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Synthetic studies on oligosaccharides composed of 5-thioglucopyranose units

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This article is dedicated to Professor Koji Nakanishi on his receipt of the Tetrahedron Prize.

Abstract—Glycosylation reactions of 5-thioglucopyranosyl trichloroacetimidates bearing ethereal protective groups at the 2-*O*-position **14**–**15**, and **37** proceed smoothly to give α-glycosides stereoselectively by using a catalytic amount of silyl triflate. This methodology allowed us to achieve syntheses of sulfur-substituted isomaltotetraoside **2** and maltotetraoside **3**. These studies also revealed that benzoyl-protected 5-thioglucopyranosyl trichloroacetimidate **12** underwent β-selective glycosylation with C6-OH glucopyranosyl acceptors upon activation by BF_3OEt_2. This was applied for preparation of sulfur-substituted gentiobiosides **1** and **46**.

1. Introduction

A number of carbohydrate analogues, the so-called carbomimetics, have been developed as effective molecular probes for mechanistic investigations of glycosidases as well as lead compounds in the search for pharmaceutical drugs targeting, for example, digestive diseases.[1,2] Most of them were designed[3–6] as inhibitors against *exo*-glycosidases, which cleave the terminal glycosidic linkages in sugar chains. There also exists the other glycosidase called *endo*-glycosidase, which hydrolyzes internal glycosidic linkages by recognizing only sequence patterns of the carbohydrate units.[6] In other words, there are many cleavable glycosidic bonds, especially within homo-polysaccharides such as amylose. Due to the difficulty of designing suitable probes,[4,7–10] mechanistic studies for *endo*-glycosidases relatively lag behind, whereas the character of *exo*-glycosidases has enabled researchers to develop effective molecular probes, which have served well for our understanding of the mechanism of *exo*-glycosidases in detail.

It is well known that the substrate for *endo*-glycosidases is polysaccharide. For molecular design of an analogue of oligosaccharide as an inhibitor against *endo*-glycosidases, a desirable modification has to be replacement of all enzymatically cleavable bonds with an inert functionality. Even if individual changes are insignificant, their accumulation may cause drastic structural changes. Our solution for this problem was to use a sulfur atom in place of the oxygen in a pyranose ring to raise the resistance against the glycosidases with minimal structural changes, since the six-membered ring would absorb these alterations. We anticipated that this methodology is applicable for synthesis of molecular probes for the *endo*-glycosidases.

Based on this concept, we investigated syntheses of oligosaccharides composed of 5-thioglucopyranose units.[11–13] In the course of these studies, we succeeded in developing α- and β-stereoselective glycosylation reactions with 5-thioglucose derivatives. We have previously communicated the successful preparation of sulfur-substituted analogues of gentiobioside **1**,[13] and isomaltotetraoside **2**.[14] We report, herein, the full details of these studies as well as our successful synthesis of maltotetraoside derivative **3**.

Keywords: *endo*-Glycosidases; α-selective glycosylation; β-selective glycosylation; 5-Thioglucopyranosyl trichloroacetimidates.
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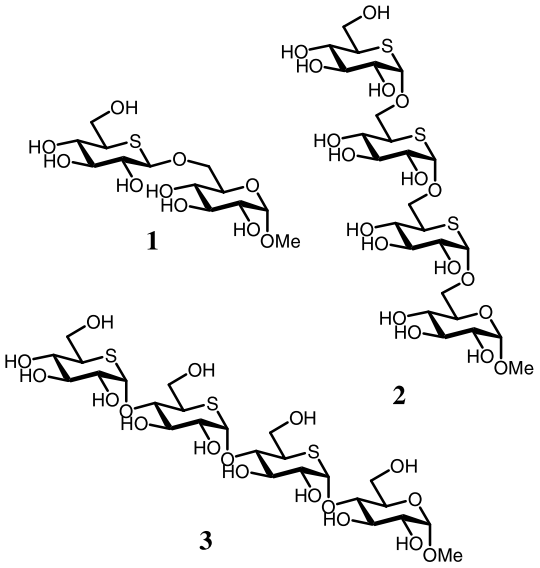
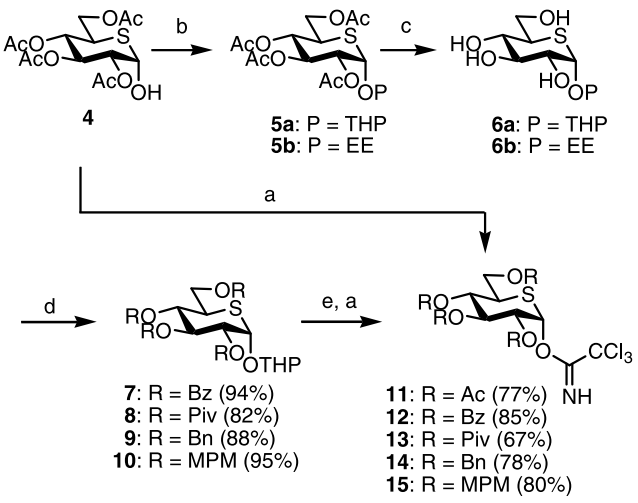




Scheme 1. Preparation of 5-thioglucopyranosyl donors. Reagents and conditions: (a) DBU, CCl_3CN, CH_2Cl_2, 0 °C, (**11**: 77%, **12**: 85%, **13**: 67%, **14**: 78%, **15**: 80%); (b) for **5a**—DHP, cat. *p*-TsOH, CH_2Cl_2, 0 °C, 95%, for **5b**—EVE, cat. PPTS, CH_2Cl_2, 0 °C, 96%; (c) NaOMe, MeOH, rt, (**6a**: 82%, **6b**: 86%); (d) for **7**—BzCl, Py, rt, 94%; for **8**—PivCl, DMAP, Py, 75 °C, 82%; for **9**—NaH, BnBr, DMF, rt, 88%; for **10**—NaH, MPMBr, DMF, rt, 95%; (e) from **7**—*p*-TsOH, MeOH, 45 °C, 85%; from **8**—*p*-TsOH, MeOH, 72%; from **9**—$HClO_4$, MeOH, rt, 90%, from **10**: HCl, MeOH, rt, 81%.

2. Results and discussion

2.1. Development of effective and stereoselective glycosylation reactions of 5-thioglucopyranosyl donors

2.1.1. Preparation of glycosyl donors and acceptors. There are many reports for preparing carbomimetics composed of 5-thiopyranoses, in most of which 2,3,4,6-tetra-*O*-acetyl-5-thioglucopyranosyl trichloroacetimidate (**11**) was used as a glycosyl donor, probably due to its synthetic feasibility.[8,15–18] Both the stereoselectivity and the chemical yield of the glycosylation of **11** depended on the acceptors employed. For example, Mehta et al. performed the glycosylation reaction in 80% yield, but with low selectivity ($\alpha:\beta = 1.5:1$),[16] while Izumi et al. obtained the α-disaccharide exclusively, but in only 22% yield.[8] These results interestingly suggest that the glycosylation of **11** has a tendency to give α-glycosides stereoselectively in spite of its equatorial C2-acetoxy group,[8,15–18] whereas this function usually results in β-selective glycosylation in regular carbohydrate chemistry by the neighboring participation.[19] It was indispensable for us to develop a general and highly stereoselective glycosylation reaction of a 5-thioglucopyranosyl donor for the synthesis of its oligomers. We first prepared a series of glycosyl donors and acceptors carrying a 5-thioglucopyranose unit in order to investigate development of efficient glycosylation reactions.

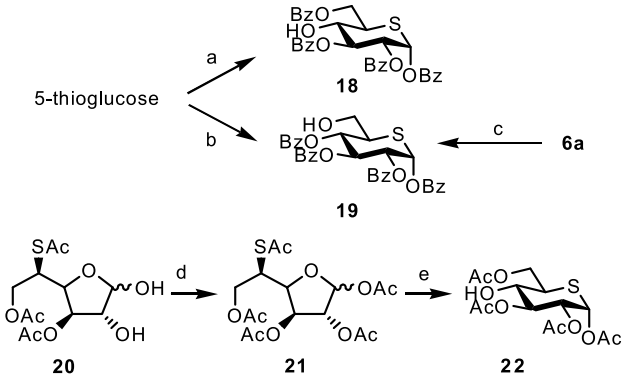
As shown in Scheme 1, synthesis of 5-thioglucosyl donors started with 2,3,4,6-tetra-*O*-acetyl-5-deoxy-5-thio-D-glucopyranose **4**, readily prepared from commercial D-glucrono-6,3-lactone by following literature procedure.[20] Trichloroacetimidate **11** was obtained by an established method.[8] The preparation of **12–14** was performed as follows. The anomeric hemithioacetal of **4** was protected as either THP (tetrahydropyranyl) or EE (ethoxyethyl) ethers to provide **5a** and **5b** (95% and 96% yields, respectively). The EE ether **5b** was used for synthesis of isomaltotetraoside derivative **2** as described later. The ^1H NMR spectrum indicated that **5a** consisted of a mixture of two isomers. In both isomers, the C1 protons (5.05 and 5.11 ppm) were determined to be of equatorial orientation according to the observed coupling constants (2.9 Hz), indicating that **5a** consisted of a diastereomeric mixture regarding the asymmetric center of the THP group (50:50). After basic methanolysis of **5a**, the resultant tetraol **6a** (82% yield) was converted to the corresponding benzoates (→**7**, 94% yield), pivaloates (→**8**, 82% yield), benzyl ethers (→**9**, 88% yield), and 4-methoxyphenylmethyl (MPM)[21] ethers (→**10**, 95% yield) by following methods. After the THP groups of **6–9** were selectively removed by acidic treatment, the C1-OH groups were converted into the corresponding trichloroacetimidates (→**12–15**) with trichloroacetonitrile in the presence of a catalytic amount of diazabicycloundec-7-ene (DBU).[22] The ^1H NMR spectra of **11–15** suggested that all trichloroacetimidate moieties possessed α-orientation. Chromatographic purification of the imidates **11–15** had to be performed quickly in order to minimize decomposition. Trichloroacetimidates **11–15** were all used for the next step immediately. The use of other glycosyl donors, such as glucosyl bromides or thioglucosides, seemed to be inappropriate as 5-thiopyranose donors because of intolerance of its sulfide functionality under the activation conditions with soft Lewis acids, such as AgOTf,[23] $HgBr_2$,[24] or NIS-TfOH.[25]

A series of glycosyl acceptors was prepared next. Acceptors with C6-OH **16a**,[26,27] **16b**,[28] and C4-OH **17**[29] were synthesized by established procedures. Acceptors with a 5-thioglucopyranose framework **18** (C4-OH), **19** (C6-

OH), and **22** (C4-OH) were also synthesized as shown in Scheme 2 in order to investigate the effects caused by the sulfur atom in the acceptors. To the best of our knowledge, the employment of 5-thioglucopyranose units as glycosyl acceptors has been reported only in our earlier communications.[14,30]

Benzoylation of 5-thioglucose under low temperature gave acceptor **18** in one step, but this gave a mixture at the anomeric position (α:β = 60:40). These isomers were separated in preparative scale by medium pressure column chromatography.

An acceptor with primary alcohol **19** was also prepared from 5-thioglucose by C6-OH triphenylmethylation (tritylation, Tr) and perbenzoylation of the remaining hydroxyl groups, followed by selective removal of the Tr group under acidic conditions. This procedure gave an inseparable mixture with the β-anomer (α:β = 83:17) besides which two extra steps required. The following sequence allowed us to obtain diastereomerically pure **19** by using **6a**: [(i) *tert*-butyldiphenylsilyl (TBDPS) ether formation with the C6-OH, (ii) benzoylation at the C2-, C3-, and C4-alcohols, (iii) acidic cleavage of the THP ether, (iv) benzoylation of the C1-OH, and (v) removal of the TBDPS group]. The secondary alcohol **22** was prepared from Driguez's intermediate **20**.[20] Acetylation of **20** gave an anomeric mixture of pentaacetate **21** (75:25, the stereochemistry was not assigned). Treatment with hydrazine acetate in *N*,*N*-dimethylformamide (DMF) resulted in selective removal of the C1-OAc and C5-SAc groups, which induced an expansion of furanose into 5-thiopyranose framework. The C1-OH was selectively acetylated to give diastereomerically pure **22** in 95% yield.



Scheme 2. Preparation of 5-thioglucopyranosyl acceptors. Reagents and conditions: (a) BzCl, Py, 40%, (b) (i) TrCl, DMAP, Py, 60 °C, 75%, (ii) BzCl, Py, 78%, (iii) *p*-TsOH, MeOH, 50 °C, 81%, (c) (i) TBDPSCl, ImH, 76%, (ii) BzCl, Py, 98%, (iii) $HClO_4$, MeOH, 81%, (iv) BzCl, Py, 97%, (v) TBAF, AcOH, 92%, (d) Ac_2O, Py, rt, quant, (e) (i) hydrazine acetate, DMF, rt, 80%, (ii) AcCl, Py, DMAP, CH_2Cl_2, 0 °C, 95%.

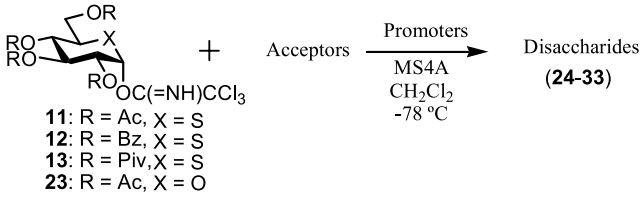
2.1.2. Glycosylation reactions of 5-thioglucopyranosyl donors bearing ester protective groups. With a series of glycosyl donors and acceptors in hand, glycosylation reactions of the 5-thioglucopyranosyl donors were investigated. We first examined the reactions with the acyl protected 5-thioglucosyl donors, because it was anticipated that the ester groups would be removed readily without affecting the sulfide functionality after glycosylation. Taking account of the steric factor, primary alcohols **16a**, **16b**, and **29** were first used as the acceptors for the reactions.

As we expected, upon activation with BF_3OEt_2 (0.5 equiv) glycosylation of acetyl protected trichloroacetimidate of regular glucopyranose **23**[31] with acceptor **16a** proceeded to give glycoside **24** in 76% yield with excellent β-stereoselectivity (α:β > 5:95) (run 1 in Table 1). However, when the corresponding 5-thio analogue **11** was subjected to this reaction, desired glycoside **25** was obtained in low yield (19%) with lower β-selectivity (α:β = 30:70, run 2). The use of triethylsilyl trifluoromethanesulfonate (TESOTf) as a promoter resulted in giving glycoside **26** with unpredicted high α-stereoselectivity (α:β > 95:5, run 3) in only 10% yield. It was found that when the reactions were activated by BF_3OEt_2, benzoyl protected imidate **12** gave β-glycosides **27**–**29** stereoselectively in good yields (runs 4–6). In contrast, trimethylsilyl trifluoromethanesulfonate (TMSOTf), TESOTf, and TfOH catalyzed the α-selective reactions to provide **27** and **29** (runs 7–9 and 11) besides the unsatisfactory yields. Reaction using zinc chloride did not provide glycoside **16a** (run 10). Reaction of imidate **13** bearing pivaloyl groups also gave β-glycosides **30** and **31** in good yields in a highly β-stereoselective manner by the use of BF_3OEt_2 (runs 12–13).

Reactions of donors **11** and **13** with the secondary alcohols **17** and **22** were not promising. Reaction of imidate **11** with C4-OH **22** gave α-glycoside **32** with high stereoselectivity (α:β > 95:5), but the yield was quite low (<5%, run 14). The reaction with the acceptor **18**, bearing sterically hindered benzoyl groups, did not produce desired glycoside **33** (run 15). A trace amount of α-glycoside **34**, missing the C2-*O*-acetyl group, and acetate **35** were also isolated after repeated chromatographic separations. In the case of **17**, the reactions by using BF_3OEt_2 gave no coupling product (runs 16 and 17), but glycal **36** was detected (run 17). A similar pathway leading to thioglycal formation has been reported by Nishizawa and Yamada in their synthesis of baiyunoside.[32]

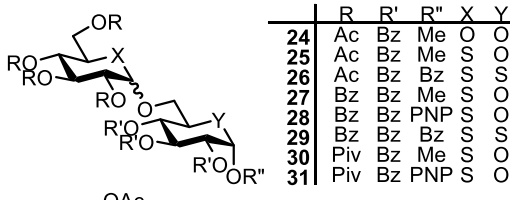
Our results implied that the glycosylation reactions of the acyl protected 5-thioglucopyranosyl donors proceeded through the less reactive species than that corresponding to regular glucopyranoses. This was considered by molecular modeling calculations.[33] In order to simplify the discussion and save time for the calculations, methyl glycosides **Ia** and **Ib** and cyclic acyloxonium intermediates **IIa** and **IIb**, bearing *O*-acetyl groups only at the C2 position (gluco-type), were used as model compounds (Table 2). Prior to *ab initio* calculations, a conformational search employing semi-empir-

Table 1. Glycosylation of ester protected 5-thioglucopyranosyl trichloroacetimidates

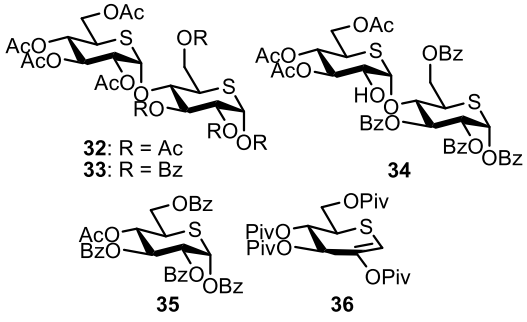


11: R = Ac, X = S
12: R = Bz, X = S
13: R = Piv, X = S
23: R = Ac, X = O

Run	Donors	Acceptors	Promoters	Disaccharides (yield α:β)	Other products
Primary alcohol					
1	**23**	**16a**	BF_3OEt_2	**24** (76%, >5:95)	
2	**11**	**16a**	BF_3OEt_2	**25** (19%, 30:70)	
3	**11**	**19**	TESOTf	**26** (10%, >95:5)	
4	**12**	**16a**	BF_3OEt_2	**27** (77%, 17:83)	
5	**12**	**16b**	BF_3OEt_2	**28** (82%, 15:85)	
6	**12**	**19**	BF_3OEt_2	**29** (62%, >5:95)	
7	**12**	**16a**	TESOTf	**27** (38%, 84:16)	
8	**12**	**16a**	TMSOTf	**27** (11%, >95:5)	
9	**12**	**16a**	TfOH	**27** (33%, 89:11)	
10	**12**	**16a**	$ZnCl_2$	No adduct	
11	**12**	**19**	TESOTf	**29** (38%, 84:16)	
12	**13**	**16a**	BF_3OEt_2	**30** (69%, >5:95)	
13	**13**	**16b**	BF_3OEt_2	**31** (86%, >5:95)	
Secondary alcohol					
14	**11**	**22**	TESOTf	**32** (5%, >95:5)	
15	**11**	**18**	TESOTf	**33** (0%)	**34**, **35** (trace)
16	**11**	**17**	BF_3OEt_2	No adduct	
17	**13**	**17**	BF_3OEt_2	No adduct	**36** (trace)



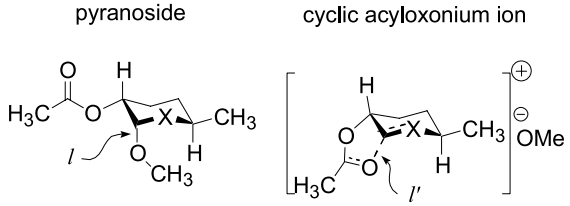
	R	R'	R"	X	Y
24	Ac	Bz	Me	O	O
25	Ac	Bz	Me	S	O
26	Ac	Bz	Bz	S	S
27	Bz	Bz	Me	S	O
28	Bz	Bz	PNP	S	O
29	Bz	Bz	Bz	S	S
30	Piv	Bz	Me	S	O
31	Piv	Bz	PNP	S	O



ical AM1 was performed for each model to provide initial geometries for the optimization. Then these were further calculated employing MP2/6-31G* taking into account the localized *d* orbital in the sulfur atom.

These calculations indicated that the length for the glycosidic bonding (*l*, see Table 2) of **Ib** (X = S) is almost identical to that of **Ia** (X = O). In contrast, the corresponding bond length (*l*′) of cyclic thiocarbenium ion (**IIb**, X = S) is ca. 3% shorter than the corresponding C–O bonding of cyclic oxocarbenium ions (**IIa**, X = O). It is suggested that the glycosidic oxygen and

Table 2. The C1–O bond length of cyclic carbenium ions and glucosides estimated by MP2/6-31G*

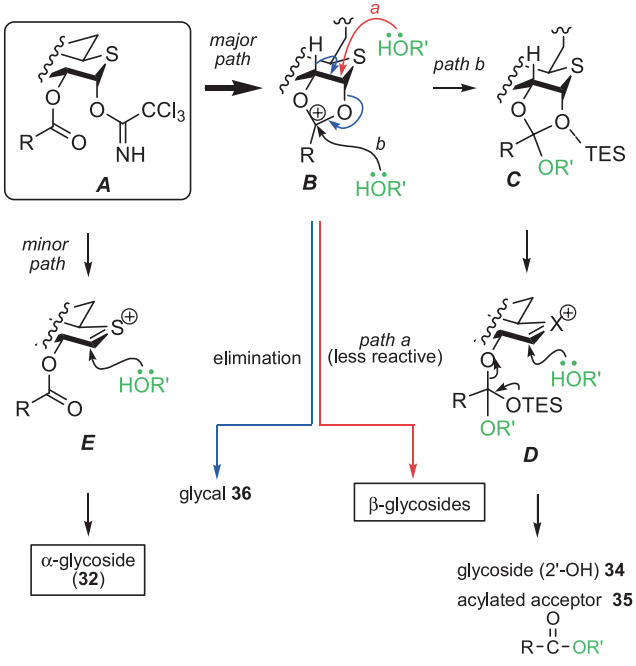


Ia: (X = O)
Ib: (X = S)
IIa: (X = O)
IIb: (X = S)

	l (Å)		*l*′ (Å)	
X = O	1.406	*−0.004*	1.608	*0.048*
X = S	1.410		1.560	

the C1 atom of **IIb** are bonded more tightly than those of **IIa**. Because cleavage of this C–O bond must precede the glycosylation reaction, the calculation results would explain the reason why the ester protected 5-thioglucopyranosyl donors were less reactive than the corresponding regular glucopyranosyl donors, such as **23**.

Since the β-glycosides were obtained stereoselectively in practical yields by reaction with primary alcohols using BF_3OEt_2 as a promoter (runs 2, 4, 6, 12, and 13 in Table 1), it would be evidence that the cyclic oxocarbenium ***B*** was generated in the glycosylation reaction (Scheme 3). On the other hand, by the use of TESOTf for glycosylation of ***A***, the corresponding intermediate ***B*** would be formed, but it could be much less reactive for β-glycosylation according to the obtained elimination product such as glycal **36**. Furthermore, the intermediate ***B*** also underwent transformation into the intermediate ***D***, likely



Scheme 3.

through the orthoester ***C***, to provide C2-deprotected α-glycoside **34** and acylated acceptor **35**. It was proposed that the α-glycosides were derived from the non-cyclic minor intermediate ***E*** (runs 3, 7, 8, 11, and 14 in Table 1).

2.1.3. Glycosylation reactions of 5-thioglucopyranosyl donors bearing ethereal protective groups. We next investigated glycosylation of 5-thioglucopyranosyl donors bearing ethereal protective groups instead of the acyl protected donors. It was found that upon treatment with a catalytic amount of TESOTf at −78 °C, glycosylation of **14** bearing benzyl ethers with acceptor **19** proceeded smoothly to provide α-glycoside **38** with high stereoselectivity (α:β > 95:5) in 81% yield (run 1 in Table 3). The coupling constant for the C′1-H signal of this sample (2.9 Hz) in the ^{1}H NMR spectrum, showed that stereochemistry of the newly formed glycosidic bond is of α-orientation. No signal corresponding to the β-isomer was detected in the spectrum. Glycosylation of donor **14** was also performed with the secondary alcohol **22** to afford glycoside **39** in 94% yield in a highly α-stereoselective manner. Donor with MPM ethers **15** also gave α-glycosides **40–43** smoothly with various acceptors (runs 3–6). Both the yields and stereoselectivities did not depend on the acceptors in these reactions. The reaction with MOM ether **37** was found to provide glycoside **44** in 79% yield, but with lower stereoselectivity (α:β = 80:20).[30] Presumably, the MOM group partially contributes to the neighboring participation to generate the intermediate **45** which preferentially produced the β-glycoside. Thus, we concluded that glycosylation using 5-thioglucosyl trichloroacetimidates with Bn or MPM groups is general and applicable for the synthesis of sulfur-substituted oligosaccharides.

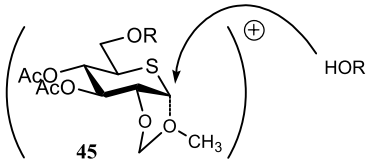
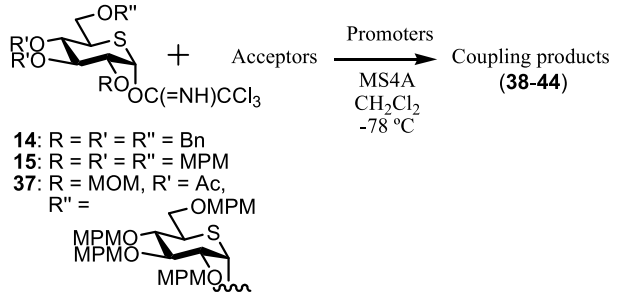
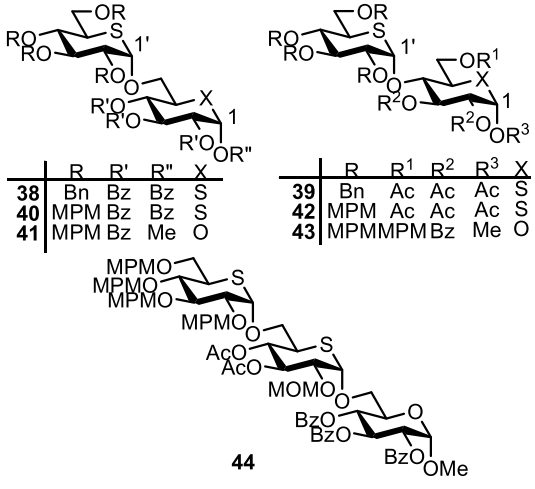


Table 3. Glycosylation of 5-thioglucopyranosyl donors bearing ethereal protective group

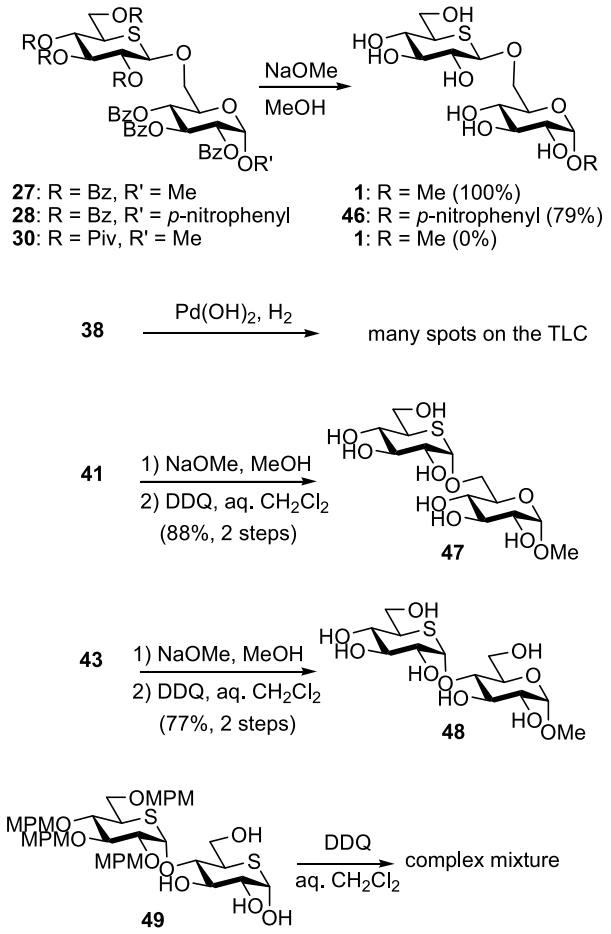


Run	Donors	Acceptors	Promoters	Disaccharides (Yield, α:β)
1	**14**	**19**	TESOTf	**38** (81%, >95:5)
2	**14**	**22**	TESOTf	**39** (94%, >95:5)
3	**15**	**19**	TESOTf	**40** (94%, >95:5)
4	**15**	**16a**	TESOTf	**41** (82%, 88:12)
5	**15**	**22**	TESOTf	**42** (60%, >95:5)
6	**15**	**17**	TESOTf	**43** (87%, >95:5)
7	**37**	**16a**	TMSOTf	**44** (79%, 80:20)[30]

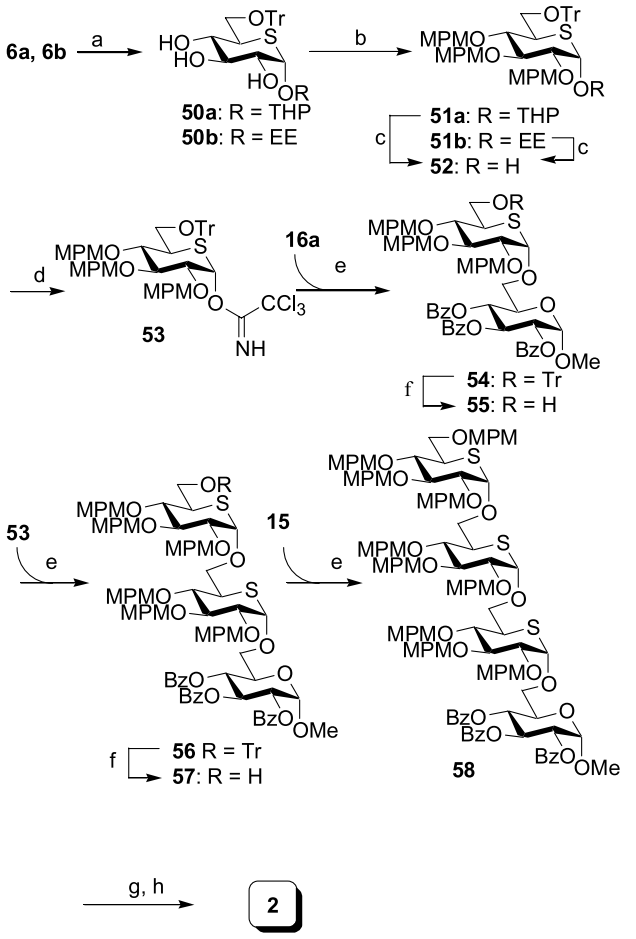


2.1.4. Development of an effective deprotection reaction of thiosaccharides. Removal of the protecting groups from sulfur-containing saccharides was also studied. Since cleavage for the acetates of the glycosides, such as **25**, was not determined due to the low yields of the glycosylation, we first attempted deprotection of **27** and **28**. Basic hydrolysis (NaOMe in MeOH) of **27** and **28** cleaved all the ester groups smoothly to give sulfur-substituted methyl gentiobiosides **1** and its *p*-nitrophenyl derivative **46** in high yields (Scheme 4). However, basic methanolysis of pivaloate **30** was not fruitful under similar conditions to provide only a complex mixture.

Hydrogenolysis of **38** was performed with 20% $Pd(OH)_2$ in MeOH. No reaction was observed at 1 atm H_2 and reaction at 5 atm of H_2 gave many spots on the silica gel TLC, probably due to partial deprotection. Extended reaction time did not promote further reaction. The sluggishness of this reaction was most likely caused by poisoning of catalyst with the sulfide. Deprotection of the MPM masked disaccharides was attempted next. Basic removal of the benzoyl groups of **41** was followed by oxidative cleavage of MPM ethers with excess 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in aqueous CH_2Cl_2 to give fully deprotected disaccharide **47** in 88% yield in two steps without affecting the sulfide function. Disaccharide **43** was subjected to the treatment similar to that used for **41** to provide deprotected disaccharide **48** in 77% yield. The negative-FABMS spectra of **47** and **48** clearly showed pseudo-molecular ion signals both at $m/z = 371$ ($[M-H]^-$). It can be concluded that DDQ treatment did not affect the oxidation-susceptible sulfide function in thiosaccharides. On the other hand, the following sequence for deprotection involved a difficulty in purification. When DDQ treatment of **38** was performed prior to basic hydrolysis, the polarity of the product was the same as that of a considerable amount of hydroquinone (DDQH), the coproduct de-



Scheme 4.



Scheme 5. Synthesis of thioisomaltotetraoside **2**. Reagents and conditions: (a) TrCl, DMAP, Py, rt, 80% (for **50a**), 81% (for **51b**); (b) NaH, MPMBr, DMF, rt, 56% (for **51a**), 62% (for **51b**); (c) (from **51a**) *p*-TsOH, EtOH, rt, 50%, (from **51b**) PPTS, EtOH, PrOH, rt, then EtOH, 92% (see text); (d) CCl_3CN, DBU, CH_2Cl_2, rt, 82%; (e) TESOTf, CH_2Cl_2, −78 °C, 67% (for **54**), 47% (for **56**), 67% (67% for **58**); (f) *p*-TsOH, MeOH, rt, 71% (for **55**), 67% (for **57**), (g) NaOMe, MeOH, rt; (h) DDQ, aq CH_2Cl_2, rt, 65% (2 steps).

rived from DDQ. Furthermore, DDQ treatment gave only a complex mixture in which the 5-thioglucopyranose unit must be of *S*,*O*-acetal form.

2.2. Synthesis of methyl thioisomaltotetraoside

We first applied these methodologies to the synthesis of thioisomaltotetraoside **2**. We planned to place a regular methyl α-glucopyranoside unit at the reducing end, because *endo*-glycosidases were anticipated not to cleave the glycosidic bond at the reducing terminus by considering its nature, and due to the synthetic feasibility. Furthermore, this α-methyl glucoside moiety meets the requirement at the DDQ oxidation stage of MPM ethers (see Section 2.1.4). The use of the sole α-isomer would simplify analysis of segments cleaved by glycosidases (Scheme 5).

We prepared trichloroacetimidate **53**, a 5-thioglucose donor with properly protected hydroxyl groups, which would serve the further elongation of the thiosaccharide chain at the C6 position. Selective tritylation of the C6 primary alcohol of **6a** (→**50a**)[34] was followed by the protection of all the remaining free hydroxyl groups as MPM ethers with MPMBr/NaH (→**51a**).[35,36] The excess MPMBr had to be completely destroyed by MeOH/triethylamine prior to silica gel column chromatography. Otherwise, MPMBr-derived hydrogen bromide can decompose the product during chromatographic purification. Since acidic removal of the THP group was accompanied by considerable cleavage of the Tr ether, hemithioacetal **52** was obtained with a maximum yield of 30%. Preparation of **53** through EE **51b** was next examined by using **6b** as a starting material, to which the sequence similar to that employed for the conversion from **6a**, was successfully applied. Ethoxyethyl ether **51b** was readily prepared from **6b**. It was found that the EE group of **51b** was removed selectively in 92% yield by (i) treatment with PPTS in a mixture of ethanol and 1-propanol (3:1) at room temperature, (ii) concentration directly in vacuo, and (iii) re-dilution with ethanol and stirring at room temperature. Treatment of **51b** with PPTS in either methanol or ethanol alone was not satisfactory because of poor solubility of **51b** in these solvents. Although 1-propanol dissolved **51b** well, the reaction was very slow at room temperature and elevation of temperature declined the selectivity. The hydroxyl group of **52** was smoothly converted into

trichloroacetimidate **53** in 82% yield under usual conditions.[22] Partial decomposition of imidate **53** took place during silica gel column chromatography. Based on its ^{1}H NMR spectrum, imidate **53** was obtained as a single α-isomer.

