Concise synthesis of a tetrasaccharide related to the repeating unit of the cell wall *O*-antigen of *Salmonella enterica* O60

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Graphical Abstract

Concise synthesis of a tetrasaccharide related to the repeating unit of the cell wall *O*-antigen of *Salmonella enterica* O60

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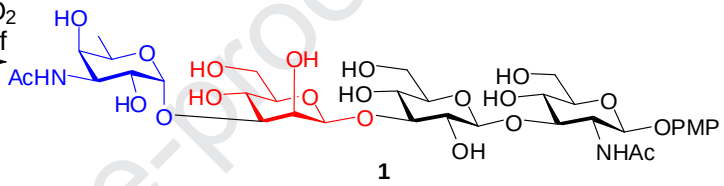
Suitably functionalized D-glucose, D-mannose, 3-amino-3-deoxy-D-fucose thioglycoside donors and functionalized D-glucosamine acceptor

NIS, $HClO_4$-SiO_2 or NIS, TMSOTf



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Concise synthesis of a tetrasaccharide related to the repeating unit of the cell wall *O*-antigen of *Salmonella enterica* O60

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Abstract— Synthesis of a tetrasaccharide related to the repeating unit of the cell wall *O*-antigen of *Salmonella enterica* O60 has been achieved by sequential glycosylations in very good yield. Use of *p*-methoxybenzyl group (PMB) as an *in situ* removable protecting group allowed obtaining the desired compound in less number of steps. Synthesis of a beta-D-mannosidic linkage present in the molecule has been successfully achieved using D-mannosyl thioglycoside donor having a *p*-methoxybenzyl (PMB) group at remote C-3 position. A combination of *N*-iodosuccinimide (NIS) and perchloric acid supported over silica ($HClO_4$-SiO_2) has been used as thiophilic glycosylation promoter in glycosylation reactions. Thioglycoside of 3-amino-3-deoxy-D-fucose has been prepared and used in the synthetic scheme for its incorporation in α-glycosidic linkage.

Keywords: Tetrasaccharide; glycosylation; beta-mannoside; 3-amino-3-deoxy-D-fucose; *Salmonella enterica* O60.
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1. Introduction

Food borne illness and diarrhoeal outbreaks caused by bacterial infections are serious concern worldwide.[1] The common causes for gastrointestinal infections include intake of contaminated food and water as well as lack of adequate sanitation.[2,3] *Salmonella* has been identified as one of the major pathogens among several diarrhoea causing bacteria such as *Shigella*, *E. coli*, *Vibrio cholerae*, *Proteus* strains causing millions of deaths annually.[4] The Salmonella infections are commonly termed as salmonellosis[5] and treated with antimicrobial agents. Due to the emergence of the multi-drug resistant bacterial strains [6,7] it is essential to develop alternate mechanism for controlling of salmonellosis. Based on the structure of the cell wall polysaccharides or *O*-antigens *Salmonella enterica* has been classified in several strains.[8] Since the cell wall *O*-polysaccharides are responsible for the virulence properties of *Salmonella*, they have been considered as important target for the development of glycoconjugate based vaccine candidates.[9,10] Although a number of reports appeared in the past on the effective vaccinations against bacterial infections such as pneumococcal infections,[11] influenza,[12] meningitis,[13] Shigellosis,[14] Cholera[15] etc. using bacterial cell wall glycoconjugates, there is no such vaccine available against salmonellosis.[16] Consequently, structures of the cell wall polysaccharides of several *Salmonella enterica* strains have been reported earlier.[8] The structure of the repeating unit of the cell wall *O*-antigen of *Salmonella enterica* O60 has been reported by Perepelov *et al.*[17] It is a tetrasaccharide repeating unit comprising β-linked D-glucosamine, β-linked D-glucose, β-linked D-mannose and α-linked 3-amino-3-deoxy-D-fucosamine moieties (Figure 1).

α-D-Fucp3NFo
1
↓
3
→2)-β-D-Manp-(1→3)-β-D-Glcp-(1→3)-β-D-GlcpNAc-(1→
Fucp3NFo: 3-formamido-3,6-dideoxygalactose

Figure 1: Structure of the repeating unit of the cell wall polysaccharide of *Salmonella enterica* O60.

Conventionally, the oligosaccharides can be obtained by bacterial fermentation with some inherent drawbacks, such as handling of living organisms, lack of adequate purity in terms of biological contamination, insufficient quantity and lack of homogeneity.[18] Therefore, development of concise chemical synthesis is the best option for getting access to the sufficient quantity of required oligosaccharides with adequate purity avoiding the above mentioned shortcomings. It has been demonstrated that glycoconjugates prepared using synthetic oligosaccharide fragments of the bacterial cell wall could serve as effective vaccine candidate similar to the vaccines prepared using cell wall polysaccharides obtained by fermentation process. Recently, glycoconjugate vaccine candidates have been reported against *Salmonella* infections using chemically synthesized oligosaccharides.[19,20] In this context, a concise synthesis of the tetrasaccharide related to the *O*-antigen of *Salmonella enterica* O60 reported herein by applying a number of recently reported glycosylation conditions. Presence of a rare sugar, 3-amino-3-deoxy-D-fucosamine with α-glycosidic linkage as well as a β-D-mannosidic linkage in the tetrasaccharide poses extra challenge in the synthetic strategy, which was competently overcome during the synthesis (Figure 2).

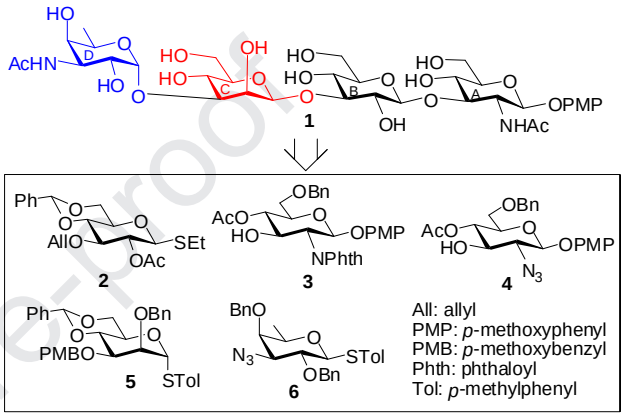


Figure 2: Structure of the synthesized tetrasaccharide and its possible synthetic intermediates.

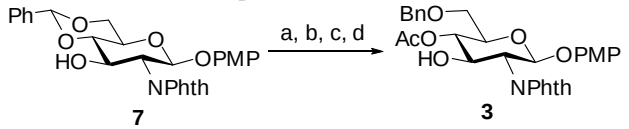
2. Results and discussion

The synthesis of the target tetrasaccharide (**1**) as its *p*-methoxyphenyl glycoside was achieved using a sequential glycosylation approach. The synthetic strategy of the target tetrasaccharide involved a challenging stereoselective beta-glycosylation of a D-mannose moiety as well as preparation of a suitably functionalized 3-amino-3-deoxy-D-fucose moiety together with other constituents such as D-glucose and D-glucosamine intermediates.

