

Carbohydrate-derived thiols as protic polarity-reversal catalysts for enantioselective radical-chain reactions

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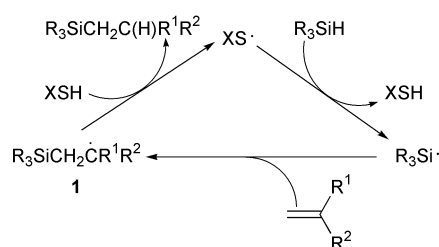
A variety of novel homochiral carbohydrate-derived thiols, in which the SH group is attached to the anomeric carbon atom, have been prepared and characterised. These thiols have been evaluated as protic polarity-reversal catalysts to mediate the enantioselective radical-chain addition of triphenylsilane to the $\text{H}_2\text{C}=\text{CR}^1\text{R}^2$ group in prochiral methylenelactones to give chiral adducts of the general type $\text{Ph}_3\text{SiCH}_2\text{CHR}^1\text{R}^2$; chemical yields were uniformly high. Systematic changes in the structures of the thiols were made with the aim of increasing the enantioselectivity of hydrogen-atom abstraction from the SH group by the prochiral alkyl radical $\text{Ph}_3\text{SiCH}_2\dot{\text{C}}\text{R}^1\text{R}^2$. Although adducts could be obtained in high enantiomeric excess in reactions carried out at 60 °C, no significant improvement in enantioselectivity could be achieved over that obtainable using simple tetra-*O*-acetyl- β -glucopyranose and - β -mannopyranose thiols as catalysts. It was found that the α -anomers of the pyranose thiols were ineffective at mediating enantioselective hydrogen-atom transfer to the radical $\text{Ph}_3\text{SiCH}_2\dot{\text{C}}\text{R}^1\text{R}^2$. All the β -pyranose thiols gave asymmetric induction in the same sense, but two β -mannofuranose thiols with less polar substituents gave asymmetric induction in the opposite sense. It is concluded that both steric and dipole-dipole interactions between the prochiral carbon-centred radical and the thiol are important in determining enantioselectivity and that these interactions can act in opposition as well as co-operatively; solvent effects are also shown to be important.

Enantioselective transfer of an atom or group G from an enantiomerically pure donor $\text{X}^*\text{-G}$ to a prochiral carbon-centred radical abcC^\bullet [eqn. (1)] represents a potentially useful, though



presently underexploited,^{1,2} route to the non-racemic chiral product $\text{abcC}^*\text{-G}$.

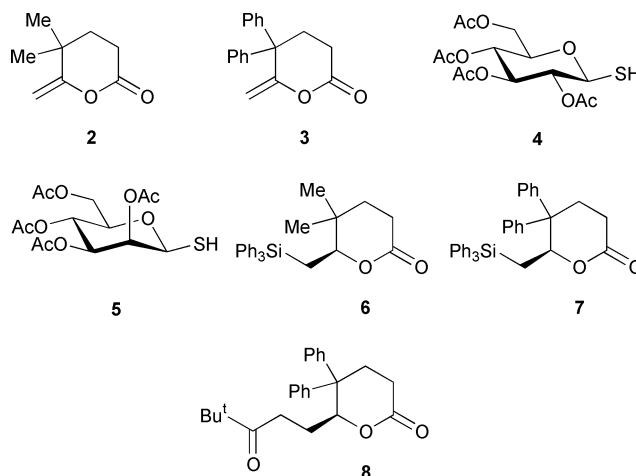
We have reported recently³⁻⁵ that thiols act as protic polarity-reversal catalysts⁶ to promote the radical-chain hydrosilylation of alkenes, via the propagation cycle shown in Scheme 1. For



Scheme 1

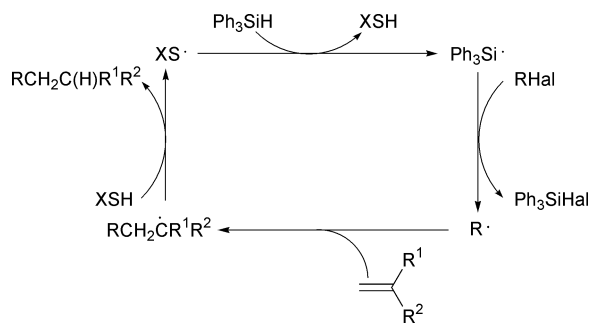
addition to a prochiral alkene of the type $\text{R}^1\text{R}^2\text{C}=\text{CH}_2$ the stereogenic carbon centre in the product silane $\text{R}_3\text{SiCH}_2\text{C(H)R}^1\text{R}^2$ is set by hydrogen-atom transfer from the thiol catalyst to the prochiral radical **1**. When the thiol is homochiral this hydrogen-atom abstraction will become enantioselective and the product silane will then be non-racemic. We have previously examined a limited number of homochiral thiols as catalysts for the enantioselective addition of triphenylsilane and of tris(trimethylsilyl)silane to the methylenelactones **2** and **3** at 60 °C, when the carbohydrate-derived thiols **4** and **5** proved to be the most

effective catalysts for asymmetric induction.⁵ For example, in hexane solvent the enantiomeric excess (ee) of the (*R*)-(-)-silane **6** derived from **2** was found to be 50% using the β -glucose thiol **4** and 76% with the β -mannose thiol **5** (5 mol% of each), although somewhat lower ees were obtained in more polar solvents (e.g. the ee of **6** was 40% with **4** as catalyst in 1,4-dioxane).⁵ For the more sterically demanding methylenelactone **3**, the ee of the (*R*)-(-)-addition product **7** was 80–87% (depending on solvent) using **4** as catalyst, rising to 93–95% with the β -mannose thiol **5**.



Enantioselective hydrogen-atom transfer from **4** and **5** also resulted in non-racemic products from the thiol-catalysed reductive alkylation of **2** and **3**.⁷ This type of reaction involves treatment of the alkene with triphenylsilane and an α -halogeno carbonyl compound, in the presence of the thiol, and the propagation cycle is shown in Scheme 2. For example, the ee of the (*S*)-(-)-adduct **8** obtained from **3** and $\text{Bu}^t\text{C(O)CH}_2\text{Br}$

† Correspondence concerning the X-ray crystallography should be directed to this Author.



Scheme 2

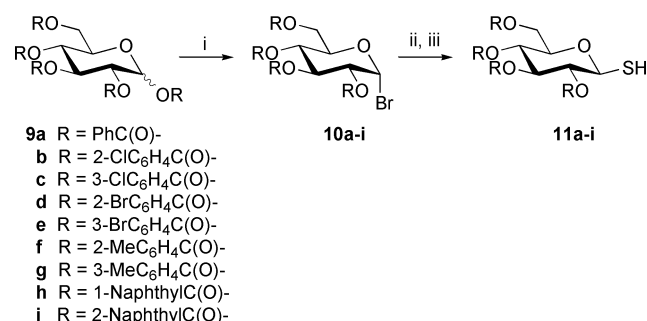
was 54% using the β -glucose thiol **4** as catalyst and 53% with the β -mannose thiol **5**.

There is clearly a need to identify those structural factors that are important in determining the enantioselectivity of hydrogen-atom abstraction from a homochiral thiol and, thereby, to be in a position to design more effective and generally applicable chiral catalysts. To this end we have now prepared a variety of carbohydrate-based thiols and screened these as protic polarity-reversal catalysts for the enantioselective addition of triphenylsilane to **2** and **3**.

Results and discussion

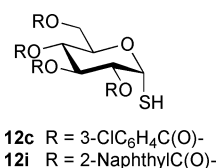
Encouraged by the significant increase in ee found previously⁵ for hydrosilylation of **2** and **3** when the catalyst was changed from the β -glucose thiol **4** to the β -mannose thiol **5**, we concentrated our efforts first on varying the nature of the ester groups in these thiols, in particular the nature of the group attached to C(2) on the pyranose ring, because the thiols **4** and **5** differ only in the configuration at this centre adjacent to the SH group.

Initially, a variety of tetra-*O*-aroyl- β -glucose thiols were prepared by the route shown in Scheme 3. Reactions of the



Scheme 3 Reagents and conditions: i, HBr–HOAc, CH₂Cl₂, room temp., 6 h; ii, thiourea, acetone, reflux, 4–8 h; iii, K₂S₂O₅, CCl₄–H₂O (1 : 1), reflux, 2 h.

penta-*O*-aroylglucopyranosides **9a–i** (prepared as mixtures of the α - and β -anomers) with HBr in acetic acid gave the α -bromoglucosides **10a–i**, that were then treated with thiourea to give the corresponding isothiuronium salts as epimeric mixtures in which the β -anomer predominated (β : α = ca. 85 : 15). These isothiuronium salts were then hydrolysed with potassium metabisulfite in a two-phase CCl₄–water system to afford an epimeric mixture of thiols from which the pure β -anomers **11a–i** were isolated, along with two α -anomers, **12c** and **12i**.



These thiols were then screened as catalysts for the enantioselective addition of triphenylsilane to the methylenelactone **2**.

Table 1 Enantioselective addition of triphenylsilane to 5,5-dimethyl-6-methylenetetrahydropyran-2-one **2** at 60 °C to give **6**, using various 2,3,4,6-tetra-*O*-acylated glucopyranose thiol catalysts^a

Entry	Thiol ^b	Solvent ^c	Ee of 6 (%) ^{d, e}
1	4	D	38 ^f
2	4	H	53 ^g
3	11a	D	34
4	11a	H	39
5	11b	D	35
6	11c	D	37
7	11d	D	39
8	11d	H	45
9	11e	D	37
10	11f	D	34
11	11g	D	37
12	11h	D	37
13	11i	D	37
14	12c	D	5
15	12i	D	4
16	16a	D	36
17	16a	H	39
18	16b	D	32

^a Molar ratio Ph₃SiH : **2** = 1.1 : 1.0. ^b 5 Mol% based on **2**. ^c D = 1,4-dioxane, H = hexane. ^d Determined by ¹H NMR spectroscopic analysis using Eu(hfc)₃ or by chiral-stationary-phase HPLC analysis using a Chiralpak-AD column and hexane–isopropyl alcohol (97.5 : 2.5 v/v) mobile phase. ^e The isolated yield was 85–95% in all cases. ^f An ee of 40% and an isolated yield of 63% were reported in ref. 5. ^g An ee of 50% and an isolated yield of 72% were reported in ref. 5.

Hydrosilylation reactions were carried out at 60 °C, generally in 1,4-dioxane because of the greater solubility of reactants, products and catalysts in this solvent as compared with hexane. In most runs, the molar ratio of methylenelactone to triphenylsilane was 1.0 : 1.1 and 5 mol% thiol catalyst (based on alkene) was used; the initiator was di-*tert*-butyl hyponitrite⁸ (Bu'ON=NOBu', TBHN, 5 mol%) which acts as a thermal source of *tert*-butoxyl radicals under mild conditions. All the thiols are extremely effective as protic polarity-reversal catalysts and isolated chemical yields of the silane adduct were often over 90%; the results are summarised in Table 1. As control experiments, it was confirmed that no hydrosilylation of **2** occurred in the absence of a thiol catalyst and that no racemisation of an enantiomerically pure sample⁵ of the adduct **6** was detectable after this compound had been subjected to the reaction conditions for its formation in the presence of the β -glucose thiol **4**, indicating that the ee of **6** was not being degraded⁹ during the hydrosilylation process. In a similar experiment replacing the glucose thiol by the achiral triphenylsilanethiol (Ph₃SiSH, 5 mol%), there was also no racemisation of **6**. Triphenylsilanethiol is likely to be produced at the end of the hydrosilylation reaction, when all the alkene has been consumed, because the residual triphenylsilane will then desulfurise the carbohydrate thiol catalyst.^{5,10} Other possible consequences of silanethiol formation are discussed later.

Two main conclusions can be drawn from these results. First, all the β -glucose thiols investigated afford the adduct **6** with surprisingly similar enantiomeric purities (32–39% in 1,4-dioxane solvent) and, second, the two α -glucose thiols investigated (**12c** and **12i**, entries 14 and 15) gave very low ees of ca. 5%. With the β -glucose thiols, moving from dioxane to hexane as solvent improved the ee somewhat, e.g. raising it from 39% to 45% with **11d** as catalyst (entries 7 and 8).

