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Synthesis and enzymatic evaluation of modified acceptors of recombinant blood group A and B glycosyltransferases

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Abstract

The disaccharide α-L-Fuc*p*-(1→2)-β-D-Gal*p*-(1→*O*)-Octyl (**1**) is an acceptor for the human blood group A and B glycosyltransferases. Seven analogues of **1**, containing deoxy, methoxy and arabino modifications of the Fuc residue, were chemically synthesized and kinetically evaluated in radioactive enzymatic assays. Both the enzymes tolerate modification of the 3′-OH on the fucose residue. The 2′-OH was found to be key to the recognition of the acceptors by these enzymes. The arabino derivative was recognized as an acceptor by the A transferase (K_m of 200 μM), but not the B transferase and is the first synthetic acceptor capable of distinguishing between the two enzyme activities.

Keywords: Glycosyltransferase; Human blood group; Synthesis; Enzyme; Acceptor, enzyme

1. Introduction

The blood group A and B glycosyltransferases are two enzymes responsible for the biosynthetic formation of the human blood group A and B antigens from the common acceptor, the blood group O(H) antigen. They are morphologically typical of the glycosyltransferase family of enzymes as they possess a cytoplasmic tail consisting of 16 amino acids, a trans-membrane region with 21 amino acids, a stem region and a large C-terminal catalytic domain consisting of 316 amino acids located inside the Golgi apparatus [1–4]. The great interest generated in understanding the involvement of blood group antigens in the invasion and metastasis of tumor cells led us to take a closer look at some of the glycosyltransferases that synthesize these structures in vivo, viz., the blood group A and B glycosyltransferases, respectively, the α-(1→3)-*N*-acetylgalactosaminyl and the α-(1→3)-galactosyltransferase. In recent years, the genes coding for these enzymes have been cloned using cDNA libraries. These studies have shown that the number of amino acids is the same in both the enzymes, and they differ in their amino acid sequences at only four positions in the catalytic domain of the proteins [5–7]. In vivo, the B transferase transfers Gal from UDP-Gal, and the A transferase uses UDP-GalNAc as the donor to form the B and the A antigens, respectively. These carbohydrate structures are found on the surfaces of erythrocytes and other cells and in soluble form in the cytoplasm [8]. The disaccharide, α-L-Fuc*p*-(1→2)-β-D-Gal*p*-*O*R, serves as the common acceptor for both the

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enzymes, R being a glycoprotein or a glycolipid in vivo. Various alkyl groups can be used as the aglycon without loss of acceptor activity [9]. Prior to this study, it was not known whether these two enzymes differed in their acceptor specificity, although it had been shown that the B transferase is in general less tolerant of changes in the acceptor structure [10,11].

The blood group A and B glycosyltransferases represent an ideal system for the study of a glycosyltransferase active site and the design and synthesis of specific glycosyltransferase inhibitors since they differ in their sequence by only four amino acids and because they have been cloned and expressed in *E. coli* [12,13], giving us access to substantial amounts of these enzymes. To identify the sites of molecular recognition on the protein in the active site, the hydroxyl groups on the acceptor and/or the donor structure can be modified to see which part of these compounds is required in the recognition process. In order to gain a detailed understanding of the interactions between the acceptor substrate and the enzyme, we designed and synthesized modified acceptors to probe the enzyme active site, an approach that has been used frequently in our group [14–18]. The systematic modification on the galactose moiety had already been described as part of the initial work on these enzymes [10,11]. For the present project it was decided that the hydroxyl groups on the Fuc residue would be replaced with H and *O*-methyl groups, and the C-6′ methyl on the Fuc residue would be replaced by H.

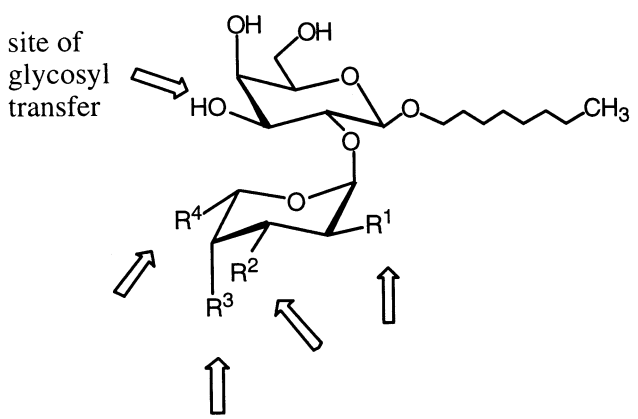


Fig. 1. Some modified disaccharides synthesized for this study.

1 $R^1 = R^2 = R^3 = OH$, $R^4 = CH_3$ (native)
2 $R^1 = R^2 = OH$, $R^3 = OMe$, $R^4 = CH_3$ (4′-methoxy)
3 $R^1 = R^2 = OH$, $R^3 = H$, $R^4 = CH_3$ (4′-deoxy)
4 $R^1 = R^3 = OH$, $R^2 = OMe$, $R^4 = CH_3$ (3′-methoxy)
5 $R^1 = R^3 = OH$, $R^2 = H$, $R^4 = CH_3$ (3′-deoxy)
6 $R^2 = R^3 = OH$, $R^1 = OMe$, $R^4 = CH_3$ (2′-methoxy)
7 $R^2 = R^3 = OH$, $R^1 = H$, $R^4 = CH_3$ (2′-deoxy)
8 $R^1 = R^2 = R^3 = OH$, $R^4 = H$ (arabino)

This report describes the synthesis of some analogues of the minimum acceptor structure recognized by these two enzymes, α-L-Fuc*p*-(1→2)-β-D-Gal*p*-*O*-Octyl (**1**) and their enzymatic evaluation. Several acceptor analogues were synthesized by modifying the hydroxyl groups on the fucose residue (Fig. 1) and assayed with these enzymes in order to determine the functional group specificities, i.e., the steric and hydrogen-bonding requirements in the active site of the enzymes. Deoxy analogues of compound **1** were prepared to assess the H-bonding interactions between the hydroxyl groups on the Fuc moiety and polar groups in the active site. Moreover, a hydrogen is non-polar and the smallest group that can replace a hydroxyl [19,20]. Methoxy groups can be H-bond acceptors but not donors and they also probe the steric requirements of the active site. Additionally, they are more hydrophobic than the native hydroxyl group [21]. The arabino analogue was prepared to determine the role of the 6′-methyl group on the Fuc residue. The octyl aglycon facilitates the purification of these compounds by reverse-phase C_{18} cartridges. It also permitted the use of radioactive Sep-Pak assays [22] of these synthetic analogues with the glycosyltransferases being studied. The biochemical evaluations of these compounds are discussed and an analysis of the results obtained is presented.

2. Results and discussion

Chemical synthesis of the disaccharide analogues.—The monosaccharide building blocks were synthesized using established protection–deprotection strategies. In order to obtain the

required disaccharides modified at the 2-, 3-, and 4-positions of the Fuc residue, an octyl β-D-galactopyranoside (**25**) protected at the 3-, 4-, and 6-positions was coupled with suitably protected Fuc and Ara derivatives using halide ion-catalyzed glycosylation or thioglycoside activation with dimethylmethylthiosulfonium triflate (DMTST) [23,24]. Under these conditions, formation of β-fucosides was not observed. Instead of using individually O-methylated and deoxygenated fucose donors, temporary protecting groups that can be removed after glycosylation were used. Methylation and deoxygenation were performed on the disaccharides, followed by deprotection to obtain the target compounds. Retrosynthetically, fucose with the 3-OH or the 4-OH free can be obtained regioselectively from a common precursor, in a single step, and this route was chosen instead of preparing them individually by two separate chemical manipulations. Phase-transfer catalysis was utilized in this step, and the precursor was obtained by the hydrolysis of the isopropylidene group on the 2-*O*-benzyl derivative of fucose. The free hydroxyl groups were then protected prior to glycosylation.

To prepare the donors, ethyl 1-thio-fucopyranoside was treated with 2,2-dimethoxy propane and a catalytic amount of camphorsulfonic acid to give compound **10** (88%). It was alkylated with benzyl bromide (93%) and hydrolyzed [32] to give compound **11** (84%).

To prepare both the analogues in one step, compound **11** was mono-benzylated under phase-transfer catalysis using a quaternary ammonium salt [33], which gave both the 3-*O*-benzyl (**12**) and 4-*O*-benzyl (**13**) compounds (88%).

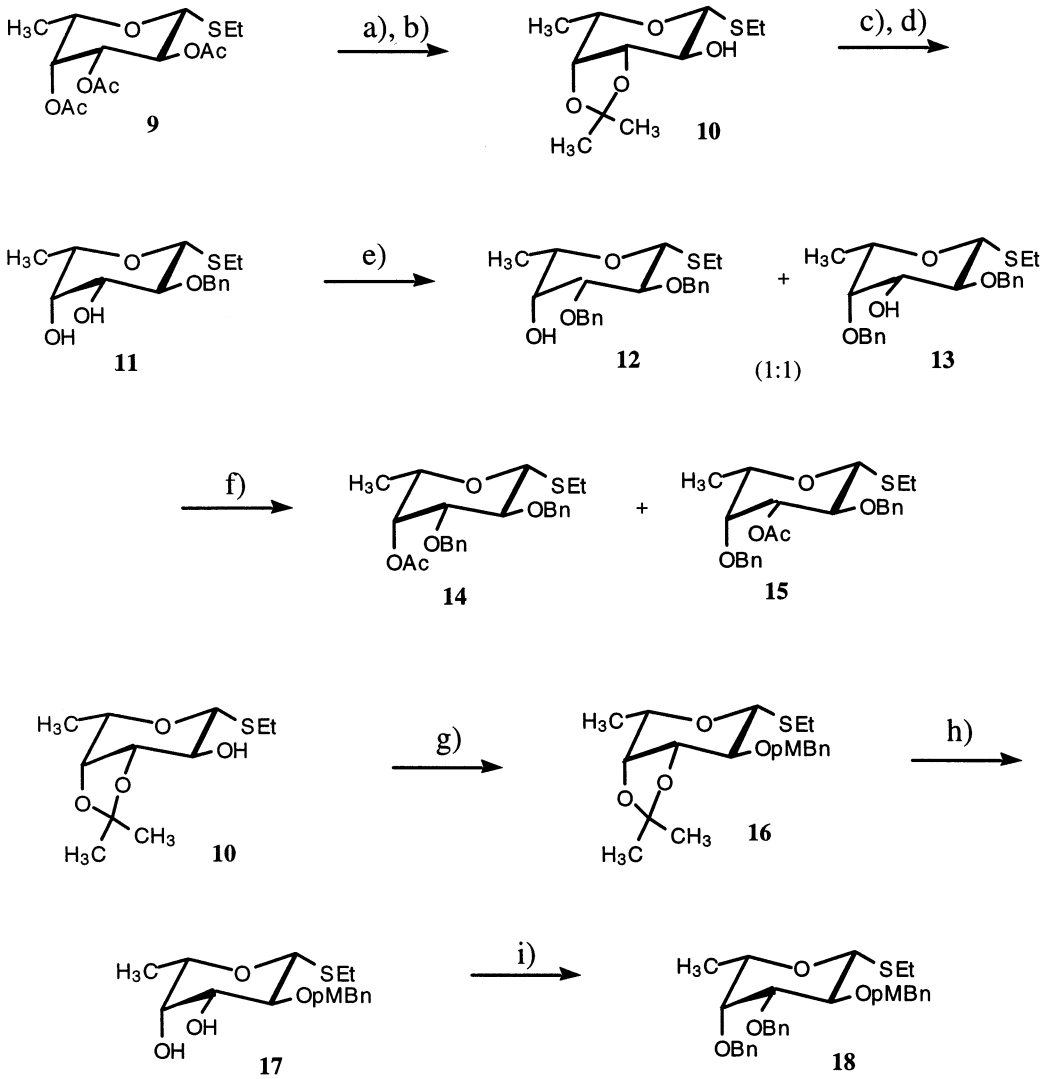
The two compounds were acetylated (in 90% yield) to produce the donors and to ascertain the identity of these compounds (Scheme 1). Based on the downfield shift of H-3′ in compound **15** and H-4′ in compound **14** in their proton NMR spectra, their structures were unambiguously assigned.

The synthesis of the acceptor **25** began with galactose pentaacetate, which was first converted to galactosyl bromide **19** with hydrogen bromide in acetic acid and then to the orthoester **20** with methanol and lutidine [25,26]. Compound **20** was deacetylated with sodium methoxide in methanol and benzylated with benzyl bromide to give compound **22** in an overall yield of 72%. As shown in Scheme 2, the orthoester was converted to 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl bromide (**23**) with tetrabutylammonium bromide and acetyl bromide [27–31]. Compound **23** was glycosylated with octanol under Helferich glycosylation conditions to give compound **24** (70% over two steps), followed by deacetylation with sodium methoxide in methanol to give **25** (97%).

Retrosynthetic analysis of the 2′-hydroxyl-modified disaccharides leads to a fucose precursor with a non-participating protecting group at the 2-OH that would survive glycosylation conditions, and can be removed in the presence of a glycosidic bond and the other protecting groups. The *p*-methoxybenzyl group was considered suitable for this purpose. Ethyl 3,4-di-*O*-isopropylidene-1-thio-β-D-galactopyranoside (**10**) was alkylated with *p*-methoxybenzyl chloride [34] to give compound **16** (89%), which was then hydrolyzed to remove the isopropylidene group and benzylated to obtain compound **18** in 55% (Scheme 1).

Alcohol **25** was coupled with compound **14** to give compound **26** (71%). Compound **27** was obtained by deacetylation of **26** in sodium methoxide in methanol (95%). Compound **27** was methylated with iodomethane to give compound **28** (76%). Compound **28** was hydrogenolyzed to give compound **2** in 91% yield (Scheme 3).

Barton's radical deoxygenation method [35,36] was used to obtain all the deoxy derivatives. The precusor alcohols were first converted to the thiocarbonyl derivatives using pentafluorophenyl chlorothionoformate with pyridine and dimethyl aminopyridine in dichloromethane. The thiocarbonates were then treated with tributyltin hydride and azobisisobutyronitrile (AIBN) to obtain the deoxygenated compounds. Compound **27** was converted into the pentafluorophenylchlorothiono derivative (**29**) in 98% yield and deoxygenated with tributyltin hydride [37,38] to give compound **30** (66%). Debenzylation of this compound gave the disaccharide **3** in 90% (Scheme 3).



