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DAST-Mediated Regioselective Anomeric Group Migration in Saccharides

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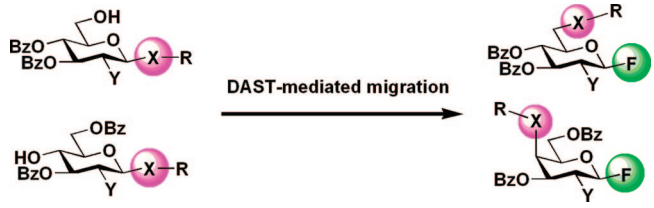

When saccharides bearing a sulfur, selenium, or oxygen substituent at the anomeric center and an unprotected hydroxyl group either at C-4 or C-6 were subjected to fluorination with DAST in dichloromethane, a regioselective migration of the anomeric substituent to the C-4 or C-6 position was observed. Certain saccharides gave a mixture of migration and normal fluorination products whereas others yielded mainly or exclusively migration products (β-glycosyl fluorides). The high thermal and chemical stability of migrated glycosyl fluorides were demonstrated to be an important precursor for many significant carbohydrate analogies. It is therefore suggested that these migrations may have useful applications in organic synthesis.

Introduction

Introduction of a fluorine atom or fluorinated group into organic molecules changes the physical, chemical, and physiological properties of the derived molecules due to the greater stability of the C−F bond and lipophilicity of the fluorinated moiety.[1] The presence of a fluorine atom in the vicinity of the anomeric position in saccharides reinforces the glycosidic bond, which enhances the therapeutic value of sugar- or nucleoside-based pharmaceuticals.[2] Furthermore, the unique specificities of the fluorine atom combined with its ability to form hydrogen bonds make fluorine an ideal substituent for hydrogen or hydroxyl groups in substrates because fluorine can enhance binding efficacy and selectivity in pharmaceuticals.[3] Apart from these desirable characteristics, a fluorine atom at the anomeric position of saccharides constitutes a very important class of glycosyl donor having potential application in the synthesis of oligosaccharides due to its increased stability during storage and increased reactivity upon activation with a variety of reagents.[4] Elemental F_2, however, is extremely reactive (even with glass) and hazardous and thus has become obsolete; it has been replaced with safe and selective agents for fluorination of organic molecules, and these agents are compatible with ordinary laboratory equipment.[5] Nucleophilic reagents, including 2,2-difluoro-1,3-dimethylimidazolidine[6] and bis(2-methoxyethyl)-aminosulfur trifluoride,[7] and a wide range of electrophilic reagents bearing R_2N-F or R_3N^+-F units such as 1-chloromethyl-4-fluorodiazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)[8] have been developed and utilized as safer alternatives to F_2.

Diethylaminosulfur trifluoride (DAST, Et_2NSF_3)[9] has long been used as a nucleophilic fluorinating agent that transforms alcohols into monofluorides. In carbohydrate chemistry, DAST

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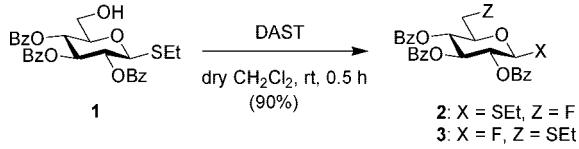
SCHEME 1. DAST-Mediated 1,6-Anomeric Thiol Group Migration



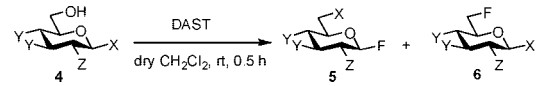
has been mainly used to prepare glycosyl fluoride donors[10a] and to replace nonanomeric hydroxyl groups by fluorines.[10b] In addition, DAST-mediated 1,2-migration of the anomeric substituent has been applied in the synthesis of oligosaccharides as demonstrated by the seminal work of Nicolaou et al.[11] Although DAST-mediated C1→C2 migrations are common in saccharides, the corresponding C1→C4 and C1→C6 migrations have been less well characterized—only a few reports described the migration of the anomeric methoxy group to the C-6 position in galactobioside[12] and lactoside.[13] To date, there have been no systematic studies on the scope of this reaction. Herein, we report a serendipitous observation of a C1→C6 migration in a monosaccharide, which prompted us to focus on DAST-mediated migration.

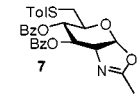
Results and Discussion

Initially, compound **1** was designed as a precursor to synthesize compound **2** by fluorination with DAST. However, thioglycoside **1** exposured to DAST (1.5 equiv) at 0 °C in dichloromethane followed by gradual warming of the reaction to room temperature over 30 min, resulting in a single compound in 90% yield that was identified as migration product **3** instead of the expected substitution product **2** (Scheme 1). The stereochemistry at C1 in **3** was expected based on mechanistic grounds, and this compound gave the anticipated ^{1}H and ^{13}C NMR and high-resolution mass spectra. The data unambiguously identified **3** as the β-glycosyl fluoride. Briefly, the anomeric proton of compound **3** exhibited a large downfield shift and split into a double−doublet with a large coupling constant (δ_H 5.65, dd, $J_{H-F} = 51.2$, 6 Hz), and the ^{13}C chemical shift of C1 was observed in the expected region as a doublet (δ_C 106.60, d, $J_{C-F} = 219$ Hz), which is typical for a β-fluoride.[14] Extensive evaluation of a variety of reaction conditions, for example increasing the DAST molar ratio to 10 equiv, lowering the reaction temperature to −30 °C, or performing the reaction at ambient temperature, suggested that compound **3** was the sole reaction product. Thus, the standard reaction conditions for C1→C6 migrations in glycosides entailed using DAST (1.5 equiv) at room temperature in dichloromethane for 0.5 h.

Accordingly, a variety of glucosides **4a**−**l** (X = STol, SBn, SePh, OMe, *O*-allyl, or N_3) were prepared by standard protection−deprotection methods[15] to achieve fluorination with DAST (Table 1). When these 6-hydroxy saccharides were subjected to the DAST reaction conditions, the corresponding C1→C6 migration glycosyl fluorides **5a**−**e** and **5g**−**k** were isolated in high yields as mainly or exclusively the β-anomer except when using **4f**. Moreover, the DAST-mediated C1→C6 migration tolerated a variety of C2 substituents (e.g., OBz, OBn, NHTroc, and NPhth). However, *O*-methyl- or *O*-allylglycosides (**4d**,**e**) gave mixtures of both migration and substitution products with poor selectivities (**5d/6d** = 5:3 and **5e/6e** = 1:1). The poor selectivity most likely resulted from the lower nucleophilicity of oxygen atom compared to sulfur atom, which benefits the reaction efficiency. Changes to the reaction conditions did not lead to the predominant formation of migration product over substitution product. For example, performing the reaction at −30 °C or in different solvents (THF and CH_3CN) yielded a mixture of both migration and substitution products. In a saccharide having an azido moiety at the anomeric center (**4f**), the azido group did not migrate even in the presence of a large excess of DAST (10 equiv), which yielded only substitution product **6f** (Table 1, entry 6). Notably, the C2 benzyl ether-protected thioglycoside **4g** gave mixtures of anomers **5g** (α/β = 2:3) in reasonable yields (Table 1, entry 7). Furthermore, this powerful migration reaction proved to be feasible for 2-deoxy-2-amino-protected sugars (Table 1, entries 8−12). Although the 2-deoxy-2-azido derivative (**4k**) delivered both migration and substitution products in 76% yield (Table 1, entry 11), 2-*N*-acetylamino-β thioglucoside **4l** produced oxazoline derivative **7** as the only isolated product in 69% yield (Table 1, entry 12) under identical reaction conditions. Thus, the results in Table 1 indicate that a sulfur, selenium, or oxygen substituent at the anomeric center can reliably affect a smooth C1→C6 migration of the anomeric group in saccharides.

