RESEARCH FRONT

Full Paper

CSIRO PUBLISHING

Aust. J. Chem. **2009**, *62*, 558–574

www.publish.csiro.au/journals/ajc

Synthesis of ABO Histo-Blood Group Type V and VI Antigens*

Peter J. Meloncelli[A] *and Todd L. Lowary*[A,B]

[A]Department of Chemistry and Alberta Ingenuity Centre for Carbohydrate Science, Gunning-Lemieux Chemistry Centre, University of Alberta, Edmonton, AB T6G 2G2, Canada.

[B]Corresponding author. Email: tlowary@ualberta.ca

The ABO histo-blood group antigens have long been of interest to chemists, biochemists, and evolutionary biologists. However, to date, a complete synthesis of all ABO histo-blood group antigens has not been conducted, despite the potential for such a panel to provide a more detailed understanding of the biological roles of these glycan motifs. Here we report the chemical synthesis of the A, B, and H type V and VI antigens in multi-milligramme quantities as part of an overall goal to prepare all 18 A, B, and H antigens. The A and B type V and VI antigens were prepared with a 7-octen-1-yl linker, to enable future conjugation to a protein or solid support. The H type V and VI antigens were prepared as the octyl glycoside, to facilitate detailed enzyme kinetics studies.

Manuscript received: 28 January 2009.
Final version: 11 March 2009.

Introduction

Despite the discovery of the ABO histo-blood group system by Landsteiner over 100 years ago,[1] questions still remain unanswered. This includes the prevalence, distribution, and antibody affinity of the ABO subtypes, as well as the kinetics of the enzymes responsible for their synthesis.[2] The structures of the carbohydrates responsible for the ABO histo-blood group system were elucidated by Morgan and Watkins in 1957.[3] Their work demonstrated that the H antigen is a disaccharide consisting of L-fucose and D-galactose (**1**, Fig. 1), whereas A and B antigens (**2** and **3**) are trisaccharides containing this disaccharide linked to an additional *N*-acetyl galactosamine or galactose residue, respectively. All individuals, with the exception of those of the Bombay phenotype, are capable of producing the core H antigen structure;[4,5] people with the O blood type are only able to produce the H antigen. Individuals who are blood group A possess the glycosyltransferase GTA, which attaches an *N*-acetyl galactosamine residue to the 3-OH group of the galactose moiety of the H antigen. Alternatively, blood group B individuals possess a different glycosyltransferase, GTB, which attaches galactose to this same hydroxyl group.[4,6,7] It was not until the 1990s that the genetic basis for the ABO blood group antigens was determined.[8–10] A direct comparison of the genes responsible for coding GTA and GTB showed a 99% sequence homology, differing by only seven base pairs, with three of those resulting in silent mutations. Thus, the proteins differ only by four amino acids.[2]

The ABO histo-blood group system can be further subtyped according to the carbohydrate residue present at the reducing end, into what is now referred to as type I through to type VI (Table 1).[4,11,12] To date, limited studies have been done to determine the biological importance of these structural subtypes. However, those studies that have been carried out suggest, not surprisingly, that these structural differences do influence biochemical function. For example, Palcic and coworkers showed that this minor structural variation can have a significant effect on the kinetics of GTA and GTB.[13] In that study, the kinetics of GTA and GTB were measured for both the H type I and type II antigens and it was shown for both enzymes that the rate of transfer was significantly higher for the H type I antigen.[13] Another study, by Oriol and coworkers, explored the cross reactivity of Anti-Le^a and Anti-Le^b antibodies with several Lewis and histo-blood group antigens, showing a significant variation in binding between subtypes.[14]

To date, numerous synthetic investigations have been undertaken towards the synthesis of the histo-blood group antigens. Most of these studies have focussed on the preparation of the disaccharide H antigens and trisaccharide A and B antigens.[15–17] When the trisaccharide H antigen and tetrasaccharide A and B antigens have been synthesized, the more prevalent type I and type II structures have been the target of most synthetic efforts.[18–22] In other investigations, the B type III and type IV tetrasaccharide determinants were prepared by Bovin and coworkers via a [3 + 1] block chemical synthesis,[23] while an earlier synthesis by the same group reported the synthesis of the A, B, and H type III determinants.[24] In addition, the syntheses of both H type V and type VI antigens have been previously reported by several groups[25–27] and the enzymatic synthesis of the A type V and type VI structures was reported by Thiem and coworkers.[27] In the present paper, we report the chemical synthesis of the A, B, and H type V and type VI antigens (**4**–**9**, Fig. 2), as part of a larger program to complete the synthesis of all 18 histo-blood group antigens in quantities suitable for detailed biochemical studies (~100 mg). Access to such quantities of this material would enable, for example, the direct comparison of GTA and GTB kinetics for the H antigens and antibody affinity studies to be conducted on the A, B, and H determinants as a function of type I–VI subtype.

*Dedicated to Professor Robert V. Stick on the occasion of his retirement.

10.1071/CH09058 0004-9425/09/060558

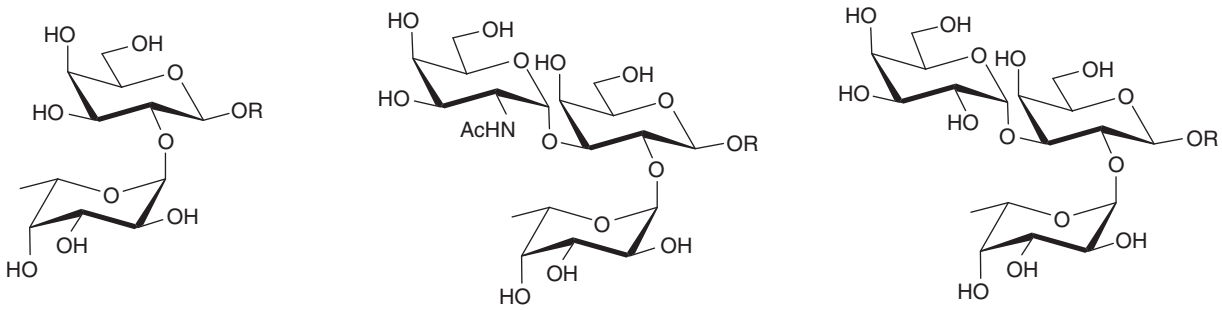


Fig. 1. Carbohydrate structures for A, B, and H antigens. R = glycoprotein or glycolipid.

Table 1. Carbohydrate moieties responsible for the six subtypes of human blood, where R are the ABO blood group antigens[4]

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

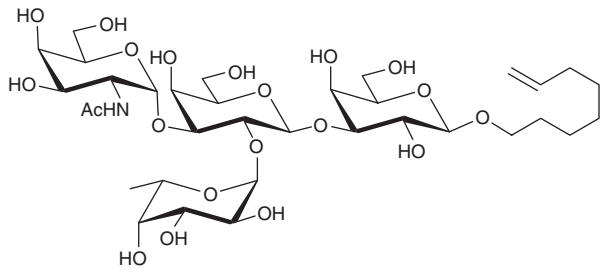
Results and Discussion

To prepare **4**–**9**, it was decided that a linear chemical synthesis would offer the most expedited synthesis while still allowing appreciable quantities to be produced. Although a block synthesis of the tetrasaccharides, where, for example, a donor consisting of the non-reducing-end trisaccharide was added to a monosaccharide would be more convergent, such an approach would not allow access to the H structures, which were also targets. A versatile group at the reducing end was required to ensure that the targets could be used in a wide range of studies, and for this reason a 7-octen-1-yl linker was chosen. This group would enable ready access to the octyl glycoside for enzyme kinetic studies,[28] while still enabling the attachment of a linker to enable conjugation to a protein or solid support. As part of a larger project within our group, developing tolerogens for ABO-incompatible transplants, we have been able to successfully attach the A type I antigen to stainless steel stents and nanoparticles (M. Jeyakanthan, V. W. Wright, P. J. Meloncelli, et al., unpubl. data). It is anticipated that the A and B type V and VI antigens could also be attached in a similar manner.

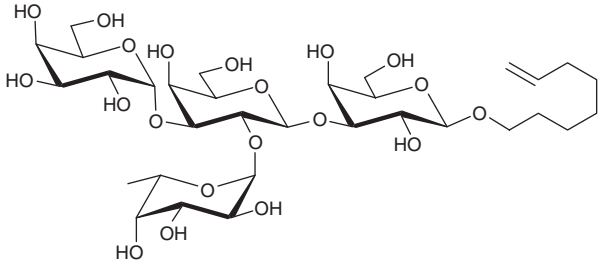
Synthesis of Type V Antigens

Key to the synthesis of the type V antigens was the preparation of the β-D-galactopyranoside derivative **18** (Scheme 1). The benzyl ethers and benzylidene acetal in this intermediate were selected to enable their one-step removal at the end of the sequence. The octenyl glycoside **11** was prepared directly from the known trichloroacetimate **10**[29] with subsequent deacetylation to afford the tetrol **12** in 73% yield over the two steps. Introduction of the benzylidene acetal was achieved using benzaldehyde dimethyl acetal and catalytic *p*-toluenesulfonic acid to give, in 72% yield, the diol **13**. With the diol in hand, it was necessary to differentiate the two secondary hydroxyl groups. Introduction of the benzyl group on the C-2 hydroxyl group was achieved by first selectively protecting the C-3 hydroxyl group as a *p*-methoxybenzyl ether. This approach was inspired by similar work reported by Nakashima and coworkers, the only difference being the presence of an *n*-pentenyl glycoside instead of the *n*-octenyl glycoside in **13**.[30] This transformation was achieved by the preparation of a stannylene acetal by heating **13** with di-*n*-butyltin oxide at reflux in toluene, followed by reaction with *p*-methoxybenzyl chloride, which led to the formation of a mixture of **14** and **15** in a 1:2 ratio in a combined yield of 95%. Fortunately, conversion of the undesired isomer **14** into **13** was possible by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), analogously to the conversion of **16** into **18** (see below). Confirmation of the regioselectivity of the reaction was achieved by acetylation of **15** and observation of the downfield shift of the resonance from H2 from a multiplet between 3.91 and 4.06 ppm to a doublet of doublets at 5.34 ppm. With the correct regiochemistry confirmed, benzylation of **15** (benzyl bromide, sodium hydride) afforded **16** in 89% yield. Removal of the *p*-methoxybenzyl ether to give **18** was achieved in good yield (95%) using DDQ in a mixture of dichloromethane and water.

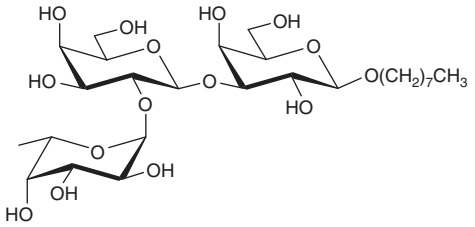
Selection of the appropriate donor for the introduction of the galactose core was key to the efficient synthesis of the target. Treatment of the previously prepared acceptor **18** with trichloroacetimidate donor **19**[31] and the appropriate promoter ($BF_3 \cdot OEt_2$) afforded the disaccharide **20** with complete stereoselectivity (Scheme 2). Deacetylation to afford **21** was necessary to facilitate separation from the trichloroacetimidate by-product, the glycosyl *N*-trichloroacetamide. Selective protection of the 3′ position of **21** was achieved using trimethylacetyl chloride in pyridine, similarly to previous work reported by Zhang and coworkers.[32] This strategy, although counter-intuitive at first, effectively circumvents the difficulties that could be observed by complex protecting group manipulations at a later stage in the synthesis. Introduction of the α-L-fucopyranosyl linkage was achieved using β-L-fucopyranosyl trichloroacetimidate **23**, which has been successfully used by Schmidt and coworkers to prepare several α-L-fucopyranosides in a stereoselective manner.[33] Removal of the pivaloate ester from **24** proved to be more problematic than anticipated. Its cleavage required the forcing conditions of refluxing lithium methoxide in methanol



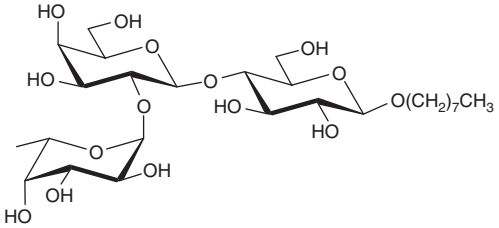
4
A type V antigen



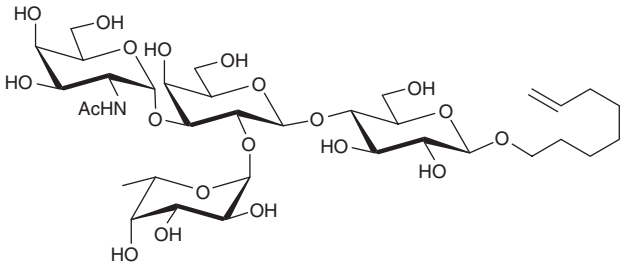
5
B type V antigen



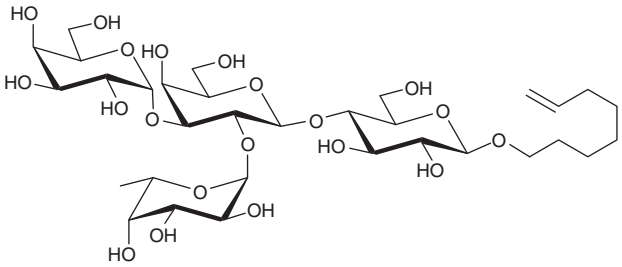
6
H type V antigen



7
H type VI antigen



8
A type VI antigen



9
B type VI antigen

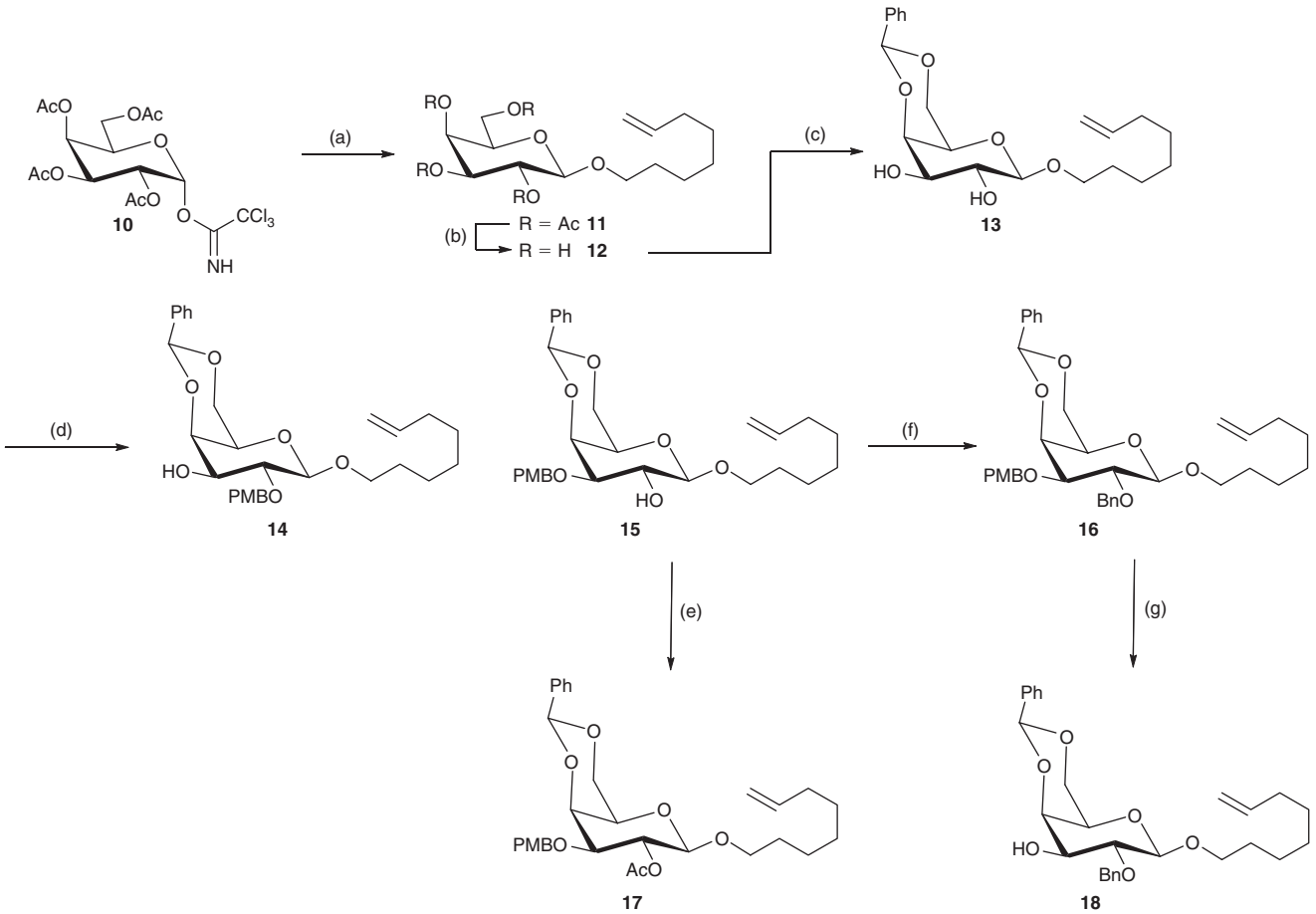
Fig. 2. Histo-blood group antigen targets, A, B, and H type V and VI.

to provide **25** in moderate (58%) yield; however, some starting material (**24**) was recovered and could be recycled.

With trisaccharide **25** in hand, the H type V antigen was prepared with the view of undertaking enzyme kinetic studies with GTA and GTB. For these investigations, the octyl glycoside **6** was required and this compound was obtained as illustrated in Scheme 3. First, removal of the benzylidene acetals and benzyl ethers using a Birch reduction, followed by reduction of the alkene by hydrogenation afforded **6** in 49% yield. The low yield can be attributed to the low solubility of **25** under the reaction conditions, and a significant portion (33%) of starting material was recovered, and could be recycled. Although direct hydrogenation of **25** provided **6**, surprisingly, it was not possible to isolate **25** in adequate purity when the protecting groups were removed in this manner and thus we employed this two-step approach.

In addition to being used for the synthesis of the H type V antigen, trisaccharide **25** also served as the precursor to the corresponding A and B structures. Access to the A type V antigen (Scheme 4) was achieved by glycosylation of **25** using the known trichloroacetimidate **26**[34] to afford the tetrasaccharide with complete stereoselectivity. Purification of the product at this stage proved difficult owing to contamination with by-products arising from trichloroacetimidate **26**. Thus, the azide was reduced and the product amine was acetylated, generating the expected *N*-acetyl derivative **27**, in 51% overall yield from **25** and **26**. Deacetylation, followed by a Birch reduction, afforded tetrasaccharide **4** in good (90%) yield. The solubility problems that plagued the deprotection of **25** were not problematic here.

