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Note

Synthesis of mixed glycosyl disulfides/selenenylsulfides using benzyltriethylammonium tetrathiomolybdate as a sulfur transfer reagent

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ABSTRACT

An easy and mild method has been developed for the synthesis of mixed glycosyl disulfides/selenenylsulfides from glycosyl halides and diaryl/dialkyl dichalcogenides in the presence of benzyltriethylammonium tetrathiomolybdate [$(BnEt_3N)_2MoS_4$]. The salient feature of this method is the sulfur transfer from $[BnEt_3N]_2MoS_4$ to form glycosyl disulfides which with excess tetrathiomolybdate further undergo exchange reaction with other dichalcogenides in a one-pot operation.

The disulfide linkage plays an important role in carbohydrate chemistry for the study glycopeptides,[1] lectin binding,[2,3] and carbohydrate structure.[4,5] Moreover, in metabolic and other enzymatic studies, sugar disulfides are significantly important entities.[6,7] Many natural products and biologically active compounds have disulfide linkage as a vital functional motif.[8–10] Mixed glycosyl disulfides have received attention as a new class of glycosyl donors in solution and in solid phase synthesis.[11] Davis et al. reported the advantages of mixed disulfides over thioglycosides.[11] Due to the flexible nature of mixed disulfide linkage, the cleavage of disulfide bond could be adjusted according to the reacting partner.[12] When the mixed disulfide is used as a linker in solid-supported glycosylation, the anomeric mixed disulfide linkage would allow bidirectional (reductive or hydrolytic) cleavage, that would be of great advantage in both the analysis and use of solid supported glycosylation systems. Due to the presence of two sulfur atoms in mixed disulfides, the coordination potential of thiophile may offer enhanced reactivity over single sulfur thioglycoside systems. On the other hand, glycosyl selenenylsulfides have been used in protein glycoconjugation, which allows glycoconjugation with mono- and oligosaccharides of up to seven saccharide units in size at single and multiple sites in a variety of proteins.[13]

Usually, the synthesis of mixed disulfides involves the nucleophilic substitution of thiol onto sulfenyl derivatives. Sulfenyl derivatives such as sulfenyl halides,[14–18] sulfenic acids,[19] *S*-alkyl thiosulfates and *S*-aryl thiosulfates (Bunte salts),[20] *S*-(alkylsulfanyl)isothioureas,[21,22] benzothiazol-2-yl disulfides,[23] benzotriazolyl sulfides,[24] dithioperoxyesters,[25] (alkylsulfanyl)dialkylsulfonium salts,[26] alkyl aryldithiopyridine *N*-oxides,[27] *N*-alkyltetrazolyl disulfides, sulfenamides,[28] sulfenyl thiocyanates,[29] 4-nitroarenesulfenanilides,[30] thiolsulfinates and thiolsulfonates,[31,32] sulfanylsulfinamidines,[33] thionitrites,[34] sulfenyl thiocarbonates,[35] thioimides, thiophosphonium salts,[36,37] and thio-phthalimides[38] are used for this purpose.[39–45] Although sulfenyl derivatives are widely used, they have problems such as stability, multistep synthesis, and use of expensive reagents which limits the use of these reagents.

Disulfide exchange reaction is one of the useful methods for the synthesis of unsymmetrical disulfides which circumvents the use of malodorous thiols. Yamaguchi and Arisawa reported $RhH(PPh_3)_4$ catalyzed disulfide exchange reaction between two structurally different disulfides to give unsymmetrical disulfides (Scheme 1).[46] However, the limitation of this method is the use of expensive phosphine rhodium complex and it is applicability to only a few substrates. Hence, the search for alternative methods which are more convenient is clearly warranted.

Our continuing efforts to explore the utility of benzyltriethylammonium tetrathiomolybdate, $(BnNEt_3)_2MoS_4$ **1** as a reagent in

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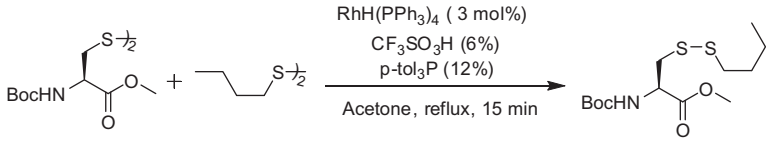


Scheme 1. Functionalization of cysteine via unsymmetrical disulfide exchange reaction.

organic synthesis led to the discovery of a number of useful methodologies.[47–58] Earlier, we have demonstrated the synthesis of sugar disulfides using **1** as a sulfur transfer reagent.[48] Also, we have shown the application of **1** in tandem sulfur transfer reaction followed by Michael addition in a one-pot fashion.[49] Later the utility of **1** has been demonstrated in the synthesis of unsymmetrical β-sulfonamido disulfides from aziridines and disulfides.[47] To further explore the usefulness of the reagent **1**, we planned the synthesis of mixed glycosyl disulfides/selenenylsulfides via sulfur transfer-dichalcogenide exchange reaction in one-pot (Scheme 2).

Reaction of glucosyl bromide **2a** with disulfides **3** in the presence of **1**: We commenced our study by reacting glucose derived anomeric bromide **2a** (1 equiv) with tetrathiomolybdate **1** (2.2 equiv, CH_3CN, 25 °C, 2 h) followed by the addition of diphenyl disulfide **3a** (2 equiv),[59] and it gave the desired mixed disulfide **4aa** (3 h) in 70% yield (Scheme 3).

The mechanism of the reaction is similar to the one proposed in our earlier work on the synthesis of functionalized unsymmetrical β-sulfonamido disulfides from aziridines and disulfides in the presence of tetrathiomolybdate.[47] In light of this, it is visualized that the intermediate **A** formed during the reaction of **2a** with tetrathiomolybdate **1** undergoes an exchange reaction with disulfide **3a** (via intermediates **B** and **C**) to furnish the corresponding mixed disulfide **4aa** (Scheme 4).

Encouraged by this result, we further studied the scope of this reaction with other disulfides (**3b**–**3h**). The outcome of this detailed study is summarized in Table 1. It was observed that disulfides **3d**, **3e** bearing electron withdrawing groups (–Cl, $-NO_2$) gave the corresponding mixed disulfides **4ad** and **4ae** in lower yields (Table 1, entries 3 and 4)[60,61] compared to disulfides **3b**, **3c** containing electron donating groups (–Me, –OMe) (Table 1, entries 1 and 2). Heteroaromatic disulfide such as dipyridyl disulfide **3f** gave only 35% of the desired mixed disulfide **4af** (Table 1, entry 5). Aliphatic disulfides, dibenzyl disulfide **3g**, and dimethyl disulfide **3h** reacted smoothly with **2a** in the presence of **1** to give the corresponding mixed disulfides **4ag** and **4ah** respectively (Table 1, entries 6 and 7).

In general, most of the methods reported on the synthesis of mixed glycosyl dichalcogenides provide only moderate yields.[11,18,22,62] However, the methodologies that give very good yield of mixed dichalcogenides[19,24,38,63,64] use free chalcogenols as the reaction partner. Hence, the present protocol that avoids the use of free chalcogenols compares favorably with the existing methods.