TABLE 1. DAST-Mediated Regioselective C1→C6 Migrations in Saccharides



Entry	Compound	X	Y	Z	Product	Yield (%)
1	**4a**	STol	OBz	OBz	**5a**	90
2	**4b**	SBn	OBz	OBz	**5b**	76
3	**4c**	SePh	OBz	OBz	**5c**	77
4	**4d**	OMe	OBz	OBz	**5d : 6d** = 5:3[a]	80
5	**4e**	O-allyl	OBz	OBz	**5e : 6e** = 1:1[a]	71
6	**4f**	N_3	OBz	OBz	**6f**[a]	80
7	**4g**	STol	OBn	OBn	**5g** [α/β] = 2:3	84
8	**4h**	STol	OBz	PhthN	**5h : 6h** = 1 : 1	70
9	**4i**	STol	OBz	TrocHN	**5i**	62
10	**4j**	STol	OBn	PhthN	**5j**	70
11	**4k**	STol	OBz	N_3	**5k : 6k** = 3:2	76
12	**4l**	STol	OBz	NHAc	 **7**	69

[a] DAST (10 equiv), rt, CH_2Cl_2, 1 h.

Next, β-thiogalactosides **8** and **9** with a free hydroxyl at C-6 were subjected to DAST-mediated C1→C6 migration (Scheme 2). Again, smooth migration of the arylthiol from C1 to C6 was observed using a C2 benzoylated β-thiogalactoside **8** to

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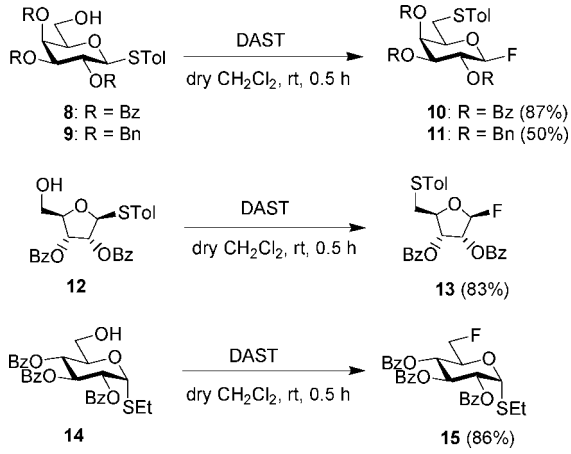
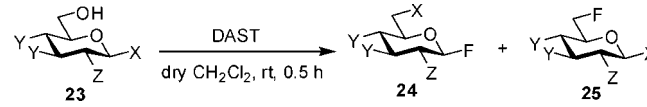
SCHEME 2. Outcomes of DAST-Mediated Reactions onto Galactosyl, Glucosyl, and Furanosyl Thioglycosides

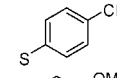
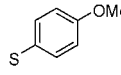
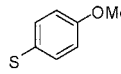


produce β-galactosyl fluoride **10** in high yield (87%). However, C2 benzyl ether-protected galactoside **9** produced a β-galactosyl fluoride, **11**, in a moderate yield (50%) in conjunction with a mixture of unidentified products, one of which presumably contained the α-anomer. Furthermore, to extend the reaction and its scope, a regioselective C1→C5 migration was performed onto furanoside **12** to produce the migration product **13** in 83% yield under similar reaction conditions. However, α-thioglucoside **14** gave only substitution product **15** in a good yield of 86%. These findings suggested a mechanism for DAST mediated C1→C6 migration because under similar reaction conditions the corresponding β-anomer **1** gave only migration product **3** (Scheme 1).

Mechanistically, we surmised that the free hydroxyl group in saccharide **4** reacted with DAST to produce an alkoxy-*N,N*-dialkylaminodifluorosulfane intermediate **16** (Scheme 3).[16] Intermediate **16** adopts the $^1C_4$ chair conformation (**17**) to facilitate the formation of thiol-bridged ring intermediate **18**. As shown in Scheme 3, through route a, subsequent neighboring group participation of the C2-*O*-acyl protecting group (OR = OBz) led to formation of a more stable cyclic benzoxonium ion **19** in which the anomeric oxygen is oriented axially.[11a] Attack by fluoride ion at the anomeric carbon on **19** led to the exclusive formation of β-glycosyl fluoride, such as **5a**. The formation of oxazoline product **7** (Table 1, entry 12) further supports the proposed neighboring group participation mechanism (route c). However, in chair conformation **22**, derived from α-thioglycoside **14**, the leaving group and thiol nucleophile are antiperilanar, which only produced substitution product **15**. Thus, formation of β-glycosyl fluorides is stereoselective, and this mechanism accounts well for the selectivities observed during C−F bond formation. Furthermore, the nature of the C2 protecting group overrides the controlling effect of stereoselective glycosyl fluoride formation. In route b of Scheme 3, the resonance of the ring oxygen lone-pair electrons allowed the formation of a cyclic alkoxycarbenium **20**, in which fluoride ion can attack at either faces of the anomeric center to give an anomeric mixture of products. For example, **4g**, without a participating group (*Z* = Bn) at C2, yielded fluorides **5g** with α/β = 2/3 (Table 1, entry 7). However, through participation of the C2 *N*-acetylamido group, the DAST-induced anomeric group migration provided a stable oxazoline derivative **7**, which was found not susceptible to be attacked by the fluoride ion (Table 1, entry 12). Notably, electron-withdrawing substituents (NPhth vs NHTroc) at C2 weakened the nucleophilicity of the anomeric S atom and inhibited the C1→C6 migration (Table 1, entries 8 vs 9). However, this effect can be overcome by changing the hydroxyl-protecting group as electron-donating group (Table 1, entries 8 vs 10).

TABLE 2. Effect of the Nature of Anomeric Groups on DAST-Mediated Regioselective C1→C6 Migration



Entry	Compound	X	Y	Z	Product	Yield (%)
1	**23a**		OBz	OBz	**24a** [a,b]	85
2	**23b**		OBz	OBz	**24b**	95
3	**23c**		OBn	OBn	 **26**	73
4	**23d**	SAc	OAc	OAc	**25d**	51

[a] Reaction performed at −30 to −20 °C; 78% yield of **24a**. [b] Yields of **25a** in THF and acetonitrile are 60% and 44%, respectively.

To gain insight into the electronic effect of the anomeric S-substituent, we synthesized saccharides **23a−d** with different electronic properties of anomeric S-substituents (Table 2). DAST-mediated reactions indicated that electron-withdrawing 4-chlorophenyl thiol **23a** produced only migration product **24a** in 85% yield (Table 2, entry 1), whereas the relatively stronger nucleophile, electron-donating 4-methoxyphenyl thiol (**23b**, Table 2, entry 2), enhanced the yield of the migration product to 95%. Additionally, the nature of the C-2 protecting group also determined the stereochemical outcome of the reaction, only producing β-anomer. Interestingly, thioglycoside **23c** bearing an electron-donating benzyl ether protecting group at C2 produced 1,6-dideoxy-1,6-epithio glycoside **26** (Table 2, entry 3), indicating the formation of proposed intermediate **18**.[17] However, the less nucleophilic *S*-acetyl protecting group in **23d** did not migrate at all, giving substitution product **25d** in a moderate 51% yield (Table 2, entry 4).

To study the solvent effect on DAST-mediated migration, saccharide **23a** (Table 2, entry 1) was subjected to standard reaction conditions except that the reaction temperature was maintained between −30 and −20 °C. As expected, migration product **24a** was only obtained in a 78% yield. However, a change of solvent from less polar (dichloromethane) to more polar (THF and acetonitrile) led to predominant formation of substitution product **25a** (see footnote b in Table 2). This may due to the better solvation nature of polar solvents, which suppresses migration by enhancing the nucleophilicity of the fluoride ion.

