An Effective Synthesis of 2-Trifluoromethyl- or 2-(1,1-Difluoroalkyl)thiophenes

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Various thiophenecarboxylates carrying a 2-trifluoromethyl, 2-(1,1-difluoroalkyl) or 2-polyfluoroalkyl group are synthesized conveniently from reaction of α-fluoroalkyl ketones **1**, aldehydes **2** or ethyl α-fluoroalkylacetates **3** with methyl (or ethyl) 2-sulfanylacetates **4**. A possible reaction pathway is suggested.

Fluorine-containing heterocyclic compounds are important in both academic and industrial fields. Regioselective replacement of hydrogen in a molecule by a fluorine or fluoroalkyl group may have profound influence on the biological and physical properties of such compounds.[1] Synthesis of thiophenes carrying a fluorinated side chain has received considerable attention in recent years.[2] Trifluoromethylthiophenes have been synthesized, for example, by fluorination of thiophenecarboxylic acid with sulfur tetrafluoride,[3] trifluoromethylation of thiophenes,[4] substitution of halogen on thiophene by trifluoromethyl group,[5] condensation of trifluoromethylated acetylenic esters with 2-sulfanylacetates[6] and the reaction of certain fluorine-containing unsaturated compounds with phosphorus pentasulfide.[7] However, methods for synthesis of such compounds are still quite limited and usually hazardous reagents, complicated products or long synthetic routes were involved.

α-Fluoroalkyl ketones **1**, aldehydes **2**, and acetates **3** have been proved to be versatile precursors in our previous synthesis of fluoroalkyl-containing pyrimidines[8] and pyrazoles.[9] Here we report the synthesis of 2-fluoroalkylthiophenes from reaction of such compounds with alkyl 2-sulfanylacetates **4**.

In the presence of sodium methoxide, α-fluoroalkylcarbonyl compounds **1**,[10] **2** and **3**[11] reacted with methyl 2-sulfanylacetate **(4a)** in methanol at r.t. for about 5 hours to afford compounds **5**, **6** or **7** in high yields. The results are summarized in the Table and expressed in Schemes 1 and 2.

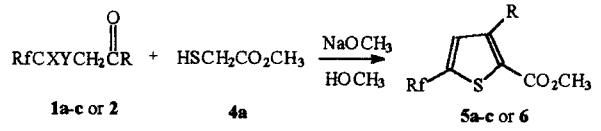
Such a condensation reaction proceeded smoothly with α-fluoroalkyl ketones **1** to give products **5** in good yields (Scheme 1). ^{19}F NMR spectra of **5** revealed that the fluoroalkyl group contained one less carbon than that of the corresponding starting material **1**, ^{1}H NMR showed an aromatic proton at δ = 7.0–7.8 and UV spectrum showed absorption at λ_{max}: 260–280 nm. All these suggested the presence of a thiophene system. α-Fluoroalkyl cycloketones **1d–f** gave the aliphatic ring-fused 2-trifluoromethyl- (or 2-chlorodifluoromethyl)thiophene derivatives **5d–f**.

The reaction also fitted well with α-fluoroalkyl aldehydes **2**. Compounds **2a** and **2b** furnished **6a** and **6b** in 60% and 54% yield respectively (entry 6 and 7). The lower yield was attributed to the vulnerability of such an aldehyde under basic conditions.

