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Copper-catalyzed three component C—S/C—N coupling for the synthesis of trifluorothioacetamides

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ABSTRACT

A copper-catalyzed three component C—S/C—N coupling reaction of imines with sulfur and CFC-113a was developed. The reaction involves amination and C═S double bond formation of CFC-113a, leading to biologically important trifluorothioacetamides. The method features efficient construction of trifluorothioacetyl moiety from cheap sulfur and CFC-113a, and safe disposal for environmentally persistent Freon

1. Introduction

Thioamides are essential structural motifs found in a variety of biologically active molecules [1], natural products (closthioamide) [2] and pharmaceuticals [3], with remarkable biological and medicinal properties, including antibacterial, and inhibitor properties [1–3]. Furthermore, many thioamides derivatives have demonstrated wide applications in diverse areas of science (fluorescence probes, supra molecular scaffolds, metal-ions sensors) [4], as well as building blocks in organic synthesis [5]. Consequently, considerable efforts have been devoted to the development of efficient methods for the preparation of thioamides and their derivatives [6]. However, the synthesis of trifluorothioacetamides is rarely reported [[7]] although the incorporation of CF_3 group into organic molecules often enhances their biological activity and has become a powerful strategy in drug design [8]. For example, some trifluorothioacetamide-containing peptides were reported as general tight-binding sirtuin probes [9], and some trifluorothioacetamides were used in antipsychotic disease drugs and pesticides [10]. Up to now, only two examples were applied to their synthesis, including the thionation of trifluoroacetamides with Lawesson's reagent (Scheme 1, eq. 1) [7a] and the nucleophilic addition of isothiocyanates with $TMSCF_3$ (eq. 2) [7b] Therefore, the development of efficient and practical strategy for the synthesis of trifluorothioacetamides, particularly from new sulfur and CF_3 source, remains highly desirable.

In environment field, the presence of large amounts of chlorofluorocarbons (CFCs) presents a major challenge, and Montreal Protocol was achieved to phase out CFCs and other substances which destroy stratospheric ozone [11]. Therefore, many efforts have been directed to the safe disposal of these compounds [12]. However, CFCs could also be considered as raw materials for various useful chemicals, and their transformation can provide an opportunity for their use. For example, trifluorotrichloroethane (CFC-113a), one of the most inexpensive and abundant industrial raw material, is commonly used for the preparation of various trifluoromethylated compounds (such as trifluoroacetic acid) [13]. In general, CFC-113a is a fluorine-containing C2 synthon which could be regarded as an ideal CF_3 group source for trifluoromethylated molecules. Herein, we wish to report a copper-catalyzed three component C–S/C—N coupling reaction of imines with CFC-113a and elemental sulfur, which represents a novel method for the practical synthesis of trifluorothioacetamides (eq. 3).

2. Results and discussion

2.1. Screening of optimal reaction conditions

We began investigation by examining the reaction of *N*, 1-diphenylmethanimine **1a** with S_8 and CFC-113a to screen the optimal reaction conditions, and the results are summarized in Table 1. Initially, the reaction was carried out in the presence of 10 mol % of CuI, 20 mol % of 1,10-phen, 2.0 equiv of K_3PO_4 in 1,4-dioxane at 120 °C, the product **2a** was isolated in 30 % yield (entry 1). Subsequently, a variety of copper

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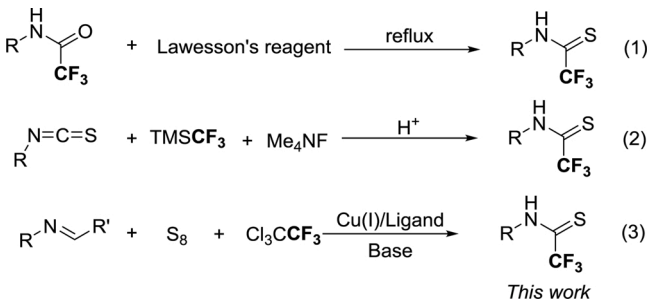
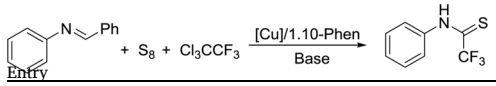


Scheme 1. Synthetic Methods for Trifluorothioacetamides.

Table 1
Screening of optimal reaction conditions[a].