3-Amino-3-deoxy-D-fucose is rarely found in nature. It can be found as a part of the polysaccharide chain of cell wall in few bacterial strains. Being essential components of a variety of antibiotics, deoxy sugars play critical roles in their biological function. Dube and co-workers[21] summarized biological roles of a variety of deoxy amino sugars in the bacterial polysaccharides and their possible links in the pathogenesis. Although the deoxyamino sugars are biosynthesized in nature, it is quite difficult to synthesize them chemically. A number of reports appeared from Kulkarni and co-workers[22,23] and Andreana and co-workers[24] on the synthetic aspects of rare deoxy aminosugars.[22-24] However, there is no report available in the literature on the synthesis of 3-amino-3-deoxy-D-fucose derivative for its use in the glycosylation. Suitably functionalized monosaccharide intermediates **2,**[25] **3, 4**,

5[26] and **6** were prepared using reaction conditions available in the literature. Preparation of compounds **2**[25] and **5**[26] were carried out using the earlier reported reaction conditions. Compounds **3**, **4** and **6** were synthesized from earlier reported monosaccharide derivatives **7**,[27] **8**[28] and **9**[29] respectively.

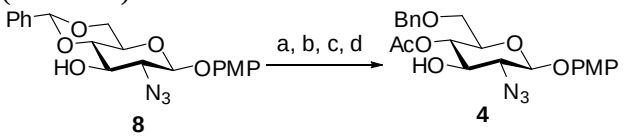
p-Methoxyphenyl 4-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (**3**) was synthesized from *p*-methoxyphenyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (**7**)[27] using a sequence of reactions, involving esterification of the C-3 hydroxyl group using levulinic acid in the presence of DIC and DMAP;[30] reductive ring opening of 4,6-*O*-benzylidene acetal using a combination of triethylsilane and trifluoroacetic acid;[31] acetylation of the resulting C-4 hydroxyl group and finally removal of the levulinic ester using hydrazine acetate[32] in 62% over all yield. NMR spectroscopic analysis confirmed the formation of compound **3** (Scheme 1).



7 **3**

Scheme 1: Preparation of 2-deoxy-2-*N*-phthalimido-D-glucose intermediate as glycosyl acceptor. Reagents and conditions: (a) levulinic acid, DIC, DMAP, CH_2Cl_2, r t, 5 h; (b) Et_3SiH, TfOH, CH_2Cl_2, 0 °C, 3 h; (c) Ac_2O, pyridine, r t, 2 h; (d) AcOH, $NH_2NH_2 \cdot H_2O$, CH_3OH-CH_2Cl_2 (1:1), 0 °C, 8 h, 62% in four steps.

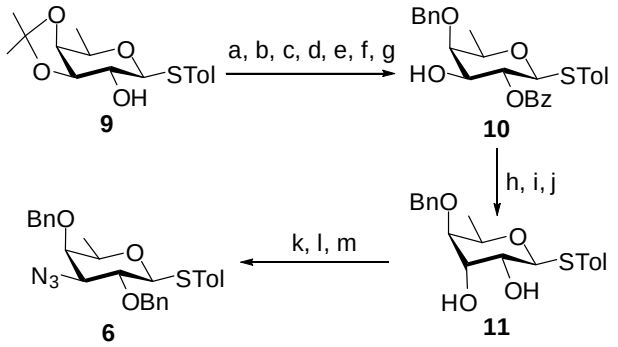
p-Methoxyphenyl 4-*O*-acetyl-2-azido-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (**4**) was synthesized from *p*-methoxyphenyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**8**)[28] using a sequence of reactions, involving allylation using allyl bromide in the presence of sodium hydride;[33] reductive ring opening of 4,6-*O*-benzylidene acetal using a combination of triethylsilane and trifluoroacetic acid;[31] acetylation of the resulting C-4 hydroxyl group and finally removal of the allyl ether using palladium chloride[34] in 53% over all yield. NMR spectroscopic analysis confirmed the formation of compound **4** (Scheme 2).



8 **4**

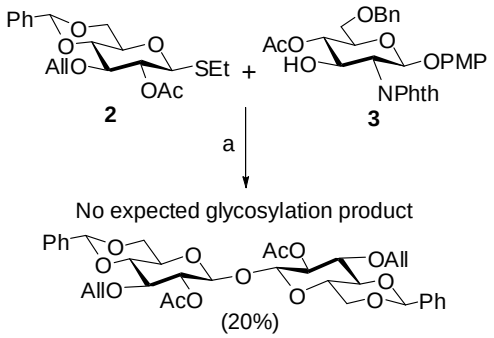
Scheme 2: Preparation of 2-azido-2-deoxy-D-glucose intermediate as glycosyl acceptor. Reagents and conditions: (a) Allyl bromide, NaH, DMF, 0 °C to r t, 2 h; (b) Et_3SiH, TfOH, CH_2Cl_2, 0 °C, 3 h; (c) Ac_2O, pyridine, r t, 2 h; (d) $PdCl_2$, CH_3OH, r t, 3 h, 53%.

Tolyl 3-azido-2,4-di-*O*-benzyl-3-deoxy-1-thio-β-D-fucopyranoside (**6**) was synthesized from literature known tolyl 3,4-*O*-isopropyl-1-thio-β-D-fucopyranoside (**9**)[29] in thirteen steps using functional groups manipulation of the hydroxyl groups. In order to achieve compound **6**, initially it was decided to benzylate the C-2 hydroxy group of compound **9** followed by functionalization of the remaining hydroxyl groups and inversion of C-3 hydroxyl group using minimum number of steps. However, it was observed that no inversion product was obtained in case of 2-*O*-benzylated derivative except formation of a complex mixture. Earlier, similar observation was reported by Ramström and co-workers.[35,36] The inversion reaction of triflate group proceeded smoothly only when an ester group was present at the carbon adjacent to the carbon atom carrying the leaving triflate group. On the contrary, a complex mixture was formed rapidly without formation of the inversion product when benzyl groups were employed. These results suggested that a neighboring ester group is essential to induce or activate the inversion reaction, whereas an ether derivative is unable to produce this effect. It was also shown[35,36] that the inversion reaction proceeded smoothly regardless of the triflate configuration. Therefore, it was decided to re-design the synthetic scheme by functionalizing the C-2 hydroxy group with a benzoyl group to achieve better yield of the inversion steps, although the number of steps increased. Compound **9** was subjected to a series of reactions comprising (a) treatment of 2-naphthylmethyl (NAP) bromide in the presence of sodium hydride;[37] (b) removal of isopropylidene group using 80% aq. acetic acid;[38] (c) selective benzylation of the axial hydroxyl group at C-4 using a phase transfer reaction condition; (d) esterification of the remaining hydroxyl group at C-3 using levulinic acid in the presence of DIC and DMAP;[30] (e) oxidative removal of the NAP group using DDQ;[39] (f) benzoylation of the free hydroxyl group followed by (g) removal of the levulinic ester using hydrazine acetate[32] to give tolyl 2-*O*-benzoyl-4-*O*-benzyl-1-thio-β-D-fucopyranoside (**10**) in 45% over all yield. The free hydroxyl group at C-3 in compound **10** was epimerized by the treatment of triflic anhydride in the presence of pyridine followed by S_N2 substitution of the triflate group by hydroxyl group in the presence of sodium nitrite[40] and removal of benzoyl group using sodium methoxide furnished compound **11** in 58% over all yield. The equatorial C-2 hydroxyl group in the diol derivative **11** was selectively benzylated via stannylidene acetal[41] formation. The C-3 hydroxyl group was treated with triflic anhydride in the presence of pyridine to give triflate derivative which was subjected to the S_N2 inversion using sodium azide[42] to furnish compound **6** in 60% over all yield. NMR spectroscopic analysis confirmed the formation of compound **6** (Scheme 3).



