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Synthesis of GD3-lactam: a potential ligand for the development of an anti-melanoma vaccine

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Abstract

The novel sialyl donor methyl (ethyl 4,7,8,9-tetra-*O*-acetyl-5-*N*,*N*-diacetylamino-3,5-dideoxy-2-thio-3-thiophenyl-D-*erythro*-β-L-*gluco*-non-2-ulopyranosid)onate was used for glycosylation of a lactosyl acceptor to give the GM3-trisaccharide derivative in 83% yield. Introduction of an azido group at C-9″ of the GM3-trisaccharide derivative, transformation into a glycosyl acceptor, and sialylation with the above mentioned novel sialyl donor gave a GD3-trisaccharide in 50% yield. Reduction of the azido group gave the corresponding amine, which underwent spontaneous lactamization to the GD3-[1‴–9″]-lactam in an overall yield of 86%. Removal of protecting groups of over five steps, followed by per-*O*-acetylation gave an acetylated GD3-[1‴–9″]-lactam TMSEt glycoside in 27% overall yield. The acetylated GD3-[1‴–9″]-lactam TMSEt glycoside is suitable for glycosylation of linker-arms and the resulting linker-glycosides are planned to be coupled to carrier proteins, thus providing immunogens for trial vaccinations against malignant melanoma.

Keywords: Melanoma; Antigen; GD3; GD3-lactam; Glycosylation

1. Introduction

Gangliosides (sialic acid-containing glycosphingolipids) are well-known tumor-associated antigens.[1–5] However, gangliosides having an intact sialic acid terminal unit are only weakly immunogenic, thus reducing their potential as vaccine candidates against cancer.[4,5] Since gangliosides are hydroxy-carboxylic acids, they form lactones on treatment with acids (such as acetic acid) and the lactones have been reported to be much more immunogenic than the ganglioside saccharide itself.[6] It was recently reported that immunization of melanoma patients with a GD3-lactone:KLH neoglycoconjugate induced a strong immune response towards GD3 and GD3-lactone, while immunization with the corresponding GD3:KLH conjugate did not.[7] These results further emphasize the relevance of ganglioside lactones as tumor immunogens. Lactones are unstable and undergo easy hydrolysis back to the hydroxy acid form, which reduces the usefulness of ganglioside lactones as immunogens. We introduced lactam analogs of ganglioside lactones[8] (Fig. 1) as hydrolytically stable alternatives and found that these ganglioside lactams are highly immunogenic; some of the anti-GM3-lactam antibodies formed were shown to cross-react with the corresponding ganglioside lactone,[9] indicating a close structural similarity between the lactone and the lactam; the antibodies were capable of staining melanoma cells, demonstrating the presence of lactones on the cell surface.[10] An ether analog of GM3-lactone has also been reported[11] as a hydrolytically stable lactone analog (Fig. 1). We now wish to report our synthesis of a lactam analog of one of the possible lactones of GD3 ganglioside, which is a tumor-associated antigen on

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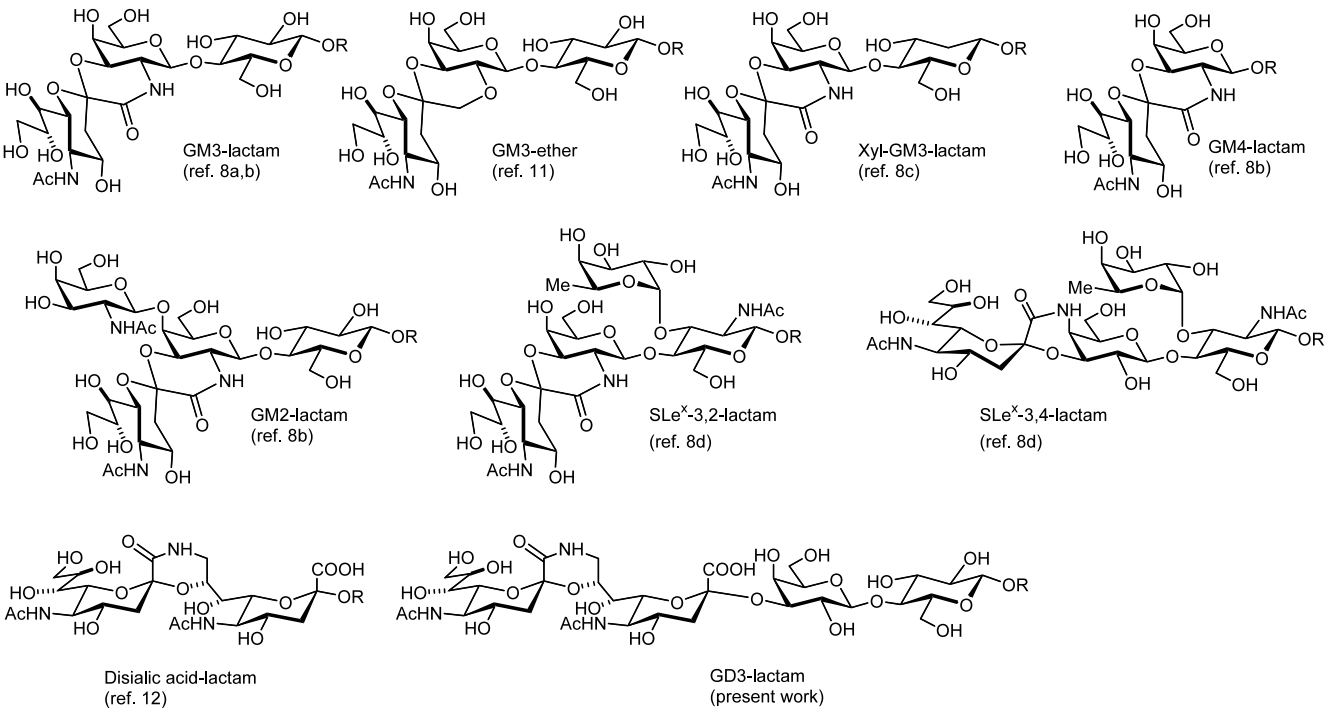


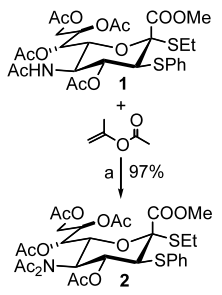
Fig. 1. Synthetic analogs of ganglioside lactones. Examples of the aglycon residue R include alkyl, aryl, ceramide, linkers, and linked protein.

human malignant melanoma cells.[6] In order to create the quite demanding α-(2→8)-bond between the two terminal sialic acid units in GD3, novel sialic acid donors were developed.[12,13] The GD3-tetrasaccharide has been synthesized by others.[14]

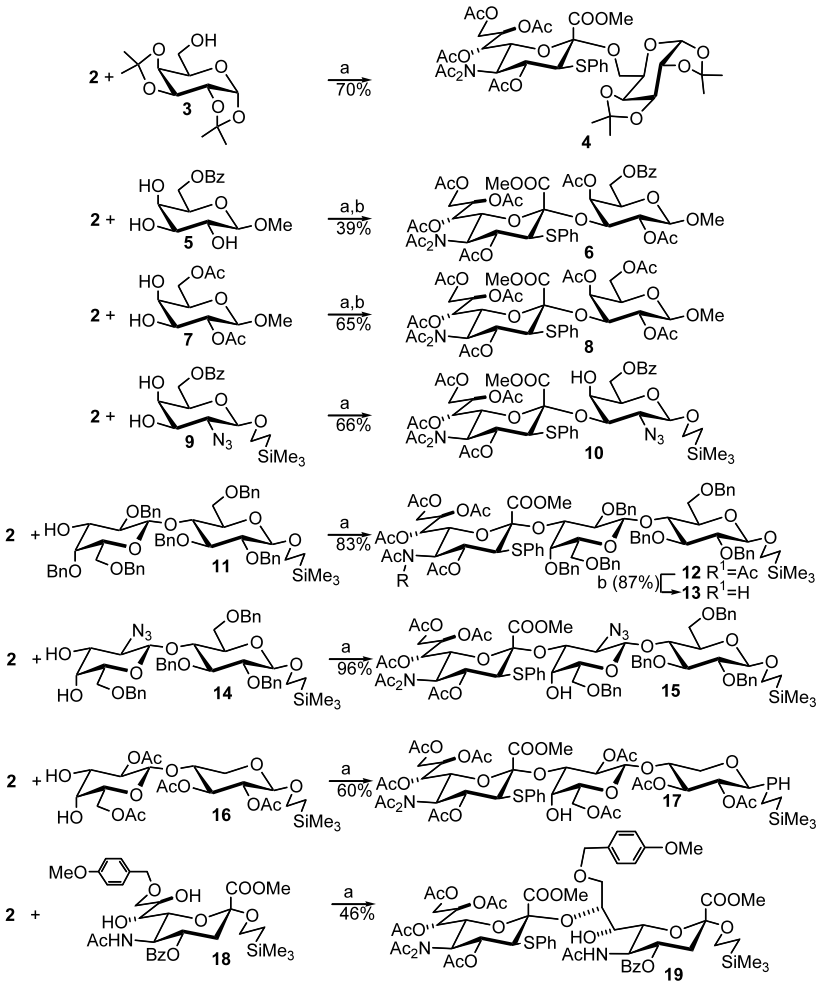
2. Results and discussion

Synthesis of a novel sialyl donor.—Glycosylation with *N*-acetyl-neuraminic acid donors (sialylation) is more difficult than other glycosylations, especially when another *sialic* acid moiety is used as acceptor. In order to avoid losses of donor (via side reactions) and also to improve the α,β-ratio in sialylations, donors were introduced that carry a thiophenyl substituent at C-3.[14b,15] It is believed that the thiophenyl substituent decreases the acidity of H-3 and also leads to the formation of a reactive episulfonium intermediate that can only be attacked by the acceptor molecule from the α-side of the donor. The original donors were *O*-benzylated,[14b,15] whereas two recent donors (**1** and its derivative **2**; Scheme 1) carry *O*-acetyl protecting groups.[12,13] In a comparative study of **1** and traditional sialyl donors that lack the thiophenyl group, we found that only **1** gave sialylated products in the form of pure α-glycosides; the other donors gave α-glycosides contaminated by a small amount (4–6%) of the corresponding β-glycosides.[12] Although donor **1** had the power to sialylate the sterically hindered acceptor **18** (Scheme 2), the yield of the desired α-(2→8)-linked bis-sialic acid was rather low (28%).[12] Another attempt towards improved sialyl donors includes the use of a phenoxy-thiocarbonyl group at C-3.[16]

It was recently reported[17] that the nitrogen atom of the acetamido residue of sialic acid donors can undergo alkylation by the strongly electrophilic reagents normally used for activation of the anomeric thioalkyl group. To avoid *N*-alkylation, an extra *N*-acetyl group was introduced, which reduced the nucleophilicity of the amide nitrogen, and sialylations could be performed in high yield. In a comparative study with different sialic acid acceptors, the α-Neu5Ac-(2→8)-Neu5Ac moiety was obtained in ~60% yield, but the α,β-ratio was low.[18] Following the glycosylation step, the extra *N*-acetyl group was easily removed by methanolic sodium methoxide to furnish the intact sialic acid moiety.[17,18] We have reported a further elaboration on this



Scheme 1. (a) $MePhSO_3H$, 55 °C, 30 h.



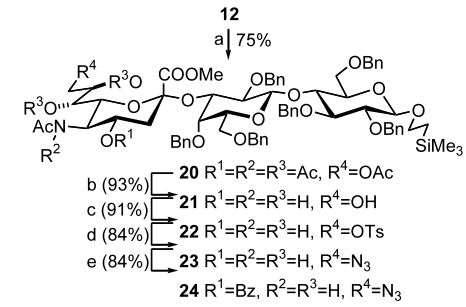
Scheme 2. (a) AgOTf, MeSBr, MS 3 Å, MeCN, CH_2Cl_2, −45 °C, 3 h. (b) Ac_2O, pyridine.

theme and introduced the donor **2**, carrying both a thiophenyl group and an extra acetyl group on the nitrogen atom[13] (Scheme 1).

