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A Michael Addition and Peterson Olefination Sequence Using 1-Silylethenyl Sulfides and Sulfoxide

Shuji KANEMASA,* Hiroshi KOBAYASHI, Junji TANAKA, and Otohiko TSUGE*
Institute of Advanced Material Study, and Department of Molecular Science and Technology,
Interdisciplinary Graduate School of Engineering Sciences,
Kyushu University, Kasugakoen, Kasuga 816
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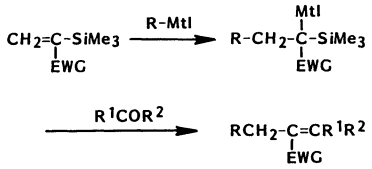
Reaction of organolithiums with a 1-(trimethylsilyl)ethenyl sulfide produces 1,2-bis(trimethylsilyl)-cyclopropanes, while use of 1-silylethenyl sulfides bearing a bulkier silyl moiety results in exclusive formation of the corresponding Michael adduct anions which are then quenched with aldehydes to give vinyl sulfides. On the contrary, a 1-(trimethylsilyl)ethenyl sulfoxide undergoes smooth Michael addition with a variety of organometallics and the resulting carbanion intermediates can be quenched with aldehydes to produce vinyl sulfoxides. Scope and limitations of these sequential reactions are discussed.

Development of a step-saving procedure for the sequence including several reaction steps is important from a standpoint of efficiency and simplification of synthetic route. Especially attractive is a one-flask procedure in which more than two steps of carbon–carbon bond forming processes are involved.

In a previous communication,[1] we reported the Michael addition–Peterson olefination sequence of methyl 2-(trimethylsilyl)acrylate (Eq. 1, EWG=COOMe). Thereafter we have been continuing our research program aiming at a wide extension of this consecutive reaction to other systems using electrophilic olefins such as 1-silylethenyl sulfides,[2] sulfoxides,[2] and ketones.



(1)

Meantime Ager reported Michael additions of phenyl 1-silylethenyl sulfide with organolithiums followed by alkylations or Peterson olefinations.[3,4] His two reports stimulated us to present our own results obtained in a similar research using the same 1-silylethenyl sulfide, its derivatives, and a silylethenyl sulfoxide. As discussed below, our results differ from the Ager's ones in some points.

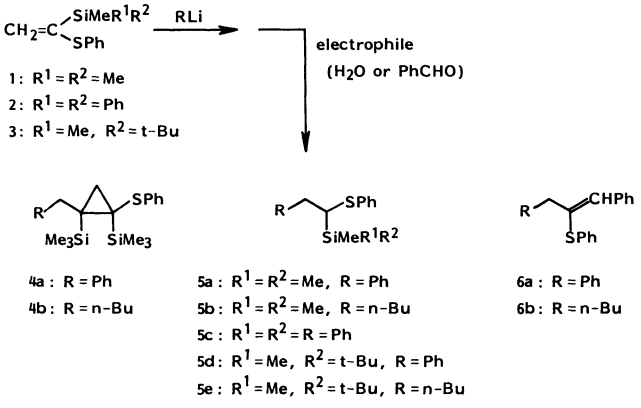
The Michael addition of 1-silyl-1-alkenyl sulfides was first reported by Seebach who briefly investigated the Michael addition–Peterson olefination sequence of a 1-silylethenyl sulfide.[5] Later this reaction was applied to a synthetic approach of sulfines[6] and 1-silylalkyl sulfides.[7] Although yields of the Michael addition step were unsatisfactory at the early stage of these investigations, they were improved by slow addition of a diluted solution of the Michael acceptors to excess nucleophiles.[7]

Compared with the relatively many reaction examples on 1-silyl-1-alkenyl sulfides, the corresponding sulfoxides and sulfones[6] with higher oxidation levels have been rarely utilized in the related reaction sequence. As 1-silylalkyl sulfoxides are labile compounds[6] so as to undergo sila-Pummerer rearrangement under mild conditions, the Michael addition to 1-silyl-1-alkenyl sulfoxides must be useful as a new method of generating 1-silyl-1-sulfinyl carbanions.[8]

The present article describes the scope and limitation of the Michael addition–Peterson olefination sequence of 1-silylethenyl sulfides and sulfoxide.

Results and Discussion

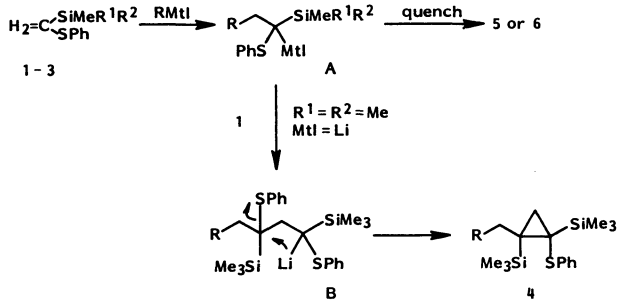
Michael Reactions of 1-Silylethenyl Sulfides. In the first place, the reactivity of phenyl 1-(trimethylsilyl)ethenyl sulfide (**1**) in Michael additions was examined by use of nucleophiles such as phenyllithium and phenylmagnesium bromide; the resulting anionic adduct was quenched with water. Although silane **1** was recovered quantitatively in the reaction with the Grignard reagent, phenyllithium underwent a smooth addition in diethyl ether or tetrahydrofuran (THF) in the presence of *N,N,N′,N′*-tetramethyl-1,2-ethanediamine (TMEDA) to afford **4a** as a single product (Scheme 1). The product **4a** which consisted of two stereoisomers in a 4.3:1 ratio was assigned not to be the expected 1-silylalkyl sulfide **5a** but 1-benzyl-2-phenylthio-1,2-bis(trimethylsilyl)cyclopropane (**4a**) on



Scheme 1.

the basis of spectral data. The maximum yield of **4a** reached 88% when the reaction was carried out in THF (Table 1, Entry 2). Nevertheless the formation of neither **4a** nor related compounds was reported in the previous works accomplished by Ager[3,4,7] and others.[5,6]

As shown in Scheme 2, phenyllithium adds to the β-carbon of vinylsilane **1** to provide carbanion intermediate **A** (R=Ph, R^1=R^2=Me, Mtl=Li). Exclusive formation of cyclopropane **4a** indicates that the resulting carbanion **A**, stabilized by both silyl and phenylthio moieties, is much more nucleophilic than the starting phenyllithium. Thus relatively rapid addition of **A** to **1** leads to bisadduct **B** (R=Ph) followed by internal nucleophilic substitution into **4a**. A related cyclopropanation has been recently demonstrated by Cohen who carried out the reactions of vinylsilane **1** with 1-(phenylthio)allyllithiums.[9] Use of two equivalents of phenyllithium also gave cyclopropane **4a** as a sole product (Table 1, Entry 3). Even when **1** was slowly added to excess phenyllithium (2 equiv) in a period of 1 h, **4a** was the major product (62%); the 1:1 adduct **5a** was obtained only in 17% yield (Entry 4).



Scheme 2.

Use of butyllithium instead of phenyllithium in the Michael addition of **1** in diethyl ether and subsequent hydrolytic quench furnished a 1:1 mixture of cyclopropane **4b** and the expected Michael adduct **5b** (Scheme 1 and Table 1, Entry 6). They can be separated from each other by column chromatography. On the other hand, both the same reaction in THF (Entry 7) and the reaction using a catalytic amount of copper(I) chloride (Entry 8) in diethyl ether produced only cyclopropane **4b**.

