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Additive Pummerer Reactions of Vinylic Sulfoxides. Synthesis of γ-Hydroxy-α,β-Unsaturated Esters, α-Hydroxyketones, and 2-Phenylsulfenyl Aldehydes and Primary Alcohols[1]

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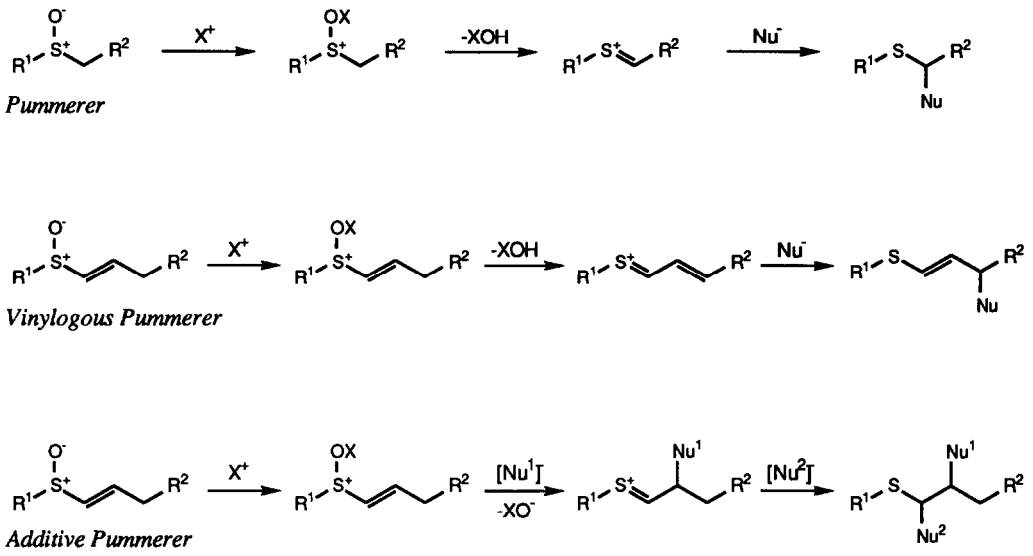
Abstract: Treatment of β-monosubstituted vinylic sulfoxides **1** with trifluoroacetic anhydride in dichloromethane gave excellent yields of 1,2-bis(trifluoroacetoxy)thioethers **6**. Mildly basic methanolysis of 2-alkyl-substituted **6** gave α-hydroxyaldehydes **11** as monomer–dimer mixtures; similar treatment of the 2-aryl analogues afforded aryl (hydroxymethyl) ketones **12**. Compounds **11** underwent Wittig reactions with methoxycarbonylmethylenetriphenylphosphorane to give high yields of γ-hydroxy-α,β-unsaturated esters **13**, predominantly as the *E*-isomers. β-Monosubstituted vinylic sulfoxides **1** possessing a β-aryl group, and β-disubstituted vinylic sulfoxides **3** reacted with trifluoromethanesulfonic anhydride–sodium acetate in acetic anhydride to give 2-(phenylsulfenyl)acylals **14**. These gave 2-phenylsulfenyl aldehydes **15** upon basic methanolysis, and the corresponding primary alcohols **16** on reduction with sodium borohydride. Reaction of both geometric isomers of enantiomerically pure vinylic sulfoxide **1o** with TFAA gave racemic **6o** as a mixture of diastereomers. Reaction of optically pure (*E*)- and (*Z*)-**1p** with trifluoromethanesulfonic anhydride–sodium acetate in acetic anhydride gave acylal **19** in 10.5 and 23% e.e., respectively.

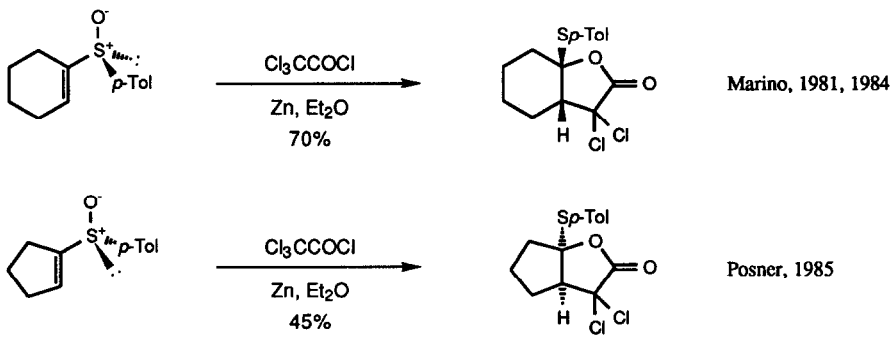
INTRODUCTION

The Pummerer reaction has emerged as a versatile and effective method for the generation of cationic reactive intermediates from sulfoxide precursors.[2] 'Normal' Pummerer reactions involve initial activation of the sulfoxide by reaction at oxygen with an electrophilic reagent. This substantially labilizes the protons α- to sulfur, and elimination of the elements of XOH from the intermediate oxysulfonium species generates a thionium ion. This is trapped by one of the nucleophilic species present to give an α-substituted thioether in an overall redox process. The attacking species in the final step may be negatively-charged or neutral, heteroatom- or carbon-centred, and may be inter- or intramolecularly disposed with respect to the electrophilic α-carbon atom. With α,β-unsaturated sulfoxide substrates the initially-formed oxysulfonium ion may suffer reaction via two divergent pathways. In the vinylogous Pummerer reaction[3] γ-proton loss occurs concomitantly with sulfoxide S–O bond scission to yield an unsaturated thionium ion which is then intercepted by a nucleophile at the now electrophilic γ-position. In the additive Pummerer reaction initial nucleophilic attack occurs at the electrophilic β-



Scheme 1

carbon atom, giving rise to a saturated, β-functionalized thionium species. Trapping with a nucleophile yields the product of formal sequential attack by two nucleophiles on an α,β-dication (Scheme 1). The additive Pummerer reaction has successfully been deployed for the formation of heteroatom–carbon[4] and carbon–carbon[5] bonds. Reaction of vinylic sulfoxides with silyl ketene acetals[5(a)] and disubstituted olefins[5(b)] in the presence of oxaphilic Lewis acids, and with Grignard reagents[5(c),5(d)] has been reported to give the products of sequential C–C bond-forming processes at the β- and α-positions of the vinylic group. In definitive early work it was demonstrated that exposure of vinylic sulfoxides to dichloroketene generated in situ resulted in sequential sulfoxide activation with formation of a dichloroenolate, β-C–C bond formation via intramolecular delivery of the enolate, and trapping of the resulting thionium ion by the carboxylate so formed. This gave γ-lactones in high yields and with essentially complete asymmetric induction from sulfur to carbon (Scheme 2).[6]



Scheme 2

We have been looking at the additive Pummerer reaction with a view to assessing its viability as a general strategy for the synthesis of carbo- and heterocyclic ring systems. In particular, we are keen to determine whether activated vinylic sulfoxides may be used as electrophilic 'triggers' which serve to initiate tandem carbon–carbon/carbon–carbon and carbon–carbon/carbon–heteroatom bond-forming processes. We consider this to be a particularly attractive goal in the context of potential asymmetric synthesis because of the ready availability of enantiomerically pure vinylic sulfoxide substrates.[7] In the initial phase of these studies we probed the behaviour of simple vinylic sulfoxides towards oxaphilic reagents. We recently described the reactions of such substrates with trifluoroacetic anhydride (TFAA),[8] and with trifluoromethanesulfonic anhydride–sodium acetate in acetic anhydride.[9] We now report in full the results of these investigations, and describe also the outcome of attempts to carry out these new reactions in the asymmetric mode.

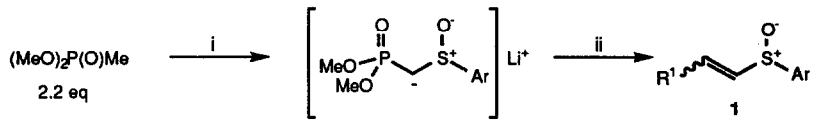
RESULTS AND DISCUSSION

Synthesis of Vinylic Sulfoxides

At the outset of our studies a short, efficient and versatile method was required for the preparation of vinylic sulfoxide substrates **1**. It was considered essential that the chosen method should be adaptable to the synthesis of both enantiomers of **1** in optically pure form. The Wadsworth-Emmons reaction[10] of dialkyl (arylsulfinyl)methylphosphonates with aldehydes had previously been reported[11] to be effective for the generation of mixtures of geometric isomers. In this work the requisite sulfinylphosphonate precursors had been formed in a separate step, by oxidation of the corresponding sulfides,[11(a)] or by reaction of lithiated phosphonates with arylsulfinyl esters.[11(c)] It occurred to us that the formation and Wadsworth-Emmons reaction of sulfinylphosphonate anions with aldehydes could be carried out in a single synthetic operation by using two equivalents of the nucleophilic/basic carbanion in the reaction with the sulfinate ester and quenching directly with aldehydes. In practice this was found to be an effective method which was successful with a variety of aldehydes **2** to give chromatographically separable mixtures of **1** (Table 1).[12] For aliphatic aldehydes (entries 1–6) the reactions were poorly *Z*-selective, whereas substituted benzaldehydes gave predominantly (*E*)-**1**, again with low to moderate stereoselectivity (entries 7–13). Enantiomerically pure (*R*)-**1** were synthesized using this one-pot method by using (-)-$(S)_S$-menthyl *p*-tolylsulfinate[13] in place of racemic isopropyl phenylsulfinate (entries 14–16). The reaction was much less efficient for the synthesis of β-disubstituted vinylic sulfoxides **3** from ketones **5**, since isomerization of initially formed **3** to β,γ-unsaturated isomers **4** competed significantly under a variety of reaction conditions (Table 2).[14]

Reaction of β-Monosubstituted Vinylic Sulfoxides 1 with Trifluoroacetic Anhydride

TFAA-Mediated additive Pummerer reactions of vinylic sulfoxides possessing an additional electron-withdrawing group at the α-position have been described.[15] In these cases the additional α-substituent presumably accelerated β-attack by enhancing the polarization of the unsaturated linkage. We were keen to establish whether the diastereoselectivity of the additive Pummerer reaction was affected by the geometry of **1**, since it was felt that this would provide mechanistic evidence concerning the rate of bond formation at the β-position relative to trapping of the ensuing thionium ion. In some cases it was possible to obtain by chromatographic separation geometrically pure samples of **1** on which to carry out the reactions with TFAA. Treatment of dichloromethane solutions of **1** with 1.3–2 equivalents of TFAA at 0°C or ambient temperature resulted in each



Reagents and conditions: (i) *n*-BuLi (2.1 eq), THF, -78°C; add ArS(O)OR (1 eq), -78°C; (ii) add **2** (1.1–2 eq), THF, -78°C→ 0°C; aq NH_4Cl.

Entry	R	Ar	aldehyde	R^1	yield of **1** (%)	*E*:*Z* ratio of **1**[16]
1	*i*-Pr	Ph	**2a**	Me	**1a** 90	1:1.3
2	*i*-Pr	Ph	**2b**	*n*-C_6H_{13}	**1b** 85	1:2.7
3	*i*-Pr	Ph	**2c**	*i*-Pr	**1c** 90	1:13.5
4	*i*-Pr	Ph	**2d**	*t*-Bu	**1d** 73	1:2
5	*i*-Pr	Ph	**2e**	$BnOCH_2$	**1e** 77	1:1
6	*i*-Pr	Ph	**2f**	(*E*)-MeCH=CH	**1f** 79	1:1.2
7	*i*-Pr	Ph	**2g**	Ph	**1g** 85	1.7:1
8	*i*-Pr	Ph	**2h**	4-MeC_6H_4	**1h** 94	1.8:1
9	*i*-Pr	Ph	**2i**	4-$MeOC_6H_4$	**1i** 80	3.1:1
10	*i*-Pr	Ph	**2j**	4-ClC_6H_4	**1j** 75	1.1:1
11	*i*-Pr	Ph	**2k**	4-$O_2NC_6H_4$	**1k** 57	1.8:1
12	*i*-Pr	Ph	**2l**	4-$MeSC_6H_4$	**1l** 80	1.8:1
13	*i*-Pr	Ph	**2m**	3-$MeOC_6H_4$	**1m** 76	1.4:1
14	menth[17]	*p*-Tol	**2a**	Me	**1n** 75	1:1.3[18]
15	menth	*p*-Tol	**2b**	*n*-C_6H_{13}	**1o** 85	1:6.7
16	menth	*p*-Tol	**2g**	Ph	**1p** 77	1.5:1

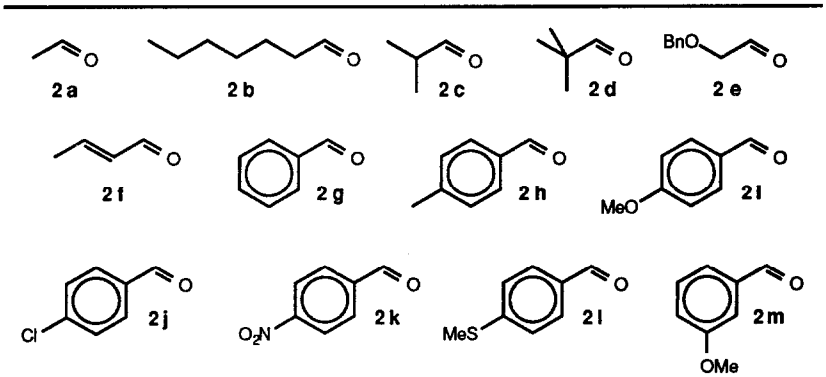
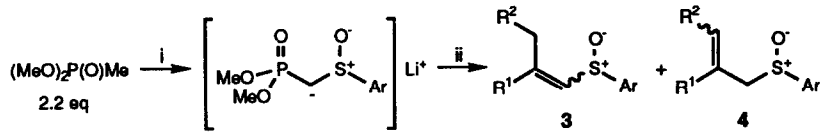


Table 1. Synthesis of β-Monosubstituted Vinylic Sulfoxides **1** from Aldehydes **2**.



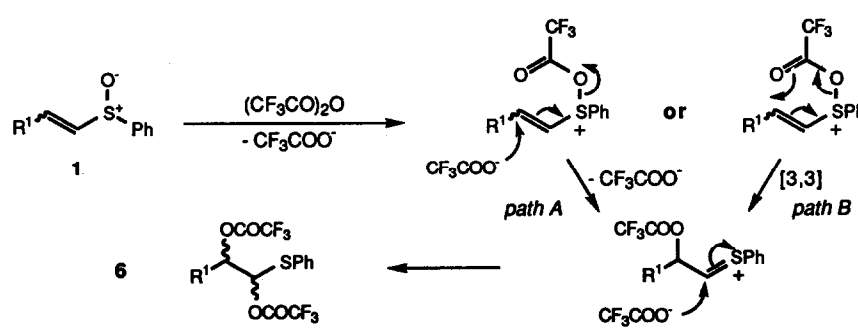
Reagents and conditions: (i) *n*-BuLi (2.1 eq), THF, -78°C; add PhS(O)O*i*-Pr (1 eq), -78°C; (ii) add **5** (1–3 eq), THF, -78°C → 0°C, 1–3 h; aq NH_4Cl.

Entry	ketone	yield of 3+ 4 (%)	R^1	R^2	ratio of 3:4[16]	*E*:*Z* ratio of 3[16]
1	**5a**	74	Me	H	3.7:1	-
2	**5b**	77	Et	H	2.7:1[19]	1.4:1
3	**5c**	42	-$(CH_2)_3$-		1.5:1	-
4	**5d**	92	-$(CH_2)_4$-		45:1	-

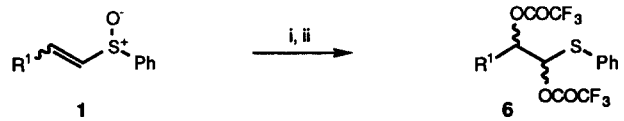
Table 2. Synthesis of β-Disubstituted Vinylic Sulfoxides **3** from Ketones **5**.

case in the disappearance of starting material and the formation of a much less polar component as demonstrated by thin-layer chromatography (tlc). The use of one equivalent of TFAA resulted only in partial conversion of **1**, presumably because of competing hydrolysis of the reagent. In most cases the best results were obtained by initial treatment of **1** with one equivalent of TFAA, followed by addition of a second equivalent after ten minutes. Mildly basic aqueous work-up gave crude material shown by ^1H nmr analysis (270 MHz) to consist exclusively of 1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)alkanes **6** as mixtures of diastereomers (Table 3). The highly acid-sensitive nature of **6** was such as to preclude purification on silica gel.

Two distinct mechanistic pathways may be invoked for the formation of **6** from **1** (Scheme 3). In path A, *O*-trifluoroacetylation of **1** is followed by attack by liberated trifluoroacetate ion at the electrophilic β-position of the sulfoxonium intermediate, forming a thionium ion and regenerating trifluoroacetate, which then intercepts the



Scheme 3



1 6

Reagents and conditions: (i) TFAA (1.3–2.0 eq), CH_2Cl_2, 0°C or 20°C; (ii) aq $NaHCO_3$.

Entry	vinylic sulfoxide 1	*E*:*Z* ratio of 1[16]	eq TFAA	T (°C)	t(min)	yield of 6 (%)[20]	R^1	diastereomer ratio of 6[16,21]
1	H_2C=CHS(O)Ph[22]	-	1.3	0	30	99	H (**6x**)	-
2	**1a**	1:1.5	2.0	0	25	88	Me	1:1
3	**1b**	1:0	2.0	0	25	95	*n*-C_6H_{13}	1.7:1
4	**1b**	0:1	2.0	0	25	93	*n*-C_6H_{13}	1:3.5
5	**1c**	1:13.5	2.0	0	25	95	*i*-Pr	1.2:1
6	**1d**	1:0	1.5	0	90	93	*t*-Bu	1.8:1
7	**1d**	0:1	1.5	0	90	93	*t*-Bu	1:1.6
8	**1e**	1.3:1	1.5	0	40	97	$BnOCH_2$	1.6:1
9	**1g**	1:0	2.0	0	60	97	Ph	6.3:1
10	**1g**	0:1	2.0	0	25	96	Ph	1:4
11	**1h**	1:2.4	1.5	0	60	97	4-MeC_6H_4	1.2:1
12	**1i**	2.8:1	1.3	0	5	97	4-$MeOC_6H_4$	1:1
13	**1j**	1:0	2.0	20	45	96	4-ClC_6H_4	1.1:1
14	**1k**	1:1.4	2.0	20	360	95	4-$O_2NC_6H_4$	1:1

Table 3. Reaction of β-Monosubstituted Vinylic Sulfoxides **1** with TFAA.

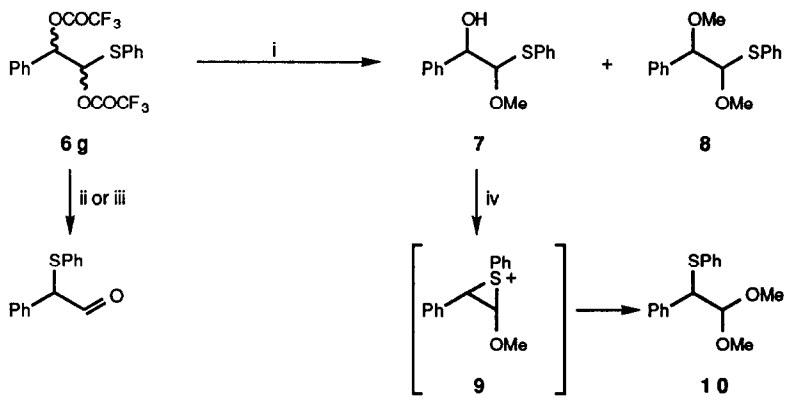
thionium ion to give **6**. In path B, the initially formed sulfoxonium intermediate undergoes [3,3]-sigmatropic rearrangement, delivering trifluoroacetate to the β-position and generating the α-electrophilic thionium species. The reactions of of vinylic sulfoxides with isopropenyl acetate[23] and with dichloroketene[6] have been shown to proceed via [3,3]-sigmatropic rearrangements. In contrast, reaction with acetyl chloride[4(d)] gave exclusively α-acetoxy-β-chlorothioethers via attack first by chloride, and subsequently at the α-position by acetate.

Most of the sulfoxide substrates exhibited similar reactivity towards TFAA (Table 3, entries 1–11). Substrate **1i**, derived from 4-methoxybenzaldehyde was significantly more reactive (entry 12) whereas sulfoxides **1j** and **1k** possessing electron-withdrawing groups on the aromatic nucleus reacted more sluggishly (entries 13, 14). This might suggest that the sulfoxide β-substituent accelerates formation of the thionium ion from the sulfoxonium intermediate by assisting sulfur–oxygen bond cleavage. The reaction failed with vinylic sulfoxide **1f** derived from 2-butenal: treatment with TFAA gave a complex mixture which ^1H nmr indicated to contain unsaturated α,β-, γ,δ- and α,δ-bis(trifluoroacetoxy)thioethers. In three cases isomerically pure substrates **1** (R^1 = *n*-C_6H_{13}, *t*-Bu, Ph) were subjected to the reaction conditions (entries 3 and 4; 6 and 7; 9 and 10). ^1H Nmr analysis of the crude products indicated the formation of different ratios of the diastereomers of **6** from the separate geometric isomers of **1**, with the modest diastereoeselectivity observed in the reactions of the *E*-isomers reversed in those of the *Z*-compounds. This may indicate trapping of the putative thionium

species by trifluoroacetate at a rate which is comparable with that of C_α–C_β bond rotation, so that the reacting conformation of the thionium ion reflects to some extent the geometry of the vinylic sulfoxide precursor.

