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Reactions of phenyl and ethyl 2-*O*-sulfonyl-1-thio-α-D-manno- and β-D-glucopyranosides with thionucleophiles

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ABSTRACT

Persubstituted derivatives of phenyl and ethyl 2-*O*-sulfonyl-1-thio-α-D-manno- and β-D-glucopyranosides were synthesized and reacted either with PhSNa or with MeSNa. The phenyl-1-thio compounds afforded the dithio-1,2-*cis*-axial/equatorial-α-D-glucopyranosides or dithio-1,2-*cis*-equatorial/axial-β-D-mannopyranosides by means of S_N2 type of reactions. Starting from the ethyl-1-thio derivatives intramolecular 1,2-thio-migration took place predominantly. In the case of mannosides both nucleophilic reagents facilitate the formation of 1-SPh- or 1-SEt glycals by elimination. The formation of unsubstituted glycal could also be observed from the ethyl-1-thio derivatives, especially by using PhSNa as a nucleophile. The 1,2-dithio-glycosides are glycosyl donors affording 1,2-*trans*-2-thio-glycosides.

1. Introduction

Our present interest in the field of carbohydrate chemistry is the synthesis of sugar-sulfonic[1–4] and sugar methylsulfonic acids[5–8] and their utilization for the preparation of oligosaccharide sulfonic acids.

Among the synthetic processes of sugar 2-sulfonic acids the 1,2-thiomigration procedures[9–11] offer very attractive possibilities. Whenever a suitable thioglycoside bearing a good leaving group at position 2 is reacted with the appropriate nucleophile (MeONa, NaN_3, and Me_3SiN_3), the thio group migrates into position 2 while the nucleophile attacks the anomeric position. Using readily removable thiol protecting groups [*p*-methoxybenzyl, (2-naphthyl)methyl, trityl, allyl, trimethylsilylethyl, and acetyl] the obtained 2-thio group can be deprotected and can be oxidized to a sulfonate. In our laboratory *gluco*- and *manno*-2-sulfonic acid derivatives were successfully prepared using this method.[2–4]

The application of alkoxide- and N_3-nucleophiles resulted in derivatives which cannot be utilized as glycosyl donors. Since our goal was to prepare 2-thio compounds that are convertible to 2-sulfonic acids and, at the same time, could serve as glycosyl donors, the study of the applicability of thionucleophiles in 1,2-thiomigration reactions was decided. Therefore, phenyl and ethyl 2-*O*-sulfonyl-1-thio-α-D-manno- and -β-D-glucopyranoside model compounds were synthesized and reacted either with PhSNa or with MeSNa.

2. Results and discussion

Methanesulfonylation of the known[12–14] compounds **1–4** resulted in the 2-*O*-mesyl thioglycosides **5–8** that were characterized by ^{1}H NMR spectra and TLC (Scheme 1).

Treatment of compound **5** with PhSNa (5 equiv) in DMF at 40 °C for 24 h gave only a single product **9** (Scheme 2). Both the ^{1}H and the ^{13}C NMR spectra showed the presence of two SPh groups and the 3-*O*-benzyl group, and the 4,6-*O*-benzylidene skeleton was also present. The simple NMR spectra did not provide sufficient information about the configuration of either C-2 or the anomeric carbon. The disappearance of the large $^3J_{2,3}$ coupling constant suggested the *manno*-configuration for compound **9**. The β-configuration was verified by the measured 155.4 Hz value for $^1J_{H1-C1}$.[15] These data confirmed that compound **9** was phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-phenyl-1-thio-β-D-mannopyranoside, isolated with 47% yield. A 1,2-diphenylthio derivative can be formed from **5** either in an intramolecular 1,2-thiomigration induced by the nucleophilic attack of the thiophenolate at the anomeric position or by means of an intermolecular nucleophilic substitution of the 2-*O*-mesylate with the thiophenolate. The β-anomeric configuration of compound **9** proves the latter mechanism, since the 1,2-thiomigration would result in inversion of the anomeric configuration via an episulfonium intermediate, or would afford an anomeric mixture via an oxocarbenium ion intermediate.[3,12]

Treatment of **5** with MeSNa (5 equiv) in DMF at 50 °C for 3 h resulted again in a 1,2-dithio compound (**10**), whose structure determination was performed similarly to that of compound **9**. The observed data were as follows: $[\alpha]_D$ +41.8; $^1J_{C1-H1}$ 155.6 Hz

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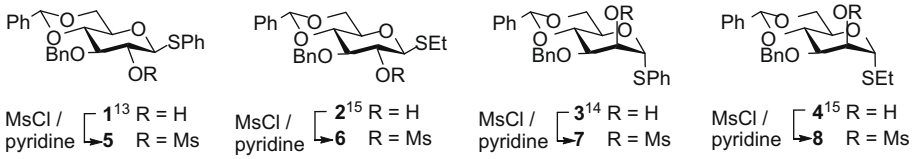
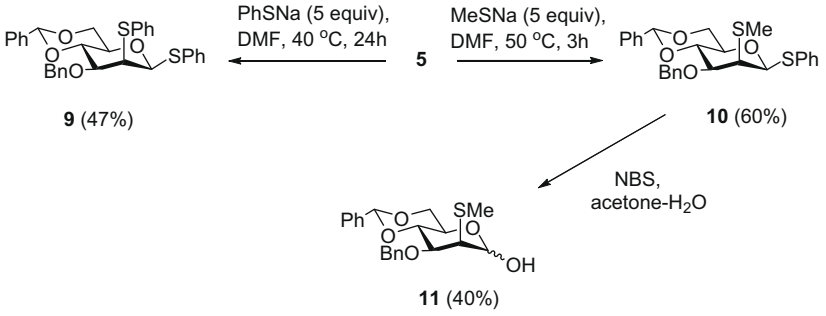


Scheme 1.



Scheme 2.

