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Synthesis and NMR studies on the ABO histo-blood group antigens: synthesis of type III and IV structures and NMR characterization of type I–VI antigens

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Dedicated to Professor András Lipták on the occasion of his 75th birthday

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ABSTRACT

The ABO histo-blood group antigens are best known for their important roles in solid organ and bone marrow transplantation as well as transfusion medicine. Here we report the synthesis of the ABO type III and IV antigens with a 7-octen-1-yl aglycone. Also described is an NMR study of the ABO type I to VI antigens, which were carried out to probe differences in overall conformation of the molecules. These NMR investigations showed very little difference in the ^{1}H chemical shifts, as well as ^{1}H–^{1}H coupling constants, across all compounds, suggesting that these ABO subtypes adopt nearly identical conformations in solution.

1. Introduction

Arguably one of the most important antigen families, the ABO histo-blood group system has been the focus of much interest since its discovery by Landsteiner in 1900.[1] Despite the plethora of literature on the ABO antigens, many important questions remain unanswered. For example, it is still unclear what role the ABO subtypes I–VI (see below) play, and whether these structural differences are biologically relevant. One challenge to addressing this question systematically is that, to the best of our knowledge, no complete set of all 18 ABO antigen subtypes with a consistent aglycone is available.

The underlying carbohydrate epitopes (**1–3**, Fig. 1) responsible for the ABO histo-blood group system were determined by Watkins and Morgan in 1957.[2] This work demonstrated that the H(O) antigen is a disaccharide consisting of L-fucose α-(1→2) linked to D-galactose (**3**, Fig. 1). The A and B blood group structures (**2**, **3**) result from further elaboration of the H antigen. Individuals with the A and/or B histo-blood group genotype each produce one additional enzyme, an *N*-acetyl-galactosaminyltransferase (GTA) or a galactosyltransferase (GTB);[3] these enzymes transfer either an *N*-acetyl D-galactosamine or D-galactose residue to the H antigen.

The ABO antigens can be further subdivided into six subtypes (I–VI), based on the carbohydrate moiety at the reducing end (Table 1).[4] Of these, type I–IV are considered to be the most important.[5] These antigens are differentially expressed on erythrocyte and tissue surfaces.[6] For example, type II antigens are expressed on the human lung vascular endothelial cells while type I, III and IV moieties are not.[7] In bronchial epithelial cells, secretors, individuals who excrete their blood group structures in their bodily fluids and secretions, express type I, III/IV, but not type II, antigens.[7] In the case of erythrocytes, type I–IV structures are expressed on the cell surface.[8] The expression of different subtypes of ABO epitopes is believed to have important biological implications. For example, individuals who are of the A blood group can be broken down into two subgroups, A_1 and A_2. In a study of the differences between these blood group subtypes, it was shown by Enholm and co-workers that A_1 individuals have a higher antigen density than those with the A_2 blood type.[9] Subsequently, Schachter and co-workers demonstrated that A_1 and A_2 individuals have two different *N*-acetyl-galactosaminyl transferases, termed GTA_1 and GTA_2, respectively.[10] Later, in a qualitative study, Clausen and co-workers showed that GTA_2 was unable to affect transfer on the H type III precursor, suggesting that the differential glycosylation of the H type I–IV antigens by GTA_1 and GTA_2 results in a greater A antigen density in A_1 individuals.[11]

Differences between the biological roles of the type I–VI subgroups could be the result of conformational changes induced by the variable monosaccharide residue at the reducing end of the antigen. Although conformational studies of these antigens have been carried out, a systematic investigation of all of them has not been reported; rather the focus has been on a relatively few

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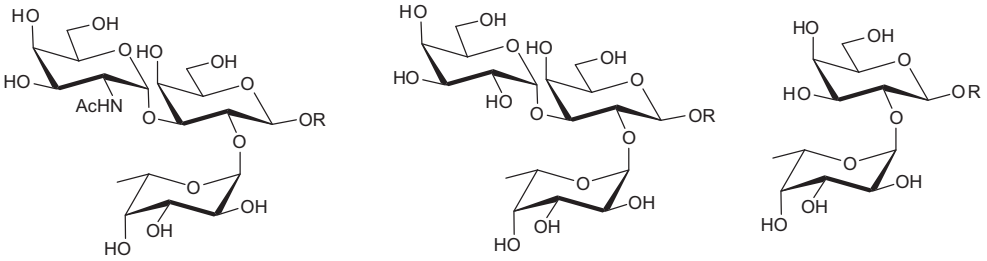


Figure 1. Structures of the A, B and H(O) antigens. R = glycoprotein, glycolipid or free oligosaccharide.

Table 1
Carbohydrate moieties responsible for the six subtypes (I–VI) of the ABO histo-blood group antigens

Type	Carbohydrate
Type I	ABO-β-(1→3)-β-D-Glc*p*NAc
Type II	ABO-β-(1→4)-β-D-Glc*p*NAc
Type III	ABO-β-(1→3)-α-D-Gal*p*NAc
Type IV	ABO-β-(1→3)-β-D-Gal*p*NAc
Type V	ABO-β-(1→3)-β-D-Gal*p*
Type VI	ABO-β-(1→4)-β-D-Glc*p*

antigens. In 1982, Lemieux and co-workers examined the three-dimensional structure of the blood group B trisaccharide methyl glycoside (**4**) using molecular dynamics and NMR spectroscopy.[12] Capitalizing on this work, in 1999, Otter and co-workers refined the structural study, taking advantage of the significant developments in NMR spectroscopy that had occurred over the nearly 20 year period (Fig. 2).[13] In addition, this latter report provided a structure obtained by X-ray crystallography, which closely matched the structure obtained from the NMR investigations.

Conformational studies have also been conducted on other blood group epitopes. Of particular note is a study by Duus and co-workers on the H type I antigen **5**.[14] These studies examined the conformation and NOE interactions of the H type I antigen **5**, compared to the structural variants **6**–**8** (Fig. 3). In **5**, the substituent at the 2 position of the reducing end is an *N*-acetyl group, in **6** it is a hydroxyl group and **7** is the 2-deoxy analogue. In **8**, the reducing end moiety was removed completely providing a disaccharide. This work showed that in the case of **5**, a strong NOE interaction existed between the H3 of the fucose residue and the reducing end *N*-acetyl group. This was supported by a 0.16 ppm upfield shift of the fucose H3, compared to the H disaccharide **8**. In the case of **6** and **7**, only a small deviation was observed. This study highlights the subtle conformational differences between the H type I trisaccharide antigen (**5**) and the H disaccharide structure, **8**. An important point to note is that in all of the molecules, the fucose ring is spatially orientated so that H3, H5, and H6 are in close proximity to the reducing end moiety.

Systematically probing the effect of the non-reducing residue in these tetrasaccharides on the overall conformation of the antigen requires access to all 18 structures, ideally attached to the same aglycone to minimize ambiguities arising from the presence of different groups at the reducing end. Although the synthesis of the ABO histo-blood group antigens by either chemical and chemoenzymatic approaches has been the subject of a number of investigations, the vast majority of attention has focused on the type I and II subtypes.[15–19] In contrast, much less work has focussed on the important type III and IV structures. In 1990, Bovin and Khorlin reported the synthesis of the A type III antigen.[20] Almost 20 years later, the same laboratory reported the synthesis of the B type III and IV antigens.[17] Both of these convergent syntheses used a [3+1] block approach to enable ready access to these structures. In addition to these chemical synthetic approaches, a chemoenzymatic synthesis of the A type IV tetrasaccharide was reported by Mazid and co-workers.[19] In this study, a synthetically prepared H type IV trisaccharide was used as a substrate for a porcine GTA, affording the target antigen. We report here the synthesis of the ABO type III and IV histo-blood group antigens (**9**–**14**, Fig. 4) attached to an octen-1-yl aglycone. This work complements earlier work from our group on the synthesis of the Type I, II, V, and VI structures.[21,22]

2. Results and discussion

To prepare **9**–**14**, we decided to employ a linear chemical synthesis, similar to that used in our previous syntheses of type I, II,

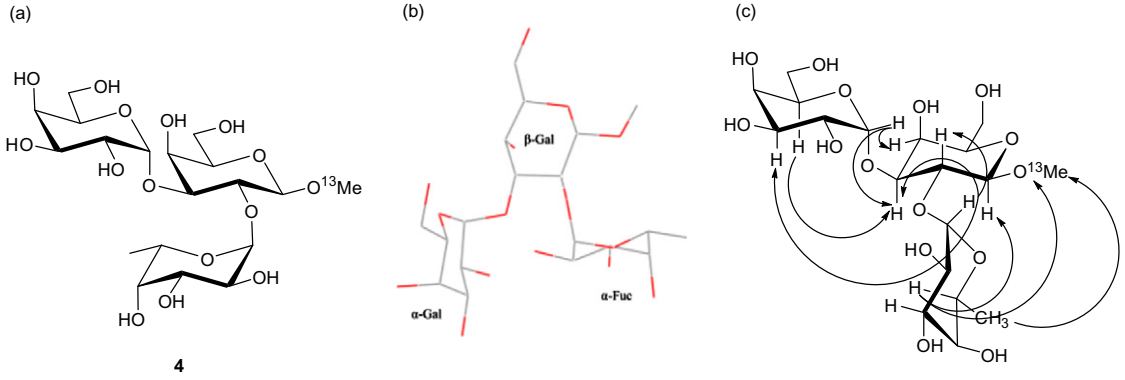


Figure 2. Crystal structure (b) and important NOE interactions (c) of B trisaccharide histo-blood group antigen **4**.[13]

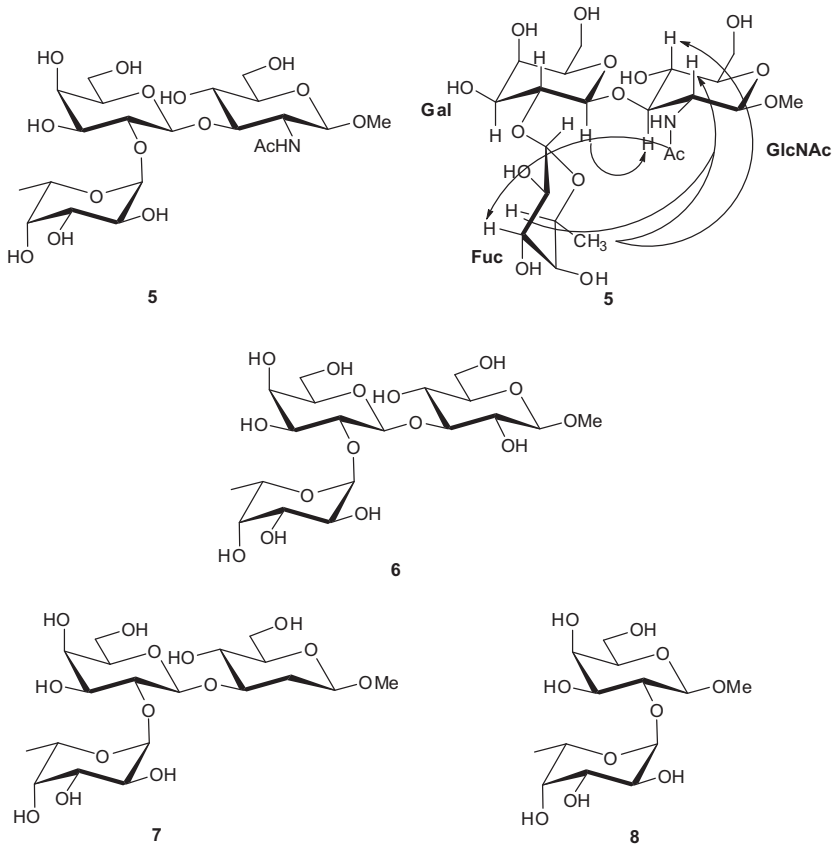


Figure 3. Schematic representation of NOE interactions of **5** and structures **6**, **7** and **8**.[14]

V, and VI antigens.[21,22] We also selected a 7-octen-1-yl aglycone, identical that used in our type I/II[22] and type V/VI[21] syntheses. This aglycone can be readily converted, by catalytic hydrogenation into the corresponding octyl glycoside, which is a useful substrate for enzyme kinetic studies.[23] The alkene can also be used to introduce a reactive linker via a thiol-ene 'click reaction'.[24]

2.1. Synthesis of type III antigens

The synthesis of the ABO type III antigens (**9**–**11**) commenced from the known trichloroacetimidate **15** (Scheme 1).[25] Preparation of the 7-octen-1-yl glycoside was achieved using standard conditions to afford **16** as an inseparable mixture of anomers (α:β, 52:48). Deacetylation under Zemplén conditions afforded the triol **17** (87% yield from **15**), which was immediately converted into the benzylidene acetals **18** and **19** in an excellent 98% combined yield. At this stage it was possible to separate the α- and β-anomers using silica gel chromatography. The poor stereoselectivity observed in the glycosylation reaction was fortuitous in some respects as it enabled preparation of the reducing end moiety for both the type III and IV antigens, which differ in the anomeric stereochemistry of this residue.

Glycosylation of acceptor **18** with trichloroacetimidate **20**[22] yielded disaccharide **21** (Scheme 2). To facilitate purification, the product **21** was subjected to Zemplén deactylation to afford the diol **22** in good yield (88%) and with complete stereoselectivity. The stereochemistry of the newly formed glycosidic linkage was confirmed using NMR spectroscopy; the ^{1}H NMR spectrum of **22** showed an anomeric signal at 4.59 ppm as a doublet with a coupling constant of 7.6 Hz, consistent with the β-stereochemistry. Selective protection of the 3′-hydroxyl group of **22** was achieved by reaction with trimethylacetyl chloride in pyridine exclusively providing **23** in 94% yield.

Introduction of the α-L-fucopyranoside residue was accomplished using trichloroacetimidate **24** yielding the trisaccharide **25**.[26] This technique for preparing α-L-fucopyranosides was crucial to the synthesis of all the type I–VI antigens. The ability to prepare these linkages with excellent stereoselectivity and high yields outweighed the limited disadvantages of the approach. The β-L-fucopyranosyl trichloroacetimidate **24** can be straightforwardly synthesized in large (10 g) quantitites; the only difficult step is its isolation in pure form. With due care, chromatographic purification of a highly activated fucopyranosyl trichloroacetimidate is possible as reported.[26] The stereochemistry of the α-L-fucopyranoside residue was confirmed from the ^{1}H NMR spectrum, which displayed an anomeric signal for this moiety at 5.39 ppm as a doublet with J = 3.4 Hz.

Removal of the pivaloate ester was achieved under forcing conditions, using lithium methoxide in methanol at reflux. The main disadvantage of this reaction was that prolonged reaction times (7 days) were required to ensure complete conversion. This was similar to what was observed in the syntheses of both the type I and II[22] and type V and VI[21] antigens. Despite the length of this deacylation reaction, the process gave an excellent yield (78%) of the product **26** and thus alternatives were not explored.

Access to the H type III antigen was achieved firstly by conversion of the azide group in **26** into an *N*-acetyl group upon treatment with thiolacetic acid in pyridine (Scheme 3). Unfortunately, some acetylation of the alcohol in **27** was also observed; this side reaction necessitated a second deacetylation step to convert the O-acetylated product into **27** in 78% yield over the two steps. Global deprotection of the resulting trisaccharide alcohol was achieved using Birch reduction, affording **11** in excellent yield (92%). For our conjugation studies,[27] the 7-octen-1-yl aglycone was desired. However, as discussed above, for studies such as the examination of GTA and GTB kinetics, the octyl glycoside was

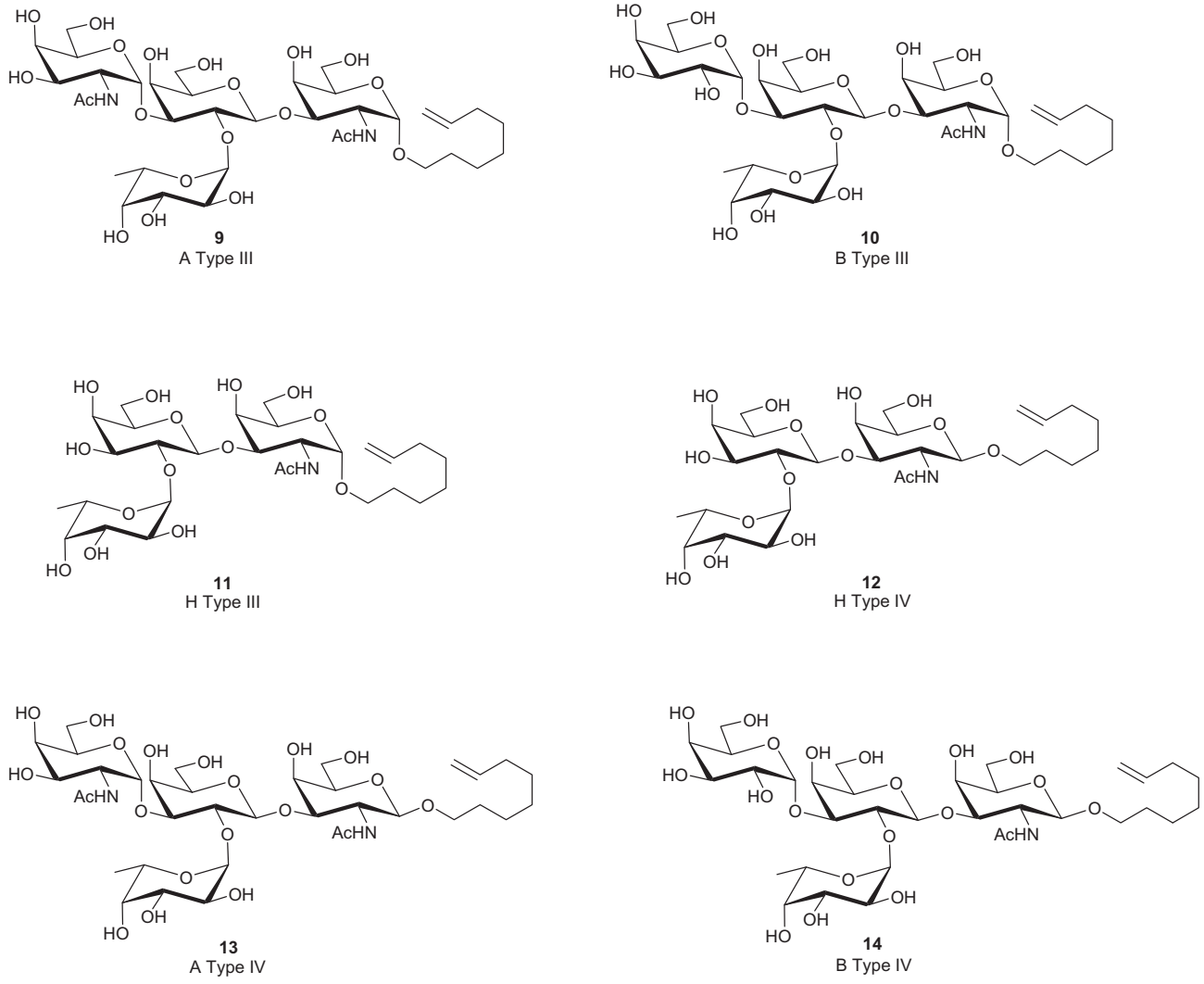
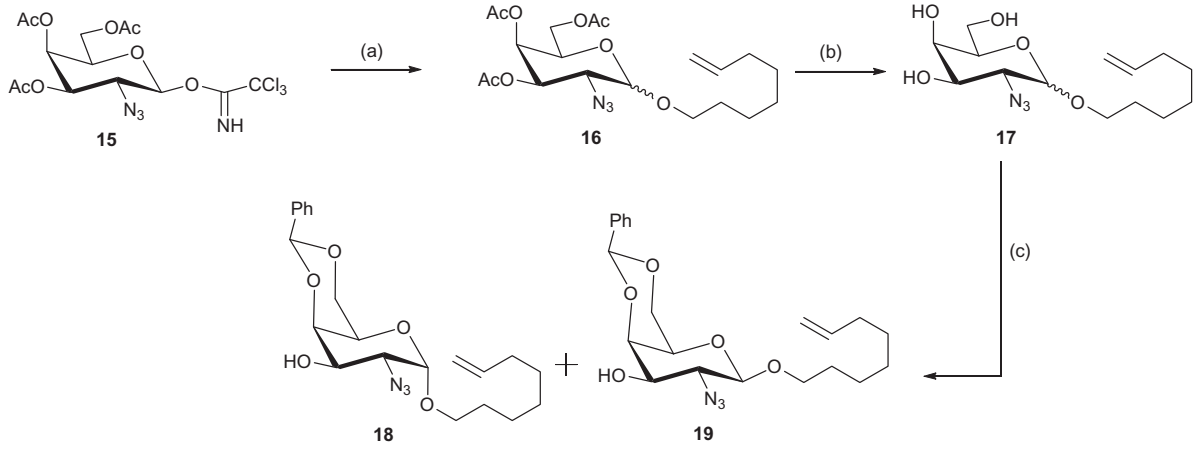


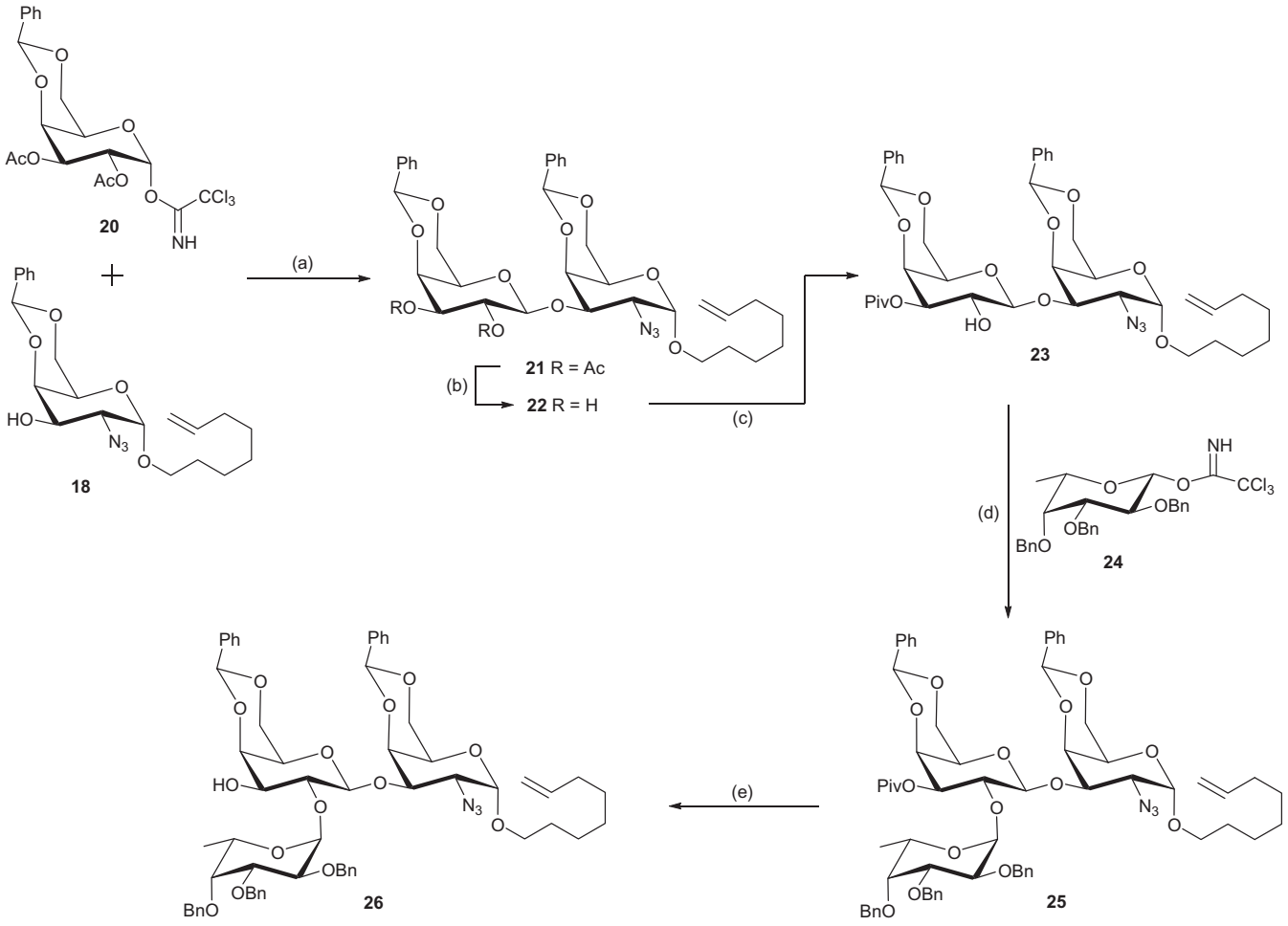
Figure 4. Structure of the ABO type III and IV histo-blood group antigens targeted for synthesis.



