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Reactivity of a β-trifluoromethyl β-thioacrolein with various electrophiles

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Abstract

Novel classes of trifluoromethylthiophenes and thiopyrans have been prepared by the reaction of a β-trifluoromethyl β-thioacrolein with different electrophiles, i.e. phenacyl bromide, enones or activated β-chlorovinylpropenes.

Keywords: β-Trifluoromethyl β-thioacrolein; Trifluoromethylthiophenes; Trifluoromethylpyrans; NMR spectroscopy; IR spectroscopy, Mass spectrometry

1. Introduction

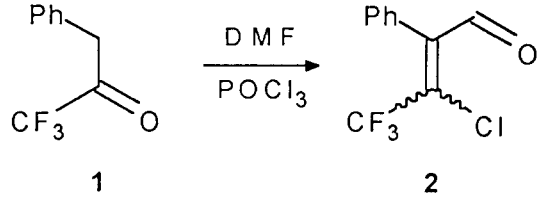
During the past few years considerable attention has been devoted to the synthesis of trifluoromethylated heterocyclic compounds, due to their unique potential biological activity [1].

In short communications, we reported that 3-chloro-3-trifluoromethylacroleins are available from the Vilsmeier reaction on trifluoromethylketones [2]. The substitution of the 3-chloro group by a thiol function allows the synthesis of a wide range of trifluoromethylated thiophenes and thiopyranes. In this paper, we describe the stabilisation of this starting material and different cyclizations.

2. Results and discussion

The Vilsmeier reaction on trifluoromethylbenzylketone (**1**) produced the 3-chloro-4,4,4-trifluoro-2-phenylbutenal (**2**) [2] (Scheme 1).

Substitution of the chloro atom in **2** via reaction with Na_2S under mild conditions led to an unstable red oil which could be stabilised in several ways and then used synthetically. Metal ions yielded the *cis*-chelates **3** (Scheme 2).



1 **2**

Scheme 1.

Reaction with dicyclohexylamine gave the thiolate **4** (yield 53%) and the enaminothione **5** in a much lower amount (yield 10%). Reaction with primary amines gave compounds **6** in relatively low yields. ^1H NMR spectra indicate intramolecular hydrogen bonding between the nitrogen and the sulfur atom.

The thiolate **4** is a useful reagent for the synthesis of various trifluoromethyl heterocyclic compounds. Nucleophilic attack of this thiolate anion on phenacyl bromides **7** proceeded by substitution of the bromo atom, followed immediately by an aldolic cyclisation reaction to give thiophenes **8a–e** (Scheme 3).

Reactions of thiolate **4** with several acroleins or enones **9** allowed the formation of the 3-acyl-substituted 2*H*-thiopyrans **10** (Scheme 4).

β-Chlorovinylpropenes **11** activated with an electron-withdrawing group reacted with thiolate **4** to give the substituted 2-methylene-2*H*-thiopyranes **12** (Scheme 5).