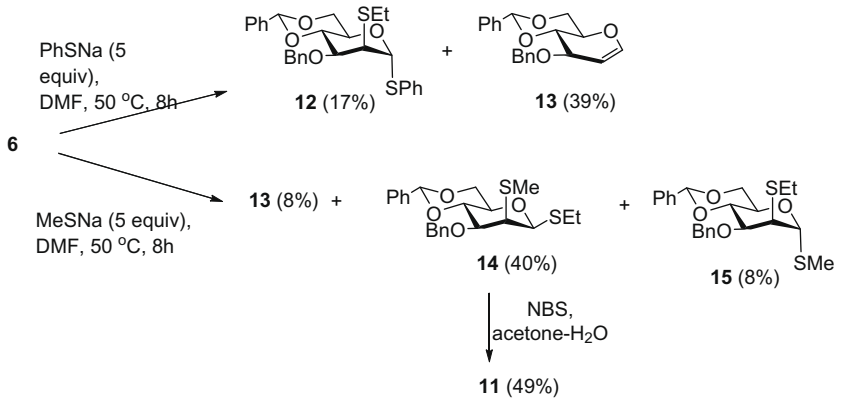
suggesting the β-anomeric configuration. However, one question to be answered remained: the substituents of the thio groups at the anomeric center and at C-2. It is known that thioglycosides can be selectively cleaved with NBS.[16] Following this procedure from compound **10**, 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-methyl-α,β-D-mannopyranose (**11**) could be isolated and characterized. The presence of the methylthio group at C-2 of **11** proves that an intermolecular nucleophilic displacement reaction occurred.

We also studied the reactivity of compound **6** toward PhSNa (Scheme 3). Two products were formed, the 1,2-thiomigrated compound **12** ($[\alpha]_D$ +114.1 and $^1J_{C1-H1}$ 170.4 Hz) and the glycal **13** in a ratio of ~1:2.

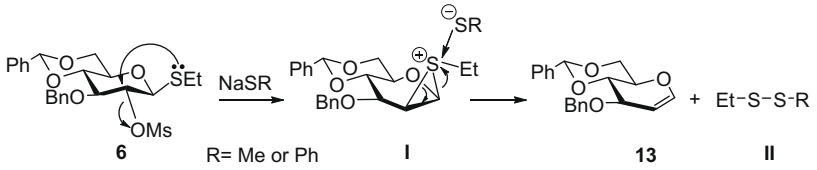
The ^1H and ^{13}C NMR data confirmed the structure of **12** as phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-ethyl-1-thio-α-D-mannopyranoside resulting from an intramolecular nucleophilic rearrangement reaction. The main product, 1,5-anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-*arabino*-hex-1-enitol (**13**: $[\alpha]_D$ −27.6) formed in an elimination reaction. The elimination presumably goes via vicinal intramolecular nucleophilic substitution to give an episulfonium ion **I** which is then attacked by a free sulfide to form a disulfide **II** and the glycal product **13** (Scheme 4). Compound **13** was first isolated by Sinaÿ and coworkers[17] using reductive lithiation at C-1, followed by a rapid elimination of the C-2 substituent of the fully protected phenyl thioglycopyranoside.

Treatment of **6** with 5 equiv of MeSNa in DMF at 50 °C for 8 h resulted in three products (Scheme 3). The major component **14** ($[\alpha]_D$ +4.9; $^1J_{C1-H1}$ 151.1 Hz) was an 1,2-*cis*-dithio-derivative, whose NBS-mediated hydrolysis delivered, again, the cyclic-hemiacetal **11**, showing that the primary product **14** was ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-methyl-1-thio-β-D-mannopyranoside. The second component, the methyl thio-α-D-mannopyranoside (**15**, $[\alpha]_D$ +102.7; $^1J_{C1-H1}$ 168.8 Hz) was a 1,2-*trans*-dithio compound formed upon an intramolecular 1,2-thiomigration reaction. The third compound in the reaction mixture was the elimination product **13**.

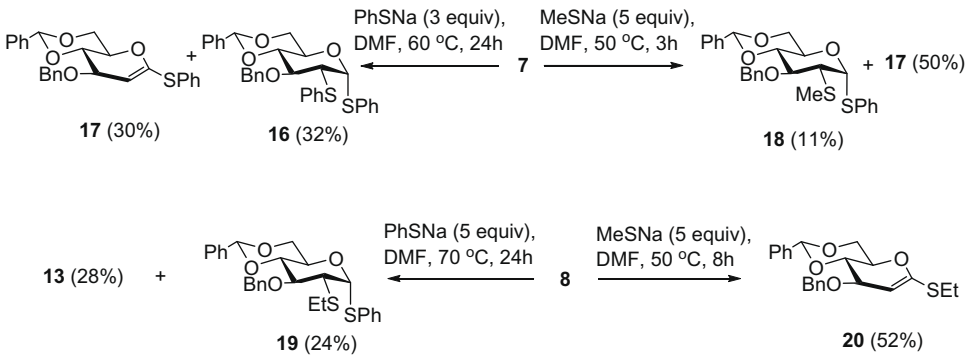
The α-D-mannopyranoside-type starting compounds, such as **7** and **8** were also investigated (Scheme 5). Compound **7** was reacted with 3 equiv of PhSNa at 60 °C for 24 h and two products could be detected (**16** and **17**). Compound **16** ($^3J_{1,2}$ 4.9 Hz; $^1J_{C1-H1}$ 169.4 Hz and $[\alpha]_D$ +283.6) proved to be phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-phenyl-1-thio-α-D-glucopyranoside, produced by an S_N2 intermolecular nucleophilic displacement reaction. This reaction did not affect the anomeric center, but changed the configuration at C-2. The second product **17** was an unsaturated sugar and proved to be phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-D-*arabino*-hex-1-enopyranoside. Preparation of such type of compounds was published[18] most recently. The formation of the above-mentioned unsaturated compounds is explained by the elimination of methanesulfonic acid.



Scheme 3.



Scheme 4.



Scheme 5.

The mesyl ester **7** was also treated with MeSNa (5 equiv) at 50 °C for 3 h, and again, two products could be isolated. The 1,2-*cis*-axial/equatorial dithio-derivative proved to be phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-methyl-1-thio-α-D-glucopyranoside (**18**; $J_{1,2}$ 5.3 Hz; $^{1}J_{C1-H1}$ 169.9 Hz; $[\alpha]_D$ +209.9) and the second component was **17**.

