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Synthesis of tri- and tetrasaccharide fragments of the *Shigella dysenteriae* type 1 O-antigen deoxygenated and fluorinated at position 3 of the methyl α-D-galactopyranoside terminus[1]

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Abstract

The blockwise synthesis of methyl alpha tri- and tetrasaccharide analogs of the biochemical repeating unit of the *Shigella dysenteriae* type 1 O-polysaccharide is described. Modifications include deoxygenation and deoxyfluorination at position 3 of the galactopyranoside residue. Methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*xylo*-hexopyranoside (**8**) and methyl 4,6-*O*-benzylidene-3-deoxy-3-fluoro-α-D-galactopyranoside (**9**) were condensed with (2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl chloride to give, after deprotection, the target trisaccharide methyl α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-3-deoxy-α-D-*xylo*-hexopyranoside and the corresponding fluorinated oligosaccharide. For the tetrasaccharide synthesis, the glycosyl acceptors **8** and **9** were condensed with the temporarily protected (2,4-di-*O*-benzoyl-3-*O*-chloroacetyl-α-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl chloride. Removal of the chloroacetyl group was followed by condensation of the resulting selectively deblocked trisaccharides with 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl chloride. Reduction and deprotection then gave the free methyl 2-acetamido-2-deoxy-α-D-glucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→2)-3-deoxy-α-D-*xylo*-hexopyranoside and the fluorinated analog.

Keywords: *Shigella dysenteriae* type 1; Deoxygenated oligosaccharides; Deoxyfluorinated oligosaccharides

1. Introduction

Shigella dysenteriae type 1 is common in developing countries where it causes devastating epidemics, especially in children. The O-specific polysaccharide (O-SP) portion of its lipopolysaccharide (LPS) interacts directly with the host. It was suggested that immunization with the O-antigen conjugated to a carrier protein could confer protective immunity [2]. We have studied the affinity of the *S. dysenteriae* type 1 O-SP for a number of monoclonal immunoglobulins elicited by this bacterium [3,4].

The repeating unit of the organism's O-antigen is the tetrasaccharide **I** [5,6]. Recent data [3] show

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[1] Part 10 of the series Synthesis of ligands related to the O-specific antigen of *Shigella dysenteriae* type 1. For part 9 see ref [1].

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disaccharide **II** to be the antigenic determinant for a monoclonal IgM and an IgG [4] antibody, but somewhat longer fragments bearing the galactopyranose unit may be needed for optimal recognition by other antibodies.

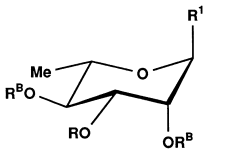
A B C D
3)-α-D-Glc*p*NAc-(1→3)-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→2)-α-D-Gal*p*-(1→

I

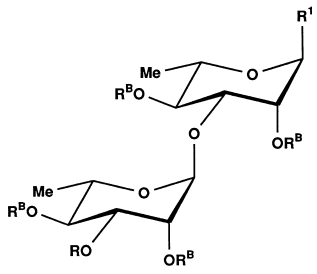
3)-α-L-Rha*p*-(1→2)-α-D-Gal*p*-(1→

II

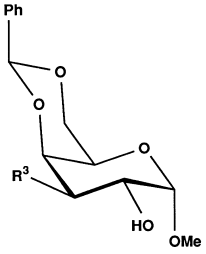
Deoxy and deoxyfluoro sugars have been used as probes to investigate the hydrogen bonding network between carbohydrate determinants and protein epitopes [7,8]. We reported on the contribution of the various hydroxyl groups in **II** to binding with a monoclonal IgM antibody [1], and showed the 3-OH of the galactopyranosyl residue to be critical for binding. In order to examine the effect of a fluorine atom at C-3 of the galactopyranose unit on binding of α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→2)-α-D-Gal*p*-OMe and of α-D-Glc*p*NAc-(1→3)-α-L-Rha*p*-(1→3)-α-L-Rha*p*-(1→2)-α-D-Gal*p*-OMe, the trisaccharide **15** and the tetrasaccharide **29** were prepared. Their synthesis is reported here, together with that of the corresponding deoxygenated derivatives **12** and **25**, respectively.



	R^B	R^1	R
1	H	OMe	H
2	Bz	OMe	H
3	Bz	OMe	ClAc
4	Bz	Cl	ClAc



	R^B	R^1	R
5	Bz	OMe	ClAc
6	Bz	Cl	ClAc
7	Bz	Cl	Bz



8 R^3 = H
9 R^3 = F

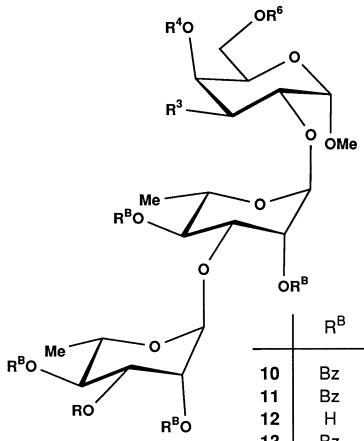
2. Results and discussion

For the construction of the deoxygenated targets **12** and **25**, compound **8** prepared in seven steps from methyl α-D-galactopyranoside [9], was used as the glycosyl acceptor. By analogy, the preparation of the fluorinated derivatives **15** and **29** involved the use of the fluorinated nucleophile **9** prepared from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose in three steps [10].

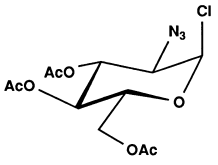
Condensation of **8** and **9** respectively with the known [11] rhamnobiosyl chloride **7** was performed under base-deficient conditions [12]. The use of **7** as the donor rather than the fully acetylated rhamnobiosyl glycosyl bromide [13] avoids the transesterification known to occur [14] with 2-*O*-acetylated glycoside halides under the conditions of silver trifluoromethanesulfonate mediated glycosylation conditions. Thus, the fully protected trisaccharides **10** and **13** were obtained in 88 and 92% yield, respectively. Hydrogenolysis (**10**→**11**, 92% and **13**→**14**, 94%) followed by Zemplén debenzoylation gave the desired deoxygenated trisaccharide **12** (91% from **11**) and its corresponding fluorinated trisaccharide **15** (92% from **14**). Experimental single bond $^1J_{C\text{-}1,H\text{-}1}$ coupling constants were 174.2 Hz (A), 171.2 Hz (B), 172.3 Hz (C) and 176.8 Hz (A), 173.3 Hz (B), 171.8 Hz (C) for compounds **12** and **15**, respectively.

By analogy with the preparation of compounds **12** and **15**, tetrasaccharides **25** and **29** were synthesized using the fully protected rhamnobiosyl chloride **6** as a common building block. In both cases, the *N*-acetyl glucosamine residue was introduced last.

This strategy required a rhamnopyranosyl donor **4** bearing a selectively removable blocking group [15] at position 3 with differing protecting groups elsewhere. The use of the known dibenzoylated precursor **2** [16] prevented acyl migration later during regioselective deblocking of the chloroacetyl group at position 3 (**2**→**3**, 89%), while allowing anchimeric assistance when replacing the leaving group at C-1. The chloride **4** was easily obtained by cleavage [17] with dichloromethyl methyl ether (DCMME) in the presence of zinc chloride (88%). Condensation of **4** with the glycosyl acceptor **2** promoted by silver trifluoromethanesulfonate then gave the methyl glycoside **5** (84%) which was converted to the chloride **6** (66%) again by selective cleavage with DCMME/$ZnCl_2$.



	R^B	R	R^3	R^4	R^6
10	Bz	Bz	H	- CHPh -	
11	Bz	Bz	H	H	H
12	H	H	H	H	H
13	Bz	Bz	F	- CHPh -	
14	Bz	Bz	F	H	H
15	H	H	F	H	H
16	Bz	ClAc	H	- CHPh -	
17	Bz	H	H	- CHPh -	
18	Bz	ClAc	F	- CHPh -	
19	Bz	H	F	- CHPh -	



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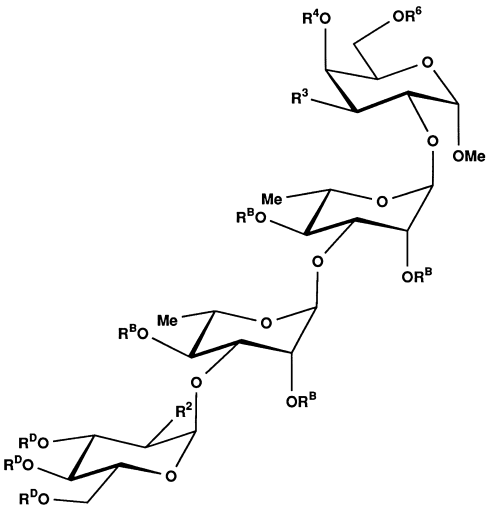

	R^B	R^D	R^2	R^3	R^4	R^6
21	Bz	Ac	N_3	H	- CHPh -	
22	Bz	Ac	NH_2	H	- CHPh -	
23	Bz	Ac	NHAc	H	- CHPh -	
24	Bz	Ac	NHAc	H	H	H
25	H	H	NHAc	H	H	H
26	Bz	Ac	N_3	F	- CHPh -	
27	Bz	Ac	NHAc	F	- CHPh -	
28	Bz	Ac	NHAc	F	H	H
29	H	H	NHAc	F	H	H

By analogy with the synthesis of trisaccharides **10** and **13**, condensation of the glycosyl acceptors **8** and **9** with the rhamnobiosyl donor **6** was promoted by silver trifluoromethanesulfonate under base-deficient conditions, to give trisaccharides **16** (80%) and **18** (74%), respectively. Selective *O*-dechloroacetylation in **16** and **18**, using thiourea, afforded both the selectively deblocked **17** (88%) and **19** (96%). Further chain extension, took advantage of the nonparticipating nature of the 2-azido group during chemical glycosylation with the chloride **20** [18] under silver trifluoromethanesulfonate promoted Koenigs–Knorr conditions. Yields of the corresponding deoxy- (**21**, 69%) and deoxyfluoro- (**26**, 85%) tetrasaccharides with the desired 1,2-*cis* linkage, were comparable to that of the reference compound bearing a non-modified galactopyranoside unit [19]. The *N*-acetylated tetrasaccharides **23** and **27** were readily obtained from the azido precursors **21** and **26** by triphenylphosphine reduction of the azido moiety to the amino group (**21**→ **22**, 79%) followed by *N*-acetylation (**22**→**23**, 96% and **26**→**27**, 71% overall yield). Subsequent hydrogenolysis of the benzylidene acetal gave diols **24** (99%) and **28** (89%) which were fully deacylated under Zemplén conditions to give the target tetrasaccharides **25** (63%) and **29** (88%), respectively. Experimental single bond $^1J_{C\text{-}1,H\text{-}1}$ coupling constants were 175.1 Hz (A), 171.0 Hz (B), 172.2 Hz (C), 174.9 Hz (D) and 178.8 Hz (A), 173.3 Hz (B), 171.3 Hz (C), 174.0 Hz (D) for compounds **25** and **29**, respectively.

The anomeric purity of both the tri- and tetrasaccharide glycosides was confirmed by ^{13}C and ^1H NMR spectroscopy. Consideration of the glycosyl halides and reaction conditions [19] employed to synthesize **12**, **15**, **25** and **29** led us to expect high anomeric purity. Based on the observation [20] that α-linked pyranoses have single bond $^1J_{C\text{-}1,H\text{-}1}$ values $\approx$170 Hz whilst those that are β-linked have $^1J_{C\text{-}1,H\text{-}1} \approx 160$ Hz, this is indeed the case. Single bond $^1J_{C\text{-}1,H\text{-}1}$ coupling constants for all four compounds did confirm the α-anomeric configuration at all linkages.

