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Tetrahedron
Tetrahedron 62 (2006) 829–832

Stereoselective preparation of trifluoromethyl containing 1,4-oxathiolane derivatives through ring expansion reaction of 1,3-oxathiolanes

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Received 25 August 2005; revised 19 October 2005; accepted 21 October 2005

Available online 8 November 2005

Abstract—Trifluoromethyl containing 1,4-oxathiolanes are synthesized in excellent yields and high stereoselectivities from the expansion reactions of sulfur ylide intermediates, which were prepared from the reaction of 2-diazo-3,3,3-trifluoro-propionic acid methyl ester and 1,3-oxathiolanes in the presence of $Rh_2(OAc)_4$.

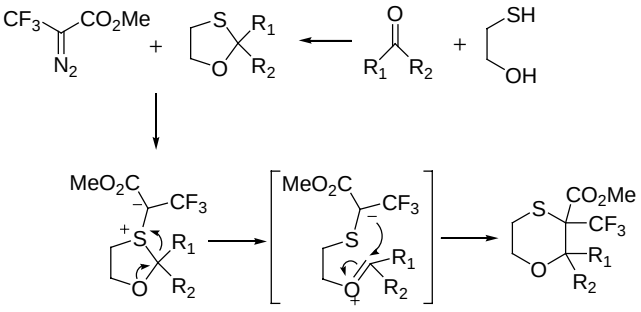
1. Introduction

Considerable attention has been given to trifluoromethyl containing organic compounds as agrochemical and pharmaceutical agents due to their unique properties arising from altered electron density, acidity, and lipophilicity.[1] Accordingly, the development of new methods for the synthesis of the trifluoromethyl containing organic compounds is continuous to be a an important area of research in agricultural, medicinal, and organic chemistry.[2] 1,4-Oxathiolanes are important heterocycles occurring in natural and medicinal molecules,[3] for example, RNA polymerase inhibitor tagetitoxin.[4] Although the preparation of nonfluoro-1,4-oxathiolane are well documented, however, the stereoselective ratio of the products mostly is still low, in particular to those containing quaternary carbons.[5] Furthermore, it is difficult to introduce fluorine atoms into 1,4-oxathiolanes.[6]

2. Results and discussion

As part of a project on synthesis of fluorine-containing molecules using fluorinated diazocompounds, we wish to develop a method to synthesize trifluoromethyl containing 1,4-oxathiolane through ring expansion of 1,3-oxathiolane started from 2-diazo-3,3,3-trifluoro-propionic acid methyl ester.

Porter et al. reported 1,4-oxathiolanes could be synthesized from the reaction of 1,3-oxathiolanes and a silylated diazoacetate in the presence of a copper catalyst in moderate yield and low diastereomeric ratio.[5] In this paper, we will report the stereoselective synthesis trifluoromethyl containing 1,4-oxathiolane from the reaction of 2-diazo-3,3,3-trifluoro-propionic acid methyl ester and 1,3-oxathiolanes (Scheme 1).



Scheme 1.

1,3-Oxathiolane **2** can be readily obtained from the reaction of 2-mercapto ethanol and carbonyl compounds in the presence of CAN in excellent yields. Initial studies were focus on the reaction of 1,3-oxathiolanes **2** derived from aromatic aldehydes and diazocompounds **1**. To a refluxing benzene solution of 1,3-oxathilane **2** and catalyst was added a benzene solution of diazocompound **1** in 2 h. The stirring continues for an additional 2 h. $Rh_2(OAc)_4$ is a superior catalyst than the copper catalysts, for example, $Cu(acac)_2$, which is contradict to the results reported by Porter.[5]

Keywords: Stereoselective synthesis; Diastereomeric ratio; Lipophilicity; Sulfur ylide; Diazo; Trifluoromethyl; 1,4-Oxathiolane.
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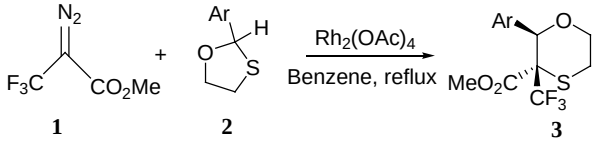
doi:10.1016/j.tet.2005.10.050

