Synthesis and reactivity of β-sulfonylvinylselenonium salts: a simple stereoselective synthesis of β-functionalized (*Z*)-vinyl sulfones

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The treatment of alkynylselenonium salt with benzenesulfinic acid in ^{i}PrOH gives (*Z*)-β-sulfonylvinylselenonium salts in good yields. The alkenylselenonium salts thus prepared react with nucleophiles such as alkoxides, halides, and acetylides to produce β-functionalized (*Z*)-vinyl sulfones in high yields. Furthermore, we succeeded in the simple stereoselective one-step synthesis of various chiral (*Z*)-β-alkoxyvinyl sulfones by the use of chiral alcohols.

Introduction

Vinyl sulfones are one of the most important synthons in organic synthesis because of their versatile utility,[1] and various synthetic methods towards vinyl sulfones have been developed.[1a–c,2] However, there have been few reports on the introduction of a substituent at the β-position by manipulation of a simple vinyl sulfone.[3] In particular, Back *et al.* demonstrated that the β-(phenylseleno)vinyl sulfones, prepared by addition of *Se*-phenyl toluene-*p*-selenosulfonate to alkynes, could be transformed into a variety of β-substituted vinyl sulfones.[4] Replacement of the SePh group was accomplished using selenocuprates RCu(SePh)Li or a combination of *m*-chloroperbenzoic acid and nucleophiles to afford β-functionalized vinyl sulfones with retention of configuration. However, these methods have significant drawbacks. In the former case, the selenocuprates have to be prepared by complicated procedures, and, in the latter case, the range of usable nucleophiles is limited. We attempted to prepare β-functionalized vinyl sulfones using β-sulfonylvinylselenonium salts because the selenonium group is an effective leaving group. Since the synthesis and reactivity of vinylselenonium salts have hardly been studied until now, we had great interest in them.[5] Ochiai's group had succeeded in the preparation of vinyl sulfones based on a similar concept, namely that iodonium group or the iodinane moieties are 'hyperleaving groups.'[6]

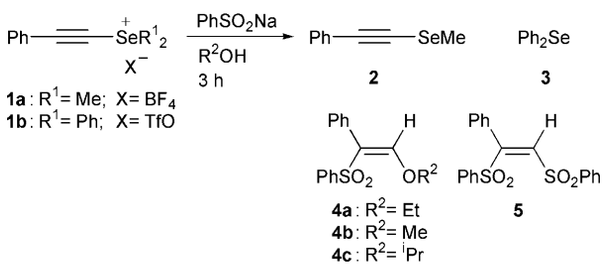
We previously reported the reactions of diphenyl(phenylethynyl)selenonium triflate with several nucleophiles such as carbanions,[7] halides,[8] and thiolate anions.[9] In each case, the selenonium moiety acted as a good leaving group and the corresponding selenide was released. In this paper, we describe the synthesis of β-sulfonylvinylselenonium salts and their utilization for the preparation of various β-functionalized vinyl sulfones.

Results and discussion

It is known that alkenylselenonium salts act as useful Michael acceptors toward nucleophiles.[5b] Alkynylselenonium salts are expected to function similarly. On the other hand, sulfinic acids and their sodium salts are good nucleophiles that easily undergo nucleophilic attack on activated double bonds as well as carbonyl compounds and alkyl halides.[10] Therefore, the reactions of dimethyl- and diphenyl-alkynylselenonium salts with sodium benzenesulfinate in various solvents were investigated with the aim of a one-pot preparation of β-alkoxyvinyl sulfones (Scheme 1). First, we conducted the reactions in alcohols as protic solvents. The results are shown in Table 1. The reactions of dimethylalkynylselenonium salt **1a**[5d] at room temperature afforded (*Z*)-ethoxyvinyl sulfone **4a** as the main product together with methyl phenylethynyl selenide **2** as a minor product produced by demethylation of **1a**. The demethylation product **2** was hardly obtained at all from the reaction at low temperature in entry 2, and the yield of the desired compound was very high, whereas the reaction at 60 °C gave **2** (33%), **4a** (25%), and **5** (20%). The reactions in other solvents at room temperature also afforded (*Z*)-alkoxyvinyl sulfones **4b** and **4c** in

Table 1 The reactions of alkynylselenonium salts **1** with sodium benzenesulfinate in protic solvents (see Scheme 1)

Entry	Selenonium salt	Solvent	Temp. (*T*/°C)	Products (% yield)
1	**1a**	EtOH	rt	**2** (21) **4a** (74)
2	**1a**	EtOH	−78	**2** (4) **4a** (92)
3	**1a**	EtOH	60	**2** (33) **4a** (25) **5** (20)
4	**1a**	MeOH	rt	**2** (25) **4b** (60)
5	**1a**	^{i}PrOH	rt	**2** (12) **4c** (68)
6	**1b**	EtOH	rt	**3** (73) **4a** (69) **5** (7)
7	**1b**	EtOH	−78	**3** (67) **4a** (64)
8	**1b**	EtOH	60	**3** (73) **4a** (64) **5** (5)
9	**1b**	MeOH	rt	**3** (80) **4b** (64) **5** (7)
10	**1b**	^{i}PrOH	rt	**3** (80) **4c** (71) **5** (12)



Scheme 1

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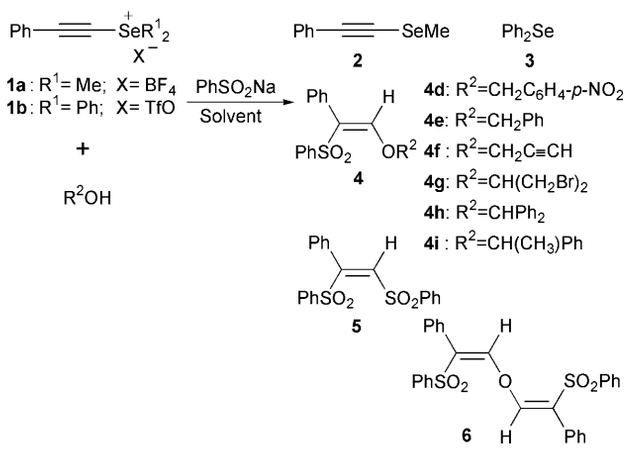
Table 2 The reactions of alkynylselenonium salts **1** and various alcohols with sodium benzenesulfinate in aprotic solvents (see Scheme 2)

Entry	1	R^2OH (equiv.)	Solvent	Temp. (*T*/°C)	Time (*t*/h)	Products (% yield)[a]
1	**1b**	*p*-$NO_2C_6H_4CH_2OH$ (1.5)	THF	rt	3.0	Complex mixture
2	**1b**	*p*-$NO_2C_6H_4CH_2OH$ (1.5)	DMSO	rt	3.0	Complex mixture
3	**1b**	*p*-$NO_2C_6H_4CH_2OH$ (1.0)	MeCN	rt	0.5	**4d** (91) **3** (93)
4	**1b**	$PhCH_2OH$ (1.5)	MeCN	rt	0.5	**4e** (90) **3** (95)
5	**1b**	$HC{\equiv}CCH_2OH$ (1.5)	MeCN	rt	0.33	**4f** (96) **3** (94)
6	**1b**	$(BrCH_2)_2CHOH$ (1.5)	MeCN	rt	0.5	**4g** (83) **3** (90)
7	**1b**	Ph_2CHOH (1.5)	MeCN	rt	0.33	**4h** (73) **3** (79)
8	**1b**	(±)-PhCH(Me)OH (1.5)	MeCN	rt	1.0	**4i** (51) **3** (88) **5** (21) **6** (5)
9	**1b**	(±)-PhCH(Me)OH (3.0)	MeCN	rt	2.0	**4i** (50) **3** (100) **5** (24) **6** (5)
10	**1b**	(±)-PhCH(Me)OH (5.0)	MeCN	rt	2.0	**4i** (48) **3** (96) **5** (23) **6** (3)
11	**1a**	(±)-PhCH(Me)OH (1.5)	MeCN	rt	0.5	**4i** (56) **2** (28) **5** (12) **6** (5)
12	**1a**	(±)-PhCH(Me)OH (1.5)	MeCN	−30	18	**4i** (63) **2** (20) **5** (6)
13	**1a**	(±)-PhCH(Me)OH (1.5)	THF	rt	0.5	**4i** (30) **2** (41) **5** (24) **6** (4)
14	**1a**	(±)-PhCH(Me)OH (1.5)	DMF	rt	0.5	**4i** (41) **2** (26) **5** (14) **6** (3)
15	**1b**	(−)-Menthol (1.0)	MeCN	rt	1.0	**3** (62) **5** (27) **6** (17)

[a] Isolated yield based on selenonium salt **1**.

good yields together with demethylation product **2**. Next, we conducted the reaction of diphenylalkynylselenonium salt **1b**[7a] with sodium benzenesulfinate under the same conditions as mentioned above because selenonium salt **1a** suffered some demethylation. As we had expected, the dephenylation of **1b** did not occur, and the desired alkoxyvinyl sulfones were obtained in good yields (entries 6–10). In some cases, a small amount of (*Z*)-bis(phenylsulfonyl)styrene **5** was obtained as a by-product. The geometrical structure of **4a** was determined by a nuclear Overhauser effect (NOE) experiment, which showed enhancement of the *ortho*-protons of the *Z*-phenyl group (11.4%) and of the methylene protons of the geminal ethoxy group (7.5%) on irradiation of the vinyl proton.

