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Radical Cyclisations of Dienes and Enynes using Phosphorus- and Sulfur-Centred Radicals

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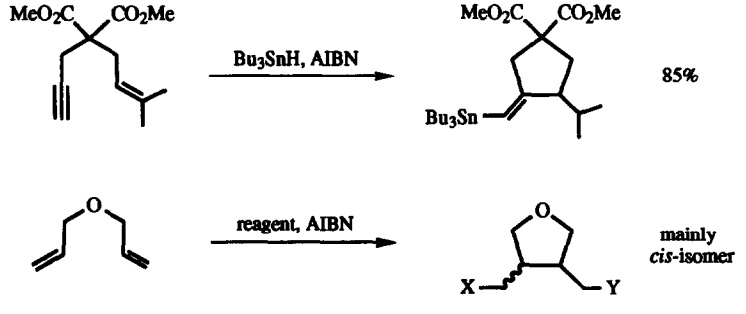
Abstract: Reaction of a number of 1,6-diene or enyne systems with $TolSO_2SePh$, under free radical conditions, results in selenosulfonylation with concomitant C–C bond formation, to give cyclised alkyl or vinyl sulfones containing the synthetically useful phenylselenyl functionality. Similar cyclisations are possible by using Ph_2PH in place of $TolSO_2SePh$, resulting in the formation of cyclic phosphine or vinyl phosphine products, although in these reactions the diene substrates give rather modest yields.

The use of carbon-centred radicals in organic synthesis has become widespread in recent years, as the value of radical reactions, particularly for ring formation, has been fully recognised.[1] One area of radical cyclisation chemistry which attracted our attention involves the cyclisation of certain doubly unsaturated substrates, especially 1,6-dienes or enynes, by reaction with a range of radical-chain carrying agents including sulfonyl halides and silicon and tin hydrides, e.g. Scheme 1.[2]



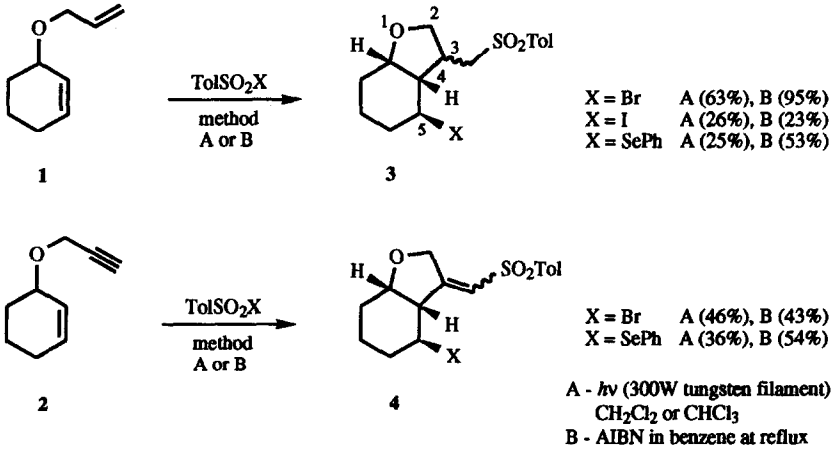
Scheme 1

Such reactions are appealing, because in one simple step, useful functionality is introduced, a new C–C bond is formed (usually stereoselectively) and two unsaturated appendages with similar, or identical, reactivity are distinguished. We recently reported two novel variants on this theme, which involve the use of Ph_2PH[3] or $TolSO_2SePh$[4] as the source of radicals for the cyclisation and here we describe in full our studies in this area.

Cyclisations with $TolSO_2SePh$

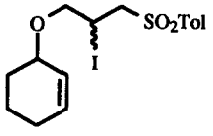
Prior to our involvement in this area, a range of cyclisations involving sulfonyl halides had been described, although we were aware of only two isolated examples involving the use of the corresponding selenosulfonates.[5] These latter reactions, described by Kice and coworkers, involved transannular cyclisation of 1,5-cyclooctadiene or cyclisation of 1,6-heptadiene using $TolSO_2SePh$, the yields of cyclised products being rather modest in each case (*ca.* 40%). It is well established that the success of radical cyclisation reactions involving sulfonyl halides depends critically on the rate of the radical chain transfer step. The chemistry is usually most successful with sulfonyl bromides, since in this case the radical chain transfer step is of a rate appropriate to allow cyclisation of the initially formed carbon-centred radical (with sulfonyl iodides the chain transfer step is usually too rapid to allow efficient cyclisation, whereas the use of sulfonyl chlorides usually requires rather vigorous conditions or the inclusion of copper salts).[6] Therefore we commenced our study by briefly comparing the efficiency of cyclisations using $TolSO_2Br$ and $TolSO_2I$ with analogous reactions using $TolSO_2SePh$.

The two simple ether systems **1** and **2**, readily available from 3-bromocyclohexene, were chosen to provide initial tests of the sulfonyl radical cyclisation with diene and enyne systems under thermolytic and photolytic conditions, Scheme 2.



Scheme 2

In the case of diene **1**, each of the $TolSO_2X$ reagents provided the desired bicyclic tetrahydrofuran product **3** as a diastereomeric mixture (*ca.* 1.5–2.1:1 ratio), the yields ranging from modest to excellent. Cyclisation of the enyne system **2** also occurred in the expected sense to give the vinyl sulfones **4** in reasonable yield and as *ca.* 3–4:1 mixtures of (*Z*):(*E*) isomers. In the case of the reaction of **1** with $TolSO_2I$ under photolytic conditions the uncyclised adduct **5** was also isolated in 48% yield, this type of adduct not being observed in significant amounts in the other reactions. In general, the thermolytic reactions employing AIBN as initiator proved more satisfactory than those under photolytic conditions, the yields of desired products being significantly higher in several cases. The thermal conditions were therefore employed in subsequent cyclisations of other substrates.



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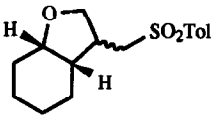

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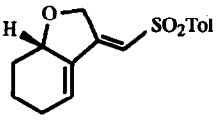

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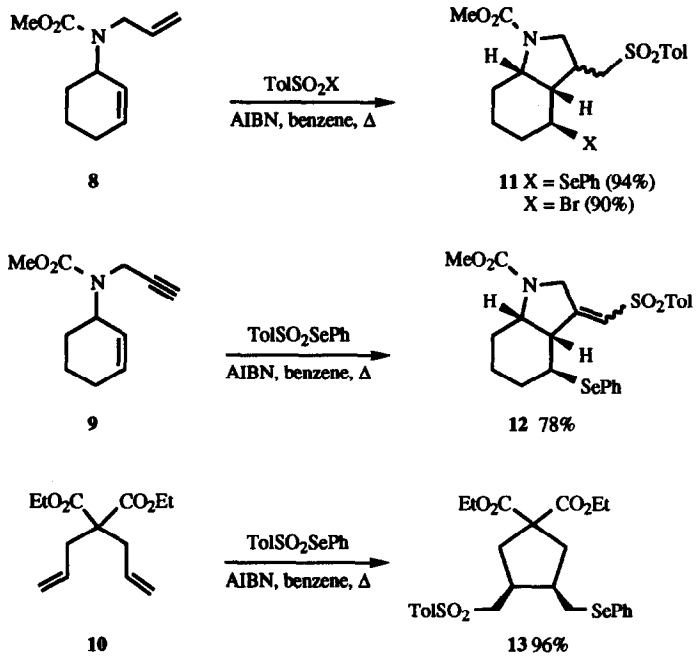
Initially, although the adducts **3** could be assumed to have a *cis*-fused ring junction, it was uncertain if the diastereoisomers were epimeric at C-3 or C-5. A typical sample of the bromide **3** (X = Br) was therefore subjected to reduction with Bu_3SnH, the sulfone product **6** being isolated in 96% yield and as an epimeric mixture having the same diastereoisomeric ratio as the starting material. The adducts **3** are therefore epimeric at C-3 (assuming analogy within the series), the major isomer probably having the CH_2SO_2Tol substituent in an *endo*-orientation in accord with previous assignments in related reactions.[7] The high stereoselectivity observed at C-5 is presumably a consequence of atom transfer to the least hindered *exo*-face of the bicyclic intermediate carbon-centred radical.

In the case of vinyl sulfone products **4**, we expected the (*Z*)-geometric isomer to predominate since the intermediate (*Z*)-β-sulfonyl vinyl radical would be expected to cyclise more readily than the corresponding (*E*)-isomer. This assignment is supported by the downfield shift seen for the C_4–H in the minor (*E*)-isomers of **4** (δ 3.02 for both X = Br and X = SePh) compared to the shift of the corresponding hydrogen in the major isomers (δ 2.85 for X = Br and δ 2.60 for X = SePh), in accord with the known *syn*-deshielding effect of the sulfonyl group in vinyl sulfones. We also carried out oxidation of the crude mixture of vinyl sulfone product **4** (X = SePh) with mCPBA which resulted in selenoxide elimination to give the dienyl sulfone **7** as mainly a single isomer (presumed to be the (*Z*)-product shown) in 70% yield.

Having demonstrated the viability of the $TolSO_2SePh$-mediated cyclisation of **1** and **2**, we proceeded with several related examples shown in Scheme 3.

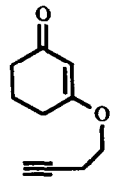


Scheme 3

Cyclisations of the nitrogen-containing enyne and diene systems **8** and **9** gave the desired products in excellent yield, these reactions being noticeably more efficient than those of the analogous ethers **1** and **2**. In the case of **8** we again compared the effectiveness of $TolSO_2SePh$ and $TolSO_2Br$ under comparable conditions, very similar yields and isomer ratios (*ca.* 1.2:1) being obtained. As with the earlier cyclisations of enynes, in the case of vinyl sulfone **12** we assigned the major product as the (*Z*)-isomer. In this case the (*Z*):(*E*) ratio appeared to be about 6:1, although we were unable to isolate the minor component and fully characterise it.

