1,1-Bis(ethylsulfanyl)perfluorobut-1-ene as Starting Material for the Synthesis of Substituted 2-Trifluoromethylfurans and -pyrroles[‡]

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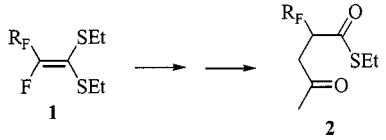
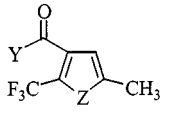
In a two-step sequence (condensation with acetone enolate/acid hydrolysis), 1,1-bis(ethylsulfanyl)perfluorobut-1-ene was converted into the corresponding *S*-ethyl 4-oxo-2-pentafluoroethylpentanethioate. This thioester proved to be a versatile intermediate, leading, in the presence of aliphatic amine, to substituted 2-trifluoromethylfurans and/or -pyrroles. The selectivity of these heterocyclisations depends on the reaction conditions and on the basicity/nucleophilicity balance of the amine.

We previously reported the synthesis[1] and some applications[2,3] of perfluoroketene dithioacetals **1a**. Whereas the initial work on such compounds involved the first term of the series (**1**, R_F = F),[4,5] the higher homologue **1a** was shown to be an excellent building block for the synthesis of α-trifluoromethyl-γ-lactones[2] and -lactams.[3] The dual reactivity of ketene dithioacetals,[6] along with the easy nucleophilic displacement of the vinylic fluorine, are the keys to the chemistry of compound **1a**, which is easily converted in two high yielding steps into the bifunctionalized intermediate **2a** (Scheme 1).



Scheme 1

The homologous perfluoroketene dithioacetal **1b** and the corresponding bifunctional intermediate **2b** were expected to offer further developments, since an additional easy HF elimination should occur under basic conditions. Indeed, when **2b** was treated with amines, which behave as basic as well as nucleophilic reagents, the formation of trifluoromethyl-substituted heterocycles (furans and pyrroles) was observed. Owing to the importance of trifluoromethylated heterocycles in general,[7] and furans and pyrroles in particular, we have investigated this reaction in order to assess the parameters which could control the selectivity and possibly lead to a preparative methodology towards either of these heterocycles. The present paper reports on the three-step conversion of the perfluoroketene dithioacetal **1b** into 5-methyl-2-trifluoromethylfurans and -pyrroles of general formula **3**.



3

Y = SEt, NHR (R = Alkyl)
Z = O, NR (R = Alkyl)

Besides some direct fluorination[8] or trifluoromethylation[9] methodologies, most of the syntheses of 2-(trifluoromethyl)furans reported so far are based on various building block strategies.[10] Among compounds bearing a carboxylic function on C-3, we could find only three examples exhibiting a substitution pattern similar to the general structure **3** (Z = O). These examples were built from substituted ethyl trifluoroacetoacetates[11] as fluorinated building blocks.

As far as 2-(trifluoromethyl)pyrroles are concerned, a considerable literature, from both academic and industrial areas, reveals the interest of such a structure, especially for agrochemical and pharmaceutical applications.[12] Here too, the building block strategy from various fluorinated intermediates was used. Considering only compounds related to the general structure **3** (Z = NR), a cycloaddition reaction is often a key step of their preparation.[13]

[‡] Fluorinated Ketene Dithioacetals, 8. Part 7: J.-P. Bouillon, Y. G. Shermolovich, C. Portella, *Tetrahedron Lett.* **2001**, *42*, 2133−2135.

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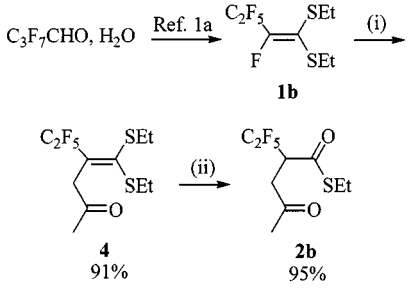
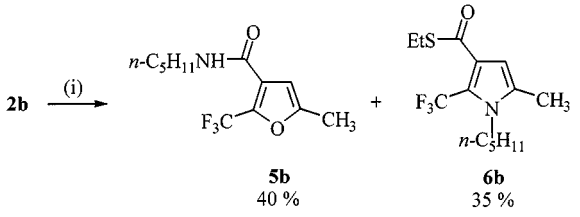
Results and Discussion

1,1-Bis(ethylsulfanyl)perfluorobut-1-ene (**1b**), prepared from heptafluorobutanal hydrate or -hemiacetal,[1a] was converted into the γ-keto thioester **2b** in a two-step procedure similar to the one already reported.[2,3] Treatment of **1b** with the potassium enolate of acetone led to the ketene dithioacetal **4**, which was hydrolysed under acidic conditions to give the expected γ-keto-α-pentafluoroethyl thioester **2b** (Scheme 2).