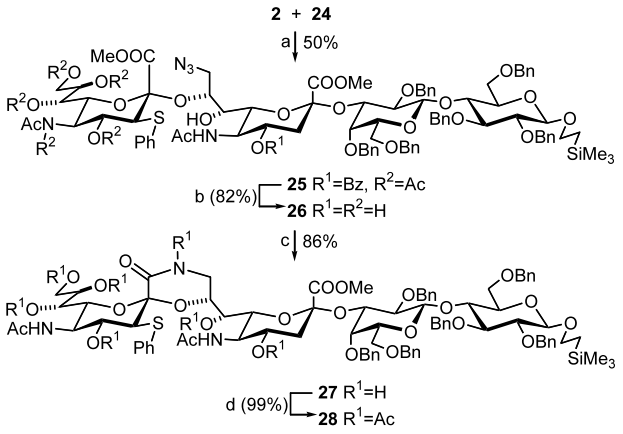
The preparation of **2** was performed according to the procedure used for *N*-acetylation of traditional sialyl donors.[17–19] The known[12] sialyl donor **1** was dissolved in isopropenyl acetate, a catalytic amount of *p*-toluenesulfonic acid was added, and the mixture was stirred at 55 °C for 30 h. Residual isopropenyl acetate was then removed, which gave pure **2** in 97% yield.

Sialylations with the novel donor **2**.—The efficiency of **2** as a sialyl donor was investigated by reaction with a series of glycosyl acceptors (**3**,[12] **5**,[12] **7**,[12] **9**,[8b] **11**,[12] **14**,[12] **16**,[8c] **18**,[12b]; Scheme 2), having different protecting-group patterns. After some experimentation, it was found that activation of **2** with AgOTf–methylsulfenyl bromide, in the presence of the acceptor and with $MeCN–CH_2Cl_2$ as the solvent, furnished the desired α-sialylated compounds **4**, **6**, **8**, **10**, **12**, **15**, **17**, and **19** in 39–96% yield after chromatographic purification. In no case was the corresponding β-glycoside observed (TLC and ^1H NMR).

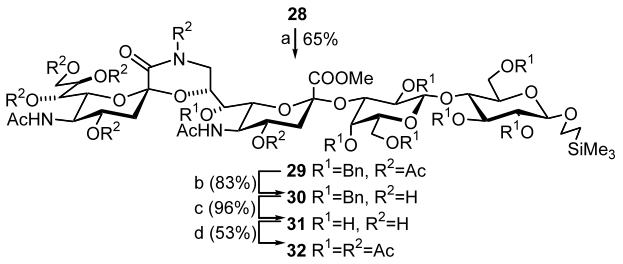
Synthesis of the GD3-lactam.—The GM3-trisaccharide **12** (Scheme 2) was treated with $Ph_3SnH–AIBN$ to remove the auxiliary thiophenyl group, which gave **20** (75%; Scheme 3). Compound **20** was de-*N*- and *O*-acetylated by treatment with MeONa–MeOH to give the tetraol **21** (93%). Regioselective 9-*O*-tosylation of **21** provided the tosylate **22** (91%) and treatment of **22**



Scheme 3. (a) Ph_3SnH, AIBN, toluene, 120 °C, 4 h. (b) MeONa, MeOH, 22 °C, 3 h. (c) $MePhSO_2Cl$, pyridine, CH_2Cl_2, −78 °C, 48 h. (d) NaN_3, 18-crown-6, DMF, 60 °C, 24 h. (e) BzCl, Et_3N, CH_2Cl_2, −45 °C, 24 h.



Scheme 4. (a) AgOTf, MeSBr, MS 3 Å, MeCN, CH_2Cl_2, −45 °C, 3 h. (b) MeONa, MeOH, 22 °C, 3 h. (c) Ph_3P, THF, H_2O, 40 °C, 24 h. (d) Ac_2O, pyridine, DMAP, 22 °C, 10 h.



Scheme 5. (a) Ph_3SnH, AIBN, toluene, 120 °C, 5 h. (b) MeONa, MeOH, 22 °C, 12 h. (c) H_2, Pd–C, EtOH, 22 °C, 10 h. (d) Ac_2O, pyridine, DMAP, 22 °C, 10 h.

with NaN_3 furnished the 9-azido-9-deoxy derivative **23** (84%). Since the reactivity order of the hydroxyl groups of sialic acids is HO-9 ≫ HO-4 > HO-8 ≫ HO-7,[12,14d] compound **23** could be regioselectively 4-*O*-benzoylated, which gave **24** (84%). The diol **24** was regioselectively sialylated with donor **2** to furnish the GD3-tetrasaccharide **25** in 50% yield (Scheme 4). (In comparison, sialylation of the diol **24** with the donor **1** gave only 28% of the corresponding tetrasaccharide.) De-*O*-acylation of **25** then gave the azidohexaol **26** (82%), which was treated with Ph_3P to reduce the azido group; the resulting amino compound underwent spontaneous ring closure to yield the lactam **27** (86%). In order to simplify the purification, **27** was *O*-acetylated to give **28** (99%), which to our surprise had also undergone *N*-acetylation; this is to the best of our knowledge the first example of *N*-acetylation of an amide nitrogen under *O*-acetylation conditions (Ac_2O, pyridine). The thiophenyl auxiliary group of **28** was removed by treatment with Ph_3SnH–AIBN (as in the preparation of **20**) to give **29** in 65% yield (Scheme 5). De-*O*-acetylation of **29** gave the hexaol lactam **30** (83%) and hydrogenolytic removal of the *O*-benzyl groups furnished the GD3-tetrasaccharide lactam **31** (96%). Treatment of **31** with Ac_2O–pyridine yielded the *O*- (and *N*-) acetylated GD3 saccharide **32** (53%), suitable for transformation into linker-arm saccharides for further coupling to protein. The protein conjugates should be potentially useful immunogens for trial vaccinations against malignant melanoma.[4,5]

3. Experimental

General methods.—The structures of all new compounds were determined by careful NMR analyses, including 2D-methods such as COSY, TOCSY, HETCOR, long-range HETCOR, and NOESY. NMR spectra were recorded with a Bruker ARX 400 MHz spectrometer. Melting points are uncorrected. Molecular sieves were activated by drying under vacuum. Dichloromethane was dried and distilled from CaH_2 prior to use. MeCN was kept over 3 Å molecular sieved for a few days and distilled from CaH_2 prior to use. DMF was dried over 4 Å molecular sieved and distilled from P_2O_5. Dichloroethane was distilled from P_2O_5. Br_2 was distilled from P_2O_5. MeSBr was prepared in 1,2-dichloroethane to give a 2 M solution. Et_3N was distilled prior to use. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. High-resolution FAB mass spectra were obtained on a JEOL JMS SX 102 spectrometer. Concentrations were made using rotary evaporation with bath temperature at or below 40 °C. TLC was performed on Kieselgel 60 F_{254} plates (E. Merck). Column chromatography was performed using SiO_2 (Matrex LC-gel, 60A, 35-70 MY, Grace).

Methyl (ethyl 4,7,8,9-tetra-O-*acetyl-5*-N,N-*diacetylamino-3,5-dideoxy-3-phenylthio-2-thio*-D-erythro-*β*-L-gluco-*non-2-ulopyranosid)onate* (**2**).—To a mixture of compound **1**[12] (1.287 g, 2.0 mmol) and isopropenyl acetate (10 mL) was added *p*-toluenesulfonic acid (19 mg). The mixture was stirred at 60 °C for 20 h, then cooled to rt. Et_3N (1 drop) was added and the mixture was concentrated. The residue was chromatographed (19:1 → 4:1 toluene–MeCN) to give **2** (1.33 g, 97%). $[\alpha]_D^{23}$ + 72° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.61–7.17 (m, 10 H, Ar), 5.79 (dd, 1 H, *J* 9.8, 10.8 Hz, H-4), 5.30 (m, 1 H, H-8), 5.12 (dd, 1 H, *J* 1.8, 8.4 Hz, H-7), 4.83 (dd, 1 H, *J* 1.8, 10.6 Hz, H-6), 4.33 (dd, 1 H, *J* 10.6, 9.8 Hz, H-5), 4.27 (dd, 1 H, *J* 2.8, 12.6 Hz, H-9), 4.14 (dd, 1 H, *J* 4.9, 12.6 Hz, H-9′), 3.94 (s, 3 H, $COOCH_3$), 3.42 (d, 1 H, *J* 10.8 Hz, H-3), 2.98–2.76 (m, 2 H, SCH_2CH_3), 2.36, 2.28, 2.17, 2.11, 2.03, 1.86, (6s, 3 H each, Ac), 1.27 (t, 3 H, *J* 7.5 Hz, SCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 174.6, 174.3, 171.1, 170.6, 170.5, 170.4, 167.9, 137.9, 132.0, 129.5, 129.4, 128.7, 127.8, 125.7, 87.5, 72.3, 71.8, 68.9, 67.4, 62.1, 60.5, 57.5, 53.5, 28.5, 27.0, 23.8, 21.5, 21.4, 21.2, 21.0, 14.3; HRMS *m/z* Calcd for $C_{30}H_{39}O_{13}NS_2Na$ [M + Na] 708.1760. Found 708.1744.

(Methyl 4,7,8,9-tetra-O-*acetyl-5*-N,N-*diacetylamino-3,5-dideoxy-3-phenylthio*-D-erythro-*β*-L-gluco-*non-2-ulopyranosylonate)-(2→6)-1,2;3,4-di*-O-*isopropylidene-α*-D-*galactopyranose* (**4**).—Donor **2** (132 mg, 0.193 mmol), and acceptor **3**[12] (42 mg, 0.161 mmol) were dissolved in a mixture of MeCN (3 mL) and CH_2Cl_2 (1.5 mL) and powdered 3 Å molecular sieves (250 mg) were added. The reaction mixture was stirred at rt for 5 min under N_2 and cooled to −45 °C. AgOTf (110 mg, 0.426 mmol) was dissolved in MeCN (1 mL) and the solution was added to the reaction mixture. After 5 min, a 2 M solution of MeSBr in 1,2-dichloroethane[20] (0.194 mL) was added over a period of 5 min. The reaction mixture was stirred at −45 °C for 3 h. Diisopropyl amine (0.1 mL) was added and the reaction mixture was stirred for 45 min at −45 °C. The temperature was raised to 22 °C, the mixture was filtered, the solid material was washed with MeCN, and the filtrate was concentrated. The residue was chromatographed (19:1→9:1 toluene–MeCN) to give pure **4** (100 mg, 70%). $[\alpha]_D^{23}$ +8° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): *δ* 7.60–7.15 (m, 5 H, Ar), 5.88 (dd, 1 H, *J* 8.7, 9.7 Hz, H-4′), 5.53 (d, 1 H, *J* 5.0 Hz, H-1), 5.33 (ddd, 1 H, *J* 3.0, 5.3, 7.6 Hz, H-8′), 5.17 (dd, 1 H, *J* 1.6, 10.2 Hz, H-6′), 5.10 (dd, 1 H, *J* 1.6, 7.6 Hz, H-7′), 4.58 (dd, 1 H, *J* 2.3, 7.9 Hz, H-3), 4.38 (t, 1 H, *J* 10.2 Hz, H-5′), 4.31 (dd, 1 H, *J* 5.0, 2.3 Hz, H-2), 4.25 (dd, 1 H, *J* 3.0, 12.4 Hz, H-9′), 4.20 (dd, 1 H, *J* 1.0, 7.9 Hz, H-4), 4.13 (dd, 1 H, *J* 5.3, 12.4 Hz, H-9′), 4.07–3.94 (m, 3 H, H-5,6), 3.86 (s, 3 H, $COOCH_3$), 3.32 (d, 1 H, *J* 8.7 Hz, H-3′), 2.39, 2.27, 2.11, 2.08, 2.02, 1.96 (6s, 3 H each, Ac), 1.46, 1.44, 1.34, 1.32 (4s, 3 H each, Me); ^{13}C NMR ($CDCl_3$): *δ* 174.9, 174.1, 171.0, 170.4, 170.3, 170.1, 167.7, 133.5, 129.4, 128.2, 109.7, 109.0, 101.1, 96.7, 72.1, 71.6, 71.1, 71.0, 70.1, 69.3, 67.8, 67.5, 64.6, 62.2, 59.5, 57.3, 52.9, 28.4, 26.6, 26.44, 26.41, 25.5, 24.9, 21.4, 21.3, 21.2, 21.0; (C-1′, $^3J_{C\text{-}1'\text{–}H\text{-}3'ax}$ 4.9 Hz; cf. Refs. 12a, 21); HRMS *m*/*z* Calcd for $C_{40}H_{53}NNaO_{19}S$ [M + Na] 906.2830. Found 906.2823.

