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Studies on the sialylation of galactoses with different *C*-5 modified sialyl donors

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ABSTRACT

Synthetic sialylated glycans provide useful tools to study carbohydrate-mediated biological recognition; however chemical sialylation is the most challenging practice in preparative carbohydrate chemistry, which is often associated with low yields and poor stereoselectivity. Herein, we conducted extensive studies on sialylation with five types of 5-N-modified sialyl donors and four types of galactosyl acceptors. Our studies have shown that a good combination between the donor and the acceptor seems necessary to achieve high yield and stereoselectivity. None of the donors or acceptors showed 'universal' utility toward the sialylation reaction.

1. Introduction

Sialic acids (Neu5Ac, *N*-acetyl-neuraminic acid) are present in many cell-surfaced glycoconjugates and secreted glycoproteins. They are involved in many cellular events, such as viral infection, inflammation and cell-cell adhesion.[1] Sialic acids reside in the termini of glycans and they serve as the essential determinant for glycan–protein interactions. Thus, synthetic homogeneous sialic acid-containing glycans are valuable tools to unravel the glycan's cellular functions.[2] Naturally occurring glycosidic linkage between sialic acids and other sugars is via α orientation. Synthetically, the glycosylation that involves a sialic acid donor is the most challenging practice in preparative carbohydrate chemistry, often with low yields and poor selectivity.[3] The electron-withdrawing property of the carboxylate groups at the anomeric position destabilizes the oxocarbonium ion glycosyl intermediate generated from glycosylation, thereby challenging the coupling reaction. In addition, the glycal derived from the elimination reaction is often the significant byproduct.[4] On the other hand, the stereoselectivity of the coupling product is difficult to control, due to the lack of a directing group at the adjacent position (*C*-3) (Fig. 1).

Over the past decades, many advances have been developed to improve the stereoselectivity and coupling efficiency.[3a] Researchers have extensively studied the effect of the leaving group of the sialic acid donor on glycosylation,[3b] and temporary directing groups (i.e., I, SPh) have been introduced to enhance the stereoselectivity.[5] More recently, it has been observed that the nature of the 5-N-protecting group, other than 5-*N*-acetamido (5-NHAc), can greatly influence the sialylation efficiency, including yields and stereoselectivity.[6]

For a research program toward the development of a practical synthesis of *N*-glycan structures, we started to evaluate the various sialic acid donors with *C*-5 modifications and different acceptors. The *N*-glycan present on glycoproteins via the asparagine side chain is important for correct protein folding and also mediates many cellular events.[7] The most common motif in *N*-glycan structures is that sialic acid is linked to a galactose via 2,6- or 2,3-linkage, thus our studies have been focused on searching for the best combination of the sialic acid donor and the galactosyl acceptor to produce Neu5Ac-α-(2,3)-Gal and Neu5Ac-α-(2,6)-Gal disaccharides (Fig. 2).

2. Results and discussion

The synthesis of sialyl donors is straightforward. We used *p*-toluenethiosialoside as the sialyl donor due to their easy preparation and stability,[8] and four sialyl donors varying at the 5-N-protecting groups (**D1**, **D2**, **D3**, and **D5**) were chosen. Recently, Wong and Wu's group reported a highly α-selective sialyl phosphate donor,[9] so we also synthesized a sialyl donor of this type (**D4**). The preparation of sialyl donors is shown in Scheme 1. The Neu5Ac thioglycoside **D1**[10] was converted into **1** by acidolysis. Acylation of **1** with methyl trifluoroacetate, and 4-nitrophenylchloroformate produced **2**,[11] and **3**,[12] respectively, while the azido transfer reaction with imidazole-1-sulfonyl azide hydrochloride gave **4**.[13] After O-acetylation with acetic anhydride and pyridine, 5-trifluoroacetamido sialyl donor **D2**,[11] and 5-azido sialyl donor **D5**,[13] were obtained in high yields. The *O*-acetylated sialoside intermediate **5**[12] was easily converted to *N*-acetyl-5-*N*,4-*O*-carbonyl-protected sialyl donor **D3**[12] and phosphate donor **D4**[9] via N-acetylation with acetyl chloride in the presence of Hunig's base and glycosylated with dibutyl phosphate promoted by *N*-iodosuccinimide (NIS) and triflic acid (TfOH), respectively.

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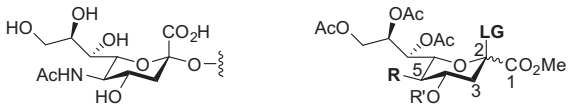


Figure 1. Naturally occurring sialic acid and sialyl donor for the chemical synthesis.

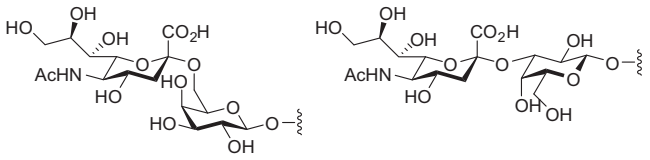
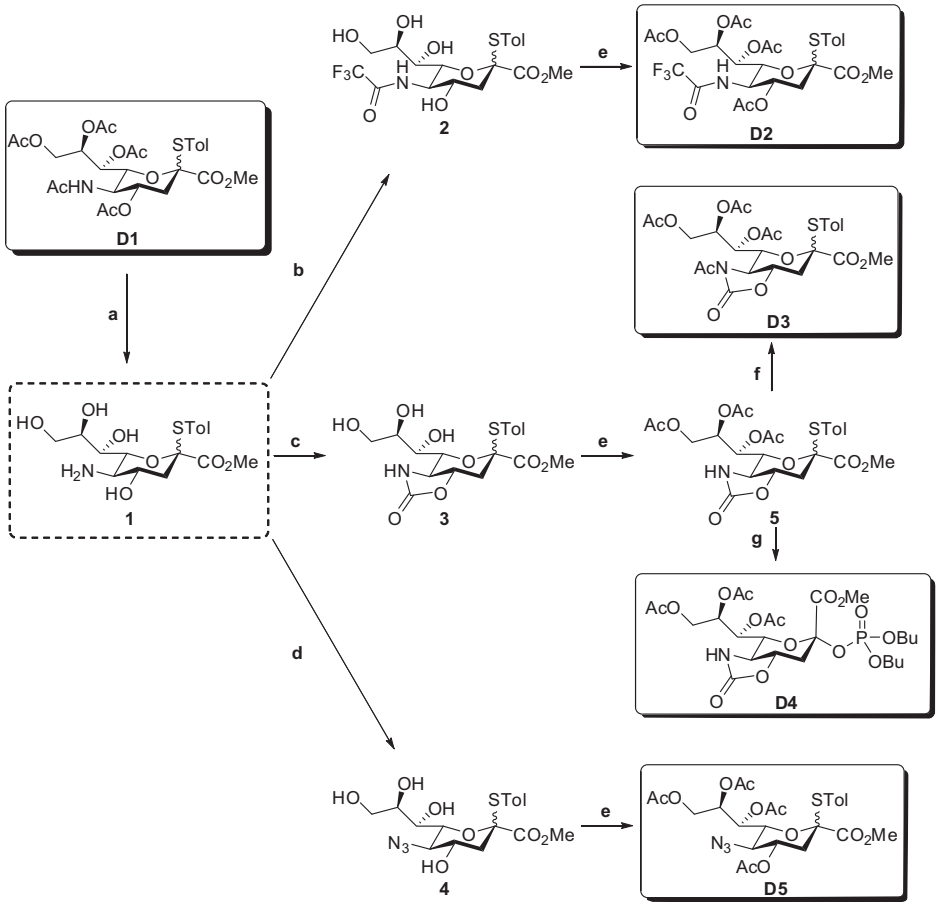


Figure 2. Neu5Ac-α-Gal components present in the *N*-glycan structures.

In addition, we have prepared, according to the literature protocol,[14–16] various galactosyl acceptors, **A1**–**A4**, including 3-OH and 6-OH building blocks. The 4-methoxyphenyl (MP) and 2-(trimethylsilyl)ethyl (TMSE) groups are selected for the temporary anomeric hydroxyl protecting groups, because they could be readily removed and modified for further elongation.[17,18] For the elongation of the resultant sialyl disaccharide to synthesize sialic acid-LacNAc, the glucosamine derivative **A5**[19] was also prepared as the acceptor (Fig. 3).