Scheme 2. (i) KH, acetone, THF; (ii) TFA, H_2O, Δ

In a first experiment, **2b** was reacted with a slight excess (2 equiv.) of *n*-pentylamine under mild conditions (method 1) to give two trifluoromethylated compounds. These compounds were separated and characterized as the 2-trifluoromethyl-3-(carboxamido)furan **5b** and the 2-trifluoromethyl-3-(ethylthiocarbonyl)pyrrole **6b**, in 40% and 35% yield, respectively (Scheme 3 and Table 1, entry 3). Structural data for these compounds are depicted in Table 2 and 3.



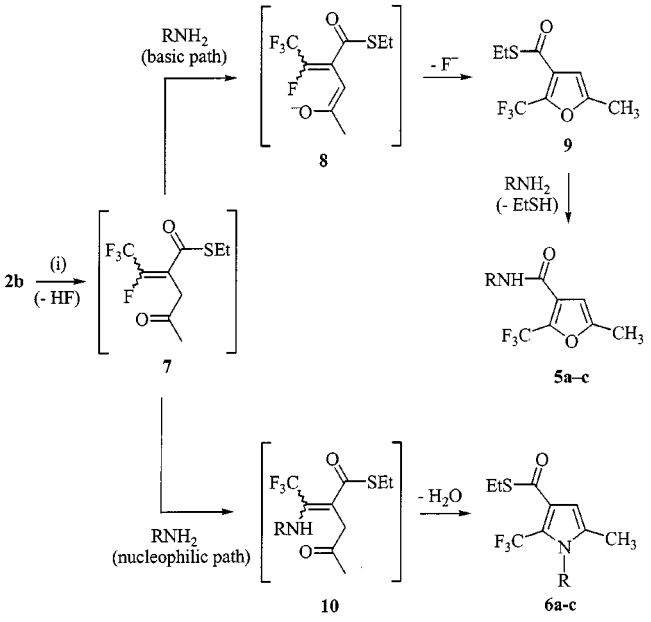
Scheme 3. (i) Method 1: n-$C_5H_{11}NH_2$ (2 equiv.), Et_2O, room temp., 24h

Table 1. Reaction of compound **2b** with primary amines

Entry	R	pK_a (amine)[16]	Conv. (%)	Furan **5** (%)[a]	Pyrrole **6** (%)[a]
1	*p*(MeO)C_6H_4	5.34	0	–	–
2	Bn	9.37	100	**5a** (25)	**6a** (48)
3	n-C_5H_{11}	10.63	95	**5b** (40)	**6b** (35)
4	*i*Pr	10.72	100	**5c** (57)	**6c** (24)

[a] Method 1: amine (2 equiv.), Et_2O, 24 h, 25 °C.

In order to try to make the reaction selective, we had to determine the parameters, in other words the reaction pathways, leading to such results. A plausible mechanism is depicted in Scheme 4. Owing to the enhanced acidity of the α-hydrogen in compound **2b**, the first step is an easy HF



Scheme 4. (i) Method 1: RNH_2 (2 equiv.), Et_2O, 24 h, 25 °C

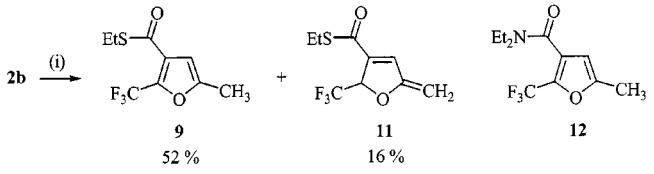
elimination leading to the multifunctionalized intermediate **7**,[14] which exhibits interesting features: a conjugated system and an activated allylic hydrogen. Such an intermediate can react as a Michael acceptor or as a proton donor. If the amine acts as a base, the reaction evolves towards the furan **9** via the intermediate enolate **8** and an intramolecular Michael addition/fluoride elimination sequence (Scheme 4, basic path). Further nucleophilic displacement of the ethylsulfanyl group can occur giving the 3-carboxamide derivative **5**. If the amine acts as a nucleophile, however, a Michael addition/elimination followed by an intramolecular condensation leads to the corresponding pyrrole **6** via the enaminone **10**[15] (Scheme 4, nucleophilic path).

