Chapter 3

Synthesis of the Oligosaccharide Repeating Units of the O-Antigenic Polysaccharides of Escherichia coli Strains
3.1. Introduction

*Escherichia coli* (*E. coli*) are a group of gram-negative bacteria that colonize at infant’s gastrointestinal tract within hours of life.\(^1\) *Escherichia* as a genus is defined by a series of physiological and morphological behaviors. But it is very difficult to describe accurately a single strain without knowing its serotyping due to the presence of high heterogeneity of this genus. The subdivision of the immunologically active site of the bacterial surface structure was introduced by Kauffmann.\(^2\) He characterized *E. coli* group based on the serotyping scheme. *E. coli* strains have been classified based on three types of antigens which are as follows: (i) somatic (*O*) antigen, (ii) capsular (*K*) antigen and (iii) flagellar (*H*) antigen. Initially, Kauffmann described 25 *O*, 55 *K* and 20 *H* antigens.\(^4\) Because of the emergence of several strains of *E. coli* currently 173 *O* antigens, *K* antigens 103 and *H* antigens 56 are present in the literature.\(^5\)\(^6\) The somatic *O*-antigens are composed of lipopolysaccharide complexes, which is an important component of the cell wall of *E. coli*. The immunogenicity of the cell-wall polysaccharides appear from the *O*-antigens. Kauffmann and Vahlne introduced the term *K*-antigen as a symbol for the envelope or capsular antigens.\(^7\) In general, *K*-antigens are acidic polysaccharides, serologically different from the *O*-antigens. Acidic capsular polysaccharides of *E. coli* are divided into two groups: group I polysaccharides similar to the capsule of *Klebsiella* species and Group II polysaccharides similar to the capsule of *Haemophilus influenza* and *Neisseria meningitidis*.\(^8\)\(^9\) The antigenic diversity of *H*-antigens is based on the different types of flagellin present in the flagellar structure. The *O*, *K*, and *H* antigens can be found in nature in many of the possible combinations. Although, the final number of *E. coli* serotype is very high 50,000-100,000 or more,\(^2\) the numbers of pathogenic serotypes are limited.

*E. coli* are versatile bacteria, which are typical component of human colonic flora. The diversity of *E. coli* pathotypes is due to the presence of specific subsets of virulence-associated genes, which are considered to be largely absent from the normal-flora *E. coli* strains. These virulence genes are usually carried by a variety of pathogenicity islands (PAIs), bacteriophages, plasmids and/or transposons.\(^10\) However, the pathogenic types of *E. coli* can cause both enteric and diarrhoeal disease. Based on their nature of infections, the enteropathogenic strain of *E. coli* have been classified in several classes,\(^11\)\(^12\) which include (a) enteropathogenic *E. coli* (EPEC), (b) enteroinvasive *E. coli* (EIEC), (c) enterotoxigenic *E. coli* (ETEC), (d) enteroaggregative *E. coli* (EAEC), (e) diffusely adherent *E. coli* (DAEC), and (f) enterohemorrhagic *E. coli* (EHEC) etc. Enterohemorrhagic *E. coli* (EHEC) are mostly responsible for diarrhoea with life threatening complications e.g. haemorrhagic colitis (HC) and haemolytic-uraemic syndrome (HUS).\(^11\)\(^12\)
EHEC strains are also called as “verotoxigenic E. coli” (VTEC) because of their toxic effect on the cultured Vero cells. They also produce a bacteriophage-mediated Shiga-like toxin and termed as “Shiga toxin-producing E. coli” (STEC). 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 associated with several outbreak of disease in the Europe, America and Japan. It is the major cause of hemolytic–uremic syndrome (HUS), a multisystemic disorder that is characterized by the onset of acute renal failure, microangiopathic hemolytic anemia and thrombocytopenia. The majority of outbreaks of human E. coli O157:H7 HUS cases resulted from the consumption of undercooked meat, raw milk, water, contaminated food or by direct contact with animals or people infected with the bacterium and EHEC epidemiology is invariably associated with the E. coli being an intestinal reservoir in cattle and other animals. The key virulence factors of the E. coli O157:H7 pathogen include verotoxins (Vt) together with effectors and adhesions associated with type III secretion systems, while the role of LPS in the EHEC pathogenesis appears to be relatively minimal. Besides E. coli O157:H7, several other E. coli serotypes have been reported to be associated with the STEC category. Although, E. coli is confined to the intestinal lumen, it causes infection in a debilitated or immuno-suppressed host or when the bacteria are introduced to other tissues, even normal “nonpathogenic” strains of E. coli can cause infection. E. coli infections may be limited to the mucosal surface or can disseminate throughout the body. The three general clinical syndromes caused by the pathogenic E. coli strains are urinary tract infections, sepsis/meningitis, and enteric/diarrheal diseases.

In the recent past, glycoconjugates derived from the O-antigenic oligosaccharides from the bacterial cell-wall have been used to develop antibacterial vaccine candidates. Several biological experiments are necessary for a detailed understanding of the relationship between the O-antigen with the pathogenicity of a particular bacterial strain, which in turn demands substantial quantities of oligosaccharides in hand. The oligosaccharides isolated from the natural source can not meet such requirement. Therefore, development of concise chemical synthetic strategy is essential to provide the large quantity of a particular oligosaccharide. In this context, oligosaccharide structures of the cell-wall of the following strains have been selected for chemical synthesis using a number of recently developed synthetic methodologies:

(i) Pentasaccharide repeating unit of the O-antigenic polysaccharide of enterohemorrhagic Escherichia coli O113.

(ii) Two structurally close tetrasaccharides corresponding to the O-antigen of Escherichia coli O127 and Salmonella enterica O13.
3.2. Convergent Synthesis of the Pentasaccharide Repeating Unit of the O-Antigenic Polysaccharide of Enterohemorrhagic Escherichia coli O113
3.2.1. Introduction

Enterohaemorrhagic *Escherichia coli* (EHEC) are one of the major causative agents of diarrhoea with life-threatening complications e.g. haemorrhagic colitis and haemorrhagic uremic syndrome.\textsuperscript{11,12} EHEC acquire their virulent action due to the release of vero-toxin or Shiga-toxin.\textsuperscript{13} The action of this toxin on the endothelial cells of the host leads to the pathological lesions associated with haemorrhagic colitis and haemorrhagic uremic syndrome. The young and elderly people are susceptible for the EHEC infections and suffer from nonbloody diarrhoea, bloody diarrhoea, and haemorrhagic uremic syndrome. The most cited EHEC strain is O157:H7, which is associated with several diarrhoeal outbreaks in the developed countries.\textsuperscript{14-17} Besides this, several EHEC strains have been identified for their pathogenic potential to cause severe diarrhorral infections, which include *E. coli* O4, O5, O16, O26, O46, O48, O55, O91, O98, O111ab, O113, O117, O118, O119, O125, O126, O128, O145 etc.\textsuperscript{30} It has been established that the bacterial virulence comes up from the *O*-specific polysaccharides (*O*-antigens) present in their cell membrane. As a consequence, a large number of reports appeared on the structural characterization of the *O*-antigens of various pathogenic bacteria as well as their application in the development of glycoconjugate based therapeutics.\textsuperscript{23-29} The structure of the pentasaccharide repeating unit of the *O*-specific lipopolysaccharide of *E. coli* O113 has been established by Parolis \textit{et al.} (Figure 1).\textsuperscript{31} It is an acidic oligosaccharide having a D-galacturonic acid moiety with three 1,2-\textit{cis} glycosyl linkage present in it. Cell wall *O*-antigens are considered as important class of molecules for the development of glycoconjugate based therapeutics. In this context, it would be pertinent to carry out several biological experiments using this pentasaccharide fragment to establish its pathological implications in the diarrhoeal infections. Since, the large quantity of the required pentasaccharide can not be isolated from the natural source, development of an efficient chemical synthetic strategy is essential. An efficient chemical synthesis of the pentasaccharide as its *p*-methoxyphenyl glycoside (1) corresponding to the *O*-antigen of the enterohaemorrhagic *E. coli* O113 is presented (Figure 2).

\[
\rightarrow 4\)\textsuperscript{-}\textit{α}-D-GalpNAC-(1→4)\textit{α}-D-GalpA-(1→3)\textit{α}-D-Galp-(1→3)\textit{β}-D-GlcpNAC-(1→3)\beta-\textit{D}-Galp
\]

\textbf{Figure 1:} Structure of the pentasaccharide repeating unit of the *O*-antigen of *E. coli* O113.
3.2.2. Results and Discussion

The synthesis of the pentasaccharide 1 as its p-methoxyphenyl glycoside was carried out using a convergent [3+2] block glycosylation strategy. A disaccharide glycosyl acceptor (14) was stereoselectively condensed with a trisaccharide glycosyl donor (19). The retrosynthetic strategy for the synthesis of pentasaccharide repeating unit of *E. coli* O113 as its p-methoxyphenyl glycoside led to a number of differentially protected monosaccharide intermediates, which were prepared from the commercially available monosaccharides using a number of protecting group manipulations (Scheme 1). The presence of α-D-galactosamine, α-D-galacturonic acid and α-D-galactose moieties make the synthesis of the target molecule challenging. A number of noteworthy features can be found in the present synthetic strategy, such as: (a) application of p-methoxybenzyl (PMB) ether as a temporary protecting group and its removal by tuning the glycosylation reaction condition in one-pot;32 (b) stereoselective [3+2] block glycosylation; (c) application of perchloric acid supported over silica (HClO₄-SiO₂)33 as a solid acid catalyst in the glycosylation of trichloroacetimidate derivative34 and thioglycoside;35 benzylidene acetal formation36 and direct conversion of benzylidene acetal to O-acetylated derivative;37 (d) the D-galactosamine moiety has been derived from tri-O-acetyl-D-galactal using azido-nitration technique reported earlier;38 (e) preparation of the α-D-galacturonic acid moiety at the late stage of the synthetic strategy using a TEMPO mediated oxidation protocol under phase transfer reaction condition39,40 and (f) use of p-methoxyphenyl group as temporary anomeric protecting group.41
3.2.2.1. Preparation of \( p \)-methoxyphenyl 4,6-benzylidene-2-deoxy-2-N phthalimido-\( \beta \)-D-glucopyranoside (5)\(^{42}\)

Treatment of \( \text{D-glucosamine hydrochloride} \) (2) with phthalic anhydride in the presence of sodium hydroxide\(^{43}\) followed by acetylation\(^{44}\) using acetic anhydride in presence of anhydrous sodium acetate resulted in the formation of 1,3,4,6-tetra-O-acetyl-2-deoxy-2-N-phthalimido-\( \beta \)-D-
glucopyranose (3) in 90% yield, which on treatment with p-methoxyphenol in the presence of borontrifluoride diethyl etherate\(^4\) furnished \(p\)-methoxyphenyl 3,4,6-tri-O-acetyl-2-deoxy-2-\(N\)phthalimido-\(\beta\)-D-glucopyranoside (4) in 86% yield. De-\(O\)-acetylation\(^4\) of compound 4, followed by benzylideneation using benzaldehyde dimethyl acetal in the presence of \(\text{HClO}_4\)-\(\text{SiO}_2\)\(^3\) furnished compound 5 in 78% overall yield (Scheme 2).

**Scheme 2:** Reagents: (a) (i) Phthalic anhydride, \(\text{NaOH}, \text{H}_2\text{O}, \text{rt}, 24\) h; (ii) \(\text{Ac}_2\text{O}, \text{NaOAc}, \text{reflux}, 30\) min, 90% in two steps; (b) \(p\)-methoxy phenol, \(\text{BF}_3\cdot\text{OEt}_2, \text{CH}_2\text{Cl}_2, \text{rt}, 5\) h, 86%; (c) (i) 0.01 M \(\text{CH}_3\text{ONa}, \text{CH}_3\text{OH, rt, 20}\) min; (ii) \(\text{PhCH}((\text{OCH}_3)_2, \text{HClO}_4-\text{SiO}_2, \text{CH}_3\text{CN, rt, 10}\) h, 78%.

### 3.2.2.2. Preparation of ethyl 2,3,4,6-tetra-O-acetyl-1-thio-\(\beta\)-D-galactopyranoside (7)\(^4\) and ethyl 2-\(O\)-benzyl-4,6-\(O\)-benzylidene-3-\(O\)-(\(p\)-methoxybenzyl)-1-thio-\(\beta\)-D-galactopyranoside (9)\(^4\)

Ethyl 2,3,4,6-tetra-O-acetyl-1-thio-\(\beta\)-D-galactopyranoside (7) was prepared from D-galactose (6) by successive treatment with acetic anhydride and ethanethiol in the presence of borontrifluoride diethyl etherate\(^4\) in 88% yield. Removal of acetyl groups\(^4\) from compound 7 using sodium methoxide followed by benzylidene acetal formation using benzaldehyde dimethyl acetal and \(\text{HClO}_4-\text{SiO}_2\)\(^3\) gave ethyl 4,6-\(O\)-benzylidene-1-thio-\(\beta\)-D-galactopyranoside (8) in 78% yield. Selective \(p\)-methoxybenzylation of compound 8 via stannylidene acetal formation\(^4\) followed by benzylation using benzyl bromide and sodium hydroxide\(^5\) furnished compound 9 in 90% overall yield (Scheme 3).

**Scheme 3:** Reagents: (a) (i) \(\text{Ac}_2\text{O}, \text{BF}_3\cdot\text{OEt}_2, \text{rt}, 1\) h; (ii) \(\text{EtSH, CH}_2\text{Cl}_2, 0\) \(^\circ\)C-\(\text{rt}, 5\) h, 88%; (b) \(\text{CH}_3\text{ONa, CH}_3\text{OH, rt, 20}\) min; (c) \(\text{PhCH(OOMe)}_2, \text{HClO}_4-\text{SiO}_2, \text{CH}_3\text{CN, rt, 10}\) h, 78%; (d) (i) \(\text{Bu}_3\text{SnO, CH}_3\text{OH, 80}\) \(^\circ\)C, 3 h; (ii) \(p\)-methoxy benzyl chloride, \(\text{CsF, DMF, 80}\) \(^\circ\)C, 10 h; (e) benzyl bromide, \(\text{NaOH, TBAB, THF, rt, 4}\) h, over all 90%.
3.2.2.3. Preparation of \( p \)-methoxyphenyl 2,3,6-tri-\( O \)-benzyl-\( \beta \)-D-\( \ \ \text{galactopyranoside (12)} \)\textsuperscript{51}

Acetylation of \( \text{D-galactose} \) \textsuperscript{6} using acetic anhydride and anhydrous sodium acetate\textsuperscript{44} furnished \( \text{D-galactose pentaacetate} \), which on treatment with \( p \)-methoxyphenol in the presence of boron trifluoride diethyletherate\textsuperscript{45} furnished \( p \)-methoxyphenyl 2,3,4,6-tetra-\( O \)-acetyl-\( \beta \)-D-galactopyranoside (10) in 90% yield. Compound 10 was subjected to a series of reactions involving deacetylation,\textsuperscript{46} 3,4-\( O \)-isopropylidene ketal formation\textsuperscript{52} using 2,2-dimethoxypropane in the presence of \( p \)-toluenesulfonic acid and benzylation\textsuperscript{50} using benzyl bromide in the presence of sodium hydroxide to furnish \( p \)-methoxyphenyl 2,6-di-\( O \)-benzyl-3,4-\( O \)-isopropylidene-\( \beta \)-D-galactopyranoside (11) in 75% yield. Removal of isopropylidene group\textsuperscript{53} from compound 11 using 80% aq. acetic acid followed by selective benzylation via stannylidene acetal formation\textsuperscript{49} furnished \( p \)-methoxyphenyl 2,3,6-tri-\( O \)-benzyl-1-thio-\( \beta \)-D-galactopyranoside (12) in 85% yield (Scheme 4).

Scheme 4: Reagents: (a) (i) \( \text{Ac}_2\text{O}, \text{NaOAc} \), reflux, 1 h; (ii) \( p \)-methoxyphenol, \( \text{BF}_3\cdot\text{OEt}_2 \), \( \text{CH}_2\text{Cl}_2 \), 0 °C-rt, 5 h, 90%; (b) (i) \( \text{CH}_3\text{ONa}, \text{CH}_3\text{OH} \), rt, 5 h; (ii) 2,2-dimethoxypropane, DMF, \( p \)-TsOH, rt, 12 h; (iii) benzyl bromide, \( \text{NaOH} \), rt, 12 h, 75% in three steps; (c) (i) 80% aq. AcOH, 75 °C, 1.5 h; (ii) \( \text{Bu}_2\text{SnO} \), \( \text{CH}_3\text{OH} \), 80 °C, 2 h; (iii) benzyl bromide, TBAB, DMF, 80 °C, 10 h 85%.

3.2.2.4. Preparation of 2,3,4-tri-\( O \)-acetyl-2-azido-2-deoxy-\( \beta \)-D-galactopyranosyl trichloroacetimidate (13)\textsuperscript{54}

Please see page no. 68.

3.2.2.5. Synthesis of \( p \)-methoxyphenyl (2-\( O \)-benzyl-4,6-\( O \)-benzylidene-\( \alpha \)-D-galactopyranosyl)-(1→3)-4,6-\( O \)-benzylidene-2-deoxy-2-N-phthalimido-\( \beta \)-D-glucopyranoside (14)

\( p \)-Methoxyphenyl 4,6-\( O \)-benzylidene-2-deoxy-2-N-phthalimido-\( \beta \)-D-glucopyranoside (5) was allowed to couple with ethyl 2-\( O \)-benzyl-4,6-\( O \)-benzylidene-3-\( O \)-(\( p \)-methoxybenzyl)-1-thio-\( \beta \)-D-galactopyranoside (9) in the presence of a combination of \( N \)-iodosuccinimide (NIS) and trifluoromethane sulfonic acid (TfOH).\textsuperscript{32,55,56} Controlling the reaction condition initially at low
temperature and then at high temperature furnished the disaccharide derivative (14) in a 72% yield, in which stereoselective glycosylation and removal of p-methoxybenzyl group was achieved in one pot. A minor quantity (~8%) of 1,2-trans isomer of compound 14 was also formed, which was separated by column chromatography. It is worth mentioning that after stereoselective glycosylation at low temperature, the elevation of temperature resulted in the clean removal of p-methoxybenzyl group by TfOH present in the reaction medium. Appearance of signals in the NMR spectra confirmed the formation of compound 14 [signals at $\delta$ 5.70 (d, $J = 8.5$ Hz, H-1A), 5.48 (d, $J = 3.5$ Hz, H-1B) in $^1$H NMR and $\delta$ 98.1 (C-1B), 97.8 (C-1A) in the $^{13}$C NMR spectra] (Scheme 5).

