Pergamon

Tetrahedron Vol. 51, No. 21, pp. 6071-6098, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00267-7

Asymmetric Intramolecular Diels–Alder Reactions of Sulfoximine-activated Trienes

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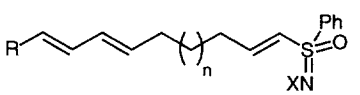
Abstract: A series of *N*-substituted sulfoximidoyl-1,6,8-nonatrienes and 1,7,9-decatrienes were synthesised and subjected to thermal intramolecular Diels–Alder (IMDA) reactions to give diastereomeric mixtures of substituted bicyclo[4.3.0]nonanes and -[4.4.0]decanes. The reactions showed varying selectivities. Endo/exo selectivity was interpreted in terms of a combination of steric factors and the asynchronous nature of the cycloadditions. Diastereofacial selectivity could be rationalised by considering attack by the diene on the less hindered face of the conformationally extended vinylic sulfoximine dienophile.

INTRODUCTION

The synthetic utility of the intramolecular Diels–Alder (IMDA) reaction stems largely from its ability to deliver structurally complex cyclic systems with frequently excellent stereoselectivities. The stereochemical outcome of IMDA processes may readily be understood in terms of diene/dienophile geometry, and concepts of asynchronicity which enable an understanding of which of the potential non-bonded interactions in the putative transition-state are likely to be important.[1] In the asymmetric mode, stereochemical information contained in the substrate (in the chain linking the diene and dienophile, or in a chiral auxiliary group) or in an external agent such as a catalyst may be conveyed to multiple asymmetric centres in the product.[2,3] The majority of research following the chiral auxiliary approach has been concerned with the covalent attachment of the auxiliary to the dienophile electron-withdrawing group, which is usually a carboxylic acid derivative. In connection with our studies on IMDA reactions of sulfonyl-substituted trienes,[4] we have investigated the thermal IMDA reactivity of trienes terminally substituted with a sulfoximine group.[5] It occurred to us that the diastereoselectivities observed in the IMDA reactions of many of the sulfone-containing substrates could usefully be expressed in absolute stereochemical terms if the sulfoximine group showed similar stereodirecting tendencies.[6] Herein we report in full[7] on our studies of asymmetric intramolecular Diels–Alder (AIMDA) reactions of sulfoximine-substituted trienes of the types shown below, and show that with careful choice of diene and dienophile substituents some members of this class of substrate exhibit synthetically useful levels of AIMDA reactivity and selectivity.

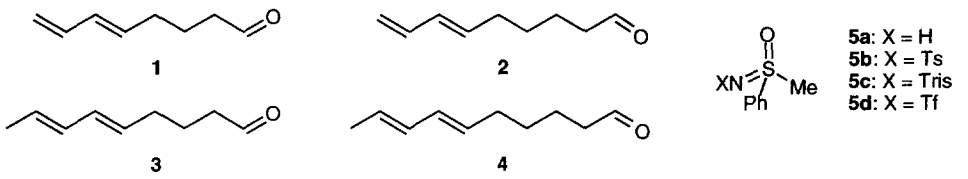


n = 1, 2
R = H, Me
X = 4-$MeC_6H_4SO_2$ (Ts), 2,4,6-(i-Pr)$_3C_6H_2SO_2$ (Tris)
F_3CSO_2 (Tf)

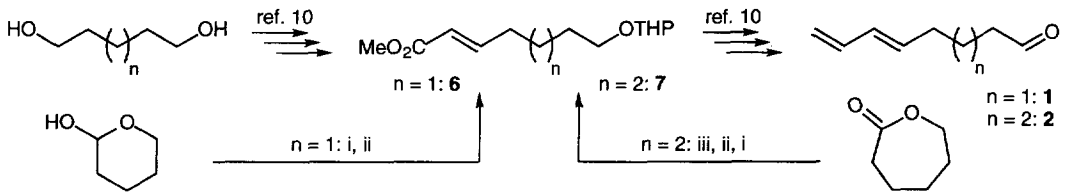
RESULTS AND DISCUSSION

Synthesis of trienes

By direct analogy with our sulfonyltriene studies, dienals **1-4** and *S*-methyl-*S*-phenylsulfoximines **5** were identified as the requisite starting materials for the synthesis of sulfoximine-substituted trienes. Initial studies focused on the terminally unsubstituted aldehydes **1** and **2**, since preparation of geometrically pure methylated dienals **3** and **4** had previously been found to be problematic.[4] *N*-(4-Tolylsulfonyl)sulfoximine **5b** was chosen as the sulfur-containing fragment; this was readily available in either enantiomerically pure form by resolution[8] of the thioanisole-derived[9] racemate followed by *N*-tosylation. Analogues **5c** and **5d** were prepared simply by reaction of the parent *N*-unsubstituted compound **5a** with the corresponding sulfonating agent.



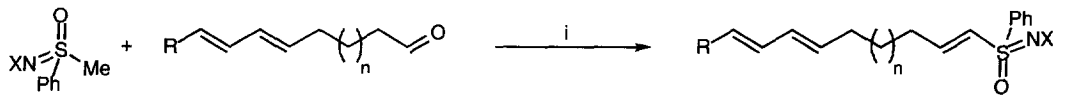
Aldehydes **1** and **2** could be accessed from respectively 1,5-pentanediol and 1,6-hexanediol,[10] or from tetrahydro-2*H*-pyran-2-ol[11] and ε-caprolactone via unsaturated esters **6** and **7** respectively. Aldehydes **3** and **4** were prepared using related sequences in which the diene portion was constructed using the Julia olefination reaction.[4] The syntheses of **1** and **2** are summarised in Scheme 1.



Reagents and conditions: (i) $Ph_3P{=}CHCO_2Me$, CH_2Cl_2; (ii) 3,4-dihydro-2*H*-pyran, CSA; (iii) DIBAL-H, PhMe.

Scheme 1

Initial attempts to introduce the vinylic sulfoximine dienophile group followed the work of Jackson,[12] but problems of removal of 1-(methylsulfonyl)butane (which is formed presumably by reaction of excess *n*-butyllithium with the sulfonating agent) from the products prompted a search for alternative methods. We had previously developed a one-pot method for the synthesis of vinylic sulfoxides via Wadsworth–Emmons reactions in which the phosphonylsulfoxide reagent was generated in situ by the reaction of a phosphorus-stabilised anion with a sulfinate ester.[13] We reasoned that a similar procedure could be applied to the synthesis of vinylic sulfoximines by reversing the polarity of the phosphorus- and sulfur-containing fragments. Thus, lithiation of (S_S)-**5b** in the usual way and and addition of one equivalent of potassium *tert*-butoxide as an auxiliary base[14] prior to treatment with diethyl chlorophosphate generated the conjugate base of (S_S)-*S*-(diethylphosphonylmethyl)-*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximine **8**. Compound **8** could be obtained in modest yield by simple proton quench; more usually, dienals were added directly to the reaction mixture to give selectively all-*E*-trienylsulfoximines in good yields after simple extractive work-up.[15] The reaction could be applied also to the synthesis of racemic *N*-(2,4,6-triisopropylphenylsulfonyl)trienylsulfoximines, although the yields were slightly lower than for the tosyl analogues in the three cases examined. The syntheses of sulfoximine-subsituted trienes **9b**, **9c**, **10b**, **10c** and **12c** are summarised in Scheme 2.



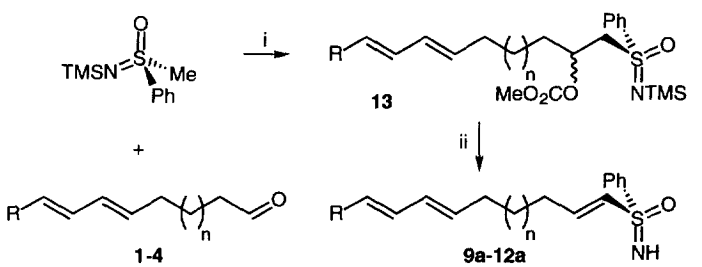
Reagents and conditions: (i) add *n*-BuLi to **5** in THF, -78°C; add *t*-BuOK, -78°C; add $(EtO)_2P(O)Cl$, -78°C; add dienal, -78°C → rt.

sulfoximine	enal	triene product	R	n	X	% yield of triene	1*E* : 1*Z* ratio[16]
(*S*S)-**5b**	**1**	**9b**	H	1	Ts	57	93:7
(*S*S)-**5b**	**2**	**10b**	H	2	Ts	60	94:6
(±)-**5c**	**1**	**9c**	H	1	Tris	55	93:7
(±)-**5c**	**2**	**10c**	H	2	Tris	51	93:7
(±)-**5c**	**4**	**12c**	Me	2	Tris	39	93:7

Scheme 2

Disappointingly, attempts to apply this methodology to the synthesis of the hitherto unreported *N*-triflyl sulfoximine-substituted trienes met with repeated failure. The high-yielding conversion of **5a** to **5d** had demonstrated that *N*-triflylation of *N*-unsubstituted sulfoximines was a facile process, and therefore we sought a method for the generation of *N*-unsubstituted vinylic sulfoximines. Such intermediates could in principle be converted into a range of AIMDA substrates with varied substituents on nitrogen. Treatment of *N*-unsubstituted β-methoxycarbonyloxysulfoximines with base has been reported[17] to give free *N*-H vinylic sulfoximines. The same authors reported that in an attempt to make cyclic sulfoximines by treatment of *N*-(trimethylsilyl) β-methoxycarbonyloxysulfoximines either with caesium fluoride or under thermal conditions *N*-unsubstituted vinylic sulfoximines were obtained as the only products.[18] No experimental details were provided. It occurred to us that treatment with base of *N*-(trimethylsilyl) β-methoxycarbonyloxysulfoximines derived from dienals followed by acid work-up would give the desired *N*-unsubstituted compounds. In the event, reaction of the lithio-derivative of the *N*-(trimethylsilyl) analogue of **5a**[19] with dienals, followed by quenching with methyl chloroformate gave crude carbonates **13** as diastereomeric mixtures. Potassium *tert*-butoxide-mediated elimination and work-up with aqueous HCl to effect desilylation followed by extraction from alkaline solution gave free *N*-H vinylic sulfoximines **9a-12a** in high yields and with complete selectivity for the 1*E*-isomers. The syntheses of **9a-12a** are summarised in Scheme 3.

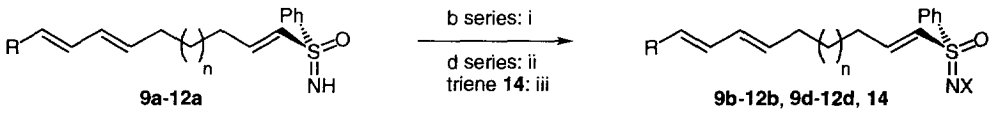
enal	R	n	triene	yield (%)
1	H	1	**9a**	87
2	H	2	**10a**	66
3	Me	1	**11a**	74
4[20]	Me	2	**12a**[21]	78



Reagents and conditions: (i) *n*-BuLi, Et_2O, -78°C → 0°C → -78°C; add enal, -78°C → rt → -78°C; MeO_2COCl, -78°C → rt; (ii) *t*-BuOK, THF, -78°C; aq HCl.

Scheme 3

Having developed an efficient route to the parent trienes **9a-12a**, it remained to functionalise the sulfoximine nitrogen atom. Triflylation occurred uneventfully on treatment of the free *N*-H trienes with triflic anhydride–pyridine to give the *N*-triflyl derivatives **9d-12d**. Because the 1*E*:1*Z* ratios of trienes obtained using the two-stage method were superior to those from the Wadsworth–Emmons route, it was decided also to prepare trienes **9b-12b** from the *N*-unsubstituted materials. The tosylation reactions were more sluggish than the triflylations, but good yields could be obtained by the use of excess tosyl chloride in the presence of catalytic quantities of *N,N*-dimethyl-4-aminopyridine (DMAP). In order to assess the effect on AIMDA reactivity of a bulky, non-sulfonyl group on nitrogen, a pivalyl derivative **14** was prepared by reaction of **10a** with pivalyl chloride–pyridine. Scheme 4 summarises the derivatisation reactions of trienes **9a-12a**.



9a-12a **9b-12b, 9d-12d, 14**

Reagents and conditions: (i) TsCl (2-4.5 eq), py, DMAP, CH_2Cl_2, 0°C → rt; (ii) Tf_2O (1.5 eq), py, CH_2Cl_2, 0°C → rt; (iii) *t*-BuCOCl, py, 0°C → rt.

triene substrate	triene product	yield (%)	R	n	X
9a	**9b**	65	H	1	Ts
10a	**10b**	65	H	2	Ts
11a	**11b**	72	Me	1	Ts
12a	**12b**	72	Me	2	Ts
9a	**9d**	75	H	1	Tf
10a	**10d**	79	H	2	Tf
11a	**11d**	63	Me	1	Tf
12a[22]	**12d**[21]	77	Me	2	Tf
10a	**14**	77	H	2	*t*-BuCO

Scheme 4

Intramolecular Diels–Alder reactions

IMDA Reactions of trienes **9-12** were carried out in the usual way[4] initially by heating rigorously dry, degassed d_8-toluene solutions in sealed, base-washed nmr tubes. Reaction temperatures and times were established by ^{1}H nmr analysis, after which preparative-scale experiments were carried out in resealable Carius tubes. Ratios of IMDA products were determined in all cases by nmr analysis of crude reaction mixtures, chromatography of which gave the purified products as diastereomeric mixtures. Single diastereomers could be obtained from some of the mixtures by fractional crystallisation of the chromatographed product. Also, HPLC was found in many cases to be an effective means of obtaining pure samples of all four diastereomeric bicycles. In some cases, reactions were carried out initially on racemic trienes prepared from unresolved **5** prior to investigations using the enantiomerically pure substrates. Where structural assignments of racemates were initially made by X-ray crystallography, the proof of the stereochemistry of the enantiomerically pure materials prepared subsequently followed from the identity of their ^{1}H nmr spectra with those of the racemates.

Reactions of 1,6,8-nonatrienes. Thermolysis of a toluene solution of the tosyl-substituted triene (S_S)-**9b** gave in 72% chromatographed yield a 39:31:25:5 mixture of four bicyclic products. The two major components

(39% and 31% of product mixture) exhibited in the ^{1}H nmr spectra one-proton signals at 3.83 and 3.51 ppm respectively, corresponding to the methine hydrogens α- to the sulfoximine group at C-5. The appearance of these resonances as triple-doublets, with two large (ca. 11 Hz) and one medium-sized (ca. 6 Hz) coupling constants led to the conclusion that these two diastereomers were trans-fused, since only structures with this type of ring-junction would have large dihedral angles between H-5 and *two* vicinal hydrogen atoms. The H-5 signals for the two remaining diastereomers appeared as quartets (J 6 Hz) at 3.76 ppm (25% of product) and 3.69 ppm (5% of product), consistent with cis-ring junction stereochemistry (Figure 1).

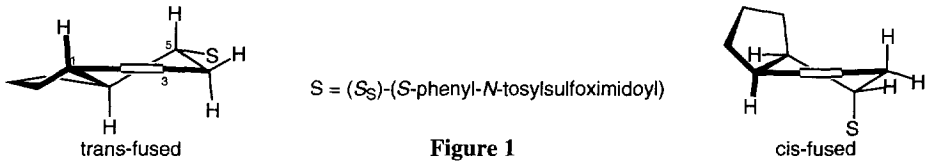
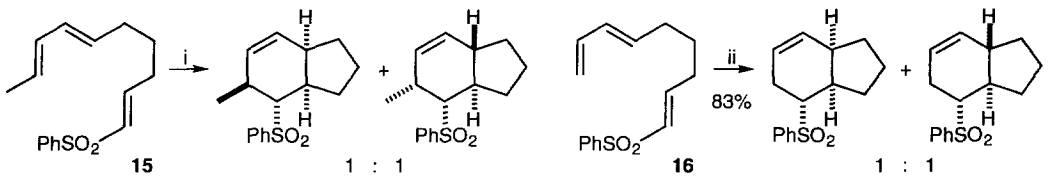


Figure 1

If the assignments made on the basis of the ^{1}H nmr spectra were correct, the IMDA reaction of **9b** had exhibited selectivity corresponding to a 30:70 cis:trans ratio, in line with the tendency of nonatrienes terminally substituted with an electron-withdrawing group to give predominantly trans-fused products.[23] Because sulfone **15** had previously been shown to undergo non-selective IMDA reaction, a control experiment was carried out. Thus, IMDA reaction of **16** (synthesised in good yield from (*E*)-5,7-octadienal and (phenylsulfonyl)methane as described previously)[4] gave in high yield a 1:1 mixture of products (Scheme 5). This suggested that that the increased trans-selectivity observed in the cyclisation of (*S*S)-**9b** compared with that of **16** was a direct consequence of the replacement of the sulfonyl moiety with a sulfoximine group. Roush has found that in IMDA reactions of 1,6,8-nonatrienes the selectivity for trans-fused products increases with increasing electron-withdrawing character of the dienophile-activating group.[24] The greater selectivity observed for sulfoximine-substituted (*S*S)-**9b** than for sulfonyl-substituted **16** suggests that the former dienophile substituent is more activating than the latter, and this is consistent with the comparative pK_a values of substances possessing these groups.[25]



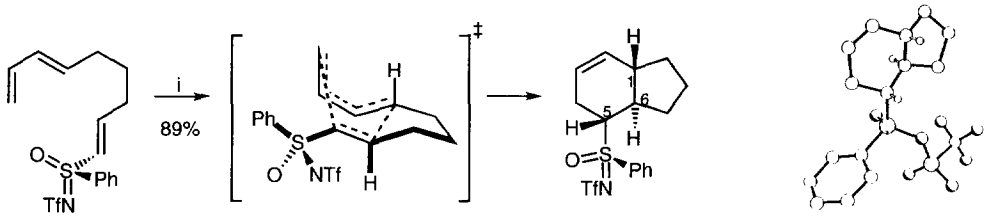
Reagents and conditions: (i) ref 4; (ii) PhMe, 140°C, 44 h.