Methyl (methyl 4,7,8,9-tetra-O-*acetyl-5*-N,N-*diacetylamino-3,5-dideoxy-3-phenylthio*-D-erythro-*β*-L-gluco-*non-2-ulopyranosylonate)-(2→3)-2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranoside* (**6**).—Donor **2** (110 mg, 0.161 mmol), and acceptor **5**[12] (40 mg, 0.134 mmol) were dissolved in a mixture of MeCN (3 mL) and CH_2Cl_2 (1.5 mL) and powdered 3 Å molecular sieves (250 mg) were added. The mixture was treated essentially as in the preparation of **4**, using 0.161 mL of the 2 M MeSBr solution, AgOTf (91 mg, 0.354 mmol). Workup and chromatographic purification (19:1→4:1 toluene–MeCN), followed by *O*-acetylation (Ac_2O–pyridine) and chromatography furnished **6** (52 mg, 39%). $[\alpha]_D^{23}$ +51° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): *δ* 8.16–7.15 (m, 10 H, Ar), 5.75 (dd, 1 H, *J* 11.0, 9.6 Hz, H-4′), 5.53–5.47 (m, 2 H, H-8′,4), 5.28 (dd, 1 H, *J* 8.0, 10.0 Hz, H-2), 5.18 (dd, 1 H, *J* 2.4, 9.2 Hz, H-7′), 4.92 (dd, 1 H, *J* 10.0, 3.7 Hz, H-3), 4.63 (d, 1 H, *J* 8.0 Hz, H-1), 4.62 (dd, 1 H, *J* 2.4, 10.5 Hz, H-6′), 4.42 (dd, 1 H, *J* 10.5, 9.6 Hz, H-5′), 4.03 (dd, 1 H, *J* 4.8, 12.6 Hz, H-9″), 3.95 (s, 3 H, $COOCH_3$), 3.59 (s, 3 H, OMe), 3.06 (d, 1 H, *J* 11.0 Hz, H-3′), 2.37, 2.27, 2.23, 2.15, 2.06, 2.01, 1.88, 1.83 (8s, 3 H each, Ac); ^{13}C NMR ($CDCl_3$): *δ* 174.3, 174.0, 171.03, 170.99, 170.92, 170.88, 170.2, 170.1, 167.6, 166.2, 138.3, 133.6, 131.6, 130.23, 130.18, 129.5, 129.4, 128.8, 128.7, 127.4, 125.7, 102.2, 98.8, 72.9, 71.8, 70.9, 69.8, 68.1, 67.7, 67.0, 62.6, 62.4, 60.3, 57.4, 56.5, 53.3, 28.5, 27.5, 21.8, 21.6, 21.3, 21.2, 21.0, 20.9. (C-1′, $^3J_{C\text{-}1'\text{–}H\text{-}3'ax}$ 6.0 Hz; cf. Refs. 12a, 21); HRMS *m*/*z* Calcd for $C_{46}H_{55}NNaO_{22}S$ [M + Na] 1028.2834. Found 1028.2849.

Methyl (methyl 4,7,8,9-tetra-O-*acetyl-5*-N,N-*diacetylamino-3,5-dideoxy-3-phenylthio*-D-erythro-*β*-L-gluco-*non-2-ulopyranosylonate)-(2→3)-2,4,6-tri*-O-*acetyl-β*-D-*galactopyranoside* (**8**).—Donor **2** (121 mg, 0.177 mmol), and acceptor **7**[12] (41 mg, 0.147 mmol) were dissolved in a mixture of MeCN (3 mL) and CH_2Cl_2 (1.5 mL) and activated powdered 3 Å molecular sieves (250 mg) were added. The mixture was treated essentially as in the preparation of **4**, using 0.177 mL of the 2 M MeSBr solution, AgOTf (100 mg, 0.388 mmol). Workup and chromatographic purification (19:1→3:1 toluene–MeCN), followed by *O*-acetylation (Ac_2O–pyridine) and chromatography furnished **8** (90 mg, 65%). $[\alpha]_D^{23}$ +72° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): *δ* 7.54–7.15 (m, 5 H, Ar), 5.75 (dd, 1 H, *J* 9.6, 10.9 Hz, H-4′), 5.48 (ddd, 1 H, *J* 9.2, 2.6, 4.8 Hz, H-8′), 5.34 (dd, 1 H, *J* 3.8, 1.0 Hz, H-4), 5.23 (dd, 1 H, *J* 8.0, 10.0 Hz, H-2), 5.19 (dd, 1 H, *J* 2.4, 9.2 Hz, H-7′), 4.87 (dd, 1 H, *J* 10.0, 3.8 Hz, H-3), 4.61 (dd, 1 H, *J* 10.5, 2.4 Hz, H-6′), 4.56 (d, 1 H, *J* 8.0 Hz, H-1), 4.41 (dd, 1 H, *J* 9.6, 10.5 Hz, H-5′), 4.32 (dd, 1 H, *J* 2.6, 12.6 Hz, H-9′), 4.15 (brd, 2 H, *J* 6.8 Hz, H-6.6′), 4.02 (dd, 1 H, *J* 4.8, 12.6 Hz, H-9″), 3.99 (s, 3 H, $COOCH_3$), 3.95 (m, 1 H, H-5), 3.57 (s, 3 H, OMe), 3.05 (d, 1 H, *J* 10.9 Hz, H-3′), 2.36, 2.26, 2.22, 2.19, 2.07, 2.05, 2.00, 1.86, 1.79 (9s, 3 H each, Ac); ^{13}C NMR ($CDCl_3$): *δ* 174.3, 174.0, 171.04, 171.00, 170.97, 170.91, 170.88, 170.20, 170.15, 167.6, 138.2, 131.5, 129.4, 128.7, 127.4, 125.7, 102.0, 98.8, 72.8, 71.8, 71.1, 70.8, 69.9, 68.1, 67.9, 67.0, 62.9, 62.4, 60.2, 57.3, 56.5, 53.4, 28.6, 27.5, 21.9, 21.6, 21.3, 21.21, 21.16, 21.0, 20.9; HRMS *m*/*z* Calcd for $C_{41}H_{53}NNaO_{22}S$ [M + Na] 966.2677. Found 966.2688.

2-(Trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-O-*acetyl-5*-N,N-*diacetylamino-3,5-dideoxy-3-phenylthio*-D-erythro-*β*-L-gluco-*non-2-ulopyranosylonate)-(2→3)-2-azido-6*-O-*benzoyl-2-deoxy-β*-D-*galactopyranoside* (**10**).—Donor **2** (100 mg, 0.146 mmol) and acceptor **9**[8b] (30 mg, 0.073 mmol) were dissolved in a mixture of MeCN (1 mL) and CH_2Cl_2 (0.7 mL) and activated powdered 3 Å molecular sieves (200 mg) were added. The mixture was treated essentially as in the preparation of **4**, using 0.147 mL of the 2 M MeSBr solution, AgOTf (83 mg,

0.322 mmol). Workup and chromatographic purification (19:1→4:1 toluene–MeCN) furnished **10** (50 mg, 66%). $[\alpha]_D^{23}$ +27° (*c* 0.46, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.08–7.15 (m, 10 H, Ar), 5.92 (dd, 1 H, *J* 10.7, 10.0 Hz, H-4′), 5.43 (ddd, 1 H, *J* 8.7, 2.8, 5.0 Hz, H-8′), 5.18 (dd, 1 H, *J* 1.9, 8.7 Hz, H-7′), 5.11 (dd, 1 H, *J* 1.9, 10.2 Hz, H-6′), 4.48 (t, 1 H, *J* 10.0 Hz, H-5′), 3.95 (s, 3 H, $COOCH_3$), 3.45 (d, 1 H, *J* 10.8 Hz, H-3′), 2.39, 2.36, 2.29, 2.09, 2.07, 2.03 (6s, 3 H each, Ac), 1.12–0.96 (m, 2 H, CH_2Si), −0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 174.8, 174.0, 171.0, 170.5, 170.3, 167.9, 166.6, 136.0, 133.5, 131.9, 130.5, 130.1, 129.8, 129.5, 128.8, 128.7, 128.4, 101.0, 100.6, 75.8, 72.1, 70.4, 70.3, 68.7, 67.6, 67.5, 67.1, 64.1, 63.1, 62.4, 59.3, 57.0, 53.2, 28.5, 26.7, 21.4, 21.3, 21.2, 21.0, 18.5, −0.2. (C-1′, $^3J_{C\text{-}1'\text{–}H\text{-}3'ax}$ 6.9 Hz; cf. Refs. 12a, 21); HRMS *m*/*z* Calcd for $C_{46}H_{60}N_4NaO_{19}SSi$ [M + Na] 1055.3239. Found 1055.3239. A sample of **10** (40 mg, 0.0387 mmol) was treated with Ac_2O–pyridine and the crude product was purified by chromatography (19:1→4:1 toluene–MeCN) to give 2-(trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-*O*-acetyl-5-*N*,*N*-diacetylamino-3,5-dideoxy-3-phenylthio-D-*erythro*-β-L-*gluco*-non-2-ulopyranosylonate)-(2→3)-4-*O*-acetyl-2-azido-6-*O*-benzoyl-2-deoxy-β-D-galactopyranoside (38 mg, 91%). $[\alpha]_D^{23}$ +28° (*c* 0.55, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.08–7.15 (m, 10 H, Ar), 5.85 (dd, 1 H, *J* 9.7, 10.9 Hz, H-4′), 5.51 (d, 1 H, *J* 3.4 Hz, H-4), 5.48 (m, 1 H, H-8′), 5.19 (dd, 1 H, *J* 2.0, 8.8 Hz, H-7′), 4.93 (dd, 1 H, *J* 10.1, 3.6 Hz, H-3), 4.74 (dd, 1 H, *J* 2.0, 10.3 Hz, H-6′), 4.44 (d, 1 H, *J* 8.2 Hz, H-1), 4.37 (t, 1 H, *J* 10.0 Hz, H-5′), 3.96 (s, 3 H, $COOCH_3$), 3.33 (d, 1 H, *J* 11.0 Hz, H-3′), 2.36, 2.25, 2.11, 2.06, 2.04, 1.91, 1.89 (7s, 3 H each, Ac), 1.10 (m, 2 H, CH_2Si), 0.02 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 174.5, 174.0, 171.1, 170.9, 170.64, 170.60, 170.5, 167.4, 166.3, 138.3, 138.2, 133.6, 132.9, 132.1, 132.0, 131.3, 130.19, 130.15, 129.5, 129.4, 128.8, 128.7, 127.8, 127.5, 125.7, 100.7, 98.9, 77.7, 73.6, 71.5, 71.0, 69.8, 68.6, 68.1, 67.4, 66.9, 63.5, 62.6, 62.4, 59.3, 57.0, 53.4, 28.5, 26.9, 21.7, 21.2, 21.1, 20.9, 18.6, −0.2; HRMS *m*/*z* Calcd for $C_{48}H_{62}N_4NaO_{20}SiS$ [M + Na] 1097.3345. Found 1097.3326.

