Glycoconj J
DOI 10.1007/s10719-015-9635-1

ORIGINAL ARTICLE

An expeditious synthesis of blood-group antigens, ABO histo-blood group type II antigens and xenoantigen oligosaccharides with amino type spacer−arms

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Received: 7 August 2015 / Revised: 30 October 2015 / Accepted: 2 November 2015

Abstract Blood group oligosaccharides are one of the most clinically important antigen families and they may also act as secondary ligands for bacterial toxins from *Escherichia coli* and *Vibrio cholerae*. Herein we report the synthesis of spacered (sp = $CH_2CH_2CH_2NH_2$) glycosides of **A antigen** {α-D-GalNAc-(l→3)-[α-L-Fuc-(l→2)]-β-D-Gal-}, **B antigen** {α-D-Gal-(l→3)-[α-L-Fuc-(l→2)]-β-D-Gal-}, **LewisX** {α-D-Gal-(l→4)-[α-L-Fuc-(l→3)]-β-D-GlcNAc-}, **A type-II** {α-D-GalNAc-(l→3)-[α-L-Fuc-(l→2)]-β-D-Gal-(1→4)-β-D-GlcNAc-}, **B type-II** {α-D-Gal-(l→3)-[α-L-Fuc-(l→2)]-β-D-Gal-(1→4)-β-D-GlcNAc-}, **H type-II** {α-L-Fuc-(l→2)-β-D-Gal-(1→4)-β-D-GlcNAc-}, **xenoantigen** {α-D-Gal-(l→3)-β-D-Gal-(1→4)-[α-L-Fuc-(l→2)]-β-D-GlcNAc-} and **Linear B Type II** {α-D-Gal-(l→3)-β-D-Gal-(1→4)-β-D-GlcNAc-} useful for a range of biochemical investigations. This linker was chosen so as to facilitate the future conjugation of the antigens to proteins or other molecules. We also measured the affinities of some synthesized oligosaccharides against El Tor CTB strain from *V. cholera*.

Keywords Blood group antigen · Oligosaccharide · Glycosylation · Xenoantigen · Aminopropyl

Introduction

The ABO blood group system, discovered by Karl Landsteiner, has interested biologists and medical scientists for over a century now. The ABH antigens of the blood group have shown remarkable differences in antigenicity, based on subtle changes in their structure. The detailed antigen structures, essential to determine the specificity of blood group were established by Walter J. Morgan, Winifred M. Watkins, Elvin Kabat and their colleagues, during the 1950s [1–3].

The antigens consist of three oligosaccharide epitopes *i.e.* Antigen H (O), A and B. Antigen H is a disaccharide consisting of L-fucose and D-galactose, whereas antigens A and B are trisaccharides containing the disaccharide H antigen along with an additional *N*-acetyl-galactosamine or a galactose residue, respectively. The ABO antigens are fucosylated oligosaccharide structures, carried on both glycolipids and glycoproteins (Fig. 1).

These blood group antigens are of important clinical consideration for both blood transfusion and organ transplantation in humans [4, 5]. Adding to this, their distribution is not only restricted to the surface of red blood cells, showing their additional presence on various body fluids and tissues. They are also present on the intestinal epithelial cell surface, the major site of *V. cholerae* and enterotoxigenic *Escherichia coli* (ETEC) infections, in close proximity to GM1 gangliosides [6–8]. They also function as receptor targets by various pathogens such as *Campylobacter jejuni*, *Heliobacter pylori* and Norwalk virus and are expressed aberrantly in oncogenesis of various organs and in various vascular inflammatory processes [9–11]. Along with these oligosaccharides, the

Electronic supplementary material The online version of this article (doi:10.1007/s10719-015-9635-1) contains supplementary material, which is available to authorized users.

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Published online: 14 November 2015

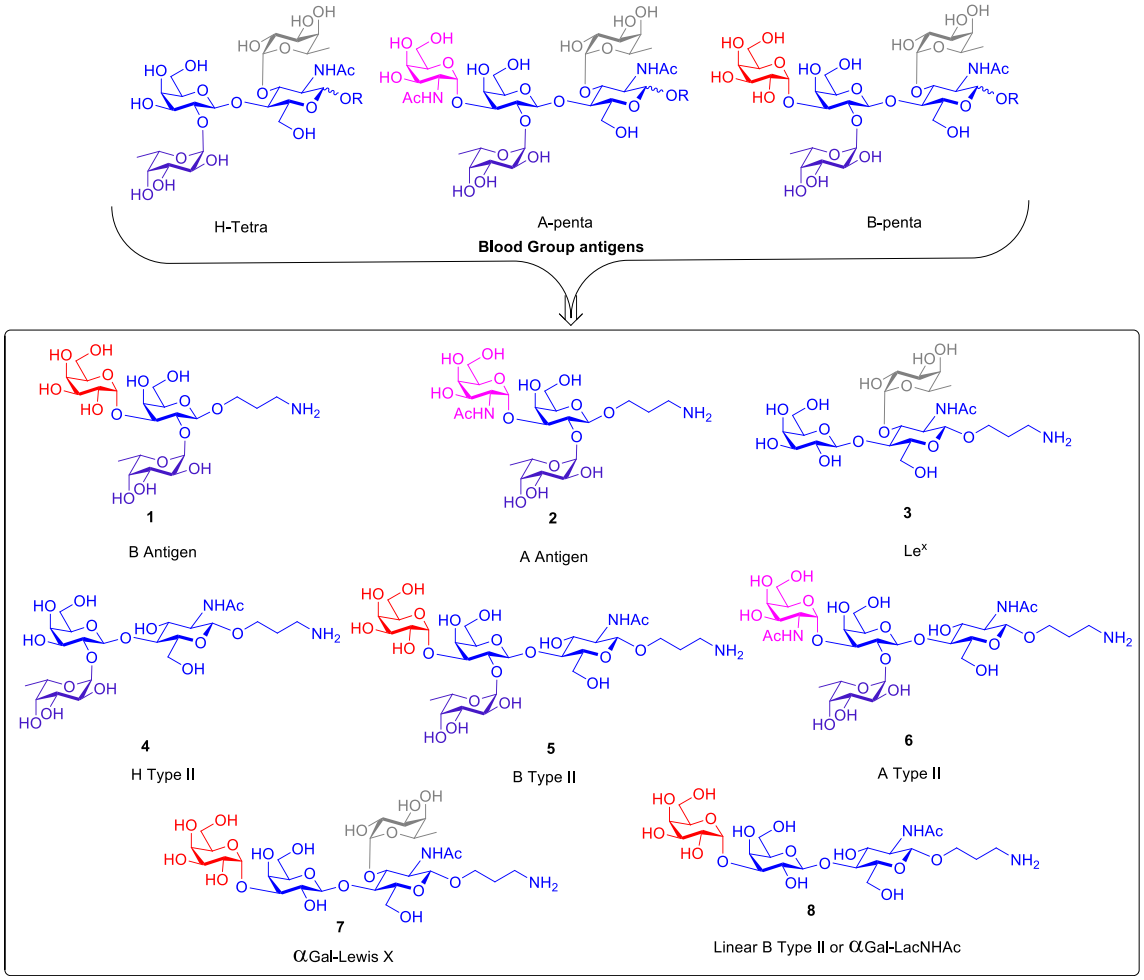


Fig. 1 Target to synthesise blood-group antigen, ABO Histo-blood group type II antigen and xenoantigen oligosaccharides

xenoantigenic epitopes consisting of trisaccharides αGal(1–3)βGal(1–4)GluNAc, a fucosylated structure, αGal-Lewis X, are an important factor to be considered during xenotransplantation of organs. Their recognition by human xenoreactive natural antibodies plays an important role in organ hyperacute rejection [12].

Recently, there have been reports showing the ability of specific members of this family of oligosaccharides to present themselves as diagnostic and prognostic markers for a variety of diseases [13, 14]. One of which includes, type II Lewis-y oligosaccharide, which is a tumour-associated antigen prevalent in several different types of cancer [15]. Furthermore, blood group A oligosaccharides based on the Lewis-y core tetrasaccharide have been identified as ligands for a number of proteins like B-subunit of *E. coli* heat-labile toxin (LTB) [16], analogous to B-subunit of cholera toxin (CTB) [17] and a hybrid protein derived from LTB. This discovery could provide an insight to the blood group dependence of diarrhoeal diseases, in which it has been observed that patients with blood group O are more susceptible to certain strains of cholera than those in blood groups A or B [18, 19].

The new information about the molecular recognition of blood-group antigens by Cholera Toxin should encourage medicinal chemists to develop improved drug design strategies towards novel pharmacological agents that inactivate cholera toxin. Development of such antagonists against cholera toxin could pave way for a more effective combination therapy, along with GM1 antagonists. This could also be useful as a tool to understand the variability of susceptibility to Cholera infection within the blood group phenotype of individuals.

As protein–carbohydrate interactions are an essential prerequisite for cell entry and toxin activity, the development of inhibitors for these interactions has attracted much interest over recent years. Even though having potential utility in understanding these various circumstances, studies involving physiological interactions and pathological implications of ABO blood group antigens at molecular level has been rather slow, mainly due to the lack of pure antigens in substantial amounts. To date, several comprehensive chemical [20–32] and chemoenzymatic [33, 34] syntheses of different types of blood group antigens have been reported.

In our previous report [35], we had described basic structural interactions between Lewis-y tetrasaccharide and blood group B pentasaccharide antigens with cholera toxin. Adding to it, herein we report efficient synthesis of blood group oligosaccharide fragments (**1**–**8**, Fig. 1) hosting an aminopropyl aglycone, which are supposed to be useful in future for the further synthesis of various glycoprobes [36].

To improve accessibility to those antigens, we designed a synthetic strategy to synthesize all target compounds employing a Divisive Hierarchical model, using only three disaccharide acceptors. From these disaccharide acceptors we easily synthesized blood group oligosaccharide fragments (**1**–**8**, Fig. 1) as well as a range of protected tri- and tetrasaccharides that are suitable for further elaboration to synthesise blood group A and B derivatives of the Lewis-y core structure in minimum number of synthetic steps.

Though Lemieux's bromide anomerisation protocol provides excellent stereoselectivity in the synthesis of these sterically congested oligosaccharides, [37–41] it typically demands large excess of glycosyl donor [23] and/or very prolonged reaction times [40, 41]. It also significantly increases the length of synthesis to prepare the fucosyl donors. On the other hand, our synthetic strategy involved easy handling and short time reactions of fucosylation of partially protected 3 or 2′-hydroxy group of a lactosamine derivative using thioglycoside donors owing to their high stability prior to activation, and toluene as a solvent, which had a very dramatic effect on the yields of these glycosylation reactions [35, 49].

Results and discussion

Synthesis of blood group antigens (1 & 2)

Synthesis of the target ABO blood group antigens (**1** and **2**) were carried out by stereoselective glycosylation of suitably protected monosaccharide intermediates which were prepared from the reducing sugars following the literature reported reaction conditions (Scheme 1). Transformation of 3-(Benzyloxycarbonyl)aminopropyl 4,6-*O*--benzylidene-β-D-galactopyranoside (**9**) [42] into 3-(Benzyloxycarbonyl)aminopropyl 3-*O*-benzoyl-4,6-*O*--benzylidene-β-D-galactopyranoside (**10**) was carried out with yield of 88 % by the treatment with benzoyl chloride in the presence of pyridine in dichloromethane.

Stereoselective glycosylation of the compound **10** with known thiofucoside donor **11** [43] in the presence of NIS-TfOH [44, 45] in toluene furnished disaccharide derivative **12** in 81 % yield together with a minor quantity (~5 %) of its other isomer, which was separated by column chromatography. Stereoselective formation of compound **12** was supported by its spectral analysis [signals at δ 5.47 (s, PhC*H*), 5.41 (d, J = 3.6 Hz, H-1_B), 4.57 (d, J = 7.7 Hz, H-1_A), and at δ 102.1 (C-1_A), 100.8 (Ph*C*H), 97.5 (C-1_B) in the ^{1}H and ^{13}C NMR spectra respectively]. De-*O*-benzoylation of compound **12** using sodium methoxide furnished disaccharide acceptor **13** in 92 % yield. Glycosylation of compound **13** with thioglycoside **14** [46] in the presence of NIS-TfOH [44, 45] furnished trisaccharide derivative **16** in 67 % yield together with its other isomer in a minor quantity (8 %), which was separated by column chromatography (Scheme 1).

Stereoselective formation of compound **16** was supported by its spectral analysis [signals at δ 5.47 (d, J = 3.4 Hz, H-1_B), 5.42 (s, PhC*H*), 5.34 (d, J = 3.6 Hz, H-1_C), 4.26 (d, J = 7.7 Hz, H-1_A), and at δ 102.3 (C-1_A), 101.3 (Ph*C*H), 97.9 (C-1_B), 92.6 (C-1_C), in the ^{1}H and ^{13}C NMR spectra respectively].

Hydrogenolysis of triasaccharide derivative **16** over Pearlman's catalyst [47] furnished trisaccharide **1** as its 3-amiopropyl glycoside with 60 % overall yield. The presence of three anomeric protons in the ^{1}H NMR δ 5.27 (d, J = 3.5 Hz, H-1_B), 5.25 (d, J = 3.3 Hz, H-1_C), 4.59 (d, J = 7.3 Hz, H-1_A) and at δ 102.3 (C-1_A), 99.5 (C-1_B), 93.8 (C-1_C) in the ^{13}C NMR spectra confirmed the formation of compound **1** (Scheme 1).