Scheme 5

We next speculated that attachment to the triene sulfoximidoyl nitrogen of a more bulky arylsulfonyl group might increase the proportion of cis-fused isomers formed, and that there might be a corresponding increase in the selectivity for one of the cis- compounds. Thermal IMDA reaction of triene (±)-**9c** gave in high yield a 35:30:30:5 mixture of compounds. ^{1}H Nmr analysis of the mixture again revealed two pairs of signals, corresponding to the cis- and trans-fused products. As with the products from **9b**, the major cis- compound had an H-5 resonance appearing as a quartet (J 6.5 Hz) 0.12 ppm downfield from the corresponding peak in the minor cis-fused material. The H-5 methine in the major trans-fused isomer resonated as a triplet of doublets 0.29 ppm downfield from the same signal for the other trans-isomer, leading to the conclusion that the stereoselectivities were of the same order as those observed for **9b**. The marginal increase in cis-selectivity may be because of the more hindered nature of the dienophile-activating group.

Although the foregoing results showed that IMDA reactions of **9b** and **9c** to give cis-fused products were moderately selective processes (ca. 5:1) and that cyclisation to trans-products was almost non-selective, it was

not possible to determine which of the cis- and trans-fused isomers predominated because of the inseparable nature of the products. Cyclisation of the triflyl-substituted triene (S_S)-**9d** took place at a significantly lower temperature than was required for **9b** and **9c**, presumably as a consequence of the increased electron-withdrawing ability of the *N*-triflylsulfoximidoyl group. A 38:32:22:8 mixture of cycloadducts was formed in excellent yield which was separated by HPLC to give samples of pure isomers. The major trans-fused isomer was shown by X-ray diffraction analysis to have the (S_S,1*S*,5*R*,6*R*) configuration (Scheme 6, Figure 2).



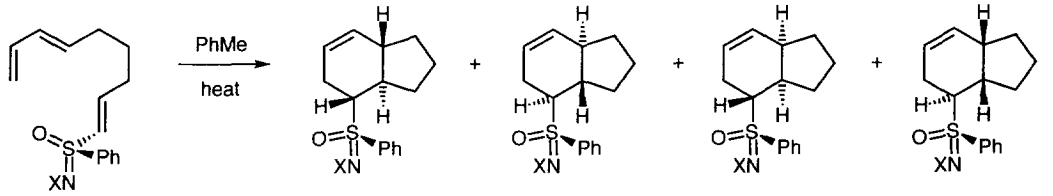
(S_S)-**9d** major product: **17d** X-ray structure of **17d**

Reagents and conditions: PhMe, 123°C, 46 h.

Figure 2

Scheme 6

It may be seen from Scheme 6 that the major (1*S*,5*R*,6*R*)-configured product **17d** must arise via attack of the si-face of C-4 of the diene on the si-face of the dienophile β-carbon atom. The close similarity in the selectivities observed for the reactions of trienes **9b-d**, together with the consistent differences in the ^{1}H nmr spectra lead us to conclude that the major trans-products formed in the reactions of **9b** and **9c** are respectively **17b** and **17c**. We suggest also that the major cis-product in all three IMDA reactions results from approach of the opposite C-4 diene diastereoface to the same si-face of the dienophile β-carbon atom. This inference was strongly supported by solid-state evidence from IMDA reactions of decatriene substrates, whose products had similar ^{1}H nmr characteristics (see below). The results of the IMDA reactions of trienes **9** as concluded on the basis of these arguments are shown in Scheme 7.



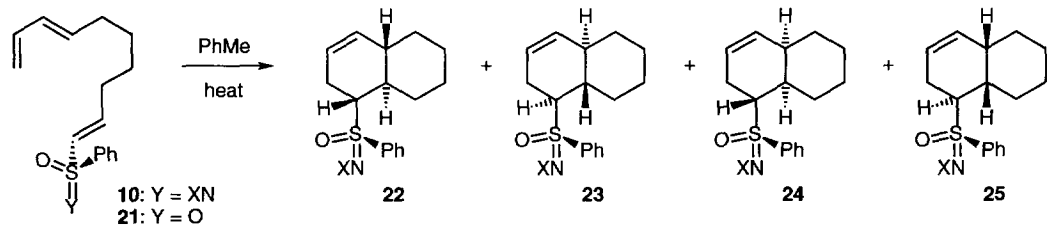
9 **17** **18** **19** **20**

triene	X	T (°C)	t (h)	yield (%)[26]	Ratio 17:18:19:20	$\delta_{H\text{-}5}$ 17	$\delta_{H\text{-}5}$ 18	$\delta_{H\text{-}5}$ 19	$\delta_{H\text{-}5}$ 20
9b	Ts	142	46	72	39 : 31 : 25 : 5	3.82	3.51	3.76	3.69
9c[27]	Tris	141	44	79	35 : 30 : 30 : 5	3.78	3.49	3.62	3.50
9d	Tf	123	46	89	38 : 32 : 22 : 8	3.82	3.60	3.67	3.51

Scheme 7

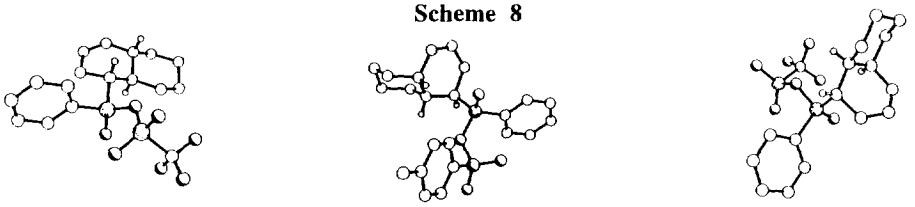
Reactions of 1,7,9-decatrienes. The IMDA reactions of the homologous trienes **10b-d** were selective for the cis-fused isomeric products, as was that of the sulfone analogue **21**; the latter compound was synthesised analogously to the lower homologue **16**. This may be explained in terms of a preferred exo-orienatation for the diene because of the bulky dienophile substituent; IMDA reactions of trienes terminally-substituted with less sterically demanding electron-withdrawing groups show no cis-bias.[28] Selectivity for the major cis-fused

product was generally lower than was observed for the lower homologues **9**; formation of the trans-fused compounds was a more selective process. As with the 1,6,8-nonatrienes, decatriene **10c** showed the highest cis-selectivity. The triflyl derivative **10d** was the most reactive, but its reaction was the least selective both in terms of the cis:trans ratio and the ratio of major to minor cis- and trans-isomers. In all three cases pure samples of the major cis-fused isomers **24** could be obtained simply by crystallisation of the chromatographed product. Separation into the pure components could be effected by HPLC. The structures of the major cis-fused products **24b,d** from cyclisation of trienes **10b** and **10d**, and of the major trans-product **22d** from **10d** were established unequivocally by X-ray crystallography (Figure 3), confirming the assignments made on the basis of nmr data and the structure of **17d**. The cyclisation reactions of trienes **10b-d** are summarised in Scheme 8.



triene	X	T (°C)	t (h)	yield (%)[26]	Ratio 22:23:24:25	$\delta_{H\text{-}5}$ 22	$\delta_{H\text{-}5}$ 23	$\delta_{H\text{-}5}$ 24	$\delta_{H\text{-}5}$ 25
10b	Ts	130	48	70	20 : 14 : 40 : 26	3.62	3.15	3.42	3.36
10c[27]	Tris	142	46	75	15 : 5 : 65 : 15	3.65	3.23	3.39	3.37
10d	Tf	116	46	68	24 : 21 : 35 : 20	3.66	3.33	3.49	3.45

Scheme 8

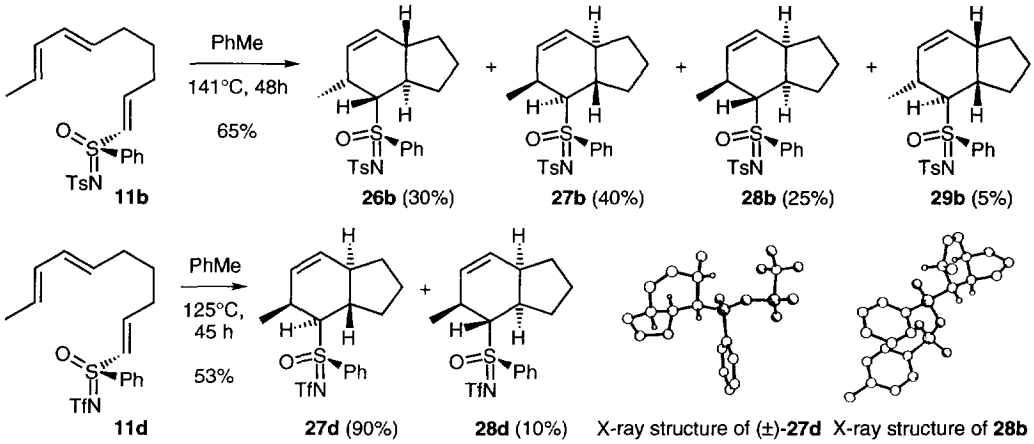


X-ray structure of **22d** X-ray structure of (±)-**24b** X-ray structure of (±)-**24d**

Figure 3

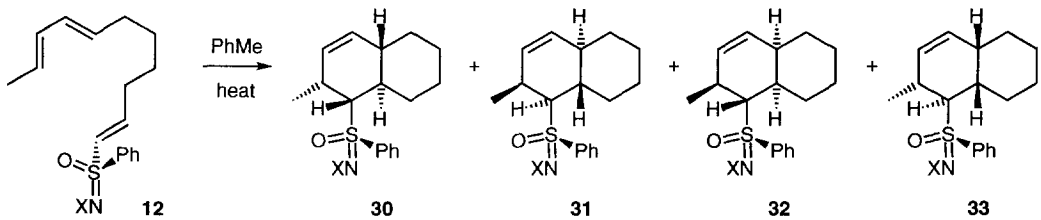
Reactions of 1,6,8-decatrienes. The IMDA reactions of 1-sulfoximidoyl-1,6,8-decatrienes **11b** and **11d** presented the opportunity for two direct comparisons. Firstly, comparison of the cyclisation behaviour of **11** with that of sulfone **15** would give an indication of the effect of the sulfoximine group on selectivity. Secondly, comparison with the reactions of 1,6,8-nonatrienes **9** would demonstrate the importance of the diene terminal methyl group, which had been shown previously to affect the stereochemical outcome of reactions of 1,7,9-decatrienes, but not of the lower homologues.[29] Thermal reaction of **11b** in the usual way gave in 65% chromatographed yield a 40:30:25:5 mixture of four compounds. Trans- and cis-fused isomers could again be assigned by examination of the ^{1}H nmr spectra. The presence of the C-4 methyl group simplified the H-5 signals, such that the trans-compounds exhibited double doublets and the cis-isomers broad singlets. These resonances paralleled exactly the corresponding signals in the analogous bicyclic sulfones.[4] Separation by HPLC gave a pure sample of the cis-fused isomer **28b**; the X-ray crystal structure is shown in Figure 4. Assignment of the major and minor trans-fused isomers was complicated by the coincidence of the H-5 signals in the nmr spectra. On the basis of all the previous IMDA reactions, the major trans-isomer initially was assigned as **26b**, since this would arise from diene attack on the si-face of the dienophile β-carbon atom. However, IMDA reaction of the triflyl analogue **11d** gave only one cis- and one trans-product, the latter having

the structure **27d** as evidenced by X-ray analysis (Figure 4). We presume that the cis-product is **28d** because of the selectivity observed with substrate **11b**; the formation of a single cis-isomer prevents comparison of the H-5 chemical shifts. The exclusive formation of **27d** might suggest that the marginally major trans-product formed from **11b** is **27b**, and not **26b** as would have been consistent with the previous reactions (Scheme 9).



Scheme 9 **Figure 4**

Reactions of 1,7,9-undecatrienes. The 1,7,9-undecatrienes were found to be the least reactive of the IMDA substrates studied. The cyclisations of trienes **12b** and **12c** were accompanied by substantial decomposition of the sulfoximine group, as evidenced by the observation of significant amounts of the corresponding sulfonamides. Triene **12b** gave a 6:1 mixture of one cis- and one trans-fused product; the trisyl analogue **12c** gave a 6:3:1 mixture of two cis-fused products and one trans-fused product. Cyclisation of the triflyl-substituted triene **12d** proceeded more rapidly and cleanly, and gave in 74% yield a 4:1 mixture of one cis- and one trans-fused isomer. Thus, trienes **12** followed the trend observed for the non-methylated analogues **10**, in that the trisyl-substituted sulfoximine **12c** showed the highest exo:endo selectivity and the triflyl derivative **12d** the lowest. On the basis of all but one (**11d**) of the reactions described above, we suggest that the stereochemical outcomes of these transformations are as summarised in Scheme 10.



triene	X	T (°C)	t (h)	yield (%)[26]	Ratio 30:31:32:33	$\delta_{H\text{-}5}$ 30	$\delta_{H\text{-}5}$ 31	$\delta_{H\text{-}5}$ 32	$\delta_{H\text{-}5}$ 33
12b	Ts	133	46	39	14 : 0 : 86 : 0	3.42	-	3.02	-
12c[27]	Tris	143	43	41	10 : 0 : 60 : 30	3.42	-	2.98	2.98
12d	Tf	123	43	74	20 : 0 : 80 : 0	3.72	-	3.09	-

Scheme 10

CONCLUSIONS

In summary, variable levels of stereoselectivity may be attained in IMDA reations of sulfoximine-substituted trienes. Like the sulfone group, the sulfoximine moiety exerts a strong exo-directing influence in those instances where there is no inherent endo-bias. Comparison of the stereoselectivities of the IMDA reactions of **10b, 10c** and **10d** shows that simply by increasing the bulk of the sulfoximine nitrogen substituent the exo-selectivity may be increased, and it is noteworthy that these three trienes may be synthesised from a common precursor. The IMDA reaction of **11d** is both highly trans-selective (9:1) and *completely* selective for one diastereomer in both trans- and cis-fused isomers; the reactions of **12b** and **12d** exhibit cis-selectivities of respectively 6:1 and 4:1, and trans-and cis-isomers are formed with 100% diastereomeric excess in both cases. Even in cases where the trans:cis selectivity is moderate, significant diastereomneric excesses are frequently observed for one or both structural types. We currently are seeking to develop asymmetric IMDA substrates which undergo ambient-temperature reactions, and we are exploring catalytic modifications as a way of increasing reactivity and selectivity. The results of these studies will be reported in due course.

ACKNOWLEDGEMENTS

We thank Rhône-Poulenc Agriculture Ltd for financial support of this research.

EXPERIMENTAL

General procedures

^{1}H, ^{13}C, ^{19}F and ^{31}P Nmr spectra were recorded on $CDCl_3$ solutions (unless stated otherwise) on either Bruker AM-500 or Bruker AS-300 spectrometers using solvent ($CHCl_3$: δ_H = 7.26 ppm; $CDCl_3$: δ_C = 77.0 ppm) or added internal references ($CFCl_3$ in $CDCl_3$: δ_F = 0 ppm; H_3PO_4 in $CDCl_3$: δ_P = 0 ppm). Infrared spectra were recorded from 4000 to 600 cm^{-1} as thin films between sodium chloride discs for oils and diluted with potassium bromide for solids, on either Perkin-Elmer 983G, or Bio-Rad FTS-7 (linked to a Bio-Rad 3240-SPC data-station) spectrometers. Mass spectra were recorded using either VG Trio or VG Quattro instruments. Microanalyses were performed by the Rhône-Poulenc Microanalytical Department, Dagenham, or by Butterworth Laboratories Ltd. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Optical rotations were measured using an Optical Activity AA-100 polarimeter. Chromatography refers to flash chromatography at 10 psi on May and Baker (40-60 microns), BDH (40-60 microns) or Merck Kieselgel 60 (230-400 mesh) silica gel. Tlc refers to analytical thin-layer chromatography performed using pre-coated glass-backed plates (Merck Kieselgel 60 F_{254}) and visualised with uv light, iodine and acidic ammonium molybdate(IV), vanillin or potassium permanganate solutions as appropriate. HPLC was carried out on Dynamax® Macro Si columns. Acetone, toluene, diethyl ether, dichloromethane, and tetrahydrofuran solvents were distilled and stored over 4Å molecular sieves. All other solvents and reagents were purified by standard procedures,[30] and obtained from commercial sources unless otherwise stated. Freshly distilled refers to bulb-to-bulb distillation under reduced pressure using a Kugelrohr apparatus. Solutions were degassed by bubbling nitrogen through the solution during sonication for 20 min. Sonication was carried out using a Semat 80 W, 50 kHz ultrasonic cleaning bath. Resealable glass tubes were base-washed before use by filling with hexamethyldisilazane, heating the sealed tube at 110°C for 24 h, rinsing with dry acetone and drying at 175°C for 18 h.

Preparation of trienes

Preparation of (±)-*S*-methyl-*S*-phenyl-*N*-(4-tolylsulfonyl)sulfilimine.

Prepared on a 400 mmol scale in 100% yield according to the method of Johnson.[9]

Preparation of (±)-*S*-methyl-*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximine ((±)-5b).

