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Convergent Synthesis of Oligosaccharide Fragments Corresponding to the Cell Wall *O*-Polysaccharide of *Salmonella enterica* O53

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Conventional glycoconjugate vaccines are prepared with polysaccharides isolated from bacterial fermentation, an approach with some significant drawbacks such as handling of live bacterial strains, the presence of biological impurities, and inter-batch variations in oligosaccharide epitope structure. However, it has been shown in many cases that a synthetic fragment of appropriate structure conjugated to a protein can be an effective vaccine that circumvents the shortcomings of using full-length oligosaccharides. The development of synthetic strategies to prepare glycoconjugate derivatives against pathogenic bacterial strains is therefore of great interest. Oligosaccharide fragments corresponding to the repeat unit of the cell wall *O*-antigen of *Salmonella enterica* strain O53 were synthesized in good yield. Sequential and block glycosylation strategies were used for the synthesis of the target compounds. A number of recently developed reaction conditions were used in the synthetic strategy. A one-pot reaction scheme was also developed for the multiple glycosylation steps. The stereoselective outcomes of all glycosylation reactions were very good.

Introduction

Foodborne illness is a serious worldwide health concern.[1] The increased rate of hospitalizations and deaths due to gastrointestinal disorders caused by bacterial infections has become a significant challenge for medical professionals.[2] Among the many pathogenic bacteria responsible for enteric diseases, *Salmonella enterica* is predominant.[3] *Salmonella* species are recognized as a major pathogen of both animals and humans, causing the foodborne illness salmonellosis.[4] Salmonella infections arise from the contamination of poultry, eggs, beef, and other foods, sometimes from unwashed fruits and vegetables.[5] Several enteric outbreaks caused by *Salmonella* have been witnessed recently in many countries.[6] There are several strains of *S. enterica*, which are classified by their cell wall *O*-polysaccharides.[7] Because these cell wall *O*-polysaccharides have a direct influence on the pathogenicity of *Salmonella* strains,[8] the structures of several *O*-polysaccharides from a number of *S. enterica* strains have been elucidated.[7] Perepelov et al.[9] reported the structure of the repeating unit of the cell wall *O*-polysaccharide of *S. enterica* strain O53; it is a tetrasaccharide composed of α-D-galactofuranose, β-D-galactosamine, 2,3-di-O-acetylated α-L-rhamnopyranose and β-D-glucosamine moieties.

Current efforts in medicinal chemistry and drug discovery programs involve the development of alternative approaches for the control of infections by antibiotic-resistant bacterial strains.[10] Although vaccines based on bacterial cell wall polysaccharides were introduced many years ago, these were ineffective in children owing to the lack of a T-cell-independent immune response. Glycoconjugate vaccines were later developed, and were found to be highly effective in both adults and children.[11] Conventional glycoconjugate vaccines are prepared by using polysaccharides isolated from bacterial fermentation. This approach has several serious drawbacks, including the handling of live bacterial strains, the presence of biological impurities, and batch-to-batch variations in the exact structure of the oligosaccharide epitope.

A synthetic oligosaccharide fragment, corresponding to the entire polysaccharide with the appropriate structure, in conjugation with a protein could lead to an efficient glycoconjugate vaccine that circumvents the above-mentioned shortcomings. In this context, the development of synthetic strategies for the preparation of glycoconjugate derivatives against *S. enterica* O53 and other related strains would be of great interest. In many cases it has been found that the full-length oligosaccharide repeat unit is not essential for generating a significant immune response; a smaller fragment can act as an immunodominant glycan.[12,13] The tetrasaccharide repeat unit of *S. enterica* O53 strain contains two *O*-acetyl groups that might influence the antigenicity of the molecule. We therefore decided to synthesize di-, tri-, and tetrasaccharide moieties corresponding to the repeat unit of the *S. enterica* O53 strain cell-wall polysaccharide, containing *O*-acetyl groups at the appropriate posi-

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tions with a 2-aminoethyl linker connected to the reducing end. In addition, we developed a one-pot synthetic strategy for the synthesis of the tetrasaccharide derivative. The 2-aminoethyl linker can serve as a readily available amine functionality for connecting the synthetic glycan moieties to a suitable protein through a spacer linkage.

Results and Discussion

Because two *O*-acetyl groups are present in the native structure of the *O*-polysaccharide, this synthetic strategy was designed for the synthesis of the target molecules with *O*-acetyl groups present at the appropriate positions. The oligosaccharide fragments **1**, **2**, and **3** were synthesized via stereoselective glycosylation of the suitably functionalized monosaccharide intermediates **4**,[14] **5**,[15] **6**,[16] **7**,[17,18] and **8** by applying recently developed glycosylation conditions (Figure 1). Compound **3** was synthesized using [2+2] block glycosylation conditions as well as a one-pot two-step glycosylation approach. The monosaccharide derivatives were prepared from the commercially available reducing sugars using published reaction conditions. To prepare the 1,2-*cis* D-galactofuranosyl linkage in compound **12**, per-O-benzylated D-galactofuranosyl trichloroacetimidate derivative **7** (α/β 1:9) was used as the glycosyl donor,[18] which was prepared from 2,3,5,6-tetra-*O*-benzyl-α/β-D-galactofuranose[19] by treatment with trichloroacetonitrile in the presence of DBU, following reaction conditions similar to those reported

