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Pentose and hexose sugars are abundant constituents of waste biomass, making them sustainable, chiral building blocks for organic synthesis. The demand for chiral saturated heterocyclic rings from the pharmaceutical industry is increasing as they provide well-defined three-dimensional frameworks that show increased metabolic resistance. Through the formation of thioacetals, sugars may be manipulated in their straight-chain form and dehydrated selectively under basic conditions at C-2. This approach was applied to an array of sugars and extended to the production of useful chiral THFs via further selective dehydration reactions.

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Regioselective Dehydration of Sugar Thioacetals under Mild Conditions

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ABSTRACT: Pentose and hexose sugars are abundant constituents of waste biomass, making them sustainable, chiral building blocks for organic synthesis. The demand for chiral saturated heterocyclic rings from the pharmaceutical industry is increasing as they provide well-defined three-dimensional frameworks that show increased metabolic resistance. Through the formation of thioacetals, sugars may be manipulated in their straight-chain form and dehydrated selectively under basic conditions at C-2. This approach was applied to an array of sugars and extended to the production of useful chiral THFs via further selective dehydration reactions.

Introduction:

Carbohydrate biomass is an abundant renewable resource which has enormous potential for the synthesis of valuable chemical building blocks. The sugars present in this material are of particular interest as a functionalised carbon source to produce chiral saturated heterocycles which are of widespread potential utility in pharmaceutical development. Whilst there are many well-established methods for converting sugars into chiral heterocycles such as tetrahydrofurans (THFs) and tetrahydropyrans (THPs), these typically rely on lengthy synthetic sequences involving the extensive use of protecting groups and high cost/energy reagents (e.g. Tf₂O). They are, therefore somewhat resource-intensive and relatively inefficient approaches, especially for the large-scale preparation of chiral building blocks, and chiral heterocycles derived from sugars remain relatively underexplored in drug discovery applications. The development of more efficient and sustainable synthetic routes to chiral building blocks from sugars is therefore of great interest, particularly if the use of protecting groups and high-cost reagents can be minimised or avoided. In this context, the identification of reactions that can be used to achieve the regioselective dehydration of sugars without the need for protecting groups is particularly important. Notably, the selective removal of one or more hydroxyl groups from the sugar backbone will lead to molecules with inherently more useful properties for pharmaceutical applications.

There have been recent reports on selective transformations of unprotected sugars and their derivatives using both biocatalytic and chemical approaches. De-oxygenation/dehydration of sugars is of particular interest and only a few approaches have been described. For example, Gagné has reported methods for the regioselective reductive cyclisation of protected sugar-derived polyols using silane reagents in the presence of Lewis acids such as B(C₆F₅)₃, leading to the formation of a range of chiral THFs and THPs which can be accessed from sugars in a few steps (Scheme 1a).
In previous work, we have developed methods for the regioselective dehydration of sugar hydrazones, e.g. 3, (Scheme 1b) to give access to a range of chiral THFs (e.g. syn-4 and anti-4) under very mild conditions. These reactions are readily scalable and provided access to useful chiral building blocks in only a few steps. Importantly, it was also observed that cyclisation of the sugar hydrazones under acidic or basic conditions provided complementary stereoselectivities. The acid-catalysed cyclisation takes place under thermodynamic control, most likely proceeding via the stabilised diazenium cation, whereas the base-mediated cyclisation appears to involve a kinetically controlled SN2 ring-opening of a cyclic carbonate intermediate which can epimerise prior to cyclisation. In this latter reaction, it was rationalised that the main role of the hydrazone is to hold the sugar in the open-chain conformation which facilitates cyclisation to the THF. We therefore envisaged that this approach could be extended to other open-chain sugars such as thioacetals. Given that the formation of dimethylhydrazones from hexoses is often slow and relatively low yielding, thioacetals might prove to be a more versatile alternative as they can readily be accessed from both pentoses and hexoses. In this paper, we describe methods for the regioselective dehydration of sugar thioacetals at C-2 and C-3 under mild and scalable conditions to provide access to novel chiral polyols and tetrahydrofurans (Scheme 1c).

Results and Discussion:

Using L-arabinose, which is available from waste sugar-beet pulp, as a test substrate, the corresponding ethyl- and phenyl thioacetals were prepared via reported procedures. Treatment of the ethyl thioacetal with K2CO3/dimethyl carbonate (DMC) led to the formation of a complex mixture of products. However, reaction of the readily formed phenyl thioacetal 5a under similar conditions led to the formation of the diphenyl ketene thioacetal 6a as a single product. In addition, purification of the phenylthioacetal derivatives could be achieved via recrystallisation, avoiding the need for column chromatography. Interestingly, unlike the reactions of the corresponding hydrazones, the THF was not formed, and a selective dehydration took place exclusively at the C-2 position to give alkene 6a in near quantitative yield (15 mmol scale, Scheme 2).
Scheme 2. Thioacetal protection of L-arabinose followed by selective dehydration under mild conditions.\textsuperscript{14,18}

![Scheme 2 Diagram](image)

The PhS groups in 5a make the C-1 proton fairly acidic, and hence, it is clear that an elimination reaction can take place readily when the C-2 hydroxyl group is activated by DMC.\textsuperscript{14} The formation of similar ketene dithioacetals has previously been reported as a problematic side reaction under harsh conditions involving reactions of protected derivatives with strong bases (e.g. sodium methylsulfinylmethylide or n-BuLi).\textsuperscript{19,20} Given that our reaction conditions are very mild, and that the reaction is selective and high yielding, this potentially offers a readily scalable method for the selective C-2 deoxygenation of sugars without the need for hydroxyl protecting groups. The scope of this approach more generally was then explored (Scheme 3).

Scheme 3. Selective dehydration of thioacetal-protected aldose sugars at the C-2 position under basic conditions.\textsuperscript{7} Isolated yields; Conversions were determined by \textsuperscript{1}H NMR spectroscopy against an internal standard of 1,4-dimethoxybenzene are shown in brackets.

![Scheme 3 Diagram](image)

Selective dehydration was carried out with an array of sugar dithioacetals, derived from aldose sugars, in moderate to excellent yields (48-99\%) for several pentose and hexose sugars (6a, 6b, 6e, 6f). However, some thioacetals, such as those derived from D-ribose (5c), L-rhamnose (5d) and D-mannose (5g), gave little to no conversion to the alkene. A common feature of the unsuccessful substrates is anti-stereochemistry at the C-2 and C-3 positions. This potentially provides a useful insight into the mechanism of the reaction, which is likely to occur via (reversible) formation of a cyclic carbonate at C-2/C-3, through reaction of the polyol with dimethyl carbonate. This then subsequently undergoes elimination by removal of the acidic C-1 proton (Scheme 4).
Scheme 4. Proposed mechanism for the selective dehydration of sugar dithioacetals with DMC and K$_2$CO$_3$, with the dehydration site shown in blue.

The stereochemical relationship between the C-2 and C-3 alcohols may well affect the ease with which the carbonate can be formed (Figure 1). As shown in structure 7c, sugars with anti stereochemistry at C-2/C-3 (e.g. D-rib) will have to form the more sterically hindered syn-cyclic carbonate. This hindered carbonate may also hinder alignment of the C-1 proton into the correct orientation for the subsequent E-2 elimination. In contrast, sugars with syn-stereochemistry at C-2/C-3 (L-ara) will form the less-hindered anti-cyclic carbonate (e.g. 7a) which can easily adopt the required conformation for E-2 elimination to generate the alkene. Preliminary DFT calculations suggest that the formation of the syn carbonate 7c from 5c is ~20.5 kJmol$^{-1}$ more endergonic than the formation of the anti carbonate 7a from 5a.

Figure 1. Intermediate carbonates formed under basic conditions with DMC from anti and syn sugar thioacetals derived from L-arabinose and D-ribose respectively. Sugar thioacetals are shown with the key stereochemical features encircled in red. DFT calculations suggest that formation of 7c from 5c is ~20.5 kJmol$^{-1}$ more endergonic than formation of 7a from 5a.

Attempts to use more reactive electrophiles such as (CDI) carbonyldiimidazole with 5c failed to give any improvement in the yield, indicating that the stereochemical relationship in these starting materials presents a significant barrier to successful dehydration under mild reaction conditions. An alternative strategy was therefore considered for anti-sugars which did not rely on the formation of a cyclic intermediate. It was envisaged that conversion of the thioacetal 5c to the corresponding peracetate could lead to sufficient activation of the C-2 alcohol for it to act as a leaving group, facilitating dehydration under basic conditions. Formation of the peracetate derivatives with pyridine/Ac$_2$O, prior to treatment with a base was explored for the D-ribose, L-rhamnose and D-mannose thioacetal derivatives (Scheme 5).