The B type V antigen was prepared in a manner analogous to the A type structure (Scheme 5). First, treatment of the trisaccharide acceptor **25** with the trichloroacetimidate **28**[35] in the presence of trimethylsilyltrifluoromethane sulfonate (TMSOTf) afforded the tetrasaccharide **29** with complete stereoselectivity. Unfortunately contamination with by-products of the trichloroacetimidate **28**, as was observed in the synthesis of **6**, again did not permit full characterization until removal of the benzyl ethers and benzylidene acetals by a Birch reduction to give **5** in 50% yield. As was seen in the deprotection of **25**, the poor yield resulted from the poor solubility of **29** under the



Scheme 1. (a) 7-octen-1-ol, 4-Å MS, TMSOTf, CH_2Cl_2; (b) $NaOCH_3$, CH_3OH, 73% (two steps); (c) $PhCH(OCH_3)_2$, *p*-TsOH, DMF, 72%; (d) *n*-Bu_2SnO, *n*-Bu_4NI, *p*-methoxybenzyl chloride, $PhCH_3$, 95%; (e) Ac_2O, pyridine, DMAP, 99%; (f) BnBr, NaH, DMF, 89%; (g) DDQ, CH_2Cl_2, H_2O, 95%.

reaction conditions; fortunately, the unreacted starting material was easily recoverable and could be submitted to the reaction again.

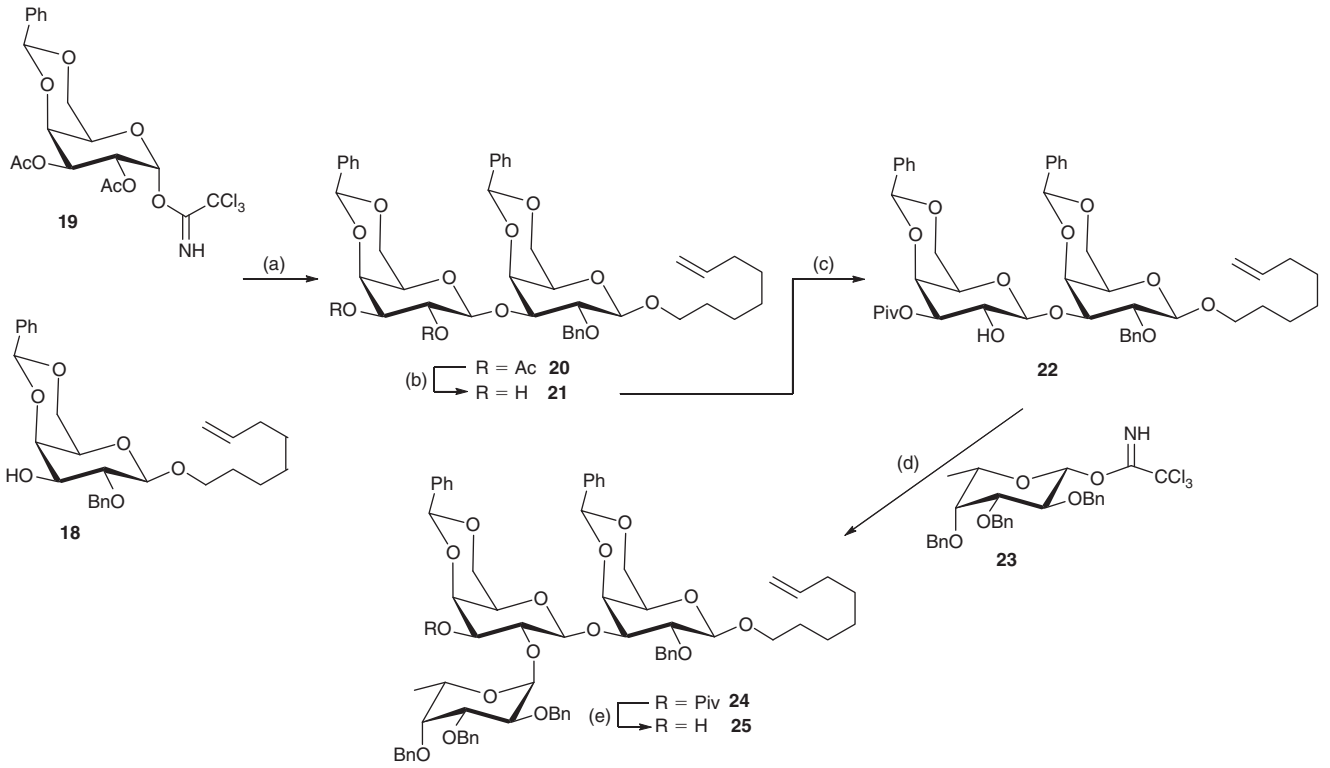
Synthesis of Type VI Antigens

A pathway analogous to the one used for the preparation of the type V structures was also employed to prepare the type VI antigens. The same building blocks were required, except that the protected galactoside acceptor **18**, the precursor to the 'reducing-end' residue, was replaced with the requisite β-D-glucopyranoside (**36**, Scheme 6). This compound was prepared commencing from the previously reported trichloroacetimidate **30**[35] by glycosidation with 7-octen-1-ol to afford the glycoside **31**. Subsequent deacetylation afforded the tetrol **32** in 57% yield over two steps. Next, introduction of the benzylidene acetal was achieved, yielding **33** in 95% yield. Benzylation of the diol under standard conditions yielded **35**, and then the opening of the benzylidene acetal provided the 2,3,6-tri-*O*-benzyl glucopyranoside derivative **36** in 63% yield over the two steps. To effect the benzylidene ring opening, several sets of conditions were explored, including the more conventional trifluoromethanesulfonic acid (TfOH)–$NaCNBH_3$ method originally reported by Kiessling.[36] However, in terms of reproducibility, the Et_3SiH–$BF_3 \cdot OEt_2$ conditions reported by Toone[37] were found to be the most effective. The regiochemistry of the benzylidene acetal ring opening was confirmed by acetylation and a downfield shift of H4 from a multiplet at 3.52–3.63 ppm to one at 4.92–5.01 ppm.

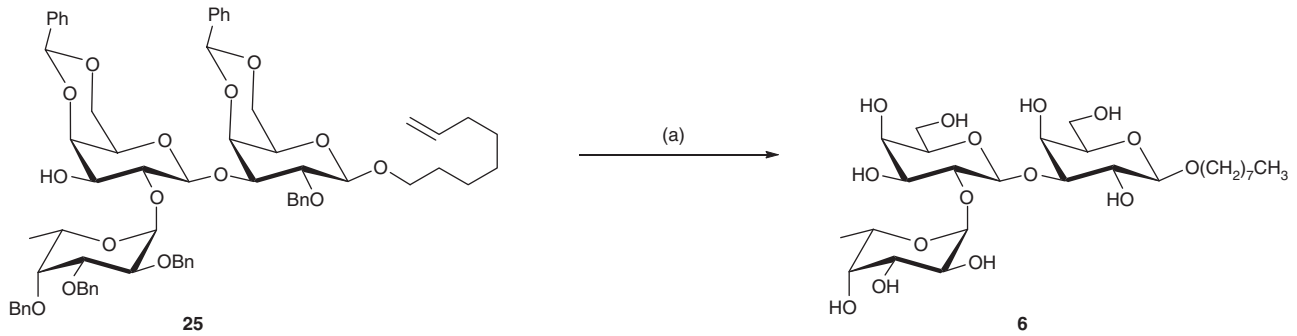
Once **36** had been synthesized, we commenced the preparation of the oligosaccharides as illustrated in Scheme 7. First, glycosylation of **36** with the trichloroacetimidate **19**[31] afforded the disaccharide product. Deacetylation was again necessary to facilitate purification as the disaccharide was contaminated by the glycosyl *N*-trichloroacetamide by-product arising from **19**. Disaccharide diol **37** was obtained in 91% yield over the two steps. Selective protection of the 3′ position with a pivaloate ester yielded alcohol **38**, which was subsequently glycosylated, in 78% yield, using β-L-fucopyranosyl trichloroacetimidate **23**.[33] Removal of the pivaloate ester in **39** afforded **40**, the low yield was again attributed to the low reactivity of **39** under the reaction conditions. Fortunately, unreacted **39** was easily recovered.

The H type VI antigen **7** was required for enzyme kinetic studies, as was its H type V counterpart. Preparation of this trisaccharide was achieved through Birch reduction of **40** followed by hydrogenation of the alkene to afford the H type VI trisaccharide **7** (Scheme 8). Although direct treatment of **40** with H_2 and Pd–C did provide **7**, it was found advantageous in terms of product purity of **7** to conduct the two-step process.

Access to the A type VI antigen was achieved by glycosylation of **40** with the trichloracetimidate **26**,[34] followed by conversion of the azide to an *N*-acetyl using thioacetic acid in pyridine (Scheme 9). Again, like the A type V counterpart, conversion of the azide was necessary to facilitate purification



Scheme 2. (a) $BF_3{\cdot}OEt_2$, CH_2Cl_2, 4-Å MS; (b) $NaOCH_3$, CH_3OH, 59% (two steps); (c) $(CH_3)_3COCl$, pyridine, 85%; (d) TMSOTf, Et_2O, 4 Å MS, 98%; (e) $LiOCH_3$, CH_3OH, 58%.

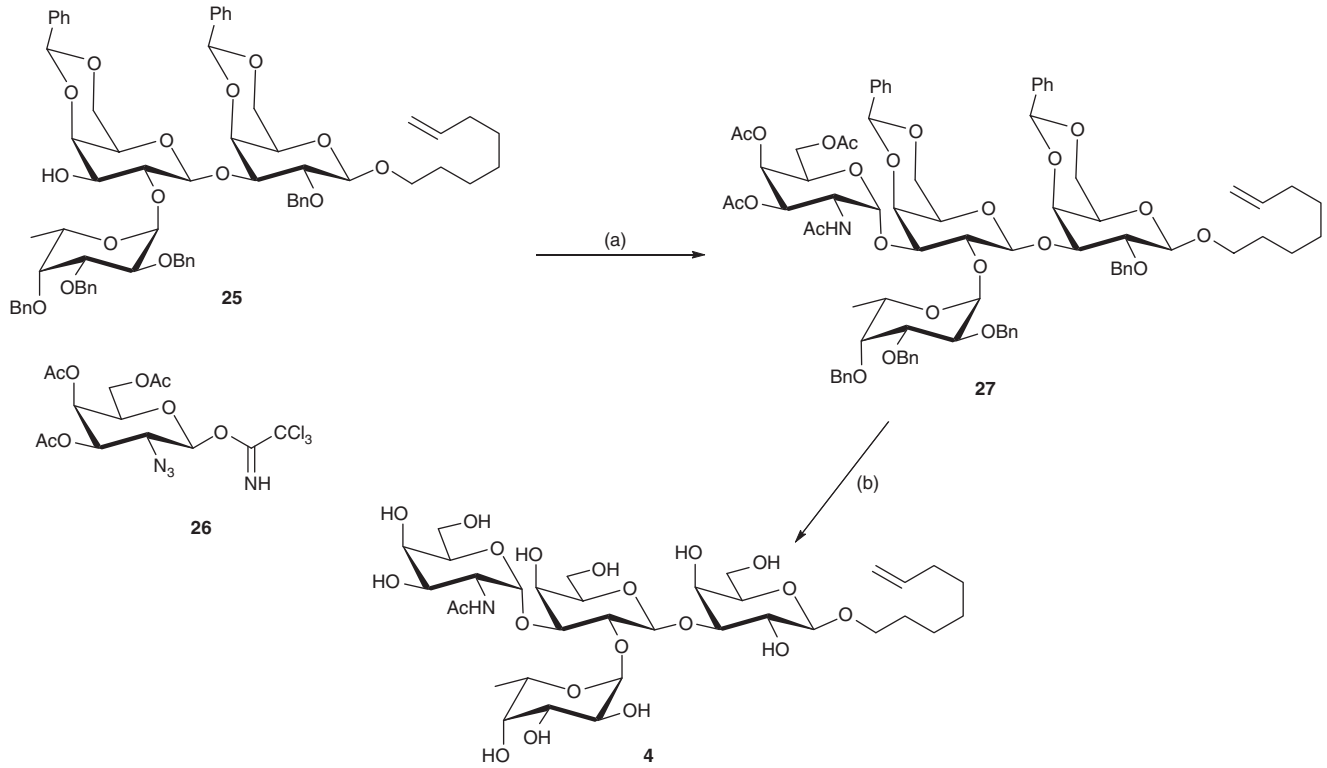


Scheme 3. (a) (i) NH_3, Na, CH_3OH, THF; (ii) H_2, 10% Pd–C, CH_3OH, 49%.

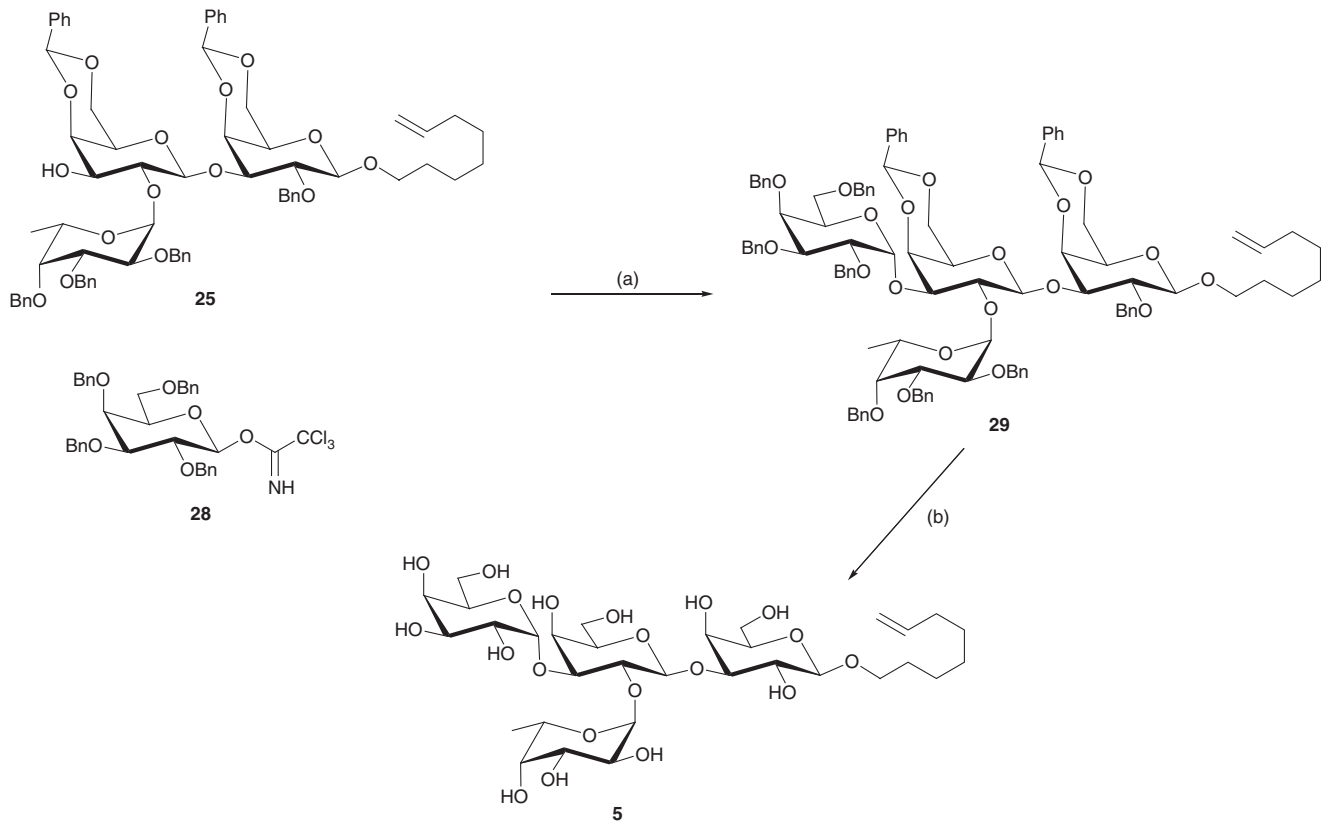
and remove by-products derived from the trichloroacetimidate **26**.[34] Deacetylation, followed by removal of the benzyl ethers and benzylidene acetals using Birch conditions afforded **8**. The B type VI antigen was accessed by glycosylation of **40** with the trichloroacetimidate **28**[35] to afford the tetrasaccharide **42** in 60% yield. Unfortunately, like the B type VI counterpart, contamination with by-products related to the trichloroacetimidate **28** prevented complete characterization. Global deprotection using Birch conditions afforded **9** in 72% yield. Unlike the B type V counterpart, the yield was not significantly affected by poor solubility of **42**.