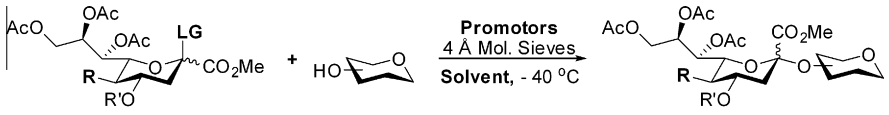
The glycosylations were performed under standard conditions. The sialyl donors and galactosyl acceptors were first mixed together with 4 Å molecular sieves and solvent (MeCN or MeCN/CH_2Cl_2), and then activated with 2.0 equiv NIS and catalytic amount of 0.20 equiv TfOH (0.30 equiv TMSOTf for **D4**), which were performed at −40 °C. After the same reaction time (1 h), the sialylation process was quenched, followed by a simple work-up. The α/β ratio of desired disaccharide was determined by ^{1}H NMR analysis of the crude reaction mixture. The configurations of the newly formed glycosidic bond of disaccharides were assigned by the long-range $^3J_{C\text{-}1,\ H\text{-}3ax}$ coupling constant.[20]

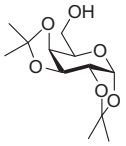
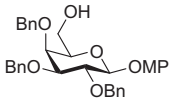
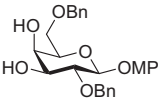
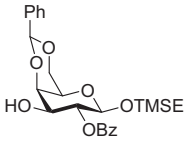
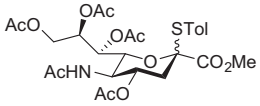
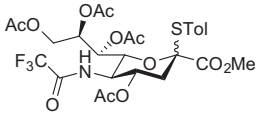
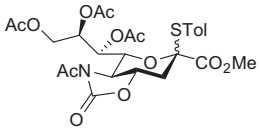
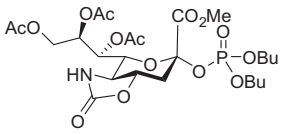
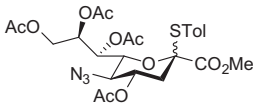
As shown in Table 1, when glycosylating with 6-OH of **A1** and **A2**, *C*-5 unmodified sialyl donor **D1** gave sialosides in good yields (83% and 86%) but with low stereoselectivity (2.4:1 and 3:1). When **D1** reacted with 3-OH of **A3** and **A4**, much lower yields (51% and 34%) were obtained with good selectivity (α only). The similar results were reported by Ito, Ando, Kiso, and Kasegawa.[22,23] When an excess amount (1.2–2.0 equiv) of donor **D1** was employed, the sialylation yield could be a little higher. In contrast with **D1**, 5-trifluoroacetamido sialyl donor **D2** gave much better stereoselectivity when reacting with 6-OH acceptors. Both **D1** and **D2** suffered from the generation of the sialyl glycal, which reduced the yield significantly. *N*-Acetyl-5-*N*,4-*O*-carbonyl-protected sialyl donor **D3** and phosphate donor **D4** can be coupled to both primary and secondary hydroxyl groups in moderate to high yields (77–99% vs 55–98%), but the glycosylation lost the stereoselectivity for 3-OH of **A3** and **A4**. This behavioral difference of **D3** was also observed by Crich and Xing.[12,26] The sialyl donor **D4** without the *N*-acetyl group is different from that phosphate donor Wong and Wu used for model studies.[9a] The reaction temperature (−40 °C) was in accord with the sialylation condition of the other four donors, but it is much higher than the reported ones (−78 °C for model study and



Scheme 1. Preparation of sialyl donors (**D1**–**D5**). Reagents and conditions: (a) MsOH, MeOH, reflux; (b) CF_3CO_2Me, Et_3N, MeOH; (c) 4-nitrophenylchloroformate, $NaHCO_3$, $MeCN/H_2O$, 0 °C; (d) imidazole-1-sulfonyl azide hydrochloride, K_2CO_3, $CuSO_4{\cdot}5H_2O$, MeOH; (e) Ac_2O, pyridine; (f) AcCl, DIPEA, CH_2Cl_2, 0 °C; (g) dibutyl phosphate, *N*-iodosuccinimide, TfOH, molecular sieves (4 Å), CH_2Cl_2, 0 °C. Overall yields (from **D1**): **D2** (85%), **D3** (46%), **D4** (36%), **D5** (67%).

Table 1
Sialylation results[a]



Disaccharide yield (%)[b]; α/β (x:1)[c] glycal yield (%)				
	D1A1[d,21] 83; 2.4:1 16	D1A2[d] 86; 3:1 10	D1A3[d,22] **51**; **α only** 30	D1A4[d,23] 34; α only 40
	D2A1[24] 95; 5:1 None[g]	D2A2 63; >10:1 10	D2A3 17; 8.3:1 32	D2A4[25] **68**; **4.5**:**1** 24
	D3A1[e,26] **99**; **α only** None[g]	D3A2[e] **77**; >**10**:**1** None[g]	D3A3[e] 79; 0.6:1 None[g]	D3A4[e] 77; 0.8:1 None[g]
	D4A1[f,27] **98**; **α only** None[g]	D4A2[f] **93**; **α only** None[g]	D4A3[f] 55; 2.8:1 None[g]	D4A4[f] 69; 3.3:1
	D5A1 99; 5:1 None[g]	D5A2 87; 1.7:1 5	D5A3 81; 2.5:1 12	D5A4 71; 1.1: 1 24

[a] General condition: donor/acceptor (1:1, M/M), 4 Å MS, MeCN, −40 °C, 2.0 equiv NIS, 0.20 equiv TfOH. The results from optimized donor/acceptor combinations are highlighted in bold form.
[b] Isolated yields.
[c] Determined by ^{1}H NMR analysis of the crude reaction mixture.
[d] 1.0 equiv TfOH (the reaction with 0.20 equiv TfOH gave no product).
[e] Reaction solvent: CH_2Cl_2/MeCN (3:2, v/v).
[f] Reaction solvent: CH_2Cl_2/MeCN (2:1, v/v); 0.30 equiv trimethylsilyl triflate (TMSOTf).
[g] Not detected from crude ^{1}H NMR analysis.

−60 °C for α(2,9) polysialic acid).[9] The different reaction temperature may account for the low selectivity of **D4** toward the secondary hydroxyl of **A3** and **A4**. The stereoselectivity of the 5-azido sialyl donor **D5** in glycosylating the selected acceptors is rather poor.

A good combination between the donor and the acceptor seems necessary to achieve high yield and selectivity. None of the donors or acceptors showed 'universal' reactivity toward sialylation reactions.

For the synthesis of Neu5Ac-α-(2,6)-Gal disaccharides, the combination of **D3** or **D4** with **A1** gave a much better yield (99% with only α isomer), while the disaccharide **D3A1** is hard for further elongation. **D4** can be glycosylated with **A2** to afford a Neu5Ac-α-(2,6)-Gal disaccharide **D4A2** in 93% yield with only α-sialoside. Furthermore, the anomeric MP group of the resultant disaccharide can be removed and subjected to further elongation.

For the synthesis of Neu5Ac-α-(2,3)-Gal disaccharides, the combination of **D2** and **A4** gave a relatively better overall yield (68% with α-sialoside preferred). Disaccharide **D2A4** will be an important substrate for the synthesis of a more complex sialylated glycan, since its anomeric TMSE group can be readily removed and modified into glycosyl trichloroacetimidates (TCA) and the benzoyl (Bz) group at *C*-2 position can ensure the *trans*-β-linkage formation for the elongating glycosylation.

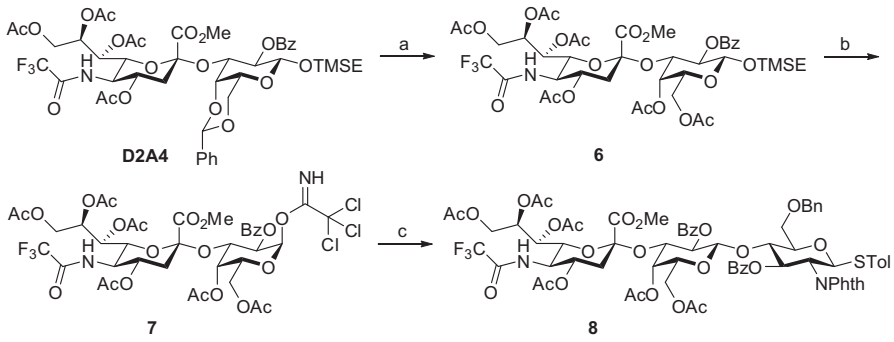
With **D2A4** in hand, we first converted 4,6-benzylidene to acetyl groups, which were more stable under anomeric TMSE cleavage conditions. After TCA donor was synthesized, it was coupled with glucosamine acceptor **A5** to afford *trans*-β-linkage of trisaccharide exclusively, which is the precursor of natural 3'-sialyl-*N*-acetyllactosamine (Scheme 2).