The cyclisation of **10** to form cyclopentane derivative **13** was very high-yielding and we were unable to detect a minor stereoisomer by NMR. Both the high level of stereoselectivity and our assignment of the major stereoisomeric cyclopentane product from this cyclisation as the *cis*-isomer shown follows ample literature precedent and is supported by analysis of the ^{13}C NMR spectrum of **13**.[8]

Systems which failed to cyclise on treatment with $TolSO_2SePh$ under our standard conditions include vinylogous ester **14**,[9] indole derivative **15**, fumaric acid derivative **16**[10] and perhaps most surprisingly the enyne **17**. In the latter case the starting material was consumed, with TLC analysis indicating the formation of several new products, but these proved unstable to column chromatography.



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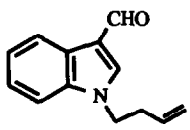

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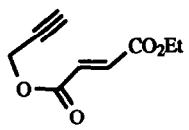

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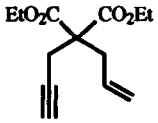
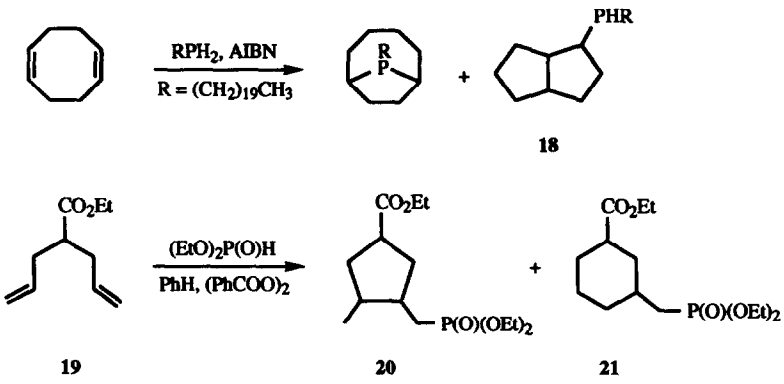


17

Following the completion of our work, a report by Chuang described his independent studies of the cyclisations of 1,6-dienes using $TolSO_2SePh$, with results in accord with those described above.[11]

Cyclisations with Ph_2PH

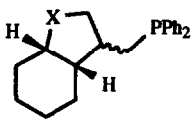
During the course of our studies concerning the use of sulfonyl-centred radicals described above, we became interested in the possibility of using other types of heteroatom-centred radicals to perform a similar role. Two isolated reports prompted us to investigate the use of phosphorus-centred radicals, Scheme 4.[12,13]



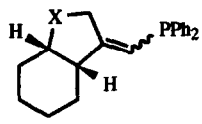
Scheme 4

Transannular cyclisation proved to be a minor pathway in the reaction of a long chain phosphine with cyclooctadiene, resulting in minor amounts of product **18** in which a new C–C bond has been formed.[12] The conversion of 1,6-diene **19** into a mixture of phosphonates **20** and **21**, by treatment with diethyl phosphite in the presence of benzoyl peroxide, reported by Cadogan and coworkers, also provided ample precedent for the desired mode of cyclisation.[13]

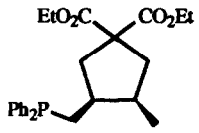
We chose to use Ph_2PH as a source of phosphinyl radicals for cyclisations, since this phosphine is readily available and is known to readily form radicals under mild conditions using AIBN as initiator.[14] The unsaturated substrates **1,2** and **8–10** described earlier were each cyclised under radical generating conditions in benzene at reflux to give the products **22–26** in the yields indicated.



22 X = O, 19% (1.2:1)
23 X = NCO_2Me, 35% (1.2:1)



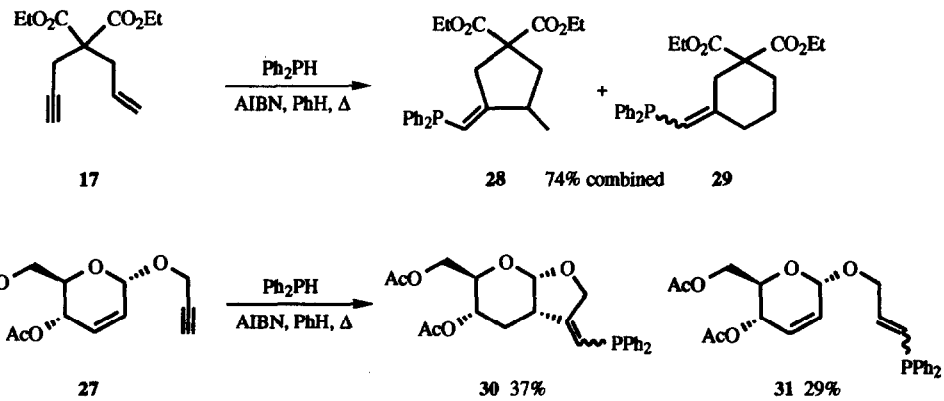
24 X = O, 66% (1.7:1)
25 X = NCO_2Me
55% major isomer
9% minor isomer



26 21% (36% based on rec'd SM)

The observed products are in accord with our expectation that a reversible addition of a Ph_2P· radical to a diene or enyne system results in the formation of an intermediate alkyl or vinyl radical, which can then cyclise to give the desired products. Clearly, enynes are much more satisfactory substrates for cyclisation by Ph_2PH than dienes, which give only modest yields of adduct. This presumably reflects the increased reactivity of the intermediate vinyl radical formed on addition to an alkyne, compared to the alkyl radical formed on addition to an alkene, which allows cyclisation to effectively compete with the elimination of Ph_2P· radical. Isolation and characterisation of these phosphine products was hampered somewhat by their tendency to undergo air oxidation to the corresponding phosphine oxides and because of complexities in their NMR spectra due to the presence of isomeric mixtures and also P–H and P–C couplings.

Two other systems which also gave the anticipated vinyl phosphine products are malonate-derived substrate **17** and the enyne **27** derived from 3,4,6-tri-*O*-acetyl-D-glucal, Scheme 5.



17 **28** 74% combined **29**

27 **30** 37% **31** 29%

Scheme 5

In the case of enyne **17** the isolated product was a mixture of the cyclopentane derivative **28** (as a single isomer) and the corresponding six-membered (formally 6-*endo*) product **29** (as two isomers) in a ratio of about 1:2. The cyclohexane product **29** is assumed to arise by initial 5-*exo-trig* cyclisation, followed by

rearrangement via a diphenylphosphinylmethyl cyclopropyl radical intermediate, as described previously by the groups of Stork and Beckwith.[15] Presumably this complication contributed to our failure to isolate products from the corresponding $TolSO_2SePh$-mediated cyclisation of **17** described in the previous section. The carbohydrate-derived system **27** underwent cyclisation in lower overall yield than the other enynes examined, although in this case the (*Z*):(*E*) ratio was increased to around 6:1.[16]

Conclusion

We have shown that the cyclisation of various dienes and enynes with either $TolSO_2SePh$ or Ph_2PH can lead to products which have undergone functionalisation with concomitant C–C bond formation. The product selenosulfones or phosphines are usually formed as mixtures of stereoisomers, although the degree of stereoselectivity observed is synthetically useful in several cases. Whilst the $TolSO_2SePh$ method appears quite generally useful, the procedure employing Ph_2PH appears to be limited to enyne systems if useful chemical yields are to be achieved.

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were obtained using a Perkin-Elmer 1720-X or Perkin-Elmer 1600 series FT-IR instrument as either liquid films or as dilute solutions in spectroscopic grade chloroform. Proton NMR spectra were recorded on either a Bruker WP 80 SY (80MHz), a Bruker WM 250 (250MHz), a Bruker AM 400 (400MHz) or a Jeol EX-270 (270MHz) spectrometer. The chemical shifts are recorded relative to an internal tetramethylsilane standard and the multiplicity of a signal is designated one of the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, multiplet. All coupling constants, *J*, are reported in Hertz. The ratios of isomer mixtures were determined using ^1H NMR spectroscopy. Carbon-13 NMR spectra were recorded on either a Bruker WM 250 (62.9MHz), Bruker AM 400 (100.6MHz) or Jeol EX-270 (67.8MHz) instrument. The spectra were recorded as dilute solutions in deuterated-solvents as stated, with chemical shifts reported relative to internal tetramethylsilane or chloroform standard on a broad band decoupled mode, and the multiplicities obtained using a DEPT sequence. The following notation is used for the multiplicities in carbon-13 spectra: q, primary-methyl; t, secondary-methylene; d, tertiary-methine; s, quaternary; in some cases additional coupling to phosphorus has been included.

Mass spectra were recorded on a AE1 MS-902 or a MM-701CF spectrometer using electron ionisation (EI) or fast atom bombardment (FAB) techniques. Microanalytical data were obtained on a Perkin-Elmer 240B elemental analyser.

Flash chromatography was performed using Merck silica gel 60 (230–400 mesh) as the stationary phase and the solvents ethyl acetate, ether, light petroleum ether (b.p. 40–60°C), hexanes, acetone and dichloromethane.

All reactions were monitored by TLC using Merck silica gel 60 F_{254} precoated glass plates which were visualised with ultraviolet light and then with either phosphomolybdic acid solution or iodine-impregnated silica gel. Solvents were purified by standard techniques.