Following acetylation, the protected sugars were stirred under basic conditions and monitored for ketene thioacetal formation. Although unreactive when using K$_2$CO$_3$, the use of the stronger nitrogen bases DBU (18-diazabicyclo[5.4.0]undec-7-ene), TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) and MeTBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene), as well as t-BuOK led to formation of the desired products 8c, 8d, and 8g in 47-96% yields. Different bases proved to be preferable for each example studied.
Scheme 5. Selective dehydration of the anti sugar thioacetals via initial acetylation\textsuperscript{21} followed by base-mediated elimination.

With a series of sugar-derived ketene dithioacetals in hand, we then went on to explore the reactivity of these novel compounds. We envisaged that reductive desulfurization of the ketene acetal group could lead to valuable chiral polyols containing a stereogenic centre bearing an ethyl group. Thus, reduction of L-arabinose derivative 6a with Raney-Ni gave a triol 9, which was isolated as the corresponding benzoate ester derivative 10 in 94\% overall yield (Scheme 6). Depending on the sugar used, chiral polyols of this general structure could be useful in the synthesis of natural products such as eicosatetraenoic acid precursor 11,\textsuperscript{22} polysaccharides found in gram-negative bacteria 12,\textsuperscript{23} and cholesterol side-chains (dihydroxyvitamins).\textsuperscript{24}

The reactivity of the dithioalkene motif in compound 6a was also explored. In principle, this alkene has the potential to react with nucleophiles or electrophiles due to the ability of the two sulfur atoms to stabilise either an anion or a cation at C-1. However, it was not possible to observe any reactivity towards amine nucleophiles such as isopropylamine, morpholine, pyridine or sodium azide. Treatment of 6a with an ‘activated’ aldehyde equivalent (benzaldehyde dimethyl acetal) under Lewis acidic conditions at high dilution (0.03 M) (Scheme 7) was then explored in the hope that condensation of one of the hydroxyl groups would deliver the electrophile to the dithioalkene leading to an intramolecular ring-closure reaction. Pleasingly, this yielded the cyclised methyl ester 13 as a single diastereoisomer but in low yield (unoptimized). Ester 13 is presumably formed by trapping of the dithiolium cation with methanol followed by hydrolytic cleavage of the C-S bonds.
Scheme 6: Reduction of L-arabinose ketene thioacetal 6a using Raney-Ni, followed by benzoylation to give 10. Chiral motifs found in useful organic molecules are highlighted.

We also hypothesised that the allylic alcohol in ketene acetals 6 might be activated by the adjacent electron-rich alkene making further selective dehydration at C-3 possible. Treatment of the glucose-derived alkene 6e with the Lewis acidic reagent B(OCH$_2$CF$_3$)$_3$ led to dehydration and cyclisation to form a diastereomeric mixture of THFs 14 (Scheme 7) with essentially complete conversion, although chromatographic purification of the THFs led to much lower isolated yields. The arabinose derived thioalkene 6a cannot undergo a similar dehydration as 6e to form a THF at C-3, but treatment of 6a with In(OTf)$_3$ led instead to cyclisation at C-1, presumably via a similar stabilised allylic cation. This leads via hydrolysis to the α,β-un saturated lactone which subsequently reacts with the liberated thiophenol to yield a diastereomeric mixture of known lactones 15 in 38% yield (unoptimized). These interesting heterocyclic compounds are potentially useful building blocks for asymmetric synthesis, with THFs 14 structurally similar to catechol-O-methyl transferase (COMT) bisubstrate inhibitor 16 and the anti-tumour natural product (+)-varitriol 17.
Scheme 7. Synthesis of chiral heterocycles from selected ketene dithioacetals via i) Lewis acid mediated reaction with electrophilic dimethyl acetal to give lactone 13 ii) borate ester B(OCH₂CF₃)₃ mediated dehydration²⁶ to give THF 14, with structural similarity to the natural product (+)-varitriol,²⁷ iii) Lewis acid mediated dehydration to give lactone 15. Catechol-O-methyltransferase (COMT) bisubstrate inhibitor²⁹, (+)-varitriol²⁷ and Branimycin intermediate²⁸ show with structurally similar glucose derived THF and arabinose-derived lactone scaffolds highlighted in red.

Similarly, lactones 15 have been widely employed previously as building blocks for asymmetric synthesis directed towards natural products such as the antibiotic 18 (Scheme 7)²⁸. Previously reported syntheses of these lactones are lengthy (6 steps) and required the use of harsh workup procedures and toxic solvents.³⁰ In contrast, using our procedure, we were able to produce 15 in only three steps with recrystallisation being the main method of purification.

In summary, we have developed scalable methods for the regioselective C-2 dehydration of sugar thioacetals. The resulting dithioketene acetals are versatile synthetic intermediates which can be used to access polyols containing a stereogenic centre bearing an ethyl group. Preliminary studies have also demonstrated that the dithioketene acetal activates the C-3 hydroxyl group for further selective dehydration reactions, and cyclisation of these compounds can be used to access chiral heterocycles (THFs, butyrolactones) that are useful building blocks for asymmetric synthesis.

Acknowledgements

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Experimental

All reagents and solvents were purchased from Sigma Aldrich, Fisher Scientific, Fluorochem and Acros Organics and used as supplied unless otherwise noted. Resins (Amberlite IRA743) were pre-washed with EtOAc, Et2O and CH2Cl2 and dried in vacuo prior to use. All reactions were monitored by TLC or 1H NMR. TLC analysis was conducted using aluminium plates pre-coated with silica gel 60 F254 (Merck KGaA). The spotted TLCs were visualised by UV light at 254 nm or appropriate staining agents. Column chromatography purification was performed using a Biotage Isolera flash purification system with Buchi FlashPure flash cartridges prepacked with silica gel (40-60 μm). Petrol mentioned in procedures is petroleum ether b.p = 40-60 °C. 1H NMR and 13C NMR spectra were recorded at 400, 500, 600 or 700 MHz (for 1H) and 151 or 176 MHz (for 13C) on Bruker AMX400, AMX500, AMX600 spectrometers at ambient temperature, unless otherwise indicated. Peaks are assigned as singlet (s), doublet (d), triplet (t), quartet (q), quintet (qn), or multiplet (m). All shifts are reported in parts per million (ppm) and compared against residual solvent signals: CHCl3 ( = 7.26 ppm, s), MeOH ( = 3.31 ppm, qn) or DMSO ( = 2.50 ppm, qn) as the internal standard. Coupling constants (J) are quoted in Hertz (Hz) to one decimal place. Mass spectrometry was performed using a Waters VG70 SE spectrometer (ES+, CI, ES- modes). Infrared spectra were obtained using a Perkin-Elmer Spectrum 100 FTIR Spectrometer operating in ATR mode, all frequencies given in reciprocal centimetres (cm⁻¹). Melting points were measured with a Gallenkamp heating block and are uncorrected. Optical rotation was measured using an AA-65 Optical Activity Ltd Polarimeter with working wavelength = 589.44 nm, all [α]D values were obtained using 10 mg/mL solutions unless otherwise stated, and are given in degrees m cm⁻³ g⁻¹ dm⁻¹.
L-Arabinose diphenyldithioacetal, (2S,3S,4R)-5,5-bis(phenylthio)pentane-1,2,3,4-tetraol [5a]:

A mixture of L-arabinose (9.0 g, 60.0 mmol) and thiophenol (13.3 mL, 130 mmol, 2.2 eq.) in a mixture of trifluoroacetic acid and water (9:1, 5.0 mL) was stirred at 50-60 °C for 12 h. The reaction solution was then concentrated in vacuo to a solid residue, which was then recrystallised from boiling EtOAc before washing with Et₂O (2 × 10 mL) to yield the desired dithioacetal (19.7 g, 56.0 mmol, 95%): m.p. = 180-183 °C (EtOAc) [183-186 °C]; [α]D21 = -20 (c = 1.00, pyridine) [-23]; ¹H NMR (700 MHz, MeOD) δ 7.46-7.42 (m, 4H, H-7), 7.31-7.20 (m, 6H, H-8, H-9), 4.76 (d, J = 7.7 Hz, 1H, H-1), 4.12 (d, J = 2.1 Hz, 1H, H-3), 4.01 (dd, J = 7.7, 2.1 Hz, 1H, H-2), 3.78 (d, J = 11.2 Hz, 1H, H-5), 3.70-3.65 (m, 1H, H-4), 3.62 (d, J = 11.2 Hz, 1H, H-5); ¹³C NMR (176 MHz, MeOD) δ 136.8 (Ar-C), 133.8 (Ar-C), 129.7 (Ar-C), 128.4 (Ar-C), 73.2 (C-2), 72.8 (C-3), 72.0 (C-4), 64.9 (C-5), 64.5 (C-1); v max (solid/cm⁻¹) 3300 (O-H), 1640 (Ar=C), 1437 (CH₂), 1085 (C-O). Data in accordance with the literature.