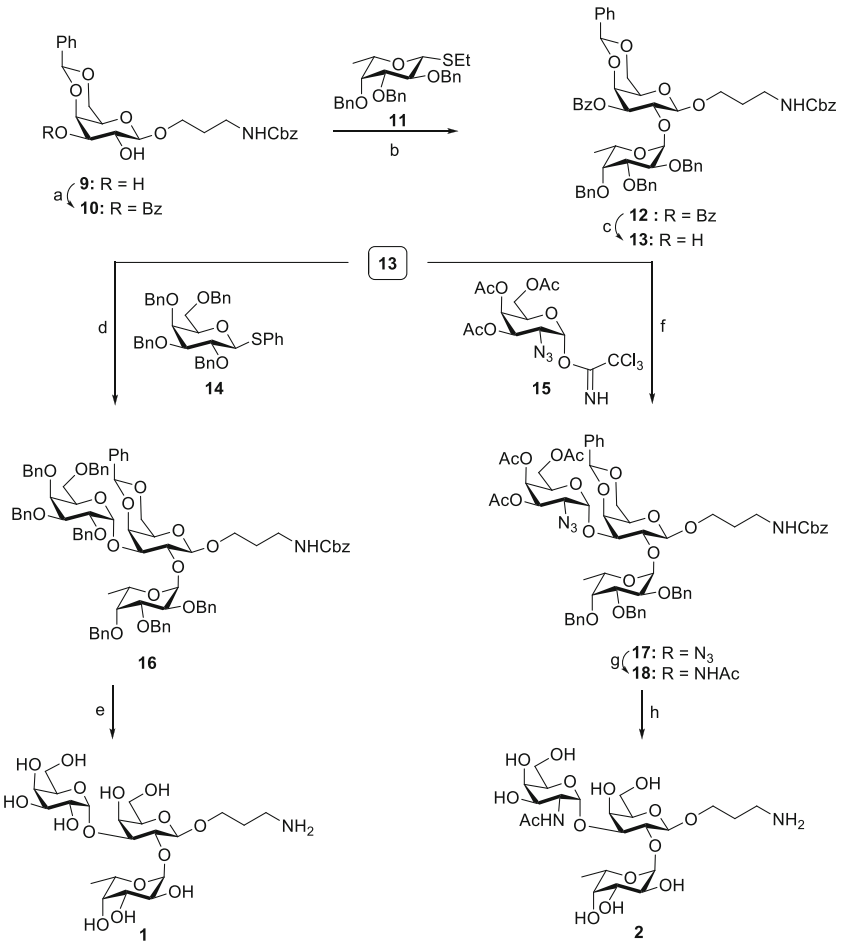
In another set of experiments, the same acceptor **13** when coupled with trichloroacetimidate donor **15** [48] in the presence of TMSOTf as glycosyl activator in CH_2Cl_2 furnished trisaccharide derivative **17** with 70 % yield together with a minor quantity (~5 %) of its other isomer, which was separated by column chromatography.

Formation of compound **17** was confirmed from its spectral analysis [signals at δ 5.54 (s, PhC*H*), 5.34 (d, J = 3.4 Hz, H-1_B), 5.30 (d, J = 3.6 Hz, H-1_C), 4.39 (d, J = 7.7 Hz, H-1_A) in the ^{1}H NMR and δ 102.0 (C-1_A), 100.8 (Ph*C*H), 98.3 (C-1_B), 94.2 (C-1_C) in the ^{13}C NMR spectra] (Scheme 1).

Conversion of the azide into *N*-acetyl groups using thiolacetic acid in pyridine afforded compound **18** in 70 % yield. Hydrogenolysis of triasaccharide derivative **18** over Pearlman's catalyst [47] followed by saponification under Zemplen conditions afforded trisaccharide **2** as its 3-aminopropyl glycoside with 53 % overall yield (Scheme 1). The presence of three anomeric protons in the ^{1}H NMR δ 5.28 (d, J = 3.7 Hz, H-1_B), 5.17 (d, J = 3.7 Hz, H-1_C), 4.58 (d, J = 7.7 Hz, H-1_A) and at δ 102.2 (C-1_A), 99.4 (C-1_B), 92.0 (C-1_C) in the ^{13}C NMR spectra confirmed the formation of compound **2** (Scheme 1).

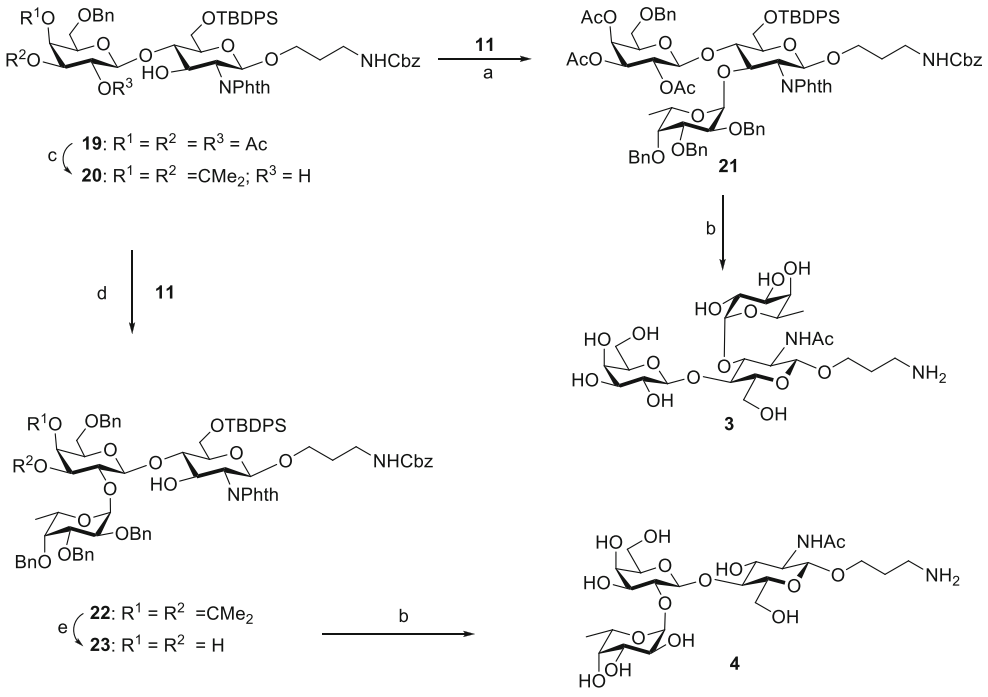
Synthesis of Lewis X and ABO Histo-blood group type II antigens (3, 4, 5 & 6)

To prepare Lewis X and histo blood group antigens **3**, **4**, **5** and **6**, we decided to employ a Divisive Hierarchical model (Scheme 2) starting with disaccharide **19** [49], similar to that used in our previous syntheses of Lewis-y oligosaccharides. To start with, first the disaccharide acceptor **19** was fucosylated at the 3-position of the glucosamine ring to



Scheme 1 Reagents and conditions: (**a**) BzCl, CH_2Cl_2, C_5H_5N, −40 °C, 1 h, 88 %; (**b**) NIS, TfOH, toluene, MS 4 Å, −10 °C, 2 h, 81 %; (**c**) 0.1 M CH_3ONa, CH_3OH, room temperature, 2 h, 92 %; (**d**) NIS, TfOH, CH_2Cl_2, MS 4 Å, −40 °C, 1 h, 67 %; (**e**) H_2, 20 % $Pd(OH)_2$-C, CH_3OH, room temperature, 24 h, 60 %; (f) TMSOTf, CH_2Cl_2, MS 4 Å, −20 °C, 1 h, 70 %; (**g**) CH_3COSH, pyridine, r t, 10 h, 70 %; (**h**) (i) 0.1 M CH_3ONa, CH_3OH, room temperature, 2 h, (ii) H_2, 20 % $Pd(OH)_2$-C, CH_3OH, room temperature, 24 h; 53 % overall yield

furnish the fully protected trisaccharide **21** in 73 % yield. The *N*-phthalimido of trisaccharide **21** was removed by treatment with hydrazine hydrate [50], followed by N-acetylation using acetic anhydride in pyridine and saponified using sodium



Scheme 2 Reagents and conditions: (**a**) donor **11**, NIS, TfOH, toluene −15 °C, 7 h, 73 %; (**b**) (i) $H_2NCH_2CH_2NH_2$, n-BuOH, 80 °C, 8 h, (ii) Ac_2O, C_5H_5N, room temperature, 3 h, (iii) 0.1 M CH_3ONa, CH_3OH, room temperature, 3 h, (iv) TBAF, THF, room temperature, 6 h, (v) H_2, 20 % $Pd(OH)_2$-C, CH_3OH, room temperature, 7 h; the five step deprotection sequence provided 49 % for **3** and 58 % for **4** respectively; (**c**) (i) 0.1 M CH_3ONa, CH_3OH, room temperature, 30 min, (ii) 2,2-dimethoxypropane, CSA, DMF, 12 h, 82 % over two steps; (**d**) 1.2 Equiv donor **11**, NIS, TfOH, toluene −30 °C, 2 h, 83 %; (**e**) 80 % AcOH (aq), 80 °C, 2 h, 87 %

methoxide. It was then desilylated using tetrabutylammonium fluoride [51] and finally completely deprotected by hydrogenolysis over Pearlman's catalyst [47] to afford pure trisaccharide **3** as its 3-aminopropyl glycoside in 49 % overall yield (Scheme 2). The presence of three anomeric protons in the ^{1}H NMR δ 5.13 (d, J = 4.0 Hz, H-1_C), 4.54 (d, J = 8.4 Hz, H-1_A), 4.47 (d, J = 7.6 Hz, H-1_B) and at δ 104.3 (C-1_B), 103.5 (C-1_A), 100.1 (C-1_C) in the ^{13}C NMR spectra confirmed the formation of compound **3** (Scheme 2).

In another set of experiments, disaccharide **19** was completely deacetylated followed by reprotection of the 3', 4'-positions with an isopropylideneacetal to give diol **20**. Reaction of the acceptor **20** with 1.2 equiv. of fucosyl donor **11** gave the 2'-fucosyl trisaccharide **22** as the major product (83 % yield). The acetonide group of a part of trisaccharide **22** was hydrolysed using 80 % AcOH to afford disaccharide **23** in 87 % yield. A portion of trisaccharide **23** was transformed to the target compound **4** in overall 58 % overall yield following a five-step sequence of reactions. Spectroscopic analysis of compound **4** unambiguously confirmed its formation [signals at δ 5.41 (d, J = 3.8 Hz, H-1_D), 4.56 (d, J = 8.1 Hz, H-1_B), 4.52 (d, J = 8.2, H-1_A) and 102.9 (C-1_B), 101.7 (C-1_A), 100.2 (C-1_D) in the ^{1}H and ^{13}C NMR spectra respectively.

On the other hand, for the synthesis of B Type II and A Type II antigens, first the trisaccharide **23** was selectively acetylated via the formation of an orthoester intermediate [52] to furnish the acceptor alcohol **24** in 79 % yield (Scheme 3). Galactosylation of **24** using thioglycoside donor **14** gave tetrasaccharide **25** in 72 % yield together with a minor quantity (~8 %) of its other isomer, which was separated by column chromatography.

Finally a five-step global deprotection sequence allowed conversion of compound **25** into target tetrasaccharide **5** in overall 55 % yield. The presence of four anomeric protons in the ^{1}H NMR δ 5.33 (d, J = 4.1 Hz, H-1_D), 5.25 (d, J = 3.4 Hz, H-1_E), 4.63 (d, J = 7.6 Hz, H-1_B), 4.50 (d, J = 7.6 Hz, H-1_A) and 101.6 (C-1_B), 100.5 (C-1_A), 99.1 (C-1_D), 93.5 (C-1_E) in the ^{13}C NMR spectra confirmed the formation of compound **5** (Scheme 3).

The A type II antigen was accessed by treatment of **24** with the trichloroacetimidate donor **15** [48] under standard conditions to give tetrasaccharide **26** in 77 % yield together with a minor quantity (~5 %) of its other isomer, which was separated by column chromatography (Scheme 3). Subsequent reduction–acetylation of the azide group using thiolacetic acid in pyridine followed by five-step complete deprotection sequence allowed conversion of compound **26** into target tetrasaccharide **6** in overall 53 % yield.

Synthesis of two xenoantigens (7 & 8)

To synthesise xenoantigens compound **7** and **8**, we decided to employ a model starting with disaccharide acceptor **27** [49] as outlined in Scheme 4. To start with, first the disaccharide acceptor **27** was fucosylated with donor **11** at the 3-position of the glucosamine ring to furnish the fully protected trisaccharide **29** in 69 % yield. This compound was then deacetylated to furnish trisaccharide diol acceptor **30**. Glycosylation of the trisaccharide acceptor **30** using thioglycoside donor **14** gave tetrasaccharide **31** in 69 % yield together with its other isomer in a minor quantity (8 %), which was separated by column chromatography.

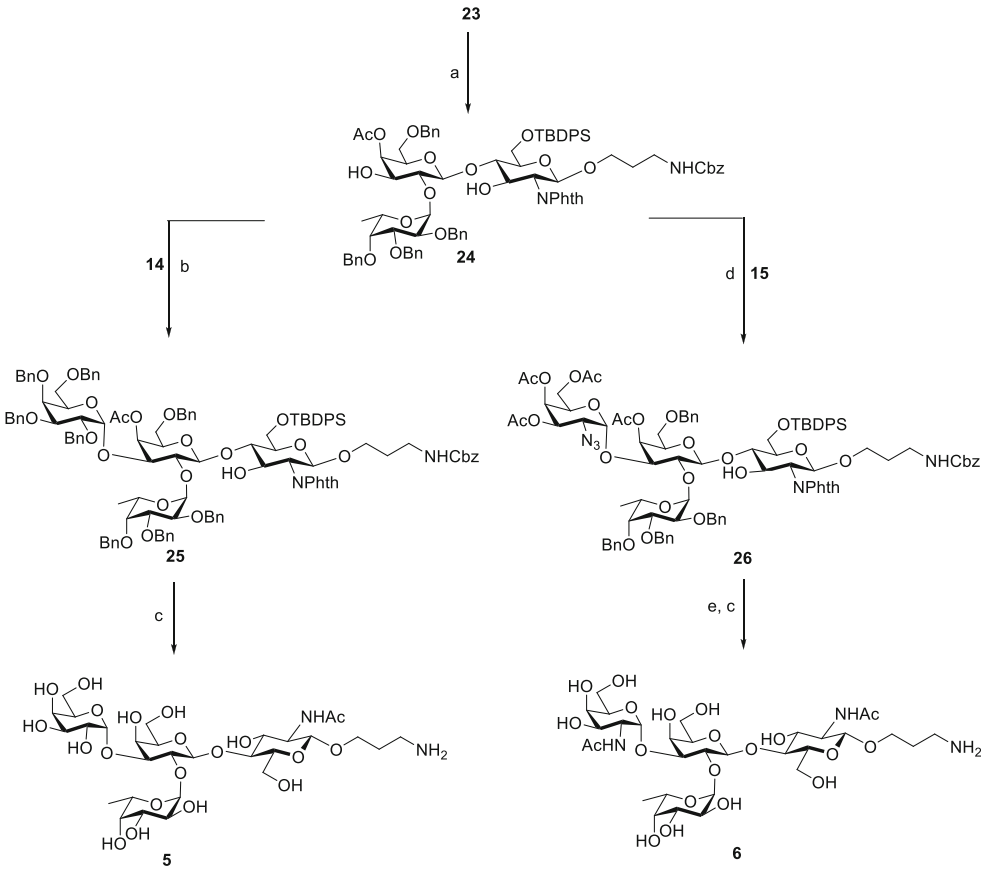
Finally, the five-step global deprotection sequence allowed conversion of compound **31** into target tetrasaccharide **7** in overall 51 % overall yield.

