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Chemo- and Regioselective Monosulfonylation of Nonprotected Carbohydrates Catalyzed by Organotin Dichloride under Mild Conditions

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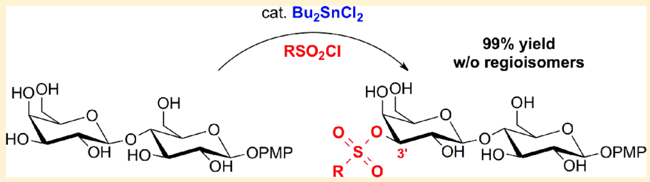
Supporting Information

ABSTRACT: The catalytic regioselective monosulfonylation of nonprotected carbohydrates using organotin dichloride under mild conditions is examined. The carbohydrates were chemo- and regioselectively converted to the corresponding monosulfonates in the presence of monoalcohols using catalytic dibutyltin dichloride. The regioselectivity of the sulfonylation is attributed to the intrinsic character of the carbohydrates derived from the relative stereochemistry between their hydroxy groups.



INTRODUCTION

The selective functionalization of polyols remains one of the most fundamental challenges for achieving the efficient access to building blocks for complex natural products and new drug development.[1] In particular, efficient chemical synthesis of carbohydrates such as pseudosugars or oligosaccharides is indispensable to clarify the mechanisms of various biological phenomena to which carbohydrates are implicated.[2] The direct regioselective functionalization of the secondary hydroxy groups in carbohydrates in the presence of originally highly reactive primary hydroxy groups with nonenzymatic catalysts is of long-standing interest because of the difficulty in functionalizing one specific hydroxy group among the multiple hydroxy groups present. Over the last several decades, progress has been made in the catalytic regioselective acylation,[3] alkylation,[4] thiocarbonylation,[5] and glycosylation[6] of nonprotected carbohydrates mediated by organo or organometal catalysts. These catalytic methods are useful for the protection or functionalization of a hydroxy group in carbohydrates in a minimum number of steps. However, some of the catalysts are not applicable to carbohydrates with nonprotected primary hydroxy groups, and the resulting monofunctionalized carbohydrates are usually not the ideal precursors for further functionalization. To resolve such problems, we began investigating the catalytic regioselective sulfonylation of nonprotected carbohydrates to afford monosulfonates, which can be used as electrophiles in the synthesis of biologically interesting pseudosugars and various building blocks for the development of novel functional materials via nucleophilic substitution reactions[7] or transition metal catalyzed C−C bond formations.[8]

Ogawa and Tsuda reported selective introduction of *p*-toluenesulfonyl group at the C(2)−OH of methyl *α*-D-glucopyranoside using $(Bu_3Sn)_2O$ to give a 53:47 mixture of 2- and 6-*O*-monosulfonates in 77% total yield or Bu_2SnO to give a 56:44 mixture of 2- and 6-*O*-monosulfonates in 50% total yield.[9a,b] However, both methods suffer from multiple sulfonylations, poor regioselectivity, use of a stoichiometric amount of organotin reagents (1−1.5 equiv), and harsh conditions for the preparation of the stannylene acetal intermediate. Martinelli reported the catalytic regioselective monosulfonylation of *α*-D-Xyl and *β*-D-Xyl in moderate yield and selectivity using catalytic Bu_2SnO.[9c,d] Onomura reported monosulfonylation of partially protected monosaccharides using catalytic Me_2SnCl_2.[3g] However, it is possible that Me_2SnCl_2 acts not as a controller of regioselectivity but as an activator of the less hindered hydroxy group in those monosaccharides.[10] More recently, Taylor reported regioselective sulfonylation using borinic acid catalysis. Unfortunately, the catalysis is not applicable to carbohydrates with nonprotected primary hydroxy groups.[9e] Herein, we report a widely useful regioselective monosulfonylation of nonprotected carbohydrates catalyzed by organotin dichloride under mild conditions.

RESULTS AND DISCUSSION

After a series of optimization studies (Table 1), we found that selective monosulfonylation at C(2)−OH of methyl *α*-D-glucopyranoside proceeded efficiently in the presence of Bu_2SnCl_2 (5 mol %), 3,5-difluorobenzenesulfonyl chloride (1.3 equiv), and 1,2,2,6,6-pentamethylpiperidine (PEMP, 2.0 equiv) in THF at 10 °C (entry 1, 98% yield with no regioisomers). In the absence of Bu_2SnCl_2 or PEMP, the desired monosulfonate **1** was obtained in 0% and <1% yield respectively without any byproducts (entries 2 and 3). The use of 1 mol % of Bu_2SnCl_2 gave monosulfonate **1** in 77% yield (entry 4). The addition of a catalytic amount of nucleophilic catalyst such as *N*,*N*-dimethylaminopyridine (DMAP) or *N*-methylimidazole (NMI) with 1 mol % of Bu_2SnCl_2 produced no significant effect under the present reaction conditions (entries 5 and 6). An

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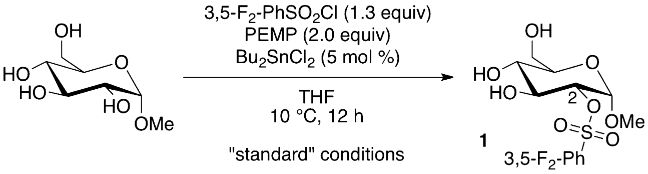
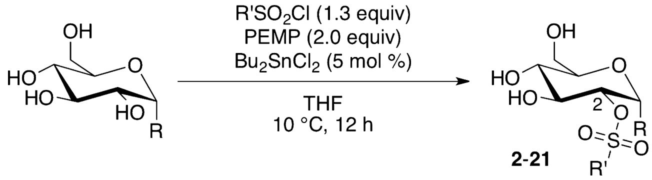
Table 1. Regioselective Sulfonylation of Methyl α-D-Glucopyranoside



entry	variation from the "standard" conditions	yield (%)
1	none	98
2	no Bu_2SnCl_2	0
3	no PEMP[a]	<1
4	1 mol % of Bu_2SnCl_2	77
5	1 mol % of Bu_2SnCl_2, 10 mol % of DMAP	70
6	1 mol % of Bu_2SnCl_2, 10 mol % of NMI	58
7	Me_2SnCl_2, instead of Bu_2SnCl_2	26[b]
8	*t*-Bu_2SnCl_2, instead of Bu_2SnCl_2	<1
9	Oc_2SnCl_2, instead of Bu_2SnCl_2	88
10	Ph_2SnCl_2, instead of Bu_2SnCl_2	<1
11	$Bu_2Sn(OTf)_2$, instead of Bu_2SnCl_2	84
12	$Bu_2Sn(OAc)_2$, instead of Bu_2SnCl_2	86
13	$Bu_2Sn(OMe)_2$, instead of Bu_2SnCl_2	91
14	Bu_2SnO, instead of Bu_2SnCl_2	47
15	Bu_2SnS, instead of Bu_2SnCl_2	87
16	*i*-Pr_2NEt, instead of PEMP	70
17	Pyridine, instead of PEMP	<1
18	2,6-Lutidine, instead of PEMP	<1
19	DME, instead of THF	76
20[c]	Dioxane, instead of THF	83
21	use of ground α-D-Glc	98
22	addition of H_2O (1.0 equiv)	24

[a]1,2,2,6,6-Pentamethylpiperidine. [b]A 49:51 mixture of 2- and 6-*O*-sulfonates was observed in 53% total yield. [c]Reaction was carried out at 20 °C.

Table 2. Scope of the Reaction of α-D-Glucopyranoside with Sulfonyl Chlorides



entry	R	R′	product	yield (%)
1[a]	OOc	3,5-F_2−Ph	**2**	80
2	OPh	3,5-F_2−Ph	**3**	91
3	OPNP[b]	3,5-F_2−Ph	**4**	90
4	SEt	3,5-F_2−Ph	**5**	95
5	Br	3,5-F_2−Ph	**6**	<1
6	OMe	Me	**7**	15 (23)[c]
7[a]	OMe	Ph	**8**	20
8[a]	OMe	2-Naphthyl	**9**	21
9[a]	OMe	2-NO_2−Ph	**10**	16
10[a]	OMe	3-NO_2−Ph	**11**	90
11[a]	OMe	4-NO_2−Ph	**12**	85
12[a]	OMe	3-CF_3−Ph	**13**	87
13[a]	OMe	3-F−Ph	**14**	80
14[a]	OMe	3-Cl−Ph	**15**	76
15[a]	OMe	3-Br−Ph	**16**	73
16[a]	OMe	3-Me−Ph	**17**	40
17[a]	OMe	4-Me−Ph	**18**	26 (34)[c]
18	OMe	3,5-$(CF_3)_2$−Ph	**19**	98
19[d]	OMe	3,5-Cl_2−Ph	**20**	91
20	OMe	Tf	**21**	0 (0)[c]

[a]Reaction was carried out at 20 °C. [b]*p*-Nitrophenyl. [c]Corresponding anhydride was used instead of sulfonyl chloride. [d]Sulfonyl chloride (1.5 equiv) was used.

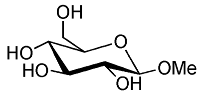
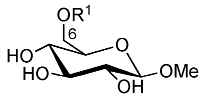
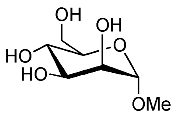
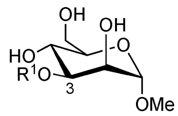
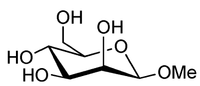
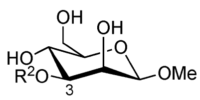
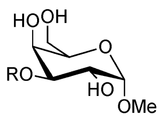
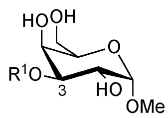
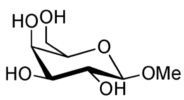
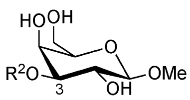
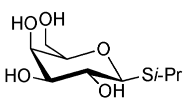
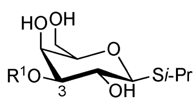
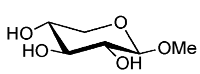
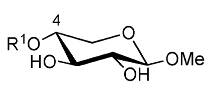
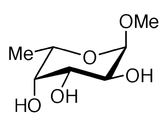
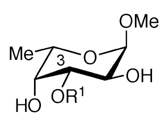
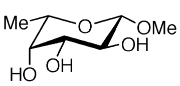
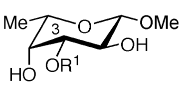
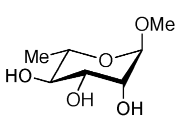
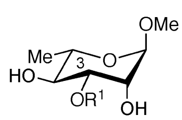
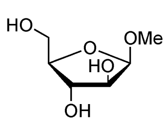
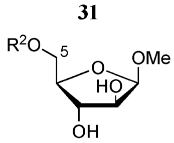
attempt to access **1** by treating methyl α-D-glucopyranoside with Me_2SnCl_2, used by Onomura,[3g] instead of Bu_2SnCl_2 led to the undesired 6-*O*-monosulfonate with **1** in 53% total yield (entry 7; 49:51 mixture of 2-*O*-sulfonate **1** and 6-*O*-sulfonate). The use of other alkyl- or aryltin dichlorides instead of Bu_2SnCl_2 gave only monosulfonate **1**, but in lower yield (entries 8−10), as did the use of $Bu_2Sn(OTf)_2$, $Bu_2Sn(OAc)_2$, $Bu_2Sn(OMe)_2$, Bu_2SnO, or Bu_2SnS (entries 11−15). Nucleophilic bases such as *i*-Pr_2NEt and pyridine also afforded **1** in lower yield (entries 16 and 17). In addition, 2,6-lutidine, which is a less nucleophilic base, did not give any products (entry 18). DME and dioxane could be used in place of THF as the solvent, at the expense of a slight decrease in yield (entries 19 and 20; 76 and 83% yield, respectively). Using ground methyl α-D-glucopyranoside, the catalysis proceeded in 98% yield without formation of regioisomers (entry 21). By addition of H_2O (1.0 equiv) in the reaction, the yield of **1** is drastically decreased without formation of the regioisomers or any byproducts (entry 22).

