# Chemoselective Glycosylations. 2. Differences in Size of Anomeric Leaving Groups Can Be Exploited in Chemoselective Glycosylations

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*Received July 7, 1997*[⊗]

We have developed a novel chemoselective glycosylation strategy. This glycosylation strategy is based on the fact that the glycosyl reactivity of an anomeric thiol group can be controlled by the bulkiness of this group whereby we have produced a new range of differentially reactive coupling substrates. It was also shown that the anomeric configuration of the thioglycosides affects the reactivity of the substrates. The new approach will enable complex oligosaccharides of biological importance to be prepared in a highly convergent manner. The versatility of this approach is demonstrated by the synthesis of pentasaccharide **34** from the building blocks **7**, **9**, **10**, **12**, and **14** without a single protecting group manipulation.

## Introduction

Oligosaccharides are involved in many vital biological processes, and not surprisingly, there is increased demand for new and more efficient methods for their chemical synthesis.[1] During the past few years, thioglycosides[2] and *n*-pentenyl glycosides[3] have attracted considerable attention in oligosaccharide synthesis. These substrates are stable under many different chemical conditions, and thus, the anomeric moiety can act as an efficient protecting group. In addition, in the presence of several electrophilic reagents, thio- and *n*-pentenyl glycosides are activated and undergo clean glycosylations with a variety of glycosyl acceptors. Another attractive feature of thio- and *n*-pentenyl glycosides is that they can be used in a chemoselective ("armed−disarmed") glycosylation strategy.[3,4] In such a glycosylation strategy, protecting group manipulations are avoided during the assembly of an oligosaccharide, and hence the number of synthetic steps can be limited.

The armed−disarmed glycosylation approach relies on the fact that C-2 ethers activate (arm) and C-2 esters deactivate (disarm) the anomeric center. Thus, coupling of a glycosyl donor having a C-2 ether protecting group (armed) with an acceptor having a C-2 ester protecting group (disarmed) proceeds highly chemoselectively to give a coupling product in high yield. The anomeric center of the resulting disarmed disaccharide can be activated with a more powerful activator, and reaction with a suitable acceptor will yield a trisaccharide. It has also been demonstrated[5] that saccharides may be regarded as disarmed when a cyclic acetal is attached to the pyranosyl ring. Recently, Ley and co-workers reported that thioglycosides, bearing a dispiroketal (dispoke)[6] or cyclohexanone-1,2-diacetal (CDA) protecting group,[7] have reactivities between armed and disarmed thioglycosides and therefore may be regarded as semi-disarmed substrates. Thus, at the moment three distinct levels of anomeric reactivity for thioglycosides have been described.

The anomeric reactivity of the glycosyl donors reported hitherto is controlled by protecting groups only, in particular the one at C-2. This feature imposes a serious limitation since the nature of the protecting group at C-2 is a major determinant of the stereochemical outcome of a glycosylation. Therefore, it will be attractive to control the anomeric reactivity of thioglycosyl donors by other means, for example by modifying the anomeric leaving group. Such an approach will give an exciting opportunity to tune glycosyl donor leaving group ability further and, thus, realize a greater potential for these glycosylation reactions.[8]

Here, we report the effect of the bulkiness of the anomeric thiol group on glycosyl reactivity whereby we have produced a new range of differentially reactive coupling substrates.[9]

## Results and Discussion

It was anticipated that structural and electronic modifications of an anomeric moiety of a thioglycoside will

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

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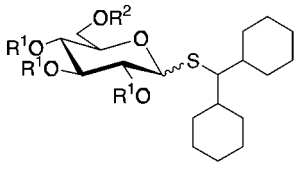
S0022-3263(97)01233-4 CCC: $14.00 



**1** $R^1 = R^2 = Ac$
**2** $R^1 = R^2 = H$
**3** $R^1 = R^2 = Bn$
**4** $R^1 = R^2 = Bz$
**5** $R^1 = H, R^2 = TBDMS$
**6** $R^1 = Bn, R^2 = TBDMS$
**7** $R^1 = Bn, R^2 = H$
**8** $R^1 = Bz, R^2 = TBDMS$
**9** $R^1 = Bz, R^2 = H$

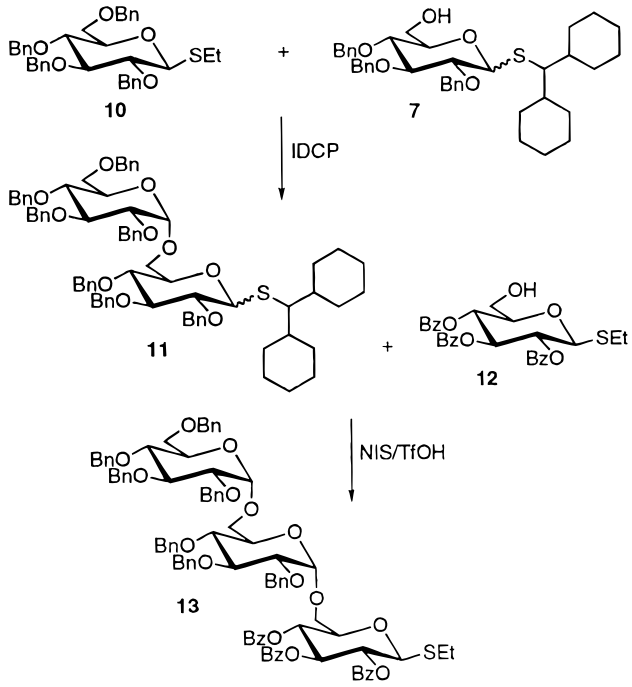
**Figure 1.** Synthesis of glycosyl donors and acceptors.

effect the anomeric leaving group ability. The glycosyl donors and acceptors **3**, **4**, **7**, and **9** were prepared to investigate the effect of the bulkiness of the anomeric thiol group on the anomeric reactivity (Figure 1). Treatment of peracetylated glucose with dicyclohexylmethanethiol[10] in the presence of trimethylsilyl triflate (TMSOTf) for 16 h at 20 °C gave, after aqeuous workup and trituration, two fractions that contained the individual anomers of **1** which were further purified by silica gel column purification to give pure **1**α (49%) and **1**$\beta$ (18%). Compound **1**α was deacetylated with NaOMe in dichloromethane (DCM)/methanol to give **2**α which was subsequently benzylated with benzyl bromide and sodium hydride in DMF to afford **3**α in an excellent yield (77%). Compound **4**α was obtained by benzoylation of **2**α with benzoyl chloride in pyridine. The 6-hydroxyl of **2**α was regioselectively protected as a *tert*-butyldimethylsilyl ether (TBDMS) by treatment with TBDMSCl in pyridine to furnish compound **5**α (76%). Compound **5**α was benzylated with sodium hydride and benzyl bromide in DMF to afford **6**α (92%), the TBDMS group of which was removed by treatment with acetic acid−water (9/1, v/v) at 60 °C to yield compound **7**α (76%). Compound **8**α was obtained by benzoylation of **5**α with benzoyl chloride in pyridine and removal of the TBDMS group with acetic acid/water (9/1, v/v) at 60 °C gave compound **9**α (76% overall yield). The $\beta$-anomers of compounds **3**, **4**, **7**, and **9** were obtained by employing similar reaction sequences but starting from the $\beta$-anomer of **1**.

Having the requisite glycosyl donors and acceptors in hand, attention was focused on chemoselective glycosylations. Iodonium dicollidine perchlorate (IDCP)-mediated glycosylation of glycosyl donor **10** with glycosyl acceptor **7**α in ether/DCM gave, after a reaction time of 2 h, disaccharide **11** in a yield of 40% as one anomer (Scheme 1). Some starting material and a small amount of a trisaccharide (3%) was isolated. Furthermore, it was observed that side products appeared after an aqueous workup procedure, probably resulting from hydrolytic degradation. Attempts to prevent the formation of these side products failed. The coupling reaction could also be performed with the more convenient activator system NIS/TfOH, but in this case only 1% of TfOH was used (10% TfOH is used under standard conditions). The use of a larger amount of acid gave a mixture of products.

To the best of our knowledge, this is the first example which demonstrates that the bulk of the anomeric leaving group has a profound effect on leaving group mobility, and the new methodology makes it now possible to couple chemoselectively benzylated thioglycosyl donors with

**Scheme 1**



benzylated thioglycosyl acceptors. This feature is of particular importance when in the subsequent glycosylation an α-anomeric linkage needs to be introduced.

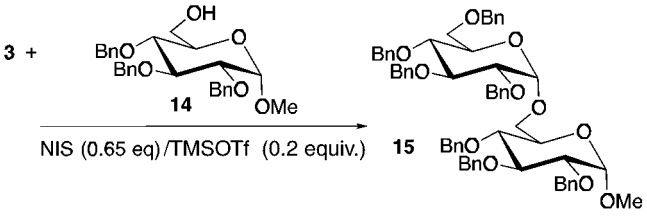
In the next stage of the research, we examined whether electronically and sterically deactivated substrates have sufficiently different reactivities to perform chemoselective glycosylations. Thus, coupling of the electronically deactivated glycosyl acceptor **12** with the sterically deactivated glycosyl donor **11**α in the presence of the powerful promoter system *N*-iodosuccinimide/triflic acid (NIS/TfOH) afforded trisaccharide **13** in a 70% yield. A reasonable α-selectivity was obtained ($\alpha/\beta$ = 6/1) when the reaction was performed in a solvent mixture containing equal amounts of diethyl ether and DCM. However, this selectivity could be significantly improved ($\alpha/\beta$ = 12/1) by increasing the proportion of diethyl ether (diethyl ether/DCM 5/1, v/v). In this respect, it is noteworthy that coupling of dicyclohexylmethyl 2,3,4,6-tetra-*O*-benzyl thioglucoside (**3**) with acceptor **12** in a mixture of diethyl ether/DCM (1/1 v/v) gave the expected disaccharide in high yield but with modest anomeric selectivity ($\alpha/\beta$ = 3/1). Thus, the glycosyl moiety at C-6 of disaccharide **11** affects the stereochemical course of the glycosylation, and a much improved α-selectivity is obtained. This directional effect probably originates from additional steric hindering at the $\beta$-face of the glycosyl donor. It has been reported[11] that bulky protecting groups at C-6 of a glucosyl donor improve the α-selectivity.

A different reaction profile was obtained when trisaccharide **13** was prepared from the $\beta$-linked dicyclohexylmethyl thioglycoside **7**$\beta$. Thus, coupling of the ethyl thioglycoside **10** with **7**$\beta$ in the presence of IDCP gave the disaccharide **11**$\beta$ in a high yield of 71%. No self-condensed or polymeric products were detected, and apart from the disaccharide **11**$\beta$ only small amounts of starting materials were isolated. The improved yield may probably be attributed to the lower reactivity of the $\beta$-linked thiodicyclohexylmethyl moiety. The trisaccharide **13** was isolated in a disappointing yield of 30% when the coupling was performed with **11**$\beta$ as the glycosyl donor. In this

(10) Dicyclohexylmethanethiol was prepared from the corresponding commercial available alcohol according to the three-step procedure of Kellogg et al.: Strijtveen, B.; Kellogg, R. M. *J. Org. Chem.* **1986**, *51*, 3664.

(11) Houdier, S.; Vottero, P. J. A. *Carbohydr. Res.* **1992**, *232*, 349.

**Table 1**



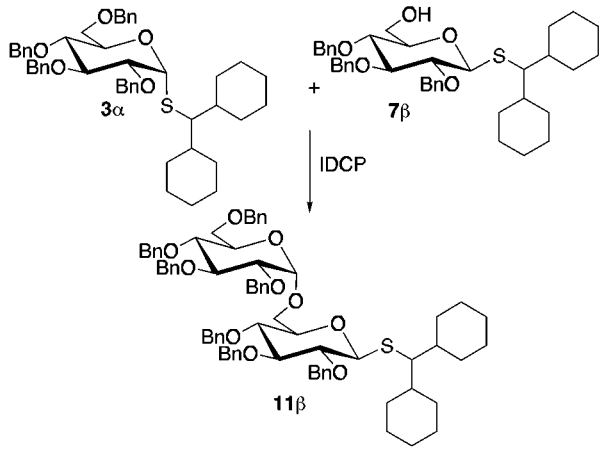

| α/β ratio of **3** | product yield (%) | recovered donor **3** (%) |
|---|---|---|
| 1/0 | 50 (α/β = 3/1) | 42 (α/β = 1/0) |
| 1/1 | 44 (α/β = 3/1) | 54 (α/β = 3/1) |
| 0/1 | 37 (α/β = 3/1) | 53 (α/β = 0/1) |

case, a substantial amount of glycosyl donor **11**$\beta$ was recovered, and it proved to be difficult to drive the reaction successfully to completion.

