Pergamon

Tetrahedron Vol. 51, No. 5, pp. 1509-1532, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/95 $9.50+0.00

0040-4020(94)01045-5

Intramolecular Diels–Alder Reactions of Internally-substituted Trienylsulfones. Synthesis of Bicyclo[4.3.0] and -[4.4.0] Systems Possessing a Bridgehead Sulfonyl Group

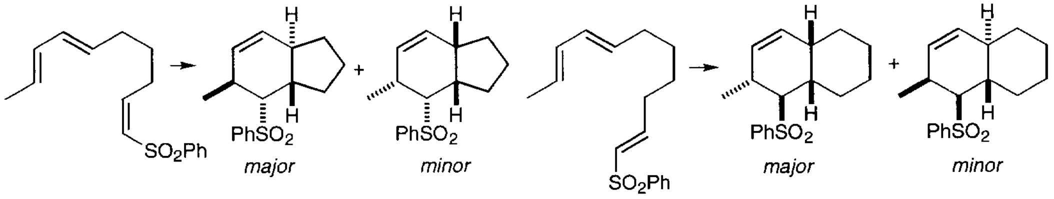
Martin C. Clasby, Donald Craig,* Alexandra M. Z. Slawin, Andrew J. P. White and David J. Williams

Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, U.K.

Abstract: A series of trienes possessing internally-activated vinylic sulfone dienophilic groups undergo intramolecular Diels–Alder (IMDA) reaction with high or complete selectivity for the cis-fused products. Incorporation of silyloxy groups within the carbon tether linking the diene and dienophile results in increased IMDA reactivity. The stereochemical outcomes of these processes are rationalised in terms of the preference for an exo-oriented phenylsulfonyl group, and a minimisation of non-bonded interactions between the silyloxy and sulfone substituents.

INTRODUCTION

The intramolecular Diels–Alder (IMDA) reaction continues to be the subject of widespread research effort in the contexts of synthetic methodology and strategy, and of total synthesis.[1] The transformation is associated with the efficient creation and multiplication of asymmetric centres within polycyclic and polyfunctional molecules, and the stereochemical outcomes of such processes are increasingly predictable on the basis of well-established concepts and empirical findings. As part of a programme for the development of new IMDA-based strategies for both synthetic methodology[2] and total synthesis,[3] we have been investigating IMDA reactions of sulfonyl-substituted trienes. Our initial studies[4] were concerned with the thermal behaviour of substrates in which the sulfonyl group is positioned at the dienophile terminus. These reactions gave selectively products arising via transition-states in which the bulky sulfonyl substituent is oriented exo to the diene group (Scheme 1). More recently, we have looked at the effect on reactivity and cyclisation selectivity of the incorporation of a phenylsulfonyl moiety at the internal end of the dienophilic C–C double bond. We now report in full[5] the results of these investigations, which demonstrate that cis-fused bicyclic systems possessing bridgehead phenylsulfonyl groups may be generated with high selectivity via IMDA reactions of appropriately-substituted triene substrates.

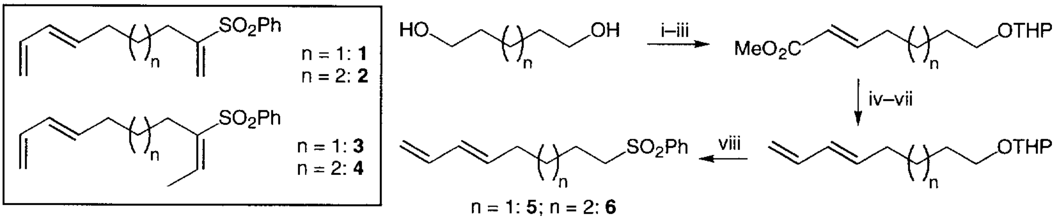


Scheme 1

RESULTS AND DISCUSSION

Synthesis of trienes

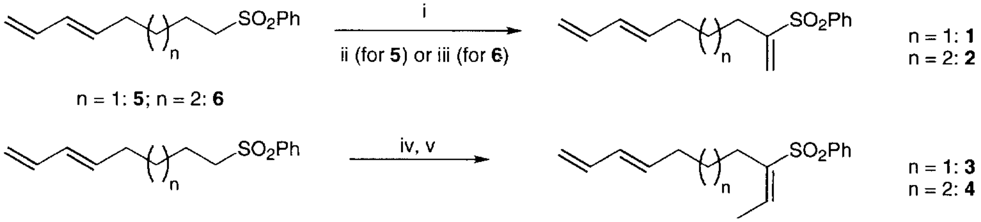
Trienes **1**–**4** were selected as the first target substrates. It was anticipated that the terminally unsubstituted diene moieties would be accessible with high selectivity for the *E*-isomers via Wittig reactions of appropriate aldehyde precursors.[6] The variation of the substituent on the β-carbon atom of the vinylic sulfone group would allow assessment of the inherent reactivity of the system, and would give an idea of the tolerance of the cyclisation process of increasing steric bulk at this position.[7] Our previous studies[4] had demonstrated the effectiveness of a hydroxyalkylation–elimination sequence for the introduction of the vinylic sulfone group, and consequently dienylsulfones **5** and **6** were identified as preliminary targets. These materials were readily prepared in good overall yields via the sequence depicted in Scheme 2.[8]



Reagents and conditions: (i) DHP, CSA, CH_2Cl_2; (ii) py·SO_3, Et_3N, DMSO; (iii) $Ph_3P{=}CHCO_2Me$, CH_2Cl_2; (iv) DIBAL-H, PhMe; (v) MnO_2, CH_2Cl_2; (vi) $Ph_3P{=}CH_2$, THF; (vii) 10-camphorsulfonic acid (CSA), MeOH; (viii) CH_3SO_2Cl, Et_3N, CH_2Cl_2; LiBr, THF; $PhSO_2Na$, DMSO.

Scheme 2

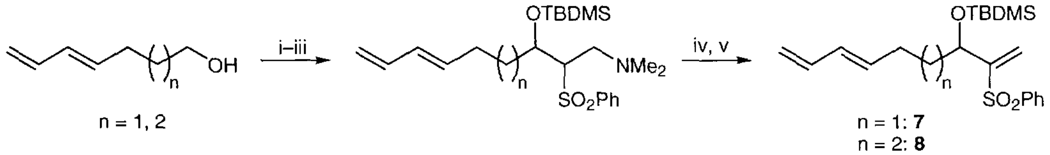
By analogy with our earlier work, it was expected that reaction of the anions derived from **5** and **6** with paraformaldehyde would generate α-(hydroxymethyl)dienylsulfones, which upon dehydration would yield the desired substrates **1** and **2**. In practice, attempted hydroxymethylation by addition of paraformaldehyde to lithiated **5** and **6** failed to yield any of the desired alcohols. In an alternative approach, **5** and **6** were phosphorylated by the addition of diethyl chlorophosphate to a solution of lithiated substrate and an additional equivalent of LDA. The product phosphonates were subjected to Wadsworth–Emmons reaction[9] by treatment with butyllithium or sodium hydride followed by paraformaldehyde, giving target trienes **1** and **2** in excellent yields. The methyl-containing analogues **3** and **4** were prepared from **5** and **6** by sequential lithiation, treatment with acetaldehyde and trapping of the resulting alkoxides with benzoyl chloride, followed by highly *E*-selective potassium *tert*-butoxide-mediated E1cB-elimination of the product esters.[10] The completion of the syntheses of trienes **1**-**4** is depicted in Scheme 3.



Reagents and conditions: (i) LDA (2.2 eq), THF, $(EtO)_2P(O)Cl$, then H^+; (ii) *n*-BuLi, $(CH_2O)_n$; (iii) NaH, $(CH_2O)_n$; (iv) *n*-BuLi, THF, MeCHO, then PhCOCl; (v) *t*-BuOK, THF.

Scheme 3

Subsequent to the investigation of the IMDA reactivity of these trienes, we became interested in the effects on reactivity and stereoselectivity of the introduction of substituents in the linking chain. In particular, we were keen to explore the chemistry of trienes **7** and **8** possessing a silyloxy substituent at the position on the carbon tether α- with respect to the dienophile C–C double bond. It was envisaged that the presence of oxygen-based functionality within the 5- or 6-membered saturated ring in the bicyclic product would provide the opportunity ultimately to fragment this ring; this would deliver the products of formal intermolecular cycloaddition, with the regio- and stereochemical advantages offered by the intramolecular variant.[11] Trienes **7** and **8** were readily prepared from the corresponding dienols synthesised as before, and the dimethylamine adduct[12] of (phenylsulfonyl)ethene[13] (Scheme 4).

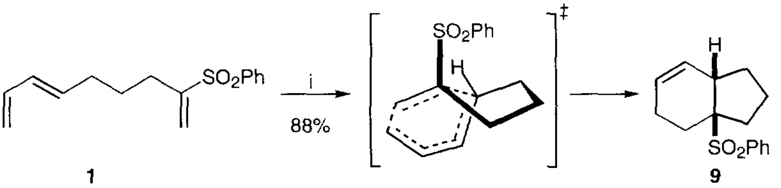


Reagents and conditions: (i) py·SO_3, Et_3N, DMSO; (ii) add aldehyde to $(Me_2NCH_2CH^-SO_2Ph)Li^+$, THF, then H^+; (iii) TBDMSOTf, py, CH_2Cl_2; (iv) MeI, Me_2CO; (v) *t*-BuOK, THF.

Scheme 4

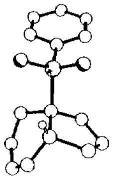
Intramolecular Diels–Alder reactions

In order to establish reaction parameters for the IMDA reactions of trienes **1-4**, **7** and **8**, preliminary cyclisation reactions were carried out on degassed d_8-toluene solutions in sealed, base-washed nmr tubes prior to preparative-scale runs in similarly-treated Carius tubes. Product ratios were determined by 500 MHz ^{1}H nmr analysis of crude reaction mixtures. Thermolysis of triene **1** gave in high yield a single cycloadduct **9**, whose structure was unambiguously determined by single-crystal X-ray analysis (Figure 1). We rationalise this selectivity in terms of the favoured disposition of the bulky phenylsulfonyl group exo with respect to the diene.[4] Also, the asynchronous nature of the IMDA reaction, together with the positioning of the electron-withdrawing sulfonyl group is such that the transition state more closely resembles a 9- rather than a 5-membered ring, whose cis-skewed conformation is energetically favoured over the alternative trans- arrangement (Scheme 5).[14]



Reagents and conditions: PhMe, 180°C, 4.5 h

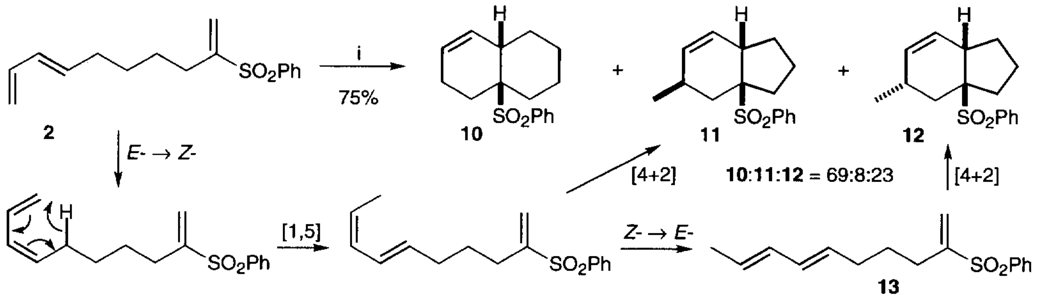
Scheme 5



X-ray structure of **9**

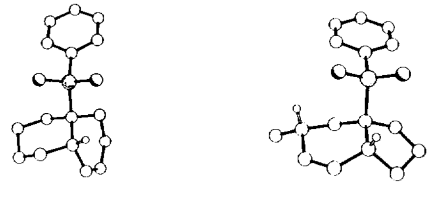
Figure 1

Heating a solution of triene **2** using the standard procedure gave a more complex product mixture. In addition to the expected cis-fused bicyclo[4.4.0] system **10**, which formed ca. 70% of product, a 3:1 mixture of two other compounds was formed, both of which clearly showed the presence of methyl doublets in the ^{1}H nmr spectrum. X-Ray crystallographic analysis (Figure 2) enabled the structural assignment of **10**, and of the major by-product **12**. We presume that the minor contaminant is the isomer **11** having the epimeric methyl-bearing carbon atom (Scheme 6). We suggest that under the thermal conditions necessary for IMDA reaction to occur triene **2** undergoes *E*- to *Z*- isomerisation followed by a [1,5]-hydrogen shift and isomerisation to the homologue **13** possessing a terminal methyl group on the diene moiety. Triene **13** undergoes IMDA reaction to give **12**; cyclisation prior to the final *Z*- to *E*- isomerisation gives rise to the by-product **11** (Scheme 6).



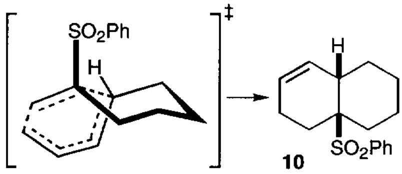
Reagents and conditions: (i) PhMe, 180°C, 36 h.

Scheme 6



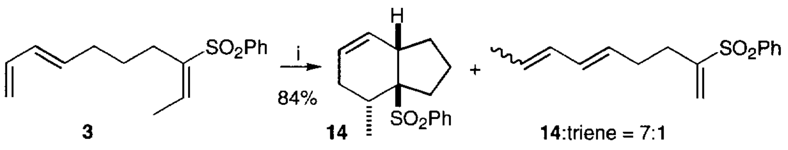
X-ray structure of **10** X-ray structure of **12**

Figure 2



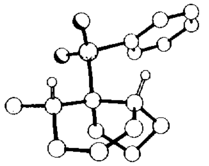
Scheme 7

Again, we attribute the highly cis-selective nature of the cycloaddition reaction of **2** (and of **13** formed in situ) to the favoured exo-orientation of the sulfonyl group with respect to the diene unit (Scheme 7). Chemical evidence for the sequence of events proposed in Scheme 6 was provided by the cyclisation reaction of the β-methyl-containing triene **3**. Thermolysis gave in high yield a ca. 7:1 mixture of the cis-fused bicyclic sulfone **14** and a mixture of acyclic compounds whose ^{1}H nmr spectra indicated the presence of a terminally-methylated diene group. (Scheme 8). IMDA Reaction of these isomers would give rise to bicyclo[4.2.0] ring-systems, and the strain associated with these structures might explain the observed inertness of the isomeric trienes. X-Ray crystallography again provided rigorous proof of the cis-fused nature of **14** (Figure 3).



Reagents and conditions: (i) PhMe, 162°C, 90 h.

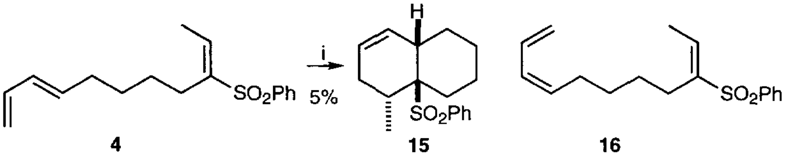
Scheme 8



X-ray structure of **14**

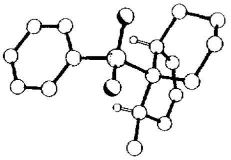
Figure 3

As anticipated, triene **4** was found to be the least reactive of the unsubstituted substrates. We attribute the observed low reactivity to a combination of steric hindrance because of the β-methyl dienophile substituent, and the presence in the linking chain of an extra carbon atom, which lowers the population of conformers disposed toward cycloaddition.[15] Cycloaddition of **4** was accompanied by extensive decomposition; cis-fused bicycle **15** was the only product isolated. The X-ray crystal structure of **15** is shown in Figure 4. Thermolysis of **4** at lower temperatures (150-160°C, 89 h) avoided decomposition, but resulted in unacceptably slow reaction; under these milder conditions **15** was formed in 6% yield, together with ca. 10% of the 2*E*,8*Z*-isomer **16**. No products arising from IMDA reaction of **16** were observed (Scheme 9).



