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Synthesis of S-linked carbohydrate analogues via a Ferrier reaction

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Abstract

In this work, the synthetic utility of the Ferrier reaction to access S-linked disaccharides and S-linked glycoamino acids has been probed. Significantly, entry to a range of 1,4- and 1,6-S-linked disaccharides has been achieved using glycals derived from glucose and galactose, and sulfur containing coupling partners derived from methyl α-D-glucopyranoside. Access to S-linked glycoamino acids and glycopeptides has also been achieved using protected cysteine and homocysteine coupling partners within the Ferrier reaction. Functionalisation of the Ferrier products, for example, via dihydroxylation using OsO_4 or amino acid coupling, and deprotection of the targets have also been achieved. In this way, entry to materials of interest as mimics of biologically interesting disaccharides and glycopeptides has been realised, including targets derived from rare sugars such as talopyranose and gulopyranose.

1. Introduction

It is now well established that carbohydrates are involved in a multitude of biological processes including cell–cell recognition, differentiation and adhesion. Moreover, the elucidation of the roles of carbohydrates in a range of disease processes such as cancer, viral and bacterial infections, and immunotherapy has received considerable recent attention.[1] As a result, it is now recognised that carbohydrates and their derivatives offer considerable potential as a new generation of therapeutic agents,[2] and much synthetic effort has been channelled into the synthesis of both natural and unnatural carbohydrates, and their mimics. In some cases carbohydrate-based drugs have demonstrated limited stability in vivo, due to processing by glycosidase enzymes, but it has been illustrated that synthetic derivatives such as S-linked glycosides, in which the interglycosidic oxygen atom has been replaced with a sulfur atom, can be of enhanced utility.[3,4] S-Linked oligosaccharides are also of interest for additional biological studies, including as hydrolytically stable structural probes for enzyme sites,[5–7] where they are able to participate in hydrogen bonding, and as accurate carbohydrate mimics. As a result of the need for S-linked carbohydrates, various methods for their preparation have been reported including Lewis acid catalysed condensation between a glycosyl acceptor containing an SH group and a suitable glycosyl donor, S_N2-like displacement of a good leaving group of a glycosyl acceptor with a 1-thiolate or of a glycosyl halide with a sugar thiolate, and Michael addition of thiolates to α,β-unsaturated systems.[6,8–12] The work reported herein advances the synthetic capability for preparing S-linked disaccharides by developing a new method for entry to such targets using a Ferrier reaction between a range of glycals and a range of sulfur containing carbohydrates.

The Ferrier reaction involves the reaction between a glycal (a carbohydrate with an endocyclic alkene) and a nucleophile in the presence of a Lewis acid or promoter. The glycal undergoes an allylic rearrangement with substitution of the nucleophile at the anomeric position.[13] Mild reaction conditions and formation of a double bond offer the potential for further functionalisation, highlighting the synthetic utility of this methodology. Oxygen, carbon and sulfur nucleophiles have already proved popular as the nucleophilic components for the synthesis of

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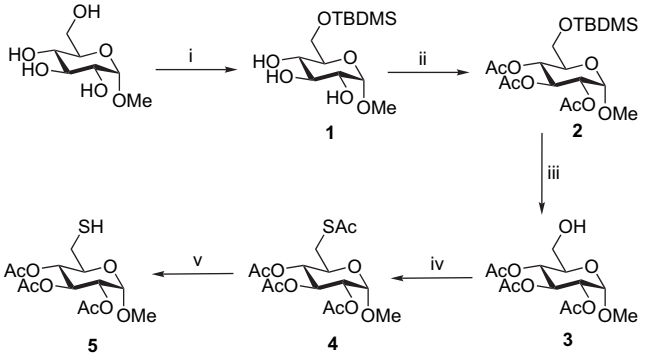
functionalised glycosides. In addition, carbohydrate derived alkenes have been incorporated to allow entry to C-linked disaccharides.[14] Although thiol nucleophiles have been incorporated within a Ferrier strategy,[15–20] the reaction has not been studied for the synthesis of S-linked disaccharides. Therefore, as an extension to this methodology and due to the biological utility of the S-linked disaccharide targets, this programme has investigated for the first time the feasibility of using sulfur containing carbohydrates as the nucleophilic components within the Ferrier reaction to allow access to S-linked disaccharides. If successful this will provide materials to further probe the hypothesis that disaccharide derivatives can potentially display more specific inhibitory activity of glycosidase enzymes compared with monosaccharide inhibitors.[21] This is believed to be a result of the disaccharides including steric and charge information of both glycosyl moieties, which are liberated during the glycosidase-catalysed hydrolysis and the aglycon to which it is attached. Monosaccharide mimics often inhibit several types of enzymes, with disaccharides and oligosaccharides being expected to be more selective for enzymes and lectins. As such disaccharide mimics represent more selective ligands for lectin and oligosaccharide receptors.[22]

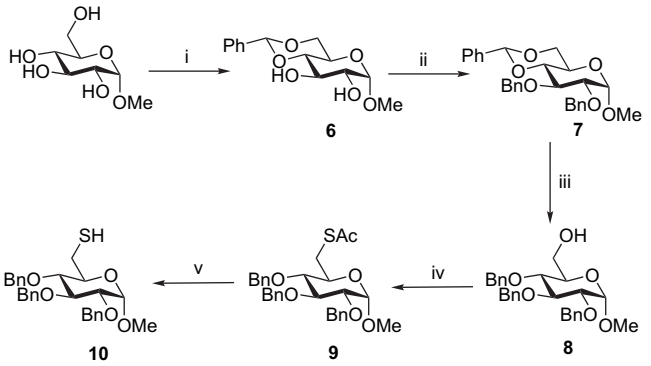
2. Results and discussion

The first stage of the research programme involved the synthesis of primary thiols **5** and **10** to potentially allow access to 1,6-S-linked disaccharides. To probe the influence of the protecting groups within the nucleophilic component on the efficiency of the Ferrier reaction, electron withdrawing (acetate) and electron donating (benzyl) protecting groups were incorporated within the thiol acceptors. The per-*O*-acetate-protected derivative (**5**)[23] and the per-*O*-benzyl protected analogue (**10**)[24,25] were prepared from methyl α-D-glucopyranoside according to the literature procedures, as illustrated in Schemes 1 and 2, respectively.



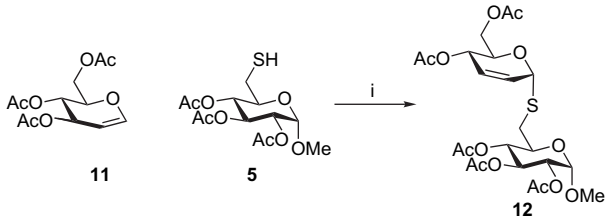
Scheme 1. Synthesis of thiol (**5**). (i) TBDMS–Cl, imidazole, DMF, overnight. (ii) Ac_2O, Py, overnight, 77% (over two steps). (iii) Aq acetic acid (80%), 50 °C, 2 h, 86%. (iv) DEAD, PPh_3, thioacetic acid, THF, overnight, 78%. (v) $N_2H_4 \cdot H_2O$, acetic acid, DMF, 0.5 h, 86%.

For both acetate and benzyl ether protected systems, the thioacetate was deprotected using hydrazine monohydrate when the material was required, therefore preventing dimerisation of the free thiol moiety.



Scheme 2. Synthesis of thiol (**10**). (i) α,α-Dimethoxytoluene, *p*-TsOH, DMF, 50 °C, 2 h, 73%. (ii) BnBr, TBAI, DMF, overnight, 86%. (iii) $LiAlH_4$, $AlCl_3$, Et_2O, CH_2Cl_2, Δ, 2 h, 74%. (iv) DEAD, PPh_3, thioacetic acid, THF, overnight, 60%. (v) $N_2H_4 \cdot H_2O$, acetic acid, DMF, 0.5 h, 96%.

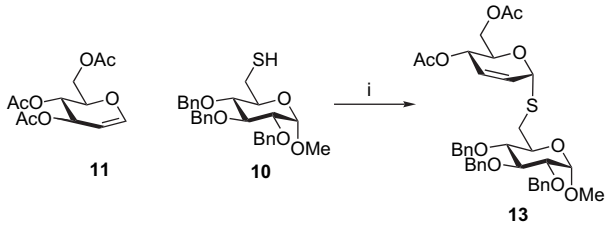
Owing to the success of $LiBF_4$ as the Lewis acid in Ferrier reactions involving sulfur nucleophiles,[15] it was decided to employ the same in the preparation of the S-linked disaccharides. First, the *O*-acetate-protected thiol (**5**) was subjected to the Ferrier reaction with tri-*O*-acetyl-D-glucal (**11**) and $LiBF_4$ (1.2 equiv) in acetonitrile (Scheme 3). After leaving the reaction mixture to stir for 8 h at room temperature, the reaction was quenched and the residue purified by column chromatography. Pleasingly, this afforded the desired 1,6-S-linked disaccharide (**12**) in 89% yield after purification by column chromatography as an anomeric mixture of 10:1, α/β as determined by ^1H NMR and NOESY spectroscopic analyses.



Scheme 3. (i) $LiBF_4$, MeCN, 8 h, 89%, α:β 10:1.

When this reaction was repeated with the benzyl protected analogue (**10**), the desired disaccharide (**13**) was afforded in 75% yield after 4 h at room temperature, in an anomeric ratio of 10:1, α/β (Scheme 4). The anomeric ratios of both reactions were consistent with the previous studies on the Ferrier reaction with sulfur nucleophiles.[15]

Presumably, the shorter reaction time of 4 h compared with 8 h for the reaction of **10** versus **5** reflects the greater nucleophilicity of the thiol (**10**). To fully probe this potential tuning



Scheme 4. (i) $LiBF_4$, MeCN, 4 h, 75%, α:β 10:1.

Table 1
Reaction of the thiol acceptors **5** and **10** with a range of glycals using $LiBF_4$ (1.2 equiv) or $BF_3{\cdot}OEt_2$ (0.1 equiv) as activator

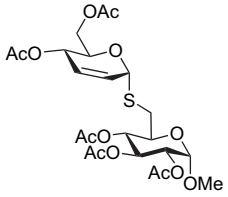
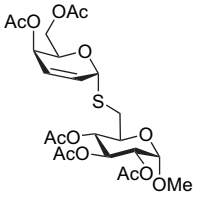
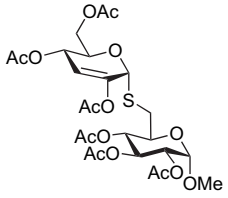
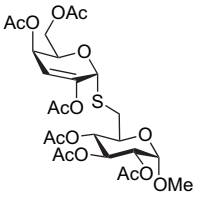
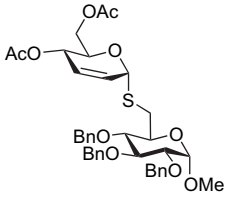
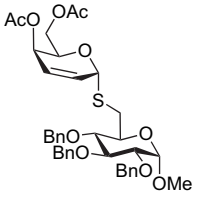
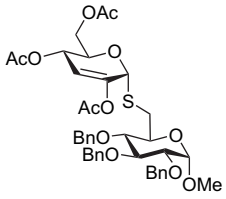
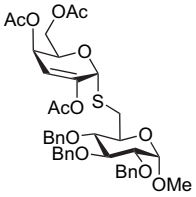
Thiol	Glycal	Reaction time	Lewis acid	Product	Yield (%), anomeric ratio (α/β)
5	**11**	8 h	$LiBF_4$	 **12**	89, 10:1
5	**14**	48 h	$LiBF_4$	 **17**	15, 10:1
5	**15**	48 h	$LiBF_4$	 **18**	15, 10:1
5	**16**	48 h	$LiBF_4$	 **19**	33, 3:2
10	**11**	4 h	$LiBF_4$	 **13**	75, 10:1
10	**14**	48 h	$LiBF_4$	 **20**	33, 10:1

Table 1 (*continued*)

Thiol	Glycal	Reaction time	Lewis acid	Product	Yield (%), anomeric ratio (α/β)
10	**15**	10 min	$BF_3{\cdot}OEt_2$	 **21**	52, α-only
10	**16**	4 h	$BF_3{\cdot}OEt_2$	 **22**	53, α-only

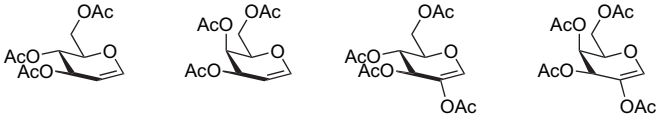


Figure 1. Glycal acceptors for the Ferrier reaction.

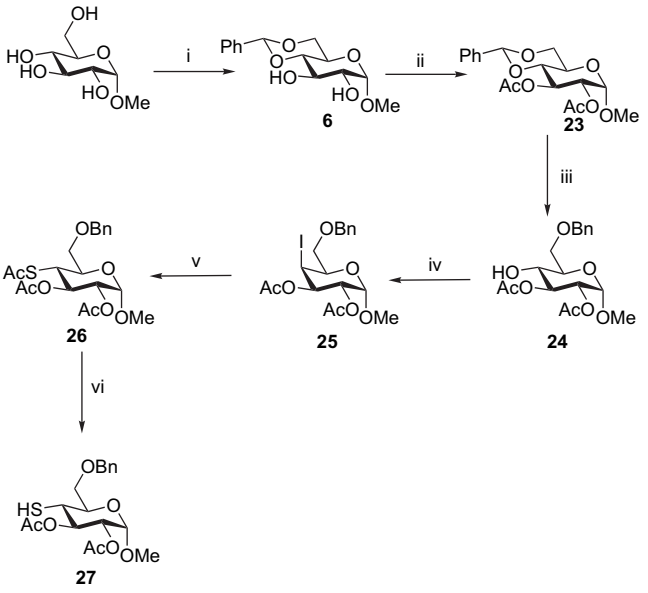
effect both the *O*-acetate and the *O*-benzyl protected thiols were subjected to further reactions with three additional glycal donors, **14**–**16** (Table 1).[26–28] Tri-*O*-acetyl-D-galactal (**14**) was commercially available, and the 2-OAc glucal (**15**) and galactal (**16**) derivatives were prepared from the respective 1-bromopyranosides after treatment with DBU (Fig. 1).[29]

Pleasingly, reaction of the *O*-acetate and *O*-benzyl protected thiols **5** and **10** with galactal (**14**) afforded the required 1,6-S-linked disaccharides **17** and **20**, however, longer reaction times were required compared to the previous studies with tri-*O*-acetyl-D-glucal. The tuning effect was still evident; hence, *O*-benzyl thiol (**10**) afforded a higher yield of **20** than that was achieved from the *O*-acetate-protected thiol (**5**) (for which 15% of disaccharide (**17**) was achieved) (Table 1). Reactions of glycals **15** and **16** using $LiBF_4$ as activator proved less successful with thiol **10** than with **5**. In an attempt to optimise the reactions, heating was applied, however, this offered no advantage. Alternative Lewis acids ($SnCl_4$, $Yb(OTf)_3$, $ZrCl_2$, $BF_3{\cdot}OEt_2$) were also utilised within the Ferrier reaction, and for the reactions of thiol (**10**) with glycals **15** and **16** this proved the key to success with $BF_3{\cdot}OEt_2$ allowing rapid entry to disaccharides **21** and **22**, respectively, with good conversion yields.

Next, a C-4 secondary thiol was also prepared from methyl α-D-glucopyranoside (Scheme 5)[24] to potentially allow access to 1,4-S-linked disaccharides via the Ferrier reaction. This extension of the methodology was expected to be particularly challenging given the reduced nucleophilicity of the secondary thiol compared to the primary thiols, owing to both steric and

electronic effects. However, 1,4-linked saccharides are of particular interest due to their common occurrence in nature and hence *S*-analogues of these targets are likely to be of significant biological interest.

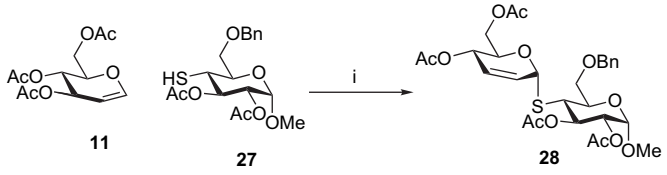
When the secondary thiol (**27**) was reacted with tri-*O*-acetyl-D-glucal and a Lewis acid, the results were surprising. Initial attempts at the reaction using $LiBF_4$ failed to yield any disaccharide product, with only starting materials being isolated from the reaction mixture. As $LiBF_4$ is reported to be a weak source of $BF_3\cdot OEt_2$,[30] it was hoped that a stronger source of $BF_3\cdot OEt_2$ may promote the desired reaction. Indeed, when $BF_3\cdot OEt_2$ was employed, a very fast reaction was observed at room temperature as evidenced by TLC analysis of the reaction mixture, but a complex mixture of products was formed. However, pleasingly, when the reaction was repeated at a lower temperature (−10 °C), the desired disaccharide (**28**) was formed in 72% yield as a single isomer (Scheme 6). Following this success, tri-*O*-acetyl-D-galactal was also subjected to the reaction with thiol (**27**). Gratifyingly, good yields of the



Scheme 5. Synthesis of (**27**). (i) α,α-Dimethoxytoluene, *p*-TsOH, DMF, 50 °C, 2 h, 73%. (ii) Ac_2O, Py, overnight, 92%. (iii) $NaCNBH_3$, HCl in Et_2O, THF, 4 Å MS, 20 min, 56%. (iv) I_2, PPh_3, imidazole, toluene, 80 °C, overnight, 62%. (v) KSAc, DMF, 90 °C, 2 h, 70%. (vi) $N_2H_4\cdot H_2O$, acetic acid, DMF, 30 min, 65%.

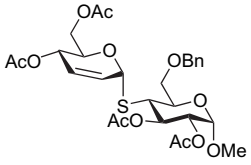
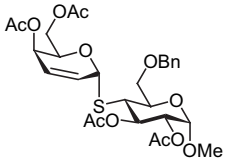
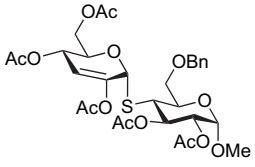
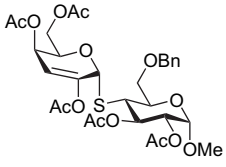
1,4-S-linked disaccharide (**29**) again resulted after only a short reaction time (Table 2). In addition, the 2-OAc glucal (**15**) and galactal (**16**) derivatives also gave good yields of their respective disaccharides **30** and **31**.

With access to a range of S-linked disaccharides achieved, functionalisation of the 2,3-glycal moiety within the



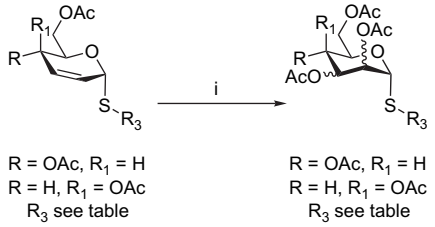
Scheme 6. $BF_3\cdot OEt_2$, CH_2Cl_2, −10 °C, 10 min, 72%.

Table 2
Ferrier reaction of the secondary thiol **27** with glycals under $BF_3\cdot OEt_2$ activation

Thiol	Glycal	Time	Temp	Product	Yield (%), anomeric ratio (α/β)
27	**11**	10 min	−10 °C	 **28**	72, α-only
27	**14**	20 min	−10 °C	 **29**	68, α-only
27	**15**	20 min	−10 °C	 **30**	58, α-only
27	**16**	2 h	rt	 **31**	65, α-only

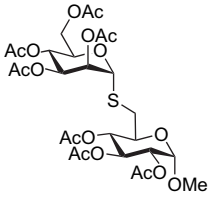
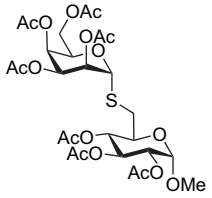
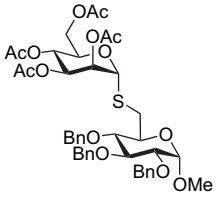
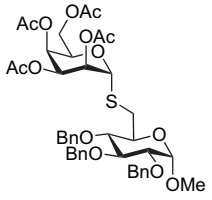
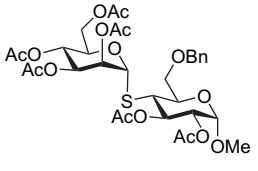
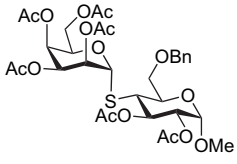
disaccharide, via dihydroxylation, was investigated. It was envisaged that this would allow access to fully hydroxylated sugar mimics, which would be of particular interest as glycosidase inhibitors and structural probes. As sulfur oxidation was not required, stoichiometric equivalents of OsO_4 were utilised to obviate the need for a co-oxidant.[31] Representative S-linked disaccharides were subjected to dihydroxylation by stirring with OsO_4 in pyridine for 24 h. The unpurified products of these reactions were treated with acetic anhydride and pyridine to effect O-acetylation and assist with isolation and purification of the hydroxylated derivatives. For the glucal systems (**12**, **13** and **28**), where both the anomeric substituent and the 4-OAc were located below the ring, all dihydroxylations occurred exclusively from the upper face of the molecule, resulting in formation of mannose derived S-linked glycoconjugates (**32**, **34** and **36**, respectively) (Scheme 7, Table 3).

For the galactal systems (**17**, **20** and **29**), where the anomeric substituent and the 4-OAc substituent were *trans*, dihydroxylation occurred from both faces with reaction from the top face predominantly affording talose derived glycoconjugates and reaction from the lower face affording gulose derived glycoconjugates. The ratio of the products was determined by ^1H NMR spectroscopic analysis and the assignment of talose or gulose was ascertained by NOESY spectroscopic analysis. Both



Scheme 7. Dihydroxylation reaction of the S-linked disaccharides. (i) OsO_4, Py, overnight, then Ac_2O, Py, overnight.

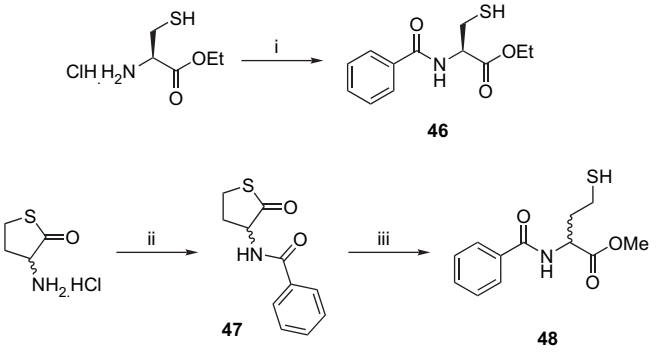
Table 3
Dihydroxylation reactions

Disaccharide	Yield (%)	Product	Tal/Gul
12	63	 **32**	n/a
17	56	 **33**	1:0.4
13	52	 **34**	n/a
20	57	 **35**	1:0.4
28	83	 **36**	n/a
29	76	 **37**	1:0.4

of these sugars are considered rare sugars and are therefore sought-after targets for biological studies.

