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Tetrahedron 61 (2005) 6982–6987
Tetrahedron

Diastereoselectivity-switchable and regiospecific hetero Diels–Alder reaction of *N*-sulfinylper(poly)fluoroalkanesulfinamides with dienes

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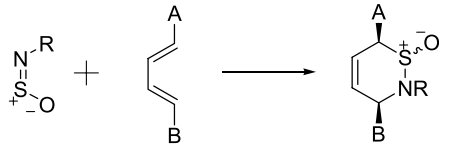
Received 29 December 2004; revised 11 May 2005; accepted 11 May 2005

Available online 4 June 2005

Abstract—*N*-Sulfinylper(poly)fluoroalkanesulfinamides reacted readily with dienes in methylene chloride at −78 °C to give the corresponding cycloadducts with complete regioselectivities and good diastereoselectivities. The diastereoselectivity of the reaction was switchable to the opposite under the catalysis of Lewis acids such as $TiCl_4$ and $SnCl_4$.

1. Introduction

Fluorine-containing heterocycles are fascinating targets for their unique bioactivities.[1] Accordingly, considerable effort has been devoted to the development of their synthetic strategies in recent years. Among various reactions available, hetero Diels–Alder reaction is an extremely useful method for the synthesis of heterocycles.[2] Hetero Diels–Alder reactions of *N*-sulfinylaniline and conjugated dienes were first described by Wichterle and Roceck in 1953. Since then a number of Diels–Alder reactions for various *N*-sulfinyl compounds have been reported (Scheme 1).[3] The cycloaddition usually takes place under mild conditions to afford dihydro-1,2-thiazine-1-oxides, which are precursors for unsaturated vicinal amino-alcohols and homoallylic amines, as well as a useful intermediate in the total synthesis of natural products and biologically active compounds.[4] Although the reactions of *N*-sulfinyl compounds are well studied, their fluorine-containing analogs are less reported.[5] To the best of our knowledge, *N*-sulfinyltrifluoromethanesulfinamide, CF_3SONSO, was first prepared in 1976.[6] However, its chemistry has not been studied yet, neither did the reaction of both *N*-sulfinylsulfinamides and their fluorinated analogs. In order to investigate the reaction of fluorine-containing *N*-sulfinyl compounds and synthesize fluorinated sulfur-containing heterocycles, *N*-sulfinylper(poly)fluoroalkanesulfinamides were prepared and their reaction with dienes was studied. The results are reported in this paper.



R=Ar, SO_2Ar, CO_2R, COPh, CN, $^+SR_2$, $PO(OR)_2$, SO_2NR_2, etc.

Scheme 1.

2. Results and discussion

N-Sulfinylper(poly)fluoroalkanesulfinamides (**5**) were prepared from per(poly)fluoroalkyl iodides (**1**) as shown in Scheme 2. Under mild conditions **1** readily reacted with sodium dithionite to give the corresponding sodium per(poly)fluoroalkanesulfinates.[7] Distillation of the sodium salts and concentrated sulfuric acid mixture gave free sulfinic acids **2**. Sulfinyl chorides **3** were obtained from **2** by the treatment with thionylchloride, which were further treated with hexamethyldisilazane to afford compound **4**. The reaction of **4** with thionylchloride gave **5** in moderate yields.

The reaction of **5** with dienes was first carried out at room temperature. In methylene chloride, compound **5** reacted

Keywords: *N*-Sulfinylper(poly)fluoroalkanesulfinamide; Hetero Diels–Alder reaction; Diene.
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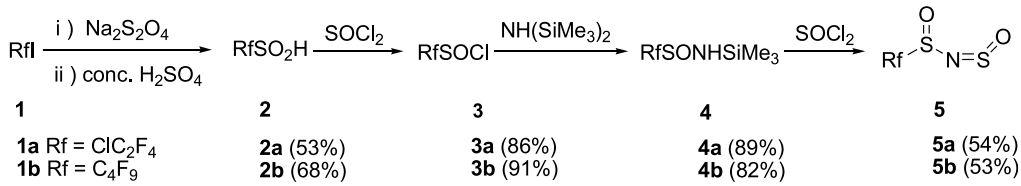
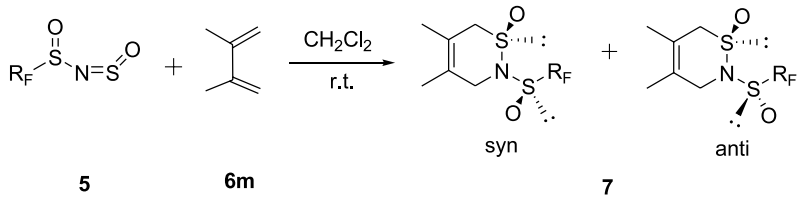
doi:10.1016/j.tet.2005.05.022



