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Synthesis of building blocks of human milk oligosaccharides. Fucosylated derivatives of the lacto- and neolacto-series

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Abstract

The synthesis of protected fucosylated derivatives of a Galβ(1→3)GlcNAc and of lactosamine Galβ(1→4)GlcNAc building blocks contained in human milk oligosaccharides is described. Both chemical and enzymatic methods have been exploited for selective protection of the disaccharide. Fucosylation of the appropriate derivatives allowed an easy and relatively short access to different products from common precursors. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Building block; Human milk; Oligosaccharide derivatives, synthesis; Lewis^x; *N*-Acetyl lactosamine; Lipases

1. Introduction

Human milk is extremely rich in oligosaccharides, more than 130 different compounds having been isolated and identified so far.[1,2] The biological significance of these compounds has largely been unappreciated, as they were thought to be nutritionally irrelevant and merely by-products due to the presence of large amounts of glycosyl transferases in the milk synthetic pathway.

Recently the great importance of these compounds has been demonstrated for breast-fed infants; during the lactation period, the oligosaccharides, among their other biological roles, inhibit bacterial adhesion to the epithelial cells' surface, which has been recognized as a crucial initial step in the infectious process.[3–9] However, it is still not clear which of the many oligosaccharides exert this function. In a project devoted to the identification of such compounds, after the synthesis of trisaccharides containing the lactose unit,[10] we focussed on the synthesis of oligosaccharide derivatives of the lacto- and neolacto-series contained in human milk.

Careful examination of the structures of the complex oligosaccharides of human milk revealed that a great number of these contain the disaccharidic units Galβ(1→3)GlcNAc and lactosamine Galβ(1→4)GlcNAc, the first bearing one/two α-fucose unit(s) linked to position 2 of Gal and/or position 4 of GlcNAc (structures **1**, **2**, **3** of Fig. 1), while the second is fucosylated in position 3 of GlcNAc and/or 2 of Gal (structures **4**, **5** of Fig. 1). Among the fucosylated derivatives of *N*-acetyl lactosamine, trisaccharides Lewis^x and H-antigen and the tetrasaccharide Lewis^y, three of the most important blood group antigens, have been extensively studied both from the biological, as well as a chemical point of view. Syntheses of Lewis^x, Lewis^y and H-antigens have employed various strategies, building blocks and protecting groups.[11–21] Lewis^x is present as such and as a core structure of many complex oligosaccharides of human milk.

Thus in order to prepare an array of the more complex oligosaccharides, we planned an efficient strategy to synthesize these units as common building blocks to which the proper peripheric unit(s) can be linked.

Moreover, we intended to exploit the enzymatic manipulation of the hydroxyl groups by regioselective introduction of acyl protecting groups, so demonstrating that such a strategy can be a useful alternative to more classical chemical methods.

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In the present paper, we describe the synthesis of the protected fucosylated derivatives of the lacto-series, corresponding to compounds **1**, **2** and **3** (Fig. 1), together with that of the neolacto-series, corresponding to compounds **4** and **5**. All these protected structures are useful building blocks for the preparation of more complex oligosaccharides contained in human milk.

2. Results and discussion

The lacto series.—The synthetic strategy adopted for the easy preparation of the target molecules was based on the fucosylation of a common disaccharidic building block precursor **8**. This compound was obtained from two easily available monosaccharides (**6** and **7**, Scheme 1), according to a procedure already described by Toepfer and Schmidt,[22] and was further elaborated to obtain the single target molecules.

The synthetic strategy planned the manipulation of compound **8** to introduce, both by chemical and enzymatic methods, the appropriate protecting groups in order to obtain the different glycosyl acceptors for the fucosylation reactions.

Compound **12**, the protected derivative of **1**, was synthesized in a straightforward manner. Removal of the benzylidene group from **8** followed by a selective acetylation of the primary position at low temperature with acetyl chloride afforded acceptor **10** in 80% yield, which was fucosylated using the efficient donor **11**[23] and TMSOTf as promoter, in excellent yield (99%). The partially acetylated fucosyl donor **11** is much more stable and easy to use with respect to the corresponding extremely reactive totally benzylated derivative (Scheme 2).

Compound **16**, the protected derivative of **2**, was obtained according to the pathway described in Scheme 3. The acetates were removed from the galactose unit of **8** and the free primary position was efficiently silylated by the introduction of a *t*-butyldiphenylsilyl group. Position 3′ and 4′ of the obtained compound **14** were then protected with an isopropylidene group affording acceptor **15**, useful for the achievement of the desired trisaccharide **16**. In fact, compound **15** was glycosylated with the same fucosyl donor **11** in the presence of TMSOTf to give compound **16** in 66% yield.

Finally, difucosylated compound **20**, corresponding to deprotected tetrasaccharide **3** (Scheme 4), was obtained exploiting the result of a recently reported study[24] on selective enzymatic protection of compound

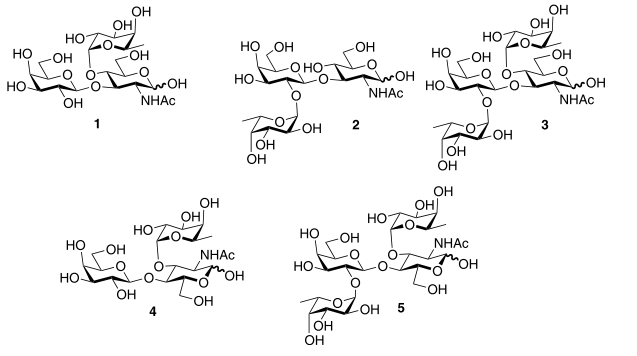
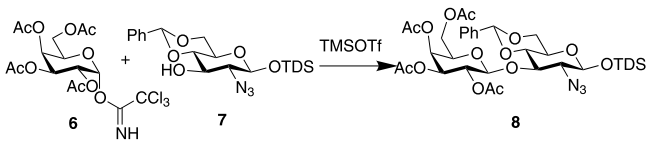
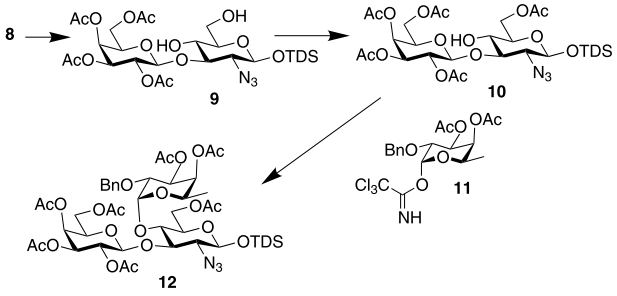


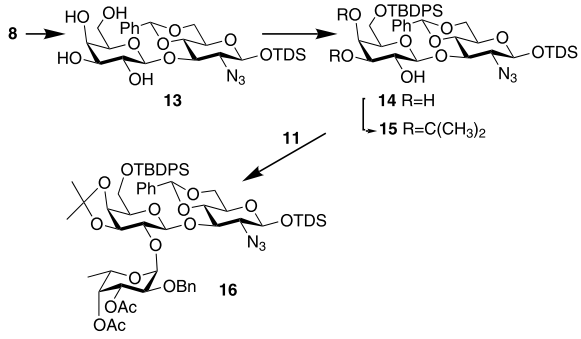
Fig. 1.



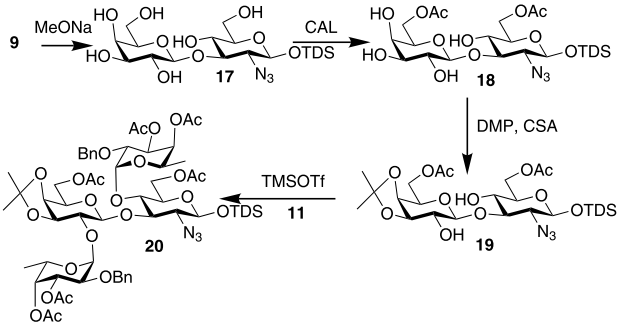
Scheme 1.



Scheme 2.



Scheme 3.

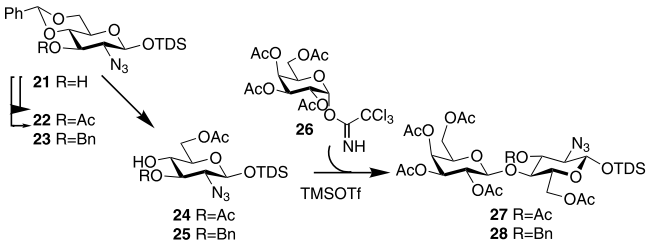


Scheme 4.

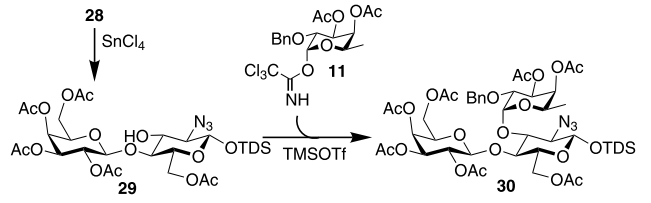
17, which can be easily obtained by deacetylation of **9**. Using lipase from *Candida antarctica* (CAL) and vinylacetate[25–27] in MeCN as solvent, it was possible to protect selectively the two primary positions of compound **17**. The 3′ and 4′ hydroxyl groups of the obtained compound **18** were then protected by the introduction of an isopropylidene group affording diol **19**. Such compound was used as acceptor for the synthesis of the desired tetrasaccharide, employing again donor **11** and TMSOTf as Lewis acid. Difucosylated compound **20** was obtained in an excellent 91% yield.

