Palladium-Catalyzed Terminal Alkyne Coupling Reaction of β-Bromo-β-phenylthio or β-Methylthio-α-trifluoromethyl Enol Ethers: a Convenient Synthesis of 2-Sulfonyl-1-buten-3-ynes

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2-Sulfonyl-1-buten-3-yne (2-sulfonyl enyne) 7 was obtained *via* the Pd-catalyzed cross-coupling reactions of β-bromo enol ethers 3 and 4 and successive oxidation with *m*-chloroperbenzoic acid.

Key words cross-coupling; fluoro enol ether; enyne; sulfide; sulfone

Conjugated enyne compounds have been widely used as a precursor of (*Z*)-enediynes and their analogs, and show a powerful antitumor activity.[1] In exploring new synthetic routes to the enediynes, preparations of various enyne compounds containing chloride,[2] chalcogenide, stannanes and other functional groups[3—5] and their transformations have been examined. We have also investigated the chemistry of the 1-sulfonyl-1-buten-3-ynes (enyne or enediyne sulfones) and reported as follows. The regioselective alkoxide addition to the enyne sulfones has given the α-alkoxy enyne sulfones,[6] which were transformed to the 3-alkynyltetrahydrofurans by treatment with *tert*-BuOK. Other transformations have been shown to afford versatile intermediates such as δ-seleno-1,3-butadiene, alkynylpyrazole,[7,8] alkynyl-cyclopropane or oxirane.[9] Other groups have also carried out intensive investigations and reported useful transformations using enyne chalcogenides.[3,10] However, 2-sulfonyl-1-buten-3-ynes (2-sulfonyl-substituted enynes or enediynes) are quite limited because of their lability in air and light. Our next approach is to prepare 2-sulfonyl enynes and explore their chemistry. We selected highly-functionalized, 2-(phenylsulfonyl)-1-(trifluoromethyl)-substituted enynes because the introduction of a trifluoromethyl group into a Diels–Alder dienophile, a diene or a tetraene[11—13] has obvious advantages in the activation of their chemical or biological reactivity. Here we report the synthesis of 2-sulfonyl-1-trifluoromethyl-1-buten-3-ynes and their reactions with nucleophiles. The β-bromo enol ethers **3** and **4** were prepared from the corresponding enol ethers **1** and **2** by addition of bromine, followed by treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (Chart 1 and Table 1).

The coupling reaction of **3** with *tert*-butylacetylene in the presence of 0.1 eq of $Pd(PPh_3)_4$ and 0.4 eq of CuI gave (*E*)-2-ethoxy-1,1,1-trifluoro-6,6-dimethyl-3-(phenylthio)hept-2-en-4-yne (**5a**) in 88% yield.[14] The structure elucidation of the enyne **5a** was achieved on the basis of spectral data showing an acetylenic absorption at ν 2250 cm^{-1}, a *tert*-butyl signal in the ^{1}H-NMR spectrum, a trifluoromethyl signal at δ 120.51 ($J_{C\text{-}F}$=277 Hz) in the ^{13}C-NMR spectrum and the molecular ion peak at *m/z* 328 ($C_{17}H_{19}F_3OS$) in the mass spectrum. The stereochemistry of **5a** was determined as *E* by the nuclear Overhauser effect (NOE) experiment. Irradiation of the methylene protons of the ethoxy group increased the intensity of the *tert*-butyl group (26%). **3** was reacted with various acetylenes and the results are shown in Table 2. The reaction of **3** with phenylacetylene afforded the enynol ether **5b** in good yield (Entry 2). Acetylenes bearing an *n*-Bu or Me_3Si group gave the coupling products **5c**, **d**, respectively. The reaction of **3** with propargyl alcohol afforded the product **5e** stereoselectively; however, benzyl propargyl ether gave a complex mixture. (*E*)-β-Methylthio derivative **4** also reacted with phenylacetylene to give the enynol ether (*E*)-**6a** in 80% yield, while the reaction of **4** (*Z*:*E*=70:30) gave (*Z*)- and (*E*)-**6a** (*Z*:*E*=70:30) in high yield. The coupling reaction was found to be stereospecific. The reactions of (*E*)- and (*Z*)-**4** (*E*:*Z*=1:1) with propargyl alcohol also afforded (*E*)-**6b** stereoselectively (Entries 9 and 10). Characterization data for

