Convenient synthesis of 2-alkynyl-cyclopropanes and -oxiranes

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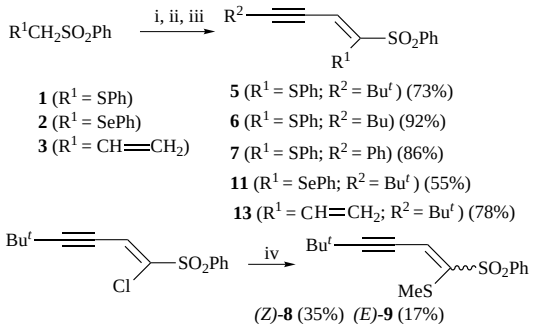
Addition of nucleophiles such as dimethylsulfoxonium methylide and Bu^{t}OOLi to the conjugate enyne sulfones 4–7, 11–14, 27–28 and 31 occurs at the β-position to the phenylsulfonyl group to give the corresponding cyclopropanes 15–17 and 19–22 and the oxiranes 33–38 in high yields. The thermal reactions of vinyloxirane 36 show an oxy-Cope rearrangement to give 2-phenylsulfonylphenol 39.

Recently, we have reported the reaction of the 1-halogeno-1-phenylsulfonylbut-1-en-3-ynes (conjugate enyne sulfones) with alkyllithium[1a] and sodium alkoxides,[2] which afford α-lithio- and α-alkoxy enyne sulfones in high yields. Here we planned to extend the reaction to other nucleophiles such as dimethylsulfoxonium methylide and peroxide. The reaction of vinyl sulfones with dimethylsulfoxonium methylide took place at the β-position to the sulfonyl group to give sulfonyl substituted cyclopropanes in good yields;[3] however, our substrates have many reactive sites in the molecule, so that it is very difficult to control the regioselectivity of the addition. A reaction of 5,5-dimethyl-1-phenylsulfonylhex-1-en-3-yne **4** and dimethylsulfoxonium methylide gave a complex mixture. We examined other enyne sulfones with dimethylsulfoxonium methylide and found that the reaction of α-phenylthio substituted enyne sulfones gave the cyclopropane derivative.

The α-phenylthio enyne sulfones **5–7** were prepared according to our previous report and that of Krause in high yields (Scheme 1).[1a,b] The α-phenylseleno- **11** and α-vinyl derivative **13**



Scheme 1 *Reagents*: i, LDA/−78 °C; ii, R^2≡CHO; iii, MsCl, DBU, −30 °C; iv, 15% MeSNa, BnEt$_3$NCl, ether

were also obtained by the same procedure. Since, however, an α-methylthio enyne sulfone could not be obtained by this method,[4] we synthesized the α-methylthio derivatives **8** and **9** under the phase-transfer catalyst conditions shown in Scheme 1. The stereochemistry of each compound was assigned from the results of NOE experiments (Fig. 1). Attempted synthesis of the (*Z*)-phenylthio enyne sulfone by the procedure described above, however, failed.

First, we examined the reaction of (*E*)-5,5-dimethyl-1-phenylthio-1-phenylsulfonylhex-1-en-3-yne **5** with dimethylsulfoxonium methylide at room temperature to give (1*S**,2*R**)-2-

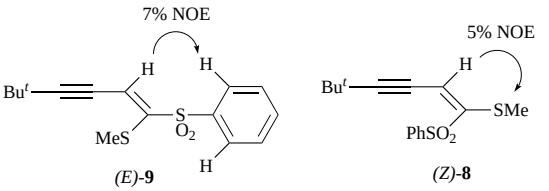


Fig. 1

(3,3-dimethylbut-1-ynyl)-1-phenylsulfonyl-1-phenylthiocyclopropane **15** (83%) (Table 1, Entry 2). The structure of the product **15** was determined on the basis of spectral evidence (IR, ^{1}H and ^{13}C NMR and mass) and elemental analysis. The IR spectrum shows the acetylenic absorption at ν/cm^{-1} 2250. The ^{1}H NMR spectrum exhibited the cyclopropane protons at δ 1.30 (dd, *J* 5 and 7 Hz), 2.19 (dd, *J* 5 and 10 Hz) and 3.20 (dd, *J* 7 and 10 Hz). The ^{13}C NMR spectrum also showed the three carbons of the cyclopropane at δ 19.96 (d), 23.65 (t) and 52.00 (s), respectively. The elemental analysis and mass spectrum showed the molecular formula to be $C_{21}H_{22}O_2S_2$. The stereochemistry of **15** was determined to be 1*S**,2*R** from NOE experiments. Irradiation of the prop-2-ynyl H of **15** increased the intensity of the aromatic *ortho* protons of the phenylsulfonyl group. The α-phenylthio enyne sulfones **6** and **7** also gave the alkynyl cyclopropanes **16** and **17**, respectively; however, the α-methylthioenyne sulfone **8** gave 5,5-dimethyl-1,3-dimethylthio-1-phenylsulfonylhexa-1,3-dienes **18** (78%) (Entry 5) not the cyclopropanes. The (*E*)-isomer **9** also afforded the diene **18**. The α-methoxy enyne sulfone **10** gave a complex mixture (Entry 7); however, the α-seleno enyne sulfone **11** gave the cyclopropane **19** (Entry 8). The reaction of the bis(phenylsulfonyl) enyne sulfone **12** resulted in a low yield of cyclopropane **20** (Entry 9). The dienyl sulfone **13** gave a stereoisomeric mixture of the vinylcyclopropane **21** (1*S**,2*R**:1*R**,2*R** = 2:1). The (*E*)-enediyne sulfone **14** also gave the cyclopropane **22** in good yield.

The mechanism for the formation of the products can be explained as follows. The nucleophilic attack preferentially occurs at the β-position to the sulfonyl group to give a betaine intermediate **23**, the anion of which, stabilized by the sulfonyl group (R^2 = SPh), attacks the α-carbon of the dimethylsulfoxonium group; successive elimination then affords the α-phenylthiocyclopropanes **24** (path a, Scheme 2). The α-methylthio enyne sulfone **23** (R^2 = SMe; Scheme 2) afforded the diene **18**; however, the diene **18** was also obtained as a minor product in the synthesis of the α-methylthio enyne sulfones **8** and **9**. This

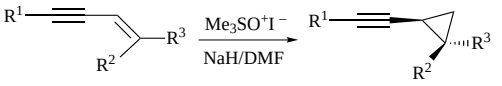
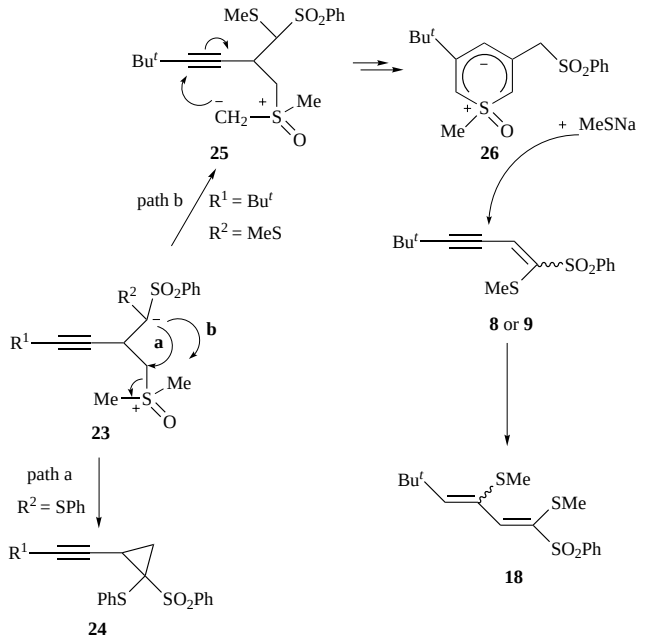


