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A stereoselective 1,2-*cis* glycosylation toward the synthesis of a novel *N*-linked glycan from the Gram-negative bacterium, *Campylobacter jejuni*

Akihiro Ishiwata,[a,b] Soichi Ohta[a] and Yukishige Ito[a,b,*]

[a]*RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan*
[b]*CREST, JST, Kawaguchi, Saitama 332-0012, Japan*

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Abstract—It has been shown that certain prokaryotes, such as *Campylobacter jejuni*, have asparagine (Asn)-linked glycoproteins. However, the structures of their glycans are distinct from those of eukaryotic origin. They consist of a bacillosamine residue linked to Asn, an α-(1→4)-Gal*p*NAc repeat, and a branching β-Glc*p* residue. In this paper, we describe a strategy for the stereoselective construction of the α-(1→4)-Gal*p*NAc repeat of a *C. jejuni N*-glycan, utilizing a pentafluoropropionyl (PFP) group as a temporary protective group of the C-4 OH group of the GalpN donor. The strategy was applied to the synthesis of the hexasaccharide α-Gal*p*-NAc-(1→4)-α-Gal*p*NAc-(1→4)-[β-Glc*p*-(1→3)]-α-Gal*p*NAc(1→4)-α-Gal*p*NAc-(1→4)-Gal*p*NAc.

Keywords: Glycoprotein; *Campylobacter jejuni*; Stereoselective synthesis; 1,2-*cis* Glycosylation; Protecting group

1. Introduction

N-Glycosylation is a well-conserved eukaryotic protein modification.[1] The tetradecasaccharide $Glc_3Man_9GlcNAc_2$ is transferred to Asn residues in Asn-Xaa-Thr/Ser motifs via the action of oligosaccharyltransferase (OST) in the endoplasmic reticulum (ER) and further modification takes place in the Golgi apparatus.[2] Contrary to previous belief, certain prokaryotes are able to produce glycosylated proteins.[3] A major non-flagellin antigenic glycoprotein designated PEB3 or Cj0289c has recently been identified in the pathogenic Gram-negative bacterium, *Campylobacter jejuni*.[4] This glycoprotein has multiple glycosylation sites with novel glycans at Asn residues in the consensus sequence Asn-Xaa-Thr/Ser, as is the case in eukaryotes.[5] The glycan is composed of α-Gal*p*NAc-(1→4)-α-Gal*p*NAc-(1→4)-[β-Glc*p*-(1→3)]-α-Gal*p*NAc(1→4)-α-Gal*p*NAc-(1→4)-α-Gal*p*NAc-(1→3)-β-Bac*p*-heptasaccharide (Fig. 1), where Bac is bacillosamine (2,4-diacetamido-2,4,6-trideoxy-D-glucopyranose). This *N*-linked glycan structure is distinct from eukaryotic glycoprotein glycans, which consist of a core pentasaccharide ($Man_3GlcNAc_2$) decorated with various sugar residues. The biosynthetic pathway of the *C. jejuni N*-glycan is, however, quite similar to that of eukaryotes. It is believed that a preassembled Und-P-P-heptasaccharide (Und = undecaprenyl) flips from the cytoplasm to the periplasm, where transfer of the heptasaccharide to the Asn moiety takes place under the control of OST.[6] The presence of this glycan on the surface of *C. jejuni* was shown to play a key role in enteric adhesion to host cells,[7] and this adhesion constitutes the first step of virulence.[8] A relationship between *C. jejuni* infection and Guillian Barré syndrome (GBS) has since been reported.[9] Very recently, the in vitro assembly of the Und-P-P-linked glycoconjugate from *C. jejuni* has been reported.[10] Here, we report a strategy for the stereoselective synthesis of the repeating

* Corresponding author. Fax: +81 48 462 4680; e-mail: yukito@riken.jp

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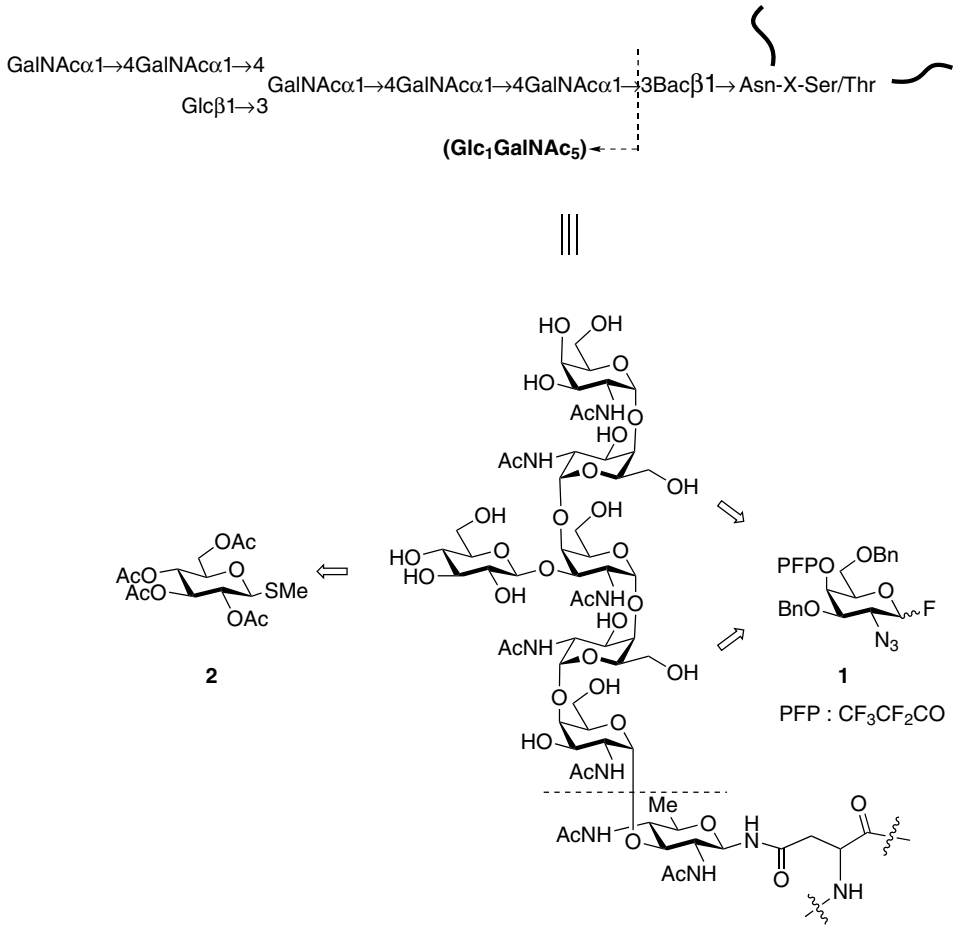


Figure 1. Structure of the *C. jejuni N*-linked glycan.

α-Gal*p*NAc-(1→4)-α-Gal*p*NAc motif, which was then applied to synthesis of the branched hexasaccharide $Glc_1GalNAc_5$.

2. Results and discussion

Construction of α-Gal*p*NAc glycosides, which constitute the linkage region of Ser/Thr-linked glycoproteins, has been examined in depth.[11,12] Conventionally, 2-azido-2-deoxy-Gal*p* derivatives,[13] which are obtainable from galactose, have been used for this purpose. More recently, Kiso and co-workers[14] reported a highly efficient approach, which allows for the nearly exclusive formation of α-Gal*p*N glycosides. In this case, donors protected with a 4,6-*O*-di-*tert*-butylsilylene group were employed. Strikingly, these donors gave α-Gal*p*N products, even when the C-2 nitrogen was protected with 1,2-*trans* directing group such as phthaloyl, trichloroethoxycarbonyl or acetyl. However, this method may not be optimally suitable for our target because it consists of (1→4)-linked Gal*p*NAc repeats and selective liberation of the C-4 hydroxyl group is required after each glycosylation. Instead, we set out to use a 4-*O*-pentafluoropropionyl (PFP) protected Gal*p*N donor, such as **1**, while the peracetylated thioglycoside **2** was adopted as the Glc*p* donor.

We recently reported the use of PFP groups as a hydroxyl-protecting group for the stepwise synthesis of oligosaccharides.[15] Removal of the PFP group can be conducted under extremely mild basic conditions, such as pyridine–EtOH or DABCO–EtOH, with complete retention of an acetyl group. It proceeds quantitatively and the byproduct, ethyl pentafluoropropionate, is volatile (bp 75–76 °C). Therefore, the product can be used for subsequent transformations immediately after evaporation. In addition to the ease of removal, its strongly electron withdrawing nature attracted our attention. Based on electrostatic considerations,[16] at the outset we expected that the PFP ester at C-4 would enhance the intrinsic α-selectivity of the 2-azido glycosyl donor to neutralize the strong dipole moment caused by a PFP group in the axial orientation, thus favoring the formation of an α-glycoside (Fig. 2).

Scheme 1 shows the preparation of the synthetic building blocks. *tert*-Butyldiphenylsilyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**3a**)[17] was used as the common precursor for the monosaccharide

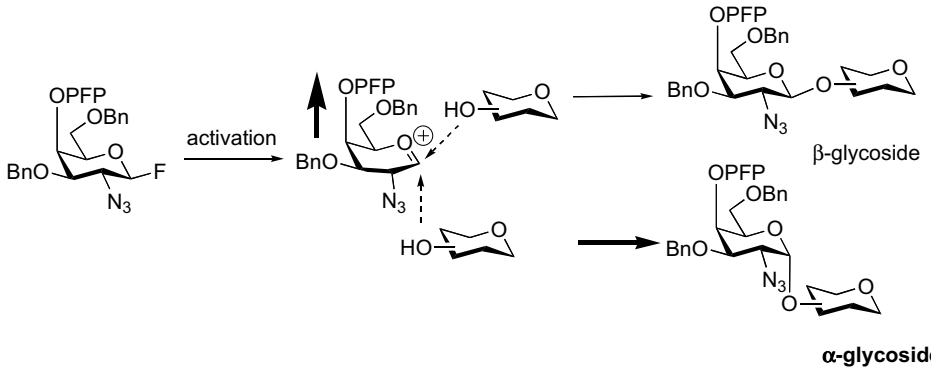
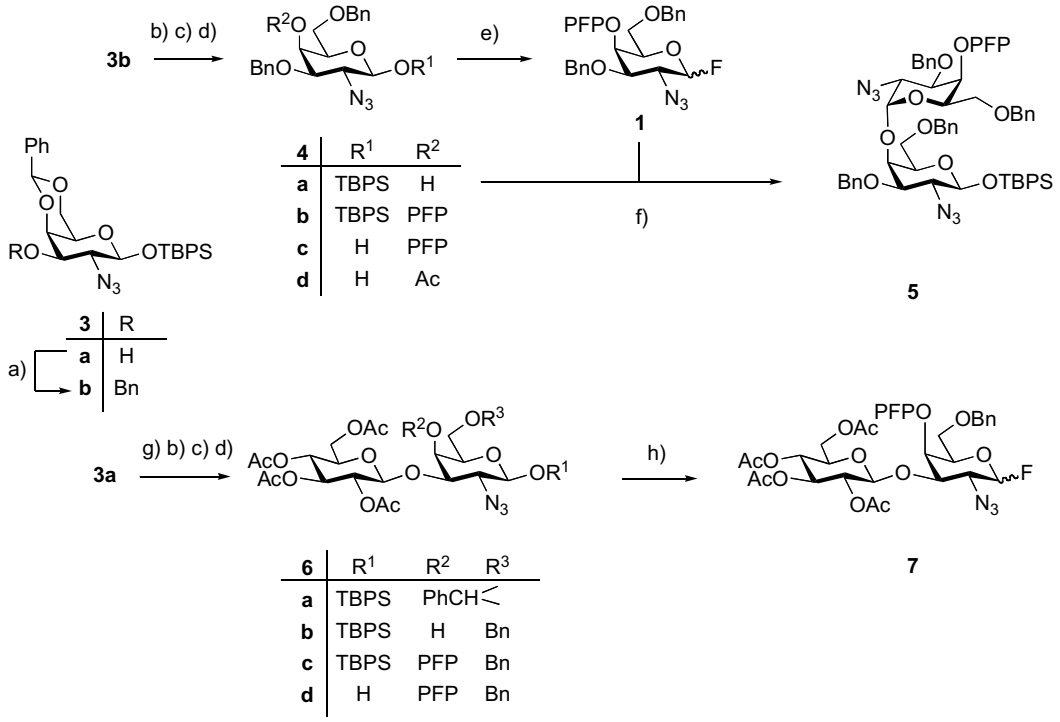


Figure 2. Stereoelectronic effect of electron-withdrawing group at the C-4 position.



Scheme 1. Synthesis of mono- and disaccharide blocks. Reagents and conditions: (a) BnBr, Ag_2O, 88%; (b) $NaBH_3CN$, HCl, 97% (**4a**), 90% (**6b**); (c) PFP_2O, pyridine, quant. (**4b**), 85% (**6c**); (d) HF, THF, 94% (**4c**), 99% (**6d**); (e) DAST, 91% (**1**), 94% (**7**); (f) **4a**, Cp_2HfCl_2, $AgClO_4$, $CHCl_3$, 92%; (g) **2**, NIS, TfOH, CH_2Cl_2–toluene, 77%.

donor **1**, acceptor **4a** as well as disaccharide donor **7**. It was first protected with a benzyl group[18] to give **3b** and reductive ring-opening of benzylidene acetal[19] gave **4a**. For synthesis of the glycosyl donor **1**, compound **4a** was treated with PFP_2O in the presence of pyridine to give PFP ester **4b**. Desilylation with HF–pyridine complex[20] in THF and subsequent fluorination of the resulting hemiacetal **4c** with DAST[21] gave **1** as a mixture of anomers ($\alpha:\beta = 31:69$). Separation by SiO_2 column chromatography gave pure β-isomer **1β**, which was used for the screening of subsequent glycosylation.

