molecules

MDPI

Article

General, Practical and Selective Oxidation Protocol for CF_3S into $CF_3S(O)$ Group

Liubov V. Sokolenko [1], Raisa K. Orlova [1], Andrey A. Filatov [1], Yurii L. Yagupolskii [1,3,*], Emmanuel Magnier [2,*], Bruce Pégot [2] and Patrick Diter [2]

1 Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmans'ka Str. 5, 02094 Kyiv, Ukraine; sokolenko.liubov@gmail.com (L.V.S.); OrlovaRaisa@ukr.net (R.K.O.); filatov@ioch.kiev.ua (A.A.F.)
2 Bâtiment Lavoisier, Université de Versailles-Saint-Quentin, 45 avenue des Etats-Unis, 78035 Versailles, France; bruce.pegot@uvsq.fr (B.P.); patrick.diter@uvsq.fr (P.D.)
3 Enamine Ltd, A. Matrosova str. 23, Kiev 01103, Ukraine
* Correspondence: yagupolskii@ioch.kiev.ua (Y.L.Y.); emmanuel.magnier@uvsq.fr (E.M.); Tel.: +38-044-559-0349 (Y.L.Y.); +33-013-925-4466 (E.M.)

Received: 14 March 2019; Accepted: 27 March 2019; Published: 30 March 2019

Abstract: A simple and efficient protocol for the oxidation of trifluoromethyl, mono- and difluoromethyl sulfides to the corresponding sulfoxides without over-oxidation to sulfones, using TFPAA prepared in situ from trifluoroacetic acid and 15% H_2O_2 aqueous solution was developed. The methodology is suitable for a wide range of aromatic and aliphatic substrates in milligram and multigram scales.

Keywords: trifluoromethylsulfides; trifluoromethylsulfoxides; oxidation; trifluoroperacetic acid; dihydrogen peroxide

1. Introduction

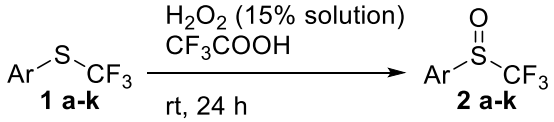
The synthesis of trifluoromethylsulfinyl containing compounds is a recent trend in current organic chemistry due to the practical significance of such compounds [1]. In particular, their biological activity is promising. They are also key intermediates for trifluoromethyl-containing sulfoximine synthesis and are excellent chiral auxiliaries [2–5]. Synthetic approaches dedicated to trifluoromethyl sulfoxides include (1) trifluoromethylation of the corresponding sulfinyl halides or sulfinic esters using $TMSCF_3$ [6–8], (2) reaction of aromatic compounds with triflinate salts [9], (3) rearrangement of aryl triflinates in the presence of $AlCl_3$ [10], (4) trifluoromethanesulfinilation using Langlois' system ($CF_3SO_2Na/POCl_3$) [11] or with 1-(trifluoromethylsulfinyl)-pyrrolidine-2,5-dione [12]. However, the most important and common method for the synthesis of trifluoromethylsulfoxides is the oxidation of the corresponding trifluoromethylsulfides using various oxidants, mainly peroxyacids, e.g. mCPBA [1]. It is noteworthy to mention that oxidation with mCPBA is sensitive to temperature. As a result, over-oxidation frequently occurs and non-negligible amounts of trifluoromethylsulfone are formed [13]. Furthermore, this reagent converts into m-chlorobenzoic acid, which is sometimes not easy to separate from the sulfoxide. Oxidation of an aliphatic sulfide was also described with Oxone® as oxidant [14]. Waste by-products formed during the oxidation reaction as well as the necessity to use silica as a component of reaction medium cause difficulties in scaling up. Trifluoroperacetic acid (TFPAA) was shown to be a convenient reagent for the oxidation of sulfides to sulfoxides, as it reacts more rapidly at low temperature than other peroxy acids [15]. To the best of our knowledge, TFPAA has not been widely applied to the oxidation of perfluoroalkyl sulfides and only a few articles [14,16–21] and patents [22–27] documented this procedure. TFPAA solution can be prepared from 30% H_2O_2 and trifluoroacetic acid or 80–90% H_2O_2 and trifluoroacetic anhydride [28,29]. On the basis of literature

data and our experience in oxidation reactions of trifluoromethyl sulfides, the use of TFPAA, obtained by both methods, has one common limitation as for mCPBA: over-oxidation readily occurs to form difficult-to-separate mixtures of trifluoromethyl sulfide, trifluoromethyl sulfoxide, and trifluoromethyl sulfone [17–19]. On the other hand, regarding the advantages of this method (easy to prepare and a cheap reagent, trifluoroacetic acid as side product), we believed there was an urgent need to exploit it. The description of a general and selective method of oxidation is especially important in the context of an exponential growth of molecules bearing a SCF_3 group [1].

Herein we propose an easy-to-handle and high-yielding procedure for the oxidation of alkyl and aryl perfluoroalkyl sulfides to the corresponding sulfoxides without over-oxidation thanks to the reappraisal of oxidation by TFPAA.

2. Results and Discussion

We postulated that a decrease in concentration, associated with a rigorous measurement of the latter, could dramatically reduce the formation of unwanted sulfone. Indeed, the use of TFPAA obtained in situ from trifluoroacetic acid and 15% H_2O_2 aqueous solution proved to be successful (see experimental part). This method was firstly applied to aryl trifluoromethyl sulfides **1** bearing both electrons donating and electron-withdrawing substituents in various positions on the aromatic ring (Scheme 1, Table 1). Corresponding aryl trifluoromethyl sulfoxides **2** were obtained in high yields whatever the nature of the substituents on the aromatic ring. In all experiments, the crude product contained less than 7% of non-reacted trifluoromethyl sulfide; at the same time, trifluoromethyl sulfone was detected in negligible amounts in only two reactions (Table 1, Entry 4, 10).



Scheme 1. Oxidation of aryl trifluoromethyl sulfides **1**.

Table 1. Oxidation of aryl trifluoromethyl sulfides **1**.

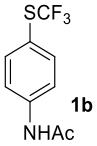
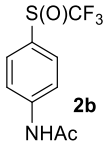
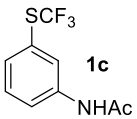
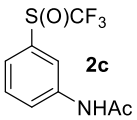
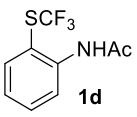
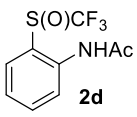
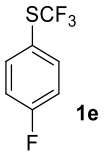
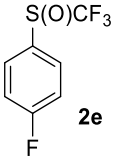
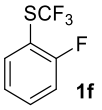
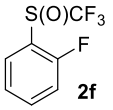
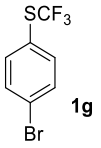
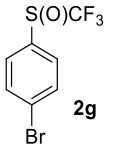
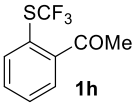
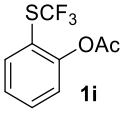
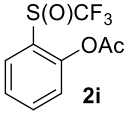
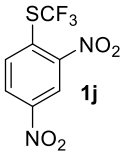
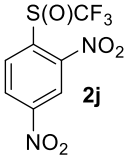
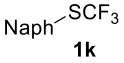
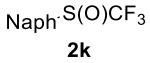
Entry	Reagent	Product	Molar ratio in Crude Product [1]			Crude[2] Yield, %	Isolated Yield, %
			1	**2**	**$ArSO_2CF_3$**		
1			5	95	0	95	-
2			7	93	0	91	85
3			4	96	0	96	-
4			2	98	traces	89	86

