Journal of Fluorine Chemistry 132 (2011) 1241–1246

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

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

# Convenient synthesis and isolation of trifluoromethylthio-substituted building blocks

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ARTICLE INFO

*Article history:*
Received 11 April 2011
Received in revised form 7 July 2011
Accepted 11 July 2011
Available online 20 July 2011

*Keywords:*
Trifluoromethylation
$CF_3I$ solution
Trifluoromethyl sulfides
Steam-distillation

Dedicated to Alain Tressaud, in honour of his ACS award, and for his great contribution to the development of fluorine chemistry.

ABSTRACT

Various aryl-, heteroaryl-, and alkyl mercaptanes (RSH, **1a**–**r**) were treated with a slight excess of NaH suspended in DMF to make the appropriate sodium thiolates (RSNa), which then reacted with 1.3 equivalent of $CF_3I$ at room temperature for overnight to afford the appropriate trifluoromethyl sulfides ($CF_3SR$, **2**) in fair to good yields. The radical chain alkylation reaction was effective without the use of UV irradiation with all but three substrates (thiosalicylic acid, **1k**; 2-mercaptobenzimidazole, **1q**; and 3-mercaptopropionic acid, **1r**).

Steam-distillation was found as an effective and easy to upscale means for the isolation of these volatile and water immiscible sulfides. The $CF_3I$ reagent gas was conveniently weighed and delivered to the reaction mixture by the balloon technique or as a preliminary made stock solution in DMF or DMSO. The sulfides **2** obtained here were assayed by GC and characterized by $^1H$, $^{13}C$, $^{19}F$ NMR and MS spectroscopy.



## 1. Introduction

The trifluoromethyl-group has been recognized as the most effective substituent for assembling fluorophilic molecules [1]. When the trifluoromethyl-group is attached to oxygen or sulphur atoms instead of carbon atoms, new functional groups such as $CF_3O$ and $CF_3S$ are born, which display rather different properties, compared to the parent $CH_3O$ and $CH_3S$ groups [2]. In the last decades fluorinated substituents have been involved in the manufacturing processes of blockbuster drugs and highly effective agrochemicals [3,4].

Much of these research activities are due to an easy access to $CF_3I$, the simplest perfluoroalkyl iodide, which is also considered as the agent of choice for refrigeration in the 21st century, since it is not controlled by the Montreal Protocol [5]. This policy facilitates the invention of novel processes where $CF_3I$ is the precursor for the synthesis of many fine chemicals and/or bulk intermediates [6]. Recent patents disclose that the reaction of $CF_3H$ and $I_2$ at elevated temperatures affords $CF_3I$ in good yields and at lower production costs [7].

The chemistry of 'fluorocarbon halides' (=perfluoroalkyl halides, including $CF_3I$) started about 60 years ago with the pioneering works of Simons [8] and Haszeldine [9]. Some 30 years later a large number of trifluoromethyl-sulfides have become accessible by the direct S-trifluoromethylations of the appropriate RSH substrates in liquid ammonia and UV initiation as described by Boiko and Yagupolskii [10].

They also demonstrated that this reaction involves a radical-ion mechanism and it has a wide scope. Thus, the trifluoromethylation of alkyl-, aryl-, and heteroaryl-mercaptanes, and the analogous selenophenols and diaryldiltellurides, or arenesulfinates afforded the appropriate sulfides ($RSCF_3$), selenides ($ArSeCF_3$) and tellurides ($ArTeCF_3$), or sulfones ($ArSO_2CF_3$) in good yields, respectively [10].

Feiring reported that perfluoroalkyl sulfides are easily formed from primary or secondary perfluoroalkyl iodides (*i*-$C_3F_7I$, *n*-$C_4F_9I$, *n*-$C_6F_{13}I$, and *n*-$C_8F_{17}I$) and alkyl- or aryl-mercaptanes without UV irradiation. Perfluoroalkyl radicals are the intermediates here as he demonstrated by trapping and inhibition studies [11].

Dolbier and co-workers reported an effective procedure for the preparation of trifluoromethyl thio- and selenoethers starting from aryl and alkyl disulfides and diselenides with the use of a $CF_3I$/TDAE couple [12].

Shorter perfluoroalkyl groups ($R_{fn}$, $C_nF_{2n+1}$, $n = 1, 4, 6$) become the key building blocks for the practice of sustainable fluorous

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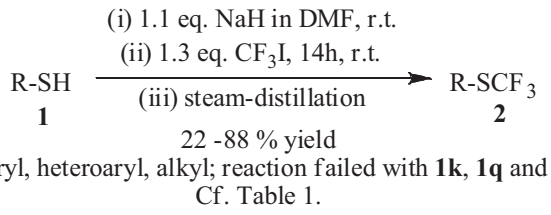
doi:10.1016/j.jfluchem.2011.07.008




**Scheme 1.** Preparation of trifluoromethyl sulfides.

chemistry as it was shown by Horváth [13], Gladysz [14], Curran [15] and others [16].

Since the $CF_3$-group receives very wide attention both in fluorous and fluorine chemistry, we aimed at using $CF_3I$ as the reagent of choice for the preparation of trifluoromethylthio-substituted building blocks.

Here we report an improved procedure for the synthesis and isolation of several $RSCF_3$ type sulfides.

