

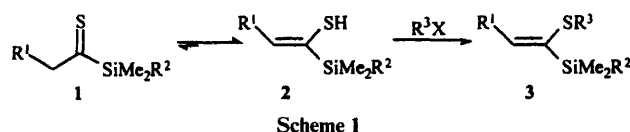
Chemistry of silyl thioketones. Part 10.¹ Synthesis and reactivity of α -silyl vinyl sulfides

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Aliphatic silyl thioketones containing an α -hydrogen atom undergo enethiolization to Z - α -silyl enethiols **2**. Compounds **2** react with a variety of halides R^3X to give open-chain α -silyl vinyl sulfides **3**. Protodesilylation of **3** was achieved upon treatment with fluoride ion to give vinyl sulfides **4**. Reaction of **3** with Grignard reagents, in the presence of an appropriate nickel catalyst, results in a series of vinylsilanes **5** with a specific geometry.

In the past years several silyl thioketones² have been synthesized and their chemistry investigated. The aliphatic derivatives **1** containing a hydrogen atom α to the carbon–sulfur double bond, undergo quantitative and stereoselective enethiolization¹ to Z - α -silyl enethiols **2** (Scheme 1). This behaviour



has been ascribed to the presence of the silyl group which favours enethiolization.^{1,3} Other methyl thiones⁴ as well as alkyl thiones do not enethiolize or give mixtures of thione and enethiol.^{4,5} We found that compounds **2** with $R^1 = (CH_2)_nX$ ($X = Cl, Br$) undergo ring closure, in the presence of solid NaOH, to give cyclic α -silyl vinyl sulfides for a range of ring sizes.^{1,3}

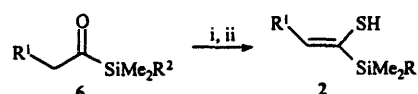
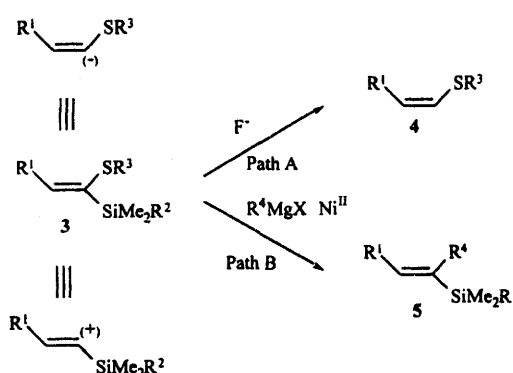
Compounds **2** ($R^1 = \text{alkyl or aryl}$) can react with a variety of halides R^3X to give open chain Z - α -silyl vinyl sulfides **3** (Scheme 1).

The Z - α -silyl vinyl sulfides **3** are intriguing species since the silyl and the thioether functions exert an opposing polarization on the olefinic bond.^{6a,h} Until now relatively few synthetic methods for these interesting polyfunctionalized compounds have been reported;^{7a,d} of these only very few give products **3** in a stereoselective manner.^{8a,h} The reaction depicted in Scheme 1 represents a new method for a highly stereoselective synthesis of trisubstituted alkenes **3**. Products **3** can be used for the generation of functionalized vinyl anions upon treatment with fluoride ions to give Z -vinyl sulfides **4** (Path A in Scheme 2). Furthermore, these compounds can serve as vinyl cation equivalents (Path B in Scheme 2) in reactions with Grignard reagents in the presence of an appropriate nickel catalyst, resulting in a series of vinylsilanes **5** with a specific geometry.

Results and discussion

In order to investigate the influence on the reactivity of **3** of the R^1 and R^2 groups present at the double bond and on the silyl moiety, two representative α -silyl enethiols **2a** and **2b** were prepared starting from 2-phenyl-1-trimethylsilyl ethanone **6a**⁹ and butanoyl(dimethylphenyl)silane **6b** (Scheme 3).

Product **6b** was prepared using a procedure developed by us¹⁰ involving the reaction of butanoyl chloride with bis(dimethyl-



Scheme 3 Reagents and conditions: i, H_2S , HCl , Et_2O ; ii, solid $NaHCO_3$

Table 1 Synthesis of (Z)- α -silyl vinyl sulfides **3**^a

Product 3	R^1	R^2	R^3	X	Yield (%)
a	Ph	Me	Me	I	98
b	Et	Ph	Me	I	95
c	Ph	Me	CH_2CO_2Et	I	100
d	Et	Ph	CH_2CO_2Et	I	80
e	Ph	Me	$(CH_2)_2CO_2Et$	Cl	100
f	Et	Ph	$(CH_2)_2CO_2Et$	Cl	80
g	Ph	Me	$CH_2CH=CH_2$	I	100
h	Et	Ph	$CH_2CH=CH_2$	I	95
i	Ph	Me	CH_2Ph	Br	100
l	Et	Ph	CH_2Ph	Br	90

^a The Z -stereochemistry of products **3** was assigned by NOE.

phenylsilyl)copper–lithium.¹¹ The Z stereochemistry was assigned to the enethiols **2** by NOE experiments. Products **3a–l** were obtained in very good yield by reactions of **2a,b** with halides R^3X in acetone in the presence of dry K_2CO_3 (1.2 equiv.) at room temperature (Scheme 1 and Table 1).

Cleavage of the silicon–vinyl carbon bond by fluoride ion is known to be difficult,^{12a,h} few examples having been reported;¹³ the presence of an anion-stabilizing group on the carbon bearing the silyl group facilitates the Si–C bond cleavage.¹³ In fact,

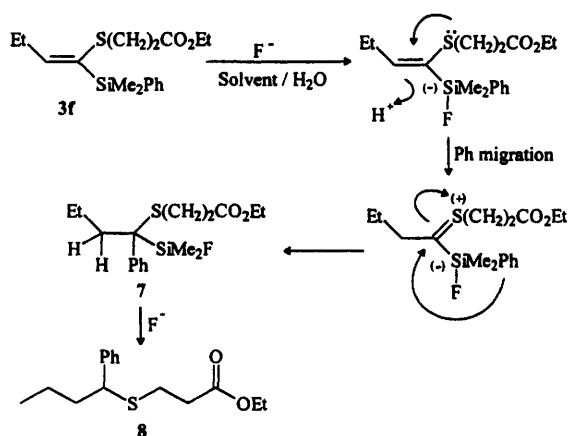
Table 2 Protodesilylation of products 3

Entry	3	F ^{-a}	Solvent	Temp. (°C)	4	R ¹	R ³	Yield (%)	Z:E ratio	Ref.
1	a	CsF	DMSO	40	a	Ph	Me	100	>98:2	14 ^b
2	b	CsF	DMSO	40	b	Et	Me	NR*		
3	b	TBAF	THF	67	b	Et	Me	46 ^c	>98:2	15 ^b
4	c	CsF	DMSO	40	c	Ph	CH ₂ CO ₂ Et	100	>98:2	16
5	d	CsF	DMSO	40	d	Et	CH ₂ CO ₂ Et	78	>98:2	17 ^d
6	e	CsF	DMSO	40	e	Ph	CH ₂ CH ₂ CO ₂ Et	100	>98:2	
7	f	CsF	DMSO	40	f	Et	(CH ₂) ₂ CO ₂ Et	NR		
8	f	TBAF	THF	67	e					
9	f	CsF	CH ₃ CN	82	e					
10	g	CsF	DMSO	40	g	Ph	CH ₂ CH=CH ₂	100	>98:2	18 ^f
11	h	CsF	DMSO	40	g					
12	h	TBAF	THF	40	h	Et	CH ₂ CH=CH ₂	85	>98:2	19 ^h
13	i	CsF	DMSO	40	i	Ph	CH ₂ Ph	100	>98:2	18 ^h
14	l	TBAF	THF	67	l	Et	CH ₂ Ph	80	>98:2	20
15	l	CsF	DMSO	40	l	Et	CH ₂ Ph	NR		

