Tetrahedron: *Asymmetry* 24 (2013) 606–611

Contents lists available at SciVerse ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Facile synthesis of a pentasaccharide repeating unit corresponding to the common *O*-antigen of *Salmonella enterica* O57 and *Escherichia coli* O51

Tamashree Ghosh [†], Abhishek Santra [†], Anup Kumar Misra [*]

Bose Institute, Division of Molecular Medicine, P-1/12, C.I.T. Scheme VII-M, Kolkata 700054, India

ARTICLE INFO

Article history:
Received 18 March 2013
Accepted 8 April 2013

ABSTRACT

A concise chemical synthetic strategy has been developed for the synthesis of a pentasaccharide present in the *O*-antigen of *Salmonella enterica* O57 and *Escherichia coli* O51 strains. A sequential glycosylation strategy has been adopted for the synthesis of the target pentasaccharide. All intermediate steps are high yielding and the glycosylation steps are stereoselective. A number of recently developed methodologies have been used in the synthesis.

1. Introduction

Diarrheal infections are a leading cause of deaths of children and elderly people in developing countries where sanitation is not adequate.[1,2] Most of the diarrheal outbrakes spread through contaminated food and water.[3,4] Microorganisms associated with the gastrointestinal infections include *Salmonella enterica* (*S. enterica*), enteropathogenic *Escherichia coli* (*E. coli*), and *Shigella* strains.[5–7] *Salmonella enterica* is considered as a leading pathogen for the outbreaks of food-borne infections in animals and humans in many countries.[8] Major sources of salmonellosis in humans are *S. enterica* infected poultry products and cattle.[9] Diarrhea causing *S. enterica* strains are divided into several serovars with similar virulence features.[10] Virulent *E. coli* strains are also important pathogens responsible for diarrheal outbreaks.[11] Diarrhea causing *E. coli* strains are divided into several pathotypes, which include enteropathogenic *E. coli* (EPEC), enterotoxigenic *E. coli* (ETEC), enteroinvasive *E. coli* (EIEC), enterohemorrhagic *E. coli* (EHEC), enteroaggregative *E. coli* (EAEC) etc.[12] Perepelov et al. characterized the structure of the pentasaccharide repeating unit of the *O*-polysaccharide of *Salmonella enterica* O57, which is identical to the repeating unit of the *O*-antigen of the enteropathogenic *E. coli* O51 strain[13] (Fig. 1). The most important component of the cell wall of a Gram-negative bacterium for its virulence property is the *O*-antigen. The *O*-antigen is a polysaccharide chain of the cell wall lipopolysaccharides, which consists of a number of repeating oligosaccharides. The pathogenic potential of the virulent bacterial strain depends on the structure of the oligosaccharide repeating units of the *O*-antigen because of its presence in the outer layer of the cell wall. The *O*-antigen plays an important role in the initial stage of adhesion of the bacteria to the host. Due to the emergence of multi-drug resistance in bacterial strains, the development of newer approach to combat bacterial infections is an important area of medicinal chemistry research. Since cell wall oligosaccharides are directly related to the bacterial virulence and infections, several studies have appeared in the literature for the development of antimicrobial agents based on glycoconjugates of cell wall oligosaccharides.[14–16] Since the repeating unit of the *O*-antigen of *S. enterica* O57 and *E. coli* O51 is identical and the pathogenic nature of the two strains is comparable, it would be worth preparing a glycoconjugate derivative corresponding to the *O*-antigen oligosaccharide. However, for the preparation of glycoconjugate derivatives, it is essential to have enough oligosaccharides corresponding to the *O*-antigens. Since a large quantity of oligosaccharides and their analogues are not accessible from natural sources, it is pertinent to develop expedient chemical synthetic strategies for the preparation of oligosaccharides with required stereochemistry at the glycosyl linkages. Herein, we report a concise chemical synthetic strategy for the synthesis of the pentasaccharide repeating unit corresponding to the *O*-antigen of *S. enterica* O57 and *E. coli* O51 (Fig. 2).

2. Results and discussion

The target pentasaccharide **1** has been synthesized as its 2-(*p*-methoxyphenoxy) ethyl glycoside using a sequential glycosylation approach from suitably protected monosaccharide intermediates **2**, **3**, **4**,[17] **5**[18], and **6**,[19] which were prepared from the commercially

β-D-GlcpNAc
1
↓
2
→3)-α-L-Rhap-(1→2)-α-L-Rhap-(1→4)-α-D-Glcp-(1→3)-β-D-GalpNAc-(1→

Figure 1. Structure of the pentasaccharide repeating unit of the *O*-antigen of *Salmonella enterica* O57 and *Escherichia coli* O51.

* Corresponding author. Tel.: +91 33 2569 3240; fax: +91 33 2355 3886.
E-mail address: akmisra69@gmail.com (A.K. Misra).
† These authors contributed equally to this work.

0957-4166/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetasy.2013.04.001

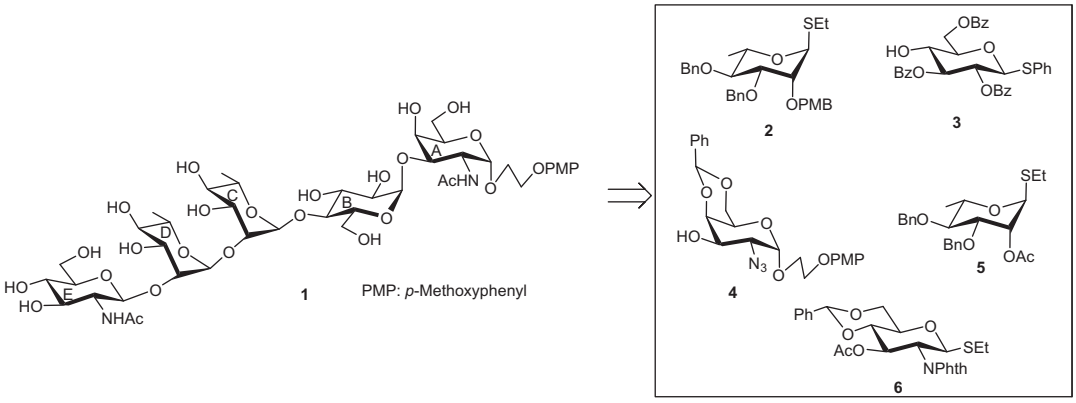
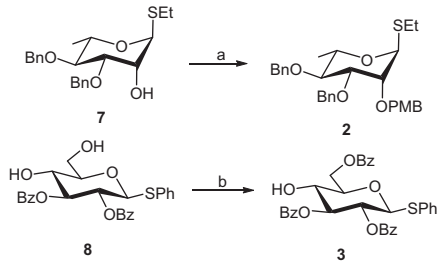


Figure 2. Structure of the synthesized pentasaccharide and its synthetic intermediates.

