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First synthesis of 3′-deoxy Lewis^{x} pentasaccharide

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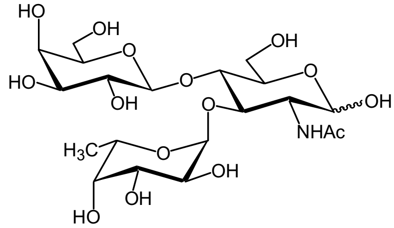
Abstract—The total synthesis of 3′-deoxy Lewis^{x} pentasaccharide is reported. 4-*O*-Acetyl-2,6-di-*O*-benzoyl-3-deoxy-β-D-xylo-hexopyranosyl trichloroacetimidate was condensed with a diol of glucosamine to give a disaccharide, which was further fucosylated to a Lewis^{x} trisaccharide analogue. Glycosylation of a lactoside diol with this trisaccharide provided a pentasaccharide, which after deprotection, afforded the target pentasaccharide.

1. Introduction

Carbohydrates are the most ubiquitous and prominently exposed molecules on the surface of living cells. They have been recognized as interaction sites in many different instances. Many of these processes are mediated by lectin or lectin-like molecules that recognize specific carbohydrate motifs. Recent advances in glycobiology revealed the existence of biologically significant carbohydrate–carbohydrate interactions, and this type of interaction could have a general, fundamental character for cell biology.[1] A typical example is the report of Hakomori,[2] who proposed that carbohydrate–carbohydrate interaction is responsible for the initial step of cell adhesion. One of the structures involved in this mechanism is the Lewis^{x} (Le^{x}) trisaccharide determinant.



Le^{x} trisaccharide

The interaction between Le^{x} and Le^{x} was found[3,4] to be homotypic, and mediated by the presence of divalent cations such as Ca^{2+}. Recently, the Le^{x}–Le^{x} interaction has gained increasing attention, using a variety of techniques including nuclear magnetic resonance (NMR) spectroscopy,[5] mass spectrometry (MS),[6] vesicle adhesion,[7] atomic force microscopy (AFM),[8] and surface plasmon resonance (SPR) spectroscopy.[9] Rat basophilic leukaemia cells pre-incubated with purified Le^{x} containing glycosphingolipids have also been used as a model.[10] However, in these studies the local environment of the Le^{x} was always very different from that existing at a typical cell surface. In cells, the Le^{x}-bearing molecules are usually composed of a ceramide connected to the Le^{x} trisaccharide through a lactose group. Very recently, using a chemically synthesized natural Le^{x}, we demonstrated by a vesicle approach that unlike the neoglycolipids,[7] which allowed a strong orientational freedom of the Le^{x} group, the natural lipid showed a restricted orientation of the Le^{x} group by which the adhesion induced by Le^{x}–Le^{x} interaction was considerably enhanced.[11] Another experiment was performed by replacing the Le^{x} by Le^{a} in which the galactose and fucose are permutated relative to the Le^{x} on one vesicle surface. The weak adhesion energy obtained for Le^{x}–Le^{a} pair showed clearly that the permutation of the

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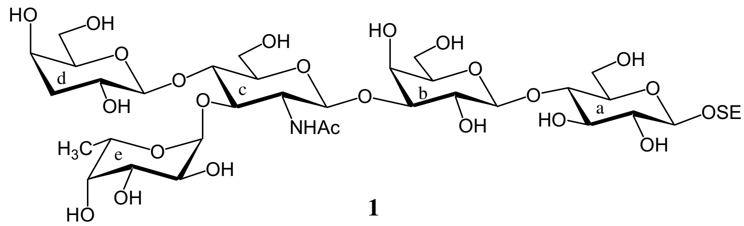

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fucose and galactose residues in the trisaccharide head-group effectively prevents specific adhesion.[11]

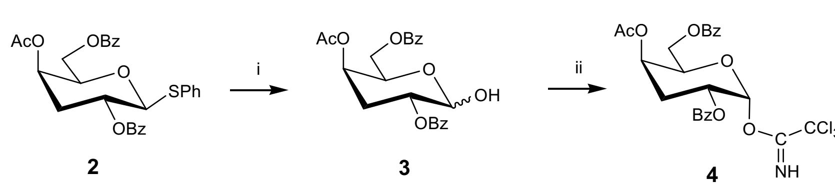
In order to understand the key role of the different hydroxyl groups on Le^x trisaccharide, it is important to have a series of pentasaccharides available in which one of the eight hydroxyl groups is replaced by a hydrogen atom, and to test the induced adhesion by interaction of these derivatives. Herein, we report the first total synthesis of 3′-deoxy Lewis^x pentasaccharide **1** to be used for a tool of carbohydrate–carbohydrate interaction study.

