Journal of Fluorine Chemistry 132 (2011) 389–393

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

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

Use of 1,3-dipolar reactions for the preparation of SF_5-substituted five-membered ring heterocycles. Pyrroles and thiophenes

William R. Dolbier Jr.*, Zhaoyun Zheng

Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, United States

ARTICLE INFO

Article history:
Received 25 January 2011
Received in revised form 7 March 2011
Accepted 10 March 2011
Available online 4 April 2011

Keywords:
Pentafluorosulfanyl group
SF_5
Pyrrole synthesis
Thiophene synthesis
1,3-Dipolar cycloadditions

ABSTRACT

In situ-generated unsubstituted, "parent" azomethine and thiocarbonyl ylides are used to prepare a large variety of 3-aryl- and alkyl-substituted, 4-pentafluorosulfanylpyrroles and 3-aryl-substituted, 4-pentafluorosulfanylthiophenes, the latter of which are to our knowledge the first reported SF_5-substituted thiophenes. The 1,3-cycloadditions of these ylides with aryl and alkyl, SF_5-alkynes produce dihydro-pyrroles and thiophenes, which without isolation can then be oxidatively aromatized to the respective pentafluorosulfanylpyrroles and thiophenes in good yield.

1. Introduction

It is now well recognized that the physicochemical and pharmacological properties of organic compounds can be significantly and often efficaciously affected simply by the incorporation of a fluorine substituent or by fluorine containing substituents such as the trifluoromethyl group [1–6]. In this respect, the pentafluorosulfanyl (SF_5) group has only recently attracted attention as a potential replacement for trifluoromethyl groups in molecules of pharmaceutical, agrochemical and materials interest. Indeed, in those cases where direct comparisons can be made, compounds where a CF_3 group has been replaced with an SF_5 substituent show at least similar, but often enhanced selectivity and biological activity [7–10].

Heterocycles comprise an important component of many pharmaceutical and agrochemical compounds, but there have been few reports of heterocycles that directly bear an SF_5 group. The synthesis of a quinoline was recently reported [10], and pyrazoles [11,12], triazoles [13], and thienothiophenes [14] have also been prepared. Triazoles tethered to an SF_5 group have also recently been reported [15]. The synthesis of basic SF_5-substituted five-membered ring heterocycles has been a particular challenge because most of the methods that have been used to prepare CF_3-substituted furans, pyrroles and thiophenes, for the most part involving condensation reactions, have not proved useful for the synthesis of their SF_5-substituted analogues, at least not in our hands. Thus far, the only methodology that has been useful in such syntheses has involved cycloaddition chemistry. Utilization of a combination of Diels–Alder and retro-Diels–Alder reactions has allowed the synthesis of SF_5-furans (Scheme 1) [16], whereas the use of a 1,3-dipolar reaction allowed the first preparation of SF_5-pyrroles (Scheme 2), in this case pyrrolecarboxylic esters [17].

At this time we would like to report an extension of this latter report, the results of which have allowed us to prepare a larger variety of SF_5-pyrroles as well as the first SF_5-substituted thiophenes.

2. Results and discussion

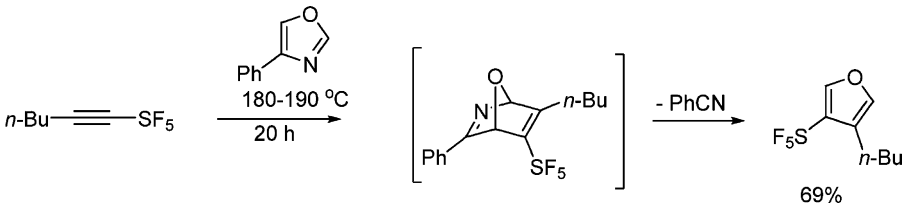
Building upon our earlier 1,3-dipolar cycloaddition work, which demonstrated that SF_5-alkynes acted as reactive dipolarophiles in their reactions with stabilized azomethine ylide **1**, two *non*-stabilized ylides were examined to determine whether they too would undergo efficient cycloaddition with the SF_5-alkynes. If successful, azomethine ylide **2** would allow the synthesis of a wide variety of 3-substituted, 4-pentafluorosulfanylpyrroles, whereas thiocarbonyl ylide **3** would allow synthesis of the first SF_5-substituted thiophenes (Scheme 3).