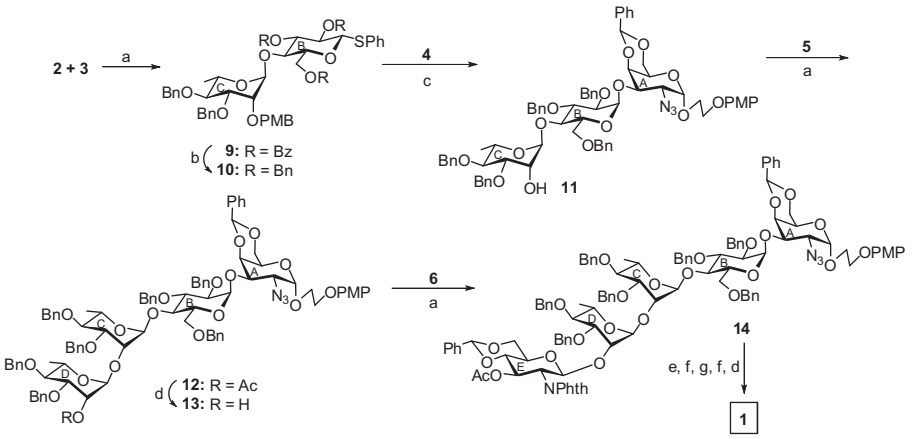
available reducing sugars (Fig. 2). This synthetic strategy has several notable features such as, (a) application of iodonium ion mediated general glycosylation conditions; (b) a minimum number of protection–deprotection steps; (c) the use of an ethylene glycol linker at the anomeric center; (d) application of an 'armed–disarmed' glycosylation technique;[20] (e) glycosylation and removal of the *p*-methoxybenzyl (PMB) group in one-pot;[21] and (f) high yield and stereoselectivity in the glycosylations.

The *p*-methoxybenzylation of ethyl 3,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside **7**[22] using *p*-methoxybenzyl chloride and sodium hydroxide furnished ethyl 3,4-di-*O*-benzyl-2-*O*-(*p*-methoxybenzyl)-1-thio-α-L-rhamnopyranoside **2** in 92% yield (Scheme 1). Phenyl 2,3-di-*O*-benzoyl-1-thio-β-D-glucopyranoside **8**[23] was selectively benzoylated at the primary hydroxyl group using benzoyl cyanide and pyridine[24] to give phenyl 2,3,6-tri-*O*-benzoylated-1-thio-β-D-glucopyranoside **3** in 86% yield (Scheme 1).



Scheme 1. Reagents and conditions: (a) *p*-methoxybenzyl chloride, NaOH, DMF, room temperature, 3 h, 92%; (b) benzoyl cyanide, pyridine, CH_2Cl_2, room temperature, 1 h, 86%.

The iodonium ion mediated stereoselective 1,2-*trans* glycosylation of thioglycoside **2** with thioglycoside **3** in the presence of a combination of *N*-iodosuccinimide (NIS) and trimethylsilyl trifluoromethanesulfonate (TMSOTf)[25] furnished disaccharide thioglycoside derivative **9** in 82% yield. Compound **2** acted as an armed glycosyl donor because of the presence of a *p*-methoxybenzyl group at the C-2 position. On the contrary, the presence of a benzoyl group at the C-2 position of compound **3** made it a disarmed glycosyl acceptor. The formation of compound **9** was confirmed from its spectroscopic analysis [signals at δ 4.87 (d, J = 10.0 Hz, H-1_B), 4.69 (br s, H-1_C) in the ^{1}H NMR and δ 99.9 (C-1_C), 85.7 (C-1_B) in the ^{13}C NMR spectra]. Compound **9** was transformed into benzylated derivative **10** in 87% yield under one-pot reaction conditions[26] for the de-*O*-acetylation and *O*-benzylation using benzyl bromide and solid sodium hydroxide in the presence of catalytic tetrabutylammonium bromide (TBAB). The 1,2-*cis* glycosylation of the thioglycoside derivative **10** with compound **4** in the presence of a combination of NIS–TMSOTf[25] in dichloromethane–diethyl ether mixture at a low temperature followed by the removal of the *p*-methoxybenzyl group[22] in the same reaction mixture by increasing the temperature furnished the trisaccharide acceptor **11** in 78% yield. The formation of compound **11** was confirmed from its spectroscopic analysis [signals at δ 5.00 (d, J = 7.5 Hz, H-1_A), 4.85 (d, J = 3.5 Hz, H-1_B), 4.49 (br s, H-1_C) in the ^{1}H NMR and δ 103.9 (C-1_C), 99.3 (C-1_A), 96.9 (C-1_B) in the ^{13}C NMR spectra]. The stereoselective glycosylation of compound **11** with L-rhamnosyl thioglycoside **5** in the presence of a combination of NIS–TMSOTf in dichloromethane furnished tetrasaccharide derivative **12** in 76% yield, which upon de-*O*-acetylation using sodium methoxide gave tetrasaccharide acceptor **13** in 95% yield. The formation of compound **12** was confirmed from its spectroscopic analysis [signals at δ 4.99 (br s, H-1_D), 4.95 (d, J = 7.5 Hz, H-1_A), 4.83 (d, J = 3.4 Hz, H-1_B), 4.46 (br s, H-1_C) in the ^{1}H NMR and δ 103.9 (C-1_C), 99.0 (C-1_D), 98.9 (C-1_A), 96.9 (C-1_B) in the ^{13}C NMR spectra]. The 1,2-*trans* glycosylation of compound **13** with thioglycoside **6** in the presence of a combination of NIS–TMSOTf in dichloromethane furnished pentasaccharide **14** in 73% yield. The stereochemistry of the glycosyl linkages in compound **14** was confirmed from its spectroscopic analysis [signals at δ 5.37 (d, J = 8.5 Hz, H-1_E), 4.88 (d, J = 8.0 Hz, H-1_A), 4.82 (br s, 2H, H-1_B, H-1_D), 4.52 (br s, H-1_C) in the ^{1}H NMR and δ 103.7 (C-1_C), 101.1 (C-1_E), 100.4 (2 C, C-1_A, C-1_D), 98.9 (C-1_B) in the ^{13}C NMR spectra]. The stereochemistry at the glycosyl linkages of compound **14** was further confirmed from the gated ^{1}H coupled ^{13}C NMR spectrum. The appearance of the anomeric coupling constant (J_{C1-H1}) values 170 Hz, 165 Hz, 168 Hz, 155 Hz and 148 Hz indicated the presence of three alpha- and two beta glycosyl linkages[27] in compound **14**. Compound **14** was subjected to a series of functional group transformations; (a) removal of the *N*-phthalimido group using ethylenediamine followed by acetylation;[28] (b) removal of the benzylidene acetal and *O*-benzyl groups and reduction of the azido group using triethylsilane and 10% palladium on charcoal (Pd–C)[29] followed by *N*-acetylation; and finally (c) saponification using sodium methoxide to give pentasaccharide **1** as its 2-(*p*-methoxyphenoxy) ethyl glycoside, which was purified over a Sephadex® LH-20 gel to give pure compound **1** in 62% yield. The formation of compound **1** was confirmed from its spectroscopic analysis [signals at δ 5.05 (br s, H-1_D), 4.83 (d, J = 4.0 Hz, H-1_B), 4.79 (br s, H-1_C), 4.59 (2 d, J = 8.5 Hz each, H-1_A, H-1_E) in the ^{1}H NMR and δ 102.7 (2 C, C-1_A, C-1_E), 100.9 (C-1_D), 99.1 (C-1_C), 98.2 (C-1_B) in the ^{13}C NMR spectra] (Scheme 2).