Coupling of the glycosyl acceptor **4a** with **1β** (1.2 equiv) was examined, with the primary focus being on the effect of the activator; the results are summarized in Table 1. When $SnCl_2$–$AgClO_4$[22] was used, the reaction was extremely slow, presumably reflecting the disarmed nature of **1β**. A combination of AgX (X = ClO_4 or OTf) with Cp_2MCl_2 (M = Hf, Zr, Ti)[23] proved to be suitable for our purposes, among which $AgClO_4$–Cp_2HfCl_2 was most efficient in providing product **5** in high yield and selectivity. Larger amounts of the promoter (entry 17) or elevated temperature (entry 15) resulted in a slightly increased yield. Although comparable results were obtained in $CHCl_3$ (entry 8), CH_2Cl_2 (entry 1) and toluene (entry 9), Et_2O (entry 10) gave lower yield. The stereoselectivity was also

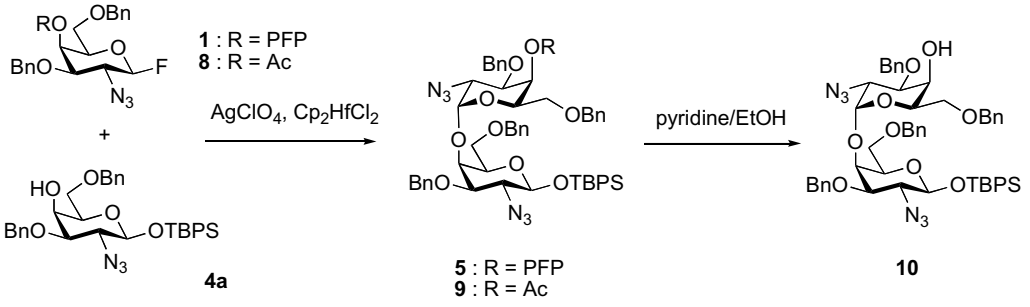
Table 1. Glycosylation of **4a** with **1β**

Entry[a]	Activator	Solvent	Temp	Yield (%)	α/β
1	$AgClO_4$ (3.6)/Cp_2HfCl_2 (1.8)	CH_2Cl_2	rt	85	93/7
2	$AgClO_4$ (3.6)/Cp_2ZrCl_2 (1.8)	CH_2Cl_2	rt	58	95/5
3	$AgClO_4$ (3.6)/Cp_2TiCl_2 (1.8)	CH_2Cl_2	rt	69	95/5
4	$AgClO_4$ (3.6)/$SnCl_2$ (1.8)	CH_2Cl_2	rt	4	86/14
5	AgOTf (3.6)/Cp_2HfCl_2 (1.8)	CH_2Cl_2	rt	75	95/5
6	$AgSbF_6$ (3.6)/Cp_2HfCl_2 (1.8)	CH_2Cl_2	rt	0	—
7	$AgPF_6$ (3.6)/Cp_2HfCl_2 (1.8)	CH_2Cl_2	rt	0	—
8	$AgClO_4$ (3.6)/Cp_2HfCl_2 (1.8)	$CHCl_3$	rt	87	95/5
9	$AgClO_4$ (3.6)/Cp_2HfCl_2 (1.8)	Toluene	rt	81	94/6
10	$AgClO_4$ (3.6)/Cp_2HfCl_2 (1.8)	Et_2O	rt	44	85/15
11	$AgClO_4$ (3.6)/Cp_2HfCl_2 (1.8)	CH_3CN	rt	0	—
12	$AgClO_4$ (3.6)/Cp_2HfCl_2 (1.8)	CPME	rt	0	—
13	$AgClO_4$ (3.6)/Cp_2HfCl_2 (1.8)	1,4-Dioxane	rt	0	—
14	$AgClO_4$ (3.6)/Cp_2HfCl_2 (1.8)	$CHCl_3$	0 °C	77	93/7
15	$AgClO_4$ (3.6)/Cp_2HfCl_2 (1.8)	$CHCl_3$	60 °C	90	94/6
16	$AgClO_4$ (2.6)/Cp_2HfCl_2 (1.3)	$CHCl_3$	rt	74	94/6
17	$AgClO_4$ (5.2)/Cp_2HfCl_2 (2.6)	$CHCl_3$	rt	92	94/6
18[b]	$AgClO_4$ (3.6)/Cp_2HfCl_2 (1.8)	$CHCl_3$	rt	87	94/6

[a] All reactions were quenched after 42 h.
[b] α-Isomer **1α** was used instead of β-isomer **1β**.

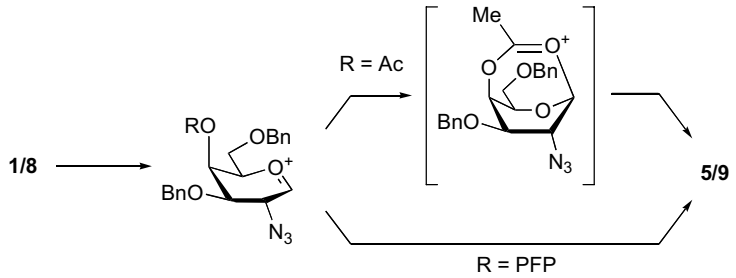
diminished in Et_2O. Other coordinating solvents, such as dioxane (entry 13), cyclopentyl methyl ether (CPME, entry 12) and acetonitrile (entry 11), were unsuitable for this reaction. α-Fluoride (**1α**) was shown to be equally effective in giving **5** in high yield (entry 18).

For comparison, the 4-*O*-acetylated donor **8**, which was prepared from **4a** via **4d**, was examined. Somewhat contrary to our expectation, glycosylation of **4a** with **8** gave the disaccharide **9** in slightly higher selectivity, albeit with lower yield, when compared with **1** (Scheme 2A, entry 2). In contrast to **1**, the selectivity was even higher in Et_2O, although the yield was unacceptable (entry 4). These results imply that reaction pathways may be different for **1** and **8**, with remote-participation



donor	solvent	product	yield (%)	α/β
1	$CHCl_3$	**5**	92	94/6
8	$CHCl_3$	**9**	80	96/4
1	Et_2O	**5**	44	85/15
8	Et_2O	**9**	13	98/2

(A)



(B)

Scheme 2. (A) Comparison of 4-*O*-PFP (**1**) and 4-*O*-Ac (**8**) protected donors. (B) Possible reaction pathways.

of 4-*O*-acetyl group[24] being the dominant factor in the latter case (Fig. 2B).

For the construction of repeating Gal*p*NAc sequence, consecutive PFP deprotection and glycosylation under the above-described conditions were performed. Deprotection of disaccharide **5** proceeded smoothly in the presence of 20 equiv of pyridine in ethanol to give **10** (Scheme 2).

Glycosylation of disaccharide acceptor **10** with common donor **1** (2.6 equiv of Cp_2HfCl_2 and 5.2 equiv of $AgClO_4$ in $CHCl_3$ at room temperature) gave trisaccharide **11a** in good yield (Scheme 3). After repeating two additional deprotection–glycosylation cycles, pentasaccharide **11e** was obtained in good overall yield and selectivity, via **11b**, **11c** and **11d**.

We then conducted the synthesis of glucose-branched hexasaccharide. For construction of the branched structure, a disaccharide donor (β-Glc*p*-(1→3)-Gal*p*N_3) **7** was used as the third component (Scheme 4). The latter was synthesized from **3a** through β-selective glucosylation with methyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**2**) under NIS–TfOH activation conditions (Scheme 1). Glycosylation of acceptor **10** with donor **7β** was briefly examined as summarized in Table 2. Although a significant reduction in selectivity was observed, isomer separation could be readily conducted by silica gel column chromatography and tetrasaccharide **12** was obtained in reasonable yield (Table 2). In addition, an α-fluoride provided a higher yield with nearly identical selectivity (Table 2, entry 8). Deprotection of the PFP group cleanly provided **13** without affecting the acetyl groups (Scheme 4). Elongation of two Gal*p*N residues was then carried out to give glucose-branched hexasaccharide **14c**.[23]

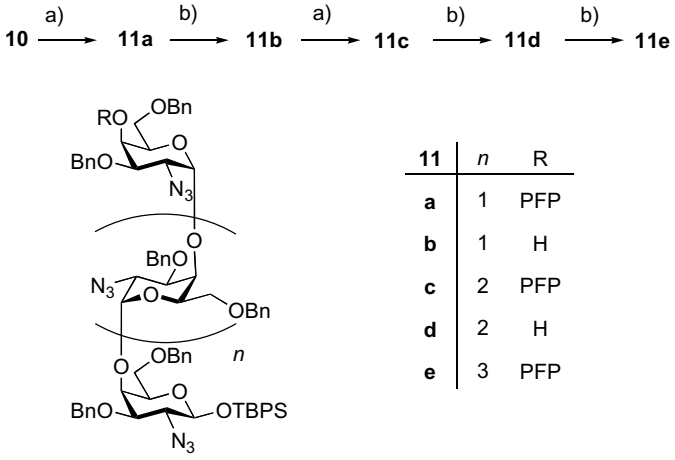
Deprotection of glucose-branched hexasaccharide **14b** was successfully conducted in a stepwise manner. Thus, methanolysis of the five esters was followed by selective reduction of the five azides under controlled hydrogenation conditions (H_2, $Pd(OH)_2$, $(i\text{-}Pr)_2NEt$, CH_3OH). Subsequent acetamide formation and hydrogenolysis of the nine benzyl groups gave free oligosaccharide **15**, which was confirmed by mass spectrometry (Scheme 4). Attempts to simultaneously reduce the azides and remove benzyl groups provided a complex mixture. In CD_3OD, the hexasaccharide gave poor ^1H NMR spectra due to severe peak broadening, even at 50 °C. This was possibly due to restricted conformer exchange, because of the extensive intramolecular hydrogen-bonding network of acetamides as suggested by molecular modeling[25] (Fig. 3). According to modeling in water, the conformation of all the pyranose rings in the heptasaccharide exists in the chair-form, possibly due to effective disruption of intramolecular hydrogen bonding. Although D_2O was unable to dissolve **15**, a mixture of CD_3OD–D_2O (1:1) gave substantially improved ^1H NMR spectra.

In conclusion, an examination of glycosylation reactions for the construction of the linear repeating Gal*p*NAc-Gal*p*NAc structure of a novel *N*-linked glycan from the Gram-negative bacterium *C. jejuni* was performed. The use of the novel Gal*p*NAc donor (**1**) having a PFP ester at position 4 was effective in giving the α-glycoside stereoselectively in good yield. Simple repetition of PFP deprotection and glycosylation afforded the penta-α-Gal*p*NAc derivative **11e**. Synthesis of glucose-branched hexasaccharide **15** was achieved using donor **7** as a third component. Further studies toward the synthesis of the complete structure of *C. jejuni*-derived *N*-glycan and its conjugation to peptide are now underway.

3. Experimental

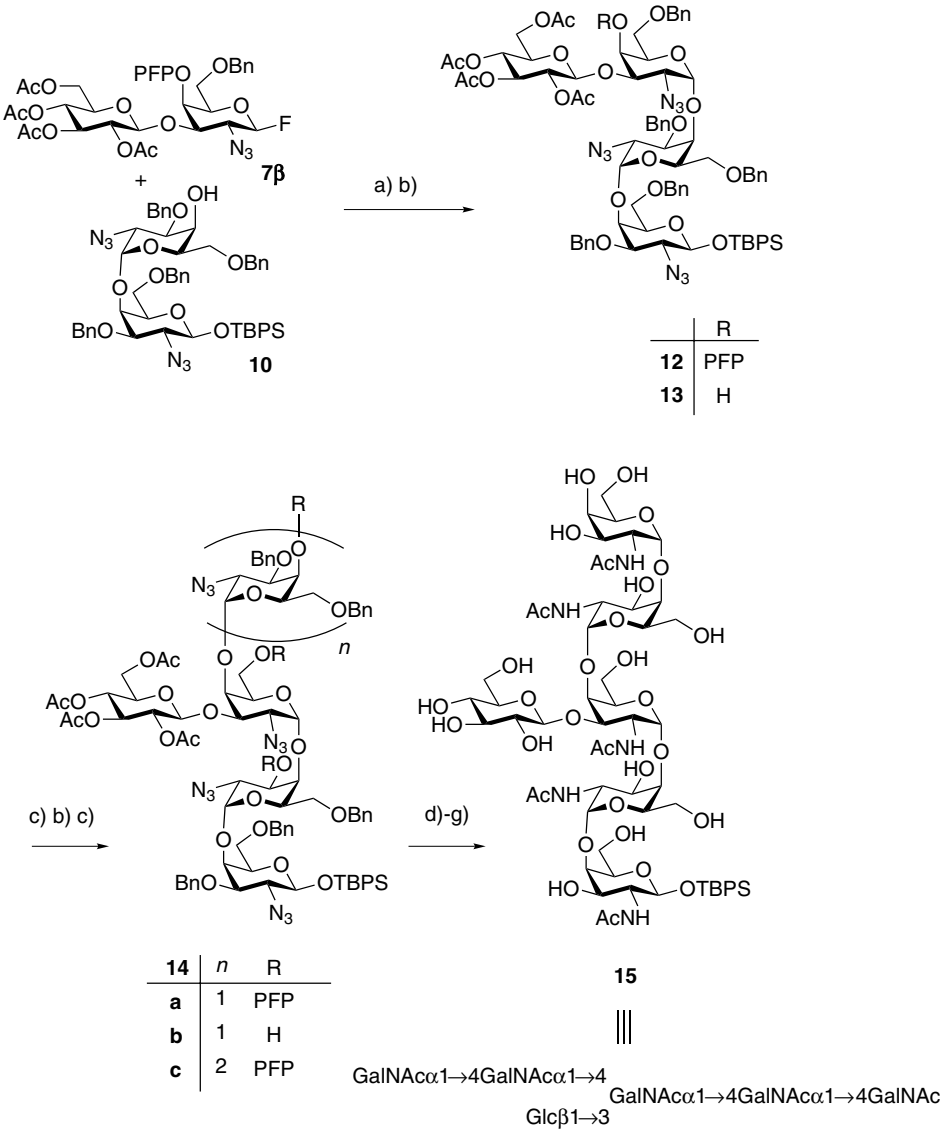
3.1. General methods

All reactions sensitive to air and/or moisture were carried out under nitrogen or argon atmosphere in



11	*n*	R
a	1	PFP
b	1	H
c	2	PFP
d	2	H
e	3	PFP

Scheme 3. Synthesis of linear pentasaccharide. Reagents and conditions: (a) **1β** (1.2 equiv) Cp_2HfCl_2 (2.6 equiv), $AgClO_4$ (5.2 equiv), $CHCl_3$, 92%, α:β = 94:6 (**11a**), 80%, α:β = 96:4 (**11c**), 70%, α:β = 95:5 (**1e**); (b) pyridine, EtOH, 80 °C, 88 h, 92% (**11b**), 99% (**11d**).



Scheme 4. Synthesis of glucose-branched hexasaccharide. Reagents and conditions: (a) see Table 2; (b) pyridine, EtOH, 80 °C, 88 h, 92% (**13**), quant. (**14b**); (c) **1β**, Cp_2HfCl_2, $AgClO_4$, $CHCl_3$, 60 °C, 84 h 96%, α:β = >95:5 (**14a**), 88%, α:β = >95:5 (**14c**); (d) $NaOCH_3$, CH_3OH; (e) H_2, $Pd(OH)_2$, Hünig base, CH_3OH; (f) Ac_2O, CH_3OH; (g) $Pd(OH)_2$, H_2, CH_3OH–$CHCl_3$–H_2O, 44% in four steps.

