Carbohydrate Research, 251 (1994) 33–67
Elsevier Science B.V., Amsterdam

Recognition of synthetic *O*-methyl, epimeric, and amino analogues of the acceptor α-L-Fuc*p*-(1 → 2)-β-D-Gal*p*-OR by the blood-group A and B gene-specified glycosyltransferases †

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(Received February 5th, 1993; accepted May 19th, 1993)

ABSTRACT

The disaccharide α-L-Fuc*p*-(1 → 2)-β-D-Gal*p*-O-$(CH_2)_7CH_3$ (**6**) is an acceptor for the glycosyltransferases responsible for the biosynthesis of the A and B blood-group antigens. These enzymes respectively transfer GalNAc and Gal in an α linkage to OH-3 of the Gal residue in **6**. All eight possible *O*-methyl, epimeric, and amino analogues of **6** having modifications on the target Gal residue were chemically synthesized and kinetically evaluated both as substrates and inhibitors for the A and B glycosyltransferases. The results support earlier findings that both enzymes will tolerate replacement of the hydroxyl groups at the 3 and 6 positions of the Gal residue. Substitution at or replacement of OH-4 of the Gal residue, however abolishes recognition. The 6-*O*-methyl and 6-amino compounds are substrates for both enzymes while the 3-epimeric (**10**) and 3-amino (**12**) compounds are inhibitors. For the B transferase, **10** is a competitive inhibitor with a K_i of 7.8 μM. Attempts to determine a K_i for **12** with the B transferase were unsuccessful because of a complex mode of inhibition. Similarly, both **10** and **12** are potent inhibitors of the A transferase, but the inhibition constants could not be calculated because of a complex mode of inhibition, resembling that for the B transferase. With the A transferase, **12** had an estimated K_i in the 200 nM range.

INTRODUCTION

The A and B blood-group antigens, respectively the trisaccharides α-D-Gal*p*-NAc-(1 → 3)-[α-L-Fuc*p*-(1 → 2)]-β-D-Gal*p*-OR (**3**) and α-D-Gal*p*-(1 → 3)-[α-L-Fuc*p*-(1 → 2)-β-D-Gal*p*-(1 → 4)-OR (**5**), (where R is a glycoprotein or glycolipid) are widely occurring oligosaccharide structures. These carbohydrate antigens are present not only on the surfaces of red blood cells but also on cells from other tissues and in soluble form in the cytoplasm[1]. The biosynthetic formation of these antigens is shown in Fig. 1 and involves the transfer of either *N*-acetylgalactosa-

† We dedicate this paper to Professor Clinton E. Ballou.
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SSDI 0008-6215(93)E0291-8

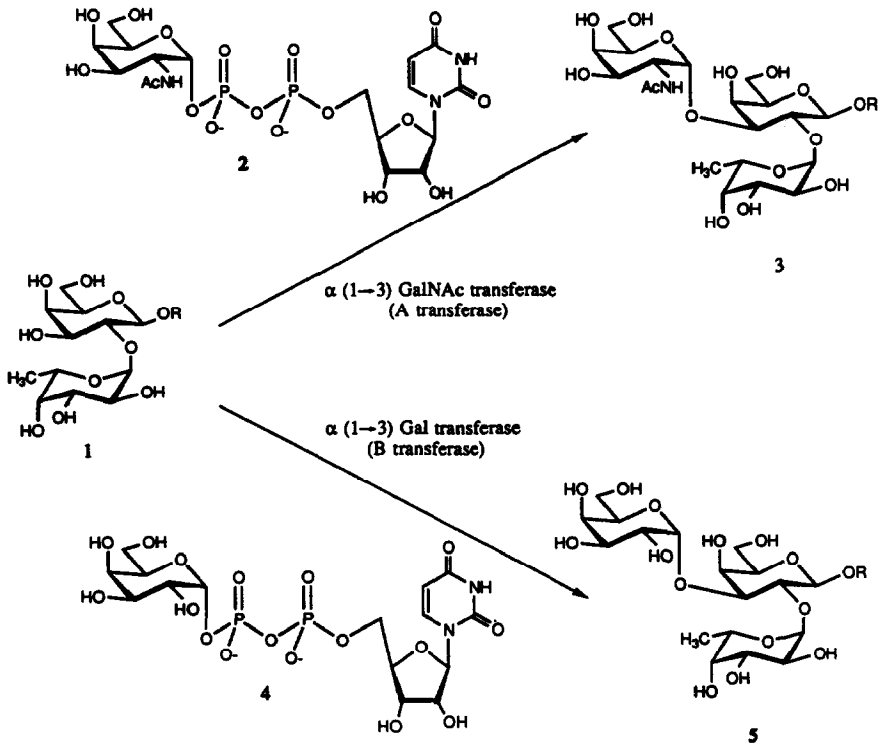


Fig. 1. Biosynthesis of the A (3) and B (5) blood-group antigens from the O(H) antigen (1).

mine or galactose from their corresponding UDP derivatives (2 and 4) to the galactosyl 3 hydroxyl group of the O-disaccharide antigen 1. Two enzymes are responsible for these reactions, namely an $\alpha(1 \rightarrow 3)$ *N*-acetylgalactosaminyl transferase (A transferase, EC 2.4.1.40) and an $\alpha(1 \rightarrow 3)$ galactosyltransferase (B transferase, EC 2.4.1.37). The amino acid sequences of these enzymes are known to differ at only four residues[2] and both have recently been cloned[2–4].

As part of our continuing studies towards developing specific glycosyltransferase inhibitors[5–9], we chose to investigate these enzymes because of the ubiquitous nature of the product carbohydrate antigens as well as the publication of reports that levels of a similar $\alpha(1 \rightarrow 3)$ Gal-transferase are elevated in patients with Ehrlich carcinoma[10] and in mouse teratocarcinoma[11]. It is believed that selective glycosyltransferase inhibitors will serve as useful tools in elucidating cell-surface oligosaccharide functions and may also be useful as potential antitumor drugs[12,13].

In order to explain the observed retention of configuration at the anomeric center during glycosyl transfer by these enzymes (the α sugar nucleotide yields an α-glycosidic linkage), we proposed[14] that the salient feature of the transfer mechanism is a two-step double-displacement (Fig. 2). The first step is the displacement

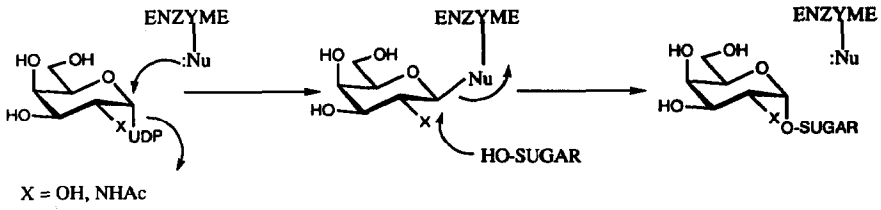


Fig. 2. Hypothesized two-step, double-displacement mechanism for the A and B transferases.

of the UDP from the sugar nucleotide by a nucleophile located in the active site thus forming a covalent glycosyl–enzyme intermediate. Transfer of the sugar residue to the growing oligosaccharide is then completed by displacement of the enzyme from the glycosyl–enzyme intermediate by the OH-3 of the acceptor Gal residue. The hypothesized presence of an essential nucleophile on the enzyme would provide a target for possible enzyme deactivation via covalent attachment of an acyl, alkyl, or other group. However, before attempting preparation of such irreversible inhibitors it is essential to determine the minimum requirements for acceptor recognition by these transferases.

The minimum acceptor structure recognized by both enzymes is the H disaccharide[1], α-L-Fuc*p*-(1 → 2)-β-D-Gal*p*-OR. In an earlier paper[14], we reported the synthesis and biochemical evaluation of six analogues of this disaccharide having R = octyl (**6**). The analogues prepared and evaluated were those in which the 3, 4, and 6 hydroxyl groups in the galactose had been replaced, independently, with hydrogen and fluorine. We chose R to be octyl because the presence of this hydrophobic group simplified the enzymatic assays by allowing the use of reverse phase (C_{18}) cartridges to separate and quantitate the product[15]. We now report the preparation and enzymic evaluation of all possible *O*-methyl (**7–9**), epimeric (**10** and **11**), and amino (**12–14**) analogues of disaccharide **6** with modifications on the Gal residue. Replacement of a hydroxyl group with an *O*-methyl group gives potential information not only about the hydrogen bonding requirements at that site but also the steric bulk the enzyme will tolerate at that position[16]. To gain additional insight into the important steric and hydrogen bonding interactions, the epimers of **6** were prepared to see if the *galacto* configuration was absolutely required by both enzymes. Finally, the amino derivatives were synthesized to probe

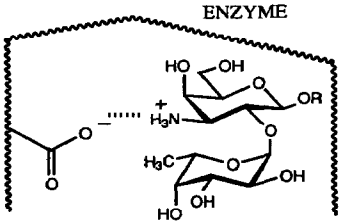


Fig. 3. Hypothetical interaction between negatively charged amino acid residue and a protonated amino group.

for the existence of a negatively charged or hydrogen-bond accepting residue in the active site. At physiological pH the amino group would be protonated, and therefore we could expect that if there were a negatively charged group near the positively charged amino function, that a strong ionic interaction might result. Such a compound could serve as a potent inhibitor of the enzyme via a tightly held enzyme–substrate complex (Fig. 3)[17].

RESULTS AND DISCUSSION

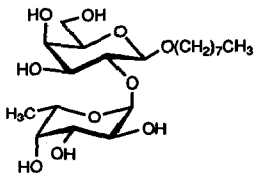
Chemical synthesis.—The preparation of compounds **7–14** followed well established synthetic procedures. The general strategy involved first the synthesis of the suitably protected modified galactose residue with OH-2 free, then fucosylation under halide-ion catalyzed conditions[18,19], and deprotection.

The synthesis of the 3-*O*-methyl derivative began with octyl 2,4,6-tri-*O*-benzyl-β-D-galactopyranoside (**15**, ref 14), which was *O*-methylated and hydrogenolyzed to provide octyl 3-*O*-methyl-β-D-galactopyranoside (**17**) in 80% yield over two steps. Protection of the 4,6-diol by benzylidenation gave alcohol **18** (72%). Fucosylation of **18** with 2,3,4-tri-*O*-benzyl α-L-fucopyransoyl bromide[19] (**19**) and deprotection by hydrogenolysis gave **7** (two steps, 47%).

To prepare the 4-*O*-methyl derivative **8**, alcohol **21** (ref 14), was methylated to give the fully protected 4-*O*-methyl derivative **22** in 92% yield. Removal of the allyl group (86%) gave **23** which was fucoslyated with **19**. Repeated attempts to purify the product by column chromatography failed and the partially purified product was therefore directly hydrogenolyzed, following which the deblocked 4-*O*-methyl disaccharide **8** could be obtained in pure form after chromatography (30% from **23**).

The synthesis of the 6-*O*-methyl derivative was straightforward and began with the benzylidenated galactoside **25** (ref 14). Reductive ring opening (76%) followed by reaction with methyl iodide gave **27** (95%). Removal of the allyl group (81%) and fucosylation provided the protected disaccharide **29** (81%). Hydrogenolysis of **29** gave the desired product **9** in 93% yield.

The preparation of the 3-epimeric disaccharide started with the conversion of the known bromide **30** (ref 20) to octyl β-D-gulopyranoside (**32**) via glycosylation and deacetylation (59% from **30**). Conversion of **32** to the diisopropylidene derivative **33** was achieved, in high yield, by reaction with an excess of 2,2-dimethoxypropane (92%). Selective hydrolysis of **33** provided diol **34**, which was then converted to the dibenzylated compound **35** (two steps, 59%). The isopropylidene group was removed (87%) and the resulting 2,3-diol was transiently protected as the methyl orthoacetate. Conversion of the orthoester by reaction with acetic acid and water gave the 3 acetate **37** (97% from **36**). Fucosylation yielded product **38**, the purification of which was not successful. The partially purified material was therefore treated with sodium methoxide and the deacetylated product **39** was



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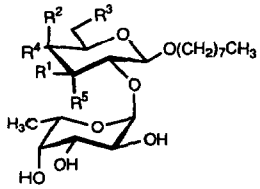
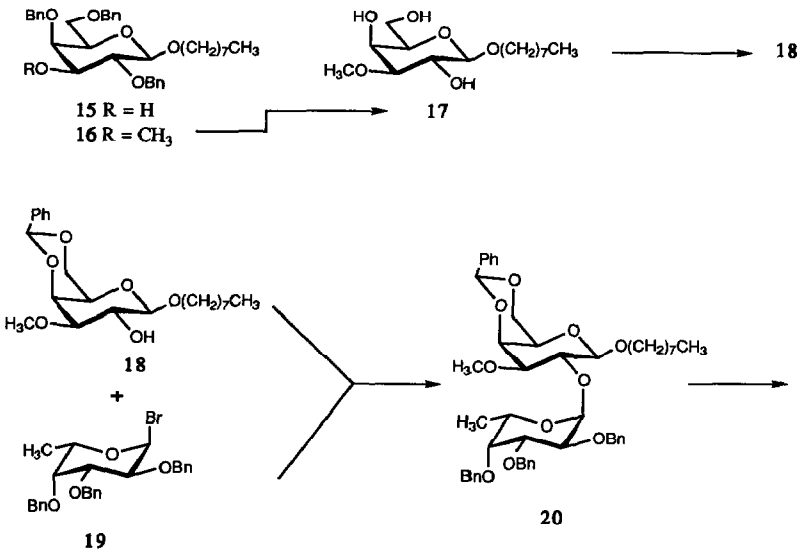


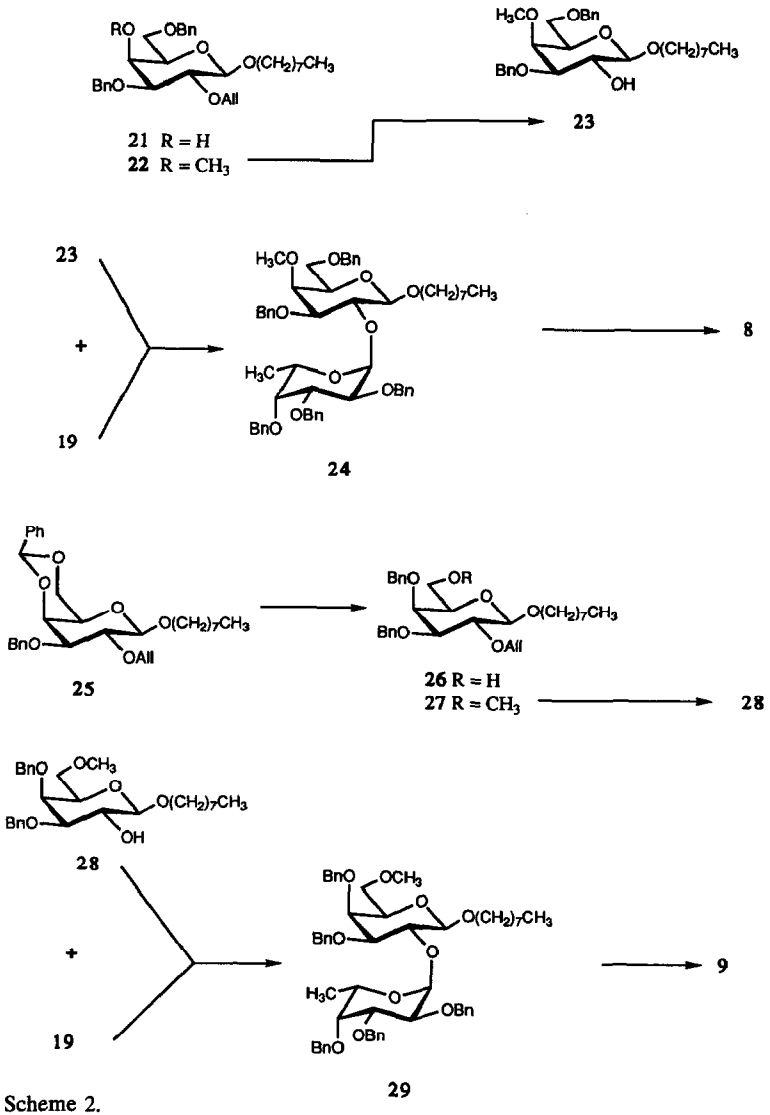
	Substrate	R^1	R^2	R^3	R^4	R^5
7	(3-O-Methyl)	OCH_3	OH	OH	H	H
8	(4-O-Methyl)	OH	OCH_3	OH	H	H
9	(6-O-Methyl)	OH	OH	OCH_3	H	H
10	(3-Epimer)	H	OH	OH	H	OH
11	(4-Epimer)	OH	H	OH	OH	H
12	(3-Amino)	NH_2	OH	OH	H	H
13	(4-Amino)	OH	NH_2	OH	H	H
14	(6-Amino)	OH	OH	NH_2	H	H



Scheme 1.

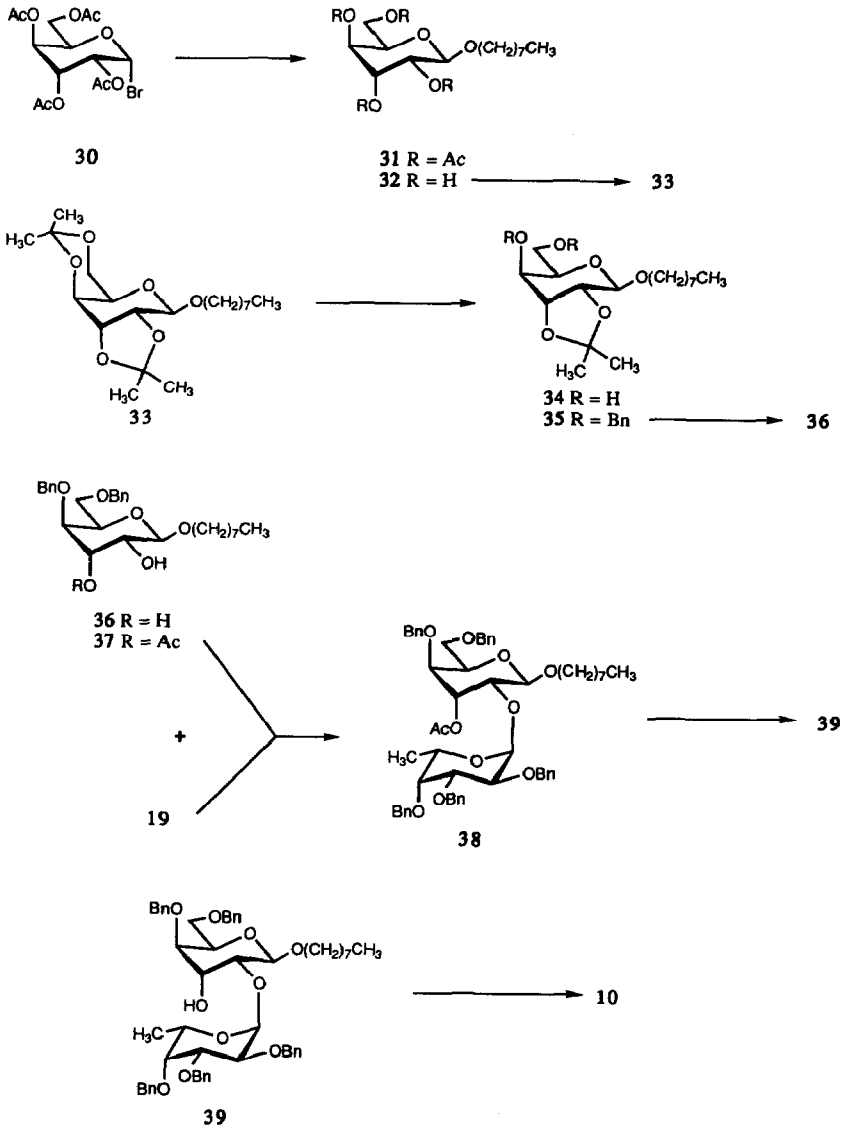
purified and characterized (78% from **37**). Hydrogenolysis afforded the gulopyranose containing disaccharide **10** (91%).