Scheme 2. Reagents and conditions: (a) *N*-iodosuccinimide (NIS), TMSOTf, CH_2Cl_2, MS 4 Å, −35 °C, 1 h, 82% for compound **9**, 76% for compound **12** and 73% for compound **14**; (b) benzyl bromide, NaOH, TBAB, DMF, room temperature, 5 h, 87%; (c) NIS, TMSOTf, CH_2Cl_2/Et_2O (1:2, v/v), MS 4 Å, −15 °C, 1 h, then 0 °C, 30 min, 78%; (d) 0.1 M CH_3ONa, CH_3OH, 2 h, room temperature, 95%; (e) ethylene diamine, ^{n}BuOH, 90 °C, 7 h; (f) acetic anhydride, pyridine, room temperature, 1 h; (g) Et_3SiH, 10% Pd-C, CH_3OH, AcOH, room temperature, 6 h, 62% in five steps.

3. Conclusion

In conclusion, a concise synthetic strategy has been developed for the synthesis of pentasaccharide **1** as its 2-(*p*-methoxyphenoxy) ethyl glycoside, corresponding to the *O*-antigen of *E. coli* O51 and *S. enterica* O57. The synthesis of target compound **1** was achieved using the minimum number of steps. The yields of the intermediate steps of the synthesis were very good and the stereochemical outcome of the glycosylation reactions was excellent.

4. Experimental

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. ^{1}H and ^{13}C NMR, DEPT 135, 2D COSY, HSQC, and gated ^{1}H coupled ^{13}C NMR spectra were recorded on Bruker Avance 300 and 500 MHz spectrometers using $CDCl_3$ and D_2O as solvents and TMS as internal reference unless stated otherwise. Chemical shift values are expressed in δ ppm. MALDI-MS were recorded on a Bruker Daltronics mass spectrometer. Elemental analysis was carried out on a Carlo Erba analyzer. Optical rotations were measured at 25 °C on a Jasco P-2000 polarimeter. Commercially available grades of organic solvents of adequate purity are used in all reactions.

4.1. Ethyl 3,4-di-*O*-benzyl-2-*O*-(*p*-methoxybenzyl)-1-thio-α-L-rhamnoside 2

To a solution of compound **7** (2.5 g, 6.43 mmol) in anhydrous DMF (10 mL) was added powdered solid NaOH (1.2 g, 30 mmol) and *p*-methoxybenzyl chloride (1.8 mL, 13.27 mmol) after which the reaction mixture was allowed to stir at room temperature for 3 h. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (100 mL). The organic layer was washed with water, dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (7:1) to give pure compound **2** (3.0 g, 92%). Colorless oil; $[\alpha]_D^{25} = -59$ (*c* 1.2, $CHCl_3$); IR (neat): 2944, 1729, 1503, 1446, 1287, 1210, 1088, 797 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz,): δ 7.35–7.28 (m, 12H, Ar-H), 6.87 (d, *J* = 9.0 Hz, 2H, Ar-H), 5.24 (br s, 1H, H-1), 4.98 (d, *J* = 11.0 Hz, 1H, PhC*H*$_2$), 4.70–4.48 (m, 5H, PhC*H*$_2$), 4.06–3.98 (m, 1H, H-5), 3.83 (s, 3H, OC*H*$_3$), 3.82–3.76 (m, 2H, H-2, H-3), 3.63 (t, *J* = 9.3 Hz each, 1H, H-4), 2.66–2.52 (m, 2H, SC*H*$_2$CH$_3$), 1.36 (d, *J* = 6.0 Hz, 3H, CC*H*$_3$), 1.27 (t, *J* = 7.4 Hz each, 3H, SCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 158.9–113.4 (Ar-C), 81.6 (C-1), 80.3 (C-2), 79.9 (C-3), 75.8 (C-4), 74.9 (PhC*H*$_2$), 71.6 (PhC*H*$_2$), 71.4 (PhC*H*$_2$), 68.0 (C-5), 54.7 (OC*H*$_3$), 24.9 (SC*H*$_2$CH$_3$), 17.5 (CC*H*$_3$), 14.6 (SCH$_2$C*H*$_3$); ESI-MS: 531.2 [M+Na$^+$]; Anal. Calcd for $C_{30}H_{36}O_5S$ (508.23): C, 70.84; H, 7.13. Found: C, 70.67; H, 7.32.