Conclusions

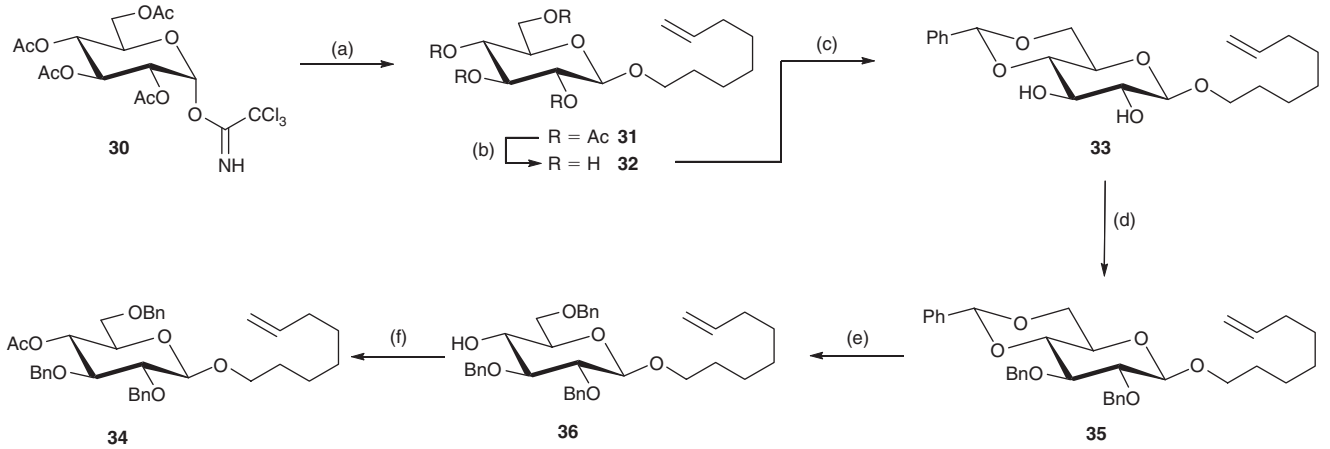
In summary, through the use of a linear chemical synthesis, we have demonstrated the syntheses of the A, B, and H type V and VI histo-blood group antigens (**4**–**9**). Key steps in the routes to these targets were the preparation of the two reducing-end building blocks **18** and **36**. Also crucial to the efficiency of this synthesis were the highly stereoselective glycosylations utilizing glycosyl trichloroacetimidates, most notably the α-L-fucopyranosyl, the 2-azido-2-deoxy-α-D-galactopyranosyl and the α-D-galactopyranosyl linkages of the H type intermediates **25** and **40**, the A type intermediates **27** and **41** and the B type intermediates **29** and **42** respectively. Importantly, the final deprotection, taking advantage of a Birch reduction, enabled the removal of the benzyl ethers and benzylidene acetals while leaving the 7-octen-1-yl linker intact. The 7-octen-1-yl linker will be important in future work aimed at conjugation of the antigens to a protein or solid support. The methodology developed here should be readily adaptable to the 12 remaining A, B, and H antigens. A range of biological investigations, including their use in binding studies with anti-A, B, and H antibodies and enzyme kinetics studies of GTA and GTB are under way.



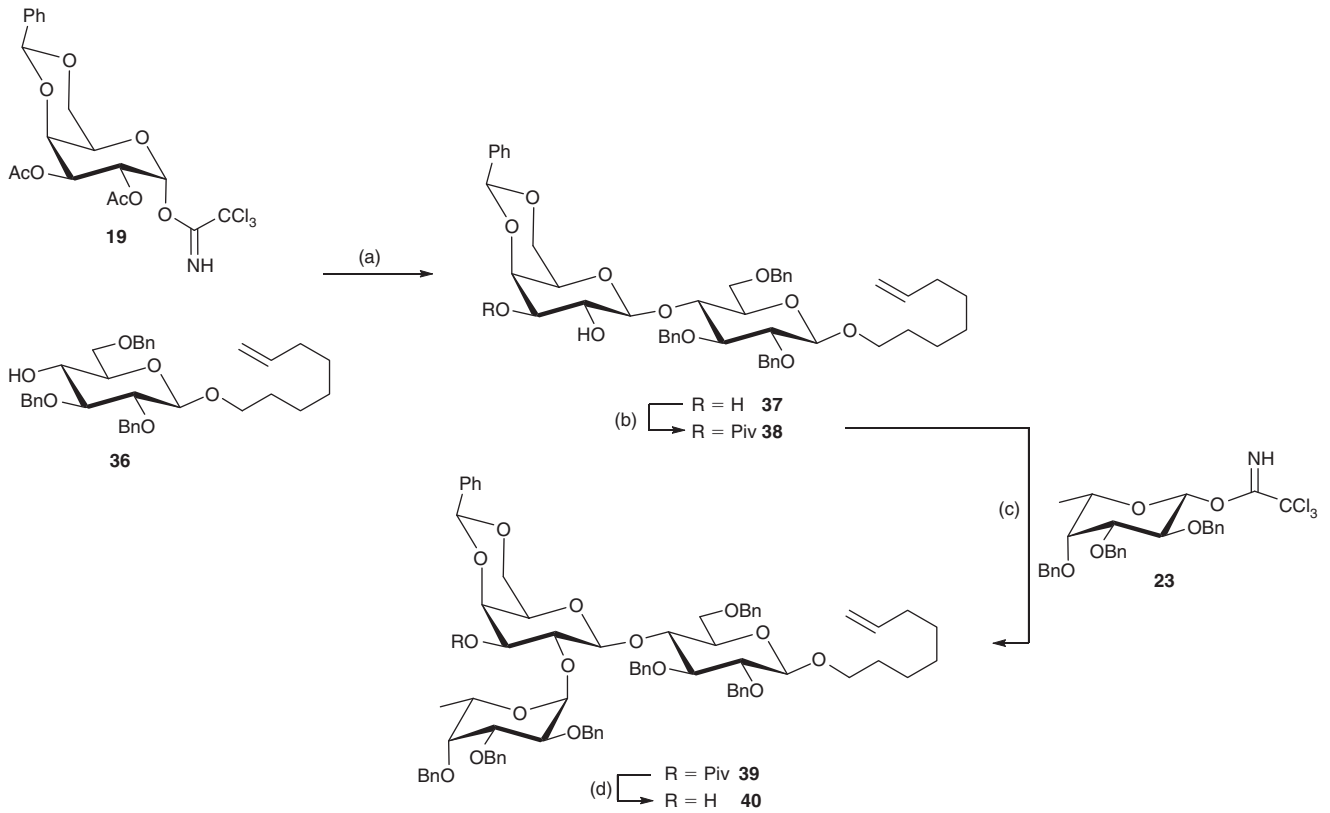
Scheme 4. (a) (i) TMSOTf, 4-Å MS, Et_2O; (ii) AcSH, pyridine, 51%; (b) (i) $NaOCH_3$, CH_3OH, 96%; (ii) Na, NH_3, CH_3OH, THF, 90%.



Scheme 5. (a) TMSOTf, Et_2O, 4-Å MS, 60%; (b) NH_3, Na, CH_3OH, THF, 50%.



Scheme 6. (a) 7-Octen-1-ol, TMSOTf, CH_2Cl_2, 4-Å MS; (b) $NaOCH_3$, CH_3OH, 57% (two steps); (c) $PhCH(OCH_3)_2$, *p*-TsOH, DMF, 95%; (d) BnBr, NaH, DMF, 98%; (e) Et_3SiH, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 64%; (f) Ac_2O, pyridine, DMAP, 88%.

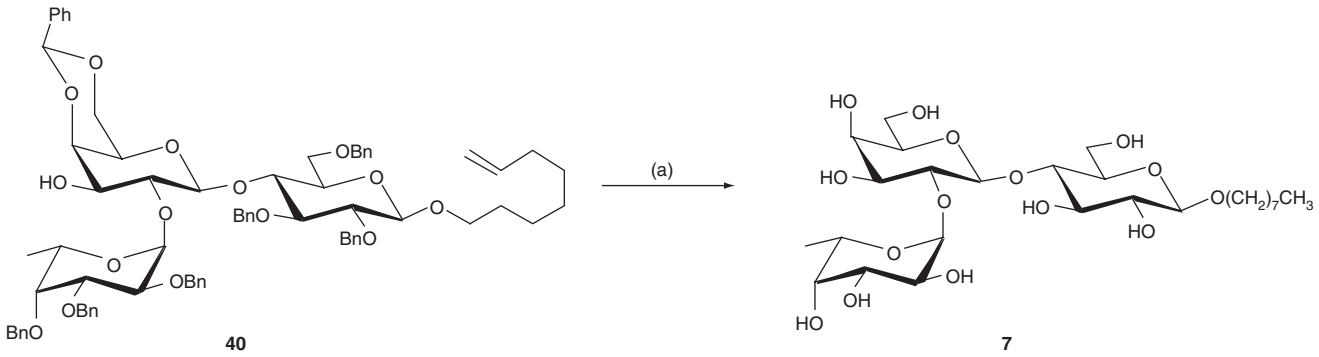


Scheme 7. (a) (i) $BF_3{\cdot}OEt_2$, CH_2Cl_2, 4-Å MS; (ii) $NaOCH_3$, CH_3OH, 91%; (b) $(CH_3)_3CCOCl$, pyridine, 95%; (c) TMSOTf, Et_2O, CH_2Cl_2, 4 Å MS, 78%; (d) $LiOCH_3$, CH_3OH, 68%.

Experimental

General Methods

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. TLC was performed on Merck silica gel 60 F_{254} aluminium-backed plates that were stained by heating (>200°C) 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). Iatrobeads refers to a beaded silica gel 6RS-8060, which is manufactured by Iatron Laboratories (Tokyo). C-18 silica gel (35–70 μm) was manufactured by Toronto Research Chemicals. Optical rotations were measured at 22 ± 2°C. ^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).



40 7

Scheme 8. (a) (i) Na, NH_3, CH_3OH, THF; (ii) H_2, Pd–C, CH_3OH, 61%.

^{13}C NMR (attached proton test) 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) or CD_3OD (49.0). All spectra were recorded in $CDCl_3$ unless specified otherwise. Melting points were measured using a Perkin–Elmer Pyris 1 Differential Scanning Calorimeter. Electrospray (ESI) mass spectra were recorded on samples suspended in mixtures of THF with CH_3OH and added NaCl.

The nomenclature for NMR assignments is shown in Fig. 3, using the A type V antigen as an example.

7-Octen-1-yl 3-O-[3-O-(2-N-Acetyl-2-deoxy-α-D-galactopyranosyl)-2-O-(α-L-fucopyranosyl)-β-D-galactopyranosyl]-β-D-galactopyranoside ***4***

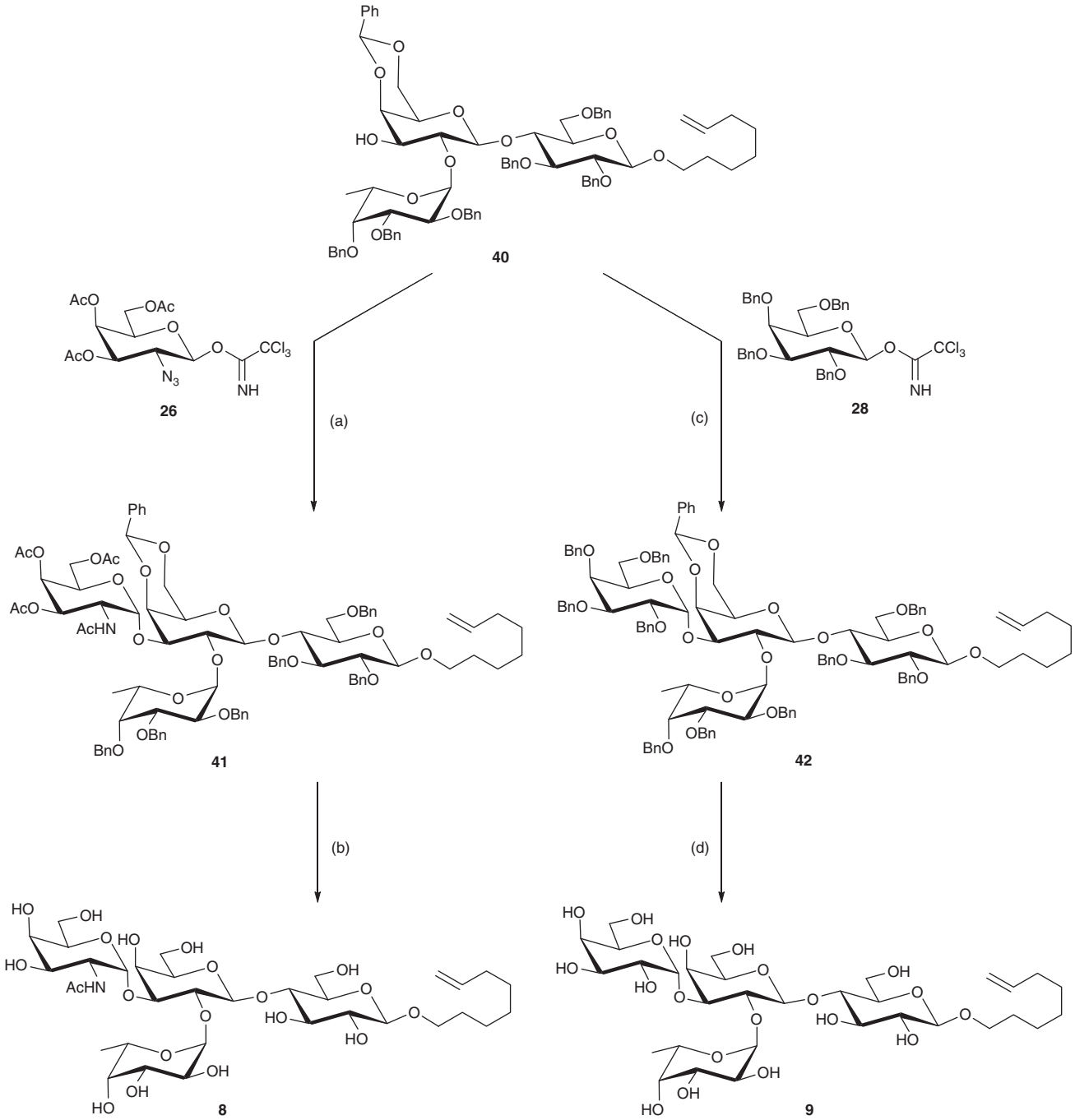
A stirred solution of the tetrasaccharide **27** (186 mg, 0.127 mmol) in CH_3OH (25 mL) was treated with a catalytic amount of $NaOCH_3$ in CH_3OH and the solution was stirred (2 h). The solution was neutralized with Amberlite IR 120 (H^+), filtered, and the residue subjected to flash chromatography (Iatrobeads, CH_2Cl_2/CH_3OH, 9:1) to afford the triol (162 mg, 96%) as a colourless oil. Redistilled liquid ammonia (20 mL) was collected in a flask cooled to −78°C and treated with sodium until the blue colour persisted. A solution of the tetrasaccharide (160 mg, 0.120 mmol) in THF (4 mL) and CH_3OH (29 μL, 0.718 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 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 tetrasaccharide **4** (85 mg, 90%) as a colourless oil. $[\alpha]$ +24.4 ($c = 0.3$, CH_3OH). δ_H (500 MHz, CD_3OD) 5.85–5.75 (1H, m, CH_2=C*H*), 5.30 (1H, d, $J_{1'',2''}$ 3.8, H1″), 5.16 (1H, d, $J_{1''',2'''}$ 3.7, H1‴), 5.01–4.93 (1H, m, CH=CH_2), 4.93–4.88 (1H, m, CH=CH_2), 4.67 (1H, d, $J_{1',2'}$ 7.7, H1′), 4.65 (1H, q, $J_{5'',6''}$ 6.5, H5″), 4.22 (1H, d, $J_{1,2}$ 6.9, H1), 4.01 (1H, dd, $J_{2',3'}$ 9.7, $J_{1',2'}$ 7.7, H2′), 4.34–4.30, 4.20–4.09, 3.95–3.80, 3.63–3.47 (22H, 4 × m, H2, H2″, H2‴, H3, H3′, H3″, H3‴, H4, H4′, H4″, H4‴, H5, H5′, H5‴, H6, H6′, H6‴, CH=$CH_2(CH_2)_5CH_2O$), 2.01 (3H, s, CH_3C=O), 2.09–2.00 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.69–1.58 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.45–1.26 (6H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.22 (3H, d, $J_{5'',6''}$ 6.5, H6″). δ_C (125 MHz, CD_3OD) 174.4 (C=O), 140.1 (CH_2=*C*H), 114.8 (*C*H_2=CH), 105.02, 104.96 (C1, C1′), 100.2 (C1″), 93.7 (C1‴), 84.2, 77.8, 76.3, 76.2, 74.0, 73.8, 72.8, 71.7, 71.6, 70.5, 70.33, 70.25, 70.0, 68.1, 64.8 (C2, C2′, C2″, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5, C5′, C5″, C5‴), 70.8 (CH=$CH_2(CH_2)_5$*C*H_2O), 63.4, 62.54, 62.51 (C6, C6′, C6‴), 51.30 (C2‴), 34.9 (CH=CH_2(*C*H_2)$_5CH_2O$), 30.8 (2C, CH=CH_2(*C*H_2)$_5CH_2O$), 30.1 (CH=CH_2(*C*H_2)$_5CH_2O$), 27.0 (CH=CH_2(*C*H_2)$_5CH_2O$), 22.9 (*C*H_3C=O), 16.8 (C6″). *m/z* (ESI) calc. $[C_{34}H_{59}NO_{20}]Na^+$: 824.3523. Found: 824.3513.

7-Octen-1-yl 3-O-[2-O-(α-L-Fucopyranosyl)-3-O-(α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-galactopyranoside ***5***

Redistilled liquid ammonia (20 mL) was collected in a flask cooled to −78°C and treated with sodium until the blue colour persisted. A solution of the tetrasaccharide **29** (260 mg, 0.157 mmol) in THF (4 mL) and CH_3OH (63 μL, 1.57 mmol) was added dropwise and the solution was stirred (−78°C, 1 h). The reaction was then quenched by the addition of CH_3OH (4 mL) and the ammonia 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 chromatography (Iatrobeads, CH_2Cl_2/CH_3OH, 1:1) to afford first unreacted **29** (104 mg, 40%); further elution (CH_2Cl_2/CH_3OH, 2:1) afforded the fully deprotected compound **5** (60 mg, 50%). $[\alpha]$ +7.2 ($c = 0.2$, CH_3OH). δ_H (500 MHz, CD_3OD) 5.85–5.75 (1H, m, CH_2=C*H*), 5.29 (1H, d, $J_{1'',2''}$ 3.8, H1″), 5.16 (1H, d, $J_{1''',2'''}$ 3.6, H1‴), 5.01–4.94 (1H, m, CH=CH_2), 4.93–4.88 (1H, m, CH=CH_2), 4.67 (1H, d, $J_{1',2'}$ 7.5, H1′), 4.61 (1H, q, $J_{5'',6''}$ 6.3, H5″), 4.23 (1H, d, $J_{1,2}$ 7.0, H1), 4.01 (1H, dd, $J_{2',3'}$ 8.1, $J_{1',2'}$ 7.5, H2′), 4.19–4.09, 3.97–3.65, 3.64–3.49 (22H, 3 × m, H2, H2″, H2‴, H3, H3′, H3″, H3‴, H4, H4′, H4″, H4‴, H5, H5′, H5‴, H6, H6′, H6‴, CH=$CH_2(CH_2)_5CH_2O$), 2.08–2.00 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.66–1.57 (2H, m, CH=$CH_2(CH_2)_5CH_2O$), 1.45–1.27 (6H, m, CH=$CH_2(CH_2)_5$ CH_2O), 0.56 (3H, d, $J_{5'',6''}$ 6.3, H6″). δ_C (125 MHz, CD_3OD) 140.1 (CH_2=*C*H), 114.8 (*C*H_2=CH), 105.04, 104.98 (C1, C1′), 100.3 (C1″), 96.1 (C1‴), 84.3, 79.4, 76.3, 76.0, 74.4, 73.8, 73.1, 71.64, 71.61, 71.4, 71.2, 70.32, 70.30, 70.0, 68.0, 66.6 (C2, C2′, C2″, C2‴, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5, C5′, C5″, C5‴), 70.8 (CH=$CH_2(CH_2)_5$*C*H_2O), 63.3, 62.56, 62.54 (C6, C6′, C6‴), 34.9 (CH=CH_2(*C*H_2)$_5CH_2O$), 30.8 (CH=CH_2(*C*H_2)$_5CH_2O$), 30.10 (2C, CH=CH_2(*C*H_2)$_5CH_2O$), 27.0 (CH=CH_2(*C*H_2)$_5CH_2O$), 16.7 (C6″). *m/z* (ESI) calc. $[C_{32}H_{56}O_{20}]Na^+$: 783.3257. Found: 783.3258.