To obtain the disaccharide with a glucosyl moiety, **11**, the 4 triflate of alcohol **40** (ref 14) was reacted with sodium benzoate to give compound **41** (73%). The allyl group was removed to give **42** (72%) and this alcohol was fucosylated to give **43**, which could not be purified. As described above for the synthesis of **10**, partially purified **43** was treated with sodium methoxide and then the deacylated product **44** was characterized. The 4-epimeric disaccharide **11** was obtained in 80% yield from **42** after hydrogenolysis.



Scheme 2.

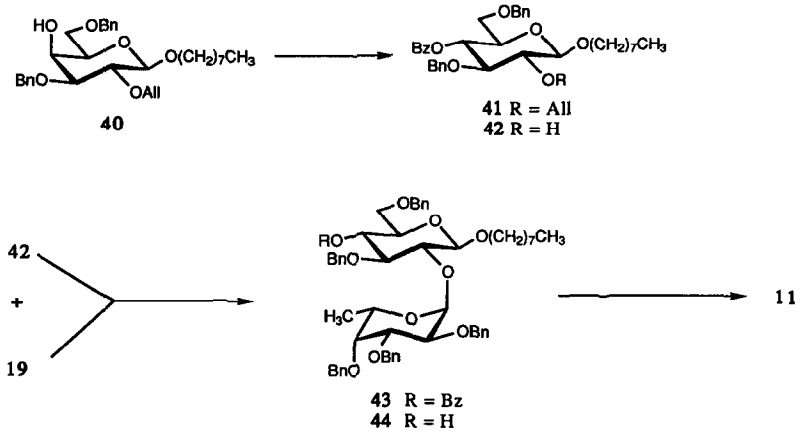
Preparation of the 3-amino disaccharide began with the known gulofuranose derivative **45** (ref 21). Reaction of the 3 triflate of **45** with sodium azide afforded azide **46** (87%). The diisopropylidene derivative was converted to peracetate **47** by treatment with trifluoroacetic acid followed by acetic anhydride and pyridine (56%). Bromide **48**, prepared by reaction of **47** with titanium tetrabromide, was treated with octanol to give octyl 2,4,6-tri-*O*-acetyl-3-azido-3-deoxygalactopyranoside (**49**) in 63% yield. Glycoside **49** was then deacetylated and the resulting triol protected as a benzylidene acetal to provide **51** (77% from **49**). Fucosylation



Scheme 3.

proceeded in modest yield (55%) to give **52** which was hydrogenolyzed providing **12** (60%).

The initial step in the synthesis of the 4-amino analogue was the displacement of the 4-triflate of **53** (ref 14) with sodium azide to give **54** (74%). Reduction of the azide and removal of the benzyl groups was achieved by hydrogenolysis to provide octyl 4-amino-4-deoxy-β-D-galactopyranoside (**55**, 59%). Preparation of alcohol **57** involved first protection of the amino group as a trifluoroacetate (78%) followed by benzoylation with dibutyltin oxide and benzoyl chloride (76%). Fucosylation of **57**



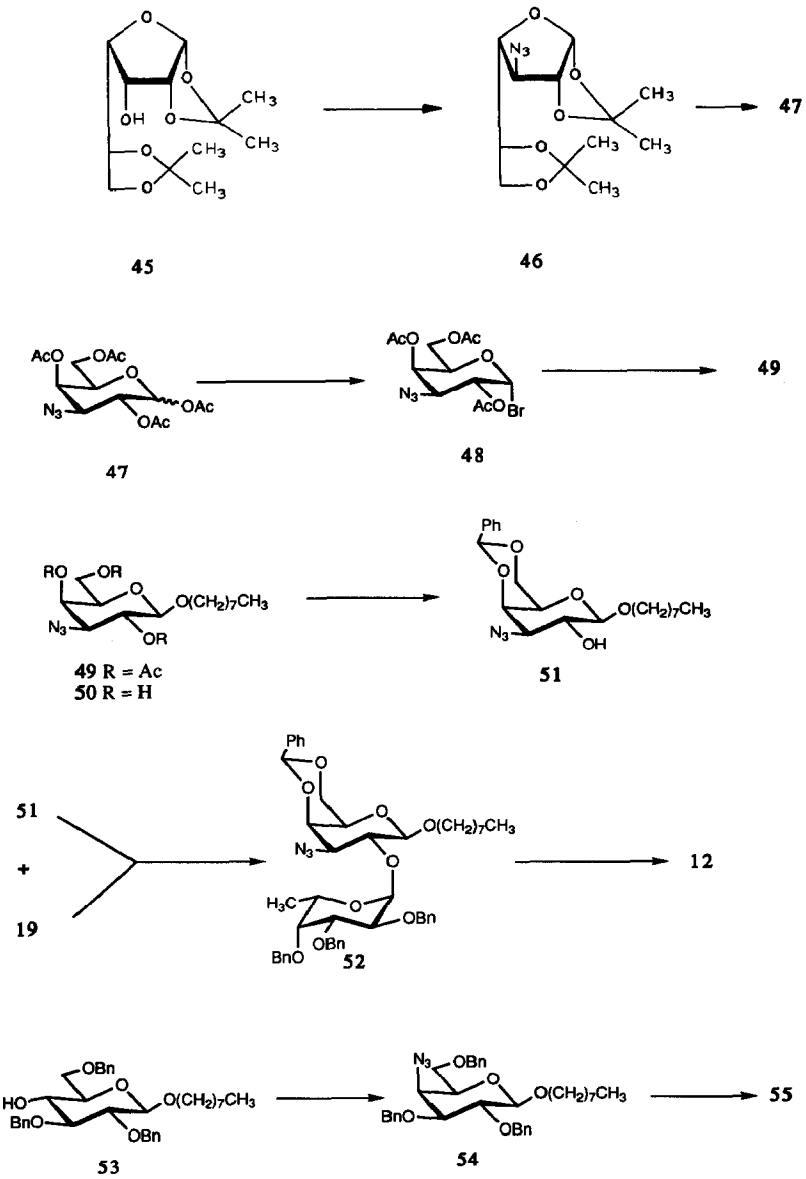
Scheme 4.

was difficult, possibly due to steric interference from an axially disposed trifluoroacetate, and halide ion catalyzed fucosylation provided only small amounts of product (< 5%). A more rigorous modification of the halide ion method[22], employing copper bromide, also gave similarly low yields of product. Finally, **58** could be obtained, albeit still in low yield (42%), using silver triflate as the promoter. Compound **58** was deprotected by hydrogenolysis and hydrolysis to give the 4-amino disaccharide **13** (77%).

The preparation of the 6-amino derivative involved first the conversion of alcohol **26**, by way of a Mitsunobu reaction with phthalimide[23], to the 6-phthalimido derivative **59** (91%). Deallylation (65%) provided alcohol **60**, which was fucosylated to give **61** (79%). The phthalimido group was removed and the amino function was protected by trifluoroacetylation (70%) to give **62**. Deprotection by hydrogenolysis and then alkaline methanolysis gave the product **14** in 61% yield.

Enzymic testing.—Preliminary screening (Table I) of compounds **7**–**14** as potential acceptors for the GalNAc and Gal transferases in human serum confirmed our previous findings that only the disaccharides with an intact 3,4-diol group are recognized as substrates. Since both epimers are inactive, it is now clear that this diol must also have the *galacto* configuration for the compound to be a substrate. Two compounds, the 6-*O*-methyl (**9**) and 6-amino (**14**) derivatives were substrates; however, the relative rates were less than those obtained for the native H-disaccharide, **6**. The products were not isolated or structurally characterized.

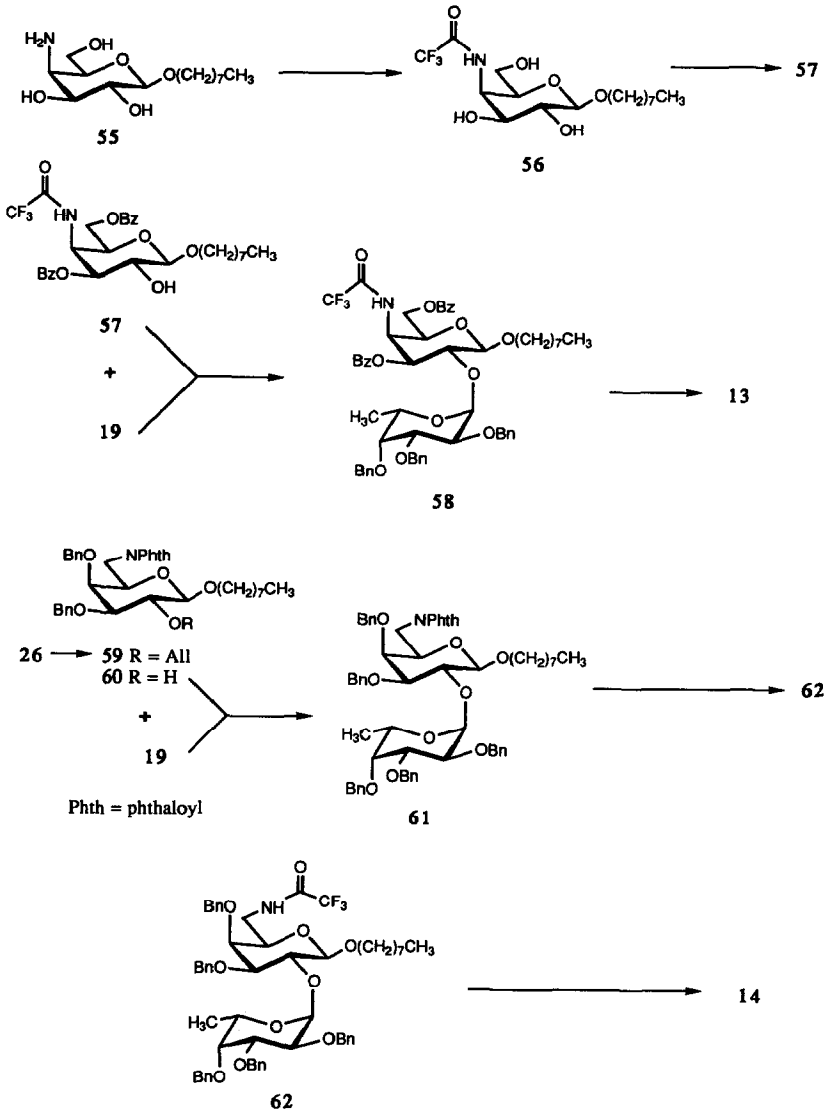
The lack of activity of the derivatives with modifications at C-4 of the galactosyl residue suggests, as was previously suggested[14], that the 4-hydroxyl group is essential for recognition by these enzymes. Of all the Gal C-3 modified derivatives, only the 3-*O*-methyl compound (**7**) is unable to react due to the lack of a suitable acceptor functional group at the 3 position. Both the 3-epimer (**10**) and the 3-amino (**12**) analogues could potentially react. The epimer could form a stable product, but it is clear from these results that the enzymes will not recognize an



Scheme 5.

axially oriented hydroxyl group at this position. The product formed from the amino analogue would have limited stability[24]. It is conceivable, therefore, that the amino derivative is in fact a substrate, but that the product is too labile to survive either in the assay mixture or the work-up procedure after the assay.

Determination of the kinetic constants (Table II) for the 6-*O*-methyl compound (**9**) showed that for both transferases, the V_{max} does not change significantly from the V_{max} of **6**. While the V_{max} for the 6-amino derivative (**14**) with the B transferase



Scheme 6.

is virtually the same as for **6**, when tested with the A transferase **14** possessed a significantly higher V_{max} than the corresponding natural disaccharide. The calculated K_m values for both **9** and **14** with both enzymes show significant increases over the value obtained with **6**. The observation that both the **9** and **14** are poor substrates suggests that an unfavorable steric interaction is probably not the only complicating factor. It is possible also that in the area occupied by OH-6 in the active site there is a positively charged residue which repels both the hydrophobic methyl group and the protonated, positively charged amino group.

TABLE I

Relative acceptor activity of disaccharides **6–14** towards the blood group A (GalNAc) and B (Gal) transferases in human serum [a]

Substrate	Relative activities (%)	
	A Transferase	B Transferase
Native disaccharide (**6**)	100	100
3-*O*-Methyl (**7**)	0.4	0
4-*O*-Methyl (**8**)	0.3	0
6-*O*-Methyl (**9**)	13.4	3.2
3-Epimer (**10**)	0	0
4-Epimer (**11**)	0	0
3-Amino (**12**)	0.8	0.1
4-Amino (**13**)	0	0.3
6-Amino (**14**)	4.7	2.0

[a] Compounds **6–14** were present at concentrations of 2.5 μM for the A transferase and 10 μM for the B transferase. Experiments were done in duplicate, with replicate runs within 10% of each other.

Results of the evaluation of disaccharides modified at the 3 and 4 positions as potential inhibitors are presented in Table III. The 4-*O*-methyl, 4-epimeric, and 4-amino derivatives were inactive, within experimental error, demonstrating that the galactosyl 4-hydroxyl group is crucial for binding to the enzyme. All of the position 3 modified derivatives possessed inhibitory ability. The 3-*O*-methyl (**7**) compound was only a very weak inhibitor and thus no effort was made to calculate K_i. The 3-epimeric (**10**) compound was determined to be a competitive inhibitor of the B transferase, possessing a K_i less than 50% of the K_m for **6** (Table IV). The 3-amino derivative (**12**) was tested as an inhibitor of the B transferase, but the observed inhibition kinetics did not follow a simple mechanism. Concomitant with an increase in inhibitor concentration, a pronounced downward curvature was observed (data not shown) in the reciprocal plots used to determine K_i. The magnitude of the curvature increased with the inhibitor concentration. As well, attempts to determine the K_i and mode of inhibition for **10** and **12** with the A

TABLE II

Calculated kinetic constants for acceptors **6**, **9**, and **12** with the blood group A (GalNAc) and B (Gal) transferases in human serum

Substrate	Kinetic constants [a]			
	A Transferase		B Transferase	
	K_m (μM)	V_{max} (pmol/min)	K_m (μM)	V_{max} (pmol/min)
Native [b] (**6**)	1.5 ± 0.2	0.61 ± 0.02	21.9 ± 3.4	0.32 ± 0.023
6-*O*-Methyl (**9**)	22.8 ± 3.0	0.58 ± 0.03	537.7 ± 18.8	0.36 ± 0.007
6-Amino (**14**)	74.5 ± 4.9	0.87 ± 0.02	565.3 ± 119.8	0.30 ± 0.003

[a] At saturating UDP-GalNAc (30 μM) and UDP-Gal (30 μM) concentrations. [b] Ref 14.

TABLE III

Relative inhibitor potency of disaccharides **7**, **8**, and **10–13** towards the blood group A (GalNAc) and B (Gal) transferases in human serum

Substrate	% Inhibition [a]	
	A Transferase [b]	B Transferase [c]
3-*O*-Methyl (**7**)	4	15
4-*O*-Methyl (**8**)	0	2.5
3-Epimer (**10**)	36	88
4-Epimer (**11**)	0	0
3-Amino (**12**)	98	93
4-Amino (**13**)	0	1.8

[a] Experiments were done in duplicate, with replicate runs within 10% of each other. [b] Concentration of potential inhibitor was 25 μM with acceptor **6** at 2.5 μM. [c] Concentration of potential inhibitor was 100 μM with acceptor **6** at 10 μM.

transferase were not successful. As in the case of the inhibition of the B transferase with **12**, a downward curvature was observed in the reciprocal plots.

Similar results were obtained with **12** when tested with A transferase serum from a different donor indicating that the effect is not related to the serum donor. To provide an estimation of the potency of these inhibitors with the A and B transferase, K_i values were estimated assuming that the inhibition was competitive, using the equation shown in Table IV[25]. A more detailed analysis of the behavior of **10** and **12** with these enzymes is in progress. That **12** is an inhibitor of both enzymes supports our hypothesis of the possible existence of a negatively charged residue in the vicinity of the Gal OH-3 in the acceptor-binding site of these transferases.

Although we have been unable to show that the 3-amino derivative is strictly speaking a competitive inhibitor, we feel that the mechanism is at least to some degree competitive. As a control, the monosaccharide precursor to **12**, octyl 3-amino-3-deoxy-β-D-galactopyranoside, was tested as an inhibitor of the enzyme and found to be inactive. We believe that this result, along with the fact that neither the 4-amino nor the 6-amino derivative inhibits the enzyme, supports a

TABLE IV

Inhibition constants (K_i) of disaccharides **10** and **12** with the blood group A and B glycosyltransferases in human serum

Enzyme	3-Epimer (**10**) K_i (μM)	3-Amino (**12**) K_i (μM)	Mode of inhibition
A Transferase	22 [a]	0.2 [a]	n.d. [b]
B Transferase	7.8±0.8	5 [a]	competitive for **10** n.d. for **12**

[a] Estimated K_i assuming the inhibition is competitive and calculated from the equation $i = [I]/([I] + K_i\{1 + [S]/K_m\})$, where i s the fractional inhibition, $[I]$ the inhibitor concentration, and $[S]$ the substrate concentration[25]. [b] Not determined.

defined recognition of the inhibitor by the enzyme; and that the inhibition is not due to another effect such as change in local pH or the binding of the inhibitor to another part of the enzyme, altering its conformation and thus decreasing it's activity.