Scheme 1. Synthesis of the modified fucosyl donors. Reagents: (a) NaOMe, MeOH. (b) 2,2-Dimethoxypropane (88%). (c) BnBr, NaH, DMF (93%). (d) 70% AcOH, 70 °C (84%). (e) 10% NaOH solution, BnBr, Bu_4NBr (88% over two steps). (f) Ac_2O, pyridine (89%).)g) *p*-$MeOC_6H_4CH_2Cl$, NaH, DMF (89%). (h) 70% AcOH, 70 °C. (i) BnBr, NaH, DMF (55% over two steps).

Disaccharide **31** was similarly obtained by coupling alcohol **25** with donor **15** with DMTST (71%). Compound **32** was obtained by Zemplén deacetylation of **31** in sodium methoxide in methanol (92%). Compound **32** was methylated with iodomethane to give compound **33** (86%). It was debenzylated with hydrogen and palladium-on-charcoal to give the disaccharide **4** in 89% yield (Scheme 4).

Disaccharide **35** was obtained by converting compound **32** to **34** with pentaflurophenyl chlorothionoformate and reducing it with tributyltin hydride and AIBN (76%). This was followed by hydrogenation to give compound **5** in 94% yield (Scheme 4).

Compounds **25** and **18** were coupled by activating the thioglycoside donor (**18**) with DMTST to yield the disaccharide **36** (67%). Compound **37** was obtained from compound **36** by removing the *p*-methoxybenzyl group with ceric ammonium nitrate (70%) [39]. The hydroxyl group was methylated using iodomethane and sodium hydride to give the disaccharide **38** (86%). Compound **38** was hydrogenated to give the target compound **6** in 89% yield (Scheme 5).

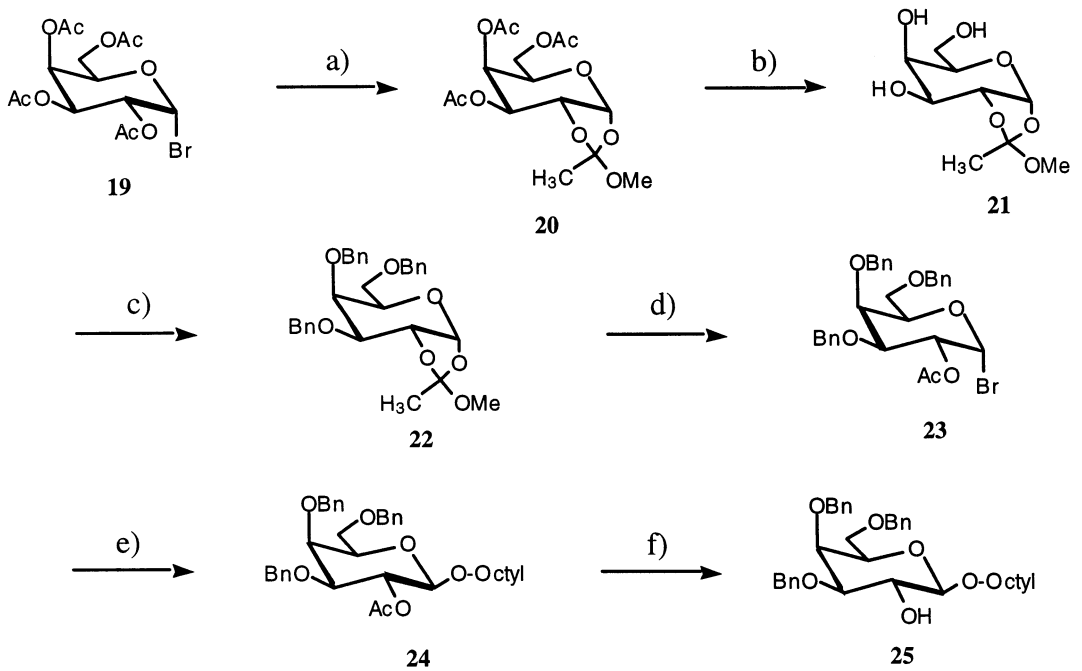
Compound **37** was acylated with pentafluorophenyl chlorothionoformate to give compound **39**. Barton deoxygenation yielded the protected disaccharide **40** in 61% over two

steps, which was then debenzylated by hydrogenolysis to give compound **7** in 84% (Scheme 5).

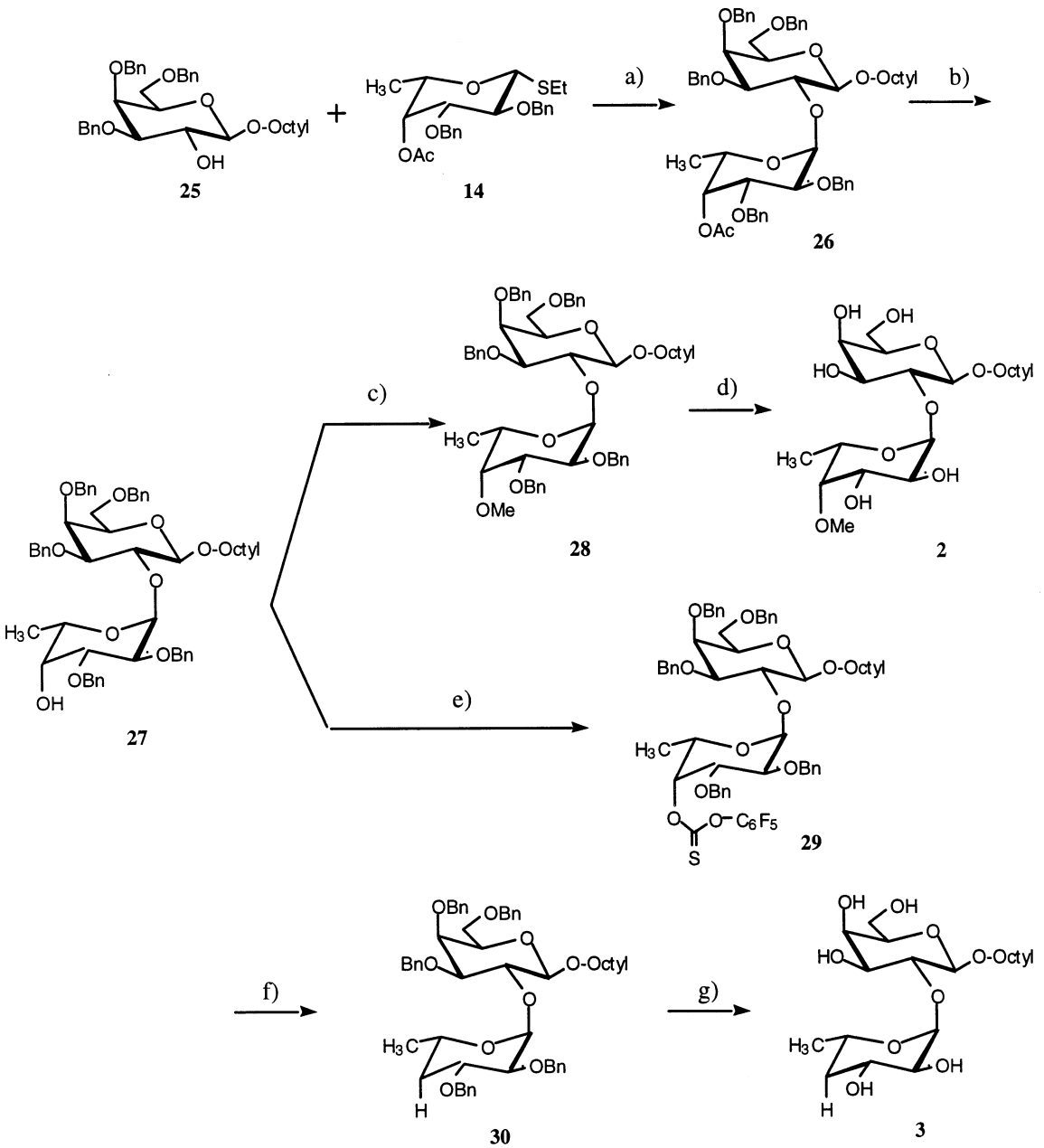
2,3,4-Tri-*O*-benzyl-D-arabinopyranose (**41**) [40] was converted into the corresponding arabinopyranosyl bromide **42** with oxalyl bromide and DMF, and this compound was directly coupled with the alcohol **25** under halide ion catalysis [41,42] to give compound **43** in 78% yield. Only β-arabinoside was observed to be formed in this reaction. Compound **43** was hydrogenolyzed to give compound **8** in 91% yield (Scheme 6).

Enzymatic assays of the disaccharide analogues.—The modified disaccharides (**2**–**8**) were screened in radioactive Sep-Pak assays to determine their activities as potential acceptors relative to the natural acceptor **1** with the recombinant blood group A and B glycosyltransferases. Compounds that were not acceptors were assayed as inhibitors. The radioactive assay technique used for this purpose quantitates the rate of transfer of radiolabeled Gal or GalNAc from the corresponding sugar nucleotides to the octyl glycosides. The potential acceptors were incubated with the A or the B enzyme and UDP-GalNAc or UDP-Gal, respectively, in a suitable buffer. After quenching the reaction, the mixtures were then loaded onto a C_{18} Sep-Pak cartridge that had been washed with methanol and water. The unreacted donor was washed away with water, and the products were eluted with methanol. The radioactivity of the eluant was determined in a liquid scintillation counter. Percentage activity was calculated as the number of decays per minute (dpm) observed for each compound relative to the native acceptor. The potential inhibitor was similarly treated after incubating with the enzyme, the corresponding donor and the native acceptor. Percentage inhibition was determined as the relative loss of activity of the native acceptor in the presence of the inhibitor.

Evaluation of the analogues as potential substrates.—Preliminary screening, the results of which are shown in Table 1, shows that the A transferase can recognize all the disaccharides as acceptors to various extents except the 2′-methoxy derivative **6**. All the analogues tested were less active than the native disaccharide except the 3′-methoxy derivative. For the B transferase, all the modifications caused loss of activity to some extent. The 2′-hydroxyl group is crucial to the recognition of the acceptor by the A enzyme. When it is replaced



Scheme 2. Synthesis of the acceptor alcohol. Reagents: (a) MeOH, 2,6-lutidine, Bu_4NBr. (b) NaOMe, MeOH. (c) BnBr, NaH, DMF (72% over three steps). (d) Et_4NBr,CH_2Cl_2, CH_3COBr. (e) *n*-Octanol, $Hg(CN)_2$, CH_3CN, (70% over two steps). (f) NaOMe, MeOH (97%).



Scheme 3. Synthesis the 4′-hydroxyl-modified analogues of **1**. Reagents: (a) DMTST, DTBMP (71%). b) NaOMe, MeOH (95%). (c) MeI, NaH, DMF (76%). (d) $H_2/Pd(OH)_2$, MeOH (91%). (e) Pentaflurophenyl chlorothionoformate, DMAP, CH_2Cl_2 (98%). (f) AIBN, Bu_3SnH, refluxing toluene (66%). (g) $H_2/Pd(OH)_2$, MeOH (90%).

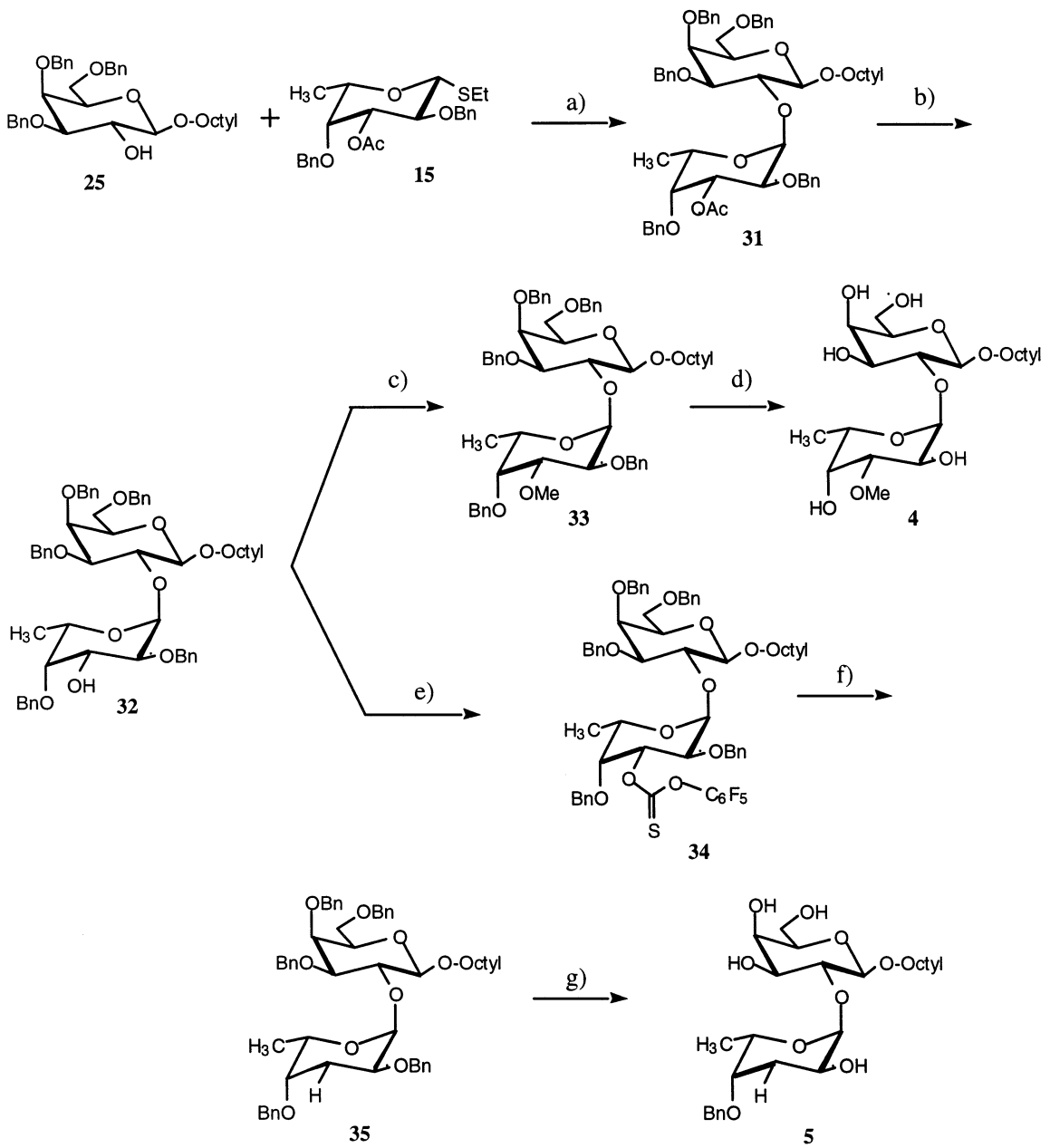
by the methoxy group, recognition is lost. This could be in part due to the steric bulk of the methoxy group at the 2-position, which is close to the active site of the enzyme and the position of transfer of the donor. The lack of reactivity can also be explained in terms of hydrogen bonding, since replacing the OH with an OMe renders it a H-bond acceptor but not a donor.

