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INTRAMOLECULAR DIELS-ALDER REACTIONS OF SULPHONYL-SUBSTITUTED TRIENES

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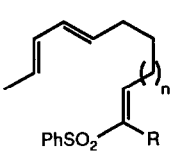
Abstract: The synthesis and thermal intramolecular Diels-Alder reactions of a series of sulphonyl-substituted deca-, undeca- and dodecatrienes have been carried out. The stereoselectivities of these reactions are discussed, and methylation reactions of the bicyclic products are described.

Introduction

The intramolecular Diels-Alder (IMDA) reaction was first reported nearly thirty years ago.[2] Since that time a large number of reports has appeared describing various aspects of this versatile reaction. IMDA Reactions of a wide variety of substrates have been examined, and have formed key parts of several total syntheses. Some important trends of reactivity and stereoselectivity have emerged, and theoretical models have been put forward to explain the observed behaviour.[3] We became interested in IMDA reactions of sulphonyl-substituted trienes for two distinct reasons. Firstly, we felt that the cyclization behaviour of these relatively unknown[4] substrates would offer further insight into the rôle of dienophile substitution in determining the stereochemical outcome of these processes. Secondly, it was considered that the diverse reactivity of the sulphone group[5] would offer rich opportunities for synthetic manipulation of the IMDA reaction products. Herein we report in full[6] the results of our investigations of thermal IMDA reactions of 1-(phenylsulphonyl)-1,6,8-decatriene and 1-(phenylsulphonyl)-1,7,9-undecatriene, and several substituted derivatives.

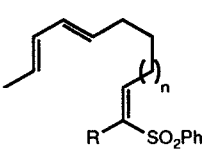
Results and Discussion



1a,b: R = H

2a,b: R = Me

a series: n = 1
b series: n = 2



3a,b: R = H

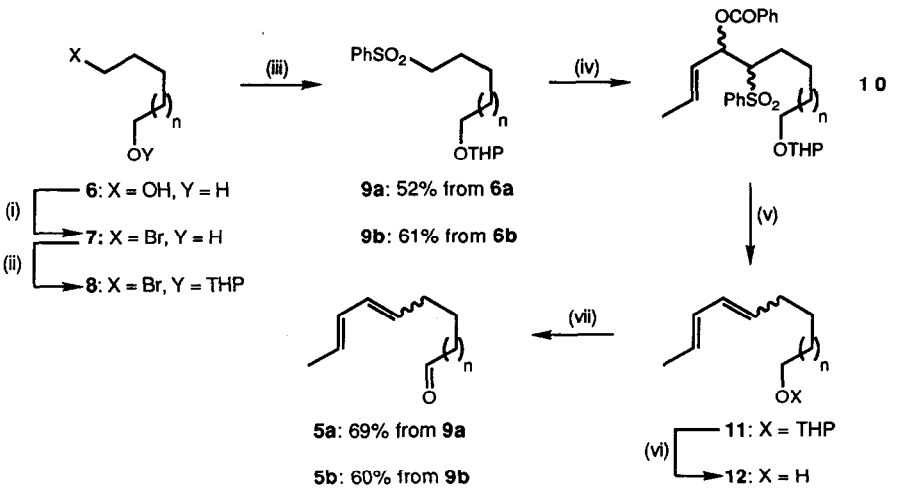
4a,b: R = Me

We have looked at thermal IMDA reactions of sulphonyl-substituted trienes **1-4** depicted above. Several factors indicated this choice of substrates. Firstly, it was considered that the lack of functionality other than the vinylic sulphone group would yield the clearest picture of the inherent effect upon IMDA reactivity of sulphonyl substituents on the dienophile. Secondly, a comparison of the cyclization behaviour of geometric isomers would give an indication of the degree of importance of dienophile geometry in determining product composition.[7]

Thirdly, the cyclization of trienes methylated α- to the sulphone group would allow some estimation of the limits of reactivity of this type of substrate. Also, the products of these reactions would enable correlation of the products of methylation reactions of α-unsubstituted IMDA products. Finally, the inclusion of the diene terminal methyl group would result in the presence in the cyclization products of a methyl group β- to the sulphone function. It was anticipated that this would aid structural assignment by virtue of the well-established tendency for the phenylsulphonyl group to cause deshielding of proximal protons.[8]

Synthesis of cyclization substrates

It was decided to pursue a synthetic approach to the desired trienes in which the dienophile part of the molecule was introduced at a late stage in the synthesis. This would allow the preparation of all eight substrates from only two homologous diene-containing synthetic precursors. Given the ready ability of the sulphone group to stabilize an adjacent carbanion[5] it was decided to couple a nucleophilic sulphonyl species with an appropriate electrophilic diene. This indicated dienals **5** as the requisite intermediates. These were synthesized in good overall yield from commercially available diols **6**. Reagents, conditions and yields are summarized in Scheme 1. Treatment of **6** with concentrated aqueous HBr in benzene under reflux with azeotropic removal of water[9] gave bromoalcohols **7**. Protection of crude **7** as the tetrahydropyranyl (THP) ethers **8**[10] followed by reaction with phenylsulphinate anion in dimethylsulphoxide (DMSO) gave the key intermediates **9** after chromatography.[11] Notably, the three-step sequences for the conversion of **6** into **9** proceeded in high overall yields on multigram scales with a single chromatographic purification step. Introduction of the diene function was carried out using Julia chemistry.[12] Deprotonation of sulphones **9** using *n*-butyllithium in tetrahydrofuran (THF) and reaction with crotonaldehyde followed by benzoyl chloride gave benzoates **10** as 1:1 diastereomeric mixtures upon simple extractive work-up. Reductive elimination of **10** using buffered sodium amalgam in THF-methanol gave the dienyl THP ethers **11** after chromatography in high overall yields for the two-step sequence from **9**.

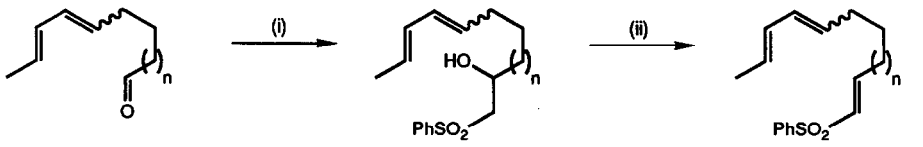


Reagents and conditions: (i) 48% aq. HBr, benzene, reflux; (ii) 3,4-dihydro-2*H*-pyran, cat. H^+, CH_2Cl_2, r.t.; (iii) $PhSO_2Na$, DMSO, r.t.; (iv) ^nBuLi, THF, -78°C, then $CH_3CH{=}CHCHO$, -78°C, then PhCOCl, -78 to 0°C; (v) 6% Na(Hg), 3:1 THF-MeOH, -20°C; (vi) cat. H^+, MeOH, r.t.; (vii) $(COCl)_2$, DMSO, CH_2Cl_2, -60°C, then add **12**, then add Et_3N, -60°C to r.t.

Scheme 1

^{1}H Nmr analysis of **11** showed the presence of both *E*- and *Z*-isomers at the newly-formed double bond in a ratio of *ca.* 6:1. Removal of the THP protecting group[10] and Swern oxidation[13] of the resulting alcohols **12** completed the synthesis of dienals **5**.[14] The synthesis required seven synthetic operations and four chromatographic purification steps. A drawback of our synthesis of **5** was the formation of a 6:1 mixture of *E*, *E*- and *Z*, *E*-dienes **11** in the reduction step of the Julia olefination procedure. In order to minimize contamination by the minor diene isomer, alcohols **12** were converted to the corresponding crystalline 3,5-dinitrobenzoate derivatives **13**. Recrystallization then yielded material further enriched in the major *E*, *E*-component. Hydrolysis of **13** gave **12** as a 20:1 mixture of *E*, *E*- and *Z*, *E*-isomers which was carried forward in the synthetic sequence as before. Full details are provided in the Experimental section.

The method employed for the introduction of the α,β-unsaturated sulphone group to complete the triene synthesis varied according to the dienophile geometry and the nature of α-substitution required. Trienes **1** were synthesized *via* a two-step sequence. Reaction of dienals **5** with with the lithio-anion derived from (phenylsulphonyl)methane followed by low-temperature proton quench gave β-hydroxysulphones **14** in excellent yields. Treatment of crude **14** with methanesulphonyl chloride in the presence of excess triethylamine[15] gave **1** in high overall yield as *ca.* 97:3 mixtures of *E*- and *Z*-$\Delta_{1,2}$ isomers (Scheme 2).



5 **14** **1a**: 82% from **5a**

1b: 69% from **5b**

Reagents and conditions: (i) Add **5** to $PhSO_2CH_2Li$, THF, -78°C, then 10% v/v AcOH-THF, -78°C; (ii) CH_3SO_2Cl, Et_3N, CH_2Cl_2, -6°C.

Scheme 2

Substrates **2** and **4** were prepared from (phenylsulphonyl)ethane and **5**. Reaction of 1-lithio-1-(phenylsulphonyl)ethane with **5** gave the expected β-hydroxysulphone adducts as *ca.* 1:1 mixtures of *erythro*- and *threo*-diastereomers **15** and **16**, which were separated by chromatography. Treatment of the purified *erythro*-diastereomers **15** with *n*-butyllithium/tosyl chloride gave tosylates **17**. Subsequent potassium *t*-butoxide-mediated E2 elimination[16] cleanly yielded the *E*, *E*, *E*-trienes **2**. ^{1}H nmr indicated the absence of any *Z*, *E*, *E*-isomer **4**. Trienes **2** prepared in this way were identical with the products of α-lithiation followed by reaction with iodomethane of unsubstituted analogues **1**.[17] Similar processing of the *threo*-diastereomers **16** initially gave tosylates **18**, which yielded **4** on base treatment as for **17**. Trienes **4** were uncontaminated by **2**, as evidenced by ^{1}H nmr. An X-ray structure of tosylate **18a** (Figure 1) confirmed its *threo* stereochemistry and the E2 nature of the elimination reaction. The conversion of **5** to **2** and **4** is summarized in Scheme 3.

Of all the cyclization substrates under investigation, unsubstituted *Z*, *E*, *E*-trienes **3** presented the most serious synthetic challenge. α-Selenenylation of a saturated sulphone followed by oxidation and *syn*-elimination would almost certainly give the *E*-isomer.[18] The use of sulphone-containing Wadsworth-Emmons reagents,[19] including the hitherto unknown bis(2,2,2-trifluoroethyl) (phenylsulphonyl)methanephosphonate[20] always resulted in the predominant formation of the undesired *E*-$\Delta_{1,2}$ isomer. The attempted model reaction of *Z*-1-lithio-1-octene[21] with phenylsulphonyl fluoride was unsuccessful under the conditions studied. At this stage it

X-ray structure of **18a**

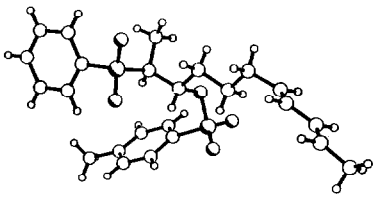
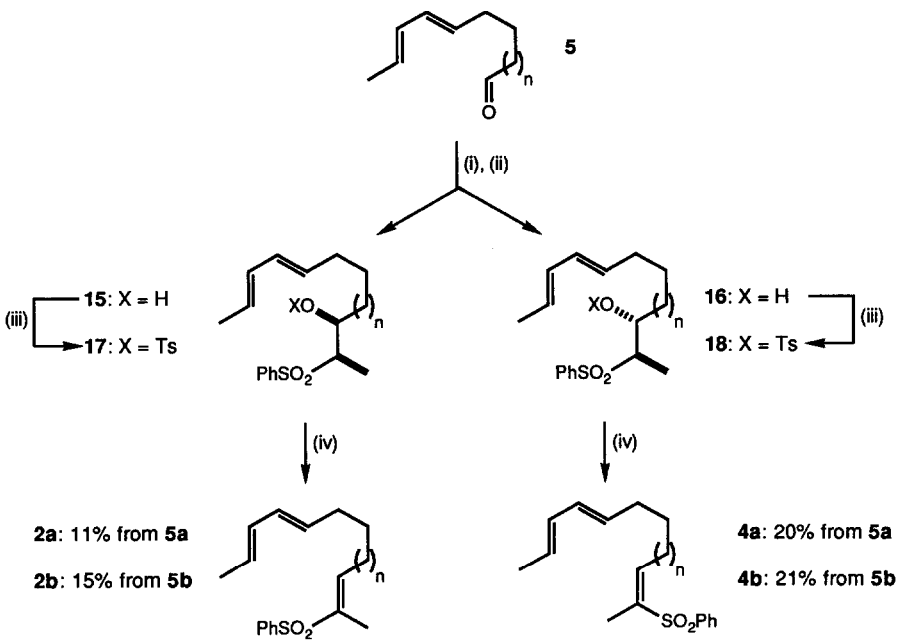


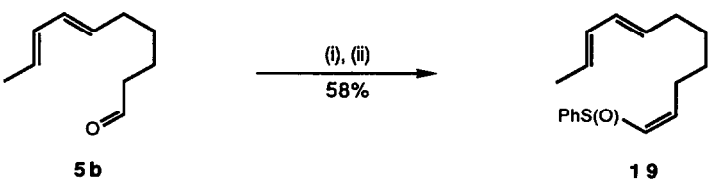
Figure 1



Reagents and conditions: (i) Add **5** to $PhSO_2CHLiCH_3$, THF, -78°C, then 10% v/v AcOH-THF, -78°C; (ii) chromatography (SiO_2); (iii) ^nBuLi, THF, -78°C, then TsCl, -78°C to r.t.; (iv) ^tBuOK, THF, -20°C.

Scheme 3

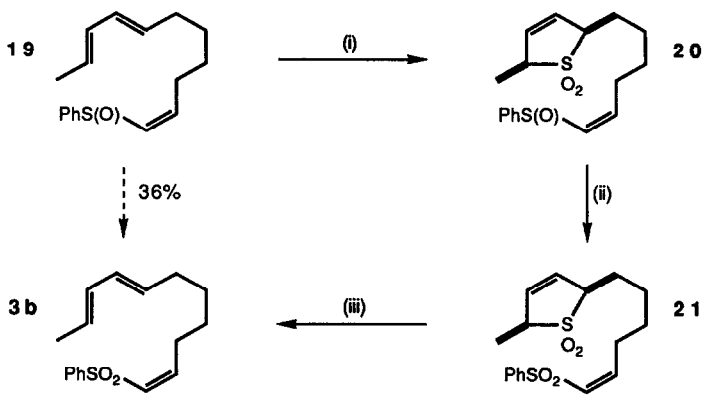
occurred to us that the geometric isomers formed in an olefination reaction at the sulphoxide oxidation level would be readily separable. Isolation of the *Z*-vinylic sulphoxide followed by *S*-oxidation would then yield *Z*-sulphones **3**. The successful realization of the first part of this strategy using our modified one-pot Wadsworth-Emmons procedure[22] is depicted in Scheme 4. Disappointingly, all attempts to oxidize chemospecifically the sulphoxide group of **19** met with failure. Reagents which were tried included peracetic acid,[23] Oxone®,[24] ruthenium tetroxide,[25] sodium perborate,[26] and H_2O_2-diphenyldiselenide.[27] Although minor ($\leq$ 15%) amounts of the desired triene **3b** could be isolated from these reactions, competing oxidation of the electron-rich diene function precluded the realization of satisfactory yields.[28] It was therefore decided to protect



Reagents and conditions: (i) $(MeO)_2P(O)Me$, ^nBuLi, THF, -78°C, then add $PhS(O)O^iPr$, -78°C, then add **5b**, -78°C to r.t.; (ii) chromatography (SiO_2).

Scheme 4

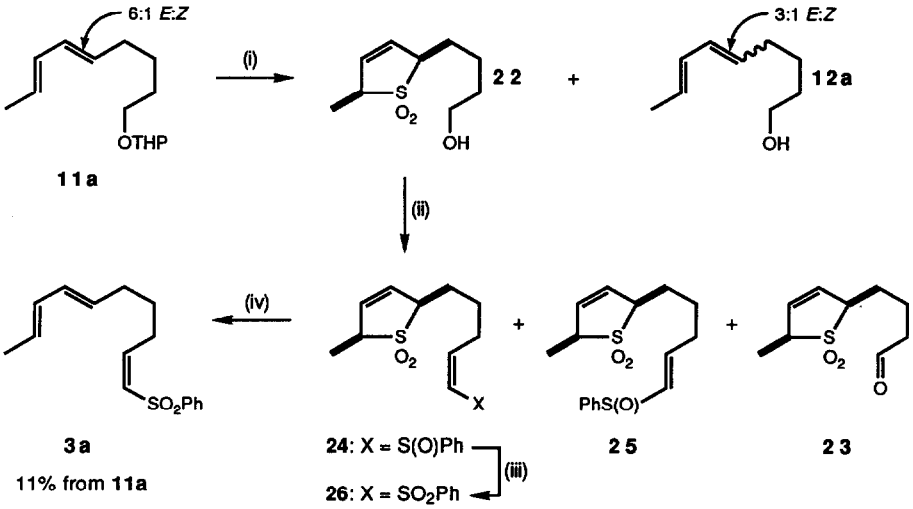
the diene function in **19** against oxidation by formation of the [4+1] chelotropic cycloadduct with sulphur dioxide.[29] This was achieved by heating **19** with SO_2 under pressure to give the dihydrothiophene *S,S*-dioxide **20** in 51% isolated yield (80% based on **19** consumed). Conversion of **20** to the corresponding sulphone **21** followed by gentle thermolysis in toluene under reflux gave triene **3b** in 21% overall yield from dienal **5b** (Scheme 5).



Reagents and conditions: (i) SO_2, 70°C; (ii) CH_3CO_3H, CH_2Cl_2, 0°C; (iii) PhMe, 80°C.

Scheme 5

We have also pursued a closely-related strategy in which the diene fragment was protected prior to the introduction of the dienophile portion of the target substrate. Thus, heating dienyl THP ethers **11a**[30] in SO_2-methanol gave the dihydrothiophene *S,S*-dioxide **22** as a single diastereomer in 46% isolated yield. Thus, the reaction of **11a** with SO_2 had simultaneously effected protection of the diene, deprotection of the THP group, and had effectively removed the minor *Z,E*-diene isomer. Interestingly, deprotected alcohol **12a** was obtained as a by-product (42%) in this reaction as a 3:1 mixture of *E,E*- and *Z,E*-isomers, indicating the lesser reactivity towards [4+1] cycloaddition of the latter. Attempts to oxidize alcohol **22** using the Swern procedure[13] resulted in apparent decomposition of the product aldehyde **23** during work-up. Accordingly, it was decided to attempt *in situ* vinylic sulphoxide formation from **23** by adding a solution of the pre-formed sulphinylphosphonate reagent[22] to the Swern reaction mixture.[31] In practice, the desired *Z*-vinylic sulphoxide **24** was obtained in 39% isolated yield, together with 23% of the unwanted *E*-isomer **25**. Oxidation of **24** as for the higher homologue **20** gave sulphone **26**, which yielded triene **3a** on heating in toluene (Scheme 6).

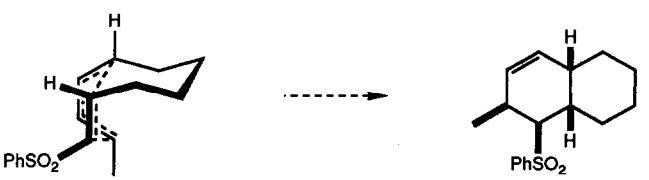


Reagents and conditions: (i) SO_2, MeOH, 84°C; (ii) $(COCl)_2$, DMSO, THF, -78°C, then add **22**, -78 to -35°C, then add Et_3N, -78°C to r.t., then add $(MeO)_2P(O)CHLiS(O)Ph$, -78°C to r.t.; (iii) CH_3CO_3H, CH_2Cl_2, 0°C; (iv) PhMe, 92°C.

Scheme 6

Cyclization reactions

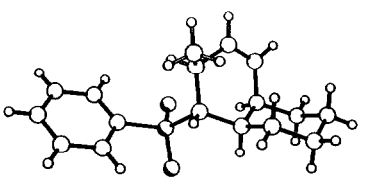
Thermal IMDA reactions were carried out in a resealable tube in dry, degassed toluene under argon. Care was taken to ensure anaerobic conditions, since the presence of oxygen even in trace amounts resulted in the formation of benzaldehyde on prolonged heating. Reactions were monitored where possible by thin-layer chromatography, or by ^1H nmr analysis of small aliquots of reaction mixture. The reaction conditions, yields and product compositions for the IMDA reactions of trienes **1-4** are summarized in Table 1. Initially we examined the IMDA reaction of **1b** (Table 1, Entry 1). This triene was used as a 6:1 mixture of *E*, *E*, *E*- and *E*, *Z*, *E*-isomers. Heating a dilute solution of **1b** at 173°C for 96 h gave a 6:1 ratio of two products as evidenced by ^1H nmr analysis of the crude reaction mixture. A consideration of the transition state possible for the IMDA reaction of *E*, *Z*, *E*-trienes such as **1b** indicates that only *cis*-fused decalins may be formed (Scheme 7).[32] It was therefore assumed that each of the triene isomers **1b** had cyclized stereospecifically. However, X-ray crystallography allowed unequivocal assignment of the structures of the major and minor products as **27c** and **27t** respectively (Figures 2 and 3). Our assumption concerning the identity of the minor product was therefore incorrect.