Table 1 A synthesis of alkynylcyclopropanes

Entry	Enyne sulfone	Alkynylcyclopropanes
1	**4** (R^1 = Bu^t, R^2 = H, R^3 = SO_2Ph)	complex mixture
2	**5** (R^1 = Bu^t, R^2 = SPh, R^3 = SO_2Ph)	**15** (83)
3	**6** (R^1 = Bu, R^2 = SPh, R^3 = SO_2Ph)	**16** (94)
4	**7** (R^1 = Ph, R^2 = SPh, R^3 = SO_2Ph)	**17** (87)
5	**8** (R^1 = Bu^t, R^2 = SO_2Ph, R^3 = SMe)	**18** (78)[a]
6	**9** (R^1 = Bu^t, R^2 = SMe, R^3 = SO_2Ph)	**18** (70)[b]
7	**10** (R^1 = Bu^t, R^2 = OMe, R^3 = SO_2Ph)	Complex mixture
8	**11** (R^1 = Bu^t, R^2 = SePh, R^3 = SO_2Ph)	**19** (79)
9	**12** (R^1 = Bu^t, R^2 = R^3 = SO_2Ph)	**20** (32)
10	**13** (R^1 = Bu^t, R^2 = vinyl, R^3 = SO_2Ph)	**21** (32)[c]
11	**14** (R^1 = Bu^t, R^2 = phenylethynyl, R^3 = SO_2Ph)	**22** (74)

[a] The products are (1*E*,3*E*)-1,3-dimethylthio-5,5-dimethyl-1-phenylsulfonylhexa-1,3-diene **18** (see Scheme 2), [(1*E*,3*E*):(1*E*,3*Z*) = 6:5]. [b] The isomer ratio for **18** was (1*E*,3*E*):(1*E*,3*Z*) = 6:5. [c] The isomer ratio for **21** was (1*S**,2*R**):(1*R**,2*R**) = 2:1.



Scheme 2

shows that MeSNa would be generated under the reaction conditions. The products in the reaction of **8** and dimethylsulfoxonium methylide were investigated in detail. The thiabenzene 1-oxide **26** was obtained as a by-product (62%) and its ORTEP drawing is shown in Fig. 2. The attack of dimethylsulfoxonium methylide obviously occurred at the β-carbon to the phenylsulfonyl group but proton abstraction and ring closure to the terminal acetylenic carbon of the enyne sulfone provides an alternative route to cyclopropane formation (path b, Scheme 2). The bond lengths between C(1)–C(2) and C(4)–C(5), between C(2)–C(3) and C(3)–C(4) are almost the same, so that the anion of the ylide **26** is delocalized to the diene.[5] The ^{13}C NMR spectrum of **26** showed signals for the 2- and 6-carbons at δ 83.33 (d) and 85.28 (d). The identification of the thiabenzene **26** shows that MeSNa is also generated from the reaction of α-methylthio enyne sulfones **8** and **9** and dimethylsulfoxonium methylide. Although the mechanism for the formation of the diene **18** proved to be by reaction of the enyne sulfone (*Z*)-**8** or (*E*)-**9** and the generated MeSNa, a mechanism for demethylation of **25** could not be established.

Next, we examined the reaction of the enyne sulfones and peroxide anion. Various peroxides were examined and it was found that Bu^{t}OOLi[6] and the enyne sulfones gave the alkynyl epoxides in good yields. First, we performed this reaction using

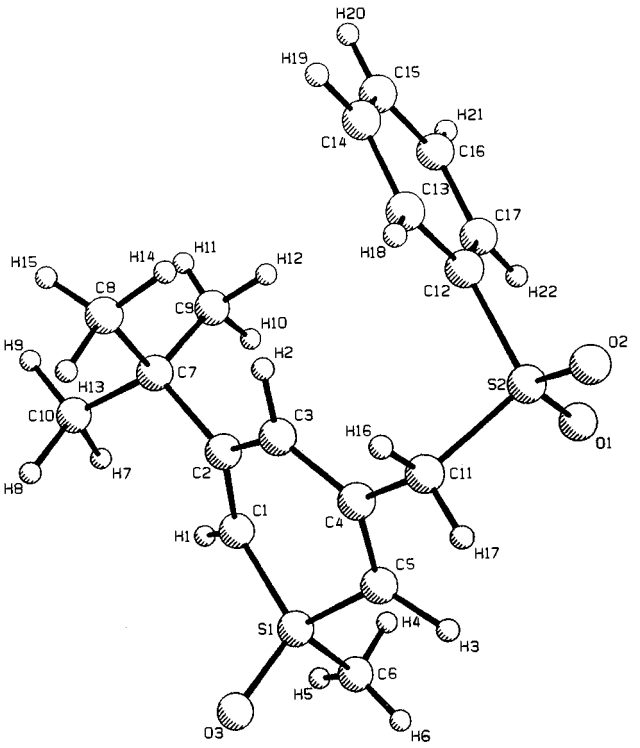


Fig. 2 ORTEP drawing of the thiabenzene 1-oxide **26**

5,5-dimethyl-1-phenylsulfonylbut-1-en-3-yne **4**, which gave (2*R**,3*R**)-3,3-dimethylbut-1-ynyl-2-phenylsulfonyloxirane **33** quantitatively. The structure of product **33** was determined as follows. The ^{1}H NMR spectrum showed the *trans*-oxirane protons at δ 4.00 (s), 4.22 (s) and the ^{13}C NMR spectrum also exhibited doublets at δ 45.25 and 69.35 due to C-2 and C-3, respectively. The stereochemistry was determined by NOE enhancement measurements. Irradiation of the prop-2-ynyl H increased the intensity of the 2-oxirane H by 4%. Other enyne sulfones, **27** and **28**, also stereoselectively afforded alkynyloxiranes, **34** and **35**, respectively. The α-vinyl enyne sulfone **13** gave the vinyl oxirane **36**, stereoselectively; however, examination of this reaction on a large scale showed that it afforded a 1:1 stereoisomeric mixture. Although the (*Z*)-isomer **31** gave the (2*S**,3*R**)-oxirane **37** stereospecifically, the methyl derivative **29** failed to undergo the epoxidation. The (*E*)-enediyne sulfone **14** also gave the *cis*-diyne epoxide **38**; however, α-sulfonyl, α-chloro- and α-thio-enyne sulfones **30**, **32** and **5** gave complex mixtures.