## 2. Results and discussion

The reaction of sodium thiolates in DMF with $CF_3I$ gives aryl- or alkyl-trifluoromethyl sulfides in good to excellent yields without any initiators as the longer perfluoroalkyl iodides gave the appropriate sulfides [11]. The use of pressure safe equipment is excluded as $CF_3I$ atmosphere is provided by the use of a simple balloon. We tested the reactivity of $CF_3I$ with several thiolates (Scheme 1) and measured the exact amount of the introduced $CF_3I$ gas. In contrast to the results obtained by the use of $CF_3Br$ by Wakselman and Tordeaux [17], we found here that the reaction of $CF_3I$ works well not only with electron rich thiophenols, but it tolerates a variety of substituents without any significant change in the isolated yields (Scheme 1 and Table 1).

**Table 1**
Yields of trifluoromethyl sulfides with references to their characterization data (bp, mp or NMR).

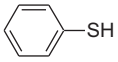
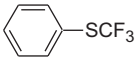
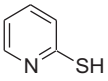
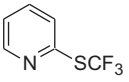
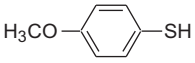
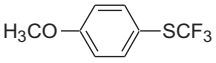
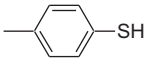
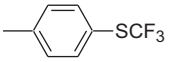
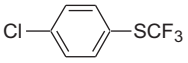
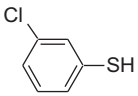
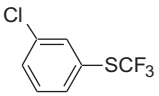
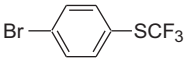
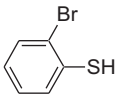
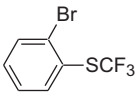
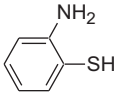
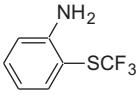
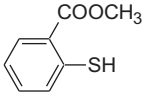
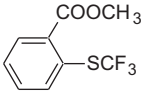
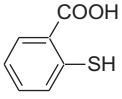
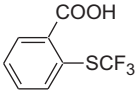
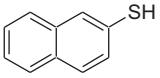
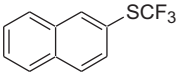
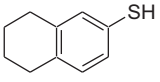
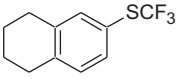
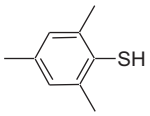
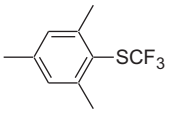
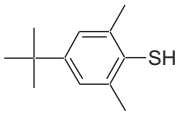
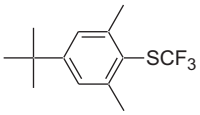
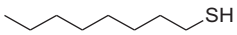
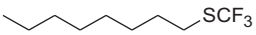
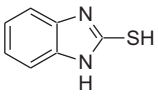
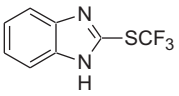
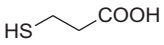
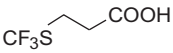
| Starting thiol (R-SH) | | Product ($R-SCF_3$) | | Isolated yield % | Lit. bp °C (mmHg) | Ref. |
|---|---|---|---|---|---|---|
| **1a** |  | **2a** |  | 77 | 140–142 | [21] |
| **1b** |  | **2b** |  | 61 | 130/760 | [22] |
| **1c** |  | **2c** |  | 88 | 90/19 | [17] |
| **1d** |  | **2d** |  | 81 | 163–167 | [23] |
| **1e** |  | **2e** |  | 88 | 173–174 | [17] |
| **1f** |  | **2f** |  | 75 | 58–62/12 | [17] |
| **1g** |  | **2g** |  | 78 | 190–191 | [21] |
| **1h** |  | **2h** |  | 62 | (oil) | [24] |
| **1i** |  | **2i** |  | 75 | 90–91/15 (mp 30–31) | [25] |
| **1j** |  | **2j** |  | 44 | 84/3 | [26] |
| **1k** |  | **2k** |  | 0 | mp 124–125/$C_6H_6$[b] | [27] |
| **1l** |  | **2l** |  | 47 | $^1H/^{19}F$ NMR (oil) | [28] |
| **1m** |  | **2m** |  | 25 | n. c.[a] (oil) | n. c. |

**Table 1** (*Continued*)

| Starting thiol (R-SH) | Product (R-$SCF_3$) | Isolated yield % | Lit. bp °C (mmHg) | Ref. |
|---|---|---|---|---|
| **1n**  | **2n**  | 62 | 89–90/10 | [29] |
| **1o**  | **2o**  | 82 | n. c.[a], mp 34–36 °C | n. c. |
| **1p**  | **2p**  | 22 | $^1H/^{19}F$ NMR (oil) | [30] |
| **1q**  | **2q**  | 0 | $^1H/^{19}F$ NMR[b] | [31] |
| **1r**  | **2r**  | 0 | $^1H/^{19}F$ NMR[b] | [32] |

[a] n. c. = new compound.
[b] UV irradiation is needed for their preparation, cf. Refs. [27,31,32].

Previously it was also reported [17] that during the synthesis of **2e** a major side reaction was observed: the $S_NAr$ substitution of the chlorine by another thiolate species. Under our experimental conditions none of the halogen substituted thiophenols showed this side reaction, in all cases only the corresponding trifluoromethyl sulfides (**2e**–**h**, Table 1) were isolated.

The aim of our work was to improve and combine the efficiency and applicability of the classic $S_{NR}1$ type methods for S-trifluoromethylation. Our method is simplified compared to the previously reported ones as neither UV irradiation [10] nor pressure safe equipment [17] is needed. It is somewhat similar to the second part of the "Tandem $CF_3I$ process", which has been introduced by Dolbier and coworkers (cf. [12a]).

