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Stereoselective Synthesis of β-Glycosyl Thiols and Their Synthetic Applications

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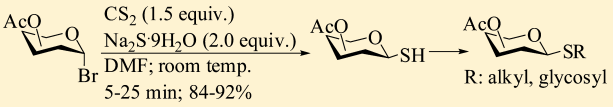
Supporting Information

ABSTRACT: A significantly fast reaction condition for the exclusive preparation β-glycosyl thiol derivatives has been developed successfully. The reaction condition is one-step, fast, high yielding, highly stereoselective, and requires only benchtop chemicals. Further reaction of glycosyl thiol derivatives with Michael acceptors and alkylating agents furnished thioglycosides and (1,1)-thiolinked trehalose analogs.



Glycosyl thiol derivatives or 1-thiosugar derivatives are important building blocks for the synthesis of various thiooligosaccharides and glycoconjugate derivatives.[1−3] Because of the exceptional stability of the sulfide linkages toward the enzymatic hydrolysis,[4] thiolinked glycoconjugates are considered as promising molecules to design therapeutics.[5] The anomeric configuration of the glycosyl thiol derivatives mostly remains unaffected[6,7] during the course of synthetic transformations in contrast to its normal sugar hemiacetal derivatives. Glycosyl thiols are being used in the preparation of a series of carbohydrate intermediates useful in the synthesis of biologically important molecules such as C-glycosides,[8] glycosyl sulfenamide/sulfonamide derivatives,[9,10] glycosyl disulfide derivatives,[11] glycosyl thionolactone derivatives' etc. They can also be transformed into new class of glycosyl donors such as glycosyl *N*-phenyltrifluorothioacetimidate[13] and glycosyl sulfenic acid[14] derivatives in the glycosylations. In the recent past, glycosyl thiols were used in the synthesis of sulfur-containing glycolipids,[15] glycopeptides, and glycoproteins[16] as well as in the radical mediated coupling with alkenes.[17]

The conventional approaches for the synthesis of glycosyl thiol derivatives include a two-step reaction sequence involving the S_N2 substitution reaction of glycosyl halide or acetate with thiourea[18,19] or thioacetate[20] and hydrolysis or de-*S*-acetylation of the resulting intermediate. Reductive removal of the benzyl group from the anomeric thiobenzyl glycoside[21] has also been explored for the preparation of glycosyl thiol derivatives. Another method for the preparation of glycosyl thiol derivatives involves bubbling of hydrogen sulfide gas through the solution of glycosyl halides in hydrogen fluoride.[22] Davis et al.[23] reported the direct preparation of glycosyl thiol derivatives on treatment of the glycosyl hemiacetal derivatives with Lawesson's reagent in moderate yields with no stereoselectivity. Zhu et al.[24,25] and Schmidt et al.[26] reported the exclusive preparation of α-glycosyl thiol derivatives by the treatment of 1,6-anhydro sugar derivative and glycosyl trichloroacetimidate derivatives with bis(trimethylsilyl)sulfide [$(TMS)_2S$] respectively. Although a number of reports appeared in the literature for the preparation of glycosyl thiol derivatives, most of the reaction conditions suffer from several shortcomings, which include longer reaction time, multiple steps, unsatisfactory yield, formation isomeric mixture, use of expensive reagent [e.g., $(TMS)_2S$], use of hazardous gas (e.g., H_2S), use of appropriately functionalized substrates, etc. Hence, there is a strong need for the stereoselective preparation of glycosyl thiol derivatives. In this context, we envisioned that S_N2 substitution of the bromide ion of glycosyl bromide with sodium carbonotrithioate, a H_2S equivalent, derived from the reaction of sodium sulfide with carbon disulfide could furnish the desired glycosyl thiol derivatives with high stereoselectivity in one-step reaction condition. In this communication, a one-step synthesis of exclusively β-glycosyl thiol derivatives, together with their applications in the Michael reaction with conjugated alkenes and preparation of thioglycosides, is presented.

Initially, carbon disulfide (CS_2) was added to sodium sulfide ($Na_2S·9H_2O$) in equimolar ratio in DMF to generate a red solution of sodium carbonotrithioate. On addition of the acetobromo-α-D-glucose (**1**; 1.0 equiv) to the in situ generated sodium carbonotrithioate solution at room temperature, the red color of the solution immediately turned into yellow. Aqueous workup of the reaction mixture furnished 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (**15**) exclusively in a 80% yield. Other commonly used solvents (e.g., CH_2Cl_2, $CHCl_3$, THF, toluene, CH_3CN, DMSO, Et_2O, CH_3OH, H_2O, etc.) have been screened and did not produce satisfactory results (Table 1). Although the yield of the product formation in DMSO and DMF were comparable, DMF has been chosen as the reaction solvent because of the shortcomings associated with DMSO (e.g., high boiling point, unpleasant odor, chance of unwanted byproduct formation, etc.). Use of alcohol or water did not furnish satisfactory yields, and degraded starting materials were obtained as the major products. To optimize the reaction condition, a series of experiments were carried out using $Na_2S·9H_2O$ (2.0 equiv) and 0.5−1.5 equiv of CS_2 in DMF at room temperature. It was observed that the yield of the formation of compound **15** can be raised to 90% by the

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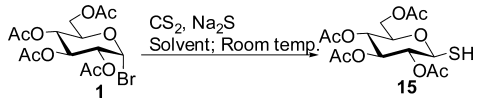
Table 1. Screening of Solvents Appropriate for the Reaction



Sl. no.	solvent	time (min)	yield (%)
1	CH_2Cl_2[a]	60	10[b]
2	$CHCl_3$[a]	60	15[b]
3	THF[a]	60	
4	CH_3CN[a]	60	25[b]
5	toluene[c]	90	
6	Et_2O[c]	90	
7	DMSO	5	85
8	DMF	5	90
9	CH_3OH	60	20[b]
10	H_2O	60	10[b]

[a]$Na_2S{\cdot}9H_2O$ partly soluble. [b]Most of the starting material degraded. [c]$Na_2S{\cdot}9H_2O$ insoluble.