D-Xylose diphenyldithioacetal, (2R,3S,4R)-5,5-bis(phenylthio)pentane-1,2,3,4-tetraol [5b]:

A mixture of D-xylose (3.00 g, 20.0 mmol) and thiophenol (4.51 mL, 40.0 mmol, 2.2 eq.) in 90% trifluoroacetic acid in water (3.00 mL) was stirred at 50-60 °C for 12 h. The reaction solution was then concentrated in vacuo to give the crude xylose diphenyldithioacetal. A solution of the crude xylose diphenyldithioacetal (8.7 g, 24.0 mmol) in NEt₃ (48 mL, 0.34 mol) and acetic anhydride (16 mL, 0.17 mol) was stirred at room temperature for 12 h. The mixture was then poured onto ice water (600 mL). After 15 min, the mixture was extracted into CH₂Cl₂ (2 × 50 mL) and the combined extracts were dried over MgSO₄ before concentrating in vacuo. A solution of the product in CH₂Cl₂ was filtered through a pad of silica, washing with CH₂Cl₂. Evaporation of the filtrate and crystallisation of the product from a 4:1 ether/petrol mixture (50 mL) at 0 °C gave a white solid as a crude product. The crude material was then purified via silica gel chromatography (2:1, EtOAc/petrol) to give D-xylose diphenyldithioacetal tetraacetate (959 mg, 160.0 mmol, 19%).

To a solution of D-xylose diphenyldithioacetal tetraacetate (959 mg, 160 mmol) in methanol (50 mL) was added sodium (10 mg); after stirring for 6 h, dry ice (2 g) was added and the mixture was filtered. The filtrate was evaporated to leave a residue, trituration of this solid with ethanol caused it to crystallise to an orange waxy solid (482 mg, 1.37 mmol, 86% crude). Recrystallisation from hot methanol gave the product as fine white crystals (134
mg, 0.38 mmol, 24%): m.p. = 113-118 °C (EtOH) [100-101 °C]; [α]_D^{21} = -12 (c = 1.00, pyridine) [-8]_; ¹H NMR (600 MHz, MeOD) δ 7.45-7.39 (m, 4H, H-7), 7.32-7.20 (m, 6H, H-8, H-9), 4.74 (d, J = 5.0 Hz, 1H, H-1), 4.15-4.10 (m, 2H, H-5), 4.07 (m, 1H, H-3), 3.97 (t, J = 5.0 Hz, 1H, H-2), 3.88 (m, 1H, H-4); ¹³C NMR (151 MHz, MeOD) δ 136.0 (Ar-C), 133.2 (Ar-C), 130.2 (Ar-C), 128.8 (Ar-C), 74.5 (C-2), 72.8 (C-3), 71.7 (C-4), 66.9 (C-5), 64.3 (C-1); v_max (solid/cm⁻¹) 3216 (O-H), 1578 (CH2), 1045 (C-O). Data in accordance with the literature.¹

L-Xylose diphenyldithioacetal, (2S,3R,4S)-5,5-bis(phenylthio)pentane-1,2,3,4-tetraol [ent-5b]:¹

A mixture of L-xylose (3.0 g, 20.0 mmol) and thiophenol (4.5 mL, 40.0 mmol, 2.2 eq.) in 90% trifluoroacetic acid in water (5.0 mL) was stirred at 50-60 °C for 12 h. The reaction solution was then concentrated in vacuo to a solid residue, which was then recrystallised from CH₂Cl₂ before washing with Et₂O (2 × 10 mL) and drying in vacuo to yield the product as a fine white powder (1.32 g, 3.7 mmol, 20%): m.p. = 111-114 °C (CH₂Cl₂); [α]_D^{12} = +12 (c = 1.00, pyridine); ¹H NMR (700 MHz, MeOD) δ 7.46-7.41 (m, 4H, H-8), 7.28-7.21 (m, 6H, H-6, H-7), 4.76 (d, J = 5.3 Hz, 1H, H-1), 4.12 (dd, J = 4.7, 3.7 Hz, 1H, H-2), 3.96-3.92 (m, 1H, H-3), 3.71 (dd, J = 6.4, 5.0, 3.7 Hz, 1H, H-4), 3.62 (dd, J = 11.2, 5.0 Hz, 1H, H-5), 3.54 (dd, J = 11.2, 6.4 Hz, 1H, H-5); ¹³C NMR (176 MHz, MeOD) δ 135.9 (Ar-C), 133.5 (Ar-C), 129.9 (Ar-C), 128.5 (Ar-C), 74.8 (C-2), 73.9 (C-3), 72.4 (C-4), 64.2 (C-5), 63.9 (C-1); v_max (solid/cm⁻¹) 3384 (O-H), 2919 (O-H), 1840 (Ar-CH), 1084 (C-O); HRMS (ESI) calcd for C₁₇H₂₀O₄S₂ [M+H]+: 353.0803, found 353.0799.

D-Ribose diphenyldithioacetal, (2R,3R,4R)-5,5-bis(phenylthio)pentane-1,2,3,4-tetraol [5c]:¹

A mixture of D-ribose (13.0 g, 86 mmol) and thiophenol (19.5 mL, 190 mmol, 2.2 eq.) in 90% trifluoroacetic acid in water (21.0 mL) was warmed at 50-60 °C for 12 h whilst stirring. The reaction solution was then concentrated in vacuo to a solid residue, which was then purified using silica gel chromatography (EtOAc/petrol 2:3) yield the product as a yellow oil (6.98 g, 19.8 mmol, 23%): [α]_D^{21} = +40 (c = 1.00, MeOH); ¹H NMR (700 MHz, MeOD) δ 7.51-7.47 (m, 2H, H-6), 7.34 (d, J = 7.6 Hz, 2H, H-7), 7.28-7.18 (m, 6H, H-8, H-9), 5.02 (d, J = 3.2 Hz, 1H, H-1), 4.41-4.39 (m, H-2), 4.18 (dt, J = 8.4, 4.3 Hz, 1H, H-4), 3.94 (dd, J = 7.9, 7.1 Hz, 1H, H-5), 3.85 (dd, J = 7.8, 7.2 Hz, 1H, H-5), 3.75 (d, J = 8.7 Hz, 1H, H-3); ¹³C NMR (176 MHz, MeOD) δ 136.5 (Ar-C), 132.9 (Ar-C), 130.1 (Ar-C), 128.5 (Ar-C), 78.2 (C-2), 75.8 (C-3), 71.4 (C-4), 65.4 (C-5),
64.1 (C-1); \( \nu_{\text{max}} \) (film/cm\(^{-1}\)) 3426 (O-H), 1713 (Ar-CH), 1434 (CH\(_2\)), 1064 (C-O). Data in accordance with the literature.\(^1\)

L-Rhamnose diphenyldithioacetal, \((2R,3R,4S,5S)-1,1\)-bis(phenylthio)hexane-2,3,4,5-tetraol [5d]:\(^1\)

\[ \text{A mixture of L-rhamnose (1.94 g, 10.0 mmol) and thiophenol (2.3 mL, 20.0 mmol, 2.2 eq.) in 90\% trifluoroacetic acid in water (5.0 mL) was stirred at 50-60 ^\circ\text{C} for 12 h. The reaction solution was then concentrated in vacuo to a solid residue, which was then recrystallised from boiling EtOAc before washing with Et\(_2\)O (2 \times 10 mL) and drying in vacuo to yield the product as white crystals (2.50 g, 6.00 mmol, 63\%): m.p. = 122-126 ^\circ\text{C} (EtOAc); [\(\alpha\)]\(_{D}\)\(^{21}\) = +52 (c = 1.00, MeOH); \(^1\)H NMR (600 MHz, MeOD) \(\delta\) 7.54-7.49 (m, 2H, H-8), 7.37-7.32 (m, 2H, H-8), 7.30-7.15 (m, 6H, H-9, H-10), 5.08 (d, \(J = 1.5\) Hz, 1H, H-1), 4.23-4.19 (m, 1H, H-2), 4.12-4.07 (m, 1H, H-3), 3.81-3.74 (m, 1H, H-4), 3.56 (m, 1H, H-5), 1.28-1.24 (m, 3H, H-6); \(^{13}\)C NMR (176 MHz, MeOD) \(\delta\) 136.7 (Ar-C), 132.7 (Ar-C), 129.2 (Ar-C), 128.0 (Ar-C), 74.7 (C-2), 74.1 (C-3), 71.0 (C-4), 69.0 (C-5), 64.7 (C-1), 20.5 (C-6); \(\nu_{\text{max}}\) (solid/cm\(^{-1}\)) 3237 (O-H), 1580 (CH\(_2\)), 1064 (C-O); HRMS (ESI) Calcd for C\(_{18}\)H\(_{22}\)O\(_4\)S\(_2\)Na [M+Na\(^+\): 389.0857, found 389.0850.

