Pergamon

Tetrahedron, Vol. 52, No. 2, pp. 695-724, 1996

0040-4020/96 $15.00 + 0.00

0040-4020(95)00920-5

Intramolecular Diels–Alder Reactions of Trienes Tethered With an Ether Linkage

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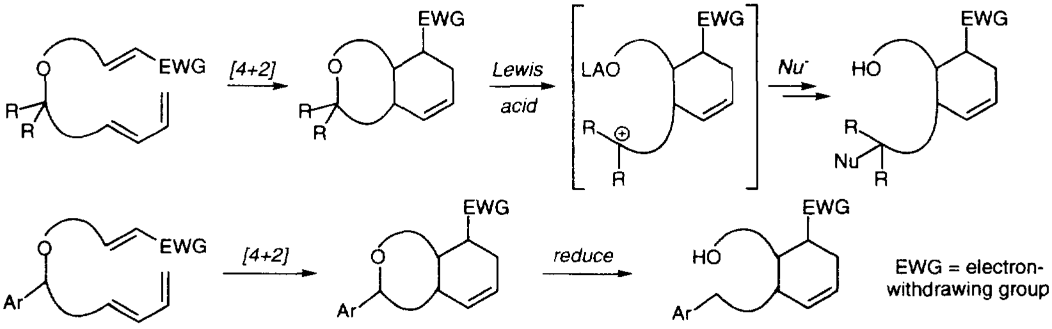
Abstract: The intramolecular Diels–Alder reactions of a series of ether-tethered trienes **3a-3o** show varying selectivities according to the nature of the dienophile-activating group and the presence of substituents in the linking chain. Some tether-cleaving reactions are reported.

INTRODUCTION

In recent years the temporary tethering of dienes and dienophiles has emerged as an effective strategy for the control of regio- and steroselectivity in Diels–Alder reactions. The products of overall in*ter*molecular processes may be accessed while exploiting the benefits of in*tra*molecularity during C–C bond formation. We have examined the utility and effectiveness of silyl acetal,[1] carbon acetal[2] and diester[3] tethers in Diels–Alder reactions. Herein we report in full[4] on our studies of intramolecular Diels–Alder (IMDA) reactions[5] of trienes tethered with ether linkages.

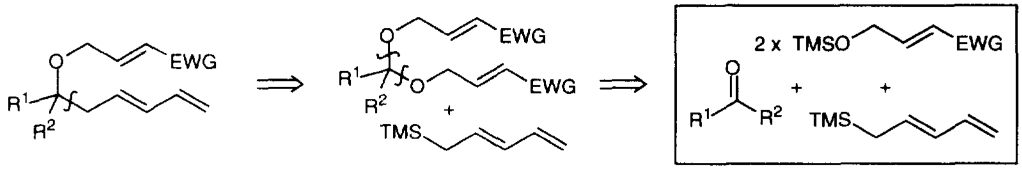
RESULTS AND DISCUSSION

An effective tethering strategy must combine high IMDA reactivity and stereoselectivity with efficient methods for introduction and removal post-cycloaddition of the linking functionality. We were particularly keen to develop approaches to IMDA substrates whose cycloaddition products would be amenable to regioselective tether cleavage. Tertiary and benzylic ether linkages appeared to be ideal (Scheme 1). In the former case it was anticipated that E1- or S_N1-type processes mediated by Lewis acids would effect selective C–O bond cleavage to



Scheme 1

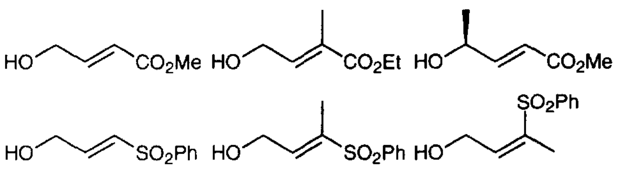
give the more stable of the alternative regiosomeric carbocations, while benzylic ethers would be cleaved selectively using hydrogenolytic or other reductive methods. It occurred to us that maximum structural diversity in such ether-tethered trienes could be achieved by using a convergent approach involving coupling of nucleophilic diene and dienophile-containing fragments with a ketone (in the case of tertiary ether tethers) or an aromatic aldehyde (for benzylic ether linkages). In this context the Sakurai coupling reaction[6] of a dienylsilane with acetals appeared to be especially attractive; the requisite acetals would be available by combining the trimethylsilyl (TMS) ethers of dienophile-containing alcohols with aldehydes or ketones in a Noyori-type acetalisation process.[7] Thus, a wide variety of trienes would be accessible simply by changing the dienophilic reagent and/or the carbonyl compound. The disconnections are outlined in Scheme 2.



Scheme 2

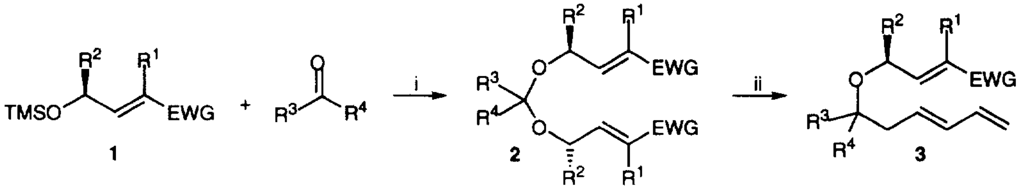
It was decided at the outset to study the IMDA reactions of ether-tethered trienes bearing two different electron-withdrawing functions on the dienophilic groups. Carboxylic esters are well-established as effective dienophile-activating units;[8] the analogous trienes possessing arylsulfonyl groups are less reactive, but unlike the ester trienes the stereochemical outcomes of their IMDA reactions are markedly influenced by dienophile geometry.[9]

Synthesis of trienes



The retrosynthetic analysis presented in Scheme 2 reduces the synthesis of ether-tethered trienes to the preparation of dienophile-containing alcohols and 5-(trimethylsilyl)-1,3-pentadiene. The alcohols prepared for this study are shown on the right. 3-(Phenylsulfonyl)-2-propenol was prepared using the literature procedure.[10] Methyl 4-hydroxy-2-butenoate and ethyl (*E*)-4-hydroxy-2-methyl-2-butenoate were synthesised by reaction of the corresponding stabilised phosphoranes with glycolaldehyde dimer.[11] The remainder were prepared either by Wittig or by Wadsworth–Emmons reactions of silyl-protected 2-hydroxyaldehydes with the appropriate substituted phosphoranes or phosphonate-stabilised anions. The trimethylsilyl ethers were prepared using standard methods. (*E*)-5-(Trimethylsilyl)-1,3-pentadiene was prepared from the potassium salt of piperylene and chlorotrimethylsilane using a modification of the method reported by Sakurai.[12] Full details are provided in the Experimental section.

The three-component method for triene synthesis is depicted in Scheme 3. Trimethylsilyl triflate (TMSOTf)-mediated reaction of TMS ethers **1** with acetone or benzaldehyde at low temperature in dichloromethane gave acetals **2**. These were isolated, and subsequently exposed to 5-(trimethylsilyl)-1,3-pentadiene in the presence of TMSOTf under similar reaction conditions to give the target trienes **3**. It occurred to us that the one-pot procedure developed by Markó[13] for the direct condensation of allyltrimethylsilane and TMS ethers with carbonyl compounds might be adaptable for the synthesis of our target compounds. After extensive experimentation, it was found that treatment with TMSOTf of a mixture of *two* equivalents of TMS ether **1** (EWG = CO_2Me, $R^1 = R^2 = H$), 5-(trimethylsilyl)-1,3-pentadiene and a ketone or aldehyde in concentrated dichloromethane solution at low temperature gave the corresponding trienes in excellent yields for the one-pot operation. The yields of all the trienes synthesised using the two-step or one-step procedures are summarised in Table 1.



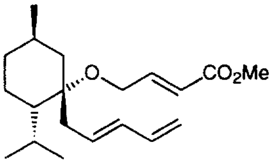
Reagents and conditions: (i) Add TMSOTf (0.2 eq) to **1** + carbonyl compound, CH_2Cl_2, -78°C, 2 h; add pyridine; (ii) Add TMSOTf (0.2 eq) to **2** + $TMSCH_2CH{=}CHCH{=}CH_2$ (2 eq), CH_2Cl_2, -78°C, 2 h; add pyridine.

Scheme 3

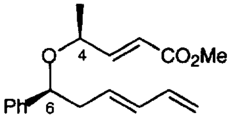
entry	R^1	R^2	R^3	R^4	EWG	% yield of 2	% yield of 3	one-pot % yield of 3[14]
a	H	H	Me	Me	CO_2Me	74	60	97
b	Me	H	Me	Me	CO_2Et	58	67	-
c	H	Me	Me	Me	CO_2Me	48	66	-
d	H	H	Me	Me	SO_2Ph	76	67	-
e	Me	H	Me	Me	SO_2Ph	48[15]	78[16]	-
f	Me	H	Me	Me	SO_2Ph	57[17]	53[18]	-
g	H	H	$(CH_2)_5$		CO_2Me	76	74	97
h	H	H	3,5-Me_2*c*-C_5H_8[19]		CO_2Me	56	75	65
i	H	H	2-*i*-Pr-5-Me*c*-C_5H_8[20]		CO_2Me	7	72[21]	17[19]
j	H	H	Ph	H	CO_2Me	70	62	98
k	Me	H	Ph	H	CO_2Et	79	86	-
l	H	Me	Ph	H	CO_2Me	72	68[22]	-
m	H	H	Ph	H	SO_2Ph	75	74	-
n	Me	H	Ph	H	SO_2Ph[15]	80	65[16]	-
o	Me	H	Ph	H	SO_2Ph[17]	86	65[18]	-

Table 1. Synthesis of Trienes **3**

Two of the triene-forming reactions had noteworthy stereochemical features. The menthone-derived substrate **3i** was formed as the same, single diastereomer in both the one-pot and stepwise processes. We tentatively assign the stereochemistry shown, since it would arise by attack via the presumably less hindered equatorial trajectory. Substrate **3l** was formed as a ca. 1.6:1 mixture of diastereomers, which could be separated in small quantities by chiral HPLC.[23] On the basis of Markó's observations,[13] and the contrasting cyclisation behaviour of the two isomers (see below), we assign the 4*S*,6*S* configuration to the major product. In all cases the yields of the one-pot reactions were markedly superior to the combined yields for the same trienes over the two-step sequences, but only if *two* equivalents of the TMS ethers **1** were used. No attempts were made to recover unconsumed **1**.



assigned structure of **3i**



[4*S*,6*S*]-**3l** (major)

Intramolecular Diels–Alder reactions

IMDA Reactions of trienes **3** were carried out in the usual way[9] by heating rigorously dry, degassed d_8-toluene solutions in sealed, base-washed nmr tubes. Reaction temperatures and times were established by ^1H nmr analysis, after which larger-scale runs were carried out at 165°C in resealable Carius tubes. Ratios of cycloadducts were determined by ^1H nmr analysis of the crude products, which were purified by flash chromatography.

Acetone-derived trienes 3a-f. The first substrates to be examined were the acetone-derived trienes **3a-f**. Heating a toluene solution of **3a** at 165°C for 7.5 h gave in high yield a single cycloadduct. ^{1}H Nmr analysis suggested that the ring-junction protons were oriented trans to each other, since the signal for H-1 appeared as a quartet of doublets with J values of respectively 11 and 4 Hz. Structure **4a** was therefore assigned. Thermolysis of the homologous α-methylated substrate **3b** gave a 6:1 mixture of products trans-**4b** and cis-**4b**, in which the former, major isomer showed two large couplings (11 and 10.5 Hz) and one smaller coupling, again indicative of a trans ring-junction. That complete asymmetric induction was attainable in a chiral substrate was conclusively demonstrated by the cyclisation of the enantiomerically pure triene **3c** to give a single, trans-fused cycloadduct **4c**. The ring-junction proton H-1 resonated as a double double doublet with J values of 10.5, 10 and 9.5 Hz, confirming both the trans-fused nature of the bicycle and the expected[24] syn relationship of H-1 and the C-2 methyl substituent. This arises from the preferred pseudoequatorial disposition of the methyl group in the transition-state. Sulfone-activated trienes **3d-f** showed significantly different IMDA selectivities. The thermolysis reaction of **3d** was moderately trans-selective, giving trans-**4d** and cis-**4d** in a 6:1 ratio. Substitution of the α-hydrogen atom for a methyl group as in **3e** resulted in a further lowering of the trans-selectivity; this effect was absent from the *Z*-isomer **3f**, which cyclised with complete selectivity for the trans isomer. The IMDA reactions of trienes **3a-3f** are summarised in Table 2.

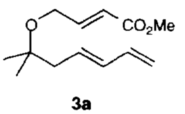
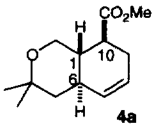
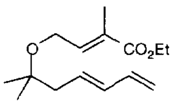
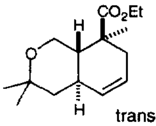
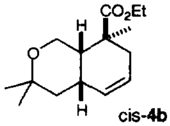
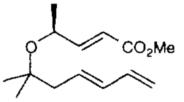
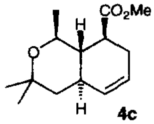
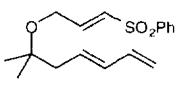
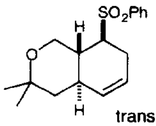
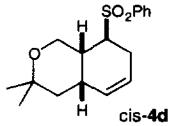
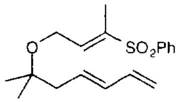
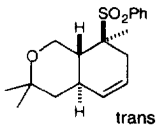
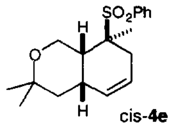
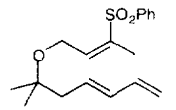
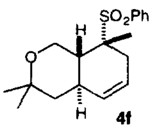
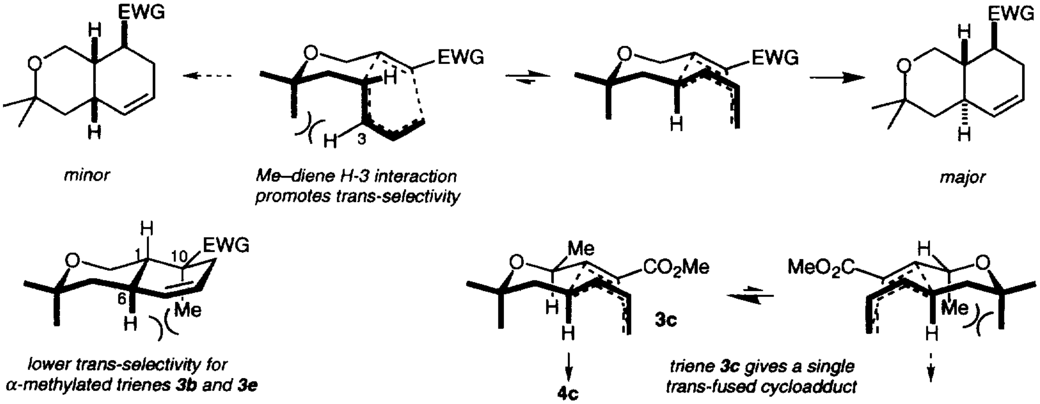
triene	reaction time (h)	% yield of cycloadducts	products (ratio)
 **3a**	7.5	80	 **4a**
 **3b**	9	95	 trans-**4b** (6:1)  cis-**4b**
 **3c**	5	97	 **4c**
 **3d**	5	84	 trans-**4d** (6:1)  cis-**4d**
 **3e**	7	84	 trans-**4e** (4:1)  cis-**4e**
 **3f**	5	92	 **4f**

Table 2. IMDA Reactions of Acetone-derived Trienes

Several trends emerged from these experiments. Firstly, all of the cycloadditions showed at least moderate, and at best complete trans-selectivity. This is in sharp contrast with previously reported IMDA reactions of both ester- and sulfone-activated trienes giving rise to bicyclo[4.4.0] systems. The former usually are moderately trans-selective, independently of dienophile geometry,[8] while the latter show modest selectivities favouring cis-fused products in the case of *E*-dienophiles, and trans-fused products in the case of the *Z*-isomers.[9] Thus, all of the reactions described in Table 2 were significantly more trans-selective than the parent systems having all-carbon tethers. We ascribe this to the geminal dimethyl group in the ether tether. Inspection of the competing reactive conformations leading to the trans- and cis-fused products shows that in the latter there is a repulsive non-bonded interaction between H-3 of the diene and the necessarily axial methyl group. With a non-bulky dienophile-activating group such as an ester (**3a**), this effect is such as to lead to complete selectivity for the trans-fused product. With an inherently cis-directing *E*-vinylic sulfone (substrate **3d**),[9] the effect is still sufficiently large to give a 6:1 trans:cis ratio. For trienes possessing ester- (**3b**) or sulfone-activated (**3e**) α-methylated *E*-dienophiles, the effect is attenuated relative to the non-methylated cases, presumably because of unfavourable 1,3-diaxial interactions between the axial C-10 methyl group and H-6. Triene **3f** combines the weakly trans-directing effect of a Z-vinylic sulfone dienophile with the strong trans bias of the geminal dimethyl tether, and complete selectivity is observed. Triene **3c** cyclises exclusively via the conformation which avoids 1,3-diaxial interactions of the dienophile γ-methyl group with one of the tether methyl substituents (Scheme 4).