According to this mechanism, one could expect that the product distribution should depend on the reaction conditions and on the dual basic/nucleophilic properties of the amines. The results obtained from reactions of **2b** with several amines under the above-described conditions (method 1) are summarized in Table 1. In order to emphasize the influence of the amine, the results are presented according to the increasing pK_a of the conjugated ammonium ion.[16] No reaction occurred with *p*-methoxyaniline, a base that is too weak to initiate the process (Table 1, entry 1). Aliphatic primary amines gave similar results as regards the reaction products, although the chemoselectivity strongly depends on the basicity of the amine. 2-(Trifluoromethyl)pyrrole (**6a**) is the major product of the reaction with benzylamine, the least basic amine, which prefers the nucleophilic path (Scheme 4 and Table 1, entry 2). In contrast, the furan derivative **5c** is the major product from the reaction with isopropylamine, which is basic enough to follow the basic path (Table 1, entry 4). These results fit well with the proposed mechanism depicted in Scheme 4, although we cannot exclude some effect of the steric bulk, which would contribute to the less nucleophilic behaviour of isopropylamine.

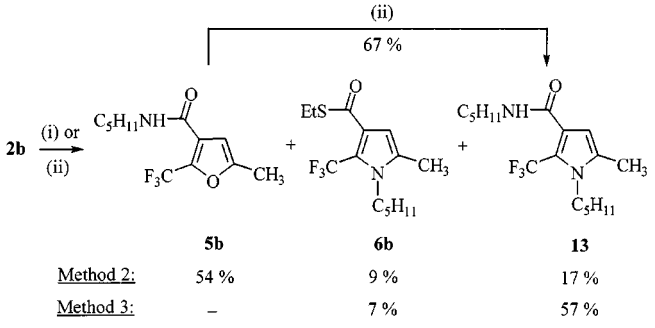
Table 2. Spectroscopic data of 2-trifluoromethylated furans **5a−c**, **9** and **12**