3. Experimental

General methods.—Melting points were determined on a Kofler hot stage. Optical rotations were measured in $CHCl_3$ solution at 25 °C, except where

indicated otherwise, with a Perkin–Elmer automatic polarimeter, Model 241 MC. TLC on precoated slides of Silica Gel G F254 (Analtech) was performed with solvent mixtures of appropriately adjusted polarity consisting of *A*, CH_2Cl_2-MeOH; *B*, hexane–EtOAc; *C*, hexane–acetone; *D*, toluene–acetone; *E*, toluene–EtOAc; *F*, water–acetonitrile. Detection was effected when applicable, with UV light, and/or by charring with 5% H_2SO_4 in EtOH. Preparative chromatography was performed by elution from columns of Silica Gel 60 (particle size 0.04–0.063 mm). Reverse phase chromatography of compounds **25** and **29** was performed by elution from columns of Silica gel Lichoprep RP 18 (particle size 25–40 μm). The NMR spectra were recorded at 25 °C for solutions in $CDCl_3$, unless stated otherwise, on a Varian Gemini-300 spectrometer (300 MHz for ^1H, 75 MHz for ^{13}C). Internal references: for solutions in $CDCl_3$, $CDCl_3$ (77.00 ppm for ^{13}C) and Me_4Si (0.00 ppm for ^1H), for solutions in D_2O, CD_3OD (49.00 ppm for ^{13}C) and HOD (4.78 ppm for ^1H). Proton-signal assignments were made by first-order analysis of the spectra, and were supported by homonuclear decoupling experiments. Of the two magnetically nonequivalent geminal protons at C-6, the one resonating at lower field is denoted H-6a and the one at higher field is denoted H-6b. The ^{13}C NMR assignments were made by two-dimensional ^{13}C–^1H correlation maps (HETCOR). Interchangeable assignments are marked with an asterisk in listing of signal assignments. Sugar residues in oligosaccharides were assigned roman numerals in ascending order starting from the one bearing the aglycon and identified by a superscript in listing of signal assignments. Low resolution chemical ionization mass spectra (CIMS) were obtained using NH_3 as the ionizing gas. Before use, AgOTf was dried at 133 Pa/50 °C for 2 h, CH_2Cl_2 was dried over drierite. Solutions in organic solvents were dried with anhyd sodium sulfate. Methyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**2**), prepared as described [16] was obtained in an overall yield of 74% starting from methyl α-L-rhamnopyranoside [21] (34.0 g, 190 mmol). 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl chloride (**20**) was prepared [22] from the corresponding β-acetate, obtained as described [18]. The disaccharide (2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl chloride (**7**) was prepared from the nucleophile **2** as described [11].

Methyl 2,4-di-O-*benzoyl-3*-O-*chloroacetyl*-α-L-*rhamnopyranoside* (**3**).—A solution of chloroacetic anhydride (31.0 g, 181.3 mmol) in DMF (30 mL) was added dropwise to a solution of methyl 2,4-di-*O*-benzoyl-α-L-rhamnopyranoside (**2**) (40.1 g, 103.9 mmol) in a mixture of DMF (140 mL) and pyridine (170 mL) at −45 °C. After 30 min, MeOH was added and the cooling bath was removed. The solution was concentrated and the residue was taken up in CH_2Cl_2. Extractive work-up followed by crystallization gave **3** (42.7 g, 89%); mp 98.5–99.5 °C (EtOH); $[\alpha]_D$ +90° (*c* 1.0); NMR: ^1H, δ 8.11–7.41 (m, 10 H, Ph), 5.65 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.1 Hz, H-3), 5.54 (m, 1 H, H-2), 5.47 (t, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 4.84 (bs, 1 H, H-1), 4.10 (dq, 1 H, $J_{5,6}$ 6.6 Hz, H-5), 3.87, 3.80 (2 d, 2 H, J_{gem} 15.0 Hz, CH_2Cl), 3.47 (s, 3 H, OCH_3), and 1.33 (d, 3 H, H-6); ^{13}C, δ 98.5 (C-1), 70.2 (C-2), 71.5 (C-4), 71.2 (C-3), 66.5 (C-5), 55.3 (OCH_3), 40.5 (CH_2Cl), and 17.6 (C-6); CIMS: *m*/*z* 480 ($[M+NH_4]^+$). Anal. Calcd for $C_{23}H_{23}ClO_8$: C, 59.69; H, 5.00. Found: C, 59.59; H, 5.03.

2,4-Di-O-*benzoyl-3*-O-*chloroacetyl*-α-L-*rhamnopyranosyl chloride* (**4**).—A solution of compound **3** (5.0 g, 10.8 mmol) in 1,2-dichloroethane (20 mL) was treated with α,α-dichloromethyl methyl ether (DCMME, 30 mL) and $ZnCl_2{\cdot}Et_2O$ complex (1.4 mL of a 2.2 M solution in CH_2Cl_2) at 65 °C for 7 h. The solution was diluted with toluene, concentrated and coevaporated with toluene three times. The residue was chromatographed (solvent *C*, 12:1) to give the known **4** (4.3 g, 88%) which NMR data were identical to those published [18].

Methyl (2,4-di-O-*benzoyl-3*-O-*chloroacetyl*-α-L-*rhamnopyranosyl)-(1→3)-2,4-di*-O-*benzoyl*-α-L-*rhamnopyranoside* (**5**).—A solution of crude **4**, prepared from **3** (16.0 g, 34.6 mmol), 2,6-di-*tert*-butyl-4-methyl pyridine (4.72 g, 23.0 mmol) and compound **2** (8.02 g, 20.8 mmol) in CH_2Cl_2 (150 mL) was added dropwise to a suspension of silver trifluoromethanesulfonate (AgOTf, 6.42 g, 25.0 mmol) in CH_2Cl_2 (30 mL) at −15 °C. After 30 min, more base (1.02 g, 5.0 mmol) was added, the cooling bath was removed and stirring was continued for 2 h, at which point very little starting material remained (TLC, solvent *E*, 9:1). CH_2Cl_2 (100 mL) was added and the mixture was filtered through a bed of Celite. The filtrate was washed with a 1:1 mixture of 5% aq $NaHCO_3$ and 5% aq $Na_2S_2O_3$, then water and satd aq NaCl. The organic phase was dried and concentrated. Chromatography of the residue (solvent *E*, 30:1) gave

disaccharide **5** (14.38 g, 84%) as a white foam, $[\alpha]_D$ +130° (*c* 1.0); NMR: ^{1}H, δ 8.25–7.34 (m, 20 H, Ph), 5.55 (t, 1 H, $J_{3,4}$ 9.8, $J_{4,5}$ 9.8 Hz, H-4^I), 5.48 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.4 Hz, H-2^I), 5.41 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 10.0 Hz, H-3^{II}), 5.29 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4^{II}), 5.15 (dd, 1 H, $J_{1,2}$ 1.7 Hz, H-2^{II}), 5.12 (bs, 1 H, H-1^{II}), 4.89 (d, 1 H, H-1^I), 4.44 (dd, 1 H, H-3^I), 4.05 (m, 2 H, H-5^I, 5^{II}), 3.71, 3.67 (2 d, 2 H, J_{gem} 15.0 Hz, C*H*$_2$Cl), 3.45 (s, 3 H, OC*H*$_3$), 1.34 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^I), and 1.15 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{II}); ^{13}C, δ 99.2 (C-1^I), 98.3 (C-1^{II}), 76.01 (C-3^I), 73.2 (C-4^I), 72.1 (C-2^I), 71.3 (C-4^{II}), 70.5 (C-3^{II}), 70.1 (C-2^{II}), 67.4 (C-5^{II}), 66.6 (C-5^I), 55.3 (O*C*H$_3$), 40.3 (*C*H$_2$Cl), 17.7 (C-6^I), and 17.4 (C-6^{II}); CIMS: *m*/*z* 834 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{43}H_{41}ClO_{14}$: C, 63.20; H, 5.06. Found: C, 63.30; H, 5.11.

(2,4-Di-O-*benzoyl-3*-O-*chloroacetyl*-α-L-*rhamnopyranosyl)-(1→3)-2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl chloride* (**6**).—$ZnCl_2{\cdot}Et_2O$ complex (1.1 mL of a 2.2 M solution in CH_2Cl_2) was added to a stirred solution of the methyl glycoside **5** (5.9 g, 7.2 mmol) and DCMME (60 mL) in dichloroethane (30 mL). The mixture was stirred at 60 °C for 1.25 h after which time TLC (solvent *B*, 9:1) showed that only traces of the starting material remained. The solution was diluted with toluene, concentrated and coevaporated repeatedly with toluene. Chromatography of the residue gave the chloride **6** (3.9 g, 66%) as a white foam, $[\alpha]_D$ +108° (*c* 1.0); NMR: ^{1}H, δ 8.21–7.35 (m, 20 H, Ph), 6.23 (bs, 1 H, H-1^I), 5.63 (m, 2 H, H-2^I, 4^I), 5.40 (dd, 1 H, $J_{2,3}$ 2.6, $J_{3,4}$ 10.0 Hz, H-3^{II}), 5.31 (t, 1 H, $J_{4,5}$ 9.8, $J_{4,3}$ 9.8 Hz, H-4^{II}), 5.17 (bs, 2 H, H-1^{II}, 2^{II}), 4.74 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.0 Hz, H-3^I), 4.34 (dq, 1 H, $J_{5,4}$ 9.8 Hz, H-5^I), 4.05 (dq, 1 H, H-5^{II}), 3.73, 3.67 (2 d, 2 H, J_{gem} 14.9 Hz, C*H*$_2$Cl), 1.38 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^I), and 1.15 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^{II}); ^{13}C, δ 99.3 (C-1^{II}), 89.5 (C-1^I), 74.6 (C-3^I), 74.2 (C-4^I), 72.4 (C-2^I), 71.1 (C-4^{II}), 70.3 (C-3^{II}), 69.9 (C-2^{II}), 69.8 (C-5^I), 67.6 (C-5^{II}), 40.2 (*C*H$_2$Cl), and 17.3 (2 C, C-6^I, 6^{II}); CIMS: *m*/*z* 838 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{42}H_{38}Cl_2O_{13}$: C, 61.39; H, 4.66; Cl, 8.63. Found: C, 61.11; H, 4.63; Cl, 9.06.

Methyl (2,3,4-tri-O-*benzoyl*-α-L-*rhamnopyranosyl-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→2)-4,6*-O-*benzylidene-3-deoxy*-α-D-xylo-*hexopyranoside* (**10**).—A solution of the glycosyl chloride **7** [11] (1.14 g, 1.34 mmol), the glycosyl acceptor **8** (306 mg, 1.15 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (295 mg, 1.44 mmol) in CH_2Cl_2 (20 mL) was added dropwise, at −20 °C, to a stirred suspension of AgOTf (473 mg, 1.84 mmol) in CH_2Cl_2 (10 mL). After 45 min, when the temperature of the bath was −5 °C, cooling was terminated. The mixture was stirred for 45 min at ambient temperature, after which time TLC (solvent *D*, 9:1) showed that only little of the acceptor remained and that **7** had completely disappeared. The mixture was filtered through a bed of Celite, and processed as described for the preparation of the disaccharide **5**. The residue was chromatographed (solvent *D*, 24:1) to afford **10** (1.09 g, 88%) as an amorphous solid, $[\alpha]_D$ +154° (*c* 1.0); NMR: ^{1}H, δ 8.24–7.16 (m, 30 H, Ph), 5.61 (t, partially overlapped, 1 H, $J_{4,5}$ 9.8 Hz, H-4^{II}), 5.57 (dd, partially overlapped, 1 H, $J_{2,3}$ 3.3, $J_{3,4}$ 10.1 Hz, H-3^{III}), 5.54 (s, 1 H, PhC*H*), 5.51 (bd, partially overlapped, 1 H, H-2^{II}), 5.48 (t, partially overlapped, 1 H, $J_{4,5}$ 9.8 Hz, H-4^{III}), 5.26 (bd, 1 H, H-2^{III}), 5.24 (bs, 1 H, H-1^{III}), 5.15 (bs, 1 H, H-1^{II}), 5.00 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1^I), 4.52 (dd, 1 H, $J_{3,4}$ 9.9, $J_{2,3}$ 3.2 Hz, H-3^{II}), 4.26 (bd, partially overlapped, 1 H, $J_{6a,6b}$ 11.9 Hz, H-6a^I), 4.20 (m, 3 H, H-2^I, 4^I, 5^{II}), 4.10 (m, 2 H, H-6b^I, 5^{III}), 3.64 (bs, 1 H, H-5^I), 3.50 (s, 3 H, OC*H*$_3$), 2.35–2.18 (m, 2 H, H-3^I), 1.35 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{II}), and 1.13 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{III}); ^{13}C, δ 101.1 (Ph*C*H), 99.2, 99.1 (C-1^I, 1^{III}), 98.1 (C-1^{II}), 76.6 (C-3^{II}), 73.4 (C-4^I), 73.0 (C-4^{II}), 72.9 (C-2^I), 72.6 (C-2^{II}), 71.5 (C-4^{III}), 70.7 (C-2^{III}), 69.5 (C-6^I), 69.3 (C-3^{III}), 67.4 (C-5^{III}), 67.1 (C-5^{II}), 61.7 (C-5^I), 55.2 (OMe), 29.8 (C-3^I), 18.0 (C-6^{II}), and 17.4 (C-6^{III}); CIMS: *m*/*z* 1096 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{61}H_{58}O_{18}$: C, 67.89; H, 5.42. Found: C, 67.88; H, 5.46.