The lack of dependence of the ee on the nature of the *O*-aroyl groups in the β -glucose thiols, particularly its insensitivity to changes in the nature of the ester group at C(2), was rather surprising since preliminary molecular mechanics studies,¹¹ in which the radical precursor of **6** was brought up to the SH group in representative tetra-*O*-aroyl- β -D-glucopyranose thiols to model the pair of diastereoisomeric transition states for H-atom transfer, indicated that significant

changes in enantioselectivity might reasonably be expected. The molecular structure of the tetra-*O*-(3-chlorobenzoyl)- β -glucose thiol **11c** (entry 6) was determined by single-crystal X-ray diffraction and the result is presented in Fig. 1. Two orient-

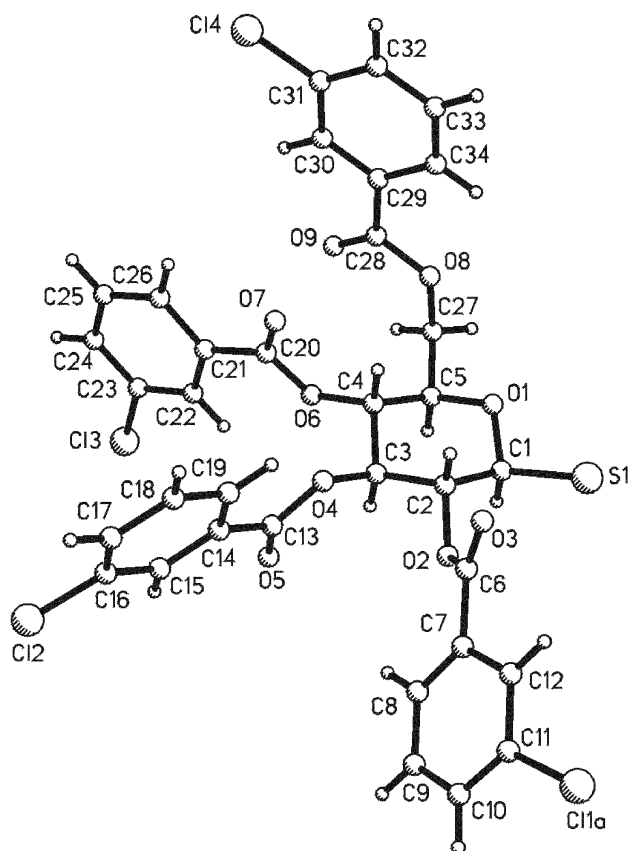
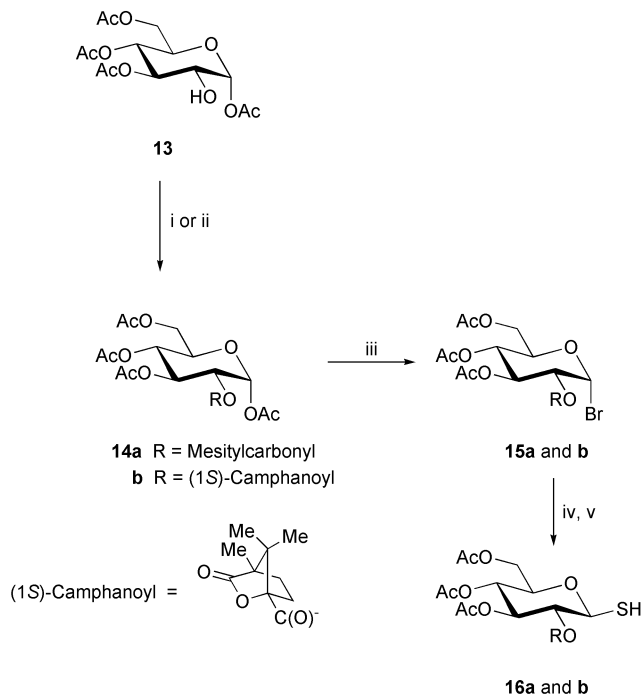


Fig. 1 Structure of 2,3,4,6-tetra-*O*-(3-chlorobenzoyl)-1-thio- β -D-glucopyranose **11c** determined by X-ray crystallography. The crystallographic numbering system differs from the conventional system used in the text. Selected geometrical parameters (bond lengths in Å, bond angles in degrees): C1–S1 1.804(5), C1–O1 1.422(5), C1–C2 1.533(6), C2–C3 1.514(7), C3–C4 1.506(7), C4–C5 1.535(6), C5–O1 1.433(5), C5–C27 1.514(7); S1–C1–C2 112.6(3), S1–C1–O1 108.4(3), O1–C1–C2 108.6(3).

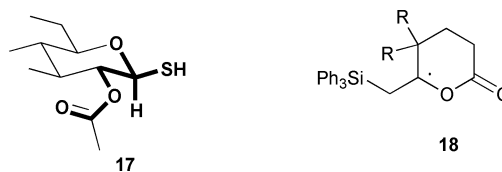
ations of the *m*-ClC₆H₄ ring in the C(2) ester group were present in the crystal, the conformation shown (77%) and a conformation that differs from it by a 180° rotation about the C(O)–C₆H₄Cl bond (23%). This suggested that symmetrically di-*ortho*- or di-*meta*-substituted aryl groups might increase enantioselectivity by restricting the freedom of the C(2) substituent to rotate to reduce interaction with the incoming prochiral radical in the transition state. The preparation of appropriate thiols containing four identical bulky ester groups proved problematic and in order to circumvent this difficulty, as well as to provide a catalyst of lower molecular weight, it was decided to work with the 3,4,6-tri-*O*-acetyl derivatives. The 2-*O*-mesitylcarbonyl thiol **16a** was prepared from 1,3,4,6-tetra-*O*-acetyl- α -D-glucopyranose **13**, as shown in Scheme 4, and the corresponding 2-*O*-[(1*S*)-camphanoyl] derivative **16b** was prepared in a similar fashion.

However, when the thiols **16a** and **16b** were used as catalysts for the addition of triphenylsilane to the methylenelactone **2** the results were disappointing (see Table 1) and no increase in ee of the adduct was found, although again the chemical yields were essentially quantitative. Even with the bulky chiral *O*-camphanoyl group present at C(2) in **16b**, when it was hoped that the combination of chirotopic elements within the same molecule might lead to an improvement in ee, none was seen. As before, moving from dioxane to hexane solvent with **16a** as catalyst resulted in an increase in ee, *e.g.* from 36 to 39% (entries 16 and 17), although the change was small. Therefore, it



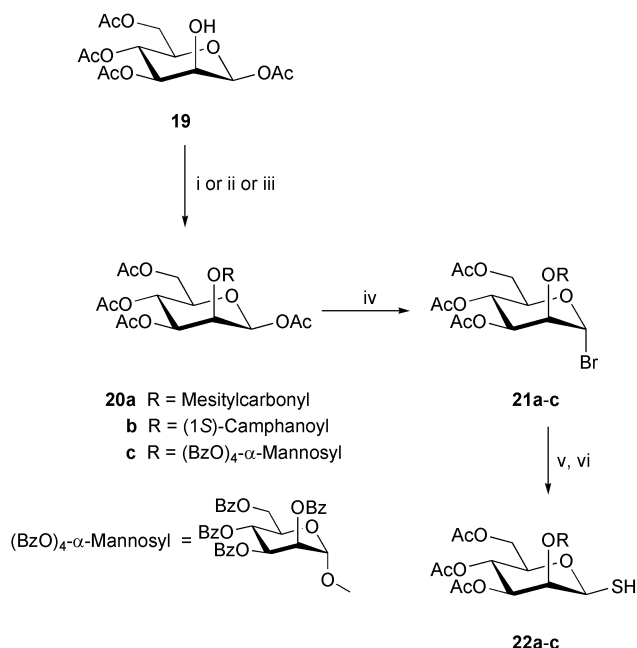
Scheme 4 Reagents and conditions: i, mesitylcarbonyl chloride, AgOTf, 2,6-lutidine, CH₂Cl₂, room temp., 4 h; ii, camphanoyl chloride, pyridine, room temp., 6 h; iii, HBr–HOAc, CH₂Cl₂, room temp., 4 h; iv, thiourea, acetone, reflux, 4–8 h; v, K₂S₂O₈, CCl₄–H₂O (1 : 1), reflux, 2 h.

appears that the same basic chiral control element present in all the β -glucosidic thiols is responsible for asymmetric induction and that this element is provided by the local environment of the SH group, as shown in bold type in structure **17**; the remaining substituents in the thiols evidently have little effect on the relative energies of the two diastereoisomeric transition states for hydrogen-atom transfer to the prochiral \ddagger β -silylalkyl radical **18**, the precursor of **6**. However, the orientation of the SH group with respect to the pyranose ring appears to be critical, because the corresponding α -glucose thiols are ineffective as enantioselective hydrogen-atom donors. The observation that enantioselectivity is decreased in more polar solvents suggests that dipole–dipole interactions between the prochiral radical **18** and the thiol catalyst may have an important influence on transition state energy.



Our preliminary findings⁵ indicated that hydrogen-atom abstraction from β -mannose thiols is more enantioselective than from their β -glucose thiol counterparts and so the three 3,4,6-tri-*O*-acetyl- β -D-mannopyranose thiols **22a–c** were synthesised starting from 1,3,4,6-tetra-*O*-acetyl- β -D-mannopyranose **19**, as shown in Scheme 5. The C(2)-OR group was chosen to be bulky (**22a**) or both bulky and homochiral (**22b** and **22c**), and molecular mechanics modelling suggested that the disaccharide **22c**, in particular, might be a promising candidate to give higher enantioselectivity than the C(2)-acetate derivative **5** investigated previously.⁵ As expected, the β -mannose thiols **22a–c** were now minor products after hydrolysis

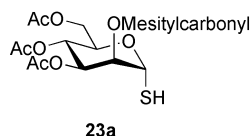
\ddagger The radical adducts **18** produced are instantaneously chiral, but stereochemically mobile and will exist in the form of rapidly interconverting enantiomeric pairs. We refer to these species as “prochiral” because it is not until the stereochemistry is fixed by hydrogen-atom transfer to the three-coordinate radical centre that the isolation of enantiomers becomes possible.



Scheme 5 Reagents and conditions: i, mesitylcarbonyl chloride, AgOTf, 2,6-lutidine, CH₂Cl₂, room temp., 4 h; ii, camphanoyl chloride, pyridine, room temp., 6 h; iii, 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl bromide, AgOTf, 2,6-di-*tert*-butyl-4-methylpyridine, −55 to −40 °C; iv, HBr–HOAc, CH₂Cl₂, room temp., 4 h; v, thiourea, acetone, reflux, 4–8 h; vi, K₂S₂O₅, CCl₄–H₂O (1 : 1), reflux, 2 h.

of the isothiuronium salts, obtained by treatment of the α-mannosyl bromides **21a–c** with thiourea, and the α-mannose thiols were the major products (α : β = *ca.* 83 : 17); however, the β-thiols could be separated by column chromatography.

Although the β-mannose thiols **22a** and **22b** gave appreciably higher ees than the corresponding β-glucose thiols when used as catalysts for the hydrosilylation of **2** (see Table 2), the ees were no greater than that obtained with the simple tetraacetate derivative **5**. Even the disaccharide thiol **22c** gave no improvement in ee (entries 6 and 7). The solvent effect on enantioselectivity was unusual with the 2-*O*-camphanoyl-substituted β-mannose thiol **22b** as catalyst, in that the product ee was reproducibly *higher* in dioxane than in hexane (entries 4 and 5). The reason for this anomalous behaviour is not clear, but it may be related to the very polar lactone function present in the camphanoyl group and to the importance of dipole–dipole interactions in determining enantioselectivity. As found for the glucose thiols, the α-mannose thiol **23a** was ineffective at transferring its chirality to the hydrosilylation product, although chemical yields were again uniformly high for both α- and β-mannose thiols. Hence, as for the glucose thiols, it is only the local environment of the SH group (*cf.* structure **17**) in the mannose thiols that is responsible for determining the enantioselectivity of the hydrogen-atom transfer.

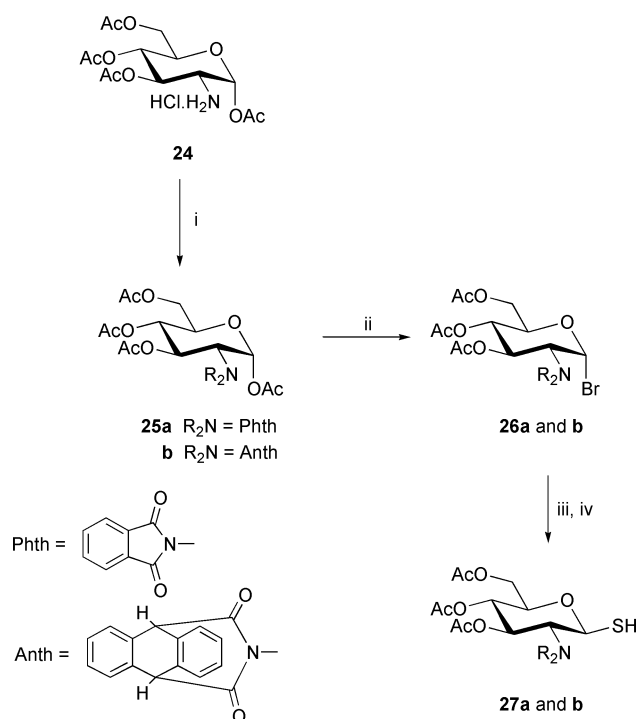


We turned our attention next to the thiols **27a** and **27b** derived from 1,3,4,6-tetra-*O*-acetyl-α-D-glucosamine **24** (see Scheme 6), in the hope that replacing the two-coordinate oxygen atom directly connected to C(2) with a three-coordinate nitrogen atom would lead to an increase in enantioselectivity. The imido groups are also highly polar which might result in an increase in dipole–dipole interaction in the transition state for hydrogen transfer. The two C(2) substituents were chosen on account of their orthogonal symmetry properties, since in **27a** the benzene ring is coplanar with the imide ring, while in **27b**

Table 2 Enantioselective addition of triphenylsilane to 5,5-dimethyl-6-methylenetetrahydropyran-2-one **2** at 60 °C to give **6**, using 3,4,6-tri-*O*-acetyl mannopyranose thiol catalysts^a

Entry	Thiol ^b	Solvent ^c	Ee of 6 (%) ^{d,e}
1	5	H	73 ^f
2	22a	H	71
3	22a	D	66
4	22b	H	46
5	22b	D	54
6	22c	H	71
7	22c	D	67
8	23a	D	5

^a Molar ratio Ph₃SiH : **2** = 1.1 : 1.0. ^b 5 Mol% based on **2**. ^c D = 1,4-dioxane, H = hexane. ^d Determined by ¹H NMR spectroscopic analysis using Eu(hfc)₃ or by chiral-stationary-phase HPLC analysis using a Chiralpak-AD column and hexane–isopropyl alcohol (97.5 : 2.5 v/v) mobile phase. ^e The isolated yield was *ca.* 90% in all cases. ^f Ees of 76% in hexane and 60% in dioxane were reported in ref. 5.



Scheme 6 Reagents and conditions: i, phthalic anhydride or 9,10-dihydroanthracene-9,10-dicarboxylic anhydride, Et₃N, pyridine; ii, HBr–HOAc, CH₂Cl₂, room temp., 6 h; iii, thiourea, acetone, reflux, 4–8 h; iv, K₂S₂O₅, CCl₄–H₂O (1 : 1), reflux, 2 h.

the two benzene rings project rigidly on either side of the imide ring. These thiols were screened as catalysts for the hydrosilylation of **2** under the standard conditions and the results are given in Table 3, along with the result of a previous preliminary experiment⁵ in which we obtained an ee of 25% for **6** using the simple, commercially available *N*-acetyl glucosamine thiol **28** as catalyst. Unfortunately, neither **27a** nor **27b** performed as well as **28** (entry 1) and the ee obtained with **27a** was particularly poor (entries 2 and 3). Although the ee obtained with **27b** (entry 4) was comparable with that using **28** as catalyst, the chemical yield with the former thiol was poor (32% isolated, 37% conversion by NMR spectroscopic analysis of the crude reaction mixture). This suggests that steric retardation of hydrogen-atom transfer reactions involving the hindered sulfur atom in **27b** and in the corresponding thiyl radical are slowing the overall chain hydrosilylation without increasing the ee of the product **6**.