2. Results and discussion

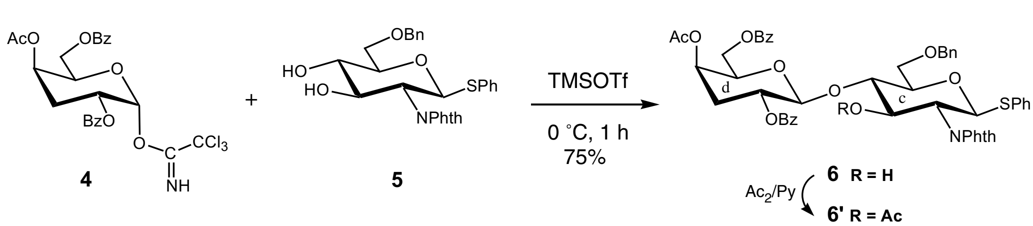
A key building block in the synthesis of pentasaccharide **1** was 4-*O*-acetyl-2,6-di-*O*-benzoyl-3-deoxy-β-D-xylo-hexopyranosyl trichloroacetimidate **4**, which can be readily prepared from the known phenyl 4-*O*-acetyl-2,6-di-*O*-benzoyl-3-deoxy-1-thio-β-D-xylo-hexopyranoside **2**,[12] by treatment with (i) $BF_3{\cdot}Et_2O$/HgO and (ii) Cl_3CCN/DBU, without further characterization of the intermediate hemiacetal **3**, in 67% yield (for two steps), as shown in Scheme 1. NMR spectra showed that the imidate was formed essentially in the α-form.

Condensation of trichloroacetimidate **4** with the previously described diol **5**,[13] according to Schmidt's method,[14] proceeded regioselectively, taking advantage of the 'stereo hindrance effect', to give the β1→4 linked disaccharide **6** in 75% yield (Scheme 2). Such a selective behaviour of phenyl 6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside **5** has previously been observed during its glycosylation with 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide.[15] Another example for this type of regioselective glycosylation was reported for phenyl 2,3,4 tri-*O*-acetyl-6-*O*-benzyl-1-thio-β-D-galactopyranoside.[16] The ^{1}H NMR spectrum of **6** showed the presence of the H-3c of the glucosamine residue at δ 4.59 (ddd, $J_{2,3} = 10.3$ Hz, $J_{3,4} = 8.2$ Hz, $J_{3,OH} = 1.0$ Hz), indicating that the position of the newly formed glycosidic linkage in the disaccharide **6** to be at OH-4 of the acceptor **5**. This regioselectivity was further confirmed from the ^{1}H NMR spectrum of **6′**—obtained from **6** by acetylation—which revealed a deshielded signal for H-3c at 5.77 ppm (t, $J_{2,3} = J_{3,4} = 9.4$ Hz), therefore confirming the position of the new glycosidic linkage in **6** as being OH-4 of the diol **5**. Its stereochemistry was determined to be the desired β-form on the basis of the H-1d, H-2d coupling constant ($J_{1d,2d} = 8.1$ Hz).