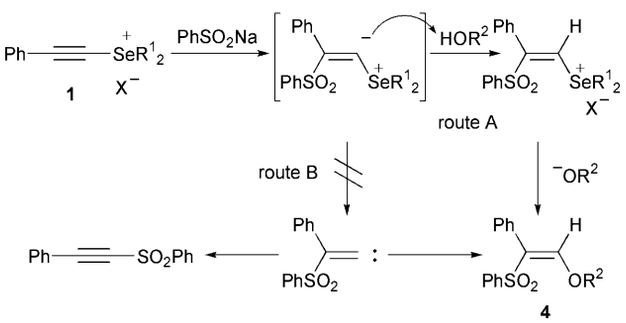
When an alcohol was used as solvent, the β-alkoxy group of the product was derived from the solvent. In order to prepare a variety of β-alkoxyvinyl sulfones, we examined the reactions of alkynylselenonium salts **1** with various alcohols and sodium benzenesulfinate in aprotic solvents (Scheme 2). The results are



Scheme 2

summarized in Table 2. The reaction of **1b** with *p*-nitrobenzyl alcohol in MeCN at room temperature only for 30 minutes produced the desired (*Z*)-β-alkoxyvinyl sulfone **4d** in a high yield (entry 3), while a complex mixture was obtained when THF or DMSO was used as solvent (entries 1 and 2). The reactions with other primary alcohols also proceeded smoothly in a short reaction time, and corresponding β-alkoxyvinyl sulfones **4e** and **4f** were given efficiently (entries 4 and 5). However, the employment of bulkier secondary alcohols brought about a decreasing yield of β-alkoxyvinyl sulfones **4g**–**i** (entries 6–8), and, in particular, no desired product was obtained when (−)-menthol, a cyclic secondary alcohol, was used (entry 15). Although increasing the amount of an alcohol could not improve the yield of compound **4i** (entries 9 and 10), the utilization of dimethylalkynylselenonium salt **1a**, which was less bulky than **1b**, gave a somewhat better yield; MeCN was the best solvent (entries 11–14). When the yield of β-alkoxyvinyl sulfone was low, 1,2-bis(phenylsulfonyl)styrene **5** and divinyl ether derivative **6** were produced as by-products. The separation of the desired compound and the by-products by TLC on silica gel was very difficult. The β-alkoxyvinyl sulfones **4** shown in Scheme 2 were only single geometrical isomers. The stereochemistry of compound **4g** was determined to be (*Z*) by the NOE enhancement between the vinyl proton and the *ortho*-protons of the *Z*-phenyl group (7.3%) or of the methyne proton of the geminal 2-bromo-1-(bromomethyl)ethoxy group (18.6%).

Two kinds of reaction pathways for the formation of β-alkoxyvinyl sulfones can be considered (Scheme 3). First,



Scheme 3

the Michael-type anti-addition of a sulfinate ion to alkynylselenonium salts would form a (*Z*)-vinylselenonium ylide intermediate. Route A contains the processes whereby protonation of the ylide with an alcohol produces a (*Z*)-vinylselenonium salt and its successive reaction with the resulting alkoxide gives product **4**. The latter process leading to (*Z*)-β-alkoxyvinyl sulfones will be discussed in detail in Scheme 8. If the reactions proceed through an alkylidene carbene intermediate in route B, phenyl phenylethynyl sulfone as a 1,2-rearrangement product[2d,11] and a mixture of (*E*)- and (*Z*)-β-alkoxyvinyl sulfones as RO-H insertion products would be formed.[12] However, alkynyl sulfone derivative and (*E*)-β-alkoxyvinyl sulfones were not obtained from the reactions mentioned above, and route B was thus excluded.

Next, in order to elucidate the reaction mechanism *via* a vinylselenonium salt intermediate, we tried to prepare vinylselenonium salts and examine their reactivity. The reactions of alkynylselenonium salts **1** with benzenesulfinic acid in propan-2-ol gave (*Z*)-β-sulfonylalkenylselenonium salts **7** in good yields

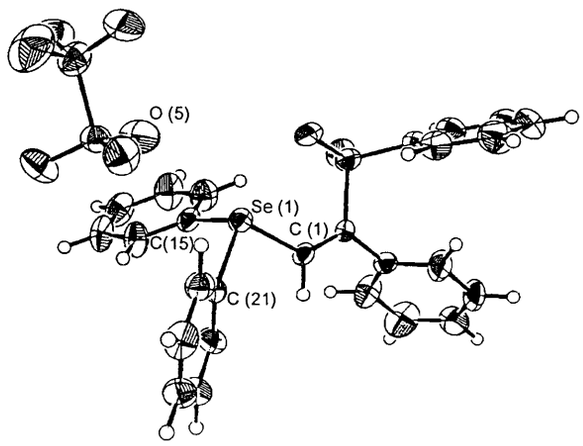
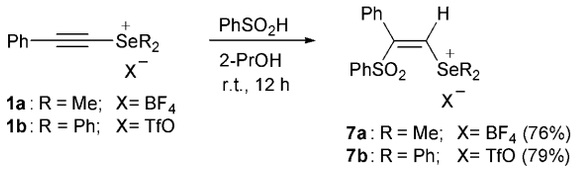


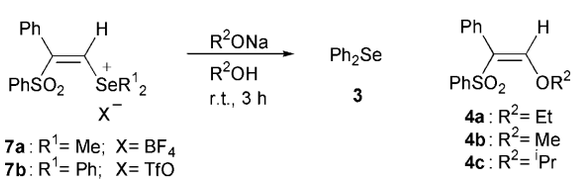
Fig. 1 ORTEP drawing of **7b**.



Scheme 4

(Scheme 4). The stereochemistry of **7** was determined as (*Z*) by NOE measurement of **7b** (8.0%) between the vinylic proton and *ortho*-protons of the *Z*-phenyl group. These results indicated that the alkynylselenonium salts underwent the anti-Michael-type addition of benzenesulfinic acid in a similar way to the general nucleophilic addition to alkynes.[2d,13] The ^{77}Se NMR spectrum showed a signal at δ 502.8 in $CDCl_3$ due to the selenonio group, which was shifted to lower field than that of the alkynylselenonium salt **1b** at δ 469.6 because of the more electron-deficient double bond bearing a sulfonyl group. Furthermore, the structure of salts **7** was established more clearly by X-ray analysis of compound **7b** (Fig. 1). The Se(1)···O (1) distance 3.074 Å is significantly shorter than the sum of the van der Waals radii (3.40 Å) of selenium and oxygen atoms. The O(5)···Se(1)–C(1) angle of 163.9° is approximately collinear, and the C(15)–Se(1)–C (21) bond angle is 99.7°. These data suggested that a weak bonding interaction, such as hypervalent bonding, existed between the oxygen atom of the triflate moiety and the selenium atom.[5c,7a,14] Thus, the configuration of the selenium atom was a slightly distorted trigonal bipyramid in which the two phenyl groups and a lone pair occupied equatorial positions and the structure was similar to a selenurane rather than to a selenonium salt.

