Diastereoselective addition reactions of racemic chiral vinyl sulfimides

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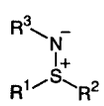
S-Aryl *S*-vinyl sulfimides are prepared by a new method *via* Horner–Wadsworth–Emmons reagents generated *in situ*. Lewis acid-catalysed Diels–Alder reaction of *S*-ethenyl-*S*-phenyl-*N*-tosylsulfimide with cyclopentadiene leads to the *endo anti* product with good diastereofacial and *endo–exo* selectivities. A range of alcohols and amines, with the limitation that they be practically usable in large excess, add to β-aryl vinyl sulfimides with modest diastereoselectivity. The major products of both the cycloaddition and the nucleophilic additions are rationalised by a model invoking addition to the least-hindered face of the s-*cis* conformation of the vinyl sulfimide.

Introduction

Compounds **1**, which have the IUPAC name "sulfimide" and



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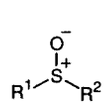

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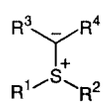

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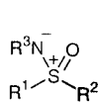

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the *Chemical Abstracts* name "sulfilimine", remain little-studied in the area of stereoselective synthesis,[1] as compared with, for example, sulfoxides **2**,[2] sulfur ylides **3**[3] and sulfoximides (sulfoximines) **4**.[4] However, there have been a number of recent reports regarding the synthesis of enantiomerically enriched sulfimides[1,5] and their application in enantioselective synthesis of non-racemic epoxides and aziridines,[6] which represent a small renaissance of interest in this field.

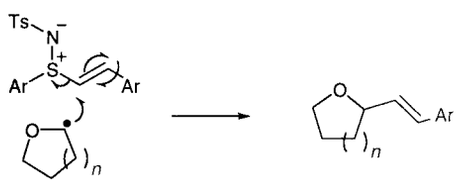
The asymmetric chemistry of chiral vinyl sulfoxides and sulfoximides is now well-established,[2,4] but the parallel chemistry of sulfimides remains largely unexplored. We decided to study the following classes of addition to the *S*-vinyl group of a sulfimide:

(i) Diels–Alder additions of dienes;
(ii) additions of nucleophiles;
(iii) additions of carbon-centred radicals.

To our knowledge, previous to our work there were no examples of classes (i) and (iii) in the sulfimide series. However, there are a number of reports from Yamamoto and co-workers of additions of alcohols, thiols, amines and doubly-stabilised carbanions to β-unsubstituted sulfimides,[7] which are useful precedents for our work on the second class (nucleophilic additions). In the β-unsubstituted examples studied by the Yamamoto group, no new chiral centre is established. We envisaged carrying out analogous reactions on β-substituted vinyl sulfimides to establish the stereochemical influence of the sulfimidyl group.

Our initial work on the third class of reactions (radical additions) has already been communicated.[8] In this case, the major product appears to result from α-addition with subsequent elimination of the sulfimidyl group (Scheme 1). A comparative study of reactions of radicals with various vinyl sulfur compounds has recently been completed and will be published separately.[9]

Herein we describe (i) a short study on the Diels–Alder reactions of two aryl vinyl sulfimides, (ii) the results of nucleophilic additions to a series of new β-substituted aryl vinyl sulfimides and (iii) a stereochemical model for the addition reactions.



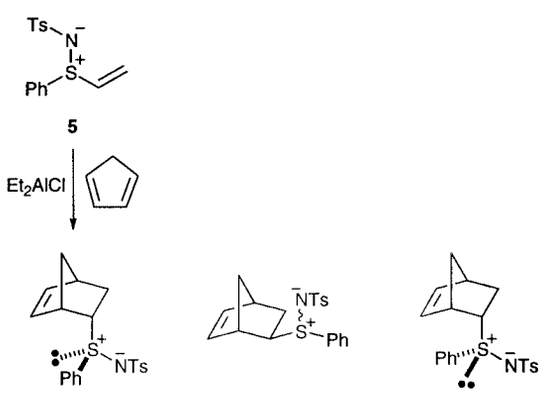
Scheme 1

Results and discussion

(i) Diels–Alder additions

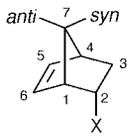
Lewis acid-catalysed reaction of **5** with cyclopentadiene was attempted in toluene at room temperature, using some of the Lewis acids proposed for the analogous cycloadditions of substituted vinyl sulfoxides.[10] With $TiCl_4$ a complex mixture of unidentified products resulted, but with $ZnCl_2$ a mixture of cycloadducts was isolated in low yield, in which an *endo* product appeared to be dominant.

Finally, using Et_2AlCl at room temperature, a 55% isolated yield of a mixture of the four possible stereoisomers **6**, which were not separated, was achieved (Scheme 2). The ^1H NMR

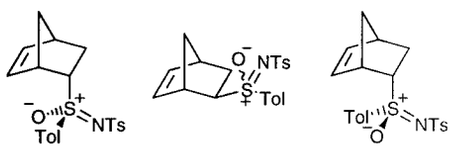


Scheme 2

Table 1 Chemical shift data for *endo* sulfimide **6a** and *endo* sulfoximides **7a** and **7d**



	6a δ/ppm	**7a** δ/ppm	**7d** δ/ppm
H-1	2.44	2.69	3.57
H-2	3.78	3.96	3.93
H-3 *endo*	1.32	1.69	1.33
H-3 *exo*	2.13	2.23	1.78
H-4	2.93	2.97	2.92
H-5 & H-6	5.97, 6.29	5.79, 6.21	5.82, 6.14
H-7 *syn*	1.25	1.25	1.27
H-7 *anti*	1.49	1.48	1.49



7a **7b + 7c** **7d**

45% 9% 9% 36% Tol = *p*-$CH_3C_6H_4$-

spectrum of the purified mixture was compared with those of the analogous sulfoxides[11] and sulfoximides,[12] which resulted from uncatalysed reactions at relatively high temperature. Not surprisingly, the closest fit, as judged by comparison of chemical shifts, was with the sulfoximides **7** (which differ only in the oxo group at sulfur and a *para* methyl group on the non-sulfonyl *S*-aryl group) and we thus used comparison with **7** to tentatively assign structures to the four isomers.

The chemical shift data for the major isomer **6a** are a reasonable match for those of both of the *endo* sulfoximides **7a** and **7d** (Table 1) and we thus confidently assign the *endo* stereochemistry to **6a**. Closer inspection reveals an excellent match between the data for **6a** and sulfoximide **7a**, with the greatest discrepancies being with those protons (H-1 and H-3*endo*) that would be expected to be the most affected by the oxo group. The configuration of another closely analogous sulfoximide was established by the Glass group by X-ray crystallography[12] and we thus believe the assignment of the relative stereochemistry of the sulfur centre to be secure. This leads us to speculate that the major product in the sulfimide case is the *endo anti* compound **6a** (adapting the terminology proposed by Montanari and co-workers[13,14] and referring to approach past the S–N rather than S–O bond).

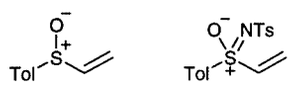
The *data* for the 11% and 5% isomers cannot be extracted completely from the spectrum, making unambiguous structural assignments difficult. Nevertheless it can be observed that the data for these two compounds are (a) quite similar and (b) best matched to the two *exo* sulfoximide analogues **7b** and **7c**. Hence we tentatively assign the *exo* stereochemistry to isomers **6b** and **6c**. Assignment of the relative stereochemistry of the sulfur centre is not possible from these data; isolation and either crystallography or stereospecific oxidation to the sulfoximide would be required. Finally, by a process of elimination we assign the *endo syn* stereochemistry to the minor isomer **6d**, but there are no independent data to confirm this.

If our assignments are correct, the Lewis acid-catalysed reaction of vinyl sulfimide **5** with cyclopentadiene proceeds with significant *endo anti* selectivity. Comparison with the thermal reactions of the corresponding sulfoxide **8** and sulfoximide **9** shows that the *endo* selectivity is as expected (Table 2). However, there is a significant change in both the magnitude and sense of the diastereofacial selectivity (Table 2). We have followed De Lucchi in extending the *syn*/*anti* nomenclature to

Table 2 Stereoselectivities in reactions of cyclopentadiene with sulfoxide **8**, sulfoximide **9** and sulfimide **5**

	endo : *exo*	*syn* : *anti*
Sulfoxide **8**	64 : 36	50 : 50
Sulfoximide **9**	81 : 19	55 : 45
Sulfimide **5**	84 : 16	7 : 93[a]

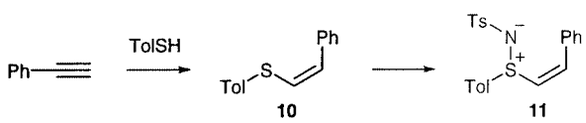
[a] Assuming 11% *exo* isomer is *syn*, otherwise 13 : 87.



8 **9**

sulfoximides by reference to the *oxo* group rather than the imido group,[14] but note that this is necessarily somewhat artificial. The variations in *syn*/*anti* selectivity (if correctly assigned) need not be surprising considering the differences in reaction conditions (115 °C for the sulfoxide, refluxing dichloromethane for the sulfoximide and Et_2AlCl at room temperature for the sulfimide). Indeed, prior conversion of the vinyl sulfoxide to a sulfoxonium salt leads to the *endo anti* product with good stereoselectivities.[11c]

We proceeded to attempt the same Et_2AlCl-catalysed reaction of the *Z*-β-substituted analogue **11**. Sulfimide **11** was prepared by imidation of the known sulfide **10** which is the isomerically pure product of addition of thiocresol to phenylacetylene (Scheme 3). Reaction with cyclopentadiene under our

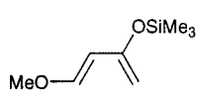


10 **11**

Scheme 3

previous best conditions led to a crude product with signals in the ^1H NMR spectrum at around 6.0 and 6.45 ppm (*cf*. 6.0 and 6.3 ppm for the alkene protons in **11**) and no signal for the upfield vinylic proton of the starting material **11** at 6.3 ppm. However, on work-up only unreacted starting material **11** could be isolated. It seems that the Diels–Alder reaction does indeed occur, but that a retro-reaction occurs during work-up to give back the starting material. This observation is significant since, as pointed out by Paquette and Magnus,[15] low yields in sulfoxide-mediated Diels–Alder reactions are often attributed to low reactivity, without consideration of the possibility of the existence of a relatively fast equilibrium. It may be that in our case the Et_2AlCl is not a true catalyst (three equivalents were used), but remains coordinated to the product, thus preventing the reverse reaction occurring until the Lewis acid is removed.

