Versatile Cyclisation Reactions Using Selenoboranes

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Tris(phenylseleno)borane and tris(methylseleno)borane reacted with terminal acetylenes to afford (*Z*)-vinyl selenides. This reaction was initiated by oxygen and the intermediates were vinyl radicals. This radical reaction could be applied to the intramolecular free radical cyclisation of enynes and some heterocycles and carbocycles were synthesised. This novel method could be also employed in the synthesis of α-kainoid derivatives.

Selenyl radicals are reactive chemical species and their addition to multiple bonds is synthetically useful.[1] The phenylselenyl radical can be readily generated by photolysis of diphenyl diselenide or by oxidation of benzeneselenol with oxygen, and adds to olefins,[2] acetylenes[3] or allenes.[4] Photochemical[5a] and thermal reactions[5b] of *Se*-phenyl areneselenosulfonates cause the free radical selenosulfonation to multiple bonds.

On the other hand, the intramolecular addition of carbon free radicals to carbon–carbon multiple bonds constructs the five- and six-membered rings.[6] In particular, the *exo*-methylene substituted five-membered rings are formed by the intramolecular capture of vinyl radicals with double bonds. The vinyl radicals are generated by addition of carbon- or heteroatom-centred radicals to acetylenes.[7] Oshima *et al.* found the facile radical additions of R_3GeH,[8] RSH[9] or R_3SnH[10] to acetylenes induced by triethylborane, and developed the method to the synthesis of five- membered rings with a R_3Ge-, RS- or R_3Sn-substituted methylene group. However, the triethylborane-induced hydroselenation of acetylenes did not give satisfactory results.[11]

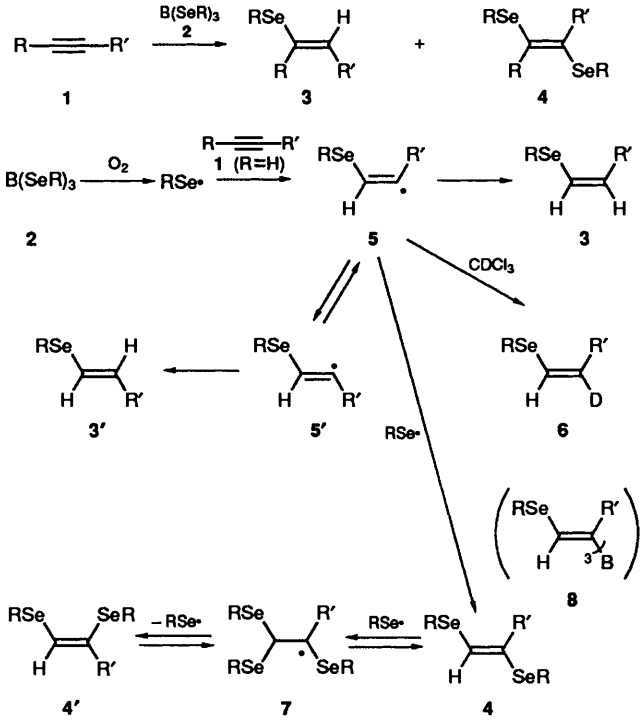
It has been reported that consecutive reactions of iodoacetylenes with bis(1,2-dimethylpropyl)borane and with alkylselenomagnesium bromide afforded vinyl selenides.[12] Recently Hevesi reported that the organoselenoboranes which are generally utilised for selenoacetalisation of aldehydes or ketones,[13] added to α,β-unsaturated ketones.[14] These reports prompted us to examine the reactions of organoselenoboranes with acetylenes and we revealed that organoselenoboranes caused free radical 1,2-addition to acetylenes.[15] We have been interested in the phenylselenomethylene-substituted five-membered ring compounds, since these compounds can be employed in the synthesis of biologically active compounds by transformation of the phenylselenomethylene group to other groups.[16] This paper gives full details of the addition reactions of organoselenoboranes and their application to radical cyclisation of some enynes.

Results and Discussion

Selenoborane reagents **2a** and **2b** were treated with acetylenes in dichloromethane at room temperature to afford mono-RSe-substituted ethylenes **3** and di-RSe-substituted ethylenes **4**. The addition reactions occurred regio- and stereo-selectively at the terminal acetylenic carbon to form *Z*-vinyl selenides in satisfactory yields. However, reactions with an acetylenic alcohol provided low yields of vinyl selenides and reactions with disubstituted acetylenes gave no addition products.[15]

The mechanism of the addition reaction was investigated by ^1H and ^{11}B NMR spectroscopy of the reaction of tris(methylseleno)borane **2a** with methyl propiolate in $CDCl_3$. The reaction did not start under an argon atmosphere but was initiated by bubbling oxygen or air. When the oxygen was exhausted, the reaction stopped. This suggests that the reaction did not progress by a radical chain mechanism. The ^{11}B NMR spectrum exhibited a peak at δ 19.07 (BF_3–diethyl ether as an external reference) due to the boron atom being bound not to the olefinic C-2 but to an oxygen atom.[17] Therefore, the reaction intermediate was found not to be vinylborane **8**. Furthermore, the ^1H NMR spectrum showed a singlet olefinic signal (δ 7.65) due to 3-H and no 2-H signal due to deuterium abstraction from $CDCl_3$.

On the basis of these results, we propose a plausible mechanism for the addition reactions of organoselenoborane as shown in Scheme 1. The RSe radical would be formed from **2**

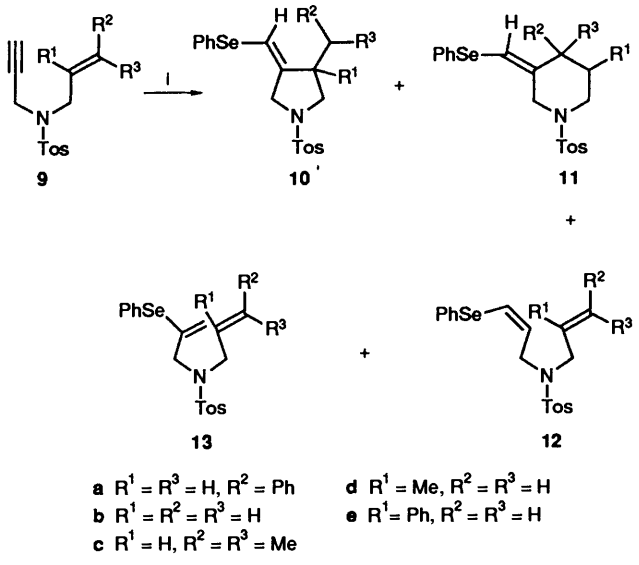


Scheme 1

and oxygen by a process similar to that for formation of alkyl radicals from trialkylboranes and oxygen.[18] The RSe radical adds to the terminal carbon of an acetylene **1** to generate vinyl radical **5**. The radical **5** abstracts a hydrogen from the solvent to give **3**. In $CDCl_3$, 2-deuterated vinyl selenide **6** is formed. Formation of *E*-vinyl selenide **3'** indicates that *Z*-vinyl radical **5** isomerises to the *E*-radical **5'**. The bis(RSe)-substituted olefin **4**

Table 1 Hydroselenation of acetylenes 1 with $B(SeR)_3$ 2

Acetylene 1		Reagent 2	Reaction	Product	$Z/Z + E$ of 3
R	R^1	R (molar ratio)	time (h)	(% yields)	(%)
H	CO_2Me	Me (0.5)	0.5	**3a** (100)	100
H	CO_2Me	Ph (0.5)	0.5	**3b** (100)	100
CO_2Me	CO_2Me	Me (0.5)	0.5	**3c** (100), **4c** (trace)	100
CO_2Me	CO_2Me	Ph (0.5)	0.5	**3d** (100)	92
H	Ph	Me (0.5)	1	**3e** (61), **4e** (18)	100
H	Ph	Ph (0.5)	1	**3f** (79), **4f** (12)	100
H	$(CH_2)_{11}Me$	Ph (0.5)	50	**3g** (72)	—
H	CH_2SO_2Ph	Ph (0.5)	3	**3h** (97)	87

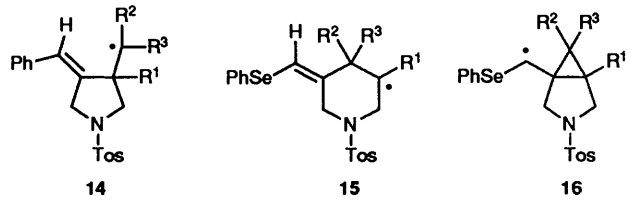


Scheme 2 *Reagents and conditions:* i; Method A: **2b**, CH_2Cl_2, room temp. or Method B: **2b**, AIBN, benzene, reflux

would be produced by radical coupling of the vinyl radical **5** and the RSe radical.