Though quench of the carbanion intermediates **A** (R^1=R^2=Me, Mtl=Li) with benzaldehyde gave the expected phenyl vinyl sulfides **6a, b** as a 1:1 mixture of *E*- and *Z*-isomers, their yields remained unsatisfactory because of the competitive formation of undesired cyclopropanes **4a, b** (Entries 5 and 10). According to the reaction pathway shown in Scheme 2, Michael acceptors bearing a bulkier silyl moiety, e.g. *t*-butyldimethylsilyl or methyldiphenylsilyl, would effectively suppress the cyclopropanation.

1-(Methyldiphenylsilyl)ethenyl phenyl sulfide (**2**) and 1-(*t*-butyldimethylsilyl)ethenyl phenyl sulfide (**3**), prepared by treating 1-(phenylthio)ethenyllithium with the corresponding silyl chlorides, reacted with phenyl- or butyllithium under similar reaction conditions to afford the Michael adducts **5a—c** after hydrolytic quench, or vinyl phenyl sulfides **6a,b** after treatment with benzaldehyde (Scheme 1 and Table 1, Entries 11—15). No cyclopropanes were even detected as expected, but water-quenched adducts **5c** and **5e** were accompanied instead (Entries 12 and 15).

Structures of phenyl vinyl sulfides **6a,b** were based on the ^{1}H and ^{13}C chemical shifts (**6a**: CH_2C=: 3.46 (*Z*), 3.79 (*E*) and 44.29 (*Z*), 37.23 (*E*); =CHPh: 6.75 (*Z*), 6.81

Table 1. Reactions of 1-Silylethenyl Sulfides **1—3** with Organolithium Compounds and Subsequent Quench with Electrophiles

Entry	Silane	RLi (equiv)	Solvent[a]	Additive (equiv)[b]	Time/h[c]	Electrophile[d]	Product (yield/%)[e]
1	**1**	PhLi (1)	DEE	TMEDA (1)	1	H_2O	**4a** (65)
2	**1**	PhLi (1)	THF	TMEDA (1)	1	H_2O	**4a** (88)
3	**1**	PhLi (2)	DEE	TMEDA (2)	1	H_2O	**4a** (69)
4	**1**	PhLi (2)	DEE	TMEDA (2)	1[f]	H_2O	**4a** (62)+**5a** (17)
5	**1**	PhLi (2)	DEE	TMEDA (2)	1[f]	PhCHO	**4a** (73)+**6a** (21, 1:1)[g]
6	**1**	*n*-BuLi (1)	DEE	TMEDA (1)	1.5	H_2O	**4b** (48)+**5b** (49)
7	**1**	*n*-BuLi (1)	THF	TMEDA (1)	1	H_2O	**4b** (88)
8	**1**	*n*-BuLi (1)	DEE	CuCl (0.03)	1	H_2O	**4b** (88)
9	**1**	*n*-BuLi (2)	DEE	TMEDA (2)	1	H_2O	**4b+5b** (45, 92:8)[h]
10	**1**	*n*-BuLi (1)	DEE	TMEDA (1)	1	PhCHO	**4b** (30)+**6b** (56, 1:1)[g]
11	**2**	PhLi (1)	DEE	TMEDA (1)	1	H_2O	**5c** (65)
12	**2**	PhLi (1)	DEE	TMEDA (1)	1	PhCHO	**5c+6a** (53, 1:3)[g]
13	**3**	PhLi (1)	DEE	TMEDA (1)	1	H_2O	**5d** (54)
14	**3**	*n*-BuLi (1)	DEE	TMEDA (1)	1	H_2O	**5e** (71)
15	**3**	*n*-BuLi (1)	DEE	TMEDA (1)	1	PhCHO	**5e+6b** (100, 3:7)[g]

a) DEE: diethyl ether; THF: tetrahydrofuran. b) TMEDA: *N,N,N′,N′*-tetramethyl-1,2-ethanediamine. c) All the reactions were carried out at 0 °C. d) After the addition of PhCHO, the reaction was continued for 1 h at 0 °C. e) Yield of isolated products. f) Silane **1** was added dropwise in a period of 1 h. g) Not separated. The ratio of two isomers of **6** was determined by ^{1}H NMR. h) Not separated. The ratio was determined by GLC.

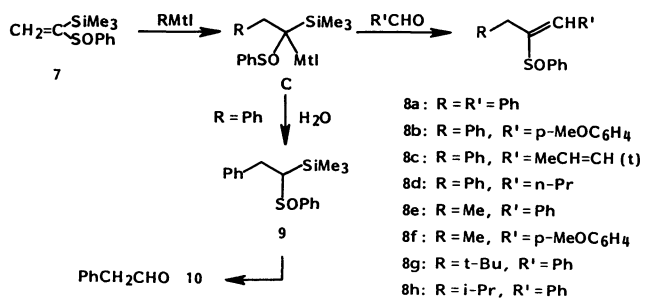
(*E*). **6b**: CH_2C=: 38.26 (*Z*), 31.06 (*E*); =CHPh: 6.60 (*Z*), 6.76 (*E*)).

Donor molecules effectively employable in the Michael reactions of 1-silylethenyl sulfide **1** are quite limited to some organolithiums. Thus Grignard reagents and lithium enolates of esters, amides, and ketones are all ineffective.[10]

A Michael Addition-Peterson Olefination Sequence of a 1-Silylethenyl Sulfoxide. 1-Silylethenyl sulfoxides must be better Michael acceptors than 1-silylethenyl sulfides because of their higher capability of stabilizing the α-anionic center by a sulfinyl moiety. Accordingly were investigated Michael additions of phenyl 1-(trimethylsilyl)ethenyl sulfoxide (**7**) which was prepared by oxidation of **1** with *m*-chloroperbenzoic acid (MCPBA).

Treatment of **7** with TMEDA and phenyllithium (both 1 equiv) in THF at −78 °C for 1 h followed by hydrolytic quench gave a mixture of 2-phenyl-1-phenylsulfinyl-1-(trimethylsilyl)ethane (**9**) and phenylacetaldehyde (**10**) whose separation from each other was unsuccessful because of their lability (Scheme 3). No formation of cyclopropane derivatives was observed. As the relative ratio of **10** was gradually increased with liberation of benzenethiol when this mixture was allowed to stand at room temperature, aldehyde **10** was presumably formed from **9** via sila-Pummerer rearrangement,[11] not from the Michael adduct anion **C** (R=Ph).

Under similar reaction conditions, the anion **C** (R=Ph) was generated and then quenched with benzaldehyde to give the expected 1-alkenyl sulfoxide **8a** as a single stereoisomer in 71% yield based on **7** (Scheme 3, Table 2, Entry 1). Although the stereostructure of **8a** could not be determined only on the basis of spectral data, its assignment as *E*-isomer was accomplished by a chemical conversion. Thus **8a** was quantitatively deoxygenated into *E*-isomer of **6a** on treatment with trifluoroacetic anhydride, sodium iodide, and triethylamine.[12]



Scheme 3.