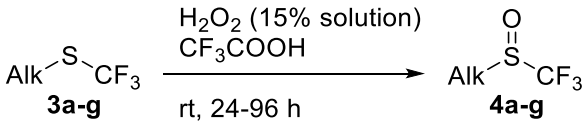
Table 1. *Cont.*

Entry	Reagent	Product	Molar ratio in Crude Product [1]			Crude[2] Yield, %	Isolated Yield, %
			1	2	$ArSO_2CF_3$		
5	 **1e**	 **2e**	3	97	0	100	96
6	 **1f**	 **2f**	0	100	0	98	-
7	 **1g**	 **2g**	3	97	0	100	96
8	 **1h**	 **2h**	3	97	0	90	85
9	 **1i**	 **2i**	3	97 [3]	0	84	70 [3]
10	 **1j**	 **2j**	7	91	2	100	83
11	 **1k**	 **2k**	0	100	0	-	87

[1] Composition of crude product on the basis of ^{19}F NMR data; [2] Crude yield is the isolated yield of product after removing the solvent before further purification; [3] Mixture of **2i** and corresponding phenol in 85:15 molar ratio (according to ^{19}F NMR data).

In most cases the crude product needs no further purification. If needed, compounds **2** were easily separated from impurities by standard methods (see experimental part for details). It should be noted that during the oxidation of acylated phenol **1i** partial hydrolysis occurred and the crude product contained ~15% of o-trifluoromethylsulfinyl phenol, which we failed to separate from **2i** by column chromatography.

Oxidation of aliphatic sulfides also proved successful (Scheme 2, Table 2).

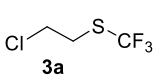
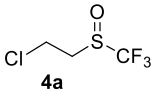
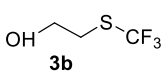
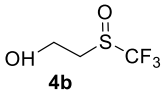
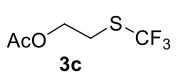
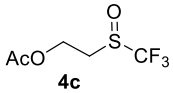
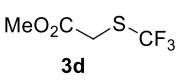
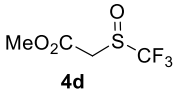
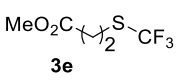
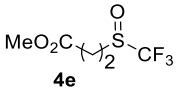
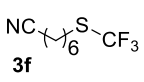
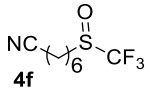
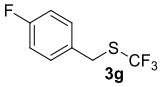
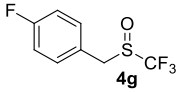


Scheme 2. Oxidation of alkyl trifluoromethyl sulfides **3**.

The thioether **3a** was oxidized by TFPAA in high yield (83%) in 24 h. This simple procedure can be favorably compared to our previous method which employed Oxone® [14]. Compound **4b** was isolated in low yield, most probably due to the high solubility of the product in water. Attempts

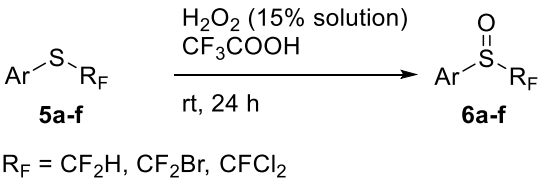
to separate **4b** from **3b** by distillation failed. Use of an acyl protective group (Table 2, Entry 3) led to a higher yield of sulfoxide **4c**. In this case, as well as in the previous one, a small amount (<3%) of trifluoromethyl sulfone was detected in the reaction mixture and the crude product. As in the experiment with acylated phenol **1i** (Table 1, Entry 9), product **4c** contains ~15% of the corresponding alcohol (Table 2, Entry 3), which we failed to separate from the ester by distillation. Oxidation of sulfide **3d** by 15% H_2O_2 solution in TFA proceeded with 90% conversion. The use of H_2O_2 in excess (1.1 equiv.) led to the same results and the sulfone was not observed in this reaction mixture. Two other examples demonstrated the efficiency of this transformation (entries 6–7).

Table 2. Oxidation of alkyl trifluoromethyl sulfides **3**.

Entry	Reagent	Product	Molar ratio in Crude Product [1]			Crude[2] Yield, %	Isolated Yield, %
			3	**4**	**$AlkSO_2CF_3$**		
1	 **3a**	 **4a**	4	96	0	-	83
2	 **3b**	 **4b**	11	89	traces	-	15 [3]
3	 **3c**	 **4c**	0	97 [4]	3	-	54 [4]
4	 **3d**	 **4d**	10	90	0	-	60 [5]
5	 **3e**	 **4e**	4	96	0	63	60
6	 **3f**	 **4f**	13	87	traces	-	85
7	 **3g**	 **4g**	0	99	1	-	85

[1] Composition of crude product on the basis of ^{19}F NMR data; [2] Crude yield is the isolated yield of product after removing the solvent before further purification; [3] Contains ~11 % of starting sulfide **3b**; [4] Mixture of **4c** and corresponding alcohol **4b** in 85:15 molar ratio (according to ^{19}F NMR data); [5] Use of 10% excess of H_2O_2 lead to the same results.

To show the scope of our oxidation procedure a number of sulfides bearing difluoromethyl **5a–c**, bromodifluoromethyl **5e**, dichlorofluoromethyl **5f**, and 1,1,2,2-tetrafluoro-2-((1,2,4-triazol)-1-yl)-ethyl **5d** groups were converted into sulfoxides (Scheme 3,Table 3).

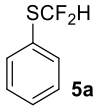
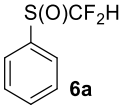
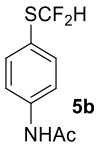
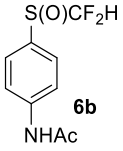
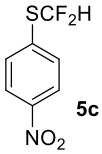
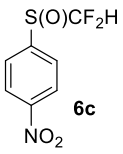
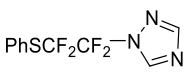
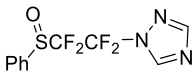
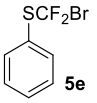
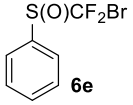
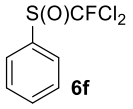


Scheme 3. Oxidation of fluoromethyl and difluoromethyl sulfides **5**.

As it is evident from Table 3, all compounds **6a–f** were obtained in high yields and the crude products were pure enough to be used without further purification. The oxidation of **5a** was strongly exothermic and the reaction was complete within 4 h at room temperature yielding pure sulfoxide **6a**, which contained neither difluoromethyl sulfide **5a** nor difluoromethyl sulfone. If this reaction was

performed at −15 °C for 6 h, with further stirring at ~10 °C for 20 h, the crude product contained ~2% of unreacted sulfide **5a**.

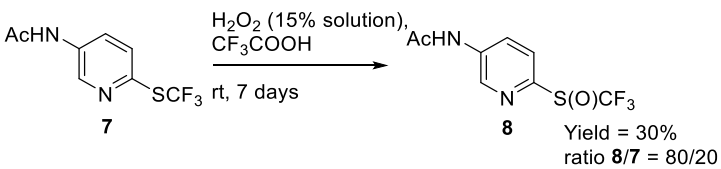
Table 3. Oxidation of fluoromethyl and difluoromethyl sulfides **5**.