Methyl (2,3,4-tri-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→2)-3-deoxy*-α-D-xylo-*hexopyranoside* (**11**).—A suspension of 10% Pd-C catalyst (250 mg) in a 1:2.5:17.5 mixture of AcOH:acetone:EtOH (42 mL) containing the fully protected **10** (850 mg, 0.79 mmol) was stirred at ambient temperature, overnight, under a hydrogen atmosphere. The suspension was filtered through a bed of Celite and the filtrate concentrated. To eliminate any residual traces of the catalyst, the residue was chromatographed on a short column of silica gel (solvent *D*, 3:1) to give **11** (719 mg, 92%) as an amorphous solid, $[\alpha]_D$ +153° (*c* 1.0); NMR: ^{1}H, δ 8.24–7.16 (m, 25 H, Ph), 5.59 (t, partially overlapped, 1 H, $J_{4,5}$ 10.0 Hz, H-4^{II}), 5.57 (dd, partially overlapped, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.1 Hz, H-3^{III}), 5.50 (bd, partially overlapped, 1 H, H-2^{II}), 5.48 (t, partially overlapped, 1 H, $J_{4,5}$ 10.0 Hz, H-4^{III}), 5.26 (dd, 1 H, $J_{1,2}$ 1.7 Hz, H-2^{III}), 5.24 (bs, 1 H, H-1^{III}), 5.15

(d, 1 H, $J_{1,2}$ 1.4 Hz, H-1^{II}), 4.93 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1^{I}), 4.51 (dd, 1 H, $J_{3,4}$ 9.8, $J_{2,3}$ 3.4 Hz, H-3^{II}), 4.22 (dq, partially overlapped, 1 H, H-5^{II}), 4.17 (m, partially overlapped, 2 H, H-2^{I}, 4^{I}), 4.09 (dq, partially overlapped, 1 H, H-5^{III}), 3.90 (bs, 2 H, H-6^{I}), 3.74 (t, 1 H, $J_{5,6a}$ 3.1, $J_{5,6b}$ 3.1 Hz, H-5^{I}), 3.45 (s, 3 H, OCH_3), 3.15 (bs, 1 H, OH), 2.07 (m, 2 H, H-3^{I}), 1.35 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^{II}), and 1.12 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^{III}); ^{13}C, δ 99.1 (C-1^{III}), 98.9 (C-1^{I}), 98.2 (C-1^{II}), 76.4 (C-3^{II}), 73.0 (2 C, C-2^{I}, 4^{II}), 72.6 (C-2^{II}), 71.5 (C-4^{III}), 70.7 (C-2^{III}), 69.4 (C-3^{III}), 69.0 (C-4^{I}), 68.5 (C-5^{I}), 67.4 (C-5^{III}), 67.2 (C-5^{II}), 64.1 (C-6^{I}), 55.5 (OMe), 32.1 (C-3^{I}), 18.0 (C-6^{II}), and 17.4 (C-6^{III}); CIMS: *m/z* 1008 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{54}H_{54}O_{18}$: C, 65.45; H, 5.49. Found: C, 65.48; H, 5.53.

Methyl α-L-*rhamnopyranosyl-(1→3)-*α-L-*rhamnopyranosyl-(1→2)-3-deoxy-*α-D-xylo-*hexopyranoside* (**12**).—A solution of **11** (560 mg, 0.56 mmol) in MeOH (5 mL) was treated with M methanolic MeONa (500 μL) and the solution was stirred at room temperature overnight. After neutralization with Amberlite IR-120 (H$^+$), and evaporation of the solvent, the crude product was chromatographed (solvent A) to give pure **12** (228 mg, 86%) as a white amorphous solid; $[\alpha]_D$ −26° (*c* 1.0, water); NMR: ^{1}H (D_2O), δ 5.03 (bs, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{III}), 4.88 (m, 2 H, $J_{1^{II},2^{II}}$ 1.9, $J_{1^{I},2^{I}}$ 3.4 Hz, H-1^{II}, 1^{I}), 4.08 (m, 1 H, $J_{4,5}$ 1.4 Hz, H-4^{I}), 4.06 (dd, 1 H, $J_{2,3}$ 3.3 Hz, H-2^{II}), 4.04 (m, 1 H, H-2^{I}), 4.02 (dd, 1 H, $J_{2,3}$ 3.5 Hz, H-2^{III}), 3.84 (m, 1 H, H-5^{I}), 3.83 (dd, 1 H, H-3^{II}), 3.80 (m, 1 H, H-3^{III}), 3.79 (m, 1 H, H-5^{III}), 3.78 (m, 1 H, $J_{4,5}$ 9.6 Hz, H-5^{II}), 3.72 (dd, 1 H, $J_{5,6a}$ 4.4 Hz, H-6a^{I}), 3.68 (dd, 1 H, $J_{5,6b}$ 7.8, $J_{6a,6b}$ 11.7 Hz, H-6b^{I}), 3.53 (t, 1 H, $J_{3,4}$ 9.7 Hz, H-4^{II}), 3.47 (s, 3 H, OCH_3), 3.45 (t, 1 H, $J_{4,5}$ 9.6, $J_{3,4}$ 9.7 Hz, H-4^{III}), 2.07 (ddd, 1 H, $J_{2,3a}$ 12.5, $J_{3a,3b}$ 13.6, $J_{3a,4}$ 3.0 Hz, H-3a^{I}), 1.93 (ddd, 1 H, $J_{2,3b}$ 5.1, $J_{3b,4}$ 3.4 Hz, H-3b^{I}), 1.32 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^{II}), and 1.28 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^{III}); ^{13}C, δ 103.4 (C-1^{III}, $J_{C,H}$ 172.3 Hz), 101.1 (C-1^{II}, $J_{C,H}$ 171.2 Hz), 89.1 (C-1^{I}, $J_{C,H}$ 174.3 Hz), 79.2 (C-3^{II}), 73.0 (C-4^{III}), 72.2 (C-4^{II}), 72.0 (C-2^{I}), 71.5 (C-5^{I}), 71.1 (3 C, C-3^{III}, 2^{II}, 2^{III}), 70.1 (C-5^{II}), 70.0 (C-5^{III}), 66.8 (C-4^{I}), 62.4 (C-6^{I}), 65.6 (OMe), 31.9 (C-3^{I}), 17.7 (C-6^{III}), and 17.5 (C-6^{II}); CIMS: *m/z* 488 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{19}H_{34}O_{13}$·0.5 H_2O: C, 47.60; H, 7.36. Found: C, 47.47; H, 7.33.

*Methyl (2,3,4-tri-*O-*benzoyl-*α-L-*rhamnopyranosyl)-(1→3)-(2,4-di-*O-*benzoyl-*α-L-*rhamnopyranosyl)-(1→2)-4,6-*O-*benzylidene-3-deoxy-3-fluoro-*α-D-*galactopyranoside* (**13**).—A solution of the glycosyl chloride **7** [11] (1.1 g, 1.30 mmol), the glycosyl acceptor **9** (284 mg, 1.0 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (287 mg, 1.4 mmol) in CH_2Cl_2 (20 mL) was added dropwise, at −20 °C, to a stirred suspension of AgOTf (461 mg, 1.8 mmol) in CH_2Cl_2 (10 mL). Cooling was terminated after 30 min, after which time TLC (solvent *D*, 19:1) showed that no starting material remained. The mixture was processed as described for the preparation of the disaccharide **5**, and the crude product was chromatographed (solvent *E*, gradient) to afford **13** (1.01 g, 92%) which crystallized on standing, mp 130–131 °C (EtOH); $[\alpha]_D$ +172° (*c* 1.0); NMR: ^{1}H, δ 8.24–7.16 (m, 30 H, Ph), 5.64 (m, 1 H, H-2^{II}), 5.59 (m, 2 H, H-4^{II}, C*H*Ph), 5.58 (dd, partially overlapped, 1 H, $J_{3,2}$ 3.2 Hz, H-3^{III}), 5.49 (t, 1 H, $J_{3,4}$ 10, $J_{4,5}$ 9.5 Hz, H-4^{III}), 5.28 (dd, 1 H, H-2^{III}), 5.25 (m, 2 H, H-1^{II}, 1^{III}), 5.06 (t, partially overlapped, 1 H, $J_{1,F}$ 3.9 Hz, H-1^{I}), 4.95 (ddd, partially overlapped, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 3.7, $J_{3,F}$ 48.5 Hz, H-3^{I}), 4.55 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.8 Hz, H-3^{II}), 4.50 (bt, 1 H, $J_{4,F}$ 4.7 Hz, H-4^{I}), 4.36 (dt, partially overlapped, 1 H, $J_{1,2}$ 3.5, $J_{2,F}$ 10.1 Hz, H-2^{I}), 4.31 (bd, partially overlapped, 1 H, $J_{6a,6b}$ 12.2 Hz, H-6a^{I}), 4.22–4.13 (m, 2 H, H-5^{II}, 5^{III}), 4.11 (bd, 1 H, H-6b^{I}), 3.71 (bs, 1 H, H-5^{I}), 3.47 (s, 3 H, OCH_3), and 1.36, 1.15 (2 d, 6 H, $J_{5,6}$ 6.1, $J_{5,6}$ 6.1 Hz, H-6^{II}, 6^{III}); ^{13}C, δ 100.8 (Ph*C*H), 99.9 (d, $J_{1,F}$ 11.2 Hz, C-1^{I}), 99.1 (2 C, C-1^{II}, 1^{III}), 87.2 (d, $J_{3,F}$ 191.1, C-3^{I}), 76.0 (C-3^{II}), 75.3 (d, $J_{2,F}$ 17.2 Hz, C-2^{I}), 74.8 (d, 16.0 Hz, C-4^{I}), 73.1 (C-4^{II}), 72.0 (C-2^{II}), 71.5 (C-4^{III}), 70.7 (C-2^{III}), 69.4 (C-3^{III}), 69.1 (C-6^{I}), 67.5, 67.4 (C-5^{II}, 5^{III}), 62.0 (d, $J_{5,F}$ 5.8 Hz, C-5^{I}), 55.6 (OMe), and 18.02, 17.4 (C-6^{II}, 6^{III}); ^{19}F, δ −46.13 (m, 1 F, $J_{F,3}$ 48.5, $J_{F,4}$ 5.1, $J_{F,2}$ 9.9 Hz, F-3^{I}); CIMS: *m/z* 1114 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{61}H_{57}FO_{18}$: C, 66.79; H, 5.24; F, 1.73. Found: C, 66.81; H, 5.43; F, 1.58.