Scheme 2.



Scheme 3.

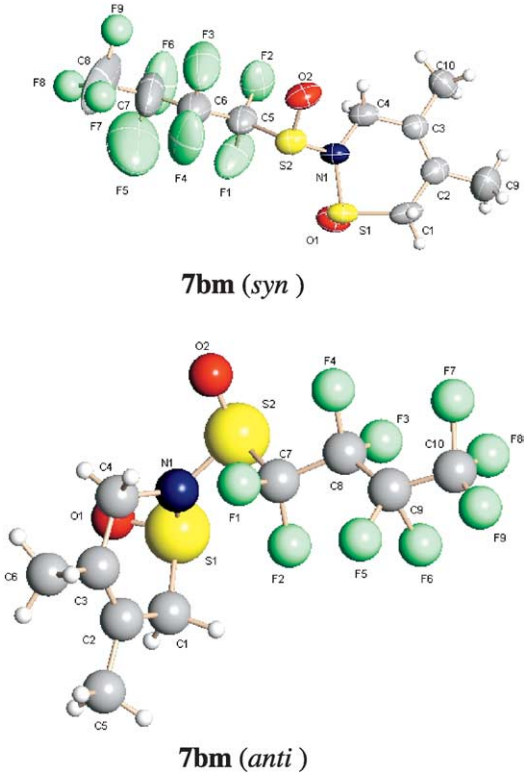


Figure 1. Molecular structure of **7bm**.

readily with 2,3-dimethyl-but-1,3-diene (**6m**) to give the corresponding cycloadduct **7** as a mixture of *syn*- and *anti*-isomers (Scheme 3). The two isomers could be separated by column chromatography. Their structures were determined on the basis of their NMR spectral and X-ray crystallographic study (Fig. 1).

To improve the stereoselectivity of the above reaction, various conditions were examined. As shown in Table 1, the ratio of two isomers changed distinctly when Lewis acids were added to the reaction mixture as a catalyst. Surprisingly it was found that opposite stereoselectivity was obtained with the addition of Lewis acids such as $TiCl_4$ and $SnCl_4$, and $TiCl_4$ gave the best result among the Lewis acids examined. Temperature also had effect on the stereoselectivity of the reaction. Much better stereoselectivities were obtained when the reaction was carried out at −78 °C (entries 7 and 9, Table 1). In all reactions, per(poly)fluoroalkanesulfinamides, R_fSONH_2, were formed as a by-product from the hydrolysis of **5** although the reaction was carried out under inert and anhydrous conditions.

The effect of $TiCl_4$ on the reaction diastereoselectivity might be explained as follows. The cycloaddition of *N*-sulfinyl compounds with dienes has been proved to be pericyclic.[8] The weight of evidence is that *N*-sulfinyl compounds exists in ground states in the *Z* configuration about the N=S double bond.[9] In the absence of $TiCl_4$, the dienophile prefers conformation **A** to minimize the electrostatic interaction between the two sulfinyl oxygens,[10]

Table 1. The reaction of **5** and **6m** under different conditions

Entry	Rf	Temperature	Catalyst	Product	Yield (%)[a]	*syn*/*anti*
1	ClC_2F_4	rt	—	**7am**	66	15:85
2	ClC_2F_4	rt	$BF_3{\cdot}Et_2O$	**7am**	71	18:82
3	ClC_2F_4	rt	$ZnCl_2$	**7am**	54	15:85
4	ClC_2F_4	rt	$AlCl_3$	**7am**	68	37:63
5	ClC_2F_4	rt	$SnCl_4$	**7am**	72	73:27
6	ClC_2F_4	rt	$TiCl_4$	**7am**	66	85:15
7	ClC_2F_4	−78 °C	—	**7am**	79	7:93
8	ClC_2F_4	−78 °C	$TiCl_4$	**7am**	59	98:2
9	C_4F_9	−78 °C	—	**7bm**	74	5:95
10	C_4F_9	−78 °C	$TiCl_4$	**7bm**	70	94:6

[a] Isolated yields based on **5**.

