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First Synthesis of a α-Trifluoromethyl Allenol Ether *via* the Julia-Lythgoe Process

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α-Trifluoromethyl allenol ethers 9a—e were prepared in moderate to good yields by the Julia-Lythgoe process using β-ethoxy-β-trifluoromethyl vinylic sulfone 3. Several reactions of 9c were examined to give α,β-unsaturated trifluoromethyl ketone derivatives 11 and 12.

Key words allene; fluoro enol ether; sulfone

Allenol ethers are important builiding blocks for the syntheses of a wide variety of synthetic precursors and natural products.[1] The transformation of allenol ethers using many kinds of organometalic reagents has been examined and provided propargylic,[2] allenic,[3] α,β-unsaturated carbonyl compounds,[4] vinyl stannanes[5] and various heterocyclic compounds.[6] Most synthetic approaches to allenol ethers have utilized the isomerization of propargylic ethers by appropriate bases.[7] Wittig-type olefination of carbonyl compounds is also known as a useful method for the preparation of allenol ethers.[8]

Recently, much attention has been focused on organofluorine compounds because of their interesting biological activities and chemical reactivities. In particular, the introduction of a trifluoromethyl group into organic molecules changes their properties due to its strong electron-withdrawing activity. However, no efforts have been described that uses the standard methods for the preparation of fluoroalkyl allenol ethers. Desulfonylation[9] and desulfinylation[10] has been used as an effective method for the formation of double bonds. In particular, the Julia-Lythgoe process involving β-acetoxy sulfones easily provides alkenyl componds by desulfonylation using SmI_2.[11] Sulfones such as shown in Fig. 1, should undergo elimination of the sulfonyl group and provide the expected fluoroalkyl allenol ethers, however, there are so far no reports of application of the Julia-Lythgoe process to allene formation. Here we report the synthesis of trifluoromethyl allenol ethers *via* the Julia-Lythgoe process of vinylic sulfones.

Preparation of the vinylic sulfones was examined as shown in Chart 1. The β-ethoxy vinylic sulfones **3** and **4** were easily obtained by mCPBA oxidation of the sulfides **1** and **2**. The sulfones were then treated with lithium 2,2,6,6-tetramethylpiperidide (LTMP) at −78 °C, followed by the successive reaction with the corresponding aldehydes to afford the allylic alcohols **5** and **6** in moderate to good yields. For preparation of allenes, we first performed the reaction of **5a** with SmI_2 at 0 °C, however, allene **9a** was obtained in low yield (Chart 2). Next, we examined reaction of the corresponding allylic acetate **7a** with SmI_2, and obtained the desired product **9a** in 73% yield. The structure of **9a** was determined by spectral data, which indicated on the allenic absorption at ν 1950 cm^{-1} in the IR spectrum, an allenic proton at δ 7.09 ppm in the ^{1}H-NMR spectrum, and a singlet carbon at δ 195.85 ppm in the ^{13}C-NMR spectrum. The reactions with other aldehydes were also examined, and the results are shown in Table 1. The *p*-chloro- and *p*-bromo-phenyl allenol

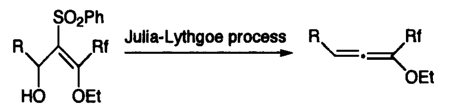
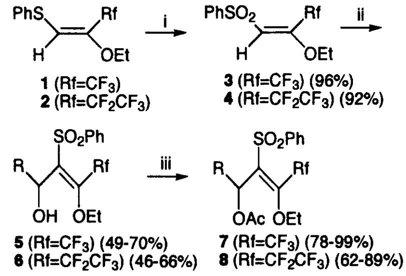
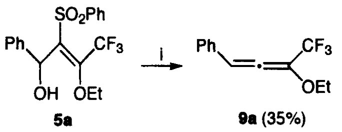


Fig. 1



Reagents: i, mCPBA/0 °C; ii, LTMP/RCHO/-78 °C; iii, Ac_2O/BF_3-$Et_2O/0$ °C

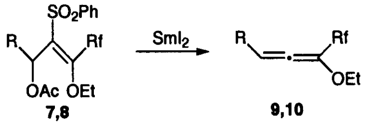
Chart 1



Reagent: i, SmI_2/THF/0 °C

Chart 2

Table 1. Syntheses of Allenol Ethers



Entry	Vinylic sulfone			Product (% yield)
		Rf	R	
1	**7a**	CF_3	Ph	**9a** (73)
2	**7b**	CF_3	*p*-Br–Ph	**9b** (49)
3	**7c**	CF_3	*p*-Cl–Ph	**9c** (70)
4	**7d**	CF_3	Phenylethynyl	**9d** (37)
5	**7e**	CF_3	(*E*)-Styryl	**9e** (57)
6	**8a**	CF_3CF_2	Ph	**10a** (15)
7	**8b**	CF_3CF_2	(*E*)-Styryl	**10b** (7)

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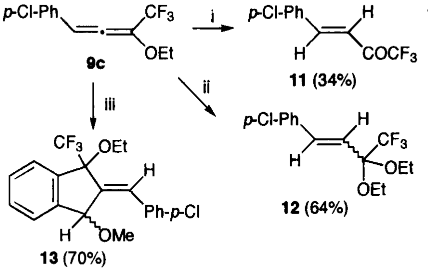

Reagent: i, HCl/EtOH-H_2O/reflux; ii, $CH(OEt)_3$/BF_3-Et_2O; iii, $PhCH(OMe)_2$/BF_3-Et_2O/$ClCH_2CH_2Cl$/0 °C

Chart 3

ethers **9b** and **9c** were readily obtained (entries 2 and 3). Phenylethynyl or cinnam-aldehydes also afforded the corresponding allenes **9d, e**, however, these compounds were found to be unstable (entries 4 and 5). The pentafluoroethyl sulfone gave low yields because they are more labile than the trifluoromethyl derivatives (entries 6 and 7).