Reaction of various glycosyl halides **2** and diphenyl dichalcogenides (**3a**, **3i**) in the presence of **1**: This methodology was further extended to various glycosyl halides (Scheme 5). The glycosyl halides **2b**–**2f** were studied for the disulfide exchange reaction with diphenyl disulfide **3a** in the presence of **1**.

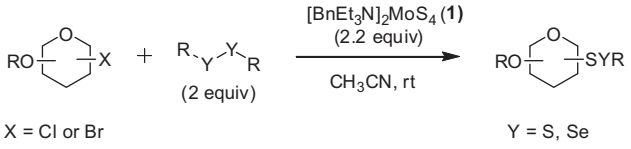
It was observed that the glycosyl halides **2b**, **2c**, **2e**, and **2f** in the presence of diphenyl disulfide **3a** and tetrathiomolybdate **1** underwent disulfide exchange reaction in 3 h to form the corresponding unsymmetrical mixed disulfides **4ba**, **4ca**, **4ea**, and **4fa**, respectively, in moderate to good yields (Table 2, entries 2, 3, 5, and 6) whereas glycosyl bromide **2d** having bromine atom at C-6 position took 8 h to furnish the mixed disulfide **4da** in 51% yield (Table 2, entry 4).

Further, we decided to extend this methodology to the synthesis of glycosyl (phenylselenenyl)sulfides. Accordingly, glycosyl halides **2a**–**2f** were treated with tetrathiomolybdate **1** (2.2 equiv) and diphenyl diselenide **3i** (2.0 equiv) in CH_3CN to give the corresponding selenenylsulfides **4ai**–**4fi** in moderate yields (Table 2). The mechanism of the reaction is similar to that of the disulfide exchange process. As in the synthesis of mixed disulfides, glycosyl bromide **2d** having bromine at C-6 position took a longer time (10 h) for sulfur-selenium exchange process and resulted in the corresponding selenenylsulfide **4di** in only 38% yield (Table 2, entry 4) compared to other glycosyl anomeric halides in which the reactions were completed in 4 h with moderate to good yields (Table 2, entries 1–3, 5, and 6).

The scope of the method was further extended to the synthesis of trisaccharide **4fj** and glycosyl amino acid **4ak** having mixed disulfide linkage. Initially lactose derived anomeric bromide **2f** was treated with **1** (2.2 equiv, CH_3CN, 25 °C, 2 h) followed by the addition of symmetrical glycosyl disulfide **3j** (2 equiv) to furnish the trisaccharide **4fj** in 51% yield (Scheme 6).

For the synthesis glycosyl amino acid mixed disulfide **4ak**, similar synthetic sequence was followed except that the starting materials were glucose derived anomeric bromide **2a** and cysteine derived Boc-Cys-OMe **3k** (Scheme 7).

In summary, we have presented a one-pot method for the synthesis of mixed glycosyl chalcogenides with sulfur transfer-dichalcogenide exchange reaction using tetrathiomolybdate **1**. The significance of this method is mild reaction conditions and avoiding the use of free chalcogenols. The application of the method has been demonstrated in the synthesis of a trisaccharide and glycosyl amino acid containing mixed disulfide linkage. Studies aimed at exploring the utility of these compounds are under progress in our laboratory.

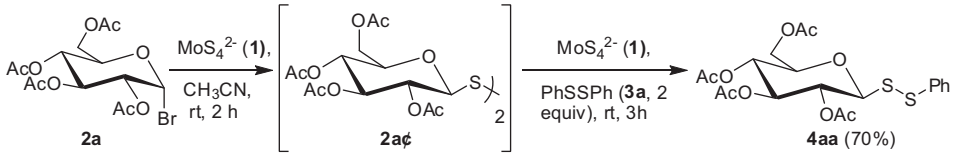


Scheme 2. General scheme for the synthesis of mixed glycosyl disulfides and selenenylsulfides.

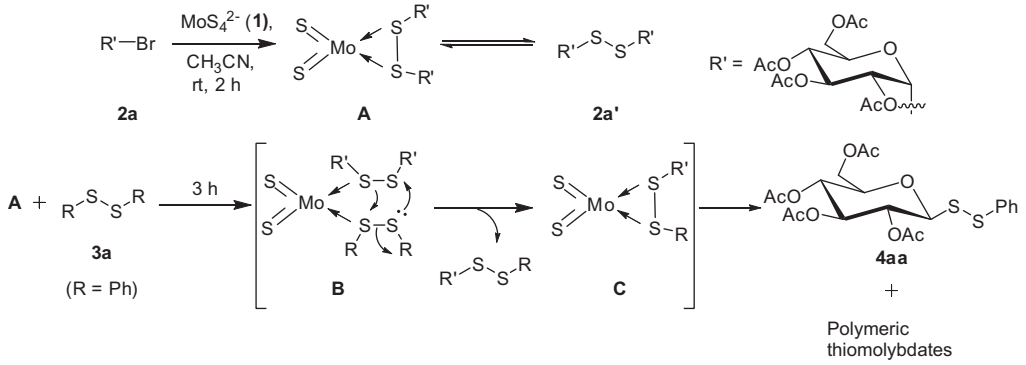
1. Experimental section

1.1. General methods

All the reactions were performed in oven dried apparatus and were stirred magnetically. Melting point values reported are uncorrected. Infrared spectra were recorded using an FTIR instrument and the frequencies are reported in wave number (cm^{-1}) and intensities of the peak are denoted as s (strong), m (medium), w (weak), and broad (br). ^1H and ^{13}C NMR spectra were recorded on a Jeol 400 MHz (100 MHz, ^{13}C) NMR spectrometer and calibrated using tetramethylsilane (TMS) for (^1H) or residual undeuterated solvent ($CDCl_3$) as an internal reference. Multiplicity is indicated using the following abbreviations: s (singlet), d (doublet),



Scheme 3. Synthesis of glucosyl phenyl disulfide **4aa**.



Scheme 4. Mechanism for the formation of unsymmetrical disulfide **4aa**.

dd (double doublet), t (triplet), m (multiplet), and bs (broad singlet). High-resolution mass spectra (HRMS) were recorded on micromass Q-TOF electrospray. Benzyltriethylammonium tetrathiomolybdate **1** was prepared as described earlier.[56,57]

1.2. General procedure for the synthesis of mixed glycosyl disulfides/selenenylsulfides

To a well-stirred solution of sugar halide (1 equiv) in CH_3CN (5 mL) benzyltriethylammonium tetrathiomolybdate **1** (1.1 equiv) was added at once and stirred for 2 h. The reaction was monitored by TLC. To this solution benzyltriethylammonium tetrathiomolybdate **1** (1.1 equiv) and diaryl(dialkyl) disulfide/diphenyl diselenide (2 equiv) were added and the stirring was continued as mentioned. The solvent was removed in vacuo and the residue was extracted repeatedly (3×10 mL) with a DCM/ether mixture (1:4). The extract was filtered through a thin pad of Celite and the filtrate was concentrated in vacuo. The reaction mixture was further purified by column chromatography using ethyl acetate/petroleum ether as eluent to yield the mixed disulfide/selenenylsulfide.