As expected, upon treatment of **53** with a catalytic amount of TESOTf in CH_2Cl_2, glycosylation with acceptor **16a** proceeded smoothly to give disaccharide **54** as an anomeric mixture (**α54/β54**, 67% and 7% yields, respectively). These isomers were separated by preparative silica gel TLC. The stereochemistry of the major isomer was confirmed as α-**54** by observing a small coupling constant for the C′1-H (2.9 Hz) in the ^{1}H NMR spectrum. On the other hand, the coupling constant for the minor isomer was 8.3 Hz, suggesting β-glycoside **β-54**. In order to prepare a stage for the next glycosylation, the Tr group of α-**54** was selectively removed by acidic treatment to liberate the free hydroxyl group (**α-54** → **55**, 71% yield). Glycosylation of **55** with donor **53** proceeded with high α-stereoselectivity to give trisaccharide **56** in 47% yield. The corresponding β-isomer of **56** was not detected in this reaction. Trisaccharide **56**, thus prepared, was successfully converted into tetrasaccharide **58** by repeating the sequence described above, that is, cleavage of the Tr ether of **56** followed by glycosylation of **57** with imidate **15** (**56** → **57**, 71% yield, **57** → **58**, 67% yield, respectively). The third glycosylation proceeded with high stereoselectivity only to provide α-glycoside **58** and the corresponding β-isomer was not detected.

Based on our established protocol, deprotection of **58** by a two-step sequence of basic methanolysis and DDQ oxidation, gave the desired isomaltotetraoside **2** in 65% yield in two steps. The ^{1}H NMR spectrum of **2** in D_2O displayed four anomeric signals with small coupling constant (2.9–3.9 Hz), which assures that the glycosylation reactions successfully proceeded with α-stereoselectivity in each step. The ^{13}C NMR spectrum displayed 25 resonances, which further supports the structural assignment. The negative FABMS spectrum of **2** evidently displayed a pseudomolecular ion (m/z = 727, $[M-H]^-$) as well as several cluster ions. These were assigned as adduct ions with chloride (m/z = 763: $[M+^{35}Cl]^-$ and 765: $[M+^{37}Cl]^-$), sodium (m/z = 749: $[M+Na-2H]^-$), and sodium chloride (m/z = 785: $[M+Na^{35}Cl-H]^-$ and 787: $[M+Na^{37}Cl-H]^-$) as shown in Figure 1. However, signals due to sulfoxides ($m/z = 727 + 16 \times n$) and/or sulfones ($m/z = 727 + 32 \times n$) were not detected. These results clearly proved that oxidation of the sulfides in the 5-thiopyranose rings did not occur throughout the synthesis.

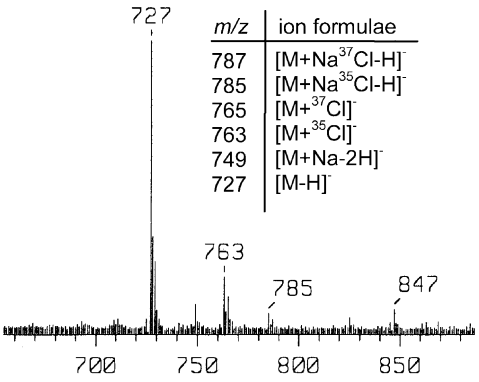
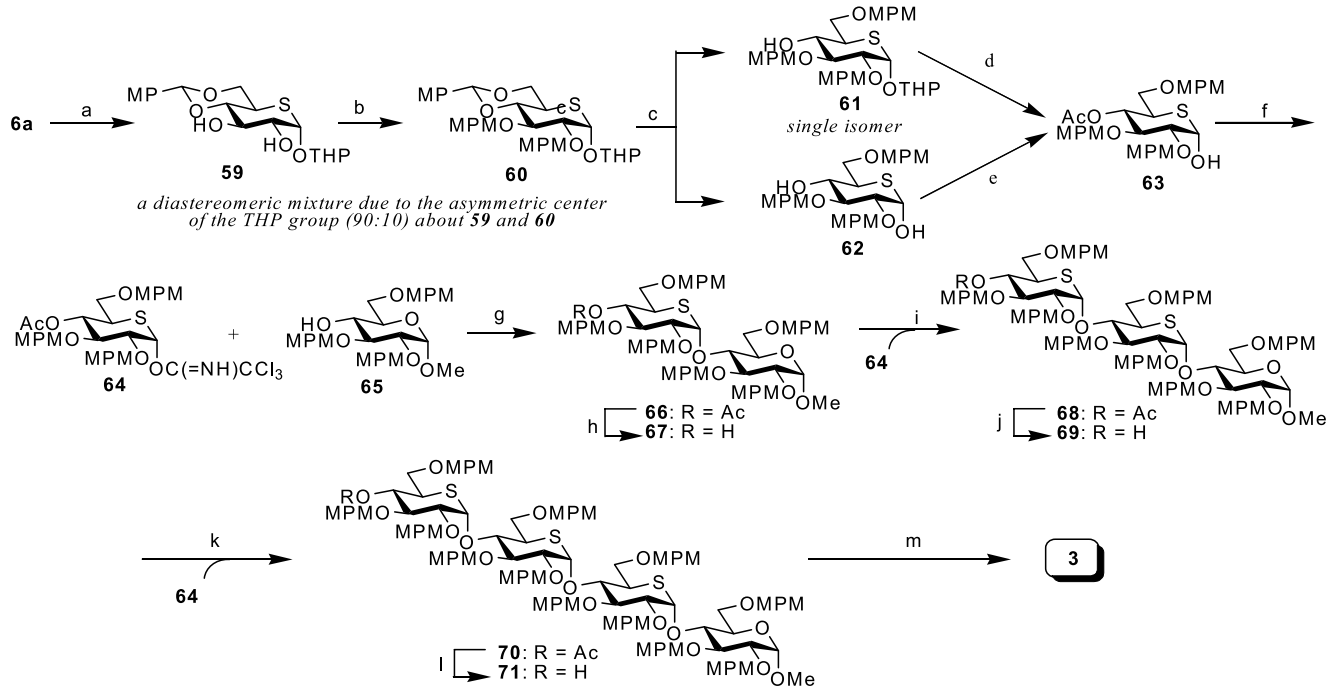


Figure 1. Region of the FABMS spectrum of **2**.

2.3. Synthesis of methyl thiomaltotetraoside

1,4-α-Glycosyl linkage appears in the most common polysaccharides in nature such as starch. With the successful completion in preparation of methyl isomaltotetraoside **2**, we next turned to investigation of the synthesis of methyl maltotetraoside **3**. Toward this end, the C4 hydroxyl group of a 5-thioglucopyranose donor has to be distinguished from all others. Reductive cleavage of 4,6-benzylidene acetal of saccharide is known to proceed regioselectively by treatment with a combination of reducing agent and acid.[15,16] By taking account of deprotection at the final stage of the synthesis, MPM ether has an advantage over benzyl ether (see Section 2.1.4); therefore, we also decided to use *O*-*p*-methoxybenzylidene acetal for protection of the C4 and C6 positions.[14–16] Treatment of **6a** with anisaldehyde dimethyl acetal in the presence of camphorsulfonic acid in DMF completed the selective acetal formation at the C4 and C6 positions to give *p*-methoxybenzylidene acetal **59** in 60% yield. The C2- and C3-OH functions were then protected as MPM ethers (→**60**). It was found that reductive cleavage of the acetal moiety in **60** proceeded regioselectively to give C4-OH **61** in 41% yield by a combination of trimethylamine borane complex, aluminum chloride[37] and acid washed molecular sieves 4A.[38] Due to the use of strong Lewis acid in this reaction, undesired cleavage of the acid-labile THP ether was not completely avoided to provide 1,4-diol **62** (28% yield). Interestingly, **61** was obtained as a single isomer, although the starting material **60** was a diastereomeric mixture with regard to the asymmetric center of the THP group. Presumably, the THP ether linkage of either isomer was selectively cleaved under the reaction conditions. Both products **61** and **62**, were independently converted into the C1-OH **63**. Acetylation of the C4-OH of **61** (97% yield) was followed by acidic cleavage of the THP ether at the anomeric position to give **63** in 71% yield. On the other hand, diacetate derived from **62** was treated with hydrazine acetate to undergo selective cleavage of the C1 acetate to provide **63** in 81% yield in two steps. The anomeric position was converted into trichloroacetimidate to provide **64** as a single α-isomer in quantitative yield (Scheme 6).

As expected, the coupling reaction of **64** with acceptor **65** proceeded to give disaccharide **66** with α-stereoselectivity (α:β = 90:10) in 79% yield by treatment with a catalytic amount of TESOTf at −78 °C. For analytical purposes pure sample **66** was obtained by HPLC (the major product: α-isomer: t_R = 92 min, the minor product: β-isomer: t_R = 85 min, μBondasphere 150 SIL-100, 7.8 (ϕ) × 300 mm, EtOAc/hexane 20:80, 4.0 mL/min flow). In the preparative scale, the minor isomer of **66**



Scheme 6. Synthesis of thiomaltotetraoside **3**. Reagents and conditions: (a) anisaldehyde dimethyl acetal, CSA, DMF, 0 °C, 60%; (b) NaH, MPMBr, DMF, rt, 100%; (c) BH_3NMe_3, $AlCl_3$, MSAW300, THF, −15 °C, 41% (**61**), 28% (**62**); (d) (i) Ac_2O, Py, rt, 97%, (ii) *p*-TsOH, MeOH-THF, rt, 71%; (e) (i) Ac_2O, Py, rt, 100%, (ii) hydrazine acetate, DMF, rt, 81%; (f) CCl_3CN, DBU, CH_2Cl_2, 0 °C, 100%; (g) TESOTf, MS4A, CH_2Cl_2, −78 °C, 79%; (h) NaOMe, MeOH-THF, 50 °C, 98%; (i) TESOTf, MS4A, CH_2Cl_2, −78 °C, 76%; (j) NaOMe, MeOH-THF, 50 °C, 75%; (k) TESOTf, MS4A, CH_2Cl_2, −78 °C, 68%; (l) NaOMe, MeOH-THF, 50 °C, 76%; (m) DDQ, aq CH_2Cl_2, 88%.

was separated at the later synthetic stage. Basic hydrolysis of the acetyl group of **66** gave acceptor **67** in 89% yield. Glycosylation of a diastereomeric mixture **67** with donor **64** under the same conditions described above gave a mixture of four possible isomers of trisaccharides containing **68** as a major isomer in 79% yield. HPLC purification allowed us to remove only two minor isomers. Fortunately, removal of the last minor isomer was made after conversion into alcohol **69**. The stereoselectivity of the second glycosylation step was estimated to be α:β = 84:16 by performing the reaction using diastereomerically pure **67**, prepared from the HPLC purified sample **66**. The third glycosylation giving a tetramer was performed. As expected, the reaction proceeded with α-stereoselectivity (α:β = 90:10) to give **70** in 68% yield. Removal of the minor isomer was made by preparative silica gel TLC after cleavage of the acetate (→**71**). Although glycosylation of **15** gave the corresponding tetrasaccharide with high α-stereoselectivity, all attempts at separation of these diastereomers resulted in failure.

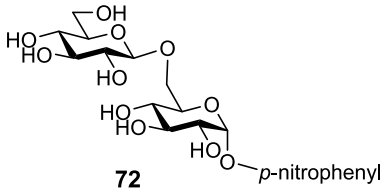
Finally, all MPM ethers of **71** were cleaved according to the protocol developed in our model studies. Treating **71** with excess DDQ in aqueous CH_2Cl_2 gave a single spot on the silica gel TLC. After washing the mixture with EtOAc, the resulting aqueous solution was passed through a SepPak ODS® to give pure maltoside analogue **3** in 88% yield, whose structure was confirmed in the same manner as described for isomaltotetraoside analogue **2**. All the data obtained supported the structural assignment.

3. Conclusion

We demonstrated that MPM-protected 5-thioglucopyranosyl trichloroacetimidates are generally applicable for α-stereoselective glycosylations promoted by TESOTf. Cleavage of MPM ethers of saccharides composed of 5-thioglucopyranose units proceeded smoothly to provide fully deprotected sulfur-substituted saccharide analogues by using DDQ without any loss of the sulfide functions. Based on the methodologies, we achieved the syntheses of sulfur-substituted analogues isomaltotetraoside **2** and maltotetraoside **3**. Benzoyl-protected 5-thioglucopyranosyl trichloroacetimidate underwent stereoselective β-glycosylation with C6-OH glucopyranosyl acceptors upon activation by BF_3OEt_2. We also achieved synthesis of sulfur-substituted gentiobiosides **1** and **46**.

However, we could not detect analogues **1**–**3** on a small scale by UV-detection on HPLC due to the absence of chromophores, which did not allow us to examine resistance against amylase using them. The *p*-nitrophenyl gentiobioside **46** was only applicable for the analysis determining that it was not hydrolyzed by β-glycosidases from almond or scallop shell, although *p*-nitrophenyl glycoside of regular gentiobioside **72** was hydrolyzed smoothly under the same conditions. In order to investigate enzymatic properties, chromophores must be introduced into these analogues. We are now intending to introduce a *p*-nitrophenyl group to the reducing terminus of **1**–**3**. Although we have succeeded in developing the basic methodology for the synthesis

of oligosaccharides composed of 5-thiopyranoses, some modifications may be required for these schemes because *p*-nitrophenyl glycoside is much less stable than methyl glycoside, especially under acidic conditions. These syntheses are in progress in our laboratories.



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4. Experimental

4.1. General methods

Melting points were determined with a Yanako MP-J3 micro melting point apparatus and were uncorrected. Optical rotations were measured on a HORIBA SEPA300 high-sensitivity polarimeter. For compounds, consisting of a mixture of diastereomers, the optical rotations were not measured. ^{1}H NMR spectra were measured on a JEOL ALPHA 400 spectrometer (400 MHz). The chemical shifts are expressed in ppm downfield from the signal of tetramethylsilane used as an internal standard in the case of employing $CDCl_3$. When other solvents were employed, the residual proton signals in deuteriosolvents C_6HD_5 (7.15 ppm), CHD_2OD (3.30 ppm), or HDO (4.63 ppm) were used as the internal standards. Splitting patterns are designated as s (*singlet*), d (*doublet*), t (*triplet*), q (*quartet*), m (*multiplet*), and br (*broad*). ^{13}C NMR spectra were recorded on a JEOL ALPHA 400 spectrometer (100 MHz). The isotopes ^{13}C in the solvents were used as the internal standard ($^{13}CDCl_3$ 77.0 ppm, $^{13}C_6D_6$ 128.0 ppm, or $^{13}CD_3OD$ 49.5 ppm). For ^{13}C NMR spectra measured in D_2O, default offset was employed and correction was not performed. Assignments of the signals are in accordance with the numbering based on IUPAC nomenclature. For carbohydrate derivatives, numbering is based on carbohydrate nomenclature. IR spectra were obtained with HORIBA FT-720 Fourier transform infrared spectrometer on a KBr cell. Measurements of electron ionization, field desorption, fast atom bombardment, or electrospray ionization mass spectra (EI-MS, FD-MS, FAB-MS, or ESI-MS, respectively) were performed on a JEOL JMS AX500 spectrometer or a JEOL JMS AX102A spectrometer at Hokkaido University. When MS spectra were measured by negative mode, 'negative mode' is indicated. Unstable compounds such as glycosyl imidates could not be subjected to MS analysis. Analytical and preparative thin-layer chromatographies were carried out using pre-coated silica gel plates, Merck silica gel 60 F_{254}. Silica gel used for column chromatography was Merck silica gel 60 or Wako gel C200. All reactions were carried out under N_2 or Ar atmosphere using dried solvents excepted for aqueous conditions or reduction with H_2. Dichloromethane and tetrahydrofuran were freshly distilled from calcium hydride and benzophenone-ketyl, respectively. Molecular sieves were finely powdered and activated (200 °C in vacuo) before use. Conversion of C1-OH 5-thioglucopyranose into the corresponding trichloro-acetimidate was performed as follows (*general procedure A*), which is similar to Izumi's report;[8] a solution of C1-OH 5-thioglucopyranose in CH_2Cl_2 was stirred with CCl_3CN in the presence of a catalytic amount of DBU at 0 °C for 1 h. The mixture was diluted with benzene and the volatiles were removed in vacuo. Purification of the residue by silica gel chromatography gave the corresponding trichloroacetimidate. Glycosylation reactions were performed as follows (*general procedure B*); a mixture of donor and acceptor was stirred with freshly activated powdered molecular sieves in CH_2Cl_2 at room temperature for 1 h under Ar atmosphere. A catalytic amount of promoter (0.05 equiv) was then added into the suspension at −78 °C. After stirring for an additional 2 hr at the same temperature, the reaction was allowed to warm to room temperature over an additional 1 h. Pyridine was added at −78 °C and the resultant mixture was passed through silica gel pad, and then concentrated in vacuo. Purification by silica gel column chromatography gave glycosides.

4.2. Tetrahydropyranyl 2,3,4,6-tetra-*O*-acetyl-5-deoxy-5-thio-α-D-glucopyranoside (5a)

A solution of 2,3,4,6-*O*-acetyl-5-deoxy-5-thioglucopyranose **4** (8.03 g, 22.0 mmol) in CH_2Cl_2 (250 mL) was stirred with 2,3-dihydropyran (2.4 mL, 26.4 mmol) and *p*-TsOH (10.0 mg, 52.6 μmol) at 0 °C. After stirring for 1.5 h, the mixture was neutralized with Et_3N (30.0 μL), and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/hexane 35:65) afforded **5a** (9.39 g, 20.9 mmol, 95%) as a syrup. The ^{1}H NMR spectrum of this sample indicated the sample consists of a mixture of diastereomers due to the asymmetric center of the THP group (50:50). IR (film) 2950, 1750, 1375, 1225, 1120, 1070, 1020, 965 cm^{-1}. ^{1}H NMR ($CDCl_3$, Signals assignable are only described.) δ 1.25–1.90 (6H, C3′H_2, C4′H_2, C5′H_2), 2.020, 2.027, 2.034, 2.038, 2.045, 2.050, 2.065, 2.071 (each 3H × 0.5, s, each CH_3CO), 3.44 (1H × 0.5, ddd, J = 3.4, 4.4, 10.7 Hz, C5H), 3.51–3.62 (1H, m, C6HH), 3.67 (1H × 0.5, ddd, J = 3.4, 4.4, 11.2 Hz, C5H), 3.96 (1H, m, C6HH), 4.03 (1H × 0.5, dd, J = 3.4, 12.2 Hz, C6H), 4.09 (1H × 0.5, dd, J = 3.4, 12.2 Hz, C6H), 4.39 (1H × 0.5, dd, J = 4.4, 12.2 Hz, C6H), 4.41 (1H × 0.5, dd, J = 4.4, 12.2 Hz, C6H), 5.05 (1H × 0.5, d, J = 2.9 Hz, C1H), 5.11 (1H × 0.5, d, J = 2.9 Hz, C1H), 5.17 (1H × 0.5, dd, J = 2.9, 10.2 Hz, C2H), 5.26 (1H × 0.5, dd, J = 2.9, 10.2 Hz, C2H), 5.31 (1H × 0.5, dd, J = 9.2, 11.2 Hz, C4H), 5.33 (1H × 0.5, dd, J = 9.2, 10.7 Hz, C4H), 5.51 (1H × 0.5, dd, J = 9.2, 10.2 Hz, C3H), 5.55 (1H × 0.5, dd, J = 9.2, 10.2 Hz, C3H). EI-MS (%, rel int) m/z 388 (0.58, [M−CH_3COOH]$^+$), 347 (1.5, [M−THPO]$^+$), 328 (2.4, [M−(2 × CH_3COOH)]$^+$), 227 (4.3, [M−(2 × CH_3COOH)-THPO]$^+$), 184 (14, [M−(2 × CH_3COOH)-THPO-CH_3CO]$^+$), 85 (100, THP$^+$). FD-MS (%, rel int) 448 (11, M$^+$), 85 (100,

$C_5H_9O^+$). EI-HRMS Found m/z = 388.1178. Calcd for $C_{17}H_{24}O_8S$: $[M-CH_3COOH]^+$, 388.1192.

4.3. 1-Ethoxyethyl 2,3,4,6-tetra-*O*-acetyl-5-deoxy-5-thio-α-D-glucopyranoside (5b)

A solution of **4** (200 mg, 549 μmol) in CH_2Cl_2 (5.0 mL) was stirred with ethyl vinyl ether (200 μL, 659 μmol) in the presence of PPTS (10.4 mg, 54.9 μmol) at room temperature. After stirring for 10 h, the mixture was neutralized with Et_3N, and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (EtOAc/hexane 35:65) afforded **5b** (229 mg, 525 μmol, 96%) as a colorless syrup. The ^1H NMR spectra indicated that the sample consists of a mixture of diastereomers due to the asymmetric center in the EE group (50:50). IR (film) 2985, 1750, 1380, 1225, 1140, 1040, 960 cm^{-1}. ^1H NMR (C_6D_6) δ: 0.99, 1.05 (each 3H × 0.5, t, J = 7.6 Hz, CH_3CH$_2$O(CH$_3$)CH), 1.11, 1.17 (each 3H × 0.5, d, J = 5, 4 Hz, CH$_3$CH$_2$O(CH_3)CH), 1.61, 1.65, 1.689, 1.691, 1.695, 1.679, 1.679, 1.703 (each 3H × 0.5, s, CH_3CO), 3.17–3.35 (2H × 0.5 + 1H × 0.5, CH$_3$CH_2O(CH$_3$)CH), 3.66 (1H × 0.5, CH$_3$CH_2O(CH$_3$)CH), 3.42, 3.56 (each 1H × 0.5, m, C5H), 3.92–3.98, 4.38–4.44 (each 2H × 0.5, C6H_2), 4.49, 4.79 (each 1H × 0.5, s, CH$_3$CH$_2$O(CH$_3$)CH), 4.68, 5.09 (each 1H × 0.5, d, C1H), 5.29, 5.36 (each 1H × 0.5, dd, C2H), 5.54–5.60 (1H, C3H), 5.82–5.90 (1H × 0.5, C4H). EI-MS (%, rel int) 376 (3, $[M-CH_3COOH]^+$), 347 (9, $[M-EEO]^+$), 73 (100, $[CH_3CH_2O{=}CHCH_3]^+$). FD-MS (%, rel int) 436 (16, M^+). EI-HRMS Found m/z = 376.1195. Calcd for $C_{16}H_{24}O_8S$: $[M-CH_3COOH]^+$, 376.1192.

4.4. Tetrahydropyranyl 5-deoxy-5-thio-α-D-glucopyranoside (6a)

A solution of **5a** (9.38 g, 20.9 mmol) in MeOH (300 mL) was stirred with NaOMe (5.65 g, 105 mmol) at room temperature. After stirring for 3.5 h, DOWEX 50W (H^+ form) was added until the solution was neutralized. The mixture was filtered and the filtrate was concentrated in vacuo. Purification of the residue by silica gel column chromatography (acetone–CH_2Cl_2 70:30) afforded **6a** (4.8 g, 17.1 mmol, 82%) as a syrup. The ^1H NMR spectra indicated that the sample consists of a mixture of diastereomers due to the asymmetric center in the THP group (50:50). IR (film) 3380, 2940, 1120, 1070, 1025, 975, 755 cm^{-1}. ^1H NMR (D_2O, Signals assignable are only described.) δ 1.20–1.80 (6H, C3′H_2, C4′H_2, C5′H_2), 2.93 (1H × 0.5, ddd, J = 3.4, 5.4, 9.8 Hz, C5H), 3.11 (1H × 0.5, ddd, J = 3.4, 5.4, 9.8 Hz, C5H), 3.57 (1H × 0.5, t, J = 8.8 Hz, C3H), 3.60 (1H × 0.5, t, J = 9.3 Hz, C3H), 3.68 (1H × 0.5, dd, J = 2.9, 9.3 Hz, C2H), 3.82 (1H × 0.5, dd, J = 5.4, 11.8 Hz, C6H), 4.77 (1H × 0.5, d, J = 2.9 Hz, C1H), 4.87 (1H × 0.5, d, J = 3.4 Hz, C1H), 4.83, 5.07 (each 1H × 0.5, br, C′1′H). EI-MS (%, rel int) 280 (0.76, M^+), 262 (1.0, $[M-H_2O]^+$), 244 (trace, $[M-(2\times H_2O)]^+$), 196 (8.1, $[M-DHP]^+$), 178 (6.4, $[M-THPOH]^+$), 85 (100, THP^+). FD-MS (%, rel int) 280 (79, M^+), 85 (100, THP^+). EI-HRMS Found m/z = 280.0957. Calcd for $C_{11}H_{20}O_6S$: M^+, 280.0981.

4.5. Ethoxyethyl 5-deoxy-5-thio-α-D-glucopyranoside (6b)

A solution of **5b** (229 mg, 525 μmol) in MeOH (7.0 mL) was stirred with NaOMe (142 mg, 2.63 mmol) at room temperature for 20 min. After the mixture was concentrated in vacuo, the residue was dissolved in H_2O and was passed through Amberlite IRC-50 column (H^+ form). The eluent was concentrated in vacuo. Purification of the residue by silica gel column chromatography (acetone/CH_2Cl_2 60:40) afforded **6b** (122 mg, 452 μmol, 86%) as a colorless syrup. The ^1H NMR spectra indicated that the sample consists of a mixture of diastereomers due to the asymmetric center in the EE group (50:50). IR (film) 3400, 2980, 2930, 1340, 1070, 1025, 950 cm^{-1}. ^1H NMR (D_2O) δ 1.07 (3H × 0.5, t, J = 7.3 Hz, CH_3CH$_2$O), 1.08 (3H × 0.5, t, J = 6.8 Hz, CH_3CH$_2$O), 2.94 (1H × 0.5, dt, J = 4.4, 9.8 Hz, C5H), 3.02 (1H × 0.5, dt, J = 4.4, 9.3 Hz, C5H), 4.67 (1H × 0.5, d, J = 3.4 Hz, C1H) 5.07 (1H × 0.5, q, J = 5.3 Hz, EtO(Me)CH). EI-MS (%, rel int) 268 (trace, M^+), 253 (trace, $[M-CH_3]^+$), 250 (0.3, $[M-H_2O]^+$), 222 (6, $[M-EtOH]^+$), 73 (100, $[CH_3CH_2O=CHCH_3]^+$). FD-MS (%, rel int) 268 (100, M^+). EI-HRMS Found m/z = 250.0846. Calcd for $C_{10}H_{18}O_5S$: $[M-H_2O]^+$, 250.0875.

4.6. Tetrahydropyranyl 2,3,4,6-tetra-*O*-benzoyl-5-deoxy-5-thio-α-D-glucopyranoside (7)

A solution of **6a** (121 mg, 430 μmol) in pyridine (4.0 mL) was stirred with benzoyl chloride (300 μL, 2.58 mmol) at room temperature for 1 h. After MeOH (500 μL) was added to decompose the excess reagent, the volatiles were removed in vacuo. The residue was dissolved in EtOAc and the resulting solution was washed with H_2O. The aqueous layer was extracted with EtOAc (× 3). The extracts were combined, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by silica gel chromatography (EtOAc/hexane 10:90) gave **7** (281 mg, 404 μmol, 94%) as a syrup. This sample consisted of the two diastereomers due to the asymmetric center in the THP group (50:50). IR (film) 2930, 2855, 1730, 1450, 1270, 1105, 1070, 1025, 710, 680 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.20–2.05 (6H, C3′H_2, C4′H_2, C5′H_2), 3.26, 3.59 (each 1H × 0.5 br d, J = 11.7 Hz, C6′HH), 3.59, 4.05 (each 1H × 0.5 br d, J = 11.7 Hz, C6′HH), 3.85, 4.09 (each 1H × 0.5, ddd, J = 3.9, 4.4, 9.8 Hz, C5H), 4.563, 4.565 (each 1H × 0.5, dd, J = 4.4, 12.2 Hz, C6HH), 4.61, 4.67 (each 1H × 0.5, dd, J = 3.9, 12.2 Hz, C6HH), 4.85, 5.23 (each 1H × 0.5, br, C2′H), 5.30, 5.41 (each 1H × 0.5, d, J = 3.4 Hz, C1H), 5.62, 5.73 (each 1H × 0.5, dd, J = 3.4, 9.8, C2H), 5.95, 5.97 (each 1H × 0.5, t, J = 9.8 Hz, C4H), 6.20, 6.24 (each 1H × 0.5, t, J = 9.8 Hz, C3H), 7.15–7.15 (20H, *aromatic protons*). FD-MS (%, rel int) 696 (2.9, $[M+H]^+$), 695 (3.4, M^+), 611 (29, $[M-THP]^+$), 85 (100, THP^+). FD-HRMS Found m/z = 696.2047. Calcd for $C_{39}H_{36}O_{10}S$: M^+, 696.2029.

4.7. Tetrahydropyranyl 2,3,4,6-tetra-*O*-pivaloyl-5-deoxy-5-thio-α-D-glucopyranoside (8)

A solution of **6a** (127 mg, 453 μmol) and DMAP (250 mg, 2.06 mmol) in pyridine (46.0 mL) was stirred

with PivCl (558 μL, 4.53 mmol) at 75 °C for 30 h. After MeOH (500 μL) was added to decompose the excess reagent, the volatiles were removed in vacuo. The residue was dissolved in EtOAc and washed with H_2O. The aqueous layer was extracted with EtOAc (×3). The extracts were combined, washed with brine dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by silica gel chromatography (EtOAc/hexane 5:95) gave **8** (228 mg, 371 μmol, 82%) as a syrup. The ^{1}H NMR spectrum indicated that this sample consisted of the two diastereomers due to the asymmetric center in the THP group (50:50). IR (film) 2970, 1740, 1480, 1395, 1365, 1280 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.10, 1.11, 1.12, 1.146, 1.146, 1.152, 1.180, 1.85 (each 9H × 0.5, s, $(CH_3)_3CCO$), 1.45–1.88 (6H, C3′ it H_2, C4′H_2, C5′H_2), 3.36, 3.64 (each 1H × 0.5, ddd, J = 2.9, 5.4, 10.7 Hz, C5*H*), 3.46, 3.55 (each 1H × 0.5, br dt, J = 4.4, 11.7 Hz, C6′*H*H), 3.74, 3.95 (each 1H × 0.5, ddd, J = 3.4, 8,3, 11.7 Hz, C6′*H*H), 4.09, 4.13 (each 1H × 0.5, J = 5.4, 12.2 Hz, C6*H*H), 4.18, 4.19 (each 1H × 0.5, dd, J = 2.9, 12.2 Hz, C6*H*H), 4.77, 5.00 (each 1H × 0.5, br, C2′*H*), 4.95, 5.52 (each 1H × 0.5, d, J = 2.9 Hz, C1*H*), 5.11, 5.21 (each 1H × 0.5, dd, J = 2.9, 9.8 Hz, C2*H*), 5.346, 5.351 (each 1H × 0.5, dd, J = 9.8, 10.7 Hz, C4*H*), 5.55, 5.58 (each 1H × 0.5, t, J = 9.8 Hz, C3*H*). FD-MS (%, rel int) 617 (6.8, $[M+H]^+$) 616 (25, M^+), 532 (15, $[M+H-Piv]^+$), 531 (47, $[M-Piv]^+$), 85 (100, Piv^+), 57 (52, $(CH_3)_3C^+$). FD-HRMS Found m/z = 616.3260. Calcd for $C_{31}H_{52}O_{10}S$: M^+, 616.3281.

4.8. Tetrahydropyranyl 2,3,4,6-tetra-*O*-benzyl-5-deoxy-5-thio-α-D-glucopyranoside (9)

To a suspension of **6a** (62.0 mg, 221 μmol) and NaH (freshly washed with hexane and dried in vacuo, 40.0 mg, 1.67 mmol) in DMF (1.0 mL), Bn Br (300 μL, 2.52 mmol) was added at room temperature. After stirring for 1 h, the mixture was poured into water and extracted with EtOAc (×3). The extracts were combined, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/hexane 20:80) afforded **9** (124 mg, 1.47 mmol, 88%) as an amorphous solid. The ^{1}H NMR spectrum indicated that this sample consists of the two diastereomers due to the asymmetric center in the THP group (50:50). IR (film) 2920, 2850, 1455, 1105, 1070, 970, 735, 700 cm^{-1}. ^{1}H NMR ($CDCl_3$, Some signals could not be assigned due to signals overlapping.) δ 1.55–1.95 (6H, C3′H_2, C4′H_2, C5′H_2), 3.22 (1H × 0.5, ddd, J = 2.5, 3.9, 10.7 Hz, C5*H*), 3.57 (1H × 0.5, C6′*H*H), 3.61 (1H × 0.5, C6′*H*H), 3.85–4.15 (5H+1H × 0.5, C2*H*, C3*H*, C4*H*, C6H_2 (for both isomers), C5*H* (for one isomer), 4.54–5.19 (8H, ArCH_2O × 4), 7.15–7.40 (20H, *aromatic protons*). EI-MS (%, rel int) 539 (0.5, $[M-THP]^+$), 538 (0.4, $[M-THPOH]^+$), 91 (100, Bn^+), 85 (59, THP^+), EI-HRMS Found m/z = 538.2184. Calcd for $C_{34}H_{34}O_4S$: $[M-THPOH]^+$, 538.2178.

