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Synthesis of a library of fucopyranosyl-galactopyranosides consisting of a complete set of anomeric configurations and linkage positions

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Abstract—A library composed of a complete set of fucopyranosyl-galactopyranosides was synthesized. A perbenzylated phenylthio fucopyranoside and a series of tri-*O*-benzyl-galactopyranosyl fluorides having single hydroxyl groups at the 2-, 3-, 4-, and 6-positions were used as the glycosyl donor and glycosyl acceptors, respectively. The chosen set of functionalities at the anomeric centers enabled rapid access to the oligosaccharides based on chemoselective activation. The first coupling reaction was achieved by the action of dimethyl(methylthio)sulfonium trifluoromethanesulfonate (DMTST). The resulting disaccharide fluoride was readily activated by hafnocene bistrifluoromethanesulfonate [$Cp_2Hf(OTf)_2$] and glycosidated with *n*-octanol.

Keywords: Fucopyranosyl-galactopyranoside; Library; Deprotection of chloroacetyl group; Anomeric mixture; Phenylthio glycosides; Glycosyl fluorides

1. Introduction

The research field of glycotechnology has expanded from fundamental chemical and biological research to one of potential pharmaceutical interest. Carbohydrates can be considered an important class of potential pharmaceuticals because a wide range of functions involved in cellular interactions are being discovered.[1] The synthesis of this class of molecules is therefore of extreme importance. Recent efforts directed at the synthesis of complex glycoconjugates have made it possible to control the stereo- and regiospecificity in glycosylation reactions using solution- and solid-phase organic synthesis.[2–7]

Naturally-occurring oligosaccharides are susceptible to degradation by hydrolases present in the bloodstream. A possible way to circumvent this problem involves the use of analogues of O-glycosides in which the exo-glycosidic atom is substituted with a sulfur or a carbon atom.[8,9] Alternatively, we propose searching for compounds in an oligosaccharide library that mimic a functional structure but resist hydrolysis. Before verifying the hypothesis, the synthesis of a library of oligosaccharides must be accomplished. State-of-the-art synthesis, however, cannot always be directly applied to combinatorial chemistry where the synthetic protocol should be extremely simple.[7,10–14]

To address the synthesis of an oligosaccharide library, we focused on the overall efficiency of the synthetic process. We decided to reduce (1) the number of protecting groups and (2) the number of reactions used throughout the synthesis. To fulfill criterion 1, benzyl groups were selected as a sole group to protect the hydroxyl groups.[15] For criterion 2, an orthogonal glycosylation reaction[16] was used (Scheme 1). Fucose-containing oligosaccharides are present in blood type antigens,[17] tumor antigens,[18] and are also ligands of *H. pylori*.[19] Thus, detailed structure–activity relationships of fucosylated oligosaccharides is quite important; however, the

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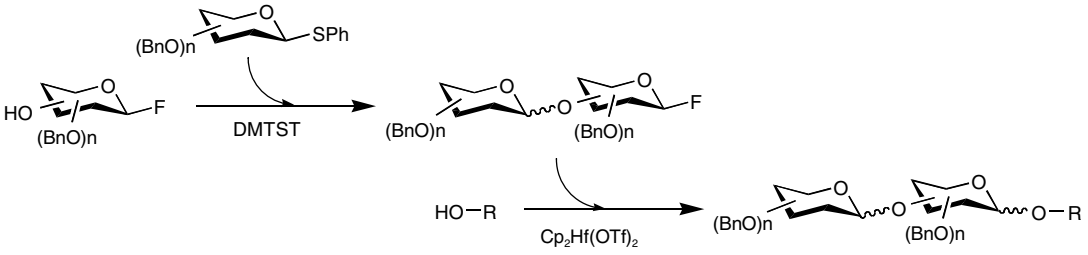


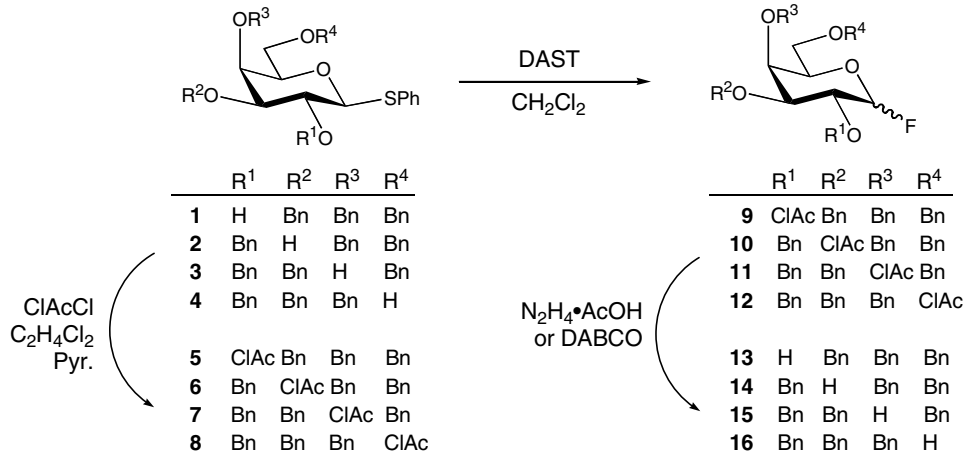
Scheme 1.

use of oligosaccharide libraries have not been applied to this problem. We therefore selected the Fuc*p*-Gal*p* sequence not only to demonstrate the synthesis of a library but also to provide a series of compounds for future biological investigations. In this paper, we report the synthesis of a library of the Fuc*p*-Gal*p* disaccharide consisting of all sets of anomeric configurations and linkages.

2. Results and discussion

For the synthesis of the library, we planned to adopt an orthogonal glycosylation strategy, which was considered to be most suitable for this type of synthesis. In the synthesis of the oligosaccharides iterative glycosylation reactions and protecting group manipulations have to be performed, and this complicates the overall synthesis due to problems associated with the selective reaction conditions that must be applied.[4] Because the orthogonal glycosylation strategy relies on only two reaction conditions to selectively activate one of the leaving groups over the other, the entire synthetic route becomes simple, which makes the method advantageous over others.[16] Although in the current report we report the synthesis of disaccharides, where only two coupling reactions are needed and thus the above consideration is not or primary concern, we envisioned future studies in which longer oligosaccharides were synthesized (Scheme 1).

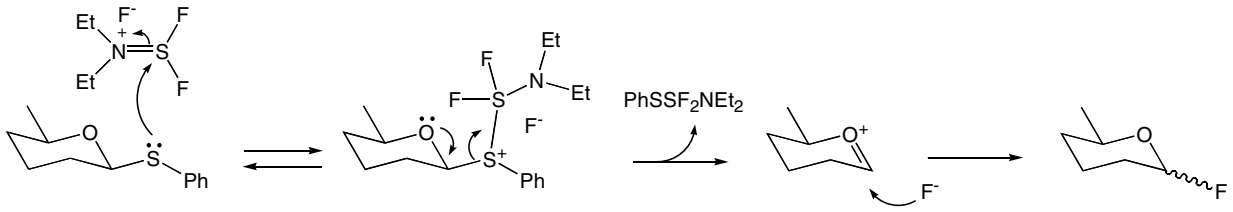
We have previously reported the synthesis of tribenzylated phenylthio galactopyranosides (**1**–**4**), which carry single hydroxyl groups at the 2-, 3-, 4-, and 6-positions, respectively.[20] To achieve orthogonal coupling, compounds **1**–**4** have to be converted into the corresponding fluorides (Scheme 2). First, each hydroxyl group in compounds **1**–**4** was protected with a chloroacetyl (ClAc) group (**5**–**8**) using chloroacetyl chloride in the presence of pyridine. Conversion of the thioglycosides into the glycosyl fluorides (**9**–**12**) was achieved by the action of *N*,*N*-diethylaminosulfur trifluoride (DAST).[21] We have found that bromonium ion, usually generated from *N*-bromosuccinimide (NBS), is not necessary for this reaction. In the absence of NBS, a higher reaction temperature (room temperature to 40 °C) was required, but the reaction was much cleaner and the desired fluoride was obtained in almost quantitative yield. We suggest that a Vilsmeir-type electrophilic sulfiminium cation species is the active agent in the reaction (Scheme 3). The next step was the deprotection of the ClAc group, which is usually achieved by treatment with thiourea,[22] 1,4-diazabicyclo[2,2,2]octane (DABCO),[23]



	R^1	R^2	R^3	R^4
1	H	Bn	Bn	Bn
2	Bn	H	Bn	Bn
3	Bn	Bn	H	Bn
4	Bn	Bn	Bn	H
5	ClAc	Bn	Bn	Bn
6	Bn	ClAc	Bn	Bn
7	Bn	Bn	ClAc	Bn
8	Bn	Bn	Bn	ClAc

	R^1	R^2	R^3	R^4
9	ClAc	Bn	Bn	Bn
10	Bn	ClAc	Bn	Bn
11	Bn	Bn	ClAc	Bn
12	Bn	Bn	Bn	ClAc
13	H	Bn	Bn	Bn
14	Bn	H	Bn	Bn
15	Bn	Bn	H	Bn
16	Bn	Bn	Bn	H