In another set of experiments, disaccharide **27** was completely deacetylated to furnished disaccharide triol acceptor **28** which was then glycosylated with thioglycoside donor **14** to afford trisaccharide **32** in 55 % yield together with its other isomer in a minor quantity (8 %), which was separated by column chromatography. A five-step deprotection sequence allowed conversion of compound **32** into trisaccharide **8**, which was isolated in 54 % overall yield.

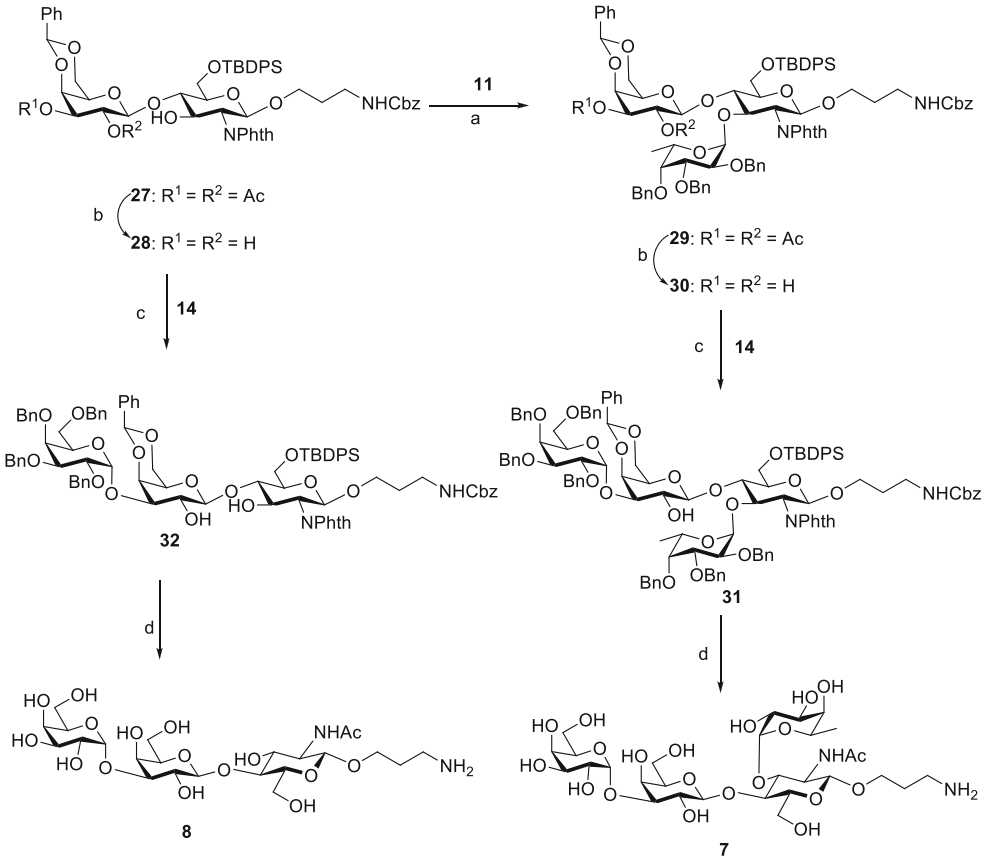
Then, the affinities of some of the synthesized oligosaccharides B Type II (**5**), A Type II (**6**) and αGal-Lewis X (**7**) were measured against El Tor CTB (100 μM) from *V. cholera*. using Isothermal Titration Calorimetry to determine a structure-activity relationship for the binding interactions of the synthesised oligosaccharides (see supporting information). Due to the low affinity binding of the compounds **5**, **6** & **7** with the E1 Tor CTB protein, relevant data were not obtained with ITC experiments. No significant heat of interactions were observed but still it cannot be concluded that inconclusive ITC experiments is a result of no binding interactions. Even weaker binding interactions may also produce such results. From the literature, it can be concluded that the presence of isoleucine-47 (E1 Tor CTB) may also lead to weaker binding interactions because of the steric hindrance caused between the ethyl moiety of isoleucine and the 2-NHAc/OH group of sugar residue E [35] in compounds **5**, **6** & **7**.

Conclusion

In summary, we carried out an efficient synthesis of human blood-group antigens and their analogues structures with a 3-aminopropyl aglycone. We employed simple thioglycoside and trichloacetimidate donors with model disaccharide acceptors obtaining the desired products in high yield. Since the monovalent interaction was inconclusive, we chose the CBz-protected aminopropyl group as an aglycone as it would allow subsequent conjugation of the oligosaccharides onto multivalent scaffolds in the glycocalyx for relevant affinities.



Scheme 3 Reagents and conditions: (**a**) (i) $(EtO)_3CH_3$, p-toluenesulfonic acid, DMF, 2 h; (ii) 80 % AcOH (aq), rt., 1 h, 79 % over two steps; (**b**) **14**, NIS, TfOH, MS4Å, CH_2Cl_2, −40 °C, 1 h, 72 %; (**c**) (i) $H_2NCH_2CH_2NH_2$, n-BuOH, 80 °C, 8 h (ii) Ac_2O, C_5H_5N, room temperature, 3 h, (iii) 0.1 M CH_3ONa, CH_3OH, room temperature, 3 h, (iv) TBAF, THF, room temperature, 6 h (v) H_2, 20 % $Pd(OH)_2$-C, CH_3OH, room temperature, 7 h; the five step deprotection sequence provided 55 % for **5**; (**d**) **15**, NIS, TMSOTf, MS4Å, CH_2Cl_2, −20 °C, 1 h, 77 %; (**e**) CH_3COSH, pyridine, then five step deprotection sequence provided 53 % for **6**



Scheme 4 Reagents and conditions: (**a**) donor **11**, NIS, TfOH, toluene, −15 °C, 7 h, 69 %; (**b**) 0.1 M CH_3ONa, CH_3OH, room temperature, 30 min, quantitative; (**c**) donor **14**, NIS, TMSOTf, CH_2Cl_2, MS 4 Å, −40 °C, 1 h, 69 % for **31** and 55 % for **32**, respectively; (**d**) (i) $H_2NCH_2CH_2NH_2$, n-BuOH, 80 °C, 8 h, (ii) Ac_2O, C_5H_5N,room temperature, 3 h, (iii) 0.1 M CH_3ONa, CH_3OH, room temperature, 3 h, (iv) TBAF, THF, room temperature, 6 h, (v) H_2, 20 % $Pd(OH)_2$-C, CH_3OH, room temperature, 7 h; the five step deprotection sequence provided trisaccharide **7** in 51 %, and tetrasaccharide **8** in 54 % yield, respectively

Experimental

General methods

All reactions were monitored by thin layer chromatography over silica gel-coated TLC plates. The spots on TLC were visualized by warming ceric sulfate [2 % $Ce(SO_4)_2$ in 5 % H_2SO_4 in EtOH]-sprayed plates on a hot plate. Silica gel 230–400 mesh was used for column chromatography. ^1H and ^{13}C NMR spectra were recorded on Brucker Avance 500 MHz and Bruker Avance 300 MHz instrument spectrometers using $CDCl_3$ and D_2O as solvents and TMS and CH_3OD as internal reference unless stated otherwise. Chemical shift values were expressed in δ ppm. Electrospray (ES+) ionisation mass spectra were obtained on a Bruker HCT-Ultra mass spectrometer, and high resolution ES+ were performed on a Bruker Daltonics MicroTOF mass spectrometer. IR spectra were recorded on Shimadzu Spectrophotometers. Optical rotations were determined on Autopol III polarimeter. Commercially available grades of organic solvents of adequate purity were used in all reactions.

3-Aminopropyl *O*-(α-D-galactopyranosyl)-(l→3)-[*O*-(α-L-fucopyranosyl)-(l→2)]-β-D-galactopyranoside (1)

To a solution of **16** (700 mg, 0.50 mmol) compound in methanol (25 mL) was added 20 % $Pd(OH)_2$-C (500 mg) and the reaction mixture was allowed to stir at room temperature under a positive pressure of H_2 for 24 h. The reaction mixture was filtered through a Celite® bed, the filtering bed was washed with CH_3OH (10 mL) and the combined filtrate was concentrated. The crude product was passed through a Sephadex® LH-20 column using CH_3OH-H_2O (4:1) as eluent to give pure trisaccharide **1** (163 mg, 60 %); White powder; $[\alpha]_D^{25}$ + 21 (*c* 1.0, H_2O); IR (KBr): 3427, 2927, 1497, 1253, 1129, 1053, 635 cm^{-1}; ^1H NMR (500 MHz, D_2O, CH_3OD internal standard at δ = 3.35 ppm): δ 5.27 (d, *J* = 3.5 Hz, 1 H, H-1_B), 5.25 (d, *J* = 3.3 Hz, 1 H, H-1_C), 4.59 (d, *J* = 7.3 Hz, 1 H, H-1_A), 4.38–4.36 (m, 1 H, H-5_B), 4.23–4.23 (m, 2 H, H-4_A, H-5_C), 4.02–3.97 (m, 3 H, H-3_A, H-2_C, H-4_C), 3.93–3.86 (m, 4 H, H-5_A, H-6_{abA}, H-4_C), 3.85–3.78 (m, 6 H, H-2_A, H-3_C, H-6_{abC}, −OCH_2-), 3.76–3.70 (m, 3 H, H-2_B, H-3_B, H-4_B), 3.17–3.14 (m, 2 H, NCH_2-), 2.03–1.99 (−CH_2-), 1.22 (d, *J* = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, D_2O, CH_3OD internal standard at δ = 49.5 ppm): δ 102.3 (C-1_A), 99.5 (C-1_B), 93.8 (C-1_C), 76.8 (C-3_A), 75.3 (C-2_A), 73.9 (C-4_B), 72.5 (C-5_A), 71.8 (C-5_C), 70.4 (C-3_C) 70.1 (C-3_B), 69.9 (C-4_C), 68.7 (C-2_C), 68.4 (C-2_B), 68.0 (−OCH_2-), 67.5 (C-5_B), 64.1 (C-4_A), 61.9 (C-6_C), 61.7 (C-6_A), 37.8 (NCH_2-), 27.6 (−CH_2-), 15.9 (CH_3); ESI-MS: $C_{21}H_{40}NO_{15}$ requires *m*/*z* 546.2320; found: *m*/*z* 546.2324 $[M + 1]^+$.

3-Aminopropyl *O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(l→3)- [*O*-(α-L-fucopyranosyl)-(l→2)]-β-D-galactopyranoside (2)

To a solution of compound **18** (600 mg, 0.49 mmol) in 0.1 M CH_3ONa in CH_3OH (10 mL) was allowed to stir at room temperature for 2 h and neutralized with Dowex-50 W X8 (H^+). The reaction mixture was filtered and evaporated to dryness and a solution of the crude mass in CH_3OH (15 mL) were added 20 % $Pd(OH)_2$-C (400 mg) and the reaction mixture was allowed to stir at room temperature under a positive pressure of H_2 for 24 h. The reaction mixture was filtered through a Celite®bed and washed with CH_3OH (10 mL) and concentrated. The crude product was passed through a Sephadex® LH-20 column using CH_3OH-H_2O (3:1) as eluent to give pure trisaccharide **2** (155 mg, 53 %); White powder; $[\alpha]_D^{25}$ + 29 (*c* 1.0, H_2O);); IR (KBr): 3020, 2462, 1753, 1467, 1116, 763, 669 cm^{-1}; ^1H NMR (500 MHz,D_2O, CH_3OD internal standard at δ = 3.35 ppm): δ 5.28 (d, *J* = 3.7 Hz, 1 H, H-1_B), 5.17 (d, *J* = 3.7 Hz, 1 H, H-1_C), 4.58 (d, *J* = 7.7 Hz, 1 H, H-1_A), 4.39–4.34 (m, 1 H, H-5_B), 4.28–4.21 (m, 3 H, H-4_A, H-2_C, H-5_C), 4.13–3.73 (m, 7 H, H-6_{abA}, H-2_B, H-4_B, H-3_C, H-4_C, −OCH_2-), 3.72–3.54 (m, 7 H, H-2_A, H-3_A, H-5_A, H-3_B, H-6_{abC}, −OCH_2-), 3.22–3.11 (m, 2 H, NCH_2-), 2.05 (s, 3 H, NHCOCH_3), 2.02–1.92 (m, 2 H, −CH_2-), 1.24 (d, *J* = 6.5 Hz, 3 H, CH_3);^{13}C NMR (125 MHz, D_2O, CH_3OD internal standard at δ = 49.5 ppm): δ 175.4 (NH*C*OCH_3), 102.2 (C-1_A), 99.4 (C-1_B), 92.0 (C-1_C), 75.5 (C-3_A), 74.9 (C-5_A), 73.1 (C-4_B), 71.8 (C-5_C), 71.1 (C-3_B), 69.8 (C-2_A), 68.6 (C-3_C), 67.8 (C-4_C), 67.4 (C-2_B),67.2 (−OCH_2-), 66.9 (C-5_B), 62.9 (C-4_A), 61.4 (C-6_C), 61.1 (C-6_A), 50.1 (C-2_C), 37.8 (NCH_2-), 27.6 (−CH_2-), 22.6 (NHCOCH_3), 15.9 (CH_3); ESI-MS: $C_{23}H_{43}N_2O_{15}$ requires *m*/*z* 587.2585; found: *m*/z 587.2589 $[M + 1]^+$.