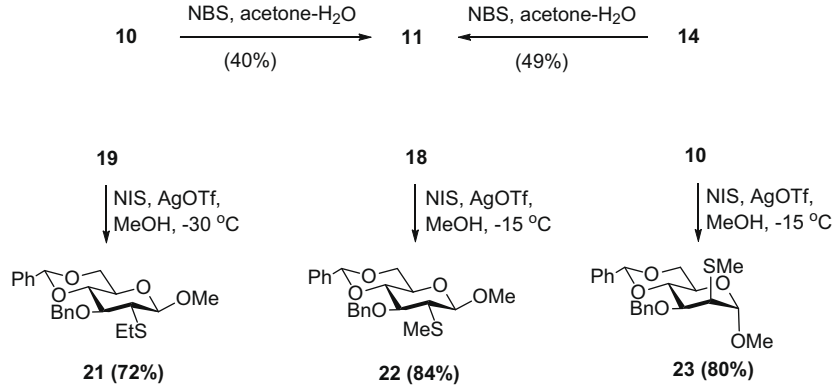
Treatment of compound **8** with PhSNa (5 equiv) at 70 °C for 24 h furnished two compounds (**19** and **13**). All measured parameters for **19** are very similar to those of compounds **16** and **18**. Characteristic data for **19** are: $^{3}J_{1,2}$ 5.3 Hz; $^{1}J_{C1-H1}$ 169.6 Hz; $[\alpha]_D$ +169.5. The second component is the unsaturated **13**, formed by the mechanism shown in Scheme 4. The formation of compound **19** was assumed in an intramolecular 1,2-thiomigration reaction via an oxocarbenium intermediate.[3,12] This type of reaction would afford both anomers, however, we could isolate only the α-product.

Using MeSNa as the nucleophilic reagent, only one compound, ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-D-*arabino*-hex-1-enopyranoside (**20**) was formed.

Determination of the structure of the products formed upon transformation of compounds **5–8** gave the opportunity to approach the mechanism of the reactions. Besides the spectroscopic methods (NMR and MS) chemical tools provided valuable information about their structure: in the case of the β-mannopyranoside derivatives (**10** and **14**) NBS cleaved the thioaglycones, but did not affect the C2-S-substituents. In the case of compounds **18** and **19** the substituents of the 1,2-dithio moieties were determined by glycosylation reactions. The NIS-AgOTf-catalyzed glycosylation reaction of **19** using MeOH as an aglycon resulted in **21**, and the glycosylation of **18** under the same conditions gave **22**. This reaction works also well with the mannosyl donor **10**, furnishing compound **23** (Scheme 6). All the three 1,2-dithio glycosyl donors afforded stereoselectively the 1,2-*trans* glycosides.

In conclusion, in the reactions of phenyl and ethyl 2-*O*-sulfonyl-1-thio-α-D-manno- and β-D-glucopyranosides with PhSNa or with MeSNa three different displacement reactions and two different elimination processes could be observed. Reactions of **5** and **7**, both with anomeric SPh group, only undergo direct nucleophilic substitution reaction, both with PhSNa and MeSNa as reagents. Only **7**, with axial leaving group, undergoes direct methanesulfonic acid elimination with both reagents, as well.

In contrast, **6** and **8**, with anomeric SEt group, typically do not show direct nucleophilic substitution reaction. With PhSNa as a reagent, both undergo intramolecular substitution to an episulfonium or an oxocarbenium intermediate, followed by a subsequent



Scheme 6.

nucleophilic attack on the anomeric carbon (leading to **12** and **19**) or on sulfur, leading to **13**. With MeSNa as a reagent, the situation is more complicated for **6**, with both substitution patterns observed as well as elimination affording **13**. With **8** having an axial leaving group, direct elimination is favored to give **20**.

3. Experimental

3.1. General methods

Optical rotations were measured at room temperature with a Perkin–Elmer 241 automatic polarimeter. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. TLC was performed on Kieselgel 60 F_{254} (Merck) with detection by immersing into 5% ethanolic sulfuric acid solution. Column chromatography was performed on Silica Gel 60 (E. Merck, 0.063–0.200 mm). The organic solutions were dried over $MgSO_4$ and concentrated in vacuo. The ^1H (360 MHz) and ^{13}C NMR (90 MHz) spectra were recorded with AM-360 spectrometer in $CDCl_3$ solution. Chemical shifts are referenced to Me_4Si (0.00 ppm for ^1H) or to the residual solvent signals (77.00 ppm for ^{13}C).

3.2. General method A for the formation of 2-*O*-methanesulfonyl derivatives (5–8)

To a solution of 3.0 mmol of the appropriate 2-OH derivative (**1–4**) in 10 mL of dry pyridine 348 μL (4.50 mmol) of methanesulfonyl chloride was added and the mixture was stirred at rt for 4 h. The mixture was diluted with 100 mL of dichloromethane and washed with 1 M aqueous HCl solution until the aqueous phase remained slightly acidic, then washed with water, saturated $NaHCO_3$ solution and water. The crude product was used for the next step without purification.

3.3. General method B for the reactions of 2-*O*-methanesulfonyl derivatives with sodium thiophenolate. Formation of 9, 12, 13, 16, 17, and 19

To a solution of 1.0 mmol of the appropriate 2-*O*-mesyl derivative (**5–8**) in 5 mL of *N*,*N*-DMF 661 mg (5 mmol) of sodium thiophenolate was added and the mixture was stirred at 40–70 °C until complete conversion of the starting material (8–24 h) was detected. The mixture was diluted with 50 mL of dichloromethane, washed with water, dried, and evaporated.

3.4. General method C for the reactions of 2-*O*-methanesulfonyl derivatives with sodium thiomethylate. Formation of 10, 13–15, 17, 18, and 20

To a solution of 1.0 mmol of 2-*O*-mesyl derivative (**5–8**) in 5 mL of *N*,*N*-DMF 350.5 mg (5 mmol) of sodium thiomethylate was added and the mixture was stirred at 50 °C until a complete conversion of the starting material (3–8 h) was detected. The mixture was diluted with 50 mL of dichloromethane, washed with water, dried, and evaporated.