Derivatization Reactions of Bis(trifluoroacetoxy)thioethers 6

It occurred to us at this stage that the hydrolytically labile bis(trifluoroacetoxy)thioethers **6** might provide a source of α-hydroxycarbonyl compounds. Solvolysis in protic solvent of both trifluoroacetate esters was expected to give α-hydroxythiohemiacetals, which would eliminate thiophenol to give 2-hydroxyaldehydes. Substrate **6g** (R^1 = Ph) was selected for these studies. Hydrolysis in either tetrahydrofuran–water or dioxan–water gave the rearranged product 2-phenyl-2-(phenylsulfenyl)ethanal in moderate yield. Reaction in methanol under reflux gave two new compounds **7** and **8**, each as a single diastereomer.[4(a),15(b)] Treatment of **7** with catalytic acid in methanol under reflux gave the rearranged acetal **10** in high yield (Scheme 4).[24] The unde-

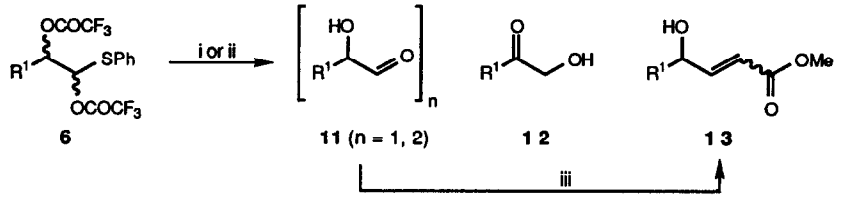


Reagents and conditions: (i) MeOH, reflux; (ii) THF–H_2O (7:1), 50°C, 20 min (38%); (iii) 1,4-dioxan–H_2O (2:1), 100°C, 10 min (42%); (iv) catalytic TsOH, MeOH, reflux, 2 h (80%).

Scheme 4

sired rearrangement reactions presumably were proceeding via episulfonium intermediates such as **9** formed by intramolecular displacement of a protonated leaving group by the neighbouring phenylsulfenyl function.[25] Therefore, it was decided to attempt the solvolysis reactions in basic media. In the event, treatment of cold dichloromethane solutions of **6** (aliphatic R^1) with methanol and a catalytic quantity of triethylamine resulted in rapid cleavage of the trifluoroacetate esters with concomitant formation of thiophenol. The products were inseparable mixtures of monomeric and dimeric α-hydroxyaldehydes **11**. In contrast, substrates with aromatic β-substituents gave aryl hydroxymethyl ketones **12** on treatment in dichloromethane with one equivalent of triethylamine in the presence of methanol at ambient temperature. The reactions of β-aryl **6** reached completion much more slowly than those of the aliphatic analogues, and presumably gave the corresponding aldehydes **11** rapidly, followed by slow base-catalyzed isomerization to the more thermodynamically stable conjugated ketones **12** (Table 4). The monomer–dimer mixtures of **11** typically exhibited weak peaks in the mass spectra corresponding to MH^+ for both the monomer and the dimer, and for ($M^+_{monomer}$-CHO). The ^1H nmr spectra varied according to the nature of R^1. Compound **11a** (R^1 = Me; Table 4, entry 2) showed the absence of a peak corresponding to an aldehyde proton, whereas the spectra of the *n*-C_6H_{13} (entry 3) and *i*-Pr (entry 4) analogues clearly showed the presence of CHO groups. In view of the presence of more than one species in the

products **11** it was decided to carry out a further synthetic transformation which would confirm their identity. Wittig reaction of the mixtures of **11** with excess methoxycarbonylmethylenetriphenylphosphorane in benzene under reflux gave good yields of the expected γ-hydroxy-α,β-unsaturated esters **13** with high or complete selectivity for the *E*-isomers. The use of methanol as solvent in place of benzene for the Wittig reaction of substrate **11a** gave in good yield a *ca.* 2:1 mixture of (*E*)-**13a** and the butenolide resulting from cyclization of the *Z*-isomer.[26] The methanolysis reactions of **6** and Wittig olefination reactions of products **11** are summarized in Table 4.



Reagents and conditions: (i) Et_3N (0.1 eq), MeOH (2.2 eq), CH_2Cl_2 (0.2M), 0°C, 5 min; (ii) Et_3N (1.1 eq), MeOH (2.2 eq), CH_2Cl_2 (0.2M), 20°C, 12 h; (iii) $Ph_3P{=}CHCO_2Me$ (3 eq), C_6H_6 (0.1M), reflux, 2.5–5 h.

Entry	Substrate	R^1	Method	Yield of **11** (%)[27]	Yield of **12** (%)	Yield of **13** (%)	*E*:*Z* ratio of **13**[16]
1	**6x**	H	(i)	62	-	44	1:0
2	**6a**	Me	(i)	85	-	84	40:1
3	**6b**	*n*-C_6H_{13}	(i)	84	-	77	1:0
4	**6c**	*i*-Pr	(i)	78	-	95	1:0
5	**6d**	*t*-Bu	(i)	48	-	69	1:0
6	**6e**	$PhCH_2OCH_2$	(i)	87	-	87	17:1
7	**6g**	Ph	(ii)	-	72	-	-
8	**6h**	4-$CH_3C_6H_4$	(ii)	-	83	-	-
9	**6i**	4-$CH_3OC_6H_4$	(ii)	-	79	-	-
10	**6j**	4-ClC_6H_4	(ii)	-	89	-	-
11	**6k**	4-$O_2NC_6H_4$	(ii)	-	53	-	-

Table 4. Basic Methanolysis Reactions of Bis(trifluoroacetoxy)thioethers **6** and Wittig Reactions of **11**.

Reaction of β-Monosubstituted Vinylic Sulfoxides 1 and 3 with Trifluoromethanesulfonic Anhydride–Sodium Acetate–Acetic Anhydride

In view of the hydrolytic instability of the bis(trifluoroacetoxy)thioethers **6** we sought at this stage to extend the reaction for the conversion of **1** to **6** to the synthesis of the diacetoxy analogues. Vinylic sulfoxide **1g** was found to be inert to acetic anhydride even after prolonged heating,[28] and on treatment with acetic anhydride–trifluoroacetic anhydride[29] gave multi-component mixtures indicated by ^1H nmr to comprise bis(trifluoroacetoxy)thioether **6g** together with the two possible regioisomeric mixed esters and the desired diacetate. Since this indicated interception of the thionium intermediate by trifluoroacetate we looked for a reagent system which would activate the sulfoxide but in which the sole effective nucleophile would be acetate

ion. Treatment of **1g** with trifluoromethanesulfonic anhydride in a mixture of excess sodium acetate and cold acetic anhydride as solvent did not result in the formation of the expected diacetate, but rather the acylal[30] **14g**. Interestingly, the initially heterogeneous reaction mixture became homogeneous only after the addition of triflic anhydride, presumably because of formation of the mixed anhydride. Attempts to perform the reaction in dichloromethane or tetrahydrofuran were unsuccessful, possibly due to the insolubility of sodium acetate in these media. The transformations of a number of vinylic sulfoxides **1** and **3** are summarized in Table 5. Further studies showed that the reaction was successful only for certain substrates **1** having an aryl group at the β-position; the reaction worked poorly when the aromatic nucleus possessed strongly electron-donating groups (entry 4). β-Disubstituted vinylic sulfoxides **3** derived from ketones also participated in this reaction. All attempts to effect the reaction on substrates **1** having single aliphatic β-substituents resulted in the formation of complex product mixtures.

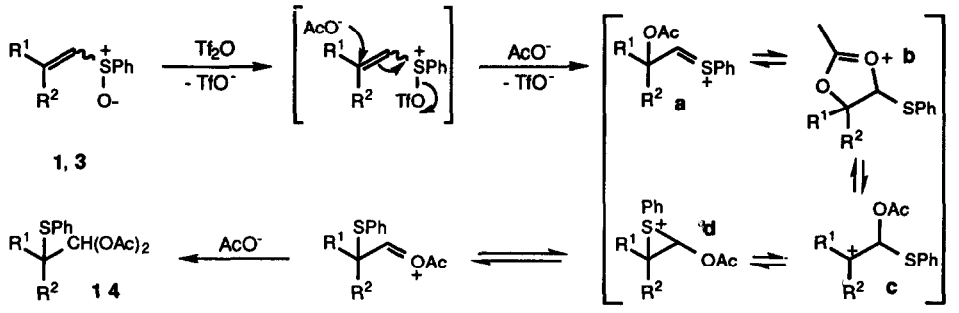
1, 3 **14**

Reagents and conditions: (i) NaOAc (2–3 eq), $(CF_3SO_2)_2O$ (1–2 eq), Ac_2O (0.2M), -40°C → 20°C; (ii) aq $NaHCO_3$.

Entry	Substrate	R^1	R^2	*E*:*Z* ratio of 1/3[16]	eq NaOAc	eq $(CF_3SO_2)_2O$	T (°C)	t (min)	Yield of **14** (%)
1	**1g**	Ph	H	0:100	3	1.5	0	15	**14g**:85
2	**1h**	4-MeC_6H_4	H	23:77	3	1.5	0	15	**14h**:80
3	**1j**	4-ClC_6H_4	H	0:100	2	1.5	0	15	**14j**: 85
4	**1m**	3-$MeOC_6H_4$	H	10:90	2	1.5	0	15	**14m**:28
5	**3a**	Me	Me	-	2	2	25	15	**14a**:60
6	**3b**	Et	Me	52:48	2	1.25	25	5	**14b**:62
7	**3c**	-$(CH_2)_4$-		-	2	2	0	15	**14c**: 66
8	**3d**	-$(CH_2)_5$-		-	2	1	0	5	**14d**:79

Table 5. Reaction of Vinylic Sulfoxides **1** and **3** with Trifluoromethanesulfonic Anhydride–Sodium Acetate–Acetic Anhydride

That formation of **14** from **1** and **3** takes place only when the carbon atom β- to sulfur is tertiary or benzylic suggests the intermediacy of a cationic species with substantial positive charge character at this position (Scheme 5). Attack by acetate at the highly electrophilic β-position of the *O*-trifluoromethanesulfonylated vinylic sulfoxide would give a thionium species **a**. Migration of acetate from the β- to the α-position might occur *via* a cyclic oxonium intermediate **b**, giving the β-cation **c**. Anchimeric charge stabilization by the phenylsulfenyl group resulting in episulfonium ion **d** would be followed by oxonium ion formation with concomitant cleavage of the C_α–sulfur bond. Finally, interception by acetate would generate **14**. The failure of the reaction when the β-aryl group in **1** is strongly electron-releasing may be because cation **c** is stabilized to the extent that sulfur migration is suppressed. In contrast, the presence of a single aliphatic group at the β-position

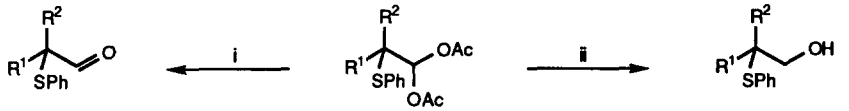


Scheme 5

fails to stabilize sufficiently the positive charge on this atom, effectively inhibiting the migration of acetate necessary for the rearrangement to take place.

Derivatization Reactions of Acylals 14

Since acylals are protected aldehydes it was decided to develop derivatization reactions of compounds **14** in which the carbonyl functionality could be unmasked and manipulated. In this context, basic methanolysis[31] of **14** using potassium carbonate in methanol followed by careful neutralization gave 2-(phenylsulfenyl) aldehydes **15** in good to excellent yields. The lower yields obtained when **14** possessed an aromatic substituent reflects the instability (presumably because of facile enolization) of the product α-aryl-α-(phenylsulfenyl) aldehydes. Acylals **14** could be reduced directly to the corresponding primary alcohols **16** by exposure to excess sodium borohydride in a mixture of 1,2-dimethoxyethane and 2-propanol. This solvent system gave the



15 **14** **16**

Reagents and conditions: (i) solid K_2CO_3 (5 eq), MeOH (0.1M), 0°C or 25°C, 10–45 min; aq NH_4Cl; (ii) $NaBH_4$ (5 eq), $MeO(CH_2)_2OMe$–*i*-PrOH (1:1; 0.1M), 25°C, 12 h.

Entry	Substrate	R^1	R^2	T (°C)	t (min)	Yield of **15** (%)	Yield of **16** (%)
1	**14g**	Ph	H	25	15	**15g** 65	**16g** 82
2	**14h**	4-MeC_6H_4	H	0	45	**15h** 65	**16h** 85
3	**14j**	4-ClC_6H_4	H	0	45	**15j** 64	**16j** 94
4	**14a**	Me	Me	0	20	**15a** 75	**16a** 78
5	**14b**	Et	Me	25	20	**15b** 82	**16b** 95
6	**14c**	-$(CH_2)_4$-		25	20	**15c** 85	**16c** 94
7	**14d**	-$(CH_2)_5$-		25	10	**15d** 85	**16d** 100

Table 6. Derivatization Reactions of Acylals **14**.

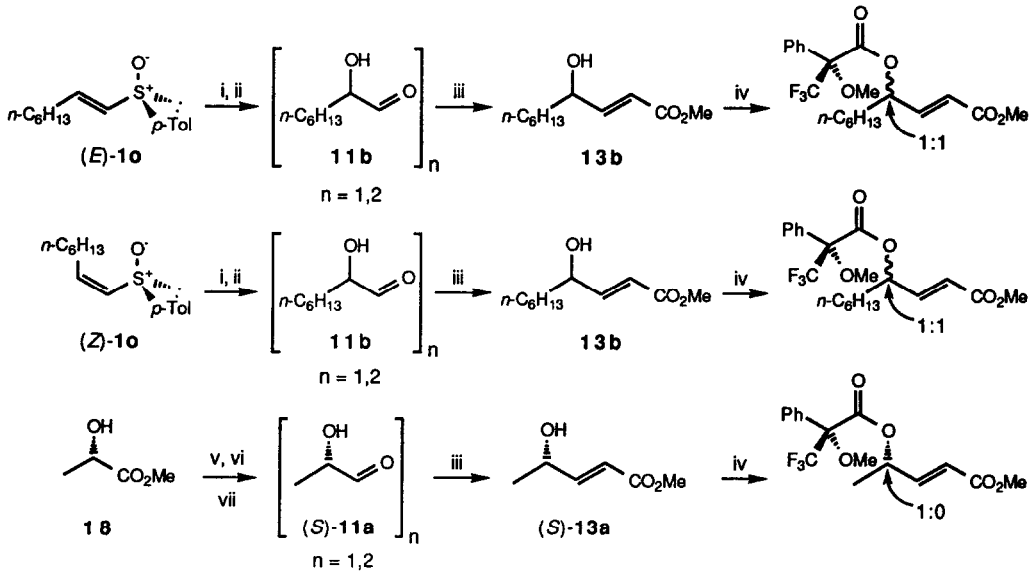
optimal combination of reaction rate and solvolysis of sodium borohydride; neat methanol gave much quicker reactions but necessitated the use of large excesses of the reducing agent. The methanolysis and reduction reactions of **14** are summarized in Table 6.

Attempted Asymmetric Additive Pummerer Reactions

Enantiomerically pure sulfoxides have found application in a number of areas of asymmetric synthesis,[7] including carbon–carbon bond-forming processes[32] and reduction reactions.[33] At the beginning of our studies, the only examples of asymmetric additive Pummerer processes taking place upon enantiomerically pure vinylic sulfoxides were the reactions with dichloroketene first reported by Marino and co-workers.[6(a)–6(d)] In view of the ready availability of enantiomerically pure vinylic sulfoxides, and the high efficiency of the reactions with both trifluoroacetic anhydride and trifluoromethanesulfonic anhydride–sodium acetate, we sought to extend these new transformations to homochiral substrates. The potential for synthesis of enantiomerically enriched α-hydroxyaldehydes and α-(phenylsulfenyl) aldehydes and alcohols was additionally attractive. In particular, the latter materials have been shown to be useful intermediates for the asymmetric synthesis of epoxides, by base-mediated ring-closure of derived sulfonium salts.[33]

Firstly, we examined the reaction of $(R)_S$-1-(*p*-tolylsulfinyl)oct-2-ene **1o** with trifluoroacetic anhydride. Substrate **1o** was prepared in high yield as a separable *ca.* 1:7 mixture of *E*- and *Z*-isomers *via* the method employed for the racemates prepared previously, using (-)-$(S)_S$-menthyl *p*-tolylsulfinate in place of isopropyl phenylsulfinate (Table 1, entry 15). Separate reaction of (*E*)- and (*Z*)-**1o** with trifluoroacetic anhydride under the usual conditions gave diastereomeric mixtures of the corresponding bis(trifluoroacetoxy)thioethers **17**. Conversion of **17** to the mixture of monomeric and dimeric 2-hydroxyoctanal **11b** was carried out as for the racemic phenylsulfenyl analogues, and **11b** then subjected to Wittig reaction as before. Mosher esterification[34] with (*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl chloride of the products **13b** from both the *E*- and *Z*-starting sulfoxides **1o** gave a 1:1 mixture of diastereomers, indicating that **13b** had been formed as racemic mixtures. Since it was impossible at this stage to eliminate the possibility that racemization had occurred in the Wittig or esterification steps, it was decided to synthesize an α-hydroxyaldehyde from an enantiomerically pure starting material, and to subject it to these transformations. Analysis of the product by Mosher ester formation would then indicate whether partial or complete scrambling of the α-stereocentre had occurred. Because of its ready availability, we chose methyl (*S*)-lactate **18** from which to prepare (*S*)-2-hydroxypropanal **11a** prior to Wittig olefination. Sequential protection of **18** as its *tert*-butyldimethylsilyl ether,[35] reduction to the protected aldehyde with diisobutylaluminium hydride,[36] and deprotection with HF–acetonitrile[37] gave a mixture of monomeric and dimeric (*S*)-**11a**. This was immediately reacted with methoxycarbonylmethylenetriphenylphosphorane to give material whose ^{1}H nmr spectrum was identical with that of methyl (*E*)-4-hydroxypent-2-enoate **13a**. Formation of the Mosher ester as for **13b** gave a single diastereomer, as evidenced by high-field (500 MHz) ^{1}H nmr (Scheme 6). Whilst this finding ruled out the possibility that racemization of **13b** had occurred in the Wittig or esterification steps, it did not unequivocally establish that epimerization α- to the aldehyde function was not taking place during the conversion of **17** to **11b**. This however seems unlikely given the use of catalytic triethylamine (0.1 equivalent) and mild conditions (0°C, 5 minutes) for this transformation. Additive Pummerer reactions of vinylic sulfoxides with dichloroketene proceed with highly efficient chirality transfer from sulfur to carbon, and this has been rationalized in terms of a [3,3]-sigmatropic rearrangement mechanism.[6] The lack of any asymmetric induction in the conversion of **1o** to **6o** and thence to **11b** might

indicate that the key Cβ–oxygen bond-forming step occurs intermolecularly, *i.e.* bimolecular attack on the activated vinylic sulfoxide by trifluoroacetate liberated in the activation process, although in some such cases diastereoselectivity has been observed in β-carbon–heteroatom bond-forming reactions despite the 'acyclic' nature of the transition state.[38] An alternative explanation is that β-carbon–oxygen bond formation is reversible, with rapid equilibration of β-epimers assisted by sulfur stabilization of the intermediate cation.

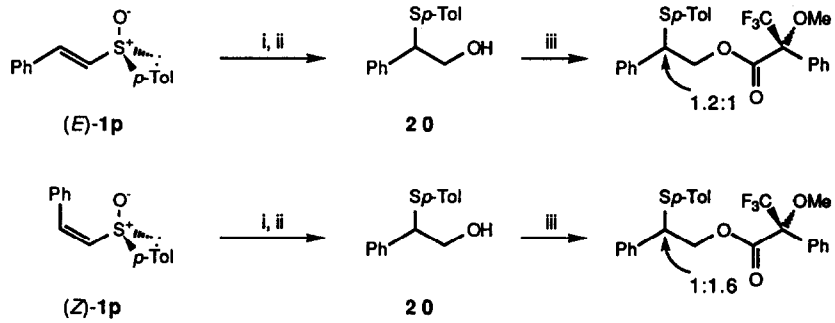


Reagents and conditions: (i) TFAA (1 eq), CH_2Cl_2, 0°C, 15 min; aq $NaHCO_3$; (ii) MeOH (2.2 eq), Et_3N (0.1 eq), CH_2Cl_2, 0°C, 5 min; (iii) $Ph_3P{=}CHCO_2Me$ (1.5 eq), C_6H_6, 80°C, 3 h; (iv) (+)-(*S*)-PhC(CF_3)(OMe)COCl (1.5 eq), pyridine (3 eq), DMAP (0.1 eq), CH_2Cl_2, 20°C, 12 h; (v) TBDMSCl (1.3 eq), Et_3N (2.6 eq), DMAP (0.1 eq), THF, 20°C, 12 h; (vi) DIBAL-H (1.3 eq), hexane, -78°C, 1.5 h; (vii) HF (*ca.* 5 eq), MeCN, 20°C, 15 min.

Scheme 6

Our attention was next directed towards the application of the acylal-forming reaction to enantiomerically pure substrates. Our studies had demonstrated that the reaction was successful with vinylic sulfoxides **1** having an aromatic β-substituent, and analogues **3** possessing two aliphatic groups at the β-position. In order to maximize the unsymmetrical nature of the vinylic group in the substrate, and therefore the prospects for asymmetric induction, vinylic sulfoxide **1p** was chosen. Substrate **1p** was synthesized in high yield as a separable mixture of geometric isomers using the standard method (Table 1, entry 16). Both (*E*)- and (*Z*)-**1p** were exposed to trifluoromethanesulfonic anhydride–sodium acetate in acetic anhydride, giving good yields of the acylal **19**. Reduction with sodium borohydride in 1,2-dimethoxyethane–2-propanol as before gave the corresponding primary alcohols. Mosher esterification of the alcohol **20** derived from the *E*-substrate gave gave a product shown by ^1H nmr (500 MHz) to contain a 1.2:1 ratio of diastereomeric esters, corresponding to 10.5% e.e. for the acylal **19**. Similar treatment of the alcohol derived from (*Z*)-**1p** gave a 1:1.6 ratio of Mosher esters, indicating 23% e.e. in the opposite sense for **19** (Scheme 7). Although we have not established the

absolute configuration of the major antipode of the alcohol **20** (and therefore of the acylal **19**), these results demonstrate clearly that the sense of chirality transfer from sulfur to carbon is the same for the two geometric isomers in that the same diastereoface (with respect to the sulfur stereocentre) is attacked irrespective of alkene geometry. The mechanism depicted in Scheme 5 would predict that the configuration is opposite to that established initially by attack of acetate, since it is postulated that sulfur migrates with inversion at the β-centre.



Reagents and conditions: (i) NaOAc (2 eq), $(CF_3SO_2)_2O$ (1 eq), Ac_2O (0.2M), 0°C, 20 min; aq $NaHCO_3$; (ii) $NaBH_4$ (5 eq), $MeO(CH_2)_2OMe$–*i*-PrOH (1:1; 0.1M), 20°C, 12 h; (iii) (+)-(*S*)-PhC(CF_3)(OMe)COCl (1.5 eq), pyridine (3 eq), DMAP (0.1 eq), CH_2Cl_2, 20°C, 12 h.