The nature of electron transfer processes in perfluoroalkyl halides reactions has been reviewed by Wakselman [18], while Savéant and coworkers reported several examples of how to identify the classical, dissociative or associative steps of the electron transfer by using electrochemical methods [19]. Proofs of the existence of an intermediate radical are based on inhibition and capture experiments [18].

Thus, to present clear proof of the $S_{NR}1$ mechanism, we carried out inhibition experiments on the reaction of $NaSC_6H_5$ and $CF_3I$ with nitrobenzene (0.1 and 2 equivalents) and 4-methylstyrene (3 equivalents). While the earlier showed no inhibition at all, the styrene derivative completely stopped the alkylation reaction.

As diaryl disulfides ($Ar_2S_2$) are possible side products of this reaction, we thought that steam-distillation would be a simple and efficient means of purification and isolation most of the target compounds (**2a**–**j**, **l**–**p**). Here we replaced the standard chromatographic work up procedure with steam-distillation, which allowed us to isolate these products in high purity with fair to excellent yields.

However, the lower yields of 2-naphthyl trifluoromethyl sulfide (**2l**), 5,6,7,8-tetrahydronaphthalene-2-yl trifluoromethyl sulfide (**2m**), and 1-octyl trifluoromethyl sulfide (**2p**) may be due to the lower solubility of their precursor sodium thiolate salts in DMF. Although in these cases two times larger volumes of DMF were needed (2 ml/1 mmol of substrate), the yields still remained lower than with the benzenethiol derivatives.

When an attempt was made to synthesize 2-trifluoromethylthio-benzoic acid (**2k**) the only isolated product was the corresponding disulfide, while with methyl thiosalicylate (**1j**), the appropriate sulfide (**2j**) was isolated in fair yield (44%). It should be noted, that **1k** was converted to **2k** in 90% yield applying an alkaline aqueous dioxane solvent system with UV irradiation [20]. In the case of other acidic group containing thiols such as 2-mercapto-benzimidazole (**1q**) and 3-mercaptopropionic acid (**1r**), the inhibition of the radical chain reaction was observed. However, with the basic thiols 2-mercapto-pyridine (**1b**) and 2-aminothiophenol (**1i**) no complications were experienced (Scheme 1 and Table 1).

The use of a stock solution of $CF_3I$ in DMSO in an industrial scale synthesis of 5-trifluoromethyluracil has been reported by Japanese authors [6a], while the first note on the use of stock solutions of $CF_3I$ and $CF_3Br$ dates back to the detailed electrochemical and mechanistic studies on perfluoroalkylation of nucleophiles by Savéant and coworkers [33]. The high solubility of $CF_3I$ in DMSO could be the manifestation of halogen-bonding between the positively polarized iodine atom of $CF_3I$ and the negatively polarized oxygen atom of DMSO as revealed by DFT calculations [34].

These precedents inspired us to test some reactions in DMSO with the addition of a $CF_3I$/DMSO solution (Table 2). In this case a smaller excess of $CF_3I$ (1.1 equiv. instead of 1.3 equiv.) was required, although larger amount of solvent was used, as the sodium-thiolate did not dissolve as well in DMSO as in DMF. The reaction mixture was worked up as previously, using steam-distillation. Although sulfide **2o** was obtained in as good yield as earlier, the purity of the steam-distilled material somewhat dropped (~95%, previously ~98%). The oxidizing potential of DMSO to convert thiolates into disulfides might also be a problem.

These results suggested, that the best solvent for S-trifluoromethylation reactions was DMF, thus the solubility of $CF_3I$ in DMF was determined. At room temperature DMF was found to dissolve approximately 30% by weight of $CF_3I$. The effect of the mode of $CF_3I$

**Table 2**
Effect of the applied conditions on the alkylation of thiol **1o**.

| Equivalents of $CF_3I$ | Mode of $CF_3I$ delivery | Purity of **2o** GC assay (%) | Yield of **2o** (%) |
|---|---|---|---|
| 1.35 | Balloon (Section 4.2) | 98 | 82 |
| 1.15 | 36% (w/w) $CF_3I$ in DMSO (Section 4.3) | 95 | 86 |
| 1.15 | 29% (w/w) $CF_3I$ in DMF (Section 4.3) | 98 | 84 |

delivery – namely the introduction of $CF_3I$ via a balloon, or the use of stock solutions of $CF_3I$ in DMSO or DMF, respectively – on the yields of trifluoromethylation of the bulky and sterically hindered 2,6-dimethyl-4-*tert*-butylbenzenethiolate (**1o**, Table 1) is shown in Table 2.

## 3. Conclusions

Trifluoromethyl sulfides can be prepared effectively in DMF with the reaction of $CF_3I$ and mercaptanes without UV irradiation. The $CF_3I$ can be introduced to the reaction mixture as a gas or as a stock solution in DMF or DMSO. Steam-distillation was used for product isolation instead of the usual chromatographic workup.

When this method failed due to an inhibition of the reaction, the activation of the same reactants by UV irradiation in liquid $NH_3$ or other solvents could afford the target sulfides in good yields (cf. [27,31,32]).