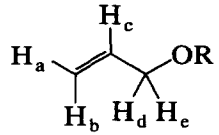
In conclusion, the results presented here corroborate our previous findings[14] that both the A and the B transferases will tolerate modifications of the galactosyl 3- and 6-hydroxyl groups without loss of recognition, and that the 4-hydroxyl group is crucial for binding. It appears therefore that the Gal OH-4 is, according to the terminology of Lemieux[26], a key polar group in the recognition by these enzymes. Furthermore, the ability of the enzymes to recognize analogues modified at OH-3 of the galactosyl residue indicates that the potential for a bidentate hydrogen bond between the galactosyl 3,4-diol function and an enzymic carboxylate or amide group, as described for other galactose recognizing proteins[27,28], is lacking, or is at least not of critical importance for recognition by these enzymes. Finally, the results with the 3-amino compound suggest that a negatively charged residue in the enzyme may be close to Gal OH-3 since, under appropriate conditions, inhibition is observed at submicromolar concentrations. Such a negatively charged residue might be catalytically important in the transfer mechanism postulated in Fig. 2, and is thus a potential site for covalent deactivation of the enzymes. Further studies of these active sites, directed towards identifying and inactivating such an active site nucleophile, are in progress.

EXPERIMENTAL

General methods.—Optical rotations were measured with a Perkin–Elmer 241 polarimeter at 22 ± 2°C. Analytical TLC was performed on Silica Gel 60-F_{254} (E. Merck, Darmstadt) with detection by quenching of fluorescence and/or by charring with H_2SO_4. All commercial reagents were used as supplied and chromatography solvents were distilled prior to use. Column chromatography was performed on Silica Gel 60 (E. Merck 40–60 μm, Darmstadt). Millex-GV (0.22 μm) filter units were from Millipore (Missisauga, ON), C_{18} Sep-Pak sample preparation cartridges were from Waters Associates (Missisauga, ON), and Ecolite was from ICN Radiochemicals (St. Laurent PQ). UDP-[6-^{3}H]Gal (specific activity 15 Ci/mmol) and UDP-[6-^{3}H]GalNAc (specific activity 10 Ci/mmol) were from American Radiolabelled Chemicals (St. Louis, MO). UDP-Gal and UDP-GalNAc were obtained from Sigma (St. Louis, MO). ^{1}H NMR spectra were recorded at 360 MHz (Bruker WM-360) or 300 MHz (Bruker AM-300) with either $(CH_3)_4Si$ (δ 0, for solutions in $CDCl_3$ and CD_3OD) or DOH (δ 4.80, for solutions in D_2O) as internal references. ^{13}C NMR spectra were recorded at 75.5 MHz (Bruker AM-300) with internal $(CH_3)_4Si$ (δ 0, for solutions in $CDCl_3$ and CD_3OD) or external 1,4-dioxane (δ 67.4, for solutions in D_2O) as references. ^{1}H NMR data are reported as though they were first order. Assignments of ^{13}C shifts are tentative and are based on comparison with published spectral data[29–31]. Unless otherwise

stated, all reactions were carried out at room temperature. In the processing of reaction mixtures solutions in organic solvents were washed with equal amounts of aqueous solutions, then dried (Na_2SO_4) prior to concentration under vacuum at < 40°C (bath). Microanalyses were carried out by the analytical services of this department and all samples submitted for elemental analyses were dried overnight under vacuum with P_2O_5 at 56°C (refluxing acetone).

Protons of the allyl group present in the compounds described in this paper are designated H_a, H_b, H_c, H_d, and H_e as defined below. These protons showed the same coupling constants and thus the same multiplicity pattern in all the compounds examined, only the chemical shifts varied. The observed couplings were as follows: H_a, (dddd, $J_{a,c}$ 10.5, $J_{a,d} = J_{a,e} = J_{a,b} = 1.5 \pm 0.5$ Hz); H_b, (dddd, $J_{b,c}$ 17.0, $J_{b,d} = J_{b,e} = J_{a,b} = 1.5 \pm 0.5$ Hz); H_c, (dddd, $J_{b,c}$ 17.0, $J_{a,c}$ 10.5, $J_{c,d} = J_{c,e} = 5.5$ Hz); H_d, (dddd, $J_{d,e}$ 13.5, $J_{c,d}$ 5.5, $J_{b,d} = J_{a,d} = 1.5 \pm 0.5$ Hz); H_e, (dddd, $J_{d,e}$ 13.5, $J_{c,e}$ 5.5, $J_{a,e} = J_{b,e} = 1.5 \pm 0.5$ Hz).



Octyl 2,4,6-tri-O-benzyl-3-O-methyl-β-D-galactopyranoside (**16**).—To a solution of octyl 2,4,6-tri-*O*-benzyl-β-D-galactopyranoside[14] (**15**, 527 mg, 0.94 mmol) in dry DMF (10 mL), NaH (85 mg, 80% in oil, 2.83 mmol) was added. After stirring for 30 min, MeI (175 μL, 2.81 mmol) was added and stirring was continued for 2 h overnight. The mixture was diluted with CH_2Cl_2 and washed with $NaHCO_3$, water, and brine. Chromatography (6:1 hexane–EtOAc) gave the product **16** (506 mg, 94%) as an oil; $[\alpha]_D$ − 9.1° (*c* 0.6, $CHCl_3$); R_f 0.37 (6:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 7.20–7.40 (m, 15 H, Ph), 4.90, 4.90, 4.74, 4.60, 4.45, 4.40 (6 d, 6 H, J_{gem} 11.5 Hz, PhCH_2), 4.25 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 3.86–3.96 (m, 2 H, H-4, OCH_2CH$_2$), 3.70 (dd, 1 H, $J_{1,2}$ 8, $J_{2,3}$ 10 Hz, H-2), 3.49–3.61 (m, 3 H, H-5, H-6a, H-6b), 3.50 (s, 3 H, OCH_3), 3.47 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.24 (dd, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 3 Hz, H-3), 1.56–1.68 (m, 2 H, OCH$_2$CH_2), 1.20–1.40 (10 H, octyl CH$_2$), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR ($CDCl_3$): δ 139.03, 138.75, 138.01 (Ph quaternary), 128.43, 128.29, 128.24, 128.15, 127.98, 127.89, 127.77, 127.49, 127.46 (Ph methine), 103.94 (C-1), 84.56 (C-3), 79.54 (C-2), 75.07, 74.42, 73.57 (PhCH$_2$), 73.37 (C-5), 72.67 (C-4), 70.05 (OCH$_2$CH$_2$), 68.94 (C-6), 58.86 (OCH$_3$), 31.85, 29.75, 29.46, 29.27, 26.18, 22.68 (octyl CH$_2$), and 14.11 (octyl CH$_3$). Anal. Calcd for $C_{36}H_{48}O_6$ (576.78): C, 74.97; H, 8.39. Found: C, 74.82, H, 8.25.

Octyl 3-O-methyl-β-D-galactopyranoside (**17**).—Compound **16** (444 mg, 0.77 mmol), was dissolved in MeOH (20 mL), 5% Pd–C (200 mg) was added, and the reaction was stirred under a flow of H_2 for 7 h. The catalyst was filtered away, the solvent evaporated, and the residue chromatographed (19:1 CH_2Cl_2–MeOH) to give **17** (201 mg, 85%) as a white solid, $[\alpha]_D$ − 14.5° (*c* 0.4, MeOH); R_f 0.20 (19:1 CH_2Cl_2–MeOH). ^1H NMR (CD_3OD): δ 4.14 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.00 (d, 1

H, $J_{3,4}$ 4 Hz, H-4), 3.81 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.60–3.70 (m, 2 H, H-6a, H-6b), 3.34–3.53 (m, 6 H, H-5, H-2, OCH_2CH$_2$, OCH_3), 3.05 (dd, 1 H, $J_{3,4}$ 4, $J_{2,3}$ 9.5 Hz, H-3), 1.46–1.61 (m, 2 H, OCH$_2$CH_2), 1.12–1.40 (10 H, octyl CH$_2$), and 0.83 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR (CD$_3$OD): δ 104.90 (C-1), 84.56 (C-3), 76.43 (C-5), 71.52 (C-2), 70.81 (OCH$_2$CH$_2$), 65.98 (C-4), 62.47 (C-6), 57.31 (OCH$_3$), 33.00, 30.82, 30.56, 30.40, 27.11, 23.70 (octyl CH$_2$), and 14.41 (octyl CH$_3$). Anal. Calcd for $C_{15}H_{30}O_6$ (306.40): C, 58.80; H, 9.87. Found: C, 58.70; H, 9.78.

*Octyl 4,6-O-benzylidene-3-O-methyl-β-*D*-galactopyranoside* (**18**).—Galactoside **17** (98 mg, 0.32 mmol) was dissolved in MeCN (10 mL). Dimethoxytoluene (50 μL, 0.33 mmol) and toluenesulfonic acid (10 mg) were added and the solution was stirred for 8 h. The reaction was quenched with Et$_3$N, and the mixture was diluted with CH$_2$Cl$_2$, then washed with water and brine. Column chromatography of the resulting clear oil (1:1 hexane–EtOAc) gave **18** (90 mg, 72%) as a white solid; $[\alpha]_D$ + 6.5° (*c* 0.5, CHCl$_3$); R_f 0.50 (1:1 hexane–EtOAc). ^{1}H NMR (CDCl$_3$): δ 7.28–7.55 (m, 5 H, Ph), 5.54 (s, 1 H, PhCHO$_2$), 4.26–4.38 (m, 3 H, H-1, H-4, H-6a), 4.08 (dd, 2 H, $J_{5,6}$ 2, $J_{6a,6b}$ 12 Hz, H-6b), 3.88–4.01 (m, 2 H, H-2, OCH_2CH$_2$), 3.45–3.56 (m, 4 H, OCH_3, OCH_2CH$_2$), 3.41 (br s, 1 H, H-5), 3.31 (dd, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 3.5 Hz, H-3), 2.48 (d 1 H, $J_{2,OH}$ 2 Hz, 2-OH), 1.58–1.72 (m, 2 H, OCH$_2$CH_2), 1.20–1.40 (10 H, octyl CH$_2$), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR (CDCl$_3$): δ 137.76 (Ph quaternary), 128.94, 128.12, 126.45 (Ph methine), 102.97 (C-1), 101.26 (PhCHO$_2$), 81.18 (C-3), 72.41 (C-4), 70.09 (C-2), 69.91 (OCH$_2$CH$_2$), 69.40 (C-6), 66.70 (C-5), 57.23 (OCH$_3$), 31.81, 29.54, 29.40, 29.22, 25.97, 22.65 (octyl CH$_2$), and 14.10 (octyl CH$_3$). Anal. Calcd for $C_{22}H_{34}O_6$ (394.51): C, 66.98; H, 8.69. Found: C, 67.16; H, 8.84.

*Octyl 4,6-O-benzylidene-3-O-methyl-2-O-(2,3,4-tri-O-benzyl-α-*L*-fucopyranosyl)-β-*D*-galactopyranoside* (**20**).—Alcohol **18** (114 mg, 0.29 mmol) and tetraethylammonium bromide (67 mg, 0.32 mmol) were dissolved in a mixture of CH$_2$Cl$_2$ (3 mL) and DMF (0.5 mL) containing crushed 4A molecular sieves (2.5 g), and the solution was stirred overnight. To this slurry was added freshly prepared 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide[19] (**19**, 1.56 mmol) in CH$_2$Cl$_2$ (3 mL) and the mixture was stirred for 2 days. Methanol (1 mL) was added, stirring was continued for 30 min, and then the mixture was filtered and taken to dryness. Column chromatography of the residue (3:2 hexane–EtOAc) gave the disaccharide **20** (180 mg, 77%) as a white solid; $[\alpha]_D$ − 72.5° (*c* 0.4, CHCl$_3$); R_f 0.53 (3:2 hexane–EtOAc). ^{1}H NMR (CDCl$_3$): δ 7.18–7.56 (m, 20 H Ph), 5.47–5.55 (m, 2 H, H-1′, PhCHO$_2$), 4.96, 4.88, 4.84, 4.74, 4.74, 4.65 (6 d, 6 H, J_{gem} 11.5 Hz, PhCH_2), 4.43 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 4.41 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 4.23–4.33 (m, 2 H, H-4, H-6a), 3.94–4.12 (m, 4 H, H-2′, H-3′, H-2, H-6b) 3.91 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.66 (br s, 1 H, H-4′), 3.54 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 3.5 Hz, H-3), 3.35–3.44 (m, 4 H, OCH_3, OCH_2CH$_2$), 3.33 (br s, 1 H, H-5), 1.48–1.61 (m, 2 H, OCH$_2$CH_2), 1.17–1.37 (10 H, octyl CH$_2$), 1.12 (d, 3 H, $J_{5',6'}$ 6.5 Hz, H-6′), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR (CDCl$_3$): δ 139.01, 138.81, 138.68,

137.68 (Ph quaternary), 128.81, 128.20, 128.11, 128.02, 127.67, 127.31, 127.25, 126.40 (Ph methine), 101.70 (C-1), 101.16 (Ph*C*HO_2), 97.06 (C-1′), 82.98 (C-3), 79.48 (C-4′), 78.03 (C-3′), 76.19 (C-3), 74.61, 72.99, 72.48 (Ph*C*H_2), 71.84 (C-2), 69.28 (C-6, O*C*H_2CH_2), 66.30 (C-5′), 66.04 (C-5), 56.18 (O*C*H_3), 31.77, 29.58, 29.43, 29.24, 26.17, 22.57 (octyl CH_2), 16.55 (C-6′), and 14.04 (octyl CH_3). Anal. Calcd for $C_{49}H_{62}O_{10}$ (811.03): C, 72.57; H, 7.70. Found; C, 72.40; H, 7.79.

*Octyl 2-*O*-α-*L*-fucopyranosyl-3-*O*-methyl-β-*D*-galactopyranoside* (**7**).—The protected disaccharide **20** (172 mg, 0.21 mmol) was dissolved in EtOH (30 mL), 5% Pd–C (80 mg) was added, and the solution was stirred under a flow of H_2 overnight. After completion of the reaction the catalyst was filtered away and the solvent evaporated. The product was purified by redissolution in water and then passing the solution through a Waters C_{18} SepPak cartridge. The cartridge was washed with water and then the product was eluted with MeOH. The MeOH eluant was evaporated, and the residue was redissolved in water, filtered through a 0.22-μm filter, and lyophilized to give the product **7** (59 mg, 61%) as a white solid. ^{1}H NMR (CD_3OD): δ 5.15 (d, 1 H, $J_{1'2'}$ 3 Hz, H-1′), 4.28 (q, 1 H, $J_{5'6'}$ 6.5 Hz, H-5), 4.25 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 3.99 (d, 1 H, $J_{3,4}$ 3 Hz, H-4), 3.82 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OC*H*$_2$CH$_2$), 3.59–3.72 (m, 5 H, H-5, H-6a, H-6b, H-2′, H-3′), 3.55 (br s, 1 H, H-4′), 3.34–3.45 (m, 5 H, H-2, OC*H*$_2$CH$_2$, OC*H*$_3$), 3.31 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 3 Hz, H-3), 1.42–1.56 (m, 2 H, OCH$_2$C*H*$_2$), 1.15–1.35 (10 H, octyl CH_2), 1.08 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6′), and 0.81 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR (CD_3OD): δ 103.44 (C-1), 100.58 (C-1′), 85.72 (C-3), 76.29 (C-3′), 75.16 (C-5), 73.81 (C-2), 71.80 (C-4′), 70.62 (O*C*H$_2$CH$_2$), 70.30 (C-2′), 67.45 (C-4), 65.79 (C-5′), 62.41 (C-6), 56.83 (O*C*H$_3$), 32.99, 30.98, 30.61, 30.41, 27.37, 23.63 (octyl CH_2), 16.72 (C-6′), and 14.41 (octyl CH_3).

*Octyl 2-*O*-allyl-3,6-di-*O*-benzyl-4-*O*-methyl-β-*D*-galactopyranoside* (**22**).—To a solution of octyl 2-*O*-allyl-3,6-di-*O*-benzyl-β-D-galactopyranoside[14] (**21**, 192 mg, 0.38 mmol) in dry DMF (10 mL), NaH (33 mg, 80% in oil, 1.1 mmol) was added. After stirring for 30 min, MeI (50 μL, 0.80 mmol) was added and stirring was continued for 2 h. At this point, more NaH (11 mg) and MeI (25 μL) were added and the mixture was stirred another 5 h. The mixture was then diluted with CH_2Cl_2 and washed with $NaHCO_3$, water, and brine. Chromatography (3:1 hexane–EtOAc) gave the product **22** (181 mg, 92%) as an oil, $[\alpha]_D$ – 19.3° (*c* 1, $CHCl_3$); R_f 0.60 (3:1 hexane–EtOAc). ^{1}H NMR ($CDCl_3$): δ 7.28–7.42 (m, 10 H, Ph), 5.96 (1 H, H_c allyl), 5.27 (1 H, H_a allyl), 5.14 (1 H, H_b allyl), 4.78, 4.71, 4.58, 4.52 (4 d, 4 H, J_{gem} 11.5 Hz, PhC*H*$_2$), 4.38 (1 H, H_d allyl), 4.25 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.22 (1 H, H_e allyl), 3.88 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OC*H*$_2$CH$_2$), 3.71 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 9.5 Hz, H-2), 3.47–3.65 (4 H, H-4, H-5, H-6a, H-6b), 3.55 (s, 3 H, OC*H*$_3$), 3.37–3.47 (m, 2 H, H-3, OC*H*$_2$CH$_2$), 1.52–1.65 (m, 2 H, OCH$_2$C*H*$_2$), 1.20–1.40 (10 H, octyl CH_2), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$): δ 138.67, 138.08 (Ph quaternary), 135.43 (CH_2=*C*HCH$_2$O), 128.46, 128.35, 127.87, 127.81, 127.61 (Ph methine), 116.53 (*C*H$_2$=CHCH$_2$O), 103.80 (C-1), 81.76 (C-3), 79.39 (C-2), 76.26 (C-5), 74.00 (CH_2=CH*C*H$_2$O), 73.65 (PhC*H*$_2$), 73.15 (C-4), 73.02 (PhC*H*$_2$),

69.88 (OCH_2CH_2), 68.55 (C-6), 61.30 (OCH_3), 31.84, 29.69, 29.40, 29.27, 26.10, 22.67 (octyl CH_2), and 14.10 (octyl CH_3). Anal. Calcd for $C_{32}H_{46}O_6$ (526.72): C, 72.97; H, 8.80. Found: C, 72.90; H, 8.77.

