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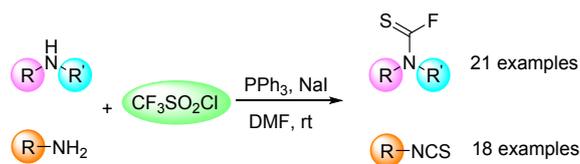
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Synthesis of Thiocarbamoyl Fluorides and Isothiocyanates using Amines with $\text{CF}_3\text{SO}_2\text{Cl}$

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ABSTRACT: A practical and efficient produce to synthesize thiocarbamoyl fluorides and isothiocyanates from amines with trifluoromethanesulfonyl chloride was developed. In the presence of reducing agent triphenylphosphine and sodium iodide, secondary amines/primary amines method thiocarbamoyl fluorides and isothiocyanates in moderate to excellent yields, respectively. A broad scope of substrates and good functional group compatibility were observed.



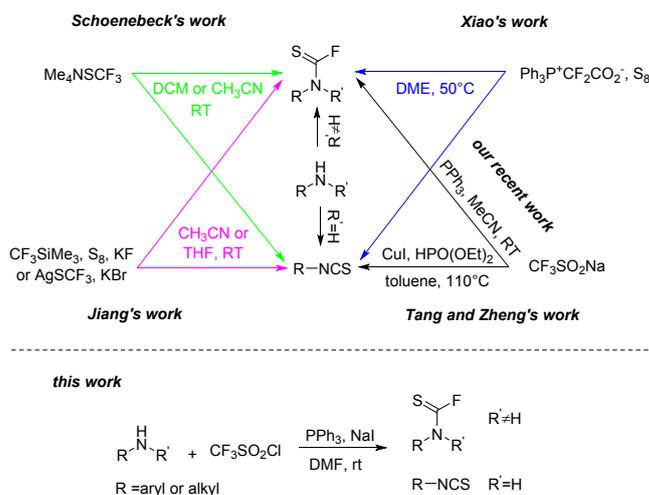
INTRODUCTION

Organofluorine compounds are important in pharmaceutical chemistry and agrochemistry because of their special chemical and biological properties.¹ In recent years, the synthesis of thiocarbamoyl fluoride has received much attention owing to the special structure, which contains nitrogen, sulfur and fluorine elements, makes it have enormous potential applications in the pharmaceuticals field.² Isothiocyanates are important organic compounds that are widely present in drugs, natural products, and material molecules.³ As one of the most important classes of organic compounds, they are widely used in biological fields and synthetic chemistry.⁴ Considering the wide applications of isothiocyanates, the use of simple and efficient methods to construct the $-\text{NCS}$ group in molecules is of great significance for the pharmaceutical and agrochemical industries. Thus, the development of synthetic methods for the synthesis of those compounds under mild conditions is highly desired.

In the last years, several strategies have been reported for the synthesis of thiocarbamoyl fluoride and/or isothiocyanates from secondary amines and/or primary amines. Until now, there are about five reagents has been development for the simultaneous synthesis of thiocarbamoyl fluorides and isothiocyanates. In 2017, the group of Schoenebeck demonstrated that amines react with Me_4NSCF_3 furnishing thiocarbamoyl fluorides and/or isothiocyanates at room temperature, respectively (Scheme 1).⁵ Afterwards the group of Xiao reported reaction of thiocarbonyl fluoride generated from $\text{Ph}_3\text{P}^+\text{CF}_2\text{CO}_2^-$, S_8 with amines (Scheme 1).⁶ Recently, Jiang's group⁷ described two pathways to access thiocarbamoyl fluorides and isothiocyanation by using CF_3SiMe_3 , S_8 , KF or AgSCF_3 , KBr (Scheme 1). Although Zheng's group⁸ has reported that Langlois reagent ($\text{CF}_3\text{SO}_2\text{Na}$) can also participate in isothiocyanation of primary amines in the presence of $\text{CuI}/\text{HPO}(\text{OEt})_2$ in 2017, a mild method for the synthesise of thiocarbamoyl fluoride using $\text{CF}_3\text{SO}_2\text{Na}$ and triphenylphosphine has recently

been reported by our group (Scheme 1)⁹. With our continuous interest in exploring construction of N-C bonds, we thought the development of efficient methods by cheap material would constitute an attractive option for the access of thiocarbamoyl fluorides and isothiocyanates.