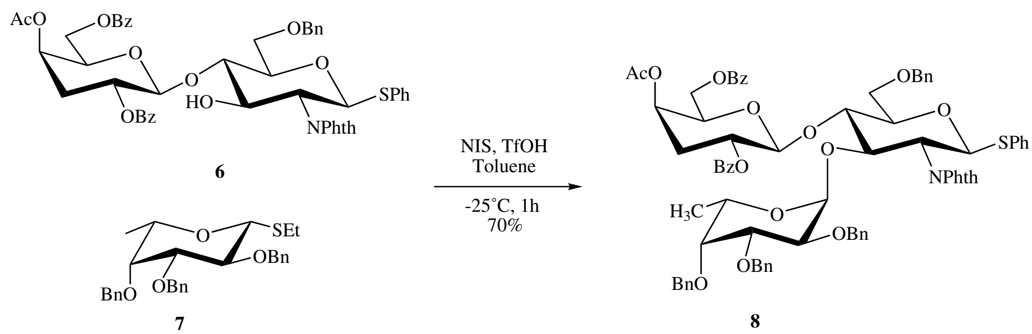
The fucosylation of **6** with ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside **7**[17] in the presence of *N*-iodosuccinimide (NIS)—trifluoromethanesulfonic acid (TfOH) in toluene for 1 h at −25 °C gave the expected trisaccharide **8** in 70% yield (Scheme 3). The stereochemistry of the newly introduced glycosidic linkage was determined to be α on the basis of the low value of the Fuc H-1, H-2 coupling constant ($J_{1e,2e} = 3.5$ Hz).



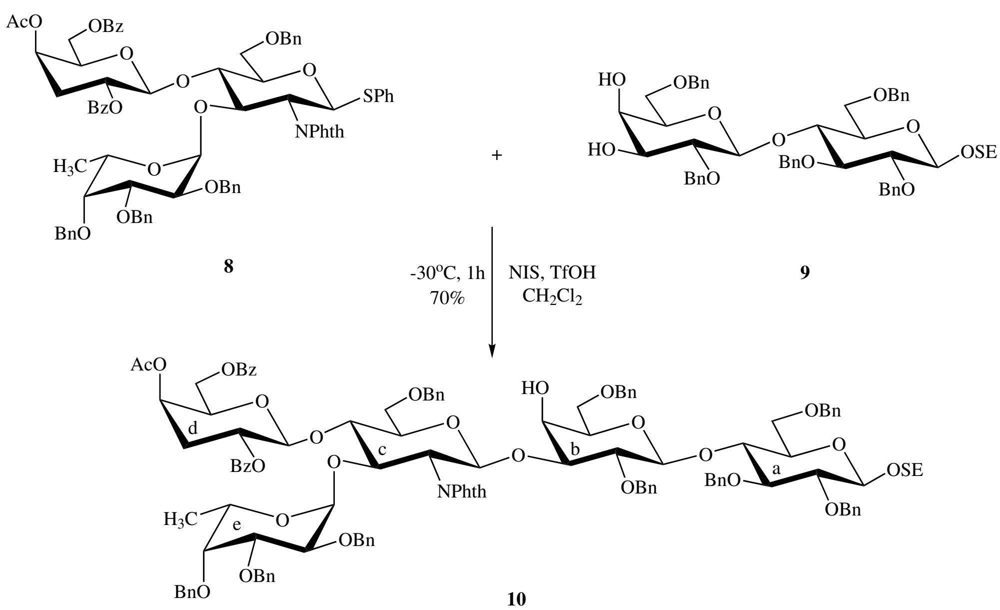
Scheme 1. Reagents and conditions: (i) $BF_3{\cdot}Et_2O$, HgO, H_2O, THF, 15 min, 70%; (ii) Cl_3CCN, DBU, DCM, 0 °C, 1 h, 95%.



Scheme 2.



Scheme 3.



Scheme 4.

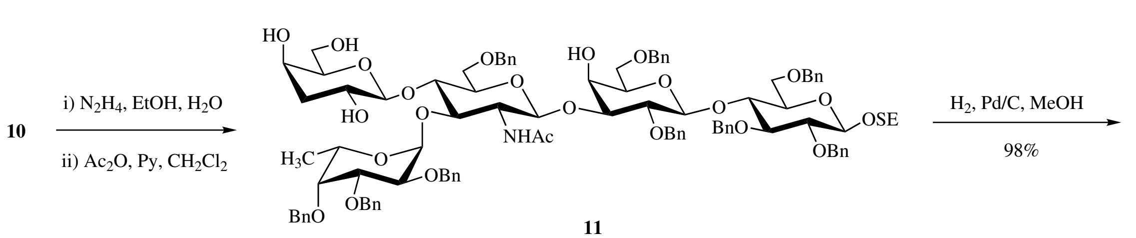
The glycosylation of diol **9**[18] with donor **8** was achieved under the conditions described above, providing the desired pentasaccharide **10** in 70% yield (Scheme 4). The stereochemistry of the newly introduced linkage was determined to be β on the basis of the GlcN H-1, H-2 coupling constant ($J_{1c,2c} = 8.5$ Hz). The regiochemistry of **10** was assigned by comparison with a very similar reaction.[19] In fact, the regioselectivity of 3-OH was usually observed during the glycosylation of the 3,4-diol of the galactose moiety, especially using a large glycosyl donor.[20]