**Scheme 5:** Reagents: (a) NIS, TfOH, CH$_2$Cl$_2$, MS 4Å, -30 °C for 45 min, then 0 °C for 30 min, 72%.

### 3.2.2.6. Synthesis of (2,3,4,6-tetra-0-acetyl-β-D-galactopyranosyl)-(1→3)-(4,6-di-0-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-0-benzyl-α-D-galactopyranosyl trichloroacetimidate (19)

In another set of experiments, stereoselective glycosylation of p-methoxyphenyl 2,3,6-tri-O-benzyl-β-D-galactopyranoside (12) with 3,4,6-tri-0-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl trichloroacetimidate (13) in the presence of HClO$_4$-SiO$_2$ in a mixture of dichloromethane-diethyl ether furnished the disaccharide derivative (15) in a 64% yield. The moderate yield of the reaction may be explained considering the less reactivity of 4-hydroxyl group of the D-galactose derivative (12). The formation of compound 15 was supported by spectral analysis [signals at $\delta$ 4.95 (d, $J = 3.5$ Hz, H-1D), 4.72 (d, $J = 7.5$ Hz, H-1C) in the $^1$H NMR and $\delta$ 103.2 (C-1C), 98.5 (C-1D) in the $^{13}$C NMR spectra]. Saponification of compound 15 using sodium methoxide followed by 4,6-O-benzylidene acetal formation using benzaldehyde dimethylacetal in the presence of HClO$_4$-SiO$_2$ gave disaccharide derivative 16 in a 77% yield. Stereoselective glycosylation of compound 16 with ethyl 2,3,4,6-tetra-0-acetyl-β-D-galactopyranoside (7) in the presence of a combination of NIS and HClO$_4$-SiO$_2$ in
dichloromethane\textsuperscript{35} afforded trisaccharide derivative 17 in a 78\% yield. Appearance of signals in the NMR spectra confirmed the formation of compound 17 [\(\delta 5.01 (d, J = 3.5 \text{ Hz}, H-1D), 4.78 (d, J = 8.0 \text{ Hz}, H-1E), 4.76 (d, J = 7.5 \text{ Hz}, H-1C)\) in the \(^1\text{H} \text{ NMR}\) and \(\delta 103.4 \text{ (C-1E)}, 103.4 \text{ (C-1C)}, 99.6 \text{ (C-1D)}\) in the \(^{13}\text{C} \text{ NMR}\) spectra]. In a one-pot de-benzylideneation and \(O\)-acyetylation reaction condition,\textsuperscript{37} compound 17 was treated with acetic anhydride in the presence \(\text{HClO}_4\)-\text{SiO}_2\textsuperscript{33} to give compound 18 in 80\% yield. Oxidative removal of \(\rho\)-methoxyphenyl group in compound 18 using ammonium cerium (IV) nitrate (CAN)\textsuperscript{41} followed by the reaction of the resulting hemiacetal with trichloroacetonitrile in the presence of DBU\textsuperscript{57} led to the formation of trisaccharide trichloroacetimidate derivate 19 in 74\% yield, which was immediately used in the next step (Scheme 6).

\begin{center}
\textbf{Scheme 6}: Reagents: (a) \(\text{HClO}_4\)-\text{SiO}_2, \(\text{CH}_2\text{Cl}_2\)-\text{Et}_2\text{O}, \(-20\ \text{°C}, 1\ \text{h}, 64\%\); (b) 0.1 M \(\text{CH}_3\text{ONa}, \text{CH}_3\text{OH}\), \(r\ t, 2\ \text{h}\); (c) \(\text{PhCl}_2(\text{OCH}_3)_2\), \(\text{HClO}_4\)-\text{SiO}_2, \(\text{CH}_3\text{CN}-\text{DMF}, r\ t, 5\ \text{h}, 77\%\) in two steps; (d) \(\text{NIS}, \text{HClO}_4\)-\text{SiO}_2, \(\text{CH}_2\text{Cl}_2\), \(\text{MS} 4\AA\), \(-40\ \text{°C}, 45\ \text{min}, 78\%\); (e) \(\text{Ac}_2\text{O}, \text{HClO}_4\)-\text{SiO}_2, \(r\ t, 30\ \text{min}, 80\%\); (f) CAN, \(\text{CH}_3\text{CN}-\text{H}_2\text{O}\), \(r\ t, 2\ \text{h}\); (g) \(\text{CCl}_3\text{CN}, \text{CH}_2\text{Cl}_2\), DBU, \(-20\ \text{°C}, 1\ \text{h}, 74\%\) in two steps.
3.2.2.7. Synthesis of \( p\)-methoxyphenyl \((\beta\text{-D-galactopyranosyl})(1\rightarrow3)-(2\text{-acetamido-2-deoxy-}\alpha\text{-D-galactopyranosyl})(1\rightarrow4)-(\text{sodium }\alpha\text{-D-galactopyranosyl uronate})(1\rightarrow3)-(\alpha\text{-D-galactopyranosyl})(1\rightarrow3)-2\text{-acetamido-2-deoxy-}\beta\text{-D-glucopyranoside (1)}\)

**Scheme 7:** Reagents: (a) HClO₄-SiO₂, CH₂Cl₂-Et₂O, -10 °C, 1 h, 68%; (b) H₂, 20% Pd(OH)₂-C, CH₃OH, r.t, 4 h; (c) Ac₂O, CH₃OH, r t, 1 h; (d) (i) TEMPO, NaBr, TBAB, NaHCO₃, NaOCl, CH₂Cl₂, H₂O, 5 °C, 3 h; (ii) NaClO₂, tert-butanol, 2-methyl-2-butene, NaH₂PO₄, r.t, 3 h; (e) NH₂NH₂·H₂O, EtOH, 80 °C, 7 h; (f) Ac₂O, pyridine, r t, 2 h; (g) H₂, 20% Pd(OH)₂-C, CH₃OH, r t, 24 h; (h) 0.1 M CH₂ONa, CH₃OH, r t, 3 h, 51%.

Stereoselective glycosylation of compound 14 with compound 19 in the presence of HClO₄-SiO₂ in a mixture of dichloromethane-diethyl ether furnished pentasaccharide derivative 20 in a 68% yield together with minor quantity (~10%) of its another isomer, which was separated by column chromatography. Spectral analysis of compound 20 confirmed its formation [signals at \( \delta \) 6.76 (d, \( J = 8.5 \) Hz, H-1₆), 5.48 (d, \( J = 3.5 \) Hz, H-1₇), 5.26 (d, \( J = 3.0 \) Hz, H-1₈), 5.08 (d, \( J = 3.5 \) Hz, H-1₉), 4.52 (d, \( J = 8.0 \) Hz, H-1₉) in the \(^{1}\text{H NMR and } \delta \) 100.7 (\( J_{C-1\beta-\text{H}-1\text{}} = 158.0 \) Hz) (C-1₆), 98.3 (\( J_{C-1\beta-\text{H}-1\text{}} = 170.0 \) Hz) (C-1₇), 98.1 (\( J_{C-1\beta-\text{H}-1\text{}} = 160.0 \) Hz) (C-1₈), 98.0 (\( J_{C-1\beta-\text{H}-1\text{}} = 169.0 \) Hz) (C-1₉), 91.7 (\( J_{C-1\beta-\text{H}-1\text{}} = 172.0 \) Hz) (C-1₉) in the \(^{13}\text{C NMR spectra}. Appearance of } J_{C-1\beta-\text{H}-1\text{}} \text{ values}^{58,59} 159 \text{ Hz and 160 Hz indicated the presence of two equatorial or } \beta\text{-glycosyl linkages and } J_{C-1\beta-\text{H}-1\text{}} \text{ values 164, 170 and 172 Hz indicated the presence of three axial or } \alpha\text{-glycosyl linkages in the compound 20. Compound 20 was subjected to a series of reactions involving (a) reduction of azido group and selective removal of benzyl groups by time dependent controlled
hydrogenation over Pd(OH)$_2$-C$^61$ followed by N-acetylation; (b) selective TEMPO mediated oxidation of the primary hydroxyl group to the carboxylic group under a phase transfer reaction condition;$^{39,40}$ (c) removal of N-phthalimido group by hydrazinolysis$^{62}$ followed by acetylation using acetic anhydride and pyridine;$^{63}$ (d) removal of benzylidene acetal by hydrogenation and finally (e) de-O-acetylation using sodium methoxide to furnish target pentasaccharide 1, which was purified over Sephadex$^\circledR$ LH-20 column using (CH$_3$OH-H$_2$O; 4:1) as eluant to give pure compound 1 in a 51% yield. Spectral analysis of compound 1 unambiguously confirmed its formation [signals at $\delta$ 5.15 (br s, H-1c), 4.90 (br s, H-1b, H-1d), 4.80-4.78 (m, H-1a), 4.32 (d, $J$ = 8.0 Hz, H-1e) in the $^1$H NMR and $\delta$ 104.9 (C-1E), 102.6 (C-1A), 99.1 (2 C, C-1B, C-1D), 96.1 (C-1C) in the $^{13}$C NMR spectra] (Scheme 7).

3.2.3. Conclusion

In conclusion, a straight forward convergent synthetic strategy has been developed for the synthesis of the pentasaccharide repeating unit corresponding to the O-antigen of enterohaemorrhagic E. coli O113 strain. A one-pot reaction protocol for the glycosylation and removal of $\beta$-methoxybenzyl ether has been adopted. HClO$_4$-SiO$_2$ has been used as an effective acid catalyst in a number of reaction steps such as benzylidene acetal formation, direct conversion of benzylidene acetal to O-acetylated derivative, to activate glycosyl trichloroacetimidate derivative and thioglycoside in combination with NIS avoiding the use of moisture sensitive protic acids. A [3+2] block glycosylation technique has been used. A late stage selective TEMPO mediated oxidation protocol has been applied for the preparation of D-galacturonic acid moiety. Over all, the target compound 1 was efficiently synthesized in minimum number steps.

3.2.4. Experimental section

3.2.4.1. General methods

Please see page no. 67.

3.2.4.2. Preparation of HClO$_4$-SiO$_2$

Please see page no. 107.
3.2.4.3. Preparation and spectral data of compounds 1-20

1,3,4,6-Tetra-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranose (3): Please see page no. 132.

p-Methoxyphenyl 3,4,6-tri-O-acetyl-2-deoxy-2-N-phthalimido-β-D-glucopyranoside (4): To the solution of compound 3 (10 g, 20.8 mmol) and p-methoxy phenol (3.4 g, 27.04 mmol) in dried CH₂Cl₂ (40 mL) was added MS 4Å (5 g) and the reaction mixture was cooled to 0 °C. To the cooled reaction mixture was added BF₃-Et₂O (8 mL, 62.8 mmol) and it was stirred at 5 °C for 5 h. The reaction mixture was filtered and washed with CH₂Cl₂ (200 mL). The organic layer was successively washed with satd. NaHCO₃ and water, dried (Na₂SO₄) and concentrated. The crude product was purified over SiO₂ using hexane-EtOAc (5:1) as eluant to give pure compound 4 (8.6 g, 86%). White solid; m. p. 70-72 °C [EtOH]; IR (KBr): 1750, 1719, 1508, 1386, 1219, 1039 cm⁻¹;¹H NMR (400 MHz, CDCl₃): δ 7.88-7.84 (m, 2 H, Ar-H), 7.76-7.71 (m, 2 H, Ar-H), 6.85 (d, J = 9.1 Hz, 2 H, Ar-H), 6.73 (d, J = 9.1 Hz, 2 H, Ar-H), 5.86 (dd, J = 10.8 Hz, 9.1 Hz, 1 H, H-3), 5.85 (d, J = 8.6 Hz, 1 H, H-1), 5.24 (dd, J = 10.2 Hz, 9.1 Hz, 1 H, H-4), 4.57 (dd, J = 10.8 Hz, 8.6 Hz, 1 H, H-2), 4.37-4.16 (m, 2 H, H-6), 3.98-3.93 (m, 1 H, H-5), 3.73 (s, 3 H, OCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 169.7, 169.6 (Phth), 156.0-114.9 (Ar-C), 102.3 (PhCH), 98.5 (C-1), 82.4 (C-4), 68.9 (2 C, C-3, C-6), 66.7 (C-)

p-Methoxyphenyl 4,6-O-benzylidene-2-deoxy-N-phthalimido-β-D-glucopyranoside (5): A solution of compound 4 (5.4 g, 10 mmol) in 0.01 M CH₂ONa in CH₂OH (60 mL) was allowed to stir at room temperature for 20 min and neutralized with Dowex-50W X8 (H⁺) resin. The reaction mixture was filtered and evaporated to dryness. The dried mass was dissolved in anhydrous CH₃CN (20 mL) and benzaldehyde dimethylacetal (1.8 mL, 12 mmol) was added to it followed by HClO₄-SiO₂ (100 mg). After stirring at room temperature for 10 hr, the reaction mixture was filtered and the solvents were removed under reduced pressure and the crude mass was purified over SiO₂ using hexane-EtOAc (3:1) as eluant to furnish pure compound 5 (3.1 g, 78 %). White solid; m. p. 128-129 °C [EtOH]; [α]D₂⁵ = 7 (c 0.9, CHCl₃);¹H NMR (500 MHz, CDCl₃): 7.87-7.20 (m, 9 H, Ar-H), 6.82 (d, J = 9.1 Hz, 2 H, Ar-H), 6.70 (d, J = 9.1 Hz, 2 H, Ar-H), 5.74 (d, J = 8.4 Hz, 1 H, H-1), 5.52 (s, 1 H, PhCH), 4.62 (m, 1 H, H-4), 4.44 (dd, J = 8.4 Hz, 10.5 Hz, 1 H, H-2), 4.34 (dd, J = 10.1 Hz each, 1 H, H-6a), 3.82 (dd, J = 9.9 Hz each, 1 H, H-6b), 3.69 (s, 3 H, OCH₃), 3.66-3.64 (m, 2 H, H-3, H-5);¹³C NMR (125 MHz, CDCl₃): δ 169.7, 169.6 (Phth), 156.0-114.9 (Ar-C), 102.3 (PhCH), 98.5 (C-1), 82.4 (C-4), 68.9 (2 C, C-3, C-6), 66.7 (C-)...
Chapter 3.2

Ethyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (7): Please see page no. 72.

Ethyl 4,6-O-benzylidene-1-thio-β-D-galactopyranoside (8): For the preparation please see page no. 72.

Ethyl 2-O-benzyl-4,6-O-benzylidene-3-O-(p-methoxybenzyl)-1-thio-β-D-galactopyranoside (9): To a solution of compound 8 (5 g, 16 mmol) in dry CH₃OH (100 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) were added CsF (2.4 g, 15.8 mmol) and p-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) and 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 CH₃OH (5 mL) and the solvents were removed under reduced pressure. The crude product was dissolved in CH₂Cl₂ (150 mL) and the organic layer was washed with water, dried (Na₂SO₄) and concentrated under reduced pressure. The crude product was purified over SiO₂ using hexane-EtOAc (8:1) as eluant to give pure compound 9 (4.5 g, 90%). White solid; m.p. 140-142 °C [EtOH]; [α]D²⁵ + 2.2 (c 1.0, CHCl₃); IR (KBr): 3441, 2863, 2361, 1616, 1515, 1456, 1400, 1352, 1254, 1172, 1096, 1058, 1028, 1005, 817, 735 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): 8 7.57-7.28 (m, 12 H, Ar-H), 6.85 (d, J = 8.5 Hz, 2 H, Ar-H), 5.47 (s, 1 H, PhCH), 4.93-4.82 (abq, J = 10.2 Hz, 2 H, PhCH₂), 4.70 (br s, 2 H, CH₂OPhCH₂), 4.44 (d, J = 9.6 Hz, 1 H, H-1), 4.30 (d, J = 12.3 Hz, 1 H, H-6A), 4.12 (d, J = 3.2 Hz, 1 H, H-4), 3.96 (d, J = 12.3 Hz, H-6b), 3.88 (t, J = 9.5 Hz, 1 H, H-2), 3.57 (dd, J = 9.2, 3.4 Hz, 1 H, H-3), 3.34 (br s, 1 H, H-5), 2.88-2.73 (m, 2 H, SCH₂CH₃), 1.36 (t, J = 7.4 Hz, 3 H, SCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃): 8 159.3, 138.5-113.8 (Ar-C), 101.4 (PhCH), 84.4 (C-1), 80.6 (C-5), 76.8 (C-3), 75.6 (PhCH₂), 74.0 (CH₂OPhCH₂), 71.4 (C-4), 69.8 (C-2), 69.4 (C-6), 55.1 (OCH₃), 23.7 (SCH₂CH₃), 15.1 (SCH₂CH₃); ESI-MS: 545.2 [M+Na⁺]; Anal. Calcd. for C₃₀H₃₄O₉S (522.21): C, 68.94; H, 6.56; found: C, 68.78; H, 6.75.

p-Methoxyphenyl 2,3,4,6-tetra-O-acetyl-β-D-galactopyranoside (10): A suspension of anhydrous NaOAc (34 g, 416 mmol) in acetic anhydride (52 mL, 556 mmol) was heated to the boiling point. D-galactose (6; 10 g, 56 mmol) was added to the reaction mixture in small portions...
with occasional shaking during 1 h. The reaction mixture was then allowed to cool to room temperature. The cooled reaction mixture was poured in ice water with stirring. The solid mass was filtered and washed with cold water. The crude product was crystallized from ethanol to give 1,2,3,4,6-penta-O-acetyl-β-D-galactopyranose (20 g). To a solution of galactose pentaacetate (15 g, 38.4 mmol) and p-methoxy phenol (7.2 g, 57.6 mmol) in anhydrous CH₂Cl₂ (100 mL) was added MS-4Å (5 g) and the solution was stirred at room temperature for 1 h under argon. To the reaction mixture was added BF₃·Et₂O (5.7 mL, 46 mmol) at 0 °C and it was allowed to stir at room temperature for 5 h. The reaction mixture was filtered and washed with CH₂Cl₂ (500 mL). The organic layer was washed with satd. aq. NaHCO₃, dried (Na₂SO₄) and concentrated under reduced pressure. Column chromatography of the crude product over SiO₂ using hexane-ETOAc (7:1) as eluent afforded pure compound 10 (14.6 g, 90%). Colorless oil; ¹H NMR (200 MHz, CDCl₃): δ 6.92, 6.77 (2 d, 4 H, J = 8.9 Hz each, Ar-H), 5.37 (m, 2 H, H-2, H-4), 5.04, (dd, J = 10.4 and 3.0 Hz, 1 H, H-3), 4.88 (d, J = 7.9 Hz, 1 H, H-1), 4.17 (d, J = 6.5 Hz, 2 H, H-6), 3.79 (m, 1 H, H-5), 3.76 (s, 3 H, OCH₃), 2.19, 2.08, 2.04, 2.01 (4 s, 12 H, COCH₃); ¹³C NMR (50 MHz, CDCl₃): δ 170.3, 170.2, 170.1, 169.2 (4 COCH₃), 156.1-114.9 (Ar-C), 101.2 (C-1), 71.2 (2 C), 69.2, 67.3, 61.5 (C-6), 55.81 (OCH₃), 21.0, 20.9, 20.9, 20.8 (4 COCH₃); ESI-MS: 477.1 [M+Na]+; Anal. Calcd. for C₂₁H₂₆O₁₁ (454): C, 55.50; H, 5.77; found: 55.41; H, 5.91.

*p-Methoxyphenyl 2,6-di-O-benzyl-3,4-O-isopropylidene-β-D-galactopyranoside (11):* A solution of compound 10 (14 g, 30.8 mmol) in 0.1 M CH₃ONa in CH₃OH (70 mL) was allowed to stir at room temperature for 5 h. The reaction mixture was neutralized with Dowex 50W-X8 (H⁺) resin, filtered and concentrated under reduced pressure. To a solution of the deacetylated product in DMF (20 mL) were added 2,2-dimethoxypropane (6.4 mL) and p-TsOH (250 mg) and it was stirred at room temperature for 12 h. The reaction was quenched with Et₃N (0.5 mL) and concentrated under pressure. To a solution of the crude product in THF (30 mL) were added benzyl bromide (5 mL) and powdered NaOH (3 g) and the reaction was stirred at room temperature for 12 h. The reaction mixture was diluted with water (200 mL) and extracted with ethyl acetate (200 mL). The organic layer was dried (Na₂SO₄) and concentrated. The crude product was purified over SiO₂ using hexane-ETOAc (8:1) as eluant furnished pure compound 11 (11.7 g, 75%). Colorless oil; [α]D²⁵ +12 (c 0.9, CHCl₃); IR (neat): 2926, 2870, 2371, 1630, 1507, 1456, 1376, 1294, 1222, 1058, 828, 736, 698, 527 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.47-7.28 (m, 10 H, Ar-H), 7.16, 6.83 (2 d, 4 H, J = 12.5 Hz each, Ar-H), 4.97, 4.91 (2 d, 2 H, J = 11.7 Hz, CH₂Ph), 4.84 (d, 1 H, J = 8.0 Hz, H-1), 4.66, 4.57 (2 d, 2 H, J = 11.7 Hz, CH₂Ph), 4.29-4.21 (m, 2 H, H-2, H-4), 4.05 (m, 1 H, H-5), 3.89-3.83 (m, 2 H, H-6), 3.80 (s, 3 H, OCH₃).
3.69 (t, 1 H, J = 12 Hz, H-2), 1.44, 1.39 (2 s, 6 H, C(CH₃)₂); ¹³C NMR (75 MHz, CDCl₃): δ 155.6, 151.8, 138.6-114.9 (Ar-C), 110.6 [C(CH₃)₂], 103.5 (C-1), 79.7, 79.5, 74.1, 74.1, 74.0, 73.0, 70.0 (C-6), 56.0 (OCH₃), 28.2, 26.8 [C(CH₃)₂]; ESI-MS: 529.3 [M+Na]+; Anal. calcd. for C₃₀H₃₄O₇ (506): C, 71.13; H, 6.76; found: C, 71.02; H, 6.60.

**p-Methoxyphenyl 2,3,6-tri-O-benzyl-β-D-galactopyranoside (12):** A solution of compound 11 (6.5 g, 12.84 mmol) in 80% aq. AcOH (150 mL) was stirred at 80 °C for 1.5 h and concentrated under reduced pressure. To a solution of the diol derivative (4 g, 8.56 mmol) in CH₃OH (100 mL) was added dibutyltinoxide (2.35 g, 9.44 mmol) and the suspension was stirred at 80 °C for 2 h. The solvents were removed under reduced pressure and the crude product was dissolved in DMF (30 mL). To the reaction mixture were added tetrabutylammonium bromide (2.76 g, 8.56 mmol) and benzyl bromide (2.54 mL, 21.44 mmol) and it was stirred at 80 °C for 10 h. The solvents were removed under reduced pressure and the crude mass was extracted with EtOAc (200 mL). The organic layer was successively washed with water, satd. NaHCO₃ and brine, dried (Na₂SO₄) and concentrated. The residue was purified over SiO₂ using hexane-EtOAc (7:1) to give pure compound 12 (4 g, 85%). White solid; m.p. 127-128 °C [EtOAc-hexane]; [α]D²⁵⁻¹⁴.3 (c 1.4, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.38-7.30 (m, 15 H), 7.05-6.79 (2 d, 4 H), 5.01 (d, J = 10.9 Hz, 1 H), 4.85 (d, J = 8.0 Hz, 1 H, H-1), 4.83 (d, 1 H), 4.75 (s, 2 H), 4.57 (s, 2 H), 4.06 (m, 1 H), 3.91 (dd, J = 9.2 Hz, 1 H, H-2), 3.84 (dd, J = 5.7, 11.3 Hz, 1 H), 3.77 (m, 1 H), 3.76 (s, 2 H), 3.66 (m, 1 H), 3.58 (dd, J = 3.4 Hz, 1 H, H-3), 2.56 (s, 1 H, OH); ¹³C NMR (125 MHz, CDCl₃): δ 155.3-114.5 (Ar-C), 102.9, 80.6, 78.7, 75.4, 73.7, 73.5, 72.5, 69.2, 66.8, 55.6; ESIMS: 579.2 [M+Na]+; Anal. Calcd. for C₃₄H₃₆O₇ (556.24): C, 73.36; H, 6.52; found: C, 73.20; H, 6.70.