Next, we examined the scope of this catalytic regioselective monosulfonylation under the optimized conditions with respect to both the anomeric substituent of the α-D-glucopyranoside and various sulfonyl chlorides as the electrophile (Table 2). When the R substituents were *O*-alkyl or *O*-aryl, monosulfonylation proceeded in 80−91% yield with no regioisomers (entries 1−3). Ethyl α-D-thioglucopyranoside,[11] a useful glycosyl donor, was converted to the corresponding monosulfonate **5** in 95% yield (entry 4). In contrast, the reaction with α-D-glucopyranosyl bromide,[12] which is a widely used partner for *O*- and *C*-glycosylation, did not afford the desired product (entry 5).

Further, we examined the scope of this catalytic monosulfonylation with respect to electron-donating and electron-withdrawing substituents R′ on the electrophile. Using methanesulfonyl chloride as an electrophile, 2-*O*-sulfonate **7** was produced in only 15% yield with 46% yield of undesired disulfonates (entry 6). The use of benzene- and 2-naphthalenesulfonyl chloride resulted in poor reactivity at C(2)−OH (entries 7 and 8). In the case of the benzenesulfonyl chloride with electron-withdrawing groups at the *meta* and *para* positions, sulfonylation proceeded in 73−98% yields without formation of regioisomers (entries 10−15, 18 and 19). Similarly, use of the benzenesulfonyl chloride with an electron-donating methyl group at the *meta* position afforded the corresponding monosulfonate **17** in good yield with great regioselectivity (entry 16). The use of 4-toluenesulfonyl chloride which is a widely used electrophile gave lower yield (entry 17). On the other hand, the benzenesulfonyl chloride with an electron-withdrawing nitro group at the *ortho* position gave a relatively poor yield (entry 9). This trend can be attributed to the effect of steric hindrance at the *ortho* position. The use of the corresponding sulfonic anhydride instead of sulfonyl chloride gave slightly better yield (entries 6 and 17). Using TfCl and Tf_2O as a sulfonyl reagent, insoluble polysaccharides like a rubber was obtained (entry 20).

Proceeding from these results, this catalytic system was used in the differentiation of primary or secondary hydroxy groups for a wide range of monosaccharides (Table 3). Monosulfonylation

Table 3. Regioselective Sulfonylation of Various Monosaccharides[a]

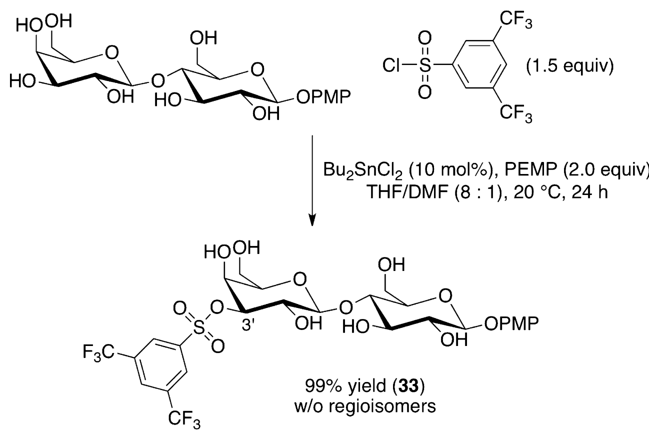
Entry	Substrate	Product[b]	Yield (%)
1[c]		 **22**	>99
2[d-e]		 **23**	95
3		 **24**	98
4[f]		 **25**	98
5[e]		 **26**	>99
6[d]		 **27**	94
7[d]		 **28**	>99
8[d]		 **29**	>99
9[d]		 **30**	>99
10		 **31**	>99
11[c-d,f]		 **32**	71

[a]For the reaction conditions, see Table 2. [b]R^1 = 3,5-difluorobenzenesulfonyl. R^2 = 3,5-bis(trifluoromethyl)benzenesulfonyl. [c]Me_2SnCl_2 was used instead of Bu_2SnCl_2. [d]In acetone. [e]Sulfonyl chloride (1.5 equiv) was used. [f]Sulfonyl chloride (1.5 equiv) and PEMP (3.0 equiv) were used.

was selectively observed only at cis-1,2-diol moieties, with equatorial−OH groups in derivatives of commercially available D-mannopyranoside (entries 2 and 3), D-galactopyranoside (entries 4 and 5), β-D-thiogalactopyranoside (entry 6), L-fucopyranoside (entries 8 and 9), and α-L-rhamnopyranoside (entry 10). Unfortunately, sulfonylation of C(2)−OH in β-D-arabinofuranoside[12] with 5 mol % of several organotin catalysts in THF or acetone was not observed (entry 11). In the case of the reactions with monosaccharides without cis-1,2-diol moieties, β-D-glucopyranoside and β-D-xylopyranoside, the less hindered hydroxy groups in the monosaccharides were selectively activated by the organotin catalyst and sulfonylated in >99% yield without formation of the regioisomers or disulfonates (entries 1 and 7).

The protocol was applied to the regioselective monosulfonylation of a dissacharide with two highly reactive primary hydroxy groups and five secondary hydroxy groups. Treatment of 4-methoxyphenyl β-D-lactopyranoside with 3,5-bis(trifluoromethyl)benzenesulfonyl chloride (1.5 equiv) and PEMP (2.0 equiv) in the presence of Bu_2SnCl_2 (10 mol %) in THF/DMF (8:1) at 20 °C for 24 h gave **33** in 99% yield with perfect regioselectivity (Scheme 1).

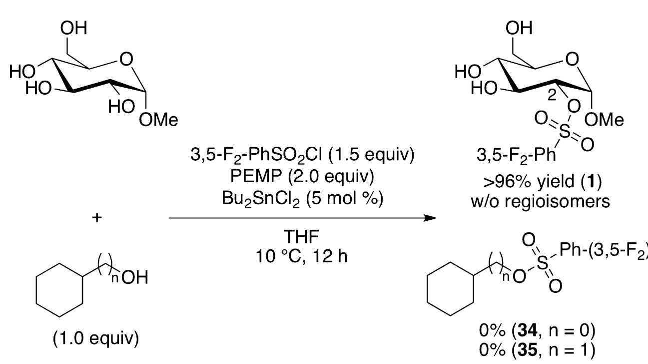
Scheme 1. Regioselective Sulfonylation of a Disaccharide



In addition, competitive sulfonylation between methyl α-D-glucopyranoside and monoalcohols in the presence of 5 mol % of Bu_2SnCl_2 proceeded to afford **1** in high yields with excellent chemo- and regioselectivities (Scheme 2).

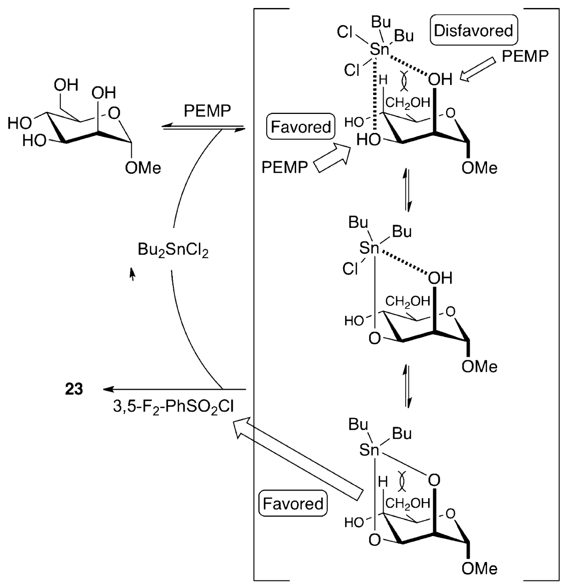
The regioselectivity of the catalytic monosulfonylation of these monosaccharides can be explained as follows. Coordination of the organotin catalyst with the cis-diol moieties in these monosaccharides is favored after moving freely among diol

Scheme 2. Competitive Sulfonylation between α-D-Glucopyranoside and Monoalcohols



moieties. As the coordination of metal ions may increase the acidity of hydroxy groups, even a weak base such as PEMP is sufficient to induce deprotonation. In addition, as an axial-H adjacent to the reacting axial−OH group in the cis-1,2-diol moiety restricts the approach of PEMP (1,3-diaxial interaction), the most accessible hydroxy group, the equatorial−OH group, may be attacked by PEMP and hence sulfonylated. Another possibility is that the deprotection can occur at both equatorial−OH and axial−OH groups and the sulfonylation proceeded rapidly at the less hindered equatorial position (Scheme 3).

Scheme 3. Plausible Explanation of the Regioselective Sulfonylation of Monosaccharides (for example, methyl α-D-mannopyranoside)



■ CONCLUSION

A catalytic process for the monosulfonylation of a wide range of nonprotected monosaccharides and a disaccharide with high yield and excellent regioselectivity under mild conditions has been developed. The motif serves as a synthetic handle for the elaboration of numerous organic functionalities. The regioselectivity of the sulfonylation was found to be intrinsic to the carbohydrate based on the stereochemical relationship among its hydroxy groups. In addition, monosaccharides were chemoselectively converted to the correspondiong monosulfonates in the presence of monoalcohols, and the catalyst regioselectively activated the particular equatrial−OH group in the *cis*-1,2-diols of pyranosides. The proposed reaction forms the basis for the development of a method for the direct functionalization of nonprotected carbohydrates and also provides new insight into carbohydrate-metal ion interactions and their activation processes.