2.1. SF_5-pyrrole synthesis

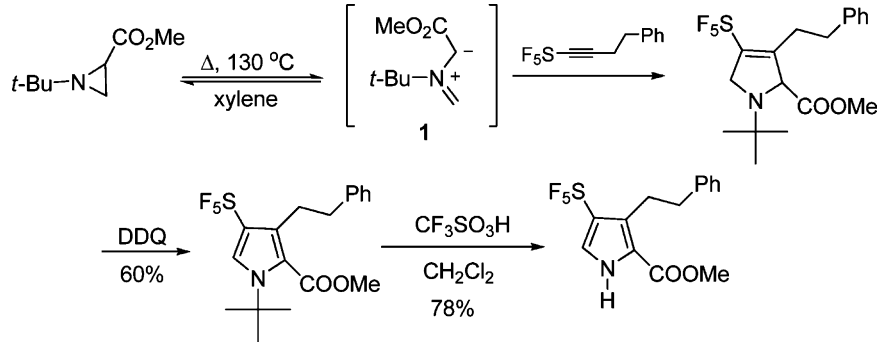
Azomethine ylide **2** was first generated by Padwa from its precursor, *N*-benzyl-*N*-(methoxymethyl)-*N*-[(trimethylsilyl)-methyl]amine (**4**), via the treatment of **4** with either LiF or CsF in acetonitrile [18]. This ylide has been widely used for the

* Corresponding author at: University of Florida, Department of Chemistry, PO Box 117200, Gainesville, FL 32611-7200, United States.
E-mail address: wrd@chem.ufl.edu (W.R. Dolbier Jr.).

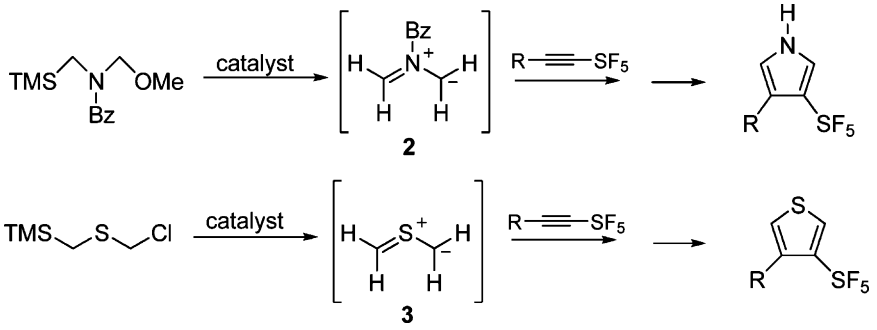
0022-1139/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2011.03.017



Scheme 1. Preparation of SF_5-substituted furans by Diels–Alder Chemistry.



Scheme 2. Preparation of SF_5-substituted pyrrolecarboxylic esters via 1,3-dipolar cycloaddition.



Scheme 3. Generation of azomethine ylide **2** and thiocarbonyl ylide **3**.

synthesis of pyrrolidines and dihydropyrroles, of particular relevance to our work are its reactions with trifluoromethylalkenes [19,20].

In our hands, as shown in Table 1 (Scheme 4), the use of these fluoride catalysts proved not to be effective in carrying out the desired cycloadditions with typical SF_5-alkyne **5a**. Instead, the reaction proceeded smoothly when **4** was treated with catalytic (0.2 eq) trifluoroacetic acid (TFA) in refluxing methylene chloride in the presence of alkyne substrate [21].

In practice the dihydropyrroles (**6a–e**) were not isolated, but were converted, *in situ*, to the respective pyrroles (**7**) by treatment with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (Scheme 5). The results of this two step, one pot process are given in Table 2.

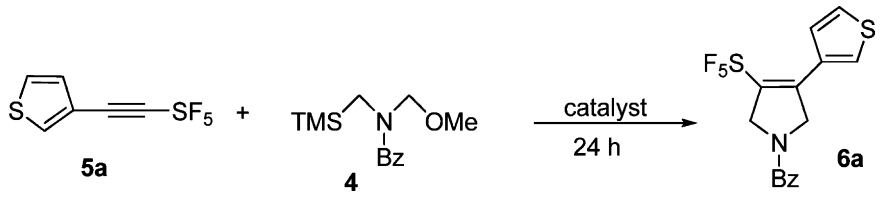
The TIPS, SF_5-acetylene **5e** produced pyrrole **7e**, which could be readily desilated to give *N*-benzyl-3-pentafluorosulfanylpyrrole, **7f** (Scheme 6).