Methyllithium as a Michael donor (Entries 8 and 9) and aromatic, α,β-unsaturated, and aliphatic aldehydes as carbonyl quenchers (Entries 6 and 7) can be employed effectively. Grignard reagents (Entries 2 and 10), a lithium cuprate (Entry 3), and magnesium cuprates (Entries 4 and 11) are also reactive albeit yields of the Michael addition steps are relatively low.

As shown in Table 2 Peterson olefinations of the silyl- and sulfinyl-stabilized intermediates **C** (Mtl=Li) derived from **7** were highly *E*-selective (Entries 1—7, 10, and 11) except for the cases where a sterically small Michael donor such as methyllithium was employed in the initial Michael additions (Entries 8 and 9). This high *E*-selectivity makes a striking contrast to the aforementioned nonstereoselective Peterson condensations of the intermediates **A** (R^1=R^2=Me, Mtl=Li) derived from **1** and also contrast to the poor

Table 2. A Michael Addition and Peterson Olefination Sequence of 1-Silylvinyl Sulfoxide **7**[a]

Entry	R-Mtl (equiv)	Michael reaction	R'CHO[b]	Peterson reaction	Product yield (%)[c]	*E*/*Z*
1	PhLi (1.5)	−78 °C, 1 h[d]	PhCHO	−78 °C, 1 h	**8a** (71)	*E*
2	PhMgBr (1.2)	−15 °C, 1 h	PhCHO	−15—0 °C, 1 h	**8a** (50)	*E*
3	Ph_2CuLi (1.2)	0 °C, 1 h	PhCHO	0 °C, 1 h	**8a** (56)	*E*
4	$Ph_2CuMgBr$ (1)	−15 °C, 1 h	PhCHO	−15—0 °C, 1 h	**8a** (68)	*E*
5	PhLi (1.5)	−78 °C, 1 h[d]	*p*-$MeOC_6H_4CHO$	−78 °C, 1 h	**8b** (92)	*E*
6	PhLi (1.5)	−78 °C, 1 h[d]	MeCH=CHCHO(*t*)	−78 °C, 1 h	**8c** (87)	*E*
7	PhLi (1.5)	−78 °C, 1 h[d]	*n*-PrCHO	−78 °C, 1 h	**8d** (86)	*E*
8	MeLi (1.5)	−78 °C, 1 h[d]	PhCHO	−78 °C, 1 h	**8e** (76)	1.7[e]
9	MeLi (1.5)	−78 °C, 1 h[d]	*p*-$MeOC_6H_4CHO$	−78 °C, 1 h	**8f** (73)	2.3[e]
10	*t*-BuMgBr (1.2)	−15 °C, 1 h	PhCHO	−15 °C, 1 h	**8g** (26)	*E*
11	*i*-$Pr_2CuMgBr$ (1.1)	−15 °C, 1 h	PhCHO	−15—0 °C, 1 h	**8h** (44)	*E*
12	CH_2=C(OLi)OEt (1)	−78 °C, 20 min	PhCHO	−78 °C, 1 h	**11a** (66)	1.8[f]
13	CH_2=C(OLi)OEt (1)	−78 °C, 20 min	*p*-$MeOC_6H_4CHO$	−78 °C, 1 h	**11b** (73)	2[e]
14	CH_2=C(OLi)OEt (1)	−78 °C, 20 min	2-furylCHO	−78 °C, 1 h	**11c** (75)	2[e]
15	CH_2=C(OLi)OEt (1)	−78 °C, 20 min	*n*-PrCHO	−78 °C, 1 h	**11d** (60)	*E*
16	CH_2=C(OLi)OEt (1)	−78 °C, 20 min	MeCH=CHCHO(*t*)	−78 °C, 1 h	**11e** (73)	*E*
17	MeCH=C(OLi)OEt (1)	−78 °C, 1 h	PhCHO	−78 °C, 1 h	**12** (33)	g)

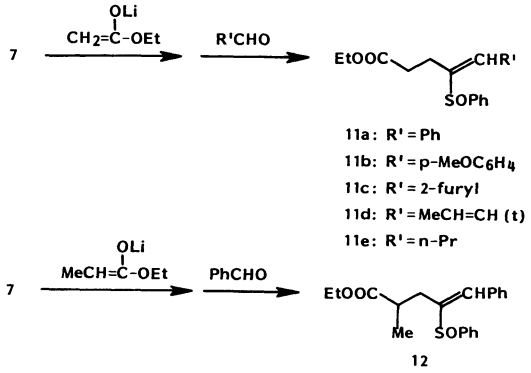
a) All reactions were carried out in dry THF under nitrogen. b) One equimolar amount of an aldehyde was used. c) Yield of isolated products. d) In the presence of TMEDA (1.5 equiv). e) Determined by ^{13}C NMR. f) Determined by ^1H NMR. g) Three diastereomers are involved (^{13}C NMR).

stereoselectivity observed in the Peterson reactions of the lithium anions derived from phenyl trimethylsilylmethyl sulfoxide.[8] Such high stereoselectivity will be discussed below.

1-Silylethenyl sulfoxide **7** also showed a high reactivity toward lithium enolates of esters. For example, the lithium enolate of ethyl acetate underwent a smooth Michael addition to **7** at −78 °C in 20 min and the resulting adduct anion was quenched with a variety of aldehydes to give vinyl sulfoxides **11a—e**, *E*-isomers as major products (Scheme 4 and Table 2, Entries 12—16). The *E*-selectivity is absolutely exclusive unless the Michael additions with a lithium enolate are followed by the Peterson olefinations with aromatic aldehydes (Entries 12—14).

Though in a low yield, a similar product **12** was obtained in the reaction of the lithium enolate of ethyl propanoate with **7** and benzaldehyde (Entry 17).

The stereoselectivity observed above is interpreted in Fig. 1. The sterically more favored intermediate adduct **D**[13] would be predominantly formed in the Michael addition step. Two chair transition states **E** and **F** are possible[14] where the bulky phenyl and silyl moieties always occupy equatorial positions. As Peterson olefination of the resulting adducts must occur, under the employed conditions, through cis-elimination of a silanol,[15] the carbonyl adducts formed via **E** and **F** should selectively lead to *E*- and *Z*-isomers, respectively, of **8**, **11**, and **12**. In the approach **F** there are two gausche interactions between R′–RCH_2 and R′–Me_3Si, whereas axial R′ in the approach **E** causes a less critical 1,3-diaxial interaction. This is the major reason for the selective or exclusive formation of *E*-olefins.



Scheme 4.

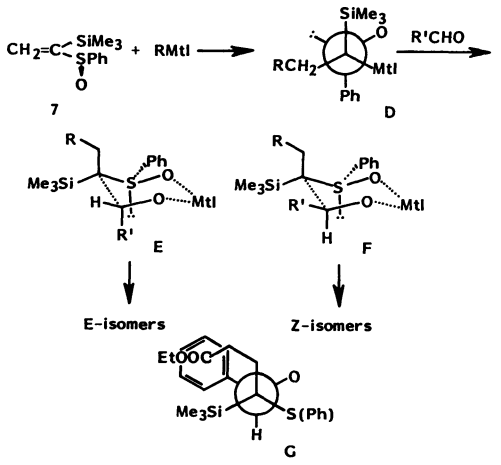


Fig. 1. Stereoselectivity in the Michael/Peterson sequences of 1-silylethenyl sulfoxide **7**.