* NR = no reaction. ^a 1.1 equiv. of fluoride ion were employed. ^b Obtained as a mixture of *E* and *Z* isomers. ^c Rather volatile compound. ^d The spectral data are not reported. ^e Product 8 was obtained: see text. ^f Obtained as a mixture of *E* and *Z* isomers together with other products. ^g Starting material and unidentified products were obtained. ^h The stereochemistry was not determined.

products 3 were protidesilylated according to path A in Scheme 2 to give vinyl sulfides 4 (Table 2) as *Z*-diastereoisomers. The same products obtained by other methods,^{14,15,17–19} were generally mixtures of *E* and *Z* isomers.

The desilylation of *Z*- α -silyl vinyl sulfides 3 ($R^1 = \text{Ph}$ and $R^2 = \text{Me}$) was achieved readily by reaction of 3a,c,e,g and i with CsF in moist DMSO at 40 °C to afford the corresponding *Z*-vinyl sulfides 4a,c,e,g and i in very good yields and in their pure state. Desilylation of compounds 3 ($R^1 = \text{Et}$ and $R^2 = \text{Ph}$), was rather difficult and it was necessary to make appropriate choices both of the fluoride ion source and the solvent. Generally, the reaction was slower than in the previous cases. For example, the desilylation of 3b, 3f and 3l with CsF in DMSO at 40 °C (entries 2, 7, 15) did not occur even after 48 h. Only with TBAF in boiling THF, could products 4b and 4l (entries 3 and 14) be obtained in 46 and 80% yield, respectively. Desilylation of 3f was accomplished only with TBAF in boiling THF or with CsF in boiling CH₃CN to give a product whose structure was deduced from analytical and spectral data and is in agreement with 8 (see Experimental section). A tentative explanation for the formation of product 8 is reported in Scheme 4, in which



Scheme 4

the reaction is initiated by protonation of the thioether 3f (protons are present in the fluoride-based reactions performed in moist solvents and the thioether will be easy to protonate). The silicon may or may not have a fluoride ion coordinated to it at this stage. The phenyl group can then migrate^{21a,b} from the silicon to the neighbouring cationic carbon giving 7. Protodesilylation of 7, with the silyl group bonded to a benzylic carbon bearing an anion-stabilizing group, gave product 8.

The reaction of product 3d with TBAF in boiling THF gave, in contrast, only the protidesilylate derivative 4d (80%). No trace of a product analogous to product 8 has been detected by ¹H NMR analysis of the crude mixture. This indicates that structural features in the ester 3f are crucial for the migration of the phenyl group.

The reaction of 3h with CsF in DMSO at 40 °C gave unchanged starting material in addition to unidentified products. In contrast, the use of TBAF in THF at 40 °C gave desilylated derivative 4h (85%) which could be fully characterized by ¹H NMR spectroscopy, but which decomposed during attempts to purify it on silica.

Compounds 3a and 3b were oxidized with oxone to their corresponding sulfones 9a and 9b. Their protidesilylation with CsF in DMSO under the same conditions as for the sulfides (40 °C) gave product 10a (100%) as a 93:7 mixture of diastereoisomers *Z*:*E* from 9a and an almost complete migration of the double bond to (*E*)-1-methylsulfonylbut-2-ene from 9b. The reaction of 9b at room temperature gave the expected protidesilylated derivative 10b in quantitative yield (Table 3).

It is known that vinyl sulfides couple with Grignard reagents in the presence of nickel(II)-phosphine complexes to give olefins, with predominant retention of configuration.^{22a–d} Phenyl vinyl sulfides containing a trimethylsilyl group in the β -position were coupled with Grignard reagents to synthesize stereospecifically monosubstituted *E*-vinylsilanes.²³ Substrates 3a,b could, in principle, afford disubstituted vinylsilanes 5 (Path B, Scheme 2). With this aim, a study of nickel-catalysed cross-coupling of 3a and 3b with Grignard reagents was carried out, the results for which are summarized in Table 4.

A large excess of the Grignard reagent was necessary for substrates 3a and 3b because of the increased reaction time observed when the amount normally employed for coupling reactions was used.^{22a–d} This extended reaction time is probably because of the bulkiness of the silyl group present on the same carbon bearing the thioether function. Methylmagnesium bromide in the presence of [Ni(PPh₃)₂Cl₂] gave high yields of products 5a and 5b with both 3a and 3b with a high degree of selectivity (entries 1 and 4). With a different catalyst, [Ni(dppe)Cl₂], at room temperature, 3a gave 5a in 94% yield (entry 7) while 3b, under identical reaction conditions, was recovered unchanged (entry 8). Moderate yields and a lower degree of stereoselectivity were obtained with ethylmagnesium bromide with both 3a (entry 2) and 3b (entry 5); a 17:1 and 1:1 *E* to *Z* ratio was observed in the ¹H NMR spectrum of the crude 5b and 5e. Butylmagnesium bromide gave a large portion of hydrogenolysis (42%) in the reaction with 3a (entry 3) and a low yield and low selectivity with 3b (entry 6). Reaction of vinyl

Table 3

$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{SiMe}_2\text{R}^2 \end{array} \xrightarrow{\text{oxone}} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{SO}_2\text{Me} \end{array} \xrightarrow{\text{F}^a} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{SO}_2\text{Me} \end{array}$ $\text{3a,b} \quad \quad \quad \text{9a,b} \quad \quad \quad \text{10a,b}$						
Entry	R ¹	R ²	Yield of 9 (%)	Desilylation temp. (°C)	Yield of 10 (%)	Z:E ratio of 10
1	Ph	Me	98	40	100	93:7
2	Et	Ph	89	40	10 ^b	>98:2
3	Et	Ph		RT	100	>98:2

^a 1 Equiv. of CsF was employed. ^b The major product was (*E*)-1-methylsulfonylbut-2-ene (90%).