In summary, we have comparably studied the sialylation with five types of 5-N-modified sialyl donors and four types of galactosyl acceptors. It was observed that the matching partner of the sialyl donor and the galatosyl acceptor is critical to afford Neu5Ac-α-Gal disaccharide in high yield and good selectivity. The combination, **D3**/**A1** and **D4**/**A2** gave the best glycosylation to produce Neu5Ac-α-(2,6)-Gal disaccharides, while **D1**/**A3** and **D2**/**A4** produced Neu5Ac-α-(2,3)-Gal disaccharides in a reasonable yield. The utility of TMSE at the reducing end would enable the transformation into TCA donors for further elongation toward the synthesis of the full *N*-glycan structure.

3. Experimental

3.1. General

^{1}H and ^{13}C NMR ($CDCl_3$) spectral analyses were performed on a Bruker 400 NMR spectrometer at room temperature using TMS as



Scheme 2. Preparation of trisaccharide (**8**). Reagents and conditions: (a) 60% HOAc, 70 °C; then Ac_2O, pyridine (88%); (b) boron trifluoride etherate ($BF_3{\cdot}OEt_2$), CH_2Cl_2, 0 °C; then trichloroacetonitrile, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), CH_2Cl_2, 0 °C (70%); (c) **A5**, TMSOTf, 4 Å Mol. Sieves, MeCN, −40 °C (57%).

an internal standard. High resolution electrospray ionization mass spectrometry (ESI-HRMS, positive mode, ion-source acceleration 4.5 kV, ion-source temperature 275 °C, sheath gas flow rate was 6 (arb. unit), methanol as solvent) mass spectra were recorded with a LTQ Orbitrap Velos spectrometer from Thermo Scientific. Analytical TLC was performed on Kieselgel 60 F_{254} (Merck). Column chromatographic purification was carried out using Kieselgel 60 (230–400 mesh, Merck). Commercial reagents were used as received, unless otherwise indicated. Molecular sieves were freshly activated under high vacuum by flame. Dichloromethane (CH_2Cl_2) was freshly distilled from calcium hydride (CaH_2). All reagents were of analytical reagent grade.

3.2. General procedure for sialylation of sialyl donors (D1–D5) with galactosyl acceptors (A1–A4)

A mixture of sialyl donor (**D1**–**D5**, 1.0 equiv), galactosyl acceptor (**A1**–**A4**, 1.0 equiv) and activated 4 Å molecular sieves (2.0 g/mmol) in dry MeCN (for **D1**, **D2** and **D5**) or CH_2Cl_2/MeCN (2:1, v/v, for **D3**) or CH_2Cl_2/MeCN (3:2, v/v, for **D4**), making the final concentration 50 mM, was stirred under argon atmosphere at room temperature for 1 h to remove any trace amounts of water. The reaction mixture was then cooled to −40 °C (MeCN in liquid N_2). *N*-Iodosuccinimide (2.0 equiv) was added followed by catalytic amount of triflic acid (0.20 equiv) to promote the sialylation process (0.30 equiv TMSOTf for **D4**). After being stirred at −40 °C for 1 h, the mixture was quenched with triethylamine, diluted with CH_2Cl_2, and filtered through a pad of Celite. The resulting filtrate was washed with 1 M aqueous $Na_2S_2O_3$ solution, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The α/β ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. The residue was purified by column chromatography on silica gel with toluene/acetone or hexane/EtOAc as eluent to give the respective disaccharide.

The disaccharides **D1A1**, **D1A3**, **D1A4**, **D2A1**, **D2A4**, **D3A1**, and **D4A1** were known compounds. The ^{1}H and ^{13}C NMR data have good consistence with those reported in references.[21–27] Following are the NMR and HRMS data for all new disaccharides.

3.2.1. Methyl 4,7,8,9-tetra-*O*-acetyl-5-azido-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2→6)-1,2;3,4-di-*O*-isopropylidene-α-galacotopyranoside (D5A1α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.49–5.52 (m, 2H), 5.37–5.41 (m, 1H), 4.83 (ddd, J = 4.7, 9.7, 14.4 Hz 1H), 4.58 (dd, J = 2.4, 7.9 Hz, 1H), 4.24–4.33 (m, 2H), 4.27 (d, J = 4.0 Hz, 1H), 4.20 (dd, J = 1.5, 7.9 Hz, 1H), 3.80–3.88 (m, 3H), 3.78 (s, 3H), 3.55 (dd, J = 6.4, 8.9 Hz, 1H), 3.22 (t, J = 10.2 Hz, 1H), 2.74 (dd, J = 4.8, 12.8 Hz, 1H), 2.18 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 1.78 (t, J = 12.5 Hz, 1H), 1.54 (s, 3H), 1.42 (s, 3H), 1.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.9, 170.0, 169.85, 169.81, 167.8 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 5.8 Hz), 109.4, 108.7, 98.5, 96.4, 71.7, 71.3, 70.8, 70.73, 70.70, 68.3, 68.0, 66.6, 63.3, 61.9, 60.1, 52.9, 37.4, 26.2, 26.1, 25.0, 24.8, 21.1, 21.0, 20.9. ESI-HRMS: Calcd for $C_{30}H_{47}N_4O_{17}$ $[M+NH_4]^+$: 735.2931. Found: 735.2941.

3.2.1.1. Methyl 4,7,8,9-tetra-*O*-acetyl-5-azido-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylonate-(2→6)-1,2;3,4-di-*O*-isopropylidene-α-galacotopyranoside (D5A1β).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.61 (dd, J = 1.7, 4.8 Hz, 1H), 5.47 (d, J = 5.0 Hz, 1H), 5.24–5.32 (m, 1H), 4.70 (dd, J = 2.3, 12.6 Hz, 1H), 4.63 (dd, J = 2.2, 8.1 Hz, 1H), 4.34 (dd, J = 1.6, 8.1 Hz, 1H), 4.24–4.31 (m, 2H), 4.06 (dd, J = 1.6, 10.4 Hz, 1H), 3.98–4.01 (m, 1H), 3.80 (s, 3H), 3.54 (t, J = 8.8 Hz, 1H), 3.47 (dd, J = 5.8, 8.3 Hz, 1H), 3.21 (t, J = 10.1 Hz, 1H), 2.60 (dd, J = 5.0, 12.9 Hz, 1H), 2.20 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.04 (s, 6H), 1.70 (dd, J = 11.7, 12.6 Hz, 1H), 1.55 (s, 3H), 1.48 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8, 170.3, 170.1, 169.8, 167.0 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 0 Hz), 109.5, 108.8, 98.1, 96.2, 71.6, 70.9, 70.7, 70.6, 70.4, 70.2, 69.3, 65.4, 62.4, 61.5, 60.2, 53.0, 36.8, 26.3, 25.9, 25.0, 24.1, 21.13, 21.11, 20.95, 20.88. ESI-HRMS: Calcd for $C_{30}H_{44}N_3O_{17}$ $[M+H]^+$: 718.2665. Found: 718.2667.

3.2.2. 4-Methoxyphenyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2→6)-2,3,4-tri-*O*-benzyl-β-galacotopyranoside (D1A2α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.39 (m, 15H), 7.07–7.09 (m, 2H), 6.79–6.82 (m, 2H), 5.35–5.39 (m, 1H), 5.29 (dd, J = 1.9, 8.1 Hz, 1H), 5.12 (d, J = 9.4 Hz, 1H), 4.97–5.02 (m, 2H), 4.67–4.90 (m, 7H), 4.30 (dd, J = 2.6, 12.4 Hz, 1H), 4.04–4.12 (m, 4H), 3.95 (d, J = 2.6 Hz, 1H), 3.90 (dd, J = 6.1, 9.4 Hz, 1H), 3.77 (s, 3H), 3.70 (t, J = 6.8 Hz, 1H), 3.66 (s, 3H), 3.63 (dd, J = 2.9, 9.8 Hz, 1H), 3.58 (dd, J = 7.6, 9.3 Hz, 1H), 2.58 (dd, J = 4.7, 12.8 Hz, 1H), 2.13 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 1.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 170.8, 170.4, 170.3, 170.0, 168.2 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 5.6 Hz), 155.2, 151.9, 139.0, 138.8, 138.6, 128.5, 128.43, 128.37, 128.28, 127.9, 127.7, 127.6, 127.5, 118.6, 114.6, 103.1, 99.0, 82.3, 79.4, 75.5, 73.4, 73.2, 73.0, 72.8, 69.1, 68.8, 67.5, 63.2, 62.6, 55.8, 53.0, 49.6, 38.0, 23.4, 21.2, 21.0, 20.9, 20.8. ESI-HRMS: Calcd for $C_{54}H_{64}NO_{19}$ $[M+H]^+$: 1030.4067. Found: 1030.4118.