Table 2. Glycosylation of **10** with **7β**

Entry[a]	Activator[b]	Temp	Yield (%)	α/β
1	$AgClO_4/Cp_2HfCl_2$	rt	50	80/20
2	$AgClO/Cp_2HfCl_2$	60 °C	72	83/17
3	$AgClO_4/Cp_2ZrCl_2$	60 °C	60	83/17
4	$AgClO_4/Cp_2TiCl_2$	60 °C	23	85/15
5	$AgOTf/Cp_2HfCl_2$	60 °C	60	87/13
6	$AgPF_6/Cp_2HfCl_2$	60 °C	0	—
7	$AgBF_4/Cp_2HfCl_2$	60 °C	0	—
8[c]	$AgClO_4/Cp_2HfCl_2$	60 °C	89	78/22

[a] All reactions were quenched after 42 h.
[b] AgX (5.2 equiv) and Cp_2MCl_2 (2.6 equiv) were used.
[c] α-Isomer **7α** was used instead of **7β**.

anhydrous solvents. Column chromatography was performed on Silica Gel 60N, 100–210 mesh (Kanto Kagaku Co., Ltd). Preparative TLC was performed on Silica Gel 60 F_{254}, 0.5 mm (E. Merck). Gel filtration was performed on Sephadex LH-20 (Pharmacia). Optical rotations were measured with a JASCO DIP 370 polarimeter. ^1H NMR spectra were recorded at 400 MHz on a JEOL JNM-AL 400 spectrometer and chemical shifts are referred to internal residual solvent signals, 7.24 ppm ($CDCl_3$) or 3.30 ppm (CD_3OD). ^{13}C NMR spectra were recorded at 100 MHz on the same instrument and chemical shifts are referred to internal $CDCl_3$ (77.0 ppm). MALDI-TOF mass spectra were recorded on a SHIMADZU Kompact MALDI AXIMA-CFR spectrometer with 2,5-dihydroxybenzoic acid as the matrix. Electrospray ionization mass spectra were recorded on a JEOL AccuTOF JMS-T700LCK with

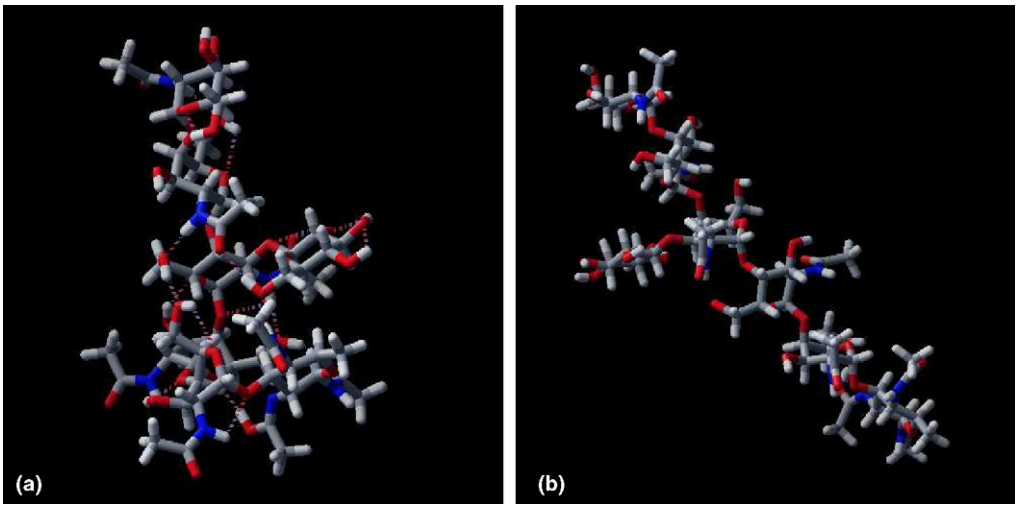


Figure 3. Results of molecular modeling of $Glc_1GalNAc_5Bac_1$-NHAc calculated by MacroModel ver 8.1. (a) In gas phase (the rings of two Gal*p*NAcs are flipped because of stabilization by intramolecular hydrogen bonding). (b) In H_2O (all pyranose rings adopt chair-form).

CF_3CO_2Na as the internal standard. Elemental analyses were performed with a Fisons EA1108 instrument.

3.2. *tert*-Butyldiphenylsilyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (3b)

To a solution of **3a** (101 mg, 0.190 mmol) in dry CH_2Cl_2 (2 mL), Ag_2O (66.1 mg, 0.285 mmol) was added at 0 °C under an Ar atmosphere and the mixture was stirred for 30 min at the same temperature. To the reaction mixture, benzyl bromide (40.0 μL, 0.33 mmol) was added and the mixture was stirred for 45 h at rt under an Ar atmosphere. The reaction mixture was filtered through Celite and concentrated in vacuo. The crude product was purified by silica gel column chromatography (9:1, hexane/EtOAc) to give **3b** as an amorphous solid (104 mg, 88%): $[\alpha]_D^{23}$ +23.7 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.15 (s, ^{t}Bu, 9H), 2.89 (s, H-5, 1H), 3.25 (dd, $J = 3.4$, 10.2 Hz, H-3, 1H), 3.80 (dd, $J = 2.0$, 12.2 Hz, H-6a, 1H), 3.91–3.96 (m, H-2, H-4, H-6b, 3H), 4.40 (d, $J = 7.8$ Hz, H-1, 1H), 4.71 (s, PhCH_2, 2H), 5.41 (s, PhCH(O)$_2$, 1H), 7.27–7.44 (m, Ar, 14H), 7.54–7.57 (m, Ar, 2H), 7.72–7.82 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.29, 26.93, 64.68, 66.22, 68.85, 71.48, 72.32, 77.71, 96.76, 101.04, 126.36, 127.17, 127.39, 127.67, 127.78, 128.16, 128.33, 128.98, 129.50, 129.64, 132.96, 133.29, 135.79, 135.95, 137.70, 137.79; MALDI-TOFMS *m*/*z* calcd for $[C_{36}H_{39}N_3O_5Si]Na^+$: 644.3. Found 644.7.

3.3. *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (4a)

To a mixture of **3b** (7.05 g, 11.3 mmol), dried powdered 3 Å molecular sieves (7.06 g) and $NaBH_3CN$ (6.06 g, 96.4 mmol) in dry THF (120 mL), 4 N HCl–dioxane (33.5 mL, 134 mmol) was added portion-wise at 0 °C under an Ar atmosphere and the mixture was stirred for 1.5 h at the same temperature. The reaction mixture was diluted with EtOAc (100 mL) and filtered through Celite. The filtrate was washed with satd aq $NaHCO_3$ (300 mL) and brine (300 mL). The washed organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel column chromatography (4:1, hexane/EtOAc) to give **4a** as an amorphous solid (6.87 g, 97%): $[\alpha]_D^{27}$ +7.0 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.12 (s, ^{t}Bu, 9H), 2.54 (br s, OH, 1H), 3.15–3.21 (m, H-3, H-5, 2H), 3.47 (dd, $J = 5.6$, 10.0 Hz, H-6a, 2H), 3.63 (dd, $J = 5.9$, 10.0 Hz, H-6b, 1H), 3.72 (dd, $J = 8.1$, 10.0 Hz, H-2, 1H) 3.91 (s, H-4, 1H), 4.31 (d, $J = 7.6$ Hz, H-1, 1H), 4.30–4.50 (m, PhCH_2, 2H), 4.60–4.75 (m, PhCH_2, 2H), 7.19–7.21 (m, Ar, 2H), 7.30–7.38 (m, Ar, 14H), 7.70–7.74 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.21, 26.84, 65.34, 65.72, 68.96, 72.02, 73.03, 73.64, 79.38, 96.81, 127.22, 127.45, 127.60 127.86, 128.06, 128.28, 128.50, 128.56, 128.74, 132.58, 133.17, 135.86, 135.91, 137.16, 137.80; MALDI-TOFMS *m*/*z* calcd for $[C_{36}H_{41}N_3O_5Si]Na^+$: 646.3. Found 646.2. Anal Calcd for $C_{36}H_{41}N_3O_5Si$: C, 69.31; H, 6.62; N, 6.74. Found: C, 69.20; H, 6.62; N, 6.63.

3.4. *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-β-D-galactopyranoside (4b)

To a solution of **4a** (3.93 g, 6.30 mmol) and pyridine (0.910 mL, 11.3 mmol) in dry CH_2Cl_2 (100 mL), pentafluoropropionic anhydride (1.97 mL, 10.1 mmol) was added portion-wise at 0 °C under an Ar atmosphere and the mixture was stirred for 2 h at 0 °C. After dilution with EtOAc (200 mL), the mixture was washed with

ice-water (300 mL), a solution of 2 N HCl (200 mL × 2) and brine (200 mL × 2), successively. The washed organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel column chromatography (6:1 to 5:1, hexane/EtOAc) to give **4b** as a syrup (4.84 g, quantitative): $[\alpha]_D^{26}$ −12.6 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.05 (s, ^{t}Bu, 9H), 3.16–3.29 (m, H-3, H-5, H-6, 4H), 3.51 (dd, $J = 7.8$, 10.2 Hz, H-2, 1H), 4.25 (s, PhCH_2, 1H), 4.28 (d, $J = 7.8$ Hz, H-1, 1H), 4.42 (d, $J = 11.2$ Hz, PhCH_2, 1H), 4.64 (d, $J = 11.2$ Hz, PhCH_2, 1H), 5.51 (d, $J =$ 2.9 Hz, H-4, 1H), 7.10–7.36 (m, Ar, 16H), 7.60–7.64 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.16, 26.77, 65.39, 65.67, 70.22, 70.83, 72.28, 73.63, 76.89, 96.77, 127.20, 127.49, 127.76 127.88, 127.95, 128.02, 128.13, 128.30, 128.37, 128.93, 129.62, 129.84, 132.37, 133.11, 135.73, 136.55 137.06, 157.54; MALDI-TOFMS *m*/*z* calcd for $[C_{39}H_{40}F_5N_3O_6Si]Na^+$: 792.3. Found 792.6. Anal Calcd for $C_{39}H_{40}F_5N_3O_6Si$: C, 60.85; H, 5.24; N, 5.46. Found: C, 60.79; H, 5.29; N, 5.32.

3.5. 2-Azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-D-galactopyranose (4c)

To a solution of **4b** (4.95 g, 6.43 mmol) in THF (210 mL), HF–pyridine (11 mL) was added at rt. After stirring for 60 h at rt, the reaction was quenched by the addition of powdered $NaHCO_3$. After dilution with EtOAc (100 mL) and water (100 mL), the reaction mixture was extracted with EtOAc (100 mL × 4) and combined organic layers were washed with brine (500 mL). The washed organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography (4:1, hexane/EtOAc,) to give **4c** as a syrup (3.20 g, 94%, α:β = 71:29): $[\alpha]_D^{23}$ +23.6 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, α-isomer): δ 3.33–3.43 (m, H-6a, 1H), 3.52 (dd, $J = 6.4$, 10.2 Hz, H-6b, 1H), 3.52 (dd, $J = 3.2$, 10.5 Hz, H-2, 1H), 3.68 (br s, OH, 1H), 3.95 (dd, $J = 3.2$, 10.5 Hz, H-3, 1H), 4.31 (t, $J = 6.0$ Hz, H-5, 1H), 4.36–4.47 (m, PhCH_2, 3H), 4.66 (d, $J = 10.7$ Hz, PhCH_2, 1H), 5.22 (br s, H-1, 1H), 5.64 (br s, H-4, 1H), 7.17–7.28 (m, Ar, 10H); β-isomer: δ 3.33–3.43 (m, H-3, H-6a, 2H), 3.50–3.54 (m, H-2, H-6b, 2H), 3.38 (t, $J = 6.0$ Hz, H-5, 1H), 4.05 (br s, OH, 1H), 4.37–4.47 (m, H-1, H-2, PhCH_2, 5H), 4.65 (d, $J = 11.5$ Hz, PhCH_2, 1H), 5.56 (br s, H-1, 1H), 7.17–7.28 (m, Ar, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 59.78, 63.74, 66.91, 67.06, 67.58, 70.14, 71.31, 71.51, 72.18, 72.38, 73.63, 73.76, 73.80, 76.94, 92.03, 96.03, 128.00, 128.04, 128.07, 128.12, 128.16, 128.20, 128.35, 128.48, 128.49, 136.26, 136.34, 136.73, 136.78, 157.60; MALDI-TOFMS *m*/*z* calcd for $[C_{23}H_{22}F_5N_3O_6]Na^+$: 554.1. Found 554.3. Anal Calcd for $C_{23}H_{22}F_5N_3O_6$: C, 51.98; H, 4.17; N, 7.91. Found: C, 51.92; H, 4.34; N, 7.83.

3.6. 2-Azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-D-galactopyranosyl fluoride (1)

To a solution of **4c** (778 mg, 1.46 mmol) in dry CH_2Cl_2 (50 mL), DAST (0.430 mL, 3.22 mmol) was added at −40 °C under an Ar atmosphere. After the reaction mixture was stirred for 2 h at −40 °C, the reaction was quenched by the addition of CH_3OH (10 mL). The reaction mixture was extracted with EtOAc (100 mL × 3) and combined organic layers were washed with water (200 mL × 2), satd aq $NaHCO_3$ (200 mL) and brine (200 mL). The washed organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel flash column chromatography (9:1, hexane/EtOAc) to give **1** (709 mg, 91%, α:β = 31:69): α-Isomer (**1α**): Amorphous solid: $[\alpha]_D^{26}$ +33.5 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.36 (t, $J = 8.8$ Hz, H-6a, 1H), 3.52–3.61 (m, H-2, H-6b, 2H), 3.92 (dd, $J = 3.0$, 10.5 Hz, H-3, 1H), 4.25 (t, $J = 6.0$ Hz, H-5, 1H), 4.39 (d, $J = 11.7$ Hz, PhCH_2, 1H), 4.43 (d, $J = 11.7$ Hz, PhCH_2, 1H), 4.47 (d, $J = 11.0$ Hz, PhCH_2, 1H), 4.70 (d, $J = 11.0$ Hz, PhCH_2, 1H), 5.57 (dd, $J = 2.4$, 52.2 Hz, H-1, 1H), 5.80 (d, $J = 2.4$ Hz, H-4, 1H), 7.18–7.31 (m, Ar, 10H); ^{13}C NMR (100 MHz $CDCl_3$): δ 58.99, 59.23, 66.46, 69.09, 70.29, 72.22, 73.46, 73.85, 77.31, 104.62, 106.89, 127.92, 128.10 128.23, 128.30, 128.44, 128.51, 135.98, 136.80, 157.38; MALDI-TOFMS *m*/*z* calcd for $[C_{23}H_{21}F_6N_3O_5]Na^+$: 556.1. Found 554.3. Anal Calcd for $C_{23}H_{21}F_6N_3O_5$: C, 51.79; H, 3.97; N, 7.88. Found: C, 52.08; H, 3.96; N, 7.66. β-Isomer (**1β**): Amorphous solid; $[\alpha]_D^{25}$ −40.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.40–3.45 (m, H-3, H-6a, 2H), 3.49–3.60 (m, H-2, H-6b, 2H), 3.76 (t, $J = 6.8$ Hz, H-5, 1H), 4.40 (dd, $J = 11.7$, 18.3 Hz, PhCH_2, 2H), 4.45 (d, $J = 11.0$ Hz, PhCH_2, 1H), 4.67 (d, $J = 11.2$ Hz, PhCH_2, 1H), 4.88 (dd, $J = 7.6$, 51.7 Hz, H-1, 1H), 5.63 (s, H-4, 1H), 7.16–7.30 (m, Ar, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 62.42, 62.62, 66.34, 69.25, 71.23, 71.28, 73.89, 76.40, 76.49, 106.52, 108.68, 127.99, 128.15 128.23, 128.25, 128.43, 128.52, 135.98, 136.70, 157.47; MALDI-TOFMS *m*/*z* calcd for $[C_{23}H_{21}F_6N_3O_5]Na^+$: 556.1. Found 556.6. Anal Calcd for $C_{23}H_{21}F_6N_3O_5$: C, 51.79; H, 3.97; N, 7.88. Found: C, 51.70; H, 3.99; N, 7.83.