The neolacto-series.—Searching for an efficient synthetic strategy for the trisaccharide **30** and the tetrasaccharide **34**, we projected two differently protected disaccharidic precursors **27** and **28** (Scheme 5), easily available from a common monosaccharidic moiety, azido glucose **21**.[28] This was converted into two glycosyl acceptors differently protected at C-3, compounds **24** and **25**, that were reacted with donor **26**[28] affording protected azidolactoses **27** and **28** in 56% and 95% yield, respectively.

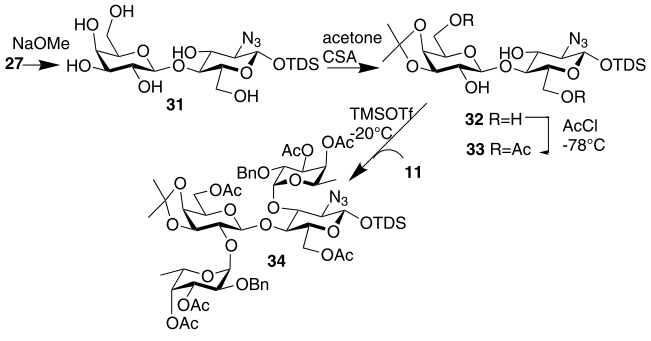
Compound **28**, containing a benzyl group at C-3, allowed to have selective access to position 3. In fact,



Scheme 5.



Scheme 6.



Scheme 7.

the benzyl group was removed[29] with $SnCl_4$ and the obtained compound **29** was readily fucosylated with donor **11**, using TMSOTf as promoter, affording the trisaccharide **30**, the protected form of **4**, in 90% yield (Scheme 6).

Finally, disaccharide **27** was used for the synthesis of the protected form of tetrasaccharide **5**. Compound **27** (Scheme 7) was fully deacetylated with sodium methoxide to compound **31**, then 3′,4′ positions were protected as isopropylidene acetal. The reaction conditions (acetone, CSA and Sikkon) were chosen in order to induce the formation of the 3′,4′- (thermodynamic control) versus the 4′,6′-acetonide. In fact, the 3′,4′ product **32** is obtained in 85% yield, while the 4′,6′ protected compound is obtained only in 15% yield. Compound **32** was selectively acetylated on the two primary positions with acetylchloride at low temperature affording acceptor **33** in 71% yield, which was finally fucosylated. Due to the unexpected lability of the acceptor during the glycosylation, many attempts were done both adopting the inverse and the direct fucosylation procedure, changing the Lewis acid (TMSOTf, $BF_3{\cdot}Et_2O$) and the temperature. The best conditions were found in the direct procedure using TMSOTf (0.01 equiv) at -20 °C. Under these conditions, tetrasaccharide **34** was obtained in 55% yield.

In conclusion, the use of a common precursor and an appropriate choice of the protecting groups and method for their introduction (either chemical or enzymatic) allowed the easy preparation of two families of fucosylated derivatives of the lacto- and neolacto-series in protected form. These compounds represent useful building blocks which can be exploited, through selective manipulation of the protective groups, to prepare a wide array of complex oligosaccharides of human milk.

3. Experimental

General methods.—^1H and ^{13}C NMR spectra were recorded on Bruker AC 300 and Varian Gemini 200 spectrometers for solution. Melting points were determined with Büchi apparatus and are not corrected. Optical rotations were measured at rt with a Perkin–Elmer 241 polarimeter. TLC was carried out on E. Merck Silica-Gel 60 F_{245} plates (0.25 mm thickness), and spots were visualized by spraying with solution containing H_2SO_4 (31 mL) ammonium molybdate (21 g) and $Ce(SO_4)_2$ (1 g) in 500 mL water, followed by heating at 110 °C for 5 min. Column chromatography was performed by the flash procedure using E. Merck Silica-gel 60 (230–400 mesh). Elemental analyses were performed using the Carlo–Erba elemental analyzer 1108.

*Thexyldimethylsilyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl-(1→3)-2-azido-4,6-*O*-benzylidene-2-de-*

*oxy-β-*D*-glucopyranoside* (**8**).—Compounds **7** (429 mg, 0.98 mmol) and **6** (1200 mg, 2.45 mmol) were mixed in a flask under inert atmosphere and dissolved in dry CH_2Cl_2 (5 ml). Then $BF_3{\cdot}Et_2O$ (490 μL of a 0.1 M solution, 0.05 equiv) was added. After 15 min, the reaction was neutralized with Et_3N and the solvent was removed under reduced pressure. Chromatographic purification (7:3 petroleum ether–EtAcO) afforded 707 mg (94% yield) of pure compound **8**. Amorphous white solid; $[\alpha]_D$ −21.6° (*c* 2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.51–7.23 (m, 5 H, H-Ar), 5.54 (s, 1 H, CHPh), 5.33 (d, 1 H, $J_{3',4'}$ 3.1 Hz, H-4′), 5.26 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 10.4 Hz, H-2′), 5.00 (d, 1 H, H-3′), 4.74 (d, 1 H, H-1′), 4.60 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.27 (dd, 1 H, $J_{6b,5}$ 4.8, $J_{6b,6a}$ 10.4 Hz, H-6b), 4.09 (dd, 1 H, $J_{6'b,5'}$ 7.8, $J_{6b',6a'}$ 11.1 Hz, H-6′b) 3.89 (dd, 1 H, $J_{6'a,5'}$ 5.8 Hz, H-6′a), 3.78 (t, 1 H, $J_{6a,5}$ 10.4 Hz, H-6a), 3.58–3.75 (m, 3 H, H-3, 4, 5′), 3.29–3.41 (m, 1 H, H-5), 3.32 (dd, 1 H, $J_{2,3}$ 8.5 Hz, H-2), 2,12, 2.08, 1.98, 1.94 (4s, 12 H, CH_3CO), 1.60–1.80 (m, 1 H, CH-TDS), 0.96–0.88 (m, 12 H, CH_3-TDS), 0.22, 0.20 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.7, 170.6, 170.6, 170.0 (4 s, CO), 137.4 (s), 129.6, 128.6, 126.4 (3 d, CHAr), 101.9, 101.7, 97.95, 80.14, 79.81, 71.44, 71.09, 69.70, 69.10, 67.32, 66.85 (11 d, C-1, 2, 3, 4, 5, 1′, 2′, 3′, 4′, 5′, CHPh), 68.92, 61.38 (2t, C-6, 6′), 34.28 (d, CH-TDS), 25.19 (s, C_q-TDS), 21.10, 21.01, 20.94, 20.94, 20.32, 20.19, 18.87, 18.75, −1.744, −2.826 (10q, 4 CH_3CO, 6 CH_3-TDS). Anal. Calcd for $C_{35}H_{51}N_3O_{14}Si$: C, 54.88; H, 6.71; N, 5.49. Found: C, 55.00; H, 6.78; N, 5.41.

*Thexyldimethylsilyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl-(1→3)-2-azido-2-deoxy-β-*D*-glucopyranoside* (**9**).—Compound **8** was dissolved in CH_2Cl_2 (15 mL) and 70% CF_3COOH (3 mL) was added. After 10 min, a saturated solution of Na_2CO_3 was added until basic pH was reached. After phase separation, the water layer was extracted with CH_2Cl_2. The combined organic phases were washed with water, dried with anhyd $NaSO_4$, filtered and the solvent was removed under reduced pressure. Chromatographic purification (1:1 petroleum ether–EtAcO) afforded 548 mg (87% yield) of pure **9**. Amorphous white solid; $[\alpha]_D$ +3.9° (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.39 (d, 1 H, $J_{3',4'}$ 3.4 Hz, H-4′), 5.26 (dd, 1 H, $J_{1',2'}$ 7.9, $J_{2',3'}$ 10.5 Hz, H-2′), 5.05 (dd, 1 H, H-3′), 4.58 (d, 1 H, H-1′), 4.57 (d, 1 H, $J_{1,2}$ 7.2 Hz, H-1), 4.19–4.06 (m, 2 H, H-6′a, 6′b), 4.00 (bt, 1 H, H-5′), 3.88 (dd, 1 H, $J_{6b,5}$ 3.7, $J_{6b,6a}$ 11.8 Hz, H-6b), 3.73 (dd, 1 H, $J_{6a,5}$ 5.3 Hz, H-6a), 3.53 (m, 1 H, H-5), 3.34–3.21 (m, 3 H, H-2, 3, 4), 2.18, 2.11, 2.07, 2.00 (4 s, 12 H, CH_3CO), 1.60–1.80 (m, 1 H, CH-TDS), 0.94–0.88 (m, 12 H, CH_3-TDS), 0.22, 0.20 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.4, 170.1, 170.1, 169.5 (5s, CH_3CO), 102.4, 97.05 (2 d, C-1, 1′), 86.25, 75.28, 71.23, 70.65, 69.72, 68.56, 67.29, 66.89 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 62.84, 61.69 (2 t, C-6, 6′), 33.85 (d, CH-TDS), 24.77 (s, Cq-TDS), 20.45–18.31, −2.085, −3.231 (CH_3CO, CH_3-TDS, CH_3Si). Anal. Calcd for $C_{28}H_{47}N_3O_{14}Si$: C, 49.61; H, 6.99; N, 6.20. Found: C, 49.58; H, 6.96; N, 6.17.

*Thexyldimethylsilyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl-(1→3)-6-*O*-acetyl-2-azido-2-deoxy-β-*D*-glucopyranoside* (**10**).—Compound **9** (474 mg, 0.70 mmol) was dissolved in dry CH_2Cl_2 (10 mL) under inert atmosphere and the temperature was lowered to −78 °C; then Py (452 μL, 5.6 mmol) and AcCl (223 μL, 3.5 mmol) were added in the order. After 1 h, MeOH was added (1 mL) and the solvent was removed under reduced pressure. Chromatographic purification (1:1 petroleum ether–EtAcO) afforded 400 mg (80% yield) of pure **10**. $[\alpha]_D$ +10.2° (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.39 (d, 1 H, $J_{3',4'}$ 3.3 Hz, H-4′), 5.26 (dd, 1 H, $J_{1',2'}$ 7.8, $J_{2',3'}$ 10.4 Hz, H-2′), 5.05 (dd, 1 H, H-3′), 4.58 (d, 1 H, H-1′), 4.52 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1), 4.43 (dd, 1 H, $J_{6b,5}$ 2.0, $J_{6b,6a}$ 12.0 Hz, H-6b), 4.17 (dd, 1 H, $J_{6a,5}$ 7.5 Hz, H-6a), 4.20–4.00 (m, 2 H, H-6′a, 6′b), 3.99 (bt, 1 H, H-5′), 3.82, (s, 1 H, OH), 3.48 (dd, 1 H, $J_{4,3}$ 7.1, $J_{4,5}$ 9.7 Hz, H-4), 3.41 (ddd, 1 H, H-5), 3.25 (dd, 1 H, $J_{3,2}$ 9.8 Hz, H-3), 3.17 (dd, 1 H, H-2), 2,15, 2.10, 2.04, 2.04, 1.97 (5 s, 15 H, CH_3CO), 1.60–1.80 (m, 1 H, CH-TDS), 0.94–0.86 (m, 12 H, CH_3-TDS), 0.22, 0.20 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.6, 170.4, 170.0, 169.9, 169.5 (5 s, CH_3CO), 102.5, 97.05 (2 d, C-1, 1′), 86.36, 73.42, 71.28, 70.63, 69.20, 68.51, 67.09, 66.86 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 63.36, 61.63 (2 t, C-6, 6′), 33.86 (d, CH-TDS), 24.78 (s, Cq-TDS), 20.73–18.31, −2.257, −3.344 (CH_3CO, CH_3-TDS, CH_3Si). Anal. Calcd for $C_{30}H_{49}N_3O_{15}Si$: C, 50.05; H, 6.86; N, 5.84. Found: C, 49.98; H, 6.79; N, 5.81.

*Thexyldimethylsilyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl-(1→3)-[3,4-di-*O*-acetyl-2-*O*-benzyl-α-*L*-fucopyranosyl-(1→4)]-6-*O*-acetyl-2-azido-2-deoxy-β-*D*-glucopyranoside* (**12**).—Compound **10** (98 mg, 0.136 mmol) was dissolved in dry CH_2Cl_2 (1 mL). The temperature was lowered to 0 °C and TMSOTf (27 μL of a 0.1 M solution, 0.02 equiv) was added. Then compound **11** (131 mg, 0.273 mmol) dissolved in dry CH_2Cl_2 (1.5 mL) was slowly added at rt. After 1 h, the reaction was neutralized with Et_3N and the solvent was removed under reduced pressure. Chromatographic purification (3:2 petroleum ether–EtAcO) afforded 140 mg (99% yield) of pure **12**. $[\alpha]_D$ −55.1° (*c* 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.35–7.23 (m, 5 H, H-Ar), 5.38 (d, 1 H, $J_{3',4'}$ 2.9 Hz, H-4′), 5.31 (d, 1 H, $J_{3'',4''}$ 2.9 Hz, H-4″), 5.17 (dd, 1 H, $J_{2'',3''}$ 10.6 Hz, H-3″), 5.10–4.99 (m, 4 H, H-1′, 2′, 3′, 5″), 4.82 (d, 1 H, $J_{1'',2''}$ 3.6 Hz, H-1″), 4.64 (d, 1 H, *J* 11.6 Hz, CHPh), 4.59 (d, 1 H, CHPh), 4.49 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1), 4.49–4.44 (m, 1 H, H-6b), 4.40 (dd, 1 H, $J_{6'b,5'}$ 6.0, $J_{6'b,6'a}$ 11.6 Hz, H-6′b), 4.23 (dd, 1 H, $J_{6'a,5'}$ 7.9 Hz, H-6′a), 4.15 (dd, 1 H, $J_{6a,5}$ 4.2, $J_{6a,6b}$ 12.0 Hz, H-6a), 3.89–3.82 (m, 2 H, H-5′, 2″), 3.69 (t, 1 H, $J_{4,3} = J_{4,5}$ 9.3 Hz, H-4), 3.59 (t, 1 H, $J_{3,2}$ 9.3 Hz, H-3), 3.44–3.41 (m, 1 H, H-5), 3. 20 (dd, 1 H, H-2), 2.15, 2.11, 2.10, 2.04, 2.04, 1.98, 1.94 (7 s, 21 H,

CH_3CO), 1.60–1.80 (m, 1 H, CH-TDS), 1.20 (d, 3 H, $J_{5'',6''}$ 5.3 Hz, H-6″), 0.96–0.88 (m, 12 H, CH_3-TDS), 0.22, 0.20 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.5, 170.2, 170.2, 170.2, 169.9, 169.5, 169.4 (7s, CO), 137.5 (s), 128.4–128.0 (CHAr), 100.8, 97.74, 96.93 (3 d, C-1, 1′, 1″), 77.05, 73.41, 73.17, 72.49, 72.03, 71.05, 70.59, 69.84, 68.87, 66.96, 64.69 (12 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′, 2″, 3″, 4″, 5″), 74.29, 61.74, 60.88 (3 t, C-6, 6′, CH_2Ph), 33.91 (d, CH-TDS), 24.78 (s, C_q-TDS), 20.73–15.73, −2.304, −3.310 (CH_3CO, CH_3-TDS, CH_3Si). Anal. Calcd for $C_{47}H_{69}N_3O_{21}Si$: C, 54.26; H, 6.69; N, 4.04. Found: C, 54.30; H, 6.72; N, 4.07.

Texyldimethylsilyl β-D-galactopyranosyl-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (**13**).—Compound **8** (330 mg, 0.43 mmol) was dissolved in dry MeOH (5 mL) under inert atmosphere, and MeNaO (43 μL of a 1 M solution in MeOH, 0.043 mmol) was added. After 30 min, the reaction was neutralized with IR 120 resin H^+ form. The resin was then filtered and the solvent was removed under reduced pressure. 249 mg (97% yield) of pure **13** were obtained. Amorphous white solid; $[\alpha]_D$ −17.0° (*c* 1.5, $CHCl_3$); ^1H NMR (CD_3OD): δ 5.60 (s, 1 H, CHPh), 4.73 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.59 (d, 1 H, $J_{1',2'}$ 7.3 Hz, H-1′), 4.24 (dd, 1 H, $J_{6b,5}$ 4.9, $J_{6b,6a}$ 10.3 Hz, H-6b), 3.79 (t, 1 H, $J_{6a,5} = J_{6a,6b}$ 10.3 Hz, H-6a), 3.55 (dd, 1 H, $J_{2',3'}$10.3 Hz, H-2′), 3.85–3.40 (m, 9 H, H-2, 3, 4, 5, 3′, 4′, 5′, 6′a, 6′b), 1.74–1.63 (m, 1 H, CH-TDS), 0.94-0.90 (m, 12 H, CH_3-TDS), 0.23, 0.20 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 136.9 (s), 129.4–126.1 (CHAr), 103.2, 101.5, 97.49 (3 d, C-1, 1′, CHPh), 78.86, 78.57, 74.07, 73.01, 71.18, 69.70, 68.56, 66.41 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 68.39, 61.36 (2 t, C-6, 6′), 33.91 (d, CH-TDS), 24.74 (s, C_q-TDS), 19.98–18.33, −2.185, −3.222 (CH_3-TDS, CH_3Si). Anal. Calcd for $C_{27}H_{43}N_3O_{10}Si$: C, 54.25; H, 7.25; N, 7.03. Found: C, 54.30; H, 7.22; N, 6.98.

Thexyldimethylsilyl 6-O-tert-butyldiphenylsilyl-β-D-galactopyranosyl-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (**14**).—Compound **13** (519 mg, 0.87 mmol) was dissolved in dry DMF (10 mL) under inert atmosphere, and imidazole (118 mg, 1.74 mmol) and *t*BuDPSCl (266 μL, 1.04 mmol) were added. After 3 h, DMF was removed under reduced pressure, the crude was dissolved in EtAcO and washed with a saturated solution of NH_4Cl then with water. The organic layer was dried over anhyd $NaSO_4$, filtered and the solvent was removed under reduced pressure. Chromatographic purification (1:1 petroleum ether–EtAcO) afforded 509 mg (70% yield) of pure **14**. White solid; $[\alpha]_D$ −3.1° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.78–7.12 (m, 15 H, H-Ar), 5.42 (s, 1 H, CHPh), 4.60 (d, 1 H, $J_{1',2'}$ 7.6 Hz, H-1′), 4.40 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.26 (dd, 1 H, $J_{6b,5'}$ 4.9, $J_{6b,6a}$ 10.5 Hz, H-6b), 4.18–3.29 (m, 11 H, H-2, 3, 4, 5, 6a, 2′, 3′, 4′, 5′, 6′a, 6′b), 3.09 (d, 1 H, *J* 2.1 Hz, OH), 2.67 (d, 1 H, *J* 5.5 Hz, OH), 2.59 (d, 1 H, *J* 3.7 Hz, OH), 1.80–1.60 (m, 1 H, CH-TDS), 1.12–0.88 (m, 21 H, CH_3-TDS, CH_3-*t*Bu), 0.21, 0.18 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 132.8–132.9 (m, CqPh), 135.6–127.8 (m, CHAr), 104.3, 97.46, 96.94 (3 d, C-1, 1′, CHPh), 85.89, 75.42, 75.42, 73.25, 71.93, 70.01, 68.56, 67.30 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 63.14, 62.90 (2 t, C-6, 6′), 33.91 (d, CH-TDS), 26.80 (q, CH_3*t*Bu), 24.85, 19.12 (2 s, C_q-TDS, *t*Bu), 19.98–18.38, −2.062, −3.134 (m, CH_3-TDS, CH_3Si). Anal. Calcd for $C_{43}H_{61}N_3O_{10}Si_2$: C, 61.76; H, 7.35; N, 5.03. Found: C, 61.71; H, 7.38; N, 4.99.