*Methyl (2,3,4-tri-*O-*benzoyl-*α-L-*rhamnopyranosyl)-(1→3)-(2,4-di-*O-*benzoyl-*α-L-*rhamnopyranosyl)-(1→2)-3-deoxy-3-fluoro-*α-D-*galactopyranoside* (**14**).—A solution of the fully protected trisaccharide **13** (788 mg, 0.72 mmol) in a 1:5 mixture of water:AcOH (6 mL) was stirred at 65 °C for 6 h. Concentration of the solution and chromatography of the residue (solvent *D*, 4:1) gave **14** (679 mg, 94%) as a white amorphous solid, $[\alpha]_D$ +168° (*c* 1.0); NMR: ^{1}H, δ 8.24–7.18 (m, 25 H, Ph), 5.61 (dd, partially overlapped, 1 H, H-2^{II}), 5.60 (t, partially overlapped, 1 H, H-4^{II}), 5.58 (dd, partially overlapped, 1 H, $J_{3,2}$ 3.2, $J_{3,4}$ 10.1 Hz, H-3^{III}), 5.48 (t, 1 H, $J_{4,5}$ 9.9 Hz, H-4^{III}), 5.28 (dd, 1 H, $J_{1,2}$

1.7 Hz, H-2^{III}), 5.26 (bs, 1 H, H-1^{III}*), 5.21 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1^{II}*), 4.98 (t, 1 H, $J_{1,F}$ 3.9 Hz, H-1^{I}), 4.85 (ddd, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 3.4, $J_{3,F}$ 49.5 Hz, H-3^{I}), 4.54 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 9.7 Hz, H-3^{II}), 4.33 (dd, 1 H, $J_{4,F}$ 6.6 Hz, H-4^{I}), 4.24 (dt, partially overlapped, 1 H, $J_{1,2}$ 3.5, $J_{2,F}$ 11.2 Hz, H-2^{I}), 4.24–4.11 (m, 2 H, H-5^{II}, 5^{III}), 4.31 (bd, partially overlapped, 1 H, $J_{6a,6b}$ 12.2 Hz, H-6a^{I}), 4.11 (bd, 1 H, H-6b^{I}), 3.71 (bs, 1 H, H-5^{I}), 3.43 (s, 3 H, OCH_3), and 1.35, 1.13 (2 d, 6 H, $J_{5,6}$ 6.1, $J_{5,6}$ 6.1 Hz, H-6^{II}, 6^{III}); ^{13}C, δ 99.4 (d, $J_{1,F}$ 8.5 Hz, C-1^{I}), 99.2 (C-1^{II}), 99.1 (C-1^{III}), 89.0 (d, $J_{3,F}$ 183.6, C-3^{I}), 76.1 (C-3^{II}), 75.6 (d, $J_{2,F}$ 16.8 Hz, C-2^{I}), 73.0 (C-4^{II}), 72.1 (C-2^{II}), 71.5 (C-4^{III}), 70.7 (C-2^{III}), 69.5 (d, $J_{4,F}$ 18.8 Hz, C-4^{I}), 69.3 (C-3^{III}), 68.6 (d, $J_{5,F}$ 5.2 Hz, C-5^{I}), 67.5, 67.4 (C-5^{II}, 5^{III}), 62.8 (C-6^{I}), 55.4 (OMe), and 17.9, 17.4 (C-6^{II}, 6^{III}); ^{19}F, δ −41.40 (m, 1 F, $J_{F,3}$ 49.4, $J_{F,4}$ 5.0, $J_{F,2}$ 10.9 Hz, F-3^{I}); CIMS: *m/z* 1026 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{45}H_{53}FO_{18}$·0.5 H_2O: C, 63.71; H, 5.34; F, 1.86. Found: C, 63.93; H, 5.36; F, 1.56.

Methyl α-L-*rhamnopyranosyl-(1→3)*-α-L-*rhamnopyranosyl-(1→2)-3-deoxy-3-fluoro*-α-D-*galactopyranoside* (**15**).—A solution of **14** (532 mg, 0.52 mmol) in MeOH (5 mL) was treated with M methanolic sodium methoxide (500 μL) as described for the preparation of **12**. Chromatography of the crude material (solvent A) gave pure **15** (230 mg, 88%) as a white amorphous solid; $[\alpha]_D$ −41° (*c* 1.0, water); NMR: ^{1}H (D_2O), δ 5.27 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{III}), 4.99 (dd, 1 H, $J_{1,2}$ 4.0 Hz, H-1^{I}), 4.94 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 4.81 (ddd, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 3.5, $J_{3,F}$ 49.0 Hz, H-3^{I}), 4.29 (ddd, 1 H, $J_{4,5}$ 1.1 Hz, H-4^{I}), 4.14 (ddd, 1 H, H-2^{I}), 4.12 (dd, 1 H, $J_{2,3}$ 3.4 Hz, H-2^{II}), 4.07 (dd, 1 H, $J_{2,3}$ 3.4 Hz, H-2^{III}), 3.84 (m, 3 H, H-3^{II}, 3^{III}, 5^{III}*), 3.80 (m, 2 H, $J_{5,6a}$ 5.0 Hz, H-5^{I}, 6a^{I}), 3.75 (dd, 1 H, $J_{5,6b}$ 7.2, $J_{6a,6b}$ 11.7 Hz, H-6b^{I}), 3.73 (m, 1 H, H-5^{II}*), 3.55 (t, 1 H, $J_{3,4}$ 9.7, $J_{4.5}$ 9.6 Hz, H-4^{II}), 3.45 (t, 1 H, $J_{3.4}$ 9.7, $J_{4,5}$ 9.6 Hz, H-4^{III}), 3.44 (s, 3 H, OCH_3), 1.33 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^{II}), and 1.29 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{III}); ^{13}C, δ 103.3 (C-1^{III}, $J_{C,H}$ 171.8 Hz), 102.9 (C-1^{II}, $J_{C,H}$ 173.3 Hz), 99.7 (d, $J_{1,F}$ 10.3, $J_{C,H}$ 176.8 Hz, C-1^{I}), 91.1 (d, $J_{3,F}$ 183.2 Hz, C-3^{I}), 79.0 (C-3^{II}), 75.4 (d, $J_{2,F}$ 17.2 Hz, C-2^{I}), 73.0 (C-4^{III}), 72.2 (C-4^{II}), 71.2 (C-2^{III}), 71.1 (C-3^{III}), 70.9 (d, $J_{3,F}$ 6.4 Hz, C-5^{I}), 70.8 (C-2^{II}), 70.4 (C-5^{III}*), 70.0 (C-5^{II}*), 68.5 (d, $J_{4,F}$ 17.1 Hz, C-4^{I}), 61.8 (C-6^{I}), 55.9 (OMe), 17.8 (C-6^{II}), and 17.6 (C-6^{III}); ^{19}F, δ −39.95 (m, 1 F, $J_{F,3}$ 49.0, $J_{F,4}$ 7.4, $J_{F,2}$ 11.5, $J_{F,1}$ 4.0 Hz, F-3^{I}); CIMS: *m/z* 506 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{19}H_{33}FO_{13}$·0.5 H_2O: C, 44.27; H, 7.04; F, 3.68. Found: C, 44.54; H, 7.14; F, 3.64.

Methyl (2,4-di-O-*benzoyl-3*-O-*chloroacetyl*-α-L-*rhamnopyranosyl-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→2)-4,6*-O-*benzylidene-3-deoxy*-α-D-xylo-*hexopyranoside* (**16**).—A solution of the glycosyl chloride **6** (3.50 g, 4.26 mmol), the glycosyl acceptor **8** (755 mg, 2.83 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (805 mg, 3.92 mmol) in CH_2Cl_2 (50 mL) was added with stirring, at −15 °C, to a suspension of AgOTf (1.29 g, 5.02 mmol) in CH_2Cl_2 (30 mL). Stirring was continued for 1.5 h, after which time the bath temperature had reached 0 °C. TLC (9:1 toluene–EtOAc) showed the complete disappearance of **8**. The mixture was processed as described for the preparation of **5**, and the crude product was chromatographed (solvent *E*, 16:1) to give pure **16** (2.39 g, 80%) as a white foam, together with a slightly contaminated fraction (300 mg, 10%) which could be used directly, $[\alpha]_D$ +110° (*c* 1.0); NMR: ^{1}H, δ 8.21–7.35 (m, 25 H, Ph), 5.57 (t, partially overlapped, 1 H, $J_{4,5}$ 10.0 Hz, H-4^{II}), 5.54 (s, 1 H, C*H*Ph), 5.49 (bs, 1 H, H-2^{II}), 5.42 (dd, 1 H, $J_{2,3}$ 2.9, $J_{3,4}$ 10.0 Hz, H-3^{III}), 5.30 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4^{III}), 5.15 (m, 3 H, H-1^{II}, 1^{III}, 2^{III}), 5.00 (bs, 1 H, H-1^{I}), 4.49 (dd, 1 H, $J_{3,4}$ 9.7, $J_{3,2}$ 2.9 Hz, H-3^{II}), 4.27–4.03 (m, 6 H, H-2^{I}, 4^{I}, 6^{I}, 5^{II}, 5^{III}), 3.70 (bs, 2 H, CH_2Cl), 3.63 (bs, 1 H, H-5^{I}), 2.31–2.17 (m, 2 H, H-3^{I}), and 1.34, 1.15 (2 d, 6 H, $J_{5,6}$ 6.1, $J_{5,6}$ 6.1 Hz, H-6^{II}, 6^{III}); ^{13}C, δ 101.0 (Ph*C*H), 99.1 (2 C, C-1^{II}, 1^{III}), 98.1 (C-1^{I}), 76.2 (C-3^{II}), 73.3 (C-4^{I}), 73.1 (C-4^{II}), 72.9 (C-2^{I}), 72.4 (C-2^{II}), 71.2 (C-4^{III}), 70.4 (C-3^{III}), 70.2 (C-2^{III}), 69.5 (C-6^{I}), 67.4 (C-5^{II}), 67.0 (C-5^{III}), 61.7 (C-5^{I}), 55.2 (OMe), 40.3 (*C*H_2Cl), 29.7 (C-3^{I}), and 17.90, 17.3 (C-6^{II}, 6^{III}); CIMS: *m/z* 1068 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{56}H_{55}ClO_{18}$: C, 63.97; H, 5.27; Cl, 3.37. Found: C, 64.00; H, 5.31; Cl, 3.34.

Methyl (2,4-di-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→2)-4,6*-O-*benzylidene-3-deoxy*-α-D-xylo-*hexopyranoside* (**17**).—A solution of the fully protected **16** (2.39 g, 2.27 mmol), thiourea (800 mg, 10.51 mmol) and *sym*-collidine (300 μL, 2.27 mmol) in a 1:1 mixture CH_2Cl_2–MeOH (30 mL) was stirred at 25 °C for 36 h. More CH_2Cl_2 (70 mL) was added and stirring was continued for 15 min. The resulting suspension was filtered through a bed of Celite. The filtrate was extracted with ice-cold 5% aq HCl, 5% aq $NaHCO_3$, water, dried and concentrated. Column chromatography (solvent *E*, 9:1) of the residue afforded **17** as an amorphous

solid (1.95 g, 88%), $[\alpha]_D$ +93° (*c* 1.0); NMR data: ^{1}H, δ 8.18–7.15 (m, 25 H, Ph), 5.54 (t, partially overlapped, 1 H, $J_{4,5}$ 9.9 Hz, H-4^{II}), 5.53 (s, partially overlapped, 1 H, C*H*Ph), 5.48 (dd, 1 H, $J_{1,2}$ 1.7 Hz, H-2^{II}), 5.20, 5.12 (2 d, 2 H, $J_{1,2}$ 1.0, $J_{1,2}$ 1.0 Hz, H-1^{II}, 1^{III}), 5.06 (t, 1 H, $J_{3,4}$ 9.8, $J_{4,5}$ 9.8 Hz, H-4^{III}), 4.98 (m, 2 H, H-1^{I}, 2^{III}), 4.45 (dd, 1 H, $J_{3,4}$ 10.0, $J_{3,2}$ 3.3 Hz, H-3^{II}), 4.25 (bd, 1 H, $J_{6a,6b}$ 13.0 Hz, H-6a^{I}), 4.19–4.15 (m, 3 H, H-2^{I}*, 6b^{I}, 5^{II}), 4.08 (bd, partially overlapped, 1 H, H-4^{I}*), 4.06 (m, partially overlapped, 1 H, H-3^{III}), 3.95 (dq, 1 H, H-5^{III}), 3.63 (bs, 1 H, H-5^{I}), 3.49 (s, 3 H, OMe), 2.24–2.14 (m, 2 H, H-3^{I}), 1.32 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^{II}), and 1.09 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6^{III}); ^{13}C, δ 101.0 (Ph*C*H), 99.2, 98.1 (C-1^{II}, 1^{III}), 99.1 (C-1^{I}), 76.6 (C-3^{II}), 75.1 (C-4^{III}), 73.4 (C-4^{I}), 73.0 (3 C, C-2^{I}, 4^{II}, 2^{III}), 72.6 (C-2^{II}), 69.5 (C-6^{I}), 68.5 (C-3^{III}), 67.1, 67.0 (C-5^{II}, 5^{III}), 61.7 (C-5^{I}), 55.2 (OMe), 29.7 (C-3^{I}), 17.9 (C-6^{II}), and 17.4 (C-6^{III}); CIMS: *m*/*z* 992 ($[M+NH_4]^+$). Anal. Calcd for $C_{54}H_{54}O_{17}$: C, 66.52; H, 5.58. Found: C, 66.59; H, 5.62.