When R is small in size (R=Me), the gauche interaction between RCH_2 and R′ is relatively reduced. On the other hand the gauche repulsion is partly cancelled by an attractive interaction between the aromatic plane and the ester moiety when R is CH_2COOEt and R′ is aryl or hetero aryl (approach **G**). In these cases, relative stability of approach **F** is increased to lead to the decrease of *E*-selectivity.

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-702 spectrometer. ^1H NMR spectra were recorded on a Hitachi R-40 (90 MHz), a JEOL FX-100 (100 MHz), or a JEOL GSX-270 instrument (270 MHz), and ^{13}C NMR on a JEOL FX-100 (25.05 MHz) or a JEOL GSX-270 spectrometer (67.94 MHz). Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL-O1SG-2 spectrometer at 70 eV of ionization energy. GC-mass spectra as well as high-resolution mass spectra were obtained on the same instrument. Elemental analyses were performed on a Hitachi 026 CHN analyzer. Thin-layer chromatography (TLC) was accomplished on 0.2 mm precoated plates of silica gel 60 F-254 (Merck) or of aluminum oxide 60 F-254 type-E (Merck). Visualization was made with ultraviolet light (254 and 365 nm), iodine, molybdophosphoric acid (5% in ethanol), or *p*-anisaldehyde (5% in ethanol containing 5% of sulfuric acid). For preparative column chromatography, Wakogel C-200, C-300 (Wako), and Silicagel 60 (Merck) were employed. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with Silicagel 60 (Merck, size: 0.04—0.063 mm). preparative high performance liquid chromatography (HPLC) was performed on a Kusano KHLC-201 apparatus with a UV-detector Uvilog-III using a column (22×300 mm) packed with silica gel (Wakogel LC-50H). Gas liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatograph (Yanagimoto) with an ionization flame detector using a glass column (SE-30, 3×2000 mm) or a glass capillary column (Silicone GE, SE-30, 0.25×50000 mm). Micro vacuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

Materials. Phenyl 1-(trimethylsilyl)ethenyl sulfide (**1**) was prepared by reaction of 1-lithioethenyl phenyl sulfide with chlorotrimethylsilane.[7] Lithium diphenylcuprate,

magnesium bromide diphenylcuprate, and magnesium bromide diisopropylcuprate were in situ prepared from two equivalents of the corresponding organometallics and copper(I) iodide. The lithium enolates of ethyl acetate and propanoate were in situ prepared from equimolar amounts of lithium diisopropylamide (LDA) and the corresponding esters. Tetrahydrofuran (THF) or diethyl ether was distilled from lithium aluminum hydride or sodium metal, respectively, immediately before use. Diisopropylamine was distilled from sodium hydride.

Phenyl 1-(Methyldiphenylsilyl)ethenyl Sulfide (2): To a freshly prepared solution of LDA (66 mmol) in hexane was added dropwise, at −78 °C under nitrogen, phenyl vinyl sulfide (9 g, 66 mmol) in dry THF (40 ml) in a period of 15 min. After stirring for 1 h, chloro(methyl)diphenylsilane (15.5 g, 66 mmol) was slowly added. The resulting mixture was stirred at −78 °C for 30 min and then at 0 °C for additional 30 min, poured into saturated aqueous sodium chloride (30 ml), and extracted with dichloromethane (35 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane–ethyl acetate (20:1 v/v) to give **2** (16.8 g, 77%): Colorless liquid; bp 215—220 °C/27 Pa; IR (neat) 1420, 1240, 1100, 875, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.73 (3H, s, SiMe), 5.40, 5.47 (each 1H, s, $=CH_2$), and 7.1—7.7 (15H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−3.88 (q, SiMe), 124.01 (t, $=CH_2$), 127.95, 128.42, 129.30, 129.77, 132.07, 134.89, 135.24, and 144.72; MS *m/z* (rel intensity, %) 332 (M^+, 22), 241 (13), 213 (10), 198 (20), 197 (base peak), 195 (17), 181 (17), 165 (13), 151 (13), 145 (16), 119 (14), 109 (12), 105 (43), 93 (11), 91 (38), and 77 (28). Found: C, 75.95; H, 6.13%. Calcd for $C_{21}H_{20}SSi$: C, 75.85; H, 6.06%.

1-(*t*-Butyldimethylsilyl)ethenyl Phenyl Sulfide (3). A similar procedure using LDA (66 mmol), phenyl vinyl sulfide (9 g, 66mmol) in THF (40 ml), and *t*-butylchlorodimethylsilane (9.9 g, 66 mmol) gave **3** (7.2 g, 61%) after vacuum distillation of the crude product: Colorless liquid; bp 73—76 °C/19 Pa; IR (neat) 1250 and 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.18 (6H, s, $SiMe_2$), 0.98 (9H, s, *t*-Bu), 5.17, 5.41 (each 1H, s, $=CH_2$), and 7.2—7.5 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−5.88 (q, $SiMe_2$), 17.00 (s, *t*-Bu), 26.83 (q, *t*-Bu), 120.30 (t, $=CH_2$), 128.41, 129.36 (each d), 132.18, 135.13 (each s), and 145.83 (s); MS *m/z* (rel intensity, %) 250 (M^+, 10), 193 (43), 177 (12), 168 (14), 167 (base peak),151 (48), 91 (24), 82 (16), 76 (23), and 75 (17).

General Procedure for the Michael Addition/Water Quench Sequence of Vinyl Sulfides 1—3 Leading to 4a,b and 5a—e. As a typical procedure, the reaction of phenyllithium with **1** is described (Entry 1 in Table 1): To a solution of *N,N,N′,N′*-tetramethyl-1,2-ethanediamine (TMEDA, 0.116 g, 1 mmol) in dry diethyl ether (3 ml) was added phenyllithium (or butyllithium) at 0 °C under nitrogen. After vinylsilane **1** (0.208 g, 1 mmol) in diethyl ether (10 ml) was added in a period of 1 h, the mixture was stirred for additional 1 h. It was poured into saturated aqueous ammonium chloride and extracted with diethyl ether (30 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was subjected to column chromatography over silica gel by using hexane to give **4a** (0.125 g, 65%). Other reactions were carried out under the reaction conditions listed in Table 1 and the results are summarized in the same table.

4a (a 4.3:1 mixture of two stereoisomers (^1H NMR)): Colorless liquid; IR (neat) 1250 and 839 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.02, 0.09, 0.14, 0.21 (18H, each s, 4.3:1:4.3:1, $SiMe_3$), 1.4—1.6 (2H, m, ring CH_2), 2.98, 3.29 (2H, each s, $PhCH_2$), and 7.0—7.3 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=0.54, 1.22 (each q, $SiMe_3$), 21.97, 24.46 (each s, ring C), 25.39 (t, ring CH_2), 39.55, 39.99 (each t, 4.3:1, $PhCH_2$), 124.32, 124.61, 125.59, 125.88, 126.66, 127.34, 127.93, 128.32, 128.80 (each d, Ph), 139.65, 140.77, and 141.89 (each s, 4.4:4.2:1, Ph); MS *m/z* (rel intensity, %) 384 (M^+, 32), 218 (21), 167 (12), 135 (15), 129 (19), 128 (15), 110 (17), 109 (17), 91 (11), and 73 (base peak). Found; C, 68.68; H, 8.45%. Calcd for $C_{22}H_{32}SSi_2$: C, 68.68; H, 8.38%.

