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First synthesis of a pentasaccharide repeating unit of the *O*-antigenic polysaccharide from enterohaemorrhagic *Escherichia coli* O48:H21

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ABSTRACT

A concise synthesis of a pentasaccharide as its 4-methoxyphenyl glycoside, found in the *O*-antigenic polysaccharide of enterohaemorrhagic *Escherichia coli* O48:H21 has been achieved for the first time in excellent yield. Most of the intermediate steps are high yielding and the stereooutcome of each glycosylation step was excellent. Stereoselective glycosylation and removal of the 4-methoxybenzyl group were achieved in one-pot by tuning the reaction conditions. A late-stage TEMPO-mediated oxidation strategy has been adopted for the oxidation of a primary hydroxyl group to carboxylic acid.

1. Introduction

Escherichia coli (*E. coli*) is a facultative Gram-negative bacterium present predominantly in the colonic flora of animals and human. The species is divided into different serotypes based on the immunogenicity of the surface oligosaccharide structures. In general, the strains are described as O:K:H serotypes, where O stands for O-antigen, that is, the polysaccharide portion of the lipopolysaccharide; K is the capsular polysaccharide, and H is the flagella antigen. To date, more than 170 different O-antigens and over 100 capsular polysaccharides have been identified within the species.[1] In general, pathogenic *E. coli* strains cause three common infections, for example, (i) enteric/diarrhoeal; (ii) urinary tract infections; and (iii) septicaemia/meningitis.[2] Virulent *E. coli* strains causing diarrhoeal diseases are classified in six classes, which are recognized as (i) enteropathogenic *E. coli* (EPEC); (ii) enteroinvasive *E. coli* (EIEC); (iii) enterotoxigenic *E. coli* (ETEC); (iv) enteroaggregative *E. coli* (EAEC); (v) diffusely adherent *E. coli* (DAEC); and (vi) enterohaemorrhagic *E. coli* (EHEC).[3]

Enterohaemorrhagic *E. coli* (EHEC) is mostly responsible for diarrhoea with life threatening complications, for example, haemorrhagic colitis (HC) and haemolytic–uraemic syndrome (HUS).[3] EHEC strains are also called 'verotoxigenic *E. coli*' (VTEC) because of their toxic effect on cultured Vero cells. They also produce a bacteriophage-mediated Shiga-like toxin and are termed as 'Shiga toxin-producing *E. coli*' (STEC).[4] The pathological symptoms due to the HC and HUS are the result of the action of Shiga toxin (Stx) on endothelial cells. The best-known Shigatoxin producing EHEC strain is *E. coli* O157:H7, which is the frequent cause of fatal intestinal infections and is associated with several outbreaks of the disease in the Europe, America and Japan.[5–8] In addition to *E. coli* O157:H7, several other *E. coli* serotypes have been reported to be associated with the STEC category.[9] Recent structural analysis of the O-antigen of enterohaemorrhagic *E. coli* (EHEC) O48:H21 showed that it contains a pentasaccharide repeating unit with a D-galactouronic acid at the non-reducing terminal through an α-linkage (Fig. 1).[10] It has been well established that the immunochemical activities of the glyco-vaccines depend on the bacterial O-antigens, which make them attractive targets for the development of glycoconjugate vaccine candidates.[11] Recently, several reports have appeared in the literature for the synthesis and evaluation of glycoconjugate vaccines against bacterial infections.[11] In order to understand the antigenicity of the O-antigen and its role in the pathogenicity on a molecular level it is necessary to have a considerable amount of the pentasaccharide in hand. As the natural source cannot provide the required quantity of the oligosaccharides for their biological evaluation, development of a chemical synthetic strategy for the preparation of the target pentasaccharide is always useful. For the immunochemical studies, it is often required to conjugate the oligosaccharide moiety with a

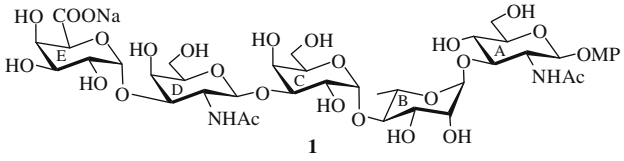

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Figure 1. Structure of the synthesized pentasaccharide repeating unit of the *O*-antigenic polysaccharide of enterohaemorrhagic *Escherichia coli* O48:H21 as its 4-methoxyphenyl (MP) glycoside.

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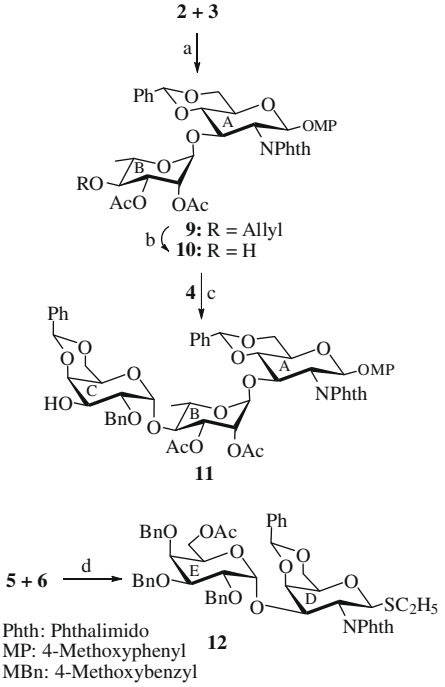
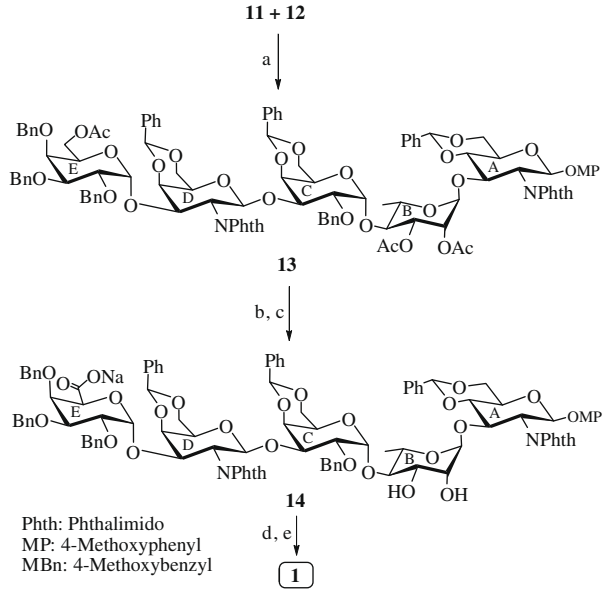
carrier protein through a spacer linker. Therefore, synthesis of an oligosaccharide moiety with a temporary protecting group at the reducing end would be useful for its ready removal whenever necessary.[12] In this direction, for the first time we herein report an efficient chemical synthesis of the pentasaccharide repeating unit of the *O*-antigenic polysaccharide from enterohaemorrhagic *E. coli* O48:H21 as its 4-methoxyphenyl glycoside using a block synthetic approach.