Scheme 7

CONCLUSIONS

The work described herein demonstrates that the TFAA-mediated additive Pummerer reaction of vinylic sulfoxides is an efficient method for the synthesis of protected α-hydroxyaldehydes and α-hydroxy arylketones. Tandem additive Pummerer–rearrangement reactions mediated by trifluoromethanesulfonic anhydride–sodium acetate give 2-(phenylsulfenyl) acylals which may be cleaved by methanol or reductively unmasked to give respectively 2-(phenylsulfenyl) aldehydes and primary alcohols. Although the former process exhibits no enantioselection when carried out on optically pure substrates, the additive Pummerer–rearrangement sequence does deliver optically enriched products, albeit with modest enantiomeric excess. Studies aimed towards increasing the levels of asymmetric induction, and experiments seeking to probe the origins of the observed stereoselectivity are currently underway.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

General Procedures

^{1}H nmr spectra were recorded in $CDCl_3$ on either Bruker AM-500, Jeol GX-270a or Bruker WM-250 spectrometers, using residual isotopic solvent ($CHCl_3$, δ_H 7.26 ppm) as an internal reference. Infra-red spectra were recorded on a Perkin-Elmer 881 spectrophotometer. Mass spectra were recorded using VG-7070B or Jeol SX-102 instruments. Elemental combustion analyses were performed in the Imperial College Chemistry Department microanalytical laboratory and at the Pfizer Central Research Physical Sciences department. Melting points were measured on a Reichert hot stage apparatus and are uncorrected. Optical rotations were measured using an Optical Activity AA-100 polarimeter. Chromatography refers to column chromatography on Merck Kieselgel 60 (230-400 mesh) or Matrex Silica 60 (35-70 micron) under pressure unless otherwise stated. Analytical thin layer chromatography was performed using pre-coated glass-backed plates (Merck Kieselgel 60 F_{254}) and visualised with ultraviolet light, iodine and acidic ammonium molybdate(IV), vanillin or potassium permanganate solutions as appropriate. Diethyl ether and tetrahydrofuran were distilled from sodium-benzophenone ketyl; dichloromethane from phosphorus pentoxide; toluene from sodium. Other solvents and reagents were purified before use according to standard procedures.[39]

Preparation of (±)$_S$-isopropyl phenylsulfinate.

To thionyl chloride (45.3 ml, 0.62 mol, 3.4 eq) at 0°C under argon was added sodium phenylsulfinate (dried for 4 h at 100°C under vacuum; 30 g, 0.18 mol, 1 eq) slowly over 1 h. After allowing the mixture to stir for a further 1 h at 0°C, the excess thionyl chloride was removed under reduced pressure by azeotropic distillation with toluene (Na-dried; 3 x 150 ml) keeping the temperature of the water bath below 30°C. The residue was diluted with ether (Na-dried; 150 ml) and the resulting suspension was added slowly over 1 h at 0°C to a stirred solution of propan-2-ol (redistilled from CaH_2 under argon onto 4Å molecular sieves; 16.8 ml, 0.22 mol, 1.2 eq) in pyridine (30 ml, 2 eq). The reaction was allowed to warm to 20°C and was allowed to stir for a further 2 h. The reaction was then quenched by the addition of water (100 ml). Ether (100 ml) was added, the organic layer was separated, washed with 20% HCl (4 x 75 ml), brine (75 ml) and dried over $MgSO_4$. Removal of the solvents under reduced pressure gave the crude product as a pale yellow oil. Purification by chromatography (25% ether–petrol) gave (±)$_S$-isopropyl phenylsulfinate (22.28 g, 66%) as a colourless oil; ν_{max} (film) 3061, 2979, 1974, 1899, 1818, 1772, 1582, 1446, 1378, 1345, 1308, 1139, 1022, 999, 911, 840, 734 cm^{-1}; δ_H (270 MHz) 7.73-7.48 (5H, m, PhS(O)), 4.60 (1H, heptet, J 6.5 Hz, $CHMe_2$), 1.38 (3H, d, J 6.5 Hz, Me), 1.22 (3H, d, J 6.5 Hz, Me); *m/z* (EI) 184 (M^+), 142 (M^+ - $(CH_3)_2C$), 125 (M^+ - $(CH_3)_2CHO$).

Preparation of (±)$_S$-2-phenyl-1-(phenylsulfinyl)ethene (1g).

To a stirred solution of redistilled dimethyl methylphosphonate (12.9 ml, 119 mmol, 2.2 eq) in dry THF (160 ml) at -78°C under argon was added, dropwise *via* syringe, *n*-BuLi (45.6 ml of a 2.5M solution in hexanes, 114 mmol, 2.1 eq). The colourless anion solution was stirred for a further 10 min at -78°C after the

addition. A solution of isopropyl phenylsulfinate (azeotropically dried with toluene [3 x 25 ml] immediately prior to use; 10.0 g, 54 mmol, 1 eq) in dry THF (80 ml) was then added slowly *via* cannula. After a further 10 min stirring at -78°C a solution of benzaldehyde (washed with 10% NaOH, saturated aqueous sodium sulfite and water followed by distillation immediately prior to use; 6.1 ml, 60 mmol, 1.1 eq) in dry THF (160 ml) was added *via* cannula to the pale yellow anion solution. The reaction mixture was immediately allowed to warm to 0°C during 10 min and then quenched by the addition of saturated aqueous ammonium chloride (200 ml). The mixture was partitioned between dichloromethane (600 ml) and water (200 ml). The aqueous layer was separated and further extracted with dichloromethane (2 x 200 ml). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give the crude products as a pale yellow oil. Purification by chromatography (25%-100% ether–petrol) gave, in order of elution, (±)$_S$-(*E*)-2-phenyl-1-(phenylsulfinyl)-ethene (*E*)-**1g** (7.12 g, 57%) as a colourless solid, mp 62-62.5°C (lit.[11(b)] mp 61.5-62°C); ν_{max} (Nujol) 2924, 2854, 1649, 1613, 1573, 1494, 1444, 1377, 1084, 1045, 998, 967, 913, 860, 822, 760, 736, 686, 666 cm^{-1}; δ_H (270 MHz) 7.70-7.33 (11H, m, PhS(O), Ph and H-2), 6.84 (1H, d, J 16 Hz, H-1); *m/z* (EI) 228 (M^+), 212 (M^+ - O), 180, 167, 135, 121, 103 (M^+ - PhS(O)), 91 ($PhCH_2$), 77 (Ph) (Found: C, 73.48; H, 5.11. $C_{14}H_{12}OS$ requires C, 73.65; H, 5.30%) and (±)$_S$-(*Z*)-2-phenyl-1-(phenylsulfinyl)ethene (*Z*)-**1g** (4.19 g, 34%) as a colourless solid, mp 79-81°C; ν_{max} (Nujol) 2925, 2855, 1606, 1571, 1494, 1461, 1445, 1377, 1301, 1170, 1083, 1038, 998, 968, 915, 850, 822, 779, 757, 734, 691 cm^{-1}; δ_H (270 MHz) 7.70-7.40 (10H, m, PhS(O) and Ph), 7.14 (1H, d, J 10 Hz, H-2), 6.45 (1H, d, J 10 Hz, H-1); *m/z* (EI) 228 (M^+), 212 (M^+ - O), 180, 178, 167, 135, 134, 121, 103 (M^+ - PhS(O)), 91 ($PhCH_2$), 77 (Ph) (Found: C, 73.50; H, 5.08. $C_{14}H_{12}OS$ requires C, 73.65; H, 5.30%).

Preparation of (±)$_S$-1-(phenylsulfinyl)prop-1-ene (1a).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (25%-100% ether–petrol) gave (±)$_S$-(*E*)-1-(phenylsulfinyl)prop-1-ene (*E*)-**1a** and (±)$_S$-(*Z*)-1-(phenylsulfinyl)prop-1-ene (*Z*)-**1a** (1:1.3 ratio of *E*:*Z* by ^1H nmr; 90%) as a colourless oil; ν_{max} (film) 3055, 2917, 1653, 1624, 1582, 1476, 1444, 1380, 1334, 1305, 1085, 1038, 998, 952, 806, 747, 709, 690 cm^{-1}; δ_H (270 MHz) (*E*-isomer) 7.57-7.39 (5H, m, PhS(O)), 6.56 (1H, dq, J 15, 6.5 Hz, H-2), 6.20 (1H, dq, J 15, 1.5 Hz, H-1), 1.84 (3H, dd, J 6.5, 1.5 Hz, H-3); (*Z*-isomer) 7.62-7.40 (5H, m, PhS(O)), 6.26 (2H, m, H-1 and H-2), 2.14 (3H, d, J 5.5 Hz, H-3); *m/z* (EI) 166 (M^+), 150 (M^+ - O), 149 (M^+ - OH), 137, 118, 109 (PhS), 78 (Found: (M^+), 166.0542. $C_9H_{10}OS$ requires (M^+), 166.0542).

Preparation of (±)$_S$-1-(phenylsulfinyl)oct-1-ene (1b).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (20%-50% ether–petrol) gave, in order of elution, (±)$_S$-(*E*)-1-(phenylsulfinyl)oct-1-ene (*E*)-**1b** (23%) as a colourless oil; ν_{max} (film) 2927, 2856, 1731, 1679, 1626, 1580, 1555, 1523, 1511, 1466, 1444, 1378, 1304, 1085, 1048, 998, 958, 747, 691 cm^{-1}; δ_H (270 MHz) 7.62-7.46 (5H, m, PhS(O)), 6.62 (1H, dt, J 15, 7 Hz, H-2), 6.22 (1H, dt, J 15, 1.5 Hz, H-1), 2.24 and 2.19 (2H, d AB quartet, J 7, 1.5 Hz, H-3), 1.51-1.39 (2H, m, H-4), 1.34-1.20 (6H, m, H-5, H-6 and H-7), 0.88 (3H, m, H-8); *m/z* (EI) 236 (M^+), 220 (M^+ - O), 149, 116, 110 (PhSH), 69 (Found: C, 71.38; H, 8.34. $C_{14}H_{18}OS$ requires C, 71.14; H, 8.53%) and *(±)$_S$-(Z)-1-*

(phenylsulfinyl)oct-1-ene (*Z*)-**1b** (62%) as a colourless oil; ν_{max} (film) 3056, 2928, 2857, 1654, 1620, 1583, 1468, 1444, 1380, 1304, 1084, 1045, 998, 922, 740, 690 cm^{-1}; δ_H (270 MHz) 7.62-7.40 (5H, m, PhS(O)), 6.21 (2H, m, H-1 and H-2), 2.72-2.46 (2H, m, H-3), 1.57-1.45 (2H, m, H-4), 1.43-1.23 (6H, m, H-5, H-6 and H-7), 0.88 (3H, br t, J 7 Hz, H-8); *m/z* (EI) 236 (M^+), 219 (M^+ - OH), 149, 110 (PhSH), 109 (PhS) (Found: C, 70.75; H, 8.71. $C_{14}H_{18}OS$ requires C, 71.14; H, 8.53%).

Preparation of (±)$_S$-3-methyl-1-(phenylsulfinyl)but-1-ene (1c).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (70% ether–petrol) gave (±)$_S$-(*E*)-3-methyl-1-(phenylsulfinyl)but-1-ene (*E*)-**1c** and (±)$_S$-(*Z*)-3-methyl-1-(phenylsulfinyl)but-1-ene (*Z*)-**1c** (1:13.5 ratio of *E*:*Z* by ^1H nmr; 90%) as a colourless oil; ν_{max} (film) 3058, 2965, 2928, 2869, 1652, 1616, 1583, 1555, 1477, 1465, 1445, 1385, 1365, 1301, 1163, 1083, 1043, 998, 928, 854, 729, 691 cm^{-1}; δ_H (270 MHz) (*E*-isomer) 7.60-7.40 (5H, m, PhS(O)), 6.59 (1H, dd, J 15.5, 7 Hz, H-2), 6.15 (1H, dd, J 15.5, 1.5 Hz, H-1), 2.47 (1H, d octet, J 7, 1.5 Hz, H-3), 1.04 (6H, d, J 7 Hz, H-4); (*Z*-isomer) 7.60-7.40 (5H, m, PhS(O)), 6.08 (1H, d, J 10 Hz, H-1), 5.99 (1H, t, J 10 Hz, H-2), 3.30 (1H, d heptet, J 10, 7 Hz, H-3), 1.12 (3H, d, J 7 Hz, H-4), 1.07 (3H, d, J 7 Hz, H-4); *m/z* (EI) 194 (M^+), 177 (M^+ - OH), 110 (PhSH), 109 (PhS), 78 (Found: C, 67.54; H, 7.37. $C_{11}H_{14}OS$ requires C, 68.00; H, 7.26%).

Preparation of (±)$_S$-3,3-dimethyl-1-(phenylsulfinyl)but-1-ene (1d).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (40%-60% ether–petrol) gave, in order of elution, (±)$_S$-(*E*)-3,3-dimethyl-1-(phenylsulfinyl)but-1-ene (*E*)-**1d** (24%) as a colourless oil; ν_{max} (film) 3055, 2960, 2867, 1619, 1582, 1476, 1444, 1393, 1365, 1304, 1266, 1230, 1201, 1084, 1048, 998, 968, 918, 830, 804, 749, 691 cm^{-1}; δ_H (270 MHz) 7.61-7.45 (5H, m, PhS(O)), 6.61 (1H, d, J 15.5 Hz, H-2), 6.13 (1H, d, J 15.5 Hz, H-1), 1.07 (9H, s, H-4); *m/z* (EI) 208 (M^+), 192 (M^+ - O), 177, 160, 159, 145, 110 (PhSH), 109 (PhS), 57 (*t*-Bu) and *(±)$_S$-(Z)-3,3-dimethyl-1-(phenylsulfinyl)but-1-ene* (*Z*)-**1d** (49%) as a colourless oil; ν_{max} (film) 3058, 2962, 2867, 1617, 1582, 1475, 1443, 1396, 1365, 1303, 1212, 1083, 1041, 998, 899, 802, 751, 692, 609 cm^{-1}; δ_H (270 MHz) 7.65-7.46 (5H, m, PhS(O)), 6.14 (1H, d, J 10.5 Hz, H-2), 6.01 (1H, d, J 10.5 Hz, H-1), 1.32 (9H, s, H-4); *m/z* (EI) 208 (M^+), 192 (M^+ - O), 191 (M^+ - OH), 177, 110 (PhSH), 109 (PhS) (Found: C, 68.91; H, 7.95. $C_{12}H_{16}OS$ requires C, 69.19; H, 7.74%).

Preparation of (±)$_S$-3-benzyloxy-1-(phenylsulfinyl)prop-1-ene (1e).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (50%-85% ether–petrol) gave *(±)$_S$-(E)-3-benzyloxy-1-(phenylsulfinyl)prop-1-ene* (*E*)-**1e** and *(±)$_S$-(Z)-3-benzyloxy-1-(phenylsulfinyl)prop-1-ene* (*Z*)-**1e** (1:1 ratio of *E*:*Z* by ^1H nmr; 77%) as a colourless oil; ν_{max} (film) 3060, 2856, 1965, 1726, 1583, 1496, 1477, 1444, 1360, 1308, 1270, 1208, 1086, 1044, 999, 945, 745, 697 cm^{-1}; δ_H (270 MHz) (*E*-isomer) 7.67-7.25 (10H, m, PhS(O), Ph), 6.68 (1H, dt, J 16, 3.5 Hz, H-2), 6.56 (1H, dt, J 16, 1 Hz, H-1), 4.54 (2H, s, OCH_2Ph), 4.20 (2H, m, H-3); (*Z*-isomer) 7.63-7.29 (10H, m, PhS(O), Ph), 6.32 (2H, m, H-1 and H-2), 4.61 (2H, s, OCH_2Ph), 4.49 (2H, m, H-3); *m/z* (EI) 272 (M^+),

256 (M^+ - O), 255 (M^+ - OH), 218, 181 (M^+ - $PhCH_2$), 166 (M^+ - PhCHO), 109 (PhS), 91 ($PhCH_2$) (Found: C, 70.42; H, 5.97. $C_{16}H_{16}O_2S$ requires C, 70.56; H, 5.92%).

Preparation of (±)$_S$-(3*E*)-1-(phenylsulfinyl)-1,3-pentadiene (1f).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (60%-75% ether–petrol) gave *(±)$_S$-(1E, 3E)-1-(phenylsulfinyl)-1,3-pentadiene* (*E*)-**1f** and *(±)$_S$-(1Z, 3E)-1-(phenylsulfinyl)-1,3-pentadiene* (*Z*)-**1f** (1:1.2 ratio of *E*:*Z* by ^1H nmr; 79%) as a colourless oil; ν_{max} (film) 3021, 2912, 2851, 1684, 1646, 1581, 1540, 1475, 1444, 1376, 1304, 1272, 1207, 1083, 1036, 998, 932, 818, 746, 690 cm^{-1}; δ_H (270 MHz) (1*E*, 3*E*-isomer) 7.65-7.46 (5H, m, PhS(O)), 6.96 (1H, m, H-4), 6.22 (1H, d, J 15 Hz, H-1), 6.11 (2H, m, H-2 and H-3), 1.83 (3H, d, J 5 Hz, H-5); (1Z, 3*E*-isomer) 7.63-7.45 (5H, m, PhS(O)), 6.90 (1H, m, J 15 Hz, H-4), 6.60 (1H, dd, J 11, 10 Hz, H-2), 6.14-6.00 (2H, m, H-1 and H-3), 1.91 (3H, dd, J 7, 1 Hz, H-5); *m/z* (EI) 192 (M^+), 176 (M^+ - O), 144, 129, 110 (PhSH), 109 (PhS) (Found: (M^+), 192.0609. $C_{11}H_{12}OS$ requires (M^+), 192.0609).

Preparation of (±)$_S$-(*E*)-2-(*p*-tolyl)-1-(phenylsulfinyl)ethene (1h).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (25%-100% ether–petrol) gave, in order of elution, *(±)$_S$-(E)-2-(p-tolyl)-1-(phenylsulfinyl)ethene* (*E*)-**1h** (60%) as a colourless solid, mp 83-84°C; ν_{max} (Nujol) 2923, 2853, 1871, 1779, 1608, 1567, 1541, 1511, 1462, 1442, 1375, 1297, 1176, 1085, 1048, 996, 975, 842, 798, 742, 710, 684, 666 cm^{-1}; δ_H (270 MHz) 7.68 (2H, m, *o*-protons on PhS(O)), 7.52 (3H, m, *m*- and *p*-protons on PhS(O)), 7.35 (2H, d, J 8 Hz, *m*-protons to Me on 4-MeAr), 7.35 (1H, d, J 16 Hz, H-2), 7.17 (2H, d, J 8 Hz, *o*-protons to Me on 4-MeAr), 6.79 (1H, d, J 16 Hz, H-1), 2.35 (3H, s, MeAr); *m/z* (EI) 242 (M^+), 226 (M^+ - O), 211, 194, 181, 178, 135, 134, 121, 115 (Found: C, 74.56; H, 5.92. $C_{15}H_{14}OS$ requires C, 74.35; H, 5.82%) and *(±)$_S$-(Z)-2-(p-tolyl)-1-(phenylsulfinyl)ethene* (*Z*)-**1h** (34%) as a colourless solid, mp 69-71°C; ν_{max} (Nujol) 2924, 2855, 1907, 1600, 1578, 1510, 1461, 1377, 1318, 1296, 1172, 1126, 1080, 1041, 848, 837, 823, 796, 752, 693, 666 cm^{-1}; δ_H (270 MHz) 7.66 (2H, m, *o*-protons on PhS(O)), 7.50 (5H, m, *m*- and *p*-protons on PhS(O) and *m*-protons to Me on 4-MeAr), 7.24 (2H, d, J 8 Hz, *o*-protons to Me on 4-MeAr), 7.10 (1H, d, J 10 Hz, H-2), 6.39 (1H, d, J 10 Hz, H-1), 2.40 (3H, s, MeAr); *m/z* (EI) 242 (M^+), 226 (M^+ - O), 211, 194, 181, 178, 135, 134, 121, 115 (Found: C, 74.61; H, 5.76. $C_{15}H_{14}OS$ requires C, 74.35; H, 5.82%).

Preparation of (±)$_S$-2-(4-methoxyphenyl)-1-(phenylsulfinyl)ethene (1i).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (60%-100% ether–petrol) gave, in order of elution, (±)$_S$-(*E*)-2-(4-methoxyphenyl)-1-(phenylsulfinyl)ethene (*E*)-**1i** (60%) as a colourless solid, mp 64-65°C (lit.[11(b)] mp 63-66°C); ν_{max} (Nujol) 2924, 1604, 1511, 1443, 1379, 1331, 1309, 1296, 1252, 1176, 1153, 1107, 1084, 1030, 996, 961, 943, 866, 843, 801, 745, 691, 666 cm^{-1}; δ_H (270 MHz) 7.63 (2H, m, *o*-protons on PhS(O)), 7.44 (3H, m, *m*- and *p*-protons on PhS(O)), 7.34 (2H, d, J 9 Hz, *m*-protons to MeO on 4-MeOAr), 7.28 (1H, d, J 16 Hz, H-2), 6.82 (2H, d, J 9 Hz, *o*-protons to MeO on 4-MeOAr), 6.67 (1H, d, J 16 Hz, H-1), 3.74 (3H, s, MeO); *m/z* (EI) 258 (M^+), 242 (M^+ - O), 227,

209, 195, 149, 133, 121 (Found: C, 69.66; H, 5.41. $C_{15}H_{14}O_2S$ requires C, 69.74; H, 5.46%) and *(±)S-(Z)-2-(4-methoxyphenyl)-1-(phenylsulfinyl)ethene* (Z)-**1i** (20%) as a colourless oil; ν_{max} (film) 3002, 2936, 2837, 2560, 2053, 1889, 1753, 1605, 1572, 1510, 1462, 1443, 1420, 1307, 1254, 1176, 1109, 1083, 1033, 997, 962, 943, 866, 842, 800, 746, 715, 690, 666 cm^{-1}; δ_H (270 MHz) 7.64 (2H, m, *o*-protons on PhS(O)), 7.54 (2H, d, J 8.5 Hz, *m*-protons to MeO on 4-MeOAr), 7.46 (3H, m, *m*- and *p*-protons on PhS(O)), 7.01 (1H, d, J 10.5 Hz, H-2), 6.92 (2H, d, J 8.5 Hz, *o*-protons to MeO on 4-MeOAr), 6.28 (1H, d, J 10.5 Hz, H-1), 3.80 (3H, s, MeO); *m/z* (EI) 258 (M^+), 242 (M^+ - O), 209, 195, 179, 165, 149, 133, 132, 121 (Found: C, 69.72; H, 5.26. $C_{15}H_{14}O_2S$ requires C, 69.74; H, 5.46%).