Entry	[Cu]	Base	Solvent	Yield(%)[b]
1	CuI	K_3PO_4	Dioxane	30
2	CuBr	K_3PO_4	Dioxane	25
3	CuCl	K_3PO_4	Dioxane	45
4	CuTc	K_3PO_4	Dioxane	35
5	$CuCl_2$	K_3PO_4	Dioxane	30
6	–	K_3PO_4	Dioxane	NR
7	CuCl	K_3PO_4	DMF	20
8	CuCl	K_3PO_4	MeCN	23
9	CuCl	K_3PO_4	DCE	Trace
10	CuCl	K_2CO_3	Dioxane	40
11	CuCl	KOAc	Dioxane	35
12	CuCl	*t*-BuOK	Dioxane	25
13[c]	CuCl	K_3PO_4	Dioxane	62
14[d]	CuCl	K_3PO_4	Dioxane	55

[a] Reaction conditions: **1a** (0.2 mmol), S_8 (0.2 mmol), Cl_3CCF_3 (4.0 mmol), catalyst (10 mol %), 1.10-phen (20 mol %) and base (0.4 mmol) in solvent (2 mL) at 120 °C under air atmosphere for 4 h.
[b] Isolated yield.
[c] 100 mg anhydrous $MgSO_4$.
[d] 100 mg 4 Å MS.

catalysts were tested, including CuBr, CuCl, CuTc, $CuCl_2$ (entries 2–5). We found that CuCl provided the best results and a 45 % yield was obtained (entry 3), while the reaction did not work in the absence of copper catalyst (entry 6). Then, various solvents were screened, DMF, MeCN and DCE were found to be inferior to dioxane (entries 7–9). A range of bases were investigated, K_2CO_3, KOAc and *t*-BuOK were all found to afford lower yields (entry 10–12). To further improve reaction yield, anhydrous $MgSO_4$ and 4 Å MS were added into the reaction (entries 13–14), we found that anhydrous $MgSO_4$ provided the best results and a 62 % yield was obtained (entry 13).

2.2. Substrate scope of trifluorothioacetamides

With the optimized reaction conditions in hand, we next examined the substrate scope of the imines. Firstly, the substitute effect of a variety of electron-donating aryl group was investigated, and good functional group tolerance was observed. For example, *N*-4-tolyl and 2-tolyl phenylmethanimines gave target product **2b** and **2c** in 55 % and 50 % yields, respectively. 4-*tert*-Bu, 4-Ph, 4-PhO, 4-MeO and 4-MeS substituted imines afforded product **2d**–**2h** in 45 %–70 % yields. Halogenated phenyl was also compatible to produce halide *N*-phenyl trifluorothio-acetamides, which could provide potential handles for further modification. Iodide product **2i** and bromide product **2j** were isolated in 55 % and 62 % yields, respectively. Chloride and fluoride thioamides **2k**–**2m** were also obtained in 59 %–62 % yields. Subsequently, strong electron-withdrawing group was examined and good yields were found for methoxycarbonyl and trifluoromethyl (**2n**, 71 % and **2o**, 68 %). Gratifyingly, N-naphthalen-1-yl phenylmethanimines underwent the reaction smoothly to provide product **2p** in 67 % yield. During the test of *N*-alkyl imines, we were pleased to find that *N*-phenylethyl thioamide **2q** was isolated as sole product, albeit in moderate yield (45 %). The similar results were also observed for *N*-cyclopentyl thioamide **2r** (31 %). The practicality of this procedure was further applied to tetrahydroisoquinolines, which were easily oxidized to 3,4-dihydroisoquinolines bearing imine moiety in the presence of CuCl and O_2 [14]. We were delighted to found that they were also suitable substrates for this reaction. 1,2,3,4-Tetrahydroisoquinoline, for instance, was conducted under standard conditions to afford desired product **2 s** in 78 % yield. Moreover, the structure of product **2 s** was confirmed by X-ray crystallography (Fig. 1). Finally, 6,7-dimethoxy and 7-bromo-substituted tetrahydroisoquinolines were also transformed to the corresponding thioamides **2t** and **2u** in 79 % and 60 % yields (Table 2).