1.2.1. Phenyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)disulfide (4aa)[18,38]

Yield 70%; R_f = 0.5 (hexanes/ethyl acetate: 60:40); white crystalline solid; mp: 120–122 °C; $[\alpha]_D^{24}$ −140.1 (*c* 0.6, $CHCl_3$); FTIR (KBr): 1746 (s), 1377 (w), 1368 (w), 1253 (m), 1229 (s), 1094 (w), 1059 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.9 Hz, 2H),7.30–7.23 (m, 3H), 5.29–5.22 (m, 2H), 5.13–5.08 (m, 1H), 4.62–4.60 (m, 1H), 4.17–4.07 (m, 2H), 3.76–3.72 (m, 1H), 2.02–1.99 (4s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.2, 169.3, 169.1, 136.8, 128.9, 128.7, 127.4, 87.8, 76.0, 73.8, 69.3, 67.9, 61.9, 20.59, 20.57, 20.5; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{20}H_{24}O_9S_2Na$ $(M+Na)^+$: 495.0759; found: 495.0758.

1.2.2. 4-Tolylphenyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) disulfide (4ab)

Yield 74%; R_f = 0.6 (hexanes/ethyl acetate: 60:40); white solid; mp: 110–112 °C; $[\alpha]_D^{22}$ −218.3 (*c* 4.9, $CHCl_3$); FTIR (KBr): 1747 (s), 1431 (w), 1368 (m), 1255 (s), 1231 (s), 1097 (m), 1059 (m), 1043 (m), 913 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.29–5.22 (m, 2H), 5.14–5.09 (m, 1H), 4.63–4.58 (m, 1H), 4.19 (dd, *J* = 12.4, 8.0 Hz, 1H), 4.10 (dd, *J* = 12.5, 1.5 Hz, 1H), 3.77–3.72 (m, 1H), 2.32 (s, 3H), 2.02–2.01 (2s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.1, 169.3, 169.1, 137.9, 133.3, 129.9, 129.5, 87.8, 76.0, 73.8, 69.3, 67.9, 61.9, 21.0, 20.60, 20.57, 20.5; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{21}H_{26}O_9S_2Na$ $(M+Na)^+$: 509.0916; found: 509.0916.

1.2.3. 4-Methoxyphenyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) disulfide (4ac)[24]

Yield 72%; R_f = 0.5 (hexanes/ethyl acetate: 60:40); white crystalline solid; mp: 138–140 °C; $[\alpha]_D^{24}$ −343.0 (*c* 0.6, $CHCl_3$); FTIR (KBr): 1749 (s), 1592 (w), 1495 (w), 1373 (m), 1248 (s), 1228 (s), 1060 (m), 1042 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 5.30–5.23 (m, 2H), 5.13 (t, *J* = 9.2 Hz, 1H), 4.61 (d, *J* = 8.8 Hz, 1H), 4.23 (dd, *J* = 12.3, 4.3 Hz, 1H), 4.13–4.09 (m, 1H), 3.80 (s, 3H), 3.77–3.75 (m, 1H), 2.06–2.00 (4s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.2, 169.3, 169.1, 160.0, 133.3, 127.5, 114.4, 87.8, 76.1, 73.8, 69.3, 68.0, 61.9, 55.4, 20.7, 20.6, 20.5; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{21}H_{26}O_{10}S_2Na$ $(M+Na)^+$: 525.0865; found: 525.0866.

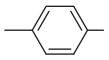
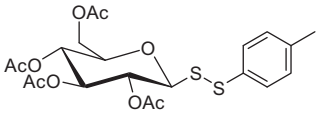
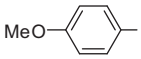
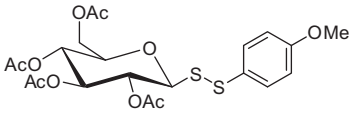
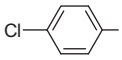
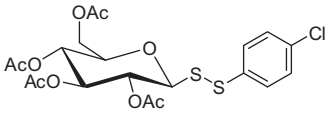
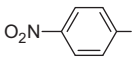
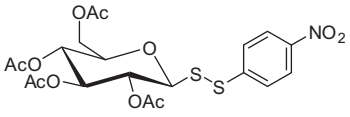
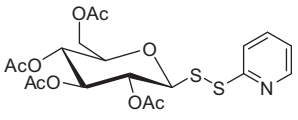
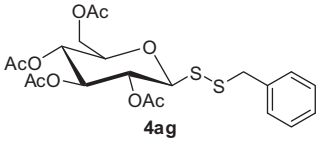
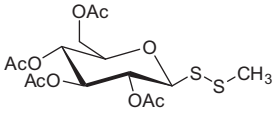
1.2.4. 4-Chlorophenyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) disulfide (4ad)

Yield 62%; R_f = 0.5 (hexanes/ethyl acetate: 60:40); white solid; mp: 132–134 °C; $[\alpha]_D^{25}$ −306.1 (*c* 1.5, $CHCl_3$); FTIR (KBr): 3462 (bs), 1746 (s), 1382 (w), 1263 (m), 1231 (s), 1092 (w), 1056 (m), 1039 (m), 913 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.30–5.23 (m, 2H), 5.09 (t, *J* = 9.3 Hz, 1H), 4.61 (d, *J* = 9.0 Hz, 1H), 4.18–4.08 (m, 2H), 3.76–3.72 (m, 1H), 2.04–2.00 (4s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4, 170.1, 169.3, 169.1, 135.4, 133.5, 130.3, 128.8, 87.4, 76.1, 73.7, 69.2, 67.8, 61.8, 20.6, 20.55, 20.53, 20.52; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{20}H_{23}ClO_9S_2Na$ $(M+Na)^+$: 529.0370; found: 529.0370.

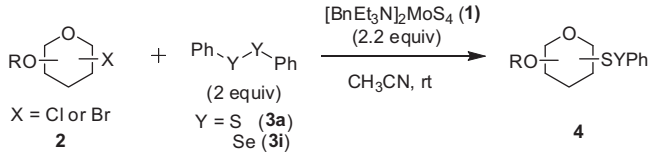
1.2.5. 4-Nitrophenyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) disulfide (4ae)

Yield 53%; R_f = 0.6 (hexanes/ethyl acetate: 50:50); Pale yellow solid; mp: 122–124 °C; $[\alpha]_D^{25}$ −269.9 (*c* 1.40, $CHCl_3$); FTIR (KBr):

Table 1
Synthesis of various mixed disulfides from glucosyl bromide **2a**

Entry	*R*–*S*–*S*–*R* (*R*–)	Time[a] (h)	Mixed disulfide	Yield (%)
1	 **3b**	3	 **4ab**	74
2	 **3c**	3	 **4ac**	72
3	 **3d**	3	 **4ad**	62
4	 **3e**	3	 **4ae**	53
5	 **3f**	8	 **4af**	35
6	 **3g**	3	 **4ag**	65
7	H_3C– **3h**	3	 **4ah**	68

[a] Time required for disulfide exchange reaction.



Scheme 5. Reaction of glycosyl halides **2** with diphenyl disulfide (**3a**)/diselenide (**3i**) in the presence of benzyltriethylammonium tetrathiomolybdate **1**.