3-Aminopropyl *O*-(β-D-galactopyranosyl)-(l→4)-[*O*-(α-L-fucopyranosyl)-(l→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside (3)

A solution of compound **21** (300 mg, 0.51 mmol) and ethylene diamine (0.2 mL) in n-butanol (5 mL) was heated at 90 °C for 8 h. The solvents were removed under reduced pressure and a solution of the crude product was re-dissolved in acetic anhydride-pyridine (2 mL; 1:1 *v*/*v*) and kept at room temperature for 3 h. The reaction mixture was evaporated and co-evaporated with toluene before treatment with 0.1 M NaOMe in MeOH (5 mL) for 3 h at room temperature. The solution was neutralized using Dowex-50 W X8 (H+) resin, filtered, and concentrated under reduced pressure. The crude mixture was redissolved in tetrabutylammonium fluoride in THF (1.0 M, 3 mL) and the reaction mixture was stirred at rt. for 6 h. The crude product was purified over SiO_2 using hexane–EtOAc (3:1) as eluent. Finally, a solution of the product in

CH_3OH (2 mL) was added 20 % $Pd(OH)_2$–C (150 mg) and the reaction mixture was allowed to stir at room temperature under a positive pressure of H_2 for 7 h. The mixture was filtered through a Celite®bed and evaporated to dryness before final purification on a Sephadex® LH-20 column using CH_3OH–H_2O (8:1 *v*/*v*) as eluent to give pure compound **3** (114 mg, 49 %). White foam; $[\alpha]_D^{25}$−71.2 (*c* 1.0, H_2O); IR: 3446, 2936, 2312, 1738, 1449, 1327, 1030, 679 cm^{-1}; ^1H NMR (500 MHz, D_2O): δ 5.13 (d, *J* = 4.0 Hz, 1 H, H-1_C), 4.85–4.83 (m, 1 H, H-5_C), 4.54 (d, *J* = 8.4 Hz, 1 H, H-1_A), 4.47 (d, *J* = 7.6 Hz, 1 H, H-1_B), 3.96–3.93 (dd, *J* = 12.4, 1.2 Hz, 2 H, H-6_{abA}), 3.88–3.78 (m, 5 H, H-2_A, H-3_A, H-4_A, H-4_B, H-3_C), 3.73–3.72 (m, 1 H, H-4_C), 3.67–3.62 (m, 5 H, H-2_C, H-6_{abB}, −OC*H*$_2$-), 3.60–3.52 (m, 3 H, H-2_B, H-3_B, H-5_B), 3.45–4.41 (m, 1 H, H-5_A), 3.03–2.99 (m, 2 H, NC*H*$_2$-), 1.97 (s, 3 H, NHCOC*H*$_3$), 1.89–1.86 (m, 2 H,-C*H*$_2$-), 1.11 (d, *J* = 6.6 Hz, 3 H, C*H*$_3$); ^{13}C NMR (75 MHz, D_2O, CH_3OD internal standard at δ = 49.5 ppm): δ 176.8 (NH*C*OCH$_3$), 104.3 (C-1_B), 103.5 (C-1_A), 100.1 (C-1_C), 77.8 (C-5_A), 77.5 (C-3_A), 77.1 (C-5_B), 75.8 (C-4_A), 74.8 (C-3_B), 74.4 (C-4_C), 73.6 (C-2_B), 71.4 (C-3_C), 70.6 (C-4_B), 70.5 (−O*C*H$_2$-), 70.1 (C-2_C), 69.3 (C-5_C), 63.5 (C-6_B), 62.1 (C-6_A), 58.3 (C-2_A), 40.1 (N*C*H$_2$-), 29.2 (−*C*H$_2$-), 24.4 (NHCO*C*H$_3$), 17.8 (*C*H$_3$); ESI-MS: $C_{23}H_{43}N_2O_{15}$ requires *m*/z 587.2585; found: *m*/*z* 587.2586 $[M + H]^+$. Compared with the physical data and checked the accuracy of synthesized compound (See supporting information) [30].

3-Aminopropyl *O*-(α-L-fucopyranosyl)-(l→2)-*O*-(β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (4)

Prepared from **23** (300 mg, 0.51 mmol), ethylene diamine (0.2 mL) in n-butanol (5 mL), acetic anhydride-pyridine (2 mL; 1:1 *v*/*v*), 0.1 M CH_3ONa in Methanol (5 mL), tetrabutylammonium fluoride in THF (1.0 M, 1 mL), 20 % $Pd(OH)_2$–C (150 mg) as described for **3**, to afford pure compound **4** (121 mg, 58 %). Glass; $[\alpha]_D^{25}$−22.6 (*c* 1.0, H_2O); IR:3445 2936, 1590, 1546, 1377, 1030, 679 cm^{-1}; ^1H NMR (500 MHz, D_2O, CH_3OD internal standard at δ = 3.35 ppm): δ 5.41 (d, *J* = 3.8 Hz,1 H, H-1_D), 4.56 (d, *J* = 8.1 Hz, 1 H, H-1_B), 4.52 (d, *J* = 8.2, 1 H, H-1_A), 4.25–4.22 (m, 1 H, H-5_D), 4.04–4.02 (m, 2 H, H-6_{abA}), 3.91–3.82 (m, 3 H,H-2_A, H-3_B, H-4_B), 3.81–3.79 (m, 6 H, H-3_A, H-4_A, H-6_{abB}, H-2_D, H-4_D), 3.78–3.67 (m, 5 H, H-2_B, H-5_B, H-3_D, −OC*H*$_2$-), 3.51–3.48 (m, 1 H, H-5_A), 3.12–3.08 (m, 2 H, NC*H*$_2$-), 2.07 (s, 3 H, NHCOC*H*$_3$), 1.98–1.92 (m, 2 H, −C*H*$_2$-), 1.25 (d, *J* = 6.6 Hz, 3 H, C*H*$_3$); ^{13}C NMR (75 MHz, D_2O, CH_3OD internal standard at δ = 49.5 ppm): δ 175.0 (NH*C*OCH$_3$), 102.9 (C-1_B), 101.7 (C-1_A), 100.2 (C-1_D), 77.3 (C-2_B), 76.3 (2 C, C-4_A, C-5_B), 74.5 (C-5_A), 73.9 (C-3_B), 73.1 (2 C, C-3_A, C-4_D), 71.1 (C-4_B), 70.4 (C-3_D), 69.5 (C-2_D), 69.8 (−O*C*H$_2$-), 68.6 (C-5_D), 61.9 (C-6_B), 61.2 (C-6_A), 56.8 (C-2_A), 38.9 (N*C*H$_2$-), 27.9 (−*C*H$_2$-), 23.1 (NHCO*C*H$_3$), 16.6 (*C*H$_3$); ESI-MS: $C_{23}H_{43}N_2O_{15}$ requires *m*/*z* 587.2658; found: *m*/*z* 587.2669 $[M + H]^+$.

3-Aminopropyl *O*-(α-D-galactopyranosyl)-(l→3)-[*O*-(α-L-fucopyranosyl)-(l→2)]-*O*-(β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (5)

Prepared from **25** (300 mg, 0.15 mmol), ethylene diamine (0.3 mL) in n-butanol (6 mL), acetic anhydride-pyridine (4 mL; 1:1 *v*/*v*), 0.1 M CH_3ONa in Methanol (5 mL), tetrabutylammonium fluoride in THF (1.0 M, 3 mL), 20 % $Pd(OH)_2$–C (150 mg) as described for **3**, to afford pure compound **5** (62 mg, 55 %); Glass; $[\alpha]_D^{25}$ + 29.2 (*c* 1.0, H_2O); IR: 3440, 2926, 2372, 1429, 1377, 1030, 679 cm^{-1}; ^1H NMR (500 MHz, D_2O): δ 5.33 (d, *J* = 4.1 Hz, 1 H, H-1_D), 5.25 (d, *J* = 3.4 Hz, 1 H, H-1_E), 4.63 (d, *J* = 7.6 Hz, 1 H, H-1_B), 4.50 (d, *J* = 7.6 Hz, 1 H, H-1_A), 4.25–4.20 (m, 2 H, H-5_D, H-5_E), 4.12 (dd, *J* = 8.6, 1.2 Hz, 1 H, H-2_B), 3.98–3.90 (m, 5 H, H-3_B, H-4_B, H-4_E, H-6_{abA}), 3.87–3.81 (m, 4 H, H-6_{abB}, H-2_E, H-3_E), 3.75–3.57 (m, 11 H, H-2_A, H-3_A, H-4_A, H-5_B, H-2_D, H-3_D, H-4_D H-6_{abE}, −OC*H*$_2$-) 3.49–3.46 (m, 1 H, H-5_A), 3.11–3.08 (m, 2 H, NC*H*$_2$-), 2.06 (s, 3 H, NHCOC*H*$_3$), 1.99–1.93 (m, 2 H, −C*H*$_2$-), 1.24 (d, *J* = 6.6 Hz, 3 H, C*H*$_3$); ^{13}C NMR (75 MHz, D_2O, CH_3OD internal standard at δ = 49.5 ppm): δ 175.1 (NH*C*OCH$_3$), 101.6 (C-1_B), 100.5 (C-1_A), 99.1 (C-1_D), 93.5 (C-1_E), 76.6 (C-2_B), 75.6 (C-2_D), 75.3 (C-2_E), 72.9 (C-3_A), 72.6 (C-3_B), 72.1 (C-3_D), 71.5 (C-3_E),70.4 (C-4_A), 69.9 (C-4_B), 69.7 (C-4_D), 68.4 (C-4_E), 68.3 (C-5_A), 68.1 (−O*C*H$_2$-), 67.2 (2 C, C-5_B, C-5_D), 63.9 (C-5_E), 61.7 (C-6_A), 61.5 (C-6_B), 60.5 (C-6_E), 55.7 (C-2_A), 38.0 (N*C*H$_2$-), 27.1 (−*C*H$_2$-), 22.6 (NHCO*C*H$_3$), 15.6 (*C*H$_3$); ESI-MS: $C_{29}H_{53}N_2O_{20}$ requires *m*/*z* 749.3186; found: *m*/*z* 749.3204 $[M + H]^+$.

3-Aminopropyl *O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(l→3)-[*O*-(α-L-fucopyranosyl)-(l→2)]-*O*-(β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (6)

A solution of tetrasaccharide **26** (355 mg, 0.201 mmol) in pyridine (2 mL) was treated with AcSH (4 mL), and the solution was stirred (12 h). The mixture was filtered, concentrated and a solution of the crude product was re-dissolved in n-butanol (5 mL) and ethylene diamine (0.4 mL) and heated at 90 °C for 8 h. The solvents were removed under reduced pressure and a solution of the crude product was re-dissolved in acetic anhydride-pyridine (6 mL; 1:1 *v*/*v*) and kept at room temperature for 3 h. The reaction mixture was evaporated and co-evaporated with toluene before treatment with 0.1 M NaOMe in MeOH (8 mL) for 3 h at room temperature. The solution was neutralized using Dowex-50 W X8

(H+) resin, filtered, and concentrated under reduced pressure. The crude mixture was redissolved in tetrabutylammonium fluoride in THF (1.0 M, 4 mL) and the reaction mixture was stirred at rt. for 6 h. The crude product was purified over SiO_2 using hexane–EtOAc (3:1) as eluent. Finally, a solution of the product in CH_3OH (2 mL) was added 20 % $Pd(OH)_2$–C (200 mg) and the reaction mixture was allowed to stir at room temperature under a positive pressure of H_2 for 7 h. The mixture was filtered through a Celite® bed and evaporated to dryness before final purification on a Sephadex® LH-20 column using CH_3OH–H_2O (8:1 *v*/*v*) as eluent to give pure compound **6** (85 mg, 53 %). Glass; $[\alpha]_D^{25}$ −9.2 (*c* 1.0, H_2O); IR: 3430, 2906, 2472, 1629, 1357, 1010, 677 cm^{-1}; ^1H NMR (500 MHz, D_2O): δ 5.30 (d, *J* = 4.1 Hz, 1 H, H-1_D), 5.19 (d, *J* = 3.7 Hz, 1 H, H-1_E), 4.61 (d, *J* = 7.6 Hz, 1 H, H-1_B), 4.51 (d, *J* = 7.8 Hz, 1 H, H-1_A), 4.34–4.32 (m, 1 H, H-5_D), 4.26–4.20 (m, 3 H, H-2_E, H-5_E, H-4_B), 4.11–4.09 (m, 3 H, H-2_B, H-3_B, H-4_E,), 4.07–3.80 (m, 7 H, H-2_A, H-6_{abA}, H-6_{abB}, H-2_D, H-3_E), 3.78–3.73 (m, 4 H, H-6_{abE}, −OCH_2-), 3.69–3.56 (m, 6 H, H-3_A, H-4_A, H-5_A, H-5_B, H-3_D, H-4_D), 3.09–3.05 (m, 2 H, NCH_2-), 2.09 (s, 3 H, NHCOCH_3), 2.01 (s, 3 H, NHCOCH_3), 1.90–1.85 (m, 2 H, −CH2-), 1.19 (d, *J* = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, D_2O, CH_3OD internal standard at δ = 49.5 ppm): δ 175.0 (NH*C*OCH$_3$), 174.9 (NH*C*OCH$_3$), 102.3 (C-1_B), 101.6 (C-1_A), 98.9 (C-1_D), 93.8 (C-1_E), 77.1 (C-5_E), 75.3 (C-5_D), 74.9 (C-2_D), 74.5 (C-3_A), 73.0 (C-4_D), 71.6 (C-4_E), 71.3 (C-4_B), 69.0 (C-4_A), 68.8 (C-3_D), 68.6 (C-3_E), 67.9 (C-3_B), 67.7 (C-5_A), 67.5 (C-5_B), 66.2 (C-2_B), 62.9 (C-6_E), 61.7 (C-6_B), 61.5 (C-6_A), 60.2 (−O*C*H$_2$-), 56.3 (C-2_A), 49.7 (C-2_E), 38.0 (N*C*H$_2$-), 27.4 (−*C*H$_2$-), 22.6 (NHCO*C*H$_3$), 22.5 (NHCO*C*-H$_3$), 15.7 (*C*H$_3$); ESI-MS: $C_{31}H_{56}N_3O_{20}$ requires *m*/*z* 790.3379; found: *m*/*z* 790.3386 $[M + H]^+$.