We wished to extend the cycloaddition chemistry to acyclic dienes, but starting material was recovered from reactions of both sulfimides **5** and **11** with Danishefsky's diene **12**.



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(ii) Nucleophilic additions to vinyl sulfimides

As mentioned in the introduction, we were interested in the stereochemical influence of the sulfimidyl group on nucleophilic additions to the β-vinylic carbon of sulfimides of general structure **13**. Since the sulfimidyl group is readily reduced to the corresponding sulfide,[16] additions of alcohols and amines would lead to derivatives of β-hydroxy- and β-aminosulfides respectively, which have potential as chiral ligands for metals.[17]

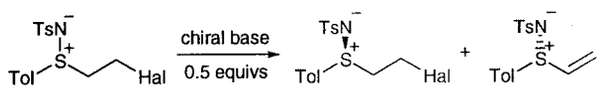
Table 3 Yields and stereoselectivities for syntheses of vinyl sulfimides **16**

	16	R	Yield (%)[a]	*E*:*Z*
	a	*p*-$MeOC_6H_4$	60	80:20
	b	Ph	48	85:15
	c	*p*-ClC_6H_4	40	95:5
	d	*p*-$O_2NC_6H_4$	5	[b]
	e	*i*-Pr	64	98:2
	f	*t*-Bu	39	98:2
	g	cyclopropyl	39	53:47

[a] Yield of (*E*:*Z*) mixture. [b] Not determined.

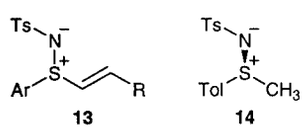
Hence, it was important that our chemistry was readily adaptable to the enantiomerically pure analogues.

The two main literature routes to vinyl sulfimides are direct imidation of sulfides, as used in Section (i) above, of which no asymmetric version yet exists for vinyl analogues,[5a] and elimination from β-halo sulfimides.[18] Although a good ee was reported for one example of an asymmetric version of this elimination reaction (Scheme 4),[18b] we did not feel that this procedure had general potential.

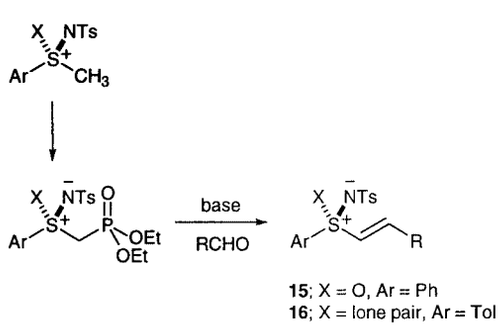


Scheme 4

At the start of our work, one of the few readily-available enantiomerically-pure sulfimides was compound **14** prepared



from the corresponding commercially available enantiomerically-pure sulfoxide using the procedure of Cram *et al.*[19] We therefore decided to use this methyl sulfimide as our starting material and to adapt the method used by Craig's group for the synthesis of related vinyl sulfoximides **15**.[20] This involves the *in situ* generation of Horner–Wadsworth–Emmons type reagents from the methyl sulfoximide and their reaction with aldehydes (Scheme 5).



Scheme 5

Using the identical conditions to Craig's group,[20] we were able to isolate a range of new racemic chiral β-substituted aryl vinyl sulfimides **16** (Table 3), albeit in lower yield than observed with the sulfoximides. In all cases the (*E*) isomer was the major product, but the selectivities varied considerably with the substituent. The aryl derivatives gave separable (*E*):(*Z*) mixtures, in which the predominance of the (*E*) product increased with increasing electron demand of the substituent (Table 3), whereas for the isopropyl and *tert*-butyl compounds, the (*Z*) isomer was not observed. However, another alkyl derivative, the cyclopropyl product **16g**, showed virtually no selectivity.

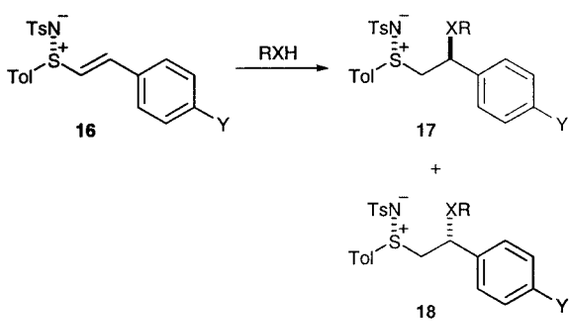
Table 4 Yields and stereoselectivites for nucleophilic additions to vinyl sulfimides **16**

	X	Y	R	Yield (%)	**17**:**18**
a	O	H	$PhCH_2$	64[a]	>97:3
b	O	H	Et	73[a]	90:10
c	O	OMe	Et	32[b]	90:10
d	NH	H	$PhCH_2$	63[a]	80:20
e	NH	Cl	$PhCH_2$	57[a]	80:20
f	NH	H	*i*-Pr	53[b]	80:20
g	NH	Cl	*i*-Pr	69[b]	80:20
h	NEt	H	Et	46[b]	70% de[c]
i	NEt	Cl	Et	56[b]	70% de[c]

[a] Isolated yield of **17**. [b] Mixture of **17** and **18**. [c] Major isomer not identified.

Although all the products described here are racemic we did undertake a small-scale preparation of **16b** using enantiomerically-enriched **14** and determined that the ees of product and starting material were the same (by integration of the *p*-tosyl methyl signals in the ^1H NMR spectrum in the presence of trifluoroanthrylethanol). Hence this method should be applicable to asymmetric synthesis.

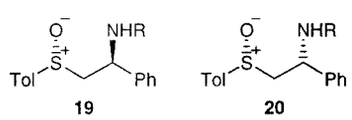
The reactions of some of the new aryl sulfimides with some representative alcohols and amines are summarised in Scheme 6



Scheme 6

and Table 4. Unfortunately, the effect of the β-substituent meant that these reactions only gave useful yields, as compared with the unsubstituted literature examples,[7] when the alcohol or amine was used as the solvent; a similar phenomenon was reported by Pyne *et al.* in the sulfoxide series.[21] Hence, the scope of this reaction is limited to cheap, volatile alcohols and amines which can feasibly be used as solvents.

The diastereoselectivities of the reactions were modest (Table 4), with the exception of the addition of benzyl alcohol which proceeded in at least 95% de. The stereochemistry of the major isomer was inferred by comparison with some sulfoxide analogues **19**.[22] The benzylic proton in Pyne *et al.*'s examples of

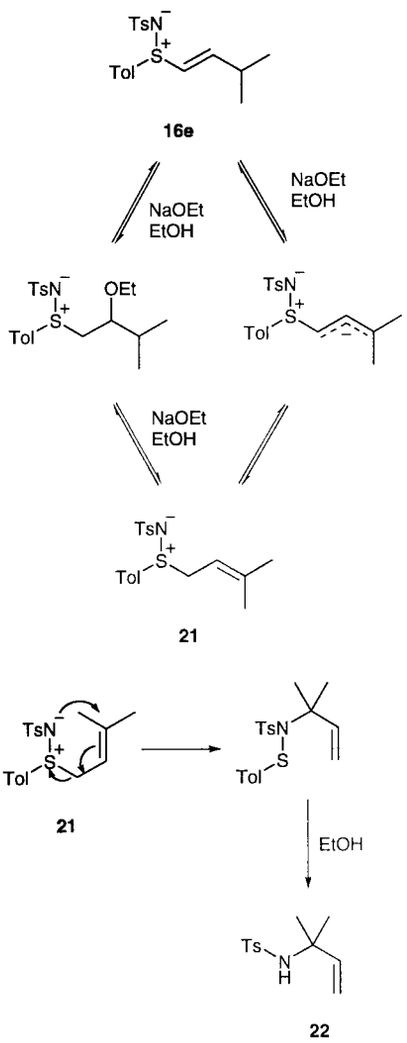


(*R*,*S*) **19** are doublets of doublets with coupling constants of around 3.0 and 10.5 Hz, in excellent agreement with our major isopropylamine adducts **17f** and **17g** (3.0 and 10.5 Hz for both examples) and the major benzylamine adducts **17d** and **17e** (2.3 and 10.7 Hz approximately). Furthermore, the major alcohol adducts **17a**–**c** have even more disparate coupling constants (2.1 and 10.9 Hz approximately). We therefore propose the (*RS*,*SR*) stereochemistry for all these adducts.

The same coupling constants for the diastereoisomeric (*R*,*R*) sulfoxides **20** are less easy to extract from the literature data, but

can be seen to be significantly closer to each other in value. With sulfimides **18f** and **18g** we were able to interpret the ^{1}H NMR data for the minor isomer; the coupling constants for the benzylic proton (dd, *J* 7.2, 7.2 Hz in both cases) resembled those of sulfoxides **20** and thus gave support to our stereochemical assignments. The equivalent multiplets for the diethylamine adducts **17h**, **17i**, **18h** and **18i** have a different pattern, presumably due to the significant increase in the steric demand of the amino group, and we are thus reluctant to assign the relative stereochemistry of these adducts.

Additions of alcohols and amines to the *tert*-butyl derivative **16f** were unsuccessful, presumably due to steric hindrance. However, the isopropyl derivative **16e** did react with ethanol, but with a different result. In this case the product was the known sulfonamide **22** which we presume to have been formed *via* alkene **21** (Scheme 7). Rearrangements of closely related allylic sulfimides are well-known.[5a,23]



Scheme 7

Finally, we wished to demonstrate that the chiral sulfimide products **17** could be readily transformed to sulfides, to permit synthesis of potentially useful chiral ligands. The most challenging substrates were the benzyl alcohol and benzylamine adducts **17a**, **17d** and **17d**, since selective hydrogenolysis of the S–N bond in the presence of the benzyl groups was required. In fact, with both **17a** and **17d** the reduction proceeded cleanly to furnish the target sulfides **23** with the *O*- and *N*-benzyl groups intact (Scheme 8).

