Journal of Fluorine Chemistry 132 (2011) 409–413

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

L-Proline catalyzed condensation–cyclization tandem process: Facile and effective synthesis of 3-polyfluoroalkanesulfonyl coumarin

Jianwei Han, Yong Xin, Jingwei Zhao, Shizheng Zhu *

Key Laboratory of Organouorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, PR China

ARTICLE INFO

Article history:
Received 26 February 2011
Received in revised form 6 April 2011
Accepted 8 April 2011
Available online 15 April 2011

Keywords:
Salicylaldehyde
Condensation
Cyclization
Polyfluoroalkanesulfonyl
Coumarin

ABSTRACT

A L-proline catalyzed condensation–cyclization tandem process is reported, which affords the potentially pharmaceutic coumarin derivatives. The mild conditions, simplicity of the purification process and satisfactory yields makes the method a facile and effective way toward the 3-polyfluoroalkanesulfonyl coumarins.

1. Introduction

Coumarin and its derivatives represent one of the most active classes of compound possessing a wide spectrum of biological activity [1–3]. Novobiocin and chlorobiocin are established antimicrobials containing a coumarin skeleton [4]. Many of these compounds have proved to be active as, antibacterial [5–7], antifungal [8], anti inflammatory [9], anticoagulant [10], anti-HIV [11] and antitumor [12]. In addition, these compounds are used as additives to food and cosmetics [13]. Coumarin derivatives are commonly used as optical whiteners, luminescence dyes [14], active media for lasers [15] and solar collector [16]. Various analogues of 4-substituted coumarin such as 4-chlorocoumarins exhibit antimicrobial activity. Thus, the synthesis of coumarin derivatives is still a popular research topic in organic chemistry. To the best of our knowledge, traditionally, these compounds are achieved by Perkin reaction, Knoevenagel reaction, Pechmann reaction, Michael reaction, Wittig reaction, Vilsmeier–Haack reaction, and Pd-catalyzed reactions. Among them, the Knoevenagel reaction represents one class of the mostly used methods, which is usually catalyzed by base or acid, such as pyridine, pyperidine, amine, acid and so on. During our research on the chemical transformation of fluorine-containing active methylene compounds, we found that they could react with aromatic aldehydes readily to give the Knoevenagel condensation products in the presence of L-proline. So it would be meaningful if the reaction could go further to afford the coumarin derivatives when reacted with salicylaldehyde.

Herein, we reported the detailed results of the reaction.

2. Results and discussion

Initially, we found that the Knoevenagel condensation between 2-((perfluorobutyl)sulfonyl) acetonitrile **1c** and benzaldehyde **2a** did not occur without any catalyst. After addition of 5 mol% of L-proline, the reaction could give the condensation product **3a** in a yield of 78%. Increasing the loading of catalyst improved the yield and shortened the reaction time (Table 1, entries 2–5). The yield began to decrease when the amount of L-proline was more than 25 mol%. Thus, the amount of the catalyst was optimized as 20 mol% (Table 1).

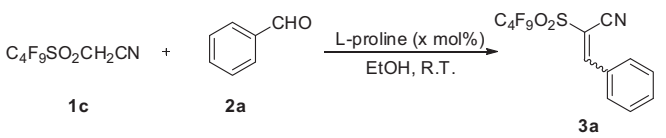
With the optimized condition in hand, we examined the scope of the fluorine-containing active methylene compounds. To our delight, they worked very well and gave the desired products in good yields (Table 2).

It was indicated in the results that the aromatic aldehyde with an electron-withdrawing group gave a lower yield than that with an electron-donating group. For instance, 3-nitrobenzaldehyde led to a yield of 73% (Table 2, entry 6), but *p*-anisaldehyde and 4-dimethylaminobenzaldehyde gave the products in yields of 89% (Table 2, entry 3) and 85% (Table 2, entry 10), respectively. Also, due to the electronic effect, 3-indolealdehyde **2h** afforded the product **3h** in a yield of 88% (Table 2, entry 8).