We examined the reactions of the (*Z*)-β-sulfonylalkenylselenonium salts **7** thus prepared with alkoxides in alcohols as a protic solvent (Scheme 5). Either dimethyl- or diphenyl-



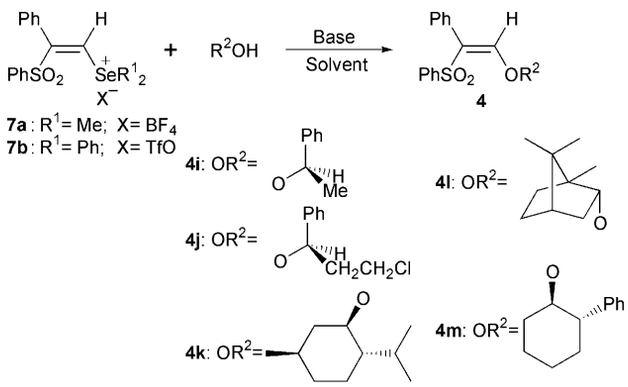
Scheme 5

selenonium salt **7a**, **7b** reacted smoothly with alkoxides prepared from NaH and the corresponding alcohols to produce (*Z*)-β-alkoxyvinyl sulfones **4** in high yields with retention of configuration. Demethylation of dimethylalkenylselenonium salt **7a** was not observed in the reactions (Table 3). Next, we planned to apply this synthetic method to prepare chiral (*Z*)-*O*-alkyl enol ethers bearing the phenylsulfonyl group at the β-position by using chiral alcohols. Chiral *O*-alkyl enol ethers

Table 3 The reactions of alkenylselenonium salts **7** with alkoxides in protic solvents (see Scheme 5)

Entry	Selenonium salt	Alkoxide (equiv.)	Solvent	Products (% yield)
1	**7a**	MeONa (1.0)	MeOH	**4b** (82)
2	**7a**	EtONa (1.0)	EtOH	**4a** (80)
3	**7a**	^{i}PrONa (1.0)	^{i}PrOH	**4c** (70)
4	**7b**	MeONa (1.0)	MeOH	**3** (75) **4b** (71)
5	**7b**	EtONa (1.0)	EtOH	**3** (79) **4a** (75)
6	**7b**	^{i}PrONa (1.0)	^{i}PrOH	**3** (92) **4c** (89)

are valuable reagents in various asymmetric reactions[15] and syntheses.[16] However, because chiral alcohols are expensive, reactions with chiral alkoxides in aprotic solvents were carried out (Scheme 6). These results are summarized in Table



Scheme 6

4. The reaction of diphenylalkenylselenonium salt **7b** with (+)-1-phenylethanol as an acyclic secondary alcohol in the presence of NaH at −30 °C for 30 minutes afforded (*Z*)-β-alkoxyvinyl sulfone **4i** in 91% yield (entry 1). The reaction with (+)-3-chloro-1-phenylpropan-1-ol produced the desired compound **4j** in a very high yield (entry 4). The reactions of alkenylselenonium salt **7b** with achiral secondary alcohols gave better results than those of alkynyl congener **1b** (compare entries 5 and 6 in Table 4 with entries 6 and 7 in Table 2). Although dimethylalkenylselenonium salt **7a** reacted with (+)-1-phenylethanol to afford **4i** in a good yield, the results were not satisfactory. These results showed that the use of alkenylselenonium salts, compared with alkynylselenonium salts, improved the yields of (*Z*)-β-alkoxyvinyl sulfones in the reactions with bulky secondary alcohols. According to this procedure, we prepared chiral (*Z*)-β-cycloalkoxyvinyl sulfones, which had not been obtained from the reactions of alkynylselenonium salt **1b**. The results are summarized in Table 5. The reactions of diphenylvinylselenonium salt **7b** with menthol and NaH in MeCN did not give good results, and the yield of the desired product **4k** was up to 47% by use of 2 mole equivalents of menthol (entries 1 and 2). On the other hand, dimethylvinylselenonium salt **7a** reacted with 1.2 mole equivalents of menthol in the presence of NaH to produce **4k** in only a 29% yield because the remaining NaH, which did not completely react with menthol, would decompose **7a** (entry 3). Therefore, the employment of excess of selenonium salt **7a** improved the yield of **4k**, up to 67% (entries 4 and 5). Phenyllithium was used as a base, and lithium menthoxide was effectively prepared. The best result was obtained from the reaction of 1.5 mole equivalents of **7a** and menthol with phenyllithium in THF at −78 °C (entry 7). Similarly, the reactions with bulky secondary cyclic alcohols, (−)-borneol and (−)-*trans* 2-phenylcyclohexanol, gave chiral (*Z*)-β-cycloalkoxyvinylsulfones **4l** and **4m** in excellent yields (entries 8 and 9).

Next, we investigated the reactions of vinylselenonium salts with other nucleophiles (Scheme 7). First, reactions with

Table 4 The reactions of alkenylselenonium salts **7** with alkoxides in MeCN[a] (see Scheme 6)

Entry	Selenonium salt	R^2OH	Temp (T/°C)	Time (t/h)	Product (% yield)[b]	Optical rotation
1	**7b**	(+)-PhCH(Me)OH	−30	0.5	**4i** (91)	$[\alpha]_D^{26}$ −94.9 (*c* 1.19 in $CHCl_3$)
2	**7a**	(+)-PhCH(Me)OH	0	0.5	**4i** (62)	
3	**7a**	(+)-PhCH(Me)OH	−30	0.5	**4i** (65)	
4	**7b**	(+)-$ClCH_2CH_2CHPhOH$	−30	2	**4j** (88)	$[\alpha]_D^{28}$ −40.8 (*c* 2.18 in $CHCl_3$)
5	**7b**	$(BrCH_2)_2CHOH$	−30	0.5	**4g** (91)	—
6	**7b**	Ph_2CHOH	−30	0.5	**4h** (90)	—

[a] Conditions: 1 equiv. of selenonium salt **7**, 1.1 equiv. of an alcohol and NaH in MeCN. [b] Isolated yield based on selenonium salt **7**.

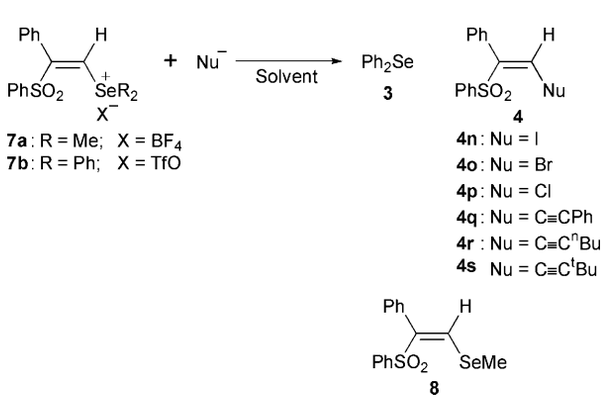
Table 5 The reactions of alkenylselenonium salts **7** with cyclic secondary alcohols[a] (see Scheme 6)

Entry	Selenonium salt (equiv.)	ROH (equiv.)	Base	Solvent	Temp. (T/°C)	Product (% yield)	Optical rotation
1	**7b** (1)	(−)-Menthol (1.5)	NaH	MeCN	−30	**4k** (39)[b]	$[\alpha]_D^{26}$ −28.6 (*c* 1.44 in $CHCl_3$)
2	**7b** (1)	(−)-Menthol (2.0)	NaH	MeCN	−30	**4k** (47)[b]	
3	**7a** (1)	(−)-Menthol (1.2)	NaH	MeCN	−30	**4k** (29)[b]	
4	**7a** (1.5)	(−)-Menthol (1)	NaH	MeCN	−30	**4k** (58)[c]	
5	**7a** (3.0)	(−)-Menthol (1)	NaH	MeCN	−30	**4k** (67)[c]	
6	**7a** (1.0)	(−)-Menthol (1)	PhLi	THF	−78	**4k** (64)[c]	
7	**7a** (1.5)	(−)-Menthol (1)	PhLi	THF	−78	**4k** (80)[c]	
8	**7a** (1.5)	(−)-Borneol (1)	PhLi	THF	−78	**4l** (96)[c]	$[\alpha]_D^{29}$ −37.6 (*c* 1.61 in $CHCl_3$)
9	**7a** (1.5)	(−)-*trans*-2-Phenylcyclohexanol	PhLi	THF	−78	**4m** (90)[c]	$[\alpha]_D^{30}$ −179.7 (*c* 0.55 in $CHCl_3$)

[a] These reactions were carried out for 12 h. [b] Isolated yield based on selenonium salt **7**. [c] Isolated yield based on alcohols.

Table 6 The reactions of alkenylselenonium salts **7** with halides (see Scheme 7)

Entry	Selenonium salt	Nucleophile (equiv.)	Solvent	Products (% yield)	
1	**7a**	$^nBu_4NBr$ (1)	$CHCl_3$		**8** (90)
2	**7a**	LiBr (1)	MeCN		**8** (88)
3	**7b**	$^nBu_4NI$ (1)	$CHCl_3$	**3** (94)	**4n** (91)
4	**7b**	$^nBu_4NBr$ (1)	$CHCl_3$	**3** (90)	**4o** (92)
5	**7b**	$^nBu_4NCl$ (1)	$CHCl_3$	**3** (85)	**4p** (88)
6	**7b**	NaI (2)	MeCN	**3** (75)	**4n** (76)
7	**7b**	LiBr (1)	MeCN	**3** (86)	**4o** (85)
8	**7b**	NaBr (2)	MeCN–MeOH	**3** (71)	**4o** (62)
9	**7b**	KBr (2)	MeCN–MeOH	**3** (43)	**4o** (39)
10	**7b**	NaCl (2)	MeCN–MeOH	**3** (53)	**4p** (45)