Octyl 3-O-[2-O-(α-L-Fucopyranosyl)-β-D-galactopyranosyl]-β-D-galactopyranoside ***6***

Redistilled liquid ammonia (10 mL) was collected in a flask cooled to −78°C and treated with sodium until the blue colour persisted. A solution of the trisaccharide **25** (330 mg,



Scheme 9. (a) (i) TMSOTf, Et_2O, 4-Å MS; (ii) AcSH, pyridine, 47%; (b) (i) $NaOCH_3$, CH_3OH, 95%; (ii) Na, NH_3, CH_3OH, THF, 90%; (c) TMSOTf, Et_2O, 4 Å MS, 60%; (d) Na, NH_3, CH_3OH, THF, 72%.

0.291 mmol) in THF (4 mL) and CH_3OH (70 μL, 1.74 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 chromatography (Iatrobeads, CH_2Cl_2/CH_3OH, 1:1) to afford first unreacted **25** (110 mg, 33%); further elution (CH_2Cl_2/CH_3OH, 2:1) afforded the alkene as a colourless oil (114 mg). The residue was then taken up in CH_3OH, treated with Pd/C (10%, 20 mg) and subjected to a H_2 atmosphere ((rt), 1 day). The mixture was then filtered and concentrated to afford the octyl glycoside **6** as a colourless oil (98 mg, 49%). [α] −30.0 ($c = 0.15$, CH_3OH). δ_H (500 MHz, $CD_3OD/CDCl_3$) 5.18 (1H, d, $J_{1'',2''}$ 2.0, H1″), 4.62 (1H, d, $J_{1',2'}$ 7.2, H1′), 4.32 (1H, q, $J_{5'',6''}$ 6.7, H5″), 4.27 (1H, d, $J_{1,2}$ 7.5, H1), 4.12 (1H, d, $J_{3',4'}$ 2.0, H4′), 3.93–3.82, 3.81–3.62, 3.63–3.47 (16H, 3 × m, H2, H2′, H2″, H3, H3′, H3″, H4, H4″, H5, H5′, H6, H6′, $CH_3(CH_2)_6CH_2O$), 1.67–1.56 (2H, m, $CH_3(CH_2)_6CH_2O$), 1.41–1.20 (10H, m, $CH_3(CH_2)_6CH_2O$), 1.24 (3H, d, $J_{5'',6''}$ 6.7, H6″), 0.89 (3H, t, J 6.8, $CH_3(CH_2)_6CH_2O$). δ_C (100 MHz) 105.1, 104.5 (C1, C1′), 102.4 (C1″), 84.9, 80.9, 76.5, 76.1, 74.7, 73.6, 71.7, 71.6, 70.9, 70.1, 70.0, 69.2 (C2, C2′, C2″, C3, C3′, C3″, C4, C4′, C4″, C5, C5′, C5″), 70.8 ($CH_3(CH_2)_6CH_2O$), 62.6, 62.5 (C6,

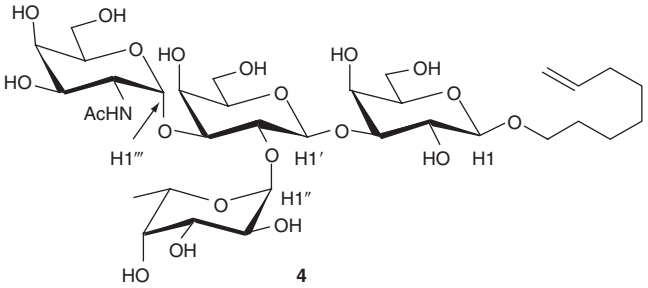


Fig. 3. Ring numbering system for NMR assignments.

C6′), 33.1 ($CH_3(CH_2)_6CH_2O$), 30.9 (2C, $CH_3(CH_2)_6CH_2O$), 30.6 ($CH_3(CH_2)_6CH_2O$), 30.5 ($CH_3(CH_2)_6CH_2O$), 27.2 ($CH_3(CH_2)_6CH_2O$), 16.8 (C6″) 14.7 ($CH_3(CH_2)_6CH_2O$). *m/z* (ESI) calc. $[C_{26}H_{48}O_{15}]Na^+$: 623.2885. Found: 623.2887.

Octyl 4-O-[2-O-(α-L-Fucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside ***7***

Redistilled liquid ammonia (10 mL) was collected in a flask cooled to −78°C and treated with sodium until the blue colour persisted. A solution of the trisaccharide **40** (370 mg, 0.301 mmol) in THF (4 mL) and CH_3OH (85 μL, 2.11 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 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 chromatography (Iatrobeads, CH_2Cl_2/CH_3OH, 1:1) to afford first unreacted **40** (120 mg, 33%); further elution afforded the alkene as a colourless oil (140 mg). The residue was then taken up in CH_3OH, treated with Pd/C (10%, 20 mg) and subjected to an H_2 atmosphere (rt, 1 day). The mixture was then filtered and concentrated to afford the octyl glycoside **7** as a colourless oil (110 mg, 61%). $[\alpha]$ −60.5 ($c = 0.26$, CH_3OH). δ_H (500 MHz, CD_3OD) 5.24 (1H, d, $J_{1'',2''}$ 3.4, H1″), 4.48 (1H, d, $J_{1',2'}$ 7.0, H1′), 4.34 (1H, d, $J_{1,2}$ 7.8, H1), 4.18 (1H, q, $J_{5'',6''}$ 6.5, H5″), 3.91–3.64, 3.59–3.45, 3.34–3.29 (16H, 3 × m, H2′, H2″, H3, H3′, H3″, H4, H4′, H4″, H5, H5′, H6, H6′, $CH_3(CH_2)_6CH_2O$), 3.25 (1H, dd, $J_{2,3}$ 8.5, $J_{1,2}$ 7.8, H2), 1.42–1.23 (2H, m, $CH_3(CH_2)_6CH_2O$), 1.65–1.57 (10H, m, $CH_3(CH_2)_6CH_2O$), 1.20 (3H, d, $J_{5'',6''}$ 6.5, H6″), 0.89 (3H, t, J 6.9, $CH_3(CH_2)_6CH_2O$). δ_C (100 MHz, CD_3OD) 104.3 (C1), 102.6 (C1), 101.7 (C1″), 78.8, 78.0, 77.0, 76.8, 76.4, 75.3, 74.8, 73.6, 71.7, 70.70, 70.66, 68.30 (C2, C2′, C2″, C3, C3′, C3″, C4, C4′, C4″, C5, C5′, C5″), 71.0 ($CH_3(CH_2)_6CH_2O$), 62.6, 61.6 (C6, C6′), 33.0 ($CH_3(CH_2)_6CH_2O$), 30.8 ($CH_3(CH_2)_6CH_2O$), 30.6 ($CH_3(CH_2)_6CH_2O$), 30.4 ($CH_3(CH_2)_6CH_2O$), 27.1 ($CH_3(CH_2)_6CH_2O$), 23.7 ($CH_3(CH_2)_6CH_2O$), 16.8 (C6″), 14.5 ($CH_3(CH_2)_6CH_2O$). *m/z* (ESI) calc. $[C_{68}H_{78}O_{15}]Na^+$: 623.2885. Found: 623.2885.

7-Octen-1-yl 4-O-[3-O-(2-N-Acetyl-2-deoxy-α-D-galactopyranosyl)-2-O-(α-L-fucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside ***8***

A stirred solution of the tetrasaccharide **41** (240 mg, 0.154 mmol) in CH_3OH (25 mL) was treated with a catalytic amount of $NaOCH_3$ in CH_3OH and the solution was stirred (2 h). The solution was neutralized with Amberlite IR 120 (H^+), filtered, and the residue subjected to flash chromatography (Iatrobeads, CH_2Cl_2/CH_3OH, 9:1) to afford the triol (210 mg, 95%) as a colourless oil. Redistilled liquid ammonia (20 mL) was collected in a flask cooled to −78°C and treated with sodium until the blue colour persisted. A solution of the tetrasaccharide (90 mg, 0.063 mmol) in THF (4 mL) and CH_3OH (18 μL, 0.44 mmol) was added dropwise and the solution was stirred (−78°C, 1 h). The reaction was then quenched by the addition of CH_3OH (4 mL) and the ammonia 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 tetrasaccharide **8** (45.0 mg, 90%) as a colourless oil. $[\alpha]$ +17.1 ($c = 0.3$, CH_3OH). δ_H (500 MHz, CD_3OD) 5.87–5.73 (1H, m, $CH_2{=}CH$), 5.34 (1H, d, $J_{1'',2''}$ 3.9, H1″), 5.16 (1H, d, $J_{1''',2'''}$ 3.9, H1‴), 5.01–4.95 (1H, m, $CH{=}CH_2$), 4.94–4.89 (1H, m, $CH{=}CH_2$), 4.52 (1H, d, $J_{1',2'}$ 7.8, H1′), 4.35–4.28 (2H, m, H2‴, H5″), 4.26 (1H, d, $J_{1,2}$ 7.8, H1), 4.00 (1H, dd, $J_{2',3'}$ 9.7, $J_{1',2'}$ 7.8, H2′), 4.20–4.15, 4.13–4.09, 3.94–3.61, 3.57–3.50, 3.32–3.23 (21H, 5 × m, H2, H2″, H3′, H3″, H3‴, H4, H4′, H4″, H4‴, H5, H5′, H5‴, H6, H6′, H6‴, $CH{=}CH_2(CH_2)_5CH_2O$), 3.46 (1H, d, $J_{2,3}$ 9.1, $J_{3,4}$ 9.1, H3), 2.01 (3H, s, $CH_3C{=}O$), 2.09–1.98 (2H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 1.65–1.58 (2H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 1.44–1.30 (6H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 1.22 (3H, d, $J_{5'',6''}$ 6.5, H6″). δ_C (125 MHz, CD_3OD) 174.5 (C=O), 140.1 ($CH_2{=}CH$), 114.8 ($CH_2{=}CH$), 104.3 (C1), 102.2 (C1′), 100.2 (C1″), 93.6 (C1‴), 78.2, 78.0, 77.0, 76.8, 76.5, 74.9, 73.6, 73.5, 72.7, 71.9, 70.6, 70.0, 67.7, 64.9 (C2, C2′, C2″, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5, C5′, C5‴), 71.0 ($CH{=}CH_2(CH_2)_5CH_2O$), 69.9 (C5″), 63.4, 62.5, 61.7 (C6, C6′, C6‴), 51.3 (C2‴), 34.8 ($CH{=}CH_2(CH_2)_5CH_2O$), 30.8 ($CH{=}CH_2(CH_2)_5CH_2O$), 30.08 ($CH{=}CH_2(CH_2)_5CH_2O$), 30.07 ($CH{=}CH_2(CH_2)_5CH_2O$), 27.0 ($CH{=}CH_2(CH_2)_5CH_2O$), 22.8 ($CH_3C{=}O$), 16.6 (C6″). *m/z* (ESI) calc. $[C_{34}H_{59}NO_{20}]Na^+$: 824.3523. Found: 824.3526.

7-Octen-1-yl 4-O-[2-O-(α-L-Fucopyranosyl)-3-O-(α-D-galactopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside ***9***

Redistilled liquid ammonia (10 mL) was collected in a flask cooled to −78°C and treated with sodium until the blue colour persisted. A solution of the tetrasaccharide **42** (160 mg, 0.091 mmol) in THF (4 mL) and CH_3OH (41 μL, 1.01 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 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 chromatography (Iatrobeads, CH_2Cl_2/CH_3OH, 1:1) to afford the fully deprotected compound **9** (50 mg, 72%). $[\alpha]$ −3.0 ($c = 1.0$, CH_3OH). δ_H (500 MHz, CD_3OD) 5.86–5.76 (1H, m, $CH_2{=}CH$), 5.33 (1H, d, $J_{1'',2''}$ 3.8, H1″), 5.17 (1H, d, $J_{1''',2'''}$ 3.7, H1‴), 5.00–4.95 (1H, m, $CH{=}CH_2$), 4.93–4.89 (1H, m, $CH{=}CH_2$), 4.53 (1H, d, $J_{1',2'}$ 7.6, H1′), 4.29 (1H, q, $J_{5'',6''}$ 6.6, H5″), 4.28 (1H, d, $J_{1,2}$ 8.2, H1), 3.47 (1H, dd, $J_{2,3}$ 9.1, $J_{3,4}$ 9.1, H3), 4.19–4.10, 4.03–3.50, 3.31–3.24 (22H, 3 × m, H2, H2′, H2″, H2‴, H3′, H3″, H3‴, H4, H4′, H4″, H4‴, H5, H5′, H5‴, H6, H6′, H6‴, $CH{=}CH_2(CH_2)_5CH_2O$), 2.09–2.00 (2H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 1.66–1.57 (2H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 1.44–1.25 (6H, m, $CH{=}CH_2(CH_2)_5CH_2O$), 1.20 (3H, d, $J_{5'',6''}$ 6.6, H6″). δ_C (125 MHz, CD_3OD) 140.1 ($CH_2{=}CH$), 114.8 ($CH_2{=}CH$), 104.3 (C1′), 102.2 (C1), 100.3 (C1″), 96.1 (C1‴), 79.8, 78.3, 77.0, 76.5, 76.4, 74.8, 73.7, 73.6, 73.1, 71.8, 71.4, 71.3, 71.0, 69.9, 67.7, 65.8

(C2, C2′, C2″, C2‴, C3, C3′, C3″, C3‴, C4, C4′, C4″, C4‴, C5, C5′, C5″, C5‴), 71.0 (CH=CH_2(CH_2)$_5$$CH_2$O), 63.3, 62.5, 61.7 (C6, C6′, C6‴), 34.8 (CH=CH_2(CH_2)$_5$$CH_2$O), 30.8 (2C, CH=$CH_2$($CH_2$)$_5$$CH_2$O), 30.1 (CH=$CH_2$($CH_2$)$_5$$CH_2$O), 27.0 (CH=$CH_2$($CH_2$)$_5$$CH_2$O), 16.6 (C6″). *m/z* (ESI) calc. [$C_{32}H_{56}O_{20}$]Na^+: 783.3257. Found: 783.3258.

7-Octen-1-yl 4,6-O-Benzylidene-β-D-galactopyranoside ***13***

A stirred solution of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate **10**[29] (20.9 g, 42.5 mmol) and 7-octen-1-ol (6.53 g, 51.0 mmol) was treated with 4-Å molecular sieves (5 g) and the mixture stirred (rt, 1 h). The mixture was then cooled (−40°C), treated with TMSOTf (0.5 mL), and the mixture was allowed to warm (rt, 1 h). The reaction was quenched by the addition of Et_3N (2 mL), filtered, and subjected to flash chromatography (EtOAc/hexanes, 2:3) to afford a colourless oil. The oil was taken up in CH_3OH (200 mL), treated with a catalytic amount of $NaOCH_3$ in CH_3OH and stirred (rt, 2 h); the $NaOCH_3$ was neutralized with Amberlite IR120 (H^+), filtered, and then concentrated. The residue was subjected to flash chromatography (EtOAc/hexanes, 5:1) to afford the tetrol **12** as a white solid (9.0 g, 73%), which was immediately used in the subsequent step. A solution of the tetrol **12** (9.0 g, 31.0 mmol) in dry DMF (100 mL) was treated with benzaldehyde dimethyl acetal (5.9 mL, 38.7 mmol), *p*-TsOH (300 mg), and the solution was stirred (40°C, 18 h). The solution was neutralized with Et_3N (1.5 mL), concentrated and subjected to flash chromatography (EtOAc/hexanes, 1:1) to afford the diol **13** (8.4 g, 72%) as a white solid. Mp 156–158°C. [α] −26.0 ($c = 0.7$, CH_2Cl_2). (Found: C 66.54, H 8.05. $C_{21}H_{30}O_6$ requires C 66.65, H 7.99%). R_f 0.37 (EtOAc/hexanes, 7:10). δ_H (500 MHz) 7.54–7.48 (2H, m, Ph), 7.40–7.34 (3H, m, Ph), 5.86–5.77 (1H, m, C*H*=CH_2), 5.56 (1H, s, PhC*H*), 5.03–4.92 (2H, m, CH=CH_2), 4.35 (1H, dd, $J_{6,6}$ 12.5, $J_{5,6}$ 1.4, H6), 4.28 (1H, d, $J_{1,2}$ 7.5, H1), 4.22 (1H, d, $J_{3,4}$ 3.8, H4), 4.10 (1H, dd, $J_{6,6}$ 12.5, $J_{5,6}$ 1.9, H6), 3.97 (1H, ddd, *J* 9.4, 6.8, 6.8, CH=CH_2(CH_2)$_5$CH_2O), 3.76 (1H, ddd, $J_{2,3}$ 9.4, $J_{1,2}$ 7.5, *J* 1.7, H2), 3.70 (1H, ddd, $J_{2,3}$ 9.4, *J* 8.9, $J_{3,4}$ 3.8, H3), 3.54–3.48 (2H, m, H5, CH=CH_2(CH_2)$_5$CH_2O), 2.51 (1H, d, *J* 8.9, OH), 2.45 (1H, d, *J* 1.7, OH), 2.10–2.02 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.72–1.63 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.46–1.30 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (125.7 MHz) 139.3 (*C*H=CH_2), 137.6 (Ph), 129.2 (Ph), 128.2 (Ph), 126.4 (Ph), 114.3 (CH=*C*H_2), 102.8 (C1), 101.4 (Ph*C*H), 75.4 (C4), 72.7, 71.7 (C2, C3), 70.0, 69.2 (C6, CH=CH_2(CH_2)$_5$*C*H_2O), 66.66 (C5), 33.7 (CH=CH_2(*C*H_2)$_5$$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$O). *m/z* (ESI) calc. [$C_{21}H_{30}O_6$]$Na^+$: 401.1935. Found: 401.1937.