**p-Methoxyphenyl (2-O-benzyl-4,6-O-benzylidene-α-D-galactopyranosyl)-(1→3)-4,6-O-benzylidene-2-deoxy-2-N-phthalimido-β-D-glucopyranoside (14):** To a solution of compound 5 (1 g, 1.98 mmol) and compound 9 (1.2 g, 2.29 mmol) in anhydrous CH₂Cl₂ (10 mL) was added MS 4Å (1 g) and the reaction mixture was stirred at room temperature under argon for 30 min. The reaction mixture was cooled to −30 °C and N-iodosuccinimide (NIS; 570 mg, 2.53 mmol) and TfOH (20 µL) were added to it. After stirring the reaction mixture at −30 °C for 45 min the temperature was raised to 0 °C and the reaction mixture was allowed to stir at 0 °C for 30 min. The reaction mixture was filtered through a Celite® bed and washed with CH₂Cl₂ (100 mL). The organic layer was successively washed with 5% Na₂S₂O₃, satd. NaHCO₃ and water, dried (Na₂SO₄) and concentrated. The crude product was purified over SiO₂ using hexane-EtOAc (4:1)
as eluant to give pure compound 14 (1.2 g, 72%). Colorless oil; $[\alpha]_D^{25} + 92.6$ (c 1.2, CHCl$_3$); IR (neat): 3033, 2980, 2933, 2876, 1780, 1742, 1717, 1502, 1459, 1400, 1099, 1031, 996, 699 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.82-6.89 (m, 19 H, Ar-H), 6.74 (d, $J = 9.0$ Hz, 2 H, Ar-H), 6.64 (d, $J = 9.0$ Hz, 2 H, Ar-H), 5.70 (d, $J = 8.5$ Hz, 1 H, H-1A), 5.48 (d, $J = 3.5$ Hz, 1 H, H-1B), 5.25 (s, 1 H, PhCH), 5.14 (s, 1 H, PhCH), 4.87 (t, $J = 9.5$ Hz, 1 H each, H-3A), 4.54 (t, $J = 9.0$ Hz, 1 H each, H-2A), 4.38 (d, $J = 12.5$ Hz, 1 H, PhCH$_2$), 3.86 (dd, $J = 9.5$, 3.0 Hz, 1 H, H-1D), 3.82 (t, $J = 9.0$ Hz, 1 H each, H-5A), 3.80 (d, $J = 3.0$ Hz, 1 H, PhCH$_2$), 3.76-3.70 (m, 2 H, H-6aA), 3.64 (s, 3 H, OCH$_3$), 3.57 (dd, $J = 10.0$, 3.5 Hz, 1 H, H-2B), 3.36 (d, $J = 12.0$ Hz, 1 H, H-6ab); 13C NMR (125 MHz, CDCl$_3$): $\delta$ 155.7-114.5 (Ar-C), 102.1 (PhCH), 100.9 (PhCH), 98.1 (C-1B), 97.8 (C-1A), 82.3 (C-4A), 75.5 (C-4b), 74.9 (C-2b), 73.8 (C-3A), 71.2 (PhCH$_2$), 68.7 (C-6b), 68.5 (C-5A), 67.4 (C-3b), 66.1 (C-6a), 62.9 (C-5b), 55.6 (C-2A), 55.3 (OCH$_3$); ESI-MS: 866.2 [M+Na]$^+$; Anal. Calcd. for C$_{48}$H$_{45}$NO$_3$ (843.29): C, 68.32; H, 5.37; found: C, 68.10; H, 5.60.

**p-Methoxyphenyl (3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (15):** A solution of compound 12 (1.4 g, 2.51 mmol) and compound 13 (1.9 g, 4.0 mmol) in anhydrous CH$_2$Cl$_2$-Et$_2$O (12 mL, 1:1 v/v) was cooled to $-20$ °C. To the cooled reaction mixture was added HClO$_4$-SiO$_2$ (200 mg) and the reaction mixture was allowed to stir at same temperature for 1 h. The reaction mixture was filtered and washed with CH$_2$Cl$_2$ (100 mL). The combined organic layer was washed with satd. NaHCO$_3$ and water, dried (Na$_2$SO$_4$) and concentrated. The crude product was purified over SiO$_2$ using hexane-EtOAc (5:1) as eluant to give pure compound 15 (1.4 g, 64%). Colorless oil; $[\alpha]_D^{25} + 73.8$ (c 1.2, CHCl$_3$); IR (neat): 7.30-7.15 (m, 15 H, Ar-H), 6.90 (d, $J = 9.0$ Hz, 2 H, Ar-H), 6.70 (d, $J = 9.0$ Hz, 2 H, Ar-H), 5.36 (d, $J = 2.0$ Hz, 1 H, H-4d), 5.30 (dd, $J = 10.5$, 3.5 Hz, 1 H, H-3d), 4.95 (d, $J = 3.5$ Hz, 1 H, H-1D), 4.94 (d, $J = 11.0$ Hz, 1 H, PhCH$_2$), 4.82 (d, $J = 11.0$ Hz, 1 H, PhCH$_2$), 4.72 (d, $J = 7.5$ Hz, 1 H, H-1c), 4.70- 4.65 (m, 2 H, H-5d), 4.45 (m, 1 H, PhCH$_2$), 4.08 (d, $J = 3.0$ Hz, 1 H, H-2c), 3.90-3.83 (m, 3 H, H-5c, H-6ac, H-6ad), 3.67 (s, 3 H, OCH$_3$), 3.60 (dd, $J = 11.0$, 4.0 Hz, 1 H, H-2d), 3.58-3.52 (m, 2 H, H-2c, H-6bd), 3.48-3.45 (m, 1 H, H-6bc), 3.40 (dd, $J = 10.0$, 3.0 Hz, 1 H, H-3c), 2.02, 1.97, 1.80 (3 s, 9 H, 3 COCH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 170.1 (2 C), 169.8 (3 COCH$_3$), 155.7-114.5 (Ar-C), 103.2 (C-1c), 98.5 (C-1b), 79.7 (C-3c), 78.7 (C-2c), 75.2 (PhCH$_2$), 73.8 (C-4c), 73.5 (PhCH$_2$), 73.3 (PhCH$_2$), 72.9 (C-5c), 68.8 (C-5b), 67.3 (C-4d), 67.0 (C-6b), 66.2 (C-5d), 60.6 (C-6c), 58.0 (C-2d), 55.6 (OCH$_3$), 20.2, 20.6 (2 C) (3
COCH$_3$); ESI-MS: 892.3 [M+Na]$^+$; Anal. Calcd. for C$_{46}$H$_{51}$N$_3$O$_{14}$ (869.34): C, 63.51; H, 5.91; found: C, 63.28; H, 6.15.

$p$-Methoxyphenyl (4,6-O-benzylidene-2-azido-2-deoxy-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (16): A solution of compound 15 (1.2 g, 1.38 mmol) in 0.1 M CH$_3$ONa in CH$_3$OH (20 mL) was allowed to stir at room temperature for 2 h. The reaction mixture was neutralized with Dowex 50W X8 (H$^+$) resin, filtered, and concentrated under reduced pressure. To a solution of the deacetylated product in anhydrous CH$_3$CN-DMF (10 mL; 1:1 v/v) was added benzaldehyde dimethyl acetal (0.4 mL, 2.66 mmol) followed by HClO$_4$-SiO$_2$ (100 mg) and the reaction mixture was allowed to stir at room temperature for 5 h. The reaction mixture was filtered and the solvents were removed under reduced pressure to give the crude product, which was purified over SiO$_2$ using hexane-EtOAc (5:1) as eluant to give pure compound 16 (880 mg, 77%). Colorless oil; [α]$_D^{25}$ + 86.8 (c 1.2, CHCl$_3$); IR (neat): 3336, 2926, 2121, 1737, 1716, 1514, 1467, 1226, 1170, 1067, 756, 699 cm$^{-1}$; $^1$H NMR (500 MHz, CDC$_3$): δ 7.38-7.17 (m, 20 H, Ar-H), 6.97 (d, $J$ = 9.0 Hz, 2 H, Ar-H), 6.72 (d, $J$ = 9.0 Hz, 2 H, Ar-H), 5.34 (s, 1 H, PhCH), 4.97 (d, $J$ = 3.5 Hz, 1 H, H-1D), 4.95 (d, $J$ = 11.5 Hz, 1 H, PhCH$_2$), 4.82 (d, $J$ = 11.5 Hz, 1 H, PhCH$_2$), 4.78 (d, $J$ = 8.0 Hz, 1 H, H-1C), 4.66-4.61 (2 d, $J$ = 12.0 Hz each, 2 H, PhCH$_2$), 4.51-4.43 (2 d, $J$ = 11.5 Hz each, 2 H, PhCH$_2$), 4.15 (d, $J$ = 2.5 Hz, 1 H, H-4p), 5.30 (dd, $J$ = 10.5, 3.0 Hz, 1 H, H-3D), 4.07 (br s, 1 H, H-5c), 4.05 (d, $J$ = 3.0 Hz, 1 H, H-4c), 3.95-3.92 (m, 1 H, H-6ac), 3.78 (t, $J$ = 10.0 Hz each, 1 H, H-2c), 3.69 (s, 3 H, OCH$_3$), 3.60-3.51 (m, 1 H, H-6bC); $^{13}$C NMR (125 MHz, CDC$_3$): δ 155.3-114.5 (Ar-C), 103.3 (C-1c), 101.0 (PhCH), 99.5 (C-1p), 80.6 (C-3c), 78.1 (C-2c), 75.6 (C-4c), 75.0 (PhCH$_2$), 73.6 (PhCH$_2$), 73.3 (C-4D), 73.1 (C-5p), 72.7 (PhCH$_2$), 68.9 (C-6c), 67.8 (C-3b), 67.0 (C-6p), 62.7 (C-5c), 61.4 (C-2b), 55.7 (OCH$_3$); ESI-MS: 854.3 [M+Na]$^+$; Anal. Calcd. for C$_{47}$H$_{49}$N$_3$O$_{11}$ (831.34): C, 67.86; H, 5.94; found: C, 67.65; H, 6.18.

$p$-Methoxyphenyl (2,3,4,6-tetra-O-acetyI-β-D-galactopyranosyl)-(1→3)-(4,6-O-benzylidene-2-azido-2-deoxy-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (17): To a solution of compound 16 (800 mg, 0.96 mmol) and compound 7 (450 mg, 1.14 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was added MS 4Å (1 g) and the reaction mixture was stirred at room temperature under argon for 30 min. The reaction mixture was cooled to −40 °C and NIS (280 mg, 1.24 mmol) and HClO$_4$-SiO$_2$ (15 mg) were added to it and the reaction mixture was allowed to stir at same temperature for 45 min. The reaction mixture was filtered through a
Celite® bed and washed with CH$_2$Cl$_2$ (50 mL). The organic layer was successively washed with 5% Na$_2$S$_2$O$_3$, satd. NaHCO$_3$ and water, dried (Na$_2$SO$_4$) and concentrated. The crude product was purified over SiO$_2$ using hexane-EtOAc (5:1) as eluant to give pure compound 17 (870 mg, 78%). Colorless oil; [α]$_D$ $^25 + 80$ (c 1.2, CHCl$_3$); IR (neat): 3474, 2932, 2868, 2117, 1757, 1502, 1226, 1100, 1056, 737, 699 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.42-7.17 (m, 20 H, Ar-H), 6.94 (d, $\text{J} = 9.0$ Hz, 2 H, Ar-H), 6.72 (d, $\text{J} = 9.0$ Hz, 2 H, Ar-H), 5.33 (d, $\text{J} = 3.5$ Hz, 1 H, H-4β), 5.31 (s, 1 H, PhCH$_2$), 3.40 (dd, $\text{J} = 8.0$ Hz each, 1 H, H-2β), 5.01 (d, $\text{J} = 3.5$ Hz, 1 H, H-1β), 4.97 (d, $\text{J} = 11.5$ Hz, 1 H, PhCH$_2$), 4.95 (dd, $\text{J} = 10.5$, 3.0 Hz, 1 H, H-3β), 4.84 (d, $\text{J} = 11.0$ Hz, 1 H, PhCH$_2$), 4.78 (d, $\text{J} = 8.0$ Hz, 1 H, H-1β), 4.76 (d, $\text{J} = 7.5$ Hz, 1 H, H-1c), 4.70-4.60 (2 d, $\text{J} = 11.5$ Hz each, PhCH$_2$), 4.49-4.41 (2 d, $\text{J} = 11.0$ Hz each, PhCH$_2$), 4.20 (d, $\text{J} = 3.0$ Hz, 1 H, H-3β), 4.17 (d, $\text{J} = 3.5$ Hz, 1 H, H-4c), 4.12-4.10 (m, 1 H, H-6αβ), 4.07-4.04 (m, 1 H, H-6αβ), 4.03 (br s, 1 H, H-5c), 3.99 (dd, $\text{J} = 10.5$, 3.0 Hz, 1 H, H-3β), 3.95-3.88 (m, 2 H, H-5β, H-6αc), 3.79-3.76 (m, 2 H, H-2c, H-2d), 3.69 (s, 3 H, OCH$_3$), 3.60-3.55 (m, 3 H, H-5β, H-6αβ, H-6βc), 3.44 (dd, $\text{J} = 10.0$, 3.0 Hz, 1 H, H-3c), 3.37-3.35 (m, 1 H, H-6αβ), 2.06, 2.00, 1.93, 1.90 (4 s, 12 H, 4 COCH$_3$); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 170.4, 170.3, 170.2, 169.5 (4 COCH$_3$), 155.4-114.5 (Ar-C), 103.4 (C-1β), 103.4 (C-1c), 100.5 (PhCH$_2$), 99.6 (C-1d), 80.6 (C-3c), 78.5 (C-2c), 76.6 (C-4d), 75.6 (C-3d), 75.0 (PhCH$_2$), 73.7 (PhCH$_2$), 73.2 (C-4c), 73.1 (C-5d), 72.7 (PhCH$_2$), 71.2 (C-3e), 70.8 (C-5e), 69.0 (C-6c), 68.8 (C-2e), 67.0 (C-4e), 66.9 (C-6d), 62.9 (C-5c), 61.5 (C-6β), 59.4 (C-2c), 56.0 (OCH$_3$), 20.9, 20.8, 20.7, 20.6 (4 COCH$_3$); ESI-MS: 1184.4 [M+Na]$^+$; Anal. Calcd. for C$_{61}$H$_{67}$N$_3$O$_2$O (1161.43): C, 63.04; H, 5.81; found: C, 62.82; H, 6.04.

$p$-Methoxyphenyl (2,3,4,6-tetra-0-acetyl-β-D-galactopyranosyl)-(1→3)-(4,6-di-0-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-0-benzyl-β-D-galactopyranoside (18): To a solution of compound 17 (850 mg, 0.73 mmol) in acetic anhydride (2 mL) was added HClO$_4$-SiO$_2$ (50 mg) and the reaction mixture was allowed to stir at room temperature for 30 min. The reaction mixture was filtered and washed with EtOAc (25 mL). The organic layer was washed with satd. NaHCO$_3$ and water, dried (Na$_2$SO$_4$) and concentrated under reduced pressure. The crude product was passed through a short pad of SiO$_2$ using hexane-EtOAc (3:1) to give pure compound 18 (675 mg, 80%). Colorless oil; [α]$_D$ $^25 + 58$ (c 1.2, CHCl$_3$); IR (neat): 3484, 3036, 2957, 2931, 1757, 1508, 1378, 1244, 1179, 1093, 977, 698 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): δ 7.29-7.17 (m, 15 H, Ar-H), 6.90 (d, $\text{J} = 9.0$ Hz, 2 H, Ar-H), 6.71 (d, $\text{J} = 9.0$ Hz, 2 H, Ar-H), 5.41 (d, $\text{J} = 2.0$ Hz, 1 H, H-4ε), 5.30 (d, $\text{J} = 3.0$ Hz, 1 H, H-4β), 5.12 (dd, $\text{J} = 8.0$ Hz each, 1 H, H-2ε), 4.96 (dd, $\text{J} = 9.5$, 3.0 Hz, 1 H, H-3ε), 4.94 (d, $\text{J} = 11.0$ Hz, 1 H, PhCH$_2$), 4.91 (d, $\text{J} = 3.5$ Hz, 1 H, H-1D), 4.80 (d, $\text{J} = 11.0$ Hz, 1 H, PhCH$_2$), 4.72 (d, $\text{J} = 7.5$ Hz, 1 H, H-1c),
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4.70 (d, J = 11.0 Hz, 1 H, PhCH$_2$), 4.78 (d, J = 8.0 Hz, 1 H, H-1$_E$), 4.63 (d, J = 11.0 Hz, 1 H, PhCH$_2$), 4.48-4.45 (m, 1 H, H-5D), 4.43 (br s, 2 H, PhCH$_2$), 4.10-4.00 (m, 4 H, H-3D, H-4C, H-6$_{abE}$), 3.90-3.85 (m, 3 H, H-6$_{ac}$, H-6$_{abD}$), 3.75 (dd, J = 7.5 Hz each, 1 H, H-2c), 3.68 (s, 3 H, OCH$_3$), 3.59 (dd, J = 9.5, 3.0 Hz, 1 H, H-2D), 3.57-3.50 (m, 3 H, H-5C, H-5E, H-6$_b$c), 3.39 (dd, J = 10.0, 3.0 Hz, 1 H, H-3c), 2.09, 2.00, 1.95, 1.90, 1.87 (s, 18 H, 6 COCH$_3$); 13C NMR (125 MHz, CDCl$_3$): 170.4, 170.3, 170.2, 170.1, 169.7, 169.5 (6 COCH$_3$), 155.3-114.5 (Ar-C), 103.2 (C-1$_C$), 100.6 (C-1$_E$), 98.8 (C-1$_D$), 79.8 (C-3$_C$), 78.6 (C-2$_C$), 75.1 (C-5$_E$), 75.0 (PhCH$_2$), 73.9 (C-3D), 73.6 (PhCH$_2$), 73.1 (PhCH$_2$), 73.0 (C-5$_C$), 71.0 (C-3$_E$), 70.9 (C-4c), 69.3 (C-4$_c$), 68.3 (C-2$_E$), 67.0 (C-6$_C$), 66.8 (C-5$_D$), 66.7 (C-4$_D$), 61.5 (C-6$_D$), 61.0 (C-6$_E$), 60.2 (C-2$_D$), 55.6 (OCH$_3$), 21.0, 20.7 (2 C), 20.6 (2 C), 20.5 (6 COCH$_3$); ESI-MS: 1180.4 [M+Na]$^+$; Anal. Calcd. for C$_{58}$H$_{67}$N$_3$O$_{22}$ (1157.42): C, 60.15; H, 5.83; found: C, 60.00; H, 6.00.

(2,3,4,6-Tetra-O-acetyl-$\beta$-D-galactopyranosyl)-(1$\rightarrow$3)-(4,6-di-O-acetyl-2-azido-2-deoxy-$\alpha$-D-galactopyranosyl)-(1$\rightarrow$4)-2,3,6-tri-O-benzyl-$\alpha$-D-galactopyranosyl trichloroacetimidate (19): To a solution of compound 18 (650 mg, 0.56 mmol) in CH$_3$CN-H$_2$O (15 mL; 1:1 v/v) was added CAN (1 g, 1.82 mmol) and the reaction mixture was allowed to stir at room temperature for 2 h. The reaction mixture was extracted with EtOAc (50 mL). The organic layer was successively washed with satd. NaHCO$_3$ and water, dried (Na$_2$SO$_4$) and concentrated. The crude product was passed through a short pad of SiO$_2$ using hexane-EtOAc (3:1) to give trisaccharide hemiacetal derivative. To a solution of the hemiacetal derivative in anhydrous CH$_2$Cl$_2$ (5 mL) was added CCl$_3$CN (0.4 mL, 3.98 mmol) and cooled to $-20$ °C. To the cooled reaction mixture was added DBU (10 pL) and the reaction mixture was stirred at same temperature for 1 h. The solvents were removed under reduced pressure and the crude product was purified over SiO$_2$ using hexane-EtOAc (6:1) as eluant to give pure compound 19 (500 mg, 74%), which was used immediately for the next step without further characterization.