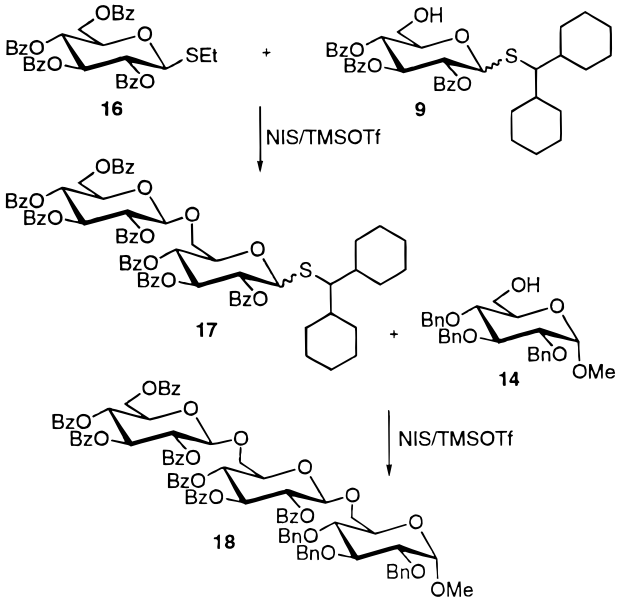
The results of these glycosylations demonstrate that the reactivity of a C-2-benzylated dicyclohexylmethyl thioglycoside is of an order of magnitude between ethyl thioglycosides having a fully armed ether and disarmed ester protecting group on C-2 which implies that these novel thioglycosides may be regarded as semi-disarmed substrates. However, it appeared that the reactivity of these novel compounds (**7** and **11**) depends on the anomeric configuration of the thio moiety. To study this observation further, the α- and $\beta$-anomers of **3** were coupled with **14**, but in these experiments only 0.7 equiv of NIS was used. As can be seen from Table 1, the α-anomer gave a higher conversion than the $\beta$-anomer. As expected, a significant amount of donor was reclaimed, the $^1$H NMR spectrum of which showed that no anomerization of the anomeric thio leaving group had occurred. This observation is in agreement with an earlier report[12] which described that thioglycosides having a bulky anomeric thio group do not anomerize during iodonium ion promoted glycosylations. The latter property provided the possibility to compare directly the reactivities of α- and $\beta$-thioglycosides by a competitive glycosylation. When a mixture of anomers of **3** (α/$\beta$ =1/1) was glycosylated with **14**, using 0.7 equiv of NIS, mainly the $\beta$-anomer of **3** (α/$\beta$ = 1/3) was reclaimed and largely the α-anomer had been glycosylated. The latter reaction was also performed as a NMR experiment which showed a similar conversion. It was also observed that treatment of compound **7**α with IDCP resulted, after a reaction time of 2 h, in a complex mixture of products containing self-condensed and hydrolyzed material and some 1,6-anhydro-2,3,4-tri-*O*-benzyl-glucose. Interestingly, no reaction was observed when the analogous $\beta$-anomer was treated with IDCP. These observations indicated that it should be possible to couple chemoselectively glycosyl donor **3**α with **7**$\beta$ to give **11**$\beta$. Indeed, when a mixture of **3**α and **7**$\beta$ was treated with IDCP, disaccharide **11**$\beta$ was isolated in a yield of 50% (Scheme 2).

On the basis of the outcome of these reactions, it can be concluded that the α-linked benzylated dicyclohexylmethyl thioglycosides are more reactive than the corresponding $\beta$-anomers. Lemieux and co-workers have reported[13] that the α- and $\beta$-anomers of glycosyl bromides have significantly different reactivities, and this property has been exploited for the synthesis of α-glycosides (in situ anomerization procedure). However, the main difference between the reactivities of glycosyl halides and

**Scheme 2**




**Scheme 3**

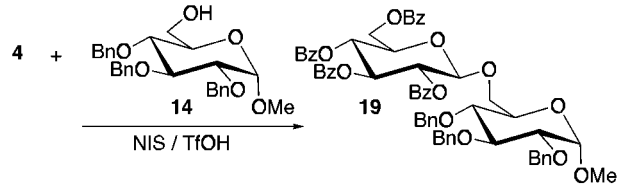



bulky thioglycosides is that during glycosylation only the α- and $\beta$-anomer glycosyl halides are in a dynamic equilibrium.

With a novel method at our disposal to control the anomeric leaving group mobility, it should be possible to create glycosyl donors or acceptors with new reactivities. We envisaged that the sterically and electronically deactivated glycosyl acceptor **9** should have a lower reactivity than the electronically deactivated glycosyl donor **16**. Indeed, coupling of glycosyl donor **16** with glycosyl acceptor **9**α in the presence of NIS/TMSOTf at rt gave disaccharide **17**α in a 64% yield (Scheme 3). A small amount of a trisaccharide was formed (3%) which was easily removed by size-exclusion column chromatography. To demonstrate that an electronically and sterically deactivated substrate is still a suitable glycosyl donor, compound **17**α was coupled with **14** in the presence of NIS/TMSOTf at room temperature and trisaccharide **18** was isolated in a good yield (73%). In this case, an excess of NIS had to be used to drive the reaction to completion. When trisaccharide **17** was prepared from glycosyl acceptor **9**, having the anomeric thio moiety in the $\beta$-configuration, a less satisfactory result was obtained and coupling of **16** with **9**$\beta$ under standard conditions gave **17**$\beta$ in a modest yield of 41%; a significant amount of self-condensation was observed. Disaccharide

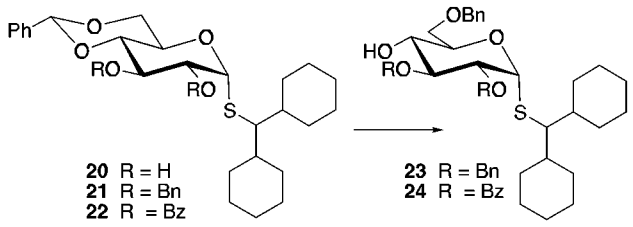
(12) Boons, G. J.; Stauch, T. *Synlett* **1996**, 906.
(13) (a) Lemieux, R. U.; Hayimi, J. L. *Can. J. Chem.* **1965**, *43*, 2162. (b) Lemieux, R. U.; Hendriks, K. B.; Stick, R. V.; James, K. *J. Am. Chem. Soc.* **1975**, *97*, 4056.

**Table 2**




| $\alpha/\beta$ ratio of **4** | product yield (%) | recovered donor **4** (%) |
|---|---|---|
| 1/0 | 30 ($\beta$ only) | 64 ($\alpha/\beta$ = 1/0) |
| 1/1 | 45 ($\beta$ only) | 52 ($\alpha/\beta$ = 1/3) |
| 0/1 | 56 ($\beta$ only) | 38 ($\alpha/\beta$ = 0/1) |

**Scheme 4**

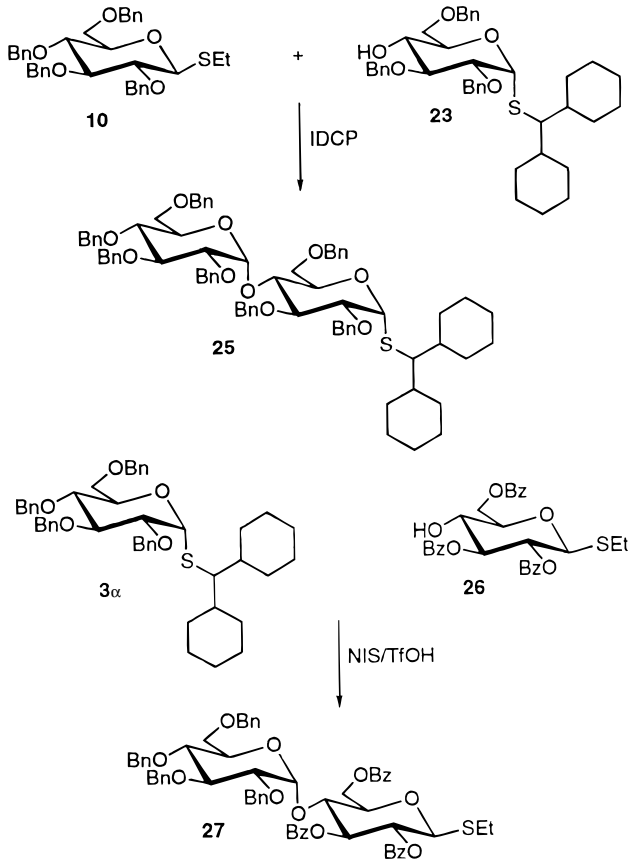



**17**$\beta$ could easily be glycosylated with **14** under standard conditions to give **18** in a good yield (73%).

These results indicate that the reactivity of acetylated dicyclohexylmethyl thioglycosides is also effected by the anomeric configuration. Indeed, NIS/TMSOTf-mediated glycosylation of an anomeric mixture of **4** ($\alpha/\beta$ =1/1) with **14** gave, apart from the expected product **19**, recovery of **4** mainly as the $\alpha$-anomer ($\alpha/\beta$ =3/1) (Table 2). Furthermore, it was observed that these thioglycosides do not anomerize during the glycosylation. Thus, these experiments clearly indicate that a benzoylated dicyclohexylmethyl thioglycoside having a $\beta$-configuration is significantly more reactive than the analogous $\alpha$-anomer. The corresponding benzylated substrates (Table 1) showed an inverse reactivity; i.e. the $\alpha$-anomer is more reactive. The differences in reactivity between benzylated and benzoylated thioglycosides may be rationalized as follows: the benzoyl protecting group at C-2 of a $\beta$-substituted dicyclohexylmethyl thioglycoside will, after activation with an iodonium ion, assist the departure of the anomeric thio group by neighboring group participation. In the case of the $\alpha$-anomer, neighboring group participation may take only place after an unfavorable conformational change of the pyran ring. In the case of a C-2-benzylated dicyclohexylmethyl thioglycoside, additional stabilization of a transition state may only be achieved by participation of a lone pair of the endocyclic oxygen. Thus, in the case of the $\alpha$-anomer, the developing positive charge at the anomeric center may be stabilized by the lone pair of the endocyclic oxygen. This stabilization of the $\beta$-anomer is only possible after an unfavorable conformational change, and hence the $\alpha$-anomer is more reactive.

Encouraged by the promising results obtained, we explored glycosylations with the less reactive glycosyl acceptors. The glucosides **23** and **24** having a 4-hydroxyl were selected as this position has the lowest glycosyl acceptor reactivity and hence represents a worse case scenario. Compound **23** was easily obtained from **2** via a three-step procedure (Scheme 4). Thus, treatment of **2** with benzaldehyde dimethyl acetal and a catalytic amount of camphorsulfonic acid gave regioselectively the partially protected saccharide **20**. Benzylation of **20** under standard conditions afforded the fully protected compound **21**, and regioselective reductive cleavage[14] of the benzylidene acetal of **21** with triethylsilane (TES) and trifluoracetic acid (TFA) yielded the required glycosyl acceptor **23**. Compound **20** was also the starting material for the preparation of glycosyl acceptor **24**. Thus, benzoylation of **20** with benzoyl chloride in pyridine gave **22**, the benzylidene acetal of which was regioselectively cleaved by treatment with $NaCNBH_4$ and HCl to yield **24**.

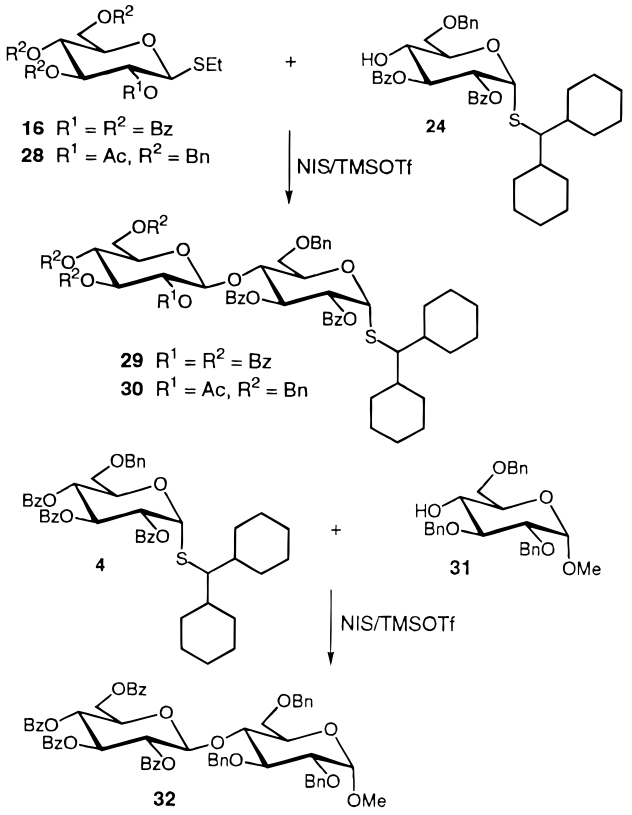
**Scheme 5**



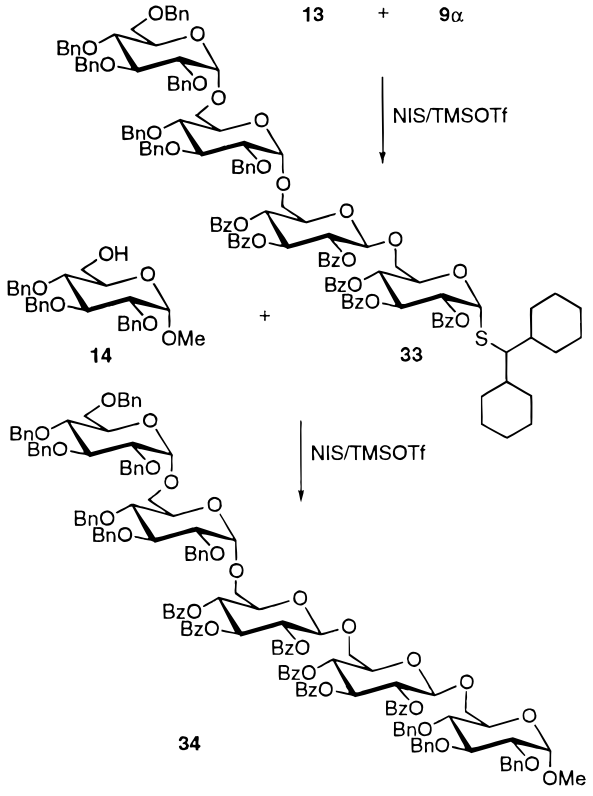

IDCP-mediated glycosylation of the activated glycosyl donor **10** with the sterically deactivated acceptor **23** in a DCM/diethyl ether mixture gave the disaccharide **25** as a single anomer in an acceptable yield of 40% (Scheme 5). No self-condensed or oligomeric material was obtained, and apart from the coupling product, some starting material was recovered together with hydrolyzed material. As expected, coupling of the sterically deactivated glycosyl donor **3**$\alpha$ with the electronically deactivated acceptor **26** proceeded in good yield to give disaccharide **27** (61%, $\alpha/\beta$ = 6/1) when the promoter system NIS/TfOH was used. Unfortunately, the coupling of the electronically deactivated substrate **16** with the doubly deactivated acceptor **24** did not result in the formation of disaccharide **29**, and mainly hydrolyzed donor and acceptor **24** were isolated (Scheme 6). The 4-hydroxyl of **24** is deactivated by the neighboring benzoyl protecting group and by the presence of the anomeric thio moiety. Also the benzoylated donor is of low reactivity. The reaction may proceed more favorably with the glycosyl donor **28**, which by the presence of the benzyl ethers at C-3, C-4, and C-6 is significantly more reactive than **16**. However, the acetyl functionality at C-2 of **28** will have a disarming effect and will perform neighboring group participation to give a $\beta$-glycoside. The coupling of **28** with **24** in the presence of NIS/TfOH gave only a small amount of coupling product **30** (19%). Fortunately, when

(14) DeNinno, M. P.; Etienne, J. B.; Duplantier, K. C. *Tetrahedron Lett.* **1995**, *36*, 669.