* Corresponding author. Tel.: +86 21 54925185; fax: +86 21 64166128.
E-mail addresses: zhusz@sioc.ac.cn, zhusz@mail.sioc.ac.cn (S. Zhu).

0022-1139/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2011.04.001

Table 1
Effect of the amount of L-proline.

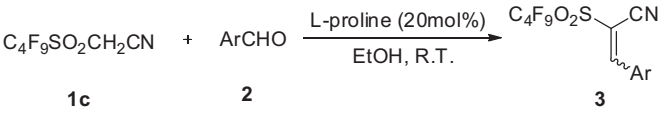


1c 2a 3a

Entry	*x*	Time (h)	Yield[a] (%)
1	0	48	Trace [b]
2	5	30	78
3	10	30	80
4	15	18	81
5	20	16	86
6	25	15	86
7	30	15	85
8	40	15	83

[a] Isolated yield after recrystallization.
[b] Determined by TLC analysis.

Table 2
Results of the Knoevenagel condensation.



1c 2 3

Entry	ArCHO	Time (h)	Product	Yield (%)[a]
1	C_6H_5 (**2a**)	16	**3a**	76
2	*p*-$CH_3C_6H_4$ (**2b**)	13	**3b**	87
3	*p*-$CH_3OC_6H_4$ (**2c**)	14	**3c**	89
4	*o*-BrC_6H_4 (**2d**)	13	**3d**	83
5	C_6H_5CH=CH (**2e**)	13	**3e**	86
6	*p*-$NO_2C_6H_4$ (**2f**)	10	**3f**	73
7	*p*-BrC_6H_4 (**2g**)	13	**3g**	85
8	3-Indole (**2h**)	14	**3h**	88
9	*o*-FC_6H_4 (**2i**)	12	**3i**	82
10	*p*-$(CH_3)_2NC_6H_4$ (**2j**)	14	**3j**	85

[a] Isolated yield after recrystallization.

Encouraged by those results, we examined the reaction between methyl 2-((perfluorobutyl)sulfonyl)acetate **1a** and salicylaldehyde **4a** under the same condition (Table 3). After stirring for 16 h, the reaction gave a product cleanly in a yield of 86%. According to the data of ^{1}H NMR spectrum, the disappearance of the peaks of C*H*O at 10.3 ppm indicated the Knoevenagel condensation proceeded successfully. Mass spectrum showed a molecular ion peak at m/z = 430 that indicated the formation of coumarin product. Other spectra data, such as elemental analysis and FT-IR, further suggested the formation of coumarin. Then we examine both the scopes of active methylene compounds and salicylaldehydes. It could be inferred that the fluoroalkylsulfonyl substituents of **1** had little influence on the yield. To our delight, not only **1a** and **1b**, but also the CN substituted substrate **1c** could react smoothly. However, due to the weak electron-withdrawing property, the reaction of **1c** with salicylaldehydes consumed more time and the yield was lower.

The proline catalyzed aldol reactions proceeded via an enamine intermediate **A**. **A** reacted with salicylaldehyde via transition state **B** to give intermediate **C**. The following dehydration and intramolecular transesterification gave the coumarin product (Scheme 1).

3. Conclusion

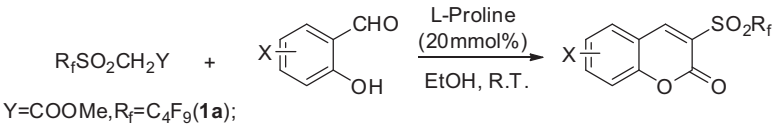
In summary, L-proline has been employed as an efficient catalyst for the preparation of 3-polyfluoroalkanesulfonyl coumarin. The reaction proceeded via a condensation–cyclization tandem process under mild conditions and gave the coumarin products in good yields. The reaction was proposed to proceed via an enamine intermediate. The simple and convenient purification procedure made the method a facile and effective way toward the 3-polyfluoroalkanesulfonyl coumarins.