In order to characterize the new trifluoromethyl allenol ethers, we examined some reactions of allenol ether **9c**, as shown in Chart 3. Hydrolysis of **9c** with 5% HCl gave the α,β-unsaturated trifluoromethyl ketone **11** in 34% yield. Reaction with ethyl orthoformate/BF_3–Et_2O gave the acetal **12** in good yield. The intermolecular reaction with benzaldehyde dimethyl acetal yielded the cyclized indene **13**, exclusively.

Experimental

^{1}H-, ^{13}C- 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 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 spectra 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.[12] The allenol ethers **9** and **10** were too labile to measure the mass spectral data.

Synthesis of (*E*)-2-Ethoxy-1,1,1-trifluoro-3-(phenylsulfonyl)prop-2-ene (3) and (*E*)-3-Ethoxy-1,1,1,2,2-pentafluoro-4-(phenylsulfonyl)but-3-ene (4). Typical Procedure mCPBA (1.92 g, 8.80 mmol) was added to a $ClCH_2CH_2Cl$ (28 ml) solution of the vinyl sulfide **1** (7.45 g, 26.6 mmol) at 0 °C. The mixture was stirred for 1 h at room temperature 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 $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt–hexane (1 : 10) to give the title compound **3** (1.02 g, 96%) as a colorless oil.

3: IR (film) cm^{-1}: 1300, 1200—1100 (SO_2). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.33 (3H, t, J=7 Hz, Me), 4.21—4.26 (2H, m, OCH_2), 6.44 (1H, s, olefinic H), 7.55—7.59 (3H, m, ArH), 7.98—8.00 (2H, m, ArH). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.03 (q), 71.22 (t), 116.95 (d, J=4 Hz, 3-C), 118.96 (s, J=280 Hz, CF_3), 127.98 (d×2), 129.24 (d×2), 134.07 (d), 141.06 (s), 150.61 (s, J=34 Hz, 2-C). ^{19}F-NMR δ: −8.04 (3F, s, CF_3); MS *m/z*: 280 (M^+). *Anal.* Calcd for $C_{11}H_{11}F_3O_3S$: C, 47.14; H, 3.96. Found: C, 47.26; H, 3.93.

4: IR (film) cm^{-1}: 1320, 1260—1080 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.40 (3H, t, J=7 Hz, Me), 4.46 (2H, q, J=7 Hz, OCH_2), 6.41 (1H, s, olefinic H), 7.57—7.61 (2H, m, ArH), 7.66—7.70 (1H, m, ArH), 7.95—7.98 (2H, m, ArH); ^{19}F-NMR δ: −40.47 (2F, s, CF_2), −4.91 (3F, s, CF_3). *Anal.* Calcd for $C_{12}H_{11}F_5O_3S$: C, 43.64; H, 3.36. Found: C, 43.72; H, 3.38. The molecular ion peak at *m/z* 330 (M^+) was not observed in the mass spectrum.

Preparations of Allylic Alcohols 5 and 6. Typical Procedure A THF (3.00 ml) solution of 2-ethoxy-1,1,1-trifluoro-3-(phenylsulfonyl)prop-2-ene (**3**) (0.51 g, 1.81 mmol) was added dropwise to a THF (6.00 ml) solution of lithium 2,2,6,6-tetramethylpiperidide (prepared from 2,2,6,6-tetramethylpiperidine (0.50 g, 3.54 mmol) and *n*-BuLi (1.80 ml, 2.68 mmol)) at −78 °C. The mixture was stirred for 10 min and a THF (3.00 ml) solution of benzaldehyde (0.38 g, 3.57 mmol) was added. The whole was then poured into water (100 ml) and the organic layer separated and the aqueous layer 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 : 20) to give (*E*)-2-ethoxy-1,1,1-trifluoro-4-phenyl-3-(phenylsulfonyl)but-2-en-4-ol (0.41 g, 61%) as a yellow oil.

5a: IR (film) cm^{-1}: 3500 (OH), 1310, 1180—1120 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ:1.45 (3H, t, J=7 Hz, Me), 4.13—4.22 (2H, m, OCH_2), 4.55 (1H, d, J=12 Hz, OH), 6.00 (1H, d, J=12 Hz, 4-H), 7.31—7.38 (7H, m, ArH), 7.49—7.56 (3H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.19 (q), 69.84 (t, J=4 Hz), 72.36 (d, 4-C), 121.02 (s, J=284 Hz, CF_3), 125.72 (d×2), 127.90 (d), 128.19 (d×2), 128.64 (d×2), 128.70 (d×2), 133.89 (d), 138.24 (s, J=2 Hz), 139.63 (s), 141.12 (s), 150.59 (s, J=34 Hz, 2-C); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −17.37 (3F, s, CF_3); MS *m/z* 357 (M^+−Et). *Anal.* Calcd for $C_{18}H_{17}F_3O_4S$: C, 55.95; H, 4.43. Found: C, 55.63; H, 4.39.