2. Results and discussion

The synthesis of the pentasaccharide **1** as its 4-methoxyphenyl glycoside (Fig. 1) was achieved using a block synthetic strategy, in which, a trisaccharide derivative **11** was stereoselectively coupled with a disaccharide thioglycoside derivative **12** under iodonium-mediated thioglycoside activation conditions to furnish the pentasaccharide derivative **13** (Schemes 1 and 2). The pentasaccharide derivative **13** was transformed to the target pentasaccharide **1** using a late-stage TEMPO-mediated oxidation of a primary hydroxyl group followed by deprotection of functional groups (Scheme 2). For this purpose, trisaccharide glycosyl acceptor **11** and disaccharide thioglycoside donor **12** were prepared from the suitably protected monosaccharide derivatives (Fig. 2, Scheme 3) derived from the commercially available reducing sugars following a sequence of reactions reported in the literature. 4-Methoxyphenyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside **2**[13] was prepared from D-glucosamine hydrochloride using reported reaction conditions. Ethyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside **7**,[14] prepared from L-rhamnose in four steps was transformed into ethyl 2,3-di-*O*-acetyl-4-*O*-allyl-1-thio-α-D-rhamnopyranoside **3** following a sequence of reactions consisting of allylation, removal of the isopropylidene ketal and acetylation in overall 90% yield. Ethyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside **8**,[15] prepared from D-galactose in four steps was subjected to a set of reaction sequences involving selective



Scheme 1. Reagents and conditions: (a) *N*-iodosuccinimide (NIS), TMSOTf, CH_2Cl_2, −20 °C, 45 min, 91%; (b) $PdCl_2$, $NaOAc{\cdot}3H_2O$, $AcOH–H_2O$, room temperature, 12 h, 79%; (c) NIS, TMSOTf, CH_2Cl_2, −50 °C, 45 min, then 0 °C for 30 min, 78%; (d) TfOH, CH_2Cl_2, −20 °C, 2 h, 85%.



Scheme 2. Reagents and conditions: (a) NIS, TMSOTf, CH_2Cl_2, −20 °C, 1 h, 75%; (b) CH_3ONa, CH_3OH, room temperature, 40 min; (c) (i) NaBr, CH_2Cl_2, H_2O, TBAB, TEMPO, $NaHCO_3$, NaOCl, 0–5 °C, 3 h ; (ii) *tert*-butanol, 2-methyl-but-2-ene, $NaClO_2$, NaH_2PO_4, room temperature, 3 h, 78%; (d) (i) ethylene diamine, *n*-butanol, 105 °C, 8 h; (ii) acetic anhydride, pyridine, room temperature, 6 h; (iii) CH_3ONa, CH_3OH, room temperature, 5 h; (e) H_2, 20% $Pd(OH)_2$–C, room temperature, 24 h, 71%.

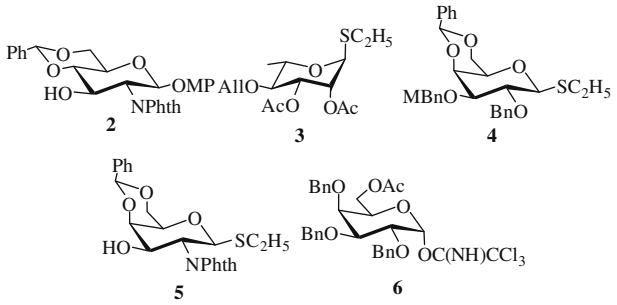
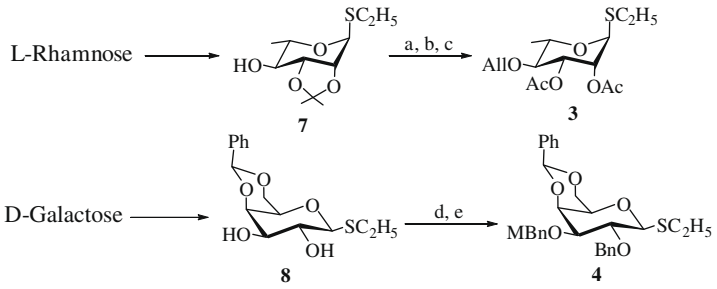


Figure 2. Suitably functionalized monosaccharide intermediates used for the construction of the pentasaccharide **1**.

4-methoxybenzylation followed by benzylation to furnish ethyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(4-methoxybenzylidene)-1-thio-β-D-galactopyranoside **4** in 88% overall yield. Compounds **5**[16] and **6**[17] were prepared following earlier literature reports (Scheme 3).

Stereoselective glycosylation of compound **2** with thioglycoside derivative **3** in the presence of *N*-iodosuccinimide (NIS) and trimethylsilyl trifluoromethanesulfonate (TMSOTf)[18] furnished disaccharide derivative **9** in 91% yield, which was confirmed from its spectroscopic analysis. The allyl ether was removed from the disaccharide derivative **9** by the reaction of palladium chloride in acetic acid–sodium acetate buffer[19] to give compound **10** in 79% yield. A one-pot 1,2-*cis* directing glycosylation of compound **10** with thioglycoside derivative **4** followed by the removal of the 4-methoxybenzyl ether protection[20] from the trisaccharide derivative formed in situ was achieved in the presence of a NIS-TMSOTf combination by tuning the reaction condition to furnish trisaccharide derivative **11** in 78% yield. The presence of signals at δ 5.76 (d, J = 8.4 Hz, 1H, H-1_A), 5.60 (s, 1H, PhC*H*), 5.52 (s, 1H, PhC*H*), 4.91 (d, J = 3.1 Hz, 1H, H-1_C), 4.69–4.52 (m, H-1_B and other protons) in ^{1}H NMR and δ 101.9 (PhCH), 100.8 (PhCH), 99.8 (C-1_C), 98.1 (C-1_A), 97.1 (C-1_B) in the ^{13}C NMR spectra confirmed the exclusive formation of



Scheme 3. Reagents and conditions: (a) allyl bromide, NaOH, TBAB, THF, room temperature, 6 h; (b) 80% aq AcOH, 80 °C, 1.5 h; (c) acetic anhydride, pyridine, room temperature, 2 h, overall 90%; (d) Bu_2SnO, CH_3OH, 80 °C, 3 h; (ii) 4-methoxybenzyl chloride, DMF, 80 °C, 10 h; (e) benzyl bromide, NaOH, TBAB, THF, room temperature, 4 h, overall 88%.

compound **11**. In this case, an exclusive formation of the α-glycoside was achieved using a non-participating benzyl group at the C-2 position of D-galactosyl thioglycoside donor **4** in the first step of the one-pot reaction (Scheme 1).