3.7. *tert*-Butyldiphenylsilyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (6a)

To a mixture of **3a** (1.37 g, 2.58 mmol) and dried powdered 3 Å molecular seives (1.50 g) in dry CH_2Cl_2 (25 mL), methyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**2**, 1.17 g, 3.09 mmol) was added at −15 °C under an Ar atmosphere. To the reaction mixture, NIS (1.48 g, 6.58 mmol) was added in dry CH_2Cl_2 (10 mL)–

dry toluene (20 mL) and trifluoromethanesulfonic acid (0.210 mL) and the mixture was stirred for 2 h at the same temperature. The reaction mixture was quenched by the addition of satd aq $NaHCO_3$ (40 mL) and filtered through Celite. The filtrate was treated with 20% $Na_2S_2O_3$ aq (40 mL) and extracted with CH_2Cl_2 (40 mL × 4). The combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (1:10, acetone/toluene) to give **6a** as an amorphous solid (1.70 g, 77%): $[\alpha]_D^{26}$ +18.9 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.13 (s, ^{t}Bu, 9H), 2.00 (s, Ac, 3H), 2.03 (s, Ac, 3H), 2.05 (s, Ac, 3H), 2.07 (s, Ac, 3H), 2.96 (s, H-5^{Gal}, 1H), 3.34 (dd, $J = 3.4$, 10.5 Hz, H-3^{Gal}, 1H), 3.64 (ddd, $J = 2.4$, 4.4, 6.8 Hz, H-5^{Glc}, 1H), 3.84–3.89 (m, H-2^{Gal}, H-6a^{Gal}, 2H), 3.96 (d, $J = 12.2$ Hz, H-6b^{Gal}, 1H), 4.12–4.15 (m, H-4^{Gal}, H-6a^{Glc}, 2H), 4.25 (dd, $J = 2.4$, 12.2 Hz, H-6b^{Glc}, 1H), 4.40 (d, $J = 7.8$ Hz, H-1^{Gal}, 1H), 4.79 (d, 7.8 Hz, H-1^{Glc}, 1H), 5.05 (dd, $J = 7.8$, 9.3 Hz, H-2^{Glc}, 1H), 5.10 (t, $J = 9.8$ Hz, H-4^{Glc}, 1H), 5.20 (t, $J = 9.3$ Hz, H-3^{Glc}, 1H), 5.48 (s, PhC*H*, 1H), 7.32–7.45 (m, Ar, 9H), 7.54–7.56 (m, Ar, 2H), 7.71–7.78 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.25, 20.65, 20.68, 20.82, 26.88, 61.61, 64.82, 66.36, 68.24, 68.66, 71.27, 71.80, 72.87, 74.86, 78.86, 96.85, 100.60, 101.76, 126.23, 127.19, 127.43, 128.08, 128.82, 129.57, 129.71, 132.85, 133.07, 135.76, 135.97, 137.83, 169.18, 169.20, 170.17, 170.33; MALDI-TOFMS *m*/*z* calcd for $[C_{43}H_{51}N_3O_{14}Si]Na^+$: 884.3. Found 884.9. Anal Calcd for $C_{43}H_{51}N_3O_{14}Si$: C, 59.92; H, 5.96; N, 4.87. Found: C, 59.91; H, 5.98; N, 4.70.

3.8. *tert*-Butyldiphenylsilyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-azido-6-*O*-benzyl-2-deoxy-β-D-galactopyranoside (6b)

To a mixture of **6a** (1.10 g, 1.28 mmol) and dried powdered 4 Å molecular seives (3.02 g) in dry THF (90 mL), $NaBH_3CN$ (718 mg, 10.9 mmol) was added at 0 °C under an Ar atmosphere, and the mixture was stirred for 30 min at the same temperature. HCl (4 N)–dioxane (6.40 mL, 25.6 mmol) was added portion-wise to the reaction mixture and the mixture was stirred for 4 h at the same temperature. The reaction mixture was diluted with EtOAc (100 mL), quenched by the addition of satd aq $NaHCO_3$ (100 mL), and filtered through Celite. The filtrate was extracted with EtOAc (50 mL × 3) and combined organic layers were washed with brine (300 mL). The washed organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography (1:1, EtOAc/$CHCl_3$) to give **6b** as an amorphous solid (990 mg, 90%): $[\alpha]_D^{24}$ +8.0 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.11 (s, ^{t}Bu, 9H), 2.01 (s, Ac, 3H), 2.03 (s, Ac, 3H), 2.05 (s, Ac, 3H), 2.09 (s, Ac, 3H), 2.59 (s, OH, 1H), 3.23 (t, $J = 5.9$ Hz, H-5^{Gal}, 1H), 3.28 (dd, $J = 3.2$, 10.3 Hz, H-3^{Gal}, 1H), 3.47 (dd, $J = 5.6$, 9.8 Hz, H-6a^{Gal}, 1H), 3.65–3.71 (m, H-2^{Gal}, H-5^{Glc}, H-6b^{Gal}, 3H), 3.93 (s, H-4^{Gal}, 1H), 4.09–4.17 (m, H-6^{Glc}, 2H), 4.31 (d, $J = 7.8$ Hz, H-1^{Gal}, 1H), 4.38 (s, PhCH_2, 2H), 4.69 (d, $J = 8.1$ Hz, H-1^{Glc}, 1H), 5.03–5.08 (m, H-2^{Glc}, H-4^{Glc}, 2H), 5.20 (t, $J = 10.0$ Hz, H-3^{Glc}, 1H), 7.18–7.20 (m, Ar, 2H), 7.26–7.40 (m, Ar, 9H), 7.69–7.73 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.10, 20.55, 20.59, 26.74, 61.69, 65.23, 67.57, 68.20, 68.81, 70.96, 71.92, 72.42, 73.01, 73.50, 77.20, 81.34, 96.73, 101.40, 127.17, 127.41, 127.53, 128.08, 128.20, 128.89, 129.54, 129.72, 132.42, 132.94, 135.77, 135.87, 137.79, 169.14, 169.23, 170.00, 170.38; MALDI-TOFMS *m*/*z* calcd for $[C_{43}H_{53}N_3O_{14}Si]Na^+$: 886.3. Found 886.8. Anal Calcd for $C_{43}H_{53}N_3O_{14}Si$: C, 59.78; H, 6.18; N, 4.86. Found: C, 59.91; H, 6.14; N, 4.58.

3.9. *tert*-Butyldiphenylsilyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-azido-6-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-β-D-galactopyranoside (6c)

To a solution of **6b** (3.73 g, 4.32 mmol) and pyridine (0.625 mL, 7.77 mmol) in dry CH_2Cl_2 (100 mL), pentafluoropropionic anhydride (1.26 mL, 6.48 mmol) was added portion-wise at 0 °C under an Ar atmosphere and the mixture was stirred for 1 h at the same temperature. The reaction was quenched by the addition of 0.2 N aq HCl (50 mL) and a separated organic layer was washed with water (80 mL) and brine (80 mL). The washed organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel column chromatography (4:1 to 7:3, hexane/EtOAc) to give **6c** as an amorphous solid (3.70 g, 85%): $[\alpha]_D^{25}$ −1.4 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.11 (s, ^{t}Bu, 9H), 2.00 (s, Ac, 6H), 2.02 (s, Ac, 3H), 2.06 (s, Ac, 3H), 3.22 (dd, $J = 2.0$, 6.3 Hz, H-6^{Gal}, 2H), 3.36 (t, $J = 6.3$ Hz, H-5^{Gal}, 1H), 3.47 (dd, $J = 3.2$, 10.2 Hz, H-3^{Gal}, 1H), 3.56–3.63 (m, H-2^{Gal}, H-5^{Glc}, 2H), 4.06 (dd, $J = 4.2$, 12.2 Hz, H-6a^{Glc}, 1H), 4.22 (dd, $J = 2.4$, 12.2 Hz, H-6b^{Glc}, 1H), 4.24 (d, $J = 11.4$ Hz, PhCH_2, 1H), 4.27 (d, $J = 11.4$ Hz, PhCH_2, 1H), 4.36 (d, $J = 7.6$ Hz, H-1^{Gal}, 1H), 4.71 (d, $J = 7.8$ Hz, H-1^{Glc}, 1H), 4.89 (dd, $J = 8.0$, 9.5 Hz, H-2^{Glc}, 1H), 5.07 (t, $J = 9.7$ Hz, H-4^{Glc}, 1H), 5.17 (t, $J = 9.5$ Hz, H-3^{Glc}, 1H), 5.51 (d, $J = 3.2$ Hz, H-4^{Gal}, 1H), 7.14–7.17 (m, Ar, 2H), 7.28–7.41 (m, Ar, 9H), 7.67–7.69 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.14, 20.49, 20.56, 20.63, 26.75, 61.19, 65.77, 67.18, 68.02, 71.18, 71.46, 71.80, 72.60, 72.93, 73.68, 77.15, 77.21, 96.79, 101.20, 127.23, 127.54, 127.79, 128.82, 128.30, 129.69, 129.93, 132.18, 132.92, 135.75, 137.14, 156.75, 168.83, 169.10, 170.15, 170.59; MALDI-TOFMS *m*/*z* calcd for $[C_{46}H_{52}F_5N_3O_{15}Si]Na^+$: 1032.3. Found 1032.2. Anal Calcd for $C_{46}H_{52}F_5N_3O_{15}Si$: C,

54.70; H, 5.19; N, 4.16. Found: C, 54.68; H, 5.21; N, 4.06.

3.10. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-azido-6-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-D-galactopyranose (6d)

To a solution of **6c** (399 mg, 0.395 mmol) in THF (15 mL), HF–pyridine (0.700 mL) was added at rt. The mixture was stirred for 24 h at the same temperature and then the mixture was quenched by the addition of powdered $NaHCO_3$, diluted with EtOAc (20 mL) and water (20 mL), and extracted with EtOAc (20 mL × 4). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (3:1 to 1:2, hexane–EtOAc) to give **6d** as an amorphous solid (301 mg, 99%, α:β = 74:26): $[\alpha]_D^{26}$ +28.2 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) α-isomer: δ 2.00–2.04 (m, Ac, 12H), 3.54–3.70 (m, H-2^{Gal}, H-5^{Glc}, H-6^{Gal}, 4H), 4.09 (dd, *J* = 4.4, 12.2 Hz, H-6a^{Glc}, 1H), 4.20 (dd, *J* = 2.9, 10.5 Hz, H-3^{Gal}, 1H), 4.27 (dd, *J* = 2.4, 8.3 Hz, H-6b^{Glc}, 1H), 4.40 (t, *J* = 5.9 Hz, H-5^{Gal}, 1H), 4.46–4.49 (m, PhCH_2, 2H), 4.78 (d, *J* = 8.1 Hz, H-1^{Glc}, 1H), 4.90 (dd, *J* = 8.1, 9.3 Hz, H-2^{Glc}, 1H), 5.09 (t, *J* = 9.8 Hz, H-4^{Glc}, 1H), 5.18 (t, *J* = 9.5 Hz, H-3^{Glc}, 1H), 5.40 (br s, H-1^{Gal}, 1H), 5.71 (d, *J* = 2.7 Hz, H-4^{Gal}, 1H), 7.18–7.36 (m, Ar, 5H); β-isomer: δ 2.00–2.04 (m, Ac, 12H), 3.54–3.70 (m, H-2^{Gal}, H-3^{Gal}, H-5^{Glc}, H-6^{Gal}, 5H), 3.81 (t, *J* = 6.6 Hz, H-5^{Gal}, 1H), 4.09 (dd, *J* = 4.4, 12.2 Hz, H-6a^{Glc}, 1H), 4.27 (dd, *J* = 2.4, 8.3 Hz, H-6b^{Glc}, 1H), 4.46–4.49 (m, PhCH_2, 2H), 4.51–4.59 (m, H-1^{Gal}, 1H), 4.76 (d, *J* = 8.6 Hz, H-1^{Glc}, 1H), 4.89 (dd, *J* = 8.6, 9.3 Hz, H-2^{Glc}, 1H), 5.09 (t, *J* = 9.8 Hz, H-4^{Glc}, 1H), 5.18 (t, *J* = 9.5 Hz, H-3^{Glc}, 1H), 5.60 (d, *J* = 3.2 Hz, H-4^{Gal}, 1H) and 7.18–7.36 (m, Ar, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.46, 20.55, 20.57, 20.61, 59.99, 61.21, 64.16, 67.42, 67.55, 67.95, 67.98, 68.02, 71.18, 71.84, 71.89, 72.54, 72.73, 72.89, 73.76, 73.84, 74.53, 74.56, 77.20, 92.08, 96.22, 101.26, 101.29, 127.97, 128.00, 128.41, 128.44, 136.83, 136.91, 156.86, 168.98, 169.15, 170.18, 170.68; MALDI-TOFMS *m*/*z* calcd for $[C_{30}H_{34}F_5N_3O_{15}]Na^+$: 794.2. Found 794.5. Anal Calcd for $C_{30}H_{34}F_5N_3O_{15}$: C, 46.70; H, 4.44; N, 5.45. Found: C, 46.84; H, 4.43; N, 5.53.