4b (a 2.2:1 mixture of two stereoisomers (^1H NMR)): Colorless liquid; IR (neat) 1250 and 839 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.08, 0.11, 0.18 (18H, each s, 2.2:3.2:1, $SiMe_3$), 0.89 (3H, t, J=6.0 Hz, n-C_5H_{11}), 1.0—1.8 (10H, m, n-C_5H_{11}), and 6.9—7.3 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=1.00, 1.12, 1.29, 1.88 (each q, 2.6:1.2:2.0:1, $SiMe_3$), 14.35 (q, n-C_5H_{11}), 21.83, 22.83 (1:2.6), 23.41, 26.88 (1:3.1), 23.71, 24.47 (1:2.6), 29.36, 29.88 (2.5:1), 32.41, 32.65 (1:2.1) 34.13, 35.35 (1:2.6), 124.36, 124.65, 126.72, 127.36, 128.48 (each d, Ph), 140.30, and 140.66 (each s, 2.5:1, Ph); MS *m/z* (rel intensity, %), 364 (M^+, 11), 73 (base peak), 44 (16), and 42 (12). Found: C, 65.67; H, 9.95%. Calcd for $C_{20}H_{30}SSi_2$: C, 65.87; H, 9.93%.

5a: Colorless liquid; IR (neat) 1250 and 841 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.16 (9H, s, $SiMe_3$), 2.7—3.1 (3H, CH_2 and CH), and 7.0—7.4 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−2.22 (q, $SiMe_3$), 36.76 (d, CH), 38.14 (t, CH_2), 125.84, 126.17, 128.13, 128.62, 129.23, 129.97 (each d, Ph), 137.62, and 140.76 (each s, Ph); MS *m/z* (rel intensity, %) 286 (M^+, 17), 195 (20), 167 (45), 135 (44), 109 (21), 91 (40), 77 (21) 73 (base peak), and 65 (22). HRMS Found: *m/z* 286.1199. Calcd for $C_{17}H_{22}SiS$: M, 286.1210.

5b: Colorless liquid; IR (neat) 1250, 858, and 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.12 (9H, s, $SiMe_3$), 0.83 (3H, t, J=5.0 Hz, n-C_5H_{11}), 1.0—1.9 (8H, m, n-C_5H_{11}), 2.45 (1H, dd, J=5.0 and 6.0 Hz, CH), and 7.0—7.5 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−1.88(q, $SiMe_3$), 14.18 (q, n-C_5H_{11}), 22.65, 28.18, 31.94, 32.12 (each t, n-C_5H_{11}), 34.65 (d, CH), 125.89, 129.01, 129.77 (each d, Ph), and 138.89 (s, Ph); MS *m/z* (rel intensity, %) 266 (M^+, 23), 183 (10), 182 (66), 167 (28), 151 (12), 135 (11), 123 (13), 109 (12), 91 (14), and 73 (base peak). Found: C, 67.39; H, 9.83%. Calcd for $C_{15}H_{26}SSi$: C, 67.60; H, 9.83%.

5c: Yellow liquid; IR (neat) 1425, 1250, and 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.00 (3H, s, SiMe), 2.0—2.7 (3H, m, CH_2 and CH), and 6.0—7.2 (20H, m, Ph); ^{13}C NMR δ=−5.03 (q, SiMe), 36.67 (d, CH), 38.48 (t, CH_2), 126.12, 126.22, 128.02, 128.12, 128.56, 129.54, 129.69, 130.56, 135.20, 137.79, and 140.57; MS *m/z* (rel intensity, %) 410 (M^+, 36), 241 (22), 197 (base peak), and 91 (22). Found: C, 79.03; H, 6.45%. Calcd for $C_{27}H_{26}SiS$: C, 78.97; H, 6.38%.

5d: Colorless liquid; IR (neat) 1250 and 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.04, 0.08 (each 3H, $SiMe_2$), 1.00 (9H, *t*-Bu), 2.7—3.3 (3H, m, CH_2 and CH), and 7.0—7.1 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−6.41, −5.76 (each q, $SiMe_2$), 17.88 (s, *t*-Bu), 27.59 (q, *t*-Bu), 35.18 (d, CH), 39.36 (t, CH_2), 125.71, 126.18, 128.18, 128.60, 129.36, 129.71 (each d, Ph), 138.30, and 141.13 (each s, Ph); MS *m/z* (rel intensity, %) 328 (M^+, 2), 167 (46), 151 (24),135 (51), 109 (31), 91 (56), 73 (base peak), 65 (33), 57 (58), and 41 (34). Found: C, 73.29; H, 8.68%. Calcd for $C_{20}H_{28}SiS$: C, 73.11; H 8.59%.

5e: Pale yellow liquid; IR (neat) 1250 and 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.04, 0.00 (each 3H, s, $SiMe_2$), 0.7—1.6 (11H, m, n-C_5H_{11}), 0.86 (9H, s, t-Bu), 2.52 (1H, dd, J=6.6 and 4.4 Hz, CH), and 6.9—7.3 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−6.00 ($SiMe_2$), 14.01 (n-C_5H_{11}), 17.68, 27.93 (t-Bu), 22.49, 27.93, 31.89, 31.92, 32.68 (n-C_5H_{11} and CH), 125.53, 128.68 129.20, and 138.73 (Ph); MS m/z (rel intensity, %) 308 (M^+, 5), 251 (20), 167 (base peak), and 73 (43). HRMS Found: m/z 308.2006. Calcd for $C_{18}H_{32}SiS$: M, 308.2018.

General Procedure for the Michael Addition/Peterson Olefination Sequence of Vinyl Sulfides 1—3 Leading to 6. The reaction of **1** with phenyllithium and benzaldehyde is described as a typical example (Entry 5 in Table 1): To a solution of TMEDA (0.232 g, 2 mmol) in dry diethyl ether (10 ml) was added phenyllithium (2 mmole) at 0 °C under nitrogen. After vinylsilane **1** (0.208 g, 1 mmol) in diethyl ether (10 ml) was added in a period of 1 h, the mixture was stirred for additional 1 h. Benzaldehyde (0.212 g, 2 mmol) in diethyl ether (2 ml) was added and stirring was continued for 1 h. The mixture was poured into saturated aqueous ammonium chloride and extracted with diethyl ether (30 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane–ethyl acetate (50:1 v/v) to give **6a** (0.064 g, 21% E:Z=1:1) and then **4a** (0.141 g, 73%). Other reactions were carried out under the reaction conditions listed in Table 1 and the results are shown in the same table.

6a (a 1:1 mixture of E- and Z-isomers (^1H NMR)): Pale yellow liquid; IR (neat) 2854 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.46, 3.79 (2H, each s, CH_2), 6.75, 6.81 (1H, each s, =CH), and 7.0—7.9 (15H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=37.23, 44.29 (each t, CH_2), 126.37, 126.46, 127.02, 127.15, 127.35, 127.68, 127.89, 128.02, 128.25, 128.29, 128.46, 128.56, 128.91, 129.05, 129.12, 129.24, 129.28, 129.69, 131.59, 132.29, 132.75, 133.50, 133.85, 134.80, 135.07, 135.16, 136.48, 136.77, 137.14, 138.50, and 138.89; MS m/z (rel intensity, %) 302 (M^+, 21), 192 (36), 191 (27), 178 (32), 165 (38), 115 (94), 109 (65), 91 (base peak), 89 (24), 78(34), 77 (38), and 65 (79). HRMS Found: m/z 302.1123. Calcd for $C_{21}H_{18}S$: M, 302.1128.