In another experiment, disaccharide thioglycoside derivative **12** was synthesized by acid-catalyzed[21] stereoselective coupling of thioglycoside derivative **5** with D-galactose derived trichloroacetimidate derivative **6** in 85% yield, which was characterized from its spectral analysis [δ 5.24 (s, PhC*H*), 5.21 (d, J = 10 Hz, H-1_D), 4.97 (d, J = 3.1 Hz, H-1_E) in the ^{1}H NMR and δ 100.9 (Ph*C*H), 98.3 (C-1_E), 80.3 (C-1_D) in the ^{13}C NMR spectra] (Scheme 1). With trisaccharide glycosyl acceptor **11** and disaccharide thioglycoside donor **12**, the iodonium ion-mediated stereoselective glycosylation of compound **11** with compound **12** in the presence of NIS-TMSOTf[18] furnished desired pentasaccharide derivative **14** in 75% yield. The formation of pentasaccharide derivative **13** was confirmed from its spectral analysis [δ 101.5 (PhCH), 100.9 (Ph*C*H), 100.3 (PhCH), 100.1 (C-1_C), 99.1 (C-1_A), 98.2 (C-1_D), 98.1 (C-1_E), 97.6 (C-1_B) in the ^{13}C NMR spectra]. Compound **13** was transformed into pentasaccharide acid derivative **14** in 78% overall yield following a sequence of reactions involving deacetylation and selective TEMPO-mediated oxidation[22] of the primary hydroxyl group to the carboxylic group in biphasic reaction conditions without affecting the secondary hydroxyl groups present in the molecule. Conversion of the *N*-phthalimido group to acetamido group[23] followed by hydrogenolysis over Pearlmann's catalyst[24] of compound **14** furnished the target pentasaccharide **1** as its 4-methoxyphenyl glycoside in 71% overall yield. The presence of signals at δ 5.47 (d, J = 7.9 Hz, H-1_A), 5.08 (d, J = 8.3 Hz, H-1_D), 4.76 (br s, H-1_B), 4.47 (br s, H-1_C), 4.26 (br s, H-1_E) in the ^{1}H NMR and at δ 100.4 (C-1_E), 100.2 (C-1_D), 99.7 (C-1_C), 97.6 (C-1_B), 97.1 (C-1_A) in the ^{13}C NMR spectra confirmed the successful formation of pentasaccharide **1** (Scheme 2).

3. Conclusion

In conclusion, the first total synthesis of a pentasaccharide repeating unit of the O-antigen of *E. coli* O48: H21 strain, as its 4-methoxyphenyl glycoside, has been achieved in a concise manner using a block synthetic strategy. Most of the intermediates are solid and all glycosylation steps are highly stereoselective and reproducible for scale-up. A one-pot reaction condition has been applied for the stereoselective glycosylation followed by removal of 4-methoxybenzyl group protection. Selective TEMPO-mediated oxidation of a primary hydroxyl group in a pentasaccharide derivative was achieved using a two-step, one-pot phase transfer oxidation protocol without affecting other secondary hydroxyl groups present in the molecules. 4-Methoxybenzyl group has been chosen as the temporary protecting group at the reducing end.

4. Experimental

4.1. General methods

All the 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 in a hot plate. Silica gel 230–400 mesh was used for column chromatography. ^{1}H and ^{13}C NMR, 2D COSY, HSQC, NOESY spectra were recorded on Brucker Advance DPX 300 MHz using $CDCl_3$ and D_2O as solvents and TMS as an internal reference unless stated otherwise. Chemical shift value is expressed in δ ppm. ESI-MS was recorded on a MICROMASS QUTTRO II triple quadrupole mass spectrometer. Elementary analysis was carried out on Carlo ERBA-1108 analyzer. Optical rotations were measured at 25 °C on a Rudolf Autopol III polarimeter. Commercially available grades of organic solvents of adequate purity are used in many reactions.

4.1.1. Ethyl 2,3-di-*O*-acetyl-4-*O*-allyl-1-thio-α-L-rhamnopyranoside 3

To a solution of compound **7** (5 g, 20.13 mmol) in anhydrous THF (25 mL) were added powdered sodium hydroxide (2.5 mg, 62.5 mmol), allyl bromide (5 mL, 57.78 mmol) and tetrabutylammonium bromide (200 mg) and the reaction mixture was allowed to stir at room temperature for 6 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (150 mL). The organic layer was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. A solution of the crude product in 80% aq AcOH (80 mL) was allowed to stir at 80 °C for 1.5 h and evaporated to dryness under reduced pressure. A solution of the crude product in acetic anhydride–pyridine (50 mL; 1:1 v/v) was stirred at room temperature for 2 h. The solvents were removed under reduced pressure and the crude product was purified over SiO_2 using hexane–EtOAc (5:1) as eluant to give pure **3** (6 g, 90%) as white solid; R_f (20% EtOAc–hexane) 0.3; mp 62–64 °C; $[\alpha]_D$ −190 (c 1.0, $CHCl_3$); ν_{max}: (KBr) 3020, 2361, 1745, 1603, 1369, 1216, 1097, 834, 762 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.92–5.79 (m, 1H, C*H*=CH_2), 5.30–5.13 (m, 5H, H-1, H-2, H-3, CH=C*H*$_2$), 4.19–4.07 (m, H-5, O–C*H*$_2$–CH=CH_2), 3.38 (t, J = 9.6 Hz, 1H, H-4), 2.69–2.55 (m, 2H, SC*H*$_2$CH$_3$), 2.14, 2.05 (2 s, 6H, 2COC*H*$_3$), 1.33 (t, J = 7.4 Hz, 3H, SCH_2CH_3), 1.28 (d, J = 6.1 Hz, 3H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 169.4 (2*C*OCH$_3$), 134.6 (*C*H=CH_2), 116.7 (CH=*C*H$_2$), 81.8 (C-1), 78.7 (C-4), 73.7 (PhC*H*$_2$), 72.1 (C-3), 71.8 (C-2), 68.2 (C-5), 25.3 (SC*H*$_2$CH$_3$), 20.9, 20.8 (2COC*H*$_3$), 17.8 (C*C*H$_3$), 14.9 (SCH_2CH_3); ESI-MS: 355.1 [M+Na]$^+$, Anal. Calcd for $C_{15}H_{24}O_6S$ (332.13): C, 54.20; H, 7.28. Found: C, 54.04; H, 7.42.

4.1.2. Ethyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(4-methoxybenzy)-1-thio-β-D-galactopyranoside 4

To a solution of compound **8** (5 g, 16 mmol) in dry CH_3OH (120 mL) was added dibutyltin oxide (4.8 g, 19.28 mmol) and the