3.5. General method D for the removal of the thio aglycone with NBS. Formation of 11

To a solution of 0.5 mmol of the thioglycoside (**10**, **14**) in acetone–water 15:1 (6 mL) 178 mg (1 mmol) of NBS was added and after 10 min the reaction was quenched by adding solid $NaHCO_3$ (390 mg). The mixture was stirred for 10 min, evaporated in vacuo at rt, and then diluted with dichloromethane (50 mL). The organic phase was washed with water until neutral pH, dried, and evaporated. The residue was purified by silica gel chromatography (CH_2Cl_2/EtOAc 95:5).

3.6. General method E for the synthesis of methyl glycosides (21–23)

To a solution of 0.5 mmol of thioglycoside (**10**, **18**, and **19**) in dichloromethane (10 mL) were added successively 3 Å molecular sieves (300 mg) and 202 μL (5 mmol) of dry MeOH, and the mixture was stirred at rt for 1 h. Then it was cooled to −15 °C (for **10** and **18**) or −30 °C (for **19**) and a mixture of 135 mg (0.6 mmol) of NIS in dry THF (300 μL) and 20 mg (0.075 mmol) of AgOTf in dry toluene (300 μL) was added. The mixture was kept at −15 to −30 °C until the TLC showed a complete conversion of the starting material (30 min). The reaction was quenched by the addition of 70 μL (1 mmol) of Et_3N. Insoluble materials were removed by filtration through Celite, the filtrate was diluted with dichloromethane, extracted three times with water, dried, and evaporated.

3.7. Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-methanesulfonyl-1-thio-β-D-glucopyranoside (5)

Compound **1** (1.35 g, 3 mmol) was converted by method **A** to give the crude **5**; ^1H NMR ($CDCl_3$): δ 7.55–7.26 (m, 15H, aromatic), 5.55 (s, 1H, PhC*H*), 4.96 and 4.74 (2d, 1-1H, PhCH_2), 4.76 (d, 1H, $^3J_{1,2}$ 9.9 Hz, H-1), 4.62 (t, 1H, $^3J_{2,3}$ 8.6 Hz, H-2), 4.37 (dd, 1H, $^3J_{5,6a}$ 5.0 Hz, $^2J_{6a,6b}$ 10.5 Hz, H-6a), 3.86 (t, 1H, $^3J_{3,4}$ 9.1 Hz, H-3), 3.78 (t, 1H, $^3J_{5,6b}$ 10.2 Hz, H-6b), 3.73 (t, 1H, $^3J_{4,5}$ 9.3 Hz, H-4), 3.48 (ddd, 1H, H-5), 3.02 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 137.3–125.9 (aromatic), 101.1 (Ph*C*H), 86.7 (C-1), 81.2, 80.0 and 79.3 (C-2, C-3 and C-4), 74.8 (PhCH_2), 70.2 (C-5), 68.3 (C-6), 39.5 (*C*H_3).

3.8. Ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-methanesulfonyl-1-thio-β-D-glucopyranoside (6)

Compound **2** (1.21 g, 3 mmol) was converted by method **A** to give the crude **6**; ^1H NMR ($CDCl_3$): δ 7.47–7.25 (m, 10H, aromatic), 5.57 (s, 1H, PhC*H*), 4.98 and 4.76 (2d, 1-1H, PhCH_2), 4.60 (t, 1H, $^3J_{2,3}$ 7.2 Hz, H-2), 4.56 (d, 1H, $^3J_{1,2}$ 9.9 Hz, H-1), 4.37 (dd, 1H, $^3J_{5,6a}$ 5.0 Hz, $^2J_{6a,6b}$ 10.5 Hz, H-6a), 3.85 (t, 1H, $^3J_{3,4}$ 9.2 Hz, H-3), 3.77 (t, 1H, $^3J_{5,6b}$ 10.3 Hz, H-6b), 3.76 (t, 1H, $^3J_{4,5}$ 9.3 Hz, H-4), 3.50 (ddd, 1H, H-5), 3.00 (s, 3H, OCH_3), 2.75 (q, 2H, CH_2), 1.29 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 137.3–125.8 (aromatic), 101.1 (Ph*C*H), 83.8 (C-1), 81.5, 79.9 and 79.4 (C-2, C-3 and C-4), 74.8 (PhCH_2), 70.3 (C-5), 68.3 (C-6), 39.4 (O*C*H_3), 24.1 (*C*H_2), 14.7 (*C*H_3).

3.9. Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-methanesulfonyl-1-thio-α-D-manno-pyranoside (7)

Compound **3** (1.35 g, 3 mmol) was converted by method **A** to give the crude **7**; ^1H NMR ($CDCl_3$): δ 7.52–7.30 (m, 15H, aromatic), 5.64 (s, 1H, PhC*H*), 5.62 (d, 1H, $^3J_{1,2}$ 1.2 Hz, H-1), 5.24 (dd, 1H, $^3J_{2,3}$ 2.9 Hz, H-2), 4.87 and 4.76 (2d, 1-1H, PhCH_2), 4.35 (ddd, 1H, H-5), 4.24 (dd, 1H, $^3J_{5,6a}$ 4.8 Hz, $^2J_{6a,6b}$ 10.3 Hz, H-6a), 4.14 (t, 1H, $^3J_{4,5}$ 9.3 Hz, H-4), 4.06 (dd, 1H, $^3J_{3,4}$ 9.9 Hz, H-3), 3.87 (t, 1H, $^3J_{5,6b}$ 10.2 Hz, H-6b), 3.02 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 137.2–126.0 (aromatic), 101.5 (Ph*C*H), 87.8 (C-1), 79.9, 78.8 and 73.8 (C-2, C-3 and C-4), 73.6 (PhCH_2), 68.2 (C-6), 65.2 (C-5), 38.7 (*C*H_3).