Table. Reaction of α-Fluoroalkyl Carbonyl Compounds with Sulfanylacetates

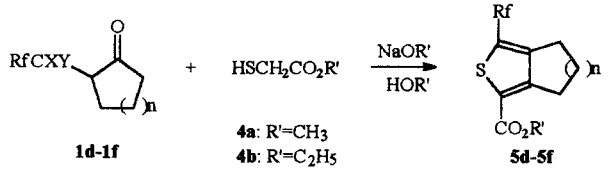
Entry	Substrate 1, 2 or 3	Time (h)	Temp. (°C)	Base/Solvent[a]	Product[b]	Yield[c] (%)
1	**1a**	4	20	A	**5a**	76
2	**1d**	4	20	A	**5b**	70
3	**1c**	3	25	A	**5c**	75
4	**1c**	4	20	$NaOCH_3$/THF	**5c**	74
5	**1c**	2	reflux	A	**5c**	60
6	**2a**	5	20	A	**6a**	60
7	**2b**	5	20	A	**6b**	54
8	**1d**	4	25	A	**5d**	70
9	**1e**	4	25	A	**5e**	78
10	**1e**	5	25	B	**5E**	75
11	**1f**	4	20	A	**5f**	77
12	**3a**	5	20	A	**7a**	75
13	**3b**	4	25	A	**7a**	72
14	**3a**	5	20	B	**7A**	80
15	**3c**	5	20	A	**7c**	75
16	**3d**	4	20	A	**7d**	72
17	**3e**	4	20	A	**7e**	83
18	**3f**	6	20	A	**7f**	72
19	**3f**	6	20	B	**7F**	70
20	**3g**	6	20	A	**7g**	80
21	**3h**	5	20	A	**7h**	71

[a] A: $NaOCH_3/HOCH_3$; B: $NaOC_2H_5/HOC_2H_5$.
[b] All new products have been characterized by ^{1}H NMR, ^{19}F NMR, IR and MS.
[c] Isolated yield based on substrate **1**, **2** or **3**.



1a-c or 2 4a 5a-c or 6

Substrate	RfCXY	R	Product	Rf
1a	CF_3CF_2	CH_3	5a	CF_3
1b	CF_3CBr_2	$C(CH_3)_3$	5b	CF_3
1c	$Cl(CF_2)_4$	$C(CH_3)_3$	5c	$Cl(CF_2)_3$
2a	$Cl(CF_2)_4$	H	6a	$Cl(CF_2)_3$
2b	$F(CF_2)_4$	H	6b	$F(CF_2)_3$

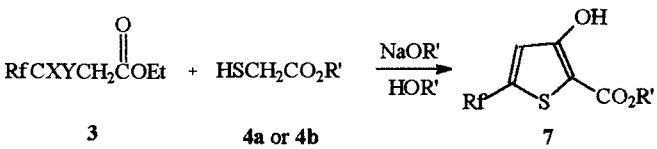


1d-1f 4a: R'=CH_3 4b: R'=C_2H_5 5d-5f

Substrate	RfCXY	n	Product	R'	Rf
1d	CF_3CF_2	1	5d	CH_3	CF_3
1e	CF_3CF_2	2	5e	CH_3	CF_3
1e	CF_3CF_2	2	5E	C_2H_5	CF_3
1f	$ClCF_2CF_2$	2	5f	CH_3	$ClCF_2$

Scheme 1

Ethyl α-fluoroalkylacetates **3** underwent a similar reaction and gave compounds **7** in good yields (Scheme 2). UV spectrum of **7** showed absorption at λ_{max}: 300–312 nm. ^{1}H NMR spectra of **7** revealed not only the presence of an aromatic proton at $\delta = 6.8–7.3$ and an aromatic hydroxyl proton at $\delta = 9.0–9.5$ but also the disappearance of ethoxyl group in the starting materials **3**. Thus the structure of **7** was suggested as 2-fluoroalkyl-4-hydroxy-5-methoxycarbonylthiophene.