reaction mixture was allowed to stir at 80 °C for 3 h and concentrated under reduced pressure. To a solution of the stannylidene acetal in anhydrous DMF (30 mL) was added 4-methoxybenzyl chloride (3.2 mL, 23.6 mmol) and the reaction mixture was allowed to stir at 80 °C for 10 h and the solvents were evaporated under reduced pressure. To a solution of the crude product in dry THF (50 mL) were added powdered NaOH (2 g, 50 mmol), benzyl bromide (3.8 mL, 31.95 mmol) and tetrabutylammonium bromide (100 mg) and the reaction mixture was allowed to stir at room temperature for 4 h. The reaction was quenched with CH_3OH (5 mL) and the solvents were removed under reduced pressure. The crude product was dissolved in CH_2Cl_2 (150 mL) and the organic layer was washed with water, dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane–EtOAc (8:1) as eluant to give pure **4** (7.4 g, 88%) as a white solid; R_f (30% EtOAc–hexane) 0.5; mp 140–142 °C; $[\alpha]_D^{25} = +2.2$ (*c* 1.0, $CHCl_3$); ν_{max}: (KBr) 3441, 2863, 2361, 1616, 1515, 1456, 1400, 1352, 1254, 1172, 1096, 1058, 1028, 1005, 817, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.57–7.28 (m, 12H, Ar-H), 6.85 (d, *J* = 8.5 Hz, 2H, Ar-H), 5.47 (s, 1H, PhC*H*), 4.93–4.82 (Abq, *J* = 10.2 Hz, 2H, PhCH_2), 4.70 (br s, 2H, CH_3OPhCH_2), 4.44 (d, *J* = 9.6 Hz, 1H, H-1), 4.30 (d, *J* = 12.3 Hz, 1H, H-6_A), 4.12 (d, *J* = 3.2 Hz, 1H, H-4), 3.96 (d, *J* = 12.3 Hz, 1H, H-6_b), 3.88 (t, *J* = 9.5 Hz, 1H, H-2), 3.57 (dd, *J* = 9.2, 3.4 Hz, 1H, H-3), 3.34 (br s, 1H, H-5), 2.88–2.73 (m, 2H, SCH_2CH_3), 1.36 (t, *J* = 7.4 Hz, 3H, SCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 138.5–113.8 (Ar-C), 101.4 (PhCH), 84.4 (C-1), 80.6 (C-5), 76.8 (C-3), 75.6 (PhCH_2), 74.0 (CH_3OPhCH_2), 71.4 (C-4), 69.8 (C-2), 69.4 (C-6), 55.1 (OCH_3), 23.7 (SCH_2CH_3), 15.1 (SCH_2CH_3); ESI-MS: 545.2 $[M+Na]^+$. Anal. Calcd for $C_{30}H_{34}O_6S$ (522.21): C, 68.94; H, 6.56. Found: C, 68.78; H, 6.75.

4.1.3. 4-Methoxyphenyl (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 **2** (5 g, 9.93 mmol) and compound **3** (4 g, 12 mmol) in anhydrous CH_2Cl_2 (60 mL) was added MS 4 Å (5 g) and the reaction mixture was allowed to stir at room temperature for 1 h under argon. The reaction mixture was cooled to −20 °C and *N*-iodosuccinimide (NIS; 3.8 g, 16.88 mmol) followed by trimethylsilyltrifluoromethane sulfonate (TMSOTf; 30 μL) was added and the reaction mixture was allowed to stir at the same temperature for 45 min. The reaction mixture was quenched with Et_3N (0.1 mL), filtered through a Celite® bed and washed with CH_2Cl_2 (150 mL). The organic layer was washed with 5% aq $Na_2S_2O_3$, satd aq $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated to dryness. The crude product was purified over SiO_2 using hexane–EtOAc (5:1) as eluant to give pure **9** (7 g, 91%) as a white solid; R_f (30% EtOAc–hexane) 0.4; mp 166–168 °C; $[\alpha]_D^{25} = +9.3$ (*c* 1.0, $CHCl_3$); ν_{max}: (KBr) 3020, 2362, 1754, 1721, 1601, 1368, 1216, 929, 760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.81–7.28 (m, 9H, Ar-H), 6.81 (d, *J* = 9.1 Hz, 2H, Ar-H), 6.72 (d, *J* = 9.0 Hz, 2H, Ar-H), 5.81 (m, 1H, -C*H*=CH_2), 5.73 (d, *J* = 8.4 Hz, 1H, H-1_A), 5.60 (s, 1H, PhC*H*), 5.24–5.10 (m, 3H, H-3_B, –CH=CH_2), 4.73–4.65 (m, 2H, H-2_B, H-3_A), 4.59–4.52 (m, 2H, H-1_B, H-2_A), 4.44–4.13 (m, 1H, H-5_A), 3.98–3.83 (m, 6H, H-4_A, H-5_B, H-6_{abA}, CH_2–CH=CH_2O), 3.71 (s, 3H, OCH_3), 3.15 (t, *J* = 9.7 Hz, 1H, H-4_B), 1.99, 1.79 (2 s, 6H, 2COCH_3), 0.74 (d, *J* = 6.1 Hz, 3H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 169.1 (2*C*OCH$_3$), 168.5, 168.4 (Phth), 155.6–134.6 (Ar-C), 134.0 (–*C*H=CH_2), 131.6–118.7 (Ar-C), 116.3 (–CH=*C*H_2), 102.0 (PhCH), 98.2 (C-1_A), 97.5 (C-1_B), 80.2 (C-4_A), 78.5 (C-4_B), 74.5 (C-3_A), 73.1 (O-*C*H_2–), 70.9 (C-3_B), 70.3 (C-2_B), 68.6 (C-6_A), 67.8 (C-5_A), 66.6 (C-5_B), 56.2 (C-2_A), 55.4 (OCH_3), 20.9, 20.5 (2COCH_3), 17.0 (CCH_3); ESI-MS: 796.3 $[M+Na]^+$. Anal. Calcd for $C_{41}H_{43}NO_{14}$ (773.27): C, 63.64; H, 5.60. Found: C, 63.48; H, 5.73.

4.1.4. 4-Methoxyphenyl (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** (6 g, 7.75 mmol) in AcOH-H_2O (90 mL; 20:1 v/v) were added NaOAc·$3H_2O$ (4.3 g, 31.62 mmol) and $PdCl_2$ (1 g, 5.64 mmol) and the reaction mixture was allowed to stir at room temperature for 12 h. The solvents were removed under reduced pressure and the crude product was purified over SiO_2 using hexane–EtOAc (4:1) as eluant to give pure **10** (4.5 g, 79%) as a white solid; R_f (30% EtOAc–hexane) 0.3; mp 100–102 °C; $[\alpha]_D^{25} = -136.8$ (*c* 1.0, $CHCl_3$); ν_{max}: (KBr) 3471, 2921, 2363, 1747, 1716, 1386, 1225, 1099, 767 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.88–7.28 (m, 9H, Ar-H), 6.82 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.72 (d, *J* = 9.0 Hz, 2H, Ar-H), 5.74 (d, *J* = 8.4 Hz, 1H, H-1_A), 5.60 (s, 1H, PhC*H*), 5.07 dd, *J* = 6.5 Hz, 1H, H-3B), 4.72–4.65 (m, 2H, H-2_B, H-3_A), 4.57–4.51 (m, 2H, H-1_B, H-2_A), 4.44–4.42 (m, 1H, H-5_A), 3.96–3.75 (m, 4H, H-4_A, H-5_B, H-6_{abA}), 3.72 (s, 3H, OCH_3), 3.52 (m, 1H, H-4_B), 1.99, 1.79 (2 s, 6H, 2COCH_3), 0.76 (d, *J* = 6.1 Hz, 3H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.1, 169.0 (2*C*OCH$_3$), 168.5, 168.4 (Phth), 155.7–114.5 (Ar-C), 102.1 (PhCH), 98.2 (C-1_A), 97.6 (C-1_B), 80.2 (C-4_A), 74.8 (C-3_A), 71.5 (C-3_B), 71.4 (C-4_B), 70.6 (C-2_B), 69.0 (C-5_A), 68.6 (C-6_A), 66.6 (C-5_B), 56.3 (C-2_A), 55.4 (OCH_3), 20.8, 20.5 (2COCH_3), 16.7 (CCH_3); ESI-MS: 756.2 $[M+Na]^+$. Anal. Calcd for $C_{38}H_{39}NO_{14}$ (733.24): C, 62.20; H, 5.36. Found: C, 62.03; H, 5.50.