4. Experimental

4.1. General information

Melting points were measured on a Temp-Melt apparatus and are uncorrected. ^{1}H and ^{19}F NMR spectra were recorded on Bruker AM-300 instruments with Me_4Si and $CFCl_3$ as the internal

Table 3
Results of the reactions between **1** and **4**.

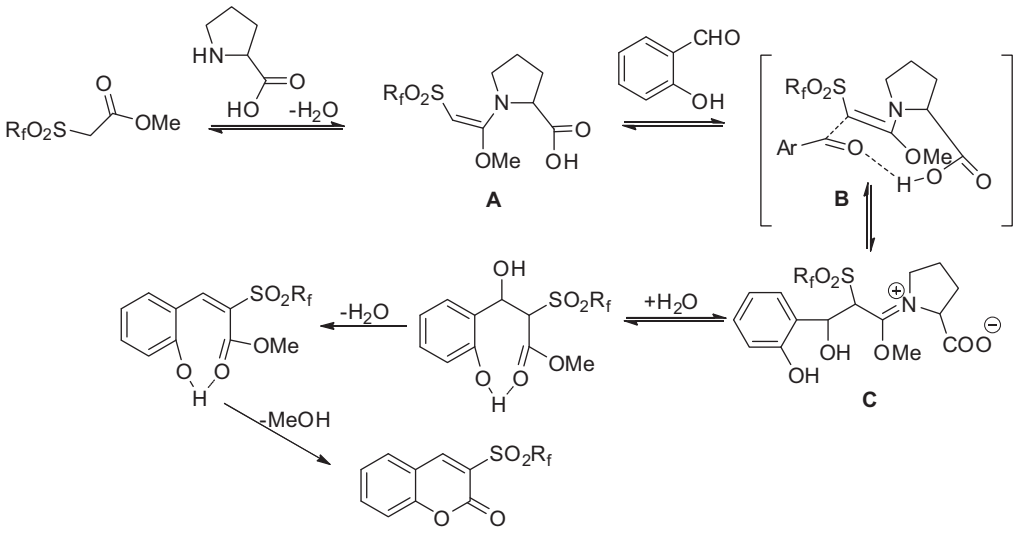


Y=COOMe, R_f=C_4F_9(**1a**);
R_f= ClC_4F_8(**1b**);
Y=CN, R_f=C_4F_9(**1c**).

1 4 5

Entry	**1**	*X*	Time (h)	Product	Yield (%)[a]
1		H (**4a**)	16	**5a**	76
2		5-Br (**4b**)	15	**5b**	74
3	**1a**	5-Cl (**4c**)	18	**5c**	73
4		4-OMe (**4d**)	18	**5d**	75
5		3,5-2Cl (**4e**)	18	**5e**	72
6		H (**4a**)	16	**5f**	74
7	**1b**	5-Br (**4b**)	17	**5g**	76
8		5-Cl (**4c**)	18	**5h**	73
9		4-OMe (**4d**)	18	**5i**	72
10		H (**4a**)	20	**5a**	58
11	**1c**	5-Br (**4b**)	20	**5b**	54
12		5-Cl (**4c**)	20	**5c**	57

[a] Isolated yield after recrystallization.



Scheme 1. The proposed mechanism of the reaction of 2-((polyfluoroalkyl)sulfonyl)acetate and salicylaldehyde.

standards and external standards, respectively. FTIR spectra were obtained with a Nicolet AV-360 spectrophotometer. Low resolution mass spectra (LRMS) were obtained on a Finnigan GC–MS 4021, using the electron impact ionization technique (70 eV). The L-proline was commercially available and used without any activation. The products **1a**, **1c**, **3a**, **3c**, **3d**, **3f**, **5a** obtained were characterized by comparison of their spectroscopic data with those reported in the literature [16–18].