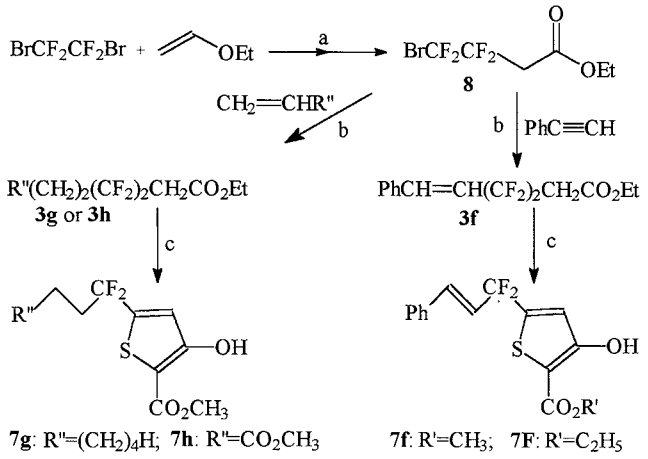


3 4a or 4b 7

Substrate	RfCXY	Rf	Product	R'
3a	CF_3CBr_2	CF_3	7a	CH_3
3b	CF_3CFBr	CF_3	7b	CH_3
3c	CF_3CF_2	CF_3	7c	C_2H_5
3d	$ClCF_2CF_2$	$ClCF_2$	7d	CH_3
3e	$Cl(CF_2)_4$	$Cl(CF_2)_3$	7e	CH_3
3f	$PhCH{=}CHCF_2CF_2$	$PhCH{=}CHCF_2$	7f	CH_3
3f	$PhCH{=}CHCF_2CF_2$	$PhCH{=}CHCF_2$	7F	C_2H_5
3g	$CH_3(CH_2)_5CF_2CF_2$	$CH_3(CH_2)_5CF_2$	7g	CH_3
3h	$CH_3O_2C(CH_2)_2CF_2CF_2$	$CH_3O_2C(CH_2)_2CF_2$	7h	CH_3

Scheme 2

Since the dihalogenated carbon β to the carbonyl group in substrates **1**, **2** and **3** became part of the thiophene skeleton with elimination of the β-halogens, 2-trifluoromethylthiophene derivatives were prepared from β,β-dihalogen-γ,γ,γ-trifluorocarbonyl compounds. Furthermore, (1,1-difluoroalkyl)thiophenes could be expected from β,β,γ,γ-tetrafluorocarbonyl compounds. Compounds **8**, derived from addition of 1,2-dibromotetrafluoroethane to ethyl vinyl ether followed by oxidation and esterification, reacted with alkenes or alkynes to afford such tetrafluoroalkylacetates in good yields.[12] Such compounds **3f**, **3g** and **3h** condensed with alkyl 2-sulfanylacetates **4** to afford 2-(1,1-difluoroalkyl)thiophenes **7f**,**7F**,**7g** and **7h**, respectively (Scheme 3).

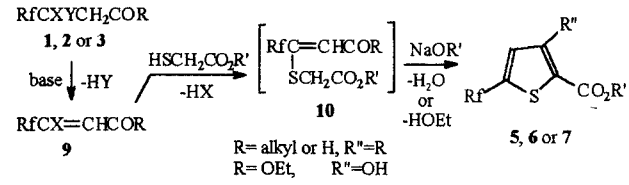


7g: R"=$(CH_2)_4H$; 7h: R"=CO_2CH_3 7f: R'=CH_3; 7F: R'=C_2H_5

a. 1) $Na_2S_2O_4$–$NaHCO_3$/CH_3CN–H_2O, 0°C 2) CrO_3–H_2SO_4/acetone, reflux 3) TsOH–benzene/EtOH, reflux
b. $BrCo(dmyH)_2$, Zn/EtOH c. $HSCH_2CO_2R'$,NaOR'/HOR'

Scheme 3

In these reactions, ethyl 2-sulfanylacetate **(4b)** could be used in ethanol instead of methyl 2-sulfanylacetate **(4a)** in methanol without any significant effect on the reaction (entry 10, 14 and 19). Reaction time could be reduced by raising the temperature. Strong base such as sodium methoxide (or sodium ethoxide) was neccessary for the one-step condensation and solvents (methanol or ethanol) should match with the base. However, when sodium carbonate, triethylamine or potassium hydroxide was used as base, the reaction of **1c** and **4a** yielded an acyclic compound **10** as the major product (63%). Compound **10** condensed intramolecularly to give **5c** in the presence of sodium methoxide (Scheme 4).



R= alkyl or H, R"=R
R= OEt, R"=OH

Scheme 4

Based on the above facts, the following reaction pathway is logically proposed (Scheme 4). Under basic conditions, compounds **1**, **2** or **3** underwent dehydrohalogenation to give intermediates **9**, which were attacked by the nucleophilic thiols **4** at the β-position and afforded intermediates **10**. Such intermediates underwent intramolecular condensation and dehydration to afford the target products **5**, **6** or **7**.