Vinyloxiranes are versatile intermediates for the synthesis of

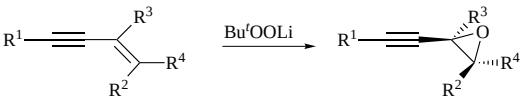
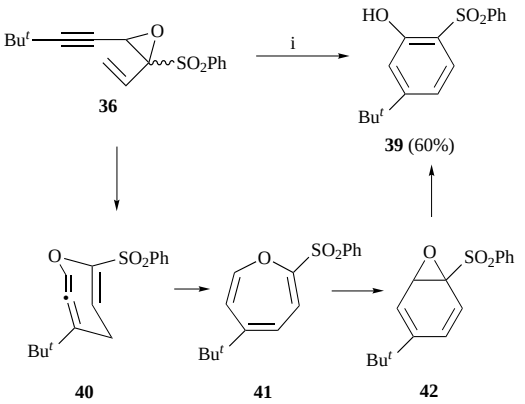


Table 2 A synthesis of 2-alkynyl-1-sulfonyl epoxides

Entry		Enyne sulfone R¹	R²	R³	R⁴	Conditions	Product (% yield)
1	**4**	Bu^t	H	H	SO_2Ph	−15 °C/2h	**33** (77)
2	**27**	Bu	H	H	SO_2Ph	−15 °C/4h	**34** (85)
3	**28**	Ph	H	H	SO_2Ph	−15 °C/2h	**35** (89)
4	**29**	Bu	Me	H	SO_2Ph	rt/2h	—
5	**13**	Bu	Vinyl	H	SO_2Ph	−15 °C/2h	**36** (81)
6	**30**	Ph	SO_2Ph	H	SO_2Ph	−20 °C/2h	decomposition
7	**31**	Bu	SO_2Ph	Me	H	−15 °C/3h	**37** (57)
8	**32**	Bu^t	Cl	H	SO_2Ph	−20 °C/4h	decomposition
9	**10**	Bu^t	OMe	H	SO_2Ph	−20 °C/2h	—
10	**14**	Bu	Phenylethynyl	H	SO_2Ph	−20 °C/2h	**38** (61)
11	**5**	Bu^t	SPh	H	SO_2Ph	−20 °C/2h	decomposition



Scheme 3 *Reagents*: i, sealed tube/180 °C/1 h

various furans[7] and allyl alcohols.[8] We examined the thermal reaction of our sulfonyl-substituted vinyloxirane **36**. The product was 5-*tert*-butyl-2-phenylsulfonylphenol **39** (60%), which was obtained from the oxy Cope rearrangement as shown in Scheme 3. The oxy Cope rearrangement of **36** affords the allenic intermediate **40** which upon isomerization gives the oxepine **41**. The oxepine **41** was equilibrated under thermal conditions to give the oxirane **42**.[9] The C–O bond of the hetero acetal was cleaved to give the trisubstituted benzene **39**.

Experimental

Mps were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. ^{1}H and ^{13}C NMR spectra were determined with a JEOL GX-270 (270 MHz) spectrometer and a Varian Gemini 2000 (200 MHz) spectrometer at the Center of Instrumentation of Gifu University. Chemical shifts are expressed in ppm with respect to tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s = singlet, d = doublet, t = triplet and q = quartet. *J* Values are given in Hz. IR spectra of solids (KBr) and liquids (film) were recorded on a JASCO IR A-100 infrared spectrometer. EI mass spectra (MS) were obtained using a JMS-SX102A spectrometer with a direct-insertion probe at an ionization voltage of 70 eV. Ether refers to diethyl ether.

Synthesis of α-phenylthio-5–9, α-phenylseleno-11, α-vinyl-13 and α-phenylethynyl enyne sulfones 14

Typical procedure. A THF (15.0 cm^3) solution of phenylsulfonyl(phenylthio)methane **1** (6.08 g, 23.0 mmol) was added to a LDA solution [prepared from diisopropylamine (3.49 g, 34.5 mmol) and BuLi (1.6 M, 23.0 cm^3) in THF (50.0 cm^3)] under an Ar atmosphere at −78 °C. A THF (8.0 cm^3) solution of 4,4-dimethylpent-2-ynal (3.80 g, 34.5 mmol) was then added dropwise to the mixture. The temperature of the mixture was then raised to −30 °C. A THF (8.0 cm^3) solution of CH_3SO_2Cl (5.27 g, 46.0 mmol) and a THF (10.0 cm^3) solution of DBU (7.00 g, 46.0 mmol) were successively added to the reaction mixture after which it was poured into water (150 cm^3). The organic layer was separated and the aqueous layer was extracted with ether (30.0 × 3 cm^3). The combined organic layer and extracts were dried ($MgSO_4$) and evaporated under reduced pressure and the residue as purified by column chromatography on silica gel eluting with AcOEt–hexane (1 : 10) to give (*E*)-5,5-dimethyl-1-phenylsulfonyl-1-phenylthiohex-1-en-3-yne **5**[2] (5.99 g, 73%) as colourless prisms.

(*E*)-1-Phenylsulfonyl-1-phenylthiooct-1-en-3-yne 6

Phenylsulfonyl(phenylthio)methane (3.00 g, 11.4 mmol) was treated with LDA [prepared from diisopropylamine (1.72 g, 17.0 mmol) and BuLi (1.6 M; 11.4 cm^3) in THF (25 cm^3)], hept-2-ynal (1.88 g, 17.0 mmol), CH_3SO_2Cl (2.60 g, 22.7 mmol) and Et_3N (2.30 g, 22.7 mmol) by the same procedure as described above for **5** to give the title compound **6** (3.72 g, 92%) as a yellow oil; ν_{max}/cm^{-1} 2210 (acetylene) and 1320, 1160 (SO_2); δ_H(200 MHz, $CDCl_3$) 0.83 (3H, t, *J* 7, CH_3), 1.26–1.40 (4H, m, 6- and 7-CH_2), 2.29 (2H, dt, *J* 2 and 7, 5-CH_2), 7.06–7.26 (5H, m, olefinic H and 4 × ArH) and 7.42–7.62 (4H, m, ArH), 7.90–7.95 (2H, m, ArH); δ_C(50 MHz, $CDCl_3$) 13.41 (q), 19.79 (t), 21.77 (t), 29.87 (t), 76.08 (s), 111.65 (s), 127.24 (d), 128.99 (d × 3), 129.04 (d × 3), 129.74 (d × 2), 130.39 (d), 132.97 (s), 133.68 (d), 138.37 (s) and 144.86 (s); *m*/*z* 356 (M^+) (Found: C, 67.22; H, 5.66. $C_{20}H_{20}O_2S_2$ requires C, 67.38; H, 5.65%).

(*E*)-4-Phenyl-1-phenylsulfonyl-1-phenylthiobut-1-en-3-yne 7

Phenylsulfonyl(phenylthio)methane (2.00 g, 7.57 mmol) was treated with LDA [prepared from diisopropylamine (1.15 g, 11.4 mmol) and BuLi (1.6 M; 7.5 cm^3) in THF (25 cm^3)], 3-phenylprop-2-ynal (1.48 g, 11.4 mmol), CH_3SO_2Cl (1.73 g, 15.1 mmol) and DBU (2.30 g, 15.1 mmol) by the same procedure as described above for **5** to give the title compound **7** (2.44 g, 86%) as pale yellow prisms (from dichloromethane–hexane), mp 91–93 °C; ν_{max}/cm^{-1} 2200 (acetylene) and 1310 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$) 7.14 (5H, s, ArH), 7.24–7.37 (5H, m, ArH), 7.48–7.52 (2H, m, ArH), 7.58–7.62 (1H, m, ArH), 7.64 (1H, s, olefinic H) and 7.95–7.98 (2H, dd, *J* 1 and 8, ArH); δ_C (100 MHz, $CDCl_3$) 84.32 (s), 108.08 (s), 121.45 (s), 127.48 (d), 128.39 (d × 3), 129.02 (d × 5), 129.97 (d × 4), 132.10 (d × 2), 132.57 (s), 133.80 (d), 138.13 (s) and 145.72 (s); *m*/*z* 376

(M^+) (Found: C, 69.93; H, 4.30. $C_{22}H_{16}O_2S_2$ requires C, 70.19; H, 4.28).