Pure (*E*)-**6a** was obtained by deoxygenation of (*E*)-**8a** with trifluoroacetic anhydride–sodium iodide–triethylamine: Pale yellow plates (hexane); mp 80—81 °C; IR (KBr) 1630, 1628, 1600, 800, 790, 780 748 and 731 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.82 (2H, s, CH_2C=), 6.85 (2H, s, =CH), and 7.1—7.6 (15H, m, Ph).

6b (a 1:1 mixture of E- and Z-isomers (^1H NMR)): Pale yellow liquid; IR (neat) 2858 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.83 (3H, t, J=6.0 Hz, n-C_5H_{11}), 1.1—1.9 (6H, m, n-C_5H_{11}), 2.1—2.5 (2H, m, n-C_5H_{11}), 6.60, 6.76 (1H, s, =CH), and 7.1—7.6 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=13.95, 13.99, 22.35, 22.42, 28.49, 28.57, 31.06, 31.49, 31.60, 38.26 (n-C_5H_{11}), 126.62, 126.75, 127.11, 127.30, 127.56, 127.96, 128.30, 128.39, 128.82, 129.07, 129.21, 130.95, 132.11, 134.26, 134.42, 136.05, 136.77, 137.17, and 139.82 (Ph); MS m/z (rel intensity, %) 282 (M^+, 44), 226 (27), 135 (43), 117 (37), 116 (47), 115 (base peak), 91 (66), and 42 (35). HRMS Found: m/z 282.1435. Calcd for $C_{19}H_{22}S$: M, 282.1430.

Phenyl 1-(Trimethylsilyl)ethenyl Sulfoxide (7):[16] To a solution of sulfide **1** (6 g, 29 mmol) in dichloromethane (60 ml) was added dropwise 3-chloroperbenzoic acid (MCPBA, 6.7 g, 29.1 mmol in dichloromethane (100 ml)) in a period of 30 min. The mixture was stirred at room temperature for 30 min, poured into saturated aqueous sodium hydrogensulfite (100 ml) and extracted with dichloromethane (60 ml×3). The combined extracts were washed with saturated sodium hydrogencarbonate, dried over magnesium sulfate, and evaporated in vacuo. The residue was chromatographed over silica gel by using hexane–ethyl acetate (10:1 v/v) to give **7** (6.16 g, 95%): Colorless liquid; IR (neat) 1240, 1040, and 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.05 (9H, s, $SiMe_3$), 6.19, 6.77 (each 1H, s, $=CH_2$), and 7.5—7.6 (5H, m, Ph);^{13}C NMR ($CDCl_3$) δ=−1.21 (q, $SiMe_3$), 126.63, 129.15, 129.24 (each d, Ph), 131.53 (t, $=CH_2$), 143.67 (s, Ph), and 157.22 (s, =C); MS m/z (rel intensity, %) 224 (M^+, 27), 167 (89), 126 (89), 77 (19), 75 (11), 73 (base peak), and 45 (12). HRMS Found: m/z 224.0683. Calcd for $C_{11}H_{16}OSiS$: M, 224.0690.

General Procedure for the Michael Addition/Peterson Olefination Sequence of Vinyl Sulfoxide 7 Leading to 8a—h, 11a—e, and 12. As a typical procedure, the reaction of **2** with phenyllithium and benzaldehyde is described (Entry 1 in Table 2): To a solution of TMEDA (0.174 g, 1.5 mmol) in dry THF (3 ml) was added phenyllithium (1.5 mmol) at −78 °C under nitrogen. After 30 min, vinyl sulfoxide **7** (0.224 g, 1 mmol) in THF (1 ml) was added in a period of 5 min and the mixture was stirred for 1 h. Benzaldehyde (0.16 g, 1.5 mmol) in THF (1 ml) was added and stirring was continued at the same temperature for 1 h. The mixture was poured into saturated aqueous ammonium chloride and extracted with diethyl ether (30 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel by using hexane–diethyl ether (20:1 v/v) to give **8a** (0.216 g, 71%) as a single isomer. Other reactions were carried out under the reaction conditions listed in Table 2. The results are also summarized in the same table.

8a: Colorless needles (hexane); mp 98—99 °C; IR (KBr) 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.46, 3.82 (each 1H, d, J_{gem}=16.5 Hz, CH_2C=), and 6.9—7.7 (16H, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=31.40 (t, CH_2C=), 125.78 (d, =CH), 129.24, 131.49, 132.81 (each d, Ph), 134.27, 136.62, 142.58 (each s, Ph), and 143.84 (s, =C); MS m/z (rel intensity, %) 318 (M^+, 2), 184 (43), 183 (78), 105 (base peak), 79 (24), 78 (31), and 77 (56). Found: C, 79.40; H, 5.94%. Calcd for $C_{21}H_{18}OS$: C, 79.21; H, 5.70%.

The sulfoxide **8a** was converted into (*E*)-**6a** by the following procedure: To a solution of **8a** (0.244 g, 0.76 mmol) in acetone (5 ml) were added sodium iodide (0.3 g, 2 mmol) and triethylamine (0.25 ml, 2 mmol). After cooled to 0 °C, trifluoroacetic anhydride (0.3 ml, 2 mmol) was slowly added. The mixture was stirred at the same temperature for 10 min and evaporated in vacuo. The residue was treated with water and extracted with diethyl ether (30 ml×3). The combined extracts were washed with diluted aqueous sodium thiosulfate and dried over magnesium sulfate. Evaporation of the ether in vacuo provided (*E*)-**6** (0.227 g, 98%).

8b: Colorless prisms (hexane); mp 91—93 °C; IR (KBr) 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.51, 3.98 (each 1H, d, J_{gem}=17.3 Hz,CH_2C=), 3.75 (3H, s, p-OMe), 6.8—6.9 (2H, m, Ar), and 6.9—7.7 (13H, m, Ar and =CH); ^{13}C NMR ($CDCl_3$) δ=31.30 (t, CH_2C=), 55.42 (q, OMe), 114.36 (d, Ar), 125.77 (d, =CH), 126.54, 127.07, 128.35, 128.36, 129.24, 131.13, 131.36 (each d, Ar), 133.13, 136.95, 141.48 (each s, Ar), 143.31 (s, =C), and 160.36 (s, Ar); MS m/z (rel intensity, %), 348 (M^+, 5), 223

(61), 222 (base peak), 207 (31), 178 (24), 116 (32), and 91 (47). Found: C, 76.01; H, 5.71%. Calcd for $C_{22}H_{20}O_2S$: C, 75.83; H, 5.78%.