3.11. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-azido-6-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-D-galactopyranosyl fluoride (7)

To a solution of **6d** (2.29 g, 2.97 mmol) in dry CH_2Cl_2 (60 mL), DAST (0.780 mL, 5.94 mmol) was added at −40 °C under an Ar atmosphere. The reaction mixture was stirred for 2 h at the same temperature, then quenched by the addition of CH_3OH (25 mL) and satd aq $NaHCO_3$ (50 mL). The reaction mixture was extracted with CH_2Cl_2 (50 mL × 4) and combined organic layers were washed with water (50 mL × 2) and satd aq $NaHCO_3$ (100 mL), successively, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by silica gel flash column chromatography (5:1 to 4:1, hexane/EtOAc) to give **7** (2.15 g, 94%, α:β = 35:65). α-Isomer (**7α**): Amorphous solid; $[\alpha]_D^{25}$ +25.3 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 2.00 (s, Ac, 3H), 2.01 (s, Ac, 3H), 2.02 (s, Ac, 3H), 2.03 (s, Ac, 3H), 3.40 (dd, *J* = 7.4, 9.8 Hz, H-6a^{Gal}, 1H), 3.55 (dd, *J* = 5.4, 9.3 Hz, H-6b^{Gal}, 1H), 3.65–3.74 (m, H-2^{Gal}, H-5^{Glc}, 2H), 4.09 (dd, *J* = 4.4, 12.2 Hz, H-6a^{Glc}, 1H), 4.16 (dd, *J* = 3.4, 10.7 Hz, H-3^{Gal}, 1H), 4.28–4.33 (m, H-5^{Gal}, H-6b^{Glc}, 2H), 4.44 (d, *J* = 11.7 Hz, PhCH_2, 1H), 4.49 (d, *J* = 11.7 Hz, PhCH_2, 1H), 4.81 (d, *J* = 7.8 Hz, H-1^{Glc}, 1H), 4.91 (t, *J* = 9.8 Hz, H-1^{Glc}, 1H), 5.10 (t, *J* = 9.8 Hz, H-4^{Glc}, 1H), 5.19 (t, *J* = 9.3 Hz, H-3^{Glc}, 1H), 5.72 (dd, *J* = 2.4, 52.2 Hz, H-1^{Gal}, 1H), 5.82 (d, *J* = 2.9 Hz, H-4^{Gal}, 1H), 7.27–7.36 (m, Ar, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.55, 20.57, 20.62, 20.63, 59.36, 59.59, 61.14, 67.03, 67.88, 69.66, 69.70, 71.16, 72.07, 72.65, 73.44, 73.82, 74.40, 77.32, 101.25, 104.58, 106.85, 127.94, 127.99, 128.42, 136.81, 156.57, 168.89, 169.11, 170.11, 170.57; MALDI-TOFMS *m*/*z* calcd for $[C_{30}H_{33}F_6N_3O_{14}]Na^+$: 796.2. Found 796.5. Anal Calcd for $C_{30}H_{33}F_6N_3O_{14}$: C, 46.58; H, 4.30; N, 5.43. Found: C, 46.51; H, 4.28; N, 5.36. β-Isomer (**7β**): Amorphous solid; $[\alpha]_D^{25}$ −11.6 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 2.00 (s, Ac, 3H), 2.02 (s, Ac, 3H), 2.03 (s, Ac, 3H), 2.04 (s, Ac, 3H), 3.45 (dd, *J* = 7.1, 9.5 Hz, H-6a^{Gal}, 1H), 3.59–3.68 (m, H-2^{Gal}, H-3^{Gal}, H-5^{Glc}, H-6b^{Gal}, 4H), 3.87 (t, *J* = 6.3 Hz, H-5^{Gal}, 1H), 4.08 (dd, *J* = 4.1, 12.4 Hz, H-6a^{Glc}, 1H), 4.29 (dd, *J* = 4.1, 12.7 Hz, H-6b^{Glc}, 1H), 4.44 (d, *J* = 11.7 Hz, PhCH_2, 1H), 4.49 (d, *J* = 11.7 Hz, PhCH_2, 1H), 4.77 (d, *J* = 7.8 Hz, H-1^{Glc}, 1H), 4.88 (dd, *J* = 8.1, 9.3 Hz, H-2^{Glc}, 1H), 5.02 (dd, *J* = 7.3, 46.3 Hz, H-1^{Gal}, 1H), 5.10 (t, *J* = 9.8 Hz, H-4^{Glc}, 1H), 5.19 (t, *J* = 9.5 Hz, H-3^{Glc}, 1H), 5.66 (br s, H-4^{Gal}, 1H), 7.27–7.34 (m, Ar, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.49, 20.57, 20.62, 61.07, 62.87, 63.09, 66.85, 67.90, 71.14, 71.85, 71.90, 71.98, 72.13, 72.50, 73.92, 76.84, 101.25, 106.53, 108.69, 128.02, 128.07, 136.74, 156.67, 168.78, 169.08, 170.13, 170.60; MALDI-TOFMS *m*/*z* calcd for $[C_{30}H_{33}F_6N_3O_{14}]Na^+$: 796.2. Found 796.4. Anal Calcd for $C_{30}H_{33}F_6N_3O_{14}$: C, 46.58; H, 4.30; N, 5.43. Found: C, 46.85; H, 4.27; N, 5.44.

3.12. Typical procedure for α-selective glycosylation: *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (5)

A mixture of $AgClO_4$ (43.1 mg, 0.208 mmol), Cp_2HfCl_2 (39.5 mg, 0.104 mmol), and dried powdered 4 Å mole-

cular sieves (225 mg) in dry $CHCl_3$ (2.10 mL) was stirred for 30 min at rt under an Ar atmosphere. To the mixture, a solution of **1β** (25.6 mg, 0.0480 mmol) and **4a** (25.0 mg, 0.0400 mmol) was added in dry $CHCl_3$ (2.1 mL) at the same temperature and the mixture was stirred for 42 h at the same temperature under an Ar atmosphere. The reaction mixture was diluted with EtOAc (10 mL), quenched by the addition of satd aq $NaHCO_3$ (10 mL), and filtered through Celite. The filtrate was extracted with EtOAc (10 mL × 3) and combined organic layers were washed with brine (30 mL). The washed organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by gel filtration chromatography (1:1, EtOAc/toluene) to give **5** as a syrup (41.8 mg, 92%, α:β = 94:6). α-Isomer (**5α**): Syrup; $[\alpha]_D^{23}$ +53.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (s, ^{t}Bu, 9H), 3.07–3.11 (m, H-3^1, H-6a^1, 2H), 3.14–3.24 (m, H-6^2, H-6b^1, 3H), 3.46 (dd, *J* = 3.4, 10.7 Hz, H-2^2, 1H), 3.63 (dd, *J* = 7.6, 10.5 Hz, H-2^1, 1H), 3.79 (t, *J* = 9.0 Hz, H-5^1, 1H), 4.01 (d, *J* = 2.9 Hz, H-4^1, 1H), 4.10 (dd, *J* = 11.7, 19.3 Hz, PhC*H*$_2$, 2H), 4.14 (dd, *J* = 2.9, 10.7 Hz, H-3^2, 1H), 4.28 (d, *J* = 7.6 Hz, H-1^1, 1H), 4.40 (s, PhC*H*$_2$, 2H), 4.50 (d, *J* = 12.2 Hz, PhC*H*$_2$, 1H), 4.60 (d, *J* = 10.2 Hz, PhC*H*$_2$, 1H), 4.67 (dd, *J* = 5.9, 8.8 Hz, H-5^2, 1H), 4.75 (d, *J* = 11.8 Hz, PhC*H*$_2$, 1H), 4.85 (d, *J* = 10.5 Hz, PhC*H*$_2$, 1H), 4.89 (d, *J* = 3.7 Hz, H-1^2, 1H), 5.90 (br s, H-4^2, 1H), 7.14–7.16 (m, Ar, 2H), 7.22–7.41 (m, Ar, 24H), 7.67–7.72 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.25, 26.79, 26.82, 26.86, 59.44, 66.23, 66.64, 66.74, 71.21, 71.98, 72.13, 72.27, 72.52, 73.32, 73.40, 77.21, 78.85, 96.92, 98.76, 127.13, 127.21, 127.42, 127.78, 127.81, 127.91, 127.99, 128.01, 128.16, 128.30. 128.31, 128.39, 128.44, 128.47, 128.49, 129.52, 129.73, 132.63, 133.23, 135.80, 135.90, 135.96, 136.42, 137.11, 137.31, 137.36; MALDI-TOFMS *m*/*z* calcd for $[C_{59}H_{61}F_5N_6O_{10}Si]Na^+$: 1159.4. Found 1159.9. Anal Calcd for $C_{59}H_{61}F_5N_6O_{10}Si$: C, 62.31; H, 5.41; N, 7.39. Found: C, 62.43; H, 5.43; N, 7.31. β-Isomer (**5β**): Syrup; $[\alpha]_D^{24}$ −11.2 (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.05 (s, ^{t}Bu, 9H), 3.14–3.20 (m, H-3^1, H-3^2, H-6a^1, H-6a^2, 4H), 3.23–3.28 (m, H-6b^1, H-6b^2, 2H), 3.39 (t, *J* = 5.9 Hz, H-5^2, 1H), 3.43–3.46 (m, H-2^2, H-5^1, 2H), 3.87 (dd, *J* = 7.8, 10.2 Hz, H-2^1, 1H), 3.95 (br s, H-4^1, 1H), 4.22–4.25 (m, PhC*H*$_2$, 4H), 4.29 (d, *J* = 7.6 Hz, H-1^1, 1H), 4.48 (d, *J* = 11.7 Hz, PhC*H*$_2$, 1H), 4.50 (d, *J* = 12.2 Hz, PhC*H*$_2$, 1H), 4.55 (d, *J* = 8.1 Hz, H-1^2, 1H), 4.67 (d, *J* = 11.7 Hz, PhC*H*$_2$, 1H), 4.72 (d, *J* = 12.2 Hz, PhC*H*$_2$, 1H), 5.53 (d, *J* = 3.6 Hz, H-4^2, 1H), 7.07–7.24 (m, Ar, 2H), 7.28–7.31 (m, Ar, 24H), 7.65–7.68 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.20, 26.81, 26.82, 63.02, 65.81, 66.60, 68.78, 70.24, 70.58, 70.76, 72.39, 73.07, 73.19, 73.67, 76.29, 77.21, 80.56, 96.92, 101.16, 127.12, 127.17, 127.40, 127.80, 127.97, 128.02, 128.15, 128.34, 128.39, 128.46, 129.45, 129.64, 132.75, 133.26, 135.85, 135.94, 136.61, 136.92, 137.69, 138.19 (Ar), 157.42; MALDI-TOFMS *m*/*z* calcd for $[C_{59}H_{61}F_5N_6O_{10}Si]Na^+$: 1159.4. Found 1160.0. Anal Calcd for $C_{59}H_{61}F_5N_6O_{10}Si$: C, 62.31; H, 5.41; N, 7.39. Found: C, 62.43; H, 5.41; N, 7.22.

3.13. 4-*O*-Acetyl-2-azido-3,6-di-*O*-benzyl-2-deoxy-D-galactopyranose (4d)

To a solution of **4a** (605 mg, 0.969 mmol) in pyridine (25 mL), Ac_2O (15 mL) was added at rt and the mixture was stirred for 12 h at the same temperature. The reaction mixture was diluted with EtOAc (50 mL), quenched by the addition of a solution of aq 1 N HCl, stirred at rt for 30 min, and extracted with EtOAc (30 mL × 3) and the organic layer was washed with brine (50 mL × 2) and water (50 mL × 2). The washed organic layer was dried over Na_2SO_4 and concentrated in vacuo. To a solution of the crude product in THF (25 mL), HF–pyridine (2.0 mL) was added at rt. After the reaction mixture was stirred for 18 h at the same temperature, the mixture was quenched by the addition of powdered $NaHCO_3$. The reaction mixture was diluted with EtOAc (20 mL) and water (30 mL) added, and the reaction mixture was extracted with EtOAc (30 mL × 3). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (4:1, hexane/EtOAc) to give **4d** as a syrup (372 mg, 90%, α:β = 61:39): $[\alpha]_D^{24}$ +33.0 (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): α-isomer: δ 2.07 (s, Ac, 3H), 3.45–3.58 (m, H-6, 2H), 3.66–3.71 (m, H-2, 1H), 3.78 (br s, OH, 1H), 3.97 (dd, *J* = 3.2, 10.5 Hz, H-3, 1H), 4.45 (t, *J* = 6.0 Hz, H-5, 1H), 4.47–4.50 (m, PhC*H*$_2$, 2H), 4.57 (d, *J* = 12.0 Hz, PhC*H*$_2$, 1H), 4.75 (d, *J* = 10.7 Hz, PhC*H*$_2$, 1H), 5.33 (t, *J* = 3.42 Hz, H-1, 1H), 5.58 (d, *J* = 3.17 Hz, H-4, 1H), 7.17–7.38 (m, Ar, 10H). β-Isomer: δ 2.08 (s, Ac, 3H), 3.35 (dd, *J* = 3.17, 10.0 Hz, H-3, 1H), 3.45–3.58 (m, H-2, H-6a, 2H), 3.66–3.71 (m, H-5, H-6b, 2H), 4.23 (br s, OH, 1H), 4.47–4.50 (m, H-1, PhC*H*$_2$, 3H), 4.57 (d, *J* = 12.0 Hz, PhC*H*$_2$, 1H), 4.73 (d, *J* = 11.2 Hz, PhC*H*$_2$, 1H), 5.49 (d, *J* = 3.2 Hz, H-4, 1H), 7.17–7.38 (m, Ar, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.82, 20.85, 59.76, 63.72, 65.61, 66.88, 68.00, 68.21, 71.67, 71.84, 72.41, 73.58, 73.67, 74.09, 77.21, 77.68, 92.22, 96.07, 127.88, 127.92, 128.00, 128.23, 128.32, 128.39, 128.43, 136.79, 136.89, 137.13, 137.20, 170.14; MALDI-TOFMS *m*/*z* calcd for $[C_{22}H_{25}N_3O_6]Na^+$: 450.2. Found 450.2. Anal Calcd for $C_{22}H_{25}N_3O_6$: C, 61.82; H, 5.90; N, 9.83. Found: C, 61.53; H, 5.72; N, 9.80.

3.14. 4-*O*-Acetyl-2-azido-3,6-di-*O*-benzyl-2-deoxy-D-galactopyranosyl fluoride (8)

To a solution of **4d** (236 mg, 0.552 mmol) in dry CH_2Cl_2 (10 mL), DAST (0.110 mL, 0.829 mmol) was added at

−40 °C under an Ar atmosphere. After the reaction mixture was stirred for 20 h at the same temperature, the reaction was quenched by the addition of CH_3OH (10 mL) and satd aq $NaHCO_3$ (30 mL). The reaction mixture was extracted with CH_2Cl_2 (50 mL × 3) and combined organic layers were washed with water (100 mL × 2) and brine (100 mL). The washed organic layer was dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by silica gel flash column chromatography (19:1, hexane/EtOAc) to give **8** (195 mg, 82%, α:β = 33:67). α-Isomer (**8α**): Syrup; $[\alpha]_D^{24}$ +48.1 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.06 (s, Ac, 3H), 3.48 (dd, *J* = 6.8, 9.5 Hz, H-6a, 1H), 3.56 (dd, *J* = 6.1, 9.5 Hz, H-6b, 1H), 3.73 (ddd, *J* = 2.7, 10.5, 25.6 Hz, H-2, 1H), 3.95 (dd, *J* = 2.9, 10.5 Hz, H-3, 1H), 4.27 (t, *J* = 6.6 Hz, H-5, 1H), 4.47 (d, *J* = 12.0 Hz, PhCH_2, 1H), 4.50 (d, *J* = 10.7 Hz, PhCH_2, 1H), 4.58 (d, *J* = 12.0 Hz, PhCH_2, 1H), 4.80 (d, *J* = 10.7 Hz, PhCH_2, 1H), 5.65 (dd, *J* = 2.7, 52.7 Hz, H-1, 1H), 5.72 (d, *J* = 2.9 Hz, H-4, 1H), 7.29–7.38 (m, Ar, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.71, 58.97, 59.21, 65.76, 67.47, 70.33, 70.36, 71.64, 73.61, 73.96, 104.89, 107.15, 127.84, 127.90, 128.03, 128.38, 128.40, 136.55, 137.19, 169.68; MALDI-TOFMS *m*/*z* calcd for $[C_{22}H_{24}FN_3O_5]Na^+$: 452.2. Found 452.9. Anal Calcd for $C_{22}H_{24}FN_3O_5$: C, 61.53; H, 5.63; N, 9.78. Found: C, 61.60; H, 5.50; N, 9.64. β-Isomer (**8β**): Syrup; $[\alpha]_D^{26}$ −28.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.09 (s, Ac, 3H), 3.44 (dd, *J* = 3.2, 10.2 Hz, H-3, 1H), 3.53 (dd, *J* = 6.8, 9.5 Hz, H-6a, 1H), 3.61 (dd, *J* = 5.9, 9.5 Hz, H-6b, 1H), 3.70 (ddd, *J* = 7.6, 10.5, 14.4 Hz, H-2, 1H), 3.78 (t, *J* = 6.6 Hz, H-5, 1H), 4.46 (d, *J* = 11.7 Hz, PhCH_2, 1H), 4.49 (d, *J* = 11.2 Hz, PhCH_2, 1H), 4.58 (d, *J* = 11.7 Hz, PhCH_2, 1H), 4.77 (d, *J* = 11.2 Hz, PhCH_2, 1H), 4.97 (dd, *J* = 7.6, 52.0 Hz, H-1, 1H), 5.58 (t, *J* = 3.2 Hz, H-4, 1H), 7.29–7.38 (m, Ar, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.43, 62.14, 62.35, 64.50, 67.08, 71.65, 72.13, 72.18, 73.44, 76.46, 76.77, 106.47, 108.60, 127.64, 127.71, 127.78, 127.97, 128.13, 136.30, 136.87, 169.50; MALDI-TOFMS *m*/*z* calcd for $[C_{22}H_{24}FN_3O_5]Na^+$: 452.2. Found 452.2. Anal Calcd for $C_{22}H_{24}FN_3O_5$: C, 61.53; H, 5.63; N, 9.78. Found: C, 61.29; H, 5.57; N, 9.53.