Methyl (2,4-di-O-*benzoyl-3*-O-*chloroacetyl*-α-L-*rhamnopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→2)-4,6*-O-*benzylidene-3-deoxy-3-fluoro*-α-D-*galactopyranoside* (**18**).—A solution of the glycosyl chloride **6** (1.50 g, 1.83 mmol), the glycosyl acceptor **9** (398 mg, 1.40 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (400 mg, 1.95 mmol) in CH_2Cl_2 (40 mL) was added dropwise, at −15 °C, to a stirred suspension of AgOTf (610 mg, 2.37 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred until it reached −5 °C, at which time the cooling bath was removed. Stirring was continued for 1 h at 25 °C. TLC (solvent *E*, 9:1) showed the complete disappearance of **9** and the presence of one major compound together with some minor ones of close chromatographic mobility to that of **18**. The suspension was filtered through a bed of Celite, and the filtrate was treated as described for the preparation of **5**. Chromatography of the residue (solvent *C*, 3.5:1) gave **18** (1.11 g, 74%) as an amorphous solid, $[\alpha]_D$ +131° (*c* 1.0); NMR: ^{1}H, δ 8.22–7.33 (m, 25 H, Ph), 5.63 (m, 1 H, H-2^{II}), 5.59 (m, partially overlapped, 1 H, $J_{3,4}$ 10.2, $J_{4,5}$ 9.5 Hz, H-4^{II}), 5.59 (s, partially overlapped, 1 H, PhC*H*), 5.44 (dd, 1 H, $J_{3,2}$ 2.7, $J_{3,4}$ 10.0 Hz, H-3^{III}), 5.33 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4^{III}), 5.24 (bs, 1 H, H-1^{II}), 5.18 (bs, 2 H, H-1^{III}, 2^{III}), 5.06 (bt, partially overlapped, 1 H, $J_{1,F}$ 3.9 Hz, H-1^{I}), 4.95 (ddd, partially overlapped, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 3.7, $J_{3,F}$ 48.6 Hz, H-3^{I}), 4.55 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.7 Hz, H-3^{II}), 4.47 (bt, 1 H, $J_{4,F}$ 4.6 Hz, H-4^{I}), 4.36 (dt, 1H, $J_{1,2}$ 3.5, $J_{2,F}$ 10.1 Hz, H-2^{I}), 4.28 (bd, 1 H, $J_{6a,6b}$ 12.5 Hz, H-6a^{I}), 4.23–4.13 (m, 2 H, H-5^{II}, 5^{III}), 4.07 (bd, 1 H, H-6b^{I}), 3.72 (d, 1 H, J_{gem} 15.0 Hz, C*H*$_2$Cl), 3.67 (bs, partially overlapped, 1 H, H-5^{I}), 3.66 (d, partially overlapped, 1 H, C*H*$_2$Cl), 3.46 (s, 3 H, OC*H*$_3$), and 1.36, 1.17 (2 d, 6 H, $J_{5,6}$ 6.2, $J_{5,6}$ 6.2 Hz, H-6^{II}, 6^{III}); ^{13}C, δ 100.6 (Ph*C*H), 99.9 (d, $J_{1,F}$ 9.1 Hz, C-1^{I}), 99.1, 99.0 (2 C, C-1^{II}, 1^{III}), 87.8 (d, $J_{3,F}$ 192.4 Hz, C-3^{I}), 75.6 (C-3^{II}), 75.3 (d, $J_{2,F}$ 16.9 Hz, C-2^{I}), 74.6 (d, $J_{4,F}$ 15.1 Hz, C-4^{I}), 73.1 (C-4^{II}), 71.8 (C-2^{II}), 71.2 (C-3^{III}), 70.4 (C-4^{III}), 70.1 (C-2^{III}), 68.9 (C-6^{I}), 67.3, 67.2 (C-5^{II}, 5^{III}), 61.9 (d, $J_{5,F}$ 5.7 Hz, C-5^{I}), 55.4 (OMe), 40.1 (*C*H$_2$Cl), and 17.7, 17.1 (C-6^{II}, 6^{III}); CIMS: *m*/*z* 1086 ($[M+NH_4]^+$). Anal. Calcd for $C_{56}H_{54}ClFO_{18}$: C, 62.89; H, 5.09; Cl, 3.32; 1.78. Found: C, 62.86; H, 5.16; Cl, 3.67; F, 1.51.

Methyl (2,4-di-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→2)-4,6*-O-*benzylidene-3-deoxy-3-fluoro*-α-D-*galactopyranoside* (**19**).—*sym*-Collidine (33 mL, 0.25 mmol) was added to a solution of the fully protected **18** (270 mg, 0.25 mmol) and thiourea (96 mg, 1.25 mmol) in 1:1 of CH_2Cl_2–MeOH (8 mL). The homogenous solution was stirred at ambient temperature for 48 h. A large excess of CH_2Cl_2 (50 mL) was added and the resulting precipitate was collected on a bed of Celite. The filtrate was washed with 5% aq $NaHCO_3$, water and satd NaCl, dried, and chromatographed (solvent *C*, 2.5:1) to give **19** (241 mg, 96%) as an amorphous solid, $[\alpha]_D$ +119° (*c* 1.0); NMR: ^{1}H, δ 8.20–7.34 (m, 25 H, Ph), 5.60 (dd, 1H, $J_{1,2}$ 1.9, $J_{2,3}$ 3.2 Hz, H-2^{II}), 5.59 (s, partially overlapped, 1 H, PhC*H*), 5.55 (t, partially overlapped, 1 H, $J_{3,4}$ 10.0, $J_{4,5}$ 9.8 Hz, H-4^{II}), 5.21 (bs, 2 H, H-1^{II}, 1^{III}), 5.07 (t, partially overlapped, 1 H, $J_{4,5}$ 9.8, $J_{3,4}$ 9.8 Hz, H-4^{III}), 5.04 (bt, partially overlapped, 1 H, $J_{1,F}$ 3.6, $J_{1,2}$ 3.6 Hz, H-1^{I}), 5.00 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.2 Hz, H-2^{III}), 4.94 (ddd, partially overlapped, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 3.7 Hz, H-3^{I}), 4.50 (dd, partially overlapped, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.7 Hz, H-3^{II}), 4.49 (m, 1 H, H-4^{I}), 4.36 (dt, partially overlapped, 1 H, $J_{1,2}$ 3.6, $J_{2,F}$ 10.2 Hz, H-2^{I}), 4.30 (bd, partially overlapped, 1 H, $J_{6a,6b}$ 12.6 Hz, H-6a^{I}), 4.16 (dq, partially overlapped, 1 H, $J_{4,5}$ 9.7 Hz, H-5^{II}), 4.08 (m, 2 H, H-6b^{I}, 3^{III}), 4.01 (dq, partially overlapped, 1 H, $J_{4,5}$ 9.6 Hz, H-5^{III}), 3.70 (bs, partially overlapped, 1 H, H-5^{I}), 3.46 (s, 3 H, OC*H*$_3$), 2.17 (d, 1 H, $J_{3,OH}$ 7.8 Hz, OH-3^{III}), 1.33 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^{II}), and 1.12 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{III}); ^{13}C, δ 100.7 (Ph*C*H), 99.9 (d, $J_{1,F}$ 9.4 Hz, C-1^{I}), 99.0 (2 C,

C-1^{II}, 1^{III}), 87.8 (d, $J_{3,F}$ 191.3 Hz, C-3^{I}), 76.0 (C-3^{II}), 75.3 (d, $J_{2,F}$ 16.7 Hz, C-2^{I}), 75.1 (C-4^{III}), 74.8 (d, $J_{4,F}$ 15.7 Hz, C-4^{I}), 73.1 (C-2^{II}), 73.0 (C-4^{II}), 72.1 (C-2^{II}), 69.1 (C-6^{I}), 68.5 (C-3^{III}), 67.3, 67.0 (C-5^{II}, 5^{III}), 62.0 (d, $J_{5,F}$ 5.5 Hz, C-5^{I}), 55.6 (OMe), and 18.0, 17.4 (C-6^{II}, 6^{III}); CIMS: *m/z* 1010 ($[M+NH_4]^+$). Anal. Calcd for $C_{54}H_{53}FO_{17}$: C, 65.31; H, 5.38; F, 1.91. Found: C, 65.25; H, 5.43; F, 2.40.

Methyl (3,4,6-tri-O-*acetyl-2-azido-2-deoxy*-α-D-*glucopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→2)-4,6*-O-*benzylidene-3-deoxy*-α-D-xylo-*hexopyranoside* (**21**).—A solution of the glycosyl acceptor **17** (370 mg, 0.35 mmol), the chloride [22] **20** (200 mg, 0.57 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (100 mg, 0.48 mmol) in CH_2Cl_2 (15 mL) was added dropwise to a suspension of AgOTf (160 mg, 0.62 mmol) in CH_2Cl_2 (5 mL) at −10 °C. The reaction mixture was stirred at 0 °C for 1 h and then overnight at ambient temperature. Although some of the glycosyl acceptor **17** subsisted in the mixture, the donor **20** was completely consumed. CH_2Cl_2 was added and the mixture was filtered through a bed of Celite. Treatment was proceeded as described for the preparation of the disaccharide **5**. The residue was chromatographed (solvent *E*, 12:1) to give pure starting material **17** (54 mg, 15%) eluting first and **21** (285 mg, 69% based on the consumed nucleophile) as an amorphous solid, $[\alpha]_D$ +157° (*c* 1.0); NMR: ^{1}H, δ 8.19–7.15 (m, 25 H, Ph), 5.47 (s, overlapped, 1 H, PhC*H*), 5.46 (dd, overlapped, 1 H, $J_{3,4}$ 9.7, $J_{4,5}$ 9.3 Hz, H-4^{II}), 5.44 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.3 Hz, H-2^{II}), 5.27 (dd, 1 H, $J_{3,4}$ 10, $J_{4,5}$ 9.8 Hz, H-4^{III}), 5.10 (bs, 1 H, H-1^{III}), 5.07 (bd, $J_{2,3}$ 3.0 Hz, H-2^{III}), 5.02 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1^{II}), 4.92 (d, 1 H, $J_{1,2}$ 2.9 Hz, H-1^{I}), 4.97 (ddd, 1 H, $J_{3,4}$ 9.7 Hz, H-3^{IV}), 4.65 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4^{IV}), 4.52 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1^{IV}), 4.41 (dd, 1 H, H-3^{II}), 4.20 (dd, 1 H, $J_{6a,6b}$ 12.3, $J_{5,6a}$ 3.1 Hz, H-6a^{I}), 4.15 (m, partially overlapped, 1 H, H-5^{II}), 4.10 (dd, 1 H, $J_{3,4}$ 9.8 Hz, H-3^{III}), 4.03–3.98 (m, 3 H, H-2^{I}, 4^{I}, 6b^{I}), 3.92 (dq, 1 H, $J_{5,6}$ 6.3 Hz, H-5^{III}), 3.68 (dd, 1 H, $J_{5,6a}$ 3.3, $J_{6a,6b}$ 12.4 Hz, H-6a^{IV}), 3.56 (bs, 1 H, H-5^{I}), 3.46 (dt, partially overlapped, 1 H, H-5^{IV}), 3.42 (s, 3 H, OMe), 3.38 (dd, 1 H, $J_{5,6b}$ 1.9 Hz, H-6b^{IV}), 2.94 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-2^{IV}), 2.14–2.00 (m, 2 H, H-3^{I}), 1.94, 1.80, 1.54 (3 s, 9 H, OAc), 1.27 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{II}), and 1.04 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{III}); ^{13}C, δ 101.0 (Ph*C*H), 99.1 (C-1^{III}), 99.0 (C-1^{I}), 98.2 (C-1^{II}), 93.9 (C-1^{IV}), 76.2 (C-3^{II}), 73.3 (d, C-4^{I}), 73.1 (C-4^{II}), 73.0 (C-3^{III}), 72.3 (C-2^{II}), 71.8 (2 C, C-2^{III}, 4^{III}), 70.2 (C-3^{IV}), 69.5 (C-6^{I}), 67.8 (C-2^{III}), 67.5 (C-4^{IV}), 67.3 (C-5^{III}), 67.2 (C-5^{II}), 67.0 (C-5^{IV}), 61.7 (C-5^{I}), 60.9 (C-6^{IV}), 60.3 (C-2^{IV}), 55.1 (OMe), 29.7 (C-3^{I}), 20.6, 20.5, 20.3 (C(O)*C*H$_3$), 17.9 (C-6^{II}), and 17.4 (C-6^{III}); CIMS: *m/z* 1305 ($[M+NH_4]_+$). Anal. Calcd for $C_{66}H_{69}N_3O_{24}$: C, 61.53; H, 5.40; N, 3.26. Found: C, 61.35; H, 5.45; N, 3.16.