(*E*)-4-(*p*-Bromophenyl)-2-ethoxy-1,1,1-trifluoro-3-(phenylsulfonyl)but-2-en-4-ol (**5b**): mp 131—134 °C (dec.), IR (KBr) cm^{-1}: 3500—3400 (OH), 1270, 1200—1060 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.43 (3H, t, J=7 Hz, Me), 4.10—4.15 (1H, m, OCH_2), 4.17—4.23 (1H, m, OCH_2), 4.52 (1H, d, J=12 Hz, OH), 5.60 (1H, d, J=12 Hz, 4-H), 7.22—7.61 (9H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.23 (q), 69.49 (d, 4-C), 72.60 (t), 120.19 (s, J=284 Hz, CF_3), 122.11 (s), 127.64 (d×2), 128.10 (d×2), 128.91 (d×2), 131.79 (d×2), 134.11 (d), 137.77 (s), 138.94 (s), 141.15 (s), 151.92 (s, 2-C); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −17.34 (3F, s, CF_3); MS *m/z* 309 (M^+−*p*-Br–Ph). *Anal.* Calcd for $C_{18}H_{16}BrF_3O_4S$: C, 46.47; H, 3.47. Found: C, 46.42; H, 3.50.

(*E*)-4-(*p*-Chlorophenyl)-2-ethoxy-1,1,1-trifluoro-3-(phenylsulfonyl)but-2-en-4-ol (**5c**): mp 98—100 °C (dec.), IR (KBr) cm^{-1}: 3504 (OH), 1327, 1189 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.43 (3H, t, J=7 Hz, Me), 4.11—4.22 (2H, m, OCH_2), 4.52 (1H, d, J=12 Hz, OH), 5.92 (1H, d, J=12 Hz, 4-H), 7.32—7.25 (4H, m, ArH) 7.35—7.44 (2H, m, ArH), 7.60—7.55 (3H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.22 (q), 69.45 (d), 72.56 (t), 120.17 (s, J=284 Hz, CF_3), 127.28 (d×2), 128.08 (d×2), 128.82 (d×2), 128.88 (d×2), 133.96 (s), 134.08 (d), 137.82 (s), 138.39 (s), 141.17 (s), 150.93 (s, J=34 Hz, 2-C); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −17.81 (3F, s, CF_3); MS *m/z* 280 (M^+−$PhSO_2$). *Anal.* Calcd for $C_{18}H_{16}ClF_3O_4S$: C, 51.37; H, 3.83. Found: C, 51.15; H, 3.70.

(*E*)-2-Ethoxy-1,1,1-trifluoro-6-phenyl-3-(phenylsulfonyl)hex-2-en-5-yn-4-ol (**6d**): IR (film) cm^{-1}: 3480 (OH), 1330—1260 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.39 (3H, t, J=7 Hz, Me), 4.10 (2H, q, J=7 Hz, OCH_2), 4.52 (1H, d, J=11 Hz, OH), 5.71 (1H, d, J=11 Hz, 4-H), 7.26—7.64 (8H, m, ArH), 8.10—8.13 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.12 (q), 59.11 (d, J=5 Hz, 4-C), 72.22 (t), 86.34 (s), 87.24 (s), 122.01 (s), 122.67 (s, J=283 Hz, CF_3), 124.64 (s), 128.42 (d×2), 128.58 (d×2), 128.92 (d×2), 129.23 (d), 131.99 (d×2), 134.08 (d), 141.11 (s), 149.65 (s, J=35 Hz, 2-C); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −16.97 (3F, s, CF_3); MS *m/z* 410 (M^+). *Anal.* Calcd for $C_{20}H_{17}F_3O_4S$: C, 58.53; H, 4.18. Found: C, 58.64; H, 4.16.

(2*E*,5*E*)-2-Ethoxy-1,1,1-trifluoro-6-phenyl-3-(phenylsulfonyl)hex-2,5-dien-4-ol (**5f**): IR (film) cm^{-1}: 3500—3450 (OH), 1310, 1200—1100 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.36 (3H, t, J=7 Hz, Me), 4.00—4.14 (2H, m, OCH_2), 4.48 (1H, d, J=11 Hz, OH), 5.49 (1H, dd, J=6, 11 Hz, 4-H), 6.52 (1H, dd, J=6, 16 Hz, 5-H), 6.71 (1H, d, J=16 Hz, 6-H), 7.63—7.25 (8H, m, ArH), 7.93—7.98 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.09 (q), 69.60 (d, J=3 Hz, 4-C), 72.14 (t), 122.67 (s, J=284 Hz, CF_3), 127.00 (d×2), 128.08 (d), 128.17 (d×2), 128.46 (d), 128.92 (d×2), 129.23 (d), 131.99 (d×2), 134.08 (d), 141.11 (s), 149.65 (s, J=35 Hz, 2-C); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −16.97 (3F, s, CF_3); MS *m/z* 410 (M^+). *Anal.* Calcd for $C_{20}H_{19}F_3O_4S$: C, 58.53; H, 4.18. Found: C, 58.64; H, 4.16.