3.15. *tert*-Butyldiphenylsilyl 4-acetyl-2-azido-3,6-di-*O*-benzyl-2-deoxy-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (9)

This compound was synthesized from **8β** and **4a** according to the general procedure for glycosylation outlined in Section 3.12 (80%, α:β = 96:4). α-Isomer (**9α**): Syrup; $[\alpha]_D^{23}$ +81.5 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.05 (s, ^{t}Bu, 9H), 1.93 (s, Ac, 3H), 3.00–3.04 (m, H-3^1, H-6a^1, 2H), 3.09 (dd, *J* = 5.1, 8.8 Hz, H-6a^2, 1H), 3.15–3.22 (m, H-6b^1, H-6b^2, 2H), 3.52 (dd, *J* = 3.4, 10.7 Hz, H-2^2, 1H), 3.61 (dd, *J* = 7.8, 10.5 Hz, H-2^1, 1H), 3.73 (t, *J* = 9.0 Hz, H-5^1, 1H), 3.97 (d, *J* = 2.4 Hz, H-4^1, 1H), 4.02 (d, *J* = 12.2 Hz, PhCH_2, 1H), 4.05 (dd, *J* = 2.7, 10.7 Hz, H-3^2, 1H), 4.20 (d, *J* = 7.8 Hz, H-1^1, 1H), 4.21 (d, *J* = 11.5 Hz, PhCH_2, 1H), 4.27 (d, *J* = 11.7 Hz, PhCH_2, 1H), 4.35 (d, *J* = 11.7 Hz, PhCH_2, 1H), 4.44 (d, *J* = 12.4 Hz, PhCH_2, 1H), 4.49 (d, *J* = 10.2 Hz, PhCH_2, 1H), 4.52 (t, *J* = 7.6 Hz, H-5^2, 1H) 4.70 (d, *J* = 12.4 Hz, PhCH_2, 1H), 4.82 (d, *J* = 10.0 Hz, PhCH_2, 1H), 4.90 (d, *J* = 3.4 Hz, H-^{1}2, 1H), 5.70 (br s, H-42, 1H), 7.11–7.37 (m, Ar, 26H), 7.60–7.65 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.22, 20.88, 26.84, 59.49, 65.84, 66.52, 66.63, 67.41, 67.81, 71.59, 71.83, 72.12, 72.63, 73.26, 73.39, 73.72, 78.75, 96.92, 99.07, 127.12, 127.31, 127.40, 127.60, 127.66, 127.77, 127.92, 127.99, 128.21, 128.36, 128.63, 129.48, 129.68, 132.66, 133.28, 135.80, 135.92, 136.99, 137.48, 169.86; MALDI-TOFMS *m*/*z* calcd for $[C_{58}H_{64}N_6O_{10}Si]Na^+$: 1055.4. Found 1056.8. Anal Calcd for $C_{58}H_{64}N_6O_{10}Si$: C, 67.42; H, 6.24; N, 8.13. Found: C, 67.51; H, 6.32; N, 7.91. β-Isomer (**9β**): Syrup; $[\alpha]_D^{24}$ −11.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.11 (s, ^{t}Bu, 9H), 2.07 (s, Ac, 3H), 3.18–3.23 (m, H-3^1, H-3^2, H-6a^1, H-6a^2, 4H), 3.35–3.40 (m, H-6b^1, H-6b^2, 2H), 3.45 (t, *J* = 6.3 Hz, H-5^1, 1H), 3.57–3.64 (m, H-2^2, H-5^2, 2H), 3.52 (dd, *J* = 3.4, 10.7 Hz, H-2^2, 1H), 3.61 (dd, *J* = 7.8, 10.5 Hz, H-2^1, 1H), 3.73 (t, *J* = 9.0 Hz, H-5^1, 1H), 3.96 (dd, *J* = 7.8, 10.5 Hz, H-2^1, 1H), 4.06 (d, *J* = 2.4 Hz, H-4^1, 1H), 4.29 to ∼4.38 (m, H-1^1, PhCH_2, 4H), 4.43 (d, *J* = 11.7 Hz, PhCH_2, 1H), 4.50 (d, *J* = 11.5 Hz, PhCH_2, 1H), 4.60 (d, *J* = 11.2 Hz, PhCH_2, 1H), 4.61 (d, *J* = 8.3 Hz, H-1^2, 1H), 4.73 (d, *J* = 12.0 Hz, PhCH_2, 1H), 4.74 (d, *J* = 11.5 Hz, PhCH_2, 1H), 5.48 (d, *J* = 3.4 Hz, H-4^2, 1H), 7.15–7.17 (m, Ar, 2H), 7.24–7.41 (m, Ar, 24H), 7.71–7.75 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 19.22, 20.86, 26.82, 63.12, 65.67, 65.69, 67.82, 69.26, 70.76, 71.90, 72.02, 72.76, 73.30, 73.44, 73.58, 77.12, 77.21, 80.51, 96.92, 101.44, 127.13, 127.31, 127.33, 127.35, 127.40, 127.69, 127.72, 127.78, 127.83, 128.00, 128.09, 128.16, 128.36, 128.39, 128.43, 129.42, 129.65, 132.71, 133.30, 135.87, 135.97, 137.17, 137.43, 137.65, 138.29, 169.98; MALDI-TOFMS *m*/*z* calcd for $[C_{58}H_{64}N_6O_{10}Si]Na^+$: 1055.4. Found 1055.4. ESIMS *m*/*z* calcd for $[C_{58}H_{64}N_6O_{10}Si]Na^+$: 1055.4351. Found 1055.4384.

3.16. General procedure for deprotection of PFP group: *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (10)

To a solution of **5α** (54.0 mg, 0.0474 mmol) in EtOH (3.00 mL), pyridine (76.7 μL, 0.950 mmol) was added

at rt. The reaction mixture was stirred at 80 °C for 88 h. After concentration in vacuo, azeotropic removal of excess pyridine and side product PFPOEt with toluene for several times gave **10** as an amorphous solid (44.7 mg, 95%); $[\alpha]_D^{26}$ +71.6 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.12 (s, ^{t}Bu, 9H), 2.98 (br s, OH, 1H), 3.07 (dd, $J = 2.7$, 10.2 Hz, H-3^1, 1H), 3.09 (dd, $J = 5.6$, 9.3 Hz, H-6a^1, 1H), 3.25 (dd, $J = 5.6$, 9.3 Hz, H-6b^1, 1H), 3.33 (dd, $J = 4.4$, 9.8 Hz, H-6a^2, 1H), 3.52 (dd, $J = 6.1$, 9.5 Hz, H-6b^2, 1H), 3.67 (dd, $J = 7.6$, 10.5 Hz, H-2^1, 1H), 3.77 (dd, $J = 3.7$, 10.7 Hz, H-2^2, 1H), 3.81 (t, $J = 9.0$ Hz, H-5^1, 1H), 4.04 (dd, $J = 2.7$, 9.8 Hz, H-3^2, 1H), 4.05 (d, $J = 2.7$ Hz, H-4^1, 1H), 4.26–4.29 (m, H-1^1, H-4^2, PhCH_2, 3H), 4.34–4.38 (m, H-5^2, PhCH_2, 3H), 4.42 (d, $J = 11.7$ Hz, PhCH_2, 1H), 4.51 (d, $J = 12.4$ Hz, PhCH_2, 1H), 4.73 (d, $J = 12.7$ Hz, PhCH_2, 1H), 4.79 (dd, $J = 11.2$, 20.5 Hz, PhCH_2, 2H), 4.98 (d, $J = 3.4$ Hz, H-1^2, 1H), 7.21–7.48 (m, Ar, 26H), 7.68–7.73 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.23, 26.84, 59.13, 65.87, 66.64, 68.32, 69.45, 71.31, 71.61, 72.02, 72.73, 73.32, 73.55, 75.51, 77.20, 78.67, 96.87, 99.11, 127.11, 127.35, 127.39, 127.65, 127.68, 127.82, 127.87, 127.99, 128.27, 128.33, 128.35, 128.49, 129.49, 129.68, 132.66, 133.28, 135.79, 135.92, 137.23, 137.42, 137.45, 137.47; MALDI-TOFMS *m*/*z* calcd for $[C_{59}H_{62}N_6O_9Si]Na^+$: 1013.4. Found 1013.9. Anal Calcd for $C_{59}H_{62}N_6O_9Si$: C, 67.86; H, 6.30; N, 8.48. Found: C, 67.80; H, 6.20; N, 8.34.

3.17. *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (11A)

This compound was synthesized from **1β** and **10** according to the general procedure for glycosylation outlined in Section 3.12 (80%, α:β = 95:5): Syrup; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.08 (s, ^{t}Bu, 9H), 2.96–3.08 (m, H-3^1, H-6^1, H-6^3, 3H), 3.11–3.14 (m, H-6^2, H-6^3, 2H), 3.20 (dd, $J = 5.6$, 9.3 Hz, H-5^1, 1H), 3.32 (dd, $J = 3.4$, 10.5 Hz, H-2^3, 1H), 3.54–3.60 (m, H-2^1, H-2^2, 2H), 3.71–3.79 (m, H-6^1, H-6^2, 2H), 3.84 (d, $J = 11.5$ Hz, PhCH_2, 1H), 3.92 (d, $J = 11.0$ Hz, PhCH_2, 1H), 3.92–4.01 (m, H-3^2, H-3^3, H-4^1, PhCH_2, 4H), 4.14 (d, $J = 12.0$ Hz, PhCH_2, 1H), 4.20 (d, $J = 7.6$ Hz, H-1^1, 1H), 4.29–4.47 (m, H-4^2, H-5^2, PhCH_2, 6H), 4.54 (dd, $J = 6.1$, 9.0 Hz, H-5^3, 1H), 4.62 (d, $J = 12.2$ Hz, PhCH_2, 1H), 4.71–4.75 (m, PhCH_2, 2H), 4.85 (d, $J = 3.7$ Hz, H-1^3, 1H), 4.89 (d, $J = 12.0$ Hz, PhCH_2, 1H), 4.97 (d, $J = 3.7$ Hz, H-1^2, 1H), 5.78 (d, $J = 1.7$ Hz, H-4^3, 1H), 7.06–7.08 (m, Ar, 2H), 7.15–7.43 (m, Ar, 34H), 7.62–7.66 (m, Ar, 4H); MALDI-TOFMS *m*/*z* calcd for $[C_{79}H_{82}F_5N_9O_{14}Si]Na^+$: 1526.6. Found 1527.4.

3.18. *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (11b)

This compound was synthesized from **11a** according to the general procedure for deprotection outlined in Section 3.16 (99%). An amorphous solid; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.09 (s, ^{t}Bu, 9H), 3.03–3.09 (m, H-3^1, H-6^1, 2H), 3.19–3.26 (m, H-6^1, H-6^2, H-6^3, 3H), 3.44 (dd, $J = 6.6$, 9.8 Hz, H-6^2, 1H), 3.57–3.65 (m, H-2^1, H-2^3, 2H), 3.72–3.78 (m, H-2^2, H-5^1, 2H), 3.83 (t, $J = 8.8$ Hz, H-6^3 1H), 3.89 (dd, $J = 2.7$, 10.5 Hz, H-3^2, 1H), 4.01 (dd, $J = 2.4$, 11.0 Hz, H-3^3, 1H), 4.04 (d, $J = 2.9$ Hz, H-4^1, 1H), 4.14–4.17 (m, PhCH_2, 3H), 4.22–4.28 (m, H-1^1, H-4^2, H-5^2, PhCH_2, 4H), 4.34 (d, $J = 11.7$ Hz, PhCH_2, 1H), 4.36 (d, $J = 2.4$ Hz, H-4^3, 1H), 4.38–4.46 (m, H-5^3, PhCH_2, 3H), 4.65 (d, $J = 12.0$ Hz, PhCH_2, 1H), 4.66 (d, $J = 11.2$ Hz, PhCH_2, 1H), 4.73 (d, $J = 12.9$ Hz, PhCH_2, 1H), 4.76 (d, $J = 12.9$ Hz, PhCH_2, 1H), 4.91 (d, $J = 12.0$ Hz, PhCH_2, 1H), 5.01 (d, $J = 3.9$ Hz, H-1^3, 1H), 5.02 (d, $J = 4.1$ Hz, H-1^2, 1H), 7.17–7.42 (m, Ar, 36H), 7.66–7.71 (m, Ar, 4H); MALDI-TOFMS *m*/*z* calcd for $[C_{76}H_{83}N_9O_{13}Si]Na^+$: 1380.6. Found 1380.7.

3.19. *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (11c)

This compound was synthesized from **1β** and **11b** according to the general procedure for glycosylation outlined in Section 3.12 (76%, α:β = 95:5). A syrup; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.07 (s, ^{t}Bu, 9H), 2.89 (dd, $J = 5.4$, 8.5 Hz, H-6^4, 1H), 2.99–3.08 (m, H-3^1, H-6^1, H-6^3, H-6^4, 4H), 3.19–3.22 (m, H-6^1, H-6^2, 2H), 3.28 (dd, $J = 3.7$, 10.7 Hz, H-2^4, 1H), 3.51–3.59 (m, H-2^1, H-2^2, H-2^3, 3H), 3.70–3.89 (m, H-3^3, H-5^1, H-6^2, H-6^3, PhCH_2, 7H), 3.91 (dd, $J = 2.9$, 10.5 Hz, H-3^4, 1H), 3.99–4.02 (m, H-3^2, H-4^1, PhCH_2, 3H), 4.10 (d, $J = 12.0$ Hz, PhCH_2, 1H), 4.14 (d, $J = 12.0$ Hz, PhCH_2, 1H), 4.19 (d, $J = 7.6$ Hz, H-1^1, 1H), 4.24 (br s, H-4^3, 1H), 4.28–4.45 (m, H-4^2, H-5^2, H-5^3, H-5^4, PhCH_2, 8H), 4.52 (d, $J = 12.2$ Hz, PhCH_2, 1H), 4.62 (d, $J = 12.2$ Hz, PhCH_2, 1H), 4.68–4.73 (dm, PhCH_2, 2H), 4.80 (d, $J = 3.7$ Hz, H-1^4, 1H), 4.84 (d, $J = 12.2$ Hz, PhCH_2, 1H), 4.94–4.97 (m, H-1^2, PhCH_2, 2H), 5.02 (d, $J = 3.7$ Hz, H-1^3, 1H), 5.76 (br s, H-4^4, 1H), 7.03–7.05 (m, Ar, 2H), 7.14–7.47 (m, Ar, 44H), 7.62–7.66 (m, Ar, 4H); MALDI-TOFMS *m*/*z* calcd for $[C_{99}H_{103}F_5N_{12}O_{18}Si]Na^+$: 1893.7. Found 1893.5.