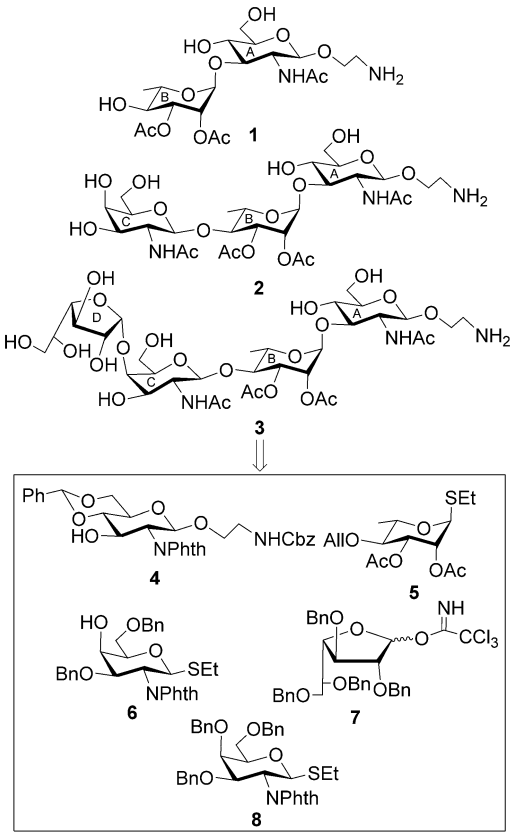
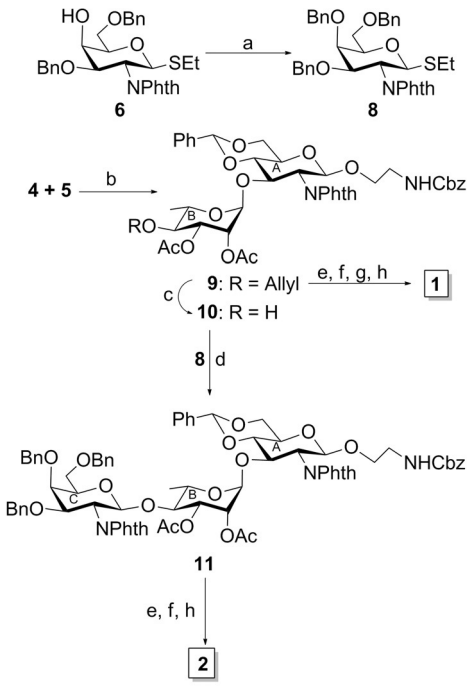


Figure 1. Structures of the synthesized oligosaccharide fragments **1**, **2**, and **3** as their 2-aminoethyl glycosides and their synthetic intermediates.

by Gandolfi-Donadío et al.[17] Disaccharide thioglycoside donor **12** was prepared by glycosylation of compound **7** with thioglycoside acceptor **6** in the presence of nitrosyl tetrafluoroborate ($NOBF_4$) as the glycosylation activator,[20] exploiting the orthogonal properties[21] of compound **6**.

Ethyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*N*-phthalimido-1-thio-β-D-galactopyranoside (**8**) was prepared in 81% yield from the previously reported compound **6**[16] by benzylation using benzyl bromide and sodium hydride.[22] Iodonium-ion-promoted stereoselective glycosylation of compound **4** with thioglycoside derivative **5** in the presence of a combination of *N*-iodosuccinimide (NIS) and perchloric acid supported over silica ($HClO_4$–SiO_2)[23,24] furnished disaccharide derivative **9** in 77% yield. NMR spectral analysis of compound **9** confirmed its formation [signals at $\delta = 5.19$ (d, $J = 8.5$ Hz, $H1_A$), 4.44 (br s, $H1_B$) in ^{1}H NMR, and at $\delta = 98.9$ ($C1_A$), 97.4 ($C1_B$) in ^{13}C NMR spectra]. Compound **9** was subjected to a series of functional group transformations, which include: a) treatment with hydrazine monohydrate at elevated temperature,[25] b) acetylation using acetic anhydride and pyridine, c) removal of the allyl ether by treatment with palladium chloride,[26] and d) catalytic transfer hydrogenation[27] using triethylsilane in the presence of Pearlman's catalyst to furnish compound **1** in 57% overall yield. NMR spectral analysis established the structure of compound **1** [signals at $\delta = 4.77$ (br s, $H1_B$), 4.44 (d, $J = 8.0$ Hz, $H1_A$) in ^{1}H NMR, and at $\delta = 100.2$ ($C1_A$), 98.4 ($C1_B$) in ^{13}C NMR spectra]. Removal of the allyl ether from compound **9** with palladium chloride[26] gave the disaccharide acceptor **10** in 67% yield. Compound **10** was allowed to couple stereoselectively with thioglycoside derivative **8** in the presence of a combination of NIS and $HClO_4$–SiO_2[23,24] to furnish the trisaccharide derivative **11** in 70% yield. Formation of compound **11** was confirmed by its spectral analysis [signals at $\delta = 5.18$ (d, $J = 8.5$ Hz, $H1_A$), 5.10 (d, $J = 8.0$ Hz, $H1_C$), 4.33 (br s, $H1_B$) in ^{1}H NMR, and at $\delta = 98.9$ ($C1_A$), 97.6 ($C1_C$), 97.0 ($C1_B$) in ^{13}C NMR spectra]. Compound **11** was subjected to a similar set of reactions used for the preparation of compound **1** from compound **9**, to furnish compound **2** in overall 55% yield. NMR spectral analysis established the structure of compound **2** [signals at $\delta = 4.95$ (br s, $H1_B$), 4.64 (d, $J = 8.5$ Hz, $H1_A$), 4.53 (d, $J = 7.5$ Hz, $H1_C$) in ^{1}H NMR, and at $\delta = 101.9$ ($C1_C$), 100.2 ($C1_A$), 98.2 ($C1_B$) in ^{13}C NMR spectra] (Scheme 1).

In another approach the tetrasaccharide **3** as its 2-aminoethyl glycoside was synthesized by applying a [2+2] block glycosylation strategy. Stereoselective glycosylation of the thioglycoside acceptor **6** with trichloroacetimidate derivative **7** in the presence of $NOBF_4$[20] furnished the disaccharide thioglycoside derivative **12** in 65% yield, together with a minor quantity (~5%) of the other isomeric product, which was separated by column chromatography. The stereochemistry of the glycosyl linkage was confirmed by its spectral analysis [signals at $\delta =$ 5.21 (d, $J = 10.5$ Hz, $H1_C$), 5.17 (d, $J = 3.5$ Hz, $H1_D$) in ^{1}H NMR, and at $\delta = 102.5$ ($C1_D$), 81.2 ($C1_C$) in ^{13}C NMR spectra]. The coupling constant ($J = 3.5$ Hz) for the D-galactofuranosyl linkage in the ^{1}H NMR spectrum of compound **12** confirmed formation of the 1,2-*cis* D-galactofuranosyl linkage.[28] Stereoselective glycosylation of disaccharide thioglycoside donor **12** with disacchar-