(*E*)-3-Ethoxy-1,1,1,2,2-pentafluoro-5-phenyl-4-(phenylsulfonyl)pent-3-en-5-ol (**6a**): mp 74—75 °C (dec.), IR (film) cm^{-1}: 3500—3450 (OH), 1310, 1180—1120 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.37 (3H, t, J=7 Hz, Me), 4.16—4.23 (1H, m, OCH_2), 4.29—4.36 (1H, m, OCH_2), 4.53 (1H, dd, J=2, 12 Hz, OH), 6.03 (1H, d, J=12 Hz, 5-H), 7.24—7.68 (10H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.23 (q), 69.49 (d, J=10 Hz, 5-C), 73.50 (t, J=4 Hz), 112.67 (s, J=40, 263 Hz, CF_2), 118.29 (s, J=36, 288 Hz, CF_3), 125.69 (d×2), 127.57 (d×3), 127.97 (d), 128.75 (d×3), 133.76 (d), 139.97 (s), 141.62 (s), 142.14 (s, J=4 Hz) 149.76 (s, J=25 Hz, 3-C); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −37.17 (1F, d, J=282 Hz, CF_2), −28.61 (1F, d, J=282 Hz, CF_2), −5.01 (3F, t, J=3 Hz, CF_3); MS *m/z* 391 (M^+−EtO). *Anal.* Calcd for $C_{19}H_{17}F_5O_4S$: C, 52.29; H, 3.93. Found: C, 51.33; H, 3.94.

(*E*)-3-Ethoxy-1,1,1,2,2-pentafluoro-7-phenyl-4-(phenylsulfonyl)hept-3-en-6-yn-5-ol (**6b**): IR (film) cm^{-1}: 3500 (OH), 1310, 1210, 1120 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.34 (3H, t, J=7 Hz, Me), 4.20 (2H, q, J=7 Hz, OCH_2), 4.52 (1H, d, J=11 Hz, OH), 5.78 (1H, d, J=10 Hz, 5-H), 7.26—7.62 (8H, m, ArH), 8.07—8.15 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.14 (q), 58.83 (d, J=9 Hz, 5-C), 73.50 (t), 86.24 (s), 87.48 (s), 111.09 (s, J=40 and 264 Hz, CF_2), 118.26 (s, J=36, 288 Hz, CF_3), 122.04 (s), 127.01 (d×2), 128.55 (d×2), 128.86 (d×2), 129.21 (d), 132.00 (d×2), 133.94 (d), 140.58 (s), 141.37 (s), 148.73 (s, J=25 Hz, 3-C); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −36.47 (1F, d, J=282 Hz, CF_2), −33.59 (1F, d, J=282 Hz, CF_2), −5.18 (3F, t, J=3 Hz, CF_3); MS m/z 415 (M^+−OEt). *Anal.* Calcd for $C_{21}H_{17}F_5O_4S$: C, 54.78; H, 3.72. Found: C, 52.94; H, 3.70.

Acetylation of Allylic Alcohols 5 and 6. Typical Procedure BF_3–Et_2O (0.29 g, 2.07 mmol) was added to a Ac_2O (1.80 g, 17.6 mmol) solution of (*E*)-2-ethoxy-1,1,1-trifluoro-4-phenyl-3-(phenylsulfonyl)but-2-en-4-ol (**5a**) (0.80 g, 2.07 mmol) at 0 °C. The mixture was stirred for 30 min and poured into $CHCl_3$ (50 ml). The organic layer was washed with a sat.$NaHCO_3$ (50×3 ml) and 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 : 20) to give (*E*)-4-acetoxy-2-ethoxy-1,1,1-trifluoro-4-phenyl-3-(phenylsulfonyl)but-2-ene (**7a**) (905 mg, 99%) as a yellow oil. IR (film) cm^{-1}: 1740 (CO), 1310, 1210—1140 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.36 (3H, t, J=7 Hz, Me), 2.24 (3H, s, Me), 3.94—4.01 (1H, m, OCH_2), 4.13—4.21 (1H, m, OCH_2), 7.26—7.61 (9H, m, ArH, 4-H), 7.67—7.69 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.08 (q), 21.01 (q), 69.40 (d, J=2 Hz, 4-C), 72.36 (t), 119.78 (s, J=283 Hz, CF_3), 126.32 (d×2), 128,24 (d), 128.40 (d×2), 128.55 (d×2), 128.61 (d×2), 133.73 (d), 136.28 (s), 136.73 (s, J=2 Hz), 141.62 (s), 151.47 (s, J=34 Hz, 2-C), 169.69 (s); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −17.20 (3F, s, CF_3); MS m/z 369 (M^+−OAc). *Anal.* Calcd for $C_{20}H_{19}F_3O_5S$: C, 56.07; H, 4.47. Found: C, 55.85; H, 4.55

(*E*)-4-Acetoxy-4-(*p*-bromophenyl)-2-ethoxy-1,1,1-trifluoro-3-(phenylsulfonyl)but-2-ene (**7b**): mp 66—69 °C (dec.), IR (film) cm^{-1}: 1730 (CO), 1320—1270 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.35 (3H, t, J=7 Hz, Me), 2.23 (3H, s, Me), 3.93—3.97 (1H, m, OCH_2), 4.10—4.18 (1H, m, OCH_2), 7.23 (1H, s, 4-H), 7.25 (2H, d, J=8 Hz, ArH), 7.43—7.47 (2H, m, ArH), 7.50 (2H, d, J=8 Hz, ArH), 7.56—7.60 (1H, m, ArH), 7.73—7.75 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.02 (q), 20.90 (q), 68.84 (d, 4-C), 71.96 (t), 119.64 (s, J=283 Hz, CF_3), 122.25 (s), 127.98 (d×2), 128.26 (d×2), 128.68 (d×2), 131.61 (d×2), 133.85 (d), 135.56 (s), 136.17 (s), 141.44 (s), 151.64 (s, J=35 Hz, 2-C), 169.49 (s); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −17.08 (3F, s, CF_3); MS m/z 365 (M^+−$PhSO_2H$). *Anal.* Calcd for $C_{20}H_{18}BrF_3O_5S$: C, 47.26; H, 3.57. Found: C, 45.74; H, 3.50.