In summary, 2-trifluoromethyl- and 2-(1,1-difluoroalkyl)thiophenecarboxylates as well as their analogues having a longer fluoroalkyl chain were synthesized. The carboxyl and hydroxyl group in these products are still reactive and thus such compounds could be considered as useful building blocks in the synthesis of compounds containing a 2-fluoroalkylthiophene moiety.

^{1}H NMR resonance spectra were obtained with $CDCl_3$ as solvent and internal TMS as standard on a FX-90Q spectrometer. ^{19}F NMR spectra were measured with external CF_3COOH as standard and with upfield shifts positive using a Varian EM-360L spectrometer at 56.4 MHz. IR spectra were recorded as film for liquid and KCl plate for solid samples on a Shimadzu IR-440 spectrometer. Mass spectra were recorded by means of a HP5989A mass spectrometer. UV spectra were measured using CH_3OH as solvent on a HP 8451A diode array spectrophotometer. The solvents and reactants were reagent grade and were used without further purification. Light petroleum refers to the fraction boiling in the range 60–90 °C.

Fluoroalkylthiophenes 5, 6 and 7; General Procedure:

To a solution of compound **1** (**2** or **3**) (5 mmol) and methyl 2-sulfanylacetate (6 mmol) in anhyd MeOH (10 mL) was added slowly NaOMe (20 mmol) and the mixture was stirred at r.t. for about 5 h (monitored by TLC or ^{19}F NMR). After that, the mixture was poured into H_2O (50 mL) and extracted with Et_2O (3 × 50 mL). The combined extracts were successively washed with sat. aq NH_4Cl and brine, dried (Na_2SO_4) and then evaporated. The remained residue was column chromatographed with light petroleum/EtOAc as eluent (100:0-100:6) to give pure products **5**, **6** or **7**.

5-Methoxycarbonyl-4-methyl-2-trifluoromethylthiophene (**5a**):

IR: ν_{max} = 2950, 1730, 1260, 1120 cm^{-1}.

^{1}H NMR: δ = 7.34 (1 H, s), 4.0 (3 H, s, CH_3), 2.70 (3 H, s).

^{19}F NMR: δ = −21.0 (s, CF_3).

MS: *m/e* = 224 (M^+, 23.18), 209 (M^+-CH_3, 2.88), 193 (M^+-OCH_3, 33.96), 165 (M^+-CO_2CH_3, 1.0).

Analysis: Calc. for $C_8H_7F_3O_2S$: C, 42.86; H, 3.13; F, 25.45; S, 14.29. Found: C, 42.58; H, 2.77; F, 25.90; S, 13.74.

4-tert-Butyl-5-methoxycarbonyl-2-trifluoromethylthiophene (**5b**):

IR: ν_{max} = 2960, 1740, 1300, 1230, 1130 cm^{-1}.

^{1}H NMR: δ = 7.41 (1 H, s), 3.90 (3 H, s, CH_3), 1.50 (9 H, s).

^{19}F NMR: δ = −21.5 (s, CF_3).

MS: *m/e* = 266 (M^+, 8.10), 251 (M^+-CH_3, 11.33), 235 (M^+-OCH_3, 6.84), 219 (M^+-$HOCH_3$-CH_3, 100), 191 (M^+-HCO_2CH_3-CH_3, 18.28).

Analysis: Calc. for $C_{11}H_{13}F_3O_2S$: C, 49.62; H, 4.89; F, 21.42; S, 12.03. Found: C, 49.22; H, 4.92; F, 21.45; S, 12.48.

4-tert-Butyl-2-(ω-chlorohexafluoropropyl)-5-methoxycarbonylthiophene (**5c**):

UV (nm): 278.

IR: ν_{max} = 2970, 1740, 1240, 1130 cm^{-1}.

^{1}H NMR: δ = 7.76 (1 H, s), 3.92 (3 H, s, CH_3), 1.50 (9 H, s).

^{19}F NMR: δ = −11.0 (2F, s, CF_2Cl), 24.0 (2F, s, CF_2C), 42.3 (2F, s).