Thexyldimethylsilyl 6-O-tert-butyldiphenylsilyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (**15**).—Compound **14** (392 mg, 0.47 mmol) was dissolved in dry MeCN (12 mL), and DMP (178 μL, 1.45 mmol) and a catalytic amount of CSA were added; after 10 min, the reaction was neutralized with Et_3N and the solvent was removed under diminished pressure. Chromatographic purification (4:1 petroleum ether–EtAcO) afforded 391 mg (95% yield) of pure **15**. Amorphous solid; $[\alpha]_D$ −3.1° (*c* 0.55, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.72–7.12 (m, 15 H, H-Ar), 5.50 (s, 1 H, CHPh), 4.61 (d, 1 H, $J_{1',2'}$ 7.4 Hz, H-1′), 4.39 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.24 (dd, 1 H, $J_{6b,5'}$ 4.9, $J_{6b,6a}$ 10.6 Hz, H-6b), 4.15–4.03 (m, 2 H, H-3′, 4′), 4.03–3.54 (m, 7 H, H-3, 4, 5, 6a, 2′, 6′a, 6′b), 3.36 (bt, 1 H, H-2), 3.35–3.28 (m, 1 H, H-5′), 2.99 (bs, 1 H, OH), 1.74–1.60 (m, 1 H, CH-TDS), 1.53, 1.36 (2 s, 6 H, $(CH_3)_2C$), 1.03 (s, 9 H, $(CH_3)_3C$), 0.91–0.88 (m, 12 H, CH_3-TDS), 0.20, 0.18 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 136.8–133.4 (m, CqPh), 135.6–125.7 (m, CHAr), 109.7 (s), 102.8, 101.1, 97.55 (3 d, C-1, 1′, CHPh), 79.56, 78.79, 78.44, 74.35, 73.44, 72.70, 68.15, 66.44 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 68.38, 62.12 (2 t, C-6, 6′), 33.81 (d, CH-TDS), 28.17, 26.22 (2 q, CH_3*i*Pr), 26.71 (q, CH_3*t*Bu), 24.79, 19.14 (2 s, C_q-TDS, *t*Bu), 19.85–19.37, −2.231, −3.211 (CH_3-TDS, CH_3Si). Anal. Calcd for $C_{46}H_{65}N_3O_{10}Si_2$: C, 63.05; H, 7.48; N, 4.80. Found: C, 63.01; H, 7.51; N, 4.83.

Texyldimethylsilyl 3,4-di-O-acetyl-2-O-benzyl-α-L-fucopyranosyl-(1→2)-6-O-tert-butyldiphenylsilyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (**16**).—Compound **15** (56 mg, 0.064 mmol) was dissolved in dry CH_2Cl_2 (1 mL). The temperature was lowered to 0 °C and TMSOTf (7 μL of a 0.1 M solution, 0.01 equiv) was added. Then, donor **11** (63 mg, 0.131 mmol) dissolved in dry CH_2Cl_2 (1.5 mL) was slowly added. After 1 h, the reaction was neutralized with Et_3N and the solvent was removed under reduced pressure. Chromatographic purification (4:1 petroleum ether–EtAcO) afforded 50 mg (66% yield) of pure **16**. Glassy solid; $[\alpha]_D$ −46.1° (*c* 2.3, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.75–7.18 (m, 20 H, H-Ar), 5.54 (d, 1 H, $J_{1'',2''}$ 3.7 Hz, H-1″), 5.40 (dd, 1 H, $J_{3'',4''}$ 3.3, $J_{3'',2''}$ 10.5 Hz, H-3″), 5.38 (s, 1 H, CHPh), 5.26 (d, 1 H, H-4″), 4.73 (d, 1 H,

$J_{1',2'}$ 7.9 Hz, H-1′), 4.71 (d, 1 H, J 12.2 Hz, CHPh), 4.65 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.63 (d, 1 H, J 12.2 Hz, CHPh), 4.51 (bq, 1 H, $J_{6'',5''}$ 6.6 Hz, H-5″), 4.11–4.27 (m, 3 H, H-4, 3′, 4′), 3.96 (t, 1 H, $J_{6b,5} = J_{6b,6a}$ 8.8 Hz, H-6b), 3.84 (dd, 1 H, H-2″), 3.66–3.82 (m, 5 H, H-3, 6a, 2′, 6′a, 6′b), 3.63–3.61 (m, 1 H, H-5), 3.37–3.30 (m, 1 H, H-5′), 3.33 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-2), 2,10, 1.99 (2 s, 6 H, CH_3CO), 1.60–1.73 (m, 1 H, CH-TDS), 1.49, 1.30 (2 s, 6 H, $(CH_3)_2C$), 1.09 (d, 3 H, H-6″), 1.05 (s, 9 H, $(CH_3)_3C$), 0.92–0.88 (m, 12 H, CH_3-TDS), 0.22, 0.20 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.5, 169.7 (2 s, CO), 138.2, 137.0, 133.4, 133.1 (4 s, CqPh), 135.7–126.1 (m, CHAr), 109.8 (s), 101.4, 99.53, 97.51, 95.14 (4d, C-1, 1′, 1″, CHPh), 80.01, 79.72, 77.01, 76.31, 73.54, 73.07, 72.38, 72.02, 69.78, 68.44, 66.37, 64.64, (12 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′, 2″, 3″, 4″, 5″), 72.50, 68.56, 62.33 (3 t, C-6, 6′, CH_2Ph), 33.85 (d, CH-TDS), 27.96, 26.81, 26.40 (3 q, 2 CH_3iPr, CH_3tBu), 24.78, 19.19 (2 s, C_q-TDS, tBu), 20.84, 20.68, 19.92, 19.81, 18.48, 18.37, 16.11, −2.254, −3.065 (9 q, 2 CH_3CO, 6 CH_3-TDS, C-6″). Anal. Calcd for $C_{63}H_{85}N_3O_{16}Si_2$: C, 63.23; H, 7.16; N, 3.51. Found: C, 63.21; H, 7.21; N, 3.46.

Thexyldimethylsilyl β-D-galactopyranosyl-(1→3)-2-azido-2-deoxy-β-D-glucopyranoside (**17**).—Compound **9** (130 mg, 0.19 mmol) was dissolved in dry MeOH (3 mL) under inert atmosphere, and MeONa (20 μL of a 1 M solution in MeOH, 0.020 mmol) was added. After 30 min, the reaction was neutralized with IR 120 resin H^+ form. The resin was then filtered and the solvent was removed under reduced pressure. Pure compound **17** (97 mg, quant.) was obtained. Amorphous white solid; $[\alpha]_D$ −11.5° (*c* 1.4, CH_3OH); ^1H NMR (CD_3OD): δ 4.58 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.48 (d, 1 H, $J_{1',2'}$ 7.1 Hz, H-1′), 3.88–3.24 (m, 12 H, H-2, 3, 4, 5, 6a, 6b, 2′, 3′, 4′, 5′, 6′a, 6′b), 1.77–1.59 (m, 1 H, CH-TDS), 0.97–0.90 (m, 12 H, CH_3-TDS), 0.21 (s, 6 H, CH_3Si); ^{13}C NMR (CD_3OD): δ 105.1, 98.41 (2 d, C-1, 1′), 84.02, 77.68, 76.98, 74.73, 72.65, 70.34, 70.00, 69.82 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 62.60, 62.60 (2 t, C-6, 6′), 35.28 (d, CH-TDS), 25.87 (s, C_q-TDS), 20.60–18.96, −1.729, −3.094 (CH_3-TDS, CH_3Si). Anal. Calcd for $C_{20}H_{39}N_3O_{10}Si$: C, 47.12; H, 7.72; N, 8.25. Found: C, 47.15; H, 7.68; N, 8.30.