3.2.2.1. 4-Methoxyphenyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylonate-(2→6)-2,3,4-tri-*O*-benzyl-β-galacotopyranoside (D1A2β).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.53 (m, 15H), 7.02–7.05 (m, 2H), 6.84–6.86 (m, 2H), 5.43–5.46 (m, 1H), 5.19–5.23 (m, 1H), 5.12 (dd, J = 2.2, 6.4 Hz, 1H), 4.97–5.02 (m, 2H), 4.68–4.90 (m, 7H), 4.57 (dd, J = 2.5, 12.5 Hz, 1H), 3.86–4.12 (m, 6H), 3.78 (s, 3H), 3.77 (s, 3H), 3.68–3.71 (m, 1H), 3.56–3.64 (m, 2H), 2.30 (dd, J = 4.8, 12.8 Hz, 1H), 2.17 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.71 (s, 3H); ^{13}C NMR ($CDCl_3$,

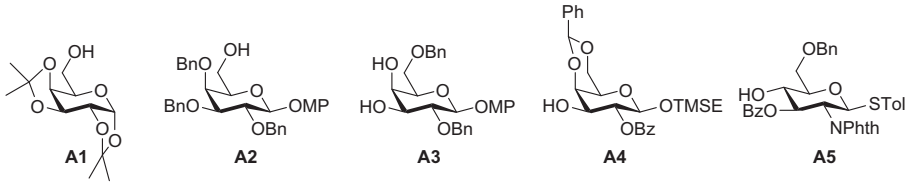


Figure 3. Galactosyl acceptors **A1**–**A4** and glucosamine acceptor **A5** used in the study (MP = 4-methoxyphenyl, TMSE = 2-(trimethylsilyl)ethyl, STol = 4-methylphenylthio, Phth = phthalimido).

100 MHz): δ 170.71, 170.68, 170.4, 170.2, 170.0, 167.7 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 0 Hz), 155.4, 151.7, 140.0, 138.6, 138.3, 128.4, 128.2, 127.8, 127.76, 127.75, 127.4, 127.1, 126.3, 118.8, 114.6, 103.4, 99.0, 82.1, 79.4, 75.6, 74.8, 74.1, 73.3, 72.2, 71.7, 70.6, 68.9, 67.2, 62.1, 62.0, 53.1, 52.9, 48.3, 37.2, 23.3, 23.1, 21.4, 20.9, 20.8. ESI-HRMS: Calcd for $C_{54}H_{64}NO_{19}$ $[M+H]^+$: 1030.4067. Found: 1030.4090.

3.2.3. 4-Methoxyphenyl (methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-trifluoroacetamido-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2→6)- 2,3,4-tri-*O*-benzyl-β-galacotopyranoside (D2A2α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26–7.38 (m, 15H), 7.07–7.09 (m, 2H), 6.78–6.83 (m, 2H), 6.55 (d, J = 9.8 Hz, 1H), 5.33–5.37 (m, 1H), 5.26 (dd, J = 2.1, 7.8 Hz, 1H), 4.98–5.05 (m, 3H), 4.67–4.89 (m, 5H), 4.32 (dd, J = 2.5, 12.5 Hz, 1H), 4.26 (dd, J = 2.0, 10.7 Hz, 1H), 4.05–4.12 (m, 2H), 3.90–4.01 (m, 3H), 3.77 (s, 3H), 3.66 (s, 3H), 3.65–3.70 (m, 1H), 3.62 (dd, J = 2.8, 9.8 Hz, 1H), 3.55 (dd, J = 7.1, 9.3 Hz, 1H), 2.62 (dd, J = 4.8, 13.0 Hz, 1H), 2.13 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.96 (s, 3H), 1.96 (t, J = 10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.0, 170.8, 170.2, 170.1, 167.9 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 6.0 Hz), 157.9, 157.5, 155.3, 151.9, 138.9, 138.7, 138.6, 128.52, 128.48, 128.36, 128.29, 127.9, 127.8, 127.6, 127.5, 118.6, 114.6, 103.2, 98.9, 82.2, 79.4, 75.5, 73.4, 73.2, 73.1, 71.9, 69.0, 68.4, 67.4, 63.4, 62.3, 55.8, 53.1, 50.4, 37.8, 21.2, 20.75, 20.73, 20.70. ESI-HRMS: Calcd for $C_{54}H_{64}F_3N_2O_{19}$ $[M+NH_4]^+$: 1101.4050. Found: 1101.4069.

3.2.4. 4-Methoxyphenyl (methyl 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→6)-2,3,4-tri-*O*-benzyl-β-D-galacotopyranoside (D3A2α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.41 (m, 15H), 7.05–7.07 (m, 2H), 6.78–6.81 (m, 2H), 5.55 (dd, J = 1.6, 7.4 Hz, 1H), 5.40 (dt, J = 3.2, 7.0 Hz, 1H), 4.99–5.02 (m, 2H), 4.70–4.89 (m, 6H), 4.57 (dd, J = 1.7, 9.4 Hz, 1H), 4.33 (dd, J = 3.0, 12.3 Hz, 1H), 4.01–4.10 (m, 3H), 3.92–3.98 (m, 3H), 3.76 (s, 3H), 3.67 (s, 3H), 3.57–3.66 (m, 2H), 2.84 (dd, J = 3.6, 12.1 Hz, 1H), 2.48 (s, 3H), 2.11 (s, 3H), 2.08–2.09 (m, 1H), 2.03 (s, 3H), 1.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.1, 170.8, 170.2, 170.1, 168.5 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 5.0 Hz), 155.3, 153.8, 151.9, 138.9, 138.7, 138.6, 128.51, 128.43, 128.36, 128.29, 127.9, 127.8, 127.7, 127.6, 118.6, 114.6, 103.2, 99.3, 82.2, 79.4, 75.9, 75.5, 75.0, 74.4, 73.4, 73.25, 73.20, 72.0, 69.5, 64.0, 63.0, 59.2, 55.8, 53.2, 36.5, 24.8, 21.2, 20.9, 20.8. ESI-HRMS: Calcd for $C_{53}H_{63}N_2O_{19}$ $[M+H]^+$: 1031.4020. Found: 1031.4052.

3.2.5. 4-Methoxyphenyl (methyl 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→6)-2,3,4-tri-*O*-benzyl-β-D-galacotopyranoside (D4A2α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24–7.40 (m, 15H), 7.08 (d, J = 9.1 Hz, 2H), 6.80 (d, J = 9.1 Hz, 2H), 5.40–5.43 (m, 2H), 5.09 (dd, J = 1.8, 9.7 Hz, 1H), 5.98–5.03 (m, 2H), 4.84–4.87 (m, 2H), 4.71–4.81 (m, 3H), 4.21–4.26 (m, 3H), 4.09 (dd, J = 7.8, 9.7 Hz, 1H), 3.89–3.96 (m, 3H), 3.76 (s, 3H), 3.65 (s, 3H), 3.62–3.64 (m, 1H), 3.60 (dd, J = 2.8, 9.7 Hz, 1H), 3.50 (dd, J = 6.6, 9.5 Hz, 1H), 3.02 (dt, J = 1.1, 10.4 Hz, 1H), 2.17 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 2.01–2.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 170.6, 169.6, 168.2 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 6.5 Hz), 159.4, 155.3, 151.9, 138.7, 138.6, 138.5, 128.5, 128.4, 128.34, 128.25, 128.0, 127.8, 127.7, 127.54, 127.50, 118.6, 114.5, 103.2, 100.1, 82.2, 79.3, 75.5, 74.3, 73.8, 73.2, 73.1, 68.9, 67.1, 63.8, 61.8, 58.0, 55.7, 53.1, 37.4, 21.1, 20.76, 20.73. ESI-HRMS: Calcd for $C_{51}H_{58}NO_{18}$ $[M+H]^+$: 972.3648. Found: 972.3677.

3.2.6. 4-Methoxyphenyl (methyl 4,7,8,9-tetra-*O*-acetyl-5-azido-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→6)-2,3,4-tri-*O*-benzyl-β-D-galacotopyranoside (D5A2α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.39 (m, 15H), 7.06 (d, J = 9.1 Hz, 2H), 6.80 (d, J = 9.1 Hz, 2H), 5.47 (dd, J = 1.5, 9.1 Hz, 1H), 5.33–5.37 (m, 1H), 4.96–5.02 (m, 2H), 4.68–4.87 (m, 7H), 4.29 (dd, J = 2.4, 12.6 Hz, 1H), 4.15 (dd, J = 4.4, 12.6 Hz, 1H), 4.07 (dd, J = 7.7, 9.7 Hz, 1H), 3.89–3.93 (m, 2H), 3.80 (dd, J = 1.6, 10.6 Hz, 1H), 3.77 (s, 3H), 3.67 (s, 3H), 3.50–3.64 (m, 3H), 3.20 (t, J = 10.2 Hz, 1H), 2.71 (dd, J = 4.8, 12.8 Hz, 1H), 2.13 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.74 (t, J = 12.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 169.9, 169.8, 169.7, 167.6 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 4.6 Hz), 155.2, 151.9, 138.8, 138.7, 138.5, 128.5, 128.43, 128.37, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 118.6, 114.5, 103.1, 98.6, 82.2, 79.4, 75.4, 74.4, 73.4, 73.2, 71.8, 71.1, 68.1, 68.0, 63.4, 62.0, 60.0, 55.8, 53.1, 37.4, 21.1, 21.0, 20.9, 20.8. ESI-HRMS: Calcd for $C_{52}H_{60}N_3O_{18}$ $[M+H]^+$: 1014.3866. Found: 1014.3896.