Allyl alcohol derived 1,6-diene 1

3-Bromocyclohexene (5.80 g, 36.0 mmol) was added to a vigorously stirred suspension of sodium bicarbonate (6.05 g, 72.0 mmol) in allyl alcohol (9.80 ml, 143.9 mmol) at 0°C, under an atmosphere of nitrogen. The reaction was stirred at room temperature for 36 h, filtered and the precipitate was washed with ether (2 x 10 ml). The filtrate and the ethereal washings were combined and the solvent and excess allyl alcohol were evaporated under reduced pressure. Flash chromatography (dichloromethane) gave the required diene **1** (3.61 g, 73%) as a colourless oil ν_{max}(film)/cm^{-1} 3026, 2937, 2862, 1648, 1453, 1317, 1136, 1077, 923 and 727; δ_H (270 MHz; $CDCl_3$) 1.47-2.16 (6H, m), 3.90 (1H, m, CHO), 4.00-4.06 (2H, m, CH_2O), 5.12-5.32 (2H, m, CH=CH_2) and 5.74-6.0 (3H, m, C*H*=C*H* and C*H*=CH_2); δ_C (67.8 MHz; $CDCl_3$) 19.0 (t), 25.0 (t), 28.1 (t), 68.9 (t, CH_2O), 71.9 (d, CHO), 116.2 (t, CH=*C*H_2), 127.6 (d), 130.5 (d) and 135.2 (d); *m/z* 137 (M^+-1, 11%), 97 (M^+-C_3H_5, 41) and 81 (M^+-C_3H_5O, 100).

Propargyl alcohol derived enyne 2

3-Bromocyclohexene (6.0 g, 37.2 mmol) was added to vigorously stirred suspension of sodium bicarbonate (6.3 g, 74.5 mmol) in propargyl alcohol (8.7 ml, 149.0 mmol) at 0°C, under an atmosphere of nitrogen. The reaction was stirred at room temperature for 48 h, filtered and the precipitate was washed with ether (2 x 10 ml). The filtrate and the ethereal washings were combined and the solvent and excess propargyl alcohol were evaporated under reduced pressure. Flash chromatography (dichloromethane) gave the enyne **2** (3.9 g, 76%) as a colourless oil ν_{max}(film)/cm^{-1} 3292, 2938, 2863, 2350, 1437, 1397, 1321, 1263, 1081, 929 and 668; δ_H (270 MHz; $CDCl_3$) 1.43-2.11 (6H, m), 2.41 (1H, t, *J* 2.3, C≡C*H*), 4.08-4.31 (3H, m, OCH and OCH_2) and 5.75-5.92 (2H, m, C*H*=C*H*); δ_C (67.8 MHz; $CDCl_3$) 18.8 (t), 25.0 (t), 27.8 (t), 55.0 (t, OCH_2), 71.5 (d), 73.8 (s, CH_2*C*CH), 80.2 (d, C*C*H), 126.9 (d) and 131.3 (d); *m/z* 135 (M^+-1, 13%), 97 (M^+-C_3H_3, 18) and 81 (M^+-C_3H_3O, 64).

Cyclisation of 1 with $TolSO_2Br$ to give 3 (X = Br)

(a) Photolytic conditions

A stirred solution of the 1,6-diene **1** (0.11 g, 0.82 mmol) and *p*-toluenesulfonyl bromide (0.25 g, 1.04 mmol) in dichloromethane (10 ml) was irradiated under an atmosphere of nitrogen for 6.25 h. The solvent was evaporated under reduced pressure. Flash chromatography (0-4% ether in dichloromethane) gave the sulfone **3** (X = Br) as a 2:1 mixture of epimers in the form of a yellow oil (0.19 g, 63%) ν_{max}(film)/cm^{-1} 2940, 2866,

1598, 1448, 1313, 1303, 1290, 1254, 1146, 1088 and 1036; δ_H (400 MHz; $CDCl_3$) 1.47-1.65 (3H, m), 1.70-1.89 (1H, m), 1.96-2.04 (1H, m), 2.19-2.45 (2H, m), 2.46 (3H, s, $PhCH_3$), 2.69 (1H, m, minor isomer, $CHCH_2SO_2$), 3.0 (1H, m, major isomer, $CHCH_2SO_2$), 3.06-3.41 (2H, m, CH_2SO_2), 3.64-4.02 (3H, m), 4.22-4.29 (1H, m, OCH_2), 7.38 (2H, d, *J* 8.2, aryl CH), 7.80 (2H, d, *J* 8.2, aryl CH, major isomer) and 7.81 (2H, d, *J* 8.2, aryl CH, minor isomer); δ_C (67.8 MHz; $CDCl_3$, major isomer) 21.2 (t), 22.0 (q, $PhCH_3$), 27.8 (t), 38.2 (d), 38.5 (t), 50.6 (d), 54.5 (d), 57.7 (t), 70.2 (t), 79.2 (d), 128.2 (d, aryl CH), 130.4 (d, aryl CH), 136.7 (s, aryl C) and 145.3 (s, aryl C); *m/z* (FAB) 373 (M^++H, 40%), 293 (M^+-Br, 11) and 217 (M^+-SO_2Tol, 14).

(b) Thermolytic conditions

A solution of 1,6-diene **1** (0.16 g, 1.16 mmol), *p*-toluenesulfonyl bromide (0.30 g, 1.28 mmol) and AIBN (0.019 g, 0.12 mmol) in benzene (14 ml) was heated under reflux, under an atmosphere of nitrogen for 20 h. The reaction was cooled and the solvent was removed under reduced pressure. Flash chromatography (0-4% ether in dichloromethane) gave the sulfone **3** (X = Br) (0.41 g, 95%) as a 2:1 mixture of epimers which was identical to that obtained previously.

Cyclisation of 1 with $TolSO_2I$ to give 3 (X = I) and uncyclised adduct 5

(a) Photolytic conditions

A stirred solution of the 1,6-diene **1** (0.15 g, 1.10 mmol) and *p*-toluenesulfonyl iodide (0.34 g, 1.20 mmol) in dichloromethane (13 ml) was irradiated under an atmosphere of nitrogen for 1.5 h. The solvent was evaporated under reduced pressure. Flash chromatography (0-4% ether in dichloromethane) gave firstly the β-iodosulfone **5** as a 1:1 mixture of diastereoisomers in the form of a yellow oil (0.22 g, 48%) ν_{max}(film)/cm^{-1} 2932, 2864, 1597, 1451, 1401, 1316, 1303, 1148, 1086, 816, 680 and 522; δ_H (250 MHz; $CDCl_3$) 1.46-2.09 (6H, m), 2.45 (3H, s, $PhCH_3$), 3.59 (1H, dd, *J* 5.6, 14.7, $CHSO_2$), 3.69-4.09 (4H, m, $CHSO_2$, OCH_2 and CHI), 4.41-4.51 (1H, m, HCO), 5.64-5.96 (2H, m, CH=CH), 7.37 (2H, d, *J* 8.2, aryl CH) and 7.79 (2H, d, *J* 8.2, aryl CH); δ_C (both isomers) (67.8 MHz; $CDCl_3$) 17.3 and 17.4 (d), 18.9 and 19.0 (t), 21.6 (q, $PhCH_3$), 25.0 (t), 28.0 and 28.2 (t), 61.7 and 61.8 (t), 71.7 and 71.8 (t), 73.1 and 73.3 (d, HCO), 127.0 and 127.1 (d), 128.0 (d), 130.0 (d), 131.3 (d), 136.2 (s, aryl C) and 145.1 (s, aryl CH); *m/z* (FAB) 421 (M^++H, 8%) and 323 (M^+-C_6H_9O, 51) followed by the sulfone **3** (X = I) as a 1.5:1 mixture of epimers in the form of a yellow oil (0.12 g, 26%) ν_{max}(film)/cm^{-1} 2936, 1597, 1303, 1145, 1087, 1038, 557 and 521; δ_H (250 MHz; $CDCl_3$) 1.26-2.65 (7H, m), 2.46 (3H, s, $PhCH_3$), 2.72-3.42 (3H, m), 3.61-4.04 (3H, m), 4.17-4.57 (1H, m), 7.39 (2H, d, *J* 7.2, aryl CH) and 7.81 (2H, d, *J* 7.2, aryl CH); *m/z* (FAB) 421 (M^++H, 32%) and 293 (M^+-I, 18).

(b) Thermolytic conditions

A solution of the 1,6-diene **1** (0.16 g, 1.16 mmol), *p*-toluenesulfonyl iodide (0.36 g, 1.28 mmol) and AIBN (0.019 g, 0.12mmol) in benzene (14 ml) was heated under reflux and under an atmosphere of nitrogen for 40 min. The reaction was cooled and the solvent was removed under reduced pressure. Flash chromatography

(0-4% ether in dichloromethane) gave the sulfone **3** (X = I) (0.11 g, 23%) which was identical to that obtained previously.