(iii) Rationalisation of the sense of stereoselectivity

Pyne and co-workers have remarked that one simple model can

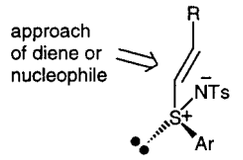
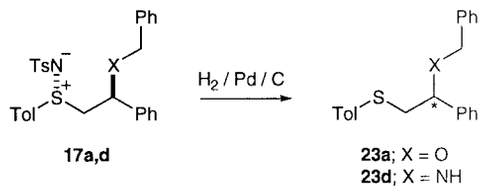


Fig. 1



Scheme 8

account for the majority of stereoselective reactions of vinyl sulfoxides.[24] Direct extension of this model leads to Fig. 1, where the reactive conformation of the vinyl sulfimide is s-*cis* and addition occurs from the least hindered face. In the cycloaddition, there is a need to invoke the usual *endo* preference and it should be noted that a Lewis acid is also involved in this case.

The model correctly predicts (i) the *anti* cycloadduct **6a** to be the major Diels–Alder product and (ii) the observed outcome of the addition of amines and alcohols to yield the (*RS*,*SR*) major products **17** (as with vinyl sulfoxides[21]).

Conclusion

S-Aryl *S*-vinyl sulfimides were prepared by a literature route and by a new method starting from *S*-aryl *S*-methyl sulfimides *via* Horner–Wadsworth–Emmons reagents generated *in situ*, this route being appropriate for the synthesis of enantiomerically enriched vinyl sulfimides.

Lewis acid-catalysed Diels–Alder reaction of one unsubstituted vinyl sulfimide with cyclopentadiene was successful, leading to the *endo anti* product with good diastereofacial and *endo–exo* selectivities, but extension to other examples failed. A range of alcohols and amines, with the limitation that they be practically usable in large excess, add to β-aryl vinyl sulfimides with modest diastereoselectivity. The major products of both the cycloaddition and the nucleophilic additions are predicted by a model invoking addition to the least-hindered face of the s-*cis* conformation of the vinyl sulfimide.

Experimental

General

Melting points were determined on a Stuart Scientific SMP1 melting point apparatus and are uncorrected. Microanalyses were performed at the University of Warwick. Mass spectra were recorded on a Kratos MS90 spectrometer. Infra-red spectra were recorded on a Perkin-Elmer 1720X Fourier transform spectrometer. NMR spectra were recorded on Bruker ACF 250 or Bruker ACP 400 instruments. Flash chromatography was performed on silica gel (Merck Kieselgel 60F_{254}, 230–400 mesh). Racemic methyl sulfimide **14** was prepared by the literature route.[23a]

S-Ethenyl-*S*-phenyl-*N*-*p*-tosylsulfimide 5[18a]

Phenyl vinyl sulfide (1.0 g, 7.3 mmol) and glacial acetic acid (0.2 cm^3, 3.5 mmol) were added to a solution of chloramine-T hydrate (2.07 g, 7.3 mmol) in absolute ethanol (200 cm^3). The mixture was stirred at 40 °C for 1 hour. The mixture was cooled to room temperature and stirred overnight. The solvent was removed and water (100 cm^3) and dichloromethane (100 cm^3) were added. The organic layer was separated, dried over anhydrous magnesium sulfate and concentrated *in vacuo* to give

the crude product. Trituration with ether followed by filtration and flash chromatography on silica gel using chloroform–ethyl acetate (8:1) as eluant furnished white crystals of sulfimide **5** (1.01 g, 45%), mp 109–110 °C (lit.,[18a] 111–113 °C); R_f 0.61 (EtOAc) (Found: C, 59.02; H, 4.94; N, 4.55. $C_{15}H_{15}NO_2S_2$ requires C, 59.02; H, 4.92; N, 4.59%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1599, 1494, 1478, 1446, 1298, 1284, 1143, 1089, 962; δ_H(250 MHz; $CDCl_3$) 2.34 (3H, s, Me), 6.03 (1H, dd, J = 8.4, 0.6 Hz, H-*trans*), 6.29 (1H, dd, J = 15.6, 0.6 Hz, H-*cis*), 6.41 (1H, dd, J = 8.4, 15.6 Hz, CHS), 7.17 (2H, AA′ of AA′BB′, J = 8.5 Hz, tosyl), 7.44–7.55 (3H, m, *meta* and *para* Ph), 7.64 (2H, m, *ortho* Ph), 7.75 (2H, BB′ of AA′BB′, J = 8.5 Hz, tosyl); δ_C(62.9 MHz; $CDCl_3$) 21.26 (Me), 126.02 (2), 126.80 (2), 129.10 (2), 129.68, 129.90 (2), 132.47, 132.78, 134.36, 141.18, 141.67; *m*/*z* (CI; NH_3) 306 (65%, MH^+), 198 (38), 189 (100), 155 (24), 137 (100), 108 (64), 91 (61), 65 (21).

Reaction of ethenyl phenyl sulfimide 5 with cyclopentadiene

Diethylaluminium chloride (0.3 cm^3 of a 1 M solution in hexanes, 0.30 mmol) was added to a solution of freshly distilled cyclopentadiene (0.10 cm^3, 0.76 mmol) and vinyl sulfimide **5** (30 mg, 0.10 mmol) in dry toluene (10 cm^3) under nitrogen at 0 °C. The mixture was stirred at 0 °C for 2 hours and then at room temperature for a further 12 hours. The solvent was removed under vacuum and the residue was subjected to flash chromatography on silica gel using chloroform–ethyl acetate (4:1) as eluant furnishing white crystals of *S*-norbornenyl-*S*-phenyl-*N*-tosylsulfimide **6** in a ratio of 82:11:5:2 (*endo anti*:*exo*:*exo*:*endo syn*), (20 mg, 55%); R_f ($CHCl_3$): 0.32 (Found: C, 64.41; H, 5.52; N, 3.44. $C_{20}H_{21}NO_2S_2$ requires C, 64.69; H, 5.66; N, 3.77%).

***endo-anti*-*S*-(Bicyclo[2.2.1]hept-5-en-2-yl)-*S*-phenyl-*N*-tosylsulfimide 6a.** δ_H(400 MHz; $CDCl_3$) 1.25 (1H, d, J = 8.9 Hz, H-7*syn*), 1.32 (1H, ddd, J = 13.6, 3.3, 3.3 Hz, H-3*endo*), 1.49 (1H, d, J = 8.9 Hz, H-7*anti*), 2.13 (1H, ddd, J = 13.1, 8.7, 3.5 Hz, H-3*exo*), 2.27 (3H, s, tosyl Me), 2.44 (1H, s, H-1), 2.93 (1H, s, H-4), 3.78 (1H, ddd, J = 8.7, 3.5, 3.5 Hz, H-2), 5.97 (1H, dd, J = 5.7, 2.7 Hz, =CH), 6.29 (1H, dd, J = 5.7, 3.1 Hz, =CH), 7.04 (2H, AA′ of AA′BB′, J = 8.1 Hz, tosyl), 7.46 (2H, m, Ph), 7.50 (1H, m, Ph), 7.59 (2H, BB′ of AA′BB′, J = 8.2 Hz, tosyl), 7.68 (2H, m, Ph); δ_C(100.6 MHz; $CDCl_3$) 21.38 (Me), 29.69 (C-3), 42.30 (C-1/C-4), 44.53 (C-1/C-4), 49.38 (C-7), 66.93 (C-2), 126.23 (2), 127.37 (2), 128.96 (2), 129.90 (2), 131.43, 132.71, 135.36, 139.72, 141.33, 141.44.

***exo*-*S*-(Bicyclo[2.2.1]hept-5-en-2-yl)-*S*-phenyl-*N*-tosylsulfimide 6b and 6c.** Discernible data for the 11% isomer: δ_H(400 MHz; $CDCl_3$) 0.82 (1H, dd, J = 12.7, 3.0, 3.0 Hz), 1.40 (1H, ddd, J = 12.0, 9.0, 4.0 Hz), 2.29 (3H, s), 2.36 (1H, s), 3.35 (1H, s), 5.70 (1H, dd, J = 5.7, 2.8 Hz), 6.22 (1H, dd, J = 5.7, 3.1 Hz), 7.10 (2H, AA′ of AA′BB′, J = 8.1 Hz), 7.39 (2H, m), 7.65 (2H, m); δ_C(100.6 MHz; $CDCl_3$) 21.38, 29.02, 42.52, 45.01, 48.29, 65.70, 126.37 (2), 127.37 (2), 129.05 (2), 129.76 (2), 131.43, 132.81, 133.95, 139.04, 141.33, 141.44. Discernible data for the 5% isomer: δ_H(400 MHz; $CDCl_3$) 1.67 (1H, ~d, J = 10.0 Hz), 1.91 (1H, ddd, J = 13.0, 4.0, 4.0 Hz), 2.42 (1H, s), 2.61 (1H, s), 3.25 (1H, s), 5.85 (1H, dd, J = 5.0, 4.0 Hz), 6.20 (1H, dd, J = 6.0, 3.6 Hz), 7.22 (2H, AA′ of AA′BB′, J = 8.0 Hz), 7.78 (2H, m); δ_C(100.6 MHz; $CDCl_3$) 21.05, 29.32, 41.94, 44.83, 46.05, 63.93.

***endo-syn*-*S*-(Bicyclo[2.2.1]hept-5-en-2-yl)-*S*-phenyl-*N*-tosylsulfimide 6d.** The only discernible peak in the ^1H NMR spectrum was: δ_H(400 MHz; $CDCl_3$) 6.15 (dd, J = 6.0, 3.6 Hz). Mixture: $\nu_{max}(CHCl_3)/cm^{-1}$ 1598, 1494, 1476, 1445, 1338, 1295, 1282, 1142, 1089, 1022, 1006, 971, 816; *m*/*z* (CI; NH_3) 372 (2%, MH^+), 203 (22), 136 (33), 84 (100), 65 (37).