$p$-Methoxyphenyl (2,3,4,6-tetra-O-acetyl-$\beta$-D-galactopyranosyl)-(1$\rightarrow$3)-(4,6-di-O-acetyl-2-azido-2-deoxy-$\alpha$-D-galactopyranosyl)-(1$\rightarrow$4)-(2,3,6-tri-O-benzyl-$\alpha$-D-galactopyranosyl)- (1$\rightarrow$3)-(2-O-benzyl-4,6-O-benzylidene-$\alpha$-D-galactopyranosyl)-(1$\rightarrow$3)-4,6-O-benzylidene-2-deoxy-2-N-phthalimido-$\beta$-D-glucopyranoside (20): A solution of compound 14 (320 mg, 0.38 mmol) and compound 19 (500 mg, 0.42 mmol) in anhydrous CH$_2$Cl$_2$-Et$_2$O (5 mL, 3:1 v/v) was cooled to $-10$ °C. To the cooled reaction mixture was added HClO$_4$-SiO$_2$ (50 mg) and the reaction mixture was allowed to stir at same temperature for 1 h. The reaction mixture was filtered and washed with CH$_2$Cl$_2$ (50 mL). The combined organic layer was washed with satd.
NaHCO₃ and water, dried (Na₂SO₄) and concentrated. The crude product was purified over SiO₂ using hexane-EtOAc (4:1) as eluant to give pure compound 20 (485 mg, 68%). Colorless oil; [α]D²⁵ + 92 (c 1.2, CHCl₃); IR (neat): 3022, 2365, 1746, 1653, 1218, 769, 677 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.91-6.92 (m, 34 H, Ar-H), 6.87 (d, J = 9.0 Hz, 2 H, Ar-H), 6.76 (d, J = 9.0 Hz, 2 H, Ar-H), 6.76 (d, J = 8.5 Hz, 1 H, H-1A), 5.48 (d, J = 3.5 Hz, 1 H, H-1B), 5.44 (d, J = 3.0 Hz, 1 H, H-4D), 5.39 (br s, 1 H, H-4E), 5.38 (s, 1 H, PhCH₂), 5.26 (d, J = 3.0 Hz, 1 H, H-1C), 5.02 (dd, J = 10.0, 3.0 Hz, 1 H, H-3B), 4.92 (t, J = 9.0 Hz, 1 H each, H-3A), 4.60-4.43 (m, 8 H, H-2A, H-5D, PhCH₂), 4.52 (d, J = 8.0 Hz, 1 H, H-1E), 4.33-4.22 (m, 3 H, H-5A, PhCH₂), 4.08-3.96 (m, 4 H, H-4C, H-6abE, H-6abD), 3.95-3.88 (m, 4 H, H-3B, H-3D, H-5C, H-6bd), 3.86-3.67 (m, 4 H, H-2B, H-3C, H-4A, H-4B, H-5E, H-6abA, H-6abC), 3.64 (s, 3 H, OCH₃), 3.52-3.45 (m, 2 H, H-2D, H-6abA), 3.38-3.33 (m, 1 H, H-6abB), 2.95-2.88 (m, 2 H, H-5B, H-6abB), 2.06, 2.00, 1.98, 1.90, 1.89, 1.82 (6 s, 18 H, 6 COCH₂); ¹³C NMR (125 MHz, CDCl₃); δ 170.3 (2 C), 170.2 (2 C), 169.6, 169.5 (6 COCH₂), 155.6-114.5 (Ar-C), 101.8 (PhCH₂), 101.2 (PhCH₂), 100.7 (Jc₁₁H₁ = 158.0 Hz) (C-1E), 98.3 (Jc₁₁H₁ = 170.0 Hz) (C-1B), 98.1 (Jc₁₁H₁ = 160.0 Hz) (C-1A), 98.0 (Jc₁₁H₁ = 169.0 Hz) (C-1D), 91.7 (Jc₁₁H₁ = 172.0 Hz) (C-1C), 82.2 (C-4A), 76.0 (C-4B), 75.5 (C-3C), 75.0 (C-2B), 73.8 (C-3A), 73.1 (PhCH₂), 72.0 (C-5C), 71.8 (PhCH₂), 71.7 (C-3D), 70.9 (C-5E), 70.6 (2 C, C-3E, C-5A), 70.5 (PhCH₂), 70.4 (C-3B), 69.1 (C-4C), 68.9 (C-2E), 68.8 (C-4D), 68.7 (2 C, C-6B, PhCH₂), 66.7 (C-2C), 66.6 (C-6C), 66.4 (C-5D), 66.1 (C-4E), 62.6 (C-5B), 61.5 (C-6A), 60.9 (2 C, C-6D, C-6E), 60.1 (C-2D), 55.6 (OCH₂), 55.2 (C-2A), 20.8, 20.7, 20.6 (2 C), 20.5 (2 C) (6 COCH₂); MALDI-MS: 1899.6 [M+Na]+; Anal. Calcd. for C₉₉H₉₉N₄O₃₃ (1876.66): C, 63.32; H, 5.58; found: C, 63.10; H, 5.84.

p-Methoxyphenyl (β-D-galactopyranosyl)-(1→3)-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→4)-(sodium α-D-galactopyranosyl uronate)-(1→3)-(α-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-glucopyranoside (1): To a solution of compound 20 (450 mg, 0.24 mmol) in CH₃OH (8 mL) was added 20% Pd(OH)₂-C (100 mg) and the reaction mixture was allowed to stir under a positive pressure of hydrogen at room temperature for 4 h. The reaction mixture was filtered through a Celite® bed and concentrated to the one third of the reaction volume. To the methanolic solution of the selectively hydrogenated product was added acetic anhydride (1 mL) and the reaction mixture was kept at room temperature for 1 h. The solvents were removed under reduced pressure to give N-acetylated and debenzyolated product. To a solution of the pentasaccharide tetraol derivative in CH₂Cl₂ (20 mL) and H₂O (5 mL) were successively added aq. NaBr (3 mL; 1 M), aq. TBAB (5 mL; 1 M),
TEMPO (150 mg, 0.96 mmol), satd. NaHCO₃ (15 mL) and 4% aq. NaOCl (15 mL) and the reaction mixture was allowed to stir at 5 °C for 3 h and neutralized with 1 N HCl. To the reaction mixture were added tert-butanol (20 mL), 2-methyl-but-2-ene (20 mL; 2 M solution in THF), aq. NaClO₂ (2.0 g/10 mL) and aq. Na₂HPO₄ (2.0 g/10 mL) and the reaction mixture was allowed to stir at room temperature for 3 h. The reaction mixture was diluted with satd. aq. Na₂HPO₄ and extracted with CH₂Cl₂ (100 mL). The organic layer was washed with water, dried (Na₂SO₄) and concentrated to dryness to give the crude product, which was passed through a short pad of SiO₂.

To a solution of the sodium salt of the oxidized product in C₂H₅OH (10 mL) was added hydrazine monohydrate (0.2 mL) and the reaction was allowed to stir at 80 °C for 7 h. The solvents were removed under reduced pressure and the crude product was dissolved in acetic anhydride and pyridine (2 mL, 1:1 v/v) and kept at room temperature for 2 h. The solvents were removed under reduced pressure and the crude product was passed through a short pad of SiO₂.

To a solution of the acetylated product in CH₃OH (5 mL) was added 20% Pd(OH)₂-C (100 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 concentrated. A solution of the crude product in 0.1 M CH₃ONa in CH₃OH (5 mL) was allowed to stir at room temperature for 3 h, neutralized with Dowex 50W X8 (H⁺) resin and then treated with Dowex 50W X8 (Na⁺) resin, filtered and evaporated to dryness. The sodium salt of the pentasaccharide was purified through a Sephadex® LH-20 column using CH₃OH-H₂O (3:1) as eluant to give pure compound 1 (130 mg, 51%). White powder; [α]D²⁵ + 67 (c 1.2, CH₃OH); IR (KBr): 2364, 2343, 1727, 1646, 1567, 1382, 1074, 838, 770, 676 cm⁻¹; ¹H NMR (500 MHz, CD₃OD): δ 6.79 (d, J = 9.0 Hz, 2 H, Ar-H), 6.73 (d, J = 9.0 Hz, 2 H, Ar-H), 5.15 (br s, 1 H, H-1c), 4.90 (br s, 2 H, H-1b, H-1d), 4.80-4.78 (m, 1 H, H-1a), 4.32 (d, J = 8.0 Hz, 2 H, H-1e), 4.27-3.89 (m, 7 H, H-2a, H-2b, H-2c, H-4c, H-4d, H-4e, H-5c), 3.90-3.72 (m, 8 H, H-2a, H-3a, H-3b, H-3c, H-3d, H-3e, H-5b, H-6abE), 3.70-3.54 (m, 8 H, H-2a, H-6abA, H-6abD, OCH₃), 3.52-3.30 (m, 7 H, H-2c, H-2b, H-3c, H-5a, H-4d, H-5b, H-6abB), 1.92 (br s, 6 H, 2 COCH₃); ¹³C NMR (125 MHz, CD₃OD): δ 174.6 (COONa), 172.7, 172.6 (2 COCH₃), 155.2-114.1 (Ar-C), 104.9 (C-1e), 102.6 (C-1a), 99.1 (2 C, C-1b, C-1d), 96.1 (C-1c), 78.8 (C-4c), 77.5 (C-3a), 76.5 (C-3d), 76.3 (C-3b), 75.3 (2 C, C-5a, C-5e), 73.3 (2 C, C-3b, C-4d), 71.3 (2 C, C-2e, C-4a), 71.1 (C-5d), 69.7 (C-4e), 68.9 (2 C, C-2c, C-3c), 68.6 (C-2a), 67.7 (C-5b), 65.2 (C-5c), 63.0 (C-4b), 61.2 (3 C, C-6a, C-6b, C-6e), 60.2 (C-6d), 55.8 (C-2p), 55.4 (C-2a), 54.7 (OCH₃), 21.5 (2 C, 2 COCH₃); ESI-MS: 1053.3 [M+H]+; Anal. Calcd. for C₄₁H₆₁N₂NaO₂₈ (1052.33): C, 46.77; H, 5.84; found: C, 47.0; H, 6.12.
3.2.5. Representative NMR spectra of synthesized compounds

$^1$H and $^{13}$C NMR spectra of p-methoxyphenyl (2-O-benzyl-4,6-O-benzylidene-α-D-galactopyranosyl)-(1→3)-4,6-O-benzylidene-2-deoxy-2-N-phthalimido-β-D-glucopyranoside (14) (CDCl$_3$).
2D COSY and 2D HSQC NMR (selected region) spectra of \( p \)-methoxyphenyl (2-\( O \)-benzyl-4,6-\( O \)-benzylidene-\( \alpha \)-D-galactopyranosyl)-(1\( \rightarrow \)3)-4,6-\( O \)-benzylidene-2-deoxy-2-\( N \)-phthalimido-\( \beta \)-D-glucopyranoside (14).
\[ ^{1}H \text{ and } ^{13}C \text{ NMR spectra of } p\text{-methoxyphenyl } (3,4,6\text{-tri-O-acetyl-2-azido-2-deoxy-}\alpha\text{-D-galactopyranosyl})\text{-}(1\rightarrow4)\text{-2,3,6-tri-O-benzyl-}\beta\text{-D-galactopyranoside (15) (CDCl}_{3}). \]
2D COSY and 2D HSQC NMR (selected region) spectra of p-methoxyphenyl (3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (15).
$^1$H and $^{13}$C NMR spectra of p-methoxyphenyl (4,6-O-benzylidene-2-azido-2-deoxy-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (16) (CDCl$_3$).
2D COSY and 2D HSQC NMR (selected region) spectra of \( p \)-methoxyphenyl \((4,6-\text{O-benzylidene-2-azido-2-deoxy-}\alpha\text{-D-galactopyranosyl})-(1 \rightarrow 4)\)-2,3,6-tri-\( \text{O} \)-benzyl-\( \beta \text{-D-galactopyranoside} \) (16).
$^1$H and $^{13}$C NMR spectra of $p$-methoxyphenyl (2,3,4,6-tetra-O-acetyl-$\beta$-D-galactopyranosyl)-(1$\rightarrow$3)-(4,6-O-benzylidene-2-azido-2-deoxy-$\alpha$-D-galactopyranosyl)-(1$\rightarrow$4)-2,3,6-tri-O-benzyl-$\beta$-D-galactopyranoside (17) (CDCl$_3$).
2D COSY and 2D HSQC NMR (selected region) spectra of p-methoxyphenyl (2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→3)-(4,6-O-benzylidene-2-azido-2-deoxy-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (17).
$^1$H and $^{13}$C NMR spectra of p-methoxyphenyl (2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→3)-(4,6-di-O-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-galactopyranoside (18) (CDCl₃).
$^{13}$C DEPT 135 and 2D HSQC NMR (selected region) spectra of $p$-methoxyphenyl (2,3,4,6-tetra-$O$-acetyl-$\beta$-$D$-galactopyranosyl)-(1$\rightarrow$3)-(4,6-di-$O$-acetyl-2-azido-2-deoxy-$\alpha$-$D$-galactopyranosyl)-(1$\rightarrow$4)-2,3,6-tri-$O$-benzyl-$\beta$-$D$-galactopyranoside (18).
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$^1$H and $^{13}$C NMR spectra of $p$-methoxyphenyl (2,3,4,6-tetra-$O$-acetyl-$\beta$-$D$-galactopyranosyl)-(1$\rightarrow$3)-(4,6-di-$O$-acetyl-2-azido-2-deoxy-$\alpha$-$D$-galactopyranosyl)-(1$\rightarrow$4)-(2,3,6-tri-$O$-benzyl-$\alpha$-$D$-galactopyranosyl)-(1$\rightarrow$3)-(2-$O$-benzyl-4,6-$O$-benzylidene-$\alpha$-$D$-galactopyranosyl)-(1$\rightarrow$3)-4,6-$O$-benzylidene-2-deoxy-2-$N$-phthalimido-$\beta$-$D$-glucopyranoside (20) (CDCl$_3$).
2D COSY and 2D HSQC NMR (selected region) spectra of p-methoxyphenyl (2,3,4,6-tetra-O-acetyl-\(\beta\)-D-galactopyranosyl)-(1\(\rightarrow\)3)-(4,6-di-O-acetyl-2-azido-2-deoxy-\(\alpha\)-D-galactopyranosyl)-(1\(\rightarrow\)4)-(2,3,6-tri-O-benzyl-\(\alpha\)-D-galactopyranosyl)-(1\(\rightarrow\)3)-(2-O-benzyl-4,6-O-benzylidene-\(\alpha\)-D-galactopyranosyl)-(1\(\rightarrow\)3)-4,6-O-benzylidene-2-deoxy-2-N-phthalimido-\(\beta\)-D-glucopyranoside (20).
$^1$H, $^{13}$C and 2D HSQC (selected region) NMR spectra of $p$-methoxyphenyl ($\beta$-D-galactopyranosyl)-(1→3)-(2-acetamido-2-deoxy-$\alpha$-D-galactopyranosyl)-(1→4)-(sodium $\alpha$-D-galactopyranosyl uronate)-(1→3)-(D-$\alpha$-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-$\beta$-D-glucopyranoside (1) (CD$_3$OD).
3.3. Expedient Synthesis of Two Structurally Close Tetrasaccharides Corresponding to the O-Antigens of Escherichia coli O127 and Salmonella enterica O13
3.3.1. Introduction

Gastrointestinal infections causing diarrhea is a serious health concern in the tropical countries. Diarrhea is one of the leading causes of death in human particularly in children in the developing countries. The microorganisms associated with several food-borne and water-borne diarrheal outbreaks in the developing and developed countries are enteropathogenic Escherichia coli (E. coli), Salmonella enterica (S. enterica) and Shigella strains. Several pathotypes of E. coli strains, responsible for the gastrointestinal infections are classified in several pathotypes. Among several virulent strains of E. coli, enteropathogenic E. coli (EPEC) causes acute infantile diarrhea in the tropical countries. Similar to EPEC, Salmonella enterica strains are also associated with the food and water borne disease worldwide. Salmonella infections are originated from the infected poultry products and household pets. Diarrhea causing S. enterica strains are divided into a subset of a number of serovars. These serovars have several virulence features that help bacteria to cause diseases by various mechanisms. Recently, Perepelov et al. established the chemical structure of the repeating unit of the O-polysaccharide of S. enterica O13 and its relationship with the repeating unit of the O-antigen of enteropathogenic E. coli O127. The O-antigen of E. coli O127 is closely similar to the O-antigen of S. enterica O13, which differs only in the presence of a D-GalpNAc moiety in place of a D-GlcNAc moiety present in S. enterica O13 (Figure 1).

\[
\rightarrow 2)-\alpha-L-Fucp-(1\rightarrow 2)-\beta-D-Galp-(1\rightarrow 3)-\alpha-D-GalpNAc-(1\rightarrow 3)-\alpha-D-GalpNAc-(1\rightarrow \]

Escherichia coli O127

\[
\rightarrow 2)-\alpha-L-Fucp-(1\rightarrow 2)-\beta-D-Galp-(1\rightarrow 3)-\alpha-D-GalpNAc-(1\rightarrow 3)-\alpha-D-GlcNAc-(1\rightarrow \]

Salmonella enterica O13

**Figure 1:** Structures of the repeating units of the O-antigens of E. coli O127 and S. enterica O13.

Emergence of multi-drug resistant (MDR) microorganisms is a serious concern in the drug discovery research. Besides the use of established therapeutics for the treatment of microbial infections, emergence of MDR bacterial strains forces researchers to develop alternative approach to eradicate the infections. O-Polysaccharides (O-antigens) are well known for their role in the pathogenicity of the bacteria as well as their involvements in the initial stages of bacterial infections. Several attempts have been made in the past to develop glycoconjugate vaccines derived from cell wall polysaccharides of bacteria. In order to develop glycoconjugate derivatives it is essential to have a significant quantity of the oligosaccharides, which is practically difficult to isolate them from their natural sources. In this context,
development of concise synthetic strategies for the chemical synthesis of oligosaccharides can provide the required quantity of materials for their biological evaluations. Since, the structures of the O-antigens of *Escherichia coli* O127 and *Salmonella enterica* O13 and their pathogenic actions are very close, expedient syntheses of two structurally close tetrasaccharides corresponding to the O-antigens of *Escherichia coli* O127 and *Salmonella enterica* O13 are presented here (Figure 2).

![Figure 2: Structure of the synthesized tetrasaccharides 1 and 2 corresponding to the repeating units of the O-antigens of *Escherichia coli* O127 and *Salmonella enterica* O13.](image)

### 3.3.2. Results and discussion

The synthesis of two tetrasaccharide 1 and 2 as their p-methoxyphenyl glycosides was achieved using stereoselective sequential glycosylations of differentially protected monosaccharide intermediates. Presence of α-D-galactosamine, α-D-glucosamine and α-L-fucose in both molecules poses challenges in their chemical synthesis. In order to construct the target compounds a number of suitably protected monosaccharide derivatives were prepared from the commercially available reducing sugars using reaction methodologies reported earlier. The notable features of the synthetic strategy include: (a) application of “unichemo protection strategy” i.e. use of similar protecting groups during the synthesis and their removal in one step; (b) use of thioglycosides as glycosyl donors in all glycosylations; (c) highly stereo selective glycosylations; (d) preparation of thioglycoside and p-methoxyphenyl glycosides of 2-azido-2-deoxy sugar derivatives and their use in the glycosylations; (e) use of a combination of perchloric acid supported over silica gel (HClO₄-SiO₂) as a solid acid and *N*-iodosuccinimide as the thiophilic activator in all glycosylations; (f) one step removal of benzylidene acetal, benzyl ethers and reduction of azido group using a combination of triethylsilane and Pearlman’s catalyst (20% Pd(OH)₂-C).
Scheme 1: Retrosynthetic strategy for the synthesis of compound 1.
Scheme 2: Retrosynthetic strategy for the synthesis of compound 2.
3.3.2.1. Preparation of \( p \)-methoxyphenyl 2-azido-4,6-\( O \)-benzylidene-2-deoxy-\( \alpha \)-D-galactopyranoside (6)\(^{79}\)

1,3,4,6-Tetra-\( O \)-acetyl-2-azido-2-deoxy-\( \alpha,\beta \)-D-galactopyranose (4)\(^{80}\) was prepared from 3,4,6-tri-\( O \)-acetyl-D-galactal (3) in 58% overall yield by azido-nitration using cerium ammonium nitrate (CAN) and sodium azide,\(^{38}\) followed by hydrolysis of the anomeric nitro group using sodium nitrite\(^{81}\) and acetylation\(^{63}\) of the hemiacetal derivative. Compound 4 was reacted with \( p \)-methoxyphenol in the presence of boron trifluoride diethyl etherate\(^{45}\) to give compound 5 in 70% yield. Deacetylation\(^{46}\) of compound 5 followed by benzylidene acetal formation\(^{82}\) using benzaldehyde dimethyl acetal and \( p \)-TsOH furnished compound 6 in 88% yield (Scheme 3).