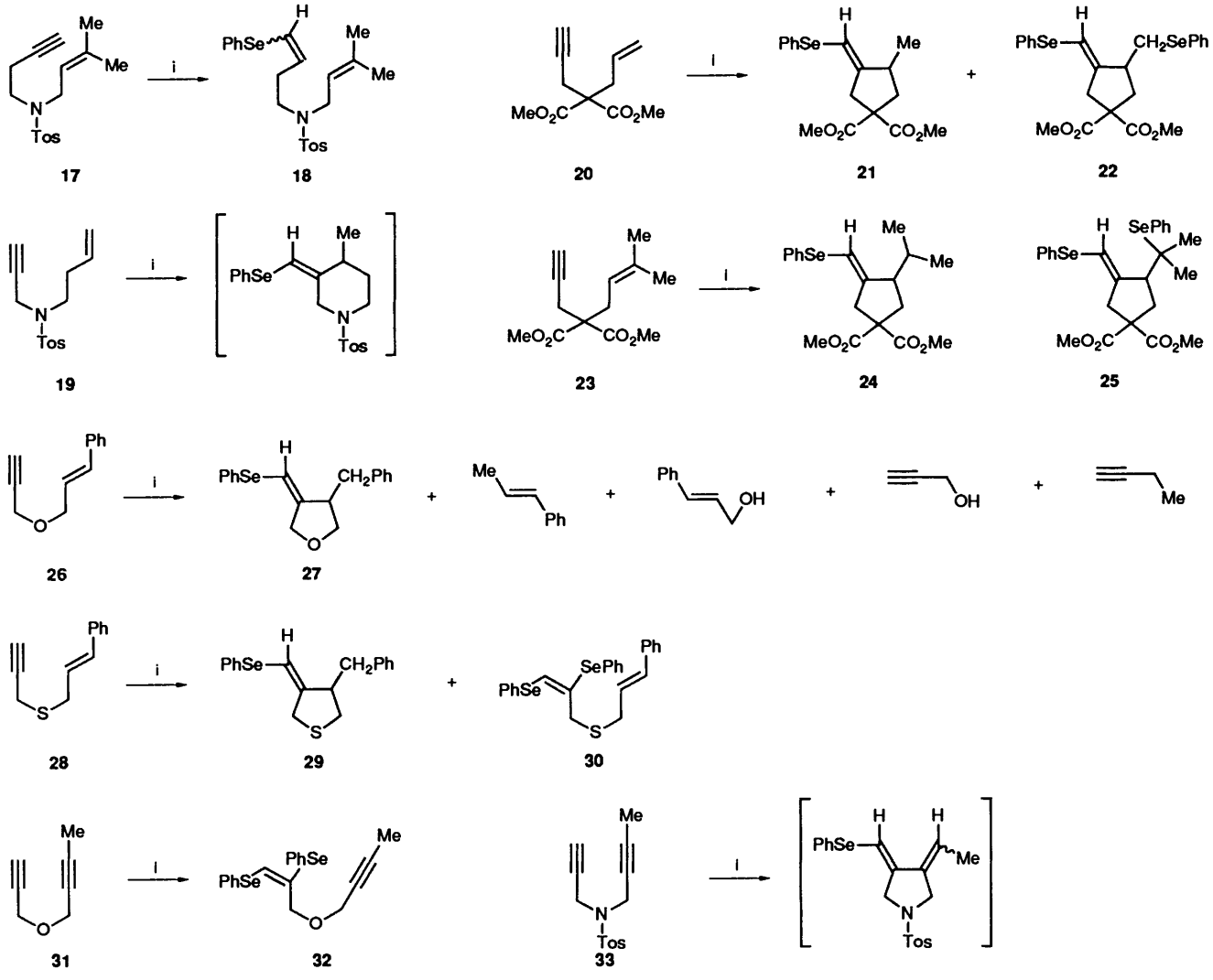
Firstly we describe the cyclisation of enynesulfonamides as an application of the addition reaction mentioned above. Cyclisation of enynesulfonamides **9** with selenoborane **2b** was carried out without azobisisobutyronitrile (AIBN) (Method A) or in the presence of AIBN (Method B). The enynes **9a–c** readily underwent cyclisation to produce the 5-*exo*-cyclised products **10a–c** exclusively. Treatment of *N*-(2-methylprop-2-enyl)-*N*-prop-2-ynylsulfonamide **9d** with selenoborane **2b** gave a non-cyclised adduct **12d** (18%) in contrast to the reaction of *N*-(2-bromoprop-2-enyl)-*N*-(2-methylprop-2-enyl)benzenesulfonamide with tributyltin hydride, which was cyclised in 6-*endo*-mode to give the piperidine derivative.[7e] We also examined the cyclisation of *N*-(2-phenylprop-2-enyl) derivative **9e** and obtained a piperidine derivative **11e** (21%) together with a non-cyclised product **13e**. The product **13e** was an unusual adduct formed by the attack of the phenylselenyl radical at the inner acetylenic carbon. The structure of **13e** was determined by the ^1H NMR spectrum showing four terminal vinyl protons at δ 5.04, 5.29, 5.32 and 5.58 as a broad singlet, respectively and by the ^{13}C NMR spectrum exhibiting two terminal vinyl carbons at δ 116.75 and 121.10 as a triplet, respectively. The ^1H NMR spectral pattern was very different from that of the adduct **12d**. We cannot explain the reasons why the phenylselenyl radical added to the inner acetylenic carbon and why the enynes **9d** and **9e** reacted with the selenoborane **2b** in different reaction modes. The 5-*exo*-cyclisation of vinyl radicals is favoured over the 6-*endo*-ring closure.[7,19] The shorter C–N or C–O bond than a C–C bond promotes the 5-*exo*-cyclisation pathway when the radical ring closure affords a nitrogen[7e] or an oxygen[21b] heterocyclic product. This preference is sometimes inverted by a mediator,[20] a solvent,[7d] or the steric hindrance of an intermediary radical.[21]

Although Malacria and Agnel reported the contribution of a cyclopropylmethyl radical for stabilisation of a homoallyl radical,[21b] the cyclopropylmethyl radical **16** would not be important for the 6-*endo*-cyclisation of the sulfonamide **9e**. Our finding of the piperidine product **11e** can be explained by the assumption that electronic stabilisation by the phenyl group exerts a more favourable effect on the *endo*-radical **15** (R^1 = Ph, benzyl radical) than on the *exo*-radical **14** (R^1 = Ph, phenethyl radical).



Other attempts to synthesise the six-membered ring were unsuccessful. Treatment of enyne **17** with selenoborane **2b** and AIBN afforded a non-cyclised adduct **18** as a mixture of *cis*- and *trans*-isomers (*cis*/*trans* = 2:1). The reaction of *N*-butenyl derivative **19** expecting the 6-*exo*-*trig* ring closure gave a complex mixture.

Next we examined the syntheses of carbocycles. The reaction of dimethyl (allyl)(prop-2-ynyl)propanedioate **20** with the selenoborane **2b** gave the cyclopentane derivatives **21** (10%) and **22** (19%). The 3,3-dimethylallyl derivative **23** also afforded the 5-*exo*-cyclised products **24** (40%) and **25** (21%). The *E*-structure of the product **24** was determined by comparison of the ^1H NMR spectral data with those of tributylstannylmethylene derivatives[22] and then the *E*-structure of **21** was established by reference to the data of **24**. Structure assignment of the product **22** was performed by the mass and NMR spectral data. Its mass spectrum showed the presence of two phenylseleno groups. The ^1H NMR spectrum exhibited a broad singlet at δ 6.33 due to the characteristic vinyl proton, two pairs of double of doublets at δ 2.12 (J 13 and 9 Hz), 2.77 (J 13 and 5 Hz) and at δ 3.00, 3.12 (both J 18 and 2 Hz) due to 5-CH_2 and 2-CH_2, respectively, and a doublet at δ 3.12 (J 7 Hz) due to the CH_2SePh group. The 4-CH was observed as a multiplet near to the 2-CH_2 group. The structure of **25** was similarly determined by analysis of its ^1H NMR spectrum which was more simple than that of **24**. The vinyl proton of **25** was observed at a lower field δ 6.60 than those of the other phenylselenomethylene-substituted 5-membered cyclic compounds described in this report because of the deshielding effect of the phenylseleno group on the isopropyl side chain.



Scheme 3 *Reagents:* i; **2b**, AIBN (Method B)

Furthermore, we conducted the reactions of the enyne ethers or enyne sulfides with selenoboranes in order to extend the radical cyclisation to the synthesis of oxygen and sulfur heterocycles. Reaction of the enyne **26** with selenoborane **2b** gave a tetrahydrofuran derivative **27** in 66% yield together with some products formed by the C–O bond cleavage. Since tris(phenylseleno)borane **2b** cleaved the C–O bond of epoxides,[23] tetrahydrofuran dihydro- and tetrahydro-pyran,[24] we were interested in the action of selenoborane **2b** on the enyne ether. The corresponding enyne sulfide **28** afforded the tetrahydrothiophene derivative **29** (41%) and the adduct **30** (4%).

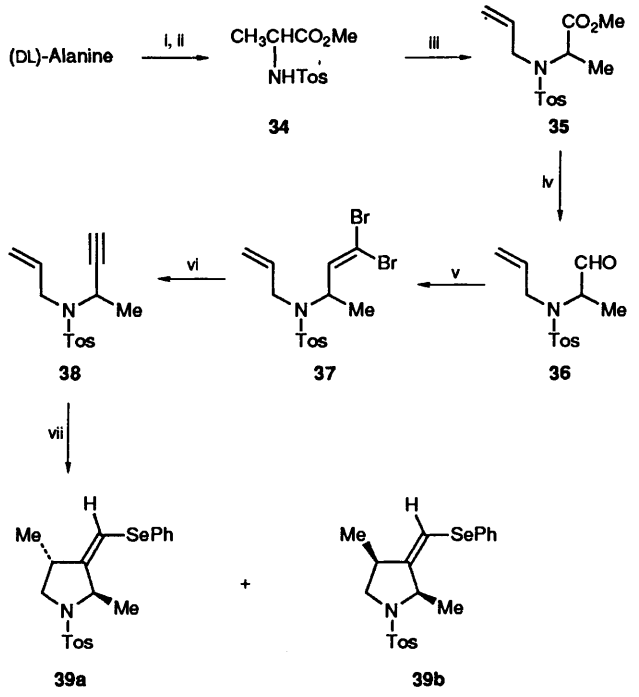
If the vinyl radical can attack the intramolecular triple bond, 1,2-bis(*exo*-methylene)-substituted cyclic compounds (*ortho*-quinoid-type butadiene) as shown in Scheme 3 are formed. Thus we attempted the cyclisation reactions of the diynes **31** and **33** with mono- and di-substituted acetylene moieties and attempted their radical cyclisation on the basis of our findings that the selenoboranes add to the terminal acetylenes only as mentioned above.

