# Direct Lithiation and Alkylation of Trifluoromethyl Enol Ethers Having a $\beta$-Sulfur Substituent

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**The direct lithiation and alkylation of $\beta$-sulfur-$\alpha$-trifluoromethyl substituted enol ethers 1—3 proceeded to give the alkylated products 4a—f, 5, 6a—c in moderate to high yields.**

**Key words** trifluoromethyl; enol ether; vinyl sulfide

In recent years, much attention has been focused on the trifluoromethyl-substituted ethenyl carbanions and their synthetic equivalents, due to the convenience of the preparation of trifluoromethyl-containing building blocks or the remarkable ability of these intermediates to function as a useful precursor for introducing the trifluoromethyl group into organic molecules.[1] Particularly, ethenyl zinc reagents have been extensively investigated and can be applied to transition metal catalyzed C–C bond formations;[2] however, their lithium reagents are quite limited because they are thermally unstable.[3] Bonnet-Delpon has also reported that the $\alpha$-ethoxy-$\alpha$-trifluoromethyl $\beta$-ethenyl carbanion is difficult to generate from a strong base, because the $\alpha$-trifluoromethyl-substituted enol ethers undergo the addition of alkyllithiums at the $\alpha$-position of the ethoxy group and afford trifluoromethyl alkenes *via* the successive elimination of lithium ethoxide.[4] Recently, a method using the halogen–lithium exchange reaction of bromovinylic ethers has been reported as an alternative route.[5] If the $\beta$-trifluoromethyl-substituted ethenyl lithiums are conveniently generated, we could provide a suitable precursor for the preparations of trifluoromethyl-substituted vinylic or allylic compounds. Thus, we preliminarily prepared $\alpha$-trifluoromethyl enol ethers having a $\beta$-sulfur substituent as a stabilizing group for the ethenyl carbanion[6] and examined their direct lithiations and alkylations. Here we report the generation of the lithiated trifluoromethyl enol ethers using alkyllithium and their alkylation reactions.

Preparation of the $\beta$-sulfur-substituted $\alpha$-trifluoromethyl enol ethers **1**—**3** are shown in Chart 1. The treatment of ethyl trifluoroacetate or *S*-ethyl trifluorothioacetate with sulfur-substituted phosphonium ylides successfully afforded **1**—**3** in good yield.[7] The spectral data of these enol ethers **1**—**3** are summarized in Table 1. The stereostructures of these enol ethers **1**—**3** were determined to be *E* by nuclear Overhauser effect (NOE) experiments. The irradiation of methylene protons of the YEt group increased the intensity of each olefinic proton as 11.8% (**1**), 7.3% (**2**) and 19.5% (**3**), respectively.

A tetrahydrofuran (THF)-solution of **1** treated with BuLi at −70 °C changed color to pale yellow, and the successive addition of methyl iodide produced the methylated enol ether **4a** in 70% yield (Table 2, entry 1). The stereostructure of **4a** was determined by the NOE experiment. Irradiation of the $\alpha$-Me group of the sulfur atom increased the intensity of the methylene protons of the EtO group. We also examined lithiations with other bases. When lithium diisopropylamide (LDA) was used as a base, the addition–elimination reaction took place at the $\alpha$-position of the ethoxy group and afforded the $\beta$-amino vinyl sulfide **7** in 24% yield (Chart 2).[7] Reactions with other electrophiles were examined using BuLi and these results are shown in Table 2. The reaction of **1** with BnBr and allyl bromide gave **4b** and **4c**, respectively (entries 2, 3). Treatment of **1** with EtOD quantitatively afforded the deuterated enol ether **4d** (entry 4). The $Me_3Si$- and MeS-groups were also introduced into the enol ethers in high yield (entries 5, 6). Next, we examined the alkylation of **2** ($R^1$=Me) with BnBr at −78 °C to give the product **5** in moderate yield (entry 7). The $\alpha,\beta$-dithiosubstituted enol ether **3** reacted with various electrophiles in high yield (entries 8—10). These products **5** and **6** were also obtained as (*E*)-stereoisomers.

In conclusion, we reported the novel lithiation and alkylation of $\alpha$-trifluoromethyl enol ethers having a $\beta$-sulfur substituent. Now we are looking into converting these enol ethers to the corresponding vinyl sulfones and investigating their vinyl sulfone chemistry.