**Scheme 6**




**Scheme 7**




TMSOTf was used instead of triflic acid, the reaction proceeded smoothly and disaccharide **30** was isolated in a yield of 56%. Finally, it was demonstrated that a doubly deactivated glycosyl donor reacts cleanly with a stericly hindered sugar alcohol and NIS/TMSOTf-mediated coupling **4**α with the methyl glucoside **31** gave the disaccharide **32** in an excellent yield of 62%.

A combined use of electronic and steric factors enables the generation of a range of thioglycosides with four distinct levels of anomeric reactivity, and it should now be possible to assemble a pentasaccharide from properly protected thioglycosides without any protecting group manipulations. To illustrate the latter feature, the pentasaccharide **34** was prepared from the building blocks **7**α, **9**α, **10**, **12**, and **14** (Schemes 1 and 7). The electronically deactivated trisaccharide donor **13** was coupled with the doubly disarmed glycosyl acceptor **9**α in the presence of the powerful promoter NIS/TMSOTf to give the tetrasaccharide **33** in a reasonable yield of 55%. In this case, only the *β*-anomer was obtained as a result of neighboring group participation of the C-2 benzoyl ester of **13**. Finally, NIS/TMSOTf-mediated glycosylation of **33** with **14** afforded the pentasaccharide **34** in a yield of 62%. The successful preparation of **34** illustrates that the chemoselective glycosylation methodology proceeds reliably also when performed with larger fragments.

## Conclusion

The research described in this paper shows, for the first time, that the reactivity of thioglycosides can be controlled by the bulkiness of the anomeric thiol group and has produced glycosyl donors and acceptors with new levels of reactivity. It was also shown that the anomeric configuration of the thioglycosides affects the reactivity of the substrates. The new methodology proved to be applicable to primary as well as secondary sugar hydroxyls, and it appeared that the α-anomers of dicyclohexylmethyl thioglycosides provide the most versatile substrates. The armed−disarmed glycosylation strategy has gained in versatility since the anomeric reactivity of glycosyl donors and acceptors can now be controlled by the bulkiness of the leaving group as well as the nature of protecting groups. A wider range of di- and trisaccharides can now be prepared by chemoselective glycosylations having differing anomeric configuration. Such saccharides will be valuable for the assembly of complex oligosaccharides. The methodology is also reliable when performed with larger fragments.

## Experimental Section

**General Methods.** Column chromatography was performed on silica gel 60 (Merck, 70−230 mesh), and reactions were monitored by TLC on Kieselgel 60 $F_{254}$ (Merck). Detection was effected by examination under UV light and by charring with 20% sulfuric acid in methanol, or with a molybdate solution (a 0.02 M solution of ammonium cerium(IV) sulfate dihydrate and ammonium molybdate(VI) tetrahydrate in aqueous 10% $H_2SO_4$). Solvents were evaporated under reduced pressure at 40 °C (bath). All solvents were distilled from the appropriate drying agents; dichloromethane, 1,2-dichloroethane, and toluene were distilled from $P_2O_5$ and stored over molecular sieves (4 Å). Diethyl ether was distilled from $CaH_2$, redistilled from $LiAlH_4$, and stored over sodium wire. *N*,*N*-Dimethylformamide was stirred with $CaH_2$ for 16 h, distilled under reduced pressure, and stored over molecular sieves (4 Å). Methanol was dried by refluxing with magnesium methoxide, distilled, and stored over molecular sieves (3 Å), and pyridine was dried by refluxing with $CaH_2$ and then distilled and stored over molecular sieves (4 Å).

**Dicyclohexylmethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-α/*β*-D-glucopyranoside (1).** To a stirred mixture of *β*-D-glucose pentaacetate (15.2 g, 38.9 mmol) and dicyclohexylmethanethiol (7.1 g, 33.4 mmol) in dry $CH_2Cl_2$ (70 mL) was added TMSOTf (7.8 mL, 42.8 mmol). After 16 h of stirring at rt, the reaction

mixture was quenched with TEA (6.2 mL, 44.5 mmol), diluted with $CH_2Cl_2$ (50 mL), and washed with $H_2O$ (3 × 25 mL). The organic layer was dried ($MgSO_4$) and filtered. The filtrate was concentrated in vacuo and triturated from $CH_2Cl_2$/petroleum ether (bp 40−60 °C) to afford a mixture of **1**$\beta$ and peracetylated glucose. Further purification by silica gel column chromatography (toluene/acetone, 95/5, v/v) afforded **1**$\beta$ as a white solid (3.3 g, 18%): $R_f$ 0.45 (toluene/acetone, 9/1, v/v); $[\alpha]^{25}_D$ −0.23° (*c* 1); FAB-MS *m*/*z* 465 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) $\delta$ 170.6−169.3 (4 *C*OCH$_3$), 87.1 (C-1), 75.6, 74.1, 71.2, and 68.7 (C-2,3,4,5), 62.6 (C-6), 62.2 (S*C*H), 40.8−26.3 (2 $C_6H_{11}$), 20.7−20.6 (4 CO*C*H$_3$); $^1$H NMR ($CDCl_3$) $\delta$ 5.20 (t, 1H, H-3, $J_{2,3}J_{3,4}$ 9.3 Hz), 5.04 (t, 1H, H-4, $J_{4,5}$ 9.7 Hz), 4.96 (dd, 1H, H-2, $J_{1,2}$ 10.1 Hz), 4.40 (d, 1H, H-1), 4.20 (dd, 1H, H-6a, $J_{5,6a}$ 5.7, $J_{6a,6b}$ −12.2 Hz), 4.11 (dd, 1H, H-6b, $J_{5,6b}$ 2.5 Hz), 3.63 (m, 1H, H-5), 2.28 (m, 1H, SC*H*), 2.07, 2.06, 2.02, and 2.00 (4 s, 12 H, 4 COC*H*$_3$), 1.90−1.00 (m, 22H, 2 $C_6H_{11}$); HR FAB-MS calcd for $C_{27}H_{42}SO_9Na$ 565.2447, found 565.2461. The remaining filtrate was concentrated in vacuo, and the residue was purified by silica gel column chromatography (toluene/acetone, 95/5, v/v) to afford **1**$\alpha$ as a white solid (8.8 g, 49%): $R_f$ 0.53 (toluene/acetone, 9/1, v/v); $[\alpha]^{25}_D$ +11.35° (*c* 1); $^{13}$C NMR ($CDCl_3$), $\delta$ 170.6−169.3 (4 *C*OCH$_3$), 85.1 (C-1), 70.8, 70.4, 68.6 and 68.0 (C-2,3,4,5), 62.0 (C-6), 61.2 (S*C*H), 41.3−26.5 (2 $C_6H_{11}$), 20.8−20.7 (4 CO*C*H$_3$); $^1$H NMR ($CDCl_3$) $\delta$ 5.48 (d, 1H, H-1, $J_{1,2}$ 5.8 Hz), 5.33 (dd, 1H, H-3, $J_{2,3}$ 10.5, $J_{3,4}$ 9.4 Hz), 5.05 (t, 1H, H-4, $J_{4,5}$ 10.2 Hz), 5.00 (dd, 1H, H-2), 4.48 (m, 1H, H-5, $J_{5,6a}$ 4.0, $J_{5,6b}$ 2.1 Hz), 4.33 (dd, 1H, H-6a, $J_{6a,6b}$ −12.4 Hz), 4.02 (dd, 1H, H-6b), 2.34 (m, 1H, SC*H*), 2.09, 2.07, 2.04, and 2.01 (4 s, 12H, 4 CO*C*H$_3$), 1.90−1.00 (m, 22H, 2 $C_6H_{11}$).

**Dicyclohexylmethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (3α).** To a solution of **1**$\alpha$ (6.5 g, 12.0 mmol) in dry $CH_2Cl_2$/MeOH (2/1, v/v, 90 mL) was added NaOMe (75 mg, 1.4 mmol). The solution was stirred for 3 h, neutralized with Dowex-50 ($H^+$) resin, and filtered. The filtrate was concentrated in vacuo and co-concentrated from $CH_2Cl_2$ (2 × 20 mL) to yield **2**$\alpha$ as a white solid (4.5 g, 100%), $R_f$ 0.59 ($CH_2Cl_2$/MeOH, 4/1, v/v). To a solution of **2**$\alpha$ (1.2 g, 3.2 mmol) in dry DMF (20 mL) were added NaH (614 mg, 26 mmol) and BnBr (2.3 mL, 19.3 mmol). The mixture was stirred for 18 h at rt, diluted with EtOAc (50 mL), and washed with $H_2O$ (3 × 20 mL). The organic layer was dried ($MgSO_4$) and filtered. The filtrate was concentrated in vacuo and co-concentrated from toluene, MeOH, and $CH_2Cl_2$ (3 × 15 mL each). Purification of the residue by silica gel column chromatography ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 3/1, v/v) afforded compound **3**$\alpha$ as a white solid (1.8 g, 77%): $R_f$ 0.41 ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 4/1, v/v); $[\alpha]^{25}_D$ +8.68° (*c* 1); FAB-MS *m*/*z* 757 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$), $\delta$ 138.9, 138.0, 137.9, and 128.4−127.5 (4 $C_6H_5CH_2$), 86.1 (C-1), 82.8, 80.0, 77.7 and 70.9 (C-2,3,4,5), 75.3, 73.6, 73.2, and 72.2 (4 $C_6H_5CH_2$), 68.5 (C-6), 59.2 (S*C*H), 41.4−26.5 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$) $\delta$ 7.42−7.09 (m, 20H, 4 $C_6H_5$), 5.30 (d, 1H, H-1, $J_{1,2}$ 3.3 Hz), 5.01−4.62 (m, 8H, 4 $C_6H_5CH_2$), 4.25 (m, 1H, H-5), 3.87−3.55 (m, 5H, H-2, H-3, H-4, H-6a, H-6b), 2.43−0.97 (m, 23H, SC*H* and 2 $C_6H_{11}$); HR FAB-MS calcd for $C_{47}H_{58}SO_9Na$ 757.3903, found 757.3890. Dicyclohexylmethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-$\beta$-D-glucopyranoside (**3**$\beta$) was obtained by the same synthetic procedure, starting from **1**$\beta$, as a white solid: $R_f$ 0.41 ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 4/1, v/v); $[\alpha]^{25}_D$ +0.42° (*c* 1); $^{13}$C NMR ($CDCl_3$) $\delta$ 138.7, 138.4, 138.2, and 128.5−127.6 (4 $C_6H_5CH_2$), 88.4 (C-1), 87.0, 82.8, 78.9, and 78.0 (C-2,3,4,5), 75.8, 75.7, 75.0, and 73.7 (4 $C_6H_5CH_2$), 69.5 (C-6), 61.0 (S*C*H), 41.4−26.3 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$), $\delta$ 7.45−7.15 (m, 20H, 4 $C_6H_5$), 4.98−4.52 (m, 8H, 4 $C_6H_5CH_2$), 4.34 (d, 1H, H-1, $J_{1,2}$ 9.5 Hz), 3.71−3.35 (m, 6H, H-2, H-3, H-4, H-5, H-6a, H-6b), 2.44−1.10 (m, 23H, SC*H*, 2 $C_6H_{11}$).

**Dicyclohexylmethyl 2,3,4,6-Tetra-*O*-benzoyl-1-thio-α-D-glucopyranoside (4α).** To a solution of **2**$\alpha$ (1.27 g, 3.39 mmol) in dry pyridine (30 mL) were added DMAP (42 mg, 0.34 mmol) and BzCl (2.2 mL, 19.0 mmol). After 18 h of stirring at rt, the reaction mixture was diluted with $CH_2Cl_2$ (50 mL) and washed with $H_2O$ (3 × 20 mL). The organic layer was dried ($MgSO_4$) and filtered. The filtrate was concentrated in vacuo and co-concentrated from toluene, MeOH, and $CH_2Cl_2$, respectively (3 × 25 mL each). The residue was purified by silica gel column chromatography ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 8/1, v/v) to afford **4**$\alpha$ as a white glass (2.2 g, 82%): $R_f$ 0.60 ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 9/1, v/v); $[\alpha]^{25}_D$ +8.52° (*c* 1); FAB-MS *m*/*z* 813 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.3−165.3 (4 $C_6H_5CO$), 133.4−128.4 (4 $C_6H_5CO$), 86.0 (C-1), 71.8, 70.8, 69.4 and 68.7 (C-2,3,4,5), 62.9 (C-6), 62.0 (S*C*H), 41.1−26.1 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$), $\delta$ 8.10−7.30 (m, 20H, 4 $C_6H_5CO$), 6.01 (t, 1H, H-3, $J_{2,3}$ 10.5, $J_{3,4}$ 10.0 Hz), 5.73 (d, 1H, H-1, $J_{1,2}$ 5.7 Hz), 5.72 (t, 1H, H-4, $J_{4,5}$ 9.8 Hz), 5.47 (dd, 1H, H-2), 4.86 (m, 1H, H-5, $J_{5,6a}$ 2.8, $J_{5,6b}$ 4.1 Hz), 4.59 (dd, 1H, H-6a, $J_{6a,6b}$ −12.3 Hz), 4.50 (dd, 1H, H-6b), 2.40−0.60 (m, 23H, SC*H*, 2 $C_6H_{11}$); HR FAB-MS calcd for $C_{25}H_{48}SSiO_5Na$ 511.2889, found 511.2866. Dicyclohexylmethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-$\beta$-D-glucopyranoside (**4**$\beta$) was obtained by the same synthetic procedure, starting from **2**$\beta$, as a white solid: $R_f$ 0.60 ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 9/1, v/v); $[\alpha]_D$ +0.90° (*c* 1); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.3−165.3 (4 $C_6H_5CO$), 133.4−128.3 (4 $C_6H_5CO$), 87.9 (C-1), 76.2, 74.2, 71.7 and 70.1 (C-2,3,4,5), 63.8 (C-6), 62.5 (S*C*H), 41.1−26.1 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$) $\delta$ 8.10−7.20 (m, 20H, 4 $C_6H_5CO$), 5.91 (t, 1H, H-3/4, *J* 9.6 Hz), 5.63−5.49 (m, 2H, H-3/4 and H-2), 4.76 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 4.60 (dd, 1H, H-6a, $J_{5,6a}$ 2.9, $J_{6a,6b}$ −12.2 Hz), 4.51 (dd, 1H, H-6b, $J_{5,6b}$ 6.2 Hz), 4.13 (m, 1H, H-5, $J_{4,5}$ 9.6 Hz), 2.30−0.60 (m, 23H, C*H*S, 2 $C_6H_{11}$).