D-Glucose diphenyldithioacetal, \((2R,3R,4S,5S)-6,6\)-bis(phenylthio)hexane-1,2,3,4,5-pentaol [5e]:\(^1\)

\[ \text{A mixture of D-glucose (1.00 g, 5.60 mmol) and thiophenol (1.3 mL, 12.3 mmol, 2.2 eq.) in 90\% trifluoroacetic acid in water (2.00 mL) was stirred at 50-60 ^\circ\text{C} for 12 h. The reaction solution was then concentrated in vacuo to a solid residue, which was then recrystallised from boiling EtOAc before washing with Et\(_2\)O (2 \times 10 mL) and drying in vacuo to yield the product as fine white crystals (12.8 g, 34.0 mmol, 80\%): m.p. = 153-156 ^\circ\text{C} (EtOAc) [158-160 ^\circ\text{C}]; [\(\alpha\)]\(_{D}\)\(^{23}\) = +44 (c = 1.00, MeOH); \(^1\)H NMR (700 MHz, MeOD) \(\delta\) 7.48-7.45 (m, 2H, H-7), 7.44-7.41 (m, 2H, H-8), 7.29-7.21 (m, 6H, H-9, H-10), 4.72 (d, \(J = 4.9\) Hz, 1H, H-1), 4.37-4.33 (m, 1H, H-3), 4.02-3.98 (m, 1H, H-2), 3.78-3.73 (m, 1H, H-4), 3.73-3.67 (m, 1H, H-5), 3.62-3.58 (m, 2H, H-6); \(^{13}\)C NMR (176 MHz, MeOD) \(\delta\) 135.8 (Ar-C), 133.5 (Ar-C), 129.8 (Ar-C), 128.4 (Ar-C), 75.8 (C-2), 73.5 (C-3), 72.9 (C-4), 71.4 (C-5), 64.6 (C-1), 64.1 (C-6); \(\nu_{\text{max}}\) (solid/cm\(^{-1}\)) 3286 (O-H), 2931 (O-H), 1438 (CH\(_2\)), 1167 (C-O). Data in accordance with the literature.\(^1\)\]
**D-Galactose diphenyldithioacetal, (2R,3S,4S,5R)-6,6-bis(phenylthio)hexane-1,2,3,4,5-pentaol [5f].**

A mixture of D-galactose (1.80 g, 10.0 mmol) and thiophenol (2.26 mL, 22.0 mmol, 2.2 eq.) in 90% trifluoroacetic acid in water (3.0 mL) was stirred at 50-60 °C for 12 h. The reaction solution was then concentrated in vacuo to a solid residue, which was then recrystallised from boiling EtOAc before washing with Et₂O (2 × 10 mL) and drying in vacuo to yield the product as a white solid (1.93 g, 5.00 mmol, 50%): m.p. = 170-174 °C (EtOAc) [175-176 °C]; [α]_D^{21} = -24 (c = 1.00, pyridine) [-32]; ¹H NMR (600 MHz, MeOD) δ 7.48-7.40 (m, 4H, H-8), 7.31-7.21 (m, 6H, H-9, H-10), 4.78-4.74 (m, 1H, H-1), 4.28 (dd, J = 9.1, 1.7 Hz, 1H, H-3), 4.04 (dd, J = 8.0, 1.7 Hz, 1H, H-2), 3.93 (td, J = 6.3 Hz, 1H, H-4) 3.68-3.65 (m, 1H, H-5), 3.64 (d, J = 6.3 Hz, 2H, H-6); ¹³C NMR (151 MHz, MeOD) δ 136.4 (Ar-C), 133.9 (Ar-C), 129.8 (Ar-C), 129.0 (Ar-C), 71.9 (C-2), 71.8 (C-4), 70.8 (C-1), 65.0 (C-5), 64.7 (C-6); v_max (solid/cm⁻¹) 3256 (O-H), 1640 (Ar-CH), 1068 (C-O). Data in accordance with the literature.

**D-Mannose diphenyldithioacetal, (2R,3R,4S,5S)-6-(cyclohexa-2,4-dien-1-ylthio)-6-(phenylthio)hexane-1,2,3,4,5-pentaol [5e].**

A mixture of D-mannose (3.0 g, 0.017 mmol) and thiophenol (3.84 mL, 0.037 mmol, 2.2 eq.) in 90% trifluoroacetic acid in water (4.30 mL, 3.3 eq) was stirred at 50-60 °C for 12 h. The reaction solution was then concentrated in vacuo. Addition of Et₂O (10 mL) resulted in crystallisation of the product as a white solid (3.55 g, 9.30 mmol, 55%): m.p. = 116-119 °C (EtzO) [140-141 °C]; [α]_D^{21} = -20 (c = 1.00, pyridine) [-30]; ¹H NMR (700 MHz, MeOD) δ 7.53-7.49 (m, 2H, H-8), 7.36-7.34 (m, 2H, H-8), 7.29-7.16 (m, 6H, H-9, H-10), 5.07 (d, J = 1.4 Hz, 1H, H-1), 4.19 (dd, J = 9.4, 0.8 Hz, 1H, H-3), 4.10 (dd, J = 9.4, 1.4 Hz, 1H, H-2), 3.81 (dd, J = 8.1 Hz, 0.8 Hz, 1H, H-4), 3.79 (dd, J = 11.1, 3.6 Hz, 1H, H-6), 3.67-3.64 (m, 1H, H-5), 3.63-3.59 (m, 1H, H-6); ¹³C NMR (176 MHz, MeOD) δ 136.8 (Ar-C), 136.7 (Ar-C), 132.8 (Ar-C), 132.7 (Ar-C), 129.9 (Ar-C), 129.8 (Ar-C), 128.1 (Ar-C), 128.0 (Ar-C), 73.9 (C-2), 73.1 (C-3), 71.2 (C-4), 71.0 (C-5), 65.0 (C-1), 64.8 (C-6); v_max (solid/cm⁻¹) 3356 (O-H), 1640 (Ar-CH), 1428 (CH₂), 1067 (C-O); HRMS (ESI) Calcd for C₁₈H₂₂O₅S₂Na [M+Na]^+ 405.0802, found 405.0802. Data in accordance with the literature.
(2S,3R)-5,5-bis(Phenylthio)pent-4-ene-1,2,3-triol [6a]:

To a mixture of L-arabinose diphenylidithioacetal (5.57 g, 15.8 mmol) in MeOH (30.0 mL), was added dimethyl carbonate (6.2 mL, 110.6 mmol, 7 eq.) and K₂CO₃ (4.37 g, 31.6 mmol, 2 eq.). The resulting mixture was stirred at room temperature for 12 h before being filtered. The residue was washed with acetone (2 × 10 mL) and the filtrate concentrated under reduced pressure to yield the product (5.24 g, 15.7 mol, 99%): m.p. = 178-181 °C (MeOH); [α]_D^21 = +60 (c = 1.00, pyridine); ¹H NMR (600 MHz, MeOD) δ 7.33-7.19 (m, 10H, H-7, H-8, H-9), 6.29 (d, J = 8.7 Hz, 1H, H-2), 4.87-4.82 (m, 1H, H-4), 3.70 (m, 2H, H-5), 3.64-3.56 (m, 1H, H-3); ¹³C NMR (151 MHz, MeOD) δ 140.7 (C-1), 133.4 (Ar-C), 132.4 (Ar-C), 130.0 (Ar-C), 129.7 (Ar-C), 128.9 (C-2), 76.2 (C-3), 72.2 (C-4), 64.4 (C-5); ν_max (solid/cm⁻¹) 3265 (O-H), 1610 (Ar-CH), 1022 (C-O); HRMS (ESI) Calcd for C₁₇H₁₈O₃S₂ [M+H]^+: 335.0770, found 335.0777.

(2R,3R)-5,5-bis(phenylthio)pent-4-ene-1,2,3-triol [6b]:

To a mixture of D-xylose diphenylidithioacetal (35 mg, 0.10 mmol) in MeOH (2.0 mL), was added dimethyl carbonate (10 μL, 0.15 mmol, 1.5 eq.) and K₂CO₃ (28 mg, 0.20 mmol, 2.0 eq.). The resulting mixture was stirred at room temperature for 12 h before being concentrated under reduced pressure and purified using silica gel chromatography (acetone/CH₂Cl₂ 2:3) to yield the product as a yellow oil (160 mg, 0.05 mmol, 48%); [α]_D^21 = -44 (c = 1.00, MeOH); ¹H NMR (700 MHz, MeOD) δ 7.31-7.23 (m, 10H, H-7, H-8, H-9), 6.23 (d, J = 8.8 Hz, 1H, H-2), 4.80 (dd, J = 8.7, 4.6 Hz, 1H, H-3), 3.62 (dd, J = 10.9, 6.9 Hz, 1H, H-5), 3.59-3.55 (m, 1H, H-4), 3.50 (dd, J = 10.9, 6.7 Hz, 1H, H-5); ¹³C NMR (176 MHz, MeOD) δ 140.3 (C-1), 134.7 (Ar-C), 134.5 (Ar-C), 134.3 (Ar-C), 133.5 (Ar-C), 132.2 (Ar-C), 130.0 (Ar-C), 129.7 (Ar-C), 129.0 (Ar-C), 128.3 (C-2), 76.1 (C-3), 71.6 (C-4), 64.2 (C-5); ν_max (film/cm⁻¹) 3329 (O-H), 1640 (Ar-CH), 1580 (C=C), 1474 (CH2), 1023 (C-O); HRMS (ESI) Calcd for C₁₇H₁₈O₃S₂ [M+H]^+: 335.0770, found 335.0776.
(2S,3S)-5,5-bis(phenylthio)pent-4-ene-1,2,3-triol [ent-6b]:

To a mixture of L-xylose diphenyldithioacetal (300 mg, 0.85 mmol) in MeOH (2.00 mL), was added dimethyl carbonate (71 µL, 1.28 mmol, 1.5 eq.) and K₂CO₃ (235 mg, 1.7 mmol, 2.0 eq). The resulting mixture was stirred at room temperature for 12 h before being filtered and washed with MeOH (2 × 5 mL). The residue was then concentrated under reduced pressure to yield the product (224 mg, 0.67 mmol, 79%): m.p. = 196-198 °C (MeOH), [α]D²⁰ = +64 (c = 1.00, pyridine); ¹H NMR (700 MHz, MeOD) δ 7.32-7.23 (m, 10H, H-7, H-8, H-9), 6.23 (d, J = 8.8 Hz, 1H, H-2), 4.79 (dd, J = 7.7, 3.8 Hz, 1H, H-3), 3.62 (dd, J = 10.9, 4.6 Hz, 1H, H-5), 3.59-3.56 (m, 1H, H-4), 3.52-3.48 (dd, J = 10.9, 4.7 Hz, 1H, H-5); ¹³C NMR (176 MHz, MeOD) δ 140.3 (C-1), 134.7 (Ar-C), 134.5 (Ar-C), 134.3 (Ar-C), 133.5 (Ar-C), 132.2 (Ar-C), 130.0 (Ar-C), 129.7 (Ar-C), 129.0 (Ar-C), 128.2 (2-C), 76.2 (C-3), 71.6 (C-4), 64.2 (C-4); νmax (solid/cm⁻¹) 3364 (O-H), 1580 (C=C), 1475 (CH₂), 1068 (C-O); HRMS (ESI) Calcd for C₁₇H₁₈O₃S₂ [M+H⁺]: 335.0770, found 335.0777.

(2R,3S,4R)-6,6-bis(phenylthio)hex-5-ene-1,2,3,4-tetraol [6e]:

To a mixture of D-glucose diphenyldithioacetal (3.54 g, 9.26 mmol) in MeOH (8.0 mL), was added dimethyl carbonate (0.81 mL, 18.51 mmol, 1.5 eq.) and K₂CO₃ (2.56 g, 18.51 mmol, 2.0 eq). The resulting mixture was stirred at room temperature for 12 h before being concentrated under reduced pressure and recrystallised from boiling EtOAc and washed with Et₂O (2 × 5 mL) to yield the product (3.19 g, 8.78 mmol, 97%): m.p. = 144-148 °C (EtOAc), [α]D²⁵ = -32 (c = 1.00, pyridine); ¹H NMR (700 MHz, MeOD) δ 7.30-7.20 (m, 10H, H-8, H-9, H-10), 6.42 (d, J = 8.6 Hz, 1H, H-2), 5.07 (d, J = 9.7 Hz, 1H, H-3), 3.80-3.75 (dd, J = 11.0, 3.3 Hz, 1H, H-6), 3.73-3.68 (m, 1H, H-6), 3.66-3.62 (m, 1H, H-4), 3.47 (dd, J = 7.7, 2.7 Hz, 1H, H-6); ¹³C NMR (176 MHz, MeOD) δ 141.4 (C-1), 133.6 (Ar-C), 133.3 (Ar-C), 132.2 (Ar-C), 130.0 (Ar-C), 129.7 (C-2), 72.5 (C-3), 69.4 (C-4), 63.3 (C-5), 62.4 (C-6); νmax (film/cm⁻¹) 3253 (O-H) 1641 (Ar-CH), 1013 (C-O); HRMS (ESI) Calcd for C₁₈H₂₀O₄S₂ [M+H⁺]: 365.0876, found 365.0898.
(2R,3R,4R)-6,6-bis(phenylthio)hex-1,2,3,4-tetraol [6f]:

![Image of molecule](image_url)

To a mixture of D-galactose diphenyldithioacetal (100 mg, 0.26 mmol) in MeOH (15.0 mL), was added dimethyl carbonate (33 µL, 0.39 mmol, 1.5 eq.) and K₂CO₃ (72 mg, 0.52 mmol, 2.0 eq). The resulting mixture was stirred at room temperature for 12 h before being concentrated under reduced pressure and purified using silica gel chromatography (acetone/CH₂Cl₂, 1:5) to yield the product (53 mg, 0.14 mmol, 53%): m.p. = 80-84 °C (CH₂Cl₂), [α]₂¹⁰D = +28 (c = 1.00, pyridine); ¹H NMR (600 MHz, MeOD) δ 7.34-7.17 (m, 10H, H-8, H-9, H-10), 6.32 (d, J = 8.7 Hz, 1H, H-2), 4.90 (dd, J = 8.7, 7.2 Hz, 1H, H-3), 3.88-3.84 (m, 1H, H-5), 3.67-3.58 (m, 2H, H-6), 3.55 (dd, J = 7.2, 3.5 Hz, 1H, H-4);

(2R,3R,4R)-5,5-bis(phenylthio)pentane-1,2,3,4-tetrayl tetraacetate:

To a mixture of D-ribose dithioacetal (1.27 g, 3.56 mmol) in dry pyridine (10 mL) was added acetic anhydride (1.7 µL, 18.0 mmol, 5 eq.) and the mixture kept overnight with stirring. The mixture was poured onto crushed ice and extracted with CH₂Cl₂ (10 mL). The organic layer was washed with aq. 15% CuSO₄ solution (10 mL) followed by brine (10 mL) before drying over MgSO₄. The mixture was filtered through silica and concentrated in vacuo to give the product as a colourless oil (1.81 g, 3.5 mmol, 98%): [α]₂¹⁰D = +52 (c = 1.00, CHCl₃); ¹H NMR (700 CDCl₃) δ 7.45-7.43 (m, 2H, H-11), 7.36-7.32 (m, 2H, H-7), 7.28-7.19 (m, 6H, H-8, H-9, H-12, H-13), 5.66 (dd, J = 7.3, 3.8 Hz, 1H, H-2), 5.41 (dd, J = 7.3, 3.5 Hz, 1H, H-3), 5.27 (m, J = 7.4, 3.6 Hz, 1H, H-4), 4.44 (d, J = 3.6 Hz, 1H, H-1), 4.23 (dd, J = 12.1, 3.4 Hz, 1H, H-5), 4.04 (dd, J = 12.1, 7.4 Hz, 1H, H-5), 2.07 (s, 3H, CH₃), 1.95 (s, 3H, CH₃), 1.94-1.91 (s, 3H, CH₃), 1.91 (s, 3H, CH₃); ¹³C NMR (176 MHz, CDCl₃) δ 170.5 (C=O), 169.9 (C=O), 169.7 (C=O), 169.2 (C=O), 133.8 (Ar-C), 132.6 (Ar-C), 128.6 (Ar-C), 128.3 (Ar-C), 128.3 (C-1), 74.4 (C-3), 72.2 (C-4), 71.5 (C-5), 64.7 (C-6); νₘₐₓ (solid/cm⁻¹) 3336 (O-H), 1578 (C=C), 1438 (CH₂); HRMS (ESI) Calcd for C₁₈H₂₀O₄S₂ [M+H]⁺: 365.0676, found 365.0668.