To explore the potential of DAST-mediated anomeric group migration at other positions in saccharides,[18] thioglycosides **27−29** were prepared and their migration efficiencies were examined (Scheme 4). Notably, the orientation of the free

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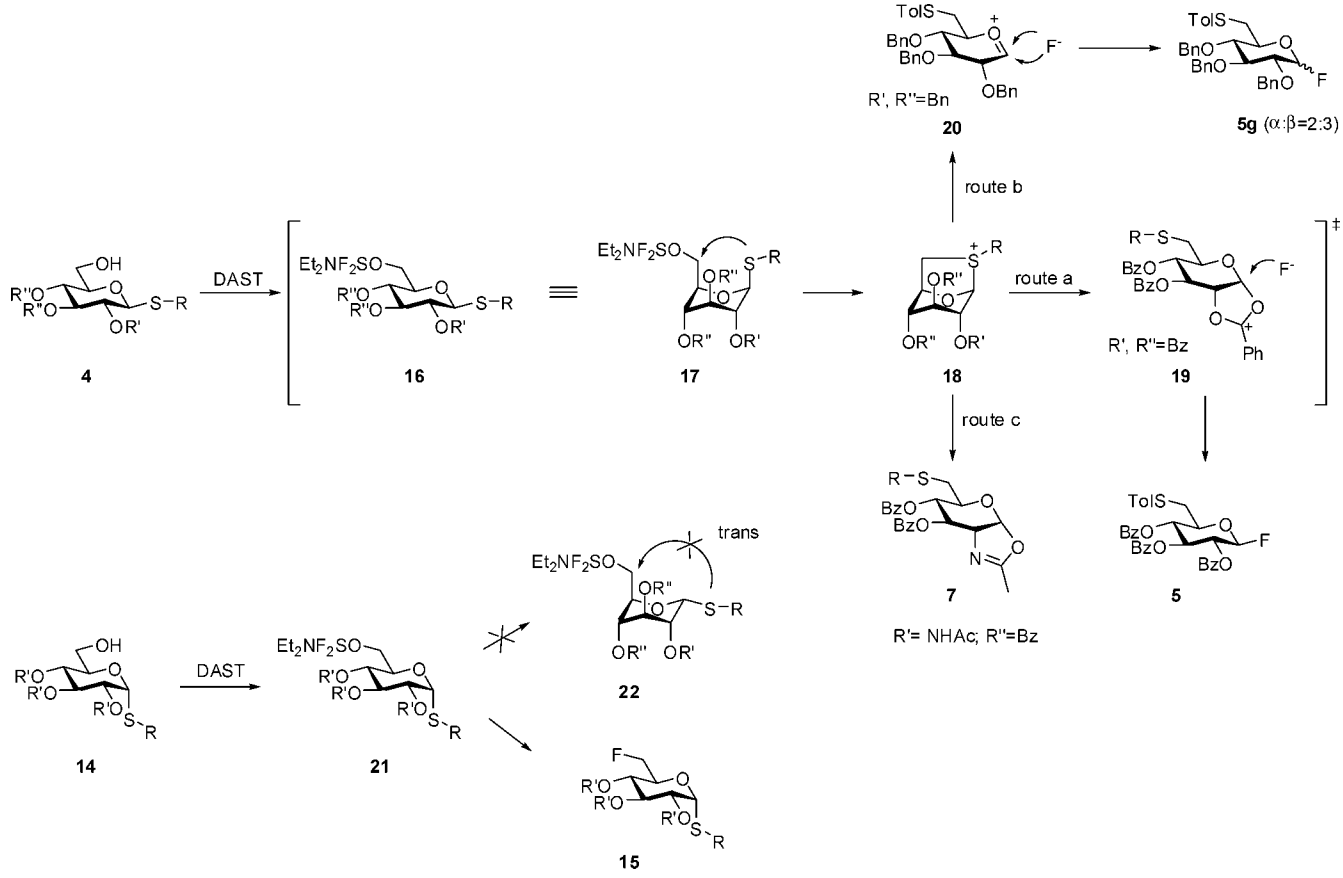
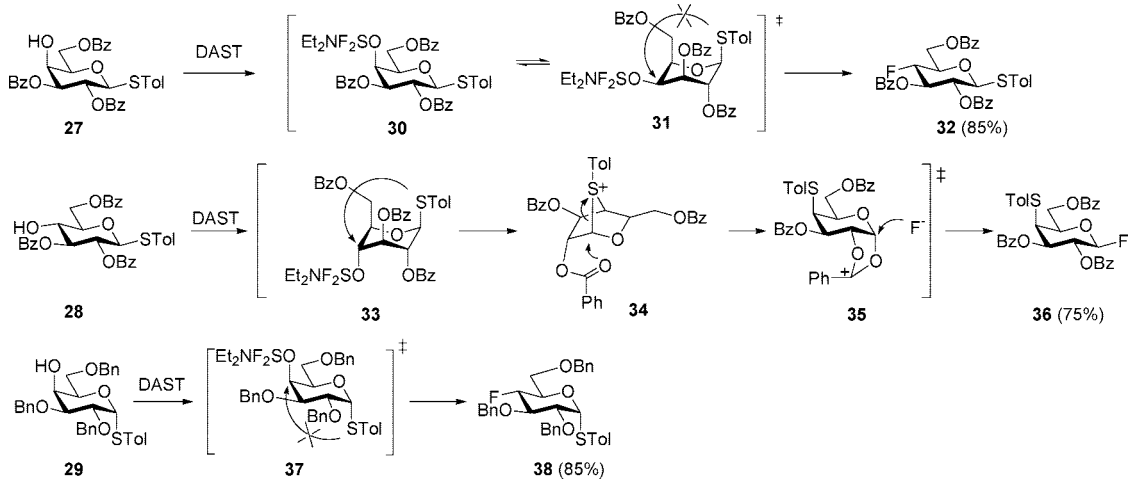
SCHEME 3. Plausible Mechanism for the C1→C6 Migrations of Anomeric Groups Mediated by DAST



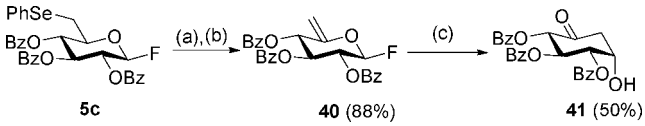
SCHEME 4. Stereoselective C1→C4 Migration of Anomeric Groups Mediated by DAST



hydroxyl in relation to the anomeric thiol group was crucial for migration. The *syn* relationship between C4-hydroxyl and C1-tolylthiol in *β*-thiogalactoside **27** resulted in formation of intermediate **30**. We propose that reactive conformation should adopt $^1C_4$ conformation to draw thiol nucleophile closing to leaving group. However, the periplanar relationship between nucleophile and leaving group makes the displacement impossible. Thus, only substitution product **32** (85%) was obtained. In contrast, *β*-thioglucoside **28** had a C4-hydroxyl *anti* to the anomeric thiol group, which could potentially form the bicyclic intermediate **34**; producing only migration product **36** (75%) stereoselectively. The stereochemistry of the newly formed anomeric fluoride was governed by the assistance of the similar C2-benzononium ion **35**, resulting in exclusive formation of *β*-anomer. However, the α-glycosidic bond in thiogalactoside **29** did not migrate and produced only substitution product **38** in 85% yield. The more stable α-thioglycosidic bond in intermediate **37** might be the factor to inhibit the migration of the anomeric S atom.

One of the notable advantages of glycosyl fluorides as glycosyl donors is their high thermal and chemical stability relative to other glycosyl halides. Therefore, several possible applications of the migration products can be envisaged on the basis of the literature (Figure 1). For example, 6-deoxy-6-thioglycosyl fluoride **5a** could be used to synthesize the corresponding oligosaccharide following desulfurization to

SCHEME 5. Synthesis of Polyhydroxylated Cyclohexanone 41[a]



[a] Key: (a) 70% *m*-chloroperoxybenzoic acid, dry CH_2Cl_2, −15 °C, 1 h; (b) dimethyl sulfide, triethylamine (2 equiv), reflux for 5 h (88% yield for two steps); (c) mercury(II) bromide, H_2O/acetone, reflux for 4.5 h, 50% yield.