**Dicyclohexylmethyl 6-*O*-(*tert*-Butyldimethylsilyl)-1-thio-α-D-glucopyranoside (5α).** Compound **2**$\alpha$ (910 mg, 2.43 mmol) was dissolved in dry pyridine (20 mL), and TBDMSCl (386 mg, 2.56 mmol) was added. The mixture was stirred for 18 h at rt, diluted with $CH_2Cl_2$ (50 mL), and washed with $H_2O$ (3 × 15 mL). The organic layer was dried ($MgSO_4$) and filtered. The filtrate was concentrated in vacuo and co-concentrated from toluene, MeOH, and $CH_2Cl_2$, respectively (3 × 15 mL each). Purification of the residue by silica gel column chromatography ($CH_2Cl_2$/acetone, 5/1, v/v) afforded **5**$\alpha$ (1.12 g, 76%) as a white glass: $R_f$ 0.28 ($CH_2Cl_2$/MeOH, 9/1, v/v); $[\alpha]_D$ +5.56° (*c* 1); FAB-MS *m*/*z* 511 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) $\delta$ 89.3 (C-1), 75.2, 72.4, 72.1, and 71.0 (C-2,3,4,5), 62.2 (C-6), 61.9 (S*C*H), 41.3, 39.7, and 32.0−26.5 (2 $C_6H_{11}$), 26.0 (SiC(*C*H$_3$)$_3$), 18.4 (Si*C*(CH$_3$)$_3$), −5.4 (Si(*C*H$_3$)$_2$); $^1$H NMR ($CDCl_3$), $\delta$ 5.21 (d, 1H, H-1, $J_{1,2}$ 5.4 Hz), 4.02 and 3.71−3.36 (m, 4H, H-2,3,4,5), 3.93 (dd, 1H, H-6a, $J_{5,6a}$ 4.1, $J_{6a,6b}$ −10.4 Hz), 3.76 (dd, 1H, H-6b, $J_{5,6b}$ 6.1 Hz), 2.36 (m, 1H, SC*H*), 2.00−1.00 (m, 22H, 2 $C_6H_{11}$), 0.92 and 0.91 (2 s, 9H, SiC(C*H*$_3$)$_3$), 0.11 and 0.10 (2 s, 6H, Si(C*H*$_3$)$_2$); HR FAB-MS calcd for $C_{25}H_{48}SSiO_5Na$ 511.2889, found 511.2866. Dicyclohexylmethyl 6-*O*-(*tert*-butyldimethylsilyl)-1-thio-$\beta$-glucopyranoside (**5**$\beta$) was obtained by the same synthetic procedure, starting from **2**$\beta$, as a white glass: $R_f$ 0.23 ($CH_2Cl_2$/MeOH, 9/1, v/v); $[\alpha]_D$ −0.87° (*c* 1); $^{13}$C NMR ($CDCl_3$) $\delta$ 88.5 (C-1), 78.1, 77.8, 73.5, and 72.6 (C-2,3,4,5), 64.7 (C-6), 61.0 (S*C*H), 41.1, 40.0 and 31.9−26.4 (2 $C_6H_{11}$), 25.8 (SiC(*C*H$_3$)$_3$), 18.2 (Si*C*(CH$_3$)$_3$), −5.5 (Si(*C*H$_3$)$_2$); $^1$H NMR ($CDCl_3$) $\delta$ 4.25 (d, 1H, H-1, $J_{1,2}$ 9.8 Hz), 3.90 (dd, 1H, H-6a, $J_{5,6a}$ 4.9, $J_{6a,6b}$ −10.4 Hz), 3.80 (dd, 1H, H-6b, $J_{5,6b}$ 6.1 Hz), 3.7−3.3 (m, 4H, H-2,3,4,5), 2.41 (m, 1H, SC*H*), 1.90−1.00 (m, 22H, 2 $C_6H_{11}$), 0.91 and 0.90 (2 s, 9H, SiC(C*H*$_3$)$_3$), 0.10 and 0.09 (2 s, 6H, Si(C*H*$_3$)$_2$).

**Dicyclohexylmethyl 2,3,4-Tri-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-α-D-glucopyranoside (6α).** To a solution of **5**$\alpha$ (365 mg, 0.75 mmol) in dry DMF (10 mL) was added NaH (104 mg, 4.50 mmol) and BnBr (0.40 mL, 3.38 mmol). After 18 h of stirring at rt, the reaction mixture was diluted with EtOAc (50 mL) and washed with $H_2O$ (3 × 15 mL). The organic layer was dried (MgSO4) and filtered. The filtrate was concentrated in vacuo and co-concentrated from toluene, MeOH, and $CH_2Cl_2$, respectively (3 × 15 mL each). Purification by silica gel column chromatography ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 3/2, v/v) afforded **6**$\alpha$ as a colorless syrup (307 mg, 92%): $R_f$ 0.70 ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 1/1, v/v); $[\alpha]^{25}_D$ +6.00° (*c* 1); FAB-MS *m*/*z* 781 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) $\delta$ 138.8, 138.6, 138.4, and 128.5−127.6 (3 $C_6H_5CH_2$), 88.3 (C-1), 87.0, 82.9, 80.0, and 77.7 (C-2,3,4,5), 75.9, 75.7, and 75.0 (3 $C_6H_5CH_2$), 62.5 (C-6), 60.7 (S*C*H), 41.5, 39.8, and 31.9−26.5 (2 $C_6H_{11}$), 26.0 (SiC(*C*H$_3$)$_3$), 18.3 (Si*C*(CH$_3$)$_3$), −5.1 and −5.5 (Si(*C*H$_3$)$_2$); $^1$H NMR ($CDCl_3$) $\delta$ 7.42−7.25 (m, 15H, 3 C6$H_5CH_2$), 5.02−4.81 (m, 6H, 3 $C_6H_5CH_2$), 4.32 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 3.84−3.19 (m, 6 H, H-2, H-3, H-4, H-5, H-6a, H-6b), 2.41 (m, 1H, SC*H*), 1.99−1.00 (m, 2 $C_6H_{11}$), 0.90 (s, 9H, SiC(C*H*$_3$)$_3$), 0.09 and 0.06 (2 s,

6H, Si(C$H_3$)$_2$); HR FAB-MS calcd for $C_{46}H_{66}SO_5SiNa$ 781.4298, found 757.3890. Dicyclohexylmethyl 2,3,4-tri-*O*-benzyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-$\beta$-D-glucopyranoside (**6**$\beta$) was obtained by the same synthetic procedure, starting from **5**$\beta$, as a colorless syrup: $R_f$ 0.61 ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 1/1, v/v); $[\alpha]^{25}_D$ +0.32° (*c* 1); $^{13}$C NMR ($CDCl_3$) $\delta$ 138.8, 138.6, 138.0, and 128.4−127.6 (3 $C_6H_5CH_2$), 85.7 (C-1), 82.7, 80.4, 77.6, and 72.1 (C-2,3,4,5), 75.9, 75.3, and 73.2 (3 $C_6H_5CH_2$), 62.1 (C-6), 58.9 (SCH), 42.0, 40.0, and 32.3−26.6 (2 $C_6H_{11}$), 26.1 (SiC(C$H_3$)$_3$), 18.4 (SiC(CH$_3$)$_3$), −5.0 (Si(C$H_3$)$_2$); $^1$H NMR ($CDCl_3$) $\delta$ 7.41−7.26 (m, 15H, 3 $C_6H_5CH_2$), 5.27 (d, 1H, H-1, $J_{1,2}$ 5.4 Hz), 4.98−4.66 (m, 6H, 3 $C_6H_5CH_2$), 4.11−3.59 (m, 6H, H-2, H-3, H-4, H-5, H-6a, H-6b), 2.40 (m, 1H, SC*H*), 2.05−1.00 (m, 22H, 2 $C_6H_{11}$), 0.92 and 0.90 (2 s, 9H, SiC(C$H_3$)$_3$), 0.05 and 0.04 (2 s, 6H, Si(C$H_3$)$_2$).

**Dicyclohexylmethyl 2,3,4-Tri-*O*-benzyl-1-thio-α-D-glucopyranoside (7α).** A solution of **6**α (1.35 g, 1.78 mmol) in HOAc/$H_2O$ (9/1, v/v, 40 mL) was stirred for 18 h at 60 °C. The solution was brought to rt, concentrated in vacuo, and co-concentrated from toluene, MeOH, and $CH_2Cl_2$, respectively (3 × 15 mL each). Purification of the residue by silica gel column chromatography ($CH_2Cl_2$/acetone, 97/3, v/v) afforded **7**α as a white glass (872 mg, 76%): $R_f$ 0.33 ($CH_2Cl_2$/acetone, 97/3, v/v); $[\alpha]^{25}_D$ +9.51° (*c* 1); FAB-MS *m*/*z* 667 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$), $\delta$ 138.8, 138.2, 137.9, and 128.6−127.6 (3 $C_6H_5CH_2$), 86.1 (C-1), 82.6, 80.1, 77.2, and 71.5 (C-2,3,4,5), 75.7, 75.3, and 73.3 (3 $C_6H_5CH_2$), 61.7 (C-6), 59.5 (SCH), 42.0, 39.7, and 32.3−26.5 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$) $\delta$ 7.40−7.26 (m, 15H, 3 $C_6H_5CH_2$), 5.24 (d, 1H, H-1, $J_{1,2}$ 5.5 Hz), 5.01−4.64 (m, 6H, 3 $C_6H_5CH_2$), 4.15 (m, 1H, H-5), 3.91−3.54 (m, 5H, H-2, H-3, H-4, H-6a, H-6b), 2.46 (m, 1H, SC*H*), 2.05−1.00 (m, 22H, 2 $C_6H_{11}$); HR FAB-MS calcd for $C_{40}H_{52}SO_5Na$ 667.3433, found 667.3426. Dicyclohexylmethyl 2,3,4-tri-*O*-benzyl-1-thio-$\beta$-D-glucopyranoside (**7**$\beta$) was obtained by the same synthetic procedure, starting from **6**$\beta$, as a colorless syrup: $R_f$ 0.41 ($CH_2Cl_2$/acetone, 97/3, v/v); $[\alpha]^{25}_D$ +1.06° (*c* 1); $^{13}$C NMR ($CDCl_3$) $\delta$ 138.5, 138.1, 137.9, and 128.5−127.6 (3 $C_6H_5CH_2$), 88.5 (C-1), 86.7, 82.7, 78.8, and 77.9 (C-2,3,4,5), 75.7, 75.7, and 75.0 (3 $C_6H_5CH_2$), 62.5 (C-6), 61.6 (SCH), 41.3, 39.7, and 31.9−26.4 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$) $\delta$ 7.41−7.26 (m, 15H, 3 $C_6H_5CH_2$), 5.03−4.57 (m, 6H, 3 $C_6H_5CH_2$), 4.39 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 3.85 (m, 1H, H-5), 3.75−3.30 (m, 5H, H-2,3,4,6a,6b), 2.37 (m, 1H, SC*H*), 2.10−1.00 (m, 22H, 2 $C_6H_{11}$).

**Dicyclohexylmethyl 2,3,4-Tri-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-α-D-glucopyranoside (8α).** To a solution of **6**α (1.20 g, 2.45 mmol) in dry pyridine (20 mL) was added DMAP (40 mg, 0.33 mmol) and BzCl (1.3 mL, 11.2 mmol). After 18 h of stirring at rt, the mixture was diluted with $CH_2Cl_2$ (60 mL) and washed with $H_2O$ (3 × 20 mL). The organic layer was dried ($MgSO_4$) and filtered. The filtrate was concentrated in vacuo and co-concentrated from toluene, MeOH, and $CH_2Cl_2$ (3 × 15 mL each). Purification of the residue by silica gel column chromatography ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 3/1, v/v) afforded **8**α as a white glass (1.78 g, 91%): $R_f$ 0.61 ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 9/1, v/v); $[\alpha]^{25}_D$ +9.51° (*c* 1); FAB-MS *m*/*z* 823 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) $\delta$ 165.8 and 165.1 (3 $C_6H_5CO$), 133.3−128.3 (3 $C_6H_5CO$), 85.7 (C-1), 72.1, 71.3, 71.0, and 69.4 (C-2,3,4,5), 62.5 (C-6), 61.8 (SCH), 41.1, 39.7, and 32.1−26.6 (2 $C_6H_{11}$), 26.0 (SiC(C$H_3$)$_3$), 18.5 (SiC(CH$_3$)$_3$), −5.5 (Si(C$H_3$)$_2$); $^1$H NMR ($CDCl_3$) $\delta$ 8.10−7.20 (m, 15H, 3 $C_6H_5CO$), 5.94 (t, 1H, H-3, $J_{2,3}$ 10.5, $J_{3,4}$ 9.8 Hz), 5.70 (d, 1H, H-1, $J_{1,2}$ 5.7 Hz), 5.63 (t, 1H, H-4, $J_{4,5}$ 9.8 Hz), 5.39 (dd, 1H, H-2), 4.53 (m, 1H, H-5), 3.9−3.7 (m, 2H, H-6a, H-6b), 2.39 (m, 1H, SC*H*), 2.00−0.70 (m, 22H, 2 $C_6H_{11}$), 0.86 (s, 9H, SiC(C$H_3$)$_3$), −0.01 and −0.02 (2 s, 6H, Si(C$H_3$)$_2$); HR FAB-MS calcd for $C_{46}H_{60}SO_8SiNa$ 823.3676, found 823.3657. Dicyclohexylmethyl 2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-$\beta$-D-glucopyranoside (**8**$\beta$) was obtained by the same synthetic procedure, starting from **6**$\beta$, as a white glass: $R_f$ 0.53 ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 9/1, v/v); $[\alpha]^{25}_D$ −3.58° (*c* 1); $^{13}$C NMR ($CDCl_3$) $\delta$ 165.8 and 165.1 (3 $C_6H_5CO$), 133.3−128.2 (3 *C*6H5CO), 87.5 (C-1), 79.4, 74.7, 71.9, and 69.7 (C-2,3,4,5), 62.9 (C-6), 61.8 (SCH), 40.8, 39.6, and 32.2−26.2 (2 $C_6H_{11}$), 26.0 (SiC(C$H_3$)$_3$), 18.3 (SiC(CH$_3$)$_3$), −5.5 (Si(C$H_3$)$_2$); $^1$H NMR ($CDCl_3$) $\delta$ 8.10−7.25 (m, 15H, 3 $C_6H_5CO$), 5.84 (t, 1H, H-3, $J_{2,3}J_{3,4}$ 9.6 Hz), 5.55 (dd, 1H, H-2, $J_{1,2}$ 9.9 $J_{2,3}$ 9.6 Hz), 5.45 (t, 1H, H-4, $J_{4,5}$ 9.6 Hz), 4.71 (d, 1H, H-1), 3.85−3.75 (m, 3H, H-5, H-6a, H-6b), 2.40−0.70 (m, 23H, SC*H*, 2 $C_6H_{11}$), 0.86 (s, 9H, SiC(C$H_3$)$_3$), 0.01 and 0.00 (2 s, 6H, Si(C$H_3$)$_2$).