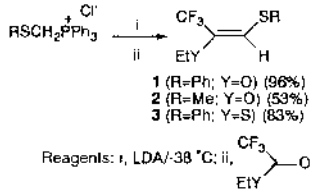


Chart 1

Table 1. NMR Data of $\beta$-Sulfur-substituted Enol Ethers **1**—**3**

| Enol | $^1$H-NMR $\delta$ Olefinic H | $^{13}$C-NMR $\delta$ | | | $^{19}$F-NMR $\delta$ |
|---|---|---|---|---|---|
| | | $CF_3$ | $\alpha$-C | $\beta$-C | |
| **1** | 6.47 (br s) | 120.41 ($J$=275 Hz) | 139.95 ($J$=34 Hz) | 117.75 ($J$=5 Hz) | −8.94 |
| **2** | 6.21 (br s) | 120.69 ($J$=274 Hz) | 139.03 ($J$=34 Hz) | 120.22 ($J$=4 Hz) | −8.75 |
| **3** | 7.61 (br s) | 122.99 ($J$=272 Hz) | 117.24 ($J$=34 Hz) | 148.22 ($J$=5 Hz) | −13.81 |

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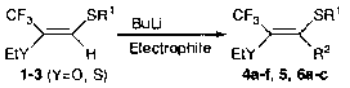
Table 2. Alkylations of $\beta$-(Thio)-$\alpha$-perfluoroalkyl Enol Ethers




| Entry | Enol ether | | | Electrophile | Product (% yield) ($R^2$) |
|---|---|---|---|---|---|
| | | Y | $R^1$ | | |
| 1 | **1** | O | Ph | MeI | **4a** (Me) (70) |
| 2 | **1** | O | Ph | BnBr | **4b** (Bn) (71) |
| 3 | **1** | O | Ph | Allyl bromide | **4c** (allyl) (62) |
| 4 | **1** | O | Ph | EtOD | **4d** (D) (quant.) |
| 5 | **1** | O | Ph | $Me_3SiCl$ | **4e** ($Me_3Si$) (quant.) |
| 6 | **1** | O | Ph | $(MeS)_2$ | **4f** (MeS) (82) |
| 7 | **2** | O | Me | BnBr | **5** (Bn) (44) |
| 8 | **3** | S | Ph | MeI | **6a** (Me) (91) |
| 9 | **3** | S | Ph | Allyl bromide | **6b** (allyl) (62) |
| 10 | **3** | S | Ph | $(MeS)_2$ | **6c** (MeS) (89) |

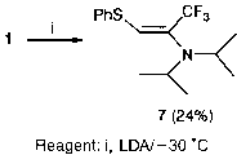



Chart 2

## Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. $^1$H- and $^{13}$C-NMR spectra were determined with a Varian Inova-400 (400 MHz) spectrometer at the Center of Instrumentation of Gifu University. Chemical shifts are expressed in parts per million (ppm) with respect to tetramethylsilane as an internal standard. Chemical shifts of $^{19}$F-NMR were reported in ppm downfield from the external trifluoroacetic acid. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet. *J*-Values are given in Hz. The IR spectra of solids (KBr) and liquids (film) were recorded on a JASCO IR A-100 infrared spectrometer. Electron impact-mass spectra (EI-MS) were obtained using a JMS-SX102A spectrometer with a direct-insertion probe at an ionization voltage of 70 eV. The stereochemistries of compounds **1**—**3**, **4a**, **5** and **6a** were determined by the NOE experiments, respectively.

**Synthesis of 2-Ethoxy-3-(phenylthio)- (1), 2-Ethoxy-3-(methylthio)- (2) and 2-(Ethylthio)-3-(phenylthio)-1,1,1-trifluoro-2-propene (3), Typical Procedure** BuLi was added dropwise to (phenylthiomethyl)triphenylphosphonium chloride (16.8 g, 40.0 mmol) in THF (140 ml) at −38 °C under an Ar atmosphere. The mixture was stirred for 10 min. Ethyl trifluoroacetate (9.52 g, 80.0 mmol) was added to the mixture. The whole was stirred for 3 d at room temperature and poured into water (150 ml). The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over $MgSO_4$. The solvent was removed under reduced pressure to form powdered triphenylphosphine oxide. The powder was filtered off and washed with pentane. The pentane extracts were evaporated and the residue was purified by coloumn chromatography on silica gel elution with hexane to give (*E*)-2-ethoxy-3-(phenylthio)-1,1,1-trifluoroprop-2-ene (**1**) (7.93 g, 80%) as a colorless oil. **1**: IR (film, cm$^{-1}$) 1630, 1330, 1180, 1120, 1080, 840, 740; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.37 (3H, t, $J$=7 Hz), 4.11 (2H, q, $J$=7 Hz, $OCH_2$), 6.48 (1H, d, $J$=1 Hz, olefinic H), 7.27—7.36 (3H, m, ArH), 7.40—7.42 (2H, m, ArH); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 15.36 (q), 69.00 (t, $J_{C\text{-}F}$=3 Hz, $OCH_2$), 117.75 (d, $J_{C\text{-}F}$=5 Hz, 3-C), 120.41 (s, $J_{C\text{-}F}$=275 Hz, $CF_3$), 127.83 (d), 129.40 (d×2), 130.45 (d×2), 133.61 (s), 139.95 (s, $J_{C\text{-}F}$=34 Hz, 2-C); $^{19}$F-NMR (376.4 MHz) $\delta$: −8.94 (3F, s, $CF_3$); MS *m/z*: 171 ($M^+$−Ph). *Anal*. Calcd for $C_{11}H_{11}F_3OS$: C, 53.22; H, 4.47. Found: C, 53.24; H, 4.50.