Scheme 1. Synthetic strategies for Thiocarbamoyl Fluorides/Isothiocyanates.



Trifluoromethanesulfonyl chloride ($\text{CF}_3\text{SO}_2\text{Cl}$), as a easy-to-handle and commercially available cheap material, has been widely used in the formation of sulfonamides and sulfonic esters,¹⁰ and also in electrophilic chlorination,¹¹ trifluoromethylation or trifluoromethyl-chlorosulfonylation etc.¹² Our group has reported its application in the electrophilic trifluoromethylthiolation of indoles, pyrroles, enamines and chloro-trifluoromethylthiolation of alkenes and alkynes.¹³ In this context, we envisioned that straightforward synthesis of thiocarbamoyl fluoride and isothiocyanates by $\text{CF}_3\text{SO}_2\text{Cl}$ can be achieved under suitable reductive conditions, we herein disclose a novel use of trifluoromethanesulfonyl chloride to prepare thiocarbamoyl fluoride and isothiocyanates.

RESULTS AND DISCUSSION

We initially investigated the treatment of *N*-methylaniline **1a** with $\text{CF}_3\text{SO}_2\text{Cl}$ **2a** (1.5 equiv) in the presence of PPh_3 (3.0 equiv) in DMF at r.t. to yield the thiocarbamoyl fluorides product **3a** in 18% yield (Table 1, entry 1). Encouraged by this result, optimisation of the reaction conditions was then carried out. Considering that iodide anion can promote the reduction of sulfonyl chloride,¹⁴ a series of iodide sources including KI, NH_4I , NaI , and I_2 were tested (Table 1, entries 2–6). and among them NaI giving the highest yield (47%, Table 1, entry 4). When KI and NH_4I was used as the catalyst, the product **3a** was obtained in 40% and 35% yield, respectively (Table 1, entries 2, 3), I_2 did not increase the yield obviously (Table 1, entry 5). Increasing the loadings of NaI to 1.5 equiv increase the product yield to 88% (Table 1, entries 6, 7). We next examined the effect of solvents on yield. After several solvents were screened, DMF proved to be the best option in the transformation. Other solvents such as MeCN, THF, and 1,2-dichloroethane were less effective for this kind of reaction (Table 1, entries 8-12). When the amount of $\text{CF}_3\text{SO}_2\text{Cl}$ **2a** is reduced to 1.2 equiv, the yield will be reduced to 61% (Table 1, entries 13). Thus, 1:1.5:3:1.5 amine/ $\text{CF}_3\text{SO}_2\text{Cl}$ / PPh_3 / NaI in DMF at r.t. for 4 h was selected as the optimized reaction conditions. Notably, the present reaction is scalable, and 1.25 g (74%) of **3a** was isolated when the reaction was performed on a 10 mmol scale (Table 1, entry 14).

Table 1. Optimization of reaction conditions^a

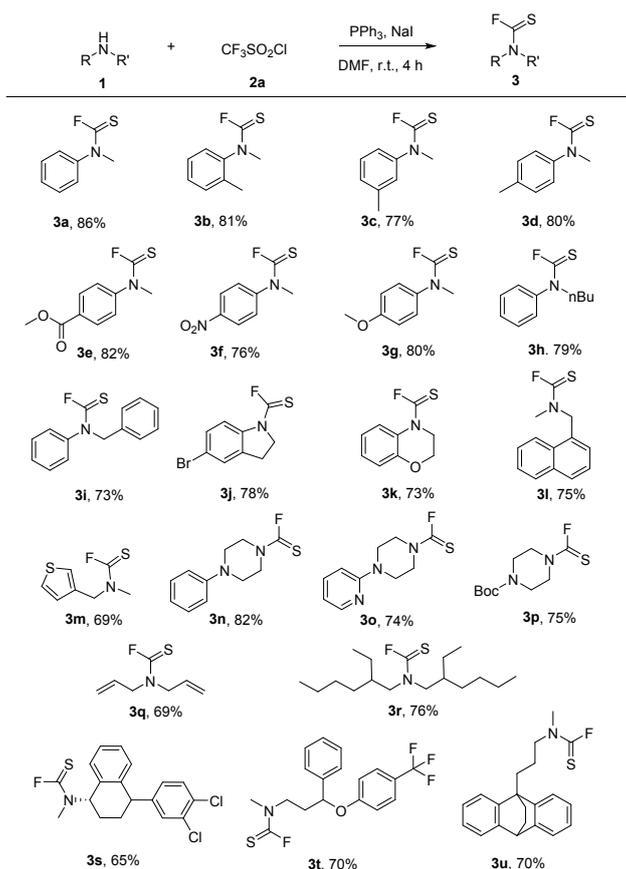
entry	additive (equiv)	solvent	yield(%) ^[b]
1	-	DMF	18
2	KI (0.5)	DMF	40