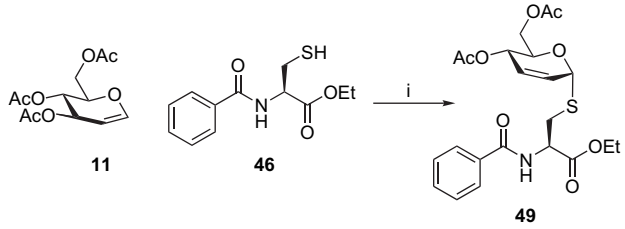
To complete the synthesis of the S-linked disaccharides, deprotection of the derivatives was required. This was achieved readily for representative acetate-protected compounds described herein, i.e., the 1,6- and 1,4-S-linked Ferrier products **12** and **17**, and **28** and **29**, as well as the dihydroxylated 1,6- and 1,4-S-linked products **32** and **33**, and **36** and **37** , to afford **38**–**45**, in near quantitative yield, via treatment with potassium carbonate in methanol for 2 h. The therapeutic utilities of these materials are now being assessed in a number of programmes within our laboratories.

As a final part of this research programme to potentially access S-linked glycoamino acids and glycopeptides, Bz–L-CysOEt (**46**) and Bz–DL-HcyOMe (**48**) were used as the nucleophilic components within the Ferrier methodology. Again, such targets have been reported in the literature to be of therapeutic potential and hence are of interest from both synthetic and biological perspectives.[8,32] The amino acids were protected before being subjected to the Ferrier reaction conditions. For both L-cysteine and DL-homocysteine, the amine functionality was first protected as a benzoyl amide, and for homocysteine the thiolactone ring was cleaved with NaOMe/MeOH affording the methyl ester of homocysteine (Scheme 8).[33]



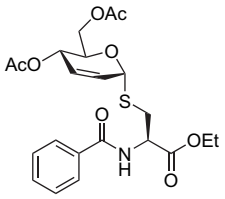
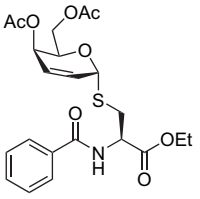
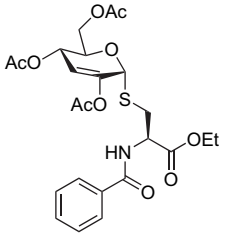
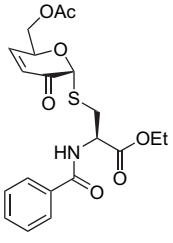
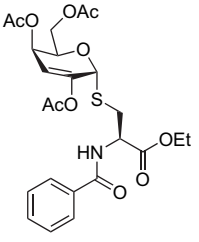
Scheme 8. Preparation of **46** and **48**. (i) Benzoic acid, oxalyl chloride, CH_2Cl_2, DMF, 30 min, then L-CysOEt·HCl, Py, CH_2Cl_2, DMF, overnight, 77%. (ii) Benzoyl chloride, CH_2Cl_2, NEt_3, overnight, 50%. (iii) NaOMe, MeOH, 30 min, quant.

As in other areas of this programme, both $LiBF_4$ and $BF_3\cdot OEt_2$ were used as the Lewis acids for the Ferrier reaction but the best results were generally observed with $BF_3\cdot OEt_2$ (Table 4). With $LiBF_4$, after 4 h at room temperature, the reaction between cysteine (**46**) and glucal (**11**) afforded the desired glycoamino acid (**49**) in 72% yield and as an anomeric ratio of 2:1, α/β (Scheme 9). When the Lewis acid was changed to



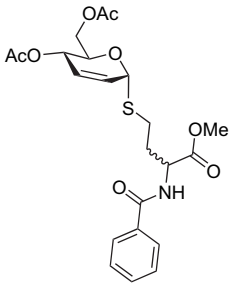
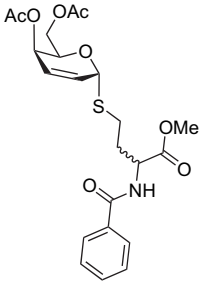
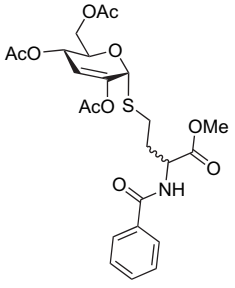
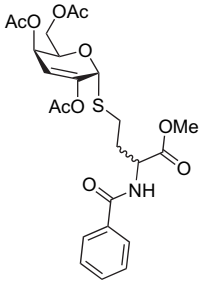
Scheme 9. (i) $LiBF_4$, MeCN, 4 h, 72%, α/β 2:1 or $BF_3\cdot OEt_2$, CH_2Cl_2, 10 min, 87%.

Table 4
Ferrier reactions with amino acids **46** and **48**

Amino acid	Glycal	Lewis acid	Reaction time	Temp	Product	Yield (%), anomeric ratio (α/β)
46	**11**	$LiBF_4$	4 h	rt	 **49**	72, 2:1
		$BF_3{\cdot}OEt_2$	10 min	rt		87, α-only
46	**14**	$LiBF_4$	16 h	rt	 **51**	60, 2:1
		$BF_3{\cdot}OEt_2$	1.5 h	rt		77, α-only
46	**15**	$LiBF_4$	16 h	50 °C	 **52**	22, 4:1
		$BF_3{\cdot}OEt_2$	10 min	rt		68, α-only
46	**16**	$LiBF_4$	16 h	60 °C	 **53**	25, 3:1
		$BF_3{\cdot}OEt_2$	2.5 h	rt	 **54**	63, α-only

(*continued on next page*)

Table 4 (*continued*)

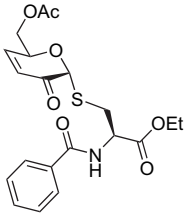
Amino acid	Glycal	Lewis acid	Reaction time	Temp	Product	Yield (%), anomeric ratio (α/β)
48	**11**	$LiBF_4$ $BF_3{\cdot}OEt_2$	16 h 10 min	rt rt	 **50**	89, 2:1 64, α-only
48	**14**	$LiBF_4$ $BF_3{\cdot}OEt_2$	48 h 1.5 h	rt rt	 **55**	65, 2:1 42, α-only
48	**15**	$LiBF_4$ $BF_3{\cdot}OEt_2$	— 2 h	50 °C rt	—  **56**	No reaction 60, α-only
48	**16**	$LiBF_4$ $BF_3{\cdot}OEt_2$	— 2 h	50 °C rt	—  **57**	No reaction 58, α-only

$BF_3{\cdot}OEt_2$ the reaction proceeded more quickly and resulted in 87% yield of the glucoamino acid (**49**) after only 10 min at room temperature.

For the homocysteine analogue (**48**), reaction with glucal (**11**) under $LiBF_4$ promotion gave the desired glycoamino acid (**50**) in 89% yield, in an anomeric ratio of 2:1, α/β (Scheme 10). Unfortunately, even after extensive purification via column chromatography, separation of the anomers was not possible. However, when using $BF_3{\cdot}OEt_2$, the reaction proceeded in 10 min at room temperature with a yield of 64% with only the α-anomer being formed.

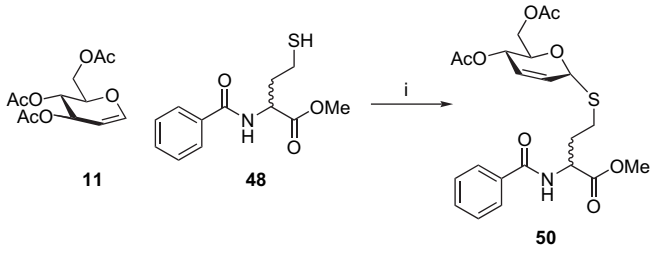
As observed previously during formation of the S-linked disaccharides using $LiBF_4$, when glycals other than **11** were utilised longer reaction times and lower yields generally resulted.

Again, the effect of heating on the reaction profile was investigated and higher temperatures served to enhance the reactions with 2-OAc glucal (**15**) and 2-OAc galactal (**16**), hence after heating overnight at 50 or 60 °C, respectively, the desired glycoamino acids **52** and **53** were obtained in 22 and 25% yields, respectively. For the 2-OAc galactal–cysteine system, elimination occurred during the reaction, resulting in the formation of an enone system **53**.[34]



53

However, when the Lewis acid was exchanged for $BF_3 \cdot OEt_2$, vastly decreased reaction times and improved yields were again observed for these systems. Moreover, the reactions now proceeded with excellent stereoselectivity and only the α-anomers were isolated from the reactions (Table 4). Most accentuated were the reactions with the 2-OAc glycals **15** and **16**, which showed increased yields for the reactions with cysteine analogues, to afford **52** and **54**. Here, yields increased from 22 and 25% to 68 and 63%, on moving from activation by $LiBF_4$ to $BF_3 \cdot OEt_2$. Further improvement was seen in the reactions between the 2-OAc glycals **15** and **16** and the homocysteine coupling partner **48**. Using $LiBF_4$, no reaction was observed as the long reaction times lead only to homocysteine thiolactone reforming in the reaction mixture. When the Lewis acid was exchanged for $BF_3 \cdot OEt_2$, the desired glycoamino acids **56** and **57** were formed after 2 h at room temperature in 60 and 58% yields, respectively.



11 **48** **50**

Scheme 10. (i) $LiBF_4$, MeCN, overnight, 89%, α/β 2:1 or $BF_3 \cdot OEt_2$, CH_2Cl_2, 10 min, 64%.

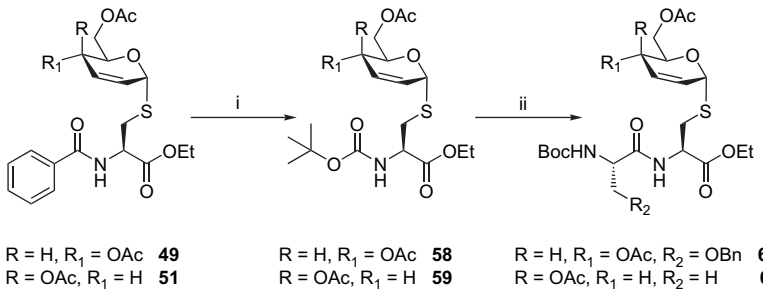
Although the full synthetic and biological potential of these compounds is still being assessed within our laboratories, initial results have shown that S-linked glycoamino acids **49** and **51** are also suitable substrates for peptide coupling reactions. Thus after removal of the *N*-Boc protecting groups from **58** and **59** and coupling with Boc(OBn)–L-SerOH or Boc–L-AlaOH in the presence of PyBOP, dipeptides **60** and **61** were accessed in 86 and 84% yield, respectively. Hence access to S-linked glycopeptides has also proved possible within this study (Scheme 11).

In addition to incorporating the disaccharides within the dihydroxylation strategy, the glycoamino acid derivatives were also oxidised to the fully hydroxylated sugars. As with the disaccharide systems, when the glucal conjugates **49** and **50** were subjected to the reaction conditions, only the mannose derivatives **62** and **64** were formed. For the galactal conjugates **51** and **55**, mixtures of talose and gulose derivatives resulted, with the talose products being favoured (Table 5).

Finally, removal of the acetate, Boc, benzoyl and ester protecting groups within the representative glycoamino acid derivatives **50** and **55**, and **58** and **59** was attempted using standard protocols. Although generally successful, racemisation of the cysteine derivatives was observed, and in some cases only partial deprotection of the ester functionality occurred. Nevertheless, entry to targets **66**, **67**, **70** and **71** was achieved, thus providing access to materials of biological interest.

3. Conclusion

The value of the Ferrier reaction for affording S-linked saccharide targets has been demonstrated, with entry to 1,6- and 1,4-S-linked disaccharides and S-linked glycoamino acids proving effective in synthetically useful yields. In many cases the reactions have proceeded with complete stereoselectivity. Further functionalisation of the Ferrier products has proved possible, for example, via peptide coupling of the glycoamino acids and dihydroxylation of the S-linked disaccharides. Again these reactions have proceeded in excellent yields to afford biologically and therapeutically interesting targets. Deprotection of the targets has also been realised to afford materials whose biological and therapeutic properties are now being assessed.



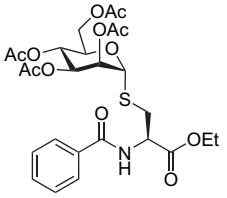
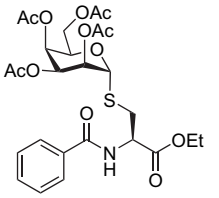
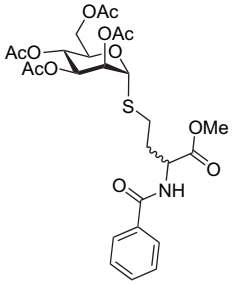
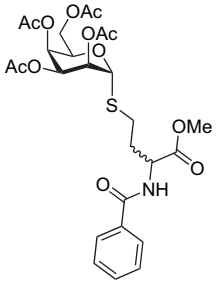
R = H, R_1 = OAc **49** R = OAc, R_1 = H **51**

R = H, R_1 = OAc **58** R = OAc, R_1 = H **59**

R = H, R_1 = OAc, R_2 = OBn **60** R = OAc, R_1 = H, R_2 = H **61**

Scheme 11. Peptide coupling of **49** and **51**. (i) Boc_2O, DMAP, THF, overnight, 92%, then $N_2H_4 \cdot H_2O$, EtOH, 0 °C, 2 h, quant. (ii) For R=H, R_1=OAc: 4 N HCl in dioxane, then, *N*-Boc–L-Ser–(OBn)–OH, PyBOP, NEt_3, CH_2Cl_2, 30 min, 86%. For R=OAc, R_1=H: 4 N HCl in dioxane, then, *N*-Boc–L-Ala–OH, PyBOP, NEt_3, CH_2Cl_2, 40 min (84%).

Table 5
Dihydroxylation reactions with the glycoamino acids

Glycoamino acid	Yield (%)	Product	Tal/Gul
49	57	 **62**	n/a
51	62	 **63**	1:0.4
50	56	 **64**	n/a
55	55	 **65**	1:0.4

4. Experimental section

4.1. The Ferrier reactions

Method A. To a stirred solution of thiol (1 equiv) and glycal (1.2 equiv) in dry acetonitrile (2 ml/mmol) under an atmosphere of argon was added lithium tetrafluoroborate solution in acetonitrile (1.2 equiv). The reaction mixture was stirred at room temperature (unless otherwise stated) until the reaction was shown to have reached completion by TLC analysis. The reaction mixture was quenched by the addition of water and then extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was subjected to purification by column chromatography.

Method B. To a stirred solution of thiol (1 equiv) and glycal (1.2 equiv) in dry CH_2Cl_2 (5 ml/mmol) under an atmosphere of argon (cooled to the specified temperature) was added $BF_3{\cdot}OEt_2$ (0.1 equiv). The reaction mixture was stirred until the reaction was shown to have reached completion by TLC analysis. The reaction was then quenched by the addition of satd aq $NaHCO_3$ and extracted with CH_2Cl_2. The combined extracts were then dried ($MgSO_4$), filtered and concentrated in vacuo. The crude residue was then subjected to purification by column chromatography.

4.1.1. Methyl 2,3,4-tri-O-acetyl-6-S-(2,3-dideoxy-4,6-di-O-acetyl-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (12)

By following *method A*, tri-*O*-acetyl-D-glucal (**11**) (74 mg, 0.27 mmol) and methyl 2,3,4-tri-*O*-acetyl-6-thio-α-D-glucopyranoside (**5**) (109 mg, 0.3 mmol) were stirred at room temperature for 8 h to afford, after purification by column chromatography (1:1 hexane/ethyl acetate), **12** as a colourless oil (133 mg, 89%, α/β 10:1). R_f 0.3 (1:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +244 (*c* 0.35, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.01 (3H, s, OC(O)CH_3), 2.04 (3H, s, OC(O)CH_3), 2.08 (3H, s, OC(O)CH_3), 2.09 (3H, s, OC(O)CH_3), 2.10 (3H, s, OC(O)CH_3), 2.69 (1H, dd, *J* 6.5, 14.0 Hz, *H*-6), 2.99 (1H, dd, *J* 3.0, 14.0 Hz, *H*-6), 3.42 (3H, s, OCH_3), 4.01 (1H, ddd, *J* 3.0, 6.5, 9.5 Hz, *H*-5), 4.14–4.18 (1H, m, *H*-6′), 4.25–4.31 (2H, m, *H*-5′, *H*-6′), 4.87 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.92 (1H, d, *J* 3.5 Hz, *H*-1), 5.06 (1H, app. t, *J* 10.0 Hz, *H*-4), 5.37 (1H, ddd, *J* 2.0, 4.0, 9.0 Hz, *H*-4′), 5.46 (1H, app. dt, 9.5, 10.0 Hz, *H*-3), 5.61–5.64 (1H, m, *H*-1′), 5.81 (1H, app. dt, *J* 2.0, 10.0 Hz, *H*-3′), 5.93 (1H, ddd, *J* 2.0, 3.0, 10.0 Hz, *H*-2′). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.7 (OAc), 20.8 (OAc), 20.8 (OAc), 21.0 (OAc), 32.1 (C-6), 55.5 (OMe), 62.8 (C-6′), 65.1 (C-4′), 66.9 (C-5′), 68.5 (C-5), 70.0 (C-3), 70.9 (C-2), 71.2 (C-4), 80.1 (C-1′), 96.6 (C-1), 127.4 (C-3′), 128.6 (C-2′), 169.8 (C=O), 170.1 (C=O), 170.2 (C=O), 170.3 (C=O), 170.8 (C=O). IR ν_{max} (thin film)/cm^{-1} 2843 (OMe), 1746 (C=O), 1371 (OMe), 732 (C=C), 605 (CS). LRMS *m/z* 549 (1%, M+H$^+$), 430 (14%), 428 (58%), 415 (100%). HRMS (CI, M+H$^+$), found: 549.1658; $C_{23}H_{33}O_{13}S$ requires: 549.1642.

4.1.2. Methyl 2,3,4-tri-O-benzyl-6-S-(2,3-dideoxy-4,6-di-O-acetyl-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (13)

By following *method A*, tri-*O*-acetyl-D-glucal (**11**) (98 mg, 0.36 mmol) and methyl 2,3,4-tri-*O*-benzyl-6-thio-α-D-glucopyranoside (**10**) (208 mg, 0.43 mmol) were stirred at room temperature for 4 h to afford, after purification by column chromatography (3:1 hexane/ethyl acetate), **13** as a colourless oil (186 mg, 75%, α/β 10:1). R_f 0.2 (3:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +104.3 (*c* 0.65, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.05 (3H, s, OC(O)CH_3), 2.09 (3H, s, OC(O)CH_3), 2.83 (1H, dd, *J* 6.5, 14.0 Hz, *H*-6), 3.14 (1H, dd, *J* 2.5, 14.0 Hz, *H*-6), 3.40 (3H, s, OCH_3), 3.50 (1H, app. t, *J* 9.5 Hz, *H*-4), 3.53 (1H, dd,

J 3.5, 9.5 Hz, *H*-2), 3.88 (1H, ddd, *J* 2.5, 6.5, 9.5 Hz, *H*-5), 4.00 (1H, app. t, *J* 9.0 Hz, *H*-3), 4.12 (1H, dd, *J* 4.5, 14.0 Hz, *H*-6′), 4.26–4.30 (2H, m, *H*-5′, *H*-6′), 5.39 (1H, ddd, *J* 1.5, 3.5, 8.5 Hz, *H*-4′), 4.58 (1H, d, *J* 3.5 Hz, *H*-1), 4.63 (1H, d, *J* 11.0 Hz, OC*H*$_2$Ph), 4.67 (1H, d, *J* 12.0 Hz, OC*H*$_2$Ph), 4.81 (1H, d, *J* 12.0 Hz, OC*H*$_2$Ph), 4.81 (1H, d, *J* 11.0 Hz, OC*H*$_2$Ph), 4.92 (1H, d, *J* 12.0 Hz, OC*H*$_2$Ph), 5.00 (1H, d, *J* 11.0 Hz, OC*H*$_2$Ph), 5.66 (1H, dd, *J* 2.0, 3.0 Hz, *H*-1′), 5.79 (1H, dt, *J* 1.5, 10.0 Hz, *H*-3′), 5.92 (1H, ddd, *J* 2.0, 3.0, 10.0 Hz, *H*-2′), 7.20–7.40 (15H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.8 (OAc), 21.0 (OAc), 32.9 (C-6), 55.3 (OMe), 62.9 (C-6′), 65.0 (C-4′), 66.8 (C-5′), 69.9 (C-5), 73.4 (OCH$_2$Ph), 75.2 (OCH$_2$Ph), 75.8 (OCH$_2$Ph), 80.1 (C-2 and C-4), 80.5 (C-1′), 81.9 (C-3), 98.0 (C-1), 127.0 (C-3′), 127.7 (ArCH), 127.9 (ArCH), 128.1 (ArCH), 128.3 (ArCH), 128.5 (ArCH), 128.9 (C-2′), 138.1 (ArC), 138.6 (ArC), 170.3 (C=O), 170.8 (C=O). IR ν_{max} (thin film)/cm^{-1} 1741 (C=O), 1370 (OMe), 755 (CH$_{arom}$), 668 (C–S). LRMS *m*/*z* 692 (4%, M+H$^+$), 572 (12%), 559 (100%), 479 (95%), 447 (30%), 341 (62%). HRMS (CI, M+H$^+$), found: 692.2644; $C_{38}H_{44}O_{10}S$ requires: 692.2655.