*Cyclisation of **1** with $TolSO_2SePh$ to give **3** (X = SePh)*

(a) Photolytic conditions

A stirred solution of the 1,6-diene **1** (0.14 g, 1.0 mmol) and *Se*-phenyl *p*-tolueneselenosulfonate (0.31 g, 1.0 mmol) in chloroform (12 ml) was irradiated under an atmosphere of nitrogen for 7 h. The solvent was evaporated under reduced pressure. Flash chromatography (5-15% ethyl acetate in light petroleum) gave firstly the major isomer of sulfone **3** (X = SePh) (0.071 g, 16%) as a yellow solid, m.p. 90-92°C (from ethyl acetate/light petroleum) $\nu_{max}(CHCl_3)/cm^{-1}$ 3542, 2943, 2857, 1597, 1314 and 1139; δ_H (250 MHz; $CDCl_3$) 1.46-1.54 (4H, m), 1.93 (1H, m), 2.11–2.19 (2H, m), 2.47 (3H, s, $PhCH_3$), 2.82-3.06 (2H, m, $CHCH_2SO_2$ and $CHSePh$), 3.21 (1H, dd, *J* 11.4, 13.6, $CHSO_2$), 3.73 (1H, dd *J* 9.3, 9.3, one of CH_2O), 3.97 (1H, m, CHO), 4.14-4.24 (2H, m, $CHSO_2$ and one of CH_2O), 7.21-7.43 (7H, m, aryl CH) and 7.80 (2H, d, *J* 8.2, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 20.4 (t), 21.6 (q, $PhCH_3$), 27.9 (t), 35.4 (t), 38.1 (d), 39.3 (d), 45.7 (d), 57.5 (t), 70.0 (t), 78.4 (d), 127.8 (d), 127.9 (d), 128.2 (s), 129.1 (d), 130.0 (d), 134.9 (d), 136.6 (s) and 144.8 (s); *m/z* (FAB) 451 (M^++H, 8%) and 293 (M^+-SePh, 16), followed by the minor isomer of sulfone **3** (X = SePh) (0.04 g, 9%) as a pale yellow oil $\nu_{max}(CHCl_3)/cm^{-1}$ 2941, 2855, 1725, 1598, 1315, 1303 and 1136; δ_H (250 MHz; $CDCl_3$) 1.49-1.58 (4H, m), 1.80 (1H, m), 1.95-2.12 (2H, m), 2.45 (3H, s, $PhCH_3$), 2.78-2.86 (2H, m), 3.15 (1H, dd, *J* 14, 9.6, $CHSO_2$), 3.29 (1H, dd, *J* 14, 4.4, $CHSO_2$), 3.63 (1H, dd, *J* 9.7, 5, one of CH_2O), 3.89 (1H, m, CHO), 4.22 (1H, dd, *J* 9.7, 7.7, one of CH_2O), 7.22-7.44 (7H, m, aryl CH) and 7.85 (2H, d, *J* 8.3, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 21.3 (t), 21.6 (q, $PhCH_3$), 27.2 (t), 33.6 (t), 39.9 (d), 45.7 (d), 49.5 (d), 60.5 (t), 71.5 (t), 76.4 (d), 127.8 (d), 127.9 (s), 128.1 (d), 128.9 (d), 129.9 (d), 135.5 (d), 136.1 (s) and 144.9 (s); *m/z* (FAB) 451 (M^++H, 6%) and 293 (M^+-SePh, 10).

(b) Thermolytic conditions

A solution of the 1,6-diene **1** (0.15 g, 1.10 mmol), *Se*-phenyl *p*-tolueneselenosulfonate (0.34 g, 1.10 mmol) and AIBN (0.018 g, 0.11 mmol) in benzene (13 ml) was heated under reflux, under an atmosphere of nitrogen for 5 h. The reaction was cooled and the solvent was removed under reduced pressure. Flash chromatography (15–20% ethyl acetate in light petroleum) gave the epimers of **3** (X = SePh) (0.16 g, 32%) of the major isomer and (0.10 g, 21%) of the minor isomer, which were identical to the products obtained previously.

*Cyclisation of **2** with $TolSO_2Br$ to give **4** (X = Br)*

(a) Photolytic conditions

A stirred solution of the enyne **2** (0.17 g, 1.24 mmol) and *p*-toluenesulfonyl bromide (0.37 g, 1.57 mmol) in dichloromethane (15 ml) was irradiated under an atmosphere of nitrogen for 7 h. The solvent was evaporated

under reduced pressure. Flash chromatography (5-20% ethyl acetate in light petroleum) gave firstly the Z-isomer of vinyl sulfone **4** (X = Br) (0.16 g, 35%) as a white solid, m.p. 111-113°C (from ethyl acetate/light petroleum) (Found: C, 51.6; H, 5.1. $C_{16}H_{19}O_3BrS$ requires C, 51.8; H, 5.2%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2948, 2862, 1648, 1598, 1304 and 1148; δ_H (250 MHz; $CDCl_3$) 1.63-1.88 (4H, m), 1.97-2.40 (2H, m), 2.45 (3H, s, $PhCH_3$), 2.85 (1H, dd, *J* 10, 4, CHC=C), 3.85 (1H, m, CHBr), 3.95 (1H, m, CHO), 4.80 (1H, dd, *J* 17.5, 2.6, one of CH_2O), 5.06 (1H, d, *J* 17.5, one of CH_2O), 6.55 (1H, m, C=CH), 7.35 (2H, d, *J* 8.2, aryl CH) and 7.78 (2H, d, *J* 8.2, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 21.2 (t), 21.6 (q, $PhCH_3$), 26.3 (t), 36.1 (t), 51.7 (d), 54.1 (d), 68.8 (t), 77.8 (d), 123.5 (d), 127.1 (d), 129.9 (d), 138.1 (s), 144.5 (s) and 157.6 (s); (Found: M^+, 370.0239. $C_{16}H_{19}O_3BrS$ requires *M*, 370.0238), followed by the *E*-isomer of vinyl sulfone **4** (X = Br) (0.05 g, 11%) as a yellow oil $\nu_{max}(CHCl_3)/cm^{-1}$ 2949, 2855, 1652, 1598, 1315, 1304 and 1147; δ_H (270 MHz; $CDCl_3$) 1.39-2.15 (6H, m), 2.45 (3H, s, $PhCH_3$), 3.02 (1H, m, CHC=C), 4.00 (1H, m, CHBr), 4.34 (1H, m, CHO), 4.73 (1H, dd, *J* 17.3, 2.0, one of CH_2O), 5.08 (1H, d, *J* 17.3, one of CH_2O), 6.47 (1H, m, C=CH), 7.35 (2H, d, *J* 8.0, aryl CH), 7.80 (2H, d, *J* 8.0, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 17.0 (t), 21.6 (q, $PhCH_3$), 25.9 (t), 32.9 (t), 48.9 (d), 49.9 (d), 70.0 (t), 76.3 (d), 122.3 (d), 127.4 (d), 129.9 (d), 138.2 (s), 144.8 (s) and 160.1 (s); (Found: M^+, 370.0192. $C_{16}H_{19}O_3BrS$ requires *M*, 370.0238).

(b) Thermolytic conditions

A solution of the enyne **2** (0.15 g, 1.10 mmol), *p*-toluenesulfonyl bromide (0.29 g, 1.21 mmol) and AIBN (0.018 g, 0.11 mmol) in benzene (13 ml) was heated under reflux and under an atmosphere of nitrogen for 20 h. The reaction was cooled and the solvent was removed under reduced pressure. Flash chromatography (5-15% ethyl acetate in light petroleum) gave the Z-isomer (0.14 g, 34%) and the E-isomer (0.035 g, 9%) of vinyl sulfone **4** (X = Br), which were identical to the products obtained previously.

Cyclisation of **2** *with* $TolSO_2SePh$ *to give* **4** *(X = SePh)*

(a) Photolytic conditions

A stirred solution of the enyne **2** (0.15 g, 1.10 mmol) and *Se*-phenyl *p*-tolueneselenosulfonate (0.34 g, 1.10 mmol) in chloroform (13 ml) was irradiated under an atmosphere of nitrogen for 8.5 h. The solvent was evaporated under reduced pressure. Flash chromatography (15% ethyl acetate in light petroleum) gave firstly the Z-isomer of vinyl sulfone **4** (X = SePh) (0.14 g, 29%) as a yellow solid, m.p. 147-148°C (from ethyl acetate/light petroleum) (Found: C, 59.1; H, 5.5. $C_{22}H_{24}O_3SSe$ requires C, 59.1; H, 5.4%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2945, 2855, 1645, 1598, 1303, 1146, 1088 and 962; δ_H (250 MHz; $CDCl_3$) 1.45-1.56 (4H, m), 1.92-2.09 (2H, m), 2.43 (3H, s, $PhCH_3$), 2.60 (1H, dd, *J* 10.3, 4.2, CHC=C), 2.90 (1H, m, C*H*SePh), 3.95 (1H, m, CHO), 4.81 (1H, dd, *J* 17.5, 2.6, one of CH_2O), 5.04 (1H, d, *J*, 17.5, one of CH_2O), 6.66 (1H, m, C=CH), 7.17-7.43 (7H, m, aryl CH) and 7.78 (2H, d, *J* 8.3, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 20.9 (t), 21.6 (q, $PhCH_3$), 26.7 (t), 33.5 (t), 43.6 (d), 50.0 (d), 68.8 (t), 77.3 (d), 123.2 (d), 127.1 (d), 127.7 (s), 128.1 (d), 129.0 (d), 129.9 (d), 135.5 (d), 138.5 (s), 144.4 (s) and 159.3 (s); *m/z* (FAB) 449 (M^++H, 21%), 448

(M^+, 24) and 291 (M^+-SePh, 38), followed by the *E*-isomer of vinyl sulfone **4** (X = SePh) (0.037 g, 7%) as a pale yellow oil $\nu_{max}(CHCl_3)/cm^{-1}$ 2839, 1598, 1303 and 1147; δ_H (270 MHz; $CDCl_3$) 1.40-1.75 (4H, m), 1.88-2.07 (2H, m), 2.39 (3H, s, $PhCH_3$), 3.02 (1H, m, CHC=C), 3.24 (1H, m, C*H*SePh), 3.89 (1H, m, CHO), 4.75 (1H, dd, *J* 17.2, 2.3, one of CH_2O), 5.14 (1H, d, *J* 17.2, one of CH_2O), 6.48-6.50 (1H, m, C=CH), 7.07-7.29 (7H, m, aryl CH) and 7.84 (2H, d, *J* 8.6, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 17.7 (t), 21.6 (q, $PhCH_3$), 26.0 (t), 30.4 (t), 45.3 (d), 49.1 (d), 70.7 (t), 76.6 (d), 121.1 (d), 127.3 (d), 127.5 (d), 128.9 (d), 129.8 (d), 131.1 (s), 134.1 (d), 138.4 (s), 144.4 (s) and 161.4 (s); *m/z* (FAB) 449 (M^++H, 28%), 448 (M^+, 11) and 291 (M^+-SePh, 23).