**Dicyclohexylmethyl 2,3,4-Tri-*O*-benzoyl-1-thio-α-D-glucopyranoside (9α).** A solution of **8**α (1.38 g, 1.72 mmol) in HOAc/$H_2O$ (9/1, v/v, 50 mL) was stirred for 16 h at 60 °C. The solution was brought to rt, concentrated in vacuo, and co-concentrated from toluene, MeOH, and $CH_2Cl_2$ (3 × 15 mL each). Purification of the residue by silica gel column chromatography (toluene/acetone, 8/1, v/v) afforded **9**α as a white glass (893 mg, 76%): $R_f$ 0.35 (toluene/acetone, 19/1, v/v); $[\alpha]^{25}_D$ +0.67° (*c* 1); FAB-MS: *m*/*z* 709 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.6 and 165.7 (3 $C_6H_5CO$), 133.8−128.3 (3 $C_6H_5CO$), 86.2 (C-1), 71.8, 70.8, 70.5, and 69.6 (C-2, 3,4,5), 62.7 (SCH), 61.0 (C-6), 41.0, 39.6, and 32.1−26.2 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$) $\delta$ 8.10−7.20 (m, 15H, 3 $C_6H_5CO$), 6.05 (t, 1H, H-3, $J_{2,3}J_{3,4}$ 10.0 Hz), 5.73 (d, 1H, H-1, $J_{1,2}$ 5.8 Hz), 5.45 (dd, 1H, H-2), 5.49 (t, 1H, H-4, $J_{4,5}$ 10.1 Hz), 4.48 (m, 1H, H-5), 3.76 (m, 2H, H-6a, H-6b), 6.31 (m, 1H, SC*H*), 2.00−0.60 (m, 22H, 2 $C_6H_{11}$); HR FAB-MS calcd for $C_{40}H_{46}SO_8Na$ 709.2811, found 709.2818. Dicyclohexylmethyl 2,3,4-tri-*O*-benzoyl-1-thio-$\beta$-D-glucopyranoside (**9**$\beta$) was obtained by the same synthetic procedure, starting from **8**$\beta$, as a white solid: $R_f$ 0.26 (toluene/acetone, 19/1, v/v); $[\alpha]^{25}_D$ +0.18° (*c* 1); $^{13}$C NMR ($CDCl_3$) $\delta$ 165.9 and 165.2 (3 $C_6H_5CO$), 133.7−128.4 (3 $C_6H_5CO$), 88.2 (C-1), 78.8, 74.2, 71.7, and 69.8 (C-2, 3,4,5), 63.1 (SCH), 62.1 (C-6), 40.8, 39.6, and 32.1−26.3 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$) $\delta$ 8.10−7.20 (m, 15H, 3 $C_6H_5CO$), 5.92 (t, 1H, H-3, $J_{2,3}J_{3,4}$ 9.6 Hz), 5.53−5.43 (m, 2H, H-2, H-4), 4.74 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 3.78 (m, 2 H, H-6a, H-6b), 2.43 (br s, 1H, O*H*), 2.32 (m, 1H, SC*H*), 2.10−0.60 (m, 22H, 2 $C_6H_{11}$).

**Dicyclohexylmethyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-1-thio-D-glucopyranoside (11). Method A.** To a stirred mixture of ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-$\beta$-D-glucopyranoside **10** (214 mg, 0.37 mmol), compound **7**α (208 mg, 0.32 mmol), and molecular sieves (4 Å, 2 g) in dry $CH_2Cl_2$/$Et_2O$ (1/5, v/v, 4 mL) was added IDCP (354 mg, 0.76 mmol). After 1 h of stirring at rt, the reaction mixture was decanted into a stirred and cooled (0 °C) solution of aqueous $Na_2S_2O_3$ (15%, w/v, 25 mL). After 1 h or stirring, the mixture was diluted with $CH_2Cl_2$ (50 mL) and transferred to a separatory funnel. The organic phase was washed with aqueous $Na_2S_2O_3$ (1 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. Size exclusion column chromatography of the residue (LH-20, $CH_2Cl_2$/MeOH, 1/1, v/v) afforded **11**α as a colorless syrup (139 mg, 40%): $R_f$ 0.72 ($CH_2Cl_2$/acetone, 99/1, v/v); $[\alpha]^{25}_D$ +9.22° (*c* 1); FAB-MS *m*/*z* 1189 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) $\delta$ 138.8−127.5 (7 $C_6H_5CH_2$), 97.5 (C-1′), 85.4 (C-1), 82.5 (C-3), 81.7 (C-3′), 80.1 (C-2/C-2′), 77.5 (C-4,4′), 71.2 (C-5), 70.4 (C-5′), 68.3 (C-6′), 66.1 (C-6), 58.2(SCH), 42.0, 39.5, and 32.2−26.4 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$) $\delta$ 7.40−7.10 (m, 35H, 7 $C_6H_5CH_2$), 5.23 (d, 1H, H-1, $J_{1,2}$ 5.5 Hz), 5.01 (d, 1H, H-1′, $J_{1',2'}$ 3.6 Hz), 5.00−4.42 (m, 14 H, 7 $C_6H_5CH_2$), 4.24 (m, 1H, H−5), 3.96 (t, 1H, H-3′, $J_{2',3'}J_{3,4'}$ 9.9 Hz), 3.95 (m, 1H, H-6a), 3.89 (t, 1H, H-3, $J_{2,3}J_{3,4}$ 9.7 Hz), 3.84−3.55 (m, 2H, H-4, H-5′), 3.71−3.64 (m, 4H, H-2, H-6b, H-4′, H-6′a), 3.64−3.54 (m, 3H, H-6b, H-2′, H-4′, H-6′a), 3.64−3.54 (m, 3H, H-2′, H-4′, H-6′), 2.43 (m, 1H, SC*H*), 2.20−0.90 (m, 22 H, 2 $C_6H_{11}$); HR FAB-MS calcd for $C_{74}H_{86}SO_{10}Na$ 1189.5839, found 1189.5827.

**Method B.** To a stirred mixture of ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-$\beta$-D-glucopyranoside **10** (121 mg, 0.21 mmol), compound **7**$\beta$ (105 mg, 0.16 mmol), and powdered molecular sieves (4 Å, 0.5 g) in dry $CH_2Cl_2$/$Et_2O$ (1/5, v/v, 3 mL) was added IDCP (226 mg, 0.48 mmol). After 2 h of stirring at rt, the reaction mixture was filtered, diluted with $CH_2Cl_2$ (75 mL), and transferred to a separatory funnel. The organic phase was washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 20 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. Size exclusion column chromatography of the residue (LH-20, $CH_2Cl_2$/MeOH, 1/1, v/v) afforded **11**$\beta$ as a colorless syrup (133 mg, 71%).

**Method C.** To a stirred mixture of compound **3**α (79 mg, 0.11 mmol), compound **7**$\beta$ (62 mg, 0.10 mmol), and molecular sieves (4 Å, 0.5 g) in dry $CH_2Cl_2$/$Et_2O$ (1/5, v/v, 3 mL) was added IDCP (60 mg, 0.13 mmol). After 2 h of stirring at rt, the reaction mixture was quenched with aqueous $Na_2S_2O_3$ (3 mL, 15%, w/v), transferred to a separatory funnel, and diluted

with $CH_2Cl_2$ (50 mL). The organic phase was washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (1 × 15 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. Silica gel column chromatography ($CH_2Cl_2$/acetone, 996/4, v/v) of the residue afforded **11**$\beta$ as a colorless syrup (63 mg, 50%): $R_f$ 0.76 ($CH_2Cl_2$/acetone, 98/2, v/v); $[\alpha]^{25}_D$ +3.26° (*c* 1); $^{13}$C NMR ($CDCl_3$) $\delta$ 138.9−127.6 (7 $C_6H_5CH_2$), 97.5 (C-1′), 88.1 (C-1), 86.8 (C-3′), 82.7 (C-2′), 81.8 (C-3), 80.2 (C-2), 79.0 (C-5′), 77.7 (C-4), 77.4 (C-5/C-4), 75.7, 75.6, 75.0, 73.5, and 71.8 (7 $C_6H_5CH_2$), 70.5 (C-5/C-4′), 68.8 (C-6), 66.1 (C-6′), 60.3 (S*C*H), 41.4, 39.5, and 32.0−26.6 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$) $\delta$ 7.45−7.15 (m, 35H, 7 $C_6H_5CH_2$), 5.20 (d, 1H, H-1′, $J_{1,2}$ 3.5 Hz), 4.99−4.46 (m, 14H, 7 $C_6H_5CH_2$), 4.34 (m, 1H, H-1, $J_{1′,2′}$ 9.7 Hz), 3.97 (t, 1H, H-3′, $J_{2′,3′}J_{3′,4′}$ 8.9 Hz), 3.88 (dd, 1H, H-6′a, $J_{5′,6′a}$ 3.5 Hz, $J_{6′a,6′b}$ −12.5 Hz), 3.81−3.76 (m, 3H, H-5, H-4′, H-6′b), 3.70 (dd, 1H, H-6a, $J_{5,6a}$ 3.8, $J_{6a,6b}$ −10.8 Hz), 3.65−3.56 (m, 4H, H-2, H-4, H-6b, H-3′), 3.32 (m, 1H, H-5′), 3.11 (dd, 1H, H-2′), 2.37 (m, 1H, C*H*S), 1.97 and 1.80−1.00 (m, 22H, 2 $C_6H_{11}$).

**Ethyl 2,3,4-Tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α/*β*-D-glucopyranosyl)-1-thio-*β*-D-glucopyranoside (13). Method A.** To a stirred mixture of ethyl 2,3,4-tri-*O*-benzoyl-*β*-D-glucopyranoside **12** (158 mg, 0.14 mmol), compound **11**α (83 mg, 0.16 mmol), and molecular sieves (4 Å, 0.5 g) in $CH_2Cl_2$/ $Et_2O$ (1/5, v/v, 2 mL) were added NIS (38 mg, 0.17 mmol) and TfOH (5 $\mu$L, 0.06 mmol). After 5 min of stirring at rt, the reaction mixture was neutralized with TEA (0.02 mL), diluted with $CH_2Cl_2$ (50 mL), and washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL). The organic phase was dried (MgSO4) and filtered. The filtrate was concentrated in vacuo. Size exclusion chromatography of the residue (LH-20, $CH_2Cl_2$/MeOH, 1/1, v/v) afforded **13** as a white glass (142 mg, 69%): $R_f$ 0.36 ($CH_2Cl_2$/acetone, 98/2, v/v); FAB-MS *m*/*z* 1491 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) $\delta$ 165.9 and 165.2 (3 $C_6H_5CO$), 139.0, 138.6, 138.4, 138.1, and 133.5−127.6 (3 $C_6H_5CO$, 7 $C_6H_5CH_2$), 97.3 and 97.0 (C-1,1′,1″), 83.7, 81.9, 81.7, 80.4, 80.0, 77.4, 74.4, 70.8, 70.3, and 69.8 (C-2,3,4,5,2′,3′,4′,5′,2″,3″,4″,5″), 75.6, 75.0, 74.8, 73.5, 73.3, and 72.0 (7 $C_6H_5CH_2$), 68.5, 66.8, and 65.6 (C-6,6′,6″), 24.4 (S$CH_2CH_3$), 14.9 (S$CH_2CH_3$); $^1$H NMR ($CDCl_3$) $\delta$ 7.89−7.04 (m, 50 H, 3 $C_6H_5CO$, 7 $C_6H_5CH_2$, 5.79 (t, 1H, H-3, $J_{2,3}J_{4,5}$ 10.0 Hz), 5.42 (t, 1H, H-4, $J_{3,4}J_{4,5}$ 10.0 Hz), 5.40 (t, 1H, H-2, $J_{1,2}$ 10.0 Hz), 4.92 (d, 1H, H-1′, $J_{1′,2′}$ 3.6 Hz), 4.89−4.33 (m, 14H, 7 $C_6H_5CH_2$), 4.68 (d, 1H, H-1, $J_{1,2}$ 10.0 Hz), 4.59 (d, 1H, H-1″, $J_{1″,2″}$ 3.6 Hz), 3.95 (m, 1H, H-5, $J_{4,5}$ 10.0, $J_{5,6a}$ 2.0, $J_{5,6b}$ 7.0 Hz), 2.89 (t, 1H, H-3″, $J_{2″,3″}J_{3″,4″}$ 9.8 Hz), 3.88 (dd, 1H, H-3′, $J_{2′,3′}$ 9.7, $J_{3′,4′}$ 9.0 Hz), 3.81−3.42 (m, 10H, H-6a, H-6b, H-4′, H-5′, H-6′a, H-6′b, H-4″, H-5″, H-6″a, H-6″b), 3.45 (dd, 1H, H-2′, $J_{2′,3′}$ 9.7 Hz), 3.32 (dd, 1H, H-2″, $J_{1″,2″}$ 3.6, $J_{2″,3″}$ 9.8 Hz), 2.70−2.55 (m, 2H, S$CH_2CH_3$), 1.10 (t, 3H, $SCH_2CH_3$, *J* 7.2 Hz); HR FAB-MS calcd for $C_{90}H_{90}SO_{18}Na$ 1513.5746, found 1513.5836.