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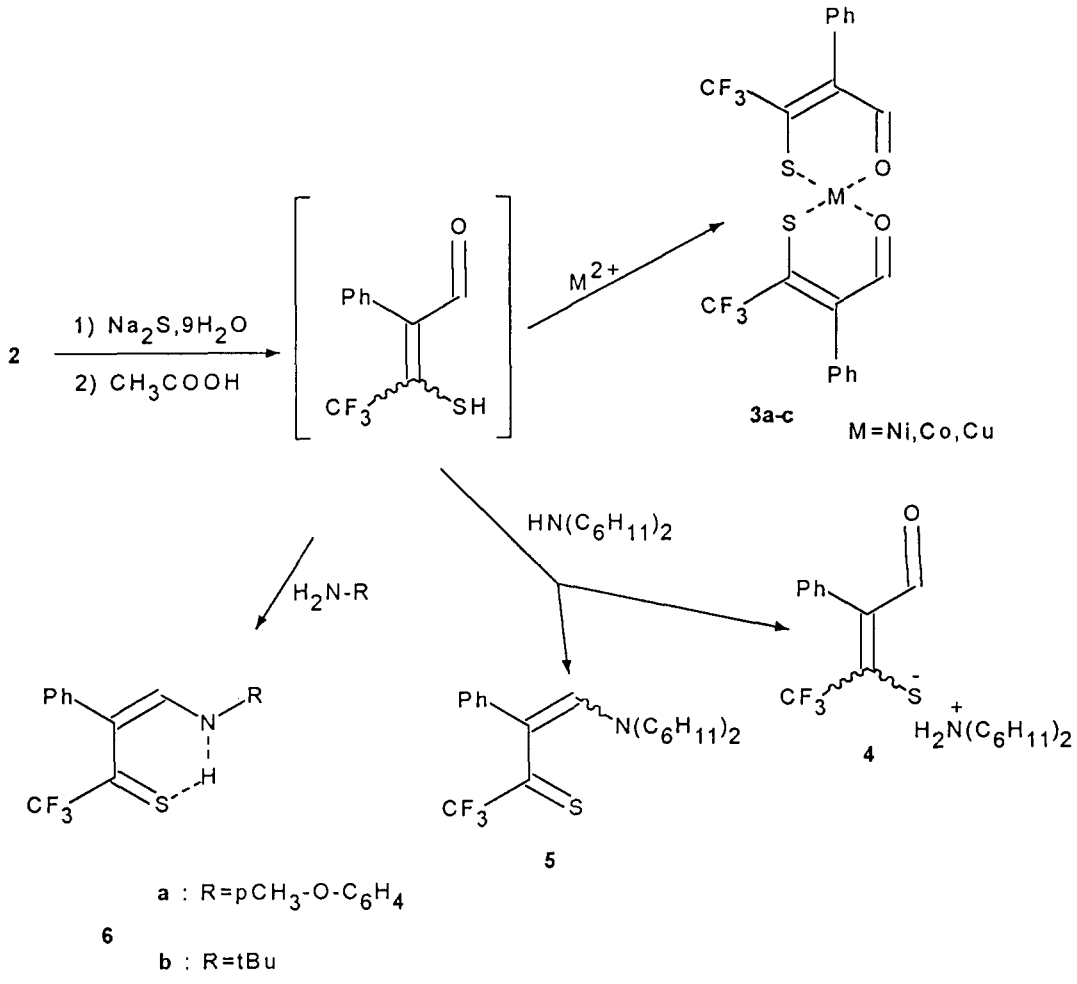
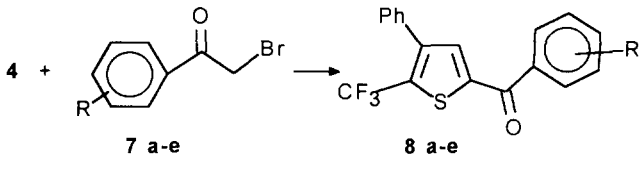
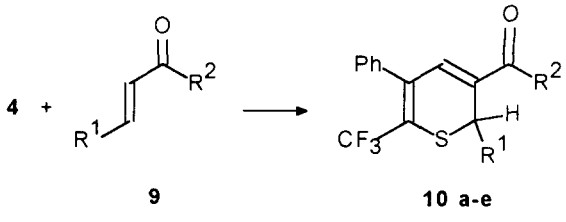


Scheme 2.



a : R=H
b : R=4-Br
c : R=3-NH_2
d : R=2-NO_2
e : R=4-F

Scheme 3.



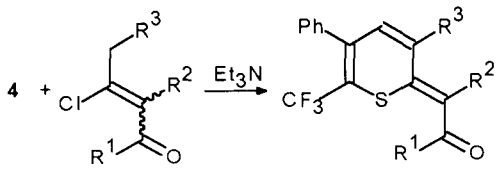
a : $R^1=R^2=H$
b : $R^1=CH_3, R^2=H$
c : $R^1=Ph, R^2=H$
d : $R^1=H, R^2=CH_3$
e : R^1-R^2=-$(CH_2)_3$-

Scheme 4.

