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4,6-*O*-Benzylidene-Directed β-Mannopyranosylation and α-Glucopyranosylation: The 2-Deoxy-2-fluoro and 3-Deoxy-3-fluoro Series of Donors and the Importance of the O2−C2−C3−O3 Interaction

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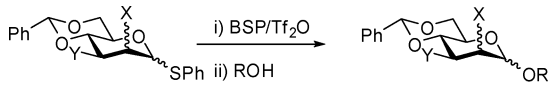

X = axial and equatorial F, Y = OBn;
X = axial and equatorial OBn, Y = F

A series of 4,6-*O*-benzylidene-protected 2-*O*-benzyl-3-deoxy-3-fluoro- and 3-*O*-benzyl-2-deoxy-2-fluorogluco- and mannopyranosyl thioglycosides were synthesized and their coupling reactions with a series of alcohols, on preactivation with 1-benzenesulfinylpiperidine and trifluoromethanesulfonic anhydride, investigated. In all cases, the selectivities were lower than those observed with the corresponding simple 4,6-*O*-benzylidene 2,3-di-*O*-benzylgluco- and mannopyranosyl thioglycosides. This leads to the conclusion that the high β-selectivity observed with 4,6-*O*-benzylidene 2,3-di-*O*-benzylmannopyranosyl donors under the same conditions is in large part derived from the compression of the O2−C2−C3−O3 torsion angle on going from the intermediate covalent glycosyl triflate to the oxacarbenium ion, as compared to the relaxation of this torsion angle in the gluco series.

Introduction

Previous work from our laboratory has drawn attention to the fact that, while the 4,6-*O*-benzylidene-protected mannosyl triflate **1** is β-selective in its glycosylation reactions, the corresponding glucosyl triflate **2** is α-selective.[1,2] This reversal of selectivity with the change in configuration at C2 is independent of the nature of the triflate precursor, thioglycoside or sulfoxide, is supported by parallel observations from other groups,[3−5] and has been the subject of computational investigations.[6,7] We consider that an understanding of this striking reversal of selectivity would help illuminate the factors involved in determining glycosylation stereoselectivity in general and so provide a necessary platform for the rational development of improved glycosylation methods. In our reflections, we were guided by our observation that the 4,6-*O*-benzylidene-2,3-*O*-carbonate **3**,[8] and its 2,3-*O*-carbonate-protected congeners in the rhamnopyranose series,[9] is highly α-selective in its homogeneous glycosylation reactions, a fact which stands in marked contrast to the β-selectivity classically observed with related 2,3-*O*-carbonate-protected mannosyl and rhamnosyl donors in glycosylations assisted by heterogeneous promoters.[10,11] While the established β-selective couplings of carbonates of this kind can be understood in terms of the heterogeneous nature of the reactions taking place on the promoter surface, we rationalize the α-selective couplings on the basis of the spectroscopically[8,9,12] and crystallographically[13] established half-chair-like

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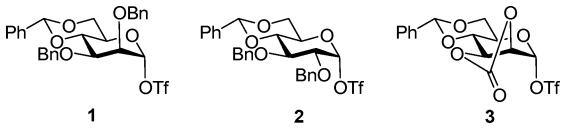
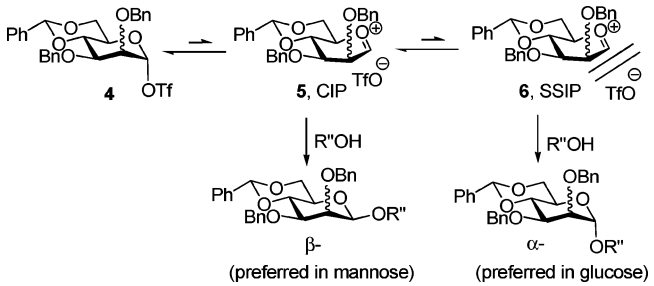
conformations imposed on these donors by the presence of the *cis*-fused carbonate group.



1 **2** **3**

In the glycosylation mechanism, as currently understood by our laboratory (Scheme 1),[14,15] the glycosyl triflate **4** serves as a reservoir for the transient contact ion pair **5**, which is the true intermediate in the formation of the β-glycosides. This contact ion pair is in equilibrium with a solvent-separated ion pair **6**, which is the source of the α-glycosides. The benzylidene acetal exerts its influence by destabilizing the oxacarbenium ion present in both ion pairs, resulting in a displacement of the complete set of equilibria further toward the covalent triflate than would be the case in donors lacking this conformational restraint.[14,16,17] According to the calculations of Nukuda, Whitfield, and co-workers, only two conformations need to be considered for the 4,6-*O*-benzylidene-protected mannosyl oxacarbenium ion, the closely related $^4H_3$ half-chair and $B_{2,5}$ boat, and two for the corresponding glucosyl oxacarbenium ion, namely, the $^4H_3$ half-chair and its close cousin the ^4E envelope.[6,7] In mannose, the conversion of the $^4C_1$ covalent triflate to the oxacarbenium ion, in either the$^4H_3$ half-chair and $B_{2,5}$ boat forms, necessitates compression of the O2−C2−C3−O3 torsion angle, which we view to be disfavorable.[18] In the carbonate **3**, this penalty has already been paid, resulting in a reduction of the activation barrier for formation of the oxacarbenium ion, a higher concentration of the CIP, and intervention of the α-selective SSIP. In glucose, on the other hand, the O2−C2−C3−O3 torsion angle is expanded on going from the covalent triflate to the oxacarbenium ion, thereby facilitating access to the CIP and the SSIP and leading to the α-selective glycosylations.[18] Our hypothesis, therefore, is that changes in the O2−C2−C3−O3 torsional interaction play a significant role in the determination of anomeric stereochemistry in these 4,6-*O*-benzylidene-protected systems. The influence of torsional interactions around the pyranoside ring on relative rates of acidic hydrolyses of simple glycosides was discussed more than 40 years ago[19−21] and was revisited recently for the spontaneous hydrolyses of aryl glycosides[22] but has not been extended to stereochemical control in glycosylation reactions prior to our recent work in the area.[18]

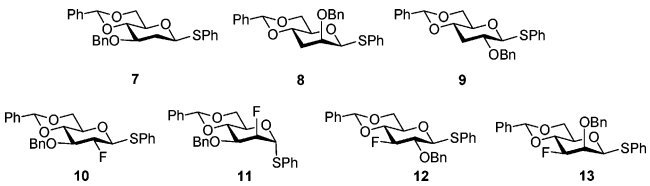
SCHEME 1. The Glycosylation Mechanism



4 **5**, CIP **6**, SSIP

β- (preferred in mannose) α- (preferred in glucose)

In a first attempt at probing the importance of the O2−C2−C3−O3 interaction, we synthesized the 2-deoxy and 3-deoxy donors **7**−**9** and studied their glycosylation reactions. As expected, the 2-deoxy donor **7** showed little or no selectivity, which is consistent with the well-known greater reactivity in this series. Both of the 3-deoxy donors **8** and **9** also displayed little selectivity in their glycosylations, thereby providing some measure of support for the general hypothesis.[18] However, the impossibility of distinguishing between the absence of the O2−C2−C3−O3 interaction and the simple absence of the electron-withdrawing C3−O3 bond as the underlying cause for the loss of selectivity in **8** and **9** prompted the synthesis and investigation of the 2-deoxy-2-fluoro and 3-deoxy-3-fluoro donors **10**−**13** on which we now report. Fluorodeoxy sugars have played important roles in the elucidation of the mechanisms of carbohydrate processing enzymes[23−28] and in the studies on the mechanism of glycoside hydrolysis[29,30] but have not been investigated in detail[31] as probes of the stereoselective chemical synthesis of glycosidic bonds.



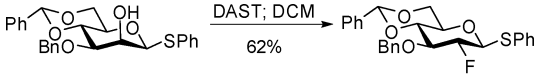
7 **8** **9**

10 **11** **12** **13**

Results

Preparation of Donors. Reaction of **14**[32] with DAST gave the 2-deoxy-2-fluoroglucose donor **10** smoothly (Scheme 2). The choice of the less common β-thioglycoside as substrate in this reaction was made based upon the need to exclude the

SCHEME 2. Synthesis of the 2-Deoxy-2-fluoroglucose Donor 10



14 **10**

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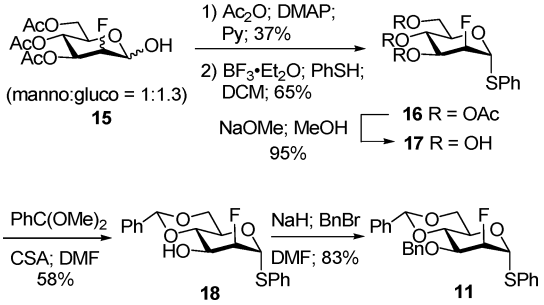
migration of the phenylthio group to the 2-position seen with related activated 2-*O*-esters of the corresponding α-glycoside.[32]

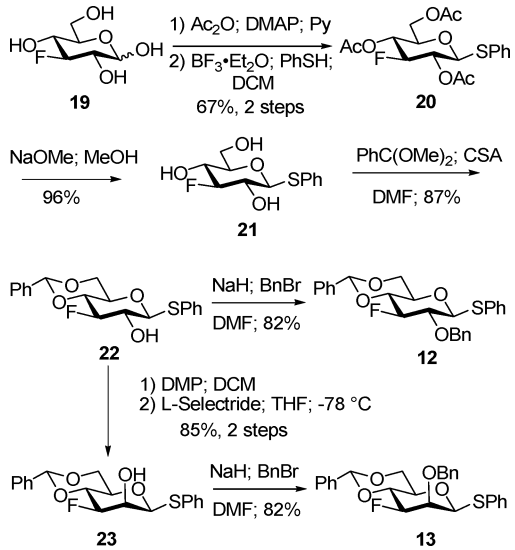
Unfortunately, attempted synthesis of the 2-deoxy-2-fluoromannose donor **11** by a parallel DAST treatment of phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside met with difficulties due to the formation of furanose isomers[33] and elimination products in significant amounts. Eventually, a synthesis was devised in which a readily available mixture of the gluco and manno isomers of tri-*O*-acetyl-2-deoxy-2-fluorohexose **15**[34,35] was acetylated to afford a separable mixture of 2-deoxy-2-fluoro tetraacetates, from which only the mannose isomer was processed through a series of routine steps to give the 2-deoxy-2-fluoromannose donor **11** (Scheme 3).

Starting from 3-deoxy-3-fluoroglucose **19**,[31,36] standard methods afforded the thioglucoside **22** (Scheme 4). This was converted to the corresponding gluco donor **12** by simple benzylation and to the corresponding manno donor **13** by Dess−Martin oxidation, stereoselective reduction with L-selectride,[37] and benzylation (Scheme 4).

