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Preparation of glycosyl disulfides and sulfides via the formation of glycosyl Bunte salts as thiol surrogates

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ABSTRACT

A convenient odourless reaction condition has been developed for the preparation of symmetrical glycosyl disulfide derivatives and aryl glycosyl disulfide derivatives from corresponding glycosyl iodides via *in situ* formation of glycosyl Bunte salts as thiol surrogates. The reaction has been further extended towards the preparation of glycosyl sulfides derivatives from corresponding Bunte salt in the presence of sodium sulphide. Most of the reactions were high yielding and suitable for scaling up.

1. Introduction

Organic disulfides are important class of compounds having wide application in the industrial production of pharmaceuticals [1] and agrochemicals [2]. Moreover, they have been used in the materials science [3] and synthetic chemistry for the construction of sulphur containing compounds by C–S bond formation [4]. Glycosyl disulfides have been used as the *O*-glycoside mimics in the glycobiology research such as lectin binding, [5] enzyme inhibition, [6] protein-carbohydrate interactions, [7] development of anti-cancer agents [8] and studies on the structural aspects of glycans [9]. Since natural glycosyl disulfides are rare they have been synthesized using a number of reaction methodologies which include, oxidation of glycosyl sulfides; [10] nucleophilic attack of glycosyl thiol onto a sulfenyl derivative (sulfonate esters); [11] use of sulfenyl halides; [12] sulfenic acids; [13] reaction of glycosyl halides with selenyl sulfides; [14] benzyltriethylammonium tetrathiomolybdate; [15] coupling of glycosyl thiols under mitsunobu reaction; [16] 1-chlorobenzotriazole-mediated reaction, [17] DDQ mediated reaction [18] and many more. Despite their synthetic utility, most of the reaction conditions suffer from several shortcomings such as, handling of malodorous thiol reagents, reactive intermediates, expensive reagents, prerequisite preparation of special reagents, handling of moisture sensitive reaction condition etc. Therefore, it is quite pertinent to develop a reaction condition for the preparation of glycosyl disulfides avoiding afore-mentioned drawbacks.

Bunte salts [19] can be considered as sulphur surrogates for the incorporation of sulphur in organic compounds under a non-malodorous reaction conditions [20]. In general, Bunte salts are stable, easy-to-handle, non-malodorous and can be considered as masked thiols. They can be prepared from alkyl halides by the treatment of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) under convenient reaction conditions [20]. Bunte salts have versatile applications in the synthetic chemistry such as they can react with samarium metal in the presence of $InCl_3$ or I_2 to give symmetrical sulfides, [21] can be hydrolyzed to thiols, [20] can react with Grignard reagent to give sulfides, [22] can act effective thiol precursor in thia-Michael reactions, [20,23] to name a few. Recently, Abbasi et al. [24] reported the one-step synthesis of symmetrical disulfides by the reaction of alkyl halides with $Na_2S_2O_3 \cdot 5H_2O$ in DMSO-H_2O.

One of the easily accessible precursor of glycosyl thiols and disulfides would be glycosyl Bunte salts namely S-glycosylthiosulfates, which can be prepared by the reaction of glycosyl halides with sodium thiosulfate. Recently, Shoda and co-workers reported the synthesis of anomeric glycosyl Bunte salt by the reaction of unprotected sugars with $Na_2S_2O_3 \cdot 5H_2O$ in the presence of 2-chloro-1,3-dimethylimidazolinium chloride (DMC) [25] and their application in the preparation of S-glycosides, glycosyl disulfides

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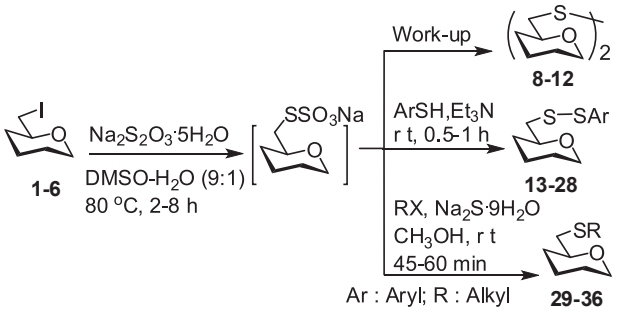
and thio-Michael adducts [26]. Based on their easy accessibility, it was decided to explore the possibility of preparing non-anomeric glycosyl Bunte salts and their use in the preparation of non-anomerically linked symmetrical as well as unsymmetrical glycosyl disulfide derivatives. Detailed experimental findings on the preparation of non-anomerically linked symmetrical as well as unsymmetrical glycosyl disulfide derivatives using glycosyl Bunte salts is presented herein (Scheme 1).

2. Results and discussion

In order to optimize the preparation of glycosyl disulfide derivative via the formation of Bunte salt, 1,2:3,4-di-*O*-isopropylidene-6-iodo-α-D-galactopyranose (**1**) was treated with varied quantities of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) in a variety of solvents and temperature. The reaction proceeded with the formation of a highly polar compound, which appeared at the base line of the TLC experiment. After a series of experimentation, it was observed that use of 1.5 equiv. of $Na_2S_2O_3 \cdot 5H_2O$ in DMSO-H_2O (9:1) at 80 °C could convert compound **1** into corresponding Bunte salt quantitatively in 8 h (Table 1). Reduction of the quantity of $Na_2S_2O_3 \cdot 5H_2O$ and lowering the temperature either delayed the formation of the Bunte salt or resulted incomplete consumption of the starting material. Use of pure DMSO did not give satisfactory conversion may be due to the poor solubility of $Na_2S_2O_3 \cdot 5H_2O$. The advantages of using DMSO-H_2O (9:1) has already been discussed earlier by Abbasi et al. [24] Due to the instability of the Bunte salt, it was not isolated and allowed to proceed for next transformation. After complete consumption of the starting material and formation of a highly polar intermediate (TLC), dilution of the reaction mixture with satd. aq. $NaHCO_3$ followed by extraction with ethyl acetate furnished symmetric disulfide derivative (**7**) in almost quantitative yield (96%). Following similar reaction conditions, a series of symmetric glycosyl disulfide derivatives (**7**–**12**) have been prepared in excellent yield (Table 2). It is noteworthy that compounds **7**–**12** could be considered as non-glycosidically disulfide linked pseudo-disaccharide derivatives, which are important class of glycomimetics [5,8]. In order to get secondary glycosyl disulfides, a number of secondary glycosyl iodide derivatives were also treated with $Na_2S_2O_3 \cdot 5H_2O$ in DMSO-H_2O (9:1) under similar reaction conditions. Unfortunately the reaction did not occur after a long reaction time (48 h) to give corresponding Bunte salts. All synthesized compounds were unambiguously characterized by NMR and mass spectroscopic analysis.

After achieving symmetric disulfide derivatives in excellent yield, it was decided to extend the reaction condition for the preparation of asymmetric glycosyl aryl disulfide derivatives using non-anomeric glycosyl Bunte salt as odourless thiol surrogate. In order to optimize the reaction condition, compound **1** was treated with $Na_2S_2O_3 \cdot 5H_2O$ (1.5 equiv.) in DMSO-H_2O (9:1) for 8 h till complete consumption of the starting material into a polar intermediate (Bunte salt). Treatment of the *in situ* generated Bunte salt with 2,6-dimethylthiophenol (1.1 equiv.) in the presence of triethyl amine (2.0 equiv.) at room temperature led to the formation of asymmetric disulfide derivative **13** in 82% yield in 45 min. Reduction in the amount of thiol and base resulted some unreacted Bunte salt, which on work up furnished symmetric disulfide (**7**). Since the reaction mixture of the Bunte salt was acidic in nature, addition of the triethyl amine is essential for the activation of thiol as well as cleavage of S–SO_3Na bond in Bunte salt. Following similar reaction conditions, a variety of glycosyl aryl disulfide derivatives (**13**–**28**) were prepared in excellent yield (Table 3). A number of glycosyl anomeric thiols were allowed to react with Bunte salts in place of aryl thiols under the reported reaction conditions. Unfortunately, no desired products were obtained after a long reaction time except degradation of the anomeric thiols, probably due to the poor nucleophilicity of the glycosyl anomeric thiols in comparison to the aromatic thiols. Spectroscopic analysis of synthesized compounds confirmed their formation.