7-Octen-1-yl 4,6-O-Benzylidene-2-O-[(4-methoxyphenyl)methyl]-β-D-galactopyranoside ***14*** *and 7-Octen-1-yl 4,6-O-Benzylidene-3-O-[(4-methoxyphenyl)methyl]-β-D-galactopyranoside* ***15***

A stirred mixture of the diol **13** (5.83 g, 15.4 mmol) and *n*-Bu_2SnO (4.21 g, 17.0 mmol) in dry toluene (200 mL) was heated at reflux with azeotropic removal of water (1 h). The solution was treated with *n*-Bu_4NI (7.95 g, 21.6 mmol) and *p*-methoxybenzyl chloride (2.9 mL, 21.6 mmol) and then heated at reflux further (4 h). The solution was partially concentrated, taken up in EtOAc (300 mL), washed with water, brine, and dried. The organic extract was then concentrated and subjected to flash chromatography (EtOAc/hexanes, 2:3) to afford first the 3-*O*-*p*-methoxybenzyl derivative **15** as a white solid (4.7 g, 62%). Mp 139–141°C. [α] +34.8 ($c = 0.6$, CH_2Cl_2). R_f 0.56 (EtOAc/hexanes, 1:1). (Found: C 70.03, H 7.79. $C_{29}H_{38}O_7$ requires C 69.86, H 7.68%). δ_H (500 MHz) 7.55–7.51 (2H, m, Ph), 7.38–7.30 (5H, m, Ph), 6.89–6.85 (2H, m, Ph), 5.86–5.76 (1H, m, C*H*=CH_2), 5.47 (1H, s, PhC*H*), 5.03–4.91 (2H, m, CH=CH_2), 4.71, 4.69 (2H, AB, *J* 12.0, PhCH_2), 4.33–4.27 (2H, m, H1, H6), 4.11 (1H, d, $J_{3,4}$ 3.5, H4), 4.06–3.91 (3H, m, H2, H6, CH=CH_2(CH_2)$_5$CH_2O), 3.80 (3H, s, CH_3O), 3.54–3.45 (2H, m, H3, CH=CH_2(CH_2)$_5$CH_2O), 3.36–3.33 (1H, m, H5), 2.45 (1H, d, *J* 1.65, OH), 2.08–2.01 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.70–1.61 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.44–1.30 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (125.7 MHz) 159.3 (Ph), 139.0 (*C*H=CH_2), 137.8 (Ph), 130.2 (Ph), 129.5 (Ph), 128.8 (Ph), 128.0 (Ph), 126.4 (Ph), 114.2 (CH=*C*H_2), 113.8 (Ph), 102.9 (C1), 101.1 (Ph*C*H), 78.8 (C3), 73.2 (C4), 71.1 (Ph*C*H_2), 70.0 (C2), 69.7, 69.3 (C6, CH=CH_2(CH_2)$_5$*C*H_2O), 66.7 (C5), 55.2 (CH_3O), 33.7 (CH=CH_2(*C*H_2)$_5$$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$$CH_2$O), 25.7 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O). *m/z* (ESI) calc. [$C_{29}H_{38}O_7$]$Na^+$: 521.2518. Found: 521.2510.

Further elution afforded the 2-*O*-*p*-methoxybenzyl derivative **14** as a white solid (2.52 g, 33%). Mp 90–92°C. [α] +17.1 ($c = 0.8$, CH_2Cl_2). R_f 0.37 (EtOAc/hexanes, 1:1). δ_H (500 MHz) 7.55–7.50 (2H, m, Ph), 7.40–7.30 (5H, m, Ph), 6.90–6.85 (2H, m, Ph), 5.86–5.77 (1H, m, C*H*=CH_2), 5.56 (1H, s, PhC*H*), 5.00–4.91 (3H, m, PhCH_2, CH=CH_2), 4.66 (1H, A of AB, *J* 10.8, PhCH_2), 4.38 (1H, d, $J_{1,2}$ 7.7, H1), 4.33 (1H, dd, $J_{6,6}$ 12.4, $J_{5,6}$ 1.3, H6), 4.20 (1H, d, $J_{3,4}$ 3.7, H4), 4.07 (1H, dd, $J_{6,6}$ 12.4, $J_{5,6}$ 1.8, H6), 4.01 (1H, ddd, *J* 9.4, 6.5, 6.5, CH=CH_2(CH_2)$_5$CH_2O), 3.80 (3H, s, CH_3O), 3.74–3.68 (1H, m, H3), 3.61 (1H, dd, $J_{2,3}$ 9.6, $J_{1,2}$ 7.7, H2), 3.52 (1H, ddd, *J* 9.4, 6.9, 6.9, CH=CH_2(CH_2)$_5$CH_2O), 3.44–3.41 (1H, m, H5), 2.48 (1H, d, *J* 7.1, OH), 2.09–2.01 (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$O), 1.49–1.32 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (125.7 MHz) 159.3 (Ph), 139.0 (*C*H=CH_2), 137.7 (Ph), 130.8 (Ph), 129.6 (Ph), 129.1 (Ph), 128.2 (Ph), 126.5 (Ph), 114.3 (CH=*C*H_2), 113.8 (Ph), 103.6 (C1), 101.4 (Ph*C*H), 78.8 (C2), 74.5 (Ph*C*H_2), 75.5, 72.4 (C3, C4), 70.0, 69.2 (C6, CH=CH_2(CH_2)$_5$*C*H_2O), 66.5 (C5), 55.3 (CH_3O), 33.7 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 29.7 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 29.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 28.9 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 26.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O). *m/z* (ESI) calc. [$C_{29}H_{38}O_7$]$Na^+$: 521.2518. Found: 521.2510.

7-Octen-1-yl 2-O-Benzyl-4,6-O-benzylidene-3-O-[(4-methoxyphenyl)methyl]-β-D-galactopyranoside ***16***

A stirred solution of the alcohol **15** (5.5 g, 11.0 mmol) in dry DMF (75 mL) was cooled (−20°C), treated with BnBr (2.10 mL, 17.6 mmol) and NaH (60%, 572 mg, 14.3 mmol) and allowed to warm (rt, 1 h). The mixture was then treated with CH_3OH (1 mL) and partially concentrated; the residue was taken up in EtOAc (250 mL) and washed with water and brine. The organic extract was dried, concentrated, and then subjected to flash chromatography (EtOAc/hexanes, 2:3) to afford the benzyl ether **16** as a white solid (5.83 g, 89%). Mp 99–103°C. [α] +42.7 ($c = 0.5$, CH_2Cl_2). R_f 0.74 (EtOAc/hexanes, 1:1). (Found: C 73.47, H 7.54. $C_{29}H_{38}O_7$ requires C 73.44, H 7.53%). δ_H (500 MHz) 7.60–7.54 (2H, m, Ph), 7.41–7.26 (10H, m, Ph), 6.88–6.82 (2H, m, Ph), 5.86–5.76 (1H, m, C*H*=CH_2), 5.50 (1H, s, PhC*H*), 5.02–4.92 (3H, m, PhCH_2, CH=CH_2), 4.78 (1H, A of AB, *J* 10.8, PhCH_2), 4.73, 4.69 (2H, AB, *J* 11.9, PhCH_2), 4.38 (1H, d, $J_{1,2}$

7.8, H1), 4.31 (1H, dd, $J_{6,6}$ 12.2, $J_{5,6}$ 1.3, H6), 4.08 (1H, d, $J_{3,4}$ 3.7, H4), 4.05–3.96 (2H, m, H6, CH=CH_2(CH_2)$_5$CH_2O), 3.85–3.80 (4H, m, H2, CH_3O), 3.54 (1H, dd, $J_{2,3}$ 9.7, $J_{3,4}$ 3.7, H3), 3.53–3.48 (1H, m, CH=CH_2(CH_2)$_5$CH_2O), 3.31 (1H, s, H5), 2.09–1.98 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.73–1.60 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.49–1.27 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (125.7 MHz) 159.2 (Ph), 139.1 (*C*H=CH_2), 139.0 (Ph), 137.9 (Ph), 130.5 (Ph), 129.3 (Ph), 128.9 (Ph), 128.2 (Ph), 128.1 (Ph), 128.0 (Ph), 127.5 (Ph), 126.5 (Ph), 114.2 (CH=*C*H_2), 113.7 (Ph), 103.7 (C1), 101.3 (Ph*C*H), 78.8, 78.5 (C2, C3), 74.1 (C4), 75.2 (Ph*C*H_2), 71.7 (Ph*C*H_2), 69.9, 69.3 (C6, CH=CH_2(CH_2)$_5$*C*H_2O), 66.42 (C5), 55.27 (CH_3O), 33.7 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 29.7 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 29.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 28.8 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 26.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O). *m/z* (ESI) calc. [$C_{36}H_{44}O_7$]$Na^+$: 611.2979. Found: 611.2977.

*7-Octen-1-yl 2-*O*-Acetyl-4,6-*O*-benzylidene-3-*O*-[(4-methoxyphenyl)methyl]-β-*D*-galactopyranoside* **17**

A stirred solution of the alcohol **15** (75.0 mg, 0.134 mmol) in pyridine (2 mL) was treated with Ac_2O (0.5 mL) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (5 mg) and stirred (rt, 2 h). The solution was treated with CH_3OH (1 mL), concentrated and subjected to flash chromatography (EtOAc/hexanes, 1:1) to afford **17** as a colourless oil (80 mg, 99%). [α] +32.8 ($c = 1.0$, CH_2Cl_2). R_f 0.62 (EtOAc/hexanes, 1:1). δ_H (500 MHz) 7.57–7.53 (2H, m, Ph), 7.39–7.32 (3H, m, Ph), 7.28–7.23 (2H, m, Ph), 6.89–6.84 (2H, m, Ph), 5.86–5.76 (1H, m, C*H*=CH_2), 5.48 (1H, s, PhC*H*), 5.34 (1H, dd, $J_{2,3}$ 10.1, $J_{1,2}$ 8.0, H2), 5.03–4.91 (2H, m, CH=CH_2), 4.57, 4.63 (2H, AB, J 12.6, PhCH_2), 4.40 (1H, d, $J_{1,2}$ 8.0, H1), 4.30 (1H, dd, $J_{6,6}$ 12.3, $J_{5,6}$ 1.3, H6), 4.14 (1H, d, $J_{3,4}$ 3.6, H4), 4.03 (1H, dd, $J_{6,6}$ 12.3, $J_{5,6}$ 1.6, H6), 3.90 (1H, ddd, J 9.5, 6.3, 6.3, CH=CH_2(CH_2)$_5$CH_2O), 3.81 (3H, s, CH_3O), 3.57 (1H, dd, $J_{2,3}$ 10.1, $J_{3,4}$ 3.6, H3), 3.45 (1H, ddd, J 9.5, 6.9, 6.9, CH=CH_2(CH_2)$_5$CH_2O), 3.33 (1H, br s, H5), 2.06 (3H, s, CH_3CO), 2.09–2.01 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.64–1.49 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.42–1.26 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (125.7 MHz) 169.3 (C=O), 159.2 (Ph), 139.00 (*C*H=CH_2), 137.7 (Ph), 130.1 (Ph), 129.1 (Ph), 128.8 (Ph), 128.0 (Ph), 126.4 (Ph), 114.1 (CH=*C*H_2), 113.7 (Ph), 101.2, 101.1 (C1, Ph*C*H), 76.8 (C3), 73.3 (C4), 70.7 (Ph*C*H_2), 70.1 (C2), 69.1, 69.0 (C6, CH=CH_2(CH_2)$_5$*C*H_2O), 66.52 (C5), 55.20 (CH_3O), 33.6 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 29.3 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 28.81 (2C, CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 28.78 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 21.0 (*C*$H_3$C=O). *m/z* (ESI) calc. [$C_{31}H_{40}O_8$]Na^+: 563.2615. Found: 563.2613.

*7-Octen-1-yl 2-*O*-Benzyl-4,6-*O*-benzylidene-β-*D*-galactopyranoside* **18**

A stirred solution of **16** (5.60 g, 9.52 mmol) in CH_2Cl_2/H_2O (19:1, 100 mL) was treated with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (2.59 g, 11.4 mmol) and the solution was stirred (2 h). The mixture was then diluted with CH_2Cl_2 (300 mL) and washed twice with saturated $NaHCO_3$ (300 mL). The solution was dried, concentrated, and subjected to flash chromatography (EtOAc/hexanes, 1:1) to afford the alcohol **18** as a white non-crystalline solid (4.22 g, 95%). [α] +9.0 ($c = 0.6$, CH_2Cl_2). R_f 0.48 (EtOAc/hexanes, 1:1). δ_H (500 MHz) 7.55–7.50 (2H, m, Ph), 7.42–7.26 (8H, m, Ph), 5.86–5.76 (1H, m, C*H*=CH_2), 5.56 (1H, s, PhC*H*), 5.03–4.92 (3H, m, PhCH_2, CH=CH_2), 4.73 (1H, A of AB, J 11.3, PhCH_2), 4.40 (1H, d, $J_{1,2}$ 7.7, H1), 4.34 (1H, dd, $J_{6,6}$ 12.4, $J_{5,6}$ 1.5, H6), 4.41 (1H, dd, $J_{6,6}$ 12.4, $J_{5,6}$ 1.9, H6), 4.22 (1H, dd, $J_{3,4}$ 3.8, $J_{4,5}$ 0.9, H4), 4.01 (1H, ddd, J 9.4, 6.5, 6.5, CH=CH_2(CH_2)$_5$CH_2O), 3.74 (1H, ddd, $J_{2,3}$ 9.6, J 7.3, $J_{3,4}$ 3.8, H3), 3.63 (1H, dd, $J_{2,3}$ 9.6, $J_{1,2}$ 7.7, H2), 3.52 (1H, ddd, J 9.4, 6.9, 6.9, CH=CH_2(CH_2)$_5$CH_2O), 3.43–3.44 (1H, m, H5), 2.53 (1H, d, J 7.3, OH), 2.08–2.01 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.61–1.73 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.49–1.30 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (125.7 MHz) 139.0 (*C*H=CH_2), 138.6 (Ph), 137.6 (Ph), 129.1 (Ph), 128.3 (Ph), 128.2 (Ph), 127.9 (Ph), 127.6 (Ph), 126.5 (Ph), 114.2 (CH=*C*H_2), 103.6 (C1), 101.4 (Ph*C*H), 79.3 (C2), 75.6 (C4), 74.8 (Ph*C*H_2), 72.5 (C3), 70.0, 69.2 (C6, CH=CH_2(CH_2)$_5$*C*H_2O), 66.5 (C5), 33.7 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 29.7 (CH=$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$$CH_2$O), 26.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O). *m/z* (ESI) calc. [$C_{28}H_{36}O_6$]$Na^+$: 491.2404. Found: 491.2402.

*7-Octen-1-yl 2-*O*-Benzyl-3-*O*-(4,6-*O*-benzylidene-β-*D*-galactopyranosyl)-4,6-*O*-benzylidene-β-*D*-galactopyranoside* **21**

A solution of the acceptor **18** (3.59 g, 7.67 mmol) in dry CH_2Cl_2 (50 mL) was stirred over 4-Å molecular sieves (3 g) and the mixture stirred (rt, 1 h). The solution was then cooled (−40°C), treated with $BF_3{\cdot}OEt_2$ (0.5 mL) followed by dropwise addition of the trichloroacetimidate **19**[31] (7.57 g, 15.34 mmol) and then the mixture allowed to warm (0°C). The mixture was neutralized with Et_3N (2 mL), concentrated, and subjected to flash chromatography (EtOAc/hexanes, 1:1) to afford a colourless oil, which was immediately used in the next step. The colourless 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, 7:3) to afford the diol **21** as a colourless oil (3.24 g, 59%). [α] +14.0 ($c = 0.4$, CH_2Cl_2). R_f 0.44 (EtOAc/hexanes, 7:3). δ_H (500 MHz) 7.60–7.23 (15H, m, Ph), 5.87–5.76 (1H, m, CH_2=C*H*), 5.56 (1H, s, Ph*C*H), 5.51 (1H, s, Ph*C*H), 5.04–4.92 (3H, m, PhCH_2, CH_2=CH), 4.70 (1H, A of AB, J 10.4, PhCH_2), 4.69 (1H, d, $J_{1',2'}$ 8.3, H1′), 4.41 (1H, d, $J_{1,2}$ 7.1, H1), 4.35 (1H, d, $J_{3,4}$ 2.8, H4), 4.31 (1H, dd, $J_{6,6}$ 12.3, $J_{5,6}$ 1.2, H6), 4.26 (1H, dd, $J_{6',6'}$ 12.4, $J_{5',6'}$ 1.1, H6′), 4.11 (1H, d, $J_{3',4'}$ 3.7, H4′), 4.08–4.00 (m, 3H, H6, H6′, CH=CH_2(CH_2)$_5$CH_2O), 3.92–3.85 (2H, m, H2, H3), 3.78 (1H, dd, $J_{2',3'}$ 8.5, $J_{1',2'}$ 8.3, H2′), 3.63–3.57 (1H, m, H3′), 3.54 (1H, ddd, J 9.4, 6.9, 6.9, CH=CH_2(CH_2)$_5$CH_2O), 3.39 (1H, s, H5), 3.31 (1H, s, H5′), 2.87 (1H, s, OH), 2.59 (1H, d, J 8.3, OH), 2.08–2.01 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.77–1.61 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.50–1.30 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (100 MHz) 139.0 (CH_2=*C*H), 138.3 (Ph), 138.0 (Ph), 137.6 (Ph), 129.2 (Ph), 128.9 (Ph), 128.7 (Ph), 128.4 (Ph), 128.3 (Ph), 128.1 (Ph), 127.9 (Ph), 126.7 (Ph), 126.3 (Ph), 114.3 (*C*H_2=CH), 103.9 (Ph*C*H), 103.7 (Ph*C*H), 101.3, 101.2 (C1, C1′), 78.4, 77.4 (C2, C3), 76.4 (C4), 75.1 (Ph*C*H_2), 75.3, 72.5, 71.8 (C2′, C3′, C4′), 70.1 (CH=CH_2(CH_2)$_5$*C*H_2O), 69.2, 69.1 (C6, C6′), 66.6, 66.5 (C5, C5′), 33.7 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 28.7 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 29.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 28.9 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 26.1 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O). *m/z* (ESI) calc. [$C_{41}H_{50}O_{11}$]$Na^+$: 741.3245. Found: 741.3245.