4.9. Tetrahydropyranyl 2,3,4,6-[tetrakis-*O*-(4-methoxyphenyl)methyl]-5-deoxy-5-thio-α-D-glucopyranoside (10)

Tetraol **6a** (261 mg, 932 μmol) was treated with MPMBr (ca. 50% solution in toluene, 2.0 mL, ca. 5 mmol) in a manner similar to that described for **9**. After stirring for 1 hr at room temperature, the excess reagents were decomposed by the addition of MeOH (ca. 1.0 mL) and Et_3N (ca. 1.0 mL). After stirring for additional 30 min, the mixture was poured into water and the resulted solution was extracted with EtOAc (×3). The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was dissolved in pyridine (3.0 mL), and the solution was stirred with Ac_2O (1.0 mL) at room temperature for 1 hr in order to convert the generated MPMOH into the corresponding acetate. After concentration in vacuo, purification of the residue by silica gel column chromatography (EtOAc/hexane = 25:75) afforded **10** (676 mg, 889 μmol, 95%) as a colorless syrup. The ^{1}H NMR spectrum indicated that this sample consists of the two diastereomers due to the asymmetric center in the THP group (50:50). IR (film) 2920, 2850, 1610, 1511, 1245, 1095, 1070, 135, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$, Some signals could not be assigned due to signals overlapping) δ: 1.40–1.87 (6H, C3′H_2, C4′H_2, C5′H_2), 3.18 (1H × 0.5, ddd, J = 2.5, 3.9, 10.3 Hz, C5*H*), 3.41 (1H × 0.5, ddd, J = 2.4, 3.4, 10.2 Hz, C5*H*), 3.48–3.58 (4H × 0.5, C6*H*H, C6′*H*H), 3.749, 3.754, 3.771, 3.774, 3.781, 3.781, 3.784, 3.789 (each 3H × 0.5, s, CH_3O), 3.73–3.97 (8H × 0.5, C2*H*, C3*H*, C4*H*, C6*H*H), 4.01, 4.05 (each, 1H × 0.5, br d, J = 9.8 Hz, C6′*H*H), 4.40–4.50 (6H × 0.5, ArCH_2O), 4.57–4.92 (10H × 0.5, ArCH_2O), 4.85 (1H × 0.5, d, J = 3.0 Hz, C1*H*), 5.03 (1H × 0.5, d, J = 2.9 Hz, C1*H*), 4.97, 5.07 (each 1H × 0.5, C′1*H*), 6.79–7.34 (16H, *aromatic protons*). FD-MS (%, rel int) 760 (6.0, M^+), 640 (82, $[M+H-MPM]^+$), 639 (100, $[M-MPM]^+$). FD-HRMS Found m/z = 640.2860. Calcd for $C_{39}H_{44}O_6S$: $[M+H-MPM]^+$, 640.2859.

4.10. 2,3,4,6-Tetra-*O*-acetyl-α-D-5-deoxy-5-thioglucopyranosyl trichloroacetimidate (11)

According to *general procedure A*, a solution of **4** (71.9 mg, 197 μmol) in CCl_3CN (200 μL, 1.97 mmol) was stirred with DBU (4.9 μL, 32.9 μmol) at 0 °C for 15 min. The mixture was diluted with benzene and the volatiles were removed in vacuo. Purification of the residue by silica gel chromatography (EtOAc/hexane = 25:75) gave **11** (77.2 mg, 152 μmol, 77%). ^{1}H NMR ($CDCl_3$) δ 2.00, 2.02, 2.06, 2.07 (each 3H, s, CH_3CO), 3.64 (1H, ddd, J = 3.4, 4.9, 11.2 Hz, C5*H*), 4.08 (1H, dd, J = 3.4, 12.2 Hz, C6*H*H), 4.39 (1H, dd, J = 4.9, 12.2 Hz, C6*H*H), 5.31 (1H, dd, J = 2.9, 9.8 Hz, C2*H*), 5.38 (1H, dd, J = 9.8, 11.2 Hz, C4*H*), 5.57 (1H, t, J = 9.8, C3*H*), 6.36 (1H, d, J = 2.9 Hz, C1*H*), 8.78 (1H, s, C(= N*H*)CCl_3). The ^{1}H NMR spectrum of this sample had good accordance with that reported in the literature.[8]

4.11. 2,3,4,6-Tetra-*O*-benzoyl-5-deoxy-5-thio-α-D-glucopyranosyl trichloroacetimidate (12)

According to *general procedure A*, a solution of **7** (596 mg, 854 μmol) in MeOH (10 mL) was stirred with *p*-TsOH (3.0 mg, 15.8 μmol) at 45 °C for 7 h. After neutralization by the addition of Et_3N (10 μL), the mixture was concentrated in vacuo. Purification of the residue by

silica gel column chromatography (EtOAc/benzene 4:96) gave 2,3,4,6-tetra-*O*-benzoyl-5-deoxy-5-thio-α-D-glucopyranose (443 mg, 728 μmol, 85%) as a syrup. $[\alpha]_D^{19}$ +58.0° (*c* 0.36, $CHCl_3$). IR (film) 3450, 1035, 2965, 1730, 1270, 1110, 1070, 705 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.62 (1H, br, O*H*), 4.15 (1H, dt, *J* = 4.9, 10.7 Hz, C5*H*), 4.57, 4.65 (each 1H, dd, *J* = 4.9, 11.7 Hz, C6H_2), 5.49 (1H, br, C1*H*), 5.64 (1H, dd, *J* = 2.4, 9.8 Hz, C2*H*), 5.97 (1H, dd, *J* = 9.8, 10.7 Hz, C3*H*), 6.27 (1H, t, *J* = 10.7 Hz, C4*H*), 7.20-8.15 (20H, *aromatic protons*). FD-MS (%, rel int) *m*/*z* 613 (26, $[M+H]^+$), 612 (20, M^+), 611 (39, $[M-H]^+$), 595 (29, $[M-OH]^+$), 491 (42, $[M-BzO]^+$), 105 (100, $PhCO^+$). FD-HRMS Found *m*/*z* = 612.1412. Calcd for $C_{34}H_{28}O_9S$: M^+, 612.1454. According to *general procedure A*, a solution of the product thus obtained (43.7 mg, 71.4 μmol) in CH_2Cl_2 (3.0 mL) was stirred with DBU (1.0 μL, 6.71 μmol) and CCl_3CN (100 μL, 990 μmol) at 0 °C for 1 h. After concentration in vacuo, purification of the residue by silica gel chromatography (EtOAc/hexane 5:95) gave **12** (36.0 mg, 47.8 μmol, 67%) as a syrup. ^1H NMR ($CDCl_3$) δ 4.07 (1H, ddd, *J* = 3.9, 4.9, 10.3 Hz, C5*H*), 4.55 (1H, dd, *J* = 4.9, 12.2 Hz, C6*H*H), 4.63 (1H, dd, *J* = 3.9, 12.2 Hz, C6*H*H), 5.81 (1H, dd, *J* = 3.0, 10.8 Hz, C2*H*), 6.03 (1H, t, *J* = 10.8 Hz, C4*H*), 6.26 (1H, t, *J* = 10.8 Hz, C3*H*), 6.64 (1H, d, *J* = 3.0 Hz, C1*H*), 7.20–8.04 (*aromatic protons*), 8.65 (1H, s, C(=N*H*)CCl_3). This sample was immediately used for the next glycosylation step.

4.12. 2,3,4,6-Tetra-*O*-pivaloyl-5-deoxy-5-thio-α-D-glucopyranosyl trichloroacetimidate (13)

Treatment of **8** (32.6 mg, 53.7 μmol) with *p*-TsOH (3.0 mg) in MeOH (1.0 mL), followed by reacting with CCl_3CN (16.3 μL, 113 μmol) according to *general procedure A*, gave **13** (21.6 mg, 32.8 μmol, 61% in two steps) as a syrup. ^1H NMR ($CDCl_3$) δ 1.10, 1.11, 1.17, 1.18 (each 9H, s, $(CH_3)_3CCO$), 3.64 (1H, ddd, *J* = 2.9, 5.4, 10.7 Hz, C5*H*), 4.11 (1H, dd, *J* = 5.4, 12.2 Hz, C6*H*H), 4.19 (1H, dd, *J* = 2.9, 12.2 Hz, C6*H*H), 5.32 (1H, dd, *J* = 3.4, 9.8 Hz, C2*H*), 5.44 (1H, dd, *J* = 9.8, 10.7 Hz, C4*H*), 5.61 (1H, t, *J* = 9.8 Hz, C3*H*), 6.30 (1H, d, *J* = 3.4 Hz, C1*H*), 8.68 (1H, s, C(=N*H*)CCl_3). This sample was immediately used for the next glycosylation step.

4.13. 2,3,4,6-Tetra-*O*-benzyl-5-deoxy-5-thio-α-D-glucopyranosyl trichloroacetimidate (14)

Treatment of **9** (115 mg, 180 μmol) with $HClO_4$ (10 mg, 100 μmol) in MeOH (1.0 mL) at room temperature for 3 h gave the corresponding alcohol (90.5 mg, 162 μmol, 90%) as a syrup. $[\alpha]_D^{27}$ +47° (*c* 0.76, $CHCl_3$). IR (film) 3420, 3030, 2915, 2865, 1500, 1450, 1400, 1360, 1140, 1100, 1060, 1025, 735, 700 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.67 (1H, br, O*H*), 3.42 (1H, ddd, *J* = 3.0, 3.9, 9.7 Hz, C5*H*), 3.59 (1H, dd, *J* = 3.0, 9.8 Hz, C6*H*H), 3.78 (1H, dd, *J* = 3.0, 9.7 Hz, C2*H*), 3.81 (1H, t, *J* = 9.7 Hz, C4*H*), 3.88 (1H, t, *J* = 9.7 Hz, C3*H*), 3.91 (1H, dd, *J* = 3.9, 9.8 Hz, C6*H*H), 4.45, 4.48 (each 1H, d, *J* = 12.2 Hz, ArCH_2O), 4.56, 4.90 (each 1H, d, *J* = 10.8 Hz, ArCH_2O), 4.66, 4.71 (each 1H, d, *J* = 11.7 Hz, ArCH_2O), 4.81, 4.86 (each 1H, d, *J* = 10.7 Hz, ArCH_2O), 4.87 (1H, d, *J* = 3.0 Hz, C1*H*), 7.15–7.40 (20H, *aromatic protons*). ^{13}C NMR ($CDCl_3$) 41.5, 68.0, 71.8, 73.2, 73.5, 75.8, 76.5, 82.2, 83.3, 84.7, 128.0, 128.1, 128.23, 128.27, 128.29, 128.39, 128.47, 128.52, 128.63, 128.66, 128.90, 128.96, 129.05, 129.08, 138.42, 138.47, 138.93, 139.44. FD-MS (%, rel int) *m*/*z* 557 (53, $[M+H]^+$), 556 (100, M^+), 539 (9.8, $[M-OH]^+$), 91 (32, Bn^+). FD-HRMS Found *m*/*z* = 556.2285. Calcd for $C_{34}H_{36}O_5S$: M^+, 556.2283. According to *general procedure A*, a solution of the alcohol (4.2 mg, 7.54 μmol) in CCl_3CN (500 μL, 4.95 mmol) with DBU (1.0 μL, 6.70 μmol) gave **14** (4.1 mg, 5.85 μmol, 78%) as a syrup. ^1H NMR ($CDCl_3$) δ 3.39 (1H, ddd, *J* = 2.9, 3.9, 9.2 Hz, C5*H*), 3.57 (1H, dd, *J* = 2.9, 10.3 Hz, C6*H*H), 3.88–4.00 (4H, C6*H*H, C4*H*, C2*H*, C3*H*), 4.49 (2H, s, ArCH_2O), 4.57, 4.90 (each 1H, *J* = 10.2 Hz, ArCH_2O), 4.65, 4.74 (each 1H, *J* = 11.7 Hz, ArCH_2O), 4.80, 4.92 (each 1H, *J* = 10.7 Hz, ArCH_2O), 6.31 (1H, br, C1*H*), 7.15–7.30 (*aromatic protons*), 8.59 (1H, s, C(=N*H*)CCl_3). This sample was immediately used for the next glycosylation.

4.14. 2,3,4,6-[Tetrakis-*O*-(4-methoxyphenyl)methyl]-5-deoxy-5-thio-α-D-glucopyranosyl trichloroacetimidate (15)

Treatment of **10** (600 mg, 789 μmol) in MeOH (50 mL) with concentrated HCl (2.0 μL) gave the corresponding alcohol (430 mg, 635 μmol, 81%) as a solid. Analytical sample was obtained by recrystallization from EtOAc/hexane (40:60) to give colorless needles. mp 103–107 °C. $[\alpha]_D^{26}$ +31° (c 0.94, $CHCl_3$). IR (KBr) 3485, 2955, 2835, 1610, 1510, 1461, 1305, 1250, 1095, 1075, 1025 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.74 (1H, br, C1O*H*), 3.38 (1H, br d, *J* = 9.8 Hz, C5*H*), 3.55 (1H, dd, *J* = 2.9, 9.8 Hz, C6*H*H), 3.74, 3.77, 3.77, 3.78 (each 3H, s, CH_3O), 3.74 (1H, dd, *J* = 2.9, 8.8 Hz, C2*H*), 3.75 (1H, t, *J* = 9.8 Hz, C4*H*), 3.80 (1H, dd, *J* = 8.8, 9.8 Hz, C3*H*), 3.87 (1H, dd, *J* = 4.4, 9.8 Hz, C6*H*H), 4.39, 4.46 (each 1H, d, *J* = 11.7 Hz, ArCH_2O), 4.46, 4.75 (each 1H, d, *J* = 10.3 Hz, ArCH_2O), 4.60, 4.66 (each 1H, d, *J* = 11.2 Hz, ArCH_2O), 4.79, 4.83 (each 1H, d, *J* = 10.2 Hz, ArCH_2O), 4.83 (1H, d, *J* = 2.9 Hz, C1*H*), 6.80–7.26 (16H, aromatic protons). ^{13}C NMR ($CDCl_3$) δ 41.3, 55.09, 55.15, 67.3, 71.5, 72.5, 72.8, 75.0, 75.7, 81.5, 82.6, 84.0, 113.65, 113.67, 113.71, 113.8, 129.31, 129.34, 129.38, 129.6, 129.8, 130.0, 130.5, 131.1, 159.0, 159.1, 159.2, 159.3. FD-MS (%, rel int) 676 (100, M^+), 675 (49, $[M-H]^+$). FD-HRMS Found m/z = 676.2688. Calcd for $C_{38}H_{44}O_9S$: M^+, 676.2706. According to *general procedure A*, treatment of the alcohol (37.5 mg, 55.4 μmol) with DBU (131 mmol/L solution in benzene, 21.4 μL, 0.1 equiv) and CCl_3CN (55.9 μL, 554 μmol) gave **15** (36.5 mg, 44.4 μmol, 80%) as a colorless syrup. IR (film) 3335, 2930, 2835, 1665, 1610, 1510, 1250, 1095, 1065, 1035, 820 cm^{-1}. ^1H NMR (C_6D_6) δ 3.26, 3.28, 3.29, 3.30 (each 3H, s, CH_3O), 3.54 (1H, dd, *J* = 2.9, 10.3 Hz, C6*H*H), 3.67 (1H, ddd, *J* = 2.9, 3.9, 10.2 Hz, C5*H*), 3.96 (1H, dd, *J* = 3.9, 10.3 Hz, C6*H*H), 3.97 (1H, dd, *J* = 3.0, 9.3 Hz, C2*H*), 4.08 (1H, dd, *J* = 9.3, 10.2 Hz, C4*H*), 4.21 (1H, t, *J* = 9.3 Hz, C3*H*), 4.22, 4.29 (each 1H, d, *J* = 11.8 Hz, ArCH_2O), 4.42, 4.53 (each 1H, d, *J* = 11.2 Hz, ArCH_2O), 4.64, 5.03 (each 1H, d,

J = 10.7 Hz, ArCH_2O), 4.91, 5.06 (each 1H, d, J = 10.8 Hz, ArCH_2O), 6.56 (1H, d, J = 3.0, C1*H*), 6.73–7.33 (16H, *aromatic protons*), 8.55 (1H, s, C(=N*H*)CCl_3). This sample was gradually decomposed in $CDCl_3$, so that it was immediately used for the next glycosylation.

4.15. 1,2,3,6-Tetra-*O*-benzoyl-5-deoxy-5-thio-D-glucopyranose (18)

A solution of 5-thioglucose (90.2 mg, 460 μmol) in pyridine (500 μL) was stirred with BzCl (120 μL, 1.03 mmol) at room temperature. After stirring for 1 h, additional BzCl (120 μL, 1.03 mmol) was added into the mixture at the same temperature and the resulting mixture was stirred for further additional 30 min. MeOH was added into the mixture and the resulting mixture was poured into water. The mixture was extracted with EtOAc (×3). Then the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/hexane 20:80) gave an anomeric mixture of **18** (110 mg, 180 μmol, 40%) as a syrup. The anomeric mixture was subjected to a medium pressure column chromatography to give α-anomer (65.2 mg) and β-anomer (44.3 mg).

4.15.1. Physical data for α-anomer of 18. $[\alpha]_D^{26}$ +226° (*c* 0.41, $CHCl_3$), IR (film) 3470, 3065, 2960, 2920, 2855, 1725, 1600, 1450, 1265, 1105, 1025, 705 cm^{-1}, ^1H NMR ($CDCl_3$) δ 3.74 (1H, ddd, J = 2.9, 3.9, 10.3 Hz, C5*H*), 4.18 (1H, t, J = 10.3 Hz C4*H*), 4.48 (1H, dd, J = 2.9, 12.2 Hz, C6*H*H) 5.16 (1H, dd, J = 3.9, 12.2 Hz, C6*H*H), 5.75 (1H, dd, J = 3.4, 10.3 Hz, C2*H*), 6.00 (1H, t, J = 10.3 Hz, C3*H*), 6.55 (1H, d, J = 3.4 Hz, C1*H*), 7.21–8.11 (20H, *aromatic protons*), FD-MS (%, rel int) 613 (58, $[M+H]^+$), 612 (41, M^+), 611 (48, $[M-H]^+$), 507 (34, $[M-PhCO]^+$), 491 (58, $[M-BzO]^+$), 105 (100, $PhCO^+$), FD-HRMS Found *m*/*z* = 613.1522, Calcd for $C_{34}H_{29}O_9S$: $[M+H]^+$, 613.1532.

4.15.2. Physical data for β-anomer of 18. $[\alpha]_D^{26}$ +33° (*c* 0.23, $CHCl_3$), IR (film) 3065, 2960, 2920, 2855, 1725, 1600, 1450, 1265, 1105, 1025, 705 cm^{-1}, ^1H NMR ($CDCl_3$) δ 3.48 (1H, dd, J = 3.4, 4.8, 8.8 Hz, C5*H*), 4.17 (1H, t, J = 8.8 Hz, C4*H*), 4.61 (1H, dd, J = 3.4, 11.7 Hz, C6*H*H), 5.04 (1H, dd, J = 4.8, 11.7 Hz, C6*H*H), 5.49 (1H, t, J = 8.8 Hz, C2*H*), 5.94 (1H, t, J = 8.8 Hz, C3*H*), 6.35 (1H, d, J = 8.8 Hz, C1*H*), 7.24–7.56 (12H, *aromatic protons*), 7.83 (2H, d, J = 8.3 Hz, *aromatic protons*), 7.93 (4H, d, J = 8.3 Hz, *aromatic protons*), 8.04 (2H, d, J = 8.3 Hz, *aromatic protons*), FD-MS (%, rel int) 613 (20, $[M+H]^+$), 612 (15, M^+), 611 (15, $[M-H]^+$), 507 (15, $[M-PhCO]^+$), 491 (21, $[M-BzO]^+$), 105 (100, $PhCO^+$), FD-HRMS Found *m*/*z* = 613.1545, Calcd for $C_{34}H_{29}O_9S$: $[M+H]^+$, 613.1532.

4.16. 1,2,3,4-Tetra-*O*-benzoyl-5-deoxy-5-thio-α-D-glucopyranose (19)

4.16.1. Preparation from 5-thioglucose. A solution of 5-thioglucose (93.0 mg, 474 μmol) in pyridine (300 μL) was stirred with TrCl (400 mg, 1.43 mmol) at 60 °C for 23 h. The mixture was concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (acetone/CH_2Cl_2 5:95) gave 5-deoxy-5-thio-6-*O*-triphenylmethylglucopyranose (156 mg, 356 μmol, 75%). ^1H NMR ($CDCl_3$) δ 3.26–3.41 (3H, C5*H*, C6H_2), 3.61–3.72 (3H, C2*H*, C3*H*, C4*H*), 4.85 (1H, br, C1*H*) 7.15–7.40 (*aromatic protons*). This sample was used for the next step without purification. A solution of 5-deoxy-5-thio-6-*O*-triphenylmethylglucopyranose (52.0 mg, 119 μmol) in pyridine (1.0 mL) was stirred with BzCl (90.0 μL, 714 μmol) at −15 °C to room temperature. After stirring for 4 h, MeOH was added into the mixture. The resulting mixture was poured into water and extracted with EtOAc (×3). Then the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/hexane 10:90) afforded 1,2,3,4-tetra-*O*-benzoyl-5-deoxy-5-thio-6-*O*-triphenylmethyl-D-glucopyranose (79.0 mg, 92.8 μmol, 78%). The ^1H NMR spectrum indicated that the sample consists of a mixture of anomers (α:β = 75:25). ^1H NMR ($CDCl_3$, a = 0.75, b = 0.25) δ 3.36 (1H × a, dd, J = 2.9, 9.8 Hz, C6*H* (α-anomer)), 3.44 (1H × a, dd, J = 3.9, 9.8 Hz, C6*H* (α-anomer)), 3.40–3.52 (3H × b, C5*H*, C6H_2(β-anomer)), 3.75 (1H, ddd, J = 2.9, 3.9, 10.3 Hz, C5*H*), 5.68 (1H × b, t, J = 8.8 Hz, C2*H* (β-anomer)), 5.87 (1H × a, dd, J = 2.9, 10.3 Hz, C2*H* (α-anomer)), 6.02–6.10 (2H × b, C3*H*, C4*H* (β-anomer)), 6.11 (1H × a, t, J = 10.3 Hz, C4*H* (α-anomer)), 6.14 (1H × a, t, J = 10.3 Hz, C3*H* (α-anomer)), 6.41 (1H × b, d, J = 8.8 Hz, C1*H* (β-anomer)), 6.63 (1H × a, d, J = 2.9 Hz, C1*H* (α-anomer)), 7.04–8.12 (*aromatic protons*). A solution of the product thus obtained (38.0 mg, 44.5 μmol) in MeOH (2.0 mL) was stirred with *p*-TsOH (2.0 mg) at room temperature. After stirring for 3 h, the mixture was neutralized by the addition of Et_3N and concentrated in vacuo. Then, the residue was diluted with EtOAc, poured into water, and extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/hexane 20:80) afforded **19** (22.0 mg, 36.0 μmol, 81%). The ^{1} spectrum disclosed that this sample consists of a mixture of anomers (α/β 83:17). ^1H NMR ($CDCl_3$, signals for the major isomer and some signals for the minor isomer are only described. a = 0.83, b = 0.17) δ 3.02 (1H, br, C6O*H*), 3.43 (1H × b, dt, J = 2.8, 10.7 Hz, C5*H* (β-anomer)), 3.63 (1H × a, ddd, J = 2.5, 2.9, 10.7 Hz, C5*H* (α-anomer)), 3.77 (1H × a, dd, J = 2.5, 13.2 Hz, C6*H*H (α-anomer)), 3.92 (1H × a, dd, J = 2.9, 13.2 Hz, C6*H*H (α-anomer)), 5.74 (1H × b, t, J = 9.3 Hz, C4*H*(β-anomer)), 5.77 (1H × a, dd, J = 9.7, 10.7 Hz, C4*H*(α-anomer)), 5.84 (1H × a, dd, J = 2.9, 10.3 Hz, C2*H* (α-anomer)), 5.91 (1H × b, t, J = 9.3 Hz, C2*H* (β-anomer) or C3*H*(β-anomer)), 6.06 (1H × b, t, J = 9.3 Hz, C2*H* (β-anomer) or C3*H* (β-anomer)), 6.34 (1H × a, dd, J = 9.7, 10.3 Hz, C3*H* (α-anomer)), 6.44 (1H × b, d, J = 9.3 Hz, C1*H* (β-anomer)), 6.63 (1H × a, d, J = 2.9 Hz, C1*H* (α-anomer)), 7.22–8.18 (20H, *aromatic protons*). The ^1H NMR signals for the major isomer consisted of that prepared as described below.

4.16.2. Preparation from 6a. A mixture of **6a** (41.0 mg, 146 μmol), TBDPSCl (114 μL, 439 μmol), and imidazole (29.9 mg, 439 μmol) in DMF (0.5 mL) was stirred at room temperature for 1 h. The mixture was poured into water and extracted with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (acetone/CH_2Cl_2 20:80) gave tetrahydropyranyl 6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-5-thio-α-D-glucopyranoside (57.3 mg, 111 μmol, 76%) as a mixture of diastereomers due to the asymmetric center in the THP moiety (50:50). ^{1}H NMR ($CDCl_3$) δ 1.05 (9H, s, $(CH_3)_3Si$), 1.50–1.82 (6H, C3′H_2, C4′H_2, C5′H_2), 3.09 (1H × 0.5, dt, J = 4.9, 10.3 Hz, C5H), 3.31 (1H × 0.5, ddd, J = 4.4, 5.8, 9.8 Hz, C5H), 3.50–3.56 (2H × 0.5, C′6HH), 3.67, 3.71 (each 1H × 0.5, t, J = 9.3 Hz, C3H), 3.78–3.91 (8H × 0.5, C2H, C4H, C6HH, C6′HH), 3.98, 4.01 (each 1H × 0.5, dd, J = 4.4, 10.3 Hz, C6HH), 4.83, 4.97 (each 1H × 0.5, d, both J = 3.4 Hz, C1H), 4.92, 4.96 (each 1H × 0.5, br t, J = 2.9 Hz, C2′H), 7.36–7.43 (6H, *aromatic protons*), 7.66 (4H, *aromatic protons*). A solution of the silyl ether thus obtained (12.9 mg, 26.5 μmol) in pyridine (0.5 mL) was stirred with BzCl (15.4 μL, 133 μmol) at room temperature for 2 h. The mixture was poured into water and extracted with EtOAc. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/hexane 20:80) gave tetrahydropyranyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyl-diphenylsilyl-5-deoxy-5-thio-α-D-glucopyranoside (21.5 mg, 26.0 μmol, 98%) as a mixture of diastereomers due to the asymmetric center in the THP moiety (50:50). ^{1}H NMR ($CDCl_3$) δ 1.03 (9H, s, $(CH_3)_3Si$), 1.49–1.82 (6H, C′3H_2, C′4H_2, C′5H_2), 3.24 (1H × 0.5, br d, J = 11.7 Hz, C′6HH), 3.48–3.58 (3H × 0.5, C5H, C6HH, C6′HH) 3.55, 4.04 (each 1H × 0.5, br t, J = 9.8 Hz, C′6HH), 3.72 (1H × 0.5, dd, J = 2.9, 11.2 Hz, C6HH), 3.78 (2H × 0.5, br d, J = 9.8 Hz, C6HH), 3.94 (1H × 0.5, br d, J = 10.3 Hz C5H), 4.81, 5.20 (each 1H × 0.5, br t, J = 2.9 Hz, C′2H), 5.28, 5.38 (each 1H × 0.5, t, both J = 2.9 Hz, C1H), 5.61, 5.71 (each 1H × 0.5, dd, both J = 2.9, 9.8 Hz, C2H), 5.96, 5.99 (each 1H × 0.5, t, both J = 9.8 Hz, C3H), 6.11, 6.14 (each 1H × 0.5, t, both J = 9.8 Hz, C4H), 7.08–7.94 (25H, *aromatic protons*). A solution of the benzoyl ester thus obtained (7.9 mg, 9.50 μmol) in MeOH (1.0 mL) was stirred with $HClO_4$ (1.0 μL) at room temperature for 24 h. After neutralization by the addition of Et_3N (5 μL), the mixture was concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/hexane 20:80) gave 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-5-thio-α-D-glucopyranose (5.8 mg, 7.70 μmol, 81%) as a syrup. $[\alpha]_D^{20}$ +35.5° (*c* 0.39, $CHCl_3$). IR (film) 3450, 3070, 2960, 2930, 2860, 1730, 1280, 1260, 1110, 1070, 1025, 730, 705, 505 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.98 (9H, s, $(CH_3)_3CSi$), 2.46 (1H, br, OH), 3.66 (1H, dd, J = 2.4, 10.7 Hz, C6HH), 3.71 (1H, ddd, J = 2.4, 3.9 Hz, 10.7 Hz, C5H), 3.90 (1H, dd, J = 3.9, 10.7 Hz, C6HH), 5.38 (1H, d, J = 2.8 Hz, C1H), 5.54 (1H, dd, J = 2.8, 10.2 Hz, C2H), 5.95, 6.10 (each 1H, t, J = 10.2 Hz, C4H, C3H), 7.03 (2H, t, J = 7.3 Hz, *aromatic protons*), 7.16 (3H, *aromatic protons*), 7.26 (7H, *aromatic protons*), 7.40 (4H, *aromatic protons*), 7.58, 7.75, 7.78, 7.87 (each 2H, dd, J = 1.5, 8.3 Hz, *aromatic protons*). FD-MS (%, rel int) 747 (5, $[M+H]^+$), 729 (3, $[M-OH]^+$), 689 (100, $[M-{}^tBu]^+$). FD-HRMS Found m/z = 747.2451. Calcd for $C_{43}H_{43}O_8SSi$: $[M+H]^+$, 747.2448. A solution of the alcohol thus obtained (213 mg, 290 μmol) in a mixture of pyridine (1.0 mL) and CH_2Cl_2 (2.0 mL) was stirred with BzCl (50.0 mg, 356 μmol) at room temperature for 12 h. The mixture was poured into saturated aqueous $NaHCO_3$ solution and extracted with EtOAc. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/hexane 18:82) gave 1,2,3,4-tetra-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-5-deoxy-5-thio-α-D-glucopyranose (240 mg, 281 μmol, 97%) as a syrup. $[\alpha]_D^{19}$ +202° (c 0.86, $CHCl_3$). IR (film) 3070, 2960, 2860, 1730, 1285, 1260, 1105, 1090, 1065, 705 cm^{-1}. NMR ($CDCl_3$) δ 1.07 (9H, s, $(CH_3)_3CSi$), 3.72–3.76 (2H, C5H, C6HH), 4.01 (1H, dd, J = 3.9, 11.2 Hz, C6HH), 5.87 (1H, dd, J = 2.9, 9.7 Hz, C2H), 6.15, 6.23 (each 1H, t, J = 9.7 Hz, C3H, C4H), 6.65 (1H, d, J = 2.9 Hz, C1H), 7.07 (2H, t, J = 7.3 Hz, *aromatic protons*), 7.24 (3H, *aromatic protons*), 7.35 (11H, *aromatic protons*), 7.50 (4H, *aromatic protons*), 7.62 (2H, *aromatic protons*), 7.83 (4H, br d, J = 7.5 Hz, *aromatic protons*), 7.89 (2H, dd, J = 1.5, 7.5 Hz, *aromatic protons*), 8.13 (2H, dd, J = 1.5, 7.5 Hz, *aromatic protons*). FD-MS (%, rel int) 851 (0.7, $[M+H]^+$), 793 (100, $[M-{}^tBu]^+$), 729 (31, $[M-PhCOO]^+$). FD-HRMS Found m/z = 851.2693. Calcd for $C_{50}H_{47}O_9SSi$: $[M+H]^+$, 851.2710. A mixture of the tetrabenzoate thus obtained (210 mg, 247 μmol), AcOH (50 mg, 833 μmol), and TBAF (1.0 M in THF, 0.4 mL) was stirred at room temperature for 12 h. The mixture was poured into water and extracted with EtOAc. The combined extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/hexane 20:80) afforded **19** (140 mg, 227 μmol, 92%) as a syrup. $[\alpha]_D^{28}$ +121° (*c* 1.9, $CHCl_3$). IR (film) 3451, 2960, 2855, 1730, 1280, 1260, 1090, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.02 (1H, br, C6OH), 3.66 (1H, ddd, J = 2.5, 2.9, 10.7 Hz, C5H), 3.81 (1H, dd, J = 2.5, 13.2 Hz, C6HH), 3.92 (1H, dd, J = 2.9, 13.2 Hz, C6HH), 5.77 (1H, dd, J = 9.7, 10.7 Hz, C4H), 5.84 (1H, dd, J = 2.9, 10.3 Hz, C2H), 6.34 (1H, dd, J = 9.7, 10.3 Hz, C3H), 6.63 (1H, d, J = 2.9 Hz, C1H), 7.20–8.14 (20H, *aromatic protons*). FAB-MS (negative mode, %, rel int): 612 (3, M^-), 611 (5, $[M-H]^-$), 368 (7, $[M-PhCOOH \times 2]^-$), 121 (100, $PhCOO^-$); FAB-HRMS Found m/z = 611.1375. Calcd for $C_{34}H_{27}O_9S$: $[M-H]^-$, 611.1376.

4.17. 1,2,3,6-Tetra-*O*-acetyl-5-*S*-acetyl-glucofuranose (21)

A solution of the diol **20**[20] (336 mg, 1.04 mmol) in a mixture of Ac_2O (5.0 mL) and pyridine (10 mL) was stirred at room temperature for 1.5 h. The volatiles were azeotropically removed with toluene by rotary evaporator. Purification of the residue by silica gel chromatography (EtOAc/hexane 30:70) gave **21** (423 mg, 1.04 mmol, 100%). The ^{1}H NMR spectra suggested that the product

is an anomeric mixture (75:25). IR (film) 1750, 1700, 1370, 1220, 1050, 1010, 940, 630 cm^{-1}. ^1H NMR ($CDCl_3$, $a = 0.75$, $b = 0.25$) δ 2.06, 2.07, 2.09, 2.11, 2.32 (each 3H × a, s, CH_3CO (α-anomer)), 2.07, 2.08, 2.12, 2.125, 2.316 (each 3H × b, s, CH_3CO (β-anomer)), 4.10 (1H × a, ddd, $J = 4.4$, 5.4, 9.3 Hz, C5H (α-anomer)), 4.18 (1H × b, ddd, $J = 3.4$, 4.4, 10.7 Hz, C5H (β-anomer)), 4.27 (1H × a, dd, $J = 5.3$, 11.7 Hz, C6HH (α-anomer)), 4.32 (1H × b, dd, $J = 4.4$, 11.7 Hz, C6HH (β-anomer)), 4.42 (1H × a, dd, $J = 4.4$, 11.7 Hz, C6HH (α-anomer)), 4.44 (1H × b, dd, $J = 3.4$, 11.7 Hz, C6HH (β-anomer)), 4.51 (1H × b, dd, $J = 4.4$, 10.7 Hz, C4H (β-anomer)), 4.52 (1H × a, dd, $J = 4.4$, 9.3 Hz, C4H (α-anomer)), 5.08 (1H × b, s, C2H (β-anomer)), 5.20 (1H × a, dd, $J = 2.4$, 4.4 Hz, C2H (α-anomer)), 5.31 (1H × b, d, $J = 4.4$ Hz, C3H (β-anomer))5.47 (1H × a, dd, $J = 2.4$, 4.4 Hz, C3H (α-anomer)), 6.09 (1H × b, s, C1H (β-anomer)), 6.45 (1H × a, d, $J = 4.4$ Hz, C1H (α-anomer)). EI-MS (%, rel int) 347 (10, $[M-AcO]^+$), 43 (100, CH_3CO^+). EI-HRMS Found $m/z = 347.0772$. Calcd for $C_{14}H_{19}O_8S$: $[M-AcO]^+$, 347.0801.