■ EXPERIMENTAL SECTION

General Procedure for the Regioselective Monosulfonylation of Nonprotected Monosaccharides Catalyzed by Organotin Dichlorides. After stirring a mixture of methyl α-D-glucopyranoside (194.2 mg, 1.0 mmol) and dibutyltin dichloride (15.2 mg, 0.05 mmol) in THF (18 mL) in a vial at room temperature for 10 min, 3,5-difluorobenzenesulfonyl chloride (276.4 mg, 1.3 mmol) and 1,2,2,6,6-pentamethylpiperidine (0.361 mL, 2.0 mmol) were added to the suspension at 10 °C. After stirring vigorously for 12 h at 10 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over $MgSO_4$, filtrated, and concentrated *in vacuo*. The residue was purified by SiO_2 column chromatography (hexane/ethyl acetate = 3/1−0/1) to give methyl 2-*O*-(3,5-difluorobenzensulfonyl)-α-D-glucopyranoside **1** (361.4 mg, 98%) as a white solid and disulfonates (4.4 mg, <1%).

*Methyl 2-O-(3,5-Difluorobenzenesulfonyl)-α-D-glucopyranoside (**1**).* Yield: 361.4 mg, 98%. White solid. R_f = 0.27 (MeOH/$CHCl_3$, 10:90). Mp 38−40 °C. $[\alpha]_D^{21}$ = +94.4 (*c* 1.13, CH_3OH). ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.70−7.60 (m, 2H, 3,5-F-Ph*H*), 7.55−7.45 (m, 1H, 3,5-F-Ph*H*), 4.82 (d, *J* = 3.7 Hz, 1H, *H*-1), 4.67 (br s, 1H, O*H*), 4.48 (br s, 1H, O*H*), 4.28 (dd, *J* = 9.6, 3.7 Hz, 1H, *H*-2), 3.90−3.60 (m, 4H, *H*-3, *H*-6 and O*H*), 3.60−3.50 (m, 1H, *H*-5), 3.39 (t, *J* = 9.3 Hz, 1H, *H*-4), 3.34 (s, 3H, OC*H*$_3$). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.6 (d, *J* = 252.4 Hz), 163.5 (d, *J* = 252.4 Hz), 140.8 (t, *J* = 9.1 Hz), 112.6 (d, *J* = 19.9 Hz), 112.5 (d, *J* = 19.9 Hz), 110.2 (t, *J* = 25.7 Hz), 98.1, 82.2, 73.0, 71.7, 71.6, 62.1, 55.2. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.4 to −106.5 (m, 2F). IR (solid) 3377, 2928, 1607, 1443, 1371, 1300, 1179, 962 cm^{-1}. MS *m*/*z* (rel intensity) 371 (M + H^+, 10), 339 (20), 307 (20), 289 (15), 261 (5), 154 (100), 145 (30), 137 (90). HRMS calcd for $C_{13}H_{17}F_2O_8S$ (M + H^+): 371.0607, found 371.0629. Anal. calcd for $C_{13}H_{16}F_2O_8S$: C, 42.16; H, 4.35. Found: C, 42.37; H, 4.11.

*Octyl 2-O-(3,5-Difluorobenzenesulfonyl)-α-D-glucopyranoside (**2**).* Yield: 373.4 mg, 80%. White solid. R_f = 0.38 (MeOH/$CHCl_3$, 10:90). Mp 84−85 °C. $[\alpha]_D^{20}$ = +85.4 (*c* 1.05, CH_3OH). ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.62 (d, *J* = 4.4 Hz, 2H, 3,5-F-Ph*H*), 7.48 (t, *J* = 4.4 Hz, 1H, 3,5-F-Ph*H*), 4.92 (d, *J* = 3.7 Hz, 1H, *H*-1), 4.67 (br s, 1H, O*H*), 4.62 (br s, 1H, O*H*), 4.29 (dd, *J* = 9.8, 3.7 Hz, 1H, *H*-2), 3.84 (t, *J* = 9.2 Hz, 1H, *H*-3), 3.80−3.50 (m, 5H, *H*-4, *H*-5, *H*-6 and O*H*), 3.41 (t, *J* = 9.5 Hz, 1H, $OCH_2(CH_2)_6CH_3$), 3.32 (dt, *J* = 9.5, 6.3 Hz, 1H, $OCH_2(CH_2)_6CH_3$), 1.70−1.50 (m, 2H, $OCH_2CH_2(CH_2)_5CH_3$), 1.45−1.10 (m, 10H, $OCH_2CH_2(CH_2)_5CH_3$), 0.89 (t, *J* = 6.7 Hz, 3H, $OCH_2(CH_2)_6CH_3$). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.6 (d, *J* = 252.4 Hz), 163.4 (d, *J* = 252.4 Hz), 140.9 (t, *J* = 9.1 Hz), 112.6 (d, *J* = 19.9 Hz), 112.5 (d, *J* = 19.9 Hz), 110.1 (t, *J* = 25.7 Hz), 97.0, 82.2, 73.1, 71.7, 71.6, 68.5, 62.1, 32.5, 30.0, 29.9, 29.6, 26.8, 23.2, 14.3. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.3 to −106.4 (m, 2F). IR (solid) 3289, 2926, 1607, 1443, 1369, 1300, 1180, 1128 cm^{-1}. MS *m*/*z* (rel intensity) 469 (M + H^+, 20), 339 (25), 321 (30), 261 (45), 177 (35), 145 (100), 127 (95), 85 (35). HRMS calcd for $C_{20}H_{31}F_2O_8S$ (M + H^+): 469.1702, found 469.1720. Anal. calcd for $C_{20}H_{30}F_2O_8S$: C, 51.27; H, 6.45. Found: C, 51.09; H, 6.64.

*Phenyl 2-O-(3,5-Difluorobenzenesulfonyl)-α-D-glucopyranoside (**3**).* Yield: 391.9 mg, 91%. White solid. R_f = 0.41 (MeOH/$CHCl_3$, 10:90). Mp 145−147 °C. $[\alpha]_D^{17}$ = +127.2 (*c* 1.10, CH_3OH). ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 7.63 (d, *J* = 2.2 Hz, 2H, Ph*H*), 7.50−7.20 (m, 3H, Ph*H*), 7.20−6.95 (m, 3H, Ph*H*), 5.62 (d, *J* = 3.7 Hz, 1H, *H*-1), 4.86 (d, *J* = 4.9 Hz, 1H, O*H*), 4.61 (d, *J* = 4.9 Hz, 1H, O*H*), 4.50 (dd, *J* = 9.8, 3.7 Hz, 1H, *H*-2), 4.06 (td, *J* = 9.3, 4.9 Hz, 1H, *H*-3), 3.85−3.50 (m, 5H, *H*-4, *H*-5, *H*-6 and O*H*). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.5 (d, *J* = 252.4 Hz), 163.4 (d, *J* = 252.4 Hz), 157.5, 140.5 (t, *J* = 9.1 Hz), 130.3 (2C), 123.6, 117.8 (2C), 112.6 (d, *J* = 19.9 Hz), 112.5 (d, *J* = 19.9 Hz), 110.2 (t, *J* = 25.7 Hz), 96.5, 81.6, 74.1, 71.7, 71.3, 61.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.1 to −106.2 (m, 2F). IR (solid) 3331, 2938, 1607, 1491, 1443, 1366, 1296, 1175 cm^{-1}. MS *m*/*z* (rel intensity) 433 (M + H^+, 5), 391 (40), 321 (10), 261 (10), 167 (20), 154 (75), 149 (100), 94 (70). HRMS calcd for $C_{18}H_{19}F_2O_8S$ (M + H^+): 433.0763, found 433.0744. Anal. calcd for $C_{18}H_{18}F_2O_8S$: C, 50.00; H, 4.20. Found: C, 49.98; H, 4.41.

*4-Nitrophenyl 2-O-(3,5-Difluorobenzenesulfonyl)-α-D-glucopyranoside (**4**).* Yield: 429.0 mg, 90%. White solid. R_f = 0.41 (MeOH/$CHCl_3$, 10:90). Mp 165−166 °C. $[\alpha]_D^{21}$ = +157.6 (*c* 1.11, CH_3OH). ^1H NMR (400 MHz, $(CD_3)_2CO$) δ 8.23 (d, *J* = 9.0 Hz, 2H, 4-NO_2−Ph*H*), 7.70−7.50 (m, 2H, 3,5-F-Ph*H*), 7.50−7.30 (m, 1H, 3,5-F-Ph*H*), 7.32 (d, *J* = 9.0 Hz, 2H, 4-NO_2−Ph*H*), 5.86 (d, *J* = 3.7 Hz, 1H, *H*-1), 4.96 (br s, 1H, O*H*), 4.69 (br s, 1H, O*H*), 4.59 (dd, *J* = 9.8, 3.7 Hz, 1H, *H*-2), 4.09 (t, *J* = 8.4 Hz, 1H, *H*-3), 3.90−3.40 (m, 5H, *H*-4, *H*-5, *H*-6 and OH). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.6 (d, *J* = 252.4 Hz), 163.4 (d, *J* = 252.4 Hz), 162.0, 143.7, 140.4 (t, *J* = 9.1 Hz), 126.4 (2C), 117.6 (2C), 112.6 (d, J = 19.9 Hz), 112.6 (d, J = 19.9 Hz), 110.3 (t, J = 25.7 Hz), 96.0, 81.2, 74.8, 71.6, 71.0, 61.8. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.0 to −106.1 (m, 2F). IR (solid) 3368, 2909, 2361, 1591, 1516, 1341, 1234, 1173, 1015 cm^{-1}. MS m/z (rel intensity) 478 (M + H$^+$, 5), 307 (20), 289 (15), 154 (100), 136 (65), 107 (20), 77 (15). HRMS calcd for $C_{18}H_{18}F_2NO_{10}S$ (M + H$^+$): 478.0614, found 478.0609. Anal. calcd for $C_{18}H_{17}F_2NO_{10}S$: C, 45.29; H, 3.59; N, 2.93. Found: C, 45.02; H, 3.43; N, 2.88.