4.1.3. Methyl 2,3,4-tri-O-acetyl-6-S-(2,3-dideoxy-4,6-di-O-acetyl-α-D-galactopyranosyl)-6-thio-α-D-glucopyranoside (17)

By following *method A*, tri-*O*-acetyl-D-galactal (**14**) (121 mg, 0.27 mmol) and methyl 2,3,4-tri-*O*-acetyl-6-thio-α-D-glucopyranoside (**5**) (180 mg, 0.53 mmol) were stirred at room temperature for 48 h to afford, after purification by column chromatography (1:1 hexane/ethyl acetate), **17** as a colourless oil (36 mg, 15%, α/β 10:1). R_f 0.3 (1:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +59.0 (*c* 0.85, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.00 (3H, s, OC(O)C*H*$_3$), 2.04 (3H, s, OC(O)C*H*$_3$), 2.07 (3H, s, OC(O)C*H*$_3$), 2.08 (3H, s, OC(O)C*H*$_3$), 2.08 (3H, s, OC(O)C*H*$_3$), 2.63 (1H, dd, *J* 6.5, 14.5 Hz, *H*-6), 2.99 (1H, dd, *J* 3.0, 14.5 Hz, *H*-6), 3.43 (3H, s, OC*H*$_3$), 4.00 (1H, ddd, *J* 3.0, 6.5, 9.5 Hz, *H*-5), 4.19 (1H, dd, *J* 7.5, 11.5 Hz, *H*-6′), 4.24 (1H, dd, *J* 5.5, 11.5 Hz, *H*-6′), 4.51 (1H, ddd, *J* 2.5, 5.5, 7.5 Hz, *H*-5′), 4.87 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.91 (1H, d, *J* 3.5 Hz, *H*-1), 5.05 (1H, app. t, *J* 9.5 Hz, *H*-4), 5.08 (1H, dd, *J* 2.5, 5.0 Hz, *H*-4′), 5.46 (1H, dd, *J* 9.5, 10.0 Hz, *H*-3), 5.71 (1H, dd, *J* 1.5, 3.0 Hz, *H*-1′), 6.05 (1H, ddd, *J* 1.5, 5.0, 10.0 Hz, *H*-3′), 6.10 (1H, dd, *J* 3.0, 10.0 Hz, *H*-2′). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.7 (OAc), 20.8 (OAc), 20.9 (OAc), 31.3 (C-6), 55.5 (OMe), 62.6 (C-6′), 63.4 (C-4′), 66.8 (C-5′), 68.6 (C-5), 70.0 (C-3), 70.9 (C-2), 71.2 (C-4), 79.6 (C-1′), 96.6 (C-1), 124.2 (C-3′), 131.5 (C-2′), 169.8 (C=O), 170.1 (C=O), 170.2 (C=O), 170.3 (C=O), 170.7 (C=O). IR ν_{max} (thin film)/cm^{-1} 1746 (C=O), 1371 (OMe), 605 (C–S). LRMS *m*/*z* 571 (90%, M+Na$^+$), 393 (50%), 335 (100%, $C_{13}H_{19}O_8S$), 295 (40%), 251 (35%), 201 (37%). HRMS (ESI M+Na$^+$), found: 571.1461; $C_{23}H_{32}O_{13}SNa$ requires: 571.1461.

4.1.4. Methyl 2,3,4-tri-O-acetyl-6-S-(3-deoxy-2,4,6-tri-O-acetyl-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (18)

By following *method A*, 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**15**) (159 mg, 0.48 mmol) and methyl 2,3,4-tri-*O*-acetyl-6-thio-α-D-glucopyranoside (**5**) (195 mg, 0.58 mmol) were stirred at room temperature for 48 h to afford, after purification by column chromatography (3:2 hexane/ethyl acetate), **18** as a colourless oil (42 mg, 15%, α/β 10:1). R_f 0.5 (3:2 hexane/ethyl acetate); $[\alpha]_D^{20}$ +275 (*c* 0.35, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.00 (3H, s, OC(O)C*H*$_3$), 2.04 (3H, s, OC(O)C*H*$_3$), 2.07 (3H, s, OC(O)C*H*$_3$), 2.08 (3H, s, OC(O)C*H*$_3$), 2.10 (3H, s, OC(O)C*H*$_3$), 2.19 (3H, s, OC(O)C*H*$_3$), 2.68 (1H, dd, *J* 6.5, 14.5 Hz, *H*-6), 2.98 (1H, dd, *J* 3.0, 14.5 Hz, *H*-6), 3.42 (3H, s, OC*H*$_3$), 4.00 (1H, ddd, *J* 3.0, 6.5, 9.5 Hz, *H*-5), 4.20 (1H, dd, *J* 2.5, 12.0 Hz, *H*-6′), 4.26 (1H, dd, *J* 5.0, 12.0 Hz, *H*-6′), 4.31 (1H, ddd, *J* 2.5, 5.0, 7.5 Hz, *H*-5′), 4.84 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.90 (1H, d, *J* 3.5 Hz, *H*-1), 5.07 (1H, app. t, *J* 10.0 Hz, *H*-4), 5.43–5.50 (2H, m, *H*-3, *H*-4′), 5.66 (1H, dd, *J* 1.0, 2.5 Hz, *H*-3′), 5.72 (1H, s, *H*-1′). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.7 (OAc), 20.7 (OAc), 20.8 (OAc), 20.9 (OAc), 21.0 (OAc), 31.8 (C-6), 55.4 (OMe), 62.4 (C-6′), 64.8 (C-4′), 67.3 (C-5′), 68.5 (C-5), 69.9 (C-3), 70.8 (C-2), 71.0 (C-4), 80.0 (C-1′), 96.6 (C-1), 114.8 (C-2′), 147.1(C-3′), 168.1 (C=O), 169.8 (C=O), 170.1 (C=O), 170.2 (C=O), 170.7 (C=O). IR ν_{max} (thin film)/cm^{-1} 1745 (C=O). LRMS *m*/*z* 629 (80%, M+Na$^+$), 603 (11%), 301 (12%), 251 (100%), 223 (33%). HRMS (ESI M+Na$^+$), found: 629.1509; $C_{25}H_{34}O_{15}SNa$ requires: 629.1516.

4.1.5. Methyl 2,3,4-tri-O-acetyl-6-S-(3-deoxy-2,4,6-tri-O-acetyl-α-D-galactopyranosyl)-6-thio-α-D-glucopyranoside (19)

By following *method A*, 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-lyxo-hex-1-enitol (**16**) (107 mg, 0.32 mmol) and methyl 2,3,4-tri-*O*-acetyl-6-thio-α-D-glucopyranoside (**5**) (131 mg, 0.38 mmol) were stirred at room temperature for 48 h to afford, after purification by column chromatography (3:2 hexane/ethyl acetate), **19** as a colourless oil (64 mg, 33%, α/β 3:2). R_f 0.5 (3:2 hexane/ethyl acetate); $[\alpha]_D^{20}$ +121 (*c* 0.40, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.00 (3H, s, OC(O)C*H*$_3$), 2.03 (3H, s, OC(O)C*H*$_3$), 2.07 (3H, s, OC(O)C*H*$_3$), 2.08 (3H, s, OC(O)C*H*$_3$), 2.10 (3H, s, OC(O)C*H*$_3$), 2.18 (3H, s, OAc), 2.73 (1H, dd, *J* 3.0, 13.5 Hz, *H*-6), 2.83 (1H, dd, *J* 8.5, 13.5 Hz, *H*-6), 3.43 (3H, s, OC*H*$_3$), 3.95 (1H, ddd, *J* 3.0, 8.5, 12.5 Hz, *H*-5), 4.09 (1H, ddd, *J* 2.0, 6.0, 12.5 Hz, *H*-5′), 4.18–4.23 (2H, m, *H*-6′), 4.86 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.88–4.95 (2H, m, *H*-1, *H*-4), 5.22 (1H, dt, *J* 2.0, 6.0 Hz, *H*-4′), 5.44 (1H, dd, *J* 9.5, 10.0 Hz, *H*-3), 5.54 (1H, app. t, *J* 1.5 Hz, *H*-1′), 5.92 (1H, dd, *J* 1.5, 6.0 Hz, *H*-3′). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.7 (OAc), 20.7 (OAc), 20.8 (OAc), 30.2 (C-6), 55.5 (OMe), 62.5 (C-6′), 64.9 (C-4′), 69.1 (C-5), 70.0 (C-3), 70.9 (C-2), 71.9 (C-4), 74.0 (C-5′), 79.4 (C-1′), 95.6 (C-1), 114.1 (C-3′), 150.1 (C-2′), 168.1 (C=O), 169.7 (C=O), 170.1 (C=O), 170.2 (C=O), 170.5 (C=O), 170.7 (C=O). IR ν_{max} (thin film)/cm^{-1} 1744 (C=O). LRMS *m*/*z* 607 (1%, M+H$^+$), 487 (26%), 444 (20%), 180 (37%), 169 (100%), 130 (49%). HRMS (CI, M+H$^+$), found: 607.1691; $C_{25}H_{35}O_{15}S$ requires: 607.1697.

4.1.6. Methyl 2,3,4-tri-O-benzyl-6-S-(2,3-dideoxy-4,6-di-O-acetyl-α-D-galactopyranosyl)-6-thio-α-D-glucopyranoside (20)

By following *method A*, tri-*O*-acetyl-D-galactal (**14**) (106 mg, 0.39 mmol) and methyl 2,3,4-tri-*O*-benzyl-6-thio-α-

D-glucopyranoside (**10**) (225 mg, 0.46 mmol) were stirred at room temperature for 3 days. Column chromatography (3:1 to 2:1 hexane/ethyl acetate) failed to separate the title compound from unreacted tri-*O*-acetyl-D-galactal. For characterisation and purification purposes, the mixture was deprotected with K_2CO_3 (4 mg) in methanol (3 mL) and purified by column chromatography (1:2 hexane/ethyl acetate). The deprotected product was then reacetylated using pyridine and acetic anhydride, and after purification by column chromatography (2:1 hexane/ethyl acetate), **20** was yielded as a colourless oil (88 mg, 33% α/β 10:1). R_f 0.3 (2:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +7.6 (*c* 1.15, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 1.98 (3H, s, OC(O)CH_3), 2.08 (3H, s, OC(O)CH_3), 2.77 (1H, dd, *J* 6.5, 14.0 Hz, *H*-6), 3.12 (1H, dd, *J* 2.5, 14.0 Hz, *H*-6), 3.38 (3H, s, OCH_3), 3.47–3.56 (2H, m, *H*-2, *H*-4), 3.87 (1H, ddd, *J* 2.5, 6.5, 9.5 Hz, *H*-5), 3.98 (1H, app. t, *J* 9.5 Hz, *H*-3), 4.15 (1H, dd, *J* 7.5, 11.5 Hz, *H*-6′), 4.25 (1H, dd, *J* 6.0, 11.5 Hz, *H*-6′), 4.51 (1H, ddd, *J* 2.5, 6.0, 7.5 Hz, *H*-5′), 4.56 (1H, d, *J* 3.5 Hz, *H*-1), 4.62 (1H, d, *J* 11.0 Hz, OCH_2Ph), 4.66 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.79 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.80 (1H, d, *J* 11.0 Hz, OCH_2Ph), 4.91 (1H, d, *J* 11.0 Hz, OCH_2Ph), 4.98 (1H, d, *J* 11.0 Hz, OCH_2Ph), 5.07 (1H, dd, *J* 2.5, 5.0 Hz, *H*-4′), 5.73–5.77 (1H, m, *H*-1′), 6.02 (1H, ddd, *J* 1.5, 5.0, 10.0 Hz, *H*-3′), 6.07 (1H, dd, *J* 3.0, 10.0 Hz, *H*-2′), 7.25–7.38 (15H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.7 (OAc), 20.9 (OAc), 32.1 (C-6), 55.3 (OMe), 62.5 (C-6′), 63.3 (C-4′), 66.7 (C-5′), 70.0 (C-5), 73.4 (OCH_2Ph), 75.4 (OCH_2Ph), 75.8 (OCH_2Ph), 80.0 (C-1′), 80.0 (C-2 or C-4), 80.1 (C-2 or C-4), 81.9 (C-3), 97.9 (C-1), 123.9 (C-3′), 127.7 (ArCH), 127.9 (ArCH), 128.2 (ArCH), 128.5 (ArCH), 131.9 (C-2′), 138.1 (ArC), 138.6 (ArC), 170.3 (C=O), 170.6 (C=O). IR ν_{max} (thin film)/cm^{-1} 1744 (C=O), 1230, 1072 and 1049 (CH_{arom}). LRMS *m*/*z* 693 (3%, M+H$^+$), 662 (36%), 661 (100%), 601 (24%). HRMS (CI, M+H$^+$), found: 693.2744; $C_{38}H_{45}O_{10}S$ requires: 693.2577.

4.1.7. Methyl 2,3,4-tri-O-benzyl-6-S-(3-deoxy-2,4,6-di-O-acetyl-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (*21*)

By following *method B*, 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**15**) (41 mg, 0.12 mmol) and methyl 2,3,4-tri-*O*-acetyl-6-thio-α-D-glucopyranoside (**10**) (50 mg, 0.1 mmol) were stirred at −10 °C for 10 min to afford, after purification by column chromatography (3:1 hexane/ethyl acetate), **21** as a colourless oil (48 mg, 52%, α-only). R_f 0.3 (3:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +243 (*c* 0.14, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.04 (3H, s, OC(O)CH_3), 2.05 (3H, s, OC(O)CH_3), 2.06 (3H, s, OC(O)CH_3), 2.77 (1H, dd, *J* 6.5, 14.0 Hz, *H*-6), 3.11 (1H, dd, *J* 2.5, 14.0 Hz, *H*-6), 3.38 (3H, s, OCH_3), 3.43–3.54 (2H, m, *H*-2, *H*-4), 3.85 (1H, ddd, *J* 2.5, 6.5, 12.0 Hz, *H*-5′), 4.00 (1H, app. t, *J* 9.0 Hz, *H*-3), 4.15 (1H, dd, *J* 2.5, 12.0 Hz, *H*-6′), 4.21–4.35 (2H, m, *H*-5, *H*-6′), 4.57 (1H, d, *J* 3.5 Hz, *H*-1), 4.62 (1H, d, *J* 10.0 Hz, OCH_2Ph), 4.67 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.78 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.80 (1H, d, *J* 10.0 Hz, OCH_2Ph), 4.90 (1H, d, *J* 11.0 Hz, OCH_2Ph), 4.99 (1H, d, *J* 11.0 Hz, OCH_2Ph), 5.47 (1H, app. dt, *J* 2.0, 9.0 Hz, *H*-4′), 5.63 (1H, d, *J* 2.0 Hz, *H*-3′), 5.72 (1H, br s, *H*-1′), 7.25–7.36 (15H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.8 (OAc), 20.9 (OAc), 32.3 (C-6), 55.3 (OMe), 62.5 (C-6′), 64.8 (C-4′), 67.1 (C-5), 69.9 (C-5′), 73.2 (OCH_2Ph), 75.2 (OCH_2Ph), 75.7 (OCH_2Ph), 79.8 and 79.9 (C-2 and C-4), 80.6 (C-1′), 81.8 (C-3), 97.8 (C-1), 114.6 (C-3′), 127.7 (ArCH), 128.1 (ArCH), 128.3 (ArCH), 128.5 (ArCH), 138.0 (ArC), 138.2 (ArC), 138.3 (ArC), 138.6 (ArC), 147.3 (C-2′), 167.9 (C=O), 170.2 (C=O), 170.8 (C=O). IR ν_{max} (thin film)/cm^{-1} 1745 (C=O), 1230 (OMe), 1072 and 1049 (CH_{arom}). LRMS *m*/*z* 773 (48%, M+Na$^+$), 768 (100%, MNH$_4^+$), 732 (21%), 617 (6%), 331 (9%). HRMS (ESI, M+NH$_4^+$), found: 768.3023; $C_{40}H_{50}O_{12}NS$ requires: 768.3054.

4.1.8. Methyl 2,3,4-tri-O-benzyl-6-S-(3-deoxy-2,4,6-di-O-acetyl-α-D-galactopyranosyl)-6-thio-α-D-glucopyranoside (*22*)

By following *method B*, 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-lyxo-hex-1-enitol (**16**) (49 mg, 0.15 mmol) and methyl 2,3,4-tri-*O*-acetyl-6-thio-α-D-glucopyranoside (**10**) (60 mg, 0.12 mmol) were stirred at room temperature for 5 h to afford, after purification by column chromatography (3:1 hexane/ethyl acetate), **22** as a colourless oil (49 mg, 53%, α-only). R_f 0.5 (3:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +72 (*c* 0.33, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) 2.05 (3H, s, OC(O)CH_3), 2.06 (3H, s, OC(O)CH_3), 2.10 (3H, s, OC(O)CH_3), 2.75 (1H, dd, *J* 6.5, 14.0 Hz, *H*-6), 3.11 (1H, dd, *J* 2.0, 14.0 Hz, *H*-6), 3.39 (3H, s, OMe), 3.46–3.52 (2H, m, *H*-2, *H*-4), 3.84–3.89 (1H, m, *H*-5′), 3.99 (1H, app. t, *J* 9.5 Hz, *H*-3), 4.19 (1H, dd, *J* 4.5, 12.0 Hz, *H*-6′), 4.22–4.27 (1H, m, *H*-5), 4.37 (1H, dd, *J* 5.0, 12.0 Hz, *H*-6′), 4.57 (1H, d, *J* 3.5 Hz, *H*-1), 4.60 (1H, d, *J* 11.0 Hz, OCH_2Ph), 4.66 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.79 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.80 (1H, d, *J* 11.0 Hz, OCH_2Ph), 4.91 (1H, d, *J* 10.5 Hz, OCH_2Ph), 4.99 (1H, d, *J* 10.5 Hz, OCH_2Ph), 5.52–5.58 (1H, m, *H*-4′), 5.80–5.84 (2H, m, *H*-1′, *H*-3′), 7.25–7.52 (15H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 125 MHz) 20.7 (OAc), 20.8 (OAc), 32.2 (C-6), 55.3 (OMe), 62.1 (C-4), 64.4 (C-6′), 66.6 (C-5′), 69.9 (C-5), 73.4 (OCH_2Ph), 75.1 (OCH_2Ph), 75.7 (OCH_2Ph), 80.1 and 80.2 (C-2 and C-4), 81.9 (C-3), 84.3 (C-1′), 97.9 (C-1), 114.9 (C-3′), 127.1–129.7 (ArCH), 134.4–138.1 (ArC), 146.4 (C-2′), 170.5 (C=O), 170.9 (C=O), 171.8 (C=O). IR ν_{max} (thin film)/cm^{-1} 1746 (C=O), 1072 and 1049 (CH_{arom}). LRMS *m*/*z* 773 (62%, M+Na$^+$), 768 (100%, M+NH$_4^+$), 735 (29%), 666 (98%), 617 (63%). HRMS (ESI, M+NH$_4^+$), found: 768.3019; $C_{40}H_{50}O_{12}NS$ requires: 768.3054.

4.1.9. Methyl 6-O-benzyl-2,3-di-O-acetyl-4-S-(2,3-dideoxy-4,6-di-O-acetyl-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (*28*)

By following *method B*, methyl 2,3-di-*O*-acetyl-6-*O*-benzyl-4-thio-α-D-glucopyranoside (**27**) (165 mg, 0.4 mmol) and tri-*O*-acetyl-D-glucal (**11**) (140 mg, 0.5 mmol) were stirred at −10 °C for 10 min to afford, after purification by column chromatography (2:1 hexane/ethyl acetate), **28** as a colourless oil (184 mg, 72% α-only). R_f 0.3 (2:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +138 (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.06 (3H, s, OC(O)CH_3), 2.06 (3H, s, OC(O)CH_3), 2.07 (3H, s,

OC(O)CH_3), 2.10 (3H, s, OC(O)CH_3), 3.10 (1H, app. t, *J* 10.5 Hz, *H*-4), 3.41 (3H, s, OMe), 3.82–3.96 (2H, m, *H*-6), 3.98–4.14 (2H, m, *H*-5 and *H*-5′), 4.16–4.32 (2H, m, *H*-6′), 4.58 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.65 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.83 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.94 (1H, d, *J* 3.5 Hz, *H*-1), 5.28–5.37 (1H, m, *H*-4′), 5.48 (1H, app. t, *J* 10.5 Hz, *H*-3), 5.64–5.67 (1H, m, *H*-1′), 5.78–5.83 (2H, m, *H*-2′ and *H*-3′), 7.26–7.35 (5H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.8 (OAc), 20.8 (OAc), 21.0 (OAc), 47.0 (C-4), 55.4 (OMe), 62.5 (C-6′), 64.5 (C-4′), 67.3 (C-5′), 69.8 (C-6), 70.2 (C-5), 72.1 (C-3), 72.2 (C-2), 73.4 (OCH_2Ph), 81.3 (C-1′), 97.0 (C-1), 127.5 (C-3′), 127.7 (ArCH), 128.2 (ArCH), 128.3 (C-2′), 128.4 (ArCH), 138.0 (ArC), 169.6 (C=O), 170.2 (C=O), 170.4 (C=O), 170.7 (C=O). IR ν_{max} (thin film)/cm^{-1} 1744 (C=O), 1370 (OMe), 1241 (CH$_{arom}$). LRMS *m/z* 597 (1%, M+H$^+$), 567 (10%), 476 (20%), 463 (32%), 213 (86%), 111 (100%). HRMS (ESI, M+Na$^+$), found: 619.1799; $C_{28}H_{36}O_{12}$SNa requires: 619.1826.

*4.1.10. Methyl 6-O-benzyl-2,3-di-O-acetyl-4-S-(2,3-dideoxy-4,6-di-O-acetyl-α-D-galactopyranosyl)-6-thio-α-D-glucopyranoside (**29**)*

By following *method B*, methyl 2,3-di-*O*-acetyl-6-*O*-benzyl-4-thio-α-D-glucopyranoside (**27**) (90 mg, 0.23 mmol) and tri-*O*-acetyl-D-galactal (**14**) (76 mg, 0.28 mmol) were stirred at −10 °C for 20 min to afford, after purification by column chromatography (2:1 hexane/ethyl acetate), **29** as a colourless oil (95 mg, 68% α-only). R_f 0.4 (2:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +19.6 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.03 (3H, s, OC(O)CH_3), 2.06 (3H, s, OC(O)CH_3), 2.06 (3H, s, OC(O)CH_3), 2.08 (3H, s, OC(O)CH_3), 3.11 (1H, app. t, *J* 11.0 Hz, *H*-4), 3.41 (3H, s, O*Me*), 3.85–4.01 (3H, m, *H*-5 and *H*-6), 4.12–4.24 (2H, m, *H*-6′), 4.31 (1H, ddd, *J* 2.5, 6.5, 6.5 Hz, *H*-5′), 4.59 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.66 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.84 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.94 (1H, d, *J* 3.5 Hz, *H*-1), 5.05 (1H, dd, *J* 2.5, 5.0 Hz, *H*-4′), 5.48 (1H, app. t, *J* 10.5 Hz, *H*-3), 5.73 (1H, d, *J* 2.0 Hz, *H*-1′), 5.97–6.07 (2H, m, *H*-2′ and *H*-3′), 7.26–7.36 (5H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.8 (OAc), 20.8 (OAc), 46.6 (C-4), 55.4 (OMe), 62.3 (C-6′), 62.8 (C-4′), 67.1 (C-5′), 69.9 (C-6), 70.1 (C-5), 72.2 (C-2 and C-3), 73.3 (OCH_2Ph), 80.9 (C-1′), 97.0 (C-1), 124.0 (C-3′), 127.7 (ArCH), 128.4 (ArCH), 131.2 (C-2′), 138.1 (ArC), 169.6 (C=O), 170.2 (C=O), 170.4 (C=O), 170.5 (C=O). IR ν_{max} (thin film)/cm^{-1} 1745 (C=O), 1371 (OMe), 789 (C=C). LRMS *m/z* 597 (1%, M+H$^+$), 476 (13%), 463 (19%), 213 (100%), 153 (23%). HRMS (CI, M+H$^+$), found: 597.2023; $C_{28}H_{37}O_{12}$S requires: 597.2006.