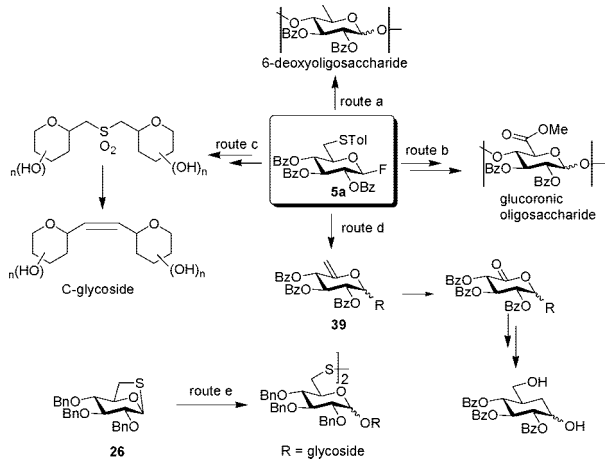
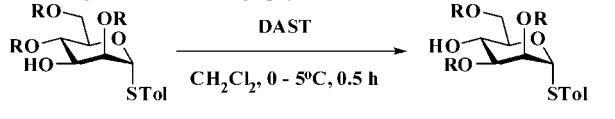


FIGURE 1. Potential application of DAST-mediated C1→C6 migration product.

generate 6-deoxysugars (Figure 1, route a).[11,19] Similarly, glycosylation followed by conversion of the arylthiol to carboxylic acid[20] would provide easy access to glucuronic oligosaccharides (Figure 1, route b). Due to the presence of the electron-withdrawing carboxylic acid function, glucuronic acid donors are less reactive and often result in a poor yield of glycosylation products.[21] DAST-mediated synthesis offers an alternative to glucuronic donors. Furthermore, aryl sulfides can be converted to sulfoxides or sulfones (Figure 1, route c), which have rich chemistry for further transformation to C-glycosides. Sulfoxides can be converted to alcohols or aldehydes, which can be further functionalized to useful saccharide intermediates.[22] Carbocyclic polyols are important components of many biologically active molecules, the effects of which range from cellular regulation to the selective inhibition of enzymes;[23] as such, various methods have been developed to obtain these bioactive molecules.[24] The synthesis of a common precursor, 6-deoxyhex-5-enopyranose derivatives, **39**, can be obtained either via elimination of the arylsulfide or arylselenide (Figure 1, route d) followed by metal catalysis to produce carbapyranoses.[25] Finally, the interesting product **26** could be used as a glycoside donor (Figure 1, route e) for the synthesis of 6-deoxy saccharides.[19]

(18) Attempts to introduce fluoride by regioselective anomeric group migration at the C3 position in mannopyranosides **42** were disappointing. While α-mannopyranoside **42a** (R = Bz) showed migration of a benzoyl ester to C3 (**43a**) under standard reaction conditions, product from **42b** (R = Bn) decomposedduring column chromatography.



We demonstrated the application of these facile migrations as shown in Scheme 5 for the synthesis of polyhydroxylated cyclohexanone **41**, which provides a practical route to a large variety of bioactive hexitols, such as aminocyclitols, and pseudosugars.[26] Thus, oxidation of the phenylselenide in **5c** with *m*-chloroperoxybenzoic acid in dichloromethane at −15 °C followed by thermal elimination of the resulting selenoxide with dimethyl sulfide in the presence of triethylamine at reflux temperature afforded 6-deoxyhex-5-enopyranoside **40**. Mercury(II)-mediated Ferrier rearrangement[27] of **40** in a mixture of H_2O/acetone at reflux temperature produced partially protected cyclohexanone derivative **41** with a newly formed hydroxyl group at the axial position.

Conclusion

In conclusion, we have systematically investigated the scope of the regioselective DAST-mediated C1→C6 and C1→C4 migrations of anomeric groups in saccharides. Our results demonstrate that an aryl or alkyl sulfide at the anomeric position in the presence of a suitable electron donor group on C2 reliably facilitates these migrations with stereoselective formation of a C−F bond. In addition, the anomeric migratory group and the free hydroxyl group should have an *anti* relationship to facilitate S_N2 attack by the migratory group. Our results suggest that these migrations would be very useful in the synthesis of various types of oligosaccharides.

Experimental Section

General Procedure for DAST-Mediated Anomeric Group Migration in Saccharides. DAST (1.5 equiv) was added to a solution of starting material (1.0 equiv) in CH_2Cl_2 (4 mL) at 0 °C, and the resulting mixture was stirred for 0.5 h. After being stirred for another 0.5 h at room temperature, the reaction mixture was quenched by aqueous $NaHCO_3$ (satd) (4 mL) and diluted with CH_2Cl_2 (10 mL). The layers were separated, the aqueous layer was extracted with CH_2Cl_2 (10 mL), the combined organic layer was dried over anhydrous $MgSO_4$ and filtered, and the solvents were evaporated at reduced pressure to give the crude product. The residue was purified by flash silica gel column chromatography eluting with a mixture *n*-hexanes and ethyl acetate to afford the pure products.

2,3,4-Tri-*O*-benzoyl-6-deoxy-6-*S*-ethyl-6-thio-β-D-glucopyranosyl fluoride (3): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.2 Hz, 2H), 7.94 (d, J = 7.2 Hz, 2H), 7.87 (d, J = 7.2 Hz, 2H), 7.56−7.30 (m, 9H), 5.83 (t, J = 8.4 Hz, 1H), 5.65 (d, J = 51.2, 6 Hz, 1H), 5.66 (t, J = 8.4 Hz, 1H), 5.58 (t, J = 8.4 Hz, 1H), 2.91

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(s, 1H), 2.90 (d, J = 6 Hz, 1H), 2.67 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.47, 165.14, 164.89, 133.56, 133.51, 133.38, 129.87, 129.81, 129.76, 129.67, 128.58, 128.45, 128.41, 128.34, 128.26, 106.60 (d, J = 219 Hz), 75.53, 75.50, 71.51, 71.42, 71.33, 71.23, 70.54, 33.20, 27.29, 14.58; HRMS (FAB) calcd for $C_{29}H_{28}FO_7S$ 539.1540 [M + H]$^+$, found 539.1530.

2,3,4-Tri-*O*-benzoyl-6-deoxy-6-*S*-(4-methylphenyl)-6-thio-β-D-glucopyranosyl fluoride (5a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.96 (m, 6H), 7.22−7.49 (m, 11H), 7.00 (d, J = 8.0 Hz, 2H), 5.85 (t, J = 8.2 Hz, 1H), 5.75−5.60 (m, 2H), 5.70 (t, J = 8.2 Hz, 1H), 4.15−4.19 (m, 1H), 3.25 (dd, J = 14.2, 3.7 Hz, 1H), 3.25 (dd, J = 14.2, 7.6 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.3, 165.0, 137.1, 133.7, 133.7, 133.6, 131.5, 131.1, 130.0, 129.9, 128.8, 128.7, 128.6, 128.5, 106.7 (d, 1J = 219 Hz), 73.9, 71.3 (d, 2J = 29.4 Hz), 71.2 (d, 3J = 7.6 Hz), 70.5, 37.2, 21.1; HRMS (FAB) calcd for $C_{34}H_{29}O_7FS$ 600.1619 [M$^+$], found 600.1618.

2,3,4-Tri-*O*-benzoyl-6-deoxy-6-*S*-benzyl-6-thio-β-D-glucopyranosyl fluoride (5b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.6 Hz, 2H), 7.91 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 7.6 Hz, 2H), 7.60−7.15 (m, 14H), 5.82 (t, J = 8.4 Hz, 1H), 5.69, 5.57 (dd, J = 48.4, 6.4 Hz), 5.63 (t, J = 8.4 Hz, 1H), 5.60 (dd, J = 6.4, 8.4 Hz, 1H), 4.07 (td, J = 9.2, 5.2 Hz, 1H), 3.83 (dd, J = 18, 13.6 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 165.49, 165.08, 164.91, 137.76, 133.57, 133.54, 133.40, 129.88, 129.83, 129.76, 129.05, 128.72, 128.65, 128.57, 128.44, 128.35, 127.06, 107.75, 105.56, 75.36, 71.60, 71.50, 71.42, 71.32, 70.60, 36.96, 32.07; HRMS (FAB) calcd for $C_{34}H_{30}FO_7S$ 601.1696 [M + H]$^+$ found 601.1705.