E, *Z*, *E*-**1b**

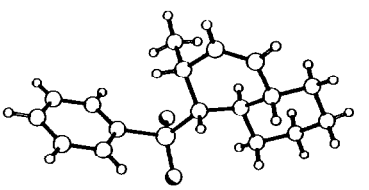
Scheme 7

Inspection of the structures of **27c** and **27t** indicates that both are derived from *E, E, E*-triene **1b**. The yield of cycloadducts after chromatography was 92%. Since **1b** used in the reaction was a 6:1, or 86:14 mixture of triene isomers, it follows that at least some of the minor *E, Z, E*-triene had been converted to **27c/27t**. ^{1}H nmr analysis of the reaction mixture at 50% conversion indicated the same 6:1 mixture of cycloadducts, effectively eliminating the possibility of the intermediacy of a rapidly-formed but short-lived diastereomeric product. Bicycle **27c** was recovered quantitatively after re-subjection to the IMDA reaction conditions.



X-ray structure of **27c**

Figure 2

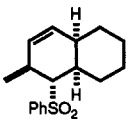
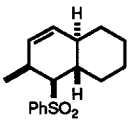
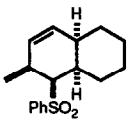
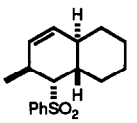
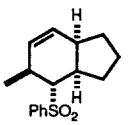
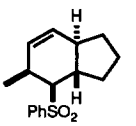
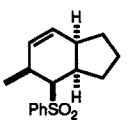
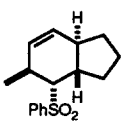
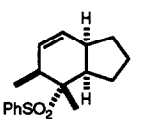
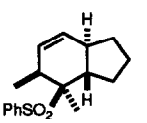
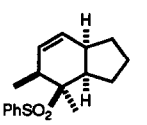
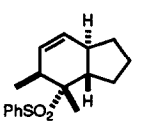
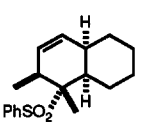
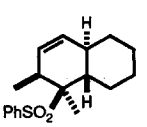
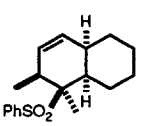
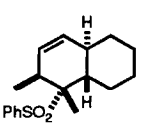


X-ray structure of **27t**

Figure 3

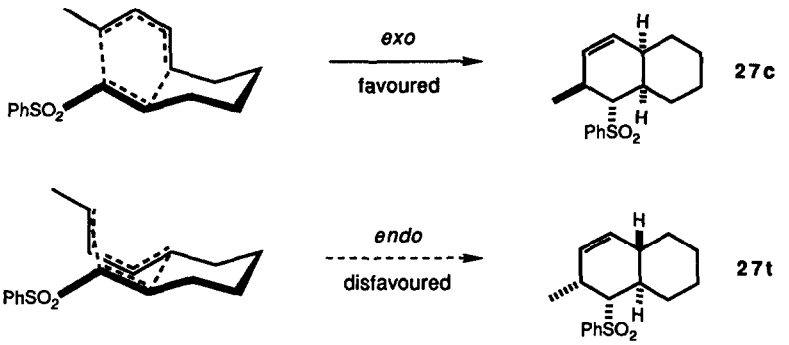
These observations suggest that *E, Z, E*-**1b** underwent isomerization to the presumably thermodynamically more stable *E, E, E*-isomer under the thermolysis conditions. Interestingly, heating a 6:1 mixture of the isomeric *t*-butyldiphenylsilyl ethers derived from **12b** at 172°C for 96 h appeared not to affect the isomer ratio. This would suggest that the presence of the vinylic sulphone group is necessary for the observed isomerization reaction of **1b**. We defer comment on the possible mechanism of this isomerization process. We note however that such transformations may be widespread in thermal IMDA reactions.[33] The ^{1}H nmr spectra of the sulphonyl-substituted decalins **27c** and **27t** showed two interesting features. Firstly, the alkene protons in **27c** resonated as a two-proton singlet. The corresponding signals in the spectrum of **27t** were well-resolved one-proton multiplets. Secondly, the CH_3 group in **27c** gave rise to a doublet at 0.95 ppm, 0.26 ppm upfield from the corresponding signal in the spectrum of **27t**. We attribute the relatively deshielded environment of the methyl group in **27t** to its *syn*-relationship with the phenylsulphonyl substituent.[8] This appeared to be a general trend in the ^{1}H nmr spectra of the cycloadducts studied, vindicating our choice of cyclization substrates.

The *cis*-selective nature of the IMDA reaction of **1b** is unusual. Thermal reactions of 1,7,9-decatrienes substituted with relatively weakly electron-withdrawing groups at the 1-position typically give *ca.* 1:1 mixtures of the two possible diastereomeric cycloadducts.[7(ii)] We attribute the predominance of **27c** over **27t** to unfavourable steric interactions between the bulky sulphone group and the diene in the *endo*-transition state leading to the latter (Scheme 8).[34] Table 1, Entry 2 lends support to this steric model. Cyclization of *Z, E, E*-triene **3b** gave in high yield a 1:3 mixture of **28c** and **28t**. For triene **3b** possessing a *Z*-dienophilic group the more sterically favourable *exo*-transition state gives rise to the *trans*-fused product. Thus, by the expedient of changing dienophile geometry a *cis*-selective IMDA reaction may be turned into a *trans*-selective one. This is in contrast with the thermal IMDA reactions of 1,7,9-decatrienes having an ester group at the 1-position, which give *ca.* 1:1 mixtures of products *regardless of dienophile geometry*.[7(ii)] The structural assignment of **28c** followed from its partial conversion into **27c** on exposure to potassium *t*-butoxide/THF. The X-ray crystal structure of **28t** is shown in Figure 4. Attention was next turned to IMDA reactions of the lower homologous trienes **1a** and **3a**. Thermolysis of **1a** gave a 1:1 mixture of cycloadducts **29c** and **29t** (Table 1, Entry 3). The structure of **29c** was implied by the observation of a 7% n.O.e. between the C-4 methine and methyl protons.

Entry	Triene	T (°C)	t (h)[a]	Yield (%)[b]	Products			
						ratio[c]		
1	**1b**	175	96	92	**27c** 	6:1		**27t**
2	**3b**	165-175[d]	146	92	**28c** 	1:3		**28t**
3	**1a**	145	48	93	**29c** 	1:1		**29t**
4	**3a**	165	60	63	**30c** 	1:7		**30t**
5	**2a**	175	120	52	**31c** 	1:1.5		**31t**
6	**4a**	190	60	95	**32c** 	1:8		**32t**
7	**2b**	170-178[d]	312	16	**33c** 	3.3:1[d]		**33t**
8	**4b**	190	120	30	**34c** 	1:2		**34t**

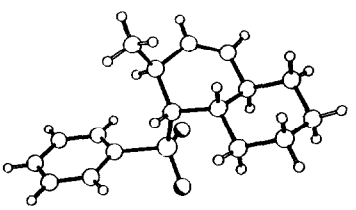
Notes: [a]total reaction time; [b]isolated yield after chromatography of combined IMDA products; [c]determined by ^{1}H nmr analysis of crude products; [d]see Experimental section for details.

Table 1: IMDA Reactions of trienes 1-4



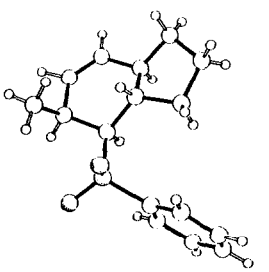
Scheme 8

This effect was absent in isomer **29t**.[35] The structure of **29t** was confirmed by X-ray crystallography (Figure 5). The stereoselectivity of the IMDA reaction of **1a** is again significantly different from that of related trienes possessing dienophile substituents other than the sulphone group. Reaction of methyl (1*E*, 6*E*, 8*E*)-11-methyl-2,7,9-dodecatrienoate gave a *ca.* 2:5 mixture of *cis*- and *trans*-fused products.[7(i)] Also, cyclization of



X-ray structure of **28t**

Figure 4

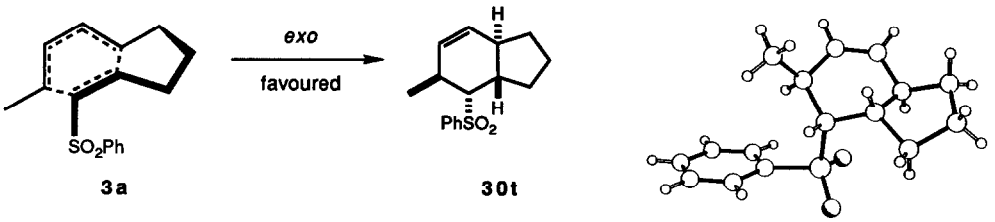


X-ray structure of **29t**

Figure 5

the nitro-substituted triene analogous to **1a** gave a 1:9 mixture in favour of the *trans*-fused isomer.[14(i)] It has been proposed that the asynchronous nature of Diels-Alder reactions[36] is such that trienes such as **1a** cyclize *via* transition states which resemble a five-membered ring more closely than the alternative nine-membered array. The greater thermodynamic stability of *trans*-1,2-disubstituted cyclopentanes accounts for the observed *trans*-selectivity. By simple analogy with the *cis*-selective cyclization of **1b**, the IMDA reaction of **1a** would be expected to be selective towards **29c**. The opposing influence of the cyclopentane-like transition state cancels out this effect, and a non-selective reaction results. Again, the cyclization of isomeric triene **3a** (Table 1, Entry 4) supported this hypothesis. Products **30c** and **30t** were obtained in a 1:7 ratio, reflecting the now cooperative nature of the steric and asynchronous effects discussed above (Scheme 9). Like the products **27-29**, **30c** and **30t** could be distinguished by the downfield resonance of the methyl group in **30c** relative to that in **30t**. The structure of **30t** was confirmed by X-ray crystallography. Thus, changing the dienophile geometry had again caused a substantial change in the stereochemical course of the IMDA reaction.

The IMDA reactions of α-methylated trienes **2** and **4** were next examined. It was expected that the presence of a substituent at the 1-position would retard intramolecular [4+2] cycloaddition because of greater diene-dienophile steric interactions in the transition states. The extent of any decrease in rate would help define more clearly the limits of reactivity of the sulphonyl-substituted trienes. In the event, thermolysis of *E*, *E*, *E*-triene **2a** gave in



Scheme 9

X-ray structure of **30t**

moderate yield a 2:3 mixture of the diastereomeric cycloadducts **31c** and **31t** (Table 1, Entry 5). As expected, the cyclization of **2a** proceeded more sluggishly than that of **1a**. The methyl doublet in the spectrum of compound **31c** appeared *ca.* 0.25 ppm upfield from the corresponding signal in the ^{1}H nmr spectrum of **31t**, consistent with previous observations. The structure of **31t** was unambiguously assigned by X-ray crystallography (Figure 6). Also, **31c** prepared *via* IMDA reaction of triene **2a** was identical with one of the

X-ray structure of **31t**

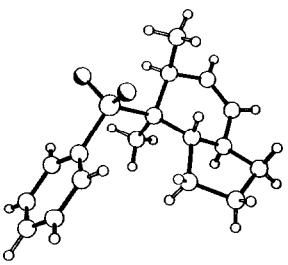
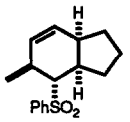
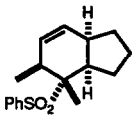
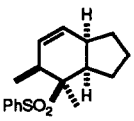
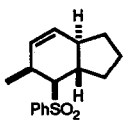
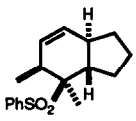
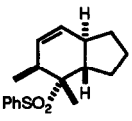
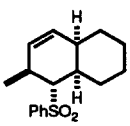
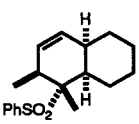
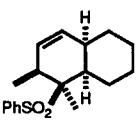
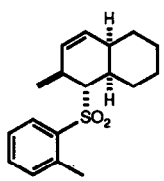
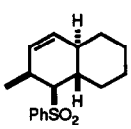
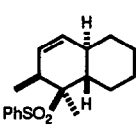
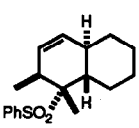
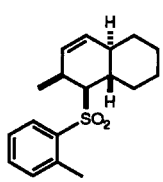
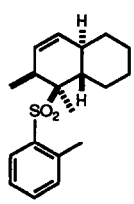


Figure 6

products of methylation of **29c** (Table 2, Entry 1). Similarly, **31t** was correlated with a product of methylation of **29t** (Table 2, Entry 2). Thus the IMDA cyclization of **2a** was slower, but exhibited similar stereoselectivity to that of the parent substrate **1a**. IMDA reaction of triene **4a** also proceeded with stereoselectivity similar to that of the parent triene, **3a**. Heating a toluene solution of **4a** gave in excellent yield a 1:8 mixture of bicyclic sulphones **32c** and **32t** (Table 1, Entry 6). The structures of both cycloadducts were again established by chemical correlation. Thus, **32c** exhibited ^{1}H nmr characteristics identical with those of the second methylation product of the unsubstituted bicycle **29c** (Table 2, Entry 1), whilst **32t** was correlated with the second product of methylation of **29t** (Table 2, Entry 2). Again, triene **4a** was observed to be a less reactive IMDA substrate than the parent triene **3a**, although the IMDA reactions showed similar stereoselectivities.

Finally, attention was focused on the IMDA cyclization reactions of the higher homologous α-methylated trienes **2b** and **4b**. Not unexpectedly, both these substrates reacted sluggishly, to the extent that the prolonged reaction times required for significant conversion of starting materials resulted in extensive decomposition and correspondingly low yields of isolated cycloadducts. Product ratios for both these IMDA reactions were determined by ^{1}H nmr analysis of crude reaction mixtures before complete conversion was attained. The yields cited in Table 1 are for purified materials whose composition differs from that indicated by the ^{1}H nmr experiments. Triene **2b** cyclized with moderate selectivity (3.3:1) for the *cis*-fused isomer **33c** (Table 1, Entry 7). Bicyclic sulphone **33c** and the minor cycloadduct **33t** were assigned by correlation with methylation products of sulphones **27c** and **27t**, respectively (Table 2, Entries 3, 4). Cyclization of *Z, E, E*-triene **4b**

Entry	Substrate	Yield (%)[a]	Products	ratio[b]
1	29c 	94	31c  32c 	54 : 46
2	29t 	81	31t  32t 	62 : 38
3	27c 	93	33c  34c 	58 : 15
			35 	27
4	27t 	77	33t  34t 	4 : 86
			36  37 	5 : 5

Notes: [a]yield of combined products; [b]based on isolated yields after chromatography of methylated products; see Experimental section for details.

Table 2: Methylation reactions of IMDA products 27 and 29

exhibited low *trans*-selectivity, giving rise to a 1:2 mixture of sulphones **34c** and **34t** (Table 1, Entry 8). The identity of **34t** was rigorously established by X-ray crystallography (Figure 7). Again, chemical correlation enabled confirmation of the assignment of the structures shown (Table 2, Entries 3, 4). The methylation reactions of **27c** and **27t** gave additional products **35-37**, resulting from reaction on the *ortho*-position of the phenyl ring (Table 2). Sulphones **32-34** possessing a methyl group *syn*- to the sulphone function again consistently showed downfield methyl signals relative to the *anti*-isomers.

X-ray structure of **34t**

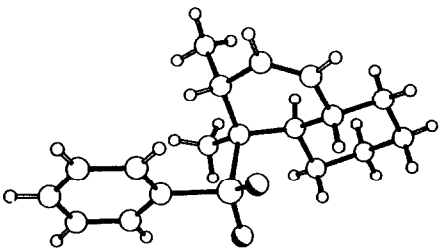


Figure 7

Conclusions

The work described herein demonstrates sulphonyl-substituted trienes to belong to a new class of thermal IMDA reaction substrate. The stereochemical course of these intramolecular [4+2] cycloaddition processes may be significantly altered simply by changing the geometry of the vinylic sulphone dienophile. We are currently investigating improved synthetic routes to the *Z, E, E*-trienes which avoid a diene protection/deprotection sequence. As well as being a stereocontrol element, the sulphonyl group may serve as a focal point for further carbon-carbon bond-forming processes, such as the methylation reactions described above. Further work aimed at gaining an understanding of the origins of the stereoselectivities observed in these lithiation/methylation reactions is under way in these laboratories. We are also seeking to apply IMDA reactions of sulphonyl-substituted trienes to the synthesis of vitamin D analogues by carrying out Julia olefination reactions[12] on the product bicyclic sulphones. Finally, we are examining the use of *sulphoximine*-bearing trienes in asymmetric IMDA reactions. The results of these and related studies will be reported in due course.

Acknowledgements

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Experimental

^{1}H nmr spectra were recorded in $CDCl_3$ using either a Bruker AM-500, Bruker WM-250 or Jeol QX-270 nmr spectrometer. Infra-red spectra were recorded on a Perkin-Elmer 881 spectrophotometer. Mass spectra were obtained using VG-7070B or Jeol SX-102 instruments. Elemental combustion analyses were performed in the Imperial College Chemistry Department microanalytical laboratory. Melting points were measured on a Reichert hot stage apparatus and are uncorrected. Chromatography refers to column chromatography on Merck Kieselgel 60 (230-400 mesh) under pressure unless otherwise stated. Tlc refers to thin-layer chromatography performed on pre-coated Merck Kieselgel 60 F_{254} glass-backed plates. Ether refers to diethyl ether and petrol to redistilled petroleum ether, bp 40-60°C. Where appropriate all solvents and reagents were purified before use according to standard procedures.[37]

Preparation of 5-bromo-1-pentanol (7a).[9] 1,5-Pentanediol **6a** (21 ml, 200 mmol) was dissolved in benzene (400 ml), aqueous hydrobromic acid (25 ml of a 48% solution, 0.75 eq.) added and the stirred mixture heated under reflux for 24 h whilst azeotropically removing the water with a Dean-Stark trap. When cool, the reaction mixture was poured into 6M aqueous sodium hydroxide (100 ml). The separated organic phase was washed with 2M HCl (3 x 100 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give **7a** as a pale yellow oil (27.65 g) which was used crude in the next step.

Preparation of 2-(5-bromopentyloxy)tetrahydro-2*H*-pyran (8a).[9] To a stirred solution of crude 5-bromo-1-pentanol **7a** (27.65 g, 165.5 mmol) in dry dichloromethane (200 ml) under argon was added a trace of 10-camphorsulphonic acid (CSA). 3,4-Dihydro-2*H*-pyran (15.5 ml, 170 mmol, 1.03 eq.) was then added dropwise *via* syringe to the solution at 0°C. After 30 min tlc (40% ether-petrol) showed the reaction to be complete and the mixture was filtered through a plug of silica gel, rinsing thoroughly with more dichloromethane (2 x 300 ml). Removal of the solvent under reduced pressure gave a pale yellow oil (37.62 g) which was used crude in the next step.

Preparation of 2-[5-(phenylsulphonyl)pentyloxy]tetrahydro-2*H*-pyran (9a). Sodium phenylsulphinate (dried *in vacuo* at 120°C for 4 h; 30 g, 181 mmol) was added to a stirred solution of crude bromide **8a** (37.62 g) in dry DMSO (170 ml) under argon at r.t. An exothermic reaction ensued and after 30 min all the sulphinate salt had dissolved, to be replaced after a further 30 min by a white precipitate of sodium bromide. The reaction mixture was poured into water (250 ml) and extracted with ethyl acetate (3 x 120 ml). The combined organic layers were washed with water (3 x 100 ml), brine (3 x 100 ml), dried ($MgSO_4$) and concentrated to give a pale yellow oil. Purification by chromatography (30% - 60% ether-petrol) gave, in order of elution, *2-[5-(phenylsulphinyloxy)pentyloxy]tetrahydro-2*H*-pyran* (2.10 g, 3% from **6a**) as an oil; υ_{max} (film) 3594, 3060, 2944, 1445, 1353, 1323, 1201, 1137, 1078, 1034 cm^{-1}; δ (270 MHz) 7.72-7.66 (2H, m, *ortho*-protons on Ph), 7.56-7.48 (3H, m, *meta*- and *para*-protons on Ph), 4.53 (1H, t, J 3Hz, H-2), 4.10-3.30 (6H, m, H-6, H-1', H-5'), 1.90-1.30 (12H, m, H-3, H-4, H-5, H-2', H-3', H-4'); *m/z* (EI) 312 (M$^+$), 249, 218, 149, 115, 110, 101, 85, 69, followed by *2-[5-(phenylsulphonyl)pentyloxy]tetrahydro-2*H*-pyran* **9a** (34.02 g, 52% from **6a**) as an oil; υ_{max} (film) 3066, 2941, 2868, 1586, 1120, 1147, 1305 cm^{-1}; δ (250 MHz) 7.94-7.85 (2H, m, *ortho*-protons on Ph), 7.68-7.51 (3H, m, *meta*- and *para*-protons on Ph), 4.55 (1H, t, J 3.4 Hz, H-2) 3.84-3.62 and 3.51-3.26 (4H, m, H-6, H-1'), 3.13-3.02 (2H, m, H-5'), 1.90-1.30 (12H, m, H-3, H-4, H-5, H-2', H-3', H-4'); *m/z* (EI) 312 (M$^+$), 227 (M$^+$ - C_5H_9O), 211 (M$^+$ - $C_5H_9O_2$), 85 ($C_5H_9O^+$) (Found: C, 61.84; H, 8.10. $C_{16}H_{24}O_4S$ requires C, 61.51; H, 7.74%).