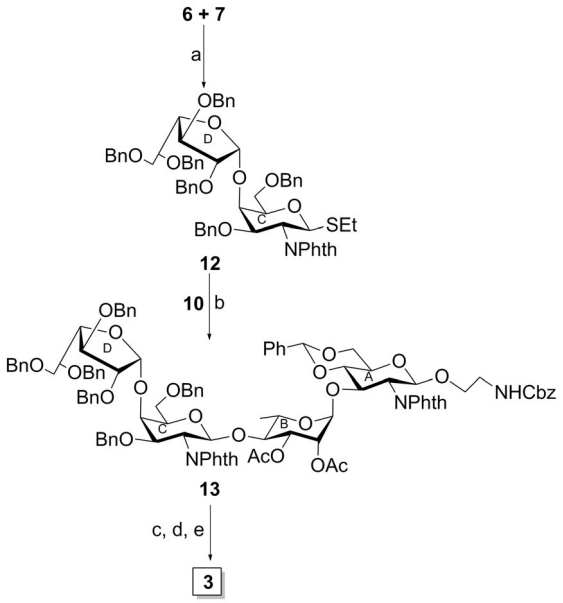


Scheme 1. *Reagents and conditions*: a) benzyl bromide, NaH, THF, 0 °C, 2 h, 81%; b) NIS, $HClO_4$–SiO_2, MS 4 Å, toluene, −15 °C, 40 min, 77%; c) $PdCl_2$, CH_3OH, RT, 1 h, 67%; d) NIS, $HClO_4$–SiO_2, MS 4 Å, CH_2Cl_2, −40 °C, 1 h, 70%; e) $NH_2NH_2{\cdot}H_2O$, EtOH, 80 °C, 8 h; f) acetic anhydride, pyridine, RT, 1 h; g) $PdCl_2$, CH_3OH, RT, 1.5 h; h) Et_3SiH, 20% $Pd(OH)_2$–C, CH_3OH, RT, 12 h, overall 57% for compound **1**, 55% for compound **2**.

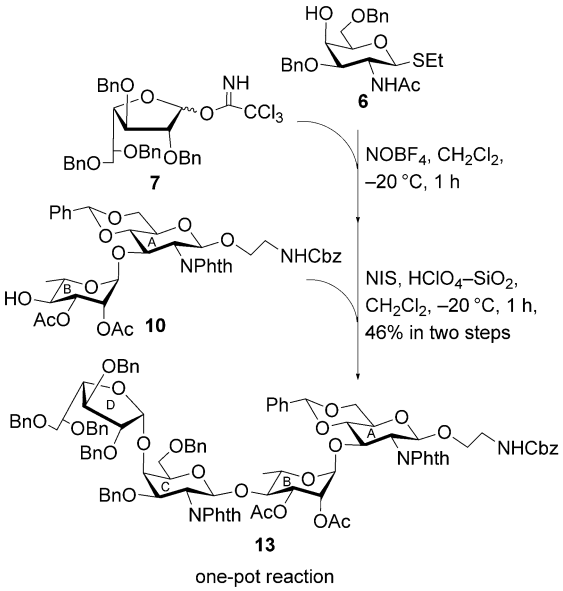
ide acceptor **10** in the presence of a combination of NIS and $HClO_4$–SiO_2[23,24] furnished tetrasaccharide derivative **13** in 66% yield, which was confirmed from its spectral analysis [signals at $\delta = 5.38$ (s, PhC*H*), 5.17 (d, $J = 8.5$ Hz, $H1_A$), 5.08 (d, $J = 4.0$ Hz, $H1_D$), 5.06 (d, $J = 10.0$ Hz, $H1_C$), 4.40 (brs, $H1_B$) in ^{1}H NMR, and at $\delta = 102.9$ ($C1_D$), 101.6 (PhCH), 98.9 ($C1_A$), 97.6 ($C1_C$), 97.5 ($C1_B$) in ^{13}C NMR spectra] (Scheme 2). In a parallel set of experiments, tetrasaccharide derivative **13** was synthesized under two-step one-pot reaction conditions. In this strategy, thioglycoside **6** was allowed to react with D-galactofuranosyl trichloroacetimidate donor **7** in the presence of $NOBF_4$ until the starting materials were consumed and a new spot appeared in the TLC plate. Compound **10** was then added to the reaction mixture followed by NIS and $HClO_4$–SiO_2, and the reaction was continued to furnish compound **13** in 46% overall yield in one pot. Compound **13** was subjected to a similar set of reactions used in the preparation of compound **1** from compound **9**, to furnish compound **3** in 50% overall yield (Scheme 3). The NMR spectral analysis of compound **3** confirmed its formation [signals at $\delta = 5.00$ (d, $J = 8.5$ Hz, $H1_A$), 4.81 (d, $J = 3.5$ Hz, $H1_D$), 4.79 (brs, $H1_B$), 4.48 (d, $J = 7.0$ Hz, $H1_C$) in ^{1}H NMR, and at $\delta = 102.6$ ($C1_D$), 100.2 ($C1_C$), 98.1 ($C1_B$), 97.6 ($C1_A$) in ^{13}C NMR spectra].

Conclusions

In summary, oligosaccharides corresponding to the cell wall *O*-polysaccharide of *Salmonella enterica* strain O53 were synthesized, maintaining the exact structural components present in



Scheme 2. *Reagents and conditions*: a) $NOBF_4$, CH_2Cl_2, −20 °C, 1 h, 65%; b) NIS, $HClO_4$–SiO_2, MS 4 Å, CH_2Cl_2, −20 °C, 1.5 h, 66%; c) $NH_2NH_2{\cdot}H_2O$, EtOH, 80 °C, 8 h; d) acetic anhydride, pyridine, RT, 1 h; e) Et_3SiH, 20% $Pd(OH)_2$–C, CH_3OH, RT, 12 h, overall 50%.



Scheme 3. Synthesis of compound **13** using two-step sequential glycosylations in a one-pot reaction.

the native polysaccharide. The tetrasaccharide derivative was also synthesized under one-pot reaction conditions. The stereoselective outcome and yields were satisfactory in all glycosylation steps.

