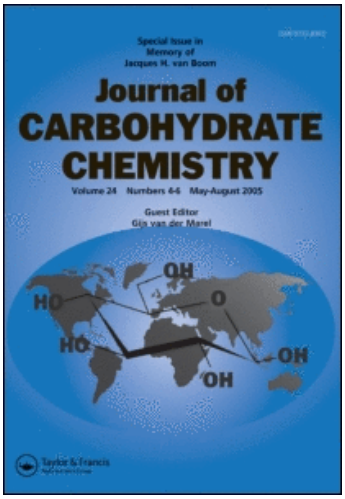

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A NEW INTRAMOLECULAR MIGRATION IN THIOSUGAR CHEMISTRY: S → O TRANSFER OF A BENZOTHIAZOL-2-YL GROUP IN SACCHARIDIC SULFONES

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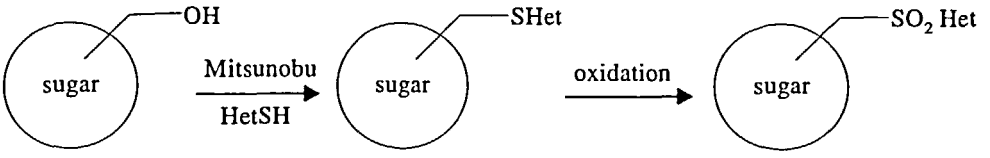
ABSTRACT

Saccharidic benzothiazol-2-yl sulfones - readily obtained through regioselective Mitsunobu thiofunctionalization followed by standard S-oxidation - can easily undergo benzothiazol-2-yl group S → O transfer when submitted to the action of a hindered base under controlled conditions. An *ipso*-substitution process is the key-step of this novel intramolecular rearrangement of saccharidic sulfones.

INTRODUCTION

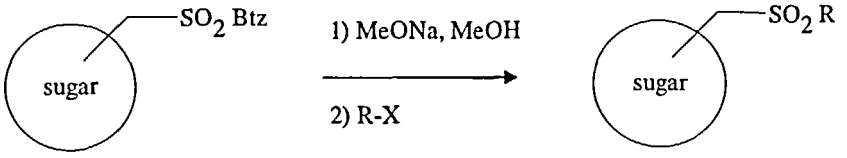
Elaboration of thio-analogs of bioactive osidic structures still remains a major concern in synthetic sugar chemistry.[1] As a continuation of earlier studies,[2] we have developed new pathways for the regioselective thiofunctionalization of sugars[3,4] via a

Mitsunobu reaction using miscellaneous thio-nucleophiles. This method has opened an access to original thiosugar / aza-heterocycle hybrids. In most cases, saccharidic sulfones can be readily obtained through standard oxidation of the corresponding heteroaryl sulfides.



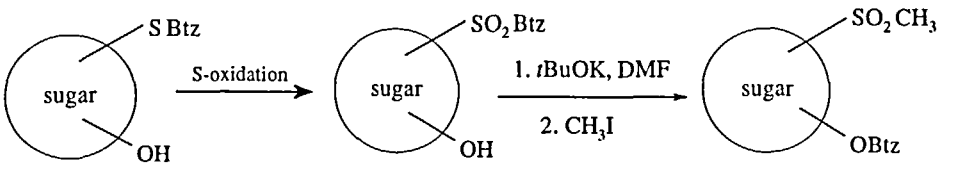
Among the diverse aza-heterocyclic moieties (Het) investigated for the present study, benzothiazol-2-yl (Btz) appeared, in agreement with the literature,[5] as the best candidate.

It has been demonstrated by S. Julia *et al.* that the benzothiazol-2-ylsulfonyl moiety is prone to undergo nucleophilic *ipso*-substitutions.[6] We have already taken advantage of this property for the synthesis of sugar derived alkyl sulfones.[7,8]



RESULTS AND DISCUSSION

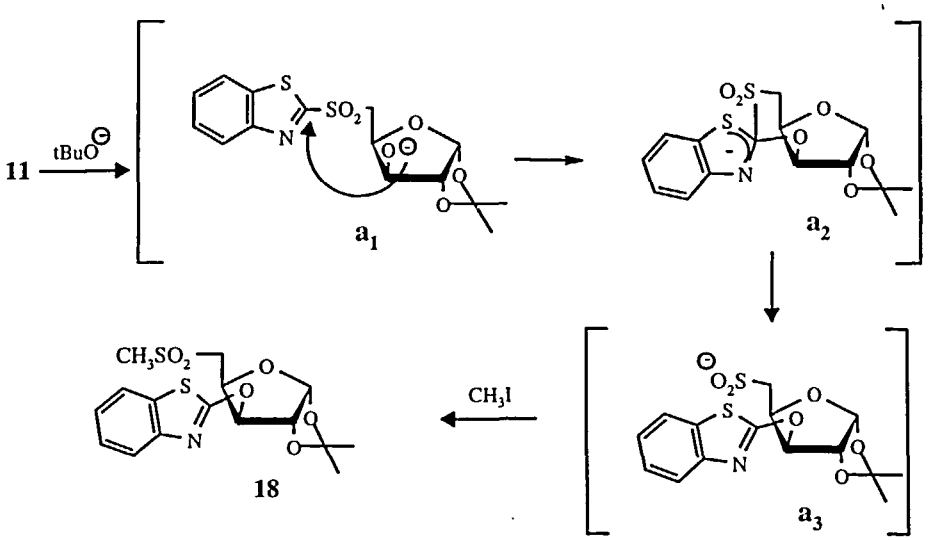
The transsulfonylation process mentioned above can also be envisaged in the form of an intramolecular S → O group transfer provided that free hydroxyl groups are available in the sugar-derived sulfones. When using a hindered base such as potassium *t*-butoxide instead of sodium methoxide,[8] the direct *ipso* attack is strongly disfavoured, so that an internal S → O transfer of the benzothiazol-2-yl group can be provoked.



1 - 7 **8 - 14** **15 - 21**

Deprotonation of the free alcohol function by *t*-BuOK being much faster in DMF than the nucleophilic interaction with the heteroaryl sulfone moiety, the transient alkoxide anion formed attacks the *ipso* carbon to afford a benzothiazol-2-yl ether. The sulfinate anion liberated is finally quenched *in situ* by an electrophilic agent, namely iodomethane.

In agreement with the literature,[5,8] it is possible to suggest a mechanism for the transfer reaction, as depicted in the selected example :



- the alkoxide anion $\mathbf{a_1}$ resulting from *t*BuOK proton-abstraction effects an *ipso*-attack on carbon C-2 of the Btz moiety, thus leading to the negatively charged spiro Meisenheimer complex $\mathbf{a_2}$.
- charge-transfer to the C-5 thio-substituent results in the formation of a sulfinate anion $\mathbf{a_3}$, and the Btz-O linkage at C-3.
- the sulfinate anion is transformed into the methyl sulfone **18** through standard alkyl halide quenching.