## 4. Experimental

### 4.1. General description of materials and methods

$CF_3I$ was prepared by reacting sodium-trifluoroacetate with iodine, according to literature process [35]. DMF was distilled from $CaH_2$ prior to use. Most of the arenethiols were purchased from Alfa-Aesar, but **13a** and **15a** were prepared with $Zn/H^+$ reduction of the precursor arenesulfonyl-chlorides as described [36,37]. $^1H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on a Bruker-Avance 400 MHz spectrometer in $CDCl_3$ at room temperature (303 K). Chemical shifts ($\delta$) are given in parts per million (ppm) units relatively to the internal standard TMS ($\delta$ = 0.00 for $^1H$, $\delta$ = 0.00 for $^{13}C$) and to $CFCl_3$ as external standard ($\delta$ = 0.00 for $^{19}F$). Gas-chromatographic analysis was run on a HP5890 Series II chromatograph (50 m × 0.2 mm × 0.5 μm PONA column, FID; Program: 120, 5, 10, 250, 5; Inj.: 250 °C, Det.: 280 °C). GC–MS measurements were run on a PerkinElmer Clarus 500 GC chromatograph (J&W DB-5MS column: 30 m × 0.25 mm × 0.25 μm, He carrier gas) coupled with a Clarus 560D mass spectrometer (ionization: EI+, 70 eV, 250 °C, interface: 250 °C). High-resolution mass spectra were obtained on a Waters-Micromass GCT spectrometer with direct injection (ionization: EI+, 70 eV; TOF resolution: >7000 FWHM at 614 *m*/*z*).

### 4.2. Synthesis of trifluoromethyl sulfides: typical procedure

Sodium-hydride (1.20 g, 28.5 mmol, 57% dispersion in oil) is washed free from the oil with pentane (3 × 10 ml) and is suspended in 25 ml of DMF. The thiol (25 mmol) is added in small portions under nitrogen atmosphere and the mixture is stirred at 20 °C for 15 min. A pre-weighed rubber balloon is charged with $CF_3I$ (6.5–7.0 g, 33–35 mmol, 1.3–1.4 equivalent) at ambient temperature and is fixed to the neck of the flask. The mixture immediately turns yellow and is stirred overnight at room temperature. To the end of stirring a white precipitate is formed, the slurry is poured to 200 ml of water and the mixture is set for distillation. The product is isolated with steam distillation, the organic layer is separated from the aqueous one, this latter is extracted with ether (2 × 15 ml), the united organic phases are washed with water (3 × 10 ml), and with brine (10 ml) and dried ($Na_2SO_4$). Upon filtration, the evaporation of ether under reduced pressure (~16 mmHg) leaves the pure product. Analytically pure samples are obtained by vacuum-distillation.

For **1k**, **1q**, and **1r** double amount of NaH was used. Finally, the reaction mixtures were acidified with 6 N HCl and worked up. The formation of the corresponding disulfide was indicated by TLC and NMR analysis.

#### 4.2.1. Phenyl trifluoromethyl sulfide (2a)

Yield: 4.80 g (77%) colorless liquid from 3.86 g (35.0 mmol) of **1a**, bp 140–141 °C (760 mmHg). GC assay: 99%, $t_{RET}$: 4.70 min. $^1H$ NMR ($CDCl_3$): $\delta$ 7.39 (t, 2H, $J$ = 7.6 Hz), 7.45 (t, 1H, $J$ = 7.4 Hz), 7.64 (d, 2H, $J$ = 7.4 Hz). $^{13}C$ NMR ($CDCl_3$): $\delta$ 124.5 (q, $J_{C,F}$ = 2.2 Hz), 115.0, 125.0 (q, $J_{C,F}$ = 308.0 Hz), 138.2, 161.9. $^{19}F$ NMR ($CDCl_3$): $\delta$ −42.8. MS (EI+): *m*/*z* (%) = 178 (52) $[M]^+$, 159 (6) $[M-F]^+$, 109 (100) $[M-CF_3]^+$, 77 (9) $[C_6H_5]^+$, 69 (17) $[CF_3]^+$, 65 (26) $[C_5H_5]^+$, 51 (13) $[C_4H_3]^+$, 39 (19) $[C_3H_3]^+$.

#### 4.2.2. 2-Pyridyl trifluoromethyl sulfide (2b)

Yield: 4.92 g (61%) colorless liquid from 5.00 g (45.0 mmol) of **1b**, only steam-distilled. GC assay: 99%, $t_{RET}$: 5.66 min. $^1H$ NMR ($CDCl_3$): $\delta$ 7.31 (dd, 1H, $J$ = 4.8 and 7.5 Hz), 7.58 (d, 1H, $J$ = 7.8 Hz), 7.72 (t, 1H, $J$ = 7.8 Hz), 8.62 (d, 1H, $J$ = 4.8 Hz). $^{13}C$ NMR ($CDCl_3$): $\delta$ 123.7, 128.0 (q, $J_{C,F}$ = 2.2 Hz), 129.4 (q, $J_{C,F}$ = 308.0 Hz), 137.6, 149.5 (q, $J_{C,F}$ = 2.9 Hz), 150.6. $^{19}F$ NMR ($CDCl_3$): $\delta$ −40.2. MS (EI+): *m*/*z* (%) = 179 (50) $[M]^+$, 160 (4) $[M-F]^+$, 110 (7) $[M-CF_3]^+$, 83 (13) [110-HCN]$^+$, 78 (100), $[M-SCF_3]^+$, 69 (13) $[CF_3]^+$, 57 (8), 51 (40), 39 (28) [aromatic marker ions].