4.18. 1,2,3,6-Tetra-*O*-acetyl-5-deoxy-5-thio-D-glucopyranose (22)

A solution of the pentaacetate **21** (199 mg, 491 μmol) in DMF (3.0 mL) was stirred with hydrazine acetate (136 mg, 1.47 mmol) at room temperature for 1 h. The mixture was poured into water and extracted with EtOAc (×3). The extracts were combined, washed with brine, and dried over $MgSO_4$. Purification of the residue by silica gel chromatography (acetone/CH_2Cl_2 7:93) gave 2,3,6-tri-*O*-acetyl-5-deoxy-5-thio-D-glucopyranose (127 mg, 393 μmol, 80%). The ^1H NMR spectra suggested that the product is an anomeric mixture (80:20). IR (film) 3450, 2960, 1740, 1370, 1240, 1025 cm^{-1}. ^1H NMR ($CDCl_3$, some signals for the minor β-isomer could not be assigned. $a = 0.8$, $b = 0.2$) δ 2.08, 2.09, 2.10 (each 3H × a, s, CH_3CO (α-isomer)), 3.05 (1H × b, ddd, $J = 3.4$, 4.9, 10.3 Hz, C5H (β-isomer)), 3.50 (1H × a, ddd, $J = 2.9$, 4.4, 10.8 Hz, C5H (α-isomer)), 3.74 (1H × a, t, $J = 9.8$ Hz, C4H (α-isomer)), 4.27 (1H × a, dd, $J = 2.9$, 11.7 Hz, C6HH (α-isomer)), 4.61 (1H × b, dd, $J = 4.9$, 11.7 Hz, C6HH (β-isomer)), 4.69 (1H × a, dd, $J = 4.4$, 11.7 Hz, C6HH (α-isomer)), 4.96 (1H × b, t, $J = 9.8$ Hz, C3H (b-isomer)) 5.11 (1H × a, d, $J = 3.0$ Hz, C1H (α-isomer)), 5.13 (1H × a, dd, $J = 3.0$, 9.8 Hz, C2H (α-isomer)), 5.40 (1H × a, t, $J = 9.8$ Hz, C3H(α-isomer)). EI-MS (%, rel int) 323 (0.7, $[M+H]^+$), 305 (2, $[M-OH]^+$), 262 (2, $[M-AcOH]^+$), 244 (16, $[M-AcOH-OH]^+$), 43 (100, CH_3CO^+). EI-HRMS Found $m/z = 323.0789$. Calcd for $C_{12}H_{19}O_8S$: $[M+H]^+$, 323.0801. A mixture of the diol thus obtained (26.2 mg, 81.3 μmol), AcCl (8.6 μL, 122 μmol), pyridine (6.3 μL, 89.4 μmol), and DMAP (1.0 mg, 8.1 μmol) was stirred in CH_2Cl_2 (1.0 mL) with at 0 °C for 6 h. Methanol (100 μL) was added into the mixture. After further stirring at room temperature for 30 min, the mixture was poured into H_2O and extracted with EtOAc (×3). The combined organic extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (acetone/CH_2Cl_2 10:90) gave **22** (28.2 mg, 77.2 μmol, 95%) and as a syrup. $[\alpha]_D^{20}$ +174° (c 0.76, $CHCl_3$). IR (film) 3480, 1750, 1370, 1220, 1025 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.00, 2.10, 2.12, 2.17 (each 3H, s, CH_3CO), 3.24 (1H, d, $J = 5.8$ Hz, C4OH), 3.40 (1H, ddd, $J = 3.4$, 4.4, 10.2 Hz, C5H), 3.76 (1H, dt, $J = 5.8$, 10.2 Hz, C4H), 4.22 (1H, dd, $J = 3.0$, 12.2 Hz, C6HH), 4.74 (1H, dd, $J = 4.4$, 12.2 Hz, C6HH), 5.19 (1H, dd, $J = 3.0$, 10.2 Hz, C2H), 5.32 (1H, t, $J = 10.2$ Hz, C3H), 6.11 (1H, d, $J = 3.0$ Hz, C1H). ^{13}C NMR ($CDCl_3$) δ 20.5, 20.6, 20.7, 20.9, 42.5, 61.7, 70.9, 72.5, 72.6, 72.8, 169.1, 169.7, 170.9, 171.7. EI-MS (%, rel int) 304 (3, $[M-AcOH]^+$), 245 (3, $[M-AcOH-AcO]^+$), 244 (3, $[M-AcOH\times2]^+$), 184 (30, $[M-AcOH\times3]^+$), 43 (100, CH_3CO^+). EI-HRMS Found $m/z = 304.0606$. Calcd for $C_{12}H_{16}O_7S$: $[M-AcOH]^+$, 304.0617.

4.19. Glycosylation reaction of 5-thioglycosyl donors carrying acyl protective group at C2-alcohols (Table 1)

4.19.1. Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl]-α-D-glucopyranoside (24) (run 1). A mixture of **23**[31] (17.2 mg, 34.9 μmol), **16a** (15.3 mg, 30.2 μmol), and freshly activated powdered MS4A (100 mg) in CH_2Cl_2 (1.0 mL) was stirred at room temperature for 1 h. After the mixture was cooled to −78 °C, BF_3OEt_2 (2.1 μL, 17.5 μmol, 0.5 equiv) was added to the suspension. After stirring for 2 h at −78 °C, the mixture was allowed to warm to room temperature over an additional 1 h. Pyridine was added to the mixture at −78 °C and it was passed through silica gel pad and then concentrated in vacuo. Purification by silica gel column chromatography (EtOAc/hexane 25:75) gave **24** (22.2 mg, 26.5 μmol, 76%). The ^1H NMR spectrum indicated that this sample consists of only β-isomer. ^1H NMR ($CDCl_3$) δ 1.98, 1.99, 2.00, 2.07 (each 3H, s, CH_3CO), 3.43 (3H, s, CH_3O), 3.64–3.70 (2H, C6HH, C5′H), 4.03 (2H, C6HH, C6′HH), 4.19–4.25 (2H, C5H, C6′HH), 4.56 (1H, d, $J = 8.3$ Hz, C1′H), 5.02 (1H, t, $J = 8.3$ Hz, C2′H), 5.04 (1H, t, $J = 9.8$ Hz, C4′H), 5.17–5.23 (3H, C1H, C2H, C3′H), 5.39 (1H, t, $J = 9.8$ Hz, C4H), 6.11 (1H, t, $J = 9.8$ Hz, C3H), 7.25–7.53 (9H, *aromatic protons*), 7.81–7.96 (6H, *aromatic protons*).

4.19.2. Methyl 6-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-5′-deoxy-5′-thio-D-glucopyranosyl]-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (25) (run 2). According to *general procedure B*, treatment of **11** (16.5 mg, 32.4 μmol) with **16a** (16.4 mg, 32.4 μmol) and BF_3OEt_2 (1.0 μL) in CH_2Cl_2 (700 μL) afforded **25** (5.3 mg, 4.54 μmol, 19%) as a syrup. The ^1H NMR spectrum indicated that this sample consists of a diastereomixture of anomers (α:β = 30:70). Analytical samples were obtained by preparative silica gel TLC (EtOAc/benzene/hexane 20:40:40).

4.19.2.1. Physical data for α-anomer of 25. $[\alpha]_D^{22}$ +101° (c 0.15, $CHCl_3$), $R_f = 0.50$ (above conditions), IR (film) 2920, 2850, 1730, 1220, 1095, 1030, 710 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.99, 2.01, 2.04, 2.06 (each 3H, s, CH_3CO), 3.49 (3H, s, CH_3O), 3.54 (1H, dd, $J = 1.7$, 10.7 Hz, C6HH), 3.54 (1H, ddd, $J = 2.9$,

4.9, 10.3 Hz, C′5*H*), 3.97 (1H, dd, *J* = 2.9, 12.2 Hz, C6′*H*H), 4.04 (1H, dd, *J* = 6.4, 10.7 Hz, C6*H*H), 4.28 (1H, ddd, *J* = 1.7, 6.4, 9.8 Hz, C5*H*), 4.33 (1H, dd, *J* = 4.9, 12.2 Hz, C6′*H*H), 4.83 (1H, d, *J* = 2.9 Hz, C1′*H*), 5.16 (1H, dd, *J* = 2.9, 9.8 Hz, C2′*H*), 5.20–5.25 (2H, C1*H*, C2*H*), 5.28 (1H, dd, *J* = 9.8, 10.3 Hz, C4′*H*), 5.51 (1H, t, *J* = 9.8 Hz, C4*H*), 5.53 (1H, t, *J* = 9.8 Hz, C3′*H*), 6.13 (1H, t, *J* = 9.8 Hz, C3*H*), 7.26–7.52 (9H, *aromatic protons*), 7.84–7.97 (6H, *aromatic protons*), FD-MS (%, rel int) 852 (18, M^+), 105 (100, $PhCO^+$).

4.19.2.2. Physical data for β-anomer of 25. $[\alpha]_D^{26}$ +23° (*c* 0.16, $CHCl_3$), R_f = 0.40 (above conditions), IR (film) 2920, 2850, 1730, 1220, 1095, 1030, 710 cm^{-1}, ^1H NMR ($CDCl_3$) δ 2.00, 2.00, 2.02, 2.06 (each 3H, s, CH_3CO), 3.12 (1H, ddd, *J* = 3.9, 5.4, 9.8 Hz, C′5*H*), 3.44 (3H, s, CH_3O), 3.67 (1H, dd, *J* = 6.8, 10.7 Hz, C6*H*H), 3.94 (1H, dd, *J* = 1.9, 10.7 Hz, C6*H*H), 4.10 (1H, dd, *J* = 3.9, 11.7 Hz, C6′*H*H), 4.18 (1H, ddd, *J* = 1.9, 6.8, 9.8 Hz, C5*H*), 4.24 (1H, dd, *J* = 5.4, 11.7 Hz, C6′*H*H), 4.68 (1H, d, *J* = 8.8 Hz, C1′*H*), 5.06 (1H, dd, *J* = 8.8, 9.3 Hz, C3′*H*), 5.17 (1H, d, *J* = 3.4 Hz, C1*H*), 5.20 (1H, dd, *J* = 3.4, 9.8 Hz, C2*H*), 5.27 (1H, dd, *J* = 9.3, 9.8 Hz, C4′*H*), 5.32 (1H, t, *J* = 8.8 Hz, C2′*H*), 5.40 (1H, t, *J* = 9.8 Hz, C4*H*), 6.10 (1H, t, *J* = 9.8 Hz, C3*H*), 7.24–7.53 (9H, *aromatic protons*), 7.81–7.96 (6H, *aromatic protons*), FD-MS (%, rel int) 853 (59, $[M+H]^+$), 852 (36, M^+), 794 (1.23, $[M+H-AcO]^+$), 793 (1.51, $[M-AcO]^+$), 732 (31, $[M+H-BzO]^+$), 105 (83, $PhCO^+$), FD-HRMS Found *m*/*z* = 852.2278. Calcd for $C_{42}H_{44}O_{17}S$: M^+, 852.2299.

4.19.3. 6-*O*-[2′,3′,4′,6′-Tetra-*O*-acetyl-5′-deoxy-5′-thio-α-D-glucopyranosyl]-1,2,3,4-tetra-*O*-benzoyl-5-deoxy-5-thio-α-D-glucopyranose (26) (run 3). According to *general procedure B*, treatment of **11** (5.8 mg, 11.4 μmol) with **19** (7.0 mg, 11.4 μmol) and TESOTf (114 μmol/mL solution in CH_2Cl_2, 10 μL, 0.1 equiv) in CH_2Cl_2 (200 μL) afforded **26** (1.0 mg, 1.1 μmol, 10%) as a syrup. $[\alpha]_D^{26}$ +136 (*c* 0.18, $CHCl_3$). IR (film) 1735, 1250, 1225, 1090, 1025, 710 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.99, 2.03, 2.05, 2.08 (each 3H, s, CH_3CO), 3.48 (1H, dd, *J* = 3.5, 10.7 Hz, C6*H*H), 3.56 (1H, dd, *J* = 3.0, 3.9, 10.8 Hz, C′5*H*), 3.82 (1H, dd, *J* = 3.0, 12.2 Hz, C′6*H*H), 3.88 (1H, dt, *J* = 3.5, 10.3 Hz, C5*H*), 4.19 (1H, dd, *J* = 3.5, 10.7 Hz, C6*H*H), 4.44 (1H, dd, *J* = 3.9, 12.2 Hz, C′6*H*H), 4.73 (1H, *J* = 3.4 Hz, C′1*H*), 5.07 (1H, dd, *J* = 3.4, 9.8 Hz, C′2*H*), 5.30 (1H, dd, *J* = 9.8, 10.8 Hz, C′4*H*), 5.54 (1H, t, *J* = 9.8 Hz, C′3*H*), 5.86 (1H, dd, *J* = 3.4, 10.3 Hz, C2*H*), 6.00 (1H, t, *J* = 10.3 Hz, C4*H*), 6.24 (1H, t, *J* = 10.3 Hz, C3*H*), 6.63 (1H, d, *J* = 3.4 Hz, C1*H*), 7.23–8.17 (20H, *aromatic protons*). FD-MS (%, rel int) 958 (17, M^+), 899 ($[M-AcO]^+$), 853 (32, $[M-Bz]^+$), 837 (28, $[M-PhCOO]^+$), 105 (100, $PhCO^+$); FD-HRMS Found = *m*/*z* 958.2147. Calcd for $C_{48}H_{46}O_{17}S_2$: M^+, 958.2176.

4.19.4. Methyl 6-*O*-[2′,3′,4′,6′-tetra-*O*-benzoyl-5′-deoxy-5′-thio-D-glucopyranosyl]-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (27).

4.19.4.1. Activation with BF_3OEt_2 (run 4). According to *general procedure B*, treatment of 12 (12.0 mg, 15.9 μmol) with **16a** (8.0 mg, 15.8 μmol) and BF_3OEt_2 (2.0 μL, 15.9 μmol) gave **27** (13.5 mg, 12.4 μmol, 77%) as a syrup. The ^1H NMR spectrum indicated that this sample consists of a diastereomixture of anomers (α:β = 17:83). Analytical samples were obtained by preparative silica gel TLC (EtOAc/benzene 10:90).

4.19.4.2. Treatment with TESOTf (run 7). According to *general procedure B*, treatment of **12** (16.6 mg, 21.9 μmol) with **16a** (13.9 mg, 27.0 μmol) and TESOTf (110 μmol/mL solution in CH_2Cl_2, 10 μL, 0.05 equiv) in CH_2Cl_2 (1.0 mL) gave **27** (9.2 mg, 7.99 μmol, 38%) as a syrup. The ^1H NMR spectrum indicated that this sample consists of a diastereomixture of anomers (α:β = 84:16). Analytical samples were obtained by preparative silica gel TLC (EtOAc/benzene 10:90).

4.19.4.3. Activation with TMSOTf (run 8). According to *general procedure B*, treatment of **12** (13.5 mg, 17.8 μmol) with **16a** (9.0 mg, 17.8 μmol) and TMSOTf (89.0 μmol/mL solution in CH_2Cl_2, 10 μL, 0.05 equiv) gave **27** (2.2 mg, 1.96 μmol, 11%) as a syrup. The ^1H NMR spectrum indicated that this sample consists of only α-isomer.

4.19.4.4. Activation with TfOH (run 9). According to *general procedure B*, treatment of **12** (15.6 mg, 20.6 μmol) with **15** (10.4 mg, 20.6 μmol) and TfOH (20.6 μmol/mL in CH_2Cl_2 solution, 1.0 μL, 0.01 equiv) gave **27** (7.5 mg, 6.80 μmol, 33%) as a syrup. The ^1H NMR spectrum indicated that this sample consists of a diastereomixture of anomers (α:β = 89:11). Analytical samples were obtained by preparative silica gel TLC (EtOAc/benzene 10:90).

4.19.4.5. Physical data for α-anomer of 27. $[\alpha]_D^{18}$ +136° ($CHCl_3$, *c* 0.75). R_f = 0.70 (above conditions). IR (film) 2960, 2930, 1730, 1450, 1270, 1105, 1070, 1025, 710 cm^{-1}. ^1H NMR ($CDCl_3$) 3.51 (3H, s, CH_3O), 3.64 (1H, dd, *J* = 1.5, 11.2 Hz, C6*H*H), 4.01 (1H, ddd, *J* = 3.9, 4.9, 10.7 Hz, C′5*H*), 4.30 (1H, ddd, *J* = 1.5, 6.1, 10.3 Hz, C6*H*H), 4.48 (1H, dd, *J* = 4.8, 12.2 Hz, C′6*H*H), 4.55 (1H, dd, *J* = 3.9, 12.2 Hz, C′6*H*H), 5.07 (1H, dd, *J* = 3.9, 10.3 Hz, C2*H*), 5.15 (1H, d, *J* = 2.9 Hz, C′1*H*), 5.18 (1H, d, *J* = 3.9 Hz, C1*H*), 5.55 (1H, t, *J* = 9.8 Hz, C4*H*), 5.64 (1H, dd, *J* = 2.9, 10.3 Hz, C′2*H*), 5.94 (1H, dd, *J* = 9.8, 10.7 Hz, C′4*H*), 6.12 (1H, t, *J* = 9.8 Hz, C3*H*), 6.27 (1H, t, *J* = 9.8 Hz, C′3*H*), 7.20–8.06 (35H, *aromatic protons*). FD-MS (%, rel int) 1101 (17, $[M+H]^+$), 979 (27, $[M-BzO]^+$), 978 (17, $[M-BzOH]^+$), 105 (100, $PhCO^+$). FD-HRMS Found *m*/*z* = 1101.2983. Calcd for $C_{62}H_{53}O_{17}S$: $[M+H]^+$, 1101.3004.

4.19.4.6. Physical data for β-anomer of 27. $[\alpha]_D^{18}$ +32° ($CHCl_3$, *c* 1.85). R_f = 0.65 (above conditions). IR (film) 2950, 1730, 1450, 1270, 1095, 1070, 1025, 710 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.19 (3H, s, CH_3O), 3.60 (1H, ddd, *J* = 4.9, 5.4, 9.8 Hz, C′5*H*), 3.75 (1H, dd, *J* = 6.8, 10.7 Hz, C6*H*H), 4.06 (1H, dd, *J* = 1.5, 10.7 Hz, C6*H*H), 4.18 (1H, ddd, *J* = 1.5, 6.8, 9.3 Hz, C5*H*), 4.53 (1H, dd, *J* = 5.4, 11.7 Hz, C′6*H*H), 4.64 (1H, dd, *J* = 4.9, 11.7 Hz,

C′6*H*H), 4.93 (1H, d, *J* = 3.4 Hz, C1*H*), 5.05 (1H, d, *J* = 7.8 Hz, C′1*H*), 5.06 (1H, dd, *J* = 3.4, 10.3 Hz, C2*H*), 5.36 (1H, t, *J* = 9.3 Hz, C4*H*), 5.76 (1H, dd, *J* = 8.3, 8.8 Hz, C′3*H*), 5.87 (1H, dd, *J* = 7.8, 8.3 Hz, C′2*H*), 5.91 (1H, dd, *J* = 8.8, 9.8 Hz, C′4*H*), 6.06 (1H, dd, *J* = 9.3, 10.3 Hz, C3*H*), 7.21–7.99 (35H, *aromatic protons*). FD-MS (%, rel int) 1101 (26, $[M+H]^+$), 1085 (26, $[M-Me]^+$), 595 (15, 1-deoxy-thioglucose$^+$), 105 (100, $PhCO^+$). FD-HRMS Found *m*/*z* = 1101.3022. Calcd for $C_{62}H_{53}O_{17}S$: $[M+H]^+$, 1101.3004.

4.19.5. 4-Nitrophenyl 2,3,4-tri-*O*-benzoyl-6-*O*-[2′,3′,4′,6′-tetra-O-benzoyl-5′-deoxy-5′-thio-D-glucopyranosyl]-α-D-glucopyranose (28) (run 5). According to *general procedure B*, treatment of **12** (11.3 mg, 17.3 μmol) with **16b** (10.0 mg, 17.3 μmol) and BF_3OEt_2 (1.5 μL) in CH_2Cl_2 (700 μL) gave **28** (17.5 mg, 14.2 μmol, 82%). The ^1H NMR spectrum indicated that this sample consists of a diastereomixture of anomers (α:β = 15:85). Analytical samples were obtained by preparative silica gel TLC (EtOAc/benzene 10:90).

4.19.5.1. Physical data for α-anomer of 28. $[\alpha]_D^{20}$ +91° (*c* 2.2, $CHCl_3$). R_f = 0.65 (above conditions). IR (film) 1725, 1595, 1520, 1450, 1270, 1105, 710 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.45 (1H, dd, *J* = 1.5, 11.7 Hz, C6*H*H), 3.98 (1H, ddd, *J* = 3.9, 4.8, 10.3 Hz, C5′*H*), 4.15 (1H, dd, *J* = 5.4, 10.7 Hz, C6*H*H), 4.34 (1H, ddd, *J* = 1.5, 5.4, 10.3 Hz, C5*H*), 4.50 (1H, dd, *J* = 4.8, 11.7 Hz, C6′*H*H), 4.58 (1H, dd, *J* = 3.9, 11.7 Hz, C6′*H*H), 5.13 (1H, d, *J* = 3.4 Hz, C1′*H*), 5.28 (1H, dd,*J* = 3.4, 10.3 Hz, C2*H*), 5.56 (1H, dd, *J* = 3.4, 10.3 Hz, C2′*H*), 5.72 (1H, t, *J* = 10.3 Hz, C4*H*), 5.94 (1H, dd, *J* = 9.8, 10.3 Hz, C4′*H*), 5.96 (1H, d, *J* = 3.4 Hz, C1*H*), 6.21 (1H, t, *J* = 9.8 Hz, C3′*H*), 6.31 (1H, t, *J* = 10.3 Hz, C3*H*), 7.16–7.56 (21H, *aromatic protons*), 7.78–8.26 (16H, *aromatic protons*). FD-MS (% rel int) 1208 (3.4, $[M+H]^+$), 1070 (100, $[M+H-PNPO]^+$), 1069 (24, $[M-PNPO]^+$), 138 (17, $PNPO^+$), 105 (14, $PhCO^+$).

4.19.5.2. Physical data for β-anomer of 28. $[\alpha]_D^{25}$ +36° (*c* 0.70, $CHCl_3$). R_f = 0.60 (above conditions). IR (film) 1725, 1600, 1520, 1450, 1265, 1105, 710 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.57 (1H, ddd, *J* = 1.9, 5.4, 8.8 Hz, C5′*H*), 3.67 (1H, dd, *J* = 5.4, 10.7 Hz, C6*H*H), 4.06 (1H, dd, *J* = 1.9, 10.7 Hz, C6*H*H), 4.24 (1H, ddd, *J* = 1.9, 5.4, 10.3 Hz, C5*H*), 4.52 (1H, dd, *J* = 5.9, 11.7 Hz, C6′*H*H), 4.66 (1H, dd, *J* = 5.4, 11.7 Hz, C6′*H*H), 4.90 (1H, d, *J* = 6.8 Hz, C′1*H*), 5.21 (1H, dd, *J* = 3.4, 10.3 Hz, C2*H*), 5.53 (1H, t, *J* = 10.3 Hz, C4*H*), 5.72 (1H, dd, *J* = 7.8, 8.8 Hz, C3′*H*), 5.80 (1H, dd, *J* = 6.8, 7.3 Hz, C2′*H*)), 5.87 (1H, t, *J* = 8.8 Hz, C4′*H*), 5.92 (1H, d, *J* = 3.4 Hz, C1*H*), 6.25 (1H, t, *J* = 10.3 Hz, C3*H*), 7.21 (2H, br d, *J* = 9.3 Hz, *aromatic protons*), 7.25–7.50 (15H, *aromatic protons*), 7.78–7.96 (20H, *aromatic protons*), 8.16 (2H, br d, *J* = 9.3 Hz, *aromatic protons*). FD-MS (%, rel int) 1207 (16, M^+), 1086 (35, $[M-BzO]^+$), 1070 (100, $[M+H-PNPO]^+$), 1069 (86, $[M-PNPO]^+$), 138 (34, $PNPO^+$), 105 (31, $PhCO^+$), FD-HRMS Found *m*/*z* = 1207.2955. Calcd for $C_{67}H_{53}O_{19}NS$: M^+, 1207.2933.

4.19.6. 1,2,3,4-Tetra-*O*-benzoyl-6-*O*-[2′,3′,4′,6′-tetra-*O*-benzoyl-5′-deoxy-5′-thio-D-glucopyranosyl]-5-thio-α-D-glucopyranose (29)

4.19.6.1. Activation with BF_3OEt_2 (run 6). According to *general procedure B*, treatment of **12** (21.7 mg, 28.7 μmol) with **19** (16.0 mg, 26.1 μmol) BF_3OEt_2 (3.5 μL, 28.7 μmol) in CH_2Cl_2 (1.0 mL) gave **29** (19.5 mg, 16.2 μmol, 62%). The ^1H NMR spectrum indicated that this sample consists of only the β-anomer.

4.19.6.2. Activation with TESOTf (run 11). According to *general procedure B*, treatment of **12** (33.1 mg, 43.7 μmol) with **19** (26.0 mg, 42.4 μmol) and TESOTf (440 μmol/mL solution in CH_2Cl_2, 10 μL, 0.1 equiv) in CH_2Cl_2 (1.0 mL) gave **29** (19.4 mg, 16.1 μmol, 38%). The ^1H NMR spectrum indicated that the sample consists of a diastereomixture of anomers (α:β = 84:16). Analytical samples were obtained by preparative silica gel TLC (EtOAc/benzene 10:90).

4.19.6.3. Physical data for α-anomer of 29. $[\alpha]_D^{20}$ +210° (*c* 0.65, $CHCl_3$). R_f = 0.70 (above conditions). IR (film) 3030, 2920, 1860, 1730, 1260, 1090, 1070, 705 cm^{-1}. ^1H NMR (C_6D_6) δ 3.53 (1H, dd, *J* = 2.9, 10.2 Hz, C6*H*H), 3.90 (1H, ddd, *J* = 2.9, 3.4, 10.7 Hz, C′5*H*), 3.97 (1H, ddd, *J* = 2.9, 3.9, 10.7 Hz, C5*H*), 4.35 (1H, dd, *J* = 3.9, 10.3 Hz, C6*H*H), 4.39 (1H, dd, *J* = 3.4, 12.2 Hz, C′6*H*H), 4.51 (1H, dd, *J* = 3.9, 12.2 Hz, C′6*H*H), 4.97 (1H, d, *J* = 3.0 Hz, C′1*H*), 5.58 (1H, dd, *J* = 3.0, 10.2 Hz, C′2*H*), 5.89 (1H, dd, *J* = 3.4, 10.3 Hz, C2*H*), 5.98 (1H, dd, *J* = 9.7, 10.7 Hz, C′4*H*), 6.17 (1H, t, *J* = 9.8 Hz, C4*H*), 6.24 (1H, t, *J* = 9.8 Hz, C3*H*), 6.27 (1H, t, *J* = 9.8 Hz, C3′*H*), 6.58 (1H, d, *J* = 3.4 Hz, C1*H*), 7.20-8.20 (40H, *aromatic protons*). FD-MS (%, rel int) 1207 (27, $[M+H]^+$), 1101 (61, $[M-Bz]^+$), 1085 (87, $[M-BzO]^+$), 105 (100, $PhCO^+$). FD-HRMS Found *m*/*z* = 1207.2858. Calcd for $C_{68}H_{55}O_{17}S_2$: $[M+H]^+$, 1207.2881.

4.19.6.4. Physical data for β-anomer of 29. $[\alpha]_D^{20}$ +115° (*c* 0.20, $CHCl_3$). R_f = 0.65 (above conditions). IR (film) 2920, 1730, 1450, 1260, 1090, 1070, 1025, 705 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.55 (1H, dt, *J* = 5.4, 8.8 Hz, C′5*H*), 3.72 (1H, dd, *J* = 5.9, 10.3 Hz, C6*H*H), 3.86 (1H, ddd, *J* = 2.9, 5.9, 10.3 Hz, C5*H*), 4.14 (1H, dd, *J* = 2.9 Hz, 10.3 Hz, C6*H*H), 4.50, 4.59 (each 1H, dd, *J* = 5.4 Hz, 11.7 Hz, C′6H_2), 4.86 (1H, d, *J* = 7.3 Hz, C′1*H*), 5.49 (1H, dd, *J* = 3.4, 10.3 Hz, C2*H*), 5.71 (2H, m, *J* = 7.3, 10.3 Hz, C4*H*, C′3*H*), 5.80 (1H, t, *J* = 7.3 Hz, C′2*H*), 5.87 (1H, t, *J* = 9.8 Hz, C3*H*), 6.49 (1H, d, *J* = 3.4 Hz, C1*H*), 7.18–8.08 (40H, *aromatic protons*). FD-MS (%, rel int) 1207 (5, $[M+H]^+$), 1101 (20, $[M-Bz]^+$), 1085 (36, $[M-BzO]^+$), 595 (25, 1-deoxy-thioglucopyranose$^+$), 105 (100, $PhCO^+$). FD-HRMS Found *m*/*z* = 1207.2904. Calcd for $C_{68}H_{55}O_{17}S_2$: $[M+H]^+$, 1207.2881.

4.19.7. Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-[2′,3′,4′,6′-tetra-*O*-pivaloyl-5′-deoxy-5′-thio-β-D-glucopyranosyl]-α-D-glucopyranose (30) (run 12). According to *general procedure B*, treatment of **13** (13.9 mg, 20.5 μmol) with **16a** (10.0 mg, 20.5 μmol) and BF_3OEt_2 (3.0 μL) gave **30**

(14.4 mg, 14.1 μmol, 69%). The ^{1}H NMR spectrum indicated that this sample consists of only the β-anomer. $[\alpha]_D^{26}$ +19° (*c* 1.5, $CHCl_3$). IR (film) 2970, 1735, 1480, 1455, 1280, 1135, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.09, 1,12, 1.12, 1.17 (each 9H, s, $(CH_3)_3CCO$), 3.08 (1H, ddd, *J* = 2.9, 5.4, 10.3 Hz, C5′*H*), 3.43 (3H, s, C*H*$_3$O), 3.67 (1H, dd, *J* = 7.3, 10.3 Hz, C6*H*H), 3.87 (1H, dd, *J* = 1.5, 10.3 Hz, C6*H*H), 4.07 (1H, dd, *J* = 5.4, 11.7 Hz, C6′*H*H), 4.11 (1H, dd, *J* = 2.9, 11.7 Hz, C6′*H*H), 4.20 (1H, ddd, *J* = 1.5, 7.3, 10.3 Hz, C5*H*), 4.61 (1H, d, *J* = 8.8 Hz, C1′*H*), 5.12 (1H, d, *J* = 3.9 Hz, C1*H*), 5.13 (1H, t, *J* = 9.3 Hz, C3′*H*), 5.19 (1H, dd, *J* = 3.9, 9.8 Hz, C2*H*), 5.29 (1H, t, *J* = 8.8 Hz, C2′*H*), 5.31 (1H, dd, *J* = 9.3, 10.3 Hz, C4′*H*), 5.33 (1H, dd, *J* = 9.8, 10.3 Hz, C4*H*), 6.10 (1H, t, *J* = 9.8 Hz, C3*H*), 7.23–7.52 (14H, *aromatic protons*), 7.80–7.96 (6H, *aromatic protons*). FD-MS (%, rel int) 1021 (36, $[M+H]^+$), 1020 (11, M^+), 919 (40, $[M-PivO]^+$), 105 (40, $PhCO^+$), 85 (40, Piv^+), 57 (100, $(CH_3)_3C^+$), FD-HRMS Found *m*/*z* = 1020.4170. Calcd for $C_{54}H_{68}O_{17}S$: M^+, 1020.4177.

4.19.8. 4-Nitrophenyl 2,3,4-tri-*O*-benzoyl-6-*O*-[2′,3′,4′,6′-tetra-*O*-pivaloyl-5′-deoxy-5′-thio-β-D-glucopyranosyl]-α-D-glucopyranose (31) (run 13). According to *general procedure B*, treatment of **13** (33.0 mg, 48.9 μmol) with **16b** (30.0 mg, 48.9 μmol) and BF_3OEt_2 (3.4 μL) gave **31** (47.7 mg, 42.1 μmol, 86%). $[\alpha]_D^{26}$ +48° (*c* 1.50, $CHCl_3$). IR (film) 2970, 1730, 1275, 1250, 1130, 1110, 1035, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.09, 1.11, 1,12, 1.16 (each 9H, s, $(CH_3)_3CCO$), 3.08 (1H, ddd, *J* = 2.9, 5.4, 10.3 Hz, C5′*H*), 3.70 (1H, dd, *J* = 7.3, 10.7 Hz, C6*H*H), 3.88 (1H, dd, *J* = 2.4, 10.7 Hz, C6*H*H), 4.05 (1H, dd, *J* = 5.4, 11.7 Hz, C6′*H*H), 4.09 (1H, dd, *J* = 2.9, 11.7 Hz, C6′*H*H), 4.30 (1H, ddd, *J* = 2.4, 7.3, 9.8 Hz, C5*H*), 4.56 (1H, d, *J* = 8.3 Hz, C1′*H*), 5.10 (1H, dd, *J* = 8.3, 9.3 Hz, C3′*H*), 5.25 (1H, t, *J* = 8.3 Hz, C2′*H*), 5.29 (1H, dd, *J* = 9.3, 10.3 Hz, C4′*H*), 5.39 (1H, dd, *J* = 3.4, 10.3 Hz, C2*H*), 5.50 (1H, t, *J* = 9.8 Hz, C4*H*), 5.92, (1H, d, *J* = 3.4 Hz, C1*H*), 6.30 (1H, t, *J* = 10.3 Hz, C3*H*), 7.25–7.53 (11H, *aromatic protons*), 7.84–7.85 (6H, *aromatic protons*), 8.27 (2H, d, *J* = 9.3 Hz, *aromatic protons*). FD-MS (%, rel int) 1128 (10, $[M+H]^+$), 1127 (8.9, M^+), 991 (100, $[M+2H-PNPO]^+$), 990 (53, $[M+H-PNPO]^+$), 989 (67, $[M-PNPO]^+$), 85 (40, Piv^+), FD-HRMS Found *m*/*z* = 1127.4178. Calcd for $C_{59}H_{69}O_{19}NS$: M^+, 1127.4185.