Prepared on a 350 mmol scale in 76% yield according to the method of Johnson.[31]

Preparation of (±)-*S*-methyl-*S*-phenylsulfoximine ((±)-5a).[8]

Prepared on a 50 mmol scale in 96% yield according to the method of Johnson.[8]

Preparation of (±)-*S*-methyl-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine ((±)-5c).[32]

To a stirred solution of (±)-*S*-methyl-*S*-phenylsulfoximine **5a** (3 g, 19.4 mmol) aand DMAP (10 mg) in dry pyridine (15 ml) at -6°C under nitrogen was added 2,4,6-triisopropylphenylsulfonyl chloride (5.86 g, 19.4 mmol) in one portion. The solution was heated at 60°C during 2 h, then allowed to cool and poured into water (10 ml). The mixture was diluted with 2M aqueous HCl (100 ml) and extracted with CH_2Cl_2 (3 x 50 ml). The combined extracts were washed with 2M aqueous HCl (50 ml), water (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a cream-coloured semi-solid. Recrystallisation from EtOH–water gave *(±)-S-methyl-S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximine* **5c** (6.94 g, 85%) as a colourless solid, mp 143-144°C; υ_{max} 3022, 2959, 2879, 1612, 1568, 1474, 1366, 1305, 1229, 1152, 1105, 1065, 980 cm^{-1}; δ_H (300 MHz) 1.24 (18H, m, 3 x $(CH_3)_2CH$), 2.88 (1H, quintet, J 7.0 Hz, Me_2CH para to SO_2 on Ar), 3.41 (3H, s, CH_3S), 4.38 (2H, quintet, J 7.0 Hz, 2 x Me_2CH ortho to SO_2 on Ar), 7.11 (2H, s, meta protons to SO_2 on Ar), 7.56-7.72 (3H, m, meta- and para-protons on Ph), 7.98-8.02 (2H, m, ortho protons on Ph); *m/z* 421 (CI) 422 (MH^+), 380, 284 ($TrisNH_3^+$), 267, 266, 251, 218, 156 (100) ($PhSO(NH_2)CH_3^+$), 141, 125, 111 (Found: C, 62.66; H, 7.40; N, 3.35. $C_{22}H_{31}NO_3S_2$ requires C, 62.67; H, 7.41; N, 3.32%).

Preparation of (±)-*S*-methyl-*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximine ((±)-5d).

To a stirred solution of (±)-*S*-methyl-*S*-phenylsulfoximine **5a** (0.5 g, 3.23 mmol) and pyridine (0.48 ml, 6.46 mmol) in dry CH_2Cl_2 at 0-5°C under nitrogen was added dropwise during 15 min a solution of triflic anhydride (0.65 ml, 3.87 mmol) in dry CH_2Cl_2 (10 ml). The resultant bright yellow solution was stirred at rt during 30 min, then water (50 ml) was added dropwise. The organic layer was separated, and washed with 2M aqueous HCl (50 ml), 2M aqueous NaOH (50 ml), water (2 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a waxy solid. Recrystallisation from EtOH–water gave *(±)-S-methyl-S-phenyl-N-(trifluoromethylsulfonyl)sulfoximine* **5d** (0.52 g, 56%) as a pale yellow solid, mp 85-86°C; υ_{max} 3073, 3025, 2928, 1360, 1199, 1062 cm^{-1}; δ_H (300 MHz) 3.52 (3H, s, CH_3Ar), 7.67-7.82 (3H, m, meta- and para-protons on Ph), 8.03-8.06 (2H, m, ortho protons on Ph); δ_C (75.5 MHz) 135.5, 130.2, 127.3 (5 x ArCH), 137.1 (ArCS), 121.3, 117.1 (CF_3), 46.7 (CH_3S); δ_F (282 MHz) 79.2; *m/z* 287 (CI) 288 (MH^+), 165, 149, 141 (MH^+-CF_3SO_2N), 138, 137, 126 (100) ($PhSOH^+$) (Found: C, 33.6; H, 2.87; N, 4.90. $C_8H_8F_3NO_3S_2$ requires C, 33.5; H, 2.81; N, 4.88%).

Preparation of (+)-(S_S)-*S*-methyl-*S*-phenylsulfoximine (5a).

Prepared in 76% yield by resolution of the racemate (100 mmol) according to the method of Johnson.[8]

Preparation of (+)-(S_S)-*S*-methyl-*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximine (5b).[31]

4-Tolylsulfonyl chloride (6.64 g, 34.8 mmol) was added portionwise over 15 min to a stirred solution of (+)-(S_S)-*S*-methyl-*S*-phenylsulfoximine **5a** (5.4 g, 34.8 mmol) in dry pyridine (25 ml) at 0 to 7°C. The resultant suspension was stirred at rt for 24 h and then filtered. The filtrate was added to water (100 ml) and

extracted with CH_2Cl_2 (3 x 75 ml). The extracts were combined, washed with water (3 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow semi-solid. The semi-solid was recrystallised from absolute ethanol to yield 7.64 g (71%) of the sulfoximine **5b** as an off-white solid, mp 97-98°C; $[\alpha]_D^{22}$ +121 (*c* 1, acetone); υ_{max} 3065, 3021, 2924, 1305, 1225 cm^{-1}; δ_H (300 MHz, d_6-DMSO) 2.36 (3H, s, CH_3Ar), 3.60 (3H, s, $SOCH_3$), 7.21 (2H, d, J 8.0 Hz, meta protons to SO_2 on Tol), 7.57-7.75 (3H, m, meta and para protons on Ph), 7.85 (2H, d, J 8.5 Hz, ortho protons to SO_2 on Tol), 7.95 (2H, d, J 7.5 Hz, ortho protons on Ph); *m/z* 309 (EI) 309 (M^+), 294 (100) (M^+-CH_3), 202, 155, 139, 125.

Preparation of tetrahydro-2*H*-pyran-2-ol.

Prepared on a 600 mmol scale in 70% yield accoording to the method of Woods.[11]

Preparation of methyl (*E*/*Z*)-7-hydroxy-2-heptenoate.[33]

A solution of tetrahydro-2*H*-pyran-2-ol (20.0 g, 196 mmol) and carbomethoxymethylenetriphenylphosphorane (78.7 g, 235 mmol) in dry CH_2Cl_2 (200 ml) under argon was stirred at rt for 48 h, then evaporated to a yellow semi-solid. The semi-solid was stirred twice with EtOAc (2 x 50 ml), then the mixture was filtered and the filtrate concentrated under reduced pressure to give a yellow oil. Chromatography (3:1 petrol–EtOAc) yielded 26.82 g (87%) of a 3:1 *E*:*Z* mixture (by 300 MHz ^1H nmr) of the hydroxyester as a yellow oil; υ_{max} 3394 (br), 2937, 2868, 1728, 1656, 1441, 1270, 1205, 1165, 1071, 1035 cm^{-1}; δ_H (300 MHz) 1.53-1.57 (4H, m, H-5, H-6), 2.21-2.27 (2H, m, *E*-CH_2CH=CH), 2.64-2.71 (2H, m, *Z*-CH_2CH=CH), 3.63-3.82 (2H, m, CH_2OH), 3.72 (3H, s, CH_3O), 5.77-5.86 (1H, m, CH=$CHCO_2CH_3$), 6.20-6.29 (1H, m, *Z*-CH_2CH=CH), 6.91-7.01 (1H, m, *E*-CH_2CH=CH); *m/z* 158 (CI) 176 (100) (MNH_4^+), 159 (MH^+), 144 (MH^+-CH_3), 127, 116, 111, 102.

Preparation of methyl (*E*/*Z*)-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-heptenoate (6).[33]

A solution of crude methyl (*E*/*Z*)-7-hydroxy-2-heptenoate (26.7 g, 169 mmol), 3,4-dihydro-2*H*-pyran (16.9 ml, 186 mmol) and 10-camphorsulfonic acid (CSA) (0.5 g) in dry CH_2Cl_2 (100 ml) under argon was stirred at rt for 1 h. The solution was washed with saturated aqueous $NaHCO_3$ (50 ml), water (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow oil. Chromatography (3:1 petrol–EtOAc) yielded 34.51 g (84%) of a 83:17 *E*:*Z* mixture (by 300 MHz ^1H nmr) of the THP-protected hydroxyester **6** as a yellow oil; υ_{max} 2933, 2871, 1724, 1658, 1439, 1272, 1211, 1175, 1127, 1069, 1049 cm^{-1}; δ_H (300 MHz) 1.57-1.83 (10H, m, H-5, H-6, H-3', H-4', H-5'), 2.20-2.27 (2H, m, CH_2CH=CH), 3.35-3.51 (2H, m, H-7, H-6'), 3.70-3.97 (2H, m, H-7, H-6'), 3.72 (3H, s, CH_3O), 4.55-4.56 (1H, m, H-2'), 5.76-5.85 (1H, m, *Z*- and *E*-CH=$CHCO_2CH_3$), 6.21-6.24 (1H, m, *Z*-CH_2CH=CH), 6.97 (1H, dt, J 15.5, 7.0 Hz, *E*-CH_2CH=CH); *m/z* 242 (CI) 260 (MNH_4^+), 243 (MH^+), 176, 159, 144, 118, 102 (100) (THPOH). The *E*:*Z* ratio was increased to 16:1 by further chromatography (4:1 petrol–Et_2O) (40% yield).

Preparation of 6-[(tetrahydro-2*H*-pyran-2-yl)oxy]hexanal.[34]

To a stirred solution of ε-caprolactone (10.0 g, 96.2 mmol) in dry toluene (100 ml) at -78°C under argon was added dropwise DIBAL-H (77 ml of a 1.5M solution in toluene, 115 mmol) over 1 h. The resultant thick slurry was stirred at -78°C for 15 min, then water (75 ml) was added dropwise and the mixture allowed to warm to 0°C over 20 min. The mixture was poured onto a suspension of anhydrous $NaHCO_3$ (30 g) in EtOAc (300 ml) and the slurry stirred for 20 min. The mixture was filtered and the filtrate was dried ($MgSO_4$) and concentrated under reduced pressure to give a colourless solid (8.81 g). The solid was stirred with 3,4-dihydro-2*H*-pyran (7.59 g, 90.3 mmol) and 10-camphorsulfonic acid (0.1 g) in dry CH_2Cl_2 (100 ml) under argon for 1 h. This solution was then washed with saturated $NaHCO_3$ (50 ml), water (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow oil. Chromatography (3:1 hexane–EtOAc) yielded 13.87 g

(72%) of the *aldehyde* as a colourless oil; υ_{max} 2939, 2865, 1724, 1447, 1030 cm^{-1}; δ_H (300 MHz, d_6-DMSO) 1.25-1.76 (12H, m, H-3, H-4, H-5, H-3', H-4', H-5'), 2.43 (2H, br t, J 7.0 Hz, CH_2CH=O), 3.27-3.44 (2H, m, H-6, H-6'), 3.57-3.76 (2H, m, H-6, H-6'), 4.52 (1H, t, J 3.5 Hz, H-2'), 9.66 (1H, s, C*H*=O); *m/z* 200 (CI) 201 (MH^+), 183, 117 (100) (deprotected alcohol + H^+), 99, 85, 81. The material was identical in all respects with that prepared by oxidation of 6-[(tetrahydro-2*H*-pyran-2-yl)oxy]hexanol.[10]

Preparation of (*E*)-6,8-nonadienal (2).[28]

To a stirred solution of oxalyl chloride (0.69 ml, 7.86 mmol) in dry CH_2Cl_2 (40 ml) at -60°C was added dropwise a solution of dry DMSO (1.12 ml, 15.7 mmol) in dry CH_2Cl_2 (5 ml). The solution was stirred at -60°C for 5 min, then a solution of (*E*)-6,8-nonadienol (1.0 g, 7.14 mmol) in dry CH_2Cl_2 (5 ml) was added dropwise with stirring at -60 to -55°C over 10 min. The solution was stirred at -60°C for 15 min, then dry triethylamine (4.98 ml, 35.7 mmol) was added dropwise and the resultant suspension was allowed to warm to rt and then stirred for a further 1 h. Water (10 ml) was added and the mixture was diluted with CH_2Cl_2 (50 ml), washed with 2M HCl (50 ml), water (50 ml), saturated aqueous $NaHCO_3$ (50 ml), water (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow oil. Chromatography (3:1 hexane–EtOAc) yielded 0.84 g (86%) of the dienal **2** as a yellow oil; υ_{max} 2931, 2856, 1721, 1459, 1005, 900 cm^{-1}; δ_H (300 MHz, d_6-DMSO) 1.31-1.58 (4H, m, CH_2CH_2), 2.06 (2H, q, J 7.0 Hz, CH=CHCH_2), 2.40-2.46 (2H, m, CH_2CH=O), 4.95 (1H, d, J 10.5 Hz, CH_aH_b=CH trans to chain), 5.09 (1H, d, J 17.0 Hz, CH_aH_b=CH cis to chain), 5.71 (1H, dt, J 15.0, 7.0 Hz, CH_2=CHCH=C*H*), 6.05 (1H, dd, J 15.0, 10.0 Hz, CH_2=C*H*CH=CH), 6.31 (1H, dt, J 17.0, 10.0 Hz, CH_2=C*H*CH=CH), 9.66 (1H, t, J 3.0 Hz, CH=O); δ_C (75.5 MHz, d_6-DMSO) 203.1 (CH=O), 137.1, 134.7, 131.0 (CH_2=*C*H*C*H=*C*H), 115.0 (*C*H_2=CHCH=CH), 42.7 (CH_2CH=O), 31.6, 26.8, 21.0 ($CH_2CH_2CH_2$); *m/z* 138 (CI) 139 (MH^+), 123 (100) (MH^+-O), 121, 109.

Preparation of *S*-(diethylphosphonylmethyl)-*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximine (8).

To a stirred solution of *S*-methyl-*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximine (1.0 g, 3.24 mmol) in dry THF (30 ml), at -78°C under nitrogen, was added dropwise *n*-BuLi (1.30 ml of a 2.5M solution in hexanes, 3.24 mmol), followed by the dropwise addition of *t*-BuOK (3.24 ml of a 1M solution in THF, 3.24 mmol). A solution of diethyl chlorophosphate (0.47 ml, 3.24 mmol) in dry THF (1 ml) was added dropwise at -78°C, then the reaction was allowed to warm to 0°C and quenched by the dropwise addition of 10% aqueous NH_4Cl (20 ml). Water (50 ml) was added and the mixture extracted with CH_2Cl_2 (3 x 50 ml). The extracts were combined, dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow oil. Chromatography (1:1 hexane–EtOAc) yielded 0.61 g (42%) of the *phosphonate* **8** as a colourless solid, mp 108-109°C; υ_{max} 3057, 2981, 2916, 1311, 1275, 1239, 1148, 1099, 1044, 1006, 798 cm^{-1}; δ_H (300 MHz) 1.21-1.26 (6H, m, 2 x CH_3CH_2O), 2.39 (3H, s, CH_3Ar), 4.04-4.14 (5H, m, 2 x CH_3CH_2O and SCH_aH_bP), 4.63 (1H, t, J 16.5 Hz, SCH_aH_bP), 7.23 (2H, d, J 8.5 Hz, meta protons to SO_2 on Tol), 7.54-7.68 (3H, m, meta and para protons on PhS), 7.86 (2H, d, J 8.5 Hz, ortho protons to SO_2 on Tol), 8.00-8.04 (2H, m, ortho protons on Ph); δ_C (75.5 MHz) 143.0, 140.5, 137.1, 134.7, 129.3, 129.2, 128.7, 126.7, 63.7, 55.3, 53.5, 21.5, 16.2, 16.1; δ_P (121.5 MHz) 10.21; *m/z* 445 (CI) 446 (100) (MH^+), 310 ($PhSO(NHTs)CH_3^+$), 292, 277, 261, 243, 229, 212 (Found: C, 48.6; H, 5.48; N, 3.09. $C_{18}H_{24}NO_6PS_2$ requires C, 48.5; H, 5.43; N, 3.14%).

Standard procedure for the preparation of (S_S)-*S*-phenyl-*N*-(tolylsulfonyl) vinylic sulfoximines using Wadsworth–Emmons reagents generated in situ.

To a stirred THF solution (0.06M) of (+)-(S_S)-*S*-methyl-*S*-phenyl-*N*-(tolylsulfonyl)sulfoximine at -78°C was added *n*-BuLi (2.5M solution in hexanes, 1 eq) followed by *t*-BuOK (1M solution in THF, 1 eq). Diethyl chlorophosphate (1 eq) was added and the mixture stirred at -78°C during 10 min. A solution of freshly-distilled aldehyde (1 eq) in THF (3M) was then added dropwise, and the mixture allowed to warm to rt and stirred

during 30 min. Saturated aqueous NH_4Cl and water were added, the layers separated, and the aqueous layer extracted with three portions of CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give the crude product. Chromatography on silica gel gave the pure vinylic sulfoximine.

Preparation of (+)-(S_S)-(1*EZ*,6*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,6,8-nonatriene (9b).

Prepared on a 1.42 mmol scale according to the standard Wadsworth–Emmons procedure to give 0.335 g (57%) of a 93:7 (1*E*,6*E*):(1*Z*,6*E*) mixture (by 300 MHz ^{1}H nmr) of the triene **9b** as a colourless gum; the spectral characteristics of the (1*E*,6*E*) isomer were identical to those given below.

Preparation of (+)-(S_S)-(1*EZ*,7*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,7,9-decatriene (10b).

Prepared on a 1.62 mmol scale according to the standard Wadsworth–Emmons procedure to give 0.42 g (60%) of of a 94:6 (1*E*,7*E*):(1*Z*,7*E*) mixture (by 300 MHz ^{1}H nmr) of the triene **10b** as a colourless gum; the spectral characteristics of the (1*E*,7*E*) isomer were identical to those given below.

Preparation of (±)-(1*E*,6*E*)-1-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]-1,6,8-nonatriene (9c).

Prepared on a 4.46 mmol scale from *S*-methyl-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (±)-**5c** according to the standard Wadsworth–Emmons procedure to give 1.34 g (55%) of a 93:7 (1*E*,6*E*):(1*Z*,6*E*) mixture (by 300 MHz ^{1}H nmr) of the *triene* **9c** as a colourless gum; data for the (1*E*,6*E*) isomer: υ_{max} 3058, 2952, 2876, 1596, 1444, 1293, 1214, 1149, 1094, 1048, 1001 cm^{-1}; δ_H (300 MHz) 1.21-1.25 (18H, m, 3 x $(CH_3)_2CH$) 1.51-1.61 (2H, m, $CH_2CH_2CH_2$), 2.05-2.12 (2H, m, CH_2=CHCH=CHCH_2), 2.23-2.30 (2H, m, CH_2CH=CHS), 2.88 (1H, p, J 7.0 Hz, Me_2CH para to SO_2 on Ar), 4.38 (2H, septet, J 7.0 Hz, 2 x Me_2CH ortho to SO_2 on Ar), 4.98 (1H, d, J 10.0 Hz, CH_aH_b=CH trans to chain), 5.08 (1H, d, J 17.0 Hz, CH_aH_b=CH cis to chain), 5.60 (1H, dt, J 15.0, 7.0 Hz, CH_2=CHCH=CH), 6.00 (1H, dd, J 15.0, 10.5 Hz, CH_2=CHCH=CH), 6.28 (1H, dt, J 17.0, 7.0 Hz, CH_2=CHCH=CH), 6.41 (1H, d, J 15.0 Hz, CH=CHS), 6.99 (1H, dt, J 15.0, 7.0 Hz, CH=CHS), 7.11 (2H, s, meta protons to SO_2 on Ar), 7.52-7.66 (3H, m, meta and para protons on Ph), 7.92-7.95 (2H, m, ortho protons on Ph); *m/z* 527 (CI) 545 (MNH_4^+), 528 (MH^+), 425, 408, 312, 301 (100) ($TrisNH_2$+NH_4^+), 282, 267, 231, 220, 203, 189, 178, 159, 125, 109 (Found: C, 68.35; H, 7.71; N, 2.55. $C_{30}H_{41}NO_3S_2$ requires C, 68.27; H, 7.83; N, 2.65%).