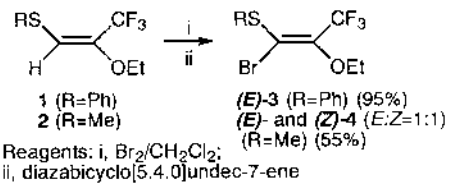

Chart 1

Table 1. Characteristic Spectroscopic Data of the Bromides **3** and **4**

Bromide	IR (Neat) ν (cm^{-1})	^{1}H NMR ($CDCl_3$) δ, *J* (Hz)	^{13}C NMR ($CDCl_3$) δ, $J_{C\text{-}F}$ (Hz)	^{19}F NMR δ
(*E*)-**3**	1180—1100	1.38 (t, *J*=7 Hz, 3H), 4.05 (q, *J*=7 Hz, 2H), 7.32—7.43 (m, 5H)	15.40 ($J_{C\text{-}F}$=3 Hz), 70.82 ($J_{C\text{-}F}$=9 Hz), 120.89 ($J_{C\text{-}F}$=279 Hz, CF_3), 128.65, 129.28, 129.40, 129.52, 131.34, 132.54, 133.70, 148.58 ($J_{C\text{-}F}$=34 Hz)	−1.02
(*E*)-**4**	1200—1100	1.38 (t, *J*=7 Hz, 3H), 3.41 (s, 3H), 3.99 (q, *J*=7 Hz, 2H)	15.22, 19.31, 70.23, 120.67, 120.74 ($J_{C\text{-}F}$=278 Hz, CF_3), 146.36	−16.36
(*Z*)-**4**	1160—1100	1.36 (t, *J*=7 Hz, 3H), 2.42 (s, 2H), 3.96 (q, *J*=7 Hz, 2H)	15.18, 17.97, 69.92, 118.02, 120.67 ($J_{C\text{-}F}$=277 Hz, CF_3), 141.75	15.20

a) All compounds gave satisfactory elemental analyses.

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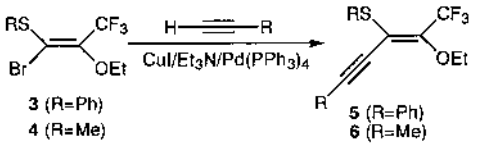
the products are shown in Table 3.

The conversion of the sulfide **5a** to the corresponding sulfone **7** proceeded in 76% yield by the oxidation with *m*-chloroperbenzoic acid (mCPBA). To characterize the titled enyne sulfone **7**, we carried out the reactions with the nucleophiles alkoxides, thiolate and selenolate anions (Chart 2). First, we examined the addition with MeONa to give the allenyl sulfone **8a** *via* the Michael addition and successive isomerization. The structure of **8a** was determined by the IR, ^{1}H-NMR, ^{19}F-NMR, and MS spectra. IR spectrum showed the characteristic allenyl absorption at ν 1960 cm^{-1}. ^{1}H-NMR spectrum exhibited two singlets at δ 5.99 and 6.02 due to the allenic protons. Furthermore, the mass spectrum showed the molecular ion peak at *m/z* 392 ($C_{18}H_{23}F_3O_4S$). The reactions with the other alkoxides afforded the allenyl sulfones **8b** (R=*iso*-Pr), **8c** (R=allyl) and **8d** (R=*tert*-Bu) in moderate to good yields. Next, we examined the reaction with MeSNa in the presence of Bu_4NHSO_4. The allenyl sulfone **9** was also obtained by the regioselective addition reaction. However, the reaction with PhSeNa (generated from $(PhSe)_2$/$NaBH_4$ in EtOH at 0 °C) afforded the δ-(phenylseleno)-1,3-butadiene **10** in stereoselectively. Sulfonyl-substituted 1,3-butadienes[15] and allenyl sulfones[16] are known to be a variety of versatile synthons and are used as the starting materials for the Diels–Alder reactions, Michael additions and cycloadditions. Now we are examining such reactions of our allenyl or dienyl sulfones. These results will be reported elsewhere.

