Enzymic glycosylation using 6-substituted glycosides as donor substrates: a novel route to functionalised disaccharides

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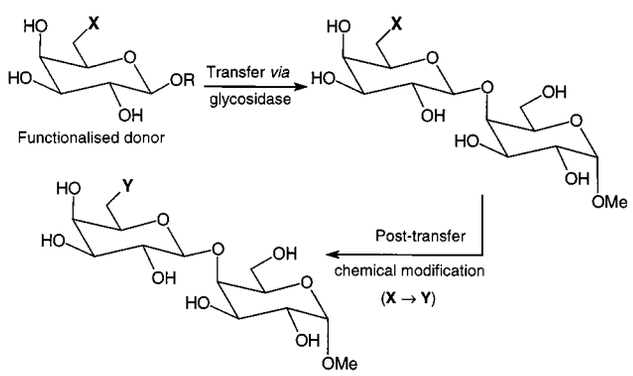
The ability of functionalised monosaccharides **1**–**10**, which include both natural and unnatural derivatives, to act as donors in glycosidase-mediated glycosylation processes has been evaluated. Using methyl α-D-galactopyranoside as the acceptor, the glycosidase-containing preparations snail acetone powder and barley extract catalysed formation of 1→4 and 1→6 disaccharides, respectively, with good to excellent levels of regioselectivity. With disaccharide formation achieved, the ability to harness the functionality resident within the donor component has been demonstrated by (i) selective reduction of the alkyne moiety of compound **19** and (ii) dihydroxylation of alkene **21**.

Introduction

In recent years a deeper understanding of the diverse roles of carbohydrates as information mediators in biochemical recognition has led to a powerful impetus for glycobiology research and created new opportunities in drug discovery.[1,2] With an increased drive towards bioactive and, in particular, novel and chemically modified oligosaccharides for structure–function relationship studies and *in vivo* evaluation, the need arises for the introduction of additional functionality to allow access to a range of structural analogues.[3–9]

Two main strategies may be envisaged for the synthesis of an oligosaccharide bearing a specific structural modification. Either the important functional moiety is incorporated at the end of the synthesis *via* regioselective manipulation or at a much earlier point in the form of a precursor monosaccharide. Both strategies involve considerable synthetic effort but the latter approach becomes more attractive once enzymes can be employed in critical glycosylation reactions leading to oligosaccharides. This way it is possible to take advantage of the high selectivity of enzymic catalysis and, by avoiding protection/deprotection, also reduce the number of steps in the overall synthetic protocol. The success of the enzymic approach, however, is highly dependent on the ability of the enzyme to accept "unnatural" substrates bearing an array of functionality. Studies with glycosyl transferases, for example, have shown that in certain cases these enzymes are able to accept modified donor substrates and produce disaccharides without compromising regio- and stereoselectivity.[10,11] Unfortunately, transferase-based methodology is constrained by both the availability of, and the requirement for regenerating, the sugar nucleotide donor.

In marked contrast, glycosidases as well as the requisite donor substrates are readily available and inexpensive. The aim of this work was to establish the feasibility of using glycosidases to achieve the transfer of chemically modified monosaccharide donors (incorporating synthetically useful functional groups) onto simple glycoside acceptors. This functionality, once incorporated as part of a disaccharide, should then be amenable to further and useful chemical manipulation. In this way, we define a versatile strategy for the synthesis of novel and unnatural disaccharides, a concept illustrated in Scheme 1.



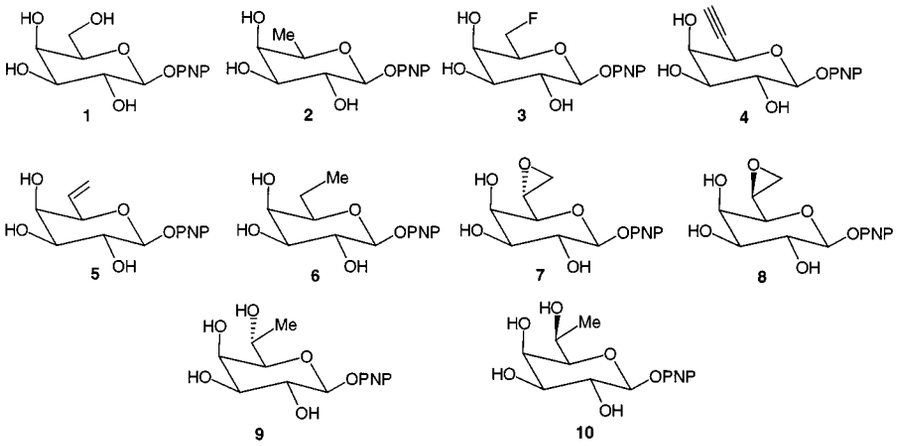
Scheme 1 Enzymic glycosylation and post-transfer modification of 6′-functionalised disaccharides.

Results and discussion

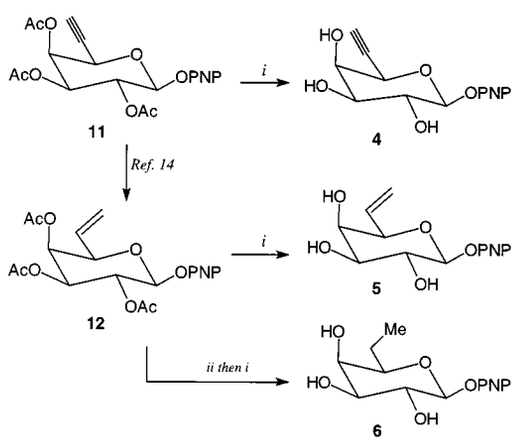
In order to establish the feasibility of enzymic transglycosylation using chemically modified glycoside donors, a series of 6-substituted *p*-nitrophenyl (PNP) β-D-galactopyranosides **1**–**10** were prepared. These sterically and electronically modified donors were then evaluated to establish their ability to be recognised (and hydrolysed) by crude enzyme preparations exhibiting β-galactosidase activity.

Synthesis of modified donors

The "parent" donor, *p*-nitrophenyl β-D-galactopyranoside **1** and the corresponding 6-deoxy analogue (*p*-nitrophenyl β-D-fucopyranoside) **2**[12] are commercially available. The novel 6-fluoro analogue **3** was obtained by direct fluorination of compound **1** using DAST,[13] a reaction that proceeded in 46% yield. To prepare the other targets in an efficient manner, the *O*-peracetylated alkyne **11**, was identified as a versatile and common intermediate. Thus, synthesis of compound **11**



(starting from di-*O*-isopropylidenegalactopyranose[14]) then afforded ready access to alkyne **4**, alkene **5** and the saturated derivative **6** (Scheme 2). Synthetic details for the diastereoisomeric epoxides **7** and **8** and the epimeric secondary alcohols **9** and **10** have already been described.[14,15] Problems were encountered in a number of cases when we attempted to carry out *O*-glycosylation with *p*-nitrophenol at a late stage. For this reason, the PNP glycoside, a group required for efficient enzyme-mediated hydrolysis and transfer, was introduced at an early point in our synthetic sequences. This offered the added advantage of streamlining the chemistry shown in Scheme 2.



Scheme 2 *Reagents and conditions*: i, MeOH, NaOMe; ii, NH_2NHTs, NaOAc, THF–water reflux.

Two crude enzyme preparations were selected for the purposes of this study: snail acetone powder (SNAP) and barley extract (sold by Sigma as "β-amylase"). These extracts exhibit a variety of glycosidase activities, including β-galactosidase activity, and in an initial assay both enzyme systems cleaved the PNP glycosides of donor substrates **1–10**. Furthermore, our preliminary studies indicated that these enzymes each displayed a different regioselectivity preference in transglycosylation reactions, an observation that was subsequently borne out in preparative-scale transfers.

Preparative-scale glycosidase-mediated transfers

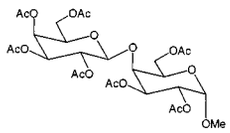
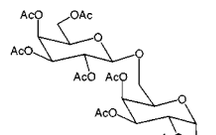
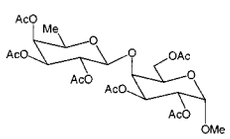
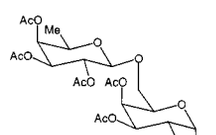
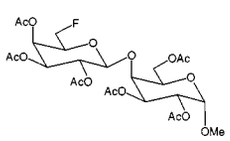
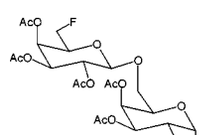
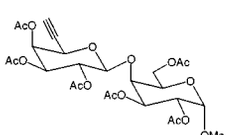
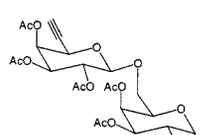
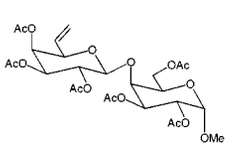
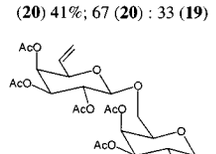
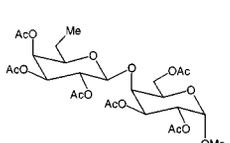
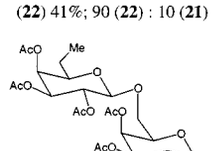
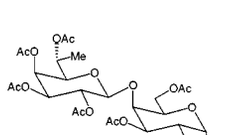
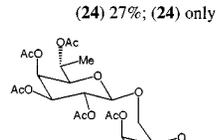
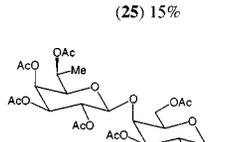
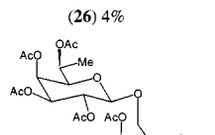
Having identified viable donors, a series of preparative-scale transfers were carried out using methyl α-D-galactopyranoside as acceptor. Transfer of *p*-nitrophenyl β-D-galactopyranoside **1** onto methyl α-D-galactopyranoside, followed by peracetylation, gave predominantly the (1→4)-linked disaccharide **13** (using SNAP) and the (1→6)-linked disaccharide **14** (using β-amylase) (Scheme 3). The procedure used to isolate disaccharides **13** and **14** involved an initial purification of the crude reaction mixture, followed by *O*-acetylation (to aid isolation and purification of isomeric products) and separation of the (1→6)- and (1→4)-disaccharide isomers by chromatography. A similar sequence was applied to the other donor substrates available, and the full range of disaccharides obtained, together with the degree of regioselectivity observed for each enzyme preparation, is shown in Table 1.

A higher degree of regioselectivity was observed using the 6-deoxy-β-D-galactopyranoside **2** which gave predominantly products **15** (using SNAP) and **16** (using β-amylase). The 6-fluoro-6-deoxy-β-D-galactopyranoside **3** underwent highly specific transfer leading to the fluorine-containing (1→4)- and (1→6)-linked disaccharides **17** and **18** using SNAP and β-amylase, respectively. Donor **3** was of interest given the importance of fluorinated derivatives as carbohydrate mimics and biochemical probes. While replacement of -OH by -F should not have a major steric effect, this change would be expected to alter the donor's hydrogen-bonding properties as compared with the parent β-D-galactoside. Nevertheless, the 6-fluoro derivative **3** was recognized and underwent efficient transfer using both enzyme systems.

The C_7 monosaccharide donors **4–6** were also found to be excellent substrates for transglycosylation reactions. Isolation and characterisation of the products showed that a similar pattern of regioselectivity was observed with these donors: the (1→4)-linked disaccharide with SNAP and the (1→6)-disaccharide with β-amylase. To our knowledge, these are the first examples of the use of 6-substituted glycosides as donors in glycosidase-catalysed transfer reactions. Two other interesting features emerge from this study. Both SNAP and the β-amylase preparation showed an improved level of regioselectivity with the "unnatural" donors **3–6** as compared with the β-D-galactose substrate **1**. Secondly, it is pertinent to note that compound **1** displayed a poorer degree of regioselectivity than did *p*-nitrophenyl β-D-fucopyranoside **2**. While the structural factors that determine these specificity differences remain unclear, our designation of enzyme specificity (*e.g.*, galactosidase *vs.* fucosidase) reflects a laboratory-based assay rather than Nature's intended function.

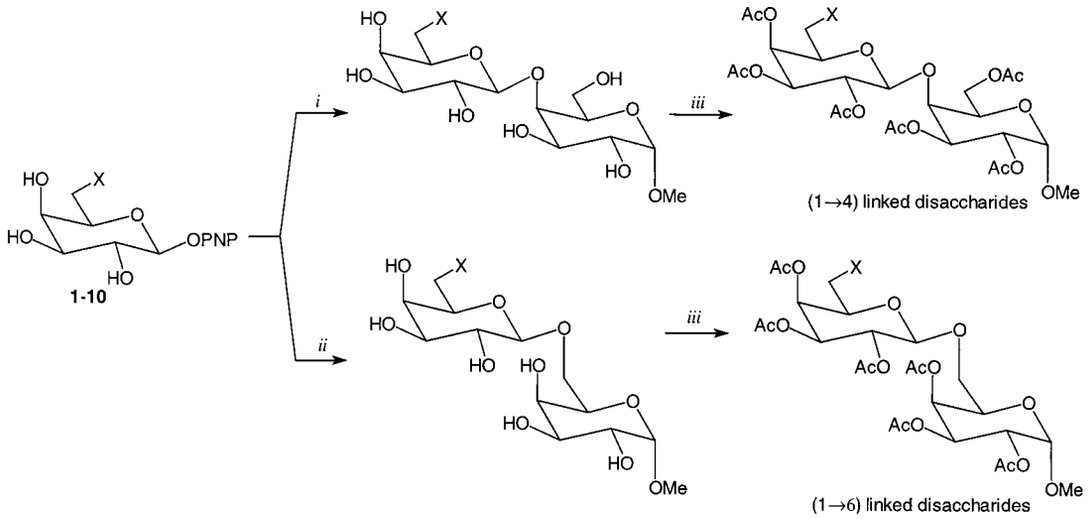
The ability of SNAP and β-amylase to accept a wide variety of substrates led us to investigate other donors, and in particular derivatives incorporating an additional stereocentre at C-6. These compounds, *p*-nitrophenyl 6,7-anhydro- D-*glycero*-β-D-*galacto*-heptopyranoside **7** and *p*-nitrophenyl 6,7-anhydro-L-*glycero*-β-D-*galacto*-heptopyranoside **8**, and *p*-nitrophenyl 7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside **9** and *p*-nitrophenyl 7-deoxy-L-*glycero*-β-D-*galacto*-heptopyranoside **10**, underwent transglycosylation reactions using methyl α-D-galactopyranoside as acceptor. Epoxides **7** and **8** proved to be good substrates for both enzyme preparations with single regioisomers (as judged by HPLC analysis) being produced in the case of substrate **7**. Further, the different retention times of the products obtained indicated that, in line with the other substrates, SNAP and β-amylase displayed different regio-