Preparation of (±)S-2-(4-chlorophenyl)-1-(phenylsulfinyl)ethene (1j).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (20%-75% ether–petrol) gave, in order of elution, (±)S-(*E*)-2-(4-chlorophenyl)-1-(phenylsulfinyl)ethene (*E*)-**1j** (39%) as a colourless solid, mp 97-98°C (lit.[11(b)] mp 94.5-95.5°C); ν_{max} (Nujol) 3029, 2923, 2854, 2052, 1962, 1905, 1680, 1655, 1609, 1590, 1466, 1442, 1407, 1378, 1306, 1084, 1027, 996, 960, 946, 849, 799, 746, 689, 665 cm^{-1}; δ_H (270 MHz) 7.67 (2H, m, *o*-protons on PhS(O)), 7.52 (5H, m, *m*- and *p*-protons on PhS(O) and *m*-protons to Cl on 4-ClAr), 7.38 (3H, m, *o*-protons to Cl on 4-ClAr and H-2), 6.82 (1H, d, J 15.5 Hz, H-1); *m/z* (EI) 264, 262 (M^+), 248, 246 (M^+ - O), 214, 211, 201, 178, 157, 155, 134, 121 (Found: C, 63.92; H, 4.28. $C_{14}H_{11}ClOS$ requires C, 64.00; H, 4.22%) and *(±)S-(Z)-2-(4-chlorophenyl)-1-(phenylsulfinyl)ethene* (Z)-**1j** (36%) as a colourless solid, mp 85-87°C; ν_{max} (Nujol) 2924, 2854, 1656, 1608, 1590, 1490, 1464, 1438, 1403, 1377, 1171, 1081, 1039, 1013, 921, 857, 829, 765, 747, 689, 666 cm^{-1}; δ_H (270 MHz) 7.67 (2H, m, *o*-protons on PhS(O)), 7.52 (5H, m, *m*- and *p*-protons on PhS(O) and *m*-protons to Cl on 4-ClAr), 7.35 (2H, d, J 7 Hz, *o*-protons to Cl on 4-ClAr), 7.07 (1H, d, J 10 Hz, H-2), 6.46 (1H, d, J 10 Hz, H-1); *m/z* (EI) 264, 262 (M^+), 248, 246 (M^+ - O), 214, 211, 201, 178, 157, 155, 134, 121 (Found: C, 64.00; H, 4.16. $C_{14}H_{11}ClOS$ requires C, 64.00; H, 4.22%).

Preparation of (±)S-2-(4-nitrophenyl)-1-(phenylsulfinyl)ethene (1k).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (2%-5% methanol-dichloromethane) gave *(±)S-(E)-2-(4-nitrophenyl)-1-(phenyl-sulfinyl)ethene* (*E*)-**1k** and *(±)S-(Z)-2-(4-nitrophenyl)-1-(phenylsulfinyl)ethene* (Z)-**1k** (1.8:1 ratio of *E*:Z by ^1H nmr; 57%) as an orange solid; ν_{max} (Nujol) 2924, 2853, 1655, 1644, 1593, 1572, 1563, 1513, 1465, 1409, 1397, 1374, 1336, 1152, 1108, 1082, 1066, 1047, 972, 953, 929, 859, 828, 808, 736, 684, 666 cm^{-1}; δ_H (270 MHz) (*E*-isomer) 8.22 (2H, d, J 9 Hz, *o*-protons to NO_2 on 4-NO_2Ar), 7.69 (2H, m, *o*-protons on PhS(O)), 7.60 (2H, m, *m*-protons to NO_2 on 4-NO_2Ar), 7.56 (3H, m, *m*- and *p*-protons on PhS(O)), 7.43 (1H, d, J 15.5 Hz, H-2), 7.02 (1H, d, J 15.5 Hz, H-1); (Z-isomer) 8.30 (2H, d, J 9 Hz, *o*-protons to NO_2 on 4-NO_2Ar), 7.75 (2H, m, *m*-protons to NO_2 on 4-NO_2Ar), 7.64 (2H, m, *o*-protons on PhS(O)), 7.56 (3H, m, *m*- and *p*-protons on PhS(O)), 7.17 (1H, d, J 10 Hz, H-2), 6.64 (1H, d, J 10 Hz, H-1); *m/z* (EI) 273 (M^+), 269, 257 (M^+ - O), 244, 225, 110 (PhSH), 109 (PhS) (Found: C, 61.50; H, 4.01; N, 5.11. $C_{14}H_{11}NO_3S$ requires C, 61.53; H, 4.06; N, 5.12%).

Preparation of (±)$_S$-2-[4-(methylsulfenyl)phenyl]-1-(phenylsulfinyl)ethene (1l).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (50%-100% ether–petrol) gave, in order of elution, *(±)$_S$-(E)-2-[4-(methylsulfenyl)phenyl]-1-(phenylsulfinyl)ethene* (*E*)-**1l** (51%) as a colourless solid, mp 88°C; ν_{max} (Nujol) 2923, 1654, 1593, 1540, 1494, 1465, 1404, 1378, 1311, 1289, 1197, 1170, 1085, 1069, 1046, 1024, 999, 959, 941, 912, 832, 792, 746, 686, 665 cm^{-1}; δ_H (270 MHz) 7.68 (2H, m, *o*-protons on PhS(O)), 7.51 (3H, m, *m*- and *p*-protons on PhS(O)), 7.36 (2H, d, J 8 Hz, *m*-protons to MeS on 4-MeSAr), 7.31 (1H, d, J 15.5 Hz, H-2), 7.20 (2H, d, J 8 Hz, *o*-protons to MeS on 4-MeSAr), 6.78 (1H, d, J 15.5 Hz, H-1), 2.47 (3H, s, MeSAr); *m/z* (EI) 274 (M^+), 258 (M^+ - O), 243, 226, 211, 178, 165, 149, 148, 134, 121 (Found: C, 65.91; H, 4.72. $C_{15}H_{14}OS_2$ requires C, 65.66; H, 5.14%) and *(±)$_S$-(Z)-2-[4-(methylsulfenyl)phenyl]-1-(phenylsulfinyl)ethene* (Z)-**1l** (29%) as a colourless oil; ν_{max} (film) 2925, 2854, 1654, 1598, 1558, 1540, 1494, 1458, 1446, 1404, 1378, 1085, 1040, 999, 960, 821, 792, 746, 704, 687 cm^{-1}; δ_H (270 MHz) 7.67 (2H, m, *o*-protons on PhS(O)), 7.51 (5H, m, *m*- and *p*-protons on PhS(O) and *m*-protons to MeS on 4-MeSAr), 7.28 (2H, d, J 8.5 Hz, *o*-protons to MeS on 4-MeSAr), 7.03 (1H, d, J 11 Hz, H-2), 6.38 (1H, d, J 11 Hz, H-1), 2.51 (3H, s, MeSAr); *m/z* (EI) 274 (M^+), 258 (M^+ - O), 243, 226, 211, 178, 165, 149, 148, 134, 121 (Found: C, 65.90; H, 4.86. $C_{15}H_{14}OS_2$ requires C, 65.66; H, 5.14%).

Preparation of (±)$_S$-2-(3-methoxyphenyl)-1-(phenylsulfinyl)ethene (1m).

Prepared according to the standard procedure described for **1g**. Purification by chromatography (60%-100% ether–petrol) gave, in order of elution, *(±)$_S$-(E)-2-(3-methoxyphenyl)-1-(phenylsulfinyl)ethene* (*E*)-**1m** (44%) as a colourless oil; ν_{max} (film) 3052, 2838, 2087, 1958, 1889, 1870, 1842, 1765, 1667, 1588, 1457, 1273, 1160, 1042, 960, 932, 841, 774, 688 cm^{-1}; δ_H (270 MHz) 7.69 (2H, m, *o*-protons on PhS(O)), 7.53 (3H, m, *m*- and *p*-protons on PhS(O)), 7.35 (1H, d, J 16 Hz, H-2), 7.27 (1H, t, J 8 Hz, H-5 on 3-MeOAr), 7.05 (1H, br d, J 8 Hz, H-4 or H-6 on 3-MeOAr), 6.97 (1H, t, J 2 Hz, H-2 on 3-MeOAr), 6.90 (1H, dd, J 8, 2 Hz, H-4 or H-6 on 3-MeOAr), 6.81 (1H, d, J 16 Hz, H-1), 3.80 (3H, s, MeO); *m/z* (EI) 258 (M^+), 242 (M^+ - O), 210, 209, 194, 165, 134, 121 (Found: C, 69.88; H, 4.96. $C_{15}H_{14}O_2S$ requires C, 69.74; H, 5.46%) and *(±)$_S$-(Z)-2-(3-methoxyphenyl)-1-(phenylsulfinyl)ethene* (Z)-**1m** (32%) as a colourless oil; ν_{max} (film) 3058, 3002, 2941, 2836, 1684, 1578, 1540, 1491, 1444, 1298, 1261, 1181, 1138, 1083, 1044, 998, 918, 861, 786, 750, 688, 629 cm^{-1}; δ_H (270 MHz) 7.67 (2H, m, *o*-protons on PhS(O)), 7.50 (3H, m, *m*- and *p*-protons on PhS(O)), 7.36 (1H, t, J 8 Hz, H-5 on 3-MeOAr), 7.14 (2H, m, H-4 or H-6 and H-2 on 3-MeOAr), 7.08 (1H, d, J 10.5 Hz, H-2), 6.96 (1H, dd, J 9, 2 Hz, H-4 or H-6 on 3-MeOAr), 6.43 (1H, d, J 10.5 Hz, H-1), 3.84 (3H, s, MeO); *m/z* (EI) 258 (M^+), 242 (M^+ - O), 210, 209, 194, 165, 150, 134, 121 (Found: C, 69.31; H, 5.30. $C_{15}H_{14}O_2S$ requires C, 69.74; H, 5.46%).

Preparation of (+)-(*R*)$_S$-1-(*p*-tolylsulfinyl)oct-1-ene (1o).

To a stirred solution of redistilled dimethyl methylphosphonate (3.24 ml, 29.9 mmol, 2.2 eq) in dry THF (40 ml) at -78°C under argon was added, dropwise *via* syringe, *n*-BuLi (12.1 ml of a 2.35M solution in hexanes, 28.5 mmol, 2.1 eq). The colourless anion solution was stirred for a further 10 min at -78°C after the

addition. A solution of (-)-(*S*)$_S$-menthyl *p*-toluenesulfinate (azeotropically dried with toluene [3 x 20 ml] immediately prior to use; 4 g, 13.6 mmol, 1 eq) in dry THF (40 ml) was then added slowly *via* cannula. After a further 10 min stirring at -78°C a solution of heptanal (stirred over flame dried sodium sulfate for 12 h followed by distillation immediately prior to use; 2.09 ml, 14.9 mmol, 1.1 eq) in dry THF (40 ml) was added *via* cannula to the pale yellow anion solution. The reaction mixture was immediately allowed to warm to 0°C during 10 min and then quenched by the addition of saturated aqueous ammonium chloride (80 ml). The mixture was partitioned between dichloromethane (240 ml) and water (80 ml). The aqueous layer was separated and further extracted with dichloromethane (2 x 80 ml). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to give the crude products as a pale yellow oil. Purification by chromatography (50%-100% ether–petrol) gave, in order of elution, (+)-(*R*)$_S$-(*E*)-1-(*p*-tolylsulfinyl)oct-1-ene (*E*)-**1o** (0.387 g, 11%) as a colourless oil, $[\alpha]_D^{20}$ +138.8 (*c* 1.37, $CHCl_3$) (lit.[40] $[\alpha]_D^{20}$ +138.2 (*c* 0.503, acetone)); ν_{max} (film) 2925, 2856, 1628, 1597, 1493, 1466, 1398, 1379, 1302, 1210, 1178, 1083, 1048, 1016, 957, 810, 727, 666 cm^{-1}; δ_H (270 MHz) 7.49 (2H, d, J 8 Hz, *o*-protons on tolyl), 7.19 (2H, d, J 8 Hz, *m*-protons on tolyl), 6.57 (1H, dt, J 16, 8 Hz, H-2), 6.19 (1H, dt, J 16, 0.5 Hz, H-1), 2.40 (3H, s, tolyl Me), 2.20 (2H, dq, J 8, 0.5 Hz, H-3), 1.50-1.22 (8H, m, H-4, H-5, H-6 and H-7), 0.87 (3H, m, J 7 Hz, H-8); *m/z* (EI) 250 (M^+), 234 (M^+ - O), 202, 163, 131, 130, 124, 91 ($PhCH_2$) and (-)-(*R*)$_S$-(*Z*)-1-(phenylsulfinyl)oct-1-ene (*Z*)-**1o** (2.515 g, 74%) as a colourless oil, $[\alpha]_D^{20}$ -275 (*c* 1.09, acetone) (lit.[40] $[\alpha]_D^{20}$ -279.6 (*c* 0.193, acetone)); ν_{max} (film) 2924, 2857, 1617, 1493, 1466, 1397, 1379, 1302, 1209, 1177, 1083, 1043, 1016, 810, 724, 622 cm^{-1}; δ_H (270 MHz) 7.47 (2H, d, J 8 Hz, *o*-protons on tolyl), 7.17 (2H, d, J 8 Hz, *m*-protons on tolyl), 6.20-6.19 (2H, m, H-1 and H-2), 2.67-2.43 (2H, m, H-3), 2.38 (3H, s, tolyl Me), 1.55-1.23 (8H, m, H-4, H-5, H-6 and H-7), 0.88 (3H, m, J 9 Hz, H-8); *m/z* (EI) 250 (M^+), 234, 233, 163, 130, 124, 91 ($PhCH_2$).

Preparation of (+)-(*R*)$_S$-2-phenyl-1-(*p*-tolylsulfinyl)ethene (1p).

To a stirred solution of dimethyl methylphosphonate (redistilled; 4.03 ml, 37.2 mmol, 2.2 eq) in dry THF (50 ml) at -78°C under argon was added, dropwise *via* syringe, *n*-BuLi (14.2 ml of a 2.5M solution in hexanes, 35.5 mmol, 2.1 eq). The colourless anion solution was stirred for a further 10 min at -78°C after the addition. A solution of (-)-(*S*)$_S$-menthyl *p*-toluenesulfinate (azeotropically dried with toluene [3 x 25 ml] immediately prior to use; 4.9796 g, 16.9 mmol, 1 eq) in dry THF (50 ml) was then added slowly *via* cannula. After a further 10 min stirring at -78°C a solution of benzaldehyde (washed with 10% NaOH, saturated aqueous sodium sulfite and water followed by distillation immediately prior to use; 1.89 ml, 18.6 mmol, 1.1 eq) in dry THF (50 ml) was added *via* cannula to the pale yellow anion solution. The reaction mixture was immediately allowed to warm to 0°C during 10 min and then quenched by the addition of saturated aqueous ammonium chloride (100 ml). The mixture was partitioned between dichloromethane (300 ml) and water (100 ml). The aqueous layer was separated and further extracted with dichloromethane (2 x 100 ml). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give the crude products as a pale yellow oil. Purification by chromatography (30%-60% ether–petrol) gave, in order of elution, (+)-(*R*)$_S$-(*E*)-2-phenyl-1-(*p*-tolylsulfinyl)ethene (*E*)-**1p** (1.881 g, 46%) as a colourless solid, mp 82-83°C (lit.[11(c)] mp 82°C), $[\alpha]_D^{20}$ +160.2 (*c* 1.35, $CHCl_3$) (lit.[11(c)] $[\alpha]_D$ +166 (*c* 1.14, $CHCl_3$)) ν_{max} (Nujol) 3019, 2926, 1649, 1593, 1573, 1492, 1445, 1378, 1302, 1178, 1082, 1047, 1015, 971, 916, 854, 807, 762, 740, 692, 664, 620 cm^{-1};

δ_H (270 MHz) 7.58 (2H, d, J 8 Hz, *o*-protons on tolyl), 7.47-7.28 (8H, m, *m*-protons on tolyl, Ph and H-2), 6.81 (1H, d, J 16 Hz, H-1), 2.40 (3H, s, tolyl Me); *m/z* (EI) 242 (M^+), 226 (M^+ - O), 211, 194, 181, 178, 103 (M^+ - *p*-TolS(O)), 91 ($PhCH_2$), 77 (Ph) and (-)-(*R*)$_S$-(*Z*)-2-phenyl-1-(*p*-tolylsulfinyl)ethene (*Z*)-**1p** (1.255 g, 31%) as a colourless solid, mp 51-52°C (lit.[11(c)] mp, 52–52.5°C), $[\alpha]_D^{20}$ -734.2 (*c* 0.98, $CHCl_3$) (lit.[11(c)] $[\alpha]_D$ -736 (*c* 1.04, $CHCl_3$)); ν_{max} (Nujol) 3029, 2922, 2854, 1656, 1607, 1593, 1571, 1492, 1445, 1397, 1378, 1349, 1306, 1286, 1211, 1180, 1155, 1118, 1077, 1033, 1012, 968, 920, 847, 809, 771, 742, 722, 694 cm^{-1}; δ_H (270 MHz) 7.60-7.39 (7H, m, *o*-protons on tolyl and Ph), 7.32 (2H, d, J 9 Hz, *m*-protons on tolyl), 7.09 (1H, d, J 10 Hz, H-2), 6.43 (1H, d, J 10 Hz, H-1), 2.41 (3H, s, tolyl Me); *m/z* (EI) 242 (M^+), 226 (M^+ - O), 211, 194, 181, 178, 121, 103 (M^+ - *p*-TolS(O)), 91 ($PhCH_2$), 77 (Ph).

Preparation of (±)$_S$-2-methyl-1-(phenylsulfinyl)prop-2-ene (4a) and (±)$_S$-2-methyl-1-(phenylsulfinyl)prop-1-ene (3a).

To a stirred solution of redistilled dimethyl methylphosphonate (137 µl, 1.3 mmol, 2.2 eq) in dry THF (1 ml) at -78°C under argon was added, dropwise *via* syringe, *n*-BuLi (490 µl of a 2.5M solution in hexanes, 1.2 mmol, 2.1 eq). The colourless anion solution was stirred for a further 10 min at -78°C after the addition. A solution of isopropyl phenylsulfinate (azeotropically dried with toluene [3 x 5 ml] immediately prior to use; 107.4 mg, 0.58 mmol, 1 eq) in dry THF (1 ml) was then added slowly *via* syringe. After a further 10 min stirring at -78°C a solution of acetone (stirred over dry calcium sulfate for 12 h followed by distillation immediately prior to use; 128 µl, 1.7 mmol, 3 eq) in dry THF (1 ml) was added *via* syringe to the pale yellow anion solution. The reaction mixture was immediately allowed to warm to 20°C during 10 min and stirring was continued for a further hour. The reaction was then quenched by the addition of saturated aqueous ammonium chloride (5 ml). The mixture was partitioned between dichloromethane (10 ml) and water (5 ml). The aqueous layer was separated and further extracted with dichloromethane (2 x 5 ml). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to give the crude products as a pale yellow oil. Purification by chromatography (70%-100% ether–petrol) gave, in order of elution, (±)$_S$-2-methyl-1-(phenylsulfinyl)prop-2-ene **4a** (17.2 mg, 16%) as a colourless oil; ν_{max} (film) 3060, 2973, 2916, 1696, 1685, 1653, 1641, 1617, 1583, 1540, 1521, 1478, 1445, 1379, 1321, 1286, 1214, 1143, 1087, 1071, 1048, 998, 903, 825, 750, 692 cm^{-1}; δ_H (270 MHz) 7.67-7.58 (2H, m, *o*-protons on PhS(O)), 7.54-7.47 (3H, m, *m*- and *p*-protons on PhS(O)), 5.02 (1H, t, J 1 Hz, H-3), 4.80 (1H, br s, H-3), 3.53 and 3.38 (2H, AB quartet, J 12.5 Hz, H-1), 1.80 (3H, s, 2-Me); *m/z* (EI) 180 (M^+), 164 (M^+ - O), 149, 132, 131, 125, 110 (PhSH), 109 (PhS) and (±)$_S$-2-methyl-1-(phenylsulfinyl)prop-1-ene **3a** (61.1 mg, 58%) as a colourless oil; ν_{max} (film) 3060, 2980, 2947, 2913, 2853, 2065, 1696, 1634, 1583, 1558, 1541, 1507, 1477, 1444, 1374, 1304, 1161, 1084, 1036, 998, 922, 851, 792, 747, 692 cm^{-1}; δ_H (270 MHz) 7.60-7.42 (5H, m, PhS(O)), 6.01 (1H, br s, H-1), 2.18 (3H, s, H-3), 1.89 (3H, s, H-3); *m/z* (EI) 180 (M^+), 164 (M^+ - O), 163 (M^+ - OH), 149, 132, 117, 110 (PhSH).

Preparation of (±)$_S$-2-methyl-1-(phenylsulfinyl)but-1-ene (3b).

Prepared according to the standard procedure described for **3a**. Purification by chromatography (50%-100% ether–petrol) gave *(±)$_S$-(E)-2-methyl-1-(phenylsulfinyl)but-1-ene* (*E*)-**3b** and *(±)$_S$-(Z)-2-methyl-1-*

(phenylsulfinyl)but-1-ene (Z)-**3b** (1.4:1 ratio of *E*:*Z* by ^{1}H nmr; 56%) as a colourless oil; ν_{max} (film) 3056, 2970, 2877, 1620, 1582, 1443, 1378, 1304, 1159, 1083, 1039, 998, 952, 920, 803, 743, 693, 666 cm^{-1}; δ_H (270 MHz) (*E*-isomer) 7.63-7.45 (5H, m, PhS(O)), 6.02 (1H, br s, H-1), 2.19 (5H, m, H-3 and 2-Me), 1.06 (3H, t, J 8 Hz, H-4); (*Z*-isomer) 7.63-7.45 (5H, m, PhS(O)), 6.00 (1H, br s, H-1), 2.69 (1H, dq, J 13.5, 7.5 Hz, H-3), 2.58 (1H, dq, J 13.5, 7 Hz, H-3), 1.89 (3H, d, J 1 Hz, 2-Me), 1.19 (3H, br t, J 7.5 Hz, H-4); *m/z* (EI) 194 (M^+), 178 (M^+ - O), 163, 130, 110 (PhSH), 91 (Found: (M^+), 194.0765. $C_{11}H_{14}OS$ requires (M^+), 194.0765).