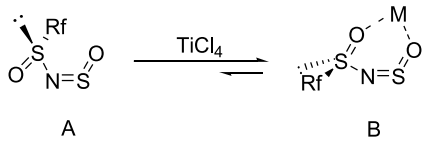


Figure 2.

electrophilic *N*-sulfinyl compounds had better regioselectivity in the hetero Diels–Alder reactions with dienes on the basis of the Hückel frontier orbital approach and experimental evidence.[8] So it is clear that the regioselectivity of this reaction is attributed to the strong electron-withdrawing ability of perfluoroalkylsulfinyl group.

Table 2. The cycloaddition reaction of **5** and asymmetrical dienes[a]

Entry	Rf	Diene	Catalyst	Product	Yield (%)[b]	*syn*/*anti*
1	ClC_2F_4	**6n**	—	**7an**	55	26:74
2	ClC_2F_4	**6n**	$TiCl_4$	**7an**	64	87:13
3	C_4F_9	**6n**	—	**7bn**	66	28:72
4	C_4F_9	**6n**	$TiCl_4$	**7bn**	62	90:10
5	ClC_2F_4	**6l**	—	**7al**	76	24:76
6	C_4F_9	**6l**	—	**7bl**	72	16:84

[a] All reactions were carried out at −78 °C.
[b] Isolated yields based on **5**.

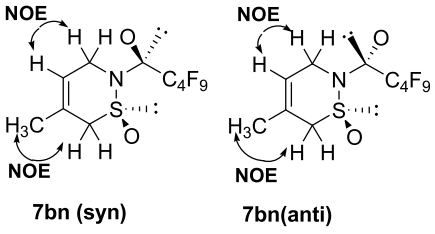


Figure 3. NOE correlations from NOESY spectra of **7bn**.

resulting in the predominant formation of *anti* cycloadducts when reacted with dienes (Fig. 2). While in the presence of $TiCl_4$ the reaction takes place through the chelating complex B, formed by the bonding of metal cation and two sulfinyl oxygens. Thus, the other side is the most accessible for the approach of the diene and opposite stereoselectivity is obtained.

To demonstrate the regioselectivity of this reaction, reactions of **5** and some asymmetrical dienes were investigated using the optimized conditions (Scheme 4). The results are summarized in Table 2. The cycloaddition of **5b** and **6n** gave only two isomers as indicated by ^{19}F NMR spectra of the crude products. Their structures were determined on the basis of NOESY spectra of purified products (Fig. 3). This indicated that the reaction proceeded in a completely regioselective manner with good diastereoselectivities. Similar results were reported in the literatures.[8,11] Hanson and Stockburn reported that less

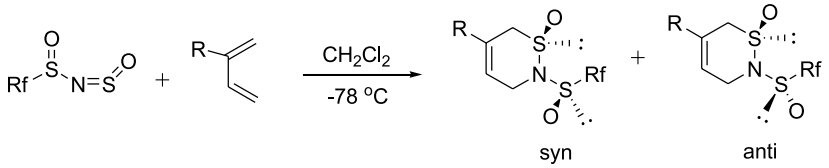
In summary, the cycloaddition reaction of *N*-sulfinylper(poly)fluoroalkanesulfinamides with dienes has been demonstrated, providing a facile method for the preparation of per(poly)fluoroalkanesulfinyl substituted dihydro-1,2-thiazine-1-oxides with complete regioselectivity and good diastereoselectivity.