2-(Trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-O-*acetyl-5*-N,N-*diacetylamino-3,5-dideoxy-3-phenylthio*-D-erythro-β-L-gluco-*non-2-ulopyranosylonate)-(2→3)-(2,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**12**).—Donor **2** (685.7 mg, 1.0 mmol) and acceptor **11**[12] (1.51 g, 1.536 mmol) were dissolved in a mixture of MeCN (3 mL) and CH_2Cl_2 (1.5 mL) and activated powdered 3 Å molecular sieves (400 mg) were added. The mixture was treated essentially as in the preparation of **4**, using AgOTf (565 mg, 2.2 mmol) in MeCN (1 mL) and 1 mL of the 2 M MeSBr solution. Workup and chromatographic purification (19:1→9:1 toluene–MeCN) furnished **12** (1.1 g, 69%; yield based on donor **2**) and recovered **11** (600 mg). When 2 equiv of **2** and 1 equiv of **11** were used, **12** was obtained in 83% yield. ^{1}H NMR ($CDCl_3$): δ 7.40–7.10 (m, 35 H, Ar), 5.87 (dd, 1 H, *J* 9.7, 11.0 Hz, H-4″), 5.52 (m, 1 H, H-8″), 5.17 (dd, 1 H, *J* 2.2, 8.4 Hz, H-7″), 5.12 (d, 1 H, *J* 11.2 Hz, CH_2Ph), 5.04 (d, 1 H, *J* 11.1 Hz, CH_2Ph), 4.91 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.79 (dd, 1 H, *J* 2.2, 10.4 Hz, H-6″), 4.74 (d, 1 H, *J* 7.4 Hz, H-1′), 4.38 (d, 1 H, *J* 8.7 Hz, H-1), 4.24 (dd, 1 H, *J* 2.4, 12.9 Hz, H-9″), 3.93 (s, 3 H, $COOCH_3$), 3.30 (d, 1 H, *J* 11.0 Hz, H-3″), 2.39, 2.28, 2.09, 1.96, 1.92, 1.77 (6s, 3 H each, Ac), 1.03 (m, 2 H, CH_2Si), 0.03 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 174.4, 174.2, 170.9, 170.7, 170.6, 170.2, 168.0, 140.0, 139.7, 139.6, 139.2, 139.1, 139.0, 137.8, 131.8, 129.3, 128.7, 128.63, 128.6, 128.53, 128.48, 128.41, 128.36, 128.3, 127.93, 127.85, 127.83, 127.81, 127.73, 127.66, 127.6, 127.5, 127.4, 103.4, 103.1, 99.9, 83.3, 82.5, 80.0, 75.7, 75.6, 75.4, 75.3, 75.2, 75.0, 73.4, 73.3, 72.7, 71.9, 70.0, 69.6, 68.8, 68.5, 67.8, 67.2, 62.1, 60.3, 56.9, 53.2, 28.6, 27.3, 21.6, 21.2, 21.1, 21.0, 18.9, -0.10. (C-1″, $^3J_{C\text{-}1''\text{–}H\text{-}3''ax}$ 6.1 Hz; cf. Refs. 12a, 21); HRMS *m*/*z* Calcd for $C_{87}H_{103}NNaO_{24}SSi$ [M + Na] 1628.6257. Found 1628.6261.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-4,7,8,9-tetra-O-*acetyl-3,5-dideoxy-3-phenylthio*-D-erythro-β-L-gluco-*non-2-ulopyranosylonate)-(2→3)-(2,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**13**).—Compound **12** (20 mg, 0.012 mmol) was dissolved in MeOH (0.5 mL) and 1 M NaOMe in MeOH (0.009 mL) was added. The mixture was left at 22 °C for 4 h and neutralized with Duolite C26 (H^+) resin. The resin was filtered off and washed with MeOH. The filtrate was concentrated and the residue was treated with Ac_2O in pyridine to give **13** (17 mg, 87%) after chromatographic purification. The physical properties of **13** were identical with those reported.[12b]

2-(Trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-O-*acetyl-5*-N,N-*diacetylamino-3,5-dideoxy-3-phenylthio*-D-erythro-β-L-gluco-*non-2-ulopyranosylonate)-(2→3)-(2-azido-6*-O-*benzyl-2-deoxy-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**15**).—Donor **2** (80 mg, 0.116 mmol) and acceptor **14**[12] (80 mg, 0.097 mmol) were dissolved in a mixture of MeCN (2 mL) and CH_2Cl_2 (1 mL) and activated powdered 3 Å molecular sieves (200 mg) were added. The mixture was treated essentially as in the preparation of **4**, using AgOTf (66 mg, 0.255 mmol) in MeCN (1 mL), 0.116 mL of the 2 M MeSBr solution, and ^{i}Pr$_2$NH (0.1 mL). Workup and chromatographic purification (19:1→9:1 toluene–acetone) furnished **15** (135 mg, 96%). $[\alpha]_D^{23}$ + 13° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.56–7.15 (m, 25 H, Ar), 5.95 (dd, 1 H, *J* 10.7, 9.9 Hz, H-4″), 5.45 (ddd, 1 H, *J* 2.5, 5.5, 8.3 Hz, H-8″), 5.18 (dd, 1 H, *J* 1.7, 8.3 Hz, H-7″), 5.08 (dd, 1 H, *J* 1.7, 10.2 Hz, H-6″), 5.01 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.93 (d, 1 H, *J* 10.9 Hz, CH_2Ph), 4.84 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.54 (d, 1 H,

J 8.1 Hz, H-1′), 4.41 (d, 1 H, *J* 8.0 Hz, H-1), 4.28 (dd, 1 H, *J* 2.5, 12.6 Hz, H-9″), 3.96 (s, 3 H, $COOCH_3$), 3.44 (d, 1 H, *J* 10.7 Hz, H-3″), 2.41, 2.31, 2.22, 2.20, 1.95, 1.77 (6s, 3 H each, Ac), 1.07 (m, 2 H, CH_2Si), 0.05 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 174.7, 174.0, 170.9, 170.49, 170.45, 170.0, 167.7, 139.7, 139.1, 139.0, 138.7, 136.4, 132.0, 129.7, 127.5, 128.72, 128.68, 128.54, 128.52, 128.48, 128.2, 128.13, 128.10, 128.04, 127.99, 127.95, 127.86, 127.8, 127.5, 125.8, 103.5, 100.91, 100.87, 83.4, 82.7, 76.2, 75.5, 75.4, 75.3, 73.74, 73.67, 73.0, 70.8, 70.4, 69.6, 69.04, 68.99, 67.8, 67.5, 67.2, 64.2, 62.4, 59.3, 57.1, 53.3, 28.5, 26.7, 21.9, 21.4, 21.1, 21.0, 19.0, −0.1. A sample of **15** was acetylated and the crude product was purified by chromatography (19:1 → 4:1 toluene–MeCN) to give 2-(trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-*O*-acetyl-5-*N*,*N*-diacetylamino-3,5-dideoxy-3-phenylthio-D-*erythro*-β-L-*gluco*-non-2-ulopyranosylonate)-(2 → 3)-(2-azido-4-*O*-acetyl-6-*O*-benzyl-2-deoxy-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (110 mg 79%). $[\alpha]_D^{23}$ +20° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.48–7.15 (m, 25 H, Ar), 5.89 (dd, 1 H, *J* 9.7, 10.9 Hz, H-4″), 5.52 (ddd, 1 H, *J* 2.6, 5.4, 8.5 Hz, H-8″), 5.45 (d, 1 H, *J* 3.6 Hz, H-4′) 5.19 (dd, 1 H, *J* 1.8, 8.5 Hz, H-7″), 5.02 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.88 (d, 1 H, *J* 11.4 Hz, CH_2Ph), 4.78 (dd, 1 H, *J* 1.9, 10.4 Hz, H-6″), 4.62 (d, 1 H, *J* 12.0 Hz, CH_2Ph), 4.44 (d, 1 H, *J* 7.8 Hz, H-1), 4.30 (dd,1 H, *J* 2.6, 12.6 Hz, H-9″), 4.02 (s, 3 H, $COOCH_3$), 3.44 (dd,1 H, *J* 7.9, 9.1 Hz, H-2), 3.37 (d,1 H, *J* 10.9 Hz, H-3″), 2.37, 2.27, 2.18, 2.11, 2.05, 1.98, 1.87 (7s, 3 H each, Ac), 1.13–1.01 (m, 2 H, CH_2Si), 0.06 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 174.4, 174.1, 171.0, 170.6, 170.5, 170.4, 170.3, 167.1, 139.7, 139.1, 139.0, 138.52, 138.46, 131.0, 129.5, 129.4, 128.74, 128.71, 128.67, 128.6, 128.5, 128.1, 128.0, 127.93, 127.91, 127.8, 127.6, 127.3, 125.8, 103.5, 100.7, 99.1, 83.3, 82.7, 75.4, 75.34, 75.29, 73.9, 73.60, 73.55, 72.1, 71.7, 69.8, 69.6, 68.6, 67.9, 67.8, 67.5, 67.0, 64.8, 62.5, 59.0, 57.0, 28.5, 27.0, 21.9, 21.6, 21.2, 21.1, 20.9, 19.0, −0.1, (C-1″, $^3J_{C\text{-}1''\text{–}H\text{-}3''ax}$ 6.1 Hz, cf. Refs. 12a, 21); HRMS *m*/*z* Calcd for $C_{75}H_{92}O_{24}N_4SSiNa$ [M + Na] 1515.5489. Found 1515.5514.

2-(Trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-O-*acetyl-5*-N,N-*diacetylamino-3,5-dideoxy-3-phenylthio*-D-erythro-*β*-L-gluco-*non-2-ulopyranosylonate)-(2→3)-(2,6-di*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-2,3-di*-O-*acetyl-β*-D-*xylopyranoside* (**17**).—Donor **2** (170 mg, 0.248 mmol) and acceptor **16**[8c] (72 mg, 0.124 mmol) were dissolved in a mixture of MeCN (1.5 mL) and CH_2Cl_2 (1 mL) and activated powdered 3 Å molecular sieves (250 mg) were added. The mixture was treated essentially as in the preparation of **4**, using AgOTf (140 mg, 0.546 mmol) in MeCN (1 mL), 0.248 mL of the 2 M MeSBr solution, and $^iPr_2NH$ (0.1 mL). Workup and chromatographic purification (19:1 → 4:1 toluene–MeCN) furnished **17** (90 mg, 60%). $[\alpha]_D^{23}$ +30° (*c* 0.60, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.53–7.20 (m, 5 H, Ar), 5.78 (dd, 1 H, *J* 9.6, 10.9 Hz, H-4″), 5.46 (m, 1 H, H-8″), 5.07 (dd, 1 H, *J* 8.0, 9.9 Hz, H-2′), 4.84 (dd, 1 H, *J* 7.3, 9.0 Hz, H-2), 4.56 (d, 1 H, *J* 8.0 Hz, H-1′), 4.42 (d, 1 H, *J* 7.3 Hz, H-1), 4.35 (dd, 1 H, *J* 2.5, 12.4 Hz, H-9″), 4.09 (dd, 1 H, *J* 5.3, 11.9 Hz, H-5), 3.95 (s, 3 H, $COOCH_3$), 3.31 (dd, 1 H, *J* 9.9, 11.9, Hz, H-5), 3.18 (d, 1 H, *J* 10.9 Hz, H-3″), 2.35, 2.26, 2.19, 2.12, 2.09, 2.05, 2.04, 2.03, 2.01, 1.87 (10s, 3 H each, Ac), 0.09–0.83 (m, 2 H, CH_2Si), −0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 174.4, 173.9, 171.2, 171.0, 170.8, 170.6, 170.5, 170.3, 170.2, 169.9, 167.8, 136.8, 131.6, 129.6, 127.9, 101.4, 100.9, 99.5, 76.5, 74.9, 73.1, 72.4, 71.8, 71.4, 70.4, 70.1, 68.3, 68.26, 67.6, 67.2, 63.8, 63.7, 62.8, 59.9, 56.4, 53.4, 28.6, 27.4, 21.7, 21.5, 21.3, 21.24, 21.18, 21.1, 20.9, 18.4, −0.1 (C-1″, $^3J_{C\text{-}1''\text{–}H\text{-}3''ax}$ 6.1 Hz; cf. Refs. 12a, 21); HRMS *m*/*z* Calcd for $C_{52}H_{73}NNaO_{27}SSi$ [M + Na] 1226.3757. Found 1226.3781. A sample of **17** was per-*O*-acetylated with Ac_2O–pyridine and the crude product was chromatographed (9:1 → 3:1 toluene–MeCN) to give 2-(trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-*O*-acetyl-5-*N*,*N*-diacetylamino-3,5-dideoxy-3-phenylthio-D-*erythro*-β-L-*gluco*-non-2-ulopyranosylonate)-(2 → 3)-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,4-di-*O*-acetyl-β-D-xylopyranoside (26 mg, 97%). $[\alpha]_D^{23}$ +38° (*c* 0.55, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.52–7.15 (m, 5 H, Ar), 5.73 (dd, *J* 5.8, 10.9 Hz, 1 H, H-4″), 5.54 (m, 1 H, H-8″), 5.26 (dd, *J* 1.0, 3.7 Hz, 1 H, H-4′), 4.84 (dd, 1 H, *J* 10.1, 3.7 Hz, H-3′), 4.67 (d, *J* 8.0 Hz, 1 H, H-1′), 4.60 (dd, *J* 10.6, 2.5 Hz, 1 H, H-6″), 4.14 (dd, 1 H, *J* 5.1, 11.9 Hz, H-5), 3.98 (s, 3 H, $COOCH_3$), 3.56 (m, 1 H, OCH_2CH_2Si); 3.35 (dd, 1 H, *J* 9.9, 11.9 Hz, H-5), 3.04 (d, 1 H, *J* 10.9 Hz, H-3″), 2.35, 2.26, 2.22, 2.18, 2.08, 2.06, 2.05, 2.02, 1.87, 1.80 (10s, 3 H each, Ac), 1.00–0.85 (m, 2 H, CH_2Si), 0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 174.3, 174.0, 171.12, 171.05, 170.99, 170.90, 170.86, 170.6, 170.4, 170.2, 169.8, 167.5, 138.3, 131.6, 129.5, 129.4, 128.7, 127.5, 101.8, 101.0, 98.7, 73.3, 72.6, 71.8, 71.3, 70.7, 69.8, 68.0, 67.72, 67.66, 67.3, 63.7, 63.0, 62.8, 60.1, 56.3, 53.5, 28.6, 27.5, 21.9, 21.4, 21.32, 21.26, 21.21, 21.19, 21.15, 21.0, 20.9, 18.4, -1.0; HRMS *m*/*z* Calcd for $C_{54}H_{75}O_{28}NSSiNa$ [M + Na] 1268.3863. Found 1268.3876.