Preparation of (±)-(1*E*,7*E*)-1-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]-1,7,9-decatriene (10c).

Prepared on a 2.46 mmol scale from *S*-methyl-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (±)-**5c** according to the standard Wadsworth–Emmons procedure to give 0.681 g (51%) of a 93:7 (1*E*,7*E*):(1*Z*,7*E*) mixture (by 300 MHz ^{1}H nmr) of the *triene* **10c** as a colourless solid, mp 80-81°C; data for the (1*E*,7*E*) isomer: υ_{max} 3077, 2971, 2935, 1601, 1445, 1310, 1235, 1155, 1066, 897, 707 cm^{-1}; δ_H (300 MHz) 1.14-1.42 (22H, m, $CH_2CH_2CH_2CH_2$ and 3 x $(CH_3)_2CHAr$), 1.97-2.07 (2H, m, CH_2=CHCH=CHCH_2), 2.15-2.20 (2H, m, CH_2CH=CHS), 2.80 (1H, p, J 7.0 Hz, Me_2CH para to SO_2 on Ar), 4.31 (1H, p, J 7.0 Hz, Me_2CH 2 x ortho to SO_2 on Ar), 4.96 (1H, d, J 10.0 Hz, CH_aH_b=CH trans to chain), 5.03 (1H, d, J 17.0 Hz, CH_aH_b=CH cis to chain), 5.56 (1H, dt, J 15.0, 7.0 Hz, CH_2=CHCH=CH), 5.95 (1H, dd, J 15.0, 10.0 Hz, CH_2=CHCH=CH), 6.21 (1H, dt, J 17.0, 10.0 Hz, CH_2=CHCH=CH), 6.34 (1H, d, J 15.0 Hz, CH=CHS), 6.91 (1H, dt, J 15.0, 7.0 Hz, CH=CHS), 7.03(2H, s, meta protons to SO_2 on Ar), 7.43-7.58 (2H, m, meta

and para protons on Ph), 7.86-7.91 (2H, m, ortho protons on Ph); *m/z* 541 (CI) 559 (MNH_4^+), 542 (MH^+), 425, 408, 301 (100) ($TrisNH_2+NH_4^+$), 282, 267, 203, 159, 135, 108 (Found: C, 68.72; H, 8.00; N, 2.59. $C_{31}H_{43}NO_3S_2$ requires C, 68.75; H, 7.93; N, 2.61%).

Preparation of (±)-(1*E*,7*E*,9*E*)-1-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]-1,7,9-undecatriene (12c).

Prepared on a 1.97 mmol scale from *S*-methyl-*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximine (±)-**5c** according to the standard Wadsworth–Emmons procedure to give 0.425 g (39%) of a 93:7 (1*E*,7*E*,9*E*):(1*Z*,7*E*,9*E*) mixture (by 300 MHz ^1H nmr) of the *triene* **12c** as a colourless gum; data for the (1*E*,7*E*,9*E*) isomer: υ_{max} 2959, 2870, 1602, 1459, 1378, 1309, 1234, 1148, 1107, 1062, 986 cm^{-1}; δ_H (300 MHz) 1.21-1.25 (18H, m, 3 x $(CH_3)_2CH$) 1.34-1.50 (4H, m, $CH_2CH_2CH_2CH_2$), 1.72 (3H, d, J 6.5 Hz, CH_3CH=CHCH=CH), 2.02 (2H, q, J 7.0 Hz, CH_3CH=CHCH=CHCH_2), 2.21-2.26 (2H, m, CH_2CH=CHS), 2.87 (1H, p, J 7.0 Hz, Me_2CH para to SO_2 on Ar), 4.38 (2H, p, J 6.5 Hz, 2 x Me_2CH ortho to SO_2 on Ar), 5.42-5.71 (2H, m, CH_3CH=CHCH=CHCH$_2$), 5.91-6.01 (2H, m, CH_3CH=CHCH=CHCH$_2$), 6.38 (1H, d, J 15.0 Hz, CH=CHS), 6.99 (1H, dt, J 15.0, 7.0 Hz, CH=CHS), 7.10 (2H, s, meta protons to SO_2 on Ar), 7.51-7.65 (3H, m, meta and para protons on Ph), 7.91-7.94 (2H, m, ortho protons on Ph); *m/z* 555 (CI) 556 (MH^+), 518, 490, 408, 312, 284 (100) ($TrisNH_3^+$), 282, 267, 242, 205, 189, 172, 149, 127, 111 (Found: C, 69.46; H, 8.30; N, 2.55. $C_{32}H_{45}NO_3S_2$ requires C, 69.15; H, 8.16; N, 2.52%).

Preparation of (+)-(S_S)-*S*-methyl-*S*-phenyl-*N*-(trimethylsilyl)sulfoximine.[19]

To a stirred solution of (+)-(S_S)-*S*-methyl-*S*-phenylsulfoximine **5a** (4.0 g, 25.8 mmol) in dry CH_3CN (20 ml) was added dropwise *N*,*N*-diethyl(trimethylsilyl)amine (5.43 ml, 28.7 mmol). The mixture was stirred at 65°C during 10 min and allowed to cool during 30 min. Concentration under reduced pressure gave 5.99 g (100%) of the sulfoximine as a yellow oil; $[\alpha]_D^{20}$ +90.6 (*c* 0.71, acetone); υ_{max} 2958, 1323, 1292, 1254, 1162, 1091, 847, 744 cm^{-1}; δ_H (300 MHz) 0.10 (9H, s, $(CH_3)_3Si$), 3.11 (3H, s, $CH_3S(O)$), 7.52-7.63 (3H, m, meta and para protons on Ph), 7.94-8.03 (2H, m, ortho protons on Ph); *m/z* 227 (CI) 228 (MH^+), 156 (100) ($PhSO(NH_2)CH_3^+$), 141, 116, 111.

Standard procedure for the preparation of (S_S)-*S*-phenyl *N*-unsubstituted (*E*)-vinylic sulfoximines.

To a stirred solution of (+)-(S_S)-*S*-methyl-*S*-phenyl-*N*-(trimethylsilyl)sulfoximine in ether (0.07M) at -78°C was added *n*-BuLi (2.5M in hexanes, 1 eq). The solution was allowed to warm to 0°C during 10 min and then re-cooled to -78°C. Freshly-distilled aldehyde (1 eq) was added, and the mixture allowed to warm to rt and stirred for 2 h. The mixture was again cooled to -78°C and methyl chloroformate (1 eq) added. The resulting suspension was allowed to warm to rt and stirred for 30 min. Water was added, and the mixture was diluted with ether. The layers were separated and the organic layer washed with water and dried ($MgSO_4$). Concentration under reduced pressure gave the crude β-(methoxycarbonyloxy)sulfoximine as a mixture of diastereomers. This was dissolved in THF (0.1M) and the solution cooled to -78°C and treated with *t*-BuOK (1M in THF, 1 eq). The mixture was stirred at -78°C during 30 min, aqueous HCl (2M; 1.5 ml per mmol substrate) added and the mixture allowed to warm to rt and stirred for 30 min. The mixture was then diluted with ether and extracted three times with aqueous HCl (2M). The combined extracts were washed with ether, adjusted to pH 11 with aqueous NaOH (2M), and extracted with three portions of CH_2Cl_2. The CH_2Cl_2 extracts were dried ($MgSO_4$), concentrated under reduced pressure and chromatographed on silica gel to give the pure *N*-unsubstituted vinylic sulfoximine.

Preparation of (-)-(S_S)-(*E*,*E*)-1-(*S*-phenylsulfoximidoyl)-1,6,8-nonatriene (9a).

Prepared on a 4.02 mmol scale according to the standard procedure to give 0.908 g (87%) of the *triene* **9a** as a colourless hygroscopic oil; $[\alpha]_D^{20}$ -7.6 (*c* 0.40, CH_2Cl_2); υ_{max} 3270 (br), 2930, 1648, 1440, 1226, 1121, 1034, 1006, 967, 749, 694 cm^{-1}; δ_H (300 MHz) 1.51-1.61 (2H, m, $CH_2CH_2CH_2$), 2.05-2.12 (2H, m, CH_2=CHCH=CHCH_2), 2.20-2.27 (2H, m, CH_2CH=CHS), 2.76 (1H, br s, N*H*), 4.97 (1H, d, J 10.0 Hz, CH_aH_b=CH trans to chain), 5.07 (1H, d, J 17.0 Hz, CH_aH_b=CH cis to chain), 5.61 (1H, dt, J 15.0, 7.0 Hz, CH_2=CHCH=C*H*), 5.99 (1H, dd, J 15.0, 10.0 Hz, CH_2=CHC*H*=CH), 6.27 (1H, dt, J 17.0, 10.0 Hz, CH_2=C*H*CH=CH), 6.38 (1H, d, J 15.0 Hz, CH=C*H*S), 6.92 (1H, dt, J 15.0, 7.0 Hz, C*H*=CHS), 7.48-7.65 (3H, m, meta and para protons on Ph), 7.86-8.03 (2H, m, ortho protons on Ph); *m/z* 261 (CI) 262 (100) (MH^+), 247 (MH^+-NH), 231, 214, 199, 158, 156 ($PhSO(NH_2)CH_3^+$), 142 ($PhSONH_3^+$), 136, 126 ($PhSOH^+$), 109 (Found: (MH^+), 262.1265. $C_{15}H_{19}NOS$ requires (MH^+), 262.1266).

Preparation of (-)-(S_S)-(*E*,*E*)-1-(*S*-phenylsulfoximidoyl)-1,7,9-decatriene (10a).

Prepared on a 5.93 mmol scale according to the standard procedure to give 1.078 g (66%) of the *triene* **10a** as a colourless hygroscopic oil; $[\alpha]_D^{20}$ -11.4 (*c* 0.83, CH_2Cl_2); υ_{max} 3270 (br), 2928, 1444, 1224, 1117, 1073, 1003 cm^{-1}; δ_H (300 MHz) 1.33-1.51 (4H, m, $CH_2CH_2CH_2CH_2$), 2.03-2.09 (2H, m, CH_2=CHCH=CHCH_2), 2.19-2.26 (2H, m, CH_2CH=CHS), 2.70 (1H, br s, N*H*), 4.96 (1H, d, J 10.0 Hz, CH_aH_b=CH trans to chain), 5.08 (1H, d, J 17.0 Hz, CH_aH_b=CH cis to chain), 5.63 (1H, dt, J 15.0, 7.0 Hz, CH_2=CHCH=C*H*), 6.01 (1H, dd, J 15.0, 10.5 Hz, CH_2=CHC*H*=CH), 6.28 (1H, dt, J 17.0, 10.0 Hz, CH_2=C*H*CH=CH), 6.39 (1H, d, J 15.0 Hz, CH=C*H*S), 6.92 (1H, dt, J 15.0, 7.0 Hz, C*H*=CHS), 7.48-7.65 (3H, m, meta and para protons on Ph), 7.85-8.03 (2H, m, ortho protons on Ph); *m/z* 275 (CI) 276 (100) (MH^+), 261 (MH^+-NH), 245, 214, 208, 159, 156 ($PhSO(NH_2)CH_3^+$), 152, 141, 126 ($PhSOH^+$), 108 (Found: (MH^+), 276.1422. $C_{16}H_{21}NOS$ requires (MH^+), 276.1422).

Preparation of (-)-(S_S)-(*E*,*E*,*E*)-1-(*S*-phenylsulfoximidoyl)-1,6,8-decatriene (11a).

Prepared on a 6.15 mmol scale according to the standard procedure to give 1.253 g (74%) of the *triene* **11a** as a hygroscopic yellow oil; $[\alpha]_D^{20}$ -9.6 (*c* 1.2, CH_2Cl_2); υ_{max} 3291 (br), 3106, 2932, 2852, 1447, 1230, 1118, 1091, 981, 781 cm^{-1}; δ_H (300 MHz) 1.48-1.58 (2H, m, $CH_2CH_2CH_2$), 1.71 (3H, d, J 6.5 Hz, CH_3CH=CHCH=CH), 2.01-2.07 (2H, m, CH_3CH=CHCH=CHCH_2), 2.18-2.25 (2H, m, CH_2CH=CHS), 2.77 (1H, br s, N*H*), 5.40-5.56 (2H, m, CH_3CH=CHCH=C*H*CH_2), 5.88-6.02 (2H, m, CH_3CH=C*H*C*H*=CHCH_2), 6.36 (1H, d, J 15.0 Hz, CH=C*H*S), 6.91 (1H, dt, J 15.0, 7.0 Hz, C*H*=CHS), 7.48-7.62 (3H, m, meta and para protons on Ph), 7.94-7.98 (2H, m, ortho protons on Ph); *m/z* 275 (CI) 276 (MH^+), 261 (MH^+-NH), 207, 194, 181, 168, 156 ($PhSO(NH_2)CH_3^+$), 147, 142 ($PhSONH_3^+$), 134, 126 (100) ($PhSOH^+$), 119, 115, 107 (Found: (MH^+), 276.1422. $C_{16}H_{21}NOS$ requires (MH^+), 276.1422).

Preparation of (-)-(S_S)-(1*E*,7*E*,9*E*)-1-(*S*-phenylsulfoximidoyl)-1,7,9-undecatriene and (-)-(S_S)-(1*E*,7*Z*,9*E*)-1-(*S*-phenylsulfoximidoyl)-1,7,9-undecatriene (12a).

Prepared on a 2.42 mmol scale according to the standard procedure to give 0.544 g (78%) of a 6:1 (1*E*,7*E*,9*E*):(1*E*,7*Z*,9*E*) mixture (by 300 MHz ^1H nmr) of the *triene* **12a** as a colourless, hygroscopic gum; $[\alpha]_D^{20}$ -9.7 (*c* 1.3, CH_2Cl_2). Data for the (1*E*,7*E*,9*E*) isomer: υ_{max} 3279 (br), 3016, 2915, 2857, 1629, 1448, 1216, 1098, 990 cm^{-1}; δ_H (300 MHz) 1.37-1.78 (4H, m, $CH_2CH_2CH_2CH_2$), 1.72 (3H, d, J 7.0 Hz, CH_3CH=CH), 2.00-2.17 (2H, m, CH=CH-CH=CHCH_2), 2.18-2.23 (2H, m, CH_2CH=CHS), 2.79 (1H, br s, N*H*), 5.19-5.71 (2H, m, CH_3C*H*=CH-CH=C*H*CH_2), 5.91-6.04 and 6.23-6.31 (2H, m, CH_3CH=C*H*-C*H*=CHCH_2), 6.38 (1H, d, J 15.0 Hz, CH=C*H*S), 6.92 (1H, dt, J 15.0, 7.0 Hz, C*H*=CHS), 7.48-7.60 (3H, m, meta and para protons on Ph), 7.94-8.04 (2H, m, ortho protons on Ph); *m/z* 289 (CI) 290 (MH^+), 275

(MH^+-NH), 259, 224 (100) 210, 196, 179, 166, 156 ($PhSO(NH_2)CH_3^+$), 142 ($PhSONH_3^+$), 126 ($PhSOH^+$), 109 (Found: (MH^+), 290.1579. $C_{17}H_{23}NOS$ requires (MH^+), 290.1579).

Preparation of (+)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(trimethylacetyl)sulfoximidoyl]-1,7,9-decatriene (14).

To a stirred solution of (-)-(S_S)-(*E*,*E*)-1-(*S*-phenylsulfoximidoyl)-1,7,9-decatriene **10a** (0.38 g, 1.38 mmol) in dry pyridine (5 ml) at 0°C under nitrogen was added dropwise trimethylacetyl chloride (0.17 g, 1.40 mmol). The resultant suspension was stirred at rt for 24 h, then poured into water (100 ml) and extracted with CH_2Cl_2 (3 x 50 ml). The extracts were combined and washed with 2M HCl (50 ml), water (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a yellow oil. Chromatography (3:1 hexane–EtOAc) yielded 0.382 g (77%) of the *triene* **14** as a colourless solid, mp 0-1°C; $[\alpha]^{20}_D$ +18.5 (*c* 1.64, CH_2Cl_2); υ_{max} 2947, 1643, 1472, 1291, 1228, 1176, 1106, 1005, 980, 881 cm^{-1}; δ_H (300 MHz) 1.23 (9H, s, $(CH_3)_3C$), 1.26-1.54 (4H, m, $CH_2CH_2CH_2CH_2$), 2.03-2.10 (2H, m, CH_2=CHCH=CHCH_2), 2.24-2.31 (2H, m, CH_2CH=CHS), 4.97 (1H, d, J 10.0 Hz, C$H_a$$H_b$=CH trans to chain), 5.08 (1H, d, J 16.5 Hz, $CH_a$$H_b$=CH cis to chain), 5.63 (1H, dt, J 15.0, 7.0 Hz, CH_2=CHCH=C*H*), 6.02 (1H, dd, J 15.0, 10.5 Hz, CH_2=CHC*H*=CH), 6.26 (1H, dt, J 17.0, 10.0 Hz, CH_2=C*H*CH=CH), 6.35 (1H, d, J 15.0 Hz, CH=C*H*S), 6.98 (1H, dt, J 15.0, 7.0 Hz, C*H*=CHS), 7.51-7.63 (3H, m, meta and para protons on Ph), 7.87-7.91 (2H, m, para protons on Ph); *m/z* 359 (CI) 360 (MH^+), 276 (MH^+-$(CH_3)_3CCO$), 243, 227, 210, 159, 152, 135, 119 (100), 102 (Found: (MH^+), 360.1997. $C_{21}H_{29}NO_2S$ requires (MH^+), 360.1997).