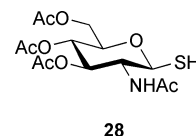
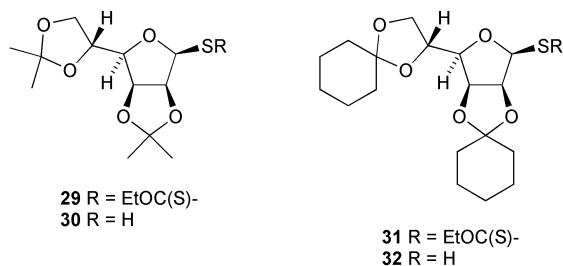


Table 3 Enantioselective addition of triphenylsilane to 5,5-dimethyl-6-methylenetetrahydropyran-2-one **2** at 60 °C to give **6**, using other thiol catalysts^a

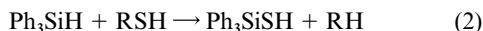
Entry	Thiol ^b	Solvent ^c	Ee of 6 (%) ^d	Isolated yield (%)
1 ^e	28	H + D (7 : 1)	25	67
2	27a	H ^f	5	70
3	27a	D	5	95
4	27b	D	20	32
5	30	H	9 ^g	95
6	32	H	9 ^g	92

^a Molar ratio Ph₃SiH : **2** = 1.1 : 1.0. ^b 5 Mol% based on **2**. ^c D = 1,4-dioxane, H = hexane. ^d Determined by ¹H NMR spectroscopic analysis using Eu(hfc)₃ or by chiral-stationary-phase HPLC analysis using a Chiralpak-AD column and hexane-isopropyl alcohol (97.5 : 2.5 v/v) mobile phase. ^e Data from ref. 5. ^f The thiol dissolved only after the reaction mixture was stirred at 60 °C. ^g The major enantiomer is the (S)-antipode of (–)-**6**.

In the hope that the relatively rigid bicyclo[3.3.0]octyl framework, with the SH in an *endo* position at C(1) on the furanose ring, might improve the enantioselectivity of hydrogen-atom transfer, the two mannofuranose thiols **30** and **32** were investigated. These thiols were prepared by alkaline hydrolysis of the known¹² dithiocarbonates **29** and **31**. The chemical yields of silane adduct were again essentially quantitative using either thiol as catalyst, but the ee was only 9% with both the isopropylidene- and cyclohexylidene-protected derivatives, although it was now the (S)-(+)-antipode of **6** that was formed in excess (Table 3, entries 5 and 6). The low enantioselectivity and the reversal of the sense of asymmetric induction obtained with these relatively non-polar thiols, compared with the results obtained with the more polar ester-substituted pyranose thiols, provides further support for the importance of factors other than steric interactions in determining the energy difference between the diastereoisomeric transition states for hydrogen-atom transfer to the polar lactone radical **18** derived from **2**.



We have reported recently¹⁰ that the radical-chain reaction between triphenylsilane and an alkanethiol provides a useful synthesis of triphenylsilanethiol [eqn. (2)].



Any such conversion of the homochiral thiol catalyst to the achiral Ph₃SiSH during the hydrosilylation could result in a reduction in the enantiomeric purity of the adduct produced. Silanethiol formation would occur by S_H2 attack of the Ph₃Si[•] on the homochiral thiol RSH, to displace R[•], in competition with addition of the silyl radical to the lactone. Although the latter reaction is expected to be much the more rapid process,¹³ the effect of increasing the relative concentration of the lactone was investigated. For example, with the thiol **22a** as catalyst under the conditions of entry 2 in Table 2, the ee of the adduct **6** obtained was 71%. However, when the concentration of the methylenelactone **2** was doubled (molar ratio Ph₃SiH : **2** = 1.1 : 2.0), under otherwise identical conditions, the ee of the product **6** decreased to 45%. When the experiment was repeated, but now replacing half the methylenelactone **2** with the saturated γ-caprolactone, so that the molar ratio Ph₃SiH : **2**

Table 4 Enantioselective addition of triphenylsilane to 5,5-diphenyl-6-methylenetetrahydropyran-2-one **3** at 60 °C to give **7**, using various thiol catalysts^a

Entry	Thiol ^b	Solvent ^c	Ee of 7 (%) ^d	Isolated yield (%)
1 ^e	5	H + D (5 : 1)	95	90
2	11d	H + D (4 : 1)	85	73
3	22a	H + D (4 : 1)	94	87
4	30	H + D (4 : 1)	53 ^f	82
5	32	H + D (4 : 1)	58 ^f	74

^a Molar ratio Ph₃SiH : **3** = 1.1 : 1.0. ^b 5 Mol% based on **3**. ^c D = 1,4-dioxane, H = hexane. ^d Determined by chiral-stationary-phase HPLC analysis using a Chiralcel-OD column and hexane-isopropyl alcohol (90 : 10 v/v) mobile phase. ^e Data from ref. 5. ^f The major enantiomer is the dextrorotatory (S)-antipode of (–)-**7**. The enantiomeric product mixture from entry 4 showed [α]_D²⁰ +105.5 (c 1.4, CHCl₃); that from entry 5 showed [α]_D²⁰ +116.0 (c 1.7, CHCl₃).

was returned to 1.1 : 1.0, the ee of **6** was 58%, still significantly less than under the conditions of Table 2, entry 2. It appears that conversion of the homochiral catalyst to achiral triphenylsilanethiol is not a complication under the conditions used, but that the presence of excess polar lactone seems to lower the ee of the product **6**, providing further evidence suggestive of the involvement of dipole–dipole interactions in determining the enantioselectivity of H-atom abstraction from the thiol.

The addition of triphenylsilane to the more sterically demanding methylenelactone **3** was investigated using a representative selection of the homochiral thiols as catalysts and the results are gathered in Table 4; the lactone **3** is relatively insoluble and mixtures of hexane and dioxane were used as solvents. Although the absolute configuration of the (–)-adduct **7** has not been proved rigorously to be *R*, there is little doubt that it is the same as that of **6** which has been verified by X-ray diffraction.⁵ The compound (–)-**8**, formed by reductive alkylation of **3**, also has the topologically analogous configuration (now *S* rather than *R*, because of the priority change according to the Cahn–Ingold–Prelog rules).

Our best previous result for the hydrosilylation of **3** was obtained using the β-mannopyranose thiol **5** as catalyst (entry 1), when the adduct (–)-**7** was formed in high chemical yield with an ee of 95%.⁵ When all five acetyl protecting groups in **5** were replaced with relatively bulky *o*-bromobenzoyl groups the ee of the product **7** was reduced to 85% (entry 2); the chemical yield was also reduced, indicating steric hindrance to H-atom transfer from the thiol to the relatively bulky radical **18** derived by addition of Ph₃Si[•] to the lactone **3**.

The β-mannopyranose thiol **22a**, in which the 2-*O*-acetyl group in **5** has been replaced by a very bulky mesitylcarbonyl group, gave **7** with the same high ee as obtained using **5** as catalyst (entry 3). This result is again consistent with the importance of factors other than the steric demands of the thiol in determining the enantioselectivity of H-atom transfer from the thiol to the prochiral adduct radical **18**, a conclusion supported by the results obtained with the bulky, but less polar, thiols **30** and **32** (entries 4 and 5). Not only was the ee obtained using either of these mannofuranose thiols significantly smaller than obtained using the β-mannopyranose thiols but, as for the hydrosilylation of **2** catalysed by the mannofuranose thiols, the sense of the asymmetric induction was reversed and the (+)-(*S*)-antipode of **7** was now produced in excess. Thus, it appears that van der Waals and dipole–dipole interactions can operate in opposition as well as co-operatively to determine the enantioselectivity of H-atom transfer from the thiol.

Conclusions

Enantioselective hydrogen-atom transfer from a homochiral thiol catalyst to a prochiral carbon-centred radical offers a potentially attractive, metal-free route to enantiomerically

enriched organic compounds. However, the design and synthesis of suitable thiols, capable of yielding products in high enantiomeric purity from prochiral radicals with limited steric or dipolar asymmetry around the radical centre, presents a considerable challenge. Careful positioning of relatively rigid steric and dipolar control elements in the vicinity of the SH group will be required to maximise differentiation between the enantiotopic faces of the hydrogen-abstracting radical and solvent effects will probably also need to be exploited.

Experimental

NMR spectra were recorded using a Bruker ADVANCE 500 instrument (500 MHz for ^1H , 125.7 MHz for ^{13}C). The solvent was CDCl_3 and chemical shifts are reported relative to Me_4Si ; J values are quoted in Hz. Column chromatography and TLC were carried out using Merck Kieselgel 60 (230–400 mesh) and Kieselgel 60 F_{254} aluminium-backed pre-coated plates, respectively. IR spectra were obtained using a Shimadzu FTIR-8700 spectrophotometer. Determination of enantiomeric composition by high-performance liquid chromatography (HPLC) was carried out using a Chiralpak-AD or Chiralcel-OD column (both 4.6 mm \times 250 mm; Daicel Chemical Industries Ltd.) in conjunction with hexane–isopropyl alcohol eluent (flow rate 1 $\text{cm}^3 \text{min}^{-1}$); the proportion of alcohol in the eluent is given in the text and UV detection was at 254 nm. Determination of ee by ^1H NMR spectroscopy was carried out using an enantiomerically pure NMR shift reagent, europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] $[\text{Eu}(\text{hfc})_3]$, Aldrich]. Optical rotations were measured with an AA Series Polaar 2000 polarimeter (Optical Activity Ltd.) using a 1 dm cell and are given in units of $10^{-1} \text{deg cm}^2 \text{g}^{-1}$.

All manipulations and reactions of air-sensitive compounds were carried out under an atmosphere of dry argon or nitrogen and all extracts were dried over anhydrous MgSO_4 . Light petroleum refers to the fraction of bp 40–60 $^\circ\text{C}$.

Materials

1,4-Dioxane and hexane were heated under reflux over calcium hydride, then distilled and stored under argon. TBHN was prepared by the reaction of sodium hyponitrite with *tert*-butyl bromide in diethyl ether, in the presence of zinc chloride, using the method described by Mendenhall.^{8b} 5,5-Dimethyl-6-methylenetetrahydropyran-2-one^{5,14} **2** and 5,5-diphenyl-6-methylenetetrahydropyran-2-one^{5,15} **3** were prepared by the published methods. Triphenylsilane and 2,3,4,6-tetra-*O*-acetyl-1-thio- β -D-glucopyranose was obtained commercially (Aldrich or Lancaster) and were used as received. 2,3,4,6-Tetra-*O*-acetyl-1-thio- β -D-mannopyranose **5** was prepared as described previously.⁵

Preparation of homochiral thiols

The β -glucose thiols **11a–i**, **16a** and **16b** were prepared by hydrolysis of the isothiuronium salts derived from the corresponding α -glucosyl bromides and thiourea. ^1H NMR analysis of the crude thiols showed them to be mixtures of the β - and α -anomers ($\beta : \alpha = \text{ca. } 85 : 15$) and the pure compounds were isolated by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (14 : 10 : 1)]. The preparations of **11c** and its α -anomer **12c** are given below as representative procedures; **12c** and **12i** were the only α -glucose thiols isolated in a pure state.

2,3,4,6-Tetra-*O*-(3-chlorobenzoyl)-1-thio- β/α -D-glucopyranose **11c/12c**

3-Chlorobenzoyl chloride (31.7 cm^3 , 0.24 mol) was added dropwise to a stirred mixture of anhydrous D-(+)-glucose (7.21 g, 0.04 mol) and pyridine (60 cm^3) with cooling in an ice–water bath. The reaction was stirred at room temperature for

18 h, after which precipitated pyridine hydrochloride was removed by filtration and the filtrate was evaporated under reduced pressure to remove excess pyridine. The residual oil was diluted with dichloromethane (250 cm^3) and washed successively with 1 M HCl, water, saturated aqueous NaHCO_3 , water and saturated brine (100 cm^3 of each). The organic solution was dried and concentrated under reduced pressure to give penta-*O*-(3-chlorobenzoyl)-D-glucopyranose **9c** as an oil. The crude benzoate was dissolved in dichloromethane (60 cm^3) and a 30 wt% solution of hydrogen bromide in acetic acid (40 cm^3 , 0.2 mol) was added slowly, with cooling in an ice–water bath. The mixture was stirred at room temperature for 6 h and ice–water (200 cm^3) was then added. The organic layer was separated and the aqueous layer was extracted with dichloromethane ($2 \times 150 \text{ cm}^3$). The combined extracts were washed successively with water, saturated aqueous NaHCO_3 ($2 \times 100 \text{ cm}^3$) and water (100 cm^3). The dichloromethane solution was dried, concentrated under reduced pressure and the residue was purified by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (11 : 13 : 1)] to give 1-bromo-2,3,4,6-tetra-*O*-(3-chlorobenzoyl)- α -D-glucopyranose **10c** (24.6 g, 77%) as a white foam. $[\alpha]_{\text{D}}^{25} +97.7$ (c 2.0, CHCl_3); δ_{H} 4.54 (1 H, dd, J 12.5 and 4.3, $\text{H}^{\text{A-6}}$), 4.64 (1 H, dd, J 12.5 and 2.9, $\text{H}^{\text{B-6}}$), 4.73 (1 H, m, H-5), 5.32 (1 H, dd, J 9.9 and 4.1, H-2), 5.75 (1 H, t, J 10.0, H-4), 6.20 (1 H, t, J 9.8, H-3), 6.84 (1 H, d, J 4.0, H-1), 7.28–8.01 (16 H, m, Ph); δ_{C} 62.1, 68.2, 71.0, 71.5, 72.3, 86.1, 127.7, 128.0(2), 128.0(4), 129.0, 129.7, 129.8 (3 C), 129.9(1), 129.9(2), 129.9(4) (3 C), 130.1, 130.2, 131.0, 133.4, 133.6, 133.8, 133.9, 134.6 (2 C), 134.7, 134.8, 163.9, 164.0, 164.4, 164.7. (Found: C, 51.2; H, 2.8. $\text{C}_{34}\text{H}_{23}\text{BrCl}_4\text{O}_9$ requires C, 51.2; H, 2.9%).