The diyne ether **31** gave the adduct **32** as the sole product and the diyne sulfonamide **33** did not afford the cyclised product. Failure of this cyclisation may be attributable to the longer distance between the vinyl radical and the substituted acetylene than that between the radical and the olefin. We also attempted to trap the vinyl radical with an ester or a cyano group intramolecularly, but did not get the cyclised products.

In order to investigate diastereoselectivity of the cyclisation described above, the ring-closure of enyne **38** was conducted. The enyne **38** was synthesised as shown in Scheme 4.

N-Protection and esterification of (D,L)-alanine afforded the *N*-toluene-*p*-sulfonylalanine methyl ester **34**, which was allylated and then reduced with diisobutylaluminium hydride to give *N*-allyl aldehyde **36**. Transformation of the formyl group into the acetylenic group was performed by treatment with carbon tetrabromide–triphenylphosphine and then with 2 equiv. of butyllithium.[25] The cyclisation of enyne **38** with **2b** and AIBN gave pyrrolidine derivatives **39a** and **39b** as a mixture of diastereoisomers with a ratio of **39a**/**39b** = 4. The stereostructure of the isomer **39a** was determined as *trans* by the difference NOE experiments. Irradiation of the 4-methyl protons of **39a** increased the intensities of the vinyl proton, 4-CH and 5β-CH.

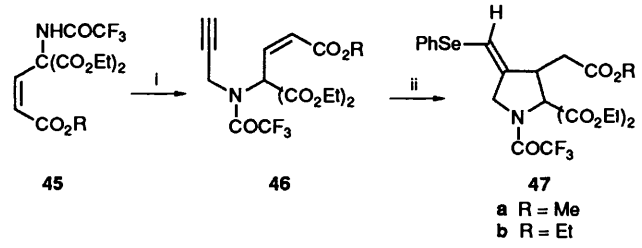
The stereoselectivity of this reaction can be explained as shown in Scheme 5. Isomerisation of (*Z*)-vinyl radical **40** to the (*E*)-radical **41** can be excluded because the 3-(*E*)-*exo*-methylene-substituted product **42** was not obtained. The 3-(*Z*)-*exo*-methylene-substituted products **39a** and **39b** are formed *via* intermediates **43** and **44**, respectively. Steric repulsion between the axial methyl group and the axial hydrogen or the vinyl group in the opposite side of the nitrogen atom in cyclisation transition state **44** would energetically disfavour formation of the *cis*-2,4-dimethylpyrrolidine derivative **39b**. Preferential formation of the *trans*-isomer **39a** stems from the absence of these steric interactions in the cyclisation transition state **43**.



Scheme 4 *Reagents:* i, NaOH, TsCl; ii, HCl, MeOH; iii, NaH, CH_2=$CHCH_2Br$ (92%); iv, Bu^i_2AlH; v, CBr_4, PPh_3 (51%); vi, 2 equiv. BuLi, 2 mol dm^{-3} H_2SO_4 (74%); vii, **2b**, AIBN (Method B) (71%)

Finally we planned to utilise the radical cyclisation of enynes for the synthesis of the kainoids, which have recently attracted considerable interest owing to their pronounced neuroexcitant properties. Baldwin *et al.* reported the syntheses of kainoids utilising radical cyclisation reactions of alkyl halides with cobalt(I) reagent.[26] We synthesised 4-phenylselenomethylene-pyrrolidinetricarboxylates **47** as shown in Scheme 6.

The enyne compounds **46** were prepared by alkylation of 4,4-diethoxycarbonyl-4-trifluoroacetamidobut-2-enoates **45** with prop-2-ynyl bromide. Cyclisation of **46a** and **46b** with



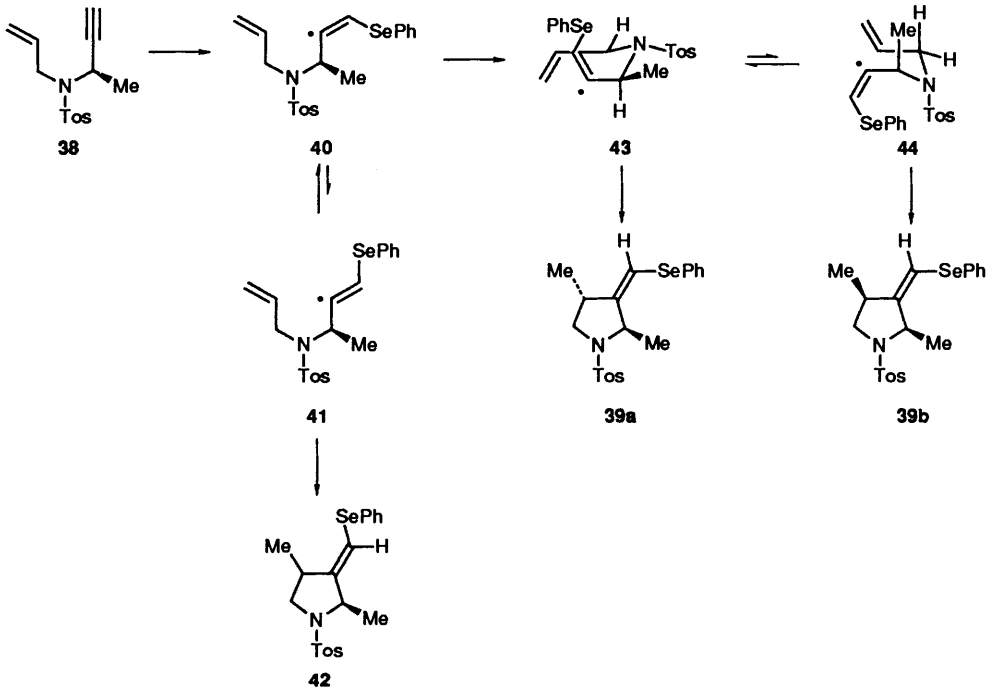
Scheme 6 *Reagents:* i, NaH, $CH{\equiv}CCH_2Br$, HMPA; ii, **2b**

tris(phenylseleno)borane **2b** and AIBN afforded the pyrrolidine derivatives **47a** and **47b** in yields of 55 and 36%, respectively. The yield of product **47a** was decreased to 16% in the absence of AIBN. The pyrrolidines can be led to kainoid derivatives by detrifluoroacetylation and hydrolysis of the esters.[27] Moreover the vinylselenide moiety can be converted into other functional groups[16] and the new kainic acid derivatives with some modifications at 4-position can be synthesised. These will be reported elsewhere.

Experimental

M.p.s were determined on Yanagimoto micro melting point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (film) were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H NMR spectra were obtained for solutions in $CDCl_3$ on a Hitachi R-20B (60 MHz) or a JEOL GX-270 (270 MHz) spectrometer with tetramethylsilane as an internal standard, unless otherwise indicated. ^{13}C NMR spectra and NOE spectrum were run on a JEOL GX-270 spectrometer. *J*-Values are given in Hz. Mass spectra were obtained using a JEOL JMS-D 300 spectrometer with a direct-insertion probe at 70 eV. All exact mass determination was obtained on the JMA 2000 on-line system.

General Procedure for Reactions of Tris(methylseleno)- **2a** *and Tris(phenylseleno)-borane* **2b** *with Acetylenes.*—Methyl propiolate (0.5 g, 5.95 mmol) was added to a CH_2Cl_2 (7 cm^3) solution



Scheme 5

of tris(methylseleno)borane **2a** (2.09 g, 7.14 mmol). After stirring for 30 min the reaction mixture was poured into water and extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by PLC on silica gel eluting with CH_2Cl_2–hexane (1:5). *Methyl* (Z)-3-*methylselenoacrylate* **3a** was obtained as a yellow oil; ν_{max}/cm^{-1} 1700 and 1200 (CO_2Me); δ_H(60 MHz; $CDCl_3$) 2.18 (3 H, s, SeMe), 3.95 (3 H, s, OMe), 6.28 (1 H, d, *J* 11, 2-olefinic H) and 7.65 (1 H, d, *J* 11, 3-olefinic H) (Found: M^+, 179.9685. $C_5H_8O_2Se$ requires *M*, 179.9689).

Methyl (Z)-2,3-*bis*(*methylseleno*)*acrylate* **4a** was obtained by using THF as solvent; ν_{max}/cm^{-1} 1700 and 1250 (CO_2Me); δ_H(60 MHz; $CDCl_3$) 2.23 (3 H, s, SeMe), 2.30 (3 H, s, SeMe), 3.75 (3 H, s, OMe) and 8.55 (1 H, s, olefinic H) (Found: M^+, 273.9029. $C_6H_{10}O_2Se$ requires *M*, 273.9011).