Reagents and conditions: (i) PhMe, 180°C, 54 h.

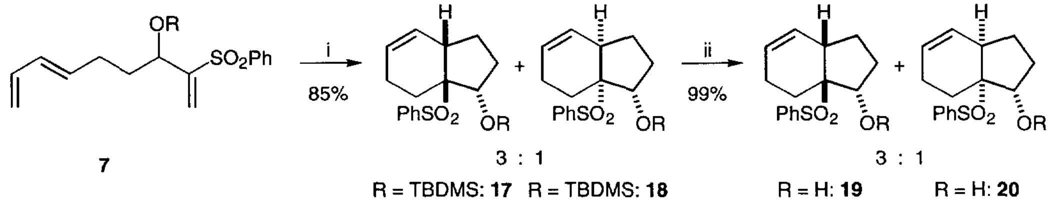
Scheme 9



X-ray structure of **15**

Figure 4

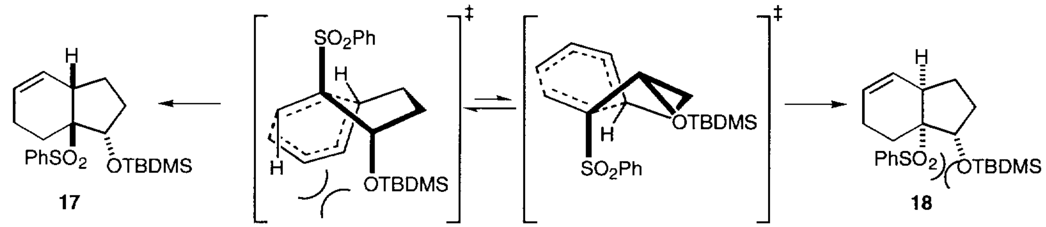
The complete cis-selectivity exhibited in the cyclisations of trienes **1-4** augured well for the success of IMDA reactions of the structurally more complex substrates **7** and **8**. An additional stereochemical issue attended these transformations, since in principle two diastereomeric cis-fused products could be formed in each case. In the event, triene **7** was found to be more reactive than all the substrates previously investigated, and gave on heating in toluene in the usual manner a 3:1 mixture of cycloadducts in high yield. By comparison of the ^1H nmr spectra of the products with that of the unsubstituted bicycle **9**, the two products were assigned as having the same cis-fused bicyclo[4.3.0] ring system. The major product was deduced to be the endo-isomer **17** on account of the appearance of the silyloxy α-methine signal in the ^1H nmr spectrum at a position 0.6 ppm downfield from the corresponding peak in the spectrum of the minor, exo-isomer **18**; the deshielding effect of a phenylsulfonyl group on syn-vicinal protons is well known,[16] and often serves as an aid to structural identification of saturated and vinylic sulfone-containing systems. The mixture of **17** and **18** was cleanly desilylated on treatment with HF in acetonitrile[17] to give the alcohols **19** and **20** as a 3:1 mixture (Scheme 10).



Reagents and conditions: (i) PhMe, 145°C, 11 h; (ii) HF, MeCN, rt.

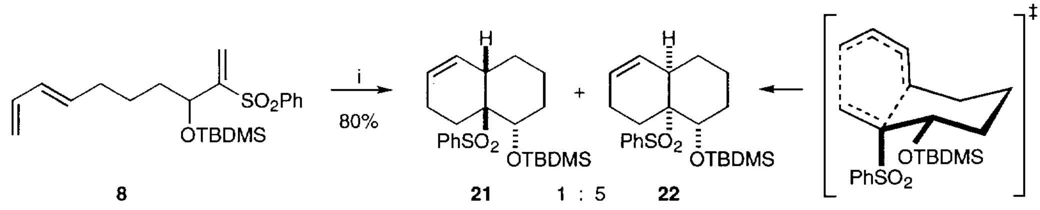
Scheme 10

The selectivity of the transformation **7** to **17** + **18** is noteworthy. The usual tendency for IMDA reactions of this class of triene substrate is for substituents α- to the dienophile C–C double bond to be oriented on the 'outside', or exo face of the bicyclo[4.3.0] products. This may be interpreted in terms either of the stability of products - the exo substituent is sterically less encumbered - or of $A_{1,3}$-strain[18] in the transition-state leading to the product with the endo-substituent. We rationalise the observed modest selectivity for **17** as being a consequence of the opposition of steric effects: in the exo-isomer **18** the silyloxy substituent is syn- with respect to the bulky bridgehead sulfonyl group, whereas **17** must be formed via a reactive conformation in which the dienophile β-hydrogen atom anti- to the sulfonyl group eclipses the silyloxy moiety (Scheme 11). Interestingly, treatment of the 3:1 mixture of alcohols **19** and **20** with catalytic potassium *tert*-butoxide resulted in quantitative conversion to a 10:1 mixture of the same compounds. This indicates the greater thermodynamic stability of **19** compared to **20**, *and demonstrates the facile, reversible cleavage of the 5-membered ring under these conditions.* We anticipate that this observation will have important consequences for the projected carbon tether-cleaving reactions for the synthesis of *monocyclic* materials using this chemistry.



Scheme 11

Finally, triene **8** was subjected to thermolysis conditions. Again, introduction of the silyloxy substituent caused an increase in reactivity relative to the parent triene **2**. Two new compounds were formed in good yield in a 5:1 ratio. The major isomer was assigned structure **22** on account of the appearance of the silyloxy α-methine signal upfield from the corresponding resonance in the spectrum of **21**. Interestingly, no isomerisation of **8** and subsequent IMDA reaction was observed, reflecting the greater reactivity of **8** compared with the unsubstituted parent compound **2**. The predominant formation of **22** may be explained in terms of the preferred pseudoequatorial disposition of the silyloxy group; the pseudoaxial orientation implied in the formation of **21** suffers destabilising interactions both with axial hydrogen atoms in the tether, and with the exo-oriented diene group (Scheme 12).



Reagents and conditions: (i) d_8-PhMe, 180°C, 9 h.

Scheme 12

CONCLUSIONS

The results described herein demonstrate that IMDA reactions of internally-substituted sulfonyltrienes provide an effective method for the assembly of cis-fused bicyclo[4.3.0] and [4.4.0] carbocyclic systems in good yield and with excellent selectivity. In view of the reactivity limitations of some of the substrates, we are currently looking at trienes possessing an additional electron-withdrawing function such as a carbonyl group within the all-carbon tether linking the diene and dienophile. It is envisaged that this extra functionality will provide also a focal point for cleavage of the tethers post-cyclisation. Finally, we are seeking to apply this chemistry to trienes activated by sulfoximine groups.[19] The results of these studies will be reported in due course.

ACKNOWLEDGEMENTS

We thank the SERC (Quota Studentship to M. C. C.), Pfizer Central Research and the ICI Strategic Research Initiative for financial support of this research, and Glaxo Research and Development for the gift of HPLC equipment. We acknowledge support from the Wolfson Foundation for the establishing of the Wolfson Centre for Organic Chemistry in Medical Science. We gratefully acknowledge the SERC Mass Spectrometry Service Centre, University College of Swansea for providing high-resolution mass spectra.

EXPERIMENTAL

General Procedures

^{1}H nmr spectra were recorded in $CDCl_3$ on either Bruker AM-500, Jeol GX-270Q or Bruker WM-250 spectrometers, using residual isotopic solvent ($CHCl_3$, δ_H 7.26 ppm) as internal reference. Infrared spectra were recorded on a Perkin-Elmer 881 spectrophotometer. Mass spectra were obtained using Jeol SX-102, VG-7070B, VG 12-253 and VG ZAB-E 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. Air- and moisture-sensitive reagents were transferred via syringe or cannula, and reactions involving these materials were carried out in oven-dried flasks under a positive pressure of argon. Liquid reagents were transferred via syringe. Chromatography refers to column chromatography on Merck Kieselgel 60 (230-400 mesh) or Matrex Silica 60 (35-70 micron) under pressure unless otherwise stated. Tlc refers to analytical thin-layer chromatography performed using pre-coated glass-backed plates (Merck Kieselgel 60 F_{254}) and visualised with ultraviolet light, iodine and acidic ammonium molybdate(IV), vanillin or potassium permanganate solutions as appropriate. High-performance liquid chromatography (HPLC) was carried out using a Rainin Instrument Co. Dynamax® column (250 x 21.4 mm) with uv detection (254 nm). Petrol refers to redistilled 40°–60° petroleum ether, and ether to diethyl ether. Ether and tetrahydrofuran were distilled from sodium–benzophenone ketyl, dichloromethane from phosphorus pentoxide, and toluene from sodium. Other solvents and reagents were purified according to standard procedures.[20]

Preparation of 4-[(tetrahydro-2*H*-pyran-2-yl)oxy]butanol.

To a stirred two-phase mixture of 1,4-butanediol (23 ml, 0.255 mol), CSA (2.96 g, 0.013 mol, 0.1 eq) in CH_2Cl_2 (260 ml) was added 3,4-dihydro-2*H*-pyran (23.6 ml, 1 eq). After stirring for 4 h the mixture became homogeneous and was diluted with CH_2Cl_2 (260 ml). The solution was washed with saturated aqueous $NaHCO_3$ (3 x 250 ml), H_2O (3 x 250 ml), and dried ($MgSO_4$). Concentration under reduced pressure followed by chromatography (20-50% ether–petrol) gave 4-[(tetrahydro-2*H*-pyran-2-yl)oxy]butanol (15.08 g, 34%) as a colourless oil; υ_{max} (film) 3400, 2942, 2659, 1651, 1445, 1350, 1323, 1261, 1201, 1121, 1026, 9 07, 869, 811 cm^{-1}; δ_H (270 MHz) 4.59 (1H, t, J 2.5 Hz, H-2'), 3.90-3.75 (2H, m) and 3.60-3.40 (2H, m, H-6', H-4), 3.66 (2H, t, J 6.0 Hz, H-1), 2.05 (1H, br s, OH), 1.90-1.48 (10H, m, H-2, H-3, H-3', H-4', H-5'); *m/z* (EI) 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 83 ($C_5H_7O^+$), 71 ($C_4H_7O^+$), 55 ($C_4H_7^+$); in agreement with previously reported data.[21]

Preparation of 5-[(tetrahydro-2*H*-pyran-2-yl)oxy]pentanol.

Prepared according to the procedure used for 5-[(tetrahydro-2*H*-pyran-2-yl)oxy]butanol on a 0.34 mol scale to give the *alcohol* (21.09 g, 33%) as a colourless oil; υ_{max} (film) 3403, 2937, 1733, 1649, 1445, 1351, 1261, 1121, 1028, 903, 868, 812 cm^{-1}; δ_H (270 MHz) 4.56 (1H, t, J 2.5 Hz, H-2'), 3.90-3.80 (1H, m) and 3.56-3.44 (1H, m, H-6'), 3.74 and 3.39 (each 1H, dt, J 10.0, 6.5 Hz, H-5), 3.64 (2H, t, J 6.5 Hz, H-1), 1.90-1.35 (13H, m, H-2, H-3, H-4, H-3', H-4', H-5', OH); *m/z* (EI) 187 (M^+-H), 170 (M^+-H_2O), 103 (M^+-C_5H_9O), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 83 ($C_5H_7O^+$) (Found: C, 63.84; H, 10.83. $C_{10}H_{20}O_3$ requires C, 63.79; H, 10.70%).

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

Prepared according to the procedure used for 5-[(tetrahydro-2*H*-pyran-2-yl)oxy]butanol on a 0.37 mol scale to give the *alcohol* (25.16 g, 34%) as a colourless oil; υ_{max} (film) 3421, 2936, 1447, 1351, 1261, 1202, 1122, 1029, 904, 868, 812 cm^{-1}; δ_H (270 MHz) 4.56 (1H, t, J 2.5 Hz, H-2'), 3.92-3.82 (1H, m) and 3.54-3.44 (1H, m, H-6'), 3.75 and 3.40 (each 1H, dt, J 9.5, 6.5 Hz, H-6), 3.65 (2H, t, J 6.5 Hz, H-1), 1.90-1.35 (14H, m, H-2, H-3, H-4, H-5, H-3', H-4', H-5'); *m/z* (EI) 202 (M^+), 201 (M^+-H), 117 (M^+-C_5H_9O), 101

($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 83 ($C_5H_7O^+$) (Found: C, 65.18; H, 11.19. $C_{11}H_{22}O_3$ requires C, 65.31; H, 10.96%).

Preparation of 4-[(tetrahydro-2*H*-pyran-2-yl)oxy]butanal.

To a stirred solution of 4-[(tetrahydro-2*H*-pyran-2-yl)oxy]butanol (10.4 g, 0.059 mol), in DMSO (150 ml) was added triethylamine (83.35 ml, 10 eq) followed by a solution of pyridine–sulfur trioxide complex (31.4 g, 3.3 eq) in DMSO (150 ml). After stirring for 10 min tlc indicated complete consumption of starting material. The reaction mixture was poured into water and the mixture was extracted with ether (3 x 500 ml). The combined organic extracts were washed with saturated aqueous $CuSO_4$ (3 x 500 ml), H_2O (3 x 500 ml), brine (2 x 500 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (50% ether–petrol) gave 4-[(tetrahydro-2*H*-pyran-2-yl)oxy]butanal (7.33 g, 71%) as a colourless oil; υ_{max} (film) 2944, 2724, 1725, 1442, 1387, 1353, 1324, 1261, 1201, 1183, 1122, 1077, 1035, 971, 906, 870, 814, cm^{-1}; δ_H (270 MHz) 9.75 (1H, t, J 1.5 Hz, H-1), 4.55 (1H, t, J 2.5 Hz, H-2'), 3.90-3.81 (1H, m) and 3.53-3.44 (1H, m, H-6'), 3.76 (1H, dt, J 9.5, 6.5 Hz) and 3.38 (1H, dt, J 9.5, 6.5 Hz, H-4), 2.44 (2H, td, J 7.0, 1.5 Hz, H-2), 1.91-1.44 (8H, m, H-3, H-3', H-4', H-5'); *m/z* (EI) 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 83 ($C_5H_7O^+$), 71 ($C_4H_7O^+$), 55 ($C_4H_7^+$); in agreement with reported data.[21]

Preparation of 5-[(tetrahydro-2*H*-pyran-2-yl)oxy]pentanal.