Preparation of (±)$_S$-(1-cyclopentenyl)(phenylsulfinyl)methane (4c) and (±)$_S$-cyclopentylidene(phenylsulfinyl)methane (3c).

Prepared according to the standard procedure described for **3a**. Purification by chromatography (50%-100% ether–petrol) gave, in order of elution, (±)$_S$-(1-cyclopentenyl)(phenylsulfinyl)methane **4c** (17%) as a colourless solid, mp 56-57°C (lit.[41] mp 56-57°C); ν_{max} (Nujol) 3050, 2953, 2849, 1647, 1624, 1536, 1442, 1410, 1291, 1135, 1085, 1039, 956, 914, 888, 857, 826, 746, 693 cm^{-1}; δ_H (270 MHz) 7.59 (2H, m, *o*-protons on PhS(O)), 7.49 (3H, m, *m*- and *p*-protons on PhS(O)), 5.57 (1H, br s, H-2 on ring), 3.66 and 3.50 (2H, AB quartet, J 13 Hz, H-1), 2.38-2.19 (4H, m, H-3 and H-5 on ring), 1.90-1.78 (2H, m, H-4 on ring); *m/z* (EI) 206 (M^+), 205 (M^+ - H), 190 (M^+ - O), 189 (M^+ - OH), 126, 110 (PhSH), 109 (PhS), 81, 79 and (±)$_S$-cyclopentylidene(phenylsulfinyl)methane **3c** (25%) as a colourless solid, mp 53-54°C (lit.[41] mp 52-54°C); ν_{max} (Nujol) 3054, 2961, 2873, 1653, 1632, 1583, 1571, 1557, 1541, 1523, 1477, 1443, 1425, 1305, 1261, 1228, 1160, 1109, 1083, 1036, 997, 952, 923, 787, 753, 694 cm^{-1}; δ_H (270 MHz) 7.57 (2H, m, *o*-protons on PhS(O)), 7.47 (3H, m, *m*- and *p*-protons on PhS(O)), 6.09 (1H, t, J 1 Hz, H-1), 2.97-2.83 (1H, m, H-2 or H-5 on ring), 2.67-2.52 (1H, m, H-2 or H-5 on ring), 2.46-2.28 (2H, m, H-2 or H-5 on ring), 1.84-1.63 (4H, m, H-3 and H-4 on ring); *m/z* (EI) 206 (M^+), 190 (M^+ - O), 189 (M^+ - OH), 158, 155, 147, 110 (PhSH), 109 (PhS).

Preparation of (±)$_S$-cyclohexylidene(phenylsulfinyl)methane (3d).

Prepared according to the standard procedure described for **3a**. Purification by chromatography (70% ether–petrol) gave (±)$_S$-cyclohexylidene(phenylsulfinyl)methane[41] **3d** (90%) as a colourless oil; ν_{max} (film) 3058, 2934, 2858, 1654, 1628, 1583, 1540, 1477, 1445, 1350, 1337, 1289, 1232, 1169, 1129, 1083, 1038, 998, 933, 905, 850, 798, 744, 694, 639 cm^{-1}; δ_H (270 MHz) 7.62-7.43 (5H, m, PhS(O)), 5.98 (1H, s, H-1), 2.81-2.60 (2H, m, H-2 or H-6 on ring), 2.26-2.14 (2H, m, H-2 or H-6 on ring), 1.82-1.55 (6H, m, H-3, H-4 and H-5 on ring); *m/z* (EI) 220 (M^+), 204 (M^+ - O), 203 (M^+ - OH), 171, 161, 147, 110 (PhSH), 95.

Preparation of 1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane (6x).

To a stirred solution of (phenylsulfinyl)ethene (100 µl, 0.75 mmol) in dry dichloromethane (1.5 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (137 µl, 0.97 mmol, 1.3 eq). After 30 min stirring at 0°C the reaction was quenched by the addition of saturated aqueous sodium hydrogencarbonate (10 ml). dichloromethane (25 ml) was added, the organic layer was separated, dried over $MgSO_4$ and the solvents were

removed under reduced pressure to give *1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane* **6x** (269 mg, 99%) as a colourless oil; ν_{max} (film) 2967, 1798, 1653, 1586, 1479, 1443, 1397, 1369, 1350, 1316, 1162, 1071, 1024, 961, 866, 774, 749, 726, 692 cm^{-1}; δ_H (270 MHz) 7.58-7.35 (5H, m, PhS), 6.34 (1H, dd, J 9, 4 Hz, H-1), 4.67 (1H, dd, J 12, 4 Hz, H-2), 4.44 (1H, dd, J 12, 9 Hz, H-2); *m/z* (EI) 362 (M^+), 253 (M^+ - PhS), 109 (PhS) (Found: (M^+), 362.0048. $C_{12}H_8F_6O_4S$ requires (M^+), 362.0048).

Preparation of 1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)propane (6a).

To a stirred solution of $(\pm)_S$-(*E*)-1-(phenylsulfinyl)prop-1-ene (*E*)-**1a** and $(\pm)_S$-(*Z*)-1-(phenylsulfinyl)prop-1-ene (*Z*)-**1a** (1:1.5 ratio by ^1H nmr; 94.3 mg, 0.57 mmol) in dry dichloromethane (1 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (80 µl, 0.57 mmol, 1 eq). The reaction was stirred at 0°C for 10 min and then TFAA (80 µl, 0.57 mmol, 1 eq) was added dropwise *via* syringe. After 15 min stirring at 0°C the reaction was quenched. Standard work-up gave *1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)propane* **6a** (1:1 ratio of diastereomers by ^1H nmr; 187.8 mg, 88%) as a colourless oil; ν_{max} (film) 2999, 1795, 1586, 1478, 1443, 1369, 1332, 1233, 1151, 1049, 1025, 960, 863, 774, 748, 722, 692 cm^{-1}; δ_H (270 MHz) (one diastereomer) 7.58-7.35 (5H, m, PhS), 6.34 (1H, d, J 4 Hz, H-1), 5.45 (1H, dq, J 6.5, 4 Hz, H-2), 1.57 (3H, d, J 6.5 Hz, H-3); (one diastereomer) 7.58-7.35 (5H, m, PhS), 6.15 (1H, d, J 8 Hz, H-1), 5.23 (1H, dq, J 8, 6.5 Hz, H-2), 1.54 (3H, d, J 6.5 Hz, H-3); *m/z* (EI) 376 (M^+), 267 (M^+ - PhS), 235, 207, 109 (PhS) (Found: (M^+), 376.0204. $C_{13}H_{10}F_6O_4S$ requires (M^+), 376.0204).

Preparation of 1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)octane (6b): from (*E*)-**1b.**

To a stirred solution of $(\pm)_S$-(*E*)-1-(phenylsulfinyl)oct-1-ene (*E*)-**1b** (38.6 mg, 0.16 mmol) in dry dichloromethane (1 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (23 µl, 0.16 mmol, 1 eq). The reaction was stirred at 0°C for 10 min and then TFAA (23 µl, 0.16 mmol, 1 eq) was added dropwise *via* syringe. After 15 min stirring at 0°C the reaction was quenched. Standard work-up gave *1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)octane* **6b** (1.7:1 ratio of diastereomers by ^1H nmr; 69.2 mg, 95%) as a colourless oil; ν_{max} (film) 2935, 2862, 1792, 1586, 1469, 1443, 1368, 1337, 1233, 1155, 1026, 927, 875, 772, 747, 692 cm^{-1}; δ_H (270 MHz) (major diastereomer) 7.55-7.32 (5H, m, PhS), 6.17 (1H, d, J 8.5 Hz, H-1), 5.25 (1H, dt, J 8.5, 3.5 Hz, H-2), 2.08-1.77 (2H, m, H-3), 1.49-1.20 (8H, m, H-4, H-5, H-6 and H-7), 0.90 (3H, m, H-8); (minor diastereomer) 7.55-7.32 (5H, m, PhS), 6.33 (1H, d, J 4 Hz, H-1), 5.40 (1H, dt, J 9, 4 Hz, H-2), 2.08-1.77 (2H, m, H-3), 1.49-1.20 (8H, m, H-4, H-5, H-6 and H-7), 0.90 (3H, m, H-8); *m/z* (EI) 446 (M^+), 207, 109 (PhS) (Found: (M^+), 446.0987. $C_{18}H_{20}F_6O_4S$ requires (M^+), 446.0987).

Preparation of 1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)octane (6b): from (*Z*)-**1b.**

To a stirred solution of $(\pm)_S$-(*Z*)-1-(phenylsulfinyl)oct-1-ene (*Z*)-**1b** (40.3 mg, 0.17 mmol) in dry dichloromethane (1 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (24 µl, 0.17 mmol, 1 eq). The reaction was stirred at 0°C for 10 min and then TFAA (24 µl, 0.17 mmol, 1 eq) was added dropwise *via* syringe. After 15 min stirring at 0°C the reaction was quenched. Standard work-up gave 1-(phenylsulfenyl)-

1,2-bis(trifluoroacetoxy)octane **6b** (1:3.5 ratio of diastereomers by ^{1}H nmr; 70.5 mg, 93%) as a colourless oil; spectroscopic data was in agreement with the previously prepared compound.

Preparation of 3-methyl-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)butane (6c).

To a stirred solution of (±)$_S$-(*E*)-3-methyl-1-(phenylsulfinyl)but-1-ene (*E*)-**1c** and (±)$_S$-(*Z*)-3-methyl-1-(phenylsulfinyl)but-1-ene (*Z*)-**1c** (1:13.5 ratio by ^{1}H nmr; 71.4 mg, 0.37 mmol) in dry dichloromethane (0.75 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (52 µl, 0.37 mmol, 1 eq). The reaction was stirred at 0°C for 10 min and then TFAA (52 µl, 0.37 mmol, 1 eq) was added dropwise *via* syringe. After 15 min stirring at 0°C the reaction was quenched. Standard work-up gave *3-methyl-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)butane* **6c** (1.2:1 ratio of diastereomers by ^{1}H nmr; 141.3 mg, 95%) as a colourless oil; ν_{max} (film) 3068, 2976, 2886, 1790, 1586, 1544, 1479, 1443, 1374, 1340, 1239, 1026, 1002, 978, 922, 878, 771, 748, 724, 692 cm^{-1}; δ_H (270 MHz) (major diastereomer) 7.58-7.33 (5H, m, PhS), 6.33 (1H, d, J 4.5 Hz, H-1), 5.22 (1H, dd, J 7, 4.5 Hz, H-2), 2.30 (1H, octet, J 7 Hz, H-3), 1.02 (3H, d, J 7 Hz, H-4), 0.93 (3H, d, J 7 Hz, H-4); (minor diastereomer) 7.58-7.33 (5H, m, PhS), 6.24 (1H, d, J 8.5 Hz, H-1), 5.17 (1H, dd, J 8.5, 3.5 Hz, H-2), 2.45 (1H, d heptet, J 7, 3.5 Hz, H-3), 1.07 (3H, d, J 7 Hz, H-4), 1.01 (3H, d, J 7 Hz, H-4); *m/z* (EI) 404 (M^+), 207, 181 (M^+ - PhS, CF_3CO_2H), 109 (PhS) (Found: (M^+), 404.0517. $C_{15}H_{14}F_6O_4S$ requires (M^+), 404.0517).

Preparation of 3,3-dimethyl-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)butane (6d): from (*E*)-1d.

To a stirred solution of (±)$_S$-(*E*)-3,3-dimethyl-1-(phenylsulfinyl)but-1-ene (*E*)-**1d** (42.4 mg, 0.2 mmol) in dry dichloromethane (1 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (43 µl, 0.31 mmol, 1.5 eq). After 90 min stirring at 0°C the reaction was quenched. Standard work-up gave *3,3-dimethyl-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)butane* **6d** (1.8:1 ratio of diastereomers by ^{1}H nmr; 79.6 mg, 93%) as a colourless oil; ν_{max} (film) 3068, 2973, 1786, 1653, 1586, 1481, 1443, 1406, 1374, 1332, 1232, 1134, 1042, 1026, 974, 940, 922, 870, 772, 747, 724, 692 cm^{-1}; δ_H (270 MHz) (major diastereomer) 7.59-7.31 (5H, m, PhS), 6.42 (1H, d, J 4 Hz, H-1), 5.17 (1H, d, J 4 Hz, H-2), 1.02 (9H, s, *t*-Bu); (minor diastereomer) 7.59-7.31 (5H, m, PhS), 6.40 (1H, d, J 4 Hz, H-1), 5.17 (1H, d, J 4 Hz, H-2), 1.11 (9H, s, *t*-Bu); *m/z* (EI) 418 (M^+), 304 (M^+ - CF_3CO_2H), 195 (M^+ - PhS, CF_3CO_2H), 109 (PhS), 57 (*t*-Bu) (Found: (M^+), 418.0673. $C_{16}H_{16}F_6O_4S$ requires (M^+), 418.0674).

Preparation of 3,3-dimethyl-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)butane (6d): from (*Z*)-1d.

To a stirred solution of (±)$_S$-(*Z*)-3,3-dimethyl-1-(phenylsulfinyl)but-1-ene (*Z*)-**1d** (147.3 mg, 0.71 mmol) in dry dichloromethane (3.5 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (150 µl, 1.06 mmol, 1.5 eq). After 90 min stirring at 0°C the reaction was quenched. Standard work-up gave *3,3*-dimethyl-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)butane **6d** (1:1.6 ratio of diastereomers by ^{1}H nmr; 275.2 mg, 93%) as a colourless oil; spectroscopic data was in agreement with the previously prepared compound.

Preparation of 3-benzyloxy-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)propane (6e).

To a stirred solution of (±)$_S$-(*E*)-3-benzyloxy-1-(phenylsulfinyl)prop-1-ene (*E*)-**1e** and (±)$_S$-(*Z*)-3-benzyloxy-1-(phenylsulfinyl)prop-1-ene (*Z*)-**1e** (1.3:1 ratio by ^{1}H nmr; 137.6 mg, 0.51 mmol) in dry dichloromethane (2.5 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (107 µl, 0.76 mmol, 1.5 eq). After 40 min stirring at 0°C the reaction was quenched. Standard work-up gave *3-benzyloxy-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)propane* **6e** (1.6:1 ratio of diastereomers by ^{1}H nmr; 236.6 mg, 97%) as a colourless oil; ν_{max} (film) 3068, 3035, 2874, 1795, 1664, 1620, 1586, 1543, 1539, 1497, 1478, 1455, 1443, 1367, 1160, 1025, 913, 866, 771, 748, 697 cm^{-1}; δ_H (270 MHz) (major diastereomer) 7.51-7.25 (10H, m, PhS and Ph), 6.46 (1H, d, J 9 Hz, H-1), 5.33 (1H, m, H-2), 4.55 (2H, s, OCH_2Ph), 3.78 (2H, m, H-3); (minor diastereomer) 7.51-7.25 (10H, m, PhS and Ph), 6.45 (1H, d, J 5.5 Hz, H-1), 5.44 (1H, m, H-2), 4.55 (2H, s, OCH_2Ph), 3.92 (2H, dd, J 12.5, 4.5 Hz, H-3); *m/z* (EI) 482 (M^+), 110 (PhSH), 91 ($PhCH_2$) (Found: (M^+), 482.0624. $C_{20}H_{16}F_6O_5S$ requires (M^+), 482.0623).

Preparation of 2-phenyl-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane (6g): from (*E*)-1g.

To a stirred solution of (±)$_S$-(*E*)-2-phenyl-1-(phenylsulfinyl)ethene (*E*)-**1g** (107.3 mg, 0.47 mmol) in dry dichloromethane (1.5 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (100 µl, 0.71 mmol, 1.5 eq). The reaction was stirred at 0°C for 45 min and then TFAA (50 µl, 0.35 mmol, 0.5 eq) was added dropwise *via* syringe. After 15 min stirring at 0°C the reaction was quenched. Standard work-up gave *2-phenyl-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane* **6g** (6.3:1 ratio of diastereomers by ^{1}H nmr; 200.1 mg, 97%) as a colourless oil; ν_{max} (film) 3070, 1796, 1586, 1542, 1535, 1499, 1479, 1459, 1443, 1370, 1148, 1025, 1003, 934, 875, 791, 763, 748, 725, 697 cm^{-1}; δ_H (270 MHz) (major diastereomer) 7.49-7.30 (10H, m, PhS and Ph), 6.46 (1H, d, J 9 Hz, H-1), 6.06 (1H, d, J 9 Hz, H-2); (minor diastereomer) 7.49-7.30 (10H, m, PhS and Ph), 6.49 (1H, d, J 5 Hz, H-1), 6.09 (1H, d, J 5 Hz, H-2); *m/z* (EI) 438 (M^+), 325 (M^+ - $OCOCF_3$), 235, 207, 109 (PhS) (Found: (M^+), 438.0360. $C_{18}H_{12}F_6O_4S$ requires (M^+), 438.0361).

Preparation of 2-phenyl-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane (6g): from (*Z*)-1g.

To a stirred solution of (±)$_S$-(*Z*)-2-phenyl-1-(phenylsulfinyl)ethene (*Z*)-**1g** (300.0 mg, 1.31 mmol) in dry dichloromethane (1.4 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (186 µl, 1.31 mmol, 1 eq). The reaction was stirred at 0°C for 10 min and then TFAA (186 µl, 1.31 mmol, 1 eq) was added dropwise *via* syringe. After 15 min stirring at 0°C the reaction was quenched. Standard work-up gave -2-phenyl-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane **6g** (1:4 ratio of diastereomers by ^{1}H nmr; 550.2 mg, 96%) as a colourless oil; spectroscopic data were in agreement with the previously prepared compound.

Preparation of 1-(phenylsulfenyl)-2-(*p*-tolyl)-1,2-bis(trifluoroacetoxy)ethane (6h).

To a stirred solution of (±)$_S$-(*E*)-2-(*p*-tolyl)-1-(phenylsulfinyl)ethene (*E*)-**1h** and (±)$_S$-(*Z*)-2-(*p*-tolyl)-1-(phenylsulfinyl)ethene (*Z*)-**1h** (1:2.4 ratio by ^{1}H nmr; 100.8 mg, 0.42 mmol) in dry dichloromethane (2 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (88 µl, 0.62 mmol, 1.5 eq). After 60 min stirring at 0°C the reaction was quenched. Standard work-up gave *1-(phenylsulfenyl)-2-(p-tolyl)-1,2-bis(trifluoroacetoxy)ethane* **6h** (1.2:1 ratio of diastereomers by ^{1}H nmr; 182.4 mg, 97%) as a colourless oil; ν_{max} (film) 2929, 1792, 1653, 1617, 1586, 1539, 1518, 1478, 1443, 1368, 1231, 1142, 1025, 931, 870, 817, 774, 749, 724, 692 cm^{-1}; δ_H (270 MHz) (major diastereomer) 7.47-7.18 (9H, m, PhS and *o*- and *m*-protons on 4-MeAr), 6.46 (1H, d, J 7 Hz, H-1), 6.03 (1H, d, J 7 Hz, H-2), 2.36 (3H, s, MeAr); (minor diastereomer) 7.47-7.18 (9H, m, PhS and *o*- and *m*-protons on 4-MeAr), 6.45 (1H, d, J 9 Hz, H-1), 6.00 (1H, d, J 9 Hz, H-2), 2.40 (3H, s, MeAr); *m/z* (EI) 452 (M$^+$), 338 (M$^+$ - CF_3CO_2H), 235, 226, 217, 207, 105, 91 (Found: (M$^+$), 452.0517. $C_{19}H_{14}F_6O_4S$ requires (M$^+$), 452.0517).

Preparation of 2-(4-methoxyphenyl)-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane (6i).

To a stirred solution of (±)$_S$-(*E*)-2-(4-methoxyphenyl)-1-(phenylsulfinyl)ethene (*E*)-**1i** and (±)$_S$-(*Z*)-2-(4-methoxyphenyl)-1-(phenylsulfinyl)ethene (*Z*)-**1i** (2.8:1 ratio by ^{1}H nmr; 103.5 mg, 0.4 mmol) in dry dichloromethane (1.5 ml) at 0°C under argon was added, dropwise *via* syringe, TFAA (74 µl, 0.52 mmol, 1.3 eq). After 5 min stirring at 0°C the reaction was quenched. Standard work-up gave *2-(4-methoxyphenyl)-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane* **6i** (1:1 ratio of diastereomers by ^{1}H nmr; 181.6 mg, 97%) as a colourless oil; ν_{max} (film) 2966, 2843, 1795, 1655, 1613, 1588, 1540, 1517, 1478, 1443, 1371, 1309, 1153, 1034, 1002, 927, 832, 776, 749, 723, 692, 606 cm^{-1}; δ_H (270 MHz) (major diastereomer) 7.49-7.27 (7H, m, PhS and *o*-protons to MeO on 4-MeOAr), 6.98-6.90 (2H, m, *m*-protons to MeO on 4-MeOAr), 6.48 (1H, d, J 9 Hz, H-1), 6.00 (1H, d, J 9 Hz, H-2), 3.85 (3H, s, MeO); (minor diastereomer) 7.49-7.27 (7H, m, PhS, *o*-protons to MeO on 4-MeOAr), 6.98-6.90 (2H, m, *m*-protons to MeO on 4-MeOAr), 6.50 (1H, d, J 7 Hz, H-1), 6.06 (1H, d, J 7 Hz, H-2), 3.82 (3H, s, MeO); *m/z* (EI) 468 (M$^+$), 359 (M$^+$ - PhS), 354 (M$^+$ - CF_3CO_2H), 242, 233, 218 (Found: (M$^+$), 468.0466. $C_{19}H_{14}F_6O_5S$ requires (M$^+$), 468.0466).

Preparation of 2-(4-chlorophenyl)-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane (6j).