(*Z*)-Phenylethenyl *p*-tolyl sulfide 10[25]

To a solution of sodium (1.85 g, 80.4 mmol) in absolute ethanol (100 cm^3) was added thiocresol (10.0 g, 80.5 mmol) and phenylacetylene (9.70 cm^3, 80.4 mmol). The mixture was refluxed for 2 days. After standing for a further 2 days, the mixture was poured into water (100 cm^3) and dichloromethane (100 cm^3) was added. The organic layer was separated, and the aqueous layer was extracted twice with dichloromethane (100 cm^3). The combined organic layers were dried over anhydrous magnesium sulfate and concentrated *in vacuo*, giving exclusively sulfide **10** (14.72 g, 81%), mp 62–64.5 °C (lit.,[25] 64–65.5 °C); R_f (MeOH): 0.80 (Found: C, 79.57; H, 6.22. $C_{15}H_{14}S$ requires C, 79.64; H, 6.19%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1599, 1588, 1494, 1445, 1358, 1094, 1019, 849, 810; δ_H(250 MHz; $CDCl_3$) 2.42 (3H, s, Me), 6.56 (1H, d, J = 10.8 Hz, CHPh), 6.64 (1H, d, J = 10.8 Hz, CHS), 7.23 (2H, AA′ of AA′BB′, J = 7.9 Hz, *p*-tolyl), 7.30 (5H, m, Ph), 7.65 (2H, BB′ of AA′BB′, J = 7.9 Hz, *p*-tolyl); δ_C(62.9 MHz; $CDCl_3$) 21.10 (Me), 126.49 (2), 127.02 (2), 127.05 (2), 128.32 (2), 128.74, 129.96, 130.50, 132.67, 136.58, 137.38; *m*/*z* (EI) 226 (100%, M^+), 211 (30), 91 (25), 77 (23).

(*Z*)-*S*-2-Phenylethenyl-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 11

An adaptation of a literature method was used.[23a] To a solution of sulfide **10** (6.00 g, 26.5 mmol) and hexadecyltributylphosphonium bromide (0.675 g, 1.3 mmol) in dichloromethane (200 cm^3) was added *N*-chloramine-T hydrate (7.75 g, 27.5 mmol) and the mixture was stirred for 2 days. The reaction mixture was washed with 5% aqueous sodium hydroxide solution (200 cm^3) and the organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was then evaporated, leaving a yellow oil, which was purified by flash chromatography on silica gel using chloroform–ethyl acetate (9:1) as eluant. White crystals of a mixture of (*E*) and (*Z*) sulfimides (10:90) were obtained which on trituration yielded (*Z*)-**11** (7.95 g, 75%); R_f ($CHCl_3$): 0.35; mp 123.5–125 °C (Found: C, 66.32; H, 5.33; N, 3.61. $C_{22}H_{21}NO_2S_2$ requires C, 66.84; H, 5.32; N, 3.54%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1597, 1492, 1446, 1297, 1284, 1143, 1088, 967; δ_H(250 MHz; $CDCl_3$) 2.32 (3H, s, tolyl Me), 2.38 (3H, s, tosyl Me), 6.33 (1H, d, J = 10.0 Hz, =CHPh), 7.10 (2H, AA′ of AA′BB′, J = 7.8 Hz, tolyl), 7.13 (1H, d, J = 10.0 Hz, =CHS), 7.27 (2H, AA′ of AA′BB′, J = 7.8 Hz, tosyl), 7.38 (5H, m, Ph), 7.54 (2H, BB′ of AA′BB′, J = 7.8 Hz, tolyl), 7.70 (2H, BB′ of AA′BB′, J = 7.8 Hz, tosyl); δ_C(62.9 MHz; $CDCl_3$) 21.30 (2 × Me), 126.05 (2), 126.24 (2), 128.76 (2), 128.99 (2), 129.43 (2), 130.09, 130.51 (2), 132.42, 132.58, 141.20, 141.36, 141.40, 142.77 (one C missing); *m*/*z* (CI; NH_3) 396 (5.4%, MH^+), 227 (100), 226 (74), 189 (34), 124 (28), 108 (21), 91 (45).

(*E*)-*S*-[2-(4-Methoxyphenyl)ethenyl]-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 16a

To a solution of *S*-methyl-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide **14** (1.0 g, 3.26 mmol) in THF (100 cm^3) at −78 °C under nitrogen were added dropwise *n*-BuLi (2.5 M, 1.3 cm^3, 3.26 mmol), potassium *tert*-butoxide (1.0 M, 3.27 cm^3, 3.26 mmol) and diethyl chlorophosphate (0.47 cm^3, 3.26 mmol). After stirring for 10 min, *p*-anisaldehyde (0.4 cm^3, 3.26 mmol) in THF (2 cm^3) was added dropwise and the reaction left to warm to 0 °C over 30 min. Saturated aqueous ammonium chloride (100 cm^3) was added, along with sufficient water to dissolve any salts precipitated, and the reaction extracted with dichloromethane (3 × 80 cm^3). The combined organic layers were washed with water (150 cm^3) and dried over magnesium sulfate, filtered and concentrated under reduced pressure. A ^1H NMR spectrum of the crude product (60% yield) showed an (*E*:*Z*) ratio of 80:20. Column chromatography of the yellow oil on silica using ether as eluant separated the stereoisomers. The major product was the (*E*) isomer **16a** (0.67 g, 48%), mp 122–124 °C; R_f 0.30 (ether) (Found: C, 64.91; H, 5.45; N, 3.29. $C_{23}H_{23}NO_3S_2$ requires C,

64.81; H, 5.39; N, 3.23%); ν_{max}(Nujol)/cm^{-1} 1602, 1512, 1465, 1307, 1293, 1170, 1136, 1087, 959, 802; δ_H(250 MHz; $CDCl_3$) 2.29 (3H, s, Me tolyl), 2.36 (3H, s, Me tosyl), 3.79 (3H, s, MeO), 6.42 (1H, dd, J = 15.1, 0.9 Hz, =CHAr), 6.85 (2H, AA′ of AA′BB′, $MeOC_6H_4$), 7.13 (AA′ of AA′BB′, tolyl), 7.25 (AA′ of AA′BB′, tosyl), 7.26 (1H, d, J = 15.1 Hz, =CHS), 7.30 (2H, BB′ of AA′BB′, $MeOC_6H_4$), 7.55 (BB′ of AA′BB′, tolyl), 7.76 (BB′ of AA′BB′, tosyl); δ_C(62.9 MHz; $CDCl_3$) 21.3 (2 × Me), 55.4 (MeO), 114.3, 119.8 (=CHAr), 125.3, 126.2, 126.6, 129.0, 129.7, 130.5, 132.3, 141.3, 141.4, 141.5, 142.9, 161.6 (=CHS); *m*/*z* (EI) 426 (2%, MH$^+$), 256 (100), 241 (21), 211 (35), 91 (76).

(*E*)-*S*-(2-Phenylethenyl)-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 16b

To a solution of *S*-methyl-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide **14** (4.0 g, 0.013 mol) in THF (300 cm^3) at −78 °C under nitrogen were added dropwise *n*-BuLi (2.5 M, 5.2 cm^3, 0.013 mol), potassium *tert*-butoxide (1.0 M, 13 cm^3, 0.013 mol) and diethyl chlorophosphate (1.88 cm^3, 2.0 mol). After stirring for 10 min, benzaldehyde (1.32 cm^3, 0.013 mmol) in THF (5 cm^3) was added dropwise and the reaction left to warm to 0 °C over 30 min. Saturated aqueous ammonium chloride (300 cm^3) was added, along with sufficient water to dissolve any salts precipitated, and the reaction extracted with dichloromethane (3 × 150 cm^3). The combined organic layers were washed with water (300 cm^3) and dried over magnesium sulfate, filtered and concentrated under reduced pressure. A ^{1}H NMR spectrum of the crude product (48% yield) showed an (*E*:*Z*) ratio of 85:15. Column chromatography of the yellow oil on silica using chloroform–ethyl acetate 4:1 as eluant separated the stereoisomers. The major product was the (*E*) isomer **16b** (1.95 g, 38%), mp 121–122 °C; R_f 0.33 (ether) (Found: C, 66.80; H, 5.35; N, 3.54. $C_{22}H_{21}NO_2S_2$ requires C, 66.90; H, 5.33; N, 3.46%); ν_{max}(Nujol)/cm^{-1} 1662, 1601, 1491, 1307, 1138, 661; δ_H(400 MHz; $CDCl_3$) 2.30 (3H, s, Me tolyl), 2.37 (3H, s, Me tosyl), 6.55 (1H, d, J = 15.2 Hz, =CHPh), 7.14 (2H, AA′ of AA′BB′, tolyl), 7.26 (2H, AA′ of AA′BB′, tosyl), 7.32 (1H, d, J = 15.2 Hz, =CHS), 7.35 (5H, m, Ph), 7.55 (2H, BB′ of AA′BB′, tolyl), 7.76 (2H, BB′ of AA′BB′, tosyl); δ_C(100.6 MHz; $CDCl_3$) 21.30 (Me tolyl), 21.38 (Me tosyl), 122.70 (=CHPh), 126.23, 126.82, 128.91, 129.07, 129.43, 130.56, 130.76, 132.00, 132.70, 141.07 (=CHS), 141.40, 141.54, 143.20; *m*/*z* (FAB) 396 (100%, MH$^+$), 227 (92), 226 (100).

The minor isomer (*Z*)-*S*-(2-phenylethenyl)-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide **11** was also isolated (9%), mp 124–125 °C; spectra identical to **11** above.