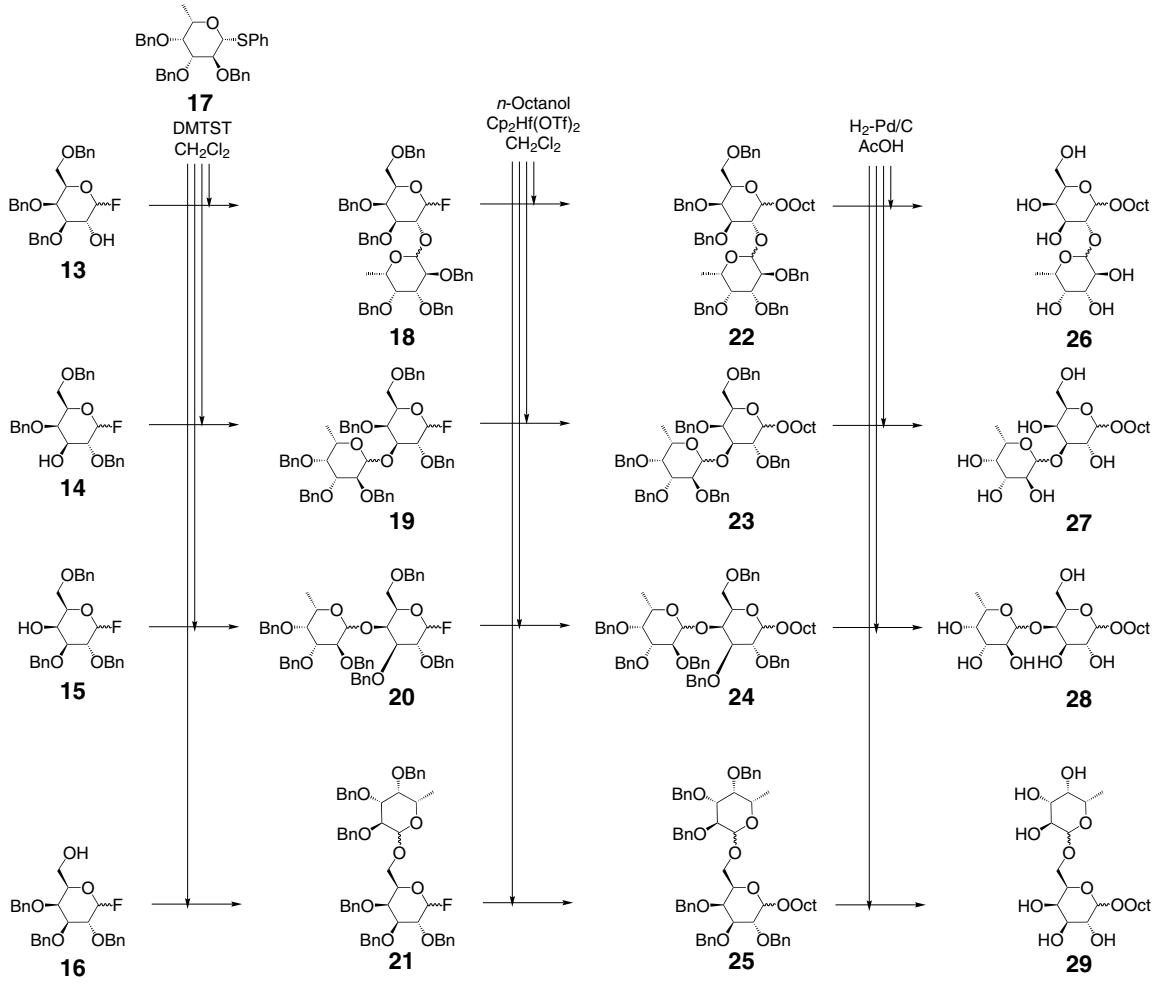
Scheme 2.



Scheme 3.

$NaOCH_3$,[24] or N_2H_4·AcOH.[25] In an effort to synthesize a series of synthetic units, we examined these reactions and found that the reactions of N_2H_4·AcOH and DABCO gave excellent results. Because the substrate for these reactions were glycosyl fluorides, we anticipated that the use of methoxide would generate anionic species next to the anomeric center in the case of compound **9**, leading to poor yield due to the loss of fluorine atom. The reaction using thiourea resulted in adequate yields (~75%) for all substrates. DABCO was the first choice for our substrates, except for the compound carrying a ClAc group at the O-2 position. In the case of compound **9**, N_2H_4·AcOH was found to give an essentially quantitative yield.

Having completed the syntheses of the monosaccharide units, we carried out the synthesis of a disaccharide library (Scheme 4). Glycosylation of compounds **13**–**16** with fucosyl donor **17** was carried out in the presence of DMTST[26,27] in dichloroethane and acetonitrile to yield disaccharides in generally good yield according by TLC. Because our intention was to synthesize all possible structures, we had determined beforehand that

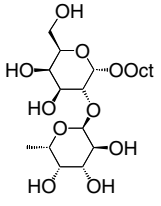
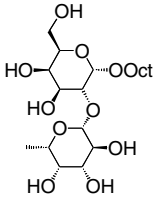
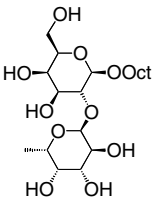
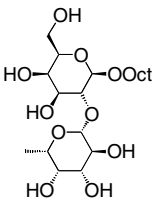
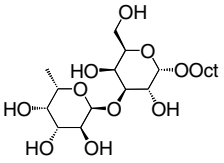
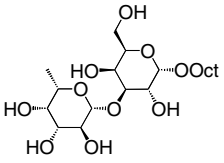
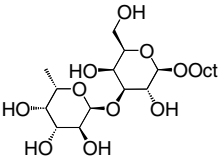
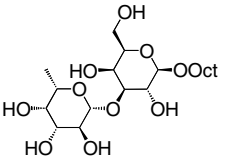
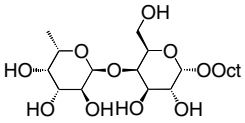
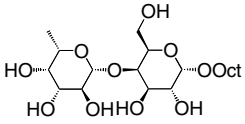
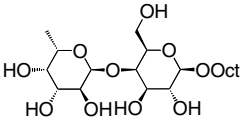
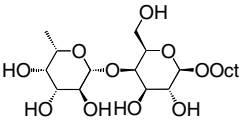
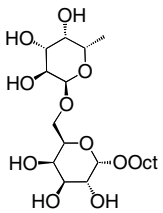
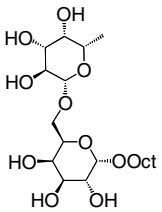
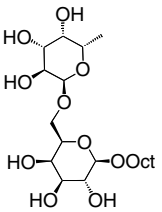
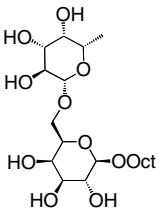


Scheme 4.

the optimal solvent system was a 1:1 mixture of dichloroethane and acetonitrile, which gave anomeric mixtures in the fucosylation reactions (data not shown). Each anomer in the disaccharide mixtures **18**–**21** was not purified at this stage to avoid unnecessary product loss, but instead were collected as a mixture. The mixtures were then used as the glycosyl donors and reacted with *n*-octanol in the presence of $Cp_2Hf(OTf)_2$.[28–30] Incorporation of an *n*-octyl group at the reducing anomeric center was based on a consideration that the final products can be distinguished easily from other hydrophilic by-products such as hydrolysis and elimination products.[31] The solvents used were dichloroethane and acetonitrile (1:1) to obtain a 'good' mixture where an equal distribution of anomers was obtained. The Fuc*p*-Gal*p*-Octyl disaccharides (**22**–**25**), were subjected to hydrogenation (58%, 49%, 40%, and 68% yields for 2-, 3-, 4-, and 6-position, respectively) and finally purified by high performance liquid chromatography (HPLC). A reverse-phase (C_{18}) column was successfully used to isolate all the anomers [designated as **i**–**iv** for α/α, β/α, α/β, and β/β Fuc*p*/Gal*p*, respectively] in each mixture (Table 1, **26**–**29**). We viewed it as rather unusual that these compounds could be successfully purified on reverse phase chromatography as these compounds have the same molecular weight. This suggests that there are differences in the partition coefficient values (log *P*) between these compounds, possible due to the packing of individual compounds.

In conclusion, we have demonstrated the synthesis of a complete library of Fuc*p*-Gal*p*-Octyl disaccharides. The extremely short syntheses were achieved using a semi-orthogonal glycosylation strategy. Although the method is neither practical nor 'efficient' in terms of stereospecific synthesis, libraries of this type may be useful as a source of potential pharmaceutical seeds or functional molecules. The NMR data of this library of compounds may also be useful in the structural characterization of newly discovered glycoconjugates. Furthermore, structural analysis and quantitative analysis of the MS/MS data obtained from the library are currently underway[32] in our laboratory using collision induced dissociation (CID) mass spectrometry, which will be reported elsewhere.

Table 1. Structures of the Fuc*p*-Gal*p* library

Linkage position	Gal	α		β	
	Fuc	α	β	α	β
Fuc-(1→2)-Gal		 **26-i**	 **26-ii**	 **26-iii**	 **26-iv**
Fuc-(1→3)-Gal		 **27-i**	 **27-ii**	 **27-iii**	 **27-iv**
Fuc-(1→4)-Gal		 **28-i**	 **28-ii**	 **28-iii**	 **28-iv**
Fuc-(1→6)-Gal		 **29-i**	 **29-ii**	 **29-iii**	 **29-iv**

3. Experimental

3.1. General methods

Analytical thin layer chromatography (TLC) was performed on Merck Art. 5715, Kieselgel 60 F_{254}/0.25 mm thickness plates. Visualization was accomplished with UV light and phosphomolybdic acid and/or sulfuric acid solution followed by heating. Column chromatography was performed with Merck Art 7734 Silica Gel 60 (70–230 mesh). Optical rotations were measured in a 1.0 dm tube with a Horiba SEPA-200 polarimeter. Melting points were measured with Yanaco MP-S3 micro-melting point apparatus. ^{1}H NMR (500 MHz) spectra were recorded with a AVANCE 500 spectrometer (Bruker Biospin Inc.) in deuterated solvents using $(CH_3)_4Si$ as the internal standard. ^{13}C NMR chemical shifts were obtained and assigned by HSQC experiments. HPLC was performed on Waters LC/MS System with following setup; Pump: Waters 2525; Makeup Pump: Waters 515 HPLC Pump; Column Oven: Senshu Scientific Co. Ltd 2120; MS: Waters Micromass ZQ. High resolution mass spectra were obtained using Q-STAR pulsar i with ESI interface (ABS) or LCMS-IT-TOF (Shimadzu). Solvents (HPLC): CH_3CN: Merck LC/MS hyper grade; H_2O: Wako HPLC grade. Columns (HPLC): Xterra C18: Waters Corp.; Chromolith Performance RP-18: Merck. Doubly deionized H_2O was prepared with a Milli-Q system (Millipore Corp.). Millex-GV syringe filters [0.22 μm × 4 mm (I.D.)] were from Nihon Millipore Ltd. Dry solvents were used in all reactions. Solutions were evaporated under reduced pressure at a bath temperature not exceeding 50 °C. Gel permeation chromatography was performed using Bio Beads SX-1 (Bio-Rad laboratories). Sep-Pak C18 was from Waters Corp.