Prepared from 5-[(tetrahydro-2*H*-pyran-2-yl)oxy]pentanol according to the procedure used for 4-[(tetrahydro-2*H*-pyran-2-yl)oxy]butanal on a 0.059 mol scale to give 5-[(tetrahydro-2*H*-pyran-2-yl)oxy]pentanal (8.99 g, 81%) as a colourless oil; υ_{max} (film) 2944, 2722, 1726, 1454, 1353, 1324, 1261, 1201, 1138, 1122, 1078, 1035, 991, 906, 870, 814 cm^{-1}; δ_H (270 MHz) 9.77 (1H, t, J 1.5 Hz, H-1), 4.55 (1H, t, J 2.5 Hz, H-2'), 3.89-3.82 (1H, m) and 3.54-3.45 (1H, m, H-6'), 3.75 (1H, dt, J 9.5, 7.0 Hz) and 3.38 (1H, dt, J 9.5, 7.0 Hz, H-5), 2.45 (2H, td, J 7.0, 1.5 Hz, H-2), 1.90-1.43 (10H, m, H-3, H-4, H-3', H-4', H-5'); *m/z* (EI) 186 (M$^+$), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 83 ($C_5H_7O^+$); in agreement with reported data.[22]

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

Prepared from 6-[(tetrahydro-2*H*-pyran-2-yl)oxy]hexanol according to the procedure used for 4-[(tetrahydro-2*H*-pyran-2-yl)oxy]butanal on a 0.059 mol scale to give 6-[(tetrahydro-2*H*-pyran-2-yl)oxy]hexanal (10.31 g, 86%) as a colourless oil; υ_{max} (film) 2940, 2723, 1727, 1459, 1352, 1262, 1123, 1077, 1032, 904, 869, 814 cm^{-1}; δ_H (270 MHz) 9.76 (1H, t, J 1.5 Hz, H-1), 4.56 (1H, t, J 2.5 Hz, H-2'), 3.89-3.81 (1H, m) and 3.53-3.45 (2H, m, H-6'), 3.74 (1H, dt, J 10.0, 6.5 Hz) and 3.38 (1H, dt, J 10.0, 6.5 Hz, H-6), 2.43 (2H, td, J 7.0, 1.5 Hz, H-2), 1.90-1.40 (12H, m, H-3, H-4, H-5, H-3', H-4', H-5'); *m/z* (EI) 201 (MH$^+$), 115 (M$^+$-C_5H_9O), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 83 ($C_5H_7O^+$); in agreement with reported data.[23]

Preparation of methyl (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenoate.

To a stirred solution of 4-[(tetrahydro-2*H*-pyran-2-yl)oxy]butanal (7.33 g, 0.043 mol) in CH_2Cl_2 (100 ml) was added a solution of methoxycarbonylmethylenetriphenylphosphorane (20 g, 0.060 mol, 1.4 eq) in CH_2Cl_2 (100 ml). The mixture was stirred for 16 h after which time tlc indicated complete consumption of starting material. The solution was evaporated to dryness and the resulting solid was triturated with petrol. The resulting suspension was filtered and the solid washed thoroughly with petrol until tlc indicated no more product in the filtrate. The combined filtrates were concentrated and the resulting residue chromatographed (10-20% ether–petrol) to give methyl (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenoate (8.63 g, 89%) as a colourless oil; υ_{max} (film) 2945, 1724, 1657, 1438, 1322, 1272, 1205, 1169, 1122, 1075, 1036, 981, 903, 814 cm^{-1}; δ_H (270 MHz) 6.99 (1H, dt, J 15.5, 7.0 Hz, H-3), 5.84 (1H, dt, J 15.5, 1.5 Hz, H-2), 4.57 (1H, t, J 2.5 Hz, H-

2'), 3.90-3.66 (2H, m, one of each H-6, H-6'), 3.78 (3H, s, CH_3O), 3.55-3.44 (1H, m, one of H-6'), 3.39 (1H, dt, J 10.0, 6.5 Hz, one of H-6), 2.31 (2H, m, H-4), 1.90-1.40 (8H, m, H-5, H-3', H-4', H-5'); *m/z* (EI) 227 (M^+-H), 213 (M^+-CH_3), 197 (M^+-CH_3O), 169 (M^+-CO_2CH_3), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 83 ($C_5H_7O^+$), 59 ($CO_2CH_3^+$); in agreement with previously reported data.[23]

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

Prepared from 5-[(tetrahydro-2*H*-pyran-2-yl)oxy]pentanal according to the procedure used for methyl (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenoate on a 0.048 mol scale to give the *ester* (9.65 g, 83%) as a colourless oil; υ_{max} (film) 2946, 1728, 1659, 1439, 1271, 1202, 1122, 1076, 1034, 984, 906, 870, 815 cm^{-1}; δ_H (270 MHz) 6.97 (1H, dt, J 15.5, 7.0 Hz, H-3), 5.83 (1H, dt, J 15.5, 1.5 Hz, H-2), 4.57 (1H, t, J 3.0 Hz, H-2'), 3.89-3.66 (2H, m, one of each H-7, H-6'), 3.72 (3H, s, CH_3O), 3.54-3.42 (1H, m, one of H-7), 3.38 (1H, dt, J 10.0, 6.5 Hz, one of H-6'), 2.24 (2H, m, H-4), 1.86-1.46 (10H, m, H-5, H-6, H-3', H-4', H-5'); *m/z* (EI) 242 (M^+), 227 (M^+-CH_3), 183 (M^+-CO_2CH_3), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 59 ($CO_2CH_3^+$) (Found: C, 64.30; H, 8.93. $C_{13}H_{22}O_4$ requires C, 64.44; H, 9.15%).

Preparation of methyl (*E*)-8-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-octenoate.

Prepared from 6-[(tetrahydro-2*H*-pyran-2-yl)oxy]hexanal according to the procedure used for methyl (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenoate on a 0.051 mol scale to give the *ester* (12 g, 91%), as a colourless oil; υ_{max} (film) 2944, 1725, 1656, 1438, 1271, 1201, 1122, 1077, 1033, 986, 906, 869, 815 cm^{-1}; δ_H (270 MHz) 6.96 (1H, dt, J 15.5, 7.0 Hz, H-3), 5.81 (1H, dt, J 15.5, 1.5 Hz, H-2), 4.56 (1H, t, J 2.5 Hz, H-2'), 3.89-3.64 (2H, m, one of each H-8, H-6'), 3.71 (3H, s, CH_3O), 3.53-3.42 (1H, m, one of H-6'), 3.37 (1H, dt, J 9.5, 6.5 Hz, one of H-8), 2.19 (2H, m, H-4), 1.86-1.37 (12H, m, H-5, H-6, H-7, H-3', H-4', H-5'), *m/z* (EI) 255 (M^+-H), 241 (M^+-CH_3), 197 (M^+-CO_2CH_3), 154 (M^+-$C_5H_{10}O_2$), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 59 ($CO_2CH_3^+$) (Found: (M^+-H), 255.1585. $C_{14}H_{23}O_4$ requires (M^+-H), 255.1596).

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

To a stirred solution of methyl (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenoate (8.62 g, 0.038 mol), in toluene (200 ml) at -78°C was added DIBAL-H (75.6 ml of a 1.5M solution in toluene, 0.114 mol, 3 eq) dropwise over 30 min. Once the addition was complete the mixture was stirred at -78°C for 30 min after which time tlc indicated complete consumption of starting material. Water (46 ml) was added cautiously over 20 min and after stirring for a further 10 min the mixture was allowed to warm to rt. The solution was diluted with EtOAc (500 ml) and solid $NaHCO_3$ was added to the vigorously stirred solution. After 20 min the resultant granular white solid was filtered, and the residue washed thoroughly with ethyl acetate until tlc indicated no more product in the filtrate. The combined filtrates were concentrated to an oil; chromatography (50% ether–petrol) gave (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenol (7.45g, 99%) as a colourless oil; υ_{max} (film) 3410, 2941, 1670, 1445, 1351, 1261, 1202, 1121, 1078, 1028, 904, 868, 812 cm^{-1}; δ_H (270 MHz) 5.77-5.60 (2H, m, H-2, H-3), 4.57 (1H, t, J 2.5 Hz, H-2'), 4.08 (2H, d, J 4.5 Hz, H-1), 4.13-3.81 (1H, m) and 3.54-3.50 (1H, m, H-6'), 3.74 (1H, dt, J 9.5, 6.5 Hz) and 3.44 (1H, dt, J 9.5, 6.5 Hz, H-6), 2.22-2.10 (2H, m, H-4), 1.95-1.61 (8H, m, H-5, H-3', H-4', H-5'); *m/z* (EI) 199 (M^+-H), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 57 ($C_3H_5O^+$); in agreement with previously reported data.[24]

Preparation of (*E*)-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-heptenol.

Prepared from methyl (*E*)-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-heptenoate according to the procedure used for (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenol to give the *alcohol* (8.35 g, 99%) as a colourless oil; υ_{max} (film) 3407, 2939, 1671, 1450, 1354, 1264, 1125, 1076, 1030, 905, 870, 812 cm^{-1}; δ_H (270 MHz)

5.75-5.55 (2H, m, H-2, H-3), 4.56 (1H, t, J 2.5 Hz, H-2'), 4.08 (2H, d, J 4.0 Hz, H-1), 3.92-3.80 (1H, m) and 3.55-3.45 (1H, m, H-6'), 3.73 (1H, dt, J 9.5, 6.5 Hz) and 3.38 (1H, dt, J 9.5, 6.5 Hz, H-7), 2.15-2.02 (2H, m, H-4), 1.90-1.20 (10H, m, H-5, H-6, H-3', H-4', H-5'); *m/z* (EI) 196 (M^+-H_2O), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 83 ($C_5H_7O^+$), 57 ($C_3H_5O^+$) (Found: C, 67.50; H, 10.01. $C_{12}H_{22}O_4$ requires C, 67.26; H, 10.35%).

Preparation of (*E*)-8-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-octenol.

Prepared from methyl (*E*)-8-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-octenoate according to the procedure used for (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenol on a 0.038 mol scale to give the *alcohol* (8.78 g, 99%) as a colourless oil; υ_{max} (film) 3406, 2937, 1656, 1440, 1353, 1121, 1077, 1029, 905, 869, 812 cm^{-1}; δ_H (270 MHz) 5.75-5.55 (2H, m, H-2, H-3), 4.57 (1H, t, J 2.5 Hz, H-2'), 4.08 (2H, d, J 4.5 Hz, H-1), 3.92-3.82 (1H, m) and 3.55-3.44 (1H, m, H-6'), 3.73 (1H, dt, J 9.5, 6.5 Hz) and 3.38 (1H, dt, J 9.5, 6.5 Hz, H-8), 2.15-2.00 (2H, m, H-4), 1.90-1.20 (12H, m, H-5, H-6, H-7, H-3', H-4', H-5'); *m/z* (EI) 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 83 ($C_5H_7O^+$), 57 ($C_3H_5O^+$) (Found: C, 68.42; H, 10.70. $C_{13}H_{24}O_3$ requires C, 68.38; H, 10.59%).

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

To a slurry of MnO_2 (28 g, 8 eq) in CH_2Cl_2 (100 ml) was added a solution of (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexen-1-ol (7.4 g, 0.037 mol) in CH_2Cl_2 (100 ml). After stirring for 24 h the mixture was filtered though a pad of Celite®, washing with CH_2Cl_2 (400 ml). Evaporation under reduced pressure followed by chromatography (20-50% ether–petrol) gave (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenal (5.02 g, 67%) as a colourless oil; υ_{max} (film) 2943, 2735, 1690, 1638, 1443, 1350, 1261, 1136, 1075, 1034, 977, 902, 813 cm^{-1}; δ_H (270 MHz) 9.51 (1H, d, J 8.0 Hz, H-1), 6.88 (1H, dt, J 15.5, 7.0 Hz, H-3), 6.13 (1H, ddt, J 15.5, 8.0, 1.5 Hz, H-2), 4.56 (1H, t, J 3.0 Hz, H-2'), 3.88-3.83 (1H, m) and 3.54-3.47 (1H, m, H-6'), 3.80 (1H, dt, J 10.0, 6.5 Hz) and 3.42 (1H, dt, J 10.0, 6.5 Hz, H-6), 2.44 (2H, m, H-4), 1.87-1.46 (8H, m, H-5, H-3', H-4', H-5'); *m/z* (EI); 197 (M^+-H), 113 (M^+-C_5H_9O), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 55 ($C_3H_3O^+$); in agreement with previously reported data.[25]

Preparation of (*E*)-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-heptenal.

Prepared according to the procedure used for (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenal on a 0.039 mol scale to give (*E*)-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-heptenal as a colourless oil (5.77 g, 70%); υ_{max} (film) 2941, 2867, 1689, 1637, 1441, 1350, 1136, 1075, 1032, 977, 905, 870, 813 cm^{-1}; δ_H (270 MHz) 9.49 (1H, d, J 8.0 Hz, H-1), 6.85 (1H, dt, J 15.5, 7.0 Hz, H-3), 6.13 (1H, ddt, J 15.5, 8.0, 1.5 Hz, H-2), 4.57 (1H, t, J 3.0 Hz, H-2'), 3.89-3.72 (2H, m) and 3.54-3.36 (2H, m, H-7, H-6'), 2.36 (2H, m, H-4), 1.90-1.51 (10H, m, H-5, H-6, H-3', H-4', H-5'); *m/z* (EI) 211 (M^+-H), 111 (M^+-$C_5H_9O_2$), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$), 83 ($C_5H_7O^+$), 55 ($C_3H_3O^+$); in agreement with previously reported data.[26]

Preparation of (*E*)-8-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-octenal.

Prepared according to the procedure used for (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenal on a 0.046 mol scale to give the *enal* as a colourless oil (7.92 g, 76%); υ_{max} (film) 2941, 2732, 1694, 1639, 1459, 1352, 1261, 1136, 1077, 1032, 977, 906, 870, 814 cm^{-1}; δ_H (270 MHz) 9.46 (1H, d, J 8.0 Hz, H-1), 6.82 (1H, dt, J 15.5, 7.0 Hz, H-3), 6.07 (1H, ddt, J 15.5, 8.0, 1.5 Hz, H-2), 3.90-3.82 (1H, m) and 3.52-3.42 (1H, m, H-6), 3.70 (1H, dt, J 9.5, 6.5 Hz) and 3.35 (1H, dt, J 9.5, 6.5 Hz, H-8), 2.33 (2H, m, H-4), 1.88-1.29 (12H, m, H-5, H-6, H-7, H-3', H-4', H-5'); *m/z* (EI) 225 (M^+-H), 125 (M^+-$C_5H_9O_2$), 101 ($C_5H_9O_2^+$), 85

($C_5H_9O^+$), 83 ($C_5H_7O^+$), 55 ($C_3H_3O^+$) (Found: (M^+-$C_5H_9O_2$), 125.0967. $C_8H_{13}O$ requires (M^+-$C_5H_9O_2$), 125.0966).

Preparation (*E*)-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,3-heptadiene.

To a suspension of methyltriphenylphosphonium iodide (15.36 g, 0.038 mol, 1.5 eq), in THF (83 ml) at 0°C was added *n*-BuLi (14.14 ml of a 2.5M solution in hexanes, 0.0357 mol, 1.4 eq) dropwise. After 10 min the deep red solution was allowed to warm to rt and stirred for a further 30 min. The mixture was cooled to -78°C and a solution of (*E*)-6-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-hexenal (5.0 g, 0.026 mol) in THF (27 ml) was added dropwise. The reaction mixture was stirred at -78°C for a further 10 min and then allowed to warm to rt. The reaction mixture was then added to saturated aqueous NH_4Cl (200 ml) and the aqueous layer was extracted with petrol (3 x 200 ml). The combined organic extracts were washed with H_2O (3 x 200 ml), brine (3 x 200 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (10% ether–petrol) gave the *diene* (4.73 g, 95%) as a colourless oil; υ_{max} (film) 2941, 1799, 1651, 1602, 1444, 1350, 1322, 1261, 1202, 1121, 1077, 1035, 900, 814 cm^{-1}; δ_H (270 MHz) 6.30 (1H, dt, J 17.0, 10.5 Hz, H-2), 6.06 (1H, dd, J 15.0, 10.5 Hz, H-3), 5.71 (1H, m, H-4), 5.07 (1H, dd, J 17.0, 1.5 Hz, H-1_{trans}), 4.95 (1H, dd, J 10.5, 1.5, H-1_{cis}), 4.57 (1H, t, J 2.5 Hz, H-2'), 3.90-3.82 (1H, m) and 3.54-3.45 (1H, m, H-6'), 3.74 (1H, dt, J 9.5, 7.0 Hz) and 3.39 (1H, dt, J 9.5, 7.0 Hz, H-7), 2.18 (2H, m, H-5), 1.90-1.42 (8H, m, H-6, H-3', H-4', H-5'); *m/z* (EI) 196 (M^+), 101 ($C_5H_9O_2^+$), 95 (M^+-$C_5H_9O_2$), 85 ($C_5H_9O^+$) (Found: (M^+), 196.1463. $C_{12}H_{20}O_2$ requires (M^+), 196.1433).