**Method B.** To a stirred mixture of ethyl 2,3,4-tri-*O*-benzoyl-*β*-D-glucopyranoside **12** (323 mg, 0.28 mmol), compound **11**$\beta$ (180 mg, 0.34 mmol), and molecular sieves (4 Å, 0.6 g) in dry $CH_2Cl_2/H_2O$ (1/1, v/v, 6 mL) were added NIS (75 mg, 0.33 mmol) and TMSOTf (5 $\mu$L, 0.03 mmol). After 30 min of stirring at rt, the reaction mixture was neutralized with TEA (0.02 mL), diluted with $CH_2Cl_2$ (50 mL), and washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL). The organic phase was dried ($MgSO_4$) and filtered. The filtrate was concentrated in vacuo. Size exclusion column chromatography of the residue (LH-20, $CH_2Cl_2$/MeOH, 1/1, v/v) afforded **13** as a white glass (125 mg, 30%).

**Dicyclohexylmethyl 2,3,4-Tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-*β*-D-glucopyranosyl)-1-thio-D-glucopyranoside (17). Method A.** To a stirred mixture of ethyl tetra-*O*-benzoyl-1-thio-*β*-D-glucopyranoside **16** (99 mg, 0.15 mmol), compound **9**α (97 mg, 0.14 mmol), and molecular sieves (4 Å, 1.0 g) in dry $CH_2Cl_2$/ $Et_2O$ (1/1, v/v, 1 mL) were added NIS (33 mg, 0.15 mmol) and TMSOTf (6 $\mu$L, 0.03 mmol). After 5 min of stirring at rt, the reaction mixture was quenched with TEA (0.02 mL), diluted with $CH_2Cl_2$ (60 mL), and washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL). The organic layer was dried (MgSO4) and filtered, and the filtrate was concentrated in vacuo. Purification of the residue by size exclusion chromatography (LH-20, $CH_2Cl_2$/MeOH, 1/1, v/v) afforded **17**α as a white glass (115 mg, 64%): $R_f$ 0.67 ($CH_2Cl_2$/acetone, 98/2, v/v); $[\alpha]^{25}_D$ +5.24° (*c* 1), FAB-MS *m*/*z* 1287 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) 166.1, 165.7, and 165.1 (7 $C_6H_5CO$), 133.5−128.3 (7 $C_6H_5CO$), 101.1 (C-1), 87.5 (C-1′), 78.6, 74.2, 72.9, 72.2, 71.5, 69.8, and 69.6 (C-2,3,4,5,2′,3′,4′,5′), 68.4 and 63.1 (C-6,6′), 61.7 (S*C*H), 41.0, 40.0, and 31.6−26.1 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$) $\delta$ 8.07−7.22 (m, 35H, 7 $C_6H_5CO$), 5.87 (t, 1H, H-3, $J_{2,3}J_{3,4}$ 9.5 Hz), 5.77 (t, 1H, H-3′, $J_{2′,3′}J_{3′,4′}$ 9.5 Hz), 5.58 (t, 1H, H-4, $J_{4,5}$ 9.5 Hz), 5.45 (dd, 1H, H-2, $J_{1,2}$ 7.9 Hz), 5.39 (dd, 1H, H-2′, $J_{1′,2′}$ 10.0, $J_{2′,3′}$9.5 Hz), 5.33 (t, 1H, H-4′), 5.06 (d, 1H, H-1), 4.64 (d, 1H, H-1′), 4.60 (dd, 1H, H-6a, $J_{5,6a}$ 3.1, $J_{6a,6b}$ −12.0 Hz), 4.43 (dd, 1H, H-6b, $J_{5,6b}$ 5.1 Hz), 4.09 (m, 1H, H-5), 4.03−3.91 (m, 3H, H-5′, H-6′a, H-6′b), 2.29 (m, 1H, SC*H*), 2.07−0.60 (m, 22H, 2 $C_6H_{11}$); HR FAB-MS calcd for $C_{74}H_{72}SO_{17}Na$ 1287.4388, found 1287.4400.

**Method B.** To a stirred mixture of ethyl tetra-*O*-benzoyl-1-thio-*β*-D-glucopyranoside **16** (111 mg, 0.17 mmol), compound **9**$\beta$ (109 mg, 0.16 mmol), and molecular sieves (4 Å, 1.0 g) in dry $CH_2Cl_2$/ $Et_2O$ (1/1, v/v, 1 mL) were added NIS (38 mg, 0.17 mmol) and TMSOTf (6 $\mu$L, 0.03 mmol). After 10 min of stirring at rt, the reaction mixture was quenched with TEA (0.02 mL), diluted with $CH_2Cl_2$ (60 mL), and washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. Purification of the residue by size exclusion column chromatography (LH-20, $CH_2Cl_2$/MeOH, 1/1, v/v) afforded **17**$\beta$ as a white glass (108 mg, 41%): $R_f$ 0.64 ($CH_2Cl_2$/acetone, 98/2, v/v); $[\alpha]^{25}_D$ +0.06° (*c* 1); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.1, 165.8, 165.4, and 165.1 (7 $C_6H_5CO$), 133.2−128.3 (7 $C_6H_5CH_2$), 101.4 (C-1), 85.5 (C-1′), 73.0 (C-3/C-3′), 72.3 (C-5′), 71.7 (C-2, 2′), 70.7 (C-3/C-3′), 69.7 (C-4′), 69.3 (C-4), 69.0 (C-5), 67.7 (C-6), 63.1 (C-6′), 61.4 (S*C*H), 41.0, 39.4, and 32.0−26.1 (2 $C_6H_{11}$); $^1$H NMR ($CDCl_3$) $\delta$ 8.20−7.20 (m, 35H, 7 $C_6H_5CO$), 5.91 (t, 2H, H-3 and H-3′ overlapping), 5.621 (t, 1H, H-4′, $J_{3′,4′}J_{4′,5′}$ 9.7 Hz), 5.615 (d, 1H, H-1, $J_{1,2}$ 5.6 Hz), 5.55 (dd, 1H, H-2′, $J_{1′,2′}$ 7.8, $J_{2′,3′}$ 9.7 Hz), 5.45 (t, 1H, H-4, $J_{3,4}J_{4,5}$ 9.7 Hz), 5.18 (dd, 1H, H-2, $J_{2,3}$ 10.5 Hz), 4.93 (d, 1H, H-1′), 4.65 (m, 1H, H-5, $J_{5,6a}$ 2.5, $J_{5,6b}$ 4.0 Hz), 4.55 (dd, 1H, H-6′a, $J_{5′,6′a}$ 3.4, $J_{6′a,6′b}$ −12.1 Hz), 4.45 (dd, 1H, H-6′b, $J_{6a,6b}$ −10.9 Hz), 4.18 (dd, 1H, H-6a), 4.10 (m, 1H, H-5′, $J_{5′,6′b}$ 5.0 Hz), 3.77 (dd, 1H, H-6b), 2.29 (m, 1H, SC*H*), 1.90−0.70 (m, 2 $C_6H_{11}$).

**Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-*β*-D-glucopyranosyl)-*β*-D-glucopyranosyl)-α-D-glucopyranoside (18). Method A.** To a stirred mixture of compound **17**α (124 mg, 0.27 mmol), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **14** (253 mg, 0.20 mmol), and molecular sieves (4 Å, 0.7 g) in dry $CH_2Cl_2$ (10 mL) were added NIS (249 mg, 1.11 mmol) and TMSOTf (30 $\mu$L, 0.17 mmol). After 30 min of stirring at rt, the reaction mixture was quenched with TEA (0.04 mL), diluted with $CH_2Cl_2$ (60 mL), and washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. Purification of the residue by silica gel column chromatography ($CH_2Cl_2$/acetone, 99/1, v/v) afforded **18** as a white glass (220 mg, 73%).

**Method B.** To a stirred mixture of compound **17**$\beta$ (181 mg, 0.14 mmol), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **14** (80 mg, 0.17 mmol), and molecular sieves (4 Å, 2.0 g) in dry $CH_2Cl_2$/ $Et_2O$ (5 mL, 1/1, v/v) were added NIS (133 mg, 0.60 mmol) and TMSOTf (21 $\mu$L, 0.12 mmol). After 10 min of stirring at rt, the reaction mixture was quenched with TEA (0.04 mL), diluted with $CH_2Cl_2$ (60 mL), and washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. Purification of the residue by silica gel column chromatography ($CH_2Cl_2$/acetone, 99/1, v/v) afforded **18** as a white glass (159 mg, 73%): $R_f$ 0.32 ($CH_2Cl_2$/acetone, 98/2, v/v); $[\alpha]^{25}_D$ +1.65° (*c* 1); FAB-MS *m*/*z* 1539 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) 166.1, 165.7, 165.4, 165.14, 165.08, and 164.8 (7 $C_6H_5CO$), 138.9, 138.4, 138.2, 133.5, 133.4, 133.2, 133.2, and 129.8−127.3 (7 $C_6H_5CO$, 3 $C_6H_5CH_2$), 101.4 (C-1), 100.7 (C-1′), 98.2 (C-1″), 81.9, 79.7, 77.0, 75.5, 74.5, 74.4, 73.5, 72.7, 72.3, 72.0, and 71.8 (C-2,3,4,5,2′,3′,4′,5′,2″,3″,4″,5″), 69.6, 69.5, and 69.4 (3 $C_6H_5CH_2$), 68.5, 67.5, and 63.0 (C-6,6′,6″), 55.4 (O$CH_3$); $^1$H NMR ($CDCl_3$) $\delta$ 8.10−6.90 (m 50H, 7 $C_6H_5CO$, 3 $C_6H_5CH_2$), 5.84 (t, 1H, H-3″, $J_{2″,3″}J_{3″,4″}$ 10.0 Hz), 5.75 (t, 1H, H-3′, $J_{2′,3′}J_{3′,4′}$ 10.0 Hz), 5.61 (t, 1H, H-4″, $J_{4″,5″}$ 9.8

Hz), 5.49 (t, 1H, H-2″, $J_{1'',2''}$ 8.0 Hz), 5.46 (t, 1H, H-2′, $J_{1',2'}$ 7.9 Hz), 5.30 (t, 1H, H-4′, $J_{4',5'}$ 9.8 Hz), 4.99 (d, 1H, H-1″), 4.59 (dd, 1H, H-6″a, $J_{6''a,6''b}$ −12.0 Hz), 4.58 (d, 1H, H-1, $J_{1,2}$ 2.8 Hz), 4.50 (d, 1H, H-1′), 4.41 (dd, 1H, H-6b″, $J_{5'',6''b}$ 5.6 Hz), 4.07 (m, 1H, H-5″), 4.02 (m, 1H, H-6′a), 3.93−3.87 (m, 2H, H5′, H6′b), 3.85 (t, 1H, H-3, $J_{2,3}J_{3,4}$ 9.2 Hz), 3.50 (m, 1H, H-5), 3.44-3.35 (m, 4H, H-2, H-4, H-6a, H-6b), 3.34 (s, 3H, OC*H*$_3$); HR FAB-MS calcd for $C_{89}H_{80}O_{23}Na$ 1539.4988, found 1539.4951.

**Dicyclohexylmethyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (21).** To a solution of **2**α (2.6 g, 7.0 mmol) in dry DMF (30 mL) were added benzaldehyde dimethyl acetal (1.3 mL, 8.7 mmol) and camphorsulfonic acid (70 mg, 0.3 mmol). The solution was stirred for 3 h at 57 °C under reduced pressure (20 mmHg). The reaction mixture was diluted with $Et_2O$ (100 mL) and washed with aqueous 1 M $NaHCO_3$ (1 × 20 mL) and $H_2O$ (1 × 20 mL). The organic phase was dried ($MgSO_4$), filtered, concentrated in vacuo, and co-concentrated from toluene. Purification of the residue by silica gel column chromatography (toluene/EtOAc, 7/3, v/v) afforded **20** as a white glass (3.2 g, 100%). Compound **20** (1.36 g, 2.94 mmol) was dissolved in dry DMF (15 mL); NaH (282 mg, 11.8 mmol) and BnBr (1.0 mL, 8.8 mmol) were added, and the mixture was stirred for 2.5 h at rt, diluted with EtOAc (175 mL), and washed with $H_2O$ (2 × 25 mL). The organic phase was dried ($MgSO_4$), filtered, concentrated in vacuo, and co-concentrated from toluene (3 × 30 mL), MeOH (3 × 20 mL), and $CH_2Cl_2$ (3 × 20 mL), respectively. Purification of the residue by silica gel column chromatography ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 3/1, v/v) afforded **21** as a white solid (1.76 g, 93%): $R_f$ 0.36 ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 3/1, v/v); $[\alpha]^{25}_D$ +8.88° (*c* 1); FAB-MS *m*/*z* 665 ($M^+$ + Na)$^+$; $^{13}C$ NMR ($CDCl_3$) δ 138.9, 138.0, 137.5, and 129.0−126.1 (3 $C_6H_5CH_2$), 101.3 ($C_6H_5CH$), 87.5, 82.1, 79.5, 79.4, and 63.3 (C-1,2,3,4,5), 75.4 and 73.3 (2 $C_6H_5CH_2$), 68.9 (C-6), 59.8 (SCH), 41.9−26.6 (2 $C_6H_{11}$); $^1H$ NMR ($CDCl_3$) δ 7.56−7.26 (m, 15H, 3 $C_6H_5CH_2$), 5.59 ($C_6H_5CH$), 5.26 (d, 1H, H-1, $J_{1,2}$ 5.6 Hz), 4.96−4.68 (m, 4H, 2 $C_6H_5CH_2$), 4.42−3.61 (m, 6H, H-2, H-3, H-4, H-5, H-6a, H-6b), 2.39−1.05 (m, 23H, SC*H*, 2 $C_6H_{11}$); HR FAB-MS calcd for $C_{40}H_{50}SO_5Na$ 665.3277, found 665.3283.