Entry	Reagent	Product	Molar ratio in Crude Product [1]			Crude[2] Yield, %	Isolated Yield, %
			5	6	$ArSO_2R_F$		
1	 **5a**	 **6a**	0	100	0	-	70 [3]
2	 **5b**	 **6b**	4	96	0	80	-
3	 **5c**	 **6c**	4	96	0	75	-
4	 **5d**	 **6d**	5	95	0	95	92
5	 **5e**	 **6e**	3	96	1	-	91
6	 **5f**	 **6f**	0	100	0	-	69

[1] Composition of crude product on the basis of ^{19}F NMR data; [2] Crude yield is the isolated yield of product after removing the solvent before further purification; [3] Reaction time 4 h.

It should be emphasized that the oxidation reactions of sulfides **1**, **3**, and **5** could be performed on a 0.05 to 50 g scale.

The application of this method to heterocyclic thioethers is highly challenging, as demonstrated by the two following preliminary results. Thus, 2-trifluoromethylsulfenyl-5-acetylamino-pyridine **7** was oxidized to sulfoxide **8** with low conversion after seven days stirring, and we failed to separate the product from the starting sulfide (Scheme 4). A study devoted to the oxidation of heterocyclic substrates is needed but falls outside the scope of the present study.



Scheme 4. Oxidation of heterocyclic trifluoromethyl sulfides.

3. Materials and Methods

3.1. General Information

The purification of products by column chromatography (CC) was performed on Silica gel, 70–230 mesh 60A (Aldrich, Saint Louis, MI, USA) or by preparative TLC chromatography. ^1H NMR

spectra were recorded at 500 MHz with Bruker AVANCE DRX 500 instrument, or at 200 MHz or 300 MHz with Bruker AC-200 or AC-300, or at 400 MHz with Varian UNITY–Plus 400 spectrometer. ^{19}F NMR spectra were recorded on Varian UNITY–Plus 400 spectrometer at 376.5 MHz or at 470 MHz with Bruker AVANCE DRX 500 instrument or at 188 MHz with Bruker AC-200 (Bruker, Billerica, MA, USA). Chemical shifts are given in ppm relative to Me_4Si and CCl_3F, respectively, as internal or external standards. ^{13}C NMR-spectra (proton decoupled) were recorded on a Bruker AVANCE DRX 500 instrument at 125.7 MHz, or on Varian UNITY–Plus 400 spectrometer at 100.6 MHz, or at 75 or 50 MHz with Bruker AC-300 or AC-200. IR spectra were recorded with a Vertex 70 (Bruker) instrument (in KBr tablet). Melting points were determined in open capillaries using SMP3 instrument (Stuart Scientific Bibby Sterlin Ltd, Stone, Staffordshire, UK). Elemental analysis was performed in the Analytical Laboratory of the Institute of Organic Chemistry, NAS of Ukraine, Kyiv.

In all experiments trifluoroacetic acid from Sigma-Aldrich, 99% (CAS 76-05-1) was used. Difluoromethyl sulfides **5a–c** were synthesized by standard method [30]. Compound **5d** was synthesized as was described in the article [31]. Fluoromethylsulfides **1k**, **3f,g**, and **5e,f** were prepared according to the described procedures [32–34]. Trifluoromethylsulfides **1a–j**, **3a–e**, **7**, and **9** were purchased from Enamine Ltd (www.enamine.net).

3.2. Important Information

It is critical to know the exact concentration of H_2O_2 used in order to avoid over dosage of reagent that led to over oxidation. A solution of 15% H_2O_2 (mass concentration) was prepared from commercial ~30–35% H_2O_2 solution by dilution with water ~1:1 *w*/*w*. The concentration of H_2O_2 solution was measured using densimetry or titration (see Supplementary Materials).

3.3. General Procedure for Oxidation of Polyfluoroalkyl Sulfides to Polyfluoroalkyl Sulfoxides

To the solution of sulfide **1**, **3**, or **5** (10 mmol) in CF_3COOH (15–20 mL) 15 mass% aqueous solution of H_2O_2 (containing 10 mmol of H_2O_2) was added dropwise very slowly (during 40–90 min) at room temperature. Reaction is strongly exothermic; H_2O_2 was added at such a rate that the temperature was kept in the range 25–28 °C inside the flask (20 °C for compounds **1k**, **3f,g**, and 0 °C for compounds **5e,f**). Reaction mixture was stirred overnight at r.t. (for compound **3d** – 96 h, for **7**–7 days), poured into water, neutralized with solid $NaHCO_3$ to pH=6–7, then extracted with ether or ethyl acetate (4 × 30 mL). Compounds **2k**, **4f,g**, and **6e,f** were extracted with dichloromethane before neutralizing the TFA with $NaHCO_3$. The organic phase was washed with water (4 × 20 mL), dried with $MgSO_4$ or Na_2SO_4. Solvent was removed at atmospheric pressure for low-boiling liquids or on a rotary evaporator for solids or high-boiling liquids. Crude product was analyzed by NMR and purified if necessary.

Phenyl Trifluoromethyl sulfoxide **2a** [13,35,36]. Colorless liquid; yield 1.8 g (95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.56–7.63 (m, 3H, Ar-H), 7.75–7.77 (m, 2H, Ar-H). ^{19}F NMR (DMSO-d_6, 376.5 MHz): δ = −76.6 (s). Compound **1a** was oxidized on a 50 g scale (in 70 mL of CF_3COOH) with the same yield.

N-(4-((Trifluoromethyl)sulfinyl)phenyl)acetamide **2b** [37,38]. Crude product was purified by column chromatography, eluent CH_2Cl_2 (R_f = 0), then methyl-tert-butyl ether (R_f = 0.6). Pale yellow solid; yield 2.1 g (85 %); m.p. 140–141 °C (Lit. 141–142 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 2.10 (s, 3H, CH_3), 7.80 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-H), 7.90 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, Ar-H), 10.41 (s, 1H, NH). ^{19}F NMR (DMSO-d_6, 376.5 MHz): δ = −75.2 (s). ^{13}C NMR (DMSO-d_6, 125.7 MHz): δ = 24.5, 119.8, 125.2 (q, $^1J_{C\text{-}F}$ = 335.6 Hz, CF_3), 127.6, 128.2, 144.8, 169.6. Compound **1b** was also oxidized on a 10 g scale (in 30 mL of CF_3COOH) with the same yield.

N-(3-((Trifluoromethyl)sulfinyl)phenyl)acetamide **2c** [37]. White solid; yield 2.4 g (96%); m.p. 101–102 °C (Lit. 104.5–105.5 °C). ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 2.08 (s, 3H, CH_3), 7.49 (d,$^3J_{H\text{-}H}$ = 8 Hz, 1H, Ar-H), 7.61 (t, $^3J_{H\text{-}H}$ = 8 Hz, 1H, Ar-H), 7.85 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1H, Ar-H), 8.24 (s, 1H, Ar-H), 10.38 (s, 1H,

NH). ^{19}F NMR (DMSO-d_6, 376.5 MHz): δ = −74.8 (s). ^{13}C NMR (DMSO-d_6, 125.7 MHz): δ = 24.0, 115.1, 120.2, 123.6, 124.7 (q, $^{1}J_{C\text{-}F}$ = 335.6 Hz, CF_3), 130.2, 135.8, 140.7, 168.9.