Table 4

$ \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{SiMe}_2\text{R}^2 \end{array} \xrightarrow[\text{cat}]{\text{R}^4\text{MgX}^a} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{SiMe}_2\text{R}^2 \end{array} \text{5} + \begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{SiMe}_3 \end{array} \text{11} $									
Entry	R ¹	R ²	R ⁴	Time (h)	Catalyst	5	Yield of 5 (%) ^c	E:Z ratio of 5	Yield of 11 (%)
1	Ph	Me	Me	7	Ni(PPh ₃) ₂ Cl ₂	a	93	>98:2	—
2	Ph	Me	Et	48	Ni(PPh ₃) ₂ Cl ₂	b	60	17:1	—
3	Ph	Me	Bu	40	Ni(PPh ₃) ₂ Cl ₂	c	44	>98:2	42
4	Et	Ph	Me	18	Ni(PPh ₃) ₂ Cl ₂	d	72	>98:2	—
5	Et	Ph	Et	12	Ni(PPh ₃) ₂ Cl ₂	e	60	1:1	—
6	Et	Ph	Bu	72	Ni(PPh ₃) ₂ Cl ₂	f	50	4.5:1	—
7	Ph	Me	Me	120 ^b	Ni(dppe)Cl ₂	a	94	>98:2	—
8	Et	Ph	Me	120 ^b	Ni(dppe)Cl ₂	d	—	—	—

^a 15 Equiv. of the Grignard reagent were used and the reactions carried out in THF at reflux temperature unless otherwise noted. ^b The reaction was carried out at room temperature. ^c The yields were determined after chromatography.

Table 5

$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{SiMe}_2\text{R}^2 \end{array} \xrightarrow[\text{[Ni(PPh}_3)_2\text{Cl}_2]]{\text{R}^4\text{MgX}^a, \text{THF}^b} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{SiMe}_2\text{R}^2 \end{array} \text{5} + \begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{SiMe}_3 \end{array} \text{11}$								
Entry	R ¹	R ²	R ⁴	5	Yield of 5 (%) ^c	E:Z ratio of 5	Yield of 11 (%) ^c	E:Z ratio of 11
1	Ph	Me	Me	a	34	>98:2	54	>98:2
2	Ph	Me	Bu	c	24	>98:2	75	>98:2

^a 15 Equiv. of Grignard reagent were used. ^b The reactions were carried out at reflux temperature. ^c The yields were determined after chromatography.

sulfones with Grignard reagents with nickel or palladium catalysts have been extensively studied by Julia and co-workers^{24a,b} for the synthesis of tri- and di-substituted olefins. The cross-coupling of α -silyl vinyl sulfones **9a** with methyl- and butylmagnesium bromide, gave, in both cases, the hydrogenolysis derivative **11** as the major product in addition to a minor amount of the coupling products **5a** and **5c**. Both **5** and **11** were formed with retention of configuration (Table 5).

Conclusions

A new stereoselective synthesis of α -silyl vinyl sulfides has been developed through thionation of enolizable acylsilanes. The synthetic utility of these compounds is demonstrated by the preparation of a variety of *Z*-vinyl sulfides through protidesilylation. The trimethylsilyl group was more readily cleaved than the dimethylphenylsilyl group as a result of competitive phenyl group migration. Furthermore, nickel-induced cross-coupling of α -silyl vinyl sulfides with a Grignard reagent constitutes a highly stereoselective route to disubstituted vinylsilanes.

Experimental

Bps and mps are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded with a Varian Gemini 200 MHz spectrometer as solutions in CDCl₃; chemical shifts (δ) are given in ppm relative to tetramethylsilane. *J* Values are given in Hz. ¹³C NMR spectral assignments were made by DEPT experiments. Mass

spectra were obtained using a VG 7070-E (EI, 70 eV) spectrometer. IR spectra were recorded on a Perkin-Elmer model 257 grating spectrometer. Reactions were conducted in oven-dried (120 °C) glassware under a positive argon atmosphere. Transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes. THF was distilled from sodium benzophenone just prior to use and stored under argon. Et₂O was distilled from phosphorus pentoxide. The reactions were monitored by TLC performed on silica gel plates (Baker-flex IB2-F). Column chromatography was performed with Merck silica gel 60 (70–230 mesh) and preparative thick layer chromatography was carried out on glass plates using a 1 mm layer of Merck silica gel 60 PF₂₅₄ or aluminium oxide F₂₅₄. Light petroleum refers to the fraction with bp 40–60 °C. In the characterization of the new compounds, elemental analysis has been performed for crystalline products. Oily products, because of the small scale used for the preparation, have been characterized by accurate mass measurements. All chemicals were used as obtained or purified by distillation as needed. Sodium hydrogen carbonate 99% and Grignard reagents were purchased from Aldrich. [NiCl₂(PPh₃)₂] was prepared according to the procedure described by L. M. Venanzi²⁵ and [NiCl₂(dppe)] was commercially available (Aldrich).

Butanoyl(dimethyl)phenylsilane **6b**

Butanoyl chloride (530 mg, 0.517 cm³, 5.0 mmol) in anhydrous THF (3 cm³), was added slowly to lithium bis(dimethylphenyl)silyl]cuprate¹¹ (5.0 mmol) at –78 °C under argon. The

mixture was stirred at -78°C for 1 h and then allowed to warm to 0°C at which temperature it was stirred for 1 h. The mixture was quenched with saturated aqueous ammonium chloride and extracted with diethyl ether. The extract was dried and concentrated under reduced pressure. Chromatography on a silica gel column [light petroleum–diethyl ether (15:1) as eluent] gave, as the higher R_F fraction, a product arising from the silyl cuprate and as the lower R_F fraction the acylsilane **1b**²⁶ (670 mg, 65%) as a yellow oil; $\delta_{\text{C}}(\text{CDCl}_3)$ -4.88 (SiMe₃), 13.61 (CH₃), 15.49 , 50.64 (CH₂), 128.02 , 129.72 , 133.84 (ArCH) and 246.17 (CO); m/z (EI) 206 (M⁺), 163 (M⁺ – C₃H₇) and 135 (SiMe₂Ph).

Synthesis of (Z)- α -silyl enethiols **2**: general method

Hydrogen chloride and hydrogen sulfide were bubbled into a solution of the acylsilane **6** (1.0 mmol) in anhydrous diethyl ether (50 cm³) at -30°C , until the starting ketone had disappeared [TLC with light petroleum–diethyl ether (10:1) as eluent]. In some cases, it was possible to see the blue colour characteristic of the thio ketone that quickly faded. After the mixture had been allowed to warm to room temperature it was treated with solid sodium hydrogen carbonate until evolution of carbon dioxide ceased; it was then left overnight. Filtration and concentration of the mixture under reduced pressure gave the pure (Z)-enethiol.

(Z)-1-Trimethylsilyl-2-phenylethenethiol 2a. From 2-phenyl-1-trimethylsilyl ethanone **6a**⁹ the title compound was obtained as an oil (95%) (Found: M⁺, 208.0751. C₁₁H₁₆SSi requires M , 208.0742; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 2550 (SH) and 1250 and 840 (SiMe₃); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.30 (9 H, s, SiMe₃), 3.05 (1 H, s, SH), 6.80 (1 H, s, vinylic H) and 7.20–7.60 (5 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ -1.29 (SiMe₃), 127.59, 128.80, 129.33 (ArCH) 128.92 (C) and 134.23 (vinylic CH); m/z (EI) 208 (M⁺), 192 (M⁺ – CH₄), 91 (PhCH₂) and 73 (SiMe₃). Irradiation of the dimethylsilyl signal at 0.30 ppm produced a significant increase (12.2%) of the intensity of the signal of the vinylic proton at 6.80 ppm.