(b) Thermolytic conditions

A solution of the enyne **2** (0.25 g, 1.84 mmol), *Se*-phenyl *p*-tolueneselenosulfonate (0.57 g, 1.84 mmol) and AIBN (0.03 g, 0.18 mmol) in benzene (22 ml) was heated under reflux, under an atmosphere of nitrogen for 5.5 h. The reaction was cooled and the solvent was removed under reduced pressure. Flash chromatography (10-15% ethyl acetate in light petroleum) gave the Z-isomer (0.36 g, 44%) and the *E*-isomer (0.078 g, 10 %) of the vinyl sulfone **4** (X = SePh), which were identical to the products obtained previously.

Reduction of ***3*** *(X = Br) with* Bu_3SnH *to give sulfone* ***6***

A solution of the bromide **3** (X = Br) as a 2:1 mixture of epimers (0.088 g, 0.24 mol), Bu_3SnH (0.08 ml, 0.28 mmol) and AIBN (0.008 g, 0.024 mmol) in benzene (24 ml) was heated under reflux, under an atmosphere of nitrogen for 30h. The reaction was cooled, the solvent was removed under reduced pressure, and the residue was partitioned between acetonitrile (10 ml) and pentane (10 ml). The acetonitrile phase was separated, washed with a further portion of pentane (10 ml) and the solvent was evaporated under reduced pressure. Flash chromatography (4% ether in dichloromethane) gave the sulfone **6** as a 2:1 mixture of epimers (0.067 g, 96%) in the form of a white solid, m.p. 114-115°C (from ethyl acetate/light petroleum) (Found: C, 65.3; H, 7.65. $C_{16}H_{22}O_3S$ requires C, 65.3; H, 7.5 %); $\nu_{max}(CHCl_3)/cm^{-1}$ 2930, 2856, 1598, 1315, 1138, 1089 and 990; δ_H (270 MHz; $CDCl_3$) 0.90-2.02 (9H, m), 2.46 (3H, s, $PhCH_3$), 2.82 (1H, m), 2.99-3.10 (1H, m, $CHSO_2$, both isomers), 3.19-3.32 (1H, m, $CHSO_2$, both isomers), 3.49 (1H, dd, *J* 9.6, 5.3, one of CH_2O, minor isomer), 3.58 (1H, dd, *J* 8.6, 8.8, one of CH_2O, major isomer), 3.86 (1H, m, CHO, minor isomer), 3.91 (1H, m, CHO, major isomer), 4.00 (1H, dd, *J* 8.6, 8.6, one of CH_2O major isomer), 4.17 (1H, dd, *J* 9.6, 8.0, one of CH_2O, minor isomer), 7.37 (2H, d, *J* 8.2, aryl CH) and 7.79 (2H, d, *J* 8.2, aryl CH); δ_C (major isomer) (67.8 MHz; $CDCl_3$) 20.0 (t), 21.6 (q, $PhCH_3$), 22.1 (t), 24.1 (t), 28.0 (t), 37.7 (d), 40.1 (d), 55.5 (t), 69.7 (t, CH_2O), 77.5 (d, CHO), 127.9 (d, aryl CH), 129.9 (d, aryl CH), 136.3 (s, aryl C) and 144.8 (s, aryl C); (Found: M^+, 294.1276. $C_{16}H_{22}O_3S$ requires *M*, 294.1290).

Selenoxide syn-elimination to give diene 7

A solution of 50% *m*CPBA (0.64 g, 1.84 mmol) in dichloromethane (2 ml) was added to a stirred solution of **4** (X = SePh) in dichloromethane (15 ml), at -78°C and under an atmosphere of nitrogen. After 0.5 h the reaction was warmed to 0°C and stirred for 2 h. Saturated sodium bicarbonate solution (20 ml) was added and the reaction was extracted into dichloromethane (3 x 30 ml), washed with water (60 ml), brine (60 ml), dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. Flash chromatography (15% ethyl acetate in light petroleum) gave the dienyl sulfone **7** (0.25 g, 70%) as a white solid, m.p. 121-123°C (from ethyl acetate/light petroleum) (Found: C, 66.3; H, 6.4. $C_{16}H_{18}O_3S$ requires C, 66.2; H, 6.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2845, 1627, 1311, 1302 and 1145; δ_H (270 MHz; $CDCl_3$, major isomer in mixture) 1.19-2.23 (6H, m), 2.43 (3H, s, $PhCH_3$), 4.10-4.20 (1H, m, CHO), 4.66 (1H, dd, *J* 16.5, 2.6, one of CH_2O), 5.17 (1H, dd, *J* 16.5, 2.3, one of CH_2O), 6.20 (1H, m, C=CH), 6.37 (1H, s, $C{=}CHSO_2$), 7.34 (2H, d, *J* 8.0, aryl CH) and 7.78 (2H, d, *J* 8.0, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 18.9 (t), 21.5 (q, $PhCH_3$), 25.4 (t), 27.8 (t), 69.7 (t), 76.8 (d), 116.0 (d), 126.5 (d), 127.0 (d), 129.8 (d), 137.9 (s), 138.5 (s), 144.3 (s) and 151.7 (s); (Found: M^+, 290.0934. $C_{16}H_{18}O_3S$ requires *M*, 290.0977).

Allylamine derived 1,6-diene 8

Allylamine (1.0 ml, 13.3 mmol) was added to 3-bromocyclohexene (1.0 g, 6.21 mmol) at 0°C and under an atmosphere of nitrogen. The reaction was stirred at 0°C for 1.5 h, at room temperature for 15 h and then excess allylamine was evaporated under reduced pressure. 1M NaOH (30 ml) was added and the reaction was extracted into ethyl acetate (2 x 30 ml), washed with water (50 ml), brine (50 ml), dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. Flash chromatography (20-40% ethyl acetate in light petroleum) gave the desired allyl Δ^2-cyclohexenyl amine as a yellow oil (0.49 g, 58%) ν_{max}(film)/cm^{-1} 3301, 3076, 3020, 2932, 2860, 2836, 1706, 1643, 1565, 1450, 917 and 725; δ_H (250 MHz; $CDCl_3$) 1.38-2.08 (6H, m), 2.40 (1H, br. s, NH), 3.20-3.40 (3H, m, CHN, CH_2N), 5.06-5.24 (2H, m, $CH{=}CH_2$) and 5.68-6.01 (3H, m, $CH{=}CHCHN$, $CH{=}CH_2$); *m/z* 137 (M^+, 14%), 136 (M^+-H, 15), 109 (M^+-C_2H_4, 34) and 81 (M^+-C_3H_6N, 54).

Triethylamine (1.33 ml, 9.53 mmol) was added to a stirred solution of this amine (0.87 g, 6.4 mmol) in dichloromethane (9 ml) at 0°C and under an atmosphere of nitrogen. After 5 min methyl chloroformate (0.59 ml, 7.6 mmol) was added dropwise and the reaction was stirred at 0°C for 1 h and room temperature for 36 h. Water (15 ml) was added and the reaction was extracted into ethyl acetate (3 x 15 ml), washed with water (40 ml), brine (40 ml), dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. Flash chromatography (5% ethyl acetate in light petroleum) gave the carbamate **8** (0.99 g, 79%) as a yellow oil ν_{max}(film)/cm^{-1} 2935, 1700, 1460, 1401, 1261 and 1195; δ_H (250 MHz; $CDCl_3$, 333K) 1.52-1.67 (2H, m), 1.76-1.89 (2H, m), 1.98-2.04 (2H, m), 3.69 (3H, s, CH_3), 3.72-3.81 (2H, m, CH_2N), 4.67 (1H, br. s, CHN), 5.04-5.12 (2H, m), 5.50 (1H, m) and 5.78-5.87 (2H, m); δ_C (67.8 MHz; $CDCl_3$) 21.3 (t), 24.4 (t), 27.7 (br. t),

45.5 (br. t), 52.2 (q), 53.3 (d), 115.1 (t, CH=CH_2), 128.2 (d), 131.0 (d), 135.9 (br. d) and 156.7 (s); *m/z* 195 (M^+, 5%) and 154 (M^+-C_3H_5, 23).

Propargylamine derived enyne 9

Propargylamine (3.0 ml, 43.7 mmol) was added to 3-bromocyclohexene (3.5 g, 21.9 mmol) at 0°C and under an atmosphere of nitrogen. The reaction was stirred at 0°C for 1 h, at room temperature for 36 h and then excess propargylamine was evaporated under reduced pressure. 1M NaOH (20 ml) was added and the reaction was extracted into ethyl acetate (3 x 20 ml), washed with water (50 ml), brine (50 ml), dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. Flash chromatography (15% ethyl acetate in light petroleum) gave the desired propargyl Δ^2-cyclohexenyl amine as a yellow oil (2.01 g, 69%) ν_{max}(film)/cm^{-1} 3296, 2933, 2860, 1703, 1599, 1449, 1395, 1374 and 1177; δ_H (250 MHz; $CDCl_3$) 1.36-2.04 (7H, m), 2.24 (1H, t, *J* 2.3, C≡CH), 3.34-3.41 (1H, m, CHN), 3.47 (2H, t, *J* 2.3, CH_2N) and 5.63-5.82 (2H, m, CH=CH); δ_C (67.8 MHz; $CDCl_3$) 19.5 (t), 24.8 (t), 28.5 (t), 34.9 (t), 51.0 (d), 70.9 (s, *C*CH), 81.9 (d, C*C*H), 128.6 (d) and 128.9 (d); *m/z* 122 (M^+-CH, 7%) and 81 (M^+-C_3H_4N, 26).