Cpd[a]	Solvent[b]	IR (film) $\tilde{\nu}$ (cm^{-1})	MS *m/z*	^{19}F NMR[c]	^{1}H NMR[c]	^{13}C NMR[c]
5a	PE/acetone (95:5)	3196, 1713, 1642, 1625	283 [M^+], 266, 192, 149	−62.5 (s)	2.12 (s, 3 H), 4.59 (d, $^3J_{H,H}$ = 6.5 Hz, 2 H), 5.95 (m, 1 H), 7.2−7.4 (m, 5 H), 9.0 (br. m, 1 H)	13.9 (s, CH_3), 48.6 (s, CH_2), 98.0 (s, C-3), 100.8 (q, $^4J_{C,F}$ = 5.7 Hz, CH), 120.8 (q, $^1J_{C,F}$ = 278.6 Hz, CF_3), 127.2 (s, 2 × CHPh), 128.0 (s, CHPh), 128.9 (s, 2 × CHPh), 136.9 (s, C_4Ph), 141.1 (q, $^2J_{C,F}$ = 33.7 Hz, C-2), 147.4 (s, C-5), 171.7 (s, CON)
5b	PE/DE (98:2)	3411, 2930, 1716, 1641	263 [M^+], 206, 193, 122	−62.8 (s)	0.92 (t, $^3J_{H,H}$ = 6.5 Hz, 3 H), 1.3−1.4 (m, 4 H), 1.66 (m, 2 H), 2.11 (s, 3 H), 3.40 (td, $^3J_{H,H}$ = 6.9, 6.5 Hz, 2 H), 5.91 (m, 1 H), 8.8 (br. m, 1 H)	13.87 (s, CH_3), 13.92 (s, CH_3), 22.2 (s, CH_2), 28.6 (s, CH_2), 30.0 (s, CH_2), 44.8 (s, CH_2), 96.6 (s, C-3), 100.8 (q, $^4J_{C,F}$ = 4.9 Hz, CH), 120.7 (q, $^1J_{C,F}$ = 278.2 Hz, CF_3), 142.0 (q, $^2J_{C,F}$ = 33.1 Hz, C-2), 146.5 (s, C-5), 171.9 (s, CON)
5c	PE/EtOAc (97:3)	3164, 2924, 1716, 1641	235 [M^+], 193, 164, 122	−62.3 (s)	1.29 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H), 2.11 (s, 3 H), 3.91 (m, 1 H), 5.90 (m, 1 H), 8.7 (br. m, 1 H)	13.8 (s, CH_3), 24.4 (s, CH_3), 47.5 (s, CH), 96.6 (s, C-3), 100.8 (q, $^4J_{C,F}$ = 5.3 Hz, CH), 120.8 (q, $^1J_{C,F}$ = 278.6 Hz, CF_3), 141.1 (q, $^2J_{C,F}$ = 33.5 Hz, C-2), 146.5 (s, C-5), 171.9 (s, CON)
9	PE/EtOAc (98:2)	2969, 1771, 1637, 1129	238 [M^+], 211, 193, 177	−59.2 (s)	1.31 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H), 2.18 (s, 3 H), 3.08 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H), 6.12 (m, 1 H)	14.1 (s, CH_3), 14.5 (s, CH_3), 28.7 (s, CH_2), 103.5 (q, $^4J_{C,F}$ = 4.7 Hz, CH), 122.5 (q, $^1J_{C,F}$ = 277.0 Hz, CF_3), 128.4 (s, C-3), 133.6 (q, $^2J_{C,F}$ = 32.9 Hz, C-2), 157.5 (s, C-5), 165.2 (s, COS).
12	PE/EtOAc (97:3)	2925, 1755, 1640, 1584	249 [M^+], 229, 178, 150	−61,3 (s)	1.12 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H), 2.11 (s, 3 H), 3.40 (q, $^3J_{H,H}$ = 7.3 Hz, 4 H), 5.95 (m, 1 H)	14.0 (s, CH_3), 14.2 (s, CH_3), 47.4 (s, CH_2), 102.3 (q, $^4J_{C,F}$ = 4.9 Hz, CH), 107.8 (s, C-3), 122.0 (q, $^1J_{C,F}$ = 281.6 Hz, CF_3), 140.4 (q, $^2J_{C,F}$ = 32.5 Hz, C-2), 150.0 (q, $^4J_{C,F}$ = 3.0 Hz, C-5), 165.8 (s, CON)

[a] Oil. Satisfactory microanalyses or an HRMS were obtained, see supporting information. [b] Solvent used for TLC and chromatographic separation (PE = petroleum ether, DE = diethyl ether). [c] NMR solvent: $CDCl_3$.



Scheme 5. (i) Method 1: *i*Pr_2NH (2 equiv.), Et_2O, room temp., 24h



Scheme 6. (i) Method 2: *n*-$C_5H_{11}NH_2$ (8 equiv.), Et_2O, 24 h, 25 °C; (ii) method 3: *n*-$C_5H_{11}NH_2$ (8 equiv.), neat, 24 h, 25 °C

Under these very mild reaction conditions, nucleophilic displacement of the ethylsulfanyl group occurs selectively with the furan derivative **9**, probably because of a weaker delocalization of the nonbonding electrons with respect to the corresponding pyrroles **6**, resulting in a higher electrophilicity.

As expected according to the previous observations, the non-nucleophilic diisopropylamine led exclusively to the furan thioester **9**, some of which was isolated as the tautomeric methylene form **11** (Scheme 5). Although we have not studied this issue further, we assume that the reaction occurs under thermodynamic control owing to the acido-basic ($R_2NH_2^+/R_2NH$) medium. As a consequence, the fully conjugated methylene derivative **11** would have a resonance energy only slightly lower than that of the corresponding furan **9**. Under the same conditions, reaction of **2b** with di-

Table 3. Spectroscopic data of 2-trifluoromethylated pyrroles **6a−c** and **13**