Table 1 Transfer experiments (using methyl α-D-galactopyranoside as the acceptor throughout)

Donor	Enzyme	Product (%)[a] (1→4) : (1→6)[b]	Donor	Enzyme	Product (%)[a] (1→6) : (1→4)[b]
(**1**)	SNAP	 (**13**) 21%; 67 (**13**) : 33 (**14**)	(**1**)	β-amylase	 (**14**) 25%; 67 (**14**) : 33 (**13**)
(**2**)	SNAP	 (**15**) 32%; 90 (**15**) : 10 (**16**)	(**2**)	β-amylase	 (**16**) 34%; 90 (**16**) : 10 (**15**)
(**3**)	SNAP	 (**17**) 33%; (**17**) only	(**3**)	β-amylase	 (**18**) 37%; (**18**) only
(**4**)	SNAP	 (**19**) 33%; (**19**) only	(**4**)	β-amylase	 (**20**) 41%; 67 (**20**) : 33 (**19**)
(**5**)	SNAP	 (**21**) 37%; 90 (**21**) : 10 (**22**)	(**5**)	β-amylase	 (**22**) 41%; 90 (**22**) : 10 (**21**)
(**6**)	SNAP	 (**23**) 25%; (**23**) only	(**6**)	β-amylase	 (**24**) 27%; (**24**) only
(**9**)[c]	SNAP	 (**25**) 15%			 (**26**) 4%
(**10**)[c]	SNAP	 (**27**) 15%			 (**28**) 9%

[a] The major product is shown with the yield (which was based on the donor) referring to the combined yield obtained for both isomers. [b] Ratio of disaccharide isomers as determined by ^{1}H NMR or HPLC. [c] In these cases, the donor substrate was not hydrolysed by β-amylase.

selectivites. However, while the epoxide moiety did not appear to cause enzyme inhibition, isolation of the disaccharides from these reaction mixtures did prove to be problematic. Significant decomposition of the products occurred on the carbon-Florisil column during work-up and, while transfer appeared to have taken place, we were unable to isolate and characterise the target disaccharides. In contrast, transfers using L- and D-*glycero* derivatives **9** and **10** were achieved with SNAP [leading to

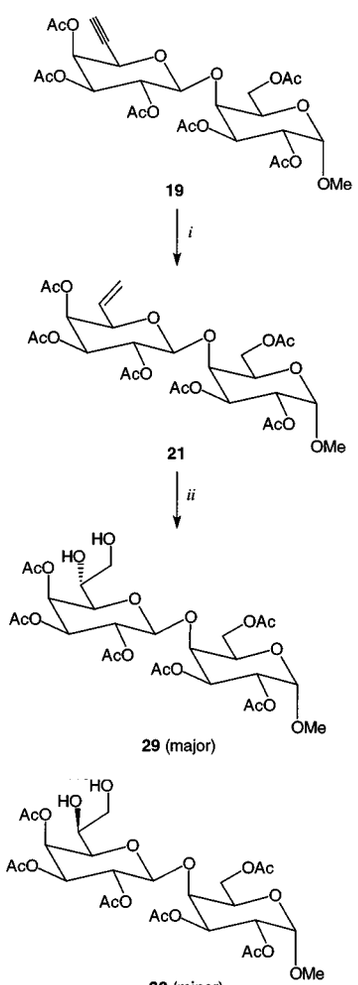


Scheme 3 *Reagents and conditions*: i, methyl α-D-galactopyranoside (8 equiv.), SNAP, citrate buffer (pH 5.2), 37 °C; ii, methyl α-D-galactopyranoside (8 equiv.), β-amylase, citrate buffer (pH 5.2), 37 °C; iii, Ac_2O, py. See Table 1 for product distributions and yields.

products **25/26** and **27/28** respectively] but not with β-amylase as biocatalyst. However, even in the successful transglycosylation reactions, a poorer degree of regioselectivity was observed compared with the other donors that were evaluated. Each of the compounds **7–10** bearing a stereocentre at C-6 have also been demonstrated to be substrates for a number of other glycosidase preparations, and studies on the diastereoselective hydrolysis of these derivatives have been reported elsewhere.[15]

Having established the feasibility of incorporating various functional groupings into disaccharides *via* enzymic transglycosylation, attention was turned to the options associated with post-transfer chemical modification. For this purpose, the two transformations shown in Scheme 4 have been examined. Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(6′,7′-dideoxy-2′,3′,4′-tri-*O*-acetyl-β-D-*galacto*-hept-6′-ynopyranosyl)-α-D-galactopyranoside **19** underwent selective alkyne reduction to give the alkenyl derivative **21** in 80% yield. The alkenyl disaccharide **21** was also used for further chemical elaboration, and osmium tetraoxide-mediated dihydroxylation afforded a 5:1 mixture of the diastereoisomeric 6′,7′-dihydroxy derivatives **29** and **30** in quantitative yield. We were only able to fully characterise the major isomer. However, comparison of the chemical shifts of the anomeric protons of the mixture with those reported by Brimacombe for similar compounds indicated that the major isomer **29** had the (6*R*) configuration and the minor isomer **30** had the (6*S*) configuration.[16] Interestingly, both ADmix-α and ADmix-β gave poorer isomer ratios of **29/30** than was observed using OsO_4.

In conclusion we have shown that glycosidases readily catalyse transfer reactions using a variety of 6-modified glycoside donors. Good yields and moderate to excellent regioselectivites were achieved in the synthesis. The feasibility of further modification of functionalised disaccharides obtained by this route was also established. In view of recent successes in the glycosidase-catalysed assembly of bioactive trisaccharides[17] and even more complex structures prepared by the combination of enzymic and chemical methods, the approach outlined here may allow direct access to functionalised structural analogues of complex oligosaccharides in just a few steps from a given modified glycoside donor.



Scheme 4 *Reagents and conditions*: i, Lindlar's catalyst, quinoline, H_2, EtOAc (80%); ii, OsO_4 in Bu′OH (10 mol%), NMO, acetone–water (**29**: 80% isolated yield).

Experimental

General

IR spectra (ν_{max}) were recorded on a Perkin-Elmer 1715 FTIR spectrometer for samples as a neat film on NaCl plates, or as a KBr disk. Mass spectra (*m*/*z*) (EI^+, CI^+ and FAB) were obtained using a Fisons/VG Analytical Autospec system (University of Bristol) and electrospray mass spectra were recorded on a VG Autospec X spectrometer (GlaxoWellcome Research and Development). NMR spectra were recorded at the field-strength setting and in the solvents indicated, using JEOL GX-270, Lambda-300 and GX-400 machines. *J*-Values

are given in Hz. Mps were recorded on a Reichert Kofler hot stage and are uncorrected, and combustion analyses were performed at the University of Bristol. Chromatography was performed on either Florisil (60–100 U.S. mesh), silica gel 60 (Merck 9385) or silica gel 60H. HPLC analysis was carried out using a Gilson 305/306 pump system equipped with a Gilson 234 autoinjector and a Sedex 55 evaporative light scattering detector. The samples were analysed with a Hypersil Hypercarb column (5 μ; 100 mm × 4.6 mm) using a linear gradient of acetonitrile–water at a flow rate of 0.75 cm^3 min^{-1}: from 100% to 90% water at 10 min, to 80% water at 15 min, to 40% water at 23 min, to 100% water at 27 min. All reagents and solvents were purified using standard methods. SNAP– and barley extract (β-amylase) were obtained from the Sigma Chemical Co. (UK). Carbohydrate products were visualised (TLC) using orcinol–$FeCl_3$ spray reagent. Petroleum spirit ('Pet SP') refers to the fraction with distillation range 40–60 °C.

Synthesis of PNP donor substrates

The synthesis of intermediates **11** and **12**, together with donors **7**, **8**, **9**, and **10** has been described.[14]

4′-Nitrophenyl 6-deoxy-6-fluoro-β-D-galactopyranoside 3. To a suspension of 4′-nitrophenyl β-D-galactopyranoside (1.00 g, 3.32 mmol) in anhydrous CH_2Cl_2 (40 cm^3) cooled to −40 °C was added DAST (2.68 g, 2.20 cm^3, 16.63 mmol). The cooling bath was removed and the reaction mixture was allowed to warm to 10 °C. (At 0 °C, the suspension dissolved and gave a yellow solution.) The reaction mixture was recooled to −40 °C, quenched with methanol (20 cm^3), allowed to warm up to rt and concentrated *in vacuo*. Purification by flash column chromatography [Pet SP–EtOAc 75:25 to 50:50, gradient] gave 4′-*nitrophenyl* 6-*deoxy*-6-*fluoro*-*β*-D-*galactopyranoside* **3** (0.46 g, 46%) as needles, mp 181 °C (from hexane–EtOAc) (Found: C, 47.2; H, 4.2; N, 4.5; F, 6.0. $C_{12}H_{14}FNO_7$ requires C, 47.5; H, 4.65; N, 4.62; F, 6.27%); δ_H[400 MHz; $(CD_3)_2CO$] 3.73 (1H, dd, $J_{3,2}$ 10 and $J_{3,4}$ 3, H-3), 3.89 (1H, dd, $J_{2,3}$ 10 and $J_{2,1}$ 8, H-2), 3.99 (1H, dd, $J_{4,3}$ 3 and $J_{4,5}$ 1, H-4), 4.19 (1H, dddd, $J_{5,F\text{-}6}$ 14, $J_{5,6B}$ 7, $J_{5,6A}$ 4 and $J_{5,4}$ 1, H-5), 4.56 (1H, ddd, $J_{6B,F\text{-}6}$ 46, $J_{6B,6A}$ 10, $J_{6B,5}$ 7, H-6B), 4.74 (1H, ddd, $J_{6A,F\text{-}6}$ 46, $J_{6A,6B}$ 10, $J_{6A,5}$ 4, H-6A), 5.20 (1H, d, $J_{1,2}$ 7, H-1), 7.29 (2H, AA′BB′, *J* 8) and 8.23 (2H, AA′BB′, *J* 8); ^{19}F NMR δ 230.1 (^{1}H coupled, ddd, $J_{F\text{-}6,H\text{-}6A}$ 46, $J_{F\text{-}6,H\text{-}6A}$ 46, $J_{5,F\text{-}6}$ 14).

4′-Nitrophenyl 6,7-dideoxy-β-D-*galacto*-hept-6-ynopyranoside 4. To a solution of 4′-nitrophenyl 2, 3, 4-tri-*O*-acetyl-6,7-dideoxy-β-D-*galacto*-hept-6-ynopyranoside[14] **11** (1.00 g, 2.38 mmol) in dry MeOH (50 cm^3) at 0 °C was added a $NaOCH_3$ solution in CH_3OH (30 cm^3; 0.87 mmol) *via* cannula. After 1 h at rt, Dowex H^+ resin was added in portions until pH 6, the resin was filtered off, and the filtrate was concentrated *in vacuo*. Purification by column chromatography (EtOAc) gave 4′-*nitrophenyl* 6,7-*dideoxy*-*β*-D-galacto-*hept*-6-*ynopyranoside* **4** (0.70 g, 90%) as needles, mp 196 °C (from EtOAc–CH_3OH) (TLC R_f 0.27 EtOAc) (Found: M + H^+, 296.0777. $C_{13}H_{14}NO_7$ requires *m*/*z*, 296.0770); δ_H(270 MHz; CD_3OD) 2.92 (1H, d, $J_{7,5}$ 2.5, H-7), 3.63 (1H, dd, $J_{3,2}$ 10 and $J_{3,4}$ 3, H-3), 3.83 (1H, dd, $J_{2,3}$ 10 and $J_{2,1}$ 7, H-2), 3.92 (1H, dd, $J_{4,3}$ 3 and $J_{4,5}$ 1, H-4), 4.67 (1H, dd, $J_{5,7}$ 2.5 and $J_{5,4}$ 1, H-5), 5.06 (1H, d, $J_{1,2}$ 7, H-1), 7.26 (2H, AA′BB′, *J* 8) and 8.24 (2H, AA′BB′, *J* 8); δ_C(75.5 MHz; CD_3OD) 68.0 (CH, C-5), 71.4 (CH, C-2), 72.5 (CH, C-4), 74.0 (CH, C-3), 76.0 (CH, C-7), 101.7 (CH, C-1), 117.7 (CH, C-2′), 126.6 (CH, C-3′), 144.7 (C, C-1′) and 163.7 (C, C-4′). The signal arising from the other acetylenic carbon (C-6) was not observed.

4′-Nitrophenyl 6,7-dideoxy-β-D-*galacto*-hept-6-enopyranoside 5. To a solution of 4′-nitrophenyl 2, 3, 4-tri-*O*-acetyl-6,7-dideoxy-β-D-*galacto*-hept-6-enopyranoside[14] **12** (1.00 g, 2.36 mmol) in dry MeOH (50 cm^3) at 0 °C was added a $NaOCH_3$ solution in CH_3OH (30 cm^3; 0.87 mmol) *via* cannula. After 1 h at rt, Dowex H^+ resin was added in portions until pH 6, the resin was filtered off, and the filtrate was concentrated *in vacuo*. Purification by column chromatography (EtOAc) gave 4′-*nitrophenyl* 6,7-*dideoxy*-*β*-D-*galacto*-*hept*-6-*enopyranoside* **5** (0.63 g, 89%) as needles, mp 173 °C (from EtOAc) (TLC R_f 0.20 EtOAc) (Found: C, 52.6; H, 5.2; N, 4.5. $C_{13}H_{15}NO_7$ requires C, 52.5; H, 5.09; N, 4.71%); δ_H(300 MHz; CD_3OD) 3.65 (1H, dd, $J_{3,2}$ 10 and $J_{3,4}$ 3, H-3), 3.84 (2H, m, H-2 and -4), 4.29 (1H, m), 5.07 (1H, d, $J_{1,2}$ 8, H-1), 5.23 (1H, ddd, $J_{7cis,6}$ 10.5, $J_{7cis,7trans}$ 1.5 and $J_{7cis,5}$ 1, H-7 *cis*), 5.35 (1H, ddd, $J_{7trans,6}$ 17, $J_{7trans,7cis}$ 1.5 and $J_{7trans,5}$ 1, H-7 *trans*), 5.97 (1H, ddd, $J_{6,7trans}$ 17, $J_{6,7cis}$ 10.5 and $J_{6,5}$ 5, H-6), 7.20 (2H, AA′BB′, *J* 8) and 8.19 (2H, AA′BB′, *J* 8); δ_C(75.5 MHz; CD_3OD) 71.7 (CH, C-2 or -4), 72.0 (CH, C-4 or -2), 74.6 (CH, C-3), 77.2 (CH, C-5), 101.9 (CH, C-1), 117.5 (CH_2, CH_2-7), 117.6 (CH, C-6), 126.6 (CH, C-2′), 135.6 (CH, C-3′), 143.8 (C, C-1′) and 163.9 (C, C-4′).