(Z)-1-[Dimethyl(phenyl)silyl]but-1-enethiol 2b. From butanoyl(dimethyl)phenylsilane **6b**²⁶ the title compound was obtained as an oil (97%) (Found: M⁺, 222.0855. C₁₂H₁₈SSi requires M , 222.0898; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 2560 (SH), 1710, 1430 and 1110 (SiPh) and 1250 (SiMe₂); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.52 (6 H, s, SiMe₂), 1.12 (3 H, t, J 8.0, CH₃), 2.30 (2 H, m, J_1 8.0, J_2 6.5, CH₂), 2.56 (1 H, s, SH), 6.03 (1 H, t, J 6.5, vinylic H) and 7.40–7.70 (5 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ -2.55 (SiMe₂), 13.68 (CH₃), 24.53 (CH₂), 128.58, 130.10, 134.82 (ArCH), 137.50 (ArC) and 142.47 (vinylic CH); m/z (EI) 222 (M⁺), 207 (M⁺ – CH₃) and 135 (SiMe₂Ph).

Synthesis of (Z)- α -silyl vinyl sulfides **3**: general method

To a solution of (Z)- α -silyl enethiol **2** (2.5 mmol) in acetone (15 cm³), solid oven-dried K₂CO₃ (3.0 mmol) and the halide (2.5 mmol) were added. The mixture was stirred at room temperature until the starting enethiol had disappeared [TLC light petroleum–ethyl acetate (20:1) as eluent]. The mixture was then quenched with water and extracted with diethyl ether. The organic layer was dried and concentrated to give the title product. Only in a few cases was the product purified by preparative thick layer chromatography (light petroleum as eluent).

(Z)-1-Methylsulfanyl-1-trimethylsilyl-2-phenylethene 3a. Yield 98% as an oil (Found: M⁺, 222.0995. C₁₂H₁₈SSi requires M , 222.0898; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1240 and 860 (SiMe₃); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.35 (9 H, s, SiMe₃), 2.20 (3 H, s, SCH₃), 6.95 (1 H, s, vinylic H) and 7.20–7.70 (5 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ 0.07 (SiMe₃), 18.19 (SCH₃), 127.75, 128.52, 129.88 (ArCH), 137.99 (C), 139.33 (vinylic CH) and 140.18 (C); m/z (EI) 222 (M⁺), 207 (M⁺ – CH₃), 105 (SSiMe₃) and 73 (SiMe₃).

(Z)-1-[Dimethyl(phenyl)silyl]-1-methylsulfanylbut-1-ene 3b. Yield 95% as an oil (Found: M⁺, 236.1045. C₁₃H₂₀SSi requires M , 236.1055; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1430 (SiPh), 1240 (SiMe₂) and 1110 (SiPh); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.48 (6 H, s, SiMe₂), 1.13 (3 H, t, J 8.0, CH₃), 2.02 (3 H, s, SCH₃), 2.42 (2 H, m, CH₂), 6.23 (1 H, t,

J 6.7, vinylic H) and 7.30–7.70 (5 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ -1.38 (SiMe₂), 14.19, 18.69 (CH₃), 24.67 (CH₂), 128.49, 129.79, 134.69 (ArCH), 135.03, 138.99 (C) and 150.96 (vinylic CH); m/z (EI) 236 (M⁺), 221 (M⁺ – CH₃), 167 (SSiMe₂Ph) and 135 (SiMe₂Ph). Irradiation of the dimethylsilyl signal at 0.48 ppm produced a significant increase (8.7%) in the intensity of the signal for the vinylic proton at 6.23 ppm.

Ethyl [(Z)-(2-phenyl-1-trimethylsilylvinyl)sulfanyl]acetate 3c. Yield 100% as an oil (Found: M⁺, 294.1107. C₁₅H₂₂O₂SSi requires M , 294.11098; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1730 (CO₂Et), 1250 (SiMe₃) and 840 and 750 (SiMe₃); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.24 (9 H, s, SiMe₃), 1.15 (3 H, t, J 7.1, CH₃), 3.22 (2 H, s, SCH₂), 4.00 (2 H, q, J 7.1, OCH₂), 7.05 (1 H, s, vinylic H) and 7.20–7.70 (5 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ -0.62 (SiMe₃), 14.53 (CH₃), 36.50 (SCH₂), 61.69 (OCH₂), 128.27, 128.68, 129.79 (ArCH), 136.79 (C), 137.82 (C), 142.98 (vinylic CH) and 169.99 (CO); m/z (EI) 294 (M⁺), 279 (M⁺ – CH₃) and 73 (SiMe₃).

Ethyl [(Z)-[1-dimethyl(phenyl)silyl]but-1-enyl]sulfanyl]acetate 3d. Yield 80% as an oil (Found: M⁺, 308.1269. C₁₆H₂₄O₂SSi requires M , 308.1266; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1730 (CO₂Et), 1430 (SiPh), 1240 (SiMe₂), 1110 (SiPh) and 870 (SiMe₂); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.48 (6 H, s, SiMe₂), 1.05 (3 H, t, J 6.6, CH₃), 1.22 (3 H, t, J 7.4, CH₃), 2.48 (2 H, m, CH₂), 3.10 (2 H, s, SCH₂), 4.10 (2 H, q, J 7.4, OCH₂), 6.38 (1 H, t, J 6.7, vinylic H), 7.3–7.4 (3 H, m, ArH) and 7.55–7.62 (2 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ -1.93 (SiMe₂), 13.94, 14.63 (CH₃), 24.78, 37.01, 61.60 (CH₂), 128.33, 129.75, 134.56 (ArCH), 131.99, 138.09 (C), 155.70 (vinylic CH) and 170.33 (CO); m/z (EI) 308 (M⁺), 293 (M⁺ – CH₃), 263 (M⁺ – OEt), 222, 179, 135 (SiMe₂Ph) and 91 (C₇H₇).

Ethyl [(Z)-(2-phenyl-1-trimethylsilylvinyl)sulfanyl]propionate 3e. Yield 100% as an oil (Found: M⁺, 308.1269. C₁₆H₂₄O₂SSi requires M , 308.1266; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1740 (CO₂Et) 1490, 1440, 1370 and 1240, 830 and 750 (SiMe₃); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.25 (9 H, s, SiMe₃), 1.20 (3 H, t, J 7.1, CH₃), 2.40 (2 H, t, J 7.4, CH₂), 2.80 (2 H, t, J 7.4, SCH₂), 4.05 (2 H, q, J 7.1, OCH₂), 7.02 (1 H, s, vinylic H), 7.20–7.38 (m, 3 H, ArH) and 7.58–7.65 (m, 2 H, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ -0.42 (SiMe₃), 14.58 (CH₃), 29.05 (CH₂), 34.88 (SCH₂), 60.97 (OCH₂), 127.95, 128.53, 129.73 (ArCH), 137.45, 137.95 (C), 141.59 (vinylic CH) and 172.17 (CO); m/z (EI) 308 (M⁺), 293 (M⁺ – CH₃), 263 (M⁺ – OEt), 207 (M⁺ – CH₂CH₂CO₂Et) and 73 (SiMe₃).