1752 (s), 1516 (m), 1346 (m), 1242 (s), 1223 (s), 1060 (m), 1045 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 5.32–5.23 (m, 2H), 5.04 (t, J = 9.5 Hz, 1H), 4.64 (d, J = 9.2 Hz, 1H), 4.07 (d, J = 3.5 Hz, 2H), 3.76–3.71 (m, 1H), 2.09 (s, 3H), 2.02 (s, 6H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 170.1, 169.3, 169.1, 146.5, 146.1, 127.1, 123.6, 87.0, 76.2, 73.5, 69.1, 67.7, 61.6, 20.6, 20.54, 20.50, 20.46; HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{23}NO_{11}S_2Na$ $(M+Na)^+$: 540.0610; found: 540.0611.

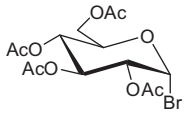
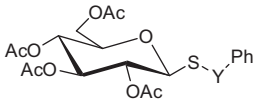
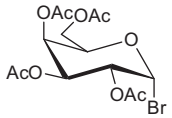
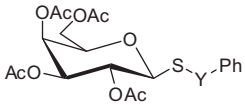
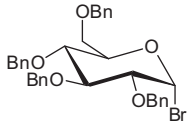
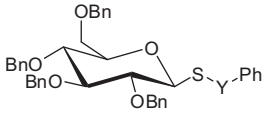
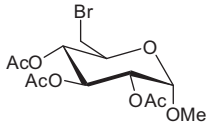
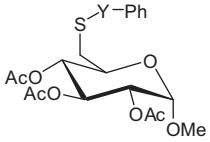
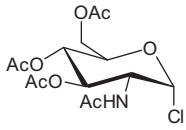
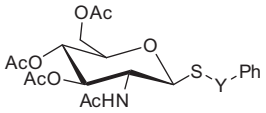
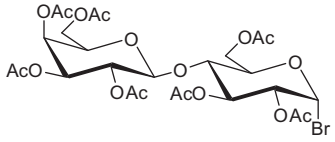
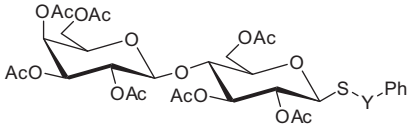
1.2.6. 2-Pyridyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) disulfide (4af)

Yield 35%; R_f = 0.4 (hexanes/ethyl acetate: 50:50); Pale yellow solid; mp: 96–98 °C; $[\alpha]_D^{25}$ −194.9 (c 0.5, $CHCl_3$); FTIR (KBr): 1748 (s), 1373 (w), 1226 (s), 1060 (s), 1038 (w), 911 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, J = 4.4 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.11–7.08 (m, 1H), 5.28–5.19 (m, 2H), 5.06 (t, J = 9.1, 1H), 4.70–4.65 (m, 1H), 4.04 (s, 2H), 3.72–3.67 (m, 1H), 2.08 (s, 3H), 2.01 (s, 6H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.3, 169.4, 169.3, 160.1, 149.0, 136.9, 121.0, 120.6, 88.3, 76.1, 73.8, 69.5, 68.0, 61.9, 20.8, 20.7, 20.6; HRMS (ESI-TOF) m/z: calcd for $C_{19}H_{23}NO_9S_2Na$ $(M+Na)^+$: 496.0712; found: 496.0719.

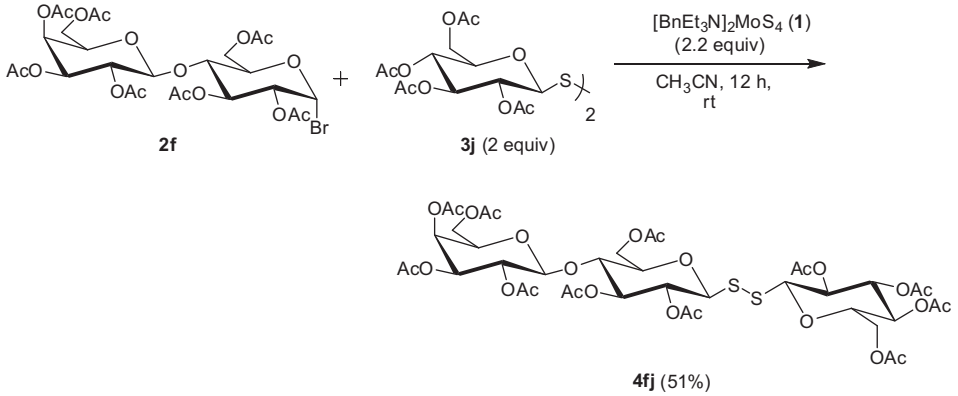
1.2.7. Benzyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)disulfide (4ag)[18]

Yield 65%; R_f = 0.5 (hexanes/ethyl acetate: 60:40); white solid; mp: 118–120 °C; $[\alpha]_D^{25}$ −207.9 (c 1.0, $CHCl_3$); FTIR (KBr): 1747 (s), 1367 (w), 1255 (s), 1228 (s), 1061 (m), 1041 (m), 912 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32 (bs, 5H), 5.32 (t, J = 9.4 Hz, 1H), 5.24 (t, J = 9.3 Hz, 1H), 5.13 (t, J = 9.6 Hz, 1H), 4.49 (d, J = 9.6 Hz, 1H), 4.27 (dd, J = 12.4, 4.8 Hz, 1H), 4.18 (dd, J = 12.4, 1.6 Hz, 1H), 4.03 (s, 2H), 3.75–3.70 (m, 1H), 2.09–2.02 (4s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.2, 169.4, 169.1, 136.7, 129.4, 128.5, 127.6, 87.8, 76.1, 73.8, 69.1, 68.0, 62.0, 44.4, 20.7, 20.64,

Table 2
Synthesis of glycosyl mixed disulfides and selenenylsulfides from **3a** and **3i**

Entry	Glycosyl halide		Glycosyl mixed disulfide/selenenylsulfide		Time[a] (h)	Yield (%)
1		**2a**		Y = S (**4aa**)	3	70
				=Se (**4ai**)	4	52
2		**2b**		Y = S (**4ba**)	3	72
				=Se (**4bi**)	4	55
3		**2c**		Y = S (**4ca**)	3	66
				=Se (**4ci**)	4	49
4		**2d**		Y = S (**4da**)	8	51
				=Se (**4di**)	10	38
5		**2e**		Y = S (**4ea**)	3	63
				=Se (**4ei**)	4	50
6		**2f**		Y = S (**4fa**)	3	68
				=Se (**4fi**)	4	51

[a] Time required for disulfide exchange reaction.



Scheme 6. Synthesis of trisaccharide containing mixed disulfide **4fj** derived from **2f** and **3j**.

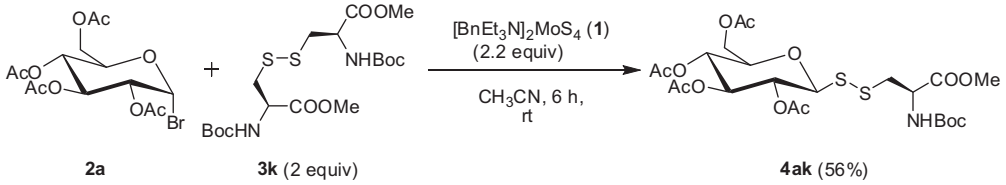
20.59, 20.56; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{21}H_{26}O_9S_2Na$ $(M+Na)^+$: 509.0916; found: 509.0913.