*4.1.11. Methyl 6-O-benzyl-2,3-di-O-acetyl-4-S-(3-deoxy-2,4,6-tri-O-acetyl-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (**30**)*

By following *method B*, methyl 2,3-di-*O*-acetyl-6-*O*-benzyl-4-thio-α-D-glucopyranoside (**27**) (90 mg, 0.23 mmol) and 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**15**) (76 mg, 0.28 mmol) were stirred at −10 °C for 20 min to afford, after purification by column chromatography (2:1 hexane/ethyl acetate), **30** as a colourless oil (88 mg, 58%, α-only). R_f 0.3 (2:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +99 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.05 (3H, s, OC(O)CH_3), 2.06 (3H, s, OC(O)CH_3), 2.07 (3H, s, OC(O)CH_3), 2.09 (3H, s, OC(O)CH_3), 2.13 (3H, s, OC(O)CH_3), 3.12 (1H, app. t, *J* 10.5 Hz, *H*-4), 3.40 (3H, s, O*Me*), 3.81–3.93 (3H, m, *H*-5 and *H*-6), 4.02 (1H, dd, *J* 2.5, 12.0 Hz, *H*-6′), 4.04–4.10 (1H, m, *H*-5′), 4.17 (1H, dd, *J* 4.0, 12.0 Hz, *H*-6′), 4.59 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.65 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.81 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.93 (1H, d, *J* 3.5 Hz, *H*-1), 5.45 (1H, app. dt, *J* 2.0, 9.5 Hz, *H*-4′), 5.55 (1H, app. t, *J* 10.5 Hz, *H*-3), 5.64 (1H, d, *J* 1.5 Hz, *H*-3′), 5.71 (1H, s, *H*-1′), 7.28–7.35 (5H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.8 (OAc), 20.8 (OAc), 20.9 (OAc), 21.0 (OAc), 45.6 (C-4), 55.4 (OMe), 52.1 (C-6′), 64.3 (C-4′), 69.7 (C-6), 70.0 (C-5), 72.2 (C-2), 72.7 (C-3), 73.5 (OCH_2Ph), 80.7 (C-1′), 97.0 (C-1), 115.7 (C-3′), 127.7 (ArCH), 127.7 (ArCH), 128.5 (ArCH), 138.0 (ArC), 145.7 (C-2′), 168.0 (C=O), 169.7 (C=O), 170.1 (C=O), 170.3 (C=O), 170.6 (C=O). IR ν_{max} (thin film)/cm^{-1} 1746 (C=O), 1217 (CH$_{arom}$), 756 (C=C). LRMS *m/z* 643 (9%), 623 (6%, M$^+$−OMe), 595 (100%), 535 (75%), 521 (68%), 395 (46%), 271 (75%), 169 (66%). HRMS (CI, M$^+$−OMe), found: 623.1804; $C_{29}H_{35}O_{13}$S requires: 623.1798.

*4.1.12. Methyl 6-O-benzyl-2,3-di-O-acetyl-4-S-(3-deoxy-2,4,6-tri-O-acetyl-α-D-galactopyranosyl)-4-thio-α-D-glucopyranoside (**31**)*

By following *method B*, methyl 2,3-di-*O*-acetyl-6-*O*-benzyl-4-thio-α-D-glucopyranoside (**27**) (56 mg, 0.14 mmol) and 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-lyxo-hex-1-enitol (**16**) (57 mg, 0.17 mmol) were stirred at room temperature for 2 h to afford, after purification by column chromatography (2:1 hexane/ethyl acetate), **31** as a colourless oil (62 mg, 65%, α-only). R_f 0.2 (2:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +44.8 (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.03 (3H, s, OC(O)CH_3), 2.06 (3H, s, OC(O)CH_3), 2.08 (3H, s, OC(O)CH_3), 2.09 (3H, s, OC(O)CH_3), 2.15 (3H, s, OC(O)CH_3), 3.11 (1H, app. t, *J* 10.5 Hz, *H*-4), 3.40 (3H, s, O*Me*), 3.82–4.00 (3H, m, *H*-5 and *H*-6), 4.17 (2H, d, *J* 6.5 Hz, *H*-6′), 4.53 (1H, ddd, *J* 2.5, 6.5, 6.5 Hz, *H*-5′), 4.60 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.65 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.82 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.93 (1H, d, *J* 3.5 Hz, *H*-1), 5.24 (1H, dd, *J* 2.5, 6.0 Hz, *H*-4′), 5.56 (1H, app. t, *J* 10.5 Hz, *H*-3), 5.80 (1H, s, *H*-1′), 5.84 (1H, d, *J* 6.0 Hz, *H*-3′), 7.26–7.36 (5H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 21.0 (OAc), 21.0 (OAc), 21.0 (OAc), 21.1 (OAc), 45.5 (C-4), 55.6 (OMe), 62.0 (C-6′), 64.1 (C-4′), 67.2 (C-5′), 70.0 (C-5), 70.2 (C-6), 72.4 (C-2), 73.0 (C-3), 73.6 (OCH_2Ph), 80.8 (C-1′), 97.1 (C-1), 113.2 (C-3′), 127.8 (ArCH), 127.9 (ArCH), 128.0 (ArCH), 128.6 (ArCH), 128.7 (ArCH), 138.3 (ArC), 148.8 (C-2′), 168.0 (C=O), 169.9 (C=O), 170.4 (C=O), 170.6 (C=O), 170.6 (C=O). IR ν_{max} (thin film)/cm^{-1} 1745 (C=O), 1371 (OMe), 1237 (CH$_{arom}$). LRMS *m/z* 677 (76%, M+Na$^+$), 672 (100%, M+NH$_4^+$), 570 (16%), 521 (22%), 331 (7%). HRMS (ESI, M+NH$_4^+$), found: 672.2303; $C_{30}H_{42}O_{14}$NS requires: 672.2326.

4.2. General method for dihydroxylation

To a stirred solution of the S-linked glycoconjugate (1 equiv) in anhydrous pyridine (3 mL) under an atmosphere of argon was added osmium(VIII) tetroxide (1 equiv) in anhydrous pyridine (3 mL). The reaction mixture was stirred at room temperature until the reaction was shown to have reached completion by TLC analysis (ethyl acetate) and then 40% aq sodium hydrogen sulfite (3 mL), water (3 mL) and pyridine (1 mL) were added, and the mixture was stirred for a further 2 h. The mixture was then diluted with water (5 mL) and extracted with CH_2Cl_2 (3×10 mL). The combined extracts were dried ($MgSO_4$), filtered and concentrated in vacuo. The crude product was then per-*O*-acetylated by dissolving in pyridine (6 mL) and acetic anhydride (3 mL). The solution was stirred overnight at room temperature and then concentrated in vacuo. The residue was taken up in ethyl acetate (5 mL) and washed with 1 N HCl (5 mL) and brine (3 mL), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was then subjected to purification by column chromatography.

4.2.1. Methyl 2,3,4-tri-O-acetyl-6-S-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-6-thio-α-D-glucopyranoside (32)

Following the general method, methyl 2,3,4-tri-*O*-acetyl-6-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (**12**) (55 mg, 0.1 mmol) was stirred with osmium tetroxide (25 mg, 0.1 mmol) at room temperature for 2 h. Subsequent per-O-acetylation afforded, after purification by column chromatography (1:1 to 1:2 hexane/ethyl acetate), **32** as a colourless oil (42 mg, 63%). R_f 0.2 (1:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +99 (*c* 0.65, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 1.98 (3H, s, OC(O)CH_3), 2.00 (3H, s, OC(O)CH_3), 2.03 (3H, s, OC(O)CH_3), 2.06 (3H, s, OC(O)CH_3), 2.08 (3H, s, OC(O)CH_3), 2.10 (3H, s, OC(O)CH_3), 2.17 (3H, s, OC(O)CH_3), 2.65 (1H, dd, *J* 7.5, 14.0 Hz, *H*-6), 2.83 (1H, dd, *J* 3.0, 14.0 Hz, *H*-6), 3.42 (3H, s, O*Me*), 3.96 (1H, ddd, *J* 3.0, 7.5, 10.5 Hz, *H*-5), 4.07 (1H, dd, *J* 1.5, 12.0 Hz, *H*-6′), 4.27–4.38 (2H, m, *H*-5′ and *H*-6′), 4.87 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.91 (1H, d, *J* 3.5 Hz, *H*-1), 4.99 (1H, app. t, *J* 9.5 Hz, *H*-4), 5.26 (1H, dd, *J* 3.5, 9.5 Hz, *H*-4′), 5.28–5.36 (3H, m, *H*-1′, *H*-2′ and *H*-3′), 5.45 (1H, app. t, *J* 9.5 Hz, *H*-3). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.6 (OAc), 20.7 (OAc), 20.9 (OAc), 31.5 (C-6), 55.6 (OMe), 62.3 (C-6′), 66.1 (C-2′ or C-3′), 68.2 (C-5), 69.2 (C-5′), 69.3 (C-4′), 69.9 (C-3), 70.8 (C-2′ or C-3′), 70.8 (C-2), 71.3 (C-4), 82.3 (C-1′), 96.9 (C-1), 169.7 (C=O), 169.8 (C=O), 169.8 (C=O), 169.9 (C=O), 170.1 (C=O), 170.2 (C=O), 170.7 (C=O). IR ν_{max} (thin film)/cm^{-1}1746 (C=O), 1370 (OMe). HRMS (CI, M^+-OAc), found: 607.1696; $C_{25}H_{35}O_{15}S$ requires: 607.1697.

4.2.2. Methyl 2,3,4-tri-O-acetyl-6-S-(2,3,4,6-tetra-O-acetyl-α-D-talopyranosyl)-6-thio-α-D-glucopyranoside (33)

Following the general method, methyl 2,3,4-tri-*O*-acetyl-6-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-galactopyranosyl)-6-thio-α-D-glucopyranoside (**17**) (45 mg, 0.08 mmol) was stirred with osmium tetroxide (21 mg, 0.08 mmol) at room temperature overnight. Subsequent per-O-acetylation afforded, after purification by column chromatography (1:1 to 1:2 hexane/ethyl acetate), **33** as a colourless oil (31 mg, 56%). R_f 0.1 (1:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +171.8 (*c* 0.43, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.00 (3H, s, OC(O)CH_3), 2.03 (3H, s, OC(O)CH_3), 2.07 (3H, s, OC(O)CH_3), 2.07 (3H, s, OC(O)CH_3), 2.08 (3H, s, OC(O)CH_3), 2.13 (3H, s, OC(O)CH_3), 2.16 (3H, s, OC(O)CH_3), 2.61 (1H, dd, *J* 6.5, 14.5 Hz, *H*-6), 2.84 (1H, dd, *J* 3.0, 14.5 Hz, *H*-6), 3.41 (3H, s, O*Me*), 3.95 (1H, ddd, *J* 3.0, 6.5, 9.5 Hz, *H*-5), 4.08 (1H, dd, *J* 7.0, 11.5 Hz, *H*-6′), 4.16 (1H, dd, *J* 5.5, 11.5 Hz, *H*-6′), 4.69 (1H, ddd, *J* 1.5, 5.5, 7.0 Hz, *H*-5′), 4.85 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.90 (1H, d, *J* 3.5 Hz, *H*-1), 5.02 (1H, dd, *J* 1.5, 4.0 Hz, *H*-4′), 5.04 (1H, app. t, *J* 9.5 Hz, *H*-4), 5.24 (1H, app. t, *J* 3.5 Hz, *H*-3′), 5.32 (1H, dd, *J* 3.5, 6.0 Hz, *H*-2′), 5.46 (1H, app. t, *J* 9.5 Hz, *H*-3), 5.59 (1H, d, *J* 6.0 Hz, *H*-1′). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.7 (OAc), 20.7 (OAc), 21.0 (OAc), 31.6 (C-6), 55.3 (OMe), 61.9 (C-6′), 64.8 (C-5′), 66.6 (C-2′ and C-3′), 68.2 (C-4′), 68.4 (C-5), 70.0 (C-3), 70.8 (C-2), 71.1 (C-4), 82.2 (C-1′), 96.6 (C-1), 169.2 (C=O), 169.5 (C=O), 169.7 (C=O), 169.8 (C=O), 170.1 (C=O), 170.2 (C=O), 170.5 (C=O). IR ν_{max} (thin film)/cm^{-1} 1746 (C=O), 1370 (OMe). LRMS *m*/*z* 689 (61%, $M+Na^+$), 684 (100%, $M+NH_4^+$), 516 (5%), 331 (10%). HRMS (ESI^-, M−H), found: 665.1769; $C_{27}H_{37}O_{17}S$ requires: 665.1752.

4.2.3. Methyl 2,3,4-tri-O-benzyl-6-S-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-6-thio-α-D-glucopyranoside (34)

Following the general method, methyl 2,3,4-tri-*O*-benzyl-6-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (**13**) (73 mg, 0.1 mmol) was stirred with osmium tetroxide (27 mg, 0.1 mmol) at room temperature overnight. Subsequent per-O-acetylation afforded, after purification by column chromatography (2:1 to 1:1 hexane/ethyl acetate), **34** as a colourless oil (44 mg, 52%). R_f 0.3 (1:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +110 (*c* 0.21, $CHCl_3$). H NMR ($CDCl_3$, 400 MHz) 1.98 (3H, s, OC(O)CH_3), 1.99 (3H, s, OC(O)CH_3), 2.10 (3H, s, OC(O)CH_3), 2.13 (3H, s, OC(O)CH_3), 2.71 (1H, dd, *J* 6.5, 14.0 Hz, *H*-6), 3.00 (1H, dd, *J* 2.5, 14.0 Hz, *H*-6), 3.37 (3H, s, O*Me*), 3.45–3.52 (2H, m, *H*-2, *H*-4), 3.82 (1H, ddd, *J* 2.5, 6.5, 9.5 Hz, *H*-5), 3.98 (1H, app. t, *J* 9.0 Hz, *H*-3), 4.05 (1H, dd, *J* 7.0, 11.5 Hz, *H*-6′), 4.14 (1H, dd, *J* 6.0, 11.5 Hz, *H*-6′), 4.48 (1H, d, *J* 3.5 Hz, *H*-1), 4.61 (1H, d, *J* 11.0 Hz, OCH_2Ph), 4.67 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.78 (1H, d, *J* 12.0 Hz, OCH_2Ph), 4.79 (1H, d, *J* 11.0 Hz, OCH_2Ph), 4.91 (1H, d, *J* 11.0 Hz, OCH_2Ph), 4.99 (1H, d, *J* 11.0 Hz, OCH_2Ph), 5.02 (1H, dd, *J* 2.0, 4.5 Hz, *H*-4′), 5.22 (1H, app. t, *J* 3.5 Hz, *H*-3′), 5.32 (1H, dd, *J* 3.5, 6.0 Hz, *H*-2′), 5.60 (1H, d, *J* 6.0 Hz, *H*-1′), 7.26–7.38 (15H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.7 (OAc), 20.9 (OAc), 32.2 (C-6), 55.1 (OMe), 61.7 (C-6′), 64.8 (C-5′), 66.6 and 66.8 (C-2′ and C-3′), 68.2 (C-4′), 69.9 (C-5), 73.2 (OCH_2Ph), 75.1 (OCH_2Ph), 75.7 (OCH_2Ph), 79.8 and 79.9 (C-2 and C-4), 81.8 (C-3), 82.3 (C-3′), 97.8 (C-1), 127.7–128.4 (ArCH), 138.1 (ArC), 138.6 (ArC), 170.1 (C=O), 170.2 (C=O), 170.3 (C=O), 170.8 (C=O). IR ν_{max} (thin film)/cm^{-1} 1744 (C=O), 1371 (OMe), 1237 (CH_{arom}). LRMS *m*/*z* 833 (47%, $M+Na^+$), 828 (100%,

M+NH_4^+), 649 (24%), 489 (37%), 395 (8%). HRMS (ESI^-, M−H), found: 809.2859; $C_{42}H_{50}O_{14}S$ requires: 809.2843.

4.2.4. Methyl 2,3,4-tri-O-benzyl-6-S-(2,3,4,6-tetra-O-acetyl-α-D-talopyranosyl)-6-thio-α-D-glucopyranoside (*35*)

Following the general method, methyl 2,3,4-tri-*O*-benzyl-6-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-galactopyranosyl)-6-thio-α-D-glucopyranoside (**20**) (30 mg, 0.04 mmol) was stirred with osmium tetroxide (12 mg, 0.04 mmol) at room temperature overnight. Subsequent per-O-acetylation afforded, after purification by column chromatography (2:1 to 1:1 hexane/ethyl acetate), **35** as a colourless oil (20 mg, 57%). R_f 0.3 (1:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +59 (*c* 0.13, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) 1.99 (3H, s, OC(O)C*H*$_3$), 2.04 (3H, s, OC(O)C*H*$_3$), 2.05 (3H, s, OC(O)C*H*$_3$), 2.15 (3H, s, OC(O)C*H*$_3$), 2.74 (1H, dd, *J* 6.5, 14.0 Hz, *H*-6), 3.00 (1H, dd, *J* 2.5, 14.0 Hz, *H*-6), 3.37 (3H, s, O*Me*), 3.49 (1H, app. t, *J* 9.0 Hz, *H*-4), 3.55 (1H, dd, *J* 3.5, 9.5 Hz, *H*-2), 3.81−3.75 (1H, m, *H*-5), 3.98 (1H, app. t, *J* 9.5 Hz, *H*-3), 4.01−4.05 (1H, m, *H*-6′), 4.24−4.34 (2H, m, *H*-5′, *H*-6′), 4.55 (1H, d, *J* 3.5 Hz, *H*-1), 4.59 (1H, d, *J* 11.0 Hz, OC*H*$_2$Ph), 4.66 (1H, d, *J* 12.0 Hz, OC*H*$_2$Ph), 4.76−4.81 (2H, m, OC*H*$_2$Ph), 4.91 (1H, d, *J* 11.0 Hz, OC*H*$_2$Ph), 4.98 (1H, d, *J* 11.0 Hz, OC*H*$_2$Ph), 5.26 (1H, dd, *J* 3.0, 10.0 Hz, *H*-4′), 5.31 (1H, app. t, *J* 9.5 Hz, *H*-3′), 5.35 (1H, dd, *J* 1.5, 3.0 Hz, *H*-2′), 5.36−5.39 (1H, m, *H*-1′), 7.24−7.37 (15H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.6 (OAc), 20.7 (OAc), 20.9 (OAc), 32.0 (C-6), 55.3 (OMe), 62.3 (C-6′), 66.2 (C-5′), 69.1 (C-2′ and C-3′), 69.3 (C-4′), 69.7 (C-5), 73.5 (OCH_2Ph), 75.2 (OCH_2Ph), 75.7 (OCH_2Ph), 79.8 and 80.2 (C-2 and C-4), 81.8 (C-3), 82.7 (C-3′), 97.3 (C-1), 127.6 (ArCH), 127.9 (ArCH), 128.1 (ArCH), 128.4 (ArCH), 138.1 (ArC), 138.6 (ArC), 170.1 (C=O), 170.2 (C=O), 170.3 (C=O), 170.8 (C=O). IR ν_{max} (thin film)/cm^{-1} 1745 (C=O), 1371 (OMe), 1237 (CH_{arom}). LRMS *m/z* 833 (37%, M+Na^+), 828 (100%, M+NH_4^+), 779 (6%), 483 (7%), 331 (8%). HRMS (ESI^-, M−H), found: 809.2839; $C_{42}H_{50}O_{14}S$ requires: 809.2843.

4.2.5. Methyl 6-O-benzyl-2,3-di-O-acetyl-4-S-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-6-thio-α-D-glucopyranoside (*36*)

Following the general method, methyl 6-*O*-benzyl-2,3-di-*O*-acetyl-4-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (**28**) (50 mg, 0.08 mmol) was stirred with osmium tetroxide (21 mg, 0.08 mmol) at room temperature for 20 min. Subsequent per-O-acetylation afforded, after purification by column chromatography (2:1 to 1:1 hexane/ethyl acetate), **36** as a colourless oil (50 mg, 83%). R_f 0.3 (1:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +95 (*c* 0.3, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) 2.00 (3H, s, OC(O)C*H*$_3$), 2.05 (3H, s, OC(O)C*H*$_3$), 2.06 (3H, s, OC(O)C*H*$_3$), 2.07 (3H, s, OC(O)C*H*$_3$), 2.09 (3H, s, OC(O)C*H*$_3$), 2.13 (3H, s, OC(O)C*H*$_3$), 3.10 (1H, app. t, *J* 10.5 Hz, *H*-4), 3.40 (3H, s, O*Me*), 3.78−3.93 (3H, m, *H*-5 and *H*-6), 3.95 (1H, dd, *J* 2.5, 12.5 Hz, *H*-6′), 4.09 (1H, app. t, *J* 2.5, 4.5, 10.0 Hz, *H*-5′), 4.23 (1H, dd, *J* 4.5, 12.5 Hz, *H*-6′), 4.59 (1H, d, *J* 12.0 Hz, OC*H*$_2$Ph), 4.62 (1H, d, *J* 12.0 Hz, OC*H*$_2$Ph), 4.81 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.93 (1H, d, *J* 3.5 Hz, *H*-1), 5.15 (1H, dd, *J* 3.5, 10.0 Hz, *H*-3′), 5.22 (1H, dd, *J* 1.5, 3.5 Hz, *H*-2′), 5.29 (1H, d, *J* 1.5 Hz, *H*-1′), 5.46 (1H, app. t, *J* 10.0 Hz, *H*-3), 7.26−7.37 (5H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.6 (OAc), 20.7 (OAc), 20.8 (OAc), 20.9 (OAc), 47.0 (C-4), 55.5 (OMe), 62.0 (C-6), 65.8 (C-3′), 69.4 (C-5), 70.1 (C-5′), 70.2 (C-6), 71.0 (C-3), 71.6 (C-2′), 72.2 (C-2), 73.5 (OCH_2Ph), 83.4 (C-1′), 97.0 (C-1), 127.7 (ArCH), 127.8 (ArCH), 128.4 (ArCH), 137.9 (ArC), 169.6 (C=O), 169.7 (C=O), 169.9 (C=O), 170.3 (C=O), 170.5 (C=O). IR ν_{max} (thin film)/cm^{-1} 1746 (C=O), 1370 (OMe), 1223 (CH_{arom}). LRMS *m/z* 732 (100%, M+NH_4^+), 583 (5%), 483 (8%), 331 (21%). HRMS (ESI^-, M−H), found: 713.2137; $C_{32}H_{41}O_{16}S$ requires: 713.2116.