After successful achievements on the synthesis of glycosyl aryl disulfide derivatives (**13**–**28**), attention was given towards the preparation of glycosyl alkyl sulfide derivatives using glycosyl Bunte salt as thiol precursor. Taking clue from the Shoda et al. [26] it was envisioned that use of a sulfide source may substitute the thiosulfonate functionality resulting in the formation of a thiolate anion, which on treatment with alkyl halide could furnish alkyl sulfides derivative. With this thought, compound **1** was transformed into Bunte salt intermediate by the treatment with $Na_2S_2O_3 \cdot 5H_2O$ (1.5 equiv.) in DMSO-H_2O (9:1). The reaction mixture was diluted with CH_3OH and treated with benzyl bromide (1.5 equiv.) in the presence of sodium sulfides nonahydrate ($Na_2S \cdot 9H_2O$) (3.0 equiv.) at room temperature. Gratifyingly formation of 6-*S*-benzyl-1,2:3,4-di-*O*-isopropylidene-6-thio-α-D-galactopyranose (**29**) was observed in 85% yield in 1 h. Reduction of the quantity of $Na_2S \cdot 9H_2O$ led to an incomplete reaction mixture, which on work-up furnished desired compound **29** (46%) together with a symmetric disulfide derivative **7** (40%) generated from the unreacted Bunte salt. Therefore, treatment glycosyl Bunte salts derived from corresponding halides (**1**–**3**) were treated with ($Na_2S \cdot 9H_2O$) (3.0 equiv.) and alkyl halide (1.5 equiv.) in CH_3OH furnished satisfactory yield of the glycosyl alkyl sulfides derivatives (**29**–**36**) (Table 4). All synthesized compounds were characterized by their NMR spectral analysis.



Scheme 1. Preparation of non-anomerically linked symmetric and asymmetric glycosyl aryl disulfides and glycosyl alkyl sulfides derivatives from glycosyl halides through *in situ* generation of glycosyl Bunte salt.

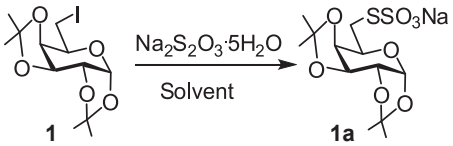
3. Conclusions

In summary, a series of non-anomerically linked symmetrical glycosyl disulfide derivatives, unsymmetrical glycosyl aryl disulfide derivatives and glycosyl alkyl sulfide derivatives have been synthesized in excellent yield from glycosyl Bunte salts, generated *in situ* by the treatment of glycosyl halides with sodium thiosulfate in DMSO-H_2O (9:1). Synthesized compounds may be considered as useful glycomimetics for their use in glycobiology research. Since the reaction condition is simple, reasonably fast, odourless and easy to scale up, it may be considered as better alternative in comparison to the methods available in the literature.

4. Experimental

General methods: All reactions were monitored by thin layer chromatography over silica gel coated TLC plates. The spots on TLC were visualized by warming ceric sulphate (2% $Ce(SO_4)_2$ in 2 N

Table 1
Optimization of the reaction condition for the formation of Bunte salt.



Sl. No.	$Na_2S_2O_3{\cdot}5H_2O$ (Equiv.)	Solvent	Temp. (°C)	Time (h)	Bunte salt of compd. 1[a]
1	1.0	CH_3OH	70	6	20
2	1.1	CH_3OH–H_2O (3:1)	70	6	20
3	1.5	DMSO	80	8	50
4	1.5	DMSO-H_2O (9:1)	80	8	98
5	1.2	DMSO-H_2O (9:1)	80	8	90
6	1.5	DMSO-H_2O (9:1)	60	8	60
7	1.5	DMF	80	8	30

[a] Not isolated. Yield based on the formation of the spot of polar compound and consumption of starting material in TLC.

H_2SO_4) sprayed plates in hot plate. Silica gel 230–400 mesh was used for column chromatography. NMR spectra were recorded on Bruker Avance 500 MHz using $CDCl_3$ as solvent and TMS as internal reference unless stated otherwise. Chemical shift value is expressed in δ ppm. The complete assignment of proton and carbon spectra was carried out by using a standard set of NMR experiments, e.g. ^{1}H NMR, ^{13}C NMR, ^{13}C DEPT 135 etc. ESI-MS were recorded on a Water Xevo G2-S Q-TOF LC-MS instrument. Optical rotations were recorded in a Jasco P-2000 spectrometer. Commercially available grades of organic solvents of adequate purity are used in all reactions.

Typical reaction condition for the preparation of symmetrical glycosyl disulfide (7): To a solution of compound **1** (185 mg, 0.5 mmol) in DMSO-H_2O (5 mL; 9:1 v/v) was added $Na_2S_2O_3{\cdot}5H_2O$ (188 mg, 0.75 mmol) and the reaction mixture was stirred at 80 °C for 8 h (Table 2). After complete consumption of the starting material (formation of a spot at the base line of TLC plate; hexane-EtOAc 1:2), the reaction mixture was diluted with satd. aq. $NaHCO_3$ (10 mL) and extracted with EtOAc (10 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was passed through a short pad of SiO_2 using hexane-EtOAc (6:1) as eluant to give pure symmetrical glycosyl disulfide derivative (**7**) (265 mg, 96%). Following similar reaction conditions, compound (**8**–**12**) were prepared (Table 2).

Analytical data of symmetrical glycosyl disulfide derivative (**7**–**12**):

Since compounds **7**–**12** are symmetrical in nature, the integration of each proton signal is two, although they appeared as one in the NMR spectra.

Bis-(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranosyl)-6,6′-disulfide (7): Yield: 265 mg, 96%; Colorless oil. $[\alpha]_D$ + 43 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.44 (d, *J* = 5.0 Hz, 1 H, H-1), 4.55 (dd, *J* = 7.0 Hz, 1.0 Hz, 1 H, H-3), 4.29 (dd, *J* = 8.0 Hz, 1.0 Hz, 1 H, H-2), 4.23–4.22 (m, 1 H, H-4), 3.98–3.96 (m, 1 H, H-5), 2.86–2.85 (m, 2 H, H-6_{ab}), 1.48 (s, 3 H, C*H*$_3$), 1.36 (s, 3 H, C*H*$_3$), 1.27 (s, 3 H, C*H*$_3$), 1.26 (s, 3 H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1–126.9 (Ar–C), 109.2 [*C*$(CH_3)_2$], 108.7 [*C*$(CH_3)_2$], 96.6 (C-1), 71.5 (C-3), 70.9 (C-4), 70.5 (C-5), 66.5 (C-2), 43.4 (C-6), 26.1 (*C*H$_3$), 26.0 (*C*H$_3$), 25.0 (*C*H$_3$), 24.5 (*C*H$_3$); HRMS for $C_{24}H_{38}O_{10}S_2$ $[M+H]^+$: Calcd. 551.1984; found: 551.1968.

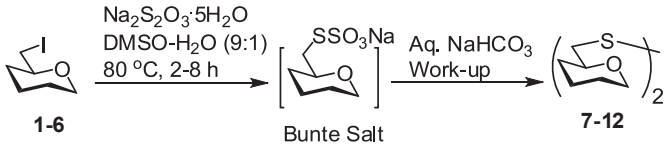
Bis-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-6,6′-disulfide (8): Yield: 452 mg, 94%; Colorless oil. $[\alpha]_D$ + 27 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.17 (m, 15 H, Ar–H), 4.95 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.86 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.77 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.73 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.61 (d, *J* = 12.5, 1 H, PhC*H*), 4.56 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.52 (d, *J* = 3.5 Hz, 1 H, H-1), 3.95 (t, *J* = 9.5 Hz, 1 H, H-4), 3.84–3.79 (m, 1 H, H-5), 3.47 (dd, *J* = 10 Hz, 3.5 Hz, 1 H, H-2), 3.35 (s, 3 H, OC*H*$_3$), 3.28 (t, *J* = 9.5 Hz, 1 H, H-3), 3.12 (dd, *J* = 13.5 Hz, 8.5 Hz, 1 H, H-6_a), 2.73 (dd, *J* = 13.5 Hz, 2 Hz, 1 H, H-6_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6–127.6 (Ar–C), 97.7 (C-1), 81.9 (C-2), 80.6 (C-4), 80.1 (C-3), 75.7 (PhCH_2), 74.9 (PhCH_2), 73.2 (PhCH_2), 69.1 (C-5), 55.3 (OCH_3), 42.2 (C-6); HRMS for $C_{56}H_{62}O_{10}S_2$ $[M+H]^+$: Calcd. 959.3862; found: 959.3846.