*Ethyl 2-O-(3,5-Difluorobenzenesulfonyl)-α-D-thioglucopyranoside (**5**).* Yield: 381.5 mg, 95%. White solid. R_f = 0.33 (MeOH/CHCl$_3$, 10:90). Mp 128−129 °C. $[\alpha]_D^{23}$ = +154.7 (c 1.03, CH_3OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.66 (d, J = 4.6 Hz, 2H, 3,5-F-PhH), 7.60−7.40 (m, 1H, 3,5-F-PhH), 5.44 (d, J = 5.6 Hz, 1H, H-1), 4.78 (br s, 1H, OH), 4.54 (br s, 1H, OH), 4.52 (dd, J = 9.8, 5.6 Hz, 1H, H-2), 4.00−3.88 (m, 1H, H-5), 3.87−3.50 (m, 4H, H-3, H-6 and OH), 3.41 (t, J = 9.3 Hz, 1H, H-4), 2.70−2.45 (m, 2H, SCH_2CH$_3$), 1.22 (t, J = 7.3 Hz, 3H, SCH$_2$CH_3). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.6 (d, J = 252.4 Hz), 163.4 (d, J = 252.4 Hz), 140.7 (t, J = 9.1 Hz), 112.8 (d, J = 19.9 Hz), 112.7 (d, J = 19.9 Hz), 110.3 (t, J = 25.7 Hz), 83.0, 81.4, 73.9, 72.5, 71.6, 62.1, 24.5, 14.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.2 to −106.4 (m, 2F). IR (solid) 3308, 2910, 1609, 1443, 1300, 1179, 1128, 988 cm^{-1}. MS m/z (rel intensity) 401 (M + H$^+$, 15), 339 (45), 321 (40), 261 (30), 177 (35), 145 (100), 127 (75). HRMS calcd for $C_{14}H_{19}F_2O_7S_2$ (M + H$^+$): 401.0535, found 401.0568. Anal. calcd for $C_{14}H_{18}F_2O_7S_2$: C, 41.99; H, 4.53. Found: C, 42.15; H, 4.24.

*Methyl 2-O-Methanesulfonyl-α-D-glucopyranoside (**7**).*[9b,13] Yield: 40.2 mg, 15%. White solid. R_f = 0.19 (MeOH/CHCl$_3$, 10:90). Mp 105−106 °C (lit.[9b] 120−121 °C). $[\alpha]_D^{26}$ = +99.4 (c 0.50, CH_3OH) {lit.[13] $[a]_D^{RT}$ = +106.4 (c 1.00, CH_3OH)}. ^{1}H NMR (400 MHz, CD_3OD) δ 4.90 (d, J = 3.7 Hz, 1H, H-1), 4.28 (dd, J = 9.8, 3.7 Hz, 1H, H-2), 3.82 (dd, J = 12.0, 2.3 Hz, 1H, H-6a), 3.79 (t, J = 9.3 Hz, 1H, H-3), 3.68 (dd, J = 12.0, 5.6 Hz, 1H, H-6b), 3.60−3.50 (m, 1H, H-5), 3.45−3.35 (m, 1H, H-4), 3.42 (s, 3H, OCH_3), 3.14 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CD_3OD) δ 99.3, 81.5, 73.5, 72.3, 71.9, 62.3, 55.7, 38.3. IR (solid) 3368, 1470, 1381, 1175, 1119, 1028, 953, 887 cm^{-1}. MS m/z (rel intensity) 295 (M + Na$^+$, 5), 194 (20), 154 (100), 137 (70), 107 (25), 88 (20), 77 (20). HRMS calcd for $C_8H_{16}O_8S$ (M + Na$^+$): 295.0464, found 295.0463.

*Methyl 2-O-Benzenesulfonyl-α-D-glucopyranoside (**8**).*[9b] Yield: 66.8 mg, 20%. White solid. R_f = 0.19 (MeOH/CHCl$_3$, 10:90). Mp 180−182 °C (lit.[9b] 201−203 °C). $[\alpha]_D^{19}$ = +97.6 (c 0.53, CH_3OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.97 (d, J = 8.1 Hz, 2H, PhH), 7.77 (t, J = 7.3 Hz, 1H, PhH), 7.67 (t, J = 7.3 Hz, 2H, PhH), 4.65 (d, J = 3.7 Hz, 1H, H-1), 4.56 (br s, 1H, OH), 4.40 (br s, 1H, OH), 4.19 (dd, J = 9.5, 3.7 Hz, 1H, H-2), 3.85−3.70 (m, 2H, H-3 and H-6a), 3.70−3.55 (m, 2H, H-6b and OH), 3.55−3.50 (m, 1H, H-5), 3.38 (t, J = 9.8 Hz, 1H, H-4), 3.23 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 138.0, 134.7, 130.1 (2C), 128.7 (2C), 98.1, 81.3, 73.0, 71.8, 71.7, 62.2, 55.2. IR (solid) 3383, 2934, 1449, 1358, 1186, 1175, 1024, 966 cm^{-1}. MS m/z (rel intensity) 335 (M + H$^+$, 5), 319 (5), 307 (30), 289 (20), 154 (100), 137 (50), 107 (25), 77 (25). HRMS calcd for $C_{13}H_{19}O_8S$ (M + H$^+$): 335.0795, found 335.0829.

*Methyl 2-O-(2-Naphthalene)sulfonyl-α-D-glucopyranoside (**9**).* Yield: 81.4 mg, 21%. White solid. R_f = 0.29 (MeOH/CHCl$_3$, 10:90). Mp 39−40 °C. $[\alpha]_D^{18}$ = +78.0 (c 1.05, CH_3OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.62 (s, 1H, Naph$H$), 8.19 (d, J = 8.0 Hz, 1H, Naph$H$), 8.16 (d, J = 8.8 Hz, 1H, Naph$H$), 8.08 (d, J = 8.0 Hz, 1H, Naph$H$), 7.94 (dd, J = 8.8, 2.0 Hz, 1H, Naph$H$), 7.80−7.68 (m, 2H, Naph$H$), 4.70 (d, J = 3.4 Hz, 1H, H-1), 4.56 (br d, J = 4.9 Hz, 1H, OH), 4.41 (br d, J = 4.6 Hz, 1H, OH), 4.25 (dd, J = 9.8, 3.4 Hz, 1H, H-2), 3.82 (ddd, J = 9.8, 8.8, 5.1 Hz, 1H, H-3), 3.77−3.70 (m, 1H, H-6a), 3.70−3.58 (m, 2H, H-6b and OH), 3.55−3.45 (m, 1H, H-5), 3.36 (ddd, J = 9.8, 8.8, 4.9 Hz, 1H, H-4), 3.21 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 136.2, 135.0, 132.9, 130.4, 130.3, 130.3, 130.3, 128.9, 128.7, 123.8, 98.2, 81.4, 73.0, 71.8, 71.7, 62.2, 55.2. IR (solid) 3372, 2932, 1456, 1352, 1175, 1028, 966, 864 cm^{-1}. MS m/z (rel intensity) 385 (M+H$^+$, 5), 353 (5), 279 (10), 191 (20), 167 (20), 149 (100), 127 (30), 115 (10). HRMS calcd for $C_{17}H_{21}O_8S$ (M + H$^+$): 385.0952, found 385.0964.

*Methyl 2-O-(2-Nitrobenzenesulfonyl)-α-D-glucopyranoside (**10**).* Yield: 61.6 mg, 16%. White solid. R_f = 0.20 (MeOH/CHCl$_3$, 10:90). Mp 44−46 °C. $[\alpha]_D^{21}$ = +34.4 (c 1.04, CH_3OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.29 (d, J = 7.8 Hz, 1H, 2-NO$_2$−PhH), 8.10−7.90 (m, 3H, 2-NO$_2$−PhH), 4.82 (d, J = 3.7 Hz, 1H, H-1), 4.65 (d, J = 5.1 Hz, 1H, OH), 4.56 (d, J = 5.1 Hz, 1H, OH), 4.42 (dd, J = 9.8, 3.7 Hz, 1H, H-2), 3.95−3.85 (m, 1H, H-3), 3.85−3.75 (m, 1H, H-6a), 3.79 (br s, 1H, OH), 3.75−3.60 (m, 1H, H-6b), 3.60−3.50 (m, 1H, H-5), 3.44 (ddd, J = 9.8, 9.0, 4.9, 1H, H-4), 3.29 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 149.1, 136.2, 133.4, 131.9, 130.4, 125.6, 98.0, 82.7, 72.9, 71.8, 71.7, 62.0, 55.2. IR (solid) 3385, 2936, 1541, 1443, 1364, 1184, 1026, 959 cm^{-1}. MS m/z (rel intensity) 380 (M + H$^+$, 5), 348 (10), 307 (20), 289 (15), 186 (10), 154 (100), 149 (45), 137 (55). HRMS calcd for $C_{13}H_{18}NO_{10}S$ (M + H$^+$): 380.0646, found 380.0667. Anal. calcd for $C_{13}H_{17}NO_{10}S$: C, 41.16; H, 4.52; N, 3.69. Found: C, 41.06; H, 4.23; N, 3.59.

*Methyl 2-O-(3-Nitrobenzenesulfonyl)-α-D-glucopyranoside (**11**).* Yield: 341.9 mg, 90%. White solid. R_f = 0.33 (MeOH/CHCl$_3$, 10:90). Mp 55−57 °C. $[\alpha]_D^{21}$ = +34.4 (c 1.04, CH_3OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.72 (t, J = 2.2 Hz, 1H, 3-NO$_2$−PhH), 8.61 (ddd, J = 8.3, 2.2, 1.0 Hz, 1H, 3-NO$_2$−PhH), 8.39 (ddd, J = 7.8, 2.2, 1.0 Hz, 1H, 3-NO$_2$−PhH), 8.10−7.95 (m, 1H, 3-NO$_2$−PhH), 4.83 (d, J = 3.7 Hz, 1H, H-1), 4.61 (d, J = 5.1 Hz, 1H, OH), 4.45 (d, J = 4.9 Hz, 1H, OH), 4.30 (dd, J = 9.8, 3.7 Hz, 1H, H-2), 3.85−3.73 (m, 2H, H-3 and H-6a), 3.73−3.60 (m, 2H, H-6b and OH), 3.60−3.47 (m, 1H, H-5), 3.44−3.30 (m, 1H, H-4), 3.32 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 149.1, 139.4, 134.6, 131.9, 129.1, 123.9, 98.1, 82.2, 73.0, 71.8, 71.6, 62.1, 55.2. IR (solid) 3383, 2936, 1609, 1533, 1350, 1186, 1026, 962 cm^{-1}. MS m/z (rel intensity) 380 (M + H$^+$, 5), 348 (10), 307 (15), 289 (20), 167 (20), 154 (100), 145 (80), 137 (75). HRMS calcd for $C_{13}H_{18}NO_{10}S$ (M + H$^+$): 380.0646, found 380.0657. Anal. calcd for $C_{13}H_{17}NO_{10}S$: C, 41.16; H, 4.52; N, 3.69. Found: C, 41.39; H, 4.18; N, 3.64.