Lastly, it was desirous to demonstrate the ability to remove the protective benzyl group from the pyrrole products. However, catalytic hydrogenolysis of the *N*-benzylpyrroles using either Pd/C or $Pd(OH)_2$/C catalysis proved unsuccessful. Instead it was found necessary to carry out the debenzylation at the dihydropyrrole stage by a method developed by Olofson and Senet to dealkylate tertiary amines using the reagent α-chloroethyl chloroformate (Scheme 7) [22]. Debenzylated dihydropyrrole **8** could then be aromatized in the usual manner by treatment with DDQ to form pyrrole **9**.

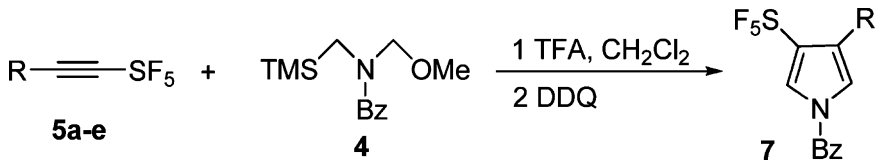
Table 1
Conditions for generation of azomethine ylide **2** from precursor **4**, and its cycloaddition with SF_5-alkyne **5a** to form dihydropyrrole **6a**.

Entry	**4** (eq)	Catalyst	Solvent	*T* (°C)	Conversion (%)
1	2	CsF (2 eq)	CH_3CN	rt	NR
2	2	CsF (2 eq)	CH_3CN	Reflux	NR
3	2	LiF (2 eq)	CH_3CN	rt	NR
4	2	LiF (2 eq)	CH_3CN	Reflux	NR
5	2	TBAF (2 eq)	THF	rt	100[a]
6	2	TFA (0.2 eq)	CH_2Cl_2	rt	65
7	4	TFA (0.2 eq)	CH_2Cl_2	rt	100
8	2.5	TFA (0.2 eq)	CH_2Cl_2	Reflux	100[b]

[a] No desired product obtained.
[b] Isolated yield is 96%.

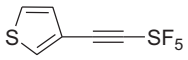
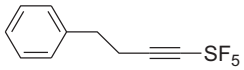
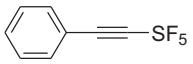
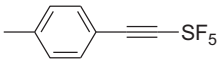
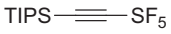


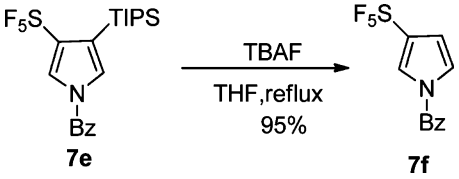
Scheme 4. Use of precursor **4** to generate azomethine ylide **2** for use in 1,3-dipolar cycloadditions with SF_5-alkyne **5a**.



Scheme 5. Two step, one pot synthesis of SF_5-pyrroles.

Table 2
Synthesis of *N*-benzylpyrroles (**7**).

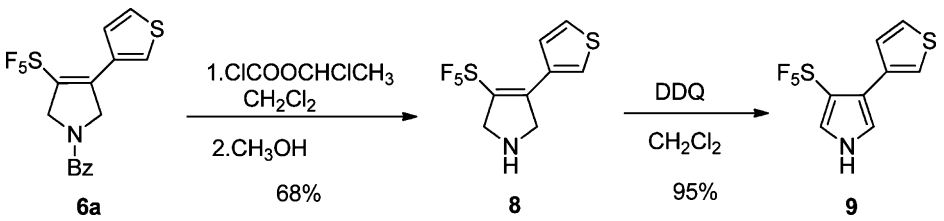
Entry	Substrate	Product yield (%)
1	 **5a**	**7a**, 96
2	 **5b**	**7b**, 79
3	 **5c**	**7c**, 80
4	 **5d**	**7d**, 88
5	 **5e**	**7e**, 78



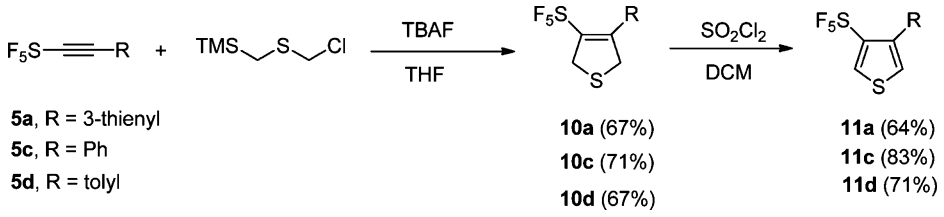
Scheme 6. Removal of TIPS group from pyrrole **7e**.