This intramolecular migration has been investigated considering various parameters: shape of the cyclic sugar, location of the heteroaryl moiety, distance between OH and benzothiazol-2-yl groups. The reaction was shown to occur in miscellaneous structural situations associated with diverse sugar series.

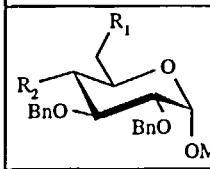
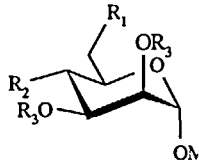
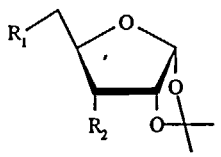
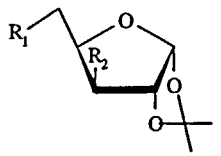
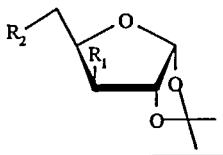
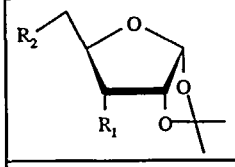
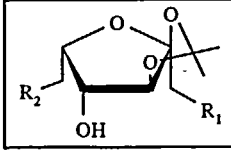
Benzothiazol-2-yl sulfones **8-14** (see Table) could be readily obtained by standard peracid oxidation of the corresponding aza-heterocycle / thiosugar hybrids **1-7**, produced through Mitsunobu thiofunctionalization of the corresponding alcohols. The primary hybrids **1-4** were obtained via regioselective substitution[3,4] whereas the secondary hybrids **5** and **6** required preliminary selective protection of the primary alcohol function[9] prior to Mitsunobu inversion, followed by unmasking of the primary hydroxyl group.

The results of the transfer reaction reported in the Table can be commented on as follows :

- pyranosidic primary sulfone **8** is able to transfer efficiently the benzothiazol-2-yl group from the 6- to the equatorial 4-position (yield 73 %).
- applying the same conditions to the 2,3,4-trihydroxylated sulfone **9** resulted in a comparable 6- to 4- Btz transfer; in addition, some *trans*-cyclic transfer from the 6- to the axial 2-position was also observed (yield 9 %) which led to the **16b** regioisomer.
- in the case of furanosidic primary sulfones **10** and **11**, the 5- to 3-position transfer was quite efficient and no significant difference in yield (74 and 78 %) could be observed between the D-*ribo* and the D-*xylo* series.
- in contrast, furanosidic secondary sulfones **12** and **13** did not undergo the reciprocal 3 → 5 transfer with good yields. However, the efficiency of the transfer was shown to be far superior in the D-*ribo* case (**20**) than in the D-*xylo* case (**19**).
- finally, the reaction proved highly regioselective with the L-*sorbo* sulfone **14** : the « primary to primary » 1 → 6 transfer was strongly favored and no 1 → 4 transfer could be observed.

From the examples presented, it appears that the heteroaryl group transfer is more effective when leaving a primary site to reach another one, either primary or secondary.

Table. Thiosugar moieties involved in the study

Sugar templates	Hybrids (R_1=SBtz ; R_2=OH) *Yield (%) of Mitsunobu*	Sulfones prepared (R_1=SO_2Btz ; R_2=OH) *Yield (%) of oxidation*	Rearranged compounds (R_1=SO_2CH_3 ; R_2=OBtz) *Yield (%) of transfer reaction*
	**1** *70*	**8** *72*	**15** *73*
	**2** (R_3 = H) *66*	**9** (R_3 = H) *72*	**16a** (R_3 = Ac) *70*
	**3** *84*	**10** *62*	**17** *74*
	**4** *89*	**11** *42*	**18** *78*
	**5** *89*	**12** *68*	**19** *33*
	**6** *56*	**13** *62*	**20** *49*
	**7** *90*	**14** *93*	**21** *57*

CONCLUSION

We have described a new intramolecular transsulfonylation process in several sugar series and diverse structural situations. This S → O transfer of a benzothiazol-2-yl moiety is believed to occur through an *ipso*-substitution mechanism involving a transient Meisenheimer complex.

Carbohydrate chemistry contains many examples of intramolecular migration of O-substituents.[10] The transfer of acyl groups, involving orthoacid intermediates, is the best-known in this regard. In the field of thio-sugars, this is to our knowledge the first hetero-migration (from sulfur to oxygen) reported. In contrast with the usually favoured rearrangement of acyl groups from secondary to primary positions, the benzothiazol-2-yl migration occurs preferably from primary to secondary positions.

EXPERIMENTAL

General Procedures. Evaporation: *in vacuo*, conducted with a Büchi rotary evaporator. TLC: precoated silica gel 60F-254 plates (Merck), detection by UV light (254 nm) and spraying with a 10% solution of concentrated sulfuric acid in methanol followed by heating. Specific rotations: Perkin-Elmer polarimeter 141, measured at 20 °C. ^{1}H (250 MHz) and ^{13}C (62.89 MHz) NMR: Bruker AVANCE DPX 250; chemical shifts (δ) in ppm relative to tetramethylsilane as internal standard in $CDCl_3$ solution. Mass spectra: low resolution mass spectra (MS) were measured on a Perkin-Elmer SCIEX API 300 (ion spray or heated nebulizer) and high resolution mass spectra (HRMS) on a VG analytical 70-SV.

General procedure for the synthesis of sulfides 1 to 7. To a solution of the sugar (0.2 g) in pyridine (2 mL) was successively added triphenylphosphine (2 eq), diisopropyl azodicarboxylate (2 eq) and 2-mercaptobenzothiazole (2 eq). The reaction mixture was heated at 80 °C under argon. After solution concentration and toluene coevaporation of pyridine, the residue was chromatographed on silica gel.