3-Aminopropyl *O*-(α-D-galactopyranosyl)-(l→3)-*O*-(β-D-galactopyranosyl)-(1→4)-[*O*-(α-L-fucopyranosyl)-(l→3)]-2-acetamido-2-deoxy-β-D-glucopyranoside (7)

Prepared from **31** (500 mg, 0.31 mmol),ethylene diamine (0.4 mL) in n-butanol (6 mL), acetic anhydride-pyridine (4 mL; 1:1 *v*/*v*), 0.1 M CH_3ONa in Methanol (5 mL), tetrabutylammonium fluoride in THF (1.0 M, 3 mL), 20 % $Pd(OH)_2$–C (250 mg) as described for **3**, to afford pure compound **7** (100 mg, 51 %); Glass; $[\alpha]_D^{25}$−29.2 (*c* 1.0, H_2O); IR: 3442, 2925, 2361, 1516, 1429, 679 cm^{-1};^1H NMR (500 MHz, D_2O, CH_3OD internal standard at δ = 3.35 ppm): δ 5.11 (d, *J* = 3.9 Hz, 1 H, H-1_C), 5.09 (d, *J* = 3.7 Hz, 1 H, H-1_E), 4.77–4.76 (m, 1 H, H-5_C), 4.51 (d, *J* = 7.8 Hz, 1 H, H-1_B), 4.50 (d, *J* = 7.6 Hz, 1 H, H-1_A), 4.17–4.11 (m, 2 H, H-5_E, H-4_B), 3.99–3.87 (m, 6 H, H-6_{abA}, H-2_B, H-3_B, H-4_E, H-2_E), 3.86–3.80 (m, 4 H, H-6_{abB}, H-3_E, H-2_C), 3.75–3.64 (m, 8 H, H-2_A, H-4_A, H-3_C, H-4_C, H-6_{abE}, −OCH_2-), 3.57–3.55 (m, 3 H, H-3_A, H-5_A,H-5_B), 3.03–2.97 (m, 2 H, NCH_2-), 2.01 (s, 3 H, NHCOCH_3), 1.90–1.86 (m, 2 H, −CH2-), 1.16 (d, *J* = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, D_2O, CH_3OD internal standard at δ = 49.5 ppm): δ 175.2 (NH*C*OCH$_3$), 103.2 (C-1_B), 102.0 (C-1_A), 99.2 (C-1_C), 96.0 (C-1_E), 78.1 (C-3_B), 77.7 (C-3_A), 75.6 (C-5_B), 75.2 (C-5_A), 73.9 (C-4_A), 72.6 (C-4_C), 71.4 (C-5_E), 70.0 (C-2_B), 69.7 (2 C, C-3_C, C-3_E), 68.6 (C-4_E), 68.4 (C-2_E), 68.3 (−O*C*H$_2$-), 67.1 (2 C, C-2_C, C-5_C), 65.9 (C-4_B), 61.8 (C-6_B), 61.4 (C-6_E), 60.1 (C-6_A), 56.2 (C-2_A), 38.1 (N*C*H$_2$-), 27.6 (−*C*H$_2$-), 22.7 (NHCO*C*H$_3$), 15.8 (*C*H$_3$); ESI-MS: $C_{29}H_{53}N_2O_{20}$ requires *m*/*z* 749.3186; found: *m*/*z* 749.3219 $[M + H]^+$. Compared with the physical data and checked the accuracy of synthesized compound (See supporting information) [32].

3-Aminopropyl *O*-(α-D-galactopyranosyl)-(l→3)-*O*-(β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranoside (8)

Prepared from **32** (300 mg, 0.20 mmol), ethylene diamine (0.2 mL) in n-butanol (5 mL), acetic anhydride-pyridine (2 mL; 1:1 *v*/*v*), 0.1 M CH_3ONa in Methanol (5 mL), tetrabutylammonium fluoride in THF (1.0 M, 1 mL), 20 % $Pd(OH)_2$–C (150 mg) as described for **3**, to afford pure compound **8** (65 mg, 54 %); Glass; $[\alpha]_D^{25}$−21.7 (*c* 1.0, H_2O); IR: 3446, 2915, 2461, 1816, 1419, 699 cm^{-1};^1H NMR (500 MHz, D_2O): δ 5.10 (d, *J* = 3.7 Hz, 1 H, H-1_E), 4.76 (d, *J* = 7.6 Hz, 1 H, H-1_B), 4.49 (d, *J* = 7.8 Hz, 1 H, H-1_A), 4.18–4.12 (m, 2 H, H-5_E, H-4_B), 3.92–3.89 (m, 3 H, H-6_{aA}, H-2_B, H-3_B), 3.87–3.81 (m, 3 H, H-6bA, H-6_{aB}, H-4_E), 3.80–3.76 (m, 3 H, H-6_{bB}, H-2_E, H-3_E), 3.75–3.65 (m, 6 H, H-2_A, H-4_A, H-6_{abE}, −OCH_2-), 3.57–3.52 (m, 3 H, H-3_A, H-5_A, H-5_B), 3.15–3.10 (m, 2 H, NCH_2-), 1.99 (s, 3 H, NHCOCH_3), 1.80–1.76 (m, 2 H, −CH2-); ^{13}C NMR (75 MHz, D_2O, CH_3OD internal standard at δ = 49.5 ppm): δ 175.1 (NH*C*OCH$_3$), 103.9 (C-1_B), 102.2 (C-1_A), 96.5 (C-1_E), 78.3 (C-4_A), 77.2 (C-3_B), 76.1 (C-5_B), 73.9 (C-5_A), 72.8 (C-3_A), 72.1 (C-5_E), 70.1 (2 C, C-2_B, C-3_E), 69.9 (C-4_E), 69.3 (−O*C*H$_2$-), 67.8 (C-2_E), 66.1 (C-4_B), 63.3 (C-6_B), 61.3 (C-6_E), 61.1 (C-6_A), 56.9 (C-2_A), 38.5 (N*C*H$_2$-), 27.7 (−*C*H2-), 22.8 (NHCO*C*H$_3$); ESI-MS: $C_{23}H_{43}N_2O_{16}$ requires *m*/*z* 603.2534; found: *m*/*z* 603.2562 $[M + H]^+$.]$^+$. Compared with the physical data and checked the accuracy of synthesized compound (See supporting information) [32].

3-(Benzyloxycarbonylamino)propyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside (10)

A solution of *diol* **9** (5.0 g, 10.9 mmol) and pyridine (945 μL, 11.89 mmol) in dry CH_2Cl_2 (70 mL) was allowed to stir at −40 °C. Benzoyl chloride (1.66 ml, 11.98 mmol) was added and the reaction mixture, allowed to stir at same temperature for 1 h. When TLC showed complete consumption of the starting material, the reaction mixture was diluted with

CH_2Cl_2 (100 mL) and washed with 1 M HCl, satd. $NaHCO_3$ and water,. The solution was then dried (Na_2SO_4) and evaporated. The crude product was purified over SiO_2 using hexane −EtOAc (4.5:1) as eluent to furnish pure *benzoate* **10** (5.4 g, 88 %); $[\alpha]_D^{25}$−35 (*c* 1.5, $CHCl_3$); IR: 3428, 2831, 1725, 1552, 1370, 1276, 1013, 1045, 822, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.36–8.26 (m, 2 H, Ar-H), 7.45–7.24 (m, 13 H, Ar-H), 5.48 (s, 1 H, PhC*H*), 5.33–5.29 (m, 1 H, N*H*Cbz), 5.12 (dd, *J* = 3.7, 10.1 Hz, 1 H, H-3_A), 5.05 (brs, 2 H, COOCH_2Ph), 4.44 (d, *J* = 3.5 Hz, 1 H, H-4_A), 4.36 (d, *J* = 7.7 Hz, 1 H, H-1_A), 4.28 (dd, *J* = 1.2, 12.4 Hz, 1 H, H-6_{aA}), 4.16–4.08 (m, 1 H, −OCH_2-), 4.01 (dd, *J* = 1.1, 12.5 Hz, 1 H, H-6_{bA}), 3.99–3.94 (m, 1 H, −OCH_2-), 3.58–3.55 (m, 1 H, H-2_A), 3.47 (brs, 1 H, H-5_A), 3.44–3.34 (m, 1 H, NCH_2-), 3.24–3.16(m, 1 H, NCH_2-), 1.80–1.68 (m, 2 H, −CH_2-); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.6 (*C*OPh), 156.9 (NH*C*OOCH$_2$Ph), 137.9–126.2 (Ar-C), 103.2 (C-1_A), 100.8 (Ph*C*H), 74.5 (C-3_A), 73.7 (C-4_A), 69.1 (−O*C*H$_2$-), 68.6 (C-2_A), 66.9 (C-6_A), 66.7 (COO*C*H$_2$Ph), 66.5 (C-5_A), 37.9 (N*C*H$_2$-), 29.6 (−*C*H$_2$-); ESI-MS: $C_{31}H_{33}NNaO_9$ requires *m*/*z* 586.2155; found: *m*/*z* 586.2161 $[M + Na]^+$.

3-(Benzyloxycarbonylamino)propyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 2)-3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside (12)

To a solution of compound **10** (6 g, 10.66 mmol) and thioglycoside donor **11** (6.1 g, 12.79 mmol) in toluene (90 mL) was added MS-4 Å (6 g) and the reaction mixture was allowed to stir at room temperature under argon for 30 min. The reaction mixture was cooled to −10 °C and *N*-iodosuccinimide (3.5 g, 15.34 mmol) and TfOH (90 μL) were added to it. After stirring the reaction mixture at the same temperature for 2 h, it was filtered through a Celite® bed and washed with CH_2Cl_2 (200 mL). The organic layer was washed with 5 % $Na_2S_2O_3$ (150 mL), satd. $NaHCO_3$ (150 mL) and water (100 mL) in succession, dried (Na_2SO_4) and evaporated to dryness. The crude mass was purified over SiO_2 using hexane−EtOAc (4:1) as eluent to furnish pure **12** (8.45 g, 81 %); $[\alpha]_D^{25}$ –14.2 (*c* 1.5, $CHCl_3$); IR: 2835, 1618, 1614, 1407, 1125, 1057, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.14–8.12 (m, 2 H, Ar-H), 7.49–7.12 (m, 28 H, Ar-H), 5.47 (s, 1 H, PhC*H*), 5.41 (d, *J* = 3.6 Hz, 1 H, H-1_B), 5.34 (dd, *J* = 10.1, 3.6 Hz, 1 H, H-3_A), 5.33–5.31 (m, 1 H, N*H*Cbz), 5.06 (brs, 2 H, COOCH_2Ph), 4.90 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.57 (d, *J* = 7.7 Hz, 1 H, H-1_A), 4.58–4.53 (m, 3 H, PhCH_2), 4.48 (d, *J* = 3.4 Hz, 1 H, H-4_A), 4.38–4.22 (m, 5 H, PhCH_2, H-2_A, H-6_{aA}, H-5_B), 4.04–3.91 (m, 3 H, H-6_{bA}, H-2_B, −OCH_2-), 3.84–3.81 (m, 1 H, H-3_B), 3.66 (brs, 1 H, H-5_A), 3.59–3.55 (m, 1 H, −OCH_2-), 3.52 (brs, 1 H, H-4_B), 3.28–3.23 (m, 2 H, NCH_2-), 1.81–1.68 (m, 2 H, −CH_2-), 1.11 (d, *J* = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0 (*C*OPh), 156.6 (*C*OOCH$_2$Ph), 139.1–126.3(Ar-C), 102.1 (C-1_A), 100.8 (Ph*C*H), 97.5 (C-1_B), 79.3 (C-3_B), 77.9 (C-2_A), 76.3 (C-2_B), 75.5 (C-4_A), 74.9 (Ph*C*H$_2$), 73.7 (C-4_B), 73.1 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 71.8 (C-3_A), 69.0 (−O*C*H$_2$-), 67.0 (C-5_B), 66.5 (COO*C*H$_2$Ph), 66.4 (C-6_A), 66.3(C-5_A), 37.9 (N*C*H$_2$-), 29.5 (−*C*H$_2$-) 16.7 (*C*H$_3$); ESI-MS: $C_{58}H_{61}NNaO_{13}$ requires *m*/*z* 1002.4143; found: *m*/*z* 1002.4149 $[M + Na]^+$.