*Methyl 2-O-(4-Nitrobenzenesulfonyl)-α-D-glucopyranoside (**12**).*[14] Yield: 322.0 mg, 85%. White solid. R_f = 0.33 (MeOH/CHCl$_3$, 10:90). Mp 151−153 °C (lit.[14] 148 °C). $[\alpha]_D^{20}$ = +98.0 (c 1.15, CH_3OH) {lit.[14] $[a]_D^{23}$ = +107.0 (c 1.58, $(CH_3)_2CO$)}. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.49 (d, J = 9.2 Hz, 2H, 4-NO$_2$−PhH), 8.26 (d, J = 9.2 Hz, 2H, 4-NO$_2$−PhH), 4.79 (d, J = 3.7 Hz, 1H, H-1), 4.57 (d, J = 5.1 Hz, 1H, OH), 4.43 (d, J = 4.9 Hz, 1H, OH), 4.29 (dd, J = 9.8, 3.7 Hz, 1H, H-2), 3.85−3.70 (m, 2H, H-3 and H-6a), 3.70−3.60 (m, 2H, H-6b and OH), 3.55−3.45 (m, 1H, H-5), 3.41−3.34 (m, 1H, H-4), 3.30 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 143.2, 130.4 (2C), 125.2 (3C), 98.1, 82.3, 73.1, 71.8, 71.7, 62.1, 55.2. IR (solid) 3343, 2905, 1533, 1352, 1320, 1186, 1015, 988 cm^{-1}. MS m/z (rel intensity) 380 (M + H$^+$, 5), 348 (5), 307 (20), 289 (15), 154 (100), 137 (70), 107 (20), 77 (15). HRMS calcd for $C_{13}H_{18}NO_{10}S$ (M + H$^+$): 380.0646, found 380.0646. Anal. calcd for $C_{13}H_{17}NO_{10}S$: C, 41.16; H, 4.52; N, 3.69. Found: C, 41.09; H, 4.41; N, 3.61.

*Methyl 2-O-(3-Trifluoromethylbenzenesulfonyl)-α-D-glucopyranoside (**13**).* Yield: 351.0 mg, 87%. White solid. R_f = 0.36 (MeOH/CHCl$_3$, 10:90). Mp 36−38 °C. $[\alpha]_D^{21}$ = +82.6 (c 1.06, CH_3OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.35−8.20 (m, 2H, 3-CF$_3$−PhH), 8.12 (d, J = 7.8 Hz, 1H, 3-CF$_3$−PhH), 7.95 (t, J = 7.8 Hz, 1H, 3-CF$_3$−PhH), 4.80 (d, J = 3.7 Hz, 1H, H-1), 4.68 (d, J = 5.1 Hz, 1H, OH), 4.51 (d, J = 4.9 Hz, 1H, OH), 4.29 (dd, J = 9.8, 3.7 Hz, 1H, H-2), 3.90−4.60 (m, 4H, H-3, H-6 and OH), 3.60−3.50 (m, 1H, H-5), 3.45−3.35 (m, 1H, H-4), 3.29 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 139.0, 132.6, 131.7 (q, J = 33.1 Hz), 131.5, 131.3 (q, J = 4.1 Hz), 125.5 (q, J = 4.1 Hz), 124.3 (q, J = 272.3 Hz), 98.1, 81.9, 72.9, 71.7, 71.5, 62.1, 55.2. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −62.3 (s, 3F). IR (solid) 3356, 2938, 1435, 1368, 1325, 1179, 1128, 1026 cm^{-1}. MS m/z (rel intensity) 403 (M + H$^+$, 5), 391 (60), 371 (40), 353 (40), 293 (40), 209 (75), 149 (100), 145 (85). HRMS calcd for $C_{14}H_{18}F_3O_8S$ (M + H$^+$): 403.0669, found 403.0679. Anal. calcd for $C_{14}H_{17}F_3O_8S$: C, 41.79; H, 4.26. Found: C, 41.51; H, 4.33.

*Methyl 2-O-(3-Fluorobenzenesulfonyl)-α-D-glucopyranoside (**14**).* Yield: 280.1 mg, 80%. White solid. R_f = 0.32 (MeOH/CHCl$_3$, 10:90). Mp 36−39 °C. $[\alpha]_D^{19}$ = +93.2 (c 1.07, CH_3OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.84 (dd, J = 1.7, 1.0 Hz, 1H, 3-F-PhH), 7.80−7.70 (m, 2H, 3-F-PhH), 7.65−7.50 (m, 1H, 3-F-PhH), 4.75 (d, J = 3.7 Hz, 1H, H-1), 4.66 (d, J = 5.1 Hz, 1H, OH), 4.49 (d, J = 4.9 Hz, 1H, OH), 4.24 (dd, J = 9.8, 3.7 Hz, 1H, H-2), 3.90−3.60 (m, 4H, H-3, H-6 and OH), 3.52 (ddd, J = 9.8, 4.9, 2.4 Hz, 1H, H-5), 3.40 (ddd, J = 9.8, 4.9, 1.0 Hz, 1H, H-

4), 3.45 (s, 3H, OC*H*$_3$). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.0 (d, *J* = 249.1 Hz), 139.7 (d, *J* = 7.4 Hz), 132.3 (d, *J* = 8.3 Hz), 124.9 (d, *J* = 3.3 Hz), 121.8 (d, *J* = 21.5 Hz), 115.9 (d, *J* = 25.7 Hz), 98.1, 81.7, 73.0, 71.7, 71.6, 62.1, 55.2. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −110.4 to −110.6 (m, 1F). IR (solid) 3385, 2934, 1439, 1364, 1229, 1177, 1024, 964 cm^{-1}. MS *m*/*z* (rel intensity) 353 (M + H$^+$, 10), 321 (40), 303 (15), 243 (20), 149 (100), 145 (90), 137 (65), 127 (75). HRMS calcd for $C_{13}H_{18}FO_8S$ (M + H$^+$): 353.0701, found 353.0704. Anal. calcd for $C_{13}H_{17}FO_8S$: C, 44.32; H, 4.86. Found: C, 44.55; H, 5.11.

*Methyl 2-O-(3-Chlorobenzenesulfonyl)-α-D-glucopyranoside (**15**).* Yield: 281.4 mg, 76%. White solid. R_f = 0.30 (MeOH/CHCl$_3$, 10:90). Mp 38−39 °C. $[\alpha]_D^{23}$ = +88.8 (*c* 1.05, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.05−7.90 (m, 2H, 3-Cl-Ph*H*), 7.80 (ddd, *J* = 8.1, 2.0, 1.0 Hz, 1H, 3-Cl-Ph*H*), 7.70 (t, *J* = 8.1 Hz, 1H, 3-Cl-Ph*H*), 4.77 (d, *J* = 3.7 Hz, 1H, *H*-1), 4.72 (br s, 1H, O*H*), 4.55 (br s, 1H, O*H*), 4.27 (dd, *J* = 9.8, 3.7 Hz, 1H, *H*-2), 3.82 (t, *J* = 9.3 Hz, 1H, *H*-3), 3.80 (br s, 1H, O*H*), 3.79 (dd, *J* = 11.8, 2.2 Hz, *H*-6a), 3.68 (dd, *J* = 11.8, 4.9 Hz, 1H, *H*-6b), 3.54 (ddd, *J* = 9.8, 4.9, 2.2 Hz, 1H, *H*-5), 3.42 (t, *J* = 9.8 Hz, 1H, *H*-4), 3.29 (s, 3H, OC*H*$_3$). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 139.4, 135.3, 134.6, 131.8, 128.4, 127.2, 98.0, 81.6, 72.8, 71.6, 71.4, 62.0, 55.2. IR (solid) 3372, 2934, 1462, 1362, 1180, 1026, 964, 851 cm^{-1}. MS *m*/*z* (rel intensity) 369 (M + H$^+$, 10), 337 (40), 319 (15), 259 (15), 175 (40), 145 (100), 137 (80), 127 (85). HRMS calcd for $C_{13}H_{18}ClO_8S$ (M + H$^+$): 369.0405, found 369.0425. Anal. calcd for $C_{13}H_{17}ClO_8S$: C, 42.34; H, 4.65. Found: C, 42.05; H, 4.55.

*Methyl 2-O-(3-Bromobenzenesulfonyl)-α-D-glucopyranoside (**16**).* Yield: 300.0 mg, 73%. White solid. R_f = 0.31 (MeOH/CHCl$_3$, 10:90). Mp 37−39 °C. $[\alpha]_D^{23}$ = +78.1 (*c* 1.18, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.11 (s, 1H, 3-Br-Ph*H*), 7.96 (dd, *J* = 15.1, 8.1, 2H, 3-Br-Ph*H*), 7.64 (t, *J* = 8.1 Hz, 1H, 3-Br-Ph*H*), 4.75 (d, *J* = 3.7 Hz, 1H, *H*-1), 4.70 (d, *J* = 5.1 Hz, 1H, O*H*), 4.51 (d, *J* = 4.9 Hz, 1H, O*H*), 4.25 (dd, *J* = 9.8, 3.7 Hz, 1H, *H*-2), 3.90−3.60 (m, 4H, *H*-3, *H*-6 and O*H*), 3.60−3.50 (m, 1H, *H*-5), 3.48−3.35 (m, 1H, *H*-4), 3.29 (s, 3H, OC*H*$_3$). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 139.7, 137.6, 132.0, 131.2, 127.6, 123.1, 98.0, 81.7, 72.9, 71.7, 71.5, 62.1, 55.2. IR (solid) 3366, 2932, 1460, 1362, 1180, 1024, 964, 849 cm^{-1}. MS *m*/*z* (rel intensity) 413 (M + H$^+$, 5), 383 (15), 381 (15), 307 (15), 154 (100), 145 (35), 137 (75), 127 (25). HRMS calcd for $C_{13}H_{18}BrO_8S$ (M + H$^+$): 412.9900, found 412.9914. Anal. calcd for $C_{13}H_{17}BrO_8S$: C, 37.78; H, 4.15. Found: C, 37.68; H, 3.86.

*Methyl 2-O-(3-Toluenesulfonyl)-α-D-glucopyranoside (**17**).* Yield: 138.8 mg, 40%. White solid. R_f = 0.35 (MeOH/CHCl$_3$, 10:90). Mp 33−35 °C. $[\alpha]_D^{23}$ = +68.0 (*c* 1.07, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.85−7.70 (m, 2H, 3-Me-Ph*H*), 7.65−7.50 (m, 2H, 3-Me-Ph*H*), 4.63 (d, 3.7 Hz, 1H, *H*-1), 4.63 (br s, 1H, O*H*), 4.49 (br s, 1H, O*H*), 4.18 (dd, *J* = 9.8, 3.7 Hz, 1H, *H*-2), 3.90−3.60 (m, 4H, *H*-3, *H*-6 and O*H*), 3.58−3.45 (m, 1H, *H*-5), 3.39 (t, *J* = 8.4 Hz, 1H, *H*-4), 3.22 (s, 3H, OC*H*$_3$), 2.46 (s, 3H, 3-C*H*$_3$-Ph). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 140.3, 137.8, 135.3, 129.9, 128.9, 125.8, 98.0, 81.1, 72.9, 71.7, 71.5, 62.1, 55.2, 21.1. IR (solid) 3368, 2930, 1435, 1358, 1172, 1026, 968, 873 cm^{-1}. MS *m*/*z* (rel intensity) 349 (M + H$^+$, 10), 317 (65), 299 (20), 281 (10), 239 (15), 155 (85), 127 (100), 91 (100). HRMS calcd for $C_{14}H_{21}O_8S$ (M + H$^+$): 349.0952, found 349.0937. Anal. calcd for $C_{14}H_{20}O_8S\cdot0.5\,H_2O$: C, 47.05; H, 5.92. Found: C, 47.16; H, 6.24.