The reaction gives 1,4-oxathiolanes **3** in high yields with excellent diastereomeric ratio. 1,3-Oxathiolanes derived from the aromatic aldehydes substituted with electron-withdrawing groups lead to the products in relatively higher yields than those electron-donating ones, but with lower diastereometric ratio (Table 1, entries 6–8). Chemical shift data from the NMR spectrum of the products suggests that the major isomer is the one in which the carbmethoxy and phenyl groups are trans-oriented. Those electron-rich substrates give 1,4-oxathiolanes in higher trans/cis ratio than those electron-poor ones. For example, it gives to almost exclusively trans diastereoselective products when the aromatic ring was substituted with methoxy group (Table 1, entry 8). The nitro-substituted substrate, however, it gives only 3:2 trans/cis diastereoselective ratio (Table 1, entry 8).

Table 1.

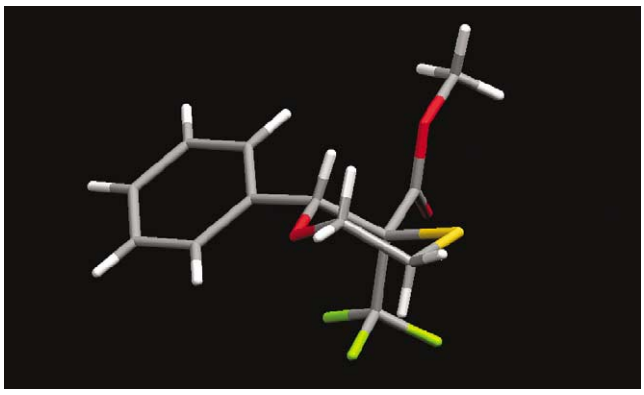


1 **2** **3**

Entry	1,3-Oxathiolanes	Product	Yield (%)[a]	trans/cis[b]
1	Ar=Ph (**2a**)	**3a**	93	96:4
2	Ar=*o*-F–C_6H_4–(**2b**)	**3b**	65	97:3
3	Ar=*o*-Cl–C_6H_4–(**2c**)	**3c**	75	98:2
4	Ar=*o*-Br–C_6H_4–(**2d**)	**3d**	75	97:3
5	Ar=*p*-Br–C_6H_4–(**2e**)	**3e**	92	92:8
6	Ar=*p*-NO_2–C_6H_4–(**2f**)	**3f**	100	2:1
7	Ar=*p*-CH_3–C_6H_4–(**2g**)	**3g**	88	92:8
8	Ar=*p*-MeO–C_6H_4–(**2h**)	**3h**	83	>99:1

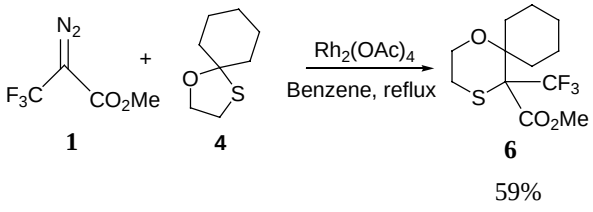
[a] All products were fully characterized by spectroscopic methods. The yields were isolated yields.
[b] Determined by ^{1}H NMR integration of the reaction mixture.

The relative stereochemistry of **3** was further confirmed by a X-ray crystal diffraction analysis of compound **3a** (Scheme 2). The structural analysis clearly shows the 1,4-oxathiolane ring of **3a** keeps in a thermodynamic stable chair conformation. The large groups, methoxyl carbonyl and phenyl ring, lie in the equatorial position of six-member ring. Trifluoromethyl group, smaller than methoxyl carbonyl group, situates in the axial position. What resulted in the low diastereomeric ratio (2:1) with regard to the reaction of 2-(4-nitro-phenyl)-1,3-oxathiolane with 1,4-oxathiolane? We know that the trifluoromethyl and aromatic ring are in cis position according to the crystallographic study. The electrostatic repulsion between the trifluoromethyl and nitrophenyl, an electron-deficient group, makes the relatively bulky methoxyl carbonyl group tend to be axial set, in order to reduce such repulsion.



Scheme 2. The molecular structure of **3a**.