4.2.6. Methyl 6-O-benzyl-2,3-di-O-acetyl-4-S-(2,3,4,6-tetra-O-acetyl-α-D-talopyranosyl)-6-thio-α-D-glucopyranoside and methyl 6-O-benzyl-2,3-di-O-acetyl-4-S-(2,3,4,6-tetra-O-acetyl-α-D-gulopyranosyl)-6-thio-α-D-glucopyranoside (*37*)

Following the general method, methyl 6-*O*-benzyl-2,3-di-*O*-acetyl-4-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-galactopyranosyl)-6-thio-α-D-glucopyranoside (**29**) (32 mg, 0.05 mmol) was stirred with osmium tetroxide (14 mg, 0.05 mmol) at room temperature for 18 h. Subsequent per-O-acetylation afforded, after purification by column chromatography (2:1 to 1:1 hexane/ethyl acetate), **37** as a colourless oil (29 mg, 76%, 1:0.4 Tal/Gul). *Tal*: R_f 0.2 (2:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +118 (*c* 0.105, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) 2.01 (3H, s, OC(O)C*H*$_3$), 2.03 (3H, s, OC(O)C*H*$_3$), 2.03 (3H, s, OC(O)C*H*$_3$), 2.05 (3H, s, OC(O)C*H*$_3$), 2.12 (3H, s, OC(O)C*H*$_3$), 2.14 (3H, s, OC(O)C*H*$_3$), 2.99 (1H, app. t, *J* 10.5 Hz, *H*-4), 3.41 (3H, s, O*Me*), 3.82−3.98 (3H, m, *H*-5, *H*-6), 4.02−4.08 (2H, m, *H*-6′), 4.46 (1H, ddd, *J* 1.5, 6.5, 6.5 Hz, *H*-5′), 4.59 (1H, d, *J* 12.0 Hz, OC*H*$_2$Ph), 4.67 (1H, d, *J* 12.0 Hz, OC*H*$_2$Ph), 4.82 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.93 (1H, d, *J* 3.5 Hz, *H*-1), 4.95 (1H, dd, *J* 1.5, 4.0 Hz, *H*-4′), 5.22 (1H, app. t, *J* 3.5 Hz, *H*-3′), 5.25 (1H, dd, *J* 3.0, 6.0 Hz, *H*-2′), 5.47 (1H, app. t, *J* 10.5 Hz, *H*-3), 5.59 (1H, d, *J* 6.0 Hz, *H*-1′), 7.27−7.38 (5H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.6 (OAc), 20.7 (OAc), 20.8 (OAc), 20.8 (OAc), 20.9 (OAc), 46.5 (C-4), 55.4 (OMe), 61.9 (C-6′), 66.2 (C-3′), 66.4 (C-2′), 67.9 (C-4′), 69.7 (C-6), 70.6 (C-5), 71.9 (C-3), 72.2 (C-2), 73.4 (OCH_2Ph), 82.7 (C-1′), 97.0 (C-1), 127.7 (ArCH), 127.7 (ArCH), 128.4 (ArCH), 138.1 (ArC), 169.0 (C=O), 169.4 (C=O), 169.8 (C=O), 170.3 (C=O). IR ν_{max} (thin film)/cm^{-1} 1752 (C=O). *Gul*: R_f 0.2 (2:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +56 (*c* 0.11, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) 1.99 (3H, s, OC(O)C*H*$_3$), 2.02 (3H, s, OC(O)C*H*$_3$), 2.05 (3H, s, OC(O)C*H*$_3$), 2.08 (3H, s, OC(O)C*H*$_3$), 2.11 (3H, s, OC(O)C*H*$_3$), 2.12 (3H, s, OC(O)C*H*$_3$), 3.10 (1H, app. t, *J* 11.0 Hz, *H*-4), 3.40 (3H, s, O*Me*), 3.81−3.98 (3H, m, *H*-5, *H*-6), 4.09 (2H, d, *J* 6.5 Hz, *H*-6′), 4.31 (1H, app. dt, *J* 1.5, 6.5 Hz, *H*-5′), 4.59 (1H, d, *J* 12.0 Hz, OC*H*$_2$Ph), 4.64 (1H, d, *J* 12.0 Hz, OC*H*$_2$Ph), 4.82 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 4.93 (1H, d, *J* 3.5 Hz, *H*-1), 5.04−5.11 (2H, m, *H*-2′ and *H*-4′), 5.21−5.29 (1H, m, *H*-3′), 5.42−5.44 (1H, m, *H*-1′), 5.47 (1H, app. t, *J* 10.0 Hz, *H*-3), 7.26−7.36 (5H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.5

(OAc), 20.6 (OAc), 20.7 (OAc), 20.8 (OAc), 20.9 (OAc), 46.6 (C-4), 55.4 (OMe), 61.4 (C-6′), 65.4 (C-2′ or C-4′), 65.6 (C-3′), 68.2 (C-5′), 69.4 (C-6), 69.5 (C-2′ or C-4′), 70.6 (C-5), 72.2 (C-2), 73.4 (OCH_2Ph), 83.7 (C-1′), 97.0 (C-1), 127.6 (ArCH), 128.4 (ArCH), 138.1 (ArC), 169.0 (C=O), 169.4 (C=O), 169.8 (C=O), 170.3 (C=O). IR ν_{max} (thin film)/cm^{-1} 1752 (C=O), 1223 (CH_{arom}). LRMS *m/z* 737 (55%, $M+Na^+$), 732 (100%, $M+NH_4^+$), 688 (9%), 571 (8%), 483 (7%), 331 (22%). HRMS (ESI^-, M−H), found: 713.2130; $C_{32}H_{41}O_{16}S$ requires: 713.2116.

4.3. Ferrier reactions with cysteine and homocysteine

4.3.1. N-Benzoyl-S-(2,3-dideoxy-4,6-di-O-acetyl-α-D-glycopyranosyl)-L-cysteine ethyl ester (49)

Following *method A*, *N*-benzoyl-L-cysteine ethyl ester (**46**) (120 mg, 0.47 mmol) and tri-*O*-acetyl-D-glucal (**11**) (107 mg, 0.39 mmol) were stirred at room temperature for 4.5 h to afford, after purification by column chromatography (2:1 hexane/ethyl acetate), **49** as a white powder (131 mg, 72%, α/β 2:1).

Following *method B*, *N*-benzoyl-L-cysteine ethyl ester (**46**) (50 mg, 0.19 mmol) and tri-*O*-acetyl-D-glucal (**11**) (64 mg, 0.24 mmol) were stirred at room temperature for 10 min to afford, after purification by column chromatography (2:1 hexane/ethyl acetate), **49** as a white powder (80 mg, 87% α-only). R_f 0.4 (2:1 hexane/ethyl acetate); mp 124–126 °C; $[\alpha]_D^{20}$ +117.8 (*c* 1.2, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) 1.31 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 1.96 (3H, s, OC(O)CH_3), 2.08 (3H, s, OC(O)CH_3), 3.18 (1H, dd, *J* 3.0, 15.0 Hz, SCH_2), 3.44 (1H, dd, *J* 5.0, 15.0 Hz, SCH_2), 4.16–4.32 (5H, m, *H*-5, *H*-6, OCH_2CH_3), 5.29–5.36 (2H, m, NHC*H*, *H*-4), 5.54 (1H, dt, *J* 2.0, 3.0 Hz, *H*-1), 5.80 (1H, dt, *J* 2.0, 10.0 Hz, *H*-3), 5.95 (1H, ddd, *J* 2.0, 3.0, 10.0 Hz, *H*-2), 7.40–7.46 (2H, m, ArC*H*), 7.48–7.53 (1H, m, ArC*H*), 7.75 (1H, d, *J* 9.0 Hz, N*H*), 7.86–7.91 (2H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 14.3 (OCH_2CH_3), 20.5 (OAc), 21.0 (OAc), 36.8 (SCH_2), 52.8 (C-4), 61.8 (OCH_2CH_3), 62.8 (C-6), 64.5 (NH*C*H), 67.9 (C-5), 82.4 (C-1), 127.0 (ArCH), 127.4 (C-3), 128.4 (C-2), 128.5 (ArCH), 131.8 (ArCH), 133.8 (ArC), 167.2 (C=O), 170.1 (C=O), 170.2 (C=O), 170.8 (C=O). IR ν_{max} (thin film)/cm^{-1} 1734 (C=O), 1654 (C=O), 1524 (NHCO), 908 (CH_{arom}), 732 (CH_{arom}). LRMS *m/z* 466 (64%, $M+H^+$), 345 (100%), 332 (33%), 252 (21%), 213 (53%). HRMS (CI, $M+H^+$), found: 466.1548; $C_{22}H_{28}NO_8S$ requires: 466.1535.

4.3.2. N-Benzoyl-S-(2,3-dideoxy-4,6-di-O-acetyl-α-D-glucopyranosyl)-DL-homocysteine methyl ester (50)

Following *method A*, *N*-benzoyl-DL-homocysteine methyl ester (**48**) (100 mg, 0.39 mmol) and tri-*O*-acetyl-D-glucal (**11**) (129 mg, 0.47 mmol) were stirred at room temperature overnight to afford, after purification by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine), **50** as a colourless oil (161 mg, 89%, α/β 2:1).

Following *method B*, *N*-benzoyl-DL-homocysteine methyl ester (**48**) (85 mg, 0.33 mmol) and tri-*O*-acetyl-D-glucal (**11**) (109 mg, 0.4 mmol) were stirred at room temperature for 10 min to afford, after purification by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine), **50** as a colourless oil (100 mg, 64% α-only). R_f 0.3 (2:1 hexane/ethyl acetate). ^1H NMR ($CDCl_3$, 400 MHz) 2.07 (3H, s, OC(O)CH_3), 2.08 (3H, s, OC(O)CH_3), 2.10–2.22 (1H, m, SCH_2CH_2), 2.33–2.39 (1H, m, SCH_2CH_2), 2.67–2.86 (2H, m, SCH_2CH_2), 3.79 (3H, s, O*Me*), 4.17–4.29 (3H, m, *H*-5, *H*-6), 4.91–4.96 (1H, m, NHC*H*), 5.28 (1H, ddd, *J* 2.5, 5.5, 8.0 Hz, H-4_β), 5.36 (1H, ddd, *J* 2.0, 4.5, 9.0 Hz, *H*-4), 5.43 (1H, d, *J* 3.0 Hz, H-1_β), 5.55–5.57 (1H, m, *H*-1), 5.79 (1H, dt, *J* 1.5, 10.0 Hz, *H*-3), 5.87–5.95 (3H, m, *H*-3, H-2), 6.85 (1H, dd, *J* 8.0, 13.5 Hz, N*H*), 6.93–6.97 (1H, m, NH_β), 7.42–7.55 (3H, m, ArC*H*), 7.80–7.85 (2H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.7 (OAc), 20.8 (OAc), 21.0 (OAc), 27.9 and 28.4 (SCH_2CH_2), 33.0 and 33.2 (SCH_2CH_2), 51.8, 52.0 and 52.2 (NH*C*H), 52.7 (OMe), 62.8 and 63.1 (C-6), 65.0 (C-4), 66.9 (C-5), 79.4, 80.3 and 81.0 (C-1), 127.1 (ArCH), 127.2 (ArCH), 127.7 and 127.8 (C-3), 128.6 (C-2), 130.0 (ArCH), 131.9 (ArCH), 133.7 (ArC), 167.1 (C=O), 167.2 (C=O), 170.3 (C=O), 170.9 (C=O), 172.5 (C=O), 172.6 (C=O). IR ν_{max} (thin film)/cm^{-1} 1739 (C=O), 1661 (C=O), 669 (CH_{arom}). LRMS *m/z* 466 (1%, $M+H^+$), 345 (23%), 252 (32%), 213 (37%), 153 (57%), 111 (100%). HRMS (CI, $M+H^+$), found: 466.1533; $C_{22}H_{28}NO_8S$ requires: 466.1536.

4.3.3. N-Benzoyl-S-(2,3-dideoxy-4,6-di-O-acetyl-α-D-galactopyranosyl)-L-cysteine ethyl ester (51)

Following *method A*, *N*-benzoyl-L-cysteine ethyl ester (**46**) (194 mg, 0.7 mmol) and tri-*O*-acetyl-D-galactal (**14**) (173 mg, 0.6 mmol) were stirred at room temperature overnight to afford, after purification by column chromatography (3:1 to 1:1 pentane/ethyl acetate), **51** as a white powder (155 mg, 60%, α/β 2:1).

Following *method B*, *N*-benzoyl-L-cysteine ethyl ester (**46**) (50 mg, 0.19 mmol) and tri-*O*-acetyl-D-galactal (**14**) (64 mg, 0.24 mmol) were stirred at room temperature for 1.5 h to afford, after purification by column chromatography (2:1 hexane/ethyl acetate), **51** as a white powder (70 mg, 77% α-only). R_f 0.3 (2:1 hexane/ethyl acetate); mp 157–159 °C; $[\alpha]_D^{20}$ −5.3 (*c* 0.73, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) 1.27 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 1.90 (3H, s, OC(O)CH_3), 2.06 (3H, s, OC(O)CH_3), 3.14 (1H, dd, *J* 3.5, 14.5 Hz, SCH_2), 3.46 (1H, dd, *J* 4.5, 14.5 Hz, SCH_2), 4.05–4.13 (1H, m, *H*-6), 4.18–4.29 (3H, m, H-6, OCH_2CH_3), 4.48 (1H, ddd, *J* 2.5, 4.0, 7.5 Hz, *H*-5), 5.04 (1H, dd, *J* 2.5, 5.5 Hz, *H*-4), 5.24 (1H, ddd, *J* 3.5, 4.5, 8.5 Hz, NHC*H*), 5.59 (1H, dd, *J* 2.0, 3.5 Hz, *H*-1), 6.00 (1H, ddd, *J* 2.0, 5.5, 10.0 Hz, *H*-3), 6.10 (1H, dd, *J* 3.5, 10.0 Hz, *H*-2), 7.38–7.46 (2H, m, ArC*H*), 7.49 (1H, tt, *J* 1.0, 6.5 Hz, ArC*H*), 7.57 (1H, d, *J* 8.5 Hz, N*H*), 7.83–7.88 (2H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 14.4 (OCH_2CH_3), 20.6 (OAc), 20.9 (OAc), 36.5 (SCH_2), 52.9 (NH*C*H), 61.9 (OCH_2CH_3), 62.8 (C-6), 63.2 (C-4), 68.0 (C-5), 82.3 (C-1), 123.8 (C-3), 127.5 (ArCH), 128.6 (ArCH), 131.6 (ArCH), 132.0 (C-2), 134.1 (ArC), 167.5 (C=O), 170.2 (C=O), 170.3 (C=O), 170.9 (C=O). IR ν_{max} (thin film)/cm^{-1} 1749 (C=O), 1655 (C=O). HRMS (CI, $M+H^+$), found: 466.1530; $C_{22}H_{28}NO_8S$ requires: 466.1535.

*4.3.4. N-Benzoyl-S-(3-deoxy-2,4,6-tri-O-acetyl-α-D-glucopyranosyl)-L-cysteine ethyl ester (**52**)*

Following *method A*, *N*-benzoyl-L-cysteine ethyl ester (**46**) (74 mg, 0.29 mmol) and 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**15**) (81 mg, 0.24 mmol) were stirred at 50 °C to afford, after purification by column chromatography (3:1 to 1:1 pentane/ethyl acetate), **52** as a colourless oil (37 mg, 22%, α/β 4:1).

Following *method B*, *N*-benzoyl-L-cysteine ethyl ester (**46**) (57 mg, 0.23 mmol) and 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**15**) (62 mg, 0.18 mmol) were stirred at room temperature for 15 min to afford, after purification by column chromatography (3:2 hexane/ethyl acetate), **52** as a colourless oil (80 mg, 68%, α-only). R_f 0.5 (3:2 hexane/ethyl acetate); $[\alpha]_D^{20}$ +134.5 (*c* 1.15, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) 1.30 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 1.97 (3H, s, $OC(O)CH_3$), 2.08 (3H, s, $OC(O)CH_3$), 2.17 (3H, s, $OC(O)CH_3$), 3.18 (1H, dd, *J* 3.0, 15.0 Hz, SCH_2), 3.46 (1H, dd, *J* 4.5, 15.0 Hz, SCH_2), 4.15–4.36 (5H, m, H-5, H-6, OCH_2CH_3), 5.30 (1H, ddd, *J* 3.0, 4.5, 8.0 Hz, NHC*H*), 5.43 (1H, dt, *J* 2.0, 9.0 Hz, *H*-4), 5.52 (1H, br s, *H*-1), 5.66 (1H, d, *J* 2.0 Hz, *H*-3), 7.39–7.46 (2H, m, ArC*H*), 7.49–7.55 (1H, m, ArC*H*), 7.61 (1H, d, *J* 8.0 Hz, N*H*), 7.84–7.89 (2H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 14.2 (OCH_2CH_3), 20.5 (OAc), 20.9 (OAc), 20.9 (OAc), 36.6 (SCH_2), 52.8 (NH*C*H), 61.9 (OCH_2CH_3), 62.5 (C-6), 64.4 (C-4), 68.2 (C-5), 82.4 (C-1), 115.1 (C-3), 127.3 (ArCH), 128.5 (ArCH), 131.9 (ArCH), 133.7 (ArC), 146.2 (C-2), 167.3 (C=O), 168.9 (C=O), 169.9 (C=O), 170.1 (C=O), 170.7 (C=O). IR ν_{max} (thin film)/cm^{-1} 1742 (C=O), 1651 (C=O). LRMS *m/z* 524 (50%, $M+H^+$), 464 (21%), 422 (100%), 404 (26%), 131 (19%). HRMS (CI, $M+H^+$), found: 524.1588; $C_{24}H_{30}NO_{10}S$ requires: 524.1590.

*4.3.5. N-Benzoyl-S-(3-deoxy-2,4,6-tri-O-acetyl-α-D-galactopyranosyl)-L-cysteine ethyl ester (**54**)*

Following *method B*, *N*-benzoyl-L-cysteine ethyl ester (**46**) (50 mg, 0.2 mmol) and 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-lyxo-hex-1-enitol (**16**) (78 mg, 0.24 mmol) were stirred at room temperature for 2.5 h to afford, after purification by column chromatography (2:1 to 3:2 hexane/ethyl acetate), **54** as a white powder (65 mg, 63%, α-only). R_f 0.2 (2:1 hexane/ethyl acetate); mp 167–169 °C; $[\alpha]_D^{20}$ −9.7 (*c* 0.35, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) 1.30 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 1.93 (3H, s, $OC(O)CH_3$), 2.08 (3H, s, $OC(O)CH_3$), 2.18 (3H, s, $OC(O)CH_3$), 3.16 (1H, dd, *J* 3.5, 15.0 Hz, SCH_2), 3.51 (1H, dd, *J* 4.5, 15.0 Hz, SCH_2), 4.12 (1H, dd, *J* 8.0, 12.0 Hz, H-6), 4.25 (2H, q, *J* 7.0 Hz, OCH_2CH_3), 4.29 (1H, dd, *J* 4.0, 12.0 Hz, H-6), 4.50 (1H, ddd, *J* 2.5, 4.0, 8.0 Hz, H-5), 5.26 (1H, dd, *J* 2.5, 6.0 Hz, H-4), 5.25–5.30 (1H, m, NHC*H*), 5.61 (1H, d, *J* 1.0 Hz, H-1), 5.84 (1H, dd, *J* 1.0, 6.0 Hz, H-3), 7.42–7.54 (4H, m, NH and ArCH), 7.85–7.89 (2H, m, ArCH). ^{13}C NMR ($CDCl_3$, 100 MHz) 14.2 (OCH_2CH_3), 20.4 (OAc), 20.8 (OAc), 21.0 (OAc), 36.4 (SCH_2), 52.8 (NH*C*H), 61.9 (OCH_2CH_3), 62.4 (C-6), 64.4 (C-4), 67.9 (C-5), 82.6 (C-1), 112.4 (C-3), 127.3 (ArCH), 128.5 (ArCH), 131.9 (ArCH), 133.6 (ArC), 149.0 (C-2), 167.5 (C=O), 167.8 (C=O), 169.9 (C=O), 170.1 (C=O), 170.8 (C=O). IR ν_{max} (thin film)/cm^{-1} 1741 (C=O), 1647 (C=O), 771 (C=C). LRMS *m/z* 524 (100%, $M+H^+$), 464 (11%), 422 (47%), 404 (35%), 271 (7%). HRMS (CI, $M+H^+$), found: 524.1605; $C_{24}H_{30}NO_{10}S$ requires: 524.1590.