4.2. General experimental procedures for the synthesis of 1a and 1b

A solution of 1,1,1,2,2,3,3,4,4-nonafluoro-4-(methylsulfonyl)-butane (10 mmol, 2.98 g) in anhydrous THF (15 ml) was added dropwise to the anhydrous THF (35 ml) containing NaH (60% in mineral oil, 22 mmol, 0.8 g) at 0 °C under N_2 atmosphere. After 30 min a solution of methyl chloroformate (10 mmol, 0.95 g) in anhydrous THF (15 ml) was added dropwise at −15 °C the resulting mixture was warmed to room temperature and after 2 h was hydrolyzed at 0 °C by addition of saturated NH_4Cl. The aqueous layer was extracted with ether. The combined organic layers were washed with brine, dried with Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by flash chromatography over silica gel.

2-((perfluorobutyl)sulfonyl)acetonitrile **1c** was prepared following the Subramanian's procedure [18].

4.2.1. Methyl (4-chloro-1,1,2,2,3,3,4,4-octafluorobutyl-1-sulfonyl)-acetate (1b)

Colorless oil. Yield: 79%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.31 (s, 2H, CH_2), 3.92 (s, 3H, CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.8 (m, 2F, CF_2Cl), −109.1 (m, 2F, CF_2–SO_2), −119.2 to −120.5 (m, 4F, CF_2CF_2). IR (film) cm^{-1}: 3013, 2963, 1757, 1440, 1383, 1288, 1204, 1144, 1082, 961, 696. MS (70 eV, EI) *m*/*z* (%): 341 (M^+−OMe, 18), 235 (6), 137 (33). Anal. Calcd. for $C_7H_5F_8ClO_3S$ (%): C 22.55, H 1.34; Found: C 22.66, H 1.70.

4.3. General experimental procedures for the synthesis of 2-aryl-(perfluorobutylsulfonyl l)-acrylonitriles

To a solution of (nonafluorobutanesulfonyl) acetonitrile **1c** (2 mol, 646 mg) and benzaldehyde **2a** (2 mol, 212 mg) in EtOH (8 ml) was added L-proline (0.4 mmol, 46 mg) and the solution was stirred at r.t. until completion of reaction as indicated by TLC. The reaction mixture was directly recrystallized to afford the product **3a**.

4.3.1. (E)-2-(perfluorobutylsulfonyl)-3-(p-methylphenyl)-acrylonitrile (3b)

Light yellow solid, mp 102–103 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.26–7.01 (m, 4H), 2.51 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.6 (m, 3F, CF_3), −109.6 (m, 2F, CF_2–SO_2), −120.7 (m, 2F, CF_2CF_2–SO_2), −125.8 (m, 2F, CF_2CF_3). IR (KBr) cm^{-1}: 3040, 2224, 1583, 1420, 1371, 1302, 1117, 1041, 980, 947, 816, 737, 648. MS (70 eV, EI) *m*/*z* (%): 425 (M^+, 18), 206 (89), 142 (100), 115 (62), 69 (21). Anal. Calcd. for $C_{14}H_8F_9NO_2S$: C 39.54, H 1.90, N 3.29; Found: C 39.46, H 1.89, N 3.37.

4.3.2. (2E,4E)-2-(perfluorobutylsulfonyl)-3-(1,3-butadienyl-phenyl)-acrylonitrile (3e)

Yellow solid, mp 93–94 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.99–8.03 (d, 1H), 7.40–7.62 (m, 6H), 7.18–7.24 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.6 (m, 3F, CF_3), −110.2 (2F, m, CF_2–SO_2), −120.7 (m, 2F, CF_2CF_2–SO_2), −125.8 (m, 2F, CF_2CF_3). IR (KBr) cm^{-1}: 3027, 2223, 1607, 1578, 1554, 1376, 1354, 1234, 1140, 999, 752, 683, 619. MS (70 eV, EI) *m*/*z* (%): 437 (M^+, 22.6), 218 (28.8), 154 (62.9), 137 (100.0). Anal. Calcd. for $C_{15}H_8F_9NO_2S$: C 41.20, H 1.84, N 3.20; Found: C 41.15, H 1.93, N 3.29.