2.2. SF_5-thiophene synthesis

Chloromethyl trimethylsilylmethyl sulfide was first devised and used as a parent thiocarbonyl ylide synthon by Sakurai in 1986 [23,24], being utilized to prepare di- and tetrahydrothiophenes via 1,3-dipolar cycloadditions by treatment with CsF in acetonitrile in the presence of appropriate dipolarophiles [25]. Indeed, when various SF_5-aryl-substituted alkynes were used as substrates, the cycloadditions proceeded smoothly to form the respective dihydrothiophenes, **10a**, **c** and **d** (Scheme 8). Alkynes substituted with alkyl groups proved to be unsatisfactory substrates.



Scheme 7. Removal of benzyl group from dihydropyrrole **6a**.



Scheme 8. Synthesis of SF_5-dihydrothiophenes and thiophenes.

Conversion of the dihydrothiophenes to the respective thiophenes proved more difficult than was the case for the pyrroles. DDQ was ineffective, and the method which was finally successful was treatment of the dihydrothiophenes with SO_2Cl_2 in methylene chloride. Although this two step procedure is not as general as we had hoped, nevertheless the synthesis depicted in Scheme 8 comprises, to our knowledge, the first reported preparation of SF_5-substituted thiophenes [26].

3. Conclusion

In conclusion, by means of the 1,3-dipolar cycloadditions of *in situ*-generated unsubstituted, "parent" azomethine and thiocarbonyl ylides **2** and **3** it has been possible to synthesize a variety of 3-aryl- and alkyl-substituted, 4-pentafluorosulfanylpyrroles and 3-aryl-substituted, 4-pentafluorosulfanylthiophenes, the latter to our knowledge being the first reported SF_5-substituted thiophenes.

4. Experimental

NMR spectra were obtained in $CDCl_3$ using TMS as the internal standard for ^1H (300 MHz) and ^{13}C NMR (75 MHz) and $CFCl_3$ for ^{19}F NMR (282 MHz). Melting points were uncorrected. Starting material SF_5-alkynes **5a–e** were prepared according to the previous literature [17,27].

4.1. Preparation of 1-pentafluorosulfanyl-2-(3-thienyl)-acetylene (5a)

This new alkyne was prepared according to the literature [17]: (60%) ^1H NMR δ 7.18–7.20 (dd, J = 1.2, 3.6 Hz, 1H), 7.32–7.34 (dd, J = 3.0, 2.1 Hz, 1H), 7.73–7.34 (m, 1H); ^{13}C NMR δ 126.7, 129.8 (m), 134.0 (m); ^{19}F NMR δ 83.6 (m, 4F), 76.9 (m, 1F).

4.2. General procedure for preparation of pyrroles 7a–f

Trifluoroacetic acid solution (0.9 mL, 0.2 eq, 1 M in CH_2Cl_2) was slowly added to a mixture of **5** (4.27 mmol, 1 eq) and *N*-(methoxymethyl)-*N*-(trimethylsilylmethyl)-*N*-benzylamine **4** (10 mmol, 2.5 eq) in 10 mL CH_2Cl_2. After addition, the reaction mixture was refluxed for 24 h, and then cooled with an ice-water bath. DDQ (4.7 mmol, 1.1 eq) was then carefully added to the light-yellow solution. After stirring for another 2 h, the dark-red mixture was diluted with 10 mL CH_2Cl_2 and poured into saturated $NaHCO_3$ solution (20 mL), the organic phase separated and solvent evaporated. Column chromatography allowed isolation of the product as either a white solid or a colorless liquid.

The intermediate **6a** was separated and characterized by NMR analysis prior to its oxidative conversion to pyrrole **7a**.

4.3. Yields, spectral and analytical data for pyrrole products

4.3.1. N-benzyl-3-pentafluorosulfanyl-4-(3-thienyl)-2,5-dihydropyrrole (6a)

^1H NMR δ 3.79 (s, 2H), 3.84–3,87 (m, 2H), 4.00–4.03 (t, J = 4.2 Hz, 2H), 7.13–7.14 (d, J = 4.8 Hz, 1H), 7.26–7.36 (m, 7H); ^{13}CNMR δ 60.1, 61.8 (m), 64.8, 125.5 (m), 125.7, 127.6 (m), 127.7, 128.8, 128.9, 132.5, 137.0 (m), 138.1, 144.4 (m); ^{19}F NMR δ 83.9 (p, J = 164 Hz, 1F), 66.4 (d, J = 166 Hz, 4F).