(*Z*)-5,5-Dimethyl-1-phenylseleno-1-phenylsulfonylhex-1-en-3-yne 11

Phenylseleno(phenylsulfonyl)methane (2.00 g, 6.43 mmol) was treated with LDA [prepared from diisopropylamine (0.98 g, 9.65 mmol) and BuLi (1.6 M; 6.4 cm^3) in THF (30 cm^3)], 4,4-dimethylpent-2-ynal (1.06 g, 9.65 mmol), CH_3SO_2Cl (1.47 g, 12.9 mmol) and DBU (1.96 g, 12.9 mmol) by the same procedure as described above for **5** to give the title compound **11** (1.42 g, 55%) as pale-yellow needles (from dichloromethane–hexane), mp 120–123 °C; ν_{max}/cm^{-1} 2220 (acetylene) and 1310 and 1150 (SO_2); δ_H(400 MHz, $CDCl_3$) 1.11 (9H, s, $CH_3 \times 3$), 7.09–7.18 (5H, m, ArH), 7.45–7.53 (2H, m, ArH), 7.56 (1H, s, olefinic H), 7.57–7.65 (1H, m, ArH) and 7.92–7.95 (2H, m, ArH); δ_C(100 MHz, $CDCl_3$) 28.70 (s), 30.09 (q × 3), 75.54 (s), 118.08 (s), 127.50 (d), 128.92 (d × 3), 129.05 (d × 3), 131.28 (d), 131.76 (d × 2), 133.54 (d), 135.83 (s), 138.35 (s) and 141.21 (s); *m*/*z* 404 (M^+) (Found: C, 59.43; H, 4.96. $C_{20}H_{20}O_2SSe$ requires C, 59.55; H, 5.00).

(*E*)-7,7-Dimethyl-3-phenylsulfonylocta-1,3-dien-5-yne 13

Allyl phenyl sulfone (1.00 g, 7.57 mmol) was treated with LDA [prepared from diisopropylamine (0.83 g, 8.24 mmol) and BuLi (1.6 M; 7.6 cm^3) in THF (30 cm^3)], 4,4-dimethylpent-2-ynal (0.91 g, 8.24 mmol), CH_3SO_2Cl (1.26 g, 11.0 mmol) and DBU (1.67 g, 11.0 mmol) by the same procedure as described above for **5** to give the title compound **13** (1.17 g, 78%) as a yellow oil; ν_{max}/cm^{-1} 2200 (acetylene) and 1310 and 1180 (SO_2); δ_H(400 MHz, $CDCl_3$) 1.28 (9H, s, $CH_3 \times 3$), 5.47 (1H, d, *J* 12, olefinic H), 6.11 (1H, d, *J* 18, olefinic H), 6.52 (1H, dd, *J* 12 and 18, olefinic H), 6.89 (1H, s, olefinic H), 7.50–7.62 (3H, m, ArH) and 7.84–7.86 (2H, m, ArH); δ_C(100 MHz, $CDCl_3$) 28.76 (s), 30.39 (q × 3), 74.59 (s), 116.48 (s), 120.59 (d), 122.48 (t), 126.10 (d), 127.72 (d × 2), 129.05 (d × 2), 133.32 (d), 139.78 (s) and 145.85 (s) [Found: M^+, 275.1095. $C_{16}H_{18}O_2S$ requires *M* (FAB) 275.1105].

Syntheses of (*E*) and (*Z*)-5,5-dimethyl-1-methylthio-1-phenylsulfonylhex-1-en-3-yne 8 and 9

An Et_2O (20.0 cm^3) solution containing (*E*)-1-chloro-5,5-dimethyl-1-phenylsulfonylbut-1-en-3-yne **5** (1.00 g, 3.54 mmol), $BnNEt_3Cl$ (0.20 g, 0.88 mmol), 18-crown-6 (0.20 g, 0.76 mmol) and CH_3SNa (15%, 16.0 cm^3) was stirred for 2 days. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer and the extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel (AcOEt–hexane 1:10) to give (*Z*)-5,5-dimethyl-1-methylthio-1-phenylsulfonylhex-1-en-3-yne **8** (0.37 g, 35%) as white powder, mp 68–70 °C, (*E*)-5,5-dimethyl-1-methylthio-1-phenylsulfonylhex-1-en-3-yne **9** (0.18 g, 17%) as a yellow oil and (1*E*,3*E*)-, (1*E*,3*Z*)-5,5-dimethyl-1,3-bis(methylthio)-1-phenylsulfonylbuta-1,3-diene **18** (0.15 g, 12%) as colourless prisms.

(*Z*)-5,5-Dimethyl-1-methylthio-1-phenylsulfonylhex-1-en-3-yne 8

Mp 68–70 °C (from dichloromethane–hexane); ν_{max}/cm^{-1} 2220 (acetylene) and 1300 and 1150 (SO_2); δ_H(400 MHz, $CDCl_3$) 1.32 (9H, s, $CH_3 \times 3$), 2.34 (3H, s, SCH_3), 6.34 (1H, s, olefinic H), 7.27–7.62 (3H, m, ArH) and 7.98–8.00 (2H, m, ArH); δ_C(100 MHz, $CDCl_3$) 16.00 (q), 28.76 (s), 30.10 (q × 3), 71.88 (s), 118.56 (s), 124.73 (d), 127.52 (d × 2), 128.86 (d × 2), 133.04 (d), 136.39 (s) and 142.12 (s); *m*/*z* 294 (M^+) (Found: C, 61.00; H, 6.16. Calc. for $C_{15}H_{18}O_2S_2$: C, 61.19; H, 6.16%).

(*E*)-5,5-Dimethyl-1-methylthio-1-phenylsulfonylhex-1-en-3-yne 9

A pale-yellow oil, ν_{max}/cm^{-1} 2230 (acetylene) and 1320 and 1150 (SO_2); δ_H(400 MHz, $CDCl_3$) 1.26 (9H, s, $CH_3 \times 3$), 2.41 (3H, s, SCH_3), 6.47 (1H, s, olefinic H), 7.52–7.56 (2H, m, ArH), 7.61–7.64 (1H, m, ArH) and 7.99–8.01 (2H, m, ArH); δ_C(100 MHz, $CDCl_3$) 16.43 (q), 28.31 (s), 30.15 (q × 3), 73.09 (s), 112.39 (s), 125.48 (d), 127.13 (d × 2), 128.77 (d × 2), 133.18 (d), 140.67 (s) and 141.11 (s); *m*/*z* 294 (M^+) (Found: C, 59.85; H, 6.19. Calc. for $C_{15}H_{18}O_2S_2$: C, 61.19; H, 6.16%).