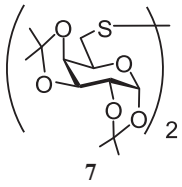
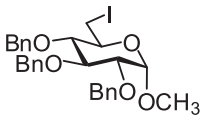
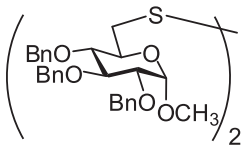
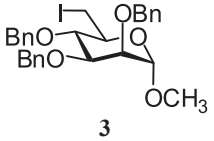
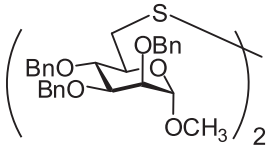
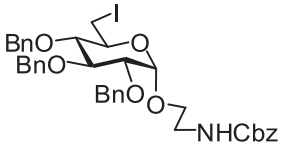
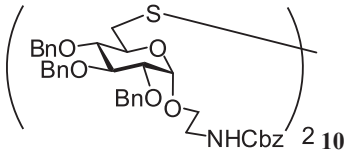
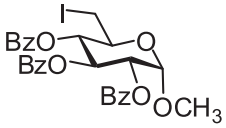
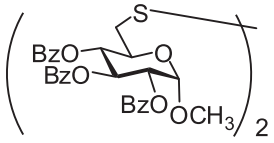
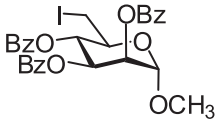
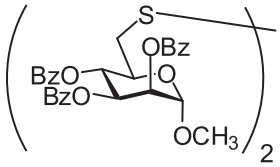
Bis-(methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-6,6′-disulfide (9): Yield: 460 mg, 96%; Colorless oil. $[\alpha]_D$ + 67 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23–7.17 (m, 15 H, Ar–H), 4.91 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.69 (ABq, *J* = 10.5 Hz, 2 H, 2 PhC*H*), 4.65 (d, *J* = 1.5 Hz, 1 H, H-1), 4.57 (br s, 2 H, 2 PhC*H*), 4.54 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 3.84 (dd, *J* = 9.5 Hz, 3.0 Hz, 1 H, H-3), 3.80–3.77 (m, 1 H, H-5), 3.74 (br s, 1 H, H-2), 3.73 (t, *J* = 9.5 Hz, 1 H, H-4), 3.29 (s, 3 H, OC*H*$_3$), 3.15 (dd, *J* = 13.0 Hz, 2.0 Hz, 1 H, H-6_a), 2.84 (dd, *J* = 13.0 Hz, 1.2 Hz, 1 H, H-6_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4–127.5 (Ar–C), 98.8 (C-1), 80.2 (C-5), 77.7 (C-4), 74.8 (C-3), 74.7 (PhCH_2), 72.7 (PhCH_2), 72.1 (PhCH_2), 70.4 (C-2), 54.8 (OCH_3), 41.5 (C-6); HRMS for $C_{56}H_{62}O_{10}S_2$ $[M+H]^+$: Calcd. 959.3862; found: 959.3846.

Bis-(2-benzyloxycarbonylamino 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-6,6′-disulfide (10): Yield: 578 mg, 90%; Colorless oil. $[\alpha]_D$ + 33 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22–7.17 (m, 20 H, Ar–H), 5.32 (br s, 1 H, N*H*), 5.01 (br s, 2 H, 2 PhC*H* (Cbz)), 4.87 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.78 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.69 (d, *J* = 10.5 Hz, 1 H, PhC*H*), 4.62 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.53 (d, *J* = 3.0 Hz, 1 H, H-1), 4.48–4.45 (m, 2 H, 2 PhC*H*), 3.85 (t, *J* = 9.5 Hz, 1 H, H-3), 3.77–3.74 (m, 1 H, H-5), 3.41 (dd, *J* = 8.0 Hz, 4.5 Hz, 1 H, H-2), 3.37–3.26 (m, 3 H, 2 OC*H*, NC*H*), 3.21–3.17 (m, 1 H, H-6_a), 3.03–3.00 (m, 1 H, H-6_b), 2.60–2.55 (m, 1 H, NC*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.3 (PhCO), 138.6–127.6 (Ar–C), 97.0 (C-1), 81.8 (C-2), 80.5 (C-3), 80.3 (C-4), 75.6 (PhCH_2), 75.0 (PhCH_2), 73.3 (PhCH_2), 69.3 (C-5), 67.6 [PhCH_2(Cbz)], 66.7 (OCH_2), 41.8 (NCH_2), 40.7 (C-6); HRMS for $C_{74}H_{80}N_2O_{14}S_2$ $[M+H]^+$: Calcd. 1285.5129; found: 1285.5110.

Bis-(methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranosyl)-6,6′-disulfide (11): Yield: 500 mg, 96%; Colorless oil. $[\alpha]_D$ – 13 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83–7.18 (m, 15 H, Ar–H), 6.08 (t, *J* = 9.5 Hz, 1 H, H-3), 5.35 (t, *J* = 9.5 Hz, 1 H, H-4), 5.21 (dd, *J* = 9.5 Hz, 4.0 Hz, 1 H, H-2), 5.14 (d, *J* = 3.5 Hz, 1 H, H-1), 4.29–4.19 (m, 1 H, H-5), 3.46 (s, 3 H, OC*H*$_3$), 2.96–2.94 (m, 2 H, H-6_{ab}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6 (PhCO), 165.4 (2 C; 2 PhCO), 133.4–128.2 (Ar–C), 96.8 (C-1), 72.2 (C-2), 72.0 (C-3), 70.3 (C-4), 68.2 (C-5), 55.6 (OCH_3), 41.6 (C-6); HRMS for $C_{56}H_{50}O_{16}S_2$ $[M+H]^+$: Calcd. 1043.2618; found: 1043.2600.

Table 2
Preparation of non-anomerically linked symmetric glycosyl disulfides from glycosyl halide via the formation of corresponding Bunte salt.



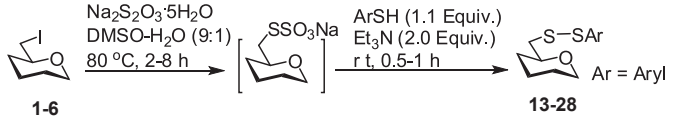
Sl. No.	Glycosyl halide	Product	Time (h)[a]	Yield (%)[b]
1	 **1**	 **7**	8	96
2	 **2**	 **8**	2	94
3	 **3**	 **9**	2	96
4	 **4**	 **10**	4	90
5	 **5**	 **11**	6	96
6	 **6**	 **12**	6	95

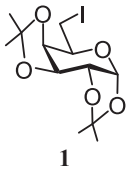
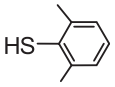
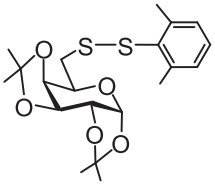
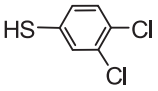
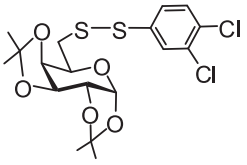
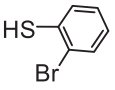
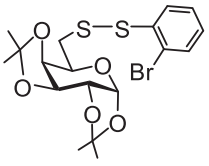
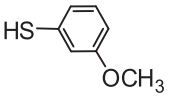
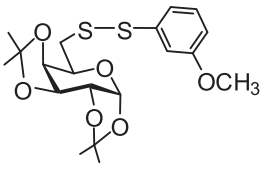
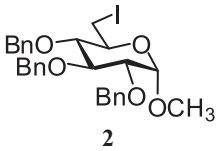
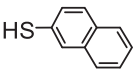
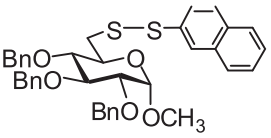
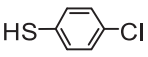
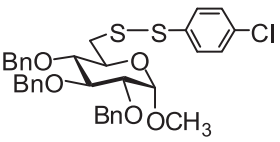
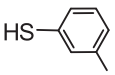
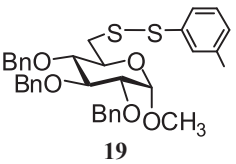
[a] Time required for the formation of corresponding Bunte salt.
[b] Isolated yield.

