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Total synthesis of 4d-deoxy Lewis^x pentasaccharide

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Abstract

Total synthesis of 4d-deoxy Lewis^x pentasaccharide is described. *O*-(2,3,6-Tri-*O*-benzoyl-4-deoxy-α-D-xylo-hexopyranosyl)trichloroacetimidate was condensed with a diol of glucosamine to give regioselectively a β1 → 4 linked disaccharide, which was further fucosylated to a protected deoxy Lewis^x trisaccharide. A highly stereo- and regioselective glycosylation of this trisaccharide onto a lactoside diol was performed to provide a pentasaccharide in excellent yield. After deprotection, this pentasaccharide afforded the target oligosaccharide. ***To cite this article: Y. Luo et al., C. R. Chimie 11 (2008).***

Résumé

La synthèse totale du 4d-déoxy Lewis^x pentasaccharide est décrite. Le *O*-(2,3,6-tri-*O*-benzoyl-4-déoxy-α-D-xylo-hexopyranosyl)trichloroacétimidate a été condensé avec un diol de la glucosamine pour donner régiosélectivement un disaccharide β1 → 4, qui a été ensuite fucosylé, conduisant à un Lewis^x trisaccharide désoxygéné protégé. Une glycosylation hautement stéréo- et régiosélective de ce trisaccharide sur un diol du lactoside a été effectuée pour conduire à un pentasaccharide, avec un excellent rendement. Après déprotection, ce pentasaccharide a fourni l'oligosaccharide cible. ***Pour citer cet article : Y. Luo et al., C. R. Chimie 11 (2008).***

Keywords: Glycosylation; Lewis^x; Pentasaccharide; Synthesis

Mots-clés : Glycosylation ; Lewis^x ; Pentasaccharide ; Synthèse

1. Introduction

Homotypic interactions between biopolymers such as nucleic acid–nucleic acid and protein–protein are the basis for bio-recognition and cell functioning, as they mediate such processes as transcription, signal

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transduction and cell membrane formation. It is well known that cell surface carbohydrates play a role in cell–cell adhesion and communication [1]. Several models for cell interactions based on carbohydrates have been proposed. In most of them, the carbohydrate binds to selectins, galectins, and other carbohydrate-binding proteins [2]. 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 [3]. A typical example is the report of Hakomori, who proposed that carbohydrate–carbohydrate interaction is responsible for the initial step of cell adhesion [4]. Embryogenesis, metastasis, and other proliferation processes are, according to Hakomori, mediated by carbohydrate–carbohydrate interactions [4]. One of the structures involved in this novel mechanism is the Lewis^x (Le^x) trisaccharide determinant (Galβ1 → 4[Fucα1 → 3]GlcNAcβ1). The Lewis^x antigen – previously defined as the Stage-Specific Embryonic Antigen 1 (SSEA-1) – is found in a wide variety of systems such as human cancers, pre-implantation mouse embryos, embryonic carcinoma cells, and human erythrocytes [5].

The interaction between Le^x and Le^x was found to be homotypic and mediated by the presence of divalent cations such as Ca^{2+} [6,7]. Recently, the Le^x–Le^x interaction has increasingly been studied, using a variety of techniques including nuclear magnetic resonance (NMR) spectroscopy [8], mass spectrometry (MS) [9], vesicle adhesion [10], atomic force microscopy (AFM) [11], and surface plasmon resonance (SPR) spectroscopy [12]. Rat basophilic leukaemia cells pre-incubated with purified Le^x containing glycosphingolipids have also been used as a model [13]. Another model system, ''Glycosylated Foldamer'', has been demonstrated very recently to study the carbohydrate–carbohydrate interaction in terms of individual carbohydrate motifs [14]. To demonstrate the homotypic characterization of this kind of interactions, we recently performed an experiment using the vesicle technique [15]. In this study, the Le^x was replaced 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 the Le^x–Le^a pair showed clearly that the permutation of the fucose and galactose residues in the trisaccharide headgroup effectively prevents specific adhesion [15].

To date, however, the molecular detail of these weak, Ca^{2+}-dependent interactions remains unclear, necessitating the new models to probe the nature of this phenomenon in terms of key role of the different hydroxyl groups on Le^x trisaccharide involved in the Le^x–Le^x interaction. Our objective has been to prepare a series of Le^x pentasaccharides in which one of the eight hydroxyl groups of Le^x trisaccharide is replaced by an hydrogen atom (Fig. 1) and to test the induced adhesion by interaction of these derivatives, in order to gain an insight into the functions played by the hydroxyl groups of the Le^x trisaccharide.

Taking the cost of different sugar residues of Lewis^x pentasaccharide into account, the synthetic work was started from the chemical modification of the galactose residue. After successful synthesis of 3d-deoxy Lewis^x pentasaccharide [16], we describe here the first total synthesis of 4d-deoxy Lewis^x pentasaccharide **1** (Fig. 2), which is a useful tool for carbohydrate–carbohydrate interaction study.

Classic strategy for oligosaccharide assembly is involved in the manipulation of the protecting groups between each glycosylation step. Such a manipulation is a consequence of increased linearity and inefficiency of oligosaccharide assembly. In order to increase assembly efficiency of complex oligosaccharides by avoiding various unnecessary manipulations of each glycosylation step, an intelligent strategy is to use highly stereo- and regioselective glycosylation of partially or unprotected acceptors [17] based on differences in reactivity of the hydroxyl groups followed by analysis of the structures using modern 2D NMR techniques.

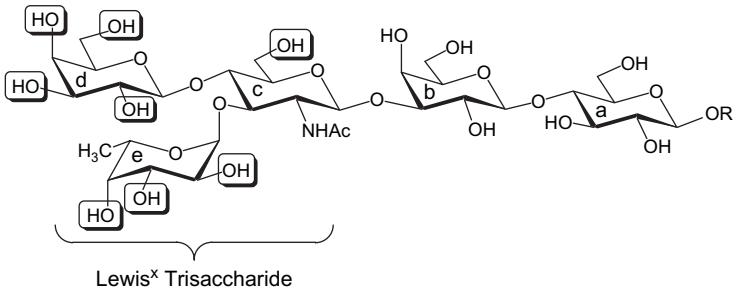


Fig. 1. Lewis^x pentasaccharide.