8c: Pale yellow liquid; IR (neat) 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.82 (3H, d, J=5.1 Hz, Me), 3.33, 3.67 (each 1H, d, J_{gem}=15.3 Hz, CH_2C=), 6.14 (1H, dq, J=15.0 and 5.1 Hz, MeCH=), 6.24 (1H, dd, J=15.0 and 10.6 Hz, =CH), and 6.9—7.7 (11H, m, Ar and =CH); ^{13}C NMR ($CDCl_3$) δ=18.36 (q, Me), 29.88 (t, CH_2C=), 124.95 (d, =CH), 125.34, 125.93, 127.98, 128.07, 128.71, 130.61 (each d, Ph), 133.40, 137.84 (each d, =CH), 137.59, 140.87 (each s, Ph), and 142.83 (s, =C); MS m/z (rel intensity, %) 282 (M^+, 16), 157 (29), 142 (25), 141 (43), 129 (43), 128 (37), 126 (19), 125 (19), 116 (61), 97 (27), 91 (base peak), 78 (80), 77 (80), and 65 (44). Found: C, 76.40; H, 6.57%. Calcd for $C_{18}H_{18}OS$: C, 76.56; H, 6.42%.

8d: Colorless liquid; IR (neat) 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.80 (3H, t, J=7.0 Hz, n-Pr), 1.2—1.8, 1.9—2.4 (each 2H, m, n-Pr), 3.15, 3.52 (each 1H, d, J_{gem}=15.6 Hz, CH_2C=), 6.57 (1H, t, J=6.0 Hz, =CH), and 6.8—7.6 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=13.38 (q, n-Pr), 21.53, 29.78 (each t, n-Pr), 30.18 (t, CH_2C=), 124.95, 125.98, 128.17, 128.80, 130.66, 137.20 (each d, Ph and =CH), 137.59, 142.77 (each s, Ph), and 143.55 (s, =C); MS m/z (rel intensity, %) 284 (M^+, 23), 159 (base peak), 130 (28), 126 (86), 117 (89), 115 (32), 91 (98), 89 (72), 78 (23), 77 (21), 71 (67), and 56 (41). HRMS Found: m/z 284.1231. Calcd for $C_{18}H_{20}OS$: M, 284.1234.

8e (a 1.7:1 mixture of E- and Z-isomers (^{13}C NMR)): Pale yellow liquid; IR (neat) 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (1/2.7×3H, t, J=7.6 Hz, Et (Z)), 1.05 (1.7/2.7×3H, t, J=7.6 Hz, Et (E)), 1.8—2.8 (2H, m, Et), 7.00 (1/2.7H, br s, =CH (Z)), and 7.2—7.8 (10H+1.7/2.7H, m, Ph and =CH (E)); ^{13}C NMR ($CDCl_3$) δ=12.87, 13.10 (each q, Et), 18.84, 19.01 (each t, Et),124.26, 125.43, 126.72, 126.90, 128.18, 128.30, 128.41, 128.65, 128.99, 129.12, 129.47, 130.17, 131.10, 134.56, 135.08, 142.98 (s, Ph), 143.98 (s, Ph), 147.60, and 148.25 (each s, =C); MS m/z (rel intensity, %) 256 (M^+, 5), 131 (42), 116 (32), 115 (56), 91 (base peak) 79 (62), 78 (34), 77 (90), and 52 (61). Found: C, 74.75; H, 6.37%. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29%.

8f (a 2.3:1 mixture of E- and Z-isomers (^{13}C NMR)): Pale yellow liquid; IR (neat) 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (1/3.3×3H, t, J=7.0 Hz, Et (Z)), 0.97 (2.3/3.3×3H, t, J=7.0 Hz, Et (E)), 2.38 (1/3.3×2H, q, J=7.0 Hz, Et (Z)), 2.40 (2.3/3.3×2H, t, J=7.0 Hz, Et (E)), 3.80 (3H, s, p-OMe), 6.7—7.0 (2H, m, Ar), 7.24 (1/3.3H, s, =CH (Z)), and 7.3—7.8 (8H+2.3/3.3H, m, Ar and =CH (E)); ^{13}C NMR ($CDCl_3$) δ=13.09 (q, Et), 18.65 (t, Et), 55.37 (q, OMe), 114.16, 114.40 (each d, Ar), 124.61, 125.63 (each d, =CH), 127.25, 128.71, 129.30, 130.37, 131.00, 131.15, 131.34, 131.69, 135.20, 143.75, 145.36, and 160.16 (s, Ar); MS m/z (rel intensity, %) 286 (M^+, 9), 161 (77), 145 (44), 125 (47), 121 (43), 117 (32), 103 (37), 97 (33), 91(58), 78 (44), and 77 (base peak). Found: C, 71.03; H, 6.16%. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.33%.

8g: Colorless prisms (hexane); mp 115—116 °C; IR (KBr) 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (9H, s, t-Bu), 1.58, 2.85 (each 1H, d, J_{gem}=14.7 Hz, CH_2C=), 7.3—7.4 (5H, m, Ph), 7.4—7.5 (3H, m, Ph), and 7.7—7.8 (3H, m, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=30.40 (t-Bu), 33.51 (t-Bu), 39.18 (CH_2C=), 126.63, 127.82, 128.51, 128.97, 129.36, 129.87, 131.64, 135.88, 143.74, and 144.32 (=C); MS m/z (rel intensity, %) 298 (M^+, 1), 131 (22), 126 (23), 125 (27), 117 (21), 116 (51), 115 (base peak), 91 (31), 78 (33), and 77 (29). Found: C, 76.30; H, 7.46%. Calcd for $C_{19}H_{22}OS$: C, 76.47; H, 7.43%.

8h: Colorless liquid; IR (neat) 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.82, 0.85 (each 3H, d, J=6.6Hz, i-Pr), 1.8—2.0 (2H, m, i-Pr and one of CH_2C=) 2.48 (1H, dd, J=14.3 and 6.6 Hz, the other of CH_2C=), 7.3—7.4 (5H, m, Ph), 7.4—7.5 (4H, m, Ph and =CH), and 7.6—7.7 (2H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=22.15, 22.69 (each i-Pr), 27.07 (i-Pr), 35.12 (CH_2C=), 125.99, 128.16, 128.59, 129.05, 129.27, 130.28, 131.37, 135.06, 143.34 (Ph and =CH), and 145.39 (=C); MS m/z (rel intensity, %) 284 (M^+, 8), 117 (25), 115 (29), 108 (78), 107 (59), 103 (21), 91 (61), 79 (base peak), 78 (22), 77 (65), and 51 (37). Found: C, 75.92; H, 7.30%. Calcd for $C_{18}H_{20}OS$: C, 76.02; H, 7.09%.

11a (a 1.8:1 mixture of E- and Z-isomers (^1H NMR)): Pale yellow liquid; IR (neat) 1730 and 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.16 (1/2.8×3H, t, J=7.2 Hz, OEt (E)), 1.17 (1.8/2.8×3H, t, J=7.2 Hz, OEt (Z)), 2.0—2.8 (4H, m, CH_2CH_2), 4.19 (1/2.8×2H, q, J=7.2 Hz, OEt (Z)), 4.25 (1.8/2.8×2H, q, J=7.2 Hz, OEt (E)), 7.02 (1/2.8H, br s, =CH (Z)), and 7.2—7.8 (10H+1.8/2.8H, m, Ph and =CH (E)); ^{13}C NMR ($CDCl_3$) δ=14.06 (q, OEt), 20.88, 32.65 (each t, CH_2CH_2 (E)), 22.65, 33.83 (each t, CH_2CH_2 (Z)), 60.48, 60.59 (each t, OEt), 124.42, 125.54 (each d, =CH), 128.72, 129.01, 129.13, 129.42, 129.71, 130.60, 131.42, 132.89, 134.30, 137.19, 143.07 (s), 144.95, 145.42 (each s, =C), 172.07, and 172.42 (each s, COOEt); MS m/z (rel intensity, %) 312 (M^+ −16, 4), 283 (2), 223 (37), 203 (38), 149 (base peak), 110 (50), 109 (42), 84 (30), 76 (38), 73 (31), and 43 (43). Found: C, 69.45; H, 6.16%. Calcd for $C_{19}H_{20}O_3S$: C, 69.49; H, 6.14%.