Bis-(methyl 2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl)-6,6′-disulfide (12): Yield: 495 mg, 95%; Colorless oil. $[\alpha]_D$ + 77 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 8.09–7.21 (m, 15 H, Ar–H), 5.81 (dd, J = 10.0 Hz, 3.5 Hz, 1 H, H-3), 5.67 (t, J = 10.0 Hz, 1 H, H-4), 5.59 (br s, 1 H, H-2), 4.86 (br s, 1 H, H-1), 4.29–4.25 (m, 1 H, H-5), 3.49 (s, 3 H, OCH_3), 3.03–3.02 (m, 2 H, H-6_{ab}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5 (PhCO), 165.2 (PhCO), 165.1 (PhCO), 133.4–128.2 (Ar–C), 98.5 (C-1), 70.5 (C-5), 69.9 (C-3), 69.8 (C-4), 69.2 (C-2), 55.4 (OCH_3), 41.9 (C-6); HRMS for $C_{56}H_{50}O_{16}S_2$ $[M+H]^+$: Calcd. 1043.2618; found: 1043.2600.

Typical reaction condition for the preparation of glycosyl aryl disulfide (13): To a solution of compound **1** (370 mg, 1.0 mmol) in DMSO-H_2O (5 mL; 9:1 v/v) was added $Na_2S_2O_3 \cdot 5H_2O$ (375 mg, 1.5 mmol) and the reaction mixture was stirred at 80 °C for 8 h. The

Table 3
Preparation of non-anomerically linked glycosyl aryl disulfides from glycosyl iodides via the formation of Bunte salt.



Sl. No.	Glycosyl halide	Aryl thiol	Product	Time (min)[a]	Yield (%)[b]
1	 **1**		 **13**	45	82
2	**1**		 **14**	60	80
3	**1**		 **15**	30	84
4	**1**		 **16**	45	86
5	 **2**		 **17**	60	78
6	**2**		 **18**	30	83
7	**2**		 **19**	30	88

(*continued on next page*)

Table 3 (*continued*)

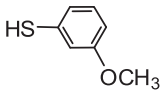
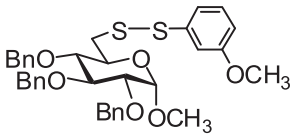
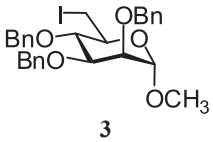
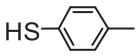
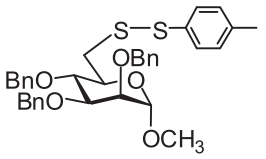
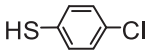
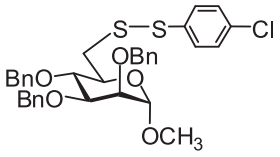
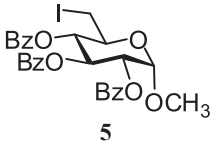
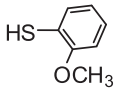
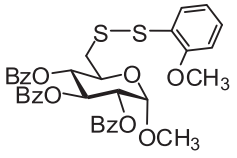
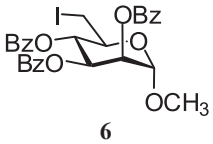
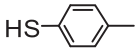
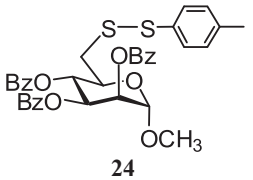
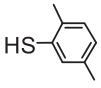
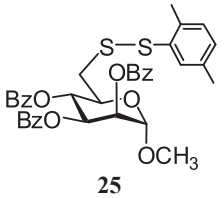
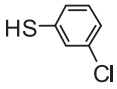
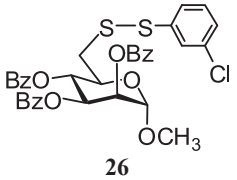
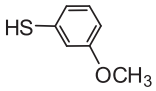
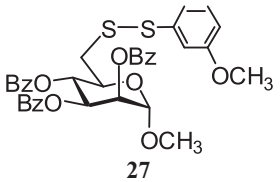
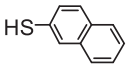
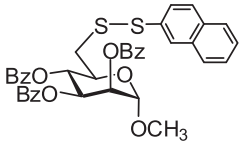
Sl. No.	Glycosyl halide	Aryl thiol	Product	Time (min)[a]	Yield (%)[b]
8	**2**		 **20**	30	82
9	 **3**		 **21**	30	86
10	**3**		 **22**	30	82
11	 **5**		**22**  **23**	45	80
12	 **6**		 **24**	30	85
13	**6**		 **25**	30	84
14	**6**		 **26**	30	80
15	**6**		 **27**	45	86

Table 3 (*continued*)

Sl. No.	Glycosyl halide	Aryl thiol	Product	Time (min)[a]	Yield (%)[b]
16	**6**		 **28**	60	78

[a] Time required after the formation of Bunte salt.
[b] Isolated yield.

reaction mixture was cooled to room temperature and 2,6-dimethylthiophenol (155 mg, 1.1 mmol) and Et_3N (0.2 mL, 2 mmol) were added to it. After stirring the reaction mixture at room temperature for 45 min (Table 3), it was diluted with satd. aq. $NaHCO_3$ (10 mL) and extracted with EtOAc (10 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was passed through a short pad of SiO_2 using hexane-EtOAc (6:1) as eluant to give pure symmetrical glycosyl disulfide derivative (**13**) (338 mg, 82%). Following similar reaction conditions, compounds **14**–**28** were prepared (Table 3).

Analytical data of symmetrical glycosyl disulfide derivative (**13**–**28**):

6-Deoxy-6-(2,6-dimethylphenyldithio)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (13): Yield: 338 mg, 82%; Colorless oil. $[\alpha]_D$ + 30 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–6.86 (m, 3 H, Ar–H), 5.44 (d, J = 5.0 Hz, 1 H, H-1), 4.55 (dd, J = 8.0 Hz, 2.0 Hz, 1 H, H-3), 4.28 (dd, J = 7.5 Hz, 1.5 Hz, 1 H, H-2), 4.23 (dd, J = 5.0 Hz, 2.5 Hz, 1 H, H-4), 4.05–4.03 (m, 1 H, H-5), 2.82–2.80 (m, 2 H, H-6_{ab}), 2.27 (s, 6 H, 2 CH_3), 1.45 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.27 (s, 6 H, 2 CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.2–127.9 (Ar–C), 109.3 [$(CH_3)_2C(O)_2$], 108.7 [$(CH_3)_2C(O)_2$], 96.6 (C-1), 71.5 (C-3), 70.9 (C-4), 70.6 (C-2), 66.3 (C-5), 37.6 (C-6), 26.0 (2 *C*H_3), 25.0 (*C*H_3), 24.5 (*C*H_3), 21.1 (*C*H_3), 19.5 (*C*H_3); HRMS for $C_{20}H_{28}O_5S_2$ $[M+H]^+$: Calcd. 413.1456; found: 413.1438.

6-Deoxy-6-(3,4-dichlorophenyldithio)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (14): Yield: 361 mg, 80%; Colorless oil. $[\alpha]_D$ + 44 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56–7.19 (m, 3 H, Ar–H), 5.44 (d, J = 5.0 Hz, 1 H, H-1), 4.55 (dd, J = 8.0 Hz, 2.5 Hz, 1 H, H-3), 4.24 (dd, J = 5.0 Hz, 2.5 Hz, 1 H, H-2), 4.20–4.18 (m, 1 H, H-6_a), 3.97–3.89 (m, 1 H, H-5), 2.88–2.85 (m, 1 H, H-6_b), 1.41 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.2–126.5 (Ar–C), 109.4 [$(CH_3)_2C(O)_2$], 108.7 [$(CH_3)_2C(O)_2$], 96.6 (C-1), 71.6 (C-3), 70.9 (C-4), 70.4 (C-2), 66.3 (C-5), 38.7 (C-6), 25.9 (2 *C*H_3), 24.9 (*C*H_3), 24.5 (*C*H_3); HRMS for $C_{18}H_{22}Cl_2O_5S_2$ $[M+H]^+$: Calcd. 453.0364; found: 453.0346.