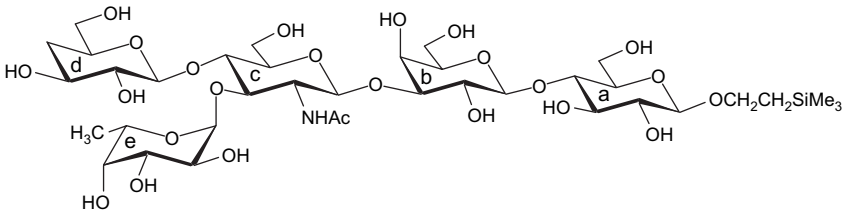


Fig. 2. 4d-Deoxy Lewis^x pentasaccharide **1**.

Another useful strategy is to employ two-directional glycosylation, which exploits both the differences in the reactivities of an anomeric leaving group and the subtle control of nucleophilicities of sugar hydroxyl groups [18]. The major purpose of these strategies is to overcome the traditional, tedious multi-step protection/deprotection schemes and provide an efficient way for the complex oligosaccharide synthesis. These strategies have been successfully demonstrated in our first synthesis of 3d-deoxy Lewis^x pentasaccharide [16] and were proved to be effective in our following syntheses of disaccharide and pentasaccharide.

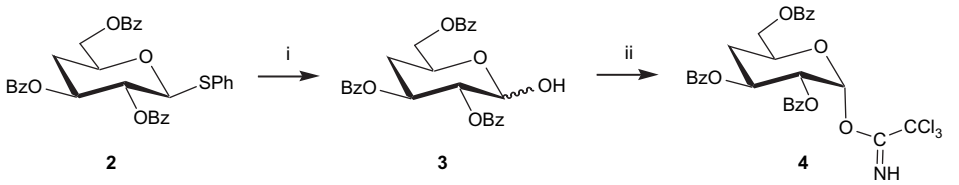
2. Results and discussion

O-(2,3,6-Tri-*O*-benzoyl-4-deoxy-α-D-xylo-hexopyranosyl)trichloroacetimidate (**4**) was chosen as galactosyl donor to construct a lactosamine building block for the synthesis of the pentasaccharide **1**. This imidate *per se* was prepared from phenyl 2,3,6-tri-*O*-benzoyl-4-deoxy-1-thio-β-D-xylo-hexopyranoside **2** [19]. Thus treatment of **2** with $BF_3 \cdot Et_2O$ in the presence of HgO gave the hemiacetal **3** as a mixture of α/β isomers in 88% yield, which were not separated and further characterized. Compound **3** was then treated with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) as a base to provide the trichloroacetimidate **4** in 77% yield, as outlined in Scheme 1.

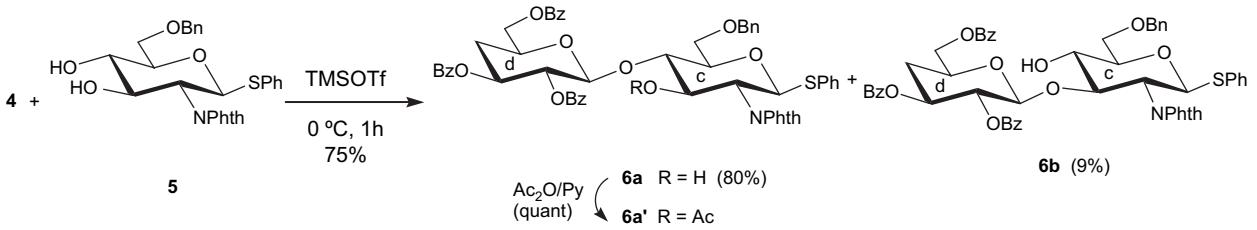
The NMR spectra showed that only the α-trichloroacetimidate was formed on the basis of the H-1, H-2 coupling constant ($J_{1,2} = 3.7$ Hz). This is because an axial trichloroacetimidate is the thermodynamically more stable isomer [20]. However, a thermodynamically unstable equatorial imidate could also be occasionally isolated in a similar reaction [21].

As illustrated in Scheme 2, condensation of the trichloroacetimidate **4** with the previously reported diol **5** [22], according to the Schmidt glycosylation procedure [23], using TMSOTf as a promoter without affecting the SPh group of the acceptor **5**, proceeded regioselectively, taking advantage of the ''stereo hindrance effect'', to give the β1 → 4 linked disaccharide **6a** in 80% yield; the by-product β1 → 3 linked disaccharide **6b** was isolated as a minor product (9%). 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 [24] or with *O*-(3-*O*-acetyl-2,6-di-*O*-benzoyl-3-deoxy-α-D-xylo-hexopyranosyl)trichloroacetimidate [16]. 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 [25].

The ^{1}H NMR spectrum of **6a** showed the presence of H-3c of the glucosamine residue at δ 4.54 (ddd, $J_{2c,3c} = 10.3$ Hz, $J_{3c,4c} = 8.3$ Hz, $J_{3c,OH} = 1.0$ Hz), indicating the position of the newly formed glycosidic linkage in the disaccharide **6a** to be at OH-4 of the acceptor **5**. This regioselectivity was further confirmed from the ^{1}H NMR spectrum of **6a′** − obtained from **6a** by acetylation − which revealed a deshielded signal for H-3c at 5.78 ppm (dd, $J_{2c,3c} = 10.1$ Hz, $J_{3c,4c} = 9.2$ Hz), confirming therefore the position of the new glycosidic linkage in **6a** as being OH-4 of the diol **5**. Its stereochemistry was determined to be desired β on the basis of the H-1d, H-2d coupling constant ($J_{1d,2d} = 7.9$ Hz).