(*E*)-*S*-[2-(4-Chlorophenyl)ethenyl]-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 16c

To a solution of *S*-methyl-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide **14** (4.0 g, 0.013 mol) in THF (300 cm^3) at −78 °C under nitrogen were added dropwise *n*-BuLi (2.5 M, 5.2 cm^3, 0.013 mol), potassium *tert*-butoxide (1.0 M, 13 cm^3, 0.013 mol) and diethyl chlorophosphate (1.88 cm^3, 2.0 mol). After stirring for 10 min, benzaldehyde (1.32 cm^3, 0.013 mmol) in THF (5 cm^3) was added dropwise and the reaction left to warm to 0 °C over 30 min. Saturated aqueous ammonium chloride (300 cm^3) was added, along with sufficient water to dissolve any salts precipitated, and the reaction extracted with dichloromethane (3 × 150 cm^3). The combined organic layers were washed with water (300 cm^3) and dried over magnesium sulfate, filtered and concentrated under reduced pressure. A ^{1}H NMR spectrum of the crude product (40% yield) showed an (*E*:*Z*) ratio of 95:5. Column chromatography of the yellow oil on silica using chloroform–ethyl acetate 4:1 as eluant was used to isolate the (*E*) isomer (1.95 g, 38%), mp 108–109 °C; R_f 0.43 (ether) (Found: C, 61.16; H, 4.66; N, 3.18. $C_{22}H_{20}ClNO_2S_2$ requires C, 61.45; H, 4.69; N, 3.18%); ν_{max}(Nujol)/cm^{-1} 1652, 1491, 1307, 1138, 955, 803, 774, 661; δ_H(400 MHz; $CDCl_3$) 2.32 (3H, s, Me tolyl), 2.40 (3H, s, Me tosyl), 6.54 (1H, d, J = 15.1 Hz, =CHPh), 7.16 (2H, AA′ of AA′BB′, tolyl), 7.26 (1H, d, J = 15.1 Hz, =CHS), 7.31 (6H, m, tosyl and *p*-ClC_6H_4), 7.55 (2H, BB′ of AA′BB′, tolyl), 7.76 (2H, BB′ of AA′BB′, tosyl); δ_C(100.6 MHz; $CDCl_3$) 21.4 (Me tolyl and tosyl), 123.26 (=CHPh), 126.11, 126.80, 129.02, 129.07, 129.21, 131.22, 131.61, 132.07, 136.32, 139.07, 141.36 (=CHS), 141.58, 143.21; *m*/*z* (FAB) 430 (49%, MH$^+$).

(*E*)-*S*-(3-Methylbut-1-enyl)-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 16e

To a solution of *S*-methyl-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide **14** (1.0 g, 3.26 mmol) in THF (100 cm^3) at −78 °C under nitrogen were added dropwise *n*-BuLi (2.5 M, 1.3 cm^3, 3.26 mmol), potassium *tert*-butoxide (1.0 M, 3.27 cm^3, 3.26 mmol) and diethyl chlorophosphate (0.47 cm^3, 3.26 mmol). After stirring for 10 min, isobutyraldehyde (0.30 cm^3, 3.26 mmol) in THF (1 cm^3) was added dropwise and the reaction left to warm to 0 °C over 30 min. Saturated aqueous ammonium chloride (100 cm^3) was added, along with sufficient water to dissolve any salts precipitated, and the reaction extracted with dichloromethane (3 × 80 cm^3). The combined organic layers were washed with water (150 cm^3) and dried over magnesium sulfate, filtered and concentrated under reduced pressure. A ^{1}H NMR spectrum of the crude product (64% yield) showed an (*E*:*Z*) ratio of >98:2. Column chromatography of the yellow oil on silica using ether as eluant separated the stereoisomers. The major product was the (*E*) isomer **16e** (0.41 g, 35%), mp 108–110 °C; R_f 0.37 (ether); ν_{max}(Nujol)/cm^{-1} 1602, 1490, 1284, 1138, 1088, 1021, 962; δ_H(250 MHz; $CDCl_3$) 0.97 (6H, 2 × d, J = 7.0 Hz, Me), 2.33 (3H, s, Me tolyl), 2.36 (3H, s, Me tosyl), 2.41 (1H, m, C*H*Me), 5.94 (1H, dd, J = 15.0, 1.3 Hz, =CHS), 6.55 (1H, dd, J = 15.0, 6.4 Hz, =CHR), 7.15 (AA′ of AA′BB′, tolyl), 7.25 (AA′ of AA′BB′, tosyl), 7.47 (BB′ of AA′BB′, tolyl), 7.72 (BB′ of AA′BB′, tosyl); δ_C(62.9 MHz; $CDCl_3$) 20.8 (Me), 20.9 (Me), 21.3 (2 × ArMe), 31.3 (*C*HMe), 123.1 (=CHR), 126.2, 126.5, 129.0, 130.4, 132.0, 141.1, 141.5, 142.9, 151.7 (=CHS); *m*/*z* (CI/NH_3) 362 (100%, MH$^+$).

(*E*)-*S*-(3,3-Dimethylbut-1-enyl)-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 16f

To a solution of *S*-methyl-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide **14** (1.0 g, 3.26 mmol) in THF (100 cm^3) at −78 °C under nitrogen were added dropwise *n*-BuLi (2.5 M, 1.3 cm^3, 3.26 mmol), potassium *tert*-butoxide (1.0 M, 3.27 cm^3, 3.26 mmol) and diethyl chlorophosphate (0.47 cm^3, 3.26 mmol). After stirring for 10 min, pivalaldehyde (0.354 cm^3, 3.26 mmol) in THF (1 cm^3) was added dropwise and the reaction left to warm to 0 °C over 30 min. Saturated aqueous ammonium chloride (100 cm^3) was added, along with sufficient water to dissolve any salts precipitated, and the reaction extracted with dichloromethane (3 × 80 cm^3). The combined organic layers were washed with water (150 cm^3) and dried over magnesium sulfate, filtered and concentrated under reduced pressure. A ^{1}H NMR spectrum of the crude product (39% yield) showed an (*E*:*Z*) ratio of >98:2. After column chromatography of the yellow oil on silica using ether as eluant, the major product was the (*E*) isomer **16f** (0.48 g, 39%), mp 146–147 °C; R_f 0.46 (ether) (Found: C, 63.96; H, 6.76; N, 3.73. $C_{20}H_{25}NO_2S_2$ requires C, 63.82; H, 6.66; N, 3.71%); ν_{max}(Nujol)/cm^{-1} 1598, 1492, 1284, 1141, 1089, 1021, 962; δ_H(250 MHz; $CDCl_3$) 0.98 (9H, s, Me), 2.32 (3H, s, Me tolyl), 2.36 (3H, s, Me tosyl), 5.89 (1H, d, J = 15.0 Hz, =CHS), 6.53 (1H, d, J = 15.0 Hz, =CHR), 7.15 (AA′ of AA′BB′, tolyl), 7.25 (AA′ of AA′BB′, tosyl), 7.47 (BB′ of AA′BB′, tolyl), 7.73 (BB′ of AA′BB′, tosyl); δ_C(62.9 MHz; $CDCl_3$) 21.3 (2 × ArMe), 28.3 (Me), 126.2 (=CHR), 126.5, 126.6, 129.0, 130.4, 132.1, 141.4, 141.6, 142.9, 155.3 (=CHS); *m*/*z* (CI/NH_3) 376 (100%, MH$^+$), 220 (43), 207 (26), 206 (17).

S-(2-Cyclopropylethenyl)-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 16g

To a solution of *S*-methyl-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide **14** (614 mg, 2.0 mmol) in THF (40 cm^3) at −78 °C under nitrogen were

added dropwise *n*-BuLi (2.5 M, 0.80 cm^3, 2.0 mmol), potassium *tert*-butoxide (1.0 M, 2.0 cm^3, 2.0 mmol) and diethyl chlorophosphate (0.29 cm^3, 2.0 mmol). After stirring for 10 min, cyclopropanecarbaldehyde (0.149 cm^3, 2.0 mmol) in THF (1 cm^3) was added dropwise and the reaction left to warm to 0 °C over 30 min. Saturated aqueous ammonium chloride (40 cm^3) was added, along with sufficient water to dissolve any salts precipitated, and the reaction extracted with dichloromethane (3 × 50 cm^3). The combined organic layers were washed with water (100 cm^3) and dried over magnesium sulfate, filtered and concentrated under reduced pressure. A ^1H NMR spectrum of the crude product (39% yield) showed an (*E*:*Z*) ratio of 53:47. Column chromatography of the yellow oil on silica using ether as eluant led to a mixture of inseparable stereoisomers (0.28 g, 39%) (Found: MH^+ 360.1104. $C_{20}H_{25}NO_2S_2$ requires 360.1092); ν_{max}(Nujol)/cm^{-1} 1606, 1292, 1280, 1142, 1089, 981, 734, 661.

(*E*)-*S*-(2-Cyclopropylethenyl)-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 16g. δ_H(250 MHz; $CDCl_3$) 0.59 (2H, m, CH_2), 0.99 (2H, m, CH_2), 2.03 (1H, m, CH), 2.36 (3H, s, Me tolyl), 2.39 (3H, s, Me tosyl), 5.58 (1H, dd, *J* = 10.8, 9.0 Hz, =CHR), 6.04 (1H, dd, *J* = 9.0, 0.6 Hz, =CHS), 7.18 (AA′ of AA′BB′, tolyl), 7.28 (AA′ of AA′BB′, tosyl), 7.57 (BB′ of AA′BB′, tolyl), 7.79 (BB′ of AA′BB′, tosyl); δ_C(62.9 MHz; $CDCl_3$) 8.7 (CH_2), 9.1 (CH_2), 12.4 (CH), 21.3 (2 × ArMe), 123.9 (=CHR), 125.9, 126.3, 129.0, 130.4, 132.6, 141.3, 141.7, 142.3, 150.6 (=CHS).

(*Z*)-*S*-(2-Cyclopropylethenyl)-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide. δ_H(250 MHz; $CDCl_3$) 0.58 (2H, m, CH_2), 0.93 (2H, m, CH_2), 1.53 (1H, m, CH), 2.35 (3H, s, Me tolyl), 2.38 (3H, s, Me tosyl), 6.01 (1H, dd, *J* = 10.8, 14.5 Hz, =CHR), 6.02 (1H, d, *J* = 14.5 Hz, =CHS), 7.16 (AA′ of AA′BB′, tolyl), 7.26 (AA′ of AA′BB′, tosyl), 7.49 (BB′ of AA′BB′, tolyl), 7.74 (BB′ of AA′BB′, tosyl); δ_C(62.9 MHz; $CDCl_3$) 8.7 (2 × CH_2), 14.5 (CH), 21.3 (2 × ArMe), 121.2 (=CHR), 126.2, 126.5, 129.0, 130.4, 132.3, 141.3, 141.6, 142.7, 150.7 (=CHS); *m*/*z* (FAB) 360 (100%, MH^+), 190 (14), 123 (46).