Triethylamine (3.1 ml, 22.3 mmol) was added to a stirred solution of this amine (2.01 g, 14.9 mmol) in dichloromethane (20 ml) at 0°C under an atmosphere of nitrogen. After 5 mins methyl chloroformate (1.38 ml, 17.9 mmol) was added dropwise and the reaction was stirred at 0°C for 1 h and at room temperature for 15 h. Water (20 ml) was added and the reaction was extracted into ethyl acetate (2 x 50 ml), washed with water (100 ml), brine (100 ml), dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. Flash chromatography (5% ethyl acetate in light petroleum) gave the carbamate **9** as a yellow oil (2.18 g, 76%) ν_{max}(film)/cm^{-1} 3289, 3249, 2937, 2863, 1698, 1454, 1402 and 1261; δ_H (250 MHz; $CDCl_3$) 1.64-2.02 (6H, m), 2.20 (1H, t, *J* 2.4, C≡CH), 3.75 (3H, s, CH_3), 3.78-4.04 (2H, m), 4.64-4.79 (1H, br. m), 5.53 (1H, d, *J* 9.8) and 5.91-5.95 (1H, m); δ_C (67.8 MHz; $CDCl_3$) 21.1 (t), 24.4 (t), 27.3 (br. t), 32.3 (br. t), 52.6 (q), 53.0 (d), 70.1 (s, *C*CH), 81.3 (d, C*C*H), 127.4 (d), 132.1 (d) and 156.1 (s); *m/z* 193 (M^+, 8%) and 154 (M^+-C_3H_3, 100).

Cyclisation of 8 to give sulfone 11 (X = Br)

A solution of the carbamate **8** (0.23 g, 1.18 mmol), *p*-toluenesulfonyl bromide (0.31 g, 1.30 mmol) and AIBN (0.02 g, 0.12 mmol) in benzene (14 ml) was heated under reflux, under an atmosphere of nitrogen for 6 h. The reaction was cooled and the solvent was evaporated under reduced pressure. Flash chromatography (35% ethyl acetate in light petroleum) gave the sulfone **11** (X = Br) as a 1.1:1 mixture of epimers and as a white solid (0.46 g, 90%) m.p. 163-164°C (ethyl acetate/light petroleum) (Found: C, 50.05; H, 5.8; N, 3.1. $C_{18}H_{24}NO_4BrS$ requires C, 50.2; H, 5.6; N, 3.3%); ν_{max}($CHCl_3$)/cm^{-1} 2952, 1688, 1456, 1316 and 1149; δ_H (400 MHz; $CDCl_3$, 338K) 1.31-4.44 (14H, m), 2.45 (3H, s), 3.66 (3H, s, major isomer), 3.67 (3H, s, minor isomer), 7.36 (2H, m, aryl CH) and 7.79 (2H, d, *J* 8.2, aryl CH); δ_C (major isomer) (100 MHz; $CDCl_3$,

338K) 19.1 (t), 21.6 (q), 27.4 (t), 35.5 (d), 37.8 (t), 50.3 (d), 51.2 (t), 52.0 (d), 52.2 (q), 54.3 (d), 59.4 (t), 128.0 (d), 130.2 (d), 136.9 (s), 145.2 (s) and 155.0 (s); *m/z* (FAB) 432 (M^++1, ^{81}Br, 29%), 430 (M^++1, ^{79}Br, 31) and 274 (M^+-SO_2Tol, ^{79}Br, 15).

Cyclisation of ***8*** *to give sulfone* ***11*** *(X = SePh)*

A solution of the carbamate **8** (0.204 g, 1.05 mmol), *Se*-phenyl-*p*-tolueneselenosulfonate (0.36 g, 1.15 mmol) and AIBN (0.02 g, 0.11 mmol) in benzene (13 ml) was heated under reflux, under an atmosphere of nitrogen for 6 h. The reaction was cooled and the solvent was evaporated under reduced pressure. Flash chromatography (20-30% ethyl acetate in light petroleum) gave the sulfone **11** (X = SePh) as a white solid and as a 1.3:1 mixture of epimers (0.50 g, 94%) m.p. 142-144°C (ether/light petroleum) (Found: C, 56.85; H, 5.85; N, 2.65. $C_{24}H_{29}NO_4SSe$ requires C, 56.9; H, 5.8; N, 2.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2946, 2863, 1688, 1457, 1316, 1303 and 1145; δ_H (400 MHz; $CDCl_3$, 338K) 1.24-2.04 (6H, m), 2.44 (3H, s, major isomer), 2.45 (3H, s, minor isomer), 2.69-3.49 (5H, m), 3.65 (3H, s, major isomer), 3.66 (3H, s, minor isomer), 3.67-4.10 (3H, m), 7.21-7.28 (3H, m, aryl CH), 7.35 (2H, d, *J* 8.1, aryl CH), 7.41-7.51 (2H, m, aryl CH), 7.76 (2H, d, *J* 8.1, aryl CH, major isomer) and 7.77 (2H, d, *J* 8.1, aryl CH, minor isomer); δ_C (major isomer) (100 MHz; $CDCl_3$, 338K) 20.0 (t), 21.6 (q), 27.4 (t), 27.6 (t), 35.9 (d), 41.3 (d), 46.1 (d), 51.0 (t), 52.2 (q), 54.5 (d), 59.5 (t), 128.1 (d), 128.1 (d), 129.3 (d), 129.7 (s), 130.2 (d), 135.0 (d), 137.0 (s), 145.1 (s) and 155.1 (s); *m/z* (FAB) 508 (M^++1, ^{80}Se, 40%), 506 (M^++1, ^{78}Se, 24) and 350 (M^+-SePh, 54).

Cyclisation of ***9*** *to give vinyl sulfone* ***12***

A solution of the carbamate **9** (0.2 g, 1.02 mmol), *Se*-phenyl-*p*-tolueneselenosulfonate (0.35 g, 1.12 mmol) and AIBN (0.017 g, 0.10 mmol) in benzene (13 ml) was heated under reflux, under an atmosphere of nitrogen for 6 h. The reaction was cooled and the solvent was evaporated under reduced pressure. Flash chromatography (20-25% ethyl acetate in light petroleum) gave the vinyl sulfone **12** as white solid (0.40 g, 78%) m.p. 166-167°C (ethyl acetate/light petroleum) (Found: C, 57.1; H, 5.6; N, 3.0. $C_{24}H_{27}NO_4SSe$ requires C, 57.1; H, 5.4; N, 2.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 2946, 2858, 1694, 1461, 1303, 1145 and 1116; δ_H (250 MHz; $CDCl_3$) 1.46-1.75 (4H, m), 1.99-2.07 (2H, m), 2.44 (3H, s, $PhCH_3$), 3.08 (1H, br. m), 3.72 (3H, s, CH_3O), 3.76 (1H, br. s), 4.38 (1H, br. s), 4.54 (1H, dm, *J* 18.8, CH_2N), 4.67 (1H, dm, *J* 18.8, CH_2N), 6.14 (1H, d, *J* 2.5, C=CH), 7.23-7.41 (5H, m, aryl CH), 7.48-7.53 (2H, m, aryl CH) and 7.77 (2H, d, *J* 8.3, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 19.4 (t), 21.5 (q), 26.0 (t), 27.3 (br. t), 39.8 (d), 47.8 (t), 49.4 (br. d), 52.4 (q), 53.9 (d), 122.7 (br. d, C=*C*H), 127.1 (d), 128.0 (d), 128.7 (s), 129.3 (d), 129.9 (d), 134.5 (d), 138.0 (s), 144.6 (s), 154.5 (s) and 155.3 (br. s); *m/z* (FAB) 506 (M^++1, ^{80}Se, 25%), 504 (M^++1, ^{78}Se, 17), 350 (M^+-SO_2Tol, ^{80}Se, 33) and 348 (M^+-SO_2Tol, ^{78}Se, 25).