3.10. Ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-methanesulfonyl-1-thio-α-D-mannopyranoside (8)

Compound **4** (1.21 g, 3 mmol) was converted by method **A** to give the crude **8**; ^1H NMR ($CDCl_3$): δ 7.51–7.30 (m, 10H, aromatic), 5.63 (s, 1H, PhC*H*), 5.41 (d, 1H, $^3J_{1,2}$ 0.9 Hz, H-1), 5.08 (dd, 1H, $^3J_{2,3}$ 3.0 Hz, H-2), 4.83 and 4.72 (2d, 1-1H, PhCH_2), 4.27–4.19 (m, 2H,

H-5 and H-6a), 4.09 (t, 1H, $^3J_{4,5}$ 9.2 Hz, H-4), 4.00 (dd, 1H, $^3J_{3,4}$ 9.2 Hz, H-3), 3.88 (t, 1H, H-6b), 3.02 (s, 3H, OCH_3), 2.65 (q, 2H, CH_2), 1.29 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 137.3–126.0 (aromatic), 101.5 (PhCH), 84.3 (C-1), 80.4, 78.9 and 73.9 (C-2, C-3 and C-4), 73.6 (PhCH_2), 68.3 (C-6), 64.6 (C-5), 38.7 (OCH_3), 25.9 (CH_2), 14.9 (CH_3).

3.11. Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-phenyl-1-thio-β-D-mannopyranoside (9)

Compound **5** (529 mg, 1 mmol) was converted by method **B**. The crude product was purified by silica gel chromatography (hexane/EtOAc 95:5) to give 255 mg of **9** (47%); R_f 0.41 (hexane/EtOAc 8:2); $[\alpha]_D$ +4.5 (*c* 0.11, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.73–7.08 (m, 20H, aromatic), 5.62 (s, 1H, PhC*H*), 5.07 (d, 1H, $^3J_{1,2}$ 1.4 Hz, H-1), 4.54 and 4.42 (2d, 1-1H, PhCH_2), 4.30 (dd, 1H, $^3J_{5,6a}$ 4.8 Hz, $^2J_{6a,6b}$ 10.4 Hz, H-6a), 4.13 (t, 1H) and 3.89–3.84 (m, 3H) (H-2, H-3, H-4 and H-6b), 3.40 (ddd, 1H, H-5); ^{13}C NMR ($CDCl_3$): δ 137.7–125.9 (aromatic), 101.4 (PhCH), 90.1 (C-1, $^1J_{C1-H1}$ 155.4 Hz), 79.3 and 78.2 (C-3 and C-4), 72.2 (PhCH_2), 72.1 (C-5), 68.3 (C-6), 59.3 (C-2). Anal. Calcd for $C_{32}H_{30}O_4S_2$ (542.71): C, 70.82; H, 5.57. Found: C, 71.09; H, 5.59.

3.12. Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-methyl-1-thio-β-D-mannopyranoside (10)

Compound **5** (529 mg, 1 mmol) was converted by method **C**. The crude product was purified by silica gel chromatography (hexane/EtOAc 95:5) followed by crystallization from ethanol to give 288 mg of **10** (60%); mp 166–168 °C; R_f 0.35 (hexane/EtOAc 85:15); $[\alpha]_D$ +41.8 (*c* 0.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.47–7.26 (m, 15H, aromatic), 5.61 (s, 1H, PhC*H*), 5.03 (d, 1H, $^3J_{1,2}$ 1.8 Hz, H-1), 4.87 and 4.74 (2d, 1-1H, PhCH_2), 4.30 (dd, 1H, $^3J_{5,6a}$ 4.8 Hz, $^2J_{6a,6b}$ 10.4 Hz, H-6a), 4.18 (t, 1H), 3.92–3.81 (m, 2H) and 3.45–3.33 (m, 2H) (H-2, H-3, H-4, H-5 and H-6b), 2.41 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 138.1–126.0 (aromatic), 101.4 (PhCH), 90.2 (C-1, $^1J_{C1-H1}$ 155.6 Hz), 79.7 and 78.9 (C-3 and C-4), 72.9 (PhCH_2), 72.1 (C-5), 68.4 (C-6), 56.4 (C-2), 19.1 (CH_3). Anal. Calcd for $C_{27}H_{28}O_4S_2$ (480.64): C, 67.47; H, 5.87. Found: C, 67.21; H, 5.93.

3.13. 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*S*-methyl-α,β-D-mannopyranose (11)

Compound **10** (240 mg, 0.5 mmol) was converted by method **D** to give 78 mg of **11** (40%) and compound **14** (216 mg, 0.5 mmol) was converted by method **D** to give 95 mg of **11** (49%); R_f 0.41 (CH_2Cl_2/EtOAc 9:1); ^{1}H NMR ($CDCl_3$): δ 7.51–7.25 (m, 10H, aromatic), 5.63 and 5.59 (2s, 0.6H and 0.4H, PhCH_α and PhCH_β), 5.40 (s, 0.6H, H-1_α), 4.94–4.63 (m, 2.4H, PhC$H_{2\alpha,\beta}$) and H-1_β), 4.32–3.74 (m, 5H, H-$3_{\alpha,\beta}$, H-$4_{\alpha,\beta}$, H-$5_{\alpha,\beta}$, H-$6a_{\alpha,\beta}$ and H-$6b_{\alpha,\beta}$), 3.39–3.31 (m, 0.4H, OH_β), 3.24–3.22 (m, 1H, H-$2_{\alpha,\beta}$), 2.97 (s, 0.6H,OH_α), 2.29 and 2.26 (2s, 3H, C$H_{3\alpha,\beta}$); ^{13}C NMR ($CDCl_3$): δ 138.4–126.0 (aromatic), 101.5 and 101.4 (PhC$H_{\alpha,\beta}$), 95.9 and 93.5 (C-$1_{\alpha,\beta}$), 80.1, 79.9, 77.6 and 74.8 (C-$3_{\alpha,\beta}$ and C-$4_{\alpha,\beta}$), 73.2 and 72.9 (PhC$H_{2\alpha,\beta}$), 68.8 and 68.4 (C-$6_{\alpha,\beta}$),67.2 and 64.4 (C-$5_{\alpha,\beta}$), 59.3 and 53.2 (C-$2_{\alpha,\beta}$). Anal. Calcd for $C_{21}H_{24}O_5S$ (388.48): C, 64.93; H, 6.23. Found: C, 63.87; H, 6.44.