A stirred solution of **10c** (22.5 g, 28.2 mmol) and thiourea (2.79 g, 36.7 mmol) in acetone (50 cm^3) was heated under reflux for 8 h. The reaction was cooled to room temperature, after which the solvent was removed under reduced pressure to give the isothiuronium salt as a white solid. To a suspension of this salt in water (35 cm^3) and carbon tetrachloride (35 cm^3) was added $\text{K}_2\text{S}_2\text{O}_5$ (9.79 g, 44 mmol) and the mixture was stirred under reflux for 2 h until all the solid had dissolved. The reaction was cooled to room temperature, the carbon tetrachloride layer was separated and the aqueous layer was extracted with dichloromethane ($2 \times 30 \text{ cm}^3$). The combined organic phase was dried and concentrated under reduced pressure. The ^1H NMR spectrum of the residue showed the presence a mixture of the β - and α -anomers ($\beta : \alpha = 82 : 18$) and these compounds were isolated by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (14 : 10 : 1)]; their characteristics and the yields from the pyranosyl bromides are given below.

2,3,4,6-Tetra-*O*-(3-chlorobenzoyl)-1-thio- β -D-glucopyranose **11c.** Foam, yield 61%, $[\alpha]_{\text{D}}^{25} +42.3$ (c 2.0, CHCl_3); δ_{H} 2.50 (1 H, d, J 9.9, SH), 4.21 (1 H, m, H-5), 4.53 (1 H, dd, J 12.3 and 4.7, $\text{H}^{\text{A-6}}$), 4.62 (1 H, dd, J 12.3 and 3.3, $\text{H}^{\text{B-6}}$), 4.93 (1 H, t, J 9.8, H-1), 5.51 (1 H, t, J 9.6, H-2), 5.69 (1 H, t, J 9.8, H-4), 5.86 (1 H, t, J 9.5, H-3), 7.22–7.96 (16 H, m, Ph); δ_{C} 63.3, 69.6, 74.2, 74.3, 76.2, 79.0, 127.7(2), 127.7(9), 127.8(3), 127.8(9), 129.6(6), 129.7(0) (4 C), 129.7(6) (2 C), 129.8(3), 130.0(7), 130.0(9), 130.4, 131.0, 133.2, 133.5, 133.6(0), 133.6(3), 134.4(7), 134.5(1), 134.6 (2 C), 163.9, 164.1, 164.5, 164.8; IR (KBr disc) 2563 cm^{-1} (SH str.). (Found: C, 54.2; H, 3.0. $\text{C}_{34}\text{H}_{24}\text{Cl}_4\text{O}_9\text{S}$ requires C, 54.4; H, 3.2%).

2,3,4,6-Tetra-*O*-(3-chlorobenzoyl)-1-thio- α -D-glucopyranose **12c.** Foam, yield 9%, $[\alpha]_{\text{D}}^{25} +70.9$ (c 2.0, CHCl_3); δ_{H} 2.12 (1 H, d, J 5.8, SH), 4.52 (1 H, dd, J 12.3 and 4.4, $\text{H}^{\text{A-6}}$), 4.62 (1 H, dd, J 12.3 and 3.1, $\text{H}^{\text{B-6}}$), 4.87 (1 H, m, H-5), 5.50 (1 H, dd, J 10.2 and 5.7, H-2), 5.67 (1 H, t, J 9.9, H-4), 6.03 (1 H, t, J 9.9, H-3), 6.20 (1 H, t, J 5.7, H-1), 7.27–8.00 (16 H, m, Ph); δ_{C} 62.9, 68.5, 69.4, 70.7, 71.3, 77.4, 127.8, 127.9 (2 C), 128.0, 129.8 (7 C), 129.9, 130.0, 130.2, 130.3, 131.1, 133.3, 133.6, 133.7, 133.8, 134.6 (2 C), 134.7, 134.8, 164.0 (2 C), 164.5, 164.9; IR (KBr

disc) 2577 cm⁻¹ (SH str.). (Found: C, 54.4; H, 3.1. C₃₄H₂₄Cl₄O₉S requires C, 54.4; H, 3.2%).

The characteristics of the remaining α -glucosyl bromides and the glucose thiols are given below. The yields of pyranosyl bromides are based on penta-*O*-aroylglucose and those of the thiols are based on the pyranosyl bromide.

1-Bromo-2,3,4,6-tetra-*O*-(2-chlorobenzoyl)- α -D-glucopyranose

10b. Foam, yield 82%, $[\alpha]_D^{19} +113.3$ (c 2.0, CHCl₃); δ_H 4.64 (2 H, m, H-6), 4.69 (1 H, m, H-5), 5.32 (1 H, dd, *J* 9.9 and 4.1, H-2), 5.81 (1 H, t, *J* 9.9, H-4), 6.23 (1 H, t, *J* 9.8, H-3), 6.87 (1 H, d, *J* 4.0, H-1), 7.23–7.96 (16 H, m, Ph); δ_C 62.6, 68.1, 70.8, 71.5, 72.3, 86.2, 126.7(0), 126.7(2), 126.7(4), 126.8, 127.3, 128.6, 128.7, 129.2, 131.0, 131.1(1), 131.1(3), 131.4(0), 131.4(1), 131.5, 131.7, 132.4, 132.9, 133.0, 133.2, 133.6, 133.8, 133.9, 134.0, 134.8, 163.5, 164.1, 164.4, 164.9. (Found: C, 51.0; H, 2.7. C₃₄H₂₃BrCl₄O₉ requires C, 51.2; H, 2.9%).

1-Bromo-2,3,4,6-tetra-*O*-(2-bromobenzoyl)- α -D-glucopyranose

10d. Foam, yield 79%, $[\alpha]_D^{19} +93.7$ (c 2.0, CHCl₃); δ_H 4.64 (2 H, m, H-6), 4.70 (1 H, m, H-5), 5.32 (1 H, dd, *J* 9.9 and 4.1, H-2), 5.81 (1 H, t, *J* 9.9, H-4), 6.23 (1 H, t, *J* 9.7, H-3), 6.87 (1 H, d, *J* 4.1, H-1), 7.28–7.98 (16 H, m, Ph); δ_C 62.3, 68.2, 70.8, 71.5, 72.2, 86.2, 121.8, 121.9 (2 C), 122.7, 127.3 (2 C), 127.4, 127.5, 129.1, 130.6 (2 C), 131.2, 131.5, 131.6, 131.7, 132.5, 132.9, 133.1, 133.2, 133.6, 134.3 (2 C), 134.4, 134.7, 164.0, 164.6, 164.8, 165.4. (Found: C, 42.2; H, 2.3. C₃₄H₂₃Br₂O₉ requires C, 41.9; H, 2.4%).

1-Bromo-2,3,4,6-tetra-*O*-(3-bromobenzoyl)- α -D-glucopyranose

10e. Foam, yield 85%, $[\alpha]_D^{19} +79.5$ (c 1.9, CHCl₃); δ_H 4.54 (1 H, dd, *J* 12.6 and 4.4, H^A-6), 4.64 (1 H, dd, *J* 12.6 and 2.9, H^B-6), 4.72 (1 H, dt, *J* 10.0 and 3.7, H-5), 5.31 (1 H, dd, *J* 10.0 and 4.1, H-2), 5.74 (1 H, t, *J* 10.0, H-4), 6.19 (1 H, t, *J* 9.8, H-3), 6.84 (1 H, d, *J* 4.1, H-1), 7.20–8.16 (16 H, m, Ph); δ_C 62.2, 68.3, 71.0, 71.5, 72.3, 86.2, 122.5 (2 C), 122.6 (2 C), 128.2, 128.3, 128.4, 128.5, 130.0 (2 C), 130.1 (4 C), 130.3, 131.1, 132.7 (3 C), 132.9, 136.2, 136.5, 136.7, 136.8, 163.7, 163.9, 164.2, 164.6. (Found: C, 41.8; H, 2.2. C₃₄H₂₃Br₂O₉ requires C, 41.9; H, 2.4%).

1-Bromo-2,3,4,6-tetra-*O*-(2-methylbenzoyl)- α -D-glucopyranose 10f. Foam, yield 79%, $[\alpha]_D^{19} +115.1$ (c 2.0, CHCl₃); δ_H 2.34 (3 H, s, Me), 2.46 (3 H, s, Me), 2.56 (3 H, s, Me), 2.62 (3 H, s, Me), 4.57 (2 H, m, H-6), 4.70 (1 H, dt, *J* 10.2 and 3.6, H-5), 5.30 (1 H, dd, *J* 10.0 and 4.0, H-2), 5.76 (1 H, t, *J* 10.0, H-4), 6.25 (1 H, t, *J* 9.8, H-3), 6.89 (1 H, d, *J* 4.0, H-1), 7.10–8.00 (16 H, m, Ph); δ_C 21.2, 21.5, 21.7, 21.9, 61.7, 67.7, 70.2, 71.3, 72.8, 87.2, 125.7, 125.8 (2 C), 125.9, 127.3, 127.8, 128.3, 128.9, 130.5, 130.8 (2 C), 131.5, 131.6, 131.7, 131.8, 132.2, 132.3, 132.6, 132.8, 132.9, 140.3, 140.4, 140.9, 141.3, 165.5, 165.8, 166.2, 166.9. (Found: C, 64.1; H, 5.0. C₃₈H₃₅BrO₉ requires C, 63.8; H, 4.9%).

1-Bromo-2,3,4,6-tetra-*O*-(3-methylbenzoyl)- α -D-glucopyranose 10g. Foam, yield 81%, $[\alpha]_D^{19} +102.9$ (c 2.0, CHCl₃); δ_H 2.29 (3 H, s, Me), 2.34 (3 H, s, Me), 2.35 (3 H, s, Me), 2.40 (3 H, s, Me), 4.51 (1 H, dd, *J* 12.5 and 4.6, H^A-6), 4.63 (1 H, dd, *J* 12.5 and 2.8, H^B-6), 4.72 (1 H, m, H-5), 5.29 (1 H, dd, *J* 10.0 and 4.0, H-2), 5.78 (1 H, t, *J* 10.0, H-4), 6.25 (1 H, t, *J* 9.8, H-3), 6.87 (1 H, d, *J* 4.0, H-1), 7.19–7.86 (16 H, m, Ph); δ_C 21.0 (2 C), 21.1, 21.2, 61.9, 68.0, 70.5, 71.5, 72.7, 86.9, 126.8, 126.9, 127.0, 127.1, 128.1, 128.3 (3 C), 128.4 (2 C), 128.7, 129.3, 130.1, 130.2, 130.3, 130.5, 133.9, 134.0, 134.3, 134.5, 138.0, 138.1, 138.2 (2 C), 165.1, 165.4, 165.6, 166.1. (Found: C, 64.1; H, 5.1. C₃₈H₃₅BrO₉ requires C, 63.8; H, 4.9%).

1-Bromo-2,3,4,6-tetra-*O*-(1-naphthoyl)- α -D-glucopyranose

10h. Foam, yield 85%, $[\alpha]_D^{19} +125.7$ (c 1.7, CHCl₃); δ_H 4.77 (1 H, dd, *J* 12.5 and 2.9, H^A-6), 4.82 (1 H, dd, *J* 12.5 and 4.4, H^B-6), 4.91 (1 H, m, H-5), 5.54 (1 H, dd, *J* 10.0 and 4.0, H-2), 6.05 (1 H, t, *J* 10.0, H-4), 6.54 (1 H, t, *J* 9.8, H-3), 7.07 (1 H, d, *J* 4.0,

H-1), 7.21–8.94 (28 H, m, Np); δ_C 62.2, 68.1, 70.6, 71.6, 72.9, 87.2, 124.4, 124.6 (3 C), 125.2, 125.4 (3 C), 125.9 (2 C), 126.1 (2 C), 126.2, 126.3 (3 C), 127.6, 127.9, 128.0, 128.2, 128.3, 128.5 (2 C), 128.6, 130.1, 130.7, 130.8, 131.1, 131.4 (2 C), 131.5, 131.7, 133.5, 133.6, 133.7 (2 C), 133.8 (2 C), 134.2, 134.5, 165.7, 165.8, 166.4, 166.8. (Found: C, 70.1; H, 4.3. C₅₀H₃₅BrO₉ requires C, 69.9; H, 4.1%).

1-Bromo-2,3,4,6-tetra-*O*-(2-naphthoyl)- α -D-glucopyranose

10i. Foam, yield 83%, $[\alpha]_D^{19} +105.4$ (c 2.0, CHCl₃); δ_H 4.68 (1 H, dd, *J* 12.4 and 4.6, H^A-6), 4.80 (1 H, dd, *J* 12.4 and 3.1, H^B-6), 4.91 (1 H, m, H-5), 5.51 (1 H, dd, *J* 9.9 and 4.1, H-2), 6.01 (1 H, t, *J* 10.0, H-4), 6.47 (1 H, t, *J* 9.8, H-3), 7.00 (1 H, d, *J* 4.1, H-1), 7.43–8.62 (28 H, m, Np); δ_C 62.4, 68.6, 71.0, 71.7, 72.8, 87.0, 125.0, 125.1 (2 C), 125.2, 125.6, 125.8, 126.0, 126.5 (2 C), 126.7 (3 C), 127.5, 127.6, 127.7 (2 C), 128.2 (2 C), 128.3 (2 C), 128.4 (2 C), 128.5, 128.6, 129.4 (2 C), 129.5 (2 C), 131.5 (2 C), 131.8, 132.1, 132.2, 132.3, 132.4 (2 C), 135.6 (2 C), 135.7, 135.9, 165.3, 165.5, 165.8, 166.2. (Found: C, 69.8; H, 4.0. C₅₀H₃₅BrO₉ requires C, 69.9; H, 4.1%).