4′-Nitrophenyl 2, 3, 4-tri-*O*-acetyl-6,7-dideoxy-β-D-*galacto*-heptopyranoside. A solution of 4′-nitrophenyl 2, 3, 4-tri-*O*-acetyl-6,7-dideoxy-β-D-*galacto*-hept-6-enopyranoside[14] **12** (0.12 g, 0.28 mmol) and toluene-4-sulfonyl hydrazide (0.63 g, 3.40 mmol) in 1:1 THF–water (10 cm^3) was heated at reflux, and over a period of 3 h a solution of sodium acetate (0.47 g, 5.67 mmol) in water (2 cm^3) was added dropwise. The reaction mixture was cooled to rt and concentrated *in vacuo* (to a volume of 5 cm^3), poured into saturated aq. NH_4Cl (10 cm^3), and extracted with CH_2Cl_2 (3 × 10 cm^3). The combined organic extracts were washed with brine (20 cm^3), dried (Na_2SO_4), and concentrated *in vacuo*. Purification by flash column chromatography (Pet SP–EtOAc 100:0 to 70:30, gradient) gave 4′-*nitrophenyl* 2,3,4-*tri*-*O*-*acetyl*-6,7-*dideoxy*-*β*-D-*galacto*-*hepto*-*pyranoside* (0.10 g, 83%) as needles, mp 170 °C (from Pet SP–CH_2Cl_2) [TLC R_f 0.23 Pet SP–EtOAc (1:1)] (Found: C, 53.7; H, 5.6; N, 3.5. $C_{19}H_{23}NO_{10}$ requires C, 53.65; H, 5.45; N, 3.29%); δ_H(400 MHz; $CDCl_3$) 1.00 [3H, t, $J_{CH_3\text{-}7,6A}$ 7 and $J_{CH_3\text{-}7,6B}$ 7, CH_3-7], 1.56 [1H, m, H-6A], 1.74 [1H, m, H-6B], 3.74 (1H, ddd, $J_{5,6A}$ 8, $J_{5,6B}$ 6 and $J_{5,4}$ 1, H-5), 5.14 (1H, dd, $J_{3,2}$ 11, $J_{3,4}$ 4, H-3), 5.17 (1H, d, $J_{1,2}$ 7, H-1), 5.42 (1H, dd, $J_{4,3}$ 4 and $J_{4,5}$ 1, H-4), 5.52 (1H, dd, $J_{2,3}$ 11 and $J_{2,1}$ 7, H-2), 7.08 (2H, AA′BB′, *J* 8) and 8.22 (2H, AA′BB′, *J* 8); δ_C(75.5 MHz; $CDCl_3$) 10.1 (CH_3, CH_2CH_3), 20.6 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 23.4 (CH_2, CH_2CH_3), 68.6 (CH, C-2, -3 or -4), 68.7 (CH, C-3, -4 or -2), 71.1 (CH, C-4, -2 or -3), 75.5 (CH, C-5), 98.6 (CH, C-1), 116.4 (CH, C-2′), 125.8 (CH, C-3′), 143.0 (C, C-1′), 161.4 (C, C-4′), 169.4 (C, $OCOCH_3$), 170.1 (C, $OCOCH_3$) and 170.4 (C, $OCOCH_3$).

4′-Nitrophenyl 6,7-dideoxy-β-D-*galacto*-heptopyranoside 6. To a solution of 4′-nitrophenyl 2,3,4-tri-*O*-acetyl-6,7-dideoxy-β-D-*galacto*-heptopyranoside (1.00 g, 2.35 mmol) in dry MeOH (30 cm^3) at 0 °C was added a $NaOCH_3$ solution in CH_3OH (30 cm^3; 0.87 mmol) *via* cannula. After 2 h at rt, Dowex H^+ resin was added in portions until pH 6, the resin was filtered off, and the filtrate was concentrated *in vacuo*. Purification by column chromatography (EtOAc) gave 4′-*nitrophenyl* 6,7-*dideoxy*-*β*-D-*galacto*-*heptopyranoside* **6** (0.64 g, 90%) as needles, mp 180 °C (from EtOAc–CH_3OH) (TLC R_f 0.20 EtOAc) (Found: M + H^+, 300.1084. $C_{13}H_{18}NO_7$ requires *m*/*z*, 300.1083); δ_H(400 MHz; CD_3OD) 1.04 [3H, t, $J_{CH_3\text{-}7,6A}$ 8 and $J_{CH_3\text{-}7,6B}$ 8, CH_3-7], 1.68 [1H, m, $J_{6A,CH_3\text{-}7}$ 8, H-6A], 1.82 [1H, m, $J_{6B,CH_3\text{-}7}$ 8, H-6B], 3.64 (2H, m, H-3 and -5), 3.82 (1H, d, $J_{4,3}$ 3, H-4), 3.86 (1H, dd, $J_{2,1}$ 8 and $J_{2,3}$ 7, H-2), 5.05 (1H, d, $J_{1,2}$ 7, H-1), 7.24 (2H, AA′BB′, *J* 8, 2 × H-2′) and 8.25 (2H, AA′BB′, *J* 8, 2 × H-3′); δ_C(75.5 MHz; CD_3OD) 10.7 (CH_3, CH_2CH_3), 24.6 (CH_2, CH_2CH_3), 71.4 (CH, C-4), 72.0 (CH, C-2), 74.9 (CH, C-3 or -5), 78.0 (CH, C-5 or -3), 101.9 (CH, C-1), 117.5 (CH, C-2′), 126.6 (CH, C-3′), 143.7 (C, C-1′) and 163.9 (C, C-4′).

Enzymic transglycosylation

In a typical experiment the PNP donor glycoside (100 mg) and methyl α-D-galactopyranoside (8 equiv.) were dissolved in a minimum volume of citrate buffer (50 mM, pH 5.2) at 37 °C. SNAP (40 mg) or barley extract (β-amylase) (20 mg) was added and the mixture was incubated at 37 °C until the donor had been consumed (as determined by HPLC analysis). The reaction mixture was applied to a carbon–Florisil column (2.5 cm internal diameter chromatography column packed with 15 cm of 1:1 carbon–Florisil) and eluted with water (300 cm^3) followed by ethanol–water (50:50 v/v; 200 cm^3). The ethanol–water fraction was evaporated *in vacuo* and the residue was acetylated as follows.

To an ice-cold solution of the crude disaccharide (100 mg) in pyridine (5 cm^3) was added dropwise acetic anhydride (2.5 cm^3). The reaction mixture was warmed to rt and stirred for 18 h, then was cooled to 0 °C; water (2.5 cm^3) was added and the mixture was extracted with CH_2Cl_2 (3 × 10 cm^3). The extracts were washed successively with 1M hydrochloric acid (2 × 10 cm^3), water (2 × 10 cm^3) and saturated aq. $NaHCO_3$ (2 × 10 cm^3) and dried (Na_2SO_4). The solvents were removed *in vacuo* and the acetylated mixture was purified by silica chromatography [elution with $CHCl_3$ followed by $CHCl_3$–MeOH (100:1 v/v]. Regiochemical assignments were based on ^1H and ^{13}C NMR analysis (^1H–^1H and ^1H–^{13}C correlation spectroscopy) which served to identify, most importantly, H-6 *vs*. H-4 and the corresponding ^{13}C shifts, and this allowed assignment of the site of coupling. When key signals in ^1H NMR spectra (using $CDCl_3$) were overlapping or obscured, then full assignments were possible using C_6D_6 as solvent. This option proved valuable in a number of cases and, where appropriate, data from both solvent systems are presented. Comparison of data with structurally related disaccharides, such as methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-galactopyranosyl)-β-D-galactopyranoside[18] and methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside,[19] was also carried out.

The ratios of isomers and yields obtained are shown in Table 1 and characterisation data for the individual compounds, together with the weight of product isolated (to indicate the scale of the transfer experiment) are provided below. The ratio of isomers was determined by ^1H NMR but isomers, when present, were separated prior to full characterisation.

Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-galactopyranoside 13. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] gave *methyl* 2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′,6′-*tetra-O-acetyl-β*-D-*galactopyranosyl*)-*α*-D-*galactopyranoside* **13** (38 mg using SNAP) as a foam [TLC R_f 0.19 Pet SP–EtOAc (1:1)] (Found: MNH_4^+, 668.2413. $C_{27}H_{42}NO_{18}$ requires *m*/*z*, 668.2402); δ_H(400 MHz; C_6D_6) 1.58 (3H, s, $OCOCH_3$), 1.71 (3H, s, $OCOCH_3$), 1.73 (3H, s, $OCOCH_3$), 1.77 (3H, s, $OCOCH_3$), 1.80 (3H, s, $OCOCH_3$), 1.89 (3H, s, $OCOCH_3$), 2.17 (3H, s, $OCOCH_3$), 3.05 (3H, s, OCH_3), 3.31 (1H, br t, $J_{5',6A'}$ 7 and $J_{5',6B'}$ 7, H-5′), 3.91 (1H, br dd, $J_{5,6A}$ 7 and $J_{5,6B}$ 4, H-5), 4.01 (1H, br s, H-4), 4.17 (1H, dd, $J_{6A',6B'}$ 11.5 and $J_{6A',5'}$ 7, H-6A′), 4.24 (1H, dd, $J_{6B',6A'}$ 11.5 and $J_{6B',5'}$ 7, H-6B′), 4.39 (1H, dd, $J_{6A,6B}$ 14 and $J_{6A,5}$ 7, H-6A), 4.41 (1H, d, $J_{1',2'}$ 7, H-1′), 4.59 (1H, dd, $J_{6B,6A}$ 14 and $J_{6B,5}$ 4, H-6B), 4.69 (1H, br d, $J_{1,2}$ 3, H-1), 5.24 (1H, dd, $J_{3',2'}$ 10.5 and $J_{3',4'}$ 3, H-3′), 5.54 (3H, m, H-2, -3 and -4′) and 5.73 (1H, dd, $J_{2',3'}$ 10.5 and $J_{2',1'}$ 7, H-2′); δ_C(75.5 MHz; C_6D_6) 19.9 (CH_3, $OCOCH_3$), 20.3 (CH_3, $OCOCH_3$), 20.4 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 54.8 (CH_3, OCH_3), 61.3 (CH_2, CH_2-6′), 64.4 (CH_2, CH_2-6), 67.2 (CH), 68.1 (CH, C-5′), 68.4 (CH), 69.2 (CH, C-2), 70.7 (CH), 70.9 (CH, C-5), 71.3 (CH, C-3), 76.3 (CH, C-4′), 97.7 (CH, C-1), 102.6 (CH, C-1′), 169.2 (C, $OCOCH_3$), 169.5 (C, $OCOCH_3$), 169.6 (C, $OCOCH_3$), 169.8 (C, $OCOCH_3$), 169.9 (C, $OCOCH_3$), 169.9 (C, $OCOCH_3$) and 170.2 (C, $OCOCH_3$); δ_H(400 MHz; $CDCl_3$) 2.00 (3H, s, $OCOCH_3$), 2.05 (3H, s, $OCOCH_3$), 2.08 (6H, s, 2 × $OCOCH_3$), 2.11 (3H, s, $OCOCH_3$), 2.11 (3H, s, $OCOCH_3$), 2.17 (3H, s, $OCOCH_3$), 3.39 (3H, s, OCH_3), 3.84 (1H, br t, $J_{5',6A'}$ 6.5 and $J_{5',6B'}$ 6.5, H-5′), 4.02 (1H, br dd, $J_{5,6B}$ 12 and $J_{5,6A}$ 8, H-5), 4.10 (2H, d, $J_{6',5'}$ 6.5, CH_2-6′), 4.19 (1H, dd, $J_{6A,5}$ 8 and $J_{6A,6B}$ 4.5, H-6A), 4.20 (1H, br d, $J_{4,3}$ 3, H-4), 4.34 (1H, dd, $J_{6B,5}$ 12 and $J_{6B,6A}$ 4.5, H-6B), 4.40 (1H, d, $J_{1',2'}$ 8, H-1′), 4.86 (1H, d, $J_{1,2}$ 3, H-1), 4.98 (1H, dd, $J_{3',2'}$ 10.5 and $J_{3',4'}$ 3, H-3′), 5.18 (1H, dd, $J_{2,3}$ 11 and $J_{2,1}$ 3, H-2), 5.20 (1H, dd, $J_{3,2}$ 11 and $J_{3,4}$ 3, H-3), 5.24 (1H, dd, $J_{2',3'}$ 10.5 and $J_{2',1'}$ 8, H-2′) and 5.37 (1H, br d, $J_{4',3'}$ 3, H-4′); δ_C(75.5 MHz; $CDCl_3$) 20.6 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 20.9 (CH_3, $OCOCH_3$), 55.2 (CH_3, OCH_3), 61.4 (CH_2, CH_2-6), 63.8 (CH_2, CH_2-6′), 66.8 (CH, C-4), 67.4 (CH, C-5′), 67.6 (CH, C-2′), 68.6 (CH, C-2), 70.1 (CH, C-3′), 70.6 (CH, C-3), 70.7 (CH, C-5), 75.1 (CH, C-4′), 97.1 (CH, C-1), 101.8 (CH, C-1′), 169.2 (C, $OCOCH_3$), 169.5 (C, $OCOCH_3$), 169.6 (C, $OCOCH_3$), 169.8 (C, $OCOCH_3$), 169.9 (C, $OCOCH_3$), 169.9 (C, $OCOCH_3$) and 170.2 (C, $OCOCH_3$).