Scheme 7

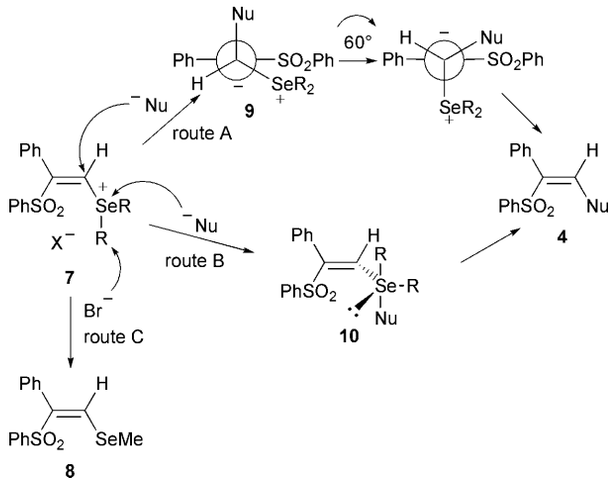
various halides were conducted (Table 6). The reaction of dimethylvinylselenonium salt **7a** with tetrabutylammonium bromide as a phase-transfer catalyst or lithium bromide as an inorganic salt gave the demethylation product **8** in high yields, while the β-halogenovinyl sulfone was not obtained at all (entries 1 and 2). In contrast, the reactions of diphenylvinylselenonium salt **7b** proceeded easily to produce corresponding (*Z*)-β-halogenovinyl sulfones **4n**–**p** in high yields except with sodium chloride or potassium bromide because of their insolubility in organic solvents (entries 3–10). The stereochemistry of the β-halogenovinyl sulfones was determined as being *Z* by

Table 7 The reactions of diphenylalkenylselenonium salt **7b** with acetylides (see Scheme 7)

Entry	Nucleophile (equiv.)	Solvent	Temp. (T/°C)	Products (% yield)	
1	PhC≡CLi (1.2)	THF	−78	**3** (73)	**4p** (52)
2	^nBuC≡CLi (1.2)	THF	−78	**3** (86)	**4r** (49)
3	^tBuC≡CLi (1.2)	THF	−78	**3** (82)	**4s** (53)

NOE measurement of **4n**, which showed enhancement (5.3%) between the vinylic proton and *ortho*-protons of the *Z*-phenyl group. The reactivity of acetylides as carbanions with the vinylselenonium salts was also examined (Table 7). The reaction of diphenylvinylselenonium salt **7b** with 1.2 mole equivalents of lithium phenylacetylide, prepared from the reaction of phenylacetylene and *n*-butyllithium in THF at −78 °C, afforded (*Z*)-β-alkynylvinyl sulfone **4q** in 52% yield (entry 1). The reactions with other acetylides similarly gave corresponding (*Z*)-enyne sulfone derivatives in good yields (entries 2 and 3). The *Z* configuration was determined by NOE experiment on **4s**, showing the enhancement of the *ortho*-protons of the *Z*-phenyl group (6.1%) upon irradiation of the vinyl proton.

A plausible mechanism for the formation of the β-substituted (*Z*)-vinyl sulfones **4** from the reactions of vinylselenonium salts **7** with nucleophiles is shown in Scheme 8. Route A proceeds *via* the pathway whereby the Michael-type addition of



Scheme 8

a nucleophile to the β-carbon in the vinyl sulfonyl moiety forms betaine **9** and the subsequent elimination of a selenide leads to the (*Z*)-vinyl sulfones with retention of configuration.[6b,17] Another pathway, route B, involves the formation of the selenurane intermediate **10**, *via* direct attack of the nucleophile to the selenium atom in the vinylselenonium salt, followed by ligand coupling between the Nu and the vinyl group of **10**.[18] Both pathways provide feasible explanations of the stereochemical outcome observed in these reactions. On the other hand, demethylation product **8** was formed by the S_N2 reaction shown because the selenonio group was a good leaving group.

Conclusions

We showed that (*Z*)-β-sulfonylvinylselenonium salts, which were prepared easily from the reaction of alkynylselenonium salts with benzenesulfinic acid in ^{i}PrOH, acted as useful intermediates in the synthesis of β-functionalized (*Z*)-vinyl sulfones. By means of this method, we developed a simple, efficient, and stereoselective one-step synthesis of various (*Z*)-β-substituted vinyl sulfones in good yields. In particular, it is very valuable that the *Z* configuration products, which are thermodynamically unstable, are accessible, and that diphenyl selenide, which was recovered in a high yield, was reused as one of the starting materials for the preparation of alkynylselenonium salt **1b**.

Experimental

General

Mps were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (NaCl) were recorded on a JASCO IRA-100 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL GX-270 (270 MHz) or a JEOL EX-400 (400 MHz) spectrometer with tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded on the JEOL GX-270 (68 MHz) or the JEOL EX-400 (100 MHz) spectrometer with chloroform as internal standard. The ^{77}Se NMR spectrum of salt **7b** was recorded on the JEOL EX-400 (76 MHz) spectrometer with dimethyl selenide as external standard. The *J*-values are given in Hz. Mass spectra (MS and HRMS) were obtained with electron impact (EI, 70 eV) or fast-atom bombardment (FAB, glycerol or 3-nitrobenzyl alcohol as matrix) techniques. Elemental analyses of new compounds were performed by a Yanaco CHN Corder MT-5. Optical rotations were measured on a JASCO DIP-360 digital polarimeter for $CHCl_3$ solution. All chromatographic isolations were accomplished with either Kieselgel 60 (Merck) or BW-127ZH (Fuji Silysia) for column chromatography or Kieselgel 60 PF_{254} containing gypsum (Merck) for preparative TLC (PLC).

Dimethyl(phenylethynyl)selenonium tetrafluoroborate 1a

Trimethyloxonium tetrafluoroborate (2.04 g, 13.8 mmol) was added to a stirred solution of methyl phenylethynyl selenide[19] (2.54 g, 13.8 mmol) in dichloromethane (10 cm^3) at room temperature. The mixture was stirred in an atmosphere of nitrogen overnight. After the solvent had been evaporated under reduced pressure, the residue was washed with diethyl ether several times and purified by recrystallization from dichloromethane–diethyl ether to give the selenonium salt **1a** (2.54 g, 62%) as colourless prisms, mp 132–135 °C (Found: C, 40.4; H, 3.7. $C_{10}H_{11}BF_4Se$ requires C, 40.5; H, 3.7%); ν_{max} (KBr)/cm^{-1} 2180 and 1140–1040; δ_H (400 MHz; $CDCl_3$) 3.33 (6 H, s, $SeCH_3$), 7.41 (2 H, t, *J* 7.3, ArH), 7.51 (1 H, t, *J* 7.3, ArH) and 7.59 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; CD_3CN) 29.0 (q), 65.3 (s), 104.8 (s), 119.6 (s), 129.9 (d), 132.8 (d) and 133.5 (d); *m*/*z* (FAB) 221 ([M − BF_4]$^+$, 100%) and 136 (53).

General procedure for the reactions of alkynylselenonium salts with sodium benzenesulfinate in alcohols. A typical example (Table 1, entry 1): (*Z*)-β-ethoxy-α-(phenylsulfonyl)styrene 4a

Sodium benzenesulfinate (82 mg, 0.5 mmol) was added to a stirred solution of the dimethyl(phenylethynyl)selenonium tetrafluoroborate **1a** (148 mg, 0.5 mmol) in ethanol (5 cm^3) at room temperature. The resulting mixture was stirred at the same temperature for 3 h, poured into water and extracted with ethyl acetate. The extracts were washed with brine and dried over $MgSO_4$. After the solvent had been evaporated under reduced pressure, the residue was separated by PLC (5:1 hexane–ethyl acetate) to give **2** (20 mg, 21%) and the vinyl sulfone **4a** (107 mg, 74%). Compound **4a**: colourless oil [HRMS Calc. for $C_{16}H_{16}O_3S$: *M*, 288.0820. Found: M$^+$, 288.0809]; ν_{max} (NaCl)/cm^{-1} 1631, 1302, 1227, 1150 and 1084; δ_H (400 MHz; $CDCl_3$) 1.23 (3 H, t, *J* 6.8, CH_2CH_3), 3.99 (2 H, q, *J* 6.8, CH_2CH_3), 6.57 (1 H, s, C=CH), 7.30–7.40 (5 H, m, ArH), 7.46 (2 H, t, *J* 7.3, ArH), 7.56 (1 H, t, *J* 7.3, ArH) and 7.90 (2 H, d, *J* 7.3, ArH); δ_C (68 MHz; $CDCl_3$) 14.8 (q), 71.3 (t), 121.2 (s), 127.4 (d), 127.9 (d), 128.0 (d), 128.2 (d), 130.6 (d), 131.5 (s), 132.5 (d), 142.2 (s) and 154.7 (d); *m*/*z* (EI) 288 (M$^+$, 100%), 260 (40), 119 (65) and 91 (83).