Treatment of pentasaccharide **10** with hydrazine in boiling ethanol, followed by acetylation, then led to the derivative **11** in 80% overall yield from **10**. Catalytic hydrogenolysis of **11** and purification of the product on Sephadex G25-150 afforded the desired pentasaccharide **1** in almost quantitative yield (Scheme 5).

3. Experimental

3.1. General methods

Optical rotations were measured at 20 ± 2 °C with a Perkin–Elmer Model 241 digital polarimeter, using a 10 cm, 1 mL cell. Chemical ionisation (CI, ammonia)



Scheme 5.

and Fast Atom Bombardment (FAB) mass spectra were obtained with a JMS-700 spectrometer. Elemental analyses were performed by Service de microanalyze de l'Université Pierre et Marie Curie, 4 Place Jussieu, 75005 Paris, France. ^{1}H NMR spectra were recorded with a Bruker DRX 400 spectrometer at ambient temperature. Assignments were aided by COSY experiments. ^{13}C NMR spectra were recorded at 100.6 MHz with a Bruker DRX 400 for solutions in $CDCl_3$ or D_2O. Flash column chromatography was performed on silica gel 60 (230–400 mesh, Merck).

3.2. 4-*O*-Acetyl-2,6-di-*O*-benzoyl-3-deoxy-β-D-xylo-hexopyranosyl trichloroacetimidate 4

To a solution of **3** (5.16 g, 14.81 mmol) in 220 mL of dry dichloromethane were added at 0 °C, 17.08 mL of trichloroacetonitrile and 2.23 mL of DBU, dropwise. The mixture was stirred at 0 °C for 1 h. After concentration, the residue was purified by flash chromatography, eluting with toluene–ethyl acetate–triethylamine (600:100:0.7) to give compound **4** as a white foam in 95% yield: R_f 0.53 (toluene–ethyl acetate 4:1), $[\alpha]_D = +20$ (*c* 0.9, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (s, 1H, NH), 8.01–7.99 (m, 4H, arom), 7.58–7.54 (m, 2H, arom), 7.45–7.40 (m, 4H, arom), 6.65 (d, 1H, $J_{1,2} = 3.2$ Hz, H-1), 5.60–5.54 (m, 1H, H-2), 5.41 (br, 1H, H-4), 4.55–4.51 (m, 1H, H-5), 4.46–4.37 (m, 2H, H-6a, H-6b), 2.45–2.43 (m, 1H, H-3a), 2.42–2.41 (m, 1H, H-3e), 2.19 (s, 3H, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.16 (C=O, Ac), 166.03, 165.49 (2C=O, Bz), 160.69 (C=NH), 133.51–128.39 (aromatic C, CH), 93.06 (C-1), 69.57 (C-5), 67.34 (C-4), 66.52 (C-2), 62.36 (C-6), 28.36 (C-3), 20.96 (CH_3). HRMS Calcd for $C_{24}H_{22}Cl_3NO_8$ ($M+Na^+$): 580.0303. Found 580.0316.

3.3. Phenyl(4-*O*-acetyl-2,6-di-*O*-benzoyl-3-deoxy-β-D-xylo-hexopyranosyl)-(1→4)-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside 6