Reaction of **2a** *with Phenylacetylene*.—The reaction of **2a** (0.29 g, 0.98 mmol) with phenylacetylene (0.20 g, 1.96 mmol) in CH_2Cl_2 (3 cm^3) afforded (Z)-β-*methylselenostyrene* **3e** (0.24 g, 61%) as a yellow oil and (E)-α,β-*bis*(*methylseleno*)*styrene* **4e** (0.10 g, 18%) as a yellow oil. **3e**: δ_H(60 MHz; $CDCl_3$) 2.13 (3 H, s, SeMe), 6.48 (1 H, d, *J* 11, β-olefinic H), 6.85 (1 H, d, *J* 11, α-olefinic H) and 7.10–7.40 (5 H, m, ArH) (Found: M^+, 197.9946. $C_9H_{10}Se$ requires *M*, 197.9946). **4e**: δ_H(270 MHz; $CDCl_3$) 2.02 (3 H, s, SeMe), 2.14 (3 H, s, SeMe), 6.67 (1 H, s, olefinic H) and 7.24–7.45 (5 H, m, ArH) (Found: M^+, 291.9268. $C_{10}H_{12}Se_2$ requires *M*, 291.9268).

Reaction of Tris(*phenylseleno*)*borane* **2b** *with Methyl Propiolate*.—The reaction of tris(phenylseleno)borane **2b** (0.54 g, 1.1 mmol) and methyl propiolate (0.17 g, 2.0 mmol) in CH_2Cl_2 (3 cm^3) afforded methyl (Z)-3-phenylselenoacrylate **3b** (0.48 g, 100%) as a yellow oil; ν_{max}/cm^{-1} 1700 (CO); δ_H(60 MHz; $CDCl_3$) 3.73 (3 H, s, OMe), 6.33 (1 H, d, *J* 9, 2-H), 7.20–7.68 (5 H, m, ArH) and 7.70 (1 H, d, *J* 9, 3-H) (Found: M^+, 241.9817. $C_{10}H_{10}O_2Se$ requires *M*, 241.9845).

Reaction of **2b** *with Dimethyl Acetylenedicarboxylate*.—The reaction of **2b** (0.41 g, 0.85 mmol) and dimethyl acetylenedicarboxylate (0.21 g, 1.5 mmol) afforded *dimethyl* 2-*phenylselenofumarate* **3d** (0.41 g, 92%) as a yellow oil and *dimethyl* 2-*phenylselenomaleate* as a yellow oil; **3d**: ν_{max}/cm^{-1} 1730 (CO_2Me); δ_H(270 MHz; $CDCl_3$) 3.10 (3 H, s, OMe), 3.69 (3 H, s, OMe), 6.42 (1 H, s, olefinic H), 7.18–7.27 (3 H, m, ArH) and 7.48–7.51 (2 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 51.57 (q), 51.77 (q), 117.51 (d), 127.51 (d), 128.58 (d), 128.80 (d), 134.31 (s), 135.76 (d), 150.71 (s), 165.15 (s) and 165.93 (s) (Found: M^+, 299.9913. $C_{12}H_{12}O_4Se$ requires *M*, 299.9900). *Dimethyl* 2-*phenylselenomaleate*: ν_{max}/cm^{-1} 1730 (CO); δ_H(270 MHz; $CDCl_3$) 3.65 (3 H, s, OMe), 3.67 (3 H, s, OMe), 5.76 (1 H, s, olefinic H) and 7.27–7.66 (5 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 51.87 (q), 52.68 (q), 118.13 (d), 124.44 (s), 129.10 (d), 129.81 (d), 130.13 (d), 136.68 (d), 136.97 (d), 147.31 (s), 163.86 (s) and 166.25 (s) (Found: M^+, 299.9927. $C_{12}H_{12}O_4Se$ requires *M*, 299.9901).

Reaction of **2b** *with Phenylacetylene*.—The reaction of **2b** (0.49 g, 1.0 mmol) and phenylacetylene (0.18 g, 1.8 mmol) in CH_2Cl_2 (3 cm^3) afforded (Z)-β-*phenylselenostyrene* **3f** (0.37 g, 79%) as a yellow oil and (E)-α,β-*bis*(*phenylseleno*)*styrene* **4f** (0.09 g, 12%) as a yellow oil. **3f**: δ_H(60 MHz; $CDCl_3$) 6.68 (1 H, d, *J* 10, olefinic H), 6.91 (1 H, d, *J* 10, olefinic H) and 7.08–7.60 (5 H, m, ArH) (Found: M^+, 260.0110. $C_{14}H_{12}Se$ requires *M*, 260.0104). **4f**: δ_H(270 MHz; $CDCl_3$) 7.03–7.59 (16 H, m, ArH and olefinic H); δ_C(67.5 MHz; $CDCl_3$) 126.00 (d), 126.62 (d), 127.27 (d), 127.40 (d), 127.44 (d), 127.83 (d), 128.26 (d), 128.62 (d), 129.15 (d), 129.24 (d), 129.37 (d), 130.52 (s), 130.66 (s), 130.87 (d), 131.62 (s), 132.10 (d), 133.18 (d), 133.58 (d) and 139.54 (s) (Found: M^+, 415.9544. $C_{20}H_{16}Se_2$ requires *M*, 415.9580).

Reaction of **2b** *with Dodecyne*.—The reaction of **2b** (0.54 g, 1.1 mmol) and dodecyne (0.39 g, 2.0 mmol) afforded a mixture of (E)- and (Z)-1-*phenylselenododec*-1-*ene* **3g** (0.57 g, 72%) as a yellow oil; ν_{max}/cm^{-1} 2850–2950 (alkyl); δ_H(270 MHz; $CDCl_3$) 0.85–0.90 [3 H, m, (*E*)- and (*Z*)-Me], 1.26–1.43 (20 H, m, CH_2), 2.11–2.19 (2 H, m, CH_2), 6.00–6.43 (4 H, m, olefinic H) and 7.20–7.52 (5 H, m, ArH) (Found: M^+, 352.1686. $C_{20}H_{32}Se$ requires *M*, 352.1669). The product ratio of (*E*)-and (*Z*)-olefins could not be determined because the peaks of (*E*)- and (*Z*)-olefins overlapped.

Reaction of **2b** *and* 3-*Phenylsulfonylprop*-1-*yne*.—The reaction of **2b** (0.24 g, 0.5 mmol) and 3-phenylsulfonylprop-1-yne (0.18 g, 1.0 mmol) in dry CH_2Cl_2 (2 cm^3) afforded (Z)-3-*phenylsulfonyl*-1-*phenylselenoprop*-1-*ene* **3h** (0.29 g, 84%), m.p. 89–90 °C, as white needles; ν_{max}/cm^{-1} 1300 and 1150 (SO_2); δ_H(270 MHz; $CDCl_3$) 2.01 (2 H, d, *J* 7, CH_2) and 7.02–7.81 (11 H, m, ArH and olefinic H) (Found: C, 53.3; H, 4.2. $C_{15}H_{14}O_2SSe$ requires C, 53.4; H, 4.1%).

N-*Cinnamyl*-N-*prop*-2-*ynyltoluene*-p-*sulfonamide* **9a**.—A DMF (8 cm^3) solution of *N*-cinnamyltoluene-*p*-sulfonamide[28] (2.0 g, 7.0 mmol) was dropwise added to the DMF (4 cm^3) suspension of NaH (0.25 g, 10.4 mmol) at 0 °C. After stirring for 15 min at room temperature, the DMF (8 cm^3) solution of prop-2-ynyl bromide (0.92 g, 7.7 mmol) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred overnight, poured into water, and extracted with benzene–hexane (4:1). The extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt–hexane (1:5). The title compound **9a** (1.42 g, 62%) was obtained as white prisms, m.p. 80–81 °C; ν_{max}/cm^{-1} 3250 (HC≡C) and 2100 (C≡C); δ_H(270 MHz; $CDCl_3$) 2.05 (1 H, t, *J* 2, C≡CH), 2.42 (3 H, s, Me), 3.99 (2 H, d, *J* 6, CH_2C=), 4.12 (2 H, d, *J* 2, $CH_2C{\equiv}C$), 6.07 (1 H, dt, *J* 6 and 16, CH_2CH=), 6.57 (1 H, d, *J* 16, =CHPh), 7.24–7.32 (7 H, m, ArH) and 7.76 (2 H, d, *J* 8, ArH); δ_C(67.5 MHz; $CDCl_3$) 21.51 (q), 35.84 (t), 48.52 (t), 73.85 (s), 76.50 (d), 122.82 (d), 126.49 (d), 127.72 (d), 128.02 (d), 128.56 (d), 129.47 (d), 134.85 (d), 136.03 (s) and 143.59 (s) (Found: C, 70.0; H, 5.8; N, 4.3. $C_{19}H_{19}NO_2S$ requires C, 70.1; H, 5.9; N, 4.3%).

N-(3-*Methylbut*-2-*enyl*)-N-*prop*-2-*ynyltoluene*-p-*sulfonamide* **9c**.—*N*-(3-Methylbut-2-enyl)toluene-*p*-sulfonamide[25] was treated with prop-2-ynyl bromide by the same procedure described above for **9a** to give the title compound **9c** as an orange oil (70%); ν_{max}/cm^{-1} 3350 (C≡CH), 2100 (C≡C), 1340 and 1160 (SO_2); δ_H(270 MHz; $CDCl_3$) 1.70 (6 H, br s, $Me_2C{\equiv}C$), 1.97 (1 H, t, *J* 2, HC≡C), 2.40 (3 H, s, Me), 3.80 (2 H, d, *J* 7, CH_2), 4.05 (2 H, d, *J* 2, $HC{\equiv}CCH_2$), 4.90–5.30 (1 H, m, $Me_2C{\equiv}CH$), 7.25 (2 H, d, *J* 8, ArH) and 7.70 (2 H, d, *J* 8, ArH) (Found: M^+, 277.1148. $C_{15}H_{19}NO_2S$ requires *M*, 277.1038).