Spiro structures existed in many medicinally or biologically important molecules.[7] How to efficiently synthesize such compounds is still a challenge subject. It is in particular difficult to introduce fluorine atom into spiro-molecules. Spiro 1,3-oxathiolanes can be easily available from cyclic ketone with 2-mercapto ethanol. Based on the above experiments, the [1,2]-rearrangement of the intermediate sulfur ylides of spiro 1,3-oxathiolanes should give the trifluoromethyl containing spiro 1,4-oxatiolane. Under the same reaction conditions, the spiro compound **6** was indeed obtained in 59% yield, which was in line with our initial speculations (Scheme 3).



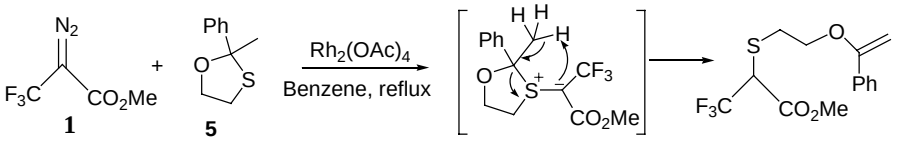
1 **4** **6**

59%

Scheme 3.

For comparison, 1,3-oxathiolane **5** was treated with trifluoromethyl diazoacetate **1** under similar reaction conditions, no [1,2]-rearrangement of intermediate sulfur ylides was not observed. The elimination product **7** was dominant (48%) (Scheme 4). The reaction might be preceded through a five-membered ring intermediate.

In summary, we have developed an efficient method for the stereoselective synthesis of trifluoromenthyl 1,4-oxathiolane through ring expansion of 1,3-oxathiolane ylide using



1 **5** **7**

48%

Scheme 4.

trifluoromethyl diazoactetate in the presence of $Rh_2(OAc)_4$. This catalytic, stereoselective and mild reaction will be the method of choice in many instances.

3. Experimental

Melting points were measured on a Temp-Melt apparatus and are uncorrected. Solvents were dried before use. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on a Varian-360L instrument or Bruker DRX-400 spectrometer with TMS and TFA ($\delta CFCl_3 = \delta TFA + 76.8$) as the internal and external standards and the upfield as negative. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Low-resolution mass spectra and high-resolution mass spectra (HRMS) were obtained on a Finnigan GC–MS 4021 and Finnigan MAT-8430 instrument, respectively. The X-ray structural analysis was performed with a Rigaku/AFC 7R Diffractometer. Elemental analyses were performed by this Institute.

3.1. General procedure for ring expansion

A mixture of 1,3-oxathiolane (**2**) (1 mmol) and $Rh_2(OAc)_4$ (5 mg, 0.01 mmol) in dry benzene (2 mL) was heated to reflux under a nitrogen atmosphere. A solution of 2-diazo-3,3,3-trifluoro-propionic acid methyl ester (**1**) (201 mg, 1.2 mmol) in benzene (2 mL) was added dropwise over 2 h through syringe. Reflux was continued for 2 h, and then the mixture was allowed to cool to rt. The solvent was removed under reduced pressure and the residue was purified by a flash chromatography on silica gel (petroleum–ethyl acetate) to give the ring expansion product 1,4-oxathiolane (**3**). The procedure for the preparation of products **6** and **7** are similar to that of **3**.

3.1.1. 2-Phenyl-3-trifluoromethyl-1,4-oxathiinane-3-carboxylic acid methyl ester (3a). Colorless crystal with mp: 59–61 °C, yield: 93%, IR (KBr): 2987, 2957, 2924, 1747, 1498, 1455, 1432, 1253, 1164 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.44 (d, 1H, $J=13.5$ Hz), 3.41 (t, 1H, $J=12.3$ Hz), 3.80 (s, 3H), 4.07 (t, 1H, $J=11.7$ Hz), 4.49 (d, 1H, $J=11.4$ Hz), 5.49 (s, 1H), 7.32–7.46 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.7, 53.4, 55.8 (d, $J_{F-C}=24.8$ Hz), 69.5, 82.4, 125.1 (q, $J_{F-C}=283.3$ Hz), 127.2, 128.0, 128.5, 137.5, 166.1 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.89 (s) ppm. EI-MS (*m*/*z*, %): 306 (M^+, 6), 200 (100), 172 (21), 105 (42), 77 (15), 59 (21). Anal. Calcd for $C_{13}H_{13}F_3O_3S$: C; 50.98, H; 4.28%. Found: C; 51.10, H; 4.25%.