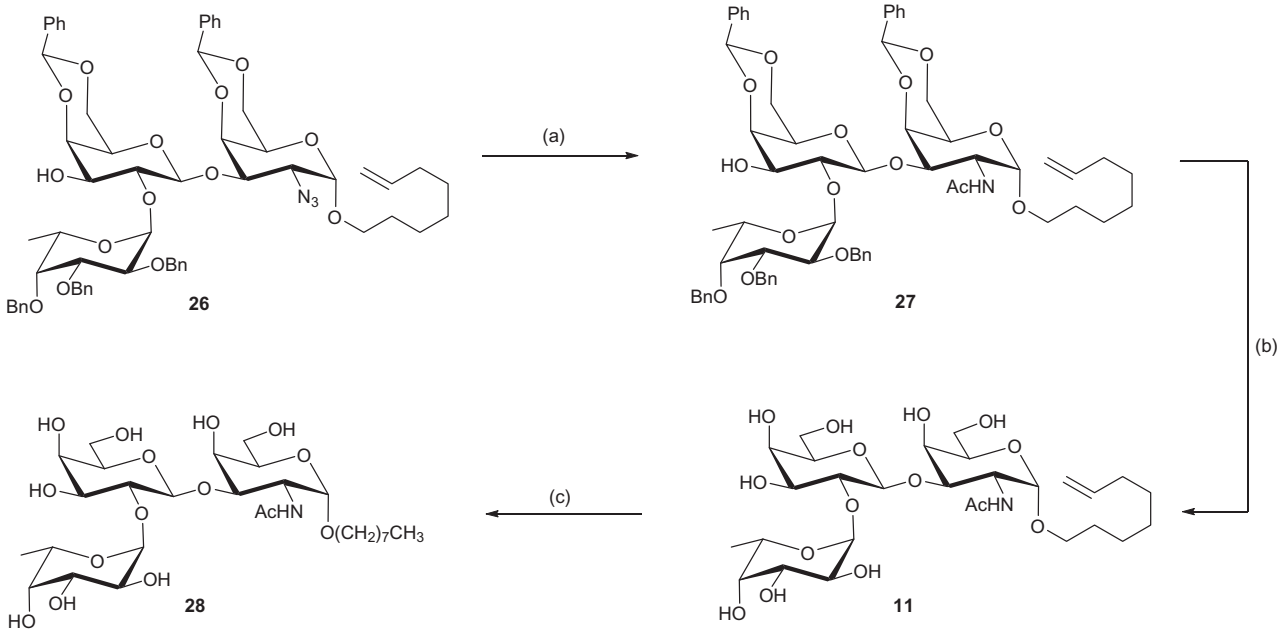
Scheme 1. Reagents: (a) $HO(CH_2)_6CH{=}CH_2$, 4 Å MS, TMSOTf, CH_2Cl_2, (α:β, 52:48); (b) $NaOCH_3$, CH_3OH, 87% (two steps); (c) $PhCH(OCH_3)_2$, *p*-TsOH, DMF, 98%.

desired. Reduction of the alkene was therefore achieved using catalytic hydrogenation to afford a 93% yield of octyl glycoside **28**.

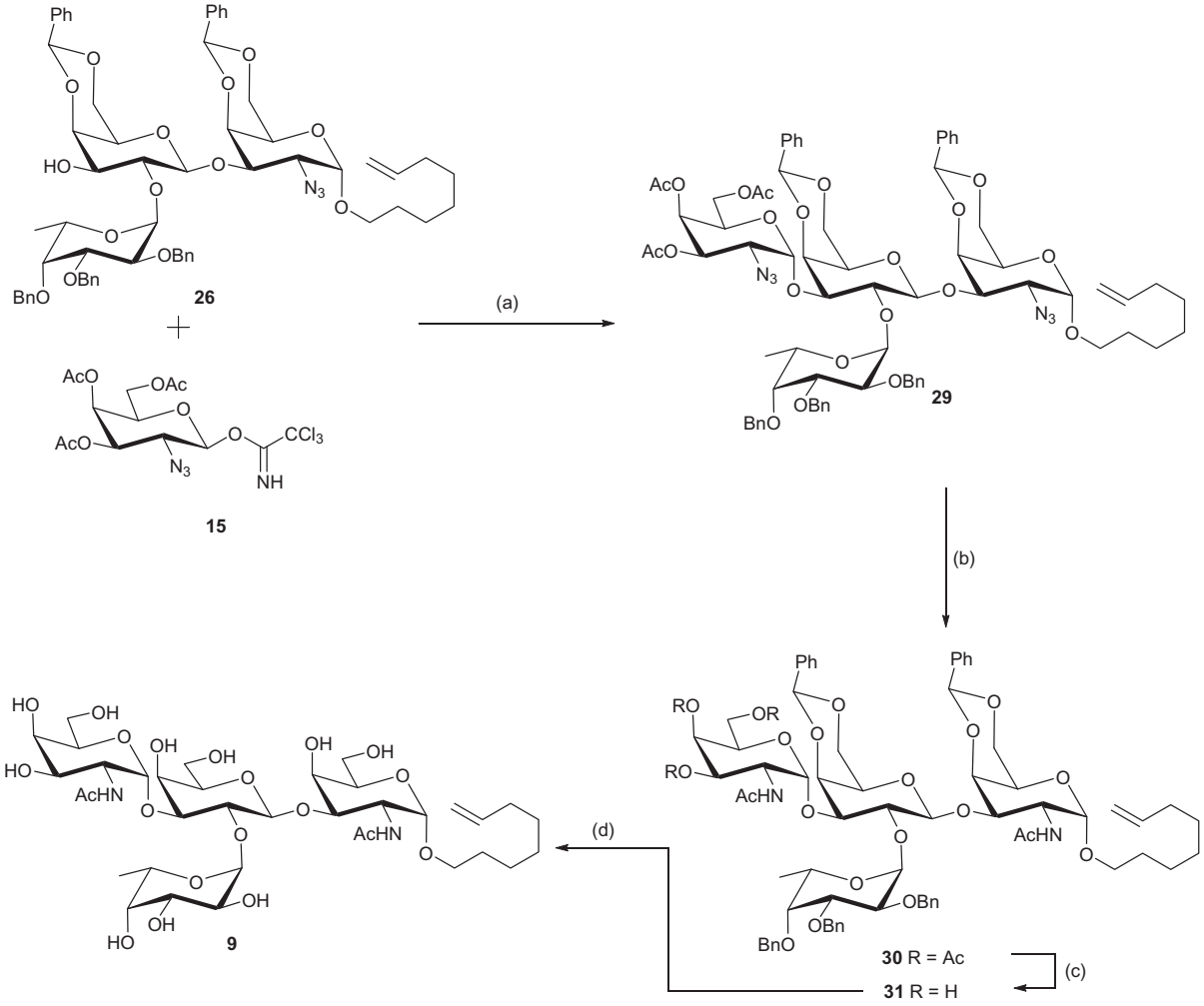
The A type III antigen was accessed from the trisaccharide intermediate **26**. Glycosylation using the trichloroacetimidate **15** under standard conditions afforded the near pure tetrasaccharide **29** in moderate (71%) yield (Scheme 4). To facilitate purification and removal of trichloroacetimidate related impurities (<5% by ^1H NMR spectroscopy) produced during the glycosylation, the two azido



Scheme 2. Reagents: (a) TMSOTf, 4 Å MS, CH_2Cl_2; (b) $NaOCH_3$, CH_3OH, 88%; (c) $(CH_3)_3CCOCl$, pyridine, 94%; (d) TMSOTf, 4 Å MS, Et_2O, 72%; (e) $LiOCH_3$, CH_3OH, 78%.



Scheme 3. Reagents: (a) (i) AcSH, pyridine; (ii) $NaOCH_3$, CH_3OH, 78%; (b) Na, NH_3, CH_3OH, THF, 92%; (c) 10% Pd–C, H_2, CH_3OH, 93%.



Scheme 4. Reagents: (a) TMSOTf, 4 Å MS, Et_2O, 71%; (b) AcSH, pyridine, 76%; (c) $NaOCH_3$, CH_3OH, 99%; (d) Na, NH_3, CH_3OH, THF, 96%.

groups in **29** were converted, in 76% yield, into the corresponding acetamides using thiolacetic acid in pyridine. Confirmation of the glycosidic linkage stereochemistry was possible at this stage; the $^3J_{1,2}$ for the terminal GalNAc residue was 3.7 Hz, indicative of the α-stereochemistry. Deacetylation of **30** was achieved using standard Zemplén conditions to afford **31**. Final global deprotection was achieved using a dissolving metal reduction to provide the A type III antigen **9** in 95% overall yield from **30**.

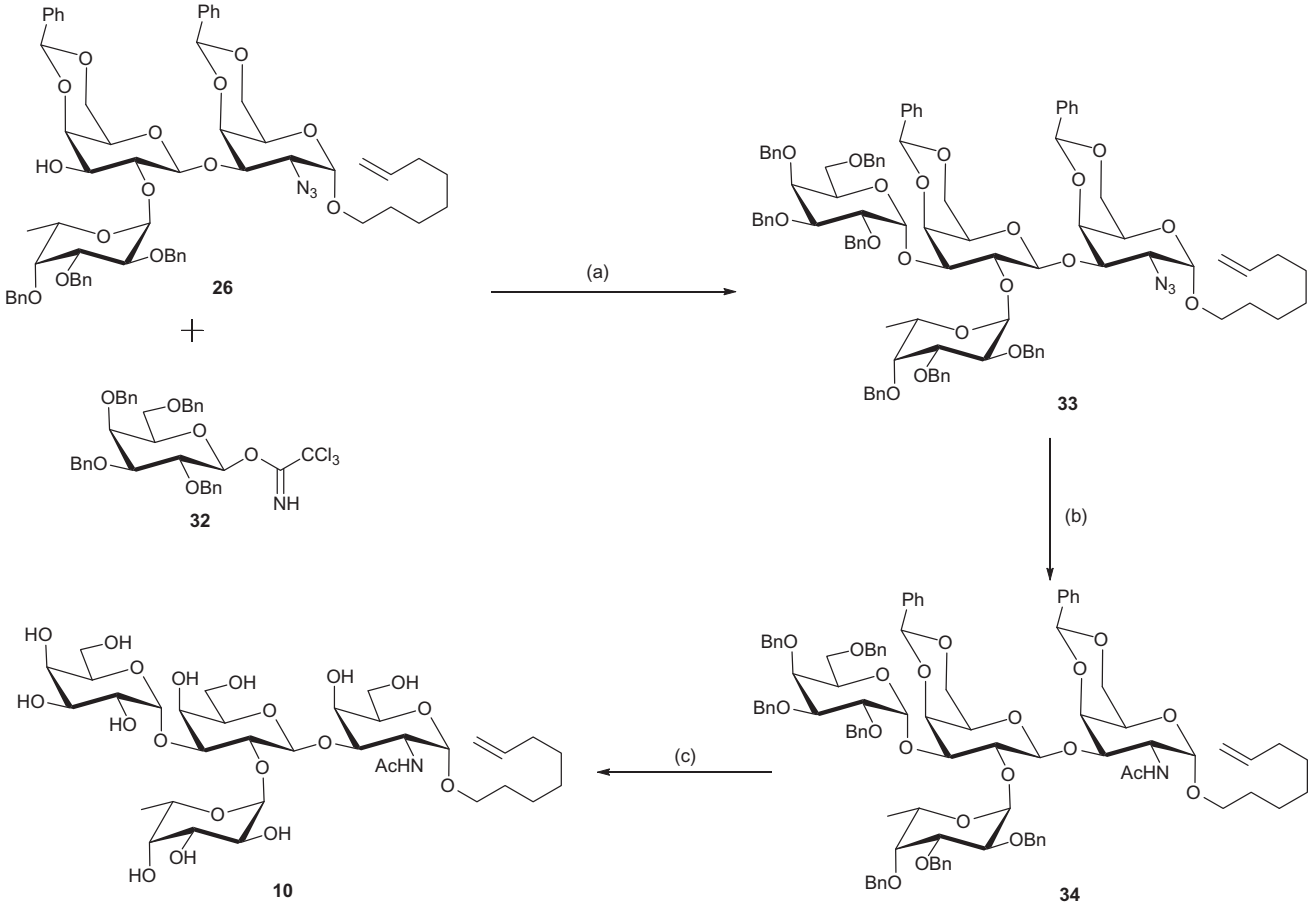
Access to the B type III antigen commenced from the trisaccharide intermediate **26**. Treatment of **26** with the galactosyl trichloroacetimidate **32**[28] using TMSOTf as the promoter afforded the tetrasaccharide **33** (Scheme 5). As was the case with the preparation of **29**, trace amounts of trichloroacetimidate related byproducts (<5% by ^{1}H NMR spectroscopy) hampered obtaining **33** in pure form. A small amount of the acceptor was isolated as the TMS ether, which explains the modest yield (68%) of this glycosylation. To facilitate the purification, the azide moiety was converted into an *N*-acetyl group, enabling the isolation of **34** in high purity, but in moderate yield over the two steps (52%). Complete debenzylation and removal of the benzylidene acetals in **34** using Birch reduction afforded **10** in excellent yield (92%).

2.2. Synthesis of type IV antigens

The type IV antigens are very similar to the type III structures, the only difference is in the anomeric configuration of the reducing end acceptor. Not unsurprisingly, therefore, the preparation of the type IV structures mirrored the approach described above for the Type III antigens, using a different starting monosaccharide. In the latter case the 7-octenyl-α-glycoside **18** was used, while in the former case the corresponding β-glycoside (**19**) was used.

As detailed in Scheme 6, the synthesis of the type IV antigens commenced from the acceptor **19**. Glycosylation using the trichloroacetimidate **20**[22] afforded the disaccharide **35**. To facilitate purification and isolation, Zemplén deacetylation was conducted to provide **36** in 76% yield over the two steps. Protection of the 3-OH group of the galactose ring at the non-reducing end of the molecule using trimethylacetyl chloride provided **37** in excellent yield (98%). Installation of the α-L-fucopyranoside moiety was achieved in 75% yield using activation of the glycosyl donor **24** with TMSOTf, described initially by Gerhard and Schmidt.[26] Removal of the pivaloate ester from **38** was achieved, as it was in the case of the Type III structures, by heating in lithium methoxide in methanol at reflux to provide **39** in 80% yield.

Access to both 7-octen-1-yl and octyl glycoside analogues of the H type IV antigen first required conversion of the azide in **39** to an *N*-acetyl group (Scheme 7). Thiolacetic acid in pyridine was again used to affect this conversion. As was the case in the H type III antigen synthesis, some acetylation of the galactopyranose 3-OH group was observed, but this problem could be remedied using a Zemplén deacetylation step to afford **40** in 60% yield over the two steps. The lower yield was due to difficulties in forcing the



Scheme 5. Reagents: (a) TMSOTf, 4 Å MS, Et_2O, 68%; (b) AcSH, pyridine, 76%; (c) Na, NH_3, CH_3OH, THF, 92%.

reaction to completion; unreacted starting material (28%) was recovered and the structure confirmed by ^{1}H NMR spectroscopy. Complete deprotection using a dissolving metal reduction provided (87% yield) the H type IV antigen with the 7-octen-1-yl aglycone required for conjugation to a linker. Catalytic reduction of the alkene in **12** resulted in the successful preparation of the octyl glycoside **41**.

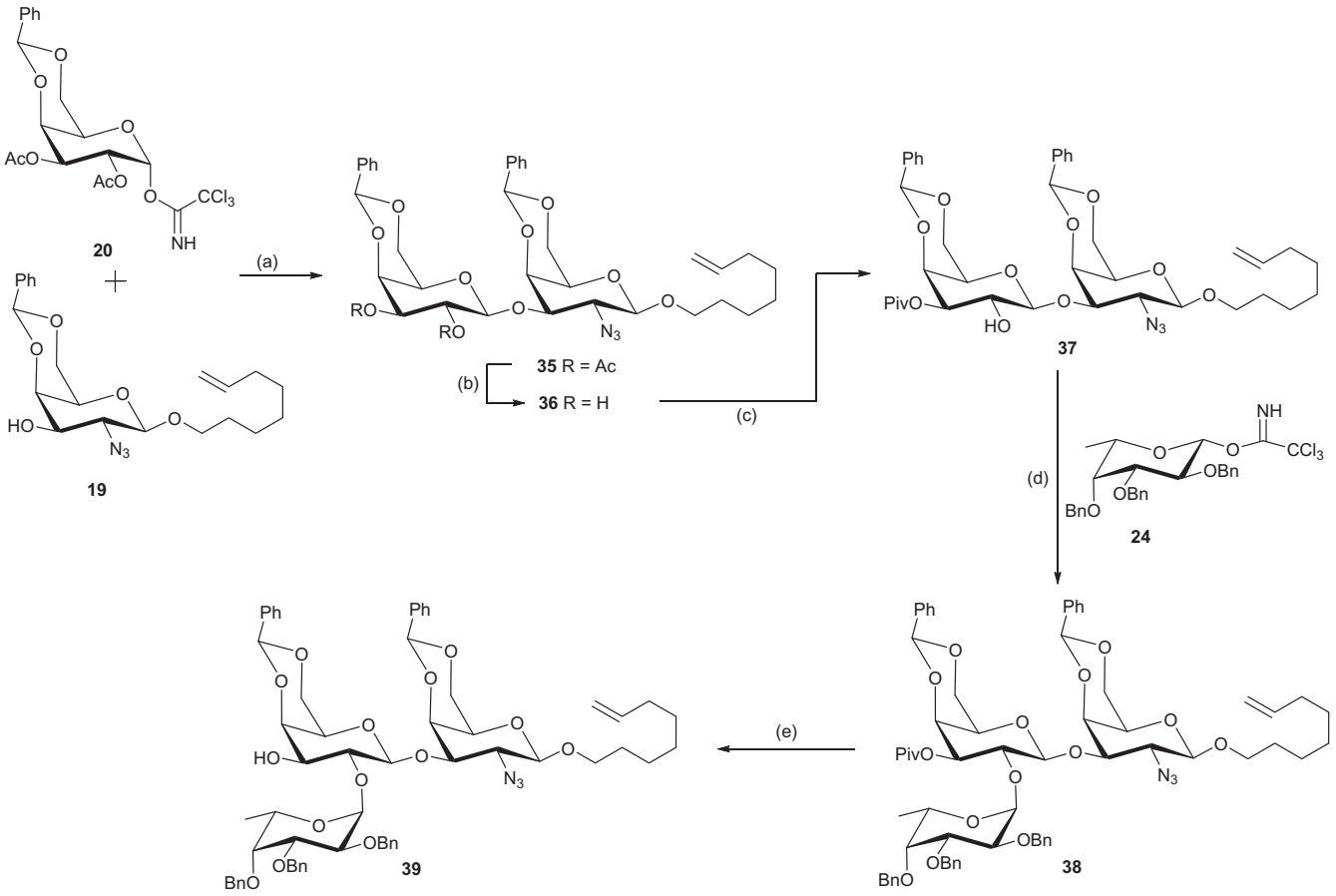
Using intermediate **39**, glycosylation with trichloroacetimidate **15** provided the near pure tetrasaccharide **42** (Scheme 8) in 79% yield. Again, as was the case in the A type III synthesis, contamination with trichloroacetimidate related impurities (<5% by ^{1}H NMR spectroscopy) was observed. Consequently, treatment of **42** with thiolacetic acid in pyridine resulted in conversion of the two azide groups into the expected acetamides and the preparation, in 83% yield, of pure **43**. Exhaustive deprotection, firstly by Zemplén deacetylation and secondly by Birch reduction provided the A type IV antigen **13** in 84% yield. At this stage the stereochemistry of the newly formed glycosidic linkage could be confirmed using ^{1}H NMR spectroscopy; the anomeric signal appeared as a doublet at 5.15 ppm with a coupling constant of 3.7 Hz.

Access to the B type IV antigen was achieved from the trisaccharide **39**. Glycosylation with the trichloroacetimidate **32** afforded the tetrasaccharide **45** (Scheme 9), which was contaminated with trichloroacetimidate related impurities (<5% by ^{1}H NMR spectroscopy). Instead, conversion of the azide in the partially purified product into an *N*-acetyl group was required to enable isolation of the pure tetrasaccharide in 78% yield from **39**. The anomeric signal of the newly formed α-D-galactopyranoside appeared as a doublet at 5.33 ppm with a coupling constant of 3.6 Hz. Final deprotection of the benzyl ethers and benzylidene acetals using a Birch reduction afforded **14** in excellent (94%) yield.