A solution of **5** (1.4 g, 2.84 mmol) and **4** (2.38 g, 4.26 mmol, 1.5 equiv) in 51 mL of dry CH_2Cl_2 was stirred with 5.5 g of ground molecular sieves 4 Å for 40 min at room temperature under an argon atmosphere. Trimethylsilyl triflate (773.2 μL, 4.26 mmol, 1.5 equiv) was added at 0 °C, and stirring continued for an additional hour. The mixture was filtered through Celite and the solids then washed with CH_2Cl_2. The filtrate was washed with a saturated $NaHCO_3$ solution, then with water, dried over $MgSO_4$ and concentrated. The residue was eluted from a column of silica gel with (toluene–ethyl acetate 9:1) to give **6** (75%): R_f 0.4 (toluene–ethyl acetate 4:1); $[\alpha]_D = +17.4$ (*c* 1.0, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–7.20 (m, 24H, arom), 5.63 (d, 1H, $J_{1,2} = 10.5$ Hz, H-1c), 5.36 (m, 1H, H-2d), 5.23 (m, 1H, H-4d), 4.82 (d, 1H, $J = 8.1$ Hz, H-1d), 4.66 (dd, 1H, $J_{5,6} = 3.3$ Hz, $J_{6,6'} = 11.6$ Hz, H-6d), 4.65 (d, 1H, $J = 1$ Hz, exch. D_2O, OH-3c), 4.59 (ddd, 1H, $J_{2,3} = 10.3$ Hz, $J_{3,4} = 8.2$ Hz, H-3c), 4.39 (dd, 1H, H-2c), 4.33, 4.27 (2d, 2H, $J = 12$ Hz, $PhCH_2$), 4.20 (dd, 1H, $J_{5,6} = 8.6$ Hz, H-6′d), 4.15 (ddd, 1H, $J_{4,5} = 1.1$ Hz, H-5d), 3.81 (dd, 1H, $J_{4,5} = 9.5$ Hz, H-4c), 3.73 (ddd, 1H, $J_{4,5} = 9.8$ Hz, $J_{5,6} = 4.2$ Hz, $J_{5,6'} = 1.3$ Hz, H-5c), 3.693 (dd, 1H, $J_{6,6'} = 11$ Hz, H-6c), 3.63 (dd, 1H, H-6′c), 2.57 (ddd, 1H, $J_{2,3} = 5.2$ Hz, $J_{3,3'} = 14.3$ Hz, $J_{3,4} = 3.1$ Hz, H-3d), 2.19 (s, 3H, CH_3), 1.93 (ddd, 1H, $J_{2,3'} = 11.9$ Hz, $J_{3',4} = 3.1$ Hz, H-3′d); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 169.96 (C=O, Ac), 167.96, 167.41 (2C=O, NPht), 166.19, 164.90 (C=O, Bz), 138.26, 132.14, 131.69, 131.54, 129.28, 128.98 (aromatic C), 133.97, 133.89, 133.45, 133.15, 132.29, 129.72, 129.70, 129.54, 128.93, 128.70, 128.48, 128.43, 128.36, 128.18, 128.12, 127.65, 127.41, 127.28, 125.19, 123.48, 123.19 (aromatic *C*H), 103.04 (C-1d), 83.28 (C-1c), 82.20 (C-4c), 77.96 (C-5c), 75.10 (C-5d), 72.98 (PhCH_2), 70.86 (C-3c), 68.26 (C-6c), 67.65 (C-2d), 67.08 (C-4d), 62.96 (C-6d), 54.95 (C-2c), 32.94 (C-3d), 20.83 (CH_3). HRMS (CI, NH_3) Calcd for $C_{49}H_{49}N_2O_{13}S$ ($M + NH_4^+$): 905.2955. Found 905.2969.

3.4. Phenyl(4-*O*-acetyl-2,6-di-*O*-benzoyl-3-deoxy-β-D-xylo-hexopyranosyl)-(1→4)-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside 8