Preparation of (*E*)-8-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,3-octadiene

Prepared from (*E*)-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-heptenal according to the procedure used for (*E*)-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,3-heptadiene on a 0.027 mol scale to give the *diene* (5.46 g, 96%) as a colourless oil; υ_{max} (film) 3087, 2940, 1652, 1603, 1561, 1440, 1351, 1261, 1201, 1121, 1077, 1033, 900, 814 cm^{-1}; δ_H (270 MHz) 6.30 (1H, dt, J 17.0, 10.5 Hz, H-2), 6.05 (1H, dd, J 15.0, 10.5 Hz, H-3), 5.70 (1H, m, H-4), 5.08 (1H, dd, J 17.0, 1.0 Hz, H-1_{trans}), 4.95 (1H, dd, J 10.0, 1.0 Hz, H-1_{cis}), 4.57 (1H, t, J 2.5 Hz, H-2'), 3.90-3.83 (1H, m) and 3.54-3.46 (1H, m, H-6), 3.73 (1H, dt, J 9.5, 7.0 Hz) and 3.39 (1H, dt, J 9.5, 7.0 Hz, H-8), 2.12 (2H, m, H-5), 1.90-1.44 (10H, m, H-6, H-7, H-3', H-4', H-5'); *m/z* (EI) 210 (M^+), 109 (M^+-$C_5H_9O_2$), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$) (Found: (M^+-$C_5H_9O_2$), 109.1020. $C_{13}H_{22}O_2$ requires (M^+-$C_5H_9O_2$), 109.1017).

Preparation of (*E*)-9-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,3-nonadiene.

Prepared from (*E*)-8-[(tetrahydro-2*H*-pyran-2-yl)oxy]-2-octenal according to the procedure used for (*E*)-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,3-heptadiene on a 0.065 mol scale to give (*E*)-9-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,3-nonadiene (14.16 g, 97%) as a colourless oil; υ_{max} (film) 3086, 2938, 1653, 1603, 1440, 1353, 1262, 1137, 1077, 1033, 900, 814 cm^{-1}; δ_H (270 MHz) 6.3 (1H, dt, J 17.0, 10.0 Hz, H-2), 6.05 (1H, dd, J 15.0, 10.0 Hz, H-3), 5.69 (1H, m, H-4), 5.07 (1H, dd, J 17.0, 1.0 Hz, H-1_{trans}), 4.95 (1H, dd, J 10.0, 1.0 Hz, H-1_{cis}), 4.56 (1H, t, J 2.5 Hz, H-2'), 3.90-3.82 (1H, m) and 3.53-3.46 (1H, m, H-6'), 3.73 and 3.38 (2H, dt, J 10.0, 7.0 Hz, H-9), 2.11 (2H, m, H-5), 1.91-1.32 (12H, m, H-6, H-7, H-8, H-3', H-4', H-5'); *m/z* (EI) 224 (M^+), 122 (M^+-$C_5H_9O_2$), 101 ($C_5H_9O_2^+$), 85 ($C_5H_9O^+$); in agreement with previously reported data.[27]

Preparation of (*E*)-4,6-heptadienol.

To a stirred solution of (*E*)-7-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,3-heptadiene (0.563 g, 2.87 mmol) in methanol (7.14 ml) at rt was added CSA (35 mg, 0.05 eq). The mixture was stirred at rt for 16 h after which time tlc indicated complete consumption of starting material. The reaction mixture was diluted with ether (50 ml) and the resulting solution washed with H_2O (3 x 20 ml), saturated aqueous $NaHCO_3$ (3 x 20 ml), brine (3 x 20 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (50% ether–petrol) gave (*E*)-4,6-heptadienol (273.7 mg, 85%) as a colourless oil; υ_{max} (film) 3339, 3086, 2936, 1795, 1651, 1602, 1441, 1038, 1003, 951, 899 cm^{-1}; δ_H (270 MHz) 6.31 (1H, dt, J 17.0, 10.5 Hz, H-6), 6.08 (1H, dd, J 15.0, 10.5 Hz, H-5), 5.71 (1H, m, H-4), 5.09 (1H, dd, J 17.0, 1.0 Hz, H-7$_{trans}$), 4.97 (1H, dd, J 10.5, 1.0 Hz, H-7$_{cis}$), 3.66 (2H, t, J 6.5 Hz, H-1), 2.17 (2H, m, H-3), 1.70 (2H, m, H-2); *m/z* (EI) 112 (M$^+$), 94 (M$^+$-H_2O), 79 (M$^+$-CH_2OH), 53 ($C_4H_5^+$); in agreement with previously reported data.[25]

Preparation of (*E*)-5,7-octadienol.

Prepared from (*E*)-8-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,3-octadiene according to the procedure used for (*E*)-4,6-heptadienol on a 0.032 mol scale to give (*E*)-5,7-octadienol (3.83 g, 94%) as a colourless oil; υ_{max} (film) 3345, 3087, 2935, 2328, 1806, 1718, 1652, 1603, 1450, 1062, 1005, 952, 898 cm^{-1}; δ_H (270 MHz) 6.30 (1H, dt, J 16.5, 10.5 Hz, H-7), 6.05 (1H, dd, J 15.5, 10.5 Hz, H-6), 5.70 (1H, m, H-5), 5.09 (1H, dd, J 16.5, 1.0 Hz, H-8$_{trans}$), 4.95 (1H, dd, J 10.5, 1.0 Hz, H-8$_{cis}$), 3.65 (2H, t, J 6.5 Hz, H-1), 2.12 (2H, m, H-4), 1.65-1.40 (4H, m, H-2, H-3); *m/z* (EI) 126 (M$^+$), 108 (M$^+$-H_2O), 95 (M$^+$-CH_2OH), 54 ($C_4H_6^+$); in agreement with previously reported data.[28]

Preparation of (*E*)-6,8-nonadienol.

Prepared from (*E*)-9-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,3-nonadiene according to the procedure used for (*E*)-4,6-heptadienol on a 0.063 mol scale to give (*E*)-6,8-nonadienol (7.5 g, 84%) as a colourless oil; υ_{max} (film) 3345, 3087, 2933, 1799, 1652, 1603, 1459, 1055, 1004, 952, 897 cm^{-1}; δ_H (270 MHz) 6.30 (1H, dt, J 17.0, 10.5 Hz, H-8), 6.05 (1H, dd, J 15.0, 10.5 Hz, H-7), 5.70 (1H, m, H-6), 5.07 (1H, dd, J 17.0, 1.0 Hz, H-9$_{trans}$), 4.95 (1H, dd, J 10.5, 1.0 Hz, H-9$_{cis}$), 3.60 (2H, t, J 7.0 Hz, H-1), 2.10 (2H, m, H-5), 1.75-1.20 (6H, m, H-2, H-3, H-4); *m/z* (EI) 140 (M$^+$), 122 (M$^+$-H_2O), 107 (M$^+$-CH_2OH), 54 ($C_4H_6^+$) in agreement with previously reported data.[27]

Preparation of (*E*)-9-(phenylsulfonyl)-1,3-nonadiene (6) and (*E*)-9-(phenylsulfinyloxy)-1,3-nonadiene.

To a stirred solution of (*E*)-6,8-nonadienol (7.5 g, 0.054 mol) in CH_2Cl_2 (180 ml) at -15°C was added triethylamine (12 ml, 0.08 mol, 1.5 eq) followed by methanesulfonyl chloride (5 ml, 0.058 mol, 1.1 eq). A white precipitate was formed and after 1 h tlc indicated complete consumption of starting material. Water (300 ml) was added and the aqueous layer was extracted with CH_2Cl_2 (3 x 300 ml). The combined organic extracts were washed with saturated aqueous NH_4Cl (3 x 300 ml), H_2O (3 x 300 ml) and dried ($MgSO_4$). Evaporation under reduced pressure gave a colourless oil which was dissolved in THF (50 ml) and added to a THF solution of lithium bromide (23.3 g, 0.26 mol, 5 eq). After stirring for 16 h tlc indicated complete consumption of starting material. Water (300 ml) was added and the aqueous layer was extracted with ether (3 x 300 ml). The combined organic extracts were washed with H_2O (3 x 300 ml), brine (3 x 300 ml) and dried ($MgSO_4$). Evaporation under reduced pressure gave an orange oil which was dissolved in DMSO (20 ml) and added to a solution of sodium phenylsulfinate (10.0 g, 0.059 mol, 1.1 eq) in DMSO (62 ml). After stirring for 20 h tlc indicated complete consumption of starting material. Water (300 ml) was added and the aqueous layer was extracted with ether (3 x 300 ml). The combined organic extracts were washed with H_2O (3 x 300 ml), brine (3 x 300 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (20-50% ether–petrol) gave, in order of elution, the *sulfinate* (1.0 g, 7%) as a colourless oil; υ_{max} (film) 2934, 2859, 1652, 1604, 1445, 1381, 1306, 1135, 1082, 1005, 950, 897, 754, 697 cm^{-1}; δ_H (270 MHz) 7.71 (2H, m, *ortho*-Ph), 7.54 (3H, m, *para, meta*-Ph), 6.30 (1H, dt, J 17.0, 10.5 Hz, H-2), 6.03 (1H, m, H-3), 5.70 (1H, m, H-4), 5.07 (1H, d, J 17.0 Hz, H-1_{trans}), 4.96 (1H, d, J 10.5 Hz, H-1_{cis}), 4.03 (1H, m) and 3.60 (1H, m, H-9), 2.08 (2H, m, H-5), 1.73-1.52 (2H, m, H-8), 1.47-1.22 (4H, m, H-6, H-7); *m/z* (EI) 139 (M^+-PhSO), 122 (M^+-$PhSO_2H$), 77 (Ph^+), 53 ($C_4H_5^+$) (Found: (M^+-$PhSO_2H$), 122.1096. $C_{15}H_{20}O_2S$ requires (M^+-$PhSO_2H$), 122.1096), and the *sulfone* **6** (12.1 g, 85%) as a colourless oil; υ_{max} (film) 2936, 2859, 1652, 1603, 1448, 1305, 1148, 1087, 1007, 954, 900, 727, 690 cm^{-1}; δ_H (270 MHz) 7.93 (2H, m, *ortho*-Ph), 7.71-7.53 (3H, m, *para, meta*-Ph), 6.27 (1H, dt, J 17.0, 10.0 Hz, H-2), 6.00 (1H, dd, J 15.5 10.0 Hz, H-3), 5.61 (1H, m, H-4), 5.07 (1H, dd, J 17, 1.0 Hz, H-1_{trans}), 4.95 (1H, dd, J 10.0, 1.0 Hz, H-1_{cis}), 3.07 (2H, m, H-9), 2.05 (2H, m, H-5), 1.72 (2H, m, H-8), 1.37 (4H, m, H-6, H-7); *m/z* (EI) 264 (M^+), 122 (M^+-$PhSO_2H$), 77 (Ph^+), 53 ($C_4H_5^+$) (Found: C, 68.40; H, 7.80. $C_{15}H_{20}O_2S$ requires C, 68.14; H, 7.62%).

Preparation of (*E*)-8-(phenylsulfonyl)-1,3-octadiene (5) and (*E*)-8-(phenylsulfinyloxy)-1,3-octadiene.

Prepared from (*E*)-5,7-octadienol according to the procedure used for (*E*)-9-(phenylsulfonyl)-1,3-nonadiene on a 0.0296 mol scale to give, in order of elution, the *sulfinate* (0.624 g, 6%) as a colourless oil; υ_{max} (film) 2943, 1652, 1603, 1446, 1380, 1135, 1082, 1006, 897, 813, 754, 698 cm^{-1}; δ_H (270 MHz) 7.72 (2H, m, *ortho*-Ph), 7.55 (3H, m, *para, meta*-Ph), 6.28 (1H, dt, J 17.0, 10.5 Hz, H-2), 6.00 (1H, dd, J 15.0, 10.5, H-3), 5.63 (1H, m, H-4), 5.07 (1H, d, J 17.0 Hz, H-1_{trans}), 4.96 (1H, d, J 10.5, H-1_{cis}), 4.03 (1H, dt, J 10.0, 6.5) and 3.60 (1H, dt, J 10.0, 6.5 Hz, H-8), 2.08 (2H, m, H-5), 1.65 (2H, m, H-7), 1.45 (4H, m, H-6); *m/z* (EI) 125 (M^+-PhSO), 108 (M^+-$PhSO_2H$), 77 (Ph^+), 53 ($C_4H_5^+$) (Found: (M^+-PhSO), 125.0966. $C_8H_{13}O$ requires (M^+-PhSO), 125.0966), and the *sulfone* **5** (5.8 g, 78%) as a colourless oil; υ_{max} (film) 2940, 2354, 1815, 1697, 1604, 1448, 1409, 1306, 1149, 1087, 1007, 954, 902, 793, 729, 690 cm^{-1}; δ_H (270 MHz) 7.91 (2H, m, *ortho*-Ph), 7.70-7.53 (3H, m, *para, meta*-Ph), 6.26 (1H, dt, J 17, 10.5 Hz, H-2), 6.00 (1H, dd, J 15.0 10.5 Hz, H-3), 5.59 (1H, m, H-4), 5.07 (1H, dd, J 17, 1.0 Hz, H-1_{trans}), 4.97 (1H, dd, J 10.5, 1.0 Hz, H-1_{cis}), 3.08 (2H, m, H-8), 2.08 (2H, m, H-5), 1.75 (2H, m, H-7), 1.49 (2H, H-6); *m/z* (EI) 250 (M^+), 108 (M^+-$PhSO_2H$), 77 (Ph^+), 53 ($C_4H_5^+$) (Found: C, 67.40; H, 7.20. $C_{14}H_{18}O_2S$ requires C, 67.16; H, 7.24%).

Preparation of (*E*)-9-(diethylphosphonyl)-9-(phenylsulfonyl)-1,3-nonadiene.

To *N,N*-diisopropylamine (10.82 ml of a 1.43M solution in THF, 15.48 mmol, 2.2 eq) at 0°C was added *n*-BuLi (6.2 ml of a 2.5M solution in hexanes, 15.48 mmol, 2.2 eq) dropwise and the resultant mixture stirred for 30 min. This solution was added to a stirred solution of (*E*)-9-(phenylsulfonyl)-1,3-nonadiene **6** (1.86 g, 7.035 mmol) in THF (10 ml) at -78°C dropwise over 15 min to give a bright yellow solution. Diethyl chlorophosphate (1.12 ml, 7.74 mmol, 1.1 eq) was added and after 15 min tlc indicated complete consumption of starting material. The reaction mixture was allowed to warm to rt and was quenched by the addition of AcOH (4 ml of a 1.74 M solution, 7.74 mmol, 1.1 eq). Water (100 ml) was added and the aqueous layer was extracted with ether (3 x 100 ml). The combined organic extracts were washed with H_2O (3 x 100ml), brine (3 x 100 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (ether) gave the *phosphonylsulfone* (2.7 g, 96%) as a colourless oil; υ_{max} (film) 2930, 1652, 1602, 1448, 1318, 1258, 1153, 1025, 972, 901, 727, 690 cm^{-1}; δ_H (270 MHz) 7.92 (2H, m, *ortho*-Ph), 7.70-7.63 (1H, m, *para*-Ph), 7.63-7.54 (2H, m, *meta*-Ph), 6.28 (1H, dt, J 17.5, 10.5 Hz, H-2), 6.01 (1H, dd, J 15.0, 10.5 Hz, H-3), 5.63 (1H, m, H-4), 5.08 (1H, d, J 17.5 Hz, H-1_{trans}), 4.96 (1H, d, J 10.5 Hz, H-1_{cis}), 4.25-4.05 (4H, m, CH_3CH_2O), 3.45 (1H, dt, J 19.5, 5.5 Hz, H-9), 2.15-1.90 (4H, m, H-5, H-8), 1.65-1.30 (4H, m, H-6, H-7), 1.26 (6H, td, J 7.0, 2.5 Hz, CH_3CH_2O); *m/z* (EI) 400 (M^+), 355 (M^+-CH_3CH_2O), 259 (M^+-$PhSO_2$), 137 ($(CH_3CH_2O)_2PO^+$), 77 (Ph^+), 53 ($C_4H_5^+$) (Found: (M^+), 400.1473. $C_{19}H_{29}O_5PS$ requires (M^+), 400.1473).