(*E*)-4-Acetoxy-4-(*p*-chlorophenyl)-2-ethoxy-1,1,1-trifluoro-3-(phenylsulfonyl)but-2-ene (**7c**): mp 61—63 °C (dec.), IR (KBr) cm^{-1}: 1740 (CO), 1310, 1240—1120 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.36 (3H, t, J=7 Hz, Me), 2.24 (3H, s, Me), 3.93—4.01 (1H, m, OCH_2), 4.09—4.20 (1H, m, OCH_2), 7.24 (1H, s, 4-H), 7.29 (2H, d, J=9 Hz, ArH), 7.35 (2H, d, J=9 Hz, ArH), 7.44—7.48 (2H, m, ArH), 7.57—7.62 (1H, m, ArH), 7.71—7.74 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.15 (q), 21.05 (q), 68.94 (d, 4-C), 72.08 (t), 119.76 (s, J=283 Hz, CF_3), 127.81 (d×2), 128.40 (d×2), 128.77 (d×2), 128.79 (d×2), 133.91 (d), 134.27 (s), 135.07 (s), 136.37 (s), 141.62 (s), 151.77 (s, J=35 Hz, 2-C), 169.49 (s); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −17.12 (3F, s, CF_3); MS m/z 321 (M^+−$PhSO_2H$). *Anal.* Calcd for $C_{20}H_{18}ClF_3O_5S$: C, 51.90; H, 3.92. Found: C, 51.84; H, 3.96.

(*E*)-4-Acetoxy-2-ethoxy-1,1,1-trifluoro-6-phenyl-3-(phenylsulfonyl)hex-2-en-5-yne (**7d**): IR (film) cm^{-1}: 1770 (CO), 1320, 1220—1140 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.24 (3H, t, J=7 Hz, Me), 2.26 (3H, s, Me), 3.77—3.82 (1H, m, OCH_2), 3.89—3.94 (1H, m, OCH_2), 7.15 (1H, s, 4-H), 7.32—7.55 (8H, m, ArH, 4-H), 8.09—8.12 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.15 (q), 21.69 (q), 61.85 (t), 84.19 (s), 110.12 (s), 121.34 (s, J=290 Hz, CF_3), 121.84 (s), 127.35 (d), 128.58 (d×2), 128.66 (d×2), 130.21 (d×2), 132.17 (d×2), 133.51 (d), 142.06 (s), 143.12 (s), 168.17 (s); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: 0.47 (3F, s, CF_3), MS m/z 393 (M^+−OAc). *Anal.* Calcd for $C_{22}H_{19}F_3O_5S$: C, 58.40; H, 4.23. Found: C, 52.72; H, 3.83.

(*Z*)-4-Acetoxy-2-ethoxy-1,1,1-trifluoro-6-phenyl-3-(phenylsulfonyl)hex-2-en-5-yne (**7d**): mp 132—133 °C (dec.), IR (KBr) cm^{-1}: 1780 (CO), 1320, 1200—1140 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.91 (3H, t, J=7 Hz, Me), 2.02 (3H, s, Me), 3.42—3.50 (1H, m, OCH_2), 3.77—3.81 (1H, m, OCH_2), 7.26—7.35 (3H, m, ArH), 7.46—7.54 (4H, m, ArH), 7.57—7.61 (1H, m, ArH), 7.74 (1H, s, 4-H), 7.90—7.93 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.74 (q), 20.67 (q), 61.17 (t), 83.59 (s), 118.51 (s), 121.73 (s), 121.88 (s, J=294 Hz, CF_3), 127.58 (d), 128.27 (d×2), 129.00 (d×2), 129.22 (d×2), 130.62 (d), 132.43 (d×2), 133.21 (d), 141.34 (s), 142.98 (s), 166.03 (s); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −0.95 (3F, s, CF_3); MS m/z 393 (M^+−OAc). *Anal.* Calcd for $C_{22}H_{19}F_3O_5S$: C, 58.40; H, 4.23. Found: C, 57.97; H, 4.18.

(2*E*,5*E*)-4-Acetoxy-2-ethoxy-1,1,1-trifluoro-6-phenyl-3-(phenylsulfonyl)hex-2,5-diene (**7e**): IR (film) cm^{-1}: 1770 (CO), 1300, 1200—1120 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.95 (3H, t, J=7 Hz, Me), 2.03 (3H, s, Me), 3.44—3.52 (1H, m, OCH_2), 3.73—3.77 (1H, m, OCH_2), 7.14 (1H, d, J=15 Hz, 6-H), 7.23—7.36 (1H, m, ArH), 7.39—7.43 (3H, m, ArH), 7.47—7.56 (4H, m, ArH), 7.56—7.58 (1H, m ArH), 7.90—7.92 (2H, m, ArH), 8.09 (1H, d, J=11 Hz, 4-H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.57 (q), 21.31 (q), 61.06 (t), 121.18 (d), 121.71 (s, J=293 Hz, CF_3), 127.95 (d×2), 128.18 (d×2), 128.61 (d×2), 129.97 (d×2), 130.50 (d), 131.60 (s), 132.76 (d), 135.33 (s), 142.10 (s), 146.32 (d), 147.74 (d), 165.48 (s); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −0.79 (3F, s, CF_3); MS m/z 395 (M^+−OAc). *Anal.* Calcd for $C_{22}H_{21}F_3O_5S$: C, 58.14; H, 4.66. Found: C, 58.21; H, 4.69.