(*RS*,*SR*)-*S*-[2-Phenyl-2-(phenylmethoxy)ethyl]-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 17a

A solution of vinyl sulfimide **16b** (200 mg, 0.5 mmol) and sodium hydride (60%; hexane washed, 4 mg, 20 mol%) in benzyl alcohol (30 cm^3) was stirred at room temperature for 3 days. Water (50 cm^3) was added and then the aqueous solution was extracted with CH_2Cl_2 (3 × 20 cm^3). The combined organic extracts were dried over magnesium sulfate and evaporated to dryness to leave a white residue (>95% de). Column chromatography on silica with 10% chloroform–ethyl acetate as eluant followed by recrystallisation from ether–petroleum ether yielded **17a** as a white powder (165 mg, 64%), mp 146–148 °C; R_f 0.44 (10% chloroform–ethyl acetate) (Found: C, 68.83; H, 5.79; N, 2.77. $C_{29}H_{29}NO_3S_2$ requires C, 69.15; H, 5.80; N, 2.78%) (Found: 504.1670; MH^+ requires 504.1669); ν_{max}(Nujol)/cm^{-1} 1283, 1140, 1116, 1090, 967, 725, 656; δ_H(400 MHz; $CDCl_3$) 2.33 (3H, s, Me tolyl), 2.35 (3H, s, Me tosyl), 3.15 (dd, *J* = 10.7, 12.8 Hz, CH^aS), 3.27 (1H, dd, *J* = 2.3, 12.8 Hz, CH^bS), 4.05 (1H, AB, *J* = 10.5, CH_2Ph), 4.20 (1H, AB, *J* = 10.5 Hz, CH_2Ph), 4.84 (1H, dd, *J* = 2.3, 10.7 Hz, CHPh), 7.18 (2H, AA′ of AA′BB′, tolyl), 7.25 (2H, AA′ of AA′BB′, tosyl), 7.30 (10H, m, Ar), 7.60 (2H, BB′ of AA′BB′, tolyl), 7.81 (2H, BB′ of AA′BB′, tosyl); δ_C(100.6 MHz; $CDCl_3$) 21.27 (Me tolyl), 21.34 (Me tosyl), 62.43 (CH_2S), 70.99 (CH_2Ph), 74.96 (CH), 125.89, 126.80, 126.52, 127.74, 127.81, 128.25, 128.74, 128.99, 129.13, 130.45, 132.10, 137.23, 137.98, 141.28, 141.50, 142.99; *m*/*z* (CI/NH_3) 504 (35%, MH^+).

(*RS*,*SR*)-*S*-(2-Phenyl-2-ethoxyethyl)-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 17b

A solution of vinyl sulfimide **16b** (200 mg, 0.5 mmol) and sodium hydride (60%; hexane washed, 4 mg, 20 mol%) in ethanol (40 cm^3) was stirred at room temperature for 5 days. Water (40 cm^3) was added and then the aqueous solution was extracted with CH_2Cl_2 (3 × 40 cm^3). The combined organic extracts were dried over magnesium sulfate and evaporated to dryness to leave a white residue (80% de). Column chromatography on silica with ether–petroleum ether (8:1) as eluant followed by recrystallisation from ether–petroleum ether (8:1) yielded **17b** as a white powder (165 mg, 73%), mp 127–129 °C; R_f 0.33 (ether–petroleum ether) (Found: C, 64.96; H, 6.04; N, 3.34. $C_{24}H_{27}NO_3S_2$ requires C, 65.28; H, 6.16; N, 3.17%); ν_{max}(Nujol)/cm^{-1} 1295, 1282, 1140, 1090, 969, 722, 656; δ_H(400 MHz; $CDCl_3$) 1.07 (3H, dd, *J* = 7.0, 7.0 Hz), 2.33 (3H, s, Me tolyl), 2.35 (3H, s, Me tosyl), 2.96 (dq, *J* = 8.8, 7.0 Hz, CH_2O), 3.05 (dd, *J* = 10.9, 12.9 Hz, CH^aS), 3.19 (1H, dd, *J* = 2.3, 12.9 Hz, CH^bS), 3.23 (1H, dq, *J* = 8.8, 7.0 Hz, CH_2O), 4.60 (1H, dd, *J* = 2.3, 10.9 Hz, CHPh), 7.18 (2H, AA′ of AA′BB′, tolyl), 7.24 (2H, AA′ of AA′BB′, tosyl), 7.25 (5H, m, Ph), 7.60 (2H, BB′ of AA′BB′, tolyl), 7.82 (2H, BB′ of AA′BB′, tosyl); δ_C(100.6 MHz; $CDCl_3$) 15.0 (Me), 21.2 (Me tolyl), 21.3 (Me tosyl), 62.3 (CH_2S), 64.6 (CH_2O), 74.6 (CH), 125.9, 126.3, 128.4, 128.7, 129.0, 130.4, 132.4, 138.5, 141.3, 141.4, 142.9; *m*/*z* (CI/NH_3) 442 (12%, MH^+).

(*RS*,*SR*)-*S*-[2-(4-Methoxyphenyl)-2-ethoxyethyl]-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 17c

A solution of vinyl sulfimide **16a** (50 mg, 0.12 mmol) and sodium hydride (60%; hexane washed, ~1 mg) in ethanol (5 cm^3) was stirred at room temperature for 5 days. Water (10 cm^3) was added and then the aqueous solution was extracted with CH_2Cl_2 (3 × 10 cm^3). The combined organic extracts were dried over magnesium sulfate and evaporated to dryness to leave a white residue (80% de). Column chromatography on silica with ethyl acetate–petroleum ether (2:3) as eluant followed by recrystallisation from ethyl acetate–petroleum ether (2:3) yielded a mixture of inseparable diastereoisomers **17c** and **18c** as a white gum (18 mg, 32%), R_f 0.33 (ethyl acetate–petroleum ether 2:3); δ_H(for **17c** only; 400 MHz; $CDCl_3$) 1.05 (3H, dd, *J* = 7.0, 7.0 Hz), 2.33 (3H, s, Me tolyl), 2.35 (3H, s, Me tosyl), 2.92 (dq, *J* = 8.8, 7.0 Hz, CH_2O), 3.04 (dd, *J* = 10.9, 12.8 Hz, CH^aS), 3.17 (1H, dd, *J* = 1.8, 12.8 Hz, CH^bS), 3.20 (1H, dq, *J* = 8.8, 7.0 Hz, CH_2O), 3.76 (3H, s, MeO), 4.55 (1H, dd, *J* = 1.8, 10.9 Hz, CHAr), 6.83 (2H, AA′ of AA′BB′, $MeOC_6H_4$), 7.17 (2H, BB′ of AA′BB′, $MeOC_6H_4$), 7.18 (2H, AA′ of AA′BB′, tolyl), 7.25 (2H, AA′ of AA′BB′, tosyl), 7.60 (2H, BB′ of AA′BB′, tolyl), 7.81 (2H, BB′ of AA′BB′, tosyl).

(*RS*,*SR*)-*S*-[2-Phenyl-2-(phenylmethylamino)ethyl]-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 17d

A solution of vinyl sulfimide **16b** (20 mg, 0.05 mmol) and sodium hydride (60%; hexane washed, 0.5 mg, 20 mol%) in benzylamine (4 cm^3) was stirred at room temperature for 24 h. Water (5 cm^3) was added and then the aqueous solution was extracted with dichloromethane (3 × 4 cm^3). The combined organic extracts were dried over magnesium sulfate and evaporated to dryness to leave a white residue (60% de). The major isomer was isolated by column chromatography on silica with 10% chloroform–ethyl acetate as eluant followed by recrystallisation from ether–petroleum ether to yield **17d** as a white powder (16.1 mg, 63%), mp 146–148 °C; R_f 0.66 (10% EtOAc–$CHCl_3$) (Found: C, 69.27; H, 6.07; N, 5.50. $C_{29}H_{30}N_2O_2S_2$ requires C, 69.29; H, 6.02; N, 5.57%); ν_{max}(Nujol)/cm^{-1} 3321, 1283, 1140, 1116, 1090, 813, 725; δ_H(400 MHz; $CDCl_3$) 2.25 (3H, s, Me tolyl), 2.35 (3H, s, Me tosyl), 3.13 (1H, dd, *J* = 10.5, 12.9 Hz, CH^aS), 3.35 (1H, dd, *J* = 2.2, 12.9 Hz, CH^bS), 4.06 (1H, AB, *J* = 10.5 Hz, CH_2Ph), 4.27 (1H, AB, *J* = 10.5 Hz, CH_2Ph), 4.81 (1H, dd, *J* = 2.2, 10.5 Hz, CHPh), 7.10 (2H, AA′ of AA′BB′, tolyl), 7.24 (2H, AA′ of AA′BB′, tosyl), 7.30 (10H, m, Ph), 7.66 (2H, BB′ of AA′BB′, tolyl), 7.84

(2H, BB′ of AA′BB′, tosyl); δ_C(100.6 MHz; $CDCl_3$) 21.2 (Me tolyl), 21.3 (Me tosyl), 62.5 (CH_2S), 71.0 (CH_2Ph), 74.96 (CH), 125.90, 126.34, 126.89, 127.58, 127.77, 128.26, 128.96, 129.10, 130.45, 132.2, 134.04, 138.0, 139.14, 139.94, 141.12, 141.92; *m*/*z* (CI/NH_3) 503 (3%, MH^+), 310 (42), 210 (53), 188 (100).