In order to further understand the mechanism of this reaction, we conducted a series of control experiments (Scheme 2). When aniline was used in the reaction instead of imine under standard conditions, only trifluoroacetamide **3** was isolated in 27 % yield and the desired product **2a** could not be detected (eq. 4). Moreover, the reaction of **3** with sulfur did not work under standard reaction conditions (eq. 5). These results demonstrated that the product **2a** might not be produced through the hydrolysis of imine or the thiolation transformation of carbonyl into thiocarbonyl. The compound **3** was isolated in 35 % yield when substrate **2a** was treated with 0.1 ml H_2O under standard reaction conditions (eq. 6), indicating that water could promote the hydrolysis of product **2** to form trifluoroacetamide. Furthermore, the reaction of substrate **1 s** was conducted with 0.1 ml $H_2^{18}O$ under standard reaction conditions (eq. 7). A mixture of the product ^{18}O-**2s** and ^{16}O-**2s** was isolated in 65 % yield with a 52:48 ratio and was confirmed by HRMS, which suggested that a hydrolysis process occurred in the three component C–S/C-N coupling reaction.

2.3. Possible mechanism

On the basis of the obtained results and related precedents [6d], a possible mechanism is proposed as outlined in Scheme 3. In the presence of CuCl and base, CF_3CCl_3 is decomposed to yield carbine :$CClCF_3$ under high temperature [15], which is combined with sulfur to produce trifluorothioacetyl chloride **A** (confirmed by ^{19}F NMR) [16]. The coordination of imine **1a** with CuCl affords complex **B** [17], which undergo an oxidative addition with trifluorothioacetyl chloride **A** to provide Cu (III) complex **C** [18]. The following reductive elimination gives intermediate **D**. However, the path of direct nucleophilic substitution of **1a** with **A** to generate **D** can not be ruled out. Finally, the hydrolysis of imine ion **D** affords product **2a**, benzaldehyde and hydrogen proton, which undergo neutralization with base to regenerate water.

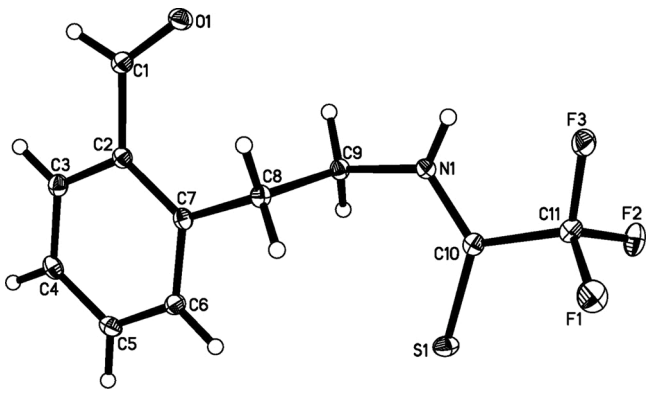
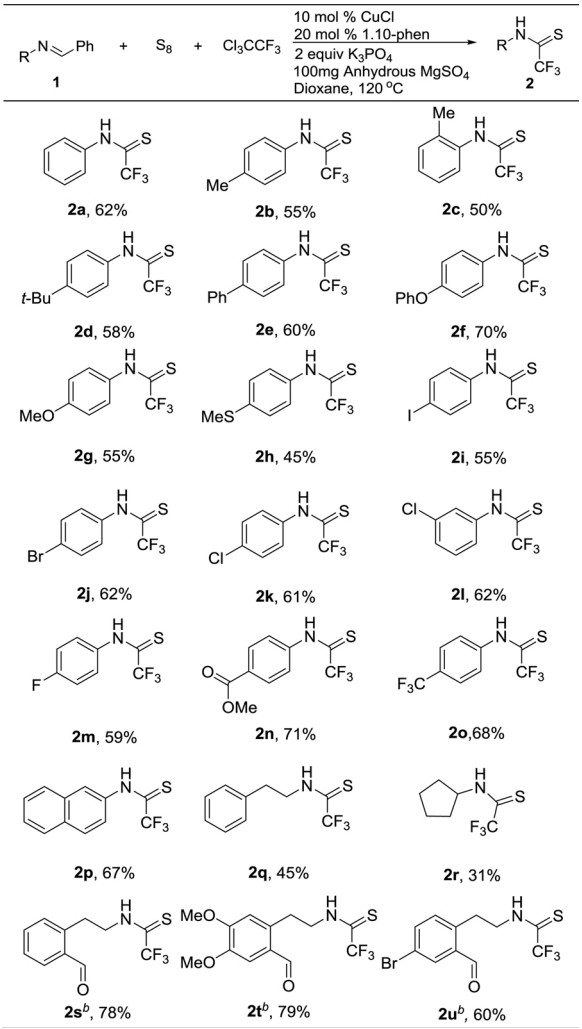
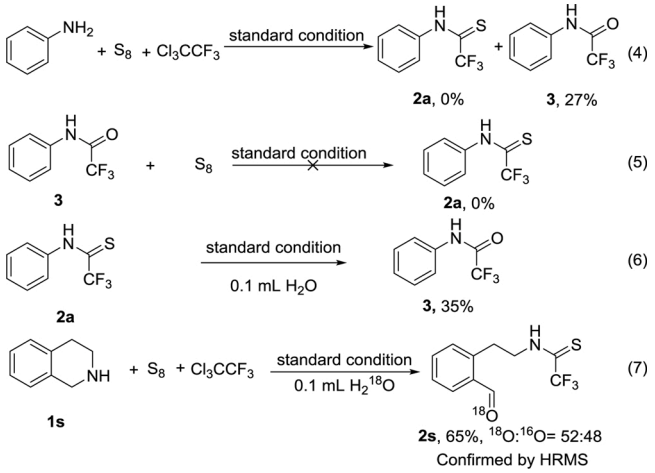