Cpd[a]	Solvent[b]	IR (film) $\tilde{\nu}$ (cm^{-1})	MS *m/z*	^{19}F NMR[c]	^{1}H NMR[c]	^{13}C NMR[c]
6a	PE/acetone (95:5)	2930, 1673, 1508, 1426	327 [M^+], 308, 266, 174	−55.5 (s)	1.34 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H), 2.12 (s, 3 H), 3.02 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H), 5.24 (s, 2 H), 6.45 (s, 1 H), 6.91 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H), 7.2−7.4 (m, 3 H)	12.1 (s, CH_3), 14.7 (s, CH_3), 23.7 (s, CH_2), 49.1 (s, CH_2), 109.6 (s, CH), 118.4 (q, $^2J_{C,F}$ = 38.1 Hz, C-2), 120.7 (q, $^1J_{C,F}$ = 269.8 Hz, CF_3), 125.1 (s, C-5), 125.3 (s, 2 × CHPh), 127.6 (s, CHPh), 128.8 (s, 2 × CHPh), 133.3 (s, C-3), 136.2 (s, C_4 Ph), 186.6 (s, COS)
6b	PE/EtOAc (98:2)	2931, 1676, 1428, 1155	307 [M^+], 288, 247, 176	−55.6 (s)	0.92 (t, $^3J_{H,H}$ = 6.5 Hz, 3 H), 1.2−1.4 (m, 7 H), 1.69 (m, 2 H), 2.24 (s, 3 H), 2.98 (q, $^3J_{H,H}$ = 6.5 Hz, 2 H), 3.91 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H), 6.34 (s, 1 H)	12.1 (s, CH_3), 13.8 (s, CH_3), 14.7 (s, CH_3), 22.1 (s, CH_2), 23.6 (s, CH_2), 28.8 (s, CH_2), 30.6 (s, CH_2), 46.2 (s, CH_2), 109.3 (s, CH), 117.5 (q, $^2J_{C,F}$ = 39.4 Hz, C-2), 120.9 (q, $^1J_{C,F}$ = 269.8 Hz, CF_3), 124.7 (s, C-5), 132.2 (s, C-3), 186.6 (s, COS)
6c	PE/EtOAc (96:4)	2929, 1678, 1416, 1161	279 [M^+], 238, 219, 176	−54.4 (s)	1.31 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H), 1.52 (d, $^3J_{H,H}$ = 7.3 Hz, 6 H), 2.37 (s, 3 H), 2.98 (q, $^3J_{H,H}$ = 7.6 Hz, 2 H), 4.65 (sept, $^3J_{H,H}$ = 7.3 Hz, 1 H), 6.25 (s, 1 H)	14.7 (s, 2 × CH_3), 21.7 (s, CH_3), 23.9 (s, CH_2), 50.0 (q, $^4J_{C,F}$ = 2.0 Hz, CH), 111.0 (s, CH), 117.2 (q, $^2J_{C,F}$ = 37.6 Hz, C-2), 120.9 (q, $^1J_{C,F}$ = 268.8 Hz, CF_3), 125.0 (s, C-5), 132.4 (s, C-3), 187.7 (s, COS)
13	PE/DE (94:6)	3130, 2927, 1654, 1625	332 [M^+], 275, 205, 191	−62.5 (s)	0.8−1.0 (m, 6 H), 1.2−1.4 (m, 8 H), 1.5−1.7 (m, 4 H), 2.10 (s, 3 H), 3.37 (td, $^3J_{H,H}$ = 6.9, 6.5 Hz, 2 H), 3.56 (t, $^3J_{H,H}$ = 7.6 Hz, 2 H), 5.66 (m, 1 H), 9.8 (br. m, 1 H)	13.1 (s, CH_3), 13.9 (s, CH_3), 14.0 (s, CH_3), 22.3 (s, CH_2), 22.4 (s, CH_2), 28.8 (s, CH_2), 29.1 (s, CH_2), 29.6 (s, CH_2), 30.1 (s, CH_2), 39.9 (s, CH_2), 44.5 (s, CH_2), 97.2 (q, $^4J_{C,F}$ = 4.9 Hz, CH), 101.2 (s, C-3), 121.2 (q, $^1J_{C,F}$ = 278.6 Hz, CF_3), 131.8 (s, C-5), 140.9 (q, $^2J_{C,F}$ = 31.5 Hz, C-2), 169.1 (s, CON)

[a] Oil. Satisfactory microanalyses or an HRMS were obtained, see supporting information. [b] Solvent used for TLC and chromatographic separation (PE = petroleum ether, DE = diethyl ether). [c] NMR solvent: $CDCl_3$.

ethylamine led to the furan **9** (21%) accompanied by the corresponding diethylamide **12** (38%).