3. Experimental

Melting points were uncorrected. ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker AM-300 spectrometer (300 MHz) with TMS as internal standard. ^{19}F NMR spectra were taken on a Bruker AM-300 (282 MHz) spectrometer using $CFCl_3$ as external standard. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Mass spectra and high resolution mass spectra (HRMS) were obtained on a Finnigan GC-MS 4021 and a Finnigan MAT-8430 spectrometer, respectively. Dichloromethane was distilled from CaH_2 and reagents were purified before use. Compound **5** was easy to hydrolyse and stored in CH_2Cl_2 solution.

3.1. General procedure for the synthesis of per(poly)-fluoroalkanesulfinic acids 2

With magnetic stirring, a mixture of $Na_2S_2O_4$ (34.8 g, 0.2 mol) and $NaHCO_3$ (16.8 g, 0.2 mol) was added to the mixture of per(poly)fluoroalkyl iodides **1** (0.15 mol), 180 mL H_2O and 120 mL CH_3CN at room temperature.



5 **6** **7**

5a Rf = ClC_2F_4 **6n** R = CH_3
5b Rf = C_4F_9 **6l** R = $CH_2CH_2CH{=}C(CH_3)CH_3$

Scheme 4.

After addition, the mixture was stirred for a few hours at room temperature to the completion of reaction (monitored by ^{19}F NMR). The resulting mixture was extracted with ethyl acetate (100 mL×4). The combined organic layer was washed with saturated aqueous NaCl solution (100 mL×3) and dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was dissolved in 120 mL of concentrated H_2SO_4 and distilled under reduced pressure to give **2** as a colorless oil.

3.1.1. 2-Chlorotetrafluoroethanesulfinic acid (2a). Colorless oil. Bp 62–63 °C/1 Torr. FT-IR (film): 2910, 1273, 1167 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 10.28 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −68.30 (m, 2F), −122.34 (m, 2F). EIMS (*m/z*, %): 201 (M^++1, 0.74), 135 (17.37), 116 (15.21), 100 (34.39), 85 (46.53), 65 (100.00), 50 (17.45), 48 (22.70), 45 (15.82). Anal. Calcd for $C_2HClF_4O_2S$: C, 11.98; H, 0.50. Found: C, 12.07; H, 0.66.

3.1.2. Nonafluorobutanesulfinic acid (2b).[12] Colorless oil. Bp 65–66 °C/1 Torr. FT-IR (film): 3397, 1299, 1254, 1291, 1141 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.60 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −81.21 (t, J=7.6 Hz, 3F), −122.77 (m, 2F), −123.24 (m, 2F), −126.59 (m, 2F). EIMS (*m/z*, %): 285 (M^++1, 0.67), 169 (16.24), 150 (19.38), 131 (30.83), 119 (28.92), 100 (29.85), 69 (100.00), 65 (78.37), 45 (44.44).

3.2. General procedure for the synthesis of perfluoroalkanesulfinyl chlorides 3

Perfluoroalkanesulfinic acid **2** (0.1 mol) was added dropwise to thionylchloride (7.4 mL, 0.1 mol) with stirring at 0 °C. After the addition, stirring was continued for 2 h at room temperature. The product was purified by distillation under reduced pressure.

3.2.1. 2-Chlorotetrafluoroethanesulfinyl chloride (3a). Colorless oil. Bp 58 °C/160 Torr. FT-IR (film): 1262, 1202, 1176, 1121, 1010, 792 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ −66.98 (m, 2F), −110.55, −117.60 (AB, J_{AB}= 218.8 Hz, 2F). EIMS (*m/z*, %): 218 (M^+, 0.26), 151 (17.33), 137 (34.02), 135 (100.00), 100 (28.19), 87 (20.08), 85 (81.31), 83 (69.59), 48 (22.11). Anal. Calcd for $C_2Cl_2F_4OS$: C, 10.97. Found: C, 10.94.

3.2.2. Nonafluorobutanesulfinyl chloride (3b).[12] Colorless oil. Bp 33–34 °C/40 Torr. FT-IR (film): 1719, 1351, 1239, 1140, 111, 747, 723 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ −81.4 (m, 3F), −111.2, −117.3 (AB, J_{AB}=233.57 Hz, 2F), −120.8 (m, 2F), −126.5 (m, 2F). EIMS (*m/z*, %): 169 (14.44), 131 (41.30), 119 (20.89), 100 (26.67), 69 (100.00), 65 (74.98), 48 (13.85), 47 (20.63).