3.2. Phenyl 3,4,6-tri-*O*-benzyl-2-*O*-chloroacetyl-1-thio-β-D-galactopyranoside (5)

To a solution of **1**[33] (1.01 g, 1.86 mmol) in $C_2H_4Cl_2$ (18 mL) and pyridine (1 mL) was added ClAcCl (300 μL, 3.73 mmol) at 0 °C and the mixture was stirred at rt for 30 min. The reaction mixture was diluted with EtOAc and extracted with N HCl, satd aq $NaHCO_3$, and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by chromatography on silica gel (5:1, hexane/EtOAc) to give **5** (1.14 g, 99%) as needles; mp: 121.5–122.0 °C; $[\alpha]_D^{27}$ +15.9 (*c* 1.0, $CHCl_3$); R_f 0.26 (5:1, hexane/EtOAc); ^{1}H NMR ($CDCl_3$): δ 7.48–7.20 (m, 20H, aromatic H), 5.43 (t, 1H, $J_{2,3}$ 9.7 Hz, H-2), 4.92 (d, 1H, *J* 11.5 Hz, PhC*H*$_2$), 4.67 (d, 1H, *J* 12.2 Hz, PhC*H*$_2$), 4.63 (d, 1H, $J_{1,2}$ 10.0 Hz, H-1), 4.56 (d, 1H, *J* 11.6 Hz, PhC*H*$_2$), 4.49 (d, 1H, *J* 11.9 Hz, PhC*H*$_2$), 4.45 (d, 1H, *J* 12.6 Hz, PhC*H*$_2$), 4.42 (d, 1H, *J* 11.6 Hz, PhC*H*$_2$), 4.00 (br d, 1H, *J* 2.7 Hz, H-4), 3.98 (d, 1H, *J* 14.8 Hz, ClC*H*$_2$CO), 3.90 (d, 1H, *J* 14.8 Hz, ClC*H*$_2$CO), 3.64–3.62 (m, 3H, H-5, H-6, H-6′), 3.59 (dd, 1H, $J_{3,4}$ 2.7 Hz, H-3); ^{13}C NMR ($CDCl_3$): δ 165.9 (ClCH$_2$*C*O), 138.3–127.5 (aromatic C), 86.2 (C-1), 81.2 (C-3), 77.6 (C-5), 74.4, 73.6 (Ph*C*H$_2$ × 2), 72.7 (C-4), 72.0 (Ph*C*H$_2$), 71.4 (C-2), 68.6 (C-6), 40.8 (Cl*C*H$_2$CO); ESIMS: *m*/*z* calcd for $[C_{35}H_{35}ClO_6]Na^+$: 641.1735. Found: 641.1732.

3.3. 3,4,6-Tri-*O*-benzyl-2-*O*-chloroacetyl-α,β-D-galactopyranosyl fluoride (9)

To a solution of **5** (213.5 mg, 345 μmol) in CH_2Cl_2 (3.5 mL) was added DAST (85 μL, 69 μmol) at 0 °C and the mixture was stirred at 40 °C for 3.5 h. The reaction mixture was diluted with EtOAc and extracted with satd aq $NaHCO_3$ and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated. The residue was purified by chromatography on silica gel (5:1, hexane/EtOAc) to give **9** (181.5 mg, quant., α/β = 1.00/0.32) as a pale yellow syrup; $[\alpha]_D^{23}$ +44.8 (α-anomer, *c* 1.0, $CHCl_3$); R_f 0.36 (α-anomer), 0.16 (β-anomer) (5:1, hexane/EtOAc); ^{1}H NMR ($CDCl_3$): δ 7.38–7.24 (m, 30H, aromatic H), 5.77 (dd, 1H, $J_{1,2}$ 2.7 Hz, $^2J_{1,F}$ 54.5 Hz, H-1α), 5.48 (ddd, 1H, $J_{2,3}$ 10.0 Hz, $^3J_{2,F}$ 12.3 Hz, H-2β), 5.40 (ddd, 1H, $J_{2,3}$ 10.4 Hz, $^3J_{2,F}$ 24.3 Hz, H-2α), 5.15 (dd, 1H, $J_{1,2}$ 7.0 Hz, $^2J_{1,F}$ 53.1 Hz, H-1β), 4.93 (d, 1H, *J* 11.3 Hz, PhC*H*$_2$-α), 4.92 (d, 1H, *J* 11.5 Hz, PhC*H*$_2$-β), 4.71 (d, 1H, *J* 12.0 Hz, PhC*H*$_2$-α), 4.67 (d, 1H, *J* 12.2 Hz, PhC*H*$_2$-β), 4.62 (d, 1H, *J* 12.0 Hz, PhC*H*$_2$-α), 4.58 (d, 1H, *J* 11.5 Hz, PhC*H*$_2$-β), 4.57 (d, 1H, *J* 11.3 Hz, PhC*H*$_2$-α), 4.51–4.42 (m, 5H, PhC*H*$_2$-α × 2, PhC*H*$_2$-β × 3), 4.12 (br t, 1H, *J* 6.6 Hz, H-5α), 4.07–3.92 (m, 7H, H-3α, H-4α,β, ClC*H*$_2$CO-α,β), 3.71 (m, 1H, H-5β), 3.66 (m, 2H, H-6β, H-6′β), 3.59 (d, 2H, *J* 6.5 Hz, H-6α, H-6′α), 3.57 (dd, $J_{3,4}$ 2.4 Hz, H-3β); ^{13}C NMR ($CDCl_3$): δ 166.8 (ClCH$_2$*C*O-α), 165.9 (ClCH$_2$*C*O-β), 137.9–127.5 (aromatic C), 107.0 (d, $J_{C\text{-}1,F}$ 219 Hz, C-1β), 104.5 (d, $J_{C\text{-}1,F}$ 226 Hz, C-1α), 78.7 (d, $^3J_{C\text{-}3,F}$ 12 Hz, C-3β), 75.8 (C-3α), 74.9 (Ph*C*H$_2$-α), 74.6 (Ph*C*H$_2$-β), 74.0 (d, $^3J_{C\text{-}5,F}$ 2 Hz, C-5β), 73.6 (C-4, Ph*C*H$_2$-β), 73.5 (Ph*C*H$_2$-α), 72.9 (d, $^2J_{C\text{-}2,F}$ 24 Hz, C-2α), 72.7 (Ph*C*H$_2$-α), 72.2 (Ph*C*H$_2$-β), 72.1 (d, $^2J_{C\text{-}2,F}$ 25 Hz, C-2α), 71.9 (d, $^3J_{C\text{-}5,F}$ 3 Hz, C-5α), 68.0 (C-6β), 67.9 (C-6α), 40.6 (Cl*C*H$_2$CO-α,β); ESIMS: *m*/*z* calcd for $[C_{29}H_{30}ClFO_6]Na^+$: 551.1607. Found: 551.1596.

3.4. 3,4,6-Tri-*O*-benzyl-α,β-D-galactopyranosyl fluoride (13)

To a solution of **9** (46.7 mg, 88.3 μmol) in DMF (0.88 mL) was added N_2H_4·AcOH (25 mg, 269 μmol) at rt, and stirred overnight at rt. The reaction mixture was diluted with EtOAc and extracted with satd aq $NaHCO_3$ and brine. The organic layer was dried (Na_2SO_4), filtered, and concentrated to give **13**[34]

(39.9 mg, quant., α/β = 1.00/0.29) as a light brown syrup, which was crystallized from hexane/EtOAc to give **13α** as needles; mp: 60.0–61.0 °C (α-anomer); $[\alpha]_D^{26}$ +58.7 (α-anomer, *c* 1.0, $CHCl_3$); R_f 0.24 (3:1, hexane/EtOAc); ^{1}H NMR ($CDCl_3$): δ 7.38–7.26 (m, 30H, aromatic H), 5.69 (dd, 1H, $J_{1,2}$ 2.7 Hz, $^2J_{1,F}$ 54.3 Hz, H-1α), 5.06 (dd, 1H, $J_{1,2}$ 7.1 Hz, $^2J_{1,F}$ 53.7 Hz, H-1β), 4.88 (d, 1H, *J* 11.3 Hz, PhCH_2-α), 4.87 (d, 1H, *J* 11.5 Hz, PhCH_2-β), 4.76–4.71 (m, 2H, PhCH_2-α,β), 4.64–4.42 (m, 8H, PhCH_2-α × 4, PhCH_2-β × 4), 4.20 (br dd, 1H, $J_{2,3}$ 9.1 Hz, $^3J_{2,F}$ 24.8 Hz, H-2α), 4.13 (br t, 1H, $J_{5,6}$ 6.6 Hz, H-5α), 4.09–4.03 (m, 2H, H-2β, H-4α), 3.95 (br s, 1H, H-4β), 3.76 (dd, 1H, $J_{2,3}$ 10.1 Hz, *J* 2.5 Hz, H-3α), 3.69–3.57 (m, 5H, H-5β, H-6α,β, H-6′α,β), 3.42 (dd, 1H, $J_{2,3}$ 9.8 Hz, *J* 2.4 Hz, H-3β), 2.49 (br s, 1H, OHβ), 2.24 (br s, 1H, OHα); ^{13}C NMR ($CDCl_3$): δ 138.1–127.7 (aromatic C), 109.6 (d, $J_{C\text{-}1,F}$ 213 Hz, C-1β), 107.3 (d, $J_{C\text{-}1,F}$ 224 Hz, C-1α), 81.1 (d, $^3J_{C\text{-}3,F}$ 11 Hz, C-3β), 78.6 (C-3α), 74.8 (Ph*C*H_2-α), 74.6 (Ph*C*H_2-β), 73.7 (d, $^3J_{C\text{-}5,F}$ 5 Hz, C-5β), 73.6 (Ph*C*H_2-β), 73.5 (Ph*C*H_2-α), 73.0 (C-4α), 72.4 (Ph*C*H_2-β), 72.2 (Ph*C*H_2-α), 72.0 (C-4β), 72.0 (d, $^3J_{C\text{-}5,F}$ 3 Hz, C-5α), 71.0 (d, $^2J_{C\text{-}2,F}$ 25 Hz, C-2β), 68.4 (d, $^2J_{C\text{-}2,F}$ 12 Hz, C-2α), 68.1 (C-6α,β); ESIMS: *m*/*z* calcd for $[C_{27}H_{29}FO_5]Na^+$: 475.1891. Found: 475.1887.

3.5. Phenyl 2,4,6-tri-*O*-benzyl-3-*O*-chloroacetyl-1-thio-β-D-galactopyranoside (6)

Compound **6**[24] was prepared according to the method described for the synthesis of compound **5** using compound **2**[24] (1.01 g, 1.86 mmol), $C_2H_4Cl_2$ (18 mL), pyridine (1 mL), and ClAcCl (300 μL, 3.73 mmol). Column chromatography (5:1, hexane/EtOAc); (1.14 g, 99%) as a pale yellow syrup; $[\alpha]_D^{26}$ +37.0 (*c* 1.0, $CHCl_3$); R_f 0.33 (5:1, hexane/EtOAc); ^{1}H NMR ($CDCl_3$): δ 7.59–7.20 (m, 20H, aromatic H), 4.98 (dd, 1H, $J_{3,4}$ 3.0 Hz, H-3), 4.83 (d, 1H, *J* 11.1 Hz, PhCH_2), 4.68 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1), 4.56 (s, 2H, PhCH_2), 4.52 (d, 1H, *J* 11.1 Hz, PhCH_2), 4.52 (d, 1H, *J* 11.8 Hz, PhCH_2), 4.45 (d, 1H, *J* 11.7 Hz, PhCH_2), 4.05 (br d, 1H, *J* 2.9 Hz, H-4), 3.95 (t, 1H, $J_{2,3}$ 9.7 Hz, H-2), 3.74 (br t, 1H, *J* 6.6 Hz, H-5), 3.67 (br d, 2H, *J* 6.6 Hz, H-6, H-6′), 3.60 (d, 1H, *J* 14.8 Hz, ClCH_2CO), 3.56 (d, 1H, *J* 14.8 Hz, ClCH_2CO); ^{13}C NMR ($CDCl_3$): δ 166.5 ($ClCH_2$*C*O), 138.1–127.3 (aromatic C), 87.6 (C-1), 78.4 (C-3), 76.7 (C-5), 75.3 (Ph*C*H_2), 75.2 (C-2), 74.9 (Ph*C*H_2), 74.2 (C-4), 73.5 (Ph*C*H_2), 67.8 (C-6), 40.4 (Cl*C*H_2CO); ESIMS: *m*/*z* calcd for $[C_{35}H_{35}ClO_6]Na^+$: 641.1735. Found: 641.1744.