The results of these reactions also depend strongly on the stoichiometry of the reactants. Reaction of **2b** with eight equivalents of *n*-pentylamine in ether at room temperature (method 2) led, as we expected, to a larger amount of amide derivatives **5b** and **13** (Scheme 6), with 2-trifluoromethylfuran (**5b**) still being the major product. Interestingly, 2-trifluoromethyl-3-carboxamide pyrrole (**13**) was produced in good yield and selectivity when the reaction was performed in neat amine (Scheme 6, method 3). In the previous experiments (Scheme 4), the pyrrole derivatives **6** proved to be inert towards amidation. Thus the question arose about the origin of **13**. As a matter of fact, under these conditions, **13** does not result from a nucleophilic displacement of the thiolate group of **6b**, but from oxygen substitution on **5b**. Indeed, treatment of the furan **5b** in neat *n*-pentylamine led cleanly to the pyrrole **13** (Scheme 6). The conversion of non-fluorinated furans[17] and benzofurans[18] into the corresponding pyrroles has already been reported.

From a kinetic viewpoint, a simple increase of *n*-pentylamine concentration (methods 1 and 2), all other conditions being the same, should affect each pathway equally. The formation of the furan **5b** as the major reaction product in the presence of an excess of *n*-pentylamine, whereas both basic and nucleophilic pathways were equivalent in stoichiometric conditions (method 1), seems to indicate that the mechanism could be more complicated than the one described in Scheme 4. A possible explanation would be that in the presence of an excess of amine, a second basic pathway from the intermediate **10**, via the corresponding enolate, contributes to the formation of the furan **9**.

Conclusions

This study extends the field of applications of perfluoroketene dithioacetals **1**. The synthon **1b**, like its homologue **1a**, is easily converted into the γ-keto thioester **2b**, a bifunctional intermediate which actually behaves as the trifunctional intermediate **7** in the presence of aliphatic amines (Scheme 4). The versatility of these intermediates is exemplified by the possible syntheses of 2-trifluoromethylfurans and/or -pyrroles bearing a thioester or a carboxamide group. The selectivity of the reaction is controlled by the reaction conditions (methods 1−3) and the basicity/nucleo-

philicity balance of the amine (Table 1). This study and the preceding reports in this series disclose only a few aspects of the scope of this chemistry. Other applications are under investigation.

Experimental Section

General Remarks: See ref.[19] for general experimental procedures. Compounds **1b**,[1a] **4**[2] and **2b**[3] were prepared according to published procedures.

5,5-Bis(ethylthio)-4-pentafluoroethylpent-4-en-2-one (4): Yield: 91% (8.79 g). Oil; b.p. 99 °C/0.4 Torr. ^{1}H NMR: δ = 1.21 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H), 1.29 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H), 2.21 (s, 3 H), 2.85 (q, $^3J_{H,H}$ = 7.3 Hz, 4 H), 3.75 (t, $^4J_{H,F}$ = 1.5 Hz, 2 H). Selected ^{13}C NMR spectroscopic data: δ = 14.5 (s, CH_3), 14.7 (s, CH_3), 28.3 (s, CH_2), 29.2 (s, CH_2), 29.7 (s, CH_3), 47.0 (m, CH_2), 148.2 [m, *C*(SEt)$_2$], 202.3 (s, CO). ^{19}F NMR: δ = −82.8 (m, 3F, CF_3), −106.9 (m, 2F, CF_2). MS: *m*/*z* = 322 [M$^+$], 278, 198.

***S*-Ethyl 4-Oxo-2-pentafluoroethylpentanethioate (2b):** Yield: 95% (5.28 g). Oil; b.p. 71 °C/10 Torr. ^{1}H NMR: δ = 1.24 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H), 2.19 (s, 3 H), 2.8−3.0 (m, 3 H), 3.27 (dd, $^2J_{H,H}$ = 18.7, $^3J_{H,H}$ = 10.3 Hz, 1 H), 3.90 (m, 1 H). ^{13}C NMR: δ = 14.0 (s, CH_3), 24.3 (s, CH_2), 29.6 (s, CH_3), 39.4 (s, CH_2), 49.5 (t, $^2J_{C,F}$ = 20.9 Hz, CH), 105−115 (m, CF_2), 118.7 (q, $^1J_{C,F}$ = 287.5 Hz, CF_3), 192.9 (s, COS), 202.8 (s, CO). ^{19}F NMR: δ = −82.4 (m, 3F, CF_3), −115.1 (ddm, $^2J_{F,F}$ = 274.7, $^3J_{H,F}$ = 15.3 Hz, 1 F, CF_AF$_B$), −116.8 (ddm, $^2J_{F,F}$ = 274.7, $^3J_{H,F}$ = 15.3 Hz, 1 F, CF$_A$$F_B$). IR (film): $\tilde{\nu}$ = 2973, 2936, 1730, 1680, 1265 cm^{-1}. MS: *m*/*z* = 278 [M$^+$], 219, 189, 75. $C_9H_{11}F_5O_2S$ (278.237): calcd. C 38.85, H 3.98; found C 39.05, H 3.79.

