Synthesis and conformational and configurational studies of diastereoisomeric O-
protected 4-(arylsulfonylimidoyl)butane-1,2,3-triols

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Abstract

Chiral sulfoximines have applications as transition-state mimicking enzyme inhibitors, as peptide isosteres and as chiral auxiliaries in synthesis. To access the required O-protected 4-
(arylsulfonylimidoyl)butane-1,2,3-triols, 4S,5S-di(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane (prepared from diethyl R,R-tartrate) was converted into its monobenzyl ether. Mitsunobu-like coupling with thiophenols gave 4S,5R-4-(benzyloxymethyl)-2,2-dimethyl-5-(arylthiomethyl)-1,3-dioxolanes. Sulfoxidation and S-imination (trifluoroacetamide, iodosobenzene diacetate, rhodium acetate) proceeded without stereoselectivity, giving inseparable diastereomeric mixtures of 4S,5R,S(±)-4-(benzyloxymethyl)-2,2-dimethyl-5-(N-(trifluoroacetyl)arylsulfony-
imidoylmethyl)-1,3-dioxolanes. Removal of the trifluoroacetyl protection allowed chromatographic separation of the diastereomeric 4S,5R,S(±)-4-(benzyloxymethyl)-2,2-dimethyl-5-(aryl sulfonylimidoylmethyl)-1,3-dioxolanes. The configurations at sulfur were determined by X-ray crystallography and some analysis of the solution and solid-state conformations was carried out. The resulting O-protected 4-(arylsulfonylimidoyl)butane-1,2,3-triols are of use in developing enzyme inhibitors.

Keywords: Sulfoximine, butanetriol, X-ray crystallography, conformation, diastereoisomer.

1. Introduction

Sulfoximines have attracted chemical and biological attention since the discovery of αS,S(S)-methionine sulfoximine 1 (Figure 1) as the toxic agent in agenised flour in the 1950s.1 This compound inhibits glutamine synthetase,2 the enzyme responsible for the formation of Gln
from Glu and ammonia, and \(\gamma\)-glutamylcysteine synthetase,\(^3\) which catalyses the first step in the biosynthesis of glutathione. Later studies showed that the homologue, \(\alpha S,S(S)\)-buthionine sulfoximine 2 is a more potent and selective inhibitor of \(\gamma\)-glutamylcysteine synthetase.\(^4,5\) In 1 and 2, the tetrahedral sulfoximine unit is acting as a mimic of the transition state or intermediate of the enzyme-catalysed process.\(^2-4\) Sulfoximines are configurationally stable. More recently, sulfoximines have been used in asymmetric synthesis as chiral ligands or chiral auxiliaries,\(^6-8\) as peptidomimetics (e.g. 3, Figure 1)\(^9,10\) and as transition-state mimics in the design of other enzyme inhibitors.\(^11\) As part of our programme of design and synthesis of selective enzyme inhibitors,\(^12-14\) we required the individual diastereoisomers of O-protected \(2S,3R\)-4-(arylsulphonimidoyl)butane-1,2,3-triols with different configurations at sulfur.

2. Synthesis

The synthetic approach to the target O-protected sulfoximine triols is shown in Scheme 1. We proposed that the four-carbon unit bearing the two carbon chiral centres could be introduced from a precursor available from the chiral pool. The sulfoximine chiral centre could be created by diastereoselective sulfoxidation of the intermediate aryl sulfide, followed by imination or, less efficiently, by generation of a mixture of diastereoisomeric sulfides and selective imination of one diastereoisomer.

Diethyl \(R,R\)-tartrate 4 contains the required secondary alcohols in the configurations corresponding to those in the synthetic targets 12 and 13. These were protected as the acetonide by ketal exchange with 2,2-dimethoxypropane; the esters (mixed methyl and ethyl esters) were then reduced with lithium aluminium hydride to give the \(C_2\)-symmetric \(S,S\)-dial 5. Desymmetrisation by monobenzylation with sodium hydride and benzyl bromide in DMF afforded 7 in 71% yield, which could be readily separated from the small quantity of dibenzyl ether 6 produced. The next step involved displacement of the primary OH with (substituted)thiophenols, for which it would be necessary to convert it into a good leaving group. Treatment of 7 with tetrabromomethane and triphenylphosphine efficiently converted it into the bromo compound

![Figure 1. Structures of \(\alpha S,S(S)\)-methionine sulfoximine 1, \(\alpha S,S(S)\)-buthionine sulfoximine 2 and a peptidomimetic 3 containing a sulfoximine.](image-url)
under a variety of forcing conditions; study of the required angle of approach of the nucleophile to the electrophilic CH₂ in 8 in an SN₂ process indicated that steric crowding between the dioxolane and the incoming aromatic ring may preclude reaction. In contrast, displacement of the primary OH of with the arylthio nucleophiles was achieved directly from 6 under Mitsunobu conditions (arylthiol, tributylphosphine, 1,1’-(azodicarbonyl)dipiperidine) to give the sulfoxides 9a and 9b in good yields.

At this point, it had been anticipated that the chirality of the sulfides could be exploited to drive the sulfoxidation in a diastereoselective manner. However, no conditions could be found to achieve this diastereoselection, so 9a was treated with 3-chloroperoxybenzoic acid to give a high yield of the sulfoxides 10a as an inseparable 1:1 mixture of diastereoisomers. Similar reaction of the bromophenylsulfide 9b gave the corresponding sulfoxides 10b, also as an inseparable equimolar mixture. A variety of reagents and conditions have been used to generate sulfoximines from sulfoxides, including sodium azide / hot conc. sulfuric acid and O-(2,4,6-trimethylbenzenesulfonyl)hydroxylamine but many are incompatible with the protecting
groups used here. Okamura and Bolm have developed a very mild sulfoximation in which PhI=NCOCF<sub>3</sub> is generated in situ from iodosobenzene diacetate and trifluoroacetamide and Rh-catalysed transimination converts sulfoxides into N-trifluoroacetyl sulfoximines. Application of this method to the mixture of diastereoisomeric Ph-unsubstituted sulfoxides 10a gave a mixture of diastereoisomers of the N-trifluoroacetyl sulfoximine 11a; the ratio of the diastereoisomers shifted from 1:1 in 10a to 3:2 in 11a, indicating that one diastereoisomer had reacted slightly more efficiently, but the isomers again could not be separated. In parallel, the bromophenylsulfoxides 10b were converted into the inseparable N-trifluoroacetyl sulfoximines 11b with no change in the 1:1 ratio of diastereoisomers.