Methyl 6-*S*-(Benzothiazol-2-yl)-2,3-di-*O*-benzyl-6-thio-α-D-glucopyranoside (1). Starting from methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside,[11] this procedure gave **1** (0.196 g, 70 %) as a colorless syrup: $[\alpha]_D$ - 112 (*c* 1, $CHCl_3$); ^1H NMR: 3.40 (s, 1H, OH), 3.43 (s, 3H, OCH_3), 3.47 (d, 1H, J_{6a-6b} = 14.5 Hz, H-6b), 3.53 (dd, 1H, J_{1-2} = 3.0 Hz, J_{2-3} = 9.2 Hz, H-2), 3.63 (dd, 1H, J_{3-4} = 9.0 Hz, J_{5-4} = 2.7 Hz, H-4), 3.94 (ft, 1H, H-3), 3.98 (d, 1H, H-6a), 4.05 (m, 1H, H-5), 4.64(d, 1H, H-1), 4.67 and 4.82 (2d, 2H, J_{gem} = 12.2 Hz, CH_2Ph), 4.93 (2d, 2H, J_{gem} = 11.4 Hz, CH_2Ph), 7.24-7.44 (m, 12H, H_{benzyl}, H-6_{Btz} and H-5_{Btz}), 7.73 (d, 1H, $J_{7Btz-6Btz}$ = 7.2 Hz, H-7_{Btz}), 7.84 (d, 1H, $J_{4Btz-5Btz}$ = 8.1 Hz, H-4_{Btz}); ^{13}C NMR: 37.2 (C-6), 57.1 (OCH_3), 71.9 (C-5), 73.6 (C-4), 75.2 and 77.5 (2 CH_2), 80.8 (C-2), 82.5 (C-3), 100.4 (C-1), 122.7 and 122.8 (C-4_{Btz}) and (C-7_{Btz}), 126.4 (C-6_{Btz}), 128.0 (C-5_{Btz}), 129.3-130.1 (C_{benzyl}), 136.7 (C-$3a_{Btz}$), 140.0 and 140.6 (C_{benzyl}), 153.8 (C-$7a_{Btz}$), 171.0 (C-2_{Btz}); HRMS Calcd for $C_{28}H_{29}NO_5S_2$ (523.1487). Found (523.1491).

Methyl 6-*S*-(Benzothiazol-2-yl)-6-thio-α-D-mannopyranoside (2). Starting from commercially available methyl α-D-mannopyranoside (1 g, 5.2 mmol), the same experiment gave **2** (1.271 g, 66 %) as a colorless syrup: $[\alpha]_D$ - 105 (*c* 1, $CHCl_3$); ^1H NMR: 3.40 (s, 3H, OCH_3), 3.52 (dd, 1H, J_{6a-6b} = 14.7 Hz, H-6b), 3.83 (d, 1H, J_{3-4} = 9.7 Hz, H-4), 3.94 (d, 1H, J_{2-3} = 3.3 Hz, H-3), 4.00 (m, 2H, H-2 and H-5), 4.05 (dd, 1H, H-6a), 4.76 (s, 1H, H-1), 7.21 (td, 1H, $J_{6Btz-7Btz} = J_{6Btz-5Btz}$ = 7.8 Hz, $J_{6Btz-4Btz}$ = 1.3 Hz , H-6_{Btz}), 7.32 (td, 1H, H-5_{Btz}), 7.69 (d, 1H, H-7_{Btz}), 7.79 (d, 1H, H-4_{Btz}); HRMS Calcd for $C_{14}H_{17}NO_5S_2$ (343.0548). Found (343.0539).

5-*S*-(Benzothiazol-2-yl)-1,2-*O*-isopropylidene-5-thio-α-D-ribofuranose (3) and **5-*S*-(Benzothiazol-2-yl)-1,2-*O*-isopropylidene-5-thio-α-D-xylofuranose (4)** have been already described in reference 4.

3-*S*-(Benzothiazol-2-yl)-1,2-*O*-isopropylidene-3-thio-5-*O*-trityl-α-D-xylofuranose (5). Starting from 1,2-*O*-isopropylidene-5-*O*-trityl-α-D-ribofuranose[12] (0.2 g, 0.462 mmol) the same experiment gave **5** (0.24 g, 89 %): mp 68-70 °C, $[\alpha]_D$ - 3 (*c* 1, $CHCl_3$); ^1H NMR: 1.34 and 1.61 (2s, 6H, 2 CH_3), 3.34 (dd, 1H, J_{5a-5b} = 9.8 Hz, J_{5-4} = 5.0 Hz, H-5b), 3.54 (dd, 1H, H-5a), 4.67-4.74 (m, 2H, H-4 and H-3), 4.86 (d, 1H, J_{1-2} = 3.6 Hz, H-2), 5.95 (d, 1H, H-1), 7.15-7.50 (m, 17H, H_{trityl}, H-5_{Btz} and H-6_{Btz}), 7.76 (d, 1H,

$J_{7Btz\text{-}6Btz}$ = 8.0 Hz, H-7_{Btz}), 7.90 (d, 1H, $J_{4Btz\text{-}5Btz}$ = 8.0 Hz, H-4_{Btz}); ^{13}C NMR: 26.4 and 26.7 (2 CH_3), 53.8 (C-3), 62.8 (C-5), 78.1 (C-4), 87.0 (C-2), 104.8 (C-1), 112.2 (C_{iso}), 121.0 (C-7_{Btz}), 122.0 (C-4_{Btz}), 124.5 (C-6_{Btz}), 126.1 (C-5_{Btz}),127.0-128.7 (C_{trityl}), 135.3 (C-$3a_{Btz}$), 143.6 (C-$7a_{Btz}$), 153.0 (C_{trityl}), 164.0 (C-2_{Btz}); HRMS Calcd for $C_{34}H_{31}NO_4S_2$ (581.1694). Found (581.1688).

3-*S*-(Benzothiazol-2-yl)-1,2-*O*-isopropylidene-3-thio-5-*O*-trityl-α-D-ribofuranose (6). Starting from 1,2-*O*-isopropylidene-5-*O*-trityl-α-D-xylofuranose[12] (1.03 g, 2.384 mmol) the same experiment gave **6** (0.782 g, 56 %): mp 78-80 °C, $[\alpha]_D$ + 34 (*c* 1, $CHCl_3$); ^{1}H NMR: 1.40 and 1.56 (2s, 6H, $2CH_3$), 3.20 (dd, 1H, $J_{5a\text{-}5b}$ = 10.9 Hz, $J_{5\text{-}4}$ = 4.3 Hz, H-5b), 3.45 (dd, 1H, H-5a), 4.23 (m, 1H, H-4), 4.75 (dd, 1H, $J_{3\text{-}2}$ = 10.4 Hz, $J_{3\text{-}4}$ = 4.7 Hz, H-3), 5.04 (t, 1H, $J_{2\text{-}1}$ = 10.4 Hz, H-2), 6.06 (d, 1H, H-1), 7.05-7.40 (m, 17H, H_{trityl}, H-5_{Btz} and H-6_{Btz}), 7.63 (dd, 1H, $J_{7Btz\text{-}6Btz}$ = 8.0 Hz, $J_{7Btz\text{-}5Btz}$ = 0.8 Hz, H-7_{Btz}), 7.74 (dd, 1H, $J_{4Btz\text{-}5Btz}$ = 7.6 Hz, $J_{4Btz\text{-}6Btz}$ = 1.1 Hz, H-4_{Btz}); ^{13}C NMR: 26.6 and 26.5 ($2CH_3$), 48.4 (C-3), 62.1 (C-5), 80.6 (C-4), 86.6 (C-2), 104.6 (C-1), 112.4 (C_{iso}), 120.9 (C-7_{Btz}), 121.7 (C-4_{Btz}), 124.4 (C-6_{Btz}), 126.0 (C-5_{Btz}), 127.0-129.0 (C_{trityl}), 135.6 (C-$3a_{Btz}$), 143.7 (C_{trityl}), 152.7 (C-$7a_{Btz}$), 164.6 (C-2_{Btz}); HRMS Calcd for $C_{34}H_{31}NO_4S_2$ (581.1694). Found (581.1695).