3.6. 2,4,6-Tri-*O*-benzyl-3-*O*-chloroacetyl-α,β-D-galactopyranosyl fluoride (10)

Compound **10** was prepared according to the method described for the synthesis of compound **9** using compound **6** (55.1 mg, 89.0 μmol), CH_2Cl_2 (0.89 mL), and DAST (22 μL, 18 μmol). Column chromatography (5:1, hexane/EtOAc); yield (43.9 mg, 93%, α/β = 1.00/0.10) as a light brown syrup; $[\alpha]_D^{27}$ +55.4 (α/β = 25/1, *c* 1.0, $CHCl_3$); R_f 0.33 (5:1, hexane/EtOAc); NMR data for α-anomer: ^{1}H NMR ($CDCl_3$): δ 7.37–7.23 (m, 15H, aromatic H), 5.61 (dd, 1H, $J_{1,2}$ 2.6 Hz, $^2J_{1,F}$ 53.1 Hz, H-1), 5.29 (dd, 1H, $J_{3,4}$ 3.0 Hz, H-3), 4.69 (d, 1H, *J* 12.1 Hz, PhCH_2), 4.66 (d, 1H, *J* 12.2 Hz, PhCH_2), 4.58 (d, 1H, *J* 11.5 Hz, PhCH_2), 4.54 (s, 1H, PhCH_2), 4.52 (s, 1H, PhCH_2), 4.46 (d, 1H, *J* 11.9 Hz, PhCH_2), 4.24 (br t, 1H, *J* 6.8 Hz, H-5), 4.14 (br d, 1H, *J* 2.3 Hz, H-4), 4.04 (ddd, 1H, $J_{2,3}$ 10.4 Hz, $^3J_{2,F}$ 24.4 Hz, H-2), 3.80 (d, 1H, *J* 14.8 Hz, ClCH_2CO), 3.72 (d, 1H, *J* 14.8 Hz, ClCH_2CO), 3.58 (br d, 2H, *J* 6.2 Hz, H-6, H-6′); ^{13}C NMR ($CDCl_3$): δ 166.5 ($ClCH_2$*C*O), 137.7–127.8 (aromatic C), 105.6 (d, $J_{C\text{-}1,F}$ 228 Hz, C-1), 75.2 (Ph*C*H_2), 74.5 (C-4), 73.5, 73.4, 73.3 (C-2, C-3, Ph*C*H_2 × 2), 70.9 (d, $^3J_{C\text{-}5,F}$ 3 Hz, C-5), 67.4 (C-6), 40.6 (Cl*C*H_2CO); HRTOFMS calculated for $[C_{29}H_{30}ClFO_6]Na^+$: 551.1607. Found: 551.1598.

3.7. 2,4,6-Tri-*O*-benzyl-α,β-D-galactopyranosyl fluoride (14)

To a solution of **10** (131 mg, 248 μmol) in EtOH/pyridine (5:1, 2.5 mL) was added DABCO (85 mg, 743 μmol) at room temperature, and stirred for overnight at 70 °C. The reaction mixture was diluted with EtOAc and extracted with N HCl, satd aq $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give **14** (110 mg, quant., α/β = 1.00/0.08) as a light brown syrup; $[\alpha]_D^{27}$ +27.5 (α/β = 25/1, *c* 1.0, $CHCl_3$); R_f 0.30 (3:1, hexane/EtOAc); NMR data for α-anomer: ^{1}H NMR ($CDCl_3$): δ 7.37–7.27 (m, 15H, aromatic H), 5.63 (dd, 1H, $J_{1,2}$ 2.5 Hz, $^2J_{1,F}$ 53.7 Hz, H-1), 4.81 (d, 1H, *J* 11.5 Hz, PhCH_2), 4.74 (d, 1H, *J* 11.7 Hz, PhCH_2), 4.69 (d, 1H, *J* 11.7 Hz, PhCH_2), 4.62 (d, 1H, *J* 11.5 Hz, PhCH_2), 4.52 (d, 1H, *J* 11.9 Hz, PhCH_2), 4.45 (d, 1H, *J* 11.9 Hz, PhCH_2), 4.16 (br t, 1H, *J* 6.5 Hz, H-5), 4.07 (ddd, 1H, $J_{3,4}$ 3.3 Hz, $J_{3,OH}$ 4.6 Hz, H-3), 4.00 (br d, 1H, *J* 2.3 Hz, H-4), 3.80 (ddd, 1H, $J_{2,3}$ 10.0 Hz, $^3J_{2,F}$ 25.2 Hz, H-2), 3.61–3.55 (m, 2H, H-6, H-6′), 2.27 (d, 1H, $J_{2,OH}$ 5.0 Hz, OH); ^{13}C NMR ($CDCl_3$): δ 138.1–127.7 (aromatic C), 105.1 (d, $J_{C\text{-}1,F}$ 227 Hz, C-1), 76.5 (d, $^2J_{C\text{-}2,F}$ 24 Hz, C-2), 75.9 (C-4), 75.1, 73.3, 72.9 (Ph*C*H_2 × 3), 71.5 (d, $^3J_{C\text{-}5,F}$ 3 Hz, C-5), 69.7 (C-3), 68.1 (C-6); ESIMS: *m*/*z* calcd for $[C_{27}H_{29}FO_5]Na^+$: 475.1891. Found: 475.1891.

3.8. Phenyl 2,3,6-tri-*O*-benzyl-4-*O*-chloroacetyl-1-thio-β-D-galactopyranoside (7)

Compound **7** was prepared according to the method described for the synthesis of compound **5** using compound **3**[35] (1.02 g, 1.88 mmol), $C_2H_4Cl_2$ (18 mL),

pyridine (1 mL), and ClAcCl (300 μL, 3.73 mmol). Column chromatography (5:1, hexane/EtOAc); yield (1.08 g, 93.3%) as a pale yellow syrup; $[\alpha]_D^{23}$ +2.7 (*c* 1.0, $CHCl_3$); R_f 0.32 (5:1, hexane/EtOAc); ^1H NMR ($CDCl_3$): δ 7.57–7.25 (m, 20H, aromatic H), 5.70 (br d, 1H, *J* 2.9 Hz, H-4), 4.77 (d, 1H, *J* 10.9 Hz, PhCH_2), 4.74 (d, 1H, *J* 10.2 Hz, PhCH_2), 4.70 (d, 1H, *J* 10.2 Hz, PhCH_2), 4.68 (d, 1H, $J_{1,2}$ 9.6 Hz, H-1), 4.56 (d, 1H, *J* 11.6 Hz, PhCH_2), 4.49 (d, 1H, *J* 10.9 Hz, PhCH_2), 4.45 (d, 1H, *J* 11.6 Hz, PhCH_2), 4.05 (d, 1H, *J* 15.0 Hz, ClCH_2CO), 3.98 (d, 1H, *J* 15.0 Hz, ClCH_2CO), 3.78 (br t, 1H, *J* 6.5 Hz, H-5), 3.67 (dd, 1H, $J_{2,3}$ 9.1 Hz, $J_{3,4}$ 3.2 Hz, H-3), 3.64–3.58 (m 2H, H-2, H-6), 3.52 (dd, 1H, $J_{5,6}$ 7.4 Hz, $J_{6,6'}$ 9.3 Hz, H-6′); ^{13}C NMR ($CDCl_3$): δ 166.8 (ClCH$_2$*C*O), 138.0–127.6 (aromatic C), 87.7 (C-1), 81.0 (C-3), 76.6 (C-2), 75.8 (Ph*C*H$_2$), 75.4 (C-5), 73.7, 72.2 (Ph*C*H$_2$ × 2), 68.8 (C-4), 67.5 (C-6), 40.8 (Cl*C*H$_2$CO); ESIMS: *m*/*z* calcd for $[C_{35}H_{35}ClO_6]Na^+$: 641.1735. Found: 641.1745.

3.9. 2,3,6-Tri-*O*-benzyl-4-*O*-chloroacetyl-α,β-D-galactopyranosyl fluoride (11)

Compound **11** was prepared according to the method described for the synthesis of compound **9** using compound **7** (62.3 mg, 101 μmol), CH_2Cl_2 (1 mL), and DAST (25 μL, 20 μmol). Column chromatography (5:1, hexane/EtOAc); yield (47.6 mg, 89%, α/β = 1.00/0.03) as a pale brown syrup; $[\alpha]_D^{26}$ +17.2 (α-anomer, *c* 1.0, $CHCl_3$); R_f 0.34 (5:1, hexane/EtOAc); NMR data for α-anomer: ^1H NMR ($CDCl_3$): δ 7.37–7.29 (m, 15H, aromatic H), 5.73 (br d, 1H, *J* 2.5 Hz, H-4), 5.58 (dd, 1H, $J_{1,2}$ 2.6 Hz, $^2J_{1,F}$ 53.0 Hz, H-1), 4.83 (d, 1H, *J* 11.8 Hz, PhCH_2), 4.78 (d, 1H, *J* 11.1 Hz, PhCH_2), 4.67 (d, 1H, *J* 11.8 Hz, PhCH_2), 4.55 (d, 1H, *J* 11.1 Hz, PhCH_2), 4.55 (d, 1H, *J* 11.9 Hz, PhCH_2), 4.42 (d, 1H, *J* 11.9 Hz, PhCH_2), 4.26 (br t, 1H, *J* 6.4 Hz, H-5), 4.01 (d, 1H, *J* 14.8 Hz, ClCH_2CO), 3.98 (dd, 1H, $J_{3,4}$ 3.2 Hz, H-3), 3.94 (d, 1H, *J* 14.9 Hz, ClCH_2CO), 3.73 (ddd, 1H, $J_{2,3}$ 10.0 Hz, $^3J_{2,F}$ 25.3 Hz, H-2), 3.53 (dd, 1H, $J_{5,6}$ 5,7 Hz, $J_{6,6'}$ 9.4 Hz, H-6), 3.45 (dd, 1H, $J_{5,6'}$ 7.3 Hz, H-6); ^{13}C NMR ($CDCl_3$): δ 166.5 (ClCH$_2$*C*O), 137.7–127.8 (aromatic C), 106.0 (d, $J_{C\text{-}1,F}$ 227 Hz, C-1), 75.4 (C-3), 74.5 (d, $^2J_{C\text{-}2,F}$ 24 Hz, C-2), 73.9, 73.6, 72.2 (Ph*C*H$_2$ × 3), 69.5 (d, $^3J_{C\text{-}5,F}$ 3 Hz, C-5), 69.2 (C-4), 67.2 (C-6), 40.7 (Cl*C*H$_2$CO); ESIMS: *m*/*z* calcd for $[C_{29}H_{30}ClFO_6]Na^+$: 551.1607. Found: 551.1590.