![Scheme 3](image)

**Scheme 3:** Reagents: (a) (i) CAN, NaN\(_3\), CH\(_3\)CN, -20 °C, 1 h; (ii) NaNO\(_2\), dioxane-H\(_2\)O (10:1), 80 °C, 12 h; (iii) Ac\(_2\)O, pyridine, r.t, 1 h, 58% in three steps; (b) \( p \)-methoxy phenol, BF\(_3\)-Et\(_2\)O, CH\(_2\)Cl\(_2\), 0-15 °C, 12 h, 70%; (c) (i) 0.1 M CH\(_3\)ONa, CH\(_3\)OH, r.t, 3 h; (ii) PhCH(OCH\(_3\))\(_2\), \( p \)-TsOH, CH\(_3\)CN, r.t, 2 h, 88 %.

3.3.2.2. Preparation of \( p \)-methoxyphenyl 2-azido-4,6-\( O \)-benzylidene-2-deoxy-\( \alpha \)-D-glucopyranoside (9)\(^{83}\)

Preparation of 1,3,4,6-tetra-\( O \)-acetyl-2-azido-2-deoxy-\( \alpha,\beta \)-D-glucopyranose (7) has been described in page no.110. Compound 7 was reacted with \( p \)-methoxyphenol in the presence of boron trifluoride diethyl etherate\(^{45}\) to give compound 8 in 70% yield. Deacetylation\(^{46}\) of compound 8 followed by benzylidene acetal formation\(^{82}\) using benzaldehyde dimethyl acetal and \( p \)-TsOH furnished compound 9 in 77% overall yield (Scheme 4).

![Scheme 4](image)

**Scheme 4:** Reagents: (a) \( p \)-Methoxy phenol, BF\(_3\)-Et\(_2\)O, CH\(_2\)Cl\(_2\), 0 °C-15 °C, 18 h, 70%; (b) (i) 0.1 M CH\(_3\)ONa, CH\(_3\)OH, r.t, 3 h; (ii) PhCH(OCH\(_3\))\(_2\), \( p \)-TsOH, CH\(_3\)CN, r.t, 8 h, 77%.
3.3.2.3. Preparation of \( p \)-methylphenyl 3-\( O \)-acetyl-2-azido-4,6-\( O \)-benzylidene-2-deoxy-1-thio-\( \beta \)-D-galactopyranoside (11)

1,3,4,6-Tetra-\( O \)-acetyl-2-azido-\( \alpha \),\( \beta \)-D-galactopyranose (4) was treated with \( p \)-thiocresol in the presence of boron trifluoride diethyl etherate \(^{84} \) to give \( p \)-methylphenyl 3,4,6-tri-\( O \)-acetyl-2-azido-2-deoxy-1-thio-\( \beta \)-D-galactopyranoside (10) in 51% yield. De-\( O \)-acetylation \(^{46} \) of compound 10 followed by benzylidene acetal formation \(^{82} \) using benzaldehyde dimethyl acetal and \( p \)-TsOH and acetylation \(^{63} \) furnished compound 11 in 86% over all yield (Scheme 5).

**Scheme 5:** Reagents: (a) \( p \)-Thiocresol, BF\(_3\)-OEt\(_2\), CH\(_2\)Cl\(_2\), 0 °C to rt, 24 h, 51%; (b) 0.1 M CH\(_3\)ONa, CH\(_3\)OH, rt, 4 h; (c) PhCH(OCH\(_3\))\(_2\), p-TsOH, DMF, rt, 24 h; (d) Ac\(_2\)O, pyridine, rt, 2 h, 86% over all yield.

3.3.2.4. Preparation of ethyl 2-\( O \)-acetyl-3-\( O \)-benzyl-4,6-\( O \)-benzylidene-1-thio-\( \beta \)-D-galactopyranoside (14) \(^{85} \)

Preparation of compound 12 has been described in page no. 72. Removal of acetyl groups \(^{46} \) from compound 12 using sodium methoxide followed by benzylidene acetal formation \(^{82} \) using benzaldehyde dimethyl acetal and \( p \)-TsOH gave compound 13 in 78% yield. Selective 3-\( O \)-benzylation of compound 13 via stannylidene acetal formation \(^{49} \) followed by acetylation \(^{63} \) furnished compound (14) in 88% yield (Scheme 6).

**Scheme 6:** Reagents: (a) (i) 0.1 M CH\(_3\)ONa, CH\(_3\)OH, rt, 3 h; (ii) PhCH(O\(_{\text{Me}}\))\(_2\), p-TsOH, CH\(_3\)CN, rt, 10 h, 78%; (b) (i) Bu\(_2\)SnO, CH\(_3\)OH, 80 °C, 3 h; (ii) benzyl bromide, CsF, DMF, 80 °C, 10 h; (iii) Ac\(_2\)O, pyridine, rt, 2 h; overall 88%.
### 3.3.2.5. Preparation of ethyl 2,3,4-tri-O-benzyl-1-thio-β-L-fucopyranoside (17)\(^{86}\)

Acetylation of L-fucose using acetic anhydride in the presence of boron trifluoride diethyletherate furnished 1,2,3,4-tetra-O-acetyl-α-L-rhamnopyranose, which on treatment with ethanethiol in the presence of boron trifluoride diethyletherate\(^{47}\) in one-pot gave ethyl 2,3,4-tri-O-acetyl-1-thio-β-L-fucopyranoside (16) in 90% overall yield. Ethyl 2,3,4-tri-O-benzyl-1-thio-β-L-fucopyranoside (17) was prepared from compound 16 following a one-pot, two-step deacetylation-benzylation reaction condition\(^{50}\) using benzyl bromide and sodium hydroxide in 88% yield (Scheme 7).

![Scheme 7](image)

**Scheme 7:** Reagents: (a) (i) Ac\(_2\)O, BF\(_3\)-OEt\(_2\), r t, 1 h; (ii) EtSH, BF\(_3\)-OEt\(_2\), CH\(_2\)Cl\(_2\), 5 °C, 5 h, 90% in two steps; (b) benzyl bromide, NaOH, THF, r t, 3 h, 95%.

### 3.3.2.6. Preparation of 6-methoxyphenyl (α-L-fucopyranosyl)-(1→2)-(β-D-galactopyranosyl)-(1→3)-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (1)

Stereoselective glycosylation of compound 6 with compound 11 in the presence of a combination of N-iodosuccinimide (NIS) and HClO\(_4\)-SiO\(_2\)\(^{35}\) using dichloromethane-diethyl ether (1:1) as the reaction solvent furnished disaccharide derivative 18 in 78% yield together with a minor quantity (~6%) of its β-isomer, which was separated by column chromatography. Stereoselective formation of compound 18 was confirmed from its spectral analysis [signals at δ 5.64 (d, J = 3.0 Hz, H-1\(_A\)), 5.40 (d, J = 3.5 Hz, H-1\(_B\)) in the \(^1\)H NMR and δ 98.0 (C-1\(_A\)), 95.4 (C-1\(_B\)) in the \(^13\)C NMR spectra]. Saponification of compound 18 with sodium methoxide in methanol resulted in the formation of disaccharide acceptor 19 in a quantitative yield. Iodonium ion promoted glycosylation of compound 19 with thioglycoside derivative 14 in the presence of NIS and HClO\(_4\)-SiO\(_2\) in dichloromethane afforded trisaccharide derivative 20 in 83% yield, which was de-acetylated using sodium methoxide to give trisaccharide acceptor 21 in a 96% yield. Formation of compound 20 was confirmed from its spectral analysis [signals at δ 5.61 (d, J = 3.0 Hz, H-1\(_A\)), 5.39 (d, J = 3.5 Hz, H-1\(_B\)), 4.73 (d, J = 8.0 Hz, H-1\(_C\)) in the \(^1\)H NMR and δ 102.2 (C-1\(_C\)), 97.6 (C-1\(_A\)), 94.7 (C-1\(_B\)) in the \(^13\)C NMR spectra]. Glycosylation of compound 21
with thioglycoside derivative 17 in the presence of NIS and HClO4-SiO2 in CH2Cl2-Et2O furnished tetrasaccharide derivative 22 in 71% yield. Stereoselective formation of compound 22 was confirmed from its spectral analysis [signals at δ 5.62 (d, J = 3.0 Hz, H-1A), 5.57 (d, J = 3.0 Hz, H-1B), 5.47 (d, J = 3.0 Hz, H-1D), 4.76 (d, J = 8.0 Hz, H-1C) in the 1H NMR and at δ 102.4 (C-1C), 97.5 (C-1A), 97.2 (C-1B), 94.8 (C-1D) in the 13C NMR spectra]. Removal of benzylidene acetals, benzyl ethers and reduction of azido group in one step using triethylsilane in the presence of 20% Pd(OH)2-C78 followed by N-acetylation using acetic anhydride in methanol furnished fully deprotected tetrasaccharide 1 as its p-methoxyphenyl glycoside in 64% overall yield. The structure of the tetrasaccharide 1 was unambiguously confirmed from its spectral analysis [signals at δ 5.39 (d, J = 3.5 Hz, H-1A), 5.12 (d, 4.0 Hz, H-1D), 4.99 (d, J = 3.0 Hz, H-1B), 4.54 (d, J = 8.0 Hz, H-1C) in the 1H NMR and at δ 102.1 (C-1C), 99.2 (C-1D), 97.1 (C-1A), 93.2 (C-1B) in the 13C NMR spectra] (Scheme 8).

Scheme 8: Reagents: (a) N-iodosuccinimide (NIS), HClO4-SiO2, MS 4Å, CH2Cl2-Et2O (1:1), -18 °C, 1 h, 78% for compound 18 and 71% for compound 22; (b) 0.1 M CH3ONa, CH3OH, r t, 2 h, quantitative for compound 19 and 96% for compound 21; (c) NIS, HClO4-SiO2, MS 4Å, CH2Cl2, -30 °C, 1.5 h, 83%; (d) Et3SiH, 20% Pd(OH)2-C, CH2Cl2-CH3OH (1:1), r t, 6 h; (e) Ac2O, CH3OH, r t, 1 h, 64%.
3.3.2.7. Preparation of p-methoxyphenyl (α-L-fucopyranosyl)-(1→2)-(β-D-galactopyranosyl)-(1→3)-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (2)

In another experiment, iodonium ion promoted stereoselective glycosylation of compound 9 with compound 11 in the presence of NIS and HClO₄-SiO₂ using dichloromethane-diethyl ether (1:1) as the reaction solvent exclusively furnished disaccharide derivative 23 in 73% yield. Formation of compound 23 was confirmed from its spectral analysis [signals at δ 5.60 (d, J = 2.5 Hz, H-1B), 5.45 (d, J = 3.5 Hz, H-1A) in the ¹H NMR and at δ 99.7 (C-1B), 98.7 (C-1A) in the ¹³C NMR spectra]. Removal of O-acetyl group using sodium methoxide gave disaccharide acceptor 24 in quantitative yield. Stereoselective glycosylation of compound 24 with thioglycoside derivative 14 in the presence of NIS and HClO₄-SiO₂ in dichloromethane afforded trisaccharide derivative 25 in 77% yield, which was de-acetylated using sodium methoxide to give trisaccharide acceptor 26 in a quantitative yield. Formation of compound 25 was confirmed from its spectral analysis [signals at δ 5.67 (d, J = 3.0 Hz, H-1B), 5.50 (d, J = 3.0 Hz, H-1A), 4.81 (d, J = 8.0 Hz, H-1C) in the ¹H NMR and at δ 101.7 (C-1C), 99.8 (C-1B), 98.5 (C-1A) in the ¹³C NMR spectra]. Glycosylation of compound 26 with thioglycoside derivative 17 using NIS and HClO₄-SiO₂ combination as glycosylation promoter in CH₂Cl₂-Et₂O furnished tetrasaccharide derivative 27 in 75% yield together with a minor quantity (~5%) of its β-isomer, which was separated by column chromatography. Stereoselective formation of compound 27 was confirmed from its spectral analysis [signals at δ 5.63 (d, J = 3.0 Hz, H-1B), 5.50 (d, J = 3.5 Hz, H-1D), 5.45 (d, J = 3.0 Hz, H-1A), 4.76 (d, J = 8.0 Hz, H-1C) in the ¹H NMR and at δ 102.3 (C-1C), 100.1 (C-1D), 98.5 (C-1B), 97.0 (C-1A) in the ¹³C NMR spectra]. Removal of benzylidene acetals, benzyl ethers and reduction of azido group in one step using triethylsilane in the presence of 20% Pd(OH)₂-C₇₈ followed by N-acetylation using acetic anhydride in methanol furnished fully deprotected tetrasaccharide 2 as its p-methoxyphenyl glycoside in 62% over all yield. The structure of the tetrasaccharide 2 was unambiguously confirmed from its spectral analysis [signals at δ 5.30 (d, J = 3.5 Hz, H-1A), 5.28 (d, J = 3.5 Hz, H-1B), 5.05 (d, J = 3.5 Hz, H-1D), 4.47 (d, J = 7.5 Hz, H-1C) in the ¹H NMR and at δ 102.0 (C-1C), 99.3 (C-1D), 97.1 (C-1B), 96.8 (C-1A) in the ¹³C NMR] (Scheme 9).
3.3.3. Conclusion

In summary, two structurally close tetrasaccharides corresponding to the O-antigens of *Escherichia coli* O127 and *Salmonella enterica* O13 have been synthesized using similar reaction conditions exploiting a “unichemo approach” with minimum number of reaction steps. A generalized glycosylation condition has been applied in all glycosylation reactions. High yields of α-glycosides were achieved in both cases. All glycosylation reactions were high yielding and highly stereoselective.

3.3.4. Experimental section

3.3.4.1. General methods

Please see page no. 67.

3.3.4.2. Preparation of HClO₄-SiO₂
3.3.4.3. Preparation and spectral data of compounds 1-27

1,3,4,6-Tetra-O-acetyl-2-azido-2-deoxy-α,β-D-galactopyranose (4): To a solution of compound 3 (6 g, 22 mmol) and sodium azide (2.3 g, 35.2 mmol) in dry CH₃CN (75 mL) was added ceric ammonium nitrate (36.4 g, 66 mmol) at -20 °C and the reaction mixture was allowed to stir at the same temperature for 1 h under argon atmosphere. The reaction mixture was diluted with ethyl acetate (80 mL) and the organic layer was washed with water and satd. NaHCO₃ solution successively. The organic layer was dried (Na₂SO₄), filtered and concentrated under reduced pressure. To a solution of the crude product in dioxane-water (50 mL, 10:1 v/v) was added sodium nitrite (4.8 g, 66 mmol) and the reaction mixture was heated at 80 °C for 12 h. The reaction mixture was concentrated, diluted with CH₂Cl₂ (70 mL) and washed with water and brine respectively. The organic layer was dried (Na₂SO₄), filtered and concentrated. A solution of the crude material in acetic anhydride (15 mL) and pyridine (15 mL) was stirred for 1 h at room temperature. The solvents were evaporated and co-evaporated with toluene and the crude product was purified over SiO₂ using hexane-EtOAc (3:1) as eluant to give pure compound 4 (4.8 g, 58%) as a colorless oil; spectral analysis was in agreement with the literature data.⁷⁹

p-Methoxyphenyl 3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-galactopyranoside (5): To a solution of compound 4 (3.4 g, 9.18 mmol) and p-methoxyphenol (1.4 g, 10.98 mmol) in dry CH₂Cl₂ (18 mL) was added BF₃·OEt₂ (2.4 ml, 18.4 mmol) at 0 °C and the reaction mixture was stirred at 15 °C for 12 h. The reaction mixture was diluted with CH₂Cl₂ (100 mL) and washed successively with water and satd. NaHCO₃. The organic layer was dried (Na₂SO₄) and concentrated to give the crude product, which was purified over SiO₂ using hexane-EtOAc (3:1) as eluant to give pure compound 5 (2.8 g, 70%). Colorless oil; [α]₀^25 + 146 (c 1.0, CHCl₃); IR (neat): 3021, 2360, 2112, 1750, 1216, 761, 670 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.04 (d, J = 9.1 Hz, 2 H, Ar-H), 6.83 (d, J = 9.1 Hz, 2 H, Ar-H), 5.55 (dd, J = 11.1, 3.2 Hz, 1 H, H-3), 5.50 (d, J = 3.2 Hz, 1 H, H-1), 5.50 (br s, 1 H, H-4), 4.43-4.37 (m, 1 H, H-5), 4.16-4.03 (m, 2 H, H-6ab), 3.78 (s, 3 H, OCH₃), 3.74 (dd, J = 11.3, 3.6 Hz, 1 H, H-2), 2.17, 2.09, 1.99 (3 s, 9 H, 3 COCH₃); ¹³C NMR (75 MHz, CDCl₃): δ 170.0, 169.7, 169.5 (3 C, 3 COCH₃), 155.6 (Ar-C), 150.2 (Ar-C), 118.2 (2 C, Ar-C), 114.6 (2 C, Ar-C), 98.0 (C-1), 68.1 (C-4), 67.4 (C-6), 67.3 (C-3), 61.3 (C-5), 57.3 (OCH₃), 55.5 (C-2), 20.6 (3 C, 3 COCH₃); ESI-MS: 460.3 [M+Na]⁺; Anal. Calcd. for C₁₉H₂₃N₃O₉ (437.1): C, 52.17; H, 5.30; found: C, 52.0; H, 5.50.
p-Methoxyphenyl 2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (6): A solution of compound 5 (2.6 g, 5.88 mmol) in 0.1 M CtbONa in CH₃OH (40 mL) was allowed to stir at room temperature for 3 h, neutralized with Dowex-50W X-8 (H⁺), filtered and evaporated to dryness. To a solution of the deacetylated product in dry acetonitrile (15 mL) were added benzaldehyde dimethylacetal (1.3 ml, 1.47 mmol) and p-TsOH (300 mg) and the reaction mixture was allowed to stir at room temperature for 8 h. The reaction was quenched with Et₃N (0.5 mL) and the solvents were removed under reduced pressure. The crude product was purified over SiCh using hexane-EtOAc (7:2) as eluant to give pure compound 6 (2 g, 88%). White solid; m.p. 72-73 °C [EtOH]; [α]D²⁵ − 22 (c 1.0, CHCl₃); IR (KBr): 2935, 2362, 2104, 1508, 1452, 1249, 1218, 1103, 1041, 827, 796, 755, 701 cm⁻¹; *H NMR (300 MHz, CDC1₃): δ 7.50-7.45 (m, 2 H, Ar-H), 7.38-7.34 (m, 3 H, Ar-H), 7.0 (d, J = 9.1 Hz, 2 H, Ar-H), 6.80 (d, J = 9.1 Hz, 2 H, Ar-H), 5.54 (s, 1 H, PhCtf), 5.51 (d, J = 3.2 Hz, 1 H, H-1), 4.38-4.27 (m, 2 H, H-3 and H-5), 4.22 (dd, J = 12.7, 1.1 Hz, 1 H, H-6a), 4.00 (dd, J = 12.5, 1.4 Hz, 1 H, H-2a), 3.82 (br s, 1 H, H-4), 3.75 (s, 3 H, OCH₃), 3.62 (dd, J = 10.3, 3.2 Hz, 1 H, H-6b), 2.66 (d, J = 10.4 Hz, 1 H, OCH₃); ¹³C NMR (75 MHz, CDC1₃): δ 155.3-114.7 (Ar-C), 101.2 (PhCH), 98.3 (C-1), 75.4 (C-4), 69.1 (C-6), 67.3 (C-3), 63.4 (C-5), 60.4 (C-2), 55.5 (OCH₃); ESI-MS: 422.4 [M+Na]⁺; Anal. Calcd. for C₂₀H₂₁N₃O₆ (399.1): C, 60.14; H, 5.30; found: C, 59.93; H, 5.52.

p-Methoxyphenyl 3,4,6-tri-O-acetyl-2-azido-2-deoxy-α-D-glucopyranoside (8): To a solution of compound 7 (6.85 g, 18.36 mmol) and p-methoxyphenol (2.8 g, 22 mmol) in dry CH₂Cl₂ (45 mL) was added BF₃·OEt₂ (4.5 ml, 36.72 mmol) at 0 °C and the reaction mixture was stirred at 15 °C for 18 h. The reaction mixture was diluted with CH₂Cl₂ (100 mL) and the organic layer was successively washed with water and satd. NaHCO₃. The organic layer was dried (Na₂SO₄) and concentrated to give the crude product, which was purified over SiCh using hexane-EtOAc (3:1) as eluant to give pure compound 8 (5.1 g, 70%). Colorless oil; [α]D²⁵ + 116 (c 1.0, CHCl₃); IR (neat): 3021, 2360, 2112, 1750, 1216, 761, 670 cm⁻¹; *H NMR (400 MHz, CDC1₃): δ 7.04 (d, J = 9.1 Hz, 2 H, Ar-H), 6.85 (d, J = 9.1 Hz, 2 H, Ar-H), 5.70 (dd, J = 11.5 Hz each, 1 H, H-3), 5.46-5.15 (t, J = 12.9, 11.4 Hz, 1 H, H-4), 4.30-4.26 (m, 1 H, H-6a), 4.20-4.17 (m, 1 H, H-5), 4.08-4.05 (m, 1 H, H-6b) 3.77 (s, 3 H, OCH₃), 3.74 (dd, J = 4.5, 12.9 Hz, 1 H, H-2), 2.11, 2.05, 2.04 (3 s, 9 H, 3 COCH₃); ¹³C NMR (75 MHz, CDC1₃): δ 170.4, 170.0, 169.6 (3 C, 3 COCH₃), 155.6 (Ar-C), 149.9 (Ar-C), 117.8 (2 C, Ar-C), 114.7 (2 C, Ar-C), 97.4 (C-1), 70.2 (C-4), 68.2 (C-6), 68.1 (C-3), 61.6 (C-5), 60.7 (OCH₃), 55.6 (C-2), 20.6 (3 C, 3 COCH₃); ESI-MS: 460.3 [M+Na]⁺; Anal. Calcd. for C₁₉H₂₁N₃O₉ (437.1): C, 52.17; H, 5.30; found: C, 52.0; H, 5.50.
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**p-Methoxyphenyl 2-azido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (9):** A solution of compound 8 (4 g, 9.15 mmol) in 0.1 M CH₃ONa in CH₃OH (30 mL) was allowed to stir at room temperature for 3 h, neutralized with Dowex 50W X8 (H⁺) resin and concentrated under reduced pressure. To a solution of the crude product in anhydrous CH₂CN (25 mL) were added benzaldehyde dimethylacetal (2.7 mL, 18.0 mmol) and p-TsOH (500 mg) and the reaction mixture was allowed to stir at room temperature for 8 h. The reaction was quenched with Et₃N (2 mL) and evaporated to dryness under reduced pressure to give the crude product, which was purified over SiO₂ using hexane-EtOAc (4:1) as eluant to give pure compound 9 (2.8 g, 77%).