2,3,4-Tri-*O*-benzoyl-6-deoxy-6-*Se*-phenyl-6-seleno-β-D-glucopyranosyl fluoride (5c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 7.8 Hz, 2H), 7.85 (d, J = 7.8 Hz, 2H), 7.56−7.18 (m, 14H), 5.80 (t, d, J = 8.4 Hz, 1H), 5.71, 5,58 (dd, J = 48.4, 5.6 Hz, 1H), 5.65 (t, J = 8.8 Hz, 1H), 5.55 (m, 1H), 4.17 (ddd, J = 8, 8, 4 Hz, 1H), 3.28 (dd, J = 13.2, 3.6 Hz, 1H), 3.22 (dd, J = 13.2, 8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.42, 165.13, 164.87, 133.58, 133.52, 133.40, 133.15, 129.87, 129.83, 129.77, 129.47, 129.13, 128.69, 128.62, 128.56, 128.43, 128.41, 128.35, 127.38, 107.64, 105.45, 74.37, 74.33, 71.49, 71.29, 71.20, 71.11, 29.22; HRMS (FAB) calcd for $C_{23}H_{27}FO_7Se$ 634.0906 [M$^+$], found 634.0904.

2,3,4-Tri-*O*-benzoyl-6-methyl-β-D-glucopyranosyl fluoride (5d) and methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-fluoro-β-D-glucopyranoside (6d): ^{1}H NMR (400 MHz, $CDCl_3$) migration product δ 8.00−7.94 (m, 4H), 7.90 (d, J = 8 Hz, 2H), 7.54−7.26 (m, 9H), 5.87 (t, J = 10 Hz, 1H), 5.74, 5.61 (dd, J = 51.6(H−F), 6 Hz, 1H), 5.67 (t, J = 10 Hz, 1H), 5.61 (t, J = 10 Hz, 1H), 4.19 (quint, J = 5.2 Hz, 1H), 3.70 (d, J = 4.4 Hz, 2H), 3.40 (s, 3H); substitution product δ 8.00−7.94 (m, 4H), 7.83 (d, J = 4.4 Hz, 2H), 7.54−7.26 (m, 9H), 5.93 (t, J = 10 Hz, 1H), 5.53 (t, J = 10 Hz, 1H), 5.52 (dd, J = 10, 7.6 Hz, 1H), 4.63 (d, J = 8 Hz, 1H), 4.69 (d, J = 3.6 Hz, 1H), 4.57 (d, J = 4 Hz, 1H), 4.07 (ddt, J = 20, 10, 4 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.75, 165.49, 165.21, 165.13, 165.06, 164.89, 133.54, 133.50, 133.37, 133,22, 133.19, 129.88, 129.80, 129.75, 129.70, 129.24, 128.73, 128.64, 128.45, 128.41, 128.33, 128.30, 128.26, 101.68, 105.49, 101.91, 82.41, 80.66, 73.99, 73.31, 73.11, 72.80, 71.68, 71.57, 71.47, 71.28, 68.88, 68.81, 68.60, 59.53, 57.10; HRMS (FAB) calcd for $C_{28}H_{26}FO_8$ 509.1612 [M + H]$^+$, found 509.1622.

2,3,4-Tri-*O*-benzoyl-6-(2-propen-1-yl)-β-D-glucopyranosyl fluoride (5e) and 2-propen-1-yl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-fluoro-β-D-glucopyranoside (6e): ^{1}H NMR (400 MHz, $CDCl_3$) substitution product δ 7.97−7.81 (m, 6H), 7.54−7.26 (m, 9H), 5.91 (t, J = 9.5 Hz, 1H), 5.86−5.76 (m, 1H), 5.56−5.48 (m, 2H), 5.29−5.17 (m, 2H), 4.91 (d, J = 7.6 Hz, 1H), 4.55 (d, J = 4.8 Hz, 2H), 4.42 (dd, J = 13.0, 4.4 Hz, 1H), 4.19 (dd, J = 13.0, 6.2 Hz, 1H), 4.02 (d, J = 6 Hz, 1H); migration product δ 8.00−7.82 (m, 6H), 7.55−7.26 (m, 9H), 5.87−5.83 (m, 1H), 5.60−5.70 (m, 1H), 5.58 (dd, J = 44.0, 9.6 Hz, 1H), 5.61−5.58 (m, 2H), 5.52 (t, J = 9.6 Hz, 1H), 5.21 (dd, J = 10.2, 4.2 Hz, 2H), 4.67 (d, J = 4.8 Hz, 2H), 4.21 (dd, J = 14.0, 6.0 Hz, 1H), 3.75 (d, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.76, 165.50, 165.23, 165.12, 165.01, 164.91, 133.99, 133.56, 133.51, 133.48, 133.38, 133.23, 133.21, 133.19, 129.89, 129.80, 129.75, 129.25, 128.85, 128.74, 128.67, 128.62, 128.46, 128.42, 128.32, 128.27, 117.89, 117.73, 106. 0 (d, J = 219 Hz), 99.67, 81.21 (d, J = 175 Hz), 74.12, 73.31, 73.11, 72.80, 72.66, 71.70, 71.57, 71.24, 70.03, 68.91, 68.82, 68.62; HRMS (FAB) for $C_{30}H_{28}O_8F$ 535.1755 [M + H]$^+$, found 535.1768.

2,3,4-Tri-*O*-benzoyl-6-deoxy-6-fluoro-β-D-glucopyranosyl azide (6f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.97 (m, 4H), 7.80−7.83 (m, 2H), 7.50−7.54 (m, 2H), 7.36−7.44 (m, 5H), 7.25−7.29 (m, 2H), 5.93 (t, J = 9.7 Hz, 1H), 5.57 (t, J = 9.7 Hz, 1H), 5.48 (dd, J = 9.7, 8.8 Hz, 1H), 4.96 (d, J = 8.8 Hz, 1H), 4.54−4.71 (m, 2H), 4.09−4.18 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 165.1, 164.9, 133.7, 133.5, 133.4, 129.9, 129.8, 129.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 88.2, 81.1 (d, ^1J = 175.5 Hz), 75.3 (d, ^2J = 19.5 Hz), 72.6, 71.1, 68.2 (d, ^3J = 6.7 Hz); HRMS (FAB) calcd for $C_{27}H_{23}O_7N_3F$ 520.1517 [M + H]$^+$, found 520.1520.

2,3,4-Tri-*O*-benzoyl-6-deoxy-6-*S*-(4-methylphenyl)-6-thio-α-D-glucopyranosyl fluorides (5g(α)): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.35 (m, 13H), 7.23−7.25 (m, 2H), 7.18−7.21 (m, 2H), 7.04−7.07 (m, 2H), 5.51 (dd, J = 53.0, 2.6 Hz, 1H), 4.95 (d, J = 10.9 Hz, 1H), 4.90 (d, J = 11.0 Hz, 1H), 4.82 (d, J = 10.9 Hz, 1H), 4.78 (d, J = 11.8 Hz, 1H), 4.70 (d, J = 11.8 Hz, 1H), 4.55 (d, J = 11.0 Hz, 1H), 4.05 (ddd, J = 9.3, 6.6, 2.8 Hz, 1H), 3.97 (t, J = 9.3 Hz, 1H), 3.50−3.59 (m, 2H), 3.31 (dd, J = 14.8, 2.8 Hz, 1H), 3.01 (dd, J = 14.8, 6.6 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.3, 137.9, 137.6, 136.4, 132.6, 130.3, 129.7, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 105.0 (d, ^1J = 226.5 Hz), 81.3, 79.6 (d, ^2J = 24.6 Hz), 79.2, 75.7, 75.0, 73.5, 72.0, 36.5, 20.9; HRMS (FAB) calcd for $C_{34}H_{36}O_4FS$ 559.2313 [M + H]$^+$, found 559.2318.

2,6-Dideoxy-3,4-di-*O*-benzoyl-2-*N*-phthalimido-6-*S*-(4-methylphenyl)-6-thio-β-D-glucopyranosyl fluoride (5h): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67−7.87 (m, 8H), 7.20−7.43 (m, 8H), 7.03 (d, J = 7.9 Hz, 2H), 6.18 (dd, J = 52.3, 7.8 Hz, 1H), 6.17 (t, J = 9.6 Hz, 1H), 5.55 (t, J = 9.6 Hz, 1H), 4.60−4.68 (m, 1H), 4.06−4.11 (m, 1H), 3.22−3.25 (m, 1H), 3.13 (dd, J = 14.3, 7.9 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 165.5, 165.2, 137.0, 134.4, 133.9, 133.6, 133.4, 131.4, 130.9, 129.7, 128.5, 128.4, 128.3, 123.7, 104.3 (d, J = 216 Hz), 73.4, 70.1 (d, J = 10.3), 54.9 (d, J = 24 Hz), 36.6, 21.0; HRMS (FAB) calcd for $C_{35}H_{28}O_7NFS$ 625.1561 [M$^+$], found 625.1571.