(2R,3R,4R)-5,5-bis(phenylthio)pentane-1,2,3,4-tetrayl tetraacetate:

To a mixture of D-ribose dithioacetal (1.27 g, 3.56 mmol) in dry pyridine (10 mL) was added acetic anhydride (1.7 µL, 18.0 mmol, 5 eq.) and the mixture kept overnight with stirring. The mixture was poured onto crushed ice and extracted with CH₂Cl₂ (10 mL). The organic layer was washed with aq. 15% CuSO₄ solution (10 mL) followed by brine (10 mL) before drying over MgSO₄. The mixture was filtered through silica and concentrated in vacuo to give the product as a colourless oil (1.81 g, 3.5 mmol, 98%): [α]₂¹⁰D = +52 (c = 1.00, CHCl₃); ¹H NMR (700 CDCl₃) δ 7.45-7.43 (m, 2H, H-11), 7.36-7.32 (m, 2H, H-7), 7.28-7.19 (m, 6H, H-8, H-9, H-12, H-13), 5.66 (dd, J = 7.3, 3.8 Hz, 1H, H-2), 5.41 (dd, J = 7.3, 3.5 Hz, 1H, H-3), 5.27 (m, J = 7.4, 3.6 Hz, 1H, H-4), 4.44 (d, J = 3.6 Hz, 1H, H-1), 4.23 (dd, J = 12.1, 3.4 Hz, 1H, H-5), 4.04 (dd, J = 12.1, 7.4 Hz, 1H, H-5), 2.07 (s, 3H, CH₃), 1.95 (s, 3H, CH₃), 1.94-1.91 (s, 3H, CH₃), 1.91 (s, 3H, CH₃); ¹³C NMR (176 MHz, CDCl₃) δ 170.5 (C=O), 169.9 (C=O), 169.7 (C=O), 169.2 (C=O), 133.8 (Ar-C), 132.6 (Ar-C), 128.6 (Ar-C), 128.3 (Ar-C), 72.2 (C-4), 70.1 (C-3), 61.8 (C-4), 61.3 (C-5), 20.8 (CH₃), 20.7 (CH₃), 20.7 (CH₃), 20.6 (CH₃); νₘₐₓ (film/cm⁻¹) 1739 (C=O), 1643 (Ar-CH), 1367 (CH₂), 1197 (C-O); HRMS (ESI) Calcd for C₂₅H₂₆O₈S₄ [M+H]⁺: 521.1226, 521.1336 found.
D-Ribose diphenyldithioacetal tetraacetate (1.8 g, 3.5 mmol) was dissolved in DMSO-d$_6$ (10 mL), followed by addition of DBU (1.1 mL, 7.0 mmol, 2.0 eq). The resulting mixture was stirred at rt for 12 h to yield the thioacetal ketene. The mixture was added to water (10 mL) and the product extracted with Et$_2$O (5 x 10 mL), dried over MgSO$_4$ and concentrated in vacuo to yield the isolated product as a yellow oil (1.55 g, 3.4 mmol, 96%). [$\alpha$]$_D^{21} +96$ (c = 1.00, CHCl$_3$); $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 7.36-7.21 (m, 10H, H$_6$, H$_7$, H$_8$, H$_9$, H$_{10}$, H$_{11}$, H$_{12}$, H$_{13}$), 6.11 (dd, $J = 8.8$, 5.7 Hz, 1H, H$_2$), 5.83 (d, $J = 8.8$ Hz, 1H, H$_4$), 5.28 (ddd, $J = 6.5$, 5.8, 3.8 Hz, 1H, H$_3$), 4.26 (dd, $J = 12.0$, 3.7 Hz, 1H, H$_5$), 4.17 (dd, $J = 12.0$, 6.3 Hz, 1H, H$_5$), 2.07 (s, 3H, CH$_3$), 2.051 (s, 3H, CH$_3$), 2.049 (s, 3H, CH$_3$); $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 170.7 (C=O), 170.0 (C=O), 169.6 (C=O), 140.4 (C=O), 134.2 (Ar-C), 134.1 (Ar-C), 132.7 (Ar-C), 132.5 (Ar-C), 129.5 (Ar-C), 129.2 (Ar-C), 128.9 (Ar-C), 128.5 (Ar-C), 128.0 (C-2), 71.3 (C-3), 70.8 (C-4), 62.2 (C-5), 21.0 (CH$_3$), 21.0 (CH$_3$), 20.9 (CH$_3$); $\nu_{max}$ (film/cm$^{-1}$) 1745 (C=O), 1672 (C=C), 1370 (CH$_2$); HRMS (ESI) Calcd for C$_{23}$H$_{26}$O$_6$S$_2$ [M+H]$^+$: 461.1048, 461.1113 found.

(2R,3R,4S,5S)-1,1-bis(phenylthio)hexane-2,3,4,5-tetrayl tetraacetate:

To a mixture of l-rhamnose dithioacetal (500 mg, 1.26 mmol) in anhydrous pyridine (HOW MUCH) was added acetic anhydride (596 µL, 6.30 mmol, 5 eq.) and the mixture stirred at RT for 4 h. An additional aliquot of acetic anhydride (596 µL, 6.30 mmol, 5 eq.) was added and the mixture stirred for a further 4 h. The resulting mixture was poured onto crushed ice and extracted with CH$_2$Cl$_2$ (10 mL). The organic layer was washed with aq. 15% CuSO$_4$ solution (10 mL) followed by brine (10 mL) before drying over MgSO$_4$. The mixture was filtered through silica and concentrated in vacuo. The mixture was purified via column chromatography (3:2 EtOAc/Petrol) to give pure product as a yellow oil (630 mg, 1.18 mmol, 94%). [$\alpha$]$_D^{25} +92$ (c = 1.00, CHCl$_3$); $^1$H NMR (700 MHz, CDCl$_3$) $\delta$ 7.58-7.56 (m, 2H, H$_8$), 7.36-7.30 (m, 5H, H$_{12}$, H$_{13}$, H$_{14}$), 7.26 (m, 3H, H$_9$, H$_{10}$), 5.88 (dd, $J = 8.6$, 1.8 Hz, 1H, H$_3$), 5.33 (dd, $J = 8.6$, 2.9 Hz, 1H, H$_2$), 5.20 (dd, $J = 8.3$, 1.8 Hz, 1H, H$_4$), 4.88-4.81 (m, 1H, H$_5$), 4.38 (d, $J = 2.9$ Hz, 1H, H$_1$), 2.06 (s, 3H, CH$_3$), 2.01 (s, 3H, CH$_3$), 1.98 (s, 6H, CH$_3$ x 2), 1.16 (d, $J = 6.4$ Hz, 3H, H$_6$); $^{13}$C NMR (176 MHz, CDCl$_3$) $\delta$ 170.0 (C=O), 170.2 (C=O), 169.8 (C=O), 134.2 (Ar-C), 133.9 (Ar-C), 133.5 (Ar-C), 129.1 (Ar-C), 128.4 (Ar-C), 71.5 (C-2), 71.4 (C-3), 69.0 (C-4), 67.3 (C-5), 61.6 (C-1), 21.3 (CH$_3$), 20.9 (CH$_3$), 20.8 (CH$_3$), 20.8 (CH$_3$), 20.8 (CH$_3$), 20.8 (CH$_3$), 20.8 (CH$_3$), 20.8 (CH$_3$).
16.6 (C-6); \( \nu_{\text{max}} \) (film/cm\(^{-1}\)) 1730 (C=O), 1371 (CH\(_3\)), 1235 (C-O), 1043 (C-O); HRMS (ESI) Calcd for C\(_{26}\)H\(_{30}\)O\(_8\)S\(_2\)Na [M \(+Na^+\)]: 557.1274, found 557.1274.

(2S,3R,4S)-6,6-bis(Phenylthio)hex-5-ene-2,3,4-triyl triacetate [8d]:

\[
\begin{align*}
\text{L-Rhamnose diphenyldithioacetal tetraacetate triacetate (900 mg, 1.68 mmol) was dissolved} \\
\text{in DMSO-}d_6 (10 \text{ mL}), \text{ followed by addition of triazabicyclodecene (350 mg, 2.52 mmol, 2.0} \\
\text{eq). The resulting mixture was stirred at RT for 8 h. The mixture was added to water (10 \text{ mL})} \\
\text{and the product extracted with Et}_2\text{O (5 x 10 mL), dried over MgSO}_4 \text{ and concentrated in vacuo} \\
to yield the isolated product as a yellow oil (680 mg, 1.43 mmol, 85%): [\alpha]_{D}^{25} = +96 \text{ (c = 0.80, CHCl}_3) \text{;} \\
\text{1H NMR (700 MHz, CDCl}_3) \delta 7.36-7.28 \text{ (m, 10H, H-8, H-9, H-10), 6.17 (dd, J = 8.7, 5.0} \\
\text{Hz, 1H, H-3), 5.69 (d, J = 8.7 Hz, 1H, H-4), 5.04-5.02 (m, 1H, H-5), 2.07 (s, 3H, CH}_3) \text{;} \\
\text{13C NMR (176 MHz, CDCl}_3) \delta 170.2 \text{ (C=O), 170.0 \text{ (C=O), 169.7 \text{ (C=O), 133.8 (Ar-C), 132.2} (Ar-C),} \\
129.3 \text{ (Ar-C), 129.0 \text{ (Ar-C), 128.6 (C-1), 127.9 (C-2), 74.7 (C-3), 70.3 (C-4), 67.9 (C-5), 21.2} (CH}_3) \text{, 21.1 (CH}_3) \text{, 20.8 (CH}_3) \text{, 16.0 (C-6);} \\
\text{\nu_{max} (film/cm}^{-1}) 1746 \text{ (C=O), 1653 (C=C), 1370 (CH}_3})
\end{align*}
\]