Preparation of 2-[(7*E*)-6-benzoyloxy-5-(phenylsulphonyl)-7-nonenyloxy]tetrahydro-2*H*-pyran (10a). Sulphone **9a** (32.04 g, 103.22 mmol) was dissolved in dry THF (300 ml) under argon and cooled to -78°C. The stirred solution was treated with *n*-butyllithium (44.2 ml of a 2.57M solution in hexanes, 1.1 eq.) dropwise *via* syringe to give a lemon yellow solution of the anion. To this was added redistilled crotonaldehyde (9.4 ml, 113.54 mmol, 1.1 eq.), causing the colour to fade slowly. After 30 min, redistilled benzoyl chloride (13.2 ml, 113.54 mmol, 1.1 eq.) was added slowly *via* syringe and the reaction allowed to stir at -78°C for a further 2.5 h. The cooling bath was removed and after 3 h at r.t. the reaction was quenched with saturated aqueous sodium hydrogencarbonate (300 ml) and allowed to stir for 12 h. The organic phase was separated and the aqueous layer extracted with dichloromethane (3 x 100 ml). The combined organic layers were then washed with water (2 x 250 ml), dried ($MgSO_4$), and concentrated under reduced pressure to give the benzoyloxysulphones **10a** (*ca.* 1:1 mixture of diastereomers by ^1H nmr; 51.83 g) as a pale yellow oil which was used crude in the following step.

Preparation of 2-[(5*E*, 7*E*)-5,7-nonadienyloxy]tetrahydro-2*H*-pyran and 2-[(5*Z*, 7*E*)-5,7-nonadienyloxy]tetrahydro-2*H*-pyran (11a). Crude benzoyloxysulphones **10a** (51.83 g, *ca.* 103 mmol) were dissolved in dry THF (700 ml) under argon in a dry flask equipped with a large "rugby football"-shaped magnetic stirrer bar. Dry methanol (300 ml) and disodium hydrogenphosphate (60 g, 103 mmol, 1 eq.) was added and the mixture was cooled to -20°C. 6% Sodium amalgam (160 g, 412 mmol Na, *ca.* two-fold excess) was added as two batches of finely-ground powder. Stirring became increasingly difficult until finally the mixture was allowed to stand overnight at -20°C. Water (700 ml) was added and the solution was decanted away from the mercury residues. The organic phase was separated and the aqueous layer extracted with petrol (3 x 250 ml). The combined organic layers were washed alternately with water (3 x 250 ml) and brine (3 x 250 ml), then dried ($MgSO_4$) and concentrated under reduced pressure to give a pale yellow oil (24 g). This was purified by chromatography (5% - 20% ether-petrol) to give the *dienes* **11a** (6:1 ratio by ^1H nmr; 17.7 g, 77% from **9a**) as a colourless oil; υ_{max} (film) 3017, 2940, 2870, 1035, 987 cm^{-1}; δ (270 MHz) (5*E*, 7*E*-isomer) 6.10-5.90 (2H, m, H-6', H-7'), 5.60-5.40 (2H, m, H-5', H-8'), 4.58 (1H, br. s, H-2), 3.95-3.66 and 3.55-3.30 (4H, m, H-6, H-1') 2.09 (2H, q, J 6 Hz, H-4), 1.72 (3H, d, J 6 Hz, H-9), 1.70-1.35 (10H, m, H-3, H-4, H-5, H-2', H-3'); *m/z* (EI) 224 (M^+), 140 (M^+ - C_5H_8O), 123 (M^+ - $C_5H_7O_2$) (Found: (M^+), 224.1782. $C_{14}H_{24}O_2$ requires (M^+), 224.1778).

Preparation of (5*E*, 7*E*)-5,7-nonadien-1-ol and (5*Z*, 7*E*)-5,7-nonadien-1-ol (12a). A solution of the THP ethers **11a** (20.7 g, 92.2 mmol) in dry methanol (150 ml) containing a trace of CSA was stirred under argon at r.t. for 3 h, when tlc (50% ether-petrol) showed the absence of starting material. The solution was concentrated under reduced pressure to one quarter of its original volume and then filtered through a pad of silica gel. The pad was washed exhaustively with ether (4 x 200 ml) and the combined filtrate and washings concentrated under reduced pressure to give an oil which was purified by chromatography (20% - 50% ether-petrol) to give the *alcohols* **12a** (6:1 ratio by ^1H nmr; 12.2 g, 94%) as a colourless oil; υ_{max} (film) 3332 (br.), 3017, 2935, 1625, 1436, 1377, 1143, 1060, 986, 948, 926 cm^{-1}; δ (270 MHz) (5*E*, 7*E*-isomer) 6.05-5.93 (2H, m, H-6, H-7), 5.62-5.46 (2H, m, H-5, H-8), 3.60 (2H, t, J 6 Hz, H-1), 2.09 (2H, q, J 6 Hz, H-4), 1.88 (1H, br. s, OH), 1.72 (3H, d, J 6 Hz, H-9), 1.55-1.38 (4H, m, H-2, H-3); *m/z* (EI) 140 (M^+), 122, 107, 93, 81, 79, 68 (Found: C, 77.13; H, 11.62. $C_9H_{16}O$ requires C, 77.09; H, 11.50%).

Preparation of (5*E*, 7*E*)-5,7-nonadienyl 3,5-dinitrobenzoate and (5*Z*, 7*E*)-5,7-nonadienyl 3,5-dinitrobenzoate (13a). To a stirred solution of 3,5-dinitrobenzoyl chloride (8.73 g, 37.8 mmol, 1.1 eq.) and *N,N*-dimethyl-4-aminopyridine (DMAP) (92 mg, 0.8 mmol, 0.02 eq.) in dry dichloromethane (100 ml) at r.t. under argon was added a solution of alcohols **12a** (4.82 g, 34.4 mmol) in dichloromethane (50 ml). Triethylamine (5.3 ml, 37.8 mmol, 1.1 eq.) was added and the solution stirred for 30 min at r.t.. The reaction

was then poured into saturated aqueous sodium hydrogencarbonate (300 ml) and the aqueous phase extracted with dichloromethane (3 x 100 ml). The combined organic layers were washed with saturated aqueous sodium hydrogencarbonate (3 x 100 ml), water (3 x 100 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a dark orange oil. This was purified by chromatography (10% ether-petrol) to give a yellow solid which was crystallized to give the *3,5-dinitrobenzoates* **13a** (12:1 ratio by ^1H nmr; 6.72 g, 58%) as yellow crystals, mp 42-43°C (ether-petrol); υ_{max} (film) 3104, 3018, 2928, 1731, 1630, 1599, 1541, 1456, 1346, 1277, 1167, 1075, 991, 922, 825, 722 cm^{-1}; δ (500 MHz) (5*E*, 7*E*-isomer) 9.22 (1H, t, J 2 Hz, H-4), 9.14 (2H, d, J 2 Hz, H-2, H-6), 6.05-5.95 (2H, m, H-6', H-7'), 5.63-5.49 (2H, m, H-5', H-8'), 4.45 (2H, t, J 6.5 Hz, H-1'), 2.15 (2H, q, J 7 Hz, H-4'), 1.84 (2H, m, H-2'), 1.72 (3H, d, J 6.5 Hz, H-9'), 1.58-1.51 (2H, m, H-3'); *m/z* (EI) 334 (M^+), 195 ($C_7H_3N_2O_5$), 149, 139 (M^+ - $C_7H_3N_2O_5$), 121, 107, 94, 81, 75 (Found: (M^+), 334.1165. $C_{16}H_{18}N_2O_6$ requires (M^+), 334.1165).

Preparation of (5*E*, 7*E*)-5,7-nonadienal and (5*Z*, 7*E*)-5,7-nonadienal (5a). To a stirred solution of oxalyl chloride (3.45 ml, 39.6 mmol, 2 eq.) in dry dichloromethane (40 ml) under argon at -60°C was added a solution of DMSO (5.62 ml, 79.2 mmol, 4 eq.) in dichloromethane (50 ml) dropwise *via* cannula. After 5 min a solution of alcohols **12a** (2.78 g, 19.8 mmol) in dichloromethane (100 ml) was added and the reaction stirred for 15 min at -60°C. Triethylamine (13.80 ml, 99 mmol, 5 eq.) was added and the mixture allowed to warm to r.t.. The mixture was poured into water (200 ml) and extracted with ether (3 x 200 ml). The combined organic layers were then washed with saturated aqueous ammonium chloride (3 x 100 ml), water (3 x 100 ml), brine (2 x 100 ml), dried ($MgSO_4$) and concentrated under reduced pressure with ice-cooling to give a pale yellow oil. This was purified by chromatography (2.5% - 10% ether-petrol) to give the aldehydes **5a** (6:1 ratio by ^1H nmr; 2.72 g, 96%) as a colourless oil; υ_{max} (film) 3020, 2930, 2855, 2720, 1725, 1450, 990 cm^{-1}; δ (250 MHz) (5*E*, 7*E*-isomer) 9.76 (1H, t, J 2 Hz, H-1), 6.08-5.90 (2H, m, H-6, H-7), 5.80-5.33 (2H, m, H-5, H-8), 2.43 (2H, td, J 7, 2 Hz, H-2), 2.10 (2H, q, J 7 Hz, H-4), 1.73 (3H, d, J 6 Hz, H-9), 1.82-1.60 (2H, m, H-3); *m/z* (EI) 138 (M^+), 137 (M^+ - H), 94 (M^+ - C_2H_4O), 81 (M^+ - C_3H_5O), in agreement with data previously reported.[14]

Preparation of (6*E*, 8*E*)-1-(phenylsulphonyl)-6,8-decadien-2-ol and (6*Z*, 8*E*)-1-(phenylsulphonyl)-6,8-decadien-2-ol (14a). To a stirred solution of (phenylsulphonyl)methane (dried *in vacuo* over P_2O_5; 729 mg, 4.66 mmol, 1.1 eq.) in THF (20 ml) under argon at -78°C was added dropwise *via* syringe *n*-butyllithium (3.28 ml of a 2.57M solution in hexanes, 4.66 mmol, 1.1 eq.) to give a colourless solution of the anion. After 10 min a solution of aldehydes **5a** (freshly distilled, $bp_{0.5}$ 85°C; 586 mg, 4.24 mmol) in THF (5 ml) was added *via* cannula, rinsing with further THF (5 ml). After 15 min the reaction was quenched by the addition of a solution of acetic acid in THF (4.0 ml of a 1.75M solution, 1.3 eq.). The mixture was allowed to warm to r.t. and poured into a 1:1 mixture of dichloromethane and saturated aqueous sodium hydrogencarbonate (100 ml). The layers were separated, and the aqueous layer was extracted with dichloromethane (2 x 50 ml) The combined organic layers were washed with water (3 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a colourless oil. This was purified by chromatography (45% - 50% ether-petrol) to give the *hydroxysulphones* **14a** (6:1 ratio by ^1H nmr; 1.12 g, 90%) as a viscous, colourless oil; υ_{max} (film) 3516 (br.), 3067, 3017, 2931, 1653, 1625, 1481, 1447, 1307, 1151, 1087, 1025, 991, 783, 746, 720 cm^{-1}; δ (250 MHz) (6*E*, 8*E*-isomer) 7.98-7.88 (2H, m, *ortho*-protons on Ph), 7.65-7.52 (3H, m, *meta*- and *para*-protons on Ph), 6.02-5.86 (2H, m, H-7, H-8), 5.60-5.38 (2H, m, H-6, H-9), 4.20-4.10 (1H, m, H-2), 3.38 (1H, d, J 2.5 Hz, OH), 3.15-3.05 (2H, m, H-1), 2.00 (2H, q, J 7 Hz, H-5), 1.82 (3H, d, J 6.5 Hz, H-10), 1.60-1.30 (4H, m, H-3, H-4); *m/z* (EI) 276 (M^+ - H_2O), 205, 199, 185, 156, 141, 135, 94, 77 (Found: C, 65.36; H, 7.79. $C_{16}H_{22}O_3S$ requires C, 65.27; H, 7.53%).

Preparation of (1*E*, 6*E*, 8*E*)-1-(phenylsulphonyl)-1,6,8-decatriene and (1*E*, 6*Z*, 8*E*)-1-(phenylsulphonyl)-1,6,8-decatriene (1a). To a stirred solution of hydroxysulphones **14a** (1.26 g, 4.085 mmol) in dry dichloromethane (30 ml) under argon at -6°C was added, dropwise *via* syringe triethylamine (5.56 ml, 40.85 mmol, 10 eq.) followed immediately by methanesulphonyl chloride (0.96 ml, 12.26 mmol, 3 eq.). A light yellow precipitate developed and the reaction was allowed to warm to r.t.. After 90 min the mixture was poured into saturated aqueous ammonium chloride (100 ml) and extracted with dichloromethane (3 x 50 ml). The combined organic layers were washed with saturated aqueous ammonium chloride (2 x 100 ml), water (100 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by chromatography (20% ether-petrol) to give the *trienes* **1a** (6:1 ratio by ^1H nmr; 1.08 g, 91%) as a viscous, colourless oil; υ_{max} (film) 3020, 2925, 2855, 1625, 1445, 1305, 1150, 990 cm^{-1}; δ (500 MHz) (1*E*, 6*E*, 8*E*-isomer) 7.90 (2H, m, *ortho*-protons on Ph), 7.61 (1H, m, *para*-proton on Ph), 7.54 (2H, m, *meta*-protons on Ph), 6.99 (1H, dt, J 14.5, 6.5 Hz, H-2), 6.21 (1H, d, J 14.5 Hz, H-1), 6.03-5.81 (2H, m, H-7, H-8), 5.61-5.53 and 5.50-5.41 (2H, m, H-6, H-9), 2.24 (2H, q, J 6.5 Hz, H-3), 2.06 (2H, q, J 6.5 Hz, H-5), 1.72 (3H, d, J 6.5 Hz, H-10), 1.59-1.52 (2H, m, H-4); *m/z* (EI) 276 (M^+), 195 (M^+ - C_6H_9), 135 (M^+ - SO_2Ph), 95 (M^+ - $C_3H_4SO_2Ph$) (Found: C, 69.60; H, 7.02. $C_{16}H_{20}O_2S$ requires C, 69.53; H, 7.29%).

Preparation of 6-bromo-1-hexanol (7b). This was prepared analogously to 5-bromo-1-pentanol **7a** on a 422 mmol scale to give a nearly colourless oil (97%) which was used crude in the following step.

Preparation of 2-(6-bromohexyloxy)tetrahydro-2*H*-pyran (8b). This was prepared analogously to the lower homologue **8a** on a 410 mmol scale to give a colourless oil (81%) which was used crude in the following step.

Preparation of 2-[6-(phenylsulphonyl)hexyloxy]tetrahydro-2*H*-pyran (9b). Sodium phenylsulphinate (dried *in vacuo* at 120°C for 4 h; 73 g, 443 mmol, 1.1 eq.) was dissolved in dry DMSO (400 ml) under argon with gentle heating. To the stirred solution was added a solution of crude bromide **8b** (107 g, *ca.* 403 mmol) in DMSO (100 ml) *via* cannula, rinsing the flask with further DMSO (2 x 50 ml). After 2 h, tlc (75% ether-petrol) showed no starting material to be present. The reaction mixture was poured into water (1000 ml) and extracted with ethyl acetate (3 x 300 ml). The combined organic layers were washed with water (3 x 300 ml), brine (3 x 250 ml), dried ($MgSO_4$) and concentrated to give a nearly colourless oil. Purification by column chromatography (30% - 60% ether-petrol) gave, in order of elution, *2-[6-(phenylsulphinyloxy)-hexyloxy]tetrahydro-2*H*-pyran* (6.9 g, 5% from **6b**) as a colourless oil; υ_{max} (film) 2940, 1724, 1445, 1323, 1262, 1201, 1136, 1034, 975, 904, 756, 698 cm^{-1}; δ (270 MHz) 7.72-7.62 (2H, m, *ortho*-protons on Ph), 7.54-7.45 (3H, m, *meta*- and *para*-protons on Ph), 4.52 (1H, t, J 2.5 Hz, H-2), 4.05-3.28 (6H, m, H-6, H-1', H-6'), 1.85-1.25 (14H, m, H-3, H-4, H-5, H-2', H-3', H-4', H-5'); *m/z* (EI) 326 (M^+), 307, 271, 243, 225, 209, 195, 185, 181, 170, 156, 143, 125, 101, 85 (Found: (M^+ - C_5H_9O), 241.0904. $C_{17}H_{24}O_4S$ requires (M^+ - C_5H_9O), 241.0898), and *2-[6-(phenylsulphonyl)hexyloxy]tetrahydro-2*H*-pyran* **9b** (84.2 g, 61% from **6b**) as a colourless oil; υ_{max} (film) 2943, 2867, 1586, 1448, 1353, 1307, 1201, 1147, 1087, 1034 cm^{-1}; δ (250 MHz) 7.85 (2H, m, *ortho*-protons on Ph), 7.65-7.45 (3H, m, *meta*- and *para*-protons on Ph), 4.55 (1H, t, J 3 Hz, H-2), 3.85-3.20 (4H, m, H-6, H-1'), 3.05 (2H, m, H-6'), 1.80-1.20 (14H, m, H-3, H-4, H-5, H-2', H-3', H-4', H-5'); *m/z* (EI) 326 (M^+), 325 (M^+ - H), 308 (M^+ - H_2O), 241 (M^+ - C_5H_9O), 225, 209, 197, 169, 155 ($PhSO_2CH_2^+$), 143, 101, 85 ($C_5H_9O^+$), 77 (Found: C, 62.26; H, 8.30. $C_{17}H_{26}O_4S$ requires C, 62.54; H, 8.03%) (Found: (M + NH_4^+), 344.1896. $C_{17}H_{26}O_4S$ requires (M + NH_4^+), 344.1896).

Preparation of 2-[(8*E*)-7-benzoyloxy-6-(phenylsulphonyl)-8-decenyloxy]tetrahydro-2*H*-pyran (10b). To a stirred solution of THP ether **9b** (41.88 g, 128 mmol) in dry THF (220 ml) under argon at -78°C, was added *n*-butyllithium (99.1 ml of a 1.42M solution in hexanes, 141 mmol, 1.1 eq.) *via* cannula. After 10 min, freshly distilled crotonaldehyde (11.7 ml, 141 mmol, 1.1 eq.) was added to the yellow solution. After a further 30 min benzoyl chloride (16.4 ml, 141 mmol, 1.1 eq.) was added. The reaction mixture was stirred at -78°C for a further 3 h and allowed to warm to r.t. Saturated aqueous sodium hydrogencarbonate (200 ml) was added and the mixture was stirred overnight. The layers were separated and the aqueous phase extracted with dichloromethane (3 x 75 ml). The combined organic layers were washed with water (3 x 100 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give the benzoyloxysulphones **10b** (*ca.* 1:1 mixture of diastereomers by ^1H nmr; 75.9 g) as a pale yellow oil which was used crude in the following step.

Preparation of 2-[(6*E*, 8*E*)-6,8-decadienyloxy]tetrahydro-2*H*-pyran and 2-[(6*Z*, 8*E*)-6,8-decadienyloxy]tetrahydro-2*H*-pyran (11b). Crude benzoyloxysulphones **10b** (72.9 g, *ca.* 146 mmol) were dissolved in THF (1000 ml) and methanol (400 ml) in a flask together with disodium hydrogenphosphate (60 g) and the mixture cooled to -20°C with overhead stirring. Freshly ground 6% sodium amalgam (224 g, 582 mmol of sodium, *ca.* two-fold excess) was added in two batches an hour apart. The thick suspension was stirred at -20°C for 12 h and then carefully decanted away from the mercury residues into water (1000 ml). The aqueous phase was extracted with petrol (3 x 500 ml). The combined extracts were washed with water (3 x 500 ml), brine (2 x 250 ml) and dried ($MgSO_4$). Concentration under reduced pressure and purification by chromatography (5% - 10% ether-petrol) gave the *dienes* **11b** (6:1 ratio by ^1H nmr; 24.3 g, 79%) as a colourless oil; υ_{max} (film) 3016, 2934, 2856, 1452, 1441, 1353, 1201, 1137, 1120, 1078, 1036, 986, 906, 870, 816 cm^{-1}; δ (250 MHz) (*E*, *E*-isomer) 6.10-5.90 (2H, m, H-7', H-8'), 5.70-5.45 (2H, m, H-6', H-9'), 4.57 (1H, br. s, H-2), 3.95-3.65 and 3.55-3.32 (4H, m, H-6, H-1'), 2.08 (2H, q, J 5.5 Hz, H-5'), 1.73 (3H, d, J 6.5 Hz, CH_3), 1.90-1.20 (12H, m, H-3, H-4, H-5, H-2', H-3', H-4'); *m/z* (EI) 238 (M^+), 220 (M^+ - H_2O), 154 (M^+ - C_5H_8O), 136 (M^+ - C_5H_8O - H_2O), 85 ($C_5H_9O^+$) (Found: C, 75.33; H, 11.21. $C_{15}H_{26}O_2$ requires C, 75.58; H, 11.00%).