Scheme 1. Reagents and conditions: (*i*) $BF_3 \cdot Et_2O$, HgO, H_2O, THF, RT, 1 h, 88%; (*ii*) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 1 h, 85%.



Scheme 2.

For construction of trisaccharide, the disaccharide **6a** was fucosylated by the known ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside **7** [26] in toluene using *N*-iodosuccinimide (NIS)−trifluoromethanesulfonic acid (TfOH) as catalysts. The chemical yield of this glycosylation was found to be temperature dependent; the best yield was obtained when the reaction was run at −20 °C for 1 h, giving the expected trisaccharide **8** in 57% 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).

The next glycosylation of the diol **9** [27] with the donor **8** was performed under the similar conditions described above, using dichloromethane as solvent instead of toluene. Again the outcome of this reaction was proved to be temperature dependent. The glycosylation was started at −30 °C by addition of the promoters into the reaction mixture, the temperature was then slowly raised to room temperature, the desired pentasaccharide **10** was isolated in excellent 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 ($J_{1c,2c} = 8.4$ Hz). The regiochemistry of **10** was assigned from the ^{1}H NMR spectrum of **10′** − obtained from **10** by acetylation − which revealed a deshielded signal for H-4b at 5.42 ppm (d, $J_{3b,4b} = 3.5$ Hz, $J_{4b,5b}$ being close to zero), confirming therefore the position of the new glycosidic linkage in **10** as being OH-3b of the diol **9**. In fact, the regioselectivity of 3-OH was usually observed for glycosylation of the 3,4-diol of the galactose moiety, especially using a large glycosyl donor [28,29].

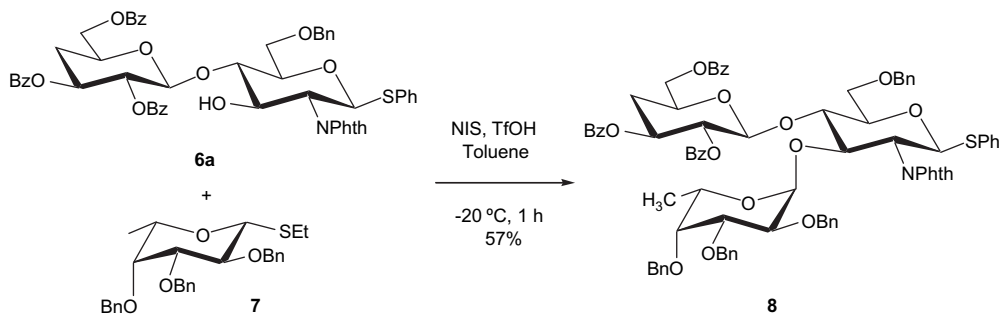
The final route to target oligosaccharide **1** is outlined in Scheme 5. Treatment of pentasaccharide **10** with hydrazine in boiling ethanol, followed by a selective *N*-acetylation, afforded the derivative **11** in 89% overall yield from **10**. Catalytic hydrogenolysis of **11** in methanol for 13 h, followed by purification on Sephadex G25-150, provided the desired pentasaccharide **1** as a white amorphous solid in almost quantitative yield.

The structure and purity of the synthesized compounds were established by two-dimensional ^{1}H−^{1}H homonuclear correlation, ^{1}H−^{13}C heteronuclear correlation experiments and HR-FAB mass spectroscopy.

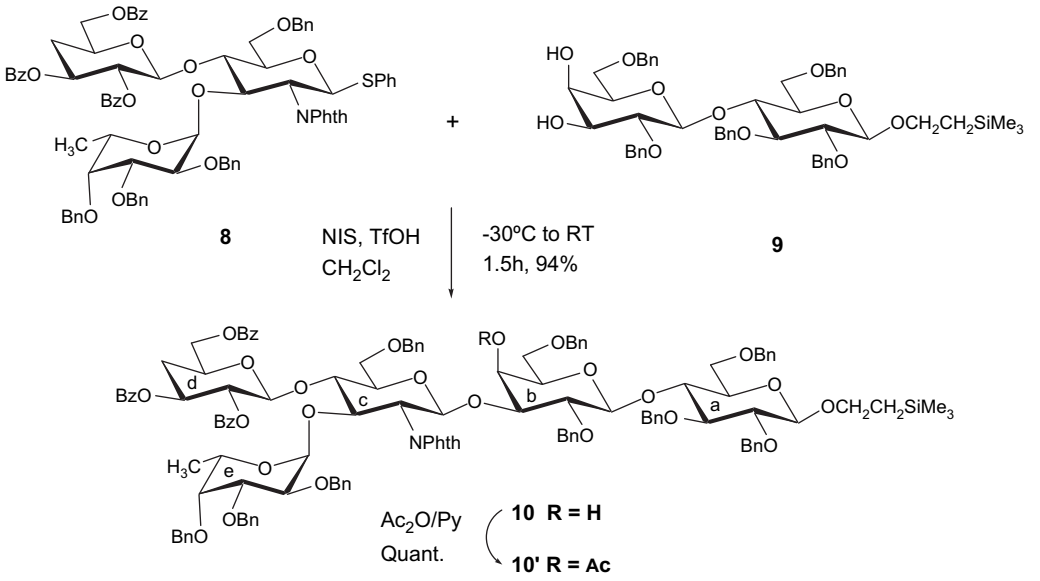
3. Experimental section

3.1. General methods

Optical rotations were measured at 20 ± 2 °C with a PerkinElmer Model 241 digital polarimeter, using a 10-cm, 1-mL cell. Fast Atom Bombardment (FAB) mass spectra were obtained with a JMS-700 spectrometer. ^{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



Scheme 3.



Scheme 4.