(2R,3R,4S,5S)-6,6-bis(phenylthio)hexane-1,2,3,4,5-pentayl pentaacetate:

\[
\begin{align*}
\text{To a mixture of d-mannose dithiaoacet al (293 mg, 0.766 mmol) in anhydrous pyridine (HOW MUCH) was added} \\
\text{acetic anhydride (1.74 mL, 18.40 mmol, 24 eq.), added over 4 h. The resultant} \\
mixture was stirred overnight before it was poured onto crushed ice and extracted with CH}_2\text{Cl}_2 (10 \text{ mL}). \\
The organic layer was washed with \text{aq. 15% CuSO}_4 solution (10 \text{ mL}) followed by brine (10 \text{ mL}) before} \\
drying over MgSO\text{. The mixture was filtered through silica} \text{ and concentrated in vacuo to give pure product} \\
as a colourless oil (421 mg, 0.765 mmol, 99%): [\alpha]_{D}^{25} = +32 \text{ (c = 1.00, CHCl}_3) \text{;} \\
\text{1H NMR (700 MHz, MeOD) \delta 7.58-7.53 \text{ (m, 4H, H-18), 7.38-7.23 \text{ (m, 6H, H-19, H-20), 5.84 (dd, J = 8.3, 1.3} \\
\text{Hz, 1H, H-3), 5.44 (dd, J = 9.1, 1.2 Hz, 1H, H-4), 5.33 \text{ (dd, J = 8.2, 3.5 Hz, 1H, H-2), 5.05-4.99 (m, 1H, H-5),} \\
4.42 \text{ (d, J = 3.5 Hz, 1H, H-1), 4.19 (dd, J = 12.5, 2.6 Hz, 1H, H-6), 4.03 \text{ (dd, J = 12.5, 5.1 Hz, 1H, H-6), 2.10} (s, 3H, CH}_3) \text{, 2.03} \\
\text{ (s, 3H, CH}_3) \text{, 2.00 (s, 3H, CH}_3) \text{, 1.99 (s, 3H, CH}_3) \text{, 1.96 \text{ (s, 3H, CH}_3) \text{;} \\
\text{13C NMR (176 MHz, MeOD) \delta 170.7 \text{ (C=O), 170.1 (C=O), 170.1 (C=O), 169.74 (C=O x 2), 134.0 (Ar-C), 133.8 (Ar-C), 133.5} (Ar-C), 133.4 (Ar-C), 129.2 (Ar-C), 129.1 (Ar-C), 128.5 (Ar-C), 128.4 (Ar-C), 71.5 (C-3), 69.0}
\end{align*}
\]
(C-5), 68.1 (C-2), 67.7 (C-4), 62.0 (C-6), 61.3 (C-1), 21.1 (CH₃), 20.9 (CH₃), 20.8 (CH₃), 20.7 (CH₃); ν_max (film/cm⁻¹) 1744 (C=O), 1667 (Ar-CH), 1368 (CH₂), 1209 (C-O), 1043 (C-O); HRMS (ESI) Calcd for C₂₆H₃₀O₉S₂Na [M+Na]⁺: 573.1223, found 573.1223.

(2R,3S,4R)-6,6-bis(Phenylthio)hex-5-ene-1,2,3,4-tetrayl tetraacetate [8g]:

D-Mannose diphenyldithioacetal pentaacetate (21 mg, 0.0382 mmol) was dissolved in DMSO-d₆ (1 mL), followed by addition of tBuOK (10 mg, 0.0870 mmol, 4.4 eq). The resulting mixture was stirred at RT for 12 h to yield the thioacetal ketene. The mixture was added to water (5 mL) and the product extracted with Et₂O (4 × 5 mL), dried over MgSO₄ and concentrated in vacuo to yield the product as an unseparable mixture of the product with starting material as a yellow oil (4 mg, 0.018 mmol, 47%). Yield calculated by ¹H NMR, via addition of an internal standard (1,4-DMB):

¹H NMR (700 MHz, CDCl₃) δ 7.38 - 7.26 (m, 10H, H-18, H-19, H-20), 6.20 (dd, J = 8.5, 3.5 Hz, 1H, H-3), 5.62 (d, J = 8.5 Hz, 1H, H-2), 5.30 (dd, J = 8.0, 3.6 Hz, 1H, H-4), 4.22 (dd, J = 12.4, 2.6 Hz, 1H, H-5), 2.06 (s, 3H, CH₃), 2.05 (s, 3H, CH₃), 2.04 (s, 3H, CH₃), 2.04 (s, 3H, CH₃); ¹³C NMR (176 MHz, CDCl₃) δ 170.7 (C=O), 170.0 (C=O), 169.7 (C=O), 169.5 (C=O), 139.1 (C-1), 133.6 (C-2), 133.5 (Ar-C), 132.8 (Ar-C), 127.9 (Ar-C), 71.3 (C-4), 70.0 (C-5), 68.7 (C-3), 62.1 (C-6), 21.1 (CH₃), 20.9 (CH₃), 20.8 (CH₃); HRMS (ESI) Calcd for C₂₆H₃₀O₉S₂ [M+H]⁺: 533.1298, found 533.1297.

(2R,3S,4R)-6,6-bis(Phenylthio)hex-5-ene-1,2,3,4-tetrayl tetraacetate [8g]:

To a mixture of d-glucose dithioacetal ketene (100 mg, 0.275 mmol) in anhydrous pyridine (HOW MUCH) was added acetic anhydride (130 µL, 1.37 mmol, 6 eq.), and this addition repeated every hour for 4 h. The resultant mixture was stirred overnight before it was poured onto crushed ice and mixed with CH₂Cl₂ (10 mL). The organic layer was washed with aq. 15% CuSO₄ solution (10 mL) followed by brine (10 mL) before drying over MgSO₄. The mixture was filtered through silica and concentrated in vacuo to give the product as a colourless oil (64 mg, 0.12 mmol, 44%): [α]D²⁵ = -20 (c = 1.00, CHCl₃); ¹H NMR (700 MHz, CDCl₃) δ 7.38-7.35 (m, 2H, H-20), 7.33-7.26 (m, 8H, H-18, H-19), 6.20 (dd, J = 8.5, 3.5 Hz, 1H, H-3), 5.62 (d, J = 8.5 Hz, 1H, H-2), 5.30 (dd, J = 8.0, 3.6 Hz, 1H, H-4), 5.21 (m, 1H, H-5), 4.22 (dd, J = 12.4, 2.6 Hz, 1H, H-6), 4.16 (dd, J = 12.4, 5.4 Hz, 1H, H-6), 2.06 (s, 1H, CH₃), 2.05 (s, 1H,
CH₃), 2.04 (s, 1H, CH₃), 2.04 (s, 1H, CH₃); ¹³C NMR (176 MHz, CDCl₃) δ 170.7 (C=O), 170.0 (C=O), 169.7 (C=O), 169.5 (C=O), 139.1 (C-1), 133.6 (C-2), 132.8 (Ar-C), 132.2 (Ar-C), 132.0 (Ar-C), 129.3 (Ar-C), 129.0 (Ar-C), 128.7 (Ar-C), 128.6 (Ar-C), 127.9 (Ar-C), 71.3 (C-4), 70.0 (C-5), 68.7 (C-3), 62.1 (C-6), 21.0 (CH₃), 20.9 (CH₃), 20.8 (CH₃), 20.7 (CH₃); νmax (film/cm⁻¹) 1744 (C=O), 1660 (C=C), 1370 (CH₂), 1210 (C-O), 1024 (C-O), 774 (C=C); HRMS (ESI) Calcd for C₃H₂NO₅S₂ [M+H]⁺: 533.1298, found 533.1298. Data in accordance with compound pre-8g.

(2S, 3R)-2,3-Dihydroxypentyl benzoate [10]:⁴⁵

A solution of 6a (67 mg, 0.2 mmol) in EtOH (2 mL) with Raney-Ni (2 g) was stirred at RT for 12 h. The mixture was filtered through a plug of silica and washed with EtOH (5 mL). The filtrate was concentrated in vacuo and dissolved in pyridine (3 mL) at 0 °C under an inert atmosphere. To the stirred solution was added benzoyl chloride (23 μL, 0.2 mmol) dropwise. The resultant mixture was stirred at 0 °C for 2 h and then at RT for 12 h. The solvent was evaporated and then co-evaporated with toluene (5 mL). The residue was slowly poured into vigorously stirring water. The product was extracted with EtOAc (3 × 5 mL) before washing with brine (5 mL) and sat. aq. NaHCO₃ (5 mL). The mixture was dried using MgSO₄ and concentrated in vacuo. The crude product was purified using column chromatography (20% EtOAc/petrol) to yield the product as a colourless oil (42 mg, 0.19 mmol, 94%): [α]₀²⁵ = +4 (c = 1.00, pyridine), ¹H NMR (700 MHz, CDCl₃) δ 8.06 (d, J = 7.8 Hz, 2H, H-8), 7.59 (t, J = 7.3 Hz, 1H, H-10), 7.46 (t, J = 7.5 Hz, 2H, H-9), 4.52 (d, J = 4.8 Hz, 2H, H-5), 3.94-3.88 (m, 1H, H-4), 3.67 (m, 1H, H-3), 2.54 (d, J = 4.7 Hz, 1H, OH), 2.15 (d, J = 4.5 Hz, 1H, OH), 1.72-1.65 (m, 1H, H-2), 1.61-1.56 (m, 1H, H-2), 1.04 (t, J = 7.4 Hz, 3H, H-1); ¹³C NMR (176 MHz, CDCl₃) δ 167.4 (C-6), 133.5 (Ar-C), 130.0 (Ar-C), 129.8 (Ar-C), 128.6 (Ar-C), 74.0 (C-5), 73.1 (C-4), 66.3 (C-3), 25.6 (C-2), 10.3 (C-1); νmax (film/cm⁻¹) 3386 (O-H), 1680 (C=O), 1582 (CH₂), 1067 (C-O); HRMS (ESI) Calcd for C₁₂H₁₆O₄Na [M+Na]⁺: 247.0491, found 247.0491.