*7-Octen-1-yl 2-*O*-Benzyl-3-*O*-(4,6-*O*-benzylidene-3-*O*-pivaloyl-β-*D*-galactopyranosyl)-4,6-*O*-benzylidene-β-*D*-galactopyranoside* **22**

A solution of the diol **21** (2.7 g, 3.76 mmol) in pyridine (50 mL) was treated with trimethylacetal chloride (0.69 mL, 5.64 mmol)

and the solution was stirred. A further addition of trimethylacetal chloride (0.69 mL, 5.64 mmol) was required to ensure completion. The solution was concentrated and subjected to flash chromatography (EtOAc/hexanes, 1:1) to afford the alcohol **22** as a white solid (2.55 g, 85%). [α] +62.7 ($c = 2.2$, CH_2Cl_2). R_f 0.59 (EtOAc/hexanes, 3:2). δ_H (500 MHz) 7.57–7.28 (15H, m, Ph), 5.85–5.76 (1H, m, CH_2=C*H*), 5.56 (1H, s, PhC*H*), 5.50 (1H, s, PhC*H*), 5.03–4.92 (3H, m, CH_2=CH, PhCH_2), 4.82 (1H, d, $J_{1',2'}$ 7.8, H1′), 4.79 (1H, dd, $J_{2',3'}$ 10.2, $J_{3',4'}$ 3.8, H3′), 4.68 (1H, A of AB, J 10.0, PhCH_2), 4.40 (1H, d, $J_{1,2}$ 7.5, H1), 4.35–4.25 (4H, m, H4, H4′, H6, H6′), 4.07–3.99 (4H, m, H2′, H6, H6′, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.92 (1H, dd, $J_{2,3}$ 9.9, $J_{3,4}$ 3.4, H3), 3.87 (1H, dd, $J_{2,3}$ 9.9, $J_{1,2}$ 7.5, H2), 3.52 (1H, ddd, J 9.2, 7.0, 7.0, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.40–3.37 (2H, m, H5, H5′), 2.69 (1H, s, OH), 2.08–2.01 (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), 1.48–1.31 (6H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.24 (9H, s, (CH$_3$)$_3$C). δ_C (100 MHz) 178.4 (C=O), 139.0 (CH_2=*C*H), 138.2 (Ph), 137.9 (Ph), 137.8 (Ph), 128.9 (Ph), 128.8 (Ph), 128.7 (Ph), 128.5 (Ph), 128.1 (Ph), 128.0 (Ph), 127.9 (Ph), 126.6 (Ph), 125.9 (Ph), 114.2 (*C*H$_2$=CH), 103.9 (Ph*C*H), 103.6 (Ph*C*H), 101.2 (C1′), 100.4 (C1), 78.5 (C3), 76.2 (C2), 75.1 (PhCH_2), 73.3, 73.2 (3C, C3′, C4, C4′), 70.1 (CH=CH$_2$(CH$_2$)$_5$CH_2O), 69.09, 69.07 (C6, C6′), 68.9 (C2′), 66.5 (2C, C5, C5′), 39.0 ((CH$_3$)$_3$*C*), 33.7 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.7 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.0 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 27.1 ((*C*H$_3$)$_3$C), 26.1 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O). *m/z* (ESI) calc. [$C_{46}H_{58}O_{12}$]Na^+: 825.3820. Found: 825.3830.

7-Octen-1-yl 2-O-Benzyl-3-O-[4,6-O-benzylidene-2-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-3-O-pivaloyl-β-D-galactopyranosyl]-4,6-O-benzylidene-β-D-galactopyranoside ***24***

A solution of the alcohol **22** (1.74 g, 2.16 mmol) in dry Et_2O/CH_2Cl_2 (9:1, 50 mL) was treated with 4-Å molecular sieves (1 g) and the mixture stirred (rt, 1 h). The mixture was then cooled (−10°C), treated with TMSOTf (100 μL), followed by dropwise addition of the trichloroacetimidate **23**[33] (3.65 g, 6.50 mmol) in dry Et_2O (15 mL). The mixture was treated with Et_3N (0.5 mL), filtered, and subjected to flash chromatography (EtOAc/hexanes, 1:3) to yield the trisaccharide **24** as a colourless oil (2.60 g, 98%). [α] −62.7 ($c = 0.3$, CH_2Cl_2). R_f 0.17 (EtOAc/hexanes, 1:1). δ_H (500 MHz) 7.53–7.44 (6H, m, Ph), 7.39–7.13 (24H, m, Ph), 5.87–5.76 (1H, m, CH_2=C*H*), 5.51 (1H, s, PhC*H*), 5.44 (1H, s, PhC*H*), 5.46 (1H, d, $J_{1'',2''}$ 3.5, H1″), 5.13 (1H, d, $J_{1',2'}$ 8.0, H1′), 5.03–4.92 (2H, m, CH_2=CH), 4.89 (1H, dd, $J_{2',3'}$ 9.8, $J_{3',4'}$ 3.8, H3′), 4.82 (1H, A of AB, J 9.6, PhCH_2), 4.79 (1H, A of AB, J 12.0, PhCH_2), 4.74 (1H, A of AB, J 11.7, PhCH_2), 4.63–4.54 (4H, m, PhCH_2), 4.43 (1H, d, $J_{1,2}$ 7.7, H1), 4.36–4.24 (7H, m, H2′, H4, H4′, H5″, H6, H6′, PhCH_2), 4.12–3.94 (6H, m, H2″, H3, H3″, H6, H6′, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.79 (1H, dd, $J_{2,3}$ 9.9, $J_{1,2}$ 7.7, H2), 3.57 (1H, ddd, J 9.4, 7.0, 7.0, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.38 (1H, s, H5), 3.23 (1H, s, H5′), 3.20 (1H, d, J 1.3, H4″), 2.11–2.02 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.80–1.69 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.54–1.34 (6H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.13 (9H, s, (CH$_3$)$_3$C), 0.54 (3H, d, $J_{5'',6''}$ 6.4, H6″). δ_C (100 MHz) 178.0 (C=O), 139.1 (Ph), 139.0 (CH_2=*C*H), 138.9 (Ph), 138.5 (Ph), 137.9 (Ph), 137.6 (Ph), 129.3 (Ph), 129.1 (Ph), 128.8 (Ph), 128.6 (Ph), 128.3 (Ph), 128.21 (Ph), 128.16 (Ph), 128.1 (2C, Ph), 128.0 (Ph), 127.9 (Ph), 127.4 (Ph), 127.34 (Ph), 127.30 (Ph), 127.2 (Ph), 127.14 (Ph), 127.08 (Ph), 127.0 (Ph), 125.9 (Ph), 114.3 (*C*H$_2$=CH), 103.8 (C1), 101.9, 101.3, 100.4 (3C, C1′, Ph*C*H), 96.4 (C1″), 79.9 (C2), 79.3 (C3), 78.6 (C4″), 76.7, 76.4, 76.1, 74.3, 73.1 (C2″, C3′, C3″, C4, C4′), 75.3 (PhCH_2), 75.0 (PhCH_2), 73.0 (Ph*C*H$_2$), 72.6 (PhCH_2), 70.2 (CH=CH$_2$(CH$_2$)$_5$*C*H$_2$O), 69.03, 68.97 (C6, C6′), 68.9 (C5″), 66.52, 66.5, 66.3 (C2′, C5, C5′), 38.9 ((CH$_3$)$_3$*C*), 33.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.0 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.9 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 27.1 ((*C*H$_3$)$_3$C), 26.3 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 15.89 (C6″). *m/z* (ESI) calc. [$C_{73}H_{86}O_{16}$]Na^+: 1241.5808. Found: 1241.5808.

7-Octen-1-yl 2-O-Benzyl-3-O-[4,6-O-benzylidene-2-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl]-4,6-O-benzylidene-β-D-galactopyranoside ***25***

A stirred solution of **24** (3.21 g, 2.62 mmol) in CH_3OH (150 mL) was treated with catalytic $LiOCH_3$ (200 mg) and the solution was heated at reflux (5 days). The solution was allowed to cool, neutralized with Amberlite IR 120 (H^+), filtered, and subjected to flash chromatography (EtOAc/hexanes, 1:3) to afford first unreacted **24** (350 mg, 11%); further elution (EtOAc/hexanes, 1:2) afforded alcohol **25** as a colourless oil (1.72 g, 58%). [α] −50.3 ($c = 0.4$, CH_2Cl_2). R_f 0.77 (EtOAc/hexanes, 1:1). δ_H (500 MHz) 7.56–7.47 (6H, m, Ph), 7.40–7.18 (24H, m, Ph), 5.88–5.78 (1H, m, CH_2=C*H*), 5.58 (1H, d, $J_{1'',2''}$ 3.55, H1″), 5.55 (1H, s, PhC*H*), 5.53 (1H, s, PhC*H*), 5.05–4.94 (3H, m, H1′, CH_2=CH), 4.82, 4.76 (2H, AB, J 11.5, PhCH_2), 4.90, 4.64 (2H, AB, J 9.6, PhCH_2), 4.61, 4.53 (2H, AB, J 12.0, PhCH_2), 4.85, 4.45 (2H, AB, J 11.6, PhCH_2), 4.42 (1H, d, $J_{1,2}$ 7.8, H1), 4.31 (1H, d, $J_{3,4}$ 3.4, H4), 4.34–4.18 (3H, m, H5″, H6, H6′), 4.11 (1H, d, $J_{3',4'}$ 3.8, H4′), 4.10–3.97 (6H, m, H2″, H3, H3″, H6, H6′, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.93 (1H, dd, $J_{2',3'}$ 8.4, $J_{1',2'}$ 8.2, H2′), 3.83 (1H, dd, $J_{2,3}$ 9.7, $J_{1,2}$ 7.8, H2), 3.78–3.73 (1H, m, H3′), 3.55 (1H, ddd, J 9.1, 6.9, 6.9, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.39 (1H, s, H5), 3.33 (1H, d, J 1.8, H4″), 3.29 (1H, d, J 7.5, OH), 3.24 (1H, s, H5′), 2.13–2.03 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.80–1.67 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.55–1.32 (6H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 0.70 (3H, d, $J_{5'',6''}$ 6.4, H6″). δ_C (100 MHz) 139.03 (CH_2=*C*H), 138.9 (Ph), 138.5 (Ph), 138.3 (Ph), 137.6 (Ph), 129.1 (Ph), 129.0 (Ph), 128.8 (Ph), 128.4 (Ph), 128.32 (Ph), 128.25 (Ph), 128.22 (Ph), 128.17 (Ph), 128.12 (2C, Ph), 128.09 (Ph), 128.0 (2C, Ph), 127.8 (Ph), 127.41 (Ph), 127.40 (Ph), 127.34 (Ph), 127.29 (Ph), 126.9 (Ph), 126.4 (Ph), 114.3 (*C*H$_2$=CH), 103.9 (C1), 101.5, 101.4, 101.2 (3C, C1′, Ph*C*H), 97.8 (C1″), 79.8, 79.5 (C2, C3), 78.3 (C4″), 76.7, 76.2, 75.9, 75.2, 74.8, 74.4 (C2′, C2″, C3′, C3″, C4, C4′), 75.0 (PhCH_2), 74.8 (PhCH_2), 73.0 (Ph*C*H$_2$), 72.8 (PhCH_2), 70.1 (CH=CH$_2$(CH$_2$)$_5$*C*H$_2$O), 69.1, 69.0 (C6, C6′), 66.8, 66.64, 66.61 (C5, C5′, C5″), 33.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.0 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.9 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 26.2 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 16.14 (C6″). *m/z* (ESI) calc. [$C_{68}H_{78}O_{15}$]Na^+: 1157.5233. Found: 1157.5237.

7-Octen-1-yl 3-O-[3-O-(2-N-Acetyl-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-O-benzyl-4,6-O-benzylidene-β-D-galactopyranoside ***27***

A solution of the acceptor **25** (359 mg, 0.316 mmol) in dry Et_2O (15 mL) was treated with 4-Å molecular sieves (300 mg) and the

mixture stirred (rt, 1 h). The mixture was then cooled (−10°C), treated with TMSOTf (10 μL, 0.058 mmol); the trichloroacetimidate **26**[34] (457 mg, 0.965 mmol) in dry Et_2O (15 mL) was then added dropwise and the mixture 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 partially pure tetrasaccharide as a colourless oil (270 mg, 65%). The residue was taken up in pyridine (4 mL) and treated with AcSH (2 mL) and the solution was stirred (3 days). The solution was concentrated and subjected to flash chromatography (CH_2Cl_2/CH_3OH, 20:1) to afford **27** as a colourless oil (205 mg, 78%). [α] +11.7 ($c = 0.6$, CH_2Cl_2). R_f 0.38 (EtOAc/hexanes, 3:1). δ_H (500 MHz) 7.59–7.11 (30H, m, Ph), 5.89–5.77 (1H, m, CH_2=C*H*), 5.57 (1H, d, J_{NH} 10.8 NH), 5.51 (1H, d, $J_{1'',2''}$ 3.7, H1″), 5.55 (1H, s, PhC*H*), 5.44 (1H, s, PhC*H*), 5.13–5.08 (2H, m, H1‴, PhCH_2), 5.07–5.02 (3H, m, H1′, H4‴, CH=CH_2), 4.92–5.01 (3H, m, H3‴, PhCH_2, CH=CH_2), 4.90, 4.89 (2H, AB, J 10.0, PhCH_2), 4.79 (1H, A of AB, J 11.4, PhCH_2), 4.78 (1H, A of AB, J 12.2, PhCH_2), 4.64 (1H, ddd, J_{NH} 10.8, $J_{2''',3'''}$ 10.6, $J_{1''',2'''}$ 3.6, H2‴), 4.52 (1H, A of AB, J 11.8, PhCH_2), 4.45 (1H, d, $J_{1,2}$ 7.8, H1), 4.44–4.39 (2H, m, H5″, PhCH_2), 4.35–4.22 (5H, m, H3′, H4, H4′, H6, H6′), 4.18 (1H, dd, $J_{2'',3''}$ 10.2, $J_{1'',2''}$ 3.7, H2″), 4.13–4.01 (6H, m, H3, H3″, H5‴, H6, H6′, CH=CH_2(CH_2)$_5$CH_2O), 3.87–3.81 (2H, m, H2, H2′), 3.71 (1H, dd, $J_{6''',6'''}$ 11.5, $J_{5''',6'''}$ 7.8, H6‴), 3.57 (1H, ddd, J 9.1, 7.0, 7.0, CH=CH_2(CH_2)$_5$CH_2O), 3.32 (1H, s, H4″), 3.40, 3.27 (2H, 2 × s, H5, H5′), 3.10 (1H, dd, $J_{6''',6'''}$ 11.5, $J_{5''',6'''}$ 2.6, H6‴), 2.09, 1.97, 1.78, 1.57 (12H, 4 × s, CH_3C=O), 2.12–2.04 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.80–1.67 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.53–1.35 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 0.56 (3H, d, $J_{5'',6''}$ 6.2, H6″). δ_C (100 MHz) 170.7 (C=O), 170.3 (C=O), 170.1 (C=O), 170.0 (C=O), 139.3 (Ph), 139.0 (CH_2=*C*H), 138.9 (Ph), 138.41 (2C, Ph), 138.39 (Ph), 137.4 (Ph), 129.4 (Ph), 129.2 (Ph), 128.72 (Ph), 128.71 (Ph), 128.33 (Ph), 128.30 (Ph), 128.26 (Ph), 128.23 (Ph), 128.17 (2C, Ph), 128.0 (Ph), 127.9 (Ph), 127.44 (Ph), 127.38 (Ph), 127.2 (Ph), 127.1 (Ph), 126.9 (Ph), 126.0 (Ph), 114.3 (*C*H_2=CH), 103.8 (C1), 102.0, 101.6, 100.7 (C1′, Ph*C*H), 98.1 (C1″), 92.1 (C1‴), 80.2, 79.8 (C2, C3), 78.2 (C4″), 75.3 (Ph*C*H_2), 75.0 (Ph*C*H_2), 74.1 (Ph*C*H_2), 72.2 (Ph*C*H_2), 76.3, 76.1, 76.0, 75.0, 70.7, 69.9 (C2′, C2″, C3′, C3″, C4, C4′), 70.3 (CH=CH_2(CH_2)$_5$*C*H_2O), 69.2, 69.0 (C6, C6′), 68.9 (C3‴), 67.6 (C4‴), 67.3 (C5″), 66.9 (C5‴), 66.5, 66.2 (C5, C5′), 62.5 (C6‴), 46.4 (C2‴), 33.8 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 29.8 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 29.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 28.9 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 26.2 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 22.8 (*C*$H_3$C=O), 20.74 (*C*$H_3$C=O), 20.71 (*C*$H_3$C=O), 20.66 (*C*$H_3$C=O), 15.91 (C6″). *m/z* (ESI) calc. [$C_{82}H_{97}NO_{23}$]Na^+: 1486.6344. Found: 1486.6348.

7-Octen-1-yl 2-O-Benzyl-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]-4,6-O-benzylidene-β-D-galactopyranoside ***29***

A solution of the acceptor **25** (310 mg, 0.273 mmol) in dry Et_2O (5 mL) was treated with 4-Å molecular sieves and the mixture stirred (rt, 1 h). The mixture was then cooled (−10°C), treated with TMSOTf (10 μL, 0.058 mmol); the trichloroacetimidate **28**[35] (700 mg, 1.02 mmol) in dry Et_2O (10 mL) was then added dropwise and the mixture 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 partially pure tetrasaccharide **29** (270 mg, 60%) as a colourless oil.