3	NH ₄ I (0.5)	DMF	35
4	NaI (0.5)	DMF	47
5	I ₂ (0.5)	DMF	13
6	NaI (1.0)	DMF	68
7	NaI (1.5)	DMF	88
8	NaI (1.5)	MeCN	22
9	NaI (1.5)	THF	41
10	NaI (1.5)	1,4-dioxane	trace
11	NaI (1.5)	DCE	40
12	NaI (1.5)	AcOH	18
13	NaI (1.5)	DMF	61 ^[c]
14	NaI (1.5)	DMF	74 ^[d]

^aReaction conditions: N-methylaniline (0.5 mmol), CF₃SO₂Cl (0.75 mmol), PPh₃ (1.5 mmol), DMF (2.5 mL), r.t. for 4h. ^bYield determined by ¹⁹F NMR using *p*-fluorotoluene as an internal standard on crude products. ^cCF₃SO₂Cl (0.6 mmol), PPh₃ (1.2 mmol) was used. ^dYield was obtained at 10 mmol scale.

With the optimized reaction conditions in hand, we next investigated the substrate scope. Various secondary amines, including N-phenyl (**3a–3k**), N-benzyl (**3l–3m**) and N-alkyl (**3n–3r**) amines, were converted into the corresponding thiocarbamoyl fluorides with good yields (Scheme 2). Substrates bearing electron-donating and electron-withdrawing substituents on aryl rings also proceeded well. A good range of functional groups, including ester (**3e**), nitro (**3f**), ether (**3g**), and bromide (**3j**), were well tolerated under the mild reaction conditions. The conversion is not particularly sensitive to steric effects, as evidenced by the good yields of **3b**, **3c**, and **3d**. Notably, heterocyclic and heterocycle-containing amines and amino acid derivative were also successfully employed to provide the corresponding products in 71–83% yields (**3m–3p**). Alkyl amines (**3q**, **3r**) were also suitable for this reaction. It was worth mentioning that products **3s–3u**, which are the thiocarbamoyl fluorides of the drug-like molecules, was obtained without affecting the core structure of these molecules. Indeed antidepressants such as sertraline and fluoxetine proceeded smoothly to provide the corresponding product **3s** and **3t** with yields 69% and 70%, respectively. Maprotiline, bearing an alkyl chain amine group, was also successfully transformed (**3u**).

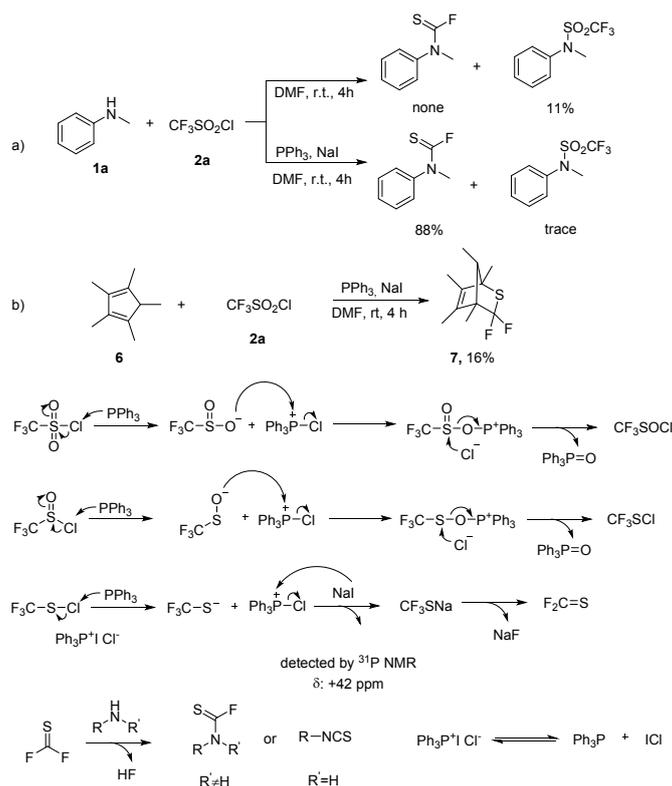
Scheme 2. Scope of secondary amines^a



^aReaction conditions: secondary amine (0.5 mmol), $\text{CF}_3\text{SO}_2\text{Cl}$ (0.75 mmol), PPh_3 (1.5 mmol), NaI (0.75 mmol) in DMF (2.5 mL) at r.t. for 4h; isolated yields.