N-β-*Methylallyl*-N-*prop*-2-*ynyltoluene*-p-*sulfonamide* **9d**.—A mixture of toluene-*p*-sulfonamide, 3-chloro-2-methylallylpropane and K_2CO_3 in acetone was heated at reflux overnight. The mixture was poured into water and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica gel using AcOEt–hexane (1:5) to give N-β-*methylallyltoluene*-p-*sulfonamide* (70%) as white prisms (dichloromethane–hexane), m.p. 50–52 °C; ν_{max}/cm^{-1} 3300 (NH), 1320 and 1160 (SO_2); δ_H(60 MHz; $CDCl_3$) 1.70 (3 H, s, Me), 2.45 (3 H, s, Me), 3.50 (2 H, d, *J* 6, CH_2), 7.30 (2 H, d, *J* 8, ArH) and 7.75 (2 H, d, *J* 8, ArH) (Found: C, 58.6; H, 6.8; N, 6.2. $C_{11}H_{15}NO_2S$ requires C, 58.6; H, 6.7; N, 6.2%).

N-β-Methylallyltoluene-*p*-sulfonamide was treated with prop-2-ynyl bromide by the same procedure as described above

for **9a** to give the title compound **9d** (89%) as white prisms (dichloromethane–hexane), m.p. 64–65 °C; ν_{max}/cm^{-1} 3350, 2100 (C≡CH), 1340 and 1160 (SO_2); δ_H(60 MHz; $CDCl_3$) 1.77 (3 H, br s, Me), 1.99 (1 H, t, *J* 3, C≡CH), 2.40 (3 H, s, Me), 3.70 (2 H, s, CH_2), 4.05 (2 H, d, *J* 8, CH_2), 4.98 (2 H, br s, C=CH_2), 7.25 (2 H, d, *J* 8, ArH) and 7.75 (2 H, d, *J* 8, ArH) (Found: C, 63.6; H, 6.5; N, 5.3. $C_{14}H_{17}NO_2S$ requires C, 63.85; H, 6.5; N, 5.3%).

N-β-*Styrylmethyl*-N-*prop*-2-*ynyltoluene*-p-*sulfonamide* **9e**.—Toluene-*p*-sulfonamide was treated with β-styrylmethyl bromide by the same procedure as described above with β-methylallyl bromide. N-β-*Styrylmethyltolune*-p-*sulfonamide* was obtained as colourless needles (55%) (dichloromethane–hexane), m.p. 81–83 °C; ν_{max}/cm^{-1} 3250 (NH), 1315 and 1160 (SO_2); δ_H(60 MHz; $CDCl_3$) 2.45 (3 H, s, Me), 4.00 (2 H, d, *J* 6, CH_2), 4.80–5.10 (1 H, m, NH), 5.30 (2 H, d, *J* 9, =CH_2), 7.20–7.40 (7 H, m, ArH) and 7.75 (2 H, d, *J* 8, ArH) (Found: C, 66.8; H, 6.0; N, 4.9. $C_{16}H_{17}NO_2S$ requires C, 66.9; H, 6.0; N, 4.9%). The *N*-Styrylmethylsulfonamide was allowed to react to give the title compound **9e** (quant.) by the same procedure as described above for **9a**. Colourless needles (dichloromethane–hexane), m.p. 72–73.5 °C; ν_{max}/cm^{-1} 1340, 1320 and 1150 (SO_2); δ_H(60 MHz; $CDCl_3$) 1.90 (1 H, t, *J* 2, HC≡C), 2.40 (3 H, s, Me), 3.95 (2 H, d, *J* 2, ≡CCH_2), 4.20 (2 H, s, CH_2), 5.40 (2 H, d, *J* 12, =CH_2), 7.10–7.55 (7 H, m, ArH) and 7.70 (2 H, d, *J* 8, ArH) (Found: C, 70.0; H, 5.9; N, 4.3. $C_{19}H_{19}NO_2S$ requires C, 70.1; H, 5.9; N, 4.3%).

N-*Butyn*-3-*yl*-N-(3-*methylbut*-2-*enyl*)*toluene*-p-*sulfonamide* **17**.—To a dry THF (8 cm^3) solution of *N*-(3-methylbut-2-enyl)toluene-*p*-sulfonamide[7e] (2.0 g, 8.4 mmol), but-3-yn-1-ol (0.88 g, 12.5 mmol) and triphenylphosphine (2.2 g, 8.4 mmol) was added a solution of diethyl azodicarboxylate (1.46 g, 8.4 mmol) in THF (8 cm^3) over 30 min under an Ar atmosphere. After stirring for 2 h, the solvent was removed under reduced pressure. Purification of the residue by column chromatography eluting with AcOEt–hexane (1:10) afforded the title compound **17** (1.2 g, 50%) as a yellow oil; ν_{max}/cm^{-1} 1340 and 1150 (SO_2); δ_H(60 MHz; $CDCl_3$) 1.65 (6 h, br s, =CMe_2), 2.00 (1 H, t, *J* 2, HC≡C), 2.20–2.70 (2 H, m, NCH_2CH_2), 2.40 (3 H, s, Me), 3.20 (2 H, d, *J* 8, NCH_2CH), 3.80 (2 H, t, *J* 7, NCH_2CH_2), 4.80–5.20 (1 H, m, CH=), 7.30 (2 H, d, *J* 8, ArH) and 7.70 (2 H, d, *J* 8, ArH); *m*/*z* 252 (M^+ − HC≡CCH_2). The molecular ion peak was not observed.

Reactions of **2b** *with Enyne Sulfonamides* **9**. *General Procedure* (*Method A*).—*N*-Cinnamyl-*N*-prop-2-ynyltoluene-*p*-sulfonamide **9a** (0.20 g, 0.6 mmol) was added to a dry CH_2Cl_2 (1 cm^3) solution of **2b** (0.53 g, 1.1 mmol) under an N_2 atmosphere. The reaction mixture was stirred overnight, poured into water (100 cm^3) and extracted with CH_2Cl_2. The extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by PLC on silica gel eluting with AcOEt–hexane (1:10). 4-*Benzyl*-3-(*phenylselenomethylene*)-1-*toluene*-p-*sulfonylpyrrolidine* **10a** (0.28 g, 90%), m.p. 89–90 °C was obtained as colourless needles; ν_{max}/cm^{-1} 1340 and 1160 (SO_2); δ_H(270 MHz; $CDCl_3$) 2.40 (3 H, s, Me), 2.58 (1 H, m, 2-H), 2.95 (2 H, m, 2-H and 4-H), 3.06 (1 H, dd, *J* 9 and 5, 5-H), 3.25 (1 H, dd, *J* 9 and 7, 5-H), 3.90 (2 H, d, *J* 9, CH_2Ph), 6.16 (1 H, br s, olefinic H) and 7.07–7.75 (14 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 21.4 (q), 38.9 (t), 45.9 (d), 51.1 (t), 53.0 (t), 112.0 (d) and ArC (Found: C, 62.0; H, 5.2; N, 2.9. $C_{25}H_{25}NO_2SSe$ requires C, 62.2; H, 5.2; N, 2.9%). In the case of Method B the enyne **9a** also afforded the pyrrolidine derivative **10a** (94%). The general procedure for Method B is shown below.

Reaction of **2b** *with* N-*Allyl*-N-*prop*-2-*ynylbenzenesulfonamide* **9b**. *General Procedure* (*Method B*).—To a benzene (3 cm^3) solution of **2b** (0.53 g, 1.1 mmol) and AIBN (16 mg, 0.1 mmol) was added the enyne sulfonamide **9b**[7e] (0.24 g, 1.0 mmol). The reaction mixture was heated at reflux for 4 h under an N_2 atmosphere, poured into water (100 cm^3), extracted with CH_2Cl_2 and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by PLC on silica gel eluting with AcOEt–hexane (1:5). 4-*Methyl*-3-(*phenylselenomethylene*)-1-*benzenesulfonylpyrrolidine* **10b** (0.17 g, 42%) was obtained as white prisms (dichloromethane–hexane), m.p. 75–77 °C; ν_{max}/cm^{-1} 1350 and 1160 (SO_2); δ_H(270 MHz; $CDCl_3$) 1.07 (3 H, d, *J* 6, 4-Me), 2.72–2.81 (2 H, m, 5-CH_2), 3.53–3.64 (1 H, m, 4-H), 3.76 (1 H, br d, *J* 15, 2-H), 3.94 (1 H, dd, *J* 15 and 1, 2-H), 6.24 (1 H, br s, olefinic H) and 7.22–7.86 (10 H, m, ArH) (Found: C, 54.8; H, 5.0; N, 3.5. $C_{18}H_{19}NO_2SSe$ requires C, 55.1; H, 4.9; N, 3.6%).

Reaction of N-β-*Methylallyl*-N-*prop*-2-*ynyltoluene*-p-*sulfonamide* **9d** *with* **2b**.—N-β-*Methylallyl*-N-[3-(*phenylseleno*)-*allyl*]*toluene*-p-*sulfonamide* **12d** (18%) was obtained as a yellow oil by Method B; ν_{max}/cm^{-1} 1340 and 1160 (SO_2); δ_H(60 MHz; $CDCl_3$) 1.70 (3 H, s, =CH*Me*), 2.40 (3 H, s, Me), 3.70 (2 H, br s, CH_2C=CH_2), 3.80–4.10 (2 H, m, =CHCH_2N), 4.90 (2 H, br s, CH_2=C), 5.60–6.05 (1 H, m, =CH), 6.53 (1 H, d, *J* 9, PhSe*CH*), 7.15–7.55 (7 H, m, ArH) and 7.70 (2 H, d, *J* 8, ArH) (Found: M^+, 421.0590. $C_{20}H_{23}NO_2SSe$ requires *M*, 421.0820).