(*E*)-2-Ethoxy-3-(methylthio)-1,1,1-trifluoroprop-2-ene (**2**): A pale yellow oil, 53%, IR (film, cm$^{-1}$) 1180—1060 (C–O–C); $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.33 (3H, t, $J$=7 Hz, Me), 2.35 (3H, s, Me), 4.02 (2H, q, $J$=7 Hz, $OCH_2$), 6.21 (1H, br s, olefinic H); $^{13}$C-NMR (100 MHz,$CDCl_3$) $\delta$: 15.36 (q), 16.98 (q), 68.53 (t), 120.22 (d, $J_{C\text{-}F}$=4 Hz, 3-C), 120.69 (s, $J_{C\text{-}F}$=274 Hz, $CF_3$), 139.03 (s, $J_{C\text{-}F}$=34 Hz, 2-C); $^{19}$F-NMR (376.4 MHz) $\delta$: −8.70 (3F, s, $CF_3$); MS *m/z*: 186 ($M^+$).

(*E*)-2-(Ethylthio)-3-(phenylthio)-1,1,1-trifluoroprop-2-ene (**3**): IR (film, cm$^{-1}$) 1580, 1320—1240, 1200—1100; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.33 (3H, t, $J$=7 Hz, Me), 2.86 (2H, q, $J$=7 Hz, $CH_2$), 7.24—7.40 (3H, m, ArH), 7.43—7.47 (2H, m, ArH), 7.61 (1H, d, $J$=1 Hz, olefinic H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.91 (q), 28.62 (t), 117.24 (s, $J_{C\text{-}F}$=34 Hz), 122.99 (s, $J_{C\text{-}F}$=273 Hz, $CF_3$), 128.80 (d), 129.74 (d×2), 131.61 (d×2), 133.00 (s), 147.99 (d, $J_{C\text{-}F}$=3 Hz, 2-C); $^{19}$F-NMR (376.4 MHz) $\delta$: −13.81 (3F, s, $CF_3$); MS *m/z*: 264 ($M^+$). *Anal*. Calcd for $C_{11}H_{11}F_3S_2$: C, 49.98; H, 4.19. Found: C, 50.23; H, 4.28.

**Alkylation of (*E*)-2-Ethoxy-3-(phenylthio)-1,1,1-trifluoroprop-2-ene (1) with BuLi/MeI, a Typical Procedure** Under an Ar atmosphere, BuLi (1.00 ml, 1.50 mmol) was added to a THF (2.00 ml) solution of **1** (0.25 g, 1.00 mmol) at −78 °C. The reaction mixture was stirred for 10 min and then a THF (1.00 ml) solution of MeI (0.71 g, 5.00 mmol) was added to the mixture. The whole was stirred for 10 min and poured into water (100 ml) and the organic layer was separated. The aqueous layer was extracted with ether. 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 elution with hexane to give (*E*)-2-ethoxy-3-(phenylthio)-1,1,1-trifluorobut-2-ene (**4a**) (0.22 g, 84%) as a yellow oil. **4a**: IR (film, cm$^{-1}$) 1220—1100 (C–O–C); $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.37 (3H, t, $J$=7 Hz, Me), 1.79 (3H, q, $J$=2 Hz, Me), 3.98 (2H, q, $J$=7 Hz, $OCH_2$), 7.32—7.36 (3H, m, ArH), 7.43—7.46 (2H, m, ArH); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 15.46 (q), 16.01 (q), 69.48 (t), 121.98 (s, $J_{C\text{-}F}$=227 Hz, $CF_3$), 128.98 (d), 129.33 (d×2), 130.68 (s), 131.30 (s), 135.04 (d×2), 137.58 (s, $J_{C\text{-}F}$=34 Hz, 2-C); $^{19}$F-NMR (376.4 MHz) $\delta$: −16.58 (3F, s, $CF_3$); MS *m/z*: 233 ($M^+$−Et). *Anal.* Calcd for $C_{12}H_{13}F_3OS$: C, 54.95; H, 5.00. Found: C, 54.99; H, 5.00.