4.1.5. 4-Methoxyphenyl (2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-(1→4)-(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** (3 g, 4.08 mmol) and compound **4** (2.6 g, 4.97 mmol) in anhydrous CH_2Cl_2 (60 mL) was added MS 4 Å (5 g) and the reaction mixture was allowed to stir at room temperature for 1 h under argon. The reaction mixture was cooled to −50 °C and NIS (1.3 g, 5.77 mmol) followed by TMSOTf (25 μL) was added to it and the reaction mixture was allowed to stir at the same temperature for 45 min. After consumption of the starting materials (TLC; 20% EtOAc–hexane) the reaction mixture was warmed up to 0 °C and allowed to stir at 0 °C for 30 min. The reaction mixture was filtered through a Celite® bed and washed with CH_2Cl_2 (100 mL). The organic layer was washed with 5% aq $Na_2S_2O_3$, satd aq $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated to dryness. The crude product was purified over SiO_2 using hexane–EtOAc (5:1) as eluant to give pure **11** (3.4 g, 77%) as a white solid; R_f (30% EtOAc–hexane) 0.3; mp 121–123 °C; $[\alpha]_D^{25} = -4$ (*c* 1.0, $CHCl_3$); ν_{max}: (KBr) 3471, 2929, 2361, 1747, 1717, 1386, 1223, 1097, 1044, 767 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.88–7.29 (m, 19H, Ar-H), 6.82 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.73 (d, *J* = 9.0 Hz, 2H, Ar-H), 5.76 (d, *J* = 8.4 Hz, 1H, H-1_A), 5.60 (s, 1H, PhC*H*), 5.52 (s, 1H, PhC*H*), 5.21 (m, 1H, H-3_B), 4.91 (d, *J* = 3.1 Hz, 1H, H-1_C), 4.74 (d, *J* = 11.7 Hz, 1H, PhCH_{2a}), 4.69–4.52 (m, 5H, H-1_B, H-2_A, H-3_A, H-2_B, PhCH_{2b}), 4.43 (dd, *J* = 4.3 Hz, 1H, H-5_A), 4.18 (d, *J* = 2.7 Hz, 1H, H-4_C), 4.13 (d, *J* = 12.8 Hz, 1H, H-6_{aC}), 4.01–3.93 (m, 2H, H-3_C, H-6_{bC}), 3.91–3.76 (m, 5H, H-2_C, H-4_A, H-5_B, H-6_{abA}), 3.72 (s, 3H, OCH_3), 3.68 (br s, 1H, H-5_C), 3.28 (t, *J* = 9.1 Hz, 1H, H-4_B), 1.98, 1.83 (2 s, 6H, 2COCH_3), 0.94 (d, *J* = 6.1 Hz, 3H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.6, 169.0 (2*C*OCH$_3$), 168.5, 168.4 (Phth), 155.6–114.4 (Ar-C), 101.9 (PhCH), 100.8 (PhCH), 99.8 (C-1_C), 98.1 (C-1_A), 97.1 (C-1_B), 80.3 (C-4_B), 80.2 (C-4_A), 77.7 (C-3_C), 76.1 (C-5_B), 74.3 (C-3_A), 73.3 (C-4_C), 70.5 (PhCH_2), 69.8 (C-2_B), 69.1 (C-3_B), 68.6 (C-6_C), 68.4 (C-6_A), 67.3 (C-5_A), 66.5 (C-2_C), 63.3 (C-5_C), 56.1 (C-2_A), 55.3 (OCH_3), 21.1, 20.4 (2COCH_3), 17.4 (CCH_3); ESI-MS: 1096.3 $[M+Na]^+$. Anal. Calcd for $C_{58}H_{59}NO_{19}$ (1073.37): C, 64.86; H, 5.54. Found: C, 64.68; H, 5.75.

4.1.6. Ethyl (6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-1-thio-β-D-galactopyranoside 12

To a solution of compound **5** (2 g, 4.37 mmol) and compound **6** (4.2 g, 6.60 mmol) in anhydrous CH_2Cl_2 (40 mL) was added MS 4 Å (4 g) and the reaction mixture was allowed to stir at room temperature for 20 min. under argon. The reaction mixture was cooled to −20 °C and TfOH (50 μL) was added after which it is allowed to stir at the same temperature for 2 h. The reaction mixture was quenched with Et_3N (0.1 mL), filtered through a Celite® bed and washed with CH_2Cl_2 (100 mL). The organic layer was washed with satd aq $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated to dryness. The crude product was purified over SiO_2 using hexane–EtOAc (6:1) as eluant to give pure **12** (3.4 g, 85%) as a white solid; R_f (30% EtOAc–hexane): 0.4; mp 142–144 °C; $[\alpha]_D^{25} = +81$ (*c* 1.0, $CHCl_3$); ν_{max}: (KBr) 33427, 3020, 2361, 1360, 1216, 726, 670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.79–7.67 (m, 4H, Ar-H), 7.48–7.15 (m, 20H, Ar-H), 5.24 (s, 1H, PhC*H*), 5.21 (d, *J* = 10 Hz, 1H, H-1_D), 4.97 (d, *J* = 3.1 Hz, 1H, H-1_E), 4.82 (d, *J* = 11.5 Hz, 1H, PhCH_{2a}), 4.78 (t, *J* = 10.9 Hz, 1H, H-2_D), 4.71–4.67 (m, 2H, PhCH_2), 4.60–4.51 (m, 3H, H-3_D, PhCH_2), 4.43 (d, *J* = 11.5 Hz, 1H, PhCH_{2a}), 4.31–4.27 (m, 2H, H-4_D, H-4_E), 3.94–3.91 (m, 1H, H-2_E), 3.83 (d, *J* = 11.9 Hz, 1H, H-6_{aE}), 3.77–3.71 (m, 2H, H-3_E, H-6_{aD}), 3.60–3.54 (m, 2H, H-5_D, H-6_{bE}), 3.46 (s, 1H, H-5_E), 3.27–3.24 (m, 1H, H-6_{bD}), 2.85–2.68 (m, 2H, SCH_2CH$_3$), 1.23 (t, *J* = 7.5 Hz, 3H, SCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8 (*C*OCH$_3$), 168.6, 168.4 (Phth), 138.6–123.3 (Ar-C), 100.9 (PhCH), 98.3 (C-1_E), 80.3 (C-1_D), 78.6 (C-3_E), 76.2 (C-3_D), 75.6 (C-2_E), 74.4 (PhCH$_2$), 74.2 (C-5_D), 73.4 (C-4_D), 73.3 (PhCH$_2$), 73.1 (PhCH$_2$), 70.2 (C-5_E), 69.6 (C-4_E), 69.5 (C-6_D), 22.7 (SCH_2CH$_3$), 20.8 (CO*C*H$_3$), 14.9 (SCH$_2$CH_3); ESI-MS: 938.4 $[M+Na]^+$. Anal. Calcd for $C_{52}H_{53}NO_{12}S$ (915.33): C, 68.18; H, 5.83. Found: C, 68.0; H, 6.0.