N-(2-((Trifluoromethyl)sulfinyl)phenyl)acetamide **2d**. Crude product was purified by column chromatography, eluent methyl-tert-butyl ether (R_f = 0.6). White solid; yield 2.1 g (86%); m.p. 68–69 °C. IR (KBr): 3295, 3103, 2999, 2765, 2387, 2310, 2116, 1685, 1586, 1512, 1474, 1431, 1377, 1304, 1266, 1180, 1136, 1074, 1044, 1007, 889, 853, 776, 670, 603, 576, 549, 522, 476, 455, 431 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.17 (s, 3H, CH_3), 7.20 (t, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 1H, Ar-H), 7.39 (d, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 1H, Ar-H), 7.61 (t, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 1H, Ar-H), 8.55 (d, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 1H, Ar-H), 10.00 (s, 1H, NH). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ = -72.3 (s). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 24.9, 118.1, 123.0, 123.6, 125.4 (q, $^{1}J_{C\text{-}F}$ = 337 Hz, CF_3), 128.5, 135.1, 142.2, 168.9. Anal. Calcd for $C_9H_8F_3NO_2S$: C, 43.03; H, 3.21; N, 5.58. Found: C, 43.00; H, 3.18; N, 5.57.

1-Fluoro-4-((trifluoromethyl)sulfinyl)benzene **2e** [9]. Crude product contains 97 mol% of **2e** and 3 mol% of starting sulfide, which may be removed in vacuum (1 mBar) to give pure sulfoxide **2e**. Light yellow liquid; yield 1.9 g (96%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.25–7.29 (m, 2H, Ar-H), 7.76–7.80 (m, 2H, Ar-H). ^{19}F NMR (DMSO-d_6, 376.5 MHz): δ = −75.7 (s, 3F, CF_3), −104.8 (s, 1F, Ar-F). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 117.2 (d, $^{2}J_{C\text{-}F}$ = 22 Hz), 124.6 (q, $^{1}J_{C\text{-}F}$ = 335 Hz, CF_3), 128.5 (d, $^{3}J_{C\text{-}F}$ = 9 Hz), 131.1, 166.0, (d, $^{1}J_{C\text{-}F}$ = 254.5 Hz, C-F). Compound **1e** was oxidized on a 50 g scale (in 70 mL of CF_3COOH) with the same yield.

1-Fluoro-2-((trifluoromethyl)sulfinyl)benzene **2f**. White solid; yield 2.0 g (98%); m.p. 44–45 °C. IR (KBr): 3094, 2124, 1986, 1948, 1820, 1724, 1633, 1598, 1474, 1449, 1261, 1141, 955, 867, 823, 762, 706, 673, 579, 544, 490, 459, 430 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.19–7.23 (m, 1H, Ar-H), 7.42–7.46 (m, 1H, Ar-H), 7.61–7.67 (m, 1H, Ar-H), 7.94–7.98 (m, 1H, Ar-H). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ = −75.9 (s, 3F, CF_3), −114.5 (s, 1F, Ar-F). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 116.4 (d, $^{2}J_{C\text{-}F}$ = 20 Hz), 123.5 (dq, $^{3}J_{C\text{-}F}$ = 15 Hz, $^{4}J_{C\text{-}F}$ 2.5 Hz), 124.9 (qd, $^{1}J_{C\text{-}F}$ = 335.5 Hz, $^{4}J_{C\text{-}F}$ = 3.8 Hz, CF_3),125.6 (d, $^{4}J_{C\text{-}F}$ = 3.8 Hz), 127.2, 135.5 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz), 159.7 (d, $^{1}J_{C\text{-}F}$ = 252.7 Hz, C-F). Anal. Calcd for $C_7H_4F_4OS$: C, 39.63; H, 1.90; S, 15.11. Found: C, 39.62; H, 1.91; S, 15.11.

1-Bromo-4-((trifluoromethyl)sulfinyl)benzene **2g** [30,38]. Crude product contains 97 mol% of **2g** and 3 mol% of starting sulfide, which may be removed by washing with pentane to give pure product **2g**. White solid; yield 2.6 g (96%); m.p. 57–58 °C (Lit. 56–57 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.66 (d, $^{3}J_{H\text{-}H}$ = 8.5 Hz, 2H, Ar-H), 7.75 (d, $^{3}J_{H\text{-}H}$ = 8.5 Hz, 2H, Ar-H). ^{19}F NMR ($CDCl_3$, 470 MHz): δ = −74.4 (s). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 124.4 (q, $^{1}J_{C\text{-}F}$ = 335.6 Hz, CF_3), 127.3, 128.6, 133.0, 134.7. Compound **1g** was oxidized on a 15 g scale (in 35 mL of CF_3COOH) with the same yield.

2-((Trifluoromethyl)sulfinyl)-acetophenone **2h**. Crude product contains 97 mol% of **2h** and 3 mol% of starting sulfide, which may be removed by washing with pentane to give pure product **2h**. Pale yellow solid; yield 2 g (85 %); m.p. 97–98 °C. IR (KBr): 3080, 2968, 1675, 1585, 1468, 1438, 1359, 1280, 1187, 1130, 1073, 961, 885, 772, 663, 602, 571, 483, 434 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.68 (s, 3H, CH_3), 7.74 (t, $^{3}J_{H\text{-}H}$= 7 Hz, 1H, Ar-H), 7.88 (t, *J* = 7 Hz, 1H, Ar-H), 8.04 (d, $^{3}J_{H\text{-}H}$ = 7 Hz, 1H, Ar-H), 8.36 (d, $^{3}J_{H\text{-}H}$= 7 Hz, 1H, Ar-H). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ = −70.0 (s). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 26.2, 125.1 (q, $^{1}J_{C\text{-}F}$ = 340 Hz, CF_3), 126.0, 131.0, 132.4, 134.2, 135.4, 140.3, 198.3. Anal. Calcd for $C_9H_7F_3O_2S$: C, 45.76; H, 2.99; S, 13.57. Found: C, 45.78; H, 3.01; S, 13.60.

2-((Trifluoromethyl)sulfinyl)phenyl acetate **2i**. Crude product was purified by column chromatography, eluent hexane-methyl-tert-butyl ether, 2:1 (R_f = 0.5), but the product contains ~15% of the corresponding phenol. Pale yellow oil; yield 1.8 g (70 %). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.33 (s, 3H, CH_3), 7.05 (d, $^{3}J_{H\text{-}H}$ = 8 Hz, 1H, Ar-H), 7.53 (t, $^{3}J_{H\text{-}H}$ = 8 Hz, 1H, Ar-H), 7.68 (t, $^{3}J_{H\text{-}H}$ = 8 Hz, 1H, Ar-H), 8.03 (d, $^{3}J_{H\text{-}H}$ = 8 Hz, 1H, Ar-H). ^{19}F NMR ($CDCl_3$, 470 MHz): δ = −73.5 (s). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 20.5, 123.4, 124.9 (q, $^{1}J_{C\text{-}F}$ = 336 Hz, CF_3), 126.8, 127.0, 127.8, 134.5, 148.6, 167.8.

2,4-Dinitro-1-((trifluoromethyl)sulfinyl)benzene **2j**. Crude product was purified by column chromatography, eluent hexane-methyl-*tert*-butyl ether, 5:1 (R_f = 0.2). Pale yellow solid; yield 2.4 g (83%), m.p. 85–87 °C. IR (KBr): 3110, 3039, 2883, 1611, 1544, 1347, 1224, 1186, 1134, 1074, 917, 896, 860, 835, 742, 678, 602, 574, 531, 496, 439 cm^{-1}. ^1H NMR (DMSO-d_6, 500 MHz): δ = 8.46 (d, $^3J_{H-H}$ = 8 Hz, 1H, Ar-H), 8.92 (d,$^3J_{H-H}$ = 8 Hz, 1H, Ar-H), 8.97 (s, 1H, Ar-H). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ = −68.5 (s). ^{13}C NMR (DMSO-d_6, 125.7 MHz): δ = 121.0, 125.7 (q, $^1J_{C-F}$ = 342 Hz, CF_3), 128.8, 130.4, 142.1, 146.9, 150.8. Anal. Calcd for $C_7H_3F_3N_2O_5S$: C, 29.59; H, 1.06; N, 9.86; S, 11.28. Found: C, 29.58; H, 1.05; N, 9.87; S, 11.29.