X-ray data of **3a**

$C_{13}H_{13}F_3O_3S$: $M_w=306.29$, CCDC no. 284941, orthorhombic, space group: $P2(1)2(1)2(1)$, $a=6.755(10)$ Å $b=7.867(11)$ Å, $c=12.937(18)$ Å; $\alpha=91.464(3)°$, $\beta=92.651(3)°$, $\gamma=108.662(2)°$; $V=650.06(16)$ Å^3, $Z=1$, $D_c=1.794$ g/cm^3, $F(000)=348$. Radiation, Mo Kα ($\lambda=0.71073$ Å). Crystal dimension, $0.58\times0.44\times0.34$ mm.

Intensity data were collected at 293(2) K with a Bruker P4 four-circle diffractometer with graphite monochromator and Mo Kα radiation ($\lambda=0.71073$ Å). A total of 8147 independent reflection were measured in range $2.36<\theta<27.0°$. The structure was solved by directed methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically, hydrogen atoms were included but not refined. The final cycle of fullmatrix least-square refinement was base on F^2. The final R and wR value were 0.0490 and 0.1128, respectively. All calculations were performed using the SHELX-97 program.

3.1.2. 2-(2-Fluoro-phenyl)-3-trifluoromethyl-1,4-oxathiinane-3-carboxylic acid methyl ester (3b). Colorless crystal with mp: 71–73 °C, yield: 65%, IR (KBr): 3001, 2955, 2923, 1750, 1491, 1458, 1434, 1258, 1164 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.48 (d, 1H, $J=13.2$ Hz), 3.43 (t, 1H, $J=15.0$ Hz), 3.77 (s, 3H), 4.06 (t, 1H, $J=12.0$ Hz), 4.49 (d, 1H, $J=11.7$ Hz), 5.48 (s, 1H), 6.94–7.59 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.1, 53.6, 57.2 (d, $J_{F-C}=26.5$ Hz), 70.0, 82.3, 114.4, 114.7, 123.9, 129.1 (q, $J_{F-C}=283.4$ Hz), 129.5, 130.8, 130.9, 165.0 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −60.3 (s, 3F) −116.8 (s, 1F) ppm. EI-MS (*m*/*z*, %): 324 (M^+, 6), 200 (100), 172 (23), 123 (46), 113 (12), 59 (45). Anal. Calcd for $C_{13}H_{12}F_4O_3S$: C; 48.15, H; 3.73%. Found: C; 47.97, H; 3.84%.

3.1.3. 2-(2-Chloro-phenyl)-3-trifluoromethyl-1,4-oxathiinane-3-carboxylic acid methyl ester (3c). Colorless crystal, mp: 69–71 °C, yield: 75%, IR (KBr): 3011, 2958, 2967, 1934, 1740, 1478, 1437, 1258, 1160 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.49 (d, 1H, $J=12.6$ Hz), 3.47 (t, 1H, $J=13.5$ Hz), 3.75 (s, 3H), 4.06 (t, 1H, $J=11.7$ Hz), 4.49 (d, 1H, $J=11.7$ Hz), 5.59 (s, 1H), 7.25–7.65 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.7, 54.0, 58.1, 70.2, 79.8, 125.4 (q, $J_{F-C}=282.9$ Hz), 126.4, 128.5, 129.8, 130.5, 132.8, 135.3, 164.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.7 (s, 3F) ppm. EI-MS (*m*/*z*, %): 340 (M^+, 2), 200 (100), 172 (20), 139 (27), 113 (11), 59 (34). Anal. Calcd for $C_{13}H_{12}ClF_3O_3S$: C; 45.82, H; 3.55%. Found: C; 45.85, H; 3.62%.