reaction of compound **1** with a premixed mixture of CS_2 (1.5 equiv) and $Na_2S{\cdot}9H_2O$ (2.0 equiv) in DMF at room temperature in 5 min (Scheme 1) (Table 2). Use of less amount of CS_2 (0.5 equiv) resulted in the significant formation of symmetrical bis-glycosyl sulfide derivative (**15a**), may be due to the condensation of unreacted glycosyl bromide with the in situ generated glycosyl thiol (**15**). In a control experiment, compound **1** was treated with $Na_2S{\cdot}9H_2O$ (2.0 equiv) in DMF at room temperature without addition of CS_2. The reaction did not proceed even after 12 h and only degraded starting material was obtained (Table 2). The exclusive formation of glycosyl thiol (**15**) using 2.0 equiv of CS_2 and bis-glycosyl disulfide (**15a**) using 0.5 equiv of CS_2 confirmed that use of excess CS_2 increased the rate of the glycosyl thiol formation, minimizing the chances of the reaction of glycosyl thiol with unreacted glycosyl bromide in the reaction mixture as well as hydrolysis of glycosyl bromide. In earlier reports,[27] reaction of glycosyl bromide with $Na_2S{\cdot}9H_2O$ in a phase transfer reaction at high temperature furnished bis-glycosyl sulfide derivatives instead of giving glycosyl thiol derivative. Following the optimized reaction condition, a series of glycosyl thiol derivatives (**15**–**25**) were prepared in excellent yield (Table 3). The reaction is equally effective in D- and L-sugar derivatives as well as in disaccharide derivatives. Although most of the glycosyl bromides furnished corresponding glycosyl thiol derivatives, treatment of 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl bromide (**12**) with CS_2 and $Na_2S{\cdot}9H_2O$ resulted in the exclusive formation of 3,4,6-tri-*O*-acetyl-D-glucal (**26**) in a 94% yield. This unexpected outcome may be explained either by considering the elimination of sodium bromide followed by elimination of hydrazoic acid (HN_3) from compound **12** or considering the instability of azido group in the presence of sodium carbonotrithioate formed in situ and elimination of HBr under the basic reaction condition. However, the exact mechanism for the formation of compound **26** from compound **12** is yet to be established. In contrast to the formation of compound **19** from compound **5**, reaction of 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl bromide (**13**) with CS_2 and $Na_2S{\cdot}9H_2O$ furnished only a mixture of oxazoline derivative (**13a**) and hemiacetal derivative without formation of the expected thiol derivative, presumably due to the faster rate of intramolecular cyclization (oxazoline formation) and hydrolysis than S_N2 substitution. A scaled up preparation (10 g) of glycosyl thiol derivative **15** was achieved with similar yield as in the small-scale preparation. Commonly used hydroxyl protecting groups (e.g., acetyl, benzoyl, benzyl, *N*-phthalimido etc.) remained unaffected under the reaction condition. The stereochemistry of the anomeric center of the glycosyl thiol derivatives were determined from the coupling constant ($J_{1,2}$) of the H-1 as well as SH ($J_{\text{H-1,SH}}$ = 8−10 Hz for β-glycosyl thiol and $J_{\text{H-1,SH}}$ = 4−5 Hz for α-glycosyl thiol). Another noteworthy point is that β-D-mannosidic thiol and β-L-rhamnosidic thiol derivatives can be achieved exclusively under the reaction condition, avoiding the formation of anomerized or oxidized products. In case of D-mannose and L-rhamnose derived glycosyl thiol derivatives, the anomeric configurations were determined using $J_{\text{SH–H1}}$ in the ^{1}H spectra and $J_{\text{C-1,H-1}}$ values from the ^{1}H coupled ^{13}C NMR spectra.[28] Appearance of $J_{\text{C-1,H-1}}$ values 141.2 and 141.4 Hz in the ^{1}H coupled ^{13}C NMR spectra of compounds **17** and **20**, respectively, confirmed the β-configuration of the thiol derivatives ($J_{\text{C-1,H-1}}$ less than 160 Hz).[28] The exclusive formation of β-glycosyl thiol derivatives could be explained by considering the S_N2 displacement of the bromide ion by the carbonotrithioate ion derived from the reaction of CS_2 and $Na_2S{\cdot}9H_2O$, followed by elimination of CS_2 in situ. Because all glycosyl bromides used in this study have α-configuration, β-glycosyl thiol was formed as the exclusive products. It is worth mentioning that the reaction condition is significantly fast and the exclusive formation of β-glycosyl thiols was observed from α-glycosyl bromides (Scheme 2). The

Scheme 1. Reaction of Glycosyl Bromides with Carbon Disulfide and Sodium Sulfide to Furnish β-Glycosyl Thiols

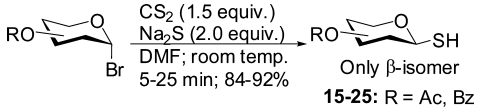
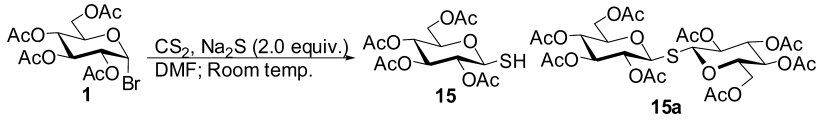


Table 2. Optimization of the Quantity of CS_2 for the Preparation Glycosyl Thiol Derivative



				product (%)	
Sl. no.	CS_2 (equiv)	$Na_2S{\cdot}9H_2O$(equiv)	time (min)	**15**	**15a**
1	0.5	2.0	5		60
2	1.0	2.0	5	50	30
3	1.5	2.0	5	90	
4		2.0	720		

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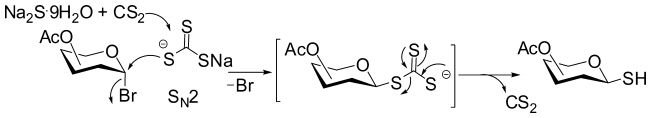
Scheme 2. Plausible Mechanism for the Stereoselective Formation of Glycosyl Thiol Derivatives

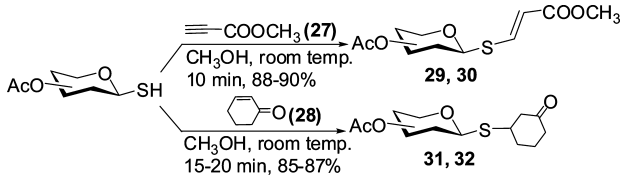


anomeric configuration of the glycosyl thiols was not influenced by the functional group (neighboring group participating or nonparticipating) present at C-2 position of the sugar backbone, which was established by the formation of exclusive β-thiol derivative (**25**) from the per-*O*-benzylated-α-D-gluco-pyranosyl bromide (**11**) (entry 11, Table 3). Contrary to the earlier report,[27] formation of oxidized product such as bis-glycosyl sulfide or glycosyl disulfide was not observed during the reaction. The glycosyl thiol derivatives were quite stable and have been used successfully for the preparation of unsymmetrical sulfide derivatives.