(1*E*,3*E*)- and (1*E*,3*Z*)-5,5-Dimethyl-1,3-dimethylthio-1-phenylsulfonylbuta-1,3-diene 18

Colourless prisms, mp 112–115 °C; ν_{max}/cm^{-1} 2210 (acetylene) and 1310 and 1150 (SO_2); δ_H(400 MHz, $CDCl_3$) 1.17 (s, 3*E*-CH_3), 1.20 (s, 3*Z*-CH_3), 1.87 (s, 3*E*-CH_3), 1.93 (s, 3*Z*-CH_3), 2.21 (s, 3*E*-CH_3), 2.32 (s, 3*Z*-CH_3), 6.02 (d, *J* 2 Hz, 3*Z*-olefinic H), 6.09 (d, *J* 2, 3*E*-olefinic H), 6.44 (d, *J* 2 Hz, 3*E*-olefinic H), 6.62 (d, *J* 2, 3*Z*-olefinic H), 7.49–7.63 (m, ArH) and 7.85–7.88 (m, ArH); δ_C(100 MHz, $CDCl_3$) 15.90 (q), 18.97 (q), 29.22 (q × 3), 40.17 (s), 118.55 (d), 121.50 (d), 127.39 (d × 2), 128.90 (d × 2), 132.98 (d), 141.94 (s) and 156.10 (s); *m*/*z* 342 (M^+) (Found: C, 56.36; H, 6.46. Calc. for $C_{16}H_{22}O_2S_3$: C, 56.10; H, 6.47%).

Cyclopropanations of the enyne sulfones 4–14

Typical procedure. NaH (60%; 0.59 g, 14.7 mmol) was added to a dry DMF (40.0 cm^3) solution of trimethylsulfoxonium iodide (3.24 g, 14.7 mmol) and the reaction mixture was stirred for 1 h. A dry DMF (20.0 ml) solution of (*E*)-5,5-dimethyl-1-phenylsulfonyl-1-phenylthiohex-1-en-3-yne **4** (3.50 g, 9.80 mmol) was added dropwise to the mixture of 0 °C after which the whole was stirred for 2 h at room temperature. It was then poured into water (150 cm^3) and extracted with AcOEt (30.0 × 3 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure and the residue was purified by column chromatography on silica gel eluting with AcOEt–hexane (1:10) to afford (1*S**,2*R**)-2-(3,3-dimethylbut-1-ynyl)-1-phenylsulfonyl-1-phenylthiocyclopropane **15** (3.03 g, 83%) as colourless prisms (mp 96–99 °C).

(1*S,2*R**)-2-(3,3-Dimethylbut-1-ynyl)-1-phenylsulfonyl-1-phenylthiocyclopropane 15.** The product was recrystallized from dichloromethane-hexane; ν_{max}/cm^{-1} 2250 (acetylene) and 1320 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$) 1.09 (9H, s, Me × 3), 1.29 (1H, dd, *J* 5 and 7, 3-H), 2.19 (1H, dd, *J* 5 and 10, 3-H), 3.01 (1H, dd, *J* 7 and 10, 2-H), 7.18–7.23 (3H, m, ArH), 7.29–7.33 (2H, m, ArH), 7.50–7.54 (2H, m, ArH), 7.62–7.66 (1H, m, ArH) and 7.92–7.95 (2H, m, ArH); δ_C(100 MHz, $CDCl_3$) 19.96 (d), 23.65 (t), 27.38 (s), 30.71 (q × 3), 52.00 (s), 73.97 (s), 91.44 (s), 127.22 (d), 127.60 (d), 128.60 (d), 128.83 (d), 128.92 (d), 129.47 (d), 129.64 (d), 130.32 (d), 132.99 (s), 133.85 (d), 136.63 (d) and 137.83 (s); *m*/*z* 370 (M^+) (Found: C, 67.80; H, 6.01. Calc. for $C_{21}H_{22}O_2S_2$: C, 68.07; H, 5.98%).

(1*S,2*R**)-2-Hex-1-ynyl-1-phenylsulfonyl-1-phenylthiocyclopropane 16**

(*E*)-1-Phenylsulfonyl-1-phenylthiooct-1-en-3-yne **6** (1.00 g, 2.80 mmol) was treated with dimethylsulfoxonium methylide [prepared from trimethylsulfoxonium iodide (0.92 g, 4.20 mmol) and NaH (0.17 g, 4.20 mmol) in DMF (12 cm^3)] by the same procedure as described above for **4** to give the title compound **16** (0.98 g, 94%) as a pale-yellow oil; ν_{max}/cm^{-1} 2250 (acetylene) and 1320 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$) 0.84 (3H, t, *J* 7, CH_3), 1.29–1.39 (4H, m, 4′- and 5′-CH_2) 2.11 (2H, br t, *J* 6, 3′-CH_2), 2.24 (2H, dd, *J* 1 and 4, 3-CH_2), 2.96–3.01 (1H, m, 2-CH), 7.19–7.24 (3H, m, ArH), 7.33–7.37 (2H, m, ArH), 7.50–7.54 (2H, m, ArH), 7.62–7.66 (1H, m, ArH) and 7.92–7.95 (2H, m, ArH); δ_C(100 MHz, $CDCl_3$) 13.52 (q), 18.38 (t), 20.37 (d), 21.77 (t), 23.41 (t), 30.49 (t), 52.05 (s), 75.16 (s), 83.46 (s), 127.38 (d), 128.70 (d × 2), 128.89 (d × 2), 129.52 (d × 2), 130.61 (d × 2), 132.78 (s), 133.81 (d) and 137.69 (s); *m*/*z* 370 (M^+) (Found: C, 60.18; H, 5.44. $C_{21}H_{22}O_2S_2$: C, 60.43; H, 5.31%).

(1*S,2*R**)-2-Phenylethynyl-1-phenylsulfonyl-1-phenylthiocyclopropane 17**

(*E*)-4-Phenyl-1-phenylsulfonyl-1-phenylthio-but-1-en-3-yne **7** (0.50 g, 1.33 mmol) was treated with dimethylsulfoxonium methylide [prepared from trimethylsulfoxonium iodide (0.44 g, 2.00 mmol) and NaH (0.11 g, 2.66 mmol) in DMF (4 cm^3)] by the same procedure as described above for **4** to give the title compound **17** (0.52 g, 87%) as a pale yellow oil; ν_{max}/cm^{-1} 2230 (acetylene) and 1310 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$) 1.47 (1H, dd, *J* 6 and 7, 3-CH_2), 2.36 (1H, dd, *J* 6 and 10, 3-CH_2), 3.22 (1H, dd, *J* 7 and 10, 2-CH), 7.20–7.31 (8H, m, ArH), 7.36–7.40 (2H, m, ArH), 7.52–7.56 (2H, m, ArH), 7.62–7.66 (1H, m, ArH) and 7.67–7.99 (2H, dd, *J* 1 and 8, ArH); δ_C(100 MHz, $CDCl_3$) 20.57 (t), 23.61 (d), 52.70 (s), 82.55 (s), 85.01 (s), 122.48 (s), 127.63 (d), 128.18 (d × 2), 128.33 (d), 128.84 (d × 2), 128.97 (d × 2), 129.60 (d × 2), 130.95 (d × 2), 131.71 (d × 2), 132.47 (s), 133.96 (d) and 137.47 (s); *m*/*z* 390 (M^+) (Found: C, 70.54; H, 4.78. $C_{23}H_{18}O_2S_2$: C, 70.74; H, 4.65%).