3.1.4. 2-(2-Bromo-phenyl)-3-trifluoromethyl-1,4-oxathiinane-3-carboxylic acid methyl ester (3d). Colorless crystal, mp: 97–99 °C, yield: 75%, IR (KBr): 3062, 2995, 2920, 1745, 1474, 1431, 1262, 1225, 1170, 1153, 1095 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.48 (d, 1H, $J=13.8$ Hz), 3.46 (t, 1H, $J=12.0$ Hz), 3.75 (s, 3H), 4.05 (t, 1H, $J=12.0$ Hz), 4.49 (d, 1H, $J=11.7$ Hz), 5.59 (s, 1H), 7.15–7.56 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.7, 54.1, 58.0, 70.2, 82.4, 123.6, 125.5 (q, $J_{F-C}=285.1$ Hz), 126.9, 130.1, 130.9, 131.8, 136.9, 164.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.5 (s) ppm. EI-MS (*m*/*z*, %): 340/342 (M^+, 1/1), 200 (100), 185 (15), 183 (16), 172 (19), 113 (8), 59 (29). Anal. Calcd for $C_{13}H_{12}BrF_3O_3S$: C; 40.54, H; 3.14%. Found: C; 40.69, H; 3.27%.

3.1.5. 2-(4-Bromo-phenyl)-3-trifluoromethyl-1,4-oxathiinane-3-carboxylic acid methyl ester (3e). Colorless crystal, mp: 62–64 °C, yield: 92%, IR (KBr): 2996, 2957, 1749, 1489, 1338, 1249, 1173, 1162, 1099 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.44 (d, 1H, $J=13.5$ Hz), 3.37 (t, 1H, $J=12.3$ Hz), 3.78 (s, 3H), 4.02 (t, 1H, $J=11.7$ Hz), 4.46 (d, 1H, $J=11.7$ Hz), 5.41 (s, 1H), 7.24–7.26 (m, 2H), 7.41–7.44 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.0, 53.7, 55.3, 69.4, 85.8, 125.0 (q, $J_{F-C}=283.4$ Hz),

129.1, 131.0, 131.4, 136.6, 166.0 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.8 (s) ppm. EI-MS (*m/z*, %): 340/342 (M^+, 4/4), 200 (100), 185 (26), 183 (24), 172 (21), 113 (17), 77 (7), 59 (35). HR-EI-MS calcd for $C_{13}H_{12}BrF_3O_3S$ (M^+): 383.9643; found: 383.9657.

3.1.6. 2-(4-Nitro-phenyl)-3-trifluoromethyl-1,4-oxathiinane-3-carboxylic acid methyl ester (3f). Colorless crystal, mp: 77–79 °C, yield: 100%, IR (KBr): 3000, 2961, 2914, 1751, 1744, 1608, 1517, 1350, 1251, 1157, 1104, 1032 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.50 (d, 1H, J=13.8 Hz), 3.42 (t, 1H, J=12.3 Hz), 3.83 (s, 3H), 4.06 (t, 1H, J=12.0 Hz), 4.52 (d, 1H, J=11.7 Hz), 5.57 (s, 1H), 7.58–7.61 (m, 2H), 8.14–8.18 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.7, 53.8, 55.2, 69.3, 80.9, 123.0, 126.8, 130.5, 144.6, 147.8, 165.9 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.7 (s) ppm. EI-MS (*m/z*, %): 351 (M^+, 1), 200 (100), 172 (17), 113 (3), 77 (1), 59 (5). Anal. Calcd for $C_{13}H_{12}NF_3O_5S$: C; 44.45, H; 3.44, N; 3.99%. Found: C; 44.36, H; 3.27, N; 3.89%.

3.1.7. 2-(4-Methyl-phenyl)-3-trifluoromethyl-1,4-oxathiinane-3-carboxylic acid methyl ester (3g). Pale yellow liquid, yield: 88%, IR (KBr): 3009, 2958, 2865, 2253, 1749, 1715, 1616, 1516, 1437, 1363, 1264, 1224, 1171, 1105 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.44 (d, 1H, J=12.6 Hz), 3.42 (t, 1H, J=11.2 Hz), 3.80 (s, 3H), 4.06 (t, 1H, J=11.7 Hz), 4.49 (d, 1H, J=12.0 Hz), 5.45 (s, 1H), 7.12–7.15 (m, 2H), 7.26–7.35 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.2, 24.7, 53.5, 55.8, 69.6, 82.4, 123.3, 127.1, 128.6, 134.6, 138.2, 166.2 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.9 (s) ppm. EI-MS (*m/z*, %): 320 (M^+, 8), 200 (100), 172 (15), 119 (50), 91 (17), 84 (19), 59 (27). HR-MALDI-MS calcd for $C_{14}H_{15}F_3O_3SNa$ ($M+Na^+$): 343.0592; found: 343.0593.