2-((Trifluoromethyl)sulfinyl)naphthalene **2k**. Product was purified by column chromatography, eluent Et_2O-petroleum ether, 1:9 (R_f = 0.6). Pale yellow liquid; yield 1.4 g (87%). IR (KBr): 2940, 1171, 1126, 1073, 813, 744,639 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.67 (m, 2H, Ar-H), 7.75 (d, $^3J_{H-H}$ = 8.6 Hz, 1H, Ar-H), 7.85–7.96 (m, 2H, Ar-H), 7.99 (d, $^3J_{H-H}$ = 8.7 Hz, 1H, Ar-H), 8.31 (s, 1H, Ar-H). ^{19}F NMR (188 MHz, $CDCl_3$): δ = −74.5 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.4, 124.9 (q, $^1J_{C-F}$ = 335 Hz, CF_3), 127.7, 127.8, 128.2, 128.8, 129.0, 129.9, 132.4, 132.5, 132.6, 135.5. HRMS: calcd. for $C_{11}H_7F_3SONa$ 267.0063; found 267.0067 [M − Na]+ (δ = −1.5).

1-Chloro-2-((trifluoromethyl)sulfinyl)ethane **4a** [14]. Product was purified by distillation. Colorless liquid; yield 1.5 g (83%); b.p. 68–70 °C (10 Torr). ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.21–3.24 (m, 1H, CH_2), 3.43–3.48 (m, 1H, CH_2), 3.95–4.00 (m, 2H, CH_2). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ = −73.6 (s). Compound **3a** was oxidized on a 15 g scale (in 35 mL of CF_3COOH) with the same yield.

2-(Trifluoromethyl)sulfinyl-ethanol **4b**. Crude product was purified by distillation, but the product contains 11% of starting sulfide. Colorless liquid; yield 0.25 g (15%); b.p. 108–110 °C (10 Torr). IR (KBr): 3417, 2893, 1396, 1293, 1174, 1138, 1047, 1004, 946, 844, 749, 645, 563, 442 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 3.02–3.20 (m, 2H, CH_2), 3.67 (s, 1H, OH), 4.09–4.13 (m, 2H, CH_2). ^{19}F NMR ($CDCl_3$, 470 MHz): δ = −73.6 (s). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 51.2, 54.4, 125.5 (q, $^1J_{C-F}$ = 332 Hz, CF_3).

2-((Trifluoromethyl)sulfinyl)ethyl acetate **4c**. Crude product was purified by distillation, but the product contains 15% of the corresponding alcohol. Colorless liquid; yield 1.1 g (54%); b.p. 100–102 °C (10 Torr). ^1H NMR ($CDCl_3$, 500 MHz): δ = 2.10 (s, 3H, CH_3), 3.20–3.33 (m, 2H, CH_2), 4.47–4.64 (m, 2H, CH_2). ^{19}F NMR ($CDCl_3$, 470 MHz): δ = −73.7 (s). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 20.4, 48.2, 55.9, 125.3 (q, $^1J_{C-F}$ = 333 Hz, CF_3), 170.3.

Methyl 2-((trifluoromethyl)sulfinyl)acetate **4d** [16]. Product was purified by distillation. Colorless liquid; yield 1.1 g (60%); b.p. 90 °C (10 Torr). ^1H NMR ($CDCl_3$, 500 MHz): δ = 3.79 (s, 3H, CH_3), 3.87 (d, $^2J_{H-H}$ = 15 Hz, 1H, CH_2), 3.94 (d, $^2J_{H-H}$ = 15 Hz, 1H, CH_2). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ = −73.8 (s). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 53.5, 53.6, 125.1 (q, $^1J_{C-F}$ = 334.5 Hz, CF_3), 164.2.

Methyl 3-((trifluoromethyl)sulfinyl)propanoate **4e**. Product was purified by distillation. Colorless liquid; yield 1.25 g (60%); b.p. 96–98 °C (10 Torr). IR (KBr): 2959, 1735, 1440, 1367, 1173, 1136, 1074, 980, 828, 746, 661, 564, 450 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.77–2.97 (m, 2H, CH_2), 3.17–3.27 (m, 2H, CH_2), 3.72 (s, 3H, CH_3). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ = −74.2 (s). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 25.6, 43.2 (q, $^3J_{C-F}$ = 2.5 Hz, CH_2-S(O)CF_3), 52.4, 125.4 (q, $^1J_{C-F}$ = 334.5 Hz, CF_3), 170.8. Anal. Calcd for $C_5H_7F_3O_3S$: C, 29,42; H, 3,46; S, 15.70. Found: C, 29.43; H, 3.44; S, 15.72.

7-((Trifluoromethyl)sulfinyl)heptanenitrile **4f**. Compound **3f** was oxidized on a 0.12 g scale. Product was purified by preparative TLC chromatography, eluent Et_2O-petroleum ether, 1:9 (R_f = 0.1). Pale yellow liquid; yield 0.11 g (85%). IR (KBr): 2936, 2864, 2239, 1171, 1143, 1080 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.40–1.56 (m, 4H, CH_2 -CH_2), 1.56–1.76 (m, 2H, CH_2), 1.74–1.92 (m, 2H, CH_2), 2.31 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, CH_2), 2.73–2.90 (m, 1H, CH), 2.93–3.11 (m, 1H, CH). ^{19}F NMR ($CDCl_3$, 188 MHz): δ = −74.1 (s). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 17.0, 21.5, 24.9, 27.8, 28.1, 48.2, 119.5, 125.3 (q, $^1J_{C-F}$ = 333 Hz, CF_3). HRMS: calcd. for $C_8H_{12}NF_3SONa$ 250.0477; found 250.0489 [M − Na]+ (δ = 0.4).

1-Fluoro-4-(((trifluoromethyl)sulfinyl)methyl)benzene **4g** [39]. Compound **3g** was oxidized on a 0.05 g scale. Product was purified by preparative TLC chromatography, eluent Et_2O-petroleum ether, 1:9 (R_f = 0.3). Pale yellow solid; yield 0.041 g (85%); m.p. 80 °C (Lit. 81–82 °C). IR (KBr): 2983, 2927, 1600, 1507, 1243, 1178, 1139, 1050, 1011, 842, 745 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.20 (AB syst., $^2J_{H-H}$ = 13.2 Hz, 2H, CH_2), 7.11 (t, $^3J_{H-H}$ = $^3J_{H-F}$= 8.4 Hz, 2H, Ar-H), 7.35 (dd, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-F}$ = 5.3 Hz, 2H, Ar-H). ^{19}F NMR ($CDCl_3$, 188 MHz): δ = −73.11 (s, 3F, CF_3), −112.25(m, 1F, Ar-F). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 54.7 (q, $^3J_{C-F}$ = 3.1 Hz), 116.5 (d, $^2J_{C-F}$ = 21.9 Hz), 123.3 (d, $^4J_{C-F}$ = 3.3 Hz), 125.3 (q, $^1J_{C-F}$ = 335.0 Hz, CF_3), 132.3 (d, $^3J_{C-F}$ = 8.5 Hz), 163.4 (d, $^1J_{C-F}$ = 249.3 Hz, C-F).