1.2.8. Methyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)disulfide (4ah)[65]

Yield 68%; R_f = 0.5 (hexanes/ethyl acetate: 60:40); white solid; mp: 89–90 °C; $[\alpha]_D^{22}$ −92.2 (*c* 4.3, $CHCl_3$); FTIR (KBr): 1748 (s), 1380 (m), 1250 (s), 1228 (s), 1087 (m), 1054 (m), 1039 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.34–5.24 (m, 2H), 5.15–5.05 (m, 1H), 4.58 (d, *J* = 9.2 Hz, 1H), 4.23 (dd, *J* = 12.4, 4.6 Hz, 1H), 4.17 (dd, *J* = 12.3, 1.7 Hz, 1H), 3.78–3.74 (m, 1H), 2.49 (s, 3H), 2.09 (s, 3H), 2.04 (s, 6H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.2, 169.4, 169.1, 87.9, 76.0, 73.8, 68.9, 68.0, 62.0, 24.6, 20.7, 20.63, 20.58, 20.5; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{15}H_{22}O_9S_2Na$ $(M+Na)^+$: 433.0603; found: 433.0605.

1.2.9. Phenyl-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl) disulfide (4ba)[63]

Yield 72%; R_f = 0.4 (hexanes/ethyl acetate: 70:30); white solid; mp: 120–122 °C; $[\alpha]_D^{25}$ −239.3 (*c* 3.2, $CHCl_3$); FTIR (KBr): 1759



2a **3k** (2 equiv) **4ak** (56%)

Scheme 7. Synthesis of glycosyl amino acid mixed disulfide **4ak** derived from **2a** and **3k**.

(m), 1746 (m), 1728 (m), 1373 (w), 1254 (m), 1238 (s), 1219 (s), 1077 (w), 1050 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.63–7.60 (m, 2H), 7.32–7.23 (m, 3H), 5.47–5.41 (m, 2H), 5.08 (dd, J = 10.0, 3.4 Hz, 1H), 4.61 (d, J = 9.9 Hz, 1H), 4.04–3.93 (m, 3H), 2.16 (s, 3H), 2.04 (s, 3H), 1.99 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.1, 170.0, 169.3, 137.1, 129.3, 128.8, 127.6, 89.6, 74.7, 71.8, 67.1, 66.8, 61.3, 20.7, 20.62, 20.59, 20.5; HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{24}O_9S_2Na$ $(M+Na)^+$: 495.0759; found: 495.0756.

1.2.10. Phenyl-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl) disulfide (4ca)[64]

Yield 66%; R_f = 0.4 (hexanes/ethyl acetate: 70:30); Gummy; $[\alpha]_D^{26}$ −149.3 (c 4.6, $CHCl_3$); FTIR (neat): 3063 (w), 3031 (w), 2917 (w), 2865 (w), 1454 (w), 1361 (w), 1086 (s), 1027 (m), 738 (m), 697 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (dd, J = 8.1, 1.3 Hz, 2H), 7.40–7.16 (m, 23H), 4.90–4.80 (m, 5H), 4.72 (d, J = 10.2 Hz, 1H), 4.62–4.51 (m, 3H), 3.80–3.63 (m, 4H), 3.54–3.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 138.2, 138.0, 137.9, 137.4, 128.8–127.1 (Ar-C), 89.4, 86.7, 80.1, 79.5, 77.6, 75.8, 75.5, 75.2, 73.6, 69.0; HRMS (ESI-TOF) m/z: calcd for $C_{40}H_{40}O_5S_2Na$ $(M+Na)^+$: 687.2215; found: 687.2217.

1.2.11. Phenyl-(3,4,6-tri-*O*-acetyl-2-acetamido-2-deoxy-β-D-glucopyranosyl)disulfide (4ea)

Yield 63%; R_f = 0.4 (ethyl acetate); white solid; mp: 188–190 °C; $[\alpha]_D^{25}$ −142.8 (c 7.3, $CHCl_3$); FTIR (KBr): 1750 (m), 1538 (w), 1378 (m), 1372 (m), 1237 (s), 1085 (m), 1052 (s), 910 (w), 742 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 7.6 Hz, 2H), 7.29–7.20 (m, 3H), 6.35 (d, J = 8.9 Hz, 1H), 5.33 (t, J = 9.8 Hz, 1H), 5.08 (t, J = 9.7 Hz, 1H), 4.85 (d, J = 10.3 Hz, 1H), 4.25 (q, J = 9.8 Hz, 1H), 4.14 (dd, J = 12.3, 4.6 Hz, 1H), 4.07 (dd, J = 12.3, 1.8 Hz, 1H), 3.80–3.76 (m, 1H), 2.03–1.94 (4s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.6, 170.4, 169.3, 137.1, 128.7, 128.6, 127.3, 88.9, 75.8, 73.3, 68.3, 62.1, 52.8, 23.2, 20.7, 20.6, 20.5; HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{25}NO_8S_2Na$ $(M+Na)^+$: 494.0919; found: 494.0919.

1.2.12. Phenyl-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2′,3′,6′-tri-*O*-acetyl-β-D-glucopyranosyl)disulfide (4fa)

Yield 68%; R_f = 0.5 (hexanes/ethyl acetate: 20:80); white solid; mp: 96–97 °C; $[\alpha]_D^{25}$ −161.4 (c 4.8, $CHCl_3$); FTIR (KBr): 1751 (s), 1440 (w), 1371 (m), 1230 (s), 1056 (m), 911 (w), 745 (w), 603 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 7.4 Hz, 2H), 7.30–7.21 (m, 3H), 5.34 (d, J = 2.6 Hz, 1H), 5.24 (t, J = 9.1 Hz, 1H), 5.17 (t, J = 9.4 Hz, 1H), 5.09 (dd, J = 10.4, 7.8 Hz, 1H), 4.94 (dd, J = 10.3, 3.3 Hz, 1H), 4.59 (d, J = 9.6 Hz, 1H), 4.48–4.45 (m, 2H), 4.15–4.01 (m, 3H), 3.87–3.79 (m, 2H), 3.68–3.64 (m, 1H), 2.15–2.05 (3s, 9H), 2.03 (s, 6H), 1.97 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.2, 170.1, 170.0, 169.7, 169.4, 169.0, 136.9, 128.7, 128.2, 127.2, 101.0, 87.5, 76.9, 75.8, 73.6, 70.9, 70.7, 69.6, 69.0, 66.5, 61.9, 60.7, 20.75, 20.66, 20.60, 20.57, 20.5; HRMS (ESI-TOF) m/z: calcd for $C_{32}H_{40}O_{17}S_2Na$ $(M+Na)^+$: 783.1605; found: 783.1606.

1.2.13. Phenyl-2,3,4,6-tetra-*O*-acetyl-1-selenenylsulfide-β-D-glucopyranoside (4ai)[13]

Yield 52%; R_f = 0.4 (hexanes/ethyl acetate: 60:40); white solid; mp: 110–111 °C; $[\alpha]_D^{25}$ −194.24 (c 0.75, $CHCl_3$); FTIR (KBr): 1752 (m), 1572 (w), 1376 (w), 1227 (s), 1054 (m), 1038 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70–7.68 (m, 2H), 7.27 (bs, 3H), 5.29–5.21 (m, 2H), 5.12 (t, J = 9.4 Hz, 1H), 4.62 (d, J = 9.0 Hz, 1H), 4.16 (dd, J = 12.5, 4.7 Hz, 1H), 4.08 (dd, J = 12.4, 1.9 Hz, 1H), 3.78–3.74 (m, 1H), 2.02–2.00 (3s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.2, 169.4, 169.2, 132.1, 131.3, 128.9, 128.0, 85.7, 76.0, 73.7, 70.7, 68.0, 61.9, 20.62, 20.58, 20.5; HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{24}O_9SSeNa$ $(M+Na)^+$: 543.0204; found: 543.0202.