(1*S,2*R**)-2-(3,3-Dimethylbut-1-ynyl)-1-phenylseleno-1-phenylsulfonylcyclopropane 19**

(*Z*)-5,5-Dimethyl-1-phenylseleno-1-phenylsulfonyl-hex-1-en-3-yne **11** (0.40 g, 0.99 mmol) was treated with dimethylsulfoxonium methylide [prepared from trimethylsulfoxonium iodide (0.33 g, 1.50 mmol) and NaH (0.07 g, 1.98 mmol) in DMF (4 cm^3)] by the same procedure as described above for **4** to give the title compound **19** (0.33 g, 80%) as colourless needles (from CH_2Cl_2–hexane), mp 85–87 °C; ν_{max}/cm^{-1} 2250 (acetylene) and 1320 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$), 1.15 (9H, s, CH_3 × 3), 1.19 (1H, dd, *J* 6 and 7, 3-CH_2), 2.12 (1H, dd, *J* 6 and 10, 3-CH_2), 2.93 (1H, dd, *J* 7 and 10, 2-CH), 7.13–7.27 (5H, m, ArH), 7.49–7.53 (2H, m, ArH), 7.61–7.65 (1H, m, ArH) and 7.93 (2H, dd, *J* 1 and 8, ArH); δ_C(100 MHz, $CDCl_3$) 18.58 (d), 23.01 (t), 27.41 (s), 30.81 (q × 3), 47.66 (s), 75.23 (s), 90.97 (s), 127.99 (d), 128.79 (d × 2), 128.87 (d × 2), 129.64 (d × 2), 133.37 (d × 2), 133.56 (s), 133.68 (d) and 137.98 (s); *m*/*z* 418 (M^+) (Found: C, 60.18; H, 5.44. $C_{21}H_{22}O_2SSe$: C, 60.43; H, 5.31%).

Reaction of (*E*)-7,7-dimethyl-3-phenylsulfonylocta-1,3-dien-5-yne 13 and dimethylsulfoxonium methylide

(*E*)-7,7-Dimethyl-3-phenylsulfonylocta-1,3-dien-5-yne **13** (0.27 g, 1.00 mmol) was treated with dimethylsulfoxonium methylide [prepared from trimethylsulfoxonium iodide (0.33 g, 1.50 mmol) and NaH (0.08 g, 2.00 mmol) in DMF (4 cm^3)] by the same procedure as described above for **4** to give (1*S**,2*R**)-2-(3,3-dimethylbut-1-ynyl)-1-phenylsulfonyl-1-vinylcyclopropane (1*S**,2*R**)-**21** (0.06 g, 22%) (from ether–hexane), mp 158–163 °C as white prisms and its isomer (1*R**,2*R**)-**21** (0.03 g, 10%) as a colourless oil.

Compound (1*S,2*R**)-21.** ν_{max}/cm^{-1} 2210 (acetylene) and 1320 and 1140 (SO_2); δ_H(400 MHz, $CDCl_3$) 1.13 (9H, s, CH_3 × 3), 1.25 (1H, dd, *J* 5 and 6, 3-CH_2), 1.86 (1H, ddd, *J* 1 and 5 and 10, 2-CH), 2.68 (1H, dd, *J* 6 and 10, 3-CH_2), 5.12 (1H, dd, *J* 1 and 17, olefinic H), 5.40 (1H, dd, *J* 1 and 10, olefinic H), 6.02 (1H, ddd, *J* 1 and 10 and 17, olefinic H), 7.49–7.68 (3H, m, ArH) and 7.78–7.84 (2H, m, ArH); δ_C(100 MHz, $CDCl_3$) 14.80 (d), 19.02 (t), 27.28 (s), 30.93 (q × 3), 49.08 (s), 73.94 (s), 90.81 (s), 124.13 (t), 126.24 (s), 128.29 (d), 128.87 (d × 3), 129.28 (d) and 133.57 (d); *m*/*z* 288 (M^+) (Found: C, 70.52; H, 7.05. $C_{17}H_{20}O_2S$: C, 70.80; H, 6.99%).

Compound (1*R,2*R**)-21.** ν_{max}/cm^{-1} 2210 (acetylene) and 1320 and 1150 (SO_2); δ_H(400 MHz, $CDCl_3$) 1.29 (9H, s, CH_3 × 3), 1.48 (1H, dd, *J* 5 and 9, 3-CH_2), 1.97 (1H, dd, *J* 7 and 9, 3-CH_2), 2.13 (1H, dd, *J* 5 and 7, 2-CH), 5.03 (1H, dd, *J* 1 and 17, olefinic H), 5.20 (1H, dd, *J* 1 and 10, olefinic H), 6.14 (1H, ddd, *J* 1 and 10 and 17, olefinic H), 7.47–7.67 (3H, m, ArH) and 8.01–8.06 (2H, m, ArH) (Found M^+, 289.1272. $C_{17}H_{21}O_2S$ requires *M*, 289.1263).

(1*S,2*R**)-2-Hex-1-ynyl-1-phenylethynyl-1-phenylsulfonylcyclopropane 22**

(*E*)-1-Phenyl-3-phenylsulfonyl-dec-3-ene-1,5-diyne **14** (0.50 g, 1.43 mmol) was treated with dimethylsulfoxonium methylide [prepared from trimethylsulfoxonium iodide (0.47 g, 2.20 mmol) and NaH (0.11 g, 2.86 mmol) in DMF (4 cm^3)] by the same procedure as described above for **4** to give the title compound **22** (0.52 g, 74%) as a pale yellow oil; ν_{max}/cm^{-1} 2200 (acetylene) and 1310 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$) 0.76 (3H, t, *J* 7, CH_3), 1.24–1.42 (4H, m, 4′- and 5′-CH_2), 1.54 (1H, dd, *J* 5 and 7, 3-CH_2), 2.12–2.16 (3H, m, 3-CH_2 and 3′-CH_2), 2.71–2.76 (1H, m, 2-CH), 7.26–7.35 (5H, m, ArH), 7.56–7.60 (2H, m, ArH), 7.67–7.70 (1H, m, ArH), 7.99 (2H, dd, *J* 1 and 8, ArH); δ_C(100 MHz, $CDCl_3$) 13.48 (q), 18.10 (d), 18.42 (t), 21.78 (t), 23.38 (t), 30.67 (t), 42.72 (s), 75.03 (s), 81.73 (s), 82.59 (s), 86.10 (s), 122.09 (s), 128.22 (d), 128.98 (d × 3), 129.07 (d × 3), 131.90 (d × 2), 133.96 (d) and 137.94 (s); *m*/*z* 362 (M^+) (Found: C, 76.15; H, 6.15. $C_{23}H_{22}O_2S$: C, 76.21; H, 6.12%).

Reaction of (*Z*)-5,5-dimethyl-1-methylthio-1-phenylsulfonylhex-1-en-3-yne 8 with dimethylsulfoxonium methylide

Treatment of (*Z*)-5,5-dimethyl-1-methylthio-1-phenylsulfonyl-hex-1-en-3-yne **8** (0.27 g, 0.91 mmol) with dimethylsulfoxonium methylide [prepared from trimethylsulfoxonium iodide (0.39 g, 1.79 mmol) and NaH (0.10 g, 2.38 mmol) in DMF (3 cm^3)] by the same procedure as described above for **4** to give (1*E*,3*E*)- and (1*E*,3*Z*)-5,5-dimethyl-1,3-dimethylthiobut-1,3-diene **18** (0.12 g, 78%) and 5-*tert*-butyl-1-methyl-3-phenylsulfonyl-methylthiabenzene 1-oxide **26** (0.09 g, 62%) as pale yellow prisms ($CHCl_3$–Et_2O), mp 75–77 °C. Reaction of the (*E*)-isomer **9** (0.17 g, 0.57 mmol) with dimethylsulfoxonium methylide [prepared from trimethylsulfoxonium iodide (0.19 g, 0.86 mmol) and NaH (0.05 g, 1.14 mmol) in DMF (3 cm^3)] also afforded the diene **18** (0.07 g, 70%) and the thiabenzene 1-oxide **26** (0.10 g, 65%). The isomer ratio of **18** were determined by the intensities of MeS groups in the ^1H NMR spectrum.