Application of the glycosyl thiol derivatives in the Michael addition was explored to prepare thio-linked glycoconjugate derivatives. Treatment of a series of glycosyl thiol derivatives with α,β-unsaturated ester or ketone in methanol at room temperature furnished excellent yield of Michael addition products without requirement of any catalyst (Scheme 3, Table 4). Reaction of glycosyl thiols with methyl propiolate (**27**) furnished exclusively *E*-isomer of the Michael addition products (entries 1, 2; compounds **29**, **30**; Table 4), whereas reactions of glycosyl thiols with 2-cyclohexenone (**28**) furnished mixture of diastereomeric products (entries 3, 4; compounds **31**, **32**; Table 4), which were confirmed from the NMR spectral analysis. This methodology has the potential to find application in the conjugation of carbohydrate derivatives to protein/peptide[17,29] through a spacer linker or to immobilize glycans to solid support.[30]

In another approach, β-glycosyl thiol derivatives were allowed to react with a variety of alkyl halides in the presence of catalytic amount of triethylamine in DMF to furnish alkyl β-

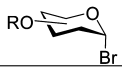
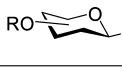
Scheme 3. Reaction of β-Glycosylthiol Derivatives with Conjugated Alkene Derivatives



thioglycoside derivatives (Scheme 4) (entries 1−4, Compounds **33**−**36**, Table 5). Yields were excellent in all reactions, and formation of anomerization products of the thioglycosides was not observed. Similarly, reaction of β-glycosyl thiol derivatives with a diastereomeric mixture of lactic acid ester triflate salt furnished thio-linked β-thioglycosyl lactate derivatives in excellent yields as a diastereomeric mixtures and the diastereomeric ratios (dr) were confirmed from the integration values of the anomeric protons and methyl group of the lactate moiety in the ^{1}H NMR spectra (Scheme 4) (entries 5, 6; compounds **37**, **38**; Table 5). It is worth noting that exclusive formation of β-D-mannopyranosyl thiolactate derivative (**38**) (appearance of $J_{C\text{-}1,H\text{-}1}$ = 155.0 Hz in the ^{1}H coupled ^{13}C NMR spectrum)[28] was achieved using the present reaction condition which is difficult to obtain using other methodologies. Further treatment of β-glycosyl thiol derivative with α-glycosyl bromide derivatives in DMF in the presence of triethylamine furnished unsymmetrical 1,1-thio-linked di- and trisaccharide derivatives (trehalose analogues) in excellent yield (Scheme 4) (compounds **39**, **40**; Table 5). The structural characterization of all synthesized products was carried out using NMR spectral data.

In summary, an expedient one-step reaction condition for the synthesis of exclusive β-glycosyl thiol derivatives has been developed by treating glycosyl bromide derivatives with a mixture of CS_2 and $Na_2S{\cdot}9H_2O$ at room temperature. The reaction is significantly fast and high yielding with high stereoselectivity. The β-glycosyl thiol derivatives were reacted with alkyl halides and triflate derivative to furnish β-thioglyco-

Table 3. Stereoselective synthesis of β-Glycosyl Thiol Derivatives in DMF

Sl. No.	Substrate 	Product 	Time (min)	Yield (%)[a]	α/β[b]
1	Per-*O*-acetyl-α-D-gluco- **(1)**	Per-*O*-acetyl-β-D-gluco- **(15)**[23]	5	90 (88)[c]	0/1
2	Per-*O*-acetyl-α-D-galacto- **(2)**	Per-*O*-acetyl-β-D-galacto- **(16)**[31]	5	90	0/1
3	Per-*O*-acetyl-α-D-manno- **(3)**	Per-*O*-acetyl-β-D-manno- **(17)**[17a]	5	85	0/1
4	Per-*O*-benzoyl-α-D-gluco- **(4)**	Per-*O*-benzoyl-β-D-gluco- **(18)**[32]	10	88	0/1
5	Per-*O*-acetyl-2-deoxy-2-*N*-phthalimido-α-D-gluco- **(5)**	Per-*O*-acetyl-2-deoxy-2-*N*-phthalimido-β-D-gluco- **(19)**[33]	15	84	0/1
6	Per-*O*-acetyl-α-L-rhamno-**(6)**	Per-*O*-acetyl-β-L-rhamno- **(20)**[34]	5	90	0/1
7	Per-*O*-acetyl-α-L-fuco- **(7)**	Per-*O*-acetyl-β-L-fuco- **(21)**[23]	5	90	0/1
8	Per-*O*-acetyl-α-D-lacto- **(8)**	Per-*O*-acetyl-β-D-lacto- **(22)**[35]	10	88	0/1
9	Per-*O*-acetyl-α-D-malto- **(9)**	Per-*O*-acetyl-β-D-malto- **(23)**[36]	10	92	0/1
10	Per-*O*-acetyl-α-D-melibio- **(10)**	Per-*O*-acetyl-β-D-melibio- **(24)**	10	90	0/1
11	Per-*O*-benzyl-α-D-gluco- **(11)**	Per-*O*-benzyl-β-D-gluco- **(25)**	5	82	0/1
12	3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-gluco- **(12)**	--[d]	5	--	--
13	2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-gluco- **(13)**	--[e]	10	--	--

[a]Yield of isolated product. [b]α/β ratio of the crude reaction mixture. [c]Yield in parentheses is 10 g scale. [d]Exclusive formation of 3,4,6-tri-*O*-acetyl-D-glucal (**26**) (94%) in 5 min. [e]Formation of a mixture of oxazoline derivative (**13a**) and hemiacetal derivative in 10 min.