1.2.14. Phenyl-2,3,4,6-tetra-*O*-acetyl-1-selenenylsulfide-β-D-galactopyranoside (4bi)[13]

Yield 55%; R_f = 0.4 (hexanes/ethyl acetate: 60:40); white solid; mp: 120–122 °C; $[\alpha]_D^{23}$ −226.2 (c 3.7, $CHCl_3$); FTIR (KBr): 1750 (s), 1369 (w), 1221 (s), 1083 (w), 1055 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72–7.69 (m, 2H), 7.29–7.27 (m, 3H), 5.45–5.40 (m, 2H), 5.08 (dd, J = 10.0, 3.3 Hz, 1H), 4.64 (d, J = 9.8 Hz, 1H), 4.03–3.94 (m, 3H), 2.17–1.99 (4s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.1, 170.0, 169.4, 132.3, 131.7, 128.9, 128.1, 87.5, 74.7, 71.8, 68.1, 67.1, 61.3, 20.7, 20.64, 20.61, 20.5; HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{24}O_9SSeNa$ $(M+Na)^+$: 543.0204 Found: 543.0208.

1.2.15. Phenyl-2,3,4,6-tetra-*O*-benzyl-1-selenenylsulfide-β-D-glucopyranoside (4ci)

Yield 49%; R_f = 0.4 (hexanes/ethyl acetate: 80:20); Gummy; $[\alpha]_D^{26}$ −169.2 (c 2.0, $CHCl_3$); FTIR (neat): 2863 (w), 1751 (w), 1454 (w), 1361 (w), 1089 (s), 1072 (s), 1028 (w), 736 (m), 697 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.74–7.15 (m, 25H), 4.92–4.75 (m, 5H), 4.59–4.41 (m, 4H), 3.74–3.49 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 138.2, 138.0, 137.8, 132.5, 131.5, 131.0, 129.2, 128.9, 128.44, 128.39, 128.3, 128.2, 127.92, 127.86, 127.8, 127.7, 127.6, 127.5, 127.5, 88.0, 86.6, 81.4, 79.5, 77.6, 77.2, 75.7, 75.4, 75.0, 73.5, 68.9; HRMS (ESI-TOF) m/z: calcd for $C_{40}H_{40}O_5SSeNa$ $(M+Na)^+$: 735.1659 found: 735.1658.

1.2.16. Phenyl-3,4,6-tri-*O*-acetyl-2-acetamido-2-deoxy-1-selenenylsulfide-β-D-glucopyranoside (4ei)[64]

Yield 50%; R_f = 0.4 (ethyl acetate); white solid; mp: 178–180 °C; $[\alpha]_D^{26}$ −237.3 (c 4.0, $CHCl_3$); FTIR (KBr): 3373 (br), 1748 (s), 1656 (m), 1542 (m), 1377 (m), 1239 (s), 1084 (m), 1053 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71–7.69 (m, 2H), 7.29–7.25 (m, 3H), 5.98 (d, J = 9.0 Hz, 1H), 5.30 (t, J = 9.8 Hz, 1H), 5.10 (t, J = 9.7 Hz, 1H), 4.80 (d, J = 10.1 Hz, 1H), 4.27–4.19 (m, 1H), 4.16 (dd, J = 12.3, 4.6 Hz, 1H), 4.07 (dd, J = 12.2, 2.0 Hz,1H), 3.80–3.76 (m, 1H), 2.03–1.91 (4s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0, 170.7, 170.3, 169.3, 132.4, 131.2, 129.0, 127.9, 86.8, 75.9, 73.4, 68.3, 62.2, 54.2, 23.2, 20.72, 20.68, 20.6; HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{25}NO_8SSeNa$ $(M+Na)^+$: 542.0364; found: 542.0366.

1.2.17. Phenyl-2,3,6-tri-*O*-acetyl-4-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosyl)-1-selenenylsulfide-β-D-glucopyranoside (4fi)

Yield 51%; R_f = 0.4 (hexanes/ethyl acetate: 70:30); white solid; mp: 74–76 °C; $[\alpha]_D^{25}$ −58.4 (c 2.2, $CHCl_3$); FTIR (KBr): 1750 (s), 1371 (m), 1231 (s), 1055 (m), 912 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.66–7.63 (m, 2H), 7.27–7.25 (m, 3H), 5.34 (d, J = 3.1 Hz, 1H), 5.25 (t, J = 9.2 Hz, 1H), 5.14–5.07 (m, 2H), 4.94 (dd, J = 10.4, 3.4 Hz, 1H), 4.60 (d, J = 9.7 Hz, 1H), 4.47–4.44 (m,

2H), 4.15–4.02 (m, 3H), 3.87–3.80 (m, 2H), 3.69–3.66 (m, 1H), 2.15–1.96 (7s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.32, 170.26, 170.1, 170.0, 169.7, 169.5, 169.0, 132.1, 130.7, 129.0, 127.8, 101.0, 85.5, 76.8, 75.9, 73.5, 71.0, 70.9, 70.6, 69.0, 66.5, 62.0, 60.7, 20.8, 20.70, 20.66, 20.62, 20.59, 20.5; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{32}H_{40}O_{17}SSeNa$ $(M+Na)^+$: 831.1049; found: 831.1049.

1.2.18. *S*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-*O*-(2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranosyl)-(1→4)-1,2,3,6-tetra-*O*-acetyl-β-D-galactopyranose (4fj)

Yield 51%; R_f = 0.4 (ethyl acetate); Gummy; $[\alpha]_D^{22}$ −54.5 (*c* 2.7, $CHCl_3$); FTIR (neat): 3411 (bs), 1752 (m), 1601 (m), 1437 (w), 1370 (w), 1225 (s), 1020 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.35 (d, *J* = 2.2 Hz, 1H), 5.30–5.06 (m, 6H), 4.97 (dd, *J* = 10.4, 3.3 Hz, 1H), 4.61 (dd, *J* = 9.9, 4.2 Hz, 2H), 4.54 (d, *J* = 7.9 Hz, 1H), 4.33–4.05 (m, 6H), 3.91–3.67 (m, 4H), 2.18–1.97 (10s, 33H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 170.4, 170.3, 170.2, 170.1, 170.0, 169.6, 169.5, 169.3, 169.0, 100.9, 87.1, 86.9, 77.2, 76.0, 75.7, 73.83, 73.78, 71.0, 70.6, 70.1, 69.7, 69.0, 67.8, 66.5, 61.6, 61.5, 60.6, 20.9, 20.8, 20.75, 20.67, 20.6, 20.54, 20.48; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{40}H_{54}O_{26}S_2Na$ $(M+Na)^+$: 1037.2242; found: 1037.2242.