3.10. 2,3,6-Tri-*O*-benzyl-α,β-D-galactopyranosyl fluoride (15)

Compound **15** was prepared according to the method described for the synthesis of compound **14** using compound **11** (73.6 mg, 139 μmol), EtOH/pyridine (5:1, 1.4 mL), and DABCO (48 mg, 42 μmol); yield (63.0 mg, quant., α/β = 1.00/0.05) as a pale yellow syrup; $[\alpha]_D^{27}$ +14.9 (α-anomer, *c* 1.1, $CHCl_3$); R_f 0.32 (3:1, hexane/EtOAc); NMR data for α-anomer: ^1H NMR ($CDCl_3$): δ 7.36–7.26 (m, 15H, aromatic H), 5.59 (dd, 1H, $J_{1,2}$ 2.4 Hz, $^2J_{1,F}$ 52.1 Hz, H-1), 4.82 (d, 1H, *J* 11.8 Hz, PhCH_2), 4.76 (d, 1H, *J* 11.6 Hz, PhCH_2), 4.73 (d, 1H, *J* 11.8 Hz, PhCH_2), 4.71 (d, 1H, *J* 11.6 Hz, PhCH_2), 4.57 (d, 1H, *J* 12.0 Hz, PhCH_2), 4.54 (d, 1H, *J* 12.0 Hz, PhCH_2), 4.12 (br s, 1H, H-4), 4.08 (br t, 1H, *J* 5.7 Hz, H-5), 3.89 (ddd, 1H, $J_{2,3}$ 9.8 Hz, $^3J_{2,F}$ 27.5 Hz, H-2), 3.86 (br s, 1H, H-3), 3.73 (dd, 1H, $J_{5,6}$ 5.6 Hz, $J_{6,6'}$ 10.0 Hz, H-6), 3.68 (dd, 1H, $J_{5,6'}$ 5.9 Hz H-6′), 2.75 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$): δ 137.8–127.7 (aromatic C), 106.0 (d, $J_{C\text{-}1,F}$ 226 Hz, C-1), 77.0 (C-3), 75.0 (d, $^2J_{C\text{-}2,F}$ 24 Hz, C-2), 73.6, 73.6, 72.5 (Ph*C*H$_2$ × 3), 70.7 (d, $^3J_{C\text{-}5,F}$ 3 Hz, C-5), 69.0 (C-6), 67.4 (C-4); ESIMS: *m*/*z* calcd for $[C_{27}H_{29}FO_5]Na^+$: 475.1891. Found: 475.1888.

3.11. Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-chloroacetyl-1-thio-β-D-galactopyranoside (8)

Compound **8** was prepared according to the method described for the synthesis of compound **5** using compound **4**[36] (1.01 g, 1.86 mmol), $C_2H_4Cl_2$ (18 mL), pyridine (1 mL), and ClAcCl (300 μL, 3.73 mmol). Column chromatography (5:1, hexane/EtOAc); yield (1.09 g, 95%) as a pale yellow solid, which was crystallized from hexane/EtOAc; mp: 72.5–73.0 °C; $[\alpha]_D^{27}$ −8.3 (*c* 1.0, $CHCl_3$); R_f 0.19 (5:1, hexane/EtOAc); ^1H NMR ($CDCl_3$): δ 7.57–7.22 (m, 20H, aromatic H), 5.00 (d, 1H, *J* 11.6 Hz, PhCH_2), 4.83 (d, 1H, *J* 10.2 Hz, PhCH_2), 4.81–4.75 (m, 3H, PhCH_2), 4.64 (d, 1H, *J* 11.6 Hz, PhCH_2), 4.63 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1), 4.36 (dd, 1H, $J_{5,6}$ 7.1 Hz, $J_{6,6'}$ 11.2 Hz, H-6), 4.13 (dd, 1H, $J_{5,6'}$ 5.4 Hz, H-6′), 3.95 (t, 1H, $J_{2,3}$ 9.4 Hz, H-2), 3.94 (d, 1H, *J* 14.7 Hz, ClCH_2CO), 3.90 (d, 1H, *J* 15.0 Hz, COCH_2Cl), 3.83 (br d, 1H, *J* 2.2 Hz, H-4), 3.62–3.59 (m, 2H, H-2, H-5); ^{13}C NMR ($CDCl_3$): δ 166.8 (ClCH$_2$*C*O), 138.0–127.3 (aromatic C), 87.8 (C-1), 84.0 (C-3), 77.3 (C-2), 75.7 (Ph*C*H$_2$), 75.5 (C-5), 74.1, 73.2 (Ph*C*H$_2$ × 2), 72.9 (C-4), 64.8 (C-6), 40.6 (Cl*C*H$_2$CO); ESIMS: *m*/*z* calcd for $[C_{35}H_{35}ClO_6]Na^+$: 641.1735. Found: 641.1733.

3.12. 2,3,4-Tri-*O*-benzyl-6-*O*-chloroacetyl-α,β-D-galactopyranosyl fluoride (12)

Compound **12** was prepared according to the method described for the synthesis of compound **9** using compound **8** (46.6 mg, 75.3 μmol), CH_2Cl_2 (0.75 mL), and DAST (19 μL, 15 μmol). Column chromatography (5:1, hexane/EtOAc); yield (38.0 mg, 95%, α/β = 1.00/0.01) as a pale brown syrup; $[\alpha]_D^{25}$ −2.6 (α/β = 12/1, *c* 1.1, $CHCl_3$); R_f 0.25 (5:1, hexane/EtOAc); NMR data for α-anomer: ^1H NMR ($CDCl_3$): δ 7.41–7.28 (m, 15H, aromatic H), 5.58 (dd, 1H, $J_{1,2}$ 2.6 Hz, $^2J_{1,F}$

53.5 Hz, H-1), 4.98 (d, 1H, *J* 11.4 Hz, PhCH_2), 4.89 (d, 1H, *J* 11.7 Hz, PhCH_2), 4.86 (d, 1H, *J* 11.8 Hz, PhCH_2), 4.79 (d, 1H, *J* 11.7 Hz, PhCH_2), 4.73 (d, 1H, *J* 11.8 Hz, PhCH_2), 4.62 (d, 1H, *J* 11.4 Hz, PhCH_2), 4.25 (dd, 1H, $J_{5,6}$ 6.5 Hz, $J_{6,6'}$ 10.8 Hz, H-6), 4.13–4.02 (m, 3H, H-2, H-5, H-6′), 3.98–3.91 (m, 3H, H-3, ClCH_2CO), 3.91 (br s, 1H, H-4); ^{13}C NMR ($CDCl_3$): δ 166.8 (ClCH_2CO), 138.1–127.6 (aromatic C), 106.0 (d, $J_{C\text{-}1,F}$ 227 Hz, C-1), 78.2 (C-3), 75.6 (d, $^2J_{C\text{-}2,F}$ 24 Hz, C-2), 74.5 (PhCH_2), 73.8 (PhCH_2), 73.7 (C-4), 73.5 (PhCH_2), 70.6 (d, $^3J_{C\text{-}5,F}$ 3 Hz, C-5), 64.5 (C-6), 40.6 (ClCH_2CO); ESIMS: *m*/*z* calcd for $[C_{29}H_{30}ClFO_6]Na^+$: 551.1607. Found: 551.1600.

3.13. 2,3,6-Tri-*O*-benzyl-α,β-D-galactopyranosyl fluoride (16)

Compound **16** was prepared according to the method described for the synthesis of compound **14** using compound **12** (71.2 mg, 135 μmol), EtOH/pyridine (5:1, 1.4 mL), and DABCO (46.0 mg, 402 μmol); yield (60.9 mg, quant., α/β = 1.00/<0.01) as a pale yellow syrup; $[\alpha]_D^{26}$ +2.0 (α/β = 25/1, *c* 1.2, $CHCl_3$); R_f 0.27 (2:1, hexane/EtOAc); NMR data for α-anomer: ^{1}H NMR ($CDCl_3$): δ 7.40–7.26 (m, 15H, aromatic H), 5.61 (dd, 1H, $J_{1,2}$ 2.6 Hz, $^2J_{1,F}$ 53.9 Hz, H-1), 4.97 (d, 1H, *J* 11.5 Hz, PhCH_2), 4.86 (d, 2H, *J* 11.7 Hz, PhCH_2), 4.77 (d, 1H, *J* 11.8 Hz, PhCH_2), 4.73 (d, 1H, *J* 11.8 Hz, PhCH_2), 4.64 (d, 1H, *J* 11.5 Hz, PhCH_2), 4.06 (ddd, 1H, $J_{2,3}$ 9.8 Hz, $^3J_{2,F}$ 25.2 Hz, H-2), 3.96–3.91 (m, 3H, H-3, H-4, H-5), 3.73 (dd, 1H, $J_{5,6}$ 6.3 Hz, $J_{6,6'}$ 11.3 Hz, H-6), 3.53 (dd, 1H, $J_{5,6'}$ 5.6 Hz, H-6′); ^{13}C NMR ($CDCl_3$): δ 138.2–127.5 (aromatic C), 106.1 (d, $J_{C\text{-}1,F}$ 226 Hz, C-1), 78.4 (C-3), 75.7 (d, $^2J_{C\text{-}2,F}$ 24 Hz, C-2), 74.5 (PhCH_2), 74.2 (C-4), 73.7, 73.3 (PhCH_2 × 2), 73.0 (d, $^3J_{C\text{-}5,F}$ 3 Hz, C-5), 61.8 (C-6); ESIMS: *m*/*z* calcd for $[C_{27}H_{29}FO_5]Na^+$: 475.1891. Found: 475.1902.