3. Experimental details

3.1. General

^1H NMR spectra were recorded either on a Varian EM 360 (60 MHz) or a Bruker AC 200 (200.13 MHz) spectrometer and are reported in δ units (ppm) with tetramethylsilane as internal standard and $CDCl_3$ as solvent. IR spectra were recorded (ν in cm^{-1}) in $CHCl_3$ (unless otherwise stated) on a Perkin-Elmer infrared spectrometer or on a Specord M80 (Carl Zeiss). UV spectra were measured on a UV–vis. Specord instrument and are reported in λ nm (units log ϵ). Mass spectra were taken on a Varian MAT CH6 or on a VG 12-



11 a-d 12 a-d

a : R^1=H, R^2=CH_3, R^3=H
b : R^1=H, R^2=C_6H_5, R^3=H
c : R^1=H, R^2-R^3=-$(CH_2)_3$-
d : R^1=CH_3O, R^2=H, R^3=CO_2CH_3

Scheme 5.

250 (Masslab) at 70 eV. Column chromatographies were carried out on silica gel (Merck, 230–400 mesh) using light petroleum ether (b.p. 45–65 °C) or light petroleum ether/diethyl ether (9:1).

The preparation of trifluoromethylketone (**1**) has already been described [2a].

*3.2. Preparation of bis(2-phenyl-3-sulfur-4,4,4-trifluoro-but-2-ene-1-al) metal chelates (**3a–c**)*

The metal acetate (0.001 mol) was dissolved in 10 ml of a mixture of methanol and water and added to a stirred solution consisting of 0.002 mol of crude thiol in ether (prepared from the chloro compound **2** and sodium sulfide according to the procedure described [3]). The reaction mixture was warmed for a short time and evaporated. The dry residue was dissolved in CH_2Cl_2 and filtered. The solvent was evaporated, the residue dried under vacuum and recrystallised from petroleum ether (b.p. 80–110 °C).

Nickel chelate **3a**: Violet crystals, yield, 30%; m.p. 223–225 °C. UV–vis. λ_{max}: 572 nm (ϵ=3.00). IR (KBr) (cm^{-1}): 1565 (CO). MS *m/z*: 520 ($M^{+\cdot}$). Analysis: Calc. for $C_{20}H_{12}F_6O_2S_2Ni$ (521.1): C, 46.10; H, 2.32; S, 12.31%. Found: C, 46.32; H, 3.30; S, 12.65%.

Cobalt chelate **3b**: Yield, 35%; m.p. 201–203 °C. IR (KBr) (cm^{-1}): 1595 (CO). MS *m/z*: 521 ($M^{+\cdot}$); 231 ($C_{10}H_6F_3OS^+$).

Copper chelate **3c**: Yield, 35%; m.p. 98–100 °C. IR (KBr) (cm^{-1}): 1605 (CO). MS *m/z*: 231 ($C_{10}H_6F_3OS^+$).

*3.3. Preparation of 2-phenyl-3-(dicyclohexylammonium-thiolyl)-4,4,4-trifluoro-but-2-ene-1-al (**4**)*

To a stirred, refluxing solution of 0.03 mol of sodium sulfide nonahydrate in 50 ml of methanol was added a solution at 0.02 mol of 3-chloro-4,4,4-trifluoro-2-phenyl-butenal (**2**) in 10 ml of ether. The mixture became dark red and refluxing was continued for 1 h. After removing the solvents in vacuum, the solid residue was dissolved in 200 ml of water. The resulting solution was filtered, treated with a 50 ml portion of ether and stirred, followed by careful addition of acetic acid until a pH value $\leqslant$7 was attained. Stirring was then continued for about 5 min when the mixture was allowed to become two-phase which was separated. The aqueous phase was extracted with a 50 ml portion of ether. To the combined stirred ether solution was now added dropwise 0.02 mol of dicyclohexylamine in a liquid condition [pure, or preferably freshly distilled, amine in a molten condition (m.p. 18 °C)]. The product precipitated a short time after addition of the amine and was separated by filtration and washed with a small portion of dry ether. Yellow crystals were obtained on recrystallisation from an ethanol/water mixture. Yield, 55%; m.p. 154–157 °C. UV–vis. (EtOH) λ_{max}: 377 nm (ϵ=4.14). IR (cm^{-1}): 1580 (CO); 3420 (NH). ^{1}H NMR δ: 1.09 (m, 20H); 1.73 (m, 2H); 7.19 (m, 5H); 9.90 (q, 1H, J_{HF}=3.5 Hz, (*E*)-C*H*O); 10.5 (s, 1H, (*Z*)-C*H*O) ppm. Analysis: Calc. for $C_{22}H_{30}F_3NOS$: C, 63.90; H, 5.31; N, 3.39%. Found: C, 63.90; H, 5.28, N, 3.55%.