Methyl [2-(trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-O-*acetyl-5*-N,N-*diacetylamino-3,5-dideoxy-3-phenylthio*-D-erythro-*β*-L-gluco-*non-2-ulopyranosylonate)-(2→8)-5-acetamido-4*-O-*benzoyl-3,5-dideoxy-9*-O-*p-methoxybenzyl*-D-glycero-*α*-D-galacto-*non-2-ulopyranosid]onate* (**19**).—Donor **2** (138 mg, 0.201 mmol) and acceptor **18**[12b] (65 mg, 0.100 mmol) were dissolved in a mixture of MeCN (1.5 mL) and CH_2Cl_2 (1 mL) and activated powdered 3 Å molecular sieves (250 mg) were added. The mixture was treated essentially as in the preparation of **4**, using AgOTf (114 mg, 0.441 mmol) in MeCN (1.2 mL), 0.20 mL of the 2 M MeSBr solution,

and $^{i}Pr_2NH$ (0. 1 mL). Workup and chromatographic purification (19:1→3:1 toluene–MeCN) furnished **19** (58 mg, 46%). $[\alpha]_D^{23}$ +20° (*c* 0.60, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.08–6.82 (m, 14 H, Ar), 6.07 (d, 1 H, *J* 9.3 Hz, NH), 5.88 (t, 1 H, *J* 9.8 Hz, H-4′), 5.32 (m, 1 H, H-8′), 5.19 (m, 1 H, H-4), 5.14 (dd, 1 H, *J* 1.5, 8.6 Hz, H-7′), 4.97 (dd, 1 H, *J* 1.5, 10.3 Hz, H-6′), 4.94 (m, 1 H, H-8), 4.32 (m, 2 H, H-5,5′), 3.88, 3.84, 3.79 (3s, 3 H each, $COOCH_3$, OCH_3), 3.53 (d, 1 H, *J* 9.9 Hz, H-3′), 3.40 (m, 1 H, OCH_2CH_2Si), 2.78 (dd, 1 H, *J* 12.8, 4.8 Hz, H-3eq), 2.38, 2.36, 2.21, 2.12, 2.06, 2.05, 1.90 (7s, 3 H each, Ac), 0.82 (t, 2 H, *J* 7.8 Hz, CH_2Si), −0.03 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 174.8, 174.0, 172.2, 171.4, 170.6, 170.4, 168.9, 168.6, 167.0, 159.3, 137.0, 133.8, 132.3, 131.5, 130.2, 129.5, 129.3, 129.2, 128.9, 128.7, 127.6, 125.7, 114.0, 100.9, 99.1, 77.7, 75.8, 75.7, 72.7, 72.0, 71.2, 70.3, 70.2, 69.2, 67.3, 62.4, 62.3, 59.6, 57.3, 55.6, 52.93, 52.91, 51.0, 38.3, 28.5, 26.6, 23.5, 21.5, 21.20, 21.16, 21.0, 18.3, −0.1; HRMS *m*/*z* Calcd for $C_{60}H_{78}N_2NaO_{24}SSi$ [M + Na] 1293.4322. Found 1293.4326. A sample of **19** was acetylated with Ac_2O in pyridine and the crude product was chromatographed (19:1→3:1 toluene–MeCN) to give the corresponding *O*-acetylated compound in 90% yield. $[\alpha]_D^{23}$ +44° (*c* 0.37, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.05–6.84 (m, 14 H, Ar), 6.30 (d, 1 H, *J* 9.4 Hz, NH), 5.80 (dd, 1 H, *J* 9.8, 10.8 Hz, H-4′), 5.69 (t, 1 H, *J* 1.7 Hz, H-7), 5.46 (m, 1 H, H-8′), 5.23 (m, 1 H, H-8), 5.17 (dd, 1 H, *J* 1.5, 9.2 Hz, H-7′), 5.05 (m, 1 H, H-4), 4.93 (dd, 1 H, *J* 1.5, 10.4 Hz, H-6′), 4.52 (d, 1 H, *J* 11.5 Hz, CH_2Ph), 4.37 (t, 1 H, *J* 10.1 Hz, H-5′), 4.18 (t, 1 H, *J* 9.8 Hz, H-5), 3.96 (s, 3 H, $COOCH_3$), 3.87 (s, 3 H, $COOCH_3$), 3.79 (s, 3 H, OMe), 3.47 (d, 1 H, *J* 4.7, 12.7 Hz, H-3′), 3.39 (m, 1 H, OCH_2CH_2Si), 2.87 (dd, 1 H, *J* 4.7, 12.7 Hz, H-3′), 2.38, 2.25, 2.17, 2.04, 2.03, 1.98, 1.86, 1.84 (8s, 3 H each, Ac), 0.90–0.75 (m, 2 H, CH_2Si), −0.3 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 174.7, 174.0, 171.4, 171.3, 170.52, 170.50, 170.48, 170.0, 168.9, 168.7, 166.6, 138.0, 133.6, 131.9, 131.6, 130.3, 130.2, 129.5, 129.1, 129.0, 128.9, 128.7, 127.1, 114.1, 99.8, 99.2, 77.7, 74.7, 74.4, 72.0, 71.6, 71.2, 70.64, 70.61, 70.2, 69.2, 66.9, 62.4, 62.3, 60.2, 57.4, 55.7, 53.2, 53.0, 49.6, 38.3, 28.5, 26.8, 23.6, 21.8, 21.2, 21.14, 21.08, 20.9, 18.3, −0.1.

2-(Trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-O-*acetyl-5*-N,N-*diacetylamino*-*3,5*-*dideoxy*-D-glycero-α-D-galacto-*non*-*2*-*ulopyranosylonate)*-*(2→3)*-*(2,4,6*-*tri*-O-*benzyl*-β-D-*galactopyranosyl)*-*(1→4)*-*2,3,6*-*tri*-O-*benzyl*-β-D-*glucopyranoside* (**20**).—Compound **12** (500 mg, 0.311 mmol) was treated with triphenyltin hydride (0.318 mL) in the presence of AIBN (51 mg, 0.311 mmol) in toluene (5 mL) at 120 °C for 4 h. The solvent was removed and the residue was chromatographed (19:1→4:1 toluene–MeCN) to give **20** (350 mg, 75%). $[\alpha]_D^{23}$ −4° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.40–7.12 (m, 30 H, Ar), 5.56 (m, 1 H, H-4″), 5.43 (m, 1 H, H-8″), 5.15 (dd, 1 H, *J* 1.5, 8.2 Hz, H-7″), 4.63 (d, 1 H, *J* 7.6 Hz, H-1′), 4.41 (d, 1 H, *J* 7.7 Hz, H-1), 4.20 (t, 1 H, *J* 9.8 Hz, H-5″), 2.68 (dd, 1 H, *J* 5.2, 13.1 Hz, H-3eq), 2.39, 2.33, 2.13, 1.99, 1.97, 1.82 (6s, 3 H each, Ac), 1.05 (m, 2 H, CH_2Si), 0.05 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 174.6, 174.4, 170.9, 170.6, 170.2, 170.0, 168.2, 140.0, 139.6, 139.5, 139.2, 139.1, 138.7, 128.73, 128.71, 128.7, 128.51, 128.49, 128.44, 128.39, 128.2, 128.04, 128.00, 127.96, 127.9, 127.8, 127.6, 127.5, 103.5, 103.1, 99.6, 83.5, 82.4, 79.2, 77.3, 77.1, 76.6, 75.74, 75.67, 75.39, 75.37, 75.3, 73.7, 73.6, 73.1, 70.0, 69.4, 68.4, 67.79, 67.4, 67.2, 62.1, 57.2, 53.4, 37.5, 28.5, 26.8, 21.5, 21.21, 21.16, 21.0, 18.9, −0.1 (C-1″, $^3J_{C\text{-}1''\text{–}H\text{-}3''ax} = 6.1$ Hz; cf. Refs. 12a, 21); HRMS *m*/*z* Calcd for $C_{62}H_{80}N_2NaO_{25}SSi$ [M + Na] 1335.4437. Found 1335.4434.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-*3,5-dideoxy*-D-glycero-α-D-galacto-*non*-*2*-*ulopyranosylonate)*-*(2→3)*-*(2,4,6*-*tri*-O-*benzyl*-β-D-*galactopyranosyl)*-*(1→4)*-*2,3,6*-*tri*-O-*benzyl*-β-D-*glucopyranoside* (**21**).—Compound **20** (500 mg, 0.334 mmol) was dissolved in MeOH (3 mL) and 1 M NaOMe in MeOH (0.05 mL) was added. The mixture was left at 22 °C for 3 h and neutralized with Duolite C26 (H^+) resin. The resin was filtered off and washed with MeOH. The filtrate was concentrated and the residue was chromatographed (19:1→1:2 toluene–acetone) to give **21** (401 mg, 93%). $[\alpha]_D^{23}$ −4° (*c* 0.89, $CHCl_3$); ^1H NMR ($CDCl_3$ + CD_3OD): δ 7.34–7.06 (m, 30 H, Ar), 4.96 (d, 1 H, *J* 10.6 Hz, CH_2Ph), 4.87 (d, 1 H, *J* 11.4 Hz, CH_2Ph), 4.86 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.72–4.66 (m, 3 H, CH_2Ph), 4.63 (d, 1 H, *J* 10.7 Hz, CH_2Ph), 4.54 (d, 1 H, *J* 11.9 Hz, CH_2Ph), 4.44 (d, 1 H, *J* 11.4 Hz, CH_2Ph), 4.42 (d, 1 H, *J* 8.0 Hz, H-1′), 4.41 (d, 1 H, *J* 11.8 Hz, CH_2Ph), 4.33 (d, 1 H, *J* 11.8 Hz, CH_2Ph), 4.32 (d, 1 H, *J* 7.8 Hz, H-1), 4.17 (d, 1 H, *J* 11.8 Hz, CH_2Ph), 3.98 (dd, 1 H, *J* 3.1, 9.9 Hz, H-3′), 3.99–3.94 (m, 1 H, OCH_2CH_2Si), 3.88 (brt, 1 H, *J* 9.3 Hz, H-4), 3.81 (m, 1 H, H-8″), 3.77–3.69 (m, 5 H, H-4,6), 3.72 (s, 3 H, $COOCH_3$), 3.65 (dd, 1 H, *J* 4.5, 12.0 Hz, H-9), 3.59 (dd, 1 H, *J* 7.7, 9.8 Hz, H-2′), 3.58–3.49 (m, 4 H, H-4,4″,9″, OCH_2CH_2Si), 3.48 (t, 1 H, *J* 9.1 Hz, H-3), 3.42–3.32 (m, 4 H, H-2), 3.29 (m, 1 H, H-5), 2.59 (dd, 1 H, *J* 4.7, 13.3 Hz, H-3″eq), 1.99 (s, 3 H, Ac), 1.98 (brt, 1 H, *J* 13.3 Hz, H-3″ax), 0.99 (m, 2 H, CH_2Si), −0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$ + CD_3OD): δ 174.3, 170.2, 139.6, 139.5, 139.2, 139.0, 138.7, 138.6, 128.8, 128.72, 128.70, 128.63, 128.57, 128.54, 128.47, 128.4, 128.13, 128.06, 128.02, 127.97, 127.91, 127.85, 127.7, 127.5, 103.5, 103.0, 100.2, 83.3, 82.2, 78.7, 77.7, 77.3, 77.0, 76.6, 75.8, 75.5, 75.43, 75.36, 74.7, 73.6, 73.0, 68.6, 68.5, 67.8, 64.0, 53.7, 53.0, 38.6, 23.2, 18.9, -0.1; HRMS *m*/*z* Calcd for $C_{71}H_{89}NNaO_{19}Si$ [M + Na] 1310.5696. Found 1310.5743.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-*3,5-dideoxy*-*9*-p-*toluenesulfonyl*-D-glycero-α-D-galacto-*non*-*2*-*ulopyranosylonate)*-*(2→3)*-*(2,4,6*-*tri*-O-*benzyl*-β-D-