(*E*)-5-Acetoxy-3-ethoxy-1,1,1,2,2-pentafluoro-5-phenyl-4-(phenylsulfonyl)pent-3-ene (**8a**): IR (film) cm^{-1}: 1740 (CO), 1320, 1180—1120 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.39 (3H, t, J=7 Hz, Me), 2.23 (3H, s, Me), 4.26—4.34 (2H, m, OCH_2), 7.26—7.53 (8H, m, 5H and ArH), 7.53—7.57 (1H, m, ArH) 7.71—7.74 (2H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.18 (q), 20.84 (q), 69.22 (d, J=5 Hz, 5-C), 74.00 (t), 109.80 (s, J=40, 265 Hz, CF_2), 118.10 (s, J=36, 287 Hz, CF_3), 125.80 (d), 128.00 (d×2), 128.02 (d×2), 128.52 (d×2), 128.58 (d×2), 133.70 (d), 136.53 (s), 140.76 (s), 141.75 (s), 151.74 (s, J=25 Hz, 3-C), 169.56 (s); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −33.86 (1F, d, J=284 Hz CF_2), −30.05 (1F, d, J=284 Hz CF_2), −3.68 (3F, t, J=19 Hz, CF_3); MS m/z 337 (M^+−$PhSO_2H$). *Anal.* Calcd for $C_{21}H_{19}F_5O_5S$: C, 52.61; H, 3.99. Found: C, 50.94; H, 3.86.

(3*E*,6*E*)-5-Acetoxy-3-ethoxy-1,1,1,2,2-pentafluoro-7-phenyl-4-(phenylsulfonyl)hept-3,6-diene (**8b**): IR (film) cm^{-1}: 1780 (CO), 1310, 1240—1120 (SO_2); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.04 (3H, t, J=7 Hz, Me), 2.05 (3H, s, Me), 3.41—3.49 (1H, m, OCH_2), 3.67—3.75 (1H, m, OCH_2), 7.14 (1H, d, J=15 Hz, 7-H), 7.21—7.45 (5H, m, ArH), 7.47—7.58 (3H, m, ArH), 7.85—7.92 (2H, m, ArH), 8.08 (1H, d, J=11 Hz, 5-H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.62 (q), 21.58 (q), 61.96 (t), 118.75 (s, J=35, 322 Hz, CF_3), 121.41 (d), 128.03 (d×2), 128.43 (d×2), 128.57 (d), 129.35 (d×2), 130.58 (d×2), 131.94 (s), 132.93 (d), 135.41 (s), 142.22 (s), 147.15 (d), 147.89 (d), 165.93 (s); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −40.61 (2F, s, CF_2), −0.93 (3F, s, CF_3); MS m/z 363 (M^+−$PhSO_2H$). *Anal.* Calcd for $C_{23}H_{21}F_5O_5S$: C, 54.65; H, 4.19. Found: C, 54.67; H, 4.25.

Preparations of Allenol Ethers 9 and 10 from Acetates 7 and 8 with SmI_2. Typical Procedure SmI_2 (5.00 ml, 0.20 mol/l THF solution) was added dropwise to a THF (2.0 ml) solution of (*E*)-4-acetoxy-2-ethoxy-1,1,1-trifluoro-4-phenyl-3-(phenylsulfonyl)but-2-ene (**7a**) (0.15 g, 0.35 mmol) at room temperature. The reaction mixture was stirred for 30 min and poured into water (150 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 removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with hexane to afford 2-ethoxy-1,1,1-trifluoro-4-phenylbut-2,3-diene (**9a**) (58 mg, 73%) as a colorless oil.

9a: IR (film) cm^{-1}: 1950 (allene), 1200—1100 (ether); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.32 (3H, t, J=7 Hz, Me), 3.77 (2H, q, J=7 Hz, OCH_2), 7.09 (1H, q, J=3 Hz, allenic H), 7.25—7.41 (5H, m, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.57 (q), 65.98 (t), 113.72 (d, 4-C), 120.95 (s, J=273 Hz, CF_3), 128.09 (d×2), 129.17 (d×2), 129.35 (d), 131.14 (s), 195.85 (s, 3-C); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −0.01 (3F, s, CF_3). *Anal.* Calcd for $C_{12}H_{11}F_3O$: C, 63.16; H, 4.89. Found: C, 62.88; H, 4.51.

4-(*p*-Bromophenyl)-2-ethoxy-1,1,1-trifluorobut-2,3-diene (**9b**): IR (film) cm^{-1}: 1950 (allene), 1200—1100 (ether); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.32 (3H, t, J=7 Hz, Me), 3.68—3.82 (2H, m, OCH_2), 7.03 (1H, q, J=3 Hz, allenic H), 7.24 (2H, brd, J=8 Hz, ArH), 7.48 (2H, brd, J=8 Hz, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.50 (q), 66.10 (t), 112.74 (d, 4-C), 120.79 (s, J=273 Hz, CF_3), 123.44 (s), 127.32 (s, J=40 Hz, 2-C), 129.47 (d×2), 132.09 (s), 132.35 (d×2), 190.84 (s, 3-C); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −0.01 (3F, s, CF_3). *Anal.* Calcd for $C_{12}H_{10}BrF_3O$: C, 49.63; H, 3.28. Found: C, 49.24; H, 3.19.