3.14. Synthesis of octyl L-fucopyranosyl-(1→2)-D-galactopyranosides (26)

3.14.1. Glycosylation of 3,4,6-tri-*O*-benzyl galactopyranosyl fluoride with phenyl 2,3,4-tri-*O*-benzyl-1-thiofucopyranoside. A mixture of compound **17** (58 mg, 0.11 mmol), **13** (50 mg, 0.11 mmol), and AW300 molecular sieves (500 mg) in $C_2H_4Cl_2$ (1.0 mL) and CH_3CN (1.0 mL) was stirred for 3 h under an N_2 atmosphere. To this mixture, MeSSMe (19.9 μL, 0.22 mmol) and MeOTf (25.0 μL, 0.22 mmol) were added at 0 °C and the mixture was stirred for further 4 h. Et_3N was added to the reaction mixture, the mixture was filtered through Celite pad and washed with CH_2Cl_2, which was washed with satd aq $NaHCO_3$. The organic layer was dried ($MgSO_4$) and concentrated to dryness. The residue was purified on silica gel column chromatography (15:1, toluene/EtOAc) to yield **18** (86 mg, 0.99 mmol; 90%). The mixture of fluorides showed anomeric protons around 5.1–5.7 ppm with typical coupling constants ($J_{1,2}$ ~ 3.5 and ~7.8 Hz) corresponding to the α- and β-anomers and those of $J_{1,F}$ (~53 Hz).

3.14.2. Glycosylation of *n*-octanol reaction with disaccharide fluoride. Mixture A: Compound **18** (34 mg, 39.2 μmol) and *n*-octanol (12.3 μL, 78.3 μmol) dissolved in CH_3CN (1.0 mL) was stirred in the presence of AW300 molecular sieves (500 mg) for 2 h under a N_2 atmosphere. Mixture B: To a mixture of AgOTf (30.0 mg, 118 μmol) and AW300 molecular sieves (500 mg) in $C_2H_4Cl_2$ (1.0 mL), which was stirred for 2 h under a N_2 atmosphere, was added Cp_2HfCl_2 (22.2 mg, 58.8 μmol), and the mixture was further stirred for 2 h. The mixture was then centrifuged at 2000 rpm for 10 min to remove precipitated AgCl. To mixture A, a supernatant of a mixture B was added at −20 °C, and resulting mixture was stirred for 4 h. The reaction was terminated by adding Et_3N, the mixture was filtered through Celite pad and washed with CH_2Cl_2. The solution was washed with satd aq $NaHCO_3$ and the organic layer was dried over $MgSO_4$ and concentrated. The residue was purified on a column of Bio Beads SX-1 (toluene) to afford **22**, 55 mg, as an anomeric mixture.

3.14.3. Hydrogenation of disaccharide. Compound **22** (55 mg, mixture) dissolved in AcOH (4.0 mL) was stirred in the presence of 5% Pd/C (60 mg) for 12 h under a H_2 atmosphere. The mixture was filtered through Celite pad and washed with CH_3OH. After concentration, the residue was purified on a Sep-Pak C_{18} (elution with H_2O and then CH_3OH). The latter solution, containing the desired octyl glycoside of the disaccharide, was concentrated. The residue was dissolved in H_2O, filtered through Millex GV filter, and concentrated to give compound **26** (11 mg, 25.1 μmol; 58%; three steps). Ratio: **26-i**:**26-ii**:**26-iii**:**26-iv** 12:1:37:21 (estimated by LC–MS, based on assumption that these compounds are similarly ionized).

3.14.4. Isolation of isomers using HPLC. Compound **26** was purified using HPLC–MS. Flow rate: 1.0 mL/min; column: Cadenza CD-C18, 3 μm, 75 mm (L) × 4.6 mm (I.D.); mobile phase: CH_3CN/H_2O (17:83); column temperature: 15 °C; detection (*m*/*z*): 461.3 $[M+Na]^+$; retention times (min): 46.4 (**26-ii**; β-Fuc-α-Gal), 49.0 (**26-iv**; β-Fuc-β-Gal), 73.3 (**26-i**; α-Fuc-α-Gal), and 93.3 (**26-iii**; α-Fuc-β-Gal).

3.14.4.1. Octyl α-L-fucopyranosyl-(1→2)-α-D-galactopyranoside (26-i). ^{1}H NMR (D_2O): δ 5.05 (d, 1H, $J_{1',2'}$ 3.6 Hz, H-1′), 5.02 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.09 (q, 1H, $J_{5',6'}$ 6.5 Hz, H-5′), 4.00 (br d, 1H, H-4), 3.97 (dd, 1H, H-3), 3.91–3.85 (m, 2H, H-3′, H-5), 3.81–3.74 (m, 4H, H-2, H-2′, H-4′, OCH_2CH_2(CH_2)$_5$CH_3), 3.72

(d, 2H, $J_{5,6a}$, $J_{5,6b}$ 5.8 Hz, H-6a, H-6b), 3.48 (q, 1H, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 1.62 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.38–1.21 (m, 13H, H-6′,OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 0.85 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D$_2$O): δ 102.0 (C-1′), 98.3 (C-1), 78.3 (C-2), 72.2 (C-4′), 71.2 (C-5), 69.8 (C-4), 69.7 (C-3′), 69.0 (C-3), 69.0 (C-2′), 68.8 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 67.8 (C-5′), 61.5 (C-6), 31.4 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 29.0 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.9 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.8 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.5 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 16.1 (C-6′), 13.9 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [C$_{20}$H$_{38}$O$_{10}$]Na$^+$: 461.2357. Found: 461.2353.

3.14.4.2. Octyl β-L-fucopyranosyl-(1→2)-α-D-galactopyranoside (26-ii). ^{1}H NMR (D$_2$O): δ 5.08 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.45 (d, 1H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.01 (br d, 1H, $J_{3,4}$ 2.8 Hz, H-4), 3.98 (dd, 1H, $J_{2,3}$ 7.0 Hz, H-2), 3.93–3.88 (m, 2H, H-3, H-5), 3.77 (q, 1H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.74–3.66 (m, 4H, H-4′, H-6a, H-6b, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.61 (dd, 1H, $J_{3',4'}$ 3.0 Hz, H-3′), 3.53 (m, 1H, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.49 (dd, 1H, $J_{2',3'}$ 9.8 Hz, H-2′), 1.59 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.34–1.21 (m, 13H, H-6′, OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 0.83 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D$_2$O): δ 101.5 (C-1′), 96.0 (C-1), 75.6 (C-2), 72.7 (C-3′), 71.1 (C-4′), 71.0 (C-5′), 70.7 (C-3), 70.5 (C-2′), 68.9 (C-4), 68.3 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 68.0 (C-5), 61.0 (C-6), 31.1 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 28.7 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.8 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.2 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 15.4 (C-6′), 13.6 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [C$_{20}$H$_{38}$O$_{10}$]Na$^+$: 461.2357. Found: 461.2354.

3.14.4.3. Octyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranoside (26-iii).[37] ^{1}H NMR (D$_2$O): δ 5.26 (d, 1H, $J_{1',2'}$ 3.6 Hz, H-1′), 4.62 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.34 (q, 1H, $J_{5',6'}$ 6.4 Hz, H-5′), 3.93–3.88 (m, 2H, H-4, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.85–3.82 (m, 2H, H-3, H-3′), 3.78–3.71 (m, 4H, H-2′, H-4′, H-6a, H-6b), 3.66–3.63 (m, 2H, H-5, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.57 (t, 1H, $J_{2,3}$ 8.6 Hz, H-2), 1.60 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.30–1.26 (m, 10H, OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 1.20 (d, 3H, $J_{5',6'}$ 6.6 Hz, H-6′), 0.85 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D$_2$O): δ 102.0 (C-1), 99.6 (C-1′), 76.7 (C-2), 75.3 (C-5), 74.2 (C-3), 72.3 (C-2′), 71.0 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 70.0 (C-3′), 69.3 (C-4), 68.7 (C-4′), 67.2 (C-5′), 61.3 (C-6), 31.4 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 29.3 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.9 (OCH$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 25.7 (OCH$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 22.4 (OCH$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 15.7 (C-6′), 13.9 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [C$_{20}$H$_{38}$O$_{10}$]Na$^+$: 461.2357. Found: 461.2355.

3.14.4.4. Octyl β-L-fucopyranosyl-(1→2)-β-D-galactopyranoside (26-iv). ^{1}H NMR (D$_2$O): δ 4.67 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.54 (m, 1H, $J_{1,2}$ 7.3 Hz, H-1), 3.95–3.91 (m, 2H, H-4, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.79–3.72 (m, 4H, H-4′, H-5′, H-6a, H-6b), 3.71–3.61 (m, 5H, H-2, H-3, H-3′, H-5, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.48 (t, 1H, $J_{2',3'}$ 8.4 Hz, H-2′), 1.62 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.35–1.24 (m, 13H, H-6′, OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 0.84 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D$_2$O): δ 106.4 (C-1), 102.4 (C-1′), 77.4 (C-2), 75.2 (C-5), 73.3 (C-3′), 72.1 (C-3), 71.7 (C-4′), 71.2 (C-5′), 71.2 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 71.2 (C-2′), 68.6 (C-4), 61.2 (C-6), 31.1 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 29.1 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.2 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 15.8 (C-6′), 13.9 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [C$_{20}$H$_{38}$O$_{10}$]Na$^+$: 461.2357. Found: 461.2354.

3.15. Synthesis of octyl L-fucopyranosyl-(1→3)-D-galactopyranosides (27)

The title compound was synthesized according to the procedure described for the synthesis of compound **26**. Overall yield: 49% (three steps after Sep-Pak). Ratio: **27-i**:**27-ii**:**27-iii**:**27-iv** 1.0:1.0:1.7:1.6 (estimated by LC–MS based on assumption that these compounds are similarly ionized). HPLC conditions follows; flow rate: 1.0 mL/min; column: [Chromolith Performance RP-18e, 200 mm (L) × 4.6 mm (I.D.) (two columns were connected)]; mobile phase: CH$_3$CN/H$_2$O 17:83; column temperature: 30 °C; detection (*m*/*z*): 461.3 [M+Na]$^+$; retention times (min): 74.2 (**27-iii**; α-Fuc-β-Gal), 87.4 (**27-i**; α-Fuc-α-Gal), 123 (**27-iv**; β-Fuc-β-Gal), and 140 (**27-ii**; β-Fuc-α-Gal).