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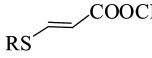
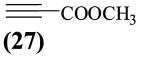
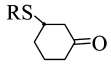
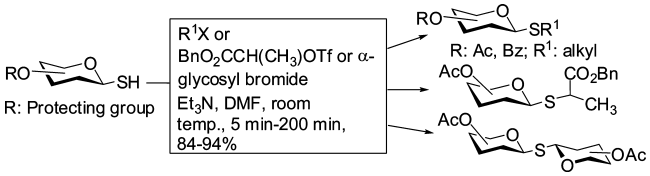
Table 4. Michael Addition of β-Glycosyl Thiols with Activated Alkenes

Sl. No.	Thiol	alkene	Product	Time (min)	Yield (%)	E/Z
						E/Z
1	**18**		R = per-*O*-benzoyl-β-D-glucopyranosyl (**29**)	10	88	1/0
2	**20**	**(27)**	R = per-*O*-acetyl-β-L-rhamnopyranosyl (**30**)	10	90	1/0
						d. r.
3	**18**		R = per-*O*-benzoyl-β-D-glucopyranosyl (**31**)	15	87	1:1
4	**22**	**(28)**	R = per-*O*-acetyl-β-D-lactopyranosyl (**32**)	20	85	1:1

Scheme 4. Reaction of β-Glycosyl Thiols with Alkyl Halide, Triflate and Glycosyl Halide Derivatives



side derivatives. The reaction has been further extended toward the preparation of (1,1)-thiolinked di- and trisaccharide derivatives. Present methodology will be considered as an attractive alternative in this area because of the above-mentioned advantages over the existing methodologies for the synthesis of β-glycosyl thiol derivatives and their use in the preparation of thiolinked glycomimetics.

EXPERIMENTAL SECTION

General Comments. All reactions were monitored by thin layer chromatography over silica gel coated TLC plates. The spots on TLC were visualized by warming ceric sulfate (2% $Ce(SO_4)_2$ in 2N H_2SO_4) sprayed plates in hot plate. Silica gel 230−400 mesh was used for column chromatography. ^1H and ^{13}C NMR and 2D COSY and HSQC spectra were recorded on a 500 NMR spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C) using $CDCl_3$ as solvent and TMS as internal reference unless stated otherwise. Chemical shift value is expressed in δ ppm. ESI-MS were recorded on a Micromass mass spectrometer. Commercially available grades of organic solvents of adequate purity are used in all reactions.

General Experimental Condition for the Preparation of β-Glycosyl Thiol Derivatives. To a solution of sodium sulfide (2.0 mmol) in DMF (5 mL) was dropwise added carbon disulfide (1.5 mmol) at room temperature. On addition of the glycosyl bromide (1.0 mmol) to the resulting red-colored solution, the color of the reaction became yellow and the reaction mixture was stirred at room temperature for an appropriate time as mentioned in Table 1. The reaction mixture was diluted with water and extracted with EtOAc (50 mL), dried (Na_2SO_4), and concentrated to furnish the crude product, which was purified over SiO_2 using hexane−EtOAc as eluant. Analytical data for the new compounds are as follows:

Compound ***24***. Yield 590 mg (90%); eluant, hexane−EtOAc (4:1); white solid; mp 204−205 °C (Et_2O−hexane); $[\alpha]_D^{25}$ +150 (*c* 1.0, $CHCl_3$). IR (KBr): 2568, 1753, 1374, 1225, 1165, 1051, 915 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.35 (d, *J* = 2.0 Hz, 1 H, H-4_B), 5.25 (dd, *J* = 11.0,3.0 Hz, 1 H, H-3_B), 5.14 (d, *J* = 3.0 Hz, 1 H, H-1_B), 5.08 (t, *J* = 9.5 Hz each, 1 H, H-2_A), 5.00 (t, *J* = 10.0 Hz each, 1 H, H-4_A), 4.98 (dd, *J* = 10.5, 3.0 Hz, 1 H, H-2_B), 4.81 (t, *J* = 9.5 Hz each, 1 H, H-3_A), 4.42 (t, *J* = 10.0 Hz each, 1 H, H-1_A), 4.18−4.16 (m, 1 H, H-5_B), 4.01−3.98 (m, 2 H, H-6_{abB}), 3.64−3.55 (m, 3 H, H-5_A, H-6_{abA}), 2.19 (d, *J* = 10.0 Hz, 1 H, SH), 2.07, 2.06, 2.02, 2.00, 1.96, 1.94, 1.92 (7 s, 21 H, 7 $COCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.3, 170.1, 170.0, 169.9, 169.7, 169.4, 169.1 (7 $COCH_3$), 96.1 (C-1_B), 78.5 (C-1_A), 77.1 (C-5_A), 73.6 (2 C, C-3_A, C-4_A), 68.6 (C-2_A), 68.2.(C-2_B), 67.9 (C-4_B), 67.4 (C-3_B), 66.3 (C-5_B), 65.9 (C-6_A), 61.4 (C-6_B), 20.9, 20.7, 20.6 (2 C), 20.5 (3 C) (7 $COCH_3$). ESI-MS: 675.1 $[M + Na]^+$. Anal. Calcd for $C_{26}H_{36}O_{17}S$ (652.16): C, 47.85; H, 5.56. Found: C, 47.70; H, 5.75.

Compound ***25***. Yield 456 mg (82%); eluant, hexane−EtOAc (7:1); white solid; mp 60−62 °C (Et_2O−hexane); $[\alpha]_D^{25}$ +57 (*c* 1.0, $CHCl_3$). IR (KBr): 2556, 1756, 1372, 1222, 1145, 915 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.37−7.13 (m, 20 H, Ar−H), 4.97−4.53 (m, 8 H, 4 $PhCH_2$), 4.50 (t, *J* = 9.0 and 8.0 Hz, 1 H, H-1), 3.74−3.68 (m, 2 H, H-3, H-4), 3.67−3.63 (m, 2 H, H-6_{ab}), 3.48−3.46 (m, 1 H, H-5), 3.73 (t, *J* = 9.0 Hz each, 1 H, H-2), 2.29 (d, *J* = 8.0 Hz, 1 H, *SH*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8−127.6 (Ar−C), 86.5 (C-1), 84.8 (C-5), 79.8 (C-3), 79.5 (C-4), 77.7 (C-2), 75.7 (2 C, 2 $PhCH_2$), 75.0 ($PhCH_2$), 73.5 ($PhCH_2$), 68.7 (C-6). ESI-MS: 579.2 $[M + Na]^+$. Anal. Calcd for $C_{34}H_{36}O_5S$ (556.22): C, 73.35; H, 6.52. Found: C, 73.18; H, 6.75.