Preparation of (6*E*, 8*E*)-6,8-decadien-1-ol and (6*Z*, 8*E*)-6,8-decadien-1-ol (12b). To a stirred solution of THP ethers **11b** (20.62 g, 86.5 mmol) in dry methanol (155 ml) was added a trace of CSA. After 3 h tlc (50% ether-petrol) indicated the reaction to be complete and the solution was concentrated to one third of its original volume. The solution was filtered through a pad of silica gel which was rinsed exhaustively with ether. The solvent was removed under reduced pressure and the product purified by chromatography (20% - 25% ether-petrol) to give the alcohols **12b** (12.2 g, 91%) as a colourless oil which solidified on refrigeration at -5°C. The product gave spectral data identical with those reported previously.[14]

Preparation of (6*E*, 8*E*)-(6,8-decadien-1-yl) 3,5-dinitrobenzoate and (6*Z*, 8*E*)-(6,8-decadien-1-yl) 3,5-dinitrobenzoate (13b). This was carried out on a *ca.* 70 mmol scale in exactly analogous fashion to the lower homologues **13a** to give the *3,5-dinitrobenzoates* **13b** (20:1 ratio by ^1H nmr; 24.26 g, 52%) as yellow crystals, mp 57-59°C (ether-petrol); υ_{max} (film) 2926, 1728, 1627, 1462, 1377, 1346, 1290, 1170 cm^{-1}; δ (250 MHz) (*E*, *E*-isomer) 9.24 (1H, t, J 3 Hz, H-4), 9.15 (2H, J 3 Hz, H-2, H-6), 6.08-5.80 (2H, m, H-7', H-8'), 5.60-5.45 (2H, m, H-6', H-9'), 4.45 (2H, t, J 7 Hz, H-1'), 2.15-2.05 (2H, m, H-5'), 1.90-1.80 (2H, m, H-2'), 1.72 (3H, t, J 7 Hz, CH_3), 1.50-1.40 (4H, m, H-3', H-4'); *m/z* (EI) 348 (M^+), 195 ($C_7H_3N_2O_5^+$), 149, 135, 121, 107, 93, 81, 75, 68 (Found: (M^+), 348.1321. $C_{17}H_{20}N_2O_6$ requires (M^+), 348.1321).

Saponification of dinitrobenzoate ester (13b) To a solution of dinitrobenzoate ester **13b** (3.0 g, 8.61 mmol) in THF (75 ml) was added 10% aqueous potassium hydroxide (100 ml, 178 mmol, *ca.* 20 eq.). The colour of the mixture changed immediately from yellow to dark red and after 40 min tlc (20% ether-petrol) showed the reaction to be complete. The solution was poured into water (100 ml), the organic phase separated and the aqueous layer extracted with ether (3 x 50 ml). The combined organic layers were washed with water (3 x 50 ml), brine (50 ml), dried ($MgSO_4$), and concentrated under reduced pressure. The product was purified by chromatography (15% - 20% ether-petrol) to give (6*E*, 8*E*)-6,8-decadien-1-ol **12b** (contaminated with *ca.* 5% of the 6*Z*, 8*E*-isomer; 1.266 g, 95%) as a colourless oil.

Preparation of (6*E*, 8*E*)-6,8-decadienal (5b). Swern oxidation was performed on an 8.2 mmol scale analogously to the lower homologue **5a** to give the product (contaminated with *ca.* 5% of the 6*Z*, 8*E*-isomer; 1.04 g, 84%) as a colourless oil, $bp_{0.2}$ 80°C. Spectral data were identical with those reported previously.[14]

Preparation of (7*E*, 9*E*)-1-(phenylsulphonyl)-7,9-undecadien-2-ol (14b). The procedure was carried out on a 3.8 mmol scale analogously to the lower homologue **14a** to give the product (contaminated with *ca.* 5% of the 6*Z*, 8*E*-isomer; 1.40 g) as a viscous, colourless oil which was used crude in the next step.

Preparation of (1*E*, 7*E*, 9*E*)-1-(phenylsulphonyl)-1,7,9-undecatriene (1b). Crude (7*E*, 9*E*)-1-(phenylsulphonyl)-7,9-undecadien-2-ol **14b** (1.40 g) was treated analogously to the lower homologue **14a** to give the product **1b** (contaminated with *ca.* 5% of the 1*E*, 6*Z*, 8*E*-isomer; 762 mg, 69% from (6*E*, 8*E*)-6,8-decadienal) as a viscous, colourless oil; υ_{max} (film) 3015, 2928, 2857, 1655, 1625, 1572, 1540, 1447, 1319, 1307, 1148, 1087, 989, 819, 752, 716, 688 cm^{-1}; δ (270 MHz) 7.92-7.84 (2H, m, *ortho*-protons on Ph), 7.65-7.50 (3H, m, *meta*- and *para*-protons on Ph), 6.98 (1H, dt, J 16, 7 Hz, H-2), 6.31 (1H, dt, J 16, 1.5 Hz, H-1), 6.08-5.90 (2H, m, H-8, H-9), 5.68-5.42 (2H, m, H-7, H-10), 2.23 (2H, m, H-3), 2.04 (2H, q, J 7 Hz, H-6), 1.72 (3H, d, J 7 Hz, CH_3), 1.55-1.32 (4H, m, 4-H, 5-H); *m/z* (EI) 290 (M^+), 195 (M^+ - C_7H_{11}), 81 (C_6H_9), 77 (Ph), 67 ($C_5H_7^+$) (Found: C, 70.43; H, 7.84. $C_{17}H_{22}O_2S$ requires C, 70.31; H, 7.64%).

Preparation of [2R*, 3S*]-(7*E*, 9*E*)-2-(phenylsulphonyl)-7,9-undecadien-3-ol (15a) and [2R*, 3R*]-(7*E*, 9*E*)-2-(phenylsulphonyl)-7,9-undecadien-3-ol (16a).
(Phenylsulphonyl)ethane[38] (dried *in vacuo* over P_2O_5; 935 mg, 4.49 mmol, 1.1 eq.) was dissolved in dry THF (20 ml) under argon and cooled to -78°C. *n*-Butyllithium (3.9 ml of a 1.42M solution in hexanes, 5.49 mmol, 1.1 eq.) was added dropwise *via* syringe. After 10 min a solution of (5*E*, 7*E*)-5,7-nonadienal **5a** (freshly distilled; 690 mg, 4.99 mmol) in dry THF (5 ml) was added *via* cannula, rinsing with further dry THF (5 ml). The yellow anion colour faded slowly over the course of an hour to give a nearly colourless solution to which was added acetic acid in THF (4.6 ml of a 1.75 M solution, 1.3 eq.). The reaction mixture was allowed to warm to r.t., poured into saturated aqueous sodium hydrogencarbonate (50 ml) and the aqueous layer extracted with dichloromethane (3 x 50 ml). The combined organic layers were washed with water (2 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by chromatography (35% - 40% ether-petrol) to give the *hydroxysulphones* (1:1 ratio by ^1H nmr; 1.298 g combined yield, 84%) as a viscous, colourless oil; less polar [2R*, 3S*]-isomer **15a**: υ_{max} (film) 3516, 2935, 1630, 1448, 1302, 1146, 1086, 990, 760, 734, 690 cm^{-1}; δ (250 MHz) 7.90 (2H, dd, J 8, 1.5 Hz, *ortho*-protons on Ph), 7.73-7.54 (3H, m, *meta*- and *para*-protons on Ph), 6.05-5.86 (2H, m, H-8, H-9), 5.65-5.40 (2H, m, H-7, H-10), 4.30-4.18 (1H, m, H-3), 3.02 (1H, qd, J 7, 1 Hz, H-2), 2.90 (1H, d, J 2.5 Hz, OH), 2.02 (2H, br. q, J 7 Hz, H-6), 1.73 (3H, d, J 7 Hz, H-11), 1.60-1.40 (4H, m, H-4, H-5), 1.32 (3H, d, J 7 Hz, H-1); *m/z* (EI) 308 (M^+), 307 (M^+ - H), 290 (M^+ - H_2O), 225, 213, 199, 181, 149, 141, 125, 94, 79, 77 (Found: (M^+), 308.1451. $C_{17}H_{24}O_3S$ requires (M^+), 308.1446); more polar [2R*, 3R*]-isomer **16a**: υ_{max} (film) 3516, 2926, 2858, 1630, 1448,

1305, 1147, 1083, 990, 734, 690 cm^{-1}; δ (250 MHz) 7.90 (2H, dd, J 8, 1.5 Hz, *ortho*-protons on Ph), 7.74-7.52 (3H, m, *meta*- and *para*-protons on Ph), 6.05-5.89 (2H, m, H-8, H-9), 5.70-5.40 (2H, m, H-7, H-10), 4.08-3.95 (1H, m, H-3), 3.85 (1H, d, J 2.5 Hz, OH), 3.15 (1H, quintet, J 7 Hz, H-2), 2.10-2.00 (2H, m, H-6), 1.72 (3H, d, J 6.5 Hz, H-11), 1.60-1.35 (4H, m, H-4, H-5), 1.12 (3H, d, J 7 Hz, H-1); *m/z* (EI) 308 (M^+), 307 (M^+ - H), 290 (M^+ - H_2O), 225, 213, 199, 149, 143, 107, 94, 79 (Found: C, 66.29; H, 8.03. $C_{17}H_{24}O_3S$ requires C, 66.20; H, 7.84%).

Preparation of [2R*, 3S*]-(7*E*, 9*E*)-2-(phenylsulphonyl)-7,9-undecadien-3-ol (4-methylphenylsulphonate) (17a). Hydroxysulphone **15a** (azeotropically dried with toluene (2 x 5 ml); 473 mg, 1.54 mmol) was dissolved in THF (15 ml) together with 1,10-phenanthroline (2 crystals) and the solution cooled to -78°C under argon. *n*-Butyllithium (560 μl of a 2.5M solution in hexanes, 1.4 mmol, 0.91 eq.) was added dropwise to the stirred solution until a rust brown colour just persisted. After 5 min a solution of tosyl chloride (381 mg, 2.0 mmol, 1.3 eq.) in THF (5 ml) was added *via* cannula. The reaction mixture was allowed to warm to 0°C whereupon saturated aqueous ammonium chloride (10 ml) was added. The aqueous phase was extracted with dichloromethane (3 x 50 ml) and the combined organic layers were washed with 1M aqueous sodium hydroxide (2 x 50 ml), water (3 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by chromatography (5% - 50% ether-petrol) to give, in order of elution, *(2E, 7E, 9E)-2-(phenylsulphonyl)-2,7,9-undecatriene* **2a** (46.3 mg, 11%), as a colourless oil; υ_{max} (film) 3019, 2927, 2855, 1652, 1446, 1304, 1146, 1076, 1024, 990, 761, 728, 690 cm^{-1}; δ (250 MHz) 7.86 (2H, dd, J 8, 2.5 Hz, *ortho*-protons on Ph), 7.64-7.48 (3H, m, *meta*- and *para*-protons on Ph), 6.89 (1H, td, J 6.5, 2.5 Hz, H-3), 6.06-5.88 (2H, m, H-8, H-9), 5.70-5.30 (2H, m, H-7, H-10), 2.18 (2H, br. q, J 6.5 Hz, H-4), 2.08 (2H, br. q, J 6.5 Hz, H-6), 1.80 (3H, s, H-1), 1.72 (3H, d, J 6.5 Hz, H-11), 1.58 (2H, m, H-5); *m/z* (EI) 209 (M+ - C_6H_9), 149 (M^+ - SO_2Ph), 77 (Ph^+) (Found: C, 70.48; H, 7.68. $C_{17}H_{22}O_2S$ requires C, 70.31; H, 7.64%), followed by *[2R*, 3S*]-(7E, 9E)-2-(phenylsulphonyl)-7,9-undecadien-3-ol 3-(4-methylphenylsulphonate)* **17a** (286.3 mg, 40%) as a colourless oil; υ_{max} (film) 2936, 2905, 1598, 1446, 1360, 1306, 1189, 1175, 1148, 1085, 924, 765, 731, 690 cm^{-1}; δ (270 MHz) 7.95-7.50 (7H, m, Ph and *ortho*-protons on Tol), 7.32 (2H, *meta*-protons on Tol), 6.00-5.90 (2H, m, H-8, H-9), 5.64-5.30 (2H, m, H-7, H-10), 5.05 (1H, td, J 7, 3.5 Hz, H-3), 3.30 (1H, qd, 7, 2.5 Hz, H-2), 2.42 (3H, s, Tol *para*-methyl), 2.05-1.90 (2H, m, H-6), 1.75 (3H, d, J 6.5 Hz, H-11), 1.40-1.05 (4H, m, H-4, H-5), 1.27 (3H, d, J 7 Hz, H-1); *m/z* (EI) 462 (M^+), 290 (M^+ - TsOH), 213, 149, 94, 91, 77 (Found: (M + NH_4^+), 480.1878. $C_{29}H_{30}O_5S_2$ requires (M + NH_4^+), 480.1878).

Preparation of (2*E*, 7*E*, 9*E*)-2-(phenylsulphonyl)-2,7,9-undecatriene (2a). An inseparable mixture of hydroxysulphone **15a**, tosyloxysulphone **17a** and (phenylsulphonyl)ethane (286 mg, 0.619 mmol **17a**) was dissolved in THF (10 ml) under argon and treated with a solution of potassium *t*-butoxide (513 μl of a 1.0M solution in THF, 0.513 mmol, 0.83 eq.) at r.t. After 20 min the reaction mixture was poured into water (25 ml) and extracted with dichloromethane (3 x 20 ml). The combined organic layers were washed with water (3 x 20 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The product was purified by chromatography (15% - 50% ether-petrol) to give the title compound as a colourless oil (58.2 mg, 32%), identical with material previously prepared, followed by a mixture of **15a**, **17a** and (phenylsulphonyl)ethane (177.5 mg, 0.223 mmol **17a**). This mixture was re-subjected to the elimination conditions to give further **2a** (58 mg, 32%; total yield 64%).

Preparation of [2R*, 3R*]-(7*E*, 9*E*)-2-(phenylsulphonyl)-7,9-undecadien-3-ol 3-(4-methylphenylsulphonate) (18a). Hydroxysulphone **16a** (azeotropically dried with toluene (2 x 20 ml); 378 mg, 1.225 mmol) and 1,10-phenanthroline (2 crystals) was dissolved in dry THF (15 ml) under argon and cooled to -78°C. To the stirred solution was added *n*-butyllithium (480 μl of a 2.5M solution in hexanes, 1.23

mmol, *ca.* 1 eq.) until a rust-brown colour just persisted. A solution of tosyl chloride (408 mg, 2.141 mmol, 1.5 eq.) in THF (10 ml) was added to the anion solution, causing slow discharge of the colour. The reaction was allowed to warm to r.t., poured into water (50 ml) and extracted with dichloromethane (3 x 50 ml). The combined organic layers were washed with water (3 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a colourless oil (687 mg). The product was purified by chromatography (15% - 50% ether-petrol) to give, in order of elution, *(2Z, 7E, 9E)-2-(phenylsulphonyl)-2,7,9-undecatriene* **4a** (10 mg, 3%) as a colourless oil; υ_{max} (film) 3064, 2928, 2859, 1445, 1367, 1303, 1148, 1023, 997, 760, 723, 690 cm^{-1}; δ (250 MHz) 7.90 (2H, dd, J 8, 2.5 Hz, *ortho*-protons on Ph), 7.70-7.50 (3H, m, *meta*- and *para*-protons on Ph), 6.11-5.92 (3H, m, H-3, H-8, H-9), 5.70-5.45 (2H, m, H-7, H-10) 2.68 (2H, br. q, J 6.5 Hz, H-4), 2.09 (2H, br. q, J 6.5 Hz, H-6), 1.99 (3H, br. s, H-1), 1.75 (3H, d, J 6.5 Hz, H-11), 1.48 (2H, quintet, J 6.5 Hz, H-5); *m/z* (EI) 290 (M^+), 209 (M^+ - C_6H_9), 196 (M^+ - C_7H_{10}), 179, 149 (M^+ - SO_2Ph), 95, 79, 77 (Found: (M^+), 290.1341. $C_{17}H_{22}O_2S$ requires (M^+), 290.1341), and *[2R*, 3R*]-(7E, 9E)-2-(phenylsulphonyl)-7,9-undecadien-3-ol 3-(4-methylphenylsulphonate)* **18a** (398 mg, 70%) as a colourless oil which crystallized from ether at -18°C, mp 92-94°C (ether-petrol); υ_{max} (film) 2928, 2868, 1716, 1596, 1446, 1367, 1307, 1254, 1189, 1176, 1150, 1095, 1080, 914, 879, 816, 707, 688 cm^{-1}; δ (500 MHz) 7.88 (2H, dd, J 8, 2.5 Hz, *ortho*-protons on SO_2Ph), 7.75-7.60 (5H, m, *meta*- and *para*-protons on SO_2Ph and *ortho*-protons on Tol), 7.32 2H, d, J 8 Hz, *meta*-protons on Tol), 5.97 (1H, ddd, J 15, 11.5, 1.5 Hz, H-9), 5.85 (1H, dd, J 15, 11 Hz, H-8), 5.58 (1H, dq, J 15, 6.5 Hz, H-10), 5.32 (1H, dt, J 15, 6.5 Hz, H-7), 4.81 (1H, dt, J 13, 2 Hz, H-3), 3.72 (1H, qd, J 7, 3 Hz, H-2), 2.45 (3H, s, Tol *para*-methyl), 1.87-1.68 (3H, m, H-4 [one proton] and H-6), 1.74 (3H, d, J 6.5 Hz, H-11), 1.62 (1H, m, H-4), 1.30 (3H, d, J 6.5 Hz, H-1), 1.18 (1H, m, H-5), 0.90 (1H, m, H-5); *m/z* (EI) 462 (M^+), 307 (M^+ - Ts), 290 (M^+ - TsOH), 255, 239, 225, 209, 196, 149, 94, 81, 77 (Found: C, 62.15; H, 6.41. $C_{24}H_{30}O_5S_2$ requires C, 62.31; H, 6.54%).

Preparation of (2*Z*, 7*E*, 9*E*)-2-(phenylsulphonyl)-2,7,9-undecatriene (4a). Tosyloxysulphone **18a** (232 mg, 0.502 mmol) was dissolved in dry THF (5 ml) under argon and cooled to 0°C. To the stirred solution was added potassium *t*-butoxide (500 µl of a 1.0M solution in THF, 0.5 mmol, 1 eq) dropwise *via* syringe. This caused the appearance of a yellow colour followed by formation of a white precipitate. The reaction mixture was immediately poured into water (25 ml) and the aqueous layer extracted with dichloromethane (3 x 25 ml). The combined organic layers were washed with water (3 x 30 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a colourless oil (140 mg). The product was purified by chromatography (15% - 40% ether-petrol) to give, in order of elution, the title compound (84 mg, 58%), identical with previously prepared material, followed by a mixture of trienes **2a** and **4a** (31 mg), followed by recovered **18a** (6.4 mg, 3%). The **2a/4a** mixture was re-chromatographed to furnish further **4a** (16 mg; overall yield 100 mg, 69%).