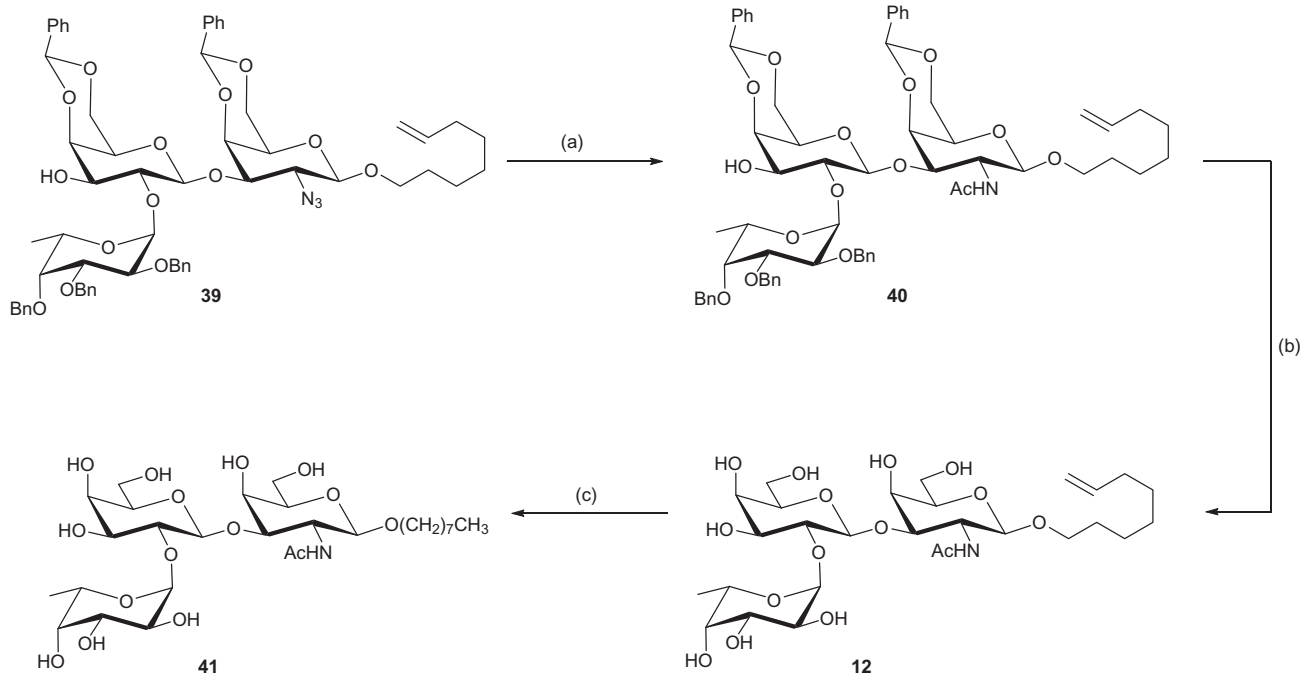
2.3. NMR analysis of ABO type I–VI antigens

With a collection of all 18 ABO type I–VI antigens in hand, provided as described above, or through our previous work,[21,22] our attention shifted to NMR studies aimed at assessing any conformational differences between the subtypes. As an initial gauge of differences or similarities, ^{1}H chemical shifts and ^{1}H–^{1}H coupling constants were measured on all 18 compounds under identical conditions. One of the main complications in carrying out these analyses was the significant spectral overlap in the ^{1}H NMR spectra. To overcome this problem a gradient-enhanced chemical shift selective filtering (ge-CSSF) technique was used. In previous studies, 1D-ge-CSSF-TOCSY experiments have been shown[29,30] to be effective in assigning the coupling constants and chemical shifts for the type I and II antigens,[22] as well as other oligosaccharides.[31–33] A sample 1D-ge-CSSF-TOCSY is included in Supplementary data. This technique is essentially a 1D version of the standard 2D-TOCSY, with each carbohydrate ring presented as a single 1D ^{1}H NMR spectrum. However, significantly better resolution can be obtained. The main limitation of this technique is the same as that of a traditional TOCSY experiment: the signal transfer throughout each ring is dependent upon the size of the coupling constants. In systems such as glucose, this is typically not a problem. Galactose and fucose, on the other hand, when irradiated at H1, suffer poor signal transfer from H3 to H4 (due to $^3J_{H3,H4}$ <3 Hz). In most cases this problem could be partially circumvented by irradiating at other proton signals (H4, H5 or H6).

The chemical shift and coupling constant data are presented in three sets of two tables (Tables 2–7). The first table of each set (Tables, 2, 4 and 6) details the ^{1}H chemical shift and multiplicity for each of the antigens; the second table of each set (Tables 3, 5

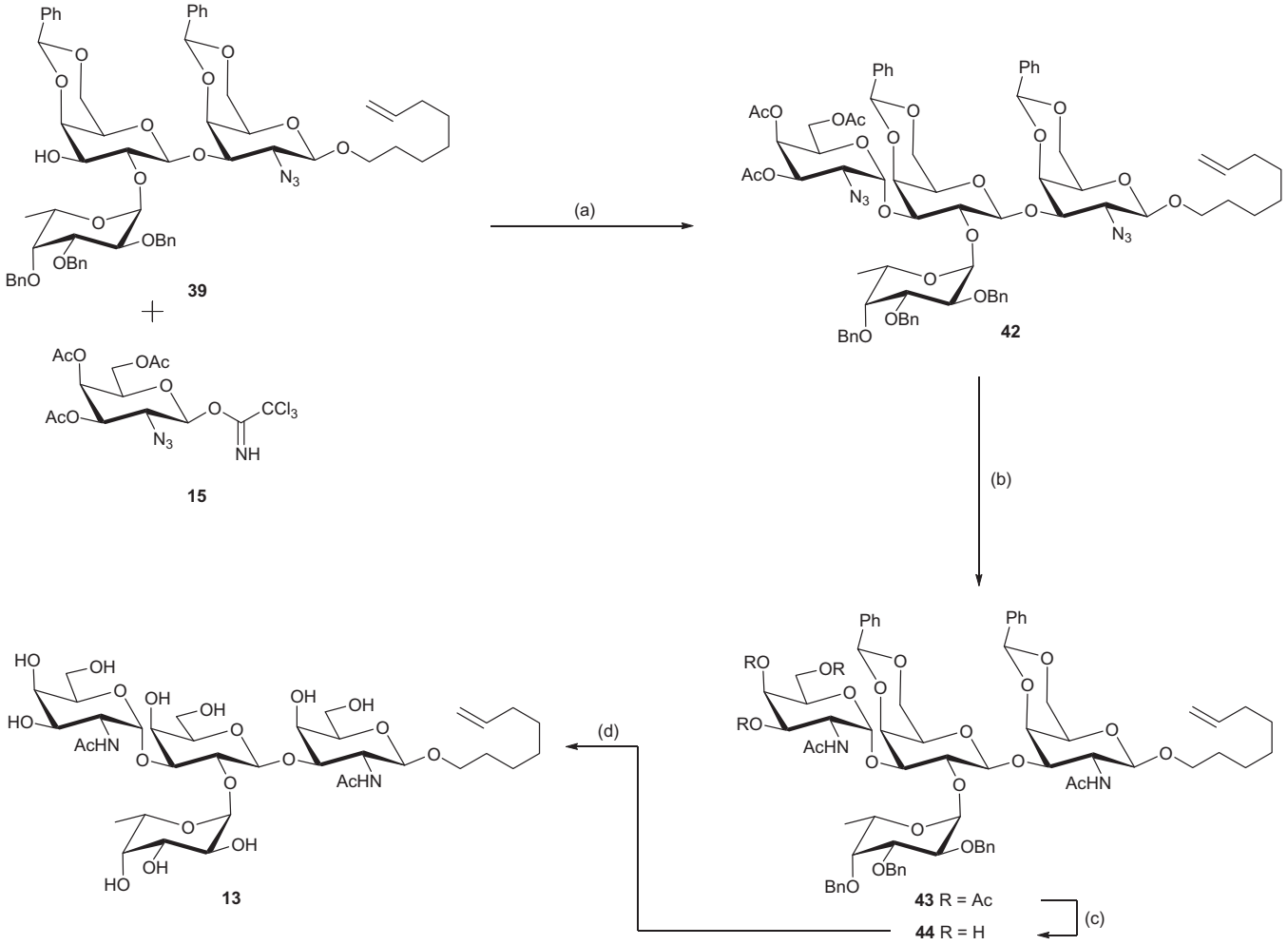


Scheme 6. Reagents: (a) TMSOTf, 4 Å MS, CH_2Cl_2; (b) $NaOCH_3$, CH_3OH, 76%; (c) $(CH_3)_3CCOCl$, pyridine, 98%; (d) TMSOTf, 4 Å MS, Et_2O, 75%; (e) $LiOCH_3$, CH_3OH, 80%.



Scheme 7. Reagents: (a) (i) AcSH, pyridine; (ii) $NaOCH_3$, CH_3OH, 60%; (b) Na, NH_3, CH_3OH, THF, 87%; (c) Pd–C, H_2, CH_3OH, 73%.

and 7) details the ^1H–^1H coupling constants. Figure 6 details the nomenclature system used for the NMR spectroscopic data, using tetrasaccharide **14** as an example. The work by Duus and co-workers, described above, showed that the H3, H5 and H6 signals of the fucose on the H type I antigen were the most prone to variation, albeit small.[14] In the case of the A and B antigens



Scheme 8. Reagents: (a) TMSOTf, 4 Å MS, Et_2O, 79%; (b) AcSH, pyridine, 83%; (c) $NaOCH_3$, CH_3OH, 92%; (d) Na, NH_3, CH_3OH, THF, 91%.

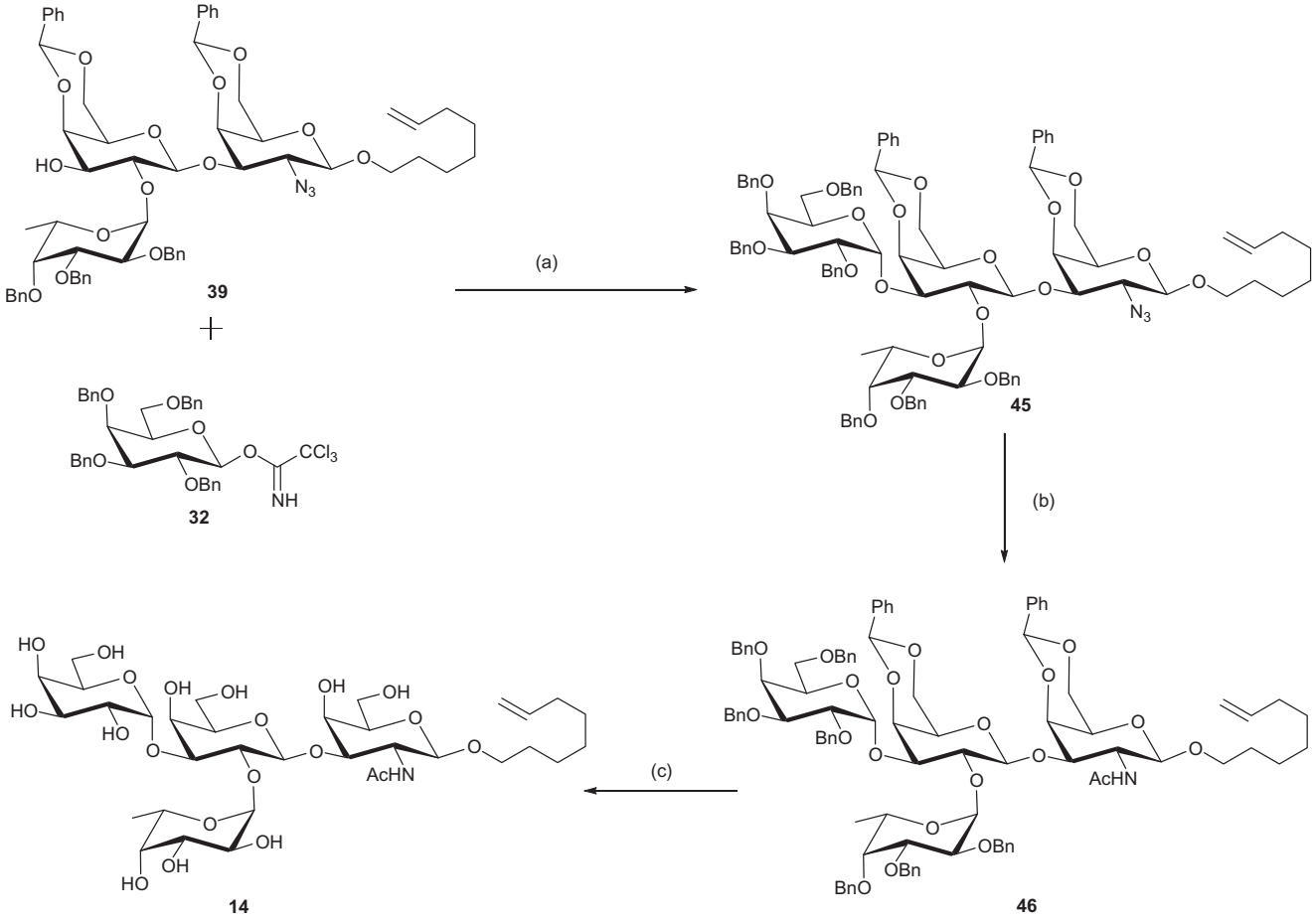
studied here (Tables 2–4), there is very little variation in both the chemical shifts and coupling constants. The only significant variation observed was in the chemical shifts of the A and B type V antigens. The chemical shift of the H5 proton of the fucose residue of A type V resonated at 4.65 ppm, a deviation of 0.33 ppm from the 4.32 ppm average (Table 2). A similar observation was made of the fucose H5 in the B type antigen series (Table 4). The H3 and H6 protons of the fucose residue also showed some minor deviation in the case of the A and B type V antigens, although this was far less pronounced than was the case with the H5 proton. In the H antigen series, very little deviation across the subtypes was observed, even in the fucose H3, H5 and H6 signals. As shown in Tables 3, 5 and 7, the ^1H–^1H coupling constants across all antigen subtypes were also nearly identical.

In addition to the 1D-ge-CSSF-TOCSY experiments, we also conducted 2D TROESY experiments on both the A type IV **13** and A type V **47** antigens. The A type V antigen was chosen as it showed the most significant deviation in ^1H NMR chemical shifts in the previous experiments. The A type IV antigen was chosen as a point of comparison. Not surprisingly, the vast majority of the interactions were identical in both the A type IV and the A type V antigens. The only difference is that in the case of the A type IV antigen a strong ROSEY interaction between H1′ and H5 was observed. A summary of the main interactions is shown in Figure 5, more detailed ROSEY data are included in Supplementary data.

The conclusion that can be drawn from the chemical shift and coupling constant data reported in Tables 2–7 is that, with a very limited number of exceptions, the reducing end moiety in these antigen subtypes does not appear to influence significantly the conformation of the canonical A, B and O(H) antigens. Therefore, it does not appear that differential recognition of these structures by various proteins or receptors, such as the different catalytic activities of GTA_1 and GTA_2 observed by Clausen and co-workers,[11] arises from conformational differences.

2.4. Conclusions

In summary, we report the linear synthesis of the ABO type III and IV histo-blood group antigens with a 7-octen-1-yl linker. The syntheses described here complete the goal of preparing all 18 known ABO antigens attached to a common aglycone.[21,22] The high yields and stereoselectivity observed with the trichloroacetimidate glycosylations ensured each antigen was prepared in an efficient manner. Of particular note was the glycosylation using the β-L-fucopyranosyl trichloroacetimidate **24**, originally developed by Gerhard and Schmidt,[26] which was used to stereoselectively introduce the α-L-fucopyranosyl moiety in **25** and **38**. The use of an azido precursor for the amino group enabled the later conversion to an *N*-acetyl group using mild conditions. In addition, Birch reduction was effectively used on several occasions to remove all of the benzyl ethers and benzylidene acetals without any reduction of the 7-octen-1-yl aglycone. Finally, NMR analysis was conducted on all 18 ABO antigens. The ^1H chemical shift and ^1H–^1H coupling constant data obtained indicate that residue at the reducing end of



Scheme 9. Reagents: (a) TMSOTf, 4 Å MS, Et_2O, 86%; (b) AcSH, pyridine, 91%; (c) Na, NH_3, CH_3OH, THF, 94%.

the molecule influence the global conformation of the molecule very little. One exception is the chemical shift for H5 of the fucose residue of the A type V tetrasaccharide, which resonated around 4.65 ppm, a deviation of 0.33 ppm from the 4.32 ppm average. The significance of this observation is currently unclear.

3. Experimental

All reagents were purchased from commercial sources and were used without further purification, unless otherwise stated. Reaction solvents were purchased and were used without purification; dry solvents were purified by successive passage through columns of alumina and copper under nitrogen. All reactions were carried out at room temperature under a positive pressure of argon, unless otherwise stated. Thin layer chromatography (TLC) was performed on Merck Silica Gel 60 F_{254} aluminum-backed plates that were stained by heating (>200°) with either *p*-anisaldehyde in 5% sulfuric acid in EtOH or 10% ammonium molybdate in 10% sulfuric acid. Unless otherwise indicated, all column chromatography was performed on Silica Gel 60 (40–60 μM). C_{18} silica gel (35–70 μM) was manufactured by Toronto Research Chemicals. Optical rotations were measured at 589 nm, at 22 ± 2 °C and are in units of deg dm^{-1} cm^3 g^{-1}, in all cases the concentrations are in the units g/100 mL.

^1H NMR spectra were recorded at 400 and 500 MHz, chemical shifts were referenced to the peak for TMS (0.0 ppm, $CDCl_3$) or CD_3OD (3.30 ppm, CD_3OD). For final compounds, NMR analysis was conducted using 1D-ge-CSSF-TOCSY[29,30] at 600 MHz, to identify individual proton resonances. Samples for 1D-ge-CSSF-TOCSY experiments were prepared in CD_3OD at a concentration of 21 mg/mL. Spectra were obtained using CD_3OD as the solvent as spectra obtained using D_2O exhibited significant line broadening that interfered with the selective irradiation of the desired proton. On average, each of the 18 antigens required approximately 8 h of instrument time on a Varian Direct Drive three channel 600 MHz spectrometer. ^{13}C NMR (APT) spectra were recorded at 125 or 100 MHz, and ^{13}C chemical shifts were referenced to the peak for internal $CDCl_3$ (77.1 ppm, $CDCl_3$) or CD_3OD (49.0, CD_3OD). All spectra were recorded in $CDCl_3$ unless specified otherwise. Melting points were measured using a PerkinElmer Thermal Analysis. Electrospray mass spectra were recorded on samples suspended in mixtures of THF with CH_3OH and added NaCl.

3.1. 7-Octen-1-yl 2-acetamido-3-*O*-(3-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (9)

A solution of the tetrasaccharide **30** (400 mg, 0.283 mmol) in CH_3OH (20 mL) was treated with a catalytic amount of $NaOCH_3$ in CH_3OH and the solution was stirred for 2 h. The solution was then neutralized with Amberlite IR 120 (H^+), filtered and the residue subjected to flash chromatography (CH_2Cl_2–CH_3OH 10:1) to afford **31** (360 mg, 99%) as a colorless oil. Redistilled liquid ammonia (20 mL) was collected in a flask cooled to (−78 °C) and treated with sodium until the blue color persisted. A solution of the tetrasaccharide **31** (271 mg, 0.210 mmol) in THF (4 mL) and CH_3OH (42 μL, 1.05 mmol) was added dropwise and the mixture was stirred

Table 2
^{1}H Assignments (ppm) of the A type I–VI antigens, recorded at 600 MHz with CD_3OD as solvent

Proton	A Type I	A Type II	A Type III	A Type IV	A Type V	A Type VI
H1‴	5.15 (d)	5.15 (d)	5.13 (d)	5.15 (d)	5.15 (d)	5.15 (d)
H2‴	4.29 (dd)	4.32 (dd)	4.31 (dd)	4.30 (dd)	4.32 (dd)	4.32 (dd)
H3‴	3.85 (dd)	3.82 (dd)	3.87 (dd)	3.84 (dd)	3.83 (dd)	3.82 (dd)
H4‴	3.87 (d)	3.89 (d)	3.90 (d)	3.88 (d)	3.90 (d)	3.89 (d)
H5‴	4.20 (dd)	4.16 (dd)	4.27–4.24 (m)	4.21–4.17 (m)	4.17 (dd)	4.16 (dd)
H6‴	3.75 (dd)	3.76 (dd)	3.74–3.67 (m)	3.68 (dd)	3.75 (dd)	3.76 (dd)
H6‴	3.68 (dd)	3.68 (dd)	3.74–3.67 (m)	3.79–3.72 (m)	3.69 (dd)	3.69 (dd)
H1″	5.23 (s)	5.33 (d)	5.20 (d)	5.26 (d)	5.29 (d)	5.34 (d)
H2″	3.69 (dd)	3.72 (dd)	3.73 (dd)	3.70 (dd)	3.71 (dd)	3.73 (dd)
H3″	3.65 (dd)	3.68 (dd)	3.63 (dd)	3.59 (dd)	3.81 (dd)	3.67 (dd)
H4″	3.72 (d)	3.69 (d)	3.63 (d)	3.73 (d)	3.71 (d)	3.69 (d)
H5″	4.36 (q)	4.32 (q)	4.31 (q)	4.32 (q)	4.65 (q)	4.31 (q)
H6″	1.19 (d)	1.21 (d)	1.23 (d)	1.22 (d)	1.13 (d)	1.21 (d)
H1′	4.57 (d)	4.52 (d)	4.64 (d)	4.56 (d)	4.66 (d)	4.51 (d)
H2′	3.91 (dd)	3.99 (dd)	3.91 (dd)	3.98 (dd)	4.01 (dd)	4.00 (dd)
H3′	3.86 (dd)	3.90 (dd)	3.87 (dd)	3.87 (dd)	3.90 (dd)	3.91 (dd)
H4′	4.09 (d)	4.09 (d)	4.09 (d)	4.10 (d)	4.11 (d)	4.11 (d)
H5′	3.49 (dd)	3.29–3.25 (m)	3.48 (dd)	3.51 (dd)	3.48 (dd)	3.53 (dd)
H6′	3.77–3.73 (m)	3.81–3.77 (m)	3.73 (dd)	3.78–3.71 (m)	3.73 (dd)	3.76 (dd)
H6′	3.66–3.65 (m)	3.72–3.66 (m)	3.69 (d)	3.78–3.71 (m)	3.69 (dd)	3.67 (dd)
H1	4.25–4.20 (m)	4.39 (d)	4.89 (d)	4.19 (d)	4.23–4.20 (m)	4.26 (d)
H2	3.86–3.79 (m)	3.71 (dd)	4.25 (dd)	4.07 (dd)	3.61–3.54 (m)	3.25 (dd)
H3	3.86–3.79 (m)	3.69 (dd)	3.97 (dd)	3.79–3.72 (m)	3.61–3.54 (m)	3.45 (dd)
H4	3.41–3.37 (m)	3.59 (dd)	4.19 (d)	4.10 (d)	4.11 (s)	3.65 (dd)
H5	3.32–3.28 (m)	3.28 (dd)	3.84 (dd)	3.46 (dd)	3.54–3.50 (m)	3.28 (ddd)
H6	3.78–3.74 (m)	3.90 (d)	3.74–3.67 (m)	3.73 (dd)	3.75–3.71 (m)	3.89 (dd)
H6	3.69–3.66 (m)	3.78 (d)	3.74–3.67 (m)	3.69 (dd)	3.75–3.71 (m)	3.75 (dd)
CH_2O	3.91–3.87 (m)	3.86–3.83 (m)	3.74–3.66 (m)	3.90–3.83 (m)	3.89–3.86 (m)	3.56–3.51 (m)
CH_2O	3.44–3.40 (m)	3.45–3.41 (dt)	3.37–3.32 (dt)	3.45–3.38 (m)	3.57–3.53 (m)	3.91–3.85 (m)
CH=CH_2	4.99–4.95 (m)	5.00–4.94 (m)	5.00–4.95 (m)	4.99–4.94 (m)	5.00–4.95 (m)	5.00–4.95 (m)
CH=CH_2	4.91–4.89 (m)	4.92–4.88 (m)	4.92–4.88 (m)	4.92–4.88 (m)	4.93–4.88 (m)	4.92–4.88 (m)
CH=CH_2	5.84–5.76 (dddd)	5.84–5.76 (dddd)	5.84–5.76 (dddd)	5.80 (dddd)	5.85–5.76 (dddd)	5.85–5.76 (dddd)
$(CH_2)_5$	2.08–2.01 (m)	2.07–2.01 (m)	2.07–2.02 (m)	2.06–2.01 (m)	2.07–2.01 (m)	2.08–2.01 (m)
$(CH_2)_5$	1.57–1.47 (m)	1.58–1.48 (m)	1.60–1.53 (m)	1.58–1.47 (m)	1.65–1.58 (m)	1.65–1.57 (m)
$(CH_2)_5$	1.42–1.26 (m)	1.42–1.27 (m)	1.44–1.29 (m)	1.42–1.27 (m)	1.43–1.29 (m)	1.43–1.29 (m)
CH_3CO	1.99 (s)	2.00 (s)	1.99 (s)	2.00 (s)	2.00 (s)	2.00 (s)
CH_3CO	1.99 (s)	1.96 (s)	1.98 (s)	1.98 (s)		