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-galactopyranoside 14. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 65:35, gradient)] gave *methyl* 2, 3, 4-*tri-O-acetyl*-6-*O*-(2′,3′,4′,6′-*tetra-O-acetyl-β*-D-*galactopyranosyl*)-*α*-D-*galactopyranoside* **14** (40 mg using β-amylase) as a foam [TLC R_f 0.12 Pet SP–EtOAc (1:1)] (Found: MNH_4^+, 668.2377); δ_H(400 MHz; C_6D_6) 1.61 (3H, s, $OCOCH_3$), 1.67 (3H, s, $OCOCH_3$), 1.70 (3H, s, $OCOCH_3$), 1.71 (3H, s, $OCOCH_3$), 1.77 (3H, s, $OCOCH_3$), 1.79 (3H, s, $OCOCH_3$), 1.89 (3H, s, $OCOCH_3$), 3.20 (3H, s, OCH_3), 3.40 (1H, br t, $J_{5',6A'}$ and $J_{5',6B'}$ 7, H-5′), 3.81 (2H, d, $J_{6,5}$ 6, CH_2-6), 4.05 [1H, br t, $J_{5,CH_2\text{-}6}$ 6, H-5], 4.13 (1H, dd, $J_{6A',6B'}$ 11 and $J_{6A',5'}$ 7, H-6A′), 4.19 (1H, dd, $J_{6B',6A'}$ 11 and $J_{6B',5'}$ 7, H-6B′), 4.28 (1H, d, $J_{1',2'}$, 8, H-1′), 5.17 (1H, d, $J_{1,2}$ 3.5, H-1), 5.18 (1H, dd, $J_{3',2'}$ 10 and $J_{3',4'}$ 3.5, H-3′), 5.51 (1H, br d, *J* 2.5, H-4′), 5.57 (1H, dd, $J_{2,3}$ 11 and $J_{2,1}$ 3.5, H-2), 5.60 (1H, br d, *J* 2.5, H-4), 5.66 (1H, dd, $J_{2',3'}$ 10 and $J_{2',1'}$ H-2′) and 5.75 (1H, dd, $J_{3,2}$ 11 and $J_{3,4}$ 3.5 H-3); δ_C(75.5 MHz; C_6D_6) 20.1 (CH_3, $OCOCH_3$), 20.3 (CH_3, $OCOCH_3$), 20.3 (CH_3, $OCOCH_3$), 20.4 (CH_3, $OCOCH_3$), 20.5 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 55.4 (CH_3, OCH_3), 61.5 (CH_2, CH_2-6′), 67.5 (CH, CH-4′), 67.8 (CH), 67.9 (CH_2, C-6), 68.5 (CH, C-3), 69.1 (CH), 69.2 (CH), 69.3 (CH), 71.2 (CH, C-5′), 71.5 (CH), 97.8 (CH, C-1), 101.6 (CH, C-1′), 169.2 (C, $OCOCH_3$), 169.7 (C, $OCOCH_3$), 169.8 (C, $OCOCH_3$), 170.0 (C, $OCOCH_3$) and 170.3 (C, $OCOCH_3$).

The synthesis and ^1H NMR data of (1→6)-disaccharides **14** have been reported previously.[20] Data presented above are available for purposes of comparison with the related, but novel (1→6)-linked disaccharides described below.

Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′-tri-*O*-acetyl-β-D-fucopyranosyl)-α-D-galactopyranoside 15. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 50:50, gradient)] gave *methyl* 2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′-*tri-O-acetyl-β*-D-*fucopyranosyl*)-*α*-D-*galactopyranoside* **15** (73 mg using SNAP) as a foam which was recrystallised as spars, mp 196.5 °C (from CH_2Cl_2– Pet SP) [TLC R_f 0.13 Pet SP–EtOAc (1:1)] (Found: MNa^+, 615.1904. $C_{25}H_{36}NaO_{16}$ requires *m*/*z*, 615.1901); δ_H(400 MHz; C_6D_6) 1.00 (3H, d, $J_{6',5'}$ 6.5, CH_3-6′), 1.61 (3H, s, $OCOCH_3$), 1.69 (3H, s, $OCOCH_3$), 1.70 (3H, s, $OCOCH_3$), 1.78 (3H, s,$OCOCH_3$), 1.89 (3H, s, $OCOCH_3$), 2.19 (3H, s, $OCOCH_3$), 2.93 [1H, qd, $J_{5',CH_3\text{-}6'}$ 6.5 and $J_{4',5'}$ 1, H-5′], 3.05 (3H, s, OCH_3), 3.92 (1H, br dd, $J_{5,6A}$ 7 and $J_{5,6B}$ 4, H-5), 4.01 (1H, br d, $J_{4,3}$ 3, H-4), 4.33 (1H, d, $J_{1',2'}$ 8, H-1′), 4.43 (1H, dd, $J_{6A,6B}$ 12 and $J_{6A,5}$ 7, H-6A), 4.59 (1H, dd, $J_{6B,6A}$ 12 and $J_{6B,5}$ 4, H-6B), 4.68 (1H, d, $J_{1,2}$ 3.5, H-1), 5.20 (1H, dd, $J_{3',2'}$ 11 and $J_{3',4'}$ 3, H-3′), 5.28 (1H, dd, $J_{4',3'}$ 3 and $J_{4',5'}$ 1, H-4′), 5.52

(1H, dd, $J_{3,2}$ 11 and $J_{3,4}$ 3, H-3), 5.56 (1H, dd, $J_{2,3}$ 11 and $J_{2,1}$ 3.5, H-2) and 5.70 (1H, dd, $J_{2',3'}$ 11 and $J_{2',1'}$ 8, H-2′); δ_C(75.5 MHz; C_6D_6) 16.0 (CH_3, CH_3-6′), 19.9 (CH_3, OCO*C*H$_3$), 20.3 (CH_3, OCO*C*H$_3$), 20.5 (CH_3, OCO*C*H$_3$), 20.6 (CH_3, OCO*C*H$_3$), 20.8 (CH_3, OCO*C*H$_3$), 54.8 (CH_3, OCH_3), 64.4 (CH_2, CH_2-6), 68.1 (CH, C-5), 68.4 (CH), 69.2 (CH, C-5′), 69.3 (CH), 70.2 (CH, C-2′), 70.9 (CH, C-4′), 71.7 (CH, C-3′), 75.8 (CH, C-4), 97.7 (CH, C-1), 102.5 (CH, C-1′), 169.0 (C, O*C*OCH$_3$), 169.8 (C, O*C*OCH$_3$), 170.0 (C, O*C*OCH$_3$) and 170.7 (C, O*C*OCH$_3$); δ_H(400 MHz; $CDCl_3$) 1.15 (3H, d, $J_{6',5'}$ 6.5, CH_3-6′), 1.99 (3H, s, OCOCH$_3$), 2.06 (3H, s, OCOCH$_3$), 2.07 (3H, s, OCOCH$_3$), 2.10 (3H, s, OCOCH$_3$), 2.10 (3H, s, OCOCH$_3$), 2.17 (3H, s, OCOCH$_3$), 3.39 (3H, s, OCH_3), 3.71 [1H, qd, J(5′,CH_3-6′) 6.5 and $J_{4',5'}$ 1, H-5′], 4.01 (1H, br dd, $J_{5,6A}$ 7 and $J_{5,6B}$ 5, H-5), 4.19 (1H, br s, H-4), 4.22 (1H, dd, $J_{6A,6B}$ 12 and $J_{6A,5}$ 7, H-6A), 4.34 (1H, d, $J_{1',2'}$ 8, H-1′), 4.35 (1H, dd, $J_{6B,6A}$ 12 and $J_{6B,5}$ 5, H-6B), 4.86 (1H, br d, $J_{1,2}$ 2.5, H-1), 4.97 (1H, dd, $J_{3',2'}$ 10.5 and $J_{3',4'}$ 3.5, H-3′) and 5.19 (4H, m, H-2, -2′, -3 and -4′); δ_C(75.5 MHz; $CDCl_3$) 15.9 (CH_3, CH_3-6′), 20.7 (CH_3, OCO*C*H$_3$), 20.7 (CH_3, OCO*C*H$_3$), 20.8 (CH_3, OCO*C*H$_3$), 20.9 (CH_3, OCO*C*H$_3$), 20.9 (CH_3, OCO*C*H$_3$), 55.2 (CH_3, OCH_3), 63.7 (CH_2, CH_2-6), 67.5 (CH, C-5), 67.7 (CH), 68.8 (CH), 69.1 (CH, C-5′), 70.0 (CH), 70.3 (CH), 71.2 (CH, C-3′), 74.6 (CH, C-4), 97.2 (CH, C-1), 101.7 (CH, C-1′), 169.5 (C, O*C*OCH$_3$), 169.8 (C, O*C*OCH$_3$), 170.2 (C, O*C*OCH$_3$), 170.4 (C, O*C*OCH$_3$), 170.6 (C, O*C*OCH$_3$) and 170.8 (C, O*C*OCH$_3$).

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2′,3′,4′-tri-*O*-acetyl-β-D-fucopyranosyl)-α-D-galactopyranoside 16. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] gave *methyl* 2,3,4-*tri-O-acetyl*-6-*O*-(2′,3′,4′-*tri-O-acetyl-β*-D-*fucopyranosyl*)-α-D-*galactopyranoside* **16** (77 mg using β-amylase) as a foam [TLC R_f 0.15 Pet SP–EtOAc (1:1)] (Found: MNH_4^+, 610.2359. $C_{25}H_{40}NO_{16}$ requires *m*/*z*, 610.2347); δ_H(400 MHz; C_6D_6) 0.97 (3H, d, $J_{6',5'}$ 6.5, CH_3-6′), 1.64 (3H, s, OCOCH$_3$), 1.65 (3H, s, OCOCH$_3$), 1.70 (3H, s, OCOCH$_3$), 1.79 (6H, s, 2 × OCOCH$_3$), 1.92 (3H, s, OCOCH$_3$), 3.09 [1H, qd, $J_{5',CH_3\text{-}6'}$ 6.5 and $J_{5',4'}$ 1, H-5′], 3.19 (3H, s, OCH_3), 3.81 (1H, dd, $J_{6A,6B}$ 10.5 and $J_{6A,5}$ 7, H-6A), 3.85 (1H, dd, $J_{6B,6A}$ 10.5 and $J_{6B,5}$ 5, H-6B), 4.03 (1H, br t, $J_{5,6A}$ 7 and $J_{5,6B}$ 5, H-5), 4.31 (1H, d, $J_{1',2'}$ 8, H-1′), 5.17 (1H, br d, $J_{1,2}$ 3, H-1), 5.18 (1H, dd, $J_{3',2'}$ 10.5 and $J_{3',4'}$ 3, H-3′), 5.27 (1H, dd, $J_{4',3'}$ 3 and $J_{5',4'}$ 1, H-4′), 5.56 (1H, dd, $J_{2,3}$ 11 and $J_{2,1}$ 3, H-2), 5.60 (1H, br d, $J_{4,3}$ 3, H-4), 5.64 (1H, dd, $J_{2',3'}$ 10.5 and $J_{2',1'}$ 8, H-2′) and 5.75 (1H, dd, $J_{3,2}$ 11 and $J_{3,4}$ 3, H-3); δ_C(75.5 MHz; C_6D_6) 16.1 (CH_3, CH_3-6′), 20.0 (CH_3, OCO*C*H$_3$), 20.1 (CH_3, OCO*C*H$_3$), 20.4 (CH_3, OCO*C*H$_3$), 20.4 (CH_3, OCO*C*H$_3$), 20.5 (CH_3, OCO*C*H$_3$), 20.6 (CH_3, OCO*C*H$_3$), 55.2 (CH_3, OCH_3), 67.4 (CH_2, CH_2-6), 67.8 (CH, C-5), 68.3 (CH, C-3), 69.0 (CH), 69.2 (CH), 69.2 (CH), 69.3 (CH, C-5′), 70.5 (CH, C-4′), 71.8 (CH, C-3′), 97.6 (CH, C-1), 101.2 (CH, C-1′), 169.4 (C, O*C*OCH$_3$), 169.7 (C, O*C*OCH$_3$), 170.0 (C, O*C*OCH$_3$), 170.1 (C, O*C*OCH$_3$), 170.3 (C, O*C*OCH$_3$) and 170.5 (C, O*C*OCH$_3$); δ_H(400 MHz; $CDCl_3$), 1.22 (3H, d, $J_{6',5'}$ 6, CH_3-6′), 1.97 (3H, s,OCOCH$_3$), 1.98 (3H, s, OCOCH$_3$), 2.04 (3H, s, OCOCH$_3$), 2.09 (3H, s, OCOCH$_3$), 2.14 (3H, s, OCOCH$_3$), 2.17 (3H, s, OCOCH$_3$), 3.40 (3H, s, OCH_3), 3.62 (1H, dd, $J_{6A,6B}$ 11 and $J_{6A,5}$ 7.5, H-6A), 3.80 [1H, br q, $J_{5',CH_3\text{-}6'}$ 6 and $J_{5',4'}$ 1, H-5′], 3.83 (1H, dd, $J_{6B,6A}$ 11 and $J_{6B,5}$ 4, H-6B), 4.18 (1H, ddd, $J_{5,6A}$ 7.5, $J_{5,6B}$ 4 and $J_{5,4}$ 1, H-5), 4.46 (1H, d, $J_{1',2'}$ 8, H-1′), 4.97 (1H, br d, $J_{1,2}$ 3.5, H-1), 4.99 (1H, dd, $J_{3',2'}$ 10.5 and $J_{3',4'}$ 3.5, H-3′), 5.13 (1H, dd, $J_{2,3}$ 11 and $J_{2,1}$ 3.5, H-2), 5.17 (1H, dd, $J_{2',3'}$ 10.5 and $J_{2',1'}$ 8, H-2′), 5.22 (1H, dd, $J_{4',3'}$ 3.5 and $J_{4',5'}$ 1, H-4′), 5.33 (1H, dd, $J_{3,2}$ 11 and $J_{3,4}$ 3.5, H-3) and 5.42 (1H, dd, $J_{4,3}$ and $J_{4,5}$ 1, H-4); δ_C(75.5 MHz; $CDCl_3$) 16.0 (CH_3, CH_3-6′), 20.7 (CH_3, OCO*C*H$_3$), 20.7 (CH_3, OCO*C*H$_3$), 20.8 (CH_3, OCO*C*H$_3$), 20.9 (CH_3, OCO*C*H$_3$), 55.4 (CH_3, OCH_3), 67.5 (CH, C-5), 67.6 (CH, C-3), 68.0 (CH_2, CH_2-6), 68.3 (CH), 68.7 (CH), 68.8 (CH, C-4), 69.3 (CH, C-5′), 70.1 (CH, C-4′), 71.2 (CH, C-3′), 97.0 (CH, C-1), 101.1 (CH, C-1′), 169.4 (C, O*C*OCH$_3$), 169.8 (C, O*C*OCH$_3$), 170.1 (C, O*C*OCH$_3$), 170.2 (C, O*C*OCH$_3$), 170.5 (C, O*C*OCH$_3$) and 170.7 (C, O*C*OCH$_3$).

Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′-tri-*O*-acetyl-6′-deoxy-6′-fluoro-β-D-galactopyranosyl)-α-D-galactopyranoside 17. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] gave *methyl* 2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′-*tri-O-acetyl*-6′-*deoxy*-6′-*fluoro*-β-D-*galactopyranosyl*)-α-D-*galactopyranoside* **17** (73 mg using SNAP) as a foam [TLC R_f 0.22 Pet SP–EtOAc (1:1)] (Found: MNH_4^+, 628.2242. $C_{25}H_{39}FNO_{16}$ requires *m*/*z*, 628.2253); δ_H(400 MHz; C_6D_6) 1.55 (3H, s, OCOCH$_3$), 1.71 (3H, s, OCOCH$_3$), 1.76 (3H, s, OCOCH$_3$), 1.77 (3H, s, OCOCH$_3$), 1.91 (3H, s, OCOCH$_3$), 2.18 (3H, s, OCOCH$_3$), 3.04 (3H, s, OCH_3), 3.23 (1H, m, H-5′), 3.90 (1H, m, H-5), 4.04 (1H, br s, H-4), 4.10 (1H, ddd, $J_{6A',F\text{-}6'}$ 46, $J_{6A',5'}$ 4, H-6A′), 4.35 (1H, ddd, $J_{6B'F\text{-}6'}$ 46, $J_{6B',6A'}$ 10 and $J_{6B',5'}$ 7, H-6B′), 4.40 (1H, dd, $J_{6A,6B}$ 11 and $J_{6A,5}$ 7, H-6A), 4.43 (1H, d, $J_{1',2'}$ 8, H-1′), 4.57 (1H, dd, $J_{6B,6A}$ 11 and $J_{6B,5}$ 5, H-6B), 4.67 (1H, br d, $J_{1,2}$ 2, H-1), 5.18 (1H, dd, $J_{3',2'}$ 11 and $J_{3',4'}$ 4, H-3′), 5.40 (1H, br d, $J_{3',4'}$ 4, H-4′), 5.54 (2H, m, H-2 and -3) and 5.69 (1H, dd, $J_{2',3'}$ 11 and $J_{2',1'}$ 8, H-2′); δ_C(75.5 MHz; C_6D_6) 19.7 (CH_3, OCO*C*H$_3$), 20.2 (CH_3, OCO*C*H$_3$), 20.4 (CH_3, OCO*C*H$_3$), 20.6 (CH_3, OCO*C*H$_3$), 20.6 (CH_3, OCO*C*H$_3$), 54.8 (CH_3, OCH_3), 64.0 (CH_2, CH_2-6), 67.3 (CH, d, $J_{C\text{-}4',F\text{-}6'}$ C-4′), 67.8 (CH, C-5), 68.4 (CH, C-2 or -3), 69.2 (CH, C-2′), 70.7 (CH, C-3 or -2), 71.1 (CH, C-3′), 71.9 (CH, d, $J_{C\text{-}5',F\text{-}6}$ 22, C-5′), 76.1 (CH, C-4), 81.5 (CH_2, d, $J_{C\text{-}6',F\text{-}6}$ 172, C-6′), 97.7 (CH, C-1) and 102.5 (CH, C-1′); δ_H(500 MHz; $CDCl_3$) 2.00 (3H, s, OCOCH$_3$), 2.05 (3H, s, OCOCH$_3$), 2.08 (3H, s, OCOCH$_3$), 2.11 (6H, s, 2 × OCOCH$_3$), 2.16 (3H, s, OCOCH$_3$), 3.39 (3H, s, OCH_3), 3.90 (1H, m, H-5′), 4.06 (1H, m, H-5), 4.19 (1H, dd, $J_{6A,6B}$ 11 and $J_{6A,5}$ 7, H-6A), 4.23 (1H, br d, $J_{4,3}$ 3, H-4), 4.34 (1H, dd, $J_{6B,6A}$ 11 and $J_{6B,5}$ 5, H-6B), 4.40 (1H, ddd, $J_{6A',F\text{-}6'}$ 46, $J_{6A',6B'}$ 10 and $J_{6A',5'}$ 4, H-6A′), 4.41 (1H, ddd, $J_{6B',F\text{-}6'}$ 46, $J_{6B',6A'}$ 10 and $J_{6B',5'}$ 7, H-6B′), 4.43 (1H, d, $J_{1',2'}$ 8, H-1′), 4.86 (1H, d, $J_{1,2}$ 3, H-1), 5.00 (1H, dd, $J_{3',2'}$ 10 and $J_{3',4'}$ 3, H-3′), 5.18 (1H, dd, $J_{2,3}$ 10 and $J_{2,1}$ 3, H-2), 5.24 (1H, dd, $J_{3,2}$ 10 and $J_{3,4}$ 3, H-3), 5.26 (1H, dd, $J_{2',3'}$ 10 and $J_{2',1'}$ 8, H-2′) and 5.39 (1H, br d, $J_{4',3'}$ 3, H-4′); δ_C(75.5 MHz; $CDCl_3$) 20.6 (CH_3, OCO*C*H$_3$), 20.6 (CH_3, OCO*C*H$_3$), 20.7 (CH_3, OCO*C*H$_3$), 20.8 (CH_3, OCO*C*H$_3$), 20.8 (CH_3, OCO*C*H$_3$), 55.3 (CH_3, OCH_3), 63.2 (CH_2, CH_2-6), 67.0 (CH, d, $J_{C\text{-}4',F\text{-}6'}$ 7, C-4′), 67.2 (CH, C-5), 67.7 (CH), 68.8 (CH), 70.1 (CH), 70.7 (CH, C-3′), 71.7 (CH, d, $J_{C\text{-}5',F\text{-}6'}$ 22, C-5′), 75.0 (CH, C-4), 81.05 (CH, d, $J_{C\text{-}6',F\text{-}6'}$ 172, C-6′), 97.2 (CH, C-1) and 101.6 (CH, C-1′).

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2′,3′,4′-tri-*O*-acetyl-6′-deoxy-6′-fluoro-β-D-galactopyranosyl)-α-D-galactopyranoside 18. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] gave *methyl* 2,3,4-*tri-O-acetyl*-6-*O*-(2′,3′,4′-*tri-O-acetyl*-6′-*deoxy*-6′-*fluoro*-β-D-*galactopyranosyl*)-α-D-*galactopyranoside* **18** (12 mg using β-amylase) as a foam [TLC R_f 0.19 Pet SP–EtOAc (1:1)] (Found: MNH_4^+, 628.2248); δ_H(400 MHz; C_6D_6) 1.60 (3H, s, OCOCH$_3$), 1.67 (3H, s, OCOCH$_3$), 1.71 (3H, s, OCOCH$_3$), 1.78 (3H, s, OCOCH$_3$), 1.80 (3H, s, OCOCH$_3$), 1.92 (3H, s, OCOCH$_3$), 3.20 (3H, s, OCH_3), 3.25 (1H, m, H-5′), 3.84 (2H, m, H_2-6), 4.03 (1H, m, H-5), 4.10 (1H, m, H-6A′), 4.15 (1H, m, H-6B′), 4.32 (1H, d, $J_{1',2'}$ 8, H-1′), 5.13 (1H, d, $J_{1,2}$ 3.5, H-1), 5.19 (1H, dd, $J_{3',2'}$ 10 and $J_{3',4'}$ 3, H-3′), 5.43 (1H, d, $J_{3',4'}$ 3, H-4′), 5.55–5.63 (2H, m, H-2 and -4), 5.65 (1H, dd, $J_{1',2'}$ 8 and $J_{2',3'}$ 10, H-2′) and 5.77 (1H, dd, $J_{2,3}$ 11 and $J_{3,4}$ 3, H-3); δ_C(75.5 MHz; C_6D_6) 20.0 (CH_3, OCO*C*H$_3$), 20.1 (CH_3, OCO*C*H$_3$), 20.3 (2 × CH_3, OCO*C*H$_3$), 20.4 (CH_3, OCO*C*H$_3$), 20.6 (CH_3, OCO*C*H$_3$), 55.1 (CH_3, OCH_3), 67.4 (CH_2, CH_2-6), 67.5 (CH), 68.2 (CH), 68.9 (CH), 68.95 (CH), 69.0 (CH), 70.7 (CH), 71.1 (CH), 71.8 (CH, d, $J_{C\text{-}5',F\text{-}6}$ 22, C-5′), 81.1 (CH_2, d, $J_{C\text{-}6',F\text{-}6}$ 172, C-6′), 97.6 (CH, C-1) and 102.4 (CH, C-1′); δ_H(400 MHz; $CDCl_3$) 2.01 (3H, s, OCOCH$_3$), 2.07 (3H, s, OCOCH$_3$), 2.08 (3H, s, OCOCH$_3$), 2.11 (6H, s, 2 × OCOCH$_3$), 2.23 (3H, s, OCOCH$_3$), 3.40 (3H, s,

OCH_3), 3.64 (1H, dd, $J_{6A,6B}$ 11 and $J_{6A,5}$ 7.5, H-6A), 3.85 (1H, dd, $J_{6A,6B}$ 11 and $J_{6B,5}$ 4, H-6B), 3.95 (1H, m, H-5′), 4.18 (1H, m, H-5), 4.35–4.55 (2H, m, H_2-6′), 4.52 (1H, d, $J_{1',2'}$ 8, H-1′), 4.97 (1H, d, $J_{1,2}$ 3.5, H-1), 5.01 (1H, dd, $J_{3',2'}$ 11 and $J_{3',4'}$ 3, H-3′), 5.12 (1H, dd, $J_{2,3}$ 11 and $J_{2,1}$ 3.5, H-2), 5.20 (1H, dd, $J_{2',3'}$ 11 and $J_{2',1'}$ 8, H-2′), 5.32 (1H, dd, $J_{3,2}$ 11 and $J_{3,4}$ 3.5, H-3) and 5.41–5.43 (2H, m, H-4′ and -4).

Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′-tri-*O*-acetyl-6′,7′-dideoxy-β-D-*galacto*-hept-6′-ynopyranosyl)-α-D-galactopyranoside 19. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] gave *methyl* 2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′-*tri-O-acetyl*-6′,7′-*dideoxy-β*-D-*galacto-hept*-6′-*ynopyranosyl*)-*α*-D-*galactopyranoside* **19** (88 mg using SNAP) as a foam [TLC R_f 0.16 Pet SP–EtOAc (1:1)] (Found: MNH_4^+, 620.2198. $C_{26}H_{38}NO_{16}$ requires *m/z*, 620.2191); ν_{max}(film)/cm^{-1} 3250, 2130, 1735 and 1370; δ_H(400 MHz; C_6D_6) 1.69 (3H, s, $OCOCH_3$), 1.70 (3H, s, $OCOCH_3$), 1.75 (3H, s, $OCOCH_3$), 1.76 (3H, s, $OCOCH_3$), 1.88 (3H, s, $OCOCH_3$), 1.98 (1H, d, $J_{5',7'}$ 1.5, H-7′), 2.17 (3H, s, $OCOCH_3$), 3.01 (3H, s, OCH_3), 3.54 (1H, br t, $J_{5',7'}$ 1.5 and $J_{5',4'}$ 1, H-5′), 3.93 (2H, m, H-4 and -5), 4.30 (1H, d, $J_{1',2'}$ 8, H-1′), 4.44 (1H, dd, $J_{6A,6B}$ 11.5 and $J_{6A,5}$ 7, H-6A), 4.61 (1H, dd, $J_{6B,6A}$ 11.5 and $J_{6B,5}$ 5, H-6B), 4.64 (1H, br d, $J_{1,2}$ 2.5, H-1), 5.13 (1H, dd, $J_{3',2'}$ 10.5 and $J_{3',4'}$ 3.5, H-3′), 5.52 (2H, m, H-2 and -3), 5.57 (1H, dd, $J_{4',3'}$ 3.5 and $J_{4',5'}$ 1, H-4′) and 5.69 (1H, dd, $J_{2',3'}$ 10.5 and $J_{2',1'}$ 8, H-2′); δ_C(75.5 MHz; C_6D_6) 20.0 (CH_3, $OCOCH_3$), 20.1 (CH_3, $OCOCH_3$), 20.4 (CH_3, $OCOCH_3$), 20.5 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 54.8 (CH_3, OCH_3), 63.6 (CH_2, CH_2-6), 65.4 (CH, C-5′), 68.5 (CH, C-5), 69.0 (CH, C-2 or -3), 69.6 (CH, C-2′), 70.0 (CH, C-4′), 71.2 (CH, C-3 or -2), 71.3 (CH, C-3′), 75.6 (CH, C-7′), 76.4 (CH, C-4), 98.2 (CH, C-1), 102.8 (CH, C-1′), 169.8 (C, $OCOCH_3$), 170.1 (C, $OCOCH_3$), 170.2 (C, $OCOCH_3$), 170.4 (C, $OCOCH_3$) and 170.8 (C, $OCOCH_3$) (C-6′ was not observed); δ_H(400 MHz; $CDCl_3$) 2.00 (3H, s, $OCOCH_3$), 2.03 (3H, s, $OCOCH_3$), 2.07 (3H, s, $OCOCH_3$), 2.10 (6H, s, 2 × $OCOCH_3$), 2.21 (3H, s, $OCOCH_3$), 2.42 (1H, d, $J_{7',5'}$ 2.5, H-7′), 3.38 (3H, s, OCH_3), 4.04 (1H, br dd, $J_{5,6A}$ 7 and $J_{5,6B}$ 6, H-5), 4.24 (1H, dd, $J_{6A,6B}$ 11.5 and $J_{6A,5}$ 7, H-6A), 4.25 (1H, m, H-4), 4.34 (1H, br dd, $J_{5',7'}$ 2.5 and $J_{5',4'}$ 1, H-5′), 4.36 (1H, dd, $J_{6B,6A}$ 11.5 and $J_{6B,5}$ 6, H-6B), 4.39 (1H, d, $J_{1',2'}$ 8, H-1′), 4.85 (1H, d, $J_{1,2}$ 3.5, H-1), 4.98 (1H, dd, $J_{3',2'}$ 10.5 and $J_{3',4'}$ 3.5, H-3′), 5.17 (1H, dd, $J_{2,3}$ 10.5 and $J_{2,1}$ 3.5, H-2), 5.23 (1H, dd, $J_{2',3'}$ 10.5 and $J_{2',1'}$ 8, H-2′), 5.24 (1H, dd, $J_{3,2}$ and $J_{3,4}$ 3.5, H-3) and 5.43 (1H, dd, $J_{4',3'}$ 3.5 and $J_{4',5'}$ 1, H-4′); δ_C(75.5 MHz; $CDCl_3$) 20.6 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 21.0 (CH_3, $OCOCH_3$), 55.3 (CH_3, OCH_3), 63.1 (CH_2, CH_2-6), 64.6 (CH, C-5′), 67.3 (CH, C-5), 67.7 (CH, C-2′), 68.4 (CH, C-2 or -3), 68.9 (CH, C-4′), 70.2 (CH, C-3 or -2), 74.8 (CH, C-3′), 75.1 (CH, C-4), 76.2 (CH, C-7′), 97.2 (CH, C-1), 101.6 (CH, C-1′), 169.4 (C, $OCOCH_3$), 169.8 (C, $OCOCH_3$), 170.0 (C, $OCOCH_3$), 170.2 (C, $OCOCH_3$), 170.4 (C, $OCOCH_3$) and 170.5 (C, $OCOCH_3$) (C-6′ was not observed).