To a stirred solution of (±)$_S$-(*E*)-2-(4-chlorophenyl)-1-(phenylsulfinyl)ethene (*E*)-**1j** (75.2 mg, 0.29 mmol) in dry dichloromethane (1.5 ml) at 20°C under argon was added, dropwise *via* syringe, TFAA (81 µl, 0.57 mmol, 2 eq). After 45 min stirring at 20°C the reaction was quenched. Standard work-up gave *2-(4-chlorophenyl)-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane* **6j** (1.1:1 ratio of diastereomers by ^{1}H nmr; 130.3 mg, 96%) as a colourless oil; ν_{max} (film) 2937, 1793, 1655, 1599, 1543, 1491, 1440, 1412, 1367, 1336, 1300, 1228, 1147, 1093, 1070, 1017, 1001, 933, 874, 826, 788, 772, 748, 727, 692, 604 cm^{-1}; δ_H (270 MHz) (major diastereomer) 7.48-7.29 (9H, m, PhS and *o*- and *m*-protons on 4-ClAr), 6.44 (1H, d, J 9 Hz, H-1), 6.02 (1H, d, J 9 Hz, H-2); (minor diastereomer) 7.48-7.29 (9H, m, PhS and *o*- and *m*-protons on 4-ClAr), 6.48 (1H, d, J 7 Hz, H-1), 6.07 (1H, d, J 7 Hz, H-2); *m/z* (EI) 474, 472 (M$^+$), 360, 358 (M$^+$ - CF_3CO_2H), 235, 207, 109 (PhS) (Found: (M$^+$), 471.9970. $C_{18}H_{11}ClF_6O_4S$ requires (M$^+$), 471.9971).

Preparation of 2-(4-nitrophenyl)-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane (6k).

To a stirred solution of (±)$_S$-(*E*)-2-(4-nitrophenyl)-1-(phenylsulfinyl)ethene (*E*)-**1k** and (±)$_S$-(*Z*)-2-(4-nitrophenyl)-1-(phenylsulfinyl)ethene (*Z*)-**1k** (1:1.4 ratio by ^{1}H nmr; 70.4 mg, 0.26 mmol) in dry dichloromethane (1 ml) at 20°C under argon was added, dropwise *via* syringe, TFAA (73 µl, 0.52 mmol, 2 eq). After 6 h stirring at 20°C the reaction was quenched. Standard work-up gave *2-(4-nitrophenyl)-1-(phenylsulfenyl)-1,2-bis(trifluoroacetoxy)ethane* **6k** (1:1 ratio of diastereomers by ^{1}H nmr; 118.6 mg, 95%) as a pale yellow oil; ν_{max} (film) 3091, 2996, 2862, 1793, 1688, 1583, 1531, 1474, 1349, 1228, 1148, 1069, 1024, 1016, 1001, 936, 856, 826, 786, 771, 748, 725, 693 cm^{-1}; δ_H (270 MHz) (one diastereomer) 8.33-8.25 (2H, m, *o*-protons to NO_2 on 4-NO_2Ar), 7.67-7.55 (2H, m, *m*-protons to NO_2 on 4-NO_2Ar), 7.49-7.30 (5H, m, PhS), 6.51 (1H, d, J 7 Hz, H-1), 6.20 (1H, d, J 7 Hz, H-2); (one diastereomer) 8.33-8.25 (2H, m, *o*-protons to NO_2 on 4-NO_2Ar), 7.67-7.55 (2H, m, *m*-protons to NO_2 on 4-NO_2Ar), 7.49-7.30 (5H, m, PhS), 6.47 (1H, d, J 9 Hz, H-1), 6.15 (1H, d, J 9 Hz, H-2); *m/z* (EI) 483 (M^+), 370 (M^+ - $OCOCF_3$), 369 (M^+ - CF_3CO_2H), 257, 218, 207, 110 (PhSH), 109 (PhS) (Found: (M^+), 483.0210. $C_{18}H_{11}F_6NO_6S$ requires (M^+), 483.0211).

Preparation of methyl (*E*)-4-hydroxybut-2-enoate (13x).

To a stirred solution of 1,2-bis(trifluoroacetoxy)-1-(phenylsulfenyl)ethane **6x** (216.8 mg, 0.6 mmol) in dry dichloromethane (2 ml) at 0°C under argon was added MeOH (48 µl, 1.2 mmol, 2 eq) followed by triethylamine (8 µl, 0.06 mmol, 0.1 eq). After 5 min stirring at 0°C the solvents were removed under reduced pressure. Purification by chromatography (50%-90% ether–petrol) gave 2-hydroxyethanal **11x** (22.2 mg, 62%) as an inseparable mixture of monomeric and dimeric forms. Spectroscopic data for the mixture was complicated, showing signals corresponding to both forms, therefore its identity was further implied by its participation in a Wittig reaction as follows. To a stirred solution of hydroxyethanal **11x** (mixture of monomeric and dimeric forms; 10.3 mg, 0.17 mmol) in dry benzene (0.25 ml) at 100°C under argon was added, dropwise *via* syringe, a solution of methyl (triphenylphosphoranylidene)acetate (86 mg, 0.26 mmol, 1.5 eq) in dry benzene (0.75 ml). After stirring for 5 h at 100°C, the reaction was allowed to cool and the solvents were removed under reduced pressure. Purification by chromatography (65% ether–petrol) gave methyl (*E*)-4-hydroxybut-2-enoate **13x** (8.8 mg, 44%) as a colourless oil; ν_{max} (film) 3432, 3000, 2955, 2120, 1721, 1661, 1558, 1540, 1439, 1283, 1175, 1100, 1014, 960, 928, 835, 681 cm^{-1}; δ_H (270 MHz) 7.04 (1H, dt, J 15.5, 4 Hz, H-3), 6.11 (1H, dt, J 15.5, 2.5 Hz, H-2), 4.35 (2H, br m, H-4), 3.75 (3H, s, MeO), 1.87 (1H, br t, OH); *m/z* (EI) 117 (MH^+), 116 (M^+), 85 (M^+ - MeO).

Preparation of methyl 4-hydroxypent-2-enoate (13a).

Prepared according to the standard procedure described for **13x**. Purification by chromatography (75% ether–petrol and 60% ether–petrol respectively for the two steps) gave 2-hydroxypropanal **11a** (85%) and a mixture of methyl (*E*)-4-hydroxypent-2-enoate (*E*)-**13a** and methyl (*Z*)-4-hydroxypent-2-enoate (*Z*)-**13a** (40:1 ratio of *E*:*Z*; 84%) as a colourless oil; ν_{max} (film) 3434, 2976, 2114, 1721, 1656, 1558, 1436, 1274, 1176, 1048, 1011, 979, 947, 924, 865, 841, 717 cm^{-1}; δ_H (270 MHz) (*E*-isomer) 6.96 (1H, dd, J 16, 4.5 Hz,

H-3), 6.03 (1H, dd, J 16, 2.5 Hz, H-2), 4.48 (1H, br m, H-4), 3.74 (3H, s, MeO), 1.90 (1H, br s, OH), 1.32 (3H, d, J 7 Hz, H-5); *m/z* (EI) 131 (MH^+), 130 (M^+), 99 (M^+ - MeO), 87 (M^+ - CH_3CHOH).

Preparation of methyl (*E*)-4-hydroxydec-2-enoate (13b).

Prepared according to the standard procedure described for **13x**. Purification by chromatography (40%-50% ether–petrol and 30% ether–petrol respectively for the two steps) gave 2-hydroxyoctanal **11b** (84%) and methyl (*E*)-4-hydroxydec-2-enoate **13b** (77%) as a colourless oil; ν_{max} (film) 3424, 2927, 2859, 1727, 1660, 1571, 1539, 1509, 1436, 1277, 1170, 1042, 982, 928, 859, 723 cm^{-1}; δ_H (270 MHz) 6.96 (1H, dd, J 16, 4.5 Hz, H-3), 6.04 (1H, dd, J 16, 2.5 Hz, H-2), 4.31 (1H, br m, H-4), 3.74 (3H, s, MeO), 1.74 (1H, br s, OH), 1.58 (2H, m, H-5), 1.45-1.23 (8H, m, H-6, H-7, H-8 and H-9), 0.89 (3H, t, J 7 Hz, H-10); *m/z* (EI) 200 (M^+), 182 (M^+ - H_2O), 115 ($C_6H_{13}CHOH$).

Preparation of methyl (*E*)-4-hydroxy-5-methylhex-2-enoate (13c).

Prepared according to the standard procedure described for **13x**. Purification by chromatography (30%-50% ether–petrol and 40% ether–petrol respectively for the two steps) gave 2-hydroxy-3-methylbutanal **11c** (78%) and methyl (*E*)-4-hydroxy-5-methylhex-2-enoate **13c** (95%) as a colourless oil; ν_{max} (film) 3449, 2962, 1711, 1660, 1562, 1436, 1286, 1175, 1075, 1038, 987, 917, 871, 802, 734 cm^{-1}; δ_H (270 MHz) 6.97 (1H, dd, J 15.5, 4.5 Hz, H-3), 6.03 (1H, dd, J 15.5, 2 Hz, H-2), 4.09 (1H, br m, H-4), 3.73 (3H, s, MeO), 1.89 (1H, br s, OH), 1.82 (1H, d heptet, J 7, 2 Hz, H-5), 0.94 (3H, d, J 7 Hz, H-6), 0.93 (3H, d, J 7 Hz, H-6); *m/z* (EI) 158 (M^+), 127 (M^+ - MeO), 116, 115, 87, 84 (M^+ - Me_2CHCH_2OH).

Preparation of methyl (*E*)-5,5-dimethyl-4-hydroxyhex-2-enoate (13d).

Prepared according to the standard procedure described for **13x**. Purification by chromatography (10%-50% ether–petrol and 30% ether–petrol respectively for the two steps) gave *3,3-dimethyl-2-hydroxybutanal* **11d** (48%) and *methyl (*E*)-5,5-dimethyl-4-hydroxyhex-2-enoate* **13d** (69%) as a colourless oil; ν_{max} (film) 3443, 2961, 1778, 1694, 1650, 1543, 1438, 1392, 1362, 1278, 1199, 1172, 1113, 1019, 985, 929, 890, 851, 773, 694, 665 cm^{-1}; δ_H (270 MHz) 7.02 (1H, dd, J 16, 5.5 Hz, H-3), 6.03 (1H, dd, J 16, 2 Hz, H-2), 3.92 (1H, br d, H-4), 3.75 (3H, s, MeO), 1.90 (1H, br s, OH), 0.93 (9H, s, H-6); *m/z* (EI) 141 (M^+ - MeO), 125, 116 (M^+ - *t*-Bu), 57 (*t*-Bu) (Found: (M^+ - MeO), 141.0915. $C_8H_{13}O_2$ requires (M^+ - MeO), 141.0916).

Preparation of methyl 5-benzyloxy-4-hydroxypent-2-enoate (13e).

Prepared according to the standard procedure described for **13x**. Purification by chromatography (50%-100% ether–petrol and 50% ether–petrol respectively for the two steps) gave *3-benzyloxy-2-hydroxypropanal* **11e** (87%) and a mixture of *methyl (*E*)-5-benzyloxy-4-hydroxypent-2-enoate* (*E*)-**13e** and *methyl (Z)-5-benzyloxy-4-hydroxypent-2-enoate* (*Z*)-**13e** (17:1 ratio of *E*:*Z*; 87%) as a colourless oil; ν_{max} (film) 3441, 3031, 2861, 2116, 1960, 1884, 1722, 1660, 1496, 1438, 1274, 927, 860, 820, 741, 699, 666 cm^{-1}; δ_H (270

MHz) (*E*-isomer) 7.40-7.28 (5H, m, Ph), 6.90 (1H, dd, J 16, 4.5 Hz, H-3), 6.17 (1H, dd, J 16, 2.5 Hz, H-2), 4.56 (2H, s, OCH_2Ph), 4.51 (1H, br m, H-4), 3.73 (3H, s, MeO), 3.61 (1H, ABX, J 9, 4 Hz, H-5), 3.39 (1H, ABX, J 9, 8 Hz, H-5), 2.82 (1H, br d, OH); *m/z* (EI) 218 ($M^+ - H_2O$), 206 ($M^+ - CH_2O$), 175 ($M^+ - CH_2O$, MeO), 145 ($M^+ - PhCH_2$), 115 ($M^+ - PhCH_2OCH_2$), 91 ($PhCH_2$) (Found: ($M^+ - CH_2O$), 206.0943. $C_{12}H_{14}O_3$ requires ($M^+ - CH_2O$), 206.0943).

Preparation of 2-hydroxy-1-phenylethanone (12g).

To a stirred solution of 1,2-bis(trifluoroacetoxy)-2-phenyl-1-(phenylsulfenyl)ethane **6g** (70.9 mg, 0.16 mmol) in dry dichloromethane (1 ml) at 20°C under argon was added MeOH (14 ml, 0.36 mmol, 2.2 eq) followed by triethylamine (25 ml, 0.18 mmol, 1.1 eq). The reaction was allowed to stir at 20°C for 12 h and then dichloromethane (20 ml) was added. The organic layer was washed with 2M HCl (5 ml), saturated aqueous sodium hydrogencarbonate (10 ml) and dried over $MgSO_4$. The solvents were removed under reduced pressure to give the crude product as a yellow oil. Purification by chromatography (10%-40% ether–petrol) gave 2-hydroxy-1-phenylethanone **12g** (15.9 mg, 72%) as a colourless solid, mp 89-90°C (lit.[42] mp 86-87°C); ν_{max} (Nujol) 3387, 2956, 2925, 2855, 1681, 1598, 1554, 1533, 1464, 1378, 1236, 1109, 753, 688 cm^{-1}; δ_H (270 MHz) 7.95-7.90 (2H, m, *o*-protons on Ph), 7.70 (3H, m, *m*- and *p*-protons on Ph), 4.90 (2H, br d, J 5 Hz, H-2), 3.50 (1H, br t, J 5 Hz, OH).

Preparation of 2-hydroxy-1-(*p*-tolyl)ethanone (12h).

Prepared according to the standard procedure described for **12g**. Purification by chromatography (10%-50% ether–petrol) gave 2-hydroxy-1-(*p*-tolyl)ethanone **12h** (83%) as a colourless solid, mp 104-105°C (lit.[42] mp 105-106°C); ν_{max} (Nujol) 2921 (br), 1675, 1612, 1577, 1510, 1420, 1285, 1183, 1117, 962, 839, 755 cm^{-1}; δ_H (270 MHz) 7.83 (2H, d, J 8 Hz, *m*-protons to Me on 4-MeAr), 7.31 (2H, d, J 8 Hz, *o*-protons to Me on 4-MeAr), 4.86 (2H, d, J 4.5 Hz, H-2), 3.54 (1H, t, J 4.5 Hz, OH), 2.45 (3H, s, MeAr).

Preparation of 2-hydroxy-1-(4-methoxyphenyl)ethanone (12i).

Prepared according to the standard procedure described for **12g**. Purification by chromatography (10%-50% ether–petrol) gave 2-hydroxy-1-(4-methoxyphenyl)ethanone **12i** (79%) as a colourless solid, mp 106°C (lit.[43] mp 105-106°C); ν_{max} (Nujol) 3384, 2925, 2853, 1672, 1605, 1578, 1514, 1463, 1427, 1378, 1296, 1250, 1186, 1111, 1030, 1009, 980, 836, 823 cm^{-1}; δ_H (270 MHz) 7.90 (2H, d, J 9 Hz, *m*-protons to MeO on 4-MeOAr), 6.97 (2H, d, J 9 Hz, *o*-protons to MeO on 4-MeOAr), 4.82 (2H, d, J 4.5 Hz, H-2), 3.88 (3H, s, MeO), 3.58 (1H, t, J 4.5 Hz, OH).

Preparation of 2-hydroxy-1-(4-chlorophenyl)ethanone (12j).

Prepared according to the standard procedure described for **12g**. Purification by chromatography (20%-50% ether–petrol) gave 2-hydroxy-1-(4-chlorophenyl)ethanone **12j** (89%) as a colourless solid, mp 120-122°C (lit.[42] mp 121-122°C); ν_{max} (Nujol) 3423, 2924, 2854, 1738, 1679, 1592, 1491, 1412, 1284, 1233, 1113,

1093, 980, 826, 806 cm^{-1}; δ_H (270 MHz) 7.86 (2H, d, J 8 Hz, *m*-protons to Cl on 4-ClAr), 7.47 (2H, d, J 8 Hz, *o*-protons to Cl on 4-ClAr), 4.84 (2H, s, H-2), 3.49 (1H, br s, OH).

Preparation of 2-hydroxy-1-(4-nitrophenyl)ethanone (12k).

Prepared according to the standard procedure described for **12g**. Purification by chromatography (20%-100% ether–petrol) gave 2-hydroxy-1-(4-nitrophenyl)ethanone **12k** (53%) as a yellow solid; ^1H nmr analysis of the product indicated the presence of additional 1,4-disubstituted aromatic species (*ca.* 10% by integration) which were not identified; ν_{max} (Nujol) 3389, 2923, 1682, 1597, 1511, 1447, 1407, 1377, 1340, 1300, 1236, 1109, 1078, 975, 921, 805, 753, 688 cm^{-1}; δ_H (270 MHz) 8.37 (2H, d, J 9 Hz, *o*-protons to NO_2 on 4-NO_2Ar), 8.10 (2H, d, J 9 Hz, *m*-protons to NO_2 on 4-NO_2Ar), 4.94 (2H, s, H-2), 3.39 (1H, br s, OH).

Preparation of 1,1-diacetoxy-2-phenyl-2-(phenylsulfenyl)ethane (14g).

To a stirred suspension of (±)$_S$-(Z)-2-phenyl-1-(phenylsulfinyl)ethene (Z)-**1g** (30.9 mg, 0.14 mmol) and sodium acetate (33 mg, 0.41 mmol, 3 eq) in acetic anhydride (677 µl; 0.2M) at 0°C under argon was added, dropwise *via* syringe, trifluoromethanesulfonic anhydride (23 µl, 0.14 mmol, 1 eq). The reaction was stirred at 0°C for 10 min and then trifluoromethanesulfonic anhydride (11 µl, 0.07 mmol, 0.5 eq) was added dropwise *via* syringe. After 5 min stirring at 0°C the reaction was quenched by the addition of saturated aqueous sodium hydrogencarbonate (10 ml). The aqueous layer was extracted with dichloromethane (2 x 10 ml). The combined organic layers were washed with saturated aqueous sodium hydrogencarbonate (2 x 10 ml), dried over $MgSO_4$ and the solvents removed under reduced pressure to give a brown oil. Chromatography (20% ether–petrol) gave *1,1-diacetoxy-2-phenyl-2-(phenylsulfenyl)ethane* **14g** (38 mg, 85%) as a colourless oil; ν_{max} (film) 2923, 1765, 1581, 1437, 1372, 1235, 1009, 747, 700 cm^{-1}; δ_H (270 MHz) 7.40-7.21 (10H, m, PhS and Ph), 7.16 (1H, d, J 6 Hz, H-1), 4.53 (1H, d, J 6 Hz, H-2), 1.95 (6H, s, 2 x $OCOCH_3$); *m/z* (EI) 330 (M^+), 270 (M^+ - AcOH), 228 (M^+ - Ac_2O), 221 (M^+ - PhS), 211 (M^+ - AcOH, AcO), 199 (M^+ - AcOCHOAc), 119, 110 (PhSH), 91 ($PhCH_2$) (Found: C, 65.89; H, 5.42. $C_{18}H_{18}O_4S$ requires C, 65.44; H, 5.49%).

Preparation of 1,1-diacetoxy-2-(*p*-tolyl)-2-(phenylsulfenyl)ethane (14h).

To a stirred suspension of (±)$_S$-(*E*)-2-(*p*-tolyl)-1-(phenylsulfinyl)ethene (*E*)-**1h** and (±)$_S$-(*Z*)-2-(*p*-tolyl)-1-(phenylsulfinyl)ethene (*Z*)-**1h** (1:3.3 ratio by ^1H nmr; 31.6 mg, 0.13 mmol) and sodium acetate (32 mg, 0.39 mmol, 3 eq) in acetic anhydride (652 µl; 0.2M) at 0°C under argon was added, dropwise *via* syringe, trifluoromethanesulfonic anhydride (22 µl, 0.13 mmol, 1 eq). The reaction was stirred at 0°C for 10 min and then trifluoromethanesulfonic anhydride (11 µl, 0.07 mmol, 0.5 eq) was added dropwise *via* syringe. After 5 min stirring at 0°C the reaction was quenched. Standard work-up followed by chromatography (20% ether–petrol) gave *1,1-diacetoxy-2-(p-tolyl)-2-(phenylsulfenyl)ethane* **14h** (36 mg, 80%) as a colourless oil; ν_{max} (film) 3055, 2922, 1773, 1698, 1685, 1663, 1649, 1583, 1540, 1515, 1508, 1482, 1472, 1458, 1440, 1375, 1233, 1098, 1009, 822, 740, 691 cm^{-1}; δ_H (270 MHz) 7.38 (2H, m, *o*-protons on PhS), 7.29-7.21 (5H, m, *m*- and *p*-protons on PhS and *m*-protons to Me on 4-MeAr), 7.15-7.10 (3H, m, *o*-protons to Me on 4-MeAr and H-1), 4.52 (1H, d, J 5 Hz, H-2), 2.32 (3H, s, MeAr), 1.97 (3H, s, $OCOCH_3$), 1.95 (3H, s,

$OCOCH_3$); *m/z* (EI) 344 (M^+), 284 (M^+ - AcOH), 242 (M^+ - Ac_2O), 235 (M^+ - PhS), 225 (M^+ - AcOH, AcO), 213 (M^+ - AcOCHOAc), 133, 109 (PhS), 105, 91 ($PhCH_2$) (Found: C, 66.01; H, 5.96. $C_{19}H_{20}O_4S$ requires C, 66.26; H, 5.85%).

Preparation of 1,1-diacetoxy-2-(4-chlorophenyl)-2-(phenylsulfenyl)ethane (14j).