7-Octen-1-yl 4,6-O-Benzylidene-β-D-glucopyranoside ***33***

A stirred solution of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate **30**[38] (33.9 g, 69 mmol) and 7-octen-1-ol (11.0 g, 86 mmol) was treated with 4-Å molecular sieves (5 g) and the mixture stirred (rt, 1 h). The mixture was then cooled (−40°C), treated with TMSOTf (0.5 mL) and the mixture was allowed to warm (rt, 1 h). The reaction was quenched by the addition of Et_3N (2 mL), filtered, and subjected to flash chromatography (EtOAc/hexanes, 2:3) to afford a colourless oil. The oil was taken up in CH_3OH (200 mL), treated with a catalytic amount of $NaOCH_3$ in CH_3OH and stirred (rt, 2 h); the $NaOCH_3$ was neutralized with Amberlite IR120 (H^+), filtered, and then concentrated. The residue was subjected to flash chromatography (EtOAc/hexanes, 5:1) to afford the tetrol **32** as a white solid (11.3 g, 57%), which was immediately used in the subsequent step. A solution of the tetrol **32** (11.3 g, 38.9 mmol) in dry DMF (200 mL) was treated with benzaldehyde dimethyl acetal (7.2 mL, 48 mmol), *p*-TsOH (300 mg), and the solution was stirred (40°C, 18 h). The solution was neutralized with Et_3N (1.5 mL), concentrated and subjected to flash chromatography (EtOAc/hexanes, 1:1) to afford the diol **33** (14.0 g, 95%) as a white solid. Mp 149–151°C. [α] −46.8 ($c = 0.3$, CH_2Cl_2). R_f 0.82 (EtOAc/hexanes, 7:10). δ_H (500 MHz) 7.52–7.48 (2H, m, Ph), 7.41–7.35 (3H, m, Ph), 5.86–5.77 (1H, m, C*H*=CH_2), 5.55 (1H, s, PhC*H*), 5.03–4.92 (2H, m, CH=CH_2), 4.41 (1H, d, $J_{1,2}$ 8.0, H1), 4.35 (1H, dd, $J_{6,6}$ 10.5, $J_{5,6}$ 4.9, H6), 3.93–3.77 (3H, m, H3, H6, CH=CH_2(CH_2)$_5$CH_2O), 3.61–3.43 (4H, m, H2, H4, H5, CH=CH_2(CH_2)$_5$CH_2O), 2.71 (1H, d, J 2.2, OH), 2.51 (1H, d, J 2.4, OH), 2.10–2.01 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.71–1.59 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.47–1.28 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (125 MHz) 139.0 (*C*H=CH_2), 136.9 (Ph), 129.3 (Ph), 128.3 (Ph), 126.3 (Ph), 114.3 (CH=CH_2), 103.1 (C1), 101.9 (Ph*C*H), 80.6 (C4), 73.2, 70.5, 64.6 (C2, C3, C5), 68.7 (CH=CH_2(CH_2)$_5$*C*H_2O), 66.4 (C6), 33.7 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 29.5 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 28.83 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 28.77 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 25.8 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O). *m/z* (ESI) calc. [$C_{21}H_{30}O_6$]$Na^+$: 401.1935. Found: 401.1934.

7-Octen-1-yl 4-O-Acetyl-2,3,6-tri-O-benzyl-β-D-glucopyranoside ***34***

A solution of the alcohol **36** (15.8 mg, 0.028 mmol) in pyridine (1.5 mL) was treated with Ac_2O (0.5 mL) and DMAP (2 mg) (rt, 2 h). The solution was then treated with CH_3OH (1 mL), concentrated, and subjected to flash chromatography (EtOAc/hexanes, 1:3) to afford the ester **34** as a colourless oil (15 mg, 88%). [α] +1.7 ($c = 0.6$, CH_2Cl_2). R_f 0.73 (EtOAc/hexanes, 3:7). δ_H (500 MHz) 7.37–7.22 (15H, m, Ph), 5.85–5.76 (1H, m, *C*H=CH_2), 5.01–4.92 (m, 4H, H4, CH=CH_2, PhCH_2), 4.71 (1H, A of AB, J 11.1, PhCH_2), 4.82, 4.62 (2H, AB, J 11.6, PhCH_2), 4.55, 4.52 (2H, AB, J 12.1, PhCH_2), 4.42 (1H, d, $J_{1,2}$ 7.9, H1), 3.99–3.93 (1H, m, CH=CH_2(CH_2)$_5$CH_2O), 3.60 (dd, $J_{2,3}$ 9.4, $J_{3,4}$ 9.3, H3), 3.57–3.51 (4H, m, H5, H6, CH=CH_2(CH_2)$_5$CH_2O), 3.48 (1H, dd, $J_{2,3}$ 9.4, $J_{1,2}$ 7.9, H2), 1.83 (3H, s, CH_3C=O), 2.07–2.01 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.71–1.62 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.45–1.30 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (125 MHz) 167.2 (C=O), 136.5 (*C*H=CH_2), 135.9 (Ph), 135.8 (Ph), 135.5 (Ph), 125.82

(Ph), 125.80 (Ph), 125.79 (Ph), 125.6 (Ph), 125.27 (Ph), 125.26 (Ph), 125.2 (Ph), 125.1 (Ph), 125.0 (Ph), 111.7 (CH=*C*H_2), 101.0 (C1), 79.5, 79.2 (C2, C3), 72.5 (Ph*C*H_2), 72.4 (Ph*C*H_2), 71.1 (Ph*C*H_2), 70.9, 68.6 (C4, C5), 67.7, 67.4 (C6, CH=CH_2(CH_2)$_5$*C*H_2O), 31.2 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 27.3 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 26.4 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 26.3 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 23.5 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O), 18.3 ($CH_3$). *m/z* (ESI) calc. [$C_{37}H_{46}O_7$]$Na^+$: 625.3138. Found: 625.3136.

*7-Octen-1-yl 4,6-*O*-Benzylidene-2,3-di-*O*-benzyl-β-D-glucopyranoside* ***35***

A stirred solution of the diol **33** (13.0 g, 34.4 mmol) in DMF (200 mL, −20°C) was treated with BnBr (12.2 mL, 0.103 mmol) and NaH (60%, 3.44 g, 86 mmol) and the mixture stirred (rt, 6 h). The mixture was cooled (−20°C), treated with CH_3OH (10 mL) and allowed to stand (rt, 10 min). The solution was concentrated, taken up in EtOAc (500 mL) and washed with water (400 mL), and brine (400 mL). The organic extract was dried and then concentrated and subjected to flash chromatography (EtOAc/hexanes, 1:9) to afford the dibenzyl ether **35** as a white solid (18.8 g, 98%). Mp 49–51°C. [α] −27.8 ($c = 1.2$, CH_2Cl_2). R_f 0.56 (EtOAc/hexanes, 1:5). δ_H (500 MHz) 7.52–7.49 (2H, m, Ph), 7.43–7.26 (13H, m, Ph), 5.86–5.76 (1H, m, C*H*=CH_2), 5.59 (1H, s, PhC*H*), 5.04–4.91 (4H, m, PhCH_2, CH=CH_2), 4.83 (1H, A of AB, *J* 10.9, PhCH_2), 4.79 (1H, A of AB, *J* 11.0, PhCH_2), 4.57 (1H, d, $J_{1,2}$ 7.9, H1), 4.37 (1H, dd, $J_{6,6}$ 10.3, $J_{5,6}$ 5.1, H6), 3.93 (1H, ddd, *J* 9.4, 6.5, 6.5, CH=CH_2(CH_2)$_5$CH_2O), 3.81 (1H, dd, $J_{6,6}$ 10.3, $J_{5,6}$ 5.1, H6), 3.77 (1H, dd, $J_{2,3}$ 8.6, $J_{3,4}$ 9.1, H3), 3.71 (1H, dd, $J_{4,5}$ 9.2, $J_{3,4}$ 9.1, H4), 3.58 (1H, ddd, 1H, *J* 9.4, 6.9, 9.4, CH=CH_2(CH_2)$_5$CH_2O), 3.48 (1H, dd, $J_{2,3}$ 8.6, $J_{1,2}$ 7.9, H2), 3.43 (1H, ddd, $J_{5,6}$ 9.9, $J_{4,5}$ 9.4, $J_{5,6}$ 5.1, H5), 2.09–2.02 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.72–1.62 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.47–1.31 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (125 MHz) 139.0 (*C*H=CH_2), 138.6 (Ph), 138.4 (Ph), 137.4 (Ph), 128.9 (Ph), 128.4 (Ph), 128.32 (Ph), 128.27 (Ph), 128.2 (Ph), 128.0 (Ph), 127.7 (Ph), 127.6 (Ph), 126.0 (Ph), 114.3 (CH=*C*H_2), 104.2 (C1), 101.1 (Ph*C*H), 82.2, 81.5, 90.9 (C2, C3, C4), 75.3 (Ph*C*H_2), 75.1 (Ph*C*H_2), 70.6 (CH=CH_2(CH_2)$_5$*C*H_2O), 68.8 (C6), 66.0 (C5), 33.7 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 29.7 (CH=$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$$CH_2$O), 26.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O). *m/z* (ESI) calc. [$C_{35}H_{42}O_6$]$Na^+$: 581.2874. Found: 581.2876.

*7-Octen-1-yl 2,3,6-Tri-*O*-benzyl-β-D-glucopyranoside* ***36***

A stirred solution of the alkene **35** (7.47 g, 13.3 mmol) in dry CH_2Cl_2 (200 mL) was treated with 4-Å molecular sieves (5 g) and the mixture stirred (rt, 1 h). The mixture was then cooled (0°C) and treated with triethylsilane (10.7 mL, 66.9 mmol) and $BF_3{\cdot}OEt_2$ (3.3 mL, 26.6 mmol) and the mixture stirred (rt, 5 h). The mixture was neutralized with Et_3N (5 mL), diluted with CH_2Cl_2 (300 mL), and washed with saturated $NaHCO_3$, water and then brine. The organic extract was concentrated and subjected to flash chromatography (EtOAc/hexanes, 1:4) to afford the alcohol **36** as a colourless oil (4.7 g, 64%). [α] −18.0 ($c = 0.3$, CH_2Cl_2). R_f 0.73 (EtOAc/hexanes, 3:7). δ_H (500 MHz) 7.40–7.26 (15H, m, Ph), 5.87–5.76 (1H, m, C*H*=CH_2), 5.03–4.93 (4H, m, PhCH_2, CH=CH_2), 4.75 (1H, A of AB, *J* 11.4, PhCH_2), 4.73 (1H, A of AB, *J* 10.7, PhCH_2), 4.62, 4.58 (2H, AB, *J* 12.3, PhCH_2), 4.43 (1H, d, $J_{1,2}$ 7.2, H1), 3.99–3.93 (1H, m, CH=CH_2(CH_2)$_5$CH_2O), 3.79 (1H, dd, $J_{6,6}$ 10.4, $J_{5,6}$ 3.9, H6), 3.72 (1H, dd, $J_{6,6}$ 10.4, $J_{5,6}$ 5.4, H6), 3.63–3.52 (2H, m, H4, CH=CH_2(CH_2)$_5$CH_2O), 3.50–3.40 (3H, m, H2, H3, H5), 2.54 (1H, d, *J* 2.1, OH), 2.09–2.01 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.72–1.62 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.47–1.30 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (125 MHz) 139.0 (*C*H=CH_2), 138.7 (Ph), 138.5 (Ph), 138.0 (Ph), 128.5 (Ph), 128.40 (Ph), 128.36 (Ph), 128.1 (Ph), 128.0 (Ph), 127.8 (Ph), 127.71 (Ph), 127.69 (2C, Ph), 114.2 (CH=*C*H_2), 103.7 (C1), 84.1, 81.7 (C2, C3), 75.3 (Ph*C*H_2), 74.7 (Ph*C*H_2), 74.0 (C4), 73.7 (Ph*C*H_2), 71.7 (C5), 70.4, 70.2 (C6, CH=CH_2(CH_2)$_5$*C*H_2O), 33.7 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 29.7 (CH=$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$$CH_2$O), 26.0 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O). *m/z* (ESI) calc. [$C_{35}H_{44}O_6$]$Na^+$: 583.3030. Found: 583.3031.

*7-Octen-1-yl 4-*O*-(4,6-*O*-Benzylidene-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside* ***37***

A solution of the acceptor **36** (4.02 g, 7.19 mmol) in dry CH_2Cl_2 (50 mL) was stirred over 4-Å molecular sieves (rt, 1 h). The solution was then cooled (−40°C), treated with $BF_3{\cdot}OEt_2$ (0.5 mL), followed by dropwise addition of the trichloroacetimidate **19**[31] (8.90 g, 18.0 mmol) and then the mixture was allowed to warm (0°C). The mixture was neutralized with Et_3N (2 mL), concentrated, and subjected to flash chromatography (EtOAc/hexanes, 1:1) to afford a colourless oil, which was immediately used in the next step. The colourless 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, 7:3) to afford the diol **37** as a colourless oil (5.3 g, 91%). [α] −3.1 ($c = 1.4$, CH_2Cl_2). R_f 0.68 (EtOAc/hexanes, 7:3). δ_H (500 MHz) 7.50–7.21 (20H, m, Ph), 5.86–5.77 (1H, m, CH_2=C*H*), 5.46 (1H, s, PhC*H*), 5.03–4.91 (5H, m, PhCH_2, CH_2=CH), 4.73 (1H, A of AB, *J* 10.1, PhCH_2), 4.74, 4.62 (2H, AB, *J* 12.3, PhCH_2), 4.58 (1H, d, $J_{1',2'}$ 8.5, H1′), 4.40 (1H, d, $J_{1,2}$ 8.1, H1), 4.06–3.99 (4H, m, H4, H4′, H6, H6′), 3.95 (1H, ddd, *J* 9.5, 6.4, 6.4, CH=CH_2(CH_2)$_5$CH_2O), 3.80 (1H, dd, $J_{6,6}$ 11.6, $J_{5,6}$ 1.9, H6), 3.75 (1H, dd, $J_{6',6'}$ 12.5, $J_{5',6'}$ 1.5, H6′), 3.73–3.68 (2H, m, H3, H5), 3.64 (1H, dd, $J_{2',3'}$ 9.0, $J_{1',2'}$ 8.5, H2′), 3.54 (1H, ddd, *J* 9.5, 6.8, 6.8, CH=CH_2(CH_2)$_5$CH_2O), 3.51–3.44 (3H, m, H2, H3′, OH), 2.87 (1H, s, H5′), 2.49 (1H, d, *J* 7.3, OH), 2.10–2.01 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.74–1.61 (2H, m, CH=CH_2(CH_2)$_5$$CH_2$O), 1.49–1.29 (6H, m, CH=CH_2(CH_2)$_5$$CH_2$O). δ_C (125 MHz) 139.2 (CH_2=*C*H), 139.0 (Ph), 138.4 (Ph), 137.69 (Ph), 137.67 (Ph), 129.1 (Ph), 128.4 (Ph), 128.3 (Ph), 128.2 (Ph), 128.1 (2C, Ph), 128.0 (Ph), 127.8 (Ph), 127.6 (Ph), 127.2 (2C, Ph), 126.4 (Ph), 114.3 (*C*H_2=CH), 103.9, 103.5 (C1, C1′), 101.3 (Ph*C*H), 83.7 (C3), 82.1 (C2), 77.6 (C4), 75.2 (Ph*C*H_2), 75.1, 74.2 (C4′, C5), 74.9 (Ph*C*H_2), 73.5 (Ph*C*H_2), 72.7, 72.5 (C2′, C3′), 70.10 (CH=CH_2(CH_2)$_5$*C*H_2O), 68.9, 68.5 (C6, C6′), 66.7 (C5′), 33.7 (CH=CH_2(*C*H_2)$_5$$CH_2$O), 29.7 (CH=$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$$CH_2$O), 26.1 (CH=$CH_2$(*C*$H_2$)$_5$$CH_2$O). *m/z* (ESI) calc. [$C_{48}H_{58}O_{11}$]$Na^+$: 833.3871. Found: 833.3872.

*7-Octen-1-yl 4-*O*-(4,6-*O*-Benzylidene-3-*O*-pivaloyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside* ***38***

A stirred solution of the diol **37** (5.93 g, 7.32 mmol) in pyridine (50 mL) was treated with trimethylacetyl chloride

(1.16 mL, 9.52 mmol) and the solution was stirred. The solution was concentrated and subjected to flash chromatography (EtOAc/hexanes, 1:1) to afford the alcohol **38** as a white solid (6.22 g, 95%). [α] +42.4 ($c = 0.5$, CH_2Cl_2). R_f 0.55 (EtOAc/hexanes, 3:2). δ_H (500 MHz) 7.52–7.18 (20H, m, Ph), 5.86–5.77 (1H, m, CH_2=C*H*), 5.40 (1H, s, PhC*H*), 5.05–4.90 (5H, m, CH_2=CH, PhCH_2), 4.73 (1H, A of AB, *J* 11.9, PhCH_2), 4.72 (1H, A of AB, *J* 10.9, PhCH_2), 4.67–4.63 (2H, m, H1′, H3′), 4.59 (1H, A of AB, *J* 12.4, PhCH_2), 4.39 (1H, d, $J_{1,2}$ 7.8, H1), 4.17 (1H, d, $J_{3',4'}$ 3.7, H4′), 4.04–3.90 (4H, m, H4, H6, H6′, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.87 (1H, dd, $J_{2',3'}$ 9.7, $J_{1',2'}$ 7.9, H2′), 3.78 (1H, dd, $J_{6,6}$ 11.6, $J_{5,6}$ 2.0, H6), 3.73–3.65 (2H, m, H3, H6′), 3.49–3.42, 3.60–3.50 (4H, 2 × m, H2, H5, OH, CH=CH$_2$(CH$_2$)$_5$CH_2O), 2.81 (1H, s, H5′), 2.09–2.01 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.72–1.61 (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), 1.22 (9H, s, (CH$_3$)$_3$C). δ_C (125 MHz) 178.3 (C=O), 139.2 (Ph), 139.0 (CH$_2$=*C*H), 138.4 (Ph), 137.9 (Ph), 137.5 (Ph), 128.6 (Ph), 128.4 (Ph), 128.3 (Ph), 128.2 (Ph), 128.14 (Ph), 128.12 (Ph), 127.92 (Ph), 127.86 (Ph), 127.6 (Ph), 127.1 (Ph), 126.9 (Ph), 126.0 (Ph), 114.3 (*C*H$_2$=CH), 103.9 (2C, C1, C1′), 100.4 (Ph*C*H), 83.9 (C3), 82.2 (C2), 77.7 (C4), 75.1 (Ph*C*H$_2$), 74.8 (Ph*C*H$_2$), 74.0, 73.4, 73.1 (C3′, C4′, C5), 73.7 (Ph*C*H$_2$), 70.1 (CH=CH$_2$(CH$_2$)$_5$*C*H$_2$O), 69.5 (C2′), 68.8 (2C, C6, C6′), 66.5 (C5′), 38.7 ((CH$_3$)$_3$*C*), 33.7 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.7 (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), 27.1 ((*C*H$_3$)$_3$C), 26.0 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O). *m/z* (ESI) calc. [$C_{53}H_{66}O_{12}$]Na^+: 917.4446. Found: 917.4449.