4.1.7. 4-Methoxyphenyl (6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl)-(1→3)-(4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-D-galactopyranosyl)-(1→3)-(2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-(1→4)-(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 **11** (1.5 g, 1.38 mmol) and compound **12** (1.5 g, 1.64 mmol) in anhydrous CH_2Cl_2 (20 mL) was added MS 4 Å (2 g) and the reaction mixture was allowed to stir at room temperature for 1 h under argon. The reaction mixture was cooled to −20 °C and NIS (450 mg, 2.0 mmol) followed by TMSOTf (5 μL) was added to it and the reaction mixture was allowed to stir at the same temperature for 1 h. The reaction mixture was quenched with Et_3N (0.1 mL), filtered through a Celite® bed and washed with CH_2Cl_2 (100 mL). The organic layer was washed with 5% aq $Na_2S_2O_3$, satd aq $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated to dryness. The crude product was purified over SiO_2 using hexane–EtOAc (3:1) as eluant to give pure **13** (2 g, 75%) as a white solid; R_f (30% EtOAc–hexane) 0.3; mp 127–129 °C; $[\alpha]_D^{25} = +66$ (*c* 1.0, $CHCl_3$); ν_{max}: (KBr) 3469, 2926, 2860, 2361, 1717, 1457, 1387, 1225, 1099, 1046, 725 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.90–6.92 (m, 43H, Ar-H), 6.81 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.74 (d, *J* = 9.0 Hz, 2H, Ar-H), 5.74 (d, *J* = 8.3 Hz, 1H, H-1_D), 5.59 (d, *J* = 8.5 Hz, 1H, H-1_A), 5.56 (s, 1H, PhC*H*), 5.51 (s, 1H, PhC*H*), 5.28 (s, 1H, PhC*H*), 5.25–5.22 (m, 1H, H-2_B), 5.18–5.09 (m, 1H, H-3_B), 5.07–4.96 (m, 2H, H-1_E, PhCH_{2a}), 4.88–4.82 (m, 2H, H-4_C, PhCH_{2b}), 4.78–4.66 (m, 3H, H-1_C, H-2_A, H-3_D), 4.64–4.54 (m, 7H, H-1_B, H-2_D, H-3_A, 2PhCH_2), 4.51–4.42 (m, 3H, H-3_C, PhCH_2), 4.34–4.17 (m, 3H, H-4_D, H-4_E, H-6_{aE}), 4.12–4.04 (m, 2H, H-5_A, H-6_{bE}), 3.97–3.92 (m, 4H, H-2_E, H-4_A, H-6_{abA}), 3.89–3.84 (m, 2H, H-2_C, H-6_{aC}), 3.82–3.75 (m, 2H, H-3_E, H-6_{bC}), 3.73 (s, 3H, OCH_3), 3.67–3.54 (m, 3H, H-5_B, H-5_C, H-6_{aD}), 3.52–3.34 (m, 2H, H-5_D, H-5_E), 3.32–3.23 (m, 2H, H-4_B, H-6_{bD}), 1.90, 1.89, 1.84 (3 s, 9H, 3CO*C*H$_3$), 0.90 (d, *J* = 6.0 Hz, 3H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 169.1, 169.0 (3*C*OCH$_3$), 168.8–167.2 (Phth), 155.6–114.5 (Ar-C), 101.5 (PhCH), 100.9 (PhCH), 100.3 (PhCH), 100.1 (C-1_C), 99.1 (C-1_A), 98.2 (C-1_D), 98.1 (C-1_E), 97.6 (C-1_B), 80.2 (C-2_E), 79.7 (C-5_B), 78.6 (C-4_C), 78.5 (C-2_B), 77.2 (C-2_C), 76.0 (C-4_A), 75.6 (C-3_A), 75.3 (C-5_A), 74.3 (2C, 2PhCH_2), 74.1 (C-4_E), 73.4 (C-4_D), 73.2 (PhCH_2), 72.8 (PhCH_2), 70.5 (C-3_D), 69.7 (C-3_B), 69.5 (C-6_C), 69.2 (C-6_A), 69.1 (C-3_C), 68.6 (C-6_E), 67.6 (C-4_B), 66.6 (C-5_D), 66.5 (C-5_E), 63.5 (C-3_E), 62.6 (C-5_C), 61.9 (C-6_D), 56.1 (C-2_A), 55.4 (O*C*H$_3$), 52.9 (C-2_D), 20.7 (2C), 20.4 (3CO*C*H$_3$), 17.6 (C*C*H$_3$); ESI-MS: 1949.7 $[M+Na]^+$. Anal. Calcd for $C_{108}H_{106}N_2O_{31}$ (1926.68): C, 67.28; H, 5.54. Found: C, 67.10; H, 5.70.

4.1.8. 4-Methoxyphenyl (sodium 2,3,4-tri-*O*-benzyl-α-D-galactopyranosyl uronate)-(1→3)-(4,6-*O*-benzylidene-2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→3)-(2-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl)-(1→4)-(α-L-rhamnopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-acetamido-2-deoxy-β-D-glucopyranoside 14