Experimental Section

General methods: All reactions were monitored by thin-layer chromatography over silica-gel-coated TLC plates. The spots on TLC were visualized by warming ceric sulfate (2% $Ce(SO_4)_2$ in 2 N

H_2SO_4) sprayed plates on a hot plate. Silica gel (230–400 mesh) was used for column chromatography. NMR spectra were recorded on a Bruker Avance 500 MHz instrument, using $CDCl_3$ as solvent and TMS as internal reference unless stated otherwise. Chemical shifts (δ) are expressed in ppm. The complete assignment of proton and carbon spectra was carried out by using a standard set of NMR experiments: ^{1}H NMR, ^{13}C NMR, ^{13}C DEPT 135, 2D COSY, 2D HSQC, etc. MALDI-MS data were recorded on a Bruker Daltonics mass spectrometer. Optical rotations were recorded with a Jasco P-2000 polarimeter. Microanalysis was carried out on Carlo Erba analyzer. Commercially available grades of organic solvents of adequate purity were used in all reactions. $HClO_4$–SiO_2 was prepared by following experimental conditions similar to those reported by Chakraborti et al.[24]

Ethyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*N*-phthalimido-1-thio-β-D-galactopyranoside (8): To a solution of compound **6** (1 g, 1.87 mmol) in anhydrous THF (15 mL) was added benzyl bromide (0.5 mL, 4.20 mmol) and the reaction mixture was cooled to 0 °C. To the cooled reaction mixture was added sodium hydride (60% oil coated, 225 mg, 5.61 mmol) and it was stirred at 0 °C for 2 h. The reaction was quenched by the addition of saturated aqueous NH_4Cl (50 mL), and then was extracted with CH_2Cl_2 (50 mL). The organic layer was washed with H_2O (50 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane/EtOAc (9:1) as eluent to give pure compound **8** (945 mg, 81%). Yellow oil; $[\alpha]_D^{25}$: +66 (c = 1.2, $CHCl_3$); IR (neat): 3021, 2934, 1699, 1534, 1454, 1262, 1091, 1027, 751 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.85–6.98 (m, 19H, Ar–H), 5.26 (d, J = 10.5 Hz, 1H, H-1), 4.99 (d, J = 12.5 Hz, 1H, PhC*H*), 4.81 (t, J = 10.5 Hz each, 1H, H-2), 4.62 (2d, J = 11.0 Hz each, 2H, 2PhC*H*), 4.51 (ABq, J = 12.0 Hz each, 2H, 2PhC*H*), 4.37 (dd, J = 10.5, 2.5 Hz, 1H, H-3), 4.32 (d, J = 12.0 Hz, 1H, PhC*H*), 4.09 (br s, 1H, H-4), 3.81–3.78 (m, 1H, H-6$_a$), 3.67–3.63 (m, 2H, H-5, H-6$_b$), 2.71–2.61 (m, 2H, SCH_2CH$_3$), 1.18 (t, J = 7.5 Hz each, SCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 168.3, 167.6 (PhthCO), 138.7–123.1 (Ar-*C*), 81.2 (C1), 77.5 (C3), 77.4 (C5), 74.5 (PhCH$_2$), 73.5 (PhCH$_2$), 72.2 (C4), 71.4 (PhCH$_2$), 68.6 (C6), 51.6 (C2), 23.6 (SCH_2CH$_3$), 14.8 (SCH$_2$C*H*$_3$); ESI-MS: 646.2 [M + Na]$^+$; Anal. calcd for $C_{37}H_{37}NO_6S$ (623.23): C 71.24, H 5.98%; found: C 71.10, H 6.16%.

2-(*N*-Benzyloxycarbonyl)aminoethyl *O*-(2,3-di-*O*-acetyl-4-*O*-allyl-α-L-rhamnopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (9): To a solution of compound **4** (1.5 g, 2.61 mmol) and compound **5** (1 g, 3.01 mmol) in dry toluene (20 mL) was added MS 4 Å (2 g), and the reaction mixture was cooled to −15 °C under argon. To the cooled reaction mixture were added NIS (750 mg, 3.33 mmol) and $HClO_4$–SiO_2 (50 mg), and it was allowed to stir at same temperature for 40 min. The reaction mixture was filtered and washed with CH_2Cl_2 (100 mL). The combined organic layer was successively washed with 5% $Na_2S_2O_3$ (100 mL), saturated $NaHCO_3$ (100 mL) and H_2O (100 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (5:1) as eluent to give pure compound **9** (1.7 g, 77%). White solid; mp: 117–118 °C [EtOH]; $[\alpha]_D^{25}$: −31 (c = 1.2, $CHCl_3$); IR (KBr): 3033, 2927, 1775, 1715, 1670, 1547, 1445, 1230, 1273, 1088, 1017, 712 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.77–7.25 (m, 14H, Ar-H), 5.76–5.70 (m, 1H, C*H*=CH$_2$), 5.52 (s, 1H, PhC*H*), 5.19 (d, J = 8.5 Hz, 1H, H-1$_A$), 5.15–5.06 (m, 3H, H-3$_B$, CH=C*H*$_2$), 4.98–4.87 (m, 3H, N*H*, 2PhC*H*), 4.66 (br s, 1H, H-2$_B$), 4.59 (t, J = 9.5 Hz each, 1H, H-3$_A$), 4.44 (br s, 1H, H-1$_B$), 4.36 (dd, J = 10.0, 4.5 Hz, 1H, H-6$_{aA}$), 4.28 (t, J = 9.0 Hz each, 1H, H-2$_A$), 3.93–3.88 (m, 3H, H-5$_B$, OC*H*$_2$CH=CH$_2$), 3.79–3.75 (m, 2H, H-6$_{bA}$, OC*H*-), 3.70 (t, J = 9.0 Hz each, 1H, H-4$_A$), 3.65–3.56 (m, 2H, H-5$_A$, OC*H*-), 3.26–3.21 (m, 2H, NC*H*$_2$), 3.12 (t, J = 9.5 Hz each, H-4$_B$), 1.93, 1.74 (2 s, COC*H*$_3$), 0.70 (d, J = 6.5 Hz, 3H, CC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 169.2, 169.1 (2*C*OCH$_3$), 156.1 (CbzCO), 137.0–123.6 (Ar–C), 139.9 (*C*H=CH$_2$), 116.3 (CH=*C*H$_2$), 101.9 (PhCH), 98.9 (C1$_A$), 97.4 (C1$_B$), 80.2 (C4$_A$), 78.4 (C4$_B$), 74.4 (C3$_A$), 73.1 (OCH$_2$*C*H=CH$_2$), 70.8 (C2$_B$), 70.3 (C3$_B$), 69.1 (C6$_A$), 68.5 (O*C*H$_2$), 67.8 (C5$_B$), 66.5 (2C, C5$_A$, PhCH$_2$), 56.2 (C2$_A$), 40.7 (N*C*H$_2$), 20.8, 20.5 (2C, 2CO*C*H$_3$), 17.0 (C*C*H$_3$); MALDI-MS: 867.3 [M + Na]$^+$; Anal. calcd for $C_{44}H_{48}N_2O_{15}$ (844.31): C 62.55, H 5.73%; found: C 62.40, H 6.90%.