Preparation of (*E*)-8-(diethylphosphonyl)-8-(phenylsulfonyl)-1,3-octadiene.

Prepared from (*E*)-8-(phenylsulfonyl)-1,3-octadiene **5** according to the procedure used for (*E*)-9-diethylphosphonyl-9-(phenylsulfonyl)-1,3-nonadiene on a 6.067 mmol scale to give the *phosphonylsulfone* (2.43 g, 94%) as a colourless oil; υ_{max} (film) 2984, 2342, 1651, 1604, 1448, 1393, 1318, 1258, 1153, 1025, 972, 902, 798, 730, 690 cm^{-1}; δ_H (250 MHz) 7.96 (2H, m, *ortho*-Ph), 7.69-7.62 (1H, m, *para*-Ph), 7.59-7.52 (2H, m, *meta*-Ph), 6.27 (1H, dt, J 16.5, 10.5 Hz, H-2), 6.01 (1H, dd, J 15.0, 10.5 Hz, H-3), 5.58 (1H, m, H-4), 5.08 (1H, d, J 16.5 Hz, H-1$_{trans}$), 4.97 (1H, d, J 10.5 Hz, H-1$_{cis}$), 4.20-4.00 (4H, m, CH_3CH_2O), 3.46 (1H, dt, J 19.0, 5.5 Hz, H-8), 2.15-1.87 (4H, m, H-5, H-7), 1.85-1.54 (2H, m, H-6), 1.27 (6H, td J 6.5, 2.0 Hz, CH_3CH_2O); *m/z* (EI) 386 (M^+), 341 (M^+-CH_3CH_2O), 249 (M^+-$(CH_3CH_2O)_2PO$), 245 (M^+-$PhSO_2$), 137 ($(CH_3CH_2O)_2PO^+$) 77 (Ph^+), 53 ($C_4H_5^+$) (Found: C, 55.70; H, 7.20. $C_{18}H_{27}O_5SP$ requires C, 55.94; H, 7.04%).

Preparation of (*E*)-8-(phenylsulfonyl)-1,3,8-nonatriene (1).

To a stirred solution of (*E*)-8-diethylphosphonyl-8-(phenylsulfonyl)-1,3-octadiene (1.51 g, 3.91 mmol) in THF (10 ml) at -78°C was added *n*-BuLi (1.72 ml of a 2.5M solution in hexanes, 4.29 mmol, 1.1 eq) dropwise to give a yellow solution. The reaction mixture was stirred at -78°C for 10 min and allowed to warm to 0°C. The mixture was added to a suspension of paraformaldehyde (257 mg, 8.6 mmol, 2.2 eq) in THF (5 ml + 5 ml rinse) at 0°C. The mixture was stirred at 0°C for a further 30 min after which time tlc indicated complete consumption of starting material. Water (25 ml) was added cautiously and the aqueous layer was extracted with ether (3 x 25 ml). The combined organic extracts were washed with saturated aqueous NH_4Cl (3 x 25 ml), H_2O (3 x 25 ml), brine (3 x 25 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (30% ether–petrol) gave the *triene* **1** (0.96 g, 94%) as a colourless oil; υ_{max} (film) 2935, 2328, 1821, 1651, 1602, 1446, 1308, 1142, 1082, 1007, 952, 902, 749, 691 cm^{-1}; δ_H (270 MHz) 7.87 (2H, m, *ortho*-Ph), 7.66-7.50 (3H, m, *para, meta*-Ph), 6.37 (1H, s, H-9$_{cis\ to\ sulfone}$), 6.25 (1H, dt, J 17.0, 10.0 Hz, H-2), 5.97 (1H, dd, J 15.0 10.0 Hz, H-3), 5.73 (1H, s, H-9$_{trans\ to\ sulfone}$), 5.56 (1H, m, H-4), 5.07 (1H, d, J 17.0 Hz, H-1$_{trans}$), 4.97 (1H, d, J 10.5 Hz, H-1$_{cis}$), 2.24 (2H, br t, J 8.0 Hz, H-7), 2.03 (2H, m, H-5), 1.57 (2H, m, H-6); *m/z* (EI) 262 (M^+), 142 ($PhSO_2H^+$), 120 (M^+-$PhSO_2H$), 77 (Ph^+), 53 ($C_4H_5^+$) (Found: C, 68.60; H, 6.92. $C_{15}H_{18}O_2S$ requires C, 68.67; H, 6.91%).

Preparation of (*E*)-9-(phenylsulfonyl)-1,3,9-decatriene (2).

A stirred suspension of NaH (0.26 g of a 60% dispersion in mineral oil, 6.5 mmol, 1 eq) was washed with dry petrol (3 x 20 ml). The oil-free NaH so prepared was suspended in THF (5 ml) at 0°C and a solution of (*E*)-9-(diethylphosphonyl)-9-(phenylsulfonyl)-1,3-nonadiene (2.6 g, 6.5 mmol) in THF (10 ml) was added dropwise, causing rapid effervesence followed by the formation of a white precipitate. After stirring at 0°C for 30 min a suspension of paraformaldehyde (0.39 g, 13.0 mmol, 2 eq) in THF (5 ml) was added in one portion. The reaction mixture was stirred for a further 30 min after which time tlc indicated complete consumption of starting material. Water (100 ml) was added cautiously and the aqueous layer was extracted with ether (3 x 100 ml). The combined organic extracts were washed with saturated aqueous NH_4Cl (3 x 100 ml), H_2O (3 x 100 ml), brine (3 x 100 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (30% ether–petrol) gave the *triene* **2** (1.654 g, 89%) as a colourless oil; υ_{max} (film) 2934, 2859, 2349, 1820, 1653, 1603, 1447, 1310, 1141, 1082, 1007, 952, 901, 750, 692 cm^{-1}; δ_H (270 MHz) 7.87 (2H, m, *ortho*-Ph), 7.66-7.50 (3H, m, *para, meta*-Ph), 6.37 (1H, s, H-10$_{cis\ to\ sulfone}$), 6.26 (1H, dt, J 17.0, 10.5 Hz, H-2), 5.98 (1H, dd, J 15.0, 10.5 Hz, H-3), 5.73 (1H, s, H-10$_{trans\ to\ sulfone}$), 5.61 (1H, m, H-4), 5.07 (1H, d, J 17.0 Hz, H-1$_{trans}$), 4.96 (1H, d, J 10.5, H-1$_{cis}$), 2.23 (2H, br t, J 7.0 Hz, H-8), 2.01 (2H, m, H-5), 1.45-1.30 (4H, m, H-6, H-7); *m/z* (EI) 276 (M^+), 222 (M^+-C_4H_6), 135 (M^+-$PhSO_2$), 77 (Ph^+), 53 ($C_4H_5^+$) (Found: C, 69.50; H, 7.30. $C_{16}H_{20}O_2S$ requires C, 69.53; H, 7.29%).

Preparation of (*E*)-9-(phenylsulfonyl)-1,3-undecatrien-10-yl benzoate.

To a stirred solution of (*E*)-9-(phenylsulfonyl)-1,3-nonadiene **6** (485 mg, 1.84 mmol) in THF (5 ml) at -78°C was added *n*-BuLi (0.81 ml of a 2.5M solution in hexanes, 2.02 mmol, 1.1 eq) dropwise, giving a bright yellow solution. After 15 min acetaldehyde (1.01 ml of a 2M solution in THF, 2.02 mmol, 1.1 eq) was added and the solution was stirred for a further 15 min at -78°C. Benzoyl chloride (0.24 ml, 2.02 mmol, 1.1 eq) was added and after stirring for 10 min tlc indicated complete consumption of starting material. The reaction mixture was allowed to warm to rt and H_2O (100 ml) was added. The aqueous layer was extracted with ether (4 x 100 ml). The combined organic extracts were washed with H_2O (3 x 100 ml), brine (3 x 100 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (20-50% ether–petrol) gave a 1:1 diastereomeric mixture of the *benzoyloxysulfones* (0.713 g, 94%) as a colourless oil; υ_{max} (film) 3086, 2935, 1721, 1652, 1603, 1450, 1273, 1147, 1108, 1006, 955, 900, 717, 691 cm^{-1}; δ_H (270 MHz) 7.93 (2 H one diastereomer, d, J 7.5 Hz), 7.88-7.81 (2H, m) and 7.71 (2 H one diastereomer, d, J 7.5 Hz, all comprising *ortho*-Ph), 7.66-7.30 (6H, m, *para, meta*-Ph both diastereomers), 6.40-6.17 (1H, m, H-9 both diastereomers), 6.15-5.88 (1H, m, H-8 both diastereomers), 5.75-5.50 (2H, m, H-7, H-1 both diastereomers), 5.16-4.92 (2H, m, H-10 both diastereomers), 3.47 (1H, td, J 4.5, 1.0 Hz) and 3.18 (1H, td, J 4.5, 1.0 Hz, H-2 both diastereomers), 2.23-1.85 (4H, m, H-3, H-6 both diastereomers), 1.79-1.28 (4H, m, H-4, H-5 both diastereomers), 1.53 (3H, d, J 6.0 Hz) and 1.46 (3H, d, J 6.0 Hz, H-1' both diastereomers); *m/z* (EI) 412 (M^+), 290 (M^+-$PhCO_2H$), 271 (M^+-$PhSO_2$), 122 ($PhCO_2H^+$), 105 ($PhCO^+$), 77 (Ph^+) (Found: C, 69.66; H, 6.93. $C_{24}H_{28}O_4S$ requires C, 69.87; H, 6.84%).

Preparation of (*E*)-8-(phenylsulfonyl)-1,3-decatrien-9-yl benzoate.

Prepared from (*E*)-8-(phenylsulfonyl)-1,3-octadiene **5** according to the procedure used for (*E*)-9-(phenylsulfonyl)-1,3-undecatrien-10-yl benzoate on a 4.03 mmol scale to give a 1:1 diastereomeric mixture of the *benzoyloxysulfones* (1.4 g, 87%) as a colourless oil; υ_{max} (film) 3066, 2945, 2361, 1788, 1720, 1673, 1602, 1450, 1272, 1147, 1006, 902, 715 cm^{-1}; δ_H (270 MHz) 7.96 (2 H one diastereomer, d, J 7.5 Hz), 7.89-7.81 (2H, m) and 7.70 (2 H one diastereomer, d, J 7.5 Hz, all comprising *ortho*-Ph), 7.67-7.29 (6H, m, *para, meta*-Ph both diastereomers), 6.40-5.89 (2H, m, H-7, H-8 both diastereomers), 5.74-5.50 (2H, m, H-6, H-1 both diastereomers), 5.18-4.92 (2H, m, H-9 both diastereomers), 3.48 (1H, td, J 4.5, 1.0 Hz) and 3.20 (1H, td, J 4.5, 1.0 Hz, H-2 both diastereomers), 2.25-1.20 (6H, m, H-3,H-4, H-5 both diastereomers), 1.51 (3H, d, J 6.0 Hz) and 1.45 (3H, J 6.0 Hz, H-1' both diastereomers); *m/z* (EI) 398 (M^+), 257 (M^+-$PhSO_2$), 256 (M^+-$PhSO_2H$), 105 ($PhCO^+$), 77 (Ph^+) (Found: (M^+), 398.1552. $C_{23}H_{26}O_4S$ requires (M^+), 398.1552).

Preparation of (*E,E*)-9-(phenylsulfonyl)-1,3,9-undecatriene (4).

To a stirred solution of (*E*)-9-(phenylsulfonyl)-1,3-undecatrien-10-yl benzoate (646 mg, 1.56 mmol) in THF (16 ml) at rt was added *t*-BuOK (1.57 ml of a 1M solution in THF, 1.57 mmol, 1.01 eq) dropwise until tlc indicated complete consumption of starting material. Water (100 ml) was added. The aqueous layer was extracted with ether (3 x 100 ml). The combined organic extracts were washed with H_2O (3 x 100 ml), brine (3 x 100 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (20-30% ether–petrol) gave the *triene* **4** (459 mg, 99%) as a colourless oil; υ_{max} (film) 2933, 2861, 1649, 1603, 1447, 1302, 1142, 1084, 1006, 954, 900, 727, 692 cm^{-1}; δ_H (270 MHz) 7.86 (2H, m, *ortho*-Ph), 7.64-7.47 (3H, m, *para, meta*-Ph), 6.99 (1H, q, J 7.0 Hz, H-10), 6.28 (1H, dt, J 17.0, 10.0 Hz, H-2), 5.95 (1H, dd, J 14.0, 10.0 Hz, H-3), 5.60 (1H, m, H-4), 5.07 (1H, d, J 17.0 Hz, H-1_{trans}), 4.95 (1H, d, J 10.0 Hz, H-1_{cis}), 2.23 (2H, m, H-8), 2.01 (2H, m, H-5), 1.84 (3H, d, J 7.0 Hz, H-11), 1.31 (4H, m, H-6, H-7); *m/z* (EI) 149 (M^+-$PhSO_2$), 77 (Ph^+), 53 ($C_4H_5^+$) (Found: C, 70.50; H, 7.70. $C_{17}H_{22}O_2S$ requires C, 70.31; H, 7.64%).

Preparation of (*E*,*E*)-8-(phenylsulfonyl)-1,3,8-decatriene (3).

Prepared from (*E*)-8-(phenylsulfonyl)-1,3-decatrien-9-yl benzoate according to the procedure used for (*E*,*E*)-9-(phenylsulfonyl)-1,3,9-undecatriene on a 3.34 mmol scale to give the *triene* **3** (1.4 g, 87%) as a colourless oil; υ_{max} (film) 2931, 2363, 1906, 1822, 1721, 1649, 1603, 1448, 1300, 1142, 1084, 1007, 955, 901, 854, 728 cm^{-1}; δ_H (270 MHz) 7.50 (2H, m, *ortho*-Ph), 7.63-7.48 (3H, m, *para, meta*-Ph), 6.99 (1H, q, J 7.0 Hz, H-9), 6.28 (1H, dt, J 17.0, 10.0 Hz, H-2), 5.97 (1H, dd, J 15.0, 10.0 Hz, H-3), 5.56 (1H, m, H-4), 5.07 (1H, d, J 17.0 Hz, H-1$_{trans}$), 4.97 (1H, d, J 10.0 Hz, H-1$_{cis}$), 2.21 (2H, m, H-7), 2.05 (2H, m, H-5), 1.84 (3H, d, J 7.0 Hz, H-10), 1.44 (4H, m, H-6); *m/z* (EI) 276 (M$^+$), 134 (M$^+$-PhSO$_2$H), 77 (Ph$^+$), 53 (C$_4$H$_5$$^+$) (Found: C, 69.60; H, 7.30. C$_{16}$H$_{20}$O$_2$S requires C, 69.53; H, 7.25%).

Preparation of (*E*)-4,6-heptadienal.