Table 2. Coupling Reactions of β-(Thio)-α-trifluoromethyl Enol Ethers



Entry	Enol ether	Acetylene R	Product (% yield) $(E/(E+Z)\times100)$
1	**3**	*tert*-Bu	**5a** (88) (>99)
2	**3**	Ph	**5b** (80) (>99)
3	**3**	*n*-Bu	**5c** (62) (>99)
4	**3**	Me_3Si	**5d** (87) (>99)
5	**3**	CH_2OH	**5e** (89) (>99)
6	**3**	CH_2OBn	—
7	(*E*)-**4**	Ph	(*E*)-**6a** (80) (>99)
8	(*E*)- and (*Z*)-**4**[a]	Ph	(*E*)- and (*Z*)-**6a** (93) (30)
9	(*E*)- and (*Z*)-**4**[b]	CH_2OH	(*E*)-**6b** (89) (>99)

a) *E* : *Z*=30 : 70, *b*) *E* : *Z*=50 : 50.

Experimental

^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded using a Varian Inova400 spectrometer; chemical shifts are reported in ppm using $CDCl_3$ as solvent and tetramethylsilane as internal standard. ^{19}F-NMR are reported in

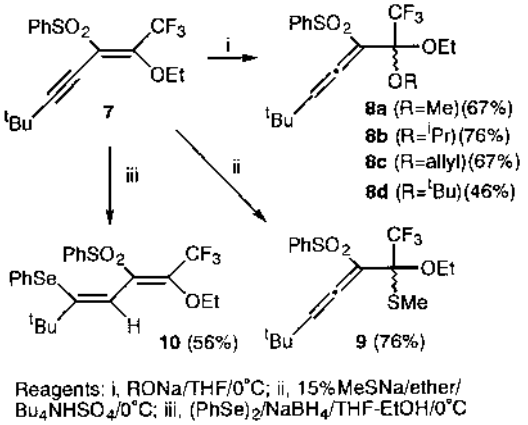


Chart 2

Table 3. Characteristic Spectroscopic Data of the Products **5** and **6**

Product[a]	IR (Neat) ν (cm^{-1})	^{1}H NMR ($CDCl_3$) δ, J (Hz)	^{13}C NMR ($CDCl_3$) δ, $J_{C\text{-}F}$ (Hz)	^{19}F NMR δ
5a	2200, 1180, 1100	1.41 (t, J=7 Hz, 3H), 4.10 (q, J=7 Hz, 2H), 6.86—6.88 (m, 2H), 7.12—7.21 (m, 3H), 7.30—7.40 (m, 3H), 7.54—7.56 (m, 2H)	15.43, 60.29, 70.09, 79.81, 102.35, 123.40 ($J_{C\text{-}F}$=276 Hz, CF_3), 121.79, 128.08, 128.81, 128.89, 129.18, 130.24, 131.23, 133.51, 135.93	−1.01
5b	2250	0.89 (s, 9H), 1.41 (t, J=7 Hz, 3H), 4.05 (q, J=7 Hz, 2H), 7.34—7.36 (m, 3H), 7.49—7.52 (m, 2H)	15.17, 29.58, 29.88, 69.61, 77.14, 112.14 ($J_{C\text{-}F}$=2 Hz), 118.84, 120.51 ($J_{C\text{-}F}$=277 Hz, CF_3), 128.49, 128.85, 130.26, 136.84, 141.39 ($J_{C\text{-}F}$=33 Hz, 2-C)	−1.02
5c	2225, 1190, 1130	0.77 (t, J=7 Hz, 3H), 1.10—1.13 (m, 4H), 1.41 (t, J=7 Hz, 3H), 2.01 (t, J=5 Hz, 2H), 4.05 (q, J=7 Hz, 2H), 7.33—7.35 (m, 3H), 7.47—7.50 (m, 2H)	13.44, 15.34, 19.07, 21.64, 29.76, 69.92, 71.17, 104.90, 119.28, 120.65 ($J_{C\text{-}F}$=326 Hz, CF_3), 128.58, 128.74, 128.88, 130.64, 135.52	−1.41
5d	2170, 1180, 1120	0.15 (s, 9H), 1.65 (t, J=7 Hz, 3H), 4.31 (q, J=7 Hz, 2H), 7.58—7.60 (m, 3H), 7.73—7.75 (m, 2H)	0.93, 32.50, 70.02, 93.59, 109.18, 120.39 ($J_{C\text{-}F}$=277 Hz, CF_3), 128.77, 128.80, 129.18, 130.18, 135.90, 143.39 ($J_{C\text{-}F}$=33 Hz, 2-C)	−14.72
5e	3600—3100, 2225, 1190, 1120	1.22 (br s, 1H), 1.42 (t, J=7 Hz, 3H), 3.98 (d, J=6 Hz, 2H), 4.09 (q, J=7 Hz, 2H), 7.37—7.40 (m, 3H), 7.51—7.53 (m, 2H)	15.30, 50.92, 70.09, 76.23, 100.71 ($J_{C\text{-}F}$=2 Hz), 117.24, 120.24 ($J_{C\text{-}F}$=277 Hz, CF_3), 128.71, 129.24, 130.21, 135.82, 142.92 ($J_{C\text{-}F}$=33 Hz, 2-C)	−13.82