3.3. General procedure for the synthesis of *N*-(trimethylsilyl)perfluoroalkanesulfinamides 4

To $NH(SiMe_3)_2$ (16 mL, 0.075 mol) was added dropwise perfluoroalkanesulfinyl chlorides (0.075 mol) at 0 °C. After addition, stirring was continued for 2 h at room temperature. The product was purified by distillation under reduced pressure.

3.3.1. *N*-Trimethylsilyl-2-chlorotetrafluoroethanesulfinamide (4a). Oil. Bp 62–63 °C/0.1 Torr. FT-IR (film): 1260, 1172, 1127, 1016, 911 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.28 (s, 9H), 5.01 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.1 (m, 2F), −110.1, −126.21 (AB, J_{AB}=232.2 Hz, 2F). EIMS (*m/z*, %): 272 (M^++1, 0.02), 100 (7.30), 85 (12.22), 73 (17.31), 66 (7.13), 64 (100.00), 48 (11.80), 47 (6.59), 46 (13.23). HRMS: calcd for $C_5H_{10}ClF_4NNaOSSi$: 293.9769. Found: 293.9767.

3.3.2. *N*-Trimethylsilyl-nonafluorobutanesulfinamide (4b).[12] Oil. Bp 52–53 °C/0.01 Torr. FT-IR (film): 3221, 1353, 1237, 1142, 852 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.31 (s, 9H), 4.82 (s, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −81.2 (m, 3F), −120.1, −128.2 (AB, J_{AB}=234.9 Hz, 2F), −122.3 (m, 2F), −126.6 (m, 2F). EIMS (*m/z*, %): 131 (13.37), 100 (10.37), 69 (40.57), 66 (7.80), 64 (100.00), 48 (21.41), 47 (7.99), 46 (19.98).

3.4. General procedure for the synthesis of *N*-sulfinylper(poly)fluoroalkanesulfinamides 5

To thionyl chloride (3.7 mL, 0.05 mol) was added slowly *N*-(trimethylsilyl)-perfluoroalkanesulfinamide (0.05 mol) by a syringe pump at room temperature. After addition, the mixture was stirred at room temperature for a few hours to the completion of reaction (monitored by ^{19}F NMR). The resulting mixture was distilled under reduced pressure to give **5**.

3.4.1. *N*-Sulfinyl-2-chlorotetrafluoroethanesulfinamide (5a). Oil. Bp 60 °C/15 Torr. FT-IR (film): 1236, 1168, 1122, 1075, 1015, 801 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ −66.8 (m, 2F), −112.6, −116.5 (AB, J_{AB}=223.1 Hz, 2F). EIMS (*m/z*, %): 245 (M^+, 2.04), 202 (37.62), 201 (8.47), 200 (100.00), 85 (11.30), 64 (93.32), 48 (23.14), 47 (12.46), 46 (33.93). Anal. Calcd for $C_2ClF_4NO_2S_2$: C, 9.78; N, 5.70. Found: C, 9.95; N, 5.90.

3.4.2. *N*-Sulfinylnonafluorobutanesulfinamide (5b). Oil. Bp 66–67 °C/15 Torr. FT-IR (film): 1353, 1236, 1212, 1141, 1109, 726, 696 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$): δ −81.2 (m, 3F), −114.1, −117.1 (AB, J_{AB}=291.5 Hz, 2F), −121.4 (m, 2F), −126.6 (m, 2F). EIMS (*m/z*, %): 329 (M^+, 4.49), 284 (100.00), 282 (13.08), 131 (10.04), 69 (31.29), 64 (91.92), 48 (39.24), 47 (13.61), 46 (44.27). HRMS: calcd for $C_4F_9NO_2S_2$: 328.9227. Found: 328.9261.