Thexyldimethylsilyl 6-O-acetyl-β-D-galactopyranosyl-(1→3)-6-O-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (**18**).—Compound **17** was dissolved in MeCN (7 mL), vinylacetate (1 mL) was added and the supported CAL was suspended. The suspension was stirred mechanically with a thermostatic shaking apparatus at 40 °C for 24 h, and the reaction was monitored by TLC (9:1 EtAcO–MeOH). The enzyme was filtered, and the solvent was removed under reduced pressure. Chromatographic purification (EtAcO) afforded 112 mg (70% yield) of pure compound **18** and 10 mg (8%) of the 6′-monoacetylated and 24 mg (16%) of the 6,2′,6′-triacetylated compounds. Colorless oil; $[\alpha]_D$ +4.7° (*c* 1.5, $CHCl_3$); ^1H NMR (CD_3OD): δ 4.59 (d, 1 H, $J_{1,2}$ 7.1 Hz, H-1), 4.44 (d, 1 H, $J_{1',2'}$ 7.1 Hz, H-1′), 4.40 (dd, 1 H, $J_{6'b,5'}$ 1.4, $J_{6'b,6'a}$ 11.4 Hz, H-6′b), 4.31 (dd, 1 H, $J_{6'a,5'}$ 8.4 Hz, H-6′a), 4.23 (dd, 1 H, $J_{6b,5}$ 4.2, $J_{6b,6a}$ 11.7 Hz, H-6b), 4.17 (dd, 1 H, $J_{6a,5}$ 7.2 Hz, H-6a), 3.88–3.78 (m, 2 H, H-4′, 5′), 3.58 (bt, 1 H, H-2′), 3.52 (dd, 1 H, $J_{3',4'}$ 3.6, $J_{3',2'}$ 10.3 Hz, H-3′), 3.54–3.46 (m, 1 H, H-5), 3.44–3.28 (m, 3 H, H-2, 3, 4), 2.05 (s, 6 H, CH_3CO), 1.75–1.60 (m, 1 H, CH-TDS), 0.95–0.86 (m, 12 H, CH_3-TDS), 0.21, 0.18 (2 s, 6 H, CH_3Si); ^{13}C NMR (CD_3OD): δ 173.0, 172.8 (2 s, CO), 105.6, 98.58 (2 d, C-1, 1′), 85.52, 75.19, 74.72, 74.43, 72.58, 70.67, 70.39, 69.63 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 65.13, 65.02 (2 t, C-6, 6′), 35.61 (d, CH-TDS), 26.19 (s, C_q-TDS), 21.09–19.29, −1.535, −2.692 (CH_3CO, CH_3-TDS, CH_3Si). Anal. Calcd for $C_{24}H_{43}N_3O_{12}Si$: C, 48.54; H, 7.30; N, 7.08. Found: C, 48.49; H, 7.31; N, 7.07.

Thexyldimethylsilyl 6-O-acetyl-3,4-O-isopropylidene-β-D-galactopyranosyl)-(1→3)-6-O-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (**19**).—Compound **18** (260 mg, 0.437 mmol) was dissolved in dry MeCN (7 mL) and DMP (170 μL, 1.38 mmol) and a catalytic amount of CSA was added; after 30 min, the reaction was neutralized with Et_3N and the solvent was removed under diminished pressure. Chromatographic purification (3:2 petroleum ether–EtAcO) afforded 213 mg (77% yield) of pure **19**. $[\alpha]_D$ +34.3° (*c* 1.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 4.54 (d, 1 H, $J_{1,2}$ 7.2 Hz, H-1), 4.48–4.04 (m, 8 H, H-6a, 6b, 1′, 2′, 3′, 4′, 6′a, 6′b), 3.68–3.60 (m, 1 H, H-5′), 3.48–3.43 (m, 2 H, H-4, 5), 3.33 (dd, 1 H, $J_{2,3}$ 10.1 Hz, H-2), 3.22 (dd, 1 H, $J_{3,4}$ 7.5 Hz, H-3), 2.10, 2.08 (2 d, 6 H, CH_3CO), 1.75–1.50 (m, 1 H, CH-TDS), 1.56, 1.38 (2 s, 6 H, $(CH_3)_2C$), 0.96–0.88 (m, 12 H, CH_3-TDS), 0.21 (s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.3 (2 s, CO), 110.7 (s), 104.1, 96.88 (2 d, C-1, 1′), 87.18, 78.63, 73.54, 73.37, 72.95, 71.59, 69.44, 66.86 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 63.37, 63.14 (2 t, C-6, 6′), 33.87 (d, CH-TDS), 27.87, 26.12 (2 q, CH_3iPr), 25.19 (s, C_q-TDS), 20.63–18.36, −2.299, −3.332 (CH_3CO, CH_3-TDS, CH_3Si). Anal. Calcd for $C_{27}H_{47}N_3O_{12}Si$: C, 51.16; H, 7.48; N, 6.63. Found: C, 51.13; H, 7.51; N, 6.68.

Thexyldimethylsilyl 3,4-di-O-acetyl-2-O-benzyl-α-L-fucopyranosyl-(1→2)-6-O-acetyl-3,4-O-isopropylidene-β-D-galactopyranosyl-(1→3)-[3,4-di-O-acetyl-2-O-benzyl-α-L-fucopyranosyl-(1→4)]-6-O-acetyl-2-azido-2-deoxy-β-D-glucopyranoside (**20**).—Compound **19** (73 mg, 0.115 mmol) was dissolved in dry CH_2Cl_2 (1 mL). The temperature was lowered to 0 °C and TMSOTf (12 μL of a 0.1 M solution, 0.01 equiv) was added. Then donor **11** (222 mg, 0.461 mmol) dissolved in dry CH_2Cl_2 (2 mL) was slowly (1 h) added. After 1 h, another equivalent of **11** (55 mg, 0.11 mmol) dissolved in dry CH_2Cl_2 (1 mL) was added. After 20 min, the reaction was neutralized with Et_3N and the solvent was removed under reduced pressure. Chromatographic purification (4:1 petroleum ether–acetone) afforded 133

mg (91% yield) of pure **20**. $[\alpha]_D$ −52.4° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.49–7.22 (m, 10 H, H-Ar), 5.48 (d, 1 H, $J_{1''',2'''}$ 3.6 Hz, H-1‴), 5.36–5.31 (m, 2 H, H-3″, 4″), 5.28 (dd, 1 H, $J_{3''',4'''}$ 3.4, $J_{3''',2'''}$ 10.6 Hz, H-3‴), 5.21 (d, 1 H, H-4‴), 4.95 (bq, 1 H, $J_{5'',6''}$ 6.6 Hz, H-5″), 4.92 (d, 1 H, $J_{1',2'}$ 8.5 Hz, H-1′), 4.84 (d, 1 H, $J_{1'',2''}$ 3.7 Hz, H-1″), 4.73 (d, 1 H, *J* 12.1 Hz, CHPh), 4.63 (d, 1 H, *J* 12.1 Hz, CHPh), 4.62 (s, 2 H, CH_2Ph), 4.52 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.48 (dd, 1 H, $J_{6b,5}$ 1.8, $J_{6b,6a}$ 12.7 Hz, H-6b), 4.49–4.42 (m, 3 H, H-6′a, 6′b, 5‴), 4.29 (dd, 1 H, $J_{6a,5}$ 4.6 Hz, H-6a), 4.24 (dd, 1 H, $J_{3',4'}$ 5.7, $J_{3',2'}$ 6.9 Hz, H-3′), 4.09 (dd, 1 H, $J_{4',5'}$ 2.3 Hz, H-4′), 3.92 (dt, 1 H, $J_{5',6'a} = J_{5',6'b}$ 6.4 Hz, H-5′), 3.88–3.82 (m, 2 H, H-2″, 2‴), 3.63 (bt, 2 H, H-3, 2′), 3.56 (t, 1 H, $J_{4,3}$ 4.5 Hz, H-4), 3.50–3.42 (m, 1 H, H-5), 3.23 (dd, 1 H, $J_{2,3}$ 9.4 Hz, H-2), 2.12, 2,10, 2.08, 2.04, 1.99, 1.92 (6 s, 18 H, CH_3CO), 1.71–1.58 (m, 1 H, CH-TDS), 1.48, 1.32 (2 s, 6 H, $(CH_3)_2C$), 1.17–1.10 (m, 6 H, H-6″, 6‴), 0.92–0.87 (m, 12 H, CH_3-TDS), 0.20, 0.19 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.9, 170.5, 170.3, 173.3, 169.4, 169.4 (6 s, CO), 138.4, 137.5 (2 s, CqPh), 128.4–127.6 (m, CHAr), 110.0 (s), 100.2, 98.56, 97.16, 96.81 (4 d, C-1, 1′, 1″, 1‴), 79.77, 77.12, 76.76, 74.60, 73.77, 73.59, 73.40, 73.04, 72.29, 71.90, 71.12, 70.42, 69.83, 69.07, 64.80, 64.58 (16 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′, 2″, 3″, 4″, 5″, 2‴, 3‴, 4‴, 5‴), 74.29, 72.09, 62.90, 62.04 (4 t, C-6, 6′, 2 CH_2Ph), 33.84 (d, CH-TDS), 28.01, 26.05 (2 q, $2CH_3$*i*Pr), 24.89 (s, C_q-TDS), 20.90–15.72 (m, 6 CH_3CO, 4 CH_3-TDS, C-6″, C-6‴), −2.197, −3.234 (2 CH_3Si). Anal. Calcd for $C_{61}H_{87}N_3O_{24}Si$: C, 57.48; H, 6.88; N, 3.30. Found: C, 57.51; H, 6.91; N, 3.27.