To a stirred solution of (*E*)-4,6-heptadienol (273.7 mg, 2.44 mmol) in DMSO (6.1 ml) was added triethylamine (3.4 ml, 24.4 mmol, 10 eq), followed by a solution of pyridine–sulfur trioxide complex (1.28 g, 8.05 mmol, 3.3 eq) in DMSO (6.1 ml). After stirring for 10 min tlc indicated complete consumption of starting material. The reaction mixture was poured into H$_2$O (20 ml) and the mixture extracted with ether (3 x 20 ml). The combined organic extracts were washed with saturated aqueous CuSO$_4$ (4 x 20 ml), H$_2$O (3 x 20 ml), brine (2 x 20 ml) and dried (MgSO$_4$). Evaporation under reduced pressure followed by chromatography (10% ether–petrol) gave the *dienal* (171.9 mg, 64%) as a colourless oil; υ_{max} (film) 3068, 3009, 2917, 2828, 2726, 2317, 1725, 1442, 1094, 1005, 902 cm^{-1}; δ_H (270 MHz) 9.77 (1H, t, J 1.5 Hz, H-1), 6.30 (1H, dt, J 17.0, 10.0 Hz, H-6), 6.09 (1H, dd, 15.5 10.0 Hz, H-5), 5.68 (1H, m, H-4), 5.12 (1H, d, J 17.0 Hz, H-7$_{trans}$), 5.00 (1H, d, J 10.0 Hz, H-7$_{cis}$), 2.59-2.51 (2H, m, H-2), 2.47-2.37 (2H, m, H-3); *m/z* (EI) 110 (M$^+$), 109 (M$^+$-H), 81 (M$^+$-CHO), 57 (M$^+$-C$_4$H$_5$), 53 (C$_4$H$_5$$^+$) (Found: (M$^+$-H), 109.6526. C$_7H_9$O requires (M$^+$-H), 109.6534).

Preparation of (*E*)-5,7-octadienal.

Prepared from (*E*)-5,7-octadienol according to the procedure used for (*E*)-4,6-heptadienal on a 2.47 mmol scale to give the *dienal* (242 mg, 79%) as a colourless oil; υ_{max} (film) 3086, 3007, 2936, 2722, 1724, 1651, 1603, 1412, 1006, 955, 901 cm^{-1}; δ_H (270 MHz) 9.77 (1H, t, J 1.5 Hz, H-1), 6.30 (1H, dt, J 17.0, 10.0 Hz, H-7), 6.09 (1H, dd, J 15.5 10.0 Hz, H-6), 5.64 (1H, m, H-5), 5.10 (1H, d, J 17.0 Hz, H-8$_{trans}$), 4.97 (1H, d, J 10.0 Hz, H-8$_{cis}$), 2.45 (2H, td, J 7.5, 1.5 Hz, H-2), 2.13 (2H, m, H-4), 1.74 (2H, m, H-3); *m/z* (EI) 124 (M$^+$), 123 (M$^+$-H), 93 (M$^+$-CHO), 53 (C$_4$H$_5$$^+$) (Found: (M$^+$), 124.0889. C$_8H_{12}$O requires (M$^+$), 124.0888).

Preparation of *N*,*N*-dimethyl-2-(phenylsulfonyl)ethylamine.

To a stirred solution of (phenylsulfonyl)ethene (0.977 g, 5.81 mmol) in absolute ethanol (4.4 ml) at rt was added dimethylamine (1.7 ml of a 33% w/w solution in methylated spirits, 16.4 mmol, 2.8 eq). After stirring for 5 min tlc indicated complete consumption of starting material. The solution was concentrated under reduced pressure and filtered though a pad of silica gel, washing with ethanol until tlc of the filtrate indicated no more product. Evaporation of the combined filtrates under reduced pressure gave the *amine* (1.17 g, 95%) as a yellow oil; υ_{max} (film) 3607, 3063, 2944, 2774, 1587, 1449, 1407, 1379, 1319, 1225, 1150, 1088, 1047, 1004, 900, 857, 796, 747, 691 cm^{-1}; δ_H (270 MHz) 7.92 (2H, m, *ortho*-Ph), 7.68-7.59 (1H, *para*-Ph), 7.59-7.53 (2H, m, *meta*-Ph), 3.26 (2H, m, H-2), 2.69 (2H, m, H-1), 2.16 (6H, s, (CH$_3$)$_2$N); *m/z* (EI) 213 (M$^+$), 168 (M$^+$-(CH$_3$)$_2$NH), 71 (M$^+$-PhSO$_2$H), 44 ((CH$_3$)$_2$N$^+$) (Found: (M$^+$), 213.0823. C$_{10}$H$_{15}$NO$_2$S requires (M$^+$), 213.0823).

Preparation of (*E*)-1-(*N*,*N*-dimethylamino)-2-(phenylsulfonyl)-6,8-nonadien-3-ol.

To a stirred solution of *N*,*N*-dimethyl-2-(phenylsulfonyl)ethylamine (0.69 g, 3.24 mmol, 2.2 eq) in THF (7.2 ml) at -78°C was added *n*-BuLi (1.29 ml of a 2.5M solution in hexanes, 3.24 mmol, 2.2 eq) dropwise giving a pale yellow solution. After 10 min a solution of (*E*)-4,6-heptadienal (161.9 mg, 1.47 mmol) in THF (5 ml + 2.2 ml rinse) was added dropwise. After stirring for a further 15 min tlc indicated complete consumption of starting material. Acetic acid (3.24 ml of a 1M solution in THF, 3.24 mmol, 2.2 eq) was added and the reaction mixture allowed to warm to rt. Saturated aqueous $NaHCO_3$ (30 ml) was added and the aqueous layer was extracted with ether (3 x 30 ml). The combined organic extracts were washed with H_2O (3 x 30 ml), brine (3 x 30 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (ether) gave a 1:1 diastereomeric mixture of the *alcohols* (337.6 mg, 71%) as a colourless oil; υ_{max} (film) 3518, 2947, 2832, 2779, 1810, 1650, 1602, 1449, 1377, 1304, 1147, 1084, 1006, 955, 902, 855, 813, 757, 722, 690 cm^{-1}; δ_H (270 MHz) 7.91-7.84 (2H, m, *ortho*-Ph both diastereomers), 7.70-7.62 (1H, *para*-Ph both diastereomers), 7.60-7.53 (2H, m, *meta*-Ph both diastereomers), 6.38-6.20 (1H, m, H-8 both diastereomers), 6.13-5.89 (1H, m, H-7 both diastereomers), 5.77-5.58 (1H, m, H-6 both diastereomers), 5.09 (1H, d with additional fine structure, J 17.0 Hz, H-9_{trans} both diastereomers), 4.97 (1H, d with additional fine structure, J 10.0 Hz, H-9_{cis} both diastereomers), 4.18 (1H, m, H-3 one diastereomer), 3.97 (1H, dt with additional fine structure, J 10.5, 1.5 Hz, H-3 one diastereomer), 3.58 (1H, dt, J 12.0, 3.5 Hz, H-2 one diastereomer), 3.20-3.09 (2H, one of H-1, H-2 one diastereomer), 2.88-2.80 (1H, m, one of H-1), 2,72-2.63 (2H, m, two of H-1), 2.51-2.04 (4H, m, H-4, H-5 both diastereomers), 2.21 (3H, s) and 2.12 (3H, s, $(CH_3)_2N$ both diastereomers); *m/z* (EI) 323 (M^+), 212 ($PhSO_2CHCH_2N(CH_3)_2^+$), 182 (M^+-$PhSO_2$), 181 (M^+-$PhSO_2H$), 141 ($PhSO_2^+$), 110 ($C_7H_{10}O^+$), 45 ($(CH_3)_2NH^+$) (Found: (M^+), 323.1555. $C_{17}H_{25}NO_3S$ requires (M^+), 323.1555).

Preparation of (*E*)-1-(*N*,*N*-dimethyl)-2-(phenylsulfonyl)-7,9-decadien-3-ol.

Prepared from *N*,*N*-dimethyl-2-(phenylsulfonyl)ethylamine and (*E*)-5,7-octadienal according to the procedure used for (*E*)-1-(*N*,*N*-dimethylamino)-2-(phenylsulfonyl)-6,8-nonadien-3-ol on a 1.95 mmol scale to give a 1:1 diastereomeric mixture of the *alcohols* (481.8 mg, 73%) as a colourless oil; υ_{max} (film) 3510, 2942, 2777, 1721, 1650, 1602, 1451, 1377, 1304, 1147, 1083, 1006, 954, 900, 855, 812, 756, 722, 690 cm^{-1}; δ_H (270 MHz) 7.92-7.85 (2H, m, *ortho*-Ph both diastereomers), 7.73-7.63 (1H, *para*-Ph both diastereomers), 7.62-7.54 (2H, m, *meta*-Ph both diastereomers), 6.45-6.20 (1H, m, H-9 both diastereomers), 6.14-5.94 (1H, m, H-8 both diastereomers), 5.77-5.58 (1H, m, H-7 both diastereomers), 5.10 (1H, d with additional fine structure, J 17.0 Hz, H-10_{trans}), 4.97 (1H, d with additional fine structure, J 10.0 Hz, H-10_{cis}), 4.19 (1H, m, H-3 one diastereomer), 4.02 (1H, dt with additional fine structure, J 10.5, 1.5 Hz, H-3 one diastereomer), 3.58 (1H, dt, J 12.0, 3.5 Hz, H-2 one diastereomer), 3.36-3.07 (3H, one of H-1, H-2 one diastereomer, O*H*), 2.89-2.80 (1H, m, one of H-1), 2,75-2.57 (2H, m, two of H-1), 2.40-1.40 (6H, m, H-4, H-5, H-6 both diastereomers), 2.18 (3H, s) and 2.12 (3H, s, $(CH_3)_2N$ both diastereomers); *m/z* (EI) 337 (M^+), 212 ($PhSO_2CHCH_2N(CH_3)_2^+$), 196 (M^+-$PhSO_2$), 195 (M^+-$PhSO_2H$), 141 ($PhSO_2^+$) 45 ($(CH_3)_2NH^+$) (Found: (M^+), 337.1731. $C_{18}H_{27}NO_3S$ requires (M^+), 337.1712).

Preparation of *N*,*N*-dimethyl-(*E*)-3-(*tert*-butyldimethylsilyloxy)-2-(phenylsulfonyl)-6,8-nonadienamine.

To a solution of (*E*)-1-(*N*,*N*-dimethylamino)-2-(phenylsulfonyl)-6,8-nonadien-3-ol (317 mg, 0.981 mmol) in CH_2Cl_2 at 0°C was added pyridine (87 μl, 1.08 mmol, 1.1 eq) followed by *tert*-butyldimethylsilyl triflate (247 μl, 1.08 mmol, 1.1 eq). After stirring for 30 min tlc indicated complete consumption of starting material. Saturated aqueous $NaHCO_3$ (10 ml) was added and the aqueous layer was extracted with DCM (3 x 10 ml). The combined organic extracts were washed with H_2O (3 x 10 ml), saturated aqueous $CuSO_4$ (3 x 10 ml), H_2O (3 x 10 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (ether) gave a 4:3 diastereomeric mixture of the *amines* (346 mg, 80%) as a colourless oil; υ_{max} (film) 2932, 2771, 1806, 1652, 1603, 1465, 1364, 1306, 1256, 1148, 1074, 1004, 952, 899, 835, 778, 725, 691, 665 cm^{-1}; δ_H (270 MHz) 7.92-7.82 (2H, m, *ortho*-Ph both diastereomers), 7.61-7.43 (3H, *para, meta*-Ph both diastereomers), 6.39-6.21 (1H, m, H-8 both diastereomers), 6.14-5.97 (1H, m, H-7 both diastereomers), 5.76-5.55 (1H, m, H-6 both diastereomers), 5.11 (1H, m, H-9$_{trans}$ both diastereomers), 5.00 (1H, m, H-9$_{cis}$), 4.63 (1H, m, H-3 minor diastereomer), 4.39 (1H, dt, J 9.5, 2.5 Hz, H-3 major diastereomer), 3.31 (1H, dt, J 8.5, 3.0 Hz, H-2 major diastereomer), 3.14 (1H, td, J 6.5, 1.5 Hz, H-2 minor diastereomer), 2.98 (1H, dd, J 12.5, 9.5 Hz, one of H-1 major diastereomer), 2.78 (2H, d, J 5.5 Hz, H-1 minor diastereomer), 2.59 (1H, dd, J 12.5, 3.5 Hz, one of H-1 major diastereomer), 2.33-1.04 (4H, m, H-4, H-5), 1.94 (6H, s, $(CH_3)_2N$ major diastereomer), 1.91 (6H, s, $(CH_3)_2N$ minor diastereomer), 0.90 (9H, s, *t*-Bu minor diastereomer), 0.87 (9H, s, *t*-Bu major diastereomer), 0.15 (3H, s) and 0.10 (3H, s, *t*-Bu$(CH_3)_2$Si minor diastereomer), 0.04 (3H, s) and 0.02 (3H, s, *t*-Bu$(CH_3)_2$Si major diastereomer); *m/z* (EI) 437 (M$^+$), 380 (M$^+$-*t*-Bu), 58 (*t*-BuH$^+$) (Found: (M$^+$), 437.2372. $C_{23}H_{39}NO_3SSi$ requires (M$^+$), 437.2419).

Preparation of *N,N*-dimethyl-(*E*)-3-(*tert*-butyldimethylsilyloxy)-2-(phenylsulfonyl)-7,9-decadienamine.

Prepared from (*E*)-1-(*N,N*-dimethylamino)-2-(phenylsulfonyl)-7,9-decadien-3-ol according to the procedure used for *N,N*-dimethyl-(*E*)-3-(*tert*-butyldimethylsilyloxy)-2-(phenylsulfonyl)-6,8-nonadienamine on a 1.95 mmol scale to give a diastereomeric mixture of the *amines* (467.9 mg, 72%) as a colourless oil; υ_{max} (film) 2932, 2857, 2823, 2771, 1801, 1651, 1603, 1463, 1364, 1306, 1256, 1148, 1078, 1004, 950, 837, 777, 726, 691, 665 cm^{-1}; δ_H (270 MHz) 7.95-7.86 (2H, m, *ortho*-Ph both diastereomers), 7.62-7.44 (3H, *para, meta*-Ph both diastereomers), 6.41-6.21 (1H, m, H-9 both diastereomers), 6.14-5.98 (1H, m, H-8 both diastereomers), 5.78-5.57 (1H, m, H-7 both diastereomers), 5.10 (1H, d, J 17.0 Hz, H-10$_{trans}$ both diastereomers), 4.97 (1H, d, J 10.5 Hz, H-10$_{cis}$ both diastereomers), 4.61 (1H, m, H-3 minor diastereomer), 4.39 (1H, m, H-3 major diastereomer), 3.30 (1H, dt, J 8.5, 3.0 Hz, H-2 major diastereomer), 3.09 (1H, td, J 6.0, 1.5 Hz, H-2 minor diastereomer), 2.95 (1H, dd, J 13.0, 9.5 Hz, one of H-1 major diastereomer), 2.78 (2H, d, J 6.0 Hz, H-1 minor diastereomer), 2.59 (1H, dd, J 13.0, 3.5 Hz, one of H-1 major diastereomer), 2.21-1.10 (6H, m, H-4, H-5, H-6), 1.94 (3H, s, $(CH_3)_2N$ major diastereomer), 1.91 (3H, s, $(CH_3)_2N$ minor diastereomer), 0.89 (9H, s, *t*-Bu minor diastereomer), 0.85 (9H, s, *t*-Bu major diastereomer), 0.18 (3H, s) and 0.09 (3H, s, *t*-Bu$(CH_3)_2$Si minor diastereomer), 0.05 (3H, s) and 0.03 (3H, s, *t*-Bu$(CH_3)_2$Si major diastereomer); *m/z* (EI) 451 (M$^+$), 394 (M$^+$-*t*-Bu), 58 (*t*-BuH$^+$) (Found: (M$^+$), 451.2594. $C_{24}H_{41}NO_3SSi$ requires (M$^+$), 451.2576).