The 2′-deoxy compound has a relative rate of about two-thirds of that of the natural acceptor, since it is no longer a H-bond donor, but it does not hinder the transfer of the donor, probably due to its minimal steric demand. The A transferase also tolerates modifications on the 3- and the 4-hydroxyl groups of fucose. The 3′-methoxy, 3′-deoxy, and 4′-methoxy compounds have relative rates that are quite close to that of the native acceptor. This probably indicates that the 3-

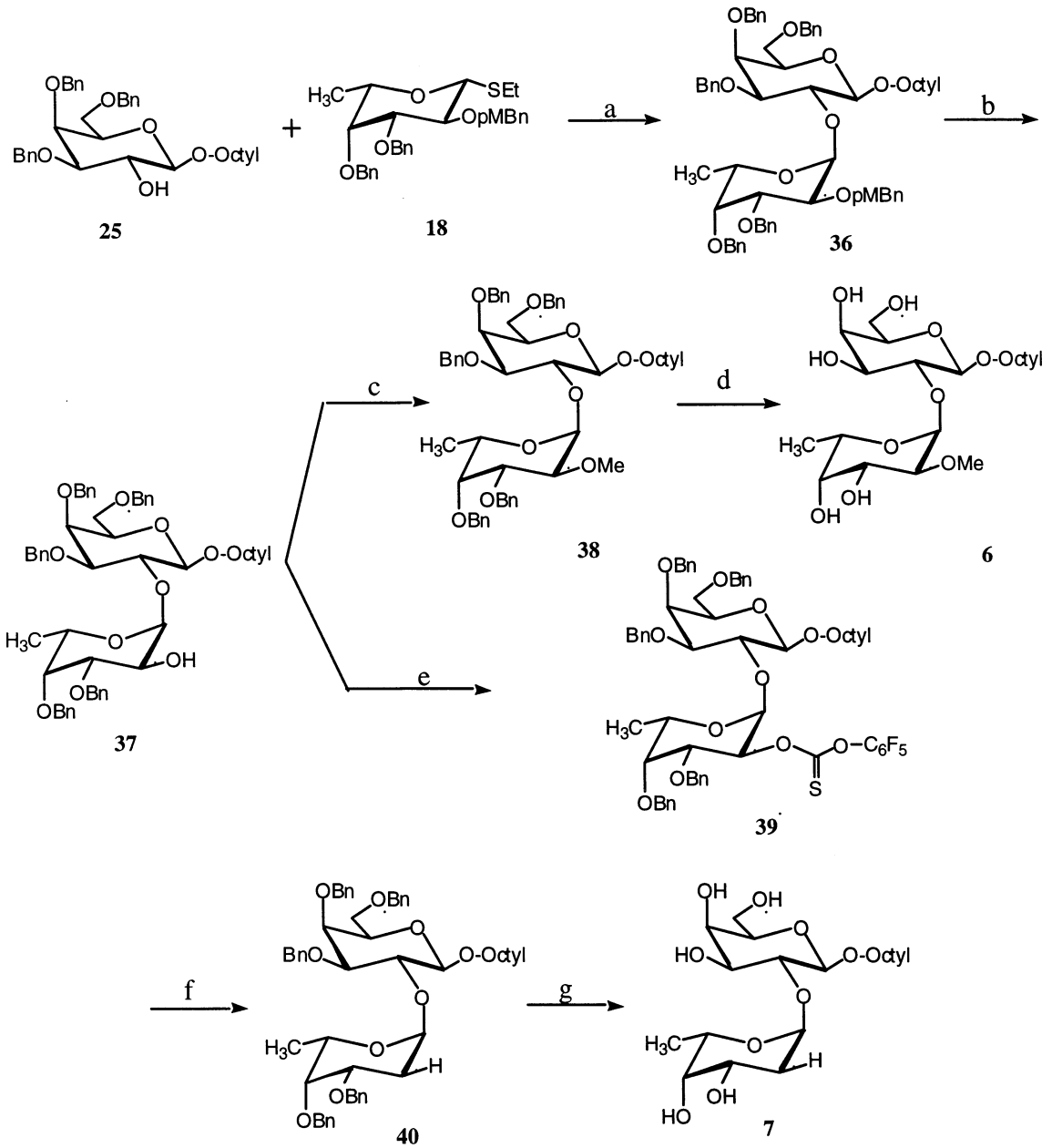
and 4-hydroxyl groups of fucose are not close enough to the active site to be able to perturb it in any significant way.

The 3′-OH is probably not a key polar group since both the methoxy and deoxy analogues are good acceptors. It might be a hydrogen-bond acceptor, since the deoxy compound loses some activity compared with the methoxy, but its contribution to the stability of the enzyme substrate complex is unlikely to be significant. The 4′-deoxy compound has a relative rate of half that of compound **1**, which is lower than that of the methoxy derivative. This could indicate that 4′-OH is also a hydrogen-bond acceptor. The arabino analogue is an acceptor for the A transferase with a high relative rate; thus, the methyl group on the fucose is not critical for recognition by the A transferase.

As observed before for the galactose modifications, the B transferase is less amenable to modifications of the hydroxyl groups on fu-



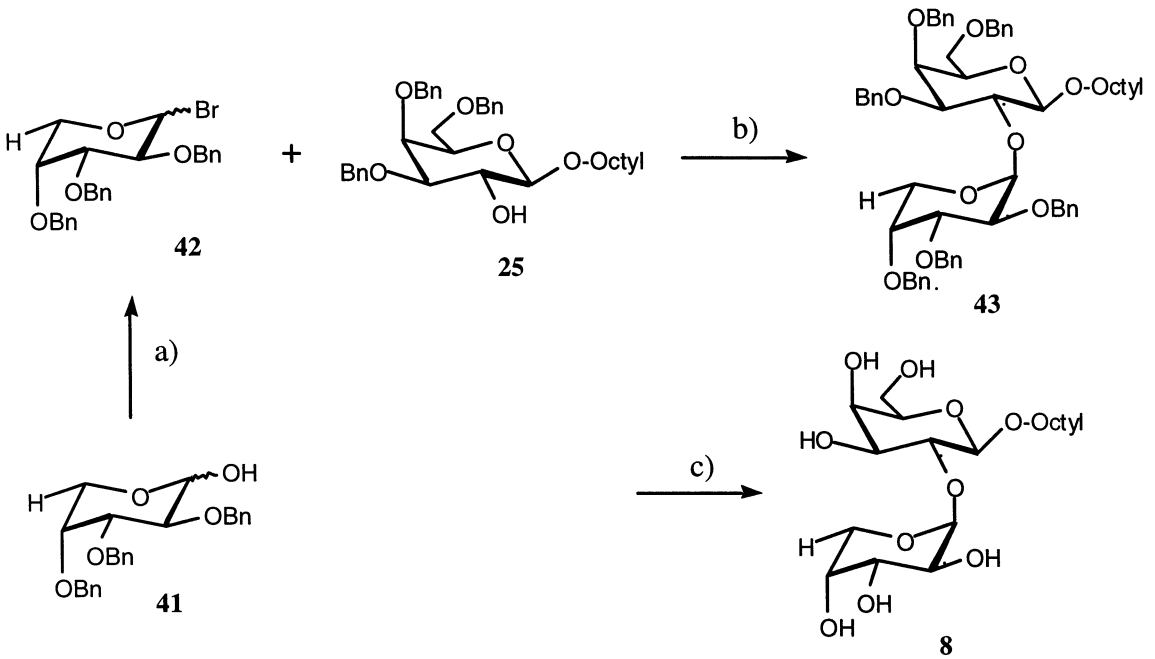
Scheme 4. Synthesis of the 3′-hydroxyl-modified analogues of **1**. Reagents: (a) DMTST, DTBMP (71%). (b) NaOMe, MeOH (92%). (c) MeI, NaH, DMF (86%). (d) $H_2/Pd(OH)_2$, MeOH (89%). (e) Pentaflurophenyl chlorothionoformate, DMAP, CH_2Cl_2 (98%). (f) AIBN, Bu_3SnH, refluxing toluene (76%). (g) $H_2/Pd(OH)_2$, MeOH (94%).



Scheme 5. Synthesis of the 2′-hydroxyl-modified analogues of **1**. Reagents: (a) DMTST, DTBMP (67%). (b) Ceric ammoniumnitrate, 9:1 $CH_3CN–H_2O$ (70%). (c) MeI, NaH, DMF (86%). (d) $H_2/Pd(OH)_2$, MeOH (89%). (e) Pentaflurophenyl chlorothionoformate, DMAP, CH_2Cl_2 (93%). (f) AIBN, Bu_3SnH, refluxing toluene (61%). (g) $H_2/Pd(OH)_2$, MeOH (84%).

cose as well. The 2′-OH is again crucial for recognition, and recognition of the acceptor is lost when either modification is made. Thus, it seems likely that apart from strict steric requirements for the groups that are tolerated at this position, the 2′-OH is likely to be both a hydrogen-bond acceptor and donor. The 3′-OH is again the least significantly involved in steric interactions in the active site, and since the 3′-methoxy is a good acceptor for the B enzyme, the 3′-OH is probably a hydrogen-bond acceptor in the active site. No other analogues are acceptors at all or marginally so. The 4′-OH is also probably involved in hydrogen-bonding interactions in the active site. The 6′-methyl group is required for the acceptor to bind to the B transferase. Thus, although the arabino derivative is an acceptor for the A enzyme, it is not recognized by the B enzyme as an acceptor.

The binding constants of the synthetic analogues most often parallel the percentage ac-



Scheme 6. Synthesis of **8**, the arabino analogue of **1**. Reagents: (a) oxalyl bromide, DMF, CH_2Cl_2. (b) Et_4NBr, CH_2Cl_2, DMF, 4 Å molecular sieves (76%). (c) $H_2/Pd(OH)_2$, MeOH (91%).

tivities of these compounds with the exception of the 4′-methoxy and the 4′-deoxy analogues, which have K_m values of about 1140 and 700 μM, respectively, with the A transferase (Table 2). The K_m values of the other analogues range from 20 to 200 μM, which is about 2–20 fold higher than the native acceptor. Not surprisingly, the 3′-methoxy analogue has the lowest K_m value of all the modified acceptors. It is not clear, however, why the 4′-methoxy compound is required at such a high concentration for it to bind to the enzyme.

The K_m value for the arabino compound **8** is about 208 μM, with a relative rate that is about 2.5 times higher than the native disaccharide. The rates of the reactions in all cases are comparable with that of the natural acceptor. The 4′-methoxy compound has the highest reaction velocity among all the synthesized analogues, while the 3′-deoxy compound reacts at the slowest rate, about 2.5 and 0.6 times of compound **1**, respectively.

The 3′-methoxy and the 3′-deoxy derivatives were the only acceptors for the B transferase with K_m values of about 200 and 400 μM, respectively. The relative rates of the three modified acceptors on which kinetic studies could be performed were higher than that of the native disaccharide. The K_m values of the other compounds could not be determined since they were insoluble at the high concentrations that were required for the assays.

Evaluation of the analogues as potential inhibitors.—Since the 2′-methoxy derivative was concluded not to be an acceptor for either the A or the B transferase, it was assayed as an inhibitor for the two enzymes. The B enzyme failed to recognize it as an inhibitor. The compound showed a calculated K_i value of about 1 mM for the A transferase.

Table 1
Relative acceptor activities of disaccharides **1**–**8** towards cloned blood group A and B glycosyltransferases [a,b]

Substrate	A transferase (% activity)	B transferase (% activity)
2′-Methoxy (**6**)	4	1
2′-Deoxy (**7**)	66	6
3′-Methoxy (**4**)	108	78
3′-Deoxy (**5**)	84	27
4′-Methoxy (**2**)	86	11
4′-Deoxy (**3**)	57	5
Arabino- (**8**)	75	5
Native disaccharide (**1**)	100	100

[a] UDP-*N*-acetylgalactosamine and UDP-galactose were used as donors for the A and the B enzymes, respectively.
[b] Both donors were used at a fixed (saturation) concentrations.

Table 2
Calculated kinetic constants for the modified acceptors with blood group A and B glycosyltransferases

Substrate	A transferase		B transferase	
	K_m (μM)	V_{max} (nmol/min/μg)	K_m (μM)	V_{max} (nmol/min/μg)
2′-Deoxy (**7**)	170 ± 23	3.5 ± 0.17		
3′-Methoxy (**4**)	20 ± 3	3.9 ± 0.4	200 ± 25	8.1 ± 0.9
3′-Deoxy (**5**)	84 ± 13	1.8 ± 0.09	400 ± 52	1.7 ± 0.06
4′-Methoxy (**2**)	1140 ± 182	7.7 ± 0.07	4000 ± 640	2.29 ± 0.16
4′-Deoxy (**3**)	722 ± 115	2.6 ± 0.13		
Arabino (**8**)	208 ± 6	7.4 ± 0.11		
Native disaccharide (**1**)	12.9 ± 1.2	2.9 ± 0.08	110 ± 12	0.24 ± 0.02

None of the modifications made on the disaccharide resulted in the loss of the acceptor property, that is, the 3-OH remained active. Therefore, the loss of or modification in the activities of the analogues was a result of the perturbation of the interactions around the site of transfer in the active site. Molecular modeling of the native disaccharide shows that the 2′-OH is in close proximity to the 3-OH group [9]; thus, it has the most significant effect on the transfer reaction.

To summarize the results, the modifications on the Fuc residue show that an intact 2′-OH is necessary for recognition by the enzymes, particularly by the B enzyme. Modifications on the 3′-OH are tolerated by both enzymes, more so by the A enzyme. 4′-OH and C-6′ are crucial for recognition by B, but modifications are tolerated well by the A enzyme. Thus, a fair amount of flexibility was observed in recognition of the Fuc residue by the two enzymes. Results obtained from previous work on the acceptor specificity of these enzymes [10,11] showed that the 4-hydroxyl group is essential for binding, while modifications on the 3- and 6-hydroxyl groups are tolerated by both enzymes without loss of recognition. It is likely, therefore, that the galactosyl 4-hydroxyl and the fucosyl 2-hydroxyl are the key polar groups involved in the recognition of the acceptor by these enzymes (Fig. 2). In addition, the two enzymes recognized the arabino and the 4′-deoxy compounds differentially as acceptors. Therefore, the acceptor specificity of the enzymes was shown to be determined by their amino acid sequence.