3.2.6.1. 4-Methoxyphenyl (methyl 4,7,8,9-tetra-*O*-acetyl-5-azido-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylonate)-(2→6)-2,3,4-tri-*O*-benzyl-β-D-galacotopyranoside (D5A2β).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.41 (m, 15H), 7.01–7.03 (m, 2H), 6.84–6.86 (m, 2H), 5.54 (dd, J = 1.4, 7.2 Hz, 1H), 5.24–5.30 (m, 2H), 5.10 (d, J = 10.9 Hz, 1H), 4.98–5.03 (m, 2H), 4.76–4.90 (m, 7H), 4.67 (d, J = 11.8 Hz, 1H), 5.64 (d, J = 10.9 Hz, 1H), 4.50 (dd, J = 2.2, 12.6 Hz, 1H), 4.16 (dd, J = 5.1, 12.6 Hz, 1H), 4.10 (dd, J = 7.7, 9.7 Hz, 1H), 4.02–4.06 (m, 2H), 3.83 (d, J = 2.8 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.58–3.65 (m, 4H), 3.47–3.56 (m, 3H), 3.30 (t, J = 10.2 Hz, 1H), 2.59 (dd, J = 5.1, 12.9 Hz, 1H), 2.20 (s,3H), 2.12 (s,3H), 2.01 (s,3H), 1.89 (s,3H), 1.72 (dd, J = 11.6, 12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.4, 170.0, 169.7, 167.3 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 0 Hz), 155.5, 151.8, 138.8, 138.7, 138.5, 128.8, 128.6, 128.5, 128.45, 128.36, 127.8, 127.7, 127.65, 119.1, 114.7, 103.5, 98.9, 82.3, 79.4, 75.5, 74.9, 73.7, 73.2, 72.8, 70.9, 70.6, 69.7, 68.6, 62.7, 61.9, 60.1, 55.8, 53.0, 21.1, 21.0, 20.9, 20.8. ESI-HRMS: Calcd for $C_{52}H_{60}N_3O_{18}$ $[M+H]^+$: 1014.3866. Found: 1014.3862.

3.2.7. 4-Methoxyphenyl (methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-trifluoroacetamido-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→3)-2,6-di-*O*-benzyl-β-galacotopyranoside (D2A3α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29–7.40 (m, 10H), 7.00–7.04 (m, 2H), 6.77–6.81 (m, 2H), 6.53 (d, *J* = 10.2 Hz, 1H), 5.28–5.38 (m, 3H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.88–4.91 (m, 2H), 4.74 (d, *J* = 11.0 Hz, 1H), 4.56–4.59 (m, 2H), 4.47 (dd, *J* = 2.2, 10.6 Hz, 1H), 4.08–4.18 (m, 2H), 3.97–4.02 (m, 2H), 3.78–3.93 (m, 3H), 3.77 (s, 3H), 3.58–3.63 (m, 2H), 3.50 (s, 3H), 2.67 (dd, *J* = 4.6, 13.4 Hz, 1H), 2.31 (d, *J* = 7.7 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.94–1.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 170.8, 170.7, 169.9, 166.9 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 4.9 Hz), 158.0, 157.7, 155.5, 151.5, 138.5, 137.9, 133.8, 131.8, 130.3, 130.2, 128.64, 128.56, 128.4, 128.0, 127.91, 127.85, 118.6, 114.7, 103.1, 99.8, 75.5, 73.9, 73.0, 71.6, 70.1, 69.6, 69.0, 68.5, 62.7, 55.8, 53.0, 49.8, 37.0, 29.9, 21.1, 20.9, 20.8, 20.7. ESI-HRMS: Calcd for $C_{47}H_{58}N_2O_{19}$ $[M+NH_4]^+$: 1011.3580. Found: 1011.3604.

3.2.8. 4-Methoxyphenyl (methyl 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→3)-2,6-di-*O*-benzyl-β-galacotopyranoside (D3A3α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.40 (m, 10H), 7.00–7.04 (m, 2H), 6.78–6.82 (m, 2H), 5.50–5.52 (m, 1H), 5.40–5.42 (m, 2H), 5.01 (s, 2H), 4.94 (d, *J* = 11.1 Hz, 1H), 4.88 (d, *J* = 7.7 Hz, 1H), 4.72 (d, *J* = 11.1 Hz, 1H), 4.66 (dd, *J* = 2.4, 12.1 Hz, 1H), 4.55–4.62 (m, 3H), 4.51 (dd, *J* = 2.6, 9.2 Hz, 1H), 4.07 (brs, 1H), 3.96–4.01 (m, 2H), 3.83–3.88 (m, 3H), 3.77 (s, 3H), 3.68–3.73 (m, 2H), 3.48 (s, 3H), 3.36–3.38 (m, 1H), 2.86 (dd, *J* = 3.6, 12.5 Hz, 1H), 2.48 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 171.1, 170.8, 169.9, 166.5 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 6.2 Hz), 155.5, 153.9, 151.5, 138.2, 137.9, 135.9, 129.1, 128.8, 128.6, 128.5, 128.4, 128.0, 127.9, 127.8, 118.5, 114.7, 103.2, 99.4, 79.4, 75.8, 75.4, 74.5, 73.9, 73.3, 73.2, 71.2, 70.2, 69.6, 63.4, 59.4, 55.8, 53.0, 36.1, 29.8, 24.9, 21.2, 21.0, 20.9. ESI-HRMS: Calcd for $C_{46}H_{54}NO_{19}$ $[M+H]^+$: 924.3285. Found: 924.3295.

3.2.8.1. 4-Methoxyphenyl (methyl 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylonate)-(2→3)-2,6-di-*O*-benzyl-β-galacotopyranoside (D3A3β).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.40 (m, 10H), 7.03–7.06 (m, 2H), 6.79–6.83 (m, 2H), 5.57 (dd, *J* = 1.5, 7.6 Hz, 1H), 5.46 (dt, *J* = 2.7, 7.2 Hz, 1H), 4.77–5.08 (m, 5H), 4.56–4.59 (m, 3H), 4.50 (dd, *J* = 1.6, 9.4 Hz, 1H), 4.43 (dd, *J* = 2.7, 12.3 Hz, 1H), 4.15 (dd, *J* = 3.2, 9.6 Hz, 1H), 3.90–4.06 (m, 3H), 3.82–3.87 (m, 2H), 3.81 (s, 3H), 3.65–3.78 (m, 5H), 3.77 (s, 3H), 2.82 (dd, *J* = 3.5, 12.4 Hz, 1H), 2.48(s, 3H), 2.23 (t, *J* = 12.9 Hz, 1H), 2.11 (s, 3H), 2.00 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 170.9, 170.5, 169.9, 168.5 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 0 Hz), 155.4, 153.7, 151.7, 138.8, 138.2, 128.8, 128.6, 128.5, 128.4, 128.1, 127.9, 127.8, 118.8, 114.6, 103.1, 98.9, 79.0, 76.3, 75.9, 75.2, 75.1, 75.0, 73.9, 73.8, 73.3, 72.1, 69.7, 69.3, 68.5, 63.3, 59.0, 55.8, 53.5, 35.1, 29.7, 24.8, 21.3, 20.9, 20.7. ESI-HRMS: Calcd for $C_{46}H_{54}NO_{19}$ $[M+H]^+$: 924.3285. Found: 924.3289.