*4.3.6. Ethyl 3-((2R)-6-(acetoxymethyl)-3-oxo-3,6-dihydro-2H-pyran-2-ylthio)-2-benzamidopropanoate (**53**)*

Following *method A*, *N*-benzoyl-L-cysteine ethyl ester (**46**) (144 mg, 0.57 mmol) and 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-lyxo-hex-1-enitol (**16**) (156 mg, 0.47 mmol) were stirred at 60 °C to afford, after purification by column chromatography (3:1 to 1:1 pentane/ethyl acetate), **53** as a colourless oil (60 mg, 25%, α/β 3:1). R_f 0.3 (1:1 pentane/ethyl acetate). ^1H NMR ($CDCl_3$, 500 MHz) 1.29 (3H, t, *J* 7.0 Hz, OCH_2CH_3 minor), 1.31 (3H, t, *J* 7.0 Hz, OCH_2CH_3 major), 1.94 (3H, s, $OC(O)CH_3$ minor), 1.96 (3H, s, $OC(O)CH_3$ major), 3.09 (1H, dd, *J* 5.5, 14.0 Hz, SCH_2 minor), 3.32 (1H, dd, *J* 3.5, 14.5 Hz, SCH_2 major), 3.44 (1H, dd, *J* 5.0, 14.5 Hz, SCH_2 major), 3.50 (1H, dd, *J* 4.5, 14.5 Hz, SCH_2 minor), 4.13–4.33 (10H, m, OCH_2CH_3, H-5, H-6 major and minor), 5.23–5.28 (1H, m, NHC*H* minor), 5.33 (1H, ddd, *J* 3.5, 5.0, 8.5 Hz, NHC*H* major), 5.49 (1H, s, *H*-1 major), 5.64 (1H, s, *H*-1 minor), 5.85 (1H, dd, *J* 1.0, 6.0 Hz, *H*-3 minor), 6.18 (1H, dd, *J* 3.0, 10.5 Hz, *H*-3 major), 6.46 (1H, d, *J* 3.5 Hz, *H*-4 minor), 6.95 (1H, dd, *J* 1.5, 10.5 Hz, *H*-4 major), 7.18 (1H, d, *J* 7.5 Hz, N*H* minor),7.36–7.56 (6H, m, ArC*H* major and minor), 7.62 (1H, d, *J* 8.5 Hz, N*H* major), 7.78–7.93 (4H, m, ArC*H* major and minor). ^{13}C NMR ($CDCl_3$, 100 MHz) 14.0 (OCH_2CH_3 major and minor), 21.0 (OAc major), 21.5 (OAc minor), 34.1 (SCH_2 minor), 36.4 (SCH_2 major), 52.4 (NH*C*H minor), 52.7 (NH*C*H major), 61.8 (OCH_2CH_3 minor), 62.1 (OCH_2CH_3 major), 64.2 (C-6 major), 64.3 (C-6 minor), 67.5 (C-5 major), 67.9 (C-5 minor), 82.4 (C-1 minor), 85.9 (C-1 major), 110.6 (C-4 minor), 113.0 (C-3 minor), 127.2 (C-3 major), 127.1 (ArCH), 127.5 (ArCH), 127.9 (ArCH), 128.3 (ArCH), 128.7 (ArCH), 131.0 (ArC), 131.1 (ArC), 131.7 (ArC), 131.9 (ArC), 132.0 (ArC), 147.8 (C-4 major), 166.9 (C=O), 167.1 (C=O), 170.1 (C=O), 170.4 (C=O), 170.6 (C=O), 177.2 (C=O). IR ν_{max} (thin film)/cm^{-1} 1741 (C=O), 1648 (C=O). HRMS (CI, $M+H^+$), found: 422.1287; $C_{20}H_{23}NO_7S$ requires: 422.1273.

*4.3.7. N-Benzoyl-S-(2,3-dideoxy-4,6-di-O-acetyl-D-galactopyranosyl)-DL-homocysteine methyl ester (**55**)*

Following *method A*, *N*-benzoyl-DL-homocysteine methyl ester (**48**) (244 mg, 0.96 mmol) and tri-*O*-acetyl-D-galactal (**14**) (314 mg, 1.2 mmol) were stirred at room temperature for 48 h to afford, after purification by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine), **55** as a colourless oil (290 mg, 65%, α/β 2:1).

Following *method B*, *N*-benzoyl-DL-homocysteine methyl ester (**48**) (85 mg, 0.33 mmol) and tri-*O*-acetyl-D-galactal (**14**) (109 mg, 0.4 mmol) were stirred at room temperature for 1.5 h to afford, after purification by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine), **55** as a colourless oil (65 mg, 42% α-only). R_f 0.3 (2:1 hexane/ethyl acetate). ^1H NMR ($CDCl_3$, 400 MHz) 2.01 (3H, s, $OC(O)CH_3$), 2.09 (3H, s, $OC(O)CH_3$), 2.11–2.27 (1H, m, SCH_2CH_2), 2.31–2.46

(1H, m, SCH_2CH_2), 2.64–2.76 (1H, m, SCH_2CH_2), 2.78–2.91 (1H, m, SCH_2CH_2), 3.08 and 3.09 (3H, s, O*Me* anomers), 4.13–4.29 (2H, m, *H*-6 anomers), 4.47–4.54 (1H, m, *H*-5), 4.86–4.99 (1H, m, NHC*H*), 5.06–5.10 (1H, m, *H*-4), 5.62–5.66 (1H, m, *H*-1), 6.01–6.12 (2H, m, *H*-2, *H*-3 anomers), 6.84 (1H, t, *J* 8.5 Hz, N*H*), 7.42–7.57 (3H, m, ArC*H*), 7.79–7.91 (2H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.6–21.0 (OAc), 26.9–27.7 (SCH_2CH_2), 32.3 (SCH_2CH_2), 51.8 (NH*C*H), 62.6 (C-6), 63.2 (C-4), 66.8 (C-5), 79.1 (C-1_β), 80.3 (C-1_α), 124.4 (C-3), 127.0 (ArCH), 127.5 (ArCH), 127.9 (ArCH), 128.2 (ArCH), 128.6 (ArCH), 131.5 (C-2), 131.9 (C-2), 131.7 (ArC), 167.5 (C=O), 170.7 (C=O), 171.0 (C=O), 172.9 (C=O). IR ν_{max} (thin film)/cm^{-1} 1740 (C=O), 1651 (C=O). LRMS *m/z* 505 (45%), 466 (68%, M+H$^+$), 346 (44%), 252 (57%), 213 (100%), 153 (78%). HRMS (CI, M+H$^+$), found: 466.1520; $C_{22}H_{27}NO_8S$ requires: 466.1535.

4.3.8. *N*-Benzoyl-*S*-(3-deoxy-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl)-DL-homocysteine methyl ester (**56**)

Following *method B*, *N*-benzoyl-DL-homocysteine methyl ester (**48**) (125 mg, 0.5 mmol) and 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**15**) (195 mg, 0.6 mmol) were stirred at room temperature for 2 h to afford, after purification by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine), **56** as a colourless oil (155 mg, 60%). R_f 0.3 (2:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.04 (3H, s, OC(O)CH_3), 2.08 (3H, s, OC(O)CH_3), 2.14 (3H, s, OC(O)CH_3), 2.12–2.23 (1H, m, SCH_2CH_2), 2.28–2.39 (1H, m, SCH_2CH_2), 2.63–2.87 (2H, m, SCH_2CH_2), 2.11–2.27 (1H, m, SCH_2CH_2), 2.31–2.46 (1H, m, SCH_2CH_2), 2.64–2.76 (1H, m, SCH_2CH_2), 2.78–2.91 (1H, m, SCH_2CH_2), 3.78 and 3.79 (3H, s, O*Me* epimers), 4.10–4.38 (3H, m, *H*-5, *H*-6), 4.84–4.98 (1H, m, NHC*H*), 5.33–5.51 (1H, m, *H*-4), 5.58 (1H, d, *J* 9.0 Hz, *H*-3), 5.65 (1H, br s, *H*-1), 6.96–7.17 (1H, m, N*H* epimers), 7.36–7.55 (3H, m, ArC*H*), 7.78–7.87 (2H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.7 (OAc), 20.9 (OAc), 27.7 and 28.4 (SCH_2CH_2), 32.2–33.2 (SCH_2CH_2), 52.6 (NH*C*H), 52.7 (OMe), 62.4 (C-6), 64.7 (C-4), 67.3 (C-5), 81.0 (C-1), 115.9 (C-3), 127.1 (ArCH), 128.6 (ArCH), 131.8 (ArCH), 133.6 (ArC), 146.8 (C-2), 167.3 (C=O), 168.3 (C–O), 170.0 (C=O), 170.7 (C=O), 172.4 (C=O). IR ν_{max} (thin film)/cm^{-1} 1744 (C=O), 1650 (C=O). LRMS *m/z* 566 (17%), 524 (100%, M+H$^+$), 505 (62%), 404 (57%), 169 (20%). HRMS (CI, M+H$^+$), found: 524.1586; $C_{24}H_{30}NO_{10}S$ requires: 524.1590.

4.3.9. *N*-Benzoyl-*S*-(3-deoxy-2,4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-DL-homocysteine methyl ester (**57**)

Following *method B*, *N*-benzoyl-DL-homocysteine methyl ester (**48**) (125 mg, 0.5 mmol) and 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-lyxo-hex-1-enitol (**16**) (195 mg, 0.6 mmol) were stirred at room temperature for 2 h to afford, after purification by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine), **57** as a white powder (149 mg, 58%). R_f 0.4 (2:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz) 2.02 (3H, s, OC(O)CH_3), 2.08 (3H, s, OC(O)CH_3), 2.15 (3H, s, OC(O)CH_3), 2.29–2.43 (1H, m, SCH_2CH_2), 2.62–2.90 (3H, m, SCH_2CH_2, SCH_2CH_2), 3.77 and 3.79 (3H, s, O*Me* epimers), 4.06–4.13 (1H, m, *H*-5), 4.16–4.33 (2H, m, *H*-6), 4.48–4.55 (1H, m, NHC*H*), 5.22–5.29 (1H, m, *H*-4), 5.67 (1H, d, *J* 10.0 Hz, *H*-1), 5.84 (1H, d, *J* 5.5 Hz, *H*-3), 6.96–7.17 (1H, m, N*H* epimers), 7.37–7.56 (3H, m, ArC*H*), 7.77–7.88 (2H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.6 (OAc), 20.7 (OAc), 20.9 (OAc), 27.2 and 27.7 (SCH_2CH_2), 32.2 and 34.9 (SCH_2CH_2), 52.5 (NH*C*H), 52.7 (OMe), 62.2 (C-6), 64.4 (C-4), 67.0 (C-5), 80.6 (C-1), 112.3 (C-3), 127.1 (ArCH), 128.6 (ArCH), 131.9 (ArCH), 133.5 (ArC), 149.6 (C-2), 167.1 (C=O), 167.9 (C–O), 170.5 (C=O), 170.6 (C=O), 172.4 (C=O). IR ν_{max} (thin film)/cm^{-1} 1745 (C=O), 1651 (C=O). LRMS *m/z* 524 (62%, M+H$^+$), 506 (28%), 505 (100%), 404 (51%), 169 (19%). HRMS (CI, M+H$^+$), found: 524.1567; $C_{24}H_{30}NO_{10}S$ requires: 524.1590.

4.3.10. *N*-tert-Butoxycarbonyl-*O*-benzyl-L-serine-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-glucopyranosyl)-L-cysteine ethyl ester (**60**)

To a stirred solution of *N-tert*-butoxycarbonyl-*S*-(2,3-deoxy-4,6-tri-*O*-acetyl-α-D-glucopyranosyl)-L-cysteine ethyl ester (**58**) (25 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) was added 4 N HCl in dioxane (3 mL). The solution was stirred for 2 h and then concentrated in vacuo. The residue was taken up in CH_2Cl_2 (3 mL), and *N-tert*-butoxy-*O*-benzyl-L-serine (17 mg, 0.06 mmol), PyBOP (33 mg, 0.07 mmol) and triethylamine (0.02 mL, 0.14 mmol) were added with stirring. The resultant solution was stirred for 1 h and diluted with CH_2Cl_2 (10 mL), washed with 0.5 M HCl (10 mL), $NaHCO_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), filtered and concentrated in vacuo. The crude product was purified by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine) to yield **60** as a colourless oil (33 mg, 95%). R_f 0.4 (2:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +158 (*c* 0.25, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 1.27 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 1.44 (9H, s, $C(CH_3)_3$), 2.07 (3H, s, OC(O)CH_3), 2.11 (3H, s, OC(O)CH_3), 3.09–3.21 (2H, m, SCH_2), 3.59 (1H, dd, *J* 5.0, 9.0 Hz, OCH_2), 3.98 (1H, dd, *J* 3.5, 9.0 Hz, OCH_2), 4.13–4.45 (6H, m, H-5, H-6, OCH_2CH_3, Ser–NHC*H*), 4.52 (2H, AB, *J* 12.0 Hz, OCH_2Ph), 4.97 (1H, app. dt, *J* 4.0, 8.0 Hz, Cys–NHC*H*), 5.22–5.29 (1H, m, *H*-4), 5.35–5.40 (1H, m, *H*-1), 5.53 (1H, d, *J* 6.5 Hz, Ser–N*H*), 5.64–5.72 (2H, m, *H*-2, *H*-3), 7.28–7.38 (5H, m, ArC*H*), 7.58 (1H, d, *J* 8.0 Hz, Cys–N*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 14.2 (OCH_2CH_3), 20.8 (OAc), 21.0 (OAc), 28.3 ($C(CH_3)_3$), 35.3 (SCH_2), 52.9 (Cys–NH*C*H), 54.5 (Ser–NH*C*H), 61.8 (OCH_2CH_3), 62.9 (C-6), 65.0 (C-4), 67.7 (C-5), 70.5 (OCH_2), 73.5 (OCH_2Ph), 80.4 ($C(CH_3)_3$), 81.6 (C-1), 126.5 (C-3), 127.9 (ArCH), 128.5 (ArCH), 128.9 (C-2), 137.5 (ArC), 155.5 (C=O), 169.6 (C=O), 170.2 (C=O), 170.3 (C=O), 171.0 (C=O). IR ν_{max} (thin film)/cm^{-1} 1740 (C=O), 1664 (C=O). HRMS (EI, M+Na$^+$), found: 661.2393; $C_{30}H_{42}N_2O_{11}SNa$ requires: 661.2407.

4.3.11. *N*-tert-butoxycarbonyl-L-alanine-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-galactopyranosyl)-L-cysteine ethyl ester (**61**)

To a stirred solution of *N-tert*-butoxycarbonyl-*S*-(2,3-deoxy-4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-L-cysteine ethyl ester

(**59**) (34 mg, 0.07 mmol) in CH_2Cl_2 (3 ml) was added 4 N HCl in dioxane (3 mL). The solution was stirred for 2 h and then concentrated in vacuo. The residue was taken up in CH_2Cl_2 (3 mL), and *N*-*tert*-butoxy-L-alanine (15 mg, 0.08 mmol), Py-BOP (46 mg, 0.09 mmol) and triethylamine (0.02 mL, 0.18 mmol) were added with stirring. The resultant solution was stirred for 1 h and diluted with CH_2Cl_2 (10 mL), washed with 0.5 M HCl (10 mL), $NaHCO_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), filtered and concentrated in vacuo. The crude product was purified by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine) to yield **61** as a white solid (35 mg, 94%). R_f 0.3 (2:1 hexane/ethyl acetate); mp 96–99 °C. ^{1}H NMR (CDCl, 400 MHz) 1.28 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 1.39 (3H, d, *J* 7.0 Hz, Ala–*Me*), 1.44 (9H, s, $C(CH_3)_3$), 2.08 (3H, s, $OC(O)CH_3$), 2.11 (3H, s, $OC(O)CH_3$), 3.11 (1H, dd, *J* 4.0, 14.5 Hz, SCH_2), 3.26 (1H, dd, *J* 5.0, 14.5 Hz, SCH_2), 4.22 (2H, q, *J* 7.0 Hz, OCH_2CH_3), 4.20–4.25 (1H, m, Ala–NHC*H*), 4.26 (1H, dd, *J* 7.5, 11.5 Hz, *H*-6), 4.37 (1H, dd, *J* 5.5, 11.5 Hz, *H*-6), 4.45 (1H, ddd, *J* 2.5, 5.5, 7.5 Hz, *H*-5), 4.93 (1H, app. dt, *J* 4.0 8.0 Hz, Cys–NHC*H*), 5.06 (1H, dd, *J* 2.5, 5.0 Hz, *H*-4), 5.16 (1H, d, *J* 5.5 Hz, Ala–N*H*), 5.52–5.56 (1H, m, *H*-1), 6.01 (1H, ddd, *J* 1.5, 5.0, 10.0 Hz, *H*-3), 6.07 (1H, dd, *J* 3.0, 10.0 Hz, *H*-2), 7.23 (1H, d, *J* 8.0 Hz, Cys–N*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 14.2 (OCH_2CH_3), 18.6 (Ala–Me), 20.8 (OAc), 28.3 ($C(CH_3)_3$), 35.0 (SCH_2), 50.1 (Ala–NHCH), 52.4 (Cys–NHCH), 61.9 (OCH_2CH_3), 62.5 (C-6), 63.0 (C-4), 67.5 (C-5), 80.1 ($C(CH_3)_3$), 81.4 (C-1), 123.8 (C-3), 131.4 (C-2), 155.3 (C=O), 169.9 (C=O), 170.3 (C=O), 170.8 (C=O), 172.6 (C=O). IR ν_{max} (thin film)/cm^{-1} 1740 (C=O), 1677 (C=O), 756 (C=C). HRMS (CI, M+H$^+$), found: 533.2172; $C_{23}H_{37}N_2O_{10}S$ requires: 533.2169.

4.3.12. *N*-Benzoyl-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-L-cysteine ethyl ester (**62**)

Following the general method, *N*-benzoyl-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-glycopyranosyl)-L-cysteine ethyl ester (**49**) (148 mg, 0.3 mmol) was stirred with osmium tetroxide (100 mg, 0.4 mmol) at room temperature overnight. Subsequent per-O-acetylation afforded, after purification by column chromatography (1:1 to 1:2 hexane/ethyl acetate), **62** as a colourless oil (106 mg, 57%). R_f 0.4 (1:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +56 (*c* 1.25, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 1.31 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 1.95 (3H, s, $OC(O)CH_3$), 1.99 (3H, s, $OC(O)CH_3$), 2.05 (3H, s, $OC(O)CH_3$), 2.15 (3H, s, $OC(O)CH_3$), 3.22 (1H, dd, *J* 3.5, 14.5 Hz, SCH_2), 3.39 (1H, dd, *J* 4.5, 14.5 Hz, SCH_2), 4.18–4.22 (2H, m, *H*-6), 4.27 (2H, q, *J* 7.0 Hz, OCH_2CH_3), 4.33 (1H, ddd, *J* 3.5, 5.0, 10.0 Hz, *H*-5), 5.17 (1H, dd, *J* 3.5, 10.0 Hz, *H*-3), 5.23–5.32 (3H, m, H-1, H-4, NHC*H*), 5.38 (1H, dd, *J* 1.5, 3.5 Hz, *H*-2), 7.39–7.48 (3H, m, ArC*H*, N*H*), 7.53 (1H, tt, *J* 2.0, 7.5 Hz, ArC*H*), 7.85–7.90 (2H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 14.2 (OCH_2CH_3), 20.5 (OAc), 20.6 (OAc), 20.7 (OAc), 20.9 (OAc), 36.1 (SCH_2), 52.1 (NHCH), 62.1 (OCH_2CH_3), 62.4 (C-6), 66.0 (C-4), 69.0 (C-2), 70.0 (C-5), 71.2 (C-3), 84.2 (C-1), 127.3, 128.5 and 132.0 (ArCH), 133.6 (ArC), 167.0 (C=O), 169.7 (C=O), 169.8 (C=O), 169.9 (C=O), 170.1 (C=O), 170.6 (C=O). IR ν_{max} (thin film)/cm^{-1} 1746 (C=O), 1664 (C=O), 1224 (CH_{arom}). LRMS *m*/*z* 584 (37%, M+H$^+$), 403 (19%), 331 (100%), 251 (23%), 218 (25%), 169 (57%). HRMS (CI, M+H$^+$), found: 584.1788; $C_{26}H_{34}NO_{12}S$ requires: 584.1802.

4.3.13. *N*-Benzoyl-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-talopyranosyl)-L-cysteine ethyl ester (**63**)

Following the general method, *N*-benzoyl-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-galactopyranosyl)-L-cysteine ethyl ester (**51**) (53 mg, 0.1 mmol) was stirred with osmium tetroxide (28 mg, 0.1 mmol) at room temperature overnight. Subsequent per-O-acetylation afforded, after purification by column chromatography (1:1 to 1:2 hexane/ethyl acetate), **63** as a colourless oil (41 mg, 62%). R_f 0.2 (1:1 hexane/ethyl acetate); $[\alpha]_D^{20}$ +87 (*c* 0.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 1.31 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 1.86 (3H, s, $OC(O)CH_3$), 2.07 (3H, s, $OC(O)CH_3$), 2.13 (3H, s, $OC(O)CH_3$), 2.16 (3H, s, $OC(O)CH_3$), 2.99 (1H, dd, *J* 3.0, 15.0 Hz, SCH_2), 3.46 (1H, dd, *J* 4.5, 15.0 Hz, SCH_2), 3.98 (1H, dd, *J* 8.0, 11.5 Hz, *H*-6), 4.19–4.35 (3H, m, H-6, OCH_2CH_3), 4.66 (1H, ddd, *J* 1.5, 4.0, 8.0 Hz, *H*-5), 4.99 (1H, dd, *J* 1.5, 4.0 Hz, *H*-4), 5.25 (1H, app. t, *J* 3.5 Hz, *H*-3), 5.28–5.31 (1H, m, NHC*H*), 5.32 (1H, dd, *J* 3.5, 6.0 Hz, *H*-2), 5.46 (1H, d, *J* 6.0 Hz, *H*-1), 7.40–7.53 (3H, m, ArC*H*), 7.59 (1H, d, *J* 9.0 Hz, N*H*), 7.85–7.89 (2H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 14.3 (OCH_2CH_3), 20.4 (OAc), 20.7 (OAc), 20.8 (OAc), 20.9 (OAc), 37.9 (SCH_2), 52.9 (NHCH), 61.7 (OCH_2CH_3), 62.4 (C-6), 65.9 (C-5), 66.4 (C-2 or C-3), 66.6 (C-2 or C-3), 68.3 (C-4), 85.3 (C-1), 127.4, 128.5 and 131.9 (ArCH), 133.8 (ArC), 167.4 (C=O), 168.9 (C=O), 169.4 (C=O), 169.8 (C=O), 170.1 (C=O), 170.7 (C=O). IR ν_{max} (thin film)/cm^{-1} 1745 (C=O), 1656 (C=O), 1216 (CH_{arom}), 758 (CH_{arom}). LRMS *m*/*z* 584 (7%, M+H$^+$), 403 (11%), 331 (29%), 180 (76%), 180 (100%). HRMS (CI, M+H$^+$), found: 584.1821; $C_{26}H_{34}NO_{12}S$ requires: 584.1831.