7-Octen-1-yl 4-O-[4,6-O-Benzylidene-2-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-β-D-galactopyranosyl]-2,3,6-tri-O-benzyl-β-D-glucopyranoside ***40***

A solution of the alcohol **38** (2.90 g, 3.24 mmol) in dry Et_2O/CH_2Cl_2 (9:1, 50 mL) was treated with 4-Å molecular sieves (2 g) and the mixture was stirred (rt, 1 h). The mixture was then cooled (−10°C), treated with TMSOTf (100 μL), followed by dropwise addition of the trichloroacetimidate **23**[33] (5.20 g, 9.01 mmol) in dry ether (15 mL). The mixture was treated with Et_3N (0.5 mL), filtered, and subjected to flash chromatography (EtOAc/hexanes, 1:3) to yield the trisaccharide as a colourless oil (3.34 g, 78%). The oil was taken up in CH_3OH (100 mL), treated with catalytic $LiOCH_3$ (150 mg), and the solution was heated at reflux (5 days). The solution was allowed to cool, neutralized with Amberlite IR 120 (H^+), filtered, and subjected to flash chromatography (EtOAc/hexanes, 1:3) to afford first unreacted starting material (480 mg, 16%); further elution (EtOAc/hexanes, 1:2) afforded the alcohol **40** as a colourless oil (1.96 g, 68%). [α] −40.8 ($c = 0.4$, CH_2Cl_2). R_f 0.44 (EtOAc/hexanes, 3:2). δ_H (500 MHz) 7.58–7.09 (35 H, m, Ph), 5.87–5.76 (1H, m, CH_2=C*H*), 5.58 (1H, s, PhC*H*), 5.16 (1H, A of AB, *J* 10.4, PhCH_2), 5.05 (1H, d, $J_{1'',2''}$ 3.4, H1″), 5.03–5.01, 4.97–4.93 (3H, m, PhCH_2, CH_2=CH), 4.82 (1H, A of AB, *J* 11.6, PhCH_2), 4.81 (1H, A of AB, *J* 12.1, PhCH_2), 4.76–4.70 (4H, m, PhCH_2), 4.89, 4.64 (2H, AB, *J* 10.9, PhCH_2), 4.67, 4.43 (2H, AB, *J* 12.4, PhCH_2), 4.42 (1H, d, $J_{1',2'}$ 7.9, H1′), 4.35 (1H, d, $J_{6',6'}$ 12.4, H6′), 4.34 (1H, d, $J_{1,2}$ 7.9, H1), 4.14 (1H, d, $J_{3',4'}$ 3.6, H4′), 4.07 (1H, dd, $J_{2'',3''}$ 6.8, $J_{1'',2''}$ 3.4, H2″), 4.09–4.00 (2H, m, H4, H4″), 3.98 (1H, dd, $J_{6',6'}$ 12.4, $J_{5',6'}$ 1.5, H6′), 3.97–3.87 (4H, m, H3″, H5″, H6, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.81 (1H, dd, $J_{2',3'}$ 9.7, $J_{1',2'}$ 7.9, H2′), 3.69–3.57 (3H, m, H3′, H6, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.54–3.46 (2H, m, H3, OH), 3.41 (1H, dd, $J_{2,3}$ 9.1, $J_{1,2}$ 8.0, H2), 3.31–3.26 (1H, m, H5), 3.13 (1H, s, H5′), 2.06–2.01 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.72–1.59 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.47–1.29 (6H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.08 (3H, d, $J_{5'',6''}$ 6.5, H6″). δ_C (125 MHz) 139.0 (CH$_2$=*C*H), 138.8 (Ph), 138.74 (Ph), 138.69 (Ph), 138.6 (Ph), 138.3 (Ph), 138.1 (Ph), 137.5 (Ph), 129.0 (Ph), 128.9 (Ph), 128.6 (Ph), 128.43 (Ph), 128.42 (Ph), 128.32 (2C, Ph), 128.27 (Ph), 128.24 (Ph), 128.19 (Ph), 128.10 (Ph), 128.06 (Ph), 128.0 (Ph), 127.7 (Ph), 127.64 (Ph), 127.60 (Ph), 127.57 (Ph), 127.54 (Ph), 127.43 (Ph), 127.38 (Ph), 126.6 (Ph), 114.2 (*C*H$_2$=CH), 103.7 (C1), 101.4, 101.2 (C1′, Ph*C*H), 99.2 (C1″), 82.9, 81.7 (C2, C3), 79.0, 78.1, 77.6, 77.3, 76.3 (C2′, C2″, C3″, C4, C4″), 75.8 (C4′), 76.0 (Ph*C*H$_2$), 75.11 (Ph*C*H$_2$), 75.07 (C5), 74.8 (Ph*C*H$_2$), 74.1 (Ph*C*H$_2$), 73.4 (Ph*C*H$_2$), 73.0 (Ph*C*H$_2$), 72.9 (C3′), 70.0 (CH=CH$_2$(CH$_2$)$_5$*C*H$_2$O), 69.0, 68.1 (C6, C6′), 67.3, 66.5 (C5′, C5″), 33.7 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.7 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 29.0 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 28.8 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 26.0 (CH=CH$_2$(*C*H$_2$)$_5$CH$_2$O), 16.8 (C6″). *m/z* (ESI) calc. [$C_{75}H_{86}O_{15}$]Na^+: 1249.5859. Found: 1249.5855.

7-Octen-1-yl 4-O-[3-O-(2-N-Acetyl-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]-2,3,6-tri-O-benzyl-β-D-glucopyranoside ***41***

A solution of the acceptor **40** (365 mg, 0.297 mmol) in dry Et_2O (15 mL) was treated with 4-Å molecular sieves (250 mg) and the mixture stirred (rt, 1 h). The mixture was then cooled (−10°C), treated with TMSOTf (10 μL, 0.058 mmol); the trichloroacetimidate **26**[34] (457 mg, 0.965 mmol) in dry Et_2O (15 mL) was then added dropwise and the mixture 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 partially pure tetrasaccharide as a colourless oil (330 mg, 67%). The residue was taken up in pyridine (4 mL) and treated with AcSH (2 mL) and the solution was stirred (3 days). The solution was concentrated and subjected to flash chromatography (CH_2Cl_2/CH_3OH, 20:1) to afford **41** as a colourless oil (230 mg, 70%). [α] −3.4 ($c = 0.3$, CH_3OH). δ_H (500 MHz) 7.55–7.12 (35H, m, Ph), 5.87–5.75 (1H, m, CH_2=C*H*), 5.47 (1H, d, $J_{1'',2''}$ 3.9, H1″), 5.43 (1H, s, PhC*H*), 5.42 (1H, d, *J* 9.7, NH), 5.23–5.17 (2H, m, PhCH_2), 5.10 (1H, d, $J_{1''',2'''}$ 3.7, H1‴), 5.03–4.93 (6H, m, H3‴, H4‴, PhCH_2, CH=CH_2), 4.89 (1H, A of AB, *J* 10.6, PhCH_2), 4.74 (1H, A of AB, *J* 10.5, PhCH_2), 4.74 (1H, A of AB, *J* 11.8, PhCH_2), 4.70–4.57 (7H, m, H1′, H2‴, PhCH_2), 4.40–4.34 (2H, m, H5″, H6′), 4.35 (1H, d, $J_{1,2}$ 8.0, H1), 4.29 (1H, d, $J_{3',4'}$ 3.8, H4′), 4.25 (1H, dd, $J_{2'',3''}$ 10.1, $J_{1'',2''}$ 3.9, H2″), 4.21 (1H, dd, $J_{2',3'}$ 9.6, $J_{1',2'}$ 8.1, H2′), 4.12 (1H, dd, $J_{3,4}$ 9.1, $J_{4,5}$ 9.1, H4), 4.14–4.07 (1H, m, H5‴), 4.02–3.94 (2H, m, H6′, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.90 (1H, dd, $J_{6,6}$ 11.5, $J_{5,6}$ 3.7, H6), 3.86 (1H, dd, $J_{2'',3''}$ 10.1, $J_{3'',4''}$ 2.6, H3″), 3.84 (1H, dd, $J_{2',3'}$ 9.4, $J_{3',4'}$ 3.8, H3′), 3.71–3.64 (3H, m, H4″, H6, H6‴), 3.59 (1H, ddd, *J* 9.5, 6.8, 6.8, CH=CH$_2$(CH$_2$)$_5$CH_2O), 3.50 (1H, dd, $J_{2,3}$ 9.0, $J_{3,4}$ 9.1, H3), 3.49 (1H, dd, $J_{2,3}$ 9.0, $J_{1,2}$ 8.0, H2), 3.20–3.14 (2H, m, H5, H5′), 3.04 (1H, dd, $J_{6''',6'''}$ 11.5, $J_{5''',6'''}$ 3.6, H6‴), 2.09, 1.97, 1.81, 1.46 (12H, 4 × s, CH_3C=O), 2.10–2.01 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.74–1.66 (2H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.48–1.38 (6H, m, CH=CH$_2$(CH_2)$_5$CH$_2$O), 1.16 (3H, d, $J_{5'',6''}$ 6.6, H6″). δ_C (125 MHz) 170.4 (C=O), 170.3 (C=O), 170.1 (C=O), 170.0 (C=O), 139.4 (Ph), 139.0 (CH$_2$=*C*H), 138.6 (Ph), 138.52

(Ph), 138.50 (Ph), 138.4 (Ph), 138.3 (Ph), 137.7 (Ph), 129.1 (Ph), 129.0 (Ph), 128.42 (Ph), 128.36 (Ph), 128.32 (3C, Ph), 128.29 (Ph), 128.25 (Ph), 128.20 (Ph), 128.19 (Ph), 127.8 (Ph), 127.7 (Ph), 127.55 (Ph), 127.53 (Ph), 127.40 (2C, Ph), 127.36 (Ph), 127.3 (Ph), 126.4 (Ph), 126.3 (Ph), 114.3 (CH_2=CH), 103.8 (C1), 101.3, 100.8 (C1′, PhCH), 98.3 (C1″), 92.1 (C1‴), 83.0, 71.7 (C2, C3), 79.9, 77.2, 76.5, 75.8, 75.5, 75.5, 71.3, 70.6 (C2′, C2″, C3′, C3″, C4, C4′, C4″, C5), 76.2 (PhCH_2), 75.3 (PhCH_2), 74.7 (PhCH_2), 7.36 (PhCH_2), 73.4 (PhCH_2), 72.1 (PhCH_2), 70.1 (CH=$CH_2(CH_2)_5CH_2$O), 69.0, 67.9 (C6, C6′), 68.8, 67.7, 67.4 (C3‴, C4‴, C5‴), 66.7, 66.4 (C5′, C5″), 63.0 (C6‴), 46.5 (C2‴), 33.8 (CH=$CH_2(CH_2)_5CH_2$O), 29.8 (CH=$CH_2(CH_2)_5CH_2$O), 29.0 (CH=$CH_2(CH_2)_5CH_2$O), 28.9 (CH=$CH_2(CH_2)_5CH_2$O), 26.1 (CH=$CH_2(CH_2)_5CH_2$O), 22.6 (CH_3C=O), 20.69 (CH_3C=O), 20.66 (CH_3C=O), 20.6 (CH_3C=O), 16.7 (C6″). *m/z* (ESI) calc. $[C_{89}H_{105}NO_{23}]Na^+$: 1578.6970. Found: 1578.6986.

7-Octen-1-yl 4-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]-2,3,6-tri-O-benzyl-β-D-glucopyranoside ***42***

A solution of the acceptor **40** (320 mg, 0.261 mmol) in dry Et_2O (5 mL) was treated with 4-Å molecular sieves and the mixture stirred (rt, 1 h). The mixture was then cooled (−10°C), treated with TMSOTf (10 μL, 0.058 mmol); the trichloroacetimidate **28**[35] (700 mg, 1.02 mmol) in dry Et_2O (10 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 partially pure tetrasaccharide **42** (270 mg, 60%) as a colourless oil.

Acknowledgements

The present work was supported by the Natural Sciences and Engineering Research Council of Canada, the Canadian Institutes of Health Research, and the Alberta Ingenuity Centre for Carbohydrate Science.

References

[1] K. Landsteiner, *Zentralbl. Bakteriol.* **1900**, *27*, 357.
[2] N. L. Rose, M. M. Palcic, *J. Chem. Educ.* **2005**, *82*, 1846.
[3] W. M. Watkins, W. T. J. Morgan, *Nature* **1957**, *180*, 1038. doi:10.1038/1801038A0
[4] A. Blancher, W. W. Socha, in *Molecular Biology and Evolution of Blood Group and MHC Antigens in Primates* **1997**, pp. 30. (Springer-Verlag: Berlin)
[5] Y. M. Bhende, C. K. Deshpande, H. M. Bhatia, R. Sanger, R. R. Race, W. T. J. Morgan, W. M. Watkins, *Lancet* **1952**, *259*, 903.
[6] C. Race, D. Ziderman, W. M. Watkins, *Biochem. J.* **1968**, *107*, 733.
[7] H. Tuppy, W. L. Staudenbauer, *Nature* **1966**, *210*, 316. doi:10.1038/210316A0
[8] F. Yamamoto, H. Clausen, T. White, J. Marken, S. Hakomori, *Nature* **1990**, *345*, 229. doi:10.1038/345229A0
[9] F. Yamamoto, P. D. McNeill, S. Hakomori, *Glycobiology* **1995**, *5*, 51. doi:10.1093/GLYCOB/5.1.51
[10] F. Yamamoto, J. Marken, T. Tsuji, T. White, H. Clausen, S. Hakomori, *J. Biol. Chem.* **1990**, *265*, 1146.
[11] V. P. Rege, T. J. Painter, W. M. Watkins, W. T. J. Morgan, *Nature* **1963**, *200*, 532. doi:10.1038/200532A0
[12] T. J. Painter, V. P. Rege, W. T. J. Morgan, *Nature* **1963**, *199*, 569. doi:10.1038/199569A0
[13] J. A. Letts, N. L. Rose, Y. R. Fang, C. H. Barry, S. N. Borisova, N. O. L. Seto, M. M. Palcic, S. V. Evans, *J. Biol. Chem.* **2006**, *281*, 3625. doi:10.1074/JBC.M507620200
[14] A. H. Good, O. Yau, L. R. Lamontagne, R. Oriol, *Vox Sang.* **1992**, *62*, 180. doi:10.1111/J.1423-0410.1992.TB01195.X
[15] R. Lemieux, D. R. Bundle, D. A. Baker, *US Patent 4238473* **1980**.
[16] X. Qian, K. Sujino, A. Otter, M. M. Palcic, O. Hindsgaul, *J. Am. Chem. Soc.* **1999**, *121*, 12063. doi:10.1021/JA993004G
[17] N. O. L. Seto, C. A. Compston, A. Szpacenko, M. M. Palcic, *Carbohydr. Res.* **2000**, *324*, 161. doi:10.1016/S0008-6215(99)00297-9
[18] C. A. Compston, C. Condon, H. R. Hanna, M. Mazid, *Carbohydr. Res.* **1993**, *239*, 167. doi:10.1016/0008-6215(93)84212-O
[19] O. Hindsgaul, T. Norberg, J. Le Pendu, R. U. Lemieux, *Carbohydr. Res.* **1982**, *109*, 109. doi:10.1016/0008-6215(82)84034-2
[20] W. M. Macindoe, H. Iijima, Y. Nakahara, T. Ogawa, *Tetrahedron Lett.* **1994**, *35*, 1735. doi:10.1016/0040-4039(94)88332-7
[21] W. M. Macindoe, Y. Nakahara, T. Ogawa, *Carbohydr. Res.* **1995**, *271*, 207. doi:10.1016/0008-6215(95)00092-8
[22] E. A. Khatuntseva, Y. E. Tsvetkov, A. A. Grachev, N. E. Nifant'ev, *Russ. J. Org. Chem.* **2005**, *41*, 1814. doi:10.1007/S11178-006-0043-7
[23] I. M. Ryzhov, E. Y. Korchagina, K. A. Byrgazov, I. S. Popova, N. V. Bovin, in *24th International Carbohydrate Symposium*, *Oslo, Norway* **2008**, pp. A-P071.
[24] T. V. Zemlianukhina, N. V. Bovin, *Bioorg. Khim.* **1990**, *16*, 1096.
[25] X. Zeng, T. Murata, T. Usui, *J. Carbohydr. Chem.* **2003**, *22*, 309. doi:10.1081/CAR-120023474
[26] A. M. Scheppokat, M. Morita, J. Thiem, H. Bretting, *Tetrahedron: Asymm.* **2003**, *14*, 2381. doi:10.1016/S0957-4166(03)00521-4
[27] H. Bretting, F. Buck, G. Jacobs, S. Meinke, A. M. Scheppokat, J. Thiem, *Chem. Eur. J.* **2007**, *13*, 7144. doi:10.1002/CHEM.200700440
[28] M. M. Palcic, L. D. Heerze, M. Pierce, O. Hindsgaul, *Glycoconj. J.* **1988**, *5*, 49. doi:10.1007/BF01048331
[29] P.-H. Amvam-Zollo, P. Sinay, *Carbohydr. Res.* **1986**, *150*, 199. doi:10.1016/0008-6215(86)80016-7
[30] T. Yoshida, T. Chiba, T. Yokochi, K. Onozaki, T. Sugiyama, I. Nakashima, *Carbohydr. Res.* **2001**, *335*, 167. doi:10.1016/S0008-6215(01)00222-1
[31] S. Figueroa-Pérez, V. Vérez-Bencomo, *Carbohydr. Res.* **1999**, *317*, 29. doi:10.1016/S0008-6215(99)00022-1
[32] Y. Zhang, Q. Yao, C. Xia, X. Jiang, P. G. Wang, *ChemMedChem* **2006**, *1*, 1361. doi:10.1002/CMDC.200600135
[33] A. Toepfer, R. R. Schmidt, *J. Carbohydr. Chem.* **1993**, *12*, 809. doi:10.1080/07328309308020096
[34] G. Gerhard, R. R. Schmidt, *Liebigs Ann.* **1984**, 1826.
[35] B. Wegmann, R. R. Schmidt, *J. Carbohydr. Chem.* **1987**, *6*, 357. doi:10.1080/07328308708057926
[36] N. L. Pohl, L. L. Kiessling, *Tetrahedron Lett.* **1997**, *38*, 6985. doi:10.1016/S0040-4039(97)01670-5
[37] S. D. Debenham, J. Crossrow, E. J. Toone, *J. Org. Chem.* **1999**, *64*, 9153. doi:10.1021/JO991096M
[38] R. R. Schmidt, M. Josef, *Angew. Chem.* **1980**, *92*, 763. doi:10.1002/ANGE.19800920933