Preparation of (+)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,6,8-nonatriene (9b).

To a stirred solution of (-)-(S_S)-(*E*,*E*)-1-(*S*-phenylsulfoximidoyl)-1,6,8-nonatriene **9a** (0.30 g, 1.15 mmol), dry pyridine (0.19 ml, 2.30 mmol, 2 eq) and DMAP (10 mg) in dry CH_2Cl_2 (20 ml) at 0°C was added portionwise 4-tolylsulfonyl chloride (0.22 g, 1.16 mmol, 1.01 eq). The resultant solution was allowed to warm to rt, then stirred at rt for 24 h. Dry pyridine (0.30 ml, 3.71 mmol, 3.2 eq), and further 4-tolylsulfonyl chloride (0.20 g, 1.05 mmol, 0.9 eq) was added and the solution stirred at rt for a further 72 h. The solution was diluted with CH_2Cl_2 (100 ml), washed with 2M HCl (50 ml), water (50 ml), 2M aqueous NaOH (50 ml), water (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. Chromatography (3:1 hexane–EtOAc) yielded 0.312 g (65%) of the *triene* **9b** as a colourless gum; $[\alpha]_D^{20}$ +9.9 (*c* 0.91, CH_2Cl_2); υ_{max} 3056, 2930, 1607, 1445, 1322, 1240, 1240, 1159, 1093, 1021, 821, 757 cm^{-1}; δ_H (300 MHz) 1.52-1.62 (2H, m, $CH_2CH_2CH_2$), 2.05-2.12 (2H, m, CH_2=CHCH=CHCH_2), 2.23-2.31 (2H, m, CH_2CH=CHS), 2.39 (3H, s, CH_3Ar), 4.98 (1H, d, J 10.0 Hz, C$H_a$$H_b$=CH trans to chain), 5.08 (1H, d, J 17.0 Hz, $CH_a$$H_b$=CH cis to chain), 5.60 (1H, dt, J 15.0, 7.0 Hz, CH_2=CHCH=C*H*), 5.99 (1H, dd, J 15.0, 10.5 Hz, CH_2=CHC*H*=CH), 6.26 (1H, dt, J 17.0, 10.5 Hz, CH_2=C*H*CH=CH), 6.42 (1H, d, J 15.0 Hz, CH=C*H*S), 6.98 (1H, dt, J 15.0, 7.0 Hz, C*H*=CHS), 7.25 (2H, d, J 8.0 Hz, meta protons to SO_2 on Tol), 7.53-7.67 (3H, m, meta and para protons on Ph), 7.83 (2H, d, 8.5 Hz, ortho protons to SO_2 on Tol), 7.93-7.96 (2H, m, para protons on Ph); *m/z* 415 (CI) 416 (MH^+), 324, 296, 278, 263, 172 ($TsNH_3^+$), 155, 143, 121 (100) (Found: (MH^+), 416.1354. $C_{22}H_{25}NO_3S_2$ requires (MH^+), 416.1354) (Found: C, 63.50; H, 6.18; N, 3.49. $C_{22}H_{25}NO_3S_2$ requires C, 63.59; H, 6.06; N, 3.37%).

Preparation of (+)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,7,9-decatriene (10b).

To a stirred solution of (-)-(S_S)-(*E*,*E*)-1-(*S*-phenylsulfoximidoyl)-1,7,9-decatriene **10a** (0.157 g, 0.571 mmol), dry pyridine (0.53 ml, 6.55 mmol, 11.5 eq) and DMAP (10 mg) in dry CH_2Cl_2 (10 ml) at 0°C was added portionwise 4-tolylsulfonyl chloride (0.50 g, 2.62 mmol, 4.6 eq). The resultant suspension was allowed

to warm to rt, then stirred at rt for 72 h. The suspension was diluted with CH_2Cl_2 (100 ml), washed with 2M HCl (50 ml), water (50 ml), 2M aqueous NaOH (50 ml), water (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a brown oil. Chromatography (3:1 hexane–EtOAc) yielded 0.160 g (65%) of the *triene* **10b** as a colourless gum; $[\alpha]_D^{20}$ +142.9 (*c* 0.49, CH_2Cl_2); υ_{max} 3010, 2890, 2805, 1599, 1558, 1422, 1295, 1160, 1068, 1035 cm^{-1}; δ_H (300 MHz) 1.23-1.50 (4H, m, $CH_2CH_2CH_2CH_2$), 2.03-2.10 (2H, m, CH_2=CHCH=CHCH_2), 2.23-2.30 (2H, m, CH_2CH=CHS), 2.39 (3H, s, CH_3Ar), 4.97 (1H, d, J 10.0 Hz, CH_aH_b=CH trans to chain), 5.09 (1H, d, J 17.0 Hz, CH_aH_b=CH cis to chain), 5.63 (1H, dt, J 15.0, 7.0 Hz, CH_2=CHCH=CH), 6.02 (1H, dd, J 15.0, 10.0 Hz, CH_2=CHCH=CH), 6.28 (1H, dt, J 17.0, 10.0 Hz, CH_2=CHCH=CH), 6.41 (1H, d, J 15.0 Hz, CH=CHS), 6.98 (1H, dt, J 15.0, 7.0 Hz, CH=CHS), 7.24 (2H, d, J 8.0 Hz, meta protons to SO_2 on Tol), 7.53-7.75 (3H, m, meta and para protons on Ph), 7.83 (2H, d, J 8.5 Hz, ortho protons to SO_2 on Tol), 7.91-8.01 (2H, m, para protons on Ph); *m/z* 429 (CI) 430 (MH^+), 391, 313, 261 (MH^+-TsN), 245, 206, 189 (100) $TsNH_2$+NH_4^+), 175, 152, 135, 125, 108 (Found: C, 63.80; H, 6.15; N, 3.34. $C_{23}H_{27}NO_3S_2$ requires C, 64.31; H, 6.33; N, 3.34%).

Preparation of (+)-(S_S)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,6,8-decatriene (11b).

To a stirred solution of (-)-(S_S)-(*E*,*E*,*E*)-1-(*S*-phenylsulfoximidoyl)-1,6,8-decatriene **11a** (0.50 g, 1.82 mmol), dry pyridine (10.62 ml, 20.0 mmol, 11 eq) and DMAP (10 mg) in dry CH_2Cl_2 (20 ml) at 0°C was added portionwise 4-tolylsulfonyl chloride (1.29 g, 8.19 mmol, 4.5 eq). The resultant solution was allowed to warm to rt under nitrogen, then stirred at rt for 70 h. The solution was diluted with CH_2Cl_2 (100 ml), washed with 2M HCl (50 ml), water (50 ml), 2M aqueous NaOH (50 ml), water (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a colourless gum. Chromatography (3:1 hexane–EtOAc) yielded 0.565 g (72%) of the *triene* **11b** as a colourless gum; $[\alpha]_D^{20}$ +18 (*c* 3.5, CH_2Cl_2); υ_{max} 3020, 2929, 1451, 1312, 1239, 1095, 1057, 997 cm^{-1}; δ_H (300 MHz) 1.51-1.59 (2H, m, $CH_2CH_2CH_2$), 1.72 (2H, d, J 7.0 Hz, CH_3CH=CHCH=CH), 2.02-2.06 (2H, m, CH_3CH=CHCH=CHCH_2), 2.22-2.29 (2H, m, CH_2CH=CHS), 2.39 (3H, s, CH_3Ar), 5.46-5.60 (2H, m, CH_3CH=CHCH=CH), 5.88-5.99 (2H, m, CH_3CH=CHCH=CH), 6.40 (1H, d, J 15.0 Hz, CH=CHS), 6.97 (1H, dt, J 15.0, 7.0 Hz, CH=CHS), 7.23 (2H, d, J 8.0 Hz, meta protons to SO_2 on Tol), 7.52-7.67 (3H, m, meta and para protons on Ph), 7.83 (2H, d, 8.5 Hz, ortho protons to SO_2 on Tol), 7.92-7.95 (2H, m, para protons on Ph); *m/z* 429 (CI) 447 (MNH_4^+), 430 (MH^+), 313, 261 (MH^+-TsN), 245, 206, 189 (100) ($TsNH_2$+NH_4^+), 159, 135, 125, 108 (Found: (MNH_4^+), 447.1776. $C_{23}H_{27}NO_3S_2$ requires (MNH_4^+), 447.1776).

Preparation of (+)-(S_S)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,7,9-undecatriene (12b).

To a stirred solution of (-)-(S_S)-(1*E*,7*E*,9*E*)-1-(*S*-phenylsulfoximidoyl)-1,7,9-undecatriene (contaminated with ca. 15% (-)-(S_S)-(1*E*,7*Z*,9*E*)-1-(*S*-phenylsulfoximidoyl)-1,7,9-undecatriene) **12a** (0.20 g, 0.692 mmol), dry pyridine (0.62 ml, 7.61 mmol, 11 eq) and DMAP (10 mg, 0.0811 mmol) in dry CH_2Cl_2 (15 ml) at 0°C was added portionwise 4-tolylsulfonyl chloride (0.59 g, 3.11 mmol, 4.5 eq). The resultant suspension was allowed to warm at rt under nitrogen, then stirred at rt for 96 h. The suspension was diluted with CH_2Cl_2 (100 ml), washed with 2M HCl (50 ml), water (50 ml), 2M aqueous NaOH (50 ml), water (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a colourless gum. Chromatography (3:1 hexane–EtOAc) yielded 0.221 g (72%) of a 6:1 (1*E*,7*E*,9*E*):(1*E*,7*Z*,9*E*) mixture (by 300 MHz ^{1}H nmr) of the *triene* **12b** as a colourless gum; $[\alpha]_D^{22}$ +14.3 (*c* 2.03, CH_2Cl_2); data for the (*E*,*E*,*E*-isomer): υ_{max} 3012, 2926, 2869, 1621, 1455, 1310, 1239, 1099, 1070, 992 cm^{-1}; δ_H (300 MHz) 1.23-1.50 (4H, m, $CH_2CH_2CH_2CH_2$), 1.72 (2H, d, J 6.5 Hz, CH_3CH=CHCH=CH), 2.02 (2H, q, J 6.5 Hz, CH=CHCH=CHCH_2), 2.22-2.26 (2H, m, CH_2CH=CHS), 2.39 (3H, s, CH_3Ar), 5.39-5.70 (2H, m, CH_3CH=CHCH=CH), 5.91-6.04 (2H, m, CH_3CH=CHCH=CH), 6.40 (1H, d, J 15.0 Hz, CH=CHS), 6.96 (1H, dt, J 15.0, 7.0 Hz, CH=CHS), 7.23 (2H, d, J 8.0 Hz, meta

protons to SO_2 on Tol), 7.52-7.66 (3H, m, meta and para protons on Ph), 7.85 (2H, d, 8.5 Hz, ortho protons to SO_2 on Tol), 7.92-7.95 (2H, m, para protons on Ph); *m/z* 443 (CI) 444 (MH^+), 296, 275 (MH^+-TsN), 172 (100) ($TsNH_3^+$), 155, 149, 141, 127, 111 (Found: C, 64.67; H, 6.45; N, 3.12. $C_{24}H_{29}NO_3S_2$ requires C, 64.98; H, 6.59; N, 3.19%).

Standard procedure for the preparation of (S_S)-*S*-phenyl *N*-(trifluoromethylsulfonyl) vinylic sulfoximines.

To a stirred solution of the *N*-unsubstituted vinylic sulfoximine in CH_2Cl_2 (0.09M) was added pyridine (3 eq). The solution was cooled to 0°C and trifluoromethylsulfonic anhydride (1.5 eq) added. The resulting dark orange solution was allowed to warm to rt and stirred for 1 h, after which time it was diluted with CH_2Cl_2. The mixture was washed with aqueous HCl (2M), water, aqueous NaOH (2M), water, and dried ($MgSO_4$). Concentration under reduced pressure gave an orange oil, which was purified by chromatography on silica gel.

Preparation of (-)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]-1,6,8-nonatriene (9d).

Prepared on a 2.15 mmol scale according to the standard procedure to give 0.630 g (75%) of the *triene* **9d** as a waxy yellow solid, mp 49-50°C; $[\alpha]_D^{20}$ -6.6 (*c* 0.53, CH_2Cl_2); υ_{max} 2936, 1451, 1366, 1258, 1190, 1140, 1099, 1055, 744 cm^{-1}; δ_H (300 MHz) 1.50-1.60 (2H, m, $CH_2CH_2CH_2$), 2.02-2.09 (2H, m, CH_2=CHCH=CHCH_2), 2.25-2.32 (2H, m, CH_2CH=CHS), 4.92 (1H, d, J 10.0 Hz, CH_aH_b=CH trans to chain), 4.98 (1H, d, J 17.0 Hz, CH_aH_b=CH cis to chain), 5.54 (1H, dt, J 15.0, 7.0 Hz, CH_2=CHCH=CH), 5.95 (1H, dd, J 15.0, 10.5 Hz, CH_2=CHCH=CH), 6.20 (1H, dt, 17.0, 10.0 Hz, CH_2=CHCH=CH), 6.38 (1H, d, J 15.0 Hz, CH=CHS), 7.07 (1H, dt, J 15.0, 7.0 Hz, CH=CHS), 7.54-7.70 (3H, m, meta and para protons on Ph), 7.89-7.92 (2H, m, ortho protons on Ph); δ_F (282 MHz) -79.36; *m/z* 393 (CI) 411 (100) (MNH_4^+), 394 (MH^+), 373, 339, 305, 291, 288, 262, 247 (MH^+-CF_3SO_2N), 231, 216, 186, 165, 156, 141, 121, 110, 102 (Found: (MNH_4^+), 411.1024. $C_{16}H_{18}F_3NO_3S_2$ requires (MNH_4^+), 411.1024) (Found: C, 48.53; H, 4.57; N, 3.57. $C_{16}H_{18}F_3NO_3S_2$ requires C, 48.85; H, 4.58; N, 3.61%).

Preparation of (-)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]-1,7,9-decatriene (10d).

Prepared on a 1.82 mmol scale according to the standard procedure to give 0.584 g (79%) of the *triene* **10d** as a yellow oil; $[\alpha]_D^{20}$ -5.6 (*c* 0.90, CH_2Cl_2); υ_{max} 2937, 1624, 1449, 1366, 1260, 1194, 1103, 1052, 748 cm^{-1}; δ_H (300 MHz) 1.37-1.57 (4H, m, $CH_2CH_2CH_2CH_2$), 2.05-2.12 (2H, m, CH_2=CHCH=CHCH_2), 2.31-2.39 (2H, m, CH_2CH=CHS), 4.98 (1H, d, J 10.0 Hz, CH_aH_b=CH trans to chain), 5.08 (1H, d, J 17.0 Hz, CH_aH_b=CH cis to chain), 5.64 (1H, dt, J 15.0, 7.0 Hz, CH_2=CHCH=CH), 6.03 (1H, dd, J 15.0, 10.5 Hz, CH_2=CHCH=CH), 6.29 (1H, dt, 17.0, 10.5 Hz, CH_2=CHCH=CH), 6.44 (1H, d, J 15.0 Hz, CH=CHS), 7.15 (1H, dt, J 15.0, 7.0 Hz, CH=CHS), 7.61-7.77 (3H, m, meta and para protons on Ph), 7.96-8.00 (2H, m, ortho protons on Ph); δ_F (282 MHz) -79.35; *m/z* 407 (CI) 425 (100) (MNH_4^+), 408 (MH^+), 349, 291, 261 (MH^+-CF_3SO_2N), 245, 202, 185, 152, 135, 126 ($PhSOH^+$), 109 (Found: (MNH_4^+), 425.1180. $C_{17}H_{20}F_3NO_3S_2$ requires (MNH_4^+), 425.1181).

Preparation of (-)-(S_S)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]-1,6,8-decatriene (11d).

Prepared on a 2.36 mmol scale according to the standard procedure to give 0.601 g (63%) of the *triene* **11d** as a yellow oil; $[\alpha]_D^{20}$ -3.6 (*c* 0.44, CH_2Cl_2); υ_{max} 2932, 1450, 1363, 1265, 1200, 1144, 1095, 1062, 997, 752 cm^{-1}; δ_H (300 MHz) 1.55-1.65 (2H, m, $CH_2CH_2CH_2$), 1.73 (3H, d, J 6.0 Hz,

CH_3CH=CHCH=CH), 2.05-2.10 (2H, m, CH=CHCH=CHCH_2), 2.31-2.38 (2H, m, CH_2CH=CHS), 5.40-5.62 (2H, m, CH_3CH=CHCH=$CHCH_2$), 5.91-6.00 (2H, m, CH_3CH=$CHCH$=$CHCH_2$), 6.44 (1H, d, J 15.0 Hz, CH=CHS), 7.14 (1H, dt, J 15.0, 7.0 Hz, CH=CHS), 7.61-7.77 (3H, m, meta and para protons on Ph), 7.96-7.99 (2H, m, ortho protons on Ph); δ_F (282 MHz) -79.36; *m/z* 407 (CI) 425 (100) (MNH_4^+), 408 (MH^+), 261 (MH^+-CF_3SO_2N), 245, 228, 202, 185, 167, 152, 135, 121, 108 (Found: (MNH_4^+), 425.1181. $C_{17}H_{20}F_3NO_3S_2$ requires (MNH_4^+), 425.1181) (Found: C, 50.26; H, 4.76; N, 3.26. $C_{17}H_{20}F_3NO_3S_2$ requires C, 50.11; H, 4.95; N, 3.44%).

Preparation of (-)-(S_S)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]-1,7,9-undecatriene (12d).