4-Methylphenyl 3,4-di-*O*-benzoyl-2,6-dideoxy-2-*N*-phthalimido-6-fluoro-1-thio-β-D-glucopyranoside (6h): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, J = 8.0 Hz, 2H), 7.73−7.68 (m, 6H), 7.48−7.31 (m, 6H), 7.24−7.20 (m, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.24 (t, J = 9.8 Hz, 1H), 5.81 (dd, J = 50.4, 10.4 Hz, 1H), 5.50 (t, J = 9.6 Hz, 1H), 4.65−4.63 (m, 1H), 4.56−4.50 (m, 2H), 4.16−4.12 (m, 1H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.28, 165.89, 165.39, 139.06, 134.68, 134.52, 134.16, 133.75, 133.50, 131.48, 130.06, 130.00, 128.67, 128.51, 127.20, 123.90, 83.71, 81.75 (J = 175 Hz), 72.20, 69.24, 54.01, 21.43; HRMS (ESI) calcd for $C_{35}H_{28}O_7NFNaS$ 648.1468 [M + Na$^+$], found 648.1475.

2,6-Dideoxy-3,4-di-*O*-benzoyl-2-*N*-[(2,2,2-trichloroethoxycarbonyl)amino]-6-*S*-(4-methylphenyl)-6-thio-β-D-glucopyranosyl fluoride (5i): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92−7.88 (m, 4H), 7.54−7.50 (m, 2H), 7.40−7.34 (m, 4H), 7.25 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 5.63−5.55 (m, 3H), 5.50 (dd, J = 35.2, 5.5 Hz, 1H), 4.70 (d, J = 12 Hz, 1H), 4.59 (d, J = 12 Hz, 1H), 4.14−4.07 (m, 1H), 4.04−3.99 (m, 1H), 3.26 (qd, J = 4.4, 7.4 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.78, 165.62, 154.46, 136.85, 133.64, 133.56, 132.27, 130.61, 130.12, 130.02, 129.98, 129.58, 129.07, 128.60, 128.53, 93.77 (d, J = 222 Hz), 74.80, 72.37, 71.40, 69.50, 54.79, 36.90, 21.19; HRMS (ESI) calcd for $C_{30}H_{27}O_7NFSC_{13}Na$ 692.0456 [M + Na$^+$], found 692.0466.

2,6-Dideoxy-3,4-di-*O*-benzyl-2-*N*-phthalimido-6-*S*-(4-methylphenyl)-6-thio-β-D-glucopyranosyl fluoride (5j): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68−7.66 (m, 4H), 7.34−7.27 (m, 6H), 7.08

(d, J = 6.4 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.89−6.83 (m, 4H), 5.84 (dd, J = 53.0, 7.6 Hz, 1H), 4.91 (d, J = 11.2 Hz, 1H), 4.78 (d, J = 12.0 Hz, 1H), 4.66 (d, J = 12.0 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.35 (d, J = 8.4 Hz, 1H), 4.31−4.26 (m, 1H), 3.77−3.66 (m, 2H), 3.38 (dd, J = 14.0, 2.0 Hz, 1H), 3.04 (dd, J = 13.0, 6.1 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.05, 137.70, 136.07, 134.16, 133.71, 132.74, 131.50, 130.02, 129.80, 129.51, 128.45, 128.01, 127.89, 127.32, 123.56, 105.35 (d, J = 210 Hz), 83.64, 82.07, 79.15, 75.06, 74.79, 74.26, 57.43, 36.24, 20.92; HRMS (FAB) calcd for $C_{35}H_{32}O_5NFS$ 597.1985 [M$^+$], found 597.1978.

2-Azido-2,6-dideoxy-3,4-di-*O*-benzoyl-6-*S*-(4-methylphenyl)-6-thio-β-D-glucopyranosyl fluoride (5k) and 4-methylphenyl 2-azido-2,6-dideoxy-3,4-di-*O*-benzoyl-6-fluoro-1-thio-β-D-glucopyranoside (6k): ^{1}H NMR (400 MHz, $CDCl_3$) migration product δ 7.93−7.83 (m, 4H), 7.53−7.45 (m, 2H), 7.37−7.32 (m, 4H), 7.25−7.19 (m, 2H), 7.02 (d, J = 8.0 Hz, 2H), 5.87 (d, J = 9.2 Hz, 1H), 5.44 (dd, J = 52, 9.2 Hz, 1H), 4.15 (dt, J = 9.4, 2.2 Hz, 1H), 3.63 (ddd, J = 2.4, 2.4, 2.4 Hz, 1H), 3.47 (dd, 10.6, 3.4 Hz, 1H), 3.19 (dd, J = 12.8, 30.0 Hz, 1H), 3.02 (dd, J = 14.4, 8.8 Hz, 1H), 2.28 (s, 3H); substitution product δ 7.93−7.83 (m, 4H), 7.53−7.45 (m, 2H), 7.37−7.32 (m, 4H), 7.25−7.19 (m, 2H), 7.02 (d, J = 8.0 Hz, 2H), 5.85 (d, J = 9.2 Hz, 1H), 5.43 (d, J = 9.2 Hz, 1H), 5.36 (t, J = 9.4 Hz, 1H), 4.96 (d, J = 3.2 Hz, 1H), 4.32 (dt, J = 28, 2.8 Hz, 1H), 3.88−3.84 (m, 1H), 3.12 (dd, J = 16.8, 7.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.72, 165.65, 165.54, 165.44, 137.25, 134.74, 133.81, 133.66, 133.43, 131.66, 131.36, 130.40, 130.20, 130.00, 129.25, 128.95, 128.88, 128.61, 128.59, 128.50, 106.08 (d, J = 228 Hz), 99.05, 86.48, 81.42 (d, J = 175 Hz), 72.57, 71.62, 71.59, 71.12, 70.81, 70.17, 69.19, 61.91, 61.68, 55.66, 36.75, 21.18; HRMS (ESI) calcd for $C_{27}H_{24}N_3O_5FNaS$ 544.1318 [M + Na]$^+$, found 544.1323.

2-Methyl-4,5-(3,4-di-*O*-benzoyl-6-*S*-(4-methylphenyl)-6-thio-1,2-dideoxy-α-D-glucopyrano)[2,1-*d*]-2-oxazoline (7): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.58−7.54 (m, 2H), 7.44−7.39 (m, 4H), 7.24−7.22 (m, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.06 (d, J = 7.2 Hz, 1H), 5.60 (t, J = 2.0 Hz, 1H), 5.30 (d, J = 8.5 Hz, 1H), 4.29 (d, J = 6.8 Hz, 1H), 3.36 (td, J = 8.2, 3.2 Hz, 1H), 3.26 (dd, J = 14.0, 3.2 Hz, 1H), 3.05 (dd, J = 14.0, 8.0 Hz, 1H), 2.25 (s, 3H), 1.98 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 166.67, 165.09, 164.76, 136.74, 133.47, 133.44, 131.41, 131.08, 130.92, 129.94, 129.75, 129.66, 129.28, 129.08, 128.44, 128.37, 99.59, 71.75, 70.42, 68.40, 64.73, 38.13, 20.98, 13.75; HRMS (ESI) calcd for $C_{29}H_{28}NO_6S$ 518.1637 [M + H]$^+$, found 518.1641.