Fig. 1. X-ray crystal structure of compound **2 s**.

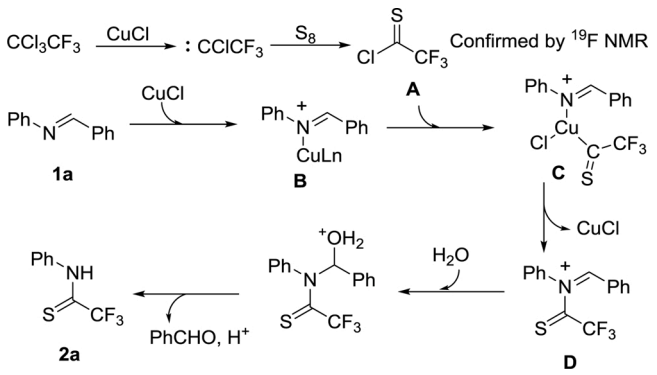
Table 2
Substrate scope of trifluorothioacetamides.



[a]Reaction conditions: **1** (0.2 mmol), S_8 (0.2 mmol), Cl_3CCF_3 (4.0 mmol), CuCl (10 mol %), 1.10-phen (20 mol %), anhydrous $MgSO_4$ (100 mg) and K_3PO_4 (0.4 mmol) in 1,4-dioxane (2 mL) at 120 °C under air atmosphere for 4 h., isolated yields.
[b]For 12 h.



Scheme 2. Control Experiments.



Scheme 3. Possible mechanism.

3. Conclusion

In summary, we have discovered copper-catalyzed three component C–S/C-N coupling reaction of imines with sulfur and CF_3CCl_3. A variety of imines including *N*-aryl or alkyl phenylmethanimines and tetrahydroisoquinolines underwent the coupling reaction successfully to afford the corresponding trifluorothioacetamides in moderate to good yields. The use of inexpensive sulfur and CFC-113a as trifluorothioacetyl group source is a significant practical advantage. The present reaction can be used for the synthesis of trifluoromethylated molecules from cheap commerce-available materials, and it also provided a new safe disposal method for environmentally persistent Freon.

4. Experimental section

4.1. General information

Chemicals were either purchased or purified by standard techniques. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on 500 or 400 MHz spectrometer (400 MHz for ^1H, 125 MHz for ^{13}C, 470 MHz for ^{19}F), using $CDCl_3$ as the solvent with trimethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS, the coupling constants *J* are given in hertz. High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometry. All reactions under air atmosphere were conducted using standard Schlenk techniques. Melting points were measured on WRS-1B melting point apparatus. Infrared data was measured by Bruker Vector-55. Column chromatography was performed using EM Silica gel 60 (300–400 mesh).

4.2. General procedure for the synthesis of trifulorothioamides

To a flame-dried Schlenk tube with a magnetic stirring bar was charged with S_8 (51.2 mg, 0.2 mmol), Cl_3CCF_3 (749.6 mg; 4.0 mmol), CuCl (1.98 mg; 0.02 mmol), 1,10-phen (7.2 mg; 0.04 mmol), K_3PO_4 (51.3 mg; 0.4 mmol) and anhydrous $MgSO_4$ (100 mg) and 1,4-dioxane (2 mL). The reaction mixture was stirred at 120 °C until complete consumption of the starting material as detected by TLC or GC–MS analysis. After the reaction was complete, the mixture was poured into ethyl acetate and evaporated under vacuum. The resulting crude product was purified by flash column chromatography on silica gel using petroleum ether/methylene chloride (10:1) as the eluent to give the pure products **2a-2 u**.