*Octyl 3,6-di-*O*-benzyl-4-*O*-methyl-β-*D*-galactopyranoside* (**23**).—To a solution of **22** (118 mg, 0.22 mol) in 7:3:1 EtOH–benzene–water (15 mL), tris(triphenylphosphine)rhodium(I) chloride (30 mg, 0.03 mmol) and 1,4-diazabicyclo[2.2.2]octane (11 mg, 0.096 mmol) were added, and the solution was refluxed for 23 h. The solvent was evaporated and the residue dissolved in 9:1 acetone–water (15 mL). Mercuric oxide (5 mg) and mercuric chloride (900 mg) were added and stirring was continued for 6 h. The mixture was then diluted with CH_2Cl_2 and washed with satd KI, water, and brine. Evaporation of the organic layer followed by chromatography (3:1 EtOAc–hexane) gave **23** (159 mg, 86%) as an oil; $[\alpha]_D$ − 6.3° (*c* 0.3, $CHCl_3$); R_f 0.35 (3:1 hexane–EtOAc). ^{1}H NMR ($CDCl_3$): δ 7.25–7.40 (m, 10 H, Ph), 4.78, 4.71, 4.58, 4.53 (4 d, 4 H, J_{gem} 11.5 Hz, PhCH_2), 4.20 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.80–3.90 (m, 2 H, H-6a, OCH_2CH$_2$), 3.73 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 9.5 Hz, H-2), 3.66 (d, 1 H, $J_{3,4}$ 3 Hz, H-4), 3.55–3.65 (m, 2 H, H-6b, H-5), 3.54 (s, 3 H, OCH_3), 3.47 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.40 (d, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 3 Hz, H-3), 2.40 (d, 1 H, $J_{2,OH}$ 1.5 Hz, 2-OH), 1.54–1.67 (m, 2 H, OCH$_2$CH_2), 1.20–1.37 (10 H, octyl CH_2), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$): δ 138.23, 137.98 (Ph quaternary), 128.48, 128.46, 127.87, 127.83, 127.78, 127.68 (Ph methine), 103.14 (C-1), 81.80 (C-3), 75.48 (C-5), 73.65 (PhCH_2), 73.56 (C-4), 72.39 (PhCH_2), 71.44 (C-2), 69.85 (OCH_2CH_2), 68.46 (C-6), 61.22 (OCH_3), 31.81, 29.59, 29.39, 29.22, 25.99, 22.65 (octyl CH_2), and 14.08 (octyl CH_3). Anal. Calcd for $C_{29}H_{41}O_6$ (486.65): C, 71.57; H, 8.70. Found: C, 71.41; H, 8.66.

*Octyl 2-*O*-α-*L*-fucopyranosyl-4-*O*-methyl-β-*D*-galactopyranoside* (**8**).—Alcohol **23** (101 mg, 0.21 mmol) was fucosylated as described for **18** with 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (1.408 mmol) and tetraethylammonium bromide (51 mg, 0.24 mmol). At this point it was not possible to obtain a pure product, therefore, the partially purified product, obtained by chromatography (3:1 hexane–EtOAc), was dissolved in MeOH (10 mL), 5% Pd–C (50 mg) was added, and the solution was stirred under a flow of H_2 overnight. Final purification as described for **7** gave **8** (55 mg, 30%) as a white solid. ^{1}H NMR (CD_3OD): δ 5.19 (d, 1 H, $J_{1',2'}$ 3 Hz, H-1'), 4.28 (m, 2 H, H-1, H-5'), 3.86 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.62–3.80 (m, 6 H, H-3', H-2', H-4, H-6a, H-6b, H-5), 3.60 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 9.5 Hz, H-2), 3.54 (s, 3 H, OCH_3), 3.44–3.53 (m, 3 H, H-3, H-4', OCH_2CH$_2$), 1.52–1.62 (m, 2 H, OCH$_2$CH_2), 1.25–1.45 (10 H, octyl CH_2), 1.19 (d, 3 H, $J_{5',6'}$ 6.5 Hz, H-6'), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR (CD_3OD): δ 103.51 (C-1), 101.60 (C-1'), 80.21 (C-4), 79.31 (C-2, 76.45 (C-5), 73.75 (C-4'), 72.84 (C-3), 71.75 (C-3'), 70.82 (OCH_2CH_2), 70.61 (C-2'), 67.77 (C-5'), 61.94 (OCH_3), 61.65 (C-6), 32.99, 30.96, 30.59, 30.39, 27.27, 23.68 (octyl CH_2), 16.77 (C-6'), and 14.40 (octyl CH_3).

*Octyl 2-*O*-allyl-3,4-di-*O*-benzyl-β-*D*-galactopyranoside* (**26**).—To a solution of octyl 2-*O*-allyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranoside[14] (**25**, 2.07 g,

4.05 mmol) in 1:1 CH_2Cl_2–ether (80 mL), was added $LiAlH_4$ (465 mg, 12.24 mmol). The solution was heated to reflux and then $AlCl_3$ (165 mg 12.39 mmol) in ether (25 mL) was added dropwise over 45 min. The reaction was complete after 90 min and the reaction was quenched by the addition of EtOAc, then water. The solution was diluted with CH_2Cl_2 and extracted with water, bicarbonate, and brine. Chromatography (3:1 hexane–EtOAc) gave the product **26** (1.57 g, 76%) as a solid; $[\alpha]_D - 10.2°$ (*c* 0.8, $CHCl_3$), R_f 0.18 (3:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 7.25–7.42 (m, 10 H, Ph), 5.98 (1 H, H_c allyl), 5.29 (1 H, H_a allyl), 5.16 (1 H, H_b allyl), 4.94, 4.84, 4.73, 4.65 (4 d, 4 H, J_{gem} 11.5 Hz, PhCH_2), 4.42 (1 H, H_d allyl), 4.28 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.25 (1 H, H_e allyl), 3.90 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.65–3.80 (m, 3 H, H-2, H-3, H-4), 3.40–3.51 (m, 3 H, H-6a, H-6b, OCH_2CH$_2$), 3.34 (dt, 1 H, $J_{5,6}$ 6.5, $J_{4,5}$ 1 Hz, H-5), 1.52–1.67 (m, 2 H, OCH$_2$CH_2), 1.48 (dd, 1 H, $J_{6a,OH}$ 10.5, $J_{6b,OH}$ 6 Hz, 6-OH), 1.20–1.40 (10 H, octyl CH_2), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$): δ 138.64, 138.36 (Ph quaternary), 135.37 (CH_2–*C*HCH$_2$O), 128.72, 128.46, 127.96, 127.70, 127.66 (Ph methine), 104.09 (C-1), 82.23 (C-3, 79.49 (C-2), 74.52 (C-4), 74.11 (Ph*C*H$_2$), 74.03 (Ph*C*H$_2$), 73.57 (CH_2=CH*C*H$_2$O), 73.07 (C-5), 70.18 (O*C*H$_2$CH$_2$), 62.11 (C-6), 31.85, 29.72, 29.42, 29.28, 26.09, 22.70 (octyl CH_2), and 14.12 (octyl CH_3). Anal. Calcd for $C_{31}H_{44}O_6$ (512.69): C, 72.62; H, 8.65. Found: C, 72.50; H, 8.91.

*Octyl 2-*O*-allyl-3,4-di-*O*-benzyl-6-*O*-methyl-β-*D*-galactopyranoside* (**27**).—To a solution of **26** (219 mg, 0.43 mmol) in dry DMF (5 mL), NaH (44 mg, 80% in oil, 1.46 mmol) was added. After stirring for 15 min, MeI (80 μL, 1.28 mmol) was added and stirring was continued overnight. The mixture was diluted with CH_2Cl_2 and washed with $NaHCO_3$, water, and brine. Chromatography (3:1 hexane–EtOAc) gave the product **27** (215 mg, 95%) as an oil; $[\alpha]_D + 2.3°$ (*c* 0.7, $CHCl_3$); R_f 0.59 (3:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 7.20–7.40 (m, 10 H, Ph), 5.97 (1 H, H_c allyl), 5.28 (1 H, H_a allyl), 5.15 (1 H, H_b allyl), 4.93, 4.78, 4.70, 4.64 (4 d, 4 H, J_{gem} 11.5 Hz, PhCH_2), 4.41 (1 H, H_d allyl), 4.27 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 4.24 (1 H, H_e allyl), 3.90 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.82 (d, 1 H, $J_{3,4}$ 4 Hz, H-4), 3.68 (dd, 1 H, $J_{1,2}$ 8, $J_{2,3}$ 10 Hz, H-2), 3.49–3.50 (m, 5 H, H-3, H-5, H-6a, H-6b, OCH_2CH$_2$), 3.27 (s, 3 H, OCH_3), 1.52–1.67 (m, 2 H, OCH$_2$CH_2), 1.20–1.40 (10 H, octyl CH_2), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$); δ 138.70 (Ph quaternary), 135.42 (CH_2–*C*HCH$_2$O), 128.40, 128.34, 128.12, 127.52, 126.93 (Ph methine), 116.51 (*C*H$_2$–CHCH$_2$O), 103.98 (C-1), 82.09 (C-3), 79.37 (C-2), 74.41, 73.95 (Ph*C*H$_2$), 73.62 (C-5), 73.37 (C-4), 73.14 (CH_2=CH*C*H$_2$O), 71.24 (C-6), 70.04 (O*C*H$_2$CH$_2$), 59.06 (O*C*H$_3$), 31.82, 29.66, 29.38, 29.25, 26.06, 22.66 (octyl CH_2), and 14.09 (octyl CH_3). Anal. Calcd for $C_{32}H_{46}O_6$ (526.72): C, 72.97; H, 8.80. Found: C, 72.87; H, 8.68.

*Octyl 3,4-di-*O*-benzyl-6-*O*-methyl-β-*D*-galactopyranoside* (**28**).—To a solution of **27** (173 mg, 0.33 mmol) in 7:3:1 EtOH–benzene–water (10 mL), tris(triphenylphosphine)rhodium(I) chloride (49 mg, 0.05 mmol) and 1,4-diazabicyclo[2.2.2]octane (19 mg, 0.14 mmol) were added, and the solution was refluxed for 20 h. The solvent was evaporated and the residue dissolved in 9:1 acetone–water (10 mL).

Mercuric oxide (5 mg) and mercuric chloride (1.5 g) were added, and stirring was continued at room temperature overnight. The mixture was then diluted with CH_2Cl_2 and washed with satd KI, water, and brine. Evaporation of the organic layer followed by chromatography (3:1 EtOAc–hexane) gave **28** (130 mg, 81%) as a white solid; $[\alpha]_D$ + 9.4° (*c* 0.9, $CHCl_3$); R_f 0.24 (3:1 hexane–EtOAc). ^{1}H NMR ($CDCl_3$): δ 7.24–7.40 (m, 10 H, Ph), 4.91, 4.75, 4.67, 4.65 (4 d, 4 H, J_{gem} 11.5 Hz, PhCH_2), 4.22 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.94 (ddd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 9.5, $J_{2,OH}$ 2 Hz, H-2), 3.84–3.92 (m, 2 H, H-4, OCH_2CH_2), 3.46–3.54 (m, 4 H, H-5, H-6a, H-6b, OCH_2CH_2), 3.44 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 3 Hz, H-3), 3.30 (s, 3 H, OCH_3), 2.34 (d, 1 H, $J_{2,OH}$ 2 Hz, 2-OH), 1.57–1.68 (m, 2 H, OCH$_2$CH_2), 1.20–1.40 (10 H, octyl CH_2), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$): δ 138.60, 138.24 (Ph quanternary), 128.54, 128.34, 128.22, 127.80, 127.68, 127.61 (Ph methine), 103.32 (C-1), 81.96 (C-3), 74.56 (PhCH_2), 73.76 (C-5), 73.01 (C-4), 72.44 (PhCH_2), 71.51 (C-2), 71.12 (C-6), 70.04 (OCH_2CH_2), 59.14 (OCH_3), 31.85, 29.59, 29.42, 29.24, 25.98, 22.68 (octyl CH_2), and 14.11 (octyl CH_3). Anal. Calcd for $C_{29}H_{42}O_6$ (486.65): C, 71.57; H, 8.70. Found: C, 71.65; H, 8.66.

*Octyl 3,4-di-*O*-benzyl-6-*O*-methyl-2-*O*-(2,3,4-tri-*O*-benzyl-α-*L*-fucopyranosyl)-β-*D*-galactopyranoside* (**29**).—Alcohol **28** (77 mg, 0.16 mmol) was fucosylated as described for **18** with 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (0.635 mmol) and tetraethylammonium bromide (37 mg, 0.18 mmol). Column chromatography of the mixture (3:1 hexane–EtOAc) gave the disaccharide **29** (116 mg, 81%) as an oil; $[\alpha]_D$ − 60.5° (*c* 0.2, $CHCl_3$); R_f 0.40 (3:1 hexane–EtOAc). ^{1}H NMR ($CDCl_3$): δ 6.96–7.40 (m, 20 H, Ph), 5.71 (d, 1 H, $J_{1'2'}$ 3.5 Hz, H-1′), 4.95 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.40–4.88 (m, 11 H, H-1, H-5, 9 PhCH_2), 4.24 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 10 Hz, H-2), 4.03 (dd, 1 H, $J_{1'2'}$ 3.5, $J_{2'3'}$ 10 Hz, H-2′), 3.96 (dd, 1 H, $J_{2'3'}$ 10, $J_{3'4'}$ 2.5 Hz, H-3′), 3.92 (d, 1 H, $J_{3,4}$ 2.5 Hz, H-4), 3.89 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 3.74 (dd, $J_{2,3}$ 10, $J_{3,4}$ 2.5 Hz, H-3), 3.65 (br s, 1 H, H-4′), 3.45–3.56 (m, 3 H, H-5, H-6a, H-6b), 3.38 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 3.23 (s, 3 H, OCH_3), 1.45–1.58 (m, 2 H, OCH$_2$CH_2), 1.20–1.35 (10 H, octyl CH_2), 1.12 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6′), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$): δ 139.01, 138.87, 138.44, 138.30, 138.06 (Ph quaternary), 128.43, 128.37, 128.29, 128.25, 128.14, 128.03, 127.79, 127.55, 127.37, 127.25, 126.33 (Ph methine), 102.17 (C-1), 97.14 (C-1′), 84.55 (C-3), 79.70 (C-2), 78.20 (C-4′), 75.76 (C-3′), 74.76, 74.33 (PhCH_2), 73.38 (C-4), 73.07, 72.62 (PhCH_2), 72.09 (C-2′), 71.93 (C-5), 71.26 (PhCH_2), 71.18 (C-6), 69.75 (OCH_2CH_2), 66.20 (C-5′), 59.13 (OCH_3), 31.88, 29.73, 29.55, 29.35, 26.31, 22.67 (octyl CH_2), 16.55 (C-6′), and 14.12 (octyl CH_3). Anal. Calcd for $C_{56}H_{70}O_{10}$ (903.17): C, 74.47; H, 7.81. Found: C, 74.08; H, 7.84.

*Octyl 2-*O*-α-L-fucopyranosyl-6-*O*-methyl-β-D-galactopyranoside* (**9**).—The protected disaccharide **29** (80 mg, 0.09 mmol) was dissolved in MeOH (5 mL), 5% Pd–C (20 mg) was added, and the solution was stirred under a flow of H_2 overnight. The catalyst was filtered away, and the product purified as described for **7** to give **9** (37 mg, 93%) as a white solid. ^{1}H NMR (CD_3OD): δ 5.19 (d, 1 H, $J_{1'2'}$ 2 Hz, H-1′), 4.31 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), 4.29 (q, 1 H, $J_{5'6'}$ 6.5 Hz, H-5), 3.85 (dt, 1

H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.70–3.80 (m, 3 H, H-3, H-4, H-2′), 3.55–3.70 (m, 6 H, H-2, H-3′, H-4′, H-5, H-6a, H-6b), 3.50 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.37 (s, 3 H, OCH_3), 1.53–1.65 (m, 2 H, OCH$_2$CH_2), 1.24–1.43 (10 H, octyl CH$_2$), 1.18 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6′), and 0.88 (t, 3 H, J_{viz} 7 Hz, octyl CH$_3$); ^{13}C NMR (CD$_3$OD): δ 103.53 (C-1), 101.58 (C-1′), 79.00 (C-2), 75.62 (C-5), 74.77 (C-3), 73.74 (C-3′), 72.93 (C-6), 71.76 (C-4′), 70.83 (OCH$_2$CH$_2$), 70.62 (C-2′), 70.60 (C-4), 67.78 (C-5′), 59.45 (OCH$_3$), 33.00, 30.98, 30.58, 30.39, 27.28, 23.69 (octyl CH$_2$), 16.77 (C-6′), and 14.41 (octyl CH$_3$).

*Octyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-gulopyranoside* (**31**).—Silver triflate (609 mg, 2.37 mmol, dried in vacuo over P_2O_5 for 1 h), was stirred with collidine (155 μL, 1.27 mmole) and *n*-octanol (746 μL, 4.74 mmol) in CH$_2$Cl$_2$ (10 mL) containing crushed 3A molecular sieves (2.5 g), under N_2 at −30°C for 20 min. To this solution was added dropwise 2,3,4,6-tetra-*O*-acetyl-α-D-gulopyranosyl bromide[20] (**30**, 650 mg, 1.58 mmol) in CH$_2$Cl$_2$ (5 mL). The mixture was stirred under N_2 and warmed to room temperature. After stirring overnight the reaction was quenched with collidine (200 μL), and the mixture was filtered and evaporated. The residue was then chromatographed (4:1 hexane–EtOAc) to give the product **31** (478 mg, 66%) as an oil; $[\alpha]_D$ − 26.6° (*c* 0.7, CHCl$_3$); R_f 0.42 (4:1 hexane–EtOAc). ^{1}H NMR (CDCl$_3$): δ 5.39 (t, 1 H, $J_{3,4} = J_{2,3} = 3.5$ Hz, H-3), 5.01 (dd, 1 H, $J_{2,3}$ 3.5, $J_{1,2}$ 8 Hz, H-2), 4.97 (dd, 1 H, $J_{3,4}$ 3.5, $J_{4,5}$ 1 Hz, H-4), 4.75 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 4.13–4.30 (m, 3 H, H-5, H-6a, H-6b), 3.88, 3.50 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 2.15 (s, 6 H, acetate CH$_3$), 2.07, 2.02 (2 s, 6 H, acetate CH$_3$), 1.50–1.65 (m, 2 H, OCH$_2$CH_2), 1.20–1.40 (10 H, octyl CH$_2$), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR (CDCl$_3$): δ 170.47, 169.60, 169.43, 168.94 (C=O), 98.61 (C-1), 70.35 (C-5), 70.06 (OCH$_2$CH$_2$), 68.49 (C-3), 67.84 (C-4), 67.74 (C-2), 61.93 (C-6), 31.82, 29.52, 29.32, 29.26, 25.89, 22.66 (octyl CH$_2$), 20.74, 20.63 (acetate CH$_3$), and 14.09 (octyl CH$_3$). Anal. Calcd for $C_{22}H_{36}O_{10}$ (460.52): C, 57.38; H, 7.88. Found: C, 57.52; H, 7.98.