2,3,4,6-Tetra-*O*-benzoyl-1-thio- β -D-glucopyranose 11a. Foam, yield 67%, $[\alpha]_D^{23} +62.1$ (c 2.0, CHCl₃); δ_H 2.48 (1 H, d, *J* 9.8, SH), 4.18 (1 H, m, H-5), 4.48 (1 H, dd, *J* 12.3 and 5.0, H^A-6), 4.63 (1 H, dd, *J* 12.3 and 2.9, H^B-6), 4.90 (1 H, t, *J* 9.8, H-1), 5.51 (1 H, t, *J* 9.6, H-2), 5.72 (1 H, t, *J* 9.8, H-4), 5.89 (1 H, t, *J* 9.6, H-3), 7.26–8.05 (20 H, m, Ph); δ_C 63.1, 69.4, 73.8, 74.2, 76.7, 79.1, 128.2 (2 C), 128.3 (2 C), 128.4 (4 C), 128.7, 129.0, 129.6 (3 C), 129.7 (5 C), 129.8 (2 C), 133.1, 133.2, 133.4 (2 C), 165.1, 165.4, 165.7, 166.1; IR (KBr disc) 2560 cm⁻¹ (SH str.). (Found: C, 66.6; H, 4.5. C₃₄H₂₈O₉S requires C, 66.7; H, 4.6%).

2,3,4,6-Tetra-*O*-(2-chlorobenzoyl)-1-thio- β -D-glucopyranose

11b. Foam, yield 66%, $[\alpha]_D^{20} +23.7$ (c 2.0, CHCl₃); δ_H 2.50 (1 H, d, *J* 10.0, SH), 4.15 (1 H, m, H-5), 4.57 (1 H, dd, *J* 12.4 and 4.8, H^A-6), 4.63 (1 H, dd, *J* 12.4 and 2.7, H^B-6), 4.85 (1 H, t, *J* 9.8, H-1), 5.49 (1 H, t, *J* 9.6, H-2), 5.72 (1 H, t, *J* 9.8, H-4), 5.88 (1 H, t, *J* 9.5, H-3), 7.25–7.94 (16 H, m, Ph); δ_C 63.2, 69.4, 73.8, 74.3, 76.3, 78.9, 126.6(4), 126.6(6), 126.6(9), 126.7(4), 128.4, 128.6, 128.8, 129.3, 130.9(5), 131.0(0), 131.0(3), 131.0(6), 131.5 (2 C), 131.6, 131.7, 132.8, 133.1 (3 C), 133.8, 133.9 (2 C), 134.0, 164.1, 164.2, 164.4, 165.0; IR (KBr disc) 2561 cm⁻¹ (SH str.). (Found: C, 54.1; H, 3.1. C₃₄H₂₄Cl₄O₉S requires C, 54.4; H, 3.2%).

2,3,4,6-Tetra-*O*-(2-bromobenzoyl)-1-thio- β -D-glucopyranose

11d. Foam, yield 69%, $[\alpha]_D^{21} +16.2$ (c 2.0, CHCl₃); δ_H 2.51 (1 H, d, *J* 10.1, SH), 4.14 (1 H, m, H-5), 4.57 (1 H, dd, *J* 12.4 and 4.8, H^A-6), 4.64 (1 H, dd, *J* 12.4 and 2.7, H^B-6), 4.85 (1 H, t, *J* 9.9, H-1), 5.49 (1 H, t, *J* 9.6, H-2), 5.72 (1 H, t, *J* 9.8, H-4), 5.88 (1 H, t, *J* 9.5, H-3), 7.29–7.82 (16 H, m, Ph); δ_C 63.4, 69.5, 73.9, 74.4, 76.3, 79.0, 121.8(7), 121.9(1), 122.0(8), 122.1(1), 127.2(6) (2 C), 127.2(9), 127.4, 130.2, 130.6, 130.7, 131.4, 131.6, 131.7(0), 131.7(3), 131.9, 132.8, 133.1(1), 133.1(5), 133.2(1), 134.3(3) (2 C), 134.3(7), 134.4(2), 164.6, 164.7, 164.8, 165.5; IR (KBr disc) 2557 cm⁻¹ (SH str.). (Found: C, 43.8; H, 2.6. C₃₄H₂₄Br₄O₉S requires C, 44.0; H, 2.6%).

2,3,4,6-Tetra-*O*-(3-bromobenzoyl)-1-thio- β -D-glucopyranose

11e. Foam, yield 65%, $[\alpha]_D^{21} +36.0$ (c 2.0, CHCl₃); δ_H 2.47 (1 H, d, *J* 10.1, SH), 4.18 (1 H, m, H-5), 4.51 (1 H, dd, *J* 12.3 and 4.8, H^A-6), 4.59 (1 H, dd, *J* 12.3 and 3.3, H^B-6), 4.89 (1 H, t, *J* 9.8, H-1), 5.47 (1 H, t, *J* 9.6, H-2), 5.65 (1 H, t, *J* 9.8, H-4), 5.83 (1 H, t, *J* 9.5, H-3), 7.18–8.13 (16 H, m, Ph); δ_C 63.3, 69.7, 74.2, 74.4, 76.3, 79.0, 122.4(9) (2 C), 122.5(8), 122.6(0), 128.2, 128.3(0), 128.3(4), 128.4, 129.9(8), 130.0(2), 130.0(7) (2 C), 130.2(7), 130.2(9), 130.6, 131.2, 132.6(6), 132.7(0) (2 C), 132.8, 136.2, 136.5, 136.6(1), 136.6(4), 163.8, 164.1, 164.4, 164.8; IR (KBr disc) 2561 cm⁻¹ (SH str.). (Found: C, 43.9; H, 2.4. C₃₄H₂₄Br₄O₉S requires C, 44.0; H, 2.6%).

2,3,4,6-Tetra-*O*-(2-methylbenzoyl)-1-thio- β -D-glucopyranose 11f. Foam, yield 64%, $[\alpha]_{\text{D}}^{20} + 34.5$ (*c* 2.0, CHCl_3); δ_{H} 2.28 (3 H, s, CH_3), 2.42 (3 H, s, CH_3), 2.48 (3 H, s, CH_3), 2.48 (1 H, d, *J* 9.9, SH), 2.60 (3 H, s, CH_3), 4.13 (1 H, m, H-5), 4.51 (1 H, dd, *J* 12.3 and 5.0, $\text{H}^{\text{A-6}}$), 4.56 (1 H, dd, *J* 12.3 and 2.9, $\text{H}^{\text{B-6}}$), 4.87 (1 H, t, *J* 9.8, H-1), 5.48 (1 H, t, *J* 9.6, H-2), 5.67 (1 H, t, *J* 9.8, H-4), 5.87 (1 H, t, *J* 9.6, H-3), 7.09–7.96 (16 H, m, Ph); δ_{C} 21.0, 21.2, 21.3, 21.6, 62.6, 68.7, 73.3, 73.7, 76.5, 78.9, 125.6 (4C), 127.8, 127.9, 128.3, 128.8, 130.3, 130.5 (2 C), 130.7, 131.3, 131.4(0), 131.4(2), 131.4(8), 132.0, 132.1(8), 132.2(1), 132.3, 140.1(0), 140.1(2), 140.1(7), 140.6, 165.4, 165.9, 166.2, 166.7; IR (KBr disc) 2559 cm^{-1} (SH str.). (Found: C, 68.2; H, 5.4. $\text{C}_{38}\text{H}_{36}\text{O}_9\text{S}$ requires C, 68.3; H, 5.4%).

2,3,4,6-Tetra-*O*-(3-methylbenzoyl)-1-thio- β -D-glucopyranose 11g. Foam, yield 67%, $[\alpha]_{\text{D}}^{21} + 47.2$ (*c* 2.0, CHCl_3); δ_{H} 2.27 (3 H, s, CH_3), 2.31 (3 H, s, CH_3), 2.36 (3 H, s, CH_3), 2.38 (3 H, s, CH_3), 2.47 (1 H, d, *J* 9.7, SH), 4.17 (1 H, m, H-5), 4.48 (1 H, dd, *J* 12.3 and 5.2, $\text{H}^{\text{A-6}}$), 4.60 (1 H, dd, *J* 12.3 and 3.2, $\text{H}^{\text{B-6}}$), 4.89 (1 H, t, *J* 9.7, H-1), 5.49 (1 H, t, *J* 9.6, H-2), 5.67 (1 H, t, *J* 9.8, H-4), 5.87 (1 H, t, *J* 9.6, H-3), 7.16–7.84 (16 H, m, Ph); δ_{C} 20.9(8), 21.0(2), 21.0(7), 21.1(3), 63.2, 69.5, 73.7, 74.2, 76.7, 79.1, 126.8(0), 126.8(9) (2 C), 126.9(3), 128.1(0), 128.1(5), 128.1(9), 128.2(4), 128.7 (2 C), 128.9, 129.5, 130.1(4), 130.1(8), 130.2(7), 130.3(2), 133.8, 133.9, 134.0(9), 134.1(3), 137.9, 138.0(2), 138.0(7), 138.1(3), 165.2, 165.5, 165.8, 166.2; IR (KBr disc) 2561 cm^{-1} (SH str.). (Found: C, 68.0; H, 5.3. $\text{C}_{38}\text{H}_{36}\text{O}_9\text{S}$ requires C, 68.3; H, 5.4%).

2,3,4,6-Tetra-*O*-(1-naphthoyl)-1-thio- β -D-glucopyranose 11h. Foam, yield 58%, $[\alpha]_{\text{D}}^{20} + 33.4$ (*c* 2.0, CHCl_3); δ_{H} 2.62 (1 H, d, *J* 9.8, SH), 4.35 (1 H, m, H-5), 4.77 (2 H, m, H-6), 5.06 (1 H, t, *J* 9.8, H-1), 5.74 (1 H, t, *J* 9.6, H-2), 5.96 (1 H, t, *J* 9.8, H-4), 6.17 (1 H, t, *J* 9.5, H-3), 7.17–8.93 (28 H, m, Np); δ_{C} 63.2, 69.3, 73.7, 74.1, 76.7, 79.2, 124.2(7), 124.3(8), 124.4(1) (2 C), 125.0, 125.2(7), 125.3(0) (2 C), 125.5, 125.7, 126.0 (2 C), 126.1(1), 126.1(7), 126.2(3), 126.2(6), 127.5, 127.7(7), 127.8(2), 127.8(9), 128.2(7), 128.3(3), 128.3(9), 128.4(4), 130.2, 130.4, 130.5, 130.6, 131.0, 131.1, 131.2, 131.3, 133.4, 133.5(3) (2 C), 133.5(6), 133.6(5), 133.6(7), 133.7(3), 134.0, 165.7, 166.1, 166.5, 166.9; IR (KBr disc) 2559 cm^{-1} (SH str.). (Found: C, 73.8; H, 4.2. $\text{C}_{50}\text{H}_{36}\text{O}_9\text{S}$ requires C, 73.9; H, 4.5%).

2,3,4,6-Tetra-*O*-(2-naphthoyl)-1-thio- β -D-glucopyranose 11i. Foam, yield 56%, $[\alpha]_{\text{D}}^{21} + 79.1$ (*c* 2.0, CHCl_3); δ_{H} 2.57 (1 H, d, *J* 9.7, SH), 4.37 (1 H, m, H-5), 4.67 (1 H, dd, *J* 12.2 and 5.0, $\text{H}^{\text{A-6}}$), 4.76 (1 H, dd, *J* 12.2 and 3.7, $\text{H}^{\text{B-6}}$), 5.06 (1 H, t, *J* 9.7, H-1), 5.68 (1 H, t, *J* 9.6, H-2), 5.90 (1 H, t, *J* 9.8, H-4), 6.09 (1 H, t, *J* 9.5, H-3), 7.42–8.56 (28 H, m, Np); δ_{C} 63.6, 69.9, 74.0, 74.4, 76.6, 79.3, 124.9 (2 C), 125.1, 125.2, 125.7(6), 125.8(1), 126.0, 126.4 (2 C), 126.5, 126.6 (2 C), 127.4(5), 127.5(3), 127.5(8), 127.6(2), 128.0 (2 C), 128.1(6), 128.2(1) (2 C), 128.2(8), 128.4, 128.5, 129.2(7), 129.3(3) (2 C), 129.3(7), 131.3, 131.5, 131.6, 131.7, 132.1, 132.2, 132.3 (2 C), 135.4(7) (2 C), 135.5(6), 135.6(4), 165.3, 165.6, 165.9, 166.3; IR (KBr disc) 2559 cm^{-1} (SH str.). (Found: C, 73.7; H, 4.3. $\text{C}_{50}\text{H}_{36}\text{O}_9\text{S}$ requires C, 73.9; H, 4.5%).