A mixture of **6** (1 g, 1.12 mmol, 1 equiv) and **7** (1.34 g, 2.81 mmol, 2.5 equiv), 4 Å powdered molecular sieves (7 g) and dry toluene (36 mL) was stirred at room temperature for 30 min and then cooled to −25 °C under argon. NIS (518 mg, 2.3 equiv) and then TfOH (20.5 μL, 0.23 equiv) were added. The reaction mixture was neutralized (Et_3N) after 1 h, diluted with dichloromethane, filtered through Celite, washed with aqueous thiosulfate, water, brine, dried over $MgSO_4$ and concentrated. The residue was eluted from a column of silica gel with (toluene–ethyl acetate 9:1) to give **8** (62%): R_f 0.62 (cyclohexane–ethyl acetate 3:2); $[\alpha]_D = +3.3$ (*c* 1.0, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.07 (m, 39H, arom), 5.48 (d, 1H, $J_{1,2} = 10.6$ Hz, H-1c), 5.14 (ddd, 1H, $J_{1,2} = 8.4$ Hz, $J_{2,3} = 5.1$ Hz, $J_{2,3'} = 11.8$ Hz, H-2d), 5.11 (m, 1H, H-4d), 4.93 (d, 1H, H-1d), 4.91 (d, 1H, $J = 3.7$ Hz, H-1e), 4.90, 4.67 (2d, 2H, $J = 11.8$ Hz, $PhCH_2$), 4.85, 451 (2d, 2H, $J = 12.0$ Hz, $PhCH_2$), 4.84 (q, 1H, $J_{4,5} <$ 1 Hz, $J_{5,6} = 6.4$ Hz, H-5e), 4.78 (dd, 1H, $J_{2,3} = 10.0$ Hz, $J_{3,4} = 9.3$ Hz, H-3c), 4.69, 4.65 (2d, 2H, $J = 11.9$ Hz, $PhCH_2$), 4.54 (dd, 1H, H-2c), 4.40 (dd, 1H, $J_{5,6} = 3.9$ Hz, $J_{6,6'} = 11.0$ Hz, H-6d), 4.24 (dd, 1H, $J_{4,5} = 9.2$ Hz, H-4c), 4.19 (dd, 1H, $J_{5,6'} = 6.9$ Hz, H-6′d), 4.07 (dd, 1H, $J_{2,3} = 10.3$ Hz, $J_{3,4} = 2.5$ Hz, H-3e), 4.01 (dd, 1H, $J_{5,6} = 2.9$ Hz, $J_{6,6'} = 11.3$ Hz, H-6c), 3.88 (dd, 1H, H-2e), 3.82–3.78 (m, 2H, H-5d, H-6′c), 3.72 (dd, 1H, H-4e), 3.56 (dd, 1H, H-5c), 2.42 (ddd, 1H, $J_{3,3'} = 14.0$ Hz, $J_{3,4} = 3.0$ Hz, H-3d), 1.90 (s, 3H, CH_3), 1.66 (ddd, 1H, $J_{3',4} = 3.2$ Hz, H-3′d), 1.29 (d, 3H, H-6e); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 169.71 (C=O, Ac), 165.85, 164.84 (2C=O, Bz), 138.93, 138.63, 138.18, 137.98, 132.46, 129.47 (C-arom), 134.08, 133.39, 133.27, 132.23, 129.75, 129.51, 128.74, 128.70, 128.50, 128.48, 128.23, 128.18, 128.07, 127.86, 127.62, 127.41, 127.03, 126.78 (CH arom), 100.89 (C-1d), 97.80 (C-1e), 84.32 (C-1c), 79.70 (C-3e), 79.33 (C-4e), 77.53 (C-5c), 74.99 (C-4c), 74.34 (C-2e), 73.91 (C-3c), 73.67 (C-5d), 74.13, 73.54, 72.98, 72.43 (4Ph*C*H_2), 67.95 (C-2d), 67.87 (C-6c), 66.98 (C-4d), 66.45 (C5-e), 61.45 (C-6d), 55.51 (C-2c), 32.98 (C-3d), 20.84 (CH_3), 16.82 (C-6e). HRMS (FAB) Calcd for $C_{76}H_{73}NO_{17}SNa$ (M+Na^+): 1326.4497. Found 1326.4515.

3.5. 2-(Trimethylsilyl)ethyl(4-*O*-acetyl-2,6-di-*O*-benzoyl-3-deoxy-β-D-xylo-hexopyranosyl)-(1→4)-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-phtalimido-β-D-glucopyranoside-(1→3)-(2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside 10