*3.4. Preparation of 1-N,N-dicyclohexyl-2-phenyl-4,4,4-trifluoro-1,3-enaminothione (**5**)*

This was obtained from the mother liquor after isolation of **4**, evaporating a part of the solvent, separating by column chromatography (using neutral Al_2O_3 and toluene), complete evaporation of the solvents and recrystallisation of the red–orange residue from petroleum ether (b.p. 50–80 °C). Yield, 10%; m.p. 165–168 °C. UV–vis. λ_{max}: 414 nm (ϵ=4.12). ^{1}H NMR δ: 1.64 (m, 20H); 2.86 (m, 2H); 7.76 (s, 1H); 7.26 (m, 5H) ppm. Analysis: Calc. for $C_{22}H_{28}F_3NS$: C, 66.81; H, 7.14; N, 3.54; S, 8.10%. Found: C, 66.81; H, 7.08; N, 3.66; S, 8.22%.

*3.5. Preparation of enaminothiones **6***

A solution consisting of 0.006 mol of the amine in 10 ml of ethanol was added to the ether solution of the crude thiol (about 0.006 mol) prepared from the chloro compound **2**. The mixture was warmed for 15 min and then allowed to cool to room temperature. The residue was collected by filtration and crystallised.

1-*N*-(*p*-CH_3-O-C_6H_4)-2-phenyl-4,4,4-trifluoro-1,3-enaminothione (**6a**): Using *p*-anisidine according to the general procedure, red crystals were isolated from ethanol. Yield, 29%; m.p. 122.123 °C. UV–vis. λ_{max}: 452 nm (ϵ=4.24). IR (cm^{-1}): 1115 (C=S); 3350 (NH). ^{1}H NMR δ: 3.69 (s, 3H, aliphat.); 7.56 (d, 1H); 16.12 (d, 1H, NH) ppm. MS *m/z*: 337 ($M^{+\cdot}$). Analysis: Calc. for $C_{17}H_{14}F_3NOS$: C, 60.53; H, 4.19; N, 4.15; S, 9.50%. Found: C, 60.43; H, 4.29; N, 4.34; S, 9.86%.

1-*N*-t-butyl-2-phenyl-4,4,4-trifluoro-1,3-enaminothione (**6b**): Using t-butylamine according to the general procedure, orange–red crystals were isolated from ethanol. Yield, 35%; m.p. 118–120 °C. UV–vis. λ_{max}:

411 nm ($\epsilon = 4.29$). IR (cm^{-1}): 1105 (C=S); 3365 (NH). ^1H NMR δ: 1.40 (s, 9H); 7.44 (d, 1H); 14.99 (d, 1H, NH) ppm. MS *m/z*: 287 ($M^{+\cdot}$). Analysis: Calc. for $C_{14}H_{16}F_3NS$: C, 58.82; H, 5.61; N, 4.88; S, 11.16%. Found: C, 58.46; H, 5.63; N, 5.12; S, 11.69%.

3.6. Preparation of 2-acyl-4-phenyl-5-trifluoromethyl-thiophenes 8

To a solution consisting of 0.003 mol of the phenacyl bromide in 20 ml of ethanol, a solution of 0.0025 mol of thiolate **4** in 10 ml of ethanol was added. The mixture was stirred, first at room temperature and subsequently warmed to 50 °C for about 10 min. After cooling, the precipitate (dicyclohexylamine hydrobromide) was separated by filtration. Evaporation of the solvent gave a solid residue which was recrystallised or purified by column chromatography.

Compound **8a** (R=H): According to the general procedure, colourless crystals after chromatography (Al_2O_3/toluene) and following recrystallisation from an ethanol/water mixture. Yield, 62%; m.p. 79–82 °C. IR (KBr) (cm^{-1}): 1640 (CO). ^1H NMR δ: 7.09 (s, 1H) ppm. MS *m/z*: 332 ($M^{+\cdot}$); 312 ($M^+ - HF$); 263 ($M^+ - CF_3$); 255 ($M^+ - C_6H_5$). Analysis: Calc. for $C_{18}H_{11}F_3OS$: C, 65.05; H, 3.34; S, 9.65%. Found: C, 65.20; H, 3.25; S, 9.43%.