**Dicyclohexylmethyl 2,3-Di-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-α-D-glucopyranoside (22).** To a solution of **20** (1.54 g, 3.33 mmol) in dry pyridine (15 mL) were added BzCl (1.2 mL, 10.3 mmol) and DMAP (81 mg, 0.66 mmol). After 18 h of stirring at rt, the reaction mixture was diluted with EtOAc (50 mL) and washed with $H_2O$ (3 × 15 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (petroleum ether (bp 40−60 °C), 1/1, v/v) afforded **22** as a white solid (2.06 g, 92%): $R_f$ 0.38 ($CH_2Cl_2$/petroleum ether (bp 40−60 °C), 1/1, v/v); $[\alpha]^{25}_D$ +1.59° (*c* 1); FAB-MS *m*/*z* 693 ($M^+$ + Na); $^{13}C$ NMR ($CDCl_3$) δ 165.8, 165.4 (2 $C_6H_5CO$), 136.8 and 133.3−126.0 (2 $C_6H_5CO$), 101.4 ($C_6H_5CH$), 86.8 (C-1), 79.3, 72.2, 69.8, and 63.4 (C-2,3,4,5), 68.6 (C-6), 62.1 (SCH), 40.9, 39.3, and 31.9−26.1 (2 $C_6H_{11}$); $^1H$ NMR ($CDCl_3$) δ 8.10−7.20 (m, 10H, 2 $C_6H_5CO$), 5.91 (t, 1H, H-3, $J_{2,3}J_{3,4}$ 10.3 Hz), 5.64 (d, 1H, H-1, $J_{1,2}$ 5.9 Hz), 5.59 (s, 1H, $C_6H_5CH$), 5.42 (t, 1H, H-2), 4.56 (m, 1H, H-5), 4.30 (dd, 1H, H-4, $J_{4,5}$ 4.8 Hz), 3.90 (m, 2H, H-6a, H-6b), 2.30 (m, 1H, SC*H*), 2.0−0.6 (2 $C_6H_{11}$); HR FAB-MS calcd for $C_{40}H_{46}SO_7Na$ 693.2862, found 693.2860.

**Dicyclohexylmethyl 2,3,6-Tri-*O*-benzyl-1-thio-α-D-glucopyranoside (23).** To a stirred and cooled (0 °C) solution of **21** (1.63 g, 2.54 mmol) and triethylsilane (2.0 mL, 12.5 mmol) in $CH_2Cl_2$ (20 mL) was added TFA (1.0 mL, 13.0 mmol). The solution was stirred for 15 min, diluted with $CH_2Cl_2$ (60 mL), transferred to a separating funnel, and washed with aqueous $NaHCO_3$ (2 × 15 mL, 10%, w/v) and $H_2O$ (2 × 15 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography ($CH_2Cl_2$/acetone 98/2, v/v, 1/1) afforded **23** as a white solid (1.4 g, 85%): $R_f$ 0.54 ($CH_2Cl_2$/acetone, 96/4, v/v); $[\alpha]^{25}_D$ +8.02° (*c* 1); FAB-MS *m*/*z* 667 ($M^+$ + Na); $^{13}C$ NMR ($CDCl_3$) δ 138.9, 138.2, 137.9, and 128.6−127.7 (3 $C_6H_5CH_2$), 86.1 (C-1), 82.1, 79.6 and 70.7 (C-2,3,4,5), 75.5, 73.7, and 73.0 (3 $C_6H_5CH_2$), 69.4 (C-6), 59.1 (SCH), 41.9, 39.8, and 38.5−26.4 (2 $C_6H_{11}$); $^1H$ NMR ($CDCl_3$) δ 7.45−7.22 (m, 15 H, 3 $C_6H_5CH_2$), 5.31 (d, 1H, H-1, $J_{1,2}$ 5.8 Hz), 5.03−4.88 (m, 6H, 3 $C_6H_5CH_2$), 4.22 (m, 1H, H-5), 3.81−3.57 (m, 5H, H-2, H-3, H-4, H-6a, H-6b), 2.36 (d, 1H, O*H*, $J_{4,OH}$ 2.0 Hz), 2.44−1.00 (m, 23H, SC*H*, 2 $C_6H_{11}$); HR FAB-MS calcd for $C_{40}H_{52}SO_5Na$ 667.3433, found 667.3422.

**Dicyclohexylmethyl 2,3-Di-*O*-benzoyl-6-*O*-benzyl-1-thio-α-D-glucopyranoside (24).** To a stirred mixture of compound **22** (5.6 g, 8.4 mmol) and molecular sieves (4 Å, 10 g) in dry THF (80 mL) was added $NaCNBH_4$ (5.9 g, 94.0 mmol). After 30 min of stirring at rt, a solution of HCl in dry $Et_2O$ was added dropwise (50 mL, 1.0 M). The mixture was filtered over Celite, diluted with $Et_2O$ (100 mL), and washed with $H_2O$ (2 × 40 mL), aqueous $NaHCO_3$ (4 × 40 mL, 10%, w/v), and $H_2O$ (2 × 40 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated. Purification of the residue by silica gel column chromatography ($CH_2Cl_2$) afforded **24** as a white glass (4.28 g, 76%): $R_f$ 0.68 ($CH_2Cl_2$/acetone, 99/1, v/v); $[\alpha]^{25}_D$ +2.56° (*c* 1); FAB-MS *m*/*z* 695 ($M^+$ + Na); $^{13}C$ NMR ($CDCl_3$) δ 167.0 and 165.9 (2 $C_6H_5CO$), 137.8 and 133.4−127.7 (2 $C_6H_5CO$, $C_6H_5CH_2$), 85.9 (C-1), 74.3, 71.3, 70.9, and 70.6 (C-2,3,4,5), 73.8 ($C_6H_5CH_2$), 69.3 (C-6), 62.0 (SCH), 41.0 and 40.0 (2 $C_6H_{11}$), 41.0, 40.0, and 32.1−26.1 (2 $C_6H_{11}$); $^1H$ NMR ($CDCl_3$) δ 8.1−7.2 (m, 15H, 2 $C_6H_5CO$ and $C_6H_5CH_2$), 5.61 (d, 1H, H-1, $J_{1,2}$ 5.7 Hz), 5.60 (t, 1H, H-3, $J_{2,3}$ 9.6, $J_{3,4}$ 9.6 Hz), 5.40 (dd, 1H, H-2), 4.68 and 4.58 (2 d, 2H, $C_6H_5CH_2$, *J* 12.1 Hz), 4.43 (m, 1H, H-5), 4.02 (dt, 1H, H-4, $J_{4,OH}$ 4.0, $J_{4,5}$ 9.6 Hz), 3.89 (dd, 1H, H-6a, $J_{5,6a}$ 3.7, $J_{6a,6b}$ −10.3 Hz), 3.74 (dd, 1H, H-6b, $J_{5,6b}$ 3.7 Hz), 2.98 (d, 1H, O*H*), 2.33 (t, 1H, SC*H*, *J* 5.9 Hz), 1.9−0.6 (m, 22H, 2 $C_6H_{11}$); HR FAB-MS calcd for $C_{40}H_{48}SO_7Na$ 695.3018, found 695.3003.

**Dicyclohexylmethyl 2,3,6-Tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-1-thio-α-D-glucopyranoside (25).** To a stirred mixture of compound **10** (135 mg, 0.23 mmol), compound **23** (110 mg, 0.16 mmol), and molecular sieves (4 Å, 3 g) in dry $CH_2Cl_2$/$Et_2O$ (1/5, v/v, 5 mL) was added IDCP (220 mg, 0.47 mmol). After 1.5 h of stirring at rt, the reaction mixture was decanted into a stirred and cooled (0 °C) solution of aqueous $Na_2S_2O_3$ (15%, w/v, 25 mL). After 2 h of stirring, the mixture was diluted with $CH_2Cl_2$ (50 mL) and transferred to a seporatory funnel. The organic phase was washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (1 × 15 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by size exclusion column chromatography (LH-20, $CH_2Cl_2$/MeOH, 1/1, v/v) afforded **25**α as a colorless syrup (77 mg, 31%): $R_f$ 0.72 ($CH_2Cl_2$/acetone, 99/1, v/v); $[\alpha]^{25}_D$ +8.33° (*c* 1); FAB-MS *m*/*z* 1190 ($M^+$ + Na); $^{13}C$ NMR ($CDCl_3$) δ 138.9−138.0 and 128.3−126.4 (7 $C_6H_5CH_2$), 96.7 (C-1′), 86.1 (C-1), 82.6, 81.9, 80.2, 79.6, 77.7, 72.2, 70.9, and 70.5 (C-2,3,4,5,2′,3′,4′,5′), 75.5−73.1 (7 $C_6H_5CH_2$), 68.9 and 68.2 (C-6,6′), 59.9 (SCH), 39.9 and 29.7−26.3 (2 $C_6H_{11}$); $^1H$ NMR ($CDCl_3$) δ 7.30−7.00 (m, 35H, 7 $C_6H_5CH_2$), 5.65 (d, 1H, H-1′, $J_{1,2}$ 2.3 Hz), 5.24 (d, 1H, H-1, $J_{1',2'}$ 3.3 Hz), 4.99−4.16 (7 $C_6H_5CH_2$), 4.26 (m, 1H, H-5′), 4.01 (dd, 1H, H-4′, $J_{3',4'}J_{4',5'}$ 7.4 Hz), 3.90−3.81 (m, 3H, H-3, H-6a, H-3′), 3.77 (dd, 1H, H-2′, $J_{1',2'}$ 4.1, $J_{2',3'}$ 7.4 Hz), 3.70 (m, 1H, H-5), 3.59 (dd, 1H, H-4, $J_{3,4}$ 6.7, $J_{4,5}$ 7.4 Hz), 3.51 (dd, 1H, H-6b, $J_{5,6b}$ 1.5, $J_{6a,6b}$ −8.1 Hz), 3.42 (dd, 1H, H-2, $J_{1,2}$ 2.7, $J_{2,3}$ 7.3 Hz), 3.40 (dd, 1H, H-6′a, $J_{5',6'a}$ 2.0, $J_{6'a,6'b}$ −8.3 Hz), 3.31 (dd, 1H, H-6′b, $J_{5',6'b}$ 1.3 Hz), 2.4 (m, 1H, SC*H*), 2.0−0.9 (m, 22H, 2 $C_6H_{11}$); HR FAB-MS calcd for $C_{74}H_{86}SO_{10}Na$ 1189.5839, found 1189.5817.

**Ethyl 2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (27).** To a stirred mixture of ethyl 2,3,6-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside **26** (101 mg, 0.19 mmol), compound **3**α (132 mg, 0.18 mmol), and molecular sieves (4 Å, 0.3 g) in dry $CH_2Cl_2$/$Et_2O$ (1/1, v/v, 4 mL) were added NIS (46 mg, 0.20 mmol) and TfOH (5.5 μL, 0.06 mmol). After 5 min of stirring at rt, the reaction mixture was quenched with TEA (0.02 mL), diluted with $CH_2Cl_2$ (60 mL), transferred to a separatory funnel, and washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL). The organic phase was collected, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by size exclusion column chromatography (LH-20, $CH_2Cl_2$/MeOH, 1/1) afforded **27** as a white glass (116 mg, 61%): $R_f$ 0.44 ($CH_2Cl_2$/acetone, 98/2, v/v); CI-MS *m*/*z* 1076 ($M^+$ + $NH_4$); $^{13}C$ NMR ($CDCl_3$) δ 165.9, 165.6, and 165.5 (3 $C_6H_5CO$), 138.7, 138.4, 138.1, 137.9, 133.3, 133.1, 133.0, and 130.0−127.6 (4 $C_6H_5CH_2$, 3 $C_6H_5CO$), 99.9 (C-1′), 83.6 (C-1), 81.3 (C-3′), 78.9 (C-2′), 77.6 (C-5), 77.2 (C-4′), 76.8 (C-4), 75.3 (C-3), 71.8 (C-

5′), 70.8 (C-2), 68.5 (C-6′), 63.8 (C-6), 24.3 (S*C*$H_2$CH$_3$), and 14.9 (SCH$_2$*C*H$_3$); $^1$H NMR ($CDCl_3$) $\delta$ 8.20−7.10 (4 C$_6$*H*$_5$CH$_2$, 3 C$_6$*H*$_5$-CO), 5.94 (t, 1H, H-3, $J_{2,3}J_{3,4}$ 9.2 Hz), 5.60 (t, 1H, H-2, $J_{1,2}$ 9.2 Hz), 4.96 (m, 1H, H-6a, $J_{6a,6b}$ −12.2 Hz), 4.95 (m, 1H, H-1′, $J_{1',2'}$ 3.0 Hz), 4.82 (d, 1H, H-1), 4.67 (m, 1H, H-6b), 4.25 (t, 1H, H-4, $J_{4,5}$ 9.0 Hz), 3.99 (m, 1H, H-5, $J_{5,6a}$ 2.0, $J_{5,6b}$ 4.6 Hz), 3.98 (m, 1H, H-3′), 3.94 (m, 1H, H-5′), 3.62 (m, 2H, H-6a′, H-6b′, $J_{6a,6b}$ −12.2 Hz), 3.60 (m, 1H, H-4′), 3.31 (dd, 1H, H-2′), 2.77 (m, 2H, SC*H*$_2$CH$_3$), 1.27 (m, 3H, SCH$_2$C*H*$_3$). Anal. Calcd for $C_{63}H_{62}SO_{13}$: C, 71.48; H, 5.90. Found: C, 71.05; H, 6.07.