3.15.1. Octyl α-L-fucopyranosyl-(1→3)-α-D-galactopyranoside (27-i). ^{1}H NMR (D$_2$O): δ 5.13 (d, 1H, $J_{1',2'}$ 4.0 Hz, H-1′), 4.94 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.17 (q, 1H, $J_{5',6'}$ 6.7 Hz, H-5′), 4.05 (br d, 1H, $J_{3,4}$ 2.9 Hz, H-4), 3.99–3.91 (m, 3H, H-2, H-3′, H-5), 3.86 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 2.9 Hz, H-3), 3.81 (br d, 1H, $J_{3',4'}$ 2.7 Hz, H-4′), 3.77 (dd, 1H, $J_{2',3'}$ 10.4 Hz, H-2′), 3.74–3.70 (m, 3H, H-6a, H-6b, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.52 (m, 1H, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 1.61 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.36–1.26 (m, 10H, OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 1.19 (d, 3H, $J_{5',6'}$ 6.6 Hz, H-6′), 0.84 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D$_2$O): δ 101.4 (C-1′), 98.6 (C-1), 78.5 (C-3), 72.4 (C-4′), 71.3 (C-5), 69.8 (C-3′), 69.8 (C-4), 69.0 (C-2′), 68.8 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 67.8 (C-2), 67.5 (C-5′), 61.5 (C-6), 31.4 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 28.7 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.8 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.2 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 15.8 (C-6′), 13.9 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [C$_{20}$H$_{38}$O$_{10}$]Na$^+$: 461.2357. Found: 461.2350.

3.15.2. Octyl β-L-fucopyranosyl-(1→3)-α-D-galactopyranoside (27-ii). ^{1}H NMR (D$_2$O): δ 4.97 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 4.67 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.18

(br d, 1H, $J_{3,4}$ 2.7 Hz, H-4), 4.02 (dd, 1H, $J_{2,3}$ 10.1 Hz, $J_{3,4}$ 2.7 Hz, H-3), 3.92 (m, 2H, H-2, H-5), 3.78 (q, 1H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.74–3.69 (m, 4H, H-4′, H-6a, H-6b, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.65 (dd, 1H, $J_{2,3}$ 9.9 Hz, $J_{3,4}$ 3.4 Hz, H-3′), 3.52 (m, 2H, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 1.62 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.37–1.24 (m, 13H, H-6′,OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 0.85 (t, 3H, OCH$_2$-CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D$_2$O): δ 100.9 (C-1′), 98.3 (C-1), 77.7 (C-3), 73.3 (C-3′), 71.8 (C-4′), 71.4 (C-5′), 71.0 (C-5), 70.9 (C-2′), 68.8 (O*C*H$_2$CH$_2$(CH$_2$)$_5$-CH$_3$), 67.2 (C-2), 67.2 (C-4), 61.4 (C-6), 31.4 (OCH$_2$-CH$_2$(*C*H$_2$)$_5$CH$_3$), 28.8 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.7 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.7 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.9 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 15.7 (C-6′), 13.9 (OCH$_2$-CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [C$_{20}$H$_{38}$O$_{10}$]-Na$^+$: 461.2357. Found: 461.2358.

3.15.3. Octyl α-L-fucopyranosyl-(1→3)-β-D-galactopyranoside (27-iii). ^{1}H NMR (D$_2$O): δ 5.15 (d, 1H, $J_{1',2'}$ 3.9 Hz, H-1′), 4.43 (m, 1H, $J_{1,2}$ 7.4 Hz, H-1), 4.18 (q, 1H, $J_{5',6'}$ 6.6 Hz, H-5′), 4.00 (br d, 1H, H-4), 3.94–3.89 (m, 2H, H-3′, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.81 (br d, 1H, $J_{3',4'}$ 3.0 Hz, H-4′), 3.78–3.62 (m, 7H, H-2, H-2′, H-3, H-5, H-6a, H-6b, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 1.61 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.34–1.26 (m, 10H, OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 1.19 (d, 3H, $J_{5',6'}$ 6.6 Hz, H-6′), 0.84 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D$_2$O): δ 102.8 (C-1), 101.3 (C-1′), 81.3 (C-3), 75.4 (C-5), 72.2 (C-4′), 71.0 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 70.5 (C-2), 69.8 (C-3′), 69.0 (C-4), 68.8 (C-2′), 67.6 (C-5′), 61.2 (C-6), 31.1 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 28.9 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.4 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.2 (OCH$_2$CH$_2$-(*C*H$_2$)$_5$CH$_3$), 15.7 (C-6′), 13.9 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [C$_{20}$H$_{38}$O$_{10}$]Na$^+$: 461.2357. Found: 461.2349.

3.15.4. Octyl β-L-fucopyranosyl-(1→3)-β-D-galactopyranoside (27-iv). ^{1}H NMR (D$_2$O): δ 4.49 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.42 (d, 1H, $J_{1,2}$ 8.0 Hz, H-1), 4.12 (br d, 1H, $J_{3,4}$ 3.2 Hz, H-4), 3.91 (q, 1H, OCH_2CH$_2$-(CH$_2$)$_5$CH$_3$), 3.84 (dd, 1H, $J_{2,3}$ 9.0 Hz, H-3), 3.80–3.72 (m, 4H, H-4′, H-5′, H-6a, H-6b), 3.69–3.64 (m, 3H, H-3′, H-5, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.59 (t, 1H, H-2), 3.52 (t, 1H, $J_{2',3'}$ 8.8 Hz, H-2′), 1.61 (m, 2H, OCH$_2$-CH_2(CH$_2$)$_5$CH$_3$), 1.35–1.24 (m, 13H, H-6′,OCH$_2$-CH$_2$(CH_2)$_5$CH$_3$), 0.84 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D$_2$O): δ 102.9 (C-1), 101.0 (C-1′), 80.5 (C-3), 75.2 (C-3′), 73.3 (C-5), 71.7 (C-4′), 71.6 (C-5′), 71.0 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 70.9 (C-2′), 69.8 (C-2), 66.6 (C-4), 61.2 (C-6), 31.4 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 28.9 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$-CH$_3$), 25.4 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.2 (OCH$_2$CH$_2$-(*C*H$_2$)$_5$CH$_3$), 15.9 (C-6′), 13.9 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [C$_{20}$H$_{38}$O$_{10}$]Na$^+$: 461.2357. Found: 461.2362.

3.16. Synthesis of octyl L-fucopyranosyl-(1→4)-D-galactopyranosides (28)

The title compound was synthesized according to the procedure described for the synthesis of compound **26**. Overall yield: 40% (three steps after Sep-Pak). Ratio: **28-i**:**28-ii**:**28-iii**:**28-iv** 1.0:3.1:7.8:4.2 (estimated by LC–MS based on assumption that these compounds are similarly ionized). HPLC conditions follows; flow rate: 1.0 mL/min; column: [Chromolith Performance RP-18e, 200 mm (L) × 4.6 mm (I.D.) (two columns were connected)]; mobile phase: CH$_3$CN/H$_2$O 20:80; column temperature: 30 °C; detection (*m*/*z*): 461.3 [M+Na]$^+$; retention times (min): 36.9 (**28-iv**; β-Fuc-β-Gal), 49.8 (**28-ii**; β-Fuc-α-Gal), 54.4 (**28-iii**; α-Fuc-β-Gal), and 62.4 (**28-i**; α-Fuc-α-Gal).

3.16.1. Octyl α-L-fucopyranosyl-(1→4)-α-D-galactopyranoside (28-i). ^{1}H NMR (D$_2$O): δ 5.12 (d, 1H, $J_{1',2'}$ 4.0 Hz, H-1′), 4.94 (d, 1H, $J_{1,2}$ 3.1 Hz, H-1), 4.13 (q, 1H, H-5′), 4.04 (br d, 1H, H-4), 3.99 (dd, 1H, $J_{5,6a}$ 4.2 Hz, $J_{5,6b}$ 7.6 Hz, H-5), 3.89 (m, 3H, H-2, H-3, H-3′), 3.82 (m, 2H, H-2′, H-4′), 3.76–3.68 (m, 3H, H-6a, H-6b, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.53 (m, 1H, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 1.62 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$-CH$_3$), 1.39–1.23 (m, 10H, OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 1.22 (d, 3H, $J_{5',6'}$ 6.5 Hz, H-6′), 0.85 (t, 3H, OCH$_2$-CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D$_2$O): δ 101.8 (C-1′), 98.6 (C-1), 79.8 (C-4), 72.1 (C-4′), 71.4 (C-5), 70.7 (C-3), 70.0 (C-6), 69.7 (C-3′), 69.5 (C-2), 69.3 (C-2′), 68.8 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 67.9 (C-5′), 31.1 (OCH$_2$-CH$_2$(*C*H$_2$)$_5$CH$_3$), 28.7 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.7 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.1 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 15.7 (C-6′), 12.4 (OCH$_2$-CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [C$_{20}$H$_{38}$-O$_{10}$]Na$^+$: 461.2357. Found: 461.2355.

3.16.2. Octyl β-L-fucopyranosyl-(1→4)-α-D-galactopyranoside (28-ii). ^{1}H NMR (D$_2$O): δ 4.95 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1), 4.33 (d, 1H, $J_{1',2'}$ 7.8 Hz, H-1′), 4.15 (br d, 1H, H-4), 4.02 (t, 1H, $J_{5,6a}$, $J_{5,6b}$ 6.2 Hz, H-5), 3.84–3.78 (m, 5H, H-2, H-3, H-5′, H-6a, H-6b), 3.74–3.69 (m, 2H, H-4′, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.64 (dd, 1H, $J_{3',2'}$ 10.0 Hz, $J_{3',4'}$ 3.8 Hz, H-3′), 3.52 (m, 2H, H-2′, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 1.61 (m, 2H, OCH$_2$CH_2-(CH$_2$)$_5$CH$_3$), 1.34–1.23 (m, 13H, H-6′, OCH$_2$CH$_2$-(CH_2)$_5$CH$_3$), 0.85 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D$_2$O): δ 103.5 (C-1′), 98.9 (C-1), 79.5 (C-4), 73.1 (C-3′), 71.8 (C-4′), 71.4 (C-5), 71.4 (C-5′), 71.1 (C-2′), 69.5 (C-2), 69.5 (C-3), 69.1 (O*C*H$_2$CH$_2$(CH$_2$)$_5$-CH$_3$), 61.1 (C-6), 31.4 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 28.6 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.7 (OCH$_2$CH$_2$(*C*H$_2$)$_5$-CH$_3$), 15.8 (C-6′), 12.4 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [C$_{20}$H$_{38}$O$_{10}$]Na$^+$: 461.2357. Found: 461.2348.