*Octyl β-*D*-gulopyranoside* (**32**).—Guloside **31** (373 mg, 0.81 mmol), was dissolved in MeOH (10 mL) and NaOMe (60 mg) added. After stirring for 48 h, the solution was neutralized by the addition of prewashed Amberlite IR 120 (H^+) resin. The solvent was evaporated and the residue was redissolved in water, then passed through a SepPak eluted first with water and then with MeOH. The MeOH eluent was evaporated, redissolved in water, filtered, and lyophilized to give the **32** (218 mg, 92%) as a gum; $[\alpha]_D$ − 60.9° (*c* 1, MeOH). ^{1}H NMR (CD$_3$OD): δ 4.57 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 3.94 (t, 1 H, $J_{2,3} = J_{3,4} = 3.5$ Hz, H-3), 3.82–3.92 (m, 2 H, H-4, OCH_2CH$_2$), 3.64–3.77 (m, 3 H, H-5, H-6a, H-6b), 3.60 (dd, 1 H, $J_{1,2}$ 8, $J_{2,3}$ 3.5 Hz, H-2), 3.51 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 1.55–1.68 (m, 2 H, OCH$_2$CH_2), 1.20–1.42 (10 H, octyl CH$_2$), and 0.89 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR (CD$_3$OD): δ 102.32 (C-1), 74.80 (C-5), 73.13 (C-3), 71.18 (C-4), 70.60 (OCH$_2$CH$_2$), 69.62 (C-2), 62.57 (C-6), 32.95, 30.83, 30.54, 30.35, 27.10, 23.66 (octyl CH$_2$), and 14.40 (octyl CH$_3$). Anal. Calcd for $C_{14}H_{28}O_6$ (292.37): C, 57.51; H, 9.65. Found: C, 57.71; H, 9.62.

*Octyl 2,3-*O*-isopropylidene-β-*D*-gulopyranoside* (**34**).—Compound **32** (191 mg,

0.65 mmol), was dissolved in DMF (5 mL) and 2,2-dimethoxypropane (2.25 mL, 18.3 mmol) was added. Toluenesulfonic acid (160 mg) was added and the mixture stirred for 1 h. The mixture was then neutralized with Et_3N (500 μL), the solvent was evaporated, and the residue chromatographed (3:1 hexane–EtOAc) to give **33** (223 mg, 92%) as an oil; R_f 0.65 (3:1 hexane–EtOAc). ^{1}H NMR showed four isopropylidene methyl signals (1.50, 1.48, 1.42, and 1.35), indicating the product to be the 2,3:4,6-diisopropylidene derivative. This product was not further characterized but rather was dissolved in MeOH (20 mL), then water (1 mL), and toluenesulfonic acid (10 mg) were added and the mixture was stirred for 5 h. The mixture was then neutralized with Et_3N (200 μL), then the solvent was evaporated and the residue chromatographed (3:1 hexane–EtOAc) to give **34** (147 mg, 74%) as an oil; $[\alpha]_D$ − 31.9° (*c* 0.3, $CHCl_3$); R_f 0.30 (3:1 hexane–EtOAc). ^{1}H NMR ($CDCl_3$): δ 4.84 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), 4.38 (dd, 1 H, $J_{2,3}$ 6.5, $J_{3,4}$ 2 Hz, H-3), 4.26 (dd, 1 H, $J_{2,3}$ 6.5, $J_{1,2}$ 3 Hz, H-2), 4.02 (ddd, 1 H, $J_{4,5}$ 1, $J_{5,6a}$ 6, $J_{5,6b}$ 7 Hz, H-5), 3.93 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 3.77–3.93 (m 3 H, H-4, H-6a, H-6b), 3.51 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 2.20 (dd, 1 H, $J_{6,OH}$ 10, $J_{6,OH}$ 4 Hz, 6-OH), 1.55–1.65 (m, 3 H, 4-OH, OCH_2CH_2), 1.50 (s, 3 H, $(CH_3)_2CO_2$), 1.20–1.35 (10 H, octyl CH_2), 1.35 (s, 3 H, $(CH_3)_2CO_2$), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$): δ 109.32 ($(CH_3)_2CO_2$), 99.12 (C-1), 74.85 (C-5), 73.40 (C-3), 71.99 (C-4), 69.48 (OCH_2CH_2), 67.61 (C-2), 63.65 (C-6), 31.77, 29.46, 29.30, 29.15 (octyl CH_2), 26.78 ($(CH_3)_2CO_2$), 25.94, (octyl CH_2), 24.59 ($(CH_3)_2CO_2$), 22.60 (octyl CH_2), and 14.04 (octyl CH_3). Anal. Calcd for $C_{17}H_{32}O_6$ (332.44): C, 61.42; H, 9.70. Found: C, 61.43; H, 9.96.

*Octyl 4,6-di-*O*-benzyl-2,3-*O*-isopropylidene-β-*D*-gulopyranoside* (**35**).—Compound **34** (75.4 mg, 0.23 mmol) was dissolved in dry DMF (3 mL). Sodium hydride (45 mg, 80% dispersion in oil, 1.50 mmol) was added and the mixture was stirred for 15 min. Benzyl bromide (162 μL, 1.36 mmol) was added and stirring was continued for 15 h. The solution was then cooled to 0°C, quenched with water, diluted with CH_2Cl_2, and washed with $NaHCO_3$, water, and brine. Evaporation of the organic layer gave a brown liquid, which was chromatographed (9:1 hexane–EtOAc) to give **35** (106 mg, 91%) as a colorless oil; $[\alpha]_D$ − 86.3° (*c* 0.5, $CHCl_3$); R_f 0.32 (9:1 hexane–EtOAc). ^{1}H NMR ($CDCl_3$): δ 7.22–7.47 (m, 10 H, Ph), 4.68, 4.54, 4.52, 4.46 (4 d, 4 H, J_{gem} 11.5 Hz, $PhCH_2$), 4.40 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), 4.32 (dd, 1 H, $J_{3,4}$ 2, $J_{2,3}$ 5.5 Hz, H-3), 4.00 (dd, 1 H, $J_{2,3}$ 5.5, $J_{1,2}$ 7 Hz, H-2), 3.81–3.95 (m, 2 H, H-5, OCH_2CH_2), 3.74 (br t, 1 H, $J_{4,5} = J_{3,4} = 2$ Hz, H-4), 3.70 (dd, 1 H, $J_{5,6a}$ 6.5, $J_{6a,6b}$ 10 Hz, H-6a), 3.62 (dd, 1 H, $J_{5,6b}$ 6, $J_{6a,6b}$ 10 Hz, H-6b), 3.48 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 1.54–1.70 (m, 2 H, OCH_2CH_2), 1.48, 1.34 (2 s, 6 H, $(CH_3)_2CO_2$), 1.20–1.40 (10 H, octyl CH_2), 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$): δ 138.25, 137.78 (Ph quaternary), 128.38, 128.13, 127.91, 127.63 (Ph methine), 109.28 ($(CH_3)_2CO_2$), 102.60 (C-1), 74.97 (C-5), 74.42 (C-4), 73.48, 72.98 ($PhCH_2$), 72.92 (C-3), 72.84 (C-2), 69.69 (OCH_2CH_2), 69.04 (C-6), 31.84, 29.61, 29.43, 29.25 (octyl CH_2), 28.08 26.11 ($(CH_3)_2CO_2$), 25.95, 22.67, (octyl CH_2), and

14.11 (octyl CH_3). Anal. Calcd for $C_{31}H_{44}O_6$ (512.69): C, 72.63; H, 8.65. Found: C, 72.61; H, 8.74.

Octyl 4,6-di-O-benzyl-β-D-gulopyranoside (**36**).—Compound **35** (320 mg, 0.63 mmol) was dissolved in CH_2Cl_2 (5 mL) and then water (500 μL) and 99% CF_3CO_2H (2 mL) added. After stirring for 30 min, the mixture was evaporated to dryness and the product purified by chromatography (3:1 hexane–EtOAc) to give **36** (258 mg, 87%) as a white solid; $[\alpha]_D - 53.3°$ (*c* 0.5, $CHCl_3$); R_f 0.28 (3:1 hexane–EtOAc). ^{1}H NMR ($CDCl_3$): δ 7.20–7.38 (m, 10 H, Ph), 4.42–4.64 (m, 5 H, PhCH_2, H-1), 4.18 (t, 1 H, $J_{2,3} = J_{3,4} = 3$ Hz, H-3), 4.11 (dt, 1 H, $J_{4,5}$ 1.5 $J_{5,6a} = J_{5,6b} = 6.5$ Hz, H-5), 3.90 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.73 (dd, 1 H, $J_{2,3}$ 3, $J_{1,2}$ 8 Hz, H-2), 3.67 (dd, 1 H, $J_{5,6a}$ 6.5, $J_{6a,6b}$ 10 Hz, H-6a), 3.62 (dd, 1 H, $J_{5,6b}$ 6.5, $J_{6a,6b}$ 10 Hz, H-6b), 3.60 (dd, 1 H, $J_{4,5}$ 1.5 $J_{3,4}$ 3 Hz, H-4), 3.46 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 2.64, 2.50 (br s, 1 H, 2-OH, 3-OH), 1.54–1.70 (m, 2 H, OCH$_2$CH_2), 1.20–1.40 (10 H, octyl CH_2), 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$): δ 138.28, 137.98 (Ph quaternary), 128.36, 128.03, 127.83, 127.68, 127.61 (Ph methine), 100.27 (C-1), 75.77 (C-5) 73.43, 72.93 (PhCH_2), 72.37 (C-4), 69.81 (C-3), 69.65 (OCH_2CH$_2$), 68.99 (C-2), 68.26 (C-6), 31.84, 29.67, 29.43, 29.25, 26.03, 22.67, (octyl CH_2), and 14.11 (octyl CH_3). Anal. Calcd for $C_{28}H_{40}O_6$ (472.62): C, 71.16; H, 8.53. Found: C, 71.43; H, 8.69.

Octyl 3-O-acetyl-4,6-di-O-benzyl-β-D-gulopyranoside (**37**).—Compound **36** (227 mg, 0.48 mmol) was dissolved in benzene (5 mL) and then triethyl orthoformate (1.4 mL, 8.4 mmol) added followed by *p*-toluenesulfonic acid (5 mg). After stirring for 1 h TLC indicated the presence of one carbohydrate spot (R_f 0.67, 3:1 hexane–EtOAc). The reaction was then neutralized with Et_3N (100 μL), and the mixture was diluted with ether and washed with water, $NaHCO_3$, and brine. After drying, the solvent was evaporated and the residue was dissolved in aq 80% acetic acid (5 mL). The solution was stirred for 10 min and then evaporated. The product was purified by chromatography (3:1 hexane–EtOAc) to give **37** (240 mg, 97%) as a clear oil; R_f 0.34 (3:1 hexane–EtOAc). ^{1}H NMR ($CDCl_3$): δ 7.00–7.20 (m, 10 H, Ph), 5.32 (t, 1 H, $J_{2,3} = J_{3,4} = 3.5$ Hz, H-3), 4.60 (d, 1 H, J_{vic} 11.5 Hz, PhCH_2), 4.50 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 4.42, 4.40, 4.34 (3 d, 3 H, J_{vic} 11.5 Hz, PhCH_2), 3.74–3.88 (m, 3 H, H-2, H-5, OCH_2CH$_2$), 3.49–3.60 (m, 3 H, H-4, H-6a, H-6b), 3.48 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 2.14, (d, 1 H, $J_{2,OH}$ 3.5 Hz, 2-OH), 2.06 (s, 3 H, acetate CH_3), 1.54–1.70 (m, 2 H, OCH$_2$CH_2), 1.20–1.40 (10 H, octyl CH_2), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3).

Octyl 4,6-di-O-benzyl-2-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-β-D-gulopyranoside (**39**).—Alcohol **37** (200 mg, 0.39 mmol) was fucosylated as described for **18** using 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (1.56 mmol) and tetraethylammonium bromide (90 mg, 0.43 mmol). At this point it was not possible to obtain **38** as a pure product, therefore the partially purified product (obtained by chromatography in 3:1 hexane–EtOAc, R_f 0.55) was dissolved in MeOH (10 mL), and NaOMe (15 mg) was added. The residue left after neutralization with Amberlite IR-120 (H^+) resin and solvent evaporation was chromatographed (6:1 hexane–

EtOAc) to give **39** (269 mg, 78%) as an oil; $[\alpha]_D$ – 95.3° (*c* 0.2, $CHCl_3$); R_f 0.35 (3:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 7.20–7.45 (m, 25 H, Ph), 4.98 (d, 1 H, J_{vic} 11.5 Hz, PhCH_2), 4.42–4.84 (m, 11 H, H-1, H-1′, 4.5 PhCH_2), 4.20 (q, 1 H, $J_{5'6'}$ 6.5 Hz, H-5′), 4.09 (dt, 1 H, $J_{5,6a} = J_{5,6b} = 6.5$, $J_{4,5}$ 1.5 Hz, H-5), 4.04 (dd, 1 H, $J_{2',3'}$ 10, $J_{3',4'}$ 3.5 Hz, H-3′), 3.91–3.99 (m, 2 H, H-2′, H-3), 3.86 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.74 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 3.5 Hz, H-2), 3.58–3.70 (m, 4 H, H-4, H-4′, H-6a, H-6b), 3.37 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 1.46–1.58 (m, 2 H, OCH$_2$CH_2), 1.18–1.35 (10 H, octyl CH$_2$), 1.11 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6′), an 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR ($CDCl_3$): δ 138.70, 138.39, 138.22, 138.10 (Ph quaternary) 128.52, 128.42, 128.39, 128.35, 128.27, 128.24, 128.13, 127.96, 127.86, 127.66, 127.58, 127.39 (Ph methine), 98.98 (C-1), 94.74 (C-1′), 79.92 (C-2), 77.66 (C-4′), 76.12 (C-5), 75.63 (C-2′), 74.85, 74.36 (PhCH$_2$), 73.37, 73.24, 72.85 (PhCH$_2$), 71.99 (C-4), 69.09 (OCH$_2$CH$_2$), 69.04 (C-6), 66.83 (C-3), 65.52 (C-5′), 31.89, 29.84, 29.51, 29.38, 26.19, 22.70 (octyl CH$_2$), 16.54 (C-6′), and 14.13 (octyl CH$_3$). Anal. Calcd for $C_{55}H_{68}O_{10}$ (889.15): C, 74.30; H, 7.71. Found: C, 74.49; H, 7.74.

Octyl 2-O-α-L-fucopyranosyl-β-D-gulopyranoside (**10**).—The protected disaccharide **39** (87 mg, 0.098 mmol) was dissolved in MeOH (5 mL), 5% Pd–C (20 mg) was added and the solution was stirred under a flow of H_2 for 15 h. The catalyst was filtered away, and the product purified as described for **7** to give **10** (39 mg, 91%) as a white solid. ^1H NMR (D_2O): δ 5.01 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 4.78 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 4.34 (q, 1 H, $J_{5'6'}$ 6.5 Hz, H-5′), 4.21 (t, 1 H, $J_{2,3} = J_{3,4} = 3$ Hz, H-3), 4.00 (t, 1 H, $J_{5,6a} = J_{5,6b} = 6.5$ Hz, H-5), 3.92 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.72–3.91 (m, 6 H, H-4, H-6a, H-6b, H-2′, H-3′, H-4′), 3.70 (dd, 1 H, $J_{1,2}$ 8, $J_{2,3}$ 3 Hz, H-2), 3.60 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 1.53–1.66 (m, 2 H, OCH$_2$CH_2), 1.24–1.50 (10 H, octyl CH$_2$), 1.22 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6′), and 0.86 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR (CD_3OD): δ 100.55 (C-1), 97.24 (C-1′), 74.90 (C-5), 73.98 (C-3′), 73.79 (C-3), 71.70 (C-4′), 70.51 (C-4), 70.30 (OCH$_2$CH$_2$), 69.99 (C-2), 69.71 (C-2′), 67.66 (C-5′), 62.54 (C-6), 33.00, 31.02, 30.59, 30.45, 27.42, 23.68 (octyl CH$_2$), 16.61 (C-6′), and 14.40 (octyl CH$_3$).

Octyl 2-O-allyl-4-O-benzoyl-3,6-di-O-benzyl-β-D-glucopyranoside (**41**).—To a solution of octyl 2-*O*-allyl-3,6-di-*O*-benzyl-β-D-galactopyranoside[14] (**40**, 926 mg, 1.81 mmol), in 19:1 CH_2Cl_3–pyridine (40 mL) at 0°C, was added dropwise triflic anhydride (1.30 mL, 7.7 mmol) in CH_2Cl_2 (5 mL). After stirring for 45 min TLC showed that the starting material was replaced by a new spot (R_f 0.55, 4:1 hexane–EtOAc). The mixture was then extracted with ice-cold 5% HCl and water, dried with Na_2SO_4, and evaporated to an orange liquid. This product was directly dissolved in dry DMF (100 mL), cooled to 0° C, and treated with sodium benzoate (2 g, 13.7 mmol). After stirring for 15 h and warming to room temperature, the mixture was diluted with CH_2Cl_2 and washed with water, $NaHCO_3$, and brine. The solvent was evaporated and the residue chromatographed (39:1 toluene–EtOAc) to give **41** (817 mg, 73%) as an oil; $[\alpha]_D$ – 55.7° (*c* 0.3, $CHCl_3$); R_f 0.35 (39:1 toluene–EtOAc). ^1H NMR ($CDCl_3$): δ 7.00–8.00 (m, 15 H, Ph), 5.96 (1 H,

H_c allyl), 5.30 (1 H, H_a allyl), 5.20 (t, 1 H, $J_{3,4} = J_{4,5} = 10$ Hz, H-4), 5.18 (1 H, H_b allyl), 4.79, 4.62, 4.51, 4.46 (4 d, 4 H, J_{gem} 11.5 Hz, PhCH_2), 4.43 (1 H, H_d allyl), 4.42 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.22 (1 H, H_e allyl), 3.96 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.69 (t, 1 H, $J_{3,4} = J_{2,3} = 10$ Hz, H-3), 3.56–3.68 (m, 3 H, H-5, H-6a, H-6b), 3.54 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.43 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 10 Hz, H-2), 1.58–1.70 (m, 2 H, OCH$_2$CH_2), 1.20–1.45 (10 H, octyl CH$_2$), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR (CDCl$_3$): δ 165.42 (C=O), 138.08, 137.94 (Ph quaternary), 135.01 (CH$_2$=*C*HCH$_2$O), 133.12, 129.79, 128.37, 128.24, 128.14, 128.06, 127.65, 127.51 (Ph methine), 117.01 (*C*H$_2$=CHCH$_2$O), 103.54 (C-1), 81.80 (C-3), 81.44 (C-2), 75.07 (Ph*C*H$_2$), 73.73 (C-5), 73.65 (Ph*C*H$_2$), 71.51 (C-4), 70.30 (O*C*H$_2$CH$_2$), 69.94 (C-6), 31.85, 29.73, 29.39, 29.28, 26.11, 22.68 (octyl CH$_2$), and 14.12 (octyl CH$_3$). Anal. Calcd for $C_{38}H_{48}O_7$ (616.80): C, 74.00; H, 7.84. Found: C, 73.71; H, 8.13.