Preparation of [2R*, 3S*]-(8*E*, 10*E*)-2-(phenylsulphonyl)-8,10-dodecadien-3-ol (15b) and [2R*, 3R*,]-(8*E*, 10*E*)-2-(phenylsulphonyl)-8,10-dodecadien-3-ol (16b). (Phenylsulphonyl)-ethane (dried *in vacuo* over P_2O_5; 790 mg, 4.63 mmol, 1.1 eq.) was dissolved in dry THF (50 ml) and the solution cooled to -78°C. *n*-Butyllithium (1.85 ml of a 2.5M solution in hexanes, 4.63 mmol, 1.1 eq.) was added dropwise *via* syringe with stirring, causing the solution to turn yellow. After 5 min a solution of aldehyde **5b** (freshly distilled; 642 mg, 4.21 mmol) in THF (5 ml + 2 ml rinse) was added *via* cannula to the reaction mixture. The reaction mixture was stirred for 1 h at -78°C after which time it was quenched by the addition of acetic acid in THF (4.9 ml of a 1.75M solution, 2 eq.) and allowed to warm to r.t.. The mixture was poured into saturated aqueous sodium hydrogencarbonate (50 ml) and extracted with dichloromethane (3 x 50 ml). The combined organic layers were washed with water (3 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a colourless oil. The crude product was purified by chromatography (35% - 40% ether-petrol) to give, in order of elution, *[2R*, 3S*]-(8E, 10E)-2-(phenylsulphonyl)-8,10-dodecadien-3-ol*

15b (642 mg, 47%) as a colourless oil; υ_{max} (film) 3517, 2930, 2896, 1683, 1605, 1446, 1299, 1143, 1088, 990, 760, 735 cm^{-1}; δ (500 MHz) 7.92 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.70-7.56 (3H, m, *meta*- and *para*-protons on Ph), 6.03-5.92 (2H, m, H-9, H-10), 5.58 (1H, m) and 5.48 (1H, m, both comprising H-8, H-11), 4.26-4.21 (1H, m, H-3), 3.02 (1H, qd, J 7, 2 Hz, H-2), 2.88 (1H, d, J 2.5 Hz, OH), 2.01 (2H, br. q, J 7 Hz, H-7), 1.73 (3H, d, J 7 Hz, H-12), 1.65-1.56 (2H, m, H-4), 1.46-1.20 (4H, m, H-5, H-6), 1.31 (3H, d, J 7 Hz, H-1); *m/z* (EI) 322 (M^+), 265, 254, 239, 225, 213, 199, 180, 170, 163, 107, 95, 81, 77 (Found: C, 67.04; H, 8.13. $C_{18}H_{26}O_3S$ requires C, 67.04; H, 8.13%), followed by *[2R*, 3R*]-(8*E*, 10*E*)-2-(phenylsulphonyl)-8,10-dodecadien-3-ol* **16b** (513 mg, 38%) as a colourless oil; υ_{max} (film) 3507, 2935, 1688, 1448, 1304, 1147, 1083, 999, 734, 691 cm^{-1}; δ (500 MHz) 7.90 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.70-7.55 (3H, m, *meta*- and *para*-protons on Ph), 6.04-5.94 (2H, m, H-9, H-10), 5.61-5.47 (2H, m, H-8, H-11), 4.04-3.98 (1H, m, H-3), 3.82 (1H, dd, J 3, 1 Hz, OH), 3.17 (1H, dq, J 8, 7 Hz, H-2), 2.05 (2H, br. q, J 7 Hz, H-7), 1.72 (3H, br. d, J 7 Hz, H-12), 1.65-1.55 (2H, m, H-4), 1.50-1.32 (4H, m, H-5, H-6), 1.14 (3H, d, J 7 Hz, H-1); *m/z* (EI) 322 (M^+), 225 (M^+ - C_7H_{13}), 199 ($C_9H_{11}O_3S^+$), 181, 143, 141 ($PhSO_2^+$), 107, 94, 81, 77 (Found: (M^+ - C_7H_{13}), 225.0590. $C_{18}H_{26}O_3S$ requires (M^+ - C_7H_{13}), 225.0585).

Preparation of [2R*, 3S*]-(8*E*, 10*E*)-2-(phenylsulphonyl)-8,10-dodecadien-3-ol 3-(4-methylphenylsulphonate) (17b). Hydroxysulphone **15b** (589 mg, 1.828 mmol) and 1,10-phenanthroline (2 crystals) were dissolved in dry THF (30 ml) under argon and cooled to -78°C. *n*-Butyllithium (720 µl of a 2.57M solution in hexanes, 1.85 mmol, 1.01 eq.) was added to the stirred solution until a rust brown colour just persisted. After 5 min a solution of tosyl chloride (524 mg, 2.742 mmol, 1.5 eq.) in dry THF (10 ml) was added *via* cannula, slowly discharging the colour. When allowed to warm to r.t. a near-colourless solution resulted. The reaction was poured into saturated aqueous ammonium chloride (30 ml) and the aqueous phase was extracted with dichloromethane (3 x 50 ml). The combined organic layers were washed with water (3 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The product was purified by chromatography (5% - 60% ether-petrol), to give, in order of elution: *(2*E*, 8*E*, 10*E*)-2-(phenylsulphonyl)-2,8,10-dodecatriene* **2b** as a colourless oil (46.7 mg, 8%); υ_{max} (film) 2928, 2857, 1652, 1624, 1447, 1304, 1144, 1072 cm^{-1}; δ (250 MHz) 7.90-7.80 (2H, m, *ortho*-protons on Ph), 7.64-7.48 (3H, m, *meta*- and *para*-protons on Ph), 6.88 (1H, td, J 8, 1.5 Hz, H-3), 6.08-5.90 (2H, m, H-9, H-10), 5.65-5.40 (2H, m, H-8, H-11), 2.18 (2H, br. q, J 7 Hz, H-4), 2.08 (2H, br. q, J 7 Hz, H-7), 1.82 (3H, d, J 1Hz, H-1), 1.74 (3H, d, J 7.5 Hz, H-12), 1.50-1.30 (4H, m, H-5, H-6); *m/z* 304 (M^+), 291 (M^+ - CH_3), 267, 238, 176, 143, 135, 125, 121, 109, 95, 91, 81, 77, followed by the *title compound* **17b** (1:1 mixture of **15b** and **17b** by ^1H nmr; 492 mg, 37% **17b**) as a colourless oil; υ_{max} (film) 3062, 2935, 1597, 1584, 1446, 1405, 1362, 1306, 1189, 1175, 1146, 1087, 997, 783, 731, 690 cm^{-1}; δ (500 MHz) 7.84 (2H, dd, J 8.5, 1.5 Hz, *ortho*-protons on Ph) 7.77 (2H, d, J 8.5 Hz, *ortho*-protons on Tol), 7.70-7.50 (3H, m, *meta*- and *para*-protons on Ph), 7.32 (2H, d, J 8.1 Hz, *meta*-protons on Tol), 6.02-5.90 (2H, m, H-9, H-10), 5.58 (1H, m) and 5.42 (1H, m, all comprising H-8, H-11), 5.03 (1H, td, J 6.5, 3.5 Hz, H-3), 3.29 (1H, qd, J 7, 3.5 Hz, H-2), 2.44 (3H, s, Tol *para*-methyl), 1.94 (2H, br. q, J 7 Hz, H-7), 1.78-1.70 (5H, m, H-4, H-12), 1.35-1.20 (4H, m, H-5, H-6), 1.27 (3H, d, J 7 Hz, H-1); *m/z* (positive FAB) 499 (MNa^+), 289, 193, 154, 107.

Preparation of (2*E*, 8*E*, 10*E*)-2-(phenylsulphonyl)-2,8,10-dodecatriene (2b). A mixture of hydroxysulphone **15b**, tosyloxysulphone **17b** and (phenylsulphonyl)ethane (294 mg of **17b** by ^1H nmr, 0.617 mmol) was dissolved in THF (10 ml) and cooled to -20°C under argon. Potassium *t*-butoxide (700 µl of a 1.0M solution in THF, 0.7 mmol, 1.13 eq.) was added dropwise to the stirred solution. When the reaction appeared to be complete by tlc (2 x 50% ether-petrol) water (10 ml) was added to the rapidly stirred solution. The mixture was extracted with dichloromethane (3 x 25 ml), washed with water (3 x 25 ml), dried ($MgSO_4$) and concentrated under reduced pressure to give a colourless oil (327 mg). Purification by chromatography

(15% - 50% ether-petrol) gave, in order of elution, the title compound (157 mg, 84%) identical to material previously prepared, and an inseparable mixture of **15b** and (phenylsulphonyl)ethane (135 mg).

Preparation of [2R*, 3R*]-(8*E*, 10*E*)-2-(phenylsulphonyl)-8,10-dodecadien-3-ol 3-(4-methylphenylsulphonate) (18b). Hydroxysulphone **16b** (513 mg, 1.59 mmol) and 1,10-phenanthroline (2 crystals) were azeotropically dried with toluene (2 x 20 ml), dissolved in THF (16 ml) under argon and the solution cooled to -78°C. *n*-Butyllithium (620 µl of a 2.57M solution in hexanes, 1.59 mmol, 1.0 eq.) was added dropwise *via* syringe until a rust brown colour just persisted. After 5 min a solution of tosyl chloride (455 mg, 2.39 mmol, 1.5 eq.) in THF (5 ml) was added *via* cannula which caused the colour to fade slowly. The reaction was allowed to warm to r.t. over 40 min whereupon it was quenched by the addition of saturated aqueous ammonium chloride (50 ml). The aqueous phase was extracted with dichloromethane (3 x 50 ml) and the combined organic layers were washed with water (3 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the crude product (5% - 50% ether petrol) gave, in order of elution, the *title compound* (567 mg, 75%) as a colourless oil; υ_{max} (film) 3060, 2939, 2864, 1721, 1596, 1446, 1366, 1307, 1250, 1189, 1176, 1150, 1096, 901, 817, 735, 690, 662 cm^{-1}; δ (270 MHz) 7.88 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.75-7.45 (4H, m, *meta*- and *para*-protons on Ph and *ortho*-protons on Tol), 7.32 (2H, d, J 8.5 Hz, *meta*-protons on Tol), 6.05- 5.85 (2H, m, H-9, H-10), 5.66-5.30 (2H, m, H-8, H-11), 4.78 (1H, ddd, J 9.5, 3, 2 Hz, H-3), 3.76 (1H, qd, J 7, 3 Hz, H-2), 2.45 (3H, s, *para*-methyl on Tol), 1.90-1.80 (3H, m, H-4 [one proton], H-7), 1.75 (3H, d, J 7 Hz, H-12), 1.62 (1H, m, H-4), 1.32 (3H, d, J 7 Hz, H-1), 1.20-1.00 (3H, m) and 0.90-0.70 (1H, m, all comprising H-5, H-6); *m/z* (EI) 476 (M^+), 304 (M^+ - TsOH), 172, 163 (M^+ - TsOH - $PhSO_2$), 107, 94, 91, 81, 77 (Found: C, 63.18; H, 6.69. $C_{25}H_{32}O_5S_2$ requires C, 62.99; H, 6.77%), and recovered **16b** (15.3 mg, 3%).

Preparation of (2*Z*, 8*E*, 10*E*)-(2-phenylsulphonyl)-2,8,10-dodecatriene (4b). Tosylate **18b** (572 mg, 1.20 mmol) was dissolved in THF (15 ml) and cooled to -20°C under argon. Potassium *t*-butoxide (1.2 ml of a 1.0M solution in THF, 1.2 mmol, 1.0 eq.) was added to the stirred solution dropwise *via* syringe. The reaction was quenched by the rapid addition of water (10 ml) and allowed to warm to r.t.. The aqueous phase was extracted with dichloromethane (3 x 50 ml), and the combined organic layers were washed with water (3 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Purification of the product by chromatography (15% - 50% ether-petrol) gave, in order of elution, the *title compound* (265 mg, 72%) as a colourless oil; υ_{max} (film) 3014, 2926, 2851, 1642, 1447, 1305, 1145, 1083 cm^{-1}; δ (250 MHz) 7.92-7.85 (2H, m, *ortho*-protons on Ph), 7.65-7.48 (3H, m, *meta*- and *para*-protons on Ph), 6.05-5.95 (3H, m, H-3, H-9, H-10), 5.55 (2H, m, H-8, H-11), 2.65 (2H, m, H-4), 2.05 (2H, m, H-7), 1.95 (3H, d, J 1 Hz, H-1), 1.74 (3H, d, J 7 Hz, H-12), 1.45-1.30 (4H, m, H-5, H-6); *m/z* (EI) 304 (M^+), 209, 196, 179, 163 (M^+ - SO_2Ph), 125, 109, 81, 79 (Found: C, 71.14; H, 8.05. $C_{18}H_{24}O_2S$ requires C, 71.01; H, 7.95%), followed by (2*E*, 8*E*, 10*E*)-(2-phenylsulphonyl)-2,8,10-dodecatriene **2b** (29 mg, 8%) and finally recovered **18b** (13 mg, 2%).

Preparation of (1*E*, 7*E*, 9*E*)-1-(phenylsulphinyl)-1,7,9-undecatriene and (1*Z*, 7*E*, 9*E*)-1-(phenylsulphinyl)-1,7,9-undecatriene (19). Freshly distilled dimethyl methanephosphonate (1.10 g, 8.86 mmol, 2.1 eq.) was dissolved in dry THF (80 ml) under argon. The stirred solution was cooled to -78°C and treated with *n*-butyllithium (3.4 ml of a 2.57M solution in hexanes, 8.65 mmol, 2.05 eq.) dropwise *via* syringe. To the colourless solution was added a solution of isopropyl phenylsulphinate (azeotropically dried with toluene (2 x 5 ml); 816 mg, 4.43 mmol, 1.05 eq.) in dry THF (10 ml) *via* cannula. After 5 min a solution of (6*E*, 8*E*)-6,8-decadienal **5b** (freshly distilled; 642 mg, 4.22 mmol) in THF (10 ml) was added *via* cannula and the reaction was then allowed to warm to r.t. whereupon it was quenched by the addition of saturated aqueous ammonium chloride (75 ml). The mixture was extracted with dichloromethane (3 x 50 ml). The

combined extracts were washed with water (3 x 50 ml), dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by chromatography (40% - 60% ether-petrol) to give, in order of elution, the *E*- and *Z*-vinylic sulphoxides (1:2 ratio by ^1H nmr; 1.005 g combined yield, 87%) as a colourless oil; *(1E, 7E, 9E)-1-(phenylsulphinyl)-1,7,9-undecatriene*: υ_{max} (film) 3013, 2926, 2855, 1617, 1580, 1442, 1084, 1041, 989, 745, 690 cm^{-1}; δ (250 MHz) 7.65-7.40 (5H, m, Ph), 6.70 (1H, dt, J 15, 6 Hz, H-2), 6.22 (1H, dt, J 15, 1.5 Hz, H-1), 6.00-5.90 (2H, m, H-8, H-9), 5.65-5.40 (2H, m, H-7, H-10), 2.30-2.15 (2H, m, H-3), 2.10-2.00 (2H, m, H-6), 1.85 (3H, d, J 7 Hz, CH_3), 1.50-1.30 (4H, m, H-4, H-5); *m/z* (EI) 274 (M^+), 257, 149, 123, 81, 79, 77 (Found: C, 74.29; H, 8.36. $C_{17}H_{22}OS$ requires C, 74.40; H, 8.08%); *(1Z, 7E, 9E)-1-(phenylsulphinyl)-1,7,9-undecatriene* **19**; υ_{max} (film) 2926, 1620, 1443, 1080, 1045, 989, 690 cm^{-1}; δ (250 MHz) 7.65-7.30 (5H, m, Ph), 6.30 (4H, m, H-1, H-2, H-8, H-9), 5.80-5.45 (2H, m, H-7, H-10), 2.70-2.50 (2H, m, H-3), 2.20-2.05 (2H, m, H-6), 1.75 (3H, d, J 7 Hz, CH_3), 1.55-1.40 (4H, m, H-4, H-5); *m/z* (EI) 274 (M^+), 257, 177, 149, 123, 105, 81, 79, 77 (Found C, 74.64; H, 8.37. $C_{17}H_{22}OS$ requires C, 74.40; H, 8.08%).

Reaction of *Z*-sulphoxide (19) with neat SO_2. *Z*-Sulphoxide **19** (187 mg, 0.68 mmol) and hydroquinone (2 mg, 0.014 mmol, 2 mol%) were placed inside a teflon-lined steel autoclave together with a magnetic stirrer bar. Liquid sulphur dioxide (4 ml) was introduced *via* cannula and the system was sealed and heated to 70°C for 12 h. The resultant brown oil was extracted from the autoclave with dichloromethane, the solvent and excess sulphur dioxide removed under reduced pressure and the product purified by chromatography (40% - 100% ether-petrol, then 75% - 100% ethyl acetate-petrol) to give, in order of elution, recovered **19** (67 mg, 36%), and *[2R*,5S*]-2,5-dihydro-2-methyl-5-[(5Z)-6-(phenylsulphinyl)-5-hexenyl]thiophene S,S-dioxide* **20** (117 mg, 51%, 80% based on recovered **19**) as a colourless oil; υ_{max} (film) 2930, 1654, 1618, 1445, 1304, 1131, 1084, 1039 cm^{-1}; δ (270 MHz) 7.65-7.45 (5H, m, Ph), 6.25-6.15 (2H, m, H-5', H-6'), 5.94 (2H, m, H-3, H-4), 3.80 (1H, q, J 7 Hz, H-2), 3.68 (1H, m, H-5), 2.80-2.65 (1H, m, H-4'), 2.60-2.45 (1H, m, H-4'), 1.80-1.50 (6H, m, H-1', H-2', H-3'), 1.40 (3H, d, J 7 Hz, CH_3); *m/z* (EI) 274 ($M^+ - SO_2$), 149, 123, 81, 79, 77 (Found: ($M^+ - SO_2$), 274.1396. $C_{17}H_{22}O_3S_2$ requires ($M^+ - SO_2$), 274.1391. Found: C, 56.64; H, 5.99. $C_{17}H_{22}O_3S_2$ requires C, 56.44; H, 5.92%).

Oxidation of *Z*-sulphoxide (20). *Z*-Sulphoxide **20** (117 mg, 0.346 mmol) was dissolved in dichloromethane (10 ml), anhydrous sodium acetate (31 mg, 0.381 mmol, 1.1 eq.) added and the mixture cooled to 0°C. Peracetic acid (160 μl of a 32 wt.% solution in dilute acetic acid, 0.518 mmol, 1.5 eq.) was added *via* syringe and the reaction was allowed to stir for 12 h, after which time tlc (75% ethyl acetate-petrol) showed complete reaction. The mixture was poured into water (30 ml) and extracted with dichloromethane (3 x 20 ml). The combined organic layers were washed with 10% aqueous sodium thiosulphate (3 x 20 ml), saturated aqueous sodium hydrogencarbonate (3 x 20 ml), dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by chromatography (50% - 80% ethyl acetate-petrol) to give *[2R*, 5S*]-2,5-dihydro-2-methyl-5-[(5Z)-6-(phenylsulphonyl)-5-hexenyl]thiophene S,S-dioxide* **21** (104 mg, 85%) as a colourless oil; υ_{max} (film) 3064, 2929, 2865, 1625, 1448, 1305, 1147 cm^{-1}; δ (250 MHz) 7.90 (2H, m, *ortho*-protons on Ph), 7.70-7.50 (3H, m, *meta*- and *para*-protons on Ph), 6.35-6.20 (2H, m, H-5', H-6'), 5.92 (2H, br. s, H-3, H-4), 3.85-3.60 (2H, m, H-2, H-5), 2.75-2.60 (2H, m, H-4'), 1.90-1.50 (6H, m, H-1', H-2', H-3'), 1.40 (3H, d, J 7 Hz, CH_3); *m/z* (EI) 354 (M^+), 336, 322, 293, 165, 149, 64, 79, 71, 64 (SO_2) (Found: C, 57.68; H, 6.41. $C_{17}H_{22}O_4S_2$ requires C, 57.60; H 6.26%) (Found: ($M + NH_4^+$), 372.1303. $C_{17}H_{22}O_4S_2$ requires ($M + NH_4^+$), 372.1303).

Cycloelimination of SO_2 from *Z*-sulphone (21). *Z*-Sulphone **21** (61 mg, 0.172 mmol) was dissolved in toluene (10 ml) and the solution heated to 80°C for 1.5 h after which time tlc (75% ethyl acetate-petrol) indicated complete reaction. The solution was concentrated under reduced pressure to one tenth of its original volume and the residue chromatographed (15% ether-petrol) to give *(1Z, 7E, 9E)-1-(phenylsulphonyl)-1,7,9-undecatriene* **3b** (42 mg, 84%) as a colourless oil; υ_{max} (film) 3015, 2928, 2859, 1625, 1587, 1555, 1447, 1306, 1148, 1086, 990, 779, 754 cm^{-1}; δ (250 MHz) 7.92 (2H, dd, J 8, 1.5 Hz, *ortho*-protons on Ph), 7.66-7.50 (3H, m, *meta*- and *para*-protons on Ph), 6.33-6.18 (2H, m, H-1, H-2), 6.10-5.90 (2H, m, H-8, H-9), 5.66-5.42 (2H, m, H-7, H-10), 2.68 (2H, m, H-3), 2.04 (2H, m, H-6), 1.73 (3H, d, J 6.5 Hz, CH_3), 1.44-1.35 (4H, m, H-4, H-5); *m/z* (EI) 290 (M^+), 223 (M^+ - C_5H_7), 209 (M^+ - C_6H_9), 195 (M^+ - C_7H_{11}), 182, 165, 149 (M^+ - SO_2Ph), 81 (Found: (M^+), 290.1341. $C_{17}H_{22}O_2S$ requires (M^+), 290.1341).