To a stirred suspension of (±)$_S$-(*Z*)-2-(4-chlorophenyl)-1-(phenylsulfinyl)ethene (*Z*)-**1j** (37.4 mg, 0.14 mmol) and sodium acetate (23 mg, 0.28 mmol, 2 eq) in acetic anhydride (712 µl; 0.2M) at 0°C under argon was added, dropwise *via* syringe, trifluoromethanesulfonic anhydride (24 µl, 0.14 mmol, 1 eq). The reaction was stirred at 0°C for 10 min and then trifluoromethanesulfonic anhydride (12 µl, 0.07 mmol, 0.5 eq) was added dropwise *via* syringe. After 5 min stirring at 0°C the reaction was quenched. Standard work-up followed by chromatography (20% ether–petrol) gave *1,1-diacetoxy-2-(4-chlorophenyl)-2-(phenylsulfenyl)ethane* **14j** (43.9 mg, 85%) as a colourless oil; ν_{max} (film) 3027, 2928, 1769, 1651, 1584, 1554, 1521, 1511, 1493, 1439, 1410, 1375, 1235, 1197, 1090, 1012, 830, 743, 691 cm^{-1}; δ_H (270 MHz) 7.37-7.21 (9H, m, PhS and *o*- and *m*-protons on 4-ClAr), 7.12 (1H, d, J 5 Hz, H-1), 4.48 (1H, d, J 5 Hz, H-2), 1.99 (3H, s, $OCOCH_3$), 1.97 (3H, s, $OCOCH_3$); *m/z* (EI) 366, 364 (M^+), 306, 304 (M^+ - AcOH), 264, 262 (M^+ - Ac_2O), 257, 255 (M^+ - PhS), 247, 245 (M^+ - AcOH, AcO), 235, 233 (M^+ - AcOCHOAc), 197, 155, 153, 127, 125, 110 (PhSH), 109 (PhS) (Found: C, 59.00; H, 4.61. $C_{18}H_{17}ClO_4S$ requires C, 59.26; H, 4.70%).

Preparation of 1,1-diacetoxy-2-(3-methoxyphenyl)-2-(phenylsulfenyl)ethane (14m).

To a stirred suspension of (±)$_S$-(*E*)-2-(3-methoxyphenyl)-1-(phenylsulfinyl)ethene (*E*)-**1m** and (±)$_S$-(*Z*)-2-(3-methoxyphenyl)-1-(phenylsulfinyl)ethene (*Z*)-**1m** (1:9 ratio by ^1H nmr; 23.7 mg, 0.09 mmol) and sodium acetate (15 mg, 0.18 mmol, 2 eq) in acetic anhydride (459 µl; 0.2M) at 0°C under argon was added, dropwise *via* syringe, trifluoromethanesulfonic anhydride (15 µl, 0.09 mmol, 1 eq). The reaction was stirred at 0°C for 10 min and then trifluoromethanesulfonic anhydride (8 µl, 0.05 mmol, 0.5 eq) was added dropwise *via* syringe. After 5 min stirring at 0°C the reaction was quenched. Standard work-up followed by chromatography (20% ether–petrol) gave *1,1-diacetoxy-2-(3-methoxyphenyl)-2-(phenylsulfenyl)ethane* **14m** (9.1 mg, 28%) as a colourless oil; ν_{max} (film) 3064, 2922, 1770, 1697, 1684, 1676, 1654, 1650, 1645, 1602, 1588, 1557, 1540, 1534, 1519, 1511, 1506, 1493, 1465, 1458, 1437, 1374, 1316, 1234, 1201, 1110, 1045, 1009, 923, 883, 776, 743, 693 cm^{-1}; δ_H (270 MHz) 7.40-7.35 (2H, m, *o*-protons on PhS), 7.28-7.22 (4H, m, *m*- and *p*-protons on PhS and *m*-proton to MeO on 3-MeOAr), 7.14 (1H, d, J 8 Hz, H-1), 4.48 (1H, d, J 8 Hz, H-2), 3.77 (3H, s, MeO), 1.95 (3H, s, $OCOCH_3$), 1.93 (3H, s, $OCOCH_3$); *m/z* (EI) 360 (M^+), 300 (M^+ - AcOH), 258 (M^+ - Ac_2O), 251 (M^+ - PhS), 241 (M^+ - AcOH, AcO), 229 (M^+ - AcOCHOAc), 149, 110 (PhSH), 91 ($PhCH_2$), 43 (CH_3CO).

Preparation of 1,1-diacetoxy-2-methyl-2-(phenylsulfenyl)propane (14a).

To a stirred suspension of (±)$_S$-2-methyl-1-(phenylsulfinyl)prop-1-ene **3a** (17.9 mg, 0.1 mmol) and sodium acetate (16 mg, 0.2 mmol, 2 eq) in acetic anhydride (494 µl; 0.2M) at 20°C under argon was added, dropwise *via* syringe, trifluoromethanesulfonic anhydride (17 µl, 0.1 mmol, 1 eq). The reaction was stirred at

20°C for 10 min and then trifluoromethanesulfonic anhydride (17 µl, 0.1 mmol, 1 eq) was added dropwise *via* syringe. After 5 min stirring at 20°C the reaction was quenched. Standard work-up followed by chromatography (20% ether–petrol) gave *1,1-diacetoxy-2-methyl-2-(phenylsulfenyl)propane* **14a** (16.9 mg, 60%) as a colourless oil; ν_{max} (film) 3063, 2981, 2935, 2873, 1762, 1585, 1574, 1558, 1541, 1477, 1440, 1371, 1208, 1138, 1075, 1004, 923, 754, 706, 695 cm^{-1}; δ_H (270 MHz) 7.58 (2H, m, *o*-protons on PhS), 7.41-7.29 (3H, m, *m*- and *p*-protons on PhS), 6.84 (1H, s, H-1), 2.05 (6H, s, 2 x $OCOCH_3$), 1.27 (6H, s, H-3); *m/z* (EI) 282 (M^+), 223 (M^+ - AcO), 181 (MH^+ - Ac_2O), 173 (M^+ - PhS), 163 (M^+ - AcOH, AcO), 151 (M^+ - AcOCHOAc), 131, 110 (PhSH), 109 (PhS) (Found: C, 59.48; H, 6.37. $C_{14}H_{18}O_4S$ requires C, 59.55; H, 6.43%).

Preparation of 1,1-diacetoxy-2-methyl-2-(phenylsulfenyl)butane (14b).

To a stirred suspension of (±)$_S$-(*E*)-2-methyl-1-(phenylsulfinyl)but-1-ene (*E*)-**3b** and (±)$_S$-(*Z*)-2-methyl-1-(phenylsulfinyl)but-1-ene (*Z*)-**3b** (1.1:1 ratio by ^1H nmr; 38.3 mg, 0.2 mmol) and sodium acetate (32 mg, 0.39 mmol, 2 eq) in acetic anhydride (986 µl; 0.2M) at 20°C under argon was added, dropwise *via* syringe, trifluoromethanesulfonic anhydride (41 µl, 0.25 mmol, 1.25 eq). After 5 min stirring at 20°C the reaction was quenched. Standard work-up followed by chromatography (20% ether–petrol) gave *1,1-diacetoxy-2-methyl-2-(phenylsulfenyl)butane* **14b** (36.2 mg, 62%) as a colourless oil; ν_{max} (film) 3058, 2976, 2939, 2882, 1765, 1583, 1573, 1474, 1439, 1372, 1237, 1008, 788, 752, 705, 694, 665 cm^{-1}; δ_H (270 MHz) 7.59 (2H, m, *o*-protons on PhS), 7.40-7.27 (3H, m, *m*- and *p*-protons on PhS), 6.89 (1H, s, H-1), 2.03 (3H, s, $OCOCH_3$), 2.02 (3H, s, $OCOCH_3$), 1.64 (2H, q, J 7 Hz, H-3), 1.14 (3H, s, 2-Me), 1.09 (3H, t, J 7 Hz, H-4); *m/z* (EI) 296 (M^+), 237 (M^+ - AcO), 236 (M^+ - AcOH), 195 (MH^+ - Ac_2O), 194 (M^+ - Ac_2O), 187 (M^+ - PhS), 178 (M^+ - AcO, AcO), 165 (M^+ - AcOCHOAc), 145, 123, 110 (PhSH), 109 (PhS) (Found: C, 60.92; H, 6.91. $C_{15}H_{20}O_4S$ requires C, 60.79; H, 6.80%).

Preparation of 1-(diacetoxymethyl)-1-(phenylsulfenyl)cyclopentane (14c).

To a stirred suspension of (±)$_S$-cyclopentylidene(phenylsulfinyl)methane **3c** (32.5 mg, 0.16 mmol) and sodium acetate (26 mg, 0.32 mmol, 2 eq) in acetic anhydride (788 µl; 0.2M) at 0°C under argon was added, dropwise *via* syringe, trifluoromethanesulfonic anhydride (27 µl, 0.16 mmol, 1 eq). The reaction was stirred at 0°C for 10 min and then trifluoromethanesulfonic anhydride (27 µl, 0.16 mmol, 1 eq) was added dropwise *via* syringe. During the addition of the anhydride, a purple colour appeared which slowly faded to yellow. The purple colour persisted when the addition was complete. After 5 min stirring at 0°C the reaction was quenched. Standard work-up followed by chromatography (20% ether–petrol) gave *1-(diacetoxymethyl)-1-(phenylsulfenyl)cyclopentane* **14c** (32 mg, 66%) as a colourless oil; ν_{max} (film) 3058, 2962, 2870, 1765, 1695, 1683, 1653, 1623, 1576, 1552, 1533, 1505, 1476, 1439, 1375, 1309, 1238, 1008, 753, 694 cm^{-1}; δ_H (270 MHz) 7.60 (2H, m, *o*-protons on PhS), 7.36-7.27 (3H, m, *m*- and *p*-protons on PhS), 6.97 (1H, s, AcOCHOAc), 2.12-1.86 (4H, m), 1.86-1.63 (4H, m), 2.03 (6H, s, 2 x $OCOCH_3$); *m/z* (EI) 308 (M^+), 249 (M^+ - AcO), 207 (MH^+ - Ac_2O), 199 (M^+ - PhS), 190 (M^+ - AcO, AcO), 189 (M^+ - AcOH, AcO), 177 (M^+ - AcOCHOAc), 157, 139, 110 (PhSH) (Found: C, 61.99; H, 6.35. $C_{16}H_{20}O_4S$ requires C, 62.32; H, 6.54%).

Preparation of 1-(diacetoxymethyl)-1-(phenylsulfenyl)cyclohexane (14d).

To a stirred suspension of (±)S-cyclohexylidene(phenylsulfinyl)methane **3d** (26.8 mg, 0.12 mmol) and sodium acetate (20 mg, 0.24 mmol, 2 eq) in acetic anhydride (608 µl; 0.2M) at 0°C under argon was added, dropwise *via* syringe, trifluoromethanesulfonic anhydride (20 µl, 0.16 mmol, 1 eq). During the addition of the anhydride, a purple colour appeared which slowly faded to yellow. The purple colour persisted when the addition was complete. After 5 min stirring at 0°C the reaction was quenched. Standard work-up followed by chromatography (20% ether–petrol) gave *1-(diacetoxymethyl)-1-(phenylsulfenyl)cyclohexane* **14d** (30.9 mg, 79%) as a colourless oil; ν_{max} (film) 3059, 2937, 2859, 1765, 1583, 1572, 1475, 1439, 1371, 1202, 1121, 1081, 1010, 913, 875, 850, 753, 705, 694, 663 cm^{-1}; δ_H (270 MHz) 7.62 (2H, m, *o*-protons on PhS), 7.36-7.28 (3H, m, *m*- and *p*-protons on PhS), 6.86 (1H, s, AcOCHOAc), 2.08-1.47 (8H, m), 2.00 (6H, s, 2 x $OCOCH_3$), 1.32-1.15 (2H, m); *m/z* (EI) 322 (M^+), 263 (M^+ - AcO), 221 (MH^+ - Ac_2O), 220 (M^+ - Ac_2O), 213 (M^+ - PhS), 204 (M^+ - AcO, AcO), 203 (M^+ - AcOH, AcO), 202 (M^+ - AcOH, AcOH), 191 (M^+ - AcOCHOAc), 171, 153, 123, 111, 110 (PhSH) (Found: C, 63.11; H, 6.95. $C_{17}H_{22}O_4S$ requires C, 63.33; H, 6.88%).

Preparation of 2-phenyl-2-(phenylsulfenyl)ethanal (15g).

To a stirred solution of 1,1-diacetoxy-2-phenyl-2-(phenylsulfenyl)ethane **14g** (80.2 mg, 0.24 mmol) in dry methanol (2.43 ml; 0.1M) at 20°C was added solid potassium carbonate (168 mg, 1.21 mmol, 5 eq). The reaction was allowed to stir at 20°C for 15 min and was then brought to pH 7 by the addition of saturated aqueous ammonium chloride. The aqueous layer was extracted with dichloromethane (2 x 10 ml). The combined organic layers were washed with water (5 ml), brine (5 ml), dried over $MgSO_4$ and the solvents were removed under reduced pressure to give the crude product as a pale yellow oil. Purification by chromatography (10% ether–petrol) gave 2-phenyl-2-(phenylsulfenyl)ethanal **15g** (36 mg, 65%) as a colourless oil; ν_{max} (film) 3061, 2825, 1792, 1721, 1642, 1600, 1583, 1547, 1482, 1453, 1440, 1376, 1278, 1175, 1078, 1025, 1002, 928, 839, 746 cm^{-1}; δ_H (270 MHz) 9.55 (1H, d, J 5 Hz, CHO), 7.55-7.20 (10H, m, PhS and Ph), 4.72 (1H, d, J 5 Hz, H-2); *m/z* (EI) 228 (M^+), 199 (M^+ - CHO), 184, 165, 121, 110 (PhSH), 109 (PhS), 91 ($PhCH_2$) (Found: (M^+), 228.0612. $C_{14}H_{12}OS$ requires (M^+), 228.0609).

Preparation of 2-(*p*-tolyl)-2-(phenylsulfenyl)ethanal (15h).

Prepared according to the standard procedure described for **15g**. Purification by chromatography (10% ether–petrol) gave *2-(*p*-tolyl)-2-(phenylsulfenyl)ethanal* **15h** (65%) as a colourless oil; ν_{max} (film) 3058, 2921, 2824, 1718, 1684, 1655, 1629, 1608, 1584, 1555, 1539, 1513, 1482, 1441, 1414, 1379, 1277, 1182, 1112, 1089, 1070, 1025, 1000, 904, 816, 787, 744, 691 cm^{-1}; δ_H (270 MHz) 9.53 (1H, d, J 4.5 Hz, CHO), 7.46-7.17 (9H, m, PhS and *o*- and *m*-protons on 4-MeAr), 4.70 (1H, d, J 4.5 Hz, H-2), 2.36 (3H, s, MeAr); *m/z* (EI) 242 (M^+), 218, 213 (M^+ - CHO), 185, 133 (M^+ - PhS), 119, 110 (PhSH), 109 (PhS), 91 ($PhCH_2$) (Found: (M^+), 242.0765. $C_{15}H_{14}OS$ requires (M^+), 242.0765).

Preparation of 2-(4-chlorophenyl)-2-(phenylsulfenyl)ethanal (15j).

Prepared according to the standard procedure described for **15g**. Purification by chromatography (10% ether–petrol) gave *2-(4-chlorophenyl)-2-(phenylsulfenyl)ethanal* **15j** (64%) as a colourless oil; ν_{max} (film) 3062, 2922, 2818, 1722, 1683, 1652, 1624, 1589, 1558, 1493, 1439, 1409, 1286, 1209, 1179, 1093, 1025, 1015, 825, 745, 691 cm^{-1}; δ_H (270 MHz) 9.55 (1H, d, J 4.5 Hz, CHO), 7.46-7.20 (9H, m, PhS and *o*- and *m*-protons on 4-ClAr), 4.70 (1H, d, J 4.5 Hz, H-2); *m/z* (EI) 264, 262 (M^+), 235, 233 (M^+ - CHO), 218, 197, 155, 153 (M^+ - PhS), 141, 139, 127, 125, 110 (PhSH), 109 (PhS) (Found: (M^+), 262.0219. $C_{14}H_{11}ClOS$ requires (M^+), 262.0219).

Preparation of 2-methyl-2-(phenylsulfenyl)propanal (15a).

Prepared according to the standard procedure described for **15g**. Purification by chromatography (10% ether–petrol) gave 2-methyl-2-(phenylsulfenyl)propanal **15a** (75%) as a colourless oil; ν_{max} (film) 3058, 2965, 2933, 2870, 1718, 1583, 1473, 1450, 1439, 1385, 1335, 1306, 1275, 1210, 1145, 1109, 1068, 1025, 909, 750, 691 cm^{-1}; δ_H (270 MHz) 9.36 (1H, s, CHO), 7.32-7.26 (5H, m, PhS), 1.32 (6H, s, H-3); *m/z* (EI) 180 (M^+), 151 (M^+ - CHO), 123, 117, 110 (PhSH), 109 (PhS).

Preparation of 2-methyl-2-(phenylsulfenyl)butanal (15b).

Prepared according to the standard procedure described for **15g**. Purification by chromatography (5% ether–petrol) gave 2-methyl-2-(phenylsulfenyl)butanal **15b** (82%) as a colourless oil; ν_{max} (film) 3059, 2971, 2931, 2879, 2804, 2709, 1720, 1583, 1474, 1454, 1439, 1386, 1306, 1205, 1103, 1069, 1025, 904, 750, 692, 665 cm^{-1}; δ_H (270 MHz) 9.34 (1H, s, CHO), 7.41-7.27 (5H, m, PhS), 1.77 (1H, dq, J 14.5, 7 Hz, H-3), 1.66 (1H, dq, J 14.5, 7.5 Hz, H-3), 1.25 (3H, s, 2-Me), 1.00 (3H, dd, J 7.5, 7 Hz, H-4); *m/z* (EI) 194 (M^+), 165 (M^+ - CHO), 123, 110 (PhSH), 109 (PhS).

Preparation of 1-(phenylsulfenyl)cyclopentanecarbaldehyde (15c).

Prepared according to the standard procedure described for **15g**. Purification by chromatography (10% ether–petrol) gave 1-(phenylsulfenyl)cyclopentanecarbaldehyde **15c** (85%) as a colourless oil; ν_{max} (film) 3060, 2953, 2872, 2804, 2715, 1717, 1681, 1620, 1585, 1561, 1539, 1476, 1440, 1307, 1069, 1026, 750, 693 cm^{-1}; δ_H (270 MHz) 9.47 (1H, s, CHO), 7.41-7.25 (5H, m, PhS), 2.18-2.05 (2H, m), 1.96-1.57 (6H, m); *m/z* (EI) 206 (M^+), 177 (M^+ - CHO), 123, 110 (PhSH), 109 (PhS).

Preparation of 1-(phenylsulfenyl)cyclohexanecarbaldehyde (15d).

Prepared according to the standard procedure described for **15g**. Purification by chromatography (5% ether–petrol) gave 1-(phenylsulfenyl)cyclohexanecarbaldehyde **15d** (85%) as a colourless oil; ν_{max} (film) 3058, 2932, 2855, 2800, 2704, 1713, 1583, 1574, 1473, 1439, 1335, 1294, 1273, 1252, 1212, 1163, 1140, 1111, 1068, 1042, 1025, 977, 955, 928, 832, 750, 704, 692 cm^{-1}; δ_H (270 MHz) 9.26 (1H, s, CHO), 7.41-7.26 (5H, m, PhS), 1.90-1.25 (10H, m); *m/z* (EI) 220 (M^+), 191 (M^+ - CHO), 123, 110 (PhSH), 109 (PhS), 81.

Preparation of 2-phenyl-2-(phenylsulfenyl)ethanol (16g).

To a stirred solution of 1,1-diacetoxy-2-phenyl-2-(phenylsulfenyl)ethane **14g** (38.5 mg, 0.12 mmol) in a mixture of propan-2-ol and dimethoxyethane (1:1; 1.165 ml; 0.1M) at 20°C was added sodium borohydride (22 mg, 0.58 mmol, 5 eq). The reaction was allowed to stir at 20°C for 12 h and was then quenched by the addition of methanol (1 ml). Water (5 ml) was added to the mixture and the aqueous layer was extracted with dichloromethane (2 x 10 ml). The combined organic layers were dried over $MgSO_4$ and the solvents were removed under reduced pressure to give the crude product as a colourless oily solid. Purification by chromatography (20% ether–petrol) gave *2-phenyl-2-(phenylsulfenyl)ethanol* **16g** (22.1 mg, 82%) as a colourless oil; ν_{max} (film) 3382, 3059, 2932, 1733, 1661, 1583, 1555, 1541, 1524, 1481, 1452, 1439, 1171, 1055, 1024, 746, 694 cm^{-1}; δ_H (270 MHz) 7.38-7.22 (10H, m, PhS and Ph), 4.32 (1H, t, J 6 Hz, H-2), 3.92 (2H, br m, H-1), 2.08 (1H, br t, OH); *m/z* (EI) 230 (M^+), 199 (M^+ - CH_2OH), 184, 165, 121 (M^+ - PhS), 120, 110 (PhSH), 103, 91 ($PhCH_2$) (Found: (M^+), 230.0765. $C_{14}H_{14}OS$ requires (M^+), 230.0765).

Preparation of 2-(*p*-tolyl)-2-(phenylsulfenyl)ethanol (16h).

Prepared according to the standard procedure described for **16g**. Purification by chromatography (25% ether–petrol) gave *2-(p-tolyl)-2-(phenylsulfenyl)ethanol* **16h** (85%) as a colourless oil; ν_{max} (film) 3366, 3058, 2922, 1613, 1584, 1556, 1513, 1478, 1438, 1379, 1181, 1059, 1022, 815, 742, 692 cm^{-1}; δ_H (270 MHz) 7.36 (2H, m, *o*-protons on PhS), 7.29-7.10 (7H, m, *m*- and *p*-protons on PhS and *o*- and *m*-protons on 4-MeAr), 4.30 (1H, t, J 7 Hz, H-2), 3.90 (2H, br m, H-1), 2.34 (3H, s, MeAr), 2.00 (1H, br t, OH); *m/z* (EI) 244 (M^+), 213 (M^+ - CH_2OH), 197, 165, 149, 135 (M^+ - PhS), 117, 110 (PhSH), 105, 91 ($PhCH_2$) (Found: (M^+), 244.0922. $C_{15}H_{16}OS$ requires (M^+), 244.0920).

Preparation of 2-(4-chlorophenyl)-2-(phenylsulfenyl)ethanol (16j).