4.2. Phenyl 2,3,6-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside 3

To a solution of compound **8** (4.0 g, mmol, 8.32) in CH_2Cl_2 (20 mL) were added pyridine (4 mL) and benzoyl cyanide (1.1 g, 8.38 mmol) at 0 °C and the reaction mixture was allowed to stir at room temperature for 30 min. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (100 mL). The organic layer was washed with satd. $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (9:1) as eluant to give pure compound **3** (4.2 g, 86%). White solid; mp 172–74 °C [EtOH]; $[\alpha]_D^{25} + 56$ (*c* 1.2, $CHCl_3$); IR (KBr): 3022, 2904, 1621, 1512, 1464, 1229, 757, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz,): δ 8.11–7.15 (m, 20H, Ar-H), 5.50 (t, *J* = 9.5 Hz each, 1H, H-2), 5.44 (t, *J* = 9.5 Hz each, 1H, H-3), 5.0 (d, *J* = 9.6 Hz, 1H, H-1), 4.80–4.68 (m, 2H, H-6$_{ab}$), 3.90–3.80 (m, 2H, H-4, H-5), 3.55 (br s, 1H, O*H*); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.9, 166.2, 164.6 (3 PhCO), 133.0–127.7 (Ar-C), 85.5 (C-1), 78.2 (C-5), 77.6 (C-3), 69.6 (C-4), 69.1 (C-2), 63.1 (C-6); ESI-MS: 607.1 [M+Na$^+$]; Anal. Calcd for $C_{33}H_{28}O_8S$ (584.15): C, 67.79; H, 4.83. Found: C, 67.65; H, 5.0.

4.3. Phenyl [3,4-di-*O*-benzyl-2-*O*-(*p*-methoxybenzyl)-α-L-rhamnopyranosyl]-(1→3)-2,3,6-tri-benzoyl-1-thio-β-D-glucopyranoside 9

To a solution of compound **2** (2.2 g, 4.32 mmol) and compound **3** (2.5 g, 4.27 mmol) in anhydrous CH_2Cl_2 (20 mL) was added MS-4 Å (2.0 g) and the reaction mixture was allowed to stir at room temperature for 30 min under argon. The reaction mixture was cooled to −35 °C. To the cooled reaction mixture were added NIS (1.0 g, 4.44 mmol) and TMSOTf (20 μl) and then stirred at the same temperature for 1 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and filtered through a Celite® bed and washed with CH_2Cl_2. The combined organic layer was successively washed with

5% $Na_2S_2O_3$, satd. $NaHCO_3$, and water, dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (5:1) as eluant to give pure compound **9** (3.6 g, 82%). Yellow oil; $[\alpha]_D^{25} = -21$ (*c* 1.2, $CHCl_3$); IR (neat): 3013, 2932, 1731, 1513, 1453, 1267, 1216, 1088, 1028, 755, 711 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.11–7.08 (m, 32H, Ar-H), 6.75 (d, 2H, Ar-H), 5.62 (t, *J* = 9.5 Hz each, 1H, H-3_B), 5.27 (t, *J* = 9.5 Hz each, 1H, H-2_B), 4.87 (d, *J* = 10.0 Hz, 1H, H-1_B), 4.79 (d, *J* = 11.5 Hz, 1H, PhCH_2), 4.69 (br s, 1H, H-1_C), 4.62–4.55 (m, 4H, H-6_{aB}, PhCH_2), 4.48 (d, *J* = 11.5 Hz, 1H, PhCH_2), 4.43 (d, *J* = 11.5 Hz, 1H, PhCH_2), 4.11–4.08 (m, 1H, H-6_{bB}), 3.92 (t, *J* = 9.5 Hz each, 1H, H-4_B), 3.78–3.75 (m, 1H, H-5_B), 3.73 (s, 3H, OCH_3), 3.68 (br s, 1H, H-2_C), 3.63 (dd, *J* = 9.0, 2.5 Hz, 1H, H-3_C), 3.48–3.43 (m, 1H, H-5_C), 3.37 (t, *J* = 9.0 Hz each, 1H, H-4_C), 0.73 (d, *J* = 6.0 Hz, 3H, CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.8, 165.7, 165.0 (3 PhCO), 159.3–113.7 (Ar-C), 99.9 (C-1_C), 85.7 (C-1_B), 80.1 (C-4_C), 79.1 (C-3_C), 77.7 (C-5_B), 75.2 (C-2_C), 74.7 (C-4_B), 74.6 (PhCH_2), 74.5 (C-3_B), 72.6 (PhCH_2), 72.3 (PhCH_2), 70.7 (C-2_B), 69.2 (C-5_C), 62.6 (C-6_B), 55.0 (OCH_3), 17.4 (CCH_3); MALDI-MS: 1053.3 [M+Na^+]; Anal. Calcd for $C_{61}H_{58}O_{13}S$ (1030.35): C, 71.05; H, 5.67. Found: C, 70.88; H, 5.86.

4.4. Phenyl [3,4-di-*O*-benzyl-2-*O*-(*p*-methoxybenzyl)-α-L-rhamnopyranosyl]-(1→3)-2,3,6-tri-benzyl-1-thio-β-D-glucopyranoside 10

To a solution of compound **9** (3.0 g, 2.91 mmol) in dry DMF (20 mL) were added powdered NaOH (1.2 g, 30 mmol), benzyl bromide (2.1 mL, 17.65 mmol), and TBAB (250 mg) and the reaction mixture was allowed to stir for 5 h at room temperature. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (100 mL). The organic layer was washed with water, dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (7:1) as eluant to give pure compound **10** (2.5 g, 87%). Yellow oil; $[\alpha]_D^{25} = -29$ (*c* 1.2, $CHCl_3$); IR (neat): 3009, 2916, 1611, 1514, 1454, 1249, 1217, 1079, 753, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.57–7.21 (m, 32H, Ar-H), 6.79 (d, *J* = 9.0 Hz, 2H, Ar-H), 5.00 (br s, 1H, H-1_C), 4.91–4.87 (m, 3H, PhCH_2), 4.76 (d, *J* = 10.5 Hz, 1H, PhCH_2), 4.70 (d, *J* = 10.5 Hz, 1H, PhCH_2), 4.62 (d, *J* = 9.0 Hz, 1H, H-1_B), 4.60–4.52 (m, 7H, PhCH_2), 3.90–3.86 (m, 1H, H-5_C), 3.83–3.77 (m, 2H, H-3_C, H-4_B), 3.75 (s, 3H, OCH_3), 3.71 (br s, 1H, H-2_C), 3.63–3.61 (m, 1H, H-6_{aA}), 3.56–3.49 (m, 4H, H-2_B, H-3_B, H-4_C, H-6_{bB}), 3.38–3.34 (m, 1H, H-5_B), 1.04 (d, *J* = 6.0 Hz, 3H, CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.2–113.7 (Ar-C), 98.6 (C-1_C), 87.5 (C-1_B), 84.9 (C-4_C), 81.1 (C-5_B), 80.6 (C-3_C), 79.6 (C-4_B), 79.5 (C-3_B), 75.5 (PhCH_2), 75.2 (PhCH_2), 75.1 (PhCH_2), 74.8 (C-2_B), 74.2 (C-2_C), 73.59 (PhCH_2), 72.2 (PhCH_2), 72.0 (PhCH_2), 68.8 (2 C, C-5_C, C-6_B), 55.1 (OCH_3), 17.8 (CCH_3); MALDI-MS: 1011.3 [M+Na^+]; Anal. Calcd for $C_{61}H_{64}O_{10}S$ (988.42): C, 74.06; H, 6.52. Found: C, 73.87; H, 6.73.