MS: *m/e* = 382 (M^+, 14.28), 367 (M^+-CH_3, 17.97), 351 (M^+-OCH_3, 9.27), 335 (M^+-$HOCH_3$-CH_3, 100), 307 (M^+-HCO_2CH_3-CH_3, 8.14).

Analysis: Calc. for $C_{13}H_{13}ClF_6O_2S$: C, 40.78; H, 3.40; F, 29.80; S, 8.37. Found: C, 40.50; H, 3.28; F, 30.17; S, 8.28.

2-(ω-Chlorohexafluoropropyl)-5-methoxycarbonylthiophene (**6a**):

IR: ν_{max} = 2900, 1720, 1280, 1180 cm^{-1}.

^{1}H NMR: δ = 7.76 (1 H, d, *J* = 3 Hz), 7.40 (1 H, d, *J* = 3 Hz), 3.93 (3 H, s).

^{19}F NMR: δ = −11.3 (2F, s), 23.3 (2F, s), 42.0 (2F, s).

MS: *m/e* = 326 (M^+, 20.04), 295 (M^+-OCH_3, 30.63), 191 (M^+-$ClCF_2CF_2$, 100).

HRMS: Calc. for $C_9H_5{}^{35}ClF_6O_2S$: 325.9603, Found: 325.9617; for $C_9H_5{}^{37}ClF_6O_2S$: 327.9573, Found: 327.9554.

2-Heptafluoropropyl-5-methoxycarbonylthiophene (**6b**):

^{1}H NMR: δ = 7.76 (1 H, d, *J* = 3.0 Hz), 7.40 (1 H, d, *J* = 3.0 Hz), 3.96 (3 H, s).

^{19}F NMR: δ = 2.10 (3F, s), 25.5 (2F, s), 48.5 (2F, s).

MS: *m/e* = 310 (M^+, 37.66), 291 (M^+-F, 5.96), 279 (M^+-OCH_3, 72.67), 191 (M^+-CF_3CF_2, 100), 160 (4.07), 132 (28.66).

HRMS: Calc. for $C_9H_5F_7O_2S$: 309.9935, Found: 309.9899. Analysis: Calc. for $C_9H_5F_7O_2S$: C, 34.84; H, 1.61; Found: C, 34.88; H, 1.86.

5-Methoxycarbonyl-3,4-propylene-2-trifluoromethylthiophene (**5d**):

^{1}H NMR: δ = 3.91 (3 H, s, CH_3), 2.90 (4 H, m), 2.46 (2 H, m).

^{19}F NMR: δ = −21.8.

MS: *m/e* = 250 (M^+, 52.99), 232 (M^+-F+1, 21.71), 214 (15.16), 199 (24.47), 149 (40.14), 91 (100).

Analysis: Calc. for $C_{10}H_9F_3O_2S$: C, 48.0; H, 3.60; F, 22.8; S, 12.80. Found: C, 47.98; H, 3.59; F, 22.78; S, 12.81.

3,4-Butylene-5-methoxycarbonyl-2-trifluoromethylthiophene (**5e**):

UV (nm): 280.

^{1}H NMR: δ = 3.90 (3 H, s, CH_3), 3.03 (2 H, m), 2.81 (2 H, m), 1.76 (4 H, m).

^{19}F NMR: δ = −21.6.

MS: *m/e* = 264 (M^+, 100), 249 (M^+-CH_3, 95.26), 233 (M^+-OCH_3, 32.94), 205 (M^+-CO_2CH_3, 53.39), 185 (10.66), 165 (26.30).

Analysis: Calc. for $C_{11}H_{11}F_3O_2S$: C, 50.0; H, 4.17; F, 21.59; S, 12.12. Found: C, 49.99; H, 4.09; F, 21.15; S, 12.08.

3,4-Butylene-5-ethoxycarbonyl-2-trifluoromethylthiophene (**5E**):

^{1}H NMR: δ = 4.26 (2 H, q, CH_2), 3.0 (2 H, m), 2.76 (2 H, m), 1.73 (4 H, m), 1.35 (3 H, t).

^{19}F NMR: δ = −21.6.