3-(Benzyloxycarbonylamino)propyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 2)-4,6-*O*-benzylidene-β-D-galactopyranoside (13)

A solution of compound **12** (7.5 g, 7.67 mmol) in 0.1 M CH_3ONa (130 mL) was allowed to stir at room temperature for 2 h and neutralized with Amberlite-IR 120 (H^+) resin. The reaction mixture was filtered and evaporated to dryness to give the crude product, which was passed through a short column of SiO_2 using hexane–EtOAc (1:1) as eluent to give pure **13** (6.2 g, 92 %); colorless syrup; $[\alpha]_D^{25}$ –22.7 (*c* 1.5, $CHCl_3$); IR (neat): 2903, 2272, 2042, 1861, 1671,1455, 1215, 988, 611 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.53–7.50 (m, 2 H, Ar-H), 7.35–7.18 (m, 23 H, Ar-H), 5.54 (s, 1 H, PhC*H*), 5.41–5.37 (m, 1 H, N*H*Cbz), 5.13 (d, *J* = 3.6 Hz, 1 H, H-1_B), 5.05 (brs, 2 H, COOCH_2Ph), 4.95 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 4.79–4.72 (dd, *J* = 11.6 Hz, 4 H, PhCH_2), 4.64 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 4.34 (d, *J* = 7.7 Hz, 1 H, H-1_A), 4.27–4.26 (m, 1 H, H-6_{aA}), 4.18 (d, *J* = 3.3 Hz, 1 H, H-4_A), 4.09–4.01 (m, 3 H, H-2_A, H-6_{bA}, H-5_B), 3.98–3.90 (m, 2 H, H-2_B, −OCH_2-), 3.82–3.76 (m, 2 H, H-3_A, H-3_B), 3.66 (brs, 1 H, H-5_A), 3.58–3.56 (m, 1 H, −OCH_2-), 3.38 (brs, 1 H, H-4_B), 3.30–3.25 (m, 2 H, NCH_2-), 1.81–1.75 (m, 2 H, −CH_2-), 1.10 (d, *J* = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.7 (*C*OOCH$_2$Ph), 138.6–126.6 (Ar-C), 101.9 (C-1_A), 101.5 (Ph*C*H), 99.8 (C-1_B), 79.7 (C-3_B), 78.5 (C-2_A), 77.7 (C-2_B), 77.1 (C-4_A), 75.6 (C-3_A), 75.0 (Ph*C*H$_2$), 74.1 (Ph*C*H$_2$), 73.2 (C-4_B), 73.0 (Ph*C*H$_2$), 69.3 (−O*C*H$_2$-), 67.5 (C-5_B), 66.7 (C-5_A), 66.5 (COO*C*H$_2$Ph), 66.4 (C-6_A), 38.0 (N*C*H$_2$-), 29.5 (−*C*H$_2$-), 16.9 (*C*H$_3$); ESI-MS: $C_{51}H_{57}NNaO_{12}$ requires *m*/*z* 898.3881; found: *m*/*z* 898.3891$[M + Na]^+$.

3-(Benzyloxycarbonylamino)propyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-(l → 3)-[*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 2)-4,6-*O*-benzylidene-β-D-galactopyranoside (16)

To a solution of compound **13** (1.5 g, 1.7 mmol) and thioglycoside donor **14** (1.4 g, 2.23 mmol) in CH_2Cl_2 (30 mL) was added MS-4 Å (800 mg) and the reaction mixture was allowed to stir at room temperature under N_2 for 30 min. The reaction mixture was cooled to −40 °C and *N*-iodosuccinimide (602 mg, 2.67 mmol) and TfOH (30 μL) were added to it. After stirring the reaction mixture at the same

temperature for 1 h, it was filtered through a Celite® bed and washed with CH_2Cl_2 (100 mL). The organic layer was washed with 5 % $Na_2S_2O_3$ (100 mL), satd. $NaHCO_3$ (100 mL) and water (100 mL) in succession, dried (Na_2SO_4) and evaporated to dryness. The crude mass was purified over SiO_2 using hexane−EtOAc (5:1) as eluent to furnish pure **16** (1.6 g, 67 %); $[\alpha]_D^{25}$ –16.3 (*c* 1.5, $CHCl_3$); IR: 2830, 2708, 1852, 1619, 1407, 1393, 1216, 1059, 909, 697, cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.54–7.01 (m, 45 H, Ar-H), 5.47 (d, *J* = 3.4 Hz, 1 H, H-1_B), 5.42 (s, 1 H, PhC*H*), 5.34 (d, *J* = 3.6 Hz, 1 H, H-1_C), 5.33–5.30 (m, 1 H, N*H*Cbz), 5.09–5.02 (m, 2 H, COOCH_2Ph), 4.88 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.83 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.76 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 4.66 (d, *J* = 11.7 Hz, 2 H, PhCH_2), 4.63(d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.59 (d, *J* = 11.6 Hz, 2 H, PhCH_2), 4.48(dd, *J* = 11.6 Hz, 2 H, PhCH_2), 4.44–4.36 (m, 4 H, PhCH_2), 4.32 (d, *J* = 3.1 Hz, 1 H, H-4_A), 4.26 (d, *J* = 7.7 Hz, 1 H, H-1_A), 4.22–4.19 (m, 1 H, H-5_B), 4.09–4.05 (m, 1 H, H-2_C), 4.00–3.84 (m,8 H, H-2_A, H-5_A, H-6_{abA}, H-3_B, H-3_C, H-4_C, H-6_{aC},), 3.61 (brs, 1 H, H-5_C), 3.55–3.48 (m, 4 H, H-2_B, H-4_B, H-6bC, −OCH_2-), 3.27–3.23 (m, 2 H, NCH_2-), 3.18–3.14 (m, 1 H, −OCH_2-), 3.09 (brs, 1 H, H-3_A), 1.81–1.66 (m, 2 H, −CH_2-), 1.14 (d, *J* = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7 (*C*OOCH$_2$Ph), 139.2–126.5 (Ar-C), 102.3 (C-1_A), 101.3 (Ph*C*H), 97.9 (C-1_B), 92.6 (C-1_C), 80.0 (C-3_C), 78.4(C-3_B), 78.1 (C-2_A), 76.8 (C-2_B), 76.6 (C-2_C), 75.5 (C-4_C), 75.4 (C-4_A), 75.0 (2 C, C-4_B, C-3_C), 74.6 (Ph*C*H$_2$), 73.9 (Ph*C*H$_2$), 73.3 (Ph*C*H$_2$), 73.1 (Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.8(Ph*C*H$_2$), 72.0 (C-3_A),71.5 (Ph*C*H$_2$), 70.3 (C-5_C), 70.1 (−O*C*H$_2$-), 69.5 (C-6_A), 66.6 (C-5_B), 66.6 (C-6_C), 66.3 (COO*C*H$_2$Ph), 66.2 (C-5_A), 37.9 (N*C*H$_2$-), 29.8 (−*C*H$_2$-), 16.9 (*C*H$_3$);ESI-MS: $C_{85}H_{91}NlNaO_{17}$ requires *m*/*z* 1420.6287; found: *m*/*z* 1420.6295 $[M + Na]^+$.

3-(Benzyloxycarbonylamino)propyl *O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-(l → 3)-[*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 2)-4,6-*O*-benzylidene-β-D-galactopyranoside (17)

To a solution of compound **13** (2.4 g, 2.74 mmol) and **15** (1.7 g, 3.57 mmol) in dry CH_2Cl_2 (50 mL) was added MS-4 Å (2 g) and the reaction mixture was allowed to stir under N_2 at room temperature for 3 h. and the reaction mixture was cooled to −20 °C. To the cooled reaction mixture was added TMSOTf (50 μL) and the reaction mixture was allowed to stir at same temperature for 1 h. when TLC showed complete consumption of the acceptor **21** then the reaction mixture was diluted with CH_2Cl_2 (100 mL) and the reaction mixture was filtered through a Celite® bed and the organic layer was washed with satd. $NaHCO_3$ and water, dried (Na_2SO_4) and evaporated to dryness. The crude product was purified over SiO_2 using hexane−EtOAc (5:1) as eluent to furnish pure compound **17** (2.30 g, 70 %); yellow oil; $[\alpha]_D^{25}$ + 21.9 (*c* 1.5, $CHCl_3$); IR (neat): 2859,2108, 1852, 1619, 1507, 1363, 1216, 1059, 909 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.56–7.54 (m, 2 H, Ar-H), 7.44–7.41 (m, 2 H, Ar-H), 7.40–7.22 (m, 21 H, Ar-H), 5.54 (s, 1 H, PhC*H*), 5.34 (d, *J* = 3.4 Hz, 1 H, H-1_B), 5.33–5.31 (m, 1 H, H-3_C), 5.30 (d, *J* = 3.6 Hz, 1 H, H-1_C), 5.22 (d, *J* = 2.8 Hz, 1 H, H-4_C), 5.07 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 5.06–5.03 (m, 2 H, COOCH_2Ph), 4.92 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 4.82 (dd, *J* = 11.6 Hz, 2 H, PhCH_2), 4.73 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.61 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 4.39 (d, *J* = 7.7 Hz, 1 H, H-1_A), 4.35–4.30 (m, 3 H, H-4_A, H-6_{aA}, H-5_C), 4.27–4.24 (m, 1 H, H-5_B), 4.11–4.04 (m, 3 H, H-6_{bA}, H-2_B, H-3_B), 3.96–3.89 (m, 2 H, H-6_{abC}), 3.86–3.81 (m, 2 H, H-3_A, H-4_B), 3.75–3.69 (m, 1 H, H-2_A), 3.56–3.52 (m, 2 H, −OCH_2-, H-2_C), 3.40–3.36 (m, 2 H, −OCH_2-, H-5_A), 3.24–3.22 (m, 2 H, NCH_2-), 2.09 (s, 3 H, COCH_3), 2.02 (s, 3 H, COCH_3), 1.95 (s, 3 H, COCH_3), 1.81–1.67 (m, 2 H, −CH_2-), 1.12 (d, *J* = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5 (*C*OCH$_3$), 169.9 (*C*OCH$_3$), 169.6 (*C*OCH$_3$), 156.7 (*C*OOCH$_2$Ph), 139.4–126.2 (Ar-C), 102.0 (C-1_A), 100.8 (Ph*C*H), 98.3 (C-1_B), 94.2 (C-1_C), 80.4 (C-3_B), 77.8 (C-2_A), 76.8 (C-2_B), 76.2 (C-4_B), 74.9 (Ph*C*H$_2$), 74.2 (Ph*C*H$_2$), 73.3 (C-3_C) 72.8 (Ph*C*H$_2$), 71.9 (C-5_A), 69.3 (−O*C*H$_2$-), 68.7 (C-5_B), 68.2 (C-2_C), 67.6 (C-5_C), 67.0 (C-3_A), 66.7 (C-6_A), 66.2 (C-4_A), 63.2 (C-6_C), 62.8 (COO*C*H$_2$Ph), 57.9 (C-4_C), 37.6 (N*C*H$_2$-), 29.5 (−*C*H$_2$-), 20.9 (CO*C*-H$_3$), 20.7 (2 C, CO*C*H$_3$), 16.9 (*C*H$_3$); ESI-MS: $C_{63}H_{72}N_4NaO_{19}$ requires *m*/*z* 1211.4791; found: *m*/*z* 1211.4803 $[M + Na]^+$.

3-(Benzyloxycarbonylamino)propyl *O*-(2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-galactopyranosyl)-(l → 3)-[*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 2)-4,6-*O*-benzylidene-β-D-galactopyranoside (18)

A solution of azidotrisaccharide **17** (1.4 g, 1.18 mmol) in pyridine (8 mL) was treated with AcSH (16 mL), and the solution was stirred 10 h. The mixture was filtered, concentrated. The crude product was purified over SiO_2 using hexane −EtOAc (1:2) as eluent to give pure **18** (1.0 g, 70 %).; $[\alpha]_D^{25}$ + 46.7 (*c* 1.5, $CHCl_3$); IR (neat): 2946, 2022,1756, 1509, 1473, 1333, 1187, 923 cm − 1; ^{1} H NMR (500 MHz, $CDCl_3$): δ 7.45–7.20 (m, 25 H, Ar-H), 5.47 (d, *J* = 9.4 Hz, 1 H, N*H*COCH$_3$), 5.43 (s, 1 H, PhC*H*), 5.35 (d, *J* = 3.8 Hz, 1 H, H-1_B), 5.32–5.29 (m, 1 H, N*H*Cbz), 5.11 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 5.09–5.03 (m, 4 H, COOCH_2Ph, H-1_C, H-4_C), 4.97 (dd, *J* = 3.3, 10.2, Hz, 1 H, H-3_C), 4.94 (d, *J* = 11.7 Hz,

1 H, PhCH_2), 4.83 (d, J = 11.6 Hz, 1 H, PhCH_2), 4.78 (d, J = 11.7 Hz, 1 H, PhCH_2), 4.72 (d, J = 11.6 Hz, 1 H, PhCH_2), 4.62 (d, J = 11.6 Hz, 1 H, PhCH_2), 4.60–4.56 (m, 1 H, H-2_C), 4.42 (d, J = 7.7 Hz, 1 H, H-1_A), 4.34–4.29 (m, 3 H, H-4_A, H-5_B, H-5_C), 4.23–4.15 (m, 2 H, H-2_B, H-3_B), 4.08–4.02 (m, 2 H, H-6_{abA}), 3.98–3.94 (m, 2 H, −OCH_2-, H-4_B), 3.88–3.86 (m, 1 H, H-3_A), 3.77–3.72 (m, 2 H, H-6_{abC}), 3.62–3.58 (m, 1 H, −OCH_2-), 3.39 (brs, 1 H, H-5_A), 3.31–3.25 (m, 3 H, H-2_A, NCH_2-), 2.11 (s, 3 H, COCH_3), 1.96 (s, 3 H, COCH_3), 1.92 (s, 3 H,. COCH_3), 1.91–1.83 (m, 2 H, −CH_2-), 1.45 (s, 3 H, NHCOCH_3), 1.16 (d, J = 6.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5 (*C*OCH$_3$), 170.4 (*C*OCH$_3$), 170.3 (*C*OCH$_3$), 170.2 (*C*OCH$_3$), 156.5 (*C*OOCH$_2$Ph), 139.3–126.4 (Ar-C), 102.1 (C-1_A), 101.3 (Ph*C*H), 98.7 (C-1_B), 92.3 (C-1_C), 80.3 (C-3_B), 77.5 (C-2_A), 76.4 (C-2_B), 74.9 (2 C, PhCH$_2$, C-4_B), 74.1 (PhCH$_2$), 72.9 (PhCH$_2$), 72.8 (C-3_C), 70.5 (C-5_A), 69.4 (−OCH$_2$-), 68.8 (C-5_B), 67.9(C-5_C), 67.4(C-3_A), 66.9 (C-4_A), 66.6 (2 C, C-6_A, COOCH$_2$Ph), 66.1(C-4_C), 63.0 (C-6_C), 46.9 (C-2_C), 37.9 (NCH$_2$-), 29.7 (−CH$_2$-), 22.8 (NHCOCH$_3$), 20.9 (COCH$_3$), 20.8 (COCH$_3$), 20.7 (COCH$_3$), 16.8 (CH$_3$); ESI-MS: $C_{65}H_{76}N_2NaO_{20}$ requires *m*/*z* 1227.4991; found: *m*/*z* 1227.4501 $[M + Na]^+$.