Compound **8b** (R=4-Br): Colourless solid after recrystallisation ethanol. Yield, 60%; m.p. 80–81 °C. IR (KBr) (cm^{-1}): 1650 (CO). ^1H NMR δ: 7.05 (s, 1H) ppm. MS *m/z*: 410 ($M^{+\cdot}$); 412 (isotope peak); 391 ($M^+ - F$); 341 ($M^+ - CF_3$); 255 ($M^+ - C_6H_4Br$). Analysis: Calc. for $C_{18}H_{10}BrF_3OS$: C, 52.57; H, 2.45; S, 7.80; Br, 19.43%. Found: C, 52.70; H, 2.38; S, 8.4; Br, 19.78%.

Compound **8c** ($R = 3\text{-}NH_2$): In contrast to the general procedure, the product and the amine hydrobromide precipitated together. For this reason, the residue was separated by filtration and treated with ether. Filtration and evaporation of the etheral solution gave, after recrystallisation from ethanol, a colourless solid compound. Yield, 50%; m.p. 140–142 °C. IR (KBr) (cm^{-1}): 1650 (CO). ^1H NMR δ: 7.03 (s, 1H) ppm. MS *m/z*: 377 ($M^{+\cdot}$); 255 ($M^+ - C_6H_4NO_2$). Analysis: Calc. for $C_{18}H_{10}F_3NO_3S$: C, 57.30; H, 2.67; N, 3.71; S, 8.49%. Found: C, 57.15; H, 2.85; N, 4.01; S, 8.41%.

Compound **8d** ($R = 2\text{-}NO_2$): Colourless crystals from methanol. Yield, 30%; m.p. 89–91 °C. IR (KBr) (cm^{-1}): 1645 (CO). ^1H NMR δ: 6.99 (s, 1H) ppm. MS *m/z*: 377 ($M^{+\cdot}$); 255 ($M^+ - C_6H_4NO_2$). Analysis: Calc. for $C_{18}H_{10}F_3NO_3S$: C, 57.30; H, 2.67; N, 3.71; S, 8.49%. Found: C, 57.30; H, 3.00; N, 3.77; S, 8.36%.

Compound **8e** (R=4-F): Colourless solid after recrystallisation from methanol. Yield, 20%; m.p. 83–85 °C. IR (KBr) (cm^{-1}): 1645 (CO). ^1H NMR δ; 7.08 (s, 1H) ppm. MS *m/z*: 350 ($M^{+\cdot}$); 281 ($M^+ - CF_3$); 255 ($M^+ - C_6H_4F$). Analysis: Calc. for $C_{18}H_{10}F_4OS$: C, 61.40; H, 2.86; S, 9.10%. Found: C, 61.66; H, 3.10; S, 9.27%.

3.7. Preparation of 2H-3-acyl-5-phenyl-6-trifluoromethyl-thiopyrans 10

To a stirred solution consisting of 0.01 mol of the dicyclohexylammonium salt **4** in 25 ml of methanol, was added dropwise at room temperature 0.01 mol of an unsaturated carbonyl compound, e.g. acrolein. The mixture became muddy in colour and was subsequently stirred for 2 h with heating in a water bath maintained at 50 °C. After evaporation of the solvent, the liquid residue was purified by column chromatography using silica gel and toluene or other suitable solvents.

Compound **10a** ($R^1 = R^2 = H$): According to the general procedure, using acrolein as reagent and a solvent mixture of toluene/acetic acid (3:1) for chromatography, followed by final purification by recrystallisation from methanol, a yellow solid compound was obtained. Yield, 80%; m.p. 72–74 °C. UV–vis. λ_{max}: 382 nm ($\epsilon = 3.56$). IR (KBr) (cm^{-1}): 1675 (CO). ^1H NMR δ: 3.63 (s, 2H); 6.98 (s, 1H); 9.64 (s, 1H, CHO) ppm. MS *m/z*: 270 ($M^{+\cdot}$); 241 ($M^+ - CHO$); 172 ($M^+ - CHO - CF_3$). Analysis: Calc. for $C_{13}H_9F_3OS$: C, 57.77; H, 3.36; S, 11.87%. Found: C, 57.77; H, 3.43; S, 11.67%.