(*Z*)-β-Methoxy-α-(phenylsulfonyl)styrene 4b. White powder, mp 89–90 °C (Found: C, 65.6; H, 5.3. $C_{15}H_{14}O_3S$ requires C, 65.7; H, 5.1%); ν_{max} (NaCl)/cm^{-1} 1625, 1305, 1250, 1132 and 1081; δ_H (400 MHz; $CDCl_3$) 3.82 (3 H, s, CH_3), 6.51 (1 H, s, C=CH), 7.27–7.35 (5 H, m, ArH), 7.47 (2 H, t, *J* 7.3, ArH), 7.56 (1 H, t, *J* 7.3, ArH) and 7.87 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 62.5 (q), 121.8 (s), 127.6 (d), 128.2 (d), 128.4 (d), 128.5 (d), 131.0 (d), 131.7 (s), 132.7 (d), 142.5 (s) and 155.9 (d); *m*/*z* (EI) 274 (M$^+$, 75%) and 118 (100).

(*Z*)-β-Isopropoxy-α-(phenylsulfonyl)styrene 4c. *White powder*, mp 91–94 °C (Found: C, 67.4; H, 6.0. $C_{17}H_{18}O_3S$ requires C, 67.5; H, 6.0%); ν_{max} (NaCl)/cm^{-1} 1623, 1305, 1227, 1145 and 1082; δ_H (400 MHz; $CDCl_3$) 1.19 (6 H, d, *J* 6.4, CH_3CHCH_3), 4.09 (1 H, m, *J* 6.4, CH_3CHCH_3), 6.60 (1 H, s, C=CH), 7.32–7.40 (5 H, m, ArH), 7.47 (2 H, t, *J* 7.3, ArH), 7.56 (1 H, t, *J* 7.3, ArH) and 7.93 (2 H, d, *J* 7.3, ArH); δ_C (68 MHz; $CDCl_3$) 22.0 (q), 78.6 (t), 121.5 (s), 127.7 (d), 128.01 (d), 128.04 (d), 128.1 (d) 130.6 (d), 131.7 (s), 132.5 (d), 142.7 (s) and 153.4 (d); *m*/*z* (EI) 302 (M$^+$, 20%), 260 (100) and 119 (47).

(*Z*)-α,β-Bis(phenylsulfonyl)styrene 5. Colourless needles, mp 83–85 °C {HRMS Calc. for $C_{20}H_{17}O_4S_2$: ([M + H]$^+$), 385.0568. Found: *m*/*z*, 385.0564}; ν_{max} (NaCl)/cm^{-1} 1583, 1331 and 1159; δ_H (400 MHz; $CDCl_3$) 6.88 (1 H, s, C=CH), 7.20 (2 H, d, *J* 7.3, ArH), 7.26 (2 H, t, *J* 7.8, ArH), 7.35–7.48 (3 H, m, ArH), 7.55–7.61 (3 H, m, ArH), 7.67–7.73 (3 H, m, ArH) and 8.10 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 128.2 (q), 128.3 (d), 128.9 (d), 129.1 (d), 129.2 (d), 129.5 (d), 130.3 (d),

132.4 (s), 133.9 (d), 134.3 (d), 138.1 (s), 140.8 (d), 141.4 (s) and 152.2 (s); *m/z* (FAB) 385 ([M + H]$^+$, 55%), 289 (19) and 136 (60).

General procedure for the reactions of alkynylselenonium salts and various alcohols with sodium benzenesulfinate in aprotic solvents. A typical example (Table 2, entry 3): (*Z*)-β-(*p*-nitrobenzyloxy)-α-(phenylsulfonyl)styrene 4d

Sodium benzenesulfinate (36 mg, 0.22 mmol) was added to a stirred solution of diphenyl(phenylethynyl)selenonium trifluoromethanesulfonate **1b** (97 mg, 0.2 mmol) and *p*-nitrobenzyl alcohol (31 mg, 0.2 mmol) in acetonitrile (3 cm^3) at room temperature. The resulting mixture was stirred at the same temperature for 0.5 h, poured into water and extracted with ethyl acetate. The extracts were washed with brine and dried over $MgSO_4$. After the solvent had been evaporated under reduced pressure, the residue was separated by PLC (chloroform) to give **3** (43 mg, 93%) and the vinyl sulfone **4d** (72 mg, 91%). **4d**: *colourless prisms*, mp 113–114 °C (Found: C, 63.7; H, 4.5; N, 3.5. $C_{21}H_{17}NO_5S$ requires C, 63.8; H, 4.3; N, 3.5%); ν_{max} (NaCl)/cm^{-1} 1620, 1520, 1350, 1280 and 1139; δ_H (400 MHz; $CDCl_3$) 5.12 (2 H, s, OCH_2), 6.63 (1 H, s, C=CH), 7.27–7.39 (7 H, m, ArH), 7.43 (2 H, t, *J* 7.8, ArH), 7.57 (1 H, t, *J* 7.3, ArH), 7.84 (2 H, d, *J* 7.3, ArH) and 8.16 (2 H, d, *J* 8.8, ArH); δ_C (100 MHz; $CDCl_3$) 75.1 (t), 123.4 (s), 123.8 (d), 127.5 (d), 127.6 (d), 128.2 (d), 128.6 (d), 128.7 (d), 130.8 (d), 131.1 (s), 132.9 (d), 142.1 (s), 142.5 (s), 147.7 (s) and 153.5 (d); *m/z* (EI) 395 (M$^+$, 17%), 254 (54), 125 (78) and 77 (100).

(*Z*)-β-Benzyloxy-α-(phenylsulfonyl)styrene 4e. *White powder*, mp 107–108 °C (Found: C, 71.8; H, 5.2. $C_{21}H_{18}O_3S$ requires C, 72.0; H, 5.2%); ν_{max} (NaCl)/cm^{-1} 1635, 1301 and 1143; δ_H(400 MHz; $CDCl_3$) 4.99 (2 H, s, OCH_2), 6.63 (1 H, s, C=CH), 7.13–7.15 (2 H, m, ArH), 7.26–7.35 (8 H, m, ArH), 7.39 (2 H, t, *J* 7.3, ArH), 7.53 (1 H, t, *J* 7.3, ArH) and 7.84 (2 H, d, *J* 7.3, ArH); δ_C 100 MHz; $CDCl_3$) 76.7 (t), 122.5 (s), 127.4 (d), 127.7 (d), 128.2 (d), 128.4 (d), 128.5 (d), 128.6 (d), 128.7 (d), 130.8 (s), 131.6 (s), 132.7 (d), 135.2 (s), 142.5 (s) and 154.1 (d); *m/z* (FAB) 351 ([M + H]$^+$, 14%), 289 (20) and 136 (55).

(*Z*)-α-Phenylsulfonyl-β-(prop-2-ynyloxy)styrene 4f. *Pale yellow oil* (Found: C, 68.3; H, 4.7. $C_{17}H_{14}O_3S$ requires C, 68.4; H, 4.7%); ν_{max} (NaCl)/cm^{-1} 2125, 1628, 1306 and 1142; δ_H (400 MHz; $CDCl_3$) 2.55 (1 H, t, *J* 2.4, C≡CH), 4.58 (2 H, d, *J* 2.4, OCH_2), 6.72 (1 H, s, C=CH), 7.27–7.38 (5 H, m, ArH), 7.46 (2 H, t, *J* 7.3, ArH), 7.56 (1 H, t, *J* 7.3, ArH) and 7.87 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 61.3 (t), 76.5 (d), 77.6 (s), 123.9 (s), 127.7 (d), 128.3 (d), 128.5 (d), 128.6 (d), 130.9 (d), 131.5 (s), 132.9 (d), 142.2 (s) and 152.3 (d); *m/z* (FAB) 299 ([M + H]$^+$, 20%) and 136 (62).

(*Z*)-β-[2-Bromo-1-(bromomethyl)ethoxy]-α-(phenylsulfonyl)-styrene 4g. *Colourless plates*, mp 103–105 °C (Found: C, 44.2; H, 3.5. $C_{17}H_{16}Br_2O_3S$ requires C, 44.4; H, 3.5%); ν_{max} (KBr)/cm^{-1} 1634, 1287 and 1142; δ_H (400 MHz; $CDCl_3$) 3.44 (2 H, dd, *J* 6.4 and 11.2, CH_2Br), 3.55 (2 H, dd, *J* 5.4 and 11.2, CH_2Br), 4.15–4.21 (1 H, m, OCH), 6.63 (1 H, s, C=CH), 7.30–7.40 (5 H, m, ArH), 7.48 (2 H, t, *J* 7.3, ArH), 7.59 (1 H, t, *J* 7.3, ArH) and 7.93 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 31.2 (t), 84.2 (d), 123.5 (s), 128.0 (d), 128.4 (d), 128.6 (d), 128.7 (d), 130.8 (d), 131.2 (s), 133.0 (d), 142.3 (s) and 152.3 (d); *m/z* (FAB) 461 ([M + 2 + H]$^+$, 33%), 261 (40) and 136 (62).