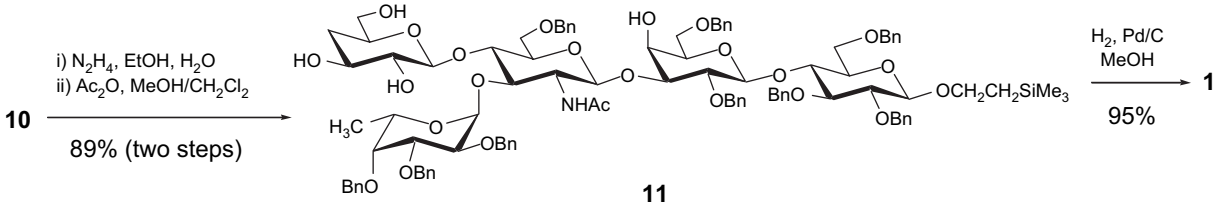
DRX 400 for solutions in $CDCl_3$ or D_2O. Reactions were monitored by thin-layer chromatography (TLC) on a precoated aluminium plate of silica gel 60 F_{254} (layer thickness 0.2 mm, E. Merck, Darmstadt, Germany) and detection by charring with sulfuric acid. Flash column chromatography was performed on silica gel 60 (230–400 mesh, E. Merck).

3.2. O-(2,3,6-Tri-O-benzoyl-4-deoxy-α-D-xylo-hexopyranosyl)trichloroacetimidate (4)

Trichloroacetonitrile (4.76 mL, 46.5 mmol) was added to a solution of **3** (1.67 g, 3.5 mmol) in 62 mL of dry dichloromethane at 0 °C, then DBU (0.62 mL, 4.0 mmol) was added dropwise. The mixture was stirred at 0 °C for 1 h. After concentration, the residue was purified by flash column chromatography (toluene–ethyl acetate–triethylamine 150:10:0.1) to afford **4** (1.83 g, 85%) as a white foam; $R_f = 0.50$ (toluene–ethyl acetate 9:1); $[\alpha]_D$ +100 (*c* 0.45, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H, NH), 8.10–7.30 (m, 15H, aromatic), 6.80 (d, 1H, $J_{1,2} = 3.7$ Hz, H-1), 5.96–5.88 (m, 1H, H-3), 5.64 (dd, 1H, $J_{1,2} = 3.7$ Hz, $J_{2,3} = 10.1$ Hz, H-2), 4.69–4.65 (m, 1H, H-5), 4.56–4.48 (m, 2H, H-6, H-6′), 2.65 (ddd, 1H, $J_{3,4} = 4.9$ Hz, $J_{4,5} = 2.5$ Hz, $J_{gem} = 12.7$ Hz, H-4), 2.08 (q, 1H, $J = 12.7$ Hz, H-4′); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 166.12, 165.76, 165.62 (3C=O, Bz), 160.68 (C=NH), 133.65–128.36 (aromatic CH), 94.28 (C-1), 70.90 (C-2), 68.47 (C-3), 68.27 (C-5), 65.50 (C-6), 32.56 (C-4); FAB-HRMS (*m/z*) Calcd for $C_{29}H_{24}Cl_3NO_8Na$ ($M + Na^+$): 644.0442. Found: 644.0428.

3.3. Phenyl (2,3,6-tri-O-benzoyl-4-deoxy-β-D-xylo-hexopyranosyl)-(1 → 4)-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (6a) and phenyl (2,3,6-tri-O-benzoyl-4-deoxy-β-D-xylo-hexopyranosyl)-(1 → 3)-6-O-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (6b)

A solution of **5** (0.79 g, 1.6 mmol, 1.0 equiv) and **4** (1.48 g, 2.4 mmol, 1.5 equiv) in 29 mL of dry dichloromethane was stirred with 4-Å powdered molecular



Scheme 5.

sieves (2 g) for 40 min at room temperature under an argon atmosphere. Trimethylsilyl triflate (87.6 μL, 0.48 mmol, 0.3 equiv) was added dropwise at 0 °C. The mixture was stirred for 40 min and then filtered through Celite. The filtrate was washed with a saturated aqueous $NaHCO_3$ and then with water, dried over $MgSO_4$ and concentrated. The residue was submitted to flash column chromatography and eluted with toluene–ethyl acetate (9:1). The earlier fractions contained the compound **6a**; on concentration, these fractions gave a white foam (1.21 g, 80%); $R_f = 0.50$ (toluene–ethyl acetate 4:1); $[\alpha]_D$ +47 (*c* 1, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–7.20 (m, 29H, aromatic), 5.60 (d, 1H, $J_{1,2} = 10.3$ Hz, H-1c), 5.50 (dd, 1H, $J_{1,2} = 7.8$ Hz, $J_{2,3} = 9.8$ Hz, H-2d), 5.43–5.39 (m, 1H, H-3d), 4.81 (d, 1H, $J_{1,2} = 7.8$ Hz, H-1d), 4.66 (dd, 1H, $J_{gem} = 11.8$ Hz, PhCH), 4.60 (d, 1H, $J = 0.9$ Hz, exch. D_2O, OH-3c), 4.54 (ddd, 1H, $J_{2,3} = 10.3$ Hz, $J_{3,4} = 8.3$ Hz, $J_{3,OH} = 0.9$ Hz, H-3c), 4.35 (t, 1H, $J_{1,2} = 10.3$ Hz, $J_{2,3} = 10.3$ Hz, H-2c), 4.23–4.08 (m, 4H, H-5d, H-6d, H-6d′, PhCH), 3.82–3.80 (m, 1H, H-4c), 3.71–3.67 (m, 1H, H-5c), 3.56–3.48 (m, 2H, H-6c, H-6c′), 2.47 (ddd, 1H, $J_{3,4} = 5.1$ Hz, $J_{4,5} = 1.7$ Hz, $J_{gem} = 11.7$ Hz, H-4d), 1.85 (q, 1H, $J = 11.7$ Hz, H-4d′); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 168.06, 167.44, 166.23, 165.71, 165.11 (5C=O, NPhth, Bz), 138.25, 134.48, 132.19, 131.81, 131.66, 129.06, 129.02 (aromatic C), 134.48, 133.99, 133.93, 133.50, 133.37, 133.19, 132.40, 129.84, 129.83, 129.69, 128.73, 128.52, 128.42, 128.27, 127.70, 127.51, 127.36, 123.56, 123.58 (aromatic CH), 101.76 (C-1d), 83.29 (C-1c), 82.41 (C-4c), 77.80 (C-5c), 72.88 (C-6c), 72.28 (C-2d), 70.97 (C-3d), 70.89 (C-3c), 70.53 (C-5d), 68.18 (C-6d), 65.41 ($PhCH_2$), 55.02 (C-2c), 32.31 (C-4d); FAB-HRMS (*m/z*) Calcd for $C_{54}H_{51}N_2O_{13}S$ ($M + NH_4^+$): 967.3112. Found: 967.3116.