3.2.9. 4-Methoxyphenyl (methyl 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→3)-2,6-di-*O*-benzyl-β-galacotopyranoside (D4A3α)

Selected ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.38 (m, 10H), 7.01–7.04 (m, 2H), 6.78–6.80 (m, 2H), 5.50–5.54 (m, 1H), 5.10 (dd, *J* = 1.8, 9.4 Hz, 1H), 4.93 (d, *J* = 7.8 Hz, 1H), 7.81–7.91 (m, 4H), 4.25 (dd, *J* = 1.9, 12.7 Hz, 1H), 3.04 (t, *J* = 10.2 Hz, 1H), 2.91 (dd, *J* = 3.4, 12.2 Hz, 1H), 2.70 (brs, 3H), 2.13 (s, 3H), 2.03 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 170.6, 169.9, 168.8 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 5.0 Hz), 159.3, 155.4, 151.6, 138.9, 138.2, 128.6, 128.5, 128.4, 128.3, 127.8, 127.7, 127.7, 118.6, 114.6, 102.9, 99.2, 76.4, 75.0, 73.9, 73.7., 73.0, 69.3, 69.0, 68.1, 67.2, 62.0, 57.9, 55.8, 53.3, 36.6, 21.2, 20.8, 20.6. ESI-HRMS: Calcd for $C_{44}H_{52}NO_{18}$ $[M+H]^+$: 882.3179. Found: 882.4072.

3.2.9.1. 4-Methoxyphenyl (methyl 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylonate)-(2→3)-2,6-di-*O*-benzyl-β-galacotopyranoside (D4A3β).

Selected ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.38 (m, 10H), 7.02–7.04 (m, 2H), 6.78–6.81 (m, 2H), 5.32–5.35 (m, 1H), 5.16 (t, *J* = 3.4 Hz, 1H), 4.40 (dd, *J* = 3.1, 9.8 Hz, 1H), 3.22 (brs, 3H), 3.09 (t, *J* = 10.6 Hz, 1H), 2.83 (dd, *J* = 3.7, 12.5 Hz, 1H), 2.14 (s, 3H), 2.08 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 170.8, 170.4, 166.4 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 0 Hz), 159.5, 155.4, 151.5, 138.0, 134.6, 128.6, 128.5, 128.4, 128.0, 127.8, 127.6, 127.5, 118.5, 114.6, 103.1, 100.5, 76.5, 75.4, 73.8, 73.6, 73.2, 71.8, 70.5, 70.1, 69.6, 62.4, 58.4, 55.8, 52.9, 37.1, 21.0, 20.8, 20.7. ESI-HRMS: Calcd for $C_{44}H_{52}NO_{18}$ $[M+H]^+$: 882.3179. Found: 882.4072.

3.2.10. 4-Methoxyphenyl (methyl 4,7,8,9-tetra-*O*-acetyl-5-azido-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→3)-2,6-di-*O*-benzyl-β-galacotopyranoside (D5A3α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.39 (m, 10H), 7.02–7.04 (m, 2H), 6.78–6.80 (m, 2H), 5.48 (dd, *J* = 1.6, 8.8 Hz, 1H), 5.38–5.42 (m, 1H), 4.91 (d, *J* = 7.7 Hz, 1H), 4.77–4.92 (m, 4H), 4.57 (s, 2H), 4.29 (dd, *J* = 2.3, 12.6 Hz, 1H), 4.14 (dd, *J* = 3.3, 9.6 Hz, 1H), 4.05 (dd, *J* = 4.7, 12.6 Hz, 1H), 3.83–3.86 (m, 1H), 3.82 (s, 3H), 3.78–3.80 (m, 2H), 3.77 (s, 3H), 3.71–3.76 (m, 2H), 3.20 (t, *J* = 10.1 Hz, 1H), 2.72 (dd, *J* = 4.8, 13.0 Hz, 1H), 2.11 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H), 1.83 (t, *J* = 12.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.0, 169.7, 169.6, 168.2 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 5.0 Hz), 155.4, 151.7, 138.9, 138.2, 128.5, 123.4, 128.1, 127.85, 127.80, 127.7, 118.7, 114.6, 102.9, 98.0, 75.9, 75.2, 73.8, 73.3, 72.0, 69.5, 68.5, 68.2, 68.1, 62.2, 59.9, 55.8, 53.3, 36.4, 21.2, 21.0, 20.9, 20.6. ESI-HRMS: Calcd for $C_{45}H_{57}N_4O_{18}$ $[M+NH_4]^+$: 941.3662. Found: 941.3669.

3.2.10.1. 4-Methoxyphenyl (methyl 4,7,8,9-tetra-*O*-acetyl-5-azido-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylonate)-(2→3)-2,6-di-*O*-benzyl-β-galacotopyranoside (D5A3β).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27–7.41 (m, 10H), 6.98–7.03 (m, 2H), 6.76–6.80 (m, 2H), 5.51 (dd, *J* = 2.1, 4.5 Hz, 1H), 5.37–5.44 (m, 1H), 5.31–5.35 (m, 1H), 4.95 (d, *J* = 11.0 Hz, 1H), 4.87 (d, *J* = 7.0 Hz, 1H), 4.81 (d, *J* = 11.0 Hz, 1H), 4.77 (dd, *J* = 2.5, 12.4 Hz, 1H), 4.58 (s, 2H), 4.20 (dd, *J* = 2.1, 10.4 Hz, 1H), 4.10 (dd, *J* = 7.5, 12.4 Hz, 1H), 3.95 (brs, 1H), 3.78–3.86 (m, 4H), 3.76 (s, 3H), 3.71–3.75 (m, 1H), 3.53 (s, 3H), 3.30 (t, *J* = 10.1 Hz, 1H), 3.01 (d, *J* = 3.8 Hz, 1H), 2.81 (dd, *J* = 4.8, 13.3 Hz, 1H), 2.18 (s, 3H), 2.11 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.78 (dd, *J* = 11.7, 13.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.4, 169.9, 169.8, 167.0 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 0 Hz), 155.3, 151.5, 138.3, 138.1, 128.7, 128.5, 128.3, 127.9, 127.80, 127.78, 118.5, 114.6, 102.9, 99.5, 78.0, 75.3, 73.8, 73.4, 71.2, 71.0, 70.7, 70.1, 69.9, 68.9, 62.6, 60.2, 55.8, 53.0, 36.6, 29.8, 21.1, 20.9, 20.8. ESI-HRMS: Calcd for $C_{45}H_{57}N_4O_{18}$ $[M+NH_4]^+$: 941.3662. Found: 941.3679.

3.2.11. 2-(Trimethylsilyl)ethyl (methyl 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galacotopyranoside (D3A4α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11–8.13 (m, 2H), 7.54–7.59 (m, 3H), 7.43–7.47 (m, 2H), 7.34–7.39 (m, 3H), 5.57 (d, *J* = 2.7 Hz, 1H), 5.47 (dd, *J* = 8.0, 10.1 Hz, 1H), 5.39 (s, 1H), 4.73 (d, *J* = 8.0 Hz, 1H), 4.56 (dd, *J* = 3.7, 10.1 Hz, 1H), 4.44–4.50 (m, 2H), 4.32 (dd, *J* = 1.3, 12.2 Hz, 1H), 4.17 (dd, *J* = 1.4, 12.2 Hz, 1H), 4.07 (d,

J = 3.5 Hz, 1H), 3.98–4.04 (m, 2H), 3.71–3.75 (m, 1H), 3.51–3.61 (m, 3H), 3.47 (s, 3H), 2.95 (dd, *J* = 3.2, 12.0 Hz, 1H), 2.44 (s, 3H), 2.20 (s, 3H), 2.06 (s, 3H), 1.82 (s, 3H), 1.80 (dd, *J* = 12.1, 13.4 Hz, 1H), 0.82–0.90 (m, 2H), −0.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 171.1, 170.6, 170.2, 168.9 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 4.7 Hz), 165.4, 137.9, 133.1, 130.7, 130.0, 129.1, 128.5, 126.7, 101.0, 100.7, 97.0, 75.2, 75.0, 73.2, 72.9, 71.6, 70.6, 69.2, 68.2, 67.1, 66.2, 63.9, 59.0, 53.0, 37.2, 24.8, 21.5, 21.0, 20.7, 18.1, −1.36. ESI-HRMS: Calcd for $C_{44}H_{59}N_2O_{19}Si$ $[M+NH_4]^+$: 947.3476. Found: 947.3498.