A solution of compound **13** (1.5 g, 0.78 mmol) in 0.05 M CH_3ONa in CH_3OH (100 mL) was allowed to stir at room temperature for 45 min. and neutralized with Dowex-50W X8 (H^+) resin. The reaction mixture was filtered and concentrated under reduced pressure. To a solution of the crude product in CH_2Cl_2 (20 mL) and H_2O (3.5 mL) were added aq solution of NaBr (1 mL; 1 M), aq solution of TBAB (2 mL; 1 M), TEMPO (80 mg, 0.5 mmol), satd aq solution of $NaHCO_3$ (8 mL) and 4% aq NaOCl (10 mL) in succession and the reaction mixture was allowed to stir at 0–5 °C for 3 h. The reaction mixture was neutralized by the addition of 1 M aq HCl solution. To the reaction mixture were added *tert*-butanol (25 mL), 2-methyl-but-2-ene (30 mL; 2 M solution in THF), aq. solution of $NaClO_2$ (1 g in 5 mL) and aq solution of NaH_2PO_4 (1 g in 5 mL) and the reaction mixture was allowed to stir at room temperature for 3 h. The reaction mixture was diluted with satd aq NaH_2PO_4 and extracted with CH_2Cl_2 (100 mL). The organic layer was washed with water, dried (Na_2SO_4) and concentrated to dryness. The crude product was purified over SiO_2 using toluene–EtOAc (1:1) as eluant to give pure **14** (1.1 g, 78%) as a yellow oil; R_f (50% EtOAc–toluene) 0.2; $[\alpha]_D^{25} = +47$ (*c* 1.0, $CHCl_3$); ν_{max}: (neat) 3430, 3020, 2361, 1596, 1350, 1216, 960, 761, 670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.74–6.78 (m, 43H, Ar-H), 6.73 (d, *J* = 9.0 Hz, 2H, Ar-H), 6.64 (d, *J* = 9.0 Hz, 2H, Ar-H), 5.66 (d, *J* = 8.5 Hz, 1H, H-1_D), 5.50 (d, *J* = 8.5 Hz, 1H, H-1_A), 5.46 (br s, 2H, 2PhC*H*), 5.31 (s, 1H, PhC*H*), 4.79–4.64 (m, 4H, 2PhCH_2), 4.61–4.48 (m, 3H, H-1_B, H-1_C, H-1_E), 4.46–4.26 (m, 10H, H-2_A, H-2_D, H-3_A, H-3_C, H-3_D, H-4_C, 2PhCH_2), 4.16 (d, *J* = 11.6 Hz, 1H, H-6_{aD}), 4.12–4.04 (m, 3H, H-4_D, H-4_E, H-5_A), 4.02–3.87 (m, 4H, H-2_E, H-3_E, H-4_A, H-6_{bD}), 3.86–3.69 (m, 5H, H-2_C, H-6_{abA}, H-6_{abC}), 3.68–3.62 (m, 1H, H-3_B), 3.61 (s, 3H, OCH_3), 3.58–3.50 (m, 3H, H-2_B, H-5_B, H-5_C), 3.45–3.43 (m, 1H, H-5_E), 3.34–3.29 (m, 2H, H-4_B, H-5_D), 0.70 (d, *J* = 6.0 Hz, 3H, CCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4–167.8 (Phth), 155.5–114.3 (Ar-C), 101.5 (PhCH), 100.5 (PhCH), 100.2 (PhCH), 99.6 (3C, C-1_B, C-1_C, C-1_E), 99.2 (C-1_A), 97.9 (C-1_D), 80.3 (2C, C-2_E, C-5_B), 77.7 (C-2_B), 77.1 (C-4_C), 76.3 (C-2_C), 75.3 (C-4_A), 75.3 (C-5_A), 75.0 (2C, C-3_A, C-4_D), 74.5 (C-4_E), 74.2 (C-3_D), 73.3 (PhCH$_2$), 72.3 (PhCH$_2$), 71.5 (3C, C-3C, 2PhCH$_2$), 70.3 (C-3_B), 69.3 (2C, C-6_A, C-6_C), 68.9 (C-4_B), 68.4 (C-6_D), 66.4 (2C, C-5_D, C-5_E), 66.3 (C-3_E), 63.6 (C-5_C), 56.2 (C-2_A), 55.4 (O*C*H$_3$), 53.3 (C-2_D), 17.0 (C*C*H$_3$); ESI-MS: 1837.0 $[M+1]^+$. Anal. Calcd for $C_{102}H_{97}N_2NaO_{29}$ (1836.61): C, 66.66; H, 5.32. Found: C, 66.47; H, 5.50.

4.1.9. 4-Methoxyphenyl (sodium α-D-galactopyranosyl uronate)-(1→3)-(2-acetamido-2-deoxy-β-D-galactopyranosyl)-(1→3)-(α-D-galactopyranosyl)-(1→4)-(α-L-rhamnopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside 1

To a solution of compound **15** (1 g, 0.54 mmol) in *n*-butanol (25 mL) was added ethylene diamine (0.2 mL, 3.0 mmol) and the

reaction mixture was allowed to stir at 105 °C for 8 h and the solvents were removed under reduced pressure. A solution of the crude mass in acetic anhydride–pyridine (20 mL, 1:1 v/v) was kept at room temperature for 6 h and the solvents were removed under reduced pressure. A solution of the crude mass in 0.1 M sodium methoxide (30 mL) was allowed to stir at room temperature for 5 h and neutralized with Amberlite IR-120 (H^+) resin. The reaction mixture was filtered and evaporated to dryness. To a solution of the crude product in CH_3OH (30 mL) was added 20% $Pd(OH)_2$–C (300 mg) and the reaction mixture was allowed to stir at room temperature under a positive pressure of hydrogen for 24 h. The reaction mixture was filtered through a Celite® bed and then washed with CH_3OH–H_2O (60 mL; 3:1 v/v). The combined filtrate was evaporated under reduced pressure to furnish compound **1**, which was purified through a Sephadex LH-20 column using CH_3OH–H_2O (4:1) as eluant to give pure compound **1** (415 mg, 71%) as a white amorphous powder; R_f (CH_2Cl_2–CH_3OH–H_2O = 10:5:1) 0.3; $[\alpha]_D^{25} = +77$ (*c* 1.0, H_2O); ν_{max}: (KBr) 3432, 2943, 1607, 1377, 1145, 1089, 665 cm^{-1}; ^1H NMR (300 MHz, D_2O): δ 6.42 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.21 (d, *J* = 8.8 Hz, 2H, Ar-H), 5.47 (d, *J* = 7.9 Hz, 1H, H-1_A), 5.08 (d, *J* = 8.3 Hz, 1H, H-1_D), 4.76 (br s, 1H, H-1_B), 4.47 (br s, 1H, H-1_C), 4.40 (br s, 1H, H-4_D), 4.26 (br s, 1H, H-1_E), 4.08–3.85 (m, 5H, H-2_A, H-2_D, H-3_A, H-3_D, H-4_E), 3.76–3.44 (m, 9H, H-3_B, H-4_C, H-5_A, H-5_B, H-5_C, H-6_{abA}, H-6_{abC}), 3.43–3.22 (m, 9H, H-2_B, H-2_C, H-2_E, H-3_C, H-3_E, H-4_A, H-5_E, H-6_{abD}), 3.16 (s, 3H, OCH_3), 3.15–3.10 (m, 1H, H-5_D), 2.98–2.91 (m, 1H, H-4_B), 1.89 (s, 6H, 2NHCOCH_3), 0.72 (d, *J* = 6.1 Hz, 3H, CCH_3); ^{13}C NMR (75 MHz, D_2O): δ 174.6, 174.2 (2NH*C*OCH$_3$), 174.0 (*C*OONa), 154.7–114.6 (Ar-C), 100.4 (C-1_E), 100.2 (C-1_D), 99.7 (C-1_C), 97.6 (C-1_B), 97.1 (C-1_A), 80.7 (C-4_B), 79.4 (C-5_C), 78.7 (C-3_A), 76.4 (C-2_C), 74.8 (C-4_D), 74.6 (C-5_A), 72.0 (C-2_B), 70.6 (C-3_B), 70.5 (C-5_D), 70.2 (C-5_B), 69.2 (2C, C-3_C, C-4_E), 68.8 (2C, C-4_C, C-5_E), 68.3 (C-3_E), 67.5 (C-4_A), 67.0 (C-3_D), 65.4 (C-2_E), 60.9 (C-6_A), 60.6 (2C, C-6_C, C-6_D), 55.8 (C-2_A), 55.4 (O*C*H$_3$), 52.3 (C-2_D), 23.2, 23.0 (2NHCO*C*H$_3$), 16.7 (*C*CH$_3$); ESI-MS: 1037.5 $[M+1]^+$. Anal. Calcd for $C_{41}H_{61}N_2NaO_{27}$ (1036.64): C, 47.49; H, 5.93. Found: C, 47.27; H, 6.18.