*Methyl 2-O-(4-Toluenesulfonyl)-α-D-glucopyranoside (**18**).*[9b] Yield: 90.6 mg, 26%. White solid. R_f = 0.23 (MeOH/CHCl$_3$, 10:90). Mp 135−137 °C (lit.[9b] 140−142 °C). $[\alpha]_D^{27}$ = +79.0 (*c* 0.60, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.84 (d, *J* = 8.2 Hz, 2H, 4-Me-Ph*H*), 7.47 (d, *J* = 8.2 Hz, 2H, 4-Me-Ph*H*), 4.64 (d, 3.7 Hz, 1H, *H*-1), 4.57 (br s, 1H, O*H*), 4.47 (br s, 1H, O*H*), 4.15 (dd, *J* = 9.8, 3.7 Hz, 1H, *H*-2), 3.83−3.70 (m, 1H, *H*-6a), 3.79 (t, *J* = 9.2 Hz, 1H, *H*-3), 3.65 (br s, 1H, O*H*), 3.65 (dd, *J* = 11.5, 5.1 Hz, 1H, *H*-6b), 3.51 (dd, *J* = 10.1, 5.1 Hz, 1H, *H*-5), 3.38 (t, *J* = 9.3 Hz, 1H, *H*-4), 3.24 (s, 3H, OC*H*$_3$), 2.46 (s, 3H, 4-C*H*$_3$-Ph). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 145.7, 135.1, 130.6 (2C), 128.8 (2C), 98.1, 81.0, 73.0, 71.8, 71.7, 62.2, 55.2, 21.5. IR (solid) 3383, 2928, 1687, 1358, 1175, 1032, 970, 849 cm^{-1}. MS *m*/*z* (rel intensity) 349 (M + H$^+$, 15), 317 (100), 299 (25), 281 (10), 239 (15), 155 (90), 145 (95), 127 (90). HRMS calcd for $C_{14}H_{21}O_8S$ (M + H$^+$): 349.0952, found 349.0942.

*Methyl 2-O-[3,5-Bis(trifluoromethyl)benzenesulfonyl]-α-D-glucopyranoside (**19**).* Yield: 460.2 mg, 98%. White solid. R_f = 0.31 (MeOH/CHCl$_3$, 10:90). Mp 108−109 °C. $[\alpha]_D^{17}$ = +79.5 (*c* 1.29, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.55 (s, 2H, 3,5-CF$_3$−Ph*H*), 8.47 (s, 1H, 3,5-CF$_3$−Ph*H*), 4.88 (d, *J* = 3.7 Hz, 1H, *H*-1), 4.66 (br s, 1H, O*H*), 4.45 (br s, 1H, O*H*), 4.37 (dd, *J* = 9.8, 3.7 Hz, 1H, *H*-2), 3.79 (t, *J* = 9.3 Hz, 1H, *H*-3), 3.85−3.72 (m, 2H, *H*-6a and O*H*), 3.65 (dd, *J* = 11.7, 5.1 Hz, 1H, *H*-6b), 3.54−3.50 (m, 1H, *H*-5), 3.36 (t, *J* = 9.3 Hz, 1H, *H*-4), 3.36 (s, 3H, OC*H*$_3$). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 140.4, 133.0 (q, *J* = 34.8 Hz, 2C), 129.7 (q, *J* = 3.3 Hz, 2C), 128.4 (sept, *J* = 3.3 Hz), 123.6 (q, *J* = 272.3 Hz, 2C), 98.2, 82.5, 73.1, 71.8, 71.6, 62.1, 55.2. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −62.4 (s, 6F). IR (solid) 3377, 2932, 1381, 1362, 1279, 1179, 1134, 974 cm^{-1}. MS *m*/*z* (rel intensity) 471 (M + H$^+$, 10), 421 (35), 361 (30), 277 (30), 213 (35), 154 (25), 145 (100), 127 (70). HRMS calcd for $C_{15}H_{17}F_6O_8S$ (M + H$^+$): 471.0543, found 471.0559. Anal. calcd for $C_{15}H_{16}F_6O_8S$: C, 38.30; H, 3.43. Found: C, 38.29; H, 3.14.

*Methyl 2-O-(3,5-Dichloro)benzenesulfonyl-α-D-glucopyranoside (**20**).* Yield: 336.8 mg, 91%. White solid. R_f = 0.35 (MeOH/CHCl$_3$, 10:90). Mp 51−53 °C. $[\alpha]_D^{22}$ = +86.6 (*c* 1.05, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.00−7.80 (m, 3H, 3,5-Cl-Ph*H*), 4.84 (d, *J* = 3.7 Hz, 1H, *H*-1), 4.76 (br s, 1H, O*H*), 4.55 (br s, 1H, O*H*), 4.31 (dd, *J* = 9.8, 3.7 Hz, 1H, *H*-2), 3.90−3.75 (m, 3H, *H*-3, *H*-6a and O*H*), 3.75−3.60 (m, 1H, *H*-6b), 3.60−3.50 (m, 1H, *H*-5), 3.42 (t, *J* = 8.9 Hz, 1H, *H*-4), 3.34 (s, 3H, OC*H*$_3$). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 140.6, 136.4 (2C), 134.3, 127.3 (2C), 98.1, 82.2, 72.9, 71.7, 71.5, 62.1, 55.2. IR (solid) 3354, 2934, 1570, 1369, 1184, 1144, 1026, 962 cm^{-1}. MS *m*/*z* (rel intensity) 403 (M + H$^+$, 5), 391 (10), 371 (10), 307 (10), 289 (10), 154 (100), 145 (35), 137 (90). HRMS calcd for $C_{13}H_{17}Cl_2O_8S$ (M + H$^+$): 403.0016, found 403.0026. Anal. calcd for $C_{13}H_{16}O_8S$: C, 38.72; H, 4.00. Found: C, 38.44; H, 3.79.

*Methyl 6-O-(3,5-Difluorobenzenesulfonyl)-β-D-glucopyranoside (**22**).* Yield: 368.5 mg, >99%. White solid. R_f = 0.21 (MeOH/CHCl$_3$, 10:90). Mp 63−64 °C. $[\alpha]_D^{19}$ = −16.3 (*c* 1.00, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.70−7.40 (m, 3H, 3,5-F-Ph*H*), 4.51 (dd, *J* = 12.7, 2.0 Hz, 1H, *H*-6a), 4.50 (br s, 1H, O*H*), 4.45−4.25 (m, 3H, *H*-6b and O*H*), 4.16 (d, *J* = 7.8 Hz, 1H, *H*-1), 3.45−3.55 (m, 1H, *H*-5), 3.45−3.25 (m, 2H, *H*-3 and *H*-5), 3.39 (s, 3H, OC*H*$_3$), 3.15−3.00 (m, 1H, *H*-2). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.8 (d, *J* = 252.4 Hz), 163.6 (d, *J* = 252.4 Hz), 140.2 (t, *J* = 9.1 Hz), 112.5 (d, *J* = 19.9 Hz), 112.4 (d, *J* = 19.9 Hz), 110.3 (t, *J* = 25.7 Hz), 104.8, 77.5, 74.5, 74.2, 71.8, 70.4, 56.7. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −105.9 to −106.1 (m, 2F). IR (solid) 3347, 2922, 1607, 1443, 1364, 1300, 1180, 988 cm^{-1}. MS *m*/*z* (rel intensity) 371 (M + H$^+$, 15), 339 (35), 321 (30), 289 (10), 154 (100), 136 (85), 107 (30), 77 (30). HRMS calcd for $C_{13}H_{17}F_2O_8S$ (M + H$^+$): 371.0607, found 371.0619. Anal. calcd for $C_{13}H_{16}F_2O_8S$: C, 42.16; H, 4.35. Found: C, 42.37; H, 4.06.

*Methyl 3-O-(3,5-Difluorobenzenesulfonyl)-α-D-mannopyranoside (**23**).* Yield: 352.3 mg, 95%. White solid. R_f = 0.32 (MeOH/CHCl$_3$, 10:90). Mp 29−32 °C. $[\alpha]_D^{26}$ = +24.1 (*c* 1.05, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.70−7.55 (m, 2H, 3,5-F-Ph*H*), 7.46 (tt, *J* = 9.0, 2.4 Hz, 1H, 3,5-F-Ph*H*), 4.79 (br s, 1H, O*H*), 4.67 (d, *J* = 1.7 Hz, 1H, *H*-1), 4.64 (dd, *J* = 9.8, 3.3 Hz, 1H, *H*-3), 4.53 (br d, *J* = 5.4 Hz, 1H, O*H*), 4.10−4.06 (m, 1H, *H*-2), 3.98 (td, *J* = 9.8, 6.1 Hz, 1H, *H*-4), 3.78 (dd, *J* = 11.5, 2.3 Hz, 1H, *H*-6a), 3.69 (dd, *J* = 11.5, 4.9 Hz, 1H, *H*-6b), 3.55−3.45 (m, 1H, *H*-5), 3.34 (s, 3H, OC*H*$_3$), 3,14 (br s, 1H, O*H*). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.5 (d, *J* = 252.4 Hz), 163.4 (d, *J* = 252.4 Hz), 141.2 (t, *J* = 9.1 Hz), 112.5 (d, *J* = 19.9 Hz), 112.4 (d, *J* = 19.9 Hz), 110.0 (t, *J* = 25.7 Hz), 102.0, 85.6, 74.2, 70.2, 65.2, 62.2, 54.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.4 to −106.6 (m, 2F). IR (solid) 3406, 2938, 1368, 1300, 1179, 1128, 1055, 961 cm^{-1}. MS *m*/*z* (rel intensity) 371 (M + H$^+$, 20), 339 (35), 307 (15), 289 (15), 249 (15), 154 (100), 149 (30), 137 (90). HRMS calcd for $C_{13}H_{17}F_2O_8S$ (M + H$^+$): 371.0607, found 371.0614. Anal. calcd for $C_{13}H_{16}F_2O_8S$: C, 42.16; H, 4.35. Found: C, 42.44; H, 4.07.