(*RS*,*SR*)-*S*-[2-(4-Chlorophenyl-2-(phenylmethylamino)ethyl]-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 17e

A solution of vinyl sulfimide **16c** (21.5 mg, 0.05 mmol) and sodium hydride (60%; hexane washed, 0.5 mg, 20 mol%) in benzylamine (4 cm^3) was stirred at room temperature for 24 h. Water (5 cm^3) was added and then the aqueous solution was extracted with dichloromethane (3 × 4 cm^3). The combined organic extracts were dried over magnesium sulfate and evaporated to dryness to leave a yellow oil (60% de). The major isomer was isolated by column chromatography on silica with 10% chloroform–ethyl acetate as eluant followed by recrystallisation from ether–petroleum ether to yield **17e** as a yellow solid (18.2 mg, 57%); R_f 0.64 ($CHCl_3$–EtOAc 4:1) (Found: C, 64.24; H, 5.27; N, 5.26. $C_{29}H_{29}ClN_2O_2S_2$ requires C, 64.85; H, 5.44; N, 5.21%); ν_{max}(Nujol)/cm^{-1} 3321, 1281, 1142, 1090, 813, 755, 736; δ_H(400 MHz; $CDCl_3$) 2.33 (3H, s, Me tolyl), 2.35 (3H, s, Me tosyl), 2.92 (1H, AB, CH_2Ph), 3.04 (1H, dd, *J* = 10.9, 12.8 Hz, CH^aS), 3.18 (1H, dd, *J* = 2.4, 12.8 Hz, CH^bS), 3.35 (1H, AB, CH_2Ph), 4.62 (1H, dd, *J* = 2.4, 10.9 Hz, CHAr), 6.83 (2H, AA′ of AA′BB, *p*-ClC_6H_4), 7.17 (2H, BB′ of AA′BB′, *p*-ClC_6H_4), 7.18 (2H, AA′ of AA′BB′, tolyl), 7.24 (2H, AA′ of AA′BB′, tosyl), 7.35 (5H, m, Ar), 7.60 (2H, BB′ of AA′BB′, tolyl), 7.81 (2H, BB′ of AA′BB′, tosyl); δ_C(100.6 MHz; $CDCl_3$) 21.2 (Me tolyl), 21.3 (Me tosyl), 62.45 (CH_2S), 71.09 (CH_2Ph), 75.06 (CH), 125.98, 126.84, 127.00, 127.67, 127.97, 128.00, 128.47, 128.96, 129.19, 130.49, 132.42, 134.08, 138.0, 139.98, 141.22, 143.12; *m*/*z* (CI/NH_3) 538 (5%, MH^+).

General procedure for the reaction of vinyl sulfimides 16 with isopropylamine

Vinyl sulfimide **16** was stirred with a small amount of NaH in isopropylamine (15 cm^3) under nitrogen at room temperature. The reaction was monitored by TLC. On completion (about 6 h) the excess amine was removed *in vacuo*. The remaining solid was extracted into ether (30 cm^3) and washed with water (2 × 20 cm^3), dried using magnesium sulfate and concentrated *in vacuo* yielding a yellow oil. The crude product was purified by column chromatography on silica gel (chloroform–ethyl acetate 4:1).

***S*-[2-Phenyl-2-(isopropylamino)ethyl]-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 17f (*RS*,*SR*) and 18f (*RR*,*SS*).** Using vinyl sulfimide **16b** (90 mg, 0.22 mmol), the desired product was obtained as a yellow oil as an inseparable mixture of the two diastereoisomers **17f** and **18f** (80:20) (55.7 mg, 53%); R_f 0.43 (Found: C, 60.04; H, 6.62; N, 5.82. $C_{25}H_{30}N_2O_2S_2$ requires C, 59.99; H, 6.65; N, 6.06%); ν_{max}(Nujol)/cm^{-1} 3431 (N–H stretch), 1598, 1342, 1089, 803; δ_H(400 MHz; $CDCl_3$) 0.82 (d, *J* = 6.1 Hz, Me(**17**)), 0.92 (m, Me(**17**), 2 × Me(**18**)), 2.32 (s, Me tolyl(**17**)), 2.34 (s, Me tolyl(**18**)), 2.35 (s, Me tosyl(**17**)), 2.38 (s, Me tosyl(**18**)), 2.48 (m, C*H*Me(**17**) and C*H*Me(**18**)), 3.02 (m, CH^aS(**17**) and CH^aS(**18**)), 3.23 (dd, *J* = 3.0, 12.8 Hz, CH^bS(**17**)), 3.47 (dd, *J* = 7.5, 12.8 Hz, CH^bS(**18**)), 3.79 (dd, *J* = 7.2, 7.2 Hz, CHPh(**18**)), 4.24 (dd, *J* = 3.0, 10.5 Hz, CHPh(**17**)), 7.00 (AA′ of AA′BB, *J* = 8.0 Hz, tolyl), 7.13 (AA′ of AA′BB, *J* = 8.0 Hz, tosyl), 7.24 (m, Ph), 7.68 (BB′ of AA′BB′, *J* = 8.2 Hz, tolyl), 7.73 (BB′ of AA′BB′, *J* = 8.2 Hz, tosyl); δ_C(for **17f**; 100.6 MHz; $CDCl_3$) 21.44 (Me tolyl), 22.57 (Me tosyl), 23.82 (Me), 29.59 (Me), 45.53 (CH_2S), 55.30 (*C*HMe), 61.72 (CHPh), 126.04, 126.70, 126.83, 127.71, 128.13, 128.96, 129.43, 130.29, 131.01, 139.95, 141.29, 143.33; *m*/*z* (EI) 455 ($M^{+\bullet}$, 15.2%).

***S*-[2-(4-Chlorophenyl)-2-(isopropylamino)ethyl]-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 17g (*RS*,*SR*) and 18g (*RR*,*SS*).** Vinyl sulfimide **16c** (21.5 mg, 0.05 mmol) gave the desired product as a yellow oil as an inseparable mixture of the two diastereoisomers **17g** and **18g** (80:20) (18.3 mg, 69%); R_f 0.54 (Found: C, 61.37; H, 5.96; N, 5.76. $C_{25}H_{29}ClN_2O_2S_2$ requires C, 61.39; H, 5.98; N, 5.73%); ν_{max}(Nujol)/cm^{-1} 3431 (N–H), 1598, 1342, 1089, 809; δ_H(400 MHz; $CDCl_3$) 0.82 (d, *J* = 6.1 Hz, Me(**17**)), 0.92 (m, Me(**17**), 2 × Me(**18**)), 2.32 (s, Me tolyl(**17**)), 2.34 (s, Me tolyl(**18**)), 2.35 (s, Me tosyl(**17**)), 2.38 (s, Me tosyl(**18**)), 2.48 (m, C*H*Me(**17**) and C*H*Me(**18**)), 3.02 (m, CH^aS(**17**) and CH^aS(**18**)), 3.25 (dd, *J* = 3.0, 12.8 Hz, CH^bS(**17**)), 3.47 (dd, *J* = 7.2, 12.8 Hz, CH^bS(**18**)), 3.79 (dd, *J* = 7.2, 7.2 Hz, CHAr(**18**)), 4.24 (dd, *J* = 3.0, 10.5 Hz, CHAr(**17**)), 6.83 (AA′ of AA′BB, *p*-ClC_6H_4), 7.01 (BB′ of AA′BB′, *p*-ClC_6H_4), 7.17 (AA′ of AA′BB′, *J* = 8.2 Hz, tolyl), 7.28 (AA′ of AA′BB′, *J* = 8.2 Hz, tosyl), 7.68 (BB′ of AA′BB′, *J* = 8.2 Hz, tolyl), 7.73 (BB′ of AA′BB′, *J* = 8.2 Hz, tosyl); δ_C(for **17g**; 100.6 MHz; $CDCl_3$) 21.32 (Me tolyl), 22.47 (Me tosyl), 23.75 (Me), 29.59 (Me), 45.65 (CH_2S), 54.77 (*C*HMe), 61.32 (CHPh), 123.90, 126.25, 126.64, 128.24, 128.99, 129.43, 130.46, 130.96, 133.88, 138.32, 141.29, 143.09; *m*/*z* (EI) 454 (65%, M − $Cl^{+\bullet}$).

General procedure for the reaction of vinyl sulfimides 16 with diethylamine

Vinyl sulfimide **16** was stirred with a small amount of NaH in diethylamine (5 cm^3) under nitrogen at room temperature. The reaction was refluxed (3 days), then the excess amine was removed *in vacuo* and the resulting white solid extracted into ether (10 cm^3) and washed with water (2 × 10 cm^3) and dried using magnesium sulfate. The ether layer was concentrated *in vacuo* to yield a brown solid. The product was purified by column chromatography on silica using chloroform–ethyl acetate 4:1.

***S*-[2-Phenyl-2-(diethylamino)ethyl]-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 17h and 18h.** Using vinyl sulfimide **16b** (20 mg, 0.05 mmol), the desired product was obtained as a yellow oil as an inseparable mixture of the two diastereoisomers **17h** and **18h** (11.4 mg, 46%) in 70% de. The configurations of the two isomers are uncertain. ^1H NMR data for the minor isomer are indicated by a prime; R_f 0.78 ($CHCl_3$–EtOAc 4:1) (Found: C, 66.60; H, 6.81; N, 5.95. $C_{26}H_{32}N_2O_2S_2$ requires C, 66.63; H, 6.88; N, 5.98%); ν_{max}(neat)/cm^{-1} 3030, 1455, 1337, 1092, 805; δ_H(400 MHz; $CDCl_3$) 1.29–1.42 (m, 2 × Me and 2 × Me′), 2.31 (s, Me tolyl), 2.34 (s, Me tolyl′), 2.35 (s, Me tosyl), 2.37 (s, Me tosyl′), 2.85 (m, CH^aS and CH^aS'), 3.00 (m, 2 × CH_2N and 2 × CH_2N'), 3.54 (m, CH^bS and CH^bS'), 4.67 (dd, *J* = 6.2, 12.9 Hz, CHPh), 5.00 (dd, *J* = 6.2, 6.2 Hz, CHPh′), 7.01 (AA′ of AA′BB′, *J* = 8.4 Hz, tolyl), 7.14 (AA′ of AA′BB′, *J* = 8.4 Hz, tosyl), 7.24 (m, Ph), 7.52 (BB′ of AA′BB′, *J* = 8.4 Hz, tolyl), 7.80 (BB′ of AA′BB′, *J* = 8.4 Hz, tosyl); δ_C(major isomer only; 100.6 MHz; $CDCl_3$) 22.99 (Me tolyl), 23.22 (Me tosyl), 29.01 (Me), 30.01 (Me), 41.85 (CH_2S), 51.14 (2 × CH_2N), 61.57 (CH), 125.71, 126.64, 127.50, 127.96, 128.32, 129.00, 129.43, 130.46, 130.96, 133.88, 138.32, 141.29; *m*/*z* (EI) 468 (100%, $M^{+\bullet}$).