General Experimental Condition for the Michael Addition of Glycosyl Thiol Derivatives with Activated Alkenes. A mixture of

Table 5. Reaction of β-Glycosyl Thiols with Alkyl Halides, Triflate, and Glycosyl Bromide

Sl. no.	thiol	alkylating agent	thioglycoside	time (min)	yield (%)
1	**15**	allyl bromide	allyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**33**)[37]	30	94
2	**16**	benzyl bromide	benzyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (**34**)[37]	30	90
3	**21**	β-methallyl chloride	methallyl 2,3,4-tri-*O*-acetyl-1-thio-β-L-fucopyranoside (**35**)	30	90
4	**22**	benzyl bromide	benzyl per-*O*-acetyl-1-thio-β-D-lactopyranoside (**36**)[38]	30	90
5	**15**	$CH_3CH(OTf)COOBn$	benzyl-2-methyl-propanoyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**37**)[a]	5	90
6	**17**	$CH_3CH(OTf)COOBn$	benzyl-2-methyl-propanoyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-mannopyranoside (**38**)[a]	5	88
7	**21**	1	(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-(1→1)-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**39**)	180	86
8	**23**	1	(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-2,3,4,2′,3′,4,6′-hepta-*O*-acetyl-1-thio-β-D-maltopyranoside (**40**)	200	84

[a]dr: 1.4:1.

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glycosyl thiol derivative (1.0 mmol) and conjugated alkene derivative (1.1 mmol) in methanol was allowed to stir at room temperature for appropriate time as mentioned in the Table 2. After formation of thio-adduct (monitored by TLC), the reaction mixture was concentrated under reduced pressure to give the crude product, which was purified over SiO_2 using hexane−EtOAc as eluant. Analytical data for the new compounds are as follows:

Compound ***29***. Yield 600 mg (88%); eluant, hexane−EtOAc (6:1); white solid; mp 142−144 °C (Et_2O−hexane); $[\alpha]_D^{25}$ −2 (*c* 1.0, $CHCl_3$). IR (KBr): 2925, 1732, 1601, 1583, 1451, 1315, 1268, 1175, 1088, 1068, 1026, 802, 708, 685 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.72−7.18 (m, 21 H, Ar−H, =*H*C−CO), 5.89 (d, *J* = 10.0 Hz, 1 H, S−C*H*=), 5.85 (t, *J* = 9.5 Hz each, 1 H, H-2), 5.64 (t, *J* = 10.0 Hz each, 1 H, H-3), 5.61 (t, *J* = 10.0 Hz each, 1 H, H-4), 4.90 (d, *J* = 9.5 Hz, 1 H, H-1), 4.58 (dd, *J* = 12.0, 2.0 Hz, 1 H, H-6_a), 4.41 (dd, *J* = 12.0, 5.0 Hz, 1 H, H-6_b), 4.18−4.16 (m, 1 H, H-5), 3.63 (s, 3 H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5 ($COOCH_3$), 165.9, 165.6, 165.0, 164.7 (4 PhCO), 142.6 (*S*CH=), 133.4−128.3 (Ar-*C*), 115.1 (=*C*HCO), 83.3 (C-1), 76.9 (C-5), 73.9 (C-2), 70.6 (C-3), 69.3 (C-4), 63.0 (C-6), 51.4 ($COOCH_3$). ESI-MS: 719.1 $[M + Na]^+$. Anal. Calcd for $C_{38}H_{32}O_{11}S$ (696.16): C, 65.51; H, 4.63. Found: C, 65.35; H, 4.80.

Compound ***30***. Yield 340 mg (90%); eluant, hexane−EtOAc (5:1); yellow oil; $[\alpha]_D^{25}$ +92 (*c* 1.0, $CHCl_3$). IR (neat): 2986, 1747, 1704, 1586, 1437, 1372, 1222, 1170, 1055, 981, 933, 758, 707 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.20 (d, *J* = 10.5 Hz, 1 H, =*CH*CO), 5.87 (d, *J* = 10.0 Hz, 1 H, SC*H*=), 5.45 (d, *J* = 3.0 Hz, 1 H, H-2), 4.99 (t, *J* = 10.0 Hz each, 1 H, H-4), 4.93 (dd, *J* = 10.0, 3.5 Hz, 1 H, H-3), 4.74 (br s, 1 H, H-1), 3.65 (s, 3 H, $COOCH_3$), 3.55−3.52 (m, 1 H, H-5), 2.10, 1.98, 1.90 (3 s, 9 H, 3$COCH_3$), 1.21 (d, *J* = 6.0 Hz, 3 H, CCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7, 169.5 (3 $COCH_3$), 166.6 ($COOCH_3$), 144.4 (SCH=), 114.1 (=CHCO), 82.1 (C-1), 75.6 (C-3), 71.7 (C-4), 70.0 (C-2), 69.9 (C-5), 51.4 ($COOCH_3$), 20.7, 20.6, 20.5 (3 $COCH_3$), 17.6 (CCH_3). ESI-MS: 413.0 $[M + Na]^+$. Anal. Calcd for $C_{16}H_{22}O_9S$ (390.09): C, 49.22; H, 5.68. Found: C, 49.08; H, 5.85.

Compound ***31***. (dr: 1:1) 600 mg (87%); eluant, hexane−EtOAc (6:1); white solid; mp 80−82 °C (Et_2O−hexane). IR (KBr): 2952, 1729, 1601, 1451, 1315, 1271, 117, 1091, 1068, 1026, 708 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) (diastereomeric mixture): δ 7.97−7.19 (m, 20 H, Ar−H), 5.85 (d, *J* = 9.5 Hz, 1 H, H-1), 5.56 (t, *J* = 10.0 Hz each, 1 H, H-2), 5.45 (t, *J* = 10.0 Hz each, 1 H, H-3), 4.87 (t, *J* = 10.0 Hz each, 1 H, H-4), 4.60−4.43 (m, 2 H, H-6_{ab}), 4.12−4.08 (m, 1 H, H-5), 3.28−3.23 (m, 1 H, C*H*), 2.70−2.65 (m, 1 H, CH_2), 2.38−1.47 (m, 7 H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.5 (CO), 165.2, 165.1, 165.08, 165.0 (PhCO), 133.4−128.3 (Ar−C), 83.4 (C-1), 76.5 (C-5), 73.9 (C-3), 70.5 (C-4), 69.5 (C-2), 63.2 (C-6), 48.8 (CH_2), 42.7 (CH), 40.7 (CH_2), 32.5 (CH_2), 24.3 (CH_2). ESI-MS: 731.2 $[M + Na]^+$. Anal. Calcd for $C_{40}H_{36}O_{10}S$ (708.20): C, 67.78; H, 5.12. Found: C, 67.62; H, 5.30.