4.5. 2-(*p*-Methoxyphenoxy) ethyl (3,4-di-*O*-benzyl-α-L-rhamno)-(1→4)-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside 11

To a solution of compound **4** (850 mg, 1.92 mmol) and compound **10** (2.0 g, 2.02 mmol) in anhydrous CH_2Cl_2/Et_2O (15 mL; 1:2 v/v) was added MS-4 Å (2.0 g) and the reaction mixture was allowed to stir at room temperature for 30 min under argon. The reaction mixture was cooled to −15 °C. To the cooled reaction mixture were added NIS (500 mg, 2.22 mmol) and TMSOTf (15 μl) and it was then stirred at the same temperature for 1 h. The temperature of the reaction mixture was raised and it was stirred at 0 °C for 30 min. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and filtered through a Celite® bed and washed with CH_2Cl_2. The combined organic layer was washed successively with 5% $Na_2S_2O_3$, satd. $NaHCO_3$, and water, dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (6:1) as eluant to give pure compound **11** (1.8 g, 78%). Yellow oil; $[\alpha]_D^{25} = -16$ (*c* 1.2, $CHCl_3$); IR (neat): 3016, 2917, 1508, 1455, 1216, 1048, 756, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.35–7.21 (m, 30H, Ar-H), 6.84–6.79 (m, 4H, Ar-H), 5.00 (d, *J* = 7.5 Hz, 1H, H-1_A), 4.97 (s, 1H, PhC*H*), 4.93 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.85 (d, *J* = 3.5 Hz, 1H, H-1_B), 4.83 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.73–4.54 (m, 7H, PhCH_2), 4.49 (br s, 1H, H-1_C), 4.46 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.22–4.17 (m, 1H, H-5_C), 4.14–4.10 (m, 2H, OCH_2), 3.97–3.88 (m, 3H, H-4_A, OCH_2), 3.87–3.80 (m, 4H, H-3_A, H-3_B, H-6_{abA}), 3.77–3.72 (m, 3H, H-2_A, H-3_C, H-4_B), 3.74 (s, 3H, OCH_3), 3.68–3.64 (m, 1H, H-6_{aB}), 3.62–3.56 (m, 2H, H-2_B, H-6_{bB}), 3.54 (br s, 1H, H-2_C), 3.52–3.50 (m, 1H, H-5_B), 3.38–3.35 (m, 2H, H-4_C, H-5_A),0.99 (d, *J* = 6.0 Hz, 3H, CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.6–114.6 (Ar-C), 103.9 (C-1_C), 99.3 (2 C, C-1_A, PhCH), 96.9 (C-1_B), 80.5 (C-4_C), 80.1 (C-3_C), 79.8 (C-3_B), 79.7 (C-4_B), 75.5 (C-4_A), 75.4 (C-2_A), 75.3 (C-3_A), 75.0 (3 C, C-5_A, C-5_B, PhCH_2), 73.6 (2 C, 2 PhCH_2), 73.1 (PhCH_2), 71.9 (2 C, C-2_C, PhCH_2), 70.2 (C-5_C), 68.6 (2 C, C-6_A, C-6_B), 67.9 (C-2_B), 67.6 (OCH_2), 66.4 (OCH_2), 55.6 (OCH_3), 17.7 (CCH_3); MALDI-MS: 1224.5 [M+Na^+]; Anal. Calcd for $C_{69}H_{75}N_3O_{16}$ (1201.51): C, 68.93; H, 6.29. Found: C, 68.76; H, 6.50.

4.6. 2-(*p*-Methoxyphenoxy) ethyl (2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside 12