2,3,4,6-Tetra-*O*-(2-naphthoyl)-1-thio- α -D-glucopyranose 12i. Foam, yield 12%, $[\alpha]_{\text{D}}^{19} + 74.7$ (*c* 2.0, CHCl_3); δ_{H} 2.19 (1 H, d, *J* 5.8, SH), 4.66 (1 H, dd, *J* 12.2 and 4.7, $\text{H}^{\text{A-6}}$), 4.76 (1 H, dd, *J* 12.2 and 3.4, $\text{H}^{\text{B-6}}$), 5.04 (1 H, m, H-5), 5.68 (1 H, dd, *J* 10.1 and 5.7, H-2), 5.89 (1 H, t, *J* 9.8, H-4), 6.28 (1 H, t, *J* 9.8, H-3), 6.33 (1 H, t, *J* 5.7, H-1), 7.42–8.60 (28 H, m, Np); δ_{C} 63.1, 68.9, 69.6, 70.5, 71.4, 77.7, 125.0 (3 C), 125.2, 125.8, 125.9, 126.0, 126.5 (2 C), 126.6 (2 C), 127.5, 127.6 (3 C), 128.1 (2 C), 128.2 (2 C), 128.3 (2 C), 128.4, 128.5, 129.3 (2 C), 129.4, 129.5, 131.4, 131.5, 131.6, 131.9, 132.2 (2 C), 132.3 (2 C), 135.5 (2 C), 135.6, 135.7, 165.4, 165.5, 165.9, 166.3; IR (KBr disc) 2571 cm^{-1} (SH str.). (Found: C, 73.9; H, 4.3. $\text{C}_{50}\text{H}_{36}\text{O}_9\text{S}$ requires C, 73.9; H, 4.5%).

3,4,6-Tri-*O*-acetyl-2-*O*-mesitylcarbonyl-1-thio- β -D-glucopyranose 16a

Mesitylcarbonyl chloride (2.36 g, 12.9 mmol) was added to a stirred mixture of 1,3,4,6-tetra-*O*-acetyl- α -D-glucopyranose¹⁶ (3.0 g, 8.6 mmol), silver triflate (4.42 g, 17.2 mmol) and 2,6-lutidine (3.0 cm^3 , 25.8 mmol) in dry dichloromethane (45 cm^3), with cooling in an ice–water bath. After being stirred at room temperature for 4 h, the reaction mixture was filtered through Celite and the filter cake was washed thoroughly with dichloromethane. The filtrate was washed with water and saturated brine, then dried and concentrated under reduced pressure. The residue was purified by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (10 : 14 : 1)] to give 1,3,4,6-tetra-*O*-acetyl-2-*O*-mesitylcarbonyl- α -D-glucopyranose **14a** (3.57 g, 84 %) as a white foam. $[\alpha]_{\text{D}}^{21} + 117.4$ (*c* 2.1, CHCl_3); δ_{H} 2.03 (3 H, s, Ac), 2.04 (3 H, s, Ac), 2.10 (3 H, s, Ac), 2.13 (3 H, s, Ac), 2.21 (6 H, s, $2 \times \text{CH}_3$), 2.27 (3 H, s, CH_3), 4.10 (1 H, dd, *J* 12.6 and 2.2, $\text{H}^{\text{A-6}}$), 4.13 (1 H, m, H-5), 4.31 (1 H, dd, *J* 12.6 and 4.0, $\text{H}^{\text{B-6}}$), 5.19 (1 H, t, *J* 9.8, H-4), 5.38 (1 H, dd, *J* 10.4 and 3.7, H-2), 5.59 (1 H, t, *J* 9.8, H-3), 6.54 (1 H, d, *J* 3.7, H-1), 6.83 (2 H, s, Ph); δ_{C} 19.6 (2 C), 20.5, 20.6, 20.7, 20.8, 21.0, 61.3, 68.3, 69.3, 69.4, 69.7, 88.5, 128.5 (2 C), 129.2, 135.3 (2 C), 140.0, 168.6 (2 C), 169.5, 170.0, 170.5. (Found: C, 58.2; H, 6.1. $\text{C}_{24}\text{H}_{30}\text{O}_{11}$ requires C, 58.3; H, 6.1%).

To a solution of 1,3,4,6-tetra-*O*-acetyl-2-*O*-mesitylcarbonyl- α -D-glucopyranose (3.5 g, 7.1 mmol) in dry dichloromethane (15 cm^3) was added a 30 wt% solution of hydrogen bromide in acetic acid (5.66 cm^3 , 28.4 mmol). The mixture was stirred at room temperature for 4 h and ice–water (50 cm^3) was then added. The organic layer was separated and the aqueous layer was extracted with dichloromethane ($2 \times 50 \text{ cm}^3$). The combined extracts were washed successively with water, saturated aqueous NaHCO_3 ($2 \times 40 \text{ cm}^3$) and water (40 cm^3). The dichloromethane solution was dried and concentrated under reduced pressure and the residue was purified by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (10 : 13 : 2)] to give 1-bromo-3,4,6-tri-*O*-acetyl-2-*O*-mesitylcarbonyl- α -D-glucopyranose **15a** (3.36 g, 92%) as a white foam. $[\alpha]_{\text{D}}^{22} + 207.0$ (*c* 2.0, CHCl_3); δ_{H} 2.02 (3 H, s, Ac), 2.05 (3 H, s, Ac), 2.12 (3 H, s, Ac), 2.28 (9 H, s, $3 \times \text{CH}_3$), 4.16 (1 H, dd, *J* 12.4 and 1.9, $\text{H}^{\text{A-6}}$), 4.34 (1 H, m, H-5), 4.37 (1 H, dd, *J* 12.4 and 4.0, $\text{H}^{\text{B-6}}$), 5.12 (1 H, dd, *J* 10.1 and 4.0, H-2), 5.22 (1 H, t, *J* 9.8, H-4), 5.63 (1 H, t, *J* 9.7, H-3), 6.82 (1 H, d, *J* 4.0, H-1), 6.85 (2 H, s, Ph); δ_{C} 19.9 (2 C), 20.5, 20.7 (2 C), 21.1, 60.9, 67.5, 70.2, 71.1, 72.1, 86.5, 128.5 (2 C), 129.1, 135.3 (2 C), 140.1, 169.0, 169.6 (2 C), 170.5. (Found: C, 51.4; H, 5.1. $\text{C}_{22}\text{H}_{27}\text{BrO}_9$ requires C, 51.3; H, 5.3%).

The thiol **16a** was prepared from the bromide **15a** (3.30 g, 6.40 mmol) and thiourea according to the general procedure described. ^1H NMR spectroscopy showed that the crude thiol was a mixture of the β - and α -anomers ($\beta : \alpha = 83 : 17$) and the β -anomer was isolated by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (10 : 13 : 2)] as a white foam (1.84 g, 61%). $[\alpha]_{\text{D}}^{19} + 51.7$ (*c* 1.9, CHCl_3); δ_{H} 2.02 (6 H, s, $2 \times \text{Ac}$), 2.10 (3 H, s, Ac), 2.28 (3 H, s, CH_3), 2.31 (6 H, s, $2 \times \text{CH}_3$), 2.48 (1 H, d, *J* 9.9, SH), 3.77 (1 H, m, H-5), 4.15 (1 H, dd, *J* 12.4 and 2.2, $\text{H}^{\text{A-6}}$), 4.28 (1 H, dd, *J* 12.4 and 4.8, $\text{H}^{\text{B-6}}$), 4.60 (1 H, t, *J* 9.7, H-1), 5.12 (1 H, dd, *J* 10.1 and 9.1, H-4), 5.29 (1 H, t, *J* 9.2, H-3), 5.36 (1 H, t, *J* 9.5, H-2), 6.85 (2 H, s, Ph); δ_{C} 20.1 (2 C), 20.4, 20.6, 20.7, 21.0, 61.8, 68.7, 73.2, 73.5, 75.9, 78.7, 128.5 (2 C), 129.3, 135.4 (2 C), 139.8, 168.3, 169.5, 169.9, 170.5; IR (KBr disc) 2600 cm^{-1} (SH str.). (Found: C, 56.3; H, 5.7. $\text{C}_{22}\text{H}_{28}\text{O}_9\text{S}$ requires C, 56.4; H, 6.0%).

3,4,6-Tri-*O*-acetyl-2-*O*-[(1*S*)-camphanoyl]-1-thio- β -D-glucopyranose 16b

(1*S*)-(–)-Camphanoyl chloride (2.99 g, 13.8 mmol) was added to a stirred mixture of 1,3,4,6-tetra-*O*-acetyl- α -D-glucopyranose¹⁶ (4.0 g, 11.5 mmol) and pyridine (25 cm^3) cooled in an

ice–water bath. After being stirred at room temperature for 6 h, the reaction mixture was concentrated under reduced pressure. The residue was diluted with dichloromethane (100 cm³) and washed successively with 1 M HCl, water, saturated aqueous NaHCO₃, water and saturated brine (50 cm³ of each). The organic solution was dried and concentrated under reduced pressure to give the crude product as a white foam, which was purified by recrystallisation from dichloromethane–light petroleum to afford 1,3,4,6-tetra-*O*-acetyl-2-*O*-(1*S*)-camphanoyl]- α -D-glucopyranose **14b** (4.9 g, 81%) as a white solid. Mp 169–171 °C; $[\alpha]_D^{19} + 87.6$ (*c* 2.0, CHCl₃); δ_H 0.89 (3 H, s, CH₃), 0.98 (3 H, s, CH₃), 1.09 (3 H, s, CH₃), 1.67 (1 H, m, CH₂), 1.87 (1 H, m, CH₂), 1.99 (1 H, m, CH₂), 2.01 (3 H, s, Ac), 2.04 (3 H, s, Ac), 2.09 (3 H, s, Ac), 2.17 (3 H, s, Ac), 2.26 (1 H, m, CH₂), 4.10 (1 H, dd, *J* 12.4 and 2.2, H^A-6), 4.14 (1 H, m, H-5), 4.28 (1 H, dd, *J* 12.4 and 4.0, H^B-6), 5.15 (1 H, t, *J* 9.8, H-4), 5.23 (1 H, dd, *J* 10.2 and 3.8, H-2), 5.53 (1 H, t, *J* 9.8, H-3), 6.41 (1 H, d, *J* 3.7, H-1); δ_C 9.2, 16.0, 16.2, 20.1, 20.2 (2 C), 20.3, 28.3, 30.2, 53.5, 54.2, 60.9, 67.4, 69.3, 69.4, 69.6, 88.1, 90.2, 165.7, 168.2, 169.0, 169.4, 170.0, 177.0. (Found: C, 54.4; H, 6.2. C₂₄H₃₂O₁₃ requires C, 54.5; H, 6.1%).

To a solution of **14b** (4.9 g, 9.3 mmol) in dry dichloromethane (20 cm³) was added a 30 wt% solution of hydrogen bromide in acetic acid (7.4 cm³, 37 mmol). The mixture was stirred at room temperature for 4 h and ice–water (60 cm³) was then added. The organic layer was separated and the water layer was extracted with dichloromethane (2 \times 60 cm³). The combined extracts were washed successively with water, saturated aqueous NaHCO₃ (2 \times 50 cm³) and water (50 cm³). The dichloromethane solution was dried and concentrated under reduced pressure and the residue was purified by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (6 : 12 : 7)] to give 1-bromo-3,4,6-tri-*O*-acetyl-2-*O*-(1*S*)-camphanoyl]- α -D-glucopyranose **15b** (4.75 g, 93%) as a white foam. $[\alpha]_D^{18} + 154.8$ (*c* 2.0, CHCl₃); δ_H 0.96 (3 H, s, CH₃), 1.00 (3 H, s, CH₃), 1.11 (3 H, s, CH₃), 1.70 (1 H, m, CH₂), 1.91 (1 H, m, CH₂), 2.03 (3 H, s, Ac), 2.04 (1 H, m, CH₂), 2.06 (3 H, s, Ac), 2.10 (3 H, s, Ac), 2.46 (1 H, m, CH₂), 4.14 (1 H, dd, *J* 12.4 and 1.4, H^A-6), 4.31 (1 H, m, H-5), 4.35 (1 H, dd, *J* 12.4 and 4.2, H^B-6), 4.99 (1 H, dd, *J* 10.0 and 4.1, H-2), 5.18 (1 H, t, *J* 9.8, H-4), 5.63 (1 H, t, *J* 9.7, H-3), 6.67 (1 H, d, *J* 4.1, H-1); δ_C 9.3, 16.4 (2 C), 20.2, 20.3 (2 C), 28.5, 30.4, 53.8, 54.5, 60.5, 66.8, 69.6, 70.9, 72.0, 85.8, 90.3, 165.9, 169.1, 169.3, 170.1, 177.0. (Found: C, 47.9; H, 5.3. C₂₂H₂₉BrO₁₁ requires C, 48.1; H, 5.3%).

The thiol **16b** was prepared in the usual way starting from the bromide **15b** (4.75 g, 8.6 mmol) and thiourea (0.78 g, 10.3 mmol). ¹H NMR spectroscopy showed that the crude thiol was a mixture of the β - and α -anomers (β : α = 60 : 40) from which the β -anomer (2.02 g, 47%) was isolated by recrystallisation from methanol at –18 °C. Mp 153–155 °C; $[\alpha]_D^{19} + 17.5$ (*c* 2.0, CHCl₃); δ_H 0.98 (3 H, s, CH₃), 1.06 (3 H, s, CH₃), 1.11 (3 H, s, CH₃), 1.70 (1 H, m, CH₂), 1.92 (1 H, m, CH₂), 2.00 (3 H, s, Ac), 2.02 (3 H, s, Ac), 2.03 (1 H, m, CH₂), 2.10 (3 H, s, Ac), 2.33 (1 H, d, *J* 10.0, SH), 2.38 (1 H, m, CH₂), 3.75 (1 H, m, H-5), 4.14 (1 H, dd, *J* 12.5 and 2.2, H^A-6), 4.27 (1 H, dd, *J* 12.5 and 4.8, H^B-6), 4.62 (1 H, t, *J* 9.9, H-1), 5.10 (1 H, t, *J* 9.6, H-4), 5.12 (1 H, t, *J* 9.7, H-2), 5.27 (1 H, t, *J* 9.4, H-3); δ_C 9.6, 16.6, 16.7, 20.5 (2 C), 20.7, 28.8, 31.1, 54.3, 54.9, 61.9, 68.1, 73.3, 74.3, 76.4, 78.3, 90.6, 166.5, 169.4, 169.7, 170.6, 177.6; IR (KBr disc) 2581 cm^{–1} (SH str.). (Found: C, 52.4; H, 6.0. C₂₂H₃₀O₁₁S requires C, 52.6; H, 6.0%).