The successful reaction of $\text{CF}_3\text{SO}_2\text{Cl}$ with secondary amines prompted us to investigate its reaction with primary amines, to our delight, the protocol was also efficient for the primary amines to form isothiocyanates (Scheme 3). A variety of primary amines with electron-donating or electron-withdrawing groups conducted under the optimized condition and proceeded in good yields. Para-substituted amines with functional groups such as fluoride (**5d**), chloride (**5e**), bromine (**5f**), phenyl (**5g**), methoxy (**5h**), alkynyl (**5i**), cyano (**5j**), and nitro (**5k**) groups reacted to generate the corresponding products with yields ranging from 77% to 86%. Pyridin-3-amine was also applied in the reaction successfully to afford **5l** with satisfactory results. Then alkyl amines were also investigated, affording the corresponding isothiocyanate products **5m-5o** in moderate yields. In particular, antiviral and antiparkinsonian drug amantadine was also tolerated (**5o**). Moreover, intramolecular thiocarbamides (**5p-5r**) could also be obtained from the corresponding amines.

Scheme 3. Scope of primary amines^a



CONCLUSIONS

In summary, we have developed a convenient method for the synthesis of thiocarbamoyl fluorides and isothiocyanates with amines using trifluoromethanesulfonyl chloride. The reaction system consists of a reducing agent, PPh_3 and NaI , all reagents used in this process were widely available, and the reactions occurred smoothly under mild conditions. The highly efficient and concise nature of the reaction process along with the mild conditions employed, are the major advantages of this new method.

EXPERIMENTAL SECTION

General information

All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are identified by appropriate technique such as ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, ^{19}F NMR and compared with previously reported data. All unknown compounds are characterized by ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, ^{19}F NMR and HRMS. Analytical thin-layer chromatography is performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{19}F NMR spectra were recorded on a 500 MHz Bruker DRX 500 and tetramethylsilane (TMS) was used as a reference. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0). and chemical shifts are reported in ppm. GC-MS data was recorded on a ISQ LT Single Quadrupole Mass Spectrometer, coupled with a Trace 1300 Gas Chromatograph (Thermo Fisher Scientific). Melting points were measured on a melting point apparatus and were uncorrected. High resolution mass spectral data were acquired on Waters Micromass GCT Premier spectrometer (electro ionization: EI) and Waters Q-ToF microTM (electrospray ionization: ESI).

A typical procedure for preparation of thiocarbamoyl fluorides or isothiocyanates

A 10 mL oven-dried reaction vessel was charged with PPh_3 (1.5 mmol, 393 mg, 3 equiv.) and NaI (0.75

mmol, 112.5 mg, 1.5 equiv.) under N₂, *N*-Methylaniline (0.5 mmol, 54 mg, 1.0 equiv.) was dissolved in DMF (1.25 mL) and the solution was added to the vessel by syringe, CF₃SO₂Cl (0.75 mmol, 126 mg, 1.5 equiv.) was dissolved in DMF (1.25 mL) and the solution was added to the vessel by syringe. The resulting solution was stirred at room temperature for 4h. After that, the reaction mixture was diluted with water and extracted with CH₂Cl₂, the organic layers were washed with brine and concentrated under reduced pressure. Then the residue was purified by column chromatography to give the corresponding products.

A typical procedure of gram-scale synthesis for thiocarbamoyl fluorides

In a 150 mL oven-dried reaction vessel was consecutively placed PPh₃ (30 mmol, 7.86 g, 3 equiv), NaI (15 mmol, 2.25 g, 1.5 equiv) under N₂, *N*-Methylaniline **1a** (1.07 g, 10 mmol, 1 equiv) dissolved in DMF (40 mL) was added to the sealed reaction vessel by syringe, then the mixture was cooled to 0 °C under stirring. CF₃SO₂Cl (15 mmol, 2.52 g, 1.5 equiv.) dissolved in DMF (10 mL) was then slowly added via syringe. The resulting mixture was then allowed to warm to room temperature and stirred for 5h. Upon completion, the reaction mixture was diluted with water (300ml) and extracted with CH₂Cl₂ (300ml), the organic layers were washed with brine (300ml) three times and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to obtain **3a** in 74% yield (1.25 g).