A mixture of **8** (153 mg, 0.117 mmol), **9** (104 mg, 0.117 mmol), 4 Å powdered molecular sieves (0.7 g) and CH_2Cl_2 (7.3 mL) was stirred at room temperature for 30 min. NIS (2 equiv, 52.7 mg, 0.234 mmol) was added at room temperature. The reaction mixture was cooled at −30 °C. Triflic acid (0.035 mmol, 4 μL) was added. The reaction mixture was stirred at −30 °C for 1 h, neutralized (Et_3N), filtered through Celite, washed with aqueous thiosulfate, water, brine, dried over $MgSO_4$ and concentrated. The residue was flash chromatographed (toluene–ethyl acetate 6:1) to give **10** (70%) as an amorphous powder: R_f 0.33 (toluene–ethyl acetate 6:1); $[\alpha]_D = +6.2$ (*c* 1.0, chloroform); ^1H NMR (400 MHz, $CDCl_3$): δ 8.05–7.18 (m, 59H, arom), 5.30 (d, 1H, $J_{1,2} = 8.4$ Hz, H-1c); 5.14 (m, 2H, H-4d, H-2d); 4.95, 4.70 (2d, 2H, $J = 10.5$ Hz, Ph*C*H_2), 4.91 (d, 1H, $J_{1,2} = 8.2$ Hz, H-1d), 4.87 (d, 1H, $J_{1,2} = 3.7$ Hz, H-1e), 4.80 (m, 1H, H-5e), 4.77 (dd, 1H, $J_{2,3} = 10.4$ Hz, $J_{3,4} = 8.7$ Hz, H-3c), 4.28 (d, 1H, $J_{1,2} = 7.6$ Hz, H-1a), 4.26 (d, 1H, $J_{1,2} = 8.2$ Hz, H-1b), 4.50 (dd, 1H, H-2c), 4.49 (d, 1H, $J = 12.1$ Hz, PhC*H_2*), 4.79, 4.45 (2d, 2H, $J = 12.0$ Hz, $PhCH_2$), 4.46, 4.23 (2d, 2H, $J = 11.9$ Hz, $PhCH_2$), 4.20 (dd, 1H, $J_{4,5} = 9.2$ Hz, H-4c), 4.29–4.14 (m, 4H, PhC*H_2*), 4.04 (m, 1H, H-5c), 4.05–3.92 (m, 3H), 3.73–3.67 (m, 3H), 3.59–3.44 (m, 4H), 3.42–3.30 (m, 6H), 3.00 (m, 1H), 2.44 (ddd, 1H, $J_{2,3} = 5.0$ Hz, $J_{3,3'} = 14.4$ Hz, $J_{3,4} = 3.1$ Hz, H-3d), 1.91 (s, 3H, CH_3), 1.67 (ddd, 1H, $J_{2,3'} = 11.6$ Hz, $J_{3',4} = 3.2$ Hz, H-3′d), 1.29 (d, 3H, $J_{5,6} = 6.4$ Hz, H-6e), 1.06–0.95 (m, 2H, CH_2Si), 0.03 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 169.73 (C=O, Ac), 165.88, 164.83 (2C=O, Bz), 139.00, 138.91, 138.74, 138.62, 138.47, 138.27, 138.19, 137.69, 131.13, 129.52 (aromatic C), 133.73, 133.39, 133.33, 129.77, 129.50, 128.71, 128.58, 128.54, 128.34, 128.24, 128.21, 128.18, 128.17, 128.07, 128.05, 128.00, 127.94, 127.84, 127.73, 127.62, 127.53, 127.43, 127.42, 127.35, 127.14, 127.04, 127.00, 126.77, 126.52, 126.21 (aromatic CH), 102.97 (C-1b), 101.93 (C-1a), 100.93 (C-1d), 98.89 (C-1c), 97.69 (C-1e), 83.14, 82.78, 81.82, 79.58, 77.98, 77.54, 75.88, 75.17, 74.87, 74.58, 73.78, 72.75, 72.53, 68.01, 67.50, 66.97, 66.45, (CH), 75.33, 74.85, 74.14, 74.01, 73.75, 73.27, 72.86, 72.42, 68.40 (Ph*C*H_2), 68.10 (OCH_2Si), 67.96, 67.77, 67.18 (C-6a, C-6b, C-6c), 61.52 (C-6d), 56.25 (C-2c), 33 (C-3d), 20.84 (OAc), 18.37 (CH_2Si), 16.84 (C-6e), −1.47 ($Si(CH_3)_3$). HRMS (FAB) Calcd for $C_{122}H_{131}NO_{28}SiNa$ (M+Na^+) 2109.8525. Found 2108.8557.