The later fractions contained **6b** as a syrup (142 mg, 9.4%); $R_f = 0.43$ (toluene–ethyl acetate 4:1); $[\alpha]_D$ +102 (*c* 1, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19–7.13 (m, 29H, aromatic), 5.43 (d, 1H, $J_{1,2} =$ 10.4 Hz, H-1c), 5.38 (dd, 1H, $J_{1,2} = 7.8$ Hz, $J_{2,3} =$ 9.8 Hz, H-2d), 5.34–5.28 (m, 1H, H-3d), 4.72 (d, 1H, $J_{1,2} = 7.8$ Hz, H-1d), 4.68–4.58 (m, 5H, H-3c, H-6d, OH-4c, $PhCH_2$), 4.41 (t, 1H, $J_{1,2} = 10.4$ Hz, $J_{2,3} =$ 10.4 Hz, H-2c), 4.33 (dd, 1H, $J_{gem} = 12.0$ Hz, $J_{5,6} =$ 7.6 Hz, H-6d′), 4.20–4.14 (m, 1H, H-5d), 3.97 (d, 1H, $J = 10.4$ Hz, H-5c), 3.80–3.70 (m, 3H, H-4c, H-6c, H-6c′), 2.41 (ddd, 1H, $J_{3,4} = 5.2$ Hz, $J_{4,5} = 1.8$ Hz, $J_{gem} = 12.8$ Hz, H-4d), 1.84 (q, 1H, $J = 12.8$ Hz, H-4d′); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 168.53, 166.70, 166.13, 165.63, 164.85 (5C=O, NPhth, Bz), 138.48, 132.68, 130.79, 130.71, 129.21, 128.85, 128.76 (aromatic C), 133.93, 133.56, 133.33, 133.25, 132.62, 131.71, 130.03, 129.47, 128.72, 128.30, 128.24, 128.15, 127.49, 127.46, 127.36, 123.40, 122.81 (aromatic CH), 101.28 (C-1d), 83.90 (C-1c), 83.64 (C-3c), 79.85 (C-4c), 73.37 ($PhCH_2$), 72.58 (C-2d), 71.04 (C-3d), 70.41 (C-5d), 69.87 (C-5c), 69.78 (C-6c), 65.33 (C-6d), 53.78 (C-2c), 32.25 (C-4d); FAB-HRMS (*m/z*) Calcd for $C_{54}H_{47}NO_{13}SNa$ ($M + Na^+$): 972.2666. Found: 972.2687.

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

A solution of **6a** (100 mg) in 1 mL of pyridine and 0.5 mL of acetic anhydride was stirred at room temperature for 4 h and then concentrated, co-evaporated with toluene and dried. Compound **6a′** was obtained in quantitative yield (104 mg); $R_f = 0.55$ (toluene–ethyl acetate 4:1); $[\alpha]_D$ +30 (*c* 0.7, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13–7.21 (m, 29H, aromatic), 5.78 (dd, 1H, $J_{3,4} = 9.2$ Hz, $J_{2,3} = 10.1$ Hz, H-3c), 5.67 (d, 1H, $J_{1,2} = 10.6$ Hz, H-1c), 5.39–5.35 (m, 1H, H-2d), 5.32–5.26 (m, 1H, H-3d), 4.78 (d, 1H, $J_{1,2} = 7.9$ Hz, H-1d), 4.71 (d, 1H, $J_{gem} = 12.1$ Hz, PhCH), 4.54–4.43 (m, 2H, H-6d, PhCH), 4.40–4.31 (m, 2H, H-2c, H-6d′), 4.11 (t, 1H, $J_{3,4} = J_{4,5} = 9.2$ Hz, H-4c), 3.90–3.84 (m, 1H, H-5d), 3.76 (dd, 1H, $J_{5,6} = 3.3$ Hz, $J_{gem} = 11.2$ Hz, H-6c), 3.64–3.57 (m, 2H, H-5c, H-6c′), 2.41 (ddd, 1H, $J_{3,4} = 7.7$ Hz, $J_{4,5} = 1.9$ Hz, $J_{gem} = 12.6$ Hz, H-4d), 1.90–1.80 (m, 4H, H-4d′, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.08 (C=O, Ac), 167.73, 167.15, 166.19, 165.81, 164.88 (5C=O, Bz, NPhth), 138.05, 131.69, 131.54, 131.23, 129.49, 129.27, 129.25 (aromatic C), 134.29, 134.07, 133.41, 133.23, 132.93, 129.69, 128.82, 128.65, 128.56, 128.42, 128.38, 128.04, 127.99, 127.83, 123.68, 123.50 (aromatic CH), 100.64 (C-1d), 83.05 (C-1c), 78.70 (C-5c), 75.32 (C-4c), 73.45 (PhCH), 72.49 (C-2d), 71.73 (C-3d), 71.65 (C-3c), 69.55 (C-5d), 67.51 (C-6c), 65.52 (C-6d), 53.98 (C-2c), 32.75 (C-4d), 20.46 (CH_3, OAc); FAB-HRMS (*m/z*) Calcd for $C_{56}H_{49}NO_{14}SNa$ ($M + Na^+$): 1014.2771. Found: 1014.2797.