To a solution of compound **5** (600 mg, 1.39 mmol) and compound **11** (1.5 g, 1.25 mmol) in anhydrous CH_2Cl_2 (10 mL) was added MS-4 Å (1.0 g) and the reaction mixture was allowed to stir at room temperature for 30 min under argon. The reaction mixture was then cooled to −35 °C. To the cooled reaction mixture were added NIS (350 mg, 1.55 mmol) and TMSOTf (5 μl) and then stirred at same temperature for 1 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and filtered through a Celite® bed and washed with CH_2Cl_2. The combined organic layer was successively washed with 5% $Na_2S_2O_3$, satd. $NaHCO_3$, and water, dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (6:1) as eluant to give pure compound **12** (1.5 g, 76%). Yellow oil; $[\alpha]_D^{25} = -4$ (*c* 1.2, $CHCl_3$); IR (neat): 3017, 2930, 1740, 1508, 1455, 1216, 1054, 756, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.34–7.15 (m, 40H, Ar-H), 6.81–6.77 (m, 4H, Ar-H), 5.52 (br s, 1H, H-2_D), 4.99 (br s, 2H, H-1_D, PhC*H*), 4.95 (d, *J* = 7.5 Hz, 1H, H-1_A), 4.94–4.84 (m, 2H, PhCH_2), 4.83 (d, *J* = 3.4 Hz, 1H, H-1_B), 4.73–4.48 (m, 12H, PhCH_2), 4.46 (br s, 1H, H-1_C), 4.18–4.08 (m, 3H, H-5_C, OCH_2), 3.95–3.86 (m, 5H, H-3_A, H-4_A, H-5_D, OCH_2), 3.84–3.74 (m, 7H, H-2_A, H-3_B, H-3_C, H-3_D, H-4_B, H-6_{abA}), 3.73 (s, 3H, OCH_3), 3.66–3.63 (m, 1H, H-6_{aB}), 3.58–3.52 (m, 3H, H-2_B, H-2_C, H-6_{bB}), 3.51–3.47 (m, 1H, H-5_B), 3.37–3.33 (m, 3H, H-4_C, H-4_D, H-5_A), 2.11 (s, 3H, COCH_3), 1.20, 1.00 (2 d, *J* = 6.0 Hz each, 6H, 2 CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.8 (*C*OCH$_3$), 155.3–114.6 (Ar-C), 103.9 (C-1_C), 99.3 (PhCH), 99.0 (C-1_D), 98.9 (C-1_A), 96.9 (C-1_B), 80.7 (C-4_B), 80.0 (2 C, C-4_D, C-5_A), 79.8 (C-4_C), 77.7 (2 C, C-3_C, C-3_D), 75.4 (PhCH_2), 75.3 (2 C, C-3_B, PhCH_2), 75.1 (2 C, C-2_A, PhCH_2), 75.0 (C-5_B), 74.7 (C-4_A), 74.6 (C-3_A), 73.4 (PhCH_2), 73.0 (PhCH_2), 71.9 (PhCH_2), 71.8 (PhCH_2), 68.9 (2 C, C-2_C, C-5_D), 68.7 (C-2_D), 68.5 (C-5_C), 68.3 (2 C, H-2_B, H-6_B), 67.7 (C-6_A), 67.6 (OCH_2), 66.3 (OCH_2), 55.5 (OCH_3), 21.1 (COCH_3), 18.0, 17.8 (2 CCH_3); MALDI-MS: 1592.6 [M+Na^+]; Anal. Calcd for $C_{91}H_{99}N_3O_{21}$ (1569.67): C, 69.58; H, 6.35. Found: C, 69.40; H, 6.50.

4.7. 2-(*p*-Methoxyphenoxy) ethyl (3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside 13

A solution of compound **12** (1.2 g, 0.76 mmol) in 0.1 M CH_3ONa in CH_3OH (15 mL) was allowed to stir at room temperature for 2 h. The reaction mixture was neutralized with Dowex 50 W-X8 (H^+) resin, filtered and concentrated. The crude product was passed through a small pad of SiO_2 using hexane/EtOAc (1:1) as eluant to give pure compound **13** (1.1 g, 95%). Yellow oil; $[\alpha]_D^{25} = -10$ (*c* 1.2, $CHCl_3$); IR (neat): 3018, 2918, 1508, 1216, 1052, 758 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.32–7.16 (m, 40H, Ar-H), 6.81–6.78 (m, 4H, Ar-H), 5.04 (d, *J* = 7.5 Hz, 1H, H-1_A), 5.00 (s, 1H, PhC*H*), 4.96 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.94 (br s, 1H, H-1_D), 4.86 (d, *J* = 3.5 Hz, 1H, H-1_B), 4.85–4.81 (m, 2H, PhCH_2), 4.72–4.50 (m, 11H, PhCH_2), 4.48 (br s, 1H, H-1_C), 4.20–4.07 (m, 4H, H-2_D, H-5_C, OCH_2), 3.95–3.86 (m, 4H, H-3_A, H-5_D, OCH_2), 3.85–3.74 (m, 8H, H-2_A, H-3_B, H-3_C, H-3_D, H-4_A, H-4_B, H-6_{abA}), 3.73 (s, 3H, OCH_3), 3.68–3.63 (m, 1H, H-6_{aB}), 3.58–3.54 (m, 3H, H-2_C, H-5_B, H-6_{bB}), 3.52–3.47 (m, 1H, H-2_B), 3.44 (t, *J* = 9.0 Hz each,1H, H-4_C), 3.38–3.30 (m, 2H, H-4_D, H-5_A), 1.21 (d, *J* = 6.0 Hz, 3H, CCH_3), 0.99 (d, *J* = 6.0 Hz, 3H, CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.2–114.6 (Ar-C), 103.9 (C-1_C), 100.7 (PhCH), 100.6 (C-1_D), 98.9 (C-1_A), 96.8 (C-1_B), 80.7 (C-4_B), 80.4 (C-4_D), 80.1 (2 C, C-4_C, C-5_A), 79.6 (C-3_C), 79.5 (C-3_D), 75.4 (PhCH_2), 75.3 (PhCH_2), 75.2 (C-3_A), 75.1 (C-3_B), 75.0 (C-5_B), 74.6 (2 C, C-4_A, PhCH_2), 73.4 (PhCH_2), 73.0 (PhCH_2), 72.2 (PhCH_2), 72.1 (PhCH_2), 68.7 (2 C, C-2_C, C-5_D), 68.6 (C-6_B), 68.5 (C-2_D), 67.9 (2 C, C-2_B, C-5_C), 67.7 (C-6_A), 67.6 (*C*H$_2$), 66.3 (*C*H$_2$), 55.6 (2 C, C-2_A, O*C*H$_3$), 18.0 (*C*CH$_3$), 17.9 (*C*CH$_3$); MALDI-MS: 1550.6 [M+Na^+]; Anal. Calcd for $C_{89}H_{97}N_3O_{20}$ (1527.66): C, 69.92; H, 6.40. Found: C, 69.76; H, 6.58.