4-(*p*-Chlorophenyl)-2-ethoxy-1,1,1-(trifluoro)but-2,3-diene (**9c**): IR (film) cm^{-1}: 1950 (allene), 1180—1060 (ether); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.32 (3H, t, J=7 Hz, Me), 3.69—3.82 (2H, m, OCH_2), 7.05 (1H, q, J=3 Hz, allenic H), 7.31 (2H, d, J=8 Hz, ArH), 7.34 (2H, d, J=8 Hz, ArH); ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.52 (q), 66.10 (t), 112.66 (d, 4-C), 120.84 (s, J=273 Hz, CF_3), 129.22 (d×2), 129.40 (d×2), 131.67 (s), 135.24 (s), 190.82 (s, 3-C); ^{19}F-NMR (376.4 MHz, $CDCl_3$) δ: −0.01 (3F, s, CF_3). *Anal.* Calcd for $C_{12}H_{10}ClF_3O$: C, 54.87; H, 3.84. Found: C, 54.50; H, 3.85.

2-Ethoxy-1,1,1-trifluoro-6-phenylhexa-2,3-dien-5-yne (**9d**): IR (film) cm^{-1}: 1940 (allene), 1200—1100 (ether); ^{1}H-NMR (400 MHz, CDCl$_3$) δ: 1.36 (3H, t, J=7 Hz, Me), 3.79 (2H, q, J=7 Hz, OCH$_2$), 6.54 (1H, q, J=2 Hz, allenic H), 7.25—7.36 (3H, m, ArH), 7.47—7.49 (2H, m, ArH); ^{13}C-NMR (100 MHz, CDCl$_3$) δ: 14.47 (q), 66.39 (t), 81.50 (s), 93.80 (s), 95.45 (d, 4-C), 120.48 (s, J=274 Hz, CF$_3$), 122.49 (s), 128.64 (d×2), 129.30 (d), 132.02 (d×2), 200.47 (s, 3-C); ^{19}F-NMR (376.4 MHz, CDCl$_3$) δ: −0.09 (3F, s, CF$_3$); MS m/z 252 (M$^+$). *Anal.* Calcd for $C_{14}H_{11}F_3O$: C, 66.66; H, 4.40. Found: C, 66.31; H, 4.61.

(*E*)-2-Ethoxy-1,1,1-trifluoro-6-phenylhexa-2,3,5-triene (**9e**): IR (film) cm^{-1}: 1940 (allene), 1200—1100 (ether); ^{1}H-NMR (400 MHz, CDCl$_3$) δ: 1.33 (3H, t, J=7 Hz, Me), 3.71—3.77 (2H, m, OCH$_2$), 6.63 (1H, dd, J=10, 16 Hz, olefinic H), 6.75 (1H, d, J=16 Hz, olefinic H), 6.89 (1H, dd, J=3, 10 Hz, allenic H), 7.25—7.29 (1H, m, ArH), 7.30—7.36 (2H, m, ArH), 7.43—7.44 (2H, m, ArH); ^{13}C-NMR (100 MHz, CDCl$_3$) δ: 14.53 (q), 65.86 (t), 113.56 (d, 4-C), 120.85 (s, J=273 Hz, CF$_3$), 123.73 (d), 127.07 (d×2), 128.84 (d), 128.99 (d×2), 136.33 (s), 136.78 (d), 200.47 (s, 3-C); ^{19}F-NMR (376.4 MHz, CDCl$_3$) δ: −0.01 (3F, s, CF$_3$); MS m/z 255 (M$^+$+1). *Anal.* Calcd for $C_{14}H_{13}F_3O$: C, 66.14; H, 5.15. Found: C, 66.01; H, 5.17.

3-Ethoxy-1,1,1,2,2-pentafluoro-5-phenylpenta-3,4-diene (**10a**): IR (film) cm^{-1}: 1960 (allene), 1210—1160 (ether); ^{1}H-NMR (400 MHz, CDCl$_3$) δ: 1.31 (3H, t, J=7 Hz, Me), 3.69—3.89 (2H, m, OCH$_2$), 7.11 (1H, d, J=4 Hz, allenic H), 7.24—7.40 (5H, m, ArH); ^{19}F-NMR (376.4 MHz, CDCl$_3$) δ: −39.93 (1F, d, J=3 Hz, CF$_2$), −39.86 (1F, d, J=3 Hz, CF$_2$), −5.40 (3F, t, J=2 Hz, CF$_3$). *Anal.* Calcd for $C_{13}H_{11}F_5O$: C, 56.12; H, 3.99. Found: C, 56.98; H, 4.43.

3-Ethoxy-1,1,1,2,2-pentafluoro-7-phenylhepta-3,4,6-triene (**10c**): IR (film) cm^{-1}: 1940 (allene), 1220 (ether); ^{1}H-NMR (400 MHz, CDCl$_3$) δ: 1.32 (3H, t, J=7 Hz, Me), 3.71—3.79 (2H, m, OCH$_2$), 6.61 (1H, dd, J=11, 16 Hz, 6-H), 6.76 (1H, d, J=16 Hz, 5-H), 6.91 (1H, dt, J=3, 11 Hz, allenic H), 7.27—7.37 (3H, m, ArH), 7.43—7.47 (2H, m, ArH); ^{19}F-NMR (376.4 MHz, CDCl$_3$) δ: −39.86—−39.86 (2F, m, CF$_2$), −5.42 (3F, t, J=2 Hz, CF$_3$).