Reaction of THP ethers (11a) with SO_2-methanol. A solution of THP ethers **11a** (456 mg, 2.13 mmol) in methanol (5 ml) was heated to 84°C in a steel autoclave containing hydroquinone (5 mg, 0.041 mmol, 2 mol %) and liquid sulphur dioxide (1 ml, 20 mmol, 9.4 eq.) for 5 h. When cool the dark oil was dissolved in dichloromethane and the solvent and excess sulphur dioxide evaporated under reduced pressure. The residue was purified by chromatography (20% - 100% ethyl acetate-petrol) to give, in order of elution, *E*, *E*- and *Z*, *E*-alcohols **12a** (3:1 ratio by ^1H nmr; 118 mg, 42%), identical with material prepared previously, and *[2'R*, 5'S*]-4-(2,5-dihydro-5-methylthiophen-2-yl)-1-butanol S,S-dioxide* **22** (192 mg, 46%); υ_{max} (film) 3384 (br.), 2940, 1653, 1453, 1300, 1127, 1078 cm^{-1}; δ (270 MHz) 5.93 (2H, m, H-3', H-4'), 3.78 (1H, m, H-5'), 3.73-3.64 (3H, m, H-1, H-2'), 2.00-1.90 (1H, m, H-4), 1.70-1.50 (6H, m, H-2, H-3, H-4 [one proton], OH), 1.39 (3H, d, J 7 Hz, CH_3); *m/z* (EI) 205 (MH^+), 186 (M^+ - H_2O), 174, 155, 140 (M^+ - SO_2), 122, 94, 81, 79, 77 (Found: C, 53.20; H, 8.08. $C_9H_{16}O_3S$ requires C, 52.91; H, 7.90%).

Swern Oxidation of alcohol (22) with *in situ* olefination. Oxalyl chloride (285 µl, 3.26 mmol, 2.2 eq.) was added to THF (10 ml) under argon at -78°C. After addition of dimethyl sulphoxide (463 µl, 6.53 mmol, 4.4 eq.) the stirred solution was allowed to warm to -35°C for 3 min then re-cooled to -78°C. A solution of the alcohol **22** (303 mg, 1.48 mmol) in THF (5 ml) was added dropwise *via* cannula to give a cloudy white suspension. The reaction was allowed to warm to -35°C and stirred for 20 min. After re-cooling to -78°C, triethylamine (1.36 ml, 9.79 mmol, 6.6 eq.) was added in one portion and the mixture warmed to r.t. Analysis of the reaction mixture by tlc (75% ethyl acetate-petrol) showed it to be complete after 20 min and the mixture was again cooled to -78°C. In a separate flask, dimethyl methanephosphonate (freshly distilled; 1.55 g, 12.46 mmol, 8.4 eq.) was dissolved in THF (60 ml) under argon, cooled to -78°C and treated with *n*-butyllithium (4.82 ml of a 2.5M solution in hexanes, 12.16 mmol, 8.2 eq.). After 5 min a solution of isopropyl phenylsulphinate (azeotropically dried with toluene (2 x 5 ml); 1.09 g, 5.93 mmol, 4.0 eq.) was added dropwise *via* cannula. This pale yellow solution was then added *via* cannula at -78°C to the stirred Swern reaction mixture prepared above. The reaction mixture was allowed to warm to r.t. after 5 min, and stirred for a further hour. The mixture was poured into saturated aqueous ammonium chloride (200 ml) and extracted with ethyl acetate (3 x 100 ml). The combined organic layers were washed with saturated ammonium chloride (3 x 100 ml) and water (3 x 100 ml) alternately, followed by brine (100 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The resulting crude oil was purified by chromatography (45% - 100% ethyl acetate-petrol) to give, in order of elution, *[2'R*, 5'S*]-4-(2,5-dihydro-5-methylthiophen-2-yl)butanal S,S-dioxide* **23** (28 mg, 9%) as a colourless oil; υ_{max} (film) 2934, 1720, 1451, 1304, 1129, 1078, 739, 641 cm^{-1}; δ (270 MHz) 9.77 (1H, t, J 1 Hz, H-1), 5.96-5.89 (2H, m, H-3', H-4'), 3.79 (1H, qt, J 7, 1 Hz, H-5'), 3.71-3.64 (1H, m, H-2'), 2.54 (2H, tt, J 7, 1 Hz, H-2), 2.00-1.60 (4H, m, H-3, H-4), 1.39 (3H, dd, J 7, 2 Hz, CH_3); *m/z* (EI) 203 (MH^+), 185 (MH^+ - H_2O), 174, 167, 157, 153, 138 (M^+ - SO_2), 123, 109, 94, 81 (Found: C, 53.27; H, 6.81. $C_9H_{14}O_3S$ requires C, 53.44; H 6.98%) (Found: (M + NH_4^+), 220.1007. $C_9H_{14}O_3S$ requires (M + NH_4^+), 220.1007), followed by *[2R*, 5S*]-2,5-dihydro-2-methyl-5-[(4E)-5-(phenylsulphinyl)-4-pentenyl]thiophene*

S,S-dioxide **25** (127 mg, 22.6%) as a colourless oil; υ_{max} (film) 2935, 1616, 1445, 1303, 1131, 1039, 750, 691, 640 cm^{-1}; δ (500 MHz) 7.64-7.60 (2H, m, *ortho*-protons on Ph), 7.55-7.45 (3H, m, *meta*- and *para*-protons on Ph), 6.59 (1H, ddt, J 15, 7, 3 Hz, H-4'), 6.29 (1H, dd, J 15, 0.5 Hz, H-5'), 6.00-5.88 (2H, m, H-3, H-4), 3.83-3.64 (2H, m, H-2, H-5), 2.36-2.28 (2H, m, H-3'), 1.80-1.62 (4H, m, H-1', H-2'), 1.41 (3H, d, J 7 Hz, CH_3); *m/z* (EI) 324 (M^+), 260, 232, 179, 166, 149, 123, 91, 79, 64 (Found C, 59.53; H, 6.31%. $C_{16}H_{20}O_3S_2$ requires C, 59.23; H, 6.21%) (Found: (M^+ - SO_2), 260.1231. $C_{16}H_{20}O_3S_2$ requires (M^+ - SO_2), 260.1235), and finally *[2R*, 5S*]-2,5-dihydro-2-methyl-5-[(4Z)-5-(phenylsulphinyl)-4-pentenyl]thiophene S,S-dioxide* **24** (217 mg, 38.6%) as a colourless oil; υ_{max} (film) 2936, 1623, 1558, 1444, 1303, 1131, 1086, 1037, 747, 691, 641 cm^{-1}; δ (500 MHz) 7.64-7.60 (2H, m, *ortho*-protons on Ph), 7.55-7.45 (3H, m, *meta*- and *para*-protons on Ph), 6.30-6.18 (2H, m, H-4', H-5'), 5.94 (2H, m, H-3, H-4), 3.85-3.68 (2H, m, H-2, H-5), 2.75 (1H, m, H-3'), 2.63 (1H, m, H-3'), 2.05-1.68 (4H, m, H-1', H-2'), 1.42 (3H, d, J 7 Hz, CH_3); *m/z* (EI) 260 (M^+ - SO_2), 243, 232, 200, 179, 166, 149, 135, 123, 116, 109, 81, 64 (Found: C, 58.99; H, 6.25. $C_{16}H_{20}O_3S_2$ requires C, 59.23; H, 6.21%) (Found: (M^+ - SO_2), 260.1231. $C_{16}H_{20}O_3S_2$ requires (M^+ - SO_2), 260.1235). The presence of minor amounts of unidentified by-products in both product sulphoxides has not been taken into account when calculating the yields cited.

Oxidation of Z-sulphoxide (24). To a stirred solution of *Z*-sulphoxide **24** (124 mg, 0.382 mmol) in dichloromethane (3.8 ml) containing anhydrous sodium acetate (47 mg, 0.573 mmol, 1.5 eq.) at 0°C was added peracetic acid (117 μl of a 32 wt.% solution in dilute acetic acid, 0.573 mmol, 1.5 eq.) *via* syringe. After 20 min the mixture was allowed to warm to r.t. and stirred for a further 8 h. The reaction was poured into water (50 ml) and extracted with dichloromethane (3 x 50 ml). The combined organic layers were then washed with 10% aqueous sodium thiosulphate (3 x 50 ml), saturated aqueous sodium hydrogencarbonate (3 x 50 ml), water (50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by chromatography (50% - 75% ethyl acetate-petrol) to give *[2R*, 5S*]-2,5-dihydro-2-methyl-5-[(Z)-5-(phenylsulphonyl)-4-pentenyl]thiophene S,S-dioxide* **26** (86.4 mg, 66%) as a colourless oil; υ_{max} (film) 3061, 2933, 1624, 1448, 1305, 1147, 1085, 783, 756, 689, 638 cm^{-1}; δ (270 MHz) 7.91 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.66-7.52 (3H, m, *meta*- and *para*-protons on Ph), 6.36-6.20 (2H, m, H-4', H-5'), 5.92 (2H, m, H-3, H-4), 3.84-3.69 (2H, m, H-2, H-5), 2.76 (2H, m, H-3'), 1.96-1.91 (1H, m, H-1'), 1.79-1.55 (3H, m, H-1', H-2'), 1.40 (3H, d, J 8 Hz, CH_3); *m/z* (EI) 276 (M^+ - SO_2), 233, 221, 209, 195, 182, 165, 149, 147, 135, 95, 81, 77, 64 (SO_2) (Found: (M^+ - SO_2), 276.1180. $C_{16}H_{20}O_4S$ requires (M^+ - SO_2), 276.1184).

Cycloelimination of SO_2 from Z-sulphone (26). *Z*-Sulphone **26** (18.7 mg, 0.055 mmol) was dissolved in dry toluene (2 ml) and heated to 92°C for 2 h, after which time tlc (50% ethyl acetate-petrol) indicated the reaction to be complete. Concentration of the solution under reduced pressure and chromatography of the residue (20% ether-petrol) gave *(1Z, 6E, 8E)-1-(phenylsulphonyl)-1,6,8-decatriene* **3a** (13.7 mg, 92%) as a colourless oil; υ_{max} (film) 3014, 2920, 1624, 1448, 1306, 1146, 1086, 990, 753, 688 cm^{-1}; δ (500 MHz) 7.91 (2H, dd, J 8, 1.5 Hz, *ortho*-protons on Ph), 7.66-7.60 (1H, m, *para*-proton on Ph), 7.58-7.52 (2H, m, *meta*-protons on Ph), 6.30 (1H, br. d, J 11 Hz, H-1), 6.25 (1H, dt, J 11, 7 Hz, H-2), 6.05-5.95 (2H, m, H-7, H-8), 5.55-5.63 (1H, m, H-6), 5.48 (1H, m, H-9), 2.67 (2H, br. q, J 7 Hz, H-3), 2.07 (2H, br. q, J 7 Hz, H-5), 1.74 (3H, d, J 7 Hz, CH_3), 1.52-1.48 (2H, m, H-4); *m/z* (EI) 276 (M^+), 221 (M^+ - C_4H_7), 209, 195, 182, 165, 149, 147, 135, 95, 81, 79, 77 (Found: (M^+), 276.1180. $C_{16}H_{20}O_2S$ requires (M^+), 276.1184).

IMDA reaction of (1*E*, 7*E*, 9*E*)-1-(phenylsulphonyl)-1,7,9-undecatriene (1b). A solution of triene **1b** (azeotropically dried with toluene (3 x 50 ml); 497 mg, 1.71 mmol) in dry toluene (30 ml) was rigorously degassed by alternate sonification for 5 min, followed by degassing with argon for 5 min, repeated three times. The solution was then transferred *via* cannula to a dry, argon-filled resealable pressure tube and the system sealed. The tube was heated (Woods' metal bath) to 175°C for 96 h. After cooling, the toluene was evaporated under reduced pressure to give a pale crystalline solid. ^{1}H nmr (250 MHz) analysis of the crude product indicated the presence of a 6:1 mixture of cycloadducts. Purification by chromatography (20% ether-petrol) gave a white solid (457 mg, 92%) which was recrystallized to give *[3R*, 4S*, 5S*, 10S*]-3-methyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene* **27c** (270 mg, 54%), mp 133-134°C (benzene-petrol); υ_{max} (film) 3014, 2927, 2856, 1558, 1446, 1307, 1291, 1143, 1085, 935, 784, 746, 718, 690, 646, 616 cm^{-1}; δ (500 MHz) 7.92 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.70-7.50 (3H, m, *meta*- and *para*-protons on Ph), 5.52 (2H, br. s, H-1, H-2), 2.80 (1H, m, H-4), 2.77 (1H, m, H-10), 2.69 (1H, m, H-3), 2.49 (1H, m, H-5), 1.74-1.42 (5H, m) and 1.28-1.17 (3H, m, all comprising H-6, H-7, H-8, H-9), 0.95 (3H, d, J 7.5 Hz, CH_3); *m/z* (EI) 290 (M^+), 258, 226, 148 (M^+ - HSO_2Ph) (Found: C, 70.11; H 7.57. $C_{17}H_{22}O_2S$ requires C, 70.31; H, 7.65%). Repeated recrystallization (benzene-petrol) of the residue from the mother liquor gave *[3R*, 4R*, 5R*, 10S*]-3-methyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene* **27t**, mp 133-134.5°C (benzene-petrol); υ_{max} (film) 2923, 1651, 1446, 1300, 1144, 1086 cm^{-1}; δ (500 MHz) 7.88 (2H, dd, J 8, 1.5 Hz, *ortho*-protons on Ph), 7.65-7.60 (1H, m, *para*-proton on Ph), 7.55 (2H, m, *meta*-protons on Ph), 5.49 (1H, ddd, J 10, 5, 2.5 Hz, H-2), 5.33 (1H, d, J 10 Hz, H-1), 3.44 (1H, dd, J 10, 4.5 Hz, H-4), 2.41 (1H, m, H-3), 2.33 (1H, dd, J 12.5, 2.5 Hz, H-6_{eq}), 1.90 (1H, m, H-5), 1.86 (1H, m, H-10), 1.80-1.70 (3H, m, H-7_{eq}, H-8_{eq}, H-9_{eq}), 1.35 (1H, m, H-7_{ax}), 1.25 (1H, m, H-8_{ax}) 1.21 (3H, d, J 7 Hz, CH_3), 1.12 (1H, qd, J 12, 3.5 Hz, H-9_{ax}), 1.02 (1H, qd, J 12, 3.5 Hz, H-6_{ax}); *m/z* (EI) 290 (M^+), 225, 199, 169, 165, 149 (M^+ - SO_2Ph), 81, 79, 77 (Found: C, 70.41; H, 7.68. $C_{17}H_{22}O_2S$ requires C, 70.31; H 7.65%).

IMDA reaction of (1*Z*, 7*E*, 9*E*)-1-(phenylsulphonyl)-1,7,9-undecatriene (3b). A solution of triene **3b** (azeotropically dried with toluene (2 x 10 ml); 32.4 mg, 0.116 mmol) in dry toluene was degassed as above and transferred to a dry, argon-filled resealable pressure tube *via* cannula. The solution was heated at 160°C for 70 h, 165°C for 48 h, and then 175°C for 28 h. After cooling, the solvent was evaporated under reduced pressure. ^{1}H nmr analysis of the crude material indicated the presence of a 3:1 mixture of cyclization products. Purification by chromatography (15% ether-petrol) gave a solid (30 mg, 92%) which was recrystallized to give the major adduct *[3R*, 4S*, 5R*, 10S*]-3-methyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene* **28t**, mp 118-119°C (benzene-petrol); υ_{max} (film) 3008, 2914, 2848, 1638, 1539, 1480, 1443, 1368, 1303, 1287, 1145, 1108, 1083, 740, 726, 688 cm^{-1}; δ (500 MHz) 7.92 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.65-7.50 (3H, m, *meta*- and *para*-protons on Ph), 5.50 (1H, br. d, J 10 Hz, H-1), 5.43 (1H, m, H-2), 3.06 (1H, d, J 7 Hz, H-4), 2.64 (1H, m, H-3), 2.39 (1H, m, H-10), 2.05 (1H, qd, J 13, 3.5 Hz, H-6_{ax}), 1.90-1.80 (2H, m, H-7_{eq}, H-9_{eq}), 1.78-1.68 (3H, m, H-5, H-6_{eq}, H-8_{eq}), 1.38 (1H, qt, J 13, 3.5 Hz, H-8_{ax}), 1.21 (1H, qt, J 13, 3.5 Hz, H-7_{ax}), 0.97 (3H, d, J 7 Hz, CH_3), 0.95 (1H, m, H-9_{ax}); *m/z* (EI) 290 (M^+), 258, 249, 225, 208, 165, 148 (M^+ - HSO_2Ph), 133, 105, 91, 81, 77 (Found: C, 70.05; H, 7.80. $C_{17}H_{22}O_2S$ requires C, 70.31; H, 7.64%) (Found: (M^+), 290.1341. $C_{17}H_{22}O_2S$ requires (M^+), 290.1341). The minor adduct, *[3R*, 4R*, 5S*, 10S*]-3-methyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene* **28c** could not be isolated in a pure state from the mixture; δ (500 MHz) (*inter alia*) 7.92 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.68-7.55 (3H, m, *meta*- and *para*-protons on Ph), 5.60 (1H, dt, J 10, 3.5 Hz, H-1), 5.36 (1H, d, J 10 Hz, H-2), 3.33 (1H, dd, J 6.5, 2.5 Hz, H-4), 2.76-2.70 (1H, m, H-3), 2.28-2.20 (2H, m) and 2.18-2.14 (1H, m, all comprising H-5, H-10, H-6_{eq}), 1.62 (1H, m, H-6_{ax}), 1.44 (3H, d, J 7.5 Hz, CH_3), 1.08 (1H, m, H-9_{ax}).

IMDA reaction of (1*E*, 6*E*, 8*E*)-1-(phenylsulphonyl)-1,6,8-decatriene (1a). A solution of triene **1a** (azeotropically dried with toluene (2 x 10 ml); 10 mg, 0.036 mmol) in dry xylene (10 ml) was degassed as above and transferred to a dry, argon-filled resealable pressure tube *via* cannula. The solution was heated at 145°C for 48 h. ^{1}H nmr analysis of the crude product indicated the presence of a 1:1 mixture of diastereomers. The product was purified by chromatography (15% ether-petrol) to give a colourless solid (9.3 mg, 0.034 mmol, 93%) which was fractionally crystallized to give *[3R*, 4S*, 5S*, 9S*]-3-methyl-4-(phenylsulphonyl)bicyclo[4.3.0]-2-nonene* **29c**, mp 130-131.5°C (benzene-petrol); υ_{max} (film) 2962, 1640, 1443, 1282, 1243, 1140, 1083, 763, 738, 717, 690 cm^{-1}; δ (500 MHz) 7.92 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.70-7.50 (3H, m, *meta*- and *para*-protons on Ph), 5.45 (2H, br. s, H-1, H-2), 3.17 (1H, t, J 2.0 Hz, H-4), 2.82-2.74 (1H, m, H-3), 2.63 (1H, m, H-5), 2.55 (1H, m, H-9), 1.89-1.80 (1H, m), 1.78-1.70 (1H, m), 1.63-1.55 (2H, m) and 1.51-1.45 (2H, m; all comprising H-6, H-7, H-8), 1.10 (3H, d, J 7 Hz, CH_3); *m/z* (EI) 276 (M^+), 223, 205, 182, 165, 149, 143, 141, 135 (M^+ - SO_2Ph), 119, 105, 93 (Found: (M + NH_4^+), 294.1528. $C_{16}H_{20}O_2S$ requires (M + NH_4^+), 294.1528), and *[3R*, 4R*, 5R*, 9S*]-3-methyl-4-(phenylsulphonyl)bicyclo[4.3.0]-2-nonene* **29t**, mp 132-134°C (benzene-petrol); υ_{max} (film) 3021, 2966, 1641, 1443, 1285, 1243, 1108, 1082, 1024, 841, 796, 764, 738, 716, 690 cm^{-1}; δ (500 MHz) 7.92 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.68-7.50 (3H, m, *meta*- and *para*-protons on Ph), 5.73 (1H, d, J 9.5 Hz, H-1), 5.50 (1H, ddd, J 9.5, 5, 2.5 Hz, H-2), 3.50 (1H, dd, J 10, 4 Hz, H-4), 2.77 (1H, m, H-3), 1.98-1.55 (6H, m), 1.18 (1H, qd, J 10.5, 8.5 Hz) and 0.93 (1H, qd, J 10.5, 9.5 Hz, all comprising H-5, H-6, H-7, H-8, H-9), 1.28 (3H, d, J 7 Hz, CH_3); *m/z* (EI) 276 (M^+), 223, 149, 143, 135 (M^+ - SO_2Ph), 119, 107, 93, 79, 77 (Found: C, 69.56; H, 7.47. $C_{16}H_{20}O_2S$ requires C, 69.53; H, 7.29%).