3. Experimental

General methods.—Analytical thin-layer chromatography (TLC) was performed on Silica Gel 60-F_{254} (E. Merck, Darmstadt) with detection by quenching of fluorescence (aromatic compounds), charring with 5% H_2SO_4 or ninhydrin. Unless otherwise noted, column chromatography was performed on Silica Gel 60 (E. Merck). Iatrobeads were from Iatron Laboratories Inc. (Japan). Millex-GV (0.22 μm) filters were from Millipore (Missisauga, ON), C_{18} Sep-Pak (reversed-phase) cartridges were from Waters Associates (Missisauga, ON). All commercial reagents were used as supplied, and all chromatography solvents were distilled prior to use. Ecolite scintillation cocktail was from ICN Radiochemicals (St. Louis, MO) UDP-[6-^{3}H]-Gal (specific activity 1 Ci/mmol) and UDP-[6-^{3}H]-GalNAc (specific

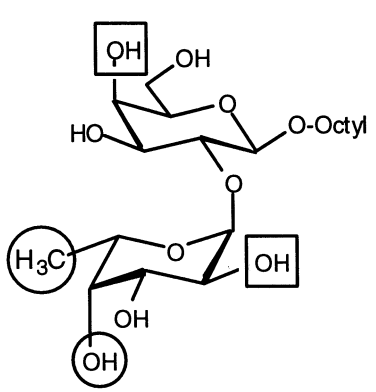


Fig. 2. Recognition of the acceptor α-L-Fuc*p*-(1→2)-β-D-Gal*p*-1-*O*-Octyl (**1**) by the blood group A and B glycosyltransferases, key polar groups shown. (Squares indicate hydroxyl groups essential for recognition by both the enzymes. Circles indicate key polar groups for the B transferase.)

activity 1 Ci/mmol) were from American Radiolabelled Chemicals (St. Louis, MO). UDP-Gal and UDP-GalNac were from Sigma Chemical Co. Optical rotation measurements were done on a Perkin–Elmer 241 polarimeter at 22 ± 2 °C. ^{1}H NMR spectra were recorded at 360 megahertz (MHz) on a Bruker WM-360, 500 MHz (Varian unity 500) or 300 MHz (Varian i300) in solutions of $CDCl_3$ (proton chemical shifts referenced to residual proton signal of chloroform at δ 7.26), CD_3OD (residual proton signal of CD_2HOD at δ 3.30) or D_2O (DOH at δ 4.85 at 22 °C or referenced to external acetone at δ 2.225). ^{13}C NMR spectra were recorded at 75 MHz (Bruker AM 300), or 125 MHz (Varian unity 500) in $CDCl_3$ (δ 77.07), CD_3OD (δ 49.0) or D_2O (external acetone at δ 31.07). Fast-atom bombardment (FAB) mass spectra were recorded on a Kratos AEIMS9 instrument with Xe as the bombarding gas and glycerol as the matrix. Electrospray-ionization mass spectra (performed either in positive- or negative-ion mode) were recorded on a Zabspec Hybrid Sector–Time of Flight instrument from Micromass (Manchester, UK). For exact mass measurements, the spectra were obtained by voltage scan over a narrow mass range. Data acquisition and processing was done using the OPUS software package on a Digital Alpha station with VMS operating system. Elemental analyses were performed on a Carlo Erba EA1108 instrument.

Ethyl 4-O-*acetyl-2,3-di*-O-*benzyl-1-thio*-α-L-*fucopyranoside* (**14**) *and ethyl 3*-O-*acetyl-2,3-di*-O-*benzyl-1-thio*-α-L-*fucopyranoside* (**15**).—Ethyl 2-*O*-benzyl-1-thio-α-L-fucopyranoside (1.1 g, 3.35 mmol) was dissolved in 60 mL of CH_2Cl_2. A 5% soln of aq NaOH (5 mL), BnBr (0.63 mL, 50 mmol) and Bu_4NHSO_4 (0.23 g, 0.67 mmol) were added and the mixture was stirred at room temperature (rt) for 1 day. Additional BnBr (0.45 mL) was added, and stirring was continued for another 24 h. After extraction with CH_2Cl_2 and washing the extract with water, drying and evaporation of the solvent yielded a syrup that was chromatographed (15:1, 10:1, 5:1, 2:1 pentane–EtOAc) to yield compounds **12** (500 mg) and **13** (600 mg) in a combined yield of 88%. Each of the two compounds was acetylated without characterization to give the required **14** and **15**, respectively. Data for compound **14**: $[\alpha]_D$ −28.8° (*c* 0.4 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.2–7.4 (m, 10 H, ArC*H*), 5.38 (d, 1 H, $J_{3,4}$ 2.5 Hz, H-4) 4.81, 4.75, 4.72, 4.50 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.42 (d, 1 H, $J_{1,2}$ 9.0 Hz, H-1), 3.64 (q, 1 H, $J_{5,6}$ 6.5 Hz, H-5), 3.53–3.61 (m, 2 H, H-2, H-3), 2.7–2.8 (m, 2 H, SCH_2), 2.19 (s, 3 H, CH_3CO), 1.30 (t, 3 H, J_{vic} 7.5 Hz, SCH_2CH_3), 1.20 (d, 3 H, $J_{5,6}$ 6.5 Hz, H-6); ^{13}C NMR ($CDCl_3$): δ 170.9 (*C*OCH$_3$), 138.3, 137.8 (Ar*C*), 128.4, 128.3, 128.1, 128.0 (Ar*C*H), 85.0 (C-1), 81.5, 75.8, 73.0, 71.8, 69.9 (C-3, C-4, C-5, *C*H$_2$O), 24.9, 21.0 (*C*H$_3$CO), 16.7 (C-6), 15.06 (SCH_2CH_3). Anal. Calcd for $C_{24}H_{30}O_5S$ (430.56): C, 66.95; H, 7.02. Found: C, 67.33; H, 6.92. ESIMS for $C_{24}H_{30}O_5SNa$: Calcd 453.1711. Found 453.1718.

Data for compound **15**: $[\alpha]_D$ −42.4° (*c* 0.4 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.20–7.38 (m, 10 H, ArC*H*), 4.89 (dd, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 3.0 Hz, H-3) 4.87 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.57–4.67 (m, 3 H, PhC$H_2 \times 3$), 4.43 (d, 1 H, $J_{1,2}$ 9.8 Hz, H-1), 3.79 (t, 1 H, *J* 9.8 Hz, H-2), 4.89 (dd, 1 H, $J_{3,4}$ 3.0, $J_{4,5}$ 0.8 Hz, H-3), 3.60 (dq, 1 H, $J_{5,6}$ 6.5, $J_{4,5}$ 0.8 Hz, H-5), 2.7–2.8 (m, 2 H, SCH_2), 1.89 (s, 3 H, CH_3CO), 1.38 (t, 3 H, J_{vic} 7.5 Hz, SCH_2CH_3), 1.22 (d, 3 H, $J_{5,6}$ 6.5 Hz, H-6); ^{13}C NMR ($CDCl_3$): δ 170.3 (*C*OCH$_3$), 138.1, 138.0 (Ar*C*), 128.1, 128.1, 128.1, 129.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.67 (Ar*C*H), 84.8 (C-1), 77.4, 76.4, 76.2, 75.2, 74.1, (C-3, C-4, C-5, *C*H$_2$O), 24.7, 21.7 (*C*H$_3$CO), 16.7 (C-6), 14.8 (SCH_2CH_3). Anal. Calcd for $C_{24}H_{30}O_5S$ (430.56): C, 66.95; H, 7.02. Found: C, 66.99; H, 7.02. ESIMS for $C_{24}H_{30}O_5SNa$: Calcd 453.171166. Found 453.171697.

Ethyl 3,4-O-*isopropylidene-2*-O-p-*methoxybenzyl-1-thio*-β-L-*fucopyranoside* (**16**).—Ethyl 3,4-*O*-isopropylidene-1-thio-β-L-fucopyranoside (300 mg, 1.2 mmol) was dissolved in DMF (4 mL), 0.115 g of 50% NaH was added, and the mixture was stirred in a cold water bath for 10 min. *p*-Methoxybenzyl chloride (0.325 mL) was added slowly and stirred for another 3 h. After completion of the reaction, excess NaH was destroyed with MeOH. The reaction mixture was extracted with CH_2Cl_2 and washed with water and dried (Na_2SO_4), and concentrated in vacuo. The

residue was chromatographed (10:1, 7:1, 5:1 pentane–EtOAc) and **16** was obtained (387 mg, 89%). $[\alpha]_D$ −42.4° (*c* 0.4 $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.35 (d, 2 H, J_{ortho} 9.0 Hz, ArC*H*), 6.85 (d, 2 H, J_{ortho} 9.0 Hz, ArC*H*), 4.76 (d, 1 H, J_{gem} 11.0 Hz, PhCH_2), 4.67 (d, 1 H, J_{gem} 11.0 Hz, PhCH_2), 4.34 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 4.15 (dd, 1 H, $J_{2,3}$ 6.5, $J_{3,4}$ 5.5 Hz, H-3), 4.01 (dd, 1 H, $J_{3,4}$ 5.5, $J_{4,5}$ 2.0 Hz, H-4), 3.78 (dq, 1 H, $J_{5,6}$ 6.5, $J_{4,5}$ 2.0 Hz, H-5), 3.76 (s, 3 H, CH_3O), 3.39 (dd, 1 H, $J_{1,2}$ 9.5, $J_{2,3}$ 6.5 Hz, H-2), 2.60–2.78 (m, 2 H, SCH_2), 1.38, 1.35 (s, 3 H, CH_3C), 1.34 (d, 3 H, $J_{5,6}$ 6.5 Hz, H-6), 1.27 (t, 3 H, J_{vic} 7.5 Hz, SCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 159.2 (Ar*C*OCH$_3$), 130.1 (Ar*C*), 129.9, 113.6 (Ar*C*H), 109.5 (Me_2C) 83.4 (C-1), 79.8, 78.6, 76.5, 73.1, 72.4, (C-3, C-4, C-5, *C*H_2O), 55.2 (O*C*H_3) 28.0, 26.4, 24.4, 16.8 (C-6), 14.8 (SCH_2CH_3). ESIMS for $C_{19}H_{28}O_5SNa$: Calcd 391.1555. Found 391.1555.

Ethyl 2-O-p-*methoxybenzyl-1-thio-β*-L-*fucopyranoside* (**17**).—Compound **16** (331 mg; 0.89 mmol) was dissolved in 50% aq AcOH (20 mL) and heated with stirring at 60 °C for 2 h. After completion of reaction, the solvent was evaporated and subsequently co-evaporated with toluene to dryness to give a syrup. It was chromatographed with 2:1 pentane–EtOAc to give compound **17**. $[\alpha]_D$ −11.2° (*c* 0.4 $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.32 (d, 2 H, J_{ortho} 9.0 Hz, ArC*H*), 6.88 (d, 2 H, J_{ortho} 9.0 Hz, ArC*H*), 4.88, 4.60 (d, 1 H, J_{gem} 10.5 Hz, PhCH_2), 4.36 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 3.79 (s, 3 H, CH_3O), 4.71 (bs, 1 H, H-4), 3.58 (m, 2 H, H-3, H-5), 3.41 (t, 1 H, *J* 9.5 Hz, H-2), 2.67–2.82 (m, 2 H, SCH_2), 2.55, 2.28 (bs, 1 H, OH), 1.31 (t, 3 H, J_{vic} 7.5 Hz, SCH_2CH_3), 1.30 (d, 3 H, $J_{5,6}$ 6.5 Hz, H-6); ^{13}C NMR ($CDCl_3$): δ 159.5 (Ar*C*OCH$_3$), 130.2 (Ar*C*), 130.0, 114.0 (Ar*C*H), 84.7 (C-1), 78.4, 75.1, 74.8, 71.7 (C-3, C-4, C-5, *C*H_2O), 55.2 (O*C*H_3), 24.9, 16.5 (C-6), 14.9 (SCH_2CH_3). ESIMS for $C_{16}H_{24}O_5SNa$: Calcd 351.1242. Found 351.1247.

Ethyl 3,4-di-O-*benzyl-2*-O-p-*methoxybenzyl-1-thio-β*-L-*fucopyranoside* (**18**).—Compound **17** (250 mg, 0.89 mmol) was dissolved in DMF (5 mL), 0.2 g NaH (50% suspension in oil) was added, and the mixture was stirred for 10 min at 0 °C. Benzyl bromide (0.5 mL) was added slowly, and stirring was continued for another 3 h at rt. The reaction mixture was then cooled in an ice-bath and MeOH was added. The mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was dried (Na_2SO_4) and evaporated in vacuo to obtain a syrup that was chromatographed with (15:1 pentane–ethylacetate) to obtain compound **18** (200 mg, 55% from 16). $[\alpha]_D$ −1.5° (*c* 0.4 $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.25–7.45 (m, 12 H, ArC*H*), 6.86 (d, 2 H, ArC*H*), 5.00, 4.82, 4.79, 4.47, 4.73, 4.70 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.38 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 3.81 (t, 1 H, *J* 9.5 Hz, H-2), 3.80 (s, 3 H, CH_3O), 3.61 (dd, 1 H, $J_{3,4}$ 2.5, $J_{4,5}$ 0.9 Hz, H-4), 3.57 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 2.5 Hz, H-3), 3.47 (dq, 1 H, $J_{5,6}$ 6.5, $J_{4,5}$ 0.9 Hz, H-5), 2.82–2.65 (m, 2 H, SCH_2), 1.35 (t, 3 H, J_{vic} 7.5 Hz, SCH_2CH_3), 1.20 (d, 3 H, $J_{5,6}$ 6.5 Hz, H-6); ^{13}C NMR ($CDCl_3$): δ 158.9 (Ar*C*OCH$_3$), 138.4, 138.2, 132.9, 130.3 (Ar*C*), 129.6, 129.1, 128.0, 127.9, 127.8, 127.2, 127.1, 126.5 (Ar*C*H), 84.6 (C-1), 84.1, 77.7, 76.3, 74.9, 74.2, 74.1, 72.4, (C-2, C-3, C-4, C-5, *C*H_2O), 54.8 (O*C*H_3), 24.2, 16.9 (C-6), 14.7 (SCH_2CH_3). Anal. Calcd for $C_{30}H_{36}O_5S$ (508.65): C, 70.84; H, 7.13. Found: C, 70.51; H, 7.31. ESIMS for $C_{30}H_{36}O_5SNa$: Calcd 531.2181. Found 531.2179.