3.1.8. 2-(4-Methoxyl-phenyl)-3-trifluoromethyl-1,4-oxathiinane-3-carboxylic acid methyl ester (3h). Pale yellow solid with mp: 82–84 °C, yield: 83%, IR (KBr): 3021, 2982, 2841, 1743, 1616, 1515, 1436, 1293, 1261, 1171, 1156, 1103 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.45 (d, 1H, J=13.5 Hz), 3.41 (t, 1H, J=12.0 Hz), 3.80 (s, 6H), 4.06 (t, 1H, J=11.7 Hz), 4.49 (d, 1H, J=13.5 Hz), 5.41 (s, 1H), 6.82–6.85 (m, 2H), 7.27–7.31 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.8, 53.4, 55.2, 55.7, 69.6, 82.1, 113.2, 125.2 (q, J_{F-C}=281.2 Hz), 128.5, 129.6, 159.6, 166.2 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −59.8 (s) ppm. EI-MS (*m/z*, %): 336 (M^+, 18), 200 (100), 172 (16), 136 (98), 135 (82), 113 (10), 77 (9), 59 (21). Anal. Calcd for $C_{14}H_{15}F_3O_4S$: C; 50.00, H; 4.50%. Found: C; 50.00, H; 4.47%.

3.1.9. 5-Trifluoromethyl-1-oxa-4-thia-spiro[5.5]undecane-5-carboxylic acid methyl ester (6). Pale yellow liquid, yield: 59%, IR (KBr): 3403, 2959, 2881, 1750, 1708, 1440, 1354, 1282, 1252, 1147, 1111 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38–1.87 (m, 6H), 2.01–2.05 (m, 2H) 2.30–2.34 (m, 2H), 2.86–3.04 (m, 2H), 3.76 (s, 3H), 3.86 (t, 1H, J=5.7 Hz), 4.18 (t, 1H, J=8.1 Hz) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.6, 22.6, 27.6, 32.9, 53.2, 60.0, 77.1, 124.0 (q, J_{F-C}=277.7 Hz), 165.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −52.1 (dd, J^1=10.1 Hz, J^2=36.7 Hz) ppm. EI-MS (*m/z*, %): 298 (M^+, 3), 200 (100), 188 (20), 159 (18), 142 (71), 91 (29), 59 (53), 45 (64). HR-MALDI-MS calcd for $C_{12}H_{17}F_3O_3SNa$ ($M+Na^+$): 321.0748; found: 321.0759.

3.1.10. 3,3,3-Trifluoro-2-[2-(1-phenyl-vinyloxy)-ethylsulfanyl]-propionic acid methyl ester (7). Pale yellow oil (152 mg, 48%), IR (KBr): 3467, 2959, 1751, 1713, 1686, 1439, 1361, 1269, 1147, 1111 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.21 (q, 2H, J=4.8 Hz), 3.80 (s, 3H), 3.82 (s, 1H), 4.10 (t, 2H, J=6.0 Hz), 4.23 (d, 1H, J=3.0 Hz), 4.72 (d, 1H, J=3.3 Hz), 7.34–7.62 (m, 5H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.4, 49.7, 53.2, 63.2, 83.2, 127.8 (q, J_{F-C}=282.8 Hz), 125.0, 125.4, 128.2, 128.6, 159.6, 165.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ −52.5 ppm. EI-MS (*m/z*, %): 321 (M^+, 15), 201 (100), 179 (6), 141 (17), 77 (5), 59 (8). HR-MALDI-MS calcd for $C_{14}H_{15}F_3O_3SNa$: 343.0592; found: 343.0598.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (NNSFC) (Nos. 20372077 and 20472106).

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