(*E*)-2-Ethoxy-4-phenyl-3-(phenylthio)-1,1,1-trifluorobut-2-ene (**4b**): IR (film, cm$^{-1}$) 1220—1100 (C–O–C); $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.40 (3H, t, $J$=7 Hz, Me), 3.58 (2H, s, $CH_2$), 4.07 (2H, q, $J$=7 Hz, $OCH_2$), 6.86—6.89 (2H, m, ArH), 7.15—7.22 (7H, m, ArH), 7.26—7.29 (1H, m, ArH); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 15.53 (q), 34.24 (t), 69.85 (t), 121.70 (s, $J_{C\text{-}F}$=277 Hz, $CF_3$), 126.61 (d), 128.35 (d×2), 128.37 (d×2), 128.83 (d), 129.04 (d×2), 130.18 (s), 133.97 (s), 135.02 (d×2), 137.23 (s), 139.69 (s, $J_{C\text{-}F}$=33 Hz, 2-C); $^{19}$F-NMR (376.4 MHz) $\delta$: −16.69 (3F, s, $CF_3$); MS *m/z*: 338 ($M^+$). *Anal.* Calcd for $C_{18}H_{17}F_3OS$: C, 63.89; H, 5.06. Found: C, 63.81; H, 5.13.

(*E*)-2-Ethoxy-3-(phenylthio)-1,1,1-trifluorohex-2,5-diene (**4c**): IR (film, cm$^{-1}$) 1220—1100 (C–O–C); $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.37 (3H, t, $J$=7 Hz, Me), 2.92—2.95 (2H, m, $CH_2$), 4.00 (2H, q, $J$=7 Hz, $OCH_2$), 4.86 (1H, dd, $J$=2, 15 Hz, olefinic H), 4.98 (1H, dd, $J$=1, 10 Hz, olefinic H), 5.57—5.64 (1H, m, olefinic H), 7.31—7.35 (3H, m, ArH), 7.41—7.44 (2H, m, ArH); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 15.46 (q), 32.69 (t), 69.76 (t), 117.06 (t), 121.62 (s, $J_{C\text{-}F}$=278 Hz, $CF_3$), 128.88 (d), 129.27 (d×2), 130.78 (s), 133.14 (s, $J_{C\text{-}F}$=3 Hz, 3-C), 133.97 (d), 134.73 (d×2), 139.29 (s, $J_{C\text{-}F}$=34 Hz, 2-C); $^{19}$F-NMR (376.4 MHz) $\delta$: −7.52 (3F, s, $CF_3$); MS *m/z*: 288 ($M^+$). *Anal.* Calcd for $C_{14}H_{15}F_3OS$: C, 58.32; H, 5.24. Found: C, 57.31; H, 5.25.

(*E*)-2-Ethoxy-3-deuterio-3-(phenylthio)-1,1,1-trifluoroprop-2-ene (**4d**): IR (film, cm$^{-1}$) 1220—1100 (C–O–C); $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.37 (3H, t, $J$=7 Hz, Me), 4.11 (2H, q, $J$=7 Hz, $OCH_2$), 7.26—7.34 (3H, m, ArH), 7.38—7.40 (2H, m, ArH); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 15.54 (q), 69.19 (t), 117.79 (s, $J_{C\text{-}F}$=27 Hz, 3-C), 120.63 (s, $J_{C\text{-}F}$=275 MHz, $CF_3$), 128.02 (d), 129.60 (d×2), 130.61 (d×2), 133.78 (s), 140.11 (s, $J_{C\text{-}F}$=34 Hz, 2-C); $^{19}$F-NMR (376.4 MHz) $\delta$: −8.83 (3F, s, $CF_3$); MS *m/z*: 249 ($M^+$). *Anal.* Calcd for $C_{11}H_{10}DF_3OS$: C, 53.00; H, 4.04. Found: C, 52.92; H, 4.40.