Preparation of (*E*)-7-(*tert*-butyldimethylsilyloxy)-8-(phenylsulfonyl)-1,3,8-nonatriene (7).

To a solution of *N,N*-dimethyl-(*E*)-3-(*tert*-butyldimethylsilyloxy)-2-(phenylsulfonyl)-6,8-nonadienamine (203 mg, 0.464 mmol) in acetone (2 ml) was added MeI (2 ml). The resultant solution was stirred in the dark for 6 h, after which time tlc indicated complete consumption of starting material. Evaporation under reduced pressure gave a white foam which was dissolved in THF (23 ml). The solution was cooled to 0°C, *t*-BuOK (464 μl of a 1M solution in THF, 0.464 mmol, 1 eq) was added and the resultant mixture stirred for 10 min. The reaction mixture was allowed to warm to rt, saturated aqueous NH_4Cl (60 ml) was added and the aqueous layer was extracted with ether (3 x 60 ml). The combined organic extracts were washed with H_2O (3 x 60 ml), brine (3 x 60 ml) and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (20% ether–petrol) gave the *triene* **7** (133 mg, 73%) as a colourless oil; υ_{max} (film) 2930, 2857, 1651, 1603, 1467, 1446, 1381, 1320, 1256, 1154, 1101, 1004, 970, 900, 836, 779, 751, 690, 665 cm^{-1}; δ_H (500 MHz) 7.87 (2H, m, *ortho*-Ph), 7.65-7.54 (2H, m, *para*-Ph), 7.53-7.51 (2H, m, *meta*-Ph), 6.42 (1H, s, H-9$_{cis\ to\ sulfone}$), 6.25 (1H, dt, J 17.0, 10.5 Hz, H-2), 6.12 (1H, d, J 1.0 Hz, H-9$_{trans\ to\ sulfone}$), 5.98 (1H, dd, J 15.5, 10.5 Hz, H-3), 5.59 (1H, m, H-4), 5.09 (1H, d, J 17.0 Hz, H-1$_{trans}$), 4.97 (1H, d, J 10.5, H-1$_{cis}$), 4.36 (1H, dt, J

7.5, 1.0 Hz, H-7), 2.07 (2H, m, H-5), 1.82-1.75 (1H, m) and 1.62-1.56 (1H, m, H-6), 0.80 (9H, s, *t*-Bu), -0.17 (3H, s) and -0.36 (3H, s, *t*-Bu(C*H*$_3$)$_2$Si); *m/z* (EI) 377 (M$^+$-CH$_3$), 335 (M$^+$-*t*-Bu), 77 (Ph$^+$), 53 ($C_4H_5^+$) (Found: (M$^+$-CH$_3$), 377.1621. $C_{20}H_{29}O_3SSi$ requires (M$^+$-CH$_3$), 377.1607)

Preparation of (*E*)-8-(*tert*-butyldimethylsilyloxy)-9-(phenylsulfonyl)-1,3,9-decatriene (8).

Prepared from *N,N*-dimethyl-(*E*)-3-(*tert*-butyldimethylsilyloxy)-2-(phenylsulfonyl)-7,9-decadienamine according to the standard procedure used for triene **7** on a 0.116 mmol scale to give the *triene* **8** (33.1 mg, 70%) as a colourless oil; υ_{max} (film) 2931, 2319, 1814, 1651, 1603, 1466, 1368, 1320, 1256, 1151, 1101, 1005, 956, 896, 837, 779, 751, 691, 664 cm^{-1}; δ_H (270 MHz) 7.88 (2H, m, *ortho*-Ph), 7.66-7.59 (2H, m, *para*-Ph), 7.55-7.51 (2H, m, *meta*-Ph), 6.40 (1H, s, H-10$_{cis\ to\ sulfone}$), 6.28 (1H, dt, J 17.0, 10.5 Hz, H-2), 6.11 (1H, d, J, 1.0 Hz, H-10$_{trans\ to\ sulfone}$), 5.98 (1H, dd, J 15.0, 10.5 Hz, H-3), 5.58 (1H, m, H-4), 5.08 (1H, d, J 17.0 Hz, H-1$_{trans}$), 4.96 (1H, d, J 10.5, H-1$_{cis}$), 4.38 (1H, m, H-8), 2.02-1.93 (2H, m, H-5), 1.67-1.16 (4H, m, H-6, H-7), 0.76 (9H, s, *t*-Bu), -0.15 (3H, s) and -0.33 (3H, s, *t*-Bu(*CH$_3$*)$_2$Si); *m/z* (EI) 391 (M$^+$-CH$_3$), 349 (M$^+$-*t*-Bu), 77 (Ph$^+$), 53 ($C_4H_5^+$) (Found: (M$^+$-CH$_3$), 391.1772. $C_{21}H_{31}O_3SSi$ requires (M$^+$-CH$_3$), 391.1763).

Preparation of [1*R**,6*R**]-6-(phenylsulfonyl)bicyclo[4.3.0]-2-nonene (9).

A solution of triene **1** (223 mg, 0.843 mmol) in toluene (35 ml) was degassed (by alternate sonication/bubbling argon though the solution, 3 cycles over 30 min) and flame-sealed in a hexamethyldisilazane-washed carius tube. The tube was heated at 180°C for 4.5 h and allowed to cool to rt, whereupon the tube was opened and the solution concentrated under reduced pressure. Chromatography of the residue (5-20% ether–petrol) gave the *bicycle* **9** (196 mg, 88%) as a colourless solid, mp 103-106°C (benzene–petrol); υ_{max} (CH_2Cl_2) 3095, 3031, 2962, 2870, 1714, 1656, 1580, 1444, 1346, 1290, 1137, 1075, 1033, 999, 891, 824, 764, 696 cm^{-1}; δ_H (500 MHz) 7.91 (2H, m, *ortho*- Ph), 7.66-7.62 (1H, m, *para*-Ph), 7.56-7.53 (2H, m, *meta*-Ph), 5.75-5.72 (1H, m, H-2), 5.59-5.55 (1H, m, H-3), 3.18 (1H, m, H-1), 2.51-2.45 (1H, m, one of H-4), 2.19-2.11 (2 H,m), 2.04-1.92 (2H, m) and 1.76-1.42 (5H, m, all comprising one of H-4, H-5, H-7, H-8, H-9); *m/z* (EI) 262 (M$^+$), 121 (M$^+$-PhSO$_2$), 120 (M$^+$-PhSO$_2$H), 77 (Ph$^+$) (Found: C, 68.60; H, 6.87. $C_{15}H_{18}O_2S$ requires C, 68.67; H, 6.91%).

Preparation of [1*R**,6*R**]-6-(phenylsulfonyl)bicyclo[4.4.0]-2-decene (10) and [1*R**, 4*R**, 6*R**]-5-methyl-6-(phenylsulfonyl)bicyclo[4.3.0]-2-nonene (12).

A solution of triene **2** (235 mg, 0.852 mmol) in toluene (35 ml) degassed as described above was heated at 180°C for 36 h in a sealed tube and allowed to cool to rt, whereupon the tube was opened and the solution concentrated under reduced pressure to give a 69:23:8 mixture (determined by 500 MHz ^{1}H nmr) of three compounds (177.4 mg, 75%). Purification by HPLC (5% 2-propanol in petrol) gave, in order of elution, *bicycle* **12** (37.2 mg, 16%) as a colourless solid, mp 68-70°C (benzene–petrol); υ_{max} (CH_2Cl_2) 3016, 2953, 2872, 2360, 2223, 1709, 1687, 1633, 1582, 1539, 1448, 1373, 1299, 1140, 1080, 999, 758, 731, 692 cm^{-1}; δ_H (500 MHz) 7.91 (2H, m, *ortho*- Ph), 7.67-7.63 (1H, m, *para*-Ph), 7.56-7.52 (2H, m, *meta*-Ph), 5.71-5.68 (1H, m, H-3), 5.59-5.57 (1H, m, H-2), 3.17-3.13 (1H, m, H-1), 2.60-2.54 (1H, m, H-4), 2.46 (1H, m), 2.11-2.04 (2H, m), 1.67-1.39 (4H, m) and 1.12 (1H, dd, J 15.0, 11.5 Hz, all comprising H-5, H-7, H-8, H-9), 0.95 (3H, d, 7.0 Hz, C-4 CH$_3$); *m/z* (EI) 141 (PhSO$_2^+$), 134 (M$^+$-PhSO$_2$), 77 (Ph$^+$); (Found: (M$^+$-PhSO$_2$H), 134.1090. $C_{10}H_{14}$ requires (M$^+$-PhSO$_2$H), 134.1095), followed by *bicycle* **10** (115.3 mg, 48.4%) as a colourless solid, mp 98-101°C (benzene–petrol); υ_{max} (DCM) 3069, 2932, 1731, 1700, 1653, 1587, 1537, 1506, 1446, 1294, 1141, 1077, 1033, 996, 756, 720, 691 cm^{-1}; δ_H (500 MHz) 7.88 (2H, m, *ortho*-Ph), 7.65-7.62 (1H, m, *para*-Ph), 7.56-7.53 (2H, m, *meta*-Ph), 5.65-5.62 (1H, m, H-3), 5.40-5.37 (1H, m, H-2), 2.92 (1H, br s, H-1), 2.54-2.43 (1H, m) and 2.15-1.20 (11H, m, H-4, H-5, H-7, H-8, H-9, H-10); *m/z* (EI) 141

($PhSO_2^+$), 135 (M^+-$PhSO_2$), 77 (Ph^+) (Found: C, 69.21; H 7.08. $C_{16}H_{20}O_2S$ requires C, 69.53; H, 7.29%); the minor isomer (presumed to be **11**: see Results and Discussion) was not obtained pure.

Preparation of [1*R**,5*S**,6*R**]-5-methyl-6-(phenylsulfonyl)bicyclo[4.3.0]-2-nonene (14) and (*E,E*)-8-(phenylsulfonyl)-2,4,8-decatriene.

A solution of triene **3** (213 mg, 0.772 mmol) in toluene (30 ml) degassed as described above was heated at 162°C for 90 h in a sealed tube and allowed to cool to rt, whereupon the tube was opened and the solution concentrated under reduced pressure to give a 7:1 mixture (determined by 500 MHz ^1H nmr) of two compounds (178.3 mg, 83.6%). Recrystallisation (benzene–petrol) gave the *bicycle* **14** (128 mg, 60%) as a colourless solid, mp 79-81°C; υ_{max} (CH_2Cl_2) 2961, 2878, 2332, 1460, 1300, 1150, 980, 940, 910, 770, 740, 700 cm^{-1}; δ_H (500 MHz) 7.91 (2H, m, *ortho-* Ph), 7.65-7.61 (1H, m, *para*-Ph), 7.56-7.53 (2H, m, *meta*-Ph), 5.66-5.63 (1H, m, H-2), 5.49-5.46 (1H, m, H-3), 3.14 (1H, br s, H-1), 2.47 (1H, m, one of H-4), 2.03-1.85 (4 H,m), 1.79-1.68 (2H, m), 1.59-1.50 (1H, m) and 1.29-1.21 (1H, all comprising one of H-4, H-5, H-7, H-8, H-9), 1.19 (3H, d, J 7.0 Hz, C-5 CH_3) triene *inter alia* 7.85 (2H, m, *ortho*-Ph), 7.05-7.01 (1H, m, H-1); *m/z* (EI) 276 (M^+),141 ($PhSO_2^+$), 135 (M^+-$PhSO_2$), 77 (Ph^+) (Found: C, 69.60; H, 7.30. $C_{16}H_{20}O_2S$ requires C, 69.53; H, 7.29%).

Preparation of [1*R**,5*S**,6*R**]-5-methyl-6-(phenylsulfonyl)bicyclo[4.4.0]-2-decene (15).

A solution of triene **4** (229 mg, 0.789 mmol) in toluene (35 ml) degassed as described above was heated at 180°C for 48 h in a sealed tube and allowed to cool to rt. The tube was opened and the solution concentrated under reduced pressure. Chromatography of the residue (5-20% ether–petrol) gave the *bicycle* **15** (11.5 mg, 5%) as a colourless solid, mp 117-118°C (benzene–petrol); υ_{max} (CH_2Cl_2) 2932, 1733, 1686, 1653, 1617, 1579, 1538, 1447, 1388, 1292, 1136, 756, 691 cm^{-1}; δ_H (500 MHz) 7.93 (2H, m, *ortho-* Ph), 7.64-7.61 (1H, m, *para*-Ph), 7.56-7.53 (2H, m, *meta*-Ph), 5.60-5.56 (1H, m, H-3), 5.28-5.25 (1H, m, H-2), 2.78 (1H, br s, H-1), 2.55-2.48 (2H, m, H-4), 2.01-1.91 (2H, m), 1.86-1.78 (1H, m), 1.63-1.38 (4H, m, all comprising H-5, H-7, H-8, H-9, H-10), 1.20 (3H, d, J 6.5 Hz, C-5 CH_3); *m/z* (EI) 149 (M^+-$PhSO_2$), 141 ($PhSO_2^+$), 77 (Ph^+) (Found: C, 70.20; H 7.50. $C_{17}H_{22}O_2S$ requires C, 70.31; H, 7.64%).

Preparation of [1*R**,6*R**,7*R**]-6-(phenylsulfonyl)-7-(*tert*-butyldimethylsilyloxy)bicyclo-[4.3.0]-2-nonene (17) and [1*R**,6*R**,7*S**]-6-(phenylsulfonyl)-7-(*tert*-butyldimethylsilyloxy)bicyclo[4.3.0]-2-nonene (18).

A solution of triene **7** (111 mg, 0.282 mmol) in toluene (12 ml) degassed as described above was heated at 145°C for 11 h in a sealed tube and allowed to cool to rt. The tube was opened and the solution concentrated under reduced pressure. Chromatography of the residue gave a 3:1 mixture of *bicycles* **17** and **18** (94.1 mg, 85%) as a colourless solid, υ_{max} (CH_2Cl_2) 3066, 3024, 2931, 2856, 1658, 1586, 1444, 1365, 1298, 1255, 1139, 1082, 1025, 1004, 929, 836, 779, 719, 690 cm^{-1}; δ_H (500 MHz) 7.94 (2H, *ortho*-Ph **18**), 7.90 (2H, *ortho-* Ph **17**), 7.62-7.59 (1H, m, *para*-Ph **17**), 7.58-7.50 (3H, m, *meta*-Ph **17**, *para*-Ph **18**), 7.49-7.45 (2H, m, *meta*-Ph **18**), 5.85-5.81 (1H, m, H-2 **17**), 5.62-5.56 (3H, m, H-3 **17**, H-2, H-3 **18**), 4.83 (1H, dd, J 8.0, 6.5 Hz, H-7 **17**), 4.23 (1H, dd, J 10.5, 8.0 Hz, H-7 **18**), 3.48-3.37 (1H, m, H-1 **18**), 3.20 (1H, m, H-1 **17**), 2.39-2.36 (1 H **17**, m) and 2.25-1.40 (8 H **17**, 7 H **18**, m, H-4, H-5, H-8, H-9), 0.78 (9H, s, *t*-Bu **18**), 0.72 (9H, s, *t*-Bu **17**), 0.03 (3H, s) and -0.05 (3H, s, *t*-BuCH_3Si **17**), 0.11 (3H, s) and -0.16 (3H, s, *t*-BuCH_3Si **18**), unidentified product *inter alia* 4.85-4.80 (2H, m), 4.63 (1H, d, J 6.0 Hz), 0.82 (9H, s); *m/z* (EI) 392 (M^+), 377 (M^+-CH_3), 335 (M^+-C_4H_9), 251 (M^+-$PhSO_2$), 77 (Ph^+) (Found: (M^+), 392.1831. $C_{21}H_{32}O_3SSi$ requires (M^+), 392.1841).