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

A mixture of **6a** (1.19 g, 1.25 mmol, 1 equiv), **7** (1.52 g, 3.18 mmol, 2.5 equiv) and 4 Å powdered

molecular sieves (2 g) in dry toluene (40.7 mL) was stirred at room temperature under argon for 40 min, then cooled to −20 °C. NIS (582.2 mg, 2.87 mmol, 2.3 equiv) and then TfOH (22.76 μL, 0.28 mmol, 0.23 equiv) were added. The mixture was stirred at −20 °C for 1 h, then neutralized with Et_3N, filtered through Celite, and concentrated. The residue was washed with aqueous thiosulfate, water, brine and then dried over $MgSO_4$ and concentrated. After purification by flash column chromatography (cyclohexane–ethyl acetate 5:1), compound **8** was obtained (0.97 g, 57%) as a white amorphous solid; $R_f = 0.50$ (cyclohexane–ethyl acetate 2:1); $[\alpha]_D$ −1 (*c* 0.94, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14–7.09 (m, 44H, aromatic), 5.51 (d, 1H, $J_{1,2} = 10.6$ Hz, H-1c), 5.39–5.33 (m, 1H, H-2d), 5.30–5.24 (m, 1H, H-3d), 5.04 (d, 1H, $J_{1,2} = 3.5$ Hz, H-1e), 4.99 (d, 1H, $J_{1,2} = 8.1$ Hz, H-1d), 4.86 (d, 1H, $J_{gem} = 12.0$ Hz, PhCH), 4.80–4.76 (m, 2H, H-3c, PhCH), 4.70–4.66 (m, 1H, H-5e), 4.56–4.52 (m, 10H, H-2c, H-4c, H-6d, H-6d′, 2PhCH, $2PhCH_2$), 3.97–3.91 (m, 2H, H-3e, H-6c), 3.84–3.73 (m, 3H, H-2e, H-5d, H-6c′), 3.67 (d, 1H, $J = 1.5$ Hz, H-4e), 3.47 (d, 1H, $J = 9.5$ Hz, H-5c), 2.48–2.44 (m, 1H, H-4d), 1.77–1.69 (m, 1H, H-4d′), 1.33 (d, 3H, $J_{5,6} = 6.5$ Hz, H-6e); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 166.02, 165.77, 164.75 (3C=O, Bz), 138.76, 138.23, 137.88, 132.30, 131.75, 129.60, 129.28, 129.24 (aromatic C), 133.98, 133.35, 133.21, 133.17, 132.34, 129.76, 129.68, 129.62, 128.70, 128.65, 128.55, 128.43, 128.35, 128.24, 128.21, 128.18, 128.05, 127.99, 127.97, 127.91, 127.88, 127.78, 126.83, 123.47 (aromatic CH), 99.50 (C-1d), 97.73 (C-1e), 83.94 (C-1c), 79.53 (C-3e), 79.13 (C-5c), 78.30 (C-4e), 75.14 (C-4c), 75.02 (C-2e), 74.75, 73.55, 72.79, 72.09 ($4PhCH_2$), 74.69 (C-3c), 72.69 (C-2d), 71.67 (C-3d), 69.46 (C-5d), 67.86 (C-6c), 66.60 (C-5e), 65.54 (C-6d), 55.30 (C-2c), 33.32 (C-4d), 16.82 (C-6e); FAB-HRMS (*m/z*) Calcd for $C_{81}H_{75}NO_{17}SNa$ ($M + Na^+$): 1388.4653. Found: 1388.4667.

*3.6. 2-(Trimethylsilyl)ethyl(2,3,6-tri-O-benzoyl-4-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-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** (50.7 mg, 0.037 mmol, 1 equiv), **9** (50 mg, 0.056 mmol, 1.5 equiv) and 4-Å powdered molecular sieves (100 mg) in dry dichloromethane (3.4 mL) was stirred at room temperature under argon for 40 min, then cooled to −30 °C. NIS (16.7 mg, 0.08 mmol, 2.2 equiv) and then TfOH (1.2 μL, 0.012 mmol, 0.33 equiv) were added at −30 °C. The temperature was raised slowly to room temperature during 30 min. The mixture was neutralized with Et_3N after stirring at room temperature for an additional hour, filtered through Celite and then concentrated. The residue was washed with aqueous thiosulfate, water, and brine and then dried over $MgSO_4$ and concentrated. After purification by flash column chromatography (toluene–ethyl acetate 9:1), compound **10** was obtained (74.7 mg, 94%) as a white foam; $R_f = 0.64$ (toluene–ethyl acetate 4:1); $[\alpha]_D$ −1 (*c* 1.1, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12–7.20 (m, 64H, aromatic), 5.35 (dd, 1H, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 9.6$ Hz, H-2d), 5.32 (d, 1H, $J_{1,2} = 8.4$ Hz, H-1c), 5.30–5.24 (m, 1H), 5.01 (d, 1H, $J_{1,2} = 3.4$ Hz, H-1e), 4.95 (d, 1H, $J_{1,2} = 7.9$ Hz, H-1d), 4.94–4.67 (m, 7H), 4.60 (dq, 1H, $J_{4,5} < 1$ Hz, $J_{5,6} = 6.5$ Hz, H-5e), 4.50–4.16 (m, 16H), 4.29 (d, 1H, $J_{1,2} = 7.9$ Hz, H-1a), 4.26 (d, 1H, $J_{1,2} = 8.1$ Hz, H-1b), 4.00 (s_{br}, 1H, H-4b), 3.98–3.81 (m, 5H), 3.76 (dd, 1H, $J_{gem} = 10.1$ Hz, PhCH), 3.68 (dd, 1H, $J = 7.1$ Hz, $J = 9.5$ Hz, 1H of OCH_2), 3.63–3.56 (m, 2H), 3.52 (dd, 1H, $J_{gem} = 10.5$ Hz, PhCH), 3.49–3.29 (m, 9H), 3.02–3.00 (m, 1H), 2.73 (s, 1H, OH), 2.47–2.44 (m, 1H, H-4d), 1.76–1.67 (m, 1H, H-4d′), 1.29 (d, 3H, $J_{5,6} = 6.5$ Hz, H-6e), 1.03–0.98 (m, 2H, OCH_2CH_2Si), 0.02 (s, 9H, $SiMe_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 166.03, 165.76, 164.73 (3C=O, Bz), 139.01, 138.74, 138.72, 138.48, 138.47, 138.26, 138.25, 137.59, 131.28, 129.23, 129.22 (aromatic C), 133.63–123.09 (64 aromatic CH), 102.95 (C-1b), 101.88 (C-1a), 99.48 (C-1d), 98.71 (C-1c), 97.61 (C-1e), 83.28, 82.79, 81.83, 79.44, 78.21, 77.96, 75.93, 75.35, 75.21, 74.64, 74.60, 73.70, 72.75, 72.51, 69.57 (CH), 75.29, 74.81, 74.73, 74.02, 73.74, 73.24, 72.84, 72.71, 72.07 ($PhCH_2$), 71.63 (C-2d), 68.38, 67.94, 67.81, 67.13, 65.51 (4C-6, OCH_2), 67.42 (C-4b), 66.62 (C-5e), 56.08 (C-2c), 33.25 (C-4d), 18.35 (OCH_2CH_2Si), 16.83 (C-6e), −1.49 ($SiMe_3$); FAB-MS (*m/z*) Calcd for $C_{127}H_{133}NO_{28}SiNa$ ($M + Na^+$): 2171.8714. Found: 2171.8.