4.3.3. (E)-2-(perfluorobutylsulfonyl)-3-(p-bromophenyl)-acrylonitrile (3g)

Light yellow solid, mp 102–103 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.77–7.98 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.5 (m, 3F, CF_3), −109.6 (m, 2F, CF_2–SO_2), −120.6 (m, 2F, CF_2CF_2–SO_2), −125.7 (m, 2F, CF_2CF_3). IR (KBr) cm^{-1}: 2223, 1609, 1582, 1578, 1488, 1456, 1369, 1360, 1209, 1140, 1056, 956. MS (70 eV, EI) *m*/*z* (%): 489 (M^+), 272 (41), 270 (40), 208 (40), 206 (42), 127 (100), 69 (22). Anal. Calcd. for $C_{13}H_5BrF_9NO_2S$: C 31.86, H 1.03, N 2.86; Found: C 31.87, H 1.07, N 2.90.

4.3.4. (E)-2-(perfluorobutylsulfonyl)-3-indole-acrylonitrile (3h)

Yellow solid, mp 196–197 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.66 (br. s, 1H), 8.81 (s, 1H), 8.53 (s, 1H), 7.41–7.81 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.6 (m, 3F, CF_3), −110.6 (m, 2F, CF_2–SO_2), −120.7 (m, 2F, CF_2CF_2–SO_2), −125.8 (m, 2F, CF_2CF_3). IR (KBr) cm^{-1}: 3387, 2220, 1589, 1560, 1504, 1422, 1379, 1351, 1203, 1135, 1056. MS (70 eV, EI) *m*/*z* (%): 450 (M^+), 367 (3), 231 (15), 167 (50), 140

(100), 69 (15). Anal. Calcd. for $C_{15}H_5F_9N_2O_2S$: C 41.01, H 1.57, N 6.22. Found: C 39.93, H 1.48, N 6.13.

*4.3.5. (E)-2-(perfluorobutylsulfonyl)-3-(o-fluorophenyl)-acrylonitrile (**3i**)*

Yellow solid, mp 78–79 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (s, 1H), 7.19–7.73 (m, 4H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.5 (m, 3F, CF_3), −108.4 (m, 1F), −109.6 (m, 2F, CF_2–SO_2), −120.6 (m, 2F, CF_2CF_2–SO_2), −125.7 (m, 2F, CF_2CF_3). IR (KBr) cm^{-1}: 3057, 2224, 1608, 1593, 1568, 1480, 1462, 1388, 1375, 1353, 1292, 1170, 1135, 1033, 853, 783, 770, 740. MS (70 eV, EI) *m*/*z* (%): 429 (M^+, 8), 210 (50), 146 (100), 126 (54). Anal. Calcd. for $C_{13}H_5F_{10}NO_2S$: C 36.38, H 1.17, N 3.26; Found: C 36.23, H 1.07, N 2.90.

*4.3.6. (E)-2-(perfluorobutylsulfonyl)-3-(p-(dimethylamino)phenyl)-acrylonitrile (**3j**)*

Yellow solid, mp 146–147 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.86–7.89 (d, *J* = 9.3, 2H), 7.79 (s, 1H), 7.66–7.69 (d, *J* = 9.3, 2H), 3.15 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.5 (m, 3F, CF_3), −109.6 (m, 2F, CF_2–SO_2), −120.6 (m, 2F, CF_2CF_2–SO_2), −125.7 (m, 2F, CF_2CF_3). IR (KBr) cm^{-1}: 3087, 2210, 1612, 1539, 1514, 1442, 1391, 1331, 1239, 1199, 1152, 1040, 996, 942, 816, 738. MS (70 eV, EI) *m*/*z* (%): 454 (M^+, 13), 171 (100), 69 (8). Anal. Calcd. for $C_{13}H_5BrF_9NO_2S$: C 39.66, H 2.44, N 6.17; Found: C 39.63, H 2.64, N 6.15.