((Difluoromethyl)sulfinyl)benzene **6a** [40]. Colorless liquid; yield 1.2 g (70%); b.p. 130 °C (10 Torr). ^1H NMR ($CDCl_3$, 400 MHz): δ = 6.02 (t, $^2J_{H-F}$ = 55.6 Hz, 1H, CHF_2), 7.55-7.60 (m, 3H, Ar-H), 7.69–7.71 (m, 2H, Ar-H). ^{19}F {H} NMR ($CDCl_3$, 376.5 MHz): δ = −119.4 (d, $^2J_{F-F}$ = 260 Hz, 1F, CHF_2), -120.2 (d, $^2J_{F-F}$ = 260 Hz, 1F, CHF_2). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 120.8 (dd, $^1J_{C-F}$= 288 Hz, 287 Hz, CHF_2), 125.4, 129.5, 132.8, 136.6 (t, $^3J_{C-F}$ = 4 Hz).

N-(4-((Difluoromethyl)sulfinyl)phenyl)acetamide **6b** [30]. Pale yellow solid; yield 1.9 g (80%); m.p. 166–167 °C (Lit. 170–171 °C). ^1H NMR (DMSO-d_6, 500 MHz): δ = 2.09 (s, 3H, CH_3), 6.89 (t, $^2J_{H-F}$ = 54 Hz, 1H, CHF_2), 7.70 (d, $^3J_{H-H}$ = 8 Hz, 2H, Ar-H), 7.85 (d, $^3J_{H-H}$ = 8 Hz, 2H, Ar-H), 10.34 (s, 1H, NH). ^{19}F NMR (DMSO-d_6, 376.5 MHz): δ = -121.4 (dd, $^2J_{F-F}$ = 257 Hz, $^2J_{H-F}$ = 54 Hz, 1F, CHF_2), -125.5 (dd, $^2J_{F-F}$ = 257 Hz, $^2J_{H-F}$ = 54 Hz, 1F, CHF_2). ^{19}F {H} NMR ($CDCl_3$, 376.5 MHz): δ = −121.5 (d, $^2J_{F-F}$ = 257 Hz, 1F, CHF_2), -123.3 (d, $^2J_{F-F}$ = 257 Hz, 1F, CHF_2). ^{13}C NMR (DMSO-d_6, 125.7 MHz): δ = 24.6, 119.8, 120.6 (t, $^1J_{C-F}$ = 292 Hz, CHF_2), 120.9 (t, $^1J_{C-F}$ = 280 Hz, CHF_2), 127.2, 127.3, 129.9, 143.8, 169.5.

1-((Difluoromethyl)sulfinyl)-4-nitrobenzene **6c** [30]. Pale yellow solid; yield 1.7 g (75%); m.p. 84–85 °C (Lit. 81–83 °C). ^1H NMR (DMSO-d_6, 500 MHz): δ = 7.08 (t, $^2J_{H-F}$ = 56 Hz, 1H, CHF_2), 8.04 (d, $^3J_{H-H}$ = 6.5 Hz, 2H, Ar-H), 8.46 (d, $^3J_{H-H}$ = 6.5 Hz, 2H, Ar-H). ^{19}F NMR (DMSO-d_6, 376.5 MHz): δ = −120.8 (dd, $^2J_{F-F}$ = 254 Hz, $^2J_{H-F}$ = 56 Hz, 1F, CHF_2), -125.9 (dd, $^2J_{F-F}$ = 254 Hz, $^2J_{H-F}$ = 56 Hz, 1F, CHF_2). ^{19}F {H} NMR (DMSO-d_6, 376.5 MHz): δ = −120.8 (d, $^2J_{F-F}$ = 254 Hz, 1F, CHF_2), −125.9 (d, $^2J_{F-F}$ = 254 Hz, 1F, CHF_2). ^{13}C NMR (DMSO-d_6, 125.7 MHz): δ = 120.4 (t, $^1J_{C-F}$ = 284 Hz, CHF_2), 120.6 (t, $^1J_{C-F}$ = 287 Hz, CHF_2), 124.7, 124.9, 127.4, 127.5, 133.9, 144.3, 150.4.

(1,1,2,2-Tetrafluoro-2-((1,2,4-triazol)-1-yl)-ethyl)-sulfinylbenzene **6d**. Crude product was purified by column chromatography, eluent CH_2Cl_2, then methyl-tert-butyl ether (R_f = 0.7). Pale yellow solid; yield 2.7 g (92%); m.p. 77–78 °C. IR (KBr): 3105, 2872, 1819, 1688, 1582, 1512, 1477, 1453, 1403, 1378, 1294, 1262, 1221, 1191, 1140, 1111, 1070, 981, 903, 830, 756, 691, 667, 629, 591, 514, 482, 449 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.56–7.65 (m, 3H, Ar-H), 7.77 (d, 2H, Ar-H), 8.15 (s, 1H, Het-H), 8.59 (s, 1H, Het-H). ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ = −94.0 (d, $^2J_{F-F}$ = 226 Hz, 1F, CF_2), −94.6 (d, $^2J_{F-F}$ = 226 Hz, 1F, CF_2), −112.5 (d, $^2J_{F-F}$ = 237 Hz, 1F, CF_2), 124.3 (d, $^2J_{F-F}$ = 237 Hz, 1F, CF_2). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 113.0 (tt, $^1J_{C-F}$ = 271 Hz, $^2J_{C-F}$ = 31 Hz, CF_2), 116.9 (ddt, $^1J_{C-F}$ = 318 Hz, $^1J_{C-F}$ = 308 Hz, $^2J_{C-F}$ 38 Hz, CF_2), 126.7, 129.5, 133.8, 135.0, 143.4, 154.1. Anal. Calcd for $C_{12}H_{12}F_4N_3OS$: C, 44.72; H, 3.75; N, 13.04; S, 9.95. Found: C, 44.74; H, 3.76; N, 13.02; S, 9.98.

((Bromodifluoromethyl)sulfinyl)benzene **6e** [41]. Compound **5e** was oxidized only on a 50 mmol scale. Crude product was purified by column chromatography, eluent petroleum ether-diethyl ether, 8:2 (R_f = 0.6). Yellow oil; yield 8.1 g (91%). IR (KBr):1443, 1114, 1073, 1056, 854, 827, 742, 687 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ= 7.52 (m, 3H, ArH), 7.72 (m, 2H, ArH). ^{19}F NMR ($CDCl_3$, 188 MHz): δ = -53.49 and -55.56 (2F, CF_2Br, syst. AB $^2J_{C-F}$ = 145 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 126.2, 128.4 (dd, $^1J_{C-F}$ = 355 Hz, 350.5Hz), 129.1, 133.4, 136.7 (dd, $^3J_{C-F}$ = 3 Hz, 1 Hz).

((Dichlorofluoromethyl)sulfinyl)benzene **6f** [42]. Compound **5f** was oxidized only on a 50 mmol scale. Crude product was purified by column chromatography, eluent petroleum ether-diethyl ether, 8:2 (R_f = 0.5). Yellow oil; yield 10.6 g (69%). IR (KBr): 1445, 1104, 1061, 840, 792, 744, 684 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ = 7.61 (m, 3H, Ar-H), 7.82 (m, 2H, Ar-H). ^{19}F NMR ($CDCl_3$, 188 MHz): δ = −62.8

(s). ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 126.9 (d, $^1J_{C-F}$ = 340 Hz), 126.9 (d, $^4J_{C-F}$ = 1.5 Hz), 128.9, 133.5, 137.4 (d, $^3J_{C-F}$ = 1.5 Hz).