#### 4.2.3. 4-Methoxyphenyl trifluoromethyl sulfide (2c)

Yield: 6.60 g (88%) colorless liquid from 5.05 g (36.0 mmol) of **1c**, only steam-distilled. GC assay: 99%, $t_{RET}$: 8.43 min. $^1H$ NMR ($CDCl_3$): $\delta$ 3.82 (s, 3H), 6.92 (d, 2H, $J$ = 8.9 Hz), 7.56 (d, 2H, $J$ = 8.7 Hz). $^{13}C$ NMR ($CDCl_3$): $\delta$ 55.3, 114.8 (q, $J_{C,F}$ = 2.2 Hz), 115.0, 129.7 (q, $J_{C,F}$ = 308.0 Hz), 138.2, 161.9. $^{19}F$ NMR ($CDCl_3$): $\delta$ −44.0. MS (EI+): *m*/*z* (%) = 208 (70) $[M]^+$, 189 (5) [M−F], 139 (100) $[M-CF_3]^+$, 124 (21) $[M-CF_3-CH_3]^+$, 108 (7), [M−$CF_3$−$OCH_3$], 95 (35) [M−$CSCF_3$], 77 (8) $[C_6H_5]^+$, 69 (26) $[CF_3]^+$, 63 (12) $[C_5H_3]^+$, 50 (8) $[C_4H_2]^+$, 45 (10) $[HCS]^+$.

#### 4.2.4. 4-Methylphenyl trifluoromethyl sulfide (2d)

Yield: 3.89 g (81%) colorless liquid from 3.11 g (25.0 mmol) of **1d**, only steam distilled. GC assay: 99%, $t_{RET}$: 5.93 min. $^1H$ NMR ($CDCl_3$): $\delta$ 2.37 (s, 3H), 7.20 (d, 2H, $J$ = 8.2 Hz), 7.52 (d, 2H, $J$ = 8.1 Hz). $^{13}C$ NMR ($CDCl_3$): $\delta$ 21.3, 120.9 (q, $J_{C,F}$ = 22.1 Hz), 129.7 (q, $J_{C,F}$ = 308.0 Hz), 130.2, 136.3, 141.4. $^{19}F$ NMR ($CDCl_3$): $\delta$ −43.2. MS (EI+): *m*/*z* (%) = 192 (92) $[M]^+$, 173 (10) $[M-F]^+$, 123 (100) $[M-CF_3]^+$, 108 (10) $[M-CF_3-CH_3]^+$, 91 (43) $[C_7H_7]^+$, 77 (31) $[C_6H_5]^+$, 69 (23) $[CF_3]^+$, 65 (12) $[C_5H_5]^+$, 51 (12) $[C_4H_3]^+$, 45 (36) $[HCS]^+$, 39 (17) $[C_3H_3]^+$.

#### 4.2.5. 4-Chlorophenyl trifluoromethyl sulfide (2e)

Yield: 4.67 g (88%) colorless liquid from 3.62 g (25.0 mmol) of **1e**, only steam-distilled. GC assay: 99%, $t_{RET}$: 6.78 min. $^1H$ NMR ($CDCl_3$): $\delta$ 7.4 (d, 2H, $J$ = 8.7 Hz), 7.57 (d, 2H, $J$ = 8.7 Hz). $^{13}C$ NMR ($CDCl_3$): $\delta$ 122.8 (q, $J_{C,F}$ = 2.2 Hz), 129.8, 137.5, 137.7, 129.3 (q, $J_{C,F}$ = 310.0 Hz). $^{19}F$ NMR ($CDCl_3$): $\delta$ −42.8. MS (EI+): *m*/*z* (%) = 212 (86) $[M]^+$, 193 (47) $[M-F]^+$, 143 (80) $[M-CF_3]^+$, 108 (100) $[M-CF_3-Cl]^+$, 99 (40) $[C_5H_4Cl]^+$, 75 (38) $[C_6H_3]^+$, 69 (84) $[CF_3]^+$, 63 (51) $[C_5H_3]^+$, 50 (40) $[C_4H_2]^+$, 45 (17) $[HCS]^+$.

#### 4.2.6. 3-Chlorophenyl trifluoromethyl sulfide (2f)

Yield: 3.99 g (75%) colorless liquid from 3.62 g (25.0 mmol) of **1f**, only steam-distilled. GC assay: 98%, $t_{RET}$: 6.62 min. $^1H$ NMR ($CDCl_3$): $\delta$ 7.34 (t, 1H, $J$ = 8.0 Hz), 7.46 (d, 1H, $J$ = 8.1 Hz), 7.53 (d, 1H, $J$ = 7.8 Hz), 7.65 (s 1H). $^{13}C$ NMR ($CDCl_3$): $\delta$ 126.1 (q, $J_{C,F}$ = 2.2 Hz), 129.3 (q, $J_{C,F}$ = 308.0 Hz), 130.5, 131.1, 134.2, 135.1, 135.8. $^{19}F$ NMR ($CDCl_3$): $\delta$ −42.4. MS (EI+): *m*/*z* (%) = 212 (69) $[M]^+$, 193 (6) $[M-F]^+$, 143 (90) $[M-CF_3]^+$, 108 (100) $[M-CF_3-Cl]^+$, 99 (17) $[C_5H_4Cl]^+$, 75 (18) $[C_6H_3]^+$, 69 (36) $[CF_3]^+$, 63 (28) $[C_5H_3]^+$, 50 (16) $[C_4H_2]^+$, 45 (9) $[HCS]^+$.