11b (a 2:1 mixture of E- and Z-isomers (^{13}C NMR)): Pale yellow liquid; IR (neat) 1730 and 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20 (3H, t, J=7.0 Hz, OEt), 2.0—2.8 (4H, m, CH_2CH_2), 3.80 (3H, s, p-OMe), 4.06 (2H, q, J=7.0 Hz, OEt), 6.7—7.0 (2H, m, Ar), 7.00 (1/3H, s, =CH (Z)), and 7.2—7.8 (7H+2/3H, m, Ar and =CH (E)); ^{13}C NMR ($CDCl_3$) δ=14.18 (q, OEt), 20.88, 32.71 (each t, CH_2CH_2, (E)), 23.00, 34.12 (each t, CH_2CH_2 (Z)), 55.42 (q, OMe), 60.71 (t, OEt), 114.24, 114.60 (each d, Ar), 124.60, 125.54, 126.89, 129.42, 130.60, 131.07, 131.30, 142.36, 143.42 (s, =C), 160.25 (s, Ar), 172.42, and 174.66 (each s, COOEt); MS m/z (rel intensity, %) 342 (M^+ −16, 5), 313 (12), 233 (base peak), 204 (28), 203 (42), 191 (38), 163 (61), 161 (23), 159 (22), 145 (52), 116 (25), and 77 (22). Found: C, 66.91; H, 6.27%. Calcd for $C_{20}H_{22}O_4S$: C, 67.02; H, 6.19%.

11c (a 2:1 mixture of E- and Z-isomers (^{13}C NMR)): Yellow liquid; IR (neat) 1730 and 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.18 (2/3×3H, t, J=7.0 Hz, OEt (E)), 1.20 (1/3×3H, t, J=7.0 Hz, OEt (Z)), 2.0—3.0 (4H, m, CH_2CH_2), 4.04 (2/3×2H, q, J=7.0 Hz, OEt (E)), 4.08 (1/3×2H, q, J=7.0 Hz, OEt (Z)), 6.0—6.7 (2H, m, Ar), 7.16 (1/3H, br s, =CH), and 7.3—7.8 (6H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=14.24 (q, OEt), 21.77, 33.41 (each t, CH_2CH_2 (E)), 22.12, 34.06 (each t, CH_2CH_2 (Z)) 60.65 (t, OEt), 114.36, 119.54 (each d), 124.24, 125.83 (each d), 141.60, 142.50 (s, =C), 144.48 (d), and 172.60 (s, COOEt); MS m/z (rel intensity, %) 273 (M^+ −45, 4), 193 (42), 164 (30), 125 (19), 123 (70), 109 (20), 107 (67), 91 (base peak), 78 (56), 77 (63), and 65 (49). Found: C, 63.90; H, 5.70%. Calcd for $C_{17}H_{18}O_4S$: C, 64.13; H, 5.70%.

11d: Pale yellow liquid; IR (neat) 1725 and 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.22 (3H, t, J=7.0 Hz, OEt), 1.88 (3H, dd, J=6.6 and 1.1 Hz, Me), 2.0—2.6 (4H, m, CH_2CH_2), 4.07 (2H, q, J=7.0 Hz, OEt), 6.15 (1H, dq, J=15.0 and 6.6 Hz,

MeCH=), 6.29 (1H, ddd, J=15.0, 6.6, and 1.1 Hz, =CH), and 7.1—7.7 (6H, m, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=14.80 (q, OEt), 18.77 (q, Me), 29.36, 34.00 (each t, CH_2CH_2), 60.59 (t, OEt), 125.24, 129.36 (each d, =CH), 131.19, 134.13, 138.54 (each d), 141.24 (s), 143.48 (s, =C), and 172.31 (s, COOEt); MS m/z (rel intensity, %) 247 (M^+ −45, 17), 167 (57), 97 (base peak), 95 (50), 93 (42), 91 (35), 78 (58), and 77 (37). Found: C, 65.72; H, 6.99%. Calcd for $C_{16}H_{20}O_3S$: C, 65.73; H, 6.89%.

11e: Colorless liquid; IR (neat) 1720 and 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.95 (3H, t, J=7.0 Hz, n-Pr), 1.09 (3H, t, J=7.0 Hz, OEt), 1.4—1.7 (2H, m, n-Pr), 1.7—2.6 (6H, m, CH_2CH_2 and n-Pr), 4.04 (2H, q, J=7.0 Hz, OEt), 6.46 (1H, t, J=7.5 Hz, =CH), and 7.3—7.7(5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=13.82 (q, n-Pr), 14.18 (q, OEt), 19.94, 22.18, 30.30, 33.77 (each t, n-Pr and CH_2CH_2), 60.59 (t, OEt), 125.19, 129.36, 131.13 (each d), 137.17(d), 143.42 (s), 143.83 (s, =Ct), and 172.42 (s, COOEt); MS m/z (rel intensity, %), 294 (M^+, 3), 249 (25), 169 (base peak), 141 (29), 123 (27), 95 (37), and 81 (56). Found: C, 65.09; H, 7.60%. Calcd for $C_{16}H_{22}O_3S$: C, 65.28; H, 7.53%.

12 (a mixture of three isomers including E- and Z-isomers (^{1}H and ^{13}C NMR)): Pale yellow liquid; bp 250 °C/80 Pa (bulb-to-bulb); IR (neat) 1730 and 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.04, 1.16 (3H, each d, J=6.6 Hz, Me), 1.18, 1.19 (3H, each t, J=7.0 Hz, OEt), 1.9—3.1 (3H, m, $CHCH_2$), 3.97, 4.04 (2H, each q, J=7.0 Hz, OEt), 7.00 (0.5H, br s, =CH (Z)), and 7.0—7.8 (10H+0.5H, m, Ph and =CH (E)); ^{13}C NMR ($CDCl_3$) δ=14.12, 16.71, 16.82, 17.59 (each q), 29.47, 29.83, 31.28 (each t, CH_2), 37.77, 38.06, 39.53 (each d, CH), 60.42, 60.59, 60.71 (each t, OEt), 124.48, 125.89, 126.01 (each d), 128.72, 128.89, 129.13, 129.24, 129.48, 129.71, 130.60, 131.66, 132.30 (each d), 134.42, 134.60, 134.72, 137.48 (each s), 143.36, 143.42, 143.78 (each s), 175.24, 175.54, and 176.01 (each s, COOEt); MS m/z (rel intensity, %) 326 (M^+ −16, 10), 297 (16), 217 (base peak), 143 (34), 133 (55), 129 (28), 128 (47), 116 (42), and 91 (35). Found: C, 70.23; H, 6.55%. Calcd for $C_{20}H_{22}O_3S$: C, 70.15; H, 6.48%.

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