2-(*N*-Benzyloxycarbonyl)aminoethyl *O*-(2,3-di-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (10): To a solution of compound **9** (1 g, 1.18 mmol) in anhydrous CH_3OH (20 mL) was added $PdCl_2$ (125 mg, 0.70 mmol) and the reaction mixture was allowed to stir at room temperature for 1 h. The reaction mixture was filtered through a Celite bed and the filtering bed was washed with CH_3OH (50 mL). The combined filtrate was concentrated to give the crude product, which was purified over SiO_2 using hexane/EtOAc (4:1) as eluent to give pure compound **10** (640 mg, 67%). White solid; mp: 89–90 °C [EtOH]; $[\alpha]_D^{25}$: −21 (c = 1.2, $CHCl_3$); IR (KBr): 3453, 2926, 1775, 1714, 1387, 1243, 1083, 754 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.78–7.25 (m, 14H, Ar–*H*), 5.53 (s, 1H, PhC*H*), 5.21 (d, J = 8.5 Hz, 1H, H-1$_A$), 5.02 (dd, J = 10.0, 3.5 Hz, 1H, H-3$_B$), 4.98–4.88 (m, 3H, N*H*, 2PhC*H*), 4.64 (br s, 1H, H-2$_B$), 4.59 (t, J = 9.5 Hz each, 1H, H-3$_A$), 4.48 (br s, 1H, H-1$_B$), 4.36 (dd, J = 10.5, 4.5 Hz, 1H, H-6$_{aA}$), 4.26 (t, J = 9.0 Hz each, 1H, H-2$_A$), 3.82–3.76 (m, 3H, H-5$_B$, H-6$_{bA}$, OC*H*-), 3.70–3.55 (m, 3H, H-4$_A$, H-5$_A$, OC*H*-), 3.26–3.23 (m, 2H, NC*H*$_2$), 3.12 (t, J = 9.5 Hz each, 1H, H-4$_B$), 1.93, 1.74 (2 s, 6H, 2COC*H*$_3$), 0.70 (d, J = 6.5 Hz, 3H, CC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.0, 169.1 (2C, 2*C*OCH$_3$), 156.1 (CBzCO), 137.0–123.7 (Ar–*C*), 102.0 (PhCH), 98.9 (C1$_A$), 97.5 (C1$_B$), 80.2 (C4$_A$), 74.6 (C3$_A$), 71.4 (C4$_B$), 71.3 (C3$_B$), 70.6 (C2$_B$), 69.2 (C6$_A$), 69.0 (C5$_B$), 68.5 (O*C*H$_2$), 66.5 (2C, C5$_A$, PhCH$_2$), 56.2 (C2$_A$), 40.7 (N*C*H$_2$), 20.8, 20.4 (2C, 2*C*OCH$_3$), 16.6 (C*C*H$_3$); MALDI-MS: 827.2 [M + Na]$^+$; Anal. calcd for $C_{41}H_{44}N_2O_{15}$ (804.27): C 61.19, H 5.51%; found: C 61.05, H 5.70%.

2-(*N*-Benzyloxycarbonyl)aminoethyl *O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-*N*-phthalimido-β-D-galactopyranosyl)-(1→4)-*O*-(2,3-di-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (11): To a solution of compound **10** (300 mg, 0.37 mmol) and compound **8** (260 g, 0.42 mmol) in dry CH_2Cl_2 (8 mL) was added MS 4 Å (0.5 g) and the reaction mixture was cooled to −40 °C under argon. To the cooled reaction mixture were added NIS (110 mg, 0.49 mmol) and $HClO_4$–SiO_2 (10 mg) and it was allowed to stir at same temperature for 1 h. The reaction mixture was filtered and washed with CH_2Cl_2 (50 mL). The combined organic layer was successively washed with 5% $Na_2S_2O_3$ (25 mL), saturated $NaHCO_3$ (25 mL) and H_2O (25 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (5:1) as eluent to give pure compound **11** (350 mg, 70%). Yellow oil; $[\alpha]_D^{25}$: −7 (c = 1.2, $CHCl_3$); IR (neat): 2926, 1764, 1634, 1434, 1215, 1077, 757 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.89–6.98 (m, 33H, Ar–H), 5.51 (s, 1H, PhC*H*), 5.18 (d, J = 8.5 Hz, 1H, H-1$_A$), 5.10 (d, J = 8.0 Hz, 1H, H-1$_C$), 5.00–4.88 (m, 5H, N*H*, H-3$_B$, 3PhC*H*), 4.62–4.53 (m, 3H, H-2$_B$, H-2$_C$, PhC*H*), 4.48–4.42 (m, 4H, H-3$_A$, 3PhC*H*), 4.37 (dd, J = 10.5, 5.0 Hz, H-6$_{aA}$), 4.33 (br s, 1H, H-1$_B$), 4.31–4.28 (m, 2H, H-3$_C$, PhC*H*), 4.18 (t, J = 9.5, 9.0 Hz, 1H, H-2$_A$), 4.01 (br s, 1H, H-4$_C$), 3.88–3.85 (m, 1H, H-5$_B$), 3.78–3.65 (m, 5H, H-4$_A$, H-5$_C$, H-6$_{bA}$, H-6$_{aC}$, OC*H*<C->), 3.61–3.55 (m, 3H, H-5$_A$, H-6$_{bC}$, OC*H*<C->), 3.50 (t, J = 9.5 Hz each, 1H, H-4$_B$), 3.26–3.23 (m, 2H, NC*H*$_2$), 1.88, 1.69 (2 s, 6H, 2COC*H*$_3$), 0.53 (d, J = 6.5 Hz, 3H, CC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 169.1, 168.7 (2C, 2*C*OCH$_3$), 168.1, 167.5 (2C, PhthCO), 156.1 (CBzCO), 138.8–122.5

(Ar–*C*), 101.9 (PhCH), 98.9 ($C1_A$), 97.6 ($C1_C$), 97.0 ($C1_B$), 80.0 ($C4_A$), 76.4 ($C3_C$), 74.7 ($PhCH_2$), 74.0 ($C4_B$), 73.8 ($C3_A$), 73.5 ($PhCH_2$), 73.1 ($C4_C$), 72.5 ($C5_C$), 71.6 ($PhCH_2$), 70.5 ($C3_B$), 70.1 ($C2_B$), 69.1 ($C6_A$), 68.7 (OCH_2), 68.5 ($C6_C$), 67.2 ($C5_B$), 66.6 ($C5_A$), 66.5 ($PhCH_2$), 56.1 ($C2_A$), 53.1 ($C2_C$), 40.7 (NCH_2), 20.8, 20.5 (2C, $2COCH_3$), 16.5 (CCH_3); MALDI-MS: 1388.4 $[M+Na]^+$; Anal. calcd for $C_{76}H_{75}N_3O_{21}$ (1365.49): C 66.80, H 5.53%; found: C 66.64, H 5.70%.