Octyl 2-O-*acetyl-3,4,6,-tri*-O-*benzyl-β*-D-*galactopyranoside* (**24**).—2-*O*-Acetyl-3,4,6,-tri-*O*-benzyl-β-D-galactopyranosyl bromide (13 g, 23.4 mmol) was dissolved in 100 mL acetonitrile, and 3 Å molecular sieves (powdered, 12 g) and octanol (11 mL, 70.2 mmol) were added and the mixture stirred under argon for 20 min. $Hg(CN)_2$ (8.3 g, 32.8 mmol) and $HgBr_2$ (catalytic amount) were added and the reaction mixture was stirred overnight. The mixture was diluted with three times its volume of CH_2Cl_2 and filtered through Celite. The filtrate was collected and washed successively with water, 8% aq KI and aq $NaHCO_3$. Drying (Na_2SO_4) and concentration yielded a syrup that was chromatographed (15:1, 10:1, 8:1, 5:1 pentane–EtOAc) to yield **24** (8.8 mg, 74%) as a white solid. $[\alpha]_D$ +6.1° (*c* 3.3 $CHCl_3$); R_f 0.45 (3:1 hexane–EtOAc). ^1H NMR ($CDCl_3$): δ 7.2–7.4 (m, 15 H, ArC*H*), 5.35 (dd, 1 H, $J_{2,3}$ 10.0, $J_{1,2}$ 8.0 Hz, H-2), 4.94, 4.67, 4.59, 4.51, 4.46, 4.41 (d, 1 H, J_{gem} 11.5

Hz, PhCH_2), 4.32 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.94 (d, 1 H, $J_{3,4}$ 2.8, $J_{4,5}$ 0.8 Hz, H-4), 3.83 (dt, 1 H, J_{gem} 9.8, J_{vic} 6.9 Hz, CH_2O), 3.53–3.65 (m, 3 H, H-5, H-6b, H-6b), 3.50 (dd, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 2.8 Hz, H-3), 3.39 (dt, 1 H, J_{gem} 9.8, J_{vic} 6.9 Hz, CH_2O), 2.02 (s, 3 H, CH_3CO), 1.52 (m, 2 H, CH_2CH$_2$O), 1.25 (bs, 10 H, CH_2 octyl), 0.87 (t, 3 H, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 169.5 (*C*OCH$_3$), 138.5, 138.0, 137.9, (Ar*C*), 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5, 127.4, (Ar*C*H), 101.4 (C-1), 80.4 (C-2), 74.7, 74.4, 73.7, 73.6, 72.6, 71.9, 71.5, 69.4, 68.7, (C-3, C-4, C-5, C-6, *C*H$_2$O × 5), 31.8, 29.5, 29.4, 29.3, 25.9, 22.6 (*C*H$_2$ octyl), 21.0 (*C*H$_3$CO), 14.4 (*C*H$_3$ octyl). Anal. Calcd for $C_{37}H_{48}O_7$ (604.75): C, 73.53; H, 8.00. Found: C, 73.53; H, 8.15.

Octyl 3,4,6,-tri-O-*benzyl*-β-D-*galactopyranoside* (**25**).—Compound **24** (8.8 g, 14.5 mmol) was deacetylated with NaOMe (0.02 M) in dry MeOH (Zemplén deacetylation) to yield compound **25** as a white solid (8.8 g, 97%). $[\alpha]_D$ −0.8° (*c* 1.6 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.2–7.4 (m, 15 H, ArC*H*), 4.89, 4.73, 4.68, 4.61, 4.49, 4.43 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.22 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.95 (dd, 1 H, $J_{1,2}$ 7.5, $J_{2,3}$ 10.0 Hz, H-2), 3.92 (d, 1 H, $J_{3,4}$ 2.8 Hz, H-4), 3.86 (dt, 1 H, J_{gem} 9.8, J_{vic} 6.9 Hz, CH_2O), 3.55–3.63 (m, 3 H, H-5, H-6a, H-6b), 3.48 (m, 1 H, CH_2O), 3.44 (dd, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 2.8 Hz, H-3), 2.25 (d, 1 H, $J_{H\text{-}2,OH}$ 1.8 Hz, OH), 1.61 (m, 2 H, CH_2CH$_2$O), 1.28 (bs, 10 H, CH_2 octyl), 0.89 (t, 3 H, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 169.7 (*C*OCH$_3$), 138.2, 137.8, 137.6 (Ar*C*), 128.4, 128.5, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3 (Ar*C*H), 102.0 (C-1), 80.2 (C-2), 74.6, 74.4, 73.6, 72.7, 72.1, 69.1, 68.0, 62.3, 56.6 (C-3, C-4, C-5, C-6, *C*H$_2$O x5), 21.05 (*C*H$_3$CO), 33.0, 31.4, 30.6, 30.4, 27.3, 23.7 (*C*H$_2$ octyl), 16.8 (C-6′), 14.4 (*C*H$_3$ octyl). ESIMS for $C_{37}H_{52}O_{13}N_2Na$: Calcd 585.336710. Found 585.336560. Anal. Calcd for $C_{37}H_{48}O_7$ (604.75): C, 73.53; H, 8.00. Found: C, 73.53; H, 8.15. ESIMS for $C_{35}H_{46}O_6Na$: Calcd 585.3192. Found 585.3185.

Octyl 4-O-*acetyl-2,3-di*-O-*benzyl*-α-L-*fucopyranosyl*-*(1→2)*-*3,4,6*-*tri*-O-*benzyl*-β-D-*galactopyranoside* (**26**).—Compounds **25** (145 mg, 0.26 mmol) and **14** (200 mg, 0.46 mmol, 1.8 equiv) were dissolved in dry CH_2Cl_2 (10 mL), and the mixture was stirred for 1 h with 400 mg 4 Å molecular sieves. DMTST (356 mg, 1.38 mmol) and DTBMP (190 mg, 0.92 mmol) were then added and stirring continued for another 3 h. Upon completion, the reaction mixture was filtered through Celite, washed with (Na_2SO_4), and evaporated. Column chromatography (10:1, 6:1, 4:1 pentane–EtOAc) gave compound **26** (170 mg, 71%). $[\alpha]_D$ −42.2° (*c* 0.76 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.20–7.40 (m, 25 H, Ar*H*), 5.69 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 5.42 (bd, 1 H, $J_{3',4'}$ 2.5 Hz, H-4′), 4.93, 4.85, 4.82, 4.78, 4.75, 4.67, 4.65 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.44–4.58 (m, 3 H, PhCH_2), 4.27 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.1 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 4.00 (dd, 1 H, $J_{2,3}$ 10.5, $J_{3,4}$ 3.0 Hz, H-3), 3.85–3.95 (m, 3 H, H-2, H-4, H-6a), 3.77 (dd, 1 H, $J_{2',3'}$ 10.0 Hz, $J_{1',2'}$ 3.5 Hz, H-2′), 3.72 (dd, 1 H, $J_{2',3'}$ 10.0, $J_{3',4'}$ 2.5 Hz, H-3′), 3.51–3.64 (m, 3 H, H-5, H-6b, CH_2O), 3.40 (dt, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 2.10 (s, 3 H, CH_3CO), 1.60 (m, 2 H, CH_2CH$_2$O), 1.30 (bs, 10 H, CH_2 octyl), 1.12 (d, 2 H, $J_{5'6'}$ 6.5 Hz, H-6′), 0.88 (t, 3 H, J_{vic} 6.9 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 159.7 (CH$_3$*C*O), 129.3, 139.2, 138.8, 138.1, 138.0, 128.4, 128.3, 128.1, 128.0, 127.9 × 2, 127.8, 127.7, 127.6, 127.4, 127.3, 127.2 × 2, (Ar*C*), 103.5 (C-1), 99.3 (C-1′), 81.1, 79.5, 79.4, 76.8, 75.3, 74.9, 74.2, 74.0, 74.0, 73.3, 72.7, 71.3, 71.0, 70.0, 69.7 (C-2, C-3, C-4, C-5, C-6, C-3′, C-4′, C-5′, *C*H$_2$O), 32.3, 30.3, 30.2, 30.0, 29.2, 27.2 (*C*H$_2$ octyl), 21.7 (*C*H$_3$CO), 16.7 (C-6′), 14.6 (*C*H$_3$ octyl). ESIMS for $C_{57}H_{70}O_{11}Na$: Calcd 953.4815. Found 953.4815.

Octyl 2,3-di-O-*benzyl-4*-O-*methyl*-α-L-*fucopyranosyl*-*(1→2)*-*3,4,6*-*tri*-O-*benzyl*-β-D-*galactopyranoside* (**28**).—Compound **26** (140 mg, 0.15 mmol) was dissolved in dry MeOH (10 mL), 2 mL of a 0.5 M soln of NaOMe in MeOH was added, and the mixture was stirred at rt for 4 h. The reaction mixture was neutralized with Dowex 50 (H^+) resin and filtered. The solvent was evaporated to obtain a syrup (compound **27**) that was methylated directly with iodomethane and NaH in DMF to obtain compound **28** (102 mg, 73% from **26**). $[\alpha]_D$ −47.2° (*c* 1.1 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.20–7.40 (m, 25 H, Ar*H*), 5.71 (d,

1 H, $J_{1',2'}$ 2.4 Hz, H-1′), 4.84, 4.83, 4.78, 4.76, 4.72, 4.61, 5.59, 4.55 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.52 (s, 2 H, PhCH_2), 4.47 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.43 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 4.25 (dd, 1 H, $J_{2,3}$ 10.0, $J_{1,2}$ 7.8 Hz, H-2), 3.97 (bd, 1 H, $J_{3,4}$ 2.5 Hz, H-4), 3.94 (m, 1 H, H-6a), 3.91 (dd, 1 H, $J_{2',3'}$ 9.8, $J_{1',2'}$ 2.4 Hz, H-2′), 3.73 (dd, 1 H, $J_{2',3'}$ 9.8, $J_{3',4'}$ 2.5 Hz, H-3′), 3.55–3.65 (m, 5 H, H-2, H-3, H-5, H-6a, CH_2O), 3.61 (s, 3 H, OCH_3), 3.40 (dt, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 1.55 (m, 2 H, CH_2CH$_2$O), 1.32 (bs, 10 H, CH_2 octyl), 1.21 (d, 2 H, $J_{5'6'}$ 6.5 Hz, H-6′), 0.90 (t, 3 H, J_{vic} 6.9 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 138.9, 138.4, 138.3, 138.0, 137.9, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.4, 127.3, 127.2, 127.2, 127.0, 126.35 (Ar*C*), 103.6 (C-1), 97.0 (C-1′), 84.5, 80.9, 79.2, 76.0, 74.3, 73.6, 73.3, 72.9, 72.8, 72.6, 72.1, 71.2, 70.3, 70.0, 69.7 (C-2, C-3, C-4, C-5, C-6, C-3′, C-4′, C-5′, *C*H$_2$O), 61.6 (O*C*H$_3$), 31.8, 29.7, 29.5, 29.3, 26.2, 22.6 (*C*H$_2$ octyl), 16.2 (C-6′), 14.0 (*C*H$_3$ octyl). Anal. Calcd for $C_{56}H_{70}O_{10}$ (903.18): C, 74.47; H, 7.81. Found: C, 74.54; H, 7.84.

Octyl 4-O-*methyl*-α-L-*fucopyranosyl*-*(1→2)*-β-D-*galactopyranoside* (**2**).—Compound **28** (80 mg, 0.088 mmol) was dissolved in MeOH and hydrogenated in a flow of hydrogen overnight in presence of palladium hydroxide-on-charcoal. After completion of the reaction, the catalyst was filtered off on a 0.22-μm Millipore filter, the solvent was evaporated, the residue was dissolved in water and passed through Waters C_{18} Sep-Pak cartridges and eluted with 60:40% MeOH–water. The solution was evaporated, the residue was redissolved in water, and the solution was filtered on a 0.22-μm Millipore filter, and lyophilized to give compound **2** (36 mg, 91%). ^{1}H NMR (CD_3OD): δ 5.17 (d, 1 H, $J_{1',2'}$ 3.8 Hz, H-1′), 4.40 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.28 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 3.85–3.93 (m, 2 H, H-4, CH_2O), 3.78–3.83 (m, 2 H, H-4′, H-6a), 3.69–3.74 (m, 3 H, H-6b, H-2′, H-3′), 3.61–3.67 (m, 2 H, H-2, H-3), 3.56 (s, 3 H, OCH_3), 3.45–3.51 (m, 2 H, H-5, CH_2O), 1.55–1.64 (m, 2 H, CH_2CH$_2$O), 1.26–1.36 (m, 10 H, CH_2 octyl), 1.19 (d, 2 H, $J_{5'6'}$ 6.5 Hz, H-6′), 0.0.87–0.93 (m, 3 H, CH_3 octyl); ^{13}C NMR (CD_3OD): δ 104.4 (C-1), 101.5 (C-1′), 84.5, 83.4, 79.0, 76.5, 75.7, 72.2, 70.9, 70.8, 70.4, 67.9 (C-2, C-3, C-4, C-5, C-6, C-3′, C-4′, C-5′, *C*H$_2$O), 62.38 (O*C*H$_3$), 32.9, 30.9, 30.5, 30.3, 27.2, 23.6 (*C*H$_2$ octyl), 16.8 (C-6′), 14.4 (*C*H$_3$ octyl). ESIMS for $C_{21}H_{40}O_{10}Na$: Calcd 475.2519. Found 475.2512.

Octyl benzyl-*2*-O-*(2,3-di*-O-*benzyl*-α-L-xylo-*hexopyranosyl*-*(1→2)*-β-D-*galactopyranoside* (**30**).—Compound **26** (483 mg, 0.52 mmol) was deacetylated with NaOMe in MeOH as before to give **27**. After evaporation and drying of the mixture, it was acylated with pentafluorophenylchlorothionoformate (175 μL, 1.08 mmol) and DMAP (250 mg, 0.05 mmol) in CH_2Cl_2 (**29**). Compound **28** was deoxygenated with AIBN (88 mg, 0.52 mmol) and Bu_3SnH (700 μL, 2.5 mmol) in refluxing toluene to give **30** (207 mg; 65% from alcohol) after column chromatography (10:1, 6:1 pentane–EtOAc). $[\alpha]_D$ −15.2° (*c* 0.9). ^{1}H NMR ($CDCl_3$): δ 7.20–7.40 (m, 25 H, Ar*H*), 5.69 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1′), 4.85, 4.79, 4.74, 4.66, 4.64, 4.60, 4.56, 4.49 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.47 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.45 (s, 2 H, PhCH_2), 4.25 (dd, 1 H, $J_{2,3}$ 9.8 Hz, $J_{1,2}$ 7.8 Hz, H-2), 3.89 (m, 3 H, H-4, H-6a, CH_2O), 3.76 (dd, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 2.7 Hz, H-3) 3.57–3.65 (m, 4 H, H-5, H-6b, H-2′, H-3′), 3.40–3.45 (m, 2 H, H-5′, CH_2O), 2.10 (m, 1 H, H-4′a), 1.05 (m, 1 H, H-4′b), 1.59 (m, 2 H, CH_2CH$_2$O), 1.30 (bs, 10 H, CH_2 octyl), 1.16 (d, 2 H, $J_{5'6'}$ 6.5 Hz, H-6′), 0.90 (t, 3 H, J_{vic} 6.9 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 139.0, 138.4, 138.2, 138.1, 137.9, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.3, 127.2, 126.4 (Ar*C*), 102.2 (C-1), 97.3 (C-1′), 84.5, 80.1, 75.5, 74.3, 73.6, 73.3, 72.3 × 2, 72.2 × 2, 72.1, 71.3, 69.8, 68.9, 63.3 (C-2, C-3, C-4, C-5, C-6, C-2′, C-3′ C-5′, *C*H$_2$O), 39.1 (C-4′), 31.8, 29.7, 29.5, 29.3, 26.2, 22.6 (*C*H$_2$ octyl), 20.8 (C-6′), 14.0 (*C*H$_3$ octyl). Anal. Calcd for $C_{55}H_{69}O_9$ (873.54): C, 75.66; H, 7.85. Found: C, 75.67; H, 7.69.