4.19.9. 4-*O*-[2′,3′,4′,6′-Tetra-*O*-acetyl-5′-deoxy-5′-thio-α-D-glucopyranosyl]-1,2,3,6-tetra-*O*-acetyl-5-deoxy-5-thio-α-D-glucopyranose (32) (run 14). According to *general procedure B*, treatment of **11** (20.8 mg, 40.9 μmol) with **22** (14.9 mg, 40.9 μmol) and TESOTf (402 μmol/mL solution in CH_2Cl_2, 10.2 μL, 0.1 equiv) in CH_2Cl_2 (400 μL) gave **32** (1.4 mg, 2.05 μmol, 5.0%) as a syrup. $[\alpha]_D^{26}$ +300° (*c* 0.18, $CHCl_3$). IR (film) 2960, 1750, 1375, 1045, 1020 cm^{-1}. ^{1}H NMR (C_6D_6) δ 1.52, 1.61, 1.63, 1.66, 1.69, 1.71, 1.76, 1.92 (each 3H, s, C*H*$_3$CO), 3.29 (1H, ddd, *J* = 3.4, 5.4, 10.2 Hz, C5*H*), 3.63 (1H, ddd, *J* = 2.9, 3.9, 10.3 Hz, C′5*H*), 4.08 (1H, dd, *J* = 3.4, 12.2 Hz, C6*H*H), 4.15 (1H, dd, *J* = 9.3, 10.2 Hz, C4*H*), 4.21 (1H, dd, *J* = 2.9, 12.2 Hz, C′6*H*H), 4.26 (1H, dd, *J* = 5.4, 12.2 Hz, C6*H*H), 4.61 (1H, dd, *J* = 3.9, 12.2 Hz, C′6*H*H), 5.22 (1H, dd, *J* = 2.9, 9.3 Hz, C2*H*), 5.36 (1H, d, *J* = 3.9 Hz, C′1*H*), 5.46 (1H, dd, *J* = 3.9, 9.8 Hz, C′2*H*), 5.63 (1H, dd, *J* = 9.8, 10.3 Hz, C′4*H*), 5.80 (1H, t, *J* = 9.3 Hz, C3*H*), 5.87 (1H, t, *J* = 9.8 Hz, C′3*H*), 6.25 (1H, d, *J* = 2.9 Hz, C1*H*), FD-MS (%, rel int) 711 (27, $[M+H]^+$), 710 (26, M^+), 651 (100, $[M-AcO]^+$), 650 (86, $[M-AcOH]^+$). FD-HRMS Found *m*/*z* = 710.1520. Calcd for $C_{28}H_{38}O_{17}S_2$: M^+, 710.1550.

4.19.10. 4-*O*-[2′,3′,4′,6′-Tetra-*O*-acetyl-5′-deoxy-5′-thio-α-D-glucopyranosyl]-1,2,3,6-tetra-*O*-benzoyl-5-deoxy-5-thio-α-D-glucopyranose (33) (run 15). According to *general procedure B*, treatment of **11** (10.4 mg, 16.2 μmol) with **18** (8.2 mg, 16.2 μmol) and TESOTf (162 μmol/mL solution in CH_2Cl_2, 10 μL, 0.1 equiv) in CH_2Cl_2 (400 μL) gave C2 deprotected α-glycoside **34** (0.1 mg) and acetate **35** (0.1 mg). Signals corresponding to the desired disaccharide **33** were not detected in the ^{1}H NMR spectrum.

4.19.10.1. Physical data of 4-*O*-[3′,4′,6′-tri-*O*-acetyl-5′-deoxy-5′-thio-α-D-glucopyranosyl]-1,2,3,6-tetra-*O*-benzoyl-α-D-glucopyranose (34). $[\alpha]_D^{26}$ +168° (*c* 0.14, $CHCl_3$). IR (film) 3455, 2920, 1725, 1265, 1105, 1070, 1025, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.94, 1.98, 2.01 (each 3H, s, C*H*$_3$CO), 3.36 (1H, br, C5′*H*), 3.62 (1H, br, C2′*H*), 3.80 (1H, dd, *J* = 2.9, 12.2 Hz, C6′*H*H), 3.87 (1H, ddd, *J* = 3.4, 4.3, 10.3 Hz, C5*H*), 4.31 (1H, dd, *J* = 4.3, 12.2 Hz, C6′*H*H), 4.53 (1H, dd, *J* = 9.8, 10.3 Hz, C4*H*), 4.55 (1H, dd, *J* = 3.4, 11.7 Hz, C6*H*H), 4.77 (1H, dd, *J* = 4.3, 11.7 Hz, C6*H*H), 5.11 (1H, d, *J* = 3.9 Hz, C1′*H*), 5.13–5.16 (2H, C3′*H*, C4′*H*), 5.75 (1H, dd, *J* = 3.4, 10.3 Hz, C2*H*), 6.24 (1H, t, *J* = 9.8 Hz, C3*H*), 6.56 (1H, d, *J* = 3.4 Hz, C1*H*), 7.16–8.17 (15H, *aromatic protons*). FD-MS (%, rel int) 916 (18, M^+), 857 (30, $[M-AcO]^+$), 811 (19, $[M-PhCO]^+$), 795 (18, $[M-BzO]^+$), 595 (35, $[M-thioglucose]^+$), 105 (100, $PhCO^+$), FD-HRMS Found *m*/*z* = 916.2111. Calcd for $C_{46}H_{44}O_{16}S_2$: M^+, 916.2071.

4.19.10.2. Physical data of 1,2,3,6-tetra-*O*-benzoyl-4-*O*-acetyl-5-deoxy-5-thio-α-D-glucopyranose (35). $[\alpha]_D^{22}$ +222° (*c* 0.33, $CHCl_3$). IR (film) 2960, 2920, 1730, 1265, 1090, 1070, 1020, 710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.90 (3H, s, C*H*$_3$CO), 3.91 (1H, ddd, *J* = 3.4, 4.9, 10.3 Hz, C5*H*), 4.50 (1H, dd, *J* = 3.4, 12.2 Hz, C6*H*H), 4.58 (1H, dd, *J* = 4.9, 12.2 Hz, C6*H*H), 5.76 (1H, dd, *J* = 3.4, 10.3 Hz, C2*H*), 5.78 (1H, t, *J* = 10.3 Hz, C4*H*), 6.11 (1H, t, *J* = 10.3 Hz, C3*H*), 6.58 (1H, d, *J* = 3.4 Hz, C1*H*), 7.22–7.53 (12H, *aromatic protons*), 7.79, 7.90, 8.07, 8.11 (each 2H, d, *J* = 7.3 Hz, *aromatic protons*), FD-MS (%, rel int) 654 (4.0, M^+), 595 (19, $[M-AcO]^+$), 549 (20, $[M-PhCO]^+$), 533 (77, $[M-BzO]^+$), 105 (100, $PhCO^+$).

4.19.11. 2,3,4,6-Tetra-*O*-pivaloyl-5-deoxy-5-thio-D-glucal (36) (run 17). According to *general procedure B*, treatment of **13** (31.8 mg, 47.0 μmol) with **17** (35.2 mg, 69.6 μmol) and BF_3OEt_2 (2.5 μL) in CH_2Cl_2 (1.0 mL) gave **36** (2.5 mg, 4.7 μmol, 10%) as a syrup. Signals corresponding to the desired disaccharide were not detected in the ^{1}H NMR spectrum, and alchol **17** (29.4 mg) was recovered. $[\alpha]_D^{22}$ +28° (*c* 0.11, $CHCl_3$), IR (film) 2970, 1740, 1480, 1275, 1130 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ

1.18, 1.18, 1.20, 1.20 (each 9H, s, $(CH_3)_3CCO$), 3.54 (1H, dd, J = 5.9, 7.3, Hz, C5*H*), 4.23, (1H, dd, J = 5.9, 11.7 Hz, C6*H*H), 4.41 (1H, dd, J = 7.3, 11.7 Hz, C6*H*H), 5.33 (1H, dd, J = 3.9, 5.9 Hz, C4*H*), 5.52 (1H, d, J = 3.9 Hz, C3*H*), 6.02 (1H, s, C1*H*), FD-MS (%, rel int) 515 (38, $[M+H]^+$), 514 (100, M^+), 430 (21, $[M+H-Piv]^+$), 429 (67, $[M-Piv]^+$), 85 (75, Piv^+), 57 (13, $(CH_3)_3C^+$), FD-HRMS Found m/z = 514.2576. Calcd for $C_{26}H_{42}O_8S$: M^+, 514.2600.

4.20. Glycosylation reaction of 5-thioglycosyl donor bearing ethereal protective group at C2-alcohols (Table 3)

4.20.1. 1,2,3,4-Tetra-*O*-benzoyl-6-*O*-[2′,3′,4′,6′-tetra-*O*-benzyl-5′-deoxy-5′-thio-α-D-glucopyranosyl]-5-deoxy-5-thio-α-D-glucopyranose (38) (run 1). According to *general procedure B*, a mixture of **14** (7.5 mg, 10.7 μmol) with **19** (9.5 mg, 15.5 μmol) and freshly activated powdered MS4A (100 mg) in CH_2Cl_2 (0.5 mL) was stirred at room temperature for 1 h. After the mixture was cooled to −78 °C, TESOTf (42.8 μmol/mL solution in CH_2Cl_2, 10 μL, 0.04 equiv) was added to the suspension. After stirring for 2 h at −78 °C, the mixture was allowed to warm to room temperature over additional 1 h. Pyridine was added to the mixture at −78 °C and it was passed through silica gel pad and then concentrated in vacuo. Purification by silica gel column chromatography (EtOAc/hexane 25:75) gave **38** (10.0 mg, 8.67 μmol, 81%) as amorphous powder. $[\alpha]_D^{25}$ +109° (*c* 0.68, $CHCl_3$). IR (film) 2920, 2860, 1730, 1260, 1090, 1070, 705 cm^{-1}. ^1H NMR ($CDCl_3$) δ 3.16 (1H, ddd, J = 2.4, 2.9, 10.3, C′5*H*), 3.32 (1H, dd, J = 2.4, 10.3 Hz, C′6*H*), 3.52 (1H, dd, J = 2.9, 9.8 Hz, C6*H*H), 3.74 (1H, dd, J = 2.9, 10.3 Hz, C′2*H*), 3.78 (1H, t, J = 10.3 Hz, C′4*H*), 3.90 (1H, t, J = 10.3 Hz, C3′*H*), 3.90 (1H, dd, J = 2.9, 10.3 Hz, C′6*H*H), 4.00 (1H, ddd, J = 2.9, 6.5, 10.3, C5*H*), 4.08 (1H, dd, J = 6.5, 9.8 Hz, C6*H*H), 4.32 (1H, d, J = 2.9 Hz, C′1*H*), 4.40 (2H, s, $ArCH_2O$), 4.55, 4.87 (each 1H, d, J = 10.7 Hz, $ArCH_2O$), 4.57, 4.69 (each 1H, d, J = 12.2 Hz, $ArCH_2O$), 4.77, 4.87 (each 1H, d, J = 10.7 Hz, $ArCH_2O$), 5.82 (1H, dd, J = 2.9, 10.3 Hz, C2*H*), 5.94 (1H, t, J = 10.3 Hz, C4*H*), 6.24 (1H, t, J = 10.3 Hz, C3*H*), 6.64 (1H, d, J = 2.9 Hz, C1*H*), 7.00–8.20 (40H, *aromatic protons*). FD-MS (%, rel int) 1151 (65, $[MH]^+$), 1150 (100, M^+), 1043 (86, $[M-BnO]^+$). FD-HRMS Found m/z = 1150.3633. Calcd for $C_{68}H_{62}O_{13}S_2$: M^+, 1150.3632.

4.20.2. 1,2,3,6-Tetra-*O*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-benzyl-5′-deoxy-5′-thio-α-D-glucopyranosyl]-5-deoxy-5-thio-α-D-glucopyranose (39) (run 2). According to *general procedure B*, treatment of **14** (9.0 mg, 11.9 μmol) with **22** (5.1 mg, 14.0 μmol) and TESOTf (59.5 μmol/mL in CH_2Cl_2 solution, 10 μL, 0.05 equiv) gave **39** (10.1 mg, 11.2 μmol, 94%) as a syrup. $[\alpha]_D^{25}$ +119° (*c* 0.74, $CHCl_3$). IR (film) 3030, 2920, 2860, 1751, 1455, 1365, 1215, 1065, 740, 701 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.89, 1.97, 1.98, 2.16 (each 3H, s, CH_3CO), 3.14 (1H, br, C′5*H*), 3.50 (1H, dd, J = 1.9, 9.7 Hz, C′6*H*H), 3.60 (1H, ddd, J = 3.9, 4.4, 10.2 Hz, C5*H*), 3.79–3.84 (3H, C′2*H*, C′3*H*, C′4*H*), 3.89 (1H, dd, J = 3.9, 9.7 Hz, C′6*H*H), 4.34 (1H, dd, J = 9.2, 10.2 Hz, C4*H*), 4.40–4.50 (2H, $C6H_2$), 4.42, 4.45 (each 1H, d, J = 12.2 Hz, $ArCH_2O$), 4.55, 4.88 (each 1H, d, J = 10.8 Hz, $ArCH_2O$), 4.69, 4.73 (each 1H, d, J = 11.7 Hz, $ArCH_2O$), 4.78, 4.84 (each 1H, d, J = 10.2 Hz, $ArCH_2O$), 5.03 (1H, d, J = 1.9 Hz, C′1*H*), 5.21 (1H, dd, J = 3.4, 10.3 Hz, C2*H*), 5.26 (1H, dd, J = 9.2, 10.3 Hz, C3*H*), 6.07 (1H, d, J = 3.4 Hz, C1*H*), 7.12–7.35 (20H, *aromatic protons*). FD-MS (%, rel int) 903 (67, $[M+H]^+$), 902 (87, M^+), 901 (100, $[M-H]^+$), 843 (39, $[M-AcO]^+$), 795 (49, $[M-BnO]^+$). FD-HRMS Found m/z = 902.3013. Calcd for $C_{48}H_{54}O_{13}S_2$: M^+, 902.3006.

4.20.3. 1,2,3,4-Tetra-*O*-benzoyl-6-*O*-[2′,3′,4′,6′-[tetrakis-*O*-(4-methoxyphenyl)methyl]-5′-deoxy-5′-thio-α-D-glucopyranosyl]-5-deoxy-5-thio-α-D-glucopyranose (40) (run 3). According to *general procedure B*, treatment of **15** (3.4 mg, 4.1 μmol) with **19** (5.3 mg, 8.7 μmol, α:β = 83:17) and TESOTf (20.5μmol/mL in CH_2Cl_2 solution, 10 μL, 0.05 equiv) gave **40** (4.9 mg, 3.9 μmol, 94%) as a syrup. The ^1H NMR spectrum disclosed that this sample consists of an anomeric mixture at the C1 position (α:β = 83:17) however, β-isomer, due to the glucosyl linkage newly formed, was not observed. $[\alpha]_D^{26}$ +136° (*c* 0.28, $CHCl_3$). IR (film) 2923, 1730, 1610, 1510, 1250, 1090, 710 cm^{-1}. ^1H NMR ($CDCl_3$, signals for the main isomer and some for the minor isomer are described. Only for the signal of the minor isomer, 'minor isomer' is mentioned. a = 0.83, b = 0.17) δ 3.13 (1H × a, dd, J = 2.9, 3.9, 10.7 Hz, C′5*H*), 3.28 (1H × a, dd, J = 2.9, 10.2 Hz, C′6*H*H), 3.52 (1H × a, dd, J = 2.9, 9.7 Hz, C6*H*H), 3.66 (1H × a, dd, J = 2.9, 9.8 Hz, C′2*H*), 3.66–3.82 (2H × a, C′3*H*, C′4*H*), 3.73, 3.75, 3.78, 3.78 (each 3H × a, s, CH_3O), 3.83 (1H × a, dd, J = 3.9, 10.7 Hz, C′6*H*H), 3.95–4.05 (2H × a, C5*H*, C6*H*H), 4.21 (1H × a, d, J = 2.9 Hz, C′1*H*), 4.25(1H × b, d, J = 2.9 Hz, C′1*H* (minor isomer)), 4.32, 4.37 (each 1H × a, d, J = 11.8 Hz, $ArCH_2O$), 4.42, 4.75 (each 1H × a, d, J = 10.3 Hz, $ArCH_2O$), 4.47, 4.59 (each 1H × a, d, J = 11.7 Hz, $ArCH_2O$), 4.66, 4.74 (each 1H × a, d, J = 10.2 Hz, $ArCH_2O$), 5.78 (1H × a, dd, J = 3.4, 10.3 Hz, C2*H*), 5.86 (1H × b, dd, J = 8.3, 9.8 Hz, C2*H* (minor isomer)), 5.87 (1H × a, t, J = 10.3 Hz, C4*H*), 5.99 (1H × b, t, J = 8.8 Hz, C′3*H* or C4′*H* (minor isomer)), 6.20 (1H × a, t, J = 10.3 Hz, C3*H*), 6.39 (1H × b, d, J = 8.3 Hz, C1*H* (minor isomer)), 6.62 (1H × a, d, J = 3.4 Hz, C1*H*), 7.05–8.14 (36H, *aromatic protons*). ^{13}C NMR ($CDCl_3$) δ 41.44, 41.47, 55.21, 55.26, 71.28, 71.92, 72.68, 72.76, 72.80, 74.14, 75.06, 75.71, 81.00, 81.52, 82.73, 83.89, 113.67, 113.71, 113.77, 113.81, 128.21, 128.28, 128.35, 128.72, 128.76, 129.23, 129.35, 129.48, 129.57, 129.72, 129.84, 129.97, 130.02, 130.46, 130.89, 131.43, 133.08, 133.24, 133.66, 133.84, 158.98, 159.10, 159.19, 159.26, 164.69, 165.20, 165.21, 165.85. FD-MS (%, rel int) 1271 (9.0, $[M+H]^+$), 1270 (13, M^+), 1149 (100, $[M-PhCOO]^+$). FD-HRMS Found m/z = 1270.4017. Calcd for $C_{72}H_{70}O_{17}S_2$: M^+, 1270.4054.

4.20.4. Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-[2′,3′,4′,6′-[tetrakis-*O*-(4-methoxyphenyl)methyl]-5′-deoxy-5′-thio-α-D-glucopyranosyl]-α-D-glucopyranoside (41) (run 4). According to *general procedure B*, treatment of **15** (9.9 mg, 12.1 μmol) with **16a** (12.2 mg, 24.1 μmol) and TESOTf (60.5 μmol/mL solution in CH_2Cl_2,

10 μL, 0.05 equiv) gave **41** (11.5 mg, 9.90 μmol, 82%, α:β = 88:12) as a syrup. Analytical sample was prepared by preparative silica gel TLC (EtOAc/benzene 7:93).

4.20.4.1. Physical data for α-isomer of 41. $[\alpha]_D^{26}$ +74° (*c* 0.55, $CHCl_3$). R_f = 0.65 (above conditions). IR (film) 2930, 1730, 1510, 1250, 1095, 1065, 1030, 710 cm^{-1}. ^1H NMR (C_6D_6) δ 3.12 (3H, s, C1OC*H*$_3$), 3.28, 3.30, 3.310, 3.311 (each 3H, s, C*H*$_3$O), 3.49 (2H, br d, *J* = 8.8 Hz, C′5*H*, C6′*H*H), 3.57 (1H, dd, *J* = 2.0, 11.2 Hz, C6*H*H), 3.96 (2H, br dd, *J* = 3.4, 9.8 Hz, C′2*H*, C′6*H*H), 4.08 (1H, dd, *J* = 9.3, 9.8 Hz, C′4*H*), 4.15 (1H, dd, *J* = 4.9, 11.2 Hz, C6*H*H), 4.23, 4.295 (each 1H, d, *J* = 11.7 Hz, ArC*H*$_2$O), 4.298 (1H, t, *J* = 9.3 Hz, C′3*H*), 4.35 (1H, ddd, *J* = 1.9, 4.9, 10.3 Hz, C5*H*), 4.53, 4.59 (each 1H, d, *J* = 11.3 Hz, ArC*H*$_2$O), 4.54 (1H, d, *J* = 3.4 Hz, C′1H), 4.67, 5.070 (each 1H, d, *J* = 11.2 Hz, ArC*H*$_2$O), 4.95, 5.074 (each 1H, d, *J* = 10.2 Hz, ArC*H*$_2$O), 5.31 (1H, d, *J* = 3.4 Hz, C1*H*), 5.45 (1H, dd, *J* = 3.4, 10.3 Hz, C2*H*), 6.07 (1H, t, *J* = 10.3 Hz, C4*H*), 6.64 (1H, t, *J* = 10.3 Hz, C3*H*), 6.73–8.15 (31H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 41.9, 54.70, 54.70, 54.73, 54.73, 55.2, 67.7, 68.1, 69.3, 70.0, 71.4, 72.4, 72.9, 75.3, 75.9, 72.8, 81.3, 82.5, 83.6, 85.2, 97.5, 113.89, 113.93, 114.07, 114.18, 128.41, 128.47, 128.53, 129.51, 129.56, 129.63, 129.68, 129.79, 129.81, 129.96, 130.16, 130.19, 130.7, 131.4, 131.9, 132.4, 132.9, 133.11, 133.14, 159.5, 159.6, 159.7, 159.8, 165.4, 165.8, 166.3. FD-MS (%, rel int) 1165 (15, $[M^+ + H]^+$), 1164 (31, 1044 (28, $[M+H-MPM]^+$), 1043 (100, $[M-MPM]^+$). FD-HRMS Found *m*/*z* = 1164.4172. Calcd for $C_{66}H_{68}O_{17}S$: M^+, 1164.4177.

4.20.4.2. Physical data for β-isomer of 41. $[\alpha]_D^{26}$ +34° (*c* 0.25, $CHCl_3$). R_f = 0.60 (above conditions). IR (film) 2915, 1730, 1515, 1280, 1245, 1095, 1070, 1035, 710 cm^{-1}. ^1H NMR (C_6D_6) δ 2.88 (1H, ddd, *J* = 3.4, 4.9, 9.3 Hz, C′5H), 3.10 (3H, s, C1OC*H*$_3$), 3.297, 3.299, 3.299, 3.31 (each 3H, s, C*H*$_3$O), 3.58 (1H, dd, *J* = 7.8, 9.3 Hz, C′3*H*), 3.62 (1H, dd, *J* = 3.4, 9.8 Hz, C′6*H*H), 3.82 (1H, dd, *J* = 4.9, 9.8 Hz, C′6*H*H), 3.87 (1H, dd, *J* = 6.3, 11.2 Hz, C6*H*H), 4.01 (1H, t, *J* = 9.3 Hz, C′4*H*), 4.05 (1H, t, *J* = 7.8 Hz, C′2*H*), 4.20 (1H, dd, *J* = 2.4, 11.2 Hz, C6*H*H), 4.26, 4.32 (each 1H, d, *J* = 11.7 Hz, ArC*H*$_2$O), 4.40 (1H, ddd, *J* = 2.4, 6.3, 10.3 Hz, C5*H*), 4.58, 4.91 (each 1H, d, *J* = 10.8, ArC*H*$_2$O), 4.66 (1H, d, *J* = 7.8 Hz, C′1*H*), 4.81, 5.11 (each 1H, d, *J* = 11.2, ArC*H*$_2$O), 4.88, 5.01 (each 1H, d, *J* = 10.3, ArC*H*$_2$O), 5.28 (1H, d, *J* = 3.4 Hz, C1*H*), 5.53 (1H, dd, *J* = 3.4, 10.3 Hz, C2*H*), 5.88 (1H, t, *J* = 10.2 Hz, C4*H*), 6.68 (1H, t, *J* = 10.3 Hz, C3*H*), 6.76–8.15 (31H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 44.6, 54.7, 54.7, 54.7, 54.7, 55.4, 69.2, 69.8, 70.4, 71.3, 72.6, 73.0, 74.9, 75.1, 75.5, 81.6, 86.0, 86.2, 86.5, 97.4, 113.9, 113.9, 114.0, 114.1, 128.4, 128.5, 128.6, 128.8, 129.3, 129.5, 129.6, 129.7, 129.81, 129.88, 129.91, 130.6, 130.13, 130.16, 130.7, 131.6, 131.7, 131.9, 133.0, 133.18, 133.22, 159.5, 159.6, 159.7, 159.8, 165.7, 165.9, 166.2. FD-MS (%, rel int) 1165 (32, $[M+H]^+$), 1164 (51, M^+), 1044 (53, $[M+H-MPM]^+$), 1043 (100, $[M-MPM]^+$). FD-HRMS Found *m*/*z* = 1164.4142. Calcd for $C_{66}H_{68}O_{17}S$: M^+, 1164.4177.

4.20.5. 1,2,3,6-Tetra-*O*-acetyl-4-*O*-[2′,3′,4′,6′-[tetrakis-*O*-(4-methoxyphenyl)methyl]-5′-deoxy-5′-thio-α-D-glucopyranosyl]-5-deoxy-5-thio-α-D-glucopyranose (42), (run 5). According to *general procedure B*, treatment of **15** (7.6 mg, 9.3 μmol) with **22** (6.0 mg, 16.5 μmol) and TESOTf (46.5 μmol/mL, 10 μL, 0.05 equiv) gave **42** (5.7 mg, 5.6 μmol, 60%) as a syrup. $[\alpha]_D^{26}$ +83° (*c* 0.40, $CHCl_3$). IR (film) 2915, 2850, 1750, 1610, 1510, 1245, 1220, 1095, 1030, 821 cm^{-1}. ^1H NMR (C_6D_6) δ 1.49, 1.61, 1.63, 1.64 (each 3H, s, C*H*$_3$CO), 3.25, 3.256, 3.262, 3.27 (each 3H, s, C*H*$_3$O), 3.54 (1H, ddd, *J* = 2.4, 4.4, 10.3 Hz, C′5*H*), 3.60 (1H, ddd, *J* = 3.4, 5.4, 10.3 Hz, C5*H*), 3.67 (1H, dd, *J* = 2.4, 9.8 Hz, C′6*H*H), 3.95 (1H, dd, *J* = 2.9, 9.3 Hz, C′2*H*), 4.01 (1H, dd, *J* = 4.4, 9.8 Hz, C′6*H*H), 4.07 (1H, dd, *J* = 9.3, 10.3 Hz, C4′*H*), 4.18 (1H, t, *J* = 9.3, C′3*H*), 4.28, 4.31 (each 1H, d, *J* = 11.7 Hz, ArC*H*$_2$O), 4.32 (1H, dd, *J* = 8.8, 10.3 Hz, C4*H*), 4.54 (1H, dd, *J* = 5.4, 12.2 Hz, C6*H*H), 4.60, 4.75 (each 1H, d, *J* = 11.7 Hz, ArC*H*$_2$O), 4.65 (1H, dd, *J* = 3.4, 12.2 Hz, C6*H*H), 4.66, 5.01 (each 1H, d, *J* = 10.7 Hz, ArC*H*$_2$O), 4.94, 4.98 (each 1H, d, *J* = 10.7 Hz, ArC*H*$_2$O), 5.14 (1H, d, *J* = 3.0 Hz, C′1*H*), 5.40 (1H, dd, *J* = 2.9, 9.8 Hz, C2*H*), 5.88 (1H, dd, *J* = 8.8, 9.8 Hz, C3*H*), 6.28 (1H, d, *J* = 2.9 Hz, C1*H*), 6.73-7.33 (16H, *aromatic protons*). FD-MS (%, rel int) 1023 (27, $[MH]^+$), 1022 (19, M^+), 1021 (22, $[M-H]^+$), 901 (100, $[M-MPM]^+$). FD-HRMS Found *m*/*z* = 1022.3392. Calcd for $C_{52}H_{62}O_{17}S_2$: M^+, 1022.3428.

4.20.6. Methyl 2,3-di-*O*-benzoyl-6-*O*-(4-methoxy-phenyl)methyl-4-*O*-[2′,3′,4′,6′-tetrakis-*O*-(4-methoxy-phenyl)-methyl-5′-deoxy-5′-thio-α-D-glucopyranosyl]-α-D-glucopyranoside (43) (run 6). According to *general procedure B*, treatment of **15** (46.7 mg, 56.9 μmol) with **17** (52.4 mg, 100 μmol) and TESOTf (210 μmol/mL solution in CH_2Cl_2, 13.5 μL, 0.05 equiv) gave **43** (58.6 mg, 49.6 μmol, 87%) as a syrup. $[\alpha]_D^{26}$ +78° (*c* 0.74, $CHCl_3$). IR (film) 2950, 1725, 1610, 1515, 1275, 1250, 1100, 1070, 1035 cm^{-1}. ^1H NMR (C_6D_6) δ 2.96 (3H, s, C1OC*H*$_3$), 3.28, 3.29, 3.30, 3.30, 3.31 (each 3H, s, C*H*$_3$O), 3.51 (1H, dd, *J* = 2.5, 9.7 Hz, C′6*H*H), 3.63 (1H, br dt, *J* = 3.4, 9.3 Hz, C′5*H*), 3.73 (1H, br d, *J* = 11.3 Hz, C6*H*H), 3.84 (1H, dd, *J* = 2.9, 9.3 Hz, C′2*H*), 3.95 (1H, dd, *J* = 4.4, 9.7 Hz, C′6*H*H), 4.01 (1H, t, *J* = 10.3 Hz, C′4*H*), 4.10 (1H, br d, *J* = 9.8 Hz, C5*H*), 4.13 (1H, t, *J* = 9.3 Hz, C′3*H*), 4.19 (1H, dd, *J* = 3.5, 11.3 Hz, C6*H*H), 4.24, 4.32 (each 1H, d, *J* = 11.7 Hz, ArC*H*$_2$O), 4.32, 4.58 (each 1H, d, *J* = 11.7 Hz, ArC*H*$_2$O), 4.49, 4.56 (each 1H, d, *J* = 11.7 Hz, ArC*H*$_2$O), 4.61, 5.01 (each 1H, d, *J* = 10.7 Hz, ArC*H*$_2$O), 4.80, 4.84 (each 1H, d, *J* = 10.7 Hz, ArC*H*$_2$O), 4.98 (1H, t, *J* = 9.8 Hz, C4*H*), 5.23 (1H, d, *J* = 3.4 Hz, C1*H*), 5.45 (1H, d, *J* = 2.9 Hz, C′1*H*), 5.54 (1H, dd, *J* = 3.4, 9.8 Hz, C2*H*), 6.65 (1H, t, *J* = 9.8 Hz, C3*H*), 6.73–8.17 (30H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 42.1, 54.34, 54.38, 54.5, 54.6, 67.8, 69.0, 70.4, 71.8, 72.7, 72.9, 73.2, 73.3, 73.6, 75.1, 75.3, 79.4, 81.9, 83.0, 84.4, 97.0, 113.5, 113.6, 113.7, 113.8, 113.9, 128.1, 128.2, 129.1, 129.27, 129.31, 129.9, 130.2, 130.3, 130.51, 130.53, 131.4, 131.9, 132.68, 132.75, 159.1, 159.3, 159.38, 159.44, 159.5, 165.7, 165.8. FD-MS (%, rel int) 1180 (28, M^+), 1060 (79, $[M+H-MPM]^+$), 1059 (72, $[M-MPM]^+$). FD-HRMS

Found m/z = 1180.4487. Calcd for $C_{67}H_{72}O_{17}S$: M^+, 1180.4490.

4.21. Methyl 6-*O*-(deoxy-5′-thio-β-D-glucopyranosyl)-α-D-glucopyranoside (1)

A solution of β-**27** (13.7 mg, 12.4 μmol) in MeOH (2.0 mL) was stirred with NaOMe (5.0 mg) at room temperature for 1 h. After DOWEX 50W (H^+ form) was added until the solution was neutralized, the mixture was filtered and the filtrate was concentrated in vacuo. The residue was passed through a SepPak ODS® to give **1** (4.6 mg, 12.4 μmol, 100%). Since this sample was soluble in only H_2O, IR spectrum was not measured. $[\alpha]_D^{22}$ +33° (*c* 0.29, H_2O), ^1H NMR (D_2O) δ 2.98 (1H, ddd, *J* = 3.4, 6.7, 9.8 Hz, C5′*H*), 3.35 (1H, t, *J* = 9.3 Hz, C3′*H*), 3.46 (3H, s, C*H*$_3$O), 3.51 (1H, t, *J* = 9.8 Hz, C4*H*), 3.58 (1H, dd, *J* = 3.9, 9.8 Hz, C2*H*), 3.62 (1H, dd, *J* = 9.3, 9.8 Hz, C4′*H*), 3.693 (1H, t, *J* = 9.8 Hz, C3*H*), 3.696 (1H, t, *J* = 9.3 Hz, C2′*H*), 3.81 (1H, ddd, *J* = Hz, C5*H*), 3.87 (1H, dd, *J* = 6.4, 11.7 Hz, C6′*H*H), 3.93 (1H, dd, *J* = 4.9, 11.2 Hz, C6*H*H), 3.97 (1H, dd, *J* = 3.4, 11.7 Hz, C6′*H*H), 4.11 (1H, dd, *J* = 2.0, 11.2 Hz, C6*H*H), 4.68 (1H, d, *J* = 9.3 Hz, C1′*H*), 4.82 (1H, d, *J* = 3.9 Hz, C1*H*), ^{13}C NMR (D_2O) δ 45.5, 55.5, 60.5, 69.5, 69.9, 70.7, 71.3, 73.1, 73.3, 76.7, 76.8, 83.4, 99.6, FAB-MS (negative mode, %, rel int) 371 (26, $[M-H]^-$), FAB-HRMS (negative mode) Found m/z = 371.1017. Calcd for $C_{13}H_{23}O_{10}S$: $[M-H]^-$, 371.1012.

4.22. 4-Nitrophenyl 6-*O*-(5′-deoxy-5′-thio-β-D-glucopyranosyl)-α-D-glucopyranoside (46)

A solution of β-**28** (20.5 mg, 17.0 μmol) in MeOH (2.0 mL) was stirred with NaOMe (5.0 mg) at room temperature for 1 h. After DOWEX 50W (H^+ form) was added until the solution was neutralized, the mixture was filtered and the filtrate was concentrated in vacuo. The residue was passed through a SepPak ODS® to give **46** (6.5 mg, 13.5 μmol, 79%). Since this sample was soluble in only H_2O, IR spectrum was not measured. $[\alpha]_D^{26}$ +31° (*c* 0.67, H_2O). ^1H NMR (D_2O) δ 2.87 (1H, ddd, *J* = 3.4, 5.8, 10.2 Hz, C5′*H*), 3.27 (1H, t, *J* = 8.8 Hz, C3′*H*), 3.51 (1H, dd, *J* = 8.8, 10.2 Hz, C4′*H*), 3.58 (1H, t, *J* = 8.8 Hz, C2′*H*), 3.59 (1H, t, *J* = 8.8 Hz, C4*H*), 3.76 (1H, dd, *J* = 5.8, 11.7 Hz, C6′*H*H), 3.83 (1H, dd, *J* = 3.4, 9.8 Hz, C2*H*), 3.85 (1H, dd, *J* = 3.4, 11.7 Hz, C6′*H*H), 3.88–4.02 (4H, C3*H*, C5*H*, C6H_2), 4.56 (1H, d, *J* = 8.8 Hz, C1′*H*) 5.87 (1H, d, *J* = 3.4 Hz, C1*H*), 7.33, 8.30 (each 2H, d, *J* = 9.3 Hz, *aromatic protons*), ^{13}C NMR (D_2O) δ 46.2, 61.2, 70.2, 71.1, 71.8, 72.7, 73.8, 72.9, 77.4, 77.7, 84.1, 97.3, 117.8, 127.0, FAB-MS (negative mode, %, rel int) 479 (3.9, M^-), 478 (2.3, $[M-H]^-$), FAB-HRMS (negative mode) Found m/z = 479.1115. Calcd for $C_{18}H_{25}O_{12}NS$: M^-, 479.1097.