Reaction of N-(3-*Methylbut*-2-*enyl*)-N-*prop*-2-*ynyltolune*-p-*sulfonamide* **9c** *and* **2b**.—4-*Isopropyl*-3-(*phenylselenomethylene*)-1-*toluene*-p-*sulfonylpyrrolidine* **10c** (quant.) was obtained as a yellow oil by Method B; ν_{max}/cm^{-1} 1340 and 1160 (SO_2); δ_H(270 MHz; $CDCl_3$) 0.83 (3 H, d, *J* 7, Me), 0.90 (3 H, d, *J* 7, Me), 1.76–1.83 (1 H, m, *CH*Me_2), 2.42 (3 H, s, Me), 2.55–2.57 (1 H, m, *CH*$CHMe_2$), 3.24–3.29 (2 H, br d, 4-CH_2), 3.73–3.87 (2 H, br d, 2-CH_2), 6.25–6.27 (1 H, m, C=CH), 7.23–7.38 (7 H, m, ArH) and 7.71 (2 H, d, *J* 8, ArH); δ_C(67.5 MHz; $CDCl_3$) 18.35 (q), 20.54 (q), 30.24 (d), 50.00 (t), 50.60 (d), 52.39 (t), 111.95 (d), 127.03 (d), 127.66 (d), 129.18 (d), 129.60 (d), 130.55 (s), 131.45 (d), 132.57 (s), 143.54 (s) and 143.82 (s) (Found: M^+, 435.0740. $C_{21}H_{25}NO_2SSe$ requires *M*, 435.0770).

Reaction of N-*Styrylmethyl*-N-*prop*-2-*ynyltoluene*-p-*sulfonamide* **9e** *and* **2b**.—3-(*Phenylselenomethylene*)-5-*phenyl*-1-*toluene*-p-*sulfonylpiperidine* **11e** (21%) as white needles, m.p. 151–152 °C, and N-(2-*phenylpropenyl*)-N-[2-(*phenylseleno*)-*propenyl*]*toluene*-p-*sulfonamide* **13e** (21%) as a yellow oil were obtained by Method B. **11e**: ν_{max}/cm^{-1} 1340 and 1160 (SO_2); δ_H(270 MHz; $CDCl_3$) 2.35–2.40 (1 H, m, 4-CH), 2.43 (3 H, s, Me), 2.53–2.65 (2 H, m, 4-H and 6-H), 2.83–2.94 (1 H, m, Ph*CH*), 3.03 (1 H, d, *J* 13, 2-H), 3.89–3.98 (1 H, m, 6-H), 4.76 (1 H, d, *J* 13, 2-H), 6.36 (1 H, br s, olefinic H), 7.14–7.34 (10 H, m, ArH), 7.44–7.48 (2 H, m, ArH) and 7.62–7.71 (2 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 21.52 (q), 40.72 (t), 42.25 (d), 48.83 (t), 52.04 (t), 126.98 (d), 127.08 (d), 127.20 (d), 127.69 (d), 128.69 (d), 129.24 (d), 129.72 (d), 130.73 (s), 131.75 (d), 131.92 (d), 133.90 (s), 136.93 (s), 141.25 (s) and 143.56 (s) (Found: C, 62.0; H, 5.3; N, 2.9. $C_{25}H_{25}NO_2SSe$ requires C, 62.2; H, 5.2; N, 2.9%). **13e**: ν_{max}/cm^{-1} 1340 and 1160 (SO_2); δ_H(270 MHz; $CDCl_3$) 2.40 (3 H, s, Me), 3.88 (2 H, s, =PhCH_2), 4.29 (2 H, s, =SePhCH_2), 5.04 (1 H, br s, olefinic H), 5.29 (1 H, br s, olefinic H), 5.32 (1 H, br s, olefinic H), 5.58 (1 H, br s, olefinic H), 7.20–7.28 (10 H, m, ArH), 7.43–7.47 (2 H, m, ArH) and 7.58 (2 H, d, *J* 8, ArH); δ_C(67.5 MHz; $CDCl_3$) 21.48 (q), 51.71 (t), 52.85 (t), 116.75 (t), 121.10 (t), 126.40 (d), 127.36 (d), 127.79 (d), 127.88 (d), 128.27 (d), 128.31 (s), 129.27 (d), 129.49 (d), 133.98 (d), 135.83 (s), 136.64 (s), 138.43 (s), 142.16 (s) and 143.24 (s) (Found: M^+, 483.0683. $C_{25}H_{25}NO_2SSe$ requires *M*, 483.0663).

Reaction of N-*But*-3-*ynyl*-N-(3-*methylbut*-2-*enyl*)*toluene*-p-*sulfonamide* **17** *and* **2b**.—N-(3-*Methylbut*-2-*enyl*)-N-3-(*phenylselenobutenyl*)*toluene*-p-*sulfonamide* **18** (7%) (*cis*/*trans* = 2:1) was obtained as a yellow oil by Method B. The ratio of stereoisomers was determined by the intensities of olefinic protons in the ^{1}H NMR spectrum; ν_{max}/cm^{-1} 1340 and 1160 (SO_2); δ_H(270 MHz; $CDCl_3$) 1.60, 1.64, 1.66, 1.70 (each s, *cis* and *trans* C=CMe_2), 2.42 (s, Me), 3.13–3.28 (m, NCH_2), 3.59 (d, *J* 7, NCH_2C=), 3.77–3.84 (m, NCH_2CH_2), 5.00–5.03, 5.06–5.12 (each m, *cis* and *trans* PhSeC=*CH*), 5.87–6.00 (m, Me_2C=*CH*), 6.42 (d, *J* 15, PhSeCH_{trans}), 6.52 (d, *J* 9, PhSeCH_{cis}), 7.22–7.33 (m, ArH), 7.43–7.55 (m, ArH) and 7.58–7.72 (m, ArH); δ_C(67.5 MHz; $CDCl_3$) 17.71 (q), 21.44 (q), 25.71 (q), 33.92 (q), 37.69 (t), 45.86 (t), 46.91 (t), 47.61 (t), 118.31 (d), 118.96 (d), 119.40 (t), 127.10 (d), 127.82 (d), 128.63 (s), 129.14 (d), 129.28 (d), 129.54 (3), 134.25 (d), 134.44 (s), 136.91 (s), 137.10 (s), 137.70 (s), 139.01 (s), 142.97 (s) and 143.16 (s). A small M^+ was observed at *m*/*z* 449 but was too small for the exact mass spectrum to be measured.

Reaction of Dimethyl (*Allyl*)(*prop*-2-*ynyl*)*propanedioate* **20** *and* **2b**.—(E)-*Dimethyl* 4-*methyl*-3-*phenylselenomethylene-cyclopentane*-1,1-*dicarboxylate* **21** (10%) and (E)-*dimethyl* 4-*phenylselenomethyl*-3-*phenylselenomethylene cyclopentane*-1,1-*dicarboxylate* **22** (19%), as a yellow oil, were obtained by Method B. **21**: ν_{max}/cm^{-1} 1730 and 1250 (CO_2Me); δ_H(270 MHz; $CDCl_3$) 1.09 (3 H, d, *J* 6, Me), 2.58–3.15 (5 H, m, 2-H, 4-H, 5-H), 3.67 (6 H, s, MeO × 2), 6.14 (1 H, br s, olefinic H), 7.18–7.20 (3 H, m, ArH), 7.36–7.39 (2 H, m, ArH) (Found: M^+, 368.0517. $C_{17}H_{20}O_4Se$ requires *M*, 368.0525). **22**: ν_{max}/cm^{-1} 1730 and 1250; δ_H(270 MHz; $CDCl_3$) 2.12 (1 H, dd, *J* 13 and 9, 5-H), 2.77 (1 H, dd, *J* 13 and 5, 5-H), 2.87 (1 H, d, *J* 7, 2-H), 3.00 (1 H, dd, *J* 18 and 2, 2-H), 2.87–3.0 (1 H, m, 4-H), 3.12 (1 H, dd, *J* 18 and 2, 2-H), 3.21 (2 H, d, *J* 7, CH_2), 6.33 (1 H, br s, olefinic H), 7.23–7.31 (6 H, m, ArH) and 7.41–7.52 (4 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 32.06 (t), 40.49 (t), 40.63 (t), 44.04 (d), 52.92 (q), 58.14 (q), 60.38 (s), 112.37 (d), 126.93 (d), 127.14 (d), 129.13 (d), 129.22 (d), 130.06 (s), 131.06 (s), 131.09 (s), 131.61 (d), 133.07 (d), 147.15 (s), 171.66 (s) and 171.77 (s); *m*/*z*: 524 (M^+) and 367 (base). A small M^+ peak was observed but was too small for the exact mass spectrum to be measured.