galactopyranosyl)-(1→4)-2,3,6-tri-O-*benzyl*-β-D-*gluco-pyranoside* (**22**).—Compound **21** (505 mg, 0.392 mmol) was dissolved in CH_2Cl_2 (3 mL) and pyridine (1.5 mL), the mixture was cooled to −78 °C, and *p*-toluenesulfonyl chloride (149.5 mg, 0.784 mmol) was added. The mixture was stirred for 50 min and kept at −78 °C for 2 days. Water (0.095 mL) was added and the mixture was stirred at −78 °C for 20 min and at 22 °C for 30 min. The reaction mixture was concentrated and the residue was chromatographed (19:1→2:1 toluene–MeCN) to give **22** (512 mg, 91%). $[\alpha]_D^{23}$ −4° (*c* 0.62, $CHCl_3$); ^{1}H NMR ($CDCl_3 + CD_3OD$): δ 7.72–7.05 (m, 34 H, Ar), 4.94 (d, 1 H, *J* 10.7 Hz, C*H*$_2$Ph), 4.85 (d, 1 H, *J* 11.1 Hz, C*H*$_2$Ph), 4.84 (d, 1 H, *J* 11.4 Hz, C*H*$_2$Ph), 4.70–4.61 (m, 4 H, C*H*$_2$Ph), 4.51 (d, 1 H, *J* 12.3 Hz, C*H*$_2$Ph), 4.40 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.39 (d, 1 H, *J* 7.7 Hz, H-1′), 4.38 (d, 1 H, *J* 12.0 Hz, C*H*$_2$Ph), 4.31 (d, 1 H, *J* 7.7 Hz, H-1), 4.29 (d, 1 H, *J* 11.6 Hz, C*H*$_2$Ph), 4.15 (dd, 1 H, *J* 2.6, 10.2 Hz, H-9″), 4.14 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.06 (dd, 1 H, *J* 5.1, 10.2 Hz, H-9″), 3.70 (s, 3 H, $COOCH_3$), 2.58 (dd, 1 H, *J* 4.6, 13.3 Hz, H-3″eq), 2.38 (s, 3 H, SO_2PhMe), 2.00 (s, 3 H, Ac), 1.95 (brt, 1 H, *J* 12.0 Hz, H-3″ax), 0.99 (m, 2 H, C*H*$_2$Si), −0.01 (s, 9 H, Si*Me*$_3$); ^{13}C NMR ($CDCl_3$): δ 173.6, 169.6, 145.0, 139.1, 139.0, 138.7, 138.5, 138.2, 132.1, 129.9, 128.9, 128.24, 128.16, 128.1, 128.0, 127.9, 127.84, 127.80, 127.7, 127.5, 127.4, 127.3, 127.2, 127.0, 125.2, 103.0, 102.4, 99.5, 82.8, 81.7, 78.1, 76.6, 76.5, 76.3, 75.2, 75.1, 75.0, 74.9, 74.8, 73.8, 73.0, 72.4, 71.4, 69.3, 68.1, 67.84, 67.77, 67.6, 67.4, 53.3, 52.8, 38.1, 22.9, 21.6, 18.4, -1.5; HRMS *m*/*z* Calcd for $C_{78}H_{95}NO_{21}SSiNa$ [M + Na] 1464.5785. Found 1464.5747.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-9-azido-3,5,9-trideoxy-D-glycero-α-D-galacto-*non-2-ulopyranosylonate)-(2→3)-(2,4,6-tri*-O-*benzyl*-β-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**23**).—To a solution of **22** (430 mg, 0.298 mmol) in DMF (3 mL) was added 18-crown-6 (32 mg) followed by NaN_3 (97 mg, 1.490 mmol) and the reaction mixture was stirred at 60 °C for 24 h. The mixture was cooled to 22 °C, filtered, and the filtrate was concentrated. The residue was chromatographed (19:1→2:1 toluene–MeCN) to give **23** (330 mg, 84%). $[\alpha]_D^{23}$ −1° (*c* 0.73, $CHCl_3$); IR (neat); *ν* 2090 cm^{-1}; ^{1}H NMR ($CDCl_3 + CD_3OD$): δ 7.35–7.08 (m, 30 H, Ar), 4.98 (d, 1 H, *J* 10.7 Hz, C*H*$_2$Ph), 4.88 (d, 2 H, *J* 11.2 Hz, C*H*$_2$Ph), 4.73–4.63 (m, 4 H, C*H*$_2$Ph), 4.56 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.46 (d, 1 H, *J* 11.5 Hz, C*H*$_2$Ph), 4.44 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.43 (d, 1 H, *J* 7.7 Hz, H-1′), 4.35 (d, 1 H, *J* 11.8 Hz, C*H*$_2$Ph), 4.34 (d, 1 H, *J* 7.8 Hz, H-1), 4.20 (d, 1 H, *J* 11.8 Hz, C*H*$_2$Ph), 3.73 (s, 3 H, $COOCH_3$), 2.60 (dd, 1 H, *J* 4.7, 13.3 Hz, H-3″eq), 2.03 (s, 3 H, Ac), 1.99 (brdd, 1 H, *J* 12.1, 13.0 Hz, H-3″ax), 1.01 (m, 2 H, C*H*$_2$Si), 0.01 (s, 9 H, Si*Me*$_3$); ^{13}C NMR ($CDCl_3$): δ 173.5, 169.6, 139.2, 139.1, 138.8, 138.6, 138.3, 138.2, 128.41, 128.35, 128.30, 128.25, 128.16, 128.1, 128.0, 127.8, 127.73, 127.67, 127.61, 127.55, 127.4, 127.3, 127.2, 103.2, 102.6, 99.7, 82.9, 81.8, 78.4, 76.8, 76.7, 76.6, 75.3, 75.2, 75.1, 75.0, 74.2, 73.2, 72.6, 71.0, 69.1, 68.2, 68.1, 67.9, 67.5, 53.5, 53.4, 52.8, 38.4, 23.1, 18.5, -1.4; HRMS *m*/*z* Calcd for $C_{71}H_{88}N_4O_{18}SiNa$ [M + Na] 1335.5737. Found 1335.5763.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-9-azido-4-O-*benzoyl-3,5,9-trideoxy*-D-glycero-α-D-galacto-*non-2-ulopyranosylonate)-(2→3)-(2,4,6-tri*-O-*benzyl*-β-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**24**).—Compound **23** (330 mg, 0.251 mmol) was dissolved in CH_2Cl_2 (1.0 mL) and the mixture was cooled to −45 °C. Et_3N (88 μL) and benzoyl chloride (0.044 mL, 0.379 mmol) were added and the mixture was kept at −45 °C for 24 h. MeOH (200 μL) was added and the temperature was raised to 22 °C. The mixture was concentrated and the residue was dissolved in EtOAc (20 mL), washed successively with satd aq $NaHCO_3$ solution (3 × 3 mL) and water (3 mL), dried (Na_2SO_4), filtered, and concentrated. The residue was chromatographed (19:1→4:1 toluene–MeCN) to give **24** (300 mg, 84%). Mp 76–79 °C; $[\alpha]_D^{23}$ −32° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3 + CD_3OD$): δ 7.98–7.46 (m, 5 H, Ar), 7.34–7.03 (m, 30 H, Ar), 5.12 (ddd, 1 H, *J* 4.9, 10.5, 11.7 Hz, H-4″), 4.99 (d, 1 H, *J* 10.7 Hz, C*H*$_2$Ph), 4.90–4.87 (m, 2 H, C*H*$_2$Ph), 4.73 (d, 1 H, *J* 11.4 Hz, C*H*$_2$Ph), 4.72 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 4.66 (d, 1 H, *J* 11.4 Hz, C*H*$_2$Ph), 4.62 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.58 (d, 1 H, *J* 11.1 Hz, C*H*$_2$Ph), 4.48 (d, 1 H, *J* 11.4 Hz, C*H*$_2$Ph), 4.46 (d, 1 H, *J* 7.7 Hz, H-1′), 4.43 (d, 1 H, *J* 12.0 Hz, C*H*$_2$Ph), 4.35 (d, 1 H, *J* 7.9 Hz, H-1), 4.21 (d, 1 H, *J* 11.8 Hz, C*H*$_2$Ph), 4.18 (brt, 1 H, *J* 10.3 Hz, H-5″), 4.07 (dd, 1 H, *J* 3.3, 10.0 Hz, H-3′), 4.00 (m, 1 H, H-8″), 3.99 (m, 1 H, OC*H*$_2$CH$_2$Si), 3.92 (brt, 1 H, *J* 9.4 Hz, H-4), 3.89 (s, 3 H, $COOCH_3$), 3.77–3.74 (m, 1 H, H-9″), 3.69 (dd, 1 H, *J* 7.4, 10.1 Hz, H-2′), 3.60–3.46 (m, 8 H, H-2,5, OC*H*$_2$CH$_2$Si), 2.50 (dd, 1 H, *J* 4.9, 13.2 Hz, H-3″eq), 2.25 (brt, 1 H, *J* 13.0 Hz, H-3″ax), 1.93 (s, 3 H, Ac), 1.01 (m, 2 H, C*H*$_2$Si), 0.00 (s, 9 H, Si*Me*$_3$); ^{13}C NMR ($CDCl_3$): δ 173.1, 169.1, 167.0, 139.0, 138.7, 138.4, 138.3, 138.2, 133.9, 129.8, 128.7, 128.5, 128.2, 128.1, 128.0, 127.94, 127.85, 127.7, 127.5, 127.41, 127.37, 127.3, 127.2, 127.0, 103.0, 102.4, 99.6, 82.8, 81.7, 78.3, 77.0, 76.4, 76.3, 75.2, 75.0, 74.9, 74.8, 74.3, 73.2, 73.1, 72.5, 70.7, 69.7, 68.9, 68.2, 67.8, 67.2, 53.5, 53.3, 50.8, 34.9, 22.9, 18.4, −1.5.