Thexyldimethylsilyl 2,3,4,6-tetra-O-*acetyl-β*-D-*galactopyranosyl-(1→4)-3,6-di*-O-*acetyl-2-azido-2-deoxy-β*-D-*glucopyranoside* (**27**).—Compounds **24** (719 mg, 1.67 mmol) and **26** (1.23 g, 2.50 mmol) were mixed in a flask under inert atmosphere and dissolved in dry CH_2Cl_2 (8 mL). Then TMSOTf (333 μL of a 0.1 M solution in CH_2Cl_2, 0.02 equiv) was added. After 40 min the reaction was neutralized with Et_3N and the solvent was removed under diminished pressure. Chromatographic purification (3:2 petroleum ether–EtAcO) afforded 707 mg (56% yield) of pure **27**. Amorphous white solid; $[\alpha]_D$ +2.5° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.33 (d, 1 H, $J_{3',4'}$ 3.3 Hz, H-4′), 5.10 (dd, 1 H, $J_{1',2'}$ 7.6, $J_{2',3'}$ 10.3 Hz, H-2′), 4.97 (dd, 1 H, $J_{3,4}$ 8.6, $J_{3,2}$ 10.3 Hz, H-3), 4.96 (d, 1 H, H-3′), 4.58 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.46 (d, 1 H, H-1′), 4.46 (dd, 1 H, $J_{6b,5}$ 2.0, $J_{6b,6a}$ 11.7 Hz, H-6b), 4.21–4.05 (m, 3 H, H-6a, 6′a, 6′b), 3.87 (bt, 1 H, *J* 6.6 Hz, H-5′), 3.67 (t, 1 H, $J_{4,5}$ 8.6 Hz, H-4), 3.62–3.51 (m, 1 H, H-5), 3.32 (dd, 1 H, H-2), 2.16, 2.09, 2.08, 2.07, 2.04, 1.98 (6 s, 18 H, CH_3CO), 1.78–1.57 (m, 1 H, CH-TDS), 0.94–0.88 (m, 12 H, CH_3-TDS), 0.20, 0.18 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.2, 170.2, 170.2, 170.0, 169.4, 168.8 (6 s, CO), 100.8, 96.67 (2d, C-1, 1′), 76.45, 71.79, 70.87, 70.66, 70.37, 69.08, 66.66, 66.43 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 62.10, 60.94 (2 t, C-6, 6′), 33.80 (d, CH-TDS), 24.73 (s, C_q-TDS), 20.74–18.30, −2.440, −3.442 (6 CH_3CO, 4 CH_3-TDS, 2 CH_3Si). Anal. Calcd for $C_{32}H_{51}N_3O_{16}Si$: C, 50.44; H, 6.75; N, 5.52. Found: C, 50.39; H, 6.78; N, 5.47.

Thexyldimethylsilyl 2,3,4,6-tetra-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-6*-O *-acetyl-2-azido-3*-O-*benzyl-2-deoxy-β*-D-*glucopyranoside* (**28**).—Compounds **25** (258 mg, 0.54 mmol) and **26** (344 mg, 0.70 mmol) were mixed in a flask under inert atmosphere and dissolved in dry CH_2Cl_2 (6 mL). Then TMSOTf (54 μL of a 0.1 M solution in CH_2Cl_2, 0.01 equiv) was added. After 3 h, the reaction was neutralized with Et_3N and the solvent was removed under diminished pressure. Chromatographic purification (7:3 petroleum ether–EtAcO) afforded 413 mg (95% yield) of pure **28**. Amorphous white solid; $[\alpha]_D$ −2.3° (*c* 0.66, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.40–7.21 (m, 5 H, HAr), 5.30 (d, 1 H, $J_{3',4'}$ 3.0 Hz, H-4′), 5.18 (dd, 1 H, $J_{1',2'}$ 7.9, $J_{2',3'}$ 10.5 Hz, H-2′), 4.95 (dd, 1 H, H-3′), 4.92 (d, 1 H, *J* 10.9 Hz, CHPh), 4.82 (d, 1 H, *J* 10.9 Hz, CHPh), 4.62 (d, 1 H, H-1′), 4.47 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.43 (dd, 1 H, $J_{6b,5}$ 1.8, $J_{6b,6a}$ 11.7 Hz, H-6b), 4.05 (dd, 1 H, $J_{6'b,5'}$ 6.7, $J_{6'b,6'a}$ 11.0 Hz, H-6′b), 3.69 (dd, 1 H, $J_{6'a,5'}$ 8.0 Hz, H-6′a), 3.84 (dd, 1 H, $J_{6a,5}$ 6.2 Hz, H-6a), 3.73–3.67 (m, 2 H, H-3, 5′), 3.46 (ddd, 1 H, $J_{5,4}$ 8.0 Hz, H-5), 3.37 (bt, 1 H, H-4), 3.29 (dd, 1 H, $J_{2,3}$ 9.3 Hz, H-2), 2.16. 2.11, 2.06, 1.97 (4 s, 15 H, CH_3CO), 1.78–1.57 (m, 1 H, CH-TDS), 0.94–0.88 (m, 12 H, CH_3-TDS), 0.20, 0.18 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.3, 170.0, 170.0, 170.0, 169.3 (5 s, CO), 138.2 (s), 128.3–127.3 (CHAr), 100.8, 96.69 (2 d, C-1, 1′), 80.83, 77.93, 72.73, 70.93, 70.70, 69.55, 68.45, 66.78 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 74.69, 62.43, 60.65 (3 t, C-6, 6′, CH_2Ph), 33.86 (d, CH-TDS), 24.73 (s, C_q-TDS), 20.52–18.27, −2.353, −3.392 (5 CH_3CO, 4 CH_3-TDS, 2 CH_3Si). Anal. Calcd for $C_{37}H_{55}N_3O_{15}Si$: C, 54.86; H, 6.85; N, 5.19. Found: C, 54.91; H, 6.88; N, 5.22.

Thexyldimethylsilyl 2,3,4,6-tetra-O-*acetyl-β*-D-*galactopyranosyl-(1→4)-6*-O-*acetyl-2-azido-2-deoxy-β*-D-*glucopyranoside* (**29**).—Compound **28** (400 mg, 0.493 mmol) was dissolved in dry CH_2Cl_2 (20 mL) under inert atmosphere. Then $SnCl_4$ (0.115 μL, 0.986 mmol) was added. After 24 h, another 2 equiv (0.115 μL) of $SnCl_4$ were added and the reaction was left stirring for 12 h. Then, the reaction mixture was poured in an ice cold saturated solution of $NaHCO_3$ and a solution of sodium and potassium tartrate was added. The organic layer was washed with HCl 5% and water, dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. Chromatographic purification (7:3 petroleum ether–EtAcO) afforded 170 mg (48% yield) of pure **29**. Amorphous white solid; $[\alpha]_D$ +18.2° (*c* 0.60, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.37 (d, 1 H, $J_{3',4'}$ 3.2 Hz, H-4′), 5.21 (dd, 1 H, $J_{1',2'}$ 8.1, $J_{2',3'}$ 10.4 Hz, H-2′), 4.99 (dd, 1 H, H-3′), 4.53 (d, 1 H, H-1′), 4.45 (d,

1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.26 (dd, 1 H, $J_{6b,5}$ 1.5, $J_{6b,6a}$ 11.7 Hz, H-6b), 4.22–4.10 (m, 3 H, H-5′, 6′a, 6′b), 3.98 (dd, 1 H, $J_{6a,5}$ 6.5 Hz, H-6a), 3.54 (dd, 1 H, $J_{3,4}$ 8.1, $J_{3,2}$ 9.6 Hz, H-3), 3.50–3.46 (m, 1 H, H-5), 3.40 (t, 1 H, $J_{4,5}$ 8.1 Hz, H-4), 3.22 (dd, 1 H, H-2), 2.18, 2.11, 2.09, 2.00 (4 s, 15 H, CH_3CO), 1.72–1.57 (m, 1 H, CH-TDS), 0.92–0.88 (m, 12 H, CH_3-TDS), 0.19, 0.16 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.4, 170.4, 169.8, 169.8, 169.4 (CO), 102.0, 96.35 (2 d, C-1, 1′), 82.82, 73.70, 71.68, 71.48, 70.75, 68.71, 67.68, 66.83 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 62.68, 61.79 (2 t, C-6, 6′), 33.91 (d, CH-TDS), 24.83 (s, C_q-TDS), 20.98–11.37, −2.341, −3.374 (5 CH_3CO, 4 CH_3-TDS, 2 CH_3Si). Anal. Calcd for $C_{30}H_{49}N_3O_{15}Si$: C, 50.05; H, 6.86; N, 5.84. Found: C, 50.00; H, 6.88; N, 5.79.