Table 3
$^2J_{H,H}$, $^3J_{H,H}$ (Hz) of the A type I–VI antigens, recorded at 600 MHz with CD_3OD as solvent

Coupling	A Type I	A Type II	A Type III	A Type IV	A Type V	A Type VI
$^3J_{H\text{-}1‴,H\text{-}2‴}$	3.8	3.7	3.7	3.7	3.7	3.6
$^3J_{H\text{-}2‴,H\text{-}3‴}$	10.8	11.0	10.8	10.9	11.0	11.0
$^3J_{H\text{-}3‴,H\text{-}4‴}$	3.4	3.0	3.2	3.2	3.1	3.0
$^3J_{H\text{-}4‴,H\text{-}5‴}$	0.0	0.0	0.0	0.0	0.0	0.0
$^3J_{H\text{-}5‴,H\text{-}6a‴}$	7.6	7.2	m	4.2	7.4	7.4
$^3J_{H\text{-}5‴,H\text{-}6b‴}$	4.1	4.5	m	m	4.5	4.3
$^2J_{H\text{-}6a‴,H\text{-}6b‴}$	11.7	11.5	m	11.6	11.6	11.5
$^3J_{H\text{-}1″,H\text{-}2″}$	3.9	3.9	4.0	4.1	3.9	3.9
$^3J_{H\text{-}2″,H\text{-}3″}$	10.5	9.5	9.8	10.2	10.2	9.9
$^3J_{H\text{-}3″,H\text{-}4″}$	3.1	3.3	3.5	3.2	3.2	3.1
$^3J_{H\text{-}5″,H\text{-}6″}$	6.5	6.6	6.6	6.6	6.4	6.6
$^3J_{H\text{-}1′,H\text{-}2′}$	7.3	7.7	7.2	7.5	7.7	7.7
$^3J_{H\text{-}2′,H\text{-}3′}$	9.9	9.8	9.6	9.9	9.8	9.8
$^3J_{H\text{-}3′,H\text{-}4′}$	3.1	3.0	2.9	3.1	3.0	2.9
$^3J_{H\text{-}5′,H\text{-}6a′}$	7.9	m	6.8	6.0	7.0	7.1
$^3J_{H\text{-}5′,H\text{-}6b′}$	4.3	m	5.6	6.0	5.1	4.9
$^2J_{H\text{-}6a′,H\text{-}6b′}$	m	m	11.2	m	11.4	11.3
$^3J_{H\text{-}1,H\text{-}2}$	m	8.4	3.6	8.4	m	7.8
$^3J_{H\text{-}2,H\text{-}3}$	m	9.3	11.2	10.8	m	8.5
$^3J_{H\text{-}3,H\text{-}4}$	m	8.9	3.1	3.1	m	9.1
$^3J_{H\text{-}4,H\text{-}5}$	m	9.8	0.0	0.0	m	9.4
$^3J_{H\text{-}5,H\text{-}6a}$	m	4.9	6.1	6.0	m	4.9
$^3J_{H\text{-}5,H\text{-}6b}$	m	0.0	6.1	6.0	m	1.1
$^2J_{H\text{-}6a,H\text{-}6b}$	m	11.2	m	m	m	11.9
CH_2O	m	9.7, 6.6	10.0, 6.4	m	m	m
CH=CH_2	17.1, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7

Table 4
^{1}H Assignments (ppm) of the B type I–VI antigens, recorded at 600 MHz with CD_3OD as solvent

Proton	B Type I	B Type II	B Type III	B Type IV	B Type V	B Type VI
H1‴	5.14 (d)	5.15 (d)	5.14 (d)	5.14 (d)	5.15 (d)	5.15 (d)
H2‴	3.83 (dd)	3.84 (dd)	3.86–3.80 (m)	3.84 (dd)	3.85 (dd)	3.85 (dd)
H3‴	3.81 (dd)	3.78 (dd)	3.86–3.80 (m)	3.80 (dd)	3.80 (dd)	3.81 (dd)
H4‴	3.89 (dd)	3.9 (d)	3.91 (d)	3.89 (d)	3.91 (d)	3.90 (d)
H5‴	4.16 (dd)	4.14–4.10 (m)	4.23 (dd)	4.16 (dd)	4.16 (dd)	4.14–4.10 (m)
H6‴	3.73 (dd)	3.76–3.71 (m)	3.76–3.71 (m)	3.75–3.71 (m)	3.73 (dd)	3.75–3.72 (m)
H6‴	3.68 (dd)	3.70–3.66 (m)	3.71–3.67 (m)	3.70–3.66 (m)	3.69 (dd)	3.70–3.67 (m)
H1″	5.21 (d)	5.32 (m)	5.20 (d)	5.25 (d)	5.29 (d)	5.33 (d)
H2″	3.7 (dd)	3.73 (m)	3.71 (dd)	3.71 (dd)	3.72 (dd)	3.73 (dd)
H3″	3.65 (dd)	3.69–3.66 (m)	3.63 (dd)	3.58 (dd)	3.80 (dd)	3.69–3.66 (m)
H4″	3.71 (d)	3.69–3.66 (m)	3.61 (d)	3.72 (d)	3.71 (d)	3.69–3.66 (m)
H5″	4.45 (q)	4.29 (q)	4.29 (q)	4.31 (q)	4.61 (q)	4.29 (q)
H6″	1.18 (d)	1.20 (d)	1.22 (d)	1.21 (d)	1.20 (d)	1.19 (d)
H1′	4.60–4.56 (m)	4.53 (d)	4.63 (d)	4.57 (d)	4.66 (d)	4.52 (d)
H2′	3.93–3.87 (m)	3.98 (dd)	3.93–3.86 (m)	3.98 (dd)	4.01 (dd)	3.98 (dd)
H3′	3.93–3.87 (m)	3.94 (dd)	3.93–3.86 (m)	3.91 (dd)	3.93 (dd)	3.94 (dd)
H4′	4.10 (s)	4.12 (d)	4.10 (d)	4.11 (d)	4.13 (d)	4.13 (d)
H5′	3.54 (dd)	3.60–3.54 (m)	3.53 (dd)	3.53–3.48 (m)	3.53 (m)	3.58–3.54 (m)
H6′	3.79 (dd)	3.79 (dd)	3.75–3.53 (m)	3.77–3.71 (m)	3.74–3.65 (m)	3.72–3.65 (m)
H6′	3.68 (dd)	3.67 (dd)	3.75–3.53 (m)	3.77–3.71 (m)	3.74–3.65 (m)	3.84–3.75 (m)
H1	4.25–4.19 (m)	4.36 (d)	4.87 (d)	4.19 (d)	4.23–4.20 (m)	4.26 (d)
H2	3.86–3.77 (m)	3.70 (dd)	4.24 (dd)	4.07 (dd)	3.61–3.55 (m)	3.25 (dd)
H3	3.86–3.77 (m)	3.59 (dd)	3.95 (dd)	3.77 (dd)	3.61–3.55 (m)	3.46 (dd)
H4	3.41–3.37 (m)	3.66 (dd)	4.18 (d)	4.08 (d)	4.12 (s)	3.65 (dd)
H5	3.31–3.28 (m)	3.30–3.26 (m)	3.84 (dd)	3.53–3.48 (m)	3.54–3.51 (m)	3.28 (ddd)
H6	3.93–3.83 (m)	3.90 (dd)	3.72–3.69 (m)	3.77–3.71 (m)	3.74–3.65 (m)	3.89 (dd)
H6	3.76–3.64 (m)	3.77 (dd)	3.72–3.69 (m)	3.77–3.71 (m)	3.74–3.65 (m)	3.76 (dd)
CH_2O	3.92–3.83 (m)	3.91–3.83 (m)	3.74–3.66 (m)	3.90–3.83 (m)	3.91–3.85 (m)	3.92–3.85 (m)
CH_2O	3.46–3.37 (m)	3.45 (dt)	3.35 (dt)	3.42 (dt)	3.59–3.51 (m)	3.57–3.51 (m)
CH=CH_2	4.99–4.95 (m)	5.00–4.95 (m)	4.99–4.95 (m)	5.00–4.94 (m)	5.00–4.95 (m)	4.99–4.94 (m)
CH=CH_2	4.92–4.89 (m)	4.93–4.88 (m)	4.92–4.89 (m)	4.92–4.88 (m)	4.93–4.88 (m)	4.92–4.87 (m)
C*H*=CH_2	5.84–5.75 (dddd)	5.84–5.76 (dddd)	5.80 (dddd)	5.80 (dddd)	5.84–5.76 (dddd)	5.84–5.76 (dddd)
$(CH_2)_5$	2.07–2.01 (m)	2.08–2.01 (m)	2.07–2.01 (m)	2.07–2.01 (m)	2.07–2.01 (m)	2.08–1.99 (m)
$(CH_2)_5$	1.57–1.46 (m)	1.58–1.49 (m)	1.60–1.54 (m)	1.59–1.46 (m)	1.65–1.59 (m)	1.66–1.57 (m)
$(CH_2)_5$	1.42–1.27 (m)	1.43–1.25 (m)	1.45–1.27 (m)	1.43–1.27 (m)	1.43–1.31 (m)	1.43–1.24 (m)
CH_3CO	1.99 (s)	1.95 (s)	1.99 (s)	1.99 (s)	2.00 (s)	
CH_3CO						

Table 5
$^2J_{H,H}$, $^3J_{H,H}$ (Hz) of the B type I–VI antigens, recorded at 600 MHz with CD_3OD as solvent

Coupling	B Type I	B Type II	B Type III	B Type IV	B Type V	B Type VI
$^3J_{H\text{-}1‴,H\text{-}2‴}$	3.5	3.8	2.8	3.6	3.7	3.7
$^3J_{H\text{-}2‴,H\text{-}3‴}$	10.2	10.1	m	10.1	10.1	10.1
$^3J_{H\text{-}3‴,H\text{-}4‴}$	3.1	2.9	1.3	3.0	3.1	3.1
$^3J_{H\text{-}4‴,H\text{-}5‴}$	0.8	0.0	0.0	0.0	0.0	0.0
$^3J_{H\text{-}5‴,H\text{-}6a‴}$	7.3	m	6.7	6.7	7.1	m
$^3J_{H\text{-}5‴,H\text{-}6b‴}$	4.3	m	5.7	4.6	4.6	m
$^2J_{H\text{-}6a‴,H\text{-}6b‴}$	11.4	m	m	m	11.4	m
$^3J_{H\text{-}1″,H\text{-}2″}$	4.1	3.9	4.0	4.1	3.9	4.0
$^3J_{H\text{-}2″,H\text{-}3″}$	9.3	9.9	9.4	10.2	10.1	10.7
$^3J_{H\text{-}3″,H\text{-}4″}$	3.3	m	3.2	3.0	3.2	m
$^3J_{H\text{-}5″,H\text{-}6″}$	6.6	6.6	6.5	6.5	6.6	6.6
$^3J_{H\text{-}1′,H\text{-}2′}$	m	7.4	6.7	7.6	7.6	7.7
$^3J_{H\text{-}2′,H\text{-}3′}$	m	9.7	m	9.6	9.6	9.7
$^3J_{H\text{-}3′,H\text{-}4′}$	0.0	2.7	2.0	2.8	2.9	2.9
$^3J_{H\text{-}5′,H\text{-}6a′}$	7.8	7.3	6.5	m	m	m
$^3J_{H\text{-}5′,H\text{-}6b′}$	4.4	3.9	5.3	m	m	m
$^2J_{H\text{-}6a′,H\text{-}6b′}$	11.4	11.6	m	m	m	m
$^3J_{H\text{-}1,H\text{-}2}$	m	8.4	3.7	8.4	m	7.8
$^3J_{H\text{-}2,H\text{-}3}$	m	10.4	11.1	10.8	m	9.2
$^3J_{H\text{-}3,H\text{-}4}$	m	8.8	3.0	3.0	m	9.3
$^3J_{H\text{-}4,H\text{-}5}$	m	9.2	0.0	0.0	m	9.3
$^3J_{H\text{-}5,H\text{-}6a}$	m	5.0	5.5	m	m	4.8
$^3J_{H\text{-}5,H\text{-}6b}$	m	1.8	5.5	m	m	1.7
$^2J_{H\text{-}6a,H\text{-}6b}$	m	11.9	m	m	m	11.9
CH_2O	m	9.7, 6.6	10.0, 6.3	9.6, 6.7	m	m
C*H*=CH_2	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7

Table 6
^{1}H Assignments (ppm) of the O type I–VI antigens, recorded at 600 MHz with CD_3OD as solvent

Proton	H Type I	H Type II	H Type III	H Type IV	H Type V	H Type VI
H1″	5.20 (d)	5.21 (d)	5.12 (d)	5.21 (d)	5.18 (d)	5.23 (d)
H2″	3.73 (dd)	3.77–3.71 (m)	3.76 (dd)	3.74 (dd)	3.76 (dd)	3.76 (dd)
H3″	3.68 (dd)	3.77–3.71 (m)	3.70 (dd)	3.66 (dd)	3.79 (dd)	3.73 (dd)
H4″	3.71–3.69 (m)	3.66 (d)	3.65 (d)	3.69 (d)	3.67 (d)	3.66 (d)
H5″	4.29 (q)	4.17 (q)	4.22 (q)	4.25 (q)	4.35 (q)	4.17 (q)
H6″	1.19 (d)	1.20 (d)	1.28 (d)	1.23 (d)	1.23 (d)	1.20 (d)
H1′	4.54–4.51 (m)	4.50–4.44 (m)	4.59 (d)	4.53 (d)	4.63 (d)	4.47 (d)
H2′	3.71–3.65 (m)	3.75–3.68 (m)	3.69–3.64 (m)	3.71 (dd)	3.72 (dd)	3.73 (dd)
H3′	3.71–3.65 (m)	3.75–3.68 (m)	3.69–3.64 (m)	3.67 (dd)	3.69 (dd)	3.70 (dd)
H4′	3.80–3.78 (m)	3.78 (d)	3.82 (d)	3.80 (d)	3.83 (d)	3.78 (d)
H5′	3.52 (dd)	3.54 (dd)	3.54 (dd)	3.53–3.48 (m)	3.52 (dd)	3.55–3.52 (m)
H6′	3.67–3.64 (m)	3.65–3.61 (m)	3.75–3.66 (m)	3.82–3.68 (m)	3.78–3.71 (m)	3.69–3.62 (m)
H6′	3.77–3.74 (m)	3.75–3.73 (m)	3.75–3.66 (m)	3.82–3.68 (m)	3.78–3.71 (m)	3.69–3.62 (m)
H1	4.28–4.22 (m)	4.37 (d)	4.96 (d)	4.23 (d)	4.26 (d)	4.26 (d)
H2	3.84–3.78 (m)	3.72 (dd)	4.25 (dd)	4.10 (dd)	3.64 (dd)	3.24 (dd)
H3	3.84–3.78 (m)	3.59 (dd)	3.98 (dd)	3.82 (dd)	3.60 (dd)	3.48 (dd)
H4	3.42–3.38 (m)	3.69 (dd)	4.17 (d)	4.06 (d)	4.10 (d)	3.65 (dd)
H5	3.32–3.28 (m)	3.33–3.29 (m)	3.83 (dd)	3.51 (dd)	3.54–3.52 (m)	3.31 (ddd)
H6	3.74–3.65 (m)	3.89 (dd)	3.74–3.68 (m)	3.82–3.68 (m)	3.78–3.71 (m)	3.70–3.62 (m)
H6	3.92–3.84 (m)	3.83 (dd)	3.74–3.68 (m)	3.82–3.68 (m)	3.78–3.71 (m)	3.90–3.85 (m)
CH_2O	3.45–3.37 (m)	3.47–3.42 (m)	3.36 (dt)	3.43 (dt)	3.59–3.51 (m)	3.55–3.52 (m)
CH_2O	3.91–3.83 (m)	3.91–3.82 (dt)	3.74–3.65 (m)	3.87 (m)	3.91–3.86 (m)	3.91–3.82 (m)
CH=CH_2	4.99–4.93 (m)	4.99–4.94 (m)	5.00–4.94 (m)	4.99–4.94 (m)	5.00–4.95 (m)	5.00–4.95 (m)
CH=CH_2	4.92–4.88 (m)	4.92–4.88 (m)	4.93–4.89 (m)	4.93–4.89 (m)	4.92–4.88 (m)	4.92–4.88 (m)
CH=CH_2	5.84–5.75 (dddd)	5.83–5.75 (dddd)	5.80 (dddd)	5.80 (dddd)	5.80 (dddd)	5.80 (dddd)
$(CH_2)_5$	2.07–2.00 (m)	2.07–2.01 (m)	2.08–2.02 (m)	2.08–2.01 (m)	2.07–2.01 (m)	2.07–2.00 (m)
$(CH_2)_5$	1.58–1.46 (m)	1.58–1.48 (m)	1.59–1.51 (m)	1.59–1.47 (m)	1.66–1.57 (m)	1.65–1.57 (m)
$(CH_2)_5$	1.41–1.26 (m)	1.41–1.28 (m)	1.42–1.30 (m)	1.43–1.27 (m)	1.43–1.26 (m)	1.43–1.26 (m)
CH_3CO	1.97 (s)	1.96 (s)	1.98 (s)	1.96 (s)		

Table 7
$^2J_{H,H}$, $^3J_{H,H}$ (Hz) of the O type I–VI antigens, recorded at 600 MHz with CD_3OD as solvent

Coupling	H Type I	H Type II	H Type III	H Type IV	H Type V	H Type VI
$^3J_{H\text{-}1'',H\text{-}2''}$	3.8	3.3	3.8	3.9	3.3	3.4
$^3J_{H\text{-}2'',H\text{-}3''}$	10.0	m	10.0	10.0	10.2	10.2
$^3J_{H\text{-}3'',H\text{-}4''}$	3.1	2.8	3.3	3.5	2.9	2.8
$^3J_{H\text{-}5'',H\text{-}6''}$	6.6	6.6	6.6	6.5	6.5	6.5
$^3J_{H\text{-}1',H\text{-}2'}$	m	m	6.5	7.3	7.2	6.9
$^3J_{H\text{-}2',H\text{-}3'}$	m	m	m	9.6	9.6	9.4
$^3J_{H\text{-}3',H\text{-}4'}$	m	4.0	2.7	3.1	3.0	3.0
$^3J_{H\text{-}5',H\text{-}6a'}$	7.7	7.6	6.6	m	6.3	m
$^3J_{H\text{-}5',H\text{-}6b'}$	4.3	4.0	5.6	m	4.7	m
$^2J_{H\text{-}6a',H\text{-}6b'}$	m	m	m	m	m	m
$^3J_{H\text{-}1,H\text{-}2}$	m	8.4	3.6	8.4	7.6	7.8
$^3J_{H\text{-}2,H\text{-}3}$	m	10.5	11.2	10.8	9.6	9.2
$^3J_{H\text{-}3,H\text{-}4}$	m	8.8	3.0	3.0	3.0	9.4
$^3J_{H\text{-}4,H\text{-}5}$	m	10.4	0.0	0.0	0.0	9.4
$^3J_{H\text{-}5,H\text{-}6a}$	m	4.4	6.5	6.0	m	4.2
$^3J_{H\text{-}5,H\text{-}6b}$	m	1.9	6.5	6.0	m	1.9
$^2J_{H\text{-}6a,H\text{-}6b}$	m	12.0	m	m	m	m
CH_2O	m	9.6, 6.6	10.0, 6.3	9.7, 6.6	m	m
CH=CH_2	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7	17.0, 10.2, 6.7, 6.7

(−78 °C, 1 h). The reaction was then quenched by the addition of CH_3OH (4 mL) and the ammonia evaporated. The solution was taken up in CH_3OH (100 mL), neutralized with Amberlite IR 120 (H^+), filtered and the residue subjected to C_{18} chromatography (CH_3OH–H_2O 1:1) to afford the fully deprotected tetrasaccharide **9** (170 mg, 96%) as a colorless oil. [α] +253.8 (*c* 0.4, CH_3OH); ^{1}H NMR data see Tables 2 and 3. ^{13}C NMR (CD_3OD, 125.7 MHz): δ_C 174.4 (C=O), 173.3 (C=O), 140.0 (CH_2=*C*H), 114.8 (*C*H_2=CH), 104.2 (C1′), 100.5 (C1″), 98.1 (C1), 93.9 (C1‴), 77.6, 77.4, 76.2, 75.8, 73.4, 72.7, 71.8, 71.6, 70.6, 70.1, 70.0, 69.9, 68.4, 64.9 (C2′, C2‴, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5, C5′, C5″, C5‴), 68.9 (CH=CH_2(CH_2)$_5$*C*H_2O), 63.4, 62.9, 62.5 (C6, C6′, C6‴), 51.4, 50.9 (C2, C2‴), 34.9 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 30.6 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 30.1 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 30.0 (CH=$CH_2$($CH_2$)$_5$$CH_2$O), 27.2 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 22.85 (*C*$H_3$CO), 22.84 (*C*$H_3$CO), 16.8 (C6″). ESIMS: *m/z* Calcd [$C_{36}H_{62}N_2O_{20}$]Na^+: 865.3788. Found: 865.3785.