2,2,2-trifluoro-N-phenylethanethioamide **(2a)** [7b]: Yellow oil. (25.4 mg, 62 % yield); ^1H NMR (500 MHz, $CDCl_3$) δ 9.24 (s, 1 H), 7.66 (d, J =8.0 Hz, 2 H), 7.36 (d, J =7.5 Hz, 2 H), 7.27 – 7.24 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.4 (q, J =35.0 Hz), 136.5, 129.3, 128.1, 123.1, 117.4 (q, J =279.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.75 (s); IR (thin film) ν_{max} 3405, 1163, 829, 715. LRMS (EI, 70 eV) *m/z* (%): 205 (M^+, 85), 204 (100), 184 (34), 77 (66).

2,2,2-trifluoro-N-(p-tolyl)ethanethioamide **(2b)** [19a]: Yellow solid (24.1 mg, 55 % yield), mp 54.9–55.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.30 (s, 1 H), 7.62 (d, J =8.0 Hz, 2 H), 7.25 (d, J =8.0 Hz, 2 H), 2.37 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.2 (q, J =35.0 Hz), 138.3, 134.0, 129.9, 123.0, 117.5 (q. J = 279.0 Hz), 21.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.72 (s); IR (thin film) ν_{max} 3409, 2911, 1507, 1158, 823, 710. LRMS (EI, 70 eV) *m/z* (%): 219 (M^+, 100), 198 (30), 150 (26), 91 (88).

2,2,2-trifluoro-N-(o-tolyl)ethanethioamide **(2c)** [19b]: Yellow oil. (21.9 mg, 50 % yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (s, 1 H), 7.59 – 7.43 (m, 1 H), 7.24 (d, J =6.5 Hz, 3 H), 2.21 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.3 (q, J =35.0 Hz), 134.7, 133.5, 131.3, 128.9, 127.0, 125.6, 117.6 (q, J = 279.0 Hz), 17.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.59 (s); IR (thin film) ν_{max} 3411, 2901, 1163, 818, 721. LRMS (EI, 70 eV) *m/z* (%): 219 (M^+, 41), 204 (100), 184 (34), 166 (14).

N-(4-(tert-butyl)phenyl)-2,2,2-trifluoroethanethioamide **(2d)**: Yellow oil. (30.3 mg, 58 % yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.28 (s, 1 H), 7.70 (d, J =8.5 Hz, 2 H), 7.46 (d, J =8.5 Hz, 2 H), 1.33 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.8 (q, J =35.0 Hz), 151.4, 134.0, 126.2, 122.5, 117.5 (q, J = 279.0 Hz), 34.8, 31.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.74 (s); LRMS (EI, 70 eV) *m/z* (%): 261 (M^+, 41), 246 (100), 106 (81), 123 (25); IR (thin film) ν_{max} 3408, 2914, 1507, 1159, 835, 712. HRMS (ESI) Calcd for $C_{12}H_{15}F_3NS^+$ ($[M+H]^+$) 262.0872, Found: 262.0865.

N-([1,1′-biphenyl]-4-yl)-2,2,2-trifluoroethanethioamide **(2e):** Yellow solid. (33.7 mg, 60 % yield), mp 107.5–108.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.26 (s, 1 H), 7.78 (d, J =8.5 Hz, 2 H), 7.58 (d, J =8.5 Hz, 2 H), 7.51 (d, J =7.5 Hz, 2 H), 7.39 – 7.36 (m, 2 H), 7.31 – 7.28 (m, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.0 (q, J =35.0 Hz), 141.0, 139.8, 135.7, 129.0, 127.9, 127.8, 127.1, 123.1, 117.5 (q, J =279.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.68 (s); LRMS (EI, 70 eV) *m/z* (%): 281 (M^+, 100), 212 (18), 185 (34), 152 (70); IR (thin film) ν_{max} 3406, 1340, 1166, 834, 719. HRMS (ESI) Calcd for $C_{14}H_{11}F_3NS^+$ ($[M+H]^+$) 282.0559, Found: 282.0563.