Scheme 4

Benzaldehyde-derived trienes 3j-o. Attention was turned next to the IMDA reactions of the analogous benzaldehyde-derived trienes **3j-o**. These transformations presented an additional stereochemical issue because of the stereocentre in the benzylic ether linkage. Thermolysis of the ester-activated substrate **3j** gave in excellent yield two of the four possible products in a 2:1 ratio. The major component displayed in the ^{1}H nmr spectrum a resonance at 1.85 ppm corresponding to H-1, which appeared as a quartet of doublets with J values of 11 and 3.5 Hz. This clearly indicated its trans-fused nature. The corresponding signal in the minor component overlapped with the H-6 and H-10 resonances. In both isomers the benzylic proton appeared to be oriented axially on the pyran ring, as evidenced by the J values of 11 and 2.5 Hz (major) and 11.5 and 2 Hz (minor). This strongly suggested that the two cycloadducts had the structures trans-**4j** and cis-**4j** (Table 3). These arise by respectively endo- and exo-attack by the diene on the same diastereoface of the dienophile, via a transition-state in which the phenyl substituent is pseudoequatorially disposed (Scheme 5). Similar stereoselectivity was observed in the IMDA reaction of the α-methylated ethyl ester **3k**, with the previously observed small diminution of the trans-selectivity. Carrying out the IMDA reactions of **3j** and **3k** under Lewis acidic rather than thermal conditions resulted in complete trans-selectivity, in line with published findings;[25] it is noteworthy

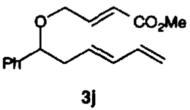
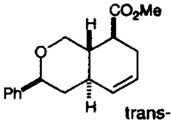
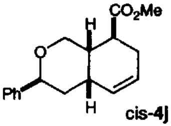
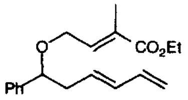
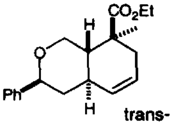
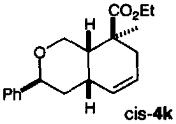
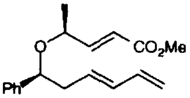
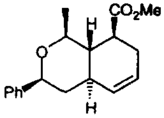
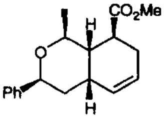
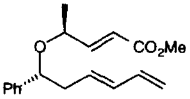
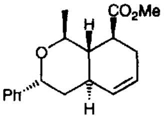
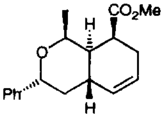
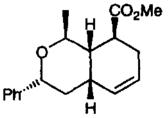
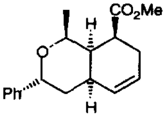
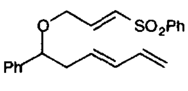
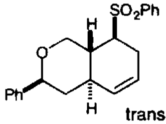
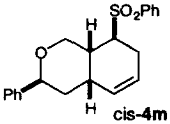
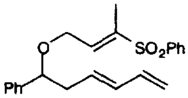
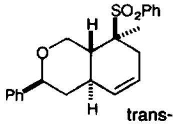
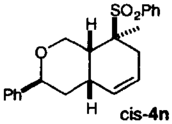
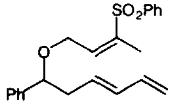
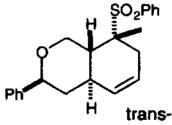
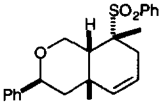
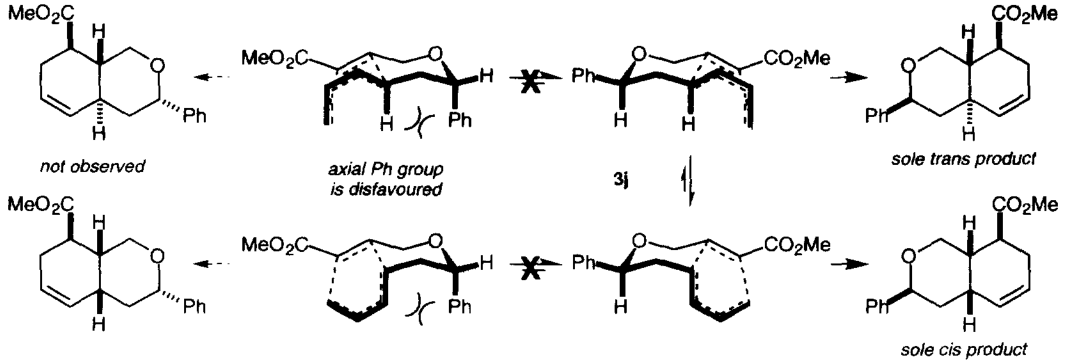
triene	reaction time (h)	% yield of cycloadducts	products (ratio)		
 **3j**	9 (36)[26]	91 (92)[26]	 trans-**4j**	(2:1) (1:0)	 cis-**4j**
 **3k**	10 (36)[26]	89 (93)[26]	 trans-**4k**	(1.6:1) (1:0)	 cis-**4k**
 [4*S*,6*S*]-**3l**	7	88	 [1*S*,2*S*,4*S*]-trans-**4l**	(2:1)	 [1*S*,2*S*,4*S*]-cis-**4l**
 [4*S*,6*R*]-**3l**	7.5	88	 [1*S*,2*S*,4*R*]-trans-**4l**  [1*R*,2*S*,4*R*]-trans-**4l**	(6 : 3) : : (2 : 1)	 [1*S*,2*S*,4*R*]-cis-**4l**  [1*R*,2*S*,4*R*]-cis-**4l**
 **3m**	7	90	 trans-**4m**	(1:1)	 cis-**4m**
 **3n**	12	89	 trans-**4n**	(1:1)	 cis-**4n**
 **3o**	7	86	 trans-**4o**	(3.5:1)	 cis-**4o**

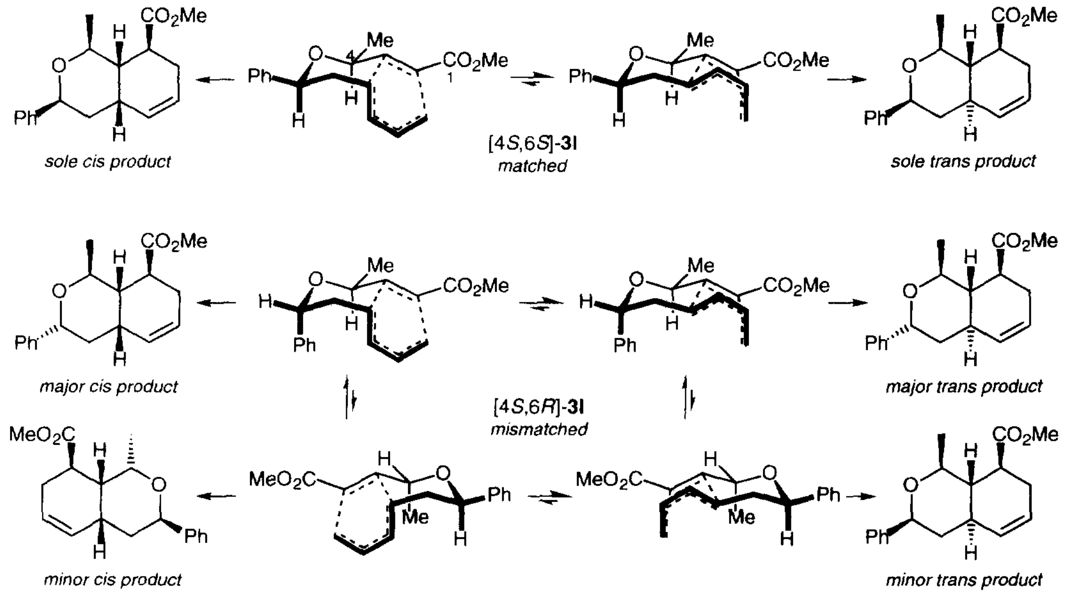
Table 3. IMDA Reactions of Benzaldehyde-derived Trienes

that the potentially labile benzylic ether tether withstood these highly electrophilic reaction conditions. Substrates **3l** presented an opportunity to assess the relative magnitude of the stereodirecting effects of the C-4 methyl and C-6 phenyl substituents. The cyclisation of the methylated, acetone-derived triene **3c** had been observed to be completely specific; IMDA reaction of **3j** had resulted only in the formation of the two isomers arising via transition-states in which the phenyl substituent was equatorial. Therefore, the major triene **3l** form-



Scheme 5

ulated as having the 4*S*,6*S*-configuration would be expected to be a matched substrate, since its IMDA reaction could proceed through a reactive conformation in which both the C-4 and C-6 substituents were equatorial. In the event, [4*S*,6*S*]-**3l** gave in high yield on thermolysis a 2:1 mixture of single trans- and cis-fused diastereomers, as evidenced by ^{1}H nmr analysis. The minor isomer, previously assigned as [4*S*,6*R*]-**3l** gave a



Scheme 6

mixture of all four possible diastereomeric products. The ratio of combined trans-fused to combined cis-fused isomers was 2:1. For the trans isomers, the major (2:1) product was [1*S*,2*S*,4*R*]-trans-**4l**; this has an equatorial C-2 methyl substituent and an axial C-4 phenyl group. The major cis-fused isomer [1*S*,2*S*,4*R*]-cis-**4l** possesses the C-2 methyl group on the convex, outer face of the bicyclic structure, while the C-4 phenyl

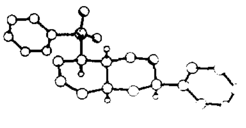


Figure 1
X-Ray structure
of trans-**4m**

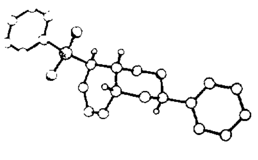
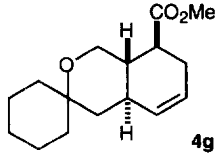


Figure 2
X-Ray structure
of cis-**4m**

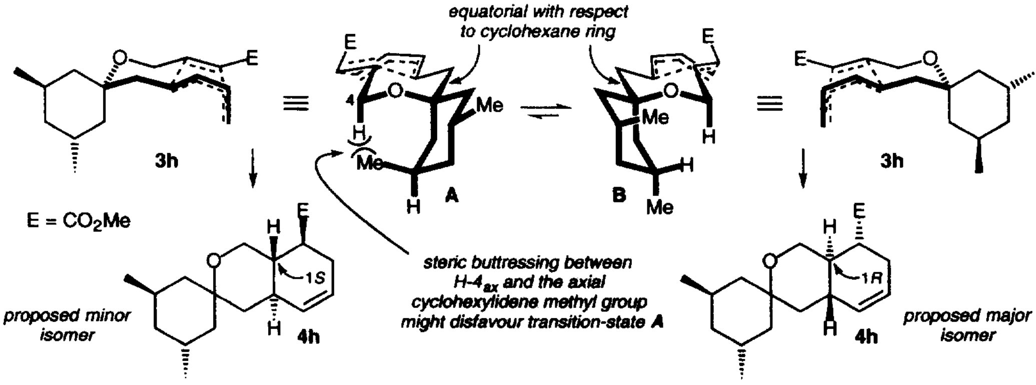
moiety is on the concave, inner face. It would appear therefore that the C-4 methyl group exerts a marginally stronger directing effect than the C-6 phenyl substituent in formation of both trans and cis isomers. Thus, [4*S*,6*S*]-**3l** was indeed shown to be a matched substrate, strongly supportive of its original structural assignment. The isomeric triene [4*S*,6*R*]-**3l** gave a mixture of all the four possible IMDA cycloadducts, and as such was shown to be a mismatched substrate, as expected (Scheme 6). Sulfonyl-activated trienes **3m** and **3n** gave 1:1 mixtures of trans- and cis-fused products as single diastereomers. The X-ray crystal structures of trans-**4m** and cis-**4m** are shown in Figures 1 and 2. As with the acetone-derived sulfone-activated substrate **3f**, *Z*-triene **3o** underwent a more trans-selective IMDA reaction than its *E*-counterpart **3n**. The IMDA reactions of all the benzaldehyde-derived trienes are summarised in Table 3.

Cyclohexanone-derived trienes 3g-3i. Most of the acetone- and benzaldehyde-derived trienes studied to date had been achiral or racemic. Substrates **3c** and **3l** were enantiomerically pure, but the stereochemical information was derived directly from that present in the lactate-derived[11] TMS ether precursor. In view of the high diastereoselectivities observed with many of the IMDA reactions, we were keen to design systems in which these selectivities could be expressed in absolute terms by the incorporation of chirality in the tethering unit. It occurred to us that ether-tethered trienes derived from chiral cyclohexanones might be suitable substrates, if a sufficiently conformationally restricted six-membered ring-system could be found. Substrates **3g-3i** could be made using the standard two-step method used for all the other trienes, but the yields were markedly better if the one-pot procedure was used (Table 1). For (-)-menthone-derived triene **3i**, the yield of 17% for the one-step process was superior to that of 5% for the stepwise method; in the latter sequence the first, acetalisation step was low-yielding, while incorporation of the diene using the Sakurai procedure worked in similar yield to those obtained for the other triene substrates.

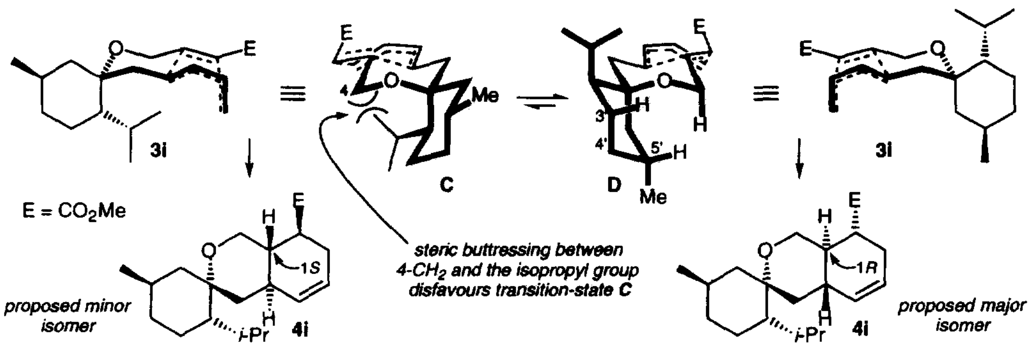


4g

The cyclohexanone-derived triene **3g** served as an initial model compound on which to assess the basic reactivity of this modified class of IMDA substrates. Thermolysis at 165°C for 3 hours gave in excellent yield a single (>95:5), trans-fused diastereomer **4g** as shown by ^{1}H nmr analysis. This was expected on the basis of the model developed for the acetone-derived trienes. Enantiomerically pure triene **3h** was more reactive: IMDA reaction was complete after 2.25 hours, and gave an inseparable 3:2 mixture of trans-fused products in similarly high yield. Finally, thermolysis of the (-)-menthone-derived substrate **3i** caused rapid cycloaddition to take place, giving in high yield a 10:1 mixture of products whose ^{1}H nmr spectrum again strongly supported the assignment of trans ring-junction stereochemistry. In the reactions of both **3h** and **3i** we were unable to assign completely the stereochemistry of the products. However, for the reaction of **3h** we propose that the major isomer is [1*R*]-**4h** as shown in Scheme 7. If it is assumed in the competing IMDA transition-states of **3h** that the diene-containing substituent is disposed equatorially on the dimethylated cyclohexane ring, then two reactive conformations **A** and **B** are



Scheme 7

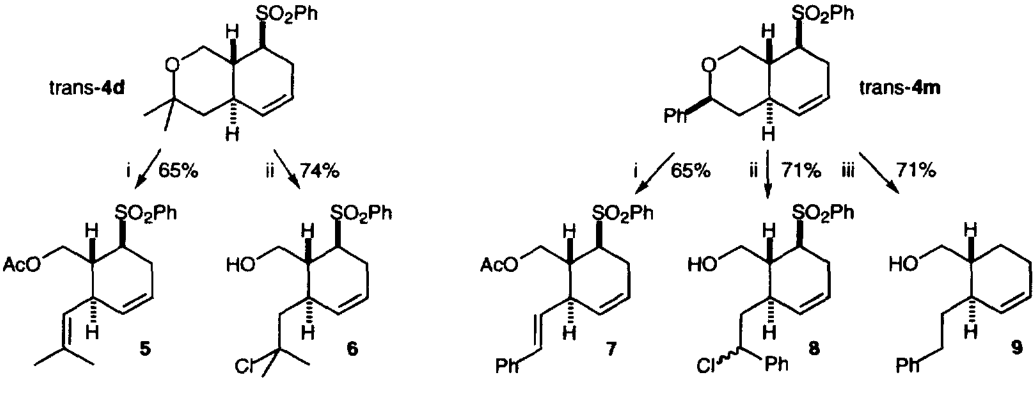


Scheme 8

possible. In conformer **A** there is marginally more steric buttressing between H-4 and the axial cyclohexylidene methyl group than in **B**, which is therefore proposed as the major product. A similar model may be formulated for substrate **3i** (Scheme 8). Transition-state **C** is disfavoured because of repulsive interactions between C-4 of the dienophile and the isopropyl substituent from the menthylidene group; examination of models reveals that these are in close mutual proximity. Therefore, we propose that the major cycloadduct from IMDA reaction of **3i** is [1*R*]-**4i** as shown in Scheme 8. These arguments rest on the assumption that the stereochemistry of **3i** is as shown, i.e. that the pentadienyl substituent is anti with respect to the isopropyl group. Some support for this contention came from the appearance of the resonances corresponding to the H-3'$_{\text{axial}}$ and H-5'$_{\text{axial}}$ menthylidene protons at relatively low fields in the ^{1}H nmr spectrum. For example, H-3'$_{\text{axial}}$ appeared as a quartet of doublets at 1.62 ppm, whereas the trans-diaxially related H-4'$_{\text{axial}}$ signal appeared at 0.8 ppm. This anomalously deshielded environment is consistent with the 1,3-diaxial relationship of H-3'$_{\text{axial}}$ and the dienophile-bearing ether oxygen atom at C-1' as formulated for **3i**. All attempts (hydrogenation, hydrolysis, 3,5-dinitrobenzoylation of the derived primary alcohol) to make crystalline derivatives of the major product of IMDA reaction of **3i** gave oily products, precluding unambiguous structural assignment by X-ray analysis.

De-tethering reactions of IMDA reaction products

The final phase of our study centred on the development of methods for cleavage of the ether tethers. We were keen to establish conditions which would give monocyclic materials possessing functionality with potential for further elaboration. Since most of the projected methods would involve the use of electrophilic, Lewis acidic reagents, attention was focused on sulfonyl-substituted tethered IMDA products; it was anticipated that the more



Reagents and conditions: (i) FeCl$_3$ (0.1 eq), Ac$_2$O, 0°C, 30 min; (ii) BCl$_3$ (1 eq), CH$_2$Cl$_2$, -78°C→0°C; MeOH, -78°C; (iii) Na, NH$_3$ (l), 25 min; solid NH$_4$Cl.

Scheme 9

strongly Lewis basic ester groups[27] in the alternative series would cause side-reactions to occur which might obscure the findings from the de-tethering reactions.

Treatment of an acetic anhydride solution of trans-**4d** with a catalytic amount of iron(III) chloride[28] gave in good yield the unsaturated ester **5**. Similar treatment of the benzaldehyde-derived IMDA product trans-**4m** gave the analogous olefin **7** exclusively as the trans isomer. Alternatively, exposure of the same cycloadducts to boron trichloride in dichloromethane[29] followed by quenching with methanol gave respectively chloroalcohols **6** and **8**. Compound **8** was formed as a 1:1 mixture of diastereomers. Finally, reduction of trans-**4m** using sodium–liquid ammonia gave alcohol **9** in good yield. Compound **9** may be regarded as the product of a completely regioselective in*ter*molecular Diels–Alder reaction of allyl alcohol and 6-phenyl-1,3-hexadiene. The derivatisation reactions of trans-**4d** and trans-**4m** are summarised in Scheme 9.

CONCLUSIONS

In conclusion, the work presented herein demonstrates that ether-tethered trienes are readily accessible, reactive substrates which enter into IMDA reactions with mostly high and sometimes complete stereoselectivities. The stereochemical outcomes of these processes may be understood in terms of well-established concepts of preferred equatorially-disposed substituents on chair-like chains linking the diene and dienophile. The synthesis of an enantiomerically pure triene in which the chirality resides within the ketone-derived tethering unit is low-yielding, but its cycloaddition is highly selective. Further work is underway to identify a more readily accessible chiral substrate which undergoes a similarly selective IMDA reaction. Cleavage of the tethers post-cycloaddition delivers the overall products of completely regioselective and highly stereoselective bimolecular processes.

ACKNOWLEDGEMENTS

We thank SERC/EPSRC (Quota Studentships to P. J. A. and J. C. R.) and the ICI Strategic Research Initiative for financial support of this research. We gratefully acknowledge the SERC/EPSRC 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; $PhCD_2H$, δ_H 2.03 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. Optical rotation measurements were carried out using an Optical Activity AA-100 polarimeter. 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 or nitrogen. 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. 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.[30]

Preparation of trienes

Preparation of (*E*)-5-(trimethylsilyl)-1,3-pentadiene.[6]

Potassium metal (3.91 g, 0.1 mol, 1 eq) was heated in THF (14.22 g, 16.27 ml, 0.2 mol, 2 eq) under reflux with vigorous stirring, until the surface of the metal was shiny. The flask was cooled to room temperature and Et_3N (13.94 ml, 10.12 g, 0.1 mol, 1 eq) added, followed by the dropwise addition of freshly distilled piperylene (19.93 ml, 13.62 g, 0.2 mol, 2 eq) at a rate which maintained gentle reflux. The solution was heated at reflux for 5 h, during which time an orange/red solution was formed. The mixture was then cooled to 0°C, and freshly distilled chlorotrimethylsilane (13.96 ml, 11.95 g, 0.11 mol, 1.1 eq) added dropwise. The solution was stirred at 0°C for 1 h during which time a white precipitate formed. The reaction was worked up by the addition of saturated aqueous ammonium chloride (50 ml). The layers were separated, the aqueous layer extracted with ether (2 x 30 ml), and the dried ($MgSO_4$) organic layers partially concentrated by evaporation with cooling. The resultant pale yellow oil was purified by distillation under reduced pressure, to afford (*E*)-5-(trimethylsilyl)-1,3-pentadiene (11.64 g, 83%) as a colourless oil, bp_{112} 105°C; υ_{max} (film) 3086, 2958, 1730, 1645, 1548, 1506, 1451, 1409, 1251, 1148, 1034, 999, 967, 894, 851, 755, 695 cm^{-1}; δ_H (270 MHz) 6.31 (1H, dt, J 17, 10.5 Hz, H-2), 5.87 (1H, dd, J 15, 10.5 Hz, H-3), 5.72 (1H, dt, J 15, 7.5 Hz, H-4), 5.01 (1H, d, J 17 Hz, H-1_{trans}), 4.89 (1H, d, J 10.5 Hz, H-1_{cis}), 1.57 (2H, d, J 7.5 Hz, H-5), 0.00 (9H, s, $Si(CH_3)_3$); *m/z* (EI) 140 (M^+), 125 (M^+-CH_3), 97, 86, 73 ($Si(CH_3)_3$) (Found: (M^+), 140.1021. $C_8H_{16}Si$ requires (M^+), 140.1021).