3.14. Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-ethyl-1-thio-α-D-mannopyranoside (12) and 1,5-anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-*arabino*-hex-1-enitol (13)

Compound **6** (481 mg, 1 mmol) was converted using method **B** to give a mixture of **12** and **13** which were separated by silica gel chromatography (hexane/EtOAc 9:1 and CH_2Cl_2/EtOAc 99.5:0.5). Compound **12** was isolated with 17% yield (84 mg); R_f 0.40 (hexane/EtOAc 85:15); $[\alpha]_D$ +114.1 (*c* 0.24, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.50–7.29 (m, 15H, aromatic), 5.65 and 5.63 (2s, 1-1H, H-1 and PhC*H*), 4.86 and 4.76 (2d, 1-1H, PhCH_2), 4.37 (ddd, 1H, H-5), 4.26–4.13 (m, 3H) and 3.86 (t, 1H) (H-3, H-4, H-6a and H-6b), 3.49 (d, 1H, $^3J_{2,3}$ 3.9 Hz, H-2), 2.71 (q, 2H, CH_2), 1.25 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 138.1-126.0 (aromatic), 101.5 (PhCH), 89.4 (C-1, $^1J_{C1-H1}$ 170.4 Hz), 80.1 and 75.1 (C-3 and C-4), 72.9 (PhCH_2), 68.4 (C-6), 65.6 (C-5), 52.0 (C-2), 27.9 (CH_2) 14.6 (CH_3). Anal. Calcd for $C_{28}H_{30}O_4S_2$ (494.67): C, 67.99; H, 6.11. Found: C, 68.44; H, 5.97.

The crystalline **13** was isolated with 39% yield (127 mg); mp 104–105 °C (ethanol); R_f 0.41 (hexane/EtOAc 85:15); $[\alpha]_D$ −7.6 (*c* 0.11, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.52–7.25 (m, 10H, aromatic), 6.50 (d, 1H, H-1), 5.64 (s, 1H, PhC*H*), 4.83–4.70 (m, 3H, H-2 and PhCH_2), 4.39–4.35 (m, 2H), 4.03 (t, 1H) and 3.92–3.82 (m, 2H) (H-3, H-4, H-5, H-6a and H-6b); ^{13}C NMR ($CDCl_3$): δ 144.4 (C-1), 138.4–126.0 (aromatic), 102.3 (C-2), 101.2 (PhCH), 80.0 and 73.1 (C-3 and C-4), 72.0 (PhCH_2), 68.6 (C-5), 68.4 (C-6). Anal. Calcd for $C_{20}H_{20}O_4$ (324.37): C, 74.06; H, 6.21. Found: C, 74.25; H, 6.39.

3.15. Ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-methyl-1-thio-β-D-mannopyranoside (14) and methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-ethyl-1-thio-α-D-mannopyranoside (15)

Compound **6** (481 mg, 1 mmol) was converted using method **C** to give a mixture of **13**, **14**, and **15** which were separated by silica gel chromatography (hexane/EtOAc 9:1 and CH_2Cl_2/hexane 8:2). Compound **13** was isolated with 8% yield (26 mg).

Compound **14** was isolated with 40% yield (173 mg); R_f 0.33 (hexane/EtOAc 85:15); $[\alpha]_D$ +4.9 (*c* 0.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.50–7.25 (m, 10H, aromatic), 5.61 (s, 1H, PhC*H*), 4.87 and 4.76 (2d, 1-1H, PhCH_2), 4.82 (d, 1H, $^3J_{1,2}$ 1.5 Hz, H-1), 4.27 (dd, 1H, $^3J_{5,6a}$ 4.8 Hz, $^2J_{6a,6b}$ 10.5 Hz, H-6a), 4.14 (t, 1H, $^3J_{4,5}$ 9.4 Hz, H-4), 3.89 (dd, 1H, $^3J_{3,4}$ 9.5 Hz, H-3), 3.84 (t, 1H, $^3J_{5,6b}$ 10.3 Hz, H-6b), 3.39 (ddd, 1H, H-5), 3.28 (dd, 1H, $^3J_{2,3}$ 4.2 Hz, H-2), 2.72 (q, 2H, CH_2), 2.36 (s, 3H, SCH_3) 1.27 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 138.2–125.9 (aromatic), 101.4 (PhCH), 87.3 (C-1, $^1J_{C1-H1}$ 151.1 Hz), 79.8 and 79.0 (C-3 and C-4), 72.8 (PhCH_2), 72.2 (C-5), 68.4 (C-6), 56.2 (C-2), 26.1 (CH_2), 19.0 (SCH_3), 15.0 (CH_3). Anal. Calcd for $C_{23}H_{28}O_4S_2$ (432.60): C, 63.86; H, 6.52. Found: C, 64.11; H, 6.74.

Compound **15** was isolated with 8% yield (35 mg); R_f 0.39 (hexane/EtOAc 85:15); $[\alpha]_D$ +102.7 (*c* 0.13, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.51–7.26 (m, 10H, aromatic), 5.62 (s, 1H, PhC*H*), 5.33 (s, 1H, H-1), 4.82 and 4.71 (2d, 1-1H, PhCH_2), 4.23–4.09 (m, 4H) and 3.88 (t, 1H) (H-3, H-4, H-5, H-6a and H-6b), 3.33 (d, 1H, $^3J_{2,3}$ 3.9 Hz, H-2), 2.72 (q, 2H, CH_2), 2.12 (s, 3H, SCH_3) 1.27 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 138.2–125.9 (aromatic), 101.5 (PhCH), 87.2 (C-1, $^1J_{C1-H1}$ 168.8 Hz), 80.2 and 75.2 (C-3 and C-4), 72.9 (PhCH_2), 68.7 (C-6), 64.7 (C-5), 51.6 (C-2), 27.9 (CH_2), 14.6 and 14.1 (SCH_3 and CH_3). Anal. Calcd for $C_{23}H_{28}O_4S_2$ (432.60): C, 63.86; H, 6.52. Found: C, 64.24; H, 6.71.