2,2,2-trifluoro-N-(4-phenoxyphenyl)ethanethioamide **(2f)**: Yellow solid. (41.6 mg, 70 % yield), mp 46.3–47.7 °C ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.24 (s, 1 H), 7.61 (d, J =9.0 Hz, 2 H), 7.29 – 7.26 (m, 2 H), 7.08 – 7.05 (m, 1 H), 6.99 – 6.87 (m, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.2 (q, J =35.0 Hz), 156.9, 156.3, 131.3, 130.0, 124.8, 124.2, 119.6, 118.7, 117.5 (q, J = 279.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.60 (s); LRMS (EI, 70 eV) *m/z* (%): 297 (M^+, 100), 264 (28), 141 (32), 77 (53); IR (thin film) ν_{max} 3421, 1178, 1050, 833, 709. HRMS (ESI) Calcd for $C_{14}H_{10}F_3NOSNa^+$ ($[M + Na]^+$) 320.0327, Found: 320.0325.

2,2,2-trifluoro-N-(4-methoxyphenyl)ethanethioamide **(2 g)** [19b]: Yellow oil. (25.9 mg, 55 % yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (s, 1 H), 7.63 (d, J =9.0 Hz, 2 H), 6.94 (d, J =9.0 Hz, 2 H), 3.81 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.6 (q, J =35.0 Hz), 158.9, 129.4, 124.8, 117.6 (q, J = 279.0 Hz), 114.4, 55.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.61 (s); IR (thin film) ν_{max} 3401, 2810, 1507, 1174, 1013, 829, 713. LRMS (EI, 70 eV) *m/z* (%): 235 (M^+, 100), 202 (30), 166 (21), 125 (22).

2,2,2-trifluoro-N-(4-(methylthio)phenyl)ethanethioamide **(2 h)**: Yellow oil. (22.6 mg, 45 % yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (s, 1 H), 7.60 (d, J =8.5 Hz, 2 H), 7.19 (d, J =8.5 Hz, 2 H), 2.41 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.9 (q, J =35.0 Hz), 139.0, 133.5, 126.6, 123.4, 117.4 (q, J = 279.0 Hz), 15.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.63 (s); LRMS (EI, 70 eV) *m/z* (%): 251 (M^+, 100), 218 (22), 182 (15), 141 (23). IR (thin film) ν_{max} 3406, 2935, 1162, 835, 716. HRMS (ESI) Calcd for $C_9H_8F_3NS_2Na^+$ ($[M+H]^+$) 273.9942, Found: 273.9942.

2,2,2-trifluoro-N-(4-iodophenyl)ethanethioamide **(2i)** [19b]: Yellow solid. (36.3 mg, 55 % yield), mp 81.4–82.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (s, 1 H), 7.67 (d, J =8.5 Hz, 2 H), 7.46 (d, J =8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.4 (q, J =35.0 Hz), 138.4, 136.2, 124.6, 117.3 (q, J = 279.0 Hz), 92.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.68 (s); IR (thin film) ν_{max} 3421, 1178, 1050, 833, 709. LRMS (EI, 70 eV) *m/z* (%): 331 (M^+, 100), 262 (14), 202 (28), 109 (35).

N-(4-bromophenyl)-2,2,2-trifluoroethanethioamide **(2 j)** [19b]: Yellow solid. (35.1 mg, 62 % yield), mp 46.1–47.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (s, 1 H), 7.59 – 7.57 (m, 2 H), 7.49 – 7.47 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.5 (q, J =35.0 Hz), 135.5, 132.5, 124.6, 121.2, 117.4 (q, J = 279.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.72 (s); IR (thin film) ν_{max} 3425, 1175, 1061, 832, 713. LRMS (EI, 70 eV) *m/z* (%): 283/285 (M^+, 95), 234 (100), 157 (35), 109 (54).

N-(4-chlorophenyl)-2,2,2-trifluoroethanethioamide **(2k)** [19b]: Yellow oil. (29.1 mg, 61 % yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (s, 1 H), 7.65 (d, J =8.5 Hz, 2 H), 7.34 (d, J =8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.6 (q, J =35.0 Hz), 134.0, 132.4, 128.5, 123.3, 116.3 (q, J = 279.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.74 (s); IR (thin film) ν_{max} 3413, 1169, 1086, 835, 716. LRMS (EI, 70 eV) *m/z* (%): 239 (M^+, 100), 218 (23), 144 (40), 111 (51).

N-(3-chlorophenyl)-2,2,2-trifluoroethanethioamide **(2 l)**: Yellow oil. (29.6 mg, 62 % yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.19 (s, 1 H), 7.81 (s, 1 H), 7.52 (d, J =8.0 Hz, 1 H), 7.32 – 7.29 (m, 1 H), 7.24 (d, J =8.0 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.7 (q, J =35.0 Hz), 137.5, 135.0, 130.3, 128.2, 123.1, 121.2, 118.3 (q, J = 279.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.77 (s); LRMS (EI, 70 eV) *m/z* (%): 239 (M^+, 79), 238 (100), 218 (25), 170 (32), 110 (58); IR (thin film) ν_{max} 3413, 1165, 1089, 832, 711. HRMS (ESI) Calcd for $C_8H_6ClF_3NS^+$ ($[M+H]^+$) 239.9856, Found: 239.9854.