IMDA reaction of (1*Z*, 6*E*, 8*E*)-1-(phenylsulphonyl)-1,6,8-decatriene (3a). A solution of triene **3a** (34.3 mg, 0.124 mmol) in toluene (6 ml) degassed as above was transferred to a dry, argon-filled resealable pressure tube *via* cannula. The solution was heated to 165°C for 60 h, after which time ^{1}H nmr analysis of the crude material indicated the presence of a 7:1 mixture of diastereomeric products. Chromatography (15% ether-petrol) gave a crystalline solid (21.7 mg, 63%) which was recrystallized to give the major isomer, *[3R*, 4S*, 5R*, 9S*]-3-methyl-4-(phenylsulphonyl)bicylo[4.3.0]-2-nonene* **30t**, mp 114-115°C (benzene-petrol); υ_{max} (film) 2960, 2873, 1624, 1593, 1448, 1295, 1193, 1164, 1145, 1084, 1025, 952, 764, 690 cm^{-1}; δ (500 MHz) 7.92 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.68-7.7.60 (1H, m, *para*-proton on Ph), 7.60-7.52 (2H, m, *meta*-protons on Ph), 5.88 (1H, d, J 10 Hz, H-1), 5.43 (1H, dt, J 10, 3 Hz, H-2), 3.34 (1H, d, J 4 Hz, H-4), 2.74 (1H, m, H-3), 2.65-2.57 (1H, m, H-5), 2.20-2.10 (1H, m, H-9), 1.98-1.89 (1H, m, H-6), 1.86-1.65 (4H, m, H-6, H-7, H-8 [one proton]), 1.15-1.08 (1H, m, H-8), 0.95 (3H, d, J 7.5 Hz, CH_3); *m/z* (EI) 276 (M^+), 211, 183, 143, 141 (SO_2Ph^+), 134 (M^+ - HSO_2Ph) (Found: (M^+), 276.1180. $C_{16}H_{20}O_2S$ requires (M^+), 276.1184). The minor isomer, *[3R*, 4R*, 5S*, 9S*]-3-methyl-4-(phenylsulphonyl)bicylo[4.3.0]-2-nonene* **30c** gave *inter alia* the following ^{1}H nmr data: δ (500 MHz) 5.61 (1H, ddd, J 10, 5, 2 Hz, H-1), 5.37 (1H, dt, J 10, 2 Hz, H-2), 3.53 (1H, dd, J 5, 4 Hz, H-4), 2.38 (1H, qd, J 7.5, 4 Hz, H-3), 1.43 (3H, d, J 7.5 Hz, CH_3).

IMDA reaction of (2*E*, 7*E*, 9*E*)-2-(phenylsulphonyl)-2,7,9-undecatriene (2a). A solution of triene (142 mg, 0.487 mmol) in dry toluene (10 ml) was degassed as above and transferred to an argon-filled resealable pressure tube *via* cannula. The solution was heated to 175°C for 120 h, allowed to cool and concentrated under reduced pressure. ^{1}H nmr analysis of the crude product indicated the presence of a 1:1.5 mixture of cycloadducts. Purification by chromatography (20% ether-petrol) gave a semi-solid (73 mg, 52%) which was re-chromatographed (15% ether-petrol) to give, in order of elution, *[3R*, 4R*, 5R*, 9S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.3.0]-2-nonene* **31t** (29 mg, 20%) as a crystalline solid, mp 132-133°C (benzene-petrol); υ_{max} (film) 2950, 2900, 1600, 1300, 1150, 1120, 1080 cm^{-1}; δ (270 MHz) 7.95 (2H, dd, J 8,

2 Hz, *ortho*-protons on Ph), 7.65-7.45 (3H, m, *meta*- and *para*-protons on Ph), 5.68 (1H, br. d, J 10 Hz, H-1), 5.52 (1H, ddd, J 10, 5, 2 Hz, H-2), 2.40 (1H, m, H-3), 2.12 (1H, td, J 12, 6 Hz, H-9), 2.00-1.60 (6H, m) and 1.05 (1H, m, all comprising H-5, H-6, H-7, H-8), 1.40 (3H, d, J 7 Hz, C-3 CH_3), 1.27 (3H, s, C-4 CH_3); *m/z* (EI) 223, 205, 176, 167, 149 (M^+ - SO_2Ph), 133, 121, 107, 93, 79, 77 (Found: C, 70.23; H, 7.82. $C_{17}H_{22}O_2S$ requires C, 70.30; H, 7.64%), followed by a mixture of the two isomers (10 mg, 7%), and finally *[3R*, 4S*, 5S*, 9S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.3.0]-2-nonene* **31c** (21.3 mg, 15%) as a crystalline solid, mp 126-132°C (benzene-petrol); υ_{max} (film) 2960, 1585, 1448, 1381, 1299, 1129, 1075, 760, 733, 693 cm^{-1}; δ (500 MHz) 7.92 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.70-7.48 (3H, m, *meta* and *para*-protons on Ph), 5.50 (2H, s, H-1, H-2), 2.91-2.82 (2H, m, H-5, H-9), 2.37 (1H, q, J 7.5 Hz, H-3), 1.91-1.83 (1H, m) and 1.70-1.40 (5H, m, all comprising H-6, H-7, H-8), 1.37 (3H, s, C-4 CH_3), 1.15 (3H, d, J 7.5 Hz, C-3 CH_3); *m/z* (EI) 149 (M^+ - SO_2Ph), 133, 119, 107, 93, 86, 81, 79, 77, 49 (Found: C, 70.11; H, 7.40. $C_{17}H_{22}O_2S$ requires C, 70.30; H, 7.64%).

IMDA reaction of (2*Z*, 7*E*, 9*E*)-2-(phenylsulphonyl)-2,7,9-undecatriene (4a). A solution of triene **4a** (84.3 mg, 0.289 mmol) in dry xylene (10 ml) was degassed as above and transferred *via* cannula to a dry, argon-filled resealable pressure tube. The solution was heated to 190°C for 60 h, allowed to cool, and then concentrated under reduced pressure. ^1H nmr analysis of the crude product indicated the presence of a 8:1 mixture of two diastereomeric cycloadducts. Purification by chromatography (15% ether-petrol) gave, in order of elution, *[3R*, 4R*, 5S*, 9S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.3.0]-2-nonene* **32c** (6.8 mg, 8%) as an oil which crystallized from ether to give a solid, mp 126-128°C (benzene-petrol); υ_{max} (film) 2944, 1623, 1448, 1379, 1300, 1149, 1127, 1073, 761, 737, 693 cm^{-1}; δ (500 MHz) 7.89 (2H, br. d, J 8 Hz, *ortho*-protons on Ph), 7.65 (1H, br. t, J 8 Hz, *para*-proton on Ph), 7.57 (2H, br. t, J 8 Hz, *meta*-protons on Ph), 5.57 (1H, ddd, J 10, 5, 2.5 Hz, H-2), 5.33 (1H, br. d, J 10 Hz, H-1), 2.56-2.48 (2H, m, H-3, H-9), 2.32-2.24 (1H, m), 2.12-2.04 (1H, m), 1.90 (1H, m), 1.75-1.65 (2H, m) and 1.58-1.49 (2H, m, all comprising H-5, H-6, H-7, H-8); *m/z* (EI) 290 (M^+), 149 (M^+ - SO_2Ph), 133, 107, 93, 77 (Found: (M^+), 290.1341. $C_{17}H_{22}O_2S$ requires (M^+), 290.1341), followed by a mixture of the two isomers as a colourless oil (15.4 mg, 18%), and finally *[3R*, 4S*, 5R*, 9S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.3.0]-2-nonene* **32t** (57.7 mg, 69%) as a crystalline solid, mp 147-148.5°C (benzene-petrol); υ_{max} (film) 2961, 2874, 1649, 1447, 1299, 1139, 731 cm^{-1}; δ (250 MHz) 7.90 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.65-7.50 (3H, m, *meta*- and *para*-protons on Ph), 5.84 (1H, dt, J 10, 1.5 Hz, H-1), 5.50 (1H, ddd, J 10, 5, 1.5 Hz, H-2), 2.90-2.70 (2H, m, H-3, H-9), 2.15-1.90 (2H, m), 1.80-1.60 (4H, m) and 1.22-1.08 (1H, m, all comprising H-5, H-6, H-7, H-8), 1.35 (3H, s, C-4 CH_3), 0.90 (3H, d, J 7 Hz, C-3 CH_3); *m/z* (EI) 290 (M^+), 149 (M^+ - SO_2Ph), 133, 119, 105, 91, 79, 77; (CI) 308 (M + NH_4^+), 149 (M^+ - SO_2Ph) (Found: (M + NH_4^+), 308.1684. $C_{17}H_{22}O_2S$ requires (M + NH_4^+), 308.1684).

IMDA reaction of (2*E*, 8*E*, 10*E*)-2-(phenylsulphonyl)-2,8,10-dodecatriene (2b). A solution of triene **2b** (304 mg, 1.0 mmol) in xylene (12 ml) was degassed as above and transferred *via* cannula to an argon-filled resealable pressure tube. The solution was heated to 170°C for 144 h, after which time an aliquot (*ca.* 10 mg) was withdrawn under a positive pressure of argon. ^1H nmr analysis of this crude mixture indicated *ca.* 50% conversion of **2b**, and the presence of the *cis*- and *trans*-fused cycloadducts in a 10:3 ratio. The reaction was heated to 178°C for a further 168 h, allowed to cool and the solvent evaporated under reduced pressure. ^1H nmr analysis of the resultant dark brown oil showed it to contain the same two cycloadducts together with what appeared to be a third unassignable product, also containing a methyl doublet, at *ca.* 1.23 ppm. Purification by chromatography (15% - 20% ether-petrol) gave *[3R*, 4R*, 5R*, 10S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene* **33t** (30 mg, 10%), followed by *[3R*, 4S*, 5S*, 10S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene* **33c** (18 mg, 6%) together with the unidentified product containing a methyl doublet. Both **33c** and **33t** were unambiguously identified by comparison of their ^1H nmr

spectra with those of the products of methylation of **27c** and **27t**, respectively (see below).

IMDA reaction of (2*Z*, 8*E*, 10*E*)-2-(phenylsulphonyl)-2,8,10-dodecatriene (4b). A solution of triene **4b** (236 mg, 0.776 mmol) in dry xylene (10 ml) was degassed as above and transferred *via* cannula to an argon-filled resealable pressure tube. The solution was heated to 190°C for 120 h and allowed to cool. ^{1}H nmr analysis of the crude product showed the presence of a 1:2 mixture of *cis*- and *trans*-fused cycloadducts. Purification by chromatography (15% - 20% ether-petrol) gave, in order of elution, *[3R*, 4R*, 5S*, 10S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene* **34c** (51 mg, 22%), followed by *[3R*, 4S*, 5R*, 10S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene* **34t**, (18 mg, 8%). Both **34c** and **34t** were unambiguously identified by comparison of their ^{1}H nmr spectra with those of the products of methylation of **27c** and **27t**, respectively (see below).

Methylation of [3R*, 4S*, 5S*, 9S*]-3-methyl-4-(phenylsulphonyl)bicyclo[4.3.0]-2-nonene (29c). Sulphone **29c** (contaminated with *ca.* 25 mol % **29t** (by ^{1}H nmr); 17.3 mg, 0.063 mmol) was dried *in vacuo* over P_2O_5, dissolved in THF (0.6 ml) under argon and the solution cooled to -78°C. *n*-Butyllithium (27 µl of a 2.57M solution in hexanes, 0.07 mmol, 1.1 eq.) was added dropwise to the stirred solution, giving a lemon yellow solution of the anion. Iodomethane (12 µl, 0.189 mmol, 3 eq.) was then added, causing fading of the colour. After 15 min the reaction was allowed to warm to room temperature during which time a yellow colour developed. The mixture was poured into water (15 ml) and the aqueous phase was extracted with dichloromethane (3 x 10 ml). The combined organic layers were washed with water (3 x 10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. ^{1}H nmr analysis of the crude product showed the presence of four isomeric products, indicating complete methylation of both **29c** and **29t**. Purification by chromatography (15% ether-petrol) gave, in order of elution, a mixture of **31t** and **32c** (3.2 mg and 5.8 mg, respectively (determined by ^{1}H nmr); 43% **32c** based on **29c**) followed by a mixture of **31c** and **32t** (7.0 mg and 1.0 mg, respectively (determined by ^{1}H nmr); 51% **31c** based on **29c**). Compounds **31c**, **31t**, **32c** and **32t** were unambiguously identified by comparison of their ^{1}H nmr spectra with those of the products of the IMDA reactions of trienes **2a** and **4a** (see above).

Methylation of [3R*, 4R*, 5R*, 9S*]-3-methyl-4-(phenylsulphonyl)bicyclo[4.3.0]-2-nonene (29t). Sulphone **29t** (dried *in vacuo* over P_2O_5; 33.3 mg, 0.121 mmol) was dissolved in THF (1.2 ml) under argon and the solution cooled to -78°C. *n*-Butyllithium (52 µl of a 2.56M solution in hexanes, 0.133 mmol, 1.1 eq) was added dropwise to the stirred solution, giving a lemon yellow anion colour. Iodomethane (23 µl, 0.363 mmol, 3 eq.) was then added, causing slow decolourization. After 10 min the reaction was allowed to warm to room temperature, causing the development during 30 min of a deep yellow colour. The reaction mixture was poured into water (20 ml) and the aqueous phase extracted with dichloromethane (3 x 20 ml). The combined organic layers were washed with water (3 x 20 ml), dried ($MgSO_4$), and concentrated under reduced pressure. Purification by chromatography (15% ether-petrol) gave, in order of elution, [3R*, 4R*, 5R*, 9S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.3.0]-2-nonene **31t** (13.3 mg, 38%) as a crystalline solid, identical by ^{1}H nmr to material prepared previously, followed by a colourless oil (19.8 mg) containing (by ^{1}H nmr) starting material **29t** (4.4 mg, 13%), further **31t** (4 mg, 12%; combined yield 50%) and its C-4 epimer **32t** (11 mg, 31%), and finally further **29t** (1 mg, 3%; total unreacted **29t** amounted to 16%). The oil crystallized at -18°C to give [3R*, 4S*, 5R*, 9S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.3.0]-2-nonene **32t**, identical by ^{1}H nmr to material prepared previously (see above).

Methylation of [3R*, 4S*, 5S*, 10S*]-3-methyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene (27c). A solution of sulphone **27c** (dried *in vacuo* over P_2O_5; 100 mg, 0.344 mmol) in THF (3.5 ml) was cooled to -78°C under argon. *n*-Butyllithium (266 µl of a 1.42M solution in hexanes, 0.378 mmol, 1.1 eq.) was added dropwise to the stirred solution and after 5 min iodomethane (52 µl, 0.833 mmol, 2.2 eq.) was added *via* syringe to the bright yellow anion solution. The colour discharged slowly and after 10 min the reaction was allowed to warm to room temperature over 30 min and poured into water (15 ml). The aqueous phase was extracted with dichloromethane (3 x 20 ml) and the combined organic layers were dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a colourless oil (111 mg). Purification by chromatography (15% ether-petrol) gave, in order of elution, *[3R*, 4S*, 5S*, 10S*]-3-methyl-4-(2-methylphenylsulphonyl)bicyclo-[4.4.0]-2-decene* **35** (26 mg, 25%) as a crystalline solid, mp 137-139°C (benzene-petrol); υ_{max} (film) 2926, 2856, 1597, 1506, 1449, 1312, 1291, 1148, 1130, 1060, 807, 751, 706, 690 cm^{-1}; δ (500 MHz) 8.00 (1H, dd, J 8, 2 Hz, *ortho*-proton on Ar), 7.52 (1H, td, J 8, 2 Hz, *para*-proton on Ar), 7.39 (2H, m, *meta*-protons on Ar), 5.54 (2H, s, H-1, H-2), 2.82 (2H, m, H-4, H-10), 2.69 (3H, s, Ar-CH_3), 2.68-2.60 (1H, m, H-3), 2.45-2.40 (1H, m, H-5), 1.70-1.40 (5H, m) and 1.25-1.15 (3H, m, all comprising H-6, H-7, H-8, H-9), 0.94 (3H, d, J 7.5 Hz, C-3 CH_3); *m/z* (EI) 277, 201, 183, 148 (M^+ - $C_7H_8O_2S$), 133, 119, 105, 91, 81, 77; (CI) 322 (M + NH_4^+), 174, 163, 149 (M^+ - $C_7H_7O_2S$) (Found: (M + NH_4^+), 322.1840. $C_{18}H_{24}O_2S$ requires (M + NH_4^+), 322.1840), followed by *[3R*, 4R*, 5S*, 10S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene* **34c** (14.9 mg, 14%) as an oily solid; υ_{max} (film) 2925, 2660, 2567, 2448, 2379, 1290, 1151, 1082, 760, 730, 692 cm^{-1}; δ (500 MHz) 7.88 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.70-7.50 (3H, m, *meta*- and *para*-protons on Ph), 5.62 (1H, dt, J 10, 3.5 Hz, H-2), 5.40-5.30 (1H, m, H-1), 2.70 (1H, dd, J 13, 2 Hz, H-10), 2.55-2.45 (1H, m, H-5), 2.35-2.25 (1H, m, H-3), 1.80-1.70 (2H, m, H-6_{eq}, H-9_{eq}), 1.66 (1H, m, H-9_{ax}), 1.60 (3H, d, J 7 Hz, C-3 CH_3), 1.50-1.33 (3H, m, H-7_{eq}, H-8_{eq}, H-8_{ax}), 1.30-1.18 (1H, m, H-6_{ax}), 1.23 (3H, s, C-4 CH_3), 1.10-1.05 (1H, m, H-7_{ax}); *m/z* (EI) 222, 177, 163 (M^+ - SO_2Ph), 148, 133, 199, 105, 95, 81, 77, (CI) 322 (M + NH_4^+), 163 (M^+ - SO_2Ph) (Found: (M + NH_4^+), 322.1840. $C_{18}H_{24}O_2S$ requires (M + NH_4^+), 322.1840), and finally *[3R*, 4S*, 5S*, 10S*]-3,4-dimethyl-4-(phenylsulphonyl)-bicyclo[4.4.0]-2-decene* **33c** (57 mg, 54%) as a crystalline solid, mp 86-87°C (benzene-petrol); υ_{max} (film) 3306, 2923, 2855, 1551, 1447, 1379, 1291, 1147, 1078, 798, 754, 729, 693 cm^{-1}; δ (500 MHz) 7.85 (2H, dd, J 8, 1.5 Hz, *ortho*-protons on Ph), 7.63-7.52 (3H, m, *meta*- and *para*-protons on Ph), 5.65 (1H, dt, J 10, 3.2 Hz, H-2), 5.55-5.53 (1H, m, H-1), 3.23 (1H, m, H-10), 2.98-2.96 (1H, m, H-3), 2.01 (1H, dt, J 12.5, 4 Hz, H-5), 1.78 (1H, dt, J 13.5, 2.5 Hz, H-9_{eq}), 1.67 (1H, m, H-7_{eq}), 1.53 (1H, tt, J 13.5, 4.5 Hz, H-9_{ax}), 1.45-1.41 (2H, m, H-8_{eq}, H-6_{eq}), 1.30 (1H, qd, J 12, 3 Hz, H-6_{ax}), 1.24 (3H, s, C-4 CH_3), 1.20 (1H, qt, 13, 3.2 Hz, H-8_{ax}), 1.11 (1H, qt, J 13, 3.2 Hz, H-7_{ax}), 1.01 (3H, d, J 7.5 Hz, C-3 CH_3); *m/z* (EI) 218, 199, 184, 163 (M^+ - SO_2Ph), 162, 147, 118, 105, 95, 91, 77 (Found: C, 71.18; H, 8.03. $C_{18}H_{24}O_2S$ requires C, 71.01; H, 7.95%).

Methylation of [3R*, 4R*, 5R*, 10S*]-3-methyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene (27t). Sulphone **27t** (azeotropically dried with toluene (2 x 10 ml); 14.4 mg, 0.05 mmol) was dissolved in THF (0.8 ml) under argon and the solution cooled to -78°C. *n*-Butyllithium (39 µl of a 1.41M solution in hexanes, 0.055 mmol, 1.1 eq.) was added dropwise to give a yellow solution of the anion, followed by iodomethane (8 µl, 0.125 mmol, 2.5 eq.). The reaction was stirred at -78°C for 10 min, then allowed to warm to room temperature and stirred overnight. Water (10 ml) was added and the aqueous phase was extracted with dichloromethane (3 x 10 ml). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to give a colourless oil. Purification by chromatography (15% ether-petrol) gave, in order of elution, an inseparable mixture of *[3R*, 4R*, 5R*, 10S*]-3-methyl-4-(2-methylphenyl-sulphonyl)bicyclo[4.4.0]-2-decene* **36** and *[3R*, 4R*, 5R*, 10S*]-3,4-dimethyl-4-(2-methylphenyl-sulphonyl)bicyclo[4.4.0]-2-decene* **37** (1 mg, 7%) as a semi-solid; υ_{max} (film) (mixture of **36** and **37**) 2922, 2890, 1444, 1302, 1147, 1120, 791, 730, 690 cm^{-1}; *m/z* (CI) (**36**) 322 (M + NH_4^+), 163 (M^+ - SO_2Ph), 141

(SO_2Ph), 108, 91; (**37**) 336 ($M + NH_4^+$), 177 ($M^+ - SO_2Ph$), followed by *[3R*, 4R*, 5R*, 10S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene* **33t** (0.5 mg, 3%); υ_{max} (film) 2922, 2830, 1443, 1374, 1298, 1149, 1124, 1067, 768, 731, 690 cm^{-1}; δ (250 MHz) 7.97 (2H, dd, J 8, 2 Hz, *ortho*-protons on Ph), 7.65-7.46 (3H, m, *meta*- and *para*-protons on Ph), 5.57-5.44 (1H, m, H-1), 5.28 (1H, d, J 9 Hz, H-2), 2.70 (1H, d, J 6.5 Hz, H-3), 2.40-2.30 (1H, m, H-10), 2.20-1.70 (5H, m) and 1.50-1.10 (4H, m, all comprising H-5, H-6, H-7, H-8, H-9), 1.46 (3H, s, C-4 CH_3), 1.32 (3H, d, J 7 Hz, C-3 CH_3); *m/z* (CI) 322 ($M + NH_4^+$), 180, 163 ($M^+ - SO_2Ph$) (Found: ($M + NH_4^+$), 322.1840. $C_{18}H_{24}O_2S$ requires ($M + NH_4^+$), 322.1841), and finally *[3R*, 4S*, 5R*, 10S*]-3,4-dimethyl-4-(phenylsulphonyl)bicyclo[4.4.0]-2-decene* **34t** (10.2 mg, 67%) as a crystalline solid, mp 128-129°C (benzene-petrol); υ_{max} (film) 2922, 2850, 1590, 1444, 1379, 1356, 1301, 1146, 1125, 1078, 1040, 850, 763, 724, 693 cm^{-1}; δ (500 MHz) 7.85 (2H, dd, J 8, 1.5 Hz, *ortho*-protons on Ph), 7.62 (1H, m, *para*-proton on Ph), 7.50 (2H, m, *meta*-protons on Ph), 5.49 (1H, ddd, J 10, 4.5, 2.5 Hz, H-2), 5.42 (1H, d, J 10 Hz, H-1), 2.57 (1H, m, H-3), 2.48 (1H, t with additional fine structure, J 9 Hz, H-10), 1.98 (1H, m, $H\text{-}6_{eq}$), 1.94-1.80 (3H, m, $H\text{-}6_{ax}$, $H\text{-}7_{eq}$, $H\text{-}9_{eq}$), 1.74 (1H, m, $H\text{-}8_{eq}$), 1.50 (1H, td, J 10, 3 Hz, H-5), 1.38 (1H, m, $H\text{-}8_{ax}$), 1.34 (3H, s, C-4 CH_3), 1.17 (1H, m, $H\text{-}7_{ax}$), 0.95 (1H, qd, J 13, 3 Hz, $H\text{-}9_{ax}$), 0.89 (3H, d, J 7 Hz, C-3 CH_3); *m/z* (CI) 322 ($M + NH_4^+$), 180, 163 (Found: C, 71.11; H, 7.95. $C_{18}H_{24}O_2S$ requires C, 71.01; H, 7.74%).