Ethyl *O*-(2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalimido-1-thio-β-D-galactopyranoside (12): A solution of compound **6** (500 mg, 0.94 mmol) and compound **7** (800 mg, 1.17 mmol) in dry CH_2Cl_2 (20 mL) was cooled to −20 °C under argon. To the cooled reaction mixture was added $NOBF_4$ (80 mg, 0.68 mmol) and it was allowed to stir at same temperature for 1 h. The reaction mixture was poured into saturated $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was washed with H_2O (50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (8:1) as eluent to give pure compound **12** (645 mg, 65%). Yellow oil; $[\alpha]_D^{25}$: +42 (*c* = 1.2, $CHCl_3$); IR (neat): 2926, 1724, 1637, 1434, 1267, 1155, 757 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.68–6.89 (m, 34H, Ar–H), 5.21 (d, *J* = 10.5 Hz, 1H, H-1_C), 5.17 (d, *J* = 3.5 Hz, 1H, H-1_D), 4.80–4.57 (m, 5H, H-2_C, 4PhC*H*), 4.54–4.43 (m, 6H, 6PhC*H*), 4.39–4.33 (m, 2H, H-3_C, PhC*H*), 4.28–4.20 (m, 2H, H-4_C, PhC*H*), 4.03 (t, *J* = 5.5 Hz each, 1H, H-3_D), 3.97 (t, *J* = 5.5 Hz each, 1H, H-2_D), 3.92–3.88 (m, 2H, H-4_D, H-6_{aD}), 3.87–3.72 (m, 3H, H-5_D, H-6_{aC}, H-6_{bD}), 3.68–3.62 (m, 2H, H-5_C, H-6_{bC}), 2.72–2.62 (m, 2H, SCH_2CH_3), 1.09 (t, *J* = 7.0 Hz each, 3H, SCH_2CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 167.7, 167.5 (PhthCO), 139.3–123.0 (Ar–*C*), 102.5 (H-1_D), 83.4 ($C2_D$), 81.2 ($C1_C$), 81.1 ($C3_D$), 80.9 ($C3_C$), 78.8 ($C4_D$), 77.5 ($C5_D$), 75.5 ($C4_C$), 73.4 ($PhCH_2$), 72.9 ($PhCH_2$), 72.8 ($C5_C$), 72.5 ($PhCH_2$), 72.3 ($PhCH_2$), 72.2 ($PhCH_2$), 70.4 ($PhCH_2$), 70.1 ($C6_D$), 68.3 ($C6_C$), 51.5 ($C2_C$), 23.1 (SCH_2CH_3), 14.7 (SCH_2CH_3); MALDI-MS: 1078.4 $[M+Na]^+$; Anal. calcd for $C_{64}H_{65}NO_{11}S$ (1055.43): C 72.77, H 6.20%; found: C 72.60, H 6.40%.

2-(*N*-Benzyloxycarbonyl)aminoethyl *O*-(2,3,5,6-tetra-*O*-benzyl-α-D-galactofuranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalimido-β-D-galactopyranosyl)-(1→4)-*O*-(2,3-di-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (13): To a solution of compound **10** (300 mg, 0.37 mmol) and compound **12** (460 mg, 0.44 mmol) in dry CH_2Cl_2 (10 mL) was added MS 4 Å (0.5 g) and the reaction mixture was cooled to −20 °C under argon. To the cooled reaction mixture were added NIS (110 mg, 0.49 mmol) and $HClO_4$–SiO_2 (10 mg) and it was allowed to stir at same temperature for 1.5 h. The reaction mixture was filtered and washed with CH_2Cl_2 (50 mL). The combined organic layer was successively washed with 5% $Na_2S_2O_3$ (50 mL), saturated $NaHCO_3$ (50 mL) and H_2O (50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (5:1) as eluent to give pure compound **13** (440 mg, 66%). Yellow oil; $[\alpha]_D^{25}$: +32 (*c* = 1.2, $CHCl_3$); IR (neat): 3063, 2924, 1777, 1714, 1454, 1208, 1098, 1027, 752 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.77–7.03 (m, 48H, Ar–*H*), 5.38 (s, 1H, PhC*H*), 5.17 (d, *J* = 8.5 Hz, 1H, H-1_A), 5.08 (d, *J* = 4.0 Hz, 1H, H-1_D), 5.06 (d, *J* = 10.0 Hz, 1H, H-1_C), 5.01–4.98 (m, 1H, H-3_B), 4.93–4.84 (m, 3H, N*H*, 2PhC*H*), 4.74–4.59 (m, 5H, H-2_B, 4PhC*H*), 4.51–4.42 (m, 6H, H-3_A, H-3_C, 4PhC*H*), 4.40 (br s, 1H, H-1_B), 4.32–4.20 (m, 6H, H-2_A, H-2_D, H-3_D, H-6_{aA}, 2PhC*H*), 4.14–4.11 (m, 2H, 2PhC*H*), 4.02–4.00 (m, 1H, H-5_B), 3.93–3.91 (m, 2H, H-2_C, H-4_D), 3.81–3.72 (m, 5H, H-6_{bA}, H-6_{aC}, H-6_{aD}, OCH_2-), 3.62–3.57 (m, 6H, H-4_A, H-4_C, H-5_A, H-5_C, H-5_D, H-6_{bD}), 3.48–3.42 (m, 1H, H-6_{bC}), 3.33 (t, *J* = 10.0 Hz each, H-4_B), 3.25–3.21 (m, 2H, NCH_2), 1.76, 1.67 (2 s, 6H, $2COCH_3$), 0.57 (d, *J* = 6.0 Hz, 3H, CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 169.1, 169.0 (2C, $COCH_3$), 168.7, 168.1 (2C, PhthCO), 156.1 (CBzCO), 138.3–122.9 (Ar–*C*), 102.9 ($C1_D$), 101.6 (PhCH), 98.9 ($C1_A$), 97.6 ($C1_C$), 97.5 ($C1_B$), 83.2 ($C4_D$), 81.2 ($C2_D$), 80.6 ($C3_D$), 80.1 ($C4_A$), 78.2 ($C5_D$), 77.1 ($C4_B$), 75.1 ($C3_C$), 73.9 ($C3_A$), 73.3, 72.7, 72.6, 72.5, 72.2 (5$PhCH_2$), 71.9 ($C4_C$), 70.5 ($C6_D$), 70.1 ($PhCH_2$), 70.0 ($C2_B$), 69.9 ($C3_B$, $C5_C$), 69.8 ($C5_B$), 69.1 ($C6_A$), 68.5 (OCH_2), 67.8 ($PhCH_2$), 67.2 ($C5_A$), 66.5 ($C6_C$), 56.0 ($C2_C$), 52.7 ($C2_A$), 41.8 (NCH_2), 20.6, 20.4 (2C, $COCH_3$), 17.6 (CCH_3); MALDI-MS: 1820.6 $[M+Na]^+$; Anal. calcd for $C_{103}H_{103}N_3O_{26}$ (1797.68): C 68.77, H 5.77%; found: C 68.60, H 5.98%.