(*E*)-2-Ethoxy-3-(phenylthio)-1,1,1-trifluoro-3-(trimethylsilyl)prop-2-ene (**4e**): IR (film, cm$^{-1}$) 1220—1100 (C–O–C); $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 0.17 (9H, s, Me×3), 1.18 (3H, t, $J$=7 Hz, Me), 4.00 (2H, q, $J$=7 Hz, $OCH_2$), 7.15—7.28 (5H, m, ArH); $^{19}$F-NMR (376.4 MHz) $\delta$: −13.71 (3F, s, $CF_3$); MS *m/z*: 320 ($M^+$). *Anal.* Calcd for $C_{14}H_{19}F_3OSSi$: C, 52.48; H, 5.98. Found: C, 52.69; H, 5.86.

(*E*)-2-Ethoxy-3-(methylthio)-3-(phenylthio)-1,1,1-trifluoroprop-2-ene (**4f**): IR (film, cm$^{-1}$) 1220—1100 (C–O–C); $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.32 (3H, t, $J$=7 Hz, Me), 2.12 (3H, s, Me), 4.00 (2H, q, $J$=7 Hz, $OCH_2$), 7.31—7.33 (3H, m, ArH), 7.36—7.39 (2H, m, ArH); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 15.20 (q), 17.63 (q), 70.33 (t), 120.98 (s, $J_{C\text{-}F}$=278 Hz, $CF_3$), 127.83 (d), 128.94 (d×2), 131.34 (s), 131.92 (d×2), 132.21 (s), 145.45 (s, $J_{C\text{-}F}$=32 Hz, 2-C); $^{19}$F-NMR (376.4 MHz) $\delta$: −7.94 (3F, s, $CF_3$); MS *m/z*: 294 ($M^+$). *Anal.* Calcd for $C_{12}H_{13}F_3OS_2$: C, 48.97; H, 4.45. Found: C, 49.12; H, 4.42.

(*E*)-2-Ethoxy-3-(methylthio)-4-phenyl-1,1,1-trifluorobut-2-ene (**5**): IR (film, $cm^{-1}$) 1220—1100 (C–O–C); $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.39 (3H, t, $J$=7 Hz, Me), 2.08 (3H, s, SMe), 3.84 (2H, s, $CH_2$), 3.99 (2H, q, $J$=7 Hz, $OCH_2$), 7.22—7.25 (3H, m, ArH), 7.30—7.37 (2H, m, ArH); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 13.51 (q), 15.57 (q), 34.00 (t), 69.07 (t), 121.74 (s, $J_{C\text{-}F}$=277 Hz, $CF_3$), 126.91 (d), 127.98 (d×2), 128.89 (d×2), 133.89 (s), 137.25 (s), 138.52 (s, $J_{C\text{-}F}$=33 Hz, 2-C); $^{19}$F-NMR (376.4 MHz) $\delta$: −8.54 (3F, s, $CF_3$); MS *m*/*z*: 276 ($M^+$). *Anal.* Calcd for $C_{13}H_{15}F_3OS$: C, 56.51; H, 5.47. Found: C, 56.36; H, 5.62.

(*E*)-2-(Ethylthio)-3-(phenylthio)-1,1,1-trifluorobut-2-ene (**6a**): IR (film, $cm^{-1}$) 3100—2800, 1560, 1450, 1280, 1220, 1140, 990, 880; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.34 (3H, t, $J$=7 Hz, Me), 1.93 (3H, q, $J$=2 Hz, Me), 2.83 (2H, q, $J$=7 Hz, $SCH_2$), 7.36—7.42 (3H, m, ArH), 7.48—7.51 (2H, m, ArH); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.58 (q), 20.53 (q, $J_{C\text{-}F}$=2 Hz), 29.41 (t), 113.82 (s, $J_{C\text{-}F}$=34 Hz), 123.65 (s, $J_{C\text{-}F}$=274 Hz, $CF_3$), 129.48 (d×2), 129.83 (d), 131.22 (s), 136.16 (d×2), 160.33 (s, $J_{C\text{-}F}$=2 Hz); $^{19}$F-NMR (376.4 MHz) $\delta$: −22.68 (3F, s, $CF_3$); MS *m*/*z*: 278 ($M^+$). *Anal.* Calcd for $C_{12}H_{13}F_3S_2$: C, 51.78; H, 4.71. Found: C, 51.90; H, 4.74.