Methyl (3,4,6-tri-O-*acetyl-2-amino-2-deoxy*-α-D-*glucopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→2)-4,6*-O-*benzylidene-3-deoxy*-α-D-xylo-*hexopyranoside* (**22**).—A mixture of the azido tetrasaccharide **21** (200 mg, 0.15 mmol) and triphenylphosphine (203 mg, 0.77 mmol) in CH_2Cl_2 (10 mL) was heated for 24 h at 35 °C. Water (0.5 mL) was added and stirring was maintained at the same temperature for another 24 h. The organic phase was separated from the the aq one, dried and concentrated. Chromatography of the residue (solvent *D*, 4.5:1) afforded the amino derivative **22** as an amorphous solid (155 mg, 79%); $[\alpha]_D$ +146° (*c* 1.0); NMR: ^{1}H, δ 8.19–7.34 (m, 25 H, Ph), 5.53 (m, 2 H, $J_{4,5}$ 9.8 Hz, H-4^{II}, PhC*H*), 5.49 (dd, 1 H, $J_{1,2}$ 1.6 Hz, H-2^{II}), 5.30 (t, 1 H, $J_{3,4}$ 9.6 Hz, H-4^{III}), 5.17 (dd, 1 H, $J_{2,3}$ 2.8 Hz, H-2^{III}), 5.14 (s, 1 H, H-1^{II}), 5.08 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1^{III}), 4.98 (bt, 1 H, $J_{1,2}$ 3.1 Hz, H-1^{I}), 4.65 (dd, 1 H, $J_{3,4}$ 9.3, $J_{4,5}$ 10.2 Hz, H-4^{IV}), 4.58 (dd, 1 H, $J_{2,3}$ 10.0 Hz, H-3^{IV}), 4.51 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1^{IV}), 4.46 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.0 Hz, H-3^{II}), 4.24 (d, 1 H, $J_{6a,6b}$ 12.9 Hz, H-6a^{I}), 4.19 (m, 3 H, H-2^{I}, 4^{I}, 5^{II}), 4.10 (dd, partially overlapped, 1 H, $J_{2,3}$ 3.1 Hz, H-3^{III}), 4.07 (d, partially overlapped, 1 H, $J_{5,6b}$ 1.5 Hz, H-6b^{I}), 4.00 (dq, 1 H, $J_{4,5}$ 9.8 Hz, H-5^{III}), 3.69 (dd, 1 H, $J_{5,6}$ 3.1, $J_{6a,6b}$ 12.3 Hz, H-6a^{IV}), 3.63 (bs, 1 H, H-5^{I}), 3.48 (s, 3 H, OC*H*$_3$), 3.44 (m, 2 H, H-5^{IV}, 6b^{IV}), 2.58 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2^{IV}), 2.17 (m, 2 H, H-3^{I}), 2.01, 1.87, 1.58 (3 s, 9 H, OAc), 1.33 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{II}), and 1.12 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{III}); ^{13}C, δ 101.0 (Ph*C*H), 99.2 (d, C-1^{III}), 99.1 (C-1^{I}), 98.2 (C-1^{II}), 96.0 (C-1^{IV}), 76.1 (C-3^{II}), 73.8 (C-3^{IV}), 73.3 (C-2^{I}*), 73.1 (C-4^{II}), 73.0 (C-4^{I}*), 72.3 (C-2^{II}), 71.9 (C-4^{III}), 71.2 (C-3^{III}), 69.5 (C-6^{I}), 68.0 (C-2^{III}), 67.8 (C-4^{IV}), 67.3 (C-5^{IV}), 67.2 (C-5^{III}), 61.7 (C-5^{I}), 61.2 (C-6^{IV}), 55.1 (OMe), 53.9 (C-2^{IV}), 29.7 (C-3^{I}), 20.7, 20.6, 20.3 (OAc), 17.8 (C-6^{II}), and 17.3 (C-6^{III}); CIMS: *m/z* 1262 ($[M+H]^+$). Anal. Calcd for $C_{66}H_{71}NO_{24}$: C, 62.80; H, 5.67; N, 1.11. Found: C, 62.82; H, 5.92; N, 0.95.

Methyl (2-acetamido-3,4,6-tri-O-*acetyl-2-deoxy*-α-D-*glucopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→2)-4,6*-O-*benzylidene-3-deoxy*-α-D-xylo-*hexopyranoside* (**23**).—A mixture of the azido tetrasaccharide **21** (700 mg, 0.54 mmol) and triphenylphosphine (715 mg, 2.73 mmol) in CH_2Cl_2 (30 mL) was heated for 24 h at 35 °C. Water (2 mL) was added and stirring was maintained at the same temperature for another 24 h. The organic phase was separated from the the aqueous one, dried and concentrated. The residue was taken up in pyridine (5 mL) and acetic anhydride (2.5 mL) was added. The mixture was stirred at ambient temperature overnight. Conventional processing and chromatography of the residue gave the *N*-acetylated product **23** (678 mg, 96%) as an amorphous solid; $[\alpha]_D$ +136° (*c* 1.0); NMR: ^{1}H, δ 8.18–7.33 (m, 25 H, Ph), 5.53 (s, 1 H, H-4^{II}, PhC*H*), 5.51 (dd, 1 H, $J_{3,4}$ 9.7, $J_{4,5}$ 9.8 Hz, H-4^{II}), 5.49 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.3 Hz, 1 H, H-2^{II}), 5.26 (t, 1 H, $J_{4,5}$ 9.8, $J_{3,4}$ 9.9 Hz, H-4^{III}), 5.09 (m, 3 H, H-1^{II}, 1^{III}, 2^{III}), 4.97 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1^{I}), 4.83 (dd, 1 H, $J_{3,4}$ 9.7, $J_{4,5}$ 9.8 Hz, H-4^{IV}), 4.58 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-3^{IV}), 4.44 (dd, 1 H, $J_{2,3}$ 3.3, $J_{3,4}$ 9.9 Hz, H-3^{II}), 4.46 (dd, 1 H, $J_{1,2}$ 3.6 Hz, H-1^{IV}), 4.24 (d, 1 H, $J_{6a,6b}$ 12.7 Hz, H-6a^{I}), 4.19 (m, 2 H, H-2^{I}, 4^{I}), 4.07 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-6b^{I}), 4.03 (m, 3 H, $J_{2,3}$ 3.2 Hz, H-5^{II}, 3^{III}, 2^{IV}), 3.98 (dq, 1 H, H-5^{III}), 3.66 (dd, 1 H, $J_{5,6a}$ 3.0, $J_{6a,6b}$ 12.7 Hz, H-6a^{IV}), 3.63 (bs, 1 H, H-5^{I}), 3.48 (s, 3 H, OCH_3), 3.43 (dt, 1 H, H-5^{IV}), 3.39 (dd, 1 H, $J_{5,6b}$ 1.9 Hz, H-6b^{IV}), 2.17 (m, 2 H, H-3^{I}), 2.01, 1.87, 1.58 (3 s, 9 H, OAc), 1.33 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{II}), and 1.12 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{III}); ^{13}C, δ 101.0 (Ph*C*H), 99.0 (2 C, C-1^{I}, 1^{III}*), 98.2 (C-1^{II}*), 95.6 (C-1^{IV}), 76.3 (C-3^{II}), 73.3 (C-4^{II}), 73.1 (C-2^{I}*), 72.9 (C-3^{III}, 4^{I}*), 72.2 (C-2^{II}), 72.0 (C-4^{III}), 70.9 (C-3^{IV}), 69.5 (C-6^{I}), 68.6 (C-2^{III}), 67.6 (C-5^{IV}), 67.4 (C-5^{III}), 67.1 (C-5^{II}), 67.0 (C-4^{IV}), 61.6 (C-5^{I}), 60.8 (C-6^{IV}), 55.1 (OMe), 50.8 (C-2^{IV}), 29.7 (C-3^{I}), 22.2 (NHAc), 20.7, 20.6, 20.3 (3 C, OAc), 17.9 (C-6^{II}), and 17.4 (C-6^{III}); CIMS: *m*/*z* 1321 ([M + NH_4]$^+$). Anal. Calcd for $C_{68}H_{73}NO_{25}$: C, 62.62; H, 5.64; N, 1.08. Found: C, 62.56; H, 5.69; N, 1.03.