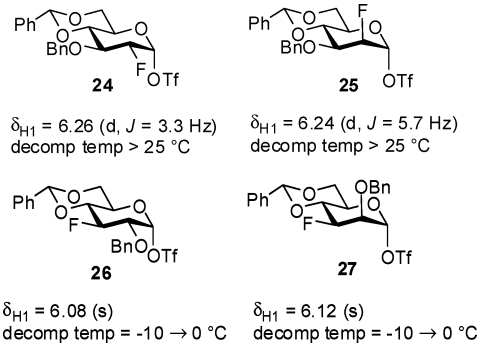
SCHEME 3. Synthesis of the 2-Deoxy-2-fluoromannose Donor 11



SCHEME 4. Synthesis of the 3-Deoxy-3-fluoroglucose and Mannose Donors 12 and 13



Investigation of Key Intermediates. Exploratory experiments conducted in CD_2Cl_2 by variable-temperature ^1H NMR spectroscopy revealed the 2-deoxy-2-fluoro donors **10** and **11** to be fully activated by the BSP/Tf_2O combination within minutes at −60 °C. The corresponding triflate intermediates **24** and **25** did not undergo decomposition on warming to 25 °C, thereby demonstrating the considerable stabilizing effect of the adjacent, powerfully electron-withdrawing C−F bond, consistent with earlier studies on the retarded hydrolysis of deoxyfluoro glycosides.[29,30] In the 3-deoxy-3-fluoro series, clean activation of both **12** and **13** by the BSP/Tf_2O couple also took place rapidly at −60 °C in CD_2Cl_2, but the putative glycosyl triflates **26** and **27** underwent decomposition at approximately 0 °C.



Glycosylation Reactions. The 2-deoxy-2-fluoro donors **10** and **11** were subjected to glycosylation under the standard conditions with preformation of the glycosyl triflates with BSP and trifluoromethanesulfonic anhydride before addition of the acceptor, leading to the results presented in Table 1. Also presented in Table 1 for ease of comparison are the results of the analogous couplings for the standard gluco and mannosyl donors, as well as for the 2-deoxy series. In all cases, the anomeric configuration of the products was readily assigned by standard ^1H NMR techniques[31] and was confirmed by the measurement of $^1J_{CH}$ anomeric coupling constants.[38,39] Comparison of columns 3, 4, and 5 of Table 1 indicates that the 2-deoxy-2-fluoro donors **10** and **11** (column 3) have little in common with the standard gluco and manno donors and approximate more closely to the corresponding 2-deoxy series in terms of stereoselectivity.

The identical series of couplings were conducted with the 3-deoxy-3-fluoro donors **12** and **13**, as reported in Table 2. Again, the results of analogous couplings to the corresponding gluco and manno donors, as well as to the 3-deoxy series, are presented for comparison. As with the 2-deoxy-2-fluoro series, the anomeric configurations of the products were readily assigned by the usual ^1H NMR techniques[31] and by the measurement of $^1J_{CH}$ anomeric coupling constants.[38,39] The only noteworthy feature in the spectra of these products was the consistent observation of a small $^4J_{H1\text{-}F3}$ heteronuclear W-type coupling in the 3-deoxy-3-fluoro α-gluco and mannopyranosides, which supports the configurational assignments. From the

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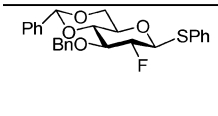
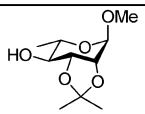
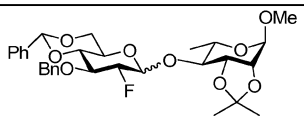
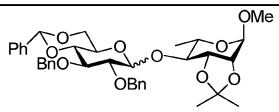
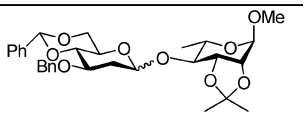
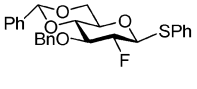
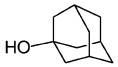
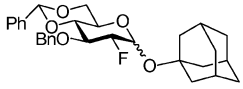
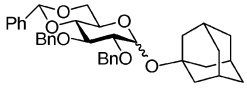
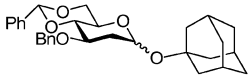
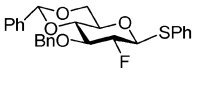
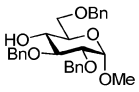
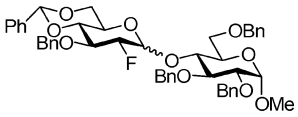
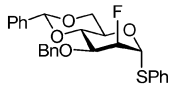
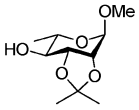
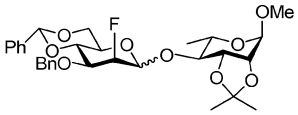
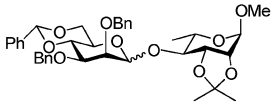
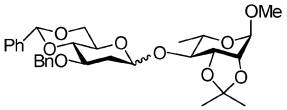
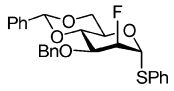
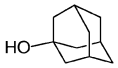
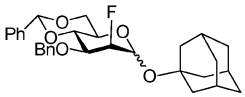
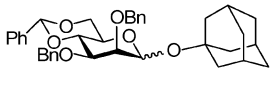
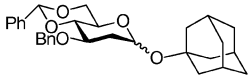
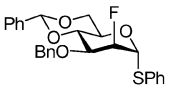
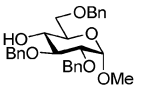
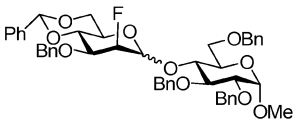
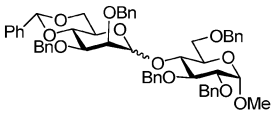
TABLE 1. Glycosylation of 2-Deoxy-2-fluoro Donors 10 and 11 and Related Donors

Donor	Acceptor	Product (yield, α/β ratio[a])	Hexose (yield, α/β ratio)	2-Deoxy Product (yield, α/β ratio)
				
10	**28**	**31** (88%, 1:2.5)	(95%, 3.2:1)[b]	(75%, 1:1.5)[c]
				
10	**29**	**32** (76%, 1:5.8)	(72%, >9:1)[d]	(30%, 1:1.9)[c]
			–	–
10	**30**	**33** (68%, 1:4.6)		
				
11	**28**	**34** (73%, 1:3.7)	(80%, 1:>10)[e]	(75%, 1:1.5)[c]
				
11	**29**	**35** (82%, 1:1.3)	(88%, 1:>9)[d]	(30%, 1:1.9)[c]
				–
11	**30**	**36** (64%, 1:3.1)	(83%, 1:>9)[f]	

[a] Determined by ^{1}H NMR spectroscopy on the crude reaction mixture. [b] Taken from ref 40. [c] Taken from ref 18. [d] Taken from ref 2. [e] Taken from ref 41 with activation by MPBT. [f] Taken from ref 42.

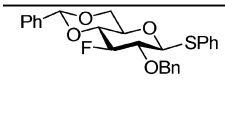
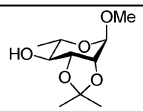
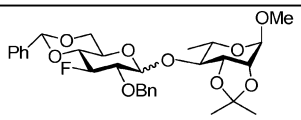
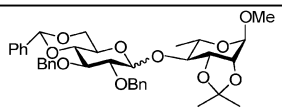
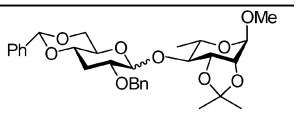
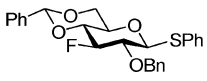
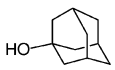
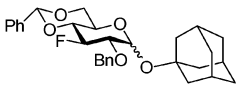
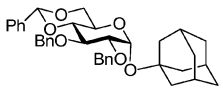
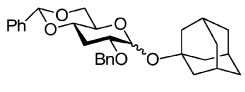
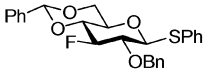
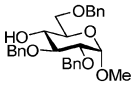
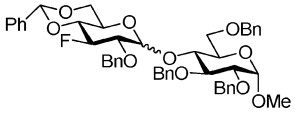
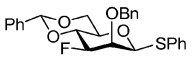
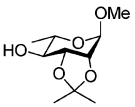
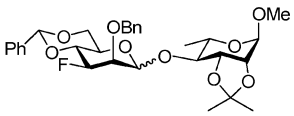
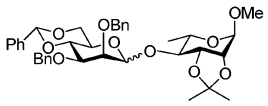
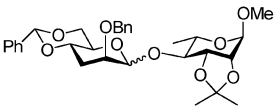
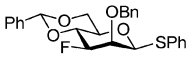
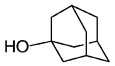
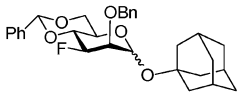
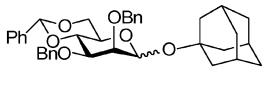
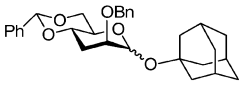
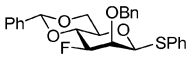
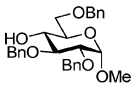
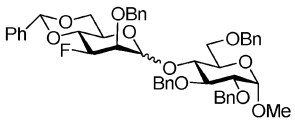
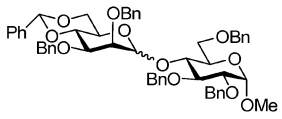
results presented, it is evident that, as in the 2-deoxy-2-fluoro series, the anomeric stereoselectivity obtained with the 3-deoxy-3-fluoro donors **12** and **13** bears no relation to that obtained with the standard gluco- and mannopyranosyl donors.

Discussion

From the results presented in Tables 1 and 2, it is apparent that both the 2-*O*-benzyl and 3-*O*-benzyl groups in the gluco- and mannopyranosyl triflates **1** and **2** play a significant role in the stereoselective couplings of these donors. Most importantly, it is clear that this role is not restricted to the electron-withdrawing nature of the C−O bonds as their replacement by the corresponding C−F bonds has a dramatic detrimental effect on selectivity in both the gluco and manno series.