4.4. General experimental procedures for the synthesis of 3-perfluoro-butanesulfonyl coumarins

To a solution of methyl (perfluorobutanesulfonyl)-acetate **1a** (1 mmol, 356 mg) and 2-hydroxybenzaldehyde **4a** (1 mmol, 122 mg) in EtOH (7 ml) was added L-proline (0.2 mmol, 23 mg) and the solution was stirred at r.t. until completion of reaction as indicated by TLC. The reaction mixture was directly recrystallized to afford the product **5a** as a colorless crystal.

*4.4.1. 6-Bromo-3-(perfluorobutylsulfonyl)-2H-chromen-2-one (**5b**)*

Light yellow crystals, mp 148–149 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (s, 1H), 7.91–7.94 (m, 2H), 7.35–7.38 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.6 (m, 3F, CF_3), −109.1 (m, 2F, CF_2–SO_2), −120.9 (m, 2F, CF_2CF_2–SO_2), −125.8 (m, 2F, CF_2CF_3). IR (KBr) cm^{-1}: 1758, 1610, 1554, 1490, 1374, 1353, 1170, 1136, 1109, 922, 757, 732. MS (70 eV, EI) *m*/*z* (%): 508 (M^++2, 22), 506 (27), 289 (100), 287 (92), 225 (67), 223 (61), 169 (78), 167 (63), 69 (72); Anal. Calcd. for $C_{13}H_{11}F_3O_4$ (%): C 54.18, H 3.85; Found: C 54.32, H, 4.05.

*4.4.2. 6-Chloro-3-(perfluorobutylsulfonyl)-2H-chromen-2-one (**5c**)*

Light yellow crystals, mp 158–159 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.76 (s, 1H), 7.77–7.82 (m, 2H), 7.42–7.45 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.6 (m, 3F, CF_3), −109.1 (m, 2F, CF_2–SO_2), −120.9 (m, 2F, CF_2CF_2–SO_2), −125.8 (m, 2F, CF_2CF_3). IR (KBr) cm^{-1}: 1758, 1610, 1554, 1453, 1374, 1283, 1170, 1136, 1109, 1031, 757, 769, 732. MS (70 eV, EI) *m*/*z* (%): 464 (M^++2, 7), 462 (18), 245 (38), 243 (100), 181 (24), 179 (73), 125 (24), 123 (79), 69 (35). Anal. Calcd. for $C_{13}H_{11}F_3O_4$ (%): C 33.75, H 0.87; Found: C 33.34, H 0.86.

*4.4.3. 7-Methoxy-3-(perfluorobutylsulfonyl)-2H-chromen-2-one (**5d**)*

Light yellow crystals, mp 163–164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.76 (s, 1H), 7.42–7.45 (m, 1H), 7.31–7.39 (m, 3H), 3.93 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.6 (m, 3F, CF_3), −109.3 (m, 2F, CF_2–SO_2), −120.9 (m, 2F, CF_2CF_2–SO_2), −125.7 (m, 2F, CF_2CF_3). IR (KBr) cm^{-1}: 1741, 1604, 1563, 1465, 1372, 1354, 1280, 1195, 1146, 1117, 982, 756, 738. MS (70 eV, EI) *m*/*z* (%): 458 (M^+, 33), 239 (35), 175 (100), 119 (32), 69 (23). Anal. Calcd. for $C_{14}H_7F_9O_5S$ (%): C 36.69, H 1.54; Found: C 36.54, H 1.67.