(*E*)-**6a**	2180, 1170, 1100	1.38 (t, J=7 Hz, 3H), 2.46 (s, 3H), 4.02 (q, J=7 Hz, 2H), 7.30—7.40 (m, 3H), 7.43—7.53 (m, 2H)	14.74, 15.35, 69.66, 78.66, 102.40, 118.02, 120.65 ($J_{C\text{-}F}$=277 Hz, CF_3), 128.47, 129.24, 131.52, 132.46, 142.56 ($J_{C\text{-}F}$=34 Hz, 2-C)	0.41
(*Z*)-**6a**		1.39 (t, J=7 Hz, 3H), 2.47 (s, 3H), 4.15 (q, J=7 Hz, 2H)		0.23
(*E*)-**6b**	3600—3100, 2800—3000	1.38 (t, J=7 Hz, 3H), 2.13 (br s, 1H), 2.38 (s, 3H), 3.98 (q, J=7 Hz, 2H), 4.51 (br s, 2H)	14.74, 15.29, 51.39, 69.63, 74.94, 100.54, 120.40 ($J_{C\text{-}F}$=276 Hz, CF_3), 120.64, 135.18	−0.23

a) All compounds gave satisfactory elemental analyses.

ppm using CF_3CO_2H as an external standard. IR spectra were obtained on a JASCO IRA-100. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. Melting points were determined on a Yanaco micromelting point apparatus and are uncorrected. Electron impact (EI) mass was obtained using a Shimadzu QP-1000 spectrometer with a direct insertion probe at an ionization voltage of 70 eV. The enol ethers **1** and **2** were prepared as in our previous report.[17)]

A Synthesis of 1-Bromo-2-ethoxy-3,3,3-trifluoro-1-(methylthio)- or 1-(phenylthio)propenes 3 and 4. General Procedure Bromine (6.38 g, 39.9 mmol) was added dropwise to a CH_2Cl_2 (46 ml) solution of the enol ether (26.6 mmol) at 0 °C. The mixture was stirred for 30 min at room temperature, and the solvent was removed under reduced pressure. The residue was diluted with dry ether (65 ml). 1,8-Diazabicyclo[5.4.0]undec-7-ene (4.89 g, 31.9 mmol) was added to the ether solution under an Ar atmosphere at 0 °C, and the whole was stirred for 30 min and poured into water (150 ml). The organic layer was separated, the aqueous layer was extracted with ether (50×3 ml), and the combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica-gel eluting with hexane to give the bromides quantitatively. The characterization data are shown in Table 1. The stereochemistries of (*E*)-**3**, (*E*)- and (*Z*)-**4** were determined by the NOE experiments. That of compound **4** was also assigned to the ^{19}F-NMR chemical shift method[18)] of the two isomers. The downfield signal exhibiting absorption at δ −15.20 was assigned as the trifluoromethyl group of *Z*-isomer which has a trifluoromethyl group with a greater steric interaction.