N-(6-((Trifluoromethyl)sulfinyl)pyridin-3-yl)acetamide **8**. Crude product was purified by column chromatography, eluent ethyl acetate (R_f = 0.5) to give compound **8** with 80 % purity (contains ~20% of starting sulfide). Yellow solid; yield 0.75 g (~30%). ^{1}H NMR (DMSO-d_6, 400 MHz): δ = 2.12 (s, 3H, CH_3), 8.02 (d, $^3J_{H-H}$ = 8.8 Hz, 1H, Het-H), 8.41 (d, $^3J_{H-H}$ = 8.8 Hz, 1H, Het-H), 10.6 (s, 1H, NH), 8.88 (s, 1H, Het-H). ^{19}F {H} NMR (DMSO-d_6, 376.5 MHz): δ = −72.7 (s). ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 24.4, 122.5, 125.3 (q, $^1J_{C-F}$ = 338 Hz, CF_3), 127.9, 139.8, 141.3, 149.3, 170.1.

4. Conclusions

In summary, a simple, convenient, and high-yielding procedure for the oxidation of fluoroalkyl sulfides to fluoroalkyl sulfoxides was developed. It was shown that the new protocol is suitable for a wide range of aliphatic and aromatic substrates on a milligram and multigram scales. In almost all cases, over-oxidation did not occur, and the crude products contained only a small quantity of starting sulfides.

Supplementary Materials: The following are available online: titration of H_2O_2 solution, NMRs and IRs of the new synthesized compounds.

Author Contributions: Y.L.Y. conceived idea of the article; L.V.S., R.K.O., A.F., B.P., P.D. performed the experiments; L.V.S. wrote the paper, Y.L.Y. and E.M. reviewed and edited the manuscript. All authors read and approved the final manuscript.

Acknowledgments: We thank Enamine Ltd (www.enamine.net) and CNRS for generous support of our research. We thank Karen Wright for the improvement of the English Manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Xu, X.-H.; Matsuzaki, K.; Shibata, N. Synthetic Methods for Compounds Having CF_3-S Units on Carbon by Trifluoromethylation, Trifluoromethylthiolation, Triflylation, and Related Reactions. *Chem. Rev.* **2015**, *115*, 731–764. [CrossRef] [PubMed]
2. Bizet, V.; Kowalczyk, R.; Bolm, C. Fluorinated sulfoximines: Syntheses, properties and applications. *Chem. Soc. Rev.* **2014**, *43*, 2426–2438. [CrossRef]
3. Shen, X.; Hu, J. Fluorinated Sulfoximines: Preparation, Reactions and Applications. *Eur. J. Org. Chem.* **2014**, 4437–4451. [CrossRef]
4. Barthelemy, A.L.; Magnier, E. Recent trends in perfluorinated sulfoximines. *C. R. Chim.* **2018**, *21*, 711–722. [CrossRef]
5. Batisse, C.; Panossian, A.; Hanquet, G.; Leroux, F. Access towards enantiopure α,α-difluoromethyl alcohols by means of sulfoxides as traceless chiral auxiliaries. *Chem. Comm.* **2018**, *54*, 10423–10426. [CrossRef]
6. Movchun, V.N.; Kolomeitsev, A.A.; Yagupolskii, Y.L. Nucleophilic trifluoromethylation of organic substrates using (trifluoromethyl)trimethylsilane in the presence of a fluoride anion II. A convenient route to aryltrifluoromethyl-sulfides, -sulfoxides and -sulfones. *J. Fluorine. Chem.* **1995**, *70*, 255–257. [CrossRef]
7. Patel, N.R.; Kirchmeier, R.L. Trifluoromethylation and pentafluorophenylation of sulfur and carbon centers using (trifluoromethyl)- and (pentafluorophenyl)trimethylsilane. *Inorg. Chem.* **1992**, *31*, 2537–2540. [CrossRef]
8. Singh, R.P.; Cao, G.; Kirchmeier, R.L.; Shreeve, J.M. Cesium Fluoride Catalyzed Trifluoromethylation of Esters, Aldehydes, and Ketones with (Trifluoromethyl)trimethylsilane. *J. Org. Chem.* **1999**, *64*, 2873–2876. [CrossRef] [PubMed]
9. Wakselman, C.; Tordeux, M.; Freslon, C.; Saint-Jalmes, L. Aryltrifluoromethylsulfoxides: Sulfinylation of Aromatics by Triflinate Salts in Acid Medium. *Synlett* **2001**, *4*, 550–552. [CrossRef]
10. Chen, X.; Tordeux, M.; Desmurs, J.-R.; Wakselman, C. Thia-Fries rearrangement of aryl triflinates to trifluoromethanesulfinylphenols. *J. Fluor. Chem.* **2003**, *123*, 51–56. [CrossRef]