3.16.3. Octyl α-L-fucopyranosyl-(1→4)-β-D-galactopyranoside (28-iii). ^{1}H NMR (D_2O): δ 5.14 (d, 1H, $J_{1',2'}$ 3.9 Hz, H-1′), 4.41 (d, 1H, $J_{1,2}$ 0.9 Hz, H-1), 4.15 (q, 1H, $J_{5',6'}$ 6.7 Hz, H-5′), 4.00 (br d, 1H, $J_{3,4}$ 2.9 Hz, H-4), 3.93–3.88 (m, 2H, H-3′, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.82 (m, 2H, H-2′, H-4′), 3.75–3.63 (m, 5H, H-3, H-5, H-6a, H-6b, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.55 (dd, 1H, $J_{2,3}$ 9.5 Hz, H-2), 1.61 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.36–1.21 (m, 10H, OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 1.21 (d, 3H, $J_{5',6'}$ 6.6 Hz, H-6′), 0.85 (t, 3H, OCH$_2$-CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D_2O): δ 102.9 (C-1), 101.4 (C-1′), 78.7 (C-4), 75.4 (C-5), 74.2 (C-3), 72.1 (C-4′), 71.8 (C-2), 71.1 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 70.0 (C-3′), 69.3 (C-2′), 67.9 (C-5′), 61.5 (C-6), 31.4 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 28.9 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.2 (OCH$_2$CH$_2$(*C*H$_2$)$_5$-CH$_3$), 22.9 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 15.7 (C-6′), 13.4 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [$C_{20}H_{38}O_{10}$]Na$^+$: 461.2357. Found: 461.2352.

3.16.4. Octyl β-L-fucopyranosyl-(1→4)-β-D-galactopyranoside (28-iv). ^{1}H NMR (D_2O): δ 4.41 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.31 (d, 1H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.10 (br d, 1H, $J_{3,4}$ 3.1Hz, H-4), 3.89 (ddd, 1H, OCH_2-CH$_2$(CH$_2$)$_5$CH$_3$), 3.85 (dd, 1H, $J_{6a,5}$ 7.7 Hz, $J_{6a,6b}$ 11.5 Hz, H-6a), 3.81–3.73 (m, 3H, H-4′, H-5, H-5′), 3.69–3.59 (m, 3H, H-3, H-3′, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.53 (dd, 1H, $J_{2',3'}$ 10.0 Hz, H-2′), 3.47 (dd, 1H, $J_{2,3}$ 9.7 Hz, H-2), 1.60 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.35–1.23 (m, 13H, H-6′, OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 0.84 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D_2O): δ 103.5 (C-1′), 103.0 (C-1), 77.8 (C-4), 75.3 (C-5), 72.9 (C-3′), 72.5 (C-3), 72.1 (C-2), 71.8 (C-4′), 71.3 (C-2′), 71.1 (C-5′), 70.9 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 60.7 (C-6), 31.3 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 29.1 (OCH$_2$-*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.4 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.3 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 15.8 (C-6′), 13.9 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [$C_{20}H_{38}O_{10}$]Na$^+$: 461.2357. Found: 461.2347.

3.17. Synthesis of octyl L-fucopyranosyl-(1→6)-D-galactopyranosides (29)

The title compound was synthesized according to the procedure described for the synthesis of compound **26**. Overall yield: 68% (three steps after Sep-Pak). Ratio: **29-i**:**29-ii**:**29-iii**:**29-iv** 1:6.4:1.9:15 (estimated by LC–MS based on assumption that these compounds are similarly ionized). HPLC conditions follows; flow rate: 1.0 mL/min; column: Xterra RP18, 5 μm, 250 mm (L) × 4.6 mm (I.D.); mobile phase: CH_3CN/H_2O 20:80; column temperature: 30 °C; detection (*m*/*z*): 461.3 [M+Na]$^+$; retention times (min): 39.7 (**29-i**; α-Fuc-α-Gal), 46.9 (**29-iii**; α-Fuc-β-Gal), 78.7 (**29-ii**; β-Fuc-α-Gal), and 82.7 (**29-iv**; β-Fuc-β-Gal).

3.17.1. Octyl α-L-fucopyranosyl-(1→6)-α-D-galactopyranoside (29-i). ^{1}H NMR (D_2O): δ 4.94 (d, 1H, $J_{1',2'}$ 3.3 Hz, H-1′), 4.90 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 4.10 (m, 1H, H-5), 4.05 (q, 1H, $J_{5',6'}$ 6.9 Hz, H-5′), 3.97 (br d, 1H, $J_{3,4}$ 1.8 Hz, H-4), 3.85–3.75 (m, 6H, H-2, H-2′, H-3, H-3′, H-4, H-6a), 3.72–3.61 (m, 2H, H-6b, OCH_2CH$_2$(CH$_2$)$_5$-CH$_3$), 3.54 (m, 1H, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 1.62 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.37–1.23 (m, 10H, OCH$_2$CH$_2$-(CH_2)$_5$CH$_3$), 1.21 (d, 3H, $J_{5',6'}$ 6.6 Hz, H-6′), 0.85 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D_2O): δ 98.9 (C-1), 98.8 (C-1′), 72.2 (C-4′), 70.0 (C-5), 69.7 (C-4), 69.7 (C-3), 69.7 (C-3′), 68.9 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 68.5 (C-2), 68.5 (C-2′), 67.2 (C-6), 67.2 (C-5′), 31.4 (OCH$_2$CH$_2$-(*C*H$_2$)$_5$CH$_3$), 28.9 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.6 (OCH$_2$-CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.7 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.1 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 15.6 (C-6′), 12.4 (OCH$_2$CH$_2$-(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [$C_{20}H_{38}O_{10}$]Na$^+$: 461.2357. Found: 461.2356.

3.17.2. Octyl β-L-fucopyranosyl-(1→6)-α-D-galactopyranoside (29-ii). ^{1}H NMR (D_2O): δ 4.91 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 4.38 (d, 1H, $J_{1',2'}$ 7.9 Hz, H-1′), 4.10 (septet, 1H, H-5), 4.02 (br d, 1H, $J_{3,4}$ 3.0 Hz, H-4), 3.95 (dd, 1H, $J_{5,6a}$ 6.8 Hz, $J_{6a,6b}$ 10.8 Hz, H-6a), 3.85–3.69 (m, 6H, H-2, H-3, H-4′, H-5′, H-6b, OCH_2-CH$_2$(CH$_2$)$_5$CH$_3$), 3.62 (dd, 1H, $J_{2',3'}$ 9.9 Hz, $J_{3',4'}$ 3.4 Hz, H-3′), 3.49 (m, 2H, H-2′, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 1.61 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.37–1.22 (m, 13H, H-6′, OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 0.85 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D_2O): δ 103.2 (C-1′), 95.3 (C-1), 73.4 (C-3′), 71.7 (C-4′), 71.4 (C-5′), 70.9 (C-2′), 69.7 (C-3), 69.6 (C-4), 69.1 (C-5), 69.0 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 68.5 (C-6), 68.5 (C-2), 31.4 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 28.9 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.6 (OCH$_2$CH$_2$-(*C*H$_2$)$_5$CH$_3$), 22.1 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 15.7 (C-6′), 12.4 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS *m*/*z* calcd for [$C_{20}H_{38}O_{10}$]Na$^+$: 461.2357. Found: 461.2349.

3.17.3. Octyl α-L-fucopyranosyl-(1→6)-β-D-galactopyranoside (29-iii). ^{1}H NMR (D_2O): δ 4.93 (d, 1H, $J_{1',2'}$ 3.9 Hz, H-1′), 4.38 (d, 1H, $J_{1,2}$ 7.9 Hz, H-1), 4.09 (q, 1H, $J_{5',6'}$ 6.1 Hz, H-5′), 3.91 (br d, 1H, $J_{3,4}$ 3.3 Hz, H-4), 3.89–3.75 (m, 7H, H-2′, H-3, H-4, H-5, H-6a, H-6b, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.69–3.61 (m, 2H, H-3, OCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 3.50 (dd, 1H, $J_{2,3}$ 9.7 Hz, H-2), 1.61 (m, 2H, OCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.35–1.26 (m, 10H, OCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 1.22 (d, 3H, $J_{5',6'}$ 6.6 Hz, H-6′), 0.85 (t, 3H, OCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (D_2O): δ 103.2 (C-1), 100.0 (C-1′), 74.0 (C-5), 73.2 (C-3), 72.1 (C-4′), 71.2 (O*C*H$_2$CH$_2$(CH$_2$)$_5$CH$_3$), 71.1 (C-2), 70.1 (C-3′), 69.2 (C-4), 68.6 (C-2′), 68.4 (C-6), 67.1 (C-5′), 31.2 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 29.0 (OCH$_2$*C*H$_2$(CH$_2$)$_5$CH$_3$), 28.6 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 25.1 (OCH$_2$CH$_2$(*C*H$_2$)$_5$CH$_3$), 22.1 (OCH$_2$CH$_2$(*C*H$_2$)$_5$-CH$_3$), 15.8 (C-6′), 12.4 (OCH$_2$CH$_2$(CH$_2$)$_5$*C*H$_3$); ESIMS

m/*z* calcd for $[C_{20}H_{38}O_{10}]Na^+$: 461.2357. Found: 461.2357.

3.17.4. Octyl β-L-fucopyranosyl-(1→6)-β-D-galactopyranoside (29-iv). ^{1}H NMR (D_2O): δ 4.39 (m, 2H, $J_{1,2}$ 7.9 Hz, $J_{1',2'}$ 7.9 Hz, H-1,1′), 4.01 (dd, 1H, $J_{5,6a}$ 8.6 Hz, $J_{6a,6b}$ 12.6 Hz, H-6a), 3.95 (br d, 1H, $J_{3,4}$ 3.4 Hz, H-4), 3.92–3.83 (m, 3H, H-5, H-6b, $OCH_2CH_2(CH_2)_5CH_3$), 3.77 (q, 1H, $J_{5',6'}$ 6.6 Hz, H-5′), 3.73 (br d, 1H, $J_{3',4'}$ 3.3 Hz, H-4′), 3.67–3.62 (m, 3H, H-3, H-3′, $OCH_2CH_2(CH_2)_5CH_3$), 3.48 (m, 2H, H-2,2′), 1.60 (m, 2H, $OCH_2CH_2(CH_2)_5CH_3$), 1.35–1.24 (m, 13H, H-6′,$OCH_2CH_2(CH_2)_5CH_3$), 0.84 (t, 3H, $OCH_2CH_2(CH_2)_5CH_3$); ^{13}C NMR (D_2O): δ 103.3 (C-1), 103.3 (C-1′), 73.5 (C-5), 73.1 (C-3), 73.1 (C-3′), 71.7 (C-4′), 71.4 (C-5′), 71.1 ($OCH_2CH_2(CH_2)_5CH_3$), 70.9 (C-2), 70.9 (C-2′), 69.1 (C-4), 69.1 (C-6), 31.3 ($OCH_2CH_2(CH_2)_5CH_3$), 28.9 ($OCH_2CH_2(CH_2)_5CH_3$), 28.6 ($OCH_2CH_2(CH_2)_5CH_3$), 25.1 ($OCH_2CH_2(CH_2)_5CH_3$), 22.1 ($OCH_2CH_2(CH_2)_5CH_3$), 15.7 (C-6′), 13.6 ($OCH_2CH_2(CH_2)_5CH_3$); ESIMS *m*/*z* calcd for $[C_{20}H_{38}O_{10}]Na^+$: 461.2357. Found: 461.2354.

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