3.5. General procedure for the reaction of *N*-sulfinylper(poly)fluoroalkanesulfinamides 5 and dienes

To a flame-dried flask were added *N*-sulfinylper(poly)fluoroalkanesulfinamide **5** (1 mmol), Lewis acid (1.2 mmol) and dry CH_2Cl_2 (5 mL) at −78 °C under N_2 atmosphere. After stirring for 30 min, diene (2 mmol) was added to the solution via a syringe and the mixture was stirred for 8 h. The reaction mixture was diluted with dichloromethane and washed with saturated aqueous $NaHCO_3$ solution and saturated aqueous NaCl solution, dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was purified by chromatography on silica gel using ethyl acetate/hexane (v/v: 1:8) as elute to give compound **7**.

3.5.1. 4,5-Dimethyl-2-(2-chlorotetrafluoroethanesulfinyl)-3,6-dihydro-2*H*-[1,2]thiazine-1-oxide (7am). *syn Isomer*. White solid, mp 72–73 °C. FT-IR (KBr): 1185, 1161, 1119, 1095, 1056, 883, 796 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.82 (s, 6H), 3.30, 3.75 (AB, J_{AB}=15.9 Hz, 2H), 3.96, 4.09 (AB, J_{AB}=15.6 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −68.0 (m, 2F), −110.1, −117.9 (AB, J_{AB}=228.0 Hz, 2F). EIMS (*m/z*, %): 328 (M^++1, 0.16), 144 (91.12), 129 (52.85), 95 (61.46), 94 (58.44), 81 (72.41), 67 (100.00), 41 (92.50), 39 (56.36). Anal. Calcd for $C_8H_{10}ClF_4O_2S_2$: C, 29.32; H, 3.08; N, 4.27. Found: C, 29.17; H, 3.35; N, 4.31.

anti Isomer. White solid, mp 61–62 °C. FT-IR (KBr): 2932, 1174, 1154, 1013, 796 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.83 (s, 6H), 3.27, 3.56 (AB, J_{AB}=16.2 Hz, 2H), 3.76, 4.05 (AB, J_{AB}=17.1 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.8 (m, 2F), −111.7, −116.9 (AB, J_{AB}=229.0 Hz, 2F). EIMS (*m/z*, %): 328 (M^++1, 42.60), 192 (80.64), 144 (100.00), 129 (72.26), 95 (67.83), 94 (53.71), 81 (64.48), 67 (63.46), 41 (68.69). Anal. Calcd for $C_8H_{10}ClF_4O_2S_2$: C, 29.32; H, 3.08; N, 4.27. Found: C, 29.46; H, 3.26; N, 4.25.

3.5.2. 4,5-Dimethyl-2-(nonafluorobutanesulfinyl)-3,6-dihydro-2*H*-[1,2]thiazine-1-oxide (7bm). *syn Isomer*. White solid, mp 74–75 °C. IR (KBr): 1249, 1221, 1196, 1108, 997, 884 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.82 (s, 6H), 3.31, 3.78 (AB, J_{AB}=16.2 Hz, 2H), 3.95, 4.11 (AB, J_{AB}=14.9 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −81.0 (m, 3F), −110.8, −119.2 (AB, J_{AB}=238.8 Hz, 2F), −122.1 (m, 2F), −126.3 (m, 2F). EIMS (*m/z*, %): 412 (M^++1, 0.20), 192 (55.40), 144 (100.00), 129 (47.89), 95 (53.78), 81 (59.71), 69 (58.95), 67 (73.08), 41 (63.63). Anal. Calcd for $C_{10}H_{10}F_9NO_2S_2$: C, 29.20; H, 2.45; N, 3.41. Found: C, 29.34; H, 2.48; N, 3.34.

anti Isomer. White solid, mp 69–70 °C. IR (KBr): 1239, 1197, 1177, 1148 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.82–1.85 (m, 6H), 3.30, 3.57 (AB, J_{AB}=16.2 Hz, 2H), 3.78, 4.06 (AB, J_{AB}=17.4 Hz, 2H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.9 (t, J=12.1 Hz, 3F), −112.1, −119.2 (AB, J_{AB}=242.5 Hz, 2F), −122.4 (m, 2F), −126.3 (m, 2F). EIMS (*m/z*, %): 412 (M^++1, 6.55), 129 (37.62), 95 (43.84), 94 (50.25), 81 (50.25), 69 (69.61), 53 (39.71), 41 (63.63). Anal. Calcd for $C_{10}H_{10}F_9NO_2S_2$: C, 29.20; H, 2.45; N, 3.41. Found: C, 29.20; H, 2.50; N, 3.37. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 248677 and 248678. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