Scheme 3: Preparation of 3-azido-3,6-dideoxy-D-galactose thioglycoside intermediate as glycosyl donor. Reagents and conditions: (a) 2-naphthylmethyl (NAP) bromide, NaH, DMF, 0 °C to r t, 2 h; (b) 80% aq. AcOH, 80 °C, 2 h; (c) benzyl bromide, 5% NaOH, CH_2Cl_2, TBAB, r t, 3 h; (d) levulinic acid, DIC, DMAP, CH_2Cl_2, r t, 5 h; (e) DDQ, CH_2Cl_2-H_2O (5:1), r t, 6 h; (f) benzoyl chloride, pyridine, r t, 2 h; (g) AcOH, $NH_2NH_2 \cdot H_2O$, CH_3OH-CH_2Cl_2 (1:1), 0 °C-r t, 3 h, 45% in seven steps; (h) Tf_2O, pyridine, CH_2Cl_2, – 10 °C, 2 h; (i) $NaNO_2$, DMF, 60 °C, 12 h; (j) 0.1 M CH_3ONa, CH_3OH, r t, 3 h, 58%; (k) (i) Bu_2SnO, CH_3OH, 65 °C, 3 h; (ii) benzyl bromide, CsF, DMF, 65 °C, 6 h; (l) Tf_2O, pyridine, CH_2Cl_2, – 10 °C, 2 h; (m) NaN_3, DMF, 60 °C, 8 h, 60% in three steps.

Having required functionalized monosaccharide intermediates, attempts were made to couple them using stereoselective glycosylations conditions. Initially, thioglycoside **2** was allowed to glycosylate with glycosyl acceptor **3** in the presence of a combination[43] of *N*-iodosuccinimide (NIS) and $HClO_4$-SiO_2[44] as thiophilic glycosylation activator. Unfortunately formation of glycosylation product was not observed after several attempts using different glycosylation promoters e.g. DMTST,[45] NIS-TfOH,[46] methyl triflate[47] except the formation of 1,1-linked self coupled disaccharide of compound **2** (~20%) (Scheme 4, Table 1). Presumably the presence of 2-*N*-phthalimido group posed extra steric hindrance to the incoming glycosyl donor towards C-3 hydroxyl group of compound **3**. Hence it was decided to use the glycosyl acceptor **4** in which the *N*-phthaloyl group was replaced by a smaller non-interactive azido group.



Scheme 4: Attempted glycosylation between glycosyl donor **2** with acceptor **3**. Reagents and conditions: NIS, $HClO_4$-SiO_2 or NIS, TfOH or DMTST, CH_2Cl_2, –40 °C to –10 °C.

Table 1: Glycosylation of glycosyl donor **2** with glycosyl activator **3** using different glycosylation activator.

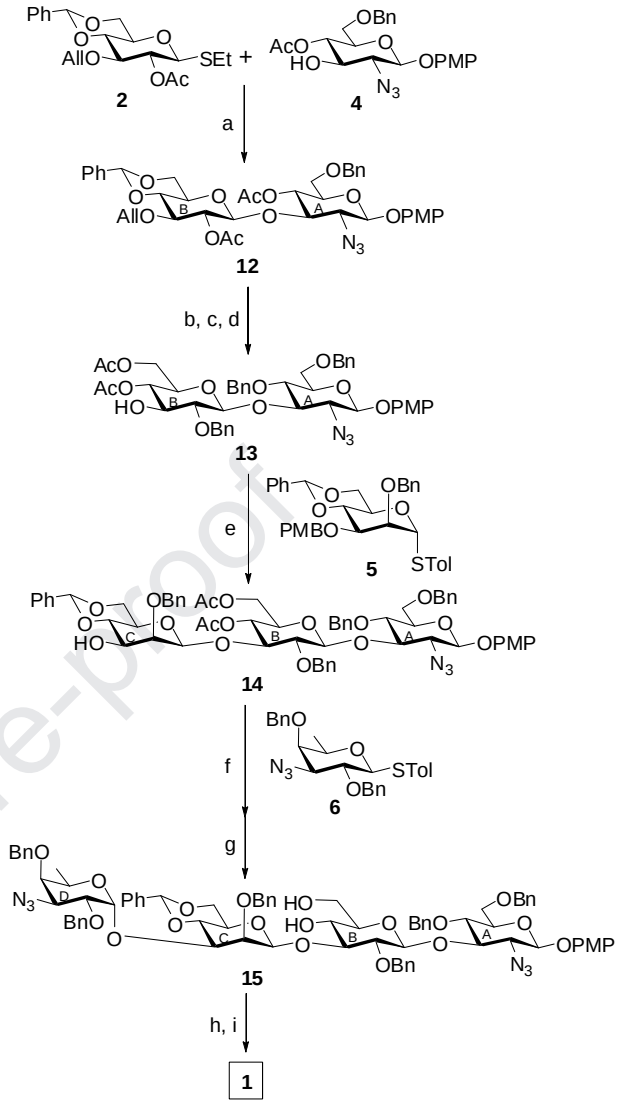
Sl. No.	Activator	Temp. (°C)	Time (min)	Yield (%)[a]
1	NIS/$HClO_4$-SiO_2	–40	60	0
2	NIS/$HClO_4$-SiO_2	–15	60	0
3	NIS/TfOH	–40	60	0
4	DMTST	–40	300	0
5	CH_3OTf	0	300	0

[a]: Acceptor fully recovered and 1,1-self coupled product of donor obtained (20%).

Stereoselective glycosylation of thioglycoside **2** with compound **4** in the presence of a combination[43] of NIS and $HClO_4$-SiO_2[44] as thiophilic glycosylation activator furnished disaccharide derivative **12** in 52% yield. Use of other glycosylation activators such as DMTST,[45] NIS-TfOH[46] did not improve the yield of the reaction. Spectroscopic data of compound **12** confirmed its formation and the stereochemistry of the newly formed glycosidic linkage. Compound **12** was subjected to a series of functional group modifications involving (a) one-pot de-*O*-acetylation and benzylation using benzyl bromide in the presence of sodium hydroxide and tetrabutylammonium bromide (TBAB);[48] (b) one-pot conversion of 4,6-*O*-benzylidene acetal into di-*O*-acetate derivative using acetic anhydride in the presence of $HClO_4$-SiO_2[49] and (c) removal of allyl group using palladium chloride[34] to give disaccharide acceptor **13** in 66% over all yield. The synthetic strategy faced another challenge at this point because of the need of incorporation of a β-D-mannosidic linkage in the molecule. In the recent past, a number of seminal reports appeared in the literature for the construction of the β-D-mannosidic linkage using mannosyl donors, which include Crich's two stage activation of thiomannosides,[50] intramolecular aglycone delivery (IAD),[51] specially designed glycosyl donor and acceptor,[52] application of thiourea ligand[53] etc. However, none of these methods can be considered as general approach. Recently, a convenient NIS-TMSOTf mediated β-mannosylation has been developed using D-mannosyl thioglycosides having remotely placed hydrogen bond mediating *p*-methoxybenzyl (PMB) group.[54] This elegant reaction condition has been successfully applied for incorporation of β-mannosidic linkage in this synthetic scheme. Stereoselective 1,2-*cis*-glycosylation of compound **13** with D-mannosyl thioglycoside **5** in the presence of a combination[46, 54] of NIS and TMSOTf at low temperature followed by removal of the PMB group[55] from the newly formed trisaccharide derivative in one-pot by raising the temperature of the reaction condition after glycosylation furnished trisaccharide acceptor **14** in 68% yield. Use of other glycosylation

activators such as a combination[43] of NIS and $HClO_4$-SiO_2,[44] DMTST[45] did not furnish satisfactory yield of the reaction. Spectral analysis of compound **14** confirmed its formation and the stereochemistry of the newly formed β-D-mannosidic linkage [signals at δ 4.67 (s, H-1_C) and 3.23-3.18 (m, H-5_C) in ^{1}H NMR and at δ 102.5 ($J_{C1,H1}$ = 158 Hz; C-1_C) in ^{13}C NMR spectra]. The $J_{C1,H1}$ = 158 Hz value of the anomeric carbon of the mannosidic moiety in the ^{1}H coupled ^{13}C NMR spectrum unambiguously confirmed its stereochemistry.[56]