Preparation of methyl (*E*)-4-(trimethylsilyloxy)-2-butenoate.

To a solution of methyl (*E*)-4-hydroxy-2-butenoate[11] (1.007 g, 8.673 mmol) and Et_3N (1.317 g, 1.813 ml, 13.010 mmol, 1.5 eq) in CH_2Cl_2 (16 ml) at 0°C was added chlorotrimethylsilane (1.037 g, 1.21 ml, 9.541 mmol, 1.1 eq). The mixture was allowed to stir for 1 h during which time a pale brown precipitate formed. The mixture was poured into a mixture of saturated aqueous sodium hydrogencarbonate (20 ml) and CH_2Cl_2 (4 ml). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 15 ml). The combined organic layers were dried ($MgSO_4$) and the solvent removed by evaporation. Purification of the residue by chromatography on silica gel (20% ether–petrol) afforded the silyl ether (1.209 g, 74%) as a colourless oil; υ_{max} (film) 2956, 2847, 1727, 1665, 1438, 1378, 1300, 1254, 1167, 1136, 1074, 1023, 964, 844, 751, 685 cm^{-1}; δ_H (270 MHz) 6.98 (1H, dt, J 15.5, 3.5 Hz, H-3), 6.06 (1H, dt, J 15.5, 2.0 Hz, H-2), 4.27 (2H, dd, J 3.5, 2.0 Hz, H-4), 3.71 (3H, s, OCH_3), 0.11 (9H, s, $Si(CH_3)_3$); *m/z* (EI) 188 (M^+), 173 (M^+-CH_3), 158 (M^+-$2CH_3$), 157 (M^+-CH_3O), 129, 89, 73 ($Si(CH_3)_3$) (Found: C, 51.04; H, 8.77. $C_8H_{16}O_3Si$ requires C, 51.03; H, 8.56%).

Preparation of (*E*)-1-(phenylsulfonyl)-3-(trimethylsilyloxy)propene.

To a solution of (*E*)-3-(phenylsulfonyl)-2-propenol[10] (3.02 g, 15.25 mmol, 1 eq) in CH_2Cl_2 (70 ml) was added Et_3N (2.31 g, 3.19 ml, 22.88 mmol, 1.5 eq) at room temperature, followed by chlorotrimethylsilane (1.82 g, 2.13 ml, 16.77 mmol, 1.1 eq). After stirring for 1 h tlc showed the reaction to be complete, and the reaction mixture was poured into saturated aqueous sodium hydrogencarbonate (70 ml) and the layers separated. The aqueous phase was further extracted with CH_2Cl_2 (3 x 30 ml) and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting oil was purified by chromatography (40% ether–petrol) to yield the tms ether (3.82 g, 93%) as a white crystals, mp 42-43°C; υ_{max} (neat) 3063, 2957, 1638, 1447, 1317, 1308, 1253, 1146, 1087, 1021, 962, 880, 845, 757, 629 cm^{-1}; δ_H (270 MHz) 7.92-7.88 (2H, m, ortho C_6H_5), 7.65-7.50 (3H, m, meta and para C_6H_5), 7.04 (1H, dt, J 14.5, 3.5 Hz, H-2), 6.61 (1H, dt, J 14.5, 2.5 Hz, H-1), 4.34 (2H, dd, J 3.5, 2.5 Hz, H-3), 0.10 (9H, s, $Si(CH_3)_3$); *m/z* (CI) 288 (MNH_4^+), 271 (MH^+), 255 (MH^+-O), 129, 113, 90, 73.

Preparation of ethyl (*E*)-2-methyl-4-(trimethylsilyloxy)-2-butenoate.

To a solution of ethyl (*E*)-2-methyl-4-hydroxy-2-butenoate[31] (1.40 g, 9.72 mmol, 1 eq) in CH_2Cl_2 (19.4 ml) at 0°C was added Et_3N (1.48 g, 2.04 ml, 14.6 mmol, 1.5 eq) followed by chlorotrimethylsilane (1.06 g, 1.23 ml, 1.1 eq). The mixture was allowed to stir for 1.5 h during which time a white precipitate formed. The mixture was poured into saturated aqueous sodium hydrogencarbonate (20 ml), the layers separated and the aqueous phase extracted with CH_2Cl_2 (3 x 10 ml). The combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting oil was purified by chromatography (25% ether–petrol), to yield *ethyl (*E*)-2-methyl-4-(trimethylsilyloxy)-2-butenoate* (1.93 g, 92%), as a colourless oil; υ_{max} (film) 2958, 2937, 1715, 1654, 1448, 1366, 1326, 1251, 1134, 1107, 1061, 887, 844, 748, 725 cm^{-1}; δ_H (270 MHz) 6.78 (1H, tq, 6.0, 1.0 Hz, H-3), 4.31 (2H, dq, J 6.0, 1.0 Hz, H-4), 4.19 (2H, q, J 7.5 Hz, OCH_2CH_3), 1.82 (3H, br s, vinylic Me), 1.30 (3H, t, J 7.5 Hz, OCH_2CH_3), 0.14 (9H, s, $Si(CH_3)_3$); *m/z* (CI) 234 (MNH_4^+), 217 (MH^+), 187 (M^+-Et), 171 (M^+-$C(Me)_3$), 144 (MH^+-$SiMe_3$), 90 (Me_3SiOH^+), 73 (CO_2Et^+) (Found (MH^+), 217.1260. $C_{10}H_{20}O_3Si$ requires (MH^+), 217.1260).

Preparation of (+)-[4*S*]-methyl (*E*)-4-(trimethylsilyloxy)-2-pentenoate.

To a solution of (+)-[4*S*]-methyl (*E*)-4-hydroxy-2-pentenoate[11] (1.5 g, 11.54 mmol, 1 eq) in CH_2Cl_2 (23.1 ml) at 0°C was added Et_3N (2.41 ml, 1.75 g, 17.31 mmol, 1.5 eq), followed by chlorotrimethylsilane (1.61 ml, 1.38 g, 14.83 mmol, 1.1 eq). The mixture was allowed to stir for 2 h during which time a white precipitate formed. The mixture was poured into saturated aqueous sodium hydrogencarbonate (20 ml), the layers separated and the aqueous phase extracted with CH_2Cl_2 (3 x 10 ml). The combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. The resulting oil was purified by chromatography (25% ether–petrol), to yield *(+)-[4S]-methyl (*E*)-4-(trimethylsilyloxy)-2-pentenoate* (2.16 g, 93%) as a colourless oil, $[\alpha]_D^{20}$ +1.91 (*c* 1.23, $CHCl_3$); υ_{max} (film) 2953, 1729, 1665, 1439, 1371, 1298, 1253, 1163, 1096, 1057, 980, 1057, 980, 926, 893, 843, 750 cm^{-1}; δ_H (270 MHz) 6.93 (1H, dd, J 15.5, 4.5 Hz, H-3), 6.00 (1H, dd, J 15.5, 1.5 Hz, H-2), 4.43 (1H, m, H-4), 3.72 (3H, s, OCH_3), 1.25 (3H, d, J 7.0 Hz, H-5), 0.12 (9H, s, $Si(CH_3)_3$); *m/z* (CI) 202 (MNH_4^+), 203 (MH^+), 187 (M^+-Me), 130 (MH^+-$SiMe_3$), 90 (Me_3SiOH^+) (Found: (MNH_4^+), 220.1366. $C_9H_{18}O_3Si$ requires (MNH_4^+), 220.1369).

Preparation of (*E*)-2-(phenylsulfonyl)-4-(trimethylsilyloxy)-2-butene and (*Z*)-2-(phenylsulfonyl)-4-(trimethylsilyloxy)-2-butene.

To a solution of (phenylsulfonyl)ethane (2.187 g, 12.86 mmol, 1 eq) in THF (26 ml) at -78°C was added LDA (28.3 ml of a 1M solution in THF, 28.3 mmol, 2.2 eq). The mixture was allowed to stir for 10 min, giving a bright yellow solution. Diethyl chlorophosphate (2.22 g, 1.86 ml, 12.86 mmol, 1 eq) was then added and the mixture allowed to stir for a further 10 min giving a rust-coloured solution. Crude 2-(trimethylsilyloxy)ethanal[32] (6.79 g, 51.46 mmol, 4 eq) in THF (5 ml) was added slowly causing gradual disappearance of the colour, and the solution was allowed to warm to room temperature. Water (50 ml) was added, the layers were separated, the aqueous layer was extracted with CH_2Cl_2 (3 x 25 ml) and the combined organic layers were dried ($MgSO_4$), and concentrated under reduced pressure to yield a pale yellow oil. Nmr analysis of the crude product showed this to be a ca. 3:2 mixture of the *Z* and *E* alcohols. The crude alcohols were dissolved in CH_2Cl_2 (13 ml) and cooled to 0°C. Triethylamine (2.6 ml, 1.95 g, 19.3 mmol, 1.5 eq), followed by chlorotrimethylsilane (1.8 ml, 1.54 g, 14.15 mmol, 1.1 eq) was added and the mixture allowed to stir for 1 h, during which time a white precipitate formed. The mixture was poured into saturated aqueous sodium hydrogencarbonate (10 ml) and the layers separated, the aqueous phase was extracted with CH_2Cl_2 (3 x 5 ml). The combined organic phases were dried ($MgSO_4$), and concentrated under reduced pressure. The resulting oil was purified by chromatography (15% ether–petrol) to give, in order of elution *(E)-2-(phenylsulfonyl)-4-(trimethylsilyloxy)-2-butene* (1.62 g, 44%) and *(Z)-2-(phenylsulfonyl)-4-(trimethyl-*

silyloxy)-2-butene (1.08 g, 30%), both as colourless oils; less polar *E*-isomer: υ_{max} (film) 3065, 2957, 2902, 1447, 1305, 1253, 1129, 1102, 1084, 1053, 1000, 845, 728, 691, 611 cm^{-1}; δ_H (270 MHz) 7.89-7.85 (2H, m, ortho $C_6H_5SO_2$), 7.65-7.50 (3H, m, meta and para $C_6H_5SO_2$), 6.91 (1H, tq, J 5.5, 1.5 Hz, H-3), 4.31 (2H, dq, J 5.5 , 1.0 Hz, H-4), 1.85 (3H, br s, H-1), 0.13 (9H, s, $Si(CH_3)_3$); *m/z* (CI) 302 (MNH_4^+), 285 (MH^+), 269 (M^+-Me), 230 ($PhSO_2C_4H_6OH+NH_4^+$)· 212 ($PhSO_2C_4H_6OH^+$), 195, 143, 127, 90, 73 ($Si(CH_3)_3^+$) (Found: (MNH_4^+), 302.1250. $C_{13}H_{20}O_3SSi$ requires (MNH_4^+), 302.1246); more polar *Z*-isomer: υ_{max} (film) 2958, 2926, 2901, 1447, 1370, 1306, 1253, 1157, 1096, 1050, 1023, 1000, 844, 728, 614 cm^{-1}; δ_H (270 MHz) 7.90-7.85 (2H, m, ortho $C_6H_5SO_2$), 7.67-7.52 (3H, m, meta and para $C_6H_5SO_2$), 6.13 (1H, tq, J 5.0, 1.5 Hz, H-3), 4.79 (2H, dq, J 5.0 , 2.0 Hz, H-4), 1.92 (3H, br s, H-1), 0.14 (9H, s, $Si(CH_3)_3$); *m/z* (CI) 302 (MNH_4^+), 285 (MH^+), 269 (M^+-Me), 212 ($PhSO_2C_4H_6OH^+$), 143, 125, 90, 73 ($SiMe_3^+$) (Found: (MH^+), 285.0980. $C_{13}H_{20}O_3SSi$ requires (MH^+), 285.0981).

Standard procedure for the preparation of acetals 2.

To a solution of silyl ether **1** (2 eq) and the carbonyl compound (1 eq) in CH_2Cl_2 (0.5 ml per mmol carbonyl compound) at -78°C was added TMSOTf (0.2 eq). The reaction mixture was stirred for 3 h, and then pyridine (0.3 eq) was added. The mixture was poured into a saturated aqueous sodium hydrogencarbonate–CH_2Cl_2 bilayer and the layers separated. Extraction of the aqueous layer with CH_2Cl_2 followed by drying ($MgSO_4$) of the combined organic layers and removal of the solvents by evaporation under reduced pressure gave the crude acetal, which was purified by chromatography.

Preparation of 2,2-bis[(*E*)-3-(methoxycarbonyl)-2-propenyloxy]propane (2a).

Acetal **2a** was prepared in 74% yield on a 1.24 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 2993, 2951, 2909, 2853, 1719, 1663, 1438, 1384, 1308, 1279, 1237, 1209, 1155, 1108, 1022, 967, 919, 870, 734, 683, 647 cm^{-1}; δ_H (270 MHz) 6.94 (2H, dt, J 15.5, 4.0 Hz, H-2), 6.07 (2H, dt, J 15.5, 2.0 Hz, H-3), 4.10 (4H, dd, J 4.0, 2.0 Hz, H-1), 3.72 (6H, s, OCH_3), 1.39 (6H, s, $C(CH_3)_2$); *m/z* (EI) 257 (M^+-CH_3), 157 ($CH_3OCOCHCHCH_2C(CH_3)_2^+$), 99 ($CH_3OCOCHCHCH_2^+$), 59 ($CH_3OCO^+$), 43 ($CH_3CO^+$) (Found: C, 57.13; H, 7.45. $C_{13}H_{20}O_6$ requires C, 57.34; H, 7.40%).

Preparation of 2,2-bis-[(*E*)-3-(ethoxycarbonyl)-2-butenyloxy]propane (2b).

Acetal **2b** was prepared in 58% yield on a 0.94 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 2988, 2360, 1714, 1659, 1558, 1540, 1455, 1368, 1326, 1256, 1034, 843, 782, 730, 668 cm^{-1}; δ_H (270 MHz) 6.77 (2H, tq, J 6.0, 1.0 Hz, H-2), 4.19 (4H, q, J 7.0 Hz, OCH_2CH_3), 4.17 (4H, dq, J 6.0, 1.0 Hz, H-1), 1.83 (6H, br s, H-4), 1.43 (6H, s, $C(CH_3)_2$), 1.29 (6H, t, J 7.0 Hz, OCH_2CH_3); *m/z* (CI) 346 (MNH_4^+), 270, 185 (M^+-$C_7H_{11}O_3$), 127 ($C_7H_{11}O_2^+$) (Found: (MNH_4^+), 346.2228. $C_{17}H_{28}O_6$ requires (MNH_4^+), 346.2229).

Preparation of (-)-[2*S*,2'*S*]-bis[(*E*)-4-methoxycarbonyl-3-buten-2-yloxy]propane (2c).

Acetal **2c** was prepared in 48% yield on a 1.46 mmol scale according to the standard procedure. Colourless oil; $[\alpha]_D^{20}$ -24.6 (*c* 1.23, $CHCl_3$); υ_{max} (film) 2988, 2952, 1726, 1661, 1436, 1377, 1349, 1297, 1274, 1196, 1163, 1091, 1046, 1016, 979 cm^{-1}; δ_H (270 MHz) 6.93 (1H, dd, J 15.5, 5.0 Hz, H-3), 5.93 (1H, dd, J 16.0, 1.5 Hz, H-4), 4.50 (1H, m, H-2), 3.74 (3H, s, OCH_3), 1.32 (6H, s, $C(CH_3)_2$), 1.25 (3H, d, J 6.5 Hz, H-1); *m/z* (CI) 318 (MNH_4^+), 301 (MH^+), 171 (M^+-$MeO_2CCHCHCH(Me)O$), 148 130, 113, 81, 58 (Found: (MH^+), 301.1646. $C_{15}H_{24}O_6$ requires (MH^+), 301.1651).

Preparation of 2,2-bis[(*E*)-3-(phenylsulfonyl)-2-propenyloxy]propane (2d).

Acetal **2d** was prepared in 76% yield on a 3.02 mmol scale according to the standard procedure. Colourless crystalline solid, mp 104-105.5°C; υ_{max} (Nujol) 1306, 1277, 1217, 1197, 1147, 1105, 1084, 1017, 969, 943, 897, 823, 766, 756, 688, 623 cm^{-1}; δ_H (500 MHz) 7.91-7.88 (4H, m, ortho $C_6H_5SO_2$), 7.65-7.62 (2H, m, para $C_6H_5SO_2$), 7.58-7.54 (4H, m, meta $C_6H_5SO_2$), 6.94 (2H, dt, J 15.0, 3.5 Hz, H-2), 6.59 (2H, dt, J 15.0, 2.0 Hz, H-3), 4.09 (4H, dd, J 3.5, 2.0 Hz, H-1), 1.34 (6H, s, $C(CH_3)_2$); *m/z* (EI) 437 (MH^+), 421 (M^+-CH_3), 354, 238 ($C_6H_5SO_2CHCHCH_2OC(CH_2)CH_3{}^+$), 198, 181 ($C_6H_5SO_2CHCHCH_2{}^+$), 169, 124, 77 (Found: C, 57.53; H, 5.37. $C_{21}H_{24}O_6S_2$ requires C, 57.78; H, 5.54%).

Preparation of 2,2-bis[(*E*)-3-(phenylsulfonyl)-2-butenyloxy]propane (2e).

Acetal **2e** was prepared in 48% yield on a 2.34 mmol scale according to the standard procedure. Colourless crystalline solid, mp 98-99.5°C; υ_{max} ($CHCl_3$) 3064, 2992, 2934, 2867, 1447, 1380, 1304, 1252, 1208, 1158, 1083, 1030, 946, 853, 734 cm^{-1}; δ_H (270 MHz) 7.89-7.84 (4H, m, ortho $C_6H_5SO_2$), 7.67-7.50 (6H, m, meta and para $C_6H_5SO_2$), 6.92 (2H, tq, J 5.5, 1.5 Hz, H-2), 4.13 (4H, dq, J 5.5, 1.0 Hz, H-1), 1.83 (6H, br s, H-4), 1.38 (6H, s, $C(CH_3)_2$); *m/z* (CI) 482 ($MNH_4{}^+$), 328, 270, 253 (M^+-$PhSO_2C(CH_3)CHCH_2O$), 230 ($PhSO_2C_4H_6OH$+$NH_4{}^+$), 195, 142, 125 (Found: ($MNH_4{}^+$), 482.1689. $C_{23}H_{28}O_6S_2$ requires ($MNH_4{}^+$), 482.1671).

Preparation of 2,2-bis[(*Z*)-3-(phenylsulfonyl)-2-butenyloxy]propane (2f).

Acetal **2f** was prepared in 57% yield on a 1.24 mmol scale according to the standard procedure. Colourless crystalline solid, mp 94-96°C; υ_{max} ($CHCl_3$) 3065, 2990, 2926, 2865, 1447, 1382, 1305, 1210, 1157, 1135, 1028, 865, 813, 730, 664 cm^{-1}; δ_H (270 MHz) 7.90-7.85 (4H, m, ortho $C_6H_5SO_2$), 7.66-7.51 (6H, m, meta and para $C_6H_5SO_2$), 6.15 (2H, tq, J 5.0, 1.5 Hz, H-2), 4.65 (4H, dq, J 5.0, 2.0 Hz, H-1), 1.92 (6H, br s, H-4), 1.41 (6H, s, $C(CH_3)_2$); *m/z* (CI) 482 ($MNH_4{}^+$), 368, 230 ($PhSO_2C_4H_6OH$+$NH_4{}^+$), 195 ($PhSO_2C_4H_6{}^+$), 125 (Found: ($MNH_4{}^+$), 482.1690. $C_{23}H_{28}O_6S_2$ requires ($MNH_4{}^+$), 482.1671).

Preparation of 1,1-bis[(*E*)-3-(methoxycarbonyl)-2-propenyloxy]cyclohexane (2g).

Acetal **2g** was prepared in 76% yield on a 0.85 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 2950, 2857, 1726, 1664, 1438, 1336, 1305, 1274, 1193, 1170, 1116, 1098, 1081, 1039, 1022 cm^{-1}; δ_H (270 MHz) 6.97 (1H, dt, J 15.5, 3.5 Hz, H-2'), 6.11 (1H, dt, J 15.5, 2.0 Hz, H-3'), 4.09 (2H, dd, J 3.5, 2.0 Hz, H-1'), 3.74 (6H, s, OCH_3'), 1.71-1.38 (10H, m, C_6H_{10}); *m/z* (CI) 330 ($MNH_4{}^+$), 197 (MH^+-$MeO_2CC_3H_4OH$), 134, 116 ($MeO_2CC_3H_4OH)^+$, 99 ($C_6H_{11}O)^+$ (Found: ($MNH_4{}^+$), 330.1918. $C_{16}H_{24}O_6$ requires ($MNH_4{}^+$), 330.1917).