3.20. *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (11d)

This compound was synthesized from **11c** according to the general procedure for deprotection outlined in Section 3.16 (99%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.27 (s, ^{t}Bu, 9H), 2.37 (br s, OH, 1H), 2.99–3.12 (m, H-3, H-6, 4H), 3.22–3.24 (m, H-6, 2H), 3.36 (dd, $J = 6.4$, 9.0 Hz, H-6, 1H), 3.58–3.62 (m, H-2, 3H), 3.71 (dd, $J = 3.4$, 10.5 Hz, H-2, 1H), 3.74–3.93 (m, H-3, H-5, H-6, 5H), 3.90–4.10 (m, PhCH_2, 2H), 4.03–4.23 (m, H-1, H-4, H-5, PhCH_2, 7H), 4.31–4.45 (m, H-4, H-5, PhCH_2, 7H), 4.55 (d, $J = 12.0$ Hz, PhCH_2, 1H), 4.62–4.76 (m, PhCH_2, 4H), 4.86 (d, $J = 12.2$ Hz, PhCH_2, 1H), 4.97–5.00 (m, H-1, PhCH_2, 3H), 5.07 (d, $J = 3.4$ Hz, H-1, 1H), 7.16–7.50 (m, Ar, 46H), 7.66–7.70 (m, Ar, 4H); MALDI-TOFMS m/z calcd for $[C_{96}H_{104}N_{12}O_{17}Si]Na^+$: 1747.7. Found 1747.0.

3.21. *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (11e)

This compound was synthesized from **1β** and **11d** according to the general procedure for glycosylation outlined in Section 3.12 (76%, α:β = 95:5): Syrup; $[\alpha]_D^{24}$ +150.0 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.09 (s, ^{t}Bu, 9H), 2.89–2.97 (m, H-6, 2H), 3.02–3.21 (m, H-3, H-6, 4H), 3.23–3.25 (m, H-6, 2H), 3.28 (dd, $J = 3.7$, 10.7, H-2^5, 1H), 3.53 (dd, $J = 3.4$, 10.7 Hz, H-2, 1H), 3.57–3.68 (m, H-2, 3H), 3.70–4.03 (m, H-3, H-4, H-5, H-6, PhCH_2, 13H), 4.11–4.18 (m, PhCH_2, 2H), 4.21–4.25 (m, H-1, H-4, H-5, 3H), 4.27–4.57 (m, H-4, H-5, PhCH_2, 13H), 4.63 (d, $J = 12.2$ Hz, PhCH_2, 1H), 4.74 (d, $J = 12.7$ Hz, PhCH_2, 1H), 4.75 (d, $J = 10.2$ Hz, PhCH_2, 1H), 4.81 (d, $J = 3.4$ Hz, H-1^5, 1H), 4.86 (d, $J = 12.2$ Hz, PhCH_2, 1H), 4.93–4.99 (m, H-1, PhCH_2, 3H), 5.01 (d, $J = 3.7$ Hz, H-1, 1H), 5.05 (d, $J = 3.4$ Hz, H-1, 1H), 5.79 (br s, H-4^5, 1H), 7.07–7.48 (m, Ar, 56H), 7.66–7.69 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.21, 26.80, 59.49, 59.70, 60.07, 65.80, 66.43, 66.69, 68.92, 69.14, 70.94, 71.38, 71.51, 71.73, 71.84, 72.02, 72.14, 72.30, 72.64, 72.98, 73.18, 73.34, 74.09, 75.23, 76.24, 77.21, 78.66, 96.85, 98.19, 98.73, 99.06, 125.22, 126.58, 126.61, 126.93, 127.08, 127.14, 127.38, 127.49, 127.58, 127.68, 127.74, 127.78, 127.82, 127.87, 128.06, 128.09, 128.15, 128.20, 128.25, 128.29, 128.35, 128.39, 128.42, 128.50, 128.96, 129.45, 129.66, 132.63, 133.24, 135.80, 135.94, 136.45, 137.12, 137.27, 137.35, 137.43, 137.50, 137.66; MALDI-TOFMS m/z calcd for $[C_{119}H_{124}F_5N_{15}O_{22}Si]Na^+$: 2260.9. Found 2261.1. ESIMS m/z calcd for $[C_{119}H_{124}F_5N_{15}O_{22}Si]Na^+$: 2260.8632. Found 2260.8534.

3.22. *tert*-Butyldiphenylsilyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-azido-6-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (12)

This compound was synthesized from **7β** and **10** according to the general procedure for glycosylation (Section 3.12) except that 2 equiv of donor was used and that the mixture was stirred at 60 °C (72%, α:β = 83:17). α-Isomer (**12α**): Amorphous solid; $[\alpha]_D^{24}$ +64.9 (c 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.14 (s, ^{t}Bu, 9H), 2.03 (s, Ac, 3H), 2.04 (s, Ac, 3H), 2.05 (s, Ac, 3H), 2.07 (s, Ac, 3H), 3.09–3.14 (m, H-3^{Gal1}, H-6^{Gal1}, H-6a^{Gal3}, 4H), 3.24 (dd, $J = 5.4$, 8.3 Hz, H-6a^{Gal2}, 1H), 3.29 (dd, $J = 5.6$, 9.3 Hz, H-6b^{Gal3}, 1H), 3.43 (dd, $J = 3.7$, 10.7 Hz, H-2^{Gal3}, 1H), 3.62–3.68 (m, H-2^{Gal1}, H-2^2, 2H), 3.76–3.81 (m, H-5^{Gal1}, H-5^{Glc}, H-6b^{Gal2}, 3H), 4.04–4.28 (m, H-1^{Gal1}, H-3^{Gal2}, H-3^{Gal3}, H-4^{Gal1}, H-6a^{Glc}, PhCH_2, 9H), 4.36–4.39 (m, H-4^{Gal2}, PhCH_2, 2H), 4.40–4.55 (m, H-5^{Gal2}, H-5^{Gal3}, H-6b^{Glc}, PhCH_2, 5H), 4.66 (d, $J = 12.0$ Hz, PhCH_2, 1H), 4.80 (d, $J = 8.4$ Hz, H-1^{Glc}, 1H), 4.81 (d, $J = 10.7$ Hz, PhCH_2, 1H), 4.92–4.97 (m, H-2^{Glc}, PhCH_2, 2H), 5.01 (d, $J = 3.7$ Hz, H-1^{Gal3}, 1H), 5.08 (d, $J = 3.2$ Hz, H-1^{Gal2}, 1H), 5.12 (t, $J = 9.8$ Hz, H-4^{Glc}, 1H), 5.21 (t, $J = 9.5$ Hz, H-3^{Glc}, 1H), 5.83 (d, $J = 2.7$ Hz, H-4^{Gal3}, 1H), 7.18–7.45 (m, Ar, 31H), 7.70–7.73 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.17, 20.45, 20.58, 20.61, 26.76, 59.54, 59.70, 61.47, 65.86, 65.90, 66.61, 66.85, 66.96, 67.93, 68.97, 71.19, 71.58, 71.73, 71.77, 72.04, 72.33, 72.47, 72.83, 73.19, 73.26, 73.32, 74.15, 74.81, 75.19, 77.20, 78.77, 96.81, 98.11, 99.08, 101.17, 127.05, 127.07, 127.13, 127.37, 127.70, 127.77, 127.84, 127.92, 128.16, 128.32, 128.34, 128.40, 128.49, 129.46, 129.67, 132.54, 133.14, 135.77, 135.89, 137.05, 137.41, 137.43, 156.28, 168.90, 169.07, 170.11, 170.58; MALDI-TOFMS m/z calcd for $[C_{86}H_{94}F_5N_9O_{23}Si]Na^+$: 1766.6. Found 1766.3. Anal Calcd for $C_{86}H_{94}F_5N_9O_{23}Si$: C, 59.20; H, 5.43; N, 7.22. Found: C, 59.05; H, 5.22; N, 7.06. β-Isomer (**12β**): Amorphous solid; $[\alpha]_D^{25}$ +41.2 (c 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.13 (s, ^{t}Bu, 9H), 2.03 (s, Ac, 3H), 2.04 (s, Ac, 3H), 2.05 (s, Ac, 3H), 2.06 (s, Ac, 3H), 3.04–3.10 (m, H-3^{Gal1}, H-6a^{Gal2}, 2H), 3.19–3.26 (m, H-6a^{Gal1}, H-6b^{Gal2}, 2H), 3.31–3.37 (m, H-6a^{Gal3}, H-6b^{Gal1}, 2H), 3.41 (dd, $J = 3.4$, 10.2 Hz, H-3^{Gal3}, 1H), 3.47–3.60 (m, H-2^{Gal3}, H-5^{Gal1}, H-6b^{Gal3}, 3H), 3.66–3.71 (m, H-2^{Gal1}, H-5^{Glc}, 2H), 3.79 (t, H-5^{Gal2}, 1H), 3.91 (dd, $J = 3.4$, 10.7 Hz,

H-2^{Gal2}, 1H), 4.04 (d, $J = 2.7$ Hz, H-4^{Gal1}, 1H), 4.06–4.19 (m, H-1^{Gal1}, H-3^{Gal2}, H-6a^{Glc}, 3H), 4.21–4.33 (m, H-6b^{Glc}, PhCH_2, 5H), 4.39 (d, $J = 11.7$ Hz, PhCH_2, 1H), 4.45–4.52 (m, H-4^{Gal2}, H-5^{Gal3}, PhCH_2, 3H), 4.66 (d, $J = 7.8$ Hz, H-1^{Gal3}, 1H), 4.72–4.82 (m, H-1^{Glc}, PhCH_2, 3H), 4.86–4.93 (m, H-2^{Glc}, PhCH_2, 2H), 5.01 (d, $J = 3.4$ Hz, H-1^{Gal3}, 1H), 5.11 (t, $J = 9.5$ Hz, H-4^{Glc}, 1H), 5.22 (t, $J = 9.5$ Hz, H-3^{Glc}, 1H), 5.57 (d, $J = 3.2$ Hz, H-4^{Gal3}, 1H), 7.17–7.50 (m, Ar, 30H), 7.69–7.74 (m, Ar, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.21, 20.43, 20.54, 20.61, 26.84, 59.84, 61.27, 63.34, 65.88, 66.70, 66.92, 68.02, 68.10, 69.15, 70.91, 70.94, 71.02, 71.14, 71.28, 71.59, 71.78, 71.86, 72.27, 72.52, 72.71, 72.97, 73.37, 73.72, 76.58, 76.88, 77.21, 78.01, 96.82, 98.78, 100.98, 101.20, 125.19, 126.97, 127.07, 127.12, 127.17, 127.29, 127.36, 127.41, 127.47, 127.54, 127.59, 127.64, 127.69, 127.73, 127.75, 127.83, 127.87, 127.91, 127.94, 127.97, 128.06, 128.11, 128.14, 128.18, 128.23, 128.30, 128.34, 128.36, 128.40, 128.45, 128.50, 128.58, 128.77, 128.92, 129.45, 129.65, 132.63, 132.65, 133.33, 135.77, 135.89, 136.94, 137.35, 137.43, 137.46, 137.49, 138.13, 156.54, 168.78, 169.10, 170.10, 170.54; MALDI-TOFMS m/z calcd for $[C_{86}H_{94}F_5N_9O_{23}Si]Na^+$: 1766.6. Found 1766.4. Anal Calcd for $C_{86}H_{94}F_5N_9O_{23}Si$: C, 59.20; H, 5.43; N, 7.22. Found: C, 59.37; H, 5.23; N, 7.17.

3.23. *tert*-Butyldiphenylsilyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2-azido-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (13)

This compound was synthesized from **12α** according to the general procedure for deprotection outlined in Section 3.16 (92%). Amorphous solid; $[\alpha]_D^{24}$ +74.6 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.10 (s, ^{t}Bu, 9H), 2.02 (s, Ac, 3H), 2.03 (s, Ac, 3H), 2.05 (s, Ac, 3H), 2.06 (s, Ac, 3H), 3.03–3.09 (m, H-3^{Gal1}, H-6a^{Gal2}, 2H), 3.25–3.30 (m, H-6b^{Gal2}, H-6^{Gal3}, 3H), 3.55–3.67 (m, H-2^{Gal1}, H-2^{Gal2}, H-2^{Gal3}, H-6a^{Gal1}, 4H), 3.71–3.77 (m, H-5^{Gal2}, H-5^{Glc}, H-6b^{Gal1}, 3H), 4.00–4.13 (m, H-3^{Gal2}, H-3^{Gal3}, H-4^{Gal1}, 3H), 4.17–4.26 (m, H-1^{Gal1}, H-4^{Gal2}, H-6^{Glc}, PhCH_2, 8H), 4.32–4.46 (m, H-4^{Gal3}, H-5^{Gal1}, H-5^{Gal3}, PhCH_2, 6H), 4.62 (d, $J = 12.2$ Hz, PhCH_2, 1H), 4.75 (d, $J = 12.9$ Hz, PhCH_2, 1H), 4.78 (d, $J = 7.8$ Hz, H-1^{Glc}, 1H), 4.94 (d, $J = 12.2$ Hz, PhCH_2, 1H), 5.03–5.12 (m, H-1^{Gal2}, H-1^{Gal3}, H-2^{Glc}, H-4^{Glc}, 4H), 5.21 (t, $J = 9.3$ Hz, H-3^{Glc}, 1H), 7.19–7.45 (m, Ar, 31H), 7.67–7.70 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.19, 20.62, 20.66, 26.77, 58.79, 59.55, 61.67, 65.81, 66.71, 67.06, 68.04, 68.08, 68.56, 69.06, 70.99, 71.23, 71.49, 71.62, 71.89, 71.99, 72.55, 72.80, 73.14, 73.27, 73.30, 74.64, 77.20, 78.33, 78.60, 78.67, 96.82, 98.61, 98.98, 101.28, 125.19, 127.07, 127.10, 127.37, 127.42, 127.55, 127.57, 127.65, 127.71, 127.76, 127.80, 127.83, 127.98, 128.12, 128.18, 128.29, 128.33, 128.38, 128.42, 128.93, 129.44, 129.66, 132.58, 133.20, 135.79, 135.93, 137.18, 137.24, 137.42, 137.44, 137.74, 169.18, 169.23, 170.06, 170.52; MALDI-TOFMS m/z calcd for $[C_{83}H_{95}N_9O_{22}Si]Na^+$: 1620.6. Found 1621.1. ESIMS m/z calcd for $[C_{83}H_{95}N_9O_{22}Si]Na^+$: 1620.6259. Found 1620.6249.