3.2. 7-Octen-1-yl 2-acetamido-3-*O*-(2-*O*-(α-L-fucopyranosyl)-3-*O*-(α-D-galactopyranosyl)-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (10)

Redistilled liquid ammonia (25 mL) was collected in a flask cooled to −78 °C and treated with sodium until the blue color persisted. A solution of the tetrasaccharide **34** (281 mg, 0.0.175 mmol)

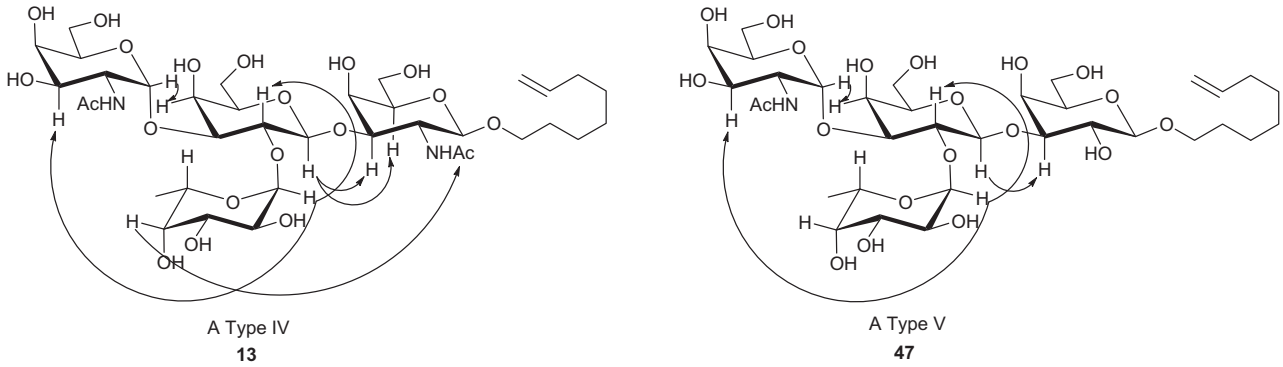


Figure 5. Summary of main ROSEY interactions between **13** and **47**.

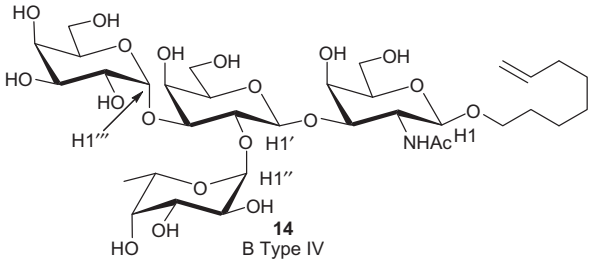


Figure 6. Nomenclature system used for NMR spectroscopic data, using B type IV antigen **14** for illustrative purposes.

in THF (4 mL) and CH_3OH (63 μL, 1.57 mmol) was added dropwise and the solution stirred (−78 °C, 1 h). The reaction was then quenched by the addition of CH_3OH (4 mL) and the ammonia was evaporated. The solution was taken up in CH_3OH (100 mL), neutralized with Amberlite IR 120 (H^+), filtered and the residue subjected to C_{18} chromatography (CH_3OH–H_2O 1:1) to afford the fully deprotected tetrasaccharide **10** (132 mg, 94%) as a colorless oil. [α] +106.8 (*c* 0.7, CH_3OH); ^1H NMR data see Tables 4 and 5. ^{13}C NMR (CD_3OD, 125.7 MHz): δ_C 173.3 (C=O), 140.0 (CH_2=*C*H), 114.8 (*C*H_2=CH), 104.2 (C1′), 100.5, 98.1 (C1, C1″), 96.3 (C1‴), 79.2, 77.6, 76.0, 75.7, 73.4, 73.0, 71.8, 71.6, 71.31, 71.26, 70.0 (3C), 68.3, 65.6 (C2′, C2″, C2‴, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5, C5′, C5″, C5‴), 68.9 (CH=CH_2(CH_2)$_5$*C*H_2O), 63.3, 62.9, 62.5 (C6, C6′, C6‴), 50.9 (C2), 34.9 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 30.5 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 30.1 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 30.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 27.2 (CH=$CH_2$-(*C*$H_2$)$_5$$CH_2$O), 22.9 (*C*$H_3$CO), 16.8 (C6″). ESIMS: *m/z* Calcd $[C_{97}H_{109}NO_{20}]Na^+$: 824.3523. Found: 824.3517.

3.3. 7-Octen-1-yl 2-acetamido-3-*O*-(2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (11)

Redistilled liquid ammonia (10 mL) was collected in a flask cooled to −78 °C and treated with sodium until the blue color persisted. A solution of the trisaccharide **27** (175 mg, 0.161 mmol) in THF (4 mL) and CH_3OH (33 μL, 0.806 mmol) was added dropwise and the solution was stirred (−78 °C, 2 h). The reaction was then quenched by the addition of CH_3OH (4 mL) and the ammonia was evaporated to dryness. The solution was taken up in CH_3OH (100 mL), neutralized with Amberlite IR 120 (H^+), filtered and the residue subjected to C-18 chromatography (CH_3OH–H_2O, 1:1) to afford the fully deprotected trisaccharide **11** as a colorless oil (95 mg, 92%). [α] +32.9 (*c* 0.8, CH_3OH); ^1H NMR data see Tables 6 and 7. ^{13}C NMR (CD_3OD, 125.7 MHz): δ_C 173.4 (C=O), 140.0 (CH_2=*C*H), 114.8 (*C*H_2=CH), 103.7 (C1), 101.9, 98.0 (C1, C1″), 80.8, 77.8, 76.6, 74.9, 73.3, 71.8, 71.6, 70.6, 70.1, 69.1, 69.0 (C2′, C2″, C3, C3′, C3″, C4, C4′, C4″, C5, C5′, C5″), 68.9 (CH=CH_2(CH_2)$_5$*C*H_2O), 62.8, 62.5 (C6, C6′), 51.1 (C2), 34.9 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 30.6 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 30.1 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 30.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 27.2 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 22.8 (*C*$H_3$CO), 16.9 (C6″). ESIMS: *m/z* Calcd $[C_{28}H_{49}NO_{15}]Na^+$: 662.2994. Found: 662.29867.

3.4. 7-Octen-1-yl 2-acetamido-3-*O*-(2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-β-D-galactopyranoside (12)

Redistilled liquid ammonia (10 mL) was collected in a flask cooled to −78 °C and treated with sodium until the blue color persisted. A solution of the trisaccharide **40** (254 mg, 0.2341 mmol) in THF (4 mL) and CH_3OH (47 μL, 1.17 mmol) was added dropwise and the solution was stirred (−78 °C, 2 h). The reaction was then quenched by the addition of CH_3OH (4 mL) and the ammonia was evaporated to dryness. The solution was taken up in CH_3OH (100 mL), neutralized with Amberlite IR 120 (H^+), filtered and the residue subjected to C-18 chromatography (CH_3OH–H_2O, 1:1) to afford the fully deprotected trisaccharide **12** as a colorless oil (130 mg, 87%). [α] −67.2 (*c* 0.4, CH_3OH); ^1H NMR data see Tables 6 and 7. ^{13}C NMR (CD_3OD, 125.7 MHz): δ_C 173.2 (C=O), 140.1 (CH_2=*C*H), 114.8 (*C*H_2=CH), 104.1, 103.7 (C1, C1′), 101.2 (C1″), 79.2, 78.5, 76.8, 76.4, 75.4, 73.5, 71.5, 70.6, 70.4, 69.7, 68.3 (C2′, C2″, C3, C3′, C3″, C4, C4′, C4″, C5, C5′, C5″), 70.5 (CH=CH_2(CH_2)$_5$*C*H_2O), 62.6 (2C, C6, C6′), 52.7 (C2), 34.9 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 30.7 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 30.2 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 30.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 27.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 23.4 (*C*$H_3$CO), 16.7 (C6″). ESIMS: *m/z* Calcd $[C_{28}H_{49}NO_{15}]Na^+$: 662.2994. Found: 662.2995.

3.5. 7-Octen-1-yl 2-acetamido-3-*O*-(3-*O*-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-β-D-galactopyranoside (13)

A solution of tetrasaccharide **43** (490 mg, 0.346 mmol) in CH_3OH (20 mL) was treated with a catalytic amount of $NaOCH_3$ in CH_3OH and the solution was stirred for 2 h. The solution was then neutralized with Amberlite IR 120 (H^+), filtered and the residue subjected to flash chromatography (CH_2Cl_2–CH_3OH 10:1) to afford **44** (410 mg, 92%) as a colorless oil. Redistilled liquid ammonia (20 mL) was collected in a flask cooled to (−78 °C) and treated with sodium until the blue color persisted. A solution of the tetrasaccharide **44** (228 mg, 0.177 mmol) in THF (4 mL) and CH_3OH (36 μL, 0.885 mmol) was added dropwise and the mixture was stirred (−78 °C, 1 h). The reaction was then quenched by the addition of CH_3OH (4 mL) and the ammonia evaporated. The solution was taken up in CH_3OH (100 mL), neutralized with Amberlite IR 120 (H^+), filtered and the residue subjected to C_{18} chromatography (CH_3OH–H_2O 1:1) to afford the fully deprotected tetrasaccharide **13** (135 mg, 91%) as a colorless oil. [α] +52.6 (*c* 0.9, CH_3OH); ^1H NMR data see Tables 2 and 3. ^{13}C NMR (CD_3OD, 125.7 MHz): δ_C

174.4 (C=O), 173.3 (C=O), 140.1 (CH_2=CH), 114.7 (CH_2=CH), 104.3, 104.1 (C1, C1′), 100.1 (C1″), 93.5 (C1‴), 79.6, 77.7, 76.5, 76.4, 74.0, 72.8, 71.6, 70.6, 70.03, 69.98, 69.9, 68.0, 64.8 (C2′, C2″, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5, C5′, C5″, C5‴), 70.6 (CH=CH_2(CH_2)$_5$$CH_2$O), 63.5, 62.6, 62.5 (C6, C6′, C6‴), 52.5, 51.4 (C2, C2‴), 34.9 (CH=CH_2(CH_2)$_5$$CH_2$O), 30.7 (CH=$CH_2$($CH_2$)$_5$$CH_2$O), 30.2 (CH=$CH_2$($CH_2$)$_5$$CH_2$O), 30.0 (CH=$CH_2$($CH_2$)$_5$$CH_2$O), 27.0 (CH=$CH_2$($CH_2$)$_5$$CH_2$O), 22.8 ($CH_3$CO), 16.6 (C6″). ESIMS: *m/z* Calcd [$C_{36}H_{62}N_2O_{20}$]Na^+: 865.3788. Found: 865.3784.

3.6. 7-Octen-1-yl 2-acetamido-3-*O*-(2-*O*-(α-L-fucopyranosyl)-3-*O*-(α-D-galactopyranosyl)-β-D-galactopyranosyl)-2-deoxy-β-D-galactopyranoside (14)

Redistilled liquid ammonia (20 mL) was collected in a flask cooled to (−78 °C) and treated with sodium until the blue color persisted. A solution of the tetrasaccharide **46** (281 mg, 0.175 mmol) in THF (4 mL) and CH_3OH (63 μL, 1.57 mmol) was added dropwise and the mixture was stirred (−78 °C, 1 h). The reaction was then quenched by the addition of CH_3OH (4 mL) and the ammonia evaporated. The solution was taken up in CH_3OH (100 mL), neutralized with Amberlite IR 120 (H^+), filtered, and the residue was subjected to C_{18} chromatography (CH_3OH–H_2O 1:1) to afford the fully deprotected tetrasaccharide **14** (132 mg, 94%) as a colorless oil. [α] 12.8 (*c* 0.7, CH_3OH); ^1H NMR data see Tables 4 and 5. ^{13}C NMR (CD_3OD, 125.7 MHz): δ_C 173.3 (C=O), 140.1 (CH_2=CH), 114.7 (CH_2=CH), 104.3, 104.2 (C1, C1′), 100.2 (C1″), 96.1 (C1‴), 79.7, 79.6, 76.4, 76.2, 74.1, 73.5, 73.1, 71.6, 71.3, 70.01, 69.98, 67.9, 65.7 (C2′, C2″, C2‴, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5, C5′, C5″, C5‴), 70.6 (CH=CH_2(CH_2)$_5$$CH_2$O), 34.9 (CH=$CH_2$($CH_2$)$_5$$CH_2$O), 30.7 (CH=$CH_2$-($CH_2$)$_5$$CH_2$O), 30.2 (CH=$CH_2$($CH_2$)$_5$$CH_2$O), 30.0 (CH=$CH_2$($CH_2$)$_5$-$CH_2$O), 27.0 (CH=$CH_2$($CH_2$)$_5$$CH_2$O), 23.4 ($CH_3$CO) 16.6 (C6″). ESIMS: *m/z* Calcd [$C_{34}H_{59}NO_{20}$]Na^+: 824.3523. Found: 824.3515.

3.7. 7-Octen-1-yl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside (18) and 7-Octen-1-yl 2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside (19)

A stirred solution of the trichloroacetimidate[25] **15** (23.12 g, 48.8 mmol) and 7-octen-1-ol (8.88 mL, 59.0 mmol) in dry Et_2O (200 mL) was treated with 4 Å molecular sieves (5 g) and the mixture was stirred (rt, 1 h). The mixture was cooled (−10 °C), treated with TMSOTf (0.5 mL, 2.8 mmol) and allowed to slowly warm to 0 °C (1 h). The mixture was neutralized by the addition of Et_3N (1 mL), filtered, concentrated, and subjected to flash chromatography (EtOAc–hexanes 1:3) to give an inseparable α/β mixture (52:48, ratio determined by ^1H NMR spectroscopy) **16**, which used immediately in the subsequent step. The oil was taken up in CH_3OH (200 mL) and treated with a catalytic amount of $NaOCH_3$ in CH_3OH and the solution stirred (rt, 1 h). The solution was then neutralized with Amberlite IR 120 (H^+) and the mixture filtered; concentration followed by flash chromatography (EtOAc–hexanes 5:1) yielded the triol **17** (13.3 g, 87%) as an inseparable α/β mixture. A solution of the triol **17** (13.3 g, 42.2 mmol) in dry DMF (100 mL) was then treated with benzaldehyde dimethyl acetal (7.6 mL, 50.0 mmol) and *p*-TsOH (300 mg) and the solution stirred (50 °C, 18 h). The solution was treated with Et_3N (1.5 mL), concentrated and the residue subjected to flash chromatography (EtOAc–hexanes 1:4) to firstly afford the α-glycoside **18** as a colorless oil (8.6 g, 51%). [α] +151.6 (*c* 0.9, CH_2Cl_2); R_f 0.63 (EtOAc–hexanes, 3:7); ^1H NMR (500 MHz): δ_H 7.52–7.47 (2H, m, Ph), 7.42–7.36 (3H, m, Ph), 5.87–5.77 (1H, m, C*H*=CH_2), 5.58 (1H, s, PhC*H*), 5.03–4.98 (1H, m, CH=CH_2), 5.01 (1H, d, $J_{1,2}$ 3.4 Hz, H1), 4.96–4.93 (1H, m, CH=CH_2), 4.31–4.26 (2H, m, H4, H6), 3.70 (1H, dd, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 3.3 Hz, H3), 4.09 (1H, dd, $J_{6,6}$ 12.6 Hz, $J_{5,6}$ 1.8 Hz, H6), 3.75–3.74 (1H, m, H5), 3.71 (1H, ddd, *J* 9.7 Hz, 6.7 Hz, 6.7 Hz, CH=CH_2(CH_2)$_5$CH_2O), 3.54 (1H, dd, $J_{2,3}$ 10.4 Hz, $J_{1,2}$ 3.4 Hz, H2), 3.53–3.49 (1H, m, CH=CH_2(CH_2)$_5$CH_2O), 2.53–2.39 (1H, br s, OH), 2.11–2.03 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.69–1.58 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.43–1.30 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O); ^{13}C NMR (125.7 MHz): δ_C 138.9 (*C*H=CH_2), 137.3 (Ph), 129.3 (Ph), 128.3 (Ph), 126.2 (Ph), 114.3 (CH=*C*H_2), 101.3 (Ph*C*H), 98.6 (C1), 75.6 (C4), 69.3 (C6), 68.7 (CH=CH_2(CH_2)$_5$*C*H_2O), 67.3 (C3), 62.7 (C5), 60.7 (C2), 33.6 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 29.3 (CH=$CH_2$(*C*$H_2$)$_5$-$CH_2$O), 28.80 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 28.76 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 25.9 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), ESIMS: *m/z* Calcd [$C_{21}H_{29}N_3O_5$]$Na^+$: 426.1999. Found: 426.1997. Further elution (EtOAc–hexanes, 1:2) afforded the β-glycoside **19** as a colorless oil (8.0 g, 47%). [α] +151.6 (*c* 0.9, CH_2Cl_2); R_f 0.63 (EtOAc–hexanes, 3:7). [α] −4.5 (*c* 0.27, CH_2Cl_2); R_f 0.28 (EtOAc–hexanes, 3:7); ^1H NMR (500 MHz): δ_H 7.53–7.48 (2H, m, Ph), 7.40–7.36 (3H, m, Ph), 5.87–5.77 (1H, m, C*H*=CH_2), 5.54 (1H, s, PhC*H*), 5.03–4.98 (1H, m, CH=CH_2), 4.95–4.92 (1H, m, CH=CH_2), 4.33 (1H, dd, $J_{6,6}$ 12.5 Hz, $J_{5,6}$ 1.5 Hz, H6), 4.28 (1H, d, $J_{1,2}$ 3.4 Hz, H1), 4.15 (1H, dd, $J_{3,4}$ 3.8 Hz, $J_{4,5}$ 1.1 Hz, H4), 4.07 (1H, dd, $J_{6,6}$ 12.5 Hz, $J_{5,6}$ 1.9 Hz, H6), 3.99 (1H, ddd, *J* 9.3 Hz, 6.5 Hz, 6.5 Hz, CH=CH_2(CH_2)$_5$CH_2O), 3.54 (1H, dd, $J_{2,3}$ 10.2 Hz, $J_{1,2}$ 7.8 Hz, H2), 3.56–3.50 (2H, m, H3, CH=CH_2-(CH_2)$_5$CH_2O), 3.46–3.40 (1H, m, H5), 2.61 (1H, d, *J* 9.2 Hz, OH), 2.09–2.01 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.71–1.61 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.47–1.31 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O); ^{13}C NMR (125.7 MHz): δ_C 139.0 (*C*H=CH_2), 137.3 (Ph), 129.3 (Ph), 128.2 (Ph), 126.3 (Ph), 114.2 (CH=*C*H_2), 102.1 (C1), 101.4 (Ph*C*H), 74.6 (C4), 71.4 (C3), 70.2 (CH=CH_2(CH_2)$_5$*C*H_2O), 69.0 (C6), 66.4 (C5), 64.1 (C2), 33.6 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 29.4 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 28.82 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 28.77 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 25.7 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), ESIMS: *m/z* Calcd [$C_{21}H_{29}N_3O_5$]$Na^+$: 426.1999. Found: 426.2000.

3.8. 7-Octen-1-yl 2-azido-3-*O*-(4,6-*O*-benzylidene-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (22)

A solution of the acceptor **18** (949 mg, 2.35 mmol) in dry CH_2Cl_2 (20 mL) was stirred over 4 Å molecular sieves (1.5 g) and the mixture was stirred (rt, 1 h). The solution was then cooled (−40 °C), treated with TMSOTf (0.2 mL, 1.1 mmol) followed by dropwise addition of the trichloroacetimidate **20**[34] (2.33 g, 4.71 mmol) and then the mixture was allowed to warm to 0 °C (1 h). The mixture was neutralized with Et_3N (2 mL), concentrated and subjected to flash chromatography (EtOAc–hexanes, 1:1) to afford compound **21** as a colorless oil, which was immediately used in the next step. The colorless oil was taken up in CH_3OH (100 mL), treated with a solution of $NaOCH_3$ in CH_3OH and stirred (rt, 3 h). The solution was neutralized with Amberlite IR 120 (H^+), filtered, and subjected to flash chromatography (EtOAc–hexanes, 1:1) to afford diol **22** as a colorless oil (1.35 g, 88%). [α] +104.5 (*c* 0.4, CH_2Cl_2); R_f 0.19 (EtOAc–hexanes, 1:1); ^1H NMR (500 MHz): δ_H 7.58–7.47 (4H, m, Ph), 7.37–7.29 (6H, m, Ph), 5.87–5.76 (1H, m, CH_2=C*H*), 5.58 (1H, s, PhCH), 5.53 (1H, s, PhCH), 5.04 (1H, d, $J_{1,2}$ 3.6 Hz, H1), 5.03–4.98 (1H, m, CH_2=CH), 4.97–4.94 (1H, m, CH_2=CH), 4.59 (1H, d, $J_{1',2'}$ 7.6 Hz, H1′), 4.50 (1H, d, $J_{3,4}$ 3.2 Hz, H4), 4.28 (1H, dd, $J_{6',6'}$ 10.5 Hz, $J_{5',6'}$ 1.5 Hz, H6′), 4.25 (1H, d, $J_{6,6}$ 10.5 Hz, H6), 4.22 (1H, dd, $J_{2,3}$ 10.8 Hz, $J_{3,4}$ 3.2 Hz, H3), 4.15 (1H, dd, $J_{3',4'}$ 3.7 Hz, $J_{4',5'}$ 0.7 Hz, H4′), 4.06 (1H, dd, $J_{6',6'}$ 10.5 Hz, $J_{5',6'}$ 1.7 Hz, H6′), 4.04 (1H, d, $J_{6,6}$ 10.5 Hz, H6), 3.91 (1H, dd, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 10.8 Hz, H2), 3.79 (1H, dd, $J_{2',3'}$ 8.3 Hz, $J_{1',2'}$ 7.6 Hz, H2′), 3.74–3.64 (3H, m, H5, H3′, CH=CH_2(CH_2)$_5$CH_2O), 3.52 (1H, ddd, *J* 9.8 Hz, 6.7 Hz, 6.7 Hz, CH=CH_2(CH_2)$_5$CH_2O), 3.46–3.43 (1H, m, H5′), 2.95 (1H, s, OH), 2.67 (1H, d, *J* 7.5 Hz, OH), 2.10–2.02 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.68–1.60 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.45–1.31 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O); ^{13}C NMR (125.7 MHz): δ_C 139.0 (CH_2=CH), 137.8 (Ph), 137.7 (Ph), 129.2 (Ph), 128.9 (Ph), 128.3 (Ph), 128.2 (Ph), 126.4 (Ph), 126.4 (Ph), 114.3 (*C*H_2=CH), 104.0 (C1′), 101.3

(PhCH), 101.0 (PhCH), 98.5 (C1), 76.3 (C4), 75.1, 74.7 (C3, C4′), 72.2, 71.5 (C2′, C3′), 69.21, 69.19, 68.7 (C6, C6′, CH=$CH_2(CH_2)_5$-CH_2O), 66.7 (C5′), 63.1, 59.1 (C2, C5), 33.7, (CH=$CH_2(CH_2)_5CH_2O$), 29.4 (CH=$CH_2(CH_2)_5CH_2O$), 28.82 (CH=$CH_2(CH_2)_5CH_2O$), 28.78 (CH=$CH_2(CH_2)_5CH_2O$), 25.9 (CH=$CH_2(CH_2)_5CH_2O$). ESIMS: *m/z* Calcd $[C_{41}H_{51}N_3O_{10}]Na^+$: 676.2841. Found: 676.2839.