The β -mannose thiols **22a–c** were prepared in a similar manner, but now the α -anomer predominated (α : β = *ca.* 83 : 17). However, the β -anomers **22a–c** could be separated in a pure state by careful and sometimes repeated flash chromatography.

3,4,6-Tri-*O*-acetyl-2-*O*-mesitylcarbonyl-1-thio- β -D-mannopyranose **22a**

Mesitylcarbonyl chloride (3.3 g, 18 mmol) was added to a

stirred mixture of 1,3,4,6-tetra-*O*-acetyl- β -D-mannopyranose¹⁷ (4.2 g, 12 mmol), silver triflate (6.17 g, 24 mmol) and 2,6-lutidine (4.2 cm³, 36 mmol) in dry dichloromethane (60 cm³), with cooling in an ice–water bath. After being stirred at room temperature for 4 h, the reaction mixture was filtered through Celite and the filter cake was washed thoroughly with dichloromethane. The filtrate was washed with water and saturated brine, and the organic phase was dried and concentrated under reduced pressure. The residue was purified by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (9 : 14 : 2)] to give 1,3,4,6-tetra-*O*-acetyl-2-*O*-mesitylcarbonyl- β -D-mannopyranose **20a** (5.42 g, 91%) as a white foam. $[\alpha]_D^{20} - 43.0$ (*c* 1.7, CHCl₃); δ_H 2.03 (3 H, s, Ac), 2.04 (3 H, s, Ac), 2.05 (3 H, s, Ac), 2.11 (3 H, s, Ac), 2.31 (3 H, s, CH₃), 2.39 (6 H, s, 2 \times CH₃), 3.82 (1 H, m, H-5), 4.14 (1 H, dd, *J* 12.4 and 2.4, H^A-6), 4.22 (1 H, dd, *J* 12.4 and 5.2, H^B-6), 5.24 (1 H, dd, *J* 10.1 and 3.1, H-3), 5.32 (1 H, t, *J* 10.0, H-4), 5.75 (1 H, dd, *J* 3.1 and 1.0, H-2), 5.94 (1 H, d, *J* 1.0, H-1), 6.89 (2 H, s, Ph); δ_C 19.8 (2 C), 20.4 (3 C), 20.5, 20.9, 61.8, 65.2, 68.6, 70.7, 73.0, 90.3, 128.2 (2 C), 129.9, 135.2 (2 C), 139.5, 168.1, 168.9, 169.3, 169.6, 170.4. (Found: C, 58.3; H, 6.0. C₂₄H₃₀O₁₁ requires C, 58.3; H, 6.1%).

To a solution of **20a** (5.38 g, 10.9 mmol) in dichloromethane (20 cm³) was added a 30 wt% solution of hydrogen bromide in acetic acid (8.7 cm³, 43.6 mmol). The mixture was stirred at room temperature for 4 h and ice–water (60 cm³) was then added. The organic layer was separated and the water layer was extracted with dichloromethane (2 \times 60 cm³). The combined extracts were washed successively with water (50 cm³), saturated aqueous NaHCO₃ (2 \times 50 cm³) and water (50 cm³). The dichloromethane solution was dried and concentrated under reduced pressure and the residue was purified by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (10 : 13 : 2)] to give 1-bromo-3,4,6-tri-*O*-acetyl-2-*O*-mesitylcarbonyl- α -D-mannopyranose **21a** (4.96 g, 88%) as a white foam. $[\alpha]_D^{20} + 69.5$ (*c* 2.0, CHCl₃); δ_H 2.03 (3 H, s, Ac), 2.04 (3 H, s, Ac), 2.06 (3 H, s, Ac), 2.31 (3 H, s, CH₃), 2.35 (6 H, s, 2 \times CH₃), 4.20 (2 H, m, H-6), 4.25 (1 H, m, H-5), 5.42 (1 H, t, *J* 10.0, H-4), 5.70 (1 H, dd, *J* 3.4 and 1.5, H-2), 5.84 (1 H, dd, *J* 10.2 and 3.4, H-3), 6.43 (1 H, d, *J* 1.5, H-1), 6.89 (2 H, s, Ph); δ_C 20.1 (2 C), 20.6 (3 C), 21.1, 61.4, 65.4, 68.2, 72.7, 73.0, 83.1, 128.7 (2 C), 129.2, 135.8 (2 C), 140.2, 168.4, 169.4, 169.6, 170.4. (Found: C, 51.3; H, 5.2. C₂₂H₂₇BrO₉ requires C, 51.3; H, 5.3%).

The thiol **22a** was prepared from the bromide **21a** (4.90 g, 9.51 mmol) and thiourea according to the general procedure. ¹H NMR spectroscopy showed that the crude thiol was a mixture of the β -anomer **22a** and α -anomer **23a** in the ratio 14 : 86 and both thiols were isolated by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (7 : 16 : 2)].

3,4,6-Tri-*O*-acetyl-2-*O*-mesitylcarbonyl-1-thio- β -D-mannopyranose **22a.** Foam, yield 10%, $[\alpha]_D^{20} - 66.4$ (*c* 2.0, CHCl₃); δ_H 2.03 (3 H, s, Ac), 2.04 (3 H, s, Ac), 2.05 (3 H, s, Ac), 2.31 (3 H, s, CH₃), 2.43 (6 H, s, 2 \times CH₃), 2.58 (1 H, d, *J* 9.8, SH), 3.74 (1 H, m, H-5), 4.11 (1 H, dd, *J* 12.4 and 2.2, H^A-6), 4.23 (1 H, dd, *J* 12.4 and 5.1, H^B-6), 4.96 (1 H, dd, *J* 9.8 and 1.0, H-1), 5.19 (1 H, dd, *J* 10.3 and 3.3, H-3), 5.37 (1 H, t, *J* 10.1, H-4), 5.70 (1 H, dd, *J* 3.3 and 1.0, H-2), 6.90 (2 H, s, Ph); δ_C 20.3 (2 C), 20.5, 20.6(2), 20.6(4), 21.0, 62.3, 65.0, 72.3(8), 72.4(2), 76.4, 76.9, 128.6 (2 C), 129.8, 135.6 (2 C), 139.8, 169.2, 169.3, 170.0, 170.5; IR (KBr disc) 2576 cm^{–1} (SH str.). (Found: C, 56.1; H, 5.8. C₂₂H₂₈O₉S requires C, 56.4; H, 6.0%).

3,4,6-Tri-*O*-acetyl-2-*O*-mesitylcarbonyl-1-thio- β -D-mannopyranose **23a.** Oil, yield 68%, $[\alpha]_D^{19} + 21.0$ (*c* 3.4, CHCl₃); δ_H 2.03 (3 H, s, Ac), 2.04 (3 H, s, Ac), 2.05 (3 H, s, Ac), 2.30 (3 H, s, CH₃), 2.34 (1 H, d, *J* 6.8, SH), 2.35 (6 H, s, 2 \times CH₃), 4.14 (1 H, dd, *J* 12.4 and 2.4, H^A-6), 4.21 (1 H, dd, *J* 12.4 and 4.9, H^B-6), 4.38 (1 H, m, H-5), 5.36 (1 H, t, *J* 10.0, H-4), 5.44 (1 H, dd, *J* 10.0 and 3.2, H-3), 5.59 (1 H, dd, *J* 3.2 and 1.6, H-2), 5.70 (1

H, dd, J 6.8 and 1.6, H-1), 6.88 (2 H, s, Ph); δ_{C} 20.1 (2 C), 20.7 (3 C), 21.1, 62.1, 66.1, 68.7, 69.7, 72.4, 77.2, 128.6 (2 C), 129.5, 135.7 (2 C), 140.0, 168.8, 169.5, 169.8, 170.6; IR (KBr disc) 2571 cm^{-1} (SH str.). (Found: C, 56.3; H, 5.9. $\text{C}_{22}\text{H}_{28}\text{O}_9\text{S}$ requires C, 56.4; H, 6.0%).

3,4,6-Tri-*O*-acetyl-2-*O*-[(1*S*)-camphanoyl]-1-thio- β -D-mannopyranose **22b**

(1*S*)-(–)-Camphanoyl chloride (4.48 g, 20.7 mmol) was added to a stirred mixture of 1,3,4,6-tetra-*O*-acetyl- β -D-mannopyranose¹⁷ (6.0 g, 17.2 mmol) and pyridine (40 cm^3) cooled in an ice–water bath. After being stirred at room temperature for 6 h, the reaction mixture was concentrated under reduced pressure. The residue was diluted with dichloromethane (150 cm^3) and washed successively with 1 M HCl, water, saturated aqueous NaHCO_3 , water and saturated brine (80 cm^3 of each). The organic phase was dried and concentrated under reduced pressure to give 1,3,4,6-tetra-*O*-acetyl-2-*O*-[(1*S*)-camphanoyl]- β -D-mannopyranose **20b** as a white foam. The crude product was dissolved in dichloromethane (30 cm^3) and treated with a 30 wt% solution of hydrogen bromide in acetic acid (13.7 cm^3 , 69 mmol), with cooling in an ice–water bath. The mixture was stirred at room temperature for 4 h and ice–water (100 cm^3) was then added. The organic layer was separated and the aqueous layer was extracted with dichloromethane ($2 \times 100 \text{ cm}^3$). The combined extracts were washed successively with water, saturated aqueous NaHCO_3 ($2 \times 80 \text{ cm}^3$) and water (80 cm^3). The dichloromethane solution was dried and concentrated under reduced pressure and the residue was purified by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (6 : 12 : 7)] to give 1-bromo-3,4,6-tri-*O*-acetyl-2-*O*-[(1*S*)-camphanoyl]- α -D-glucopyranose **21b** (8.46 g, 90%) as a white foam. $[\alpha]_{\text{D}}^{19} + 77.2$ (c 2.0, CHCl_3); δ_{H} 1.08 (3 H, s, CH_3), 1.10 (3 H, s, CH_3), 1.14 (3 H, s, CH_3), 1.73 (1 H, m, CH_2), 1.96 (1 H, m, CH_2), 2.00 (3 H, s, Ac), 2.06 (3 H, s, Ac), 2.07 (1 H, m, CH_2), 2.09 (3 H, s, Ac), 2.49 (1 H, m, CH_2), 4.17 (1 H, dd, J 12.6 and 2.0, $\text{H}^{\text{A-6}}$), 4.24 (1 H, m, H-5), 4.32 (1 H, dd, J 12.6 and 3.9, $\text{H}^{\text{B-6}}$), 5.42 (1 H, t, J 10.2, H-4), 5.60 (1 H, dd, J 3.1 and 1.7, H-2), 5.78 (1 H, dd, J 10.2 and 3.1, H-3), 6.32 (1 H, d, J 1.1, H-1); δ_{C} 9.6, 16.6, 16.7, 20.5 (3 C), 28.7, 30.7, 54.4, 54.8, 60.7, 64.5, 68.1, 72.7, 72.8, 82.3, 90.6, 166.1, 169.2 (2 C), 170.4, 177.4. (Found: C, 47.9; H, 5.3. $\text{C}_{22}\text{H}_{29}\text{BrO}_{11}$ requires C, 48.1; H, 5.3%).

The thiol **22b** was prepared from the bromide **21b** (8.36 g, 15.2 mmol) and thiourea according to the general procedure. ^1H NMR spectroscopy showed that the crude thiol was a mixture of the β - and β -anomers (β : α = 20 : 80) from which the β -anomer was isolated by flash chromatography [eluent: light petroleum–dichloromethane–diethyl ether (6 : 15 : 4)] as a white foam (1.05 g, 14%). $[\alpha]_{\text{D}}^{18} - 35.7$ (c 1.9, CHCl_3); δ_{H} 1.14 (3 H, s, CH_3), 1.15 (3 H, s, CH_3), 1.16 (3 H, s, CH_3), 1.74 (1 H, m, CH_2), 1.99 (1 H, m, CH_2), 2.00 (3 H, s, Ac), 2.03 (3 H, s, Ac), 2.08 (3 H, s, Ac), 2.09 (1 H, m, CH_2), 2.55 (1 H, m, CH_2), 2.65 (1 H, d, J 9.5, SH), 3.74 (1 H, m, H-5), 4.15 (1 H, dd, J 12.4 and 2.2, $\text{H}^{\text{A-6}}$), 4.23 (1 H, dd, J 12.4 and 4.6, $\text{H}^{\text{B-6}}$), 4.96 (1 H, dd, J 9.5 and 1.0, H-1), 5.12 (1 H, dd, J 10.2 and 3.2, H-3), 5.26 (1 H, t, J 10.1, H-4), 5.55 (1 H, dd, J 3.2 and 1.0, H-2); δ_{C} 9.7, 16.8, 16.9, 20.6 (2 C), 20.7, 28.9, 31.0, 54.3, 54.9, 62.0, 64.6, 72.0, 73.0, 75.8, 76.6, 91.1, 166.8, 169.4, 169.7, 170.6, 177.7; IR (KBr disc) 2574 cm^{-1} (SH str.). (Found: C, 52.5; H, 5.9. $\text{C}_{22}\text{H}_{30}\text{O}_{11}\text{S}$ requires C, 52.6; H, 6.0%).