1-*S*-(Benzothiazol-2-yl)-2,3-*O*-isopropylidene-1-thio-L-sorbofuranose (7). A solution of 1-*S*-benzothiazol-2-yl-2,3:4,6-di-*O*-isopropylidene-1-thio-L-sorbofuranose[2] (0.2 g, 0.49 mmol) in 60 % acetic acid [13] (3 mL) was stirred 1 h at rt. Potassium carbonate was then added to the mixture. After filtration and solvent evaporation, the organic phases were dissolved in dichloromethane, dried over magnesium sulfate and concentrated. The residue was chromatographed on silica gel using petroleum ether/ethyl acetate 6 : 4 as eluent to furnish **7** (0.162 g, 90%): mp 102 °C, $[\alpha]_D$ - 48 (*c* 0.5, $CHCl_3$); ^{1}H NMR: 1.44 and 1.52 (2s, 6H, 2 CH_3), 3.66 (d, 1H, H-1b), 4.02 (dd, 1H, $J_{5\text{-}6b}$ = 7.6 Hz, $J_{6a\text{-}6b}$ = 15.2 Hz, H-6b), 4.08 (dd, 1H, $J_{5\text{-}6a}$ = 6.6 Hz, H-6a), 4.13 (d, 1H, $J_{1a\text{-}1b}$ = 14.7 Hz, H-1a), 4.42 (m, 2H, H-4 and H-5), 4.51 (s, 1H, H-3), 7.32 (ft, 1H, H-6_{Btz}), 7.42 (ft, 1H, H-5_{Btz}), 7.74 (d, 1H, $J_{6Btz\text{-}7Btz}$ = 7.9 Hz, H-7_{Btz}), 7.86 (d, 1H, $J_{4Btz\text{-}5Btz}$ = 7.9 Hz, H-4_{Btz}); HRMS Calcd for $C_{16}H_{19}NO_5S_2$ (369.0704). Found (369.0696).

General procedure for the synthesis of sulfones.

Pathway 1: To a solution of the sulfide (0.14 g) in dichloromethane / ethanol 9:1 (15 mL), magnesium monoperoxyphthalate (2 eq) was added. The reaction mixture was

stirred under reflux for 3 h. After extraction in dichloromethane / aqueous sodium hydrogencarbonate, the organic phases were dried over magnesium sulfate and concentrated. The residue was chromatographed on silica gel.

Pathway 2: To a solution of the sulfide (0.09 g) in dichloromethane (9 mL) *meta*-chloroperbenzoic acid (3 eq) was added. The reaction mixture was stirred at rt for 1 h. After extraction in dichloromethane / aqueous sodium hydrogencarbonate, the organic phases were dried over magnesium sulfate and concentrated. The residue was chromatographed on silica gel.

Methyl 6-(Benzothiazol-2-yl)sulfonyl-2,3-di-*O*-benzyl-6-deoxy-α-D-gluco-pyranoside (8). Starting from **1** (0.14 g, 0.267 mmol), this procedure (pathway 1) gave **8** (0.108 g, 72%) as a syrup: $[\alpha]_D$ + 15 (*c* 1, $CHCl_3$); ^1H NMR: 2.60 (s, 1H, OH), 3.29 (td, 1H, $J_{4-5} = J_{4-3} = 9.7$ Hz, $J_{4-OH} = 2.7$ Hz, H-4), 3.45 (dd, 1H, $J_{2-3} = 11.0$ Hz, $J_{2-1} = 3.5$ Hz, H-2), 3.51 (s, 3H, OCH_3), 3.73 (d, 1H, $J_{6a-6b} = 10.0$ Hz, H-6b), 3.79 (dd, 1H, H-3), 4.05 (dd, 1H, $J_{6a-5} = 2.0$ Hz, H-6a), 4.33 (td, 1H, H-5), 4.48(d, 1H, H-1), 4.60 et 4.70 (2d, 2H, $J_{gem} = 12.0$ Hz, CH_2Ph), 4.68 and 4.99 (2d, 2H, $J_{gem} = 11.5$ Hz, CH_2Ph), 7.61 (m, 12H, H_{benzyl}, $H\text{-}6_{Btz}$ et $H\text{-}5_{Btz}$), 8.00 (d, 1H, $J_{7Btz\text{-}6Btz} = 6.3$ Hz, $H\text{-}7_{Btz}$), 8.20 (d, 1H, $J_{4Btz\text{-}5Btz} = 6.8$, $H\text{-}4_{Btz}$); ^{13}C NMR: 56.6 and 56.8 (C-6) and (OCH_3), 66.4 (C-5), 70.5 (C-4), 73.5 and 75.9 (2 CH_2), 79.7 (C-2), 81.1 (C-3), 98.5 (C-1), 122.7 ($C\text{-}4_{Btz}$) and ($C\text{-}7_{Btz}$), 125.9 ($C\text{-}6_{Btz}$), 128.0 ($C\text{-}5_{Btz}$), 128.4-129.1 (C_{benzyl}), 137.1 ($C\text{-}3a_{Btz}$), 138.1 and 138.7 (C_{benzyl}), 153.0 ($C\text{-}7a_{Btz}$), 167.3 ($C\text{-}2_{Btz}$); HRMS Calcd for $C_{28}H_{29}NO_7S_2$ (555.1385). Found (555.1395).