#### 4.2.7. 4-Bromophenyl trifluoromethyl sulfide (2g)

Yield: 5.01 g (78%) colorless liquid from 4.73 g (25.0 mmol) of **1g**, only steam-distilled. Lit [20] bp 190–191 °C. GC assay: 99%,

$t_{RET}$: 8.30 min. $^1$H NMR ($CDCl_3$): $\delta$ 7.50 (d, 2H, $J$ = 8.5 Hz), 7.55 (d, 2H, $J$ = 8.6 Hz). $^{13}$C NMR ($CDCl_3$): 123.5 (q, $J_{C,F}$ = 21.8 Hz), 129.2 (q, $J_{C,F}$ = 308.1 Hz), 125.9, 132.8, 137.7. $^{19}$F NMR ($CDCl_3$): $\delta$ −42.7. MS (EI+): $m/z$ (%) = 256 (97) $[M]^+$, 187 (95) $[M-CF_3]^+$, 158 (25) $[M-F-Br]^+$, 108, (67) $[M-CF_3\text{-}Br]^+$, 75 (29) $[C_6H_3]^+$, 69 (100) $[CF_3]^+$, 63 (59) $[C_5H_3]^+$, 50 (56) $[C_4H_2]^+$, 45 (25) $[HCS]^+$.

*4.2.8. 2-Bromophenyl trifluoromethyl sulfide (**2h**)*

Yield: 3.82 g (62%) colorless liquid from 4.54 g (24.0 mmol) of **1h**, only steam-distilled. GC assay: 98%, $t_{RET}$: 8.76 min. $^1$H NMR ($CDCl_3$): $\delta$ 7.30 (t, 1H, $J$ = 5.9 Hz), 7.36 (t, 1H, $J$ = 6.0 Hz), 7.71 (d, 1H, $J$ = 7.8 Hz), 7.76 (d, 1H, $J$ = 7.6 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 126.4 (q, $J_{C,F}$ = 2.2 Hz), 129.3 (q, $J_{C,F}$ = 308.0 Hz), 128.3, 130.6, 132.1, 133.9, 138.0. $^{19}$F NMR ($CDCl_3$): $\delta$ −42.0. MS (EI+): $m/z$ (%) = 256 (70) $[M]^+$, 187 (56) $[M-CF_3]^+$, 158 (18) $[M-F-Br]^+$, 108 (100) $[M-CF_3-Br]^+$, 75 (12) $[C_6H_3]^+$, 69 (43) $[CF_3]^+$, 63 (16) $[C_5H_3]^+$, 50 (15) $[C_4H_2]^+$, 45 (6) $[HCS]^+$.

*4.2.9. 2-(Trifluoromethylthio)aniline (**2i**)*

Yield: 3.62 g (75%) colorless liquid from 3.13 g (25.0 mmol) of **1i**, bp 112–114 °C (20 mmHg). GC assay: 98%, $t_{RET}$: 8.52 min. $^1$H NMR ($CDCl_3$): $\delta$ 4.44 (s, 2H), 6.73 (m, 2H), 7.24 (td, 1H, $J$ = 8.1 and 1.5 Hz), 7.45 (d, 1H, $J$ = 7.6 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 106.1 (q, $J_{C,F}$ = 2.2 Hz), 115.6, 118.6, 129.5 (q, $J_{C,F}$ = 306.6 Hz), 133.0, 139.1, 150.3. $^{19}$F NMR ($CDCl_3$): $\delta$ −42.8. MS (EI+): $m/z$ (%) = 194 (18) $[M+H]^+$, 193 (100) $[M]^+$, 173 (10) $[M-HF]^+$, 154 (33) $[M-HFCN]^+$, 124 (98) $[M-CF_3]^+$, 97 (30) $[M-CF_3-HCN]^+$, 91 (12) $[C_7H_7]^+$, 80 (91) $[M-CSCF_3]^+$, 69 (32) $[CF_3]^+$, 65 (15) $[C_5H_5]^+$, 53 (31) $[C_3H_3N]^+$, 45 (18) $[HCS]^+$, 39 (25) $[C_3H_3]^+$.

*4.2.10. Methyl (2-trifluoromethythio)benzoate (**2j**)*

Yield: 2.60 g (44%) colorless liquid from 4.21 g (25.0 mmol) of **1j**, bp 119–121 °C (20 mmHg). GC assay: 99%, $t_{RET}$: 10.93 min. $^1$H NMR ($CDCl_3$): $\delta$ 3.93 (s, 1H), 7.42 (t, 1H, $J$ = 7.6 Hz), 7.52 (d, 1H, $J$ = 7.5 Hz), 7.73 (d, 1H, $J$ = 8.0 Hz), 7.91 (d, 1H, $J$ = 7.8 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 52.5, 128.2 (q, $J_{C,F}$ = 2.2 Hz), 128.7, 129.5 (q, $J_{C,F}$ = 308.0 Hz), 130.9, 132.4, 132.6, 132.7 (q, $J_{C,F}$ = 2.2 Hz), 166.6. $^{19}$F NMR ($CDCl_3$): $\delta$ −41.4. MS (EI+): $m/z$ (%) = 236 (22) $[M]^+$, 205 (39) $[M-OCH_3]^+$, 177 (6) $[M-COOCH_3]^+$, 167 (100) $[M-CF_3]^+$, 152 (22) $[M-CF_3-CH_3]^+$, 136 (22) $[M-CF_3-OCH_3]^+$, 69 (20) $[CF_3]^+$, 63 (9) $[C_5H_3]^+$, 50 (9) $[C_4H_2]^+$, 45 (5) $[HCS]^+$.