Stereoselective 1,2-*cis* glycosylation of compound **14** with thioglycoside **6** in the presence of a combination[43] of NIS and $HClO_4$-SiO_2 furnished the tetrasaccharide derivative together with hemiacetal derivative of the glycosyl donor. De-*O*-acetylated tetrasaccharide derivative **15** was obtained in 70% yield by the treatment of the product mixture with sodium methoxide. Spectral analysis of compound **15** confirmed its formation and the stereochemistry of the newly formed α-glycosidic linkage [signals at δ 5.33 (d, J = 3.5 Hz, H-1_D), 4.85 (d, J = 7.5 Hz, H-1_A), 4.69 (s, H-1_C), 4.68 (d, J = 8.0 Hz, H-1_B) in ^{1}H NMR]. Formation of β-glycosidic product was not observed under the reaction condition. It is noteworthy to mention that, this is the first report for the glycosylation using 3-azido-3-deoxy-D-fucopyranosyl donor. Finally, compound **15** was treated with thioacetic acid[57] in presence of pyridine to transform azido groups into acetamido group followed by hydrogenolized under a positive pressure of hydrogen over 20% $Pd(OH)_2$-C (Pearlman's catalyst)[58] to furnish compound **1** in 65% over all yield (Scheme 5; Table 2). The spectroscopic analysis of compound **1** confirmed the stereochemistry of the glycosidic linkages present in it [signals at δ 5.13 (d, J = 3.5 Hz, H-1_D), 5.00 (d, J = 8.5 Hz, H-1_B), 4.87 (br s, H-1_C), 4.49 (d, J = 8.0 Hz, H-1_A) in ^{1}H NMR and at δ 102.9 ($J_{C1,H1}$ = 158 Hz; C-1_A), 100.4 ($J_{C1,H1}$ = 156 Hz; C-1_C), 100.3 ($J_{C1,H1}$ = 159 Hz; C-1_B), 100.2 ($J_{C1,H1}$ = 172 Hz; C-1_D), in ^{13}C NMR spectra]. The stereochemistry of the anomeric carbons of the monosaccharide moieties in compound **1** were unambiguously confirmed from their $J_{C1,H1}$ values.[56]



Scheme 5: Synthesis of tetrasaccharide **1** by sequential glycosylations and functionalization of the intermediate glycoside derivatives. Reagents and conditions: (a) NIS, $HClO_4$-SiO_2, MS 4Å, CH_2Cl_2, –10 °C, 2 h, 52%; (b) benzyl bromide, NaOH, DMF, TBAB, r t, 3 h; (c) acetic anhydride, $HClO_4$-SiO_2, r t, 10 min; (d) $PdCl_2$, CH_3OH, r t, 3 h, 66% in three steps; (e) NIS, TMSOTf, CH_2Cl_2, –40 °C, 3 h, then at 20 °C for 30 min, 68%; (f) NIS, $HClO_4$-SiO_2, CH_2Cl_2, –10 °C, 1 h; (g) 0.1 M CH_3ONa, CH_3OH, r t, 3 h, 70% in two steps; (h) CH_3COSH, pyridine, r t, 12 h; (i) H_2, 20% $Pd(OH)_2$-C, CH_3OH, r t, 24 h, 60% in two steps.

Table 2: Comparative yields of glycosylation reactions used in the synthetic Scheme 5.

Sl. No.	Donor	Acceptor	Activator	Temp (°C)	Time (h)	Yield (%)
1	**2**	**4**	NIS/ $HClO_4$-SiO_2	–10	2	52
2	**2**	**4**	NIS/ TfOH	–10	2	50
3	**2**	**4**	DMTST	–5	5	40
4	**5**	**13**	NIS/ $HClO_4$-SiO_2	–40	3	56
5	**5**	**13**	NIS/ TMSOTf	–40	3	68
6	**5**	**13**	DMTST	–10	6	40
7	**6**	**14**	NIS/ $HClO_4$-SiO_2	–10	1	70
8	**6**	**14**	DMTST	0	5	40

3. Conclusions

In summary, a concise synthetic strategy has been developed for the synthesis of a tetrasaccharide related to the repeating unit of the cell wall *O*-antigen of *Salmonella enterica* O60 in very good yield. A combination of NIS and $HClO_4$-SiO_2 has been used as glycosylation activator. The rare sugar intermediate, 3-amino-3-deoxy-D-fucosyl thioglycoside intermediate (**6**) has been prepared from D-fucose for the first time and used in the synthetic strategy for the construction of the α-linked 3-amino-3-deoxy-D-fucose moiety in the molecule. A recently developed PMB group directed glycosylation condition has been used to achieve excellent yield of β-mannosidic linkage. Presence of the *in situ* removable PMB group in the mannosyl thioglycoside intermediate (**5**) allowed reducing the number of reaction steps.

4. Experimental

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 sulphate (2% $Ce(SO_4)_2$ in 2N H_2SO_4) sprayed plates in hot plate. Silica gel 230-400 mesh was used for column chromatography. NMR spectra were recorded on Bruker Avance 500 MHz using $CDCl_3$ as solvent and TMS as internal reference unless stated otherwise. Chemical shift value is expressed in δ ppm. The complete assignment of proton and carbon spectra was carried out by using a standard set of NMR experiments, e.g. ^{1}H NMR, ^{13}C NMR, ^{13}C DEPT 135, 2D COSY and 2D HSQC etc. ESI-MS were recorded on a Thermo Scientific Orbitrap Velos Pro TM mass spectrometer. Optical rotations were recorded in a Jasco P-2000 spectrometer. Commercially available grades of organic solvents of adequate purity are used in all reactions. $HClO_4$-SiO_2 was prepared following the reported method.[44]