MS: *m/e* = 278 (M^+, 48.62), 259 (M^+-F, 6.11), 249 (M^+-C_2H_5, 100), 231 (39.12), 223 (19.75), 205 (62.91).

3,4-Butylene-2-chlorodifluoromethyl-5-methoxycarbonylthiophene (**5f**):

^{1}H NMR: δ = 3.90 (3 H, s, CH_3), 3.03 (2 H, m), 2.85 (2 H, m), 1.76 (4 H, m).

^{19}F NMR: δ = −36.3.

MS: *m/e* = 280 (M^+, 31.26), 265 (M^+-CH_3, 16.08), 245 (M^+-Cl, 100), 229 (5.12), 217 (5.12), 185 (21.30).

Analysis: Calc. for $C_{11}H_{11}ClF_2O_2S$: C, 47.06; H, 3.92; F, 13.55; S, 11.41; Cl: 12.66. Found: C, 47.16; H, 3.93; F, 14.11; S, 11.38; Cl: 12.23.

4-Hydroxy-5-methoxycarbonyl-2-trifluoromethylthiophene (**7a**):

IR: ν_{max} = 3300 (O–H), 1680, 1570 (C=C), 1440, 1290 (C–O), 1140 (C–C, C–F) cm^{-1}.

^{1}H NMR: δ = 9.0 (1 H, s, OH), 7.33 (1 H, s), 4.0 (3 H, s, CH_3).

^{19}F NMR: δ = −20.0 (3F, s).

MS: *m/e* = 226 (M^+, 6.91), 194 (M^+-$HOCH_3$, 15.48), 178 (M^+-OH-OCH_3, 23.68), 149 (M^+-CH_3CO_2H-OH, 77.01), 57 (100).

Analysis: Calc. for $C_7H_5F_3O_2S$: C, 37.17; H, 2.21; F, 25.22; S, 14.16. Found: C, 36.87; H, 2.14; F, 25.04; S, 14.33.

5-Ethoxycarbonyl-4-hydroxy-2-trifluoromethylthiophene (**7A**):

^{1}H NMR: δ = 9.43 (1 H, s, OH), 7.0 (1 H, s), 4.30 (2 H, q, CH_2), 1.4 (3 H, t).

^{19}F NMR: δ = −20.5 (2F, s).

MS: *m/e* = 240 (M^+, 26,47), 223 (M^+-OH, 51.33), 195 (M^+-OC_2H_5, 100).

2-Chlorodifluoromethyl-4-hydroxy-5-methoxycarbonylthiophene (**7d**):

IR: ν_{max}: = 3300, 1680, 1560, 1440, 1230, 1120 cm^{-1}.

^{1}H NMR: δ = 9.50 (1 H, s, OH), 7.10 (1 H, s), 3.92 (3 H, s, CH_3).

^{19}F NMR: δ = −35.0 (2F, s).

MS: *m/e* = 242 (M^+, 58.45), 210 (M^+-$HOCH_3$, 100), 175 (210-Cl, 18.40), 154 (175-F, 22.57).

Analysis: Calc. for $C_7H_5ClF_2O_2S$: C, 34.64; H, 2.06; F, 15.70; Cl, 14.64. Found: C, 33.98; H, 1.92; F, 16.0; S, 14.35.

2-(ω-Chlorohexafluoropropyl)-4-hydroxy-5-methoxycarbonylthiophene (**7e**):

UV (nm): 312.

IR: ν_{max} = 3300, 1680, 1570, 1190, 1120 cm^{-1}.

^{1}H NMR: δ = 9.53 (1 H, s, OH), 7.10 (1 H, s), 4.0 (3 H, s, CH_3).

^{19}F NMR: δ = −10.4 (2F, s), 26.0 (2F, m), 43.0 (2F, s).

MS: *m/e* = 342 (M^+, 9.10), 310 (M^+-$HOCH_3$, 19.02), 294 (M^+-OCH_3, 9.67), 262 (18.61), 244 (51.11), 149 (69.22), 69 (100).