4.23. Methyl 6-*O*-(5′-deoxy-5′-thio-α-D-glucopyranosyl)-α-D-glucopyranoside (47)

A solution of **41** (15.0 mg, 12.9 μmol) in MeOH (1.0 mL) was stirred with NaOMe (3.5 mg, 64.4 μmol) at room temperature for 1 h. After DOWEX 50W (H^+ form) was added until the solution was neutralized, the mixture was filtered and the filtrate was concentrated in vacuo. Without further purification, the residue was stirred with DDQ (23.4 mg, 103 μmol) in a mixture of CH_2Cl_2 (1.5 mL) and H_2O (150 μL) at room temperature for 20 h. Volatiles of the reaction mixture were removed under reduced pressure. Purification of the residue by silica gel column chromatography (MeOH/EtOAc 20:80) afforded **47** (4.2 mg, 11.3 μmol, 88%, 2 steps). Since this sample was soluble in only H_2O, IR spectrum was not measured. $[\alpha]_D^{25}$ +21° (*c* 0.09, H_2O). ^1H NMR (D_2O) δ 3.10 (1H, ddd, *J* = 3.4, 4.9, 10.3 Hz,C′5*H*), 3.43 (3H, s, C*H*$_3$O), 3.49 (1H, dd, *J* = 8.8, 9.8 Hz, C4*H*), 3.57 (1H, dd, *J* = 3.9, 9.8 Hz, C2*H*), 3.64 (1H, dd, *J* = 8.8, 10.3 Hz, C′4*H*), 3.67 (1H, dd, *J* = 8.8, 9.8 Hz, C3*H*), 3.69 (1H, dd, *J* = 8.8, 9.3 Hz, C′3*H*), 3.72 (1H, dd, *J* = 2.0, 11.0 Hz, C6*H*H), 3.83 (1H, m, C5*H*), 3.85 (1H, dd, *J* = 2.9, 9.3 Hz, C′2*H*), 3.87 (1H, dd, 3.4, 11.4 Hz, C6′*H*H), 3.92 (1H, dd, *J* = 4.6, 11.2 Hz, C′6*H*H), 4.13 (1H, dd, *J* = 4.6 Hz, 11.2 Hz, C6*H*H), 4.77 (1H, *J* = 2.9 Hz, C1′*H*), 4.82 (1H, d, *J* = 3.9 Hz, C1*H*). ^{13}C NMR (D_2O) δ 43.1, 55.3, 60.2, 66.6, 69.7, 70.2, 71.3, 73.5, 73.6, 74.2, 75.4, 81.9, 99.4. FAB-MS (negative mode,%, rel int) 371 (21, $[M-H]^-$). FAB-HRMS (negative mode) Found m/z = 371.1000. Calcd for $C_{13}H_{23}O_{10}S$: ($[M-H]^-$), 371.1012.

4.24. Methyl 4-*O*-(5′-deoxy-5′-thio-α-D-glucopyranosyl)-α-D-glucopyranoside (48)

A solution of **43** (22.0 mg, 18.6 μmol) in a mixture of MeOH (2.5 mL) and 1 M NaOH aqueous solution (300 μL) was stirred vigorously at room temperature for 1.5 h. The reaction mixture was poured into brine and extracted with $CHCl_3$ (×4). The organic extracts were combined, dried over $MgSO_4$, and concentrated in vacuo. After the residue was diluted in a mixture of CH_2Cl_2 (2.5 mL) it was and H_2O (250 μL) stirred with DDQ (30.0 mg, 132 μmol) for 16 h. To the mixture, H_2O (3.0 mL) and MeOH (10 mL) were added and the mixture was stirred with a catalytic amount of concd HCl for an additional 30 min. The solution was concentrated under reduced pressure. Purification of the residue by silica gel chromatography (MeOH/EtOAc 15:85) gave **48** (5.3 mg, 14.2 μmol, 77%, 2 steps). Since this sample was soluble in only H_2O, IR spectrum was not measured. $[\alpha]_D^{27}$ + 28° (*c* 0.08, H_2O). ^1H NMR (D_2O, 38 °C δ 3.05 (1H, dt, *J* = 4.9, 9.3 Hz, C′5H), 3.42 (3H, s, C1OC*H*$_3$), 3.59 (1H, dd, *J* = 3.9, 9.7 Hz, C2*H*), 3.62–3.67 (2H, C′3*H*, C′4*H*), 3.73–3.77 (2H, C4*H*, C5*H*), 3.82–3.85 (2H, C′2*H*, C6*H*H), 3.88–3.90 (3H, C′6H_2, C6*H*H), 3.95 (1H, t, *J* = 9.7 Hz, C3*H*), 4.81 (1H, d, *J* = 3.9 Hz, C1*H*), 5.33 (1H, d, *J* = 3.4 Hz, C′1*H*). ^{13}C NMR (D_2O, 38 °) δ 43.9, 55.2, 60.2, 61.0, 70.2, 71.3, 73.4, 73.9, 74.1, 75.5, 75.6, 82.8, 99.2. FAB-MS (negative mode, %, rel int) 371 (100, $[M-H]^-$). FAB-HRMS (negative mode) Found m/z = 371.0975. Calcd for $C_{13}H_{23}O_{10}S$: ($[M-H]^-$), 371.1012.

4.25. Tetrahydropyranyl 6-*O*-triphenylmethyl-5-deoxy-5-thio-α-D-glucopyranoside (50a)

A solution of **6a** (369 mg, 1.42 mmol) in pyridine (3.5 mL) was stirred with TrCl (607 mg, 2.16 mmol)

and DMAP (17 mg, 142 μmol) at room temperature for 24 h. The mixture was concentrated under reduced pressure, diluted with water, and extracted with EtOAc (×3). The organic extracts were washed with brine, dried over $MgSO_4$, respectively, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (acetone/CH_2Cl_2 20:80) gave **50a** (589 mg, 1.14 μmol, 80%) as a syrup. The ^1H NMR spectrum of this sample indicated that the sample consists of a diastereomeric mixture due to the asymmetric center in the THP group (50:50). IR (film) 3410, 2930, 1445, 1120, 1070, 1020, 970, 755, 700 cm^{-1}. ^1H NMR ($CDCl_3$, some signals could not be assigned due to signals overlapping.) δ 1.50–1.83 (6H, C3′H_2, C4′H_2, C5′H_2), 3.06 (1H × 0.5, dt, J = 4.9, 9.3 Hz, C5H), 3.35 (1H × 0.5, dd, J = 4.9, 10.2, C6HH), 3.49 (1H × 0.5, dd, J = 4.9, 10.2 Hz, C6HH), 3.55 (1H × 0.5, C6HH), 3.66 (1H × 0.5, t, J = 9.3 Hz, C3H), 3.67 (1H × 0.5, t, J = 9.3 Hz, C3H), 3.80 (1H × 0.5, dd, J = 3.4, 9.8 Hz, C2H), 3.82 (1H × 0.5, t, J = 10.2 Hz, C4H), 3.85 (1H × 0.5, dd, J = 3.4, 9.3 Hz, C2H), 4.02 (1H × 0.5, C6′HH), 4.83 (1H × 0.5, d, J = 3.4 Hz, C1H), 4.92 (1H × 0.5, br t, J = 3.4 Hz, C2′H), 4.96 (1H × 0.5, br, C2′H), 4.97 (1H × 0.5, d, J = 3.4 Hz, C1H). FD-MS (%, rel int) 552 (100, M^+), 243 (53, Ph_3P^+). FD-HRMS Found m/z = 522.2072. Calcd for $C_{30}H_{34}O_6S$: M^+, 522.2076.

4.26. Ethoxyethyl 6-*O*-triphenylmethyl-5-deoxy-5-thio-α-D-glucopyranoside (50b)

A solution of the tetraol **6b** (122 mg, 453 μmol) in pyridine (1.0 mL) was stirred with TrCl (703 mg, 2.52 mmol) and DMAP (3.0 mg, 24 μmol) at room temperature for 16 h. After the mixture was concentrated in vacuo, purification of the residue by silica gel column chromatography (acetone/CH_2Cl_2 20:80) gave **50b** (186 mg, 365 μmol, 81%) as a pale yellow oil. The ^1H NMR spectrum of this sample indicated that the sample consists of a diastereomeric mixture due to the asymmetric center in the EE group (50:50). IR (film) 3420, 2980, 2930, 1450, 1075, 950, 760, 710 cm^{-1}. ^1H NMR ($CDCl_3$, some signals could not be assigned due to signals overlapping.) δ 1.21, 1.22 (each 3H × 0.5, t, J = 7.2 Hz, CH_3CH$_2$), 1.35, 1.38 (each 3H × 0.5, d, J = 5.4 Hz, EtOCH(-CH_3)O), 2.56, 2.72 (each 1H × 0.5, br, OH), 2.90 (2H × 0.5, br, OH × 2), 2.95 (2H × 0.5, br, OH × 2), 3.08, 3.26 (each 1H × 0.5, dt, J = 4.9, 10.3 Hz, C5H), 3.37–3.87 (14H × 0.5), 4.65 (1H × 0.5, d, J = 3.4 Hz, C1H), 4.93 (1H × 0.5, d, J = 2.9 Hz, C1H), 4.95, 5.03 (1H × 0.5, q, J = 5.4 Hz, EtOCH(Me)O), EI-MS (%, rel int) 510 (0.3, M^+), 243 (100, Ph_3C^+). EI-HRMS Found m/z = 510.2081. Calcd for $C_{29}H_{34}O_6S$: [M^+], 510.2076.

4.27. Ethoxyethyl 2,3,4-[tris-*O*-(4-methoxyphenyl)methyl]-6-*O*-triphenylmethyl-5-thio-α-D-glucopyranoside (51b)

A solution of **50b** (158 mg, 310 μmol) was added to a suspension of freshly washed NaH (80.0 mg, 3.33 mmol) that was added to a solution of DMF (3.0 mL) at room temperature. After 10 min, MPMBr (ca. 50% in toluene, 400 μL, ca. 1.6 mmol) was added to the mixture and it was stirred at room temperature. After stirring for 40 min, additional NaH (110 mg) and MPMBr (200 μL) were added into the mixture and the resulting mixture was stirred for further additional 12 h. The excess reagents were decomposed by the addition of MeOH (ca. 1.0 mL) and Et_3N (ca. 1.0 mL). After stirring for an additional 30 min, the mixture was poured into water and extracted with Et_2O (×3). The combined ethereal extracts were washed with brine and dried over $MgSO_4$. Purification of the residue by silica gel column chromatography (EtOAc/benzene 4:96) afforded **51b** (167 mg, 191 μmol, 62%) as a syrup. The ^1H NMR spectrum of this sample indicated that the sample consists of a mixture of diastereomers due to the asymmetric center in the EE group (50:50). IR (film) 2935, 1615, 1585, 1515, 1250, 1175, 1140, 1035, 760 cm^{-1}. ^1H NMR (C_6D_6) δ 1.13, 1.18 (each 3H × 0.5, t, CH_3CH$_2$OCH-(CH$_3$)O), 1.35, 1.44 (each 3H × 0.5, d, J = 5.4 Hz, (EtOCH(CH_3)O), 3.288, 3.290, 3.294, 3.294, 3.32, 3.32 (each 3H × 0.5, s, CH_3O), 3.50–3.66 (5H × 0.5, C5H, C6HH, CH$_3$CHHOCH(CH$_3$)O × 3), 3.71–3.75 (3H × 0.5, C6HH × 2, C5H), 3.79 (1H × 0.5, C6HH), 3.94–4.06 (4H × 0.5, C2H × 2, C4H, CH$_3$CHHOCH(CH$_3$)O), 4.11–4.24 (3H × 0.5, C3H × 2, C4H), 4.36, 4.88 (each 1H × 0.5, d, J = 10.2 Hz, ArCH_2O), 4.39, 4.91 (each 1H × 0.5, d, J = 10.7 Hz, ArCH_2O), 4.49, 4.56 (each 1H × 0.5, d, J = 11.2 Hz, ArCH_2O), 4.56, 4.59 (each 1H × 0.5, d, J = 11.3 Hz, ArCH_2O), 4.82, 5.00 (each 1H × 0.5, d, J = 10.7 Hz, ArCH_2O), 4.84, 5.03 (each 1H × 0.5, d, J = 10.7 Hz, ArCH_2O), 4.71, 5.13 (each 1H × 0.5, d, J = 2.9 Hz, C1H), 4.91, 5.18 (1H × 0.5, q, J = 4.9 Hz, EtOCH(CH$_3$)O). FD-MS (%, rel int) 870 (8, M^+), 243 (100, Ph_3C^+). FD-HRMS Found m/z = 870.3820. Calcd for $C_{53}H_{58}O_9S$: [M^+], 870.3802.

4.28. 2,3,4-Tris-*O*-(4-methoxyphenyl)methyl-6-*O*-triphenylmethyl-5-deoxy-5-thio-α-D-glucopyranose (52)

4.28.1. Preparation from 51a. A solution of **51a** (400 mg, 454 μmol) in EtOH (90 mL) was stirred with *p*-TsOH (43.4 mg, 228 μmol) at room temperature for 7 h. The mixture was neutralized with Et_3N and concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/hexane 30:70) afforded **52** (51.9 mg, 74.0 μmol, 16%) as a colorless syrup. The yield was 33% according to the recovery of **51a**. $[\alpha]_D^{26}$ +5.4° (*c* 1.00, $CHCl_3$). IR (film) 3410, 2930, 1610, 1510, 1245, 1175, 1090, 1065, 1030, 755 cm^{-1}. ^1H NMR (C_6D_6) δ 2.48 (1H, br, C1OH), 3.29, 3.30, 3.32 (each 3H, s, CH_3O), 3.64–3.70 (3H, C5H, C6H_2), 3.85 (1H, dd, J = 2.9, 9.3 Hz, C2H), 3.97 (1H, t, J = 8.8 Hz, C3H), 4.05 (1H, t, J = 8.8 Hz, C4H), 4.35, 4.82 (each 1H, d, J = 10.7 Hz, ArCH_2O), 4.38, 4.46 (each 1H, d, J = 10.7 Hz, ArCH_2O), 4.79 (1H, br, C1H), 4.83, 4.92 (each 1H, d, J = 10.7 Hz, ArCH_2O), 6.70–7.64 (27H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 42.4, 54.7, 61.9, 71.8, 72.4, 74.9, 75.9, 82.4, 83.4, 85.0, 87.1, 113.7, 113.9, 114.1, 127.3, 128.1, 129.3, 129.39, 129.41, 129.7, 144.3, 159.4, 159.5, 159.8. FD-MS (%, rel int) 798 (34, M^+). FD-HRMS Found m/z = 798.3229. Calcd for $C_{49}H_{50}O_8S$: [M^+], 798.3226.

4.28.2. Preparation from 51b. A solution of **51b** (9.5 mg, 10.9 μmol) in a mixture of EtOH (700 μL) and PrOH (250 μL) was stirred with PPTS (10.0 mg, 42.7 μmol) at room temperature for 2.5 h. After concentration in vacuo, the residue was diluted again with EtOH (1.0 mL) and then the mixture was stirred for 1 h. After concentration, purification of the residue by silica gel column chromatography (EtOAc/hexane 25:75) gave **52** (8.0 mg, 10.0 μmol, 92%) as a colorless syrup. The ^{1}H NMR and ^{13}C NMR spectra of this sample were identical with those prepared from **51a**.

4.29. 2,3,4-[Tris-*O*-(4-methoxyphenyl)methyl-6-*O*-triphenylmethyl]-5-deoxy-5-thio-α-D-glucopyranosyl trichloroacetimidate (53)

According to *general procedure A*, a solution of **52** (139 mg, 174 μmol) in CH_2Cl_2 (4.0 mL) was stirred with CCl_3CN (260 μL, 2.61 mmol) in the presence of catalytic DBU (3.7 μL, 24.9 μmol, 0.14 equiv) at 0 °C for 40 min. After the mixture was diluted with benzene, the volatiles were completely removed in vacuo. Purification of the residue by silica gel chromatography (EtOAc/hexane 15:85) gave **53** (135 mg, 143 μmol, 82%) as a colorless syrup. ^{1}H NMR ($CDCl_3$) δ 3.43 (1H, ddd, J = 2.4, 3.9, 10.3 Hz, C5*H*), 3.54 (1H, dd, J = 2.4, 9.8 Hz, C6*H*H), 3.58 (1H, dd, J = 3.9, 9.8 Hz, C6*H*H), 3.76, 3.78, 3.79 (each 3H, s, CH_3O), 3.88 (1H, t, J = 9.3 Hz, C3*H*), 3.97 (1H, dd, J = 9.3. 9.8 Hz, C4*H*), 3.99 (1H, dd, J = 2.9, 9.3 Hz, C2*H*), 4.22, 4.63 (each 1H, d, J = 10.3 Hz, ArCH_2O), 4.61, 4.72 (each 1H, d, J = 11.3 Hz, ArCH_2O), 4.67, 4.79 (each 1H, d, J = 10.3 Hz, ArCH_2O), 6.38 (1H, d, J = 2.9 Hz, C1*H*), 6.81, 6.85 (each 2H, J = 8.8 Hz, *aromatic protons*), 7.18-7.43 (23H, *aromatic protons*), 8.61 (1H, s, C(= N*H*)CCl_3). ^{13}C NMR ($CDCl_3$) δ 43.4, 55.2, 61.0, 72.0, 75.1, 75.0, 76.4, 80.9, 82.6, 83.4, 86.5, 91.2, 113.5, 113.69, 113.73, 127.1, 127.8, 128.3, 128.9, 129.2, 129.6, 129.7, 130.16, 130.21, 130.9, 143.4, 159.06, 159.11, 159.16, 161.2. This sample was immediately used for the next glycosylation step.

4.30. Methyl 6-[2′,3′,4′-tris-*O*-(4-methoxyphenyl)methyl-6′-*O*-(triphenyl)methyl-5′-deoxy-5′-thio-α-D-glucopyranosyl]-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (54)

According to *general procedure B*, a suspension of **53** (46.3 mg, 49.1 μmol) and **16a** (27.1 mg, 53.5 μmol) in CH_2Cl_2 (3.0 mL) was stirred in the presence of powdered MS4A (102 mg) for 1 h at room temperature under N_2 atmosphere. After the mixture was cooled to −78 °C, TESOTf (210 μmol/mL solution in CH_2Cl_2, 23.3 μL, 0.05 equiv) was added to the suspension. After stirring for 2 h at the same temperature, pyridine was added to the mixture and the mixture was filtered through silica gel pad and then concentrated in vacuo. Purification of the residue by silica gel chromatography (Et_2O/benzene 2:98) and subsequent preparative TLC afforded **54** (42.0 mg, 32.6 μmol, 67%) and the β-isomer (4.6 mg, 3.6 μmol, 7%) as a colorless syrup (α:β = 90:10).

4.30.1. Physical data for α-54. $[\alpha]_D^{26}$ +59° (*c* 1.10, $CHCl_3$). IR (film) 2935, 1735, 1515, 1250, 1095, 1070, 1035, 755, 710 cm^{-1}. ^{1}H NMR (C_6D_6) δ 3.11 (3H, s, C1OCH_3), 3.31, 3.32, 3.34 (each 3H, s, CH_3O), 3.46 (1H, dt, J = 2.4, 3.9, 10.3 Hz, C′5*H*), 3.53 (1H, dd, J = 2.9, 9.3 Hz, C′6*H*H), 3.58 (1H, dd, J = 2.0, 11.2 Hz, C6*H*H), 3.67 (1H, dd, J = 3.9, 9.3 Hz, C′6*H*H), 4.04 (1H, dd, J = 2.9, 9.3 Hz, C′2*H*), 4.14 (1H, dd, J = 4.9, 11.2 Hz, C6*H*H), 4.17 (1H, dd, J = 9.3, 10.3 Hz, C′4*H*), 4.25 (1H, t, J = 9.3 Hz, C′3*H*), 4.35 (1H, ddd, J = 2.0, 4.9, 9.8 Hz, C5*H*), 4.42, 4.94 (each 1H, d, J = 10.3 Hz, ArCH_2O), 4.53, 4.65 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.60 (1H, d, J = 2.9 Hz, C′1*H*), 4.89, 5.05 (each 1H, d, J = 10.8 Hz, ArCH_2O), 5.30 (1H, d, J = 3.4 Hz, C1*H*), 5.44 (1H, dd, J = 3.4, 10.3 Hz, C2*H*), 6.05 (1H, t, J = 9.8 Hz, C4*H*), 6.62 (1H, dd, J = 9.8, 10.3 Hz, C3*H*), 6.70–8.13 (42H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 42.2, 54.71, 54.75, 55.2, 61.8, 67.7, 69.3, 70.0, 71.5, 72.6, 72.7, 75.0, 76.0, 81.4, 82.4, 83.6, 85.2, 87.0, 97.5, 113.7, 113.9, 114.2, 127.3, 128.1, 128.4, 128.47, 128.53, 129.3, 129.4, 129.6, 129.7, 129.8, 129.9, 130.10, 130.14, 131.4, 131.6, 132.3, 132.9, 133.1, 133.2, 144.3, 159.4, 159.5, 159.8, 165.4, 165.8, 166.3. FD-MS (%, rel int) 1285 (15, $[M-H]^+$), 1286 (14, M^+), 1287 (10, $[M+H]^+$). FD-HRMS Found *m*/*z* = 1286.4717. Calcd for $C_{77}H_{74}O_{16}S$: [M^+], 1286.4698.

4.30.2. Physical data for β-54. $[\alpha]_D^{26}$ +29° (*c* 0.41, $CHCl_3$). IR (film) 2935, 1735, 1515, 1250, 1095, 1070, 1035, 755, 710 cm^{-1}. ^{1}H NMR (C_6D_6) δ 2.84 (1H, ddd, J = 3.9, 4.9, 9.8 Hz, C′5*H*), 3.14 (3H, s, C1OCH_3), 3.30 3.31, 3.31 (each 3H, s, CH_3O), 3.50 (1H, t, J = 8.3 Hz, C′3*H*), 3.61 (1H, dd, J = 4.9, 9.3 Hz, C′6*H*H), 3.67 (1H, dd, J = 3.4, 9.3 Hz, C′6*H*H), 3.90 (1H, dd, J = 6.8, 9.8 Hz, C6*H*H), 4.04 (1H, dd, J = 8.3, 9.8 Hz, C′4*H*), 4.06 (1H, t, J = 8.3 Hz, C′2*H*), 4.20 (1H, dd, J = 2.0, 10.8 Hz, C6*H*H), 4.33, 4.79 (each 1H, d, J = 10.3 Hz, ArCH_2O), 4.45 (1H, ddd, J = 2.0, 6.8, 9.8 Hz, C5*H*), 4.65 (1H, d, J = 8.3 Hz, C′1*H*), 4.82, 4.98 (each 1H, d, J = 10.7 Hz, ArCH_2O), 4.82, 5.13 (each 1H, d, J = 10.7 Hz, ArCH_2O), 5.28 (1H, d, J = 3.4 Hz, C1*H*), 5.54 (1H, dd, J = 3.4, 10.3 Hz, C2*H*), 5.83 (1H, dd, J = 9.8, 10.3 Hz, C4*H*), 6.70 (1H, t, J = 10.3 Hz, C3*H*), 6.70–8.17 (42H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 44.8, 54.7, 54.7, 54.7, 55.4, 62.7, 69.8, 70.1, 70.5, 71.2, 72.6, 74.8, 75.3, 75.7, 81.7, 85.8, 86.3, 86.5, 87.2, 97.4, 113.7, 113.9, 114.0, 127.3, 127.9, 128.1, 128.4, 128.52, 128.54, 128.60, 129.27, 129.30, 129.51, 129.55, 129.7, 129.8, 129.9, 130.0, 130.1, 130.2, 131.3, 131.7, 131.9, 133.0, 133.21, 133.24, 144.3, 159.50, 159.51, 159.7, 165.7, 165.9, 166.2. FD-MS (%, rel int) 1285 (25, $[M-H]^+$), 1286 (34, M^+), 1287 (25, $[M+H]^+$). FD-HRMS Found *m*/*z* = 1286.4706. Calcd for $C_{77}H_{74}O_{16}S$: [M^+], 1286.4698.

4.31. Methyl 6-*O*-[2′,3′,4′-[tris-*O*-(4-methoxyphenyl)methyl]-5′-deoxy-5′-thio-α-D-glucopyranosyl]2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (55)

A solution of **54** (57.3 mg, 44.5 μmol) in a mixture of MeOH (2.0 mL) and THF (400 μL) was stirred with *p*-TsOH (1.0 mg, 5.26 μmol) at room temperature for 5 h. After the addition of Et_3N (20 μL), the mixture was concentrated in vacuo. Purification of the residue

by silica gel chromatography (EtOAc/hexane 35:65) gave **55** (33.0 mg, 31.6 μmol, 71%) as a colorless oil. $[\alpha]_D^{26}$ +93° (*c* 0.60, $CHCl_3$). IR (film): 3520, 2935, 1735, 1615, 1515, 1455, 1280, 1250, 1175, 1095, 1035, 710 cm^{-1}. ^1H NMR (C_6D_6) δ 1.45 (1H, dd, J = 3.9, 7.8 Hz, C′6O*H*), 3.11 (3H, s, C1OCH_3), 3.27, 3.29, 3.32 (each 3H, s, CH_3O), 3.39 (1H, dt, J = 3.9, 10.8 Hz, C′5*H*), 3.53 (1H, dd, J = 2.0, 11.3 Hz, C6*H*H), 3.61 (1H, dt, J = 3.9, 11.2 Hz, C′6*H*H), 3.84–3.91 (3H, C′2*H*, C′3*H*, C′6*H*H), 4.08 (1H, dd, J = 4.9, 11.3 Hz, C6*H*H), 4.30 (1H, t, J = 9.3 Hz, C4′*H*), 4.32 (1H, ddd, J = 2.0, 4.9, 10.3 Hz, C5*H*), 4.51 (1H, d, J = 2.9 Hz, C′1*H*), 4.54, 4.59 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.70, 5.05 (each 1H, d, J = 10.7 Hz, ArCH_2O), 4.91, 5.07 (each 1H, d, J = 10.7 Hz, ArCH_2O), 5.32 (1H, d, J = 3.4 Hz, C1*H*), 5.45 (1H, dd, J = 3.4, 10.3 Hz, C2*H*), 6.09 (1H, t, J = 10.3 Hz, C4*H*), 6.45 (1H, t, J = 10.3 Hz, C3*H*), 6.74–8.15 (27H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 43.5, 54.71, 54.72, 54.75, 55.3, 62.3, 67.6, 69.3, 69.9, 71.4, 72.4, 75.4, 75.9, 72.8, 81.3, 83.1, 83.4, 85.1, 97.5, 113.9, 114.12, 114.21, 127.9, 128.1, 128.35, 128.43, 128.5, 128.6, 129.6, 129.7, 129.8, 129.9, 130.0, 130.2, 131.4, 132.2, 132.9, 133.17, 133.22, 159.5, 159.7, 159.8, 165.5, 165.8, 166.3. FD-MS (%, rel int) 1044 (33, M^+). FD-HRMS Found m/z = 1044.3584. Calcd for $C_{58}H_{60}O_{16}S$: [M^+], 1044.3602.

4.32. Methyl 6-*O*-[[6′-*O*-[2″,3″,4″-[tris-*O*-(4-methoxyphenyl)methyl]-6″-*O*-triphenylmethyl-5″-deoxy-5″-thio-α-D-glucopyranosyl]-2′,3′,4′-[tris-*O*-(4-methoxyphenyl)methyl]-5′-deoxy-5′-thio-α-D-glucopyranosyl]]-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (56)

According to *general procedure B*, a mixture of **55** (39.0 mg, 41.3 μmol) and **53** (40.2 mg, 38.5 μmol) in CH_2Cl_2 (2.7 mL) was stirred in the presence of powdered MS4A (152 mg) for 1 h at room temperature and N_2 atmosphere. After the mixture was cooled to −78 °C, TESOTf (210 μmol/L solution in CH_2Cl_2, 9.8 μL, 0.05 equiv) was added to the suspension. After stirring for 2 h at the same temperature, pyridine was added into the mixture and the resulting mixture was passed through silica gel pad and then concentrated in vacuo. Purification of the residue by silica gel chromatography (Et_2O/benzene 5:95) afforded **56** (35.1 mg, 19.2 μmol, 47%) as a colorless syrup after removal of acetoamide by silica gel column chromatography (EtOAc/hexane 27:73). $[\alpha]_D^{25}$ +96° (*c* 0.57, $CHCl_3$). IR (film) 2935, 1735, 1615, 1515, 1250, 1175, 1095, 1070, 1035, 760, 710 cm^{-1}. ^1H NMR (C_6D_6) δ 3.15 (3H, s, C1OCH_3), 3.28, 3.29, 3.29, 3.30, 3.31, 3.34 (each 3H, s, CH_3O), 3.50–3.71 (6H, C″5*H*, C′5*H*, C6*H*H, C″6H_2, C′6*H*H), 3.88 (1H, dd, J = 2.9, 9.8 Hz, C′2*H*), 4.04 (1H, dd, J = 2.9, 9.3 Hz, C″2*H*), 4.10 (1H, dd, J = 8.8, 10.3, C′4*H*), 4.11 (1H, dd, J = 4.9, 10.7 Hz, C6*H*), 4.18 (1H, dd, J = 8.8, 10.2 Hz, C″4*H*), 4.24 (1H, dd, J = 8.8, 9.3 Hz, C″3*H*), 4.30 (1H, dd, J = 8.8, 9.3 Hz, C′3*H*), 4.34 (1H, ddd, J = 2.4, 4.9, 9.8 Hz, C5*H*), 4.38, 4.92 (each 1H, d, J = 10.7 Hz, ArCH_2O), 4.44 (1H, dd, J = 4.4, 10.3 Hz, C′6*H*H), 4.493, 4.57 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.496 (1H, d, J = 2.9 Hz, C′1*H*), 4.56, 4.67 (each 1H, d, J = 11.3 Hz, ArCH_2O), 4.69 (1H, d, J = 2.9 Hz, C″1*H*), 4.88, 5.08 (each 1H, d, J = 10.7 Hz, ArCH_2O), 4.91, 5.20 (each 1H, d, J = 10.7 Hz, ArCH_2O), 4.94, 5.08 (each 1H, d, J = 10.7 Hz, ArCH_2O), 5.33 (1H, d, J = 3.9 Hz, C1*H*), 5.46 (1H, dd, J = 3.9, 9.8 Hz, C2*H*), 6.07 (1H, t, J = 9.8 Hz, C4*H*), 6.64 (1H, t, J = 9.8 Hz, C3*H*), 6.67–8.13 (54H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 41.6, 54.66, 54.66, 54.70, 54.70, 54.76, 54.76 55.3, 61.8, 67.7, 67.8, 69.4, 70.0, 71.4, 72.1, 72.5, 72.8, 75.1, 75.4, 75.96, 75.99, 80.9, 81.4, 82.2, 82.6, 83.5, 83.6, 85.2, 85.4, 87.0, 97.5, 113.6, 113.9, 114.0, 114.1, 127.2, 127.9, 128.1, 128.3, 128.46, 128.51, 128.6, 129.3, 129.48, 129.51, 129.56, 129.60, 129.7, 129.9, 130.1, 130.2, 131.4, 131.8, 132.2, 132.9, 133.1, 133.2, 144.3, 159.36, 159.43, 159.67, 159.71, 165.4, 165.8, 166.2. ESI-MS (%, rel int) 1824 (82, $[M+Na]^+$), 1863 (21, $[M+K]^+$). ESI-HRMS Found m/z = 1847.6650. Calcd for $C_{107}H_{108}O_{23}S_2Na$: $[M+Na]^+$, 1847.6621.

4.33. Methyl 6-*O*-[[6′-*O*-[2″,3″,4″-[tris-*O*-(4-methoxyphenyl)methyl]-5″-deoxy-5″-thio-α-D-glucopyranosyl]-2′,3′,4′-[tris-*O*-(4-methoxyphenyl)methyl]-5′-deoxy-5′-thio-α-D-glucopyranosyl]]-2,3,4-tris-*O*-benzoyl-α-D-glucopyranoside (57)

A solution of **56** (30.5 mg, 16.7 μmol) in a mixture of MeOH (2.5 mL) and THF (800 μL) was stirred with *p*-TsOH (1.0 mg, 5.26 μmol) for 3 h. The mixture was neutralized with Et_3N and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography (EtOAc/hexane 35:65) afforded **57** (17.7 mg, 11.2 μmol, 67%) as a colorless syrup. The yield was 78% according to recovery of **56**. $[\alpha]_D^{23}$ +121° (*c* 1.60, $CHCl_3$). IR (film) 3470, 1730, 1610, 1510, 1285, 1250, 1095, 1065, 1035 cm^{-1}. ^1H NMR (C_6D_6) δ 1.44 (1H, br, C″6O*H*), 3.16 (3H, s, C1OCH_3), 3.25, 3.29, 3.29, 3.31, 3.31, 3.33 (each 3H, s, CH_3O), 3.34 (1H, C″5*H*), 3.53–3.59 (2H, C′5*H*, C′6*H*H), 3.64 (2H, dd, J = 2.0, 11.2 Hz, C6*H*H, C6″*H*H), 3.86–3.92 (4H, C′2*H*, C″2*H*, C″4*H*, C″6*H*H), 4.08 (1H, dd, J = 9.3, 10.7 Hz, C′4*H*), 4.13 (1H, dd, J = 4.9, 11.2 Hz, C6*H*H), 4.26 (1H, t, J = 9.3 Hz, C″3*H*), 4.32 (1H, t, J = 9.3 Hz, C′3*H*), 4.35 (1H, ddd, J = 2.0, 4.9, 10.3 Hz, C5*H*), 4.40 (1H, dd, J = 4.4, 11.2 Hz, C′6*H*H), 4.50 (1H, d, J = 3.4 Hz, C′1*H*), 4.51, 4.58 (each 1H, d, J = 10.7 Hz, ArCH_2O), 4.52, 4.66 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.60 (1H, d, J = 2.9 Hz, C″1*H*), 4.69, 5.03 (each 1H, d, J = 10.7 Hz, ArCH_2O), 4.91, 5.12 (each 1H, d, J = 10.7 Hz, ArCH_2O), 4.93, 5.24 (each 1H, d, J = 11.2 Hz, ArCH_2O), 4.96, 5.09 (each 1H, d, J = 10.7 Hz, ArCH_2O), 5.34 (1H, d, J = 3.4 Hz, C1*H*), 5.48 (1H, dd, J = 3.4, 10.2 Hz, C2*H*), 6.06 (1H, t, J = 10.3 Hz, C4*H*), 6.64 (1H, t, J = 10.2 Hz, C3*H*), 6.72–8.14 (39H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 41.5, 43.9, 54.69, 54.69, 54.72, 54.72, 54.75, 54.77, 55.3, 62.2, 67.7, 69.4, 70.0, 71.4, 72.0, 72.6, 75.43, 75.45, 75.9, 76.0, 72.8, 80.7, 81.4, 82.6, 82.8, 83.4, 83.5, 85.2, 85.3, 97.5, 113.92, 113.93, 114.06, 114.11, 114.17, 127.9, 128.1, 128.4, 128.5, 128.6, 129.4, 129.5, 129.61, 129.63, 129.7, 129.8, 129.95, 130.00, 130.16, 130.20, 131.3, 131.4, 131.8, 132.0, 132.2, 132.9, 133.2, 133.3, 159.5, 159.72, 159.75, 165.4, 165.9, 166.3. FD-MS (%, rel int) 1583 (22, $[M+H]^+$), 1582 (23, M^+), 1462 (70,

[M−MPM+H]$^+$), 121 (100, MPM$^+$). FD-HRMS Found m/z = 1582.5651. Calcd for $C_{88}H_{94}O_{23}S_2$: [M$^+$], 1582.5627.