4.3.2. N-benzyl-3-pentafluorosulfanyl-4-(3-thienyl)pyrrole (7a)

(96%); mp 69–71 °C; ^1H NMR δ 5.00 (s, 2H), 6.57 (s, 1H), 7.13–7.15 (m, 2H), 7.19–7.23 (m, 3H), 7.25–7.28 (m, 1H), 7.35–7.42 (m, 3H); ^{13}C NMR δ 54.3, 117.5 (m), 120.3 (m), 122.1 (m), 123.1, 124.6, 127.9, 128.7, 129.30, 129.5 (m), 134.3, 135.9; ^{19}F NMR δ 88.4 (p, J = 168 Hz, 1F), 75.7 (d, J = 163 Hz, 4F); HRMS calcd for $C_{15}H_{12}F_5NS_2$ 365.0331, found 365.0319; anal. calcd for $C_{15}H_{12}F_5NS_2$: C, 49.31; H, 3.31; N, 3.76. Found: C, 49.58; H, 3.25; N, 3.76.

4.3.3. N-benzyl-3-pentafluorosulfanyl-4-(2-phenylethyl)pyrrole (7b)

(79%); ^1H NMR δ 2.93 (m, 4H), 4.95 (s, 2H), 6.33 (s, 1H), 7.06–7.07 (d, J = 2.4 Hz, 1H), 7.13–7.16 (m, 2H), 7.22–7.25 (m, 3H), 7.30–7.37 (m, 2H), 7.38–7.44 (m, 3H); ^{13}C NMR δ 28.6, 36.8, 54.1, 118.9 (m), 120.7 (m), 121.6 (m), 126.2, 127.6, 128.50, 128.6, 128.7, 129.2, 136.4, 142.0; ^{19}F NMR δ 89.6 (p, J = 164 Hz, 1F), 74.6 (d, J = 161 Hz, 4F). HRMS calcd for $C_{17}H_{18}F_5NS$ 387.1080; found 388.1153 (M+H); anal. calcd for $C_{17}H_{18}F_5NS$: C, 58.90; H, 4.68; N, 3.62. Found: C, 58.74; H, 4.29; N, 3.78.

4.3.4. N-benzyl-3-pentafluorosulfanyl-4-phenylpyrrole (7c)

(80%); ^1H NMR δ 5.05 (s, 2H), 6.56 (s, 1H), 7.19 (s, 1H), 7.26–7.28 (d, J = 7.5 Hz, 2H), 7.37–7.44 (m, 8H); ^{13}C NMR δ 54.3, 120.3, 121.8, 122.9, 127.3, 127.8, 127.9, 128.7, 129.3, 130.1, 134.9, 135.9; ^{19}F NMR δ 88.6 (p, J = 169 Hz, 1F), 76.2 (d, J = 163 Hz, 4F); HRMS calcd for $C_{17}H_{14}F_5NS$ 359.0767, found 359.0786; anal. calcd for $C_{17}H_{14}F_5NS$: C, 56.82; H, 3.93; N, 3.90. Found: C, 56.47; H, 3.82; N, 4.01.

4.3.5. N-benzyl-3-pentafluorosulfanyl-4-tolylpyrrole (7d)

(88%); ^1H NMR δ 2.43 (s, 3H), 5.05 (s, 2H), 6.54 (s, 1H), 7.18–7.23 (m, 3H), 7.25–7.28 (m, 2H), 7.32–7.35 (m, 2H), 7.40–7.45 (m, 3H); ^{13}C NMR δ 21.4, 54.2, 120.1, 121.6, 122.8, 127.8, 128.6, 129.2, 129.9, 131.9, 135.9, 136.9; ^{19}F NMR δ 88.6 (p, J = 160 Hz, 1F), 76.1 (d, J = 150 Hz, 4F); HRMS calcd for $C_{18}H_{16}F_5NS$ 373.0923, found 373.0921; anal. calcd for $C_{18}H_{16}F_5NS$: C, 57.90; H, 4.32; N, 3.75. Found: C, 57.65; H, 4.35; N, 3.80.

4.3.6. N-benzyl-3-pentafluorosulfanyl-4-triisopropylsilylpyrrole (7e)

(78%); mp 37–39 °C; ^1H NMR δ 1.07–1.09 (d, J = 7.2 Hz, 18H), 1.31–1.41 (m, 3H), 5.05 (s, 2H), 6.67 (s, 1H), 7.08–7.11 (m, 2H), 7.18–7.19 (m, 1H), 7.31–7.39 (m, 3H); ^{13}C NMR δ 12.6, 19.3, 53.8, 110.9 (m), 123.6 (m), 127.2, 128.4, 129.2, 129.4, 136.5, 142.5 (m); ^{19}F NMR δ 89.4 (p, J = 164 Hz, 1F), 72.6 (d, J = 156 Hz, 4F); HRMS calcd for $C_{20}H_{30}F_5NSSi$ 439.1788, found 440.1859 (M+H); anal. calcd for $C_{20}H_{30}F_5NSSi$: C, 54.64; H, 6.88; N, 3.19. Found: C, 54.67; H, 6.62; N, 3.19.