3.9. 7-Octen-1-yl 2-azido-3-*O*-(4,6-*O*-benzylidene-3-*O*-pivaloyl-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (23)

A solution of diol **22** (660 mg, 1.01 mmol) in dry pyridine (10 mL) was treated with trimethylacetyl chloride (150 μL, 1.2 mmol) and the solution was stirred (rt, 2 h). The solution was concentrated and the residue was subjected to flash chromatography (EtOAc–hexanes, 1:3) to afford **23** as a colorless oil (700 mg, 94%). [α] +127.7 (*c* 0.6, CH_2Cl_2); R_f 0.41 (EtOAc–hexanes, 3:7); ^{1}H NMR (500 MHz): δ_H 7.55–7.54 (4H, m, Ph), 7.36–7.26 (6H, m, Ph), 5.87–5.77 (1H, m, CH_2=C*H*), 5.57 (1H, s, PhC*H*), 5.52 (1H, s, PhC*H*), 5.06 (1H, d, $J_{1,2}$ 3.4 Hz, H1), 5.04–4.98 (1H, m, CH_2=CH), 4.97–4.94 (1H, m, CH_2=CH), 4.85 (1H, dd, $J_{2',3'}$ 10.2 Hz, $J_{3',4'}$ 3.8 Hz, H3′), 4.68 (1H, d, $J_{1',2'}$ 7.7 Hz, H1′), 4.50 (1H, d, $J_{3,4}$ 3.1 Hz, H4), 4.40 (1H, dd, $J_{3',4'}$ 3.8 Hz, $J_{4',5'}$ 0.7 Hz, H4′), 4.32 (1H, dd, $J_{6',6'}$ 12.4 Hz, $J_{5',6'}$ 1.4 Hz, H6′), 4.25 (1H, dd, $J_{6,6}$ 12.8 Hz, $J_{5,6}$ 1.6 Hz, H6), 4.23 (1H, dd, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 3.1 Hz, H3), 4.13–4.01 (3H, m, H2′, H6, H6′), 3.90 (1H, dd, $J_{2,3}$ 10.6 Hz, $J_{1,2}$ 3.4 Hz, H2), 3.75–3.68 (2H, m, H5, CH=$CH_2(CH_2)_5CH_2O$), 3.58–3.50 (2H, H5′, CH=$CH_2(CH_2)_5CH_2O$), 2.56 (1H, d, *J* 2.1 Hz, OH), 2.10–2.02 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.70–1.59 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.45–1.28 (6H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.22 (9H, s, $(CH_3)_3C$); ^{13}C NMR (125.7 MHz): δ_C 178.3 (C=O), 138.9 (CH_2=CH), 137.8 (Ph), 137.6 (Ph), 128.8 (Ph), 128.1 (2C, Ph), 128.1 (Ph), 126.3 (Ph), 125.9 (Ph), 114.3 (CH_2=CH), 104.3 (C1′), 100.9 (PhCH), 100.5 (PhCH), 98.4 (C1), 76.2 (C4), 75.0 (C3), 73.15, 73.10 (C3′, C4′), 69.2, 69.1 (C6, C6′), 68.7 (C2′), 68.5 (CH=$CH_2(CH_2)_5CH_2O$), 66.5 (C5′), 63.1 (C5), 59.1 (C2), 39.0 ($(CH_3)_3C$), 33.7 (CH=$CH_2(CH_2)_5$-CH_2O), 29.3 (CH=$CH_2(CH_2)_5CH_2O$), 28.81 (CH=$CH_2(CH_2)_5CH_2O$), 28.78 (CH=$CH_2(CH_2)_5CH_2O$), 27.1 ($(CH_3)_3C$), 25.9 (CH=$CH_2(CH_2)_5$-CH_2O). ESIMS: *m/z* Calcd $[C_{39}H_{51}N_3O_{11}]Na^+$: 760.3416. Found: 760.3410.

3.10. 7-Octen-1-yl 2-azido-3-*O*-(4,6-*O*-benzylidene-3-*O*-pivaloyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (25)

A solution of the alcohol **23** (640 mg, 0.870 mmol) in dry Et_2O (10 mL) was stirred over 4 Å molecular sieves (500 mg) (rt, 1 h). The mixture was then cooled (−10 °C), treated with TMSOTf (50 μL, 0.28 mmol) followed by dropwise addition of the trichloroacetimidate[26] **24** (1.50 g, 2.67 mmol) in dry Et_2O (5 mL). The mixture was stirred (1 h), treated with Et_3N (0.5 mL), filtered, and subjected to flash chromatography (EtOAc–hexanes, 1:3) to yield the trisaccharide **25** as a colorless oil (720 mg, 72%). [α] +19.6 (*c* 0.6, CH_2Cl_2); R_f 0.75 (EtOAc–hexanes, 1:1); ^{1}H NMR (500 MHz): δ_H 7.52–7.44 (4H, m, Ph), 7.38–7.22 (21H, m, Ph), 5.88–5.77 (1H, m, CH_2=C*H*), 5.59 (1H, s, PhC*H*), 5.48 (1H, s, PhC*H*), 5.39 (1H, d, $J_{1'',2''}$ 3.4 Hz, H1″), 5.09 (1H, d, $J_{1,2}$ 3.3 Hz, H1), 5.07 (1H, dd, $J_{2',3'}$ 9.4 Hz, $J_{3',4'}$ 3.7 Hz, H3′), 5.04–4.99 (2H, m, CH_2=CH), 4.94 (1H, d, $J_{1',2'}$ 7.8 Hz, H1′), 4.90, 4.54 (2H, AB, *J* 11.5 Hz, PhCH_2), 4.77, 4.60 (2H, AB, *J* 11.5 Hz, PhCH_2), 4.73, 4.67 (2H, AB, *J* 11.6 Hz, PhCH_2), 4.52–4.46 (2H, m, H4, H4′), 4.45 (1H, q, $J_{5'',6''}$ 6.5 Hz, H5″), 4.35–4.23 (4H, m, H2′, H3, H6, H6′), 4.09–4.03 (4H, m, H2″, H3″, H6, H6′), 3.79–3.71 (2H, m, H5, CH=$CH_2(CH_2)_5CH_2O$), 3.60–3.52 (3H, m, H2, H5′, CH=$CH_2(CH_2)_5CH_2O$), 3.49–3.47 (1H, m, H4″), 2.12–2.02 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.72–1.64 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.47–1.34 (6H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.10 (9H, s, $(CH_3)_3C$), 0.92 (3H, d, $J_{5'',6''}$ 6.5 Hz, H6″); ^{13}C NMR (125.7 MHz): δ_C 177.9 (C=O), 139.0 (2C, Ph), 138.9 (CH_2=CH), 138.6 (Ph), 137.9 (Ph), 137.7 (Ph), 128.94 (Ph), 128.87 (Ph), 128.3 (Ph), 128.24 (Ph), 128.17 (Ph), 128.14 (2C, Ph), 128.09 (Ph), 127.5 (Ph), 127.42 (Ph), 127.41 (Ph), 127.34 (Ph), 127.29 (Ph), 126.3 (Ph), 126.0 (Ph), 114.3 (CH_2=CH), 102.0 (C1′), 100.9 (PhCH), 100.8 (PhCH), 99.0 (C1), 97.0 (C1″), 79.5, 78.4, 76.5, 76.4, 76.1 (C2″, C3″, C4, C4′, C4″), 74.9 (PhCH_2), 73.1 (PhCH_2), 72.8 (PhCH_2), 72.5, 72.2, 70.2 (C2′, C3, C3′), 69.1, 69.0, 68.7 (C6, C6′, CH=$CH_2(CH_2)_5CH_2O$), 66.5, 66.1 (C5′, C5″), 63.3 (C5), 58.8 (C2), 38.9 ($(CH_3)_3C$), 33.7 (CH=$CH_2(CH_2)_5CH_2O$), 29.4 (CH=$CH_2(CH_2)_5CH_2O$), 28.82 (CH=$CH_2(CH_2)_5CH_2O$), 28.80 (CH=$CH_2(CH_2)_5CH_2O$), 27.0 ($(CH_3)_3$-C), 26.0 (CH=$CH_2(CH_2)_5CH_2O$), 16.3 (C6″). ESIMS: *m/z* Calcd $[C_{66}H_{79}N_3O_{15}]Na^+$: 1176.5403. Found: 1176.5396.

3.11. 7-Octen-1-yl 2-azido-3-*O*-(4,6-*O*-benzylidene-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (26)

A solution of the pivaloyl ester **25** (667 mg, 0.58 mmol) in CH_3OH (50 mL) was treated with a catalytic amount of $LiOCH_3$ (50 mg) and the solution heated at reflux (7 d). The solution was then neutralized with Amberlite IR 120 (H^+), filtered, and subjected to flash chromatography (EtOAc–hexanes, 1:3) to afford the alcohol **26** as a colorless oil (480 mg, 78%). [α] +12.6 (*c* 0.4, CH_2Cl_2); R_f 0.11 (EtOAc–hexanes, 3:7); ^{1}H NMR (500 MHz): δ_H 7.54–7.48 (4H, m, Ph), 7.38–7.22 (21H, m, Ph), 5.88–5.77 (1H, m, CH_2=C*H*), 5.61 (1H, s, PhC*H*), 5.56 (1H, s, PhC*H*), 5.37 (1H, d, $J_{1'',2''}$ 2.4 Hz, H1″), 5.07 (1H, d, $J_{1,2}$ 3.4 Hz, H1), 5.04–4.99 (1H, m, CH_2=CH), 4.98–4.94 (1H, m, CH_2=CH), 4.92 (1H, A of AB, *J* 11.6 Hz, PhCH_2), 4.82–4.78 (3H, m, PhCH_2), 4.94 (1H, d, $J_{1',2'}$ 7.2 Hz, H1′), 4.72, 4.58 (2H, AB, *J* 11.7 Hz, PhCH_2), 4.50 (1H, d, $J_{3,4}$ 3.2 Hz, H4), 4.33–4.20 (5H, m, H3, H4′, H5″, H6, H6′), 4.12–4.02 (4H, m, H2″, H3″, H6, H6′), 3.95 (1H, dd, $J_{2',3'}$ 9.5 Hz, $J_{1',2'}$ 7.2 Hz, H2′), 3.93–3.87 (1H, m, H3′), 3.77–3.70 (2H, m, H5, CH=$CH_2(CH_2)_5CH_2O$), 3.67 (1H, dd, $J_{2,3}$ 10.9 Hz, $J_{1,2}$ 3.4 Hz, H2), 3.58–3.52 (2H, m, H4″, CH=CH_2-$(CH_2)_5CH_2O$), 3.50 (1H, s, H5′), 3.41 (1H, d, *J* 6.5 Hz, OH), 2.10–2.04 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.70–1.62 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.44–1.32 (6H, m, CH=$CH_2(CH_2)_5CH_2O$), 0.95 (3H, d, $J_{5'',6''}$ 6.5 Hz, H6″); ^{13}C NMR (125.7 MHz): δ_C 139.0 (CH_2=CH), 138.9 (Ph), 138.2 (Ph), 137.8 (Ph), 137.6 (Ph), 129.2 (Ph), 128.8 (Ph), 128.31 (2C, Ph), 128.27 (Ph), 128.2 (Ph), 128.11 (Ph), 128.08 (Ph), 128.04 (Ph), 127.6 (Ph), 127.41 (2C, Ph), 127.39 (Ph), 127.38 (Ph), 126.4 (Ph), 126.3 (Ph), 114.4 (CH_2=CH), 102.0, 101.4 (C1′, PhCH), 100.7 (PhCH), 98.9, 98.7 (C1, C1″), 79.7, 78.1, 77.0 (C2″, C3″, C4″), 76.7, 76.4 (2C), 75.5, 73.7, 72.2 (C2′, C3, C3′, C4, C4′, C5″), 74.8 (PhCH_2), 73.4 (PhCH_2), 72.8 (PhCH_2), 69.2, 69.1, 68.7 (C6, C6′, CH=$CH_2(CH_2)_5CH_2O$), 66.6, 63.3 (C5, C5′), 59.2 (C2), 33.7 (CH=$CH_2(CH_2)_5CH_2O$), 29.4 (CH=$CH_2(CH_2)_5CH_2O$), 28.82 (CH=$CH_2(CH_2)_5CH_2O$), 28.80 (CH=$CH_2(CH_2)_5CH_2O$), 25.9 (CH=$CH_2(CH_2)_5CH_2O$), 16.4 (C6″). ESIMS: *m/z* Calcd $[C_{61}H_{71}N_3O_{14}]$-Na^+: 1092.4828. Found: 1092.4831.

3.12. 7-Octen-1-yl 2-acetamido-3-*O*-(4,6-*O*-benzylidene-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (27)

A solution of the azide **26** (500 mg, 0.468 mmol) in pyridine (4 mL) was treated with AcSH (2 mL) and the solution stirred (10 d). The solution was then concentrated and the residue subjected to flash chromatography (CH_2Cl_2–MeOH, 9:1) to afford predominantly **27** as a colorless oil. The oil was then taken up in MeOH and treated with a catalytic amount of NaOMe in MeOH and the solution stirred (rt, 5 h). The solution was neutralized with Amberlite IR 120 (H^+), filtered, and the residue subjected to flash chromatography (EtOAc–hexanes, 1:1) to afford **27** as a colorless oil

(400 mg, 78%). [α] +13.4 (*c* 0.6, CH_2Cl_2); R_f 0.73 (EtOAc–hexanes, 3:1); ^{1}H NMR (500 MHz): δ_H 7.64–7.58 (4H, m, Ph), 7.43–7.18 (19H, m, Ph), 7.14–7.04 (3H, m, Ph, NH), 5.84–5.75 (1H, m, CH_2=C*H*), 5.58 (1H, s, PhC*H*), 5.54 (1H, s, PhC*H*), 5.20 (1H, d, $J_{1,2}$ 3.2 Hz, H1), 5.07 (1H, d, $J_{1'',2''}$ 3.7 Hz, H1″), 5.02–4.91 (3H, m, PhCH_2, CH_2=CH), 4.82–4.75 (3H, m, PhCH_2), 4.68 (1H, A of AB, *J* 11.4 Hz, PhCH_2), 4.60 (1H, A of AB, *J* 11.6 Hz, PhCH_2), 4.56 (1H, d, $J_{1',2'}$ 7.4 Hz, H1′), 4.50 (1H, ddd, $J_{2,3}$ 11.1 Hz, J_{NH} 6.4 Hz, $J_{1,2}$ 3.2 Hz, H2), 4.38 (1H, d, $J_{3,4}$ 2.5 Hz, H4), 4.31 (1H, d, $J_{6,6}$ 11.7 Hz, H6), 4.23 (1H, d, $J_{3',4'}$ 3.4 Hz, H4′), 4.20 (1H, d, $J_{6',6'}$ 11.4 Hz, H6′), 4.12 (1H, q, $J_{5'',6''}$ 6.4 Hz, H5″), 4.08–4.00 (4H, m, H2″, H3, H6, H6′), 3.94–3.88 (2H, m, H2′, H3″), 3.77 (1H, dd, $J_{2',3'}$ 9.8 Hz, $J_{3',4'}$ 3.4 Hz, H3′), 3.70 (1H, d, $J_{3'',4''}$ 2.1 Hz, H4″), 3.67–3.59 (2H, m, H5, CH=CH_2-$(CH_2)_5CH_2O$), 3.45 (1H, s, H5′), 3.40 (1H, ddd, *J* 9.9 Hz, 6.5 Hz, 6.5 Hz, CH=$CH_2(CH_2)_5CH_2O$), 2.07–2.01 (2H, m, CH=CH_2-$(CH_2)_5CH_2O$), 1.81 (3H, s, CH_3CO), 1.56–1.46 (2H, m, CH=CH_2-$(CH_2)_5CH_2O$), 1.41–1.24 (6H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.18 (3H, d, $J_{5'',6''}$ 6.4 Hz, H6″); ^{13}C NMR (125.7 MHz): δ_C 170.5 (C=O), 138.9 (CH_2=CH), 138.7 (Ph), 138.6 (Ph), 138.0 (Ph), 137.7 (Ph), 137.1 (Ph), 129.01 (Ph), 129.00 (Ph), 128.48 (Ph), 128.47 (Ph), 128.4 (Ph), 128.2 (Ph), 128.15 (Ph), 128.07 (Ph), 128.0 (Ph), 127.6 (Ph), 127.44 (Ph), 127.38 (Ph), 127.32 (Ph), 127.26 (Ph), 126.7 (Ph), 126.5 (Ph), 126.2 (Ph), 114.4 (*C*H_2=CH), 102.9 (C1′), 101.3 (Ph*C*H), 100.8 (Ph*C*H), 99.2 (C1″), 97.6 (C1), 79.7, 79.1 (C2′, C3″), 77.5 (C4″), 75.6 (C2″, C3), 75.0, 74.7 (C4, C4′), 74.7 (PhCH_2), 74.4 (PhCH_2), 72.6 (PhCH_2), 72.4 (C3′), 69.6, 69.3, 68.3 (C6, C6′, CH=$CH_2(CH_2)_5CH_2O$), 68.5 (C5″), 66.5 (C5′), 63.0 (C5), 49.4 (C2), 33.7 (CH=CH_2(*C*H_2)$_5$-CH_2O), 29.5 (CH=$CH_2(CH_2)_5CH_2O$), 28.87 (CH=$CH_2(CH_2)_5CH_2O$), 28.86 (CH=$CH_2(CH_2)_5CH_2O$), 26.0 (CH=$CH_2(CH_2)_5CH_2O$), 22.6 (*C*H_3CO), 16.5 (C6″). ESIMS: *m/z* Calcd $[C_{63}H_{75}NO_{15}]Na^+$: 1108.5029. Found: 1108.5035.

3.13. 7-Octyl 2-acetamido-3-*O*-(2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (28)

The octenyl glycoside **11** (140 mg, 0.219 mmol) was treated with Pd–C (10%, 20 mg), taken up in MeOH (20 mL) and stirred under a H_2 atmosphere (rt, 1 d). The mixture was then filtered, concentrated, and the residue was subjected to C-18 chromatography (CH_3OH–H_2O, 1:1) to afford the octyl glycoside **28** as a colorless oil (130 mg, 93%). [α] +41.4 (*c* 0.4, CH_3OH); ^{1}H NMR (CD_3OD, 500 MHz): δ_H 5.12 (1H, d, $J_{1'',2''}$ 3.8 Hz, H1″), 4.96 (1H, $J_{1,2}$ 3.5 Hz, H1), 4.60 (1H, d, $J_{1',2'}$ 7.2 Hz, H1′), 4.25 (1H, dd, $J_{2,3}$ 11.2 Hz, $J_{1,2}$ 3.5 Hz, H2), 4.23 (1H, q, $J_{5'',6''}$ 6.6 Hz, H5″), 4.18 (1H, d, $J_{3,4}$ 2.5 Hz, H4), 3.98 (1H, dd, $J_{2,3}$ 11.2 Hz, $J_{3,4}$ 2.5 Hz, H3), 3.86–3.80, 3.78–3.63, 3.57–3.52 (13H, 3 × m, H2′, H2″, H3′, H3″, H4′, H4″, H5, H5′, H6, H6′, $CH_3(CH_2)_6CH_2O$), 3.39–3.33 (1H, m, $CH_3(CH_2)_6CH_2O$), 1.98 (3H, s, CH_3C=O), 1.62–1.52 (2H, m, $CH_3(CH_2)_6CH_2O$), 1.41–1.23 (13H, m, H6″, $CH_3(CH_2)_6CH_2O$), 0.90 (3H, t, *J* 6.8 Hz, $CH_3(CH_2)_6CH_2O$). ^{13}C NMR (125.7 MHz, CD_3OD): δ_C 173.4 (C=O), 103.7 (C1′), 101.9 (C1″), 98.0 (C1), 80.8, 76.6, 74.9, 73.3, 71.8, 71.6, 70.7, 70.1, 69.2, 69.0 (C2′, C2″, C3′, C3″, C4, C4′, C4″, C5, C5′, C5″), 77.8 (C3), 69.0 ($CH_3(CH_2)_6CH_2O$), 62.8, 62.5 (C6, C6′), 51.1 (C2), 33.1 ($CH_3(CH_2)_6CH_2O$), 30.64 ($CH_3(CH_2)_6CH_2O$), 30.59 ($CH_3(CH_2)_6CH_2O$), 30.5 ($CH_3(CH_2)_6CH_2O$), 27.4 ($CH_3(CH_2)_6$-CH_2O), 23.7 ($CH_3(CH_2)_6CH_2O$), 22.7 (*C*H_3CO), 16.9 (C6″), 14.5 (*C*$H_3(CH_2)_6CH_2O$). ESIMS: *m/z* Calcd $[C_{28}H_{51}NO_{15}]Na^+$: 664.3151. Found: 664.3145.