***p*-Methoxyphenyl (3-acetamido-3-deoxy-α-D-fucopyranosyl)-(1→3)-(β-D-mannopyranosyl)-(1→3)-(β-D-glucopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside (1)**: To a solution of compound **15** (500 mg, 0.35 mmol) in pyridine (2 mL) was added CH_3COSH (0.5 mL) and the reaction mixture was stirred at room temperature for 12 h. The solvents were removed and co-evaporated with toluene (3 x 20 mL) under reduced pressure and the crude product was passed through a short pad of SiO_2. To a solution of the *N*-acetylated product in CH_3OH (5 mL) was added 20% $Pd(OH)_2$-C (50 mg) and the reaction mixture was allowed to stir at room temperature under a positive pressure of H_2 for 24 h. The reaction mixture was filtered through a Celite bed, washed with CH_3OH-H_2O (20 mL; 2:1 v/v) and concentrated under reduced pressure. The deprotected product was passed through a Sephadex LH-20 column using CH_3OH-H_2O (3:1) as eluant to give pure compound **1** (175 mg, 60%). White powder; $[\alpha]_D$ − 17 (*c* 1.0, H_2O); ^{1}H NMR (500 MHz, D_2O): δ 6.99-6.88 (m, 4 H, Ar-*H*), 5.13 (d, *J* = 3.5 Hz, 1 H, H-1_D), 5.00 (d, *J* = 8.5 Hz, 1 H, H-1_B), 4.87 (br s, 1 H, H-1_C), 4.49 (d, *J* = 8.0 Hz, 1 H, H-1_A), 4.19-4.17 (m, 3 H, H-5_D, H-3_D, H-2_C), 4.02 (t, *J* = 9.0 Hz, 1 H, H-2_B), 3.88-3.78 (m, 5 H, H-6_{abB}, 6_{abC}, H-3_B), 3.77-3.71 (m, 2 H, H-6_{aA},H-2_D), 3.73 (s, 3 H, OCH_3), 3.70-3.64 (m, 5 H, H-4_D, H-3_A, H-4_B, H-3_C, H-6_{bA}), 3.58-3.52 (m, 2 H, H-4_A, H-5_C), 3.50-3.42 (m, 2 H, H-5_A, H-4_C), 3.38 (t, *J* = 8.5 Hz, 2 H, H-2_A, H-5_B), 1.98 (s, 3 H, NHCOCH_3), 1.96 (s, 3 H, NHCOCH_3), 1.14 (d, *J* = 6.5 Hz, 1 H, CCH_3); ^{13}C NMR (125 MHz, D_2O): δ 174.8 (NH*C*OCH$_3$), 174.4 (NH*C*OCH$_3$), 154.8-115.05 (Ar-C), 102.9 ($J_{C1,H1}$ = 158 Hz; C-1_A), 100.4 ($J_{C1,H1}$ = 156 Hz; C-1_C), 100.3 ($J_{C1,H1}$ = 159 Hz; C-1_B), 100.2 ($J_{C1,H1}$ = 172 Hz; C-1_D), 84.3 (C-3_A), 82.6 (C-3_B), 80.7 (C-3_C), 76.1 (C-5_C), 75.6 (C-5_B), 75.4 (C-5_A), 72.7 (C-2_A), 70.6 (C-3_D), 70.3 (C-4_D), 68.4 (C-4_A), 68.0 (C-4_C), 67.2 (C-2_C), 66.4 (C-2_D), 65.9 (C-4_B), 60.9 (C-6_A), 60.6 (C-6_B), 60.5 (C-6_C), 55.8 (O*C*H$_3$), 54.4 (C-2_B), 51.1 (C-5_D), 22.0 (NHCO*C*H$_3$), 21.9 (NHCO*C*H$_3$), 15.3 (CCH_3); HRMS (ESI) calcd. for $C_{35}H_{54}N_2O_{21}$ (838.3219): $[M+H]^+$ 839.3297; found: 839.3290.

***p*-Methoxyphenyl 4-*O*-acetyl-6-*O*-benzyl-2-deoxy-2-*N*-phthalimido-β-D-glucopyranoside (3):** To a solution of compound **7** (2 g, 3.97 mmol) were added levulinic acid (450 µL, 4.41 mmol), DIC (750 µL, 4.79 mmol) and DMAP (485 mg, 3.97 mmol) and the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (100 mL). The organic layer was washed with 2 M HCl (50 mL), H_2O (100 mL), dried (Na_2SO_4) and concentrated. To a solution of the crude product in CH_2Cl_2 (25 mL) were added Et_3SiH (3.82 mL, 23.96 mmol) at 0 °C followed by the addition of TfOH (1.5 mL, 19.96 mmol) and the reaction mixture was stirred at the same temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with saturated $NaHCO_3$ solution (2×50 mL), dried (Na_2SO_4), and concentrated. To the solution of the crude product in pyridine (10 mL) was added Ac_2O (5 mL) and the reaction mixture was stirred at room temperature for 2 h. The solvents were removed and co-evaporated with toluene (2×25 mL) under reduced pressure. To a solution of the acetylated product in CH_3OH-CH_2Cl_2 (20 mL; 1:1 v/v) were added AcOH (2.5 mL), hydrazine monohydrate (950 µL, 19 mmol) and the reaction mixture was stirred at 0 °C for 8 h. The reaction mixture was quenched by adding acetone (50 mL) and evaporated to dryness to give the crude product which was purified over SiO_2 using hexane-EtOAc (2:1) as eluant to give pure compound **3** (1.35 g, 62%). Colorless oil; $[\alpha]_D$ − 11 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87-6.69 (m, 13 H, Ar-*H*), 5.73 (d, *J* = 8.0 Hz, 1 H, H-1), 5.07 (t, *J* = 9.0 Hz, 1 H, H-4), 4.61 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.53 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.48-4.47 (m, 2 H, H-2, H-3), 3.88-3.85 (m, 1 H, H-5), 3.73 (s, 3

H, OC*H*$_3$), 3.70-3.64 (m, 2 H, H-6$_{ab}$), 2.03 (s, 3 H, COC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.9 (*C*O), 155.5-114.4 (Ar-C), 97.5 (C-1), 73.7 (C-4), 73.5 (*C*H$_2$Ph), 72.8 (C-5), 70.4 (C-3), 68.8 (C-6), 57.1 (C-2), 55.4 (O*C*H$_3$), 20.8 (CO*C*H$_3$); HRMS (ESI) calcd. for $C_{30}H_{29}NO_9$ (547.1842): $[M+H]^+$ 548.1920; found: 548.1930.

***p*-Methoxyphenyl 4-*O*-acetyl-2-azido-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (4):** A solution of compound **8** (2 g, 5.0 mmol) in dry DMF (5 mL) was cooled to 0 °C. To the cooled reaction mixture was added NaH (60% oil coated; 450 mg) followed by allyl bromide (0.8 mL, 9.2 mmol) and the reaction mixture was allowed to stir at room temperature for 2 h. The reaction mixture was quenched with aq. NH_4Cl, diluted with H_2O (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 under reduced pressure by co-evaporating with toluene (2×20 mL). To the solution of the crude in dry CH_2Cl_2 (25 mL) were added triethylsilane (4.8 mL, 30 mmol) at 0 °C followed by the addition of trifluoroacetic acid (1.75 mL, 22.8 mmol) and the reaction mixture was stirred at the same temperature for 3 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with saturated $NaHCO_3$ solution (2×50 mL), dried (Na_2SO_4), and concentrated. To the solution of the crude product in pyridine (5 mL) was added Ac_2O (5 mL) and the reaction mixture was stirred at room temperature for 2 h. The solvents were removed and co-evaporated with toluene (2×25 mL) under reduced pressure. To a solution of the acetylated product in anhydrous CH_3OH (10 mL) was added $PdCl_2$ (180 mg, 1.0 mmol) and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was filtered through a Celite bed and washed with CH_3OH (50 mL) and concentrated under reduced pressure to give the crude product which was purified over SiO_2 using hexane-EtOAc (as eluant to give pure compound **4** (1.2 g, 53%). Colorless oil; $[\alpha]_D$ − 7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-6.76 (m, 9 H, Ar-*H*), 4.93 (t, *J* = 9.5 Hz, 1 H, H-4), 4.73 (d, *J* = 8.0 Hz, 1 H, H-1), 4.56 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.50 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 3.76 (s, 3 H, OC*H*$_3$), 3.63-3.53 (m, 5 H, H-2, H-3, H-5, H-6$_{ab}$), 2.01 (s, 3 H, COC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5 (*C*O), 155.7-114.5 (Ar-C), 101.4 (C-1), 73.7 (C-4), 73.6 (*C*H$_2$Ph), 73.5 (C-3), 71.2 (C-2), 68.9 (C-6), 66.2 (C-5), 55.4 (O*C*H$_3$), 20.8 (CO*C*H$_3$); HRMS (ESI) calcd. for $C_{22}H_{25}N_3O_7$ (443.1693): $[M+H]^+$ 444.1771; found: 444.1780.