Prepared on a 0.865 mmol scale according to the standard procedure to give 0.281 g (77%) of a 6:1 (1*E*,7*E*,9*E*):(1*E*,7*Z*,9*E*) mixture (by 300 MHz ^{1}H nmr) of the *triene* **12d** as a yellow oil; $[\alpha]_D^{22}$ -12.1 (*c* 0.28, CH_2Cl_2). Data for (*E*,*E*,*E*) isomer: υ_{max} 2933, 2857, 1618, 1444, 1361, 1256, 1195, 1135, 1098, 1062, 997 cm^{-1}; δ_H (300 MHz) 1.26-1.58 (4H, m, $CH_2CH_2CH_2CH_2$), 1.73 (3H, d, J 6.5 Hz, CH_3CH=CH), 2.05 (2H, q, J 7.0 Hz, CH=CHCH=CHCH_2), 2.31-2.36 (2H, m, CH_2CH=CHS), 5.43-5.72 (2H, m, CH_3CH=CHCH=$CHCH_2$), 5.93-6.01 (2H, m, CH_3CH=$CHCH$=$CHCH_2$), 6.44 (1H, d, J 15.0 Hz, CH=CHS), 7.15 (1H, dt, J 15.0, 7.0 Hz, CH=CHS), 7.61-7.76 (3H, m, meta and para protons on Ph), 7.95-7.99 (2H, m, ortho protons on Ph); δ_F (282 MHz) -79.36; *m/z* 421 (CI) 439 (MNH_4^+), 422 (MH^+), 384, 291, 275 (MH^+-CF_3SO_2N), 251, 163, 150 (100) ($CF_3SO_2NH_2^+$), 141, 125, 111 (Found: (MNH_4^+), 439.1337. $C_{18}H_{22}F_3NO_3S_2$ requires (MNH_4^+), 439.1337).

IMDA reactions of sulfoximine-substituted trienes

IMDA reaction of (+)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,6,8-nonatriene (9b).

A thoroughly degassed solution of (+)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,6,8-nonatriene **9b** (0.25 g, 0.602 mmol) in dry toluene (30 ml) was heated in a sealed glass tube under nitrogen at 140°C for 44 h. The solution was allowed to cool and concentrated under reduced pressure to give a brown gum. Chromatography (3:1 petrol–EtOAc) yielded a yellow glass (0.18 g, 72%). The glass was shown by 300 MHz ^{1}H nmr to be a 39:31:25:5 mixture of the cycloadducts (S_S,1*S*,5*R*,6*R*)-5-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene **17b**, (S_S,1*R*,5*S*,6*S*)-5-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene **18b**, (S_S,1*R*,5*R*,6*R*)-5-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]bicyclo-[4.3.0]-2-nonene **19b**, and (S_S,1*S*,5*S*,6*S*)-5-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene **20b**; this mixture was inseparable by HPLC or fractional crystallisation. Data for the mixture: υ_{max} 2938, 2871, 1448, 1319, 1222, 1147, 1093, 1064, 762 cm^{-1}; δ_H (300 MHz) 1.05-1.96 (6H, m, H-7, H-8, H-9), 1.99-2.56 (4H, m, H-1, H-4, H-6), 2.39 (3H, s, CH_3Ar), 3.51 (1H, td, J 10.5, 6.5 Hz, H-5 minor trans **18b**), 3.69 (1H, q, J 6.5 Hz, H-5 **20b**), 3.76 (1H, q, J 6.0 Hz, H-5 **19b**), 3.82 (1H, td, J 11.0, 6.0 Hz, H-5 **17b**), 5.39-5.49 and 5.74-5.79 (2H, m, H-2, H-3), 7.21 (2H, d, J 8.0 Hz, meta protons on to SO_2 Tol), 7.55-7.71 (3H, m, meta and para protons on Ph), 7.82-7.85 (2H, d, J 8.5 Hz, ortho protons to SO_2 on Tol), 7.94-7.98 (2H, m, ortho protons on Ph); *m/z* 415 (CI) 416 (MH^+), 171 ($TsNH_2$), 155, 139, 121 (100), 111, 108 (Found: C, 63.81; H, 6.40; N, 3.12. $C_{22}H_{25}NO_3S_2$ requires C, 63.59; H, 6.06; N, 3.37%).

IMDA reaction of (+)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,7,9-decatriene (10b).[7]

A thoroughly degassed solution of (+)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,7,9-decatriene **10b** (0.33 g, 0.769 mmol) in dry toluene (30 ml) was heated in a sealed glass tube under argon at 130°C for 48 h. The solution was allowed to cool and concentrated under reduced pressure to give an orange

gum. Chromatography (3:1 petrol–EtOAc) yielded a colourless gum (0.23 g, 70%). The gum was shown by 300 MHz ^{1}H nmr to be a 20:14:40:26 mixture of the cycloadducts **22b**, **23b**, **24b**, and **25b**. Recrystallisation from toluene–petrol gave 92 mg (28%) of the major cis-fused diastereomer *(+)-(S$_S$,1R,5R,6R)-5-[S-phenyl-N-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **24b** as a colourless solid, mp 183-185°C; $[\alpha]_D^{22}$ +138 (*c* 0.56, CH_2Cl_2); υ_{max} 2918, 2861, 1444, 1305, 1097, 1064 cm^{-1}; δ_H (500 MHz) 1.23-1.69 (8H, m, H-7, H-8, H-9, H-10), 2.10-2.23 (2H, m, H-4), 2.37 (3H, s, ArC*H*$_3$), 2.43-2.44 (1H, m, H-1), 2.73-2.76 (1H, m, H-6) 3.41-3.42 (1H, m, H-5), 5.46 (2H, s, H-2, H-3), 7.19 (2H, d, J 8.0 Hz, meta protons to SO_2 on Tol), 7.54-7.69 (3H, m, meta and para protons on Ph), 7.79 (2H, d, J 8.0 Hz, ortho protons to SO_2 on Tol), 7.94 (2H, m, ortho protons on Ph); *m/z* 429 (CI) 430 (MH^+), 313, 261 (MH^+-TsN), 211, 189 (100) ($TsNH_2$+NH_4^+), 168, 152, 135, 108 (Found: C, 64.4; H, 6.32; N, 3.13. $C_{23}H_{27}NO_3S_2$ requires C, 64.31; H, 6.33; N, 3.26%).

Semi-preparative HPLC purification (1% 2-propanol–hexane) gave 3 fractions. The first eluted component was a mixture of the two trans-fused cycloadducts *(S$_S$,1S,5R,6R)-5-[S-phenyl-N-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **22b** and *(S$_S$,1R,5S,6S)-5-[S-phenyl-N-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **23b**, as a colourless gum; υ_{max} 2927, 2871, 1440, 1323, 1231, 1193, 1154, 1093, 1065 cm^{-1}; δ_H (500 MHz) 1.01-1.99 (8H, m, H-7, H-8, H-9, H-10), 2.04-2.45 (4H, m, H-1, H-4, H-6), 2.38 (3H, s **22b**), 2.40 (3H, s **23b**), 3.15 (1H, td, J 11.0, 5.5 Hz, H-5 minor **23b**), 3.62 (1H, td, J 10.5, 5.0 Hz, H-5 major **22b**), 5.37 (2H, s, H-2, H-3), 7.21 (2H, d, J 8.5 Hz, meta protons to SO_2 on Tol), 7.55-7.69 (3H, m, meta and para protons on Ph), 7.83 (2H, d, J 8.5 Hz, ortho protons to SO_2 on Tol), 7.94 (2H, d, J 7.5 Hz, ortho protons on Ph).

The second eluted component was the minor cis-fused cycloadduct *(+)-(S$_S$,1S,5S,6S)-5-[S-phenyl-N-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **25b** as a colourless solid, mp 60-62°C; $[\alpha]_D^{20}$ +41.4 (*c* 0.21, CH_2Cl_2); υ_{max} 2921, 2860, 1454, 1314, 1267, 1146, 1098, 1027, 807 cm^{-1}; δ_H (500 MHz) 1.12-1.70 (8H, m, H-7, H-8, H-9, H-10), 2.05-2.08 (1H, m, H-1), 2.25 (1H, d, J 14.0 Hz, H-4$_\alpha$), 2.38 (3H, s, C*H*$_3$Ar), 2.39-2.41 (1H, m, H-6), 2.72 (1H, br d, J 14.0 Hz, H-4$_\beta$), 3.34-3.38 (1H, m, H-5), 5.45-5.54 (2H, m, H-2, H-3), 7.21 (2H, d, J 8.5 Hz, meta protons to SO_2 on Tol), 7.54-7.63 (2H, m, meta protons on Ph), 7.68-7.71 (1H, m, para proton on Ph), 7.81 (2H, d, J 8.5 Hz, ortho protons to SO_2 on Tol), 7.97 (2H, d, J 8.0 Hz, ortho protons on Ph); *m/z* 429 (CI) 447 (MNH_4^+), 430 (MH^+), 364, 313, 296, 276, 245, 189 (100) ($TsNH_2$+NH_4^+), 135, 108 (Found: C, 64.64; H, 6.68; N, 3.18. $C_{23}H_{27}NO_3S_2$ requires C, 64.31; H, 6.33; N, 3.26%).

The third eluted component was the major cis-fused cycloadduct *(+)-(S$_S$,1R,5R,6R)-5-[S-phenyl-N-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **24b** as a colourless solid; spectral data agreed with that found for the recrystallised material above.

IMDA reaction of (+)-(*S*$_S$)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,6,8-decatriene (11b).

A thoroughly degassed solution of (+)-(*S*$_S$)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,6,8-decatriene **11b** (0.215 g, 0.501 mmol) in dry toluene (30 ml) was heated in a sealed glass tube under nitrogen at 130°C for 48 h. The orange solution was allowed to cool and concentrated under reduced pressure to give an orange gum. Chromatography (3:1 hexane–EtOAc) yielded an orange gum (0.140 g, 65%). The gum was shown by 300 MHz ^{1}H nmr to be a 40:30:25:5 mixture of the cycloadducts **26b**, **27b**, **28b** and **29b**.

Semi-preparative HPLC purification (1% 2-propanol–hexane) gave 2 fractions. The first eluted component was the major cis-fused cycloadduct *(S$_S$,1R,4S,5R,6R)-4-methyl-5-[S-phenyl-N-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene* **28b** as a yellow solid, mp 148-150°C; $[\alpha]_D^{20}$ +116 (*c* 1.3, CH_2Cl_2); υ_{max} 2913, 1604, 1450, 1326, 1241, 1156, 1092 cm^{-1}; δ_H (300 MHz) 1.08 (3H, d, J 7.5Hz, C*H*$_3$CH), 1.26-1.84 (6H, m, H-7, H-8, H-9), 2.23 (1H, m, H-1), 2.38 (3H, s, C*H*$_3$Ar), 2.75 (1H, m, H-6), 2.93 (1H, q, J 8.0 Hz, H-4), 3.66 (1H, s, H-5), 5.24-5.35 (2H, m, H-2, H-3), 7.20 (2H, d, J 8.0 Hz, meta protons to SO_2 on Tol), 7.51-7.66 (3H, m, meta and para protons on Ph), 7.79 (2H, d, J 8.5 Hz, ortho protons

to SO_2 on Tol), 7.90-7.93 (2H, m, ortho protons on Ph); *m/z* 429 (CI) 447 (MNH_4^+), 430 (MH^+), 313, 296, 276, 261 (MH^+-TsN), 245, 189 (100) ($TsNH_2$+NH_4^+), 175, 159, 142, 126, 108 (Found: C, 63.86; H, 5.68; N, 3.30. $C_{23}H_{27}NO_3S_2$ requires C, 64.31; H, 6.33; N, 3.26%).

The second eluted component was a mixture of the minor trans-fused diastereomer, assigned as *(S_S,1S,4R,5R,6R)-4-methyl-5-[S-phenyl-N-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene* **26b** and the major trans-fused isomer, assigned as *(S_S,1R,4S,5S,6S)-4-methyl-5-[S-phenyl-N-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene* **27b**, as a yellow glass. Data for the mixture: υ_{max} 2947, 1449, 1310, 1225, 1152, 1091, 1058 cm^{-1}; δ_H (300 MHz) 0.92 (3H, d, J 7.0 Hz, C*H*$_3$CH **26b**), 1.15 (3H, d, J 7.0 Hz, C*H*$_3$CH **27b**), 1.51-1.87 (8H, m, H-1, H-6, H-7, H-8, H-9), 2.38 (3H, s, C*H*$_3$Ar **27b**), 2.39 (3H, s, C*H*$_3$Ar **26b**), 3.20 (1H, m, H-4), 3.66 (1H, dd, J 10.7, 5.1 Hz, H-5 **26b**), 3.67 (1H, dd, J 10.5, 5.0 Hz, H-5 **27b**), 5.33 (1H, m, H-2 **26b**), 5,59 (1H, m, H-2 **27b**), 5.66-5.69 (1H, m, H-3 **26b** and **27b**), 7.17-7.22 (2H, m, meta protons to SO_2 on Tol), 7.52-7.68 (3H, m, meta and para protons on Ph), 7.73-7.80 (2H, m, ortho protons to SO_2 on Tol), 7.92-8.00 (2H, m, ortho protons on Ph); *m/z* 429 (CI) 447 (MNH_4^+), 430 (MH^+), 313, 296, 276, 261 (MH^+-TsN), 245, 206, 189 (100) ($TsNH_2$+NH_4^+), 175, 159, 142, 135, 126, 108 (Found: C, 64.26; H, 6.43; N, 3.28. $C_{23}H_{27}NO_3S_2$ requires C, 64.31; H, 6.33; N, 3.26%).

Neither recrystallisation nor semi-preparative HPLC were successful in purifying the minor cis-fused diastereomer (S_S,1*S*,4*R*,5*S*,6*S*)-4-methyl-5-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene **29b**.

IMDA reaction of (+)-(S_S)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,7,9-undecatriene (12b).

A thoroughly degassed solution of (+)-(S_S)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]-1,7,9-undecatriene **12b** (125 mg, 0.282 mmol) in dry toluene (30 ml) was heated in a sealed glass tube under nitrogen at 133°C for 46 h, with some decomposition being apparent. The resultant dark brown mixture was allowed to cool and concentrated under reduced pressure to give a brown gum. Chromatography (3:1 hexane–EtOAc) yielded 70 mg (56%) of a yellow gum. The gum was shown by 300 MHz ^{1}H nmr to be a 60:10:30 mixture of (S_S,1*R*,4*S*,5*R*,6*R*)-4-methyl-5-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene **32b**, (S_S,1*S*,4*R*,5*R*,6*R*)-4-methyl-5-[*S*-phenyl-*N*-(4-tolylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene **30b** and 4-tolylsulfonamide; the mixture was inseparable by HPLC or fractional crystallisation. Data for the mixture: δ_H (300 MHz) 0.83 (3H, d, J 7.5 Hz, C*H*$_3$CH 32b, 1.13-1.67 (9H, m, H-1, H-7, H-8, H-9, H-10), 1.14 (3H, d, J 7.0 Hz, C*H*$_3$CH **30b**), 2.37 (3H, s, C*H*$_3$Ar **30b** and **32b**), 2.43 (3H, s, C*H*$_3$Ar 4-tolylsulfonamide), 2.49 (1H, d, J 6.0 Hz, H-6), 2.83 (1H, q, J 8.0 Hz, H-4), 3.02 (1H, s, H-5 **32b**), 3.42 (1H, dd, J 10.5, 4.5 Hz, H-5 **30b**), 4.76 (2H, br s, SO_2NH_2), 5.43 (2H, s, H-2, H-3 **32b**), 5.32-5.50 (2H, m, H-2, H-3 **30b**), 7.17-7.33 (2H, m, meta protons to SO_2 on Tol), 7.55-7.70 (3H, m, meta and para protons on Ph), 7.72-7.84 (2H, m, ortho protons to SO_2 on Tol), 7.98-8.01 (2H, m, ortho protons on Ph).

IMDA reaction of (±)-(*E*,*E*)-1-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]-1,6,8-nonatriene (9c).

A thoroughly degassed solution of (±)-(*E*,*E*)-1-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]-1,6,8-nonatriene **9c** (0.221 g, 0.419 mmol) in dry toluene (30 ml) was heated in a sealed glass tube under nitrogen at 141°C for 44 h. The solution was allowed to cool and concentrated under reduced pressure to give a yellow glass. Chromatography (3:1 hexane–EtOAc) yielded a yellow glass (0.174 g, 79%). The glass was shown by 300 MHz ^{1}H nmr to be a 35:30:30:5 mixture of the cycloadducts (S_S*,1*S**,5*R**,6*R**)-5-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene **17c**, (S_S*,1*R**,5*S**,6S*)-5-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene **18c**, (S_S*,1*R**,5*R**,6*R**)-5-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene **19c**, and (S_S*,1*S**,5*S**,6*S**)-5-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-

nonene **20c**; the mixture was inseparable by HPLC or fractional crystallisation. Data for the mixture: υ_{max} 2948, 2875, 1603, 1455, 1370, 1307, 1232, 1150, 1098, 1059 cm^{-1}; δ_H (300 MHz) 1.19-1.26 (18H, m, 3 x $(CH_3)_2CHAr$), 1.27-1.63 (6H, m, H-7, H-8, H-9), 2.03-2.44 (4H, m, H-1, H-4 and H-6), 2.87 (1H, m, $ArCH(CH_3)_2$ para to SO_2), 3.49 (1H, td J 10.5, 5.0 Hz, H-5 **18c**, 3.50 (1H, q, J 6.0 Hz, H-5 **20c**), 3.62 (1H, q, J 6.0 Hz, H-5 **19c**, 3.78 (1H, td, J 11.0, 6.5 Hz, H-5 **17c**), 4.32 (2H, p, J 7.0 Hz, 2 x $ArCH(CH_3)_2$ ortho to SO_2), 5.45-5.51 (2H, m, H-2, H-3), 7.08 and 7.09 (2H, 2 x s, meta protons to SO_2 on Ar), 7.51-7.58 (2H, m, meta protons on Ph), 7.62-7.67 (1H, m, para proton on Ph), 7.86-7.87 (2H, m, ortho protons on Ph); *m/z* 527 (CI) 545 (MNH_4^+), 528 (MH^+), 425, 408, 301 (100) ($TrisNH_2+NH_4^+$), 282, 267, 247 (MH^+-TrisN), 235, 203, 189, 159, 142, 121, 108.