Preparation of (-)-[3*R*,5*R*]-3,5-dimethyl-1,1-bis-[(*E*)-3-(methoxycarbonyl)-2-propenyloxy]-cyclohexane (2h).

Acetal **2h** was prepared in 56% yield on a 0.83 mmol scale according to the standard procedure. Colourless oil; $[\alpha]_D^{20}$ -13.9 (*c* 0.99, $CHCl_3$); υ_{max} (film) 2952, 2928, 2872, 2847, 1726, 1665, 1437, 1341, 1304, 1274, 1193, 1168, 1126, 1099, 1023 cm^{-1}; δ_H (270 MHz) 6.96 (2H, dt, J 15.5, 4.0 Hz, H-2'), 6.10 (2H, dt, J 15.5, 2.0 Hz, H-3'), 4.08 (4H, dd, J 4.0, 2.0 Hz, H-1'), 3.74 (6H, s, OCH_3), 1.99-1.91 (2H, m, H-3 and H-5), 1.76 (2H, dd, J 13.5, 4.5 Hz, H-2_{eq} and H-6_{ax}), 1.46 (2H, dd, J 13.5, 7.0 Hz, H-2_{ax} and H-6_{eq}), 1.30 (2H, t, J 6.0 Hz, H-4), 0.97 (6H, d, J 7.0 Hz, C-3' and C-5' CH_3); *m/z* (CI) 358 ($MNH_4{}^+$), 283, 225 (MH^+-$MeO_2CC_3H_4OH$), 144, 134, 99.

Preparation of (+)-[2*S*,5*R*]-2-isopropyl-5-methyl-1,1-bis[(*E*)-3-(methoxycarbonyl)-2-propenyloxy]cyclohexane (2i).

Acetal **2i** was prepared in 7% yield on a 1.24 mmol scale according to the standard procedure. Colourless oil; $[\alpha]_D^{20}$ +13.1 (*c* 0.51, $CHCl_3$); υ_{max} (film) 2953, 2928, 2870, 1728, 1664, 1437, 1304, 1273, 1195, 1167, 1121, 1096, 760 cm^{-1}; δ_H (270 MHz) 6.99 (1H, dt, J 15.5, 4.0 Hz, H-2' or H-2"), 6.97 (1H, dt, J 15.5, 4.0 Hz, H-2" or H-2'), 6.15 (1H, dt, J 15.5, 2.0 Hz, H-3' or H-3"), 6.10 (1H, dt, J 15.5, 2.0 Hz, H-3" or H-3'), 4.18 (2H, dd, J 4.0, 2.0 Hz, H-1' or H-1"), 4.06 (2H, dd, J 4.0, 2.0 Hz, H-1" or H-1'), 3.77 (3H, s, OCH_3' or OCH_3"), 3.76 (3H, s, OCH_3" or OCH_3'), 1.95-1.21 (9H, m, H-2, H-3, H-4, H-5, H-6 and C-2 $C\mathit{H}(CH_3)_2$), 1.13 (3H, d, J 6.5 Hz, C 5 CH_3), 1.02 and 0.97 (both 3H, d, J 6.5, C-2 $CH(C\mathit{H}_3)_2$); *m/z* (CI) 344 (MNH_4^+), 327 (MH^+), 326 $(M)^+$, 211 $(M^+\text{-}MeO_2CC_3H_4O)^+$, 99 $(C_6H_{11}O)^+$ (Found (M^+), 326.1733. $C_{17}H_{26}O_6$ requires (M^+), 326.1729).

Preparation of bis[(*E*)-3-(methoxycarbonyl)-2-propenyloxy]phenylmethane (2j).

Acetal **2j** was prepared in 70% yield on a 3.08 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 3032, 2951, 1721, 1665, 1495, 1438, 1302, 1171, 1025, 836, 741, 703 cm^{-1}; δ_H (270 MHz) 7.50-7.47 (2H, m, ortho C_6H_5), 7.41-7.35 (3H, m, meta and para C_6H_5), 6.96 (2H, dt, J 15.5, 4.5 Hz, H-2), 6.14 (2H, dt, 15.5, 2.0 Hz, H-3), 5.71 (1H, s, $CH(OR)_2$), 4.20 (4H, dd, J 4.5, 2.0 Hz, H-1), 3.75 (6H, s, OCH_3); *m/z* (LSIMS) 647 ($2M+Li^+$), 327 ($M+Li^+$), 205, 160, 99, 71 (Found: C, 63.80; H, 6.42. $C_{17}H_{20}O_6$ requires C, 63.74; H, 6.29%).

Preparation of bis[(*E*)-3-(ethoxycarbonyl)-2-butenyloxy]phenylmethane (2k).

Acetal **2k** was prepared in 79% yield on a 1.43 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 2979, 2347, 1708, 1655, 1451, 1367, 1325, 1250, 1135, 1033, 865, 739, 703 cm^{-1}; δ_H (270 MHz) 2.53-2.46 (2H, m, ortho C_6H_5), 7.43-7.28 (3H, m, meta and para C_6H_5), 6.84 (2H, tq, J 6.0, 1.0 Hz, H-2), 5.65 (1H, s, $CH(OR)_2$), 4.20 (8H, m, H-1 and $OC\mathit{H}_2CH_3$), 1.82 (6H, br s, H-4), 1.30 (6H, t, J 7.5 Hz, $OCH_2C\mathit{H}_3$); *m/z* (CI) 394 (MNH_4^+), 270, 233 ($M^+\text{-}EtO_2CC_4H_6O$), 127 ($EtO_2CC_4H_6^+$), 105 (Found: C, 66.82; H, 7.47. $C_{21}H_{28}O_6$ requires C, 66.99; 7.50%.).

Preparation of [2*S*,2'*S*]-bis[(*E*)-4-methoxycarbonyl-3-buten-2-yloxy]phenylmethane (2l).

Acetal **2l** was prepared in 72% yield on a 2.38 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 3031, 2979, 2952, 1725, 1662, 1437, 1371, 1301, 1276, 1196, 1091, 1029, 862, 765, 703 cm^{-1}; δ_H (270 MHz) 7.49-7.31 (5H, m, C_6H_5), 6.82 and 6.80 (both 1H, dd, J 15.5, 5.0 Hz, H-3 and H-3'), 5.93 and 5.87 (both 1H, dd, J 15.5, 1.5 Hz, H-4 and H-4'), 5.51 (1H, s, $CH(OR)_2$), 4.49 and 4.20 (both 1H, m, H-2 and H-2'), 3.74 and 3.72 (both 3H, s, 2 x OCH_3), 1.31 and 1.26 (both 3H, d, J 6.5 Hz, $CHC\mathit{H}_3$); *m/z* (CI) 366 (MNH_4^+), 219 ($M^+\text{-}MeO_2CCHCHCH(Me)O$), 130, 113 (Found: C, 65.50; H, 6.65%. $C_{19}H_{24}O_6$ requires C, 65.49; H, 6.95%).

Preparation of phenylbis[(*E*)-3-(phenylsulfonyl)-2-propenyloxy]methane (2m).

Acetal **2m** was prepared in 75% yield on a 2.07 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 3062, 2960, 2897, 2854, 1743, 1634, 1476, 1446, 1395, 1360, 1313, 1281, 1206, 1147, 1085, 1026, 945, 835, 756, 717, 690, 625 cm^{-1}; δ_H (500 MHz) 7.91-7.86 (4H, m, ortho $C_6H_5SO_2$), 7.66-7.51 (6H, m, meta and para $C_6H_5SO_2$), 7.37-7.32 (5H, m, C_6H_5), 6.94 (2H, dt, J 15.0, 3.5 Hz, H-2), 6.64 (2H, dt, J 15.0, 2.0 Hz, H-3), 5.63 (1H, s, $CH(OR)_2$), 4.21 (2H, ddd, J 17.0, 3.5, 2.0 Hz, H-1, H-1') and 4.17 (2H, ddd, J 17.0, 3.5, 2.0 Hz, H-1, H-1') *m/z* (CI) 502 (MNH_4^+), 287 (M^+-$PhSO_2CHCHCH_2O$), 216, 160, 106, 78 (Found: (MNH_4^+), 502.1400. $C_{25}H_{24}O_6S_2$ requires (MNH_4^+), 502.1358).

Preparation of phenylbis[(*E*)-3-(phenylsulfonyl)-2-butenyloxy]methane (2n).

Acetal **2n** was prepared in 80% yield on a 1.70 mmol scale according to the standard procedure. Colourless, viscous oil; υ_{max} (film) 3063, 2923, 2885, 2861, 1974, 1905, 1821, 1656, 1607, 1584, 1447, 1304, 1208, 948, 733 cm^{-1}; δ_H (270 MHz) 7.88-7.83 (4H, m, ortho $C_6H_5SO_2$), 7.64-7.50 (6H, m, meta and para $C_6H_5SO_2$), 7.46-7.33 (5H, m, C_6H_5), 6.96 (6H, tq, J 5.5, 1.5 Hz, H-2), 5.64 (1H, s, $CH(OR)_2$), 4.20 (4H, dq, J 5.5, 1.0 Hz, H-1), 1.80 (6H, s, H-4); *m/z* (CI) 530 (MNH_4^+), 301 (M^+-$PhSO_2C_4H_6O$), 230 ($PhSO_2C_4H_6OH$+NH_4^+), 214, 125, 105, 78 (Found: (MNH_4^+), 530.1699. $C_{27}H_{28}O_6S_2$ requires (MNH_4^+), 530.1671).

Preparation of phenylbis[(*Z*)-3-(phenylsulfonyl)-2-butenyloxy]methane (2o).

Acetal **2o** was prepared in 86% yield on a 1.70 mmol scale according to the standard procedure. Colourless, viscous oil; υ_{max} (film) 3064, 2924, 2864, 1651, 1584, 1477, 1447, 1380, 1305, 1157, 1135, 1035, 977, 810, 732, 690 cm^{-1}; δ_H (270 MHz) 7.88-7.80 (4H, m, ortho $C_6H_5SO_2$), 7.69-7.35 (11H, m, meta and para $C_6H_5SO_2$ and C_6H_5), 6.19 (2H, tq, J 5.0, 1.5 Hz, H-2), 5.62 (1H, s, $CH(OR)_2$), 4.20 (4H, dq, J 5.0, 2.0 Hz, H-2), 1.80 (6H, br s, H-4); *m/z* (CI) 530 (MNH_4^+), 301 (M^+-$PhSO_2C_4H_6O$), 230 ($PhSO_2C_4H_6OH$+NH_4^+), 195, 125 (Found: (MNH_4^+), 530.1670. $C_{27}H_{28}O_6S_2$ requires (MNH_4^+), 530.1671).

Standard procedure for the preparation of trienes 3 from acetals 2.

To a stirred solution of acetal **2** (1 eq) and (*E*)-5-(trimethylsilyl)-1,3-pentadiene (2 eq) in CH_2Cl_2 (1 ml per mmol acetal) at -78°C was added TMSOTf (0.2 eq). The reaction mixture was stirred for 2 h, and then pyridine (0.5 eq) was added. The mixture was poured into a saturated aqueous sodium hydrogencarbonate–CH_2Cl_2 bilayer and the layers separated. Extraction of the aqueous layer with CH_2Cl_2 followed by drying ($MgSO_4$) of the combined organic layers and removal of the solvents by evaporation under reduced pressure gave the crude acetal, which was purified by chromatography.

Standard one-pot procedure for the preparation of trienes 3 from carbonyl compounds and 1.

To a solution of the silyl ether **1** (EWG = CO_2Me, $R^1 = R^2 = H$) (2 eq), the carbonyl compound (1 eq) and (*E*)-5-(trimethylsilyl)-1,3-pentadiene (1.5 eq) in CH_2Cl_2 (1 ml per mmol acetal) at -78°C was added TMSOTf (0.2 eq). The mixture was allowed to stir for 2 h, after which pyridine (1 eq) was added. The mixture was poured into dilute aqueous HCl and the layers separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were washed with saturated aqueous sodium hydrogencarbonate and water, and dried ($MgSO_4$). Concentration under reduced pressure followed by chromatography gave the trienes.

Preparation of methyl (*E,E*)-6,6-dimethyl-5-oxa-2,8,10-undecatrienoate (3a).

Triene **3a** was prepared in 60% yield on a 1.61 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 2973, 1725, 1662, 1438, 1383, 1302, 1168, 1119, 1023, 900 cm^{-1}; δ_H (500 MHz) 7.00 (1H, dt, J 15.5, 4.0 Hz, H-3), 6.33 (1H, dt, J 17.0, 10.5 Hz, H-10), 6.11 (1H, dt, J 15.5, 2.0 Hz, H-2), 6.07 (1H, dd, J 15.5, 10.5 Hz, H-9), 5.71 (1H, dt, J 15.0, 7.5 Hz, H-8), 5.11 (1H, d, J 17.5 Hz, H-11_{trans}), 5.00 (1H, d, J 10.0 Hz, H-11_{cis}), 4.09 (2H, dd, J 4.0, 2.0 Hz, H-4), 3.74 (3H, s, OCH_3), 2.29 (2H, J 7.5 Hz, H-7), 1.18 (6H, s, $C(CH_3)_2$); *m/z* (EI) 157 (M^+-$CH_2CHCHCHCH_2$), 99 ($CH_3OCOCHCHCH_2$), 59

(CH_3OCO), 43 (CH_3CO) (Found: C, 69.55; H, 9.12. $C_{13}H_{20}O_3$ requires C, 69.61; H, 8.99%). Triene **3a** was prepared in 97% yield on a 0.61 mmol scale using the standard one-pot procedure.

Preparation of ethyl (*E*,*E*)-2,6,6-trimethyl-5-oxa-2,8,10-undecatrienoate (3b).

Triene **3b** was prepared in 67% yield on a 0.42 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 3085, 2974, 1711, 1633, 1603, 1469, 1383, 1366, 1325, 1254, 1131, 1059, 1005, 897, 730 cm^{-1}; δ_H (270 MHz) 6.78 (1H, tq, J 6.0, 1.0 Hz, H-3), 6.33 (1H, dt, J 17.0, 10.5 Hz, H-10), 6.08 (1H, dd, J 15.0, 10.5 Hz, H-9), 5.72 (1H, dt, J 15.0, 7.5 Hz, H-8), 5.11 (1H, d, J 17.0 Hz, H-11$_{trans}$), 4.99 (1H, d, J 10.5 Hz, H-11$_{cis}$), 4.18 (2H, q, 7.0 Hz, OCH_2CH_3), 4.10 (2H, dd, J 6.0, 1.0 Hz, H-4), 2.30 (2H, d, J 7.5 Hz, H-7), 1.83 (3H, br s, C2 Me), 1.29 (3H, t, J 7.0 Hz, OCH_2CH_3), 1.19 (6H, s, $C(CH_3)_2$); *m/z* (CI) 253 (MH^+), 237 (M^+-Me), 185 (M^+-C_5H_7), 143 (M^+-C_8H_{13}), 127, 96, 59 (Found: (MH^+), 253.1802. $C_{15}H_{24}O_3$ requires (MH^+), 253.1804).

Preparation of (-)-[4*S*]-methyl (*E*,*E*)-4,6,6-trimethyl-5-oxa-2,8,10-undecatrienoate (3c).

Triene **3c** was prepared in 66% yield on a 0.42 mmol scale according to the standard procedure. Colourless oil; $[\alpha]_D^{25}$ -18.9 (*c* 0.88, $CHCl_3$); υ_{max} (film) 2975, 2932, 1726, 1658, 1435, 1368, 1293, 1273, 1191, 1166, 1140, 1067, 1051, 1006, 980 cm^{-1}; δ_H (270 MHz) 6.95 (1H, dd, J 15.5, 4.5 Hz, H-3), 6.31 (1H, dt, J 17.0, 10.5 Hz, H-10), 6.09 (1H, dd, J 15.0, 10.5 Hz, H-9), 5.99 (1H, dd, J 15.5, 1.5 Hz, H-2), 5.71 (1H, dt, J 15.0, 7.5 Hz, H-8), 5.10 (1H, d, J 17.0 Hz, H-11$_{trans}$), 4.99 (1H, d, J 10.5 Hz, H-11$_{cis}$), 4.29 (1H, m, H-4), 3.74 (3H, s, OCH_3), 2.29 (1H, dd, J 14.0, 7.5 Hz, H-7), 2.23 (1H, dd, J 14.0, 7.5 Hz, H-7), 1.22 (3H, d, J 6.5 Hz, H-12), 1.15 and 1.14 (both 3H, s, $C(CH_3)_2$); *m/z* (CI) 256 (MNH_4^+), 239 (MH^+), 217, 203, 171 (M^+-C_5H_7), 113, 109 (M^+-$MeO_2CC_4H_6O$), 94, 69, 44 (Found: (MNH_4^+), 256.1921. $C_{14}H_{22}O_3$ requires (MNH_4^+), 256.1913).

Preparation of (*E*,*E*)-5,5-dimethyl-1-(phenylsulfonyl)-4-oxa-1,7,9-decatriene (3d).

Triene **3d** was prepared in 67% yield on a 0.2 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 3431, 3063, 2975, 2931, 1737, 1633, 1602, 1447, 1374, 1318, 1308, 1280, 1244, 1195, 1147, 1119, 1087, 1047, 1007, 947, 900, 750, 714, 688, 616 cm^{-1}; δ_H (270 MHz) 7.92-7.87 (2H, m, ortho $C_6H_5SO_2$), 7.65-7.50 (3H, m, meta and para $C_6H_5SO_2$), 7.03 (1H, dt, J 15.0, 3.0 Hz, H-2), 6.63 (1H, dt, J 15.0, 2.5 Hz, H-1), 6.28 (1H, dt, J 17.0, 10.5 Hz, H-9), 6.04 (1H, dd, J 15.0, 10.5 Hz, H-8), 5.63 (1H, dt, J 15.0, 7.5 Hz, H-7), 5.09 (1H, d, J 17.0 Hz, H-10$_{trans}$), 4.99 (1H, d, J 10.5 Hz, H-10$_{cis}$), 4.13 (2H, dd, J 3.0, 2.5 Hz, H-3), 2.25 (2H, d, J 7.5 Hz, H-6), 1.14 (6H, s, $C(CH_3)_2$); *m/z* (EI) 291 (M^+-CH_3), 239 (M^+-C_5H_7), 197 ($OCH_2CHCHSO_2C_6H_5$), 181 ($CH_2CHCHSO_2C_6H_5$), 125 (SOC_6H_5), 91, 77; *m/z* (CI) 324 (MNH_4^+) (Found: (MNH_4^+), 324.1633. $C_{17}H_{22}O_3S$ requires (MNH_4^+), 324.1633).

Preparation of (*E*,*E*)-6,6-dimethyl-2-(phenylsulfonyl)-5-oxa-2,8,10-undecatriene (3e).

Triene **3e** was prepared in 78% yield on a 1.12 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 3065, 2973, 2930, 1652, 1601, 1447, 1383, 1304, 1222, 1161, 1085, 1006, 901, 731, 691 cm^{-1}; δ_H (270 MHz) 7.90-7.85 (2H, m, ortho $C_6H_5SO_2$), 7.64-7.49 (3H, m, meta and para $C_6H_5SO_2$), 6.93 (1H, tq, J 5.5, 1.5 Hz, H-3), 6.33 (1H, dt, 17.0, 10.5 Hz, H-10), 6.07 (1H, dd, J 15.0, 10.5 Hz, H-9), 5.70 (1H, dt, J 15.0, 7.5 Hz, H-8), 5.11 (1H, d, J 17.0 Hz, H-11$_{trans}$), 5.00 (1H, d, J 10.5 Hz, H-11$_{cis}$), 4.10 (2H, dq, J 5.5, 1.0 Hz, H-4), 2.27 (2H, d, J 7.5 Hz, H-7), 1.86 (3H, br s, H-1), 1.17 (6H, s, $C(CH_3)_2$); *m/z* (CI) 338 (MNH_4^+), 253, 230 ($PhSO_2C(Me)CHCH_2OH+NH_4^+$), 212 ($PhSO_2C(Me)CHCH_2OH^+$), 195, 142, 125, 109 ($PhS^+$) (Found: ($MNH_4^+$), 338.1780. $C_{18}H_{24}O_3S$ requires (MNH_4^+), 338.1790).