Octyl 4-O-benzoyl-3,6-di-O-benzyl-β-D-glucopyranoside (**42**).—To a solution of **41** (98 mg, 0.16 mmol) dissolved in 7:3:1 EtOH–benzene–water (10 mL), tris(triphenylphosphine)rhodium(I) chloride (21 mg, 0.02 mmol) and 1,4-diazabicyclo [2.2.2]octane (8 mg, 0.07 mmol) were added and the solution was refluxed for 20 h. The solvent was evaporated and the residue dissolved in 9:1 acetone–water (15 mL). Mercuric oxide (2 mg) and mercuric chloride (500 mg) were added and stirring was continued at room temperature overnight. The mixture was then diluted with CH_2Cl_2 and washed with satd aq KI, water, and brine. Evaporation of the organic layer followed by chromatography (4:1 EtOAc–hexane) gave **42** (65 mg, 72%) as an oil; $[\alpha]_D$ – 37.0° (*c* 0.7, $CHCl_3$); R_f 0.40 (4:1 hexane–EtOAc). ^{1}H NMR (CDCl$_3$): δ 7.00–8.00 (m, 15 H, Ph), 5.26 (t, 1 H, $J_{3,4} = J_{4,5} = 10$ Hz, H-4), 4.78, 4.70 (2 d, 2 H, J_{gem} 11.5 Hz, PhCH_2), 4.48 (s, 2 H, PhCH_2), 4.36 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.95 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.59–3.77 (5 H, H-2, H-3, H-5, H-6a, H-6b), 3.56 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 2.41 (d, 1 H, $J_{2,OH}$ 2 Hz, 2-OH), 1.60–1.72 (m, 2 H, OCH$_2$CH_2), 1.20–1.40 (10 H, octyl CH$_2$), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR (CDCl$_3$): δ 165.44 (C=O), 138.09, 137.88 (Ph quaternary), 133.23, 129.84, 129.73, 128.43, 128.28, 128.01, 127.71, 127.62, 127.56 (Ph methine), 102.74 (C-1), 81.25 (C-3), 74.59 (C-5), 74.30 (PhCH_2), 74.04 (C-2), 73.67 (PhCH_2), 71.26 (C-4), 70.37 (O*C*H$_2$CH$_2$), 69.81 (C-6), 31.85, 29.66, 29.42, 29.27, 26.04, 22.69 (octyl CH$_2$), and 14.13 (octyl CH$_3$). Anal. Calcd for $C_{35}H_{44}O_7$ (576.73): C, 72.89; H, 7.69. Found: C, 72.74; H, 7.87.

Octyl 3,6-di-O-benzyl-2-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-β-D-glucopyranoside (**44**).—Alcohol **42** (79 mg, 0.14 mmol) was fucosylated as described for **18** with 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (0.68 mmol) and tetraethylammonium bromide (32 mg, 0.15 mmol). At this point it was not possible to obtain a pure product (**43**), therefore the partially purified product was dissolved in MeOH (10 mL), and NaOMe (15 mg) added. Removal of the benzoate was sluggish and after stirring for 2 days at room temperature the solution was heated at 50°C for 12 h to complete the saponification. The residue left after neutralization with Amberlite IR-120 (H^+) resin and solvent evaporation was chro-

matographed (4:1 hexane–EtOAc) to give **44** (97 mg, 80%) as an oil; $[\alpha]_D$ – 84.4° (*c* 0.3, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.38–7.90 (m, 25 H, Ph), 5.54 (d, 1 H, $J_{1'2'}$ 3.5 Hz, H-1'), 4.50–5.00 (m, 10 H, PhCH_2), 4.44 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.40 (q, 1 H, $J_{5'6'}$ 6.5 Hz, H-5'), 4.08 (dd, 1 H, $J_{2'3'}$ 10.5, $J_{1'2'}$ 3.5 Hz, H-2'), 3.98 (dd, 1 H, $J_{2'3'}$ 10.5, $J_{3'4'}$ 2.5 Hz, H-3'), 3.86 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 3.59–3.81 (m, 6 H, H-2, H-3, H-4, H-4', H-6a, H-6b), 3.36–3.48 (m, 2 H, OCH_2CH_2, H-5), 2.57 (d, 1 H, $J_{4,OH}$ 2 Hz, 4-OH), 1.45–1.60 (m, 2 H, OCH_2CH_2), 1.20–1.35 (10 H, octyl CH_2), 1.11 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6'), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$): δ 138.83, 138.77, 138.75, 138.22, 137.81 (Ph quaternary), 128.49, 128.46, 128.35, 128.17, 128.13, 127.81, 127.75, 127.53, 127.46, 127.41, 127.11 (Ph methine), 101.93 (C-1), 97.33 (C-1'), 85.79 (C-3), 79.87 (C-2), 77.96 (C-4'), 75.87 (C-5), 74.96 (C-4), 74.80, 74.20, 73.74, 73.72 (PhCH_2), 73.64 (C-3'), 72.96 (PhCH_2), 72.64 (C-2'), 70.73 (OCH_2CH_2), 69.96 (C-6), 66.37 (C-5'), 31.87, 29.77, 29.49, 29.34, 26.26, 22.67 (octyl CH_2), 16.63 (C-6'), and 14.11 (octyl CH_3). Anal. Calcd for $C_{55}H_{68}O_{10}$ (889.14): C, 74.30; H, 7.71. Found: C, 74.01; H, 7.84.

*Octyl 2-O-α-*L*-fucopyranosyl-β-*D*-glucopyranoside* (**11**).—The protected disaccharide **44** (90 mg, 0.10 mmol) was dissolved in MeOH (5 mL), 5% Pd–C (50 mg) was added, and the solution was stirred under a flow of H_2 for 24 h. The catalyst was filtered away and the product purified as described for **7** to give **11** (33 mg, 74%) as a white solid. ^1H NMR (CD_3OD): δ 5.22 (br s, 1 H, H-1'), 4.35 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.29 (q, 1 H, $J_{5'6'}$ 6.5 Hz, H-5'), 3.91 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 3.85 (dd, 1 H, $J_{5,6}$ 2, $J_{6a,6b}$ 12 Hz, H-6a), 3.74 (m, 1 H, H-2'), 3.53–3.70 (m, 4 H, H-4, H-3', H-4', H-6b), 3.50 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 3.27–3.37 (m, 2 H, H-2, H-3), 1.50–1.70 (m, 2 H, OCH_2CH_2), 1.23–1.45 (10 H, octyl CH_2), 1.18 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6'), and 0.89 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR (CD_3OD): δ 103.06 (C-1), 101.44 (C-1'), 80.96 (C-2), 78.76 (C-3), 77.83 (C-5), 75.12 (C-4), 73.76 (C-3'), 71.74 (C-4'), 71.56 (C-3'), 70.85 (OCH_2CH_2), 70.61 (C-2'), 67.81 (C-5'), 62.73 (C-6), 33.01, 30.96, 30.63, 30.41, 27.31, 23.70 (octyl CH_2), 16.77 (C-6'), and 14.40 (octyl CH_3).

*3-Azido-3-deoxy-1:2,5:6-di-O-isopropylidene-α-*D*-galactofuranose* (**46**).—To a solution of 1:2,5:6-di-*O*-isopropylidene-α-D-gulofuranose[21] (**45**, 1.03 g, 3.96 mmol), in 19:1 CH_2Cl_2–pyridine (40 mL) at 0°C, was added dropwise triflic anhydride (2.83 mL, 16.8 mmol) in CH_2Cl_2 (2 mL). After stirring for 15 min, TLC showed that the starting material was replaced by a new spot (R_f 0.36, 3:1 hexane–EtOAc). The mixture was then extracted with ice-cold 5% HCl and water, dried with Na_2SO_4, and evaporated to an orange liquid. This product was directly dissolved in dry DMF (100 mL) and cooled to 0°C, and sodium azide (1.29 g, 19.8 mmol) was added. After stirring for 2 h and warming to room temperature the reaction mixture was diluted with CH_2Cl_2 and washed with water and brine. The residue left after evaporation was chromatographed (6:1 hexane–EtOAc) to give **46** (985 mg, 87%) as a colorless oil; $[\alpha]_D$ – 26.9° (*c* 0.5, $CHCl_3$); R_f 0.58 (3:1 hexane–EtOAc). IR ($CHCl_3$) 2108.05 cm^{-1}, N_3. ^1H NMR ($CDCl_3$): δ 5.80 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.61 (dd, 1 H $J_{1,2}$ 4, $J_{2,3}$ 2 Hz, H-2), 4.35 (dt, 1 H, $J_{5,6}$ 6.5, $J_{4,5}$ 5.5 Hz,

H-5), 4.08 (dd, 1 H, $J_{5,6}$ 6.5, $J_{6a,6b}$ 8.5 H-6a), 3.95 (dd, 1 H, $J_{2,3}$ 2, $J_{3,4}$ 5.5 Hz, H-3), 3.87 (dd, 1 H, $J_{5,6}$ 6.5, $J_{6a,6b}$ 8.5 Hz, H-6b), 3.83 (t, 1 H, $J_{4,5} = J_{3,4} = 5.5$ Hz, H-4), 1.57, 1.44, 1.38, and 1.36 (4 s, 12 H, $(CH_3)_2CO_2$). ^{13}C NMR ($CDCl_3$): δ 114.41, 110.09 ($(CH_3)_2CO_2$), 104.86 (C-1), 85.76 (C-4), 83.13 (C-2), 74.58 (C-5), 65.59 (C-6), 65.56 (C-3), 27.52, 26.90, 26.37, and 25.20 ($(CH_3)_2CO_2$). Anal. Calcd for $C_{12}H_{19}N_3O_5$ (285.30): C, 50.52; H, 6.71; N, 14.73. Found: C, 50.37; H, 6.44; N, 14.56.

*1,2,4,6-Tetra-*O*-acetyl-3-azido-3-deoxy-*D*-galactopyranose* (**47**).—Azide **46** (985 mg, 3.45 mmol), was dissolved in 90% CF_3CO_2H (10 mL) and stirred at room temperature for 15 min. The mixture was evaporated in vacuo and the resulting oil was dissolved in pyridine (30 mL) and then cooled to 0°C. To this solution Ac_2O (20 mL) was added dropwise, and the mixture was stirred overnight while being allowed to warm to room temperature. Evaporation of the solvent followed by chromatography (3:1 hexane–EtOAc) gave the product **47** (727 mg, 56%) as a mixture of anomers ($\alpha:\beta$ 1:1); R_f 0.23 (3:1 hexane–EtOAc). Partial ^{1}H NMR ($CDCl_3$): δ 6.16 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1α), 5.50 (d, 1 H, $J_{1,2}$ 8 Hz, H-1β).

*2,4,6-Tri-*O*-acetyl-3-azido-3-deoxy-α-*D*-galactopyranosyl bromide* (**48**).—Compound **47** (663 mg, 1.78 mmol), was dissolved in 10:1 CH_2Cl_2–EtOAc (44 mL). Titanium tetrabromide (1 g, 2.72 mmol) was added and the mixture was stirred at room temperature for 3 days. The reaction was quenched by adding NaOAc (1 g) and stirring for 1 h, then the suspension was diluted with CH_2Cl_2 and extracted with water. The organic layer was filtered and evaporated, and the residue chromatographed (3:1 hexane–EtOAc) to give the product **48** (585 mg, 84%) as an oil; R_f 0.36 (3:1 hexane–EtOAc). ^{1}H NMR ($CDCl_3$): δ 6.70 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.56 (dd, 1 H, $J_{3,4}$ 2.5, $J_{4,5}$ 1 Hz, H-4), 4.95 (dd, 1 H, $J_{2,3}$ 10, $J_{1,2}$ 3.5 Hz, H-2), 4.41 (t, 1 H, $J_{5,6}$ 6 Hz, H-5), 4.19 (dd, 1 H, $J_{5,6a}$ 6.5, $J_{6a,6b}$ 11 Hz, H-6a), 4.14 (dd, 1 H, $J_{2,3}$ 10, $J_{1,2}$ 3.5 Hz, H-3), 4.05 (dd, 1 H, $J_{5,6b}$ 6.5, $J_{6a,6b}$ 11 Hz, H-6b) 2.18, 2.16, and 2.07 (3 s, 9 H, acetate CH_3).

*Octyl 2,4,6-tri-*O*-acetyl-3-azido-3-deoxy-β-*D*-galactopyranoside* (**49**).—Compound **48** (644 mg, 1.74 mmol) was glycosylated as described for the conversion of **30** to **31**, using silver triflate (440 mg, 1.71 mmol), collidine (104 μL, 0.86 mmol), and *n*-octanol (710 μL, 4.5 mmol) in CH_2Cl_2 (10 mL) containing crushed 3A molecular sieves (2.5 g). After 8 h the reaction was quenched with collidine (200 μL), and the mixture was filtered and washed with 2 M HCl, water, $NaHCO_3$, and brine. After evaporation, the residue was chromatographed (3:1 hexane–EtOAc) to give the product **49** (320 mg, 63%) as an oil; $[\alpha]_D$ − 15.0 (*c* 1.0, $CHCl_3$); R_f 0.32 (4:1 hexane–EtOAc). ^{1}H NMR ($CDCl_3$): δ 5.42 (dd, 1 H, $J_{3,4}$ 3.5, $J_{4,5}$ 1 Hz, H-4), 5.17 (dd, 1 H, $J_{1,2}$ 8, $J_{2,3}$ 10.5 Hz, H-2), 4.44 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 4.13 (d, 2 H, $J_{5,6}$ 7 Hz, H-6a, H-6b), 3.83–3.93 (m, 2 H, OCH_2CH_2, H-5), 3.58 (dd, 1 H, $J_{3,4}$ 3.5, $J_{2,3}$ 10.5 Hz, H-3), 3.47 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 2.19, 2.13, 2.06 (3 s, 9 H, acetate CH_3), 1.50–1.65 (m, 2 H, OCH_2CH_2), 1.25–1.40 (m, 10 H, octyl CH_2), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3). ^{13}C NMR ($CDCl_3$): δ 170.47, 170.08, 169.25 (acetate C=O), 101.45 (C-1), 71.67 (C-5), 70.24 (OCH_2CH_2), 69.87 (C-3), 67.78

(C-4), 61.81 (C-3), 61.57 (C-6); 31.85, 29.47, 29.32, 29.29, 25.87, 22.69 (octyl CH_2), 20.79, 20.73, 20.69 (acetate CH_3), and 14.12 (octyl CH_3). Anal. Calcd for $C_{21}H_{33}N_3O_8$ (443.49): C, 54.17; H, 7.50; N, 9.47. Found: C, 54.50; H, 7.73; N, 9.38.

Octyl 3-azido-3-deoxy-β-D-galactopyranoside (**50**).—Galactoside **49** (300 mg, 0.68 mmol), was dissolved in MeOH (10 mL) and NaOMe (30 mg) was added. After stirring overnight, the solution was neutralized by the addition of prewashed Amberlite IR-120 (H^+) resin. Evaporation of the solvent followed by chromatography (19:1 CH_2Cl_2–MeOH) gave the product **50** (194 mg, 90%) as a white solid; $[\alpha]_D$ − 0.8° (*c* 0.9, MeOH); R_f 0.15 (19:1 CH_2Cl_2–MeOH). ^1H NMR (CD_3OD): δ 4.26 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.83–3.94 (m, 2 H, H-4, OCH_2CH_2), 3.63–3.75 (m, 3 H, H-2, H-6a, H-6b), 3.47–3.50 (m, 2 H, H-5, OCH_2CH_2), 3.28 (dd, 1 H, $J_{2,3}$ 10.5, $J_{3,4}$ 3 Hz, H-3), 1.57–1.68 (m, 2 H, OCH_2CH_2), 1.20–1.45 (m, 10 H, octyl CH_2), and 0.83 (t, 3 H, J_{vic} 7 Hz, octyl CH_3). ^{13}C NMR (CD_3OD): δ 105.07 (C-1), 77.09 (C-5), 70.88 (OCH_2CH_2), 70.59 (C-2), 69.40 (C-4), 66.88 (C-3), 62.25 (C-3), 32.95, 30.77, 30.51, 30.35, 27.05, 23.66 (octyl CH_2), and 14.40 (octyl CH_3). Anal. Calcd for $C_{14}H_{27}N_3O_5$ (317.39): C, 52.98; H, 8.58; N, 13.24. Found: C, 53.23; H, 8.87; N, 13.06.

Octyl 3-azido-4,6-O-benzylidene-3-deoxy-β-D-galactopyranoside (**51**).—Compound **50** (119 mg, 0.38 mmol) and benzaldehyde dimethyl acetal (171 μL, 1.14 mmol) were dissolved in MeCN (25 mL) and *p*-toluenesulfonic acid (5 mg) was added. After stirring for 30 min the mixture was neutralized with Et_3N, the solution was evaporated, and the residue was chromatographed (3:1 hexane–EtOAc) to give **51** (130 mg, 85%) as a white solid; $[\alpha]_D$ + 6.9° (*c* 0.5, $CHCl_3$); R_f 0.33 (3:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 7.31–7.55 (m, 5 H, Ph), 5.58 (s, 1 H, $PhCHO_2$), 4.33 (dd, 1 H, $J_{5,6a}$ 1.5, $J_{6a,6b}$ 11.5 Hz, H-6a), 4.30 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.21 (d, 1 H, $J_{3,4}$ 3.5 Hz, H-4), 4.08 (dd, 1 H, $J_{5,6a}$ 1.5, $J_{6a,6b}$ 1.5 Hz, H-6b), 4.02 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 10 Hz, H-2), 3.96 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 3.49 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 3.46 (br s, 1 H, H-5), 3.35 (dd, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 3.5 Hz, H-3), 2.72 (br s, 1 H, 2-OH), 1.57–1.62 (m, 2 H, OCH_2CH_2), 1.15–1.40 (m, 10 H, octyl CH_2), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3). ^{13}C NMR ($CDCl_3$): δ 137.38 (Ph quaternary), 128.99, 128.16, 126.18 (Ph methine), 103.30 (C-1), 101.15 ($PhCHO_2$), 75.17 (C-4), 70.18 (OCH_2CH_2), 69.19 (C-2), 68.84 (C-5), 67.28 (C-3) 62.25 (C-6), 31.82, 29.52, 29.40, 29.24, 25.97, 22.66 (octyl CH_2), and 14.10 (octyl CH_3). Anal. Calcd for $C_{21}H_{31}N_3O_5$ (405.40): C, 62.20; H, 7.71; N, 10.36. Found: C, 62.26; H, 7.87; N, 10.29.