3.14. 7-Octen-1-yl 2-acetamido-3-*O*-(3-*O*-(2-acetamido-2-deoxy-3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-4,6-*O*-benzylidene-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (30)

A solution of the acceptor **26** (1.04 g, 0.973 mmol) in dry Et_2O (25 mL) was treated with 4 Å molecular sieves (1 g) and the mixture was stirred (rt, 1 h). The mixture was then cooled (−10 °C), treated with TMSOTf (50 μL, 0.29 mmol); the trichloroacetimidate **15**[25] (1.38 g, 2.92 mmol) in dry Et_2O (15 mL) was then added dropwise and the mixture was allowed to stand (20 min). The mixture was neutralized with Et_3N (0.5 mL), filtered, concentrated and subjected to flash chromatography (EtOAc–hexanes 1:3) to afford the near pure tetrasaccharide **29** as a colorless oil (950 mg, 71%). A portion of the tetrasaccharide (900 mg, 0.65 mmol) was taken up in pyridine (6 mL) and treated with AcSH (3 mL) and the solution was stirred (7 d). A further addition of pyridine (2 mL) and AcSH (1 mL) was conducted and the solution stirred another 7 d. The solution was concentrated and subjected to flash chromatography (CH_2Cl_2–CH_3OH, 10:1) to afford **30** as a colorless oil (700 mg, 76%). [α] +61.0 (*c* 0.2, $CHCl_3$); R_f 0.3 (CH_2Cl_2–CH_3OH, 20:1); ^{1}H NMR (500 MHz): δ_H 7.63–7.59 (2H, m, Ph), 7.55–7.51 (2H, m, Ph), 7.45–7.20 (17H, m, Ph), 7.19–7.12 (4H, m, Ph), 5.85–5.75 (1H, m, CH_2=C*H*), 5.51 (1H, s, PhC*H*), 5.46 (1H, s, PhC*H*), 5.43 (1H, d, $J_{3''',4'''}$ 1.7 Hz, H4‴), 5.29–5.24 (2H, m, H1″, NH), 5.14 (1H, d, $J_{1,2}$ 3.2 Hz, H1), 5.12–5.07 (2H, m, H1‴, H3‴), 5.06–4.92 (4H, m, PhCH_2, CH_2=CH), 4.75 (1H, A of AB, *J* 11.6 Hz, PhCH_2), 4.72 (1H, A of AB, *J* 11.4 Hz, PhCH_2), 4.65–4.60 (1H, m, H5‴) 4.59–4.46 (6H, m, H1′, H2, H2‴, H4, PhCH_2), 4.34–4.27 (2H, m, H4′, H6), 4.23 (1H, dd, $J_{6',6'}$ 12.4 Hz, $J_{5',6'}$ 1.1 Hz, H6′), 4.12 (1H, q, $J_{5'',6''}$ 6.3 Hz, H5″), 4.10–3.90 (7H, m, H2′, H2″, H3, H6, H6′, H6‴), 3.85 (1H, dd, $J_{2',3'}$ 9.5 Hz, $J_{3',4'}$ 3.8 Hz, H3′), 3.81 (1H, dd, $J_{2'',3''}$ 10.1 Hz, $J_{3'',4''}$ 2.5 Hz, H3″), 3.74 (1H, d, $J_{3'',4''}$ 2.5 Hz, H4″), 3.66–3.61 (2H, m, H5, CH=CH_2-$(CH_2)_5CH_2O$), 3.44 (1H, s, H5′), 3.41–3.35 (1H, m, CH=CH_2-$(CH_2)_5CH_2O$), 2.14 (3H, s, CH_3CO), 2.07–2.01 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.96 (3H, s, CH_3CO), 1.88 (3H, s, CH_3CO), 1.59 (3H, s, CH_3CO), 1.56–1.46 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.41–1.25 (9H, m, CH_3CO, CH=$CH_2(CH_2)_5CH_2O$), 1.18 (1H, d, $J_{5'',6''}$ 6.3 Hz, H6″). ^{13}C NMR (125.7 MHz): δ_C 170.34 (C=O), 170.31 (C=O), 170.2 (C=O), 170.0 (C=O), 169.9 (C=O), 138.9 (CH_2=CH), 138.62 (Ph), 138.57 (Ph), 137.7 (2C, Ph), 129.5 (Ph), 128.5 (Ph), 128.35 (Ph), 128.32 (2C, Ph), 128.2 (Ph), 128.1 (Ph), 128.0 (Ph), 127.9 (2C, Ph), 127.7 (Ph), 127.5 (Ph), 127.2 (Ph), 126.9 (Ph), 126.7 (Ph), 126.4 (Ph), 114.4 (*C*H_2=CH), 104.2 (C1′), 101.6 (Ph*C*H), 101.1 (Ph*C*H), 97.7 (2C, C1, C1″), 92.2 (C1‴), 79.9, 77.8 (2C), 76.3, 76.0 (2C), 75.5, 73.2, 69.8, 67.73, 67.66, 66.9 (C2′, C2″, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5″, C5‴), 75.0 (PhCH_2), 73.5 (PhCH_2), 73.0 (PhCH_2), 69.6, 69.3, 62.7 (C6, C6′, C6‴), 68.2 (CH=$CH_2(CH_2)_5CH_2O$), 65.5 (C5′), 63.0 (C5), 49.2, 47.1 (C2, C2‴), 33.7 (CH=CH_2(*C*H_2)$_5$-CH_2O), 29.5 (CH=$CH_2(CH_2)_5CH_2O$), 28.86 (CH=$CH_2(CH_2)_5CH_2O$), 28.84 (CH=$CH_2(CH_2)_5CH_2O$), 26.0 (CH=$CH_2(CH_2)_5CH_2O$), 22.6 (*C*H_3CO), 22.4 (*C*H_3CO), 20.8 (*C*H_3CO), 20.7 (*C*H_3CO), 20.6 (*C*H_3CO), 16.7 (C6″). ESIMS: *m/z* Calcd $[C_{77}H_{94}N_2O_{23}]Na^+$: 1437.6140. Found: 1437.6116.

3.15. 7-Octen-1-yl 2-acetamido-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-α-D-galactopyranoside (34)

A solution of the acceptor **26** (928 mg, 0.868 mmol) in dry Et_2O (20 mL) was treated with 4 Å molecular sieves (0.5 g) and the mixture stirred (rt, 1 h). The mixture was then cooled (−10 °C), treated with TMSOTf (30 μL, 0.17 mmol); the trichloroacetimidate **32**[28] (1.80 g, 2.60 mmol) in dry Et_2O (15 mL) was then added dropwise and the mixture was allowed to stand (20 min). The mixture was neutralized with Et_3N (0.5 mL), filtered, concentrated, and subjected to flash chromatography (EtOAc–hexanes 1:4) to afford the near pure tetrasaccharide **33** (922 mg, 68%) as a colorless oil. A solution of the tetrasaccharide **33** (550 mg, 0.345 mmol) in dry pyridine (6 mL) was treated with AcSH (3 mL) and the solution was stirred (rt, 4 d). Further pyridine (4 mL) and AcSH (2 mL)

was added and the solution was stirred further (rt, 4 d). The solution was then concentrated and subjected to flash chromatography (CH_3OH–CH_2Cl_2 1:9) to afford **34** (420 mg, 76%) as a colorless oil. [α] +35.1 (*c* 0.5, CH_2Cl_2); R_f 0.50 (EtOAc–hexanes 3:7); ^{1}H NMR (500 MHz): δ_H 7.61–7.52 (4H, m, Ph), 7.36–7.00 (41H, m, Ph), 5.87–5.77 (1H, m, CH_2=C*H*), 5.59 (1H, s, PhC*H*), 5.52 (1H, s, PhC*H*), 5.36–5.31 (2H, m, H1″, H1‴), 5.17 (1H, d, $J_{1,2}$ 3.1 Hz, H1), 5.05–4.99 (1H, m, C*H*$_2$=CH), 4.98–4.95 (1H, m, C*H*$_2$=CH), 4.88 (1H, A of AB, *J* = 11.8 Hz, PhC*H*$_2$), 4.80 (1H, A of AB, *J* = 11.1 Hz, PhC*H*$_2$), 4.67–4.61 (2H, m, PhC*H*$_2$), 4.59–4.28 (15H, m, H1′, H2, H4, H4′, H5‴, H6, PhC*H*$_2$), 4.27–4.22 (2H, m, H6′, PhC*H*$_2$), 4.18–4.13 (2H, m, H2′, H3″), 4.12–4.06 (2H, m, H2″, H6′), 4.05–3.98 (3H, m, H3, H5″, H6), 3.94 (1H, dd, $J_{2',3'}$ 9.7 Hz, $J_{3',4'}$ 3.5 Hz, H3′), 3.88 (1H, dd, $J_{2''',3'''}$ 10.2 Hz, $J_{1''',2'''}$ 4.0 Hz, H2‴), 3.83–3.79 (2H, m, H3‴, H4″), 3.68–3.61 (2H, m, H5, CH=CH$_2$(CH$_2$)$_5$C*H*$_2$O), 3.54 (1H, dd, $J_{6''',6'''}$ 9.3 Hz, $J_{5''',6'''}$ 6.1 Hz, H6‴), 3.45–3.36 (3H, m, H5′, H6‴, CH=CH$_2$(CH$_2$)$_5$C*H*$_2$O), 3.29 (1H, br s, 1H, H4‴), 2.10–2.03 (2H, m, CH=CH$_2$(C*H*$_2$)$_5$CH$_2$O), 1.62 (3H, s, C*H*$_3$CO), 1.56–1.48 (2H, m, CH=CH$_2$(C*H*$_2$)$_5$CH$_2$O), 1.44–1.24 (6H, m, CH=CH$_2$(C*H*$_2$)$_5$CH$_2$O), 1.07 (3H, d, $J_{5'',6'''}$ 6.3 Hz, H6″). ^{13}C NMR (125.7 MHz): δ_C 170.3 (C=O), 139.1 (Ph), 138.9 (CH$_2$=*C*H), 138.8 (Ph), 138.63 (Ph), 138.57 (Ph), 138.44 (Ph), 138.40 (Ph), 137.75 (Ph), 137.72 (Ph), 129.0 (Ph), 128.5 (Ph), 128.40 (Ph), 128.37 (Ph), 128.3 (Ph), 128.24 (Ph), 128.17 (Ph), 128.06 (2C, Ph), 128.05 (2C, Ph), 128.0 (Ph), 127.9 (2C, Ph), 127.8 (Ph), 127.7 (Ph), 127.65 (Ph), 127.62 (Ph), 127.41 (Ph), 127.38 (Ph), 127.34 (Ph), 127.12 (Ph), 127.06 (Ph), 127.0 (Ph), 126.9 (Ph), 126.52 (Ph), 126.49 (Ph), 126.4 (Ph), 114.4 (*C*H$_2$=CH), 104.4 (C1′), 101.15 (PhCH), 101.07 (PhCH), 97.7 (C1), 97.1 (C1″), 91.8 (C1‴), 79.3 (2C), 78.5 (2C), 77.6 (3C), 76.5 (2C), 75.6, 70.3, 69.58 (C2′, C2″, C2‴, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5‴), 74.9 (PhCH$_2$), 74.4 (PhCH$_2$), 73.6 (PhCH$_2$), 73.01 (PhCH$_2$), 72.99 (PhCH$_2$), 72.8 (PhCH$_2$), 71.4 (PhCH$_2$), 70.2, 69.63, 69.4 (C6, C6′, C6‴), 68.2 (CH=CH$_2$(CH$_2$)$_5$CH$_2$O), 67.5, 65.9, 63.0 (C5, C5′, C5″), 49.2 (C2), 33.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.6 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.91 (CH=CH$_2$(CH$_2$)$_5$CH$_2$O), 28.87 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 26.0 (CH=CH$_2$(CH$_2$)$_5$CH$_2$O), 22.5 (*C*H$_3$CO), 16.6 (C6″). ESIMS: *m/z* Calcd [$C_{97}H_{109}NO_{20}$]Na$^+$: 1630.7435. Found: 1630.7441.

3.16. 7-Octen-1-yl 2-azido-3-*O*-(4,6-*O*-benzylidene-β-D-galactopyranosyl)-2-deoxy-β-D-galactopyranoside (36)

A solution of the acceptor **19** (949 mg, 2.35 mmol) in dry CH_2Cl_2 (20 mL) was stirred over 4 Å molecular sieves (1.5 g) and the mixture was stirred (rt, 1 h). The solution was then cooled (−40 °C), treated with TMSOTf (0.2 mL, 1.1 mmol) followed by dropwise addition of the trichloroacetimidate[34] **20** (2.33 g, 4.71 mmol) and then the mixture was allowed to warm (0 °C, 1 h). The mixture was neutralized with Et_3N (2 mL), concentrated, and subjected to flash chromatography (EtOAc–hexanes, 1:1) to afford compound **35** as a colorless oil, which was immediately used in the next step. The colorless oil was taken up in CH_3OH (100 mL), treated with a solution of $NaOCH_3$ in CH_3OH and stirred (rt, 3 h). The solution was neutralized with Amberlite IR 120 (H^+), filtered, and subjected to flash chromatography (EtOAc–hexanes, 1:1) to afford the diol **36** as a colorless oil (1.17 g, 76%). [α] +15.9 (*c* 1.1, CH_2Cl_2); R_f 0.33 (EtOAc–hexanes, 3:7); ^{1}H NMR (500 MHz): δ_H 7.57–7.43 (2H, m, Ph), 7.51–7.47 (2H, m, Ph), 7.37–7.31 (6H, m, Ph), 5.87–5.77 (1H, m, CH$_2$=C*H*), 5.57 (1H, s, PhC*H*), 5.53 (1H, s, PhC*H*), 5.03–4.98 (1H, m, C*H*$_2$=CH), 4.96–4.92 (1H, m, C*H*$_2$=CH), 4.59 (1H, d, $J_{1',2'}$ 7.6 Hz, H1′), 4.35 (1H, d, $J_{3,4}$ 3.2 Hz, H4), 4.31 (1H, d, $J_{1,2}$ 7.9 Hz, H1), 4.30 (1H, dd, $J_{6,6}$ 12.1 Hz, $J_{5,6}$ 1.5 Hz, H6), 4.27 (1H, dd, $J_{6',6'}$ 12.4 Hz, $J_{5',6'}$ 1.4 Hz, H6′), 4.15 (1H, dd, $J_{3',4'}$ 3.8 Hz, $J_{4',5'}$ 0.7 Hz, H4′), 4.05 (1H, dd, $J_{6',6'}$ 12.4 Hz, $J_{5',6'}$ 1.8 Hz, H6′), 4.03 (1H, dd, $J_{6,6}$ 12.1 Hz, $J_{5,6}$ 1.6 Hz, H6), 4.02–3.97 (1H, m, CH=CH$_2$(CH$_2$)$_5$C*H*$_2$O), 3.91 (1H, dd, $J_{2,3}$ 10.6 Hz, $J_{1,2}$ 7.9 Hz, H2), 3.79 (1H, dd, $J_{2',3'}$ 8.8 Hz, $J_{1',2'}$ 7.6 Hz, H2′), 3.71–3.66 (1H, m, H3′), 3.60 (1H, dd, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 3.2 Hz, H3), 3.53 (1H, ddd, *J* 9.4 Hz, 6.9 Hz, 6.9 Hz, CH=CH$_2$(CH$_2$)$_5$C*H*$_2$O), 3.42–3.40 (1H, m, H5′), 3.37–3.36 (1H, m, H5), 2.93 (1H, s, OH), 2.66 (1H, d, *J* 8.1 Hz, OH), 2.09–2.01 (2H, m, CH=CH$_2$(C*H*$_2$)$_5$CH$_2$O), 1.72–1.61 (2H, m, CH=CH$_2$(C*H*$_2$)$_5$CH$_2$O), 1.48–1.31 (6H, m, CH=CH$_2$(C*H*$_2$)$_5$CH$_2$O); ^{13}C NMR (125.7 MHz): δ_C 139.1 (CH$_2$=*C*H), 137.7 (Ph), 137.6 (Ph), 129.2 (Ph), 129.0 (Ph), 128.3 (Ph), 128.2 (Ph), 126.5 (Ph), 126.3 (Ph), 114.2 (*C*H$_2$=CH), 104.0 (C1′), 102.4 (C1), 101.22 (PhCH), 101.16 (PhCH), 77.5 (C3), 75.4, 75.1 (C4, C4′), 72.3, 71.5 (C2′, C3′), 70.1 (CH=CH$_2$-(CH$_2$)$_5$CH$_2$O), 69.2, 69.1 (C6, C6′), 66.8, 66.6 (C5, C5′), 62.2 (C2), 33.7, (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.4 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.9 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 25.8 (CH=CH$_2$-(*C*H$_2$)$_5$CH$_2$O). ESIMS: *m/z* Calcd [$C_{41}H_{51}N_3O_{10}$]Na$^+$: 676.2841. Found: 676.2829.

3.17. 7-Octen-1-yl 2-azido-3-*O*-(4,6-*O*-benzylidene-3-*O*-pivaloyl-β-D-galactopyranosyl)-2-deoxy-β-D-galactopyranoside (37)

A solution of the diol **36** (570 mg, 0.87 mmol) in dry pyridine (10 mL) was treated with trimethylacetyl chloride (144 μL, 1.2 mmol) and the solution was stirred (rt, 2 h). The solution was concentrated and the residue was subjected to flash chromatography (EtOAc–hexanes, 1:3) to afford **37** as a colorless oil (640 mg, 98%). [α] +45.5 (*c* 1.3, CH_2Cl_2); R_f 0.31 (EtOAc–hexanes, 1:1); ^{1}H NMR (400 MHz): δ_H 7.59–7.48 (4H, m, Ph), 7.39–7.31 (6H, m, Ph), 5.90–5.77 (1H, m, CH$_2$=C*H*), 5.58 (1H, s, PhC*H*), 5.44 (1H, s, PhC*H*), 5.05–4.93 (2H, m, C*H*$_2$=CH), 4.87 (1H, dd, $J_{2',3'}$ 10.2 Hz, $J_{3',4'}$ 3.8 Hz, H3′), 4.70 (1H, d, $J_{1',2'}$ 7.8 Hz, H1′), 4.41 (1H, d, $J_{3',4'}$ 3.7 Hz, H4′), 4.37–4.29 (4H, m, H1, H4, H6, H6′), 4.14–3.98 (4H, H2′, H6, H6′, CH=CH$_2$(CH$_2$)$_5$C*H*$_2$O), 3.90 (1H, dd, $J_{2,3}$ 10.6 Hz, $J_{1,2}$ 7.9 Hz, H2), 3.63 (1H, dd, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 3.4 Hz, H3), 3.58–3.50 (2H, m, H5′, CH=CH$_2$(CH$_2$)$_5$C*H*$_2$O), 3.40 (1H, s, H5), 2.59 (d, *J* 2.4 Hz, OH), 2.11–2.04 (2H, m, CH=CH$_2$(C*H*$_2$)$_5$CH$_2$O), 1.75–1.62 (2H, m, CH=CH$_2$(C*H*$_2$)$_5$CH$_2$O), 1.51–1.30 (6H, m, CH=CH$_2$(C*H*$_2$)$_5$CH$_2$O), 1.25 (9H, s, (CH$_3$)$_3$C); ^{13}C NMR (100 MHz): δ_C 178.6 (C=O), 139.3 (CH$_2$=*C*H), 138.0 (Ph), 137.9 (Ph), 129.15 (Ph), 129.08 (Ph), 128.4 (Ph), 128.3 (Ph), 126.7 (Ph), 126.1 (Ph), 114.4 (*C*H$_2$=CH), 104.5 (C1′), 102.7 (C1), 101.4 (PhCH), 100.7 (PhCH), 77.8 (C3), 75.5, 73.4 (C3′, C4′), 73.4 (C4), 70.4, 69.3, 69.2 (C6, C6′, CH=CH$_2$-(CH$_2$)$_5$CH$_2$O), 68.8 (C2′), 66.9 (C5, C5′), 62.4 (C2), 39.2 ((CH$_3$)$_3$*C*), 33.9 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.7 (CH=CH$_2$(CH$_2$)$_5$CH$_2$O), 29.1 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.0 (CH=CH$_2$(CH$_2$)$_5$CH$_2$O), 27.3 ((*C*H$_3$)$_3$C), 26.0 CH=CH$_2$(CH$_2$)$_5$CH$_2$O). ESIMS: *m/z* Calcd [$C_{39}H_{51}N_3O_{11}$]Na$^+$: 760.3416. Found: 760.3412.

3.18. 7-Octen-1-yl 2-azido-3-*O*-(4,6-*O*-benzylidene-3-*O*-pivaloyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-β-D-galactopyranoside (38)

A solution of the alcohol **37** (520 mg, 0.705 mmol) in dry Et_2O (15 mL) was treated with 4 Å molecular sieves (500 mg) and the mixture stirred (rt, 1 h). The mixture was then cooled (−10 °C), treated with TMSOTf (50 μL, 0.226 mmol) followed by dropwise addition of the trichloroacetimidate **24**[26] (1.50 g, 2.67 mmol) in dry Et_2O (5 mL). The mixture was stirred (1 h), was treated with Et_3N (0.5 mL), filtered, and subjected to flash chromatography (EtOAc–hexanes, 1:3) to yield the trisaccharide **38** as a colorless oil (605 mg, 75%). [α] −15.8 (*c* 0.8, CH_2Cl_2); R_f 0.52 (EtOAc–hexanes, 1:1); ^{1}H NMR (500 MHz): δ_H 7.52–7.43 (4H, m, Ph), 7.35–7.20 (21H, m, Ph), 5.87–5.75 (1H, m, CH$_2$=C*H*), 5.55 (1H, s, PhC*H*),

5.46 (1H, s, PhC*H*), 5.37 (1H, d, $J_{1'',2''}$ 3.4 Hz, H1″), 5.07 (1H, dd, $J_{2',3'}$ 9.6 Hz, $J_{3',4'}$ 4.0 Hz, H3′), 5.02–4.97 (1H, m, CH_2=CH), 4.94–4.90 (2H, m, H1′, CH_2=CH), 4.88, 4.60 (2H, AB, *J* 11.5 Hz, PhCH_2), 4.78, 4.53 (2H, AB, *J* 11.7 Hz, PhCH_2), 4.71, 4.67 (2H, AB, *J* 11.4 Hz, PhCH_2), 4.46 (1H, d, $J_{3',4'}$ 4.0 Hz, H4′), 4.37 (1H, q, $J_{5'',6''}$ 6.5 Hz, H5″), 4.34 (1H, d, $J_{1,2}$ 8.3 Hz, H1), 4.32–4.25 (4H, m, H2′, H4, H6, H6′), 4.08–3.99 (5H, m, H2″, H4″, H6, H6′, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.75 (1H, dd, $J_{2,3}$ 10.7 Hz, $J_{1,2}$ 7.8 Hz, H2), 3.62–3.58 (2H, m, H3, H3″), 3.53 (1H, ddd, *J* 9.3 Hz, 6.9 Hz, 6.9 Hz, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.48 (1H, s, H5′) 3.37 (1H, s, H5), 2.09–2.02 (2H, m, CH=CH$_2$-(CH_2)$_5$CH$_2$O), 1.76–1.62 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.47–1.30 (6H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.07 (9H, s, (CH$_3$)$_3$C), 0.85 (3H, d, $J_{5'',6''}$ 6.5 Hz, H6″); ^{13}C NMR (125.7 MHz): δ_C 178.0 (C=O), 139.0 (CH$_2$=*C*H), 138.92 (Ph), 138.89 (Ph), 138.5 (Ph), 137.91 (Ph), 137.89 (Ph), 137.6 (Ph), 129.0 (Ph), 128.9 (Ph), 128.3 (2C, Ph), 128.2 (2C, Ph), 128.0 (Ph), 127.51 (Ph), 127.45 (2C, Ph), 127.38 (Ph), 127.3 (Ph), 126.6 (Ph), 126.1 (Ph), 114.3 (*C*H$_2$=CH), 102.8 (C1), 102.0 (C1′), 101.2 (Ph*C*H), 100.8 (Ph*C*H), 97.2 (C1″), 80.0, 76.3, 76.1, 75.6, 75.5 (C2″, C3′, C3″, C4, C4″), 78.2 (C3), 75.0 (PhCH$_2$), 73.4 (PhCH$_2$), 72.9 (PhCH$_2$), 72.5 (C4′), 70.6 (C2′), 70.3 (CH=CH$_2$(CH$_2$)$_5$CH$_2$O), 69.0 68.9 (C6, C6′), 66.8, 66.6, 66.1 (C5, C5′, C5″), 62.8 (C2), 38.9 ((CH$_3$)$_3$*C*), 33.7 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.5 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.9 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 27.0 ((*C*H$_3$)$_3$C), 25.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 16.3 (C6″). ESIMS: *m/z* Calcd [$C_{66}H_{79}N_3O_{15}$]Na$^+$: 1176.5403. Found: 1176.5403.