Methyl 6-(Benzothiazol-2-yl)sulfonyl-6-deoxy-α-D-mannopyranoside (9). Starting from **2** (0.14 g, 0.267 mmol), the same experiment (pathway 1) gave **9** (0.108 g, 72%) as a syrup: $[\alpha]_D$ + 34 (*c* 1 , $CHCl_3$); ^1H NMR: 3.51 (s, 3H, OCH_3), 3.66 (d, 1H, $J_{3-4} = 9.0$ Hz, H-3), 3.77 (td, 1H, $J_{5-6b} = 9.3$ Hz, $J_{5-4} = 2.9$ Hz, H-5), 3.88 (s, 1H, H-2), 3.96 (dd, 1H, $J_{6a-6b} = 14.9$ Hz, H-6b), 4.08 (d, 1H, $J_{6a-5} = 2.0$ Hz, H-6a), 4.25 (td, 1H, H-4), 4.50(s, 1H, H-1), 7.59 (m, 2H, $H\text{-}6_{Btz}$ et $H\text{-}5_{Btz}$), 7.98 (dd, 1H, $J_{7Btz\text{-}6Btz} = 7.1$ Hz, $J_{7Btz\text{-}5Btz} = 1.9$ Hz, $H\text{-}7_{Btz}$), 8.19 (dd, 1H, $J_{4Btz\text{-}5Btz} = 7.3$ Hz, $J_{4Btz\text{-}6Btz} = 1.7$ Hz, $H\text{-}4_{Btz}$); ^{13}C NMR: 56.1 (OCH_3), 56.7 (C-6), 67.5 (C-4), 69.9 (C-3), 70.8 (C-2), 71.6 (C-5), 101.4 (C-1), 122.7 ($C\text{-}7_{Btz}$), 125.8 ($C\text{-}4_{Btz}$), 128.4 ($C\text{-}6_{Btz}$), 137.0 ($C\text{-}5_{Btz}$), 137.0 ($C\text{-}3a_{Btz}$), 152.7 ($C\text{-}7a_{Btz}$), 167.2 ($C\text{-}2_{Btz}$); HRMS Calcd for $C_{14}H_{17}NO_7S_2$ (375.0446). Found (375.0432).

5-(Benzothiazol-2-yl)sulfonyl-5-deoxy-1,2-*O*-isopropylidene-α-D-ribofuranose (10). Starting from **3** (0.288 g, 0.943 mmol) the same experiment (pathway 1) gave **10** (0.194 g, 62%): mp 149 °C, $[\alpha]_D$ - 24 (*c* = 1, $CHCl_3$); ^1H NMR: 1.29 and 1.52 (2s, 6H, 2 CH_3), 2.65 (d, 1H, J_{OH-3} = 8.3 Hz, OH), 3.80 (dd, 1H, J_{5a-5b} = 14.8 Hz, H-5b), 3.87 (m, 1H, J_{3-4} = 6.0 Hz, H-3), 3.93 (dd, 1H, J_{4-5b} = 8.1 Hz, H-5a), 4.27 (m, 1H, J_{4-5a} = 3.2 Hz, H-4), 4.50 (t, 1H, J_{2-3} = 4.7 Hz, H-2), 5.60 (d, 1H, J_{1-2} = 3.8 Hz, H-1), 7.57 (m, 2H, H-5_{Btz} and H-6_{Btz}), 7.97 (d, 1H, $J_{7Btz-6Btz}$ = 7.2 Hz, H-7_{Btz}), 8.18 (d, 1H, $J_{4Btz-5Btz}$ = 7.3 Hz, H-4_{Btz}); MS (ion spray): *m/z* = 372 (M+1); HRMS Calcd for $C_{15}H_{17}NO_6S_2$ (371.0497). Found (371.0501).

5-(Benzothiazol-2-yl)sulfonyl-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (11). Starting from **4** (0.2 g, 0.589 mmol) the same experiment (pathway 1) gave **11** (0.092 g, 42 %): mp 151 °C, $[\alpha]_D$ - 56 (*c* 1, $CHCl_3$); ^1H NMR: 1.31 and 1.48 (2s, 6H, 2 CH_3), 3.95 (dd, 1H, J_{5a-5b} = 14.7 Hz, J_{4-5b} = 8.4 Hz, H-5b), 4.03 (dd, 1H, J_{4-5a} = 5.3 Hz, H-5a), 4.46 (d, 1H, J_{3-4} = 2.8 Hz, H-3), 4.76 (m, 1H, H-4), 4.59 (d, 1H, H-2), 5.88 (d, 1H, J_{1-2} = 3.7 Hz, H-1), 7.65 (m, 2H, H-5_{Btz} and H-6_{Btz}), 8.04 (d, 1H, $J_{7Btz-6Btz}$ = 7.3 Hz, H-7_{Btz}), 8.22 (d, 1H, $J_{4Btz-5Btz}$ = 7.4 Hz, H-4_{Btz}); HRMS Calcd for $C_{15}H_{17}NO_6S_2$ (371.0497). Found (371.0489).

3-(Benzothiazol-2-yl)sulfonyl-3-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (12). Starting from **5** (0.14 g, 0.267 mmol), the same experiment (pathway 2) gave **12** (0.039 g, 68 %): mp 130-132 °C, $[\alpha]_D$ + 1 (*c* 1, $CHCl_3$); ^1H NMR: 1.32 and 1.51 (2s, 6H, 2 CH_3), 2.60 (t, 1H, J_{OH-5} = 7.3 Hz, OH), 4.22 (2d, 2H, J_{5-4} = 6.6 Hz, 2 H-5), 4.30 (d, 1H, J_{3-4} = 5.4 Hz, H-3), 4.78 (dd, 1H, H-4), 5.33 (d, 1H, J_{2-1} = 3.9 Hz, H-2), 6.03 (d, 1H, H-1), 7.62-7.74 (m, 2H, H-5_{Btz} and H-6_{Btz}), 8.06 (d, 1H, $J_{7Btz-6Btz}$ = 7.6 Hz, H-7_{Btz}), 8.28 (d, 1H, $J_{4Btz-5Btz}$ = 7.1 Hz, H-4_{Btz}); ^{13}C NMR: 26.4 and 26.6 (2 CH_3), 60.8 (C-5), 70.3 (C-3), 79.3 (C-4), 81.2 (C-2), 105.1 (C-1), 112.7 (C_{iso}), 122.4 (C-7_{Btz}), 125.8 (C-4_{Btz}), 128.1 (C-6_{Btz}), 128.6 (C-5_{Btz}), 136.9 (C-$3a_{Btz}$), 152.7 (C-$7a_{Btz}$), 164.7 (C-2_{Btz}); HRMS Calcd for $C_{15}H_{17}NO_6S_2$ (371.0497). Found (371.0492).