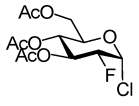
In the 2-deoxy-2-fluoro series, the glycopyranosyl donors **10** and **11** both show a small preference for the formation of the β-glycosides (Table 1). The earlier report by Kovac and co-workers that the 2-deoxy-2-fluoroglucosyl chloride **43** is less α-selective in its silver ion-promoted glycosylations than the corresponding 2-deoxy-2-chloro donor **44** is consistent with our observations if the C−Cl bond is considered isoteric with the C−OBn bond.[31] The slight preference for the formation of the β-glycosides with the 2-deoxy-2-fluoro donors **10** and **11** presumably results from the influence of the powerfully electron-withdrawing C−F bond on the glycosyl triflate/contact ion pair/solvent separated ion pair equilibrium, shifting it further toward the covalent triflate and rendering the reactions more "S_N2-like". The possibility of neighboring group participation by the C−F bond contributing to the formation of the β-glucosides and the

TABLE 2. Glycosylation of 3-Deoxy-3-fluoro Donors 12 and 13 and Related Donors

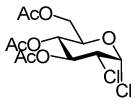
Donor	Acceptor	Product (yield, α/β ratio[a])	Hexose (yield, α/β ratio)	3-Deoxy Product (yield, α/β ratio)
				
12	**28**	**37** (93%, 1:1.8)	(95%, 3.2:1)[b]	(95%, 1.6:1)[c]
				
12	**29**	**38** (83%, 1:2.2)	(72%, >9:1)[d]	(92%, 1:1.8)[c]
			—	—
12	**30**	**39** (82%, 1:2.0)		
				
13	**28**	**40** (88%, 1.8:1)	(80%, 1:>10)[e]	(85%, 1.9:1)[c]
				
13	**29**	**41** (85%, 4.2:1)	(88%, 1:>9)[d]	(83%, 3.6:1)[c]
				—
13	**30**	**42** (82%, 1.6:1)	(83%, 1:>9)[f]	

[a] Determined by ^{1}H NMR spectroscopy on the reaction mixture. [b] Taken from ref 40. [c] Taken from ref 18. [d] Taken from ref 2. [e] Taken from ref 41 with activation by MPBT. [f] Taken from ref 42.

α-mannosides in the 2-deoxy-2-fluoro series is discounted as the selectivities are only modest, and as such, effects have been conclusively excluded in simple 2-fluoroalkyl cations.[43,44]



43



44

Overall, we conclude that a major reason for the differences in stereoselectivity observed with glycosyl triflates **1** and **2**, and with related trichloroacetimides and phosphites, are the differing changes in the O2−C2−C3−O3 torsional interaction on passage from the glycosyl triflates to the corresponding contact ion pairs (Scheme 1). In the manno series, this transition is accompanied by an increase in this torsional interaction, while in the gluco series, the interaction decreases. Accordingly, the concentration of the contact ion pair, and of other ion pairs, is lower in the manno series, resulting in the highly *β*-selective reactions typically observed. When this increase in torsional strain is limited, as with the 2,3-*O*-carbonate-protected donor **3**, or by replacing the C3−O bonds with C3−F bonds as demonstrated here, the mannosyl system is α-selective. In the 2-deoxy-2-fluoro series, the same trend of reduced *β*-selectivity in the manno series is seen, but the effect is mitigated by the powerfully electron-withdrawing nature of the C2−F bond. More subtle effects relating to shifts in the covalent triflate/ion pair equilibria and oxacarbenium ion conformations, which remain to be elucidated in detail, must be responsible for the increased *β*-selectivity seen in both the 2-deoxy-gluco and the 2-deoxy-2-fluorogluco series of donors.

(43) Ford, G. P.; Raghuveer, K. S. *Tetrahedron* **1988**, *44*, 7489−7498.
(44) Olah, G. A.; Prakash, G. K. S.; Krishnamurthy, V. V. *J. Org. Chem.* **1983**, *48*, 5116−5117.

Experimental Section

Phenyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-1-thio-β-D-glucopyranoside (10). To a cold solution (0 °C) of **14** (453 mg, 1.01 mmol) in CH_2Cl_2 (5 mL) was added DAST (0.40 mL, 3.03 mmol) dropwise with stirring. After 10 min, the cooling bath was removed, and the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was diluted with CH_2Cl_2 and quenched with excess MeOH. After 10 min, the reaction mixture was washed with H_2O, followed by saturated $NaHCO_3$ and brine. The organic layer was separated, dried over Na_2SO_4, and concentrated. Chromatographic purification on silica gel (5% ethyl acetate in hexane) afforded **10** (280 mg, 62%) as a white crystalline solid: mp 85−86 °C; $[\alpha]^{29}_D$ −59.1 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58−7.54 (m, 2H), 7.50−7.46 (m, 2H), 7.42−7.27 (m, 11H), 5.55 (s, 1H), 4.87 (d, J = 11.5 Hz, 1H), 4.83 (d, J = 12.0 Hz, 1H), 4.74−4.71 (dd, J = 3.0, 10.0 Hz, 1H), 4.42−4.39 (dd, J = 5.0, 10.5 Hz, 1H), 4.33−4.40 (ddd, J = 8.0, 10.0, 48.0 Hz, 1H), 3.90−3.83 (dt, J = 8.5, 15.5 Hz, 1H), 3.78 (t, J = 10.0 Hz, 1H), 3.61 (t, J = 9.5 Hz, 1H), 3.52−3.48 (dt, J = 5.0, 10.0 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 137.8, 137.0, 134.0, 130.6, 129.1, 128.8, 128.4, 128.3, 128.1, 127.9, 126.0, 101.3, 90.4 (d, J = 190.1 Hz), 85.3 (d, J = 25.2 Hz), 80.3 (d, J = 10.1 Hz), 80.0 (d, J = 18.9 Hz), 74.6, 70.7, 68.5; ESI-HRMS calcd for $C_{26}H_{25}FO_4SNa$ $[M + Na]^+$, 475.1356; found, 475.1372.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-fluoro-1-thio-α-D-mannopyranoside (16). To a stirred solution of **15** (404 mg, 1.31 mmol, manno/gluco = 1:1.3) and DMAP (16 mg, 0.13 mmol) in pyridine (5 mL) was added Ac_2O (0.5 mL, 5.3 mmol) at room temperature. After 5 h, the reaction mixture was concentrated, dissolved in CH_2Cl_2, and washed with saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, concentrated, and subjected to chromatographic purification on silica gel (20% ethyl acetate in hexane) to give the mannosyl tetraacetate (170 mg, 37%). To a solution of this mannosyl tetraacetate (121.7 mg, 0.35 mmol) in CH_2Cl_2 (5 mL) were added thiophenol (48 μL, 0.42 mmol) and $BF_3{\cdot}Et_2O$ (130 μL, 1.0 mmol), after which the solution was stirred at room temperature for 12 h before solid Na_2CO_3 was added and stirring continued for ∼10 min. The reaction mixture was then diluted with CH_2Cl_2, washed with saturated $NaHCO_3$ and brine, and purified by column chromatography on silica gel (20% ethyl acetate in hexane) to give 90 mg of **16** (65%): colorless oil; $[\alpha]^{20}_D$ +188.3 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.48 (m, 2H), 7.34−7.31 (m, 3H), 5.67−5.64 (dd, J = 1.5, 14.5 Hz, 1H), 5.39 (t, J = 10.0 Hz, 1H), 5.25−5.17 (ddd, J = 2.5, 10.0, 28.0 Hz, 1H), 5.10−4.99 (dt, J = 2.0, 50.0 Hz, 1H), 4.53−4.48 (ddd, J = 3.0, 5.0, 10.0 Hz, 1H), 4.32−4.30 (dd, J = 5.5, 12.5 Hz, 1H), 4.12−4.09 (dd, J = 2.5, 12.5 Hz, 1H), 2.11 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 170.7, 170.1, 169.5, 132.3, 132.0, 129.3, 128.3, 88.3 (d, J = 188.8 Hz), 85.5 (d, J = 23.9 Hz), 70.2 (d, J = 16.4 Hz), 69.6, 65.9, 62.2, 20.75, 20.73, 20.69; ESI-HRMS calcd for $C_{18}H_{21}FO_7SNa$ $[M + Na]^+$, 423.0885; found, 423.0879.

Phenyl 2-Deoxy-2-fluoro-1-thio-α-D-mannopyranoside (17). To a stirred solution of **16** (1.35 g, 3.37 mmol) in dry methanol (15 mL) was added 1.0 mL of sodium methoxide solution (25 wt % in methanol), and the resulting solution was stirred for 1 h. The mixture was neutralized with solid Amberlyst-15 ion-exchange resin, filtered, and concentrated in vacuo. The residue was recrystallized from ether and hexane to give **17** as a white crystalline solid (878 mg, 95%): mp 113−114 °C; $[\alpha]^{20}_D$ +287.2 (*c* 0.5, CH_3OH); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.53−7.51 (m, 2H), 7.35−7.28 (m, 3H), 5.61 (d, J = 14.0 Hz, 1H), 5.42 (d, J = 5.0 Hz, 1H), 5.19 (d, J = 5.0 Hz, 1H), 4.82 (d, J = 49.5 Hz, 1H), 4.62 (t, J = 6.0 Hz, 1H), 3.81 (m, 1H), 3.66−3.63 (dd, J = 5.0, 10.5 Hz, 1H), 3.56−3.46 (m, 3H); ^{13}C NMR (125.9 MHz, DMSO-d_6) δ 134.0, 132.0, 129.7, 128.1, 91.9 (d, J = 183.8 Hz), 86.0 (d, J = 22.7 Hz), 75.8, 70.7 (d, J = 18.9 Hz), 67.3, 60.9. Anal. Calcd for $C_{12}H_{15}FO_4S$: C, 52.54; H, 5.51. Found: C, 52.25; H, 5.45.

Phenyl 4,6-*O*-Benzylidene-2-deoxy-2-fluoro-1-thio-α-D-mannopyranoside (18). 17 (100 mg, 0.37 mmol), CSA (8.5 mg, 37 μmol), and benzaldehyde dimethyl acetal (66 μL, 0.44 mmol) were dissolved in DMF (2 mL) and heated to 50 °C on a rotary evaporator under water aspirator vacuum at for 5 h. DMF was then removed under vacuum, and the residue was diluted with ethyl acetate and washed with saturated $NaHCO_3$. The aqueous phase was extracted with ethyl acetate three times, and the combined organic phase was washed with water and brine, dried over Na_2SO_4, and concentrated. Chromatographic purification on silica gel (15% ethyl acetate in hexane) afforded **18** (76.7 mg, 58%) as a white solid: mp 160 °C; $[\alpha]^{22}_D$ +346.1 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.47 (m, 4H), 7.43−7.31 (m, 6H), 5.65 (d, J = 15.0 Hz, 1H), 5.60 (s, 1H), 5.11−5.01 (dt, J = 2.0, 49.5 Hz, 1H), 4.36−4.31 (dt, J = 4.5, 9.5 Hz, 1H), 4.29−4.25 (dd, J = 5.0, 10.0 Hz, 1H), 4.16−4.09 (dd, J = 10.0, 27.0 Hz, 1H), 3.99 (t, J = 9.5 Hz, 1H), 3.85 (t, J = 10.0 Hz, 1H), 2.56 (s, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 136.9, 132.7, 132.1, 129.41, 129.37, 128.4, 128.3, 126.3, 102.4, 91.2 (d, J = 186.3 Hz), 86.8 (d, J = 23.9 Hz), 78.9, 68.6 (d, J = 18.9 Hz), 68.4, 64.8. Anal. Calcd for $C_{19}H_{19}FO_4S$: C, 62.97; H, 5.28. Found: C, 62.70; H, 5.43.

Phenyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-1-thio-α-D-mannopyranoside (11). To an ice-cooled solution of **18** (306 mg, 0.85 mmol) in DMF (3 mL) was added sodium hydride (60%, 37.4 mg, 0.93 mmol) under stirring. After 10 min, benzyl bromide (121 μL, 1.0 mmol) was added and stirring continued for 6 h at room temperature. The reaction mixture was concentrated, dissolved in ethyl acetate, and washed with saturated $NaHCO_3$. The aqueous phase was extracted with ethyl acetate three times, and the combined organic phase was washed with water and brine, dried over Na_2SO_4, and concentrated. Chromatographic purification on silica gel (8% ethyl acetate in hexane) afforded **11** (320 mg, 83%) as a white solid: mp 104 °C; $[\alpha]^{22}_D$ +198.8 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57−7.53 (m, 2H), 7.49−7.30 (m, 13H), 5.67 (s, 1H), 5.66−5.63 (dd, J = 1.5, 15.0 Hz, 1H), 5.09−4.99 (dt, J = 2.0, 49.0 Hz, 1H), 4.93 (d, J = 12.0 Hz, 1H), 4.80 (d, J = 12.0 Hz, 1H), 4.38−4.33 (dt, J = 5.0, 9.5 Hz, 1H), 4.30−4.27 (dd, J = 5.0, 10.0 Hz, 1H), 4.24 (t, J = 9.5 Hz, 1H), 4.02−3.94 (ddd, J = 2.5, 10.0, 27.0 Hz, 1H), 3.90 (t, J = 10.0 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 137.7, 137.3, 132.7, 132.1, 129.4, 129.1, 128.5, 128.3, 128.2, 127.9, 126.1, 101.7, 90.0 (d, J = 187.6 Hz), 87.0 (d, J = 23.9 Hz), 78.8, 74.4 (d, J = 17.6 Hz), 73.3, 68.4, 65.3. Anal. Calcd for $C_{26}H_{25}FO_4S$: C, 69.01; H, 5.57. Found: C, 68.87; H, 5.62.

Phenyl 2,4,6-Tri-*O*-acetyl-3-deoxy-3-fluoro-1-thio-β-D-glucopyranoside (20). To a stirred solution of 3-deoxy-3-fluoro-D-glucose **19** (1.71 g, 9.4 mmol) and DMAP (106 mg, 0.9 mmol) in pyridine (10 mL) was added Ac_2O (5.3 mL, 56.3 mmol) at room temperature. After 5 h, the mixture was concentrated, dissolved in CH_2Cl_2, and washed with saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated to give the glucosyl tetraacetate. To a solution of this glucosyl tetraacetate (3.25 g, 9.3 mmol) in CH_2Cl_2 (10 mL) were added thiophenol (1.1 mL, 11.2 mmol) and $BF_3{\cdot}Et_2O$ (2.9 mL, 23.2 mmol). The solution was stirred at room temperature for 12 h, before solid Na_2CO_3 was added and stirring continued for ∼10 min. The reaction mixture was then diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated. Column chromatography on silica gel (15% ethyl acetate in hexane) provided **20**, which was recrystallized from 15% ethyl acetate in hexane to give **20** (2.50 g, 67%) as a white crystalline solid: mp 124−125 °C; $[\alpha]^{23}_D$ −15.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.48 (m, 2H), 7.32−7.29 (m, 3H), 5.16−5.06 (m, 2H), 4.63 (s, 1H), 4.63−4.49 (dt, J = 9.0, 50.0 Hz, 1H), 4.20−4.19 (m, 2H), 3.66−3.61 (m, 1H), 2.15 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 170.6, 169.2, 169.1, 133.0, 131.7, 129.0, 128.5, 92.6 (d, J = 193.9 Hz), 85.3 (d, J = 7.6 Hz), 75.2 (d, J = 6.3 Hz), 69.8 (d, J = 18.9 Hz), 68.2 (d, J = 17.6 Hz), 62.1,

20.85, 20.74, 20.67. Anal. Calcd for $C_{18}H_{21}FO_7S$: C, 53.99; H, 5.29. Found: C, 54.39; H, 5.35.

Phenyl 3-Deoxy-3-fluoro-1-thio-β-D-glucopyranoside (21). Following the general procedure for making **17**, **20** was converted to **21** (96%): white crystalline solid; mp 80−81 °C; $[\alpha]^{24}_D$ −49.6 (*c* 2.0, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 7.58−7.54 (m, 2H), 7.33−7.25 (m, 3H), 4.60 (d, *J* = 9.5 Hz, 1H), 4.34−4.20 (dt, *J* = 8.5, 52.5 Hz, 1H), 3.87 (d, *J* = 12.0 Hz, 1H), 3.71−3.67 (dd, *J* = 5.5, 12.0 Hz, 1H), 3.60−3.51 (m, 1H), 3.46−3.39 (m, 1H), 3.35−3.30 (m, 1H); ^{13}C NMR (125.9 MHz, CD_3OD) δ 133.3, 131.6, 128.5, 127.2, 98.2 (d, *J* = 185.1 Hz), 87.1 (d, *J* = 8.8 Hz), 79.6 (d, *J* = 7.6 Hz), 70.6 (d, *J* = 18.9 Hz), 68.1 (d, *J* = 18.9 Hz), 60.9. Anal. Calcd for $C_{12}H_{15}FO_4S$: C, 52.54; H, 5.51. Found: C, 52.39; H, 5.77.

Phenyl 4,6-*O*-Benzylidene-3-deoxy-3-fluoro-1-thio-β-D-glucopyranoside (22). Following the general procedure for making **18**, **21** was converted to **22** (87%): white solid; mp 106−108 °C; $[\alpha]^{22}_D$ −36.6 (*c* 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57−7.54 (m, 2H), 7.51−7.47 (m, 2H), 7.41−7.34 (m, 6H), 5.55 (s, 1H), 4.72−4.58 (dt, *J* = 9.0, 53.5 Hz, 1H), 4.63 (d, *J* = 10.0 Hz, 1H), 4.43−4.40 (ddd, *J* = 2.0, 5.0, 10.5 Hz, 1H), 3.81 (t, *J* = 10.0 Hz, 1H), 3.77−3.71 (dd, *J* = 9.5, 20.0 Hz, 1H), 3.69−3.62 (m, 1H), 3.55−3.48 (dt, *J* = 5.0, 9.5 Hz, 1H), 2.83 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 136.6, 133.4, 130.7, 129.34, 129.26, 128.8, 128.4, 126.2, 101.7, 93.3 (d, *J* = 192.6 Hz), 88.3 (d, *J* = 7.6 Hz), 78.6 (d, *J* = 17.6 Hz), 71.3 (d, *J* = 18.9 Hz), 69.8 (d, *J* = 7.6 Hz), 68.4. Anal. Calcd for $C_{19}H_{19}FO_4S$: C, 62.97; H, 5.28. Found: C, 62.87; H, 5.18.

Phenyl 4,6-*O*-Benzylidene-3-deoxy-3-fluoro-1-thio-β-D-mannopyranoside (23). To a stirred solution of **22** (200 mg, 0.55 mmol) in CH_2Cl_2 (2 mL) was added Dess Martin periodinane (281 mg, 0.66 mmol), and the resulting solution was stirred for 2 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 and washed with saturated $Na_2S_2O_3$ and brine. The organic layer was separated, dried over Na_2SO_4, and concentrated. The residue was then dissolved in 2.0 mL of THF, and L-selectride (1.1 mL, 1.0 M in THF) was added to the stirred mixture at −78 °C. The resulting solution was stirred at −78 °C for 20 min before it was quenched with H_2O and was allowed to reach room temperature. The reaction mixture was diluted with CH_2Cl_2 and washed with saturated $NaHCO_3$ and brine. The organic layer was separated, dried over Na_2SO_4, and concentrated to give the **23** (170 mg, 85%) as a white solid: mp 121−122 °C; $[\alpha]^{22}_D$ −69.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.51 (m, 2H), 7.50−7.47 (m, 2H), 7.39−7.30 (m, 6H), 5.61 (s, 1H), 4.92 (s, 1H), 4.76−4.64 (ddd, *J* = 3.5, 9.5, 50.0 Hz, 1H), 4.51 (s, 1H), 4.39−4.35 (ddd, *J* = 2.5, 5.0, 10.5 Hz, 1H), 4.32−4.26 (dd, *J* = 10.0, 20.0 Hz, 1H), 3.95 (t, *J* = 10.5 Hz, 1H), 3.48−3.43 (ddt, *J* = 1.5, 5.0, 10.0 Hz, 1H), 2.62 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 136.8, 133.6, 131.8, 129.3, 129.2, 128.4, 128.1, 126.2, 101.9, 90.5 (d, *J* = 190.1 Hz), 87.4 (d, *J* = 5.0 Hz), 76.2 (d, *J* = 17.6 Hz), 71.2 (d, *J* = 16.4 Hz), 70.5 (d, *J* = 7.6 Hz), 68.3. Anal. Calcd for $C_{19}H_{19}FO_4S$: C, 62.97; H, 5.28. Found: C, 62.91; H, 5.27.

Phenyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-1-thio-β-D-glucopyranoside (12). Following the general procedure for making **11**, **22** was converted to **12** (82%): white crystalline solid; mp 127−128 °C; $[\alpha]^{24}_D$ −28.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56−7.53 (m, 2H), 7.52−7.49 (m, 2H), 7.48−7.45 (m, 2H), 7.41−7.32 (m, 9H), 5.57 (s, 1H), 4.87−4.81 (m, 2H), 4.86−4.72 (dt, *J* = 9.0, 52.5 Hz, 1H), 4.75 (d, *J* = 10.0 Hz, 1H), 4.43−4.39 (ddd, *J* = 1.5, 5.0, 10.5 Hz, 1H), 3.84−3.74 (m, 2H), 3.64−3.57 (m, 1H), 3.48−3.44 (ddt, *J* = 1.5, 5.0, 10.0 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 137.5, 136.7, 132.7, 132.5, 129.3, 129.1 128.5, 128.4, 128.3, 128.2, 128.1, 126.2, 101.6, 94.8 (d, *J* = 190.1 Hz), 87.5 (d, *J* = 8.8 Hz), 79.1 (d, *J* = 18.9 Hz), 78.7 (d, *J* = 17.6 Hz), 75.3, 69.3 (d, *J* = 7.6 Hz), 68.5. Anal. Calcd for $C_{26}H_{25}FO_4S$: C, 69.01; H, 5.57. Found: C, 68.90; H, 5.47.

Phenyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-1-thio-β-D-mannopyranoside (13). Following the general procedure for making **11**, **23** was converted to **13** (82%): white solid; mp 156−157 °C; $[\alpha]^{22}_D$ −50.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.47 (m, 6H), 7.41−7.29 (m, 9H), 5.62 (s, 1H), 5.02 (d, *J* = 11.0 Hz, 1H), 4.89 (s, 1H), 4.81 (d, *J* = 11.0 Hz, 1H), 4.84−4.71 (ddd, *J* = 3.5, 10.0, 50.0 Hz, 1H), 4.39−4.32 (m, 3H), 3.96 (t, *J* = 10.0 Hz, 1H), 3.46−3.42 (ddt, *J* = 1.5, 5.0, 10.0 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 137.3, 137.0, 134.4, 131.5, 129.2, 129.1 128.7, 128.4, 128.1, 127.8, 126.2, 101.8, 91.8 (d, *J* = 195.1 Hz), 88.4 (d, *J* = 7.6 Hz), 78.3 (d, *J* = 15.1 Hz), 76.5 (d, *J* = 17.6 Hz), 76.1 (d, *J* = 3.8 Hz), 70.6 (d, *J* = 7.6 Hz), 68.3. Anal. Calcd for $C_{26}H_{25}FO_4S$: C, 69.01; H, 5.57. Found: C, 68.71; H, 5.44.

General Procedure for Glycosylation Using the BSP/TTBP/Tf_2O System. To a stirred solution of donor (1 equiv), BSP (1.2 equiv), TTBP (1.5 equiv), and 4 Å molecular sieves in CH_2Cl_2 (0.05 M in substrate) at −60 °C under an argon atmosphere was added Tf_2O (1.2 equiv). After 30 min of stirring at −60 °C, a solution of the glycosyl acceptor (1.5 equiv) in CH_2Cl_2 (0.02 M in acceptor) was slowly added. The reaction mixture was stirred for a further 2 h at −60 °C, then was allowed to reach room temperature. The reaction mixture was diluted with CH_2Cl_2, and the molecular sieves were filtered off and washed with saturated $NaHCO_3$ and brine. The organic layer was separated, dried over Na_2SO_4, and concentrated. Purification by column chromatography on silica gel, eluting with hexane/ethyl acetate mixtures, afforded the corresponding coupled products.

Methyl 4-*O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-α-D-glucopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (31α) and Methyl 4-*O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-glucopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (31β). Prepared by the general procedure, with a combined yield of 77.8 mg (88%, 1:2.5 α/β). **31α:** colorless oil; $[\alpha]^{22}_D$ +65.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.51 (m, 2H), 7.42−7.37 (m, 5H), 7.34−7.27 (m, 3H), 5.57 (s, 1H), 5.13 (d, *J* = 4.0 Hz, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.87 (s, 1H), 4.83 (d, *J* = 12.0 Hz, 1H), 4.58−4.46 (ddd, *J* = 4.0, 9.0, 48.5 Hz, 1H), 4.32−4.29 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.16−4.08 (m, 4H), 3.76−3.71 (m, 1H), 3.72 (t, *J* = 10.0 Hz, 1H), 3.62 (t, *J* = 9.5 Hz, 1H), 3.37 (s, 3H), 3.37−3.34 (m, 1H), 1.52 (s, 3H), 1.34 (s, 3H), 1.32 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.3, 137.3, 129.0, 128.4, 128.3, 127.9, 127.7, 126.1, 109.2, 101.4, 97.9, 97.8 (d, *J* = 24.6 Hz, $^1J_{CH}$ = 169.9 Hz), 90.6 (d, *J* = 192.6 Hz), 81.9, 81.1 (d, *J* = 8.8 Hz), 76.7, 76.6, 76.1, 74.7, 68.9, 64.7, 62.4, 54.8, 28.2, 26.4, 17.1; ESI-HRMS calcd for $C_{30}H_{37}FO_9Na$ [M + Na]$^+$, 583.2320; found, 583.2332. **31β:** colorless oil; $[\alpha]^{24}_D$ −48.6 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.48 (m, 2H), 7.41−7.38 (m, 5H), 7.34−7.26 (m, 3H), 5.57 (s, 1H), 5.16−5.14 (dd, *J* = 3.0, 7.5 Hz, 1H), 4.90−4.84 (m, 3H), 4.36−4.23 (dt, *J* = 9.0, 48.5 Hz, 1H), 4.35−4.31 (m, 1H), 4.27−4.25 (m, 1H), 4.11 (d, *J* = 5.5 Hz, 1H), 3.91−3.85 (dt, *J* = 9.0, 15.0 Hz, 1H), 3.79 (t, *J* = 10.5 Hz, 1H), 3.71−3.64 (m, 3H), 3.46−3.41 (dt, *J* = 5.0, 9.5 Hz, 1H), 3.38 (s, 3H), 1.52 (s, 3H), 1.36 (s, 3H), 1.29 (d, *J* = 5.5 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.0, 137.1, 129.1, 128.4, 128.3, 128.0, 127.8, 126.1, 109.4, 101.4, 98.8 (d, *J* = 24.6 Hz, $^1J_{CH}$ = 164.9 Hz), 97.9, 93.1 (d, *J* = 187.6 Hz), 80.6 (d, *J* = 8.8 Hz), 78.9 (d, *J* = 18.9 Hz), 78.3, 78.0, 76.0, 74.3, 68.7, 66.2, 63.7, 54.9, 27.9, 26.4, 17.6; ESI-HRMS calcd for $C_{30}H_{37}FO_9Na$ [M + Na]$^+$, 583.2320; found, 583.2339.

(1-Adamantanyl) 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-α-D-glucopyranoside (32α) and (1-Adamantanyl) 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-glucopyranoside (32β). Prepared by the general procedure with a combined yield of 65.4 mg (76%, 1:5.8 α/β). Donor **10** (3.9 mg, 5%) was recovered from this reaction. **32α:** colorless oil; $[\alpha]^{19}_D$ +49.0 (*c* 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.49 (m, 2H), 7.41−7.26 (m, 8H), 5.56 (s, 1H), 5.40 (d, *J* = 4.0 Hz, 1H), 4.87 (d, *J* = 11.0 Hz, 1H), 4.82 (d, *J* = 11.5 Hz, 1H), 4.51−4.38 (ddd, *J* = 4.0, 9.5, 49.5 Hz, 1H), 4.28−4.25 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.17−4.06 (m, 2H), 3.70 (t, *J* = 10.5 Hz, 1H), 3.59 (t, *J* = 10.0

Hz, 1H), 2.17 (s, 3H), 1.86 (d, J = 12.0 Hz, 3H), 1.80 (d, J = 12.5 Hz, 3H), 1.66 (d, J = 14.0 Hz, 3H), 1.61 (d, J = 13.5 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.5, 137.3, 129.0, 128.32, 128.25, 127.8, 127.6, 126.0, 101.3, 90.12 (d, J = 20.0 Hz), 90.06 (d, J = 193.1 Hz), 81.5 (d, J = 9.7 Hz), 78.1, 75.3, 74.7, 69.1, 62.1, 42.4, 36.2, 30.6; ESI-HRMS calcd for $C_{30}H_{36}FO_5$ $[M + H]^+$, 495.2541; found, 495.2541. **32β:** white crystalline solid; mp 146 °C; $[\alpha]^{17}_D$ −11.3 (*c* 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.48 (m, 2H), 7.42−7.26 (m, 8H), 5.55 (s, 1H), 4.88−4.83 (m, 3H), 4.38−4.25 (dt, J = 8.0, 49.5 Hz, 1H), 4.32−4.29 (dd, J = 5.0, 10.5 Hz, 1H), 3.87−3.80 (dt, J = 9.0, 15.0 Hz, 1H), 3.79 (t, J = 10.0 Hz, 1H), 3.67 (d, J = 9.5 Hz, 1H), 3.45−3.41 (dt, J = 5.0, 10.0 Hz, 1H), 2.18 (s, 3H), 1.87 (d, J = 11.0 Hz, 3H), 1.78 (d, J = 11.5 Hz, 3H), 1.66 (d, J = 12.5 Hz, 3H), 1.62 (d, J = 12.0 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.1, 137.2, 129.0, 128.33, 128.27, 128.0, 127.7, 126.1, 101.3, 94.1 (d, J = 23.9 Hz, $^1J_{CH}$ = 158.6 Hz), 93.0 (d, J = 187.6 Hz), 80.4 (d, J = 10.1 Hz), 79.2 (d, J = 18.9 Hz), 75.9, 74.3, 68.8, 66.1, 42.4, 36.2, 30.7; ESI-HRMS calcd for $C_{30}H_{35}FO_5Na$ $[M + Na]^+$, 517.2361; found, 517.2355.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-α-D-glucopyranosyl)-α-D-glucopyranoside (33α) and Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-glucopyranosyl)-α-D-glucopyranoside (33β). Prepared by the general procedure with a combined yield of 67.5 mg (68%, 1:4.6 α/β). Donor **10** (4.5 mg, 8%) was recovered from this reaction. **33α:** colorless oil; $[\alpha]^{21}_D$ +40.0 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.47 (m, 2H), 7.41−7.21 (m, 23H), 5.74 (d, J = 4.5 Hz, 1H), 5.52 (s, 1H), 5.01 (d, J = 10.5 Hz, 1H), 4.88 (d, J = 11.5 Hz, 1H), 4.82 (d, J = 12.0 Hz, 1H), 4.78 (d, J = 6.0 Hz, 1H), 4.76 (d, J = 3.5 Hz, 1H), 4.65−4.54 (m, 4H), 4.51−4.39 (ddd, J = 4.0, 9.0, 48.5 Hz, 1H), 4.08−4.02 (m, 3H), 3.93 (t, J = 9.0 Hz, 1H), 3.83−3.77 (m, 3H), 3.69 (d, J = 9.0 Hz, 1H), 3.62−3.55 (m, 3H), 3.40 (s, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.6, 138.3, 138.03, 138.00, 137.2, 129.0, 128.5, 128.43, 128.38, 128.3, 128.24, 128.18, 128.0, 127.9, 127.7, 127.6, 127.5,-127.4, 126.1, 101.3, 97.9, 97.4 (d, J = 20.0 Hz, $^1J_{CH}$ = 175.4 Hz), 90.0 (d, J = 191.3 Hz), 81.7, 81.0 (d, J = 8.6 Hz), 80.3, 76.6, 76.5, 75.3, 75.1, 74.7, 73.5 (d, J = 23.7 Hz), 69.4, 69.1, 68.7, 63.1, 54.7; ESI-HRMS calcd for $C_{48}H_{52}FO_{10}$ $[M + H]^+$, 807.3539; found, 807.3531. **33β:** colorless oil; $[\alpha]^{21}_D$ +8.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.47 (m, 2H), 7.44−7.21 (m, 23H), 5.47 (s, 1H), 4.87−4.78 (m, 5H), 4.68 (d, J = 12.0 Hz, 1H), 4.63 (d, J = 12.5 Hz, 1H), 4.61 (d, J = 4.0 Hz, 1H), 4.50−4.48 (dd, J = 3.5, 7.5 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.28−4.15 (dt, J = 8.0, 49.5 Hz, 1H), 4.03−4.00 (dd, J = 5.0, 10.5 Hz, 1H), 3.94−3.86 (m, 3H), 3.76 (d, J = 9.5 Hz, 1H), 3.66 (d, J = 10.5 Hz, 1H), 3.61−3.51 (m, 3H), 3.44 (t, J = 10.5 Hz, 1H), 3.39 (s, 3H), 3.07−3.02 (dt, J = 5.0, 9.5 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 139.2, 138.2, 138.1, 137.9, 137.2, 129.1, 128.6, 128.44, 128.38, 128.3, 128.20, 128.16, 128.0, 127.9, 127.8, 127.4, 126.1, 101.3, 101.2 (d, J = 22.7 Hz, $^1J_{CH}$ = 159.2 Hz), 98.3, 93.5 (d, J = 187.6 Hz), 80.5 (d, J = 10.1 Hz), 80.2, 79.2, 78.6 (d, J = 18.9 Hz), 77.9, 75.4, 74.2, 73.6 (d, J = 10.1 Hz), 69.6, 68.5, 67.7, 65.6, 55.3; ESI-HRMS calcd for $C_{48}H_{52}FO_{10}$ $[M + H]^+$, 807.3539; found, 807.3546.