**Dicyclohexylmethyl 2,3-Di-*O*-benzoyl-6-*O*-benzyl-4-*O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-*β*-D-glucopyranosyl)-1-thio-α-D-glucopyranoside (30).** To a stirred mixture of ethyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-1-thio-*β*-D-glucopyranoside **28** (89 mg, 0.17 mmol), compound **24** (101 mg, 0.15 mmol), and molecular sieves (4 Å, 1 g) in dry $CH_2Cl_2$/$Et_2O$ (1/1, v/v, 4 mL) were added NIS (41 mg, 0.18 mmol) and TfOH (5 $\mu$L, 0.03 mmol). After 10 min of stirring at rt, the reaction mixture was quenched with TEA (20 $\mu$L), diluted with $CH_2Cl_2$ (60 mL), transferred to a separatory funnel, and washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL). The organic phase was collected, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by size exclusion column chromatography (LH-20, $CH_2Cl_2$/MeOH, 1/1) and silica gel column chromatography ($CH_2Cl_2$/acetone, 99/1, v/v) afforded **30** as a white glass (98 mg, 56%): $R_f$ 0.48 ($CH_2Cl_2$/acetone, 98/2, v/v); FAB-MS *m*/*z* 1069 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) $\delta$ 169.2, 165.8, and 165.0 (CH$_3$*C*O, 2 C$_6$H$_5$*C*O), 138.3, 138.2, 138.0, and 133.1−127.3 (4 *C*$_6$H$_5$CH$_2$, 2 *C*$_6$H$_5$CO), 100.3 (C-1′), 85.8 (C-1), 82.9 (C-3′), 77.7 (C-4′), 75.3 (C-4), 74.9, 74.8, and 74.7 (C-5′, 2 C$_6$H$_5$*C*H$_2$), 73.8, 73.3, and 73.1 (C-2′, 2 C$_6$H$_5$*C*H$_2$), 72.3 (C-2), 71.3 (C-3), 71.1 (C-5), 68.5 and 67.7 (C-6,6′), 62.2 (S*C*H), 40.9, 39.6, and 32.0−26.1 (2 *C*$_6$H$_{11}$), 20.8 (*C*H$_3$CO); $^1$H NMR ($CDCl_3$) $\delta$ 8.03−7.97 and 7.51−7.07 (m, 30H, 4 C$_6$*H*$_5$-CH$_2$, 2 C$_6$*H*$_5$CO), 5.79 (dd, 1H, H-3, $J_{2,3}$ 10.3, $J_{3,4}$ 9.0 Hz), 5.62 (d, 1H, H-1, $J_{1,2}$ 5.9 Hz), 5.28 (dd, 1H, H-2), 4.89 (dd, 1H, H-2′, $J_{1',2'}$ 8.0, $J_{2',3'}$ 9.3), 4.9−4.1 (m, 16H, 4 C$_6$H$_5$C*H*$_2$), 4.50 (d, 1H, H-1′), 4.40 (m, 1H, H-5), 4.20 (d, 1H, H-4), 3.95 (dd, 1H, H-6a, $J_{5,6a}$ 2.9, $J_{6a,6b}$ −11.0 Hz), 3.63 (dd, 1H, H-6b, $J_{5,6b}$ 1.9 Hz), 3.56 (t, 1H, H-4′, $J_{3',4'}J_{4',5'}$ 9.2 Hz), 3.44 (t, 1H, H-3′), 3.32 (m, 2H, H-6′a, 6′b), 3.14 (dt, 1H, H-5′, $J_{5',6a'}J_{5',6'b}$ 3.0 Hz), 2.31 (t, 1H, S*CH*, *J* 5.9 Hz), 1.84 (s, 3H, C*H*$_3$CO), 1.7−0.7 (m, 22H, 2 C$_6$*H*$_{11}$); HR FAB-MS calcd for $C_{69}H_{78}SO_{13}Na$ 1169.5061, found 1169.5101.

**Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-*β*-D-glucopyranosyl)-α-D-glucopyranoside (32).** To a stirred mixture of compound **4**α (179 mg, 0.23 mmol), methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside **31** (135 mg, 0.29 mmol), and molecular sieves (4 Å, 0.8 g) in dry $CH_2Cl_2$ (8.5 mL) were added NIS (300 mg, 1.33 mmol) and TMSOTf (37 $\mu$L, 0.07 mmol). After 30 min of stirring at rt, the reaction mixture was quenched with TEA (0.05 mL), diluted with $CH_2Cl_2$ (60 mL), transferred to a separatory funnel, and washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL). The organic phase was collected, dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by size exclusion column chromatography (LH-20, $CH_2Cl_2$/MeOH, 1/1) afforded **32** as a white glass (145 mg, 62%): $R_f$ 0.20 ($CH_2Cl_2$/acetone, 8/2, v/v); $[\alpha]^{25}_D$ +2.64° (*c* 1); FAB-MS *m*/*z* 1065 ($M^+$ + Na); $^{13}$C NMR ($CDCl_3$) $\delta$ 166.0−164.8 (4 C$_6$H$_5$*C*O), 139.3−127.1 (4 *C*$_6$H$_5$CO, 3 C$_6$H$_5$*C*H$_2$), 100.4 (C-1′), 98.5 (C-1), 79.9, 78.8, 77.3, 73.2, 72.2, 72.2, 71.8, 69.9, and 69.5 (C-2,3,4,5,2′,3′,4′,5′), 75.3 and 73.6 (3 C$_6$H$_5$C*H*$_2$), 67.6 and 63.1 (C-6, 6′), 55.3 (OC*H*$_3$); $^1$H NMR ($CDCl_3$), $\delta$ 7.90−7.10 (m, 35H, 4 C$_6$*H*$_5$CO, 3 C$_6$*H*$_5$-CH$_2$), 5.54 (t, 1H, H-3′, $J_{2',3'}J_{3',4'}$ 9.6 Hz), 5.47 (t, 1H, H-4′, $J_{4',5'}$ 9.6 Hz), 5.39 (dd, 1H, H-2′, $J_{1',2'}$ 8.0 Hz), 5.00, 4.73, 4.678, 4.67, 4.51, and 4.27 (6 d, 6H, 3 C$_6$H$_5$C*H*$_2$), 4.683 (d, 1H, H-1′, $J_{1',2'}$ 8.0 Hz), 4.47 (d, 1H, H-1, $J_{1,2}$ 3.8 Hz), 4.32 (dd, 1H, H-6a′, $J_{5',6a'}$ 3.3, $J_{6'a,6'b}$ −12.2 Hz), 4.18 (dd, 1H, H-6b′, $J_{5',6b'}$ 3.3 Hz), 3.89 (dd, 1H, H-4, $J_{3,4}$ 9.2, $J_{4,5}$ 9.5 Hz), 3.80 (t, 1H, H-3, $J_{2,3}$ 9.2 Hz), 3.67−3.60 (m, 2H, H-6a, H-5′), 3.42 (m, 1H, H-5), 3.38 (dd, 1H, H-2), 3.34 (dd, 1H, H-6b, $J_{5,6b}$ 1.9, $J_{6a,6b}$ −10.8 Hz), 3.20 (s, 3H, OC*H*$_3$); HR FAB-MS calcd for $C_{62}H_{58}O_{15}Na$ 1065.3673, found 1065.3633.

**Dicyclohexylmethyl 2,3,4-Tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α/*β*-D-glucopyranosyl)-*β*-D-glucopyranosyl)-1-thio-α-D-glucopyranoside (33).** To a stirred mixture of **13** (130 mg, 0.09 mmol), **9**α (64 mg, 0.09 mmol), and molecular sieves (4 Å, 0.5 g) in dry $CH_2Cl_2$/$Et_2O$ (1/1, v/v, 2 mL) were added NIS (21 mg, 0.09 mmol) and TMSOTf (4 $\mu$L, 22 $\mu$mol). After 5 min of stirring at rt, the reaction mixture was quenched with TEA (0.02 mL), diluted with $CH_2Cl_2$ (60 mL), and washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL). The organic phase was dried (MgSO4), filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (dichloromethane/acetone, 99/1, v/v), followed by size exclusion column chromatography (LH-60, $CH_2Cl_2$/MeOH, 1/1, v/v) afforded **33** as a white glass (102 mg, 55%): $R_f$ 0.44 ($CH_2Cl_2$/acetone, 98/2, v/v); FAB-MS *m*/*z* 2139 ($M^+$ + Na); $^1$H NMR ($CDCl_3$) $\delta$ 8.10−7.10 (m, 65H, 7 C$_6$*H*$_5$CH$_2$, 6 C$_6$*H*$_5$CO), 5.86 (t, 1H, H-3, $J_{2,3}J_{3,4}$ 9.9 Hz), 5.84 (t, 1H, H-3′, $J_{2',3'}J_{3',4'}$ 9.9 Hz), 5.55 (d, 1H, H-1, $J_{1,2}$ 5.8 Hz), 5.49 (t, 1H, H-4′, $J_{4',5'}$ 9.9 Hz), 5.46 (dd, 1H, H-2′, $J_{1',2'}$ 7.9 Hz), 5.44 (t, 1H, H-4, $J_{4,5}$ 9.9 Hz), 5.05 (dd, 1H, H-2), 4.94−4.38 (m, 14H, 7 C$_6$H$_5$C*H*$_2$), 4.93 (d, 1H, H-1″, $J_{1'',2''}$ 3.5 Hz), 4.86 (d, 1H, H-1′), 4.61 (d, 1H, H-1‴, $J_{1''',2'''}$ 3.6 Hz), 4.60 (m, 1H, H-5, $J_{5,6a}$ 3.0, $J_{5,6b}$ 3.3 Hz), 4.19 (dd, 1H, H-6a), 3.92 (dd, 1H, H-3″, $J_{2'',3''}$ 10.5, $J_{3'',4''}$ 8.5 Hz), 3.89 (m, 1H, H-5′, $J_{5'a,6'a}$ 5.2 Hz, $J_{5',6'b}$ 2.7 Hz), 3.87 (dd, 1H, H-3‴, $J_{2''',3'''}$ 9.5 Hz, $J_{3''',4'''}$ 8.2 Hz), 3.81 (dd, 1H, H-6′a, $J_{6'a,6'b}$ −11.2 Hz), 3.73 (dd, 1H, H-6b), 3.71−3.56 (m, 8H, H-4″, H-5″, H-6″a, H-6″b, H-4‴, H-5‴, H-6‴a, H-6‴b), 3.54 (dd, 1H, H-6′b), 3.48 (dd, 1H, H-2″), 3.30 (dd, 1H, H-2‴), 2.21 (m, 1H, SC*H*), 1.8−0.6 (m, 22H, 2 C$_6$*H*$_{11}$); HR FAB-MS calcd for $C_{128}H_{130}SO_{26}Na$ 2137.8469, found 2137.8359.

**Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α/*β*-D-glucopyranosyl)-*β*-D-glucopyranosyl)-*β*-D-glucopyranosyl)-α-D-glucopyranoside (34).** To a stirred mixture of **33** (101 mg, 0.05 mmol), **14** (45 mg, 0.10 mmol), and molecular sieves (4 Å, 1.5 g) in dry $CH_2Cl_2$/$Et_2O$ (1/1, v/v, 3 mL) were added NIS (70 mg, 0.31 mmol) and TMSOTf (8 $\mu$L, 44 $\mu$mol). After 20 min of stirring at rt, the reaction mixture was quenched with TEA (0.01 mL), diluted with $CH_2Cl_2$ (50 mL), and washed with aqueous $Na_2S_2O_3$ (2 × 15 mL, 15%, w/v) and $H_2O$ (2 × 15 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography ($CH_2Cl_2$/acetone, 96/4), followed by size exclusion column chromatography (LH-60, $CH_2Cl_2$/MeOH, 1/1, v/v), afforded **34** as a white glass (70 mg, 62%): $R_f$ 0.39 ($CH_2Cl_2$/acetone, 96/4, v/v); FAB-MS *m*/*z* 2391 ($M^+$ + Na); $^1$H NMR ($CDCl_3$) $\delta$ 7.90−6.90 (m, 80H, 10 C$_6$*H*$_5$CH$_2$, 6 C$_6$*H*$_5$CO), 5.70 (t, 1H, H-3‴, $J_{2''',3'''}J_{3''',4'''}$ 9.5 Hz), 5.64 (t, 1H, H-3′, $J_{2',3'}J_{3',4'}$ 9.5 Hz), 5.49 (t, 1H, H-4″, $J_{4'',5''}$ 9.5 Hz), 5.37−5.31 (m, 2H, H-2′, H-2″), 5.22 (t, 1H, H-4′, $J_{4',5'}$ 9.5 Hz), 4.86 (d, 1H, H-1″, $J_{1'',2''}$ 7.3 Hz), 4.83 (d, 1H, H-1‴, $J_{1''',2'''}$ 3.5 Hz), 4.56 (d, 1H, H-1⁗, $J_{1'''',2''''}$ 3.9 Hz), 4.52 (d, 1H, H-1, $J_{1,2}$ 3.5 Hz), 4.38 (d, 1H, H-1′, $J_{1',2'}$ 7.8 Hz), 4.88−4.25 and 4.08 (m, 23H, 10 C$_6$H$_5$C*H*$_2$), 3.97 (m, 1H, H-6″a), 3.91−3.21 (m, 20H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-5′, H-6′a, H-6′b, H-5″, H-6″b, H-2‴, H-3‴, H-4‴, H-5‴, H-6‴a, H-6‴b, H-2⁗, H-3⁗, H-4⁗, H-5⁗, H-6⁗a, H-6⁗b), 3.26 (s, 3H, OC*H*$_3$); HR FAB-MS calcd for $C_{143}H_{138}O_{32}Na$ 2390.9102, found 2390.9196.

**Acknowledgment.** This work was supported by GlaxoWellcome Research and Development Ltd. (Research Studentship for R.G.).

**Supporting Information Available:** NMR and COSEY spectra (44 pages). This material is contained in libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO971233K