4.4. Preparation of N-benzyl-3-pentafluorosulfanylpyrrole (7f) from 7e

0.9 mL TBAF (1 M in THF) was added to a round flask containing **7e** (200 mg, 0.455 mmol) and 3 mL THF, and then it was heated to reflux overnight. The mixture was poured into water (5 mL),

extracted with CH_2Cl_2 (5 mL × 3), the solvent removed, and the residue purified by column chromatography. Product **7f** (0.12 g) was obtained (95%) as a colorless oil: ^{1}H NMR δ 5.04 (s, 2H), 6.43–6.45 (m, 1H), 6.60 (s, 1H), 7.05 (s, 1H), 7.15–7.18 (m, 2H), 7.32–7.42 (m, 3H); ^{13}C NMR δ 54.2, 107.3 (m), 120.1 (m), 120.4, 127.6, 128.6, 129.2, 136.2; ^{19}F NMR δ 87.6 (p, J = 162 Hz, 1F), 70.8 (d, J = 163 Hz, 4F); HRMS calcd for $C_{11}H_{10}F_5NS$ 283.0454, found 283.0458; anal. calcd for $C_{11}H_{10}F_5NS$: C, 46.64; H, 3.56; N, 4.94. Found: C, 46.82; H, 3.55; N, 5.15.

4.5. Preparation of 3-pentafluorosulfanyl-4-(3-thienyl)-2,5-dihydropyrrole (8)

Following the procedure of Renslo et al. [28], 1-chloroethyl chloroformate (156 mg, 1.1 mmol) was added to a solution of **6a** (200 mg, 0.55 mmol) and triethylamine (55 mg, 0.55 mmol) in 2 mL CH_2Cl_2 at 0 °C with stirring. The mixture was then concentrated after 30 min, dissolved in methanol (2 mL) and stirred overnight. The solvent was then removed, and the residue underwent column chromatography to produce 102 mg of colorless oil product **8** (68%): ^{1}H NMR δ 2.17 (s, 2H), 4.06 (m, 2H), 4.19–4.21 (t, J = 7.2 Hz, 2H), 7.10–7.11 (d, J = 4.8 Hz, 1H), 7.26–7.29 (m, 1H), 7.33–7.34 (m, 1H); ^{13}C NMR δ 56.9 (m), 59.8, 125.2 (m), 125.7, 127.5, 132.2, 139.1 (m), 147.1 (m); ^{19}FNMR δ 84.2 (p, J = 162 Hz, 1F), 67.4 (d, J = 164 Hz, 4F).

4.6. Preparation of 3-pentafluorosulfanyl-4-(3-thienyl)pyrrole (9)

DDQ (125 mg, 0.66 mmol) was added to a solution of **8** in CH_2Cl_2 at 0 °C with stirring, after standing for 2 h, the mixture was submitted to column directly. 95 mg of **9** as a colorless oil was obtained (95%): ^{1}HNMR ($CDCl_3$), δ 6.67 (s, 1H), 7.12–7.14 (d, J = 5.1 Hz, 1H), 7.21–7.22 (m, 2H), 7.26–7.29 (m, 1H), 8.43 (s, 1H); ^{13}CNMR, δ 117.4 (m), 119.4 (m), 123.2, 124.7, 129.6, 134.1, 136.6 (m); ^{19}FNMR, δ 87.9 (p, J = 167 Hz, 1F), 75.5 (d, J = 163 Hz, 4F). HRMS calcd for $C_8H_6F_5NS_2$ 274.9862, found 274.9864; anal. calcd for $C_8H_6F_5NS_2$: C, 34.91; H, 2.20; N, 5.09. Found: C, 35.29; H, 2.25; N, 4.75.

4.7. General procedure for preparation of 4-pentafluorosulfanylthiophenes

TBAF (1.0 M in THF, 1.3–5 eq) was added to a mixture of chloromethyl trimethylsilylmethyl sulfide (1.3–5 eq) and SF_5-alkyne (**5a**, **c** or **d**) (1 eq) in THF at room temperature. After stirring for several hours (monitoring by ^{19}F NMR), the reactions were quenched by water and submitted to column chromatography. Products **10a**, **c** or **d** were obtained as white solids.