Octyl 3-azido-4,6-O-benzylidene-3-deoxy-2-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-β-D-galactopyranoside (**52**).—Alcohol **51** (118 mg, 0.29 mmol) was fucosylated as described for **18** using 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (1.16 mmol) and tetraethylammonium bromide (67 mg, 0.32 mmol). Column chromatography of the mixture (3:1 hexane–EtOAc) gave the disaccharide **52** (130 mg, 55%) as a white solid; $[\alpha]_D$ − 22.2° (*c* 0.7, $CHCl_3$); R_f 0.42 (3:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 7.20–7.58 (m, 20 H, Ph), 5.60 (s, 1 H, $PhCHO_2$), 5.39 (d, 1 H, $J_{1'2'}$ 3.5 Hz, H-1'), 4.97, 4.88, 4.84, 4.77, 4.72, 4.66 (6 d, 6 H, J_{gem} 11.5 Hz, $PhCH_2$), 4.43 (d,

1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.27–4.38 (m, 3 H, H-5′, H-4, H-6a), 4.06–4.14 (m, 3 H, H-6b, H-2, H-2′), 3.94 (dd, 1 H, $J_{2'3'}$ 10, $J_{3'4'}$ 2.5 Hz, H-3′), 3.90 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 3.66 (d, 1 H, $J_{3'4'}$ 2.5 Hz, H-4′), 3.50 (dd, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 3.5 Hz, H-3), 3.43 (br s, 1 H, H-5), 3.39 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 1.50–1.62 (m, 2 H, OCH_2CH_2), 1.15–1.35 (m, 10 H, octyl CH_2), 1.10 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6′), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3). ^{13}C NMR ($CDCl_3$): δ 139.09, 138.79, 138.49, 137.27 (Ph quaternary), 128.96, 128.35, 128.32, 128.21, 128.18, 127.60, 127.52, 127.44, 127.40, 126.19 (Ph methine), 102.90 (C-1), 101.18 ($PhCHO_2$), 97.16 (C-1′), 79.47 (C-4′), 78.02 (C-3′), 76.29 (C-3), 75.56 (C-2′), 74.77, 73.26, 73.24 ($PhCH_2$), 71.21 (C-4), 69.74 (OCH_2CH_2), 69.23 (C-6), 66.99 (C-5′), 66.68 (C-5), 64.04 (C-3), 31.87, 29.61, 29.51, 29.33, 26.20, 22.67 (octyl CH_2), 16.64 (C-6′), and 14.12 (octyl CH_3). Anal. Calcd for $C_{48}H_{59}N_3O_9$ (822.01): C, 70.14; H, 7.23; N, 5.11. Found: C, 70.22; H, 7.43; N, 5.08.

Octyl 3-amino-3-deoxy-2-O-(α-L-fucopyranosyl)-β-D-galactopyranoside (**12**).—To a solution of protected disaccharide **52** (63 mg, 0.08 mmol) in 4:1 EtOH–CH_2Cl_2 (10 mL) was added 10% Pd–C (30 mg) and 2 M HCl (40 μL, 0.08 mmol), and the solution was stirred under a flow of H_2 overnight. After completion of the reaction the catalyst was filtered away and the solvent evaporated. Chromatography (10:4:1 $CHCl_2$–MeOH–ammonium hydroxide) followed by dissolution in water and filtration through a 22-μm filter gave the product **12** (21 mg, 60%) as a white solid; R_f 0.20 (10:4:1 CH_2Cl_2–MeOH–ammonium hydroxide). ^1H NMR (D_2O): 5.04 (d, 1 H, $J_{1'2'}$ 2.5 Hz, H-1′), 4.53 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.23 (q, 1 H, $J_{5'6'}$ 6.5 Hz, H-5′), 4.00 (d, 1 H, $J_{3,4}$ 3 Hz, H-4), 3.62–3.95 (m, 8 H, H-5, H-6a, H-6b, OCH_2CH_2, H-2′, H-3′, H-4′) 3.54 (dd, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 5 Hz, H-3), 1.60–1.70 (m, 2 H, OCH_2CH_2), 1.25–1.40 (10 H, octyl CH_2), 1.23 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6′), and 0.88 (t, 3 H J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR (D_2O): 102.69 (C-1), 102.46 (C-1′), 79.92 (C-2), 76.73 (C-5), 72.72 (C-3′), 71.45 (OCH_2CH_2), 70.46 (C-4′), 69.54 (C-2′), 68.13 (C-5′), 67.56 (C-5′), 61.33 (C-6), 57.00 (C-6), 32.12, 29.93, 29.66, 29.47, 26.16, 23.01 (octyl CH_2), 16.55 (C-6′), and 14.38 (octyl CH_3).

Octyl 4-azido-2,3,6 tri-O-benzyl-4-deoxy-β-D-galactopyranoside (**54**).—To a solution of octyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside[14] (**53**, 203 mg, 0.36 mmol), in 19:1 CH_2Cl_2–pyridine (10 mL) at 0°C, was added dropwise triflic anhydride (260 μL, 1.53 mmol) in CH_2Cl_2 (2 mL). After stirring for 30 min, TLC showed the starting material was replaced by a new spot (R_f 0.63, 4:1 hexane–EtOAc) appeared. The mixture was then extracted with ice-cold 5% HCl and water, dried with Na_2SO_4, and evaporated to an orange liquid. This product was directly dissolved in dry DMF (10 mL) and cooled to 0°C, and sodium azide (120 mg, 1.85 mmol) was added. After stirring for 15 h and warming to room temperature, the mixture was diluted with CH_2Cl_2 and washed with water and brine. The residue left after evaporation was chromatographed (4:1 hexane–EtOAc) to give **54** (157 mg, 74%) as a colorless oil; $[\alpha]_D - 4.0°$ (*c* 0.2, $CHCl_3$); R_f 0.50 (4:1 hexane–EtOAc), IR ($CHCl_3$): 2105.69 cm^{-1}, N_3. ^1H NMR ($CDCl_3$): δ 7.26–7.44 (m, 15 H, Ph), 4.89 (d, 1 H, J_{gem} 11.5 Hz, $PhCH_2$), 4.75 (s, 2 H, $PhCH_2$), 4.55 (s, 2 H,

PhCH_2), 4.72 (d, 1 H, J_{gem} 10.5 Hz, PhCH_2), 4.30 (m, 1 H, H-1), 3.98 (dd, 1 H, $J_{3,4}$ 3, $J_{4,5}$ 1 Hz), 3.89 (dt, 1 H, J_{gem} 11, J_{vic} 7 Hz, OCH_2CH$_2$), 3.52–3.70 (m, 5 H, H-2, H-3, H-5, H-6a, H-6b), 3.46 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 1.52–1.70 (m, 2 H, OCH$_2$CH_2), 1.15–1.45 (10 H, octyl CH$_2$), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR (CDCl$_3$): δ 138.57, 137.90, 137.73 (Ph quaternary), 128.52, 128.47, 128.31, 128.13, 127.94, 127.85, 127.79, 127.65 (Ph methine), 103.84 (C-1), 80.01 (C-3), 79.37 (C-2), 75.38, 73.74, 72.95 (PhCH_2), 71.57 (C-5), 70.16 (OCH_2CH$_2$), 68.69 (C-6), 60.21 (C-4), 31.85, 29.73, 29.43, 29.26, 26.16, 22.68 (octyl CH$_2$), and 14.11 (octyl CH$_3$). Anal. Calcd for $C_{35}H_{45}N_3O_5$ (587.76): C, 71.52; H, 7.72; N, 7.15. Found: C, 71.68; H, 7.99; N, 7.13.

*Octyl 4-amino-4-deoxy-β-*D*-galactopyranoside* (**55**). Galactoside **54** (1.10 g, 1.87 mmol) in EtOH (100 mL) was stirred overnight under a flow of H_2 in the presence of 5% Pd–C (550 mg) and 2 M HCl (1.87 mL, 3.74 mmol). Filtration from the catalyst followed by chromatography (10:4:1 CH_2Cl_2–MeOH–ammonium hydroxide) gave the product **55** (320 mg, 59%) as a white solid; R_f 0.52 (10:4:1 CH_2Cl_2–MeOH–ammonium hydroxide). ^{1}H NMR (D$_2$O): δ 4.35 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 3.92 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.67–3.80 (m, 4 H, H-3, H-5, H-6a, H-6b), 3.64 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.44 (dd, 1 H, $J_{1,2}$ 8, $J_{2,3}$ 10 Hz, H-2), 3.16 (d, 1 H, $J_{3,4}$ 4 Hz, H-4), 1.55–1.70 (m, 2 H, OCH$_2$CH_2), 1.20–1.40 (m, 10 H, octyl CH$_2$), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$). ^{13}C NMR (D$_2$O): δ 104.13 (C-1), 75.45 (C-5), 73.60 (C-3), 71.40 (C-2), 71.34 (OCH_2CH$_2$), 61.94 (C-6), 52.42 (C-4), 32.29, 29.93, 29.76, 29.67, 26.24, 23.12 (octyl CH$_2$), and 14.42 (octyl CH$_3$).

*Octyl 4-deoxy-4-trifluoroacetamido-β-*D*-galactopyranoside* (**56**).—Compound **55** (270 mg, 0.93 mmol) was dissolved in MeOH (75 mL) and *S*-ethyl trifluorothioacetate (400 μL, 3.13 mmol) was added at 0°C. The mixture was stirred overnight and the solvent evaporated. Chromatography (19:1 CH_2Cl_2–MeOH) gave the product **56** (280 mg, 78%) as an oil; $[\alpha]_D$ −20° (*c* 0.30, $CHCl_3$); R_f 0.54 (19:1 CH_2Cl_2–MeOH). ^{1}H NMR (CD$_3$OD): δ 4.46 (dd, 1 H, $J_{3,4}$ 4.5, $J_{4,5}$ 1 Hz, H-4), 4.26 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.91 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.74 (dd, 1 H, $J_{3,4}$ 4.5, $J_{2,3}$ 9.5 Hz, H-3), 3.70 (ddd, 1 H, $J_{5,6a}$ 5.5, $J_{5,6b}$ 6.5, $J_{6a,6b}$ 11.5 Hz, H-6a), 3.48–3.63 (m, 3 H, H-5, H-6b, OCH_2CH$_2$), 3.44 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 9.5 Hz, H-2), 1.55–1.70 (m, 2 H, OCH$_2$CH_2), 1.20–1.40 (m, 10 H, octyl CH$_2$), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$). ^{13}C NMR (CD$_3$OD): δ 160.01 (q, $J_{C,F}$ 37 Hz, C=O), 117.49 (q, $J_{C,F}$ 287 Hz, CF_3), 105.16 (C-1), 75.06 (C-5), 73.22 (C-3), 72.55 (C-2), 71.19 (OCH_2CH$_2$), 62.01 (C-6), 52.80 (C-4), 32.94, 30.81, 30.50, 30.36, 27.08, 23.66 (octyl CH$_2$), and 14.40 (octyl CH$_3$). Anal. Calcd for $C_{16}H_{28}F_3NO_6$ (387.40): C, 49.61; H, 7.29; N, 3.62. Found: C, 49.60; H, 7.37; N, 3.58.

*Octyl 3,6-di-*O*-benzoyl-4-deoxy-4-trifluoroacetamido-β-*D*-galactopyranoside* (**57**).—A mixture of compound **56** (120 mg, 0.31 mmol) and dibutyltin oxide (154 mg, 0.62 mmol) in dry benzene (30 mL) was boiled overnight under reflux through a column of 4A molecular sieves. The solution was cooled to room temperature and crushed 4A molecular sieves (500 mg) and benzoyl chloride (108 μL, 0.93 mmol)

were added. After stirring overnight the solvent was evaporated and the residue chromatographed to give the product **57** (140 mg, 76%) as a white solid; $[\alpha]_D$ − 45.3° (*c* 0.9, $CHCl_3$); R_f 0.27 (3:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 7.80–8.18 (m, 4 H, Ph), 7.31–7.63 (m, 6 H, Ph), 6.86 (d, 1 H, $J_{NH,CH}$ 10 Hz, N*H*), 5.32 (dd, 1 H, $J_{2,3}$ 10.5, $J_{3,4}$ 4.5 Hz, H-3), 4.90 (dd, 1 H, $J_{4,NH}$ 10, $J_{3,4}$ 4.5 Hz, H-4), 4.59 (dd, 1 H, $J_{5,6a}$ 6.5 $J_{6a,6b}$ 11.5 Hz, H-6a), 4.48 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.27 (dd, 1 H, $J_{5,6b}$ 6.5, $J_{6a,6b}$ 11.5 Hz, H-6b), 4.18 (dt, 1 H, $J_{5,6a} = J_{5,6b} = 6.5$, $J_{4,5}$ 1 Hz, H-5), 3.89 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 3.78 (ddd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 10.5, $J_{2,OH}$ 3 Hz, H-2), 3.58 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 2.81 (d, 1 H, $J_{2,OH}$ 3 Hz, 2-OH), 1.55–1.70 (m, 2 H, OCH_2CH_2), 1.20–1.40 (m, 10 H, octyl CH_2). 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3). ^{13}C NMR ($CDCl_3$): δ 165.95 (C=O, ester), 157.60 (q, 1 C, $J_{C,F}$ 38 Hz, C=O), 133.49, 129.79 (Ph methine), 129.21, 129.09, (Ph quaternary), 128.55, 128.46 (Ph methine), 115.73 (q, 1 C, $J_{C,F}$ 288 Hz, CF_3), 103.78 (C-1), 73.15 (C-5), 70.98 (OCH_2CH_2), 70.67 (C-3), 70.31 (C-2), 61.72 (C-6), 49.08 (C-4), 31.60, 29.55, 29.31, 29.22, 25.88, 22.65 (octyl CH_2), and 14.09 (octyl CH_3). Anal. Calcd for $C_{30}H_{36}F_3NO_8$ (595.61): C, 60.50; H, 6.09; N, 2.35. Found: C, 60.26; H, 6.08; N, 2.38.

Octyl 3,6-di-O-benzoyl-4-deoxy-2-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-4-trifluoroacetamido-β-D-galactopyranoside (**58**).—Alcohol **57** (130 mg, 0.22 mmol), silver triflate (497 mg, 1.94 mmol, dried for 1 h over P_2O_5), and 2,6-di-*tert*-butyl-4-methylpyridine (318 mg, 1.55 mmol) were stirred in CH_2Cl_2 (5 mL) with ground 4A molecular sieves (500 mg) for 15 min. The solution was cooled to −78°C and freshly prepared 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (1.29 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The solution was allowed to warm to room temperature. Although after 4 h TLC showed the presence of the starting alcohol, the reaction had stopped and therefore was quenched with collidine and the solution diluted with CH_2Cl_2. The organic solution was washed with 2 M HCl, water, $NaHCO_3$, and brine. Column chromatography of the residue left after solvent evaporation (6:1 hexane–EtOAc) gave disaccharide **58**, (93 mg, 42%) as an oil; $[\alpha]_D$ − 40.3° (*c* 0.3, $CHCl_3$); R_f 0.49 (3:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 6.80–8.10 (m, 25 H, Ph), 6.75 (d, 1 H, $J_{NH,CH}$ 9.5 Hz, N*H*), 5.52 (dd, 1 H, $J_{3,4}$ 4.5, $J_{2,3}$ 9.5 Hz, H-3), 5.34 (d, 1 H, $J_{1'2'}$ 3.5 Hz, H-1′), 4.90–4.99 (m, 2 H, H-4, $PhCH_2$), 4.76 (d, 1 H, J_{gem} 11.5 Hz, $PhCH_2$), 4.55–4.68 (m, 4 H, 4 $PhCH_2$), 4.20–4.34 (m, 4 H, H-1, H-6a, H-6b, H-5′), 4.15 (t, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 4.02 (dd, 1 H, $J_{1,2}$ 7.0, $J_{2,3}$ 9.5 Hz, H-2), 3.92 (dd, $J_{1'2'}$ 3.5, $J_{2'3'}$ 9.5 Hz, H-2′) 3.82–3.90 (m, 2 H, OCH_2CH_2, H-3′), 3.64 (d, 1 H, $J_{3'4'}$ 2 Hz, H-4′), 3.51 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 1.60–1.70 (m, 2 H, OCH_2CH_2), 1.20–1.40 (m, 10 H, octyl CH_2), 1.13 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6′), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3). ^{13}C NMR ($CDCl_3$): δ 165.94, 165.18 (C=O, ester), 157.87 (C=O, amide), 138.83, 137.77, (Ph quaternary) 133.61, 133.48, 129.83, 129.69 (Ph methine), 128.95, 128.70, (Ph quaternary), 128.58, 128.42, 128.35, 128.24, 128.14, 127.72, 127.64, 127.46, 127.39 (Ph methine), 102.65 (C-1), 97.58 (C-1′), 79.32 (C-4′), 77.82 (C-3′), 75.56 (C-2′), 74.86 ($PhCH_2$), 74.78 (C-2), 73.29, 72.70 ($PhCH_2$), 72.00 (C-3), 70.69 (OCH_2CH_2), 70.31

(C-5), 66.95 (C-5′), 61.65 (C-6), 49.16 (C-4), 31.86, 29.67, 29.41, 29.31, 26.14, 22.69 (octyl CH_2), 16.64 (C-6′), and 14.13 (octyl CH_3). Anal. Calcd for $C_{57}H_{64}F_3NO_{12}$ (1012.13): C, 67.64; H, 6.37; N, 1.38. Found: C, 67.67; H, 6.27; N, 1.45.