Methyl 4-*O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-α-D-mannopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (34α) and Methyl 4-*O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-mannopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (34β). Prepared by the general procedure with a combined yield of 45.8 mg (73%, 1:3.7 α/β). **34α:** colorless oil; $[\alpha]^{20}_D$ +59.5 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.51 (m, 2H), 7.40−7.26 (m, 8H), 5.64 (s, 1H), 5.04 (d, J = 8.0 Hz, 1H), 4.89 (d, J = 12.0 Hz, 1H), 4.85 (s, 1H), 4.76 (d, J = 12.0 Hz, 1H), 4.73 (d, J = 49.0 Hz, 1H), 4.30−4.27 (dd, J = 4.5, 10.0 Hz, 1H), 4.14−4.05 (m, 4H), 3.96−3.89 (dd, J = 9.5, 28.0 Hz, 1H), 3.83 (t, J = 10.0 Hz, 1H), 3.66−3.60 (m, 1H), 3.39−3.35 (m, 1H), 3.37 (s, 3H), 1.52 (s, 3H), 1.33 (s, 3H), 1.24 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.1, 137.5, 129.0, 128.4, 128.3, 127.8, 126.1, 109.3, 101.6, 98.9 (d, J = 15.1 Hz, $^1J_{CH}$ = 168.7 Hz), 98.0, 88.3 (d, J = 178.8 Hz), 81.1, 78.7, 76.6, 76.0, 74.2 (d, J = 16.4 Hz), 73.2, 68.7, 64.4, 63.9, 54.9, 28.1, 26.4, 17.4; ESI-HRMS calcd for $C_{30}H_{38}FO_9$ $[M + H]^+$, 561.2494; found, 561.2494. **34β:** colorless oil; $[\alpha]^{20}_D$ −30.4 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.49 (m, 2H), 7.41−7.27 (m, 8H), 5.62 (s, 1H), 5.02 (d, J = 19.0 Hz, 1H), 4.87−4.77 (dd, J = 2.5, 50.0 Hz, 1H), 4.86 (s, 1H), 4.85 (d, J = 12.5 Hz, 1H), 4.79 (d, J = 12.5 Hz, 1H), 4.32−4.29 (dd, J = 5.0, 10.5 Hz, 1H), 4.19 (t, J = 6.5 Hz, 1H), 4.12−4.08 (m, 2H), 3.92 (t, J = 10.5 Hz, 1H), 3.73−3.66 (ddd, J = 2.5, 10.0, 27.5 Hz, 1H), 3.68−3.63 (m, 2H), 3.38−3.33 (m, 1H), 3.37 (s, 3H), 1.50 (s, 3H), 1.33 (s, 3H), 1.30 (d, J = 6.0 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 137.4, 137.3, 129.0, 128.5, 128.3, 127.9, 127.8, 126.0, 109.4, 101.6, 97.8, 97.7 (d, J = 15.1 Hz, $^1J_{CH}$ = 157.4 Hz), 88.4 (d, J = 190.1 Hz), 78.4 (d, J = 25.2 Hz), 78.3, 76.2, 75.8 (d, J = 16.4 Hz), 72.4, 68.5, 67.2, 63.9, 54.8, 27.8, 26.4, 17.4; ESI-HRMS calcd for $C_{30}H_{38}FO_9$ $[M + H]^+$, 561.2494; found, 561.2494.

(1-Adamantanyl) 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-α-D-mannopyranoside (35α) and (1-Adamantanyl) 3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-mannopyranoside (35β). Prepared by the general procedure with a combined yield of 67.8 mg (82%, 1:1.3 α/β). Donor **11** (5.3 mg, 7%) was recovered from this reaction. **35α:** colorless oil; $[\alpha]^{20}_D$ +55.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.49 (m, 2H), 7.40−7.26 (m, 8H), 5.64 (s, 1H), 5.36−5.34 (dd, J = 2.0, 8.0 Hz, 1H), 4.89 (d, J = 12.0 Hz, 1H), 4.76 (d, J = 12.0 Hz, 1H), 4.67−4.56 (dt, J = 2.0, 49.5 Hz, 1H), 4.26−4.23 (dd, J = 4.5, 10.0 Hz, 1H), 4.12−3.97 (m, 3H), 3.81 (t, J = 10.0 Hz, 1H), 2.15 (s, 3H), 1.81 (d, J = 11.0 Hz, 3H), 1.76 (d, J = 10.5 Hz, 3H), 1.65 (d, J = 12.5 Hz, 3H), 1.59 (d, J = 12.0 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.3, 137.5, 128.9, 128.4, 128.2, 127.8, 127.7, 126.1, 101.5, 91.8 (d, J = 30.2 Hz, $^1J_{CH}$ = 169.6 Hz), 89.9 (d, J = 178.8 Hz), 79.1, 75.5, 74.5 (d, J = 16.4 Hz), 73.1, 68.8, 63.6, 42.3, 36.1, 30.6; ESI-HRMS calcd for $C_{30}H_{35}FO_5Na$ $[M + Na]^+$, 517.2361; found, 517.2362. **35β:** white crystalline solid; mp 86−87 °C; $[\alpha]^{17}_D$ +4.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51−7.49 (m, 2H), 7.41−7.26 (m, 8H), 5.61 (s, 1H), 4.86−4.78 (m, 3H), 4.72−4.62 (dd, J = 2.0, 50.0 Hz, 1H), 4.31−4.28 (dd, J = 5.0, 10.5 Hz, 1H), 4.10 (t, J = 10.0 Hz, 1H), 3.90 (d, J = 10.5 Hz, 1H), 3.72−3.63 (ddd, J = 2.5, 10.0, 26.5 Hz, 1H), 3.40−3.35 (dt, J = 5.0, 10.0 Hz, 1H), 2.18 (s, 3H), 1.88 (d, J = 11.5 Hz, 3H), 1.78 (d, J = 11.5 Hz, 3H), 1.66 (d, J = 12.5 Hz, 3H), 1.62 (d, J = 12.5 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 137.9, 137.4, 129.0, 128.5, 128.3, 127.8, 126.1, 101.6, 92.7 (d, J = 16.4 Hz, $^1J_{CH}$ = 153.6 Hz), 90.3 (d, J = 188.8 Hz), 78.3, 76.2 (d, J = 16.4 Hz), 76.0, 72.4, 68.7, 66.9, 42.3, 36.1, 30.7. Anal. Calcd for $C_{30}H_{35}FO_5$: C, 72.85; H, 7.13. Found: C, 73.11; H, 7.27.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-α-D-mannopyranosyl)-α-D-glucopyranoside (36α) and Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-fluoro-β-D-mannopyranosyl)-α-D-glucopyranoside (36β). Prepared by the general procedure with a combined yield of 67.5 mg (64%, 1:3.1 α/β). Donor **11** (6.0 mg, 12%) was recovered from this reaction. **36α:** colorless oil; $[\alpha]^{16}_D$ +33.3 (*c* 0.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.47 (m, 2H), 7.38−7.24 (m, 23H), 5.59 (s, 1H), 5.44−5.42 (dd, J = 1.5, 8.0 Hz, 1H), 5.00 (d, J = 11.0 Hz, 1H), 4.78 (d, J = 12.0 Hz, 1H), 4.73 (d, J = 12.0 Hz, 1H), 4.66−4.50 (m, 7H), 4.10−4.05 (m, 2H), 3.88−3.67 (m, 8H), 3.55−3.52 (dt, J = 3.5, 10.0 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.0, 137.9, 137.8, 137.4, 128.9, 128.6, 128.5, 128.39, 128.36, 128.20, 128.16, 128.1, 127.8, 127.7, 127.6, 127.0, 126.1, 101.6, 100.0 (d, J = 31.6 Hz, $^1J_{CH}$ = 173.3 Hz), 97.8, 88.4 (d, J = 180.3 Hz), 81.2, 80.2, 78.5, 77.6, 75.5, 74.0 (d, J = 16.0 Hz), 73.7, 73.2, 73.0, 69.4, 68.9, 68.5, 64.8, 55.4; ESI-HRMS calcd for $C_{48}H_{51}FO_{10}Na$ $[M + Na]^+$, 829.3364; found, 829.3387. **36β:** colorless oil; $[\alpha]^{21}_D$ +2.1 (*c* 0.15, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49−7.47 (m, 2H), 7.42−7.21 (m, 23H), 5.53 (s, 1H), 4.91 (d, J = 10.5 Hz, 1H), 4.88 (d, J = 11.5 Hz, 1H), 4.80 (d, J = 12.5 Hz, 1H), 4.72−4.54 (m, 7H), 4.41 (d, J = 12.0