Methyl (2-acetamido-3,4,6-tri-O-*acetyl-2-deoxy*-α-D-*glucopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→2)-3-deoxy*-α-D-xylo-*hexopyranoside* (**24**).—10% Palladium-on-charcoal catalyst (200 mg) was added to a solution of the *N*-acetylated **23** (310 mg, 24 μmol) in a 1:4 mixture of acetic acid–EtOH (25 mL) and the suspension was stirred in a H_2 atmosphere overnight. TLC (solvent *D*, 2.2:1) showed that the reaction was complete and a single product was formed. Filtration on a bed of Celite followed by elution on a short column of silica gel to remove any residual catalyst afforded the di-hydroxylated **24** in theoretical yield; $[\alpha]_D$ +141° (*c* 1.0); NMR: ^{1}H, δ 8.19–7.15 (m, 20 H, Ph), 5.51 (dd, partially overlapped, 1 H, $J_{3,4}$ 9.3, $J_{4,5}$ 10.4 Hz, H-4^{II}), 5.50 (dd, partially overlapped, 1 H, $J_{2,3}$ 2.8 Hz, H-2^{II}), 5.26 (t, 1 H, $J_{4,5}$ 9.8, $J_{3,4}$ 9.8 Hz, H-4^{III}), 5.09 (bd, 3 H, H-1^{II}, 1^{III}, 2^{III}), 4.92 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1^{I}), 4.83 (dd, 1 H, $J_{3,4}$ 9.8, $J_{4,5}$ 9.6 Hz, H-4^{IV}), 4.58 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-3^{IV}), 4.45 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 9.9 Hz, H-3^{II}), 4.41 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1^{IV}), 4.20 (dq, 1 H, $J_{4,5}$ 9.9, $J_{5,6}$ 6.3 Hz, H-5^{II}), 4.16 (m, 2 H, H-2^{I}, 4^{I}), 4.05 (m, 2 H, H-3^{III}, 2^{IV}), 3.97 (dq, 1 H, H-5^{III}), 3.89 (bd, 2 H, H-6^{I}), 3.73 (bs, 1 H, H-5^{I}), 3.65 (dd, 1 H, $J_{6a,6b}$ 12.4, $J_{5,6a}$ 2.8 Hz, H-6a^{IV}), 3.45 (s, 3 H, OCH_3), 3.41 (m, 1 H, H-5^{IV}), 3.40 (d, 1 H, H-6b^{IV}), 2.05 (m, 2 H, H-3^{I}), 2.00, 1.83, 1.60 (3 s, 9 H, OAc), 1.33 (d, 3 H, H-6^{II}), 1.32 (s, 3 H, NHAc), and 1.11 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{III}); ^{13}C, δ 100.1 (C-1^{III}*), 99.0 (C-1^{I}), 98.4 (C-1^{II}*), 95.6 (C-1^{IV}), 76.3 (C-3^{II}), 73.1 (2 C, C-2^{II}, 3^{III}), 73.0 (C-2^{I}), 72.3 (C-4^{II}), 72.1 (C-4^{III}), 71.0 (C-3^{IV}), 68.8 (C-4^{I}), 68.6 (C-5^{I}), 68.5 (C-2^{III}), 67.6 (C-5^{IV}), 67.4 (C-5^{III}), 67.1 (C-4^{IV}), 67.0 (C-5^{II}), 64.0 (C-6^{I}), 60.9 (C-6^{IV}), 55.0 (OMe), 50.8 (C-2^{IV}), 32.0 (C-3^{I}), 22.1 (NHAc), 20.7, 20.6, 20.3 (OAc), 17.8 (C-6^{II}), and 17.3 (C-6^{III}); CIMS: *m*/*z* 1233 ([M + NH_4]$^+$). Anal. Calcd for $C_{61}H_{69}NO_{25}$: C, 60.24; H, 5.72; N, 1.15. Found: C, 60.11; H, 5.83; N, 1.07.

Methyl (2-acetamido-2-deoxy-α-D-*glucopyranosyl)-(1→3)*-α-L-*rhamnopyranosyl-(1→3)*-α-L-*rhamnopyranosyl-(1→2)-3-deoxy*-α-D-xylo-*hexopyranoside* (**25**). A solution of **24** (180 mg, 0.14 mmol) in MeOH (5 mL) was treated with 0.5 M methanolic MeONa (500 μL) as described for the preparation of **12**. Reverse phase chromatography of the crude material (solvent *F*) followed by lyophilisation gave pure **25** (61 mg, 63%) as a white amorphous solid; $[\alpha]_D$ +51° (*c* 0.9, water); ^{1}H NMR data (D_2O): 5.07 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1^{IV}), 5.06 (s, 1 H, H-1^{III}), 4.89–3.76 (m, 7.5 H, 0.5 H-2^{IV}, 3^{III}, 3^{II}, 5^{III}, 5^{I}, 3^{IV}, 6a^{IV}, 6b^{IV}), 3.75–3.65 (m, 3 H, H-5^{II}, 6a^{I}, 6b^{I}), 3.59–3.50 (m, 3 H, H-5^{IV}, 4^{II}, 4^{III}), 3.48 (s, 3 H, OCH_3), 2.11 (m, 1 H, $J_{3a,3b}$ 13.3, $J_{2,3a}$ 3.8, $J_{3a,4}$ 3.8 Hz, H-3a^{I}), 2.06 (s, 3 H, C(=O)CH_3), 1.93 (ddd, 1 H, $J_{2,3b}$ 11.1, $J_{3b,4}$ 1.7 Hz, H-3b^{I}), and 1.33, 1.32 (2 d, 6 H, $J_{5,6}$ 6.2 Hz, H-6^{II}, 6^{III}); ^{13}C: δ 175.2

(C=O), 102.9 (C-1^{III}, $J_{C,H}$ 172.2 Hz), 100.9 (C-1^{II}, $J_{C,H}$ 171.0 Hz), 99.0 (C-1^{I}, $J_{C,H}$ 175.1 Hz), 95.1 (C-1^{IV}, $J_{C,H}$ 174.9 Hz), 79.1 (C-3^{II}), 76.0 (C-3^{III}), 72.6 (C-4^{IV}), 72.0 (C-4^{II}), 71.9 (C-2^{I}), 71.7 (C-3^{IV}), 71.4 (C-5^{I}), 71.1 (C-4^{III}), 70.9 (C-2^{II}), 70.5 (C-5^{IV}), 70.0 (2 C, C-5^{II}, 5^{III}), 67.6 (C-2^{III}), 66.7 (C-4^{I}), 62.2 (C-6^{I}), 61.0 (C-6^{IV}), 55.4 (O*C*H_3), 54.4 (C-2^{IV}), 31.7 (C-3^{I}), 22.7 (C(=O)*C*H_3), and 17.6, 17.5 (C-6^{II}, 6^{III}); *m/z* 674 ([M + H]$^+$). Anal. Calcd for $C_{27}H_{47}NO_{18}$: C, 45.31; H, 7.38; N, 1.90. Found: C, 45.17; H, 7.11; N, 1.88.

*Methyl (3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-*α*-*D*-glucopyranosyl)-(1→3)-(2,4-di-*O*-benzoyl-*α*-*L*-rhamnopyranosyl)-(1→3)-(2,4-di-*O*-benzoyl-*α*-*L*-rhamnopyranosyl)-(1→2)-4,6-*O*-benzylidene-3-deoxy-3-fluoro-*α*-*D*-galactopyranoside* (**26**).—A solution of the glycosyl acceptor **19** (550 mg, 0.51 mmol), the crude chloride **20** (314 mg, 0.90 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (164 mg, 0.80 mmol) in CH_2Cl_2 (15 mL) was added dropwise to a suspension of AgOTf (257 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) under stirring at −10 °C. Stirring was maintained at −5 °C for 1 h and then overnight when the cooling bath reached a final temperature of 15 °C. Although some of the glycosyl acceptor **19** subsisted, the reaction mixture had remained unchanged during this period. Dichloromethane was added and the mixture was filtered through a bed of Celite. Processing followed that described for the preparation of the disaccharide **5**. The residue was chromatographed (solvent *D*, 19:1) to first give pure starting material **19** (195 mg, 35%) and **26** (370 mg, 85% based on the consumed nucleophile) as an amorphous solid, $[\alpha]_D$ +174° (*c* 0.9); NMR: ^{1}H, *δ* 8.19–7.34 (m, 25 H, Ph), 5.63 (dd, 1H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.2 Hz, H-2^{II}), 5.59 (s, 1 H, Ph*C*H), 5.54 (t, 1 H, $J_{3,4}$ 9.9, $J_{4,5}$ 9.8 Hz, H-4^{II}), 5.07 (t, 1 H, $J_{4,5}$ 9.8, $J_{3,4}$ 10.0 Hz, H-4^{III}), 5.21 (bs, 3 H, H-1^{II}, 1^{III}, 2^{III}), 5.04 (bt, partially overlapped, 1 H, $J_{1,F}$ 4.9, $J_{1,2}$ 3.7 Hz, H-1^{I}), 4.93 (dd, 1 H, $J_{3,4}$ 9.3 Hz, H-3^{IV}), 4.94 (ddd, partially overlapped, 1 H, $J_{3,F}$ 44.5, $J_{2,3}$ 9.8, $J_{3,4}$ 3.7 Hz, H-3^{I}), 4.71 (dd, 1 H, $J_{4,5}$ 10.0 Hz, H-4^{IV}), 4.62 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1^{IV}), 4.50 (dd, partially overlapped, 1 H, $J_{2,3}$ 3.5, $J_{3,4}$ 9.9 Hz, H-3^{II}), 4.49 (m, 1 H, H-4^{I}), 4.34 (ddd, partially overlapped, 1 H, $J_{1,2}$ 3.6, $J_{2,F}$ 10.2 Hz, H-2^{I}), 4.30 (dd, partially overlapped, 1 H, $J_{5,6a}$ 1.7, $J_{6a,6b}$ 12.5 Hz, H-$6a^{I}$), 4.17 (dq, partially overlapped, 1 H, $J_{4,5}$ 9.8 Hz, H-5^{II}), 4.10 (dd, 1 H, $J_{5,6b}$ 1.3 Hz, H-$6b^{I}$), 4.07 (m, partially overlapped, 2 H, H-3^{III}, 5^{III}), 3.76 (dd, 1 H, $J_{5,6a}$ 3.2, $J_{6a,6b}$ 12.4 Hz, H-$6a^{IV}$), 3.70 (bs, 1 H, H-5^{I}), 3.53 (dt, 1 H, H-5^{IV}), 3.46 (s, 3 H, OCH_3), 3.44 (dd, 1 H, $J_{5,6b}$ 2.0 Hz, H-$6b^{IV}$), 3.01 (dd, 1 H, $J_{2,3}$ 10.5, $J_{1,2}$ 3.7 Hz, H-2^{IV}), 2.00, 1.86, 1.60 (3 s, 9 H, OAc), 1.33 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^{II}), and 1.15 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{III}); ^{13}C NMR: *δ* 100.9 (Ph*C*H), 99.9 (d, $J_{1,F}$ 9.2 Hz, C-1^{I}), 99.3, 99.1 (C-1^{II}, 1^{III}), 93.9 (C-1^{IV}), 88.25 (d, $J_{3,F}$ 191.2 Hz, C-3^{I}), 75.6 (C-3^{II}), 75.4 (d, $J_{2,F}$ 17.0 Hz, C-2^{I}), 74.8 (d, $J_{4,F}$ 16.0 Hz, C-4^{I}), 73.2 (C-2^{II}), 71.8 (3 C, C-2^{II}, 3^{III}, 4^{III}) 70.3 (C-3^{IV}), 69.1 (C-6^{I}), 67.8 (C-2^{III}), 67.5 (C-4^{IV}), 67.3 (2 C, C-5^{II}, 5^{III}), 67.2 (C-5^{IV}), 62.0 (d, $J_{5,F}$ 5.7 Hz, C-5^{I}), 55.6 (OMe), 20.6, 20.5, 20.3 (OAc), 17.8 (C-6^{II}), and 17.3 (C-6^{III}); CIMS: *m/z* 1323 ([M + NH_4]$^+$). Anal. Calcd for $C_{66}H_{68}FN_3O_{24}$: C, 60.69; H, 5.25; F, 1.45; N, 3.22. Found: C, 60.71; H, 5.28; F, 1.10; N, 3.14.