5-*tert*-Butyl-1-methyl-3-phenylsulfonylmethylthiabenzene 1-oxide 26. ν_{max}/cm^{-1} 1540, 1310 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$) 1.07 (9H, s, Me × 3), 3.46 (3H, s, Me), 4.14 (2H, s, CH_2SO_2), 5.32 (1H, br s, olefinic H), 5.35 (1H, dd, *J* 1 and 4, olefinic H), 5.60 (1H, dd, *J* 1 and 4, olefinic H), 7.45–7.49 (2H, m, ArH), 7.57–7.61 (1H, m, ArH) and 7.73–7.76 (2H, m, ArH); δ_C(100 MHz, $CDCl_3$) 30.36 (q × 3), 35.82 (s), 50.02 (q), 64.32 (t), 83.33 (d), 85.28 (d), 103.11 (d), 128.73 (d × 2), 128.87 (d × 2), 132.36 (s), 133.66 (d), 137.78 (s) and 156.37 (s); *m*/*z* 338 (M^+) (Found: C, 60.31; H, 6.59. $C_{17}H_{22}O_3S_2$: C, 60.32; H, 6.55%).

A synthesis of 2-alkynyl-1-phenylsulfonyloxiranes

Typical procedure: (2*R**,3*R**)-3-(3,3-dimethylbut-1-ynyl)-2-phenylsulfonyloxirane. Under an Ar atmosphere, a THF (2.0 cm^3) solution of (*E*)-5,5-dimethyl-1-phenylsulfonylhex-1-en-3-yne **4** (0.30 g, 1.2 mmol) was added dropwise to a THF (12 cm^3) solution of Bu′OOLi [prepared from Bu′OOH in toluene (3 M solution; 3.0 cm^3)[6] and BuLi (1.6 M; 3.6 cm^3)] at −78 °C. The temperature of the reaction mixture was raised to −20 °C. The mixture was then stirred for 2 h after which it was poured into water (100 cm^3). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer and extract were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was crystallized from hexane to give (2*R**,3*R**)-3-(3,3-dimethylbut-1-ynyl)-2-phenylsulfonyloxirane **33** (0.22 g, 77%) as colourless prisms.

Compound (2*R,3*R**)-33.** Colourless prisms (from ether–hexane), mp 123–124 °C; ν_{max}/cm^{-1} 2200 (acetylene) and 1310 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$), 1.20 (9H, s, Me × 3), 4.00 (1H, br s, CH), 4.22 (1H, br s, CH), 7.53–7.67 (2H, m, ArH), 7.69–7.74 (1H, m, ArH) and 7.89–7.91 (2H, m, ArH); δ_C(100 MHz, $CDCl_3$) 27.44 (s), 30.31 (q × 3), 45.25 (d), 69.35 (d), 71.20 (s), 96.07 (s), 129.31 (d × 2), 129.41 (d × 2), 134.61 (d)

and 136.20 (s); *m/z* 248 ($M^+ - O$) (Found: C, 63.73; H, 6.16. $C_{14}H_{16}O_3S$ requires C, 63.61; H, 6.10%).

(2*R,3*R**)-3-Hex-1-ynyl-2-phenylsulfonyloxirane 34**

Treatment of (*E*)-1-phenylsulfonylhex-1-en-3-yne **27** (0.13 g, 0.50 mmol) with Bu^{t}OOLi [prepared from Bu^{t}OOH in toluene (3 M solution; 1.2 cm^3) and BuLi (1.6 M; 1.5 cm^3) in THF (10 cm^3)] by the same procedure as described above for **4** afforded the title compound **34** (0.11 g, 85%) as a yellow oil; ν_{max}/cm^{-1} 2250 (acetylene) and 1310 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$) 0.89 (3H, t, *J* 7, Me), 1.31–1.55 (4H, m, $CH_2 \times 2$), 2.16–2.24 (2H, dt, *J* 2 and 7, 3′-CH_2), 4.01 (1H, dd, *J* 2 and 3, 3-H), 4.21 (1H, d, *J* 2, CH), 7.55–7.76 (3H, m, ArH) and 7.89–7.96 (2H, m, ArH); *m/z* 264 (M^+) (Found: C, 63.51; H, 6.12. $C_{14}H_{16}O_3S$ requires C, 63.61; H, 6.10%).

(2*R,3*R**)-3-Phenylethynyl-2-phenylsulfonyloxirane 35**

Treatment of (*E*)-4-phenyl-1-phenylsulfonylbut-1-en-3-yne **28** (0.13 g, 0.50 mmol) with Bu^{t}OOLi (prepared from Bu^{t}OOH in toluene (3 M solution; 0.6 cm^3) and BuLi (1.6 M; 1.5 cm^3) in THF (10 cm^3)] by the same procedure as described above for **4** afforded the title compound **35** (0.13 g, 89%) as colourless prisms, mp 72–76 °C; ν_{max}/cm^{-1} 2200 (acetylene) and 1310 and 1160 (SO_2); δ_H(200 MHz, $CDCl_3$) 4.26 (1H, d, *J* 2, CH), 4.39 (1H, d, *J* 2, CH), 7.25–7.47 (5H, m, ArH), 7.54–7.76 (3H, m, ArH) and 7.89–7.98 (2H, m, ArH); δ_C(50 MHz, $CDCl_3$) 45.27 (d), 69.32 (d), 81.10 (s), 86.41 (s), 120.69 (s), 128.40 (d × 2), 128.83 (d × 2), 129.50 (d × 3), 131.97 (d × 2), 134.77 (d) and 136.25 (s); *m/z* 284 (M^+) (Found: C, 67.68; H, 4.31. $C_{16}H_{12}O_3S$ requires C, 67.59; H, 4.25%).

(2*R,3*R**)- and (2*S**,3*R**)-3-(3,3-Dimethylbut-1-ynyl)-2-phenylsulfonyl-2-vinyloxirane 36**

Treatment of (*E*)-7,7-dimethyl-3-phenylsulfonylocta-1,3-dien-5-yne **13** (1.07 g, 3.90 mmol) with Bu^{t}OOLi [prepared from Bu^{t}OOH in toluene (3 M solution; 9.4 cm^3) and BuLi (1.6 M; 12.0 cm^3) in THF (38 cm^3)] by the same procedure as described above for **4** afforded the title compound **36** (0.90 g, 81%) as colourless needles, mp 95–97 °C. The isomer ratio was determined by the intensities of the vinyl protons in the ^{1}H NMR spectrum (2*R**:2*S** = 1:1); ν_{max}/cm^{-1} 2220 (acetylene) and 1310 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$) 1.17 (s, 2*R**-Bu^t), 1.29 (s, 2*S**-Bu^t), 4.38 (s, 2*R**-3-H), 5.02 (s, 2*S**-3-H), 5.34 (d, *J* 17, 2*R**-olefinic H), 5.48 (d, *J* 11, 2*S**-olefinic H), 5.50 (d, *J* 11, 2*R**-olefinic H), 6.10 (d, *J* 18, 2*S**-olefinic H), 6.27 (dd, *J* 11 and 17, 2*R**-olefinic H), 6.51 (dd, *J* 11 and 18, 2*S**-olefinic H), 7.50–7.62 (m, ArH), 7.65–7.70 (m, ArH) and 7.85–7.87 (m, ArH); δ_C(100 MHz, $CDCl_3$) 27.52 (s), 30.45 (q × 3), 52.15 (d), 56.66 (s), 70.32 (s), 97.67 (s), 123.94 (d), 124.02 (t), 128.99 (d × 2), 129.45 (d × 2), 134.37 (d) and 135.66 (s); *m/z* 290 (small M^+) (Found: C, 66.05; H, 6.27. $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25%).