Thexyldimethylsilyl 2,3,4,6-tetra-O-*acetyl-β*-D-*galactopyranosyl-(1→4)-[3,4-di*-O-*acetyl-2*-O-*benzyl-α*-L-*fucopyranosyl-(1→3)]-6*-O-*acetyl-2-azido-2-deoxy-β*-D-*glucopyranoside* (**30**).—Compound **29** (100 mg, 0.139 mmol) was dissolved in dry CH_2Cl_2 (1 mL), the solution was cooled to 0 °C and TMSOTf (28 μL of a 0.1 M solution in CH_2Cl_2) was added. The ice bath was then removed and donor **11** (100 mg, 0.208 mmol) dissolved in dry CH_2Cl_2 (2 mL), was added in 30 min. The reaction was neutralized with Et_3N, and the solvent was removed under reduced pressure. Chromatographic purification (3:2 petroleum ether–EtAcO) afforded 130 mg (90% yield) of pure **30**. Amorphous white solid; $[\alpha]_D$ −48.3° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.48–7.21 (m, 5 H, HAr), 5.58 (d, 1 H, $J_{1'',2''}$ 3.7 Hz, H-1″), 5.40 (d, 1 H, $J_{3',4'}$ 3.2 Hz, H-4′), 5.33 (d, 1 H, $J_{3'',4''}$ 3.1 Hz, H-4″), 5.18 (dd, 1 H, $J_{3'',2''}$ 10.5 Hz, H-3″), 5.06 (bt, 1 H, H-2′), 4.95 (dd, 1 H, $J_{2',3'}$ 10.5 Hz, H-3′), 4.90 (bq, 1 H, H-5″), 4.77 (d, 1 H, *J* 12.3 Hz, CHPh), 4.62 77 (d, 1 H, CHPh), 4.61 (bd, 1 H, H-6b), 4.54 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.46 (dd, 1 H, $J_{6'b,5'}$ 6.2, $J_{6'b,6'a}$ 11.5 Hz, H-6′b), 4.45 (d, 1 H, $J_{1',2'}$ 7.6 Hz, H-1′), 4.30 (dd, 1 H, $J_{6'a,5'}$ 7.7 Hz, H-6′a), 3.99 (dd, 1 H, $J_{6a,5}$ 5.8, $J_{6b,6a}$ 11.8 Hz, H-6a), 3.89–3.85 (m, 1 H, H-2″), 3.82–3.79 (m, 1 H, H-5′), 3.80 (t, 1 H, $J_{4,3} = J_{4,5}$ 9.7 Hz, H-4), 3.56 (t, 1 H, $J_{3,2}$ 9.7 Hz, H-3), 3.46–3.39 (m, 1 H, H-5), 3.40 (dd, 1 H, H-2), 2.15, 2.07, 2.06, 2.01, 2.00, 1.93 (6 s, 21 H, CH_3CO), 1.70–1.57 (m, 1 H, CH-TDS), 1.16 (d, 3 H, $J_{6'',5''}$ 6.5 Hz, H-6″), 0.87–0.84 (m, 12 H, CH_3-TDS), 0.15, 0.14 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.6, 170.5, 170.4, 170.0, 169.8, 169.7, 168.9 (7 s, CO), 138.0 (s), 128.2–127.7 (CHAr), 100.7, 97.16, 96.81 (3 d, C-1, 1′, 1″), 74.69, 74.23, 73.30, 72.90, 71.97, 71.17, 70.94, 70.19, 69.03, 68.86, 66.72, 64.17 (12 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′, 2″, 3″, 4″, 5″), 72.55, 61.75, 60.83 (3 t, C-6, 6′, CH_2Ph), 33.91 (d, CH-TDS), 24.78 (s, C_q-TDS), 20.73–15.77, −2.371, −3.169 (C-6″, 7 CH_3CO, 4 CH_3-TDS, 2 CH_3Si). Anal. Calcd for $C_{47}H_{69}N_3O_{21}Si$: C, 54.26; H, 6.69; N, 4.04. Found: C, 54.30; H, 6.73; N, 3.99.

Thexyldimethylsilyl β-D-*galactopyranosyl-(1→4)-2-azido-2-deoxy-β*-D-*glucopyranoside* (**31**).—Compound **27** (500 mg, 0.656 mmol) was dissolved under inert atmosphere in dry MeOH (10 mL). Then NaOMe (65 μL of a 1 M solution in MeOH, 0.1 equiv) was added. After 15 min, the reaction was neutralized with IR 120 resin (H^+ form), filtered, and the solvent was removed under reduced pressure. Compound **31** was recovered in quantitative yield (334 mg). Amorphous glassy solid; $[\alpha]_D$ −10.7° (*c* 2.6, MeOH); ^1H NMR (CD_3OD): δ 4.56 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.38 (d, 1 H, $J_{1',2'}$ 7.4 Hz, H-1′), 3.85–3.30 (m, 11 H, H-3, 4, 5, 6a, 6b, 2′, 3′, 4′, 5′, 6′a, 6′b), 3.10 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 1.71–1.67 (m, 1 H, CH-TDS), 0.94–0.91 (m, 12 H, CH_3-TDS), 0.22, 0.21 (2 s, 6 H, CH_3Si); ^{13}C NMR (CD_3OD): δ 107.2, 99.88 (2 d, C-1, 1′), 82.79, (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 62.10, 60.94 (2 t, C-6, 6′), 33.80 (d, CH-TDS), 24.73 (s, C_q-TDS), 20.74–18.30, −2.440, −3.442 (6 CH_3CO, 6 CH_3-TDS). Anal. Calcd for $C_{20}H_{39}N_3O_{10}Si$: C, 47.14; H, 7.71; N, 8.25. Found: C, 46.98; H, 7.69; N, 8.27.

Thexyldimethylsilyl 3,4-O-*isopropylidene-β*-D-*galactopyranosyl-(1→4)-2-azido-2-deoxy-β*-D-*glucopyranoside* (**32**).—Compound **31** (110 mg, 0.216 mmol) was dissolved in dry acetone (3 mL) under inert atmosphere; then Sikkon (200 mg) and a catalytic amount of CSA were added and the reaction was heated to reflux. After 1 h, the reaction was neutralized with Et_3N and the solvent was removed under diminished pressure. Chromatographic purification (10:1 EtAcO–MeOH) afforded 99 mg (84%) of pure **32** (thermodynamic product), and 20 mg (16%) of the 4′,6′-isopropylidene regioisomer. Amorphous solid; ^1H NMR ($CDCl_3$): δ 4.56 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.35 (d, 1 H, $J_{1',2'}$ 8.4 Hz, H-1′), 4.16 (dd, 1 H, $J_{4',5'}$ 1.5, $J_{4',3'}$ 6.0 Hz, H-4′), 4.10 (t, 1 H, $J_{3',2'}$ 6.0 Hz, H-3′), 4.02–3.85 (m, 5 H, H-6a, 6b, 2′, 6′a, 6′b), 3.64 (t, 1 H, $J_{3,2}$ 9.4 Hz, H-3), 3.61 (t, 1 H, *J* 8.6 Hz, H-5′), 3.49 (t, 1 H, *J* 9.4 Hz, H-4), 3.37 (dt, 1 H, *J* 3.6 Hz, H-5), 3.22 (dd, 1 H, H-2), 1.76–1.58 (m, 1 H, CH-TDS), 1.52, 1.55 (2 s, 6 H, $(CH_3)_2C$), 0.94–0.88 (m, 12 H, CH_3-TDS), 0.21, 0.18 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 110.6(s), 102.9, 96.91 (2 d, C-1, 1′), 81.39, 79.28, 74.15, 73.99, 73.70, 73.15, 73.15, 67.95 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 62.30, 61.93 (2 t, C-6, 6′), 33.90 (d, CH-TDS), 27.96, 26.12 (2 q, CH_3iPr), 24.74 (s, C_q-TDS), 19.87–18.35, −2.128, −3.276 (4 CH_3-TDS, $2CH_3Si$). Anal. Calcd for $C_{23}H_{43}N_3O_{10}Si$: C, 50.26; H, 7.88; N, 7.64. Found: C, 50.31; H, 7.85; N, 7.67.

Thexyldimethylsilyl 6-O-*acetyl-3,4*-O-*isopropylidene-β*-D-*galactopyranosyl-(1→4)-6*-O-*acetyl-2-azido-2-deoxy-β*-D-*glucopyranoside* (**33**).—Compound **32** (196 mg, 0.356 mmol) was dissolved in dry CH_2Cl_2 (5 mL) under inert atmosphere and the solution was cooled to −78 °C. Then Py (230 μL) and AcCl (152 μL) were added. After 6 h, MeOH (1 mL) was added to the reaction mixture and the temperature raised to rt; then

a saturated solution of $NaHCO_3$ was added, the organic layer was washed with HCl 5%, dried over Na_2SO_4, filtered, and the solvent was removed under diminished pressure. Chromatographic purification (1:1 petroleum ether–EtAcO) afforded 159 mg (71% yield) of pure compound **33**. Yellow oil; $[\alpha]_D$ +29° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 4.49 (bd, 1 H, *J* 12.2 Hz, H-6b), 4.45 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.40 (dd, 1 H, $J_{6'b,5'}$ 2.5, $J_{6'b,6'a}$ 12.0 Hz, H-6′b), 4.27 (dd, 1 H, $J_{6'a,5}$ 9.3 Hz, H-6′a), 4.20 (d, 1 H, $J_{1',2'}$ 8.2 Hz, H-1′), 4.14 (dd, 1 H, $J_{6a,5}$ 6.1 Hz, H-6a), 4.12–4.07 (m, 2 H, H-3′, 4′), 3.57 (bt, 1 H, H-5′), 3.51 (t, 1 H, *J* 9.6 Hz, H-3), 3.48–3.43 (m, 1 H, H-5), 3.30 (bt, 1 H, H-4), 3.19 (dd, 1 H, H-2), 2.11, 2.05 (2 s, 6 H, CH_3CO), 1.70–1.57 (m, 1 H, CH-TDS), 1.49, 1.31 (2 s, 6 H, $(CH_3)_2C$), 0.88–0.86 (m, 12 H, CH_3-TDS), 0.20, 0.18 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 171.0, 170.9 (2 s, CO), 110.7 (s), 103.5, 96.33 (2 d, C-1, 1′), 82.65, 79.08, 73.95, 73.19, 73.01, 72.55, 71.22, 67.66 (8 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′), 63.52, 63.25 (2 t, C-6, 6′), 33.96 (d, CH-TDS), 27.96, 26.17 (2 q, CH_3iPr), 24.89 (s, C_q-TDS), 20.79–18.37, −2.204, −3.296 (2 CH_3CO, 4 CH_3-TDS, 2 CH_3Si). Anal. Calcd for $C_{27}H_{47}N_3O_{12}Si$: C, 51.17; H, 7.47; N, 6.63. Found: C, 51.22; H, 7.44; N, 6.62.