3-(Benzyloxycarbonylamino)propyl *O*-(2,3,4-tri-*O*-acetyl-6-*O*-benzyl-β-D-galactopyranosyl)-(l→4)-[*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(l→3)]-6-*O*-*t*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (21)

To a solution of disaccharide **19** (1.0 g, 0.89 mmol) and ethyl 2,3,4-tri-O-benzyl-1-thio-α-L-fucopyranoside **11** (0.51 g, 1.07 mmol) in anhydrous toluene (25 mL) was added MS-4 Å (0.5 g) and the reaction mixture was allowed to stir under N_2 at room temperature for 1 h. The reaction mixture was cooled to −15 °C and *N*-iodosuccinimide (288 mg, 1.28 mmol) and TfOH (15 μl) were added in succession. The reaction mixture was allowed to stir at same temperature for 7 h before dilution with CH_2Cl_2 (50 mL). The reaction mixture was filtered through a Celite−bed and the organic layer was washed with 5 % aq $Na_2S_2O_3$, satd $NaHCO_3$ and water, dried (Na_2SO_4) and evaporated to dryness. The crude product was purified over SiO2 using hexane–EtOAc (4:1) as eluent to furnish trisaccharide **21** (1.0 g, 73 %); spectral data described previously [49].

3-(Benzyloxycarbonylamino)propyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 2)-*O*-(6-*O*-benzyl-3,4-*O*-isopropylidene-β-D-galactopyranosyl)-(1 → 4)-6-*O*-*t*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (22)

To a solution of disaccharide **20** (1.50 g, 1.45 mmol) and ethyl 2,3,4-tri-O-benzyl-1-thio-a-L-fucopyranoside **11** (0.74 g, 1.52 mmol) in anhydrous toluene (20 mL) was added MS-4 Å (1 g) and the reaction mixture was allowed to stir under N_2 at room temperature for 1 h. The reaction mixture was cooled to −30 °C and *N*-iodosuccinimide (410 mg, 1.82 mmol) and TfOH (20 μl) were added in succession. The reaction mixture was allowed to stir at same temperature for 2 h before dilution with CH_2Cl_2 (50 mL). The reaction mixture was filtered through a Celite−bed and the organic layer was washed with 5 % aq $Na_2S_2O_3$, satd $NaHCO_3$ and water, dried (Na_2SO_4) and evaporated to dryness. The crude product was purified over SiO_2 using hexane–EtOAc (5:1) as eluent to furnish tetrasaccharide **22** (2.20 g, 83 %); spectral data described previously [49].

3-(Benzyloxycarbonylamino)propyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 2)-*O*-(6-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-6-*O*-*t*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (23)

The compound **22** (2.1 g, 1.45 mmol) was dissolved in 80 % AcOH (150 mL) and stirred at 80 °C for 2 h. The solution was evaporated to give an oil which was purified over SiO_2 using hexane−EtOAc (5:1) as eluent to furnish diol **23** as a yellow oil (1.8 g, 87 %); yellow oil; $[\alpha]_D^{25}$ + 27 (*c* 1.5, $CHCl_3$); IR: 2922, 2095, 1774, 1644, 1454, 1388, 1078, 992, 699 cm^{-1}; ^{1}HNMR (500 MHz, $CDCl_3$): δ 7.42–7.26 (m, 39 H, Ar-H), 5.16 (d, J = 8.5 Hz, 1 H, H-1_A), 5.00 (brs, 2 H, COOCH_2Ph), 4.98 (d, J = 3.4 Hz, 1 H, H-1_D), 4.95–4.88(m, 2 H, PhCH_2) 4.80–4.73 (ABq, J = 11.9 Hz, 2 H, PhCH_2), 4.69 (d, J = 11.0 Hz, 1 H, PhCH_2), 4.56 (d, J = 7.6 Hz, 1 H, H-1_B), 4.57 (d, J = 11.5 Hz, 1 H, PhCH_2), 4.53–4.48 (ABq, J = 11.9 Hz, 2 H, PhCH_2), 4.43 (dd, J = 9.0, Hz, 1 H, H-3_A), 4.22 (dd, J = 8.5 Hz, 1 H, H-2_A), 4.09–4.02 (m, 2 H, H- 4_A, H-2_D), 3.89–3.83 (m, 4 H, H-6_{abA}, H-4_B, H-5_B), 3.73–3.67 (m, 2 H, H-3_B, H-3_D), 3.64–3.56 (m, 4 H, H-5_A, H-2_B, −OCH_2-), 3.52–3.48 (m, 2 H, H-6_{abB}), 3.42–3.41 (m, 1 H, H-4_D), 3.37–3.33 (m, 1 H, H-5_D), 3.15–3.11 (m, 2 H, NCH_2-), 1.77–1.66 (m, 2 H, −CH_2-), 1.02(s, 9 H, SiC(CH_3)$_3$), 0.74 (d, J = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 168.1(*C*O, Phth), 156.4 (*C*OOCH$_2$Ph), 138.5–127.7 (Ar-C), 101.6(C-1_B), 100.8 (C-1_D), 98.1 (C-1_A), 80.6 (C-3_D), 78.9 (C-2_D), 78.1 (C-2_B), 77.8 (C-4_A), 77.4 (C-5_A), 75.1 (PhCH$_2$), 74.9 (C-4_D), 74.8 (PhCH$_2$), 73.6 (PhCH$_2$), 73.4 (C-3_B), 73.2 (C-4_B), 72.8 (PhCH$_2$), 69.3 (C-3_A), 68.6 (−OCH$_2$-), 68.3(C-5_B), 68.1(C-5_D), 66.9 (C-6_B), 66.5 (COOCH$_2$Ph), 61.8 (C-6_A), 56.6 (C-2_A), 38.6 (NCH$_2$-), 29.6 (−CH$_2$-), 26.9 (SiC(CH$_3$)$_3$), 19.5 (SiC(CH$_3$)$_3$), 16.9 (CH$_3$); ESI-MS: $C_{81}H_{90}N_2NaO_{18}Si$ requires *m*/*z* 1429.5752; found: *m*/*z* 1429.5761 $[M + Na]^+$.

3-(Benzyloxycarbonylamino)propyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 2)-*O*-(4-*O*-acetyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-6-*O*-*t*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (24)

Triethyl orthoacetate (0.37 mL, 1.99 mmol) and *p*-toluenesulfonic acid (0.3 g, 1.99 mmol) were added to a solution of diol **23** (1.4 g, 0.99 mmol) in dry DMF (15 mL). The reaction mixture was stirred at room temperature for 2 h. The solvents were removed under reduced pressure and a solution of the intermediate orthoester in 80 % aqueous AcOH (50 mL) was stirred at room temperature for 1 h. The reaction mixture was evaporated to dryness and the product was purified over SiO_2 using hexane–EtOAc (3:1) as eluent to furnish **24** (1.15 g, 79 %) as a colourless syrup; $[\alpha]_D^{25}$ + 45 (*c* 1.5, $CHCl_3$); IR: 3030, 2932, 2880, 1775, 1716, 1454, 1389, 1237, 1080, 754, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.81–7.66 (m, 6 H, Ar-H), 7.36–7.24 (m, 33 H, Ar-H), 5.45(d, *J* = 3.5 Hz, 1 H, H-4_B), 5.20 (d, *J* = 8.5 Hz, 1 H, H-1_A), 5.06 (brs, 2 H, COOCH_2Ph), 4.97 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.94 (d, *J* = 3.4 Hz, 1 H, H-1_D), 4.93 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 4.81 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.80 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.74–4.72 (m, 2 H, PhCH_2), 4.66 (d, *J* = 8.0 Hz, 1 H, H-1_B), 4.60 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.53 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.48–4.46 (m, 1 H, H-3_A), 4.44 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 4.26 (dd, *J* = 8.5, 2.2 Hz, 1 H, H-2_A), 4.07–4.04 (m, 3 H, H-4_A, H-6_{aA}, H-3_D), 3.89 (d, *J* = 11.2 Hz, 1 H, H-6_{bA}), 3.86–3.83 (m, 2 H, H-5_B, H-2_D), 3.72–3.70 (m, 1 H, H-4_D), 3.60–3.57 (m, 2 H, H-2_B, H-3_B), 3.52–3.48 (m, 3 H, H-6_{aB}, −OCH_2-), 3.43–3.48 (m, 3 H, H-5_A, H-6_{bB}, H-5_D), 3.15–3.11 (m, 2 H, NCH_2-), 1.90 (S, 3 H, COCH_3), 1.72–1.69 (m, 2 H, −CH_2-), 1.02 (s, 9 H, SiC(CH_3)$_3$), 0.75 (d, *J* = 6.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3 (*C*OCH_3), 168.6, 168.1(*C*O, Phth), 156.4 (*C*OOCH_2Ph), 138–127 (Ar-C), 101.4 (C-1_B), 101.1 (C-1_D), 98.1 (C-1_A), 80.9 (C-3_B), 78.9 (C-2_B), 77.6 (2 C, C-3_A, C-2_D), 77.3(C-4_A), 75.0 (C-3_D), 74.8 (Ph*C*H_2), 74.5 (Ph*C*H_2), 73.7 (Ph*C*H_2), 73.1 (Ph*C*H_2), 72.6 (C-5_A), 72.1 (C-5_D), 69.3 (C-4_D), 69.2 (C-5_B), 68.0 (C-4_B), 67.8 (Ph*C*H_2), 67.0 (−O*C*H_2-), 66.5 (C-6_B), 61.8 (C-6_A), 56.6 (C-2_A), 38.6 (N*C*H_2-), 29.6 (−*C*H2-), 26.9 (SiC(*C*H_3)$_3$), 20.7 (CO*C*H_3), 19.5 (Si*C*(CH_3)$_3$), 16.8 (*C*H_3); ESI-MS: $C_{83}H_{92}N_2NaO_{19}Si$ requires *m*/*z* 1471.5857; found: *m*/*z* 1471.5866 $[M + Na]^+$.

3-(Benzyloxycarbonylamino)propyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-(l→3)-[*O*-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-(l→2)]-*O*-(4-*O*-acetyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-6-*O*-*t*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (25)

Prepared from compound **24** (1.3 g, 0.89 mmol), thioglycoside **14** (680 mg, 1.07 mmol), MS-4 Å (600 mg), *N*-Iodosuccinimide (NIS; 288 mg, 1.28 mmol), TfOH (35 μL) in dry CH_2Cl_2 (22 mL) as described for **16**, to afford pure compound **25** (1.3 g, 72 %); yellow oil; $[\alpha]_D^{25}$ + 5 (*c* 1.5, $CHCl_3$); IR: 2869, 2366, 1731, 1506, 1452, 1272, 1098, 1069, 708 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.26–6.94 (m, 59 H, Ar-H), 5.71 (d, *J* = 3.6 Hz, 1 H, H-1_D), 5.70–5.59 (m, 2 H, H-4_B, H-1_E), 5.23 (d, *J* = 8.1 Hz, 1 H, H-1_A), 5.19 (brs, 2 H, COOCH_2Ph), 5.09 (dd, *J* = 11.6 Hz, 2 H, PhCH_2), 4.91 (dd, *J* = 11.4 Hz. 2 H, PhCH_2), 4.77 (d, *J* = 7.8 Hz, 1 H, H-1_B), 4.76–4.71 (m, 2 H, PhCH_2), 4.63–4.44 (m, 10 H, PhCH_2), 4.35–4.19 (m, 5 H, H-2_A, H-5_A, H-6_{abA}, H-5_B), 4.18–4.05 (m, 2 H, H-2_B, H-5_E), 4.04–3.96 (m, 4 H, H-3_A,H-2_D, H-3_D, H-4_E), 3.93–3.72 (m, 6 H, H-4_A, H-6_{abB}, H-5_D, H-6_{abE}), 3.60–3.42 (m, 6 H, H-3_B, H-4_D,H-2_E, H-3_E, −OCH_2-), 3.33–3.29(m, 2 H, NCH_2-), 2.05 (s, 3 H, COCH_3), 2.02–1.95 (m, 2 H, −CH_2-), 1.21 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.99 (s,9 H, SiC(CH_3)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5 (*C*OCH_3), 168.6, 168.1(*C*O, Phth), 156.7 (*C*OOCH_2Ph), 138.4–123.0 (Ar-C), 100.6(C-1_B), 98.1 (C-1_D), 97.9 (C-1_A), 97.1 (C-1_E), 80.1 (C-2_B), 79.0 (2 C, C-2_D, C-2_E), 78.5 (C-3_A), 77.8 (C-3_B), 77.2 (2 C, C-5_B, C-3_E), 77.1 (C-3_D), 76.0 (Ph*C*H_2), 75.7 (2 C, C-4_A, C-4_D), 75.3 (C-5_D), 75.2 (2 C, Ph*C*H_2), 74.1 (Ph*C*H_2), 73.7 (Ph*C*H_2), 73.6 (Ph*C*H_2), 73.2 (Ph*C*H_2), 73.1 (Ph*C*H_2), 72.4 (C-4_E), 70.6 (C-4_B), 69.7 (C-5_A), 68.9 -(O*C*H_2-), 68.5 (COO*C*H_2Ph), 68.0 (C-6_E), 66.6 (C-5_E), 65.9 (C-6_B), 61.7 (C-6_A), 56.8 (C-2_A), 50.9 (N*C*H_2-), 29.6 (−*C*H_2-), 26.9 (SiC(*C*H_3)$_3$), 21.4 (CO*C*H_3), 19.8 (Si*C*(CH_3)$_3$), 17.1 (*C*H_3); ESI-MS: $C_{117}H_{126}N_2NaO_{24}Si$ requires *m*/*z* 1993.8472; found: *m*/*z* 1993.8466 $[M + Na]^+$.