4.34. Methyl 6-*O*-[[[6′-*O*-[[6″-*O*-[2‴,3‴,4‴,6‴-[tetrakis-*O*-(4-methoxyphenyl)methyl]-5‴-deoxy 5‴-thio-α-D-glucopyranosyl]-2″,3″,4″-[tris-*O*-(4-methoxyphenyl)methyl]-5″-deoxy-5″-thio-α-D glucopyranosyl]]-2′,3′,4′-[tris-*O*-(4-methoxyphenyl) methyl]-5′-deoxy-5′-thio-α-D-glucopyranosyl]]]-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (58)

According to *general procedure B*, a suspension of **15** (8.0 mg, 9.70 μmol) and **57** (17.5 mg, 11.0 μmol) in CH_2Cl_2 (700 μL) was stirred with MS4A (102 mg) at room temperature for 20 min. After the mixture was cooled to −78 °C, TESOTf (210 μmol/mL solution in CH_2Cl_2, 2.3 μL, 0.05 equiv) was added to the suspension. After stirring for 1 h at −78 °C, pyridine was added and the mixture was filtered through a pad of silica gel, and the pad was washed with EtOAc. After concentration in vacuo, purification of the residue by silica gel column chromatography (Et_2O/benzene 5:95) gave **58** (14.6 mg, 67%) as a colorless syrup. $[\alpha]_D^{25}$ +115° (*c* 0.28, $CHCl_3$). IR (film) 2960, 2930, 2860, 1730, 1610, 1510, 1250, 1070, 1040, 820, 710 cm^{-1}. ^{1}H NMR (C_6D_6) δ 3.11 (3H, s, C1OCH_3), 3.23, 3.241, 3.244, 3.246, 3.25, 3.27, 3.27, 3.279, 3.283, 3.29 (each 3H, s, CH_3O), 3.40–3.54 (4H, C5*H* of pyranose A, B, and C, C6*H*H of A), 3.59 (1H, m, C6*H*H of pyranose C), 3.83–3.91 (4H, C2*H* of pyranose B and C, C6*H*H of pyranose A, C6*H*H), 3.91 (1H, dd, *J* = 3.0, 9.2 Hz, C2*H* of pyranose A), 4.02 (1H, t, *J* = 9.3 Hz, C4*H* of pyranose A), 4.05 (1H, dd, *J* = 3.4, 8.8 Hz, C6*H*H), 4.10 (1H, t, *J* = 10.7 Hz, C4*H* of pyranose B), 4.08–4.10 (1H, m, C6*H*H of pyranose A), 4.16–4.33 (5H, C3*H* of pyranose A, B, and C, C5*H*, C6*H*H of pyranose B), 4.17, 4.25 (each 1H, d, *J* = 11.8 Hz, ArCH_2O), 4.37 (1H, dd, *J* = 3.9, 10.7 Hz, C6*H*H of pyranose C), 4.44, 4.54 (each 1H, d, *J* = 11.2 Hz, ArCH_2O), 4.46, 4.55 (each 1H, d, *J* = 11.7 Hz, ArCH_2O), 4.47, 4.61 (each 1H, d, *J* = 11.2 Hz, ArCH_2O), 4.48 (1H, d, *J* = 3.4 Hz, C1*H* of pyranose C), 4.53 (1H, dd, *J* = 3.4 Hz, C1*H* of pyranose B), 4.58 (1H, d, *J* = 3.0 Hz, C1*H* of pyranose A), 4.59, 5.00 (each 1H, d, *J* = 10.7 Hz, ArCH_2O), 4.88, 5.08 (each 1H, d, *J* = 10.8 Hz, ArCH_2O), 4.89, 5.22 (each 1H, d, *J* = 10.7 Hz, ArCH_2O), 4.92, 5.08 (each 1H, d, *J* = 10.2 Hz, ArCH_2O), 4.92, 5.04 (each 1H, d, *J* = 10.2 Hz, ArCH_2O), 4.93, 5.20 (each 1H, d, *J* = 10.8 Hz, ArCH_2O), 5.29 (1H, d, *J* = 3.4 Hz, C1*H*), 5.42 (1H, dd, *J* = 3.4, 10.2 Hz, C2*H*), 6.03 (1H, t, *J* = 10.2 Hz, C4*H*), 6.60 (1H, t, *J* = 10.2 Hz, C3*H*), 6.68–8.09 (55H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 41.6, 42.2, 42.5, 54.68, 54.71, 54.74, 54.75, 54.80, 55.3, 67.68, 67.71, 67.80, 68.1, 69.4, 70.0, 71.5, 72.0, 72.2, 72.5, 72.8, 73.0, 75.5, 75.6, 75.9, 76.0, 80.95, 80.99, 81.4, 82.36, 82.43, 82.7, 83.5, 83.56, 83.7, 85.26, 85.34, 85.42, 97.5, 113.89, 113.91, 114.03, 114.05, 114.12, 114.14, 114.16, 128.3, 128.4, 128.5, 128.6, 128.7, 129.46, 129.51, 129.56, 129.60, 129.69, 129.72, 129.80, 129.83, 129.96, 130.16, 130.20, 130.6, 131.39, 131.44, 131.69, 131.82, 131.88, 132.13, 132.21, 132.9, 133.1, 133.2, 159.47, 159.57, 159.58, 159.61, 159.67, 159.69, 159.71, 159.74, 165.4, 165.8, 166.3. ESI-MS (%, rel int) 2265 (100, [M+Na]$^+$). ESI-HRMS Found m/z = 2263.8147. Calcd for $C_{126}H_{136}NaO_{31}S_3$: [M+Na]$^+$, 2263.8125.

4.35. Methyl 6-*O*-[[6′-*O*-[6″-*O*-(5‴-deoxy-5‴-thio-α-D-glucopyranosyl)-5″-deoxy-5″-thio-α-D-glucopyranosyl]5′-deoxy-5′-thio-α-D-glucopyranosyl]]-α-D-glucopyranoside (2)

A solution of **58** (11.5 mg, 5.10 μmol) in MeOH (2.0 mL) was stirred with NaOMe (2.5 mg, 46.3 μmol) at room temperature for 1 h. After DOWEX 50W (H$^+$ form) was added until the solution indicated neutral, the mixture was filtered and the filtrate was concentrated in vacuo. Without further purification, the residue was stirred with DDQ (46.2 mg, 204 μmol) in a mixture of CH_2Cl_2 (1.0 mL) and H_2O (100 μL) at room temperature for 12 h. Volatiles of the reaction mixture were removed under reduced pressure. Purification of the residue by silica gel column chromatography (MeOH/EtOAc 40:60) afforded **2** (2.4 mg, 3.29 μmol, 65%, 2 steps). Since this sample was soluble in only H_2O, IR spectrum was not measured. $[\alpha]_D^{27}$ +170° (*c* 0.19, H_2O). ^{1}H NMR (D_2O, signals for the glucopyranose moiety could be assigned, except for the anomeric protons.) δ 3.24 (1H, br ddd, *J* = 3.4, 4.8, 9.8 Hz, C5*H* of thiopyranose), 3.34, 3.41 (each 1H, m, C5H × 2 of thiopyranoses), 3.50 (3H, s, C1OCH_3), 3.56 (1H, t, *J* = 9.8 Hz, C4*H*), 3.64 (1H, dd, *J* = 3.9, 9.8 Hz, C2*H*), 3.67–3.79 (7H), 3.87–4.00 (9H), 4.10–4.17 (2H), 4.22 (1H, dd, *J* = 4.9, 9.8 Hz, C6*H*H), 4.79 (1H, d, *J* = 2.9 Hz, *anomeric proton*), 4.82 (1H, d, *J* = 2.9 Hz, *anomeric proton*), 4.83 (1H, d, *J* = 2.9 Hz, *anomeric proton*), 4.88 (1H, d, *J* = 3.9 Hz, *anomeric proton*). ^{13}C NMR (D_2O) δ 40.8, 40.9, 43.3, 55.4, 66.7, 60.3, 66.9, 67.0, 69.8, 70.2, 71.4, 73.6, 73.7, 74.23, 74.25, 74.31, 74.32, 74.34, 75.28, 75.34, 75.40, 81.68, 81.71, 81.92, 99.5. FAB-MS (negative mode,%, rel int) 787 (1.0, [M+Na^{37}Cl−H]$^-$), 785 (1.0, [M+Na^{35}Cl−H]$^-$), 765 (1.8, [M+^{37}Cl]$^-$), 763 (2.4, [M+^{35}Cl]$^-$), 749 (1.6, [M+Na−2H]$^-$), 727 (19, [M−H]$^-$). FAB-HRMS (negative mode) Found m/z = 727.1591. Calcd for $C_{25}H_{43}O_{18}S_3$: [M−H]$^-$, 727.1612.

4.36. Tetrahydropyranyl 4,6-*O*-(4-methoxyphenyl)methylidene-5-deoxy-5-thio-α-D-glucopyranoside (59)

A mixture of **6a** (3.40 g, 12.1 mmol, a mixture of 90:10 diastereomers at the asymmetric center of the THP group), anisaldehyde dimethyl acetal (3.0 mL, 17.6 mmol), and in DMF (20.0 mL) was stirred with camphorsulfonic acid (10.0 mg, 43.0 μmol) at 0 °C for 2 h. After neutralization by the addition of Et_3N, the mixture was poured into H_2O and extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/benzene 40:60) gave **59** (2.90 g, 7.26 mmol, 60%) as a colorless solid. The ^{1}H NMR spectra suggested that the product consists of a pair of diastereomers due to an asymmetric center in the THP moiety (90:10). IR (KBr) 3495, 3350, 2920, 2845, 1620, 1520, 1250, 1130, 1070, 1030, 970, 825 cm^{-1}. ^{1}H NMR

($CDCl_3$, signals for the major isomer and some signals for the minor isomer are only described. $a = 0.9$, $b = 0.1$) δ 1.57–1.86 (6H, C′3H_2, C′4H_2, C′5H_2), 2.85 (1H × b, d, $J = 6.8$ Hz, C2OH), 2.96 (1H × a, d, $J = 6.8$ Hz, C2OH), 3.05 (1H × a, d, $J = 1.5$ Hz, C3OH), 3.06 (1H × b, d, $J = 1.5$ Hz, C3OH), 3.29 (1H × a, ddd, $J = 4.9$, 10.3, 11.2 Hz, C5H), 3.55 (1H × a, br d, $J = 11.2$ Hz, C′6HH), 3.71 (1H × a, t, $J = 11.2$ Hz, C6HH), 3.79 (1H × a, t, $J = 9.3$ Hz, C4H), 3.80 (3H × a, s, CH_3O), 3.91–3.98 (3H × a, C2H, C3H, C′6HH), 4.12 (1H × a, dd, $J = 4.9$, 11.2 Hz, C6HH), 4.25 (1H × b, dd, $J = 4.9$, 10.7 Hz, C6HH), 4.89 (1H × b, d, $J = 2.9$ Hz, C1H), 4.95 (1H × b, br t, $J = 3.4$ Hz, C′2H), 5.01 (1H × a, br t, $J = 3.4$ Hz, C′2H), 5.05 (1H × a, d, $J = 2.9$ Hz, C1H), 5.57 (1H, s, ArCH(OR)$_2$), 6.87–6.91 (2H, *aromatic protons*), 7.40–7.44 (2H, *aromatic protons*). ^{13}C NMR ($CDCl_3$, signals for the major isomer are described.) δ 19.5, 25.1, 30.2, 35.1, 55.3, 63.0, 68.5, 72.4, 75.5, 77.4, 83.7, 94.9, 101.8, 113.7, 127.5, 129.8, 160.2. EI-MS (%, rel int) 398 (11, M^+), 314 (18, [M−dihydropyran]$^+$), 313 (20, [M−THP]$^+$), 85 (100, THP$^+$). EI-HRMS Found m/z = 398.1368. Calcd for $C_{19}H_{26}O_7S$: M^+, 398.1399.

4.37. Tetrahydropyranyl 2,3-di-*O*-(4-methoxy)phenylmethyl-4,6-*O*-(4-methoxy)phenylmethylidene-5-droxy-5-thio-α-D-glucopyranoside (60)

To a mixture of **59** (627 mg, 1.58 mmol) and NaH (114 mg, 4.73 mmol) in DMF (10.0 mL), MPMBr (ca. 50% solution in toluene, 1.5 mL, ca. 4.73 mmol) was added at room temperature. After the mixture was stirred at the same temperature for 2 h, MeOH (0.3 mL) and Et_3N (1.0 mL) were added successively. After stirring for 30 min, the mixture was poured into H_2O and extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. The residue was dissolved in pyridine (3.0 mL), and the solution was stirred with Ac_2O (1.0 mL) at room temperature for 1 h to convert the resulting anisic alcohol into the corresponding acetate. After concentration in vacuo, purification of the residue by silica gel column chromatography (EtOAc/hexane 20:80) gave **60** (1.01g, 1.58 mmol, 100%) as a syrup. The ^{1}H NMR spectrum of this sample showed that it consists of the isomers due to the asymmetric center in the THP moiety (90:10). IR (film) 2935, 2849, 1610, 1515, 1460, 1365, 1300, 1250, 1170, 1075, 1030, 970, 825, 755 cm^{-1}. ^{1}H NMR ($CDCl_3$, signals for the major isomer and some signals for the minor isomer are only described. $a = 0.9$, $b = 0.1$) δ 1.44–1.79 (6H, C3′H_2, C4′H_2, C5′H_2), 3.23 (1H × a, ddd, $J = 4.4$, 9.3, 11.2 Hz, C5H), 3.41 (1H × a, br d, $J = 10.7$ Hz, C6′HH), 3.60 (1H × a, t, $J = 11.2$ Hz, C6HH), 3.65, 3.66, 3.67, 3.68 (each 3H × a, s, CH_3O), 3.69 (1H × a, dd, $J = 2.9$, 9.3 Hz, C2H), 3.80 (1H × a, t, $J = 9.3$ Hz, C4H), 3.92 (1H × a, t, $J = 9.3$ Hz, C3H), 3.97 (1H × a, br t, $J = 10.7$ Hz, C6′HH), 4.09 (1H × a, dd, $J = 4.4$, 11.2 Hz, C6HH), 4.16 (1H × b, dd, $J = 4.4$, 10.7 Hz, C6HH), 4.49 (1H × b, d, $J = 11.2$ Hz, ArCHHO), 4.55, 4.58 (each 1H × a, d, $J = 11.2$ Hz, ArCH_2O), 4.61 (1H × b, d, $J = 10.3$ Hz, ArCHHO), 4.67, 4.69 (each 1H × a, d, $J = 10.7$ Hz, ArCH_2O), 4.79 (1H × b, d, $J = 2.9$ Hz, C1H), 4.87 (1H × b, br t, $J = 2.9$ Hz, C2′H), 4.97 (1H × a, br t, $J = 2.9$ Hz, C2′H), 4.98 (1H × a, d, $J = 2.9$ Hz, C1H), 5.50 (1H × a, s, ArCH(OR)$_2$), 5.51 (1H × b, s, ArCH(OR)$_2$), 6.69–6.80 (6H, *aromatic protons*), 7.16–7.33 (6H, *aromatic protons*). ^{13}C NMR ($CDCl_3$, signals for the major isomer are described.) δ 18.4, 25.3, 30.0, 35.61, 55.11, 55.11, 55.16, 61.6, 68.5, 72.4, 75.8, 75.8, 79.6, 82.8, 84.9, 93.96, 101.1, 113.4, 113.5, 113.6, 127.1, 128.2, 129.4, 129.8, 130.3, 131.1, 159.1, 159.1, 159.8. EI-MS (%, rel int) 638 (0.1, M^+), 517 (2, [M−MPM]$^+$), 121 (100, MPM$^+$), 85 (45, THP$^+$). EI-HRMS Found m/z = 638.2532. Calcd for $C_{35}H_{42}O_9S$: M^+, 638.2550.

4.38. Tetrahydropyranyl 2,3,6-tri-*O*-(4-methoxyphenyl)methyl-5-deoxy-5-thio-α-D-glucopyranoside (61) and 2,3,6-tri-*O*-(4-methoxyphenyl)methyl-5-deoxy-5-thio-α-D-glucopyranose (62)

To a mixture of **60** (224 mg, 350 μmol), finely powdered molecular sieves UOP type AW300[37] (100 mg) and BH_3·NMe_3 (102 mg, 1.40 mmol) in THF (3.0 mL), $AlCl_3$ (186 mg 1.40 mmol) were added at −15 °C. Triethylamine (1.0 mL) was added to the mixture after stirring at the same temperature for 1.5 h. The mixture was filtered and the filtrate was stirred with 10% citric acid aqueous solution (10 mL) and EtOAc (20 mL). After 6 h stirring, the organic solution was separated and it was washed with H_2O and brine successively, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/benzene 5:95) gave the desired **61** (91.3 mg, 144 μmol, 41%) and **62** (55.0 mg, 98.0 μmol, 28%) both as syrups.

4.38.1. Physical data for 61. $[\alpha]_D^{26}$ +129° (c 1.10, $CHCl_3$). IR (film) 3470, 2935, 1610, 1510, 1250, 1095, 1030, 970, 820 cm^{-1}. ^{1}H NMR (C_6D_6) δ 1.25–1.80 (6H, C3′H_2, C4′H_2, C5′H_2), 3.16 (1H, br s, C4OH), 3.287, 3.290, 3.293 (each 3H, s, CH_3O), 3.45 (1H, br d, $J = 10.7$ Hz, C6′HH), 3.50 (1H, ddd, $J = 3.9$, 5.8, 9.3 Hz, C5H), 3.80 (1H, dd, $J = 3.9$, 9.8 Hz, C6HH), 3.88 (1H, dd, $J = 5.8$, 9.8 Hz, C6HH), 3.93 (1H, br dd, $J = 2.9$, 9.3 Hz, C2H), 4.05–4.12 (3H, C3H, C4H, C6′HH), 4.32 (2H, s, ArCH_2O), 4.41, 4.57 (each 1H, d, $J = 11.2$ Hz, ArCH_2O), 4.78, 5.08 (each 1H, d, $J = 10.7$ Hz, ArCH_2O), 5.22 (1H, d, $J = 2.9$ Hz, C1H), 5.31 (1H, t, $J = 2.9$ Hz, C2′H), 6.73–6.78 (6H, *aromatic protons*), 7.18–7.23 (6H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 19.1, 25.8, 30.5, 42.4, 54.7, 54.7, 54.7, 61.6, 69.4, 71.9, 73.1, 75.2, 75.3, 75.5, 82.6, 84.0, 94.1, 114.0, 114.0, 114.1, 129.4, 129.70, 129.74, 130.6, 130.9, 131.7, 159.66, 159.68, 159.7. EI-MS (%, rel int) 641 (trace, [MH]$^+$), 555 (0.3, [M−THP]$^+$), 519 (3, [M−MPM]$^+$), 121 (100, MPM$^+$), 85 (43, THP$^+$). EI-HRMS Found m/z = 519.2064. Calcd for $C_{27}H_{35}O_8S$: [M−MPM]$^+$, 519.2053.

4.38.2. Physical data for 62. $[\alpha]_D^{26}$ +32° (c 0.86, $CHCl_3$). IR (film) 3430, 2930, 2835, 1610, 1510, 1250, 1095, 1035, 820 cm^{-1}. ^{1}H NMR (C_6D_6) δ 3.03, 3.08 (each 1H, br, OH), 3.286, 3.292, 3.31 (each 3H, s, CH_3O), 3.68 (1H, ddd, $J = 4.4$, 5.4, 9.3 Hz, C5H), 3.77 (1H,

dd, $J = 2.9$, 9.3 Hz, C2*H*), 3.80 (1H, dd, $J = 4.4$, 10.2 Hz, C6*H*H), 3.85 (1H, dd, $J = 5.4$, 10.2 Hz, C6*H*H), 3.95 (1H, t, $J = 9.3$ Hz, C3*H*), 4.05 (1H, t, $J = 9.3$ Hz, C4*H*), 4.30, 4.31 (each 1H, d, $J = 10.7$ Hz, ArCH_2O), 4.39, 4.40 (each 1H, d, $J = 11.2$ Hz, ArCH_2O), 4.75, 4.99 (each 1H, d, $J = 11.2$ Hz, ArCH_2O), 4.78 (1H, d, $J = 2.9$ Hz, C1*H*), 6.75–6.80 (6H, *aromatic protons*), 7.15–7.20 (6H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 42.1, 54.72, 54.72, 54.76, 69.4, 71.8, 71.9, 73.1, 75.2, 75.6, 82.4, 84.4, 114.07, 114.17, 114.18, 129.4, 129.7, 129,9, 130.6, 130.7, 131.6, 159.7, 159.7, 159.9. EI-MS (%, rel int) 435 (0.6, $[M-MPM]^+$), 121 (100, MPM^+). EI-HRMS Found $m/z = 435.1476$. Calcd for $C_{22}H_{27}O_7S$: $[M-MPM]^+$, 435.1478.

4.39. 2,3,6-Tri-*O*-(4-methoxy)phenylmethyl-4-*O*-acetyl-5-deoxy-5-thio-α-D-glucopyranoside (63)

4.39.1. Preparation from 61. A solution of **61** (260 mg, 406 μmol) in a mixture of Ac_2O (1.0 mL), pyridine (2.0 mL) was stirred at room temperature for 6 h. After concentration in vacuo, silica gel column chromatography of the residue (EtOAc/hexane 20:80) gave the corresponding acetate (268 mg, 393 μmol, 97%) as a colorless syrup. $[\alpha]_D^{26}$ +98° (*c* 2.35, $CHCl_3$). IR (film) 2940, 2840, 1750, 1610, 1510, 1245, 1100, 1030, 970, 820 cm^{-1}. ^{1}H NMR (C_6D_6) δ 1.29–1.79 (6H, C3′H_2, C4′H_2, C5′H_2), 1.71 (3H, s, CH_3CO), 3.29 (9H, s, CH_3O × 3), 3.44 (1H, br t, $J = 11.2$ Hz, C6′*H*H), 3.54–3.66 (3H, C5*H*, C6H_2), 3.88 (1H, dd, $J = 2.9$, 9.8 Hz, C2*H*), 4.09 (1H, dt, $J = 2.4$, 11.2 Hz C6′*H*H), 4.16 (1H, t, $J = 9.8$ Hz, C3*H*), 4.24, 4.28 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 4.38, 4.48 (each 1H, d, $J = 11.2$ Hz, ArCH_2O), 4.68, 4.98 (each 1H, d, $J = 10.7$ Hz, ArCH_2O), 5.12 (1H, d, $J = 2.9$ Hz, C1*H*), 5.27 (1H, t,$J = 2.9$ Hz, C2′*H*), 5.73 (1H, t, $J = 9.8$ Hz, C4*H*), 6.76, 6.76, 6.77 (each 2H, d, $J = 8.8$ Hz, *aromatic protons*), 7.22, 7.23, 7.28 (each 2H, d, $J = 8.8$ Hz, *aromatic protons*), 7.27–7.31 (2H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 20.0, 20.7, 25.8, 30.5, 41.0, 54.8, 54.8, 54.8, 61.5, 69.2, 72.5, 73.2, 75.5, 75.2, 75.6, 80.7, 84.4, 94.0, 113.97, 114.0, 114.01, 129.1, 129.7, 129.8, 130.4, 130.9, 131.7, 159.5, 159.73, 159.76, 169.4. EI-MS (%, rel int) 597 (trace, $[M-THP]^+$), 561 (2, $[M-MPM]^+$), 121 (100, MPM^+). EI-HRMS Found $m/z = 561.2142$. Calcd for $C_{29}H_{37}O_9S$: $[M-MPM]^+$, 561.2158. A solution of the acetate thus obtained (268 mg, 393 μmol) in a mixture of MeOH (4.0 mL) and THF (1.0 mL) was stirred with cat. $HClO_4$ at room temperature for 6 h. After neutralization by addition of Et_3N, the mixture was concentrated in vacuo. Purification of residue by silica gel column chromatography (EtOAc/benzene 8:92) gave **63** (167 mg, 279 μmol, 71%) as a solid. The yield was 82% according to recovery of the starting acetate. mp 109–110 °C. $[\alpha]_D^{27}$ +38° (*c* 0.63, $CHCl_3$). IR (KBr) 3360, 2955, 2870, 1750, 1610, 1515, 1250, 1170, 1100, 1030, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.84 (3H, s, CH_3CO), 2.58 (1H, br, C1O*H*), 3.43–3.52 (3H, C3*H*, C6H_2), 3.74–3.81 (2H, C2*H*, C5*H*), 3.77, 3.776, 3.78 (each 3H, s, CH_3O), 4.33, 4.40 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 4.53, 4.75 (each 1H, d, $J = 10.8$ Hz, ArCH_2O), 4.58, 4.65 (each 1H, d, $J = 11.2$ Hz, ArCH_2O), 4.83 (1H, br, C1*H*), 5.21 (1H, br t, $J = 9.8$ Hz, C4*H*), 6.825, 6.832, 6.832 (each 2H, d, $J = 8.8$ Hz, *aromatic protons*), 7.16, 7.20, 7.22 (each 2H, d, $J = 8.8$ Hz, *aromatic protons*). ^{13}C NMR ($CDCl_3$) δ 20.9, 40.0, 55.3, 55.3, 55.3, 68.0, 71.7, 72.8, 73.9, 74.5, 75.5, 79.8, 83.7, 113.70, 113.72, 113.9, 129.2, 129.5, 129.7, 129.7, 129.8, 130.7, 159.1, 159.2, 159.4, 169.8. EI-MS (%, rel int) 597 (0.2, $[M-H]^+$), 477 (4, $[M-MPM]^+$), 121 (100, MPM^+). EI-HRMS Found $m/z = 477.1606$. Calcd for $C_{24}H_{29}O_9S$: $[M-MPM]^+$, 477.1583.

4.39.2. Preparation from 62. A solution of **62** (89.1 mg 160 μmol) in a mixture of pyridine (2.0 mL) and Ac_2O (1.0 mL) was stirred at room temperature for 6 h. After concentration under reduced pressure, silica gel column chromatography of the residue (EtOAc/hexane 5:95) gave the corresponding diacetate (103 mg, 160 μmol, 100%) as a colorless solid. mp 97–98 °C. $[\alpha]_D^{26}$ +121° (*c* 0.68, $CHCl_3$). IR (KBr) 2950, 2840, 1750, 1620, 1515, 1370, 1250, 1220, 1100, 1030, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.87 2.16 (each 3H, s, CH_3CO), 3.41–3.46 (2H, C5*H*, C6*H*H), 3.51 (1H, m, C6*H*H), 3.72 (1H, t, $J = 9.8$ Hz, C3*H*), 3.77, 3.77, 3.78 (each 3H, s, CH_3O), 3.84 (1H, dd, $J = 3.4$, 9.8 Hz, C2*H*), 4.36, 4.40 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 4.50, 4.61 (each 1H, d, $J = 10.7$ Hz, ArCH_2O), 4.51, 4.77 (each 1H, d, $J = 10.7$ Hz, ArCH_2O), 5.23 (1H, t, $J = 9.8$ Hz, C4*H*), 6.15 (1H, d, $J = 3.4$ Hz, C1*H*), 6.82, 6.85, 6.85 (each 2H, $J = 8.8$ Hz, *aromatic protons*), 7.16, 7.20, 7.22 (each 2H, $J = 8.8$ Hz, *aromatic protons*). ^{13}C NMR ($CDCl_3$) δ 20.7, 21.0, 41.1, 55.11, 55.12, 55.14, 68.0, 70.5, 72.3, 73.0, 75.3, 74.2, 79.7, 82.3, 113.6, 113.6, 113.7, 129.0, 129.39, 129.42, 129.45, 129.7, 130.6, 159.0, 159.2, 159.3, 169.3, 169.6. EI-MS (%, rel int) 519 (3.0, $[M-MPM]^+$), 121 (100, MPM^+). EI-HRMS Found $m/z = 519.1721$. Calcd for $C_{26}H_{31}O_9S$: $[M-MPM]^+$, 519.1689. A mixture of the diacetate thus obtained (100 mg, 158 μmol) and hydrazine acetate (16.6 mg, 0.18 mmol) in DMF (1.0 mL) was stirred at room temperature for 9 h. The mixture was poured into H_2O and extracted with EtOAc (×3). The combined extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. Silica gel column chromatography of the residue (EtOAc/benzene 8:92) gave **63** (72.6 mg, 129 μmol, 81%) as a solid. The ^{1}H NMR and ^{13}C NMR spectra of this sample were identical to those prepared from **61**.

4.40. 2,3,6-Tri-*O*-(4-methoxy)phenylmethyl-4-*O*-acetyl-5-thio-α-D-glucopyranosyl trichloroacetimidate (64)

According to *general procedure A*, a solution of DBU in CH_2Cl_2, (26 μM, 0.1 mL) was added at −15 °C to a mixture of **63** (32.5 mg, 54.2 μmol) and CCl_3CN (46.8 μL, 325 μmol) in CH_2Cl_2 (1.0 mL). After stirring for 30 min at the same temperature, the mixture was concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/benzene 5:95) gave **64** (40.0 mg, 53.8 μmol, 100 %) as a syrup. IR (film) 3750, 2950, 1750, 1670, 1610, 1510, 1250, 1100, 1030, 820 cm^{-1}. ^{1}H NMR (C_6D_6) δ 1.69 (3H, s, CH_3CO), 3.282, 3.286, 3.289 (each 3H, s, CH_3O), 3.53 (1H, dd,

J = 5.4, 10.3 Hz, C6*H*H), 3.56 (1H, dd, J = 4.4, 10.3 Hz, C6*H*H), 3.75 (1H, ddd, J = 4.4, 5.4, 10.7 Hz, C5*H*), 3.86 (1H, dd, J = 2.9, 9.3 Hz, C2*H*), 4.12 (1H, t, J = 9.3 Hz, C3*H*), 4.18, 4.25 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.30, 4.42 (each 1H, d, J = 11.2 Hz, ArCH_2O), 4.65, 4.92 (each 1H, d, J = 11.2 Hz, ArCH_2O), 5.74 (1H, dd, J = 9.3, 10.7 Hz, C4*H*), 6.75, 6.75, 6.76 (each 2H, d, J = 8.8 Hz, *aromatic protons*), 7.16, 7.18, 7.24 (each 2H, d, J = 8.8 Hz, *aromatic protons*), 8.58 (1H, s, C(= N*H*)CCl_3). This sample was gradually decomposed, thus it was immediately used for the next step.

4.41. Methyl 2,3,6-tri-*O*-(4-methoxyphenyl)methyl-α-D-glucopyranoside (65)

A mixture of methyl α-D-glucopyranoside (1.3 g, 6.7 mmol), anisaldehyde dimethyl acetal (1.2 mL, 7.4 mmol), and in DMF (10.0 mL) was stirred with camphorsulfonic acid (10 mg, 43.0 μmol) at 70 °C for 4 h. After neutralization by the addition of Et_3N, the mixture was poured into H_2O and extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (benzene/EtOAc 60:40) gave methyl 4,6-*O*-(4-methoxybenzylidene) glucopyranoside (1.3 g, 4.1 mmol, 62%) as a solid. ^{1}H NMR ($CDCl_3$) δ 2.21 (1H, d, J = 9.8 Hz, C2O*H*), 2.64 (1H, d, J = 2.0 Hz, C3O*H*), 3.44 (3H, s, CH_3O), 3.46 (1H, t, J = 9.3 Hz, C4*H*), 3.61 (1H, dt, J = 3.9, 9.3 Hz, C2*H*), 3.71 (1H, t, J = 9.8 Hz, C6*H*H), 3.77 (1H, C5*H*), 3.78 (1H, s, CH_3O), 3.90 (1H, dt, J = 2.0, 9.3 Hz, C3*H*), 4.26 (1H, dd, J = 4.3, 9.8 Hz, C6*H*H), 4.78 (1H, d, J = 3.9 Hz, C1*H*), 5.47 (1H, s, ArC*H*(OR)$_2$), 6.86, 6.88 (each 1H, *aromatic proton*), 7.38, 7.41 (each 1H, *aromatic proton*). To a mixture of the diol thus obtained (526 mg, 1.69 mmol) and NaH (121 mg, 5.06 mmol) in DMF (8.0 mL), MPMBr (ca. 50% solution in toluene, 1.6 mL, ca. 5.06 mmol) was added at room temperature. After the mixture was stirred at the same temperature for 2 h, MeOH (0.5 mL) and Et_3N (1.0 mL) were added successively. After stirring for 30 min, the mixture was poured into H_2O and extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/benzene 95:5) gave methyl 2,3-bis-*O*-(4-methoxy)phenylmethyl-4,6-*O*-(4-methoxybenzylidene)-α-D-glucopyranoside (881 mg, 1.64 mmol, 97%) as a solid. Analytical sample was obtained by recrystallization from hexane/EtOAc (20:80) to give colorless needles. mp 127–128 °C. $[\alpha]_D^{26}$ −48° (*c* 0.94, $CHCl_3$), IR (KBr) 2950, 2910, 1615, 1515, 1465, 1370, 1250, 1170, 1080, 1030, 825 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 3.37 (3H, s, C1OCH_3), 3.48 (1H, dd, J = 3.4, 9.3 Hz, C2*H*), 3.53 (1H, t, J = 9.3 Hz, C4*H*), 3.65 (1H, t, J = 10.3 Hz C6*H*H), 3.77 (1H, C5H), 3.77, 3.78, 3.80 (each 3H, s, CH_3O), 3.97 (1H, t, J = 9.3 Hz, C3*H*), 4.21 (1H, dd, J = 4.9, 10.3 Hz, C6*H*H), 4.45 (1H, d, J = 3.4 Hz, C1*H*), 4.60, 4.76 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.73, 4.79 (each 1H, d, J = 10.7 Hz, ArCH_2O), 5.47 (1H, s, ArC*H*(OR)$_2$), 6.82, 6.84, 6.88 (each 2H, d, J = 8.8 Hz, *aromatic protons*), 7.26, 7.27, 7.38 (each 2H, d, J = 8.8 Hz, *aromatic protons*). ^{13}C NMR ($CDCl_3$) δ 55.25, 55.26, 55.29, 55.31, 62.3, 69.0, 73.4, 75.0, 78.3, 78.7, 82.1, 99.3, 101.2, 113.5, 113.7, 113.8, 127.3, 129.6, 129.7, 130.0, 130.3, 130.9, 159.3, 159.4, 160.0. EI-MS (%, rel int) 552 (0.5, M^+), 431 (57, $[M-MPM]^+$), 121 (100, MPM^+). EI-HRMS Found m/z = 431.1715. Calcd for $C_{23}H_{27}O_8$: $[M-MPM]^+$, 431.1706. To a mixture of the MPM ether thus obtained (247 mg, 459 μmol), finely powdered molecular sieves UOP type AW300 (100 mg) and $BH_3 \cdot NMe_3$ (102 mg, 1.39 μmol) in THF (3.0 mL), $AlCl_3$ (188 mg, 1.41 μmol) were added at −15 °C. Triethylamine (1.0 mL) was added to the mixture after stirring at the same temperature for 30 min,. The mixture was filtered and the filtrate was stirred with 10% citric acid aqueous solution (10 mL) and EtOAc (20 mL). After 1 h, the organic solution was separated, and it washed with H_2O and brine successively, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/benzene 10:90) gave **65** (186 mg, 335 μmol, 73%) as a syrup. $[\alpha]_D^{27}$ +2.0° (*c* 0.16 $CHCl_3$). IR (film) 3480, 2910, 1610, 1510, 1250, 1050, 1030, 840 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.41 (1H, br, O*H*), 3.35 (3H, s, CH_3O), 3.47 (1H, dd, J = 3.9, 9.8 Hz, C2*H*), 3.53 (1H, t, J = 9.3 Hz, C4*H*), 3.58–3.68 (3H, C5H, C6H_2), 3.72 (1H, t, J = 9.3 Hz, C3*H*), 3.76, 3.77, 3.77 (each 3H, s, CH_3O), 4.45, 4.49 (each 1H, d, J = 11.2 Hz, ArCH_2O), 4.55 (1H, d, J = 3.9 Hz, C1*H*), 4.58, 4.69 (each 1H, d, J = 11.2 Hz, ArCH_2O), 4.64, 4.89 (each 1H, d, J = 11.2 Hz, ArCH_2O), 6.83, 6.84, 6.86 (each 2H, d, J = 8.8 Hz, *aromatic protons*), 7.21, 7.27, 7.27 (each 2H, d, J = 8.8 Hz, *aromatic protons*). ^{13}C NMR ($CDCl_3$) δ 55.1, 55.15, 55.18, 55.18, 69.2, 69.8, 70.7, 72.8, 73.2, 75.0, 79.2, 81.1, 98.2, 113.7, 113.8, 114.0, 129.2, 129.6, 129.7, 130.1, 130.2, 131.0, 159.2, 159.3, 159.4. EI-MS (%, rel int) 553 (trace, $[M-H]^+$), 433 (10, $[M-MPM]^+$), 313 (7.5, $[M-MPM\times2+H]^+$), 121 (100, MPM^+). EI-HRMS Found m/z = 433.1848. Calcd for $C_{23}H_{29}O_8$: $[M-MPM]^+$, 433.1862.