*Methyl 3-O-[3,5-Bis(trifluoromethyl)benzenesulfonyl]-β-D-mannopyranoside (**24**).* Yield: 459.9 mg, 98%. White solid. R_f = 0.30 (MeOH/CHCl$_3$, 10:90). Mp 47−50 °C. $[\alpha]_D^{20}$ = −52.0 (*c* 1.01, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.54 (s, 2H, 3,5-CF$_3$−Ph*H*), 8.45 (s, 1H, 3,5-CF$_3$−Ph*H*), 4.67 (dd, *J* = 8.5, 3.2 Hz, 1H, *H*-3), 4.61 (br d, *J* = 5.6 Hz, 1H, O*H*), 4.55 (s, 1H, *H*-1), 4.20−4.00 (m, 1H, O*H*), 4.13 (d, *J* = 3.2 Hz, 1H, *H*-2), 3.93 (td, *J* = 9.5, 5.1 Hz, 1H, *H*-4), 3.78 (dd, J = 11.7, 2.4 Hz, 1H, H-6a), 3.66 (dd, J = 11.7, 5.0 Hz, 1H, H-6b), 3.45 (s, 3H, OCH_3), 3.30−3.20 (m, 1H, H-5). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 140.8, 133.0 (q, J = 34.8 Hz, 2C), 129.6 (q, J = 4.1 Hz, 2C), 128.3 (sept, J = 3.3 Hz), 123.6 (q, J = 273.1 Hz, 2C), 101.3, 87.0, 77.1, 70.8, 65.4, 62.3, 56.8. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −62.3 (s, 6F). IR (solid) 3435, 2940, 1360, 1277, 1175, 1134, 1072, 943 cm^{-1}. MS m/z (rel intensity) 471 (M + H$^+$, 30), 439 (100), 421 (15), 349 (20), 277 (40), 213 (50), 145 (65), 137 (50). HRMS calcd for $C_{15}H_{17}F_6O_8S$ (M + H$^+$): 471.0543, found 471.0550. Anal. calcd for $C_{15}H_{16}F_6O_8S$: C, 38.30; H, 3.43. Found: C, 38.01; H, 3.15.

*Methyl 3-O-(3,5-Difluorobenzenesulfonyl)-α-D-galactopyranoside (**25**).* Yield: 364.2 mg, 98%. White solid. R_f = 0.32 (MeOH/CHCl$_3$, 10:90). Mp 132−133 °C. $[\alpha]_D{}^{18}$ = +152.6 (c 1.02, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.70−7.50 (m, 2H, 3,5-F-PhH), 7.50−7.35 (m, 1H, 3,5-F-PhH), 4.75−4.60 (m, 1H, H-3), 4.71 (d, J = 3.9 Hz, 1H, H-1), 4.59 (d, J = 5.1 Hz, 1H, OH), 4.22 (t, J = 3.9 Hz, 1H, H-4), 4.10−3.97 (m, 1H, H-2), 3.90−3.65 (m, 5H, H-5, H-6 and OH), 3.33 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.6 (d, J = 252.4 Hz), 163.4 (d, J = 252.4 Hz), 141.5 (t, J = 9.1 Hz), 112.5 (d, J = 19.9 Hz), 112.4 (d, J = 19.9 Hz), 110.0 (t, J = 25.7 Hz), 101.0, 84.7, 71.4, 69.2, 67.2, 61.9, 55.3. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.5 to −106.6 (m, 2F). IR (solid) 3283, 2940, 1609, 1449, 1352, 1306, 1173, 1132 cm^{-1}. MS m/z (rel intensity) 371 (M + H$^+$, 15), 339 (20), 307 (20), 289 (15), 249 (5), 154 (100), 145 (15), 137 (90). HRMS Calcd for $C_{13}H_{17}F_2O_8S$ (M + H$^+$): 371.0607, found 371.0648. Anal. calcd for $C_{13}H_{16}F_2O_8S$: C, 42.16; H, 4.35. Found: C, 42.34; H, 4.07.

*Methyl 3-O-[3,5-Bis(trifluoromethyl)benzenesulfonyl]-β-D-galactopyranoside (**26**).* Yield: 471.0 mg, >99%. White solid. R_f = 0.34 (MeOH/CHCl$_3$, 10:90). Mp 144−146 °C. $[\alpha]_D{}^{21}$ = +37.4 (c 1.10, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.53 (s, 2H, 3,5-CF$_3$−PhH), 8.45 (s, 1H, 3,5-CF$_3$−PhH), 4.64 (dd, J = 9.9 Hz, 1H, H-3), 4.58 (s, 1H, OH), 4.57 (s, 1H, OH), 4.30−4.20 (m, 1H, H-4), 4.14 (d, J = 7.6 Hz, 1H, H-1), 4.00−3.90 (m, 1H, H-5), 3.85−3.65 (m, 3H, H-2, H-6a and OH), 3.61 (dd, J = 11.7, 5.9 Hz, 1H, H-6b), 3.39 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 140.8, 132.8 (q, J = 34.8 Hz, 2C), 129.6 (q, J = 3.9 Hz, 2C), 128.2 (sept, J = 3.9 Hz), 123.6 (q, J = 272.2 Hz, 2C), 105.0, 86.7, 75.1, 69.4, 68.7, 61.7, 56.8. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −62.4 (s, 6F). IR (solid) 3445, 2922, 1358, 1277, 1198, 1134, 1074, 961 cm^{-1}. MS m/z (rel intensity) 471 (M + H$^+$, 15), 439 (35), 349 (20), 277 (15), 213 (15), 154 (100), 136 (85), 77 (35). HRMS calcd for $C_{15}H_{17}F_6O_8S$ (M + H$^+$): 471.0556, found 471.0562. Anal. calcd for $C_{15}H_{16}F_6O_8S$: C, 38.30; H, 3.43. Found: C, 38.57; H, 3.03.

*Isopropyl 3-O-(3,5-Difluorobenzenesulfonyl)-β-D-thiogalactopyranoside (**27**).* Yield: 390.5 mg, 94%. White solid. R_f = 0.39 (MeOH/CHCl$_3$, 10:90). Mp 123−125 °C. $[\alpha]_D{}^{26}$ = +16.6 (c 1.04, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.70−7.55 (m, 2H, 3,5-F-PhH), 7.45 (tt, J = 9.0, 2.2 Hz, 1H, 3,5-F-PhH), 4.62 (dd, J = 9.3, 3.2 Hz, 1H, H-3), 4.58 (d, J = 5.6 Hz, 1H, OH), 4.49 (d, J = 9.5 Hz, 1H, H-1), 4.44 (d, J = 5.6 Hz, 1H, OH), 4.30−4.20 (m, 1H, H-4), 3.93 (br s, 1H, OH), 3.85−3.60 (m, 4H, H-2, H-5, H-6), 3.18 (sept, J = 6.8 Hz, 1H, SCH(CH$_3$)$_2$), 1.25 (d, J = 6.8 Hz, 3H, SCH(CH_3)$_2$), 1.23 (d, J = 6.8 Hz, 3H, SCH(CH_3)$_2$). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.6 (d, J = 252.4 Hz), 163.3 (d, J = 252.4 Hz), 141.4 (t, J = 9.1 Hz), 112.7 (d, J = 19.9 Hz), 112.6 (d, J = 19.9 Hz), 110.0 (t, J = 25.7 Hz), 87.6, 86.4, 79.2, 69.0, 68.5, 61.9, 35.1, 24.3, 24.3. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.7 to −106.8 (m, 2F). IR (solid) 3397, 2965, 1607, 1447, 1364, 1298, 1177, 1074 cm^{-1}. MS m/z (rel intensity) 415 (M + H$^+$, 20), 397 (20), 339 (40), 307 (10), 289 (10), 249 (25), 154 (100), 136 (75). HRMS calcd for $C_{15}H_{21}F_2O_7S_2$ (M + H$^+$): 415.0691, found 415.0720. Anal. calcd for $C_{15}H_{20}F_2O_7S_2$: C, 43.47; H, 4.86. Found: C, 43.78; H, 4.87.

*Methyl 4-O-(3,5-Difluorobenzenesulfonyl)-β-D-xylopyranoside (**28**).* Yield: 340.0 mg, >99%. White solid. R_f = 0.48 (MeOH/CHCl$_3$, 10:90). Mp 133−135 °C. $[\alpha]_D{}^{21}$ = −63.1 (c 1.04, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.70−7.60 (m, 2H, 3,5-F-PhH), 7.55−7.45 (m, 1H, 3,5-F-PhH), 4.60 (br s, 1H, OH), 4.54 (br s, 1H, OH), 4.38 (td, J = 9.3, 5.4 Hz, 1H, H-4), 4.18 (d, J = 7.3 Hz, 1H, H-1), 4.05 (dd, J = 11.7, 5.4 Hz, 1H, H-5a), 3.59 (td, J = 9.3, 4.2 Hz, 1H, H-3), 3.50 (dd, J = 11.7, 10.0 Hz, 1H, H-5b), 3.42 (s, 3H, OCH_3), 3.19 (t, J = 8.1 Hz, 1H, H-2). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.6 (d, J = 252.4 Hz), 163.5 (d, J = 252.4 Hz), 140.6 (t, J = 9.1 Hz), 112.7 (d, J = 19.9 Hz), 112.6 (d, J = 19.9 Hz), 110.3 (t, J = 25.7 Hz), 105.3, 80.9, 74.6, 74.2, 63.5, 56.8. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.3 to −106.4 (m, 2F). IR (solid) 3491, 3098, 1607, 1439, 1371, 1299, 1186, 962 cm^{-1}. MS m/z (rel intensity) 341 (M + H$^+$, 10), 307 (20), 289 (15), 154 (100), 136 (85), 115 (25), 107 (25), 77 (20). HRMS calcd for $C_{12}H_{15}F_2O_7S$ (M + H$^+$): 341.0501, found 341.0529. Anal. calcd for $C_{12}H_{14}F_2O_7S$: C, 42.35; H, 4.15. Found: C, 42.41; H, 4.11.

*Methyl 3-O-(3,5-Difluorobenzenesulfonyl)-α-L-fucopyranoside (**29**).* Yield: 352.5 mg, >99%. White solid. R_f = 0.46 (MeOH/CHCl$_3$, 10:90). Mp 122−123 °C. $[\alpha]_D{}^{22}$ = −165.1 (c 1.02, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.70−55 (m, 2H, 3,5-F-PhH), 7.53−7.40 (m, 1H, 3,5-F-PhH), 4.72 (dd, J = 10.0, 2.9 Hz, 1H, H-3), 4.65 (d, J = 3.7 Hz, 1H, H-1), 4.50 (d, J = 5.6 Hz, 1H, OH), 4.05−3.85 (m, 3H, H-2, H-4 and H-5), 3.74 (d, J = 9.0 Hz, 1H, OH), 3.32 (s, 3H, OCH_3), 1.20 (d, J = 6.6 Hz, 3H, H-6). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.5 (d, J = 252.4 Hz), 163.4 (d, J = 252.4 Hz), 141.5 (t, J = 9.1 Hz), 112.4 (d, J = 19.9 Hz), 112.3 (d, J = 19.9 Hz), 109.9 (t, J = 25.7 Hz), 101.0, 84.8, 71.6, 66.8, 66.6, 55.4, 16.4. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.5 to −106.6 (m, 2F). IR (solid) 3422, 2941, 1607, 1445, 1350, 1304, 1132, 953 cm^{-1}. MS m/z (rel intensity) 355 (M + H$^+$, 15), 323 (90), 305 (20), 249 (65), 154 (100), 136 (80), 107 (30), 77 (25). HRMS calcd for $C_{13}H_{17}F_2O_7S$ (M + H$^+$): 355.0658, found 355.0689. Anal. calcd for $C_{13}H_{16}F_2O_7S$: C, 44.07; H, 4.55. Found: C, 44.22; H, 4.21.