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2′,3′,4′-tri-*O*-acetyl-6′,7′-dideoxy-β-D-*galacto*-hept-6′-ynopyranosyl)-α-D-galactopyranoside 20. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] gave *methyl* 2,3,4-*tri-O-acetyl*-6-*O*-(2′,3′,4′-*tri-O-acetyl*-6′,7′-*dideoxy-β*-D-*galacto-hept*-6′-*ynopyranosyl*)-*α*-D-*galactopyranoside* **20** (92 mg using β-amylase) as a foam [TLC R_f 0.26 Pet SP–EtOAc (1:1)] (Found: MNH_4^+, 620.2198); δ_H(400 MHz; C_6D_6) 1.66 (3H, s, $OCOCH_3$), 1.69 (3H, s, $OCOCH_3$), 1.74 (3H, s, $OCOCH_3$), 1.76 (3H, s, $OCOCH_3$), 1.79 (3H, s, $OCOCH_3$), 1.88 (3H, s, $OCOCH_3$), 1.90 (1H, br s, H-7′), 3.19 (3H, s, OCH_3), 3.70 (1H, br s, H-5′), 3.74 (1H, dd, $J_{6A,6B}$ 10 and $J_{6A,5}$ 8, H-6A), 3.77 (1H, dd, $J_{6B,6A}$ 10 and $J_{6B,5}$ 4.5, H-6B), 3.93 (1H, br dd, $J_{5,6A}$ 8 and $J_{5,6B}$ 4.5, H-5), 4.15 (1H, d, $J_{1',2'}$ 8, H-1′), 5.07 (1H, dd, $J_{3',2'}$ 10.5 and $J_{3',4'}$ 3.5, H-3′), 5.17 (1H, d, $J_{1,2}$ 3.5, H-1), 5.52 (1H, br dd, $J_{4,3}$ 3 and $J_{4,5}$ 1, H-4), 5.56 (1H, dd, $J_{2,3}$ 11 and $J_{2,1}$ 3.5, H-2), 5.58 (1H, br dd, $J_{4',3'}$ 3 and $J_{4',5'}$ 1, H-4′), 5.64 (1H, dd, $J_{2',1'}$ 8 and $J_{2',3'}$ 10.5, H-2′) and 5.75 (1H, dd, $J_{3,2}$ 11 and $J_{3,4}$ 3, H-3); δ_H(400 MHz; $CDCl_3$) 1.97 (3H, s, $OCOCH_3$), 1.99 (3H, s, $OCOCH_3$), 2.03 (3H, s, $OCOCH_3$), 2.09 (3H, s, $OCOCH_3$), 2.15 (3H, s, $OCOCH_3$), 2.20 (3H, s, $OCOCH_3$), 2.47 (1H, d, $J_{7',5'}$ 2, H-7′), 3.40 (1H, s, OCH_3), 3.65 (1H, dd, $J_{6A,6B}$ 10.5 and $J_{6A,5}$ 8, H-6A), 3.87 (1H, dd, $J_{6B,6A}$ 10.5 and $J_{6B,5}$ 3.5, H-6B), 4.18 (1H, ddd, $J_{5,6A}$ 8, $J_{5,6B}$ 3.5 and $J_{5,4}$ 1, H-5), 4.44 (1H, dd, $J_{5',7'}$ 2 and $J_{5',4'}$ 1.5, H-5′), 4.49 (1H, d, $J_{1',2'}$ 8, H-1′), 4.96 (1H, d, $J_{1,2}$ 3.5, H-1), 5.00 (1H, dd, $J_{3',2'}$ 10 and $J_{3',4'}$ 3.5, H-3′), 5.13 (1H, dd, $J_{2,3}$ 10.5 and $J_{2,1}$ 3.5, H-2), 5.19 (1H, dd, $J_{2',3'}$ 10 and $J_{2',1'}$ 8, H-2′), 5.32 (1H, dd, $J_{3,2}$ 10.5 and *J*3,4 3.5, H-3), 5.40 (1H, dd, $J_{4,3}$ 3.5 and $J_{4,5}$ 1, H-4) and 5.46 (1H, dd, $J_{4',3'}$ 3.5 and $J_{4',5'}$ 1.5, H-4′); δ_C(75.5 MHz; $CDCl_3$) 20.6 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.9 (CH_3, $OCOCH_3$), 55.4 (CH_3, OCH_3), 64.7 (CH, C-5′), 67.4 (CH, C-5), 67.6 (CH_2, CH_2-6), 68.0 (CH), 68.3 (CH), 68.3 (CH), 68.7 (CH), 69.1 (CH), 70.3 (CH), 75.3 (CH, C-7′), 97.0 (CH, C-1), 100.9 (CH, C-1′), 169.2 (C, $OCOCH_3$), 169.9 (C, $OCOCH_3$), 170.1 (C, $OCOCH_3$), 170.3 (C, $OCOCH_3$) and 170.5 (C, $OCOCH_3$) (C-6′ was not observed).

Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′-tri-*O*-acetyl-6′, 7′-dideoxy-β-D-*galacto*-hept-6′-enopyranosyl)-α-D-galactopyranoside 21. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] gave *methyl* 2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′-*tri-O-acetyl*-6′,7′-*dideoxy-β*-D-*galacto-hept*-6′-*enopyranosyl*)-*α*-D-*galactopyranoside* **21** (83 mg using SNAP) as a foam [TLC R_f 0.23 Pet SP–EtOAc (1:1)] (Found: MNH_4^+, 622.2326. $C_{26}H_{40}NO_{16}$ requires *m/z*, 622.2348); δ_H(400 MHz; C_6D_6) 1.62 (3H, s, $OCOCH_3$), 1.68 (3H, s, $OCOCH_3$), 1.70 (3H, s, $OCOCH_3$), 1.77 (3H, s,$OCOCH_3$), 1.91 (3H, s, $OCOCH_3$), 2.20 (3H, s, $OCOCH_3$), 3.06 (3H, s, OCH_3), 3.34 (1H, br m, H-5′), 3.86 (1H, br dd, $J_{5,6A}$ 7 and $J_{5,6B}$ 5, H-5), 3.93 (1H, br d, $J_{4,3}$ 1.5, H-4), 4.42 (1H, d, $J_{1',2'}$ 8, H-1′), 4.48 (1H, dd, $J_{6A,6B}$ 11 and $J_{6A,5}$ 7, H-6A), 4.52 (1H, dd, $J_{6B,6A}$ 11 and $J_{6B,5}$ 5, H-6B), 4.67 (1H, d, $J_{1,2}$ 3.5, H-1), 5.19 (1H, ddd, $J_{7'cis,6'}$ 10, $J_{7'cis,7'trans}$ 1 and $J_{7'cis,5'}$ 1, H-7′ *cis*), 5.27 (1H, dd, $J_{3',2'}$ 10.5 and $J_{3',4'}$ 3.5, H-3′), 5.47 (1H, br dd, $J_{4',3'}$ 3.5 and $J_{4',5'}$ 1, H-4′), 5.54 (3H, m, H-2, -3 and H-7′ *trans*), 5.58 (1H, ddd, $J_{6',7'trans}$ 17, $J_{6',7'cis}$ 10 and $J_{6',5'}$ 4, H-6′) and 5.76 (1H, dd, $J_{2',3'}$ 10.5 and $J_{2',1'}$ 8, H-2′); δ_C(75.5 MHz; C_6D_6) 20.0 (CH_3, $OCOCH_3$), 20.3 (CH_3, $OCOCH_3$), 20.4 (CH_3, $OCOCH_3$), 20.5 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 54.8 (CH_3, OCH_3), 64.5 (CH_2, CH_2-6), 68.0 (CH, C-5), 68.4 (CH), 69.3 (CH), 69.4 (CH), 70.8 (CH), 71.5 (CH), 73.6 (CH, C-5′), 76.1 (CH, C-4), 97.6 (CH, C-1), 102.8 (CH, C-1′), 117.8 (CH_2, CH_2-7′), 132.4 (CH, C-6′), 169.5 (C, $OCOCH_3$), 169.7 (C, $OCOCH_3$), 169.8 (C, $OCOCH_3$), 170.0 (C, $OCOCH_3$), 170.2 (C, $OCOCH_3$) and 170.4 (C, $OCOCH_3$); δ_H(400 MHz; $CDCl_3$) 2.00 (3H, s, $OCOCH_3$), 2.04 (3H, s, $OCOCH_3$), 2.08 (3H, s, $OCOCH_3$), 2.10 (3H, s, $OCOCH_3$), 2.10 (3H, s, $OCOCH_3$), 2.22 (3H, s, $OCOCH_3$), 3.39 (3H, s, OCH_3), 4.03 (1H, br t, $J_{5,6A}$ 6.5 and $J_{5,6B}$ 6.5, H-5), 4.10 (1H, br dd, $J_{5',6'}$ 5 and $J_{5',4'}$ 1, H-5′), 4.22 (1H, br s, H-4), 4.27 (1H, dd, $J_{6A,6B}$ 11.5 and $J_{6A,5}$ 7, H-6A), 4.35 (1H, dd, $J_{6B,6A}$ 11.5 and $J_{6B,5}$ 5, H-6B), 4.41 (1H, d, $J_{1',2'}$ 8, H-1′), 4.87 (1H, d, $J_{1,2}$ 2.5, H-1), 5.02 (1H, dd, $J_{3,2}$ 10.5 and $J_{3,4}$ 3.5, H-3), 5.23 (3H, m, H-2, -2′ and -3′), 5.24 (1H, dd, $J_{7'cis,6'}$ 11 and $J_{7'cis,7'trans}$ 1, H-7′ *cis*), 5.32 (1H, br d, $J_{4',3'}$ 2.5 and $J_{4',5'}$ 1, H-4′), 5.38 (1H, ddd, $J_{7'trans,6'}$ 17, $J_{7'trans,7'cis}$ 1 and $J_{7'trans,5'}$ 1, H-7′ *trans*) and 5.67 (1H, ddd, $J_{6',7'trans}$ 17, $J_{6',7'cis}$ 11 and $J_{6',5'}$ 5, H-6′).

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2′,3′,4′-tri-*O*-acetyl-6′,7′-dideoxy-β-D-*galacto*-hept-6′-enopyranosyl)-α-D-galactopyranoside 22. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 65:35, gradient)] gave *methyl* 2,3,4-*tri-O-acetyl*-6-*O*-(2′,3′,4′-*tri-O-acetyl*-6′,7′-*dideoxy-β*-D-*galacto-hept*-6′-*enopyranosyl*)-*α*-D-*galactopyranoside* **22** (92 mg using β-amylase) as a foam [TLC R_f 0.11 Pet SP–EtOAc (1:1)] (Found:

MNa^+, 627.1912. $C_{26}H_{36}NaO_{16}$ requires *m/z*, 627.1901); δ_H(400 MHz; C_6D_6) 1.64 (3H, s, $OCOCH_3$), 1.64 (3H, s, $OCOCH_3$), 1.70 (3H, s, $OCOCH_3$), 1.78 (3H, s, $OCOCH_3$), 1.79 (3H, s, $OCOCH_3$), 1.92 (3H, s, $OCOCH_3$), 3.20 (3H, s, OCH_3), 3.59 (1H, br dd, $J_{5',6'}$ 5 and $J_{5',7'}$ 1.5, H-5′), 3.81 (1H, dd, $J_{6A,6B}$ 10.5 and $J_{6A,5}$ 8, H-6A), 3.85 (1H, dd, $J_{6B,6A}$ 10.5 and $J_{6B,5}$ 5, H-6B), 4.00 (1H, ddd, $J_{5,6A}$ 8, $J_{5,6B}$ 5 and $J_{5,4}$ 1, H-5), 4.37 (1H, d, $J_{1',2'}$ 8, H-1′), 5.05 (1H, ddd, $J_{7'cis,6'}$ 10.5, $J_{7'cis,7'trans}$ 2 and $J_{7'cis,5'}$ 1.5, H-7′ *cis*), 5.17 (1H, d, $J_{1,2}$ 3.5, H-1), 5.23 (1H, dd, $J_{3',2'}$ 10.5 and $J_{3',4'}$ 3.5, H-3′), 5.29 (1H, ddd, $J_{7'trans,6'}$ 17, $J_{7'trans,7'cis}$ 2 and $J_{7'trans,5'}$ 1, H-7′ *trans*), 5.47 (1H, dd, $J_{4,3}$ 3.5 and $J_{4,5}$ 1, H-4), 5.56 (1H, dd, $J_{2,3}$ 10 and $J_{2,1}$ 3.5, H-2), 5.57 (1H, br d, $J_{4',3'}$ 3.5, H-4′), 5.60 (1H, ddd, $J_{6',7'trans}$ 17, $J_{6',7'cis}$ 10.5 and $J_{6',5'}$ 5, H-6′), 5.68 (1H, dd, $J_{2',3'}$ 10.5 and $J_{2',1'}$ 8, H-2′) and 5.74 (1H, dd, $J_{3,2}$ 10 and $J_{3,4}$ 3.5, H-3); δ_C(75.5 MHz; C_6D_6) 20.2 (CH_3, $OCOCH_3$), 20.2 (CH_3, $OCOCH_3$), 20.5 (CH_3, $OCOCH_3$), 20.5 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 55.3 (CH_3, OCH_3), 67.7 (CH_2, CH_2-6), 67.9 (CH, C-5), 68.4 (CH, C-3), 69.1 (CH, C-2), 69.3 (CH, C-2′ or -4′), 69.3 (CH, C-4′ or -2′), 69.9 (CH, C-4), 71.7 (CH, C-3′), 73.8 (CH, C-5′), 97.7 (CH, C-1), 101.4 (CH, C-1′), 117.7 (CH_2, CH_2-7′), 132.9 (CH, C-6′), 169.3 (C, $OCOCH_3$), 169.7 (C, $OCOCH_3$), 170.0 (C, $OCOCH_3$), 170.0 (C, $OCOCH_3$), 170.3 (C, $OCOCH_3$) and 170.3 (C, $OCOCH_3$).

Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′-tri-*O*-acetyl-6′,7′-dideoxy-β-D-*galacto*-heptopyranosyl)-α-D-galactopyranoside 23. Purification by flash column chromatography [Pet SP–EtOAc (100 : 0 to 70 : 30, gradient)] gave *methyl* 2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′-*tri-O-acetyl*-6′,7′-*dideoxy*-β-D-*galacto-heptopyranosyl*)-α-D-*galactopyranoside* **23** (56 mg using SNAP) as a foam [TLC R_f 0.21 Pet SP–EtOAc (1 : 1)] (Found: MNH_4^+, 624.2517. $C_{26}H_{42}NO_{16}$ requires *m/z*, 624.2504); δ_H(400 MHz; C_6D_6) 0.85 [3H, t, $J_{CH_3\text{-}7',CH_2\text{-}6'}$ 8, CH_3-7′], 1.29 [1H, m, $J_{6A',CH_3\text{-}7'}$ 8, H-6A′], 1.60 (1H, m, H-6B′), 1.61 (3H, s, $OCOCH_3$), 1.68 (3H, s, $OCOCH_3$), 1.71 (3H, s, $OCOCH_3$), 1.79 (3H, s, $OCOCH_3$), 1.90 (3H, s, $OCOCH_3$), 2.20 (3H, s, $OCOCH_3$), 2.77 (1H, br t, $J_{5'6A'}$ 6 and $J_{5',6B'}$ 6, H-5′), 3.06 (3H, s, OCH_3), 3.86 (1H, dd, $J_{5,6A}$ 7.5 and $J_{5,6B}$ 4, H-5), 4.09 (1H, br d, $J_{4,3}$ 3, H-4), 4.40 (1H, d, $J_{1',2'}$ 8, H-1′), 4.47 (1H, dd, $J_{6A,6B}$ 12 and $J_{6A,5}$ 8, H-6A), 4.59 (1H, dd, $J_{6B,6A}$ 12 and $J_{6B,5}$ 4, H-6B), 4.70 (1H, d, $J_{1,2}$ 3.5, H-1), 5.24 (1H, dd, $J_{3',2'}$ 10.5 and $J_{3',4'}$ 3, H-3′), 5.39 (1H, br d, $J_{4',3'}$ 3, H-4′), 5.52 (1H, dd, $J_{3,2}$ 10 and $J_{3,4}$ 3, H-3), 5.58 (1H, dd, $J_{2,3}$ 10 and $J_{2,1}$ 3.5, H-2) and 5.72 (1H, dd, $J_{2',3'}$ 10.5 and $J_{2',1'}$ 8, H-2′); δ_C(75.5 MHz; C_6D_6) 10.0 (CH_3, CH_2CH_3), 20.0 (CH_3, $OCOCH_3$), 20.3 (CH_3, $OCOCH_3$), 20.4 (CH_3, $OCOCH_3$), 20.5 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 23.7 (CH_2, CH_2CH_3), 54.8 (CH_3, OCH_3), 64.6 (CH_2, CH_2-6), 68.2 (CH, C-5), 68.4 (CH, C-2), 69.1 (CH, C-4′), 69.5 (CH, C-2′), 70.9 (CH, C-3), 71.7 (CH, C-3′), 74.7 (CH, C-5′), 75.9 (CH, C-4), 97.6 (CH, C-1), 102.7 (CH, C-1′), 169.4 (C, $OCOCH_3$), 169.6 (C, $OCOCH_3$), 169.9 (C, $OCOCH_3$), 169.9 (C, $OCOCH_3$), 170.1 (C, $OCOCH_3$) and 170.5 (C, $OCOCH_3$).

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2′,3′,4′-tri-*O*-acetyl-6′,7′-dideoxy-β-D-*galacto*-heptopyranosyl)-α-D-galactopyranoside 24. Purification by flash column chromatography [Pet SP–EtOAc (100 : 0 to 70 : 30, gradient)] gave *methyl* 2,3,4-*tri-O-acetyl*-6-*O*-(6′,7′-*dideoxy*-2′,3′,4′-*tri-O-acetyl*-β-D-*galacto-heptopyranosyl*)-α-D-*galactopyranoside* **24** (60 mg using β-amylase) as a foam [TLC R_f 0.21 Pet SP–EtOAc (1 : 1)] (Found: MNH_4^+, 624.2505); δ_H(400 MHz; C_6D_6) 0.93 [3H, t, $J_{CH_3\text{-}7',CH_2\text{-}6'}$ 7.5, CH_3-7′], 1.27 [1H, m, $J_{6A',CH_3\text{-}7'}$ 7.5, H-6A′], 1.54 (1H, m, $J_{6B',CH_3\text{-}7'}$ 7.5, H-6B′], 1.64 (3H, s, $OCOCH_3$), 1.66 (3H, s, $OCOCH_3$), 1.69 (3H, s, $OCOCH_3$), 1.78 (3H, s, $OCOCH_3$), 1.80 (3H, s, $OCOCH_3$), 1.92 (3H, s, $OCOCH_3$), 2.86 [1H, br t, $J_{5',CH_2\text{-}6'}$ 7.5, H-5′], 3.20 (3H, s, OCH_3), 3.85 (2H, m, CH_2-6), 4.05 [1H, br t, $J_{5,CH_2\text{-}6}$ 7, H-5], 4.32 (1H, d, $J_{1',2'}$ 8, H-1′), 5.18 (1H, d, $J_{1,2}$ 3.5, H-1), 5.20 (1H, dd, $J_{2',3'}$ 10.5 and $J_{3',4'}$ 3, H-3′), 5.40 (1H, d, $J_{4',3'}$ 3, H-4′), 5.58 (1H, dd, $J_{2,3}$ 11 and $J_{2,1}$ 3.5, H-2), 5.61 (1H, br d, $J_{4,3}$ 3, H-4), 5.66 (1H, dd, $J_{2',3'}$ 10.5 and $J_{2',1'}$ 8, H-2′) and 5.76 (1H, dd, $J_{3,2}$ 11 and $J_{3,4}$ 3, H-3); δ_C(75.5 MHz; C_6D_6) 9.9 (CH_3, CH_2CH_3), 20.2 (CH_3, $OCOCH_3$), 20.3 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 20.6 ($OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.9 (CH_3, $OCOCH_3$), 24.0 (CH_2, CH_2CH_3), 55.2 (CH_3, OCH_3), 67.5 (CH_2, CH_2-6), 68.0 (CH, C-5), 68.6 (CH), 69.2 (CH), 69.4 (CH), 69.4 (CH), 69.6 (CH), 72.1 (CH, C-3′), 74.9 (CH, C-5′), 97.9 (CH, C-1), 101.4 (CH, C-1′), 169.4 (C, $OCOCH_3$), 169.8 (C, $OCOCH_3$), 170.1 (C, $OCOCH_3$), 170.2 (C, $OCOCH_3$), 170.4 (C, $OCOCH_3$) and 170.5 (C, $OCOCH_3$); δ_H(400 MHz; $CDCl_3$) 0.93 [3H, t, $J_{CH_3\text{-}7',CH_2\text{-}6'}$ 7.5, CH_3-7′], 1.50 [1H, m, $J_{6A',CH_3\text{-}7'}$ 7.5, H-6A′], 1.66 [1H, m, $J_{6B',CH_3\text{-}7'}$ 7.5, H-6B′], 1.97 (3H, s, $OCOCH_3$), 1.98 (3H, s, $OCOCH_3$), 2.04 (3H, s, $OCOCH_3$), 2.09 (3H, s, $OCOCH_3$), 2.14 (3H, s, $OCOCH_3$), 2.15 (3H, s,$OCOCH_3$), 3.40 (3H, s, OCH_3), 3.51 [1H, br t, $J_{5',CH_2\text{-}6'}$ 7, H-5′], 3.63 (1H, dd, $J_{6A,6B}$ 11 and $J_{6A,5}$ 7, H-6A), 3.84 (1H, dd, $J_{6B,6A}$ 11 and $J_{6B,5}$ 3, H-6B), 4.19 (1H, br dd, $J_{5,6A}$ 7 and $J_{5,6B}$ 3, H-5), 4.46 (1H, d, $J_{1',2'}$ 8, H-1′), 4.96 (1H, br d, $J_{1,2}$ 4, H-1), 4.98 (1H, dd, $J_{3',2'}$ 11 and $J_{3',4'}$ 3, H-3′), 5.14 (1H, dd, $J_{2,3}$ 11 and $J_{2,1}$ 4, H-2), 5.17 (1H, dd, $J_{2',3'}$ 11 and $J_{2',1'}$ 8, H-2′), 5.31 (1H, br d, $J_{4',3'}$ 3, H-4′), 5.34 (1H, dd, $J_{3,2}$ 11 and $J_{3,4}$ 3, H-3) and 5.41 (1H, br d, $J_{4,3}$ 3, H-4); δ_C(75.5 MHz; $CDCl_3$) 9.9 (CH_3, CH_2CH_3), 20.6 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 23.3 (CH_2, CH_2CH_3), 55.3 (CH_3, OCH_3), 67.4 (CH_2, CH_2-6), 67.6 (CH, C-5), 67.7 (CH), 68.2 (CH), 68.6 (CH), 68.7 (CH), 68.9 (CH), 71.3 (CH, C-3′), 74.7 (CH, C-5′), 97.0 (CH, C-1), 101.1 (CH, C-1′), 169.4 (C, $OCOCH_3$), 169.9 (C, $OCOCH_3$), 170.1 (C, $OCOCH_3$), 170.3 (C, $OCOCH_3$), 170.4 (C, $OCOCH_3$) and 170.5 (C, $OCOCH_3$).

Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranosyl)-α-D-galactopyranoside 25. Purification by flash column chromatography [Pet SP–EtOAc (100 : 0 to 60 : 40, gradient)] gave *methyl* 2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′,6′-*tetra-O-acetyl*-7-*deoxy*-D-*glycero*-β-D-*galacto-heptopyranosyl*)-α-D-*galactopyranoside* **25** (23 mg using SNAP) as a foam [TLC R_f 0.14 Pet SP–EtOAc (1 : 1)] (Found: MNH_4^+, 682.2563. $C_{28}H_{44}NO_{18}$ requires *m/z*, 682.2558); δ_H(400 MHz; C_6D_6) 1.08 (3H, d, $J_{7',6'}$ 7, CH_3-7′), 1.52 (3H, s, $OCOCH_3$), 1.68 (3H, s, $OCOCH_3$), 1.70 (3H, s, $OCOCH_3$), 1.77 (3H, s, $OCOCH_3$), 1.89 (3H, s, $OCOCH_3$), 2.00 (3H, s, $OCOCH_3$), 2.18 (3H, s, $OCOCH_3$), 3.03 (3H, s, OCH_3), 3.13 (1H, d, $J_{5',6'}$ 8, H-5′), 4.00 (1H, m, H-5), 4.19 (1H, br s, H-4), 4.45 (1H, dd, $J_{6A,6B}$ 12 and $J_{6A,5}$ 8, H-6A), 4.53 (1H, d, $J_{1',2'}$ 8, H-1′), 4.63 (1H, dd, $J_{6B,6A}$ 12 and $J_{6B,5}$ 3, H-6B), 4.70 (1H, br s, H-1), 5.24 (1H, dd, $J_{3',2'}$ 10 and $J_{3',4'}$ 3, H-3′), 5.32 [1H, dq, $J_{6',5'}$ 8 and $J_{6',CH_3\text{-}7'}$ 7, H-6′], 5.58 (3H, m, H-2, -3 and -4′) and 5.73 (1H, dd, $J_{2',3'}$ 10 and $J_{2',1'}$ 8, H-2′); δ_C(75.5 MHz; C_6D_6) 15.9 (CH_3, CH_3-7′), 19.8 (CH_3, $OCOCH_3$), 20.2 (CH_3, $OCOCH_3$), 20.3 (CH_3, $OCOCH_3$), 20.4 (CH_3, $OCOCH_3$), 20.5 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 54.6 (CH_3, OCH_3), 64.7 (CH_2, CH_2-6), 67.4 (CH), 68.3 (CH), 68.9 (CH), 69.2 (CH), 70.8 (CH), 71.5 (CH), 74.8 (CH), 74.9 (CH), 75.8 (CH), 97.5 (CH, C-1), 102.3 (CH, C-1′), 169.6 (C, $OCOCH_3$), 169.6 (C, $OCOCH_3$), 169.7 (C, $OCOCH_3$), 170.1 (C, $OCOCH_3$), 170.2 (C, $OCOCH_3$), 170.2 (C, $OCOCH_3$) and 170.3 (C, $OCOCH_3$) δ_H(400 MHz; $CDCl_3$) 1.15 (3H, d, $J_{7',6'}$ 7, CH_3-7′), 1.98 (3H, s, $OCOCH_3$), 2.06 (3H, s, $OCOCH_3$), 2.07 (6H, s, $OCOCH_3$), 2.10 (6H, s,$OCOCH_3$), 2.18 (3H, s, $OCOCH_3$), 3.37 (3H, s, OCH_3), 3.57 (1H, dd, $J_{5',6'}$ 8 and $J_{5',4'}$ 1, H-5′), 4.03 (1H, ddd, $J_{5,5A}$ 8, $J_{5,6B}$ 3 and $J_{5,4}$ 1, H-5), 4.16 (1H, dd, $J_{6A,6B}$ 11 and $J_{6A,5}$ 8, H-6A), 4.17 (1H, br s, H-4), 4.30 (1H, dd, $J_{6B,6A}$ 11 and $J_{6B,5}$ 3, H-6B), 4.39 (1H, d, $J_{1',2'}$ 8, H-1′), 4.86 (1H, d, $J_{1,2}$ 3.5, H-1), 4.96 (1H, dd, $J_{3',2'}$ 10 and $J_{3',4'}$ 3.5, H-3′), 5.02 [1H, dq, $J_{6',5'}$ 8 and $J_{6',CH_3\text{-}7'}$ 7, H-6′], 5.20 (3H, m, H-2, -2′ and -3) and 5.41 (1H, dd, $J_{4',3'}$ 3.5 and $J_{4',5'}$ 1, H-4′).