2-(Trimethylsilyl)ethyl (methyl 4,7,8,9-tetra-O-*acetyl-5*-N,N-*diacetylamino-3,5-dideoxy-3-phenylthio*-D-erythro-β-L-gluco-*non-2-ulopyranosylonate)-(2→8)-(methyl 5-acetamido-9-azido-4*-O-*benzoyl-3,5,9-trideoxy*-D-glycero-α-D-galacto-*non-2-ulopyranosylonate)-(2→3)-(2,4,6-tri*-O-*benzyl*-β-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**25**).—The reaction was performed as described for **4** using donor

2 (319 mg, 0.46 mmol), acceptor **24** (220 mg, 0.155 mmol), MS (250 mg), CH_3CN (1.5 mL), CH_2Cl_2 (1.0 mL), AgOTf (299 mg, 1.16 mmol) in CH_3CN (1.0 mL), MeSBr (0.465 mL). After addition of MeSBr the reaction mixture was stirred at −45 °C for 3.5 h, then $^iPr_2NH$ (0.2 mL) was added the stirring was continued for 15 min and the reaction mixture was allowed to reach 22 °C. The mixture was filtered and the filtrate was concentrated. The residue was chromatographed (19:1→3:1 toluene–MeCN) to give **25** (157 mg, 50%). $[\alpha]_D^{23}$ ±0° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 8.10–7.11 (m, 40 H, Ar), 5.93 (t, 1 H, *J* 10.2 Hz, H-4‴), 5.76 (d, 1 H, *J* 8.9 Hz, NH), 5.36–5.24 (m, 2 H, H-4″, H-8‴), 5.12 (dd, 1 H, *J* 1.2, 7.8 Hz, H-7‴), 5.00 (m, 3 H, H-6‴), 4.91 (d, 1 H, *J* 11.1 Hz, C*H*$_2$Ph), 4.69 (d, 1 H, *J* 10.6 Hz, C*H*$_2$Ph), 4.28 (t, 1 H, *J* 9.9 Hz, H-5‴), 4.24 (m, 3 H, H-5″), 4.12 (dd, 1 H, *J* 2.7, 12.6 Hz, H-9‴), 3.87 (s, 3 H, $COOCH_3$), 3.82 (s, 3 H, $COOCH_3$), 3.40 (d, 1 H, *J* 10.7 Hz, H-3‴), 2.61 (dd, 1 H, *J* 5.0, 13.1 Hz, H-3″), 2.39, 2.26, 2.06, 2.05, 1.99, 1.98, 1.86 (7s, 3 H each), 1.02 (m, 2 H, C*H*$_2$Si), 0.01 (s, 9 H, Si*Me*$_3$): ^{13}C NMR ($CDCl_3$) δ 174.9, 174.1, 172.4, 171.1, 170.6, 170.4, 170.01, 169.0, 167.7, 167.2, 139.9, 139.6, 139.0, 138.9, 138.8, 131.8, 130.3, 129.7, 129.5, 129.0, 128.73, 128.69, 128.6, 128.50, 128.45, 128.4, 128.1, 128.04, 127.97, 127.9, 127.80, 127.75, 127.6, 127.5, 103.4, 101.8, 99.2, 83.4, 82.3, 78.9, 77.7, 76.8, 76.3, 76.2, 75.9, 75.7, 75.4, 73.64, 73.55, 73.2, 71.1, 70.2, 70.1,, 69.8, 68.9, 68.2, 67.8, 66.9, 62.3, 59.9, 57.8, 53.4, 52.9, 52.3, 51.2, 36.7, 28.4, 26.3, 23.5, 21.3, 21.10, 21.05, 18.9, −0.1; HRMS *m*/*z* Calcd for $C_{106}H_{125}N_5O_{32}NaSSi$ [M + Na] 2062.7695. Found 2062.7729.

2-(Trimethylsilyl)ethyl (methyl 5-acetamido-3,5-dideoxy-3-phenylthio-D-erythro-*β*-L-gluco-*non-2-ulopyranosylonate)-(2→8)-(methyl 5-acetamido-9-azido-3,5,9-trideoxy*-D-glycero-*α*-D-galacto-*non-2-ulopyranosylonate)-(2→3)-(2,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**26**).—Compound **25** (118 mg, 0.058 mmol) was dissolved in MeOH (2 mL) and 1 M NaOMe in MeOH (0.04 mL) was added. The mixture was left at 22 °C for 3.5 h and neutralized with Duolite C26 (H^+) resin. The resin was filtered off and washed with MeOH. The filtrate was concentrated and the residue was chromatographed (1–10% MeOH in CH_2Cl_2) to give **26** (82 mg, 82%). ^1H NMR (CD_3OD): δ 7.64–7.04 (m, 35 H, Ar), 4.98 (d, 1 H, *J* 10.6 Hz, C*H*$_2$Ph), 4.91–4.79 (m, 3 H, C*H*$_2$Ph), 4.71–4.66 (m 3 H, C*H*$_2$Ph), 4.56 (d, 1 H, *J* 10.5 Hz, C*H*$_2$Ph), 4.42–4.37 (m, 4 H, H-1,1′, C*H*$_2$Ph), 4.30 (s, 2 H, C*H*$_2$Ph), 4.21 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.20 (dd, 1 H, *J* 2.8, 9.8 Hz, H-3′), 3.87, 3.79 (2s, 3 H each, $COOCH_3$), 3.49 (brt, 1 H, *J* 9.1 Hz, H-3), 3.25 (dd, 1 H, *J* 7.8, 9.2 Hz, H-2), 2.77 (brdd, 1 H, *J* 4.7, 12.7 Hz, H-3″eq), 2.08, 2.03 (2s, 3 H each, Ac), 1.90 (brt, 1 H, *J* 12.6 Hz, H-3″ax), 1.00 (brt, 1 H, *J* 8.0 Hz, C*H*$_2$Si), 0.03 (s, 9 H, Si*Me*$_3$); ^{13}C NMR (CD_3OD): δ 174.4, 174.3, 169.8, 169.2, 139.6, 139.5, 139.2, 138.89, 138.85, 138.4, 135.4, 131.1, 129.3, 128.71, 128.65, 128.61, 128.58, 128.50, 128.45, 128.4, 128.3, 128.20, 128.17, 128.0, 127.93, 127.90, 127.8, 127.7, 127.6, 127.4, 103.4, 103.3, 101.5, 99.4, 83.3, 82.2, 78.8, 78.0, 77.8, 76.4, 76.2, 76.0, 75.80, 75.77, 75.6, 75.40, 75.35, 73.7, 73.5, 73.4, 72.7, 72.1, 71.3, 69.0, 68.9, 68.0, 67.9, 67.8, 66.7, 57.1, 53.5, 53.4, 52.8, 52.4, 40.2, 23.1, 22.9, 18.89, -0.10; HRMS *m*/*z* Calcd for $C_{89}H_{111}N_5NaO_{26}SSi$ [M + Na] 1748.6875. Found 1748.6895.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-3-phenylthio-D-erythro-*β*-L-gluco-*non-2-ulopyranosylonic acid)-(2→8)-(methyl 5-acetamido-9-amino-3,5,9-trideoxy*-D-glycero-*α*-D-galacto-*non-2-ulopyranosylonate)-(2→3)-(2,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside 1‴-9″-lactam* (**27**).—To a stirred solution of **26** (125 mg, 0.072 mmol) in 8:1 THF–water (0.9 mL) was added Ph_3P (76 mg, 0.2892 mmol), and the mixture was stirred at 40 °C for 24 h. The reaction mixture was co-concentrated with toluene–acetone. The residue was chromatographed (1–10% MeOH in CH_2Cl_2) to give **27** (104 mg, 86%). Mp 124–126 °C (hexane–Et_2O, MeOH); $[\alpha]_D^{23}$ −28° (*c* 0.52, $CHCl_3$); IR (film); *ν* 1735 cm^{-1} ($COOCH_3$), 1730–1620 (CONH); ^1H NMR (CD_3OD): δ 7.56–7.03 (m, 35 H, Ar), 5.00 (d, 1 H, *J* 10.6 Hz, C*H*$_2$Ph), 4.95 (d, 1 H, *J* 11.4 Hz, C*H*$_2$Ph), 4.85 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 4.78 (d, 1 H, *J* 10.6 Hz, C*H*$_2$Ph), 4.70 (d, 1 H, *J* 10.8 Hz, C*H*$_2$Ph), 4.67 (d, 1 H, *J* 10.8 Hz, C*H*$_2$Ph), 4.57 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 4.54 (d, 1 H, *J* 11.8 Hz, C*H*$_2$Ph), 4.50 (d, 1 H, *J* 11.4 Hz, C*H*$_2$Ph), 4.44–4.37 (m, 6 H, H-1,1′,4‴,8″, C*H*$_2$Ph), 4.18 (d, 1 H, *J* 12.0 Hz, C*H*$_2$Ph), 4.11 (dd, 1 H, *J* 3.0, 10.0 Hz, H-3′), 3.55 (dd, 1 H, *J* 5.9, 13.2 Hz, H-9″), 3.48 (t, 1 H, *J* 9.1 Hz, H-3), 3.46 (s, 3 H, $COOCH_3$), 3.23 (dd, 1 H, *J* 7.9, 9.1 Hz, H-2), 3.01 (d, 1 H, *J* 10.3 Hz, H-3‴), 2.61 (dd, 1 H, *J* 4.6, 13.2 Hz, H-3″eq), 2.08, 2.02 (2s, 3 H each, NAc), 2.00 (brt, 1 H, *J* 13.0 Hz, H-3″ax), 0.99 (brt, 2 H, *J* 8.0 Hz, C*H*$_2$Si), 0.04 (s, 9 H, Si*Me*$_3$); ^{13}C NMR (CD_3OD): δ 175.7, 175.4, 170.3, 169.3, 140.7, 140.4, 140.2, 140.1, 139.9, 139.7, 139.6, 132.0, 130.0, 129.7, 129.6, 129.5, 129.39, 129.36, 129.2, 129.10, 129.06, 129.0, 128.70, 128.66, 128.5, 128.4, 127.4, 104.3, 103.9, 101.4, 101.2, 84.1, 83.1, 79.7, 78.2, 77.4, 77.3, 76.5, 76.1, 75.9, 74.9, 74.4, 74.3, 74.2, 72.5, 72.4, 71.8, 70.3, 69.7, 69.3, 68.7, 68.4, 65.6, 62.2, 54.1, 54.0, 53.2, 42.2, 40.1, 23.1, 22.7, 19.4, −1.1; HRMS *m*/*z* Calcd for $C_{88}H_{109}N_3NaO_{25}Si$ [M + Na] 1690.6708. Found 1690.6698.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-3-phenylthio-D-erythro-*β*-L-gluco-*non-2-ulopyranosylonic acid)-(2→8)-(methyl 5,9-diacetamido-3,5,9-trideoxy*-D-glycero-*α*-D-galacto-*non-2-ulopyranosylonate)-(2→3)-(2,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside 1‴-9″-lactam* (**28**).—To a solution of **27** (88 mg, 0.053 mmol) in pyridine

(0.5 mL), Ac_2O (0.5 mL) and DMAP (3 mg) were added. The reaction mixture was kept at rt overnight. Methanol (1 mL) was added and the reaction was co-concentrated with toluene and methanol. The residue was chromatographed (9:1 → 1:1 toluene–acetone) to give **28** (100 mg, 99%). $[\alpha]_D^{23}$ −2° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.41–7.06 (m, 35 H, Ar), 5.63 (d, 1 H, *J* 9.5 Hz, NH), 5.57 (t, 1 H, *J* 10.7 Hz, H-4‴), 5.02 (dd, 1 H, *J* 7.1, 11.1 Hz, H-4″), 4.91 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 4.73 (d, 1 H, *J* 11.2 Hz, C*H*$_2$Ph), 4.57 (d, 1 H, *J* 12.0 Hz, C*H*$_2$Ph), 4.20 (t, 1 H, *J* 9.9 Hz, H-5‴), 3.76 (s, 3 H, $COOCH_3$), 3.30 (d, 1 H, *J* 11.0 Hz, H-3‴), 2.53 (s, 3 H, CONAc), 2.44 (dd, 1 H, *J* 5.2, 13.8 Hz, H-3″eq), 2.17, 2.03, 2.00, 1.98, 1.93, 1.90, 1.89, 1.88, (8s, 3 H each, Ac), 1.04 (m, 2 H, C*H*$_2$Si), 0.02 (s, 9 H, Si*Me*$_3$); ^{13}C NMR ($CDCl_3$): δ 171.6, 171.3, 171.0, 170.94, 170.88, 170.7, 170.4, 170.3, 170.1, 168.6, 166.9, 139.7, 139.6, 139.2, 139.0, 139.0, 138.8, 135.9, 131.3, 129.6, 129.5, 128.8, 128.7, 128.6, 128.51, 128.46, 128.39, 128.37, 128.3, 128.13, 128.07, 127.99, 127.98, 127.94, 127.92, 127.89, 127.8, 127.7, 127.4, 103.5, 103.1, 100.6, 100.2, 83.5, 82.3, 78.8, 77.7, 77.5, 77.3, 77.0, 75.7, 75.6, 75.4, 75.3, 75.2, 74.3, 73.8, 73.6, 73.4, 73.2, 72.9, 71.9, 69.8, 69.1, 69.0, 68.5, 67.8, 67.3, 62.7, 58.9, 53.3, 50.4, 50.1, 40.46, 35.9, 27.7, 23.6, 23.5, 21.3, 21.18, 21.16, 21.1, 21.0, 20.9, 18.9, −1.0.