2,2,2-trifluoro-N-(4-fluorophenyl)ethanethioamide **(2 m)** [7b]: Yellow oil. (26.3 mg, 59 % yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.34 (s, 1 H), 7.72 – 7.69 (m, 2 H), 7.15 – 7.12 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.0 (q, J =35.0 Hz), 161.4 (d, J =248.0 Hz), 132.4 (d, J =3.0 Hz), 125.4 (d, J =8.5 Hz), 117.4 (q, J = 279.0 Hz), 116.3 (d, J =23.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.71 (s, 3 F), -111.77 (s, 1 F); IR (thin film) ν_{max} 3423, 1152, 1057, 836, 711. LRMS (EI, 70 eV) *m/z* (%): 223 (M^+, 100), 202 (30), 154 (46), 95 (56).

methyl 4-(2,2,2-trifluoroethanethioamido)benzoate **(2n)**: Yellow solid. (37.3 mg, 71 % yield), mp 118.5–119.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.80 (s, 1 H), 8.09 (d, J =8.5 Hz, 2 H), 7.95 (d, J =8.5 Hz, 2 H), 3.92 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.6 (q, J =35.0 Hz), 166.3, 140.7, 130.7, 129.1, 122.4, 117.2 (q, J = 279.0 Hz), 52.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.68 (s); LRMS (EI, 70 eV) *m/z* (%): 263 (M^+, 85), 262 (100), 248 (41), 232 (28), 137 (40); IR (thin film) ν_{max} 3435, 2941, 1763, 1163, 835, 712. HRMS (ESI) Calcd for $C_{10}H_9F_3NO_2S^+$ ($[M+H]^+$) 264.0301, Found: 264.0301.

2,2,2-trifluoro-N-(4-(trifluoromethyl)phenyl)ethanethioamide **(2o)** [19b]: Yellow oil. (37.1 mg, 68 % yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (s, 1 H), 7.85 (d, J =8.5 Hz, 2 H), 7.60 (d, J =8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.4 (q, J =35.0 Hz), 139.4, 129.7 (q, J =33.0 Hz), 126.5 (q, J =3.8 Hz), 123.6 (q, J =271.0 Hz), 123.0, 117.2 (q, J = 279.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.69 (s, 3 F), -69.87 (s, 3 F); IR (thin film) ν_{max} 3445, 1480, 1155, 834, 716. LRMS (EI, 70 eV) *m/z* (%): 273 (M^+, 91), 272 (100), 252 (41), 204 (45), 177 (24).

2,2,2-trifluoro-N-(naphthalen-2-yl)ethanethioamide **(2p)**: Yellow solid. (34.2 mg, 67 % yield), mp 96.7–97.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.41 (s, 1 H), 8.53 (d, J =2.0 Hz, 1 H), 7.89 (d, J =8.5 Hz, 1 H), 7.86 – 7.83 (m, 2 H), 7.61 – 7.59 (m, 1 H), 7.55 – 7.51 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.2 (q, J =35.0 Hz), 133.9, 133.2, 132.4, 129.3, 128.2, 127.8, 127.1, 126.9, 121.3, 121.0, 117.5 (q, J = 279.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.67 (s); LRMS (EI, 70 eV) *m/z* (%): 255 (M^+, 100), 234 (23), 127 (76), 115 (38); IR (thin film) ν_{max} 3421, 1147, 826, 706. HRMS (ESI) Calcd for $C_{12}H_9F_3NS^+$ ($[M+H]^+$) 256.0402, Found: 256.0399.

2,2,2-trifluoro-N-phenethylethanethioamide **(2q)**: Yellow oil. (21.0 mg, 45 % yield) ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1 H), 7.27 – 7.25 (m, 2 H), 7.20 – 7.17 (m, 1 H), 7.13 – 7.12 (d, J =7.5 Hz, 2 H), 3.87 – 3.83 (m, 2 H), 2.94 – 2.91 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.3 (q, J =35.0 Hz), 137.3, 129.0, 128.7, 127.2, 117.3 (q, J =278.0 Hz), 46.6, 33.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.95 (s); LRMS (EI, 70 eV) *m/z* (%): 233 (M^+, 11), 104 (100), 91 (26), 78 (11); IR (thin film) ν_{max} 3441, 2916, 1156, 837, 717. HRMS (ESI) Calcd for $C_{10}H_{11}F_3NS^+$ ($[M+H]^+$) 234.0559, Found: 234.0566.