Preparation of [1*R**,6*R**,7*R**]-6-(phenylsulfonyl)bicyclo[4.3.0]-2-nonen-7-ol (19) and [1*R**,6*R**,7*S**]-6-(phenylsulfonyl)bicyclo[4.3.0]-2-nonen-7-ol (20).

To a solution of bicycles **17** and **18** (19.4 mg, 0.05 mmol) in acetonitrile (0.43 ml) at rt was added HF (365 μl of a 48% w/v solution in H_2O, 9.89 mmol, 200 eq). After stirring for 16 h tlc showed complete consumption of starting material. The reaction was quenched with solid $NaHCO_3$. Water (4 ml) was added and the aqueous layer extracted with ether (3 x 4 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (3 x 4 ml), H_2O (3 x 4 ml), brine (3 x 4 ml), and dried ($MgSO_4$). Evaporation under reduced pressure followed by chromatography (20-50% ether–petrol) gave a 3:1 mixture of *bicycles* **19** and **20** (13.7 mg, 99%) as a colourless solid; υ_{max} (CH_2Cl_2) 3468, 2922, 2855, 2343, 1652, 1444, 1391, 1278, 1131, 1080, 998, 921, 821, 761, 686 cm^{-1}; δ_H (500 MHz) 7.98 (2H, *ortho*-Ph **20**), 7.89 (2H, *ortho*-Ph **19**), 7.68-7.62 (1H, m, *para*-Ph both isomers), 7.57-7.48 (2H, m, *meta*-Ph both isomers), 5.72-5.67 (1H, m, H-3 **19**), 5.66-5.64 (2H, m, H-2, H-3 **20**), 5.63-5.57 (1H, m, H-2 **19**), 4.87 (1H, m, H-7 **19**), 4.11 (1H, d, J 6.5 Hz, H-7 **20**), 3.74 (1H, d, J 7.0 Hz, OH **20**), 3.31-3.27 (1H, m, H-1 **20**), 3.08-3.05 (1H, m, H-1 **19**), 2.25 (1H, d, J 3.5 Hz, OH **19**), 2.42-2.35 (1 H **19**, m) and 2.24-1.40 (8 H **19**, 7 H **20**, m, H-4, H-5, H-8, H-9); *m/z* (EI) 278 (M^+), 136 (M^+-$PhSO_2H$), 118 (M^+-$PhSO_2H$-H_2O), 77 (Ph^+) (Found: (M^+), 278.0972. $C_{15}H_{14}O_3S$ requires (M^+), 278.0976).

Preparation of [1*R**,6*R**,7*R**]-6-(phenylsulfonyl)-7-(*tert*-butyldimethylsilyloxy)bicyclo-[4.3.0]-2-decene (21) and [1*R**,6*R**,7*S**]-6-(phenylsulfonyl)-7-(*tert*-butyldimethylsilyloxy)-bicyclo[4.3.0]-2-decene (22).

A solution of triene **8** (13 mg, 0.032 mmol) in d_8-toluene (1 ml) degassed as described above was heated at 180°C for 9 h in a sealed nmr tube and allowed to cool to rt. The tube was opened and the solution concentrated under reduced pressure. Chromatography of the residue gave a 1:5 mixture of *bicycles* **21** and **22** (10.4 mg, 80%) as a colourless solid; υ_{max} (CH_2Cl_2) 3065, 3023, 2930, 2856, 1587, 1445, 1363, 1294, 1255, 1142, 1096, 1006, 972, 915, 878, 834, 776, 719, 690, 665 cm^{-1}; δ_H (500 MHz) 7.92 (2H, *ortho*-Ph both isomers), 7.57-7.51 (1H, m, *para*-Ph both isomers), 7.47-7.43 (2H, m, *meta*-Ph **22**), 7.43-7.38 (2H, m, *m*-Ph **21**), 5.68-5.63 (1H, m, H-3 **22**), 5.37 (1H, m, H-2 **22**), 5.12-5.09 (1H, m) and 5.00-4.95 (1H, m, H-2, H-3 **21**),.4.64 (1H, dd, J 8.5, 5.5 Hz, H-7 **21**), 3.95(1H, dd, J 9.5, 4.5 Hz, H-7 **22**), 3.39 (1H, m, H-1 both isomers), 2.66 (1 H **22**, qd, J 12.0, 3.5 Hz), 2.45-2.36 (1 H **22**, m), 2.45-2.36 (1 H **21**, m), 2.19-1.29 (9 H **21**, 8 H **22**, m, all comprising H-4, H-5, H-8, H-9, H-10 both isomers), 0.91 (9H, s, *t*-Bu **21**), 0.73 (9H, s, *t*-Bu **22**), 0.15 (3H, s) and 0.10 (3H, s, *t*-BuCH_3Si **21**), 0.01 (3H, s) and -0.26 (3H, s, *t*-BuCH_3Si **22**); *m/z* (EI) 349 (M^+-C_4H_9), 265 (M^+-$PhSO_2$), 264 (M^+-$PhSO_2H$), 77 (Ph^+) (Found: (M^+-C_4H_9), 349.1300. $C_{18}H_{25}O_3SiS$ requires (M^+-C_4H_9), 349.1293).

X-Ray Crystal Data[29]

All data were corrected for Lorentz and polarisation factors; no absorption corrections were applied. The non-hydrogen atoms were refined anisotropically. Unless stated otherwise, the positions of all hydrogen atoms were idealised, C-H = 0.96 Å, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. All methyl groups were refined as rigid bodies. All computations were carried out using the SHELXTL programme system.[30]

Compound **9**: data were measured using a Siemens P4/PC diffractometer, using Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator) using ω-scans, with $3° \le 2\theta \le 50°$. $C_{15}H_{18}O_2S$, M = 262.4, monoclinic, a = 10.283(4), b = 12.869(4), c = 10.484(3) Å, β = 103.47(2)°,V = 1349 Å^3, space group $P2_1/n$, Z = 4, D_c = 1.29 g cm^{-3}, μ(Mo-K_α) = 2.31 cm^{-1}, F(000) = 560. 2375 Independent reflections were measured of which 1573 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares to give R = 0.073, R_w = 0.078 [$w^{-1} = \sigma^2(F) + 0.0007F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.38 and -0.28 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.014 and 0.001 respectively.

Compound **10**: data were measured using a Siemens P4/PC diffractometer, using Mo-K$_\alpha$ radiation (λ = 0.71073 Å, graphite monochromator) using ω-scans, with 3° ≤ 2θ ≤ 45°. $C_{16}H_{20}O_2S$, M = 276.4, orthorhombic, a = 9.829(4), b = 15.356(6), c = 18.837(8) Å, V = 2843 Å^3, space group $Pbca$, Z = 8, D_c = 1.29 g cm^{-3}, μ(Mo-K$_\alpha$) = 2.23 cm^{-1}, F(000) = 1184. 2265 Independent reflections were measured of which 1159 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares to give R = 0.054, R_w = 0.053 [$w^{-1} = \sigma^2(F) + 0.0007F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.24 and -0.24 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.001 and 0.000 respectively.

Compound **12**: data were measured using a Siemens P4/PC diffractometer, using Cu-K$_\alpha$ radiation (λ = 1.54178 Å, graphite monochromator) using ω-scans, with 0° ≤ 2θ ≤ 116°. $C_{16}H_{20}O_2S$, M = 276.4, orthorhombic, a = 8.950(3), b = 12.138(4), c = 27.060(9) Å, V = 2940 Å^3, space group $Pbca$, Z = 8, D_c = 1.25 g cm^{-3}, μ(Cu-K$_\alpha$) = 19.13 cm^{-1}, F(000) = 1184. 1834 Independent reflections were measured of which 1351 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares to give R = 0.054, R_w = 0.056 [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.24 and -0.25 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.002 and 0.000 respectively.

Compound **14**: data were measured using a Siemens P3/PC diffractometer, using Cu-K$_\alpha$ radiation (λ = 1.54178 Å, graphite monochromator) using ω-scans, with 0° ≤ 2θ ≤ 110°. $C_{16}H_{20}O_2S$, M = 276.4, triclinic, a = 8.203(2), b = 12.036(6), c = 15.622(9) Å, α = 68.60(2), β = 84.91(2), γ = 85.65(2)°, V = 1429 Å^3, space group $P\bar{1}$, Z = 4, D_c = 1.29 g cm^{-3}, μ(Cu-K$_\alpha$) = 19.68 cm^{-1}, F(000) = 592. 3576 Independent reflections were measured of which 3095 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares to give R = 0.060, R_w = 0.067 [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.44 and -0.54 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.000 and 0.000 respectively.

Compound **15**: data were measured using a Siemens P3/PC diffractometer, using Cu-K$_\alpha$ radiation (λ = 1.54178 Å, graphite monochromator) using ω-scans, with 0° ≤ 2θ ≤ 116°. $C_{17}H_{22}O_2S$, M = 290.4, monoclinic, a = 13.686(5), b = 8.613(3), c = 13.896(5) Å, β = 114.61(2)°, V = 1489 Å^3, space group $P2_1/n$, Z = 4, D_c = 1.30 g cm^{-3}, μ(Cu-K$_\alpha$) = 19.13 cm^{-1}, F(000) = 624. 2011 Independent reflections were measured of which 1853 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares to give R = 0.045, R_w = 0.049 [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.39 and -0.57 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.002 and 0.000 respectively.

REFERENCES AND NOTES

1. For reviews of the IMDA reaction, see: Carlson, R. G. *Ann. Rep. Med. Chem.* **1974**, *9*, 270; Opplozer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10; Oppolzer, W. *Synthesis* **1978**, 793; Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63; Funk, R.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41; Ciganek, E. *Org. React.* **1984**, *32*, 1; Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183; Taber, D. F. *Intramolecular Diels–Alder Reactions and Alder Ene Reactions*; Springer: Berlin, 1984; Craig, D. *Chem. Soc. Rev.* **1987**, *16*, 187; Roush, W. R. In *Advances in Cycloaddition*, Curran, D. P., Ed.; JAI: Greenwich, CT, 1990; Vol. 2, p 91; Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: Oxford, 1991; Vol. 5, p 513.
2. Craig, D. Reader, J. C. *Synlett* **1992**, 757, and references cited therein.
3. Clasby, M. C.; Craig, D.; Marsh, A. *Angew.Chem. Int. Ed. Engl.* **1993**, *32*, 1444.
4. Craig, D.; Fischer, D. A.; Kemal, Ö.; Marsh, A.; Plessner, T. *Tetrahedron* **1991**, *47*, 3095.
5. Preliminary communication: Clasby, M. C.; Craig, D. *Tetrahedron Lett.* **1992**, *33*, 3813.
6. In our earlier studies[4] preparation via Julia olefination chemistry of dienes possessing a terminal methyl group gave ca. 6:1 mixtures of olefin isomers. In order to obtain diene samples of sufficient isomeric purity for further elaboration to trienes, it proved necessary to recrystallise repeatedly samples of the 3,5-dinitrobenzoate derivative of the dienols.
7. Our earlier investigations[4] demonstrated that a methyl group α- to the sulfone caused a marked decrease in IMDA reactivity in comparison with the non-methylated analogues.
8. Lin, Y.-T.; Houk, K. N. *Tetrahedron Lett.* **1985**, *26*, 2269.
9. For reviews, see: Wadsworth, W. S. Jr *Org. React.* **1977**, *25*, 73; Stec, W. J. *Acc. Chem. Res.* **1983**, *16*, 411. Although both the lithium- and sodium-countered phosphonate anions were found to be effective for the formation of **1** and **2**, the greater solubility of the former indicated their use for larger-scale applications. Application of the Wadsworth–Emmons reaction to the synthesis of **3** and **4** resulted in the formation of mixtures of geometric isomers.
10. Craig, D.; Smith, A. M. *Tetrahedron Lett.* **1992**, *33*, 695. For *E*-selective elimination of β-acetoxysulfones using sodium ethoxide–ethanol, see: Julia, M.; Launay, M.; Stacino, J.-P.; Verpeaux, J.-N. *Tetrahedron Lett.* **1982**, *23*, 2465.
11. For leading references to tethered IMDA reactions, see: Craig, D.; Reader, J. C. *Tetrahedron Lett.* **1992**, *33*, 6165.
12. Eisch, J. J.; Galle, J. E *J. Org. Chem.* **1980**, *45*, 4534.
13. Attempted direct α-deprotonation of (phenylsulfonyl)ethene using *n*-butyllithium or lithium diisopropylamide caused rapid polymerisation; see also reference 12.
14. Taber, D. F.; Campbell, C.; Grinn, B. P.; Chiu, I. C. *Tetrahedron Lett.* **1981**, *22*, 5141; Wu,T.-C.; Houk, K. N. *ibid.* **1985**, *26*, 2293; Brown, F. K.; Houk, K. N. *ibid.* **1985**, *26*, 2297.
15. For recent examples of both thermally-induced and Lewis acid-catalysed IMDA reactions in which an increase in tether length from four to five atoms causes a decrease in rate, see: Grieco, P. A.; Handy, S. T.; Beck, J. P. *Tetrahedron Lett.* **1994**, *35*, 2663.
16. For examples of this effect in vinylic sulfones, see: Craig, D.; Ley, S. V.; Simpkins, N. S.; Whitham, G. H.; Prior, M. J. *J. Chem. Soc., Perkin Trans 1* **1985**, 1949. For examples in saturated systems, see reference 4.
17. Newton, R. F.; Reynolds, D. P.; Finch, M. A. W.; Kelly, D. R.; Roberts, S. M. *Tetrahedron Lett.* **1979**, 3981.
18. For a review, see: Johnson, F. *Chem. Rev.* **1968**, *68*, 375.
19. For previous contributions from this laboratory in the area of synthesis and asymmetric IMDA reactions of trienylsulfoximines, see: Craig, D.; Geach, N. J. *Tetrahedron: Asymmetry* **1991**, *2*, 1177; Craig, D.; Geach, N. J. *Synlett* **1992**, 299; Craig, D.; Geach, N. J. *ibid.* **1993**, 481.

20. Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd edn.; Pergamon: Oxford, 1988.
21. Johns, A.; Murphy, J. A.; Sherburn, M. S. *Tetrahedron* **1989**, *45*, 7835.
22. Vig, O. P.; Sharma, M. L.; Gakhar, M.; Malik, N. *Ind. J. Chem. Sect. B.* **1980**, *19*, 755.
23. Sharma, G. V. M.; Rajagopal, P.; Rao, E. S. *Synth. Commun.* **1989**, *19*, 3181.
24. Sharma, G. V. M.; Shekharam, T.; Upender, V. *Tetrahedron* **1990**, *46*, 5665.
25. Marshall, J. A.; Audia, J. A.; James, E.; Grote, J.; Shearer, B. G. *Tetrahedron* **1986**, *42*, 2893.
26. Craig, D.; Roe, D. G. unpublished results.
27. Geach, N. J. Ph.D. thesis, University of London, **1993**.
28. Margol, C.; Rizzoli, M.; Schlosser, M. *Tetrahedron* **1990**, *46*, 2411.
29. 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.
30. The SHELXTL-C Programme System (Version 4.2) was used: Sheldrick, G. M.; Siemens Analytical X-Ray Instruments, Madison, Wisconsin, 1992.

(*Received in UK* 2 *November* 1994; *revised* 24 *November* 1994; *accepted* 25 *November* 1994)