2-(Trimethylsilyl)ethyl (5-acetamido-4,7,8,9-tetra-O-*acetyl-3,5-dideoxy*-D-glycero-α-D-galacto-*non-2-ulopyranosylonic acid)-(2→8)-(methyl 5,9-diacetamido-4,7-di*-O-*acetyl-3,5,9-trideoxy*-D-glycero-α-D-galacto-*non-2-ulopyranosylonate)-(2→3)-(2,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside 1‴-9″-Lactam* (**29**).—Compound **28** (65 mg, 0.033 mmol) was treated with Ph_3SnH (0.085 mL, 0.331 mmol) and AIBN (6 mg) in toluene (1.5 mL) at 120 °C for 5 h. The solvent was removed and the residue was chromatographed (9:1 → 1:1 toluene–MeCN) to give **29** (40 mg, 65%). ^{13}C NMR ($CDCl_3$): δ 171.44, 171.36, 171.2, 171.0, 170.9, 170.81, 170.77, 170.5, 170.3, 168.8, 168.5, 139.8, 139.6, 139.2, 139.0, 138.9, 138.7, 131.3, 129.6, 128.8, 128.7, 128.6, 128.52, 128.47, 128.45, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 103.5, 103.1, 100.8, 97.6, 83.5, 82.3, 78.9, 77.7, 77.3, 77.1, 76.8, 75.8, 75.5, 75.4, 75.3, 75.0, 74.3, 73.6, 73.2, 72.2, 70.4, 70.2, 69.3, 69.0, 68.3, 68.1, 67.8, 62.7, 53.2, 49.7, 49.6, 40.7, 39.8, 35.9, 27.6, 23.6, 23.4, 21.4, 21.31, 21.29, 21.2, 21.1, 20.9, 18.9, −1.0; HRMS *m*/*z* Calcd for $C_{96}H_{119}N_3NaO_{32}Si$ [M + Na] 1876.7444. Found 1876.7435.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-*non-2-ulopyranosylonic acid)-(2→8)-(methyl 5-acetamido-9-amino-3,5,9-trideoxy*-D-glycero-α-D-galacto-*non-2-ulopyranosylonate)-(2→3)-(2,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside 1‴-9″-lactam* (**30**).—To a solution of **29** (33 mg, 0.018 mmol) in MeOH (0.7 mL) was added 1 M methanolic NaOMe (0.12 mL) and the mixture was kept at 22 °C for 12 h. The mixture was neutralized with Duolite C26 (H^+) resin. The resin was filtered off and washed with MeOH. The filtrate was concentrated and the residue was chromatographed (1–12% MeOH in CH_2Cl_2) to give **30** (23 mg, 83%). $[\alpha]_D^{23}$ −22° (*c* 0.90, $CHCl_3$); ^1H NMR (CD_3OD): δ 7.39–7.06 (m, 30 H, Ar), 5.02 (d, 1 H, *J* 11.5 Hz, C*H*$_2$Ph), 5.00 (d, 1 H, *J* 10.0 Hz, C*H*$_2$Ph), 4.84 (d, 1 H, *J* 11.0 Hz, C*H*$_2$Ph), 4.78 (d, 1 H, *J* 11.4 Hz, C*H*$_2$Ph), 4.68 (d, 2 H, *J* 11.1 Hz, C*H*$_2$Ph), 4.58–4.54 (m, 3 H, C*H*$_2$Ph), 4.43 (d, 1 H, *J* 7.9 Hz, H-1′), 4.43 (m, 1 H, H-4‴), 4.40 (d, 1 H, *J* 7.7 Hz, H-1), 4.38 (d, 1 H, *J* 11.1 Hz, C*H*$_2$Ph), 4.37 (d, 1 H, *J* 11.8 Hz, C*H*$_2$Ph), 4.25 (ddd, 1 H, *J* 6.1, 10.0, 10.0 Hz, H-8″), 4.14 (d, 1 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.37 (d, 1 H, *J* 11.8 Hz, C*H*$_2$Ph), 4.10 (dd, 1 H, *J* 2.9, 9.9 Hz, H-3′), 3.99 (m, 1 H, OCH_2), 3.70 (s, 3 H, $COOCH_3$), 3.21 (brdd, 1 H, *J* 7.9, 9.1 Hz, H-2), 2.66 (dd, 1 H, *J* 4.7, 12.9 Hz, H-3″eq), 2.44 (dd, 1 H, *J* 5.3, 12.8 Hz, H-3‴eq), 2.04 (s, 3 H, Ac), 2.02 (m, 1 H, H-3″ax), 2.01 (s, 3 H, Ac), 1.83 (brt, 1 H, *J* 12.5 Hz, H-3‴ax), 0.99 (brt, 2 H, *J* 8.0 Hz, C*H*$_2$Si), 0.03 (s, 9 H, Si*Me*$_3$); ^{13}C NMR (CD_3OD): δ 175.8, 175.6, 171.1, 170.5, 141.0, 140.4, 140.3, 140.2, 140.0, 139.7, 129.84, 129.77, 129.74, 129.68, 129.5, 129.41, 129.38, 129.32, 129.30, 129.23, 129.15, 129.12, 129.11, 129.04, 128.98, 128.7, 128.5, 128.4, 104.4, 103.8, 102.1, 98.9, 84.1, 83.2, 79.8, 78.4, 77.5, 77.3, 76.5, 76.2, 76.1, 75.9, 74.5, 74.4, 74.3, 73.8, 72.0, 71.5, 69.9, 69.4, 69.3, 68.9, 68.5, 65.4, 54.4, 53.5, 53.3, 43.2, 42.1, 39.7, 23.0, 22.7, 19.5, −1.1; HRMS *m*/*z* Calcd for $C_{82}H_{105}N_3NaO_{25}Si$ [M + Na] 1582.6704. Found 1582.6733.

2-(Trimethylsilyl)ethyl (5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-*non-2-ulopyranosylonic acid)-(2→8)-(methyl 5-acetamido-9-amino-3,5,9-trideoxy*-D-glycero-α-D-galacto-*non-2-ulopyranosylonate)-(2→3)-(β-D-galactopyranosyl)-(1→4)-β-D-glucopyranoside 1‴-9″-Lactam* (**31**).—Compound **30** (40 mg, 0.026 mmol) was dissolved in EtOH (7 mL) and hydrogenated (H_2, $Pd(OH)_2$–C, 20%, 100 mg, 1 atm) at 22 °C overnight. The catalyst was filtered off, washed with MeOH and the filtrate was concentrated to give **31** (25 mg, 96%). $[\alpha]_D^{23}$ −34° (*c* 0.5, MeOH); ^1H NMR (CD_3OD): δ 4.44 (d, 1 H, *J* 7.8 Hz, H-1′), 4.43 (m, 1 H, H-4‴), 4.30 (d, 1 H, *J* 7.9 Hz, H-1), 4.14 (ddd, 1 H, *J* 6.2, 8.5, 10.7 Hz, H-8″), 3.81 (s, 3 H, $COOCH_3$), 3.21 (t, 1 H, *J* 7.9 Hz, H-2), 2.73 (dd, 1 H, *J* 4.5, 12.9 Hz, H-3″eq), 2.45 (dd, 1 H, *J* 5.6, 12.8 Hz, H-3‴eq), 2.33, 2.05 (2s, 3 H each, Ac), 1.55 (dd, 1 H, *J* 11.1, 12.6 Hz, H-3‴ax), 1.00 (m, 2 H, C*H*$_2$Si), 0.03 (s, 9 H, Si*Me*$_3$); ^{13}C NMR (CD_3OD): δ 174.6, 174.1, 169.9, 169.5, 103.9, 102.7, 99.3, 97.8, 80.0, 76.9, 75.6, 75.4, 73.8, 73.7, 73.4, 72.1, 71.2, 70.8, 69.8, 68.7, 68.4, 67.81, 67.77, 67.2, 64.3, 61.3, 61.1, 57.2, 53.2, 52.3, 41.7, 40.8, 40.1, 21.9, 21.6, 18.1, −2.4; HRMS *m*/*z* Calcd for $C_{40}H_{69}NaN_3O_{25}Si$ [M + Na] 1042.3887. Found 1042.3896.

2-(Trimethylsilyl)ethyl (5-acetamido-4,7,8,9-tetra-O-*acetyl-3,5-dideoxy*-D-glycero-α-D-galacto-*non-2-ulopy-*

ranosylonic acid)-(2→8)-(methyl 5,9-diacetamido-4,7-di-O-*acetyl-3,5,9-trideoxy*-D-glycero-α-D-galacto-*non-2-ulopyranosylonate)-(2→3)-(2,4,6-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-2,3,6-tri*-O-*acetyl-β*-D-*glucopyranoside 1‴-9″-lactam* (**32**).—To a solution of **31** (28 mg, 0.027) in pyridine (0.5 mL) was added Ac_2O (0.5 mL) followed by DMAP (1 mg) and the mixture was kept at 22 °C overnight. Methanol (1 mL) was added and the mixture was stirred at 22 °C for 5 min, and co-concentrated with toluene. The residue was chromatographed (9:1→1:1 toluene–acetone) to give **32** (23 mg, 53%). ^{1}H NMR ($CDCl_3$): δ 5.50 (m, 1 H, H-4‴), 5.30 (t, 1 H, *J* 9.3 Hz, H-3), 5.10 (m, 1 H, H-4″), 4.74 (dd, 1 H, *J* 8.1, 9.5 Hz, H-2), 4.46 (d, 1 H, *J* 8.1 Hz, H-1), 3.90 (s, 3 H, $COOCH_3$), 2.62 (dd, 1 H, *J* 5.0, 12.5 Hz, H-3‴eq), 2.59 (s, 3 H, Ac), 2.45 (dd, 1 H, *J* 5.5, 13.3 Hz, H-3″eq), 2.33, 2.14, 2.13, 2.11, 2.10, 2.05, 2.04, 2.03, 2.02, 2.01, 1.92, 1.90 (12s, 42 H, Ac), 1.74 (t, 1 H, *J* 12.5 Hz, H-3‴ax), 0.90 (m, 2 H, CH_2Si), 0.01 (s, 9 H, $SiMe_3$); ^{13}C NMR ($CDCl_3$): δ 171.6, 171.5, 171.12, 171.05, 170.84, 170.78, 170.77, 170.71, 170.65, 170.5, 170.4, 169.94, 169.88, 169.80, 169.77, 168.80, 167.1, 101.3, 100.0, 98.4, 98.0, 77.6, 77.3, 77.0, 76.1, 75.2, 73.9, 72.7, 72.5, 72.3, 71.0, 70.5, 70.2, 69.3, 68.9, 68.6, 68.0, 67.5, 66.9, 63.9, 61.71, 61.66, 53.7, 50.8, 48.9, 40.0, 38.5, 38.1, 28.0, 23.74, 23.70, 21.33, 21.25, 21.21, 21.16, 21.12, 21.08, 18.3, −1.0; HRMS *m*/*z* Calcd for $C_{66}H_{95}N_3NaO_{38}Si$ [M + Na] 1588.5260. Found 1588.5240.

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