*4.2.11. 2-Naphthyl trifluoromethyl sulfide (**2l**)*

Yield: 2.68 g (47%) colorless liquid from 4.01 g (25.0 mmol) of **1l**, only steam-distilled. GC assay: 99%, $t_{RET}$: 13.39 min. $^1$H NMR ($CDCl_3$): $\delta$ 7.53 (m, 2H, $J$ = 5.0 Hz), 7.63 (d, 1H, $J$ = 8.5 Hz), 7.82 (d, 3H, $J$ = 8.8 Hz), 8.16 (s, 1H). $^{13}$C NMR ($CDCl_3$): $\delta$ 121.5 (q, $J_{C,F}$ = 2.2 Hz), 129.8 (q, $J_{C,F}$ = 308.1 Hz), 126.9, 127.7, 127.9, 128.2, 129.2, 131.7, 133.4, 133.9, 136.9. $^{19}$F NMR ($CDCl_3$): $\delta$ −42.4. MS (EI+): $m/z$ (%) = 228 (92) $[M]^+$, 189 (12) $[M-C_3H_3]^+$, 159 (89) $[M-CF_3]^+$, 127 (10) $[M-SCF_3]^+$, 115 (100) $[M-CSCF_3]^+$, 89 (18) $[C_7H_5]^+$, 69 (27) $[CF_3]^+$, 63 (18) $[C_5H_3]^+$, 50 (12) $[C_4H_2]^+$.

*4.2.12. 2-Trifluoromethylthio-5,6,7,8-tetrahydronaphthalene (**2m**, n. c.)*

Yield: 1.45 g (25%) colorless liquid from 4.11 g (25.0 mmol) of **1m**, only steam-distilled. GC assay: 96%, $t_{RET}$: 13.20 min. $^1$H NMR ($CDCl_3$): $\delta$ 1.79 (quintett, 4H, $J$ = 3.0 Hz), 2.77 (s, 4H), 7.08 (d, 1H, $J$ = 8.5 Hz), 7.34 (s, 2H). $^{13}$C NMR ($CDCl_3$): $\delta$ 22.7, 22.8, 29.1, 29.2, 120.5 (q, $J_{C,F}$ = 2.2 Hz), 129.7 (q, $J_{C,F}$ = 308.0 Hz), 130.2, 133.2, 137.0, 138.7, 140.5. $^{19}$F NMR ($CDCl_3$): $\delta$ −43.1. MS (EI+): $m/z$ (%) = 232 (75) $[M]^+$, 213 (5) $[M-F]^+$, 204 (22) $[M-C_2H_4]^+$, 191 (9) $[M-C_3H_5]^+$, 163 (8) $[M-CF_3]^+$, 135 (19) $[M-C_2H_4CF_3]^+$, 131 (100), $[M-SCF_3]^+$, 130 (31) $[M-HSCF_3]^+$, 115 (24) $[C_9H_7]^+$, 91 (38) $[C_7H_7]^+$, 77 (8) $[C_6H_5]^+$, 69 (9) $[CF_3]^+$, 65 (7) $[C_5H_5]^+$, 51 (7) $[C_4H_3]^+$, 39 (6) $[C_3H_3]^+$. HRMS (TOF, EI+): calculated for $C_{11}H_{11}F_3S$: 232.0534; found: 232.0540.

*4.2.13. 2,4,6-Trimethylphenyl trifluoromethyl sulfide (**2n**)*

Yield: 6.94 g (63%) colorless liquid from 7.61 g (50.0 mmol) of **1n**, bp 92–93 °C/20 mmHg, solidifies at ~20 °C. GC assay: 99%, $t_{RET}$: 9.73 min. $^1$H NMR ($CDCl_3$): $\delta$ 2.28 (s, 3H), 2.52 (s, 6H), 6.98 (s, 2H). $^{13}$C NMR ($CDCl_3$): $\delta$ 21.1, 22.0, 120.1 (q, $J_{C,F}$ = 2.2 Hz), 129.6, 141.4, 145.3, 130.2 (q, $J_{C,F}$ = 310.0 Hz). $^{19}$F NMR ($CDCl_3$): $\delta$ −41.9. MS (EI+): $m/z$ (%) = 220 (91) $[M]^+$, 201 (6) $[M-F]^+$, 151 (100) $[M-CF_3]^+$, 119 (15) $[M-SCF_3]^+$, 105 (40) $[M-H_2CSCF_3]^+$, 107 (48) $[M-CSCF_3]^+$, 91 (37) $[C_7H_7]^+$, 77 (18) $[C_6H_6]^+$, 69 (12) $[CF_3]^+$, 45 (38) $[HCS]^+$, 65 (12) $[C_5H_5]^+$, 51 (12) $[C_4H_3]^+$, 39 (15) $[C_3H_3]^+$.