Octyl 4-amino-4-deoxy-2-O-(α-L-fucopyranosyl)-β-D-galactopyranoside (**13**).—To a solution of protected disaccharide **58** (82 mg, 0.08 mmol) in MeOH (10 mL), 10% Pd–C (45 mg) was added, and the solution was stirred under a flow of H_2 overnight. After completion of the reaction the catalyst was filtered away and the solvent evaporated. The residue was redissolved in MeOH (20 mL), 1 M NaOH (1 mL) was added, and the mixture stirred for 5 h. The solution was neutralized with Amberlite IR-120 (H^+) resin and evaporated, and the residue further purified as described for **7** to give the product **13** (27 mg, 77%) as a white solid. ^{1}H NMR (D_2O): δ 5.25 (d, 1 H, $J_{1'2'}$ 3.5 Hz, H-1′), 4.44 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.31 (q, 1 H, $J_{5'6'}$ 6.5 Hz, H-5′), 3.50–3.97 (m, 10 H, H-2, H-3, H-5, H-6a, H-6b, OCH_2CH_2, H-2′, H-3′, H-4′), 3.10 (d, 1 H, $J_{3,4}$ 4.5 Hz, H-4), 1.58–1.68 (m, 2 H, OCH_2CH_2), 1.23–1.45 (10 H, octyl CH_2), 1.18 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6′), and 0.88 (t, 3 H J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR (D_2O): δ 102.06 (C-1), 99.81 (C-1′), 77.10 (C-2), 74.93 (C-5), 74.07 (C-3), 73.71 (C-3′), 72.12 (C-4′), 70.49 (OCH_2CH_2), 69.83 (C-2′), 68.57 (C-5′), 66.83 (C-5), 61.27 (C-6), 51.89 (C-4), 31.57, 29.41, 29.11, 28.95, 25.75, 22.39 (octyl CH_2), 15.83 (C-6′), and 13.74 (octyl CH_3).

Octyl 2-O-allyl-3,4-di-O-benzyl-6-deoxy-6-phthalimido-β-D-galactopyranoside (**59**).—Compound **26** (238 mg, 0.46 mmol), triphenylphosphine (244 mg, 0.93 mmol), and phthalimide (107 mg (0.73 mmol) were dissolved dry THF (10 mL). To this solution was added diethyl azodicarboxylate (160 μL 0.93 mmol) and the mixture was stirred overnight. The solvent was evaporated and the residue chromatographed (3:1 hexane–EtOAc) to give the product **59** (272 mg, 91%) as an oil; $[\alpha]_D$ + 15.8° (*c* 0.8, $CHCl_3$); R_f 0.49 (3:1 hexane–EtOAc). ^{1}H NMR ($CDCl_3$): δ 7.65–7.90 (m, 4 H, Ar phthalimido), 7.20–7.40 (m, 10 H, Ph), 5.96 (1 H, H_c allyl), 5.27 (1 H, H_a allyl), 5.14 (1 H, H_b allyl), 5.04, 4.83, 4.74, 4.73 (4 d, 4 H, J_{gem} 11.5 Hz, $PhCH_2$), 4.39 (1 H, H_d allyl), 4.22 (1 H, H_e allyl), 4.18 (d, 1 H, $J_{1,2}$ 8 Hz, H-1), 4.09 (dd, 1 H, $J_{5,6a}$ 8, $J_{6a,6b}$ 13.5 Hz, H-6a), 3.61–3.79 (m, 4 H, OCH_2CH_2, H-2, H-4, H-5), 3.55 (dd, 1 H, $J_{5,6b}$ 4.5, $J_{6a,6b}$ 13.5 Hz, H-6b), 3.45 (dd, 1 H, $J_{2,3}$ 10, $J_{3,4}$ 2.5 Hz, H-3), 3.29 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH_2), 1.40–1.55 (m, 2 H, OCH_2CH_2), 1.12–1.30 (10 H, octyl CH_2), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$): δ 168.06 (C=O), 138.56, 138.48 (Ph quaternary), 135.37 (CH_2=$CHCH_2O$), 133.96 (Ph methine), 131.97 (Ph quaternary), 128.63, 128.35, 128.19, 127.60, 127.56, 123.22 (Ph methine), 116.51 (CH_2=$CHCH_2O$), 103.77 (C-1), 82.34 (C-3), 79.06 (C-2), 74.23, 73.86 ($PhCH_2$), 73.77 (C-5), 73.48 (CH_2=$CHCH_2O$), 71.50 (C-4), 69.97 (OCH_2CH_2), 38.93 (C-6), 31.75, 29.52, 29.23, 29.18, 25.95, 22.61 (octyl CH_2), and 14.07 (octyl CH_3). Anal. Calcd for $C_{39}H_{47}NO_7$ (641.81): C, 72.98; H, 7.38; N, 2.19. Found: C, 72.65; H, 7.26; N, 2.19.

Octyl 3,4-di-O-benzyl-6-deoxy-6-phthalimido-β-D-galactopyranoside (**60**).—To compound **59** (315 mg, 0.49 mmol) in 7:3:1 EtOH–benzene–water (15 mL) tris(triphenylphosphine)rhodium(I) chloride (123 mg, 0.133 mmol) and 1,4-di-

azabicyclo[2.2.2]octane (45 mg, 0.40 mmol) were added, and the solution was refluxed for 24 h. The solvent was evaporated and the residue dissolved in 9:1 acetone–water (20 mL). Mercuric oxide (5 mg) and mercuric chloride (1.5 g) were added and stirring was continued at room temperature overnight. The mixture was then diluted with CH_2Cl_2 and washed with satd aq KI, water, and brine. Evaporation of the organic layer followed by chromatography (3:1 EtOAc–hexane) gave **60** (190 mg, 65%) as a white solid; $[\alpha]_D + 19.1°$ (*c* 0.5, $CHCl_3$); R_f 0.24 (3:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 7.70–7.90 (4 H, Ar phthlimido), 7.20–7.45 (m, 10 H, Ph), 5.03, 4.80, 4.75, 4.73 (4 d, 4 H, J_{gem} 11.5 Hz, PhCH_2), 4.13 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.11 (dd, 1 H, $J_{5,6a}$ 7.5, $J_{6a,6b}$ 13.5 Hz, H-6a), 4.00 (ddd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 9.5, $J_{2,OH}$ 2 Hz, H-2), 3.79 (d, 1 H, $J_{3,4}$ 3 Hz, H-4), 3.58–3.75 (m, 3 H, H-5, H-6b, OCH_2CH$_2$), 3.42 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 3 Hz, H-3), 3.34 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 2.41 (d, 1 H, $J_{2,OH}$ 2 Hz, 2-OH), 1.40–1.59 (m, 2 H, OCH$_2$CH_2), 1.20–1.45 (10 H, octyl CH$_2$), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR ($CDCl_3$): 168.02 (C=O), 138.29, 138.05 (Ph quaternary), 133.97 (Ph methine), 131.89 (Ph quaternary), 128.49, 128.43, 128.20, 127.72, 127.60, 123.21 (Ph methine), 103.10 (C-1), 82.31 (C-3), 74.28 (PhCH_2), 73.17 (C-5), 72.81 (PhCH_2) 71.83 (C-4), 71.26 (C-2), 69.68 (OCH_2CH$_2$), 38.89 (C-6), 31.70, 29.42, 29.19, 29.11, 25.80, 22.56 (octyl CH$_3$), and 14.03 (octyl CH$_3$). Anal. Calcd for $C_{36}H_{43}NO_7$ (601.74): C, 71.86; H, 7.20; N, 2.33. Found: C, 71.96; H, 7.30; N, 2.36.

*Octyl 3,4-di-*O*-benzyl-6-deoxy-6-phthalimido-2-*O*-(2,3,4-tri-*O*-benzyl-α-*L*-fucopyranosyl)-β-*D*-galactopyranoside* (**61**).—Alcohol **60** (100 mg, 0.17 mmol) was fucosylated as described for **18** using 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (0.825 mmol) and tetraethylammonium bromide (38 mg, 0.18 mmol). Column chromatography of the mixture (3:1 hexane–EtOAc) gave the disaccharide **61** (132 mg, 79%) as an oil; $[\alpha]_D - 54.2°$ (*c* 0.3, $CHCl_3$); R_f 0.30 (3:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 7.65–7.90 (m, 4 H, Ar phthalimido), 7.00–7.40 (m, 25 H, Ph), 5.68 (d, 1 H, $J_{1'2'}$ 3.5 Hz, H-1'), 4.46–4.98 (m, 10 H, 5 PhCH_2), 4.42 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5'), 4.25–4.37 (m, 2 H, H-1, H-2), 4.10 (dd, 1 H, $J_{5,6a}$ 7, $J_{6a,6b}$ 13 Hz, H-6a), 4.04 (dd, 1 H, $J_{1'2'}$ 3.5, $J_{2',3'}$ 10 Hz, H-2'), 3.94 (dd, 1 H, $J_{2'3'}$ 10, $J_{3'4'}$ 2.5 Hz, H-3'), 3.85 (d, 1 H, $J_{3'4'}$ 2 Hz, H-4'), 3.57–3.76 (m, 5 H, H-3, H-4, H-5, H-6b, OCH_2CH$_2$), 3.23 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 1.36–1.49 (m, 2 H, OCH$_2$CH_2), 1.10–1.30 (13 H, octyl CH$_2$, H-6'), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$); ^{13}C NMR ($CDCl_3$): 168.05 (C=O), 133.99 (Ph methine), 131.99 (Ph quaternary), 138.92, 138.80, 138.30, 138.23, 137.90 (Ph quanternary), 128.63, 128.43 128.23, 128.07, 127.99, 127.33, 127.20, 126.35, 123.23 (Ph methine), 102.01 (C-1), 97.21 (C-1'), 84.73 (C-3), 79.62 (C-4'), 78.07 (C-3'), 75.73 (C-2'), 74.70, 74.10, 72.93, 72.65 (PhCH_2), 72.12 (C-3), 72.05 (C-5), 71.62 (C-4), 71.58 (PhCH_2), 69.40 (OCH_2CH$_2$), 66.21 (C-5'), 39.01 (C-6), 31.82, 29.58, 29.39, 29.28, 26.19, 22.63 (octyl CH$_2$), 16.52 (C-6'), and 14.09 (octyl CH$_3$). Anal. Calcd for $C_{63}H_{71}NO_{11} \cdot H_2O$ (1036.28): C, 73.04; H, 7.10; N, 1.35. Found: C, 73.27; H, 7.03; N, 1.29.

*Octyl 3,4-di-*O*-benzyl-6-deoxy-2-*O*-(2,3,4-tri-*O*-benzyl-α-*L*-fucopyranosyl)-6-trifluoroacetamido-β-*D*-galactopyranoside* (**62**).—Disaccharide **61** (257 mg, 0.25 mmol)

was dissolved in MeOH (10 mL) and hydrazine acetate (690 mg, 7.5 mmol) was added. The solution was refluxed for 3 h, then another portion of hydrazine acetate was added (690 mg, 7.5 mmol) and refluxing was continued for a total of 24 h. The solution was cooled, diluted with CH_2Cl_2, and washed with water and brine. The crude product, which showed no phthalimido signal in the ^1H NMR, was not further purified, but was dissolved in DMF (3 mL) and Et_3N (20 μL) was added. The solution was cooled to −30°C and then *S*-ethyl trifluorothioacetate (160 μL, 1.25 mmol) in DMF (2 mL) was added dropwise. The mixture was stirred overnight, being allowed to come to room temperature. Dilution with CH_2Cl_2 followed by extraction with water and brine gave an oil that was chromatographed (6:1 hexane–EtOAc) to furnish the disaccharide **62** (173 mg, 70%) as an oil; R_f 0.32 (6:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 7.02–7.44 (m, 25 H Ph), 6.17 (br s, 1 H, N*H*), 5.65 (d, 1 H, $J_{1'2'}$ 3.5 Hz, H-1′), 4.96, 4.91 (2 d, 2 H, J_{gem} 11.5 Hz, PhCH_2), 4.60–4.80 (m, 5 H, PhCH_2), 4.57 (m, 2 H, PhCH_2), 4.50 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.41 (m, 2 H, H-1, H-5′), 4.20 (t, 1 H, $J_{1,2}$ 8 Hz, H-2), 4.06 (dd, 1 H, $J_{1'2'}$ 8 Hz, H-2), 4.06 (dd, 1 H, $J_{1'2'}$ 3.5, $J_{2'3'}$ 10 Hz, H-2′), 3.97 (dd, 1 H, $J_{3'4'}$ 2.5, $J_{2',3'}$ 10 Hz, H-3′), 3.82 (dt, 1 H, J_{gem} 10, J_{vic} 7 Hz, OCH_2CH$_2$), 3.68–3.74 (m, 3 H, H-4, H-6a, H-6b), 3.66 (d, 1 H, $J_{3',4'}$ 2.5 Hz, H-4′), 3.34–3.57 (m, 3 H, H-3, H-5, OCH_2CH$_2$), 1.47–1.58 (m, 2 H, OCH$_2$CH_2), 1.20–1.35 (10 H, octyl CH$_2$), 1.14 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6′), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$).

Octyl 6-amino-6-deoxy-2-O-(α-L-fucopyranosyl)-β-D-galactopyranoside (**14**).—The protected disaccharide **62** (165 mg, 0.17 mmol) was dissolved in MeOH (10 mL), 5% Pd–C (100 mg) was added, and the solution was stirred under a flow of H_2 overnight. The catalyst was filtered away, and the solvent evaporated. The product was redissolved in MeOH (10 mL) and 1 M NaOH (1 mL) was added. After stirring overnight the product was neutralized with Amberlite IR-120 (H^+) resin and purified as described for **7** to give **14** (45 mg, 61%) as a white solid. ^1H NMR (D_2O): δ 5.27 (d, 1 H, $J_{1'2'}$ 3.5 Hz, H-1′), 4.49 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.36 (q, 1 H, $J_{5'6'}$ 6.5 Hz, H-5), 3.76–3.99 (m, 6 H, H-2′, H-3′, H-4, H-5, H-2, OCH_2CH$_2$), 3.52–3.73 (m, 3 H, H-4′, H-3, OCH_2CH$_2$), 2.97 (dd, 1 H, $J_{5,6a}$ 8, $J_{6a,6b}$ 13 Hz, H-6a), 2.84 (dd, 1 H, $J_{5,6b}$ 4, $J_{6a,6b}$ 13 Hz, H-6b), 1.57–1.70 (m, 2 H, OCH$_2$CH_2), 1.21–1.41 (10 H, octyl CH$_2$), 1.11 (d, 3 H, $J_{5'6'}$ 6.5 Hz, H-6′), and 0.88 (t, 3 H, J_{vic} 7 Hz, octyl CH$_3$). ^{13}C NMR (D_2O): δ 102.20 (C-1), 99.98 (C-1′), 76.36 (C-2), 74.35 (C-5), 72.70 (C-3′), 71.50 (O*C*H$_2$CH$_2$), 71.29 (C-4′), 70.36 (C-2′), 69.05 (C-4), 67.58 (C-5′), 40.88 (C-6), 31.93, 29.70, 29.40, 29.26, 26.22, 22.83 (octyl CH$_2$), 16.22 (C-6′), and 14.20 (octyl CH$_3$).

Measurement of enzyme kinetics.—Radiochemical assays were based on modification of a previously described method which takes advantage of the use of hydrophobic acceptors and products to facilitate the removal of unreacted radiolabelled donor from reaction products[15]. Human serum used as a source of the A and B transferases was prepared by allowing freshly drawn blood to clot at room temperature for 2 h, refrigerating overnight at 4°C, and centrifuging to remove clots. The serum was then stored frozen at −20°C in 100-μL aliquots. Incubations for the A and B assays were carried out in 600-μL plastic microfuge tubes at 37°C.

For the A transferase all assays were carried out in a total volume of 66 μL, with 50 mM sodium cacodylate buffer, pH 6.9, containing 20 mM $MnCl_2$, 30 μM UDP-GalNAc, 0.2 μCi UDP-[6-^{3}H]GalNAc, and 10 μL of human serum containing the A transferase (61 μU/mL serum). Under these conditions, the rate of product formation with the native disaccharide **6** was shown to be linear up to a time of 60 min. Incubations were carried out for 45 min and then quenched by the addition of EDTA (400 μL of a 23 mM solution). The mixtures were transferred to preequilibrated[15] C_{18} SepPak cartridges and the unreacted radiolabelled donor was removed by washing with dil ammonia and then water until background counts were obtained. The radiolabelled product was eluted with MeOH (1 × 3 mL) and quantitated by liquid scintillation[15]. The K_m of **6** was determined to be 1.50 μM under these conditions[14]. Assays to test activity as an acceptor were carried out at concentrations of 2.5 μM. The results are presented in Table I. To test for inhibitory activity, the potential inhibitor (25 μM) was added to **6** at 2.5 μM. The results are recorded in Table III. At concentrations of **6** greater than 25 μM, substrate inhibition was observed[14]. For compound **9** the K_m was determined over these concentrations: 100, 50, 25, 12.5, 6.25, 3.13, and 1.56 μM. Finally, in determining the K_m of **14**, the substrate concentrations used were: 259, 129.5, 64.8, 32.4 16.2, 8.1, and 4 μM.

For the B transferase assay conditions were identical to those described above except that the solution contained 30 μM UDP-Gal, 0.2 μCi UDP-[6^{3}H]Gal, 250 μM ATP, and 25 μL of human serum containing the B transferase (12.8 μU/mL serum). Using these conditions, the rate of product formation with the native disaccharide **6** was linear up to a time of 180 min. Incubations were carried out for 120 min. The K_m of **6** was 21.9 μM under these conditions[14]. Assays to test activity as an acceptor were carried out at concentrations of 10 μM. To test for inhibitory activity, the potential inhibitor (100 μM) was added to disaccharide **6** at 10 μM. At concentrations of **6** greater than 50 μM, substrate inhibition was observed[14]. The results are presented in Tables I and III. In determining K_m values, the following substrate concentrations were used. Compound **9**: 804.5, 605.4, 402.25, 302.7, 201.1, 100.6, 50.3, 25.1, and 12.5 μM. Compound **14**: 826.4, 630, 413.2, 310, 206.6, 103.3, 51.7, 25.8, and 12.9 μM. Inhibitor concentrations of 5, 10, and 15 μM were used in the determination of the a K_i for **10**.

Rate data were fit to the Michalis–Menten equation using unweighted nonlinear regression with the SigmaPlot 4.0 program to estimate the kinetic parameters shown in Table II. Unless otherwise stated, the inhibition constants shown in Table IV were calculated using the SigmaPlot 4.0 program, fitting the data to an equation for competitive inhibition.

ACKNOWLEGDMENTS

We thank Dr. O.P. Srivastava for advice on the preparation of compound **13** and S.C. Crawley, Dr. M.M. Palcic, and Dr. S. Gosselin for assistance in perform-

ing and analyzing the enzyme kinetic experiments. This work was supported by the Natural Sciences and Engineering Research Council of Canada. T.L.L. is the recipient of a studentship from the Alberta Heritage Foundation for Medical Research.

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