3.5.3. 5-Methyl-2-(2-chlorotetrafluoroethanesulfinyl)-3,6-dihydro-2*H*-[1,2]thiazine-1-oxide (7an). FT-IR (KBr): 2979, 2316, 1169, 1142, 1112 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.88 (s, 3H), 3.25, 3.53 (AB, J_{AB}=15.9 Hz, 2H), 3.96, 4.12 (AB, J_{AB}=17.1 Hz, 2H), 5.79–5.81 (m, 1H) (*anti*); 1.86 (s, 3H), 3.28, 3.68 (AB, J_{AB}=16.2 Hz, 2H), 4.03, 4.27 (AB, J_{AB}=16.5 Hz, 2H), 5.76–5.77 (m, 1H) (*syn*). ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.9 (m, 2F), −111.8, −117.0 (AB, J_{AB}=228.4 Hz, 2F) (*anti*); −67.8 (m, 2F), −109.8, −117.5 (AB, J_{AB}=222.8 Hz, 2F) (*syn*). EIMS (*m/z*, %): 361 (47.58), 360 (14.22), 359 (100.00), 289 (7.76), 237 (15.70), 209 (9.09), 176 (6.46), 135 (9.73). Anal. Calcd for $C_7H_8ClF_4NO_2S_2$: C, 26.80; H, 2.57; N, 4.46. Found: C, 26.52; H, 2.49; N, 4.57.

3.5.4. 5-Methyl-2-nonafluorobutanesulfinyl-3,6-dihydro-2*H*-[1,2]thiazine-1-oxide (7bn). *syn Isomer*. White solid, mp 70–71 °C. IR (KBr): 1352, 1237, 1202, 1181 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.88 (s, 3H), 3.32, 3.72 (AB, J_{AB}=16.5 Hz, 2H), 4.06, 4.31 (AB, J_{AB}=16.5 HZ, 2H), 5.78–5.79 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −81.0 (t, J=12.4 Hz, 3F), −110.8, −119.1 (AB, J_{AB}=238.3 Hz, 2F), −122.1 (m, 2F), −126.3 (m, 2F). EIMS (*m/z*, %): 398 (M^++1, 0.70), 178 (100.00), 130 (36.47), 115 (36.47), 82 (38.20), 81 (56.63), 80 (39.97), 67 (45.27), 53 (40.51). Anal. Calcd for $C_9H_8F_9NO_2S_2$: C, 27.21; H, 2.03; N, 3.53. Found: C, 27.16; H, 2.19; N, 3.47.

anti Isomer. White solid, mp 63–64 °C. IR (KBr): 2980, 1358, 1263, 1241 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.90 (s, 3H), 3.28, 3.54 (AB, J_{AB}=16.5 Hz, 2H), 3.98, 4.14 (AB, J_{AB}=18.3 Hz, 2H), 5.81–5.82 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −81.0 (t, J=9.3 Hz, 3F), −112.3, −119.3 (AB, J_{AB}=239.7 Hz, 2F), −122.4 (m, 2F), −126.4 (m, 2F). EIMS (*m/z*, %): 398 (M^++1, 0.32), 178 (100.00), 115 (42.25), 81 (14.52), 69 (56.52), 68 (68.58), 67 (86.68), 53 (49.56), 41 (55.38). Anal. Calcd for $C_9H_8F_9NO_2S_2$: C, 27.21; H, 2.03; N, 3.53. Found: C, 27.16; H, 2.26; N, 3.47.

3.5.5. 5-(4-Methylpent-3-enyl)-2-(2-chlorotetrafluoroethanesulfinyl)-3,6-dihydro-2*H*-[1,2]-thiazine-1-oxide (7al). FT-IR (KBr): 1162, 1120, 1014, 793 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.62 (s, 3H), 1.70 (s, 3H), 2.12–2.16 (m, 4H), 3.27–3.73 (m, 2H), 3.96–4.36 (m, 2H), 5.07–5.08 (m, 1H), 5.77–5.81 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.9 (m, 2F), −111.8, −116.6 (AB, J_{AB}=229.3 Hz, 2F) (*anti*); −67.8 (m, 2F), −111.0, −117.6 (AB, J_{AB}=222.8 Hz, 2F) (*syn*). EIMS (*m/z*, %): 183 (32.40), 169 (27.93), 134 (30.80) 133 (31.11), 107 (33.41), 105 (26.35), 80 (28.02), 67 (26.17). Anal. Calcd for $C_{12}H_{16}ClF_4NO_2S_2$: C, 37.75; H, 4.22; N, 3.67. Found: C, 37.73; H, 4.13; N, 3.71.