***p*-Methylphenyl 3-azido-2,4-di-*O*-benzyl-3-deoxy-1-thio-β-D-fucopyranoside (6):** A solution of compound **9** (3 g, 9.66 mmol) in dry DMF (10 mL) was cooled to 0 °C. To the cooled reaction mixture was added NaH (60% oil coated; 500 mg) followed by NAP bromide (2.2 g, 9.95 mmol) and the reaction mixture was allowed to stir at room temperature for 2 h. The reaction mixture was quenched with aq. NH_4Cl, diluted with H_2O (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 under reduced pressure. A solution of the crude product in 80% aq. AcOH (50 mL) was stirred at 80 °C for 2 h. The solvents were removed under reduced pressure and co-evaporated with toluene (3 x 20 mL). To a solution of the crude product in CH_2Cl_2 (50 mL) were added 5% aq. NaOH (10 mL), benzyl bromide (1.3 mL; 10.94 mmol) and TBAB (50 mg) and the biphasic reaction mixture was stirred vigorously at room temperature for 3 h. The reaction mixture was diluted with H_2O (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 under reduced pressure. To a solution of the crude product in dry CH_2Cl_2 (25 mL) were successively added levulinic acid (1.1 mL; 10.8 mmol), DIC (1.5 g, 11.88 mmol) and DMAP (1 g, 8.2 mmol) and the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (100 mL). The organic layer was washed with 2 M HCl (50 mL), H_2O (100 mL), dried (Na_2SO_4) and concentrated. To a solution of the crude product in CH_2Cl_2 (25 mL) was added a solution of DDQ (2.3 g, 10.13 mmol) in H_2O (5 mL) and the biphasic reaction mixture was stirred at room temperature for 6 h. The reaction mixture was diluted with H_2O (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. To a solution of the crude product in pyridine (15 mL) was added benzoyl chloride (1.2 mL, 10.33 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched by addition of aq. NH_4Cl (10 mL), diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (100 mL). The organic layer was successively washed with 2N HCl (50 mL), H_2O (50 mL), dried (Na_2SO_4) and concentrated. To a solution of the crude product in CH_3OH-CH_2Cl_2 (15 ml; 1:1 v/v) were added AcOH (600 µL, 10.5 mmol) and $NH_2NH_2 \cdot H_2O$ (510 µL, 10.5 mmol) and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL), successively washed with 2N HCl (50 mL), H_2O (50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane-EtOAc (8:1) as eluant to give pure compound **10** (2 g, 45%). A solution of compound **10** (2 g, 4.30 mmol) in dry CH_2Cl_2 (25 mL) was cooled to −10 °C. To the cooled reaction mixture were added pyridine (1 mL) and Tf_2O (1.5 mL, 8.93 mmol) and it was stirred at same temperature for 2 h. The solvents were removed and co-evaporated with toluene (2 x 20 mL) under reduced pressure. To a solution of the crude product in dry DMF (10 mL) was added $NaNO_2$ (2 g, 29 mmol) and it was stirred at 60 °C for 12 h. The reaction mixture was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was washed with water (50 mL), dried (Na_2SO_4) and concentrated. A solution of the crude product in 0.1 M CH_3ONa in CH_3OH (10 mL) was stirred at room temperature for 3 h, neutralized with Amberlite IR-120

(H^+) resin, filtered and concentrated. The crude product was purified over SiO_2 using hexane-EtOAc (2:1) as eluant to give pure compound **11** (900 mg, 58%). To a solution of compound **11** (900 mg, 2.49 mmol) in CH_3OH (30 mL) was added Bu_2SnO (1.5 g, 6.02 mmol) and the reaction mixture was stirred at 65 °C for 3 h. The solvents were evaporated and co-evaporated with toluene (3 x 20 mL) under reduced pressure. To a solution of the crude product in dry DMF (10 mL) were added benzyl bromide (1 mL, 8.42 mmol), CsF (380 mg, 2.5 mmol) and the reaction mixture was stirred at 65 °C for 6 h. The reaction mixture was diluted with H_2O (50 mL) and extracted with EtOAc (50 mL). The organic layer was successively washed with 2N HCl (50 mL) and H_2O (50 mL), dried (Na_2SO_4) and concentrated. A solution of the crude product in dry CH_2Cl_2 (15 mL) was cooled to −10 °C. To the cooled reaction mixture were added pyridine (0.5 mL) and Tf_2O (850 µL, 5.06 mmol) and it was stirred at same temperature for 2 h. The solvents were removed and co-evaporated with toluene (2 x 20 mL) under reduced pressure. To a solution of the crude product in dry DMF (5 mL) was added NaN_3 (1.5 g, 23 mmol) and it was stirred at 60 °C for 12 h. The reaction mixture was diluted with H_2O (50 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was washed with water (50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane-EtOAc (5:1) to give pure compound **6** (710 mg, 60%). Colorless oil; $[\alpha]_D$ + 26 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.00 (m, 14 H, Ar-*H*), 4.92 (d, *J* = 10.5 Hz, 2 H, PhC*H*$_2$), 4.67 (d, *J* = 10.0 Hz, 1 H, PhC*H*), 4.62 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.53 (d, *J* = 9.5 Hz, 1 H, H-1), 3.84 (t, *J* = 9.5 Hz, 1 H, H-2), 3.55-3.50 (m, 3 H, H-3, H-4, H-5), 2.31 (s, 3 H, C*H*$_3$), 1.24 (d, *J* = 6.5 Hz, 3 H, CC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0-127.7 (Ar-*C*), 88.2 (C-1), 77.9 (C-4), 77.2 (C-2), 75.3 (*C*H$_2$Ph), 75.1 (*C*H$_2$Ph), 75.0 (C-3), 67.6 (C-5), 21.1 (*C*H$_3$), 17.1 (C*C*H$_3$); HRMS (ESI) calcd. for $C_{27}H_{29}N_3O_3S$ (475.1930): $[M+H]^+$ 476.2008; found: 476.2000.