*Methyl (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*α*-*D*-glucopyranosyl)-(1→3)-(2,4-di-*O*-benzoyl-*α*-*L*-rhamnopyranosyl)-(1→3)-(2,4-di-*O*-benzoyl-*α*-*L*-rhamnopyranosyl)-(1→2)-4,6-*O*-benzylidene-3-deoxy-3-fluoro-*α*-*D*-galactopyranoside* (**27**).—Hydrolysis, followed by *N*-acetylation, of the azido tetrasaccharide **26** (600 mg, 0.45 mmol) was performed as described for the preparation of the deoxygenated **23**. Chromatography of the residue (solvent *C*, 2:1) gave the pure tetrasaccharide **27** (440 mg, 71%) as an amorphous solid, together with a second fraction slightly contaminated by triphenylphosphine (230 mg). Data for **27** are as follows; $[\alpha]_D$ +139° (*c* 1.0); NMR: ^{1}H, *δ* 8.17–7.14 (m, 25 H, Ph), 5.62 (bs, 1 H, H-2^{II}), 5.58 (s, 1 H, Ph*C*H), 5.52 (t, 1 H, $J_{3,4}$ 9.9, $J_{4,5}$ 9.8 Hz, H-4^{II}), 5.27 (t, 1 H, $J_{4,5}$ 9.8, $J_{3,4}$ 9.8 Hz, H-4^{III}), 5.17 (bs, 1 H, H-1^{II}), 5.11 (m, 2 H, H-1^{III}, 2^{III}), 5.04 (bt, partially overlapped, 1 H, $J_{1,F}$ 5.1 Hz, H-1^{I}), 4.92 (ddd, partially overlapped, 1 H, $J_{3,F}$ 48.4, $J_{2,3}$ 9.8, $J_{3,4}$ 3.8 Hz, H-3^{I}), 4.82 (dd, 1 H, $J_{4,5}$ 9.8 Hz, H-4^{IV}), 4.68 (dd, 1 H, $J_{3,4}$ 9.7, $J_{2,3}$ 10.0 Hz, H-3^{IV}), 4.50 (dd, partially overlapped, 1 H, $J_{2,3}$ 3.5, $J_{3,4}$ 9.5 Hz, H-3^{II}), 4.49 (m, 1 H, H-4^{I}), 4.42 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1^{IV}), 4.33 (ddd, partially overlapped, 1 H, $J_{1,2}$ 3.7, $J_{2,F}$ 10.1 Hz, H-2^{I}), 4.31 (dd, partially overlapped, 1 H, $J_{6a,6b}$ 12.9 Hz, H-$6a^{I}$), 4.16 (dq, partially overlapped, 1 H, $J_{4,5}$ 10.0, $J_{5,6}$ 6.4 Hz, H-5^{II}), 4.11 (dd, 1 H, $J_{5,6b}$ 1.3 Hz, H-$6b^{I}$), 4.07 (m, partially overlapped, 2 H, $J_{2,3}$ 3.2 Hz, H-3^{III}, 5^{III}), 3.69 (bs, 1 H, H-5^{I}), 3.66 (dd, partially overlapped, 1 H, $J_{5,6a}$ 2.0 Hz, H-$6a^{IV}$), 3.45 (s, 3 H, OCH_3), 3.44 (m, 1 H, H-5^{IV}), 3.42 (dd, 1 H, $J_{6a,6b}$ 12.6 Hz, H-$6b^{IV}$), 1.99, 1.83, 1.60 (3 s, 9 H, OAc), 1.33 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^{II}), 1.32 (s, 3 H, NHAc), and 1.15 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{III}); ^{13}C, *δ* 100.7

(Ph*C*H), 99.9 (d, $J_{1,F}$ 8.9 Hz, C-1^{I}), 99.2 (C-1^{II}), 99.0 (C-1^{III}), 95.5 (C-1^{IV}), 87.2 (d, $J_{3,F}$ 191.6 Hz, C-3^{I}), 75.7 (C-3^{II}), 75.4 (d, $J_{2,F}$ 17.1 Hz, C-2^{I}), 74.7 (d, $J_{4,F}$ 15.9 Hz, C-4^{I}), 73.2 (C-4^{II}), 72.8 (C-3^{III}), 72.0 (C-4^{III}), 71.7 (C-2^{II}), 71.0 (C-3^{IV}), 69.0 (C-6^{I}), 68.5 (C-2^{III}), 67.6 (C-5^{IV}), 67.4 (C-5^{III}), 67.2 (C-5^{II}), 67.1 (C-4^{IV}), 62.0 (d, $J_{5,F}$ 5.7 Hz, C-5^{I}), 60.8 (C-6^{IV}), 55.6 (OMe), 50.8 (C-2^{IV}), 22.2 (NHAc), 20.6, 20.4 (3 C, OAc), 17.8 (C-6^{II}), and 17.3 (C-6^{III}); CIMS: *m/z* 1339 ([M + NH_4]$^+$). Anal. Calcd for $C_{68}H_{72}FNO_{25}$: C, 61.77; H, 5.48; F, 1.44; N, 1.06. Found: C, 61.87; H, 5.57; F, 1.26; N, 0.88.

Methyl (2-acetamido-3,4,6-tri-O-*acetyl-2-deoxy*-α-D-*glucopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→3)-(2,4-di*-O-*benzoyl*-α-L-*rhamnopyranosyl)-(1→2)-3-deoxy-3-fluoro*-α-D-*galactopyranoside* (**28**).—(a) The fluorinated tetrasaccharide **27** (360 mg, 0.27 mmol) was hydrogenolyzed as described for the preparation of **24**. Chromatography (solvent *D*, 2.3:1) of the residue gave the dihydroxylated **28** (300 mg, 89%) as an amorphous solid; $[\alpha]_D$ +143° (*c* 1.0); NMR data: ^{1}H, δ 8.17–7.14 (m, 20 H, Ph), 5.61 (dd, partially overlapped, 1 H, $J_{2,3}$ 4.4 Hz, H-2^{II}), 5.51 (t, 1 H, $J_{3,4}$ 9.8, $J_{4,5}$ 9.8 Hz, H-4^{II}), 5.27 (t, 1 H, $J_{4,5}$ 9.8, $J_{3,4}$ 9.8 Hz, H-4^{III}), 5.15 (s, 1 H, H-1^{II}), 5.11 (bd, 2 H, H-1^{III}, 2^{III}), 4.96 (dd, 1 H, $J_{1,2}$ 3.7, $J_{1,F}$ 3.9 Hz, H-1^{I}), 4.83 (dd, 1 H, $J_{3,4}$ 9.7, $J_{4,5}$ 9.9 Hz, H-4^{IV}), 4.82 (ddd, 1 H, $J_{3,F}$ 49.6, $J_{2,3}$ 9.7, $J_{3,4}$ 3.3 Hz, H-3^{I}), 4.68 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-3^{IV}), 4.47 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.8 Hz, H-3^{II}), 4.42 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1^{IV}), 4.32 (m, 1 H, H-4^{I}), 4.22 (ddd, 1 H, partially overlapped, $J_{1,2}$ 3.6, $J_{2,F}$ 11.1 Hz, H-2^{I}), 4.14 (dq, partially overlapped, 1 H, $J_{4,5}$ 10.6, $J_{5,6}$ 6.3 Hz, H-5^{II}), 4.08 (m, 2 H, H-5$_{III}$, 2^{IV}), 4.04 (dd, 1 H, $J_{2,3}$ 3.1 Hz, H-3^{III}), 3.93 (m, 2 H, H-6^{I}), 3.82 (bs, 1 H, H-5^{I}), 3.65 (dd, 1 H, $J_{6a,6b}$ 12.3, $J_{5,6a}$ 2.8 Hz, H-6a^{IV}), 3.42 (m, 5 H, H-5^{IV}, 6b^{IV}, O*CH*$_3$), 3.00 (bs, 1 H, OH-4^{I}), 2.49 (bs, 1 H, OH-6^{I}), 1.93 (m, 2 H, H-3^{I}), 2.00, 1.83, 1.60 (3 s, 9 H, OAc), 1.32 (d, 3 H, H-6^{II}), 1.32 (s, 3 H, NHAc), and 1.12 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{III}); ^{13}C, δ 99.3 (2 C, $J_{1,F}$ 6.4 Hz, C-1^{I}, 1^{II}*), 98.9 (C-1^{III}*), 95.4 (C-1^{IV}), 89.7 (d, $J_{3,F}$ 185 Hz, C-3^{I}), 75.8 (C-3^{II}), 75.7 (d, $J_{2,F}$ 19.4 Hz, C-2^{I}), 73.1 (C-4^{II}), 72.8 (C-3^{III}), 72.3 (C-4^{II}), 72.0 (C-4^{III}), 71.8 (C-2^{II}), 69.3 (d, $J_{4,F}$ 17.0 Hz, C-4^{I}), 68.6 (d, $J_{5,F}$ 7.8 Hz, C-5^{I}), 68.5 (C-2^{III}), 67.6 (C-5^{IV}), 67.4 (C-5^{III}), 67.3 (C-5^{II}), 67.1 (C-4^{IV}), 62.6 (C-6^{I}), 60.9 (C-6^{IV}), 55.4 (OMe), 50.8 (C-2^{IV}), 32.0 (C-3^{I}), 22.2 (NHAc), 20.7, 20.6, 20.3 (OAc), 17.8 (C-6^{II}), and 17.4 (C-6^{III}); CIMS: *m/z* 1251 ([M + NH_4]$^+$). Anal. Calcd for $C_{61}H_{68}FNO_{25}$: C, 59.36; H, 5.55; F, 1.54; N, 1.13. Found: C, 59.34; H, 6.02; F, 1.68; N, 0.99.

Methyl (2-acetamido-2-deoxy-α-D-*glucopyranosyl)-(1→3)*-α-L-*rhamnopyranosyl-(1→3)*-α-L-*rhamnopyranosyl-(1→2)-3-deoxy-3-fluoro*-α-D-*galactopyranoside* (**29**).—A solution of **28** (180 mg, 0.15 mmol) in MeOH (5 mL) was treated with 0.5 M methanolic sodium methoxide (500 μL) as described for the preparation of **12**. Reverse phase chromatography of the crude material (solvent *F*) followed by lyophilisation gave pure **29** (89 mg, 88%) as a white amorphous solid; $[\alpha]_D$ +72° (*c* 1.0, water); ^{1}H NMR data (D_2O) δ 5.07 (bs, overlapped, 1 H, H-1^{III}), 5.06 (d, partially overlapped, 1 H, $J_{1,2}$ 3.5 Hz, H-1^{IV}), 5.00 (dd, 1 H, $J_{1,F}$ 4.1 Hz, H-1^{I}), 4.95 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1^{II}), 4.82 (ddd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 3.5, $J_{3,F}$ 48.2 Hz, H-3^{I}), 4.28 (dd, 1 H, $J_{4,F}$ 7.5 Hz, H-4^{I}), 4.20 (dd, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 3.0 Hz, H-2^{III}), 4.14 (ddd, partially overlapped, 1 H, $J_{2,F}$ 21.5, $J_{1,2}$ 4.0 Hz, H-2^{I}), 4.13 (dd, 1 H, $J_{2,3}$ 4.0 Hz, H-2^{II}), 4.02–3.74 (m, 12 H, H-2^{IV}, 3^{IV}, 4^{IV}, 6a^{IV}, 6b^{IV}, 5^{I}, 6a^{I}, 6b^{I}, 3^{II}, 5^{II}, 3^{III}, 5^{III}), 3.55 (m, overlapped, 1 H, H-5^{IV}), 3.54 (dd, partially overlapped, 1 H, $J_{4,5}$ 9.7, $J_{3,4}$ 9.6 Hz, H-4^{II}), 3.53 (t, partially overlapped, 1 H, $J_{3,4}$ 9.7, $J_{4,5}$ 9.7 Hz, H-4^{III}), 3.43 (s, 3 H, O*CH*$_3$), 2.06 (s, 3 H, Ac), 1.33 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6^{II}), and 1.32 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6^{III}); ^{13}C: δ 175.2 (C=O), 102.9 (C-1^{III}, $J_{C,H}$ 171.3 Hz), 102.7 (C-1^{II}, $J_{C,H}$ 173.3 Hz), 99.5 (d, $J_{1,F}$ 9.9 Hz, C-1^{I}, $J_{C,H}$ 168.8 Hz), 95.1 (C-1^{IV}, $J_{C,H}$ 174.0 Hz), 91.0 (d, $J_{3,F}$ 173.2 Hz, C-3^{I}), 78.9 (C-3^{II}), 76.0 (C-3^{III}), 75.1 (d, $J_{2,F}$ 17.3 Hz, C-2^{I}), 72.6 (C-4^{IV}), 71.9 (C-4^{II}), 71.7 (C-3^{IV}), 70.7 (d, $J_{5,F}$ 5.9 Hz, C-5^{I}), 70.5 (2 C, C-2^{II}, 5^{IV}), 70.2 (C-5^{II}), 70.0 (C-5^{III}), 68.3 (d, $J_{4,F}$ 16.6 Hz, C-4^{I}), 67.6 (C-2^{III}), 61.6 (C-6^{IV}), 61.0 (C-6^{I}), 55.7 (O*CH*$_3$), 54.4 (C-2^{IV}), and 17.5, 17.4 (C-6^{II}, 6^{III}); CIMS: *m/z* 692 ([M + H]$^+$). Anal. Calcd for $C_{27}H_{46}FNO_{18}\cdot 3.5H_2O$: C, 42.97; H, 7.07; N, 1.85. Found: C, 42.93; H, 6.97; N, 1.76.

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