*3.7. 2-(Trimethylsilyl)ethyl(2,3,6-tri-O-benzoyl-4-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-β-D-glucopyranoside-(1 → 3)-(4-O-acetyl-2,6-di-O-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**10′**)*

A solution of **10** (47.6 mg) in 1 mL of pyridine and 0.5 mL of acetic anhydride was stirred at room temperature for 12 h and then concentrated, co-evaporated

with toluene and dried. Compound **10′** was obtained in quantitative yield (45 mg); $R_f = 0.64$ (toluene–ethyl acetate 4:1); $[\alpha]_D$ −9 (*c* 1.2, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–7.17 (m, 64H, aromatic), 5.42 (d, 1H, $J = 3.5$ Hz, H-4b), 5.38–5.32 (m, 1H, H-2d), 5.31–5.26 (m, 1H, H-3d), 5.23 (d, 1H, $J_{1,2} = 8.3$ Hz, H-1c), 5.07 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1d), 5.00–4.94 (m, 1H), 4.95 (d, 1H, $J_{1,2} = 3.4$ Hz, H-1e), 4.90 (d, 1H, $J = 2.2$ Hz), 4.90–4.87 (m, 1H, H-4c), 4.77–4.66 (m, 5H, H-5e, H-3c), 4.58 (d, 1H, $J = 12.1$ Hz), 4.47–4.33 (m, 10H, H-2c), 4.31–4.21 (m, 7H, H-1a, H-1b), 4.04–3.95 (m, 2H, $J_{gem} = 12.1$ Hz, $PhCH_2$), 3.89–3.73 (m, 5H, H-3e, H-5d, H-2e), 3.62 (s_{br}, 1H, H-4e), 3.57–3.51 (m, 1H), 3.50–3.30 (m, 10H), 3.01–2.98 (m, 1H, PhCH), 2.49–2.45 (m, 1H, H-4d), 2.09 (s, 3H, OAc), 1.79–1.71 (m, 1H, H-4d′), 1.31 (d, 3H, $J_{5,6} = 6.4$ Hz, H-6e), 1.04–0.99 (m, 2H, OCH_2CH_2Si), 0.03 (s, 9H, $SiMe_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 169.86 (C=O, Ac), 166.01, 165.82, 164.83 (3C=O, Bz), 139.08, 138.83, 138.73, 138.42, 138.26, 138.21, 131.35, 129.63, 129.52, 129.51 (aromatic C), 133.59–127.68 (64 aromatic CH), 103.02 (C-1b), 101.94 (C-1a), 99.50 (C-1d), 98.87 (C-1c), 97.35 (C-1e), 78.42 (C-4e), 75.09 (C-4c), 75.03 (C-5e), 73.11 (C-3c), 72.60 (C-2d), 71.81 (C-3d), 69.89 (C-4b), 69.45 (C-5d), 56.47 (C-2c), 82.60, 81.73, 79.48, 78.88, 78.71, 75.73, 74.59, 72.57, 66.48 (CH), 74.88, 74.76, 74.09, 73.66, 73.56, 73.44, 72.92, 72.60, 72.13 ($PhCH_2$), 68.28, 67.68, 67.63, 67.21, 65.68 (4C-6, OCH_2), 33.42 (C-4d), 20.76 (CH_3, Ac), 18.39 (OCH_2CH_2Si), 16.83 (C-6e), −1.45 ($SiMe_3$); FAB-MS (*m/z*) Calcd for $C_{129}H_{135}NO_{29}SiNa$ ($M + Na^+$): 2213.8819. Found: 2213.8.