(*E*)-2-(Ethylthio)-3-(phenylthio)-1,1,1-trifluorohex-2,5-diene (**6b**): IR (film, $cm^{-1}$) 3050—2800, 1540, 1430, 1240, 1150, 1100, 910, 740; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.35 (3H, t, $J$=7 Hz, Me), 2.87 (2H, q, $J$=7 Hz, $SCH_2$), 3.11—3.14 (2H, m, $CH_2$), 4.76 (1H, dd, $J$=1, 17 Hz, olefinic H), 4.93—4.97 (1H, dd, $J$=1, 10 Hz, olefinic H), 5.48—5.55 (1H, m, olefinic H), 7.34—7.43 (3H, m, ArH), 7.48—7.51 (2H, m, ArH); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.60 (q), 29.52 (t), 36.09 (t, $J_{C\text{-}F}$=2 Hz), 117.24 (t), 123.53 (s, $J_{C\text{-}F}$=275 Hz, $CF_3$), 129.30 (d×2), 129.90 (d), 130.79 (s), 131.63 (s), 133.59 (d), 136.42 (d×2), 161.20 (s); $^{19}$F-NMR (376.4 MHz) $\delta$: −22.80 (3F, s, $CF_3$); MS *m*/*z*: 304 ($M^+$). *Anal.* Calcd for $C_{14}H_{15}F_3S_2$: C, 55.24; H, 4.97. Found: C, 55.40; H, 4.97.

(*E*)-2-(Ethylthio)-3-(methylthio)-3-(phenylthio)-1,1,1-trifluoroprop-2-ene (**6c**): IR (film, $cm^{-1}$) 3050—2900, 1570, 1460, 1440, 1280, 1170, 1120, 1010, 940, 840, 740, 680; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.29 (3H, t, $J$=7 Hz, Me), 2.13 (3H, s, Me), 2.83 (2H, q, $J$=7 Hz, $SCH_2$), 7.25—7.36 (3H, m, ArH), 7.39—7.42 (2H, m, ArH); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 14.55 (q), 19.07 (q), 30.51 (t), 123.09 (s, $J_{C\text{-}F}$=275 Hz, $CF_3$), 124.81 (s, $J_{C\text{-}F}$=32 Hz), 128.36 (d), 129.17 (d×2), 132.34 (d×2), 132.98 (s), 156.73 (s); $^{19}$F-NMR (376.4 MHz) $\delta$: −0.85 (3F, s, $CF_3$); MS *m*/*z*: 310 ($M^+$). *Anal.* Calcd for $C_{12}H_{13}F_3S_3$: C, 46.43; H, 4.22. Found: C, 46.46; H, 4.25.

**Reaction of Enol Ether 1 with LDA** A THF (1.0 ml) solution of **1** (0.25 g, 1.00 mmol) was added dropwise to a THF (2.0 ml) solution of LDA (1.5 mmol) at −30 °C under an Ar atmosphere. The reaction mixture was stirred for 10 min and then MeI (0.71 g, 5.0 mmol) was added dropwise to the mixture. The workup procedure afforded (*E*)-2-(diisopropylamino)-3-(phenylthio)-1,1,1-trifluoroprop-2-ene (**7**) (0.07 g, 24%) as a colorless oil, accompanied by **4a** (0.13 g, 50%). **7**: IR (film, $cm^{-1}$) 3050—2800, 1600, 1580, 1460, 1380, 1300, 1260—1050, 910, 860—820, 740, 700; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$: 1.16 (6H, s, Me×2), 1.18 (6H, s, Me×2), 3.44—3.51 (2H, m, CH), 7.11 (1H, d, $J$=1 Hz, olefinic H), 7.24—7.35 (3H, m, ArH), 7.39—7.42 (2H, m, ArH); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$: 21.30 (q×4), 49.17 (d×2), 123.25 (s, $J_{C\text{-}F}$=281 Hz, $CF_3$), 127.83 (d), 129.15 (s, $J_{C\text{-}F}$=31 Hz, 2-C), 129.49 (d×2), 130.87 (d×2), 134.93 (s), 139.70 (d, $J_{C\text{-}F}$=4 Hz, 3-C); $^{19}$F-NMR (376.4 MHz) $\delta$: −15.95 (3F, s, $CF_3$); MS *m*/*z*: 303 ($M^+$). *Anal.* Calcd for $C_{15}H_{20}F_3NS$: C, 59.38; H, 6.64; N, 4.62. Found: C, 59.53; H, 6.70; N, 4.62.

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