3.24. *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-D-galactopyranosyl-(1→4)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)]-2-azido-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (14a)

This compound was synthesized from **1β** and **13** according to the general procedure for glycosylation (Section 3.12) except that 2 equiv of donor was used and the mixture was stirred at 60 °C for 84 h (96%, α:β = >95:5). α-Isomer (**14a**): Syrup; $[\alpha]_D^{23}$ +216.6 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.09 (s, ^{t}Bu, 9H), 1.85 (s, Ac, 3H), 2.01 (s, Ac, 3H), 2.05 (s, Ac, 3H), 2.07 (s, Ac, 3H), 3.03–3.11 (m, H-2^{Gal4}, H-3^{Gal1}, H-6^{Gal1}, H-6^{Gal2}, 4H), 3.24–3.28 (m, H-6^{Gal1}, H-6^{Gal3}, 2H), 3.35 (dd, $J = 3.7$, 11.0 Hz, H-2^{Gal2}, 1H), 3.41 (t, $J = 9.0$ Hz, H-6^{Gal4}, 1H), 3.48 (t, $J = 9.5$ Hz, H-6^{Gal2}, 1H), 3.58–3.79 (m, H-2^{Gal1}, H-2^{Gal3}, H-5^{Gal1}, H-6^{Gal3}, H-6^{Gal4}, PhCH_2, 7H), 3.93 (dd, $J = 3.1$, 10.7 Hz, H-3^{Gal2}, 1H), 3.98 (dd, $J = 2.9$, 10.7 Hz, H-3^{Gal4}, 1H), 4.04–4.10 (m, H-3^{Gal3}, H-4^{Gal1}, 2H), 4.22 (d, $J = 7.6$ Hz, H-1^{Gal1}, 1H), 4.27–4.35 (m, H-4^{Gal2}, H-5^{Gal2}, H-6^{Glc}, PhCH_2, 5H), 4.41–4.48 (m, H-4^{Gal3}, H-5^{Gal3}, PhCH_2, 6H), 4.51 (d, $J = 10.7$ Hz, PhCH_2, 1H), 4.61 (d, $J = 12.2$ Hz, PhCH_2, 1H), 4.71–4.81 (m, H-1^{Gal4}, H-1^{Glc}, PhCH_2, 4H), 4.87–4.89 (m, H-5^{Gal4}, PhCH_2, 2H), 4.94 (d, $J = 12.2$ Hz, PhCH_2, 1H), 5.05 (d, $J = 3.7$ Hz, H-1^{Gal3}, 1H), 5.08 (d, $J = 3.7$ Hz, H-1^{Gal2}, 1H), 5.21–5.23 (m, H-2^{Glc}, H-3^{Glc}, H-4^{Glc}, 3H), 6.04 (br s, H-4^{Gal4}, 1H), 7.14–7.46 (m, Ar, 40H), 7.65–7.69 (m, Ar, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.19, 20.43, 20.61, 20.66, 20.74, 26.76, 59.18, 59.43, 60.25, 61.41, 65.62, 65.84, 66.09, 66.27, 66.37, 66.70, 68.04, 68.61, 69.01, 71.17, 71.32, 71.40, 71.53, 71.64, 71.89, 71.93, 72.53, 72.60, 72.85, 73.13, 73.25, 73.31, 73.56, 74.86, 76.61, 77.20, 78.65, 96.83, 98.55, 99.08, 102.47, 127.05, 127.07, 127.10, 127.37, 127.56, 127.68, 127.78, 127.79, 127.82, 127.84, 127.94, 128.06, 128.12, 128.15, 128.24, 128.30, 128.37, 128.39, 128.42, 128.47, 128.51, 129.46, 129.67, 132.58, 133.16, 135.79, 135.93, 136.75, 136.83, 137.11, 137.23, 137.42, 137.44, 137.48, 157.33, 169.21, 170.01, 170.28; MALDI-TOFMS m/z calcd for $[C_{106}H_{115}F_5N_{12}O_{27}Si]Na^+$: 2133.8. Found 2133.8. Anal Calcd for $C_{106}H_{115}F_5N_{12}O_{27}Si$: C, 60.28; H, 5.49; N, 7.96. Found: C, 60.29; H, 5.25; N, 7.77.

3.25. *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)]-2-azido-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (14b)

This compound was synthesized from **14a** according to the general procedure for deprotection outlined in Section 3.16 (quantitative): Amorphous solid; $[\alpha]_D^{25}$ +136.0 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.10 (s, ^{t}Bu, 9H), 1.82 (s, Ac, 3H), 1.98 (s, Ac, 3H), 2.04 (s, Ac, 3H), 2.07 (s, Ac, 3H), 3.03–3.09 (m, H-3^{Gal1}, H-6^{Gal1}, OH, 3H), 3.17 (dd, $J = 5.1$, 8.5 Hz, H-6^{Gal2}, 1H), 3.25–3.29 (m, H-6^{Gal1}, H-6^{Gal3}, 2H), 3.43 (dd, $J = 3.7$, 11.0 Hz, H-2^{Gal2}, 1H), 3.51 (dd, $J = 3.7$, 10.5 Hz, H-2^{Gal4}, 1H), 3.55–3.81 (m, H-2^{Gal1}, H-2^{Gal3}, H-5^{Gal1}, H-5^{Glc}, H-6^{Gal3}, 6H), 3.87–3.97 (m, H-3^{Gal2}, H-3^{Gal4}, H-6^{Gal4}, PhCH_2, 5H), 4.03–4.07 (m, H-3^{Gal3}, H-4^{Gal1}, PhCH_2, 3H), 4.11–4.18 (m, PhCH_2, 2H), 4.22 (d, $J = 7.6$ Hz, H-1^{Gal1}, 1H), 4.25–4.26 (m, H-6^{Glc}, 2H), 4.32–4.46 (m, H-4^{Gal2}, H-4^{Gal3}, H-4^{Gal4}, H-5^{Gal2}, H-5^{Gal3}, PhCH_2, 7H), 4.55–4.80 (m, H-1^{Glc}, H-5^{Gal4}, PhCH_2, 7H), 4.87 (d, $J = 12.2$ Hz, PhCH_2, 1H), 4.92–4.95 (m, H-1^{Gal4}, PhCH_2, 2H), 5.05 (d, $J = 3.7$ Hz, H-1^{Gal3}, 1H), 5.12 (d, $J = 3.7$ Hz, H-1^{Gal2}, 1H), 5.17–5.24 (m, H-2^{Glc}, H-3^{Glc}, H-4^{Glc}, 3H), 7.15–7.46 (m, Ar, 40H), 7.66–7.69 (m, Ar, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.17, 20.38, 20.61, 20.66, 20.70, 26.75, 59.07, 59.38, 60.27, 61.51, 65.76, 65.81, 66.20, 66.42, 66.70, 67.91, 68.16, 68.51, 68.82, 69.02, 71.08, 71.22, 71.51, 71.56, 71.65, 71.88, 72.53, 72.75, 72.92, 73.22, 73.30, 73.49, 74.67, 75.37, 76.84, 77.21, 78.62, 96.82, 97.44, 98.55, 99.05, 102.49, 127.06, 127.08, 127.15, 127.25, 127.35, 127.38, 127.65, 127.68, 127.77, 127.81, 127.85, 128.05, 128.08, 128.12, 128.27, 128.31, 128.34, 128.38, 128.48, 128.59, 129.44, 129.66, 132.57, 133.15, 135.77, 135.91, 137.11, 137.17, 137.34, 137.39, 137.44, 138.27, 169.12, 169.20, 170.05, 170.39; MALDI-TOFMS *m*/*z* calcd for $[C_{103}H_{116}N_{12}O_{26}Si]Na^+$: 1987.8. Found 1988.4. ESIMS *m*/*z* calcd for $[C_{103}H_{116}N_{12}O_{26}Si]Na^+$: 1987.7791. Found 1987.7720.

3.26. *tert*-Butyldiphenylsilyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-pentafluoropropionyl-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-[2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→3)]-2-azido-6-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-galactopyranosyl-(1→4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-β-D-galactopyranoside (14c)

This compound was synthesized from **1β** and **14B** according to the general procedure for glycosylation (Section 3.12) except that 2 equiv of donor was used and that the mixture was stirred at 60 °C for 84 h (88%, α:β = >95:5). Compound **14c**: Syrup; $[\alpha]_D^{25}$ +141.3 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz): δ 1.09 (s, ^{t}Bu, 9H), 1.80 (s, Ac, 3H), 2.04 (s, Ac, 3H), 2.07 (s, Ac, 3H), 2.09 (s, Ac, 3H), 2.98–3.11 (m, H-3^{Gal1}, H-6, 3H), 3.13–3.20 (m, H-2^{Gal5}, H-6, 3H), 3.21–3.28 (m, H-6, 2H), 3.32–3.38 (m, H-1, H-2, 2H), 3.52–3.84 (m, H-2, H-5, H-6, 7H), 3.86–3.97 (m, H-3, PhCH_2, 5H), 4.00–4.09 (m, H-3, H-4, H-6, PhCH_2, 5H), 4.09–4.15 (m, PhCH_2, 2H), 4.21 (d, $J = 7.8$ Hz, H-1^{Gal1}, 1H), 4.31–4.36 (m, H-5^{Glc}, H-6^{Glc}, PhCH_2, 4H), 4.39–4.49 (m, H-4, H-5, PhCH_2, 7H), 4.52–4.64 (m, H-5, PhCH_2, 4H), 4.69–4.79 (m, H-1^{Gal5}, H-1^{Glc}, PhCH_2, 4H), 4.89–4.92 (m, PhCH_2, 3H), 4.94 (d, $J = 3.4$ Hz, H-1, 1H), 5.01 (d, $J = 12.0$ Hz, PhCH_2, 1H), 5.05 (d, $J = 3.7$ Hz, H-1^{Gal1}, 1H), 5.09 (d, $J = 3.9$ Hz, H-1^{Gal1}, 1H), 5.22–5.32 (m, H-2^{Glc}, H-3^{Glc}, H-4^{Glc}, 3H), 5.78 (d, $J = 2.2$ Hz, H-4^{Gal5}, 1H), 7.09–7.52 (m, Ar, 51H), 7.66–7.69 (m, Ar, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.20, 20.36, 20.60, 20.66, 20.75, 26.78, 59.40, 60.24, 61.37, 65.84, 66.33, 66.48, 66.53, 66.72, 67.98, 68.72, 68.74, 69.03, 71.00, 71.22, 71.29, 71.48, 71.50, 71.56, 71.93, 72.43, 72.55, 72.76, 72.78, 73.21, 73.25, 73.33, 74.09, 74.56, 75.02, 76.93, 77.21, 78.67, 96.84, 97.45, 98.14, 98.52, 99.08, 102.62, 125.21, 127.05, 127.08, 127.10, 127.21, 127.23, 127.38, 127.53, 127.66, 127.69, 127.71, 127.79, 127.81, 127.84, 128.06, 128.12, 128.15, 128.17, 128.25, 128.26, 128.29, 128.38, 128.48, 128.52, 128.94, 129.47, 129.68, 132.60, 133.17, 135.80, 135.94, 136.48, 137.09, 137.12, 137.19, 137.23, 137.43, 137.47, 137.62, 137.69, 169.24, 170.01, 170.36; MALDI-TOFMS *m*/*z* calcd for $[C_{126}H_{136}F_5N_{15}O_{31}Si]Na^+$: 2500.9. Found 2501.5. ESIMS *m*/*z* calcd for $[C_{126}H_{136}F_5N_{15}O_{31}Si]Na^+$: 2500.9114. Found 2500.9196.

3.27. *tert*-Butyldiphenylsilyl 2-acetamido-2-deoxy-α-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-α-D-galactopyranosyl-(1→4)-[(β-D-glucopyranosyl)-(1→3)]-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→4)-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-galactopyranoside (15)

To a solution of **14c** (11.0 mg, 4.44 μmol) in CH_3OH/*i*-PrOH (2.5 mL, 4:1), 1 M solution of $NaOCH_3$ (50 μL) was added at rt. After stirring for 2 h at the same temperature, Amberlist H^+ resin was added to the mixture to quench excess $NaOCH_3$. The resin was filtered and the solution was concentrated. The crude mixture was then dissolved in CH_3OH (2 mL) and diisopropylethylamine (2.0 μL) was added at rt under an Ar atmosphere. The solution was stirred with $Pd(OH)_2$/C (20%, 5.5 mg) under a hydrogen atmosphere at rt for 1 h. After the atmosphere was exchanged to Ar, the catalyst was filtered off through Celite and concentrated to the half volume. To the solution, Ac_2O (50 μL) was added at rt, and the mixture was stirred for 30 min at the same temperature. The mixture was concentrated in vacuo

and diluted in $CHCl_3/CH_3OH/H_2O$ (5 mL, 2:2:1). The solution was stirred with $Pd(OH)_2/C$ (20%, 5.0 mg) under a hydrogen atmosphere at rt for 48 h. After exchanging to an Ar atmosphere, the catalyst was filtered through Celite and concentrated. To the solution of the crude mixture in CH_3OH (2 mL), Ac_2O (100 μL) was added at rt, and the mixture was stirred for 12 h at the same temperature. Ac_2O (100 μL) and $NaHCO_3$ (50.0 mg) were added to the mixture. The mixture was concentrated in vacuo and diluted in $CHCl_3/CH_3OH/H_2O$ (5 mL, 2:2:1). The solution was stirred with $Pd(OH)_2/C$ (20%, 5.0 mg) under hydrogen atmosphere at rt for 24 h. After exchanging to an Ar atmosphere, the catalyst was filtered through Celite and concentrated. The residue was purified by reversed phase column chromatography (Sep-Pac, C_{18}) using gradient solvent system (H_2O–MeOH, 1:0 to 0:1) to give the title compound as an amorphous solid (2.8 mg, 44% in four steps from **14c**); ^1H NMR (CD_3OD/D_2O, at 50 °C, 400 MHz): δ 1.01 (s, ^{t}Bu, 9H), 1.88 (s, AcNH, 3H), 2.03 (s, AcNH × 2, 6H), 2.047 (s, AcNH, 3H), 2.049 (s, AcNH, 3H), 3.25–3.90 (m, 16H), 3.92–4.02 (m, H-3^{Gal4}, H-4^{Gal1}, H-4^{Gal4}, 3H), 4.06–4.16 (m, H-1^{Gal1}, H-3^{Gal2}, H-3^{Gal3}, H-3^{Gal5}, H-4^{Gal13}, H-4^{Gal5}, 6H), 4.24–4.36 (m, H-2^{Gal3}, H-2^{Gal4}, H-2^{Gal5}, H-4^{Gal2}, 4H), 4.30–4.54 (m, 5H), 4.52 (d, $J = 7.2$ Hz, H-1^{Glc}, 1H), 4.54–4.58 (m, H-2^{Gal2}, 1H), 4.62 (d, $J = 8.0$ Hz, H-1^{Gal1}, 1H), 5.01 (d, $J = 4.0$ Hz, H-1^{Gal2}, 1H), 5.02 (d, $J = 4.0$ Hz, H-1^{Gal3}, 1H), 5.04 (d, $J = 4.0$ Hz, H-1^{Gal4}, 1H), 5.12 (d, $J = 4.0$ Hz, H-1^{Gal1}, 1H), 7.38–7.74 (m, TBPS, 10H); MALDI-TOFMS m/z calcd for $[C_{62}H_{95}N_5O_{31}Si]Na^+$: 1456.6. Found 1457.5. ESIMS m/z calcd for $[C_{62}H_{95}N_5O_{31}Si]Na^+$: 1456.5678. Found 1456.5620.

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