***p*-Methoxyphenyl (2-*O*-acetyl-3-*O*-allyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-4-*O*-acetyl-2-azido-6-*O*-benzyl-2-deoxy-β-D-glucopyranoside (12)**: To a solution of compound **2** (1.3 g, 3.29 mmol) and compound **4** (1.2 g, 2.70 mmol) in anhydrous CH_2Cl_2 (20 mL) was added MS 4Å (1 g) and the reaction mixture was cooled to − 10 °C under argon. To the cooled reaction mixture were added NIS (750 g, 3.33 mmol) and $HClO_4$-SiO_2 (50 mg) and it was stirred at same temperature for 2 h. The reaction mixture was filtered through a Celite bed, washed with CH_2Cl_2 (50 mL). The combined organic layer was successively washed with 5% $Na_2S_2O_3$ (100 mL), satd. $NaHCO_3$ (50 mL), H_2O (50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane-EtOAc (4:1) as eluant to give pure compound **12** (1.1 g, 52%). Colorless oil; $[\alpha]_D$ − 15 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44-6.77 (m, 14 H, Ar-*H*), 5.82-5.81 (m, 1 H, C*H*), 5.51 (s, 1 H, PhC*H*), 5.24 (d, *J* = 17.5 Hz, 1 H, C=C*H*), 5.13 (d, *J* = 9.5 Hz, 1 H, C=C*H*), 4.93-4.87 (m, 2 H, H-2$_B$, H-4$_A$), 4.76, 4.71 (2 d, *J* = 8.0 Hz each, 2 H, H-1$_A$, H-1$_B$), 4.51 (s, 2 H, C*H*$_2$Ph), 4.31 (s, 2 H, H-6$_{aB}$, OC*H*), 4.10 (d, *J* = 7.5 Hz, 1 H, OC*H*), 3.82 (s, 3 H, OC*H*$_3$), 3.76-3.54 (m, 7 H, H-2$_A$, H-3$_A$, H-3$_B$, H-4$_B$, H-5$_A$, H-6$_{abA}$, H-6$_B$), 3.39 (s, 1 H, H-5$_B$), 2.15 (s, 3 H, COC*H*$_3$), 1.95 (s, 3 H, COC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.0 (*C*OCH$_3$), 168.9 (*C*OCH$_3$), 155.7-114.6 (Ar-*C*), 102.0 (C-1$_B$), 101.5 (C-1$_A$), 101.2 (Ph*C*H), 81.2 (C-3$_A$), 79.7 (C-3$_B$), 78.6 (C-2$_A$), 73.7 (C-4$_B$), 73.6 (*C*H$_2$Ph), 73.1 (O*C*H$_2$), 72.8 (C-2$_B$), 69.4 (C-4$_A$), 69.3 (C-6$_B$), 68.6 (C-6$_A$), 66.1 (C-5$_B$), 65.9 (C-5$_A$), 55.5 (OC*H*$_3$), 20.81 (CO*C*H$_3$), 20.8 (CO*C*H$_3$); HRMS (ESI) calcd. for $C_{40}H_{45}N_3O_{13}$ (775.2952): $[M+H]^+$ 776.3030; found: 776.3022.

***p*-Methoxyphenyl (4,6-di-*O*-acetyl-2-*O*-benzyl-β-D-glucopyranosyl)-(1→3)-2-azido-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (13)**: To a solution of compound **12** (1 g, 1.29 mmol) in DMF (10 mL) were added powdered NaOH (200 mg, 5.0 mmol), benzyl bromide (400 µL, 3.36 mmol) and TBAB (50 mg) and the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with H_2O (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. To a solution of the crude product in acetic anhydride (5 mL) was added $HClO_4$-SiO_2 (50 mg) and it was stirred at room temperature for 10 min. The reaction mixture was filtered and concentrated under reduced pressure. To a solution of the crude product in CH_3OH (10 mL) was added $PdCl_2$ (25 mg, 0.14 mmol) and it was stirred at room temperature for 3 h. The reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane-EtOAc (5:1) as eluant to give pure compound **13** (705 mg, 66%). Colorless oil; $[\alpha]_D$ − 18 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-6.78 (m, 19 H, Ar-H), 5.02 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.99 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.97 (d, *J* = 9.0 Hz, 1 H, H-1$_B$), 4.94 (t, *J* = 10.0 Hz, 1 H, H-4$_B$), 4.77 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.72 (d, *J* = 8.0 Hz, 1 H, H-1$_A$), 4.59 (d, *J* = 12.5 Hz, 1 H, PhC*H*), 4.53 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.47 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.24 (dd, *J* = 12.5 Hz, 4.5 Hz, 1 H, H-6$_{aB}$), 4.01 (dd, *J* = 12.0 Hz, 2.0 Hz, 1 H, H-6$_{bB}$), 3.76 (s, 3 H, OC*H*$_3$), 3.75 -3.71 (m, 3 H, H-3$_A$, H-3$_B$, H-6$_{aA}$), 3.69 (dd, *J* = 11.0 Hz, 5.0 Hz, 1 H, H-6$_{aB}$), 3.63 (t, *J* = 8.5 Hz, 1 H, H-2$_A$), 3.62 (t, *J* = 7.5 Hz, 1 H, H-4$_A$), 3.58-3.54 (m, 1 H, H-5$_B$), 3.51-3.50 (m, 1 H, H-5$_A$), 3.33 (t, *J* = 8.0 Hz, 1 H, H-2$_B$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4 (*C*OCH$_3$), 170.0 (*C*OCH$_3$), 155.6-114.6 (Ar-*C*), 102.6 (C-1$_B$), 101.7 (C-1$_A$), 81.9 (C-2$_B$), 80.5 (C-3$_A$), 75.6 (C-2$_A$), 75.0 (*C*H$_2$Ph), 74.9 (H-5$_A$), 74.8 (*C*H$_2$Ph), 74.2 (C-3$_B$), 73.5 (*C*H$_2$Ph), 71.8 (C-5$_B$), 69.9 (C-4$_B$), 68.6 (C-6$_A$), 66.4 (C-4$_A$), 62.2 (C-6$_B$), 55.5 (OC*H*$_3$), 20.8 (CO*C*H$_3$), 20.6 (CO*C*H$_3$); HRMS (ESI) calcd. for $C_{44}H_{49}N_3O_{13}$ (827.3265): $[M+H]^+$ 828.3343; found: 828.3336.

***p*-Methoxyphenyl (4,6-*O*-benzylidene-2-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-(4,6-di-*O*-acetyl-2-*O*-benzyl-β-D-glucopyranosyl)-(1→3)-2-azido-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (14)**: To a solution of compound **13** (700 mg, 0.85 mmol) and compound **5** (600 mg, 1.02 mmol) in anhydrous CH_2Cl_2 (5 mL) was added MS 4Å (0.5 g) and the reaction mixture was cooled to − 40 °C under argon. To the cooled reaction mixture were added NIS (230 mg, 1.02 mmol) and TMSOTf (20 µL) and it was stirred at same temperature for 3 h. After consumption of the starting materials (TLC), the reaction mixture was allowed to stir at 20 °C for 30 min. The reaction mixture was filtered through a Celite bed, washed with CH_2Cl_2 (50 mL). The combined organic layer was successively washed with 5% $Na_2S_2O_3$ (50 mL), satd. $NaHCO_3$ (50 mL), H_2O (50 mL), 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 **14** (675 mg, 68%). Colorless oil; $[\alpha]_D$ − 6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-6.78 (m, 29 H, Ar-H), 5.44 (s, 1 H, PhC*H*), 5.06 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 5.01 (t, *J* = 8.5 Hz, 1 H, H-4$_B$), 4.97 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.97 (d, *J* = 8.0 Hz, 1 H, H-1$_A$), 4.88 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.74 (d, *J* = 8.0 Hz, 1 H, H-1$_B$), 4.67 (s, 1 H, H-1$_C$), 4.62 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.59 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.53 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.49 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.34 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.28 (dd, *J* = 10.0 Hz, 5.5 Hz, 1 H, H-6$_{aC}$), 4.26 (dd, *J* = 16.5 Hz, 4.5 Hz, 1 H, H-6$_{aB}$), 4.05 (dd, *J* = 12.0 Hz, 2.0 Hz, 1 H, H-6$_{bB}$), 3.79 (t, *J* = 10.0 Hz, 1 H, H-3$_B$), 3.76 (s, 3 H, OC*H*$_3$), 3.75 (t, *J* = 9.0 Hz, 1 H, H-3$_A$), 3.72-3.60 (m, 7 H, H-2$_B$, H-2$_C$, H-4$_A$, H-5$_B$, H-6$_{bA}$, H-6$_{abC}$), 3.52-3.48 (m, 1 H, H-5$_A$), 3.44 (t, *J* = 9.0 Hz, 1 H, H-2$_A$), 3.41 (dd, *J* = 9.0 Hz, 2.0 Hz, 1 H, H-3$_C$), 3.34 (d, *J* = 3.5 Hz, 1 H, H-4$_C$), 3.23- 3.18 (m, 1 H, H-5$_C$), 2.00 (s, 3 H, COC*H*$_3$), 1.95 (s, 3 H, COC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4 (*C*OCH$_3$), 169.3 (*C*OCH$_3$), 155.7-114.6 (Ar-*C*), 103.1 ($J_{C1,H1}$ = 159 Hz; C-1$_A$), 102.5 ($J_{C1,H1}$ = 158 Hz; C-1$_C$), 101.9 (PhCH), 101.7 ($J_{C1,H1}$ = 156 Hz; C-1$_B$), 82.5 (C-3$_C$), 80.7 (C-3$_B$), 79.7 (C-3$_A$), 79.4 (C-4$_A$), 78.4 (C-4$_C$), 75.7 (C-2$_B$), 75.5 (*C*H$_2$Ph), 75.4 (*C*H$_2$Ph), 75.0 (C-5$_A$), 74.9 (*C*H$_2$Ph), 73.5 (*C*H$_2$Ph), 71.7 (C-2$_C$), 70.6 (C-2$_A$), 68.6 (2C, C-6$_A$, C-6$_C$), 68.1 (C-4$_B$), 66.9 (C-5$_C$), 66.4 (C-5$_B$), 62.3 (C-6$_B$), 55.5 (OCH$_3$), 20.8 (COCH$_3$), 20.7 (COCH$_3$); HRMS (ESI) calcd. for $C_{64}H_{69}N_3O_{18}$ (1167.4576): $[M+H]^+$ 1168.4654; found: 1168.4664.