N-cyclopentyl-2,2,2-trifluoroethanethioamide **(2 r)**: Yellow oil. (12.2 mg, 31 % yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1 H), 4.59

–4.55 (m, 1 H), 2.23 – 2.02 (m, 2 H), 1.82 – 1.57 (m, 4 H), 1.52 – 1.48 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.3 (q, J =35.0 Hz), 117.3 (q, J =278.0 Hz), 57.2, 31.9, 24.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.88 (s); LRMS (EI, 70 eV) *m/z* (%): 197 (M^+, 100), 154 (17), 130 (57), 113 (22), 67 (47); IR (thin film) ν_{max} 3420, 2935, 1171, 829, 711. HRMS (ESI) Calcd for $C_7H_{10}F_3NSNa^+$ ($[M+H]^+$) 220.0378, Found: 220.0379.

2,2,2-trifluoro-N-(2-formylphenethyl)ethanethioamide **(2 s)**: Yellow solid. (40.7 mg, 78 % yield), mp 84.5–85.9 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.09 (s, 1 H), 9.16 (s, 1 H), 7.80 (d, J =7.5 Hz, 1 H), 7.62 – 7.59 (m, 1 H), 7.54 – 7.51 (m, 1 H), 7.38 (d, J =7.5 Hz, 1 H), 3.95 – 3.92 (m, 2 H), 3.42–3.90 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.3, 183.5 (q, J =35.0 Hz), 139.7, 135.6, 134.5, 134.4, 132.2, 127.9, 117.3 (q, J =278.0 Hz), 47.8, 30.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.86 (s); LRMS (EI, 70 eV) *m/z* (%): 261 (M^+, 12), 132 (100), 113 (30), 104 (75); IR (thin film) ν_{max} 3416, 2935, 1701, 1171, 835, 706. HRMS (ESI) Calcd for $C_{11}H_{11}F_3NOS^+$ ($[M+H]^+$) 262.0508, Found: 262.0507.

2,2,2-trifluoro-N-(2-formyl-4,5-dimethoxyphenethyl)ethanethioamide **(2 t)**: White solid. (50.7 mg, 79 % yield), mp 110.5–111.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1 H), 9.27 (s, 1 H), 7.24 (s, 1 H), 6.79 (s, 1 H), 3.97 (s, 3 H), 3.95 (s, 3 H), 3.94 –3.91 (m, 2 H), 3.39 – 3.37 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 183.5 (q, J =35.0 Hz), 154.0, 148.3, 134.7, 127.2, 117.3 (q, J =278.0 Hz), 116.6, 114.3, 56.3, 56.2, 48.0, 29.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -69.81 (s); LRMS (EI, 70 eV) *m/z* (%): 321 (M^+, 13), 192 (100), 164 (81), 149 (42); IR (thin film) ν_{max} 3405, 2916, 2802, 1730, 1160, 828, 709. HRMS (ESI) Calcd for $C_{13}H_{15}F_3NO_3S^+$ ($[M+H]^+$) 322.0719, Found: 322.0717.

N-(4-bromo-2-formylphenethyl)-2,2,2-trifluoroethanethioamide **(2 u)**: Yellow solid. (40.7 mg, 60 % yield), mp 141.2–141.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1 H), 8.92 (s, 1 H), 7.92 (d, J =2.0 Hz, 1 H), 7.73 – 7.71 (m, 1 H), 7.26 (d, J =8.0 Hz, 1 H), 3.94 – 3.90 (m, 2 H), 3.37 – 3.34 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.2, 178.4 (q, J =35.5 Hz), 133.2, 132.6, 132.1, 130.6, 128.5, 116.4, 112.1 (q, J = 278.0 HZ), 41.9, 24.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -75.06 (s); LRMS (EI, 70 eV) *m/z* (%): 389/341 (M^+, 8), 307 (15), 210 (100), 182 (72), 113 (65); IR (thin film) ν_{max} 3391, 2910, 1066, 1715, 1154, 830, 713. HRMS (ESI) Calcd for $C_{11}H_{10}BrF_3NOS^+$ ($[M+H]^+$) 339.9613, Found: 339.9613.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

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