4.3.14. *N*-Benzoyl-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-DL-homocysteine methyl ester (**64**)

Following the general method, *N*-benzoyl-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-D-glucopyranosyl)-DL-homocysteine methyl ester (**50**) (30 mg, 0.06 mmol) was stirred with osmium tetroxide (16 mg, 0.06 mmol) at room temperature overnight. Subsequent per-O-acetylation afforded, after purification by column chromatography (1:1 to 1:2 hexane/ethyl acetate, 1% triethylamine), **64** as a colourless oil (22 mg, 56%). R_f 0.2 (1:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 500 MHz) 1.98 (3H, s, $OC(O)CH_3$), 2.04 (3H, s, $OC(O)CH_3$), 2.08 (3H, s, $OC(O)CH_3$), 2.15 (3H, s, $OC(O)CH_3$), 2.13–2.19 (1H, m, SCH_2CH_2), 2.26–2.44 (1H, m, SCH_2CH_2), 2.60–2.84 (2H, m, SCH_2CH_2), 3.80 (3H, s, O*Me*), 4.00–4.17 (1H, m, *H*-6), 4.30 (1H, ddd, *J* 4.0, 5.0, 12.5 Hz, *H*-5), 4.32–4.40 (1H, m, *H*-6), 4.81–5.14 (1H, m, NHC*H*), 5.23 (1H, dd, *J* 3.5, 10.0 Hz, *H*-3), 5.25–5.31 (2H, m, *H*-1, *H*-4), 5.33 (1H, dd, *J* 1.5, 3.5 Hz, *H*-2), 6.79 (1H, app. t, *J* 8.0 Hz, N*H*), 7.41–7.56 (3H, m, ArC*H*), 7.77–7.95 (2H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 125 MHz) 20.6 (OAc), 20.7 (OAc), 20.9 (OAc), 27.4 (SCH_2CH_2), 32.7 (SCH_2CH_2), 52.5 (NHCH), 62.4 (C-6), 66.2

(C-4), 69.2 (C-5), 69.3 (C-3), 70.9 (C-2), 82.4 (C-1), 127.1–128.6 (ArCH), 131.9 (ArC), 167.1 (C=O), 169.7 (C=O), 169.7 (C=O), 169.9 (C=O), 170.6 (C=O), 172.3 (C=O). IR ν_{max} (thin film)/cm^{-1} 1745 (C=O), 1665 (C=O), 1223 (CH_{arom}). LRMS *m/z* 606 (100%, $M+Na^+$), 584 (21%, MH^+), 524 (24%), 442 (27%), 331 (32%). HRMS (ESI, $M+H^+$), found: 584.1789; $C_{26}H_{34}NO_{12}S$ requires: 584.1801.

4.3.15. *N*-Benzoyl-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-talopyranosyl)-DL-homocysteine methyl ester (**65**)

Following the general method, *N*-benzoyl-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-D-galactopyranosyl)-DL-homocysteine methyl ester (**55**) (30 mg, 0.06 mmol) was stirred with osmium tetroxide (16 mg, 0.06 mmol) at room temperature overnight. Subsequent per-O-acetylation afforded, after purification by column chromatography (1:1 to 1:2 hexane/ethyl acetate, 1% triethylamine), **65** as a colourless oil (21 mg, 55%). R_f 0.4 (1:2 hexane/ethyl acetate). ^1H NMR ($CDCl_3$, 500 MHz) 2.00 (3H, s, OC(O)CH_3), 2.04 (3H, s, OC(O)CH_3), 2.11 (3H, s, OC(O)CH_3), 2.13 (3H, s, OC(O)CH_3), 2.24–2.42 (1H, m, SCH_2CH$_2$), 2.53–2.88 (3H, m, SCH_2CH$_2$, SCH$_2$CH_2), 3.79 (3H, s, O*Me*), 4.05–4.18 (2H, m, *H*-6), 4.87–4.95 (1H, m, NHC*H*), 4.99–5.03 (1H, m, *H*-4), 5.21–5.25 (1H, m, *H*-3), 5.28–5.38 (1H, m, *H*-1), 5.46 (1H, app. t, *J* 6.5 Hz, *H*-2), 6.94 (1H, d, *J* 7.5 Hz, N*H*), 7.43–7.57 (3H, m, ArC*H*), 7.78–7.89 (2H, m, ArC*H*). ^{13}C NMR ($CDCl_3$, 125 MHz) 20.6 (OAc), 20.7 (OAc), 20.9 (OAc), 28.2 (S*C*H$_2$CH$_2$), 33.1 (SCH$_2$*C*H$_2$), 52.0 (NH*C*H), 61.8 (C-6), 66.7 (C-4), 67.9 (C-5), 68.2 (C-3), 80.6 (C-2), 82.8 (C-1), 127.1 (ArCH), 127.2 (ArCH), 128.6 (ArCH), 131.9 (ArC), 169.4 (C=O), 172.4 (C=O). IR ν_{max} (thin film)/cm^{-1} 1744 (C=O), 1655 (C=O), 1216 (CH_{arom}). LRMS *m/z* 606 (100%, $M+Na^+$), 584 (26%, MH^+), 331 (56%), 279 (8%), 169 (5%). HRMS (ESI, $M+H^+$), found: 584.1807; $C_{26}H_{34}NO_{12}S$ requires: 584.1801.

4.4. General method: deprotection

Method A. To a stirred solution of S-linked disaccharide (1 equiv) in anhydrous methanol (1 mL/mmol) under an atmosphere of argon was added K_2CO_3 (0.1 equiv) or NaOMe (0.1 equiv). The reaction mixture was stirred at room temperature until the reaction was shown to have reached completion by TLC analysis. The reaction mixture was then neutralised by the addition of Amberlite IR120 H^+, filtered and concentrated in vacuo.

Method B. A stirred solution of S-linked glycoamino acid (1 equiv) and DMAP (0.2 equiv) and di-*tert*-butyl dicarbonate (2 equiv) in anhydrous THF (3 mL/mmol) was stirred under an atmosphere of argon at room temperature overnight. The resultant solution was then diluted with ethanol (3 mL/mmol) and $N_2H_4\cdot H_2O$ (4 equiv) was added, the solution was then stirred for a further 2 h, and then poured into CH_2Cl_2 (10 mL) and washed with 1 N HCl (10 mL), $NaHCO_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was subjected to purification by column chromatography.

Method C. A stirred solution of S-linked glycoamino acid (1 equiv) and DMAP (0.2 equiv) and di-*tert*-butyl dicarbonate (2 equiv) in anhydrous THF (3 mL/mmol) was stirred under an atmosphere of argon at room temperature overnight. The resultant solution was then diluted with methanol (3 mL/mmol) and $N_2H_4\cdot H_2O$ (4 equiv) was added, the solution was then stirred for a further 2 h, and then poured into CH_2Cl_2 (10 mL) and washed with 1 N HCl (10 mL), $NaHCO_3$ (10 mL) and brine (10 mL), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was subjected to purification by column chromatography.

Method D. To a stirred solution of Boc-protected S-linked glycoamino acid (1 equiv) in anhydrous ethanol (1 mL/mmol) under an atmosphere of argon was added NaOEt (0.1 equiv). The reaction mixture was stirred at room temperature until the reaction was shown to have reached completion by TLC analysis. The reaction mixture was then neutralised by the addition of Amberlite IR120H^+, filtered and concentrated in vacuo. The crude residue was then taken up in anhydrous CH_2Cl_2 (3 mL/mmol) and cooled to 0 °C. TFA (2 equiv) was added and stirred until the reaction was shown to have reached completion by TLC analysis, and then concentrated in vacuo.

Method E. To a stirred solution of Boc-protected S-linked glycoamino acid (1 equiv) in anhydrous methanol (1 mL/mmol) under an atmosphere of argon was added NaOMe (0.1 equiv). The reaction mixture was stirred at room temperature until the reaction was shown to have reached completion by TLC analysis. The reaction was then neutralised by the addition of Amberlite IR120H^+, filtered and concentrated in vacuo. The crude residue was then taken up in anhydrous CH_2Cl_2 (3 ml/mmol) and cooled to 0 °C. TFA (2 equiv) was added and stirred until the reaction was shown to have reached completion by TLC analysis, and then concentrated in vacuo.

4.4.1. Methyl 6-*S*-(2,3-dideoxy-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (**38**)

Following *method A*, methyl 2,3,4-tri-*O*-acetyl-6-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (**12**) (14 mg, 0.02 mmol) and K_2CO_3 (3 mg, 0.002 mmol) were stirred overnight to afford **38** as a colourless oil (8 mg, quant.). $[\alpha]_D^{20}$ +103 (*c* 0.43, H_2O). ^1H NMR (D_2O, 400 MHz) 2.86 (1H, dd, *J* 8.0, 14.0 Hz, *H*-6), 3.29 (1H, dd, *J* 3.0, 14.0 Hz, *H*-6), 3.38–3.45 (1H, m, *H*-4), 3.34 (3H, s, O*Me*), 3.59 (1H, dd, *J* 4.0, 10.0 Hz, *H*-2), 3.36 (1H, dd, *J* 9.0, 10.0 Hz, *H*-3), 3.78 (1H, dd, *J* 6.0, 12.5 Hz, *H*-6′), 3.83 (1H, dd, *J* 2.5, 7.5, 10.0 Hz, *H*-5), 3.91 (1H, dd, *J* 2.5, 12.5 Hz, *H*-6′), 3.96 (1H, ddd, *J* 2.5, 6.0, 8.5 Hz, *H*-5′), 4.20 (1H, ddd, *J* 2.0, 3.5, 13.0 Hz, *H*-4′), 4.78–4.81 (1H, m, *H*-1), 5.68–5.72 (1H, m, *H*-1′), 5.90 (1H, dt, *J* 1.5, 10.0 Hz, *H*-3′), 5.96 (1H, ddd, *J* 2.0, 2.0, 10.0 Hz, *H*-2′). ^{13}C NMR (D_2O, 100 MHz) 35.2 (C-6), 58.0 (OMe), 63.7 (C-6′), 65.4 (C-4′), 73.1 (C-5), 74.1 (C-2), 74.8 (C-5′), 75.1 (C-4), 75.8 (C-3), 82.4 (C-1′), 102.1 (C-1), 130.0 (C-3′), 133.4 (C-2′). IR ν_{max} (thin film)/cm^{-1} 3443 (OH). LRMS *m/z* 339 (8%, MH^+), 180 (9%), 161 (52%), 135 (100%). HRMS (CI, $M+H^+$), found: 339.1123; $C_{13}H_{23}O_8S$ requires: 339.1114.

*4.4.2. Methyl 6-S-(2,3-dideoxy-α-D-galactopyranosyl)-6-thio-α-D-glucopyranoside (**39**)*

Following *method A*, methyl 2,3,4-tri-*O*-acetyl-6-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-galactopyranosyl)-6-thio-α-D-glucopyranoside (**17**) (20 mg, 0.04 mmol) and K_2CO_3 (1 mg, 0.004 mmol) were stirred for 2 h to afford **39** as a colourless oil (12 mg, quant.). $[\alpha]_D^{20}$ +118 (*c* 0.35, MeOH). ^{1}H NMR (D_2O, 400 MHz) 2.54 (1H, dd, *J* 7.5, 14.0 Hz, *H*-6), 2.98 (1H, dd, *J* 2.5, 14.0 Hz, *H*-6), 3.10–3.15 (1H, m, *H*-4), 3.16 (3H, s, O*Me*), 3.28 (1H, dd, *J* 3.5, 9.5 Hz, *H*-2), 3.32–3.36 (1H, m, *H*-3), 2.48–3.70 (3H, m, *H*-5, *H*-6′), 3.70 (1H, dd, *J* 2.5, 4.5 Hz, *H*-4′), 3.96 (1H, ddd, 2.5, 4.0, 6.5 Hz, *H*-5′), 4.46–4.56 (1H, m, *H*-1), 5.46 (1H, d, *J* 2.0 Hz, *H*-1′), 5.73–5.79 (2H, m, *H*-2′, *H*-3′). ^{13}C NMR (D_2O, 100 MHz) 34.4 (C-6), 57.8 (OMe), 63.9 (C-6′), 72.0 (C-4′), 73.0 (C-5), 74.0 (C-2), 74.2 (C-5′), 74.9 (C-4), 75.6 (C-3), 82.3 (C-1′), 102.0 (C-1), 130.1 (C-3′), 132.0 (C-2′). IR ν_{max} (thin film)/cm^{-1} 3443 (OH). LRMS *m*/*z* 395 (100%, M+Na$^+$), 390 (2%), 335 (9%), 331 (32%), 323 (4%). HRMS (ESI$^-$, M−H), found: 337.0952; $C_{13}H_{21}O_8S$ requires: 337.0957.

*4.4.3. Methyl 6-O-benzyl-4-S-(2,3-dideoxy-α-D-glucopyranosyl)-4-thio-α-D-glucopyranoside (**40**)*

Following *method A*, methyl 6-*O*-benzyl-2,3-di-*O*-acetyl-4-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-glucopyranosyl)-6-thio-α-D-glucopyranoside (**28**) (42 mg, 0.07 mmol) and K_2CO_3 (1 mg, 7×10^{-6} mmol) were stirred for 2 h to afford **40** as a white powder (30 mg, quant.). $[\alpha]_D^{20}$ +164 (*c* 0.13, MeOH). ^{1}H NMR (MeOD, 400 MHz) 2.77 (1H, app. t, *J* 10.5 Hz, *H*-4), 3.44 (1H, dd, *J* 3.5, 9.5 Hz, *H*-2), 3.45 (3H, s, O*Me*), 3.64 (1H, dd, *J* 7.0, 12.0 Hz, *H*-6′), 3.85–4.05 (7H, m, *H*-3, *H*-5, *H*-6, *H*-4′, *H*-5′, *H*-6′), 4.63 (2H, s, OCH_2Ph), 4.76 (1H, d, *J* 3.5 Hz, *H*-1), 5.85–5.91 (3H, m, *H*-1′, *H*-2′, *H*-3′), 7.28–7.43 (5H, m, ArC*H*). ^{13}C NMR (MeOD, 100 MHz) 49.6 (C-4), 55.7 (OMe), 62.7 (C-6′), 64.1 (C-4′ or C-3), 71.7 (C-5 or C-5′), 71.9 (C-6), 73.7 (C-4′ or C-3), 74.1 (C-5 or C-5′), 74.5 (C-2 and OCH_2Ph), 80.7 (C-1′), 101.4 (C-1), 128.2 (C-3′), 128.7 (ArCH), 128.9 (ArCH), 129.4 (ArCH), 129.4 (ArCH), 132.9 (C-2′), 139.7 (ArC). IR ν_{max} (thin film)/cm^{-1} 3443 (OH). LRMS *m*/*z* 429 (1%, M+H$^+$), 428 (5%, M), 331 (100%), 245 (10%), 169 (65%). HRMS (ESI, M+NH_4^+), found: 446.1842; $C_{20}H_{32}O_8NS$ requires: 446.1849.

*4.4.4. Methyl 6-O-benzyl-4-S-(2,3-dideoxy-α-D-galactopyranosyl)-4-thio-α-D-glucopyranoside (**41**)*

Following *method A*, methyl 6-*O*-benzyl-2,3-di-*O*-acetyl-4-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-galactopyranosyl)-6-thio-α-D-glucopyranoside (**29**) (33 mg, 0.06 mmol) and K_2CO_3 (1 mg, 6×10^{-6} mmol) were stirred for 2 h to afford **41** as a white powder (23 mg, quant.). Mp 178–182 °C; $[\alpha]_D^{20}$ +57 (*c* 1.05, MeOH). ^{1}H NMR (MeOD, 400 MHz) 3.73 (1H, app. t, *J* 10.5 Hz, *H*-4), 3.40 (1H, dd, *J* 3.5, 9.5 Hz, *H*-2), 3.41 (3H, s, O*Me*), 3.76 (2H, d, *J* 6.0 Hz, *H*-6′), 3.83 (1H, dd, *J* 2.5, 5.0 Hz, *H*-4′), 3.85–3.98 (3H, m, *H*-5, *H*-6), 4.01 (1H, app. t, *J* 10.0 Hz, *H*-3), 4.18 (1H, ddd, *J* 2.5, 6.0, 6.0 Hz, *H*-5′), 4.59 (2H, s, OCH_2Ph), 4.73 (1H, d, *J* 3.5 Hz, *H*-1), 5.94–5.97 (2H, m, *H*-1′, *H*-2′), 5.98 (1H, dd, *J* 2.5, 5.0 Hz, *H*-3′), 7.26–7.37 (5H, m, ArC*H*). ^{13}C NMR (MeOD, 100 MHz) 49.9 (C-4), 55.7 (OMe), 62.8 (C-4′), 62.8 (C-6′), 71.7 (C-5), 71.9 (C-6), 73.4 (C-3), 73.4 (C-5′), 74.5 (OCH_2Ph), 80.7 (C-1′), 101.4 (C-1), 128.7 (C-3′), 128.9 (ArCH), 129.0 (ArCH), 129.3 (ArCH), 129.3 (ArCH), 130.5 (C-2′), 139.7 (ArC). IR ν_{max} (thin film)/cm^{-1} 3443 (OH). LRMS *m*/*z* 429 (20%, M+H$^+$), 428 (43%, M), 380 (23%), 379 (100%), 129 (23%). HRMS (CI, M+H$^+$), found: 429.1578; $C_{20}H_{29}SO_8$ requires: 429.1583.

*4.4.5. Methyl 6-S-(-D-mannopyranosyl)-6-thio-α-D-glucopyranoside (**42**)*

Following *method A*, methyl 2,3,4-tri-*O*-acetyl-6-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-6-thio-α-D-glucopyranoside (**32**) (25 mg, 0.04 mmol) and K_2CO_3 (2 mg, 0.004 mmol) were stirred for 2 h to afford **42** as a white powder (14 mg, quant.). Mp 192–193.5 °C; $[\alpha]_D^{20}$ +141 (*c* 0.51, H_2O). ^{1}H NMR (D_2O, 400 MHz) 2.66 (1H, dd, *J* 8.0, 14.0 Hz, *H*-6), 3.02 (1H, dd, *J* 2.5, 14.0 Hz, *H*-6), 3.23 (1H, dd, *J* 9.0, 9.5 Hz, *H*-4), 3.28 (3H, s, O*Me*), 3.43 (1H, dd, *J* 3.5, 9.5 Hz, *H*-2), 3.46–3.51 (1H, m, *H*-4′), 3.53 (1H, app. t, *J* 9.5 Hz, *H*-3), 3.61–3.69 (3H, m, *H*-3′, *H*-5, *H*-6′), 3.73 (1H, dd, *J* 2.5, 12.5 Hz, *H*-6′), 3.84 (1H, ddd, *J* 2.5, 6.0, 8.0 Hz, *H*-5′), 3.91 (1H, dd, *J* 1.5, 3.5 Hz, *H*-2′), 4.60–4.80 (1H, m, *H*-1), 5.20 (1H, d, *J* 1.5 Hz, *H*-1′). ^{13}C NMR (D_2O, 100 MHz) 31.8 (C-6), 55.4 (OMe), 61.1 (C-6′), 67.3 (C-3), 70.3 (C-3′), 71.4 (C-5), 71.6 (C-2), 71.9 (C-2′), 72.6 (C-4), 73.3 (C-4′), 73.6 (C-5′), 84.9 (C-1′), 99.6 (C-1). IR ν_{max} (thin film)/cm^{-1} 3443 (OH). LRMS *m*/*z* 417 (100%, MCOOH), 400 (7%), 371 (26%, M−H), 348 (18%). HRMS (ESI$^-$, MCO_2H), found: 417.1070; $C_{14}H_{25}O_{12}S$ requires: 417.1067.

*4.4.6. Methyl 6-S-(-D-talopyranosyl)-6-thio-α-D-glucopyranoside (**43**)*

Following *method A*, methyl 2,3,4-tri-*O*-acetyl-6-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-talopyranosyl)-6-thio-α-D-glucopyranoside (**33**) (13 mg, 0.02 mmol) and K_2CO_3 (1 mg, 0.002 mmol) were stirred for 2 h to afford **43** as a white powder (7 mg, quant.). Mp 212–214 °C; $[\alpha]_D^{20}$ +140 (*c* 0.5, H_2O). ^{1}H NMR (D_2O, 400 MHz) 2.91 (1H, dd, *J* 8.0, 14.0 Hz, *H*-6), 3.27 (1H, dd, *J* 2.5, 14.0 Hz, *H*-6), 3.48 (1H, dd, *J* 9.0, 9.5 Hz, *H*-4), 3.53 (3H, s, O*Me*), 3.68 (1H, dd, *J* 3.5, 9.5 Hz, *H*-2), 3.70–3.77 (1H, m, *H*-4′), 3.78 (1H, app. t, *J* 9.5 Hz, *H*-3), 3.86–3.95 (3H, m, *H*-3′, *H*-5, *H*-6′), 3.99 (1H, dd, *J* 2.0, 12.0 Hz, *H*-6′), 4.10 (1H, ddd, *J* 2.0, 6.0, 8.5 Hz, *H*-5′), 4.16 (1H, dd, *J* 1.5, 3.5 Hz, *H*-2′), 4.88 (1H, d, *J* 3.5 Hz, *H*-1), 5.45 (1H, d, *J* 1.5 Hz, *H*-1′). ^{13}C NMR (D_2O, 100 MHz) 31.8 (C-6), 55.4 (OMe), 61.1 (C-6), 67.3 (C-3), 70.2 (C-4′), 71.3 (C-3′), 71.5 (C-2), 71.9 (C-2′), 72.5 (C-4), 73.2 (C-5), 73.5 (C-5′), 84.8 (C-1′), 99.5 (C-1). IR ν_{max} (thin film)/cm^{-1} 3443 (OH). LRMS *m*/*z* 395 (100%, M+Na$^+$), 331 (30%), 209 (52%), 164 (27). HRMS (ESI, M+Na$^+$), found: 395.0998; $C_{13}H_{24}O_{10}SNa$ requires: 395.0988.