3-(Benzothiazol-2-yl)sulfonyl-3-deoxy-1,2-*O*-isopropylidene-α-D-ribofuranose (13). Starting from **6** (0.05 g, 0.086 mmol) the same experiment (pathway 2) gave **13** (0.02 g, 62 %): mp 188-190 °C, $[\alpha]_D$ + 53 (*c* 1, $CHCl_3$); ^1H NMR: 1.15 and 1.28 (2s, 6H, 2CH_3), 2.14 (t, 1H, J_{OH-5} = 7.0 Hz, OH), 4.05 (m, 2H, 2H-5), 4.36 (dd, 1H, J_{3-2} = 4.6

Hz, J_{3-4} = 9.8 Hz, H-3), 5.01 (dt, 1H, J_{4-5} = 2.2 Hz, H-4), 5.10 (t, 1H, H-2), 5.90 (d, 1H, J_{1-2} = 3.7 Hz, H-1), 7.66 (m, 4H, H-5_{Btz} and H-6_{Btz}), 8.06 (dd, 1H, $J_{7Btz-6Btz}$ = 7.1 Hz, $J_{7Btz-5Btz}$ = 2.0 Hz, H-7_{Btz}), 8.22 (dd, 1H, $J_{4Btz-5Btz}$ = 7.2 Hz, $J_{4Btz-6Btz}$ = 2.7 Hz, H-4_{Btz}); ^{13}C NMR: 27.6 and 26.9 ($2CH_3$), 61.5 (C-5), 66.7 (C-3), 78.7 (C-4), 80.9 (C-2), 105.5 (C-1), 115.0 (C_{iso}), 123.4 (C-7_{Btz}), 126.6 (C-4_{Btz}), 128.9 (C-6_{Btz}), 129.3 (C-5_{Btz}), 137.8 (C-$3a_{Btz}$), 153.3 (C-$7a_{Btz}$), 168.2 (C-2_{Btz}); HRMS Calcd for $C_{15}H_{17}NO_6S_2$ (371.0497). Found (371.0492).

3-(Benzothiazol-2-yl)sulfonyl-3-deoxy-2,3-*O*-isopropylidene-L-sorbofuranose (14). Starting from **7** (0.105 g, 0.284 mmol) the same experiment (pathway 1) gave **14** (0.106 g, 93 %): mp = 185 °C, $[\alpha]_D$ + 5 (*c* 1.1, $CHCl_3$); ^{1}H NMR: 1.17 and 1.26 (2s, 6H, 2 CH_3), 3.18 (dd, 1H, J_{5-6b} = 5.7 Hz, J_{6a-6b} = 11.4 Hz, H-6b), 3.35 (dd, 1H, J_{5-6a} = 6.0 Hz, H-6a), 4.02 (m, 2H, H-4 and H-5), 4.26 (d, 1H, H-1b), 4.36 (d, 1H, J_{1a-1b} = 15.5 Hz, H-1a), 4.52 (s, 1H, H-3), 7.69 (m, 2H, H-6_{Btz} and H-5_{Btz}), 8.23 (d, 1H, $J_{6Btz-7Btz}$ = 7.9 Hz, H-7_{Btz}), 8.32 (d, 1H, $J_{4Btz-5Btz}$ = 7.9 Hz, H-4_{Btz}); HRMS Calcd for $C_{16}H_{19}NO_7S_2$ (401.0602). Found (401.0596).

General procedure for the transfer reaction: To a solution of the heteroaryl sulfone (0.051 g) in DMF (2 mL) *t*-BuOK (1.2 eq) was added. The reaction mixture was stirred at rt for 1 h, then iodomethane (10 eq) was added at rt. After 4 h, the reaction mixture was concentrated and the residue was chromatographed on silica gel.

Methyl 4-*O*-(Benzothiazol-2-yl)-2,3-di-*O*-benzyl-6-deoxy-6-methylsulfonyl-α-D-glucopyranoside (15). Starting from **8** (0.051 g, 0.0918 mmol), this procedure gave **15** (0.038 g, 73 %): mp < 48 °C, $[\alpha]_D$ + 9 (*c* 1, $CHCl_3$); ^{1}H NMR: 2.99 (s, 3H, SO_2CH_3), 3.25 (d, 1H, J_{6a-6b} = 14.2 Hz, H-6b), 3.42 (dd, 1H, J_{5-6a} = 10.5 Hz, H-6a), 3.52 (s, 3H, OCH_3), 3.62 (dd, 1H, J_{1-2} = 3.6 Hz, J_{2-3} = 9.6 Hz, H-2), 4.15 (t, 1H, J_{3-4} = 9.3 Hz, H-3), 4.49 (td, 1H, J_{4-5} = 2.1 Hz, H-5), 4.61 (d, 1H, H-1), 4.65 and 4.83 (2d, 2H, J_{gem} = 12.1 Hz, CH_2Ph), 4.73-4.87 (2d, 2H, J_{gem} = 11.0 Hz, CH_2Ph), 5.33 (t, 1H, H-4),7.08-7.42 (m, 12H, H_{benzyl}, H-6_{Btz} and H-5_{Btz}), 7.64 (dd, 1H, $J_{7Btz-6Btz}$ = 2.3 Hz, $J_{7Btz-5Btz}$ = 1.1 Hz, H-7_{Btz}), 7.67 (dd, 1H, $J_{4Btz-5Btz}$ = 2.6 Hz, $J_{4Btz-6Btz}$ = 1.0 Hz, H-4_{Btz}); ^{13}C NMR: 43.3 (CH_3), 55.8 and 55.9 (C-6) and (OCH_3), 64.9 (C-5), 73.3 and 75.3 (2 CH_2), 78.6 (C-3) and (C-2), 79.7 (C-4), 98.1 (C-1), 120.9 (C-4_{Btz}) and (C-7_{Btz}), 123.6 (C-5_{Btz}), 125.8 (C-6_{Btz}), 127.2-128.1 (C_{benzyl}), 131.5 (C-$3a_{Btz}$), 137.4 (C_{benzyl}), 148.1 (C-$7a_{Btz}$), 171.8 (C-2_{Btz}).

Anal. Calcd for $C_{29}H_{31}NO_7S_2$ (569.67): C, 61.14; H, 5.49; N, 2.46. Found: C, 60.97; H, 5.43; N, 2.44.