Compound **10b** ($R^1 = CH_3$, $R^2 = H$): According to the general procedure, using crotonaldehyde as reagent, toluene as solvent for chromatography and recrystallisation from ethanol, a yellow solid product was obtained. Yield, 68%; m.p. 62.5–65 °C. UV–vis. λ_{max}: 379 nm ($\epsilon = 3.88$). IR (KBr) (cm^{-1}): 1675 (CO). ^1H NMR δ: 1.3 (d, 3H); 4.14 (q, 1H); 6.92 (s, 1H); 9.63 (s, 1H, CHO) ppm. MS *m/z*: 284 ($M^{+\cdot}$); 269 ($M^+ - CH_3$); 255 ($M^+ - CHO$); 172 ($M^+ - CH_3 - CHO - CF_3$). Analysis: Calc. for $C_{14}H_{11}F_3OS$: C, 59.15; H, 3.90; S, 11.28%. Found: C, 59.38; H, 3.75; S, 11.21%.

Compound **10c** ($R^1 = Ph$, $R^2 = H$): According to the general procedure, using cinnamaldehyde as reagent, a yellow oil was obtained. Yield, 56%. UV–vis. λ_{max}: 383 nm (qual.). IR (cm^{-1}): 1685 (CO). ^1H NMR δ: 5.28 (s, 1H); 7.13 (s, 1H); 9.72 (s, 1H, CHO) ppm. MS *m/z*: 346 ($M^{+\cdot}$). Analysis: Calc. for $C_{19}H_{13}F_3OS$: C, 65.88; H, 3.79; S, 9.26%. Found: C, 65.81; H, 3.78; S, 9.24%.

Compound **10d** ($R^1 = H$, $R^2 = CH_3$): According to the general procedure, using methylvinylketone as reagent and a solvent mixture of benzene/methanol (5:1) for chromatography, a yellow solid product was obtained. Yield, 32%; m.p. 55–58 °C. UV–vis λ_{max}: 374 nm ($\epsilon = 3.60$). IR (KBr) (cm^{-1}): 1665 (CO). ^1H NMR δ: 2.39 (s, 3H); 3.64 (s, 2H); 7.06 (s, 1H) ppm. MS *m/z*: 284 ($M^{+\cdot}$); 241 ($M^+ - COCH_3$); 172 ($M^+ - COCH_3 - CF_3$). Analysis: Calc. for $C_{14}H_{11}FOS$: C, 59.15; H, 3.90; S, 11.28%. Found: C, 59.22; H, 3.79; S, 11.21%.

Compound **10e** ($R^1-R^2=-(CH_2)_3-$): According to the general procedure, using cyclohex-2-enone as reagent, aluminium oxide and a solvent mixture of benzene/methanol (8:1) for chromatography, followed by final recrystallization from n-pentane, a yellow solid product was obtained. Yield, 40%; m.p. 107–110 °C. UV–vis. λ_{max}: 391 nm ($\epsilon=3.51$). IR (KBr) (cm^{-1}): 1680 (CO). ^1H NMR δ: 1.85 (m, 6H); 2.55 (t, 1H); 7.25 (s, 1H) ppm. MS *m/z*: 310 ($M^{+\cdot}$); 282 (M^+-CO); 254 ($M^+-CO-C_2H_4$). Analysis: Calc. for $C_{16}H_{13}F_3OS$: C, 61.92; H, 4.22; S, 10.33%. Found: C, 62.02; H, 4.38; S, 10.16%.

3.8. Preparation of 2H-2-methylene-5-phenyl-6-trifluoromethylthiopyrans 12

To a stirred solution consisting of 0.01 mol of the dicyclohexylammonium salt **4** in 30 ml of methanol was added dropwise at room temperature first 0.01 mol of a chlorovinylcarbonyl compound **11** and then 1 ml of triethylamine. The mixture was heated to 60 °C for 2 h and then allowed to cool to room temperature. The precipitated triethylammonium chloride was separated by filtration, the solvent evaporated and the crude product purified by column chromatography and recrystallisation.