Ethyl [(Z)-[1-dimethyl(phenyl)silyl]but-1-enyl]sulfanyl]propionate 3f. Yield 80% as a yellow oil (Found: M⁺, 332.1420. C₁₇H₂₆O₂SSi requires M , 332.1422; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1730 (CO₂Et), 1430 (SiPh), 1240 (SiMe₂), 1110 (SiPh) and 870 (SiMe₂); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.45 (6 H, s, SiMe₂), 1.05 (3 H, t, J 7.0, CH₃), 1.22 (3 H, t, J 7.4, CH₃), 2.20–2.45 (4 H, m, 2 CH₂), 2.65 (2 H, t, J 9.0, CH₂), 4.10 (2 H, q, J 7.4, OCH₂), 6.35 (1 H, t, J 6.3, vinylic H) and 7.30–7.60 (5 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ -1.93 (SiMe₂), 13.90, 14.97 (CH₃), 24.74, 29.62, 35.27, 60.94 (CH₂), 128.27, 129.69, 134.42 (ArCH), 132.80, 139.22 (C), 154.17 (vinylic CH) and 172.28 (CO); m/z (EI) 322 (M⁺), 307 (M⁺ – CH₃), 277 (M⁺ – OEt), 220 (M⁺ – CH₂CH₂CO₂Et), 135 (SiMe₂Ph), 101 (CH₂CH₂CO₂Et) and 87 (CH₂CO₂Et).

(Z)-1-Allylsulfanyl-1-trimethylsilyl-2-phenylethene 3g. Yield 100% as an oil (Found: M⁺, 248.1059. C₁₄H₂₀SSi requires M , 248.1055; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1240, 830 and 750 (SiMe₃); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.22 (9 H, s, SiMe₃), 3.14 (2 H, d, J 7.4, SCH₂), 4.82–4.98 (2 H, m, J_{cis} 9.9, J_{trans} 16.9, J_{gem} 2.18, vinylic CH₂), 5.58–5.76 (1 H, m, J_{cis} 9.9, J_{trans} 16.9, J 7.4 vinylic H), 7.00 (1 H, s, vinylic H), 7.18–7.35, (3 H, m, ArH) and 7.62–7.68 (2 H, m, ArH); $\delta_{\text{C}}(\text{CDCl}_3)$ -0.60 (SiMe₃), 37.43 (SCH₂), 117.55 (vinylic CH₂), 127.89, 128.54, 129.77 (ArCH), 135.00 (vinylic CH), 137.60, 138.17 (C) and 141.28 (vinylic CH); m/z (EI) 248 (M⁺), 207 (M⁺ – CH₂CH=CH₂), 175 (M⁺ – SCH₂CH=CH₂) and 73 (SiMe₃).

(Z)-1-Allylsulfanyl-1-[dimethyl(phenyl)silyl]but-1-ene 3h. Yield 95% as an oil (Found: M⁺, 262.1215. C₁₅H₂₂SSi requires M , 262.1211; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1430 (SiPh), 1240 (SiMe₂), 1110 (SiPh) and 870 (SiMe₂); $\delta_{\text{H}}(\text{CDCl}_3)$ 0.40 (6 H, s, SiMe₂), 0.98 (3

H, t, J 7.5, CH₃), 2.38 (2 H, m, J , 7.5, J_2 6.7 CH₂), 2.98 (2 H, d, J 7.2, allylic CH₂), 4.85 (1 H, dm, vinylic H), 4.90 (1 H, br d, vinylic H), 5.60 (1 H, m, vinylic H), 6.30 (1 H, t, J 6.3, vinylic H) and 7.30–7.60 (5 H, m, ArH); δ_c (CDCl₃) –1.99 (SiMe₂), 13.94 (CH₃), 24.75, 38.37 (CH₂), 117.02 (vinylic CH₂), 128.20, 129.57, 134.53, 134.93 (3 ArCH and 1 vinylic CH), 154.22 (vinylic CH) and 132.36 and 138.32 (C); m/z (EI) 262 (M⁺), 221 (M⁺ – C₃H₅), 179 (M⁺ – 83) and 135 (SiMe₂Ph).

(Z)-1-Benzylsulfanyl-1-trimethylsilyl-2-phenylethene 3i. Yield 100% as an oil (Found: M⁺, 298.1216. C₁₈H₂₂SSi requires M , 298.12115); ν_{\max} (CCl₄)/cm^{–1} 1490, 1450, 1440 and 1240, 840 and 750 (SiMe₃); δ_H (CDCl₃) 0.20 (9 H, s, SiMe₃), 3.72 (2 H, s, SCH₂), 7.04 (1 H, s, vinylic H) and 7.10–7.77 (m, 10 H, ArCH); δ_c (CDCl₃) –0.79 (SiMe₃), 38.81 (SCH₂), 127.37, 128.00, 128.66, 129.44, 129.77 (ArCH), 138.20, 138.43 (C) and 141.27 (vinylic CH); m/z (EI) 298 (M⁺), 206 (M⁺ – HCH₂Ph), 91 (C₇H₇) and 73 (SiMe₃).

(Z)-1-Benzylsulfanyl-1-[dimethyl(phenyl)silyl]but-1-ene 3l. Yield 90% as an oil (Found: M⁺, 312.1327. C₁₉H₂₄SSi requires M , 312.1368); ν_{\max} (CCl₄)/cm^{–1} 1430 (SiPh), 1240 (SiMe₂), 1110 (SiPh) and 860 (SiMe₂); δ_H (CDCl₃) 0.48 (6 H, s, SiMe₂), 0.95 (3 H, t, J 8.5, CH₃), 2.30 (2 H, m, CH₂), 3.52 (2 H, s, CH₂), 6.30 (1 H, t, J 6.3, vinylic H), 7.1–7.22 (5 H, m, ArH), 7.4 (3 H, m, ArH) and 7.6 (2 H, m, ArH); δ_c (CDCl₃) –1.87 (SiMe₂), 13.96 (CH₃), 24.79, 39.97 (CH₂), 127.44, 128.435, 128.89, 129.54, 129.79, 134.73 (ArCH), 133.125, 138.704, 139.062 (C) and 154.518 (vinylic CH); m/z (EI) 312 (M⁺), 221 (M⁺ – C₇H₇), 135 (SiMe₂Ph) and 91 (C₇H₇).

General procedure for the protidesilylation using CsF in DMSO

To a solution of (Z)- α -silyl vinyl sulfides **3** (1 mmol) in DMSO (6 cm³) solid CsF (1.1 mmol) and a drop of water were added. The mixture was stirred at 40 °C until the starting α -silyl vinyl sulfides had disappeared [TLC, light petroleum–ethyl acetate (10:1) as eluent]. The reaction mixture was quenched with water and extracted with diethyl ether. The organic layer was dried and concentrated to give the desilylated product **4**. Chromatography [light petroleum–ethyl acetate (30:1) as eluent] was necessary only when starting from α -silyl vinyl sulfides **3** containing the SiMe₂Ph group: the higher R_F fractions were by-products arising from the SiMe₂Ph moiety.

(Z)-1-Methylsulfonyl-2-phenylethene 4a.¹⁴ Yield 100% as an oil; ν_{\max} (CS₂)/cm^{–1} 1360, 1310, 770 and 680; m/z (EI) 150 (M⁺), 135 (M⁺ – CH₃) and 91 (C₇H₇).