11. Billard, T.; Greiner, A.; Langlois, B.R. A new equivalent of the $CF_3S(O)^+$ cation. Synthesis of trifluoromethanesulfinates and trifluoromethanesulfinamides. *Tetrahedron* **1999**, *55*, 7243–7250. [CrossRef]
12. Romanenko, V.D.; Thoumazet, C.; Lavallo, V.; Tham, F.S.; Bertrand, G. Synthesis and reactivity of a stable crystalline diastereomerically pure trifluoromethanesulfinic acid derivative: (*S*)-(−)-1-trifluoromethylsulfinyl-(*R*)-4-phenyloxazolidin-2-one. *Chem. Commun.* **2003**, *14*, 1680–1681. [CrossRef]
13. Yang, J.-J.; Kirchmeier, R.L.; Shreeve, J.M. New Electrophilic Trifluoromethylating Agents. *J. Org. Chem.* **1998**, *63*, 2656–2660. [CrossRef] [PubMed]
14. Sokolenko, L.V.; Maletina, I.I.; Yagupolskii, L.M.; Yagupolskii, Yu. L. A Convenient and Efficient Synthesis of Trifluoromethyl Vinyl Sulfoxide and its Reactivity in Addition Reactions. *Synlett* **2010**, *14*, 2075–2078. [CrossRef]
15. Venier, C.G.; Squires, T.G.; Chen, Y.-Y.; Hussmann, G.P.; Shei, J.C.; Smith, B.F. Peroxytrifluoroacetic acid oxidation of sulfides to sulfoxides and sulfones. *J. Org. Chem.* **1982**, *47*, 3773–3774. [CrossRef]
16. Sokolenko, L.V.; Yagupolskii, Yu. L.; Kumanetska, L.S.; Marrot, J.; Magnier, E.; Lipetskij, V.O.; Kalinin, I.V. $CF_3S(O)_n$-Containing Enaminones as Precursors for syntheses of Pyrimidine-4(3H)-ones. *Tetrahedron Lett.* **2017**, *58*, 1308–1311. [CrossRef]
17. Tang, R.-Y.; Zhong, P.; Lin, Q.-L. A convenient conversion of pyrazolyl disulfide to sulfides by sodium dithionite and synthesis of sulfoxides. *J. Fluorine. Chem.* **2006**, *127*, 948–953. [CrossRef]
18. Scribner, R.M. Some New Sulfonyl- and Trifluoromethylthio-p-benzoquinones. Their Reactions, Polarographic Reduction Potentials, and π Acid Strengths. *J. Org. Chem.* **1966**, *31*, 3671–3682. [CrossRef]
19. Pazenok, S.V.; Kondratenko, N.V.; Popov, V.I.; Troitskaya, V.I.; Il'chenko, A.Y.; Al'perovich, M.A.; Yagupolskii, L.M. Indo- and benzindocyanine dyes with fluorine-containing substituents. *Chemistry of Heterocyclic Compounds* **1983**, *19*, 1182–1187. [CrossRef]
20. Magnier, E.; Tordeux, M.; Goumont, R.; Magder, K.; Wakselman, C. Perfluoroalkylation of 2-mercaptoethanol as a key step for a new synthesis of perfluoroalkyl vinyl sulfides, sulfoxides and sulfones. *J. Fluorine. Chem.* **2003**, *124*, 55–59. [CrossRef]
21. Moise, J.; Goumont, R.; Magnier, E.; Wakselman, C. Synthesis of Fluoroalkyl Vinyl Sulfoxides and their Use in Diels-Alder Reactions. *Synthesis* **2004**, *14*, 2297–2302. [CrossRef]
22. Meng, C.Q.; Le Hir de Fallois, L.P.; Lee, H.I.; Zhan, X.; Labrosse, J.R.; Mulhauser, M. Processes for the Preparation of 1-Aryl-5-Alkyl Pyrazole Compounds. U.S. Patent 2013/281710, 24 October 2013.
23. Lee, H.I.; Le Hir de Fallois, L.P.; Timmons, Ph.R.; Cawthorne, W.G.; de Leon, A.P. 1-Aryl-5-Alkyl Pyrazole Derivative Compounds, Processes of Making and Methods of Using Thereof. U.S. Patent 2008/031902, 7 February 2008.
24. Chou, D.T.; Knauf, W.; Maier, M.; Malaska, M.J.; Mcintyre, D.; Lochhaas, F.; Huber, S. K Pesticidal Agents on the Basis of 1-Aryl-Aminopyrrol. WO Patent 2006/000315, 5 January 2006.
25. Wu, T.-T.; Sinodis, D.N.; Timmons, P.R.; Powell, G.S.; Chou, D.T.; Newsome, P.W.; Hall, L.S. Pesticidal 1-Arylimidazoles. U.S. Patent 5223525, 29 June 1993.
26. Hatton, L.R.; Buntain, I.G.; Hawkins, D.W.; Parnell, E.W.; Pearson, C.J.; Roberts, D.A. Derivatives of N-phenylpyrazoles. U.S. Patent 5232940, 3 August 1993.
27. Huang, J.; Lowder, P.D.; Ray, N.C.; Hawkins, D.W. Pesticidal 1-Arylpyrazole Derivatives. U.S. Patent 5817688, 6 October 1998.
28. Caster, K.C.; Rao, A.S.; Mohan, H.R. Trifluoroperacetic acid. In *Handbook of Reagents for Organic Synthesis. Fluorine-Containing Reagents*; Paquette, L.A., Ed.; Wiley: Chichester, England, 2007; pp. 619–624.
29. Emmons, W.D. Peroxytrifluoroacetic Acid. I. The Oxidation of Nitrosamines to Nitramines[1]. *J. Am. Chem. Soc.* **1954**, *76*, 3468–3470. [CrossRef]
30. Sedova, L.N.; Gandel'sman, L.Z.; Alekseeva, L.A.; Yagupol'skii, L.M. Derivatives of phenyldifluoromethyl sulfide, sulfoxide, and sulfone. *Zh. Obshch. Khim.* **1969**, *39*, 2057–2062.
31. Petko, K.I.; Sokolenko, T.M.; Bezdudny, A.V.; Yagupolskii, L.M. *N*-(2-Bromotetrafluoroethyl) derivatives of five-membered nitrogen-containing heterocycles. *J. Fluorine. Chem.* **2005**, *126*, 1342–1346. [CrossRef]
32. Anselmi, E.; Blazejewski, J.-C.; Tordeux, M.; Wakselman, C. Perfluoroalkylation of aliphatic thiols in the presence of sodium hydroxymethanesulfinate. *J. Fluorine Chem.* **2000**, *105*, 41–44. [CrossRef]

33. Anselmi, E.; Simon, C.; Marrot, J.; Bernardelli, P.; Schio, L.; Pégot, B.; Magnier, E. Ionic Liquids for Fast and Solvent-Free Nucleophilic Trifluoromethylthiolation of Alkyl Halides and Alcohols. *Eur. J. Org. Chem.* **2017**, *2017*, 6319–6326. [CrossRef]
34. Pégot, B.; Urban, C.; Bourne, A.; Le, T.-N.; Bouvet, S.; Marrot, J.; Diter, P.; Magnier, E. Difluoromethyl and Chlorofluoromethyl Sulfoximines: Synthesis and Evaluation as Electrophilic Perfluoroalkylating Reagents. *Eur. J. Org. Chem.* **2015**, *2015*, 3069–3075. [CrossRef]
35. Bzhezovsky, V.M.; Penkovsky, V.V.; Rozhenko, A.B.; Iksanova, S.V.; Kondratenko, N.V.; Yagupolskii, L.M. Multinuclear NMR spectroscopy and semi-empirical MNDO-PM3 quantum chemical investigations of the compounds C_6H_5XY (X=S, SO, SO_2; Y=CF_3, CH_3). *J. Fluor. Chem.* **1994**, *69*, 41–49. [CrossRef]
36. Tordeux, M.; Magnier, E.; Guidotti, J.; Diter, P.; Wakselman, C. $^{29/28,30/28}$Silicon, $^{34/32}$sulfur and $^{80/77}$selenium isotope-induced fluorine chemical shifts through two bonds. *Magn. Reson. Chem.* **2004**, *42*, 700–703. [CrossRef] [PubMed]
37. Yagupol'skii, L.M.; Marenets, M.S.; Kondratenko, N.V. The orienting action of trifluoromethyl sulfoxide group. *Zh. Obshch. Khim.* **1965**, *62*, 377, *Chem. Abstr.* **1965**, *62*, 14551a.
38. Yagupol'skii, L.M.; Troitskaya, V.I.; Gruz, B.E.; Kondratenko, N.V. Cyanine dyes containing fluorine. XII. Cyanine dyes from derivatives of 5-trifluoromethylthio-2-methylbenzimidazole. *Zh. Obshch. Khim.* **1966**, *64*, 1644–1650, *Chem. Abstr.* **1966**, *64*, 3731c.
39. Orda, V.V.; Yagupol'skii, L.M.; Bystrov, V.F.; Stepanyants, A.U. Transmission of inductive effect of substituents SCF_3, $SOCF_3$, and SO_2CF_3, through a methylene group. *Zh. Obshch. Khim.* **1965**, *63*, 1628–1636, *Chem. Abstr.* **1965**, *63*, 17861c.
40. Surya Prakash, G.K.; Weber, C.; Chacko, S.; Olah, G.A. New Electrophilic Difluoromethylating Reagent. *Org. Lett.* **2007**, *9*, 1863–1866. [CrossRef] [PubMed]
41. Burton, D.; Wiemers, D.M. Synthesis of bromodifluoromethyl phenyl sulfide, sulfoxide and sulfone. *J. Fluorine Chem.* **1981**, *18*, 573–582. [CrossRef]
42. Saikia, A.K.; Tsuboi, S. Chemistry of Trichlorofluoromethane: Synthesis of Chlorofluoromethyl Phenyl Sulfone and Fluoromethyl Phenyl Sulfone and some of Their Reactions. *J. Org. Chem.* **2001**, *66*, 643–647. [CrossRef] [PubMed]

Sample Availability: Samples of the compounds **1–6** are available from the corresponding authors.