3.19. 7-Octen-1-yl 2-Azido-3-*O*-(4,6-*O*-benzylidene-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl))-2-deoxy-β-D-galactopyranoside (39)

A solution of the trisaccharide **38** (510 mg, 0.44 mmol) in CH$_3$OH (50 mL) was treated with a catalytic amount of LiOCH$_3$ (50 mg) and the solution was heated at reflux (7 d). The solution was then neutralized with Amberlite IR 120 (H$^+$), filtered, and subjected to flash chromatography (EtOAc–hexanes, 1:3) to afford first unreacted starting material (90 mg, 16%); further elution (EtOAc–hexanes, 1:2) afforded the alcohol **39** as a colorless oil (380 mg, 80%). [α] −36.9 (*c* 0.4, CH_2Cl_2); R_f 0.26 (EtOAc–hexanes, 1:1); ^{1}H NMR (500 MHz): δ_H 7.54–7.48 (4H, m, Ph), 7.40–7.21 (21H, m, Ph), 5.87–5.77 (1H, m, CH$_2$=C*H*), 5.58 (1H, s, PhC*H*), 5.55 (1H, s, PhC*H*), 5.35 (1H, s, H1″), 5.03–4.98 (1H, m, CH_2=CH), 4.96–4.91 (1H, m, CH_2=CH), 4.90, 4.57 (2H, AB, *J* 11.6 Hz, PhCH_2), 4.83–4.75 (4H, m, H1′, PhCH_2), 4.72 (1H, A of AB, *J* 11.6 Hz, PhCH_2), 4.33–4.22 (5H, m, H1, H4, H5″, H6, H6′), 4.21 (1H, d, $J_{3',4'}$ 2.5 Hz, H4′), 4.09 (1H, dd, $J_{6',6'}$ 12.4 Hz, $J_{5',6'}$ 1.7 Hz, H6′), 4.07–3.98 (4H, m, H2″, H3″, H6, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.94–3.87 (2H, m, H2′, H3′), 3.77 (1H, dd, $J_{2,3}$ 10.7 Hz, $J_{1,2}$ 7.9 Hz, H2), 3.67 (1H, br s, H4″), 3.57 (1H, dd, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 3.3 Hz, H3), 3.55–3.49 (1H, m, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.43 (1H, s, H5′), 3.38–3.24 (2H, m, H5, OH), 2.09–2.03 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.74–1.62 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.50–1.29 (6H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 0.94 (3H, d, $J_{5'',6''}$ 6.5 Hz, H6″); ^{13}C NMR (125.7 MHz): δ_C 139.1 (CH$_2$=*C*H), 138.9 (Ph), 138.9 (Ph), 138.2 (Ph), 137.8 (Ph), 137.6 (Ph), 129.2 (Ph), 128.8 (Ph), 128.32 (Ph), 128.31 (Ph), 128.28 (3C, Ph), 128.13 (Ph), 128.07 (Ph), 128.0 (Ph), 127.6 (Ph), 127.42 (Ph), 127.39 (Ph), 126.49 (Ph), 126.45 (Ph), 114.3 (*C*H$_2$=CH), 102.7 (C1), 102.0 (C1′), 101.4 (Ph*C*H), 101.0 (Ph*C*H), 98.9 (C1″), 80.0, 78.0 (C3″, C4″), 77.3, 76.3, 75.5, 73.8 (6C, C2′, C2″, C3, C3′, C4, C4′), 74.9 (PhCH$_2$), 73.6 (PhCH$_2$), 72.7 (PhCH$_2$), 70.2 (CH=CH$_2$-(CH$_2$)$_5$CH$_2$O), 69.2, 68.9 (C6, C6′), 66.8, 66.74, 66.69 (C5, C5′, C5″), 63.1 (C2), 33.7 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.5 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.9 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 25.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 16.3 (C6″). ESIMS: *m/z* Calcd [$C_{61}H_{71}N_3O_{14}$]-Na$^+$: 1092.4828. Found: 1092.4820.

3.20. 7-Octen-1-yl 2-acetamido-3-*O*-(4,6-*O*-benzylidene-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-β-D-galactopyranoside (40)

A solution of the azide **39** (350 mg, 0.327 mmol) in pyridine (4 mL) was treated with AcSH (2 mL) and the solution stirred (10 d). The solution was then concentrated and the residue was subjected to flash chromatography (CH_2Cl_2–MeOH, 9:1) to afford predominantly **40** as a colorless oil. The oil was then taken up in MeOH and treated with a catalytic amount of NaOMe in MeOH and the solution was stirred (rt, 5 h). The solution was then neutralized with Amberlite IR 120 (H$^+$), filtered, and the residue was subjected to flash chromatography (EtOAc–hexanes, 1:1) to afford unreacted starting material **39** (100 mg, 28%), further elution (EtOAc–hexanes, 1:1) afforded **40** as a colorless oil (210 mg, 60%). [α] −24.0 (*c* 0.4, CH_2Cl_2); R_f 0.62 (EtOAc–hexanes, 7:3); ^{1}H NMR (500 MHz): δ_H 7.54–7.46 (4H, m, Ph), 7.41–7.23 (18H, m, Ph), 7.17–7.08 (3H, m, Ph), 6.31 (1H, d, *J* 6.6 Hz, NH), 5.85–5.75 (1H, m, CH$_2$=C*H*), 5.60 (1H, s, PhC*H*), 5.55 (1H, s, PhC*H*), 5.49 (1H, d, $J_{1'',2''}$ 3.5 Hz, H1″), 5.25 (1H, d, $J_{1,2}$ 8.2 Hz, H1), 5.01–4.90 (3H, m, CH_2=CH, PhCH_2), 4.78–4.67 (4H, m, PhCH_2), 4.59–4.54 (2H, m, H3, PhCH_2), 4.45 (1H, d, $J_{1',2'}$ 7.8 Hz, H1′), 4.36 (1H, d, $J_{3,4}$ 3.4 Hz, H4), 4.31–4.25 (2H, m, H6, H6′), 4.15 (1H, d, $J_{3',4'}$ 3.7 Hz, H4′), 4.08–4.02 (4H, m, H2″, H5″, H6, H6′), 3.97 (1H, dd, $J_{2',3'}$ 9.6 Hz, $J_{1',2'}$ 7.8 Hz, H2′), 3.93–3.87 (2H, m, H3″, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.73–3.67 (1H, m, H3′), 3.51–3.40 (5H, m, H2, H4″, H5, H5′, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.37 (1H, d, *J* 8.1 Hz, OH), 2.06–2.00 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.74 (3H, s, CH$_3$CO), 1.63–1.53 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.39–1.25 (6H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 0.99 (3H, d, $J_{5'',6''}$ 6.4 Hz, H6″); ^{13}C NMR (125.7 MHz): δ_C 171.3 (C=O), 139.1 (CH$_2$=*C*H), 138.6 (2C, Ph), 138.3 (Ph), 137.62 (Ph), 137.60 (Ph), 129.2 (Ph), 128.8 (Ph), 128.4 (Ph), 128.3 (Ph), 128.24 (Ph), 128.23 (Ph), 128.20 (Ph), 128.1 (Ph), 128.0 (Ph), 128.8 (Ph), 127.6 (Ph), 127.5 (2C, Ph), 126.5 (Ph), 126.3 (Ph), 114.2 (*C*H$_2$=CH), 101.7 (C1′), 101.4 (Ph*C*H), 100.8 (Ph*C*H), 99.1 (C1), 97.1 (C1″), 79.4 (C3″), 77.4 (C4″), 77.1, 75.8, 74.8, 73.8, 73.5 (C2′, C3, C3′, C4, C4′), 75.9 (C2″), 74.8 (PhCH$_2$), 73.8 (PhCH$_2$), 73.0 (PhCH$_2$), 69.5, 69.3, 69.2 (C6, C6′, CH=CH$_2$(CH$_2$)$_5$CH$_2$O), 67.6 (C5″), 66.6, 66.5 (C5, C5′), 55.7 (C2), 33.7 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.5 (CH=CH$_2$(*C*H$_2$)$_5$-CH$_2$O), 28.90 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.89 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 25.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 23.3 (CH$_3$CO) 16.3 (C6″). ESIMS: *m/z* Calcd [$C_{63}H_{75}NO_{15}$]Na$^+$: 1108.5029. Found: 1108.5035.

3.21. 7-Octyl 2-acetamido-3-*O*-(2-*O*-(α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-β-D-galactopyranoside (41)

The octenyl glycoside **12** (95 mg, 0.149 mmol) was treated with Pd–C (10%, 20 mg), taken up in MeOH (20 mL) and to a H_2 atmosphere (rt, 1 d). The mixture was then filtered, concentrated, and the residue was subjected to C-18 chromatography (CH$_3$OH–H$_2$O, 1:1) to afford the octyl glycoside **41** as a colorless oil (70 mg, 73%). [α] −93.3 (*c* 0.2, MeOH); ^{1}H NMR (CD$_3$OD, 500 MHz): δ_H 5.21 (1H, d, $J_{1'',2''}$ 3.8 Hz, H1″), 4.53 (1H, d, $J_{1',2'}$ 7.2 Hz, H1′), 4.25 (1H, q, $J_{5'',6''}$ 6.8 Hz, H5″), 4.24 (1H, $J_{1,2}$ 8.8 Hz, H1), 4.09 (1H, dd, $J_{2,3}$ 10.2 Hz, $J_{1,2}$ 8.8 Hz, H2), 4.06 (1H, d, $J_{3,4}$ 3.2 Hz, H4), 3.92–3.64, 3.55–3.48 (15H, 2 × m, H2′, H2″, H3, H3′, H3″, H4′, H4″, H5, H5′, H6, H6′, CH$_3$(CH$_2$)$_6$CH_2O), 3.47–3.40 (1H, m, CH$_3$(CH$_2$)$_6$CH_2O), 1.97 (3H, s, CH$_3$C=O) 1.60–1.45 (2H, m, CH$_3$(CH_2)$_6$CH$_2$O), 1.40–1.26 (10H, m, CH$_3$(CH_2)$_6$CH$_2$O), 1.24 (3H, d, $J_{5'',6''}$ 6.8 Hz, H6″), 0.89 (3H, t, *J* 6.8 Hz, CH_3(CH$_2$)$_6$CH$_2$O). ^{13}C NMR (125.7 MHz, CD$_3$OD): δ_C 173.3 (C=O), 104.1 (C1), 103.8 (C1′), 101.2 (C1″), 79.2, 78.5, 76.8, 76.4, 75.5, 73.5, 71.5, 70.6, 70.4 (C2′, C2″, C3, C3′, C3″, C4, C4′, C4″, C5″), 70.6 (CH$_3$(CH$_2$)$_6$CH_2O), 69.7, 68.3 (C5, C5′), 62.6 (C6, C6′), 52.7 (C2), 33.1 (CH$_3$(*C*H$_2$)$_6$CH$_2$O), 30.7 (CH$_3$(*C*H$_2$)$_6$CH$_2$O), 30.55 (CH$_3$(CH$_2$)$_6$CH$_2$O), 30.52 (CH$_3$(*C*H$_2$)$_6$CH$_2$O),

27.2 ($CH_3(CH_2)_6CH_2O$), 23.7 ($CH_3(CH_2)_6CH_2O$), 23.4 ($CH_3C{=}O$), 16.7 (C6″), 14.5 ($CH_3(CH_2)_6CH_2O$). ESIMS: *m/z* Calcd $[C_{28}H_{51}NO_{15}]Na^+$: 664.3151. Found: 664.3146.

3.22. 7-Octen-1-yl 2-acetamido-3-*O*-(3-*O*-(2-acetamido-2-deoxy-3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-4,6-*O*-benzylidene-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-β-D-galactopyranoside (43)

A solution of the acceptor **39** (1.42 g, 1.33 mmol) in dry Et_2O (25 mL) was treated with 4 Å molecular sieves (1 g) and the mixture was stirred (rt, 1 h). The mixture was then cooled (−10 °C), treated with TMSOTf (50 μL, 0.29 mmol); the trichloroacetimidate **15**[25] (1.89 g, 3.98 mmol) in dry Et_2O (25 mL) was then added dropwise and the mixture was allowed to stand (20 min). The mixture was neutralized with Et_3N (0.5 mL), filtered, concentrated, and subjected to flash chromatography (EtOAc–hexanes 1:3) to afford the near pure tetrasaccharide **42** as a colorless oil (1.46 g, 79%). A solution of the tetrasaccharide **42** (630 mg, 0.455 mmol) in pyridine (6 mL) was treated with AcSH (3 mL) and the solution was stirred (7 d). The solution was concentrated and subjected to flash chromatography (CH_2Cl_2–CH_3OH, 10:1) to afford **43** as a colorless oil (532 mg, 83%). R_f 0.37 (CH_3OH–CH_2Cl_2 1:20); ^1H NMR (500 MHz): δ_H 7.53–7.49 (2H, m, Ph), 7.43–7.39 (2H, m, Ph), 7.37–7.24 (18H, m, Ph), 7.23–7.19 (3H, m, Ph), 5.93–5.86 (1H, s, NH), 5.85–5.76 (1H, m, $CH_2{=}CH$), 5.57 (1H, s, PhC*H*), 5.49 (1H, d, $J_{1'',2''}$ 3.9 Hz, H1″), 5.47–5.43 (2H, m, PhC*H*, NH), 5.15–5.05 (4H, m, H1, H1‴, H4‴, PhCH_2), 5.02–4.97 (1H, m, $CH_2{=}CH$), 4.96–4.92 (1H, m, $CH_2{=}CH$), 4.91–4.82 (3H, m, H3‴, PhCH_2), 4.72–4.56 (4H, m, H2‴, H3, PhCH_2), 4.51–4.46 (2H, m, H1′, PhCH_2), 4.37 (1H, d, $J_{3,4}$ 3.9 Hz, H4), 4.33–4.28 (3H, m, H4′, H6, H6′), 4.23 (1H, dd, $J_{2',3'}$ 9.6 Hz, $J_{1',2'}$ 8.1 Hz, H2′), 4.20–4.11 (2H, m, H2″, H5″), 4.09–4.03 (2H, m, H6, H6′), 4.01–3.94 (2H, m, H5‴, $CH{=}CH_2(CH_2)_5CH_2O$), 3.82–3.71 (3H, m, H3′, H3″, H6‴), 3.55–3.38 (5H, m, H2, H4″, H5, H5′, $CH{=}CH_2(CH_2)_5CH_2O$), 3.20 (1H, m, $J_{6''',6'''}$ 8.9 Hz, H6‴), 2.09 (3H, s, CH_3CO), 2.08–2.01 (2H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 1.96 (3H, s, CH_3CO), 1.94 (3H, s, CH_3CO), 1.76 (3H, s, CH_3CO), 1.69–1.58 (2H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 1.48 (3H, s, CH_3CO), 1.44–1.29 (6H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 0.79 (3H, d, $J_{5'',6''}$ 6.3 Hz, H6″); ^{13}C NMR (125.7 MHz): δ_C 170.4 (2C, C=O), 170.3 (C=O), 170.04 (C=O), 169.99 (C=O), 139.00 ($CH_2{=}CH$), 138.6 (2C, Ph), 138.4 (Ph), 138.3 (Ph), 137.4 (Ph), 129.2 (Ph), 129.0 (Ph), 128.6 (Ph), 128.31 (Ph), 128.28 (Ph), 128.20 (Ph), 128.1 (Ph), 128.0 (Ph), 127.8 (Ph), 127.65 (Ph), 127.59 (Ph), 127.55 (Ph), 127.1 (Ph), 126.7 (Ph), 126.0 (Ph), 114.3 ($CH_2{=}CH$), 102.3 (C1′), 101.1 (PhCH), 100.8 (PhCH), 99.2, 97.0 (C1, C1″) 92.1 (C1‴), 79.6, 75.94, 75.87, 75.7, 73.89, 73.7, 70.5, 68.84, 68.82, 67.42, 67.36, 66.9, 66.5, 66.4 (C2′, C2″, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5, C5′, C5″, C5‴), 74.9 (PhCH$_2$), 73.9 (PhCH$_2$), 71.7 (PhCH$_2$), 69.8, 69.3, 69.2 (C6, C6′, $CH{=}CH_2(CH_2)_5CH_2O$), 62.8 (C6‴), 55.6, 46.3 (C2, C2‴), 33.7 ($CH{=}CH_2(CH_2)_5CH_2O$), 29.6 ($CH{=}CH_2(CH_2)_5CH_2O$), 28.9 (2C, $CH{=}CH_2(CH_2)_5CH_2O$), 25.8 ($CH{=}CH_2(CH_2)_5CH_2O$), 23.4 (CH_3CO), 22.6 (CH_3CO), 20.8 (CH_3CO), 20.7 (CH_3CO), 20.6 (CH_3CO), 16.2 (C6″). ESIMS: *m/z* Calcd $[C_{77}H_{94}N_2O_{23}]Na^+$: 1437.6140. Found: 1437.6129.

3.23. 7-Octen-1-yl 2-acetamido-3-*O*-(4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-2-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl)-2-deoxy-β-D-galactopyranoside (46)

A solution of the acceptor **39** (1.49 g, 1.39 mmol) and the trichloroacetimidate **32**[28] (2.85 g, 4.18 mmol) in dry Et_2O (25 mL) was treated with 4 Å molecular sieves (rt, 1 h). The mixture was cooled (−20 °C) and treated with TMSOTf (40 μL, 0.23 mmol) and allowed to warm (0 °C). The mixture was treated with Et_3N (200 μL), filtered, concentrated, and subjected to flash chromatography (EtOAc–hexanes 1:1) to afford the tetrasaccharide **45** as a colorless oil (1.77 g, 86%). A solution of the tetrasaccharide **45** (233 mg, 0.146 mmol) in dry pyridine (4 mL) was treated with AcSH (2 mL) and stirred (rt, 14 d). Concentration followed by flash chromatography (EtOAc–CH_2Cl_2 3:7) afforded the desired **46** as a colorless oil (214 mg, 91%). R_f 0.18 (CH_3OH–CH_2Cl_2 1:20); [α] +4.3 (*c* 0.3, CH_2Cl_2); ^1H NMR (500 MHz): δ_H 7.52–7.07 (45H, m, Ph), 6.06 (1H, s, NH), 5.84–5.75 (1H, m, $CH_2{=}CH$), 5.56 (1H, d, $J_{1'',2''}$ 3.7 Hz, H1″), 5.54 (1H, s,, PhC*H*), 5.39 (1H, s,, PhC*H*), 5.33 (1H, d, $J_{1''',2'''}$ 3.6 Hz, H1‴), 5.20 (1H, d, $J_{1,2}$ 7.9 Hz, H1) 5.02–4.96 (1H, m, $CH_2{=}CH$), 4.95–4.92 (1H, m, $CH_2{=}CH$), 4.89 (1H, A of AB, *J* 11.6 Hz, PhCH_2), 4.83 (1H, A of AB, *J* 11.4 Hz, PhCH_2), 4.69–4.64 (3H, m, PhCH_2), 4.62–4.39 (7H, m H1′, H3, PhCH_2), 4.25–4.19 (2H, m, H2′, H6′), 4.13–4.07 (1H, m, H5″), 4.06–3.99 (2H, m, H2‴, H6), 3.97–3.90 (2H, m, $CH{=}CH_2(CH_2)_5CH_2O$, H6′), 3.90–3.83 (2H, m, H2″, H5‴), 3.81–3.69 (3H, m, H2, H4‴, H5, $CH{=}CH_2(CH_2)_5CH_2O$), 3.42 (1H, dd, $J_{6''',6'''}$ 9.5 Hz, $J_{5''',6'''}$ 7.2 Hz, H6‴), 3.29 (1H, s, H4″), 3.20–3.14 (2H, m, H5′, H6‴), 2.07–1.98 (2H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 1.63 (3H, s, CH_3CO), 1.61–1.53 (2H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 1.39–1.22 (6H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 0.82 (3H, d, $J_{5'',6''}$ 6.3 Hz, H6″); ^{13}C NMR (125.7 MHz): δ_C 171.3 (C=O), 139.1 (Ph), 139.0 ($CH_2{=}CH$), 138.94 (Ph), 138.92 (Ph), 138.7 (Ph), 138.63 (Ph), 138.56 (Ph), 138.5 (Ph), 138.4 (Ph), 138.2 (Ph), 137.4 (Ph), 128.9 (Ph), 128.8 (Ph), 128.5 (Ph), 128.41 (Ph), 128.40 (Ph), 128.20 (Ph), 128.18 (Ph), 128.14 (Ph), 128.11 (Ph), 128.05 (Ph), 127.99 (Ph), 127.92 (Ph), 127.87 (Ph), 127.80 (Ph), 127.75 (Ph), 127.71 (Ph), 127.66 (Ph), 127.6 (Ph), 127.50 (Ph), 127.46 (Ph), 127.4 (Ph), 127.15 (Ph), 127.08 (Ph), 126.7 (Ph), 126.1 (Ph), 114.2 ($CH_2{=}CH$), 102.5 (C1′), 101.1 (PhCH), 100.7 (PhCH), 99.3 (C1), 96.1 (C1″), 92.5 (C1‴), 79.8, 77.8, 77.5 76.4, 76.3, 75.9, 75.7, 75.0, 73.5, 72.0, 70.6 (C2′, C2″, C2‴, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5‴), 74.9 (PhCH$_2$), 74.5 (PhCH$_2$), 73.4 (PhCH$_2$), 73.0 (PhCH$_2$), 72.6 (PhCH$_2$), 72.3 (PhCH$_2$), 71.0 (PhCH$_2$), 69.8, 69.7, 69.4, 69.2 (C6, C6′, C6‴, $CH{=}CH_2(CH_2)_5CH_2O$), 66.6, 66.5, 66.4 (C5, C5′, C5″), 55.7 (C2), 33.7 ($CH{=}CH_2(CH_2)_5CH_2O$), 29.6 ($CH{=}CH_2(CH_2)_5CH_2O$), 28.90 ($CH{=}CH_2(CH_2)_5CH_2O$), 28.89 ($CH{=}CH_2(CH_2)_5CH_2O$), 25.8 ($CH{=}CH_2(CH_2)_5CH_2O$), 23.1 (CH_3CO), 16.3 (C6″). ESIMS: *m/z* Calcd $[C_{95}H_{107}NO_{19}]Na^+$: 1588.7330. Found: 1588.7356.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2011.03.008.

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