3.5.6. 5-(4-Methylpent-3-enyl)-2-nonafluorobutanesulfinyl-3,6-dihydro-2*H*-[1,2]thiazine-1-oxide (7bl). FT-IR (KBr): 1352, 1236, 1214, 1179, 1139, 1109, 1092 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.61 (s, 3H), 1.70 (s, 3H), 2.00–2.17 (m, 4H), 3.29–3.56 (m, 2H), 3.97–4.19 (m, 2H), 5.07–5.12 (m, 1H), 5.80–5.81 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.9 (m, 3F), −111.2, −119.0 (AB, J_{AB}=252.1 Hz, 1.7F, *anti isomer*), −110.8, −119.0 (AB, J_{AB}=237.7 Hz, 0.3F, *syn isomer*), −122.1 (m, 2F), −126.3 (m, 2F). EIMS (*m/z*, %): 246 (53.79), 183 (26.28), 135 (28.17), 121 (37.53), 93 (50.94), 91 (27.37), 69 (100.00), 41 (97.84). Anal. Calcd for $C_{14}H_{16}F_9NO_2S_2$: C, 36.13; H, 3.47; N, 3.01. Found: C, 36.27; H, 3.47; N, 2.98.

Acknowledgements

We thank the National Natural Science Foundation of China for financial support (No. 20172065).

References and notes

1. (a) Sloop, J. C.; Bumgardner, C. L.; Leohle, W. D. *J. Fluorine Chem.* **2002**, *118*, 135–147. (b) Zhu, S. Z.; Wang, Y. L.; Peng, W. M.; Song, L. P. *Curr. Org. Chem.* **2002**, *6*, 1057–1096.
2. (a) Amii, H.; Kobayashi, T.; Terasawa, H.; Uneyama, K. *Org. Lett.* **2001**, *3*, 3103–3105. (b) Zimmer, R.; Reissig, H. U. *J. Org. Chem.* **1992**, *57*, 339–347.
3. Garipipati, R. S.; Freyer, A. J.; Whittle, R. R.; Weinreb, S. M. *J. Am. Chem. Soc.* **1984**, *106*, 7861–7867.
4. Bayer, A.; Hansen, L. K.; Gautun, O. R. *Tetrahedron: Asymmetry* **2002**, *13*, 2407–2415.
5. Zhu, S. Z.; Liu, X. Y.; Wang, S. W. *Tetrahedron* **2003**, *59*, 9669–9676.
6. Roesky, H. W.; Holtschneider, G. *J. Fluorine Chem.* **1976**, *7*, 77–84.
7. Hu, L. Q.; Huang, W. Y. *Youji Huaxue (Chin. J. Org. Chem.)* **1991**, *11*, 126–132.
8. Hanson, P.; Stockburn, W. A. *J. Chem. Soc., Perkin Trans. 2* **1985**, 589–595.
9. (a) Caminati, W.; Mirri, A.; Maccagnani, G. *J. Mol. Struct.* **1977**, *36*, 368–374. (b) Meij, R.; Oskam, A.; Stufkens, D. *J. Mol. Struct.* **1979**, *51*, 37–49.
10. García Ruano, J. L.; Alemparte, C.; Martín Castro, A. M.; Adams, H.; Rodríguez Ramos, J. H. *J. Org. Chem.* **2000**, *65*, 7938–7943.
11. Serramedan, D.; Delmond, B.; Deleris, G. *Tetrahedron Lett.* **1990**, *31*, 7007–7010.
12. Roesky, H. W.; Tutkunkardes, S. *Chem. Ber.* **1974**, *107*, 508–517.