Yellow oil; [α]D²⁵ +120 (c 1.2, CHCl₃); IR (neat): 2963, 2944, 2116, 1752, 151, 1230, 1044, 1035, 819, 786, 543 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.49-7.36 (m, 5 H, Ar-H), 7.01 (d, J = 9.0 Hz, 2 H, Ar-H), 6.85 (d, J = 9.0 Hz, 2 H, Ar-H), 5.53 (s, 1 H, PhCH), 5.39 (d, J = 3.3 Hz, 1 H, H-1), 4.38-4.32 (m, 1 H, H-6a), 4.25-4.20 (m, 1 H, H-6b), 4.06-3.97 (m, 1 H, H-5), 3.76 (s, 3 H, OC₃H₃), 3.71 (t, J = 10.2 Hz each, 1 H, H-4), 3.55 (t, J = 9.6 Hz each, 1 H, H-3), 3.36 (dd, J = 9.9, 3.6 Hz, 1 H, H-2); ¹³C NMR (125 MHz, CDCl₃): δ 155.6-114.7 (Ar-C), 102.1 (PhCH), 98.3 (C-1), 81.7, 68.8, 68.7, 66.3, 63.1, 55.7; ESI-MS: 422.1 [M+Na]⁺; Anal. Calcd for C₂₀H₂₁N₃O₆ (399.14): C, 60.14; H, 5.30; found: C, 60.30; H, 5.50.

**p-Methylphenyl 3-O-acetyl-2-azido-4,6-O-benzylidene-2-deoxy-1-thio-β-D-galactopyranoside (11):** To a solution of compound 4 (5 g, 13.39 mmol) in anhydrous CH₂Cl₂ (30 mL) were added p-thiocresol (2.2 g, 17.71 mmol) and BF₃·OEt₂ (2.5 mL, 20.25 mmol) at 0 °C and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction mixture was poured into satd. NaHCO₃ and extracted with CH₂Cl₂ (150 mL). The organic layer was washed with water, dried (Na₂SO₄) and concentrated to give the crude product, which was purified over SiO₂ using hexane-EtOAc (8:1) as eluant to give compound 10 (3 g, 51%) and its α-isomer (2 g, 34%). A solution of compound 10 (3 g, 6.86 mmol) in 0.1 M CH₃ONa (25 mL) was stirred at room temperature for 4 h, neutralized with Dowex 50W X8 (H⁺) resin, filtered and concentrated. To a solution of the de-O-acetylated product in dry DMF (10 mL) were added benzaldehyde dimethylacetal (1.3 mL, 8.66 mmol) and p-TsOH (250 mg) and the reaction mixture was allowed to stir at room temperature for 24 h. The reaction was quenched with Et₃N (1 mL) and the solvents were removed under reduced pressure to give the crude product. A solution of the crude product in acetic anhydride-pyridine (5 mL, 1:1, v/v) was kept at room temperature for 2 h. The solvents were removed under reduced pressure and the crude product was diluted with CH₂Cl₂ (100 mL). The organic layer was successively washed with satd. NaHCO₃, water, dried (Na₂SO₄) and concentrated to give the crude product, which was purified
over SiO₂ using hexane-EtOAc (3:1) as eluant to give pure compound 11 (2.6 g, 86%). Yellow oil; [α]D²⁵ - 43 (c 1.2, CHCl₃); IR (neat): 3445, 2113, 1748, 1634, 1369, 1245, 1233, 1092, 1043, 1023, 997, 808, 769, 705 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.60 (d, J = 8.0 Hz, 2 H, Ar-H), 7.40-7.37 (m, 5 H, Ar-H), 7.05 (d, J = 8.0 Hz, 2 H, Ar-H), 5.46 (s, 1 H, PhCH), 4.77 (dd, J = 10.5, 3.5 Hz, 1 H, H-3), 4.42 (d, J = 10.0 Hz, 1 H, H-1), 4.36 (d, J = 12.5 Hz, 1 H, H-6ₗ), 4.30 (d, J = 3.0 Hz, 1 H, H-4), 3.99 (d, J = 12.5 Hz, 1 H, H-6ₜ), 3.78 (t, J = 10.0 Hz each, 1 H, H-2), 3.54-3.53 (m, 1 H, H-5), 2.34 (s, 3 H, CH₃), 2.10 (s, 3 H, COCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.2 (COCH₃), 138.6-126.1 (Ar-C), 100.9 (PhCH), 85.3 (C-1), 74.0 (C-3), 72.6 (C-4), 69.5 (C-5), 69.2 (C-6), 58.1 (C-2), 21.3 (CH₃), 20.9 (COCH₃); ESI-MS: 464.1 [M+Na]⁺; Anal. Calcd. for C₂₂H₂₃N₃O₅S (441.13): C, 59.85; H, 5.25; found: C, 59.70; H, 5.50.

Ethyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (12): Please see page no. 72.

Ethyl 4,6-O-benzylidene-1-thio-β-D-galactopyranoside (13): For the preparation please see page no. 72.

Ethyl 2-0-acetyl-3-0-benzyl-4,6-O-benzylidene-1-thio-β-D-galactopyranoside (14): To a solution of compound 13 (5 g, 16 mmol) in anhydrous CH₃OH (120 mL) was added dibutyltin oxide (4.8 g, 19.3 mmol) and the reaction mixture was allowed to stir at 80 °C for 3 h. The solvents were removed under reduced pressure and the crude mass was dissolved in anhydrous DMF (50 mL). To the reaction mixture were added CsF (2.5 g, 16.45 mmol), benzyl bromide (2.4 mL, 24 mmol) and the reaction mixture was allowed to stir at 80 °C for 10 h. The solvents were removed under reduced pressure and the crude residue was dissolved in CH₂Cl₂ (150 mL). The organic layer was washed with 1 N HCl and water in succession, dried (Na₂SO₄) and concentrated. A solution of the crude product in acetic anhydride-pyridine (6 mL, 1:1, v/v) was kept at room temperature for 2 h. The solvents were removed under reduced pressure and the crude product was diluted with CH₂Cl₂ (100 mL). The organic layer was successively washed with satd. NaHCO₃, water, dried (Na₂SO₄) and concentrated to give the crude product, which was purified over SiO₂ using hexane-EtOAc (5:1) as eluant to give pure compound 15 (4.4 g, 88%). Yellow oil; ¹H NMR (300 MHz, CDCl₃): δ 7.51-7.25 (m, 10 H, Ar-H), 5.46 (s, 1 H, PhCH), 5.44 (t, J = 9.7 Hz each, 1 H, H-2), 4.70-4.61 (ABq, J = 12.6 Hz, 2 H, PhCH₂), 4.37 (d, J = 9.8 Hz, 1 H, H-1), 4.33-4.29 (m, 1 H, H-6ₗ), 4.20 (d, J = 3.0 Hz, 1 H, H-4), 3.98-3.95 (m, 1 H, H-6ₜ), 3.61-3.58 (m, 1 H, H-3), 3.40-3.39 (m, 1 H, H-5), 2.90-2.70 (m, 2 H, SCH₂CH₃), 2.06 (s, 3 H, COCH₃), 1.27 (t, J = 7.5 Hz each, 3 H, SCH₂CH₃); ESI-MS: 467.1 [M+Na]⁺; Anal. Calcd. for C₂₄H₂₉O₆S (444.16): C, 64.84; H, 6.35; found: C, 64.70; H, 6.50.
Ethyl 2,3,4-tri-O-acetyl-1-thio-β-L-fucopyranoside (16): To a suspension of L-fucose (15) (4 g, 24.4 mmol) in acetic anhydride (16 mL) was added BF₃·OEt₂ (2 mL) and the mixture was allowed to stir at room temperature for 1 h. After consumption of the starting material, ethanethiol (3.6 mL, 48.8 mmol) and BF₃·OEt₂ (6.2 mL, 48.8 mmol) were added to it and the reaction mixture was allowed to stir at 5 °C for 5 h. The reaction mixture was diluted with CH₂Cl₂ (100 mL) and washed with aq. NaHCO₃ and water in succession. The organic layer was dried (Na₂SO₄) and concentrated under reduced pressure. The crude product was purified over SiO₂ using hexane-EtOAc (4:1) as eluant to furnish compound 16 (7.3 g, 90%). White solid; m.p. 72-73 °C [EtOH]; [α]D²⁵ + 17 (c 1.5, CHCl₃); IR (KBr): 2372, 1724, 1583, 1376, 1332, 1038, 765 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 5.25 (d, J = 3.3 Hz, 1 H, H-4), 5.19 (t, J = 9.9 Hz each, 1 H, H-2), 5.01 (dd, J = 9.9, 3.3 Hz, 1 H, H-3), 4.42 (d, J = 9.8 Hz, 1 H, H-1), 3.81 (q, J = 6.3 Hz each, 1 H, H-5), 2.77-2.66 (m, 2 H, SCH₂CH₃), 2.18, 2.06, 1.98 (3 s, 9 H, 3 COCH₃), 1.28 (t, J = 7.5 Hz each, 3 H, SCH₂CH₃), 1.21 (d, J = 6.4 Hz, 3 H, CCH₃); ¹³C NMR (75 MHz, CDCl₃): δ 170.3, 169.8, 169.3 (3 COCH₃), 83.3 (C-1), 73.1, 72.3, 70.4, 67.1, 23.7 (SCH₂CH₃), 20.7, 20.6, 20.5 (3 COCH₃), 16.4 (CCH₃), 14.7 (SCH₂CH₃); ESI-MS: 357.3 [M+Na⁺]; Anal. Calcd. for C₁₄H₂₂O₇S (334.1): C, 50.29; H, 6.63; found: C, 50.03; H, 6.82.

Ethyl 2,3,4-tri-O-benzyl-1-thio-β-L-fucopyranoside (17): To a solution of the compound 16 (2 g, 6.0 mmol) in THF (20 mL) were added powdered NaOH (1.4 g, 36.0 mmol) and benzyl bromide (2.2 mL, 18 mmol) respectively and the reaction mixture was allowed to stir at room temperature for 3 h. The reaction mixture was concentrated under reduced pressure and diluted with CH₂Cl₂ (50 mL). Then the organic layer was washed with water, dried (Na₂SO₄) and concentrated under reduced pressure. The crude product was purified over SiO₂ using hexane-EtOAc (10:1) as eluant to furnish pure compound 17 (2.7 g, 95%). White solid; m.p. 65 °C [EtOH]; [α]D²⁵ 3 (c 1.6, CHCl₃); IR (KBr): 2882, 2379, 1621, 1759, 1594, 1496, 1614, 1594, 717 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.36-7.12 (m, 15 H, Ar-H), 4.90-4.69 (m, 3 H, 3 PhCH₂), 4.65 (d, J = 11.6 Hz, 1 H, PhCH₂), 4.63 (d, J = 11.6 Hz, 1 H, PhCH₂), 4.59 (d, J = 11.6 Hz, 1 H, PhCH₂), 4.38 (d, J = 9.8 Hz, 1 H, H-1), 4.22 (dd, J = 6.6, 5.7 Hz, 1 H, H-3), 4.01 (dd, J = 5.7, 2.3 Hz, 1 H, H-4), 3.82-3.64 (m, 1 H, H-5), 3.42 (dd, J = 9.7, 6.6 Hz, 1 H, H-2), 2.65 (m, 2 H, CH₂CH₃), 1.27 (t, J = 7.5 Hz each, 3 H, SCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃): δ 137.8-128.3 (Ar-C), 82.3 (C-1), 79.5 (C-2), 78.3 (C-3), 75.7 (C-4), 74.7, 74.3, 72.5 (3 PhCH₂), 71.8 (C-5), 23.5 (CH₂CH₃), 14.6 (CH₂CH₃); ESI-MS: 501.22 [M+Na⁺]; Anal. Calcd. for C₂₉H₃₄O₄S (478.22): C, 71.12; H, 7.14; found: C, 69.63; H, 7.89.
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*p*-Methoxyphenyl (3-0-acetyl-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (18): To a solution of compound 6 (1 g, 2.50 mmol) and compound 11 (1.2 g, 2.72 mmol) in a mixture of anhydrous CH₂Cl₂ (5 mL) and Et₂O (5 mL) was added MS 4A (2 g) and the reaction mixture was allowed to stir at room temperature under argon for 20 min. The reaction mixture was cooled to −18 °C and to the cooled reaction mixture was added N-iodosuccinimide (NIS; 700 mg, 3.11 mmol) followed by HClO/i-SiCl₃ (25 mg) and the reaction mixture was allowed to stir at same temperature for 1 h. The reaction mixture was filtered through a Celite® bed and washed with CH₂Cl₂ (100 mL). The organic layer was successively washed with 5% Na₂S₂O₅, satd. NaHCO₃ and water, dried (TS^SCL) and concentrated to a crude product, which was purified over SiCₐ using hexane-EtOAc (6:1) as eluant to give pure compound 18 (1.4 g, 78%). White solid; m.p. 68-70 °C [EtOH]; [α]_D^25 +224 (c 1.2, CHCl₃); IR (KBr): 3483, 2928, 2858, 2111, 1747, 1508, 1370, 1244, 1223, 1139, 1047, 1006, 955, 828, 805, 750, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.57-7.33 (m, 10 H, Ar-H), 7.06 (d, J= 9.0 Hz, 2 H, Ar-H), 6.84 (d, J= 9.0 Hz, 2 H, Ar-H), 5.64 (d, J= 3.0 Hz, 1 H, H-1A), 5.62 (s, 1 H, PhCH), 5.56 (s, 1 H, PhCH), 5.43 (dd, J= 10.5, 3.5 Hz, 1 H, H-3B), 5.40 (d, J= 3.5 Hz, 1 H, H-1B), 4.57 (d, J= 3.0 Hz, 1 H, H-4A), 4.49 (d, J= 3.0 Hz, 1 H, H-4B), 4.46 (dd, J= 10.5, 3.5 Hz, 1 H, H-3A), 4.35 (d, J= 12.5 Hz, 1 H, H-6aA), 4.30 (d, J= 12.5 Hz, 1 H, H-6bA), 4.14 (d, J= 12.5 Hz, 1 H, H-6bB), 4.10-4.06 (m, 2 H, H-6aB, H-6bB), 4.01 (dd, J= 10.0, 3.0 Hz, 1 H, H-2A), 3.88 (dd, J= 10.0, 3.0 Hz, 1 H, H-2B), 3.87-3.86 (m, 1 H, H-5A), 3.78 (s, 3 H, OCH₃), 2.15 (s, 3 H, COCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.2 (COCH₃), 155.4-114.7 (Ar-C), 100.9 (PhCH), 100.8 (PhCH), 98.0 (C-1A), 95.4 (C-1B), 73.4 (C-4A), 71.6 (C-4B), 71.5 (C-3A), 69.3 (C-6B), 69.2 (C-6A), 68.9 (C-3B), 63.4 (C-5B), 63.3 (C-5A), 58.3 (C-2A), 56.6 (C-2B), 55.6 (OCCH₃), 20.9 (COCH₃); MALDI-MS: 739.2 [M+Na]⁺; Anal. Calcd. for C₃₃H₃₆N₃O₁₁ (716.24): C, 58.65; H, 5.06; found: C, 58.48; H, 5.20.

*p*-Methoxyphenyl (2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (19): A solution of compound 18 (1.3 g, 1.81 mmol) in 0.1 M CH₃ONa in CH₃OH (20 mL) was allowed to stir at room temperature for 2 h. The reaction mixture was neutralized with Dowex 50W X8 (H⁺) resin, filtered and concentrated to give the crude product which was passed through a short pad of SiO₂ using hexane-EtOAc (1:1) as eluant to give pure compound 19 (1.2 g, 98%). White solid; m.p. 225-226 °C [EtOH]; [α]_D^25 + 179 (c 1.2, CHCl₃); IR (KBr): 3562, 2929, 2108, 1724, 1508, 1455, 1407, 1271, 1243, 1222, 1139, 1104, 1089, 1045, 1006, 959, 832, 810, 745, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.57-7.33 (m, 10 H, Ar-H), 7.05 (d, J= 9.0 Hz, 2 H, Ar-H), 6.81 (d, J= 9.0 Hz, 2 H, Ar-H).
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9.0 Hz, 2 H, Ar-H), 5.61 (s, 2 H, 2 PhC#), 5.59 (d, J = 3.0 Hz, 1 H, H-1A), 5.33 (d, J = 3.0 Hz, 1 H, H-1b), 4.48 (br s, 1 H, H-4A), 4.44 (dd, J = 10.5, 3.5 Hz, 1 H, H-3A), 4.37 (d, J = 12.5 Hz, 1 H, H-6aA), 4.35 (br s, 1 H, H-4B), 4.30-4.25 (m, 2 H, H-3B, H-6aB), 4.12 (d, J = 12.5 Hz, 1 H, H-6bB), 4.09-4.06 (m, 1 H, H-6bA), 4.01-4.00 (m, 1 H, H-5B), 3.98 (dd, J = 10.0, 3.0 Hz, 1 H, H-2A), 3.85-3.84 (m, 1 H, H-5A), 3.77 (s, 3 H, OC#3), 3.61 (dd, J = 10.0, 3.0 Hz, 1 H, H-2B); 13C NMR (125 MHz, CDCl3): δ 155.4-114.7 (Ar-C), 101.3 (PhCH), 100.8 (PhCH), 97.8 (C-1A), 95.7 (C-1b), 75.5 (C-4b), 71.8 (C-4A), 71.7 (C-3A), 69.3 (C-6A), 69.1 (C-6b), 66.7 (C-3b), 63.7 (C-5A), 63.3 (C-5B), 60.0 (C-2A), 58.4 (C-2B), 55.5 (OCH3); ESI-MS: 697.2 [M+Na]+; Anal. Calcd. for C33H34N6O10 (674.23): C, 58.75; H, 5.08; found: C, 58.57; H, 5.25.

p-Methoxyphenyl (2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-ß-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (20): To a solution of compound 19 (1 g, 1.48 mmol) and compound 14 (760 mg, 1.71 mmol) in anhydrous CH2Cl2 (10 mL) was added MS 4A (2 g) and the reaction mixture was allowed to stir at room temperature under argon for 20 min. The reaction mixture was cooled to −30 °C and to the cooled reaction mixture was added NIS (450 mg, 2.0 mmol) followed by HClO4-SiO2 (15 mg) and the reaction mixture was allowed to stir at same temperature for 1.5 h. The reaction mixture was filtered through a Celite® bed and washed with CH2Cl2 (50 mL). The organic layer was successively washed with 5% Na2S2O3, satd. NaHCO3 and water, dried (Na2SO4) and concentrated to a crude product, which was purified over SiO2 using hexane-EtOAc (6:1) as eluant to give pure compound 20 (1.3 g, 83%). White solid; m.p. 232-234 °C [EtOH]; [α]D25 + 147 (c 1.2, CHCl3); IR (KBr): 3446, 2920, 2871, 2112, 1743, 1454, 1406, 1396, 1225, 1148, 1110, 1083, 1052, 995, 695, 824, 803, 738, 700 cm−1; 1H NMR (500 MHz, CDCl3): δ 7.58-7.30 (m, 20 H, Ar-H), 7.05 (d, J = 9.0 Hz, 2 H, Ar-H), 6.85 (d, J = 9.0 Hz, 2 H, Ar-H), 5.63 (s, 1 H, PhCH), 5.62 (s, 1 H, PhCH), 5.61 (d, J = 3.0 Hz, 1 H, H-1A), 5.46 (s, 1 H, PhCH), 5.42 (dd, J = 8.0 Hz each, 1 H, H-2c), 5.39 (d, J = 3.5 Hz, 1 H, H-1b), 4.73 (d, J = 8.0 Hz, 1 H, H-1c), 4.70-4.62 (2 d, J = 12.5 Hz each, 2 H, PhCH2), 4.57 (d, J = 2.5 Hz, 1 H, H-4A), 4.52 (d, J = 2.5 Hz, 1 H, H-4b), 4.46 (dd, J = 10.5, 3.5 Hz, 1 H, H-3A), 4.35-4.28 (m, 3 H, H-3B, H-6aA, H-6ac), 4.24 (d, J = 12.5 Hz, 1 H, H-6ab), 4.14 (d, J = 3.0 Hz, 1 H, H-4c), 4.12-4.07 (m, 3 H, H-2A, H-6bb, H-6bc), 4.00 (d, J = 12.5 Hz, 1 H, H-6ba), 3.92 (br s, 1 H, H-5), 3.90 (dd, J = 10.0, 3.0 Hz, 1 H, H-2a), 3.86 (br s, 1 H, H-5A), 3.78 (s, 3 H, CH3), 3.59 (dd, J = 10.5, 3.5 Hz, 1 H, H-3c), 3.36 (br s, 1 H, H-5c), 2.03 (s, 3 H, COCH3); 13C NMR (125 MHz, CDCl3): δ 169.4 (COCH3), 155.4-114.7 (Ar-C), 102.2 (C-1c), 101.2 (PhCH), 100.8 (PhCH), 100.6 (PhCH), 97.6 (C-1A), 94.7 (C-1B), 77.5 (C-3c), 76.0 (C-4A), 73.8 (C-4c), 73.2 (C-3b), 71.2
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(PhCH₂), 71.1 (C-4B), 70.8 (C-2C), 70.2 (C-3A), 69.3 (C-6C), 69.2 (C-6A), 69.1 (C-6B), 66.6 (C-5C), 64.2 (C-5B), 63.2 (C-5A), 58.7 (C-2A), 58.5 (C-2B), 55.7 (OCH₃), 20.9 (COCH₃); MALDI-MS: 1079.3 [M+Na]⁺; Anal. Calcd. for C₅₅H₆₈N₆O₁₆ (1056.37): C, 62.49; H, 5.34; found: C, 62.30; H, 5.55.