3.6. 2-(Trimethylsilyl)ethyl(3-deoxy-β-D-xylo-hexopyranosyl)-(1→4)-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→3)]-6-*O*-benzyl-2-deoxy-2-acetamido-β-D-glucopyranoside-(1→3)-(2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside 11

To a solution of compound **10** (480 mg, 0.23 mmol) in 68 mL of ethanol, were added 4 mL of hydrazine monohydrate and 4 mL of water. The mixture was refluxed at 80 °C for 14 h. After concentration, the residue was coevaporated with ethyl acetate and dried over P_2O_5. The residue was then dissolved in 20 mL of methanol–dichloromethane (1:1), to which 2 mL of acetic anhydride was introduced. The mixture was stirred at room temperature overnight. After concentration, the residue was dried in vacuo, and used directly for the next step.

3.7. 2-(Trimethylsilyl)ethyl(3-deoxy-β-D-xylo-hexopyranosyl)-(1→4)-[(α-L-fucopyranosyl-(1→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside-(1→3)-(β-D-galactopyranosyl)-(1→4)-2,-β-D-glucopyranoside 1

A solution of **11** (104 mg) in methanol (10 mL) was reacted over Pd/C (10%, 100 mg) under H_2 (160 kPa) for 24 h at 25 °C, filtered and evaporated. The residue was purified on a Sephadex column (G25-150) using water as eluant. Compound **1** was obtained as a white amorphous solid (99%): R_f 0.25 (isopropanol–ethyl acetate–water 3:3:1); $[\alpha]_D = -106$ (*c* 0.4, $CHCl_3$–CH_3OH 1/1); ^1H NMR (400 MHz, D_2O): δ 5.13 (d, 1H, $J = 3.97$ Hz, H-1e), 4.88 (m, 1H, H-5e), 4.87 (m, 1H), 4.72 (d, 1H, $J = 8.2$ Hz, H-1), 4.50 (d, 1H, $J = 8.1$ Hz, H-1), 4.47 (d, 1H, $J = 8.5$ Hz, H-1), 4.44 (d, 1H, $J = 8.1$ Hz, H-1), 4.16 (d, 1H, $J = 3.3$ Hz), 4.07–3.95 (m, 6H), 3.92–3.85 (m, 3H), 3.81–3.62 (m, 16H), 3.61–3.55 (m, 4H), 3.28 (m, 1H, H-2), 2.18 (ddd, 1H, $J_{2,3} = 5.0$ Hz, $J_{3,3'} = 14.1$ Hz, $J_{3,4} = 3.1$ Hz, H-3d), 2.03 (s, 3H, NHAc), 1.72 (ddd, 1H, $J_{2,3'} = 11.7$ Hz, $J_{3',4} = 3.0$ Hz, H-3′d), 1.17 (d, 3H, $J = 6.6$ Hz, H-6e), 1.02 (2dt, 2H, $J_{gem} = 12.9$ Hz, $J_{vic} = 5.4$ Hz, CH_2Si), 0.028 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (100.6 MHz, D_2O): δ 175.08 (C=O, NHAc), 103.91, 103.3, 102.92, 101.73, 99.02 (C-1a, C-1b, C-1c, C-1d, C-1e), 82.44, 78.64, 78.43, 75.52, 75.23, 75.11, 74.89, 73.18, 73.07, 72.36, 70.33, 69.57, 68.67, 68.06, 67.00, 66.10, 65.83 (CH), 68.81 (OCH_2Si), 62.08, 61.32, 60.41, 60.01 (C-6a, C-6b, C-6c, C-6d), 56.35 (C-2c), 36.94 (C-3d), 22.61 (CH_3), 17.92 (CH_2Si), 15.68 (C-6e), −2.17 ($Si(CH_3)_3$). HRMS (FAB) Calcd for $C_{37}H_{67}NO_{24}SiNa$ (M+Na^+) 960.3720 found. Anal. Calcd for $C_{37}H_{67}NO_{24}Si$ (938.01): C, 47.38; H, 7.20; N, 1.49. Found C, 47.43; H, 7.22; N, 1.51.

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