2,3,4-Tri-*O*-benzoyl-6-deoxy-6-*S*-(4-methylphenyl)-6-thio-β-D-galactopyranosyl fluoride (10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−8.08 (m, 6H), 7.32−7.63 (m, 9H), 7.25 (d, J = 7.9 Hz, 2H), 6.04 (br, 1H), 7.10 (d, J = 7.9 Hz, 2H), 5.85 (ddd, J = 12.0, 10.5, 7.0 Hz, 1H), 5.57 (dd, J = 10.5, 3.3 Hz, 1H), 5.53 (dd, J = 52.1, 7.0 Hz, 1H), 4.07 (t, J = 6.7 Hz, 1H), 3.30 (dd, J = 14.2, 6.7 Hz, 1H), 3.13 (dd, J = 14.2, 6.7 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 165.5, 165.3, 137.7, 133.9, 133.7, 133.6, 131.5, 130.7, 130.3, 130.2, 130.0, 129.0, 128.8, 128.6, 128.5, 107.5 (d, 1J = 217.5 Hz), 73.2, 71.2 (d, 3J = 10.4 Hz), 70.1 (d, 2J = 25.1 Hz), 68.3, 35.0, 21.2; HRMS (FAB) calcd for $C_{34}H_{29}O_7FS$ 600.1619 [M$^+$], found 600.1618.

2,3,4-Tri-*O*-benzyl-6-deoxy-6-*S*-(4-methylphenyl)-6-thio-β-D-galactopyranosyl fluoride (11): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.40 (m, 15H), 7.19−7.22 (m, 2H), 7.07−7.09 (m, 2H), 5.56 (dd, J = 53.7, 2.7 Hz, 1H), 5.01 (d, J = 11.1 Hz, 1H), 4.84 (d, J = 11.8 Hz, 1H), 4.83 (d, J = 11.8 Hz, 1H), 4.77 (d, J = 11.8 Hz, 1H), 4.71 (d, J = 11.8 Hz, 1H), 4.52 (d, J = 11.1 Hz, 1H), 4.13−4.14 (m, 1H), 4.03 (ddd, J = 25.2, 10.1, 2.7 Hz, 1H), 3.89−3.95 (m, 2H), 3.08 (dd, J = 13.5, 5.6 Hz, 1H), 2.99 (dd, J = 13.5, 8.5 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 138.5, 138.3, 137.1, 131.7, 130.6, 130.2, 128.7, 128.7, 128.6, 128.5, 128.2, 128.1, 128.1, 128.0, 127.8, 103.5 (d, 1J = 224.8 Hz), 79.0, 75.9 (d, 2J = 23.5 Hz), 75.3, 74.8, 74.0, 73.5, 72.3, 34.4, 21.3; HRMS (FAB) calcd for $C_{34}H_{36}O_4FS$ 559.2327 [M + H]$^+$, found 559.2318.

2,3-Di-*O*-benzoyl-6-deoxy-6-*S*-(4-methylphenyl)-6-thio-β-D-ribofuranosyl fluoride (13): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05−7.95 (m, 4H), 7.57−7.51 (m, 2H), 7.46−7.36 (m, 6H), 7.12 (d, J = 7.9 Hz, 2H), 5.77−5.75 (m, 2H), 5.45 (t, J = 2.7 Hz, 1H), 5.08 (dd, J = 44.8, 7.6 Hz, 1H), 4.39−4.34 (m, 1H), 4.15−4.09 (m, 1H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.87, 165.14, 138.46, 133.48, 133.40, 132.91, 129.94, 129.76, 128.49, 128.40, 118.97, 107.61 (d, J = 221 Hz), 71.26, 69.91, 68.60, 39.13, 21.11; HRMS (ESI) calcd for $C_{26}H_{24}O_5SF$ 467.1328 [M + H]$^+$, found 467.1323.

Ethyl 2,3,4-tri-*O*-benzoyl-6-fluoro-1-thio-α-D-glucopyranoside (15): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.96 (m, 4H), 7.86 (d, J = 7.2 Hz), 7.55−7.27 (m, 9H), 6.06 (t, J = 10 Hz, 1H), 5.95 (d, J = 6 Hz, 1H), 5.55 (t, J = 10 Hz, 1H), 5.49 (dd, J = 10, 5.6 Hz, 1H), 4.47 (dddd, J = 22, 10.4, 2.8, 4.4 Hz), 4.65, 4.54 (dm, J = 43.6 Hz (H−F), 2H), 2.65 (nintet, J = 6 Hz, 2H), 1.30 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.63, 165.39, 165.30, 133.50, 133.41. 133.14, 129.99, 129.89, 129.69, 129.17, 129.02, 128.85, 128.46, 128.29, 82.39, 80.63, 82.23, 71.63, 70.90, 69.15, 68.96, 68.80, 68.51, 24.40, 14.63; HRMS (FAB) calcd for $C_{29}H_{28}FO_7S$ 539.1540 [M + H]$^+$, found 539.1530.

2,3,4-Tri-*O*-benzoyl-6-*S*-(4-chlorophenyl)-6-deoxy-6-thio-β-D-glucopyranosyl fluoride (24a): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 7.4 Hz, 2H), 7.90 (d, J = 7.4 Hz, 2H), 7.85 (d, J = 7.4 Hz, 2H), 7.55−50 (m, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.38−7.34 (m, 4H), 7.32−7.26 (m, 4H), 7.16 (d, J = 8.4 Hz, 2H), 5.78 (t, J = 8.0 Hz, 1H), 5.65 (t, J = 8.2 Hz, 1H), 5.64 (dd, J = 51.3, 5.3 Hz, 1H), 5.56−5.52 (m, 1), 4.15−4.10 (m, 1H), 3.32 (dd, J = 14.3, 4.0 Hz, 1H), 3.24 (dd, J = 14.3, 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.34, 165.12, 164.85, 133.69, 133.57, 133.46, 132.87, 131.63, 129.87, 129.82, 129.76, 129.14, 128.61, 128.50, 128.48, 128.42, 128.37, 106.44 (d, J = 219 Hz), 73.79 (d, J = 3 Hz), 71.17, 71.00, 70.89 (d, J = 5 Hz), 70.21, 36.72; HRMS (FAB) calcd for $C_{33}H_{26}O_7ClFS$ 620.1072 [M$^+$], found 620.1062.

2,3,4-Tri-*O*-benzoyl-6-deoxy-6-*S*-(4-methoxyphenyl)-6-thio-β-D-glucopyranosyl fluoride (24b): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 7.4 Hz, 2H), 7.89−7.84 (m, 4H), 7.51 (t, J = 7.4 Hz, 2H), 7.45 (t, J = 7.4 Hz, 1H), 7.37−7.31 (m, 6H), 7.29 (d, J = 7.6 Hz, 2H), 5.76 (t, J = 8.0 Hz, 1H), 5.63 (t, J = 8.3 Hz, 1H), 5.62 (dd, J = 51.1, 5.5 Hz, 1H), 5.54−5.51 (m, 1H), 4.09−4.04 (m, 1H), 3.75 (s, 3H), 3.23 (dd, J = 14.2, 4.0 Hz, 1H), 3.16 (dd, J = 14.2, 7.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.37, 165.12, 164.86, 159.36, 134.08, 133.54, 133.53, 133.41, 129.86, 129.82, 129.76, 128.66, 128.56, 128.40, 128.35, 125.14, 114.67, 106.46 (d, J = 219 Hz), 73.73 (d, J = 3 Hz), 71.19, 70.24, 55.24, 38.28; HRMS (FAB) calcd for $C_{34}H_{29}O_8FS$ 616.1567 [M$^+$], found 616.1567.

Acetyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-fluoro-1-thio-β-D-glucopyranoside (25d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (t, J = 9.6 Hz, 1H, HC(3)), 5.28 (d, J = 10 Hz, 1H), 5.10 (dd, J = 10, 9.6 Hz, 1H), 5.09 (t, J = 9.6 Hz, 1H), 4.47 (ddd, J = 47.2, 10.8, 2.4 Hz, 1H), 4.40 (ddd, J = 47.2, 10.8, 2.4 Hz, 1H), 3.83 (dddd, J = 21.6, 10.8, 4, 2.4 Hz, 1H), 2.39 (s, 3H), 2.06, 2.03, 2.02 (s, 3H × 3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.90, 170.01, 169.25, 169.19, 81.85, 80.09, 80.16, 76.84, 74.99, 69.09, 67.95, 67.88, 30.76, 20.50; HRMS (FAB) calcd for $C_{14}H_{20}FO_8S$ 367.0863 [M + H]$^+$, found 367.0861.