Hz, 1H), 4.09−4.06 (dd, J = 5.0, 10.0 Hz, 1H), 3.98 (t, J = 9.5 Hz, 2H), 3.90 (t, J = 9.5 Hz, 1H), 3.77 (d, J = 9.0 Hz, 2H), 3.65−3.58 (m, 2H), 3.54−3.51 (dd, J = 4.0, 9.5 Hz, 1H), 3.40−3.33 (ddd, J = 2.0, 10.0, 26.0 Hz, 1H), 3.38 (s, 3H), 3.07−3.03 (dt, J = 5.0, 9.5 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 139.2, 138.2, 138.1, 137.9, 137.2, 129.1, 128.6, 128.44, 128.38, 128.3, 128.20, 128.16, 128.0, 127.9, 127.8, 127.4, 126.1, 101.3, 101.2 (d, J = 22.7 Hz, $^1J_{CH}$ = 159.2 Hz), 98.3, 93.5 (d, J = 187.6 Hz), 80.5 (d, J = 10.1 Hz), 80.2, 79.2, 78.6 (d, J = 18.9 Hz), 77.9, 75.4, 74.2, 73.6 (d, J = 10.1 Hz), 69.6, 68.5, 67.7, 65.6, 55.3; ESI-HRMS calcd for $C_{48}H_{51}FO_{10}Na$ [M + Na]$^+$, 829.3364; found, 829.3355.

Methyl 4-*O*-(2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-α-D-glucopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (37α) and Methyl 4-*O*-(2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-β-D-glucopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (37β). Prepared by the general procedure with a combined yield of 58.6 mg (93%, 1:1.8 α/β). **37α:** colorless oil; $[\alpha]^{24}_D$ +21.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.52 (m, 2H), 7.40−7.26 (m, 8H), 5.54 (s, 1H), 5.03−4.89 (dt, J = 8.5, 52.5 Hz, 1H), 4.95−4.85 (m, 3H), 4.70 (d, J = 12.0 Hz, 1H), 4.32−4.28 (ddd, J = 2.0, 5.0, 10.0 Hz, 1H), 4.16−4.10 (m, 3H), 3.76−3.64 (m, 4H), 3.35 (s, 3H), 3.32−3.28 (dd, J = 7.5, 10.0 Hz, 1H), 1.49 (s, 3H), 1.34 (d, J = 6.5 Hz, 3H), 1.33 (s, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 137.5, 136.9, 129.2, 128.5, 128.3, 128.2, 128.1, 126.3, 109.2, 101.7, 99.4 (d, J = 11.3 Hz, $^1J_{CH}$ = 173.7 Hz), 97.8, 91.7 (d, J = 186.3 Hz), 81.9, 79.7 (d, J = 16.4 Hz), 77.6 (d, J = 16.4 Hz), 76.0, 74.1, 68.9, 64.6, 61.8 (d, J = 6.3 Hz), 54,7, 28.2, 26.4, 17.2; EI-HRMS calcd for $C_{30}H_{37}FO_9$ [M]$^+$, 560.2422; found, 560.2428. **37β:** colorless oil; $[\alpha]^{24}_D$ −41.7 (*c* 0.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.49 (m, 2H), 7.41−7.29 (m, 8H), 5.54 (s, 1H), 5.07 (d, J = 7.5 Hz, 1H), 4.87 (s, 1H), 4.86 (d, J = 11.5 Hz, 1H), 4.78 (d, J = 11.5 Hz, 1H), 4.77−4.64 (dt, J = 8.5, 52.5 Hz, 1H), 4.35−4.32 (ddd, J = 2.0, 5.0, 10.0 Hz, 1H), 4.21 (t, J = 6.0 Hz, 1H), 4.10 (d, J = 5.5 Hz, 1H), 3.82−3.72 (m, 2H), 3.67−3.63 (m, 2H), 3.52−3.46 (dt, J = 8.0, 15.0 Hz, 1H), 3.42−3.39 (m, 4H), 1.51 (s, 3H), 1.35 (s, 3H), 1.29 (d, J = 5.5 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.1, 136.8, 129.3, 128.34, 128.31, 128.0, 127.7, 126.2, 109.4, 101.6, 100.9 (d, J = 10.1 Hz, $^1J_{CH}$ = 163.6 Hz), 98.0, 92.9 (d, J = 188.8 Hz), 80.4 (d, J = 7.6 Hz), 79.2 (d, J = 17.6 Hz), 78.4, 77.9, 76.0, 74.6, 68.7, 64.8 (d, J = 16.4 Hz), 63.9, 55.0, 27.9, 26.3, 17.6; EI-HRMS calcd for $C_{30}H_{37}FO_9$ [M]$^+$, 560.2422; found, 560.2425.

(1-Adamantanyl) 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-β-D-glucopyranoside (38β) and the α-Anomer. Prepared by the general procedure with a combined yield of 51.5 mg (83%, 1:2.2 α/β). **38β:** colorless oil; $[\alpha]^{15}_D$ +0.8 (*c* 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.48 (m, 2H), 7.40−7.29 (m, 8H), 5.52 (s, 1H), 4.90 (d, J = 12.0 Hz, 1H), 4.81 (d, J = 7.5 Hz, 1H), 4.78 (d, J = 11.0 Hz, 1H), 4.73−4.59 (dt, J = 9.0, 53.0 Hz, 1H), 4.34−4.30 (ddd, J = 2.0, 5.0, 10.5 Hz, 1H), 3.82−3.71 (m, 2H), 3.56−3.50 (dt, J = 8.0, 15.0 Hz, 1H), 3.42−3.37 (dt, J = 5.5, 10.0 Hz, 1H), 2.18 (s, 3H), 1.90 (d, J = 10.0 Hz, 3H), 1.80 (d, J = 11.5 Hz, 3H), 1.67 (d, J = 12.5 Hz, 3H), 1.62 (d, J = 11.5 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.0, 136.9, 129.2, 128.5, 128.3, 128.1, 127.8, 126.2, 101.5, 96.1 (d, J = 11.3 Hz, $^1J_{CH}$ = 159.1 Hz), 93.0 (d, J = 188.9 Hz), 80.5 (d, J = 16.4 Hz), 79.1 (d, J = 16.4 Hz), 76.0, 74.9, 68.8, 64.6 (d, J = 8.8 Hz), 42.7, 36.2, 30.7; ESI-HRMS calcd for $C_{30}H_{36}FO_5$ [M + H]$^+$, 495.2541; found, 495.2542. A pure sample of **38α** could not be separated, and only assignable peaks from the mixture are listed. **38α:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.53 (s, 1H), 5.26 (t, J = 3.5 Hz, 1H), 5.09−4.85 (dt, J = 9.5, 54.0 Hz, 1H), 4.28−4.22 (ddd, J = 2.0, 5.0, 10.0 Hz, 1H), 4.11−4.02 (dt, J = 5.0, 10.5 Hz, 1H), 2.18 (s, 3H), 1.90 (d, J = 10.0 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 102.1, 99.5 (d, J = 19.2 Hz), 91.3 (d, J = 10.1 Hz), 91.2 (d, J = 184.5 Hz), 72.8, 68.5, 61.3 (d, J = 7.5 Hz), 42.4, 36.2, 30.6.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-α-D-glucopyranosyl)-α-D-glucopyranoside (39α) and Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-β-D-glucopyranosyl)-α-D-glucopyranoside (39β). Prepared by the general procedure with a combined yield of 75.5 mg (82%, 1:2.0 α/β). **39α:** colorless oil; $[\alpha]^{19}_D$ +30.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.48 (m, 2H), 7.38−7.20 (m, 23H), 5.77 (t, J = 3.5 Hz, 1H), 5.50 (s, 1H), 5.03 (d, J = 12.0 Hz, 1H), 4.98−4.84 (dt, J = 9.0, 50.0 Hz, 1H), 4.77 (d, J = 11.0 Hz, 1H), 4.71−4.54 (m, 7H), 4.13−4.10 (ddd, J = 2.0, 5.0, 10.5 Hz, 1H), 4.09−4.05 (m, 2H), 3.86−3.80 (m, 3H), 3.77−3.56 (m, 5H), 3.37 (s, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.9, 138.1, 137.9, 137.4, 137.0, 129.1, 128.5, 128.4, 128.35, 128.30, 128.27, 128.2, 128.1, 128.0, 128.0, 127.8, 127.5, 127.4, 127.2, 126.2, 101.6, 97.8, 97.6 (d, J = 11.3 Hz, $^1J_{CH}$ = 177.6 Hz), 91.5 (d, J = 187.4 Hz), 82.0, 80.3, 79.7 (d, J = 17.4 Hz), 76.4, 74.3, 73.5, 73.4 (d, J = 16.4 Hz), 71.9, 69.3, 68.8, 62.5 (d, J = 7.7 Hz), 55.3; ESI-HRMS calcd for $C_{48}H_{51}FO_{10}Na$ [M + Na]$^+$, 829.3364; found, 829.3342. **39β:** colorless oil; $[\alpha]^{19}_D$ +6.3 (*c* 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50−7.47 (m, 2H), 7.40−7.21 (m, 23H), 5.45 (s, 1H), 4.88 (d, J = 10.5 Hz, 1H), 4.81−4.78 (m, 3H), 4.69−4.57 (m, 4H), 4.49−4.35 (dt, J = 9.0, 53.5 Hz, 1H), 4.34 (d, J = 8.0 Hz, 1H), 4.29 (d, J = 12.0 Hz, 1H), 4.19−4.15 (ddd, J = 2.0, 5.0, 10.0 Hz, 1H), 3.91 (t, J = 10.0 Hz, 1H), 3.88−3.85 (dd, J = 3.0, 11.0 Hz, 1H), 3.82 (t, J = 9.5 Hz, 1H), 3.64−3.58 (m, 2H), 3.52−3.50 (dd, J = 3.5, 9.5 Hz, 1H), 3.48−3.37 (m, 3H), 3.40 (s, 3H), 3.05−3.00 (dt, J = 5.0, 9.5 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 139.3, 138.3, 137.9, 137.8, 136.9, 129.3, 128.5, 128.42, 128.35, 128.3, 128.2, 128.14, 128.12, 128.08, 128.0, 127.9, 127.7, 127.4, 126.3, 101.2 (d, J = 11.1 Hz, $^1J_{CH}$ = 157.3 Hz), 98.4, 93.3 (d, J = 186.6 Hz), 81.0 (d, J = 17.9 Hz), 80.1, 79.02 (d, J = 13.7 Hz), 78.96, 77.9, 75.5, 75.0, 73.6, 73.3, 69.8, 68.6, 67.6, 64.5 (d, J = 8.7 Hz), 55.4; ESI-HRMS calcd for $C_{48}H_{51}FO_{10}Na$ [M + Na]$^+$, 829.3364; found, 829.3344.