4.8. 2-(*p*-Methoxyphenoxy) ethyl (3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside 14

To a solution of compound **6** (380 mg, 0.78 mmol) and compound **13** (1.0 g, 0.65 mmol) in anhydrous CH_2Cl_2 (5 mL) was added MS-4 Å (500 mg) and the reaction mixture was allowed to stir at room temperature for 30 min under argon. The reaction mixture was cooled to −35 °C. To the cooled reaction mixture were added NIS (200 mg, 0.88 mmol) and TMSOTf (3 μl) and then stirred at the same temperature for 1 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and filtered through a Celite® bed and washed with CH_2Cl_2. The combined organic layer was successively washed with 5% $Na_2S_2O_3$, satd. $NaHCO_3$, and water, dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane/EtOAc (5:1) as eluant to give pure compound **14** (925 mg, 73%). Yellow oil; $[\alpha]_D^{25} = -11$ (*c* 1.2, $CHCl_3$); IR (neat): 2922, 1718, 1438, 1388, 1261, 1216, 1092, 759, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.58–7.02 (m, 53H, Ar-H), 6.02 (t, *J* = 8.0 Hz each, 1H, H-3_E), 5.42 (br s, 2H, 2 PhC*H*), 5.37 (d, *J* = 8.5 Hz, 1H, H-1_E), 4.88 (d, *J* = 8.0 Hz, 1H, H-1_A), 4.86 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.82 (br s, 2H, H-1_B, H-1_D), 4.70 (d, *J* = 10.5 Hz, 1H, PhCH_2), 4.62–4.58 (m, 2H, PhCH_2), 4.56–4.53 (m, 4H, PhCH_2), 4.52 (br s, 1H, H-1_C), 4.44 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.36 (dd, *J* = 8.5 Hz each, 1H, H-2_E), 4.26 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.18–3.95 (m, 7H, H-2_D, H-5_C, H-5_E, OCH_2, PhCH_2), 3.93–3.82 (m, 3H, H-5_D, H-6_{aB}, PhCH_2), 3.81–3.74 (m, 3H, H-6_{bB}, OCH_2), 3.78 (s, 3H, OCH_3), 3.73–3.61 (m, 7H, H-2_A, H-3_A, H-3_B, H-3_C, H-3_D, H-4_B, H-4_E), 3.59–3.42 (m, 8H, H-2_B, H-2_C, H-4_A, H-5_A, H-6_{abA}, H-6_{abE}), 3.36–3.31 (m, 1H, H-5_B), 3.08–2.98 (m, 2H, H-4_C, H-4_D), 1.93 (s, 3H, COCH_3), 1.06 (d, *J* = 6.0 Hz, 3H, CCH_3), 0.88 (d, *J* = 6.0 Hz, 3H, CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.9 (*C*OCH$_3$), 155.3–121.4 (Ar-C), 103.7 (C-1_C), 101.6 (2 C, 2 PhCH), 101.1 (C-1_E), 100.4 (2 C, C-1_A, C-1_D), 98.9 (C-1_B), 85.5 (C-4_A), 82.5 (C-4_B), 82.4 (2 C, C-3_A, C-3_C), 80.6 (C-5_A), 80.5 (C-4_C), 79.2 (2 C, C-3_D, C-4_D), 79.1 (C-3_B), 78.8 (C-4_E), 77.7 (C-5_B), 77.1 (C-5_E), 75.9 (C-3_E), 75.3 (C-5_D), 75.1 (2 C, 2 PhCH_2), 75.0 (C-2_C), 74.9 (PhCH_2), 74.6 (PhCH_2), 73.4 (PhCH_2), 72.7 (PhCH_2), 71.6 (PhCH_2), 69.8 (OCH_2), 69.3 (C-2_D), 68.6 (2 C, C-6_A, C-6_E), 68.4 (OCH_2), 68.3 (C-2_B), 67.6 (C-6_B), 65.7 (C-5_C), 57.0 (2 C, C-2_A, OCH_3), 55.3 (C-2_E), 20.7 (COCH_3), 17.8, 17.7 (2 CCH_3); MALDI-MS: 1971.7 [M+Na^+]; Anal. Calcd for $C_{112}H_{116}N_4O_{27}$ (1948.78): C, 68.98; H, 6.00. Found: C, 68.80; H, 6.22.

4.9. 2-(*p*-Methoxyphenoxy) ethyl (2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-L-rhamnopyranosyl)-(1→2)-(α-L-rhamnopyranosyl)-(1→4)-(α-D-glucopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranoside 1

To a solution of compound **14** (800 mg, 0.41 mmol) in ^{n}BuOH (5 mL) was added ethylene diamine (0.5 mL, 7.49 mmol) and the reaction mixture was allowed to stir at 90 °C for 7 h. The solvents were then removed under reduced pressure. A solution of the crude product in acetic anhydride/pyridine (2 mL, 1:1 v/v) was kept at room temperature for 1 h and concentrated under reduced pressure. To the solution of the acetylated crude product in CH_3OH/AcOH (5 mL, 20:1, v/v) were added 10% Pd–C (100 mg) and Et_3SiH (2 mL, 12.5 mmol) and the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was filtered through a Celite® bed, washed with warm CH_3OH and then concentrated under reduced pressure. A solution of the crude product in acetic anhydride/pyridine (2 mL, 1:1 v/v) was kept at room temperature for 1 h and concentrated under reduced pressure. A solution of the acetylated crude product in 0.1 M CH_3ONa in CH_3OH (5 mL) was allowed to stir at room temperature for 2 h. The reaction mixture was neutralized with Dowex 50 W-X8 (H^+) resin, filtered and concentrated. The crude product was passed through a Sephadex® LH-20 column using CH_3OH/H_2O (2:1) as eluant to give pure compound **1** (260 mg, 62%). Glass; $[\alpha]_D^{25} = -1$ (*c* 1.2, H_2O); IR (KBr): 3433, 2935, 1629, 1356, 1155, 1077, 699 cm^{-1}; ^1H NMR (D_2O, 500 MHz): δ 6.96–6.85 (m, 4H, Ar-H), 5.05 (br s, 1H, H-1_D), 4.83 (d, *J* = 4.0 Hz, 1H, H-1_B), 4.79 (br s, 1H, H-1_C), 4.59 (2d, *J* = 8.5 Hz each, 2H, H-1_A, H-1_E), 4.25–4.07 (m, 1H, OCH_2), 4.02 (br s, 1H, H-2_D), 3.95–3.87 (m, 3H, H-4_A, OCH_2), 3.79 (br s, 1H, H-2_C), 3.78–3.71 (m, 6H, H-3_A, H-3_C, H-3_B, H-3_E, H-6_{abA}), 3.70 (s, 3H, OCH_3), 3.67–3.53 (m, 6H, H-2_A, H-2_E, H-5_A, H-5_C, H-6_{abB}), 3.50–3.33 (m, 8H, H-2_B, H-3_D, H-4_B, H-4_E, H-5_D, H-5_E, H-6_{abE}), 3.25–3.20 (m, 3H, H-4_C, H-4_D, H-5_B), 1.94 (s, 6H, 2 COCH_3), 1.16, 1.14 (2d, *J* = 6.0 Hz each, 6H, 2 CCH_3); ^{13}C NMR (D_2O, 125 MHz): δ 174.8 (2 C, 2 *C*OCH$_3$), 153.5–115.0 (Ar-C), 102.7 (2 C, C-1_A, C-1_E), 100.9 (C-1_D), 99.1 (C-1_C), 98.2 (C-1_B), 78.7 (C-2_D), 78.3 (C-2_C), 76.5 (C-4_B), 75.7 (2 C, C-3_D, C-5_E), 73.6 (2 C, C-3_A, C-5_A), 72.2 (C-2_B), 72.0 (C-3_B), 71.5 (2 C, C-4_E, C-5_D), 70.6 (C-5_B), 70.0 (C-3_C), 69.7 (2 C, C-4_C, C-4_D), 69.6 (C-3_E), 69.1 (C-5_C), 69.0 (C-4_A), 67.7 (OCH$_2$), 66.6 (OCH$_2$), 60.6 (2 C, C-6_A, C-6_E), 59.7 (C-6_B), 55.9 (OCH$_3$), 55.8 (2C, C-2_A, C-2_E), 22.2 (COCH$_3$), 16.6, 16.4 (2 CCH$_3$); MALDI-MS: 1051.3 [M+Na^+]; Anal. Calcd for $C_{43}H_{68}N_2O_{26}$ (1028.40): C, 50.19; H, 6.66. Found: C, 50.0; H, 6.87.