***S*-[2-(4-Chlorophenyl-2-(diethylamino)ethyl]-*S*-*p*-tolyl-*N*-*p*-tosylsulfimide 17i and 18i.** Using vinyl sulfimide **16c** (21.5 mg, 0.05 mmol), the desired product was obtained as a yellow oil as an inseparable mixture of the two diastereoisomers **17i** and **18i** (14.9 mg, 56%) in 70% de. The configurations of the two isomers are uncertain. ^1H NMR data for the minor isomer are indicated by a prime (Found: C, 62.02; H, 6.17; N, 5.52. $C_{26}H_{31}ClN_2O_2S_2$ requires C, 62.07; H, 6.21; N, 5.57%); ν_{max}(neat)/cm^{-1} 2963, 1457, 1380, 1093, 806; δ_H(400 MHz; $CDCl_3$) 1.36 (m, 2 × Me and 2 × Me′), 2.32 (s, Me tolyl), 2.34 (s, Me tolyl′), 2.35 (s, Me tosyl), 2.37 (s, Me tosyl′), 2.85 (m,

CH^aS and CH^aS'), 3.14 (m, 2 × CH_2N and 2 × CH_2N'), 3.83 (m, CH^bS and CH^bS'), 4.69 (dd, J = 6.2, 12.9 Hz, CHAr), 5.00 (dd, J = 6.2, 6.2 Hz, CHAr′), 6.83 (AA′ of AA′BB, *p*-ClC_6H_4), 7.13 (BB′ of AA′BB′, *p*-ClC_6H_4), 7.19 (AA′ of AA′BB′, J = 8.4 Hz, tolyl), 7.30 (AA′ of AA′BB′, J = 8.4 Hz, tosyl), 7.52 (BB′ of AA′BB′, J = 8.4 Hz, tolyl), 7.80 (BB′ of AA′BB′, J = 8.4 Hz, tosyl); δ_C(for major isomer only; 100.6 MHz; $CDCl_3$) 22.97 (Me tolyl), 23.21 (Me tosyl), 29.05 (Me), 30.11 (Me), 41.95 (CH_2S), 51.04 (2 × CH_2N), 61.35 (CH), 125.21, 126.61, 127.70, 127.69, 128.23, 129.08, 129.46, 130.43, 130.69, 133.68, 138.22, 141.19; *m*/*z* (EI) 502 (100%, $M^{+\bullet}$).

Reaction of vinyl sulfimide 16e with ethanol

The experimental conditions for the synthesis of **17b**, but with isopropyl sulfimide **16e** in place of **16b**, were used. The crude ^1H NMR spectrum of the product mixture showed, by comparison with the literature data,[26] that the major product was *N*-(1,1-dimethylprop-2-enyl)toluene-*p*-sulfonamide **22**.

4-Methyl-1-[2-(phenylmethoxy)-2-phenylethylsulfanyl]benzene 23a

A solution of **17a** (8 mg, 0.016 mmol) and 10% palladium on carbon (1 mg) in degassed EtOAc (2 cm^3) was stirred at room temperature under a positive pressure of hydrogen gas for 5 days. Filtration through Celite using EtOAc as eluant and concentration under reduced pressure afforded a yellow oil. Column chromatography on silica using 10% chloroform–ethyl acetate as eluant gave a pale yellow oil (3 mg, 56%); δ_H(400 MHz; $CDCl_3$) 2.30 (3H, s, Me), 3.10 (1H, dd, J = 5.2, 13.4 Hz, CH^aS), 3.35 (1H, dd, J = 8.0, 13.4 Hz, CH^bS), 4.29 (1H, AB, J = 11.8 Hz, CH_2Ph), 4.47 (1H, dd, J = 5.2, 8.0 Hz, CHPh), 4.48 (1H, AB, J = 11.8 Hz, CH_2Ph), 7.04 (2H, AA′ of AA′BB′, tolyl), 7.21 (2H, BB′ of AA′BB′, tolyl), 7.30 (10H, m, Ar); δ_C(100.6 MHz; $CDCl_3$) 20.95 (Me), 42.32 (CH_2Ph), 70.75 (CH_2S), 79.98 (CH), 126.82, 127.65, 127.83, 128.05, 128.21, 128.53, 129.60, 130.03, 132.74, 136.03, 137.96, 140.60; *m*/*z* (CI/NH_3) 352 (100%, M + NH_4^+).

4-Methyl-1-[2-(phenylmethylamino)-2-phenylethylsulfanyl]-benzene 3d

A solution of **17d** (8 mg, 0.016 mmol) and 10% palladium on carbon (1 mg) in degassed EtOAc (2 cm^3) was stirred at room temperature under a positive pressure of hydrogen gas for 5 days. Filtration through Celite using EtOAc as eluant and concentration under reduced pressure afforded a yellow oil. Column chromatography on silica using 10% chloroform–ethyl acetate as eluant gave a pale yellow oil (3 mg, 56%); δ_H(400 MHz; $CDCl_3$) 2.30 (3H, s, Me), 3.18 (1H, dd, J = 5.2, 13.4 Hz, CH^aS), 3.42 (1H, dd, J = 8.0, 13.4 Hz, CH^bS), 4.35 (1H, AB, J = 11.8 Hz, CH_2Ph), 4.52 (1H, dd, J = 5.2, 8.0 Hz, CHPh), 4.68 (1H, AB, J = 11.8 Hz, CH_2Ph), 7.04 (2H, AA′ of AA′BB′, tolyl), 7.21 (2H, BB′ of AA′BB′, tolyl), 7.30 (10H, m, Ar); δ_C(100.6 MHz; $CDCl_3$) 21.21 (Me), 42.39 (CH_2Ph), 70.80 (CH_2S), 80.02 (CH), 126.89, 127.67, 127.93, 128.15, 128.26, 128.53, 129.66, 130.02, 132.76, 136.08, 17.99, 140.63; *m*/*z* (CI/NH_3) 351 (100%, M + NH_4^+).

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References

1 P. C. Taylor, *Sulfur Rep.*, 1999, **21**, 241.
2 For a review of particular relevance to this work see V. K. Aggarwal, A. Ali and M. P. Coogan, *Tetrahedron*, 1999, **55**, 293.
3 A.-H. Li, L.-X. Dai and V. K. Aggarwal, *Chem. Rev.*, 1997, **97**, 2341.
4 S. G. Pyne, *Sulfur Rep.*, 1999, **21**, 281.
5 (*a*) H. Takada, Y. Nishibayashi, K. Ohe, S. Uemura, C. P. Baird, T. J. Sparey and P. C. Taylor, *J. Org. Chem.*, 1997, **62**, 6512; (*b*) G. Celentano, S. Colonna, N. Gaggero and C. Richelmi, *Chem. Commun.*, 1998, 701.
6 C. P. Baird and P. C. Taylor, *J. Chem. Soc., Chem. Commun.*, 1995, 893; C. P. Baird and P. C. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1998, 3399.
7 (*a*) T. Yamamoto and M. Okawara, *Chem. Lett.*, 1975, 581; (*b*) T. Yamamoto, M. Kakimoto and M. Okawara, *Tetrahedron Lett.*, 1977, 1659; (*c*) K. Ikeda, H. Satoh and T. Yamamoto, *Org. Prep. Proced. Int.*, 1992, **24**, 548.
8 A. J. Clark, S. Rooke, T. J. Sparey and P. C. Taylor, *Tetrahedron Lett.*, 1996, **37**, 909.
9 A. J. Clark, S. M. Rooke, T. J. Sparey and P. C. Taylor, unpublished results.
10 J. L. G. Ruano, J. C. Carretero, M. C. Carreno, L. M. M. Cabrejas and A. Urbano, *Pure. Appl. Chem.*, 1996, **68**, 925; S. M. Proust and D. D. Ridley, *Aust. J. Chem.*, 1984, **37**, 1677.
11 (*a*) C. Maignan and R. A. Raphael, *Tetrahedron*, 1983, **39**, 3245; (*b*) X. Ji, D. Vanderhelm, R. V. Williams and W. J. Ebey, *Acta Crystallogr., Sect. B*, 1989, **45**, 93; (*c*) B. Ronan and H. B. Kagan, *Tetrahedron: Asymmetry*, 1991, **2**, 75.
12 R. S. Glass, K. Reineke and M. Shanklin, *J. Org. Chem.*, 1984, **49**, 1527.
13 E. Bertotti, G. Luciani and F. Montanari, *Gazz. Chim. Ital.*, 1959, **89**, 1564.
14 O. De Lucchi and L. Pasquato, *Tetrahedron*, 1988, **44**, 6755.
15 L. A. Paquette, R. E. Moerck, B. Harirchian and P. D. Magnus, *J. Am. Chem. Soc.*, 1978, **100**, 1597.
16 T. L. Gilchrist and C. J. Moody, *Chem. Rev.*, 1977, **77**, 409.
17 B. M. Trost and D. L. van Vranken, *Chem. Rev.*, 1996, **96**, 395.
18 (*a*) T. Yamamoto, M. Kakimoto and M. Okawara, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 841; (*b*) R. Annunziata, M. Cinquini, S. Colonna and F. Cozzi, *J. Chem. Soc., Perkin Trans. 1*, 1981, 3118.
19 D. J. Cram, J. Day, D. R. Rayner, D. M. von Schrilz, D. J. Duchamp and D. C. Garwood, *J. Am. Chem. Soc.*, 1970, **92**, 7369.
20 D. Craig and N. J. Geach, *Synlett*, 1992, 299.
21 S. G. Pyne, R. Griffith and M. Edwards, *Tetrahedron Lett.*, 1988, **29**, 2089.
22 S. G. Pyne, P. Bloem, S. L. Chapman, C. E. Dixon and R. Griffith, *J. Org. Chem.*, 1990, **55**, 1086; S. G. Pyne and B. Dikic, *J. Org. Chem.*, 1990, **55**, 1932.
23 (*a*) C. R. Johnson, K. Mori and A. Nakanishi, *J. Org. Chem.*, 1979, **44**, 2065; (*b*) H. Takada, Y. Nishibayashi, K. Ohe and S. Uemura, *Chem. Commun.*, 1998, 1557.
24 K. A. Hellmund, S. G. Pyne, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1992, **45**, 1923; see also A. D. Briggs, W. Clegg, M. R. J. Elsegood, C. S. Frampton and R. F. W. Jackson, *Acta Crystallogr., Sect. C*, 1998, **54**, 1335.
25 W. E. Truce and J. A. Simms, *J. Am. Chem. Soc.*, 1956, **78**, 2756.
26 R. G. Shea, J. N. Fitzner, J. E. Fankhauser, A. Spaltenstein, P. A. Carpino, R. M. Peevey, D. V. Pratt, B. J. Tenge and P. B. Hopkins, *J. Org. Chem.*, 1986, **51**, 5243.

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