Compound ***32***. (dr: 1:1) 585 mg (85%); eluant, hexane−EtOAc (4:1); yellow oil. IR (neat): 2955, 2926, 1747, 1714, 1455, 1372, 1229, 1044, 760, 602 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) (*R*- and *S*-mixture): δ 5.40 (d, *J* = 4.0 Hz, 1 H, H-4_B), 5.34 (t, *J* = 10.0 Hz, 1 H, H-2_B), 5.26 (t, *J* = 10.0 Hz, 1 H, H-2_A), 5.04 (t, *J* = 10.0 Hz, 1 H, H-3_A), 4.84 (d, *J* = 9.0 Hz, 1 H, H-1_A), 4.82 (dd, *J* = 10.0, 3.0 Hz, 1 H, H-3_B), 4.63 (d, *J* = 10.0 Hz, 1 H, H-1_B), 4.50−4.45 (m, 1 H, H-5_B), 4.25−4.15 (m, 2 H, H-6_{abA}), 4.07−3.99 (m, 2 H, H-6_{abB}), 3.95 (t, *J* = 10.0 Hz, 1 H, H-4_A), 3.69−3.65 (m, 1 H, H-5_A), 3.32−3.22 (m, 1 H, C*H*), 2.80−2.70 (m, 1 H, CH_2), 2.45−2.25 (m, 3 H, CH_2), 2.15, 2.10, 2.07, 2.03, 2.02, 2.01, 2.00 (7 s, 21 H, 7 $COCH_3$), 1.75−1.70 (m, 4 H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.5 (CO), 170.4, 170.3, 170.2, 170.0, 169.7, 169.4, 169.3 (7 $COCH_3$), 95.6 (C-1_B), 82.9 (C-1_A), 76.3 (C-5_A), 76.2 (C-4_A), 72.7 (C-3_A), 70.9 (C-2_B), 70.0 (C-3_B), 69.3 (C-5_B), 68.6 (C-2_A), 68.0 (C-4_B), 63.0 (C-6_B), 61.5 (C-6_A), 49.1 (CH_2), 43.1 (CH), 40.7 (CH_2), 32.1 (CH_2), 24.3 (CH_2), 20.9 (2 C), 20.7 (2 C), 20.6 (3 C) (7 $COCH_3$). ESI-MS: 771.2 $[M + Na]^+$. Anal. Calcd for $C_{32}H_{44}O_{18}S$ (748.22): C, 51.33; H, 5.92. Found: C, 51.18; H, 6.15

General Experimental Condition for the Preparation of Thioglycoside and (1,1)-Thio Oligosaccharide Derivatives. To a solution of glycosyl thiol derivative (1.0 mmol) in DMF (5 mL) were added alkylating agent/glycosyl halide (1.1 mmol) and Et_3N (2 drops), and reaction mixture was allowed to stir at room temperature for appropriate time as mentioned in Table 3. The reaction mixture was diluted with water and extracted with CH_2Cl_2 (50 mL). The organic layer was washed with water, dried (Na_2SO_4) and concentrated to give the crude product which was purified over SiO_2 using hexane−EtOAc as eluant. Analytical data for the new compounds are as follows:

Compound ***35***. Yield 318 mg (90%); eluant, hexane−EtOAc (4:1); yellow oil; $[\alpha]_D^{25}$ +111 (*c* 1.0, $CHCl_3$). IR (neat): 2926, 2854, 1750, 1437, 1370, 1247, 1224, 1084, 1057, 918, 758 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.24 (d, *J* = 3.5 Hz, 1 H, H-4), 5.20 (t, *J* = 10.0 Hz each, 1 H, H-2), 5.01 (dd, *J* = 10.0, 3.0 Hz, 1 H, H-3), 4.88−4.85 (m, 2 H, CH_2=), 4.39 (d, *J* = 10.0 Hz, 1 H, H-1), 3.75−3.72 (m, 1 H, H-5), 3.42 (d, *J* = 13.0 Hz, 1 H, CH_2), 3.14 (d, *J* = 13.0 Hz, 1 H, CH_2), 2.17, 2.05, 1.98 (3 s, 9 H, 3 $COCH_3$), 1.81 (s, 3 H, CH_3), 1.21 (d, *J* = 6.0 Hz, 3 H, CCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 169.9, 169.4 (3 $COCH_3$), 140.5 (CH_2−C(CH_3)=), 114.3 (CH_2=), 82.0 (C-1), 73.0 (C-3), 72.4 (C-4), 70.4 (C-2), 67.2 (C-5), 37.3 (CH_2), 20.8, 20.7, 20.6 (2 C) (3 $COCH_3$, CH_3), 16.3 (CCH_3). ESI-MS: 383.1 $[M + Na]^+$. Anal. Calcd for $C_{16}H_{24}O_7S$ (360.12): C, 53.32; H, 6.71. Found: C, 53.15; H, 6.86.