IMDA reaction of (±)-(*E*,*E*)-1-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]-1,7,9-decatriene (10c).

A thoroughly degassed solution of (±)-(*E*,*E*)-1-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]-1,7,9-decatriene **10c** (0.100 g, 0.185 mmol) in dry toluene (30 ml) was heated in a sealed glass tube under nitrogen at 142°C for 46 h. The solution was allowed to cool and concentrated under reduced pressure to give a brown gum. Chromatography (3:1 hexane–EtOAc) yielded a yellow glass (75 mg, 75%). The glass was shown by 300 MHz ^1H nmr to be a 15:5:65:15 mixture of the cycloadducts **22c**, **23c**, **24c** and **25c**. Recrystallisation from toluene–hexane yielded 20.7 mg (21%) of *(S$_S$*,1R*,5R*,6R*)-5-[S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **24c** as a colourless solid, mp 205-207°C; υ_{max} 2935, 2857, 1594, 1444, 1276, 1226, 1149, 1078, 954 cm^{-1}; δ_H (500 MHz) 1.17-1.26 (18H, m, 3 x $(CH_3)_2CHAr$), 1.27-1.70 (8H, m, H-7, H-8, H-9, H-10), 2.21 (2H, br d, J 4.0 Hz, H-4), 2.62 (1H, m, H-1), 2.82-2.90 (2H, m, H-6 and $ArCH(CH_3)_2$ para to SO_2), 3.38-3.39 (1H, m, H-5), 4.23 (2H, p, J 7.0 Hz, 2 x $ArCH(CH_3)_2$ ortho to SO_2), 5.45-5.51 (2H, m, H-2, H-3), 7.08 (2H, s, meta protons to SO_2 on Ar), 7.51-7.58 (2H, m, meta protons on Ph), 7.62-7.67 (1H, m, para proton on Ph), 7.86-7.87 (2H, m, ortho protons on Ph); *m/z* 541 (CI) 542 (MH^+), 425, 408, 301 (100) ($TrisNH_2+NH_4^+$), 299, 282, 261 (MH^+-TrisN), 235, 189, 178, 159, 126, 108 (Found: C, 68.53; H, 7.87; N, 2.78. $C_{31}H_{43}NO_3S_2$ requires C, 68.72; H, 8.00; N, 2.59%).

Semi-preparative HPLC purification (1% 2-propanol–hexane) gave 4 fractions. The first eluted component was the major trans-fused diastereomer *(S$_S$*,1S*,5R*,6R*)-5-[S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sul-foximidoyl]bicyclo[4.4.0]-2-decene* **22c**, as a colourless gum; υ_{max} 2935, 2865, 1564, 1461, 1364, 1290, 1234, 1194, 1147, 1069 cm^{-1}; δ_H (500 MHz) 1.14-1.31 (18H, m, 3 x $(CH_3)_2CHAr$), 1.06-1.72 (8H, m, H-7, H-8, H-9, H-10), 1.77 (1H, br d, J 13.0 Hz, H-1), 1.89-1.91 (1H, m, H-4$_\alpha$), 2.11-2.16 (1H, m, H-6), 2.58 (1H, br d, J 13.0 Hz, H-4$_\beta$), 2.87 (1H, p, J 7.0 Hz, $ArCH(CH_3)_2$ para to SO_2), 3.65 (1H, td, J 10.5, 6.5 Hz, H-5), 4.28 (2H, p, J 7.0 Hz, 2 x $ArCH(CH_3)_2$ ortho to SO_2), 5.35 (1H, d, J 9.0 Hz, H-2), 5.39-5.43 (1H, m, H-3), 7.08 (2H, s, meta protons to SO_2 on Ar), 7.52-7.59 (2H, m, meta protons on Ph), 7.61-7.68 (1H, m, para proton on Ph), 7.86-7.88 (2H, m, ortho protons on Ph); *m/z* 541 (CI) 542 (MH^+), 425, 408, 385, 369, 301 (100) ($TrisNH_2+NH_4^+$), 282, 261 (MH^+-TrisN), 245, 226, 203, 189, 178, 152, 135, 108 (Found: C, 69.02; H, 7.75; N, 2.56. $C_{31}H_{43}NO_3S_2$ requires C, 68.72; H, 8.00; N, 2.59%).

The second eluted component was the minor trans-fused diastereomer *(S$_S$*,1R*,5S*,6S*)-5-[S-phenyl-N-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **23c**, as a colourless gum; υ_{max} 2957, 2857, 1611, 1563, 1452, 1361 1281, 1234, 1203, 1153, 1102, 1062 cm^{-1}; δ_H (500 MHz) 1.19-1.24 (18H, m, 3 x $(CH_3)_2CHAr$), 1.04-1.14 and 1.57-1.76 (8H, m, H-7, H-8, H-9, H-10), 1.84-1.88 (1H, m, H-1), 1.92 (1H, br d, J 7.5 Hz, H-4$_\alpha$), 2.29 (1H, br d, J 13.0 Hz, H-4$_\beta$), 2.36-2.44 (1H, m, H-6), 2.88 (1H, p, J 7.0 Hz, $ArCH(CH_3)_2$ para to SO_2), 3.23 (1H, td, J 10.5, 5.0 Hz, H-5), 4.35 (2H, p, J 7.0 Hz, 2 x $ArCH(CH_3)_2$ ortho to SO_2), 5.36 (1H, d, J 10.5 Hz, H-2), 5.41-5.45 (1H, m, H-3), 7.11 (2H, s, meta protons to SO_2 on Ar), 7.56-7.68 (3H, m, meta and para protons on Ph), 7.96-7.98 (2H, m, ortho protons on Ph); *m/z* 541 (CI) 559 (MNH_4^+), 542 (MH^+), 425 (100), 408, 301 ($TrisNH_2+NH_4^+$), 282, 261 (MH^+-TrisN),

245, 220, 203, 189, 178, 150, 135, 108 (Found: C, 69.11; H, 8.07; N, 2.55. $C_{31}H_{43}NO_3S_2$ requires C, 68.72; H, 8.00; N, 2.59%).

The third eluted component was the minor cis-fused diastereomer *(S_S*,1S*,5S*,6S*)-5-[S-phenyl*-N-*(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **25c**, as a colourless gum; υ_{max} 2957, 2933, 2870, 1614, 1434, 1273, 1244, 1156, 1103, 1063, 997 cm^{-1}; δ_H (500 MHz) 1.18-1.27 (18H, m, 3 x $(CH_3)_2CHAr$), 1.17-1.63 (8H, m, H-7, H-8, H-9, H-10), 2.04-2.07 (1H, m, H-1), 2.29-2.36 (1H, m, H-4α), 2.43 (1H, m, H-6), 2.82-2.90 (2H, m, $ArCH(CH_3)_2$ para to SO_2 and H-4β), 3.35-3.38 (1H, m, H-5), 4.28 (2H, p, J 7.0 Hz, 2 x $ArCH(CH_3)_2$ ortho to SO_2), 5.44 (1H, d, J 10.5 Hz, H-2), 5.50-5.54 (1H, m, H-3), 7.09 (2H, s, meta protons to SO_2 on Ar), 7.56-7.70 (3H, m, meta and para protons on Ph), 7.95-7.97 (2H, m, ortho protons on Ph); *m/z* 541 (CI) 559 (MNH_4^+), 542 (MH^+), 425, 408, 301 (100) ($TrisNH_2+NH_4^+$), 282, 261 (MH^+-TrisN), 245, 220, 203, 189, 178, 150, 135, 108 (Found: C, 68.61; H, 7.93; N, 2.73. $C_{31}H_{43}NO_3S_2$ requires C, 68.72; H, 8.00; N, 2.59%).

The fourth eluted component was the major cis-fused diastereomer *(S_S*,1R*,5R*,6R*)-5-[S-phenyl*-N-*(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **24c** as a colourless solid; spectral data agreed with that found for the recrystallised material above.

IMDA reaction of (±)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]-1,7,9-undecatriene (12c).

A thoroughly degassed solution of (±)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]-1,7,9-undecatriene **12c** (0.260 g, 0.468 mmol) was heated at 143°C for 48 h, with some decomposition being apparent. The resultant dark brown mixture was allowed to cool and concentrated under reduced pressure to give a brown gum. Chromatography (3:1 hexane–EtOAc) yielded of a yellow gum (0.210 g, 81%). The gum was shown by 300 MHz ^1H nmr to be a 5:30:15:50 mixture of (*S_S**,1*S**,4*R**,5*R**,6*R**)-4-methyl-5-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)-sulfoximidoyl]bicyclo[4.4.0]-2-decene **30c**, (*S_S**,1*R**,4*S**,5*R**,6*R**)-4-methyl-5-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)sulfoximidoyl]bicyclo-[4.4.0]-2-decene **32c**, (*S_S**,1*S**,4*R**,5*S**,6*S**)-4-methyl-5-[*S*-phenyl-*N*-(2,4,6-triisopropylphenylsulfonyl)-sulfoximidoyl]bicyclo[4.4.0]-2-decene **33c**, and 2,4,6-triisopropylphenylsulfonamide; the mixture was inseparable by HPLC or fractional crystallisation. Data for the mixture: δ_H (300 MHz) 0.81 (3H, d, J 7.5 Hz, C-4 C*H*$_3$ **33c**), 1.17 (3H, d, J 7.0 Hz, C-4 C*H*$_3$ **32c**), 1.19-1.30 (18H, m, 3 x $(CH_3)_2CHAr$), 1.35 (3H, d, J 6.5 Hz, C-4 C*H*$_3$ **30c**), 1.13-1.67 (8H, m, H-7, H-8, H-9, H-10), 2.17 (1H, m, H-1), 2.46 (1H, m, H-6), 2.61 (1H, m, H-4), 2.85-2.95 (1H, m, $(CH_3)_2CHAr$ para to SO_2), 2.98 (1H, s, H-5, **32c** and **33c**), 3.42 (1H, dd, J 10.5, 4.5 Hz, H-5, **30c**), 4.76 (2H, br s, SO_2NH_2), 5.43 (2H, s, H-2, H-3, **32c** and **33c**), 5.32-5.50 (2H, m, H-2, H-3, **30c**), 7.08 (2H, s, meta protons to SO_2 on Ar, **32c** and **33c**), 7.11 (2H, s, meta protons to SO_2 on Ar, **30c**), 7.17 (2H, s, 50% meta protons to SO_2 on $ArSO_2NH_2$), 7.55-7.70 (3H, m, meta and para protons on Ph), 7.98-8.01 (2H, m, ortho protons on Ph).

IMDA reaction of (-)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]-1,6,8-nonatriene (9d).

A thoroughly degassed solution of (-)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]-1,6,8-nonatriene **9d** (0.395 g, 1.01 mmol) in dry toluene (30 ml) was heated in a sealed glass tube under nitrogen at 123°C for 46 h. The solution was allowed to cool and concentrated under reduced pressure to give a brown oil. Chromatography (3:1 hexane–EtOAc) yielded a yellow waxy solid (0.350 g, 89%). The solid was shown by 300 MHz ^1H nmr to be a 38:32:22:8 mixture of the cycloadducts **17d**, **18d**, **19d** and **20d**.

Semi-preparative HPLC purification (1% 2-propanol–hexane) gave 4 fractions. The first eluted component was the major trans-fused diastereomer *(+)-(S_S,1S,5R,6R)-4-[S-phenyl*-N-*(trifluoromethylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene* **17d** as a colourless solid, mp 118-119°C; $[\alpha]_D^{20}$ +19.4 (*c* 1.6, CH_2Cl_2); υ_{max} 2927, 2854, 1453, 1347, 1204, 1095, 1025, 805 cm^{-1}; δ_H (500 MHz) 1.15-1.80 (6H, m, H-7,

H-8, H-9), 1.81-1.84 (1H, m, H-1), 1.89-1.96 (1H, m, H-6), 2.06-2.18 H-4$_\alpha$), 2.19-2.27 (1H, m, H-4$_\beta$), 3.82 (1H, td, J 11.0, 6.0 Hz, H-5), 5.43-5.47 (1H, m, H-3), 5.83 (1H, d, J 10.0 Hz, H-2), 7.68 (2H, t, J 8.0 Hz, meta protons on Ph), 7.78 (1H, t, J 7.5 Hz, para proton on Ph), 7.98 (2H, d, J 9.0 Hz, ortho protons on Ph); δ_F (282 MHz) -79.50; *m/z* 393 (CI) 411 (MNH_4^+), 288, 271, 270, 247 (MH^+-CF_3SO_2N), 231, 199, 190, 150 ($CF_3SO_2NH_3^+$), 133, 121 (100), 109 (Found: C, 49.09; H, 4.69; N, 3.73. $C_{16}H_{18}F_3NO_3S_2$ requires C, 48.85; H, 4.61; N, 3.56%).

The second eluted component contained 10% major trans-fused diastereomer **17d** and 90% minor cis-fused diastereomer *(+)-(S$_S$,1S,5S,6S)-5-[S-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene* **20d**, as a colourless gum; υ_{max} 2922, 2867, 1466, 1383, 1259, 1222, 1193, 1139, 1094, 1044, 1013 cm^{-1}; δ_H (500 MHz) (*inter alia*) 1.21-1.91 (6H, m, H-7, H-8, H-9), 2.35-2.41 (1H, m, H-4$_\alpha$), 2.50-2.54 (1H, m, H-1), 2.56-2.58 (1H, m, H-6), 2.60-2.62 (1H, m, H-4$_\beta$), 3.51 (1H, q, J 6.5 Hz, H-5), 5.52-5.55 (1H, m, H-3), 5.61 (1H, d, J 12.0 Hz, H-2), 7.67 (2H, t, J 8.0 Hz, meta protons on Ph), 7.78 (1H, t, J 7.5 Hz, para proton on Ph), 7.98 (2H, d, J 8.0 Hz, ortho protons on Ph); δ_F (282 MHz) -79.26; *m/z* 393 (CI) 411 (100) (MNH_4^+), 291, 174, 150 ($CF_3SO_2NH_3^+$), 138, 121, 108.

The third eluted component was the minor trans-fused diastereomer *(+)-(S$_S$,1R,5S,6S)-5-[S-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene* **18d** as a colourless gum; $[\alpha]_D^{20}$ +50.4 (*c* 0.14, CH_2Cl_2); υ_{max} 2969, 2881, 1448, 1361, 1193, 1135, 1092, 1056, 1024 cm^{-1}; δ_H (500 MHz) 1.16-2.00 (6H, m, H-7, H-8, H-9), 2.01-2.07 (1H, m, H-1), 2.08-2.18 (1H, m, H-6), 2.30-2.37 (1H, m, H-4$_\alpha$), 2.51-2.58 (1H, m, H-4$_\beta$), 3.60 (1H, td, J 11.0, 6.0 Hz, H-5), 5.51-5.55 (1H, m, H-3), 5.83 (1H, d, J 9.5 Hz, H-2), 7.68 (2H, t, J 8.0 Hz, meta protons on Ph), 7.78 (1H, t, J 7.5 Hz, para proton on Ph), 8.01 (2H, d, J 8.0 Hz, ortho protons on Ph); δ_F (282 MHz) -79.33; *m/z* 393 (CI) 411 (MNH_4^+, 100), 394 (MH^+), 247 (MH^+-CF_3SO_2N), 231, 159, 150 ($CF_3SO_2NH_3^+$), 138, 121, 108 (Found: C, 49.11; H, 4.77; N, 3.79. $C_{16}H_{18}F_3NO_3S_2$ requires C, 48.85; H, 4.61; N, 3.56%).

The fourth eluted component contained 5% minor trans-fused diastereomer **18d** and 95% major cis-fused diastereomer *(+)-(S$_S$,1R,5R,6R)-5-[S-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene* **19d** as a colourless gum; υ_{max} 3029, 2956, 2894, 2828, 1441, 1362, 1254, 1215, 1190, 1134, 1086, 1061, 1030 cm^{-1} δ_H (500 MHz) 1.34-2.03 (6H, m, H-7, H-8, H-9), 2.22-2.29 (1H, m, H-4$_\alpha$), 2.34-2.41 (1H, m, H-4$_\beta$), 2.56-2.61 (1H, m, H-1), 2.70 (1H, td, J 15, 6.5 Hz, H-6), 3.67 (1H, q, J 6.0 Hz, H-5), 5.45-5.49 (1H, m, H-3), 5.58 (1H, dq, J 10.0, 2.5 Hz, H-2), 7.64-7.68 (2H, m, meta protons on Ph), 7.76-7.79 (1H, m, para proton on Ph), 7.98-8.01 (2H, m, ortho protons on Ph); δ_F (282 MHz) -79.36; *m/z* 393 (CI) 411 (MNH_4^+), 394 (MH^+), 291, 247 (MH^+-CF_3SO_2N), 231, 159, 150 ($CF_3SO_2NH_3^+$), 138, 121 (100), 108.

IMDA Reaction of (-)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]-1,7,9-decatriene (10d).

A thoroughly degassed solution of (-)-(S_S)-(*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]-1,7,9-decatriene **10d** (415 mg, 1.02 mmol) in dry toluene (30 ml) was heated in a sealed glass tube under nitrogen at 116°C for 45 h. The solution was allowed to cool and concentrated under reduced pressure to give a brown gum. Chromatography (3:1 hexane–EtOAc) yielded a yellow gum (0.283 g, 68%). The gum was shown by 300 MHz ^{1}H nmr to be a 24:21:35:20 mixture of the cycloadducts **22d**, **23d**, **24d** and **25d**.