Compound **12a** ($R^1=H$, $R^2=CH_3$, $R^3=H$): According to the general procedure, using 3-chloro-2-methylcrotonic aldehyde (**11a**), a red oil was obtained which was insufficiently pure for elementary analysis. UV–vis. (EtOH) λ_{max}: 420 nm (qual.). Characterisation was effected by preparation of the 2,4-dinitrophenylhydrazone.

2,4-Dinitrophenylhydrazone from **12a**: M.p. 214–216 °C from methanol. UV–vis. λ_{max}: 424 nm ($\epsilon=4.37$). ^1H NMR δ: 2.05 (s, 3H); 6.18 (d, 1H, $^3J=9$ Hz); 6.92 (d, 1H, $^3J=9$ Hz); 7.64 (s, 1H); 11.31 (s, 1H, NH) ppm. Analysis: Calc. for $C_{21}H_{15}F_3N_{44}S$: C, 52.94; H, 3.17; N, 11.76%. Found: C, 52.81; H, 3.27; N, 12.50%. MS *m/z*: 476 ($M^{+\cdot}$).

Compound **12b** ($R^1=H$, $R^2=C_6H_5$, $R^3=H$): Using 3-chloro-2-phenylcrotonic aldehyde (**11b**), the crude product was purified by column chromatography using silica gel and benzene, and recrystallised from petroleum ether (b.p. 50–80 °C) to obtain red crystals. Yield, 53%; m.p. 136–138 °C. UV–vis. λ_{max}: 446 nm ($\epsilon=3.82$). IR (KBr) (cm^{-1}): 1640 (CO). ^1H NMR δ; 6.67 (d, 1H, $^3J=10$ Hz); 7.02 (d, 1H, $^3J=10$ Hz); 9.67 (s, 1H, CHO) ppm. MS *m/z*: 358 ($M^{+\cdot}$); 329 ($M^{+\cdot}-CHO$); 289 (M^+-CF_3); 260 ($M^+-CHO-CF_3$). Analysis: Calc. for $C_{20}H_{13}F_3OS$: C, 67.03; H, 3.66; S, 8.95%. Found: C, 66.68; H, 4.04; S, 9.08%.

Compound **12c** ($R^1=H$, $R^2-R^3=-(CH_2)_3-$): Starting with 3-chloro-2-(4-methoxyphenyl)crotonic aldehyde (**11c**), red crystals were obtained according to the general procedure employing purification by chromatography using silica gel and benzene, followed by recrystallisation from methanol. Yield, 47%; m.p. 105–108 °C. UV–vis. λ_{max}: 448 nm ($\epsilon=3.30$). IR (KBr) (cm^{-1}): 1645 (CO); 2840 (OCH_3) ppm. ^1H NMR δ: 3.84 (3H, OCH_3); 6.63 (d, 1H, $^3J=9$ Hz); 7.17 (d, 1H, $^3J=9$ Hz); 9.66 (s, 1H, CHO) ppm. MS *m/z*: 388 ($M^{+\cdot}$); 373 (M^+-CH_3); 359 (M^+-CHO); 319 (M^+-CF_3); 290 ($M^+-CHO-CF_3$). Analysis: Calc. for $C_{21}H_{15}F_3O_2S$: C, 64.94; H, 3.89; S, 8.26%. Found: C, 65.05; H, 3.97; S, 8.68%.

Compound **12d** ($R^1=CH_3O$, $R^2=H$, $R^3=CO_2CH_3$): Starting with dimethyl 2-chloro-propene-1,3-dicarboxylate (**11d**), the mixture was heated for 3 h and the product purified by chromatography and recrystallisation from petroleum ether (b.p. 50–80 °C) and methanol to obtain red needles. Yield, 21%; m.p. 103–105 °C. UV–vis. λ_{max}: 435 nm ($\epsilon=3.32$). ^1H NMR δ: 3.72 (s, 3H, OCH_3); 3.78 (s, 3H, OCH_3); 6.47 (s, 1H); 7.18 (m); 7.38 (s, 1H) ppm. MS *m/z*: 370 ($M^{+\cdot}$). Analysis: Calc. for $C_{17}H_{13}F_3O_4S$: C, 55.13; H, 3.54; S, 8.66%. Found: C, 55.80; H, 4.06; S, 8.30%.

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