Ethyl [(Z)-(2-phenylvinyl)sulfonyl]acetate 4c.¹⁶ Chromatography, on silica, of the crude gave as the second R_F fraction **4c**: yield 100% as an oil (Found: M⁺, 222.0716. C₁₂H₁₄O₂S requires M , 222.07145); δ_c (CDCl₃) 14.63 (CH₃), 37.09 (SCH₂), 62.20 (OCH₂), 125.53, 127.39, 127.50, 128.79, 129.21 (3 ArCH + 2 vinylic CH), 136.92 (ArC) and 169.92 (CO); m/z (EI) 222 (M⁺), 177 (M⁺ – OEt), 149 (M⁺ – CO₂Et), 134 (M⁺ – CH₃CO₂Et), 102 (134 – S), 91 (C₇H₇) and 77 (C₆H₅).

Ethyl [(Z)-but-1-enylsulfanyl]acetate 4d.¹⁷ Yield 78% as an oil (Found: M⁺, 174.0716. C₈H₁₄O₂S requires M , 174.07145); ν_{\max} (neat)/cm^{–1} 1745 (CO₂Et); δ_H (CDCl₃) 1.00 (3 H, t, J 7.5, CH₃), 1.40 (3 H, t, J 7.0, CH₃), 2.15 (2 H, m, CH₂), 3.38 (2 H, s, SCH₂), 4.20 (2 H, q, J 7.0, OCH₂), 5.65 (1 H, dt, J_1 9.4, J_2 7.2, vinylic H) and 6.00 (1 H, dt, J_1 9.4, J_2 1.3, vinylic H); δ_c (CDCl₃) 13.43, 14.145 (CH₃), 22.40, 35.31, 61.44 (CH₂), 122.26, 133.17 (vinylic CH) and 169.84 (CO); m/z (EI) 174 (M⁺) and 145 (M⁺ – C₂H₅).

Ethyl [(Z)-(2-phenylvinyl)sulfanyl]propionate 4e. Yield 100% as an oil (Found: M⁺, 236.0873. C₁₃H₁₆O₂S requires M , 236.0871); ν_{\max} (neat)/cm^{–1} 1745 (CO₂Et); δ_H (CDCl₃) 1.25 (3 H, t, J 7.2, CH₃), 2.70 (2 H, t, J 7.3, CH₂), 3.05 (2 H, t, J 7.3, CH₂), 4.18 (2 H, q, J 7.2, OCH₂), 6.23 (1 H, d, J 10.8, vinylic H), 6.48 (1 H, d, J 10.8, vinylic H) and 7.20–7.50 (5 H, m, ArH); δ_c (CDCl₃) 14.61 (CH₃), 28.38, 36.80, 63.40 (CH₂), 125.83,

127.40, 127.88, 129.12, 130.48 (3 ArCH + 2 vinylic CH), 137.08 (ArC) and 170.08 (CO); m/z (EI) 236 (M⁺), 191 (M⁺ – OEt), 149 (M⁺ – CH₂CO₂Et), 135 (149 – CH₂) and 91 (C₇H₇).

(Z)-1-Allylsulfanyl-2-phenylethene 4g.¹⁸ Yield 100% as an oil (Found: M⁺, 176.0664. C₁₁H₁₂S requires M , 176.0660); ν_{\max} (neat)/cm^{–1} 1490, 1440 and 770; δ_c (CDCl₃) 38.35 (SCH₂), 118.39 (vinylic CH₂), 126.15, 126.28, 127.12, 128.65, 129.01, 134.29 (3 ArCH + 2 vinylic CH) and 137.35 (C); m/z (EI) 176 (M⁺), 135 (M⁺ – CH₂CH=CH₂) and 91 (C₇H₇).

(Z)-1-Benzylsulfanyl-2-phenylethene 4i.¹⁸ Yield 100% as an oil (Found: M⁺, 226.0818. C₁₅H₁₄S requires M , 226.0816); ν_{\max} (neat)/cm^{–1} 1605, 1500, 1460, 780 and 700; δ_c (CDCl₃) 99.99 (SCH₂), 126.28, 126.46, 127.15, 127.84, 128.65, 129.11, 129.41 (ArCH + 2 vinylic CH) and 137.27 and 137.78 (ArC).

General procedure for the protidesilylation using TBAF in THF

A solution of tetrabutylammonium fluoride (TBAF) in THF (1.0 M; 1.1 mmol) was added to a solution of the (Z)- α -silyl vinyl sulfide **3** (1 mmol) in moist THF (6 cm³). The reaction mixture was stirred at reflux temperature for 24 h after which it was quenched with saturated aqueous ammonium chloride and extracted with diethyl ether. The extract was washed several times with water and then dried and concentrated under reduced pressure. The crude product was purified by preparative thick layer chromatography [light petroleum–ethyl acetate (30:1) as eluent] to give, as the higher R_F fractions, products arising from the SiMe₂Ph moiety and, as the lower R_F fractions, the desilylated product.

(Z)-1-Methylsulfanylbut-1-ene 4b.¹⁵ Yield 46% as an oil; m/z (EI) 102 (M⁺) 87 (M⁺ – CH₃) and 55 (M⁺ – SCH₃).

(Z)-1-Benzylsulfanylbut-1-ene 4l.¹⁹ Yield 85% as an oil; m/z (EI) 178 (M⁺) and 91 (C₇H₇).

(Z)-1-Allylsulfanylbut-1-ene 4h.¹⁹ Only decomposition products were detected when the reaction was performed at reflux temperature. In contrast, a reaction performed at 40 °C for 24 h gave product **4h** (85%) together with by-products arising from the SiMe₂Ph moiety, as detected by ¹H NMR analysis of the crude reaction mixture. **4h**: δ_H (CDCl₃) 1.05 (3 H, t, J 7.5, CH₃), 2.20 (2 H, m, CH₂), 3.32 (2 H, d, J 6.2, allylic CH₂), 5.15 (2 H, m, vinylic H), 6.63 (2 H, dt, J_{cis} 9.8, J 6.3, vinylic H) and 5.84 (2 H, m, vinylic H) (lit.,¹⁹ configuration of the double bond not assigned); m/z (EI) 128 (M⁺) and 87 (M⁺ – C₃H₅). Any attempt at purification by chromatography on silica gave only decomposition products.

Ethyl 3-(1'-phenylbutylsulfanyl)propionate 8. Chromatography on silica gel of the crude product, using light petroleum–ethyl acetate (10:1) as eluent, gave **8** as an oil (45%) (Found: M⁺, 266.1343. C₁₅H₂₂O₂S requires M , 266.13405); ν_{\max} (CCl₄)/cm^{–1} 1735 (CO₂Et); δ_H (CDCl₃) 0.85 (3 H, t, J 7.5, CH₃), 1.22 (3 H, t, J 6.8, CH₃), 1.30 (2 H, m, CH₂), 1.80 (2 H, m, CH₂), 2.48 (4 H, m, 2 CH₂), 3.80 (1 H, dd, J_1 , J_2 7.2, CH), 4.10 (2 H, q, J 6.8, OCH₂) and 7.20–7.35 (5 H, m, ArH); δ_c (CDCl₃) 13.72, 14.15 (CH₃), 20.78, 25.91, 34.57, 38.54 (CH₂), 49.57 (CH), 60.52 (CH₂), 127.05, 127.78, 128.44 (ArCH), 142.60 (ArC) and 171.93 (CO); m/z (EI) 266 (M⁺), 233 (M⁺ – OEt), 165 (M⁺ – C₂H₄OEt), 133 (M⁺ – SC₂H₄OEt) and 91 (C₇H₇). The same product **8** was also obtained (48%) when the protidesilylation was performed in boiling CH₃CN (6 cm³) with CsF (1.1 mmol).