The trifluoroacetyl groups were rapidly cleaved from 11a and 11b with ammonia, giving the free sulfoximines 12a and 12b, respectively. Now, the individual diastereoisomers contained H-bond donors and thus the diastereoisomers could be separated chromatographically, giving good yields of stereochemically pure 12a<sub>R</sub>, 12a<sub>S</sub>, 12b<sub>R</sub> and 12b<sub>S</sub>. The acetal protection was removed by acid-catalysed hydrolysis from 12a<sub>R</sub> and from 12b<sub>R</sub> to give the homochiral diols 13a<sub>R</sub> and 13b<sub>R</sub>, respectively, to demonstrate that the secondary alcohols could be revealed without loss of stereochemical integrity. However, simple examination of the 1-D <sup>1</sup>H and <sup>13</sup>C NMR spectra did not allow assignment of the configurations at sulfur of the dioxolanylmethyl sulfoximines 12 or of the diols 13.

3. X-ray crystallography and solution conformation studies

For each pair of diastereoisomeric sulfoximines 12a and 12b, one diastereoisomer was an oil but the other formed crystals (from ethanol / hexane) of quality suitable for X-ray crystallographic structure determination. The crystal structures (Figure 2) confirmed that both crystalline diastereoisomers were of S configuration at sulfur, i.e. that they were 12a<sub>S</sub> and 12b<sub>S</sub>.
The conformations of 12aS in solution in chloroform and in the crystal were compared with each other and with the solution conformation of the diastereoisomer 12aR. Similar comparisons were made for the Ar-bromo analogues 12bS and 12bR. Since it may be postulated that the N-H of the sulfoximine may form an intramolecular H-bond with the adjacent dioxolane oxygen, forming 5/6-membered fused ring structures, MM2 energy-minimised structures were calculated for 12aR and 12aS with and without the constraints of these intramolecular H-bonds (Figure 3). The predicted conformations of the two diastereoisomers without the intramolecular H-bonds are very similar to each other. In contrast, the predicted intramolecularly H-bonded conformation of 12aR is very crowded, with the 6-membered and 5-membered rings almost orthogonal, whereas that of 12aS is more open. In the predicted intramolecularly H-bonded conformation of 12aR, the dihedral angle between 4-H and 5-H of the dioxolane is ca. 90°; the observed $^3J = 8.2$ Hz coupling is inconsistent with such an angle. Thus 12aR is likely to adopt a conformation without an intramolecular H-bond in solution in chloroform,
where this dihedral angle is \( \text{ca. } 165^\circ \). The predicted conformation of the diastereoisomer 12a\(S\) in the intramolecularly H-bonded structure has the five-membered dioxolane ring in a half-chair and the six-membered ring in a twist-boat; this gives the dihedral angle between 4-H and 5-H as \( \text{ca. } 140^\circ \), whereas the corresponding angle in the non-H-bonded conformer is \( \text{ca. } 165^\circ \). The observed coupling \( ^3J = 7.9 \) Hz between these protons is consistent with both conformers. The NOESY spectrum of 12a\(S\) also did not distinguish between the possible conformers in chloroform but allowed assignment of the signals from the geminal dimethyl unit. There were cross-peaks between the 4-H signal and the upfield methyl signal at \( \delta 1.21 \) and between the 5-H signal and the downfield methyl peak at \( \delta 1.29 \), showing that the former singlet is due to the methyl \textit{cis} to the 4-CH\(_2\)OBn and the latter is due to the methyl \textit{trans} to this substituent. The NMR spectra of the Ar-bromo analogues 12b\(R\) and 12b\(S\) were very similar, showing that the remote bromine had little effect on the conformations of the diastereoisomers in solution. Overlap of some signals and poor resolution of some multiplets in the \(^1\text{H}\) NMR spectra of the deprotected derivatives 13a\(R\) and 13b\(R\) precluded any detailed analysis of their conformations in solution.

The crystal structures of 12a\(S\) and 12b\(S\) (Figure 2) are remarkably similar and show extended conformations, with intermolecular H-bonding. In the structure of 12a\(S\), the dihedral angle between the 4-CH\(_2\)OBn and the 5-CH\(_2\)SO(NH)Ph groups is \( 104^\circ \), corresponding to a half-chair conformation for the five-membered ring. The former bulky substituent almost eclipses the 5-H and that the latter large group is close to eclipsing the 4-H. The methyl \textit{cis} to the 5-CH\(_2\)SO(NH)Ph group is in the \textit{pseudo}-axial position. The crowded 5-C—CH\(_2\)S bond is in a staggered conformation, with the sulfoximine antiperiplanar to 4-C and gauche to the ring-oxygen. Interestingly, the bond from the CH\(_2\) to the sulfoximine is also staggered but with the apparently bulky groups (Ph and dioxolane) almost gauche to each other (dihedral angle \( 81^\circ \)). The structure of 12b\(S\) shows a slightly smaller dihedral angle between the 4-CH\(_2\)OBn and the 5-CH\(_2\)SO(NH)Ph groups \( (97^\circ) \) and the half-chair conformation of the dioxolane ring is distorted. The eclipsing of the 4-H and 5-H by their vicinal substituents is correspondingly diminished. The methyl \textit{cis} to the 5-CH\(_2\)SO(NH)Ph group is again in the \textit{pseudo}-axial position. The conformational arrangements of the two major side-chains are very similar to those in 12a\(S\). As expected, the sulfoximine-sulfur atoms were approximately tetrahedral. The O=S=N bond angles in 12a\(S\) and 12b\(S\) were both \( 122^\circ \). Both compounds had S=N bond lengths of 1.52 Å and S=O bond lengths of 1.46 Å.
4. Conclusions

In this paper, we have reported the synthesis of two series of diastereoisomeric O-protected 4-(arylsulfonylimidoyl)butane-1,2,3-triols, deriving the configuration of the two secondary alcohols from diethyl \(R,R\)-tartrate. A Mitsunobu reaction introduced the arylthio substituents. Peroxyacid sulfoxidation proceeded without diastereocontrol and Rh-catalysed oxidative imination gave the corresponding N-trifluoroacetyl sulfoximines as inseparable mixtures of diastereoisomers at sulfur. Removal of the TFA protection afforded the free NH sulfoximines, which were readily separated chromatographically. The configurations of the crystalline S-S dioxolanes 12a\(S\) and 12b\(S\) were established by X-ray crystallography, for both the S-Ph and S-(3-BrAr) series. However, both corresponding S-R stereoisomers 12a\(R\) and 12b\(S\) were oils. Removal of the acetonide protection exposed the secondary alcohols in 13a\(R\) and 13b\(R\). The homochiral O-protected 4-(arylsulfonylimidoyl)butane-1,2,3-triols are of potential use in developing enzyme inhibitors.

5. Experimental

5.1. General.

IR spectra were obtained on a Perkin-Elmer 782 Spectrometer as KBr discs or as liquid films. NMR spectra were recorded either on a Jeol EX270, Varian Mercury 400 or Varian United Inova 600 MHz spectrometers of samples in CDCl\(_3\), unless otherwise stated. Mass spectra were obtained by electrospray (ES), electron impact (EI) or fast atom bombardment (FAB) ionisation. Melting points were measured with a Thermo Galen Kofler block (uncorrected). Optical rotations were measured in a 1.0 dm cell on an Optical Activity Ltd. polarimeter and concentrations are expressed in g/100 mL. The chromatographic stationary phase was silica gel. THF refers to tetrahydrofuran, DMF refers to dimethylformamide. THF was dried with Na. Solutions in organic solvents were dried with MgSO\(_4\). Solvents were evaporated under reduced pressure. Experiments were conducted at ambient temperature, unless otherwise stated.

5.2. 4\(S\),5\(S\)-Di(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane (5).

Diethyl \((R,R)\)-2,3-dihydroxybutanedioate 4 (15.0 g, 70 mmol), 2,2-dimethoxypropane (32 g, 320 mmol) and TsOH.H\(_2\)O (198 mg, 1.0 mmol) in CH\(_2\)Cl\(_2\) (200 mL) were boiled under reflux in a Soxhlet apparatus for 7 d through activated 4 Å molecular sieves (33 g). Dry Na\(_2\)CO\(_3\) (83
mg, 1.0 mmol) was added. Filtration, drying, evaporation and chromatography (EtOAc / hexane, 2:3) afforded a mixture of diethyl, monoethyl-monomethyl and dimethyl esters of (4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylic acid (12 g, ca. 67%) as a pale buff oil. LiAlH₄ (2.0 M in THF, 51.5 mL, 103 mmol) was added during 1.5 h to this material in dry THF (80 mL) and the mixture was boiled under reflux for 5 h, then cooled to 0°C. Water (10 mL), aq. NaOH (4 M, 10 mL) and water (30 mL) were added cautiously in turn. The suspension was filtered and the solids were extracted with boiling 1,4-dioxane (3 × 100 mL). The solvents were evaporated from the combined extracts to give 5 (6.7 g, 85%) as a pale yellow oil with spectroscopic data identical to those reported in the literature.¹⁴,¹⁸

5.3. 4S,5S-Di(benzyloxymethyl)-2,2-dimethyl-1,3-dioxolane (6) and 4S,5S-4-benzyl-oxymethyl-5-hydroxymethyl-2,2-dimethyl-1,3-dioxolane (7).

NaH (60% in mineral oil, 1.9 g, 46 mmol, pre-washed with dry pentane) was stirred in dry DMF (20 mL) at 0°C under N₂ for 30 min. Compound 5 (6.7 g, 42 mmol) in dry DMF (20 mL) was then added dropwise and the mixture was stirred for 30 min before benzyl bromide (7.35 g, 43 mmol) was added. The mixture was stirred for 1.5 h and was poured into ice-water (250 mL) and extracted thrice with Et₂O. The combined extracts were washed with water and brine. Drying, evaporation and chromatography (hexane / Et₂O 1:1) gave 6 (500 mg, 6%) as a pale yellow oil with spectroscopic data identical to those reported in the literature.¹⁴ Further elution gave 7 (3.6 g, 71%) as a pale yellow oil with spectroscopic data identical to those reported in the literature.¹⁴

5.4. 4S,5R-4-(Benzyloxymethyl)-5-(bromomethyl)-2,2-dimethyl-1,3-dioxolane (8).

Ph₃P (353 mg, 1.3 mmol) in dry THF (1.0 mL) was added dropwise to 7 (280 mg, 1.1 mmol) and CBr₄ (409 mg, 1.2 mmol) in dry THF (2.0 mL) at 0°C under N₂ and the mixture was stirred for 3 h. Evaporation and chromatography (hexane / Et₂O 1:1) gave 8 (240 mg, 69%) as a colourless oil: ¹H NMR δ 1.43 (3 H, s, Me), 1.45 (3 H, s, Me), 3.46-3.54 (2 H, m, BrCH₂), 3.62-3.69 (2 H, m, BrCH₂), 4.04-4.12 (2 H, m, 4,5-H₂), 4.59 (2 H, s, PhCH₂), 7.30-7.38 (5 H, m, Ph-H); ¹³C NMR δ 27.1 (Me), 27.2 (Me), 34.0 (CMe₃), 70.4 (BnOCH₂), 73.6 (PhCH₂), 72.7 (5-C), 78.8 (4-C), 110.0 (CMe₂), 127.7 (Ph 3,5-C₂), 127.8 (Ph 2,6-C₂), 128.4 (Ph 4-C), 137.7 (Ph 1-C); MS (FAB) m/z 317.0563 (M + H) (C₁₄H₂₀O₃Br requires 317.0575); 316.0503 (M) (C₁₄H₁₉O₃Br requires 316.0497), 235 (M – Br), 220 (M – CH₂Br); [α]²⁰₀D = +3.6 (c 1.7, CHCl₃).
5.5. **4S,5R-4-(Benzyloxymethyl)-2,2-dimethyl-5-(phenylthiomethyl)-1,3-dioxolane (9a).**

PhSH (327 mg, 3.0 mmol) was added to Bu$_3$P (601 mg, 3.0 mmol) and 1,1'--(azodicarbonyl)-dipiperidine (749 mg, 2.97 mmol) in dry THF (7.0 mL) under Ar at 0°C and the mixture was sonicated for 30 min. During this sonication, 7 (500 mg, 2.0 mmol) in dry THF (3.0 mL) was added. The mixture was stirred at 20°C for 16 h. Filtration, evaporation and chromatography (hexane / Et$_2$O 5:1) gave 9a (300 mg, 44%) as a pale yellow oil: $^1$H NMR $\delta$ 1.40 (3 H, s, Me), 1.44 (3 H, s, Me), 3.19 (1 H, d, $J$ = 4.3 Hz, SCH), 3.20 (1 H, d, $J$ = 4.3 Hz, SCH), 3.63 (2 H, d, $J$ = 4.7 Hz, BnOCH$_2$), 4.04-4.09 (2 H, m, 4,5-H$_2$), 4.54 (1 H, d, $J$ = 14.9 Hz, PhCH), 4.57 (1 H, d, $J$ = 14.9 Hz, PhCH), 7.16-7.36 (10 H, m, 2 $\times$ Ph-H$_5$); $^{13}$C NMR $\delta$ 27.1 (Me), 27.2 (Me), 36.7 (SCH$_2$), 70.7 (BnOCH$_2$), 73.5 (PhCH$_2$), 77.0 (5-C), 79.4 (4-C), 109.7 (CMe$_2$), 126.2 (Ph-C$_2$), 127.8 (Ph-C$_2$), 128.4 (Ph-C$_2$), 128.9 (Ph-C$_2$), 129.2 (2 $\times$ P 4-C), 135.8 (Ph 1-C), 137.8 (Ph’ 1-C); MS (FAB) m/z 345.1522 (M + H) (C$_{20}$H$_{24}$O$_3$S requires 345.1519), 329 (M − CH$_3$), 109 (PhSH), 91 (Bn); $[\alpha]^{20}_D$ = +4.4 (c 2.0, CHCl$_3$).

5.6. **4S,5R-4-(Benzyloxymethyl)-2,2-dimethyl-5-(3-bromophenylthiomethyl)-1,3-dioxolane (9b).**

Compound 7 was treated with 3-bromothiophenol, as for the synthesis of 9a, to give 9b (69%) as a yellow oil. $^1$H NMR $\delta$ 1.39 (3 H, s, Me), 1.43 (3 H, s, Me), 3.16-3.19 (2 H, m, SCH$_2$), 3.59-3.66 (2 H, m, BnOCH$_2$), 4.03-4.05 (2 H, m, 4,5-H$_2$), 4.57 (2 H, s, PhCH$_2$), 7.08 (1 H, t, $J$ = 8.0 Hz, Ar 5-H), 7.22 (1 H, ddd, $J$ = 8.1, 1.8, 1.0 Hz, Ar 6-H), 7.42-7.46 (5 H, m, Ph-H$_5$), 7.48-7.51 (2 H, m, Ar 2,4-H$_2$); $^{13}$C NMR $\delta$ 27.0 (Me), 27.1 (Me), 36.3 (SCH$_2$), 70.5 (BnOCH$_2$), 73.6 (PhCH$_2$), 77.2 (5-C), 79.1 (4-C), 110.0 (CMe$_2$), 122.8 (Ar 3-C), 127.3 (CH), 127.8 (Ph 3,5-C$_2$), 128.4 (Ph 2,6-C$_2$), 129.0 (Ph 4-C), 130.2 (Ar-CH), 131.2 (Ar-CH), 132.3 (Ar-CH), 137.7 (Ph 1-C), 138.5 (Ar 1-C); $[\alpha]^{20}_D$ = +6.1 (c 2.5, CHCl$_3$).

5.7. **4S,5R,S(±)-4-(Benzyloxymethyl)-2,2-dimethyl-5-(phenylsulfinylmethyl)-1,3-dioxolane (10a).**

Compound 9a (180 mg, 0.52 mmol) was stirred with 3-chloroperoxybenzoic acid (111 mg, 0.52 mmol) in CH$_2$Cl$_2$ (15 mL) at −78°C for 5 h. The mixture was washed (aq. NaHCO$_3$, water). Drying and evaporation gave 10a (180 mg, 96%) as a 1:1 mixture of diastereoisomers as a pale yellow oil: IR $\nu_{\text{max}}$ 1265 cm$^{-1}$; $^1$H NMR $\delta$ 1.37 (1.5 H, s, Me), 1.45 (1.5 H, s, Me), 1.46 (1.5 H, s, Me), 1.47 (1.5 H, s, Me), 2.84 (0.5 H, dd, $J$ = 13.2, 9.8 Hz, SCH (isomer A)),...
3.04 (0.5 H, dd, J = 13.2, 4.2 Hz, SCH (isomer B)), 3.06 (0.5 H, dd, J = 13.2, 2.2 Hz, SCH (isomer A)), 3.22 (0.5 H, dd, J = 13.2, 7.2 Hz, SCH (isomer B)), 3.51 (0.5 H, dd, J = 9.8, 5.7 Hz, BnOCH (isomer A)), 3.62 (0.5 H, dd, J = 9.8, 4.9 Hz, BnOCH (isomer B)), 3.68 (0.5 H, dd, J = 9.5, 5.3 Hz, BnOCH (isomer A)), 3.91 (0.5 H, dt, J = 5.3, 8.3 Hz, 4-H (isomer A)), 3.97 (0.5 H, m, 5-H (isomer B)), 4.15 (0.5 H, dt, J = 5.3, 8.3 Hz, 4-H (isomer B)), 4.41 (0.5 H, ddd, J = 9.8, 8.3, 2.3 Hz, 5-H (isomer A)), 4.50 (0.5 H, d, J = 12.1 Hz, PhCH), 4.52 (0.5 H, d, J = 12.1 Hz, PhCH), 4.55 (1 H, s, PhCH$_2$), 7.23-7.35 (5 H, m, Ph-H$_5$), 7.50-7.53 (3 H, m, S-Ph 3,4,5-H$_3$), 7.65-7.67 (2 H, m, S-Ph 2,6-H$_2$); $^{13}$C NMR δ 26.8 (Me), 26.9 (Me), 27.0 (Me), 27.2 (Me), 60.2 (SCH$_2$ (isomer B)), 62.2 (SCH$_2$ (isomer A)), 69.6 (BnOCH$_2$ (isomer B)), 70.0 (BnOCH$_2$ (isomer A)), 73.2 (5-C (isomer A)), 73.5 (PhCH$_2$ (isomer B)), 73.7 (PhCH$_2$ (isomer A)), 73.9 (5-C (isomer B)), 78.6 (4-C (isomer B)), 79.0 (4-C (isomer A)), 110.0 (CMe$_2$), 110.2 (CMe$_2$), 123.8 (CH), 124.3 (CH), 127.6 (CH), 127.7 (CH), 127.8 (CH), 128.4 (CH), 129.2 (CH), 129.3 (CH), 131.2 (S-Ph 4-CH), 131.3 (S-Ph 4-CH), 137.6 (C-Ph 1-C), 137.7 (C-Ph 1-C), 143.5 (S-Ph 1-C (isomer B)), 144.5 (S-Ph 1-C (isomer A)); MS (FAB) m/z 361 (M + H), 303 (M + H − Me$_2$CO); [α]$^20_D$ = +4.4 (c 2.0, CHCl$_3$).

### 5.8. 4S,5R,S(±)-4-(Benzyloxymethyl)-2,2-dimethyl-5-(3-bromophenylsulfinylmethyl)-1,3-dioxolane (10b).

Compound 9b was treated with 3-chloroperoxybenzoic acid, as for the synthesis of 10a, to give 10b (68%) as a 3:2 mixture of diastereoisomers as a yellow oil: $^1$H NMR δ 1.16 (1.8 H, Me), 1.21 (1.2 H, Me), 1.25 (1.8 H, Me), 1.26 (1.2 H, Me), 3.42 (dd, J = 9.6, 6.8 Hz) and 3.43 (dd, J = 9.7, 6.8 Hz) (BnOCHH), 3.65 (dd, J = 10.7, 4.7 Hz) and 3.66 (dd, J = 10.2, 4.7 Hz) (BnOCHH), 3.79 (dd, J = 14.1, 8.6 Hz) and 3.81 (dd, J = 14.4, 9.7 Hz) (SCHH), 3.86-3.92 (1 H, m, 4-H), 3.99 (dd, J = 11.2, 2.3 Hz) and 4.03 (dd, J = 11.2, 2.2 Hz (SCHH), 4.14-4.19 (1 H, m, 5-H), 4.49 (2 H, s, PhCH$_2$), 7.23-7.37 (5 H, m, Ph-H$_5$), 7.54-7.60 (2 H, m, S-Ph 3,5-H$_2$), 7.70 (1 H, t, J = 8 Hz, S-Ph 4-H), 7.94 (2 H, d, J = 8 Hz, S-Ph 2,6-H$_2$); $^{13}$C NMR δ 26.4 (Me), 26.6 (Me), 58.5 (SCH$_2$), 59.3 (SCH$_2$), 69.6 (BnOCH$_2$), 69.7 (BnOCH$_2$), 72.9 (S-C), 73.3 (S-C), 73.6 (PhCH$_2$), 73.7 (PhCH$_2$), 78.1 (4-C), 78.2 (4-C), 110.8 [CMe$_2$], 127.7 (CH), 127.8 (CH), 127.9 (C-Ph 2,6-C$_2$), 128.0 (CH), 128.2 (S-Ph 2,6-C$_2$), 128.3 (CH), 128.47 (CH), 128.49 (CH), 128.53 (C-Ph 3,5-C$_2$), 129.0 (CH), 129.5 (S-Ph 3,5-C$_2$), 134.6 (S-Ph 4-C), 134.8 (S-Ph 4-C), 135.3 (S-Ph 1-C), 135.4 (S-Ph 1-C), 137.32 (C-Ph 1-C), 137.35 (C-Ph 1-C); $^{19}$F NMR δ −76.0 (1.8 F, s), −75.9 (1.2 F, s); [α]$^{20}_D$ = +3.7 (c 2.0, CHCl$_3$).
5.9. 4S,5R,S(±)-4-(Benzyloxymethyl)-2,2-dimethyl-5-(N-trifluoroacetyl)phenylsulfonimidoylmethyl)-1,3-dioxolane (11a).

PhI(OAc)₂ (242 mg, 0.75 mmol) was stirred vigorously with 10a (180 mg, 0.5 mmol), CF₃CONH₂ (113 mg, 1.0 mmol), MgO (81 mg, 2.0 mmol) and Rh₂(OAc)₄ (5.5 mg, 2.5 mol%) in CH₂Cl₂ (10 mL) for 6 d. Filtration (Celite®), evaporation and chromatography (hexane / Et₂O, 1:1) afforded 11a (176 mg, 75%) as a 3:2 mixture of diastereoisomers as a pale yellow oil: IR νmax 1422, 1265, 1173 cm⁻¹; ¹H NMR δ 1.16 (1.8 H, Me), 1.21 (1.2 H, Me), 1.25 (1.8 H, Me), 1.26 (1.2 H, Me), 3.42 (dd, J = 9.6, 6.8 Hz) and 3.43 (dd, J = 9.7, 6.8 Hz) (BnOC₂H), 3.65 (dd, J = 10.7, 4.7 Hz) and 3.66 (dd, J = 10.2, 4.7 Hz) (BnOCH₂), 3.79 (dd, J = 14.1, 8.6 Hz) and 3.81 (dd, J = 14.4, 9.7 Hz) (SC₂H), 3.86-3.92 (1 H, m, 4-H), 3.99 (0.5 H, dd, J = 11.2, 2.3 Hz, SCH) and 4.03 (0.5 H, dd, J = 11.2, 2.2 Hz, SCH), 4.14-4.19 (1 H, m, 5-H), 4.49 (2 H, s, PhCH₂), 7.23-7.37 (5 H, m, Ph-H₅), 7.70 (1 H, t, J = 8 Hz, S-Ph 4-H), 7.94 (2 H, d, J = 8 Hz, S-Ph 2,6-H₂); ¹³C NMR δ 26.4 (Me), 26.6 (Me), 58.5 (SCH₂), 59.3 (SCH₂), 69.6 (BnOCH₂), 69.7 (BnOCH₂), 72.9 (4-C), 73.3 (4-C), 73.6 (PhCH₂), 73.7 (PhCH₂), 78.1 (5-C), 78.2 (5-C), 110.8 (CMe₂), 127.7 (Ph-CH), 127.8 (Ph-CH), 127.9 (C-Ph 2,6-C₂), 128.0 (Ph-CH), 128.2 (S-Ph 2,6-C₂), 128.3 (Ph-CH), 128.47 (Ph-CH), 128.49 (Ph-CH), 128.53 (C-Ph 3,5-C₂), 129.0 (Ph-CH), 129.5 (S-Ph 3,5-C₂), 134.8 (Ph 1-C), 135.3 (Ph 1-C), 135.4 (Ph 1-C), 138.0 (Ph 1-C); ¹⁹F NMR δ -76.0 (1.8 F, s, -75.9 (1.2 F, s); MS (FAB) m/z 472.1382 (M + H) (C₂₂H₂₅NO₅F₃S requires 472.1406), 472 (M + H - O), 414 (M + H - Me₂CO); [α]²⁰D = +5.1 (c 2.6, CHCl₃).

5.10. 4S,5R,S(±)-4-(Benzyloxymethyl)-2,2-dimethyl-5-(N-trifluoroacetyl-3-bromophenylsulfonimidoylmethyl)-1,3-dioxolane (11b).

Compounds 10b were treated with trifluoroacetamide, PhI(OAc)₂ and Rh₂(OAc)₄, as for the synthesis of 11a, to give 11b (83%) as a 1:1 mixture of diastereoisomers as a pale yellow oil: IR νmax 1746, 1216, 1176 cm⁻¹; ¹H NMR δ 1.21 (1.5 H, s, Me), 1.25 (1.8 H, s, Me), 1.28 (1.5 H, s, Me), 3.49 (1 H, m, BnOCH), 3.66 (0.5 H, dd, J = 8.2, 4.8 Hz, BnOCH), 3.68 (0.5 H, dd, J = 8.2, 4.8 Hz, BnOCH), 3.70-3.75 (0.5 H, m, SCH), 3.76 (0.5 H, dd, J = 14.6, 9.8 Hz, SCH), 3.81 (1 H, m, 4-H), 4.05 (0.5 H, dd, J = 10.0, 2.2 Hz, SCH), 4.09 (0.5 H, dd, J = 9.9 Hz, 2.3 Hz, SCH), 4.14-4.22 (1 H, m, 5-H), 4.51 (2 H, s, PhCH₂), 7.27-7.40 (5 H, m, Ph-H₃), 7.43 (1 H, dt, J = 1.9, 8.0 Hz, Ar 5-H), 7.72-7.85 (2 H, m, Ar 4,6-H₂), 8.08 (0.5 H, t, J = 1.6 Hz, Ar 2-H), 8.11 (0.5 H, t, J = 1.9 Hz, Ar 2-H); ¹³C NMR δ 26.4 (Me),
26.5 (Me), 26.6 (Me), 58.6 (SCH$_2$), 59.4 (SCH$_2$), 69.5 (BnOCH$_2$), 69.6 (BnOCH$_2$), 72.9 (5-C), 73.4 (5-C), 73.8 (PhCH$_2$), 77.97 (4-C), 78.02 (4-C), 110.8 (CMe$_2$), 110.9 (CMe$_2$), 123.3 (Ar 3-C), 126.7, 126.8, 128.0, 128.1, 128.5, 128.6, 130.83 (Ar 5-C), 130.85 (Ar 5-C), 131.3 (Ar 2-CH), 131.4 (Ar 2-C), 137.2 (Ph 1-C), 137.3 (Ph 1-C), 137.4 (Ar 1-C), 137.5 (Ar 1-C), 137.7, 137.8; $^{19}$F NMR $\delta$ -76.0 (1.5 F, s, CF$_3$), -75.9 (1.5 F, s, CF$_3$); $[\alpha]^{20}_D = +4.3$ (c 1.4, CHCl$_3$).

5.11. 4$S$,5$R$,S$R$-(Benzyloxymethyl)-2,2-dimethyl-5-(phenylsulfonimidoylmethyl)-1,3-dioxolane (12a$R$) and 4$S$,5$R$,S$S$-4-(benzyloxymethyl)-2,2-dimethyl-5-(phenylsulfonimidoylmethyl)-1,3-dioxolane (12a$S$).

Compounds 11a (176 mg, 0.37 mmol) were stirred with NH$_3$ (35% in water, 2.0 mL) in MeOH (5.0 mL) for 16 h. Evaporation and chromatography (EtOAc / hexane, 2:3) yielded 12a$R$ (42 mg, 30%) as a pale yellow oil: IR $\nu_{max}$ 3332, 733 cm$^{-1}$; $^1$H NMR $\delta$ 1.33 (3 H, s, Me), 1.37 (3 H, s, Me), 3.10 (1 H, br s, NH), 3.30 (1 H, dd, $J =$ 13.6, 8.7 Hz, SCH), 3.45 (1 H, dd, $J =$ 13.6, 2.9 Hz, SCH), 3.53 (1 H, dd, $J =$ 9.8, 5.8 Hz, BnOCH), 3.67 (1 H, dd, $J =$ 9.8, 5.3 Hz, BnOCH), 3.90 (1 H, dt, $J =$ 7.7, 5.3 Hz, 4-H), 4.45 (1 H, dt, $J =$ 2.9, 8.7 Hz, 5-H), 4.51 (2 H, s, PhCH$_2$), 7.27-7.35 (5 H, m, Ph-H$_5$), 7.50 (2 H, m, S-Ph 3,5-H$_2$), 7.59 (1 H, m, S-Ph 4-H), 8.00 (2 H, m, S-Ph 2,6-H$_2$); $^{13}$C NMR $\delta$ 26.8 (Me), 26.9 (Me), 61.3 (SCH$_2$), 70.0 (BnOCH$_2$), 73.6 (PhCH$_2$), 73.7 (5-C), 78.7 (4-C), 110.4 (CMe$_2$), 127.6 (Ph 3,5-C$_2$), 127.7 (Ph 4-C), 128.4 (Ph 3,5-C$_2$), 128.5 (Ph 2,6-C$_2$), 129.0 (Ph 2,6-C$_2$), 133.1 (Ph 4-C), 137.6 (Ph 1-C), 141.5 (Ph 1-C); MS (FAB) $m/z$ 376 (M + H); MS (ES) $m/z$ 775 (2 M + Na), 399 (M + Na), 375 (M); $[\alpha]^{20}_D = +8.4$ (c 2.3, CHCl$_3$). Further elution gave 12a$S$ (47 mg, 34%) as a white solid: mp 86-88°C; IR $\nu_{max}$ 3332, 734 cm$^{-1}$; $^1$H NMR $\delta$ 1.21 (3 H, s, Me trans to CH$_2$OBn), 1.29 (3 H, s, Me cis to CH$_2$OBn), 3.39 (1 H, dd, $J =$ 14.2, 8.2 Hz, SCH), 3.50-3.54 (2 H, m, SCH + BnOCH), 3.64 (1 H, dd, $J =$ 9.7, 5.3 Hz, BnOCH), 3.93 (1 H, dt, $J =$ 7.6, 5.3 Hz, 4-H), 4.31 (1 H, dt, $J =$ 3.4, 8.2 Hz, 5-H), 4.51 (2 H, s, PhCH$_2$), 7.26-7.35 (5 H, m, Ph-H$_5$), 7.48 (2 H, m, S-Ph 3,5-H$_2$), 7.58 (1 H, m, S-Ph 4-H), 7.96 (2 H, m, S-Ph 2,6-H$_2$); $^{13}$C NMR $\delta$ 26.7 (Me), 26.8 (Me), 61.0 (SCH$_2$), 69.9 (BnOCH$_2$), 73.5 (5-C), 73.6 (PhCH$_2$), 78.6 (4-C), 110.1 (CMe$_2$), 127.6 (Ph 3,5-C$_2$), 127.7 (Ph 4-C), 128.4 (Ph 3,5-C$_2$), 128.5 (Ph 2,6-C$_2$), 128.8 (Ph 2,6-C$_2$), 133.0 (Ph 4-C), 137.6 (Ph 1-C), 141.5 (Ph 1-C); MS (FAB) $m/z$ 376 (M + H); $[\alpha]^{20}_D = +7.8$ (c 2.3, CHCl$_3$).
5.12.  $4S,5R,S(R)-4$-(Benzyloxymethyl)-2,2-dimethyl-5-(3-bromophenylsulfonimidoyl-methyl)-1,3-dioxolane (12b$^R$) and $4S,5R,S(S)-4$-(benzyloxymethyl)-2,2-dimethyl-5-(3-bromophenylsulfonimidoylmethyl)-1,3-dioxolane (12b$^S$).

Compounds 11b were treated with NH$_3$, as for the synthesis of 12a$^R$ and 12a$^S$ except that the chromatographic eluant was EtOAc / hexane (7:3), to give 12b$^R$ (29%) as a pale yellow oil:

$^1$H NMR $\delta$ 1.22 (3 H, s, Me), 1.32 (3 H, s, Me), 3.34 (1 H, dd, $J = 14.5$, 9.0 Hz, SCH), 3.46 (1 H, dd, $J = 14.5$, 2.7 Hz, SCH), 3.52 (1 H, dd, $J = 9.8$, 6.3 Hz, BnOCH), 3.69 (1 H, dd, $J = 9.8$, 5.1 Hz, BnOCH), 3.86 (1 H, ddd, $J = 7.8$, 6.3, $J = 4$ Hz, 4-H), 4.31 (1 H, ddd, $J = 8.6$, 7.8, 2.7 Hz, 5-H), 4.53 (2 H, s, PhCH$_2$), 7.29-7.37 (5 H, m, Ph-H$_5$), 7.38 (1 H, t, $J = 7.8$ Hz, Ar 5-H), 7.75 (1 H, ddd, $J = 7.8$, 2.0, 0.8 Hz, Ar 4-H or Ar 6-H), 7.82 (1 H, ddd, 7.8, 2.0, 0.8 Hz, Ar 6-H or Ar 4-H), 8.08 (1 H, t, $J = 1.9$ Hz, Ar 2-H); $^1$C NMR $\delta$ 26.7 (Me), 26.8 (Me), 59.7 (SCH$_2$), 69.9 (BnOCH$_2$), 73.6 (5-CH), 73.7 (PhCH$_2$), 78.4 (4-C), 110.3 [CMe$_2$], 122.8 (Ar 3-C), 126.9, 127.7, 127.9, 128.5, 130.4, 131.6, 136.7, 137.5 (Ph 1-C), 141.6 (Ar 1-C); MS (ES) $m/z$ 456.0642 (M + H) (C$_{20}$H$_{25}$BrNO$_4$S requires 456.0668), 455.0585 (M) (C$_{20}$H$_{24}$BrNO$_4$S requires 456.0590), 454.0669 (M + H) (C$_{20}$H$_{25}$BrNO$_4$S requires 454.0682), 453.0604 (M) (C$_{20}$H$_{24}$BrNO$_4$S requires 453.0610); [α]$^20_D$ = +3.2 (c 1.5, CHCl$_3$). Further elution gave 12b$^S$ (32%) as a white solid: mp 75-77°C; $^1$H NMR $\delta$ 1.20 (3 H, s, Me), 1.31 (3 H, s, Me), 2.32 (1 H, br s, NH), 3.38 (1 H, dd, $J = 14.3$, 8.7 Hz, SCH), 3.52 (1 H, dd, $J = 9.5$, 6.3 Hz, BnOCH), 3.54 (1 H, dd, $J = 14.3$, 3.0 Hz, SCH), 3.66 (1 H, dd, $J = 9.5$, 5.1 Hz, BnOCH), 3.89 (1 H, ddd, $J = 8.0$, 6.3, 5.1 Hz, 4-H), 4.33 (1 H, ddd, $J = 8.5$, 8.0, 2.9 Hz, 5-H), 4.53 (2 H, s, PhCH$_2$), 7.27-7.39 (5 H, m, Ph-H$_5$), 7.36 (1 H, t, $J = 8.0$ Hz, Ar 5-H), 7.70 (1 H, ddd, $J = 8.0$, 2.1, 1.0 Hz, Ar 4-H or Ar 6-H), 7.90 (1 H, ddd, $J = 8.0$, 2.1, 1.0 Hz, Ar 6-H or Ar 4-H), 8.14 (1 H, t, $J = 1.9$ Hz, Ar 2-H); $^1$C NMR $\delta$ 26.7 (Me), 26.8 (Me), 61.0 (SCH$_2$), 69.9 (BnOCH$_2$), 73.7 (PhCH$_2$ + 5-C), 78.4 (4-C), 110.3 [CMe$_2$], 122.7 (Ar 3-C), 127.2, 127.7 (Ph 3,5-C$_2$), 127.9, 128.5 (Ph 2,6-C$_2$), 130.3 (Ar 5-C), 131.8 (Ar 2-C), 136.0, 137.5 (Ph 1-C), 144.3 (Ar 1-C); Anal. Calcd. for C$_{20}$H$_{24}$BrNO$_4$S: C, 52.87; H, 5.32; N, 3.08. Found: C, 52.82; H, 5.22; N, 3.06; [α]$^20_D$ = +2.6 (c 1.5, CHCl$_3$).