Preparation of (2*Z*,8*E*)-6,6-dimethyl-2-(phenylsulfonyl)-5-oxa-2,8,10-undecatriene (3f).

Triene **3f** was prepared in 53% yield on a 1.61 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 3066, 2973, 2928, 1447, 1365, 1306, 1222, 1157, 1082, 1005, 874, 811, 759, 729, 690 cm^{-1}; δ_H (270 MHz) 7.91-7.85 (2H, m, ortho $C_6H_5SO_2$), 7.67-7.51 (3H, m, meta and para $C_6H_5SO_2$), 6.33 (1H, dt, 17.0, 10.5 Hz, H-10), 6.13 (1H, tq, J 5.0, 1.5 Hz, H-3), 6.08 (1H, dd, J 15.0, 10.5 Hz, H-9), 5.71 (1H, dt, J 15.0, 7.5 Hz, H-8), 5.12 (1H, d, J 17.0 Hz, H-11$_{trans}$), 5.00 (1H, d, J 10.5 Hz, H-11$_{cis}$), 4.59 (2H, dq, J 5.0, 2.0 Hz, H-4), 2.30 (2H, d, J 7.5 Hz, H-7), 1.92 (3H, br s, H-1), 1.19 (6H, s, $C(CH_3)_2$); *m/z* (CI) 338 (MNH_4^+), 230 ($PhSO_2C(Me)CHCH_2OH+NH_4^+$), 212 ($PhSO_2C(Me)CHCH_2OH^+$), 195, 125, 109 ($PhS^+$) (Found: ($MNH_4^+$), 338.1787. $C_{18}H_{24}O_3S$ requires (MNH_4^+), 338.1790).

Preparation of 1-[(*E*)-3-(methoxycarbonyl)-2-propenyloxy]-1-[(*E*)-2,4-pentadienyl]cyclohexane (3g).

Triene **3g** was prepared in 74% yield on a 0.64 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 2933, 2856, 1726, 1662, 1437, 1302, 1282, 1269, 1192, 1169, 1151, 115, 1068, 1022, 1005 cm^{-1}; δ_H (270 MHz) 6.99 (1H, dt, J 16.0, 4.0 Hz, H-2'), 6.31 (1H, dt, J 17.0, 10.5 Hz, H-4"), 6.18 (1H, dt, J 16.0, 2.0 Hz, H-3'), 6.08 (1H, dd, J 15.0, 10.5 Hz, H-3"), 5.65 (1H, dt, J 15.0, 7.5 Hz, H-2"), 5.12 (1H, d, J 17.0 Hz, H-5"$_{trans}$), 4.99 (1H, d, J 10.5 Hz, H-5"$_{cis}$), 4.06 (2H, dd, J 4.0, 2.0 Hz, H-1'), 3.76 (3H, s, OCH_3), 2.25 (2H, d, J 7.5 Hz, H-1"), 1.81-1.18 (10H, m, C_6H_{10}); *m/z* (CI) 282 (MNH_4^+), 265 (MH^+), 197 (M^+ - C_5H_7), 166, 149 (MH^+ - $MeO_2CC_3H_4OH$), 134, 99 $(C_6H_{11}O)^+$ (Found: (MNH_4^+), 282.2058. $C_{16}H_{24}O_3$ requires (MNH_4^+), 282.2069). Triene **3g** was prepared in 97% yield on a 0.53 mmol scale using the standard one-pot procedure.

Preparation of (-)-[3*R*,5*R*]-1-[(*E*)-3-(methoxycarbonyl)-2-propenyloxy]-3,5-dimethyl-1-[(*E*)-2,4-pentadienyl]cyclohexane (3h).

Triene **3h** was prepared in 75% yield on a 0.37 mmol scale according to the standard procedure. Colourless oil, $[\alpha]_D^{20}$ -12.5 (*c* 0.82, $CHCl_3$); υ_{max} (film) 3011, 2983, 2950, 2923, 2913, 2868, 2842, 1725, 1664, 1459, 1436, 1301, 1283, 1168, 1120 cm^{-1}; δ_H (270 MHz) 6.99 (1H, dt, J 15.5, 4.0 Hz, H-2'), 6.31 (1H, dt, J 17.0, 10.5 Hz, H-4"), 6.12 (1H, dt, J 15.5, 2.0 Hz, H-3'), 6.03 (1H, dd, J 15.0, 10.5 Hz, H-3"), 5.64 (1H, dt, J 15.0, 7.5 Hz, H-2"), 5.09 (1H, d, J 17.0 Hz, H-5"$_{trans}$), 4.98 (1H, d, J 10.5 Hz, H-5"$_{cis}$), 4.03 (2H, dd, J 4.0, 2.0 Hz, H-1'), 3.74 (3H, s, OCH_3), 2.21 (2H, d, J 7.5 Hz, H-1"), 1.98-1.82 (1H, m, H-5), 1.79 (1H, ddd, J 13.0, 4.5, 2.5 Hz, H-6$_{eq}$), 1.69 (1H, ddd, J 13.5, 3.5, 2.0 Hz, H-4$_{eq}$), 1.48 (1H, br d, J 14.0 Hz, H-2$_{eq}$), 1.31 (1H, dd, J 14.0, 6.0 Hz, H-2$_{ax}$), 1.13-0.99 (1H, m, H-3), 1.07 (3H, d, J 7.5 Hz, C-5 CH_3 or C-3 CH_3), 0.92-0.82 (2H, m, H-4$_{ax}$ and H-6$_{ax}$), 0.87 (3H, d, J 6.5 Hz, C-3 CH_3 or C-5 CH_3); *m/z* (CI) 310 (MNH_4^+), 293 (MH^+), 225 (M^+ - C_5H_7), 194, 177 (MH^+ - $MeO_2CC_3H_4OH$), 134, 99 $(C_6H_{11}O)^+$ (Found: (MH^+), 293.2126. $C_{18}H_{28}O_3$ requires (MH^+), 293.2117). Triene **3h** was prepared in 65% yield on a 0.57 mmol scale using the standard one-pot procedure.

Preparation of (+)-[1*R*,2*S*,5*R*]-1-[(2*E*)-3-(methoxycarbonyl)-2-propenyloxy]-5-methyl-1-[(*E*)-2,4-pentadienyl]-2-isopropylcyclohexane (3i).

Triene **3i** was prepared in 72% yield on a 0.08 mmol scale according to the standard procedure. Colourless oil, $[\alpha]_D^{20}$ +23.45 (*c* 0.37, $CHCl_3$); υ_{max} (film) 2990, 2952, 2925, 2869, 1726, 1663, 1454, 1437, 1299, 1285, 1270, 1169, 1115, 1023, 1006 cm^{-1}; δ_H (500 MHz) 7.00 (1H, dt, J 15.5, 3.5 Hz, H-2'), 6.31 (1H, dt, J 17.0, 10.5 Hz, H-4"), 6.13 (1H, dt, J 15.5, 2.0 Hz, H-3'), 6.07 (1H, dd, J 15.0, 10.5 Hz, H-3"), 5.57 (1H, dt, J 15.0, 7.5 Hz, H-2"), 5.11 (1H, d, J, 15.0 Hz, H-5"$_{trans}$), 5.00 (1H, d, J 10.5 Hz, H-5"$_{cis}$), 4.06 (1H, ddd, J 16.5, 3.5, 2.0 Hz, H-1'), 4.00 (1H, ddd, J 16.5, 3.5, 2.0 Hz, H-1'), 3.74 (3H, s, OCH_3), 2.52 (1H, dd, J 13.5, 7.5 Hz, H-1"), 2.29 (1H, dd, J 13.5, 7.5 Hz, H-1"), 2.13 (1H, septet, J 6.5 Hz, C-2 $C\mathit{H}(CH_3)_2$), 1.77-1.70 (2H, m, H-4$_{eq}$ and H-6$_{eq}$), 1.60 (1H, dddd, J 13.0, 12.5, 12.0, 3.5 Hz, H-3$_{ax}$), 1.54-1.47 (1H, m, H-5), 1.41 (1H, dddd, J 13.0, 6.5, 3.5, 3.0 Hz, H-3$_{eq}$), 1.13 (1H, ddd, J 12.5, 3.5, 1.5 Hz, H-2), 1.01-0.90 (4H, overlapping d and m, J 7.0 Hz, C-2 $CH(C\mathit{H}_3)_2$ and H-6$_{ax}$), 0.89-0.75 (4H, overlapping d and m, J 7.0 Hz, C-2 $CH(C\mathit{H}_3)_2$ and H-4$_{ax}$), 0.83 (3H, d, J 6.5 Hz, C-5 Me); *m/z* (CI) 338 (MNH_4^+), 321 (MH^+), 253 (M^+-C_5H_7), 205 (M^+-$MeO_2CC_3H_4O$), 163, 134, 99 ($C_6H_{11}O^+$) (Found: (MNH_4^+), 338.2690. $C_{20}H_{32}O_3$ requires (MNH_4^+), 338.2695). Triene **3i** was prepared in 17% yield on a 0.53 mmol scale using the standard one-pot procedure.

Preparation of (±)-methyl (*E*,*E*)-6-phenyl-5-oxa-2,8,10-undecatrienoate (3j).

Triene **3j** was prepared in 62% yield on a 2.09 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 3030, 2950, 2848, 1727, 1665, 1435, 1302, 1171, 1124, 1006, 964, 903, 837, 760, 703 cm^{-1}; δ_H (500 MHz) 7.36-7.33 (2H, m, ortho C_6H_5), 7.30-7.26 (3H, m, meta and para C_6H_5), 6.92 (1H, dt, J 16.0, 4.0 Hz, H-3), 6.29 (1H, dt, J 17.0, 10.5 Hz, H-10), 6.13 (1H, dt, 16.0, 2.0 Hz, H-2), 6.07 (1H, dd, J 15.5, 10.5 Hz, H-9), 5.66 (1H, dt, J 15, 7.5 Hz, Hz, H-8), 5.09 (1H, d, J 16.5 Hz, H-11$_{trans}$), 4.99 (1H, d, J 10.0 Hz, H-11$_{cis}$), 4.32 (1H, dd, J 7.5, 6.0 Hz, H-6), 4.03 (1H, ddd, J 16.0, 4.0, 2.0 Hz, H-4), 3.94 (1H, ddd, J 16.0, 4.5, 2.0 Hz, H-4), 3.74 (3H, s, OCH_3), 2.64-2.60 (1H, m, H-7), 2.48-2.43 (1H, m, H-7); *m/z* (EI) 272 (M^+), 241 (M^+-OCH_3), 205 (M^+-$CH_2CHCHCHCH_2$), 99 ($CH_2CHCHCO_2CH_3^+$), 77, 59 (Found: (M^+), 272.1414. $C_{17}H_{20}O_3$ requires (M^+), 272.1412). Triene **3j** was prepared in 98% yield on a 0.48 mmol scale using the standard one-pot procedure.

Preparation of (±)-ethyl (*E*,*E*)-2-methyl-6-phenyl-5-oxa-2,8,10-undecatrienoate (3k).

Triene **3k** was prepared in 86% yield on a 1.13 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 2978, 1712, 1655, 1604, 1494, 1453, 1367, 1323, 1253, 1134,1069, 1005, 902, 759, 702 cm^{-1}; δ_H (270 MHz) 7.40-7.24 (5H, m, C_6H_5), 6.81 (1H, tq, J 6.0, 1.0 Hz, H-4), 6.28 (1H, dt, J 17, 10.5 Hz, H-10), 6.06 (1H, dd, J 15.0, 10.5 Hz, H-9), 5.65 (1H, dt, J 15.0, 7.5 Hz, H-8), 5.12 (1H, d, J 17.0 Hz, H-11$_{trans}$), 4.99 (1H, d, J 10.5 Hz, H-11$_{cis}$), 4.29 (1H, dd, J 7.5, 6.0 Hz, H-6), 4.30 (2H, q, J 7.0 Hz, $OC\mathit{H}_2CH_3$), 4.05 (1H, ddq, J 14.5, 6.0, 1.0 Hz, H-4), 3.99 (1H, ddq, J 14.5, 6.0, 1.0 Hz, H-4), 2.55 (1H, m, H-7), 1.83 (3H, br s, H-12), 1.29 (3H, t, J 7.0 Hz, $OCH_2C\mathit{H}_3$); *m/z* (CI) 318 (MNH_4^+), 233 (M^+-C_5H_7), 197, 174, 157, 127 (Found: (MNH_4^+), 318.2085. $C_{19}H_{24}O_3$ requires (MNH_4^+), 318.2069).

Preparation of (-)-[4*S*,6*S*]-methyl (2*E*,8*E*)-4-methyl-6-phenyl-5-oxa-2,8,10-undecatrienoate ([4*S*,6*S*]-3l) and (-)-[4*S*,6*R*]-methyl (2*E*,8*E*)-4-methyl-6-phenyl-5-oxa-2,8,10-undecatrienoate ([4*S*,6*R*]-3l).

Trienes **3l** were prepared in 68% yield on a 1.72 mmol scale according to the standard procedure. The epimers were inseparable by flash chromatography, but could be separated in small quantities by chiral HPLC (elution with 3% EtOH–hexane for 35 min, followed by 12% EtOH–hexane). The first eluted, major component was [4*S*,6*S*]-**3l** as a colourless oil, retention time 37.50 min; $[\alpha]_D^{20}$ -82.7 (*c* 0.38, $CHCl_3$); υ_{max} (film) 3027, 2976, 2950, 2931, 2907, 1727, 1435, 1301, 1274, 1194, 1171, 1146, 1083, 1006, 702 cm^{-1}; δ_H (270 MHz) 7.38-7.23 (5H, m, C_6H_5), 6.82 (1H, dd, J 16.0, 7.0 Hz, H-3), 6.28 (1H, dt, J 17.0, 10.5 Hz, H-10), 6.04 (1H, dd, J 15.0, 10.5 Hz, H-9), 5.92 (1H, dd, J 16.0, 1.0 Hz, H-2), 5.60 (1H, dt, J 15.0, 7.5 Hz, H-8), 5.08 (1H, d, J 17.0 Hz, H-11$_{trans}$), 4.97 (1H, d, J 10.5 Hz, H-11$_{cis}$), 4.28 (1H, dd, J 7.0, 6.0 Hz, H-6), 3.92-3.82 (1H, m, H-4), 3.76 (3H, s, OCH_3), 2.64-2.53 (1H, m, H-7), 2.46-2.35 (1H, m, H-7), 1.20

(3H, d, J 7.0 Hz, C-4 CH_3); *m/z* (CI) 304 (MNH_4^+), 287 (MH^+), 269, 255 (M^+-OMe), 242, 219 (M^+-C_5H_7), 209 (M^+-Ph), 183, 174, 157, 113, 85 (Found: (MNH_4^+), 304.1913. $C_{18}H_{22}O_3$ requires (MNH_4^+), 304.1913). The second eluted, minor component was [4*S*,6*R*]-**3l** as a colourless oil, retention time 41.47 min; $[\alpha]_D^{20}$ -19.38 (*c* 0.33, $CHCl_3$); υ_{max} (film) 3027, 2976, 2950, 2931, 1727, 1453, 1435, 1301, 1274, 1194, 1171, 1147, 1084, 1006, 702 cm^{-1}; δ_H (270 MHz) 7.39-7.22 (5H, m, C_6H_5), 6.79 (1H, dd, J 15.5, 5.0 Hz, H-3), 6.29 (1H, dt, J 17.0, 10.5 Hz, H-10), 6.04 (1H, dd, J 15.0, 10.5 Hz, H-9), 5.97 (1H, dd, J 15.5, 2.0 Hz, H-2), 5.66 (1H, dt, J 15.0, 7.5 Hz, H-8), 5.09 (1H, d, J 17.0 Hz, H-11_{trans}), 4.98 (1H, d, J 10.5 Hz, H-11_{cis}), 4.41 (1H, dd, J 7.5, 5.5 Hz, H-6), 4.05-3.95 (1H, m, H-4), 3.71 (3H, s, OCH_3), 2.64-2.53 (1H, m, H-7), 2.46-2.35 (1H, m, H-7), 1.20 (3H, d, J 6.5 Hz, C-4 CH_3); *m/z* (CI) 304 (MNH_4^+), 287 (MH^+), 269, 255 (M^+-OMe), 219 (M^+-C_5H_7), 183, 174, 157, 113 (Found: (MNH_4^+), 304.1923. $C_{18}H_{22}O_3$ requires (MNH_4^+), 304.1913).

Preparation of (±)-(*E*,*E*)-5-phenyl-1-(phenylsulfonyl)-4-oxa-1,7,9-decatriene (3m).

Triene **3m** was prepared in 74% yield on a 0.89 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 3061, 2910, 2863, 1638, 1605, 1492, 1450, 1311, 1280, 1199, 1147, 1122, 1086, 1007, 948, 905, 837, 756, 703, 687, 618 cm^{-1}; δ_H (270 MHz) 7.92-7.88 (2H, m, ortho $C_6H_5SO_2$), 7.67-7.52 (3H, m, meta and para $C_6H_5SO_2$), 7.38-7.19 (5H, m, C_6H_5), 6.92 (1H, dt, J 15.0, 3.5 Hz, H-2), 6.68 (1H, dt, J 15.0, 2.0 Hz, H-1), 6.25 (1H, dt, J 17.0, 10.5 Hz, H-9), 6.04 (1H, dd, J 15.0, 10.5 Hz, H-8), 5.60 (1H, dt, J 15.0, 7.5 Hz, H-7), 5.07 (1H, d, J 17.0 Hz, H-10_{trans}), 4.98 (1H, dd, J 10.0, 0.5 Hz, H-10_{cis}), 4.28 (1H, dd, J 7.5, 6.0 Hz, H-5), 4.07 and 3.94 (both 1H, ddd, J 17.5, 3.5, 2.0 Hz, H-3), 2.64-2.53 (1H, m, H-6), 2.47-2.36 (1H, m, H-6); *m/z* (EI) 354 (M^+), 287 (M^+-$CH_2CHCHCHCH_2$), 210, 181 ($PhSO_2CHCHCH_2$), 157, 125 (PhSO), 110, 106 (C_6H_5CHO) (Found: C, 70.88; H, 6.35. $C_{21}H_{22}O_3S$ requires C, 71.16; H, 6.26%).

Preparation of (±)-(*E*,*E*)-6-phenyl-2-(phenylsulfonyl)-5-oxa-2,8,10-undecatriene (3n).

Triene **3n** was prepared in 65% yield on a 1.36 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 3084, 3010, 2970, 1815, 1651, 1602, 1584, 1493, 1478, 1382, 1356, 1216, 1084, 952, 842 cm^{-1}; δ_H (270 MHz) 7.88-7.83 (2H, m, ortho $C_6H_5SO_2$), 7.65-7.50 (3H, m, meta and para $C_6H_5SO_2$), 7.38-7.22 (5H, m, C_6H_5), 6.95 (1H, tq, J 5.5, 1.5 Hz, H-3), 6.28 (1H, dt, J 17.0, 10.5 Hz, H-10), 6.06 (1H, dd, J 15.0, 10.5 Hz, H-9), 5.63 (1H, dt, J 15.0, 7.5 Hz, H-8), 5.10 (1H,d, J 17.0 Hz, H-11_{trans}), 4.99 (1H, d, J 10.5 Hz, H-11_{cis}), 4.27 (1H, dd, J 7.5, 6.0 Hz, H-5), 4.05 (1H, ddq, J 12.5, 5.5, 1.0 Hz, H-4), 3.95 (1H, ddq, J 12.5, 5.5, 1.0 Hz, H-4), 2.66-2.55 (1H, m, H-7), 2.48 (1H, m, H-7), 1.73 (3H, s, H-1); *m/z* (CI) 386 (MNH_4^+), 301, 212 ($PhSO_2C(CH_3)CHCH_2OH^+$), 174 ($PhC_6H_9O^+$), 157 ($PhC_6H_8^+$), 125 ($PhSO^+$) (Found: C, 71.71; H, 6.38%. $C_{22}H_{28}O_3S$ requires C, 71.71; H, 6.56%).