Synthesis of (Z)- α -silyl vinyl sulfones **9**: general method

To a solution of the (Z)- α -silyl vinyl sulfide **3** (1.2 mmol) in methanol (10 cm³) cooled to 0 °C a solution of oxone (KHSO₅; 3.6 mmol) in water (8 cm³) was added. The mixture was allowed to warm to room temperature and after 4 h was diluted with water and extracted with chloroform. The organic layer was dried and concentrated under reduced pressure to give the vinyl sulfone.

(Z)-1-Methylsulfonyl-1-trimethylsilyl-2-phenylethene 9a. Yield 98% of a white crystalline product, mp 60–62 °C (from

diethyl ether) (Found: C, 11.25; H, 88.75. $C_{12}H_{18}O_2Si$ requires C, 11.18; H, 88.82); $\nu_{max}(CCl_4)/cm^{-1}$ 1300 (SO_2), 1250 ($SiMe_3$), 1120 (SO_2) and 860 ($SiMe_3$); $\delta_H(CDCl_3)$ 0.40 (9 H, s, $SiMe_3$), 2.60 (3 H, s, SO_2CH_3) and 7.35–7.65 (m, 6 H, ArH and vinylic H); $\delta_C(CDCl_3)$ 0.14 ($SiMe_3$) 49.72 (SO_2CH_3), 129.09, 129.89, 130.09 (ArCH), 135.38 (ArC) and 149.71 (vinylic CH); m/z (EI) 254 (M^+), 239 ($M^+ - CH_3$), 174 ($M^+ - HSO_2CH_3$), 159 ($174 - CH_3$), 137 ($M^+ - SO_2SiMe_3$) and 73 ($SiMe_3$).

(Z)-1-Dimethyl(phenyl)silyl-1-methylsulfonylbut-1-ene 9b. Yield 90% as an oil; $\nu_{max}(CCl_4)/cm^{-1}$ 1430 (SiPh), 1310, 1140 (SO_2), 1250 ($SiMe_2$) and 1110 (SiPh); $\delta_H(CDCl_3)$ 0.60 (6 H, s, $SiMe_2$), 1.05 (3 H, t, J 7.4, CH_3), 2.70 (3 H, s, SO_2CH_3), 2.65 (m, 2 H, CH_2), 6.50 (t, 1 H, J 7.6, vinylic H) and 7.30–7.62 (m, 5 H, ArH); $\delta_C(CDCl_3)$ –1.64 ($SiMe_2$), 13.75 (CH_3), 24.84 (CH_2), 45.17 (SO_2CH_3), 128.58, 130.27, 134.87 (ArCH), 136.30 (ArC), 144.70 (vinylic C) and 161.89 (vinylic CH); m/z (EI) 253 ($M^+ - CH_3$), 135 ($SiMe_2Ph$) and 105 (SiPh).

Protodesilylation of 9a and 9b

(Z)-1-Methylsulfonyl-2-phenylethene 10a.²⁷ Following the procedure described for 4a, 10a was obtained as an oil in 100% yield; a 15:1 *Z:E* ratio was determined by 1H NMR spectroscopy; $\nu_{max}(CCl_4)/cm^{-1}$ 1310 and 1160 (SO_2Me); $\delta_H(CDCl_3)$ 2.85 (3 H, s, SO_2CH_3), 6.43 (1 H, d, J 11.8, vinylic H), 7.10 (1 H, d, J 11.8, vinylic H) and 7.35–7.43 and 7.60–7.68 (5 H, m, ArH); $\delta_C(CDCl_3)$ 42.0 (SO_2Me), 128.40, 130.00 (br s), 130.20 (ArCH and vinylic CH) and 142.60 ($MeSO_2CH$); m/z (EI) 182 (M^+), 103 ($M^+ - SO_2CH_3$) and 77 (C_6H_5).

(Z)-1-Methylsulfonylbut-1-ene 10b. Following the procedure described for 4a, a mixture of two sulfones 10b and (*E*)-1-methylsulfonylbut-2-ene was obtained. Chromatography on preparative TLC [light petroleum–ethyl acetate (7:3) as eluent] gave as the higher R_F fraction a product arising from the $SiMe_2Ph$ moiety and as the second R_F fraction the title product 10b: yield 10% as an oil (Found: M^+ , 134.0403. $C_5H_{10}O_2S$ requires M , 134.04015); $\nu_{max}(CCl_4)/cm^{-1}$ 1321 and 1141 (SO_2); $\delta_H(300\text{ MHz}, CDCl_3)$ 1.11 (3 H, t, J 7.4, CH_3), 2.60–2.72 (m, J_1 7.5, J_2 1.5, J_3 1.2, CH_2), 2.97 (3 H, s, SO_2CH_3), 6.22–6.27 (1 H, dt, J_1 11.1, J_2 1.2, vinylic H) and 6.31–6.41 (1 H, dt, J_1 11.1, J_2 7.5, vinylic H); $\delta_C(CDCl_3)$ 13.72 (CH_3), 21.89 (CH_2), 44.33 (SO_2CH_3), 129.48 (vinylic CH) and 150.28 (vinylic CH); m/z (EI) 134 (M^+), 119 ($M^+ - CH_3$), 64 (SO_2) and 55 ($M^+ - SO_2CH_3$). The lower R_F fraction gave (*E*)-1-methylsulfonylbut-2-ene: 90% yield as an oil; $\delta_H(CDCl_3)$ 1.80 (3 H, d, J 7.5, CH_3), 2.85 (3 H, s, SO_2CH_3), 3.65 (2 H, d, J 7.5, CH_2), 5.60 (1 H, m, CH_2CH , J_{trans} 15.8) and 5.90 (1 H, m, CH_3CH , J_{trans} 15.8).

Product 10b left under the described conditions for 24 h, was isomerized to (*E*)-1-methylsulfonylbut-2-ene.

The protidesilylation was also performed in moist CH_3CN (6 cm^3) with solid CsF (1.1 mmol). The mixture was stirred at room temperature until the starting α -silyl vinyl sulfone had disappeared [TLC, light petroleum–ethyl acetate (7:3) as eluent] after which it was quenched with saturated aqueous ammonium chloride and extracted with diethyl ether; the organic layer was then dried and concentrated. Chromatography of the residue on silica [light petroleum–ethyl acetate (7:3) as eluent] gave, as the higher R_F fraction, products arising from the $SiMe_2Ph$ moiety and, as the second R_F fraction, the title product 10b in 100% yield.

General method for the synthesis of vinylsilanes 5 with $[NiCl_2(PPh_3)_2]$

A 3.0 M THF solution of the Grignard reagent ($RMgX$; 15 mmol) was slowly added, under argon, to a stirred suspension of $[NiCl_2(PPh_3)_2]$ (0.03 mmol) and the (*Z*)- α -silyl vinyl sulfide 3 (1 mmol) in THF (6 cm^3) at room temperature. The mixture was stirred at reflux temperature until the starting product had disappeared [TLC light petroleum–diethyl ether (20:1) as eluent] after which it was quenched with saturated aqueous ammonium

chloride and extracted with diethyl ether. The extract was dried, concentrated and purified by preparative thick layer chromatography (light petroleum as eluent).