(2*S,3*R**)-3-Hex-1-ynyl-3-methyl-2-phenylsulfonyloxirane 37**

Treatment of (*E*)-1-phenylsulfonyl-2-methyloct-1-en-3-yne **31** (0.13 g, 0.50 mmol) with Bu^{t}OOLi [prepared from Bu^{t}OOH in toluene (3 M solution; 1.2 cm^3) and BuLi (1.6 M; 1.2 cm^3) in THF (10 cm^3)] by the same procedure as described above for **4** afforded the title compound **37** (0.06 g, 57%) as a yellow oil; ν_{max}/cm^{-1} 2200 (acetylene) and 1310 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$) 0.92 (3H, t, *J* 7, Me), 1.39–1.57 (4H, m, $CH_2 \times 2$), 1.60 (3H, s, Me), 2.22 (2H, t, *J* 7, CH_2), 3.97 (1H, s, CH), 7.50–7.61 (2H, m, ArH), 7.67–7.71 (1H, m, ArH) and 7.95–7.99 (2H, m, ArH) [Found (FABMS): $M^+ + 1$, 279.1057. FABMS: $C_{15}H_{18}O_3S$ requires *M*, 279.1027].

(2*R3*R**)-3-Hex-1-ynyl-2-phenylethynyl-2-phenylsulfonyloxirane 38**

Treatment of (*E*)-1-phenyl-3-phenylsulfonyldec-3-ene-1,5-diyne **14** (0.20 g, 0.57 mmol) with Bu^{t}OOLi [prepared from Bu^{t}OOH in toluene (3 M solution; 0.8 cm^3) and BuLi (1.6 M; 1.0 cm^3) in THF (10 cm^3)] by the same procedure as described above for **4** afforded the title compound **38** (0.13 g, 61%) as colourless needles (ether–hexane), mp 53–55 °C; ν_{max}/cm^{-1} 2230 (acetylene) and 1320 and 1160 (SO_2); δ_H(400 MHz, $CDCl_3$) 0.79 (3H, t, *J* 7, Me), 1.35–1.48 (4H, m, $CH_2 \times 2$), 2.23–2.27 (2H, dt, *J* 2 and 7, 3′-CH_2), 4.44 (1H, t, *J* 2, CH), 7.31–7.40 (5H, m, ArH), 7.56–7.60 (2H, m, ArH), 7.68–7.71 (1H, m ArH) and 7.99–8.01 (2H, m, ArH); δ_C(100 MHz, $CDCl_3$) 13.34 (q), 18.45 (t), 21.66 (t), 29.99 (t), 51.88 (d), 69.84 (s), 71.76 (s), 90.31 (s × 2), 91.40 (s), 120.56 (s), 128.22 (d × 2), 128.42 (d × 3), 129.17 (d × 2), 132.21 (d × 2), 134.83 (d) and 135.43 (s); *m/z* 364 (M^+) (Found: C, 72.71; H, 5.59. Calc. for $C_{22}H_{20}O_3S$: C, 72.50; H, 5.53%).

An oxy Cope rearrangement of (2*R,3*R**)- and (2*S**,3*R**)-3-(3,3-dimethylhex-1-ynyl)-1-phenylsulfonyl-1-vinyloxirane 36**

A toluene (2 cm^3) solution of (2*R**,3*R**)- and (2*S**,3*R**)-3-(3,3-dimethylhex-1-ynyl)-1-phenylsulfonyl-1-vinyloxirane **36** (50 mg, 0.17 mmol) was heated in a sealed tube at 180 °C for 1 h. The mixture was purified by preparative TLC on silica gel eluting with AcOEt–hexane (1:10) to give 5-*tert*-butyl-2-phenylsulfonylphenol **39** (30 mg, 60%) as colourless prisms.

Compound 39. Mp 105–107 °C (from $CHCl_3$–hexane); ν_{max}/cm^{-1} 3280 (OH) and 1300 and 1150 (SO_2); ν_{max}/cm^{-1} 1.26 (9H, s, Me × 3), 6.94 (1H, d, *J* 8, 4-H), 7.48–7.60 (4H, m, ArH), 7.62 (1H, d, *J* 2, 5-H), 7.94 (2H, dd, *J* 8 and 1, 3-H) and 9.02 (1H, br s, OH); δ_C(100 MHz, $CDCl_3$) 31.15 (q × 3), 34.30 (s), 118.77 (d), 122.56 (s), 125.10 (d), 126.72 (d × 2), 129.44 (d × 2), 133.58 (d), 133.80 (d), 141.88 (s), 144.00 (s) and 153.67 (s); *m/z* 290 (M^+) (Found: C, 66.64; H, 6.50. $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25%).

X-Ray study of 5-*tert*-butyl-1-methyl-3-phenylsulfonylmethylthiabenzene 1-oxide 26

A colourless prism was mounted on a glass fibre and transferred to the diffractometer.

Crystal data. $C_{17}H_{22}O_3S_2$. *M* 338.48, Monoclinic, $a = 16.828(2)$, $b = 9.452(2)$, $c = 21.568(1)$ Å, $\beta = 94.531(6)°$, $V = 3420.0(7)$ Å^3 (from setting angles of 20 centred reflections with $75.9 \leqslant 2\theta \leqslant 79.5°$, $\lambda = 1.54178$ Å, $T = 23$ °C), space group *C*2/*c* (No 15), $Z = 8$, $D_x = 1.315$ cm^3, colourless prisms $0.18 \times 0.20 \times 0.20$ mm, μ(Cu-K$_\alpha$) = 28.48 cm^{-1}.

Data collection and processing. Rigaku AFC-5R four-circle diffractometer with 12 kW rotating anode generator, $\omega/2\theta$ scans with ω scan width $(0.94 \pm 0.30 \tan\theta)°$, graphite-monochromated Cu-Kα X-radiation; 2840 reflections measured to $2\theta_{max} = 120.1°$, 2730 unique (merging $R = 0.052$), giving 2021 with $F > 6\sigma(F)$ which were retained in all calculations. No crystal decay was observed and no corrections were applied for absorption.

Structure solution and refinement. Automatic direct methods[10] (all non-H atoms). Full-matrix least-squares refinement with all non-H atoms anisotropic.

The weighting scheme $w = 4F_o^2/\sigma^2(F_o^2)$ gave satisfactory agreement analyses. Final $R = 0.048$, $R_w = 0.063$, $S = 2.16$ for 199 refined parameters. The final ΔF synthesis showed no peaks above +0.31 or below −0.52 e Å^{-3}. The detailed crystallographic results for this study have been deposited with the Cambridge Crystallographic Data Centre and are available on request.† Any such request should be accompanied by a full bibliographic reference for this work together with the reference number 207/141.

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† For details of the Scheme, see Instructions for Authors (1997), *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, Issue 1.

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