1,6-Anhydro-6-deoxy-6-thio-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (26): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32−7.26 (m, 15H), 5.45 (s, 1H), 4.78 (d, J = 5.9 Hz, 1H), 4.68−4.54 (m, 6H), 3.65 (t, J = 4.7 Hz, 1H), 3.52 (d, J = 4.0 Hz, 1H), 3.34 (d, J = 5.6 Hz, 1H), 2.92 (q, J = 6.4, 6.2 Hz, 1H), 2.76 (d, J = 9.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.26, 138.04, 137.76, 128.45, 128.33, 127.90, 127.88, 127.83, 127.70, 127.62, 82.91, 82.43, 80.85, 79.27, 78.01, 73.24, 72.16, 71.77, 35.77; HRMS (FAB) calcd for $C_{27}H_{29}O_4S$ 449.1787 [M$^+$], found 449.1785.

4-Methylphenyl 2,3,6-tri-*O*-benzoyl-4-deoxy-4-fluoro-1-thio-β-D-glucopyranoside (32): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 6.4 Hz, 2H), 7.98 (d, J = 8 Hz, 2H), 7.95 (d, J = 8 Hz, 2H), 7.66−7.33 (m, 11H), 6.95 (d, J = 8 Hz, 2H), 5.84 (dt, J = 13.6, 9.6 Hz, 1H), 5.38 (d, J = 9.6 Hz, 1H), 4.92 (d, J = 10 Hz, 1H), 4.82 (d, J = 12 Hz, 1H), 4.78, 4.66 (dt, J = 50.8(H−F), 9.6 Hz, 1H), 4.59 (dd, J = 12, 9.6 Hz, 1H), 4.08 (ddd, J = 12, 5.6, 2.4 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.99, 165.56, 165.06, 138.71, 133.98, 133.38, 133.28, 129.85, 129.63, 129.09, 128.94, 128.42, 128.36, 127.40, 87.97, 86.09, 86.17, 75.72, 75.50, 74.30, 74.10, 62.66, 21.15; HRMS (FAB) calcd for $C_{34}H_{30}FO_7S$ 601.1696 $[M + H]^+$, found 601.1692.

2,3,6-Tri-*O*-benzoyl-4-deoxy-4-*S*-(4-methoxyphenyl)-4-thio-β-D-galactopyranosyl fluoride (36): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 6.8 Hz, 2H), 7.99 (d, J = 6.8 Hz, 2H), 7.82 (d, J = 7.2 Hz, 2H), 7.60−7.23 (m, 13H), 5.91 (ddd, J = 11.6, 9.6, 6.4 Hz, 1H), 5.58, 5.45 (dd, J = 51.6, 6.4 Hz, 1H), 5.44 (d, J = 9.6 Hz, 1H), 4.89 (d, J = 5.6 Hz, 2H), 4.46 (td, J = 5.6, 2 Hz, 1H), 4.12 (t, J = 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.12, 165.72, 164.98, 137.30, 133.50, 133.37, 133.28, 132.82, 130.17, 129.85, 129.81, 129.76, 129.44, 128.97, 128.59, 128.46, 128.39, 128.21, 108.27, 106.09, 72.89, 72.82, 69.84, 69.58, 64.25, 51.66, 29.68, 20.84; HRMS (FAB) calcd for $C_{34}H_{29}FO_7S$ 600.1618 $[M^+]$, found 600.1609.

4-Methylphenyl 2,3,6-tri-*O*-benzyl-4-deoxy-4-fluoro-1-thio-α-D-glucopyranoside (38): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.39 (17H, m), 7.04 (2H, d, J = 8.0 Hz), 5.51 (1H, dd, J = 2.9, 5.4 Hz), 4.88 (1H, d, J = 11.2 Hz), 4.83 (1H, d, J = 11.2 Hz), 4.75 (1H, d, J = 11.7 Hz), 4.70 (1H, d, J = 11.7 Hz), 4.56 (1H, d, J = 12.1 Hz), 4.55 (1H, dd, J = 51.9, 10.0 Hz), 4.51−4.49 (m, 1H), 4.48 (1H, d, J = 11.8 Hz), 3.87−3.96 (1H, m), 3.82 (1H, dd, J = 5.5, 9.7 Hz), 3.69−3.71 (2H, m), 2.30 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.38, 137.89, 137.55, 132.35, 129.91, 129.74, 128.42, 128.30, 128.07, 127.92, 127.65, 127.55, 89.55 (d, J = 182 Hz), 87.21, 80.13, 79.96, 78.56, 78.47, 75.22, 73.49, 72.76, 69.44, 69.19, 68.24, 29.67, 21.07; HRMS (FAB) calcd for $C_{34}H_{35}FO_4SNa$ $[M + Na]^+$ 581.2138, found 581.2141.

6-Deoxy-2,3,4-tri-*O*-benzoyl-β-D-*xylo*-hex-5-enopyranosyl fluoride (40): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.05 (m, 6H), 7.63−7.56 (m, 3H), 7.46−7.37 (m, 6H), 6.09 (d, J = 6 Hz, 1H), 5.99, 5,87 (ds, J = 50.4(F−H) Hz, 1H), 5.70 (dd, J = 6, 2.8 Hz, 1H), 5.50 (quint, J = 2.4 Hz, 1H), 5.08 (s, 1H), 4.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.91, 164.84, 148.77, 133.78, 133.62, 133.51, 130.07, 129.98, 129.94, 129.01, 128.76, 128.50, 128.49, 128.44, 106.16, 103.89, 99.80, 69.85, 69.26, 68.89, 67.45; HRMS (FAB) calcd for $C_{22}H_{22}FO_7$ 477.1350 $[M + H]^+$, found 477.1337.

[2*S*-(2α,3β,4α,5α)]-2,3,4-Tri-*O*-benzoyl-5-hydroxycyclohexanone (41): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, J = 7.4 Hz, 2H), 7.97 (d, J = 7.4 Hz, 2H), 7.89 (d, J = 7.4 Hz, 2H), 7.53−7.36 (m, 7H), 7.29 (t, J = 7.8 Hz, 2H), 6.38 (t, J =10.2 Hz, 1H), 5.80 (d, J = 10.4 Hz, 1H), 5.75 (dd, J = 10.1, 2.3 Hz, 1H), 4.65 (dd, J = 5.7, 3.0 Hz, 1H), 2.93(d, J = 3.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.70, 167.38, 165.64, 165.47, 133.97, 133.91, 133.84, 133.75, 133.48, 133.35, 130.34, 130.07, 129.92, 129.87, 129.69, 128.69, 128.66, 128.63, 128.59, 128.46, 128.41, 128.38, 77.08, 74.55, 70.16, 66.91, 43.24; HRMS (ESI) calcd for $C_{27}H_{23}O_8$ 475.1393 $[M + H]^+$, found 475.1401.

4-Methylphenyl 2,3,6-tri-*O*-benzoyl-1-thio-α-D-mannopyranoside (43a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30, (2H, d, J = 8.4 Hz, ArH), 8.08 (2H, d, J = 8.3 Hz, ArH), 7.97 (2H, d, J = 8.5 Hz, ArH), 7.36−7.63, (11H, m, ArH), 6.98 (2H, d, J = 8.1 Hz, ArH), 5.68 (1H, dd, J = 3.4, 3.4 Hz, H-3), 5.62 (1H, d, J = 3.4 Hz, H-2), 5.51 (1H, s, H-1), 4.91 (1H, ddd, J = 2.1, 5.3, 10.0 Hz, H-5), 4.82 (1H, dd, J = 5.3, 12.0, Hz, H-6b), 4.70 (1H, dd, J = 2.1, 12.0 Hz, H-6a), 4.30 (1H, dd, J = 3.4, 10.0, Hz, H-4), 2.02 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.86, 166.12, 164.64, 138.02, 133.71, 133.57, 133.15, 132.61, 131.30, 130.39, 129.82, 129.77, 129.05, 128.90, 128.58, 128.47, 128.37, 85.99, 71.87, 69.61, 68.02, 64.77, 64.09, 21.06; HRMS (FAB) calcd for $C_{34}H_{30}O_8SNa$ $[M + Na]^+$ 621.1559, found 621.1559.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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