Prepared according to the standard procedure described for **16g**. Purification by chromatography (25% ether–petrol) gave *2-(4-chlorophenyl)-2-(phenylsulfenyl)ethanol* **16j** (94%) as a colourless oil; ν_{max} (film) 3401, 3060, 2930, 1691, 1684, 1655, 1638, 1625, 1620, 1585, 1560, 1541, 1492, 1440, 1408, 1282, 1183, 1092, 1059, 1015, 827, 794, 743, 720, 692 cm^{-1}; δ_H (270 MHz) 7.35-7.20 (9H, m, PhS and *o*- and *m*-protons on 4-ClAr), 4.29 (1H, t, J 6.5 Hz, H-2), 3.89 (2H, br d, H-1), 2.08 (1H, br s, OH); *m/z* (EI) 266, 264 (M^+), 235, 233 (M^+ - CH_2OH), 157, 155 (M^+ - PhS), 156, 154 (M^+ - PhSH), 127, 125 (M^+ - PhSH, CHO), 110 (PhSH) (Found: (M^+), 264.0376. $C_{14}H_{13}ClOS$ requires (M^+), 264.0376).

Preparation of 2-methyl-2-(phenylsulfenyl)propan-1-ol (16a).

Prepared according to the standard procedure described for **16g**. Purification by chromatography (20% ether–petrol) gave *2-methyl-2-(phenylsulfenyl)propan-1-ol* **16a** (78%) as a colourless oil; ν_{max} (film) 3453, 3061, 2967, 2875, 1865, 1585, 1573, 1490, 1473, 1439, 1404, 1390, 1225, 1135, 1024, 906, 845, 810, 751, 692 cm^{-1}; δ_H (270 MHz) 7.51 (2H, m, *o*-protons on PhS), 7.43-7.30 (3H, m, *m*- and *p*-protons on

PhS), 3.27 (2H, d, J 6 Hz, H-1), 2.34 (1H, t, J 6 Hz, OH), 1.23 (6H, s, H-3); *m/z* (EI) 182 (M^+), 151 (M^+ - CH_2OH), 110 (PhSH), 109 (PhS), 73 (M^+ - PhS), 72 (M^+ - PhSH) (Found: C, 65.85; H, 7.61. $C_{10}H_{14}OS$ requires C, 65.89; H, 7.74%).

Preparation of 2-methyl-2-(phenylsulfenyl)butan-1-ol (16b).

Prepared according to the standard procedure described for **16g**. Purification by chromatography (20% ether–petrol) gave *2-methyl-2-(phenylsulfenyl)butan-1-ol* **16b** (95%) as a colourless oil; ν_{max} (film) 3445, 3058, 2967, 2877, 1954, 1888, 1583, 1573, 1473, 1438, 1371, 1215, 1128, 1024, 902, 811, 750, 694, 666 cm^{-1}; δ_H (270 MHz) 7.49 (2H, m, *o*-protons on PhS), 7.41-7.29 (3H, m, *m*- and *p*-protons on PhS), 3.32 and 3.24 (2H, AB quartet, J 10 Hz, H-1), 2.39 (1H, br s, OH), 1.51 (2H, q, J 8 Hz, H-3), 1.13 (3H, s, 2-Me), 1.02 (3H, t, J 8 Hz, H-4); *m/z* (EI) 196 (M^+), 165 (M^+ - CH_2OH), 123, 110 (PhSH), 86 (M^+ - PhSH) (Found: (M^+), 196.0922. $C_{11}H_{16}OS$ requires (M^+), 196.0922).

Preparation of 1-(hydroxymethyl)-1-(phenylsulfenyl)cyclopentane (16c).

Prepared according to the standard procedure described for **16g**. Purification by chromatography (20% ether–petrol) gave 1-(hydroxymethyl)-1-(phenylsulfenyl)cyclopentane **16c** (94%) as a colourless oil; ν_{max} (film) 3448, 3058, 2957, 2869, 1653, 1584, 1552, 1538, 1474, 1439, 1389, 1308, 1220, 1027, 947, 918, 750, 695 cm^{-1}; δ_H (270 MHz) 7.51 (2H, m, *o*-protons on PhS), 7.39-7.31 (3H, m, *m*- and *p*-protons on PhS), 3.33 (2H, br d, J 4.5 Hz, H-1), 2.59 (1H, br t, J 4.5 Hz, OH), 1.97-1.87 (2H, m), 1.78-1.56 (6H, m); *m/z* (EI) 208 (M^+), 205, 190, 177 (M^+ - CH_2OH), 110 (PhSH), 98 (M^+ - PhSH).

Preparation of 1-(hydroxymethyl)-1-(phenylsulfenyl)cyclohexane (16d).

Prepared according to the standard procedure described for **16g**. Purification by chromatography (20% ether–petrol) gave 1-(hydroxymethyl)-1-(phenylsulfenyl)cyclohexane **16d** (100%) as a colourless oil; ν_{max} (film) 3427, 3057, 2930, 2855, 1583, 1474, 1439, 1392, 1260, 1134, 1108, 1025, 950, 902, 882, 854, 750, 694 cm^{-1}; δ_H (270 MHz) 7.50 (2H, m, *o*-protons on PhS), 7.40-7.29 (3H, m, *m*- and *p*-protons on PhS), 3.29 (2H, br s, H-1), 2.47 (1H, br s, OH), 1.90-1.27 (10H, m); *m/z* (EI) 222 (M^+), 218, 205 (M^+ - OH), 204 (M^+ - H_2O), 191 (M^+ - CH_2OH), 124, 112 (M^+ - PhSH), 110 (PhSH).

Preparation of 1-(*p*-tolylsulfenyl)-1,2-bis(trifluoroacetoxy)octane (17).

To a stirred solution of (+)-(R)$_S$-(*E*)-1-(*p*-tolylsulfinyl)oct-1-ene (*E*)-**1o** (157.1 mg, 0.63 mmol) in dry dichloromethane (3.14 ml; 0.2M) at 0°C under argon was added, dropwise *via* syringe, TFAA (89 µl, 0.63 mmol, 1 eq). After 15 min stirring at 0°C the reaction was quenched. Standard work-up gave *1-(p-tolylsulfenyl)-1,2-bis(trifluoroacetoxy)octane* **17** (2.3:1 ratio of diastereomers by ^1H nmr; 252.4 mg, 87%) as a colourless oil; ν_{max} (film) 2932, 2861, 1795, 1494, 1466, 1366, 1227, 1169, 1019, 876, 813, 772, 725 cm^{-1}; δ_H (270 MHz) (major diastereomer) 7.41 (2H, d, J 8 Hz, *o*-protons on tolyl), 7.20 (2H, d, J 8 Hz, *m*-protons on tolyl), 6.12 (1H, d, J 9 Hz, H-1), 5.21 (1H, dt, J 9, 3.5 Hz, H-2), 2.38 (3H, s, tolyl Me), 2.08-

1.77 (2H, m, H-3), 1.44-1.19 (8H, m, H-4, H-5, H-6 and H-7), 0.91 (3H, m, H-8); (minor diastereomer) 7.39 (2H, d, J 8 Hz, *o*-protons on tolyl), 7.17 (2H, d, J 8 Hz, *m*-protons on tolyl), 6.27 (1H, d, J 4.5 Hz, H-1), 5.38 (1H, dt, J 10, 4.5 Hz, H-2), 2.36 (3H, s, tolyl Me), 2.08-1.77 (2H, m, H-3), 1.44-1.19 (8H, m, H-4, H-5, H-6 and H-7), 0.91 (3H, m, H-8); *m/z* (EI) 460 (M^+), 347 (M^+ - $OCOCF_3$), 346 (M^+ - CF_3CO_2H), 234 (M^+ - $CF_3CO_2COCF_3$), 163, 130, 124 (*p*-TolS) (Found: (M^+), 460.1143. $C_{19}H_{22}F_6O_4S$ requires (M^+), 460.1143).

Preparation of methyl (*E*)-4-hydroxydec-2-enoate (13b).

To a stirred solution of 1,2-bis(trifluoroacetoxy)-1-(*p*-tolylsulfenyl)octane **17** (257.2 mg, 0.56 mmol) in dry dichloromethane (2.79 ml; 0.2M) at 0°C under argon was added MeOH (50 µl, 1.2 mmol, 2.2 eq) followed by triethylamine (8 µl, 0.06 mmol, 0.1 eq). After 5 min stirring at 0°C the solvents were removed under reduced pressure. Purification by chromatography (40% ether–petrol) gave 2-hydroxyoctanal **11b** (71.2 mg, 88%) as a white oily solid. The product **11b** (71.2 mg, 0.49 mmol) was then dissolved in dry benzene (1.47 ml), a solution of methyl (triphenylphosphoranylidene)acetate (248 mg, 0.74 mmol, 1.5 eq) in dry benzene (1 ml; 0.2M overall) was added *via* syringe, and the reaction was heated to 110°C for 3 h. The reaction was allowed to cool and the solvents were removed under reduced pressure. Purification by chromatography (30% ether–petrol) gave methyl (*E*)-4-hydroxydec-2-enoate **13b** (71.8 mg, 73%) as a colourless oil; spectroscopic data was in agreement with the previously prepared compound.

Preparation of [(*R)-(*E*)-1-methoxycarbonylnon-1-en-3-yl] (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate.**

To a solution of methyl (*E*)-4-hydroxydec-2-enoate **13b** (49.1 mg, 0.25 mmol) and DMAP (2 mg, *ca.* 0.1 eq) in dry dichloromethane (490 µl; 0.5M) at 20°C under argon was added, dropwise *via* syringe, pyridine (59 µl , 0.73 mmol, 3 eq) followed by (+)-(*S*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoyl chloride[34] (368 µl of a 1M solution in dichloromethane, 0.21 mmol, 1.5 eq). The reaction was allowed to stir for 12 h at 20°C to ensure complete conversion of the starting material to product and thus avoid kinetic resolution. dichloromethane (5 ml) was added to the reaction, the organic layer was then washed with 1M NaOH (5 ml), 2M HCl (5 ml), dried over $MgSO_4$ and the solvents were removed under reduced pressure to give the crude product as a colourless oil. The diastereomeric ratio of the product *[(R*)-(E)-1-methoxycarbonylnon-1-en-3-yl] (R)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate* was determined by ^1H nmr analysis of the crude mixture (1:1 ratio of diastereomers, 0% d.e.); δ_H (270 MHz) 7.62-7.31 (10H, m, Ph on both diastereomers), 6.88 (1H, dd, J 16, 5.5 Hz, H-2 on one diastereomer), 6.81 (1H, dd, J 15, 5.5 Hz, H-2 on one diastereomer), 5.61 (2H, m, H-3 on both diastereomers), 3.74 (3H, s, CO_2Me for one diastereomer), 3.73 (3H, s, CO_2Me for one diastereomer), 3.56 (3H, s, MeO for one diastereomer), 3.55 (3H, s, MeO on one diastereomer), 1.83-1.62 (4H, m, H-4 on both diastereomers), 1.40-1.12 (16H, m, H-5, H-6, H-7 and H-8 for both diastereomers), 0.92-0.81 (6H, m, H-9 for both diastereomers).

Preparation of (-)-methyl (*S*)-2-[(*tert*-butyldimethylsilyl)oxy]propanoate.

To a stirred solution of (-)-(*S*)-methyl lactate **18** (2 g, 1.83 ml, 19.2 mmol) in dry THF (9.2 ml) at 20°C under argon was added, dropwise *via* syringe, triethylamine (6.96 ml, 50 mmol, 2.6 eq) followed by a solution of TBDMSCl (3.86 g, 25.5 mmol, 1.33 eq) and DMAP (235 mg, 1.92 mmol, 0.1 eq) in dry THF (10 ml; 1M overall). The reaction was allowed to stir at 20°C for 12 h and then the solvents were removed under reduced pressure. The residue was triturated with ether (100 ml) and the salts were removed by filtration, washing with ether (100 ml). The filtrate was washed sequentially with 15% acetic acid (50 ml), water (50 ml), saturated aqueous sodium hydrogencarbonate (2 x 50 ml) and water (50 ml) and then dried ($MgSO_4$). Removal of the solvents under reduced pressure followed by distillation gave (-)-methyl (2*S*)-2-[(*tert*-butyldimethylsilyl)oxy]propanoate (3.80 g, 91%) as a colourless, mobile oil, bp_{23} 95°C; $[\alpha]_D^{20}$ -31.6 (*c* 1.53, 95% ethanol) (lit.[44] $[\alpha]_D^{21}$ -31.7 (*c* 0.66, 95% ethanol)); ν_{max} (film) 2955, 2891, 2859, 1760, 1463, 1362, 1258, 1206, 1150, 1091, 1023, 834, 786, 689 cm^{-1}; δ_H (270 MHz) 4.33 (1H, q, J 7 Hz, H-2), 3.72 (3H, s, MeO), 1.40 (3H, d, J 7 Hz, H-3), 0.90 (9H, s, *t*-BuSi), 0.09 (3H, s, MeSi), 0.07 (3H, s, MeSi); *m/z* (EI) 203 (M^+ - CH_3), 161 (M^+ - *t*-Bu), 103 (M^+ - TBDMS), 89, 75, 73.

Preparation of (-)-(*S*)-2-[(*tert*-butyldimethylsilyl)oxy]propanal.

To a stirred solution of methyl (-)-(*S*)-2-[(*tert*-butyldimethylsilyl)oxy]propanoate (1.40 g, 6.4 mmol) in dry hexane (6.4 ml; 1M) at -78°C under argon was added, dropwise *via* syringe, DIBAL-H (5.56 ml of a 1.5M solution in toluene, 8.3 mmol, 1.3 eq) over 30 min. The reaction was allowed to stir at -78°C for a further 1 h after the addition and was then quenched by the addition of water (5 ml). The reaction was then warmed to 20°C, the suspension was filtered and the solids were washed with ether (100 ml). The organic layer was separated, dried over $MgSO_4$ and the solvents were removed under reduced pressure to give the crude product (-)-(*S*)-2-[(*tert*-butyldimethylsilyl)oxy]propanal (989.8 mg) as a colourless mobile oil; δ_H (270 MHz) 9.61 (1H, d, J 1 Hz, CHO), 4.10 (1H, dq, J 7, 1 Hz, H-2), 1.28 (3H, d, J 7 Hz, H-3), 0.93 (9H, s, *t*-BuSi), 0.09 (3H, s, MeSi), 0.08 (3H, s, MeSi). The crude product was taken on to the next step without further purification.

Preparation of methyl (*S*)(*E*)-4-hydroxypent-2-enoate (13a).

To a stirred solution of (-)-(*S*)-2-[(*tert*-butyldimethylsilyl)oxy]propanal (989.8 mg, 5.3 mmol assuming 100% purity) in dry acetonitrile (26.3 ml; 0.2M) at 20°C was added, dropwise *via* pipette, 48% aqueous HF solution (33 drops, *ca.* 5 eq). After 15 min stirring at 20°C, the reaction was quenched by the addition of solid sodium hydrogencarbonate (*ca.* 1 g). Stirring was continued at 20°C until no further effervescence was observed. The mixture was then filtered through a short plug of silica gel, washing with ether (50 ml). Removal of the solvents under reduced pressure gave crude 2-hydroxypropanal **11a** (310.3 mg) as a colourless oily solid. The product **11a** (81.5 mg, 1.1 mmol assuming 100% purity) was then dissolved in dry benzene (1.17 ml), a solution of methyl (triphenylphosphoranylidene)acetate (460 mg, 1.38 mmol, 1.25 eq) in dry benzene (2.5 ml; 0.15M overall) was added *via* syringe, and the reaction was heated to 110°C for 5 h. The reaction was allowed to cool and the solvents were removed under reduced pressure. Purification by

chromatography (50%-60% ether–petrol) gave methyl (*S*)(*E*)-4-hydroxypent-2-enoate **13a** (18.5:1 ratio of *E*:*Z*; 79.6 mg) as a colourless oil; spectroscopic data was in agreement with the previously prepared compound.

Preparation of [(*S*)(*E*)-1-methoxycarbonylbuten-3-yl] (*R*)-2-methoxy-2-phenyl-3,3,1-trifluoropropanoate.

Prepared from (*S*)-**13a** according to the standard procedure described above. The diastereomeric ratio of the product *[(S)(E)-1-methoxycarbonylbuten-3-yl] (R)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate* was determined by ^{1}H nmr analysis of the crude mixture (1:0 ratio of diastereomers, 100% d.e.); δ_H (500 MHz) 7.51 (2H, m, *o*-protons on Ph), 7.41 (3H, m, *m*- and *p*-protons on Ph), 6.83 (1H, dd, J 15, 4.5 Hz, H-2), 5.87 (1H, dd, J 15, 1 Hz, H-1), 5.72 (1H, dd quintet, J 6.5, 4.5, 1 Hz, H-3), 3.72 (3H, s, CO_2Me), 3.56 (3H, s, MeO), 1.46 (3H, d, J 6.5 Hz, 3-Me).

Preparation of 1,1-diacetoxy-2-phenyl-2-(*p*-tolylsulfenyl)ethane (19).

To a stirred suspension of (+)-(R)$_S$-(*E*)-2-phenyl-1-(*p*-tolylsulfinyl)ethene (*E*)-**1p** (116.8 mg, 0.48 mmol) and sodium acetate (79 mg, 0.96 mmol, 2 eq) in acetic anhydride (redistilled from P_2O_5 under argon; 2.41 ml; 0.2M) at 0°C under argon was added, dropwise *via* syringe, trifluoromethanesulfonic anhydride (81 µl, 0.48 mmol, 1 eq) over 10 min. After 10 min stirring at 0°C the reaction was quenched by the addition of saturated aqueous sodium hydrogencarbonate (10 ml). The aqueous layer was extracted with dichloromethane (2 x 10 ml). The combined organic layers were washed with saturated aqueous sodium hydrogencarbonate (2 x 20 ml), dried over $MgSO_4$ and the solvents were removed under reduced pressure to give the crude product as a brown oil. Purification by chromatography (20% ether–petrol) gave *1,1-diacetoxy-2-phenyl-2-(p-tolylsulfenyl)ethane* **19** (118.4 mg, 71%) as a colourless oil; ν_{max} (film) 3029, 1768, 1600, 1493, 1452, 1374, 1236, 1105, 1074, 1009, 812, 701 cm^{-1}; δ_H (270 MHz) 7.32 (5H, m, PhS), 7.28 (2H, d, J 8 Hz, *o*-protons on tolyl), 7.15 (1H, d, J 5.5 Hz, H-1), 7.06 (2H, d, J 8 Hz, *m*-protons on tolyl), 4.44 (1H, d, J 5.5 Hz, H-2), 2.31 (3H, s, tolyl Me), 1.97 (6H, s, 2 x $OCOCH_3$); *m/z* (EI) 344 (M^+), 284 (M^+ - AcO), 242 (M^+ - Ac_2O), 213 (M^+ - AcOCHOAc), 124, 119, 91 ($PhCH_2$) (Found: C, 65.82; H, 5.86. $C_{19}H_{20}O_4S$ requires C, 66.26; H, 5.85%).

Preparation of 2-phenyl-2-(*p*-tolylsulfenyl)ethanol (20).

To a stirred solution of 1,1-diacetoxy-2-phenyl-2-(*p*-tolylsulfenyl)ethane **19** (62 mg, 0.18 mmol) in a mixture of propan-2-ol and dimethoxyethane (1:1; 1.8 ml; 0.1M) at 20°C was added sodium borohydride (34 mg, 0.9 mmol, 5 eq). The reaction was allowed to stir at 20°C for 12 h and was then quenched by the addition of methanol (1 ml). Water (5 ml) was added to the mixture and the aqueous layer was extracted with dichloromethane (2 x 10 ml). The combined organic layers were dried over $MgSO_4$ and the solvents were removed under reduced pressure to give the crude product as an oily colourless solid. Purification by chromatography (20% ether–petrol) gave *2-phenyl-2-(p-tolylsulfenyl)ethanol* **20** (44 mg, 100%) as a colourless oil; ν_{max} (film) 3736, 3388, 3028, 2921, 1898, 1734, 1599, 1561, 1492, 1452, 1398, 1180, 1055,

1018, 810, 761, 698 cm^{-1}; δ_H (270 MHz) 7.31 (5H, m, PhS), 7.25 (2H, d, J 8 Hz, *o*-protons on tolyl), 7.06 (2H, d, J 8 Hz, *m*-protons on tolyl), 4.25 (1H, dd, J 8, 7 Hz, H-2), 3.94 and 3.88 (2H, ABX, J 10, 8, 7 Hz, H-1), 2.32 (3H, s, tolyl Me), 2.08 (1H, br s, OH); *m/z* (EI) 244 (M^+), 213 (M^+ - CH_2OH), 124, 121 (M^+ - *p*-TolS), 120 (M^+ - *p*-TolSH), 104, 103, 91 ($PhCH_2$) (Found: C, 73.77; H, 6.66. $C_{15}H_{16}OS$ requires C, 73.73; H, 6.60%).

Preparation of [(*R)-2-phenyl-2-(*p*-tolylsulfenyl)ethyl] (*R*)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate.**

Prepared from alcohol **20** according to the standard method described above. The diastereomeric ratio of the product *[(R*)-2-phenyl-2-(p-tolylsulfenyl)ethyl] (R)-2-methoxy-2-phenyl-3,3,3-trifluoropropanoate* was determined by ^1H nmr analysis of the crude mixture (1.2:1 ratio of diastereomers, 10.5% d.e.); δ_H (500 MHz) (major diastereomer) 7.45-7.23 (10H, m, 2 x Ph), 7.45 (2H, d, J 8 Hz, *o*-protons on tolyl), 7.10 (2H, d, J 8 Hz, *m*-protons on tolyl), 4.83 (1H, dd, J 11, 9.5 Hz, H-1 or H-2), 4.54 (1H, dd, J 11, 5.5 Hz, H-1 or H-2), 4.45 (1H, dd, J 9.5, 5.5 Hz, H-1 or H-2), 3.32 (3H, d, J 1 Hz, MeO), 2.33 (3H, s, tolyl Me); (minor diastereomer) 7.45-7.23 (10H, m, 2 x Ph), 7.45 (2H, d, J 8 Hz, *o*-protons on tolyl), 7.10 (2H, d, J 8 Hz, *m*-protons on tolyl), 4.78 (1H, dd, J 11, 9 Hz, H-1 or H-2), 4.63 (1H, dd, J 11, 5.5 Hz, H-1 or H-2), 4.48 (1H, dd, J 9, 5.5 Hz, H-1 or H-2), 3.33 (3H, d, J 1 Hz, MeO), 2.33 (3H, s, tolyl Me).

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