(*Z*)-β-Diphenylmethoxy-α-(phenylsulfonyl)styrene 4h. *Colourless prisms*, mp 146–148 °C (Found: C, 76.0; H, 5.3. $C_{27}H_{22}O_3S$ requires C, 76.0; H, 5.2%); ν_{max} (NaCl)/cm^{-1} 1625, 1306 and 1143; δ_H (400 MHz; $CDCl_3$) 5.89 (1 H, s, OCH), 6.69 (1 H, s, C=CH), 7.24–7.36 (17 H, m, ArH), 7.51 (1 H, t, *J* 7.3, ArH) and 7.85 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 88.5 (d), 122.9 (s), 127.0 (d), 127.9 (d), 128.2 (d), 128.4 (d), 128.5 (d), 128.7 (s), 130.9 (d), 131.7 (s), 132.6 (d), 139.4 (s), 142.6 (s) and 153.1 (d); *m/z* (FAB) 427 ([M + H]$^+$, 3%), 167 (100) and 136 (35).

{(*Z*)-β-(1-Phenylethoxy)-α-(phenylsulfonyl)styrene 4i. *White powder*, mp 92–93 °C (Found: C, 72.3; H, 5.6. $C_{22}H_{20}O_3S$ requires C, 72.5; H, 5.5%); ν_{max} (NaCl)/cm^{-1} 1632, 1304 and 1145; δ_H (400 MHz; $CDCl_3$) 1.59 (3 H, d, *J* 6.8, CH_3), 4.95 (1 H, q, *J* 6.8, OCH), 6.53 (1 H, s, C=CH), 7.05–7.07 (2 H, m, ArH), 7.25–7.30 (8 H, m, ArH), 7.49 (2 H, t, *J* 7.3, ArH), 7.60 (1 H, t, *J* 7.3, ArH) and 7.96 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 23.3 (q), 83.6 (d), 122.4 (s), 125.8 (d), 128.1 (d), 128.2 (d), 128.3 (d), 128.4 (d), 128.5 (d), 128.7 (d), 130.8 (d), 131.8 (s), 132.7 (d), 140.9 (s), 142.8 (s) and 153.2 (d); *m/z* (FAB) 365 ([M + H]$^+$, 12%), 261 (25) and 136 (62).

Bis[(*Z*)-2-phenyl-2-(phenylsulfonyl)vinyl ether 6. *White powder*, mp 152–155 °C (Found: C, 67.0; H, 4.5. $C_{28}H_{22}O_5S_2$ requires C, 66.9; H, 4.4%); ν_{max} (NaCl)/cm^{-1} 1607, 1318 and 1170; δ_H (400 MHz; $CDCl_3$) 6.66 (2 H, s, C=CH), 7.24 (4 H, d, *J* 7.3, ArH), 7.32 (4 H, t, *J* 7.3, ArH), 7.38 (2 H, d, *J* 7.3, ArH), 7.55 (4 H, t, *J* 7.3, ArH), 7.63 (2 H, t, *J* 7.3, ArH) and 8.17 (4 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 127.1 (s), 128.3 (d), 128.4 (d), 129.1 (d), 129.3 (d), 130.6 (s), 131.0 (d), 133.5 (d), 140.9 (s) and 149.4 (d); *m/z* (FAB) 503 ([M + H]$^+$, 40%), 289 (15) and 136 (65).

General procedure for the synthesis of alkenylselenonium salts. A typical example: (*Z*)-diphenyl[(*Z*)-2-phenyl-2-(phenylsulfonyl)-vinyl]selenonium trifluoromethanesulfonate 7b

Benzenesulfinic acid (1.05 g, 7.2 mmol) was added to a stirred solution of diphenyl(phenylethynyl)selenonium trifluoromethanesulfonate **1b** (2.90 g, 6.0 mmol) in propan-2-ol (70 cm^3) at room temperature. The mixture was stirred in an atmosphere of argon for 12 h. After the solvent had been evaporated under reduced pressure, the residue was washed with diethyl ether several times and purified by recrystallization from dichloromethane–diethyl ether to give the *selenonium salt* **7b** (2.99 g, 79%) as colourless prisms, mp 167 °C (Found: C, 51.8; H, 3.6. $C_{27}H_{21}F_3O_5S_2Se$ requires C, 51.8; H, 3.4%); ν_{max} (KBr)/cm^{-1} 1340–1220 and 1150; δ_H (400 MHz; $CDCl_3$) 7.22 (1 H, s, C=CH), 7.28 (2 H, t, *J* 7.3, ArH), 7.36 (1 H, t, *J* 7.3, ArH), 7.42 (2 H, t, *J* 7.3, ArH), 7.52–7.57 (3 H, m, ArH), 7.60–7.68 (6 H, m, ArH), 7.76 (2 H, d, *J* 7.3, ArH) and 7.85 (4 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 120.7 (q), 127.2 (d), 129.0 (d), 129.4 (d), 129.5 (d), 129.6 (d), 129.9 (s), 130.5 (d), 131.2 (d), 131.5 (d), 131.6 (s), 133.2 (d), 134.9 (s), 135.2 (d) and 155.0 (s); δ_{Se} (76 MHz; $CDCl_3$) 502.8; *m/z* (FAB) 477 ([M − TfO]$^+$, 75%) and 136 (63).

Dimethyl[(*Z*)-2-phenyl-2-(phenylsulfonyl)vinyl]selenonium tetrafluoroborate 7a. *Colourless needles* (from acetone–diethyl ether), mp 174–176 °C (Found: C, 43.7; H, 3.9. $C_{16}H_{17}BF_4O_2SSe$ requires C, 43.8; H, 3.9%); ν_{max} (KBr)/cm^{-1} 1350, 1150 and 1100–1050; δ_H (400 MHz; $CDCl_3$) 3.19 (6 H, s, $SeCH_3$), 7.08 (1 H, s, C=CH), 7.28 (2 H, t, *J* 7.3, ArH), 7.37 (1 H, t, *J* 7.3, ArH), 7.42–7.47 (4 H, m, ArH), 7.57 (1 H, t, *J* 7.3, ArH) and 7.73 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; CD_3OD) 26.5 (q), 129.7 (d), 129.9 (d), 130.5 (d), 130.6 (d), 131.8 (d), 132.0 (s), 136.3 (d), 137.4 (s) and 154.1 (s); *m/z* (FAB) 353 ([M − BF_4]$^+$, 100%) and 136 (73).

General procedure for the reactions of alkenylselenonium salts with alkoxides in protic solvents. A typical example (Table 3, entry 1): (*Z*)-β-methoxy-α-(phenylsulfonyl)styrene 4b

After 60% sodium hydride (8 mg, 0.2 mmol) had been added to methanol (3 cm^3) and the solution was strirred at room temperature for 0.5 h, dimethyl(phenylethynyl)selenonium

tetrafluoroborate **7a** (88 mg, 0.2 mmol) was added under argon. The resulting mixture was stirred at the same temperature for 3 h, poured into water and extracted with ethyl acetate. The extracts were washed with brine and dried over $MgSO_4$. After the solvent had been evaporated under reduced pressure, the residue was separated by PLC (hexane–ethyl acetate 3:1) to give the vinyl sulfone **4b** (45 mg, 82%).

General procedure for the reactions of alkenylselenonium salts with alkoxides in aprotic solvents. A typical example (Table 4, entry 4): (*Z*)-β-[(1*R*)-3-chloro-1-phenylpropoxy]-α-(phenylsulfonyl)styrene 4j

After 60% sodium hydride (5 mg, 0.11 mmol) had been added to a stirred solution of (+)-3-chloro-1-phenylpropan-1-ol (19 mg, 0.11 mmol) in acetonitrile (3 cm^3) and the solution stirred at room temperature for 1 h, diphenyl(phenylethynyl)-selenonium trifluoromethanesulfonate **7b** (63 mg, 0.1 mmol) was added under argon. The resulting mixture was stirred at the same temperature for 2 h, poured into water and extracted with ethyl acetate. The extracts were washed with brine and dried over $MgSO_4$. After the solvent had been evaporated under reduced pressure, the residue was separated by PLC (chloroform) to give the vinyl sulfone **4j** (37 mg, 88%) as a pale yellow oil {HRMS Calc. for $C_{23}H_{22}ClO_3S$: $[M + H^+]$ 413.0978. Found: *m/z* 413.0973}; ν_{max} (NaCl)/cm^{-1} 1626, 1305 and 1143; δ_H (400 MHz; $CDCl_3$) 2.05–2.14 (1 H, m, C*H*$_2$CH$_2$Cl), 2.29–2.38 (1 H, m, C*H*$_2$CH$_2$Cl), 3.42–3.49 (1 H, m, CH$_2$C*H*$_2$Cl), 3.55–3.62 (1 H, m, CH$_2$C*H*$_2$Cl), 5.06 (1 H, dd, *J* 4.4 and 12.8, OC*H*Ph), 6.55 (1 H, s, C=CH), 7.07–7.11 (2 H, m, ArH), 7.22–7.33 (8 H, m, ArH), 7.50 (2 H, t, *J* 7.3, ArH), 7.60 (1 H, t, *J* 7.3, ArH) and 7.93 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 40.1 (t), 40.6 (t), 84.1 (d), 122.6 (s), 126.0 (d), 127.7 (d), 128.2 (d), 128.4 (d) 128.6 (d), 128.7 (d), 128.9 (d), 130.8 (d), 131.4 (s), 132.8 (d), 138.7 (s), 142.8 (s) and 153.2 (d); *m/z* (FAB) 413 ($[M + H]^+$, 25%), 261 (55) and 136 (67).