A solution of **10a**, **c** or **d** in DCM was cooled to −30 °C, after which sulfuryl chloride (2 eq) was added slowly during 10 min. After stirring for another 30 min, the reaction was quenched by water, and the organic phase was separated and dried by Na_2SO_4. The solvent was evaporated, and the residue purified by column chromatograph to give **11a**, **c**, or **d** as white solids or colorless oils.

4.8. Spectral data for dihydrothiophenes (10)

4.8.1. 3-Pentafluorosulfanyl-4-(3′-thienyl)-dihydrothiophene (10a)

^{1}H NMR δ 3.96–4.01 (m, 2H), 4.26–4.29 (t, J = 4.8 Hz, 2H), 6.96–6.98 (d, J = 5.1 Hz, 1H), 7.19–7.20 (d, J = 1.8 Hz, 1H), 7.28–7.31 (dd, J = 5.1 Hz, 1H); ^{13}C NMR δ 39.54, 43.23, 123.82, 125.94, 127.12, 134.22, 140.91, 148.72 (m); ^{19}F NMR δ 82.97 (p, J = 161 Hz, 1F), 66.11 (d, J = 164 Hz, 4F).

4.8.2. 3-Pentafluorosulfanyl-4-phenyl-dihydrothiophene (10c)

^{1}H NMR δ 3.99–4.04 (m, 2H), 4.33–4.39 (t, J = 4.8 Hz, 2H), 7.17–7.20 (m, 2H), 7.35–7.38 (m, 3H); ^{13}C NMR δ 39.74, 44.10, 127.00, 128.36, 135.51, 145.32, 148.62 (m); ^{19}F NMR δ 83.00 (p, J = 152 Hz, 1F), 66.11 (d, J = 163 Hz, 4F).

4.8.3. 3-Pentafluorosulfanyl-4-p-tolyl-dihydrothiophene (10d)

^{1}H NMR δ 2.36 (s, 3H), 3.99 (s, 2H), 4.31–4.34 (t, J = 5.1 Hz, 2H), 7.06–7.08 (d, J = 8.1 Hz, 2H), 7.17–7.19 (d, J = 7.8 Hz, 2H); ^{13}C NMR δ 21.43, 39.68, 44.09, 126.86, 129.12, 132.40, 138.34, 145.50, 148.34 (m); ^{19}F NMR δ 83.12 (p, J = 153 Hz, 1F), 67.05 (d, J = 163 Hz, 4F).

4.9. Spectral and analytical data for thiophenes (11)

4.9.1. 3-Pentafluorosulfanyl-4-(3′-thienyl)thiophene (11a)

^{1}H NMR δ 7.07–7.08 (d, J = 4.8 Hz, 1H), 7.12–7.14 (m, 1H), 7.23–7.24 (dd, J = 1.2, 2.1 Hz, 1H), 7.28–7.31 (dd, J = 3, 1.8 Hz, 1H), 7.85–7.87 (d, J = 3.9 Hz, 1H); ^{13}C NMR δ 124.7, 125.3, 128.3, 129.3, 134.6, 135.3, 150.3; ^{19}F NMR δ 84.0 (m, 1F), 72.1 (d, J = 162 Hz, 4F). HRMS calcd for $C_8H_5F_5S_3$ 291.9474, found 291.9504.

4.9.2. 3-Pentafluorosulfanyl-4-phenylthiophene (11c)

^{1}H NMR δ 7.10–7.12 (m, 1H), 7.31–7.34 (m, 2H), 7.38–7.40 (m, 3H), 7.89–7.90 (d, J = 3.9 Hz, 1H); ^{13}C NMR δ 125.02, 127.80, 128.10, 129.81, 136.07, 139.80, 150.65 (m); ^{19}F NMR δ 84.11 (p, J = 161 Hz, 1F), 72.08 (d, J = 162 Hz, 4F); HRMS calcd for $C_{10}H_7F_5S_2$ 285.9909, found 285.9929; anal. calcd for $C_{10}H_7F_5S_2$: C, 41.95; H, 2.46. Found: C, 42.28; H, 2.49.