2-*O*-(2,3,4,6-Tetra-*O*-benzoyl- α -D-mannopyranosyl)-3,4,6-tri-*O*-acetyl-1-thio- β -D-mannopyranose **22c**

1-Bromo-2-*O*-(2,3,4,6-tetra-*O*-benzoyl- α -D-mannopyranosyl)-3,4,6-tri-*O*-acetyl- α -D-mannopyranose^{17b} **21c** was prepared according to the published procedure and converted into an anomeric mixture of α - and β -thiols following the general procedure. The β -thiol **22c** was isolated by flash chromatography [eluent: light petroleum–dichloromethane–ether (3 : 20 :

2)] as a white foam (12% yield based on **21c**). $[\alpha]_{\text{D}}^{20} - 63.6$ (c 1.9, CHCl_3); δ_{H} 2.06 (3 H, s, Ac), 2.18 (3 H, s, Ac), 2.19 (3 H, s, Ac), 2.90 (1 H, d, J 8.6, SH), 3.79 (1 H, m, H-5), 4.23 (1 H, dd, J 12.4 and 2.2, $\text{H}^{\text{A-6}}$), 4.26 (1 H, d, J 2.7, H-2), 4.33 (1 H, dd, J 12.4 and 5.2, $\text{H}^{\text{B-6}}$), 4.50 (1 H, dd, J 12.4 and 4.0, $\text{H}^{\text{A-6'}}$), 4.73 (1 H, dd, J 12.4 and 2.4, $\text{H}^{\text{B-6'}}$), 4.91 (1 H, m, H-5'), 4.96 (1 H, d, J 8.6, H-1), 5.18 (1 H, dd, J 10.0 and 2.9, H-3), 5.29 (1 H, d, J 2.2, H-1'), 5.47 (1 H, t, J 10.0, H-4), 5.87 (1 H, dd, J 2.9 and 2.2, H-2'), 6.04 (1 H, dd, J 10.2 and 3.1, H-3'), 6.22 (1 H, t, J 10.2, H-4'), 7.25–8.09 (20 H, m, Ph); δ_{C} 20.6 (2 C), 20.8, 62.5, 62.6, 65.8, 66.5, 69.3, 70.1, 70.7, 73.6, 76.7, 76.8, 80.8, 99.8, 128.2 (2 C), 128.3 (2 C), 128.4 (2 C), 128.6 (2 C), 128.8, 129.1, 129.2, 129.7 (5 C), 129.7(6) (2 C), 129.8(4) (2 C), 133.0(0), 133.0(4), 133.4, 133.5, 165.0, 165.1, 165.5, 166.1, 169.2, 170.7, 171.0; IR (KBr disc) 2573 cm^{-1} (SH str.). (Found: C, 61.0; H, 4.9. $\text{C}_{46}\text{H}_{44}\text{O}_{17}\text{S}$ requires C, 61.3; H, 4.9%).

3,4,6-Tri-*O*-acetyl-2-phthalimido-2-deoxy-1-thio- β -D-glucopyranose **27a**

To a solution containing 1,3,4,6-tetra-*O*-acetyl-2-phthalimido-2-deoxy- α -D-glucopyranose **25a**¹⁸ (10.5 g, 22 mmol) in dry dichloromethane (45 cm^3) was added a 30 wt% solution of hydrogen bromide in acetic acid (17.5 cm^3 , 88 mmol). The mixture was stirred at room temperature for 4 h and ice–water (100 cm^3) was then added. The organic layer was separated and the aqueous layer was extracted with dichloromethane ($2 \times 100 \text{ cm}^3$). The combined extracts were washed successively with water, saturated aqueous NaHCO_3 ($2 \times 80 \text{ cm}^3$) and water (80 cm^3). The dichloromethane solution was dried and concentrated under reduced pressure to afford 1-bromo-3,4,6-tri-*O*-acetyl-2-phthalimido-2-deoxy- α -D-glucopyranose **26a** as a syrup. The crude bromide was unstable on silica gel and without purification it was treated with thiourea following the general procedure. The β -thiol **27a** was separated by flash chromatography [eluent: light petroleum–dichloromethane–ether (3 : 21 : 1)] as a white foam, followed by recrystallisation from diethyl ether (yield 56% based on **25a**). Mp 127–129 °C, $[\alpha]_{\text{D}}^{19} + 66.2$ (c 2.0, CHCl_3); δ_{H} 1.86 (3 H, s, Ac), 2.03 (3 H, s, Ac), 2.12 (3 H, s, Ac), 2.25 (1 H, d, J 10.3, SH), 3.91 (1 H, m, H-5), 4.17 (1 H, dd, J 12.4 and 2.1, $\text{H}^{\text{A-6}}$), 4.30 (1 H, t, J 10.4, H-2), 4.31 (1 H, dd, J 12.4 and 4.8, $\text{H}^{\text{B-6}}$), 5.19 (1 H, t, J 9.7, H-4), 5.51 (1 H, t, J 10.3, H-1), 5.82 (1 H, dd, J 10.2 and 9.2, H-3), 7.76 (2 H, m, Ph), 7.87 (2 H, m, Ph); δ_{C} 20.4, 20.6, 20.8, 57.7, 62.1, 68.6, 71.2, 76.3(7), 76.3(9), 123.8 (2 C), 131.1, 131.4, 134.4, 134.6, 167.3, 167.6, 169.4, 170.0, 170.7; IR (KBr disc) 2587 cm^{-1} (SH str.). (Found: C, 53.4; H, 4.7; N, 2.9. $\text{C}_{20}\text{H}_{21}\text{O}_9\text{NS}$ requires C, 53.2; H, 4.7; N, 3.1%).

3,4,6-Tri-*O*-acetyl-2-imido-2-deoxy-1-thio- β -D-glucopyranose **27b**

The 1,3,4,6-tetra-*O*-acetyl-2-imido-2-deoxy- α -D-glucopyranose **25b** was prepared from 1,3,4,6-tetra-*O*-acetyl- α -D-glucosamine hydrochloride¹⁸ and 9,10-dihydroanthracene-9,10-dicarboxylic anhydride¹⁹ following the procedure used to prepare **25a**. This was then converted to the pyranosyl bromide **26b** which was treated, in a crude state, with thiourea as described for the preparation of **27a**. The β -thiol **27b** was separated by flash chromatography [eluent: light petroleum–dichloromethane–ether (2 : 22 : 1)] as a pale-yellow foam (48% yield based on **25b**). $[\alpha]_{\text{D}}^{18} + 31.1$ (c 1.9, CHCl_3); δ_{H} 1.27 (3 H, s, Ac), 1.93 (3 H, s, Ac), 2.06 (3 H, s, Ac), 2.72 (1 H, d, J 8.9, SH), 3.74 (1 H, m, H-5), 4.08 (1 H, dd, J 12.4 and 2.2, $\text{H}^{\text{A-6}}$), 4.20 (1 H, dd, J 12.4 and 4.8, $\text{H}^{\text{B-6}}$), 4.62 (1 H, dd, J 10.9 and 8.1, H-2), 4.93 (1 H, dd, J 10.1 and 8.9, H-4), 5.19 (1 H, s, PhCH), 5.33 (1 H, s, PhCH), 5.37 (1 H, t, J 8.5, H-1), 5.66 (1 H, dd, J 10.9 and 8.8, H-3), 7.28–7.52 (8 H, m, Ph); δ_{C} 19.4, 20.5, 20.7, 57.7, 59.4, 60.2, 62.1, 69.1, 69.4, 71.8, 93.4, 126.1, 126.6, 126.8, 127.4, 128.2, 128.4, 128.5, 128.6, 134.0, 134.1, 134.5, 134.7, 169.3, 169.4, 170.1, 170.7, 171.4; IR (KBr disc) 2593 cm^{-1} (SH str.).

(Found: C, 60.7; H, 4.7; N, 2.6. $C_{28}H_{27}O_9NS$ requires C, 60.8; H, 4.9; N, 2.5%).

The mannofuranose thiols **30** and **32** were prepared as described below.

2,3,5,6-Di-*O*-isopropylidene-1-thio- β -D-mannofuranose **30**

To a stirred solution of *S*-(2,3,5,6-Di-*O*-isopropylidene- β -D-mannofuranosyl) *O*-ethyl dithiocarbonate¹² **29** (3.72 g, 10.5 mmol) in ethanol (30 cm³) was added powdered potassium hydroxide (1.76 g, 31.5 mmol), with cooling in an ice–water bath. After being stirred at room temperature for 5 h, the reaction mixture was acidified to pH 5–6 with 1 M HCl and extracted with diethyl ether (3 \times 30 cm³). The combined extracts were dried, concentrated under reduced pressure and the residue was purified by flash chromatography [eluent: light petroleum–ether (5 : 1)] to afford the thiol **30** (1.88 g, 65%) as an oil, $[a]_D^{22} +93.6$ (*c* 2.5, CHCl₃); δ_H 1.32 (3 H, s, CH₃), 1.38 (3 H, s, CH₃), 1.47 (3 H, s, CH₃), 1.48 (3 H, s, CH₃), 1.95 (1 H, d, *J* 5.1, SH), 4.00 (1 H, dd, *J* 8.7 and 4.5, 6-H^A), 4.09 (1 H, dd, *J* 8.7 and 6.3, 6-H^B), 4.17 (1 H, dd, *J* 7.5 and 3.4, 4-H), 4.43 (1 H, m, 5-H), 4.66 (1 H, d, *J* 5.9, 2-H), 4.81 (1 H, dd, *J* 5.9 and 3.6, 3-H), 5.59 (1 H, d, *J* 5.1, 1-H); δ_C 24.6, 25.2, 25.9, 26.9, 66.8, 72.7, 79.7, 80.2, 84.4, 87.7, 109.3, 113.1; IR (KBr disc) 2559 cm^{−1} (SH str.). (Found: C, 52.1; H, 7.4. $C_{12}H_{20}O_5S$ requires C, 52.2; H, 7.3%).

2,3,5,6-Di-*O*-cyclohexylidene-1-thio- β -D-mannofuranose **32**

To a stirred solution of *S*-(2,3,5,6-Di-*O*-cyclohexylidene- β -D-mannofuranosyl) *O*-ethyl dithiocarbonate¹² **31** (6.63 g, 15 mmol) in ethanol (45 cm³) was added powdered potassium hydroxide (2.52 g, 45 mmol), with cooling in an ice–water bath. After being stirred at room temperature for 5 h, the reaction mixture was acidified with 1 M HCl to pH 5–6. The mixture was extracted with diethyl ether (3 \times 50 cm³), the combined extracts were dried and concentrated under reduced pressure. The residue was purified by flash chromatography [eluent: light petroleum–ether (6 : 1)] to afford the thiol **32** (3.65 g, 68%) as an oil, $[a]_D^{22} +71.6$ (*c* 2.7, CHCl₃); δ_H 1.25–1.68 (20 H, m, 2 \times C₅H₁₀), 1.95 (1 H, d, *J* 5.1, SH), 3.99 (1 H, dd, *J* 8.6 and 5.2, 6-H^A), 4.06 (1 H, dd, *J* 8.6 and 6.3, 6-H^B), 4.20 (1 H, dd, *J* 6.7 and 3.5, 4-H), 4.44 (1 H, m, 5-H), 4.63 (1 H, d, *J* 5.8, 2-H), 4.77 (1 H, dd, *J* 5.8 and 3.6, 3-H), 5.58 (1 H, d, *J* 5.1, 1-H); δ_C 23.7, 23.8(6), 23.9(1), 24.0, 25.0, 25.1, 34.3, 34.7, 35.6, 36.4, 66.2, 72.4, 79.4, 80.4, 84.5, 87.3, 109.6, 113.8; IR (KBr disc) 2558 cm^{−1} (SH str.). (Found: C, 60.6; H, 7.8. $C_{18}H_{28}O_5S$ requires C, 60.7; H, 7.9%).

Typical procedure for thiol-catalysed radical-chain hydrosilylation

The diphenylmethylenelactone **3** (0.264 g, 1.0 mmol), triphenylsilane (0.287 g, 1.1 mmol), TBHN (8.7 mg, 0.05 mmol) and the β -glucose thiol **11d** (46.4 mg, 0.05 mmol) were introduced into a dry, argon-filled 10 cm³ two-necked round-bottomed flask containing a magnetic stirrer bar and fitted with a condenser, with argon flowing slowly downwards through it. Hexane (2 cm³) and dioxane (0.5 cm³) were added to the mixture through the side arm, which was then closed with a stopper, and the flask was immersed in an oil bath pre-heated to 60 °C. The mixture was stirred under argon for 2.5 h, the solvent was removed using a rotary evaporator, and the residue was purified by flash chromatography [eluent: petroleum–dichloromethane–diethyl ether (16 : 8 : 1)] to afford the adduct 5,5-diphenyl-6-(triphenylsilylmethyl)tetrahydropyran-2-one **7^s** as a white solid (0.384 g, 73%, 85% ee), $[a]_D^{22} -165.6$ (*c* 2.0, CHCl₃).

X-Ray crystallography §

Data were collected on a Nicolet R3mV diffractometer at

20 °C using graphite-monochromated Mo-*K* α radiation. Three standard reflections were monitored throughout the data collection and these showed no variation with time. The data were corrected for Lorentz and polarisation effects. The structures were solved by direct methods (SHELXS-86)²⁰ and developed using alternating cycles of least-squares refinement and difference-Fourier synthesis (SHELXL-93).²¹ Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in idealised positions and assigned a common isotropic thermal parameter. The atom Cl(1) (Fig. 1) is disordered over two sites and was modelled with refined occupancies of 77 : 23; the major orientation [Cl(1a)] is that shown in Fig. 1.

Crystal data for 2,3,4,6-tetra-*O*-(3-chlorobenzoyl)-1-thio- β -D-glucopyranose **11c**

$C_{34}H_{24}Cl_4O_9S$, $M = 750.39$, monoclinic, space group $P2_1$, $a = 14.412(3)$, $b = 9.096(2)$, $c = 14.908(3)$ Å, $\beta = 117.43(3)^\circ$, $U = 1735$ Å³, (by least-squares refinement of diffractometer angles for 22 reflections in the range $14 < 2\theta < 29^\circ$, $\lambda = 0.71073$ Å), $Z = 2$, $F(000) = 768$, $D_c = 1.437$ g cm^{−3}, $\mu(\text{Mo-K}\alpha) = 4.55$ cm^{−1}, colourless plate $0.76 \times 0.65 \times 0.32$ mm. Full matrix least-squares refinement on 443 parameters gave $R = 0.0490$ ($R_w = 0.1232$) for 2737 independent reflections [$I > 2\sigma(I)$] and $R = 0.0628$ ($R_w = 0.1410$) for all 3264 independent reflections in the range $5 \leq 2\theta \leq 50^\circ$. The absolute configuration was determined using SHELXL-93 procedures [absolute structure parameter = $-0.01(10)$]. The final electron density map was featureless with the largest peak 0.29 e Å^{−3}.

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