General procedure for the reactions of alkenylselenonium salt 7a with cyclic secondary alkoxides. A typical example (Table 5, entry 9): (*Z*)-β-[(1*R*,2*S*)-2-phenylcyclohexyloxy]-α-(phenylsulfonyl)styrene 4m

After phenyllithium in cyclohexane–diethyl ether solution (0.85 mol dm^{-3}) (0.47 cm^3, 0.40 mmol) had been added to a stirred solution of (−)-*trans*-2-phenylcyclohexanol (71 mg, 0.40 mmol) in THF (1 cm^3) and the solution stirrred at −78 °C for 1 h, the solution was added to a stirred solution of dimethyl(phenylethynyl)selenonium tetrafluoroborate **7a** (179 mg, 0.6 mmol) with a cannula at −78 °C under argon. The resulting mixture was stirred at the same temperature for 12 h, poured into water and extracted with ethyl acetate. The extracts were washed with brine and dried over $MgSO_4$. After the solvent had been evaporated under reduced pressure, the residue was separated by PLC (chloroform) to give the *vinyl sulfone* **4m** (151 mg, 90%) as colourless prisms, mp 117–120 °C (Found: C, 74.6; H, 6.4. $C_{26}H_{26}O_3S$ requires C, 74.6; H, 6.3%); ν_{max} (NaCl)/cm^{-1} 1619, 1305 and 1145; δ_H (400 MHz; $CDCl_3$) 1.26–1.43 (2 H, m, CH), 1.47–1.70 (2 H, m, CH), 1.74–1.94 (3 H, m, CH), 2.17 (1 H, br d, *J* 13.2, CH), 2.48 (1 H, ddd, *J* 3.9, 9.2 and 13.4, CH), 3.78 (1 H, dt, *J* 4.4 and 10.7, OCH), 6.00 (1 H, s, C=CH), 6.79 (2 H, d, *J* 7.3, ArH), 6.85 (2 H, d, *J* 7.3, ArH), 7.15–7.25 (6 H, m, ArH), 7.47 (2 H, t, *J* 7.3, ArH), 7.59 (1 H, t, *J* 7.3, ArH) and 7.79 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 24.7 (t), 25.3 (t), 32.6 (t), 32.8 (t), 50.9 (d), 90.1 (d), 118.7 (s), 126.8 (d), 127.79 (d), 127.82 (d), 128.0 (d), 128.1 (d), 128.2 (d), 128.6 (d), 130.7 (d), 131.8 (s), 132.4 (d), 141.8 (s), 142.8 (s) and 154.9 (d); *m/z* (FAB) 419 ($[M + H]^+$, 15%), 261 (40) and 136 (67).

(*Z*)-β-[(1*R*,2*S*,5*R*)-Menthan-3-yloxy]-α-(phenylsulfonyl)-styrene 4k. *Colourless needles*, mp 82–84 °C (Found: C, 72.3; H, 7.6. $C_{24}H_{30}O_3S$ requires C, 72.3; H, 7.6%); ν_{max} (KBr)/cm^{-1} 1622, 1318, 1250 and 1141; δ_H (400 MHz; $CDCl_3$) 0.67 (3 H, d, *J* 6.8, CH_3), 0.84 (3 H, d, *J* 6.8, CH_3), 0.88 (3 H, d, *J* 6.8, CH_3), 0.80–1.00 (2 H, m, CH), 1.23–1.39 (3 H, m, CH), 1.64 (2 H, br d, *J* 12.2, CH), 1.70–1.78 (1 H, m, CH), 1.85 (1 H, br d, *J* 12.2, CH), 3.60 (1 H, dt, *J* 4.4 and 10.7, OCH), 6.64 (1 H, s, C=CH), 7.34–7.39 (5 H, m, ArH), 7.47 (2 H, t, *J* 7.3, ArH), 7.56 (1 H, t, *J* 7.3, ArH) and 7.91 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 15.8 (q), 20.8 (q), 21.8 (q), 22.9 (t), 25.2 (d), 31.5 (d), 33.8 (d), 41.5 (t), 47.4 (d), 86.8 (d), 121.3 (s), 127.8 (d), 128.2 (d), 128.3 (d), 130.8 (d), 131.2 (s), 132.5 (d), 143.1 (s) and 154.1 (d); *m/z* (FAB) 399 ($[M + H]^+$, 10%), 261 (40) and 136 (58).

(*Z*)-β-[(1*S*,2*R*,4*S*)-Bornan-2-yloxy]-α-(phenylsulfonyl)styrene 4l. Colourless oil {HRMS Calc. for $C_{24}H_{29}O_3S$ ($[M + H]^+$), 397.1837. Found: *m/z* 397.1833}; ν_{max} (NaCl)/cm^{-1} 1624, 1306 and 1143; δ_H (400 MHz; $CDCl_3$) 0.80 (3 H, s, CH_3), 0.83 (3 H, s, CH_3), 0.86 (3 H, s, CH_3), 1.07 (1 H, dd, *J* 2.9 and 13.4, CH), 1.24–1.32 (2 H, m, CH), 1.67 (1 H, t, *J* 4.4, CH), 1.70–1.80 (1 H, m, CH), 1.93–2.22 (1 H, m, CH), 2.14–2.23 (1 H, m, CH), 4.10 (1 H, br d, *J* 4.4, OCH), 6.62 (1 H, s, C=CH), 7.32–7.38 (5 H, m, ArH), 7.47 (2 H, t, *J* 7.3, ArH), 7.55 (1 H, t, *J* 7.3, ArH) and 7.91 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 13.1 (q), 18.5 (q), 19.4 (q), 26.4 (t), 27.7 (t), 35.7 (t), 44.4 (d), 47.9 (s), 49.6 (s), 92.8 (d), 120.1 (s), 127.2 (d), 127.9 (d), 128.3 (d), 130.6 (d), 131.9 (s), 132.4 (d), 142.9 (s) and 155.3 (d); *m/z* (FAB) 397 ($[M + H]^+$, 8%), 289 (23) and 137 (65).

General procedure for the reactions of alkenylselenonium salt 7a with halides. A typical example (Table 6, entry 2): (*Z*)-β-methylseleno-α-(phenylsulfonyl)styrene 8

Lithium bromide (17 mg, 0.20 mmol) was added to a stirred solution of dimethyl[2-phenyl-2-(phenylsulfonyl)vinyl]-selenonium tetrafluoroborate **7a** (88 mg, 0.20 mmol) in acetonitrile (3 cm^3) at room temperature. The resulting mixture was stirred at the same temperature for 5 h, poured into water and extracted with ethyl acetate. The extracts were washed with brine and dried over $MgSO_4$. After the solvent had been evaporated under reduced pressure, the residue was separated by PLC (5:1 hexane–ethyl acetate) to give the *vinyl sulfone* **8** (59 mg, 88%) as yellow powder, mp 110–112 °C (Found: C, 53.2; H, 4.2. $C_{15}H_{14}O_2SSe$ requires C, 53.4; H, 4.2%); ν_{max} (NaCl)/cm^{-1} 1554, 1299 and 1143; δ_H (400 MHz; $CDCl_3$) 2.22 (3 H, s, $SeCH_3$), 7.17–7.31 (5 H, m, ArH), 7.37 (2 H, t, *J* 7.3, ArH), 7.42 (1 H, s, C=CH), 7.53 (1 H, t, *J* 7.3, ArH) and 7.71 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 10.1 (q), 127.4 (d), 128.1 (d), 128.5 (d), 128.7 (d), 129.4 (d), 133.3 (d), 135.0 (d), 138.0 (s), 140.0 (s) and 143.7 (s); *m/z* (EI) 338 (M^+, 98%), 197 (96) and 102 (100).