Reaction of Dimethyl (3-*Methylbut*-2-*enyl*)(*prop*-2-*ynyl*)*propanedioate* **23** *and* **2b**.—(E)-*Dimethyl* 4-*isopropyl*-3-*phenylselenomethylene cyclopropane*-1,1-*dicarboxylate* **24** (40%) as a yellow oil and (E)-*dimethyl* 4-(1-*methyl*-1-*phenylselenoethyl*)-3-*phenylselenomethylene cyclopentane*-1,1-*dicarboxylate* **25** (21%) as a yellow oil were obtained by Method B. **24**: ν_{max}/cm^{-1} 1740 and 1200 (CO_2Me); δ_H(270 MHz; $CDCl_3$) 0.86 (3 H, d, *J* 7, Me), 0.96 (3 H, d, *J* 7, Me), 1.59–1.70 (1 H, m, 5-H), 1.91–2.03 (1 H, m, 4-H), 2.47–2.54 (1 H, m, 5-H), 2.65–2.67 (1 H, m, isopropyl H), 2.81 (1 H, d, *J* 17, 2-H), 3.19 (1 H, d, *J* 17, 2-H), 3.71 (3 H, s, OMe), 3.73 (3 H, s, OMe), 6.22 (1 H, br s, olefinic H), 7.20–7.28 (3 H, m, ArH) and 7.40–7.43 (2 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 17.07 (q), 21.19 (q), 29.78 (d), 34.91 (t), 41.27 (t), 49.93 (d), 52.76 (q 2), 58.31 (s), 110.56 (d), 126.60 (d), 129.14 (d), 131.19 (d), 131.76 (s), 148.69 (s), 171.90 (s) and 171.95 (s) (Found: M^+, 396.0677. $C_{19}H_{24}O_4Se$ requires *M*, 396.0677). **25**: ν_{max}/cm^{-1} 1740 and 1240 (CO_2Me); δ_H(270 MHz; $CDCl_3$) 1.37 (3 H, s, Me), 1.39 (3 H, s, Me), 2.25 (1 H, dd, *J* 9 and 13, 5-H), 2.75–3.01 (3 H, m, 2-H, 4-H, 5-H), 3.27 (1 H, d, *J* 16, 2-H), 3.69 (3 H, s, OMe), 3.76 (3 H, s, OMe), 6.60 (1 H, br s, olefinic H), 7.18–7.43 (8 H, m, ArH) and 7.61–7.64 (2 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 27.43 (q), 28.59 (q), 37.42 (t), 42.16 (t), 50.19 (s), 52.76 (q 2), 53.23 (d), 58.21 (s), 115.93 (d), 126.70 (d), 127.22 (s), 128.70 (d), 129.13 (d), 131.30 (d), 131.55 (s), 138.33 (d), 144.61 (s), 171.36 (s) and 171.57 (s); *m*/*z* M^+ (552) was not observed. 522 (M^+ − Me × 2), 395 (M^+ − PhSe) and 177 (base).

Reaction of Cinnamyl Prop-2-*ynyl Ether* **26** *with* **2b**.—4-*Benzyl*-3-*phenylselenomethylenetetrahydrofuran* **27** (66%) as a yellow oil, (*E*)-1-phenylpropene (13%) and cinnamyl alcohol (9%) were obtained by Method B. **27**: ν_{max}/cm^{-1} 1075 (C–O–C), 740 and 700 (Ph); δ_H(270 MHz; $CDCl_3$) 2.69 (1 H, dd, *J* 13 and 9, benzyl H), 2.90 (1 H, dd, *J* 13 and 6, benzyl H), 3.00–3.02 (1 H, m, 4-H), 3.67 (1 H, dd, *J* 9 and 5, 5-H), 3.89 (1 H, dd, *J* 9 and 6, 5-H), 4.33 (1 H, dd, *J* 14 and 2, 2-H), 4.40 (1 H, dd, *J* 14 and 2, 2-H), 6.18 (1 H, br s, olefinic H) and 7.14–7.43 (10 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 38.77 (t), 46.93 (d), 71.62 (t), 73.71 (t), 108.15 (d), 126.23 (d), 126.74 (d), 128.39 (d), 128.79 (d), 129.11 (d), 130.96 (s), 131.12 (s), 139.37 (s) and 148.88 (s) (Found: M^+, 330.0499. $C_{18}H_{18}OSe$ requires *M*, 330.0521).

Reaction of Cinnamyl Prop-2-*ynyl Sulfide* **28** *with* **2b**.—4-*Benzyl*-3-*phenylselenomethylenetetrahydrothiophene* **29** (41%) as a yellow oil and (E)-2,3-*bis*(*phenylseleno*)*allyl* (E)-*cinnamyl sulfide* **30** (4%) as a yellow oil were obtained. **29**: ν_{max}/cm^{-1} 3050–2850 (alkyl) and 740 (Ph); δ_H(270 MHz; $CDCl_3$) 2.59 (1 H, dd, *J* 11 and 5, 5-H), 2.71 (1 H, dd, *J* 13 and 9, benzyl H), 2.86 (1 H, dd, *J* 11 and 6, 5-H), 3.05–3.17 (1 H, m, 4-H), 3.49–3.67 (2 H, m, 2-H), 6.27–6.28 (1 H, m, olefinic H) and 7.14–7.38 (10 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 34.34 (t), 35.76 (t), 39.31 (t), 51.28 (d), 112.52 (d), 126.25 (d), 126.28 (d), 126.91 (d), 128.39 (d), 128.48 (d), 128.95 (d), 129.16 (d), 129.24 (d), 130.95 (s), 131.52 (d), 139.60 (s) and 147.50 (s) (Found: M^+, 346.0313. $C_{18}H_{18}SSe$ requires *M*, 346.0294). **30**: ν_{max}/cm^{-1} 3050–2900 (alkyl), 740 and 700 (Ph); δ_H(270 MHz; $CDCl_3$) 3.29 (2 H, dd, *J* 7 and 1, C=CCH_2), 3.30 [2 H, s, =C(SePh)CH_2], 6.11 (1 H, dt, *J* 7 and 16, olefinic H), 6.34 (1 H, d, *J* 16, olefinic H), 6.71 (1 H, s, olefinic H) and 7.12–7.54 (15 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 34.44 (t), 36.44 (t), 124.77 (d), 125.46 (d), 126.38 (d), 127.25 (d), 127.48 (d), 127.92 (d), 128.48 (d), 129.34 (d), 129.42 (d), 129.72 (s), 131.10 (s), 131.58 (d), 131.88 (s), 132.75 (d), 133.97 (d) and 136.76 (s); *m*/*z*: 502 (small M^+), 385 (M^+ − cinnamyl group) and 345 (M^+ − PhSe).

Reaction of But-2-*ynyl Prop*-2-*ynyl Ether* **31** *with* **2b**.—*But*-2-*ynyl* 1,2-*bis*(*phenylseleno*)*propenyl ether* **32** as a yellow oil was obtained in 49% yield by Method A, and in 10% yield by Method B. **32**: ν_{max}/cm^{-1} 2300, 2230 (C≡C) and 1080 (C–O–C); δ_H(270 MHz; $CDCl_3$) 1.73 (3 H, t, *J* 2, Me), 4.04 (2 H, q, *J* 2, CH_2C≡C), 4.25 [2 H, s, CH_2(SePh)C=], 6.82 (1 H, s, =CHSePh), 7.14–7.22 (6 H, m, ArH), 7.32–7.39 (2 H, m, ArH) and 7.40–7.47 (2 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 3.60 (q), 57.84 (t), 70.82 (t), 74.59 (s), 83.09 (s), 126.60 (d), 127.26 (d), 127.68 (d), 128.46 (s), 131.92 (d), 132.00 (d) and 133.61 (d) (Found: M^+, 421.9656. $C_{19}H_{18}OSe_2$ requires *M*, 421.9956).

N-*Allyl*-N-(4,4-*dibromobut*-3-*en*-2-*yl*)*toluene*-p-*sulfonamide* **37**.—*N*-Toluene-*p*-sulfonyl-(DL)-alanine methyl ester **34** was synthesised by tosylation of (DL)-analine with tosyl chloride followed by esterification with methanol and hydrogen chloride. Treatment of **34** with NaH and allyl bromide afforded *N*-allyl-*N*-toluene-*p*-sulfonyl-(DL)-alanine methyl ester **35** in 92% yield. The ester **35** (5.0 g, 16.8 mmol) in toluene–hexane (1:3) (110 cm^3) was reduced with diisobutylaluminium hydride (25 cm^3, 25.0 mmol) under an N_2 atmosphere at −78 °C for 3 h. The reaction mixture was poured into the 2 mol dm^{-3} sulfuric acid and extracted with ether. After the extracts had been dried ($MgSO_4$), the solvent was removed under reduced pressure at room temperature. The almost pure aldehyde **36** thus obtained as a colourless oil was used without further purification because of lability. To the dry CH_2Cl_2 (22 cm^3) solution of **36** and Ph_3P (13.22 g, 50.4 mmol) was added dropwise the CH_2Cl_2 (22 cm^3) solution of CBr_4 (11.14 g, 33.6 mmol) at 0–5 °C (the inner temperature) and the reaction mixture was stirred over 2 h. Pentane (100 cm^3) was added to the reaction mixture. The

precipitates were filtered off and washed with pentane. The filtrates and the washings were combined and concentrated. The residue was purified by column chromatography on silica gel eluting with AcOEt–hexane (1:5). The title compound[25] **37** (3.63 g, 51%) was obtained as a yellow oil; ν_{max}/cm^{-1} 1340 and 1160 (SO_2); δ_H(60 MHz; $CDCl_3$) 2.40 (3 H, s, Me), 3.83 (2 H, br d, *J* 6, CH_2N), 4.35–4.85 (1 H, m, NCH), 5.03–5.33 (2 H, m, olefinic H), 5.55–6.18 (1 H, m, olefinic H), 6.35 (1 H, m, olefinic H), 7.28 (2 H, d, *J* 6, ArH) and 7.70 (2 H, d, *J* 6, ArH) (Found: M^+, 420.9379. $C_{14}H_{17}Br_2NO_2S$ requires *M*, 420.9349).