Preparation of 2-Trifluoromethylated Furans 5a−c and Pyrroles 6a−c. General Procedure (method 1): The amine (15.0 mmol, 2.0 equiv.) was added to a solution of compound **2b** (2.09 g, 7.5 mmol) in ether (100 mL). A white solid precipitated immediately. The mixture was stirred for 24 h at room temperature, then diluted with ether (50 mL) and washed with brine (50 mL). The aqueous phase was extracted with ether (4 × 50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was chromatographed on silica gel using a mixture of petroleum ether/EtOAc to give the 2-trifluoromethylfurans **5a−c** and -pyrroles **6a−c** (Table 1−3).

Reaction of Compound 2b with Diisopropylamine (Scheme 5): Method 1 applied to compound **2b** (0.90 g, 3.24 mmol) and diisopropylamine (0.91 mL, 2 equiv.) gave furan **9** (0.40 g, yield: 52%) and compound **11** (0.12 g, yield: 16%) after chromatography [eluent: petroleum ether/EtOAc (98:2) for **9**, (96:4) for **11**]. Spectroscopic data for **9** are collected in Table 2.

***S*-Ethyl 5-Methylene-2-trifluoromethyl-2,5-dihydrofuran-3-carbothioate (11):** Oil. ^{1}H NMR: δ = 1.32 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H), 2.2−2.3 (m, 2 H), 4.22 (q, $^3J_{H,F}$ = 8.0 Hz, 1 H), 5.03 (d, $^2J_{H,H}$ = 2.7 Hz, 1 H), 5.34 (d, $^2J_{H,H}$ = 2.7 Hz, 1 H), 7.35 (s, 1 H). ^{13}C NMR: δ = 14.1 (s, CH_3), 27.7 (s, CH_2), 41.8 (q, $^2J_{C,F}$ = 32.9 Hz, CH), 99.8 (s, CH_2), 125.4 (q, $^1J_{C,F}$ = 279.4 Hz, CF_3), 128 (s, C-3), 138.4 (s, CH), 147.1 (q, $^4J_{C,F}$ = 7.0 Hz, C-5), 153.2 (s, COS). ^{19}F NMR: δ = −69.1 (d, $^3J_{H,F}$ = 8.0 Hz). IR (film): $\tilde{\nu}$ = 2926, 2854, 1728, 1653, 1254 cm^{-1}. GCMS: *m*/*z* = 238 [M$^+$], 178, 158, 149.

Reaction of Compound 2b with *N*-pentylamine (Scheme 6, method 2): The same procedure as method 1 except that we used an excess (8 equiv.) of *N*-pentylamine, gave furan **5b** (0.71 g, yield: 54%), and the pyrroles **6b** (0.14 g, yield: 9%) and **13** (0.28 g, yield: 17%) after chromatography (eluent: petroleum ether/EtOAc). The spectroscopic data of **5b**, **6b** and **13** are collected in Table 2 and 3.

Reaction of Compound 2b with Neat *N*-pentylamine (Scheme 6, method 3): *N*-pentylamine (3.53 mL, 30.0 mmol) was added to compound **2b** (1.05 g, 3.8 mmol) at room temperature. The reaction was exothermic (heating to 40−60 °C). The resulting mixture was stirred for 24 h at room temperature, then diluted with ether (30 mL) and washed with brine (30 mL). The aqueous phase was extracted with ether (4 × 25 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was chromatographed on silica gel using a mixture of petroleum ether/EtOAc (Table 3) to give the pyrroles **6b** (0.08 g, yield: 7%) and **13** (0.72 g, yield: 57%). The spectroscopic data of **6b** and **13** are collected in Table 3.

Reaction of Furan 5b with *N*-pentylamine (Scheme 6): The method 3 applied to compound **5b** (0.50 g, 1.90 mmol) and *N*-pentylamine (1.75 mL, 8 equiv.) gave after chromatography [eluent: petroleum ether/diethyl ether (94:6)] the pyrrole **13** (0.43 g, yield: 67%).

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