(E)-1-Phenyl-2-trimethylsilylprop-1-ene 5a.²⁸ Yield 93% as an oil, *E:Z* = 98:2 (Found: M^+ , 190.1175. $C_{12}H_{18}Si$ requires M , 190.1178); $\nu_{max}(CS_2)/cm^{-1}$ 1240 and 830 ($SiMe_3$); m/z (EI) 190 (M^+), 175 ($M^+ - CH_3$) and 73 ($SiMe_3$). The same reaction was also performed using $[NiCl_2(dppe)]$ as a catalyst (0.03 mmol for 1 mmol of 3a) at room temperature for 5 days; yield 94% *E:Z* ratio > 98:2.

(E)-1-Phenyl-2-trimethylsilylbut-1-ene 5b.²⁹ Yield 60% as an oil, *E:Z* = 17:1, $\nu_{max}(CS_2)/cm^{-1}$ 1246 and 830 ($SiMe_3$); $\delta_C(CDCl_3)$ –0.50 ($SiMe_3$), 15.26 (CH_3), 23.92 (CH_2), 126.99, 128.61, 129.10 (ArCH), 138.95 (ArC) and 137.65 (vinylic CH); m/z (EI) 204 (M^+), 189 ($M^+ - CH_3$) and 73 ($SiMe_3$).

(E)-1-Phenyl-2-trimethylsilylhex-1-ene 5c. Chromatography of the crude product, using light petroleum as eluent gave, as the higher R_F fraction an inseparable mixture of 5c and 1-phenyl-2-trimethylsilylethene 11³¹ in 44 and 42% yield respectively: 5c: *E:Z* > 98:2 (Found: M^+ , 232.1645. $C_{15}H_{24}Si$ requires M , 232.1647); $\nu_{max}(CCl_4)/cm^{-1}$ 1240 and 850 ($SiMe_3$); $\delta_H(CDCl_3)$ 0.15 (9 H, s, $SiMe_3$), 0.85 (3 H, m, CH_3), 1.35 (4 H, m, CH_2), 2.32 (2 H, t, J 9.0, allylic CH_2), 6.72 (1 H, s, vinylic H) and 7.20–7.48 (5 H, m, ArH); m/z (EI) 232 (M^+), 217 ($M^+ - CH_3$), 158 ($M^+ - HSiMe_3$) and 73 ($SiMe_3$).

(E)-2-Dimethyl(phenyl)silylpent-2-ene 5d.³⁰ Chromatography of the crude product, using light petroleum as eluent, gave, as the higher R_F fraction products arising from the $SiMe_2Ph$ moiety and as the second R_F fraction 5d, yield 72% as an oil, *E:Z* > 98:2 (Found: M^+ , 204.1338. $C_{13}H_{20}Si$ requires M , 204.1334); $\nu_{max}(CCl_4)/cm^{-1}$ 1540, 1430 (SiPh), 1244 ($SiMe_2$), 1110 (SiPh) and 852 ($SiMe_2$); $\delta_C(CDCl_3)$ –2.73 ($SiMe_2$), 14.43, 15.27 (CH_3), 22.45 (CH_2), 128.33, 129.42, 134.66 (ArCH), 133.88, 139.54 (C) and 144.16 (vinylic CH); m/z (EI) 204 (M^+), 189 ($M^+ - CH_3$), 175 ($M^+ - C_2H_5$) and 135 ($SiMe_2Ph$). The same reaction performed using $[NiCl_2(dppe)]$ as a catalyst (0.03 mmol for 1 mmol of 3b) after 5 days of stirring at room temperature gave unchanged 3b.

(E)- and (Z)-3-Dimethyl(phenyl)silylhex-3-ene 5e.¹¹ Chromatography of the crude product, using light petroleum as eluent, gave as the higher R_F fraction products arising from the $SiMe_2Ph$ moiety and as the second R_F fraction 5e, yield 60%, as an oil, *E:Z* = 1:1.

(E)- and (Z)-4-Dimethyl(phenyl)silyloct-3-ene 5f. Chromatography of the crude product, using light petroleum as eluent, gave as the higher R_F fraction products arising from the $SiMe_2Ph$ moiety and as the second R_F fraction an inseparable mixture of the (*E*)- and (*Z*)-olefin 5f in a 4.5:1 ratio; yield 50% as an oil. All the spectra were performed on the mixture of the two isomers (Found: M^+ , 246.1802. $C_{16}H_{26}Si$ requires M , 246.1804); $\nu_{max}(CS_2)/cm^{-1}$ 1430 (SiPh), 1245 ($SiMe_2$), 1110 (SiPh) and 830 ($SiMe_2$); $\delta_H(300\text{ MHz}, CDCl_3)$ 0.37 (6 H, s, $SiMe_2$ isomer *Z*), 0.42 (6 H, s, $SiMe_2$ isomer *E*), 0.77–1.07 (6 H, m), 1.22–1.52 (4 H, m), 2.12 (4 H, m), 5.87 (1 H, q, J 9.4, vinylic H, isomer *E*), 6.12 (1 H, q, J 7.5, vinylic H, isomer *Z*) and 7.32–7.42 and 7.55–7.62 (5 H, m, ArH); $\delta_C(CDCl_3)$ –2.53, –2.10 ($SiMe_2$), 14.28, 14.43, 14.61, 14.95 (CH_3), 16.00, 22.00, 23.20, 23.50, 29.70, 30.70, 32.20, 32.50 (CH_2), 128.00, 128.50, 133.50, 134.00, 134.20 (ArCH), 139.06, 140.08, 140.45 (ArC) and 143.00 and 144.20 (vinylic CH); m/z (EI) 246 (M^+), 231 ($M^+ - CH_3$), 217 ($M^+ - C_2H_5$), 168 ($M^+ - C_6H_6$) and 135 ($SiMe_2Ph$).

General method for the synthesis of vinylsilanes 5 starting from α -silyl vinyl sulfones

A 3.0 M THF solution of the Grignard reagent (15 mmol) was slowly added, under argon, to a stirred suspension of $[NiCl_2(PPh_3)_2]$ (0.03 mmol) and α -silyl vinyl sulfone 9a (1 mmol) in THF (3 cm^3) at room temperature. The mixture was stirred at reflux temperature until the starting product had

disappeared [TLC light petroleum–diethyl ether (20:1) as eluent]. The mixture was then quenched with saturated aqueous ammonium chloride and extracted with diethyl ether. The organic layer was dried, concentrated and purified by preparative thick layer chromatography using light petroleum as eluent.

(E)-1-Phenyl-2-trimethylsilyl-prop-1-ene 5a²⁸ and 1-phenyl-2-trimethylsilylethene 11.³¹ After preparative thick layer chromatography an inseparable mixture of **5a** and **11** in 34 and 54% yield respectively (calculated by ¹H NMR) was obtained.

(E)-1-Phenyl-2-trimethylsilylhex-1-ene 5c and 1-phenyl-2-trimethylsilylethene 11.³¹ After preparative thick layer chromatography an inseparable mixture of **5c** and **11** in 24 and 75% yield respectively (calculated by ¹H NMR) was obtained.

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