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References

1. (a) Edwards, P. R.; Ewing, W. H. *Identification of Enterobacteriaceae*; Burgess: Minneapolis, Minn, 1972; (b) Ørskov, F.; Ørskov, I. *Can. J. Microbiol.* **1992**, *38*, 699–704.
2. Ørskov, I.; Ørskov, F.; Jann, B.; Jann, K. *Bacteriol. Rev.* **1977**, *41*, 667–710.
3. (a) Beutin, L.; Aleksic, S.; Zimmermann, S.; Gleier, K. *Med. Microbiol. Immunol.* **1994**, *183*, 13–21; (b) Russmann, H.; Kothe, E.; Schmidth, H.; Franke, S.; Harmsen, D.; Caprioli, A.; Karch, H. *J. Med. Microbiol.* **1995**, *42*, 404–410.
4. Ludwig, K.; Sarkim, V.; Bitzan, M.; Karmali, M. A.; Bobrowski, C.; Ruder, H.; Laufs, R.; Sobottka, I.; Petric, M.; Karch, H.; Müller-Wiefel, D. E. *J. Clin. Microbiol.* **2002**, *40*, 1773–1782.
5. Ezawa, A.; Gocho, F.; Saitoh, M.; Tamura, T.; Kawata, K.; Takahashi, T.; Kikuchi, N. *J. Vet. Med. Sci.* **2004**, *66*, 779–784.
6. Grimm, L. M.; Goldoft, M.; Kobayashi, J.; Lewis, J. H.; Alfi, D.; Perdichizzi, A. M.; Tarr, P. I.; Ongerth, J. E.; Moseley, S. L.; Samadpour, M. *J. Clin. Microbiol.* **1995**, *33*, 2155–2158.
7. Kaper, J. B. *Curr. Opin. Microbiol.* **1998**, *1*, 103–108.
8. Boyce, T. G.; Swerdlow, D. L.; Griffin, P. M. *N. Engl. J. Med.* **1995**, *333*, 364–368.
9. (a) Ali, T.; Weintraub, A.; Widmalm, G. *Carbohydr. Res.* **2006**, *341*, 1878–1883; (b) Nataro, J. P.; Kaper, J. B. *Clin. Microbiol. Rev.* **1998**, *11*, 142–201; (c) Olsson, U.; Lycknert, K.; Stenutz, R.; Weintraub, A.; Widmalm, G. *Carbohydr. Res.* **2005**, *340*, 167–171; (d) Kjellberg, A.; Weintraub, A.; Widmalm, G. *Biochemistry* **1999**, *38*, 12205–12211.
10. MacLean, L. L.; Webb, A. C.; Perry, M. B. *Carbohydr. Res.* **2006**, *341*, 2543–2549.
11. (a) Becker, C. F. W.; Liu, X.; Olschewski, D.; Castelli, R.; Seidel, R.; Seeberger, P. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 8215–8219; (b) Tamborrini, M.; Werz, D. B.; Frey, J.; Pluschke, G.; Seeberger, P. H. *Angew. Chem., Int. Ed.* **2006**, *45*, 6581–6582; (c) Werz, D. B.; Seeberger, P. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 6315–6318; (d) Verez-Bencomo, V.; Fernández-Santana, V.; Hardy, E.; Toledo, M. E.; Rodríguez, M. C.; Heynngnezz, L.; Rodriguez, A.; Baly, A.; Herrera, L.; Izquierdo, M.; Villar, A.; Valdés, Y.; Cosme, K.; Deler, M. L.; Montane, M.; Garcia, E.; Ramos, A.; Aguilar, A.; Medina, E.; Toraño, G.; Sosa, I.; Hernandez, I.; Martínez, R.; Muzachio, A.; Carmenates, A.; Costa, L.; Cardoso, F.; Campa, C.; Diaz, M.; Roy, R. *Science* **2004**, *305*, 522–525; (e) Roy, R. *Drug Discovery Today: Technologies* **2004**, *1*, 327–336; (f) Pozsgay, V. *Angew. Chem., Int. Ed.* **1998**, *37*, 138–142; (g) Snippe, H.; van Dam, J. E. G.; van Houte, A. J.; Willers, J. M. N.; Kamerling, J. P.; Vliegenthart, J. F. G. *Infect. Immun.* **1983**, *42*, 842–844; (h) Jansen, W. T. M.; Hogenboom, S.; Thijssen, M. J. L.; Kamerling, J. P.; Vliegenthart, J. F. G.; Verhoef, J.; Snippe, H.; Verheul, A. F. *Infect. Immun.* **2001**, *69*, 787–793; (i) Meeks, M. D.; Saksena, R.; Ma, X.; Wade, T. K.; Taylor, R. K.; Kovác, P.; Wade, W. F. *Infect. Immun.* **2004**, *72*, 4090–4101.
12. (a) Comegna, D.; Bedini, E.; Parrilli, M. *Tetrahedron* **2008**, *64*, 3381–3391; (b) Yan, S.; Liang, X.; Diao, P.; Yang, Y.; Zhang, J.; Wang, D.; Kong, F. *Carbohydr. Res.* **2008**, *343*, 3107–3111; (c) Tamura, J.; Nakada, Y.; Taniguchi, K.; Yamane, M. *Carbohydr. Res.* **2008**, *343*, 39–47; (d) Attolino, E.; Rising, T. W. D. F.; Heidecke, C. D.; Fairbanks, A. J. *Tetrahedron: Asymmetry* **2007**, *18*, 1721–1734.
13. Nakano, T.; Ito, Y.; Ogawa, T. *Tetrahedron Lett.* **1990**, *31*, 1597–1600.
14. Veeneman, G. H.; Gomes, L. J. F.; van Boom, J. H. *Tetrahedron* **1989**, *45*, 7433–7448.
15. Sato, S.; Ito, Y.; Ogawa, T. *Carbohydr. Res.* **1986**, *155*, C1–C5.
16. Zhang, J.; Otter, A.; Bundle, D. R. *Bioorg. Med. Chem.* **1996**, *4*, 1989–2001.
17. Spijker, N. M.; Westerduin, P.; van Boeckel, C. A. A. *Tetrahedron* **1992**, *48*, 6297–6316.
18. (a) Veeneman, G. H.; van Leeuwen, S. H.; van Boom, J. H. *Tetrahedron Lett.* **1990**, *31*, 1331–1334; (b) Konradsson, P.; Udodong, U. E.; Fraser-Reid, B. *Tetrahedron Lett.* **1990**, *31*, 4313–4316.
19. Ali, A.; Channe Gowda, D.; Vishwakarma, R. A. *Chem. Commun.* **2005**, 519–521.
20. Bhattacharyya, S.; Magnusson, B. G.; Wellmar, U.; Nilsson, U. J. *J. Chem. Soc., Perkin Trans.* **2001**, 886–890.
21. Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212–236.
22. (a) Anelli, P. L.; Biffi, C.; Montanari, F.; Quici, S. *J. Org. Chem.* **1987**, *52*, 2559–2562; (b) Huang, L.; Teumelsan, N.; Huang, X. *Chem. Eur. J.* **2006**, *12*, 5246–5252.
23. Spijker, N. M.; Keuning, C. A.; Hooglugt, M.; Veeneman, G. H.; van Boeckel, C. A. A. *Tetrahedron* **1996**, *52*, 5945–5960.
24. Perlman, W. M. *Tetrahedron Lett.* **1967**, *8*, 1663–1664.