One-pot preparation of compound 13: A solution of compound **6** (250 mg, 0.47 mmol) and compound **7** (350 mg, 0.51 mmol) in dry CH_2Cl_2 (5 mL) was cooled to −20 °C under argon. To the cooled reaction mixture was added $NOBF_4$ (40 mg, 0.34 mmol) and it was allowed to stir at same temperature for 1 h. After consumption of the starting materials [TLC; hexane/EtOAc (6:1)], a solution of compound **10** (250 mg, 0.31 mmol) in CH_2Cl_2 (3 mL) was added to the reaction mixture followed by NIS (80 mg, 0.36 mmol) and $HClO_4$–SiO_2 (10 mg) and it was allowed to stir at −20 °C for 1 h. The reaction mixture was filtered and washed with CH_2Cl_2 (25 mL). The combined organic layer was successively washed with 5% $Na_2S_2O_3$ (25 mL), saturated $NaHCO_3$ (25 mL) and H_2O (25 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (5:1) as eluent to give pure compound **13** (260 mg, 46% in two steps).

2-Aminoethyl *O*-(2,3-di-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside (1): To a solution of compound **9** (500 mg, 0.59 mmol) in EtOH (10 mL) was added $NH_2NH_2{\cdot}H_2O$ (0.2 mL) and the mixture was stirred at 80 °C for 8 h. The solvents were removed under reduced pressure and a solution of the crude mass in acetic anhydride (2 mL) and pyridine (2 mL) was kept at room temperature for 1 h. The solvents were removed under reduced pressure and the crude mass was passed through a short pad of SiO_2 using EtOAc as eluent. To a solution of the acetylated product in CH_3OH (10 mL) was added $PdCl_2$ (80 mg, 0.45 mmol) and the reaction mixture was allowed to stir at room temperature for 1.5 h. The reaction mixture was filtered through a Celite bed, washed with CH_3OH (25 mL) and concentrated to give the crude product, which was passed through a short pad of SiO_2 using EtOAc as eluent. To a solution of the de-*O*-allylated product in CH_3OH (10 mL) were added 20% Pd(OH)$_2$–C (80 mg) and Et_3SiH (0.4 mL, 2.5 mmol) and the reaction mixture was allowed to stir at room temperature for 12 h. The reaction mixture was filtered through a Celite bed and the filtering bed was washed with CH_3OH/H_2O (10 mL, 2:1 *v*/*v*). The combined filtrate was concentrated under reduced pressure and passed through a Sephadex LH-20 column using CH_3OH/H_2O (2:1) as eluent to give pure compound **1** (165 mg, 57%). White powder; $[\alpha]_D^{25}$: +12 (*c* = 1.2, H_2O); IR (KBr): 3448, 2928, 1630, 1376, 1253, 1071, 696 cm^{-1}; ^1H NMR (D_2O, 500 MHz): δ = 4.93 (br s, 1H, H-2_B), 4.91 (dd, *J* = 10.0, 3.0 Hz, 1H, H-3_B), 4.77 (br s, 1H, H-1_B), 4.44 (d, *J* = 8.0 Hz, 1H, H-1_A), 4.00–3.95 (m, 1H, H-5_B), 3.90–3.86 (m, 1H, OC*H*-), 3.80–3.70 (m, 3H, H-2_A, H-6_{aA}, OC*H*-), 3.64–3.58 (m, 1H, H-6_{bA}), 3.54 (dd, *J* = 10.0, 9.5 Hz, H-4_B), 3.47–3.32 (m, 3H, H-3_A, H-4_A, H-5_A), 3.05 (m, 2H, NCH_2), 2.00, 1.91, 1.80 (3 s, 9H, $3COCH_3$), 1.15 (d, *J* = 6.0 Hz, 3H, CCH_3); ^{13}C NMR (D_2O, 125 MHz): δ = 174.7, 173.1, 172.9 (3C, $3COCH_3$), 100.2 ($C1_A$), 98.4 ($C1_B$), 82.1 ($C4_A$), 75.8 ($C3_A$), 71.3 ($C3_B$), 70.2 ($C2_B$), 69.6 ($C4_B$), 68.9 ($C5_A$), 68.3 ($C5_B$), 65.7 (OCH_2), 60.5 ($C6_A$), 50.0 ($C2_A$), 22.1, 20.2, 20.0 (3C, $3COCH_3$), 16.3 (CCH_3); ESI-MS: 517.2 $[M+Na]^+$; Anal. calcd for $C_{20}H_{34}N_2O_{12}$ (494.21): C 48.58, H 6.93%; found: C 48.76, H 7.14%.