Octyl α-L-xylo-*hexopyranosyl*-*(1→2)*-β-D-*galactopyranoside* (**3**).—Compound **30** (60 mg, 0.068 mmol) was hydrogenated and purified as described for compound **35** to give compound **3** (26.6 mg, 90%). ^{1}H NMR (CD_3OD): δ 5.16 (d, 1 H, $J_{1',2'}$ 3.8 Hz, H-1′), 4.31 (d, 1 H, $J_{1,2}$ 7.1 Hz, H-1), 4.24 (m, 1 H, H-5′), 3.89 (dt, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 3.77–3.84 (m, 2 H, H-3′, H-4), 3.70–

3.74 (m, 2 H, H-6a, H-2′), 3.61–3.67 (m, 2 H, H-2, H-3), 3.46–3.55 (m, 3 H, H-5, H-6b, CH_2O), 1.91 (ddd, 1 H, J_{gem} 12.7, J_{vic} 4.7, 2.3 Hz, H-4′a), 1.54–1.64 (m, 2 H, CH_2CH$_2$O), 1.22–1.38 (m, 11 H, H-4′b, CH_2 octyl), 1.13 (d, 1 H, $J_{5'6'}$ 6.3 Hz, H-6′), 0.86–0.94 (m, 3 H, CH_3 octyl); ^{13}C NMR (CD_3OD): δ 104.1 (C-1), 97.3 (C-1′), 80.6, 77.0, 76.3, 75.4, 73.7, 71.9, 71.1, 69.5, 62.4 (C-2, C-3, C-4, C-5, C-6, C-2′, C-3′, C-5′, CH$_2$O), 41.9 (C-4′), 33.0, 30.8, 30.5, 30.4, 27.2, 23.7 (CH$_2$ octyl), 21.1 (C-6′), 14.4 (CH$_3$ octyl). ESIMS for $C_{20}H_{38}O_9Na$: Calcd 445.2413. Found 445.2419.

*Octyl 3-*O*-acetyl-2,4-di-*O*-benzyl-α-*L*-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-*D*-galactopyranoside* (**31**).—Compound **25** (146 mg, 0.26 mmol) and **15** (200 mg, 0.46 mmol, 18 equiv) were dissolved in dry CH_2Cl_2 (10 mL), and the mixture was stirred for 1 h with 500 mg 4 Å molecular sieves. DMTST (356 mg, 1.38 mmol) and DTBMP (380 mg, 1.84 mmol) were then added and stirring continued for another 3 h. Upon completion, the reaction mixture was filtered through Celite, washed with (Na_2SO_4), and the solvent was evaporated. Column chromatography (10:1, 6:1, 4:1 pentane–EtOAc) gave compound **31** (200 mg, 71% based on alcohol). $[\alpha]_D$ −36.8° (*c* 1.9 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.20–7.40 (m, 25 H, ArH), 5.74 (d, 1 H, $J_{1',2'}$ 3.72 Hz, H-1′), 5.31 (dd, 1 H, $J_{2',3'}$ 10.6, $J_{3',4'}$ 2.8 Hz, H-3′), 4.85, 4.77 (d, 1 H, J_{gem} 11.6 Hz, PhCH_2), 4.40–4.60 (m, 8 H, PhCH_2), 4.22 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.14 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 4.09 (m, 1 H, H-6a), 4.00 (dd, 1 H, $J_{2',3'}$ 9.5, $J_{1',2'}$ 3.7 Hz, H-2′), 3.97 (bs, 1 H, H-4), 3.92 (m, 1 H, CH_2O), 3.76 (bs, 1 H, H-4′), 3.73 (dd, 1 H, $J_{2,3}$ 9.0 Hz, $J_{3,4}$ 2.6 Hz, H-3), 3.68–3.58 (m, 3 H, H-5, H-6b, H-2), 3.52–3.45 (m, 1 H, CH_2O), 2.05 (s, 3 H, CH_3CO), 1.60 (m, 2 H, CH_2CH$_2$O), 1.35 (bs, 10 H, CH_2 octyl), 1.20 (d, 2 H, $J_{5',6'}$ 6.5 Hz, H-6′), 0.95 (t, 3 H, J_{vic} 6.9 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 170.5 (CH$_3$$C$O), 139.2, 139.2, 139.1, 138.8, 138.4, 138.0, 133.3, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.7 × 2, 127.5, 127.4, 127.3, 127.0 (ArC), 103.5 (C-1), 99.1 (C-1′), 81.5, 76.6, 75.9, 75.3, 74.5, 74.4, 73.1, 72.9, 70.4, 69.9, 68.0 (C-2, C-3, C-4, C-5, C-6, C-3′, C-4′, C-5′, CH$_2$O), 31.8, 29.5, 29.3, 29.2, 26.0, 22.6 (CH$_2$ octyl), 20.9 (CH_3CO), 16.6 (C-6′), 14.1 (CH$_3$ octyl). ESIMS for $C_{57}H_{70}O_{11}Na$: Calcd 953.4815. Found 953.4817.

*Octyl 2,4-di-*O*-benzyl-α-*L*-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-*D*-galactopyranoside* (**32**).—Compound **31** (160 mg, 0.172 mmol) was deacetylated by the Zemplén method and after the usual workup, evaporation of the solvent and column chromatography of the residue (10:1, 4:1 pentane–EtOAc) gave compound **32** (140 mg, 92% from **31**). $[\alpha]_D$ −19.0° (*c* 2.4 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.18–7.43 (m, 25 H, ArH), 4.97, 4.96, 4.89, 4.86, 4.69, 4.68, 4.64, 4.57, 4.47, 4.42 (d, 1 H, J_{gem} 11.67 Hz, PhCH_2), 4.83 (d, 1 H, $J_{1',2'}$ 4.03 Hz, H-1′), 4.29 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.22 (dd, 1 H, $J_{2,3}$ 9.1, $J_{1,2}$ 7.8 Hz, H-2), 3.88 (bd, 1 H, $J_{3,4}$ 2.8 Hz, H-4), 3.82 (m, 1 H, CH_2O), 3.38–3.62 (m, 7 H, H-3, H-5, H-6a, H-6b, H-2′, H-3′, H-4′), 3.44 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 3.34 (m, 1 H, CH_2O), 2.32 (d, 1 H, $J_{H\text{-}2',OH}$ 4.3 Hz, OH), 1.55 (m, 2 H, CH_2CH$_2$O), 1.25 (bs, 10 H, CH_2 octyl), 1.22 (d, 2 H, $J_{5',6'}$ 6.4 Hz, H-6′), 0.89 (t, 3 H, J_{vic} 6.9 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 138.6, 138.3, 137.9, 137.8, 128.4, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.5, 127.5, 127.3, 127.3, 127.1 (ArC), 103.21 (C-1), 97.1 (C-1′), 81.9, 79.9, 76.0, 75.3, 74.4, 73.7, 73.6, 73.3, 73.0, 72.4, 72.3, 71.8, 71.5, 71.0, 70.4, 69.8, 68.7 (C-2, C-3, C-4, C-5, C-6, C-3′, C-4′, C-5′, CH$_2$O), 31.8, 29.6, 29.4, 29.2, 26.2, 22.6 (CH$_2$ octyl), 16.5 (C-6′), 14.0 (CH$_3$ octyl). ESIMS for $C_{55}H_{68}O_{10}Na$: Calcd 911.4710. Found 911.4707.

*Octyl 2,4-di-*O*-benzyl-3-*O*-methyl-α-*L*-fucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-*D*-galactopyranoside* (**33**).—Compound **32** (160 mg, 0.172 mmol) was methylated with MeI (25 mL, 0.4 mmol) and NaH (13 mg, 0.45 mmol) in DMF. Workup and column chromatography (10:1, 4:1 pentane–EtOAc) gave compound **33** (140 mg, 86% from **32**). $[\alpha]_D$ −8.5° (*c* 2.8 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.15–7.47 (m, 25 H, ArH), 5.69 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1′), 4.95, 4.82, 4.76, 4.64, 4.61, 4.57 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.54, 4.46 (s, 2 H, PhCH_2), 4.45 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.44 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 4.24 (dd, 1 H, $J_{2,3}$ 10.0, $J_{1,2}$ 7.8 Hz, H-2), 3.98 (dd, 1 H, $J_{2',3'}$ 9.5, $J_{1',2'}$ 3.7 Hz, H-2′), 3.96 (bs, 1 H, H-4),

3.92 (dt, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 3.81 (s, 3 H, OCH_3), 3.52–3.75 (m, 6 H, H-3, H-5, H-6a, H-6b, H-3′, H-4′), 3.41 (dt, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 1.58 (m, 2 H, CH_2CH$_2$O), 1.30 (bs, 10 H, CH_2 octyl), 1.15 (d, 2 H, $J_{5',6'}$ 6.5 Hz, H-6′), 0.91 (t, 3 H, J_{vic} 6.9 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 138.9, 138.5, 138.4, 138.1, 137.9, 128.4, 128.3, 128.2, 128.1 × 2, 128.0, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 127.2, 126.3 (Ar*C*), 102.0 (C-1), 97.2 (C-1′), 84.4, 81.5, 75.4, 74.6, 74.3, 73.6, 73.3, 69.6, 68.9, 66.1 (C-2, C-3, C-4, C-5, C-6, C-3′, C-4′, C-5′, *C*H$_2$O), 58.2 (O*C*H$_3$), 31.8, 29.7, 29.5, 29.3, 26.3, 22.6 (*C*H$_2$ octyl), 16.5 (C-6′), 14.0 (*C*H$_3$ octyl). Anal. Calcd for $C_{56}H_{70}O_{10}$ (903.16): C, 74.47; H, 7.81. Found: C, 74.32; H, 7.84.

Octyl 3-O-*methyl*-α-L-*fucopyranosyl*-*(1→2)*-β-D-*galactopyranoside* (**4**).—Compound **33** (21.7 mg, 0.024 mmol) was dissolved in 12 mL of EtOH, and 10 mg $Pd(OH)_2$-on-charcoal was added. The mixture was hydrogenated at rt and atmospheric pressure overnight. After completion of the reaction, the catalyst was filtered off on a 0.22 μm Millipore filter. The usual workup and chromatography on C_{18} Sep-Pak cartridges gave compound **4** (10 mg, 89%). ^{1}H NMR (CD_3OD): δ 5.19 (dd, 1 H, $J_{1',2'}$ 3.9 Hz, H-1′), 4.33 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1), 4.27 (q, 1 H, $J_{5',6'}$ 6.6 Hz, H-5′), 3.90 (dt, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 3.80–3.85 (m, 3 H, H-3, H-4′, H-6a), 3.62–3.76 (m, 4 H, H-2, H-4, H-5, H-2′), 3.46–3.54 (m, 2 H, H-6b, CH_2O), 3.45 (s, 3 H, OCH_3), 3.41 (dd, 1 H, $J_{2',3'}$ 10.0, $J_{3',4'}$ 3.2 Hz, H-3′), 1.56–1.64 (m, 2 H, CH_2CH$_2$O), 1.28–1.38 (m, 10 H, CH_2 octyl), 1.20 (d, 2 H, $J_{5'6'}$ 6.6 Hz, H-6′), 0.90 (t, 3 H, J_{vic} 6.7 Hz, CH_3 octyl); ^{13}C NMR (CD_3OD): δ 104.3 (C-1), 101.2 (C-1′), 84.3, 79.7, 76.4, 73.8, 71.9, 71.5, 71.1, 69.5, 68.6, 62.4 (C-2, C-3, C-4, C-5, C-6, C-3′, C-4′, C-5′, *C*H$_2$O), 57.2 (O*C*H$_3$), 33.0, 30.8, 30.6, 30.4, 27.3, 23.7 (*C*H$_2$ octyl), 16.7 (C-6′), 14.4 (*C*H$_3$ octyl). ESIMS for $C_{21}H_{40}O_{10}Na$: Calcd 475.2519. Found 475.2513.

Octyl 2,4-di-O-*benzyl*-α-L-xylo-*hexopyranosyl*-*(1→2)*-*3,4,6-tri*-O-*benzyl*-β-D-*galactopyranoside* (**35**).—Compound **32** was acetylated with pentafluorophenylchlorothionoformate (126 μL, 0.78 mmol) and 4-dimethylamino pyridine (100 mg, 0.84 mmol) in dry CH_2Cl_2 (10 mL). After 14 h the reaction mixture was extracted with CH_2Cl_2, and the extract was washed with 0.5% aq HCl, satd $NaHCO_3$, and water, dried, and concentrated to a syrup. This was directly deoxygenated as follows. To the syrup (109 mg) dissolved in toluene (10 mL), tributyltin hydride (130 μL, 0.48 mmol) and azobisisobutyronitrile (40 mg, 0.24 mmol) were added, and the mixture was refluxed at 130 °C for 4 h. Evaporation of the solvent left a syrup, which was dissolved in acetonitrile and washed with hexane. The acetonitrile layer was concentrated in vacuo and chromatographed (6:1, 4:1 pentane–EtOAc) to obtain **35** as a white solid (225 mg; 75%). $[\alpha]_D$ −2.9° (*c* 0.8 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.12–7.40 (m, 25 H, Ar*H*), 5.12 (d, 1 H, $J_{1',2a'}$ 3.3 Hz, H-1′), 4.86, 4.80, 4.64, 4.56, 4.30 (d, 1 H, J_{gem} 11.6 Hz, PhCH_2), 4.36–4.50 (m, 5 H, PhCH_2), 4.25 (d, 1 H, $J_{1,2}$ 7.97 Hz, H-1), 3.95 (bd, 1 H, $J_{3,4}$ 2.0 Hz, H-4), 3.88 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 3.77 (dd, 1 H, $J_{2',3'}$ 10.6, $J_{1',2'}$ 3.3 Hz, H-2′), 3.72 (dd, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 2.0 Hz, H-3), 3.55–3.65 (m, 5 H, H-2, H-5, H-6a, H-4′, CH_2O), 3.35–3.43 (m, 2 H, H-6b, CH_2O), 2.05 (m, 1 H, H-3′a), 1.85 (t, 1 H, *J* 10.5 Hz, H-3′b), 1.50 (m, 2 H, CH_2CH$_2$O), 1.25 (bs, 10 H, CH_2 octyl), 1.15 (d, 2 H, $J_{5',6'}$ 6.5 Hz, H-6′), 0.85 (t, 3 H, J_{vic} 6.9 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 138.5, 138.3, 137.9, 130.6, 128.9, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.4, 127.3, 126.4, 124.6 (Ar*C*), 102.2 (C-1), 96.4 (C-1′), 76.0, 75.7, 74.4, 73.6, 73.4, 72.4, 72.3, 71.5, 71.0, 70.6, 70.3, 69.7, 69.5, 65.9 (C-2, C-3, C-4, C-5, C-6, C-2′, C-4′, C-5′, *C*H$_2$O), 31.8 (C-3′), 29.7, 29.5, 29.2, 27.5, 26.2, 22.6 (*C*H$_2$ octyl), 16.3 (C-6′), 14.1 (*C*H$_3$ octyl). ESIMS for $C_{55}H_{68}O_9Na$: Calcd 895.4761. Found 895.4757.