4.42. Methyl 4-*O*-[2′,3′,6′-tri-*O*-(4-methoxyphenyl)methyl-4′-*O*-acetyl-5′-thio-α-D-glucopyranosyl]-2,3,6-tri-*O*-(4-methoxyphenyl)methyl-α-D-glucopyranoside (66)

According to *general procedure B*, a suspension of a mixture of **64** (200 mg, 371 μmol), **65** (275 mg, 370 μmol), and powdered MS4A (200 mg) in CH_2Cl_2 (4.0 mL) was stirred at room temperature for 30 min. After cooling to −78 °C, TESOTf (90 μmol/mL solution in CH_2Cl_2, 200 μL, 0.05 equiv) was added to the suspension. The mixture was stirred at the same temperature for 2 h and Et_3N (10 μL) was added. The resulting mixture was filtered through a silica gel pad, which was washed with EtOAc. After concentration in vacuo, the residue was subjected to a silica gel column chromatography (EtOAc/hexane 30:70) to give **66** (330 mg, 293 μmol, 79%) as a syrup. The ^{1}H NMR spectra of this sample suggested that the product consists of a pair of diastereomers at the newly introduced glycoside linkage (α:β = 90:10). Analytical sample for the major isomer was obtained by HPLC (μBondasphere 150 SIL-100, 7.8 (∅) × 30 mm, EtOAc/hexane 20:80, 4.0 mL/min).

However, these conditions did not provide pure minor isomer. t_R = 92 min (above conditions). $[\alpha]_D^{26}$ +68° (*c* 0.98, $CHCl_3$). IR (film) 2920, 2855, 1735, 1610, 1510, 1245, 1095, 1030, 820 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.82 (3H, s, CH_3CO) 3.10 (1H, dt, *J* = 4.4, 10.7 Hz, C5′*H*), 3.20, 3.25 (each 1H, dd, *J* = 4.4, 9.8 Hz, C6′*H*H), 3.37 (3H, s, CH_3O), 3.55 (1H, dd, *J* = 3.4, 9.3 Hz, C2*H*), 3.68, 3.73, 3.758, 3.764, 3.764, 3.77 (each 3H, s, CH_3O), 3.66 (1H, dd, *J* = 2.9, 10.3 Hz, C6*H*H), 3.71–3.78 (3H, C6*H*H, C2′*H*, C3′*H*), 3.90 (1H, br d, *J* = 9.8 Hz, C5*H*), 4.04 (1H, t, *J* = 9.3 Hz, C3*H*), 4.18 (1H, dd, *J* = 9.3, 9.8 Hz, C4*H*), 4.18, 4.29 (each 1H, d, *J* = 11.7 Hz, ArCH_2O), 4.42, 4.71 (each 1H, d, *J* = 10.7 Hz, ArCH_2O), 4.45, 4.53 (each 1H, d, *J* = 11.2 Hz, ArCH_2O), 4.46, 4.49 (each 1H, d, *J* = 11.2 Hz, ArCH_2O), 4.47 (2H, s, ArCH_2O), 4.52 (1H, d, *J* = 3.4 Hz, C1*H*), 4.55, 4.92 (each 1H, d, *J* = 11.2 Hz, ArCH_2O), 5.20 (1H, t, *J* = 10.7 Hz, C4′*H*), 5.49 (1H, d, *J* = 2.9 Hz C1′*H*), 5.71 (2H, d, *J* = 8.8 Hz, *aromatic protons*), 6.79–6.83 (10H, *aromatic protons*), 7.00 (2H, d, *J* = 8.8 Hz, *aromatic protons*), 7.10–7.16 (6H, *aromatic protons*), 7.20–7.22 (4H, *aromatic protons*). ^{13}C NMR ($CDCl_3$) δ 20.9, 40.1, 55.12, 55.15, 55.18, 55.21, 55.23, 55.23, 55.23, 67.9, 69.22, 69.25, 71.7, 72.9, 72.9, 72.97, 72.99, 73.6, 74.7, 75.3, 79.8, 79.9, 80.2, 81.7, 83.1, 97.7, 113.6, 113.72, 113.75, 113.8, 128.3, 128.8, 129.0, 129.35, 129.38, 129.78, 129.81, 129.99, 130.0, 130.3, 130.7, 130.8, 158.9, 158.96, 159.0, 159.09, 159.12, 159.4, 169.7. FD-MS (%, rel int) 1135 (12, MH^+) 1134 (7, M^+), 1133 (19, $[M-H]^+$), 1014 (63, $[M-MPM+H]^+$), 1013 (100, $[M-MPM]^+$), 893 (15, $[M-2\times MPM+H]^+$). FD-HRMS Found *m*/*z* = 1134.4657. Calcd for $C_{63}H_{74}O_{17}S$: M^+, 1134.4647.

4.43. Methyl 4-*O*-[2′,3′,6′-tri-*O*-(4-methoxyphenyl)methyl-5′-thio-α-D-glucopyranosyl]-2,3,6-tri-*O*-(4-methoxyphenyl)methyl-α-D-glucopyranoside (67)

4.43.1. Reaction using pure 66. A solution of **66** (21.5 mg, 18.9 μmol) and NaOMe (30.0 mg, 0.58 mmol) in a mixture of MeOH (2.5 mL) and THF (0.5 mL) was stirred at 40 °C for 4 h. After neutralization by the addition of 2 M HCl aqueous solution, the mixture was poured into H_2O and extracted with EtOAc (×3). The combined extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/benzene 10:90) gave an anomeric mixture of **67** (18.9 mg, 16.8 μmol, 89%) as a syrup. $[\alpha]_D^{26}$ +37° (*c* 0.68, $CHCl_3$). IR (film) 3430, 2920, 2835, 1610, 1510, 1250, 1095, 1030, 820 cm^{-1}. ^1H NMR (C_6D_6) δ 3.05 (1H, br, C′4O*H*), 3.16 (3H, s, C1OCH_3), 3.260, 3.267, 3.267, 3.272, 3.275, 3.31 (each 3H, s, CH_3O), 3.55 (1H, br dt, *J* = 4.9, 9.8 Hz, C′5*H*), 3.64 (1H, dd, *J* = 3.4, 9.8 Hz, C2*H*), 3.75 (1H, dd, *J* = 4.4, 9.8 Hz, C6′*H*H), 3.87 (1H, dd, *J* = 5.4, 9.8 Hz, C6′*H*H), 3.90 (1H, br d, *J* = 10.3 Hz, C6*H*H), 3.93 (1H, dd, *J* = 2.9, 9.3 Hz, C′2*H*), 3.99 (1H, dd, *J* = 4.4, 10.3 Hz, C6*H*H), 4.04–4.10 (2H, C′3*H*, C′4*H*), 4.15 (1H, ddd, *J* = 2.0, 4.4, 9.8 Hz, C5*H*), 4.30, 4.31 (each 1H, d, *J* = 11.7 Hz, ArCH_2O), 4.34, 4.37 (each 1H, d, *J* = 11.2 Hz, ArCH_2O), 4.49 (1H, t, *J* = 9.3 Hz, C3*H*), 4.49, 4.58 (each 1H, d, *J* = 11.7 Hz, ArCH_2O), 4.53, 4.61 (each 1H, d, *J* = 11.7 Hz, ArCH_2O), 4.68 (1H, d, *J* = 3.4 Hz, C1*H*), 4.70 (1H, dd, *J* = 9.3, 9.8 Hz, C4*H*), 4.77, 5.04 (each 1H, d, *J* = 11.0 Hz, ArCH_2O), 4.81, 5.21 (each 1H, d, *J* = 11.7 Hz, ArCH_2O), 6.02 (1H, d, *J* = 2.9 Hz, C1′*H*), 6.70–6.81 (12H, *aromatic protons*), 7.13–7.36 (12H, *aromatic protons*). ^{13}C NMR (C_6D_6) δ 42.7, 54.69, 54.69, 54.69, 54.72, 54.72, 54.9, 69.6, 70.0, 70.4, 72.1, 72.42, 72.45, 73.2, 73.3, 73.5, 75.2, 75.5, 80.3, 81.2, 82.3, 82.7, 83.7, 97.9, 114.02, 114.05, 114.07, 114.07, 114.09, 114.14, 128.2, 128.5, 129.36, 129.39, 129.6, 129.8, 130.7, 130.96, 130.99, 131.1, 131.7, 131.8, 159.3, 159.58, 159.61, 159.67, 159.71, 159.74. FD-MS (%, rel int): 1092 (22, M^+), 971 (100, $[M-MPM]^+$). FD-HRMS Found *m*/*z* = 1092.4557. Calcd for $C_{61}H_{72}O_{16}S$: M^+, 1092.4541.

4.43.2. Reaction using a mixture of isomers in preparative scale. A solution of the anomeric mixture of **66** (189 mg, 166 μmol, an anomeric mixture, α:β = 90:10), and NaOMe (31.2 mg, 0.6 mmol) in a mixture MeOH (5.0 mL) and THF (1.0 mL) was stirred at 40 °C for 4 h. After neutralization by the addition of 2 M HCl aqueous solution, the mixture was poured into H_2O and extracted with EtOAc (×3). The combined extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/benzene 10:90) gave an anomeric mixture of **67** (α:β = 90:10, 178 mg, 167 μmol, 98%) as a syrup. The major signals in the ^1H NMR spectrum of this sample were identical to those prepared from pure **66**.

4.44. Methyl 2,3,6-tri-*O*-(4-methoxyphenyl)methyl-4-*O*-[2′,3′,6′-tri-*O*-(4-methoxyphenyl)methyl-4′-*O*-[2″,3″,6″-tri-*O*-(4-methoxyphenyl)methyl-4″-*O*-acetyl-5″-thio-α-D-glucopyranosyl]-5′-thio-α-D-glucopyranosyl]-α-D-glucopyranoside (68)

4.44.1. Preparation using pure 67. According to *general procedure B*, a suspension of **67** (17.0 mg, 15.6 μmol), **64** (21.0 mg, 26.3 μmol), and MS4A (50 mg) in CH_2Cl_2 (1.0 mL) was stirred at room temperature for 30 min. After cooling to −78 °C, TESOTf (130 μmol/mL solution in CH_2Cl_2, 10 μL, 0.05 equiv) was added to the suspension. The mixture was stirred at the same temperature for 2 h and Et_3N was added. The resulting mixture was filtered through silica gel pad, which was washed with EtOAc. After concentration in vacuo, the residue was subjected to a silica gel column chromatography (EtOAc/hexane 40:60) to give an anomeric mixture of **68** (13.4 mg, 8.3 μmol, 53%) as a syrup. The yield was 80% according to recovery of **67**. The minor isomer was removed by HPLC (μBondasphere 150 SIL-100, 7.8 (ϕ) × 300 mm, EtOAc/hexane 35:65, 2.25 mL/min, t_R = 30 min). The ^1H NMR spectrum displayed small signals for the minor C1″β-anomer at δ 1.68 (CH_3CO), 3.15 (C1OCH_3), 5.73 (C″4*H*) and 6.00, 6.01 (each *anomeric proton*) ppm. Comparison of peak intensities revealed the selectivity in this reaction (α:β = 84:16). IR (film) 2925, 2830, 1740, 1610, 1510, 1250, 1100, 1035, 820 cm^{-1}. ^1H NMR (C_6D_6, Only signals for the major anomer are described.) δ 1.74 (3H, s,

CH_3CO), 3.10 (3H, s, C1OCH_3), 3.24, 3.26, 3.26, 3.27, 3.27, 3.277, 3.282, 3.288, 3.31 (each 3H, s, CH_3O), 3.54–3.58 (2H, C″6H_2), 3.64 (1H, dd, J = 3.4, 9.3 Hz, C2H), 3.75 (1H, ddd, J = 4.4, 5.9, 11.2 Hz, C″5H), 3.80–3.85 (2H, C5H, C′5H), 3.87 (1H, dd, J = 2.9, 9.8 Hz, C″2H), 4.01–4.07 (3H, C6H_2, C′2H), 4.19, 4.28 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.23–4.25 (3H, C′6H_2, C″3H), 4.33, 4.37 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.36, 4.48 (each 1H, d, J = 11.2 Hz, ArCH_2O), 4.42, 4.56 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.44 (1H, C3H), 4,45 (1H, C3′H), 4.62–4.67 (2H, ArCH_2O), 4.637, 4.69 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.642, 4.92 (each 1H, d, J = 11.2 Hz, ArCH_2O), 4.65 (1H, d, J = 3.4 Hz, C1H), 4.78 (1H, C4H), 4.78, 5.19 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.89, 5.20 (each 1H, d, J = 11.2 Hz, ArCH_2O), 4.96 (1H, t, J = 9.8 Hz, C′4H), 5.77 (1H, t, J = 9.8 Hz, C″4H), 5.79 (1H, d, J = 2.9 Hz, C′1H), 6.05 (1H, d, J = 2.9 Hz, C″1H), 6.64–7.43 (36H, *aromatic protons*). FD-MS (%, rel int) 1673 (44, $[M+H]^+$), 1672 (31, M^+), 1552 (94, $[M+H-MPM]^+$), 1551 (100, $[M-MPM]^+$). FD-HRMS Found m/z = 1673.6711. Calcd for $C_{93}H_{109}O_{24}S_2$: $[M+H]^+$, 1673.6750.

4.44.2. Reaction using a mixture of isomers. According to *general procedure B*, a suspension of **67** (136 mg, 125 μmol), **63** (115 mg, 155 μmol), and MS4A (100 mg) in CH_2Cl_2 (2.0 mL) was stirred at room temperature for 30 min. After cooling to −78 °C, TESOTf (380 μmol/mL solution in CH_2Cl_2, 20 μL, 0.05 equiv) was added to the suspension. The mixture was stirred at the same temperature for 2 h, and Et_3N was added. The resulting mixture was filtered through silica gel pad and the pad was washed with EtOAc. After concentration in vacuo, the residue was subjected to a silica gel column chromatography (EtOAc/hexane 40:60) to give an anomeric mixture of **68** (159 mg, 95.0 μmol, 76%) as a syrup. The products were subjected to a HPLC (μBondasphere 150 SIL-100, 7.8 (ϕ) × 30 mm, EtOAc/hexane 35:65, 2.25 mL/min, t_R = 30 min) to remove two minor isomers. However, the sample still contained the last minor isomer. The major signals in the ^{1}H NMR spectrum of this sample were identical to those prepared from pure **67**.

4.45. Methyl 4-*O*-[2′,3′,6′-tri-*O*-(4-methoxyphenyl)methyl-4′-*O*-[2″,3″,6″-tri-*O*-(4-methoxyphenyl)methyl-5″-thio-α-D-glucopyranosyl]-5′-thio-D-glucopyranosyl]-2,3,6-tri-*O*-(4-methoxyphenyl)methyl-α-D-glucopyranoside (69)

A solution of the anomeric mixture of **68** (105 mg, 62.7 μmol, a mixture of isomers) and NaOMe (32.0 mg, 593 μmol) in a mixture of MeOH (2.0 mL) and THF (0.5 mL) was stirred at 40 °C for 4 h. After neutralization by the addition of 2 M aqueous HCl solution, the mixture was poured into H_2O and extracted with EtOAc (×3). The combined extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (EtOAc/benzene 10:90) gave an anomeric mixture of **69** (76.8 mg, 47.1 μmol, 75%, α:β = 91:9) as a syrup. The anomeric mixture was subjected to a medium pressure column chromatography to give α-anomer (59.9 mg) and β-anomer (5.0 mg).

4.45.1. Physical data for α-anomer. $[\alpha]_D^{26}$ +99° (*c* 0.89, $CHCl_3$). IR (film) 3500, 2910, 2830, 1610, 1510, 1250, 1095, 1030, 820 cm^{-1}. ^{1}H NMR (C_6D_6, The sequence of 5-thioglucose was not assigned.) δ 3.11 (3H, s, CH_3O), 3.14 (1H, br, OH), 3.24, 3.268, 3.272, 3.274, 3.278, 3.281, 3.285, 3.30, 3.31 (each 3H, s, CH_3O), 3.58–3.69 (3H, C2H, Ca5H, Ca6HH), 3.79-3.87 (4H, C6HH, Ca6HH, Cb5H, Cb6HH), 3.93 (1H, dd, J = 2.9 and 9.3 Hz, Ca2H), 4.02–4.13 (5H, C5H, C6HH, Ca3H, Ca4H, Cb6HH), 4.22 (1H, dd, J = 4.4, 9.3 Hz, Cb6HH), 4.26, 4.29 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.35, 4.49 (each 1H, d, J = 10.5 Hz, ArCH_2O), 4.36, 4.36 (each 1H, ArCH_2O), 4.38, 4.55 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.45 (1H, t, J = 9.3 Hz, C3H), 4.48 (1H, t, J = 9.8 Hz, Cb3H), 4.50, 4.59 (each 1H, d, J = 11.2 Hz, ArCH_2O), 4.64, 4.69 (each 1H, d, J = 11.7 Hz, ArCH_2O), 4.65 (1H, d, J = 3.6 Hz, C1H), 4.77, 5.01 (each 1H, d, J = 11.2 Hz, ArCH_2O), 4.790 (1H, t, J = 9.3 Hz, C4H), 4.793, 5.20 (each 1H, d, J = 11.2 Hz, ArCH_2O), 4.78, 5.23 (each 1H, d, J = 11.2 Hz, ArCH_2O), 5.03 (1H, t, J = 9.8 Hz, Cb4H), 5.99 (1H, d, J = 2.9 Hz, Cb1H), 6.12 (1H, d, J = 2.9 Hz, Ca1H), 6.63–7.44 (36H, *aromatic protons*). FD-MS (%, rel int) 1631 (10, $[M+H]^+$), 1630 (5, M^+), 1510 (71, $[M+H-MPM]^+$), 1509 (100, $[M-MPM]^+$), FD-HRMS Found m/z = 1631.6696. Calcd for $C_{91}H_{107}O_{23}S_2$: $[M+H]^+$, 1631.6566.

4.45.2. Physical data for (α1″ → 4′, β1′ → 4)-isomer. $[\alpha]_D^{26}$ +41° (*c* 0.85, $CHCl_3$). IR (film) 3495, 2930, 2835, 1610, 1510, 1250, 1095, 1030, 820 cm^{-1}. ^{1}H NMR (C_6D_6) δ 2.87 (1H, ddd, J = 3.9, 4.9, 9.8 Hz, C5′H), 3.08 (1h, br, C4″OH), 3.19 (3H, s, CH_3O), 3.261, 3.267, 3.275, 3.28, 3.28, 3.29, 3.294, 3.31, 3.35 (each 3H, s, CH_3O), 3.57 (1H, dd, J = 3.9, 9.3 Hz, C2H), 3.54–3.58 (2H, C″6H_2), 3.77 (1H, t, J = 8.8 Hz, C3′H), 3.80 (1H, dd, J = 4.9, 9.3 Hz, C6′HH), 3.78–3.81 (2H, C5″H, C6HH), 3.90 (1H, dd, J = 2.9, 9.3 Hz, C2″H), 3.94 (1H, br d, J = 9.8 Hz, C5H), 4.077 (1H, t, J = 9.3 Hz, C3″H), 4.084 (1H, t, J = 8.8 Hz, C2′H), 4.12 (1H, dd, J = 4.9, 9.3 Hz, C6′HH), 4.15 (1H, t, J = 9.3 Hz, C4″H), 4.15 (1H, t, J = 9.8 Hz, C3H), 4.18 (1H, dd, J = 3.4,10.7 Hz, C6HH), 4.23. 4.26 (each 1H, J = 11.7 Hz, ArCH_2O), 4.34 (1H, t, J = 9.3 Hz, C4H), 4.36, 4.56 (each 1H, J = 11.7 Hz, ArCH_2O), 4.40, 4.48 (each 1H, J = 11.7 Hz, ArCH_2O), 4.44, 4.61 (each 1H, J = 11.7 Hz, ArCH_2O), 4.52-4.58 (2H, ArCH_2O), 4.63 (1H, d, J = 3.9 Hz, C1H), 4.66, 4.83 (each 1H, J = 10.7 Hz, ArCH_2O), 4.79, 5.03 (each 1H, J = 11.2 Hz, ArCH_2O), 4.94, 5.27 (each 1H, J = 10.3 Hz, ArCH_2O), 4.95, 5.16 (each 1H, J = 11.7 Hz, ArCH_2O), 4.96 (1H, t, J = 8.8 Hz, C4′H), 5.01 (1H, d, J = 8.8 Hz, C1′H), 5.95 (1H, d, J = 2.9 Hz, C1″H),6.73-7.67 (32H, *aromatic protons*), FD-MS (%, rel int) 1671 (7.3, $[M+2H+K]^+$), 1655 (11, $[M+2H+Na]^+$), 1632 (13, $[M+2H]^+$), 1511 (100, $[M+2H-MPM]^+$), FD-HRMS Found m/z = 1630.6582. Calcd for $C_{91}H_{106}O_{23}S_2$: M^+, 1630.6560.

4.46. Methyl 4-*O*-[2′,3′,6′-tri-*O*-(4-methoxyphenyl)methyl-4′-*O*-[2″,3″,6″-tri-*O*-(4-methoxyphenyl)methyl-4″-*O*-[2‴,3‴,6‴-tri-*O*-(4-methoxyphenyl)methyl-4‴-*O*-acetyl-5‴-thio-α-D-glucopyranosyl]-5″-thio-α-D-glucopyranosyl]-5′-thio-α-D-glucopyranosyl]-2,3,6-tri-*O*-(4-methoxyphenyl) methyl-α-D-glucopyranoside (70)

According to *general procedure B*, a suspension of a **69** (44.1 mg, 26.9 μmol), **64** (36.6 mg, 49.2 μmol), and MS4A (80 mg) in CH_2Cl_2 (1.0 mL) was stirred at room temperature for 30 min. After cooling to −78 °C, TESOTf (100 μmol/mL solution in CH_2Cl_2, 25 μL, 0.05 equiv) was added to the suspension. The mixture was stirred at same temperature for 2 h and Et_3N was added. The resulting mixture was filtered through silica gel pad, which was washed with EtOAc. After concentration in vacuo, the residue was subjected to a silica gel column chromatography (EtOAc/hexane 45:55) to give **70** (40.5 mg, 18.3 μmol, 68%) as a syrup. The ^1H NMR spectrum indicated that this sample consisted of a mixture of anomers. Thus, the optical rotation was not measured. IR (film) 2950, 2835, 1750, 1610, 1460, 1250, 1095, 1030, 820 cm^{-1}. NMR (C_6D_6, Assignments of the signals for the main isomer and some for the minor isomer are described. $a = 0.9$, $b = 0.1$): δ 1.73 (3H × a, s, CH_3CO), 2.92 (1H × b, ddd, $J = 4.8$, 5.4, 10.7 Hz, C5‴H), 3.10 (3H × a, s, CH_3O), 3.24, 3.25, 3.265, 3.268, 3.268, 3.272, 3.28, 3.28, 3.289, 3290, 3.312, 3.314 (each 3H × a, s, CH_3O), 3.54-3.55 (2H × a, C‴6H_2), 3.62 (1H × a, dd, $J = 3.4$, 9.3 Hz, C2H), 3.68 (1H × b, dd $J = 5.4$, 10.7, C6‴HH), 3.73 (1H × a, dt, $J = 4.4$, 10.7 Hz, C‴5H), 3.77-3.86 (5H × a, C6HH, C′6HH, C″6HH, C′5H (or C″5H), C‴2H), 3.92 (1H × a, dt, $J = 3.4$, 10.2 Hz, C′5H (or C″5H)), 3.98–4.08 (4H × a, C5H, C6HH, C′2H, C″2H), 4.185, 4.28 (each 1H × a, d, $J = 11.2$ Hz, ArCH_2O), 4.186 (1H × a, t, $J = 9.3$ Hz, C‴3H), 4.22 (1H × a, C′6HH (or C6″HH)), 4.33, 4.39 (each 1H × a, d, $J = 11.2$ Hz, ArCH_2O), 4.34, 4.78 (each 1H × a, d, $J = 11.2$ Hz, ArCH_2O), 4.36, 4.53 (each 1H × a, d, $J = 11.0$ Hz, ArCH_2O), 4.39, 4.48 (each 1H × a, d, $J = 11.2$ Hz, ArCH_2O), 4.40–4.50 (4H × a, C3H, C′3H, C″3H, C′6HH (or C6″HH)), 4.41, 4.54 (each 1H × a, d, $J = 12.2$ Hz, ArCH_2O), 4.54, 4.73 (each 1H × a, d, $J = 11.7$ Hz, ArCH_2O), 4.61, 4.68 (each 1H × a, d, $J = 11.2$ Hz, ArCH_2O), 4.61, 4.90 (each 1H × a, d, $J = 11.0$ Hz, ArCH_2O), 4.64 (1H × a, d, $J = 3.4$ Hz, C1H), 4.75 (1H × a, t, $J = 9.3$ Hz, C4H), 4.78, 5.18 (each 1H × a, d, $J = 11.7$ Hz, ArCH_2O), 4.800, 5.25 (each 1H × a, d, $J = 11.7$ Hz, ArCH_2O), 4.803, 5.15 (each 1H × a, d, $J = 10.3$ Hz, ArCH_2O), 4.96 (1H × a, t, $J = 10.2$ Hz, C′4H (or C″4H)), 5.08 (1H × a, t, $J = 9.3$ Hz, C′4H (or C″4H)), 5.72 (1H × b, t, $J = 9.8$ Hz C4‴H), 5.75 (1H × a, dd, $J = 9.8$, 10.7 Hz, C‴4H), 5.95 (1H × b, d, $J = 2.4$ Hz, *anomeric proton*), 5.97–5.98 (2H × a, C′1H (or C″1H), C‴1H), 6.08 (1H × a, d, $J = 2.9$ Hz, C′1H (or C″1H)), 6.14 (1H × b, d, $J = 2.9$ Hz, *anomeric proton*), 6.64-7.56 (48H, *aromatic protons*). ESI-MS (%, rel int) 2251 (43, $[M+2H+K]^+$), 2235 (100, $[M+2H+Na]^+$), 2114 (16, $[M+2H+Na-MPM]^+$). ESI-HRMS Found m/z = 2233.8606. Calcd for $C_{123}H_{142}O_{31}S_3Na$: $[M+Na]^+$, 2233.8595.

4.47. Methyl 4-*O*-[2′,3′,6′-tri-*O*-(4-methoxyphenyl)methyl-4′-*O*-[2″,3″,6″-tri-*O*-(4-methoxyphenyl)methyl-4″-*O*-[2‴,3‴,6‴-tri-*O*-(4-methoxyphenyl)methyl-4‴-*O*-acetyl-5‴-thio-α-D-glucopyranosyl]-5″-thio-α-D-glucopyranosyl]-5′-thio-α-D-glucopyranosyl]-2,3,6-tri-*O*-(4-methoxyphenyl)methyl-α-D-glucopyranoside (71)

A solution of the anomeric mixture of **70** (51.0 mg, 23.0 μmol) and NaOMe (14.0 mg) in a mixture MeOH (1.0 mL) and THF (0.3 mL) was stirred at 40 °C for 4 h. After neutralization by the addition of 2 M HCl aqueous solution, the mixture was poured into H_2O and extracted with EtOAc (×3). The combined extracts were washed with brine, dried over $MgSO_4$, and then concentrated in vacuo. Purification of the residue by silica gel column chromatography (benzene/EtOAc 90:10) gave an anomeric mixture of **71** (α:β = 90:10, 38.0 mg, 76%,) as a syrup. Medium pressure column chromatography gave a pure α-anomer (24.8 mg). However, pure sample of minor isomer could not be obtained. $[\alpha]_D^{26}$ +101° (c 1.61, $CHCl_3$). IR (film) 3470, 2920, 1610, 1510, 1250, 1095, 1030, 820 cm^{-1}. ^1H NMR (C_6D_6, The sequence of 5-thioglucose was not assigned) δ 3.09 (3H, s, C1OCH_3), 3.23, 3.24, 3.25, 3.258, 3.258, 3.261, 3.261, 3.27, 3.28, 3.286, 3.286, 3.30 (each 3H, s, CH_3O), 3.61 (1H, m, C5H), 3.62 (1H, dd, $J = 3.4$, 9.3 Hz, C2H), 3.65 (1H, dd, $J = 4.4$, 9.3 Hz, C6HH), 3.789 (1H, dd, $J = 2.9$, 9.8 Hz, C6HH), 3.794 (1H, m, C6HH), 3.81 (1H, m, C6HH), 3. 845 (1H, ddd, $J = 3.4$, 9.3 Hz C5H), 3.85 (1H, dd, $J =$, 9.3 Hz, C6HH), 3.91 (1H, dd, $J = 2.9$, 9.8 Hz, C2H), 3.92 (1H, ddd, $J = 2.9$, 3.9, 9.3 Hz, C5H), 4.00 (1H, dd, $J = 3.4$, 10.2 Hz, C6HH), 4.051 (1H, dd, $J = 2.9$, 9.8 Hz, C2H), 4.056 (1H, dd, $J = 2.9$, 9.8 Hz, C2H), 4.06 (1H, ddd, $J = 3.4$, Hz, C5H), 4.07 (1H, t, $J = 9.8$ Hz, C3H), 4.12 (1H, t, $J = 9.8$ Hz, C4H), 4.21 (1H, dd, $J = 3.9$, 9.8 Hz, C6HH), 4.24, 4.29 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 4.32, 4.37 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 4.34, 4.48 (each 1H, d, $J = 11.2$ Hz, ArCH_2O), 4.35, 4.54 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 4.37, 4.54 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 4.41 (1H, m, C6HH), 4.44 (1H, t, $J = 9.3$ Hz, C3H), 4.44, 4.59 (each 1H, d, $J = 11.2$ Hz, ArCH_2O), 4.46 (1H, t, $J = 9.3$ Hz, C3H), 4.51 (1H, t, $J = 9.3$ Hz, C3H), 4.55, 4.75 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 4.62, 4.69 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 4.64 (1H, d, $J = 3.4$ Hz, C1H), 4.73, 5.01 (each 1H, d, $J = 11.2$ Hz, ArCH_2O), 4.77 (1H, t, $J = 9.3$ Hz, C4H), 4.78, 5.19 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 4.79, 5.17 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 4.82, 5.25 (each 1H, d, $J = 11.7$ Hz, ArCH_2O), 5.04 (1H, t, $J = 9.3$ Hz, C4H), 5.10 (1H, t, $J = 9.3$ Hz, C4H), 5.98 (1H, d, $J = 2.9$ Hz, C1H), 6.06 (1H, br d, $J = 2.9$ Hz, C1H), 6.10 (1H, d, $J = 2.9$ Hz, C1H), 6.64–7.46 (48H, *aromatic protons*). ESI-MS (%, rel int): 2209 (24, $[M+K]^+$), 2193 (100, $[M+Na]^+$). ESI-HRMS Found m/z = 2191.8447. Calcd for $C_{121}H_{140}O_{30}S_3Na$: $[M+Na]^+$, 2191.8489.

4.48. Methyl 4-*O*-[4′-*O*-[4″-*O*-[5‴-thio-α-D-glucopyranosyl]-5″-thio-α-D-glucopyranosyl]-5′-thio-α-D-glucopyranosyl]-α-D-glucopyranoside (3)

To a solution of **71** (24.8 mg, 11.4 μmol) in CH_2Cl_2 (2.0 mL) and H_2O (0.2 mL), DDQ (62.3 mg, 274 μmol) was added at room temperature. The mixture was stir-

red at the same temperature for 24 h. After washing the mixture with EtOAc, the resulting aqueous solution was passed through a SepPak ODS® to give **3** (7.3 mg, 10.0 μmol, 88%). Since this sample was soluble in only H_2O, IR spectrum was not measured. $[\alpha]_D^{26}$ +211° (*c* 0.92, water). ^{1}H NMR (D_2O) δ 3.00–3.13 (3H), 3.32 (3H, s, C*H*$_3$O), 3.48–3.66 (6H), 3.73–3.89 (14H), 3.96 (2H, dd, *J* = 4.8, 11.2 Hz), 4.73 (1H, *J* = 3.4 Hz, *anomeric proton*), 5.17 (1H, d, *J* = 2.9 Hz, *anomeric proton*), 5.18 (1H, d, *J* = 3.4 Hz, *anomeric proton*), 5.24 (1H, d, *J* = 2.9 Hz, *anomeric proton*). ^{13}C NMR (D_2O) δ 42.6, 42.9, 44.1, 55.1, 60.1, 60.35, 60.38, 60.8, 70.1, 71.2, 73.2, 73.9, 74.0, 74.8, 75.0, 75.42, 75.49, 75.6, 75.7, 81.4, 81.7, 82.4, 83.3, 83.6, 99.1. FAB-MS (%, negative mode, rel int) 763 (2.6, $[M+Cl]^-$), 727 (3.9, $[M-H]^-$), 549 (2.5, $[M-\text{thioglucose}(C_6H_{11}O_4S)]^-$). FAB-HRMS (negative mode) Found *m*/*z* = 727.1591. Calcd for $C_{25}H_{43}O_{18}S_3$: $[M-H]^-$, 727.1612.

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