4.9.3. 3-Pentafluorosulfanyl-4-p-tolylthiophene (11d)

mp 73–75 °C; ^{1}H NMR δ 2.40 (s, 3H), 7.07 (m, 1H), 7.19 (s,, 4H), 7.87–7.88 (d, J = 3.9 Hz, 1H); ^{13}C NMR δ 21.43, 124.93, 127.90, 128.50, 129.64, 133.09, 137.85, 139.77, 150.65 (m); ^{19}F NMR δ 84.27 (p, J = 167 Hz, 1F), 72.55 (d, J = 162 Hz, 4F); HRMS calcd for $C_{11}H_9F_5S_2$ 300.0066, found 300.0060; anal. calcd for $C_{11}H_9F_5S_2$: C, 43.99; H, 3.02. Found: C, 43.91; H, 3.06.

References

[1] D. O'Hagan, Chem. Soc. Rev. 37 (2008) 308–319.
[2] M. Schlosser, Angew. Chem. Int. Ed. 110 (1998) 1496–1513.
[3] K. Mueller, C. Faeh, F. Diederich, Science 317 (2007) 1881–1886.
[4] S. Purser, P.R. Moore, S. Swallow, V. Gouverneur, Chem. Soc. Rev. 37 (2008) 320–330.
[5] K.L. Kirk, Org. Proc. Res. Dev. 12 (2008) 305–321.
[6] D. O'Hagan, J. Fluorine, Chemistry 131 (2010) 1071–1081.
[7] D.S. Lim, J.S. Choi, C.S. Pak, J.T. Welch, J. Pestic. Sci. 32 (2007) 255–259.
[8] J.T. Welch, D.S. Lim, Bioorg. Med. Chem. 15 (2007) 6659–6666.
[9] F. Micheli, d. Andreotti, S. Braggio, A. Checchia, Bioorg. Med. Chem. Lett. 20 (2010) 4566–4568.
[10] P. Wipf, T. Mo, S.J. Geib, D. Caridha, G.S. Dow, L. Gerena, N. Roncal, E.E. Milner, Org. Biomol. Chem. 7 (2009) 4163–4165.
[11] F.W. Hoover, D.D. Coffman, J. Org. Chem. 29 (1964) 3567–3570.
[12] C. Ye, G.L. Gard, R.W. Winter, R.G. Syvret, B. Twamley, J.M. Shreeve, Org. Lett. 9 (2007) 3841–3844.
[13] A.G. Williams, N.R. Foster, WO9422817 (1994) (Aventis Crop Science); Chem. Abstr. 123 (1994) 58831.
[14] S. Zahn, A.F. Nordquist, K.E. Minnich, G.S. Lal, W.F. Burgoyne, Jr., and A. Klauck-Jacobs, USP 7,241,904 (2007); Chem. Abstr. 145 (2007) 397957.
[15] Y. Huang, G.L. Gard, J.M. Shreeve, Tetrahedron Lett. 51 (2010) 6951–6954.
[16] W.R. Dolbier Jr., A. Mitani, W. Xu, I. Ghiviriga, Org. Lett. 8 (2006) 5573–5575.
[17] W.R. Dolbier Jr., Z. Zheng, J. Org. Chem. 74 (2009) 5626–5628.
[18] A. Padwa, W. Dent, J. Org. Chem. 52 (1987) 235–244.
[19] J.-P. Begue, D. Bonnet-Delpon, T. Lequeux, Tetrahedron Lett. 34 (1993) 3279–3282.
[20] D. Bonnet-Delpon, J.-P. Begue, T. Lequeux, M. Ourevitch, Tetrahedron 52 (1996) 59–70.
[21] Y. Terao, H. Kotaki, N. Imai, K. Achiwa, Chem. Pharm. Bull. 33 (1985) 2762–2766.
[22] R.A. Olofson, J.T. Martz, J.-P. Senet, M. Piteau, T. Malfroot, J. Org. Chem. 49 (1984) 2081–2082.
[23] A. Hosomi, Y. Matsuyama, H. Sakurai, J. Chem. Soc. Chem. Commun. (1986) 1073–1074.
[24] A. Hosomi, K. Miura, Bull. Chem. Soc. Jpn. 77 (2004) 835–851.
[25] S. Karlsson, H.-E. Hogberg, Org. Lett. 1 (1999) 1667–1669.
[26] W.R. Dolbier Jr., Z. Zheng, 19th Int. Symp. Fluor. Chem., 2009, Paper No. 234.
[27] W.R. Dolbier Jr., S. Ait-Mohand, T.D. Schertz, T.A. Sergeeva, J.A. Cradlebaugh, A. Mitani, G.L. Gard, R.W. Winter, J.S. Thrasher, J. Fluorine Chem. 127 (2006) 1302–1310.
[28] A.R. Renslo, H. Gao, P. Jaishankar, R. Venkatachalam, M.F. Gordeev, Org. Lett. 7 (2005) 2627–2630.