X-Ray crystal data[39]

All data were measured on a Nicolet R3m diffractometer, with Cu-K_α radiation (λ = 1.54178 Å, graphite monochromator) using ω-scans, with $2\theta \leq 116°$. The data were all corrected for Lorentz and polarization factors; no absorption corrections were applied. All structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Unless stated otherwise, the positions of all hydrogen atoms were idealized, C-H = 0.96Å, 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[40] programme system.

Crystal data for (18a): $C_{24}H_{30}O_5S_2$, M = 462.6, orthorhombic, a = 9.413(8), b = 11.967(8), c = 21.721(17) Å, V = 2447 Å^3, space group $P2_12_12_1$, Z = 4, D_c = 1.26 g cm^{-3}, μ(Cu-K_α) = 22 cm^{-1}, F(000) = 984. 1897 Independent reflections were measured of which 1853 had $|F_o| > 3\sigma(|F_o|)$, and were considered to be observed. The leading hydrogen atoms on the methyl groups on the sp^2 centres were located from an ΔF map. The absolute configuration of the molecule was determined by an R-factor test. Refinement was by block-cascade full-matrix least squares to R = 0.064, R_w = 0.064 [$w^{-1} = \sigma^2(F) + 0.00000F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.24 and -0.41 eÅ^{-3} respectively. The mean and maximum shift/error in the final refinement were 0.012 and 0.080 respectively.

Crystal data for (27c): $C_{17}H_{22}O_2S$, M = 290.4, monoclinic, a = 8.414(4), b = 9.531(4), c = 19.254(9) Å, β = 90.58(4)°, V = 1544 Å^3, space group $P2_1/c$, Z = 4, D_c = 1.25 g cm^{-3}, μ(Cu-K_α) = 18 cm^{-1}, F(000) = 624. A crystal of dimensions 0.50 x 0.27 x 0.10 mm was used. 2080 Independent reflections were measured of which 1928 had $|F_o| > 3\sigma(|F_o|)$, and were considered to be observed. Refinement was by block-cascade full-matrix least squares to R = 0.044, R_w = 0.052 [$w^{-1} = \sigma^2(F) + 0.00051F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.27 and -0.24 eÅ^{-3} respectively. The mean and maximum shift/error in the final refinement were 0.001 and 0.005 respectively.

Crystal data for (27t): $C_{17}H_{22}O_2S$, M = 290.4, monoclinic, a = 21.559(14), b = 8.203(4), c = 17.662(9) Å, β = 105.77(5)°, V = 3006 Å^3, space group $C2/c$, Z = 8, D_c = 1.28 g cm^{-3}, μ(Cu-K_α) = 19

cm^{-1}, $F(000)$ = 1248. 2025 Independent reflections were measured of which 1837 had $|F_o| > 3\sigma(|F_o|)$, and were considered to be observed. Refinement was by block-cascade full-matrix least squares to $R = 0.059$, $R_w = 0.073$ [$w^{-1} = \sigma^2(F) + 0.00080F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.31 and -0.48 $eÅ^{-3}$ respectively. The mean and maximum shift/error in the final refinement were 0.013 and 0.073 respectively.

Crystal data for (28t): $C_{17}H_{22}O_2S$, M = 290.4, orthorhombic, a = 5.849(1), b = 14.012(4), c = 19.042(5) Å, V = 1561 $Å^3$, space group $P2_1cn$, $Z = 4$, D_c = 1.24 g cm^{-3}, μ(Cu-K_α) = 18 cm^{-1}, $F(000)$ = 624. A crystal of dimensions 0.20 x 0.30 x 0.83 mm was used. 1177 Independent reflections were measured of which 1153 had $|F_o| > 3\sigma(|F_o|)$, and were considered to be observed. Refinement was by block-cascade full-matrix least squares to $R = 0.029$, $R_w = 0.033$ [$w^{-1} = \sigma^2(F) + 0.00088F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.15 and -0.24 $eÅ^{-3}$ respectively. The mean and maximum shift/error in the final refinement were 0.017 and 0.070 respectively.

Crystal data for (29t): $C_{16}H_{20}O_2S$, M = 276.4, monoclinic, a = 8.255(4), b = 10.020(7), c = 17.716(8) Å, β = 100.29(4)°, V = 1442 $Å^3$, space group $P2_1/n$, $Z = 4$, D_c = 1.27 g cm^{-3}, μ(Cu-K_α) = 19 cm^{-1}, $F(000)$ = 592. 1932 Independent reflections were measured of which 1816 had $|F_o| > 3\sigma(|F_o|)$, and were considered to be observed. Refinement was by block-cascade full-matrix least squares to $R = 0.045$, R_w = 0.055 [$w^{-1} = \sigma^2(F) + 0.00090F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.32 and -0.25 $eÅ^{-3}$ respectively. The mean and maximum shift/error in the final refinement were 0.008 and 0.038 respectively.

Crystal data for (30t): $C_{16}H_{20}O_2S$, M = 276.4, monoclinic, a = 8.457(3), b = 15.739(6), c = 10.970(4) Å, β = 96.28(3)°, V = 1451 $Å^3$, space group $P2_1/c$, $Z = 4$, D_c = 1.26 g cm^{-3}, μ(Cu-K_α) = 19 cm^{-1}, $F(000)$ = 592. A crystal of dimensions 0.07 x 0.33 x 0.37 mm was used. 1954 Independent reflections were measured of which 1792 had $|F_o| > 3\sigma(|F_o|)$, and were considered to be observed. Refinement was by block-cascade full-matrix least squares to $R = 0.041$, $R_w = 0.049$ [$w^{-1} = \sigma^2(F) + 0.00061F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.37 and -0.19 $eÅ^{-3}$ respectively. The mean and maximum shift/error in the final refinement were 0.030 and 0.288 respectively.

Crystal data for (31t): $C_{17}H_{22}O_2S$, M = 290.4, monoclinic, a = 12.952(4), b = 7.435(3), c = 15.907(6) Å, β = 101.29(3)°, V = 1502 $Å^3$, space group $P2_1/c$, $Z = 4$, D_c = 1.28 g cm^{-3}, μ(Cu-K_α) = 19 cm^{-1}, $F(000)$ = 624. A crystal of dimensions 0.33 x 0.33 x 0.67 mm was used. 2022 Independent reflections were measured of which 1843 had $|F_o| > 3\sigma(|F_o|)$, and were considered to be observed. A ΔF map revealed the positions of all the hydrogen atoms. Refinement was by block-cascade full-matrix least squares to $R = 0.048$, $R_w = 0.056$ [$w^{-1} = \sigma^2(F) + 0.00174F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.43 and -0.26 $eÅ^{-3}$ respectively. The mean and maximum shift/error in the final refinement were 0.016 and 0.142 respectively.

Crystal data for (34t): $C_{18}H_{24}O_2S$, M = 304.5, monoclinic, a = 12.995(8), b = 9.026(6), c = 14.605(12) Å, β = 107.36(6)°, V = 1635 $Å^3$, space group $P2_1/c$, $Z = 4$, D_c = 1.24 g cm^{-3}, μ(Cu-K_α) = 17 cm^{-1}, $F(000)$ = 656. 2196 Independent reflections were measured of which 2053 had $|F_o| > 3\sigma(|F_o|)$, and were considered to be observed. The bridgehead hydrogen atoms were located from a ΔF map and refined isotropically. Refinement was by block-cascade full-matrix least squares to $R = 0.075$, $R_w = 0.098$ [$w^{-1} = \sigma^2(F) + 0.00238F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.54 and -0.78 $eÅ^{-3}$ respectively. The mean and maximum shift/error in the final refinement were 0.074 and 0.320 respectively.

References and notes

1. Students of the *Deutscher Akademischer Austauschdienst*, 1987-1988.
2. (i) Brieger, G. *J. Am. Chem. Soc.*, **1963**, *85*, 3763; (ii) Klemm, L. H.; Gopinath, K. W. *Tetrahedron Lett.*, **1963**, 1243; (iii) House, H. O.; Cronin, T. H. *J. Org. Chem.*, **1965**, *30*, 1061.
3. For a review, and leading references, see: Craig, D. *Chem. Soc. Rev.*, **1987**, *16*, 187.
4. IMDA Reactions of various sulphonyl-substituted trienes have been reported. Sulphonyl-substituted dienophiles: (i) Kametani, T.; Aizawa, M.; Nemoto, H. *Tetrahedron*, **1981**, *37*, 2547; (ii) Strekowski, S.; Kong, S.; Battiste, M. A. *J. Org. Chem.*, **1988**, *53*, 901; (iii) Corey, E. J.; Da Silva Jardine, P.; Rohloff, J. C. *J. Am. Chem. Soc.*, **1988**, *110*, 3672. Sulphonyl-substituted dienes: (iv) Weichert, A.; Hoffmann, H. M. R. *J. Chem. Soc., Perkin Trans. 1*, **1990**, 2154; (v) Chou, S.-S. P.; Wey, S.-J. *J. Org. Chem.*, **1990**, *55*, 1270.
5. For reviews of general sulphone chemistry, see: (i) Magnus, P. D. *Tetrahedron*, **1977**, *33*, 2019; (ii) Trost, B. M. *Bull. Chem. Soc. Jpn.*, **1988**, *61*, 107. For a recent review of the chemistry of vinylic sulphones, see: (iii) Simpkins, N. S. *Tetrahedron*, **1990**, *46*, 6951.
6. For the preliminary account of this work, see: Craig, D.; Fischer, D. A.; Kemal, Ö.; Plessner, T. *Tetrahedron Lett.*, **1988**, *29*, 6369.
7. Trienes possessing ester substituents on the dienophilic group show thermal cyclization stereoselectivity which is largely independent of dienophile geometry: (i) Roush, W. R.; Essenfeld, A. P.; Warmus, J. S. *Tetrahedron Lett.*, **1987**, *28*, 2447, and references cited therein (bicyclo[4.3.0] systems); (ii) Roush, W. R.; Hall, S. E. *J. Am. Chem. Soc.*, **1981**, *103*, 5200; Roush, W. R.; Gillis, H. R. *J. Org. Chem.*, **1982**, *47*, 4825 (bicyclo[4.4.0] systems). For bicyclo[4.3.0] systems possessing more strongly electron-withdrawing dienophile substituents, *E*, *E*, *E*-trienes show enhanced selectivity for *trans*-fused products, whilst *Z*, *E*, *E*-trienes cyclize with low selectivity. This is because both secondary orbital effects (significant at the lower reaction temperatures) and the pseudo-five-membered cyclic transition state favour the *trans*-fusion in the case of *E*, *E*, *E*-trienes, whereas with *Z*, *E*, *E*-trienes secondary orbital overlap favours the formation of *cis*-fused products.
8. For example, in *E*-α,β-unsaturated sulphones the β-proton resonates downfield and the γ-protons upfield compared with the *Z*-isomer. See, for example: Craig, D.; Ley, S. V.; Simpkins, N. S.; Whitham, G. H.; Prior, M. J. *J. Chem. Soc., Perkin Trans. 1*, **1985**, 1949.
9. Kang, S.-K.; Kim, W.-S.; Moon, B.-H. *Synthesis*, **1985**, 1161.
10. Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981.
11. Small amounts of the phenylsulphinic esters arising from *O*-alkylation of phenylsulphinate anion were formed as by-products in these reactions. Details are provided in the Experimental section.
12. (i) Julia, M.; Paris, J. M. *Tetrahedron Lett.*, **1973**, 4833; (ii) Kocienski, P. J.; Lythgoe, B.; Ruston, S. *J. Chem. Soc., Perkin Trans. 1*, **1978**, 829; (iii) Kocienski, P. J.; Lythgoe, B.; Waterhouse, I. *ibid.*, **1980**, 1045.
13. Mancuso, A. J.; Swern, D. *Synthesis*, **1981**, 165.
14. For previous syntheses, see: (i) Kurth, M. J.; O'Brien, M. J.; Hope, H.; Yanuck, M. *J. Org. Chem.*, **1985**, *50*, 2626 (**5a**); (ii) Larsen, S. D.; Grieco, P. A. *J. Am. Chem. Soc.*, **1985**, *107*, 1768 (**5b**).
15. For a related procedure for the synthesis of vinylic sulphoximines, see: Bailey, P. L.; Clegg, W.; Jackson, R. F. W.; Meth-Cohn, O. *J. Chem. Soc., Perkin Trans. 1*, **1990**, 200.
16. Julia, M.; Launay, M.; Stacino, J.-P.; Verpeaux, J.-N. *Tetrahedron Lett.*, **1982**, *23*, 2465.
17. Eisch, J. J.; Galle, J. E. *J. Org. Chem.*, **1979**, *44*, 3279.
18. For example, see: Ley, S. V.; Anthony, N. J.; Armstrong, A.; Brasca, M. G.; Clarke, T.; Culshaw, D.; Greck, C.; Grice, P.; Jones, A. B.; Lygo, B.; Madin, A.; Sheppard, R. N.; Slawin, A. M. Z.; Williams, D. J. *Tetrahedron*, **1989**, *45*, 7161.
19. Posner, G. H.; Brunelle, D. J. *J. Org. Chem.*, **1972**, *37*, 3547.
20. *cf.* Still, W. C.; Gennari, C. *Tetrahedron Lett.*, **1983**, *24*, 4405. Bis(2,2,2-trifluoroethyl) (phenylsulphonyl)methanephosphonate was prepared as follows. A mixture of PCl_5 (1.18 g, 5.68 mmol, 3 eq.) and dimethyl (phenylsulphonyl)methanephosphonate (500 mg, 1.89 mmol, 1 eq.) under argon was heated at 70°C for 60 h. Excess PCl_5 and $POCl_3$ were removed by heating at 50°C/0.1 mm Hg for 1 h. The resulting oil was dissolved in dry benzene (1.5 ml) and treated with a solution of CF_3CH_2OH (ex $CaSO_4$/$NaHCO_3$; 290 µl, 3.97 mmol, 2.1 eq.) and $^iPr_2NEt$ (757 µl, 4.35 mmol, 2.3 eq.) in dry benzene (1 ml) under argon at 0°C. The mixture was stirred at 0°C for 1 h, after which time further CF_3CH_2OH (138 µl, 1.89 mmol, 1 eq.) and $^iPr_2NEt$ (395 µl, 2.27 mmol, 1.2 eq.) were added. After a further 30 min the reaction was quenched by the addition of saturated aqueous sodium hydrogencarbonate solution and the mixture extracted with ether (3 x 10 ml). The combined extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure to

give a yellow oil. This was purified by chromatography (30% ethyl acetate-petrol) to give *bis(2,2,2-trifluoroethyl) (phenylsulphonyl)methanephosphonate* (330 mg, 44%) as a white solid, mp 51-52.5°C (ether-petrol); δ (250 MHz) 8.05-7.96 (2H, m, *ortho*-protons on Ph), 7.78-7.58 (3H, m, *meta*- and *para*-protons on Ph), 4.49 (4H, m, OCH_2CF_3), 3.95 (2H, d, J 17.5 Hz, $PhSO_2CH_2$); *m/z* (EI) 400 (M^+), 381, 336, 316, 296 (Found: C, 32.87; H, 2.61. $C_{11}H_{11}F_6O_5PS$ requires C, 33.01; H, 2.77%). Olefination using this modified reagent typically gave 3:1 mixtures of *E*- and *Z*- vinylic sulphones, which were inseparable by chromatography.

21. Generated by *t*-BuLi treatment of *Z*-1-iodo-1-octene, which was prepared by Wittig olefination of heptanal with iodomethylenetriphenylphosphorane: Stork, G.; Zhao, K. *Tetrahedron Lett.*, **1989**, *30*, 2173.
22. Craig, D.; Daniels, K.; Marsh, A.; Rainford, D.; Smith, A. M. *Synlett*, **1990**, 531.
23. Cooper, G. D. *J. Am. Chem. Soc.*, **1954**, *76*, 3713.
24. Trost, B. M.; Braslau, R. *J. Org. Chem.*, **1988**, *53*, 532, and references cited therein.
25. Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.*, **1981**, *46*, 3936.
26. McKillop, A.; Tarbin, J. A. *Tetrahedron Lett.*, **1983**, *24*, 1505.
27. For an example of chemospecific oxidation of a sulphide to a sulphone in the presence of an isolated, disubstituted double bond using this reagent system, see: Ley, S. V.; Edwards, M. P.; Lister, S. G.; Palmer, B. D.; Williams, D. J. *J. Org. Chem.*, **1984**, *49*, 3503.
28. *Z*-Vinylic sulphoxides have been reported to undergo *S*-oxidation to vinylic sulphones significantly more slowly than the corresponding *E*-isomers: Palmer, J. T.; Fuchs, P. L. *Synth. Commun.*, **1988**, 233.
29. Backer, H.; Bottema, J. *Recl. Trav. Chim. Pays Bas*, **1932**, *51*, 294.
30. A 6:1 mixture of isomeric *E*, *E*- and *Z*, *E*- THP ethers **11a** was used in this reaction.
31. For an example of a Wittig reaction with methoxycarbonylmethylenetriphenylphosphorane of a labile aldehyde generated *in situ*, see: Ireland, R. E.; Häbich, D.; Norbeck, D. W. *J. Am. Chem. Soc.*, **1985**, *107*, 3271.
32. See, for example, Wattanasin, S.; Kathawala, F. G.; Boeckman, R. K. *J. Org. Chem.*, **1985**, *50*, 3810.
33. It should be noted that an isolated yield of cycloadducts of less than 86% might have led to the not unreasonable conclusion that *E*, *E*, *E*-**1b** had cyclized to give a 6:1 mixture of **27c** and **27t**, and that *E*, *Z*, *E*-**1b** was unreactive. We take this opportunity to stress the importance of nmr analysis of *crude* reaction mixtures when dealing with transformations of this type.
34. It has been suggested that the diastereospecificity of an in*ter*molecular Diels-Alder dimerization reaction of a sulphonyl-substituted diene may result from the preference for an *exo*- phenylsulphonyl group: Hoffmann, H. M. R.; Weichert, A.; Slawin, A. M. Z.; Williams, D. J. *Tetrahedron*, **1990**, *46*, 5591. The *endo*-selectivity of intermolecular Diels-Alder reactions of cyclopentadiene and 1,3-cyclohexadiene with (phenylsulphonyl)ethene may be rationalized in terms of the lesser steric demand associated with the planar, sp^2-hybridized diene unit compared with the sp^3-hybridized methylene groups linking the diene termini. See: Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.*, **1983**, *48*, 4976.
35. We thank Mr. Richard N. Sheppard of this department for the ^1H nmr experiments described herein.
36. Brown, F. K.; Houk, K. N. *Tetrahedron Lett.*, **1985**, *26*, 2297, and references cited therein.
37. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd edn.; Pergamon: Oxford, 1988.
38. Prepared by reaction of sodium phenylsulphinate with bromoethane in DMSO (51% after recrystallization).
39. Atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this work.
40. Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, Revision 5.2; University of Göttingen: 1985.