Octyl α-L-xylo-*hexopyranosyl*-*(1→2)*-β-D-*galactopyranoside* (**5**).—Compound **35** (15 mg, 0.017 mmol) was dissolved in 10 mL of EtOH, and 10 mg of $Pd(OH)_2$-on-charcoal was added. Compound **35** was hydrogenated at rt and atmospheric pressure overnight. After completion of the reaction, the catalyst was filtered off on a 0.22 μm Millipore filter, the solvent was evaporated, and the residue was dissolved in water and passed through

Waters C_{18} Sep-Pak cartridges and eluted with 1:1 MeOH–water. The solvent was evaporated, and the residue was redissolved in water, filtered on a 0.22-μm Millipore filter, and lyophilized to give compound **5** (6.8 mg; 94%). ^{1}H NMR (CD_3OD): δ 5.14 (dd, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 4.33 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 4.22 (q, 1 H, $J_{5',6'}$ 6.6 Hz, H-5′), 3.98 (ddd, 1 H, $J_{2',3a'}$ 17.0, $J_{1',2'}$ 3.5, $J_{2'3'b}$ 2.2 Hz, H-2′), 3.88 (dt, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 3.81 (m, 1 H, H-6a), 3.62–3.76 (m, 5 H, H-2, H-3, H-4, H-5, H-4′), 3.44–3.58 (m, 2 H, H-6b, CH_2O), 1.85–2.00 (m, 2 H, H-3a, H-3′b), 1.60 (m, 2 H, CH_2CH$_2$O), 1.25–1.40 (m, 10 H, CH_2 octyl), 1.12 (d, 2 H, $J_{5'6'}$ 6.6 Hz, H-6′), 0.90 (t, 3 H, J_{vic} 6.8 Hz, CH_3 octyl); ^{13}C NMR (CD_3OD): δ 104.9 (C-1), 101.4 (C-1′), 77.7, 75.5, 75.1, 72.5, 71.4, 70.4, 69.0, 66.2, 61.5 (C-2, C-3, C-4, C-5, C-6, C-2′, C-4′, C-5′, CH$_2$O), 37.8 (C-3′), 32.1, 29.9, 29.6, 29.5, 26.4, 23.0 (CH$_2$ octyl), 16.5 (C-6′), 14.3 (CH$_3$ octyl). ESIMS for $C_{20}H_{38}O_9Na$: Calcd 445.2413. Found 445.2417.

Octyl 3,4-di-O-*benzyl-2*-O-p-*methoxybenzyl-α*-L-*fucopyranosyl-(1→2)-3,4,6,-tri*-O-*benzyl-β*-D-*galactopyranoside* (**36**).—Compound **25** (140 mg, 0.25 mmol) and compound **18** (230 mg, 0.45 mmol, 1.8 equiv) were dissolved in dry CH_2Cl_2 (10 mL) and stirred for 1 h with 500 mg 4 Å molecular sieves. DMTST (356 mg, 1.38 mmol) and DTBMP (380 mg, 1.84 mmol) were then added, and the mixture was stirred for another 3 h. Upon completion of the reaction as determined from the TLC of the reaction mixture, the reaction was quenched with Et_3N, filtered through Celite, and the solvent was evaporated. Column chromatography of the syrup thus obtained (10:1, 6:1, 4:1 pentane–EtOAc) gave **35** (185 mg, 67% isolated yield). $[\alpha]_D$ −28.8° (*c* 0.26 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.2–7.4 (m, 25 H, ArH), 6.95, 6.61 (d, 2 H, J_{ortho} 8.6 Hz, ArH), 5.69 (d, 1 H, $J_{1',2'}$ 3.56 Hz, H-1′), 4.96, 4.85, 4.82, 4.77, 4.73, 4.66 (d, 1 H, J_{gem} 11.6 Hz, PhCH_2), 4.64, 4.54, 4.53 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.47 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.46 (s, 2 H, PhCH_2), 4.25 (dd, 1 H, $J_{2,3}$ 9.6, $J_{1,2}$ 7.8 Hz, H-2), 4.04 (dd, 1 H, $J_{2',3'}$ 10.2, $J_{1',2'}$ 3.6 Hz, H-2′), 3.95–3.99 (m, 2 H, H-5′, H-6a), 3.90 (dd, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 3.76 (dd, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 2.68 Hz, H-3), 3.72 (s, 3 H, OCH_3), 3.55–3.67 (m, 5 H, H-4, H-5, H-6b, H-3′, H-4′), 3.35–3.43 (m, 1 H, CH_2O), 1.53 (m, 2 H, CH_2CH$_2$O), 1.25 (bs, 10 H, CH_2 octyl), 1.14 (d, 2 H, $J_{5'6'}$ 6.5 Hz, H-6′), 0.90 (t, 3 H, J_{vic} 7.0 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 158.9 (ArC-OMe), 139.0, 138.8, 138.4, 138.1, 137.9, 130.3, 129.4 × 2, 128.3, 128.2, 128.1, 127.9, 127.8, 127.5, 127.3, 126.4, 113.4 (ArC), 102.1 (C-1), 97.2 (C-1′), 84.5, 79.7, 78.1, 75.1, 74.7, 74.3, 73.6, 73.3, 72.9, 72.3, 72.1, 72.0, 71.3, 69.7, 68.9, 66.1 (C-2, C-3, C-4, C-5, C-6, C-2′, C-3′, C-4′, C-5′, CH$_2$O), 55.1 (CH$_3$O), 31.8, 29.7, 29.5, 29.3, 26.3, 22.6 (CH$_2$ octyl), 16.5 (C-6′), 14.1 (CH$_3$ octyl). ESIMS for $C_{63}H_{76}O_{11}Na$: Calcd 1031.5285. Found 1031.5280.

Octyl 3,4-di-O-*benzyl-α*-L-*fucopyranosyl-(1→2)-3,4,6-tri*-O-*benzyl-β*-D-*galactopyranoside* (**37**).—Compound **36** (150 mg, 0.148 mmol) and ceric ammonium nitrate (154 mg, 0.28 mmol) were dissolved in 9:1 CH_3CN–water (10 mL) and the mixture stirred for 30 min at rt. The reaction mixture was diluted with CH_2Cl_2, washed with satd $NaHCO_3$ and water, dried (Na_2SO_4), filtered and evaporated in vacuo to yield a syrup that was chromatographed (6:1 pentane–EtOAc) to give compound **37** (100 mg, 70%). $[\alpha]_D$ −11.9° (*c* 1.2 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.2–7.4 (m, 25 H, ArH), 5.49 (d, 1 H, $J_{1',2'}$ 3.9 Hz, H-1′), 4.93, 4.85, 4.59, 4.56, 4.47, 4.43 (d, 1 H, J_{gem} 11.44 Hz, PhCH_2), 4.69 (s, 2 H, PhCH_2), 4.65, 4.62 (d, 1 H, J_{gem} 11.0 Hz, PhCH_2), 4.33 (d, 1 H, $J_{1,2}$ 7.77 Hz, H-1), 4.27 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 4.17 (m, 1 H, H-6a), 4.10 (dd, 1 H, $J_{2,3}$ 9.76, $J_{1,2}$ 7.77 Hz, H-2), 3.95 (bd, 1 H, $J_{3,4}$ 2.4 Hz, H-4), 3.86 (dd, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 3.70 (dd, 1 H, $J_{2',3'}$ 9.9, $J_{3',4'}$ 2.7 Hz, H-3′), 3.53–3.63 (m, 5 H, H-2′, H-3, H-5, H-6b, H-4′), 3.40 (dd, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 2.44 (d, 1 H, $J_{OH,H-2'}$ 7.4 Hz, OH), 1.56 (m, 2 H, CH_2CH$_2$O), 1.27 (bs, 10 H, CH_2 octyl), 1.14 (d, 2 H, $J_{5'6'}$ 6.5 Hz, H-6′), 0.89 (t, 3 H, J_{vic} 7.0 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 138.8, 138.7, 138.6, 137.6, 137.0, 128.4 × 2, 128.3, 128.2, 127.9, 127.8, 127.5 (ArC), 102.3 (C-1), 99.2 (C-1′), 83.7, 80.4, 77.0, 74.7, 74.3, 73.6, 73.4, 72.5, 72.4, 72.2, 69.9, 69.2, 68.2, 66.8 (C-2, C-3, C-4, C-5, C-6, C-2′, C-3′, C-4′, C-5′, CH$_2$O), 31.8, 29.6, 29.5, 29.3, 26.2, 22.7 (CH$_2$ octyl), 16.7 (C-6′), 14.1

(CH_3 octyl). Anal. Calcd for $C_{55}H_{68}O_{10}$ (889.09): C, 74.30; H, 7.71. Found: C, 74.06; H, 7.84.

*Octyl 3,4-di-*O*-benzyl-2-*O*-methyl-α-*L*-fucopyranosyl-(1→2)-3,4,6,-tri-*O*-benzyl-β-*D*-galactopyranoside* (**38**).—Compound **37** (200 mg, 0.225 mmol) was dissolved in DMF (10 mL) and iodomethane (0.028 mL, 0.45 mmol) and NaH (50%, 25 mg, 0.9 mmol) were added at 0 °C, the mixture was then stirred for 4 h at rt. The reaction was quenched with MeOH in the cold, and the mixture diluted with CH_2Cl_2. It was washed with water, dried (Na_2SO_4), and evaporated. Column chromatography (10:1, 6:1 pentane–EtOAc) gave **38** (176 mg, 86%). $[\alpha]_D$ −71.8° (*c* 3.0 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.20–7.45 (m, 25 H, Ar*H*), 5.70 (d, 1 H, $J_{1',2'}$ 3.8 Hz, H-1′), 4.94, 4.93, 4.81, 4.78, 4.73, 4.67, 4.61, 4.59, 4.53 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.44, 4.40 (d, 1 H, J_{gem} 11.8 Hz, PhCH_2), 4.39 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.19 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 4.17 (dd, 1 H, $J_{2,3}$ 9.8, $J_{1,2}$ 7.8 Hz, H-2), 3.92 (bd, 1 H, $J_{3,4}$ 2.5 Hz, H-4), 3.82–3.85 (m, 2 H, H-3, H-6a), 3.80 (dd, 1 H, $J_{2',3'}$ 10.0, $J_{1',2'}$ 3.8 Hz, H-2′), 3.72 (bd, 1 H, $J_{2',3'}$ 10.0 Hz, H-3′), 3.67 (bs, 1 H, H-4′), 3.55–3.61 (m, 2 H, H-5, H-6b), 3.52 (dd, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 3.43 (s, 3 H, OCH_3), 3.35 (dd, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 1.49 (m, 2 H, CH_2CH$_2$O), 1.22 (bs, 10 H, CH_2 octyl), 1.12 (d, 2 H, $J_{5'6'}$ 6.5 Hz, H-6′), 0.85 (t, 3 H, J_{vic} 7.0 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 139.0, 138.8, 138.6, 138.5, 138.0, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.5, 127.4, 127.3 × 2, 126.7 (Ar*C*), 102.0 (C-1), 97.0 (C-1′), 84.5, 78.5, 78.2, 78.0, 77.6, 74.9, 74.3, 73.6, 73.4, 73.0, 72.9, 72.4, 71.8, 69.6, 66.6 (C-2, C-3, C-4, C-5, C-6, C-2′, C-3′, C-4′, C-5′, *C*H$_2$O), 58.1 (O*C*H$_3$), 31.8, 29.6, 29.5, 29.3, 26.2, 22.6 (*C*H$_2$ octyl), 16.7 (C-6′), 14.0 (*C*H$_3$ octyl). Anal. Calcd for $C_{56}H_{70}O_{10}$ (903.08): C, 74.47; H, 7.81. Found: C, 74.57; H, 7.86.

*Octyl 2-*O*-methyl-α-*L*-fucopyranosyl-(1→2)-β-*D*-galactopyranoside* (**6**).—Compound **38** (16 mg; 0.017 mmol) was hydrogenated with hydrogen and palladium-on-charcoal in MeOH and purified as follows. The solution was filtered to remove the catalyst, and the solvent was evaporated. The crude product was dissolved in water and passed though a C_{18} column. The column was washed with water and eluted with MeOH. The fractions containing the product were pooled, and the solvent was again evaporated. The residue was re-dissolved in water, passed though a 0.22 μm Millipore filter and lyophilized to give compound **6** (7 mg, 89%). ^{1}H NMR (CD_3OD): δ 5.49 (d, 1 H, $J_{1',2'}$ 3.8 Hz, H-1′), 4.41 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.35 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 3.86–3.94 (m, 2 H, H-2, H-4), 3.68–3.80 (m, 5 H, H-3, H-6a, H-2′, H-3′, H-4′), 3.52–3.64 (m, 3 H, H-6b, CH_2O), 3.50 (s, 3 H, OCH_3), 3.45 (dd, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 1.57 (m, 2 H, CH_2CH$_2$O), 1.28 (bs, 10 H, CH_2 octyl), 1.17 (d, 2 H, $J_{5'6'}$ 6.5 Hz, H-6′), 0.86 (t, 3 H, J_{vic} 7.0 Hz, CH_3 octyl); ^{13}C NMR (CD_3OD): δ 104.6 (C-1), 100.1 (C-1′), 82.3, 80.3, 76.4, 74.5, 73.9, 72.8, 71.8, 71.0, 69.5, 62.4 (C-2, C-3, C-4, C-5, C-6, C-2′, C-3′, C-4′, C-5′, *C*H$_2$O), 61.0 (O*C*H$_3$), 38.0, 30.8, 30.6, 30.4, 27.3, 23.7 (*C*H$_2$ octyl), 16.6 (C-6′), 14.4 (*C*H$_3$ octyl). ESIMS for $C_{21}H_{40}O_{10}Na$: Calcd 475.2519. Found 475.2514.