2-Aminoethyl *O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-*O*-(2,3-di-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-2-acetam-

ido-2-deoxy-β-D-glucopyranoside (2): To a solution of compound **11** (300 mg, 0.22 mmol) in EtOH (10 mL) was added $NH_2NH_2{\cdot}H_2O$ (0.3 mL) and the mixture was stirred at 80 °C for 8 h. The solvents were removed under reduced pressure and a solution of the crude mass in acetic anhydride (2 mL) and pyridine (2 mL) was kept at room temperature for 1 h. The solvents were removed under reduced pressure and the crude mass was passed through a short pad of SiO_2 using EtOAc as eluent. To a solution of the acetylated product in CH_3OH (10 mL) were added 20% $Pd(OH)_2$–C (100 mg) and Et_3SiH (1 mL, 6.26 mmol) and the reaction mixture was allowed to stir at room temperature for 12 h. The reaction mixture was filtered through a Celite bed and the filtering bed was washed with CH_3OH/H_2O (10 mL, 2:1 *v/v*). The combined filtrate was concentrated under reduced pressure and passed through a Sephadex LH-20 column using CH_3OH/H_2O (2:1) as eluent to give pure compound **2** (85 mg, 55%). White powder; $[\alpha]_D^{25}$: −23 ($c = 1.2$, H_2O); IR (KBr): 3398, 2938, 1641, 1355, 1253, 1061, 697 cm^{-1}; ^1H NMR (D_2O, 500 MHz): $\delta = 5.14$ (dd, $J = 9.5$, 3.0 Hz, 1H, H-3_B), 5.06 (br s, 1H, H-2_B), 4.95 (br s, 1H, H-1_B), 4.64 (d, $J = 8.5$ Hz, 1H, H-1_A), 4.53 (d, $J = 7.5$ Hz, 1H, H-1_C), 4.19–4.16 (m, 1H, H-5_B), 4.10–3.88 (m, 6H, H-2_A, H-4_B, H-4_C, H-6_{aC}, OCH_2-), 3.84–3.75 (m, 5H, H-2_C, H-5_A, H-6_{abA}, H-6_{bC}), 3.68–3.51 (m, 4H, H-3_A, H-3_C, H-4_A, H-5_C), 3.29–3.24 (m, 2H, NCH_2), 2.17, 2.03, 2.02 (3 s, 12H, 4COCH_3), 1.36 (d, $J = 6.5$ Hz, 3H, CCH_3); ^{13}C NMR (D_2O, 125 MHz): $\delta = 174.6$ (2C), 172.9 (2C) (4$COCH_3$), 101.9 (C1_C), 100.2 (C1_A), 98.2 (C1_B), 82.1 (C4_A), 75.8 (2C, C3_C, C4_C), 74.6 (C3_A), 71.4 (C3_B), 70.2 (C2_B), 70.0 (C5_A), 68.2 (C5_B), 67.7 (C5_C), 67.6 (C4_B), 65.7 (OCH_2), 61.0 (C6_C), 60.5 (C6_A), 54.9 (C2_A), 52.7 (C2_C), 39.4 (NCH_2), 22.1 (2C), 20.5, 20.1 (4C, 4$COCH_3$), 16.7 (CCH_3); ESI-MS: 720.2 $[M+Na]^+$; Anal. calcd for $C_{28}H_{47}N_3O_{17}$ (697.29): C 48.20, H 6.79%; found: C 48.03, H 7.00%.

2-Aminoethyl *O*-(α-D-galactofuranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→4)-*O*-(2,3-di-*O*-acetyl-α-L-rhamnopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside (3): To a solution of compound **13** (400 mg, 0.22 mmol) in EtOH (10 mL) was added $NH_2NH_2{\cdot}H_2O$ (0.3 mL) and the mixture was stirred at 80 °C for 8 h. The solvents were removed under reduced pressure and a solution of the crude mass in acetic anhydride (2 mL) and pyridine (2 mL) was kept at room temperature for 1 h. The solvents were removed under reduced pressure and the crude mass was passed through a short pad of SiO_2 using EtOAc as eluent. To a solution of the acetylated product in CH_3OH (10 mL) were added 20% $Pd(OH)_2$–C (100 mg) and Et_3SiH (1.2 mL, 7.51 mmol) and the reaction mixture was allowed to stir at room temperature for 12 h. The reaction mixture was filtered through a Celite bed and the filtering bed was washed with CH_3OH/H_2O (10 mL; 2:1 *v/v*). The combined filtrate was concentrated under reduced pressure and passed through a Sephadex LH-20 column using CH_3OH/H_2O (2:1) as eluent to give pure compound **3** (95 mg, 50%). White powder; $[\alpha]_D^{25}$: +26 ($c = 1.2$, H_2O); IR (KBr): 3412, 2992, 1633, 1373, 1267, 1091, 687 cm^{-1}; ^1H NMR (D_2O, 500 MHz): $\delta = 5.00$ (d, $J = 8.5$ Hz, 1H, H-1_A), 4.98–4.96 (m, 2H, H-2_B, H-3_B), 4.81 (d, $J = 3.5$ Hz, 1H, H-1_D), 4.79 (br s, 1H, H-1_B), 4.48 (d, $J = 7.0$ Hz, 1H, H-1_C), 4.21–4.19 (m, 1H, H-3_D), 4.10–4.09 (m, 1H, H-5_B), 4.00–3.98 (m, 2H, H-2_C, H-2_D), 3.92–3.89 (m, 3H, H-3_A, H-4_C, OCH–), 3.79–3.62 (m, 10H, H-2_A, H-3_C, H-4_B, H-4_D, H-5_A, H-6_{abA}, H-6_{abC}, OCH-), 3.50–3.36 (m, 5H, H-4_A, H-5_C, H-5_D, H-6_{abD}), 3.12–3.06 (m, 2H, NCH_2), 2.00, 1.95, 1.90, 1.87 (4 s, 12H, 4COCH_3), 1.20–1.10 (m, 3H, CCH_3); ^{13}C NMR (D_2O, 125 MHz): $\delta = 174.6$, 173.0, 172.9, 172.8 (4C, 4$COCH_3$), 102.6 (C1_D), 100.2 (C1_C), 98.1 (C1_B), 97.6 (C1_A), 82.1 (C4_A), 80.0 (C3_C), 78.3 (C4_C), 76.1 (C4_D), 75.9 (C2_D), 75.8 (C5_D), 72.4 (C3_D), 70.8 (C3_B), 70.6 (C2_B), 69.8 (C3_A), 69.1 (C5_A), 68.3 (C5_B), 67.9 (C5_C), 66.1 (C4_B), 65.6 (OCH_2), 62.6 (C6_D), 60.4 (C6_C), 59.1 (C6_A), 54.9 (C2_A), 50.6 (C2_C), 39.3 (NCH_2), 22.1, 21.8, 20.3, 20.0 (4C, 4$COCH_3$), 16.8 (CCH_3); MALDI-MS: 882.3 $[M+Na]^+$; Anal. calcd for $C_{34}H_{57}N_3O_{22}$ (859.34): C 47.49, H 6.68%; found: C 47.30, H 6.90%.

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