*Methyl 3-O-(3,5-Difluorobenzenesulfonyl)-β-L-fucopyranoside (**30**).* Yield: 353.8 mg, >99%. White solid. R_f = 0.46 (MeOH/CHCl$_3$, 10:90). Mp 32−35 °C. $[\alpha]_D{}^{19}$ = −39.9 (c 1.10, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.70−7.55 (m, 2H, 3,5-F-PhH), 7.50−7.40 (m, 1H, 3,5-F-PhH), 4.55 (dd, J = 9.8, 3.4 Hz, 1H, H-3), 4.18 (br s, 2H, OH), 4.17 (d, J = 7.6 Hz, 1H, H-1), 3.91 (d, 1H, H-2.7 Hz, 1H, H-4), 3.74 (q, J = 6.3 Hz, 1H, H-5), 3.69 (dd, J = 9.8, 7.6 Hz, 1H, H-2), 3.41 (s, 3H, OCH_3), 1.25 (d, J = 6.3 Hz, 3H, H-6). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.3 (d, J = 251.6 Hz), 163.3 (d, J = 251.6 Hz), 141.2 (t, J = 9.1 Hz), 112.5 (d, J = 19.9 Hz), 112.4 (d, J = 19.9 Hz), 109.8 (t, J = 25.7 Hz), 104.8, 86.4, 71.1, 70.4, 68.9, 56.6, 16.5. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.7 to −106.9 (m, 2F). IR (solid) 3462, 2940, 1609, 1443, 1368, 1300, 1169, 988 cm^{-1}. MS m/z (rel intensity) 355 (M + H$^+$, 10), 323 (95), 305 (30), 249 (100), 187 (75), 154 (55), 129 (80), 101 (60). HRMS calcd for $C_{13}H_{17}F_2O_7S$ (M + H$^+$): 355.0658, found 355.0648. Anal. calcd for $C_{13}H_{16}F_2O_7S$: C, 44.07; H, 4.55. Found: C, 44.23; H, 4.83.

*Methyl 3-O-(3,5-Difluorobenzenesulfonyl)-α-L-rhamnopyranoside (**31**).* Yield: 351.8 mg, >99%. White solid. R_f = 0.48 (MeOH/CHCl$_3$, 10:90). Mp 34−35 °C. $[\alpha]_D{}^{23}$ = −16.1 (c 0.64, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.68−7.55 (m, 2H, 3,5-F-PhH), 7.55−7.40 (m, 1H, 3,5-F-PhH), 4.60 (d, J = 1.2 Hz, 1H, H-1), 4.59 (dd, J = 9.0, 3.2 Hz, 1H, H-3), 4.23 (br s, 2H, OH), 4.04 (dd, J = 3.2, 1.2 Hz, 1H, H-2), 3.65 (t, J = 9.5 Hz, 1H, H-4), 3.60−3.50 (m, 1H, H-5), 3.32 (s, 3H, OCH_3), 1.22 (d, J = 6.1 Hz, 3H, H-6). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 163.6 (d, J = 252.4 Hz), 163.5 (d, J = 252.4 Hz), 141.4 (t, J = 9.1 Hz), 112.5 (d, J = 19.9 Hz), 112.5 (d, J = 19.9 Hz), 110.0 (t, J = 25.7 Hz), 102.0, 85.4, 70.4, 70.4, 69.5, 54.9, 18.0. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −106.5 to −106.6 (m, 2F). IR (solid) 3449, 2936, 1609, 1443, 1364, 1300, 1179, 1049 cm^{-1}. MS m/z (rel intensity) 355 (M + H$^+$, 5), 323 (85), 305 (10), 247 (95), 187 (30), 154 (80), 137 (100), 129 (90). HRMS calcd for $C_{13}H_{17}F_2O_7S$ (M + H$^+$): 355.0658, found 355.0683. Anal. calcd for $C_{13}H_{16}F_2O_7S$: C, 44.07; H, 4.55. Found: C, 44.31; H, 4.42.

*Methyl 5-O-[3,5-bis(trifluoromethyl)benzenesulfonyl]-β-D-arabinofuranoside (**32**).* Yield: 312.7 mg, 71%. White solid. R_f = 0.50 (MeOH/CHCl$_3$, 10:90). Mp 65−67 °C. $[\alpha]_D{}^{25}$ = +56.2 (c 1.28, CH$_3$OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.53 (s, 2H, 3,5-CF$_3$−PhH), 8.49 (s, 1H, 3,5-CF$_3$−PhH), 4.70−4.10 (m, 1H, OH), 4.54 (d, J = 1.5 Hz, 1H, H-1), 4.54 (dd, J = 11.4, 2.9 Hz, 1H, H-5a), 4.41 (dd, J = 11.4, 6.2 Hz, 1H, H-5b), 4.04 (td, J = 6.3, 2.9 Hz, 1H, H-4), 3.95 (dd, J = 3.4, 1.5 Hz, 1H, H-2), 3.84 (dd, J = 6.3, 3.4 Hz, 1H, H-3), 3.20 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 140.0, 133.3 (q, J = 34.8 Hz, 2C), 129.5 (q, J = 4.1 Hz, 2C), 128.6 (sept, J = 3.3 Hz), 123.6 (q, J = 273.1 Hz, 2C), 110.4, 82.7, 81.9, 78.3, 72.5, 54.9. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −62.3 (s, 6F). IR (solid) 3414, 2936, 1360, 1279, 1177, 1136, 1109, 951 cm^{-1}. MS m/z (rel intensity) 441 (M + H$^+$, 5), 439 (10), 409 (55), 391 (25), 361 (30), 277 (40), 213 (60), 115 (100). HRMS Calcd for $C_{14}H_{15}F_6O_7S$ (M + H$^+$): 441.0437, found 441.0409.

Regioselective Sulfonylation of Disaccharide Catalyzed by Organtin Dichloride. After stirring the mixture of 4-methoxyphenyl β-D-lactopyranoside (224.2 mg, 0.50 mmol) and dibutyltin dichloride (15.2 mg, 0.05 mmol) in THF/DMF (18 mL, 8: 1) in vial at room temperature for 10 min, 3,5-bis(trifluoromethyl)benzenesulfonyl chloride (234.5 mg, 0.75 mmol) and 1,2,2,6,6-pentamethylpiperidine (0.181 mL, 1.0 mmol) were added to the suspension at 20 °C. After stirring vigorously for 24 h at 20 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over $MgSO_4$, filtrated, and concentrated in *vacuo*. The residue was purified by SiO_2 column chromatography (hexane/ethyl acetate = 3/1−0/1) to give 4-methoxyphenyl 3′-*O*-[3,5-bis(trifluoromethyl)benzenesulfonyl]-β-D-lactopyranoside **33** (357.9 mg, 99%) as a white solid and disulfonates (4.3 mg, <1%).

*4-Methoxyphenyl 3′-O-[3,5-Bis(trifluoromethyl)benzenesulfonyl]-β-D-lactopyranoside (**33**).* Yield: 357.9 mg, 99%. White solid. R_f = 0.50 (MeOH/$CHCl_3$, 20:80). Mp 142−145 °C. $[\alpha]_D^{24}$ = −4.8 (c 0.52, CH_3OH). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.55 (s, 2H, 3,5-CF_3−Ph*H*), 8.46 (s, 1H, 3,5-F-Ph*H*), 7.00 (dd, J = 6.8, 2.2 Hz, 2H, CH_3O-Ph*H*), 6.83 (dd, J = 6.8, 2.2 Hz, 2H, CH_3O-Ph*H*), 5.05 (br s, 1H, O*H*), 4.84 (br s, 1H, O*H*), 4.84 (d, J = 7.6 Hz, 1H, *H*-1), 4.77 (dd, J = 9.8, 3.2 Hz, 1H, *H*-3′), 4.50 (d, J = 7.8 Hz, 1H, *H*-1′), 4.27 (d, J = 3.2 Hz, 1H, *H*-4′), 3.90 (t, J = 8.8 Hz, 1H, *H*-2′), 3.87−3.40 (m, 11H, *H*-2, *H*-3, *H*-4, *H*-5, *H*-6, *H*-5′, *H*-6′ and O*H*), 3.74 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 155.9, 152.6, 140.7, 132.9 (q, J = 34.8 Hz, 2C), 129.6 (q, J = 4.1 Hz, 2C), 128.3 (sept, J = 4.1 Hz), 123.6 (q, J = 272.2 Hz, 2C), 118.8 (2C), 115.1 (2C), 104.1, 102.6, 86.1, 80.3, 76.0, 75.9, 75.5, 74.3, 69.2, 68.9, 61.9 (2C), 55.7. ^{19}F NMR (376 MHz, $(CD_3)_2CO$) δ −62.3 (s, 6F). IR (solid) 3383, 2920, 1508, 1360, 1279, 1229, 1180, 1134, 1030 cm^{-1}. MS m/z (rel intensity) 747 (M + Na$^+$, 15), 725 (M + H$^+$, 5), 601 (5), 349 (10), 277 (15), 202 (55), 124 (100). HRMS calcd for $C_{27}H_{31}F_6O_{14}S$ (M + H$^+$): 725.1333, found 725.1323. Anal. calcd for $C_{27}H_{30}F_6O_{14}S$: C, 44.76; H, 4.17. Found: C, 44.59; H, 4.33.

Competitive Sulfonylation between Methyl α-D-Glucopyranoside and Monoalcohols. 3,5-Difluorobenzenesulfonyl chloride (276.4 mg, 1.3 mmol) and 1,2,2,6,6-pentamethylpiperidine (0.361 mL, 2.0 mmol) were added to the suspension of the mixture of methyl α-D-glucopyranoside (194.2 mg, 1.0 mmol), cyclohexanemethanol (0.122 mL, 1.0 mmol) and dibutyltin dichloride (15.2 mg, 0.05 mmol) in THF (18 mL) at 10 °C in vial. After stirring vigorously for 12 h at 10 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The organic layer was washed with water and brine, dried over $MgSO_4$, filtrated, and concentrated in *vacuo*. The residue was purified by SiO_2 column chromatography (hexane/ethyl acetate = 3/1−0/1) to give methyl 2-*O*-(3,5-difluorobenzenesulfonyl)-α-D-glucopyranoside **1** (355.9 mg, 96%) as a white solid and disulfonates (14.2 mg, 3%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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