Pd(0) Catalyzed Cross-Coupling Reaction of β-Bromo-β-sulfur-α-trifluoromethyl Enol Ethers with Alkynes. General Procedure To a benzene (20.0 ml) and triethylamine (5.00 ml) solution of 3-bromo-2-ethoxy-1,1,1-trifluoroprop-2-ene (7.64 mml) was added an alkyne (15.3 mmol), CuI (0.58 g, 3.10 mmol) and $Pd(PPh_3)_4$ (1.77 g, 1.53 mmol) at room temperature. The reaction mixture was stirred for 2 h under an Ar atmosphere, poured into water (100 ml) and the organic layer separated. The aqueous layer was extracted with ether (30×3 ml). The organic layer and the extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica-gel eluting with hexane. The enyne sulfides were obtained in the yields shown in Table 2. Their characterization data are shown in Table 3.

Oxidation of Enynyl Sulfide 5a with mCPBA To a 1,2-dichloroethane (50.0 ml) solution of (*E*)-2-ethoxy-1,1,1-trifluoro-6,6-dimethyl-3-(phenylthio)hept-2-en-4-yne (**5a**) (1.91 g, 5.83 mmol) was added mCPBA (2.77 g, 12.8 mmol) at 0 °C. The mixture was stirred for 30 min and poured into $CHCl_3$ (100 ml). The $CHCl_3$ solution was washed with saturated $NaHCO_3$ (50×3 ml) solution. The organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica-gel eluting with AcOEt–hexane (1 : 40) to give (*E*)-2-ethoxy-1,1,1-trifluoro-6,6-dimethyl-3-(phenylsulfonyl)hept-2-en-4-yne (**7**), (1.93 g, 92%) as colorless oil. IR (film) cm^{-1}: 2200 (acetylene), 1330, 1220-1060 (SO_2). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.15 (9H, s, *tert*-Bu), 1.43 (3H, t, *J*=7 Hz, Me), 4.13—4.19 (2H, m, OCH_2), 7.46—7.59 (2H, m, ArH), 7.63—7.67 (1H, m, ArH), 7.91—8.03 (2H, m, ArH). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.14 (q), 29.66 (s), 29.96 (q×3), 67.75 (s), 72.68 (t), 115.98 (s), 119.83 (s, $J_{C\text{-}F}$=282 Hz, CF_3), 128.72 (d×2), 128.93 (d×2), 129.89 (s), 134.05 (d), 140.05 (s), 152.46 (s, $J_{C\text{-}F}$=34 Hz, 2-C). ^{19}F-NMR δ: −8.63 (3F, s, CF_3); MS m/z: 360 (M^+). *Anal.* Calcd for $C_{17}H_{19}F_3O_3S$: C, 56.66; H, 5.31. Found: C, 56.57; H, 5.29.