Methyl 4-*O*-(2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-α-D-mannopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (40α) and Methyl 4-*O*-(2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-β-D-mannopyranosyl)-2,3-*O*-isopropylidene-α-L-rhamnopyranoside (40β). Prepared by the general procedure with a combined yield of 54.6 mg (88%, 1.8:1 α/β). **40α:** colorless oil; $[\alpha]^{24}_D$ +45.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55−7.53 (m, 2H), 7.40−7.31 (m, 8H), 5.63 (s, 1H), 4.97−4.85 (ddd, J = 3.5, 10.0, 50.0 Hz, 1H), 4.89 (d, J = 12.5 Hz, 1H), 4.82 (s, 1H), 4.79−4.78 (dd, J = 2.0, 4.5 Hz, 1H), 4.63 (d, J = 12.5 Hz, 1H), 4.35−4.29 (q, J = 10.0 Hz, 1H), 4.29−4.25 (ddd, J = 2.5, 5.0, 10.0 Hz, 1H), 4.10−4.05 (m, 2H), 4.03−4.00 (dd, J = 5.5, 7.5 Hz, 1H), 3.95−3.93 (m, 1H), 3.87 (t, J = 10.0 Hz, 1H), 3.55−3.52 (dd, J = 6.0, 10.0 Hz, 1H), 3.34 (s, 3H), 3.27−3.24 (dd, J = 7.5, 10.0 Hz, 1H), 1.50 (s, 3H), 1.33 (s, 3H), 0.97 (d, J = 6.0 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 137.5, 137.2, 129.1, 128.6, 128.34, 128.31, 128.2, 126.3, 109.2, 101.8, 100.8 (d, J = 7.6 Hz, $^1J_{CH}$ = 171.2 Hz), 97.9, 89.1 (d, J = 191.3 Hz), 80.8, 77.2, 76.6, 76.0, 75.4 (d, J = 15.1 Hz), 74.1, 68.7, 64.5, 63.3 (d, J = 7.6 Hz), 54.9, 28.1, 26.4, 17.0; ESI-HRMS calcd for $C_{30}H_{37}FO_9Na$ [M + Na]$^+$, 583.2320; found, 583.2300. **40β:** colorless oil; $[\alpha]^{24}_D$ −1.6 (*c* 0.01, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52−7.49 (m, 2H), 7.42−7.28 (m, 8H), 5.59 (s, 1H), 5.05 (s, 1H), 4.87 (s, 1H), 4.87−4.78 (dd, J = 11.5, 33.0 Hz, 2H), 4.74−4.62 (ddd, J = 3.0, 10.0, 50.0 Hz, 1H), 4.32−4.24 (m, 2H), 4.10−4.08 (m, 3H), 3.96 (t, J = 10.0 Hz, 1H), 3.67−3.63 (m, 2H), 3.40 (s, 3H), 3.33−3.30 (m, 1H), 1.51 (s, 3H), 1.34 (s, 3H), 1.33 (d, J = 4.0 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.2, 137.0, 129.2, 128.3, 128.2, 128.1, 127.7, 126.2, 109.4, 101.7, 99.2 (d, J = 10.2 Hz) 97.9, 90.2 (d, J = 192.4 Hz), 78.3 (d, J = 5.0 Hz), 76.9 (d, J = 5.0 Hz), 76.1, 76.0, 75.3, 68.5, 64.5, 66.3 (d, J = 8.6 Hz), 64.0, 55.0, 27.9, 26.4, 17.6; ESI-HRMS calcd for $C_{30}H_{37}FO_9Na$ [M + Na]$^+$, 583.2320; found, 583.2298.

(1-Adamantanyl) 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-α-D-mannopyranoside (41α) and (1-Adamantanyl) 2-*O*-Benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-β-D-mannopyranoside (41β). Prepared by the general procedure with a combined yield of 48.4 mg (85%, 4.2:1 α/β). **41α:** colorless oil; $[\alpha]^{22}_D$ +55.7

(*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.54−7.52 (m, 2H), 7.41−7.23 (m, 8H), 5.63 (s, 1H), 5.17−5.16 (dd, J = 2.0, 4.0 Hz, 1H), 5.06−4.93 (ddd, J = 3.5, 9.5, 50.5 Hz, 1H), 4.87 (d, J = 12.0 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.31−4.26 (q, J = 9.5 Hz, 1H), 4.25−4.21 (ddd, J = 2.5, 5.0, 10.0 Hz, 1H), 4.02−3.97 (dt, J = 5.0, 10.0 Hz, 1H), 3.85 (t, J = 10.0 Hz, 1H), 3.83−3.81 (m, 1H), 2.12 (s, 3H), 1.71−1.66 (m, 6H), 1.62 (d, J = 12.0 Hz, 3H), 1.56 (d, J = 12.5 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 137.9, 137.3, 129.1, 128.5, 128.3, 128.1, 127.9, 126.2, 101.8, 93.2 (d, J = 7.6 Hz, $^1J_{CH}$ = 176.2 Hz), 89.4 (d, J = 190.1 Hz), 77.8 (d, J = 10.1 Hz), 77.7 (d, J = 11.3 Hz), 75.1, 73.9, 68.8, 63.1 (d, J = 7.6 Hz), 42.2, 36.2, 30.5; ESI-HRMS calcd for $C_{30}H_{35}FO_5Na$ $[M + Na]^+$, 517.2367; found, 517.2369. **41*β*:** colorless oil; $[\alpha]^{24}_D$ −5.0 (*c* 0.02, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.50−7.46 (m, 4H), 7.36−7.26 (m, 6H), 5.58 (s, 1H), 4.95 (d, J = 12.0 Hz, 1H), 4.88 (d, J = 12.5 Hz, 1H), 4.80 (s, 1H), 4.70−4.57 (ddd, J = 3.5, 9.5, 50.0 Hz, 1H), 4.31−4.24 (m, 2H), 3.95−3.89 (m, 2H), 3.53−3.30 (ddt, J = 1.0, 5.0, 10.0 Hz, 1H), 2.17 (s, 3H), 1.84 (d, J = 10.0 Hz, 3H), 1.75 (d, J = 11.5 Hz, 3H), 1.66 (d, J = 12.0 Hz, 3H), 1.61 (d, J = 10.0 Hz, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.2, 137.2, 129.1, 128.5, 128.3, 128.1, 127.6, 126.2, 101.7, 93.9 (d, J = 9.9 Hz), 90.4 (d, J = 194.1 Hz), 78.3 (d, J = 22.7 Hz), 77.7, 75.5, 75.0, 68.6, 65.9 (d, J = 6.9 Hz), 42.3, 36.2, 30.6; ESI-HRMS calcd for $C_{30}H_{35}FO_5Na$ $[M + Na]^+$, 517.2367; found, 517.2363.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-α-D-mannopyranosyl)-α-D-glucopyranoside (42α) and Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2-*O*-benzyl-4,6-*O*-benzylidene-3-deoxy-3-fluoro-*β*-D-mannopyranosyl)-α-D-glucopyranoside (42*β*). Prepared by the general procedure with a combined yield of 72.5 mg (82%, 1.6:1 α/*β*). **42α:** colorless oil; $[\alpha]^{24}_D$ +29.8 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.51−7.49 (m, 2H), 7.39−7.22 (m, 21H), 7.13−7.11 (m, 2H), 5.59 (s, 1H), 5.37−5.33 (dd, J = 2.0, 4.0 Hz, 1H), 5.16 (d, J = 11.5 Hz, 1H), 4.97−4.84 (ddd, J = 3.0, 10.0, 50.0 Hz, 1H), 4.71 (d, J = 12.5 Hz, 1H), 4.66−4.60 (m, 4H), 4.54 (d, J = 12.5 Hz, 1H), 4.39 (d, J = 11.5 Hz, 1H), 4.31−4.25 (q, J = 9.5 Hz, 1H), 4.14−4.09 (m, 2H), 3.94−3.91 (m, 2H), 3.85−3.77 (m, 3H), 3.75−3.68 (m, 3H), 3.59−3.56 (dd, J = 4.0, 10.0 Hz, 1H), 3.40 (s, 3H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.5, 137.9, 137.80, 137.78, 137.2, 129.1, 128.6, 128.5, 128.4, 128.3, 128.23, 128.21, 128.1, 127.7, 127.6, 127.1, 126.3, 101.8, 101.6 (d, J = 7.6 Hz, $^1J_{CH}$ = 173.7 Hz), 97.8, 89.0 (d, J = 191.3 Hz), 81.4, 80.1, 77.4, 77.2, 76.7, 75.2, 73.7, 73.2, 69.6, 68.9, 68.5, 64.5 (d, J = 7.6 Hz), 55.4; ESI-HRMS calcd for $C_{48}H_{51}FO_{10}Na$ $[M + Na]^+$, 829.3364; found, 829.3401. **42*β*:** colorless oil; $[\alpha]^{24}_D$ −16.4 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.49−7.39 (m, 2H), 7.38−7.26 (m, 23H), 5.48 (s, 1H), 5.03 (d, J = 10.5 Hz, 1H), 4.82−4.62 (m, 7H), 4.36 (s, 1H), 4.32 (d, J = 12.5 Hz, 1H), 4.31−4.18 (ddd, J = 3.0, 9.5, 49.5 Hz, 1H), 4.13−4.07 (m, 1H), 4.01−3.99 (dd, J = 3.5, 10.0 Hz, 1H), 3.88−3.84 (m, 2H), 3.58−3.37 (m, 6H), 3.42 (s, 3H), 3.03−2.99 (dt, J = 5.0, 9.5 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 139.5, 138.3, 138.1, 137.5, 137.1, 129.2, 128.7, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.5, 127.2, 126.3, 101.7, 101.0 (d, J = 9.8 Hz, $^1J_{CH}$ = 154.8 Hz), 98.4, 90.2 (d, J = 193.2 Hz), 80.3, 79.0, 78.4, 76.9, 76.3, 75.2 (d, J = 7.2 Hz), 73.7 (d, J = 8.2 Hz), 69.5, 68.4, 68.0, 65.9 (d, J = 8.6 Hz), 55.4; ESI-HRMS calcd for $C_{48}H_{51}FO_{10}Na$ $[M + Na]^+$, 829.3364; found, 829.3372.

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Supporting Information Available: Copies of NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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