Recrystallisation from toluene–hexane yielded 46.6 mg (11%) of the major cis-fused diastereomer *(+)-(S$_S$,1R,5R,6R)-5-[S-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **24d** as a colourless solid, mp 135-137°C; $[\alpha]_D^{20}$ +53.3 (*c* 1.59, CH_2Cl_2). υ_{max} 2972, 2855, 1455, 1363, 1218, 1195, 1148, 1092, 1064, 1023, 799 cm^{-1}; δ_H (500 MHz) 1.23-1.74 (8H, m, H-7, H-8, H-9, H-10), 2.19-2.30 (2H, m, H-4), 2.70 (1H, m, H-1), 2.79-2.81 (1H, m, H-6), 3.48-3.49 (1H, m, H-5), 5.50-5.54 (1H, m, H-3), 5.58 (1H, d, J 10.5 Hz, H-2), 7.57-7.72 (3H, m, meta and para protons on Ph), 7.91-7.93 (2H, m, ortho protons on Ph); δ_F (282 MHz) -79.36; *m/z* 407 (CI) 425 (MNH_4^+), 261 (MH^+-CF_3SO_2N), 245, 168, 150 ($CF_3SO_2NH_3^+$), 135 (100), 126 ($PhSOH^+$), 116, 108 (Found: C, 50.09; H, 4.88; N, 3.38. $C_{17}H_{20}F_3NO_3S_2$ requires C, 50.11; H, 4.95; N, 3.44%).

Semi-preparative HPLC purification (1% 2-propanol–hexane) gave 4 fractions. The first eluted component was the major trans-fused cycloadduct *(+)-(S_S,S,5R,6R)-5-[S-phenyl-N-(trifluoromethylsulfonyl)-sulfoximidoyl]bicyclo[4.4.0]-2-decene* **22d** as a colourless solid, mp 123-124°C; $[\alpha]_D^{20}$ +10.3 (*c* 1.06, CH_2Cl_2); υ_{max} 2918, 2854, 1345, 1199, 1154, 1092, 1062, 1024 cm^{-1}; δ_H (500 MHz) 1.07-1.89 (9H, m, H-7, H-8, H-9, H-10 and H-1), 1.96-1.99 (1H, m, H-4α), 2.15-2.21 (1H, m, H-6), 2.56 (1H, dd, J 12.5, 3.0 Hz, H-4β), 3.66 (1H, td, J 11.0, 5.5 Hz, H-5), 5.40-5.45 (2H, m, H-2, H-3), 7.68 (2H, t, J 8.0 Hz, meta protons on Ph), 7.78 (1H, t, J 7.5 Hz, para proton on Ph), 7.96 (2H, d, J 8.0 Hz, ortho protons on Ph); δ_F (282 MHz) -79.66; *m/z* 407 (CI) 425 (MNH_4^+), 261 (MH^+-CF_3SO_2N), 245, 167, 150 ($CF_3SO_2NH_3^+$), 135 (100), 125, 108 (Found: C, 49.88; H, 4.99; N, 3.32. $C_{17}H_{20}F_3NO_3S_2$ requires C, 50.11; H, 4.95; N, 3.44%).

The second eluted component was the minor cis-fused diastereomer *(+)-(S_S,1S,5S,6S)-5-[S-phenyl-N-(trifluoromethylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **25d** as a colourless solid, mp 108-110°C; $[\alpha]_D^{20}$ +122.2 (*c* 0.51, CH_2Cl_2); υ_{max} 2925, 2860, 1444, 1368, 1255, 1196, 1140, 1089, 1060, 901 cm^{-1}; δ_H (500 MHz) 1.21-1.70 (8H, m, H-7, H-8, H-9, H-10), 2.12-2.15 (1H, m, H-1), 2.34 (1H, br dd, J 20.0, 6.5 Hz, H-4α), 2.52 (1H, m, H-6), 2.80 (1H, br d, J 19.5 Hz, H-4β), 3.43-3.46 (1H, m, H-5), 5.58-5.61 (2H, m, H-2, H-3), 7.68 (2H, t, J 8.0 Hz, meta protons on Ph), 7.77 (1H, t, J 7.5 Hz, para proton on Ph), 7.99 (2H, d, J 8.0 Hz, ortho protons on Ph); δ_F (282 MHz) -79.27; *m/z* 407 (CI) 425 (MNH_4^+), 261 (MH^+-CF_3SO_2N), 245, 165, 150 ($CF_3SO_2NH_3^+$), 135 (100), 124, 116, 108 (Found: C, 50.42; H, 4.97; N, 3.66. $C_{17}H_{20}F_3NO_3S_2$ requires C, 50.11; H, 4.95; N, 3.44%).

The third eluted component was the minor trans-fused diastereomer *(+)-(S_S,1R,5S,6S)-5-[S-phenyl-N-(trifluoromethylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **23d** as a colourless solid, mp 121-123°C; $[\alpha]_D^{20}$ +102.2 (*c* 0.3, CH_2Cl_2); υ_{max} 2927, 2849, 1445, 1362, 1259, 1206, 1147, 1099, 1060, 797, 755 cm^{-1}; δ_H (500 MHz) 1.12-1.38 and 1.76-1.87 (8H, m, H-7, H-8, H-9, H-10), 1.85-1.89 (1H, m, H-1), 1.91-1.97 (1H, m, H-4α), 2.42-2.49 (1H, m, H-6), 2.51 (1H, d, J 12.0 Hz, H-4β), 3.33 (1H, td, J 10.5, 5.0 Hz, H-5), 5.43 (2H, s, H-2, H-3), 7.68 (2H, t, J 8.0 Hz, meta protons on Ph), 7.78 (1H, t, J 7.5 Hz, para proton on Ph), 7.99 (2H, d, J 7.0 Hz, ortho protons on Ph); δ_F (282 MHz) -79.34; *m/z* 407 (CI) 425 (MNH_4^+), 245, 168, 150 ($CF_3SO_2NH_3^+$), 135 (100), 126 ($PhSOH^+$), 108 (Found: C, 49.77; H, 5.06; N, 3.21. $C_{17}H_{20}F_3NO_3S_2$ requires C, 50.11; H, 4.95; N, 3.44%).

The fourth eluted component was found to be the major cis-fused diastereomer *(+)-(S_S,1R,5R,6R)-5-[S-phenyl-N-(trifluoromethylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **24d**; spectral data agreed with that found for the recrystallised material above.

IMDA reaction of (-)-(S_S)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]-1,6,8-decatriene (11d).

A thoroughly degassed solution of (-)-(S_S)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]-1,6,8-decatriene **11d** (0.200 g, 0.491 mmol) in dry toluene (30 ml) was heated in a sealed glass tube under nitrogen at 125°C for 48 h. The solution was allowed to cool and concentrated under reduced pressure to give a dark brown gum. Chromatography (3:1 hexane–EtOAc) yielded a yellow gum (106 mg, 53%). The gum was shown by 300 MHz ^1H nmr to be a 90:10 mixture of the cycloadducts **27d** and **28d**.

Semi-preparative HPLC purification (1% 2-propanol–hexane), followed by recrystallisation from toluene–hexane yielded the trans-fused cycloadduct *(S_S,1R,4S,5S,6S)-4-methyl-5-[S-phenyl-N-(trifluoromethanesulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene* **27d** as a colourless solid, mp 153-155°C; $[\alpha]_D^{20}$ +45 (*c* 2.6, CH_2Cl_2); υ_{max} 2957, 1454, 1365, 1195, 1139, 1091, 1050 cm^{-1}; δ_H (300 MHz) 1.40 (3H, d, J 7.0 Hz, CH_3CH), 1.55-1.78 (6H, m, H-7, H-8, H-9), 1.91-1.99 (2H, m, H-1, H-6), 3.29 (1H, m, H-4), 3.80 (1H, dd, J 11.0, 5.0 Hz, H-5), 5.59 (1H, dd, J 7.5, 3.0 Hz, H-2), 5.74 (1H, d, J 10.0 Hz, H-3), 7.62-7.67 (2H, m, meta protons on Ph), 7.72-7.77 (1H, m, para protons on Ph), 8.00-8.03 (2H, m, ortho protons on Ph); δ_F (282 MHz) -79.50; *m/z* 407 (CI) 425 (MNH_4^+), 261 (MH^+-CF_3SO_2N), 245, 159, 150

($CF_3SO_2NH_3^+$), 142, 135 (100), 126, 110 (Found: C, 50.09; H, 4.87; N, 3.51. $C_{17}H_{20}F_3NO_3S_2$ requires C, 50.11; H, 4.95; N, 3.44%).

The cis-fused cycloadduct *(S$_S$,1R,4S,5R,6R)-4-methyl-5-[S-phenyl-N-(trifluoromethylsulfonyl)sulfoximidoyl]bicyclo[4.3.0]-2-nonene* **28d** was not obtained pure; δ_H (300 MHz) 1.12 (3H, d, J 7.0 Hz, C*H*$_3$CH), 1.25-1.75 (6H, m, H-7, H-8, H-9), 2.41-2.49 (1H, m, H-1) 2.52-2.58 (1H, m, H-6), 2.95-2.99 (1H, m, H-4), 3.65 (1H, s, H-5), 5.38 (2H, s, H-2, H-3), 7.62-7.67 (2H, m, meta protons on Ph), 7.72-7.77 (1H, m, para protons on Ph), 8.00-8.03 (2H, m, ortho protons on Ph); δ_F (282 MHz) -79.23.

IMDA reaction of (-)-(S_S)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)sulfoximidoyl]-1,7,9-undecatriene (12d).

A thoroughly degassed solution of (-)-(S_S)-(*E*,*E*,*E*)-1-[*S*-phenyl-*N*-(trifluoromethylsulfonyl)-sulfoximidoyl]-1,7,9-undecatriene **12d** (101 mg, 0.237 mmol) in dry toluene (30 ml) was heated in a sealed glass tube under nitrogen at 123°C for 46 h. The solution was allowed to cool and concentrated under reduced pressure to give a brown gum. Chromatography (3:1 hexane–EtOAc) yielded a yellow gum (75 mg, 74%). The gum was shown by 300 MHz ^{1}H nmr to be a 20:80 mixture of the cycloadducts **30d** and **32d**.

Semi-preparative HPLC purification (1% 2-propanol–hexane) gave 2 fractions. The first eluted component was the trans-fused cycloadduct *(S$_S$,1S,4R,5R,6R)-4-methyl-5-[S-phenyl-N-(trifluoromethylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **30d** as a colourless glass; $[\alpha]_D^{20}$ +16.4 (*c* 1.2, CH_2Cl_2); υ_{max} 2926, 2857, 1445, 1350, 1187, 1152, 1086, 1055 cm^{-1}; δ_H (500 MHz) 1.10-1.74 (8H, m, H-7, H-8, H-9, H-10), 1.35 (3H, d, J 7.0 Hz, C*H*$_3$CH), 1.81-1.85 (1H, m, H-1), 1.96-2.04 (1H, m, H-6), 3.07-3.13 (1H, m, H-4), 3.72 (1H, dd, J 10.5, 4.5 Hz, H-5), 5.35 (1H, d, J 9.5 Hz, H-2), 5.60-5.63 (1H, m, H-3), 7.63-7.75 (3H, m, meta and para protons on Ph), 7.98-8.01 (2H, m, ortho protons on Ph); δ_F (282 MHz) -79.54; *m/z* 421 (CI) 439 (MNH_4^+), 422 (MH^+), 275 (MH^+-CF_3SO_2N), 259, 191, 181, 166, 149 (100) ($CF_3SO_2NH_2$), 126 ($CF_3SO_2H^+$), 109 (Found: (MNH_4^+), 39.1337. $C_{15}H_{19}NOS$ requires (MNH_4^+), 439.1337).

The second eluted component was the cis-fused diastereomer *(S$_S$,1R,4S,5R,6R)-4-methyl-5-[S-phenyl-N-(trifluoromethylsulfonyl)sulfoximidoyl]bicyclo[4.4.0]-2-decene* **32d** as a colourless gum; $[\alpha]_D^{20}$ +28.7 (*c* 2.3, CH_2Cl_2); υ_{max} 2926, 2857, 1445, 1350, 1187, 1152, 1086, 1055 cm^{-1}; δ_H (500 MHz) 0.90 (3H, d, J 7.5 Hz, C*H*$_3$CH), 1.18-1.78 (8H, m, H-7, H-8, H-9, H-10), 2.55-2.59 (1H, m, H-4), 2.72 (1H, br s, H-1), 2.89-2.92 (1H, m, H-6), 3.09 (1H, s, H-5), 5.48-5.56 (2H, m, H-2, H-3), 7.68 (2H, t, J 8.0 Hz, meta protons on Ph), 7.77 (1H, t, J 7.5 Hz, para protons on Ph), 8.00 (2H, d, J 7.5 Hz, ortho protons on Ph); δ_F (282 MHz) -79.19; *m/z* 421 (CI) 439 (MNH_4^+), 391, 275, 259, 181, 166, 149 (100), 126, 109 (Found: (MNH_4^+), 439.1337. $C_{15}H_{19}NOS$ requires (MNH_4^+), 439.1337).

X-Ray Crystal Data[35]

All data were corrected for Lorentz and polarisation factors; the non-hydrogen atoms were refined anisotropically. Unless stated otherwise, the positions of all hydrogen atoms were idealised, C-H = 0.96 Å, assigned isotropic thermal parameters, U(H) = 1.2U_{eq}(C), and allowed to ride on their parent carbon atoms. All methyl groups were refined as rigid bodies. All computations were carried out using the SHELXTL programme system.[36]

Compound **17d** has two crystallographically independent molecules that have very similar gross conformations. Data were measured using a Siemens P3/PC diffractometer, using Cu-K$_\alpha$ radiation (λ = 1.54178 Å, graphite monochromator) using ω-scans, with $0° \leq 2\theta \leq 116°$. $C_{16}H_{18}F_3NO_3S_2$, M = 393.4, monoclinic, a = 8.949(5), b = 16.965(8), c = 11.843(5) Å, β = 95.12(2)°, V = 1791 Å^3, space group $P2_1$, Z = 4, D_c = 1.46 g cm^{-3}, μ(Cu-K$_\alpha$) = 31.2 cm^{-1}, F(000) = 816. 2683 Independent reflections were measured of which 2344 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least

squares to give $R = 0.038$, $R_w = 0.039$ [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.20 and -0.19 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.010 and 0.000 respectively.

Compound **22d** has two crystallographically independent molecules that have very similar gross conformations. Data were measured using a Siemens P4/PC diffractometer, using Cu-K$_\alpha$ radiation (λ = 1.54178 Å, graphite monochromator) using ω-scans, with $0° \leq 2\theta \leq 116°$. $C_{17}H_{20}F_3NO_3S_2$, M = 407.5, orthorhombic, a = 10.346(2), b = 10.538(3), c = 36.019(6) Å, V = 3927 Å^3, space group $P2_12_12_1$, Z = 8, D_c = 1.38 g cm^{-3}, μ(Cu-K$_\alpha$) = 28.7 cm^{-1}, $F(000)$ = 1696. 3034 Independent reflections were measured of which 2652 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares to give $R = 0.043$, $R_w = 0.044$ [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.22 and -0.21 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.003 and 0.000 respectively.

Compound (±)-**24b**: data were measured using a Siemens P3/PC diffractometer, using Cu-K$_\alpha$ radiation (λ = 1.54178 Å, graphite monochromator) using ω-scans, with $3° \leq 2\theta \leq 116°$. $C_{23}H_{27}NO_3S_2$, M = 429.6, triclinic, a = 8.778(2), b = 10.517(2), c = 13.806(3) Å, α = 96.13(3), β = 105.92(3), γ = 113.04(3)°, V = 1094 Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.30 g cm^{-3}, μ(Cu-K$_\alpha$) = 24.0 cm^{-1}, $F(000)$ = 456. 2950 Independent reflections were measured of which 2327 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares to give $R = 0.069$, $R_w = 0.070$ [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.39 and -1.01 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.000 and 0.000 respectively.

Compound (±)-**24d** has a solvent toluene molecule disordered about a centre of symmetry. Data were measured using a Siemens P3/PC diffractometer, using Cu-K$_\alpha$ radiation (λ = 1.54178 Å, graphite monochromator) using ω-scans, with $0° \leq 2\theta \leq 110°$. [$C_{17}H_{20}F_3NO_3S_2$]·0.5($C_7H_8$), M = 453.5, triclinic, a = 9.302(6), b = 10.415(6), c = 12.366(7) Å, α = 82.27(2), β = 84.62(2), γ = 66.14(2)°, V = 1085 Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.39 g cm^{-3}, μ(Cu-K$_\alpha$) = 26.5 cm^{-1}, $F(000)$ = 474. 2715 Independent reflections were measured of which 2297 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares to give $R = 0.047$, $R_w = 0.054$ [$w^{-1} = \sigma^2(F) + 0.0010F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.34 and -0.27 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.000 and 0.000 respectively.

Compound (±)-**27d**: data were measured using a Siemens P4/PC diffractometer, using Cu-K$_\alpha$ radiation (λ = 1.54178 Å, graphite monochromator) using ω-scans, with $0° \leq 2\theta \leq 116°$. $C_{17}H_{20}F_3NO_3S_2$, M = 407.5, monoclinic, a = 10.229(4), b = 18.532(4), c = 11.095(3) Å, β = 114.62(2)°, V = 1912 Å^3, space group $P2_1/c$, Z = 4, D_c = 1.42 g cm^{-3}, μ(Cu-K$_\alpha$) = 29.4 cm^{-1}, $F(000)$ = 848. 2577 Independent reflections were measured of which 2111 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares to give $R = 0.048$, $R_w = 0.052$ [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.23 and -0.28 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.000 and 0.000 respectively.

Compound **28b**: data were measured using a Siemens P3/PC diffractometer, using Cu-K$_\alpha$ radiation (λ = 1.54178 Å, graphite monochromator) using ω-scans, with $0° \leq 2\theta \leq 116°$. $C_{23}H_{27}NO_3S_2$, M = 429.6, monoclinic, a =6.626(5), b = 21.739(15), c = 7.623(6) Å, β = 102.83(2)°, V = 1071 Å^3, space group $P2_1$, Z = 2, D_c = 1.33 g cm^{-3}, μ(Cu-K$_\alpha$) = 24.5 cm^{-1}, $F(000)$ = 456. 1494 Independent reflections were measured of which 1427 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares to give $R = 0.038$, $R_w = 0.041$ [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.27 and -0.26 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.000 and 0.000 respectively.

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(*Received in UK* 18 *January* 1995; *revised* 6 *April* 1995; *accepted* 7 *April* 1995)