A Reaction of Enyne Sulfone 7 with Sodium Alkoxide. Typical Procedure A MeOH (1 ml) solution of NaOMe (1.0 mmol) was added dropwise to a tetrahydrofuran (THF) (2.0 ml) solution of **7** (0.18 g, 0.50 mmol) at 0 °C. The mixture was stirred for 10 min and poured into water (100 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica-gel eluting with AcOEt–hexane (1 : 10) to give 2-ethoxy-1,1,1-trifluoro-2-methoxy-6,6-dimethyl-3-(phenylsulfonyl)hept-3,4-diene (**8a**), (0.13 g, 67%) as colorless prisms. **8a**: diastereoisomer ratio=1 : 1, mp 71—72 °C. IR (KBr) cm^{-1}: 1960 (allene), 1320, 1220—1150 (SO_2). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.10 (t, *J*=7 Hz, Me), 1.14 (s, Me), 1.15 (s, Me), 1.78 (t, *J*=7 Hz, Me), 3.29 (s, OMe), 3.36 (s, OMe), 3.38—3.72 (m, OCH_2), 5.99 (s, allenic H), 6.02 (s, allenic H), 7.48—7.57 (m, ArH), 7.58—7.60 (m, ArH), 7.88—7.92 (m, ArH). ^{19}F-NMR δ: −4.41 (s, CF_3), −4.53 (s, CF_3); MS *m/z*: 392 (M^+). *Anal*. Calcd for $C_{18}H_{23}F_3O_4S$: C, 55.09; H, 5.91. Found: C, 54.92; H, 5.87. 2-Ethoxy-1,1,1-trifluoro-6,6-dimethyl-3-(phenylsulfonyl)-2-isopropoxyhept-3,4-diene (**8b**): diastereoisomer ratio=1 : 1, IR (film) cm^{-1}: 1960 (allene), 1320, 1200—1050 (SO_2). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.82 (d, *J*=6 Hz, Me), 0.94 (d, *J*=6 Hz, Me), 1.07 (d, *J*=6 Hz, Me), 1.14 (t, *J*=7 Hz, Me), 1.15 (t, J=7 Hz, Me), 1.17 (s, *tert*-Bu), 1.18 (s, *tert*-Bu), 3.63—3.76 (m, OCH_2), 3.77—3.85 (m, OCH_2), 4.29—4.37 (m, CHO), 4.50—4.56 (m, OCH), 5.98 (s, allenic H), 6.02 (s, allenic H), 7.42—7.52 (m, ArH), 7.55—7.62 (m, ArH), 7.88—7.90 (m, ArH). ^{19}F-NMR δ: −0.75 (s, CF_3), −0.66 (s, CF_3). MS *m/z*: 361 (M^+-isopropyloxy). *Anal.* Calcd for $C_{20}H_{27}F_3O_4S$: C, 57.13; H, 6.47. Found: C, 56.89; H, 6.42. 2-Allyloxy-2-ethoxy-1,1,1-trifluoro-6,6-dimethyl-3-(phenylsulfonyl)hept-3,4-diene (**8c**): diastereoisomer ratio=1 : 1. IR (film) cm^{-1}: 1960 (allene), 1320, 1230—1050 (SO_2). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.14 (s, *tert*-Bu), 1.15 (s, *tert*-Bu), 3.54—3.78 (m, OCH_2), 3.99—4.25 (m, OCH_2), 5.15—5.18 (m, olefinic H), 5.28—5.36 (m, olefinic H), 5.75—5.88 (m, olefinic H), 5.98 (s, allenic H), 6.00 (s, allenic H), 7.45—7.53 (m, ArH), 7.55—7.59 (m, ArH), 7.88—7.90 (m, ArH). ^{19}F-NMR δ: −0.30 (s, CF_3), 0.05 (s, CF_3); MS *m/z*: 418 (M^+). *Anal*. Calcd for $C_{20}H_{25}F_3O_4S$: C, 57.40; H, 6.02. Found: C, 57.21; H, 5.96. 2-*tert*-Butoxy-2-ethoxy-1,1,1-trifluoro-6,6-dimethyl-3-(phenylsulfonyl)hept-3,4-diene (**8d**): diastereoisomer ratio=17 : 1. IR (film) cm^{-1}: 1950 (allene), 1320, 1220—1000 (SO_2). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.13 (9H, s, *tert*-Bu), 1.20 (3H, t, *J*=7 Hz, Me), 1.33 (9H, s, *tert*-Bu), 3.62—3.71 (1H, m, OCH_2), 3.82—3.90 (1H, m, OCH_2), 5.85 (1H, s, olefinic H), 7.46—7.51 (2H, m, ArH), 7.55—7.59 (1H, m, ArH), 7.88—7.92 (2H, m, ArH). ^{19}F-NMR δ: −1.38 (s, CF_3), −1.97 (s, CF_3). MS *m/z*: 361 (M^+-*tert*-BuO). *Anal*. Calcd for $C_{21}H_{29}F_3O_4S$: C, 58.05; H, 6.73. Found: C, 57.79; H, 6.49. The ratio of the diastereomers was determined by the intensities of CF_3 in the ^{19}F-NMR spectrum.