3.2.11.1. 2-(Trimethylsilyl)ethyl (methyl 5-acetamido-7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylonate)-(2→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galacotopyranoside (D3A4β). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01–8.03 (m, 2H), 7.44–7.59 (m, 5H), 7.34–7.37 (m, 3H), 5.83 (t, *J* = 2.0 Hz, 1H), 5.67 (s, 1H), 5.58 (dt, *J* = 1.8, 8.8 Hz, 1H), 5.45 (dd, *J* = 8.2, 9.8 Hz, 1H), 5.10 (dd, *J* = 2.5, 12.1 Hz, 1H), 4.66 (d, *J* = 8.2 Hz, 1H), 4.58–4.65 (m, 1H), 4.52 (dd, *J* = 2.1, 9.5 Hz, 1H), 4.47 (d, *J* = 3.6 Hz, 1H), 4.32–4.36 (m, 2H), 4.20 (dd, *J* = 1.5, 12.3 Hz, 1H), 3.97–4.04 (m, 1H), 3.92 (dd, *J* = 9.2, 12.1 Hz, 1H), 3.64 (s, 1H), 3.47–3.59 (m, 2H), 3.27 (s, 3H), 2.66 (dd, *J* = 3.6, 12.1 Hz, 1H), 2.30 (s, 3H), 2.15 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 1.87 (t, *J* = 12.3 Hz, 1H), 0.82–0.92 (m, 2H), −0.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 171.2, 171.1, 169.5, 166.0 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 0 Hz), 165.3, 137.8, 133.1, 130.6, 130.0, 129.9, 129.3, 128.43, 128.35, 126.5, 101.2, 100.3, 99.5, 76.3, 75.3, 74.6, 74.4, 74.2, 72.0, 70.8, 69.2, 67.0, 66.5, 63.3, 59.2, 52.9, 36.9, 29.8, 24.5, 21.2, 21.1, 20.8, 18.2, −1.35. ESI-HRMS: Calcd for $C_{44}H_{59}N_2O_{19}Si$ $[M+NH_4]^+$: 947.3476. Found: 947.3494.

3.2.12. 2-(Trimethylsilyl)ethyl (methyl 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galacotopyranoside (D4A4α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01–8.03 (m, 2H), 7.52–7.57 (m, 3H), 7.43–7.47 (m, 2H), 7.35–7.41 (m, 3H), 5.64 (s, 1H), 5.54 (dt, *J* = 2.0, 9.3 Hz, 1H), 5.46 (dd, *J* =8.4, 9.5 Hz, 1H), 5.20 (s, 1H), 5.17 (t, *J* = 2.3 Hz, 1H), 5.09 (dd, *J* = 2.3, 12.4 Hz, 1H), 4.67 (d, *J* = 8.1 Hz, 1H), 4.59 (dt, *J* = 2.9, 12.0 Hz, 1H), 4.36–4.39 (m, 2H), 4.25–4.28 (m, 2H), 4.15 (d, *J* = 11.5 Hz, 1H), 3.98–4.08 (m, 2H), 3.67 (s, 1H), 3.50–3.58 (m, 1H), 3.30 (s, 3H), 3.07 (t, *J* = 10.5 Hz, 1H), 2.68 (dd, *J* = 3.6, 12.2 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 1.90 (t, *J* = 12.3 Hz, 1H), 0.82–0.90 (m, 2H), −0.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 170.9, 170.5, 166.2 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 5.8 Hz), 165.3, 159.4, 137.6, 133.1, 130.6, 129.9, 129.2, 128.5, 128.4, 126.2, 100.9, 100.7, 100.3, 76.1, 75.5, 75.0, 74.8, 72.3, 70.9, 70.6, 69.1, 67.0, 66.3, 62.7, 58.0, 52.9, 37.8, 29.8, 20.9, 20.7, 18.1, −1.36. ESI-HRMS: Calcd for $C_{42}H_{57}N_2O_{18}Si$ $[M+NH_4]^+$: 905.3370. Found: 905.3385.

3.2.12.1. 2-(Trimethylsilyl)ethyl (methyl 7,8,9-tri-*O*-acetyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylonate)-(2→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galacotopyranoside (D4A4β). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07–8.09 (m, 2H), 7.52–7.59 (m, 3H), 7.44–7.48 (m, 2H), 7.35–7.40 (m, 3H), 5.54–5.58 (m, 1H), 5.41–5.46 (m,1H), 5.36 (s, 1H), 5.21 (brs, 1H), 5.11 (dd, *J* = 1.9, 10.1 Hz, 1H), 4.74 (d, *J* = 8.0 Hz, 1H), 4.48 (dd, *J* = 3.7, 10.1 Hz, 1H), 4.27–4.35 (m, 3H), 4.15 (dd, *J* = 1.5, 12.2 Hz, 1H), 4.07 (dd, *J* = 2.0, 10.0 Hz, 1H), 3.97–4.02 (m, 2H), 3.57 (dd, *J* = 3.6, 10.1 Hz, 1H), 3.49 (s, 3H), 2.99 (dd, *J* = 3.1, 12.1 Hz, 1H), 2.85 (t, *J* = 10.4 Hz, 1H), 2.26 (s, 3H), 2.08 (s, 3H), 1.84 (s, 3H), 1.78 (dd, *J* = 12.2, 13.2 Hz, 1H), 0.81–0.91 (m, 2H), −0.10 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.4, 170.7, 170.4, 168.8 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 0 Hz), 165.3, 159.2, 137.8, 133.1, 130.7, 129.9, 129.2, 128.5, 128.3, 126.6, 101.1, 100.6, 98.2, 73.6, 73.3, 72.9, 70.6, 69.3, 68.7, 67.0, 66.7, 66.2, 62.0, 57.8, 53.0, 38.1, 29.8, 20.8, 20.5, 18.1, −1.36. ESI-HRMS: Calcd for $C_{42}H_{57}N_2O_{18}Si$ $[M+NH_4]^+$: 905.3370. Found: 905.3390.

3.2.13. 2-(Trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-*O*-acetyl-5-azido-3,5-dideoxy-D-glycero-α-D-galacto-non-2-ulopyranosylonate)-(2→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galacotopyranoside (D5A4α)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52–7.54 (m, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.33–7.39 (m, 3H), 5.49–5.53 (m, 1H), 5.40–5.46 (m, 2H), 5.36 (s, 1H), 4.71 (d, *J* = 7.9 Hz, 1H), 4.67–4.72 (m, 1H), 4.49 (dd, *J* = 3.7, 10.1 Hz, 1H), 4.31–4.35 (m, 2H), 4.10–4.14 (m, 2H), 3.97–4.03 (m, 2H), 3.68 (dd, *J* = 1.6, 10.6 Hz, 1H), 3.55 (s, 3H), 3.52–3.59 (m, 2H), 3.04 (t, *J* = 10.1 Hz, 1H), 2.75 (dd, *J* = 4.5, 12.7 Hz, 1H), 2.22 (s, 3H), 2.09 (s, 3H), 2.02 (s, 3H), 1.82 (s, 3H), 1.51 (t, *J* = 12.6 Hz, 1H), 0.77–0.92 (m, 2H), −0.11 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.0, 170.5, 169.65, 169.60, 168.6 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 6.6 Hz), 165.3, 137.8, 133.0, 130.8, 130.0, 129.1, 128.4, 128.3, 126.6, 73.4, 72.5, 71.6, 70.8, 70.6, 69.3, 67.7, 67.3, 67.0, 66.2, 62.3, 59.8, 53.0, 38.1, 29.8, 21.5, 21.0, 20.9, 20.4, 18.1, −1.36. ESI-HRMS: Calcd for $C_{43}H_{59}N_4O_{18}Si$ $[M+NH_4]^+$: 947.3588. Found: 947.3596.

3.2.13.1. 2-(Trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-*O*-acetyl-5-azido-3,5-dideoxy-D-glycero-β-D-galacto-non-2-ulopyranosylonate)-(2→3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galacotopyranoside (D5A4β). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03–8.05 (m, 2H), 7.52–7.59 (m, 3H), 7.33–7.46 (m, 5H), 5.60 (s, 1H), 5.48 (d, *J* = 8.8 Hz, 1H), 5.40–5.42 (m, 1H), 5.33–5.36 (m, 1H), 5.23–5.30 (m, 1H), 4.94 (dd, *J* = 2.6, 12.4 Hz, 1H), 4.68 (d, *J* = 8.1 Hz, 1H), 4.34–4.37 (m, 2H), 4.26 (dd, *J* = 3.8, 9.8 Hz, 1H), 4.12 (d, *J* = 11.2 Hz, 1H), 3.92–4.02 (m, 3H), 3.62 (s, 1H), 3.51–3.58 (m, 2H), 3.32 (s, 3H), 3.18 (t, *J* = 10.0 Hz, 1H), 2.72 (dd, *J* = 4.6, 13.4 Hz, 1H), 2.14 (s, 3H), 2.08 (s, 6H), 2.04 (s, 3H), 1.63 (dd, *J* = 12.0, 13.1 Hz, 1H), 0.83–0.88 (m, 2H), −0.10 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.1, 170.5, 169.6, 167.3 (C-1, $^3J_{C\text{-}1,\ H\text{-}3ax}$ = 1.6 Hz), 165.1, 137.5, 133.0, 130.5, 130.0, 129.0, 128.31, 128.30, 126.4, 100.7, 100.5, 99.1, 75.0, 74.4, 71.7, 71.1, 70.7, 70.4, 70.2, 69.0, 66.9, 66.4, 62.6, 59.6, 52.8, 35.8, 29.8, 21.01, 20.97, 20.92, 20.73, 18.1, −1.37. ESI-HRMS: Calcd for $C_{43}H_{59}N_4O_{18}Si$ $[M+NH_4]^+$: 947.3588. Found: 947.3580.