3.16. Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-phenyl-1-thio-α-D-glucopyranoside (16) and phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-*arabino*-1-thio-hex-1-enopyranoside (17)

Compound **7** (529 mg, 1 mmol) was converted using method **B** to give a mixture of **16** and **17** which were separated by silica gel chromatography (CH_2Cl_2/hexane 1:1) The crystalline **16** was isolated with 32% yield (174 mg); mp 126 °C (ethanol); R_f 0.35 (CH_2Cl_2/hexane 1:1); $[\alpha]_D$ +118.6 (*c* 0.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.58–7.24 (m, 20H, aromatic), 5.60 (s, 1H, PhC*H*), 5.50 (d, 1H, $^3J_{1,2}$ 4.9 Hz, H-1), 4.94 and 4.86 (2d, 1-1H, PhCH_2), 4.51 (ddd, 1H, H-5), 4.20 (dd, 1H, $^3J_{5,6a}$ 4.7 Hz, $^2J_{6a,6b}$ 10.3 Hz, H-6a), 3.97 (t, 1H) and 3.80–3.72 (m, 3H) (H-2, H-3, H-4 and H-6b); ^{13}C NMR ($CDCl_3$): δ 137.9–125.9 (aromatic), 101.4 (PhCH), 90.0 (C-1, $^1J_{C1-H1}$

169.4 Hz), 84.0 and 78.4 (C-3 and C-4), 75.8 (PhCH$_2$), 68.7 (C-6), 64.5 (C-5), 54.9 (C-2). Anal. Calcd for $C_{32}H_{30}O_4S_2$ (542.71): C, 70.82; H, 5.57. Found: C, 70.33; H, 5.61.

The crystalline **17** was isolated with 30% yield (130 mg); mp ~160–168 °C (hexane/EtOAc 9:1) decomposed; R_f 0.39 (CH_2Cl_2/hexane 1:1); $[\alpha]_D$ +283.6 (*c* 0.21, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.55–7.22 (m, 15H, aromatic), 5.86 (dd, 1H, H-2), 5.61 (s, 1H, PhC*H*), 4.96–4.78 (m, 3H, H-3 and PhCH_2), 4.45 (m, 1H, H-5), 4.37–4.30 (m, 2H, H-4, and H-6a), 3.86 (t, 1H, H-6b); ^{13}C NMR ($CDCl_3$): δ 152.8 (C-1), 137.2–126.4 (aromatic), 102.2 (PhCH), 96.9 (C-2), 85.1 and 74.8 (C-3 and C-4), 69.6 (PhCH$_2$), 68.9 (C-6), 64.2 (C-5). Anal. Calcd for $C_{26}H_{24}O_4S$ (432.53): C, 72.20; H, 5.59. Found: C, 71.89; H, 5.47.

3.17. Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-methyl-1-thio-α-D-glucopyranoside (18)

Compound **7** (529 mg, 1 mmol) was converted using method **C** to give a mixture of **17** and **18** which were separated by silica gel chromatography (CH_2Cl_2/hexane 1:1). Compound **17** was isolated with 50% yield (216 mg).

The crystalline **18** was isolated with 11% yield (53 mg); mp 163–165 °C (ethanol); R_f 0.23 (CH_2Cl_2/hexane 1:1); $[\alpha]_D$ +209.9 (*c* 0.12, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.52–7.27 (m, 15H, aromatic), 5.60 (s, 1H, PhC*H*), 5.59 (d, 1H, H-1), 4.98 and 4.85 (2d, 1-1H, PhCH_2), 4.46 (ddd, 1H, H-5), 4.23 (dd, 1H, $^3J_{5,6a}$ 4.9 Hz, $^2J_{6a,6b}$ 10.3 Hz, H-6a), 3.93 (dd, 1H, $^3J_{3,4}$ 9.1 Hz, H-3), 3.77 (t, 1H, $^3J_{5,6b}$ 10.1 Hz, H-6b), 3.72 (t, 1H, $^3J_{4,5}$ 9.3 Hz, H-4), 3.19 (dd, 1H, $^3J_{1,2}$ 5.3 Hz, $^3J_{2,3}$ 10.7 Hz, H-2), 2.28 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 138.2–126.0 (aromatic), 101.4 (PhCH), 89.9 (C-1, $^1J_{C1-H1}$ 169.9 Hz), 84.0 and 80.3 (C-3 and C-4), 75.7 (PhCH$_2$), 68.7 (C-6), 64.3 (C-5), 53.4 (C-2), 17.6 (*C*H$_3$). Anal. Calcd for $C_{27}H_{28}O_4S_2$ (480.64): C, 67.47; H, 5.87. Found: C, 68.01; H, 5.97.

3.18. Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-ethyl-1-thio-α-D-glucopyranoside (19)

Compound **8** (481 mg, 1 mmol) was converted using method **B** to give a mixture of **13** and **19** which were separated by silica gel chromatography (hexane/EtOAc 93:7). Compound **13** was isolated with 28% yield (91 mg). The crystalline **19** was isolated with 24% yield (119 mg); mp 147–149 °C (ethanol); R_f 0.38 (hexane/EtOAc 85:15); $[\alpha]_D$ +169.5 (*c* 0.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.52–7.25 (m, 15H, aromatic), 5.61 (s, 1H, PhC*H*), 5.58 (d, 1H, $^3J_{1,2}$ 5.3 Hz, H-1), 4.97 and 4.85 (2d, 1-1H, PhCH_2), 4.47 (ddd, 1H, H-5), 4.23 (dd, 1H, $^3J_{5,6a}$ 4.9 Hz, $^2J_{6a,6b}$ 10.3 Hz, H-6a), 3.92 (dd, 1H, $^3J_{3,4}$ 9.2 Hz, H-3), 3.78 (t, 1H, $^3J_{5,6b}$ 10.3 Hz, H-6b), 3.72 (t, 1H, $^3J_{4,5}$ 9.3 Hz, H-4), 3.25 (dd, 1H, $^3J_{2,3}$ 10.6 Hz, H-2), 2.78 (q, 2H, CH_2), 1.24 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 138.3–126.0 (aromatic), 101.4 (PhCH), 90.2 (C-1, $^1J_{C1-H1}$ 169.6 Hz), 84.0 and 80.3 (C-3 and C-4), 75.9 (PhCH$_2$), 68.7 (C-6), 64.4 (C-5), 51.2 (C-2), 28.2 (*C*H$_2$), 14.6 (*C*H$_3$). Anal. Calcd for $C_{28}H_{30}O_4S_2$ (494.67): C, 67.99; H, 6.11. Found: C, 68.31; H, 6.23.