*4.2.14. 4-tert-Butyl-2,6-dimethylphenyl trifluoromethyl sulfide (**2o**, n. c.)*

Yield: 5.38 g (82%) colorless crystals from 4.86 g (25.0 mmol) of **1o**, bp 131–133 °C (20 mmHg), mp 34–36 °C. GC assay: 98%, $t_{RET}$: 13.02 min. $^1$H NMR ($CDCl_3$): $\delta$ 1.33 (s, 9H), 2.59 (s, 6H), 7.21 (s, 2H). $^{13}$C NMR ($CDCl_3$): $\delta$ 22.4, 31.1, 34.6, 120.1 (q, $J_{C,F}$ = 2.2 Hz), 125.5, 129.8 (q, $J_{C,F}$ = 307.0 Hz), 144.6, 153.9. $^{19}$F NMR ($CDCl_3$): $\delta$ −41.7. MS (EI+): $m/z$ (%) = 262 (63) $[M]^+$, 247 (100) $[M-CH_3]^+$, 219 (33) $[M-C_3H_7]^+$, 207 (11) $[M-C_4H_7]^+$, 178 (29) $[247\text{-}CF_3]^+$, 163 (18) $[178\text{-}CH_3]^+$, 161 (12) $[M-SCF_3]^+$, 146 (46) $[247\text{-}SCF_3]^+$, 131 (29) $[146\text{-}CH_3]^+$, 91 (26) $[C_7H_7]^+$, 77 (14) $[C_6H_6]^+$, 69 (15) $[CF_3]^+$, 57 (20) $[C_4H_9]^+$, 41 (38) $[C_3H_5]^+$. HRMS (TOF, EI+): calculated for $C_{13}H_{17}F_3S$: 262.1003; found: 262.0996.

*4.2.15. n-Octyl trifluoromethyl sulfide (**2p**)*

Yield: 1.18 g (22%) colorless liquid from 3.66 g (25.0 mmol) of **1p**, bp 114–115 °C (20 mmHg). GC assay: 97%, $t_{RET}$: 7.76 min. $^1$H NMR ($CDCl_3$): $\delta$ 0.88 (t, 3H, $J$ = 6.6 Hz), 1.28 (s, 9H), 1.37 (t, 2H, $J$ = 6.5 Hz), 1.68 (m, 2H), 2.87 (t, 2H, $J$ = 6.5 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 14.0, 22.6, 28.5, 28.9, 29.4, 31.75, 29.9 (q, $J_{C,F}$ = 2.2 Hz), 131.3 (q, $J_{C,F}$ = 305.0 Hz). $^{19}$F NMR ($CDCl_3$): $\delta$ −41.4. MS (EI+): $m/z$ (%) = 214 [$M^+$ not observed], 157 (17) $[M-C_4H_9]^+$, 145 (92) $[M-CF_3]^+$, 129 (15) $[M-C_6H_{13}]^+$, 115 (42) $[M-C_7H_{15}]^+$, 69 (89) $[CF_3]^+$, 84 (34), 83 (47), 71 (42), 70 (69), 57 (70), 56 (100), 55 (75), 43 (73), 41 (62), 29 (64), 27 (60) [aliphatic marker ions].

### 4.3. Inhibition experiments

*4.3.1. Reaction of PhSNa and $CF_3I$ in the presence of $PhNO_2$*

This experiment was performed according to the typical procedure, but nitrobenzene (50 mmol and 2.5 mmol) was added to the reaction mixture, and the reaction flask was covered with aluminium foil to protect it from direct light. Yield of **2a**: 76 and 77%, GC assay: 97 and 98%, respectively.

*4.3.2. Reaction of PhSNa and $CF_3I$ in the presence of 4-$CH_3C_6H_4CH{=}CH_2$*

Thiophenol (2.75 g, 25 mmol) was reacted with NaH and $CF_3I$ in the presence of 4-methylstyrene (8.85 g, 75 mmol, bp: 63–65 °C/17 mmHg) as described in the typical procedure. Steam distillation and ether extraction allowed to recover pure 4-methylstyrene as a colorless liquid (7.08 g, 80% recovery, analyzed by GC and NMR), but no $PhSCF_3$ (**2a**) was detected in the distillate. The residue was acidified with 5% aq-HCl and extracted with ether. The organic layer was separated, washed with water and dried ($Na_2SO_4$). The evaporation of the ether extract gave a yellow oil (2.20 g, 80% recovery), which was a 30:70% mixture of PhSH and $Ph_2S_2$ (GC).

### 4.4. Preparation of stock solutions of $CF_3I$

To a pre-weighed 100 ml one necked round bottom flask equipped with a magnetic stirrer bar (also weighed) DMSO is measured by weight (44.72 g). A balloon is filled with approximately 25 g of $CF_3I$, sealed and fixed to the neck of the flask. The seal is opened and the DMSO is stirred in a cold water bath for

30 min. The balloon is removed and weighed. The DMSO dissolved 24.66 g of $CF_3I$ which corresponds to a 35.5% by weight concentration of $CF_3I$. This solution can be stored in a brown glass bottle for weeks without any change. With DMF a 28.6% by weight solution was prepared by the same method.

## Acknowledgments

These investigations were supported by the Hungarian Scientific Research Foundation (OTKA K 062191 "Sustainable fluorous chemistry"). The European Union and the European Social Fund have provided financial support to the project under the grant agreement no. TÁMOP_4.2.1./B-09/1/KMR-2010-0003. Ágnes Csapó thanks the 'Sanofi-aventis/Chinoin' for a PhD scholarship.

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