Cyclisation of ***10*** *to give cyclopentane derivative* ***13***

A solution of the diallymalonate derivative **10** (0.24 g, 1.02 mmol), *Se*-phenyl-*p*-tolueneselenosulfonate (0.35 g, 1.12 mmol) and AIBN (0.017 g, 0.10 mmol) in benzene (12 ml) was heated under reflux, under an atmosphere of nitrogen for 8 h. The reaction was cooled and the solvent was evaporated under reduced pressure. Flash chromatography (20% ethyl acetate in light petroleum) gave the cyclopentane **13** as a pale yellow oil which crystallized on standing (0.54 g, 96%) m.p. 65-67°C (from ethyl acetate/light petroleum) (Found: C, 56.5; H, 5.85. $C_{26}H_{32}O_6SSe$ requires C, 56.6; H, 5.85%); ν_{max}(film)/cm^{-1} 2981, 1728, 1478, 1439, 1302, 1261, 1182, 1148 and 1089; δ_H (400 MHz; $CDCl_3$) 1.22 (3H, t, *J* 7) overlapping with 1.24 (3H, t, *J* 7), 2.26 (1H, dd, *J* 13.5, 6.5), 2.32–2.55 (5H, m), 2.45 (3H, s, $PhCH_3$), 2.68 (1H, dd, J 11.6, 9.7, one of CH_2SePh), 2.86 (1H, dd, *J* 11.6, 5.7, one of CH_2SePh), 3.07 (1H, dd, *J* 13.9, 9.1, one of CH_2SO_2), 3.18 (1H, dd, *J* 13.9, 4.3, one of CH_2SO_2), 4.16 (2H, q, *J* 7) overlapping with 4.17 (2H, q, *J* 7), 7.23–7.26 (3H, m, SePh), 7.35 (2H, d, *J* 8.5, SO_2Tol), 7.44–7.46 (2H, m, SePh) and 7.76 (2H, d, *J* 8.5, SO_2Tol); δ_C (67.8 MHz; $CDCl_3$) 13.7 (q), 21.3 (q), 27.5 (t), 36.6 (d), 37.5 (t), 38.4 (t), 41.8 (d), 55.5 (t), 58.0 (s, $C(CO_2Et)_2$), 61.3 (t), 61.4 (t), 126.8 (d), 127.7 (d), 128.8 (d), 129.2 (s), 129.6 (d), 132.5 (d), 136.1 (s), 144.4 (s), 171.5 (s, C=O) and 171.9 (s, C=O); *m/z* 552 (M^+, ^{80}Se, 30%), 550 (M^+, ^{78}Se, 17), 397 (M^+-SO_2Tol, ^{80}Se, 23) and 395 (M^+-SO_2Tol, ^{78}Se, 19).

Cyclisation of ***1*** *with* Ph_2PH *to give phosphine* ***22***

A solution of the 1,6-diene **1** (0.17 g, 1.24 mmol), diphenyl phosphine (0.22 ml, 1.24 mmol) and AIBN (0.02 g, 0.124 mmol) in benzene (15 ml) was heated under reflux and under an atmosphere of nitrogen for 24 h. Further portions of AIBN (0.01 g, 0.06 mmol) were added after 3,6 and 9 h. The reaction was cooled and the solvent was evaporated under reduced pressure. Flash chromatography (0-100% dichloromethane in ether) gave the phosphine **22** as a 1.2:1 mixture of epimers in the form of a colourless oil (0.076 g, 19%) ν_{max}(film)/cm^{-1} 2929, 2857, 1481, 1434, 1156, 1119 and 1022; δ_H (270 MHz; $CDCl_3$) 1.11-1.74 (8H, m), 1.93-2.41 (4H, m), 3.51-3.60 (1H, m, CHO), 3.83-4.15 (2H, m, CH_2O) and 7.33-7.50 (10H, m, aryl CH); (Found: M^+, 324.1674. $C_{21}H_{25}OP$ requires *M*, 324.1643).

Cyclisation of ***8*** *with* Ph_2PH *to give phosphine* ***23***

A solution of the carbamate **8** (0.20 g, 1.05 mmol), diphenyl phosphine (0.20 ml, 1.15 mmol) and AIBN (0.017 g, 0.10 mmol) in benzene (13 ml) was heated under reflux and under an atmosphere of nitrogen for 4 h. A further portion of AIBN (0.017 g, 0.10 mmol) was added and the reaction was heated for another 4.5 h. The reaction was cooled and the solvent was evaporated under reduced pressure. Flash chromatography (5-7% ethyl acetate in light petroleum) gave firstly recovered starting material **8** (0.035 g, 17%) followed by the phosphine **23** as a 1.2:1 mixture of epimers and as a colourless oil (0.14 g, 35%) ν_{max}(film)/cm^{-1} 2931, 2857, 1698, 1450, 1389, 1127, 1097, 739 and 697; δ_H (250 MHz; $CDCl_3$) 0.95-2.15 (11H, m), 2.39-2.45 (1H, m),

3.08 (1H, dd, *J* 10, one of CH_2N), 3.65 (3H, s, OCH_3), 3.58-3.83 (2H, m, CHN and one of CH_2N) and 7.30-7.46 (10H, m, aryl CH); δ_C (major isomer) (67.8 MHz; $CDCl_3$) 21.2 (t), 23.9 (t), 24.5 (t), 28.3 (t), 31.8 (t), 35.4 (d, $^2J_{PC}$ 12.2), 44.4 (d, $^3J_{PC}$ 9.7), 52.1 (t), 52.3 (q), 57.6 (d), 128.7-133.4 (10 peaks), 139.5 (s, $^1J_{PC}$ 13.5) and 155.4 (s, C=O); (Found: M^+, 381.1863. $C_{23}H_{28}NO_2P$ requires *M*, 381.1858).

Cyclisation of **2** *with* Ph_2PH *to give vinyl phosphine* **24**

A solution of the enyne **2** (0.174 g, 1.28 mmol), diphenyl phosphine (0.22 ml, 1.24 mmol) and AIBN (0.02 g, 0.124 mmol) in benzene (15 ml) was heated under reflux and under an atmosphere of nitrogen for 3 h. The reaction was cooled and the solvent was evaporated under reduced pressure. Flash chromatography (1-100% ethyl acetate in light petroleum) gave the vinyl phosphine **24** as a 1.7:1 mixture of geometric isomers in the form of a colourless oil (0.27 g, 66%) ν_{max}(film)/cm^{-1} 3069, 2932, 1641, 1586, 1480, 1434, 1052, 1029, 741 and 697; δ_H (250 MHz; $CDCl_3$) 1.21-2.08 (8H, m), 2.66 (1H, m, C*H*C=C, major isomer), 3.07 (1H, m, C*H*C=C, minor isomer), 3.96-4.06 (1H, m, CHO, both isomers), 4.35 (1H, d, *J* 14.4, minor isomer), 4.49 (1H, d, *J* 15.0, major isomer), 4.65 (1H, d, *J* 14.4, minor isomer) overlapping with 4.66 (1H, d, *J* 15.0, major isomer), 5.91 (1H, s, C=CH, minor isomer), 6.03 (1H, s, C=CH, major isomer) and 7.23-7.47 (10H, m, aryl CH); δ_C (major isomer) (67.8 MHz; $CDCl_3$) 21.3 (t), 23.3 (t), 27.3 (t), 27.8 (t), 45.6 (d), 69.4 (t), 77.6 (d), 115.0 (d, $^1J_{PC}$ 11.0, C=*C*H), 128.4-132.9 (8 peaks), 139.1 (s) and 162.2 (s, $^2J_{PC}$ 24.5); (Found: M^+, 322.1473. $C_{12}H_{23}OP$ requires *M*, 322.1486).

Oxidation of **24** *to the corresponding phosphine oxide*

A sample of the phosphine **24** was left in air for two weeks. Flash chromatography (60% ethyl acetate in light petroleum) gave the *Z*-phosphine oxide as white solid m.p. 149-150°C (Found: C, 74.4; H, 7.0. $C_{21}H_{23}O_2P$ requires C, 74.5; H, 6.85%); ν_{max}($CHCl_3$)/cm^{-1} 2940, 2858, 1640, 1170, 1121 and 1104; δ_H (270 MHz; $CDCl_3$) 1.21-1.81 (8H, m), 2.71 (1H, br. m, CHC=C), 3.98 (1H, m, CHO), 4.59 (1H, ddd, *J* 16.8, 3.0, 3.0, one of CH_2O), 4.83 (1H, d, *J* 16.8, one of CH_2O), 6.00 (1H, d, J_{PH} 24.1), 7.41-7.55 (6H, m, aryl CH) and 7.66-7.75 (4H, m, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 21.0 (t), 23.4 (t), 27.3 (t), 46.6 (d, $^3J_{PC}$ 13.4), 69.3 (t, $^3J_{PC}$ 6.1), 76.6 (d), 109.2 (d, $^1J_{PC}$ 103.7, C=*C*H), 128.6-131.9 (10 peaks), 133.9 (s, $^1J_{PC}$ 105), 134.0 (s, $^1J_{PC}$ 105) and 169.7 (s, *C*=CH).

Cyclisation of **9** *with* Ph_2PH *to give vinyl phosphine* **25**

A solution of the carbamate **9** (0.164 g, 0.85 mmol), diphenyl phosphine (0.16 ml, 0.94 mmol) and AIBN (0.014 g, 0.085 mmol) in benzene (10 ml) was heated under reflux and under an atmosphere of nitrogen for 3 h. A further portion of AIBN (0.014 g, 0.085 mmol) was added and the reaction was heated for another 1.5 h. The reaction was cooled and the solvent was evaporated under reduced pressure. Flash chromatography (10% ethyl acetate in light petroleum) gave firstly the *E*-isomer of vinyl phosphine **25** as a colourless oil

(0.029 g, 9%) ν_{max}(film)/cm^{-1} 2929, 2856, 1703, 1448, 1387, 1361, 1194, 1117, 745 and 697; δ_H (250 MHz; $CDCl_3$) 1.12-2.50 (8H, m), 3.20 (1H, m, CHC=C), 3.70 (3H, s, OCH_3), 3.88 (1H, m, CHN), 4.11-4.28 (2H, m, CH_2N), 6.03 (1H, m, C=CH) and 7.30-7.43 (10H, m, aryl CH); (Found: M$^+$, 379.1713. $C_{23}H_{26}NO_2P$ requires *M*, 379.1702) followed by the *Z*-isomer of **25** as a colourless oil (0.175 g, 55%) ν_{max}(film)/cm^{-1} 2932, 2858, 1701, 1450, 1393, 1315, 1288, 1253, 1192, 1123 and 1108; δ_H (400 MHz; $CDCl_3$, 338K) 1.05 (1H, m), 1.18-1.32 (2H, m), 1.43-1.53 (1H, m), 1.63-1.72 (2H, m), 1.96 (1H, m), 2.12 (1H, d, *J* 14.5), 2.88 (1H, br. s, CHC=C), 3.67 (3H, s, OCH_3), 4.02 (1H, m, CHN), 4.16 (1H, d, *J* 17.0, one of CH_2N), 4.30 (1H, dd, *J* 17.0, 1.5, one of CH_2N), 6.06 (1H, m, C=CH), and 7.25-7.41 (10H, m); δ_C (100 MHz; $CDCl_3$, 338K) 21.0 (t), 23.8 (t), 24.0 (t), 28.0 (t), 44.0 (d, $^3J_{PC}$ 6.2), 49.2 (t, $^3J_{PC}$ 24.0), 52.2 (q), 57.4 (d), 117.9 (d, $^1J_{PC}$ 12.4, C=*C*H), 128.4-133.2 (8 peaks), 138.8 (s, $^1J_{PC}$ 10.5), 139.6 (s, $^2J_{PC}$ 9.1) and 155.2 (s, C=O); (Found: M$^+$, 395.1698. $C_{23}H_{26}NO_3P$ requires *M*, 395.1650).