A Reaction of Enyne Sulfone 7 with Sodium Methanethiolate A 15% NaSMe solution (1 ml) was added dropwise to an ether (2 ml) solution of **7** (0.18 g, 0.50 mmol) and Bu_4NHSO_4 (0.01 g, 0.03 mmol) at 0 °C. The mixture was stirred for 30 min and poured into water (50 ml). The organic layer was separated, the aqueous layer was extracted with ether, and the combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica-gel eluting with AcOEt–hexane (1 : 20) to give 2-ethoxy-1,1,1-trifluoro-6,6-dimethyl-2-(methylthio)-3-(phenylsulfonyl)hept-3,4-diene (**9**), (0.12 g, 74%) as colorless prisms. **9**: diastereoisomer ratio=55 : 45, mp 70—72 °C. IR (KBr) cm^{-1}: 1950 (allene), 1320, 1260, 1220—1140 (SO_2). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.04 (s, *tert*-Bu), 1.09 (s, *tert*-Bu), 1.25 (t, *J*=7 Hz, Me), 1.32 (t, *J*=7 Hz, Me), 2.06 (d, *J*=1 Hz, SMe), 2.12 (d, *J*=1 Hz, SMe), 3.71—3.78 (m, OCH_2), 3.89—3.97 (m, OCH_2), 5.80 (s, allenic H), 5.90 (s, allenic H), 7.48—7.53 (m, ArH), 7.57—7.62 (m, ArH), 7.90—7.93 (m, ArH). ^{19}F-NMR δ: −4.54 (s, CF_3), −5.25 (s, CF_3). MS *m/z*: 408 (M^+). *Anal*. Calcd for $C_{18}H_{23}F_3O_3S_2$: C, 52.93; H, 5.68. Found: C, 52.80; H, 5.66.

A Reaction of Enynyl Sulfone 7 with PhSeNa An EtOH (2.00 ml) solution of PhSeNa (generated from $(PhSe)_2$ (0.13 g, 0.42 mmol) and $NaBH_4$ (52 mg, 1.38 mmol)) was added dropwise to a THF (1.00 ml) solution of the enyne sulfone **7** (0.25 g, 0.69 mmol) at 0 °C. The reaction mixture was stirred for 10 min and poured into water (100 ml). The organic layer was separated, the aqueous layer was extracted with ether, and the combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica-gel eluting with AcOEt–hexane (1 : 100) to give (2*E*,4*Z*)-2-ethoxy-1,1,1-trifluoro-6,6-dimethyl-5-(phenylseleno)-3-(phenylsulfonyl)hepta-2,4-diene (**10**) (0.20 g, 56%) as a yellow oil. IR (film) cm^{-1}: 3050—2860, 1480, 1320, 1200, 1150, 1000, 900, 860, 820, 760. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.14 (9H, s, *tert*-Bu), 1.41 (3H, t, *J*=7 Hz, Me), 3.96—4.04 (1H, m, OCH_2), 4.14—4.22 (1H, m, OCH_2), 6.20 (1H, s, olefinic H), 7.22—7.29 (3H, m, ArH), 7.49—7.59 (4H, m, ArH), 7.61—7.65 (1H, m, ArH), 8.23—8.26 (2H, m, ArH). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 10.77 (q), 29.65 (q×3), 37.57 (s), 70.81 (t), 119.70 (s, $J_{C\text{-}F}$=282 Hz, CF_3), 128.72 (d), 128.60 (d×2), 129.42 (d×2), 129.73 (d×2), 131.34 (s), 133.88 (d), 134.25 (d×2), 134.76 (s), 136.53 (s), 141.97 (s), 145.89 (s, $J_{C\text{-}F}$=33 Hz, 2-C), 155.03 (d, $J_{C\text{-}F}$=2 Hz, 4-C). MS *m/z*: 518 (M^+). *Anal*. Calcd for $C_{23}H_{25}F_3O_3SSe$: C, 53.39; H, 4.87. Found: C, 53.42; H, 4.91.

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