Preparation of (±)-(2*Z*,8*E*)-6-phenyl-2-(phenylsulfonyl)-5-oxa-2,8,10-undecatriene (3o).

Triene **3o** was prepared in 65% yield on a 1.99 mmol scale according to the standard procedure. Colourless oil; υ_{max} (film) 3031, 2961, 2924, 2854, 1650, 1494, 1381, 1305, 1157, 1082, 1006, 901, 879, 731, 689 cm^{-1}; δ_H (270 MHz) 7.88-7.84 (2H, m, ortho $C_6H_5SO_2$), 7.64-7.48 (3H, m, meta and para $C_6H_5SO_2$), 7.39-7.24 (5H, m, C_6H_5), 6.29 (1H, dt, J 17.0, 10.5 Hz, H-10), 6.16 (1H, tq, J 5.0, 1.5 Hz, H-3), 6.07 (1H, dd, J 15.0, 10.5 Hz, H-9), 5.63 (1H, dt, J 15.0, 7.5 Hz, H-8), 5.08 (1H, d, J 17.0 Hz, H-11_{trans}), 4.98 (1H, d, J 10.5 Hz, H-11_{cis}), 4.58 (1H, ddq, J 16.5, 5.0, 2.0 Hz, H-4), 4.48 (1H, ddq, J 16.5, 5.0, 2.0 Hz, H-4), 4.32 (1H, dd, J 7.5, 6.0 Hz, H-5), 2.66-2.55 (1H, m, H-7), 2.50-2.39 (1H, m, H-7), 1.90 (3H, br s, H-1); *m/z* (CI) 386 (MNH_4^+), 230 ($PhSO_2C(Me)CHCH_2OH$+NH_4^+) 212 ($PhSO_2C(Me){:}CHCH_2OH^+$), 195, 174 ($PhC_6H_9O^+$), 157 ($PhC_6H_8^+$), 121 (Found: (MNH_4^+), 386.1774. $C_{22}H_{24}O_3S$ requires (MNH_4^+), 386.1790).

Intramolecular Diels–Alder reactions

IMDA Reactions of trienes **3** (0.03-2.88 mmol) were carried out at 165°C on rigorously dry, degassed toluene solutions (0.05-0.15M) in base-washed, resealable Carius tubes as described previously.[9,11] On completion of reactions, toluene was removed under reduced pressure and the crude products analysed by high-field (500 MHz) ^{1}H nmr spectroscopy. Chromatography gave the pure cycloadduct(s).

IMDA Reaction of triene (3a).

IMDA Reaction of **3a** gave in 80% yield the trans-fused cycloadduct *[1R*,6S*,10R*]-10-(methoxycarbonyl)-4,4-dimethyl-3-oxabicyclo[4.4.0]-7-decene* **4a** as a colourless oil; υ_{max} 3020, 2972, 2846, 1736, 1437, 1367, 1314, 1263, 1169, 1145, 1108, 1073, 1023, 997, 917, 876, 815, 750, 707, 670 cm^{-1}; δ_H (500 MHz) 5.65-5.62 (1H, m, H-7 or H-8), 5.41 (1H, br dd, J 10.0, 1.5 Hz, H-8 or H-7), 3.65 (3H, s, OCH_3), 3.59 (1H, dd, J 11.5, 4.0 Hz, H-2), 3.41 (1H, t, J 11.5 Hz, H-2), 2.44-2.28 (3H, m, H-9, H-10), 2.20-2.15 (1H, m, H-6), 1.62 (1H, qd, J 11.0, 4.0 Hz, H-1), 1.58 (1H, dd, J 13.0, 3.5 Hz, H-5), 1.26 (1H, t, J 13.0 Hz, H-5), 1.22 and 1.21 (both 3H, s, C-4 Me); *m/z* (EI) 224 (M^+), 209 (M^+-CH_3), 193 (M^+-OCH_3), 166, 147, 107, 91, 67, 59, 43 (Found: C, 69.40; H, 9.07. $C_{13}H_{20}O_3$ requires C, 69.61; H, 8.99%).

IMDA Reaction of triene (3b).

IMDA Reaction of **3b** gave in 95% yield an inseparable 6:1 mixture of *[1R*,6S*,10R*]-10-(ethoxycarbonyl)-4,4,10-trimethyl-3-oxabicyclo[4.4.0]-7-decene* trans-**4b** and *[1R*,6R*,10R*]-10-(ethoxycarbonyl)-4,4,10-trimethyl-3-oxabicyclo[4.4.0]-7-decene* cis-**4b** as a colourless oil. Data for the mixture: υ_{max} (film) 3019, 2975, 2920, 2863, 1727, 1382, 1365, 1280, 1238, 1196, 1156, 1121, 1089, 1064, 1023 cm^{-1}; δ_H (500 MHz); 5.68-5.64 (1H, m, H-7 minor), 5.63-5.58 (1H, m, H-7 major), 5.56 (1H, br d, J 10.0 Hz, H-8 minor), 5.40 (1H, br d, J 10.0 Hz, H-8 major), 4.19-4.07 (2H, m, OCH_2CH_3 major), 4.05-4.00 (2H, m, OCH_2CH_3 minor), 3.71 (1H, dd, J 11.5, 5.0 Hz, H-2_{eq} minor), 3.59 (1H, t, J 11.5 Hz, H-2_{ax} minor), 3.50-3.43 (2H, m, H-2 major), 2.66 (1H, br d, J 18.5 Hz, H-9 major), 2.58 (1H, br d, J 18.0 Hz, H-9 minor), 2.51-2.46 (1H, m, H-6 minor), 2.34-2.30 (1H, m, H-1 minor), 2.26-2.20 (1H, m, H-6 minor), 1.89 (1H, br d, J 18.5 Hz, H-9 major), 1.83-1.76 (2H, overlapping ddd and m, J 11.0, 10.5, 5.0 Hz, H-1 major and H-9 minor), 1.72 (1H, dd, J 14.0, 6.0 Hz, H-5 minor), 1.64 (1H, dd, J 13.0, 3.5 Hz, H-5_{eq} major), 1.57 (1H, dd, J 13.0, 3.0 Hz, H-5 minor), 1.31 (1H, t, J 13.0 Hz, H-5_{ax} major), 1.25-1.13 (24H, m, OCH_2CH_3, C-4 and C-10 Me, major and minor); *m/z* (EI) 252 (M^+), 237 (M^+-Me), 219, 194 (M^+-$(CH_3)_2CO$), 178, 161, 121 (M^+-$(CH_3)_2O$-CO_2Et), 105, 93, 78, 55 (Found: (M^+), 252.1724. $C_{15}H_{24}O_3$ requires (M^+), 252.1725).

IMDA Reaction of triene (3c).

IMDA Reaction of **3c** gave in 97% yield the trans-fused cycloadduct *[1S,2S,6R,10S]-2,4,4-trimethyl-10-(methoxycarbonyl)-3-oxabicyclo[4.4.0]-7-decene* **4c** as a colourless oil; $[\alpha]_D^{25}$ -38.2 (*c* 0.17, $CHCl_3$); υ_{max} (film) 3023, 2972, 2921, 2850, 1739, 1462, 1437, 1380, 1367, 1264, 1202, 1190, 1165, 1146, 1089 cm^{-1}; δ_H (500 MHz) 5.65-5.61 (1H, m, H-7), 5.39 (1H, dq, J 10.0, 2.0 Hz, H-8), 3.66 (3H, s, OCH_3), 3.55 (1H, dq, J 9.5, 6.0 Hz, H-2), 2.47 (1H, td, J 10.5, 6 Hz, H-10), 2.43-2.28 (2H, m, H-9), 2.23-2.18 (1H, m, H-6), 1.57 (1H, dd, J 13.0, 3.5 Hz, H-5_{eq}), 1.43 (1H, ddd, J 20.0, 10.0, 3.5 Hz, H-1), 1.31 (1H, t, J 13.0 Hz, H-5_{ax}), 1.23 and 1.22 (both 3H, s, $C(CH_3)_2$), 1.04 (3H, d, J 6.0 Hz, C-2 Me); *m/z* (CI) 256 (MNH_4^+), 239 (MH^+), 221, 186, 175, 139, 122 (MH^+-$(CH_3)_2CO$-CO_2Me), 106, 94, 78, 58 (Found: (MH^+), 239.1662. $C_{14}H_{22}O_3$ requires (MH^+), 239.1647).

IMDA Reaction of triene (3d).

IMDA Reaction of **3d** gave in 84% yield a partially separable 6:1 mixture of _[1R*,6R*,10S*]-4,4-dimethyl-10-(phenylsulfonyl)-3-oxabicyclo[4.4.0]-7-decene_ trans-**4d** and _[1R*,6S*,10S*]-4,4-dimethyl-10-(phenylsulfonyl)-3-oxabicyclo[4.4.0]-7-decene_ cis-**4d**. Less polar trans-**4d**: mp 137-139°C (EtOAc–petrol); υ_{max} (Nujol) 1307, 1278, 1147, 1065, 768, 739, 692 cm^{-1}; δ_H (500 MHz) 7.88-7.85 (2H, m, ortho $C_6H_5SO_2$), 7.67-7.63 (1H, m, para $C_6H_5SO_2$), 7.58-7.55 (2H, m, meta $C_6H_5SO_2$), 5.51-5.47 (1H, m, H-8), 5.36 (1H, br d, J 9.5 Hz, H-7), 4.47 (1H, dd, J 12.0, 4.0 Hz, H-2), 3.66 (1H, dd, J 12.0, 11.0 Hz, H-2), 3.22-3.17 (1H, m, H-10), 2.34-2.25 (2H, m, H-6, H-9), 1.98-1.93 (1H, m, H-9), 1.81 (1H, ddd, J 21.5, 11.0, 4.0 Hz, H-1), 1.61 (1H, dd, J 13.0, 3.5 Hz, H-5), 1.29 (1H, t, J 13.0 Hz, H-5), 1.232 and 1.229 (both 3H, s, $C(CH_3)_2$); *m/z* (EI) 291 (M^+-CH_3), 165 (M^+-$SO_2C_6H_5$), 125 (SOC_6H_5), 107 (M^+-$SO_2C_6H_5$-$C(CH_3)_2O$), 91, 79, 71 (Found: C, 66.84; H, 7.29. $C_{17}H_{17}O_3S$ requires C, 66.64; H, 7.24%). More polar cis-**4d**: υ_{max} (film) 2925, 1446, 1383, 1307, 1184, 1144, 1085, 738, 692 cm^{-1}; δ_H (500 MHz) 7.92-7.90 (2H, m, ortho $C_6H_5SO_2$), 7.67-7.63 (1H, m, para $C_6H_5SO_2$), 7.59-7.53 (2H, m, meta $C_6H_5SO_2$), 5.67-5.64 (1H, m, H-6), 5.57-5.53 (1H, m, H-7), 4.22 (1H, dd, J 12.5, 5.5 Hz, H-1) and 3.68 (1H, dd, J 12.5, 4.0 Hz, H-1), 3.47-3.42 (1H, m, H-9), 2.71-2.69 (1H, m, H-5), 2.37 (1H, dddd, J 18.0, 10.5, 5.0, 2.5 Hz, H-8), 2.03 (1H, dddd, J 18.0, 8.0, 4.0, 1.5 Hz, H-8), 2.32-2.27 (1H, m, H-10), 1.59 (1H, dd, J 14.0, 4.5 Hz, H-4) and 1.37 (1H, dd, J 14.0, 9.5 Hz, H-4; AB_{SYS}), 1.23 (3H, s, CH_3), 1.21 (3H, s, CH_3); *m/z* (EI) 291 (M^+-CH_3), 182, 164 (M^+-$SO_2C_6H_5$), 146 , 143, 134, 125 (SOC_6H_5), 91, 79, 77.

IMDA Reaction of triene (3e).

IMDA Reaction of **3e** gave in 84% yield a partially separable 4:1 mixture of _[1R*,6R*,10S*]-4,4,10-trimethyl-10-(phenylsulfonyl)-3-oxabicyclo[4.4.0]-7-decene_ trans-**4e** and _[1R*,6S*,10S*]-4,4,10-trimethyl-10-(phenylsulfonyl)-3-oxabicyclo[4.4.0]-7-decene_ cis-**4e**. Less polar trans-**4e**: mp 141-142.5°C (EtOAc–petrol); υ_{max} ($CHCl_3$) 3025, 2971, 2923, 2869, 2856, 1447, 1382, 1295, 1241, 1161, 1141, 1119, 1071, 759, 732, 693 cm^{-1}; δ_H (270 MHz) 7.91-7.87 (2H, m, ortho $C_6H_5SO_2$), 7.68-7.53 (3H, meta and para $C_6H_5SO_2$), 5.51-5.43 (1H, m, H-7), 5.35 (1H, br d, J 10 Hz, H-8), 4.46 (1H, dd, J 12.0, 3.5 Hz, H-2), 3.68 (1H, dd, J 12.0, 11.0 Hz, H-2), 2.63 (1H, br d, J 17.5 Hz, H-9), 2.39-2.26 (1H, m, H-6), 1.95 (1H, td, J 11.0, 3.5 Hz, H-1), 1.66 (1H, dd, 13.0, 3.5 Hz, H-5), 1.55 (1H, br d, J 17.5 Hz, H-9), 1.37 (4H, m, H-5 and C-10 Me), 1.25 and 1.23 (both 3H, s, C-4 Me); *m/z* (CI) 338 (MNH_4^+), 321 (MH^+), 179, 161, 138, 121, 105 (Found: (MH^+), 321.1532. $C_{18}H_{24}O_3S$ requires (MH^+), 321.1524). Nmr data for more polar cis-**4e**: δ_H (270 MHz) 7.90-7.87 (2H, m, ortho $C_6H_5SO_2$), 7.68-7.53 (3H, meta and para $C_6H_5SO_2$), 5.68 (1H, br d, J 9.5 Hz, H-7), 5.65-5.58 (1H, m, H-8), 3.94 (1H, dd, J 12, 8.5 Hz, H-2), 3.72 (1H, dd, J 12, 5 Hz, H-2), 3.05-3.02 (1H, m, H-6), 2.70 (1H, br d, J 18.5 Hz, H-9), 2.37-2.29 (1H, m, H-1), 1.85 (1H, br d, J 18.5 Hz, H-9), 1.68-1.62 (2H, m, H-5), 1.25 (3H, s, C-10 Me), 1.21 and 1.18 (both 3H, s, C-4 Me).

IMDA Reaction of triene (3f).

IMDA Reaction of **3f** gave in 92% yield the trans-fused cycloadduct _[1R*,6R*,10R*]-4,4,10-trimethyl-10-(phenylsulfonyl)-3-oxabicyclo[4.4.0]-7-decene_ **4f** as a colourless crystalline solid, mp 81-81°C (EtOAc–petrol); υ_{max} (neat) 3023, 2971, 2923, 2847, 1447, 1366, 1300, 1189, 1139, 1079, 1056, 1029, 873, 760, 728 cm^{-1}; δ_H (270 MHz) 7.89-7.84 (2H, m, ortho $C_6H_5SO_2$), 7.67-7.49 (3H, meta and para $C_6H_5SO_2$), 5.58-5.52 (1H, m, H-8 or H-7), 5.48 (1H, br d, J 11.5 Hz, H-7 or H-8), 4.25 (1H, t, J 11.5 Hz, H-2_{ax}), 3.93 (1H, dd, J 12.0, 3.5 Hz, H-2_{eq}), 2.98-2.88 (1H, m, H-6), 2.52 (1H, br d, J 19.0 Hz, H-9), 2.05 (1H, br d, J 19.0 Hz, H-9), 1.78-1.66 (2H, m, H-5 and H-1), 1.35 and 1.31 (both 3H, s, C-4 Me), 1.24-1.21 (4H, overlapping m and s, H-5 and C-10 Me); *m/z* (CI) 338 (MNH_4^+), 321 (MH^+), 179, 161, 148, 121, 105 (Found: (MNH_4^+), 338.1789. $C_{18}H_{24}O_3S$ requires (MNH_4^+), 338.1790. Found: C, 67.20; H, 7.79%. $C_{18}H_{24}O_3S$ requires C, 67.48; H, 7.55%.).

IMDA Reaction of triene (3g).

IMDA Reaction of **3g** gave in 92% yield the trans-fused cycloadduct *[1R*,6S*,10R*]-10-(methoxycarbonyl)spiro[3-oxabicyclo[4.4.0]-7-decene-4,1'-cyclohexane]* **4g** as a colourless oil; ν_{max} (film) 3020, 2937, 2848, 1738, 1441, 1313, 1296, 1261, 1221, 1200, 1167, 1149, 1134, 1120, 1068 cm^{-1}; δ_H (500 MHz); 5.66-5.58 (1H, m, H-7), 5.40 (1H, br d, J 10.0 Hz, H-8), 3.65 (3H, s, OCH_3), 3.57 (1H, dd, J 11.5, 4.0 Hz, H-2$_{eq}$), 3.38 (1H, t, J 11.5 Hz, H-2$_{ax}$), 2.37-2.28 (1H, m, H-9), 2.20 (1H, td, J 11.5, 5.0 Hz, H-10), 2.05 (1H, m, H-9), 1.63 (1H, qd, J 11.5, 4.0 Hz, H-1), [1.92-1.80 (3H, m) and 1.60-1.08 (7H, m) all for H-5$_{eq}$, H-6, H-2'$_{eq}$, H-3', H-4', H-5'], 0.97 (1H, t, J 12.5 Hz, H-5$_{ax}$), 0.88-0.81 (1H, m, H-2'$_{ax}$); *m/z* (CI) 282 (MNH_4^+), 265 (MH^+), 247 (MH^+-H_2O), 233 (M^+-OMe), 221, 193, 187, 167, 107, 99 $(C_6H_{11}O)^+$, 91, 55 (Found: (MNH_4^+), 282.2087. $C_{16}H_{24}O_3$ requires (MNH_4^+), 282.2069).

IMDA Reaction of triene (3h).

IMDA Reaction of **3h** gave in 91% yield an inseparable 1.6:1 mixture of *[1R,3'R,5'R,6R,10R]-10-(methoxycarbonyl)-3',5'-dimethylspiro[3-oxabicyclo[4.4.0]-7-decene-4,1'-cyclohexane]* [1*R*]-**4h** and *[1S,3'R,5'R,6S,10S]-10-(methoxycarbonyl)-3',5'-dimethylspiro[3-oxabicyclo[4.4.0]-7-decene-4,1'-cyclohexane]* [1*S*]-**4h** as a colourless oil. Data for the mixture: ν_{max} (film) 3021, 2950, 2925, 2869, 2844, 1739, 1168, 1152, 1071, 816, 796, 770, 749, 733, 717 cm^{-1}; δ_H (500 MHz, PhMe-d_8) 5.42-5.37 (2H, m, H-7 or H-8 major and minor), 5.22-5.18 (2H, m, H-8 or H-7 major and minor), 3.67 (1H, dd, J 11.0, 4.0 Hz, H-2$_{eq}$ major), 3.62 (1H, dd, J 11.0, 4.0 Hz, H-2$_{eq}$ minor), 3.24 (1H, t, J 11.0 Hz, H-2$_{ax}$ major), 3.22 (3H, s, OCH_3 major), 3.21 (3H,s, OCH_3 minor), 3.15 (1H, t, H-2$_{ax}$ minor), [2.35-1.76 (15H, m), 1.57-1.53 (1H, m), 1.44-1.40 (4H, m), 1.21-1.12 (2H, m), 1.10-0.94 (6H, m), 0.80-0.70 (2H, m) all for H-3', H-4', H-5', H-6', H-5, H-6, H-9, and H-10 major and minor, H-2' major, and H-2'$_{eq}$ minor], 1.67-1.58 (2H, m, H-1 major and minor), 1.23 (3H, d, J 7.5 Hz, C-3' Me minor or C-5' Me minor), 1.11 (3H, d, J 7.5 Hz, C-3' Me major or C-5' Me major), 0.83 (3H, d, J 6.5 Hz, C-5' Me minor or C-3' Me minor), 0.82 (3H, d, J 6.5 Hz, C-5' Me major or C-3' Me major), 0.30 (1H, dd, J 13.5, 12.0 Hz, H-2'$_{ax}$ minor); *m/z* (CI) 310 (MNH_4^+), 293 (MH^+), 292 (M^+) 275 (MH^+-H_2O), 261 (M^+-OMe), 235, 208, 193, 167, 109, 91, 69, 58 (Found: (M^+), 292.2042. $C_{18}H_{28}O_3$ requires (M^+), 292.2038).