6-Deoxy-6-(2-bromophenyldithio)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (15): Yield: 390 mg, 84%; Colorless oil. $[\alpha]_D$ + 21 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74–6.98 (m, 4 H, Ar–H), 5.44 (d, J = 5.0 Hz, 1 H, H-1), 4.55 (dd, J = 7.5 Hz, 2.0 Hz, 1 H, H-3), 4.25–4.22 (m, 2 H, H-2, H-4), 4.08–3.98 (m, 1 H, H-5), 2.85–2.81 (m, 2 H, H-6_{ab}), 1.46 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.3–121.4 (Ar–C), 109.3 [$(CH_3)_2C(O)_2$], 108.8 [$(CH_3)_2C(O)_2$], 96.6 (C-1), 71.6 (C-3), 70.9 (C-4), 70.5 (C-2), 66.1 (C-5), 37.7 (C-6), 26.0 (2 *C*H_3), 25.0 (*C*H_3), 24.5 (*C*H_3); HRMS for $C_{18}H_{23}BrO_5S_2$ $[M+H]^+$: Calcd. 463.0248; found: 463.0233.

6-Deoxy-6-(3-methoxyphenyldithio)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (16): Yield: 356 mg, 86%; Colorless oil. $[\alpha]_D$ + 63 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz,$CDCl_3$): δ 7.15–6.66 (m, 4 H, Ar–H), 5.44 (d, J = 5.0 Hz, 1 H, H-1), 4.54 (dd, J = 7.5 Hz, 2.0 Hz, 1 H, H-3), 4.24–4.21 (m, 2 H, H-2, H-4), 4.01–3.99 (m, 1 H, H-5), 3.75 (s, 3 H, OCH_3), 2.86–2.83 (m, 2 H, H-6_{ab}), 1.44 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.26 (s, 6 H, 2 CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.1–112.5 (Ar–C), 109.3 [$(CH_3)_2C(O)_2$], 108.7 [$(CH_3)_2C(O)_2$], 96.6 (C-1), 71.6 (C-3), 70.9 (C-4), 70.5 (C-2), 66.2 (C-5), 55.2 (OCH_3), 38.2 (C-6), 26.0 (2 *C*H_3), 25.0 (*C*H_3), 24.4 (*C*H_3); HRMS for $C_{19}H_{26}O_6S_2$ $[M+H]^+$: Calcd. 415.1249; found: 415.1232.

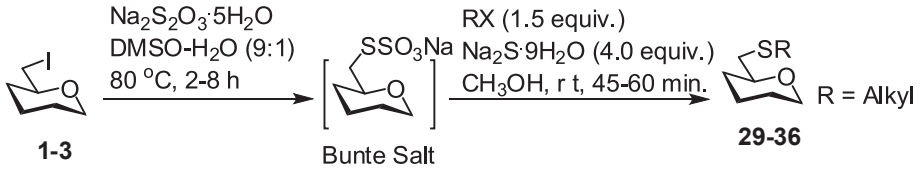
Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-(2-napthyldithio)-α-D-glucopyranoside (17): Yield: 497 mg, 78%; Colorless oil. $[\alpha]_D$ + 26 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93–6.97 (m, 22 H, Ar–H), 4.80 (d, J = 11.0 Hz, 1 H, PhC*H*), 4.63 (ABq, J = 10.0 Hz, 2 H, 2 PhC*H*), 4.59 (br s, 1 H, H-1), 4.50 (br s, 2 H, 2 PhC*H*), 4.44 (d, J = 11.0 Hz, 1 H, PhC*H*), 3.80–3.76 (m, 2 H, H-3, H-5), 3.68 (br s, 1 H, H-2), 3.65 (t, J = 9.5 Hz, 1 H, H-4), 3.24 (s, 3 H, OCH_3), 3.14 (dd, J = 13.5 Hz, 2.0 Hz, 1 H, H-6_a), 2.85 (dd, J = 13.5 Hz, 2.0 Hz, 1 H, H-6_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3–126.0 (Ar–C), 98.8 (C-1), 80.2 (C-2), 77.6 (C-3), 75.0 (PhCH_2), 74.6 (C-4), 72.7 (PhCH_2), 72.1 (PhCH_2), 70.2 (C-5), 54.7 (OCH_3), 41.2 (C-6); HRMS for $C_{38}H_{38}O_5S_2$ $[M+H]^+$: Calcd. 639.2239; found: 639.2222.

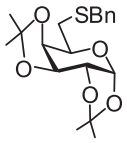
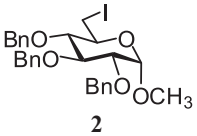
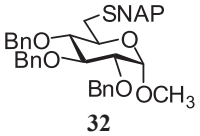
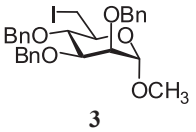
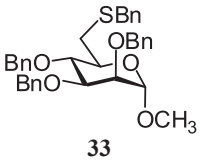
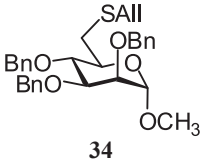
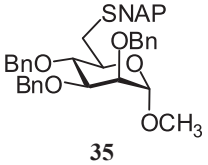
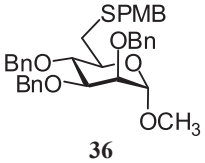
Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-(4-chlorophenyldithio)-α-D-glucopyranoside (18): Yield: 516 mg, 83%; Colorless oil. $[\alpha]_D$ + 42 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.06 (m, 19 H, Ar–H), 4.90 (d, J = 11.0 Hz, 1 H, PhC*H*), 4.80 (d, J = 11.0 Hz, 1 H, PhC*H*), 4.72–4.68 (m, 2 H, 2 PhC*H*), 4.58 (d, J = 12.0 Hz, 1 H, PhC*H*), 4.44 (d, J = 4.0 Hz, 1 H, H-1), 4.42 (d, J = 11.5 Hz, 1 H, PhC*H*), 3.90 (t, J = 9.0 Hz, 1 H, H-3), 3.82–3.79 (m, 1 H, H-5), 3.39 (dd, J = 9.5 Hz, 3.5 Hz, 1 H, H-2), 3.29 (s, 3 H, OCH_3), 3.20 (t, J = 9.5 Hz, 1 H, H-4), 3.02 (dd, J = 13.5 Hz, 3.5 Hz, 1 H, H-6_a), 2.66 (dd, J = 13.5 Hz, 3.5 Hz, 1 H, H-6_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6–127.6 (Ar–C), 97.8 (C-1), 81.8 (C-5), 80.5 (C-3), 80.0 (C-4), 75.7 (PhCH_2), 75.0 (PhCH_2), 73.3 (PhCH_2), 68.9 (C-2), 55.2 (OCH_3), 41.3 (C-6); HRMS for $C_{34}H_{35}ClO_5S_2$ $[M+H]^+$: Calcd. 623.1692; found: 623.1676.

Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-(3-methylphenyldithio)-α-D-glucopyranoside (19): Yield: 530 mg, 88%; Colorless oil. $[\alpha]_D$ + 53 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.7.31–6.93 (m, 19 H, Ar–H), 4.90 (d, J = 11.0 Hz, 1 H, PhC*H*), 4.77 (d, J = 11.0 Hz, 1 H, PhC*H*), 4.71–4.68 (m, 2 H, 2 PhC*H*), 4.57 (d, J = 12.0 Hz, 1 H, PhC*H*), 4.46 (d, J = 5.0 Hz, 1 H, PhC*H*), 4.44 (d, J = 2.0 Hz, 1 H, H-1), 3.90 (t, J = 9.0 Hz, 1 H, H-3), 3.85–3.77 (m, 1 H, H-5), 3.40 (dd, J = 9.5 Hz, 3.5 Hz, 1 H, H-2), 3.30 (s, 3 H, OCH_3), 3.22 (t, J = 9.5 Hz, 1 H, H-4), 3.07 (dd, J = 13.0 Hz, 2.0 Hz, 1 H, H-6_a), 2.69 (dd, J = 13.0 Hz, 2.0 Hz, 1 H, H-6_b), 2.24 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7–125.5 (Ar–C), 97.8 (C-1), 81.9 (C-5), 80.5 (C-3), 80.0 (C-4), 75.7 (PhCH_2), 74.9 (PhCH_2), 73.3 (PhCH_2), 69.0 (C-2), 55.2 (OCH_3), 41.6 (C-6), 21.4 (CH_3); HRMS for $C_{35}H_{38}O_5S_2$ $[M+H]^+$: Calcd. 603.2239; found: 603.2225.

Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-(3-methoxyphenyldithio)-α-D-glucopyranoside (20): Yield: 506 mg, 82%; Colorless oil. $[\alpha]_D$ + 21 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22–6.66 (m, 19 H, Ar–H), 4.89 (d, J = 11.0 Hz,

Table 4
Preparation of glycosyl alkyl sulphides from glycosyl iodides via the formation of Bunte salt.



Sl. No.	Glycosyl halide	Alkyl halide	Product	Time (min)[a]	Yield (%)[b]
1	 **1**	BnBr	 **29**	60	85
2	**1**	All Br	 **30**	60	80
3	**1**	NAPBr	 **31**	60	82
4	 **2**	NAPBr	 **32**	45	78
5	 **3**	BnBr	 **33**	45	86
6	**3**	All Br	 **34**	45	82
7	**3**	NAPBr	 **35**	60	76
8	**3**	PMBCl	 **36**	60	78

[a] Time required after the formation of Bunte salt.
[b] Isolated yield. NAP: 2-naphthylmethyl; PMB: *p*-methoxybenzyl.

1 H, PhC*H*), 4.77 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.71–4.68 (m, 2 H, 2 PhC*H*), 4.57 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.46 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.44 (d, *J* = 3.5 Hz, 1 H, H-1), 3.89 (t, *J* = 9.5 Hz, 1 H, H-3), 3.88–3.81 (m, 1 H, H-5), 3.69 (s, 3 H, OCH_3), 3.41 (dd, *J* = 9.5 Hz, 3.5 Hz, 1 H, H-2), 3.30 (s, 3 H, OCH_3), 3.26 (t, *J* = 9.5 Hz, 1 H, H-4), 3.06 (dd, *J* = 12.5 Hz, 2.0 Hz, 1 H, H-6_a), 2.69 (dd, *J* = 12.5 Hz, 2.0 Hz, 1 H, H-6_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.1–113.0 (Ar–C), 97.8 (C-1), 81.9 (C-2), 80.5 (C-3), 80.0 (C-4), 75.7 (PhCH_2), 74.9 (PhCH_2), 73.3 (PhCH_2), 69.1 (C-5), 55.2 (2 C, 2 OCH_3), 41.6 (C-6); HRMS for $C_{35}H_{38}O_6S_2$ $[M+H]^+$: Calcd. 619.2188; found: 619.2176.

Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-(4-methylphenyldithio)-α-D-mannopyranoside (21): Yield: 517 mg, 86%; Colorless oil. $[\alpha]_D$ + 48 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–6.97 (m, 19 H, Ar–H), 4.84 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.63 (ABq, *J* = 10.0 Hz, 2 H, 2 PhC*H*), 4.60 (br s, 1 H, H-1), 4.51 (br s, 2 H, 2 PhC*H*), 4.46 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 3.79–3.77 (m, 2 H, H-3, H-5), 3.68 (br s, 1 H, H-2), 3.65 (t, *J* = 9.5 Hz, 1 H, H-4), 3.24 (s, 3 H, OCH_3), 3.11 (dd, *J* = 13.5 Hz, 2.0 Hz, 1 H, H-6_a), 2.81 (dd, *J* = 13.5 Hz, 2.0 Hz, 1 H, H-6_b), 2.25 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3–127.5 (Ar–C), 98.8 (C-1), 80.2 (C-5), 77.6 (C-3), 75.0 (PhCH_2), 74.6 (C-4), 72.7 (PhCH_2), 72.1 (PhCH_2), 70.1 (C-2), 54.7 (OCH_3), 41.0 (C-6), 21.1 (CH_3); HRMS for $C_{35}H_{38}O_5S_2$ $[M+H]^+$: Calcd. 603.2239; found: 603.2227.

Methyl 2,3,4-tri-*O*-benzyl-6-deoxy-6-(4-chlorophenyldithio)-α-D-mannopyranoside (22): Yield: 510 mg, 82%; Colorless oil. $[\alpha]_D$ + 31 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.7.39–7.07 (m, 19 H, Ar–H), 4.85 (d, *J* = 11.0 Hz, 1 H, PhC*H*), 4.64 (AB_q, *J* = 10.0 Hz, 2 H, 2 PhC*H*), 4.59 (br s, 1 H, H-1), 4.52 (br s, 2 H, 2 PhC*H*), 4.45 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 3.77–3.76 (m, 2 H, H-3, H-5), 3.68 (br s, 1 H, H-2), 3.64 (t, *J* = 9.0 Hz, 1 H, H-4), 3.24 (s, 3 H, OCH_3), 3.06 (dd, *J* = 13.5 Hz, 4.5 Hz, 1 H, H-6_a), 2.81 (dd, *J* = 13.5 Hz, 4.5 Hz, 1 H, H-6_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3–127.5 (Ar–C), 98.9 (C-1), 80.2 (C-5), 77.6 (C-3), 75.1 (PhCH_2), 74.5 (C-4), 72.8 (PhCH_2), 72.1 (PhCH_2), 70.1 (C-2), 54.7 (OCH_3), 41.1 (C-6); HRMS for $C_{34}H_{35}ClO_5S_2$ $[M+H]^+$: Calcd. 623.1692; found: 623.1680.

Methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-(2-methoxyphenyldithio)-α-D-glucopyranoside (23): Yield: 528 mg, 80%; Colorless oil. $[\alpha]_D$ + 17 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96–6.69 (m, 19 H, Ar–H), 6.05 (t, *J* = 10.0 Hz, 1 H, H-3), 5.33 (t, *J* = 9.5 Hz, 1 H, H-4), 5.17 (dd, *J* = 10.5 Hz, 3.5 Hz, 1 H, H-2), 5.11 (d, *J* = 3.5 Hz, 1 H, H-1), 4.35–4.30 (m, 1 H, H-5), 3.74 (s, 3 H, OCH_3), 3.39 (s, 3 H, OCH_3), 2.94–2.92 (m, 2 H, H-6_{ab}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7 (PhCO), 165.6 (PhCO), 165.4 (PhCO), 133.2–110.8 (Ar–C), 96.7 (C-1), 72.3 (C-2), 72.1 (C-4), 70.3 (C-3), 68.2 (C-5), 55.6 (OCH_3), 55.5 (OCH_3), 42.0 (C-6); HRMS for $C_{35}H_{32}O_9S_2$ $[M+H]^+$: Calcd. 661.1566; found: 661.1552.

Methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-(4-methylphenyldithio)-α-D-mannopyranoside (24): Yield: 547 mg, 85%; Colorless oil. $[\alpha]_D$ + 73 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01–6.81 (m, 19 H, Ar–H), 5.78 (dd, *J* = 9.5 Hz, 3.0 Hz, 1 H, H-3), 5.65 (t, *J* = 10.0 Hz, 1 H, H-4), 5.56 (br s, 1 H, H-2), 4.85 (br s, 1 H, H-1), 4.33–4.29 (m, 1 H, H-5), 3.44 (s, 3 H, OCH_3), 2.93–2.91 (m, 2 H, H-6_{ab}), 2.17 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6 (PhCO), 165.3 (PhCO), 165.2 (PhCO), 137.7–128.2 (Ar–C), 98.4 (C-1), 70.6 (C-5), 69.9 (2 C, C-4, C-3), 68.7 (C-2), 55.4(OCH_3), 40.4 (C-6); HRMS for $C_{35}H_{32}O_8S_2$ $[M+H]^+$: Calcd. 645.1617; found: 645.1606.

Methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-(2,5-dimethylphenyldithio)-α-D-mannopyranoside (25): Yield: 552 mg, 84%; Colorless oil. $[\alpha]_D$ + 68 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–6.82 (m, 18 H, Ar–H), 5.77 (dd, *J* = 7.0 Hz, 2.5 Hz, 1 H, H-3), 5.65 (t, *J* = 9.0 Hz, 1 H, H-4), 5.55 (br s, 1 H, H-2), 4.84 (br s, 1 H, H-1), 4.29–4.28 (m, 1 H, H-5), 3.42 (s, 3 H, OCH_3), 2.96–2.95 (m, 2 H, H-6_{ab}), 2.26 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5 (PhCO), 165.4 (PhCO), 165.3 (PhCO), 136.0–128.2 (Ar–C), 98.4 (C-1), 70.6 (C-5), 69.9 (C-3), 69.8 (C-4), 69.0 (C-2), 55.3 (OCH_3), 40.9 (C-6), 21.0 (CH_3), 20.7 (CH_3); HRMS for $C_{36}H_{34}O_8S_2$ $[M+H]^+$: Calcd. 659.1773; found: 659.1760.

Methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-(3-chlorophenyldithio)-α-D-mannopyranoside (26): Yield: 531 mg, 80%; Colorless oil. $[\alpha]_D$ + 55 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–6.97 (m, 19 H, Ar–H), 5.76 (dd, *J* = 9.0 Hz, 2.0 Hz, 1 H, H-3), 5.66 (t, *J* = 9.0 Hz, 1 H, H-4), 5.56 (br s, 1 H, H-2), 4.86 (br s, 1 H, H-1), 4.31–4.27 (m, 1 H, H-5), 3.46 (s, 3 H, OCH_3), 3.01–2.94 (m, 2 H, H-6_{ab}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6 (PhCO), 165.3 (PhCO), 165.2 (PhCO), 138.6–126.0 (Ar–C), 98.5 (C-1), 70.5 (C-5), 69.8 (C-3), 69.7 (C-4), 69.0 (C-2), 55.5 (OCH_3), 41.2 (C-6); HRMS for $C_{34}H_{29}ClO_8S_2$ $[M+H]^+$: Calcd. 665.1070; found: 665.1056.

Methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-(3-methoxyphenyldithio)-α-D-mannopyranoside (27): Yield: 567 mg, 86%; Colorless oil. $[\alpha]_D$ + 88 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–6.59 (m, 19 H, Ar–H), 5.76 (dd, *J* = 9.0 Hz, 2.0 Hz, 1 H, H-3), 5.65 (t, *J* = 9.0 Hz, 1 H, H-4), 5.56 (br s, 1 H, H-2), 4.86 (br s, 1 H, H-1), 4.34–4.24 (m, 1 H, H-5), 3.65 (s, 3 H, OCH_3), 3.46 (s, 3 H, OCH_3), 3.02–2.96 (m, 2 H, H-6_{ab}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6 (PhCO), 165.3 (PhCO), 165.2 (PhCO), 133.4–113.3 (Ar–C), 98.5 (C-1), 70.6 (C-5), 69.9 (C-3), 69.8 (C-4), 68.9 (C-2), 55.4 (OCH_3), 55.1 (OCH_3), 40.9 (C-6); HRMS for $C_{35}H_{32}O_9S_2$ $[M+H]^+$: Calcd. 661.1566; found: 661.1554.

Methyl 2,3,4-tri-*O*-benzoyl-6-deoxy-6-(2-naphthyldithio)-α-D-mannopyranoside (28): Yield: 530 mg, 78%; Colorless oil. $[\alpha]_D$ + 62 (*c* 1.0, $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$): δ 8.06–7.11 (m, 22 H, Ar–H), 5.77 (dd, *J* = 9.8 Hz, 3.5 Hz, 1 H, H-3), 5.66 (t, *J* = 9.5 Hz, 1 H, H-4), 5.56 (br s, 1 H, H-2), 4.85 (br s, 1 H, H-1), 4.39–4.28 (m, 1 H, H-5), 3.44 (s, 3 H, OCH_3), 3.00–2.99 (m, 2 H, H-6_{ab}); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5 (PhCO), 165.4 (PhCO), 165.3 (PhCO), 133.6–126.2 (Ar–C), 98.5 (C-1), 70.5 (C-2), 69.9 (C-3), 69.8 (C-4), 68.9 (C-5), 55.4 (OCH_3), 40.6 (C-6); HRMS for $C_{38}H_{32}O_8S_2$ $[M+H]^+$: Calcd. 681.1617; found: 681.1628.

Typical reaction condition for the preparation of glycosyl alkyl sulfide (29): To a solution of compound **1** (370 mg, 1.0 mmol) in DMSO-H_2O (5 mL; 9:1 v/v) was added $Na_2S_2O_3 \cdot 5H_2O$ (375 mg, 1.5 mmol) and the reaction mixture was stirred at 80 °C for 8 h (Table 2). The reaction mixture was cooled to room temperature and diluted with CH_3OH (5 mL). To the reaction mixture were added $Na_2S \cdot 9H_2O$ (720 mg, 3.0 mmol) followed by benzyl bromide (0.18 mL, 1.5 mmol) and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was diluted with satd. aq. $NaHCO_3$ (10 mL) and extracted with EtOAc (10 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was passed through a short pad of SiO_2 using hexane-EtOAc (6:1) as eluant to give pure glycosyl alkyl sulfide derivative (**29**) (311 mg, 85%). Following similar reaction conditions, compounds **30**–**36** were prepared (Table 4).

Analytical data of symmetrical glycosyl disulfide derivative (**29**–**36**):

6-*S*-Benzyl-1,2:3,4-di-*O*-isopropylidene-6-thio-α-D-galactopyranose (29): Yield: 311 mg, 85%; Colorless oil. $[\alpha]_D$ + 32 (*c* 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23–7.18 (m, 5 H, Ar–H), 5.43 (d, *J* = 5.0 Hz, 1 H, H-1), 4.54–4.51 (m, 1 H, H-3), 4.21 (br s, 1 H, H-4), 4.15–4.11 (m, 1 H, H-2), 3.95–3.89 (m, 1 H, H-5), 3.92 (br s, 2 H, 2 PhCH_2), 2.57–2.53 (m, 2 H, H-6_{ab}), 1.50 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.25 (s, 6 H, 2 CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.2–127.4 (Ar–C), 109.2 [$(CH_3)_2C(O)_2$], 108.6 [$(CH_3)_2C(O)_2$], 96.6 (C-1), 71.5 (C-3), 70.9 (C-4), 70.5 (C-2), 66.4 (C-5), 43.3 (SPhCH_2), 37.8 (C-6), 26.1 (CH_3), 26.0 (CH_3), 25.0 (CH_3), 24.5 (CH_3); HRMS for $C_{19}H_{26}O_5S$ $[M+H]^+$: Calcd. 367.1579; found: 367.1590.

6-*S*-Allyl-1,2:3,4-di-*O*-isopropylidene-6-thio-α-D-galactopyranose (30): Yield: 253 mg, 80%; Colorless oil. $[\alpha]_D$ + 43 (*c* 1.0,

$CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.5.81–5.71 (m, 1 H, C*H*=CH_2), 5.46 (d, J = 5.0 Hz, 1 H, H-1), 5.16–5.09 (m, 2 H, CH=CH_2), 4.56–4.55 (m, 1 H, H-3), 4.27–4.24 (m, 2 H, H-2, H-4), 4.13–3.99 (m, 1 H, H-5), 3.29–3.27 (m, 2 H, SCH_2), 2.84–2.82 (m, 2 H, H-6_{ab}), 1.45 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.3 (*C*H=CH_2), 118.6 (HC=CH_2), 109.1 [$(CH_3)_2C(O)_2$], 108.7 [$(CH_3)_2C(O)_2$], 96.6 (C-1), 71.5 (C-3), 70.9 (C-4), 70.5 (C-2), 66.5 (C-5), 41.9 (SCH_2), 38.5 (C-6), 26.1 (CH_3), 25.9 (CH_3), 25.0 (CH_3), 24.4 (CH_3); HRMS for $C_{15}H_{24}O_5S$ $[M+H]^+$: Calcd. 317.1422; found: 317.1411.

6-*S*-(2-Naphthylmethyl)-1,2:3,4-di-*O*-isopropylidene-6-thio-α-D-galactopyranose (31): Yield: 341 mg, 82%; Colorless oil. $[\alpha]_D$ + 37 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.73–7.18 (m, 7 H, Ar–H), 5.44 (d, J = 5.0 Hz, 1 H, H-1), 4.50 (dd, J = 8.0 Hz, 2.5 Hz, 1 H, H-3), 4.24–4.21 (m, 1 H, H-4), 4.06 (dd, J = 8.0 Hz, 1.5 Hz, 1 H, H-2), 4.02 (br s, 2 H, 2 SPhC*H*), 3.96–3.94 (m, 1 H, H-5), 2.67–2.55 (m, 2 H, H-6_{ab}), 1.52 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3), 1.22 (s, 3 H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 134.5–125.9 (Ar–C), 109.2 [$(CH_3)_2C(O)_2$], 108.7 [$(CH_3)_2C(O)_2$], 96.6 (C-1), 71.5 (C-3), 70.8 (C-4), 70.5 (C-5), 66.5 (C-2), 43.6 (SPhCH_2), 38.1 (C-6), 26.1 (CH_3), 25.9 (CH_3), 25.0 (CH_3), 24.3 (CH_3); HRMS for $C_{23}H_{28}O_5S$ $[M+H]^+$: Calcd. 417.1735; found: 417.1726.