*3.8. 2-(Trimethylsilyl)ethyl(4-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**)*

Hydrazine monohydrate (1.5 mL) and water (1.5 mL) were added to a solution of compound **10** (140 mg, 0.065 mmol) in 10 mL of ethanol. The mixture was refluxed for 14 h. After concentration, the residue was co-evaporated with toluene and dried, then dissolved in 4 mL of methanol–dichloromethane (1:1), to which 0.5 mL of acetic anhydride was introduced. The mixture was stirred at room temperature for 2.5 h. After concentration, the residue was purified by a column of silica gel, eluted with ethyl acetate and then by a Sephadex column (LH20) using methanol–dichloromethane (1:1) as eluant. Compound **11** was obtained (101 mg, 89%) as a white amorphous solid; $R_f = 0.24$ (ethyl acetate); $[\alpha]_D$ −19 (*c* 1.1, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–7.17 (m, 45H, aromatic), 5.27 (d, 1H, $J_{1,2} = 7.3$ Hz, H-1c), 5.10–5.02 (m, 2H, H-1e, PhCH), 5.00–4.92 (m, 3H, H-3e), 4.83–4.78 (m, 4H, H-2e, 3PhCH), 4.74–4.57 (m, 8H, H-2a), 4.51–4.45 (m, 2H, H-1d, H-1a), 4.41 (d, 1H, $J_{1,2} = 9.1$ Hz, H-1b), 4.51–4.33 (m, 5H), 4.12–3.93 (m, 7H), 3.91–3.88 (m, 1H, H-5c), 3.76–3.54 (m, 17H), 3.49–3.35 (m, 4H), 3.22–3.14 (m, 2H), 1.85 (dd, 1H, $J_{gem} = 12.3$ Hz, $J_{3,4} = 4.9$ Hz, H-4d), 1.41 (s, 3H, OAc), 1.41–1.33 (m, 1H, H-4′d), 1.18 (d, 3H, $J_{5,6} = 6.4$ Hz, H-6e), 1.12–1.07 (m, 2H, OCH_2CH_2Si), 0.04 (S, 9H, $SiMe_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 170.74 (C=O, Ac), 139.08, 138.84, 138.70, 138.42, 138.30, 138.31, 138.27, 138.03, 137.27 (aromatic C), 128.49–127.07 (aromatic CH), 102.99 (C-1b), 102.10 (C-1a), 99.62 (C-1d), 99.50 (C-1c), 97.99 (C-1e), 82.83, 82.18, 81.86, 79.27, 78.89, 77.19, 76.62, 76.40, 76.23, 75.85, 75.74, 74.96, 74.73, 73.54, 72.83, 70.86, 67.81, 67.36 (ring CH), 75.21, 74.84, 74.55, 73.92, 73.51, 73.28, 73.04, 72.48 ($PhCH_2$), 70.06, 68.77, 68.25, 67.21, 64.99 (4C-6, OCH_2CH_2), 57.26 (C-2c), 33.22 (C-4d), 22.78 (CH_3, Ac), 18.38 (OCH_2CH_2Si), 16.66 (C-6e), −1.47 ($SiMe_3$); FAB-HRMS Calcd for $C_{100}H_{121}NO_{24}SiNa$ ($M + Na^+$): 1770.7946. Found: 1770.7969.

*3.9. 2-(Trimethylsilyl)ethyl(4-deoxy-β-D-xylo-hexopyranosyl)-(1 → 4)-[α-L-fucopyranosyl-(1 → 3)]-2-deoxy-2-acetamido-β-D-glucopyranoside-(1 → 3)-(β-D-galactopyranosyl)-(1 → 4)-β-D-glucopyranoside (**1**)*

A solution of **11** (40 mg) in methanol (3.85 mL) was treated with Pd/C (10%, 13.5 mg) under H_2 (160 kPa) for 13 h at 25 °C, then filtered and evaporated. The residue was purified on a Sephadex column (G25) using water as eluant. Compound **1** was obtained (20.4 mg, 95%) as a white amorphous solid; $R_f = 0.25$ (isopropanol–ethyl acetate–water 3:3:1); $[\alpha]_D$ −65 (*c* 0.88, chloroform–methanol 1:1); ^{1}H NMR (400 MHz, D_2O): δ 5.13 (d, 1H, $J_{1,2} = 4.0$ Hz, H-1e), 4.86–4.80 (m, 1H, H-5e), 4.71 (d, 1H, $J_{1,2} = 8.3$ Hz, H-1), 4.50 (d, 1H, $J_{1,2} = 8.0$ Hz, H-1), 4.46 (d, 1H, $J_{1,2} = 7.8$ Hz, H-1), 4.44 (d, 1H, $J_{1,2} = 7.8$ Hz, H-1), 4.16 (d, 1H, $J = 3.3$ Hz), 4.07–3.53 (m, 25H), 3.31–3.27 (m, 1H, H-2), 3.11 (dd, 1H, $J_{1,2} = 8.0$ Hz, $J_{2,3} = 9.0$ Hz, H-2), 2.02 (s, 3H, Ac), 1.99 (dd, 1H, $J_{gem} = 11.3$ Hz, $J_{3,4} = 5.1$ Hz, H-4d), 1.29–1.21 (m, 1H, H-4d′), 1.20 (d, 3H, $J_{5,6} = 6.6$ Hz, H-6e), 1.03 (2dt, 2H, $J_{gem} = 12.9$ Hz, $J_{vic} = 5.5$ Hz, CH_2Si), 0.034 (s, 9H, $SiMe_3$);

^{13}C NMR (100.6 MHz, D_2O): δ 175.10 (C=O, NHAc), 103.30, 102.91, 102.04, 101.73 (C-1a, C-1b, C-1c, C-1d), 99.14 (C-1e), 82.45, 78.65, 75.49, 75.45, 75.23, 75.11, 74.89, 73.51, 72.73, 72.34, 70.48, 70.33, 69.59, 68.67, 68.06, 66.81 (ring CH), 75.81 (C-2), 73.18 (C-2), 68.81 (OCH_2CH_2Si), 64.53, 61.32, 60.41, 59.97 (C-6a, C-6b, C-6c, C-6d), 56.34 (C-2c), 35.07 (C-4d), 22.63 (CH_3, Ac), 17.93 (CH_2Si), 15.80 (C-6e), −2.16 ($SiMe_3$); FAB-HRMS (*m*/*z*) Calcd for $C_{37}H_{67}NO_{24}SiNa$ ($M + Na^+$): 960.3720. Found: 960.3708.

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