Compound ***37***. (dr 1.4:1) 390 mg (90%); eluant, hexane−EtOAc (3:1); yellow oil. IR (neat) (diastereomers 1 and 2): 2996, 2944, 1757, 1441, 1351, 1232, 1088, 1056, 916, 755 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) (diastereomer 1): δ 7.38−7.25 (m, 5 H, Ar−H), 5.22 (d, *J* = 12.0 Hz, 1 H, PhCH_2), 5.12 (d, *J* = 12.0 Hz, 1 H, PhCH_2), 5.08 (t, *J* = 10.0 Hz each, 1 H, H-3), 5.02 (t, *J* = 10.0 Hz each, 1 H, H-2), 4.95 (t, *J* = 10.0 Hz each, 1 H, H-4), 4.70 (d, *J* = 10.0 Hz, 1 H, H-1), 4.18−4.14 (m, 1 H, H-6_a), 4.06−4.03 (m, 1 H, H-6_b), 3.75−3.72 (m, 1 H, C*H*), 3.61−3.58 (m, 1 H, H-5), 2.05, 2.02, 2.00, 1.98, (4 s, 12 H, 4 $COCH_3$), 1.53 (d, *J* = 6.0 Hz, 3 H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.5 (COOBn), 170.4, 169.9, 169.4, 169.1 (4 $COCH_3$), 128.7−128.1 (Ar−C), 82.9 (C-1), 75.8 (C-2), 73.9 (C-3), 69.9 (C-4), 68.1 (C-5), 67.0 (PhCH_2), 61.8 (C-6), 41.6 (*C*H), 20.7, 20.6 (2 C), 20.5 (4 $COCH_3$), 18.1 (CH_3). ^1H NMR (500 MHz, $CDCl_3$) (diastereomer 2): δ 7.38−7.25 (m, 5 H, Ar−H), 5.16 (br s, 2 H, PhCH_2), 5.09 (t, *J* = 10.0 Hz each, 1 H, H-3), 5.04 (t, *J* = 10.0 Hz each, 1 H, H-2), 4.93 (t, *J* = 10.0 Hz each, 1 H, H-4), 4.65 (d, *J* = 10.0 Hz each, 1 H, H-1), 4.18−4.15 (m, 1 H, H-6_a), 4.06−4.02 (m, 1 H, H-6_b), 3.64−3.59 (m, 1 H, C*H*), 3.45−3.43 (m, 1 H, H-5), 2.05, 2.02, 2.00, 1.98 (4 s, 12 H, 4 $COCH_3$), 1.47 (d, *J* = 6.0 Hz, 3 H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.6 (COOBn), 170.4, 169.9, 169.4, 169.1 (4 $COCH_3$), 128.7−128.1 (Ar−C), 81.9 (C-1), 75.9 (C-2), 73.8 (C-3), 69.8 (C-4), 68.0 (C-5), 66.9 (PhCH_2), 61.7 (C-6), 39.0 (*C*H), 20.7, 20.6 (2 C), 20.5 (4 $COCH_3$), 16.6 (CH_3). ESI-MS: 549.1 $[M + Na]^+$. Anal. Calcd for $C_{24}H_{30}O_{11}S$ (526.15): C, 54.74; H, 5.74. Found: C, 54.56; H, 5.90.

Compound ***38***. (dr: 1.4:1) 380 mg (88%); eluant, hexane−EtOAc (3:1); yellow oil. IR (neat) (diastereomers 1 and 2): 2938, 2856, 1760, 1457, 1377, 1257, 1220, 1088, 1067, 917 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) (diastereomer 1): δ 7.41−7.33 (m, 5 H, Ar−H), 5.30 (d, *J* = 3.5 Hz, 1 H, H-2), 5.26 (d, *J* = 12.0 Hz, 1 H, PhCH_2), 5.17 (t, *J* = 10.0 Hz each, 1 H, H-4), 5.13 (d, *J* = 12.0 Hz, 1 H, PhCH_2), 4.86 (dd, *J* = 10.0, 3.0 Hz, 1 H, H-3), 4.76 (br s, 1 H, H-1), 4.22−4.16 (m, 1 H, H-6_a), 4.09−4.04 (m, 1 H, H-6_b), 3.70−3.66 (m, 1 H, C*H*), 3.43−3.40 (m, 1 H, H-5), 2.18, 2.05, 1.97 (3 s, 12 H, 4 $COCH_3$), 1.46 (d, *J* = 6.0 Hz, 3 H, CCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.6 (COOBn), 170.6, 169.9, 169.4, 169.1 (4 $COCH_3$), 128.8−128.2 (Ar−C), 80.6 (C-1), 76.5 (C-2), 71.7 (C-3), 69.9 (C-4), 67.1 (PhCH_2), 65.6 (C-5), 62.4 (C-6), 39.4 (CH), 20.7, 20.6 (2 C), 20.5 (4 $COCH_3$), 16.4 (CH_3). ^1H NMR (500 MHz, $CDCl_3$) (diastereomer 2): δ 7.41−7.33 (m, 5 H, Ar−H), 5.35 (d, *J* = 3.5 Hz, 1 H, H-2), 5.18 (t, *J* = 10.0 Hz, 1 H, H-4), 5.16−5.13 (m, 2 H, PhCH_2), 4.96 (dd, *J* = 10.0, 3.0 Hz, 1 H, H-3), 4.86 (br s, 1 H, H-1), 4.22−4.16 (m, 1 H, H-6_a), 4.07−4.04 (m, 1 H, H-6_b), 3.62−3.56 (m, 2 H, CH, H-5), 2.17, 2.06, 2.05, 1.97 (4 s, 12 H, 4 $COCH_3$), 1.56 (d, *J* = 6.0 Hz, 3 H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.6 (COOBn), 170.6, 169.9, 169.4, 169.1 (4 $COCH_3$), 128.8−128.2 (Ar−C), 80.9 (C-1), 76.3 (C-2), 71.7 (C-3), 70.7 (C-4), 67.1 (PhCH_2), 65.6 (C-5), 62.6 (C-6), 41.2 (CH), 20.7, 20.6 (2 C),

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20.5 (4 $COCH_3$), 17.7 (CH_3). ESI-MS: 549.1 $[M + Na]^+$. Anal. Calcd for $C_{24}H_{30}O_{11}S$ (526.15): C, 54.74; H, 5.74. Found: C, 54.55; H, 5.90.

Compound ***39***. Yield 535 mg (86%); eluant, hexane−EtOAc (4:1); white solid; mp 140−142 °C (EtOH); $[\alpha]_D^{25}$ +60 (*c* 1.0, $CHCl_3$). IR (KBr): 3469, 1752, 1371, 1227, 1042, 918 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.25 (d, *J* = 2.5 Hz, 1 H, H-4_B), 5.22 (t, *J* = 10.0 Hz each, 1 H, H-2_B), 5.19 (t, *J* = 9.5 Hz each, 1 H, H-2_A), 5.09 (t, *J* = 10.0 Hz, 1 H, H-3_A), 5.01 (t, *J* = 10.0 Hz each, 1 H, H-4_A), 4.99 (dd, *J* = 10.0, 3.0 Hz, 1 H, H-3_B), 4.74 (d, *J* = 10.0 Hz, 1 H, H-1_B), 4.58 (d, *J* = 10.0 Hz, 1 H, H-1_A), 4.26−4.21 (m, 1 H, H-6_{aA}), 4.14−4.09 (m, 1 H, H-6_{bA}), 3.87−3.82 (m, 1 H, H-5_B), 3.74−3.71 (m, 1 H, H-5_A), 2.17, 2.08, 2.07, 2.03, 2.01, 2.00, 1.99 (7 s, 21 H, 7 $COCH_3$), 1.22 (d, *J* = 6.0 Hz, 3 H, CCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.0, 170.9, 170.8, 170.6, 170.3, 169.9, 169.8 (7 $COCH_3$), 81.1 (C-1_B), 81.0 (C-1_A), 76.2 (C-5_A), 74.0 (C-5_B), 73.7 (C-2_A), 72.4 (C-3_B), 70.4 (C-4_B), 70.1 (C-2_B), 68.0 (C-3_A), 67.8 (C-4_A), 62.2 (C-6_A), 20.8, 20.7 (2 C), 20.6 (2 C), 20.5 (2 C) (7 $COCH_3$), 16.3 (CCH_3). ESI-MS: 659.1 $[M + Na]^+$. Anal. Calcd for $C_{26}H_{36}O_{16}S$ (636.17): C, 49.05; H, 5.70. Found: C, 48.88; H, 5.90.