1.2.19. *N*-(*tert*-butoxycarbonyl)-L-cysteine-(2,3,4,6-tetra-*O*-acetyl-1-dithio-β-D-glucopyaranosyl disulfide) methyl ester (4ak)[64]

Yield 56%; R_f = 0.5 (hexanes/ethyl acetate: 50:50); white solid; mp: 135–137 °C; $[\alpha]_D^{22}$ +91.7 (*c* 1.7, $CHCl_3$); FTIR (KBr): 3386 (br), 1749 (s), 1690 (m), 1517 (m), 1369 (m), 1230 (s), 1166 (m), 1054 (s), 911 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.35–5.24 (m, 3H), 5.16–5.11 (m, 1H), 4.71–4.57 (m, 2H), 4.28 (dd, *J* = 12.5, 4.6 Hz, 1H), 4.16 (dd, *J* = 12.4, 1.8 Hz, 1H), 3.81 (bs, 1H), 3.77 (s, 3H), 3.31 (dd, *J* = 13.8, 4.5 Hz, 1H), 3.09–3.03 (m, 1H), 2.09–2.01 (4s, 12H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.6, 170.1, 169.3, 169.1, 155.0, 87.8, 80.2, 76.1, 73.8, 68.9, 67.8, 61.9, 52.9, 52.6, 42.6, 28.2, 20.60, 20.56, 20.5; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{23}H_{35}NO_{13}S_2Na$ $(M+Na)^+$: 620.1448; found: 620.1447.

1.3. Procedure for the synthesis of compounds 4da and 4di

To a well-stirred solution of methyl-2,3,4-tri-*O*-acetyl-6-deoxy-6-bromo-α-D-glucopyranoside **2d** (1 equiv) in CH_3CN (5 mL), benzyltriethylammonium tetrathiomolybdate **1** (1.1 equiv) was added at once and stirred for 15 h. To this solution benzyltriethylammonium tetrathiomolybdate **1** (1.1 equiv) and diphenyl disulfide/diphenyl diselenide (2 equiv) were added and the stirring was continued. The solvent was removed in vacuo and the residue was extracted repeatedly (3 × 10 mL) with a DCM/ether mixture (1:4). The extract was filtered through a thin pad of Celite and the filtrate was concentrated in vacuo. The reaction mixture was further purified by column chromatography to give the mixed disulfide/selenenylsulfide.

1.3.1. Phenyl-methyl-2,3,4-tri-*O*-acetyl-6-deoxy-6-dithio-α-D-glucopyranoside (4da)

Yield 51%; R_f = 0.5 (hexanes/ethyl acetate: 60:40); white solid; mp: 82–84 °C; $[\alpha]_D^{22}$ +276.4 (*c* 4.8, $CHCl_3$); FTIR (neat): 1749 (s), 1369 (w), 1245 (m), 1223 (s), 1068 (w), 1044 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.5 Hz, 2H), 7.35–7.24 (m, 3H), 5.48–5.43 (m, 1H), 4.91–4.84 (m, 3H), 4.10–4.05 (m, 1H), 3.39 (s, 3H), 2.85–2.84 (m, 2H), 2.07–1.95 (3s, 9H) cm^{-1}; ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 170.0 169.8, 136.4, 129.4, 129.1, 128.5, 127.4, 96.4, 71.7, 70.9, 70.0, 67.3, 55.3, 40.5, 20.7, 20.63, 20.57; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{19}H_{24}O_8S_2Na$ $(M+Na)^+$: 467.0810; found: 467.0802.

1.3.2. Phenyl-methyl-2,3,4-tri-*O*-acetyl-6-deoxy-6-selenenyl-sulfide-α-D-glucopyranoside (4di)

Yield 38%; R_f = 0.5 (hexanes/ethyl acetate: 60:40); gummy; $[\alpha]_D^{22}$ +199.9 (*c* 3.3, $CHCl_3$); FTIR (neat): 1749 (s), 1373 (m), 1245 (s), 1224 (s), 1044 (s), 739 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.4 Hz, 2H), 7.34–7.25 (m, 3H), 5.44 (t, *J* = 9.6 Hz, 1H), 4.92–4.83 (m, 3H), 4.03–3.98 (m, 1H), 3.36 (s, 3H), 3.03–2.94 (m, 2H), 2.07–1.96 (3s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 170.0, 169.8, 131.4, 130.9, 129.3, 127.9, 96.4, 71.7, 70.9, 70.0, 68.4, 55.3, 40.1, 20.7, 20.65, 20.61; HRMS (ESI-TOF) *m*/*z*: calcd for $C_{19}H_{24}O_8SSeNa$ $(M+Na)^+$: 515.0255; found: 515.0253.

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Supplementary data

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References

1. Specker, D.; Wittmann, V. *Top. Curr. Chem.* **2007**, *267*, 65–107.
2. André, S.; Pei, Z.; Siebert, H.-C.; Ramström, O.; Gabius, H.-J. *Bioorg. Med. Chem.* **2006**, *14*, 6314–6326.
3. Pei, Z.; Larsson, R.; Aastrup, T.; Anderson, H.; Lehn, J.-M.; Ramström, O. *Biosens. Bioelectron.* **2006**, *22*, 42–48.
4. Szilágyi, L.; Illyés, T.-Z.; Herczegh, P. *Tetrahedron Lett.* **2001**, *42*, 3901–3903.
5. Brito, I.; López-Rodríguez, M.; Bényei, A.; Szilágyi, L. *Carbohydr. Res.* **2006**, *341*, 2967–2972.
6. Bock, K.; Lemieux, R. U. *Carbohydr. Res.* **1982**, *100*, 63–74.
7. Gilbert, H. F. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1990**, *63*, 69–172.
8. Codelli, J. A.; Puchlopek, A. L. A.; Reisman, S. E. *J. Am. Chem. Soc.* **2012**, *134*, 1930–1933.
9. Williams, D. E.; Austin, P.; Diaz-Marrero, A. R.; van Soest, R.; Matainaho, T.; Roskelley, C. D.; Roberge, M.; Andersen, R. J. *Org. Lett.* **2005**, *7*, 4173–4176.
10. Fetrow, J. S.; Siew, N.; Skolnick, J. *FASEB J.* **1999**, *13*, 1866–1874.
11. Davis, B. G.; Ward, S. J.; Rendle, P. M. *Chem. Commun.* **2001**, 189–190.
12. Garegg, P. J. *Adv. Carbohydr. Chem. Biochem.* **1997**, *52*, 179–205.
13. Gamblin, D. P.; Garnier, P.; van Kasteren, S.; Oldham, N. J.; Fairbanks, A. J.; Davis, B. G. *Angew. Chem., Int. Ed.* **2004**, *43*, 828–833.
14. Endo, T.; Tasai, H.; Ishigami, T. *Chem. Lett.* **1975**, *4*, 813–814.
15. Harpp, D. N.; Friedlander, B. T.; Larsen, C.; Steliou, K.; Stockton, A. *J. Org. Chem.* **1978**, *43*, 3481–3485.
16. Brown, C.; Evans, G. R. *Tetrahedron Lett.* **1996**, *37*, 9101–9104.
17. Szymelfejnik, M.; Demkowicz, S.; Rachon, J.; Witt, D. *Synthesis* **2007**, 3528–3534.
18. Bell, R. H.; Horton, D.; Miller, M. J. *Carbohydr. Res.* **1969**, *9*, 201–214.
19. Aversa, M. C.; Barattucci, A.; Bonaccorsi, P. *Eur. J. Org. Chem.* **2009**, 6355–6359.
20. Hiver, P.; Dicko, A.; Paquer, D. *Tetrahedron Lett.* **1994**, *35*, 9569–9572.
21. Sirakawa, K.; Aki, O.; Tsujikawa, T.; Tsuda, T. *Chem. Pharm. Bull.* **1970**, *18*, 235–242.
22. Adinolfi, M.; Capasso, D.; Di Gaetano, S.; Iadonisi, A.; Leone, L.; Pastore, A. *Org. Biomol. Chem.* **2011**, *9*, 6278–6283.
23. Brzezinska, E.; Ternay, A. L. *J. Org. Chem.* **1994**, *59*, 8239–8244.
24. Stellenboom, N.; Hunter, R.; Caira, M. R.; Szilágyi, L. *Tetrahedron Lett.* **2010**, *51*, 5309–5312.
25. Leriverend, C.; Metzner, P. *Synthesis* **1994**, 761–762.
26. Armitage, D. A.; Clark, M. J.; Tso, C. C. *J. Chem. Soc., Perkin Trans. 1* **1972**, 680–683.
27. Barton, D. H. R.; Chen, C.; Michael Wall, G. *Tetrahedron* **1991**, *47*, 6127–6138.
28. Bao, M.; Shimizu, M. *Tetrahedron* **2003**, *59*, 9655–9659.
29. Hiskey, R. G.; Ward, B. F. J. *J. Org. Chem.* **1970**, *35*, 1118–1121.
30. Benati, L.; Montevecchi, P. C.; Spagnolo, P. *Tetrahedron Lett.* **1986**, *27*, 1739–1742.
31. Capozzi, G.; Capperucci, A.; Degl'Innocenti, A.; Del Duce, R.; Menichetti, S. *Tetrahedron Lett.* **1989**, *30*, 2995–2998.
32. Rajca, A.; Wiessler, M. *Tetrahedron Lett.* **1990**, *31*, 6075–6076.
33. Koval, I. V. *Russ. J. Org. Chem.* **2002**, *38*, 232–234.