*Octyl 3,4-di-*O*-benzyl-α-*L*-xylo-hexopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-*D*-galactopyranoside* (**40**).—Compound **37** (50 mg, 0.09 mmol) was dissolved in CH_2Cl_2 (10 mL) and 4-dimethylaminopyridine (55 mg, 0.45 mmol) and pentafluorophenylchlorothionoformate (42 μL, 0.26 mmol) were added in the cold. The mixture was stirred overnight at rt. After completion of the reaction, the reaction mixture was washed successively with 5% aq HCl, satd aq $NaHCO_3$ and water and then dried. The solvent was evaporated in vacuo, and this was taken to the next step as follows. Tributyltin hydride (39 μL, 0.52 mmol) and AIBN (42.3 mg, 0.25 mmol) were added to it in toluene and refluxed at 130 °C bath temperature for 4 h. The solvent was evaporated and chromatographed (6:1 pentane–EtOAc) to give compound **40** (50 mg, 57%). $[\alpha]_D$ −10.4° (*c* 0.74 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.12–7.40 (m, 25 H, Ar*H*), 5.50 (d, 1 H, $J_{1',2a'}$ 3.7 Hz, H-1′), 4.95, 4.84, 4.68, 4.66, 4.57, 4.49 (d, 1 H, J_{gem} 11.6 Hz, PhCH_2), 4.58, 4.42 (s, 2 H, PhCH_2), 4.24 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.22 (q, 1 H, $J_{5',6'}$ 6.5 Hz, H-5′), 4.06 (dd, 1 H, $J_{2,3}$ 9.8, $J_{1,2}$ 7.8 Hz, H-2), 3.92 (bd, 1 H, $J_{3,4}$ 2.6 Hz, H-4),), 3.84 (dd, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 3.59–3.64 (m, 2 H, H-3′, H-6a),

3.58 (bs, 1 H, H-4′), 3.53–3.56 (m, 2 H, H-5, H-6b), 3.36 (dd, 1 H, J_{gem} 10.0 Hz, J_{vic} 7.0 Hz, CH_2O), 2.09–2.18 (ddd, 1 H, J_{gem} 16.3 Hz, $J_{2'a,3'}$ 12.2 Hz, $J_{2'a,1'}$ 3.7 Hz, H-2′a), 1.89 (m, 1 H, H-2′b), 1.60 (m, 2 H, CH_2CH$_2$O), 1.25 (bs, 10 H, CH_2 octyl), 1.12 (d, 2 H, $J_{5'6'}$ 6.5 Hz, H-6′), 0.89 (t, 3 H, J_{vic} 6.9 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 139.5, 1349.4, 139.3, 139.2, 138.9, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.5, 127.2 (Ar*C*), 102.5 (C-1), 98.1 (C-1′), 84.2, 82.7, 77.2, 76.5, 74.4, 74.1, 73.6, 73.5, 72.9, 72.6, 72.1, 70.3, 69.4, 68.9 (C-2, C-3, C-4, C-5, C-6, C-3′, C-4′, C-5′, *C*H$_2$O), 33.8 (C-2′), 29.5, 29.4, 29.3, 27.3, 26.2, 22.6 (*C*H$_2$ octyl), 17.2 (C-6′), 14.1 (*C*H$_3$ octyl). Anal. Calcd for $C_{55}H_{69}O_9$ (873.05): C, 75.66; H, 7.85. Found: C, 74.39; H, 7.88.

Octyl α-L-xylo-*hexopyranosyl-(1→2)-β*-D-*galactopyranoside* (**7**).—Compound **40** (25 mg, 0.028 mmol) was hydrogenated as described for **35**. After the usual workup, it was chromatographed (10:1 CH_2Cl_2–MeOH) and then purified on reversed-phase C_{18} cartridges, as described for compound **6**, to give compound **7** (10 mg; 84%). ^{1}H NMR (CD_3OD): δ 5.38 (dd, 1 H, J_{vic} 2.2, 2.1 Hz, H-1′), 4.31 (q, 1 H, $J_{5',6'}$ 6.6 Hz, H-5′), 4.25 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.86–3.96 (m, 2 H, H-3′, CH_2O), 3.62–3.78 (m, 4 H, H-2, H-4, H-5, H-6a), 3.58 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 3.4 Hz, H-3), 3.44–3.53 (m, 3 H, H-4′, H-6b, CH_2O), 1.80–1.88 (m, 2 H, H-2′), 1.52–1.60 (m, 2 H, CH_2CH$_2$O), 1.26–1.36 (m, 10 H, CH_2 octyl), 1.17 (d, 2 H, $J_{5'6'}$ 6.6 Hz, H-6′), 0.88–0.92 (m, 3 H, CH_3 octyl); ^{13}C NMR (CD_3OD): δ 104.1 (C-1), 101.8 (C-1′), 80.6, 76.4, 73.8, 72.1, 71.2, 70.8, 69.9, 69.5, 62.4 (C-2, C-3, C-4, C-5, C-6, C-3′, C-4′, C-5′, *C*H$_2$O), 35.2 (C-2′), 31.6, 30.8, 30.5, 30.4, 27.3, 23.7 (*C*H$_2$ octyl), 17.0 (C-6′), 14.4 (*C*H$_3$ octyl). ESIMS for $C_{20}H_{38}O_9Na$: Calcd 445.2413. Found 445.2414.

Octyl 2,3,4-tri-O-*benzyl-β*-D-*arabinopyranosyl-(1→2)-3,4,6-tri*-O-*benzyl-β*-D-*galactopyranoside* (**43**).—2,3,4-Tri-*O*-benzyl-D-arabinopyranose (**41**, 238 mg, 0.566 mmol) was dissolved in CH_2Cl_2 (2 mL), and DMF (22.3 μL) was added with stirring. Oxalyl bromide (0.184 mL, 1.3 mmol) was added dropwise, and stirring was continued for 20 min after evolution of gas ceased. The reaction mixture was washed with water, the extract was dried, the solvent was partially evaporated and then dried over 4 Å molecular sieves. The resulting syrup was transferred to the reaction vessel containing compound **25** (68 mg, 0.12 mmol), Bu_4NBr (72 mg, 0.22 mmol) and 1 g 4 Å molecular sieves in 2:1 CH_2Cl_2–DMF (15 mL) and the mixture was stirred for 2 days. The mixture was filtered through Celite, and the solvents were evaporated. Column chromatography (10:1 pentane–EtOAc) gave **43** (100 mg, 76% based on alcohol). $[\alpha]_D$ −53.8° (*c* 1.6 $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 7.20–7.40 (m, 30 H, Ar*H*), 5.78 (d, 1 H, $J_{1',2'}$ 3.8 Hz, H-1′), 4.85, 4.77, 4.75, 4.72, 4.63, 4.55, 4.49, 4.45 (d, 1 H, J_{gem} 11.5 Hz, PhCH_2), 4.74, 4.61 (s, 2 H, PhCH_2), 4.46 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.25 (dd, 1 H, $J_{2,3}$ 10.0 Hz, $J_{1,2}$ 7.8 Hz, H-2), 4.08 (dd, 1 H, $J_{2',3'}$ 10.0, $J_{1',2'}$ 3.8 Hz, H-2′), 3.98 (dd, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 3.0 Hz, H-3), 3.94 (m, 1 H, H-4, H-6a), 3.89 (dt, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 3.80 m, 1 H, H-5′a), 3.74 (dd, 1 H, $J_{2',3'}$ 9.8, $J_{3',4'}$ 2.8 Hz, H-3′), 3.56–3.69 (m, 4 H, H-4, H-6b, H-4′, H-5′b), 3.42 (m, 1 H, CH_2O), 1.56 (m, 2 H, CH_2CH$_2$O), 1.26 (bs, 10 H, CH_2 octyl), 0.91 (t, 3 H, J_{vic} 6.9 Hz, CH_3 octyl); ^{13}C NMR ($CDCl_3$): δ 138.8, 138.6, 138.5, 138.4, 138.0, 137.9, 128.5, 128.4, 128.3, 128.2, 128.1 × 3, 128.0, 127.9, 127.8, 127.7 × 2, 127.6, 127.5, 127.4, 127.3, 127.2, 126.5 (Ar*C*), 102.1 (C-1), 97.5 (C-1′), 84.4, 77.6, 76.0, 74.4 × 2, 73.6, 73.3, 73.0, 72.4, 72.4, 72.1, 71.5, 71.5, 69.6, 68.8 (C-2, C-3, C-4, C-5, C-6, C-2′, C-3′ C-4′, *C*H$_2$O), 60.3 (C-5′), 31.8, 29.7, 29.4, 29.2, 26.2, 22.6 (*C*H$_2$ octyl), 14.1 (*C*H$_3$ octyl). ESIMS for $C_{61}H_{72}O_{10}Na$: Calcd 987.5502. Found 987.5502.

Octyl β-D-*arabinopyranosyl-(1→2)-β*-D-*galactopyranoside* (**8**).—Compound **43** (50 mg, 0.052 mmol) was hydrogenated as described before and purified in the usual way to give compound **8** (20 mg, 91%). ^{1}H NMR (CD_3OD): δ 5.21 (d, 1 H, $J_{1',2'}$ 2.75 Hz, H-1′), 4.32 (d, 1 H, $J_{1,2}$ 7.23 Hz, H-1), 4.15 (dd, 1 H, J_{gem} 11.72, $J_{4',5'a}$ 1.5 Hz, H-5′a), 3.89 (dt, 1 H, J_{gem} 10.0, J_{vic} 7.0 Hz, CH_2O), 3.80–3.84 (m, 2 H, H-3′, H-3), 3.76–3.79 (m, 2 H, H-4, H-2′), 3.70–3.74 (m, 2 H, H-4′, H-5′b), 3.45–3.58 (m, 3 H, H-2, H-5, CH_2O), 1.59 (m, 2 H, CH_2CH$_2$O), 1.30 (m, 10 H, CH_2 octyl), 0.90 (m, 3 H, CH_3 octyl); ^{13}C NMR (CD_3OD): δ

103.5 (C-1), 98.5 (C-1′), 77.6, 75.6, 73.0, 72.4, 71.8, 71.6, 70.4, 69.1, 68.9 (C-2, C-3, C-4, C-5, C-6, C-2′, C-3′, CH_2O), 61.5 (C-5′), 32.0, 29.8, 29.5, 29.4, 26.3, 22.9 (CH_2 octyl), 14.3 (CH_3 octyl). ESIMS for $C_{19}H_{36}O_{10}Na$: Calcd 447.2206. Found 447.2202.

Enzyme kinetics.—The enzymatic assays performed were based on a method developed that uses the rate of transfer of sugar donors incorporated with a radioisotope onto an acceptor. All the compounds synthesized had a hydrophobic aglycon and therefore C_{18} (reversed-phase) cartridges were used to separate the products from unreacted donors. The recombinant enzymes were expressed in *E. coli* and the isolation and purification was performed according to the established protocol [12,13]. They were stored at −70 °C with 1 mg/mL bovine serum albumin (BSA) until used.

All reactions were carried out in 450 μL microfuge tubes in a total volume of 33 μL. The modified derivatives were screened at 1 mM concentrations with the A and B enzymes, all activity being measured relative to the natural acceptor [octyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranoside (**1**)]. All assays were carried out in 35 mM sodium cacodylate buffer containing 0.02 M $MnCl_2$ and 1 mg/mL BSA at 37 °C. The reactions were carried out for 30 min before being quenched with water. The reaction mixture was transferred to a C_{18} Sep-Pak cartridge pre-equilibrated with MeOH and water. The cartridge was washed with water to remove unreacted donor until background counts were obtained. The products were then eluted with MeOH (3.5 mL), and the radioactivity in dpm (decays per minute) was measured in a liquid scintillation counter.

UDP-GalNAc (0.152 mM) and UDP-[6-^{3}H]GalNAc (0.2 μCi) were used as donors for the assay with the A transferase. The acceptors were used in concentrations of 1 mM. 0.25 μL of the enzyme (0.165 mg/mL) was used with 0.15 mM of UDP-GalNAc. When tested as inhibitors, the analogues were used in concentrations of 1 mM with 0.01 mM of the native acceptor **1**. Compound **1** was tested at concentrations of 0.12, 0.06, 0.03, 0.015, 0.0075, 0.00375 mM for kinetic studies, and under the conditions stated above, K_m was determined to be 1.00, 0.750, 0.500, 0.250, 0.125, 0.0625 and 0.03125 mM. K_m determination for compound **3** was carried out at concentrations of 5.00, 2.50, 1.250, 0.625, 0.3125, 0.15625, 0.07812, 0.03906 and 0.01953 mM. To determine the K_m value of compound **4**, it was used in concentrations of 1.00, 0.500, 0.250, 0.125, 0.0625, 0.03125, 0.0156, 0.0078, 0.0039 mM. Compounds **2** and **5** were assayed in concentrations of 1.00, 0.500, 0.250, 0.125, 0.0625, 0.03125, 0.0156 and 0.0078 mM and compound **7** at concentrations of 0.250, 0.125, 0.0625, 0.03125, 0.0156, 0.0078 and 0.0039 mM for K_m value determination.

UDP-Gal (0.6 mM) and UDP-[6-^{3}H]Gal (0.2 μCi) were used for assays with the B transferase. The acceptors were used in concentrations of 1 mM. 0.1 μL of the enzyme (0.997 mg/mL) was used with 0.15 mM of UDP-Gal. To test the inhibitory activities of potential inhibitors, the analogues were added in concentrations of 0.5–0.1 mM of the native acceptor **1**. To determine K_m values for compound **4**, it was used in concentrations of 0.4125, 0.2062, 0.0625, 0.03125, 0.0156, 0.0078 and 0.0039 mM. K_m determination for compound **5** was carried out at concentrations of 4.00, 2.00, 1.00, 0.500, 0.250, 0.125, 0.0625, 0.03125 and 0.0156 mM. The data obtained were then fit to the Michaelis–Menten equation using unweighted non-linear regression with the Sigma Plot 4.0 Program (Jandel Scientific) to estimate the kinetic parameters.

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