N-*Allyl*-N-*but*-1-*yn*-2-*yltoluene*-p-*sulfonamide* **38**.—To a solution of BuLi (5.20 mmol, 3.5 cm^3 of a 1.50 mmol hexane solution) in a mixture of dry THF (3.3 cm^3) and dry ether (3.3 cm^3) was added the dibromide **37** (1.0 g, 2.36 mmol) in dry THF (2.0 cm^3) at −70 °C. The reaction mixture was warmed to room temperature and then hydrolysed with aqueous 2 mol dm^{-3} sulfuric acid. The whole was extracted with ether. The extracts were washed with water and dried ($MgSO_4$). The solvent was removed and the residue was purified by column chromatography on silica gel eluting with AcOEt–hexane (1:5). The title compound **38** (0.46 g, 74%) was obtained as a yellow oil. ν_{max}/cm^{-1} 3270, 2100 (C≡CH), 1340 and 1150 (SO_2); δ_H(270 MHz; $CDCl_3$) 1.44 (3 H, d, *J* 9, Me), 2.15 (1 H, d, *J* 2, C≡CH), 2.41 (3 H, s, Me), 3.74 (1 H, dd, *J* 7 and 17, NCH_2), 3.90–3.98 (1 H, m, NCH_2), 4.89 (1 H, dq, *J* 2 and 7, N*CH*Me), 5.13 (1 H, dd, *J* 2 and 10, olefinic H), 5.26 (1 H, dd, *J* 2 and 17, olefinic H), 5.85–5.99 (1 H, m, olefinic H), 7.28 (2 H, d, *J* 8, ArH) and 7.72 (2 H, d, *J* 8, ArH); δ_C(67.5 MHz; $CDCl_3$) 21.41 (q), 22.55 (q), 46.04 (d), 47.23 (t), 73.31 (d), 81.14 (s), 117.06 (d), 127.48 (d), 129.37 (d), 135.74 (d), 136.22 (s) and 143.32 (s); *m/z*: 263 (small M^+) and 248 (M^+ − Me).

Reaction of **2b** *with Enyne Sulfonamide* **38**.—The reaction of *N*-allyl-*N*-but-3-yn-2-yltoluene-*p*-sulfonamide **38** (0.10 g, 0.4 mmol) and **2b** (0.18 g, 0.4 mmol) by Method B afforded a mixture of diastereomers of 2,4-*dimethyl*-3-*phenylselenomethylene*-N-*toluene*-p-*sulfonylpyrrolidine* **39** (0.12 g, 71%) as a yellow oil. ν_{max}/cm^{-1} 1350 and 1160 (SO_2); δ_H(270 MHz; $CDCl_3$) 1.15 (3 H, d, *J* 7, Me), 1.48 (3 H, d, *J* 6), 2.42 (3 H, s, Me), 2.50 (1 H, br q, *J* 7, 4-H), 3.21 (1 H, dd, *J* 6 and 11, 5-H), 3.53 (1 H, dd, *J* 8 and 11, 5-H), 4.42 (1 H, dq, *J* 2 and 7, 2-H), 6.15 (1 H, t, *J* 2, olefinic H), 7.24–7.35 (7 H, m, ArH) and 7.70 (2 H, d, *J* 8, ArH); δ_C(67.5 MHz; $CDCl_3$) 20.18 (q), 21.50 (q), 21.82 (q), 39.06 (d), 54.07 (t), 59.82 (d), 110.94 (d), 127.07 (s), 127.12 (d), 127.49 (d), 129.20 (d), 129.65 (d), 131.57 (d), 134.85 (s), 143.37 (s) and 152.10 (s) (Found: M^+, 421.0589. $C_{20}H_{23}NO_2SSe$ requires *M*, 421.0613).

Methyl 4,4-*Diethoxycarbonyl*-4-N-*prop*-2-*ynyl*-N-*trifluoroacetylaminobut*-2-*enoate* **46a**.—To a solution of methyl 4,4-diethoxycarbonyl-4-trifluoroacetylaminobut-2-enoate[27] **45a** (3.50 g, 9.9 mmol) in HMPA (20 cm^3) was added sodium hydride (0.36 g, 15.0 mmol) in small portions. After stirring for 1 h, a solution of prop-2-ynyl bromide (1.76 g, 14.8 mmol) in HMPA (6 cm^3) was added dropwise to the reaction mixture. After stirring for 3 days, the reaction mixture was poured into water (150 cm^3) and extracted with AcOEt. The extracts were dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt–hexane (1:10). The title compound **46a** (2.88 g, 74%) was obtained as a yellow oil; ν_{max}/cm^{-1} 3290, 2125 (HC≡), 1700–1760 (C=O), 1200 and 1145 (C–O); δ_H(60 MHz; $CDCl_3$) 1.21 (6 H, t, *J* 7, CH_2CH_3 × 2), 2.31 (1 H, t, *J* 2, ≡CH), 3.66 (3 H, s, OMe), 4.16 (4 H, q, *J* 7, CH_2CH_3 × 2), 4.50 (2 H, d, *J* 2, CH_2≡), 6.15 (1 H, d, *J* 13, olefinic H) and 6.53 (1 H, d, *J* 13, olefinic H) (Found: M^+, 393.1054. $C_{16}H_{18}F_3NO_7$ requires *M*, 393.1036).

Ethyl 4,4-*Diethoxycarbonyl*-4-(N-*prop*-2-*ynyl*-N-*trifluoroacetylamino*)*but*-2-*enoate* **46b**.—Compound **46b** was synthesised from the ethyl ester **45b** by the same way as **46a**; ν_{max}/cm^{-1} 1750, 1700, 1200, 1150, (CO_2Et), 3290 and 1965 (C≡CH); δ_H(60 MHz; $CDCl_3$) 1.25 (6 H, t, *J* 8, Me × 2), 1.28 (3 H, t, *J* 7, Me), 2.33 (1 H, t, *J* 2, C≡CH), 4.15 (2 H, q, *J* 8, CH_2), 4.21 (4 H, q, *J* 8, CH_2 × 2), 4.56 (2 H, d, *J* 2, ≡CCH_2), 6.26 (1 H, d, *J* 13, olefinic H) and 6.59 (1 H, d, *J* 13, olefinic H) (Found: M^+, 407.1154. $C_{17}H_{20}F_3NO_7$ requires *M*, 407.1190).

Reaction of Enyne **46a** *with* **2b**.—The enyne **46a** (0.15 g, 0.38 mmol) was treated with **2b** (0.18 g, 0.38 mmol) and AIBN (0.01 g, 0.1 mmol) (Method B) to afford 2-*diethoxycarbonyl*-3-(*methoxycarbonylmethyl*)-4-(*phenylselenomethylene*)-1-*trifluoroacetylpyrrolidine* **47a** (0.12 g, 54.8%) as white prisms, m.p. 72–73 °C (decomp.) (CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1755, 1730, 1700, 1290, 1240, 1215, 1160 and 1145 (CO_2); δ_H(270 MHz; $CDCl_3$) 1.26 (3 H, t, *J* 8, Me), 1.30 (3 H, t, *J* 8, Me), 2.62 (1 H, dd, *J* 8 and 17, CH_2), 2.85 (1 H, dd, *J* 6 and 17, CH_2), 3.69 (3 H, s, OMe), 3.84–3.90 (1 H, m, 3-H), 4.23 (4 H, br q, *J* 7, CH_2), 4.30 (2 H, q, *J* 7, CH_2), 4.37 (1 H, d, *J* 15, 5-H), 4.49 (1 H, d, *J* 15, 5-H), 6.45 (1 H, br s, olefinic H), 7.28–7.33 (3 H, m, ArH) and 7.37–7.42 (2 H, m, ArH); δ_C(67.5 MHz; $CDCl_3$) 13.67 (q), 33.33 (t), 47.31 (d), 50.38 (t), 52.05 (q), 62.70 (t), 62.87 (t), 74.53 (s), 113.65 (s), 115.00 (d), 117.90 (s), 127.70 (d), 129.50 (d), 131.80 (d), 138.05 (d), 164.24 (s), 165.65 (s) and 170.86 (s) (Found: C, 48.0; H, 4.4; N, 2.6. $C_{22}H_{24}F_3NO_7Se$ requires C, 48.0; H, 4.4; N, 2.5%).

Reaction of Enyne **46b** *with* **2b**.—2-*Diethoxycarbonyl*-3-(*ethoxycarbonylmethyl*)-4-(*phenylselenomethylene*)-1-*trifluoroacetylpyrrolidine* **47b** was obtained by Method B in 36% yield as white prisms, m.p. 95–98 °C (CH_2Cl_2–hexane); ν_{max}/cm^{-1} 1755, 1730, 1710, 1295, 1260, 1240, 1220, 1175 and 1150 (CO_2Et); δ_H(60 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 7, Me), 1.25 (3 H, t, *J* 6, Me), 1.29 (3 H, t, *J* 7, Me), 2.73 (2 H, d, *J* 6, 5-H), 3.75–4.50 (9 H, m, CH_2 × 2 and CH), 6.45 (1 H, m, olefinic H) and 7.18–7.50 (5 H, m, ArH) (Found: C, 49.0; H, 4.6; N, 2.5. $C_{23}H_{26}F_3NO_7Se$ requires C, 48.9; H, 4.6; N, 2.5%).

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