- Methoxyphenyl (3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (21): A solution of compound 20 (1.2 g, 1.13 mmol) in 0.1 M CH₂ONa in CH₃OH (15 mL) was allowed to stir at room temperature for 2 h. The reaction mixture was neutralized with Dowex 50W X8 (H⁺) resin, filtered and concentrated to give the crude product which was passed through a short pad of SiO₂ using hexane-EtOAc (1:1) as eluant to give pure compound 21 (1.1 g, 96%). White solid; m.p. 238-240 °C [EtOH]; [α]D ²⁵ + 190 (c 1.2, CHCｌ₃); IR (KBr): 3483, 2914, 2861, 2110, 1507, 1454, 1403, 1366, 1247, 1214, 1175, 1111, 1087, 1048, 999, 806, 752, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.57-7.28 (m, 20 Hz, Ar-H), 7.04 (d, J = 9.0 Hz, 2 H, Ar-H), 6.83 (d, J = 9.0 Hz, 2 H, Ar-H), 5.60 (s, 1 H, PhCH), 5.59 (s, 1 H, PhCH), 5.58 (d, J = 3.0 Hz, 1 H, H-1A), 5.43 (s, 1 H, PhCH), 5.41 (d, J = 3.0 Hz, 1 H, H-1B), 4.82-4.73 (2 d, J = 2.5 Hz each, 2 H, PhCH₂), 4.57 (d, J = 2.5 Hz, 1 H, H-4A), 4.55 (d, J = 8.0 Hz, 1 H, H-1C), 4.47 (br s, 1 H, H-4B), 4.43 (dd, J = 10.0, 3.0 Hz, 1 H, H-3A), 4.36 (dd, J = 10.0, 3.0 Hz, 1 H, H-3B), 4.32 (d, J = 12.0 Hz, 1 H, H-6AC), 4.28 (d, J = 12.0 Hz, 1 H, H-6Ac), 4.23 (d, J = 12.0 Hz, 1 H, H-6aA), 4.20-4.03 (m, 5 H, H-2A, H-2C, H-4C, H-6bB, H-6cB), 3.93 (br s, 1 H, H-5B), 3.79 (br s, 1 H, H-5A), 3.76 (s, 3 H, OCH₃), 3.48 (dd, J = 10.0, 3.0 Hz, 1 H, H-3C), 3.29 (br s, 1 H, H-5C); ¹³C NMR (125 MHz, CDCl₃): δ 155.4-114.7 (Ar-C), 104.3 (C-1C), 101.0 (PhCH), 100.9 (PhCH), 100.8 (PhCH), 97.6 (C-1A), 94.7 (C-1B), 78.7 (C-3C), 76.2 (C-4A), 73.8 (C-4C), 73.6 (C-3B), 71.9 (PhCH₂), 71.1 (C-4B), 71.0 (C-2C), 70.4 (C-3A), 69.2 (3 C, C-6A, C-6B, C-6C), 66.7 (C-5C), 65.3 (C-5B), 63.2 (C-5A), 58.7 (C-2B), 58.5 (C-2A), 55.6 (OCH₃); MALDI-MS: 1037.3 [M+Na]⁺; Anal. Calcd. for C₅₂H₅₄N₆O₁₆ (1014.36): C, 62.71; H, 5.36; found: C, 62.50; H, 5.55.

- Methoxyphenyl (2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-(1→2)-(3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (22): To a solution of compound 21 (1 g, 0.98 mmol) and compound 17 (550 mg, 1.15 mmol) in a mixture of anhydrous CH₂Cl₂ (4 mL) and Et₂O (4 mL) was added MS 4Å (1.5 g) and the reaction mixture was allowed to stir at room temperature under argon for 20 min. The reaction
mixture was cooled to −18 °C and to the cooled reaction mixture was added NIS (300 mg, 1.33 mmol) followed by HClO₄-SiO₂ (10 mg) and the reaction mixture was allowed to stir at same temperature for 1 h. The reaction mixture was filtered through a Celite® bed and washed with CH₂Cl₂ (50 mL). The organic layer was successively washed with 5% Na₂S₂O₃, satd. NaHCO₃ and water, dried (Na₂SO₄) and concentrated to a crude product, which was purified over SiO₂ using hexane-EtOAc (6:1) as eluant to give pure compound 22 (1 g, 71%). White solid; m.p. 128-130 °C [EtOH]; [α]D²⁵ + 99 (c 1.2, CHCl₃); IR (KBr): 3448, 3032, 2907, 2864, 2109, 1507, 1455, 1402, 1365, 1213, 1173, 1108, 1051, 1027, 806, 736, 697 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.57-7.16 (m, 35 H, Ar-H), 7.06 (d, J = 9.0 Hz, 2 H, Ar-H), 6.83 (d, J = 9.0 Hz, 2 H, Ar-H), 5.63 (s, 2 H, 2 PhCH), 5.62 (d, J = 3.0 Hz, 1 H, H-1ₐ), 5.57 (d, J = 3.0 Hz, 1 H, H-1ₐ), 5.47 (d, J = 3.0 Hz, 1 H, H-1ₐ), 5.37 (s, 1 H, PhCH), 4.84 (d, J = 11.5 Hz, 1 H, PhCH₂), 4.78 (d, J = 11.5 Hz, 1 H, PhCH₂), 4.76 (d, J = 8.0 Hz, 1 H, H-1ₐ), 4.70-4.53 (m, 7 H, H-3₂, PhCH₂), 4.52-4.46 (m, 2 H, H-3ₐ, H-4ₐ), 4.45-4.40 (m, 2 H, H-4ₐ, H-5₂), 4.32-4.29 (m, 2 H, H-6ₐ, H-6ₐ), 4.23-4.19 (m, 3 H, H-2ₐ, H-4ₐ, H-6ₐ), 4.17-4.10 (m, 2 H, H-6ₐ, H-6ₐ), 3.78 (s, 3 H, OCH₃), 3.77-3.75 (m, 1 H, H-3ₐ), 3.71 (dd, J = 10.0, 3.0 Hz, 1 H, H-5₂), 3.70 (br s, 1 H, H-5₂), 3.32 (br s, 1 H, H-5₂), 0.86 (d, J = 3.0 Hz, 3 H, CCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 155.8-114.7 (Ar-C), 102.4 (C-1ₐ), 100.9 (2 C, 2 PhCH), 100.8 (PhCH), 97.5 (C-1ₐ), 97.2 (C-1ₐ), 94.8 (C-1ₐ), 81.6 (C-3ₐ), 79.5 (C-2ₐ), 78.5 (C-5ₐ), 68.5 (C-3ₐ), 75.8 (C-3ₐ), 74.7 (PhCH₂), 72.9 (PhCH₂), 72.7 (C-4ₐ), 72.3 (PhCH₂), 71.8 (C-4ₐ), 71.7 (C-4ₐ), 71.0 (C-3ₐ), 70.9 (C-4ₐ), 70.8 (PhCH₂), 69.3 (C-6ₐ), 69.1 (C-6ₐ), 69.0 (C-6ₐ), 66.4 (C-5₂), 66.3 (C-5₂), 64.3 (C-2₁), 63.1 (C-5ₐ), 58.9 (C-2₁), 58.4 (C-2₁), 55.6 (OCH₃), 16.3 (CCH₃); MALDI-MS: 1453.5 [M+Na]⁺; Anal. Calcd. for C₈₀H₇₂N₆O₁₉ (1430.56): C, 67.12; H, 5.77; found: C, 66.94; H, 6.00.

**p-Methoxyphenyl (3-O-acetyl-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (23):** To a solution of compound 9 (1 g, 2.5 mmol) and compound 11 (1.2 g, 2.72 mmol) in a mixture of anhydrous CH₂Cl₂ (5 mL) and Et₂O (5 mL) was added MS 4Å (2 g) and the reaction mixture was allowed to stir at room temperature under argon for 20 min. The reaction mixture was cooled to −18 °C and to the cooled reaction mixture was added NIS (700 mg, 3.11 mmol) followed by HClO₄-SiO₂ (25 mg) and the reaction mixture was allowed to stir at same temperature for 1 h. The reaction mixture was filtered through a Celite® bed and washed with CH₂Cl₂ (100 mL). The organic layer was successively washed with 5% Na₂S₂O₃, satd. NaHCO₃ and water, dried (Na₂SO₄) and concentrated to a crude product, which was purified over SiO₂ using hexane-
EtOAc (6:1) as eluant to give pure compound 23 (1.3 g, 73%). White solid; m.p. 204-205 °C [EtOH]; [α]_D^{25} + 250 (c 1.2, CHCl₃); IR (KBr): 3483, 2928, 2858, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.42-7.28 (m, 10 H, Ar-H), 6.98 (d, J = 9.0 Hz, 2 H, Ar-H), 6.77 (d, J = 9.0 Hz, 2 H, Ar-H), 5.60 (d, J = 3.5 Hz, 1 H, H-1b), 5.54 (s, 1 H, PhCH), 5.46 (s, 1 H, PhCH), 5.45 (d, J = 3.5 Hz, 1 H, H-1a), 5.35 (dd, J = 10.0, 3.0 Hz, 1 H, H-3b), 4.48 (t, J = 10.0 Hz each, 1 H, H-3A), 4.40 (d, J = 3.5 Hz, 1 H, H-4b), 4.30 (d, J = 11.5 Hz, 1 H, H-6aA), 4.21 (dd, J = 10.5, 5.0 Hz, 1 H, H-6bA), 4.05-4.01 (m, 3 H, H-5a, H-5b, H-6bA), 3.80 (t, J = 9.5 Hz each, 1 H, H-4A), 3.77 (dd, J = 10.0, 3.0 Hz, 1 H, H-2b), 3.72 (s, 3 H, OCH₃), 3.60 (dd, J = 10.0, 3.0 Hz, 1 H, H-2a); 13C NMR (125 MHz, CDCl₃): δ 170.4 (COCH₃), 155.4-114.8 (Ar-C), 101.7 (PhCH), 100.7 (PhCH), 99.7 (C-1b), 98.7 (C-1a), 82.1 (C-4a), 73.6 (C-3a), 73.3 (C-4b), 69.4 (C-6b), 68.6 (C-6a), 68.5 (C-3b), 63.2 (C-5b), 63.0 (C-5a), 61.4 (C-2a), 56.9 (C-2b), 55.6 (OCH₃), 20.9 (COCH₃); ESI-MS: 739.2 [M+Na]⁺; Anal. Calcd. for C₃₅H₃₆N₆O₁₀ (716.24): C, 58.65; H, 5.06; found: C, 58.47; H, 5.25.

**p-Methoxyphenyl (2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (24):** A solution of compound 23 (1.2 g, 1.67 mmol) in 0.1 M CH₃ONa in CH₃OH (20 mL) was allowed to stir at room temperature for 2 h. The reaction mixture was neutralized with Dowex 50W X8 (H⁺) resin, filtered and concentrated to give the crude product which was passed through a short pad of SiO₂ using hexane-EtOAc (1:1) as eluant to give pure compound 24 (1.1 g, 98%). White solid; m.p. 223-224 °C [EtOH]; [α]_D^{25} + 248 (c 1.2, CHCl₃); IR (KBr): 3562, 2929, 2108, 1724, 1508, 1455, 1407, 1271, 1243, 1222, 1139, 1089, 1045, 1006, 959, 832, 810, 745, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.49-7.25 (m, 10 H, Ar-H), 7.04 (d, J = 9.0 Hz, 2 H, Ar-H), 6.85 (d, J = 9.0 Hz, 2 H, Ar-H), 5.63 (d, J = 3.5 Hz, 1 H, H-1b), 5.62 (s, 1 H, PhCH), 5.57 (s, 1 H, PhCH), 5.51 (d, J = 3.5 Hz, 1 H, H-1a), 4.53 (d, J = 9.5 Hz each, 1 H, H-3a), 4.38 (d, J = 12.5 Hz, 1 H, H-6bA), 4.34 (d, J = 3.5 Hz, 1 H, H-4b), 4.27 (dd, J = 10.5, 5.0 Hz, 1 H, H-6bA), 4.24-4.19 (m, 1 H, H-5a), 4.13-4.07 (m, 3 H, H-3b, H-5b, H-6bA), 3.87 (t, J = 9.5 Hz each, 1 H, H-4A), 3.78 (s, 3 H, OCH₃), 3.77 (t, J = 10.5 Hz each, 1 H, H-2b), 3.52 (dd, J = 10.0, 3.0 Hz, 1 H, H-2a), 3.29 (dd, J = 10.0, 3.0 Hz, 1 H, H-2a); ¹³C NMR (125 MHz, CDCl₃): δ 155.7-114.8 (Ar-C), 101.7 (PhCH), 100.7 (PhCH), 99.7 (C-1b), 98.7 (C-1a), 82.3 (C-4a), 73.4 (C-3a), 66.7 (C-5a), 63.4 (C-3b), 63.0 (C-5b), 61.7 (C-2a), 55.6 (OCH₃); ESI-MS: 697.2 [M+Na]⁺; Anal. Calcd. for C₃₃H₃₄N₆O₁₁ (716.24): C, 58.65; H, 5.06; found: C, 58.47; H, 5.25.
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*p*-Methoxyphenyl (2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (25): To a solution of compound 24 (1 g, 1.48 mmol) and compound 14 (790 mg, 1.77 mmol) in anhydrous CH₂Cl₂ (10 mL) was added MS 4Å (1.5 g) and the reaction mixture was allowed to stir at room temperature under argon for 20 min. The reaction mixture was cooled to −30 °C and to the cooled reaction mixture was added NIS (450 mg, 2.0 mmol) followed by HClO₄-SiO₂ (15 mg) and the reaction mixture was allowed to stir at same temperature for 1.5 h. The reaction mixture was filtered through a Celite® bed and washed with CH₂Cl₂ (50 mL). The organic layer was successively washed with 5% Na₂S₂O₃, satd. NaHCO₃ and water, dried (Na₂SO₄) and concentrated to a crude product, which was purified over SiO₂ using hexane-EtOAc (6:1) as eluant to give pure compound 25 (1.2 g, 77%).

White solid; m.p. 209-210 °C [EtOH]; [α]D²⁵ + 118 (c 1.2, CHCl₃); IR (KBr): 3446, 2920, 2871, 2112, 1743, 1454, 1406, 1396, 1225, 1148, 1110, 1083, 1052, 995, 824, 803, 738, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.51-7.25 (m, 20 H, Ar-H), 7.04 (d, J= 9.0 Hz, 2 H, Ar-H), 6.85 (d, J= 9.0 Hz, 2 H, Ar-H), 5.67 (d, J= 3.0 Hz, 1 H, H-1B), 5.60 (s, 1 H, PhCH), 5.57 (s, 1 H, PhCH), 5.49 (d, J= 3.0 Hz, 1 H, H-1A), 5.46 (s, 1 H, PhCH), 5.40 (t, J= 8.5 Hz each, 1 H, H-2C), 4.81 (d, J= 8.0 Hz, 1 H, H-1C), 4.69-4.61 (2 d, J= 12.5 Hz each, 2 H, PhCH₂), 4.56 (t, J= 9.5 Hz each, 1 H, H-3A), 4.52 (br s, 1 H, H-4B), 4.36-4.31 (m, 3 H, H-5A, H-6₅A, H-6₅C), 4.26 (dd, J= 10.5, 5.0 Hz, 1 H, H-6₅B), 4.16 (d, J= 2.5 Hz, 1 H, H-4C), 4.10-4.00 (m, 4 H, H-3B, H-5B, H-6₅B), 3.61 (dd, J= 10.0, 3.0 Hz, 1 H, H-3C), 3.43 (br s, 1 H, H-5C), 3.24 (dd, J= 10.0, 3.0 Hz, 1 H, H-2A), 2.00 (s, 3 H, COCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 169.4 (COCH₃), 155.7-114.8 (Ar-C), 101.7 (C-1C), 101.4 (PhCH), 101.3 (PhCH), 100.5 (PhCH), 99.8 (C-1B), 98.5 (C-1A), 82.3 (C-4A), 77.5 (C-3C), 75.8 (C-4B), 73.2 (C-4C), 72.7 (C-3A), 72.3 (C-3C), 71.2 (PhCH₂), 70.2 (C-2C), 69.4 (C-6C), 69.1 (C-6A), 68.6 (C-6B), 66.7 (C-5C), 63.9 (C-3B), 63.0 (C-5B), 61.7 (C-2A), 58.5 (C-2B), 55.6 (OCH₃), 20.9 (COCH₃); MALDI-MS: 1079.3 [M+Na]⁺; Anal. Calcd. for C₅₅H₆₅N₆O₁₆ (1056.37): C, 62.49; H, 5.34; found: C, 62.28; H, 5.57.