34. Oae, S.; Kim, Y. H.; Fukushima, D.; Shinhama, K. *J. Chem. Soc., Perkin Trans. 1* **1978**, 913–917.
35. Brois, S. J.; Pilot, J. F.; Barnum, H. W. *J. Am. Chem. Soc.* **1970**, *92*, 7629–7631.
36. Dubs, P.; Stüssi, R. *Helv. Chim. Acta* **1976**, *59*, 1307–1311.
37. Masui, M.; Mizuki, Y.; Sakai, K.; Ueda, C.; Ohmori, H. *J. Chem. Soc., Chem. Commun.* **1984**, 843–844.
38. Illyés, T.-Z.; Szabó, T.; Szilágyi, L. *Carbohydr. Res.* **2011**, *346*, 1622–1627.
39. Ternay, A. L.; Cook, C.; Brzezinska, E. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *95*, 351–352.
40. Barton, D. H. R.; Hesse, R. H.; O'Sullivan, A. C.; Pechet, M. M. *J. Org. Chem.* **1991**, *56*, 6697–6702.
41. Cragg, R. H.; Husband, J. P. N.; Weston, A. F. *J. Chem. Soc., Chem. Commun.* **1970**, 1701.
42. Boustany, K. S.; Sullivan, A. B. *Tetrahedron Lett.* **1970**, *11*, 3547–3549.
43. Harpp, D. N.; Ash, D. K.; Back, T. G.; Gleason, J. G.; Orwig, B. A.; VanHorn, W. F.; Snyder, J. P. *Tetrahedron Lett.* **1970**, *11*, 3551–3554.
44. Klose, J.; Reese, C. B.; Song, Q. *Tetrahedron* **1997**, *53*, 14411–14416.
45. Pei, Z.; Aastrup, T.; Anderson, H.; Ramström, O. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 2707–2710.
46. Arisawa, M.; Yamaguchi, M. *J. Am. Chem. Soc.* **2003**, *125*, 6624–6625.
47. Sureshkumar, D.; Ganesh, V.; Vidyarini, R. S.; Chandrasekaran, S. *J. Org. Chem.* **2009**, *74*, 7958–7961.
48. Bhar, D.; Chandrasekaran, S. *Carbohydr. Res.* **1997**, *301*, 221–224.
49. Prabhu, K. R.; Sivanand, P. S.; Chandrasekaran, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4316–4319.
50. Sridhar, P. R.; Prabhu, K. R.; Chandrasekaran, S. *Eur. J. Org. Chem.* **2004**, 4809–4815.
51. Sridhar, P. R.; Saravanan, V.; Chandrasekaran, S. *Pure Appl. Chem.* **2005**, *77*, 145–153.
52. Prabhu, K. R.; Devan, N.; Chandrasekaran, S. *Synlett* **2002**, 1762–1778.
53. Sivapriya, K.; Suguna, P.; Banerjee, A.; Saravanan, V.; Rao, D. N.; Chandrasekaran, S. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 6387–6391.
54. Sivapriya, K.; Hariharaputran, S.; Suhas, V. L.; Chandra, N.; Chandrasekaran, S. *Bioorg. Med. Chem.* **2007**, *15*, 5659–5665.
55. Nasir Baig, R. B.; Sai Sudhir, V.; Chandrasekaran, S. *Synlett* **2008**, 2684–2688.
56. Ramesha, A. R.; Chandrasekaran, S. *Synth. Commun.* **1992**, *22*, 3277–3284.
57. Ramesha, A. R.; Chandrasekaran, S. *J. Org. Chem.* **1994**, *59*, 1354–1357.
58. Sureshkumar, D.; Koutha, S. M.; Chandrasekaran, S. *J. Am. Chem. Soc.* **2005**, *127*, 12760–12761.
59. Use of less than 2 equiv. of disulfide decreases the yield of the product.
60. Lower yields obtained in the case of disulfides with electron withdrawing group are probably due to the faster disulfide cleavage resulting in the formation of the corresponding thiolate anions. These thiolate anions are less efficient to participate in the disulfide exchange process due to their internal stabilization.
61. Coyle, C. L.; Harmer, M. A.; George, G. N.; Daage, M.; Stiefel, E. I. *Inorg. Chem.* **1990**, *29*, 14–19.
62. Smith, R.; Zeng, X.; Müller-Bunz, H.; Zhu, X. *Tetrahedron Lett.* **2013**, *54*, 5348–5350.
63. Morais, R. G.; Falconer, R. A. *Tetrahedron Lett.* **2007**, *48*, 7637–7641.
64. Bernardes, G. J. L.; Grayson, E. J.; Thompson, S.; Chalker, J. M.; Errey, J. C.; El Oualid, F.; Claridge, T. D. W.; Davis, B. G. *Angew. Chem., Int. Ed.* **2008**, *47*, 2244–2247.
65. Hoang, K. L. M.; Bai, Y.; Ge, X.; Liu, X.-W. *J. Org. Chem.* **2013**, *78*, 5196–5204.