3.19. Ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-D-*arabino*-1-thio-hex-1-enopyranoside (20)

Compound **8** (481 mg, 1 mmol) was converted using method **C** and the crude product was purified by silica gel chromatography (hexane/EtOAc 9:1) to give 200 mg of **20** (52%); R_f 0.43 (hexane/EtOAc 85:15); $[\alpha]_D$ +122.9 (*c* 0.16, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.53–7.30 (m, 10H, aromatic), 5.65 (d, 1H, H-2), 5.59 (s, 1H, PhC*H*), 4.90 and 4.76 (2d, 1-1H, PhCH_2), 4.79 (d, 1H, H-3), 4.34–4.26 (m, 3H) and 3.86–3.81 (m, 1H) (H-4, H-5, H-6a and H-6b), 2.65 (m, 2H, CH_2), 1.29 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 152.0 (C-1), 137.2–126.4 (aromatic), 102.1 (PhCH), 97.3 (C-2), 81.3 and 74.9 (C-3 and C-4), 69.4 (PhCH$_2$), 69.0 (C-6), 63.6 (C-5), 26.0 (*C*H$_2$), 15.4 (*C*H$_3$). Anal. Calcd for $C_{22}H_{24}O_4S$ (384.49): C, 68.72; H, 6.29. Found: C, 69.13; H, 6.44.

3.20. Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-ethyl-β-D-glucopyranoside (21)

Compound **19** (247 mg, 0.5 mmol) was converted using method **E** and the crude product was purified by silica gel chromatography (CH_2Cl_2/EtOAc 99:1) to give 150 mg of **21** (72%); R_f 0.32 (CH_2Cl_2/EtOAc 98:2); $[\alpha]_D$ −69.5 (*c* 0.13, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.50–7.26 (m, 10H, aromatic), 5.59 (s, 1H, PhC*H*), 4.90 and 4.82 (2d, 1-1H, PhCH_2), 4.37 (d, 1H, $^3J_{1,2}$ 8.7 Hz, H-1), 4.36 (dd, 1H, $^3J_{5,6a}$ 5.1 Hz, $^2J_{6a,6b}$ 10.4 Hz, H-6a), 3.80 (t, 1H, $^3J_{5,6b}$ 10.3 Hz, H-6b), 3.71 (t, 1H, $^3J_{4,5}$ 9.1 Hz, H-4), 3.57 (s, 3H, OCH_3), 3.50 (dd, 1H, $^3J_{3,4}$ 8.9 Hz, H-3), 3.42 (ddd, 1H, H-5), 2.76 (m, 2H, CH_2), 2.72 (dd, 1H, $^3J_{2,3}$ 10.5 Hz, H-2), 1.27 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 138.3–126.0 (aromatic), 106.3 (C-1), 101.2 (PhCH), 82.8 and 79.6 (C-3 and C-4), 75.9 (PhCH$_2$), 68.8 (C-6), 65.9 (C-5), 57.6 (OCH$_3$), 52.4 (C-2), 27.3 (*C*H$_2$), 14.9 (*C*H$_3$). Anal. Calcd for $C_{23}H_{28}O_5S$ (416.53): C, 66.32; H, 6.78. Found: C, 66.89; H, 6.33.

3.21. Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-methyl-β-D-glucopyranoside (22)

Compound **18** (240 mg, 0.5 mmol) was converted using method **E** and the crude product was purified by silica gel chromatography (hexane/EtOAc 9:1) to give 170 mg of **22** (84%); R_f 0.41 (hexane/EtOAc 8:2); $[\alpha]_D$ −62.4 (*c* 0.33, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.50–7.26 (m, 10H, aromatic), 5.60 (s, 1H, PhC*H*), 4.92 and 4.82 (2d, 1-1H, PhCH_2), 4.39 (d, 1H, $^3J_{1,2}$ 8.7 Hz, H-1), 4.36 (dd, 1H, $^3J_{5,6a}$ 5.0 Hz, $^2J_{6a,6b}$ 10.6 Hz, H-6a), 3.80 (t, 1H, $^3J_{5,6b}$ 10.3 Hz, H-6b), 3.72 (t, 1H, $^3J_{4,5}$ 9.1 Hz, H-4), 3.58 (s, 3H, OCH_3), 3.52 (dd, 1H, $^3J_{3,4}$ 8.9 Hz, H-3), 3.41 (ddd, 1H, H-5), 2.66 (dd, 1H, $^3J_{2,3}$ 10.5 Hz, H-2), 2.27 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 138.2–126.0 (aromatic), 106.1 (C-1), 101.2 (PhCH), 82.9 and 79.1 (C-3 and C-4), 75.7 (PhCH$_2$), 68.7 (C-6), 65.9 (C-5), 57.5 (OCH$_3$), 54.2 (C-2), 16.5 (*C*H$_3$). Anal. Calcd for $C_{22}H_{26}O_5S$ (402.50): C, 65.65; H, 6.51. Found: C, 66.04; H, 6.40.

3.22. Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*S*-methyl-α-D-mannopyranoside (23)

Compound **10** (240 mg, 0.5 mmol) was converted using method **E** and the crude product was purified by silica gel chromatography (hexane/EtOAc 9:1) to give 161 mg of **23** (80%); R_f 0.42 (hexane/EtOAc 8:2); $[\alpha]_D$ +40.8 (*c* 0.10, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.50–7.26 (m, 10H, aromatic), 5.62 (s, 1H, PhC*H*), 4.88 (s, 1H, H-1), 4.83 and 4.72 (2d, 1-1H, PhCH_2), 4.25–4.12 (m, 3H) and 3.87–3.78 (m, 2H) (H-3, H-4, H-5, H-6a and H-6b), 3.35 (s, 3H, OCH_3), 3.22 (d, 1H, H-2), 2.27 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 137.6–126.0 (aromatic), 102.2 (C-1, $^1J_{C1-H1}$ 171.8 Hz), 101.5 (PhCH), 80.0 and 75.4 (C-3 and C-4), 72.8 (PhCH$_2$), 68.8 (C-6), 64.1 (C-5), 54.9 (OCH$_3$), 52.9 (C-2), 17.6 (*C*H$_3$). Anal. Calcd for $C_{22}H_{26}O_5S$ (402.50): C, 65.65; H, 6.51. Found: C, 65.17; H, 6.72.

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