*p*-Methoxyphenyl (3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (26): A solution of compound 25 (1 g, 1.04 mmol) in 0.1 M CH₃ONa in CH₃OH (20 mL) was allowed to stir at room temperature for 2 h. The reaction mixture was neutralized with Dowex 50W X8 (H⁺) resin, filtered and concentrated to give the crude product which was passed through a short pad of SiO₂ using hexane-EtOAc (1:1) as eluant.
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to give pure compound 26 (1 g, 99%). Colorless oil; [α]D^25 + 106 (c 1.2, CHCl₃); IR (neat): 3483, 2914, 2861, 2110, 1507, 1454, 1366, 1247, 1214, 1175, 1111, 1087, 1048, 1025, 999, 806, 752, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.44-7.18 (m, 20 H, Ar-H), 6.97 (d, J = 9.0 Hz, 2 H, Ar-H), 6.78 (d, J = 9.0 Hz, 2 H, Ar-H), 5.63 (d, J = 3.5 Hz, 1 H, H-1B), 5.52 (s, 1 H, PhCH), 5.51 (s, 1 H, PhCH), 5.43 (d, J = 3.0 Hz, 1 H, H-1A), 5.38 (s, 1 H, PhCH), 4.76-4.68 (2 d, J = 12.5 Hz each, 2 H, PhCH₂), 4.52 (d, J = 8.0 Hz, 1 H, H-1c), 4.51-4.46 (m, 2 H, PhCH₂), 4.50-4.45 (m, 5 H, H-3D, H-5D, PhCH₂), 4.39 (d, J = 12.5 Hz each, 2 H, PhCH₂), 4.29-4.18 (m, 4 H, H-5A, H-6aA, H-6bA, H-6cA), 3.82 (dd, J = 12.5 Hz, 3 H, OCH₃), 3.68 (t, J = 10.5 Hz each, 1 H, H-6bB), 3.45 (dd, 10.0, 3.0 Hz, 1 H, H-3C), 3.33 (br s, 1 H, H-5C), 3.01 (dd, J = 10.0, 3.0 Hz, 1 H, H-2A); ¹³C NMR (125 MHz, CDCl₃): δ 155.7-114.8 (Ar-C), 104.3 (C-1c), 101.8 (PhCH), 101.1 (PhCH), 99.8 (C-1B), 98.5 (C-1A), 82.4 (C-4A), 78.6 (C-3c), 76.1 (C-4B), 73.7 (2 C, C-3a, C-4c), 72.6 (C-5A), 71.9 (PhCH₂), 70.3 (C-2c), 69.4 (C-6c), 69.2 (C-6a), 68.6 (C-6b), 66.8 (C-5c), 63.8 (C-3b), 63.0 (C-5b), 61.8 (C-2a), 55.6 (OCH₃); MALDI-MS: 1037.3 [M+Na]^+; Anal. Calcd. for C₅₃H₅₄NO₁₅ (1014.36): C, 62.71; H, 5.36; found: C, 62.50; H, 5.58.

p-Methoxyphenyl (2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-(1→2)-(3-0-benzyl-4,6-0-benzylidene-p-D-galactopyranosyl)-(1→3)-(2-azido-4,6-0-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-0-benzylidene-2-deoxy-α-D-glucopyranoside (27): To a solution of compound 26 (900 mg, 0.89 mmol) and compound 17 (500 mg, 1.04 mmol) in a mixture of anhydrous CH₂Cl₂ (4 mL) and Et₂O (4 mL) was added MS 4 Å (1 g) and the reaction mixture was allowed to stir at room temperature under argon for 20 min. The reaction mixture was cooled to -18 °C and to the cooled reaction mixture was added NIS (260 mg, 1.15 mmol) followed by HC₁₀₄-SiO₂ (10 mg) and the reaction mixture was allowed to stir at same temperature for 1 h. The reaction mixture was filtered through a Celite® bed and washed with CH₂Cl₂ (mL). The organic layer was successively washed with 5% Na₂SO₃, satd. NaHCO₃ and water, dried (Na₂SO₄) and concentrated to give pure compound 27 (950 mg, 75%). Colorless oil; [α]D^25 -1 (c 1.2, CHCl₃); IR (neat): 3448, 3032, 2907, 2864, 2109, 1507, 1455, 1402, 1365, 1264, 1213, 1173, 1108, 1051, 1027, 806, 736, 697 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ 7.41-7.08 (m, 35 H, Ar-H), 7.08 (d, J = 9.0 Hz, 2 H, Ar-H), 6.78 (d, J = 9.0 Hz, 2 H, Ar-H), 5.63 (d, J = 3.0 Hz, 1 H, H-1B), 5.54 (s, 1 H, PhCH), 5.51 (s, 1 H, PhCH), 5.50 (d, J = 3.5 Hz, 1 H, H-1D), 5.45 (d, J = 3.0 Hz, 1 H, H-1A), 5.31 (s, 1 H, PhCH), 4.76 (d, J = 8.0 Hz, 1 H, H-1C), 4.74 (d, J = 12.5 Hz, 1 H, PhCH₂), 4.64-4.52 (m, 3 H, PhCH₂), 4.50-4.45 (m, 5 H, H-3D, H-5D, PhCH₂), 4.39 (d, J = 12.5 Hz,

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Hz, 1 H, PhCH₂), 4.35-4.30 (m, 1 H, H-5A), 4.28-4.20 (m, 4 H, H-3B, H-6aA, H-6ab, H-6ac), 4.18-4.14 (m, 2 H, H-2C, H-3A), 4.07-4.00 (m, 3 H, H-4B, H-6aA, H-6ac), 3.95-3.92 (m, 2 H, H-2D, H-5A), 3.91-3.88 (m, 2 H, H-3C, H-6ab), 3.82 (t, J= 9.5 Hz each, 1 H, H-4A), 3.73-3.70 (m, 2 H, H-3C, H-6bB), 3.71 (s, 3 H, OCH₃), 3.52 (dd, J= 10.0, 3.0 Hz, 1 H, H-2B), 13C NMR (125 MHz, CDCl₃): δ 156.0-114.8 (Ar-C), 102.3 (C-1c), 101.9 (PhCH), 100.9 (PhCH), 100.1 (C-1b), 98.5 (C-1a), 97.0 (C-1a), 82.4 (C-4a), 81.6 (C-3c), 79.3 (C-2D), 78.5 (C-5b), 76.4 (C-4c), 75.8 (C-3b), 74.7 (PhCH₂), 73.0 (C-4b), 72.7 (2 C, C-4D, PhCH₂), 72.4 (PhCH₂), 71.7 (C-3b), 71.4 (C-3a), 70.8 (PhCH₂), 69.3 (C-6c), 69.2 (C-6a), 68.6 (C-6b), 66.5 (C-5a), 66.3 (C-2c), 64.1 (C-5D), 63.1 (C-5c), 61.9 (C-2a), 58.5 (C-2b), 55.6 (OCH₃), 16.2 (CCH₃); MALDI-MS: 1453.5 [M+Na]+; Anal. Calcd. for C₈₀H₈₂N₆O₁₉ (1430.56): C, 67.12; H, 5.77; found: C, 66.93; H, 6.00.

\( p \)-Methoxyphenyl (\( \alpha-L \)-fucopyranosyl)-(1→2)-(\( \beta-D \)-galactopyranosyl)-(1→3)-(2-acetamido-2-deoxy-\( \alpha-D \)-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-\( \alpha-D \)-galactopyranoside (1): To a stirred solution of compound 22 (800 g, 0.56 mmol) and 20% Pd(OH)₂-C (150 mg) in a mixture of CH₂Cl₂ (3 mL) and CH₃OH (3 mL) was added drop wise Et₃SiH (1 mL, 6.26 mmol) at room temperature during 30 min and the reaction mixture was further allowed to stir at room temperature for 6 h. The reaction mixture was filtered through a Celite® bed and concentrated to dryness. To a solution of the dry mass in CH₃OH (5 mL) was added acetic anhydride (0.2 mL) and the reaction mixture was kept at room temperature for 1 h. The solvents were removed under reduced pressure to give the product, which was further purified over Sephadex LH-20 using CH₃OH-H₂O (5:1, v/v) as eluant to give pure compound 1 (300 mg, 64%). Glass; [\( \alpha \)]D²⁵ + 19 (c 1.2, H₂O); IR (KBr): 3416, 2927, 2854, 1713, 1650, 1585, 1406, 1398, 1221, 1149, 1087, 1056, 995, 695 cm⁻¹; 1H NMR (500 MHz, D₂O): δ 7.00 (d, J = 9.0 Hz, 2 H, Ar-H), 6.86 (d, J = 9.0 Hz, 2 H, Ar-H), 5.39 (d, J = 3.5 Hz, 1 H, H-1A), 5.12 (d, J = 4.0 Hz, 1 H, H-1D), 4.99 (d, J = 3.0 Hz, 1 H, H-1b), 4.54 (d, J = 8.0 Hz, 1 H, H-1c), 4.42 (dd, J = 11.0, 4.0 Hz, 1 H, H-2A), 4.17-4.08 (m, 3 H, H-2b, H-2d, H-3d), 4.04 (dd, J = 10.0, 3.5 Hz, 1 H, H-3A), 3.97 (t, J = 7.6 Hz each, 1 H, H-2c), 3.89 (dd, J = 10.0, 3.0 Hz, 1 H, H-3b), 3.85-3.83 (m, 1 H, H-5C), 3.80 (br s, 2 H, H-4A, H-4B), 3.73 (dd, J = 10.0, 3.5 Hz, 1 H, H-3c), 3.69 (s, 3 H, OCH₃), 3.67-3.60 (m, 7 H, H-4c, H-6abA, H-6abB, H-6abc), 3.59-3.50 (m, 4 H, H-4p, H-5A, H-5b, H-5d), 1.97, 1.94 (2 s, 6 H, 2 COCH₃), 1.09 (d, J = 6.0 Hz, 3 H, CCH₃); 13C NMR (125 MHz, D₂O): δ 174.4, 173.7 (2 COCH₃), 154.7-114.9 (Ar-C), 101.2 (C-1c), 99.2 (C-1D), 97.1 (C-1A), 93.2 (C-1b), 76.1 (C-5A), 75.0 (C-5b), 73.8 (C-3b), 73.5 (C-3c), 72.1 (C-3A), 71.8 (C-5D), 71.5 (C-2c), 70.9 (C-5C), 69.6 (C-4b), 69.0 (C-4A), 209
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68.8 (C-4b), 68.0 (C-2D), 66.7 (C-4c), 64.4 (C-3b), 61.1 (C-6c), 60.8 (C-6a), 60.7 (C-6b), 55.7 (OCH3), 49.0 (C-2b), 47.9 (C-2a), 22.1, 21.9 (COCH3), 15.3 (CCH3); MALDI-MS: 861.3 [M+Na]+; Anal. Calcd. for C35H54N202i (838.32): C, 50.12; H, 6.49; found: C, 49.95; H, 6.73.

**p-Methoxyphenyl (α-L-fucopyranosyl)-(1→2)-(β-D-galactopyranosyl)-(1→3)-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (2):** To a stirred solution of compound 27 (800 mg, 0.56 mmol) and 20% Pd(OH)2-C (150 mg) in a mixture of CH2Cl2 (3 mL) and CH3OH (3 mL) was added drop wise Et3SiH (1 mL, 6.26 mmol) at room temperature during 30 min and the reaction mixture was further allowed to stir at room temperature for 6 h. The reaction mixture was filtered through a Celite® bed and concentrated to dryness. To a solution of the dry mass in CH3OH (5 mL) was added acetic anhydride (0.2 mL) and the reaction mixture was kept at room temperature for 1 h. The solvents were removed under reduced pressure to give the product, which was further purified over Sephadex LH-20 using CH3OH-H2O (5:1, v/v) as eluant to give pure compound 2 (290 mg, 62%). Glass; [α]D25 + 6 (c 1.2, H2O); IR (KBr): 3428, 2926, 2853, 1710, 1652, 1587, 1400, 1396, 1223, 1056, 996 cm⁻¹; ¹H NMR (500 MHz, D2O): δ 6.94 (d, J = 9.0 Hz, 2 H, Ar-H), 6.81 (d, J = 9.0 Hz, 2 H, Ar-H), 5.30 (d, J = 3.5 Hz, 1 H, H-1A), 5.28 (d, J = 3.5 Hz, 1 H, H-1B), 5.05 (d, J = 3.5 Hz, 1 H, H-1D), 4.47 (d, J = 7.5 Hz, 1 H, H-1C), 4.07-4.00 (m, 4 H, H-2A, H-2B, H-2D, H-3D), 3.91 (t, J = 9.5 Hz each, 1 H, H-2C), 3.86 (dd, J = 10.0, 3.0 Hz, 1 H, H-3B), 3.80-3.74 (m, 1 H, H-5A), 3.76-3.74 (m, 2 H, H-4B, H-4C), 3.70-3.65 (m, 2 H, H-3C, H-4A), 3.64-3.53 (m, 7 H, H-3A, H-6abA, H-6abB, H-6abc), 3.63 (s, 3 H, OCH3), 3.52-3.44 (m, 4 H, H-4A, H-5B, H-5C, H-5D), 1.90, 1.89 (2 s, 6 H, 2COCH3), 1.10 (d, J = 6.0 Hz, 3 H, H-CH3); ¹³C NMR (125 MHz, D2O): δ 174.3, 173.6 (2 COCH3), 154.6-115.0 (Ar-C), 102.0 (C-1C), 99.3 (C-1D), 97.1 (C-1B), 96.8 (C-1A), 76.3 (C-4b), 75.7 (C-4c), 74.9 (C-2c), 73.7 (C-5b), 73.5 (C-3b), 72.4 (C-4a), 71.8 (C-5d), 71.0 (C-3a), 70.5 (C-5a), 69.6 (C-5c), 69.0 (C-4b), 68.6 (C-3b), 68.0 (C-3c), 66.8 (C-2b), 60.8 (C-6c), 60.5 (C-6a), 59.9 (C-6b), 55.8 (OCH3), 51.9 (C-2a), 49.1 (C-2b), 22.0 (COCH3), 21.9 (COCH3), 15.4 (CCH3); MALDI-MS: 861.3 [M+Na]+; Anal. Calcd. for C35H54N202i (838.32): C, 50.12; H, 6.49; found: C, 49.97; H, 6.70.
3.3.5. Representative NMR spectra of synthesized compounds

$^1$H and $^{13}$C NMR spectra of $p$-methylphenyl 3-O-acetyl-2-azido-4,6-O-benzylidene-2-deoxy-1-thio-β-D-galactopyranoside (11) (CDCl$_3$-CCl$_4$).
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$^1$H and $^{13}$C NMR spectra of $p$-methoxyphenyl (3-O-acetyl-2-azido-4,6-$O$-benzylidene-2-deoxy-$\alpha$-$D$-galactopyranosyl)-(1$\rightarrow$3)-2-azido-4,6-$O$-benzylidene-2-deoxy-$\alpha$-$D$-galactopyranoside (18) (CDCl$_3$-CCl$_4$).

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2D COSY and 2D HSQC NMR (selected region) spectra of p-methoxyphenyl (3-O-acetyl-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (18).
$^1$H and $^{13}$C NMR spectra of $p$-methoxyphenyl (2-azido-4,6-$O$-benzylidene-2-deoxy-$\alpha$-$D$-galactopyranosyl)-(1$\rightarrow$3)-2-azido-4,6-$O$-benzylidene-2-deoxy-$\alpha$-$D$-galactopyranoside (19) (CDCl$_3$-CCl$_4$).
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2D COSY and 2D HSQC NMR (selected region) spectra of $p$-methoxyphenyl (2-azido-4,6-0-benzylidene-2-deoxy-$\alpha$-D-galactopyranosyl)-(1$\rightarrow$3)-2-azido-4,6-O-benzylidene-2-deoxy-$\alpha$-D-galactopyranoside (19).
$^1$H and $^{13}$C NMR spectra of $p$-methoxyphenyl (2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-$\beta$-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-$\alpha$-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-$\alpha$-D-galactopyranoside (20) (CDCl$_3$-CCl$_4$).
2D COSY and 2D HSQC NMR (selected region) spectra of p-methoxyphenyl (2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (20).
$^1$H and $^{13}$C NMR spectra of $p$-methoxyphenyl (3-$O$-benzyl-$4,6-O$-benzylidene-$\beta$-D-galactopyranosyl)-(1$\rightarrow$3)-(2-azido-$4,6-O$-benzylidene-2-deoxy-$\alpha$-D-galactopyranosyl)-(1$\rightarrow$3)-2-azido-$4,6-O$-benzylidene-2-deoxy-$\alpha$-D-galactopyranoside (21) (CDCl$_3$, CCl$_4$).
2D COSY and 2D HSQC NMR (selected region) spectra of \(p\)-methoxyphenyl (3-\(O\)-benzyl-4,6-\(O\)-benzylidene-\(\beta\)-\(D\)-galactopyranosyl)-(1\(\rightarrow\)3)-(2-azido-4,6-\(O\)-benzylidene-2-deoxy-\(\alpha\)-\(D\)-galactopyranosyl)-(1\(\rightarrow\)3)-2-azido-4,6-\(O\)-benzylidene-2-deoxy-\(\alpha\)-\(D\)-galactopyranoside (21).
$^1$H and $^{13}$C NMR spectra of $p$-methoxyphenyl (2,3,4-tri-O-benzyl-$\alpha$-L-fucopyranosyl)-(1→2)-(3-O-benzyl-4,6-O-benzylidene-$\beta$-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-$\alpha$-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-$\alpha$-D-galactopyranoside (22) (CDCl$_3$:CCl$_4$).
2D COSY and 2D HSQC NMR (selected region) spectra of p-methoxyphenyl (2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-(1→2)-(3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (22).
$^1$H and $^{13}$C NMR spectra of $p$-methoxyphenyl (3-O-acetyl-2-azido-4,6-O-benzylidene-2-deoxy-\(\alpha\)-D-galactopyranosyl)-(1\(\rightarrow\)3)-2-azido-4,6-O-benzylidene-2-deoxy-\(\alpha\)-D-glucopyranoside (23) (CDCl$_3$-CCl$_4$).
2D COSY and 2D HSQC NMR (selected region) spectra of $p$-methoxyphenyl (3-$O$-acetyl-2-azido-4,6-$O$-benzylidene-2-deoxy-$\alpha$-$D$-galactopyranosyl)-(1$\rightarrow$3)-2-azido-4,6-$O$-benzylidene-2-deoxy-$\alpha$-$D$-glucopyranoside (23).
$^1$H and $^{13}$C NMR spectra of p-methoxyphenyl (2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (24) (CDCl$_3$-CCl$_4$).
2D COSY and 2D HSQC NMR (selected region) spectra of $p$-methoxyphenyl (2-azido-4,6-O-benzylidene-2-deoxy-$\alpha$-D-galactopyranosyl)-(1$\rightarrow$3)-2-azido-4,6-O-benzylidene-2-deoxy-$\alpha$-D-glucopyranoside (24).
$^1$H and $^{13}$C NMR spectra of $p$-methoxyphenyl (2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-$\beta$-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-$\alpha$-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-$\alpha$-D-glucopyranoside (25) (CDCl$_3$-CCl$_4$).
2D COSY and 2D HSQC NMR (selected region) spectra of p-methoxyphenyl (2-O-acetyl-3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (25).
\(^1\)H and \(^{13}\)C NMR spectra of \(p\)-methoxyphenyl (3-\(O\)-benzyl-4,6-\(O\)-benzylidene-\(\beta\)-\(D\)-galactopyranosyl)-(1\(\rightarrow\)3)-(2-azido-4,6-\(O\)-benzylidene-2-deoxy-\(\alpha\)-\(D\)-galactopyranosyl)-(1\(\rightarrow\)3)-2-azido-4,6-\(O\)-benzylidene-2-deoxy-\(\alpha\)-\(D\)-glucopyranoside (26) (CDCl\(_3\)-CCl\(_4\)).
2D COSY and 2D HSQC NMR (selected region) spectra of p-methoxyphenyl (3-O-benzyl-4,6-O-benzylidene-β-D-galactopyranosyl)-(1→3)-(2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (26).
$^1$H and $^{13}$C NMR spectra of $p$-methoxyphenyl (2,3,4-tri-$O$-benzyl-$\alpha$-L-fucopyranosyl)-(1$\rightarrow$2)-(3-$O$-benzyl-4,6-$O$-benzylidene-$\beta$-D-galactopyranosyl)-(1$\rightarrow$3)-(2-azido-4,6-$O$-benzylidene-2-deoxy-$\alpha$-D-galactopyranosyl)-(1$\rightarrow$3)-2-azido-4,6-$O$-benzylidene-2-deoxy-$\alpha$-D-glucopyranoside (27) (CDCl$_3$-CCl$_4$).
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2D COSY and 2D HSQC NMR (selected region) spectra of \( p \)-methoxyphenyl (2,3,4-tri-O-benzyl-\( \alpha \)-L-fucopyranosyl)-(1→2)-(3-\( O \)-benzyl-4,6-\( O \)-benzylidene-\( \beta \)-D-galactopyranosyl)-(1→3)-(2-azido-4,6-\( O \)-benzylidene-2-deoxy-\( \alpha \)-D-galactopyranosyl)-(1→3)-2-azido-4,6-\( O \)-benzylidene-2-deoxy-\( \alpha \)-D-glucopyranoside (27).
$^1$H and $^{13}$C NMR spectra of p-methoxyphenyl (α-L-fucopyranosyl)-(1→2)-(β-D-galactopyranosyl)-(1→3)-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (1) (D$_2$O).
2D COSY and 2D HSQC NMR (selected region) spectra of p-methoxyphenyl (α-L-fucopyranosyl)-(1→2)-(β-D-galactopyranosyl)-(1→3)-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (1).
\[ ^{1}H \text{ and } ^{13}C \text{ NMR spectra of } p\text{-methoxyphenyl} \ (\alpha-L\text{-fucopyranosyl})-(1\rightarrow2)-(\beta-D\text{-galactopyranosyl})-(1\rightarrow3)-(2\text{-acetamido-2-deoxy-}\alpha-D\text{-galactopyranosyl})-(1\rightarrow3)-2\text{-acetamido-2-deoxy-}\alpha-D\text{-glucopyranoside (2)} \ (D_2O). \]
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2D COSY and 2D HSQC NMR (selected region) spectra of p-methoxyphenyl (α-L-fucopyranosyl)-(1→2)-(β-D-galactopyranosyl)-(1→3)-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-α-D-glucopyranoside (2).
3.4. References

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