Thexyldimethylsilyl 3,4-di-O-*acetyl-2*-O-*benzyl-α*-L-*fucopyranosyl-(1→2)-6*-O-*acetyl-3,4*-O-*isopropylidene-β*-D-*galactopyranosyl-(1→4)-[3,4-di*-O-*acetyl-2*-O-*benzyl-α*-L-*fucopyranosyl-(1→3)]-6*-O-*acetyl-2-azido-2-deoxy-β*-D-*glucopyranoside* (**34**).—Compound **33** (64 mg, 0.101 mmol) and donor **11** (146 mg, 0.30 mmol) were mixed in a flask under inert atmosphere and dissolved in dry CH_2Cl_2 (4 mL). At −20 °C TMSOTf (20 μL of a 0.05 M solution in CH_2Cl_2, 0.01 equiv) was added. After 5 min, 3 equiv (146 mg) of donor were added slowly and after 10 min 2 more equiv. The reaction was neutralized with Et_3N and the solvent was removed under reduced pressure. Chromatographic purification (3:2 petroleum ether–EtAcO) afforded 70 mg (55% yield) of pure **34**. Amorphous white solid; $[\alpha]_D$ −64.9° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.45–7.22 (m, 10 H, H-Ar), 5.58 (d, 1 H, $J_{1''',2'''}$ 3.5 Hz, H-1‴), 5.48 (d, 1 H, $J_{1'',2''}$ 3.6 Hz, H-1″), 5.32 (dd, 1 H, $J_{3''',4'''}$ 3.2, $J_{3''',2'''}$ 10.7 Hz, H-3‴), 5.29 (d, 1 H, $J_{4'',3''}$ 3.4 Hz, H-4″), 5.23 (d, 1 H, H-4‴), 5.14 (dd, 1 H, $J_{3'',2''}$ 10.6 Hz, H-3″), 4.93 (bq, 1 H, $J_{5''',6'''}$ H-5‴), 4.81 (d, 1 H, *J* 12.5 Hz, CHPh), 4.67 (d, 1 H, *J* 10.0 Hz, CHPh), 4.63 (d, 1 H, *J* 10.0 Hz, CHPh), 4.60 (d, 1 H, *J* 12.5 Hz, CHPh), 4.62–4.57 (m, 1 H, H-6b), 4.59 (d, 1 H, $J_{1,2}$ 7.1 Hz, H-1), 4.53–4.45 (m, 2 H, H-6′a, 6′b), 4.30 (d, 1 H, $J_{1',2'}$ 8.2 Hz, H-1′), 4.33–4.24 (m, 2 H, H-6a, 5″), 4.12 (bt, 1 H, H-3′), 4.09 (dd, 1 H, $J_{4',5'}$ 1.6 Hz, H-4′), 3.89–3.84 (m, 1 H, H-5), 3.84 (dd, 1 H, H-2‴), 3.82 (dd, 1 H, H-2″), 3.76 (t, 1 H, $J_{4,3} = J_{4,5}$ 9.0 Hz, H-4), 3.58 (dd, 1 H, $J_{2',3'}$ 6.9 Hz, H-2′), 3.55–3.48 (m, 1 H, H-5), 3.48 (t, 1 H, $J_{2,3}$ 9.0 Hz, H-3), 3.43 (dd, 1 H, H-2), 2.10, 2.07, 2.05, 1.96, 1.93 (5 s, 18 H, CH_3CO), 1.71–1.58 (m, 1 H, CH-TDS), 1.45, 1.32 (2 s, 6 H, $(CH_3)_2C$), 1.11 (d, 3 H, $J_{6'',5''}$ 6.6 Hz, H-6″), 1.07 (d, 3 H, $J_{6''',5'''}$ 6.5 Hz, H-6‴), 0.89–0.87 (m, 12 H, CH_3-TDS), 0.20, 0.19 (2 s, 6 H, CH_3Si); ^{13}C NMR ($CDCl_3$): δ 170.6–169.6 (CO), 138.1 (CqPh), 128.3–127.7 (m, CHAr), 110.3 (s), 100.7, 97.17, 97.17, 95.77 (4 d, C-1, 1′, 1″, 1‴), 79.43, 76.31, 75.85, 75.38, 73.58, 73.58, 73.01, 72.90, 72.14, 71.68, 71.46, 69.95, 69.49, 69.03, 64.75, 64.12 (16 d, C-2, 3, 4, 5, 2′, 3′, 4′, 5′, 2″, 3″, 4″, 5″, 2‴, 3‴, 4‴, 5‴), 72.61, 72.14, 62.85, 62.16 (4 t, C-6, 6′, 2 CH_2Ph), 33.91 (d, CH-TDS), 28.01, 26.11 (2 q, 2 CH_3iPr), 24.72 (s, C_q-TDS), 20.96–15.78 (m, 6 CH_3CO, 4 CH_3-TDS, C-6″, C-6‴), −2.253, −3.224 (2 CH_3Si). Anal. Calcd for $C_{61}H_{87}N_3O_{24}Si$: C, 57.48; H, 6.88; N, 3.30. Found: C, 57.53; H, 6.90; N, 3.32.

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References

1. Newburg, D. S.; Neubaur, S. H. *Handbook of Milk Composition*; Academic: San Diego, CA, 1995; pp 273–349.
2. Stahl, B.; Thurl, S.; Zeng, J.; Karas, M.; Hillenkamp, F.; Steup, M.; Sawatzki, G. *Anal. Biochem.* **1994**, *223*, 218–226.
3. Coppa, G. V. *Abstract of Papers*, Milanopediatria 2000, Milan, Italy, May 2000.
4. Ofek, I.; Beachey, E. H. *Adv. Intern. Med.* **1980**, *25*, 503–532.
5. Boedeker, E. C. *Gastroenterology* **1982**, *83*, 489–492.
6. Gothefors, L.; Olling, S.; Winberg, J. *Acta Pediatr. Scand.* **1975**, *64*, 807–812.
7. Andersson, B.; Porras, O.; Hanson, L. A.; Lagergard, T.; Svanborg-Eden, C. *J. Infect. Dis.* **1986**, *153*, 232–237.
8. Holmgren, J.; Svennerholm, A. M.; Lindblad, M. *Infect. Immun.* **1983**, *39*, 147–154.
9. Crane, J. K.; Azar, S. S.; Stam, A.; Newburg, D. S. *J. Nutr.* **1994**, *124*, 2358–2364.
10. La Ferla, B.; Lay, L.; Poletti, L.; Russo, G.; Panza, L. *J. Carbohydr. Chem.* **2000**, *19*, 331–347.
11. Nicolaou, K. C.; Hummel, C. W.; Iwabuchi, Y. *J. Am. Chem. Soc.* **1992**, *114*, 3126–3128.
12. Jacquinet, J. C.; Sinaÿ, P. *J. Chem. Soc., Perkin Trans. 1* **1979**, 314–318.
13. Béhar, V.; Danishefsky, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1468–1470 and references therein.
14. Ichikawa, Y.; Lin, Y.-C.; Dumas, D. P.; Shen, G.-J.; Garcia-Junceda, E.; Williams, M. A.; Bayer, R.; Ketcham, C.; Walker, L. E.; Paulson, J. C.; Wong, C.-H. *J. Am. Chem. Soc.* **1992**, *114*, 9283–9298 and references therein.
15. (a) Toepfer, A.; Schmidt, R. R. *Tetrahedron Lett.* **1992**, *33*, 5161–5164;

(b) Toepfer, A.; Kinzy, W.; Schmidt, R. R. *Liebigs Ann. Chem.* **1994**, 449–464.
16. Windmüller, R.; Schmidt, R. R. *Tetrahedron Lett.* **1994**, *35*, 7927–7930.
17. Jain, R. K.; Vig, R.; Locke, R. D.; Mohammad, A.; Matta, K. L. *Chem. Commun.* **1996**, 65–67.
18. Randolph, J. T.; Danishefsky, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1470–1473.
19. Nilsson, M.; Norberg, T. *Carbohydr. Res.* **1988**, *183*, 71–82.
20. Gege, C.; Vogel, J.; Bendas, G.; Rothe, U.; Schmidt, R. R. *Chem. Eur. J.* **2000**, *6*, 111–122.
21. Hummel, G.; Schmidt, R. R. *Tetrahedron Lett.* **1997**, *38*, 1173–1176.
22. Toepfer, A.; Schmidt, R. R. *J. Carbohydr. Chem.* **1993**, *12*, 809–822.
23. Manzoni, L.; Lay, L.; Schmidt, R. R. *J. Carbohydr. Chem.* **1998**, *17*, 739–758 and references therein.
24. La Ferla, B.; Lay, L.; Russo, G.; Panza, L. *Tetrahedron: Asymmetry* **2000**, *11*, 3647–3651.
25. Degueil-Castaing, M.; De Jeso, B.; Drouillard, S.; Maillard, B. *Tetrahedron Lett.* **1987**, *28*, 953–954.
26. Wang, Y.-F.; Wong, C.-H. *J. Org. Chem.* **1988**, *53*, 3127–3129.
27. Cottaz, S.; Apparu, C.; Driguez, H. *J. Chem. Soc., Perkin Trans I* **1991**, *9*, 2235–2241.
28. Toepfer, A.; Schmidt, R. R. *J. Carbohydr. Chem.* **1993**, *12*, 809–822.
29. Hori, H.; Nishida, Y.; Ohrui, H.; Meguro, H. *J. Org. Chem.* **1989**, *54*, 1346–1353.