IMDA Reaction of triene (3i).

IMDA Reaction of **3i** gave in 94% yield a 10:1 mixture of *[1R,2'S,4R,5'R,6R,10R]-2'-isopropyl-10-(methoxycarbonyl)-5'-methylspiro[3-oxabicyclo[4.4.0]-7-decene-4,1'-cyclohexane]* [1*R*]-**4i** and *[1S,2'S,4S,5'R,6S,10S]-2'-isopropyl-10-(methoxycarbonyl)-5'-methylspiro[3-oxabicyclo[4.4.0]-7-decene-4,1'-cyclohexane]* [1*S*]-**4i** as a colourless oil. Data for the mixture: ν_{max} (film) 3020, 2949, 2925, 2866, 1740, 1454, 1437, 1365, 1311, 1263, 1199, 1167, 1142, 1119, 1072 cm^{-1}; δ_H (500 MHz) (for [1*R*]-**4i** only): 5.66-5.62 (1H, m, H-7), 5.42 (1H, br d, J 10.0 Hz, H-8), 3.65 (3H, s, OCH_3), 3.57 (1H, dd, J 11.5, 4.0 Hz, H-2$_{eq}$), 3.38 (1H, t, J 11.5 Hz, H-2$_{ax}$), 2.17 (1H, septet, J 6.5 Hz, C-2' C*H*Me$_2$), [2.45-2.27 (6H, m), 1.77-1.68 (2H, m), 1.58-1.39 (3H, m), 1.25 (1H, br s), 1.18 (1H, dd, J 12.0, 3.5 Hz), 1.01-0.92 (1H, m) all for H-1, H-2', H-3', H-4', H-5', H-6'$_{eq}$, H-5, H-6, H-9, and H-10], 0.87 (3H, d, J 7.0 Hz, C-5' Me), 0.85 (6H, d, J 6.5 Hz, C-2' CH*Me*$_2$), 0.51 (1H, dd, J 14.0, 12.5 Hz, H-6'$_{ax}$); *m/z* (CI) 338 (MNH_4^+), 221 (MH^+), 303 (MH^+-H_2O), 289 (M^+-OMe), 235, 193, 167, 137, 91 (Found: (MH^+), 321.2439. $C_{20}H_{32}O_3$ requires (MH^+), 321.2430).

Thermal IMDA reaction of triene (3j).

IMDA Reaction of **3j** gave in 91% yield a separable 2:1 mixture of *[1R*,4R*,6S*,10R*]-10-(methoxycarbonyl)-4-phenyl-3-oxabicyclo[4.4.0]-7-decene* trans-**4j** and *[1R*,4R*,6R*,10R*]-10-*

(methoxycarbonyl)-4-phenyl-3-oxabicyclo[4.4.0]-7-decene cis-**4j**, both as colourless oils. Less polar trans-**4j**: υ_{max} (film) 2926, 2844, 1736, 1606, 1496, 1436, 1367, 1307, 1263, 1227, 1200, 1171, 1075, 1021, 997, 971, 916, 814, 757, 699, 666 cm^{-1}; δ_H (500 MHz) 7.37-7.32 (4H, m, ortho, meta, para C_6H_5), 7.28-7.25 (1H, m, ortho C_6H_5), 5.69-5.65 (1H, m, H-7 or H-8), 5.50 (1H, dd, J 10.0, 1.5 Hz, H-8 or H-7), 4.43 (1H, dd, J 11.0, 2.5 Hz, H-4), 4.05 (1H, dd, J 11.0, 3.5 Hz, H-2$_{eq}$), 3.71 (3H, s, OCH_3), 3.41 (1H, t, J 11.0 Hz, H-2$_{ax}$), 2.48-2.33 (3H, m, H-9, H-10), 2.26-2.21 (1H, m, H-6), 1.97 (1H, ddd, J 13.0, 3.5, 2.5 Hz, H-5$_{eq}$), 1.85 (1H, qd, J 11.0, 3.5 Hz, H-1), 1.46 (1H, dt, J 13.0, 11.0 Hz, H-5$_{ax}$); *m/z* (EI) 272 (M^+), 241 (M^+-OCH_3), 195 (M^+-C_6H_5), 166 (M^+-C_6H_5CHO), 117, 107, 91, 79, 77, 67, 55, 41, 31 (Found: (MNH_4^+), 290.1746. $C_{17}H_{20}O_3$ requires (MNH_4^+), 290.1756). More polar cis-**4j**: υ_{max} (film) 3024, 2950, 1734, 1677, 1495, 1436, 1280, 1171, 1076, 1024, 916, 758, 701, 666 cm^{-1}; δ_H (500 MHz) 7.41-7.32 (4H, m, ortho, meta, para C_6H_5), 7.27-7.25 (1H, m, ortho C_6H_5), 5.83-5.81 (1H, m, H-7 or H-8), 5.62 (1H, d, J 10.5 Hz, H-8 or H-7), 4.37 (1H, dd, J 11.5, 2.0 Hz, H-4), 3.89 (1H, dd, J 11.0, 4.5 Hz, H-2$_{eq}$), 3.72 (3H, s, OCH_3), 3.63 (1H, t, J 11.0 Hz, H-2$_{ax}$), 2.63-2.58 (3H, m, H-1, H-6, H-10), 2.53-2.46 (1H, m, H-9), 2.11-2.06 (1H, m, H-9), 1.98-1.91 (1H, m, H-5), 1.83-1.79 (1H, m, H-5); *m/z* (EI) 272 (M^+), 241 (M^+-OCH_3), 213 (M^+-CO_2CH_3), 195 (M^+-C_6H_5), 166 (M^+-C_6H_5CHO), 117, 107, 91, 79, 77, 67, 59, 55, 41, 31 (Found: (MNH_4^+), 290.1745. $C_{17}H_{20}O_3$ requires (MNH_4^+), 290.1756).

Lewis acid-mediated IMDA reaction of triene (3j).

To a solution of triene **3j** (95 mg, 0.35 mmol, 1 eq) in CH_2Cl_2 (0.7 ml) at room temperature was added Et_2AlCl (194 µl of a 1.8M solution in PhMe, 0.35 mmol, 1 eq). The solution was stirred at room temperature for 36 h, after which time tlc indicated complete consumption of starting material. The reaction mixture was poured into ice-cold water and extracted with CH_2Cl_2 (3 x 5 ml). The combined organic extracts were washed with water (15 ml), brine (15 ml), dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the resulting oil (25% ether–petrol) gave trans-**4j** (87 mg, 92%) as a colourless oil, which had spectroscopic data identical with those of the major product formed in the thermal reaction.

Thermal IMDA reaction of triene (3k).

IMDA Reaction of **3k** gave in 89% yield an inseparable 1.6:1 mixture of *[1R*,4R*,6S*,10R*]-10-(ethoxycarbonyl)-10-methyl-4-phenyl-3-oxabicyclo[4.4.0]-7-decene* trans-**4k** and *[1R*,4R*,6R*,10R*]-10-(ethoxycarbonyl)-10-methyl-4-phenyl-3-oxabicyclo[4.4.0]-7-decene* cis-**4k** as a colourless oil. Data for the mixture: υ_{max} (film) 3062, 3021, 2979, 2930, 2910, 2847, 1726, 1453, 1236, 1194, 1158, 1116, 1087, 1025, 699 cm^{-1}; δ_H (500 MHz): (trans-**4k**) 7.39-7.23 (5H, m, C_6H_5), 5.66 (1H, m, H-7), 5.49 (1H, br d, J 10.0 Hz, H-8), 4.42 (1H, dd, J 11.0, 2.5 Hz, H-4), 4.18-4.12 (2H, m, OCH_2CH_3), 3.90 (1H, dd, J 11.0, 3.5 Hz, H-2$_{eq}$), 3.47 (1H, t, J 11.0 Hz, H-2$_{ax}$), 2.72-2.67 (1H, m, H-9), 2.31-2.26 (1H, m, H-6), 2.05-1.90 (3H, m, H-1, H-5$_{eq}$ and H-9), 1.51 (1H, q, J 11.5 Hz, H-5$_{ax}$), 1.26 (3H, t, J 7.5 Hz, OCH_2CH_3), 1.18 (3H, s, C-10 Me); (cis-**4k**) 7.39-7.23 (5H, m, C_6H_5), 5.86-5.81 (1H, m, H-7), 5.56 (1H, br d, J 10.0 Hz, H-8), 4.30 (1H, dd, J 11.0, 2.5 Hz, H-4), 4.23-4.15 (2H, m, OCH_2CH_3), 4.08 (1H, dd, J 11.0, 4.5 Hz, H-2$_{eq}$), 3.54 (1H, t, J 11.0 Hz, H-2$_{ax}$), 2.70-2.64 (1H, m, H-9), 2.63-2.57 (1H, m, H-6), 2.50 (1H, dt, 12.0, 5.0 Hz, H-1), 1.95-1.88 (1H, m, H-5), 1.80 (1H, dt, J 12.0, 3.0 Hz, H-5), 1.74 (1H, br d, J 18.5 Hz, H-9), 1.23 (3H, t, J 7.5 Hz, OCH_2CH_3), 1.20 (3H, s, C-10 Me); *m/z* (CI) 318 (MNH_4^+), 301 (MH^+), 283 (MH^+-H_2O), 272, 255, 227, 209, 194, 120, 105, 91 (Found: (MNH_4^+), 318.2079. $C_{19}H_{24}O_3$ requires (MNH_4^+), 318.2069).

Lewis acid-mediated IMDA reaction of triene (3k).

The Lewis acid-mediated IMDA reaction of triene **3k** was carried out analogously to that of **3j** on a 0.57 mmol scale to give pure trans-**4k** (145 mg, 93%), which had spectroscopic data identical with those of the major product formed in the thermal reaction.

IMDA Reaction of triene ([4*S*,6*S*]-3l).

IMDA Reaction of [4*S*,6*S*]-**3l** gave in 88% yield an inseparable 2:1 mixture of *[1S,2S,4S,6R,10S]-10-(methoxycarbonyl)-2-methyl-4-phenyl-3-oxabicyclo[4.4.0]-7-decene* [1*S*,2*S*,4*S*]-trans-**4l** and *[1S,2S,4S,6R,10S]-10-(methoxycarbonyl)-2-methyl-4-phenyl-3-oxabicyclo[4.4.0]-7-decene* [1*S*,2*S*,4*S*]-cis-**4l** as a colourless oil. Data for the mixture: υ_{max} (film) 3024, 2926, 2852, 1736, 1448, 1436, 1306, 1267, 1192, 1167, 1153, 1088, 1071, 710, 700 cm^{-1}; δ_H (500 MHz, PhMe-d_8) 7.27-7.91 (10H, m, C_6H_5 both isomers), 5.61-5.58 (1H, m, H-7 or H-8 minor), 5.38-5.33 (2H, m, H-7 or H-8 major and H-8 or H-7 minor), 5.19 (1H, br d, J 10.0 Hz, H-8 or H-7 major), 4.24 (1H, dd, J 11.5, 2.0 Hz, H-4 minor), 4.15 (1H, dd, J 11.0, 2.5 Hz, H-4 major), 3.44-3.39 (1H, m, H-2 minor), 3.29 (3H, s, OCH_3 minor), 3.27 (3H, s, OCH_3 major), 3.24-3.18 (1H, m, H-2 major), 2.49 (1H, br s, H-6 minor), 2.39-2.26 (4H, m, H-9 major, H-9 minor, H-10 major, H-10 minor), 2.15-2.12 (1H m, H-1 minor), 2.07-2.04 (1H, m, H-9 minor), 1.78-1.73 (1H, m, H-6 major), 1.67-1.49 (4H, m, H-1 major, H-5 major and minor, H-9 major), 1.23 (3H, d, J 6.0 Hz, C-2 Me major), 1,12 (3H, d, J 6.0 Hz, C-2 Me minor); *m/z* (CI) 304 (MNH_4^+), 287 (MH^+), 273 (MH^+-Me), 269 (MH^+-H_2O), 255, 242, 209, 182, 157, 104, 91, 78 (Found: (MNH_4^+), 304.1915. $C_{18}H_{22}O_3$ requires (MNH_4^+), 304.1913).

IMDA Reaction of triene ([4*S*,6*R*]-3l).

IMDA Reaction of [4*S*,6*R*]-**3l** gave in 88% yield an inseparable 6:3:2:1 mixture of *[1S,2S,4R,6R,10S]-10-(methoxycarbonyl)-2-methyl-4-phenyl-3-oxabicyclo-[4.4.0]-7-decene* [1*S*,2*S*,4*R*]-trans-**4l**, *[1S,2S,4R,6S,10S]-10-(methoxycarbonyl)-2-methyl-4-phenyl-3-oxabicyclo-[4.4.0]-7-decene* [1*S*,2*S*,4*R*]-cis-**4l**, *[1R,2S,4R,6S,10R]-10-(methoxycarbonyl)-2-methyl-4-phenyl-3-oxabicyclo-[4.4.0]-7-decene* [1*R*,2*S*,4*R*]-trans-**4l**, and *[1R,2S,4R,6R,10R]-10-(methoxycarbonyl)-2-methyl-4-phenyl-3-oxabicyclo-[4.4.0]-7-decene* [1*R*,2*S*,4*R*]-cis-**4l** as a colourless oil. Data for the mixture: υ_{max} (film) 2926, 1736, 1448, 1435, 1191, 1167, 1153, 1131, 1087, 1071, 1054, 814, 779, 758, 710 cm^{-1}; δ_H (500 MHz, PhMe-d_8) 7.28-6.91 (20H, m, C_6H_5), [5.41-5.33 (6H, m), 5.23-5.21 (2H, m), H-7 and H-8 of all isomers], 4.84 (1H, d, H-4, [1*S*,2*S*,4*R*]-trans-**4l**), 4.46 (1H, dd, J 11.5, 2.5 Hz, H-4 [1*R*,2*S*,4*R*]-trans-**4l**), 4.41-4.22 (2H, m, H-4 of [1*S*,2*S*,4*R*]-cis-**4l** and [1*R*,2*S*,4*R*]-cis-**4l**), [3.54-3.43 (2H, m), 3.34-3.27 (1H, m), 3.08-2.97 (1H, m) all for H-2 of all isomers], 3.31 (3H, s, OCH_3 [1*R*,2*S*,4*R*]-cis-**4l**), 3.29 (3H, s, OCH_3 [1*S*,2*S*,4*R*]-cis-**4l**), 3.24 (3H, s, OCH_3 [1*R*,2*S*,4*R*]-trans-**4l**), 3.22 (3H, s, OCH_3 [1*S*,2*S*,4*R*]-trans-**4l**), 2.32-1.19 (28H, m, H-1, H-5, H-6, H-9 and H-10 of all isomers), 1.17 (3H, d, J 6.5 Hz, C-2 Me [1*S*,2*S*,4*R*]-cis-**4l**), 1.15 (3H, d, J 6.5 Hz, C-2 Me [1*S*,2*S*,4*R*]-trans-**4l**), 1.13 (3H, d, J 7.0 Hz, C-2 Me [1*R*,2*S*,4*R*]-trans-**4l**), 1.08 (3H, d, J 7.0 Hz, C-2 Me [1*R*,2*S*,4*R*]-cis-**4l**); *m/z* (CI) 304 (MNH_4^+), 287 (MH^+), 269 (MH^+-H_2O), 255, 242, 209, 182, 156, 104, 91, 78 (Found: (MNH_4^+), 304.1907. $C_{18}H_{22}O_3$ requires (MNH_4^+), 304.1913).

IMDA Reaction of triene (3m).

IMDA Reaction of **3m** gave in 90% yield a separable 1:1 mixture of *[1R*,4S*,6R*,10S*]-4-phenyl-10-(phenylsulfonyl)-3-oxabicyclo[4.4.0]-7-decene* trans-**4m** and *[1R*,4S*,6S*,10S*]-4-phenyl-10-(phenylsulfonyl)-3-oxabicyclo[4.4.0]-7-decene* cis-**4m**, both as colourless, crystalline solids. Less polar trans-**4m**: mp 172-173°C (EtOAc–petrol); υ_{max} ($CHCl_3$) 3063, 3029, 2909, 2803, 1449, 1304, 1275, 1142, 1073, 1017, 833, 804, 782, 763, 740 cm^{-1}; δ_H (270 MHz) 7.92-7.89 (2H, m, ortho $C_6H_5SO_2$), 7.69-7.66 (1H, m, para $C_6H_5SO_2$), 7.61-7.58 (2H, m, meta $C_6H_5SO_2$), 7.37-7.25 (5H, m, C_6H_5), 5.54-5.51 (1H, m, H-7 or H-8), 5.45 (1H, br d, J 9.5 Hz, H-8 or H-7), 4.92 (1H, dd, J 12.0, 4.0 Hz, H-2_{eq}), 4.44 (1H, dd, J 11.0, 2.0 Hz, H-4), 3.65 (1H, dd, J 12.0, 11.0 Hz, H-2_{ax}), [3.27-3.21 (1H, m, H-10), 2.39-2.32 (2H, m), 2.08-1.96 (3H, m) and 1.53-1.46 (1H, m) all for H-1, H-5, H-6, H-9]; *m/z* (EI) 354 (M^+), 322, 287, 248 (M^+-C_6H_5CHO), 231, 212 (M^+-$SO_2C_6H_5$), 195, 165, 143, 117, 104, 91, 77 (Found: C, 70.71; H, 6.01. $C_{21}H_{22}O_3S$ requires C, 71.16; H, 6.26%). More polar cis-**4m**: mp 158-160°C (EtOAc–petrol); υ_{max} ($CHCl_3$)

3063, 3029, 2973, 2933, 2909, 2842, 1449, 1304, 1275, 1141, 1073, 1017, 804, 764, 741 cm^{-1}; δ_H (270 MHz) 7.94-7.92 (2H, m, ortho $C_6H_5SO_2$), 7.70-7.67 (1H, m, para $C_6H_5SO_2$), 7.61-7.58 (2H, m, meta $C_6H_5SO_2$), 7.35-7.24 (5H, m, C_6H_5), 5.84-5.80 (1H, m, H-8), 5.76 (1H, br d, J 10.5 Hz, H-7), 4.35 (1H, dd, J 11.5, 2.5 Hz, H-4), 3.72 (1H, dd, J 11.0, 5.0 Hz, H-2_{eq}), 3.59 (1H, t, J 11.0 Hz, H-2_{ax}), 3.13 (1H, br s, H-6), 3.05 (1H, d, J 8.0 Hz, H-10), 2.79 (1H, m, H-1), 2.63 (1H, br dd, J 20.0, 1.5 Hz, H-9), 2.27-2.18 (1H, m, H-9), 1.97 (1H, ddd, J 14.0, 11.5, 5.0 Hz, H-5_{ax}), 1.87 (1H, dt, J 14.0, 2.5 Hz, H-5_{eq}); *m/z* (EI) 353 (M$^+$), 290, 250, 248 (M$^+$-C_6H_5CHO), 231, 212 (M$^+$-$SO_2C_6H_5$), 196, 179, 144, 117, 67, 50 (Found: C, 71.34; H, 6.24. $C_{21}H_{22}O_3S$ requires C, 71.16; H, 6.26%).

IMDA Reaction of triene (3n).