Methyl-(2R,3R,4R,5S)-4-Hydroxy-5-(hydroxymethyl)-2-phenyltetrahydrofuran-3-carboxylate [13]:⁶

A mixture of 6a (200 mg, 0.60 mmol) in CH₂Cl₂ under Ar was stirred at -78 °C for 5 min before the addition of benzaldehyde dimethylacetal (100 mL, 0.66 mmol) and boron trifluoride etherate (82 μL, 0.66 mmol). The solution was left to stir for 1 h. The solution was concentrated in vacuo, followed by addition of EtOAc (5 mL). The product was extracted with EtOAc (3 × 10 mL), washed over brine (10 mL) and dried over MgSO₄. The product was purified via silica chromatography in a gradient of EtOAc/Petrol and isolated as a yellow oil.
(25 mg, 97 mol, 16%): [α]D25 = -60 (c = 1.00, pyridine). 1H NMR (700 MHz, CDCl3) δ 7.34-7.28 (m, 5H, H-9, H-10, H-11), 5.14 (d, J = 8.9 Hz, 1H, H-7), 4.21-4.18 (m, 1H, H-4), 4.07-4.01 (m, 1H, H-3), 3.88 (dd, J = 12.0, 5.3 Hz, 1H, H-5), 3.79-3.72 (m, 1H, H-5), 3.56 (s, 3H, H-6), 3.12 (dd, J = 10.0, 8.9 Hz, 1H, H-2); 13C NMR (176 MHz, CDCl3) δ 171.6 (C-1), 134.0 (Ar-C), 129.3 (Ar-C), 128.8 (Ar-C), 125.9 (Ar-C), 84.7 (C-4), 83.4 (C-7), 62.4 (C-3), 60.2 (C-5), 52.4 (C-6), 50.9 (C-2); νmax (film/cm⁻¹) 2919 (O-H), 1734 (C=O), 1461 (CH2); HRMS Calcd for C13H16O5Na [M] - 251.0697, found 251.0575.

(2R,3S,4R)-2-(2,2-bis(Phenylthio)vinyl)tetrahydrofuran-3,4-diol and (2S,3S,4R)-2-(2,2-bis(phenylthio)vinyl)tetrahydrofuran-3,4-diol [14]:

A mixture of 6a (25 mg, 0.07 mmol) in tert-amyl methyl ether (1.4 mL) with B(OCH2CF3)3 (30 μL, 200 mol%) was stirred at 120 °C for 6 h. The mixture was cooled to RT, and to the stirring solution, Amberlite IRA743 (0.5 g) was added; the resulting suspension was stirred for 0.5 h before drying over MgSO4. The solvent was removed under reduced pressure, and the crude mixture was purified via silica chromatography (1:1 EtOAc/Petrol) to give a mixture (76:24) of two diastereomers (3 mg, 0.009 mmol, 2%). (2R,3S,4R): 1H NMR (700 MHz, CDCl3) δ 7.34-7.27 (m, 10H, H-8, H-9, H-10), 6.20 (d, J = 7.9 Hz, 1H, H-2), 4.86 (dd, J = 7.9, 3.5 Hz, 1H, H-4), 4.03 (dd, J = 10.0, 4.2 Hz, 1H, H-6), 4.00 (m, 1H, H-5), 3.87 (dd, J = 10.0, 1.9 Hz, 1H, H-6). (2S,3S,4R): 1H NMR (700 MHz, CDCl3) δ 7.34-7.27 (m, 10H, H-8, H-9, H-10), 6.11 (d, J = 7.5 Hz, 1H, H-2), 5.18 (dd, J = 7.5, 3.5 Hz, 1H, H-3), 4.32 (m, 1H, H-4), 4.22 (dd, J = 10.0, 4.4 Hz, 1H H-6), 4.09 (m, 1H, H-5) 3.71 (dd, J = 10.0, 1.6 Hz, 1H, H-6); HRMS Calcd for C18H18O3S2 [M+H]+: 347.0770, found 347.0770.

(4S,5S)-5-(Hydroxymethyl)-4-(phenylthio)dihydrofuran-2(3H)-one and (4R,5S)-5-(hydroxymethyl)-4-(phenylthio)dihydrofuran-2(3H)-one [15]:

A mixture of 6a (100 mg, 0.3 mmol) in CH2Cl2 (1 mL) and In(OTf)3 (675 mg, 1.2 mmol, 4 eq.) were combined and stirred at 0 °C for 8 h, whereupon the solution was allowed to reach RT, giving a pale-pink solution. The crude mixture was concentrated in vacuo and purified using column chromatography (2:1 EtOAc/Petrol) to yield the isolated lactone as an oil, a mixture of two isomers (2:1) (25 mg, 0.11 mmol, 37%). (4R): 1H NMR (700 MHz, CDCl3) δ 4.45-4.41
(m, 1H, H-4), 3.98-3.91 (m, 2H, H-5, H-3), 3.69-3.63 (dd, J = 13.3, 3.5 Hz, 1H, H-5), 3.08-2.99 (dd, J = 17.5, 8.5 Hz, 1H, H-2), 2.63-2.56 (dd, J = 17.5, 8.4 Hz, 1H, H-2); 13C NMR (176 MHz, CDCl3) δ 174.56 (C-1) 133.1 (Ar-C), 131.4 (Ar-C), 129.6 (Ar-C), 128.7 (Ar-C), 85.0 (C-4), 62.5 (C-2), 42.2 (C-3), 36.4 (C-5). (4S): 1H NMR (700 MHz, CDCl3) δ 4.77-4.74 (m, 1H, H-4), 4.19-4.13 (m, 2H, H-5), 4.11 (dd, J = 12.6, 4.5 Hz, 1H, H-3), 4.00-3.96 (m, 1H, H-4), 2.90 (dd, J = 17.6, 8.7 Hz, 1H, H-2), 2.76 (dd, J = 17.6, 8.6 Hz, 1H, H-2); 13C NMR (176 MHz, CDCl3) δ 174.4 (C-1), 131.5 (Ar-C), 129.7 (Ar-C), 128.7 (Ar-C), 128.1 (Ar-C), 81.8 (C-4), 62.5 (C-2), 44.6 (C-3), 29.8 (C-5); vmax (film/cm-1) 3390 (O-H), 1781 (C=O), 1651 (Ar-CH), 1176 (CH2); HRMS Calcd for C18H18O3S2 [M+H]+: 225.0580, found 225.0580. Data in accordance with literature.8

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Supporting Information: $^1$H & $^{13}$C NMR

$\alpha$-Arabinose thioacetal ketene 6a:
D-Xylose thioacetal ketene 6b:
L-Xylose thioacetal ketene ent-6b:
D-Glucose thioacetal ketene 6e:
D-Galactose dithioacetal ketene 6f:
d-Ribose diphenyldithioacetal tetraacetal pre-8c:
\textbf{D-Ribose diphenylthiocetacetal ketene 8c:}
L-Rhamnose diphenylthioacetal tetraacetate, (2R,3R,4S,5S)-1,1-bis(phenylthio)hexane-2,3,4,5-tetrayl tetraacetate **pre-8d**:
(2S,3R,4S)-6,6-Bis(phenylthio)hex-5-ene-2,3,4-triy triacetate 8d:
D-Mannose diphenyldithioacetal pentaacetate pre-8g:
(2R,3S,4R)-6,6-Bis(phenylthio)hex-5-ene-1,2,3,4-tetrayl tetraacetate 8g:
(2S,3R)-2,3-Dihydroxypentyl benzoate 10:
Methyl (2R,3R,4R,5S)-4-hydroxy-5-(hydroxymethyl)-2-phenyltetrahydrofuran-3-carboxylate 13:
d-Glucose dithioacetal alkenyl THF, \(((3R,4R)-2-(2,2\text{-bis(phenylthiol)vinyl})\text{tetrahydrofuran-3,4-diol})\) via borate catalyst 14:
(4S)-5-(hydroxymethyl)-4-(phenylthio)Dihydrofuran-2(3H)-one, (4R)-5-(hydroxymethyl)-4-(phenylthio)dihydrofuran-2(3H)-one via In(OTf)$_3$ 15:
