Scope and limitation of the [1,2]-phenylsulfanyl (PhS) migration in the synthesis of tetrahydrofurans and tetrahydropyrans from common triol precursors

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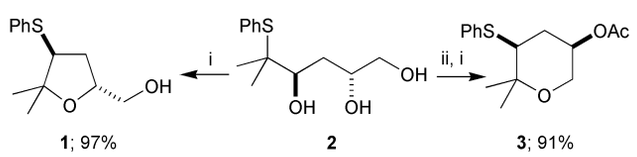
Triols containing three secondary hydroxy groups were rearranged using either (i) toluene-*p*-sulfonic acid or (ii) trimethyl orthoacetate–pyridinium toluene-*p*-sulfonate followed by toluene-*p*-sulfonic acid

In previous papers[1] we have demonstrated how enantiomerically enriched 2,4,5-triols (*e.g.* **2**) could be converted in a single step to THFs (*e.g.* **1**) (thermodynamic control) or in two-steps to THPs (*e.g.* **3**) (kinetic control–equilibration sequence) (Scheme 1). In this final paper on the subject of competition



Scheme 1 *Reagents*: i, TsOH, CH_2Cl_2, 40 °C; ii, $(MeO)_3CMe$, $C_5H_6N^+TsO^-$, CH_2Cl_2, rt.

experiments between THF and THP formation, we report in full[2] our findings on the effect of replacing the primary hydroxy at C-5 in triol **2** with a secondary alcohol. Obviously the introduction of a third stereogenic centre increases stereochemical complexity; for each series of compounds we looked at there were four possible diastereoisomers to investigate.

Given that we had previously used Sharpless asymmetric dihydroxylation[3] (AD) as a route to enantiomerically enriched triols we were keen to exploit this reaction further. In particular, we wished to prepare the styrene **4** (Fig. 1), as styrenes are well

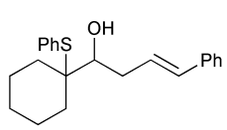


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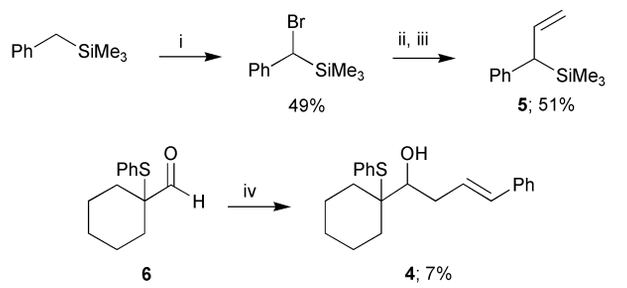
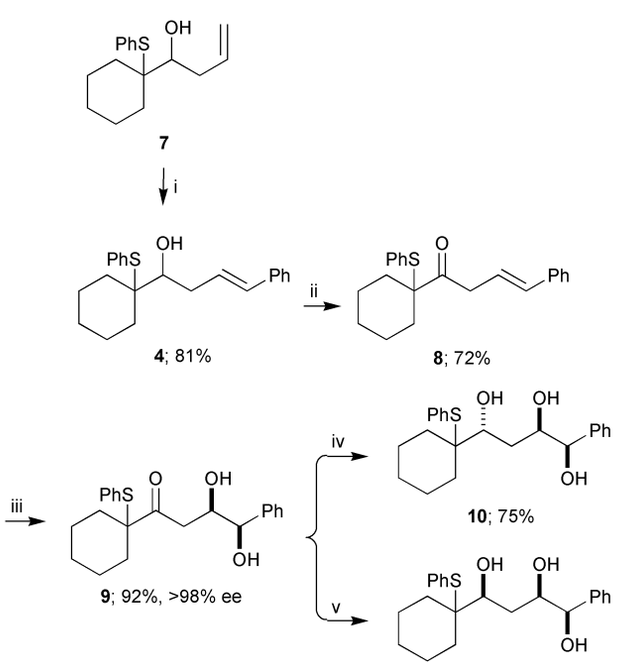
Fig. 1 Styrene target molecule **4**.

known to be amongst the best substrates for the AD reaction in terms of the high levels of enantioselectivity that may be obtained. Initial attempts to prepare this compound focused on allylic metal chemistry but were rather unsuccessful (Scheme 2). Allylsilane **5** was prepared in low yield from benzyltrimethylsilane by radical bromination with NBS[4] followed by a nickel(II) catalysed Kharasch coupling.[5] Unfortunately the Lewis acid conditions needed to promote addition of the allylsilane[6] to aldehyde **6** meant that only tiny amounts of the target styrene could be isolated and so an alternative route was sought.

Eventually we settled on preparing styrene **4** from the homoallylic alcohol **7**, reported previously,[1] by a Heck reaction with iodobenzene (Scheme 3). Oxidation of alcohol **4** to give the homoallylic ketone **8** proved troublesome with PCC, a mixture



Scheme 2 *Reagents*: i, *N*-bromosuccinimide, CCl_4, reflux, 10 h; ii, Mg, Et_2O, 0 °C; iii, Ni(dppe)Cl_2, vinyl bromide, rt, 48 h; iv, allylsilane **5**, $TiCl_4$, CH_2Cl_2, rt, 72 h.



Scheme 3 *Reagents*: i, PhI, 5 mol% $Pd(OAc)_2$, 10 mol% Ph_3P, Et_3N, MeCN, 80 °C, 24 h; ii, PDC, CH_2Cl_2, rt; iii, AD-mix-β, $MeSO_2NH_2$, Bu^tOH-H_2O, rt; iv, Me_4N^+ $BH(OAc)_3^-$, AcOH-MeCN, −20 °C, 7 days; v, Et_2BOMe, THF–MeOH, −78 °C then $NaBH_4$.

of compounds being obtained which were attributed to conjugation of the alkene with the carbonyl group. Presumably this results from the stabilisation of the extended enol by the

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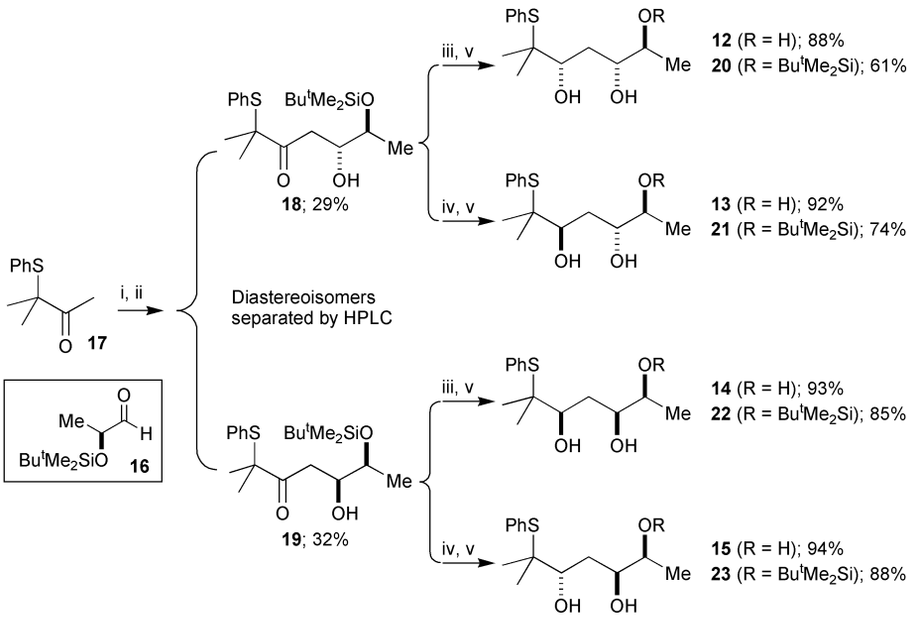


Scheme 4 *Reagents*: i, LDA, THF, −78 °C; ii, aldehyde **16**; iii, Et_2BOMe, THF–MeOH, −78 °C then $NaBH_4$; iv, Me_4N^+ $BH(OAc)_3^-$, AcOH–MeCN, −20 °C, 7 days; v, $Bu^n_4N^+$ F^-, THF, rt.

benzene ring. We were able to overcome this problem by switching to the less acidic reagent PDC.[7] The styrene **8** was dihydroxylated using the commercially available AD-mix-β to give the dihydroxyketone **9** in high yield (92%) and with excellent enantioselectivity (>98% ee) as predicted. Finally the triols **10** and **11** were obtained by the same method as used previously,[1] *i.e.* diastereoselective reduction of the β-hydroxyketone **9** (Scheme 3).[8,9]

A second series of triols **12**–**15** were prepared using aldol chemistry (Scheme 4). A short sequence of reactions starting from methyl lactate allowed us to prepare the silyl protected aldehyde **16**, a sensitive compound which was generally not purified before the aldol reaction. Unfortunately the aldol reaction of ketone **17** with aldehyde **16** gave poor diastereoselectivity and a difficult separation of the aldol diastereoisomers **18** and **19** by preparative HPLC was necessary. Similarly, Heathcock observed a low level of Felkin-Anh control[10] in the aldol reaction of the lithium enolate of pinacolone with 2-methoxypropanal (58:42 selectivity for the isomer predicted from the Felkin-Anh model).[11] The advantage of this poor selectivity was that it made both diastereoisomers immediately available and that it was possible to prepare all four diastereoisomers of the silyl-protected triol target molecules (**20**–**23**) by means of 1,3-stereocontrolled reductions (Scheme 4). The stereochemistry of the aldol products was confirmed by means of an X-ray crystal structure† (Fig. 2, Table 1) since one of the two diastereoisomers (*anti*-**18**) crystallised after the HPLC separation.

With the knowledge we had gained from the first set of substrates that we investigated,[1] we used long reaction times for the toluene-*p*-sulfonic acid catalysed rearrangement to ensure equilibrium was established. The triols in the lactic acid series (*i.e.* triols **12**–**15**) all rearranged[12] to give the THFs (**24**–**27**, respectively) as the major product (Scheme 5). We were particularly interested to establish the outcome of rearranging the ^{2,4}*anti*,^{4,5}*anti* triol **13**, since the THP **28** derived from this triol would have the maximum number of equatorial substituents (Fig. 3). Despite this 'favourable' arrangement of substituents in the THP product, the THF was still the major product, though THP **28** did account for 17% of the equilibrium.

† CCDC reference number 192685. See http://www.rsc.org/suppdata/p1/b2/b208558e/ for crystallographic files in .cif or other electronic format.

Table 1 Summary of crystal data, data collection, structure solution and refinement data for compound **18**

Empirical formula	$C_{20}H_{34}O_3SSi$
Formula weight (M)	382.62 g mol^{-1}
Crystal system	Triclinic
Unit cell dimensions	a = 10.820(3) Å α = 91.37(3)°
	b = 13.543(4) Å β = 97.96(2)°
	c = 7.720(2) Å γ = 87.39(2)°
Volume	1119.0(5) Å^3
Temperature	230(2) K
Space group	$P\bar{1}$
Z	2
Absorption coefficient (μ)	0.213 mm^{-1}
Reflections collected	6366
Independent reflections	3924 (R_{int} = 0.0415)
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0620, w$R2$ = 0.1102
R indices (all data)	$R1$ = 0.1327, w$R2$ = 0.1359

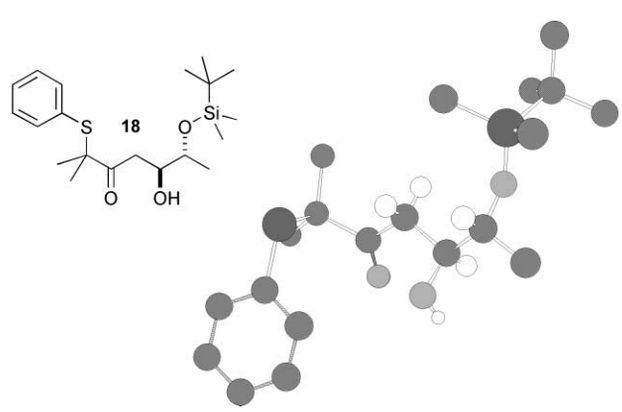


Fig. 2 X-Ray crystal structure of aldol product *anti*-**18** derived from methyl lactate.

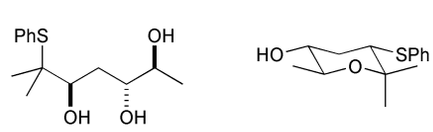
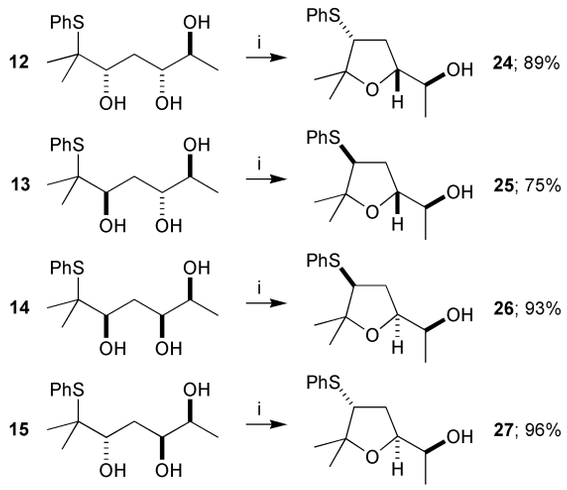
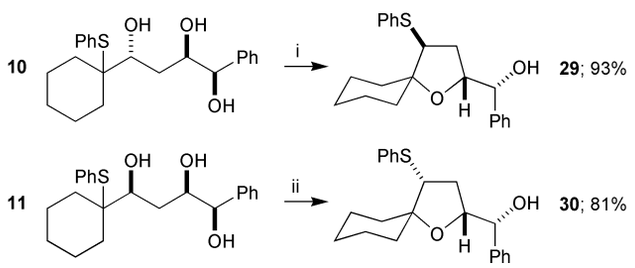


Fig. 3 THP **28**, formed from the rearrangement of triol **13**, contains the maximum number of equatorial substituents.

The rearrangement of the triols **10** and **11** required careful handling (presumably due to the benzylic hydroxy group). The ^{2,4}*anti*,^{4,5}*syn* triol **10** rearranged exclusively to THF **29** after



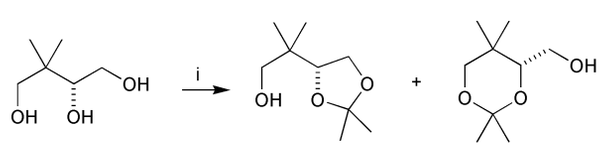
Scheme 5 *Reagents*: i, TsOH, CH_2Cl_2, 40 °C.



Scheme 6 *Reagents*: i, TsOH, CH_2Cl_2, 40 °C; ii, TsOH, CH_2Cl_2, rt.

being heated to reflux in dichloromethane for 24 hours (Scheme 6). The ^{2,4}*syn*,^{4,5}*syn* triol **11**, however, had to be rearranged at room temperature (3 days) to avoid decomposition. Again, the THF **30** was the only isolated product.

These reactions show that for the twelve 2,4,5-triols that have been investigated, six with a primary hydroxy at C-5 and six with a secondary hydroxy at C-5, the THF is always more stable than the alternative THP even when three groups can be equatorial on the THP. We believe this to be a consequence of the *gem*-disubstituted migration origin (the degree of substitution being equal for both ring sizes). In the THPs one of the C–C bonds must necessarily be axial; presumably the 1,3-diaxial interactions are too severe and the flatter THF rings are preferred. It is well known from sugar chemistry that selective 1,2- or 1,3-diol protection can be achieved either by formation of benzylidene acetals or isopropylidene ketals. For example, Lavallée showed that selective 1,2-protection of the triol **31** could be achieved by treatment with catalytic toluene-*p*-sulfonic acid in acetone.[13] The 5-ring ketal **32** was formed in preference to the 6-ring ketal **33** by a factor of 9:1. In the 6-ring ketal two methyl groups are forced to adopt axial positions (Scheme 7).



Scheme 7 *Reagents*: i, TsOH, acetone, rt.

We have calculated ground state energies for two hypothetical heterocycles **34** and **35**, in which the *gem*-dimethyl substitution has been removed (Fig. 4).[14] For the *anti*-THF **34** the energies were in the range −93.8 to −91.2 kcal mol^{-1} and for the *syn*-THP **35** −93.5 to −91.2 kcal mol^{-1}. The similar energy ranges for the two heterocycles support the theory that *gem*-dimethyl substitution raises the energy of THPs relative to THFs.

We previously published an orthoester-triggered rearrangement in which the C-4 hydroxy nucleophile is protected and

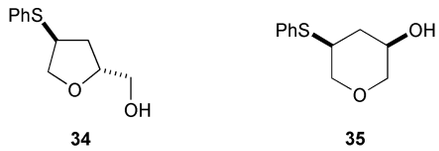
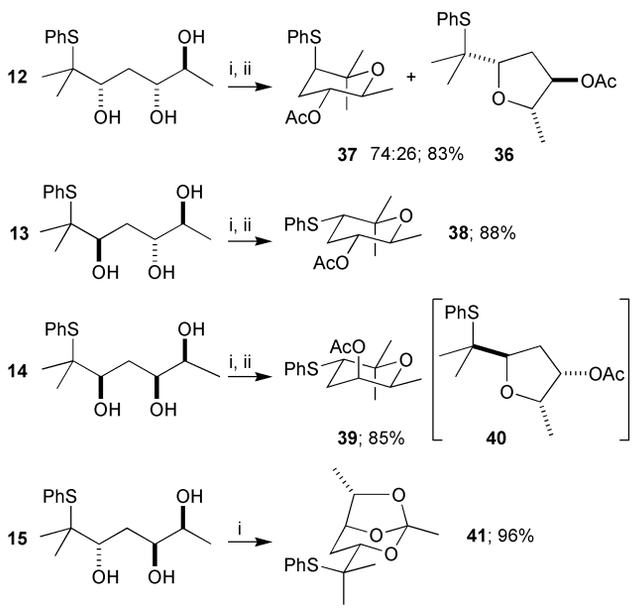


Fig. 4 Hypothetical rearrangement products: THF **34** and THP **35** lack a tertiary migration origin.

the leaving hydroxy at C-2 is activated in a single step, leaving the hydroxy at C-5 free to cyclise.[1b] Although this led to mixtures of unrearranged[12] THFs and rearranged THPs (a consequence of kinetic control) these products could be equilibrated with toluene-*p*-sulfonic acid in dichloromethane, converting the unrearranged THFs to THPs.

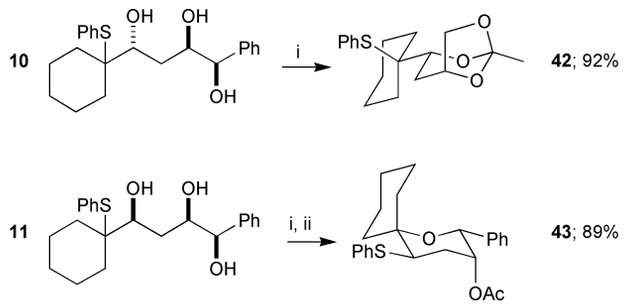
Reactions of the triols in the lactic acid series turned out to be very substrate dependent. Rearrangement of the ^{2,4}*syn*,^{4,5}*anti* triol **12** under kinetic conditions gave the unrearranged THF **36** as the major product (Scheme 8). Equilibration with toluene-



Scheme 8 *Reagents*: i, $(MeO)_3CMe$, $C_5H_6N^+\cdot TsO^-$, CH_2Cl_2, rt; ii, TsOH, CH_2Cl_2, 40 °C.

p-sulfonic acid gave only a 74:26 mixture of the rearranged THP **37** and unrearranged THF **36**. The inference here could be that it is unfavourable for the sulfanyl group to occupy an axial position, indeed sufficiently unfavourable that it can partly overcome the driving force for 'downhill' migration.[15] The ^{2,4}*anti*,^{4,5}*anti*-triol **13** behaved quite differently; after equilibration of an initial THF–THP mixture the only product identified was the THP **38**, with methyl, acetoxy and phenylsulfanyl groups all occupying equatorial positions (Scheme 8). The ^{2,4}*syn*,^{4,5}*syn*-triol **14** gave, after the two-step reaction sequence, the THP **39** with an axial acetate (the alternative THF **40** contains an unfavourable 2,3-*syn* relationship) (Scheme 8). Finally, in this series of compounds, the ^{2,4}*anti*,^{4,5}*syn*-triol **15** gave a single product after treatment with trimethyl orthoacetate and PPTS: the bicyclic orthoester **41**. Attempts to repeat the reaction at higher temperatures, or with longer reaction times, led only to decomposition products that were not characterised. It is interesting to note the stabilising effect of an *exo*-methyl group on these compounds. When triol **13** (with 2,4-*anti* stereochemistry) was reacted with the same reagent system no bicyclic orthoester intermediate was observed; presumably an *endo*-methyl group here destabilises the orthoester intermediate (if the corresponding orthoester forms at all).

The triols **10** and **11**, each containing a benzylic hydroxy group, behaved similarly to their analogues in the lactic acid



Scheme 9 *Reagents*: i, $(MeO)_3CMe$, $C_5H_6N^+\cdot TsO^-$, CH_2Cl_2, rt; ii, TsOH, CH_2Cl_2, rt.

series. Triol **11** was converted into the THP **43**, bearing an axial acetate, and triol **10** gave only the bicyclic orthoester **42** which was not successfully transformed into the target heterocycles (Scheme 9).

In summary we have demonstrated that for the general class of 2,4,5-triols under investigation THFs are formed as thermodynamic products when toluene-*p*-sulfonic acid is used as the catalyst for rearrangement regardless of the relative stereochemistry present in the triol. This is attributed to the 1,3-diaxial interactions which exist in the THPs when one of the C–C bonds of the tertiary migration origin is forced to enter an axial environment. The orthoester rearrangement has been shown to be general apart from triols with ^{2,4}*anti*,^{4,5}*syn* stereochemistry in which case the intermediate bicyclic orthoester is over-stabilised by a 6-*exo* substituent. The subsequent equilibration of THF–THP product mixtures gives THPs as exclusive products in all cases except for triol precursors with ^{2,4}*syn*,^{4,5}*anti* stereochemistry where the phenylsulfanyl group would be forced into an axial position on the THP ring.

Experimental

All solvents were distilled before use. Tetrahydrofuran and diethyl ether were freshly distilled from lithium aluminium hydride whilst dichloromethane and acetonitrile were freshly distilled from calcium hydride. Triphenylmethane was used as an indicator for tetrahydrofuran. Diisopropylamine was dried by distillation from calcium hydride and was stored over 4 Å molecular sieves. Triethylamine was dried in the same way but stored over calcium hydride granules. *n*-Butyllithium was titrated against diphenylacetic acid before use. All non-aqueous reactions were carried out under argon using oven-dried glassware.

Flash column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Thin layer chromatography was performed on commercially available pre-coated plates (Merck silica Kieselgel $60F_{254}$). Preparative HPLC was performed using a Zorbax SIL prepacked silica column (21.2 mm id × 25 cm) with a Gilson model 303 pump and a Cecil Instruments CE 212A UV detection system measuring the absorbance at 254 nm. Analytical HPLC was performed using either a Zorbax RX-C8 prepacked reverse phase silica column or a Daicel Chiralpak AD column with a Spectra-Physics SP8800 pump, a Spectra-Physics SP8450 UV detection system and a ChromJet single channel integrator.

Proton and carbon NMR spectra were recorded on Bruker DPX 250, AM 400, DRX 400 or DRX 500 Fourier transform spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per million (ppm) downfield of tetramethylsilane. Coupling constants *J* are quoted in Hz and are not rationalised. The symbol * after the proton NMR chemical shift indicates that the signal disappears after a D_2O "shake". Carbon NMR spectra were recorded with broad band proton decoupling and Attached Proton Test. The symbols $^+$ and $^-$ after the carbon NMR chemical shift indicate odd and even numbers of attached protons respectively.

Melting points were measured on a Stuart Scientific SMP1 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR spectrophotometer. Electron Impact (EI) mass spectra were recorded on a Kratos double focusing magnetic sector instrument using a DS503 data system for high-resolution analysis. Fast atom bombardment (FAB) mass spectra were obtained from a Kratos MS 890 instrument. Electrospray (+ES) mass spectra were recorded using a Brucker Bio-Apex FT-ICR instrument and LCMS using a Hewlett Packard HPLC system, eluting with an acetonitrile-water gradient, in conjunction with positive and negative ion electrospray mass spectrometry.

Optical rotations were recorded on a Perkin–Elmer 241 polarimeter (using the sodium D line; 589 nm) and $[\alpha]_D$ are given in units of 10^{-1} deg dm^2 g^{-1}.

(1*RS*,3*E*)-1-Hydroxy-4-phenyl-1-[1-(phenylsulfanyl)cyclohexyl]but-3-ene 4

A three-necked round bottomed flask, under an argon atmosphere, was charged with palladium(II) acetate (200 mg, 870 μmol, 5 mol%), triphenylphosphine (460 mg, 1.70 mmol, 10 mol%) and acetonitrile (100 cm^3). The resulting suspension was stirred to give a milky-yellow solution. Triethylamine (50 cm^3) was added, followed by iodobenzene (1.95 cm^3, 3.55 g, 17.4 mmol) and alkene **7** (5.00 g, 19.1 mmol). After addition of the alkene the solution became claret red. The solution was heated to reflux for 6 hours, during which time the solution turned black, consistent with the generation of palladium(0). The solution was then cooled to 0 °C and hydrochloric acid (2.0 mol dm^{-3}) was added until pH 4 was reached. The solution was extracted with diethyl ether (4 × 50 cm^3), washed with water (50 cm^3) and saturated brine (50 cm^3) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give a dark brown oil. This oil was redissolved in [light petroleum (bp 40–60 °C)–diethyl ether, 9:1] (30 cm^3) and filtered through a plug of silica. This process was repeated four times to yield a pale yellow solution which was evaporated under reduced pressure to give the crude product as an orange liquid. Purification by column chromatography (silica, isohexane–diethyl ether, 9:1) gave the *alcohol* **4** (5.20 g, 81%) as an oil which crystallised on standing, mp 85–89 °C (from hexane–ethyl acetate); R_f[light petroleum (bp 40–60 °C)–diethyl ether, 9:1] 0.23; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3477 (O–H), 3081, 2986, 2936, 2856, 1597 (C=C) and 1582 (PhS); δ_H(400 MHz; $CDCl_3$) 7.60–7.48 (2H, m, PhS), 7.43–7.14 (8 H, m, Ph and PhS), 6.50 (1 H, d, *J* 15.9 Hz, C*H*Ph), 6.32 (1 H, dt, *J* 15.9 and 6.5 Hz, C*H*=CHPh), 3.43 (1 H, dt, *J* 9.9 and 2.6 Hz, C*H*–OH), 2.94* (1H, dd, *J* 2.8 and 1.0 Hz, OH), 2.58 (1 H, ddt, *J* 14.3, 6.5 and 1.1 Hz, CH_AH_B), 2.38 (1 H, dddd, *J* 14.3, 9.8, 6.6 and 0.7 Hz, CH_AH_B) and 2.09–1.13 (10 H, m); δ_C(62.5 MHz; $CDCl_3$) 137.5$^-$, 137.3$^+$, 131.8$^+$ (CH=*C*HPh), 130.3$^-$, 129.1$^+$, 128.9$^+$, 128.5$^+$, 128.3$^+$ (*C*H=CHPh), 127.1$^+$, 126.1$^+$, 74.7$^+$ (CHOH), 61.1$^-$ (CSPh), 34.8$^-$ (*C*H$_2$CH=CHPh), 30.6$^-$, 29.9$^-$, 26.3$^-$ and 21.8$^-$; *m*/*z* (EI) 338 (7%, M$^+$), 320 (3, M$^+$ − H$_2$O), 211 (47), 203 (100), 191 (26, $C_6H_{10}SPh^+$), 117 (38) and 91 (30); (Found: M$^+$, 338.1706. $C_{22}H_{26}OS$ requires *M*, 338.1704).

(3*E*)-1-[1-(Phenylsulfanyl)cyclohexyl]-4-phenylbut-3-en-1-one 8

Alcohol **4** (1.00 g, 2.96 mmol) was added in one portion to a stirred suspension of pyridinium dichromate[7] (1.34 g, 3.55 mmol) in dichloromethane (25 cm^3). After stirring for 3 days, diethyl ether was added and the solution filtered through a short pad of florisil to give a crude product. Purification by column chromatography [silica, light petroleum (bp 40–60 °C), 9:1] gave the *ketone* **8** (715 mg, 72%) as a yellow oil; R_f[light petroleum (bp 40–60 °C), 9:1] 0.26; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3029, 2938, 2858, 1697 (C=O) and 1599 (C=C); δ_H(400.1 MHz, $CDCl_3$) 7.33–7.22 (10 H, m, Ph and PhS), 6.52 (1 H, d, *J* 16.0

Hz, PhC*H*=CH), 6.41 (1 H, dt, *J* 15.9 and 6.8 Hz, PhCH=C*H*), 3.71 (2 H, dd, *J* 6.6 and 0.9 Hz C*H*$_2$CH=CH), 2.04–1.20 (10 H, m, CH$_2$); δ_C(100.6 MHz; $CDCl_3$) 204.4$^-$ (C=O), 137.2$^-$, 136.5$^+$, 133.0$^+$, 130.0$^-$, 129.3$^+$, 128.8$^+$, 128.5$^+$, 127.4$^+$, 126.3$^+$, 123.7$^+$, 61.3$^-$ (CSPh), 40.3$^-$ (*C*H$_2$C=O), 32.6$^-$ (CH$_2$), 25.5$^-$ (CH$_2$) and 23.1$^-$ (CH$_2$); *m*/*z* (EI) 336 (17%, M$^+$), 227 (25), 191 (100, $C_6H_{10}SPh^+$), 123 (12), 117 (21) and 105 (37); (Found: M$^+$ 336.1561, $C_{22}H_{24}OS$ requires *M*, 336.1548).

(1*R*,2*R*)-1,2-Dihydroxy-4-[1-(phenylsulfanyl)cyclohexyl]butan-4-one 9

Alkene **8** (500 mg, 1.49 mmol) was added to a vigorously stirred solution of AD-mix-β (2.08 g) and methanesulfonamide (142 mg, 1.49 mmol) in a mixture of 2-methylpropan-2-ol (20 cm^3) and water (20 cm^3). The reaction was stirred at room temperature until judged complete by TLC or LCMS. Sodium sulfite (7.50 g, 59.3 mmol, 12 eq.) was then added and stirring continued for 30 minutes. The mixture was transferred to a separating funnel and ethyl acetate (50 cm^3) was added. The solution was extracted a further three times with ethyl acetate (25 cm^3). The combined organic extracts were washed with water (25 cm^3), saturated brine (25 cm^3) and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to give a crude product. Purification by column chromatography (silica, hexane–ethyl acetate, 2:1) gave the *diol* **9** (504 mg, 92%) as plates, mp 102–105 °C (from ethyl acetate); R_f(hexane–ethyl acetate, 2:1) 0.12; retention time/min (Chiralpak AD column; hexane–ethanol, 9:1) 17.5 (99.4%) and 20.6 (0.6); $[a]_D$ −9.0 (*c.* 0.26 in CH_2Cl_2; >98% ee); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3597 (O–H), 2938, 2958, 1686 (C=O), 1605, 1454, 1389 and 1333; δ_H(400.1 MHz, $CDCl_3$) 7.43–7.17 (10 H, m, Ph and PhS), 4.58 (1 H, dd, *J* 6.3 and 2.1 Hz, PhCH), 4.22–4.13 (1 H, m, C*H*OH), 3.48* (1 H, d, *J* 2.7 Hz, CHO*H*), 3.14 (1 H, d, *J* 2.9 Hz, PhCHO*H*), 2.91 (1 H, dd, *J* 17.8 and 3.5 Hz, CH_AH_BC=O), 2.83 (1 H, dd, *J* 17.8 and 8.4 Hz, CH_AH_BC=O), 1.92–1.55 (6 H, m) and 1.47–1.17 (4 H, m); δ_C(100.6 MHz; $CDCl_3$) 207.7$^-$ (C=O), 140.8$^-$, 136.8$^+$, 130.1$^-$, 129.9$^+$, 129.2$^+$, 129.0$^+$, 128.6$^+$, 127.3$^+$, 77.2$^+$ (Ph*C*HOH), 72.9$^+$ (CHOH), 61.3$^-$ (CSPh), 39.2$^-$ (*C*H$_2$C=O), 32.9$^-$, 25.7$^-$, 23.4$^-$ and 23.3$^-$; (Found: MNa$^+$ 393.1507, $C_{22}H_{26}O_3NaS$ requires 393.1500).

(1*R*,2*R*,4*R*)-4-[1-(Phenylsulfanyl)cyclohexyl]-1-phenylbutane-1,2,4-triol 10

Glacial acetic acid (2.5 cm^3) was added to a stirred suspension of tetramethylammonium triacetoxyborohydride[8] (569 mg, 2.16 mmol, 8 eq.) in acetonitrile (2.0 cm^3) and the resulting mixture was stirred for 30 minutes at room temperature to give a colourless solution. This solution was cooled to −30 °C and a solution of β-hydroxyketone **9** (100 mg, 0.27 mmol) in acetonitrile (0.5 cm^3) was added. The solution was then transferred to a freezer (−25 °C) for 1 week. The reaction was quenched by addition of aqueous sodium potassium tartrate solution (1.0 mol dm^{-3}, 10 cm^3) and the mixture allowed to warm slowly to room temperature. The reaction mixture was then diluted with dichloromethane (10 cm^3) and washed with saturated aqueous sodium bicarbonate solution. The aqueous layer was extracted with dichloromethane (4 × 10 cm^3), the combined organic layers dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure to give a crude product. Purification by column chromatography (silica, hexane–ethyl acetate, 2:1) gave *anti,syn-triol* **10** (75 mg, 75%) as an oil; R_f(isohexane–ethyl acetate, 2:1) 0.13; $[a]_D$ +23.6 (*c.* 0.25 in CH_2Cl_2; >98% ee); $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3564 (O–H), 3466 (O–H), 3067, 2936, 2856 and 1422; δ_H(400.1 MHz, $CDCl_3$) 7.51–7.46 (2 H, m), 7.43–7.31 (3 H, m), 7.31–7.24 (3 H, m), 7.21–7.16 (2 H, m), 4.50 (1 H, dd, *J* 7.1, 3.1 Hz, PhC*H*OH), 3.95 (1 H, ddd, *J* 14.0, 6.5 and 3.4 Hz, C*H*OH), 3.70 (1 H, dt, *J* 10.6 and 2.6 Hz, PhSCC*H*OH), 3.29* (1 H, br s, PhSCCHO*H*), 3.19* (1 H, d, *J* 6.1 Hz, CHO*H*), 3.05* (1 H, d, *J* 3.0 Hz, PhCHO*H*), 2.05–1.86 (1 H, m), 1.82–1.40 (8 H, m) and 1.31–1.06 (3 H, m); δ_C(100.6 MHz; $CDCl_3$) 140.6$^-$, 137.2$^+$, 129.9$^-$, 129.2$^+$, 129.0$^+$, 128.5$^+$, 128.0$^+$, 126.9$^+$, 77.0$^+$ (CHOH), 74.3$^+$ (CHOH), 71.6$^+$ (CHOH), 61.5$^-$ (CSPh), 32.1$^-$, 31.0$^-$, 29.4$^-$, 26.2$^-$, 21.7$^-$ and 21.7$^-$; *m*/*z* (+FAB) 372 (6%, M$^+$), 358 (9), 307 (11), 227 (48), 191 (32, $C_6H_{10}SPh^+$), 154 (100) and 111 (55); (Found: MH$^+$, 373.1830. $C_{22}H_{29}O_3S$ requires *M*, 373.1838).

(1*R*,2*R*,4*S*)-4-[1-(Phenylsulfanyl)cyclohexyl]-1-phenylbutane-1,2,4-triol 11

A 1.0 mol dm^{-3} solution of diethylmethoxyborane[9] in tetrahydrofuran (140 μl, 0.3 mmol) was added to a solution of β-hydroxyketone **9** (50 mg, 135 μmol) in tetrahydrofuran–methanol (4:1) (2.5 cm^3) at −78 °C, under an atmosphere of argon. The mixture was stirred for 5 minutes and then sodium borohydride (6 mg, 159 μmol) was added and the solution allowed to stir for 8 hours. Glacial acetic acid (3 cm^3) was added and stirring continued for a further 5 minutes. The solution was then neutralised with saturated aqueous sodium bicarbonate solution (30 cm^3) and extracted with diethyl ether (3 × 15 cm^3). The organic extracts were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure to give a crude product. This product was redissolved in methanol (5 cm^3) and stirred for 5 minutes before removing the methanol under reduced pressure. This cycle was repeated until TLC showed no spots with R_f(diethyl ether) > 0.5. Purification by column chromatography (silica, hexane–ethyl acetate, 2:1) gave *syn,syn-triol* **11** (37 mg, 74%) as an oil; R_f(hexane–ethyl acetate, 2:1) 0.21; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3553 (br, O–H), 2936, 2858, 1496, 1476, 1448, 1389 and 1026; $[a]_D$ −38.7 (*c.* 0.70 in CH_2Cl_2; >98% ee); δ_H(400.1 MHz, $CDCl_3$) 7.37–7.25 (10 H, m, Ph and PhS), 4.47 (1 H, dd, *J* 6.4 and 4.0 Hz, PhC*H*OH), 4.16* (1 H, s, OH), 3.8 (1 H, ddt, *J* 7.8, 6.4 and 1.4 Hz, C*H*OH), 3.70* (1 H, s, OH), 3.39 (1 H, dt, *J* 10.4 and 1.6 Hz, PhSCC*H*OH), 3.15* (1 H, d, *J* 3.9 Hz, OH), 1.98–1.45 (9 H, m) and 1.39–1.11 (3 H, m); δ_C(100.6 MHz; $CDCl_3$) 141.1$^-$, 137.2$^+$, 129.8$^-$, 129.1$^+$, 128.9$^+$, 128.4$^+$, 128.0$^+$, 126.9$^+$, 77.8$^+$ (CHOH), 76.5$^+$ (CHOH), 75.5$^+$ (CHOH), 60.8$^-$ (CSPh), 32.6$^-$, 30.0$^-$, 29.4$^-$, 26.1$^-$, 21.7$^-$ and 21.7$^-$; *m*/*z* (+FAB) 372 (7%, M$^+$), 245 (40), 227 (54), 191 (65, $C_6H_{10}SPh^+$), 154 (21) and 111 (100); (Found: M$^+$ 372.1752. $C_{22}H_{28}O_3S$ requires *M*, 372.1759).

(1*RS*,2*RS*,4*RS*)-4-[1-(Phenylsulfanyl)cyclohexyl]-1-phenylbutane-1,2,4-triol 10 and (1*RS*,2*RS*,4*SR*)-4-[1-(Phenylsulfanyl)cyclohexyl]-1-phenylbutane-1,2,4-triol 11

Potassium ferricyanide (8.76 g, 26.6 mmol, 3 eq.), potassium carbonate (3.68 g, 26.6 mmol, 3 eq.), osmium(III) chloride (37 mg, 124 μmol, 1.5 mol%), quinuclidine (69 mg, 621 μmol, 7 mol%) and methanesulfonamide (845 mg, 8.88 mmol, 1 eq.) were placed in a round bottom flask and stirred gently. Water (40 cm^3) and 2-methylpropan-2-ol (40 cm^3) were added, the flask was sealed and the solution stirred vigorously. Once the solids had completely dissolved the alkene **4** (3.00 g, 8.88 mmol) was added in one portion. Stirring was continued until TLC or LCMS indicated complete consumption of starting material. Sodium sulfite (40.2 g, 319 mmol) was then added in one portion and stirring continued for a further 30 minutes. The solution was transferred to a separating funnel, diluted with ethyl acetate (80 cm^3) and the aqueous layer separated. The aqueous layer was then extracted with ethyl acetate (3 × 80 cm^3). The combined organic extracts were washed with water (80 cm^3) and brine (80 cm^3), dried over anhydrous magnesium sulfate and finally, the solvent was evaporated under reduced pressure to give a crude product. Analytical HPLC (isocratic 38:62 MeCN:H_2O; 0.1% CF_3CO_2H, 0.1% Et_3N; flow rate 1 cm^3 min^{-1}) indicated an *anti*:*syn* mixture of 46:54 (retention times: 8.02 min, 10.30 min, respectively). Purification by column chromatography (silica, isohexane–ethyl acetate, 2:1) gave a white amorphous solid which was crystallised from chloroform

to give *anti-triol* **10** (1.26 g, 38%) as prisms, mp 115–117 °C (from chloroform); R_f(isohexane–ethyl acetate, 2:1) 0.13, spectroscopically identical to the enantiomerically enriched sample and *syn-triol* **11** (1.61 g, 49%) as an oil; R_f(isohexane–ethyl acetate, 2:1) 0.21, spectroscopically identical to the enantiomerically enriched sample.

(3*RS*,5*SR*,6*RS*)-2-Methyl-2-phenylsulfanylheptane-3,5,6-triol 12

Silyl ether **20** (384 mg, 1.0 mmol) was dissolved in tetrahydrofuran (20 cm^3) and tetra-*n*-butylammonium fluoride solution (1.0 cm^3, 1.0 mmol of a 1.0 mol dm^{-3} in tetrahydrofuran, containing 10% water) was added. The reaction was stirred at room temperature until judged complete by TLC (generally 1–2 h). Diethyl ether (20 cm^3) was added, followed by water (20 cm^3) and the mixture transferred to a separating funnel. The organic layer was separated and the aqueous layer extracted with diethyl ether (2 × 20 cm^3) and dichloromethane (2 × 20 cm^3). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure to give a crude product. Purification by column chromatography (silica, diethyl ether) gave the *^{3,5}syn,^{5,6}anti-triol* **12** as an oil (238 mg, 88%); R_f(diethyl ether) 0.21; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3685 (O–H), 3598 (O–H), 3482 (br, O–H), 2972, 2933, 2875, 1605, 1474, 1460, 1390, 1368, 1291, 1129, 1058 and 856; δ_H(400 MHz; $CDCl_3$) 7.52–7.47 (2 H, m, PhS), 7.43–7.30 (3 H, m, PhS), 4.02* (1 H, s, OH), 3.82–3.73 (1 H, m, C*H*Me), 3.67 (1 H, s, OH), 3.68–3.62 (1 H, m, C*H*OH), 3.53 (1 H, d, *J* 10.7 Hz, PhSCC*H*OH) 2.24* (1 H, s, OH), 1.66 (1 H, br d, *J* 14.3 Hz, CH_AH_B), 1.51 (1 H, dt, *J* 13.9 and 10.2 Hz, CH_AH_B), 1.47 (3 H, s, Me_A), 1.26 (3 H, s, Me_B) and 1.12 (3 H, d, *J* 6.4 Hz, CH*Me*); δ_C(100.6 MHz; $CDCl_3$) 137.4$^+$, 129.9$^-$ (*i*-Ph), 129.4$^+$, 128.9$^+$, 75.8$^+$ (C–O), 75.6$^+$ (C–O), 70.1$^+$ (C–O), 55.2$^-$ (CSPh), 30.1$^-$ (CH_2), 25.6$^+$ (Me), 21.7$^+$ (Me) and 17.7$^+$ (Me); *m*/*z* (+FAB) 270 (14%, M^+), 253 (82, $M^+ - OH$), 186 (100), 154 (61) and 136 (74); (Found: M^+, 270.1280. $C_{14}H_{22}O_3S$ requires *M*, 270.1290).

(3*SR*,5*SR*,6*RS*)-2-Methyl-2-phenylsulfanylheptane-3,5,6-triol 13

By the method described for compound **12**, silyl ether **21** (384 mg, 1.0 mmol) and tetra-*n*-butylammonium fluoride (1.0 cm^3, 1.0 mmol) in tetrahydrofuran (20 cm^3) gave a crude product as an oil. Purification by column chromatography (silica, diethyl ether) gave the *^{3,5}anti,^{5,6}anti-triol* **13** as an oil (248 mg, 92%); R_f(diethyl ether) 0.13; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3610 (O–H), 3489 (O–H), 2971, 2932, 1474, 1460, 1438, 1388, 1368, 1289, 1127, 1053 and 909; δ_H(400 MHz; $CDCl_3$) 7.55–7.47 (2 H, m, PhS), 7.42–7.29 (3 H, m, PhS), 3.88–3.77 (2 H, m, C*H*OH and MeC*H*OH), 3.67 (1 H, br d, *J* 10.4 Hz, C*H*OH), 3.16* (1 H, br s, OH), 2.44* (1 H, br s, OH), 2.03* (1 H, br s, OH), 1.66–1.58 (1 H, m, CH_AH_B), 1.51 (1 H, ddd, *J* 13.2, 10.5 and 2.4 Hz, CH_AH_B), 1.25 (3 H, s, Me_A), 1.20 (3 H, s, Me_B), 1.16 (3 H, d, *J* 6.1 Hz, CH*Me*); δ_C(100.6 MHz; $CDCl_3$) 137.4$^+$, 130.2$^-$ (*i*-Ph), 129.3$^+$, 128.8$^+$, 72.5$^+$ (C–O), 71.8$^+$ (C–O), 70.7$^+$ (C–O), 55.4$^-$ (CSPh), 31.8$^-$ (CH_2), 25.8$^+$ (Me), 22.2$^+$ (Me) and 17.7$^+$ (Me); *m*/*z* (+FAB) 270 (22%, M^+), 253 (98, $M^+ - OH$), 186 (24), 151 (100, Me_2CSPh^+) and 143 (91); (Found: M^+, 270.1294. $C_{14}H_{22}O_3S$ requires *M*, 270.1290).

(3*R*,5*R*,6*S*)-2-Methyl-2-phenylsulfanylheptane-3,5,6-triol 13

By the method described for compound **12**, silyl ether **21** (73 mg, 191 μmol) and tetra-*n*-butylammonium fluoride (200 μl, 200 μmol) in tetrahydrofuran (5 cm^3) gave the *^{3,5}anti,^{5,6}anti-triol* (**3***R*,5*R*,6*S*)-**13** as an oil (50 mg, 97%), spectroscopically identical to the racemic sample, retention time/min (Chiralpak AD column; hexane–ethanol, 9:1) 22.9 (100%) and 39.4 (0); $[\alpha]_D$ +21.1 (*c.* 0.47 in CH_2Cl_2; >99% ee).

(3*SR*,5*RS*,6*RS*)-2-Methyl-2-phenylsulfanylheptane-3,5,6-triol 14

By the method described for compound **12**, silyl ether **22** (384 mg, 1.0 mmol) and tetra-*n*-butylammonium fluoride solution (1.0 cm^3, 1.0 mmol) in tetrahydrofuran (20 cm^3) gave a crude product as an oil. Purification by column chromatography (silica, diethyl ether) gave the *^{3,5}syn,^{5,6}syn-triol* **14** as an oil (251 mg, 93%); R_f(diethyl ether) 0.24; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3480 (br, O–H), 2968, 2920, 2873, 1605, 1474, 1459, 1438, 1390, 1368, 1132, 1068 and 852; δ_H(400 MHz; $CDCl_3$) 7.53–7.48 (2 H, m, PhS), 7.42–7.32 (3 H, m, PhS), 4.03* (1 H, br s, OH), 3.69* (1 H, br s, OH), 3.64–3.52 (3 H, m, 3 × C*H*OH), 2.55 (1 H, br s, OH), 1.71–1.63 (1 H, m, CH_AH_B), 1.56 (1 H, ddd, *J* 14.2, 10.4 and 9.3 Hz, CH_AH_B), 1.26 (3 H, s, Me_A), 1.20 (3 H, s, Me_B) and 1.18 (3 H, d, *J* 6.2 Hz, CH*Me*); δ_C(100.6 MHz; $CDCl_3$) 137.4$^+$, 129.9$^-$ (*i*-Ph), 129.4$^+$, 128.9$^+$, 75.9$^+$ (C–O), 75.5$^+$ (C–O), 70.8$^+$ (C–O), 55.1$^-$ (CSPh), 33.0$^-$ (CH_2), 25.5$^+$ (Me), 21.8$^+$ (Me) and 19.4$^+$ (Me); *m*/*z* (+FAB) 270 (26%, M^+), 253 (88, $M^+ - OH$), 186 (55) and 143 (100); (Found: M^+, 270.1296. $C_{14}H_{22}O_3S$ requires *M*, 270.1290).

(3*RS*,5*RS*,6*RS*)-2-Methyl-2-phenylsulfanylheptane-3,5,6-triol 15

By the method described for compound **12**, silyl ether **23** (384 mg, 1.0 mmol) and tetra-*n*-butylammonium fluoride (1.0 cm^3, 1.0 mmol) in tetrahydrofuran (20 cm^3) gave a crude product as an oil. Purification by column chromatography (silica, diethyl ether) gave the *^{3,5}anti,^{5,6}syn-triol* **15** as an oil (254 mg, 94%); R_f(diethyl ether) 0.13; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3864 (O–H), 3603 (O–H), 2971, 2932, 1605, 1474, 1439, 1389, 1126, 1052 and 909; δ_H(400 MHz; $CDCl_3$) 7.52–7.48 (2 H, m, PhS), 7.41–7.30 (3 H, m, PhS), 3.71–3.58 (3 H, m, 3 × C*H*OH), 3.23* (1 H, s, OH), 2.70* (1 H, d, *J* 6.0 Hz, OH), 2.38* (1 H, d, *J* 3.9 Hz, OH), 1.66–1.53 (2 H, m, CH_AH_B and CH_AH_B), 1.25 (3 H, s, Me_A), 1.19 (3 H, s, Me_B) and 1.15 (3 H, d, *J* 6.1 Hz, CH*Me*); δ_C(100.6 MHz; $CDCl_3$) 137.4$^+$, 130.2$^-$ (*i*-Ph), 129.3$^+$, 128.9$^+$, 73.7$^+$ (C–O), 71.9$^+$ (C–O), 70.5$^+$ (C–O), 55.1$^-$ (CSPh), 33.4$^-$ (CH_2), 25.7$^+$ (Me), 22.3$^+$ (Me) and 19.2$^+$ (Me); *m*/*z* (+FAB) 270 (8%, M^+) 253 (75, $M^+ - OH$), 186 (100), 151 (71, Me_2CSPh^+) and 143 (92); (Found: M^+, 270.1301. $C_{14}H_{22}O_3S$ requires *M*, 270.1290).

(3*S*,5*S*,6*S*)-2-Methyl-2-phenylsulfanylheptane-3,5,6-triol 15

By the method described for compound **12**, silyl ether **23** (50 mg, 130 μmol) and tetra-*n*-butylammonium fluoride (130 μl, 130 μmol) in tetrahydrofuran (5 cm^3) gave the *^{3,5}anti,^{5,6}syn-triol* (**3***S*,5*S*,6*S*)-**15** as an oil (33 mg, 95%), spectroscopically identical to the racemic sample, retention time/min (Chiralpak AD column; hexane–ethanol, 9:1) 27.1 (1.4%) and 36.8 (98.6); $[\alpha]_D$ −7.9 (*c.* 1.0 in CH_2Cl_2; >97% ee).

(2*RS*)-2-(*tert*-Butyldimethylsilyloxy)propanal 16

A modification of a method reported by Kobayashi was used;[16] diisobutylaluminium hydride (1.0 mol dm^{-3} in toluene, 12 cm^3, 12 mmol) was added under argon, during a 5 minute period, to a solution of TBDMS-protected methyl lactate (2.18 g, 10 mmol) in diethyl ether (80 cm^3) at −78 °C. After stirring for 20 minutes the reaction was quenched at this temperature by the addition of methanol (1 cm^3) followed immediately by a saturated aqueous solution of potassium sodium tartrate (15 cm^3). Stirring was continued for 30 minutes during which time the solution was allowed to warm to room temperature. A further portion of the tartrate solution (50 cm^3) was added and the gelatinous mixture stirred for a further 10 minutes. The mixture was then filtered under reduced pressure, through a compacted pad of Celite, into a Buchner flask. The residues were washed twice with diethyl ether (25 cm^3) and filtered. The resulting biphasic mixture was transferred to a separating funnel and the organic layer separated. The aqueous layer was

extracted with diethyl ether (3 × 30 cm^3) and the combined extracts were dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure to give a crude product as a pale yellow liquid. This residue was purified by Kugelröhr distillation to give the aldehyde **16** (771 mg, 41%) as a liquid, bp 90 °C at 20 mmHg (lit.,[16] 90 °C at 20 mmHg); δ_H(250 MHz; $CDCl_3$) 9.62 (1 H, d, *J* 1.2 Hz, CHO), 4.09 (1 H, qd, *J* 6.9 and 1.2 Hz, CH), 1.28 (3 H, d, *J* 6.8 Hz, Me), 0.92 (9 H, s, Si^{t}Bu), 0.11 (3 H, s, Si$Me_A$$Me_B$) and 0.10 (3 H, s, $SiMe_A$$Me_B$); δ_C(100.6 MHz; $CDCl_3$) 204.1$^+$ (CHO), 73.8$^+$ (CH–O), 25.7$^+$ (SiCMe_3), 18.5$^+$ (Me), 18.2$^-$ (Si$C$$Me_3$) and −4.81$^+$ (Si$Me_A$$Me_B$ and $SiMe_A$$Me_B$); *m*/*z* (EI) 189 (1%, MH^+), 173 (5), 159 (17, M^+ − CHO), 131 (100, ^{t}$BuMe_2SiO^+$), 103 (21), 75 (44) and 73 (58); (Found: MH^+, 189.1302. $C_9H_{21}O_2Si$ requires 189.1311).

(2*S*)-2-(*tert*-Butyldimethylsilyloxy)propanal 16

By the same method used for the racemic compound, diisobutylaluminium hydride (1.0 mol dm^{-3} in toluene, 12 cm^3, 12 mmol) and TBDMS-protected (*S*)-methyl lactate (97% ee) (2.18 g, 10 mmol) in diethyl ether (80 cm^3) gave the aldehyde (**2***S*)-**16** (1.4 g, 74% crude yield) as a liquid, which was used without further purification.

2-Methyl-2-phenylsulfanylbutan-3-one 17

Alcohol **44** (5.0 g, 25.5 mmol) was added in one portion, under argon at 0 °C to a stirred solution of pyridinium chlorochromate (PCC) (7.86 g, 36.4 mmol) in dichloromethane (100 cm^3). The solution was allowed to warm to room temperature and stirred until the reaction was judged complete by TLC. Dry diethyl ether (50 cm^3) was added and the supernatant liquor decanted from a black gum. The insoluble residues were washed 5 times with ether (50 cm^3) and the combined ethereal extracts were filtered through a plug of florisil, which was washed with more diethyl ether. The solvent was removed under reduced pressure to give a crude product as a pale yellow–green oil. Purification was achieved by column chromatography [silica, light petroleum (bp 40–60 °C)–diethyl ether, 9:1] to give the *ketone* **17** (4.32 g, 87%) as a pale yellow oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 9:1) 0.27; ν_{max}(CH_2Cl_2)/cm^{-1} 3078, 3001, 2971, 2930, 2868, 1698 (C=O), 1474, 1462, 1439, 1366, 1137 and 1114; δ_H(400 MHz; $CDCl_3$) 7.37–7.26 (5 H, m, PhS), 2.39 (3 H, s, Me) and 1.41 (6 H, s); δ_C(100.6 MHz; $CDCl_3$) 206.4$^-$ (C=O), 56.5$^-$ (CSPh) and 24.5$^+$ (Me); *m*/*z* (EI) 194 (20%, M^+), 151 (100, Me_2CSPh^+) and 109 (29, PhS^+); (Found: M^+, 194.0765. $C_{11}H_{14}OS$ requires *M*, 194.0765).

(5*SR*,6*RS*)-2-Methyl-2-phenylsulfanyl-5-hydroxy-6-(*tert*-butyldimethylsiloxy)heptan-3-one 18 and (5*RS*,6*RS*)-2-Methyl-2-phenylsulfanyl-5-hydroxy-6-(*tert*-butyldimethylsiloxy)heptan-3-one 19

n-Butyllithium (3.8 cm^3 of a 1.5 mol dm^{-3} solution in hexane, 5.67 mmol) was added to a solution of diisopropylamine (547 mg, 0.80 cm^3, 5.67 mmol) in tetrahydrofuran (40 cm^3), under argon, at 0 °C. After stirring for 10 minutes the solution was cooled to −78 °C and the ketone **17** (1.00 g, 5.15 mmol) in tetrahydrofuran (5 cm^3) added over a 10 minute period. Stirring was continued for 1 hour and the aldehyde **16** (1.10 g, 5.85 mmol) in tetrahydrofuran (5 cm^3) was added over a 5 minute period. The reaction was quenched after 2 hours at −78 °C, by the addition of saturated ammonium chloride solution (30 cm^3), and the reaction allowed to warm to room temperature. The resulting slurry was transferred to a separating funnel and the residue washed in with water (10 cm^3) followed by diethyl ether (30 cm^3). The organic layer was separated and the aqueous layer extracted with diethyl ether (3 × 30 cm^3). The combined organic extracts were dried over magnesium sulfate and concentrated under reduced pressure to give a crude product as a pale yellow oil which, on standing, partly crystallised. The semi-crystalline slurry was diluted with hexane and the crystals collected by filtration. The crystals were washed twice with cold hexane (5 cm^3) to give the *ketone* **18** as prisms (276 mg, 14%), mp 67–68 °C (from hexane); ν_{max}(CH_2Cl_2)/cm^{-1} 3598 (O–H), 2956, 2931, 2896, 2857 and 1697 (C=O); δ_H(400 MHz; $CDCl_3$) 7.38–7.25 (5 H, m, PhS), 3.92–3.86 (1 H, m, C*H*–OH), 3.78 (1 H, qn, *J* 6.0 Hz, C*H*–OSiMe_2^{t}Bu), 3.11 (1 H, dd, *J* 17.4 and 2.7 Hz, CH_AH_B), 2.97* (1 H, d, *J* 2.8 Hz, OH), 2.88 (1 H, dd, *J* 17.4 and 9.3 Hz, CH_AH_B), 1.42 (3 H, s, Me), 1.40 (3 H, s, Me), 1.18 (3 H, d, *J* 6.2 Hz, Me), 0.90 (SiCMe_3), 0.09 (Si$Me_A$$Me_B$^{t}Bu) and 0.09 ($SiMe_A$$Me_B$^{t}Bu); δ_C(100.6 MHz; $CDCl_3$) 208.7$^-$ (C=O), 136.2$^+$, 131.0$^-$ (*i*-Ph), 129.4$^+$, 128.9$^+$, 72.6$^+$ (C–O), 71.0$^+$ (C–O), 56.3$^-$ (CSPh), 38.7$^-$ (CH_2), 25.9$^+$ (CMe_3), 24.4$^+$ (Me), 24.3$^+$ (Me), 19.3$^+$ (Me), 18.0$^-$ (*C*Me_3), −4.30$^+$ (Si$Me_A$$Me_B$) and −4.72$^+$ ($SiMe_A$$Me_B$); *m*/*z* (+ES) 405 (100%, MNa^+) and 383 (28, MH^+); (Found: MNa^+, 405.1880. $C_{20}H_{34}O_3NaSSi$ requires 405.1896). The hexane residue was concentrated under reduced pressure and the residue purified by column chromatography [silica, light petroleum (bp 40–60 °C)–diethyl ether, 4:1] to give a mixture of ketones **18** and **19** as an oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.21. Further purification was carried out by HPLC (hexane, 0.5% ^{i}PrOH) to give a second portion of the ketone **18** (retention time 13.0 min) as prisms (295 mg, 15%) and the *ketone* **19** (retention time 14.5 min) as an oil (630 mg, 32%), ν_{max}(CH_2Cl_2)/cm^{-1} 3560 (O–H), 2956, 2931, 2896, 2858 and 1699 (C=O); δ_H(400 MHz; $CDCl_3$) 7.38–7.25 (5 H, m, PhS), 3.95 (1 H, td, *J* 8.5 and 4.1 Hz, C*H*–OH), 3.86 (1 H, dt, *J* 10.4 and 6.2 Hz, C*H*–OSiMe_2^{t}Bu), 2.98 (1 H, dd, *J* 17.0 and 8.8 Hz, CH_AH_B), 2.90 (1 H, dd, *J* 17.0 and 3.3 Hz, CH_AH_B), 2.84* (1 H, d, *J* 4.9 Hz, OH), 1.42 (3 H, s, Me), 1.41 (3 H, s, Me), 1.17 (3 H, d, *J* 6.2 Hz, Me), 0.91 (SiCMe_3), 0.10 (Si$Me_A$$Me_B$^{t}Bu) and 0.10 ($SiMe_A$-$Me_B$^{t}Bu); δ_C(100.6 MHz; $CDCl_3$) 208.1$^-$ (C=O), 136.2$^+$, 131.1$^-$ (*i*-Ph), 129.3$^+$, 128.8$^+$, 71.9$^+$ (C–O), 70.5$^+$ (C–O), 56.3$^-$ (CSPh), 38.8$^-$ (CH_2), 25.9$^+$ (CMe_3), 24.3$^+$ (Me × 2), 19.0$^+$ (Me), 18.1$^-$ (*C*Me_3), −4.30$^+$ (Si$Me_A$$Me_B$) and −4.80$^+$ ($SiMe_A$$Me_B$); *m*/*z* (+FAB) 383 (14%, MH^+), 365 (9, $M^+ - H_2O$), 325 (20), 251 (47, M^+ − OSiMe_2^{t}Bu), 151 (100, Me_2CSPh^+) and 131 (28, ^{t}$BuMe_2SiO^+$); (Found: MH^+, 383.2069. $C_{20}H_{35}O_3SSi$ requires 383.2076).

(5*R*,6*S*)-2-Methyl-2-phenylsulfanyl-5-hydroxy-6-(*tert*-butyldimethylsiloxy)heptan-3-one 18 and (5*S*,6*S*)-2-Methyl-2-phenylsulfanyl-5-hydroxy-6-(*tert*-butyldimethylsiloxy)heptan-3- one 19

By the same method used for the racemic compounds, *n*-butyllithium (12.2 cm^3 of a 1.4 mol dm^{-3} solution in hexane, 15.5 mmol) and diisopropylamine (1.73 g, 2.41 cm^3, 17.1 mmol) in tetrahydrofuran (100 cm^3), ketone **17** (3.00 g, 15.5 mmol) in tetrahydrofuran (50 cm^3) and aldehyde (**2***S*)-**16** (*ca*. 23 mmol) in tetrahydrofuran (25 cm^3) gave the *ketone* (**5***R*,6*S*)-**18** (768 mg, 13%‡) as an oil, spectroscopically identical to the racemic sample, [*a*]$_D$ +30.3 (*c.* 0.6 in CH_2Cl_2; 97% ee) and the *ketone* (**5***S*,6*S*)-**19** (887 mg, 15%‡) as an oil, spectroscopically identical to the racemic sample, [*a*]$_D$ −18.6 (*c.* 1.01 in CH_2Cl_2; 97% ee).

(3*RS*,5*SR*,6*RS*)-2-Methyl-2-phenylsulfanyl-6-(*tert*-butyldimethylsiloxy)heptane-3,5-diol 20

Using the method described for compound **11**, ketone **18** (500 mg, 1.31 mmol), diethylmethoxyborane (1.6 cm^3, 1.6 mmol) and sodium borohydride (59 mg, 1.56 mmol) in 4:1 tetrahydrofuran–methanol (12.5 cm^3) gave a crude product as an oil. Purification by column chromatography [silica, light petroleum (bp 40–60 °C)–diethyl ether, 4:1] gave the *[3,5]syn,[5,6]anti-diol* **20** as an oil (305 mg, 61%); R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.09; ν_{max}(CH_2Cl_2)/cm^{-1} 3497 (O–H), 2956, 2929, 2856, 1463 and 1438; δ_H(400 MHz; $CDCl_3$) 7.52–7.49 (2 H, m, PhS), 7.40–7.30 (3 H, m, PhS), 3.71* (1 H, s, OH),

‡ Only part of the crude material was separated by HPLC.

3.65 (1 H, dt, *J* 11.7 and 6.0 Hz, C*H*Me), 3.61–3.52 (2 H, m, C*H*OH and C*H*OH), 3.43 (1 H, s, OH), 1.96 (1 H, br d, *J* 14.2 Hz, CH_AH_B), 1.38 (1 H, dt, *J* 14.3 and 10.2 Hz CH_AH_B), 1.26 (3 H, s, Me), 1.19 (3 H, s, Me), 1.14 (3 H, d, *J* 6.1 Hz, CH*Me*), 0.86 (9 H, s, Si^{t}Bu), 0.06 (Si*Me*$_A$Me$_B$) and 0.05 (SiMe$_A$*Me*$_B$); δ_C(100.6 MHz; $CDCl_3$) 137.5$^+$, 130.5$^-$ (*i*-Ph), 129.2$^+$, 128.8$^+$, 76.9$^+$ (C–O), 76.5$^+$ (C–O), 71.6$^+$ (C–O), 54.5$^-$ (CSPh), 32.6$^-$ (CH_2), 25.8$^+$ (C*Me*$_3$), 25.0$^+$ (Me), 23.0$^+$ (Me), 18.8$^+$ (Me), 18.0$^-$ (*C*Me$_3$), −4.32$^+$ (Si*Me*$_A$Me$_B$) and −4.78$^+$ (SiMe$_A$*Me*$_B$); *m*/*z* (+FAB) 385 (13%, MH$^+$), 367 (43, M$^+$ – OH), 309 (27), 235 (96), 151 (73, Me_2CSPh^+) and 131 (100, ^{t}BuMe$_2$SiO$^+$); (Found: MH$^+$, 385.2214. $C_{20}H_{37}O_3SSi$ requires 385.2233).

(3*SR*,5*SR*,6*RS*)-2-Methyl-2-phenylsulfanyl-6-(*tert*-butyldimethylsiloxy)heptane-3,5-diol 21

Using the method described for compound **10**, ketone **18** (500 mg, 1.31 mmol) and tetramethylammonium triacetoxyborohydride (4.14 g, 15.7 mmol) in 1:1 MeCN:AcOH (20 cm^3) gave a crude product as an oil. Purification by column chromatography [silica, light petroleum (bp 40–60 °C)–diethyl ether, 4:1] gave the *[3,5]anti,[5,6]anti-diol* **21** as an oil (372 mg, 74%); R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.07; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3568 (O–H), 2957, 2931, 2886, 2857, 1472, 1463 and 1438; δ_H(400 MHz; $CDCl_3$) 7.54–7.49 (2 H, m, PhS), 7.40–7.28 (3 H, m, PhS), 3.82–3.78 (2 H, m, C*H*OH and C*H*Me), 3.67 (1 H, d, *J* 10.3 Hz, PhSCC*H*OH), 3.01* (1 H, s, PhSCCHO*H*), 2.35* (1 H, d, *J* 3.9 Hz, CHO*H*), 1.53 (1 H, dd, *J* 13.6 and 8.7 Hz, CH_AH_B), 1.44 (1 H, ddd, *J* 13.0, 10.5 and 2.4 Hz, CH$_A$*H*$_B$), 1.24 (3 H, s, Me), 1.20 (3 H, s, Me), 1.09 (3 H, d, *J* 5.9 Hz, CH*Me*), 0.86 (9 H, s, Si^{t}Bu), 0.06 (3 H, s, Si*Me*$_A$Me$_B$) and 0.02 (3 H, s, SiMe$_A$*Me*$_B$); δ_C(100.6 MHz; $CDCl_3$) 137.5$^+$, 130.4$^-$ (*i*-Ph), 129.2$^+$, 128.8$^+$, 72.6$^+$ (C–O), 71.7$^+$ (C–O), 71.4$^+$ (C–O), 55.5$^-$ (CSPh), 32.3$^-$ (CH_2), 25.8$^+$ (C*Me*$_3$), 25.8$^+$ (Me), 22.2$^+$ (Me), 18.0$^-$ (*C*Me$_3$), 17.7$^+$ (Me), −4.30$^+$ (Si*Me*$_A$Me$_B$) and −4.80$^+$ (SiMe$_A$*Me*$_B$); *m*/*z* (+FAB) 385 (4%, MH$^+$), 367 (53), 309 (28), 235 (88), 151 (92, Me_2CSPh^+), 143 (83) and 131 (100, ^{t}BuMe$_2$SiO$^+$); (Found: MH$^+$, 385.2224. $C_{20}H_{37}O_3SSi$ requires *M*, 385.2233).

(3*R*,5*R*,6*S*)-2-Methyl-2-phenylsulfanyl-6-(*tert*-butyldimethylsiloxy)heptane-3,5-diol 21

Using the method described for compound **10**, ketone **18** (104 mg, 272 μmol) and tetramethylammonium triacetoxyborohydride (859 mg, 3.26 mmol) in 1:1 MeCN:AcOH (5.0 cm^3) gave the *diol* (**3***R*,5*R*,6*S*)-**21** as an oil (81 mg, 77%), spectroscopically identical to the racemic sample, $[a]_D$ +18.4 (*c.* 0.70 in CH_2Cl_2; 97% ee).

(3*SR*,5*RS*,6*RS*)-2-Methyl-2-phenylsulfanyl-6-(*tert*-butyldimethylsiloxy)heptane-3,5-diol 22

Using the method described for compound **11**, ketone **19** (500 mg, 1.31 mmol), diethylmethoxyborane (1.6 cm^3, 1.6 mmol) and sodium borohydride (59 mg, 1.56 mmol) in 4:1 tetrahydrofuran:methanol (12.5 cm^3) gave a crude product as an oil. Purification by column chromatography [silica, light petroleum (bp 40–60 °C)–diethyl ether, 4:1] gave the *[3,5]syn,[5,6]syn-diol* **22** as an oil (427 mg, 85%); R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.14; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3491 (O–H), 2957, 2931, 2885, 2858, 1472, 1463 and 1438; δ_H(400 MHz; $CDCl_3$) 7.52–7.48 (2 H, m, PhS), 7.39–7.28 (3 H, m, PhS), 3.81* (1 H, s, OH), 3.73 (1 H, dt, *J* 11.4 and 6.1 Hz, C*H*Me), 3.66–3.55 (2 H, m, C*H*OH and C*H*OH), 3.17* (1 H, d, *J* 3.4 Hz, OH), 1.91 (1 H, br d, *J* 14.2 Hz, CH_AH_B), 1.48 (1 H, dt, *J* 14.1 and 10.1 Hz, CH$_A$*H*$_B$), 1.26 (3 H, s, Me), 1.20 (3 H, s, Me), 1.17 (3 H, d, *J* 6.2 Hz, CH*Me*), 0.86 (9 H, s, Si^{t}Bu) 0.07 (3 H, s, Si*Me*$_A$Me$_B$) and 0.03 (3 H, s, SiMe$_A$*Me*$_B$); δ_C(100.6 MHz; $CDCl_3$) 137.6$^+$, 130.8$^-$ (*i*-Ph), 129.0$^+$, 128.7$^+$, 76.6$^+$ (C–O), 76.4$^+$ (C–O), 71.1$^+$ (C–O), 54.1$^-$ (CSPh), 32.7$^-$ (CH_2), 25.8$^+$ (C*Me*$_3$), 24.6$^+$ (Me), 23.7$^+$ (Me), 19.2$^+$ (Me), 18.0$^-$ (*C*Me$_3$), −4.27$^+$ (Si*Me*$_A$Me$_B$) and −4.83$^+$ (SiMe$_A$*Me*$_B$); *m*/*z* (+FAB) 385 (2%, MH$^+$), 367 (23, M$^+$ − OH), 309 (9), 235 (100), 151 (37, Me_2CSPh^+) and 131 (48, ^{t}BuMe$_2$SiO$^+$); (Found: MH$^+$, 385.2232. $C_{20}H_{37}O_3SSi$ requires 385.2233).

(3*RS*,5*RS*,6*RS*)-2-Methyl-2-phenylsulfanyl-6-(*tert*-butyldimethylsiloxy)heptane-3,5-diol 23

Using the method described for compound **10**, ketone **19** (500 mg, 1.31 mmol) and tetramethylammonium triacetoxyborohydride (4.14 g, 15.7 mmol) in 1:1 MeCN:AcOH (20 cm^3) gave a crude product as an oil. Purification by column chromatography [silica, light petroleum (bp 40–60 °C)–diethyl ether, 4:1] gave the *[3,5]anti,[5,6]syn-diol* **23** as an oil (441 mg, 88%); R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.09; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3562 (O–H), 2958, 2931, 2887, 2858, 1472, 1463 and 1438; δ_H(400 MHz; $CDCl_3$) 7.55–7.49 (2 H, m, PhS), 7.39–7.28 (3 H, m, PhS), 3.73–3.60 (3 H, m, C*H*Me, C*H*OH and PhSCC*H*OH), 3.07* (1 H, s, PhSCCHO*H*), 2.29* (1 H, d, *J* 5.8 Hz, OH), 1.59 (1 H, dd, *J* 13.6 and 9.4 Hz, CH_AH_B), 1.45 (1 H, dd, *J* 13.2, 10.6 and 2.3 Hz, CH$_A$*H*$_B$), 1.23 (3 H, s, Me), 1.19 (3 H, s, Me), 1.16 (3 H, d, *J* 6.0 Hz, CH*Me*), 0.87 (9 H, s, Si^{t}Bu), 0.07 (Si*Me*$_A$Me$_B$) and 0.06 (SiMe$_A$*Me*$_B$); δ_C(100.6 MHz; $CDCl_3$) 137.5$^+$, 130.6$^-$ (*i*-Ph), 129.1$^+$, 128.8$^+$, 73.0$^+$ (C–O), 72.0$^+$ (C–O), 71.8$^+$ (C–O), 55.1$^-$ (CSPh), 34.9$^-$ (CH_2), 25.8$^+$ (C*Me*$_3$), 25.6$^+$ (Me), 22.7$^+$ (Me), 20.3$^+$ (Me), 18.0$^-$ (*C*Me$_3$), −4.15$^+$ (Si*Me*$_A$Me$_B$) and −4.83$^+$ (SiMe$_A$*Me*$_B$); *m*/*z* (+FAB) 385 (9%, MH$^+$), 367 (66, M$^+$ − OH), 309 (24), 235 (84), 151 (72, Me_2CSPh^+), 143 (100) and 131 (89, ^{t}BuMe$_2$SiO$^+$); (Found: MH$^+$, 385.2230. $C_{20}H_{37}O_3SSi$ requires 385.2233).

(3*S*,5*S*,6*S*)-2-Methyl-2-phenylsulfanyl-6-(*tert*-butyldimethylsiloxy)heptane-3,5-diol 23

Using the method described for compound **10**, ketone **19** (140 mg, 366 μmol) and tetramethylammonium triacetoxyborohydride (1.16 g, 4.39 mmol) in 1:1 MeCN:AcOH (5.0 cm^3) gave the *diol* (**3***S*,5*S*,6*S*)-**23** as an oil (109 mg, 77%), spectroscopically identical to the racemic sample, $[a]_D$ −16.5 (*c.* 1.60 in CH_2Cl_2; 97% ee).

(1*RS*,2*SR*,4*SR*)-1-[5,5-Dimethyl-4-(phenylsulfanyl)tetrahydrofuran-2-yl]ethanol 24

Toluene-*p*-sulfonic acid (1.3 mg, 6.9 μmol) was added to a stirred solution of *syn*,*anti*-triol **12** (37 mg, 0.137 mmol) in dichloromethane (2 cm^3). The reaction temperature was raised to 50 °C to initiate reflux and heating continued for 48 hours. The reaction mixture was cooled to room temperature and filtered through a short plug of silica, eluting with dichloromethane, to give the *[2,4]syn-tetrahydrofuran* **24** (31 mg, 89%) as an oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 1:1] 0.23;$\nu_{max}(CH_2Cl_2)$/cm^{-1} 3561 (O–H), 3063, 2988, 2935, 2855, 1481, 1447, 1439, 1195, 1141, 1085 and 909; δ_H(400 MHz; $CDCl_3$) 7.47–7.42 (2 H, m, PhS), 7.34–7.22 (3 H, m, PhS), 3.97–3.89 (1 H, m, CH–O), 3.86 (1 H, qd, *J* 5.7 and 3.4 Hz, C*H*Me), 3.48 (1 H, dd, *J* 10.7 and 6.8 Hz, CHSPh), 2.23 (1 H, dt, *J* 12.6 and 6.1 Hz, CH_AH_B), 2.12–2.06 (2 H, m, CH$_A$*H*$_B$ and OH), 1.31 (3 H, s, Me$_A$), 1.30 (3 H, s, Me$_B$) and 1.10 (3 H, d, *J* 6.5 Hz, CH*Me*); δ_C(100.6 MHz; $CDCl_3$) 135.5$^-$ (*i*-PhS), 131.7$^+$, 129.0$^+$, 127.1$^+$, 82.6$^-$ (C–O), 80.4$^+$ (CH–O), 67.1$^+$ (CH–O), 56.1$^+$, 33.0$^-$ (CH_2), 28.0$^+$ (Me), 25.2$^+$ (Me) and 17.9$^+$ (Me); *m*/*z* (EI) 252 (57%, M$^+$), 207 (81, M$^+$ − MeCHOH), 194 (411, M$^+$ − Me_2CO), 179 (11), 163 (45), 150 (61) and 110 (100, PhSH$^+$); (Found: M$^+$, 252.1191. $C_{14}H_{20}O_2S$ requires *M*, 252.1184).

(1*RS*,2*SR*,4*RS*)-1-[5,5-Dimethyl-4-(phenylsulfanyl)tetrahydrofuran-2-yl]ethanol 25

By the method described for compound **24**, toluene-*p*-sulfonic acid (1.8 mg, 9.5 μmol) and a solution of *anti*,*anti*-triol **13** (50 mg, 185 μmol) in dichloromethane (2.5 cm^3) gave the *[2,4]anti-*

tetrahydrofuran **25** (35 mg, 75%) after 72 hours as an oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 1:1] 0.25;$\nu_{max}(CH_2Cl_2)$/cm^{-1} 3589 (O–H), 2995, 2963, 2928, 2855, 1604, 1584, 1480, 1460, 1381, 1369, 1091, 1046 and 1014; δ_H(400 MHz; $CDCl_3$) 7.45–7.38 (2 H, m, PhS), 7.33–7.19 (3 H, m, PhS), 3.97 (1 H, ddd, *J* 8.4, 5.3 and 3.0 Hz, CH–O), 3.90 (1 H, qd, 6.5 and 3.2 Hz, C*H*OH), 3.32 (1 H, t, *J* 8.9 Hz, CHSPh), 2.48 (1 H, ddd, *J* 13.1, 8.8 and 5.3 Hz, CH_AH_B), 2.01* (1 H, br s, OH), 1.96 (1 H, dt, *J* 13.0 and 8.8 Hz, CH_AH_B), 1.29 (3 H, s, Me_A), 1.28 (3 H, s, Me_B) and 1.11 (3 H, d, *J* 6.5 Hz, CH*Me*); δ_C(100.6 MHz; $CDCl_3$) 135.7$^-$ (*i*-PhS), 131.0$^+$, 129.0$^+$, 126.8$^+$, 83.1$^-$ (C–O), 79.3$^+$ (CH–O), 67.9$^+$ (CH–O), 55.1$^+$ (CSPh), 33.0$^-$ (CH_2), 27.4$^+$ (Me), 22.0$^+$ (Me) and 17.8$^+$ (Me); *m*/*z* (EI) 252 (50%, M$^+$), 207 (47, M$^+$ – MeCHOH), 194 (46, M$^+$ – Me_2CO), 163 (29), 150 (78), 136 (76) and 110 (100, PhSH$^+$); (Found: M$^+$, 252.1188. $C_{14}H_{20}O_2S$ requires *M*, 252.1184).

(1*RS*,2*RS*,4*RS*)-1-[5,5-Dimethyl-4-(phenylsulfanyl)tetrahydrofuran-2-yl]ethanol 26

By the method described for compound **24**, toluene-*p*-sulfonic acid (1.3 mg, 6.9 μmol) and a solution of *syn*,*syn*-triol **14** (37 mg, 137 μmol) in dichloromethane (2.5 cm^3) gave the ^{2,4}*syn-tetrahydrofuran* **26** (32 mg, 93%) after 72 hours as an oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 1:1] 0.21; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3577 (O–H), 3056, 2974, 2927, 2855, 1583, 1480, 1461, 1380, 1368, 1096, 1049 and 896; δ_H(400 MHz; $CDCl_3$) 7.47–7.40 (2 H, m, PhS), 7.34–7.21 (3 H, m, PhS), 3.71 (1 H, dt, *J* 9.5 and 6.7 Hz, CH–O), 3.61 (1 H, qnd, *J* 6.5 and 3.1 Hz, C*H*OH), 3.47 (1 H, dd, *J* 11.0 and 7.0 Hz, CHSPh), 2.46* (1 H, d, *J* 3.1 Hz, OH), 2.38 (1 H, dt, 12.9 and 6.7 Hz, CH_AH_B), 1.82 (1 H, ddd, *J* 12.6, 11.0 and 9.5 Hz, CH_AH_B), 1.30 (3 H, s, Me_A), 1.26 (3 H, s, Me_B) and 1.10 (3 H, d, *J* 6.3 Hz, CH*Me*); δ_C(100.6 MHz; $CDCl_3$) 135.4$^-$ (*i*-PhS), 131.5$^+$, 129.1$^+$, 127.1$^+$, 82.9$^-$ (C–O), 81.2$^+$ (C–O), 71.6$^+$ (C–O), 56.2$^+$ (CSPh), 36.7$^-$, 29.7$^-$, 27.9$^+$ (Me), 25.2$^+$ (Me), and 18.7$^+$ (Me); *m*/*z* (EI) 252 (58%, M$^+$), 220 (100), 207 (29, M$^+$ − MeCHOH), 194 (35, M$^+$ − Me_2CO), 163 (24), 150 (56) and 110 (62, PhSH$^+$); (Found: M$^+$, 252.1183. $C_{14}H_{20}O_2S$ requires *M*, 252.1184).

(1*RS*,2*RS*,4*SR*)-1-[5,5-Dimethyl-4-(phenylsulfanyl)tetrahydrofuran-2-yl]ethanol 27

By the method described for compound **24**, toluene-*p*-sulfonic acid (1.8 mg, 9.5 μmol) and a solution of *anti*,*syn*-triol **15** (50 mg, 185 μmol) in dichloromethane (2.5 cm^3) gave the ^{2,4}*anti-tetrahydrofuran* **27** (45 mg, 96%) after 72 hours as an oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 1:1] 0.25; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3574 (O–H), 2962, 2928, 1583, 1480, 1459, 1382, 1370, 1090, 1042 and 1025; δ_H(400 MHz; $CDCl_3$) 7.43–7.38 (2 H, m, PhS), 7.33–7.21 (3 H, m, PhS), 3.84 (1 H, ddd, *J* 8.4, 6.1 and 5.1 Hz, CH–O), 3.56 (1 H, qnd, *J* 6.3 and 4.7 Hz, C*H*OH), 3.36 (1 H, t, *J* 8.8 Hz, CHSPh), 2.28* (1 H, d, *J* 4.6 Hz, OH), 2.22 (1 H, ddd, *J* 13.2, 8.4 and 4.9 Hz, CH_AH_B), 2.13 (1 H, dt, *J* 13.1 and 8.7 Hz, CH_AH_B), 1.28 (3 H, s, Me_A), 1.27 (3 H, s, Me_B) and 1.14 (3 H, d, *J* 6.3 Hz, CH*Me*); δ_C(100.6 MHz; $CDCl_3$) 135.6$^-$ (*i*-PhS), 131.2$^+$, 129.1$^+$, 126.9$^+$, 83.5$^-$ (C–O), 79.7$^+$ (CH–O), 70.7$^+$ (CH–O), 55.0$^+$ (CSPh), 36.4$^-$ (CH_2), 27.8$^+$ (Me), 22.4$^+$ (Me), 19.2$^+$ (Me); *m*/*z* (EI) 252 (70%, M$^+$), 207 (72, M$^+$ − MeCHOH), 194 (63, M$^+$ − Me_2CO), 179 (20), 163 (45), 150 (100), 135 (64) and 110 (93, PhSH$^+$); (Found: M$^+$, 252.1181. $C_{14}H_{20}O_2S$ requires *M*, 252.1184).

(1*RS*,2*RS*,4*SR*)-1-Phenyl(4-phenylsulfanyl-1-oxaspiro[4.5]dec-2-yl)methanol 29

By the method described for compound **24**, toluene-*p*-sulfonic acid (1.2 mg, 6.3 μmol) and a solution of the *anti*,*syn*-triol **10** (50 mg, 134 μmol) in dichloromethane (2.5 cm^3) gave the ^{2,4}*anti-tetrahydrofuran* **29** (44 mg, 93%) after 24 hours as an oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.14; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3560 (O–H), 2928, 2855, 1584, 1480, 1455, 1377, 1196 and 909; δ_H(250 MHz; $CDCl_3$) 7.36–7.14 (10 H, m, Ph and PhS), 4.45 (1 H, d, *J* 7.0 Hz, PhC*H*OH), 4.21 (1 H, dt, *J* 7.4 and 5.8 Hz, CH–O), 3.32 (1 H, t, 7.7 Hz, PhSCH), 2.26 (1 H, ddd, 13.4, 7.7 and 5.7 Hz, CH_AH_B), 1.94 (1 H, dt, 13.3 and 7.7 Hz, CH_AH_B) and 1.83–1.15 (10 H, m); δ_C(100.6 MHz; $CDCl_3$) 140.4$^-$, 135.8$^-$, 130.7$^+$, 129.0$^+$, 128.4$^+$, 128.0$^+$, 127.2$^+$, 126.6$^+$, 84.9$^-$ (C–O), 79.5$^+$ (CH–O), 77.6$^+$ (CH–O), 54.8$^+$ (C–SPh), 37.2$^-$, 35.7$^-$, 31.5$^-$, 29.7$^-$, 25.6$^-$, 23.3$^-$ and 22.3$^-$; *m*/*z* (EI) 354 (7%, M$^+$), 247 (100, M$^+$ − PhCHOH), 203 (24), 137 (94), 119 (43) and 84 (65); (Found: M$^+$, 354.1654. $C_{22}H_{26}O_2S$ requires *M*, 354.1653).

(1*RS*,2*RS*,4*RS*)-1-Phenyl-(4-phenylsulfanyl-1-oxaspiro[4.5]dec-2-yl)methanol 30

By the method described for compound **24**, but *without* heating at reflux, toluene-*p*-sulfonic acid (0.6 mg, 3.2 μmol) and a solution of *syn*,*syn*-triol **11** (25 mg, 67.1 μmol) in dichloromethane (2.5 cm^3) gave the ^{2,4}*syn-tetrahydrofuran* **30** (19 mg, 81%) after 3 days as an oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.14; $\nu_{max}(CH_2Cl_2)$/cm^{-1} 3567 (O–H), 3063, 2986, 2936, 2859, 1584, 1480, 1449, 1439, 1388, 1194, 1145, 1085 and 909; δ_H(400 MHz; $CDCl_3$) 7.46–7.17 (10 H, m, Ph and PhS), 4.53 (1 H, dd, *J* 7.8 and 1.7 Hz, PhC*H*OH), 4.00 (1 H, br q, *J* 8.0 Hz, CH–O), 3.37 (1 H, dd, *J* 9.7 and 7.1 Hz, PhSCH), 3.12* (1 H, d, *J* 1.9 Hz, OH), 2.16 (1 H, dt, *J* 13.2 and 6.9 Hz, CH_AH_B), 1.90 (1 H, dt, *J* 12.9 and 9.5 Hz, CH_AH_B), 1.79–1.48 (9 H, m) and 1.30–1.17 (1 H, m); δ_C(100.6 MHz; $CDCl_3$) 140.1$^-$, 135.6$^-$, 131.2$^+$, 129.1$^+$, 128.4$^+$, 127.9$^+$, 127.0$^+$, 126.9$^+$, 125.9$^+$, 84.4$^-$ (C–O), 80.8$^+$, 78.7$^+$, 56.2$^+$ (CHSPh), 36.4$^-$, 36.3$^-$, 25.6$^-$, 23.1$^-$ and 22.4$^-$; *m*/*z* (EI) 354 (11%, M$^+$), 247 (100 M$^+$ − PhCHOH), 203 (26), 137 (85) and 110 (21, PhSH$^+$); (Found: M$^+$, 354.1652. $C_{22}H_{26}O_2S$ requires *M*, 354.1653).

(2*RS*,3*SR*,5*RS*)-2-Methyl-5-(1-Methyl-1-phenylsulfanylethyl)-tetrahydrofuran-3-yl ethanoate 36 and (2*RS*,3*SR*,5*SR*)-2,6,6-Trimethyl-5-phenylsulfanyltetrahydropyran-3-yl ethanoate 37

Syn,*anti*-triol **12** (41 mg, 152 μmol) was dissolved in dry dichloromethane (2.0 cm^3) and pyridinium toluene-*p*-sulfonate (10 mg, 38.0 μmol) was added. The reaction vessel was sealed with a septum and trimethyl orthoacetate (20 μl, 19.2 mg, 160 μmol) was injected in one portion. The reaction was stirred at room temperature until TLC indicated that the starting material had been completely consumed (approximately 24 hours). The reaction mixture was then filtered through a short plug of silica, eluting with dichloromethane, and the solvent was evaporated under reduced pressure to give a crude product. This product was redissolved in dichloromethane (2.5 cm^3) and toluene-*p*-sulfonic acid (2.0 mg, 10 μmol) was added. The reaction temperature was raised to 35 °C and allowed to stand at this temperature for 4 days. The reaction mixture was cooled to room temperature and filtered through a short plug of silica, again eluting with dichloromethane. The solvent was evaporated under reduced pressure to give a crude product (37 mg, 83%) which consisted of a 26:74 mixture of THF **36** and THP **37**. These compounds were not successfully separated and therefore not fully characterised. ^{1}H NMR spectroscopy on the crude mixture showed three characteristic peaks: δ_H 5.00 (1 H, td, *J* 9.6 and 5.0 Hz, $CH_{ax}OAc$, THP), 4.83 (1 H, dt, *J* 5.1 and 2.4 Hz, CHOAc, THF) and 3.27 (1 H, t, *J* 4.0 Hz, $CH_{eq}SPh$).

(2*RS*,3*SR*,5*RS*)-2,6,6-Trimethyl-5-phenylsulfanyltetrahydropyran-3-yl ethanoate 38

By the method described for compounds **36** and **37**, *anti*,*anti*-triol **13** (55 mg, 203 μmol), pyridinium toluene-*p*-sulfonate (12.8 mg, 50.8 μmol) and trimethyl orthoacetate (27 μl, 25.6 mg, 214 μmol) in dry dichloromethane (2.5 cm^3) gave a crude product after 24 h which was treated with toluene-*p*-sulfonic

acid (3.8 mg, 20.3 μmol, 10 mol%) in dichloromethane (2.5 cm^3) at 35 °C for 24 hours to give a second product. Purification by chromatography [silica, light petroleum (bp 40–60 °C)–diethyl ether, 4:1] gave the *[2,3]anti,[3,5]syn-tetrahydropyran* **38** (53 mg, 88%) as an oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.32; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2999, 2922, 2855, 1732 (C=O), 1583, 1464, 1369, 1230, 1145, 1106, 1053 and 910; δ_H(400 MHz; $CDCl_3$) 7.42–7.37 (2 H, m, PhS), 7.31–7.19 (3 H, m, PhS), 4.40 (1 H, ddd, *J* 11.2, 9.8 and 4.9 Hz, $CH_{ax}OAc$), 3.64 (1 H, dq, *J* 9.9 and 6.1 Hz, C*H*Me), 3.10 (1 H, dd, *J* 13.1 and 4.3 Hz, $CH_{ax}SPh$), 2.31 (1 H, dt, *J* 12.8 and 4.6 Hz, $CH_{ax}H_{eq}$), 2.01 (3 H, s, Ac), 1.76 (1 H, td, *J* 12.9 and 11.4 Hz, $CH_{ax}H_{eq}$), 1.40 (3 H, s, Me_A), 1.31 (3 H, s, Me_B) and 1.10 (3 H, d, *J* 6.1 Hz, CH*Me*); δ_C(100.6 MHz; $CDCl_3$) 170.1^- (C=O), 134.9^- (*i*-PhS), 132.0^+, 129.1^+, 127.3^+, 75.5^- (C–O), 73.5^+, 68.0^+, 53.5^+ (CHSPh), 33.9^-, 29.7^-, 29.1^+ (Ac), 21.1^+ (Me), 18.5^+ (Me) and 18.4^+ (Me); *m*/*z* (EI) 294 (23%, M^+), 152 (13) and 136 (100); (Found: M^+, 294.1291. $C_{16}H_{22}O_3S$ requires *M*, 294.1290).

(2*RS*,3*RS*,5*RS*)-2,6,6-Trimethyl-5-phenylsulfanyltetrahydropyran-3-yl ethanoate 39

By the method described for compounds **36** and **37**, *syn*,*syn*-triol **14** (50 mg, 185 μmol), pyridinium toluene-*p*-sulfonate (11.6 mg, 46.2 μmol) and trimethyl orthoacetate (25 μl, 23.3 mg, 194 μmol) in dry dichloromethane (2.5 cm^3) gave a crude product after 24 h which was treated with toluene-*p*-sulfonic acid (3.5 mg, 18.5 μmol) in dichloromethane (2.0 cm^3) at 35 °C for 72 hours to give a second product. Purification by chromatography [silica, light petroleum (bp 40–60 °C)–diethyl ether, 4:1] gave the *[2,3]syn,[3,5]anti-tetrahydropyran* **39** (46 mg, 85%) as an oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.22; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2999, 2852, 1732 (C=O), 1583, 1463, 1379, 1242, 1182, 1099, 1067, 1024 and 971; δ_H(400 MHz; $CDCl_3$) 7.39–7.34 (2 H, m, PhS), 7.32–7.18 (3 H, m, PhS), 4.84–4.81 (1 H, s, $CH_{eq}OAc$), 3.85 (1 H, qd, *J* 6.4 and 1.4 Hz, $CH_{ax}Me$), 3.33 (1 H, dd, *J* 13.0 and 4.3 Hz, $CH_{ax}SPh$), 2.14 (1 H, ddd, *J* 14.8, 4.2 and 3.2 Hz, $CH_{ax}H_{eq}$), 2.08 (3 H, s, Ac), 1.97 (1 H, ddd, *J* 14.8, 13.1 and 3.0 Hz, $CH_{ax}H_{eq}$), 1.43 (3 H, s, Me_A), 1.30 (3 H, s, Me_B) and 1.09 (3 H, d, *J* 6.4 Hz, CH*Me*); δ_C(100.6 MHz; $CDCl_3$) 169.6^- (C=O), 134.1^- (*i*-PhS), 130.3^+, 128.0^+, 125.9^+, 74.8^- (C–O), 69.6^+ (CHOAc), 65.7^+ (CHMe), 48.4^+ (CHSPh), 32.6^- (CH_2), 20.3^+ (Ac), 17.2^+ (Me) and 16.7^+ (Me); *m*/*z* (EI) 294 (31%, M^+), 234 (8, M^+ − AcOH), 152 (12) and 136 (100); (Found: M^+, 294.1300. $C_{16}H_{22}O_3S$ requires *M*, 294.1290).

(1*RS*,3*SR*,5*SR*,6*SR*)-1,6-Dimethyl-3-[1-methyl-1-(phenylsulfanyl)ethyl]-2,7,8-trioxabicyclo[3.2.1]octane 41

Anti,*syn*-triol **15** (70 mg, 259 μmol) was dissolved in dry dichloromethane (3.0 cm^3) and pyridinium toluene-*p*-sulfonate (16.3 mg, 64.7 μmol) was added. The reaction vessel was sealed with a septum and trimethyl orthoacetate (35 μl, 32.6 mg, 272 μmol) was injected in one portion. The reaction was stirred at room temperature for 5 minutes and the reaction mixture was then filtered through a short plug of silica, eluting with dichloromethane. The solvent was evaporated under reduced pressure to give the *orthoester* **41** as an oil (73 mg, 96%); R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.33; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3047, 2964, 2928, 2870, 1473, 1400, 1282, 1249, 1143, 1121, 1092, 1070, 949 and 909; δ_H(400 MHz; $CDCl_3$) 7.59–7.51 (2 H, m, PhS), 7.36–7.26 (3 H, m, PhS), 4.26 (1 H, dd, *J* 3.4 and 2.1 Hz, $CH_{eq}O$), 4.20 (1 H, q, *J* 6.2 Hz, C*H*Me), 3.89 (1 H, dd, *J* 11.6 and 4.0 Hz, $CH_{ax}O$), 2.11 (1 H, ddd, *J* 13.4, 11.6 and 3.5 Hz, $CH_{ax}H_{eq}$), 1.71 (1 H, ddd, *J* 13.4, 4.0 and 2.1 Hz, $CH_{ax}H_{eq}$), 1.56 (3 H, s, $MeCO_3$), 1.22 (3 H, s, Me), 1.21 (3 H, s, Me) and 1.20 (3 H, d, *J* 5.4 Hz, CH*Me*); δ_C(100.6 MHz; $CDCl_3$) 137.7^+, 131.5^- (*i*-PhS), 128.8^+, 128.4^+, 119.2^- (CO_3), 77.7^+ (CH–O), 76.1^+ (CH–O), 73.6^+ (CH–O), 50.8^- (CSPh), 29.2^- (CH_2), 25.4^+ (Me), 23.9^+ (Me), 22.7^+ (Me) and 20.3^+ (Me); *m*/*z* (EI) 294 (20%, M^+), 220 (47), 143 (100, $M^+ - Me_2CSPh$), 125 (34) and 109 (18, PhS^+); (Found: M^+, 294.1290. $C_{16}H_{22}O_3S$ requires *M*, 294.1290).

(1*RS*,3*SR*,5*SR*,6*SR*)-1-Methyl-3-(1-cyclohexyl-1-phenylsulfanyl)-6-phenyl-2,7,8-trioxabicyclo[3.2.1]octane 42

By the method described for compound **41**, *anti*,*syn*-triol **10** (45 mg, 121 μmol), pyridinium toluene-*p*-sulfonate (7.6 mg, 30.3 μmol) and trimethyl orthoacetate (16 μl, 15.3 mg, 127 μmol) in dry dichloromethane (2.5 cm^3) gave the *orthoester* **42** (44 mg, 92%) as an oil after 5 minutes; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.43; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3046, 2986, 2935, 2857, 1474, 1448, 1400, 1292, 1152, 1121, 1093, 991, 909 and 870; δ_H(400 MHz; $CDCl_3$) 7.67–7.19 (10 H, m, Ph and PhS), 4.98 (1 H, s, PhC*H*), 4.56 (1 H, br s, $CH_{eq}O$), 4.04 (1 H, dd, *J* 11.5 and 3.9 Hz, $CH_{ax}O$), 2.43 (1 H, td, *J* 11.7 and 3.4 Hz, $CH_{ax}H_{eq}CH_{ax}O$), 2.17–1.13 (11 H, m) and 1.67 (3 H, s, Me); δ_C(100.6 MHz; $CDCl_3$) 141.1^-, 137.4^+, 137.3^+, 131.8^-, 128.6^+, 128.5^+, 127.9^+, 125.8^+, 120.0^- (CO_3), 81.3^+ (CH–O), 79.7^+ (CH–O), 73.8^+ (CH–O), 56.0^- (CSPh), 31.2^-, 30.6^-, 29.0^-, 26.0^-, 22.1^+ (Me) and 21.7^-; *m*/*z* (EI) 396 (6%, M^+), 227 (62), 205 (76, $M^+ - C_6H_{10}SPh$) and 145 (100); (Found: M^+, 396.1757. $C_{24}H_{28}O_3S$ requires *M*, 396.1759).

(2*RS*,3*RS*,5*RS*)-2-Phenyl-5-phenylsulfanyl-1-oxaspiro[5.5]undecan-3-yl ethanoate 43

By the method described for compounds **36** and **37**, *syn*,*syn*-triol **11** (38 mg, 102 μmol), pyridinium toluene-*p*-sulfonate (6.4 mg, 25.5 μmol) and trimethyl orthoacetate (14 μl, 12.9 mg, 107 μmol) in dry dichloromethane (2.5 cm^3) gave a crude product after 24 h which was treated with toluene-*p*-sulfonic acid (1.9 mg, 10 μmol) in dichloromethane (2.5 cm^3) at 35 °C for 72 hours to give a second product. Purification by chromatography [silica, light petroleum (bp 40–60 °C)–diethyl ether, 4:1] gave the *[2,3]syn,[3,5]anti-tetrahydropyran* **43** (36 mg, 89%) as an oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 4:1] 0.31; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3031, 2936, 2858, 1735 (C=O), 1583, 1478, 1449, 1374, 1240, 1064, 1036 and 992; δ_H(400 MHz; $CDCl_3$) 7.42–7.35 (2 H, m, PhS), 7.34–7.18 (3 H, m, PhS), 5.31–5.24 (1 H, m, $CH_{eq}OAc$), 4.77 (1 H, s, $CH_{ax}Ph$), 3.36 (1 H, dd, *J* 11.6 and 5.9 Hz, $CH_{ax}SPh$), 2.32–2.12 (3 H, m, includes $CH_{ax}H_{eq}$ and $CH_{ax}H_{eq}$), 1.96–1.16 (9 H, m) and 1.79 (3 H, s, Ac); δ_C(100.6 MHz; $CDCl_3$) 170.6^- (C=O), 139.2^-, 135.9^-, 131.5^+, 129.4^+, 128.4^+, 127.6^+, 127.3^+, 126.3^+, 77.2^- (C–O), 71.3^+ (CHPh), 70.5^+ (CHOAc), 50.4^+ (CHSPh), 37.3^-, 33.3^-, 26.3^-, 24.7^-, 21.7^-, 21.2^+ (Ac) and 21.2^-; *m*/*z* (EI) 396 (14%, M^+), 238 (23), 162 (21), 136 (100) and 120 (45); (Found: M^+, 396.1763. $C_{24}H_{28}O_3S$ requires *M*, 396.1759).

(2*RS*)-3-Methyl-3-phenylsulfanylbutan-2-ol 44

Methyllithium (18 cm^3 of a 1.6 mol dm^{-3} solution in diethyl ether, 28.8 mmol) was added dropwise to a stirred solution of 2-methyl-2-phenylsulfanylpropionaldehyde (5.0 g, 27.8 mmol) in diethyl ether (100 cm^3), at 0 °C, under an argon atmosphere. The mixture was allowed to warm to room temperature and stirring continued for 1 hour. The reaction was then cooled to 0 °C and saturated ammonium chloride solution added (70 cm^3). The mixture was transferred to a separating funnel and the organic layer separated. The aqueous layer was extracted twice with diethyl ether (30 cm^3) and the combined organic extracts washed with water (30 cm^3) and saturated brine solution (30 cm^3). The ether solution was dried over anhydrous magnesium sulfate and the solvent evaporated under reduced pressure to give the crude product as a pale yellow oil. The product was purified by column chromatography (silica, light petroleum (bp 40–60 °C)–diethyl ether, 9:1] to give *alcohol* **44** (5.40 g, 99%) as an oil; R_f[light petroleum (bp 40–60 °C)–diethyl ether, 9:1] 0.10; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3501 (br, O–H), 3075, 2971,

2934, 2873, 1474, 1461, 1387, 1366 and 1283; δ_H(400 MHz; $CDCl_3$) 7.53–7.50 (2 H, m, PhS), 7.38–7.30 (3 H, m, PhS), 3.53 (1 H, qd, *J* 6.4 and 2.2 Hz, C*H*OH), 2.94* (1 H, br d, *J* 1.4 Hz, OH), 1.24 (3 H, s, Me), 1.18 (3 H, s, Me) and 1.12 (3 H, d, *J* 6.3 Hz, Me); δ_C(100.6 MHz; $CDCl_3$) 137.5^+ (*m*-PhS), 130.4^- (*i*-PhS), 129.2^+ (*p*-PhS), 128.8^+ (*o*-PhS), 70.7^+ (CH–OH), 55.7^- (CSPh), 26.1^+ (Me), 21.1^+ (Me) and 16.1^+ (Me); *m*/*z* (EI) 196 (22%, M^+), 151 (100, Me_2CSPh^+), 131 (17), 119 (11), 110 (84, $PhSH^+$) and 109 (32, PhS^+); (Found: M^+, 196.0923. $C_{11}H_{16}OS$ requires *M*, 196.0922).

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Notes and References

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