3-(Benzyloxycarbonylamino)propyl *O*-(3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl)-(l→3)-[*O*-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-(l→2)]-*O*-(4-*O*-acetyl-6-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-6-*O*-*t*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (26)

Prepared from compound **24** (2.0 g,1.38 mmol), trichloacetimidate donor **15** (0.79 g, 1.66 mmol), MS-4 Å (1 g), TMSOTf (50 μL) in dry CH_2Cl_2 (40 mL) as described for **17**, to afford pure compound **26** (1.85 g, 77 %); yellow oil; $[\alpha]_D^{25}$ + 26.3 (*c* 1.5, $CHCl_3$); IR (neat): 2869, 2208, 1952, 1629, 1527, 1463, 1216, 1059, 967 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.71–7.56 (m, 6 H, Ar-H), 7.37–7.25 (m, 33 H, Ar-H), 5.45 (d, *J* = 3.8 Hz, 1 H, H-1_D), 5.32 (d, *J* = 3.1 Hz, 1 H, H-1_E), 5.31–5.29 (m, 1 H, N*H*Cbz), 5.21 (d, *J* = 8.1 Hz, 1 H, H-1_A), 5.15 (brs, 2 H, COOCH_2Ph), 5.11 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 5.03–4.99 (m, 1 H, H-4_E), 4.97 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 4.94 (dd, *J* = 3.3, 10.2, Hz, 1 H, H-3_E), 4.83 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.78 (d, *J* = 11.7 Hz, 1 H, PhCH_2), 4.72 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.65 (d, *J* = 11.6 Hz, 1 H, PhCH_2), 4.62 (m, 1 H, H-3_A), 4.60–4.56 (m, 1 H, H-2_E), 4.50 (ABq, 2 H, PhCH_2), 4.42 (d, *J* = 7.7 Hz, 1 H,

H-1_B), 4.34–4.29 (m, 3 H, H-4_B, H-5_D, H-5_E), 4.26 (dd, J = 8.5, 2.2 Hz, 1 H, H-2_A), 4.23–4.15 (m, 3 H, H-2_D, H-3_D, H-4_A), 4.08–4.02 (m, 4 H, H-6_{abA}, H-6_{abB}), 3.98–3.94 (m, 2 H, −OCH_2-, H-4_D), 3.88–3.86 (m, 1 H, H-3_B), 3.77–3.72 (m, 2 H, H-6_{abE}), 3.62–3.58 (m, 3 H, H-5_A, −OCH_2-, H-2_B), 3.59 (brs, 1 H, H-5_B), 3.27–3.22 (m, 2 H, NCH_2-), 2.19 (s, 3 H, COCH_3), 2.11 (s, 3 H, COCH_3), 1.97 (s, 3 H, COCH_3), 1.93 (s, 3 H,. COCH_3), 1.91–1.83 (m, 2 H, −CH_2-), 1.21 (d, J = 6.6 Hz, 3 H, CH_3), 0.99 (s, 9 H, SiC(CH_3)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.9 (*C*OCH$_3$), 170.8 (*C*OCH$_3$), 170.5 (*C*OCH$_3$), 170.4 (*C*OCH$_3$), 168.6, 168.4(*C*O, Phth), 155.9 (*C*OOCH$_2$Ph), 139.8.-128.7(Ar-C),101.3 (C-1_B), 100.2 (C-1_A), 97.7 (C-1_D), 94.3 (C-1_E), 80.9 (C-3_D), 78.9 (C-4_A) 77.9 (C-3_B), 77.1 (C-2B) 77.8 (C-2_D), 76.3 (2 C, C-4_D, Ph*C*-H$_2$), 75.1 (Ph*C*H$_2$), 74.6 (Ph*C*H$_2$), 72.9 (2 C, C-5_A, Ph*C*H$_2$), 72.6 (C-3_E), 72.3 (C-5_D), 70.2 (C-3A), 69.5 (C-4_E), 69.2 (C-5_B), 68.4 (C-4_B), 68.2 (−O*C*H$_2$-), 68.0 (C-5_E), 67.0 (C-6_B), 66.7 (COO*C*H$_2$Ph), 65.3 (C-6_A), 63.3 (C-6_E), 58.1 (C-2_A), 54.9 (C-2E), 38.2 (N*C*H$_2$-), 29.9 (−*C*H$_2$-), 26.1 (SiC(*C*H$_3$)$_3$), 20.4 (2 C, CO*C*H$_3$), 20.2 (2 C, CO*C*H$_3$), 19.6 (Si*C*(CH$_3$)$_3$), 15.7 (*C*H$_3$); ESI-MS: $C_{93}H_{105}N_5NaO_{25}Si$ requires *m*/*z* 1743.6901; found: *m*/*z* 1743.6911 $[M + Na]^+$.

3-(Benzyloxycarbonylamino)propyl *O*-(2,3-di-O-acetyl-4,6-O-benzylidene-β-D-galactopyranosyl)-(l→4)- [*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(l→3)]- 6-*O*-*t*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (29)

To a solution of disaccharide **27** (4.5 g, 4.19 mmol) and ethyl 2, 3,4-tri-O-benzyl-1-thio-a-L-fucopyranoside **11** (2.6 g, 5.45 mmol) in anhydrous toluene (20 mL) was added MS-4 Å (2.0 g) and the reaction mixture was allowed to stir under N_2 at room temperature for 1 h. The reaction mixture was cooled to −15 °C and *N*-iodosuccinimide (1.50 g, 6.54 mmol) and TfOH (30 μL) were added in succession. The reaction mixture was allowed to stir at same temperature for 7 h before dilution with CH_2Cl_2 (80 mL). The reaction mixture was filtered through a Celite−bed and the organic layer was washed with 5 % aq $Na_2S_2O_3$, satd $NaHCO_3$ and water, dried (Na_2SO_4) and evaporated to dryness. The crude product was purified over SiO_2 using hexane–EtOAc (4:1) as eluent to furnish trisaccharide **29** (4.3 g, 69 %); spectral data described previously [49].

3-(Benzyloxycarbonylamino)propyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-(l→3)-*O*-(4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-[*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(l→3)]-6-*O*-*t*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (31)

To a solution of compound **30** (1.8 g, 1.28 mmol) and thioglycoside donor **14** (889 mg, 1.41 mmol) in CH_2Cl_2 (30 mL) was added MS-4 Å (500 mg) and the reaction mixture was allowed to stir at room temperature under N_2 for 30 min. The reaction mixture was cooled to −40 °C and *N*-iodosuccinimide (380 mg, 1.69 mmol) and TfOH (20 μL) were added to it. After stirring the reaction mixture at the same temperature for 1 h, it was filtered through a Celite® bed and washed with CH_2Cl_2 (50 mL). The organic layer was washed with 5 % $Na_2S_2O_3$ (100 mL), satd. $NaHCO_3$ (100 mL) and water (100 mL) in succession, dried (Na_2SO_4) and evaporated to dryness. The crude mass was purified over SiO_2 using hexane−EtOAc (3:1) as eluent to furnish pure **31** (1.7 g, 69 %); $[\alpha]_D^{25}$ –3.7 (*c* 1.5, $CHCl_3$); IR: 3424, 2931, 1714, 1454, 1387, 1217, 1052, 749, 698 cm^{-1};^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76–6.82 (m, 59 H, Ar-H), 5.40 (s, 1 H, PhC*H*), 5.11 (d, J = 3.4 Hz. 1 H, H-1_E), 5.03 (d, J = 8.5 Hz, 1 H, H-1_A), 5.02–4.96 (m, 4 H, COOCH_2Ph, PhCH_2), 4.82–4.73 (m, 6 H, H-1_C, PhCH_2), 4.66–4.57 (m, 6 H, H-1_B, H-5_C, PhCH_2), 4.47–4.42 (m, 4 H, H-4_B, PhCH_2),4.37–4.34 (m, 1 H, H-2_A), 4.31–4.21 (m, 2 H, H-5_A, H-3_C), 4.15–4.04 (m, 3 H, H-5_B, H-6_{abB}), 3.95–3.82 (m, 3 H, H-3_A, H-4_E, H-5_E), 3.84–3.81 (m, 1 H, H-2_B), 3.62–3.56 (m, 4 H, H-6_{abA}, H-2_C, H-3_E), 3.55–3.32 (m, 7 H, H-3_B, H-4_C, H-2_E, H-6_{abE},-OCH_2-), 3.15–3.12 (m, 1 H, H-4_A), 3.02–3.01 (m, 2 H, NCH_2-), 1.73–1.59 (m, 2 H, −CH_2-), 1.06 (s, 9 H, SiC(CH_3)$_3$), 0.98 (d, J = 6.6 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 168.1(*C*O, Phth), 156.4 (*C*OOCH$_2$Ph), 139.6.-123.7(Ar-C), 101.8 (Ph*C*-H), 99.8(C-1_B), 98.4 (C-1_C), 98.1 (C-1_A), 97.9 (C-1_E), 81.9 (C-3_E), 79.2 (C-3_C), 78.7 (2 C, C-2_E, C- 4_A), 76.5 (C-2_C), 76.0 (C-5_E), 74.9 (2 C, C-4_E, Ph*C*H$_2$), 74.8 (Ph*C*H$_2$), 74.7 (C-5_A), 74.4 (C-3_A), 73.6 (Ph*C*H$_2$), 73.5 (C-2_B), 73.1 (2 C, Ph*C*H$_2$), 72.9 (Ph*C*H$_2$), 72.2 (C-4_C), 71.4 (Ph*C*H$_2$), 70.6 (C-3_B), 69.9 (C-4_B), 69.4 (C-6_B), 69.2 (−O*C*H$_2$-), 66.6 (C-5_C), 66.5 (2 C, C-6_E, COO*C*H$_2$Ph), 61.8 (C-6_A), 56.8 (C-2_A), 38.4 (N*C*H$_2$-), 29.6 (−*C*H$_2$-), 26.9 (SiC(*C*H$_3$)$_3$), 19.8 (Si*C*(CH$_3$)$_3$), 16.4 (*C*H$_3$); ESI-MS: $C_{115}H_{122}N_2NaO_{23}Si$ requires *m*/*z* 1949.7789; found: *m*/*z* 1949.7794 $[M + Na]^+$.

3-(Benzyloxycarbonylamino)propyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-(l→3)-*O*-(4,6-*O*-benzylidene-β-D-galactopyranosyl)-(1→4)-6-*O*-*t*-butyldiphenylsilyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (32)

A mixture of compound **28** (1 g, 1.01 mmol), compound **14** (702 mg, 1.11 mmol), and MS 4 Å (500 mg) in dry CH_2Cl_2 (35 mL) was stirred under nitrogen for 1 h. NIS (300 mg, 1.33 mmol) was added, and the mixture was cooled to −40 °C followed by addition of TfOH (20 μL). The mixture was allowed to stir at −40 °C for 1 h. Then it was filtered through a Celite® bed and washed with CH_2Cl_2 (200 mL). The organic layer was washed with 5 % $Na_2S_2O_3$ (100 mL), satd. $NaHCO_3$ (100 mL) and water (100 mL) in succession, dried (Na_2SO_4) and evaporated to dryness. The crude mass

was purified over SiO_2 using hexane–EtOAc (3:1) as eluent to furnish pure **32** (850 mg, 55 %); $[\alpha]_D^{25}$ –14.7 (*c* 1.5, $CHCl_3$); IR: 3424, 2931, 1714, 1454, 1387, 1217, 1052, 749, 698 cm^{-1};^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79–7.17 (m, 44 H, Ar-H), 5.39 (s, 1 H, PhC*H*), 5.23 (d, *J* = 8.4 Hz, 1 H, H-1_A), 5.12 (d, *J* = 3.4 Hz, 1 H, H-1_E), 4.99–4.98 (m, 2 H, COOCH_2Ph), 4.94 (d, *J* = 11.5 Hz, 1 H, PhCH_2), 4.89–4.87 (m, 1 H, N*H*Cbz), 4.82 (d, *J* = 11.9 Hz, 1 H, PhCH_2), 4.75 (d, *J* = 7.7 Hz, 1 H, H-1_B), 4.71 (dd, *J* = 11.7 Hz, 2 H, PhCH_2), 4.57 (dd, *J* = 11.7, 4.3 Hz, 2 H, H-2_A, H-4_B), 4.42 (dd, *J* = 11.8 Hz, 2 H, PhCH_2), 4.34 (dd, *J* = 11.9 Hz, 2 H, PhCH_2), 4.21–4.12 (m, 5 H, H-5_E, H-2_B, H-3_E, H-6_{abA}), 3.99–3.86 (m, 5 H, H-5_A, H-5_B, H-2_E, H-6_{abE}), 3.74 (t, *J* = 8.7 Hz, 1 H, H-3_A), 3.59–3.41 (m, 5 H, OCH_2R, H-3_B, H-6_{abB}), 3.29 (brs, 1 H, H-4_E), 3.16–3.05 (m, 3 H, H-4_A, NCH_2), 1.72–1.68 (m, 2 H, −CH_2-), 1.05 (SiC(*C*H_3)$_3$; ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 168.2 (*C*O Phth), 156.5 (*C*-OOCH_2Ph), 139.1.-123.7(Ar-C), 103.9 (Ph*C*H), 101.0 (C-1_B), 98.1 (C-1_A), 96.3 (C-1_E), 81.7(C-3_E), 79.2 (C-2_e), 78.6 (C-2_B), 76.5 (C-4_E), 75.4 (C-4_A), 75.0(C-5_A), 74.9 (Ph*C*-H$_2$), 73.4 (Ph*C*H$_2$), 73.2 (Ph*C*H$_2$), 73.1 (C-3_B), 72.9 (Ph*C*H$_2$), 70.2 (C-4_B), 69.9 (C-3_A), 69.3 (C-5_E), 69.2 (−O*C*H$_2$R), 68.9 (C-6_E), 67.2 (C-6_B), 66.8 (C-5_B), 66.4 (COO*C*H$_2$Ph), 62.6 (C-6_A), 56.3 (C-2_A), 38.6(N*C*H$_2$), 29.7(−*C*H2), 27.0 (SiC(*C*-H$_3$)$_3$), 19.8 (Si*C*(CH$_3$)3); ESI-MS: $C_{88}H_{94}N_2NaO_{19}Si$ requires *m*/*z* 1533.6220; found: *m*/*z* 1533.6232 $[M + Na]^+$.

Acknowledgments Author gratefully acknowledges financial support by Department of Science and Technology (DST), India under Fast Track Proposal Scheme for Young Scientists (CS-127/2012) and SAIF Division of CSIR-CDRI for providing the spectroscopic and analytical data. CDRI communication no. 9106.

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