General procedure for the reactions of alkenylselenonium salt 7b with halides. A typical example (Table 6, entry 4): (*Z*)-β-bromo-α-(phenylsulfonyl)styrene 4o

Tetrabutylammonium bromide (48 mg, 0.15 mmol) was added to a stirred solution of diphenyl-[2-phenyl-2-(phenylsulfonyl)-vinyl]selenonium trifluoromethanesulfonate **7b** (94 mg, 0.15 mmol) in chloroform (3 cm^3) at room temperature. The resulting mixture was stirred at the same temperature for 3 h, poured into water and extracted with ethyl acetate. The extracts were dried over $MgSO_4$. After the solvent had been evaporated under reduced pressure, the residue was separated by PLC (10:1 hexane–ethyl acetate) to give **3** (32 mg, 90%), and the *vinyl sulfone* **4o** (45 mg, 92%) as a colourless oil (Found: C, 52.1; H, 3.5. $C_{14}H_{11}BrO_2S$ requires C, 52.0; H, 3.4%); ν_{max} (NaCl)/cm^{-1} 1581, 1445, 1325 and 1151; δ_H (270 MHz; $CDCl_3$) 7.02 (1 H, s, C=CH), 7.20–7.40 (5 H, m, ArH), 7.47 (2 H, t, *J* 7.3, ArH), 7.61 (1 H, t, *J* 7.3, ArH) and 7.82 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 117.2 (d), 128.3 (d), 128.8 (d), 129.5 (d), 129.9 (d), 133.7 (d), 134.0 (s), 139.7 (s) and 147.6 (s); *m/z* (EI) 324 ($M^+ + 2$, 16%), 322 (M^+, 17%), 181 (55), and 102 (100).

(*Z*)-β-Iodo-α-(phenylsulfonyl)styrene 4n. *Colourless oil* (HRMS Calc. for $C_{14}H_{11}IO_2S$: M, 369.9524. Found: M^+, 369.9517); ν_{max} (NaCl)/cm^{-1} 1560, 1444, 1321, 1149 and 1084; δ_H (400 MHz; $CDCl_3$) 7.18 (2 H, d, *J* 7.3, ArH), 7.27 (2 H, t, *J* 7.3, ArH), 7.35 (1 H, t, *J* 7.3, ArH), 7.44 (2 H, t, *J* 7.3, ArH), 7.49 (1 H, s, C=CH), 7.59 (1 H, t, *J* 7.3, ArH) and 7.77 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 88.5 (d), 128.2 (d), 128.4 (d), 128.8 (d), 129.4 (d), 129.6 (d), 133.7 (d), 135.4 (s), 139.1 (s) and 151.7 (s); *m*/*z* (EI) 370 (M^+, 18%), 229 (77) and 102 (100).

(*Z*)-β-Chloro-α-(phenylsulfonyl)styrene 4p. *Colourless oil* (HRMS Calc. for $C_{14}H_{11}ClO_2S$: *M*, 278.0168. Found: M^+, 278.0162); ν_{max} (NaCl)/cm^{-1} 1580, 1420, 1321, 1149 and 1081; δ_H (400 MHz; $CDCl_3$) 6.73 (1 H, s, C=CH), 7.25 (2 H, d, *J* 7.3, ArH), 7.34 (2 H, t, *J* 7.3, ArH), 7.40 (1 H, t, *J* 7.3, ArH), 7.48 (2 H, t, *J* 7.3, ArH), 7.61 (1 H, t, *J* 7.3, ArH) and 7.83 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 128.2 (d), 128.3 (d), 128.9 (d), 129.0 (d), 129.6 (d), 130.1 (d), 132.8 (s), 133.8 (d), 140.1 (s) and 145.1 (s); *m*/*z* (EI) 278 (M^+, 35%), 137 (100) and 102 (83).

General procedure for the reactions of alkenylselenonium salt 7b with acetylides. A typical example (Table 7, entry 1): (*Z*)-1,4-diphenyl-1-(phenylsulfonyl)but-1-en-3-yne 4q

n-Butyllithium in hexane solution (1.66 mol dm^{-3}) (0.22 cm^3, 0.36 mmol) was added to a stirred solution of phenylacetylene (37 mg, 0.36 mmol) in THF (3 cm^3) and the solution was strirred at 0 °C for 0.5 h. To the acetylenide solution thus prepared was added a solution of diphenyl(phenylethynyl)-selenonium trifluoromethanesulfonate **7b** (188 mg, 0.3 mmol) *via* cannula at −78 °C under argon. The resulting mixture was stirred at the same temperature for 3 h, poured into water and extracted with ethyl acetate. The extracts were washed with brine and dried over $MgSO_4$. After the solvent had been evaporated under reduced pressure, the residue was separated by PLC (10 : 1 hexane–ethyl acetate) to give the *vinyl sulfone* **4q** (54 mg, 52%) as a colourless oil (HRMS Calc. for $C_{22}H_{16}O_2S$: *M*, 344.0871. Found: M^+, 344.0880); ν_{max} (NaCl)/cm^{-1} 2200, 1600, 1420, 1320 and 1150; δ_H (400 MHz; $CDCl_3$) 6.44 (1 H, s, C=CH), 7.30–7.43 (10 H, m, ArH), 7.53 (1 H, t, *J* 7.3, ArH), 7.59 (2 H, d, *J* 7.3, ArH) and 7.85 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 84.8 (s), 104.2 (s), 120.5 (d), 122.3 (s), 128.0 (d), 128.2 (d), 128.5 (d), 128.8 (d), 129.3 (d), 129.6 (d), 132.1 (d), 133.4 (d), 134.1 (s), 140.5 (s) and 150.3 (s); *m*/*z* (EI) 344 (M^+, 40%), 202 (100) and 178 (33).

(*Z*)-1-Phenyl-1-(phenylsulfonyl)oct-1-en-3-yne 4r. *Colourless oil* (HRMS Calc. for $C_{20}H_{20}O_2S$: *M*, 324.1184. Found: M^+, 324.1181); ν_{max} (NaCl)/cm^{-1} 2210, 1590, 1450, 1320 and 1150; δ_H (400 MHz; $CDCl_3$) 0.95 (3 H, t, *J* 7.0, CH_3), 1.43–1.63 (4 H, m, CH_2), 2.47 (2 H, dt, *J* 2.4 and 7.0, C≡CCH_2), 6.23 (1 H, t, *J* 2.4, C=CH), 7.29–7.37 (5 H, m, ArH), 7.44 (2 H, t, *J* 7.3, ArH), 7.56 (1 H, t, *J* 7.3, ArH) and 7.83 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 13.6 (q), 20.0 (t), 22.0 (t), 30.2 (t), 76.1 (s), 107.7 (s), 121.7 (d), 128.0 (d), 128.2 (d), 128.7 (d), 129.2 (d), 129.6 (d), 133.3 (d), 134.3 (s), 140.8 (s) and 149.6 (s); *m*/*z* (EI) 324 (M^+, 2%), 141 (67) and 97 (100).

(*Z*)-5,5-Dimethyl-1-phenyl-1-(phenylsulfonyl)hex-1-en-3-yne 4s. *Colourless oil* (HRMS Calc. for $C_{20}H_{20}O_2S$: *M*, 324.1184. Found: M^+, 324.1190); ν_{max} (NaCl)/cm^{-1} 2210, 1590, 1450, 1330 and 1160; δ_H (400 MHz; $CDCl_3$) 1.34 (9 H, s, CH_3), 6.23 (1 H, s, C=CH), 7.29–7.38 (5 H, m, ArH), 7.44 (2 H, t, *J* 7.3, ArH), 7.56 (1 H, t, *J* 7.3, ArH) and 7.84 (2 H, d, *J* 7.3, ArH); δ_C (100 MHz; $CDCl_3$) 29.3 (s), 30.9 (q), 75.6 (s), 115.4 (s), 122.5 (d), 128.4 (d), 128.7 (d), 129.2 (d), 129.7 (d), 130.2 (d), 133.8 (s), 135.0 (s), 141.5 (s) and 150.0 (s); *m*/*z* (EI) 324 (M^+, 70%), 183 (35), 167 (35) and 97 (100).

Crystal-structure determination of 7b

$C_{27}H_{21}F_3O_5S_2Se$, $M = 625.54$, monoclinic, $a = 13.214(7)$, $b = 14.200(5)$, $c = 14.463(7)$ Å, $\beta = 103.31(4)°$, $V = 2641(2)$ Å^3, $T = 296$ K, space group $P2_1/n$ (#14), $Z = 4$, μ(MoKα) = 16.38 cm^{-1}, 6577 reflections measured, 6315 unique ($R_{int} = 0.078$) which were used in all calculations. The final $wR(F^2)$ was 0.033 (all data).†

† CCDC reference number 207/502. See http://www.rsc.org/suppdata/p1/b0/b007715l for crystallographic files in .cif format.

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