Methyl 2,3-di-*O*-acetyl-4-*O*-(Benzothiazol-2-yl)-6-deoxy-6-methylsulfonyl-α-D-mannopyranoside (16a). Starting from **9** (0.050 g, 0.140 mmol), the same experiment gave **16a** (0.041 g, 70 %): mp < 48 °C, $[\alpha]_D$ + 50 (*c* 1, $CHCl_3$); ^{1}H NMR $CDCl_3$: 1.89 and 2.21 (2s, 6H, 2 CH_3), 3.07 (s, 3H, SO_2CH_3), 3.34 (d, 1H, $J_{6a\text{-}6b}$ = 15.2 Hz, H-6b), 3.53 (s, 3H, OCH_3), 3.63(dd, 1H, H-6a), 4.58 (td, 1H, $J_{5\text{-}6a}$ = 10.0 Hz, $J_{4\text{-}5}$ = 2.0 Hz, H-5), 4.75 (d, 1H, $J_{1\text{-}2}$ = 1.5 Hz, H-1), 5.33 (dd, 1H, $J_{2\text{-}3}$ = 3.2 Hz, H-2), 5.55 - 5.58 (m, 2H, H-3 and H-4), 7.28 (t, 1H, $J_{6Btz\text{-}5Btz} = J_{6Btz\text{-}7Btz}$ = 7.5 Hz, H-6_{Btz}), 7.41 (t, 1H, $J_{5Btz\text{-}4Btz}$ = 7.5 Hz, H-5_{Btz}), 7.68 (ft, 2H, H-4_{Btz} and H-7_{Btz}); ^{13}C NMR: 20.6 and 20.9 (2 OAc), 43.8 (SO_2CH_3), 56.0 (OCH_3), 56.3 (C-6), 66.4 (C-3), 68.8 (C-2), 69.8 (C-5), 75.9 (C-4), 98.8 (C-1), 121.2 and 121.5 (C-4_{Btz}) and (C-7_{Btz}), 124.2 (C-5_{Btz}), 126.3 (C-6_{Btz}), 132.1 (C-$3a_{Btz}$), 148.4 (C-$7a_{Btz}$), 169.6 and 169.9 (2 CO), 172.3 (C-2_{Btz}).

Anal. Calcd for $C_{19}H_{23}NO_9S_2$ (473.51): C, 48.19; H, 4.90; N, 2.96. Found: C, 48.31; H, 4.96; N, 2.90.

The reaction also afforded the following side-product : **Methyl 3,4-di-*O*-acetyl-2-*O*-(Benzothiazol-2-yl)-6-deoxy-6-methylsulfonyl-α-D-mannopyranoside (16b).** (0.005 g, 9 %): mp < 48 °C, $[\alpha]_D$ + 11 (*c* 1, $CHCl_3$); ^{1}H NMR: 1.90 and 2.10 (2s, 6H, 2 CH_3), 3.07 (s, 3H, SO_2CH_3), 3.10 (d, 1H, $J_{6a\text{-}6b}$ = 15.0 Hz, H-6b), 3.43 (dd, 1H, $J_{6a\text{-}5}$ = 10.5 Hz H-6a),3.56 (s, 3H, OCH_3), 4.46 (td, 1H, H-5), 5.03 (d, 1H, $J_{1\text{-}2}$ = 1.8 Hz, H-1),5.29 (ft, 1H, $J_{4\text{-}5} = J_{4\text{-}3}$ = 10.0 Hz, H-4), 5.48 (dd, 1H, $J_{2\text{-}3}$ = 3.2 Hz, H-3), 5.72 (d, 1H, H-2), 7.27 (t, 1H, $J_{6Btz\text{-}5Btz} = J_{6Btz\text{-}7Btz}$ = 7.3 Hz, H-6_{Btz}), 7.38 (t, 1H, $J_{5Btz\text{-}4Btz}$ = 7.8 Hz, H-5_{Btz}), 7.68 (2d, 2H, H-4_{Btz} and H-7_{Btz}); ^{13}C NMR: 20.8 and 20.9 (2 OAc), 44.0 (SO_2CH_3), 56.3 (C-6 and OCH_3), 66.4 (C-5), 68.0 (C-4), 69.1 (C-3), 76.4 (C-2), 98.3 (C-1), 121.2 and 121.6 (C-4_{Btz} and C-7_{Btz}), 124.2 (C-5_{Btz}), 126.4 (C-6_{Btz}), 132.2 (C-$3a_{Btz}$), 148.7 (C-$7a_{Btz}$), 170.1 and 170.2 (2 CO), 171.9 (C-2_{Btz}); HRMS Calcd for $C_{19}H_{23}NO_9S_2$ (473.0821). Found (473.0810).

3-*O*-(Benzothiazol-2-yl)-5-deoxy-1,2-*O*-isopropylidene-5-methylsulfonyl-α-D-ribofuranose (17). Starting from **10** (0.093 g, 0.25 mmol) the same experiment gave **17** (0.071 g, 74 %): mp 71 °C, $[\alpha]_D$ + 97 (*c* 1, $CHCl_3$); ^{1}H NMR: 1.36 and 1.61 (2s, 6H, 2 CH_3), 3.06 (s, 3H, SO_2CH_3), 3.35 (dd, 1H, $J_{5a\text{-}5b}$ = 14.9 Hz, $J_{4\text{-}5a}$ = 2.7 Hz, H-5b), 3.44

(dd, 1H, J_{5b-4} = 8.7 Hz, H-5a), 4.75 (dd, 1H,H-4), 5.11 (t, 1H, J_{1-2} = 3.6 Hz, H-2), 5.19 (dd, 1H, J_{2-3} = 4.7 Hz, H-3), 5.91 (d, 1H, H-1), 7.27 (t, 1H, H-6_{Btz}), 7.39 (t, 1H, H-5_{Btz}), 7.67 (d, 2H, H-4_{Btz} and H-7_{Btz}); ^{13}C NMR: 26.3 and 26.5 (2 CH_3), 42.2 (SO_2CH_3), 66.3 (C-3), 69.7 (C-5), 75.0 (C-4), 79.1 (C-2), 104.6 (C-1), 114.1 (C_{iso}), 121.1 (C-7_{Btz}), 123.8 (C-4_{Btz}), 125.9 (C-6_{Btz}), 126.1 (C-5_{Btz}), 132.0 (C-$3a_{Btz}$), 149.0 (C-$7a_{Btz}$), 172.1 (C-2_{Btz}); MS (ion spray): *m/z* = 386 (M+1).

Anal. Calcd for $C_{16}H_{19}NO_6S_2$ (385.45): C, 49.85; H, 4.97; N, 3.63. Found: C, 49.68; H, 4.87; N, 3.58.

3-*O*-(Benzothiazol-2-yl)-5-deoxy-1,2-*O*-isopropylidene-5-methylsulfonyl-α-D-xylofuranose (18). Starting from **11** (0.023 g, 0.062 mmol) the same experiment gave **18** (0.016 g, 78 %) as a syrup: $[\alpha]_D$ + 31 (*c* 1, $CHCl_3$); ^{1}H NMR: 1.36 and 1.59 (2s, 6H, 2 CH_3), 3.06 (s, 3H, SO_2CH_3), 3.33 (dd, 1H, J_{5a-5b} = 15.2 Hz, H-5b), 3.44 (dd, 1H, J_{4-5a} = 9.6 Hz, H-5a), 4.93 (m, 1H,H-4), 4.86 (d, 1H, J_{1-2} = 3.9 Hz, H-2), 5.72 (dd, 1H, H-3), 6.02 (d, 1H, H-1), 7.29 (t, 1H, H-6_{Btz}), 7.42 (t, 1H, H-5_{Btz}), 7.67 (d, 2H, H-4_{Btz} and H-7_{Btz}); ^{13}C NMR: 26.3 and 26.5 (2 CH_3), 42.0 (SO_2CH_3), 66.3 (C-3), 69.7 (C-5), 75.0 (C-4), 79.1 (C-2), 104.6 (C-1), 114.1 (C_{iso}), 121.1 (C-7_{Btz}), 123.8 (C-4_{Btz}), 125.9 (C-6_{Btz}), 126.1 (C-5_{Btz}), 132.0 (C-$3a_{Btz}$), 149.0 (C-$7a_{Btz}$), 172.1 (C-2_{Btz}); MS (ion spray): *m/z* = 386 (M+1).