Compound ***40***. Yield 760 mg (84%); eluant, hexane−EtOAc (4:1); white solid; mp 96−98 °C (EtOH); $[\alpha]_D^{25}$ +53 (*c* 1.0, $CHCl_3$). IR (KBr): 2926, 2853, 1748, 1434, 1370, 1227, 1039, 759, 602 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 5.39 (d, *J* = 4.0 Hz, 1 H, H-1_C), 5.31 (t, *J* = 10.0 Hz each, 1 H, H-3_C), 5.24 (t, *J* = 10.0 Hz each, 1 H, H-3_B), 5.19 (t, *J* = 10.0 Hz each, 1 H, H-2_B), 5.07 (t, *J* = 10.0 Hz each, 1 H, H-2_A), 5.01 (2 t, *J* = 10.0 Hz each, 2 H, H-3_A, H-4_C), 4.85 (t, *J* = 10.0 Hz each, 1 H, H-4_A), 4.83 (d, *J* = 10.0 Hz, 1 H, H-1_B), 4.81 (dd, *J* = 10.0, 4.0 Hz, 1 H, H-2_B), 4.77 (d, *J* = 10.0 Hz, 1 H, H-1_A), 4.47−4.42 (m, 1 H, H-6_{aA}), 4.28−4.20 (m, H-6_{bA}, H-6_{aB}, H-$_{aC}$), 4.14−4.10 (m, 1 H, H-6_{bB}), 4.05−4.01 (m, 1 H, H-6_{bc}), 4.00 (t, *J* = 10.0 Hz each, 1 H, H-4_B), 3.94−3.90 (m, 1 H, H-5_C), 3.70−3.62 (m, 2 H, H-5_A, H-5_B), 2.16, 2.11, 2.09, 2.03, 2.02, 2.0, 1.99 (7 s, 33 H, 11 $COCH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 170.3, 170.2, 170.1, 170.0, 169.9, 169.8 (2 C), 169.7 (2 C), 169.6 (11 $COCH_3$), 95.6 (C-1_C), 80.7 (C-1_B), 80.1 (C-1_A), 76.4 (2 C, C-5_A, C-5_B), 76.2 (C-3_B), 73.8 (C-2_B), 72.7 (C-4_B), 71.0 (C-4_A), 70.1 (C-2_C), 69.9 (C-4_C), 69.2 (C-3_C), 68.6 (C-3_A), 68.1 (C-2_A), 68.0 (C-5_C), 62.9 (C-6_C), 61.9 (C-6_A), 61.4 (C-6_B), 20.7 (3 C), 20.6 (3 C), 20.5 (5 C) (11 $COCH_3$). ESI-MS: 1005.2 $[M + Na]^+$. Anal. Calcd for $C_{40}H_{54}O_{26}S$ (982.26): C, 48.88; H, 5.54. Found: C, 48.70; H, 5.70.

Preparation of 2-Methyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano)-[2,1-*d*]-2-oxazoline (13a) from Compound 13. To a solution of sodium sulfide (480 mg, 2.0 mmol) and carbon disulfide (90 μL, 1.5 mmol) in DMF (5 mL) was added compound **13** (410 mg, 1.0 mmol), and it was stirred for 10 min at room temperature. The reaction mixture was diluted with water and extracted with EtOAc (50 mL), dried (Na_2SO_4), and concentrated to furnish the crude product, which was purified over SiO_2 using hexane−EtOAc as eluant to give compound **13a** (180 mg, 54%). Yellow oil; $[\alpha]_D$ = +16 (*c* 1.2, $CHCl_3$) [Lit. $[\alpha]_D$ = +15 (*c* 1.0, $CHCl_3$)].[39]

Preparation of Bis-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-sulfide (15a). To a solution of sodium sulfide (480 mg, 2.0 mmol) and carbon disulfide (30 μL, 0.5 mmol) in DMF (5 mL) was added compound **1** (410 mg, 1.0 mmol), and it was stirred for 5 min at room temperature. The reaction mixture was diluted with water and extracted with EtOAc (50 mL), dried (Na_2SO_4), and concentrated to furnish the crude product, which was purified over SiO_2 using hexane−EtOAc as eluant to give compound **15a** (420 mg, 60%). White solid; mp 173−175 °C (EtOH) [Lit. 175−176 °C];[40] $[\alpha]_D$ = −37 (*c* 1.2, $CHCl_3$) [Lit. $[\alpha]_D$ = −35.5 ($CHCl_3$)].[40]

Preparation of Tri-*O*-acetyl-D-glucal (26) from Compound 12. To a solution of sodium sulfide (480 mg, 2.0 mmol) and carbon disulfide (90 μL, 1.5 mmol) in DMF (5 mL) was added compound **12** (395 mg, 1.0 mmol), and it was stirred for 5 min at room temperature. The reaction mixture was diluted with water and extracted with EtOAc (50 mL), dried (Na_2SO_4), and concentrated to furnish the crude product, which was purified over SiO_2 using hexane−EtOAc as eluant to give compound **26** (256 mg, 94%). White solid; mp 51−53 °C (hexane−Et_2O) [Lit. mp 50−51 °C];[41] $[\alpha]_D$ = −24 (*c* 1.2, $CHCl_3$) [Lit. $[\alpha]_D$ = −22 (*c* 4.1, $CHCl_3$)].[41]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H NMR and ^{13}C NMR spectra of compounds **15**−**26**, **29**−**40**, **13a**, and **15a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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