Analysis: Calc. for $C_9H_5ClF_6O_3S$: C, 31.53; H, 1.46; F, 33.28; S, 9.34. Found: C, 31.32; H, 1.29; F, 33.27; S, 9.34.

2-(1,1-Difluoro-3-phenylprop-2-enyl)-4-hydroxy-5-methoxycarbonylthiophene (**7f**):

IR: ν_{max} = 3260, 2900, 1670, 1560, 1340, 1170, 1040 cm^{-1}.

^{1}H NMR: δ = 9.45 (1 H, s, OH), 7.30 (5 H, m), 6.93 (1 H, d, *J* = 12 Hz), 6.85 (1 H, s), 6.0 (1 H, td, *J* = 12, 12 Hz), 3.90 (3 H, s, CH_3).

^{19}F NMR: δ = −2.20 (2F, d, *J* = 12 Hz).

MS: *m/e* = 310 (M^+, 78.02), 278 (M^+-$HOCH_3$, 100), 264 (M^+-OCH_3, 13.54), 249 (21.36), 231 (12.29), 208 (M^+-PhCCh, 29.80), 176 (208-$HOCH_3$, 95.64).

Analysis: Calc. for $C_{15}H_{12}F_2O_3S$: C, 58.06; H, 3.87; F, 12.26. Found: C, 57.71; H, 3.88; F, 12.00.

2-(1,1-Difluoro-3-phenylprop-2-enyl)-4-hydroxy-5-ethoxycarbonylthiophene (**7F**):

^{1}H NMR: δ = 9.40 (1 H, s, OH), 7.20 (5 H, m), 6.85 (1 H, d, *J* = 12 Hz), 6.77 (1 H, s), 5.92 (1 H, td, *J* = 12 Hz), 4.30 (2 H, q, CH_2), 1.38 (3 H, t, CH_3).

^{19}F NMR: δ = −1.70 (2F, d, *J* = 12, 12 Hz).

MS: *m/e* = 324 (M^+, 78.17), 278 (M^+-HOC_2H_5, 100), 261 (4.26), 177 (19.42), 159 (39.67), 133 (26.96).

2-(1,1-Difluoroheptyl)-4-hydroxy-5-methoxycarbonylthiophene (**7g**):

IR: ν_{max} = 3300, 2960, 1680, 1570, 1450, 1360, 1170 cm^{-1}.

^{1}H NMR: δ = 9.53 (1 H, s, OH), 6.85 (1 H, s), 3.95 (3 H, s), 2.10 (2 H, m), 1.34 (8 H, m), 0.90 (3 H, m).

^{19}F NMR: δ = 10.0 (2F, t, *J* = 12 Hz).

MS: *m/e* = 292 (M^+, 56.04), 260 (M^+-$HOCH_3$, 100), 245 (M^+-$HOCH_3$-CH_3, 2.72), 207 (M^+-C_6H_{13}, 55.72).

Analysis: Calc. for $C_{13}H_{18}F_2O_3S$: C, 53.42; H, 6.16; F, 13.10; S, 10.96. Found: C, 53.30; H, 6.00; F, 13.07; S, 11.52.

4-Hydroxy-5-methoxycarbonyl-2-(1,1-difluoro-3-methoxycarbonylpropyl)thiophene (**7h**):

UV (nm): 306.

IR: ν_{max} = 3300, 2950, 1740, 1670, 1560, 1440, 1300, 1160 cm^{-1}.

^{1}H NMR: δ = 9.50 (1 H, s, OH), 6.86 (1 H, s, Ha), 3.93 (3 H, s), 3.72 (3 H, s), 2.57 (4 H, m).

^{19}F NMR: δ = 13.0 (2F, t, *J* = 16 Hz).

MS: *m/e* = 294 (M^+, 79.92), 275 (M^+-F, 7.76), 262 (M^+-$CH_3O_2CCH_2CH_2$, 100), 243 (6.22), 215 (17.22), 140 (71.84).

Analysis: Calc. for $C_{11}H_{12}F_2O_5S$: C, 44.9; H, 4.08; F, 12.93; S, 10.88. Found: C, 45.05; H, 4.02; F, 13.24; S, 10.96.

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