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranosyl)-α-D-galactopyranoside 26. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] gave *methyl* 2,3,4-*tri-O-acetyl*-6-*O*-(2′,3′,4′,6′-*tetra-O-acetyl*-7-*deoxy*-D-*glycero*-β-D-*galacto-heptopyranosyl*)-α-D-*galactopyranoside* **26** (23 mg using SNAP) as a foam [TLC R_f 0.21 Pet SP–EtOAc (1:1)] (Found: MNH_4^+, 682.2566); δ_H(400 MHz; C_6D_6) 1.01 (3H, d, $J_{7',6'}$ 7, CH_3-7′), 1.55 (3H, s, $OCOCH_3$), 1.69 (3H, s, $OCOCH_3$), 1.70 (3H, s, $OCOCH_3$), 1.77 (6H, s, $OCOCH_3$), 1.87 (3H, s, $OCOCH_3$), 1.91 (3H, s, $OCOCH_3$), 3.17 (1H, dd, $J_{5',6'}$ 8 and $J_{5',4'}$ 1, H-5′), 3.25 (3H, s, OCH_3), 3.80 (2H, m, CH_2-6), 4.00 [1H, br t, $J_{5,CH_2\text{-}6}$ 6, H-5], 4.30 (1H, d, $J_{1',2'}$ 8, H-1′), 5.17 (1H, d, $J_{1,2}$ 3.5, H-1), 5.18 (1H, dd, $J_{3',2'}$ 10 and $J_{3',4'}$ 3, H-3′), 5.34 [1H, dq, $J_{6',5'}$ 8 and $J_{6',CH_3\text{-}7'}$ 7, H-6′], 5.54 (1H, dd, $J_{4',3'}$ 3 and $J_{4',5'}$ 1, H-4′), 5.56 (1H, br d, $J_{4,3}$ and $J_{4,5}$ 1, H-4), 5.57 (1H, dd, $J_{2,3}$ 10 and $J_{2,1}$ 3.5, H-2), 5.65 (1H, dd, $J_{2',3'}$ 10 and $J_{2',1'}$ 8, H-2′) and 5.72 (1H, dd, $J_{3,2}$ 10 and $J_{3,4}$ 3, H-3); δ_C(75.5 MHz; C_6D_6) 16.2 (CH_3, CH_3-7′), 20.1 (CH_3, $OCOCH_3$), 20.3 (CH_3, $OCOCH_3$), 20.5 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 21.0 (CH_3, $OCOCH_3$), 55.4 (CH_3, OCH_3), 67.8 (CH, C-4′), 68.1 (CH, C-3), 68.4 (CH, C-2′), 68.5 (CH_2, CH_2-6), 68.9 (CH, C-5), 69.3 (CH, C-6′), 69.4 (CH, C-2), 69.6 (CH, C-4), 71.9 (CH, C-3′), 75.7 (CH, C-5′), 97.7 (CH, C-1), 101.6 (CH, C-1′), 169.3 (C, $OCOCH_3$), 169.8 (C, $OCOCH_3$), 169.8 (C, $OCOCH_3$), 170.2 (C, $OCOCH_3$), 170.2 (C, $OCOCH_3$), 170.4 (C, $OCOCH_3$) and 170.5 (C, $OCOCH_3$); δ_H(400 MHz; $CDCl_3$) 1.16 (3H, d,$J_{7',6'}$ 7, CH_3-7′), 1.97 (3H, s, $OCOCH_3$), 1.97 (3H, s, $OCOCH_3$), 2.03 (3H, s, $OCOCH_3$), 2.06 (3H, s, $OCOCH_3$), 2.09 (3H, s, $OCOCH_3$), 2.13 (3H, s, $OCOCH_3$), 2.16 (3H, s, $OCOCH_3$), 3.39 (3H, s, OCH_3), 3.58 (1H, dd, $J_{5',6'}$ 8 and $J_{5',4'}$ 1, H-5′), 3.61 (1H, dd, $J_{6A,6B}$ 12 and $J_{6A,5}$ 3, H-6A), 3.77 (1H, dd, $J_{6B,6A}$ 12 and $J_{6B,5}$ 3.5, H-6B), 4.17 (1H, ddd, $J_{5,6B}$ 3.5, $J_{5,6A}$ 3 and $J_{5,4}$ 1, H-5), 4.46 (1H, d, $J_{1',2'}$ 8, H-1′), 4.96 (1H, d, $J_{1,2}$ 3, H-1), 4.98 (1H, dd, $J_{3,2}$ 10 and $J_{3,4}$ 3, H-3), 5.07 [1H, dq, $J_{6',5'}$ 8 and $J_{6',CH_3\text{-}7'}$ 7, H-6′], 5.14 (1H, dd, $J_{2,3}$ 10 and $J_{2,1}$ 3, H-2), 5.20 (1H, dd, $J_{2',3'}$ 10 and $J_{2',1'}$ 8, H-2′), 5.33 (1H, dd, $J_{3',2'}$ 10 and $J_{3',4'}$ 3, H-3′), 5.38 (1H, dd, $J_{4',3'}$ 3 and $J_{4',5'}$ 1, H-4′) and 5.41 (1H, dd, $J_{4,3}$ 3 and $J_{4,5}$ 1, H-4); δ_C(75.5 MHz; $CDCl_3$) 16.0 (CH_3, CH_3-7′), 20.5 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 20.6 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.7 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 20.9 (CH_3, $OCOCH_3$), 55.3 (CH_3, OCH_3), 66.9 (CH), 67.4 (CH), 67.6 (CH), 67.7 (CH), 68.2 (CH_2, CH_2-6), 68.5 (CH), 68.6 (CH), 68.8 (CH), 71.1 (CH), 75.1 (CH, C-5′), 96.9 (CH, C-1), 101.0 (CH, C-1′), 169.2 (C, $OCOCH_3$), 169.8 (C, $OCOCH_3$), 170.0 (C, $OCOCH_3$), 170.0 (C, $OCOCH_3$), 170.1 (C, $OCOCH_3$), 170.2 (C, $OCOCH_3$) and 170.5 (C, $OCOCH_3$).

Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-7-deoxy-L-*glycero*-β-D-*galacto*-heptopyranosyl)-α-D-galactopyranoside 27. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] gave *methyl* 2,3,6-*tri-O-acetyl*-4-*O*-(2′,3′,4′,6′-*tetra-O-acetyl*-7-*deoxy*-L-*glycero*-β-D-*galacto-heptopyranosyl*)-α-D-*galactopyranoside* **27** (19 mg using SNAP) as a foam [TLC R_f 0.19 Pet SP–EtOAc (1:1)] (Found: MNH_4^+, 682.2558); δ_H(300 MHz; $CDCl_3$) 1.32 (3H, d, $J_{7',6'}$ 7, CH_3-7′), 1.96 (3H, s, $OCOCH_3$), 1.98 (3H, s, $OCOCH_3$), 1.99 (3H, s, $OCOCH_3$), 2.00 (3H, s, $OCOCH_3$), 2.04 (3H, s, $OCOCH_3$), 2.07 (3H, s, $OCOCH_3$), 2.10 (3H, s, $OCOCH_3$), 3.39 (3H, s, OCH_3), 3.49 (1H, dd, $J_{5',6'}$ 8 and $J_{5',4'}$ 1, H-5′), 4.01 (1H, br dd, $J_{5,6A}$ 8 and $J_{5,6B}$ 3, H-5), 4.18 (2H, m, H-4 and -6B), 4.30 (1H, m, H-6A), 4.42 (1H, d, $J_{1',2'}$ 8, H-1′), 4.87 (1H, d, $J_{1,2}$ 3, H-1), 4.98 (2H, m, H-3′ and -6′), 5.20 (3H, m, H-2, -2′ and -3) and 5.42 (1H, dd, $J_{4',3'}$ 3.5 and $J_{4',5'}$ 1, H-4′); δ_C(75.5 MHz; $CDCl_3$) 17.6 (CH_3, CH_3-7′), 20.6 (CH_3, $OCOCH_3$), 20.8 (CH_3, $OCOCH_3$), 20.9 (CH_3, $OCOCH_3$), 21.0 (CH_3, $OCOCH_3$), 21.1 (CH_3, $OCOCH_3$), 21.8 (CH_3, $OCOCH_3$), 21.9 (CH_3, $OCOCH_3$), 55.2 (CH_3, OCH_3), 63.6 (CH_2, CH_2-6), 66.0 (CH), 66.5 (CH), 67.5 (CH, C-4′), 67.7 (CH), 68.7 (CH), 70.2 (CH, C-3′), 70.7 (CH), 75.0 (CH), 75.5 (CH, C-4), 97.1 (CH, C-1), 102.2 (CH, C-1′), 168.0 (C, $OCOCH_3$), 168.2 (C, $OCOCH_3$), 168.3 (C, $OCOCH_3$), 170.1 (C, $OCOCH_3$), 170.2 (C, $OCOCH_3$), 170.2 (C, $OCOCH_3$) and 170.4 (C, $OCOCH_3$).

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-7-deoxy-L-*glycero*-β-D-*galacto*-heptopyranosyl)-α-D-galactopyranoside 28. Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] gave *methyl* 2,3,4-*tri-O-acetyl*-6-*O*-(2′,3′,4′,6′-*tetra-O-acetyl*-7-*deoxy*-L-*glycero*-β-D-*galacto-heptopyranosyl*)-α-D-*galactopyranoside* **28** (37 mg using SNAP) as a foam [TLC R_f 0.24 Pet SP–EtOAc (1:1)] (Found: MNH_4^+, 682.2564); δ_H(300 MHz; $CDCl_3$) 1.16 (3H, d, $J_{7',6'}$ 7, CH_3-7′), 1.96 (3H, s, $OCOCH_3$), 1.97 (3H, s, $OCOCH_3$), 1.98 (3H, s, $OCOCH_3$), 1.98 (3H, s, $OCOCH_3$), 2.02 (3H, s, $OCOCH_3$), 2.03 (3H, s,$OCOCH_3$), 2.06 (3H, s, $OCOCH_3$), 3.36 (3H, s, OCH_3), 3.59 (1H, dd, $J_{5',6'}$ 8 and $J_{5',4'}$ 1, H-5′), 3.61 (1H, dd, $J_{6A,6B}$ 12 and $J_{6A,5}$ 3, H-6A), 3.78 (1H, dd, $J_{6B,6A}$ 12 and $J_{6B,5}$ 3.5, H-6B), 4.18 (1H, ddd, $J_{5,6B}$ 3.5, $J_{5,6A}$ 3 and $J_{5,4}$ 1, H-5), 4.46 (1H, d, $J_{1',2'}$ 8, H-1′), 4.60 (1H, d, $J_{1,2}$ 3, H-1), 4.80 (1H, dd, $J_{3,2}$ 10 and $J_{3,4}$ 3, H-3), 5.06 [1H, dq, $J_{6',5'}$ 8 and $J_{6',CH_3\text{-}7'}$ 7, H-6′], 5.13 (1H, dd, $J_{2,3}$ 10 and $J_{2,1}$ 3, H-2), 5.19 (1H, dd, $J_{2',3'}$ 10 and $J_{2',1'}$ 8, H-2′), 5.33 (1H, dd, $J_{3',2'}$ 10 and $J_{3',4'}$ 3, H-3′) and 5.40 (2H, m, H-4 and -4′).

Reduction of methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′-tri-*O*-acetyl-6′,7′-dideoxy-β-D-*galacto*-hept-6′-ynopyranosyl)-α-D-galactopyranoside 19

A solution of methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′-tri-*O*-acetyl-6′,7′-dideoxy-β-D-*galacto*-hept-6′-ynopyranosyl)-α-D-galactopyranoside **19** (10 mg, 0.062 mmol) in EtOAc (1 cm^3) containing quinoline (1 drop) and Lindlar's catalyst (3 mg) was stirred under hydrogen for 2 h. After this time, the solution was filtered through a Celite pad, the solids were washed with EtOAc, and the filtrate was concentrated *in vacuo*. The residue was purified by chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] to give alkene **21** (8 mg, 80%) which had identical spectroscopic data with those described above.

Dihydroxylation of methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′-tri-*O*-acetyl-6′,7′-dideoxy-β-D-*galacto*-hept-6′-enopyranosyl)-α-D-galactopyranoside 21

A solution of alkene **21** (10 mg, 0.016 mmol), OsO_4 (2.5% in Bu′OH, 0.16 cm^3, 0.0016 mmol, 0.1 equiv.) and NMO (4 mg, 0.033 mmol) in 8:1 acetone–water (0.5 cm^3) was stirred at rt for 2 h. After this time, dil. hydrochloric acid (2 M; 1 cm^3) was added and after 30 min the aqueous layer was removed and the organic phase was treated with saturated aq. sodium bisulfite (2 cm^3) and stirred for 1 h. The organic phase was separated, dried ($MgSO_4$), and concentrated to give a 5:1 mixture (as judged by ^1H NMR) of methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′-tri-*O*-acetyl-D-*glycero*-β-D-*galacto*-heptopyranosyl)-α-D-galactopyranoside **29** and methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′-tri-*O*-acetyl-L-*glycero*-β-D-*galacto*-heptopyranosyl)-α-D-galactopyranoside **30**.

Purification by flash column chromatography [Pet SP–EtOAc (100:0 to 60:40, gradient)] gave the major component **29** (8 mg, 80%) as a solid, δ_H(400 MHz; $CDCl_3$) 2.02 (3H, s, $OCOCH_3$), 2.07 (3H, s, $OCOCH_3$), 2.09 (3H, s, $OCOCH_3$), 2.10 (3H, s, $OCOCH_3$), 2.11 (3H, s, $OCOCH_3$), 2.21 (3H, s, $OCOCH_3$), 3.39 (3H, s, OCH_3), 3.58 (2H, br s, H_2-7′), 3.68 (1H, m, H-5), 3.85 (1H, m, H-6′), 4.02 (1H, dd, $J_{5',6'}$ 8 and $J_{5',4'}$ 1, H-5′), 4.15 (1H, br s, H-4), 4.24 (1H, dd, $J_{6A,6B}$ 11 and $J_{6A,5}$ 3, H-6A), 4.28 (1H, dd, $J_{6A,6B}$ 11 and $J_{6B,5}$ 3, H-6B), 4.45 (1H, d, $J_{1',2'}$ 8, H-1′), 4.86 (1H, d, $J_{1,2}$ 3.5, H-1), 5.04 (1H, dd, $J_{3',2'}$ 10 and $J_{3',4'}$ 3.5, H-3′), 5.16–5.28 (3H, m, H-2, -2′, -3) and 5.46 (1H, dd, $J_{4',3'}$ 3.5 and $J_{4',5'}$ 1, H-4′). We were unable to obtain

satisfactory high-resolution mass spectroscopic data for major component **29** although the corresponding deacetylated disaccharide, obtained by deprotection of compound **29** using MeONa and MeOH, was characterised by HRMS (Found: MNH_4^+, 404.1789. $C_{14}H_{30}NO_{12}$ requires *m*/*z*, 404.1768).

Partial ^{1}H NMR data for minor isomer **30**: δ_H (400 MHz; $CDCl_3$) 4.55 (1H, d, $J_{1',2'}$ 8, H-1′), 4.96 (1H, dd, $J_{3',2'}$ 10 and $J_{3',4'}$ 3.5, H-3′), 5.56 (1H, dd, $J_{4',3'}$ 3.5 and $J_{4',5'}$ 1, H-4′).

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