Hydrolysis of Allenol Ether 9c with HCl 5% HCl (1.0 ml) solution was added to 80% EtOH (1.0 ml) containing **9c** (0.10 g, 0.38 mmol). The mixture was refluxed for 1 h and poured into a sat. NaHCO$_3$ (50 ml). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer was dried over MgSO$_4$ and solvent removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–hexane (1 : 40) to give (*E*)-4-(*p*-chlorophenyl)-1,1,1-trifluorobut-3-en-2-one (**11**) (30 mg, 34%) as yellow prisms.

(*E*)-4-(*p*-Chlorophenyl)-1,1,1-trifluorobut-3-en-2-one (**11**): mp 43—46 °C, IR (KBr) cm^{-1}: 1718 (CO); ^{1}H-NMR (400 MHz, CDCl$_3$) δ: 6.98 (1H, dd, J=1, 16 Hz, 4-H), 7.37—7.45 (2H, m, ArH), 7.52—7.63 (2H, m, ArH), 7.91 (1H, d, J=16 Hz, 3-H); ^{13}C-NMR (100 MHz, CDCl$_3$) δ 116.19 (s, J=291 Hz, CF$_3$), 117.29 (d), 129.85 (d×2), 130.57 (d×2), 132.03 (s), 138.72 (s), 148.77 (d), 179.92 (s, 2-C); ^{19}F-NMR (376.4 MHz, CDCl$_3$) δ: 10.34 (3F, s, CF$_3$); MS m/z 165 (M$^+$−CF$_3$). *Anal.* Calcd for $C_{10}H_6ClF_3O$: C, 51.20; H, 2.58. Found: C, 51.15; H, 2.84.

Reaction of 9c with Triethyl Orthoformate/BF$_3$–Et$_2$O BF$_3$–Et$_2$O (0.22 g, 1.56 mmol) was added to an EtOH (1.0 ml) solution of triethyl orthoformate (0.28 g, 1.91 mmol). The mixture was refluxed for 2 h and poured into sat. NaHCO$_3$ (150 ml) solution. The work-up procedure afforded (*E*)- and (*Z*)-2,2-diethoxy-1,1,1-trifluoro-4-(*p*-chlorophenyl)but-3-ene (**12**) (75 mg, 64%) as a yellow oil.

12: *E* : *Z*=2 : 3, IR (film) cm^{-1}: 1200—1040 (ether); ^{1}H-NMR (400 MHz, CDCl$_3$) δ: 1.05 (t, J=7 Hz, *Z*-Me), 1.27 (t, J=7 Hz, *E*-Me), 3.49—3.73 (m, *E* and *Z*-OCH$_2$), 5.49 (dd, J=1, 13 Hz, *Z*-4-H), 6.05 (dd, J=1, 16 Hz, *E*-4-H), 6.77 (d, J=13 Hz, *Z*-3-H), 7.01 (d, J=16 Hz, *E*-3-H), 7.24—7.38 (m, *E* and *Z*-ArH); ^{19}F-NMR (376.4 MHz, CDCl$_3$) δ: −0.27 (s, *E*-CF$_3$), 0.69 (s, *Z*-CF$_3$). *Anal.* Calcd for $C_{14}H_{16}ClF_3O_2$: C, 54.65; H, 5.33. Found: C, 54.96; H, 5.09.

Reaction of 9c with Benzaldehyde Dimethyl Acetal/BF$_3$–Et$_2$O BF$_3$–Et$_2$O (0.11 g, 0.76 mmol) was added to a ClCH$_2$CH$_2$Cl (1.0 ml) solution of **9c** (0.10 g, 0.38 mmol) and benzaldehyde dimethyl acetal (0.12 g, 0.76 mmol) at 0 °C. The mixture was stirred for 10 min. The work-up procedure gave *cis* and *trans*-2-(*p*-chlorobenzylidene)-1-ethoxy-3-methoxy-1-(trifluoromethyl)indene (**13**) (110 mg, 70%) as a yellow oil.

13: *cis* : *trans*=1 : 1, *E* : *Z*=1 : 1, IR (film) cm^{-1}: 1280, 1150 (ether); ^{1}H-NMR (400 MHz, CDCl$_3$) δ: 0.85 (t, J=7 Hz, Me), 1.21 (t, J=7 Hz, Me), 3.07 (d, J=1 Hz, Me), 3.24 (d, J=1 Hz, Me), 3.35—3.50 (m, OCH$_2$), 3.61—3.68 (m, OCH$_2$), 4.65 (s, CHO), 4.69 (s, CHO), 6.89—6.92 (q, J=4 Hz, ArH), 7.06—7.36 (m, ArH), 7.41 (s, olefinic H), 7.43 (s, olefinic H). ^{19}F-NMR (376.4 MHz, CDCl$_3$) δ: 0.28 (s, CF$_3$), 0.60 (s, CF$_3$); MS m/z 382 (M$^+$), 353 (M$^+$−OEt). *Anal.* Calcd for $C_{20}H_{18}ClF_3O_3$: C, 62.75; H, 4.74. Found: C, 62.29, H, 4.69.

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References and Notes

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