Cyclisation of ***10*** *with* Ph_2PH *to give phosphine* ***26***

A solution of the diene **10** (0.28 g, 1.18 mmol), diphenyl phosphine (0.23 ml, 1.30 mmol) and AIBN (0.019 g, 0.11 mmol) in benzene (14 ml) was heated under reflux and under an atmosphere of nitrogen for 8 h. The reaction was cooled and the solvent was evaporated under reduced pressure. Flash chromatography (2% ethyl acetate in light petroleum) gave firstly recovered starting material (0.12 g, 43%) followed by the phosphine **26** as a yellow oil (0.10 g, 21%) ν_{max}(film)/cm^{-1} 3054, 2979, 2935, 1729, 1435, 1254 and 1181; δ_H (270 MHz; $CDCl_3$) 0.92 (3H, d, *J* 6.9, CHC*H*$_3$), 1.19 (3H, t, *J* 7.1, CH_2CH_3), 1.23 (3H, t, *J* 7.1, CH_2CH_3), 1.60-2.69 (8H, m), 4.12 (2H, q, *J* 7.0, C*H*$_2$CH$_3$), 4.17 (2H, q, *J* 7.1, C*H*$_2$CH$_3$) and 7.28-7.47 (10H, m, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 13.9 (q), 14.0 (q), 14.9 (q), 29.0 (t, $^1J_{PC}$ 12.2), 36.5 (d, J_{PC} 7.3), 39.3 (t, $^3J_{PC}$ 11.0), 39.5 (d, J_{PC} 13.4), 41.1 (t), 58.8 (s, *C*(CO$_2$Et)$_2$), 61.2 (t), 61.3 (t), 128.3-133.0 (8 peaks), 138.7 (s) and 172.8 (s); (Found: M$^+$, 426.1991. $C_{25}H_{31}O_4P$ requires *M*, 426.1960).

Cyclisation of ***17*** *with* Ph_2PH *to give cyclopentane* ***28*** *and cyclohexane* ***29***

A solution of the enyne **17** (0.35 g, 1.48 mmol), diphenyl phosphine (0.28 ml, 1.63 mmol) and AIBN (0.024 g, 0.15 mmol) in benzene (18 ml) was heated under reflux and under an atmosphere of nitrogen for 5 h. A further portion of AIBN (0.024 g, 0.15 mmol) was added and the reaction was heated for another 3 h. The reaction was cooled and the solvent was evaporated under reduced pressure. Flash chromatography (2.5-75% ethyl acetate in light petroleum) gave a mixture of products **28** and **29** (two isomers) in a ratio of 1:2 (0.39 g, 74%) (Found: M$^+$, 424.1842. $C_{25}H_{29}PO_4$ requires *M*, 424.1803). Recrystallisation (ethyl acetate/light petroleum) gave a single isomer of cyclohexane **29** as a white crystalline solid, m.p. 95-97°C ν_{max}(film)/cm^{-1} 2980, 1731, 1434, 1245, 1191, 739 and 697; δ_H (250 MHz; $CDCl_3$) 1.15 (6H, t, *J*, 7.1, CH_2CH_3), 1.81 (2H, m), 2.10 (2H, t, *J* 6.2), 2.32 (2H, t, *J* 6.2), 3.24 (2H, m), 3.85-4.18 (4H, m, C*H*$_2$CH$_3$), 6.00 (1H, d, *J* 4.3,

C=CH) and 7.25-7.47 (10H, m, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 13.9 (q), 24.1 (t), 31.4 (t), 36.0 (t, $^3J_{PC}$ 25.6), 37.7 (t, $^3J_{PC}$ 6.1), 56.5 (s, $C(CO_2Et)_2$), 61.3 (t), 123.2 (d, $^1J_{PC}$ 7.3), 128.1-132.5 (d, 5 peaks), 139.9 (s, $^1J_{PC}$ 9.8), 153.8 (s, $^2J_{PC}$ 25.6) and 171.1 (s), the residual oil contained the remaining isomer of **29** and cyclopentane **28** in a 1:1 ratio ν_{max}(film)/cm^{-1} 2979, 2935, 1731, 1434, 1245, 1191, 738 and 696; δ_H (270 MHz; $CDCl_3$) 1.11-1.28 (15H, m), 1.70-1.87 (4H, m), 2.11 (2H, m), 2.58-2.85 (5H, m), 3.12-3.37 (2H, m), 4.10-4.20 (8H, m, CH_2CH_3), 5.93-5.98 (2H, m, C=CH) and 7.25-7.38 (20H, m, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 13.9 (q), 17.9 (q), 23.7 (t), 30.9 (t), 31.1 (t), 39.2 (d, $^3J_{PC}$ 7.3), 39.6 (t, $^3J_{PC}$ 19.5), 41.5 (t), 42.7 (t, $^3J_{PC}$ 6.1), 57.0 (s), 58.3 (s), 61.2 (t), 61.4 (t), 117.5 (d, $^1J_{PC}$ 9.8), 123.6 (d, $^1J_{PC}$ 7.3), 128.0-132.8 (d, 10 peaks), 139.1 (s), 139.5 (s), 152.9 (s, $^2J_{PC}$ 25.6), 162.6 (s, $^2J_{PC}$ 24.4), 170.7 (s, C=O), 171.4 (s, C=O) and 171.6 (s, C=O).

Cyclisation of ***27*** *with* Ph_2PH *to give carbohydrate derivatives* ***30*** *and* ***31***

A solution of the enyne **27** (0.31 g, 1.15 mmol), diphenyl phosphine (0.22 ml, 1.26 mmol) and AIBN (0.019 g, 0.11 mmol) in benzene (14 ml) was heated under reflux and under an atmosphere of nitrogen for 3 h. The reaction was cooled and the solvent was evaporated under reduced pressure. Flash chromatography (20% ether in light petroleum) gave firstly a 1:2.4 mixture of the starting material and the uncyclised vinyl phosphine **31** (0.15 g) ν_{max}(film)/cm^{-1} 3281, 2909, 1742, 1371, 1235, 1101 and 1040; δ_H (250 MHz; $CDCl_3$) 2.09 (3H, s, CH_3), 2.11 (3H, s, CH_3), 3.98-4.59 (6H, m), 5.05-5.38 (2H, m), 5.81-5.95 (2H, m), 6.39-6.62 (1H, m) and 7.28-7.47 (10H, m, aryl CH); δ_C (67.8 MHz; $CDCl_3$) 20.7 (q), 20.8 (q), 62.8 (t), 65.0 (d), 66.4 (t), 66.8 (d), 94.0 (d, OCHO), 127.4-142.1 (26 peaks), 170.1 (s, C=O) and 170.6 (s, C=O); (Found: M$^+$-$Ph_2PCHCHCH_2O$, 213.0713. $C_{10}H_{13}O_5$ requires *M*, 213.0763), followed by the bicyclic vinyl phosphine **30** as a 6:1 mixture of geometric isomers (0.19 g, 37%) ν_{max}($CHCl_3$)/cm^{-1} 2926, 2854, 1738, 1366, 1121 and 976; δ_H (250 MHz; $CDCl_3$) 1.79 (1H, m), 1.92 (3H, s, CH_3), 2.08 (3H, s, CH_3), 2.28 (1H, m), 2.95 (1H, br. m), 3.98-4.07 (1H, m), 4.15 (1H, dd, *J* 12.1, 2.5, one of CH_2OAc), 4.29 (1H, dd, *J*, 12.1, 5.1, one of CH_2OAc), 4.57 (1H, dm, *J*, 14.7, one of CH_2O), 4.72-4.86 (2H, m, one of CH_2O and CHOAc), 5.42 (1H, d, *J* 4.8, OCHO), 6.15-6.17 (1H, m, C=CH) and 7.29-7.41 (10H, m, aryl CH); δ_C (major isomer) (67.8 MHz; $CDCl_3$) 20.6 (q), 20.7 (q), 29.9 (t), 41.9 (d, $^3J_{PC}$ 7.3), 62.8 (t), 65.8 (d, $^3J_{PC}$ 23.1), 68.5 (t), 69.6 (d), 100.0 (d), 118.9 (d, $^1J_{PC}$ 12.2, C=CH), 128.4-138.1 (13 peaks), 156.4 (s, $^2J_{PC}$ 25.6), 169.9 (s, C=O) and 170.6 (s, C=O); (Found: M$^+$, 454.1566. $C_{25}H_{27}O_6P$ requires *M*, 454.1545).

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