Methyl 6-*S*-(2-naphthylmethyl)-2,3,4-tri-*O*-benzyl-6-thio-α-D-glucopyranoside (32): Yield: 484 mg, 78%; Colorless oil. $[\alpha]_D$ + 32 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.78–7.12 (22 H, Ar–H), 4.87 (d, J = 10.5 Hz, 1 H, PhC*H*), 4.85–4.66 (m, 3 H, 3 PhC*H*), 4.56 (d, J = 12.0 Hz, 1 H, PhC*H*), 4.44 (d, J = 3.0 Hz, 1 H, H-1), 4.34 (d, J = 11.0 Hz, 1 H, PhC*H*), 3.95 (s, 2 H, 2 PhC*H*), 3.84 (t, J = 9.5 Hz, 1 H, H-3), 3.68–3.51 (m, 1 H, H-5), 3.39 (dd, J = 10.0 Hz, 3.5 Hz, 1 H, H-2), 3.27 (s, 3 H, OCH_3), 3.10 (t, J = 9.5 Hz, 1 H, H-4), 2.74 (dd, J = 13.5 Hz, 2.0 Hz, 1 H, H-6_a), 2.46 (dd, J = 13.5 Hz, 2.0 Hz, 1 H, H-6_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1–125.9 (Ar–C), 97.8 (C-1), 81.8 (C-2), 80.6 (C-5), 79.9 (C-3), 75.7 (PhCH_2), 74.9 (PhCH_2), 73.4 (PhCH_2), 69.3 (C-4), 55.2 (OCH_3), 43.9 (SPhCH_2), 42.3 (C-6); HRMS for $C_{39}H_{40}O_5S$ $[M+H]^+$: Calcd. 621.2674; found: 621.2662.

Methyl 6-*S*-benzyl-2,3,4-tri-*O*-benzyl-6-thio-α-D-mannopyranoside (33): Yield: 490 mg, 86%; Colorless oil. $[\alpha]_D$ + 72 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.32–7.18 (m, 20 H, Ar–H), 4.85 (d, J = 11.0 HZ, 1 H, PhC*H*), 4.66 (AB_q, J = 8.5 Hz, 2 H, 2 PhC*H*), 4.59 (br s, 1 H, H-1), 4.51 (br s, 1 H, PhC*H*), 4.48 (d, J = 11.5 Hz, 1 H, PhC*H*), 3.83 (s, 2 H, SPhC*H*), 3.77 (dd, J = 8.5 Hz, 3.0 Hz, 1 H, H-3), 3.68 (br s, 1 H, H-2), 3.66–3.62 (m, 2 H, H-4, H-5), 3.24 (s, 3 H, OCH_3), 2.88 (dd, J = 10.0 Hz, 3.5 Hz, 1 H, H-6_a), 2.71 (dd, J = 10.0 Hz, 3.5 Hz, 1 H, H-6_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3–127.3 (Ar–C), 98.9 (C-1), 80.2 (C-2), 77.6 (C-3), 74.9 (PhCH), 74.6 (C-4), 72.8 (PhCH), 72.1 (PhCH), 70.6 (C-5), 54.8 (OCH_3), 43.5 (SPhCH), 42.2 (C-6); HRMS for $C_{35}H_{38}O_5S$ $[M+H]^+$: Calcd. 571.2518; found: 571.2530.

Methyl 6-*S*-allyl-2,3,4-tri-*O*-benzyl-6-thio-α-D-mannopyranoside (34): Yield: 427 mg, 82%; Colorless oil. $[\alpha]_D$ + 66 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.27–7.18 (m, 15 H, Ar–H), 5.76–5.71 (m, 1 H, C*H*=CH_2), 5.11 (d, J = 10.0 Hz, 1 H, CH=CH_2), 5.01 (d, J = 10.0 Hz, 1 H, CH=CH_2), 4.90 (d, J = 11.0 Hz, 1 H, PhC*H*), 4.64–4.61 (m, 3 H, 2 PhC*H*, H-1), 4.53 (br s, 3 H, 3 PhC*H*), 3.80 (dd, J = 9.0 Hz, 3.0 Hz, 1 H, H-2), 3.75–3.69 (m, 3 H, H-3, H-4, H-5), 3.27–3.25 (m, 5 H, OCH_3, SCH_2), 3.11 (dd, J = 13.5 Hz, 2.0 Hz, 1 H, H-6_a), 2.88–2.80 (m, 1 H, H-6_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4–127.6 (Ar–C, *C*H=CH_2), 118.4 (CH=*C*H_2), 98.9 (C-1), 80.2 (C-2), 77.7 (C-3), 75.1 (PhCH), 74.6 (C-4), 72.8 (PhCH), 72.1 (PhCH), 70.5 (C-5), 54.8 (OCH_3), 42.1 (SCH_2), 42.0 (C-6); HRMS for $C_{31}H_{36}O_5S$ $[M+H]^+$: Calcd. 521.2361; found: 521.2350.

Methyl 6-*S*-(2-naphthylmethyl)-2,3,4-tri-*O*-benzyl-6-thio-α-D-mannopyranoside (35): Yield: 472 mg, 76%; Colorless oil. $[\alpha]_D$ + 41 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.77–7.18 (m, 22 H, Ar–H), 4.78 (d, J = 11.0 Hz, 1 H, PhC*H*), 4.65–4.59 (m, 2 H, 2 PhC*H*), 4.49 (br s, 2 H, 2 PhC*H*), 4.40 (d, J = 11.0 Hz, 1 H, PhC*H*), 3.99 (br s, 2 H, 2 SPhC*H*), 3.71–3.59 (m, 4 H, H-2, H-3, H-4, H-5), 3.26 (s, 3 H, OCH_3), 2.87 (dd, J = 13.5 Hz, 2.0 Hz, 1 H, H-6_a), 2.71 (dd, J = 13.5 Hz, 2.0 Hz, 1 H, H-6_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2–125.8 (Ar–C), 98.9 (C-1), 80.1 (C-2), 77.5 (C-3), 74.9 (PhCH_2), 74.6 (C-4), 72.8 (PhCH_2), 72.1 (PhCH_2), 70.7 (C-5), 54.8 (OCH_3), 43.9 (SPhCH_2), 42.3 (C-6); HRMS for $C_{39}H_{40}O_5S$ $[M+H]^+$: Calcd. 621.2674; found: 621.2660.

Methyl 6-*S*-(*p*-methoxybenzyl)-2,3,4-tri-*O*-benzyl-6-thio-α-D-mannopyranoside (36): Yield: 468 mg, 78%; Colorless oil. $[\alpha]_D$ + 56 (*c* 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.26–7.23 (m, 15 H, Ar–H), 7.12 (d, J = 8.5 Hz, 2 H, Ar–H), 6.71 (d, J = 8.5 Hz, 2 H, Ar–H), 4.85 (d, J = 11.5 Hz, 1 H, PhC*H*), 4.63 (AB_q, J = 8.5 Hz, 2 H, 2 PhC*H*), 4.60 (d, J = 3.0 Hz, H-1), 4.51–4.48 (m, 3 H, 3 PhC*H*), 3.79 (br s, 2 H, 2 SPhC*H*), 3.88–3.78 (m, 1 H, H-3), 3.72 (br s, 1 H, H-2), 3.68–3.61 (m, 5 H, H-4, H-5, SCH_2PhOCH_3), 3.25 (s, 3 H, OCH_3), 2.92 (dd, J = 9.0 Hz, 2.5 Hz, 1 H, H-6_a), 2.74 (dd, J = 9.0 Hz, 2.5 Hz, 1 H, H-6_b); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.9–113.9 (Ar–C), 98.9 (C-1), 80.2 (C-2), 77.6 (C-3), 75.0 (PhCH_2), 74.6 (C-4), 72.8 (PhCH_2), 72.1 (PhCH_2), 70.7 (C-5), 55.2 (OCH_3), 54.8 (OCH_3), 43.0 (SPhCH_2), 42.3 (C-6); HRMS for $C_{36}H_{40}O_6S$ $[M+H]^+$: Calcd. 601.2624; found: 601.2615.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132242.

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