*4.4.4. 6,8-Dichloro-3-(perfluorobutylsulfonyl)-2H-chromen-2-one (**5e**)*

Light yellow crystals, mp 163–164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (s, 1H), 7.67–7.69 (m, 1H), 7.31–7.39 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −80.0 (m, 3F, CF_3), −108.3 (m, 2F, CF_2–SO_2), −120.3 (m, 2F, CF_2CF_2–SO_2), −125.1 (m, 2F, CF_2CF_3). IR (KBr) cm^{-1}: 1758, 1607, 1555, 1442, 1368, 1355, 1230, 1202, 1175, 1148, 994, 866, 838, 762, 699, 641. MS (70 eV, EI) *m*/*z* (%): 458 (M^+, 33), 239 (35), 175 (100), 119 (32), 69 (23). Anal. Calcd. for $C_{14}H_7F_9O_5S$ (%): C 31.11, H 0.61; Found: C 31.38, H 0.53.

*4.4.5. 3-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutyl-1-sulfonyl)-2H-chromen-2-one (**5f**)*

Light yellow crystals, mp 172–173 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.82 (s, 1 H), 7.77–7.87 (m, 2H), 7.46–7.52 (m, 2H), ^{19}F NMR (282 MHz, $CDCl_3$): δ −68.1 (m, 2F, CF_2Cl), −113.8 (m, 2F, CF_2–SO_2), −119.7 to 120.0 (m, 4F, CF_2CF_2). IR (KBr) cm^{-1}: 1757, 1601, 1565, 1464, 1444, 1370, 1279, 1205, 1138, 1158, 1138, 1095, 1078, 932, 789, 760, 762, 616. MS (70 eV, EI) *m*/*z* (%): 476 (M^++2, 4), 474 (9), 239 (36), 175 (100), 119 (28), 85 (6). Anal. Calcd. for $C_{13}H_5ClF_8O_4S$ (%): C 35.11, H 1.13; Found: C 35.16, H 1.42.

*4.4.6. 6-Bromo-3-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutyl-1-sulfonyl)-2H-chromen-2-one (**5g**)*

Light yellow crystals, mp 155–157 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (s, 1H), 7.91–7.94 (m, 2H), 7.35–7.38 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.9 (m, 2F, CF_2Cl), −108.9 (m, 2F, CF_2–SO_2), −119.2 to 119.8 (m, 4F, CF_2CF_2). IR (KBr) cm^{-1}: 1758, 1610, 1554, 1453, 1374, 1283, 1236, 1210, 1170, 1136, 1109, 1031, 769,757, 732, 623. MS (70 eV, EI) *m*/*z* (%): 524 (M^++2, 16), 522 (13), 289 (100), 287 (94), 225 (59), 223 (64), 169 (55), 167 (58), 85 (19). Anal. Calcd. for $C_{13}H_4BrClF_8O_4S$ (%): C 29.82, H 0.77; Found: C 29.80, H 0.76.

*4.4.7. 6-Chloro-3-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutyl-1-sulfonyl)-2H-chromen-2-one (**5h**)*

Light yellow crystals; mp 147–148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.73 (s, 1H), 7.75–7.80 (m, 2H), 7.41–7.44 (m, 1H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.4 (m, 2F, CF_2Cl), −108.3 (m, 2F, CF_2–SO_2), −118.7 to 119.1 (m, 4F, CF_2CF_2). IR (KBr) cm^{-1}: 1758, 1611, 1554, 1475, 1369, 1348, 1249, 1203, 1147, 1113, 970, 956, 834, 761, 735. MS (70 eV, EI) *m*/*z* (%): 478 (M^+, 4), 243 (100), 181 (25), 179 (75), 125 (26), 123 (85), 69 (18). Anal. Calcd. for $C_{13}H_4Cl_2F_8O_4S$ (%): C 32.59, H 0.84; Found: C 32.10, H 0.64.

*4.4.8. 7-Methoxy-3-(4-chloro-1,1,2,2,3,3,4,4-octafluorobutyl-1-sulfonyl)-2H-chromen-2-one (**5i**)*

Light yellow crystals, mp 147–148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.78 (s, 1H), 7.36–7.38 (m, 3H), 4.01 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −67.9 (m, 2F, CF_2Cl), −108.9 (m, 2F, CF_2–SO_2), −119.2 to 119.8 (m, 4F, CF_2CF_2). IR (KBr) cm^{-1}: 1741, 1604, 1563, 1465, 1372, 1354, 1280, 1195, 1146, 1117, 982, 756, 738. MS (70 eV, EI) *m*/*z* (%): 474 (M^+, 18), 239 (37), 175 (100), 119 (30), 69 (19). Anal. Calcd. for $C_{14}H_7ClF_8O_5S$ (%): C 35.42, H 1.49; Found: C 35.38, H 1.48.