Anal. Calcd for $C_{16}H_{19}NO_6S_2$ (385.45): C, 49.85; H, 4.97; N, 3.63. Found: C, 49.65; H, 4.84; N, 3.68.

5-*O*-(Benzothiazol-2-yl)-3-deoxy-1,2-*O*-isopropylidene-3-methylsulfonyl-α-D-xylofuranose (19). Starting from **12** (0.02 g, 0.054 mmol) the same experiment gave **19** (0.007 g, 33 %) as a syrup: $[\alpha]_D$ + 10 (*c* 0.5, $CHCl_3$); ^{1}H NMR: 1.39 and 1.56 (2s, 6H, 2 CH_3), 3.04 (s, 3H, SO_2CH_3), 3.76 (d, 1H, J_{3-4} = 4.4 Hz, H-3), 5.00 (2d, 2H, J_{5-4} = 7.6 Hz, J_{5b-5a} = 15.4 Hz, 2 H-5), 5.15 (dd, 1H, J_{1-2} = 3.9 Hz, J_{2-3} = 0.7 Hz, H-2), 5.24 (dd, 1H, H-4), 6.08 (d, 1H, H-1), 7.25 (td, 1H, $J_{6Btz-7Btz}$ = 7.6 Hz, $J_{6Btz-4Btz}$ = 1.2 Hz, H-6_{Btz}), 7.38 (td, 1H, $J_{7Btz-5Btz}$ = 1.5 Hz, H-5_{Btz}), 7.65 (dd, 1H, H-7_{Btz}), 7.70 (dd, 1H, H-4_{Btz}); ^{13}C NMR: 26.3 and 26.7 (2CH_3), 42.0 (SO_2CH_3), 69.0 (C-3), 69.9 (C-5), 76.1 (C-4), 81.2 (C-2), 104.9 (C-1), 112.9 (C_{iso}), 121.1 and 121.3 (C-7_{Btz}) and (C-4_{Btz}), 123.7 (C-6_{Btz}), 126.0 (C-5_{Btz}), 132.2 (C-$3a_{Btz}$), 149.0 (C-$7a_{Btz}$), 171.9 (C-2_{Btz}); MS (heated nebulizer): *m/z* = 386 (M+1).

Anal. Calcd for $C_{16}H_{19}NO_6S_2$ (385.45): C, 49.85; H, 4.97; N, 3.63. Found: C, 49.71; H, 4.93; N, 3.61.

5-*O*-(Benzothiazol-2-yl)-3-deoxy-1,2-*O*-isopropylidene-3-methylsulfonyl-α-D-ribofuranose (20). Starting from **13** (0.055 g, 0.015 mmol) the same experiment gave **20** (0.028 g, 49 %): mp 108-110 °C, $[\alpha]_D$ + 64 (*c* 1, $CHCl_3$); ^1H NMR: 1.38 and 1.59 (2s, 6H, 2 CH_3), 3.17 (s, 3H, SO_2CH_3), 3.62 (dd, 1H, J_{3-4} = 10.1 Hz, J_{3-2} = 4.5 Hz, H-3), 3.70 (dd, 1H, J_{5b-4} = 4.8 Hz, J_{5b-5a} = 11.9 Hz, H-5b), 4.84 (dd, 1H, J_{4-5a} = 1.7 Hz, H-4), 5.01 (t, 1H, J_{1-2} = 4.2 Hz, H-2), 5.14 (dd, 1H, H-5a), 5.91 (d, 1H, H-1), 7.22 (td, 1H, $J_{6Btz-7Btz}$ = 7.5 Hz, $J_{6Btz-4Btz}$ = 1.2 Hz, H-6_{Btz}), 7.35 (td, 1H, $J_{7Btz-5Btz}$ = 1.4 Hz, H-5_{Btz}), 7.61-7.67 (m, 2H, H-4_{Btz} and H-7_{Btz}); ^{13}C NMR: 26.3 and 26.5 (2 CH_3), 66.3 (C-3), 69.7 (C-5), 75.0 (C-4), 79.1 (C-2), 104.6 (C-1), 114.1 (C-6), 121.1 (C-7_{Btz}), 123.8 (C-4_{Btz}), 125.9 (C-6_{Btz}), 126.1 (C-5_{Btz}), 132.0 (C-$3a_{Btz}$), 149.0 (C-$7a_{Btz}$), 172.1 (C-2_{Btz}); MS (ion spray): *m/z* = 386 (M+1).

Anal. Calcd for $C_{16}H_{19}NO_6S_2$ (385.45): C, 49.85; H, 4.97; N, 3.63. Found: C, 49.91; H, 4.94; N, 3.59.

6-*O*-(Benzothiazol-2-yl)-1-deoxy-2,3-*O*-isopropylidene-1-methylsulfonyl-L-sorbofuranose (21). Starting from **14** (0.078 g, 0.194 mmol) the same experiment gave **21** (0.046 g, 57 %) as a syrup: $[\alpha]_D$ - 14 (*c* 1, $CHCl_3$); ^1H NMR: 1.43 and 1.53 (2s, 6H, 2 CH_3), 3.07 (s, 3H, SO_2CH_3), 3.68 (d, 1H, H-1b), 3.82 (d, 1H, J_{1a-1b} = 15.7 Hz, H-1a), 4.24 (dd, 1H, J_{4-5} = 2.7 Hz, J_{4-3} = 6.3 Hz, H-4), 4.58 (m, 1H, H-5), 4.69 (dd, 1H, J_{5-6b} = 5.7 Hz, J_{6a-6b} = 11.5 Hz, H-6b), 4.80 (d, 1H, J_{OH-4} = 6.3 Hz, OH), 4.89 (s, 1H, H-3), 4.96 (dd, 1H, J_{5-6a} = 7.1 Hz, H-6a), 7.27 (ft, 1H, H-6_{Btz}), 7.39 (ft, 1H, H-5_{Btz}), 7.65 (bd, 2H, H-7_{Btz} and H-4_{Btz}); HRMS Calcd for $C_{17}H_{21}NO_7S_2$ (415.0759). Found (415.0747).

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