*4.4.7. Methyl 6-O-benzyl-4-S-(-D-mannopyranosyl)-6-thio-α-D-glucopyranoside (**44**)*

Following *method A*, methyl 6-*O*-benzyl-2,3-di-*O*-acetyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-6-thio-α-D-

glucopyranoside (**36**) (15 mg, 0.02 mmol) and K_2CO_3 (1 mg, 0.003 mmol) were stirred for 2 h to afford **44** as a colourless oil (10 mg, quant.). $[\alpha]_D^{20}$ +97 (*c* 0.21, MeOH). ^{1}H NMR (MeOD, 400 MHz) 2.83 (1H, app. t, *J* 11.0 Hz, *H*-4), 3.38 (3H, s, O*Me*), 3.44 (1H, dd, *J* 3.5, 9.5 Hz, *H*-2), 3.61 (1H, dd, *J* 3.0, 9.5 Hz, *H*-3′), 3.67 (1H, app. t, *J* 9.0 Hz, *H*-4′), 3.71 (1H, dd, *J* 6.0, 11.5 Hz, *H*-6′), 3.81–3.99 (6H, m, *H*-3, *H*-5, *H*-5′, *H*-6, *H*-6′), 4.02 (1H, dd, *J* 1.5, 3.0 Hz, *H*-2′), 4.60 (1H, d, *J* 14.0 Hz, OCH_2Ph), 4.64 (1H, d, *J* 14.0 Hz, OCH_2Ph), 4.76 (1H, d, *J* 3.5 Hz, *H*-1), 5.61 (1H, d, *J* 1.5 Hz, *H*-1′), 7.28–7.42 (5H, m, ArC*H*). ^{13}C NMR (MeOD, 100 MHz) 47.0 (C-4), 55.4 (OMe), 62.3 (C-6′), 68.4 (C-4′), 71.2 (C-3), 71.4 (C-6), 72.7 (C-3′), 73.7 (C-2′), 73.9 (C-5), 74.2 (C-2), 75.3 (C-5′), 86.3 (C-1′), 101.1 (C-1), 128.3 (ArCH), 128.6 (ArCH), 129.0 (ArCH), 137.9 (ArC). IR ν_{max} (thin film)/cm^{-1} 3443 (OH). LRMS *m/z* 485 (100%, M+Na$^+$), 483 (7%), 331 (2%), 251 (9%). HRMS (ESI$^-$, M−H), found: 461.1480; $C_{20}H_{29}O_{10}S$ requires: 461.1482.

4.4.8. Methyl 6-O-benzyl-4-S-(-D-talopyranosyl)-6-thio-α-D-glucopyranoside (45)

Following *method A*, methyl 6-*O*-benzyl-2,3-di-*O*-acetyl-4-*S*-(2,3,4,6-tetra-*O*-acetyl-α-D-talopyranosyl)-6-thio-α-D-glucopyranoside (**37**) (18 mg, 0.03 mmol) and K_2CO_3 (1 mg, 0.003 mmol) were stirred for 2 h to afford **45** as a colourless oil (12 mg, quant.). $[\alpha]_D^{20}$ +71 (*c* 0.54, MeOH). ^{1}H NMR (MeOD, 400 MHz) 2.66 (3H, app. t, *J* 9.5 Hz, *H*-4), 3.41 (3H, s, O*Me*), 3.44 (1H, dd, *J* 3.5, 9.5 Hz, *H*-2), 3.69 (1H, dd, *J* 4.5, 11.5 Hz, *H*-6′), 3.73–3.80 (2H, m, *H*-4′, *H*-6′), 3.81–3.91 (3H, m, *H*-3, *H*-3′, *H*-5′), 3.96 (1H, dd, *J* 2.0, 11.0 Hz, *H*-6), 4.01 (1H, dd, *J* 5.0, 11.0 Hz, *H*-6), 4.17 (1H, dd, *J* 3.0, 6.0 Hz, *H*-2′), 4.32–4.40 (1H, m, *H*-5), 4.59 (1H, d, *J* 11.5 Hz, OCH_2Ph), 4.63 (1H, d, *J* 11.5 Hz, OCH_2Ph), 4.73 (1H, d, *J* 3.5 Hz, *H*-1), 5.42 (1H, d, *J* 6.0 Hz, *H*-1′), 7.24–7.41 (5H, m, ArC*H*). ^{13}C NMR (MeOD, 100 MHz) 51.9 (C-4), 55.7 (OMe), 62.8 (C-6′), 67.4 (C-2′), 69.6 (C-5), 71.1 (C-4), 71.7 (C-6), 72.2, 73.1 and 73.6 (C-3, C-3′ and C-5′), 74.3 (C-2), 74.4 (OCH_2Ph), 87.6 (C-1′), 101.4 (C-1), 128.6 (ArCH), 128.9 (ArCH), 129.3 (ArCH), 138.1 (ArC). IR ν_{max} (thin film)/cm^{-1} 3443 (OH). LRMS *m/z* 485 (46%, MNa$^+$), 483 (77%), 461 (100%, M-H), 331 (2%), 251 (9%). HRMS (ESI$^-$, M−H), found: 461.1491; $C_{20}H_{29}O_{10}S$ requires: 461.1482.

4.4.9. N-tert-Butoxycarbonyl-S-(2,3-dideoxy-4,6-di-O-acetyl-α-D-glucopyranosyl)-L-cysteine ethyl ester (58)

Following *method B*, *N*-benzoyl-*S*-(2,3-dideoxy-4,6-tri-*O*-acetyl-α-D-glucopyranosyl)-L-cysteine ethyl ester (**49**) (140 mg, 0.3 mmol), DMAP (4 mg, 0.03 mmol) and di-*tert*-butyl dicarbonate (129 mg, 0.6 mmol) were stirred at room temperature overnight, after subsequent treatment with $N_2H_4\cdot H_2O$ (0.05 mL, 1.2 mmol) afforded, after purification by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine), **58** as a white solid (127 mg, 92%). R_f 0.4 (2:1 hexane/ethyl acetate); mp 134–135 °C; $[\alpha]_D^{20}$ +100.8 (*c* 0.25, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 1.27 (3H, t, *J* 7.0 Hz, OCH$_2$CH_3), 1.43 (9H, s, ^{t}*Bu*), 2.09 (3H, s, OC(O)CH_3), 2.16 (3H, s, OC(O)CH_3), 3.04 (1H, dd, *J* 3.5, 14.5 Hz, SCH_2), 3.34 (1H, dd, *J* 5.0, 14.5 Hz, SCH_2), 4.17–4.33 (5H, m, H-5, H-6, OCH_2CH$_3$), 4.62–4.69 (1H, m, *H*), 5.33 (1H, ddd, *J* 2.0, 4.0, 9.0 Hz, *H*-4), 5.46–5.51 (1H, m, *H*-1), 5.79 (1H, app. dt, *J* 2.0, 10.0 Hz, *H*-3), 5.92 (1H, ddd, *J* 2.0, 3.0, 10.0 Hz, *H*-2), 6.02 (1H, d, *J* 9.0 Hz, N*H*). ^{13}C NMR ($CDCl_3$, 100 MHz) 14.2 (OCH$_2$*C*H$_3$), 20.8 (OAc), 21.0 (OAc), 28.3 (^{t}Bu), 36.3 (SCH$_2$), 53.8 (C), 61.6 (O*C*H$_2$CH$_3$), 63.1 (C-6), 64.7 (C-4), 67.4 (C-5), 79.9 (*C*(CH$_3$)$_3$), 82.2 (C-1), 127.2 (C-3), 128.5 (C-2), 155.5 (C=O), 170.2 (C=O), 170.6 (C=O), 170.9 (C=O). IR ν_{max} (thin film)/cm^{-1} 1743.4 (C=O), 1716.1 (C=O). HRMS (EI M+Na$^+$), found: 484.1607; $C_{20}H_{31}NO_9SNa$ requires: 484.1617.

4.4.10. N-tert-Butoxycarbonyl-S-(2,3-dideoxy-4,6-di-O-acetyl-α-D-galactopyranosyl)-L-cysteine ethyl ester (59)

Following *method B*, *N*-benzoyl-*S*-(2,3-dideoxy-4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-L-cysteine ethyl ester (**51**) (75 mg, 0.16 mmol), DMAP (4 mg, 0.03 mmol) and di-*tert*-butyl dicarbonate (70 mg, 0.32 mmol) were stirred at room temperature overnight, after subsequent treatment with $N_2H_4\cdot H_2O$ (0.03 mL, 6.4 mmol) afforded, after purification by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine), **59** as a white solid (68 mg, 92%). R_f 0.4 (2:1 hexane/ethyl acetate); mp 178–182 °C; $[\alpha]_D^{20}$ −62.5 (*c* 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz) 1.28 (3H, t, *J* 7.0 Hz, OCH$_2$CH_3), 1.45 (9H, s, ^{t}*Bu*), 2.09 (3H, s, OC(O)CH_3), 2.16 (3H, s, OC(O)CH_3), 3.02 (1H, dd, *J* 3.5, 14.5 Hz, SCH_2), 3.38 (1H, dd, *J* 5.0, 14.5 Hz, SCH_2), 4.17–4.33 (4H, m, H-6, OCH_2CH$_3$), 4.49 (1H, ddd, *J* 2.5, 5.0, 7.5 Hz, *H*-5), 4.62–4.70 (1H, m, *H*-6), 5.07 (1H, dd, *J* 2.5, 5.0 Hz, *H*-4), 5.52–5.57 (1H, m, *H*-1), 6.00–6.03 (1H, m, N*H*), 6.04 (1H, ddd, *J* 1.5, 5.0, 10.0 Hz, *H*-3), 6.10 (1H, dd, *J* 3.0, 10.0 Hz, *H*-2). ^{13}C NMR ($CDCl_3$, 100 MHz) 14.2 (OCH$_2$CH$_3$), 20.8 (OAc), 20.8 (OAc), 28.3 (^{t}Bu), 36.3 (SCH$_2$), 53.8 (C), 61.6 (OCH$_2$CH$_3$), 62.9 (C-6), 63.1 (C-4), 67.5 (C-5), 79.9 (C(CH$_3$)$_3$), 82.1 (C-1), 123.9 (C-3), 131.4 (C-2), 155.5 (C=O), 170.3 (C=O), 170.6 (C=O), 170.9 (C=O). IR ν_{max} (thin film)/cm^{-1} 1743 (C=O), 1719 (C=O). HRMS (CI, MH$^+$), found: 462.1805; $C_{20}H_{32}NO_9S$ requires: 462.1798.

4.4.11. S-(2,3-Dideoxy-α-D-glucopyranosyl)-DL-cysteine (66)

Following *method D*, *N*-*tert*-butoxycarbonyl-*S*-(2,3-dideoxy-4,6-tri-*O*-acetyl-α-D-glucopyranosyl)-L-cysteine ethyl ester (**58**) (31 mg, 0.07 mmol) and NaOEt (1 mg, 0.1 mmol) were stirred for 2 h at room temperature, after cooling to 0 °C, stirring with trifluoroacetic acid (2 mL) for 30 min afforded **66** was a colourless oil (17 mg, quant.). ^{1}H NMR (D_2O, 400 MHz) 3.23 (1H, dd, *J* 3.5, 6.0 Hz, SCH_2), 3.55–3.85 (3H, m, *H*-5, *H*-6), 3.96–4.02 (1H, m, NHC*H*), 4.30 (1H, dd, *J* 4.5, 6.0 Hz, *H*-4), 5.55 (1H, br s, *H*-1), 5.73–5.84 (2H, m, *H*-2, *H*-3). ^{13}C NMR (D_2O, 100 MHz) 32.9 (SCH$_2$), 53.5 (NH*C*H), 61.1 and 62.7 (C-6), 70.1 (C-5), 72.9 (C-4), 82.0 (C-1), 114.3 and 118.9 (C-3), 126.7 and 131.4 (C-2), 163.0 and 163.5 (C=O). IR ν_{max} (thin film)/cm^{-1} 3443 (OH). LRMS *m/z* 250 (100%, M+H$^+$), 249 (26%, M$^+$), 134 (28%), 129 (43%). HRMS (ESI, MH$^+$), found: 250.0753; $C_9H_{16}NO_5S$ requires: 250.0749.

*4.4.12. S-(2,3-Dideoxy-α-D-galactopyranosyl)-DL-cysteine ethyl ester (**67**)*

Following *method D*, *N-tert*-butoxycarbonyl-*S*-(2,3-dideoxy-4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-L-cysteine ethyl ester (**59**) (32 mg, 0.07 mmol) and NaOEt (1 mg, 0.1 mmol) were stirred for 2 h at room temperature, after cooling to 0 °C, stirring with trifluoroacetic acid (2.5 mL) for 30 min afforded **67** as a colourless oil (19 mg, quant.). ^{1}H NMR (D_2O, 250 MHz) 1.09–1.19 (3H, m, OCH_2CH_3), 2.86–3.30 (3H, m, SCH_2, *H*-6), 3.62–3.71 (3H, m, NHC*H*, *H*-5, *H*-6), 3.82–3.86 (2H, m, OC*H*CH), 4.45–4.67 (1H, m, *H*-4), 5.60 (1H, br s, *H*-1), 5.87–6.00 (2H, m, *H*-2, *H*-3). ^{13}C NMR (D_2O, 63 MHz) 17.6 (OCH_2CH_3), 29.8 (SCH_2), 59.7 (NHCH), 60.4 (C-6), 61.1 (OCH_2CH_3), 64.5 (C-5), 78.4 (C-4), 82.2 (C-1), 127.8 (C-3), 137.3 (C-2), 168.5 (C=O). IR ν_{max} (thin film)/cm^{-1} 3443 (OH). LRMS *m/z* 300 (15%, M+Na$^+$), 278 (32%, MH$^+$), 277 (26%, M$^+$), 148 (23%), 129 (35%). HRMS (ESI, M), found: 277.0990; $C_{11}H_{20}NO_5S$ requires: 277.0984.

*4.4.13. N-tert-Butoxycarbonyl-S-(2,3-dideoxy-4,6-tri-O-acetyl-α-D-glucopyranosyl)-DL-homocysteine methyl ester (**68**)*

Following *method C*, *N*-benzoyl-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-glucopyranosyl)-DL-homocysteine methyl ester (**50**) (60 mg, 0.12 mmol), DMAP (1 mg, 0.03 mmol) and di-*tert*-butyl dicarbonate (56 mg, 0.25 mmol) were stirred at room temperature overnight, after subsequent treatment with $N_2H_4\cdot H_2O$ (0.03 ml, 0.5 mmol) afforded, after purification by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine), **68** as a white solid (48 mg, 80%). R_f 0.3 (2:1 hexane/ethyl acetate). ^{1}H NMR ($CDCl_3$, 400 MHz) 1.46 (9H, s, $C(CH_3)_3$), 1.91–2.06 (1H, m, SCH_2CH_2), 2.09 (3H, s, $OC(O)CH_3$), 2.10 (3H, s, $OC(O)CH_3$), 2.13–2.25 (1H, m, SCH_2CH_2), 2.62–2.83 (2H, m, SCH_2CH_2), 3.75 (3H, s, O*Me*), 4.15–4.33 (3H, m, *H*-5, *H*-6), 4.38–4.48 (1H, m, NHC*H*), 5.10 (1H, d, *J* 8.0 Hz, N*H*), 5.33–5.40 (1H, m, *H*-4), 5.52–5.57 (1H, m, *H*-1), 5.57 (1H, dd, *J* 1.5, 10.5 Hz, *H*-3), 5.87–5.95 (1H, m, *H*-2). ^{13}C NMR ($CDCl_3$, 100 MHz) 20.8 (OAc), 21.0 (OAc), 27.9 (SCH_2CH_2), 28.3 ($C(CH_3)_3$), 33.2 and 33.3 (SCH_2CH_2), 52.5 (OMe), 52.8 (NHCH), 62.9 and 63.0 (C-6), 65.0 and 65.1 (C-4), 66.9 (C-5), 80.2 and 80.3 (C-1), 81.1 ($C(CH_3)_3$), 127.3 (C-3), 128.7 (C-2), 170.3 (C=O), 170.8 (C=O), 170.9 (C=O), 172.7 (C=O). IR ν_{max} (thin film)/cm^{-1} 1744 (C=O), 1716 (C=O). LRMS *m/z* 484 (100%, M+Na$^+$), 301 (11%), 251 (24%), 239 (11%). HRMS (CI, M+H$^+$), found: 462.1799; $C_{20}H_{32}NO_9S$ requires: 462.1798.

*4.4.14. N-tert-Butoxycarbonyl-S-(2,3-dideoxy-4,6-tri-O-acetyl-α-D-galactopyranosyl)-DL-homocysteine methyl ester (**69**)*

Following *method C*, *N*-benzoyl-*S*-(2,3-dideoxy-4,6-di-*O*-acetyl-α-D-galactopyranosyl)-DL-homocysteine methyl ester (**55**) (65 mg, 0.14 mmol), DMAP (1 mg, 0.03 mmol) and di-*tert*-butyl dicarbonate (60 mg, 0.28 mmol) were stirred at room temperature overnight, after subsequent treatment with $N_2H_4\cdot H_2O$ (0.03 ml, 0.55 mmol) afforded, after purification by column chromatography (2:1 hexane/ethyl acetate, 1% triethylamine), **69** as a white solid (64 mg, 88%). R_f 0.4 (2:1 hexane/ethyl acetate); mp 151–154 °C. ^{1}H NMR ($CDCl_3$, 250 MHz) 1.44 (9H, s, $C(CH_3)_3$), 1.94–2.25 (2H, m, SCH_2CH_2), 2.09 (6H, s, $OC(O)CH_3$), 2.58–2.84 (2H, m, SCH_2CH_2), 3.75 (3H, s, O*Me*), 4.10–4.55 (4H, m, NHC*H*, *H*-5, *H*-6), 5.07 (1H, dd, *J* 2.5, 4.5 Hz, *H*-4), 5.10–5.13 (1H, m, N*H*), 5.62 (1H, br s, *H*-1), 5.59–6.13 (2H, m, *H*-2, *H*-3). ^{13}C NMR ($CDCl_3$, 63 MHz) 21.2 (OAc), 28.0 (SCH_2CH_2), 28.6 ($C(CH_3)_3$), 33.6 (SCH_2CH_2), 52.6 (OMe), 52.8 (NHCH), 63.0 (C-6), 63.7 (C-4), 67.1 (C-5), 80.1 (C-1), 80.7 ($C(CH_3)_3$), 124.4 (C-3), 132.0 (C-2), 155.7 (C=O), 170.6 (C=O), 171.0 (C=O), 173.0 (C=O). IR ν_{max} (thin film)/cm^{-1} 1743 (C=O), 1716 (C=O). LRMS *m/z* 462 (6%, M+H$^+$), 406 (11%), 284 (11%), 213 (90%), 111 (100%). HRMS (CI, MH$^+$), found: 462.1802; $C_{20}H_{32}NO_9S$ requires: 462.1798.

*4.4.15. S-(2,3-Dideoxy-α-D-glucopyranosyl)-DL-homocysteine methyl ester (**70**)*

Following *method E*, *N-tert*-butoxycarbonyl-*S*-(2,3-dideoxy-4,6-tri-*O*-acetyl-α-D-glucopyranosyl)-DL-homocysteine methyl ester (**68**) (20 mg, 0.05 mmol) and NaOMe (1 mg, 0.1 mmol) were stirred for 2 h at room temperature, after cooling to 0 °C, stirring with trifluoroacetic acid (3 mL) for 2 h afforded **70** as a colourless oil (12 mg, quant.). ^{1}H NMR (MeOD, 400 MHz) 1.95–2.09 (2H, m, SCH_2CH_2), 2.66–2.95 (2H, m, SCH_2CH_2), 3.35 (3H, s, O*Me*), 3.72–3.82 (1H, m, *H*-6), 3.83–3.93 (2H, m, *H*-5, *H*-6), 4.13–4.18 (1H, m, *H*-4), 4.21–4.34 (1H, m, NHC*H*), 5.60 (1H, br s, *H*-1), 5.83–5.91 (2H, m, *H*-2, *H*-3). ^{13}C NMR (MeOD, 100 MHz) 28.4 and 28.9 (SCH_2CH_2), 32.8 (SCH_2CH_2), 49.4 (OMe), 53.8 (NHCH), 62.3 (C-6), 62.6 (C-5), 73.1 (C-4), 80.9 (C-1), 127.9 (C-3), 132.3 (C-2), 167.2 (C=O). IR ν_{max} (thin film)/cm^{-1} 3443 (OH), 1716 (C=O). LRMS *m/z* 295 (10%, MNH$_4^+$), 278 (100%, M+H$^+$), 230 (32%), 129 (28%). HRMS (ESI$^-$, M–H), found: 276.0892; $C_{11}H_{18}NO_5S$ requires: 276.0906.

*4.4.16. S-(2,3-Dideoxy-α-D-galactopyranosyl)-DL-homocysteine methyl ester (**71**)*

Following *method E*, *N-tert*-butoxycarbonyl-*S*-(2,3-dideoxy-4,6-tri-*O*-acetyl-α-D-galactopyranosyl)-DL-homocysteine methyl ester (**69**) (24 mg, 0.05 mmol) and NaOMe (1 mg, 0.1 mmol) were stirred for 2 h at room temperature, after cooling to 0 °C, stirring with trifluoroacetic acid (3 mL) for 2 h afforded **71** as a colourless oil (13 mg, quant.). ^{1}H NMR (D_2O, 250 MHz) 1.82–2.40 (2H, m, SCH_2CH_2), 2.42–2.90 (2H, m, SCH_2CH_2), 3.62 and 3.67 (3H, s, O*Me* epimers), 3.69–4.10 (5H, m, NHC*H*, *H*-4, *H*-5, *H*-6), 5.89–5.97 (1H, m, *H*-1), 6.24–6.32 (2H, m, *H*-2, *H*-3). ^{13}C NMR (D_2O, 63 MHz) 29.3 (SCH_2CH_2), 38.2 (SCH_2CH_2), 44.2 (OMe), 51.2 (NHCH), 60.8 (C-6), 68.8 (C-5), 75.3 (C-4), 84.4 (C-1), 112.5 and 118.6 (C-3), 142.2 (C-2), 162.4 (C=O). IR ν_{max} (thin film)/cm^{-1} 3443 (OH), 1717 (C=O). LRMS *m/z* 300 (22%, M+Na$^+$), 295 (26%, MNH$_4^+$), 278 (100%, MH$^+$), 230 (28%), 129 (56%). HRMS (ESI$^-$, M–H), found: 276.0898; $C_{11}H_{18}NO_5S$ requires: 276.0906.

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