5.13.  $2S,3R,S(R)-1$-(Benzyloxy)-4-(phenylsulfonimidoyl)butane-2,3-diol (13a$^R$).

Compound 12a$^R$ (38 mg, 0.1 mmol) was stirred with aq. HCl (9 M, 1.0 mL) in MeOH (5.0 mL) for 4 h. Evaporation and chromatography (EtOAc / MeOH, 7:3) afforded 13a$^R$ (37 mg, 100%) as a pale yellow oil: IR $\nu_{max}$ 3305 cm$^{-1}$; $^1$H NMR $\delta$ 2.68 (1 H, br, OH), 3.13 (1 H, dd, $J$
= 13.8, 1.7 Hz, SCH), 3.45 (1 H, dd, J = 13.8, 10.1 Hz, SCH), 3.59-3.63 (2 H, m, BN-OCH₂), 3.69 (1 H, m, 3-H), 4.54-4.56 (3 H, m, PhCH₂ + 4-H), 7.27-7.35 (5 H, m, Ph-H₅), 7.56 (2 H, m, S-Ph 3,5-H₂), 7.64 (1 H, m, S-Ph 4-H), 7.98 (2 H, m, S-Ph 2,6-H₂); ¹³C NMR δ 59.8 (SCH₂), 66.4 (4-C), 71.0 (1-C), 72.4 (3-C), 73.5 (PhCH₂), 127.7 (Ph 3,5-C₂), 127.8 (Ph 4-C), 128.1 (Ph 3,5-C₂), 128.5 (Ph 2,6-C₂), 129.4 (Ph 2,6-C₂), 133.5 (Ph 4-C), 137.7 (Ph 1-C), 142.6 (Ph 1-C); MS (FAB) m/z 336 (M + H); MS (ES⁺) m/z 693 (2 M + Na), 671 (2 M + H), 336.1264 (M + H) (C₁₇H₂₃NO₄S requires 336.1264); MS (ES⁻) m/z 372/370 (M + Cl); MS (EI) m/z 336 (M + H), 244 (M – Bn), 214 (M – BN-OCH₂), 91 (Bn); [α]²⁰D = +5.5 (c 1.3, CHCl₃).

5.14. 2S,3R,S(R)-1-(Benzyloxy)-4-(3-bromophenylsulfonyl)butane-2,3-diol (13bR).

Compound 12bR was treated with aq. HCl, as for the synthesis of 13aR, to give 13bR (100%) as a pale yellow solid: mp 73-76°C; IR ν max 3425 cm⁻¹; ¹H NMR δ 3.00 (2 H, br, 2 ×OH), 3.13 (1 H, d, J = 14 Hz, SCH), 3.45 (1 H, dd, J = 13.9, 10.1 Hz, SCH), 3.59-3.64 (2 H, m, BN-OCH₂), 3.70 (1 H, m, 2-H), 4.52 (1 H, d, J = 11.7 Hz, PhCH), 4.54 (1 H, d, J = 11.7 Hz, PhCH), 4.55 (1 H, br d, J = 10 Hz, 3-H), 7.27-7.36 (5 H, m, Ph-H₅), 7.43 (1 H, t, J = 7.9 Hz, Ar 5-H), 7.75 (1 H, ddd, J = 8.0, 1.9, 0.8 Hz, Ar 4-H or Ar 6-H), 8.12 (1 H, t, J = 1.8 Hz, Ar 2-H); ¹³C NMR δ 59.9 (SCH₂), 66.5 (3-C), 71.0 (1-C), 72.3 (2-C), 73.6 (PhCH₂), 123.4 (Ar 3-C), 126.7, 127.9 (Ph 3,5-C₂), 128.0, 128.6 (Ph 2,6-C₂), 130.9, 131.1, 136.7, 137.6 (Ph 1-C), 141.0 (Ar 1-C); Anal. Calcd. for C₁₇H₂₂BrNO₄S: C, 49.28; H, 4.87; N, 3.38. Found: C, 49.48; H, 4.61; N, 2.95; [α]²⁰D = +2.5 (c 1.7, CHCl₃).

5.15. Crystal data for 12aS.

Crystals of quality suitable for X-ray crystallography were grown from EtOH / hexane. C₂₀H₂₅NO₄S, M = 375.47, orthorhombic, a = 5.5540(1), b = 18.4970(3), c = 19.2410(4) Å, U = 1976.67(6)Å³, T = 150(2) K, space group = P2₁2₁2₁, Z = 4, μ(Mo-Kα) = 0.188 mm⁻¹, 4490 reflections (R int = 0.04977), R₁ = 0.03581 and wR² = 0.0772 based on 3837 F² with F o > 4σ(F o). Software used: Software used: SHELLXS,¹⁹ SHEXL-97²⁰ and ORTEX.²¹ Atoms C₁₄-C₂₀ disordered in 1:1 ratio with C₁₄A-C₂₀A, respectively. H1 located and refined at 0.89 Å from N1. CCDC 654427.
5.16. Crystal data for 12bS.

Crystals of quality suitable for X-ray crystallography were grown from EtOH / hexane. C$_{20}$H$_{24}$NO$_4$SBr, $M = 454.37$, monoclinic, $a = 12.3520(2)$, $b = 5.5440(1)$, $c = 15.7540(3)$ Å, $\beta = 103.459(1)^\circ$, $U = 1049.20(3)\text{Å}^3$, $T = 150(2)$ K, space group = $P2_1$, $Z = 2$, $\mu$(Mo-K$\alpha$) = 2.083 mm$^{-1}$, 5447 reflections ($R_{int} = 0.0506$), $R1 = 0.0347$ and $wR2 = 0.0731$ based on 4752 $F^2$ with $F_o > 4\sigma(F_o)$. Software used: SHELXS, SHELXL-97 and ORTEX. H1 located and refined at 0.89 Å from N1. CCDC 654428.

Acknowledgements

We thank Dr Timothy J. Woodman (University of Bath) for the NMR spectra, Dr. James Amato (University of Bath) and the EPSRC Mass Spectrometry Centre (Swansea) for the MS spectra and the University of London School of Pharmacy Microanalysis Service for the microanalytical data. We are grateful to the University of Bath for a studentship (to JSWK).

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Graphical Abstract

Synthesis and conformational and configurational studies of diastereoisomeric O-protected 4-(arylsulfonimidoyl)butane-1,2,3-triols

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