***p*-Methoxyphenyl (3-azido-2,4-di-*O*-benzyl-3-deoxy-α-D-fucopyranosyl)-(1→3)-(4,6-*O*-benzylidene-2-*O*-benzyl-β-D-mannopyranosyl)-(1→3)-(2-*O*-benzyl-β-D-glucopyranosyl)-(1→3)-2-azido-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (15)**: To a solution of compound **14** (650 mg, 0.56 mmol) and compound **6** (340 mg, 0.71 mmol) in anhydrous CH_2Cl_2 (5 mL) was added MS 4Å (0.5 g) and the reaction mixture was cooled to − 10 °C under argon. To the cooled reaction mixture were added NIS (160 mg, 0.71 mmol) and $HClO_4$-SiO_2 (10 mg) and it was stirred at same temperature for 1 h. The reaction mixture was filtered through a Celite bed, washed with CH_2Cl_2 (50 mL). The combined organic layer was successively washed with 5% $Na_2S_2O_3$ (50 mL), satd. $NaHCO_3$ (50 mL), H_2O (50 mL), dried (Na_2SO_4) and concentrated. A solution of the crude product in 0.1 M CH_3ONa in CH_3OH (10 mL) was stirred at room temperature for 3 h, neutralized with Amberlite IR-120 (H^+) resin, filtered and concentrated. The crude product was purified over SiO_2 using hexane-EtOAc (6:1) as eluant to give pure compound **15** (560 mg, 70%). Colorless oil; $[\alpha]_D$ − 10 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39-6.73 (m, 39 H, Ar-*H*), 5.33 (d, *J* = 3.5 Hz, 1 H, H-1$_D$), 5.23 (s, 1 H, PhC*H*), 4.92 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.91 (d, *J* = 10.5 Hz, 1 H, PhC*H*), 4.85 (d, *J* = 7.5 Hz, 1 H, H-1$_A$), 4.83 (d, *J* = 12.5 Hz, 1 H, PhC*H*), 4.76 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.69 (s, 1 H, H-1$_C$), 4.68 (d, *J* = 8.0 Hz, 1 H, H-1$_B$), 4.64 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.62 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.56 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.49 (d, *J* = 12.0 Hz, 2 H, 2 PhC*H*), 4.44 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.43 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.20 (d, *J* = 12.0 Hz, 1 H, PhCH), 4.18 (dd, *J* = 9.0 Hz, 3.0 Hz, 1 H, H-6$_{aC}$), 4.10 (t, *J* = 9.0 Hz, 1 H, H-4$_D$), 3.76-3.72 (m, 4 H, H-2$_D$, H-3$_D$, H-4$_A$, H-6$_{bC}$), 3.70 (s, 3 H, OC*H*$_3$), 3.71-3.65 (m, 4 H, H-4$_C$, H-6$_{aA}$, H-6$_{abB}$), 3.59-3.54 (m, 4 H, H-2$_B$, H-3$_A$, H-3$_C$, H-5$_B$), 3.47-3.39 (m, 3 H, H-2$_C$, H-5$_A$, H-6$_{bA}$), 3.37-3.40 (m, 2 H, H-3$_B$, H-5$_D$), 3.29 (t, *J* = 8.5 Hz, 1 H, H-2$_A$), 3.51-3.21 (m, 2 H, H-4$_B$, H-5$_C$), 0.90 (d, *J* = 6.5 Hz, 1 H, CC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7-114.6 (Ar-*C*), 103.1 (2C, C-1$_A$, C-1$_C$), 102.2 (Ph*C*H), 101.8 (C-1$_B$), 96.5 (C-1$_D$), 86.5 (C-3$_A$), 81.0 (C-2$_A$), 80.4 (C-4$_C$), 78.6 (C-4$_D$), 78.4 (C-4$_A$), 78.2 (C-4$_B$), 75.7 (Ph*C*H$_2$), 75.6 (Ph*C*H$_2$), 75.3 (2C, 2 Ph*C*H$_2$), 75.2 (H-3$_C$), 75.1 (H-2$_C$), 75.0 (H-5$_C$), 74.6 (C-3$_D$), 73.8 (C-2$_D$), 73.5 (*C*H$_2$Ph), 70.4 (*C*H$_2$Ph), 69.8 (C-3$_B$), 68.5 (C-6$_A$), 68.2 (C-6$_C$), 67.4 (C-5$_D$), 66.3 (C-5$_A$), 66.2 (C-2$_B$), 62.7 (C-6$_B$), 60.8 (C-5$_B$), 55.5 (O*C*H$_3$),16.6 (C*C*H$_3$); HRMS (ESI) calcd. for $C_{80}H_{86}N_6O_{19}$ (1434.5948): $[M+H]^+$ 1435.6026; found: 1435.6017.

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Conflicts of Interest

There are no conflicts to declare.

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Concise synthesis of a tetrasaccharide related to the repeating unit of the cell wall *O*-antigen of *Salmonella enterica* O60

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Highlights

- Tetrasaccharide related to the cell wall of *Salmonella enterica* O60 was synthesized.
- A combination of NIS and $HClO_4$-SiO_2 has been used as glycosylation activator.
- 3-Amino-3-deoxy-D-fucosyl thioglycoside has been prepared from D-fucose.
- PMB group directed glycosylation has been used to achieve β-mannosidic linkage.
- The number of reaction steps was reduced by using *in situ* removable PMB group.

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Conflicts of Interest

There are no conflicts to declare.