3.2.14. 2-(Trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-trifluoroacetamido-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-β-D-galacotopyranoside (6)

The disaccharide **D2A4** (100 mg, 0.10 mmol) was suspended in aqueous 60% HOAc (5 mL) and stirred at 80 °C for 2 h. The reaction mixture was concentrated and co-evaporated with toluene three times. The concentrate was dissolved in Ac_2O–pyridine (2:3, v/v, 5 mL). After overnight stirring at room temperature, the reaction mixture was diluted with EtOAc, and then washed with 1 N HCl solution, aqueous $CuSO_4$ solution, saturated aqueous $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (CH_2Cl_2–EtOAc 5:1–1:1) to give **6** (87.7 mg, 0.088 mmol, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.1 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 7.4 Hz, 1H), 5.56–5.59 (m, 1H), 5.26 (dd, *J* = 8.2, 9.7 Hz, 1H), 5.18 (d, *J* = 9.1 Hz, 1H), 5.00 (d, *J* = 3.0 Hz, 1H), 4.76 (d, *J* = 7.9 Hz, 1H), 4.69 (dd, *J* = 3.2, 10.1 Hz, 1H), 4.35 (d, *J* = 10.9 Hz, 1H), 4.11 (d, *J* = 6.4 Hz, 1H), 3.90–3.99 (m, 2H), 3.86 (s, 3H), 3.58–3.65 (m, 1H), 2.60 (dd, *J* = 4.6, 12.6 Hz, 1H), 2.22 (s, 3H), 2.14 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.96 (s, 3H), 1.74 (t, *J* = 12.5 Hz, 1H),1.42 (s, 3H), 0.76–0.94 (m, 2H), −0.11 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.9, 170.8, 170.77, 170.6, 170.56, 170.49, 169.9, 168.0, 165.4, 158.2, 157.8, 157.5,

157.1, 133.2, 130.5, 130.3, 128.5, 100.9, 96.9, 71.7, 71.4, 71.1, 70.6, 68.8, 67.91, 67.88, 67.82, 66.4, 62.3, 62.2, 53.4, 49.7, 37.4, 29.8, 21.6, 20.9, 20.8, 20.6, 20.1, 18.2, −1.47. ESI-HRMS: Calcd for $C_{42}H_{56}F_3NO_{21}SiNa$ $[M+Na]^+$: 1018.2958. Found: 1018.2978.

3.3. 2,2,2-Trichloroacetimidate (methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-trifluoroacetamido-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-α-D-galacotopyranoside (7)

The disaccharide **6** (98.2 mg, 0.099 mmol) was dissolved in CH_2Cl_2 (5 mL). To the stirred solution was added boron trifluoride etherate (1.1 mL, 8.7×10^{-3} mmol, 0.15 equiv) at 0 °C and the reaction process was monitored by TLC. When the reaction was completed, the mixture was quenched by saturated aqueous $NaHCO_3$ solution, and diluted with CH_2Cl_2. After separation, the organic layer was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH 100:1–50:1) to afford the lactal, which was directly dissolved in dry CH_2Cl_2 (3 mL) for the next step. To the stirred solution of lactal, cooled to 0 °C, were added trichloroacetonitrile (0.15 mL, 1.5 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5 drops). The dark brown mixture was stirred for 2 h, then concentrated to get a syrup, which was purified by column chromatography on silica gel (CH_2Cl_2/MeOH 100:1–60:1) to give trichloroacetimidate donor **7** (72.5 mg, 0.070 mmol, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.59 (s, 3H), 8.14 (d, *J* = 7.1 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 3.8 Hz, 1H), 6.37 (d, *J* = 9.4 Hz, 1H), 5.55–5.59 (m, 1H), 5.50 (dd, *J* = 3.8, 10.5 Hz, 1H), 5.38 (dd, *J* = 1.9, 9.5 Hz, 1H), 5.32 (dd, *J* = 3.1, 9.8 Hz, 1H), 5.29 (dd, *J* = 3.1, 10.5 Hz, 1H), 4.98–5.02 (m, 1H), 4.58 (t, *J* = 6.4 Hz, 1H), 4.14–4.22 (m, 2H), 4.07 (dd, *J* = 7.0, 11.5 Hz, 1H), 4.00 (dd, *J* = 1.9, 10.7 Hz, 1H), 3.87–3.98 (m, 1H), 3.83 (s, 3H), 2.58 (dd, *J* = 4.7, 12.8 Hz, 1H), 2.18 (s, 3H), 2.14 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.94 (s, 3H), 1.93 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.83, 170.78, 1706, 170.1, 169.9, 169.6, 167.9, 165.9, 161.0, 158.4, 158.0, 157.6, 157.3, 133.8, 130.1, 129.6, 128.7, 96.7, 94.3, 71.9, 69.9, 68.7, 68.6, 67.7, 67.6, 66.7, 62.2, 61.9, 53.5, 50.4, 37.4, 29.8, 21.5, 20.89, 20.85, 20.82, 20.7, 20.6.

3.4. 4-Methylphenyl (methyl 4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-5-trifluoroacetamido-D-glycero-α-D-galacto-non-2-ulopyranosylonate-(2→3)-4,6-di-*O*-acetyl-2-*O*-benzoyl-α-D-galacotopyranosyl-(1→4)-4-*O*-benzoyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-glucopyranoside (8)

The trichloroacetimidate donor **7** (50.6 mg, 0.049 mmol) and glycosyl acceptor **A5** (67.1 mg, 0.11 mmol) were dissolved in dry CH_2Cl_2 (4 mL). The mixture was stirred at room temperature for 3 h in the presence of activated 4 Å molecular sieves (205 mg). After cooling to −40 °C, trimethylsilyl triflate (TMSOTf, 10 μL, 0.051 mmol) was added to initiate the glycosylation process. After stirring at −40 °C for 1 h, the reaction was quenched by $NaHCO_3$, diluted with CH_2Cl_2, and filtered through a pad of Celite. The resulting filtrate was concentrated and purified by column chromatography on silica gel (Hexane/EtOAc 3:1 to 1:1) to give trisaccharide **8** (41.0 mg, 0.028 mmol, 57%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20–8.22 (m, 2H), 7.87–7.89 (m, 2H), 7.83–7.85 (m, 1H), 7.57–7.70 (m, 4H), 7.47–7.52 (m, 3H), 7.32–7.39 (m, 7H), 7.25–7.27 (m, 2H), 6.93–6.95 (m, 2H), 5.97–6.02 (m, 2H), 5.60–5.64 (m, 2H), 5.10–5.16 (m, 2H), 4.93–4.95 (m, 2H), 4.73 (d, *J* = 3.3 Hz, 1H), 4.54 (dd, *J* = 3.4, 10.0 Hz, 1H), 4.34–4.44 (m, 2H), 4.28 (dd, *J* = 2.3, 12.5 Hz, 1H), 4.17 (t, *J* = 9.3 Hz, 1H), 3.97 (dd, *J* = 5.3, 12.5 Hz, 1H), 3.90 (d, *J* = 4.4 Hz, 1H), 3.79 (s, 1H), 3.65–3.70 (m, 1H), 3.52–3.62 (m, 2H), 3.45–3.49 (m, 1H), 3.33 (dd, *J* = 5.6, 10.6 Hz, 1H), 2.52 (dd, *J* = 4.7, 12.7 Hz, 1H), 2.26 (s, 3H), 2.13 (s, 3H), 2.03 (s, 3H), 1.94 (s, 3H), 1.92 (s, 3H), 1.86 (s, 3H), 1.68 (t, *J* = 14.7 Hz, 2H), 1.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8, 170.7, 170.5, 170.3, 170.0, 169.9, 167.9, 167.8, 167.3, 165.3, 164.8, 157.8, 157.5, 138.6, 138.4, 134.3, 134.1, 133.6, 133.5, 133.1, 131.9, 131.4, 130.4, 130.1, 129.9, 129.7, 128.7, 128.4, 128.3, 127.9, 127.6, 123.8, 123.6, 100.5, 96.9, 83.4, 78.7, 75.4, 73.0, 72.9, 71.7, 71.0, 70.4, 68.7, 68.6, 67.1, 66.4, 62.2, 61.0, 54.1, 53.4, 49.8, 37.3, 29.8, 21.5, 21.3, 20.9, 20.7, 20.6, 20.5, 20.2. ESI-HRMS: Calcd for $C_{72}H_{74}F_3N_2O_{27}S$ $[M+H]^+$ 1487.4146. Found: 1487.4176.

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Supplementary data

Supplementary data (^{1}H and ^{13}C NMR spectra of new compounds) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2012.08.007.

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