IMDA Reaction of **3n** gave in 89% yield a partially separable 1:1 mixture of *[1R*,4S*,6R*,10S*]-10-methyl-4-phenyl-10-(phenylsulfonyl)-3-oxabicyclo[4.4.0]-7-decene* trans-**4n** and *[1R*,4S*,6S*,10S*]-10-methyl-4-phenyl-10-(phenylsulfonyl)-3-oxabicyclo[4.4.0]-7-decene* cis-**4n**, both as colourless, crystalline solids. Less polar trans-**4n**: mp 143-144°C (EtOAc–petrol); υ_{max} ($CHCl_3$) 3065, 3024, 3003, 2981, 2913, 2871, 2846, 1448, 1295, 1143, 1121, 1085, 1071, 757, 731 cm^{-1}; δ_H (270 MHz) 7.95-7.90 (2H, m, ortho $C_6H_5SO_2$), 7.72-7.55 (3H, meta and para $C_6H_5SO_2$), 7.39-7.23 (5H, m, C_6H_5), 5.55-5.46 (1H, m, H-7), 5.43 (1H, br d, J 10.5 Hz, H-8), 4.92 (1H, dd, J 11.5, 3.5 Hz, H-2_{eq}), 4.45 (1H, dd, J 11.0, 2.0 Hz, H-4), 3.67 (1H, t, J 11 Hz, H-2_{ax}), 2.69 (1H, br d, 17.5 Hz, H-9), 2.39 (1H, m, H-6), 2.19 (1H, td, J 10.5, 3.5 Hz, H-1), 2.05 (1H, dt, J 12.5, 3.0 Hz, H-5_{eq}), 1.61-1.50 (2H, m, H-5_{ax} and H-9), 1.40 (3H, s, C-10 Me); *m/z* (CI) 386 (MNH_4^+), 369 (MH$^+$), 246, 227 (M$^+$-$PhSO_2$), 211, 199, 160, 121 105, 91, 78 (Found: (MNH_4^+), 386.1790. $C_{22}H_{24}O_3S$ requires (MNH_4^+), 386.1790). More polar cis-**4n**: mp 148-150°C (EtOAc–petrol); υ_{max} ($CHCl_3$) 3023, 3004, 2980, 2924, 2913, 2872, 2846, 1449, 1435, 1288, 1143, 1121, 1071, 1025, 732 cm^{-1}; δ_H (270 MHz) 7.93-7.88 (2H, m, ortho $C_6H_5SO_2$), 7.72-7.54 (3H, meta and para $C_6H_5SO_2$), 7.37-7.22 (5H, m, C_6H_5), 5.92-5.84 (1H, m, H-7), 5.78 (1H, br d, J 10.5 Hz, H-8), 4.34 (1H, quintet, J 7.5 Hz, H-4), 3.92 (1H, dd, J 11.0, 5.0 Hz, H-2_{eq}), 3.54 (1H, t, J 11.5 Hz, H-2_{ax}), 3.50 (1H, br s, H-6), 2.90 (1H, br d, 20.0 Hz, H-9), 2.46 (1H, ddd, J 11.0, 5.0, 4.5 Hz, H-1), 2.04-1.90 (3H, m, H-5 and H-9), 1.24 (3H, s, C-10 Me); *m/z* (CI) 386 (MNH_4^+), 321, 298, 266, 244, 227 (M$^+$-$PhSO_2$), 209, 196, 160, 122 105, 91, 78 (Found: C, 71.94; H, 6.60%. $C_{22}H_{24}O_3S$ requires C, 71.72; H, 6.56%).

IMDA Reaction of triene (3o).

IMDA Reaction of **3o** gave in 86% yield a partially separable 3.5:1 mixture of *[1R*,4S*,6R*,10R*]-10-methyl-4-phenyl-10-(phenylsulfonyl)-3-oxabicyclo[4.4.0]-7-decene* trans-**4o** and *[1R*,4S*,6S*,10R*]-10-methyl-4-phenyl-10-(phenylsulfonyl)-3-oxabicyclo[4.4.0]-7-decene* cis-**4o**, both as colourless, crystalline solids. Less polar cis-**4o**: mp 165-166°C (EtOAc–petrol); υ_{max} (CH_2Cl_2) 3027, 2971, 2933, 2910, 2880, 1447, 1299, 1266, 1140, 1072, 1025, 759, 728, 692, 658 cm^{-1}; δ_H (270 MHz) 7.94-7.89 (2H, m, ortho $C_6H_5SO_2$), 7.72-7.56 (3H, meta and para $C_6H_5SO_2$), 7.36-7.23 (5H, m, C_6H_5), 5.88-5.81 (1H, m, H-7), 5.62 (1H, br d, J 10.5 Hz, H-8), 4.79 (1H, dd, J 12.0, 4.5 Hz, H-2_{eq}), 4.29 (1H, dd, J 8.0, 5.5 Hz, H-4), 3.72 (1H, t, J 12.0 Hz, H-2_{ax}), 2.89 (1H, br d, J 17.0 Hz, H-9), 2.66 (1H, br s, H-6), 2.24 (1H, ddd, J 12.0, 4.5, 4.5 Hz, H-1), 2.00 (1H, br d, J 17.0 Hz, H-9), 1.93-1.86 (2H, m, H-5), 1.26 (3H, s, C-10 Me); *m/z* (CI) 386 (MNH_4^+), 369 (MH$^+$), 246, 227 (M$^+$-$PhSO_2$), 160, 105, 94, 78 (Found: (MNH_4^+), 386.1789. $C_{22}H_{24}O_3S$ requires (MNH_4^+), 386.1790). More polar trans-**4o**: mp 170-171°C (EtOAc–petrol); υ_{max} (CH_2Cl_2) 3063, 3029, 2984, 2934, 2915, 2898, 2853, 1445, 1297, 1141, 1073, 1025, 760, 727, 689, 659 cm-1; δ_H (270 MHz) 7.92-7.87 (2H, m, ortho $C_6H_5SO_2$), 7.69-7.52 (3H, meta and para $C_6H_5SO_2$), 7.38-7.25 (5H, m, C_6H_5), 5.65-5.54 (2H, m, H-7 and H-8), 4.57 (1H, dd, J 11.0 Hz, 2.0 Hz, H-2_{eq}), 4.42 (1H, dd, J 12.0, 3.5 Hz, H-4), 4.28 (1H, dd, J 12.0, 11.0 Hz, H-2_{ax}), 3.09 (1H, m, H-6), 2.54 (1H, br d, J 20.0 Hz, H-9), 2.17-2.04 (2H, m, H-5 and H-9), 1.97 (1H, ddd, J 11.0, 11.0, 3.5 Hz, H-1), 1.40 (4H, br s, H-5 and C-10 Me); *m/z* (CI) 386 (MNH_4^+), 369 (MH^+), 227 (M^+-$PhSO_2$), 209, 196 (M^+-2Ph-H_2O), 160, 121, 105, 91, 77 (Found: (MNH_4^+), 386.1786. $C_{22}H_{24}O_3S$ requires (MNH_4^+), 386.1790).

Preparation of [3*R**,4*S**,5*R**]-4-(acetoxymethyl)-3-(2-methylpropenyl)-5-(phenylsulfonyl)-cyclohexene (5).

To a solution of the bicyclic sulfone trans-**4d** (17.5 mg, 0.06 mmol, 1 eq) in acetic anhydride (500 µl) at 0°C was added $FeCl_3$ (1.0 mg, 0.1 eq). The mixture was allowed to stir for a further 30 min at 0°C. The mixture was poured into saturated aqueous sodium hydrogencarbonate (10 ml) and extracted with ether (3 x 5 ml). The combined organic layers were washed with water and dried ($MgSO_4$) and concentrated under reduced pressure giving a pale brown oil, which was purified by chromatography (20% EtOAc–petrol) to give the desired *cyclohexene* **5** (13 mg, 65%) as a colourless solid, mp 81-83°C; υ_{max} (CH_2Cl_2) 3029, 2967, 2913, 2856, 1740, 1447, 1307, 1283, 1239, 1144, 1085, 762, 737, 692 cm^{-1}; δ_H (270 MHz) 7.92-7.87 (2H, m, ortho $C_6H_5SO_2$), 7.68-7.52 (3H, meta and para $C_6H_5SO_2$), 5.62-5.54 (1H, m, H-1 or H-2), 5.41 (1H, br d, J 10.5 Hz, H-2 or H-1), 4.79 (1H, d, J 9.5 Hz, $(CH_3)_2CC\mathit{H}$), 4.52 (1H, dd, J 11.5, 2.5 Hz, $AcOC\mathit{H}_2$), 4.10 (1H, dd, J 11.5, 2.0 Hz, $AcOC\mathit{H}_2$), 3.56 (1H, td, J 11.0, 5.5 Hz, H-5), 3.21-3.11 (1H, m, H-3), 2.42-2.29 (1H, m, H-4), 2.20-1.92 (2H, m, H-6), 1.91 (3H, s, CH_3CO_2), 1.70 and 1.55 (both 3H, s, CMe_2); *m/z* (CI) 366 (MNH_4^+), 349 (MH^+), 226, 209, 147, 131, 108, 91, 78, 58 (Found: (MNH_4^+), 366.1749. $C_{19}H_{24}O_4S$ requires (MNH_4^+), 366.1739).

Preparation of [3*R**,4*R**,5*S**]-3-(2-chloro-2-methylpropyl)-4-(hydroxymethyl)-5-(phenylsulfonyl)cyclohexene (6).

A solution of the bicyclic sulfone trans-**4d** (102 mg, 0.33 mmol, 1 eq) in CH_2Cl_2 (0.7 ml) at -78°C was added BCl_3 (333 µl of 1.0M solution in CH_2Cl_2, 0.33 mmol, 1 eq). The solution was stirred at -78°C for 30 min, and then allowed to warm to 0°C and stirred for an additional 45 min. The mixture was re-cooled to -78°C and MeOH (340 µl) added via syringe. The solution was allowed to warm to room temperature and concentrated under reduced pressure. The resulting oil was purified by chromatography (25% EtOAc–petrol) to yield the *alcohol* **6** (84 mg, 74%) as a colourless solid, mp 87-88°C; υ_{max} (CH_2Cl_2) 3539, 2971, 2924, 1447, 1371, 1304, 1281, 1141, 1085, 1059, 797, 784, 762, 738, 720 cm^{-1}; δ_H (270 MHz) 7.92-7.87 (2H, m, ortho $C_6H_5SO_2$), 7.71-7.55 (3H, meta and para $C_6H_5SO_2$), 5.83 (1H, br d, J 11.0 Hz, H-1 or H-2), 5.50-5.42 (1H, m, H-2 or H-1), 4.34 (1H, dd, J 13.0, 3.0 Hz, $C\mathit{H}_2OH$), 3.79 (1H, dd, J 13.0, 2.5 Hz, $C\mathit{H}_2OH$), 3.48 (1H, m, H-5), 2.66- 2.58 (1H, m, H-3), 2.28-2.14 (1H, m, H-4), 2.06-1.67 (5H, m, H-6, $(CH_3)_2C(Cl)C\mathit{H}_2$ and OH), 1.66 and 1.63 (both 3H, s, $C(CH_3)_2$); *m/z* (CI) 360 (MNH_4^+), 343 $(MH)^+$, 324 (MNH_4^+-H_2O), 307 (MH^+-HCl), 291, 270, 220, 184, 165, 160, 147, 108, 91, 78 (Found: (MNH_4^+), 360.1415. $C_{17}H_{23}O_3S_{35}Cl$ requires (MNH_4^+), 360.1400).

Preparation of [3*R**,4*S**,5*R**]-4-(acetoxymethyl)-3-(2-phenylethenyl)-5-(phenylsulfonyl)-cyclohexene (7).

To a solution of the bicyclic sulfone trans-**4m** (17 mg, 0.05 mmol, 1 eq) in acetic anhydride (500 µl) at 0°C was added $FeCl_3$ (1 mg, 0.1 eq). The mixture was allowed to stir for 30 min at 0°C. The mixture was poured into saturated aqueous sodium hydrogencarbonate (10 ml) with vigorous stirring until effervescence ceased and then extracted with ether (3 x 5 ml). The combined organic layers were washed with water and dried ($MgSO_4$) and concentrated under reduced pressure to give a pale brown oil. This was purified by chromatography (20% EtOAc–petrol) to give the *cyclohexene* **7** (12 mg, 65%) as a colourless oil; υ_{max} (film) 3033, 2926 2853, 1739, 1447, 1372, 1306, 1283, 1250, 1145, 1085, 1046, 1026, 732, 697 cm-1; δ_H (270 MHz) 7.92-7.90 (2H, m, ortho $C_6H_5SO_2$), 7.68-7.56 (3H, meta and para $C_6H_5SO_2$), 7.47-7.21 (5H, m, C_6H_5), 6.42 (1H, d, J 15.5 Hz, $C_6H_5C\mathit{H}$), 5.93 (1h, d, J 15.5 Hz, $C_6H_5CHC\mathit{H}$), 5.71-5.67 (1H, m, H-1 or

H-2), 5.57 (1H, br d, J 9.0 Hz, H-2 or H-1), 4.57 (1H, dd, J 12.0, 3.0 Hz, AcOCH_2), 4.30 (1H, dd, J 12.0, 2.5 Hz, AcOCH_2), 3.57 (1H, td, J 11.0, 5.5 Hz, H-5), 3.10-3.05 (1H, m, H-3), 2.45-2.38 (1H, m, H-4), 2.24-2.16 (2H, m, H-6), 1.97 (3H, s, CH_3CO_2); *m/z* (CI) 414 (MNH_4^+), 397 $(MH)^+$, 366, 334, 274, 195, 160, 108, 91, 78 (Found: (MNH_4^+), 414.1725. $C_{23}H_{24}O_4S$ requires (MNH_4^+), 414.1739).

Preparation of [3*R**,4*R**,5*S**]-3-(2-chloro-2-phenylethyl)-4-(hydroxymethyl)-5-(phenylsulfonyl)cyclohexene (8).

To a solution of the bicyclic sulfone trans-**4m** (23 mg, 0.06 mmol, 1 eq) in CH_2Cl_2 (209 µl) at -78°C was added BCl_3 (65 µl of a 1M solution in CH_2Cl_2, 0.06 mmol, 1 eq). The solution was stirred at -78°C for 30 min, and then allowed to warm to 0°C and stirring continued for an additional 30 min. The mixture was re-cooled to -78°C and MeOH (70 µl) added via syringe. The solution was allowed to warm to room temperature and concentrated under reduced pressure. The resulting oil was purified by chromatography (25% EtOAc–petrol) to yield a 1:1 diastereomeric mixture of the *alcohols* **8** (18 mg, 71%) as a colourless oil; υ_{max} (film) 3529, 3063, 3031,2954, 2922, 2851, 1447, 1304, 1280, 1142, 1084, 1060, 918, 738, 719 cm^{-1}; δ_H (270 MHz) 7.88-7.80 (2H, m, ortho $C_6H_5SO_2$), 7.68-7.52 (3H, m, meta and para $C_6H_5SO_2$), 7.42-7.30 (5H, m, C_6H_5), 5.78-5.63 (1H, m, H-1 or H-2), 5.61-5.50 (1H, m, H-2 or H-1), 5.09-4.95 (1H, m, C_6H_5CHCl), 4.31 (1H, dd, J 12.5, 4.5 Hz, CH_2OH one diastereomer), 4.24 (1H, dd, J 12.5, 5.5 Hz, CH_2OH one diastereomer), 3.82 (1H, dd, J 12.5, 4.5 Hz, CH_2OH one diastereomer), 3.67 (1H, dd, J 12.5, 5.5 Hz, CH_2OH one diastereomer), 3.53-3.36 (1H, m, H-5), 2.82-2.70 (1H, m, H-3), 2.54-1.56 (4H, m, H-4, H-6 and $C_6H_5CHClCH_2$), 1.41 (1H, br s, OH); *m/z* (CI) 408 (MNH_4^+), 372 (M^+-H_2O), 355 (MH^+-HCl), 232, 213, 197, 160, 105, 91, 78 (Found: (MNH_4^+), 408.1407. $C_{21}H_{23}ClO_3S$ requires (MNH_4^+), 408.1400).

Preparation of [3*R**,4*R**]-4-(hydroxymethyl)-3-(2-phenylethyl)-cyclohexene (9).

A flask fitted with a dry-ice condenser and a KOH drying tube was purged with dry ammonia for 5 min. Ammonia was then condensed (10 ml) and a suspension of the bicyclic sulfone trans-**4m** (46 mg, 0.13 mmol) in ether (2 ml) was added. Sodium pieces were added so as to maintain a blue colour for a period of 25 min. Solid NH_4Cl was then added carefully until the blue colour had disappeared. The ammonia was allowed to evaporate and the resulting pale yellow solid suspended in ether (20 ml). The mixture was filtered, washing the residue with ether (150 ml). The filtrate was concentrated under reduced pressure and the residue purified by chromatography (20% ether–petrol) to yield the *alcohol* **9** (20 mg, 71%) as a colourless oil; υ_{max} (film) 3494, 3023, 2954, 1603, 1496, 1453, 1436, 1381, 1350, 1305, 1149, 1103, 1069, 1031, 746 cm^{-1}; δ_H (270 MHz) 7.30-7.16 (5H, m, C_6H_5), 5.75-5.71 (1H, m, H-1 or H-2), 5.68-5.65 (1H, m, H-2 or H-1), 3.67 (1H, dd, J 10.5, 5.0 Hz, CH_2OH), 3.55 (1H, dd, J 10.5, 7.0 Hz, CH_2OH), 2.72 (1H, ddd, J 13.5, 10.5, 5.5 Hz, $C_6H_5CH_2$), 2.60 (1H, ddd, J 13.5, 10.5, 5.5 Hz, $C_6H_5CH_2$), 2.04-1.96 (3H, m, H-3 and H-6), [1.85-1.75 (2H, m) and 1.58-1.47 (2H, m) $C_6H_5CH_2CH_2$, H-4, H-5 and OH]; *m/z* (CI) 234 (MNH_4^+), 198 (M^+-H_2O), 140 (MH^+-Ph), 122, 108, 91 (Found: (MNH_4^+), 234.1854. $C_{15}H_{20}O$ requires (MNH_4^+), 234.1858).

X-Ray crystal data[33]

All data were corrected for Lorentz and polarisation factors; the non-hydrogen atoms were refined anisotropically. Unless stated otherwise, the positions of all hydrogen atoms were idealised, C–H = 0.96Å, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. All methyl groups were refined as rigid bodies. All computations were carried out using the SHELXTL programme system.[34]

Compound trans-**4m**, which is racemic, crystallised in a chiral space group, indicative of spontaneous resolution upon crystallisation. The crystal chosen for diffraction studies was picked at random. Data were measured using a Siemens P4/PC diffractometer, using Cu-K_α radiation (λ = 1.54178 Å, graphite monochromator), using ω-scans, with $0° \leq 2\theta \leq 116°$. $C_{21}H_{22}O_3S$, $M = 354.4$, monoclinic, $a = 7.032(2)$, $b = 10.562(4)$, $c = 12.394(5)$ Å, $\beta = 103.28(2)°$, $V = 896$ Å^3, space group $P2_1$, $Z = 2$, $D_c = 1.31$ g cm^{-3}, μ(Cu-K$_\alpha$) = 17.4 cm^{-1}, $F(000) = 376$. 1286 Independent reflections were measured of which 1280 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares based on F to give $R = 0.037$, $R_w = 0.041$ [$w^{-1} = \sigma^2(F) + 0.0005F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.23 and -0.21 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.084 and 0.011 respectively.

Compound cis-**4m**: data were measured using a Siemens P4/PC diffractometer, using Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å, graphite monochromator), using ω-scans, with $3° \leq 2\theta \leq 50°$. $C_{21}H_{22}O_3S$, $M = 354.4$, orthorhombic, $a = 24.533(5)$, $b = 14.121(4)$, $c = 10.522(2)$ Å, $V = 3645$ Å^3, space group $Aba2$, $Z = 8$, $D_c = 1.29$ g cm^{-3}, μ(Mo-K$_\alpha$) = 1.9 cm^{-1}, $F(000) = 1504$. 1706 Independent reflections were measured of which 1399 had $|F_o| > 4\sigma(|F_o|)$, and were considered to be observed. Refinement was by full-matrix least squares based on F to give $R = 0.036$, $R_w = 0.040$ [$w^{-1} = \sigma^2(F) + 0.0007F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.21 and -0.14 eÅ^{-3} respectively. The maximum and mean shift/error ratios in the final refinement cycle were 0.002 and 0.000 respectively.

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17. *Z,Z*-isomer.
18. 1*Z*,7*E*-isomer.
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20. [2*S*,5*R*]-isomer.
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34. The SHELXTL-PC Programme System (Version 4.2) was used: Sheldrick, G. M.; Siemens Analytical X-Ray Instruments, Madison, Wisconsin, 1992.

(*Received in UK* 9 *October* 1995; *accepted* 19 *October* 1995)