Acknowledgement

We are grateful to the National Natural Science Foundation of China (NNSFC No. 21032006) for the financial support on this research.

References

[1] H. Zuo, G. Jose, Z. Boli, B. Hyunmoon, D. Soo shin, M. Ghate, Arkivoc 2 (2008) 183–189.
[2] S. Lee, K. Sivakumar, W. Seobshin, F. Xie, Q. Wang, Bioorg. Med. Chem. Lett. 16 (2006) 4596–4599.

[3] K. Moghadam, M. Mohseni, Montash. Chem. 135 (2004) 817–821.
[4] S.V. Dekic, V.S. Dekic, B.R. Dekic, M.S. Dekic, Chem. Pap. 61 (2007) 233–235.
[5] A.M.M. El-Saghier, A. Khodairy, A. Khodiyar, Phosphorus, Sulfur Silicon Relat. Elem. 160 (2000) 105–119.
[6] B. Musicki, A.M. Periers, P. Laurin, D. Ferroud, Y. Bendetti, S. Lachaud, F. Chatreaux, J.L. Haesslein, A. Iltis, C. Pierre, J. Khider, N. Tessot, P. Airault, A. Bonnefoy, P. Vicat, M. Klich, Bioorg. Med. Chem. Lett. 10 (2000) 1695–1699.
[7] J. Azizian, A. Mohammadi, I. Bidar, P. Mirazaei, Montash. Chem. 139 (2008) 805–808.
[8] V.S. Satyanarayan, P. Sreevani, A. Sivakumar, Arkivoc 17 (2008) 221–233.
[9] M.M. Garazd, O.V. Muzychka, A.I. Voyk, I.V. Nagorichna, A.S. Ogorodniichuk, Chem. Nat. Compd. 43 (2007) 19–23.
[10] G. Smitha, R. Sanjeeva, Synth. Commun. 34 (2004) 3997–4003.
[11] A. Kotali, I. Lafazanis, P. Harris, Synth. Commun. 38 (2008) 3996–4006.
[12] N. Hamdi, C. Lidrissi, M. Saoud, A.R. Nievas, H. Zarrouk, Chem. Heterocycl. Compd. 42 (2006) 320–325.
[13] M. Maheswara, V. Siddaiah, G.L. Damu, Y.K. Rao, C.V. Rao, J. Mol. Catal. A: Chem. 255 (2006) 49–52.
[14] B. Rrajitha, V. Naveen, P. Someshwar, P. Narsimha, Y. Thirupathi, Arkivoc 12 (2006) 23–27.
[15] M. Zahradnik, The Production and Application of Fluorescent Brightening Agents, John Wiley & Sons, New York, 1992.
[16] (a) P.I. Ogoiko, V.P. Nazaretyan, A.Y. Ilchenko, L.M. Yagupolskii, Zh. Org. Khim. 16 (1980) 1397–1401;
(b) C. Harzdorf, J.N. Meussdoerffer, H. Niedeprüm, M. Wechberg, Liebigs Ann. Chem. 1973 (1973) 33–39;
(c) R.J. Koshar, R.A. Mitsch, J. Org. Chem. 38 (1973) 3358–3363.
[17] R. Goumont, K. Magder, M. Tordeux, J. Marrot, F. Terrier, C. Wakselman, Eur. J. Org. Chem. 1999 (1999) 2969–2976.
[18] M. Hanack, G. Bailer, J. Hackenberg, L.R. Subramanian, Synthesis (1991) 1205–1208.