Acknowledgments

T.G. and A.S. thank CSIR, New Delhi for providing Junior and Senior Research Fellowships. This work was supported by DST, New Delhi (No. SR/S1/OC-83/2010).

References

1. Bryce, J.; Boschi-Pinto, C.; Shibuya, K.; Black, R. E. *Lancet* **2005**, *365*, 1147–1152.
2. Bern, C.; Martines, J.; de Zoysa, I.; Glass, R. I. *Bull. World Health Org.* **1992**, *70*, 705–714.
3. Lanata, C. F. *Int. J. Environ. Health Res.* **2003**, *13*, S175–S183.
4. Mirza, N. M.; Caulfield, L. E.; Black, R. E.; Macharia, W. M. *Am. J. Epidemiol.* **1997**, *146*, 776–785.
5. Salmonella: *From Genome to Function*; Porwollik, S., Ed.; Caister Academic Press: USA, 2011.
6. Dean, P.; Kenny, B. *Curr. Opin. Microbiol.* **2009**, *12*, 101–109.
7. Ogawa, M. Y.; Handa, Y.; Ashida, H.; Suzuki, M.; Sasakawa, C. *Nat. Rev. Microbiol.* **2008**, *6*, 11–16.
8. Pui, C. F.; Wong, W. C.; Chai, L. C.; Tunung, R.; Jeyaletchumi, P.; Noor Hidayah, M. S.; Ubong, A.; Farinazleen, M. G.; Cheah, Y. K.; Son, R. *Int. Food Res. J.* **2011**, *18*, 465–473.
9. Crump, J. A.; Griffin, P. M.; Angulo, F. J. *Clin. Infect. Dis.* **2002**, *35*, 859–865.
10. Hong, Y.; Liu, T.; Lee, M. D.; Hofacre, C. L.; Maier, M.; White, D. G.; Ayers, S.; Wang, L.; Berghaus, R.; Maurer, J. J. *BMC Microbiol.* **2008**, *8*, 178–185.
11. Nataro, J. P.; Kaper, J. B. *Clin. Microbiol. Rev.* **1998**, *11*, 142–201.
12. Knutton, S.; Shaw, R.; Phillips, A. D.; Smith, H. R.; Willshaw, G. A.; Watson, P.; Price, E. *J. Pediatr. Gastroenterol. Nutr.* **2001**, *33*, 32–40.
13. Perepelov, A. V.; Liu, B.; Senchenkova, S. N.; Guo, D.; Sheyeley, S. D.; Feng, L.; Shashkov, A. S.; Wang, L.; Knirel, Y. A. *Carbohydr. Res.* **2011**, *346*, 828–832.
14. Roy, R. *Drug Discovery Today Technol.* **2004**, *1*, 327–336. and references cited therein.
15. Pozsgay, V. *Angew. Chem., Int. Ed.* **1998**, *37*, 138–142.
16. Schofield, L.; Hewitt, M. C.; Evans, K.; Siomos, M.-A.; Seeberger, P. H. *Nature* **2002**, *418*, 785–789.
17. Panchadhayee, R.; Misra, A. K. *J. Carbohydr. Chem.* **2010**, *29*, 39–50.
18. Scanlan, E. M.; Mackeen, M. M.; Wormald, M. R.; Davis, B. G. *J. Am. Chem. Soc.* **2010**, *132*, 7238–7239.
19. Kihlberg, J. O.; Leigh, D. A.; Bundle, D. R. *J. Org. Chem.* **1990**, *55*, 2860–2863.
20. Fraser-Reid, B.; Lopez, J. C. *Top. Curr. Chem.* **2011**, *301*, 1–29.
21. Bhattacharya, S.; Magnusson, B. G.; Wellmar, U.; Nilsson, U. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 886–890.
22. Ghosh, S.; Misra, A. K. *Tetrahedron: Asymmetry* **2010**, *21*, 2755–2761.
23. van den Bos, L. J.; Codée, J. D. C.; van der Toorn, J. C.; Boltje, T. J.; van Boom, J. H.; Overkleeft, H. S.; van der Marel, G. A. *Org. Lett.* **2004**, *6*, 2165–2168.
24. Abbas, S. A.; Haines, A. H. *Carbohydr. Res.* **1975**, *39*, 358–363.
25. (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.
26. Madhusudan, S. K.; Agnihotri, G.; Negi, D. S.; Misra, A. K. *Carbohydr. Res.* **2005**, *340*, 1373–1377.
27. Bock, K.; Pedersen, C. *Acta Chem. Scand. B* **1975**, *29*, 258–264.
28. Kanie, O.; Crawley, S. C.; Palcic, M. M.; Hindsgaul, O. *Carbohydr. Res.* **1993**, *243*, 139–164.
29. Santra, A.; Ghosh, T.; Misra, A. K. *Beilstein J. Org. Chem.* **2013**, *9*, 74–78.