A typical procedure of gram-scale synthesis for isothiocyanates

In a 150 mL oven-dried reaction vessel was consecutively placed PPh₃ (30 mmol, 7.86 g, 3 equiv), NaI (15 mmol, 2.25 g, 1.5 equiv) under N₂, aniline **1a** (0.93 g, 10 mmol, 1 equiv) dissolved in DMF (40 mL) was added to the sealed reaction vessel by syringe, then the mixture was cooled to 0 °C under stirring. CF₃SO₂Cl (15 mmol, 2.52 g, 1.5 equiv.) dissolved in DMF (10 mL) was then slowly added via syringe. The resulting mixture was then allowed to warm to room temperature and stirred for 5h. Upon completion, the reaction mixture was diluted with water (300ml) and extracted with CH₂Cl₂ (300ml), the organic layers were washed with brine (300ml) three times and concentrated under reduced pressure.. The crude product was purified by column chromatography on silica gel to obtain **3a** in 71% yield (0.96 g).

Unsymmetrical thiocarbamoyl fluoride compounds can form two conformers 3' and 3'' which can be observed as distinct species in the NMR:



methyl(phenyl)carbamothioic fluoride 3a' and 3a''. ⁷ **3a':3a''**=5:1, yellow oil, yield 86% (72.7 mg). Eluent: ethyl acetate/petroleum ether (3:97). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.50 – 7.32 (m, 5H+3H, **3a''**+**3a'**), 7.20 (dt, *J* = 8.2, 1.3 Hz, 2H, **3a'**), 3.65 (s, 3H, **3a'**), 3.49 (d, *J* = 2.5 Hz, 3H, **3a''**). ¹⁹F NMR (470 MHz, Chloroform-*d*) δ 21.57 (**3a'**), 20.05 (**3a''**). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ 181.6 (d, *J* = 319.6 Hz, **3a'**), 145.1 (**3a''**), 142.1 (**3a'**), 131.0 (**3a''**), 130.7 (**3a'**), 129.7 (**3a''**), 129.6 (**3a'**), 127.0 (d, *J* = 1.8 Hz, **3a''**), 125.9 (**3a'**), 45.9 (d, *J* = 7.3 Hz, **3a'**), 41.9 (**3a''**).

methyl(o-tolyl)carbamothioic fluoride 3b' and 3b''. ⁷ **3b':3b''**=4:1, yellow solid, yield 81% (74.1 mg). Eluent: ethyl acetate/petroleum ether (3:97). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.22 (m, 3H+3H, **3b'**+**3b''**), 7.19 (d, *J* = 6.7 Hz, 1H, **3b''**), 7.15 – 7.08 (m, 1H, **3b'**), 3.56 (d, *J* = 1.6 Hz, 3H, **3b'**), 3.41 (d, *J* = 2.2 Hz, 3H, **3b''**), 2.29 (s, 3H, **3b''**), 2.24 (s, 3H, **3b'**). ¹⁹F NMR (470 MHz, Chloroform-*d*) δ 21.32 (**3b'**), 17.25 (**3b''**). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ 182.5 (d, *J* = 325.4 Hz, **3b''**), 182.0 (d, *J* = 318.0 Hz, **3b'**), 143.6 (**3b''**), 141.2 (**3b'**), 135.2 (**3b''**), 134.9 (**3b'**), 132.8 (**3b''**), 132.5 (**3b'**), 130.2 (**3b''**+**3b'**), 128.9

(**3b''**), 128.4 (**3b'**), 126.9 (d, $J = 2.1$ Hz, **3b''**), 126.3 (**3b'**), 45.0 (d, $J = 7.3$ Hz, **3b'**), 40.9 (d, $J = 4.2$ Hz, **3b''**), 18.2 (**3b'+3b''**).

methyl(m-tolyl)carbamothioic fluoride 3c' and 3c''. $^7\text{3c':3c''}=6:1$, yellow oil, yield 77% (70.5 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.25 (m, 1H+1H, **3c''+3c'**), 7.20 – 7.12 (m, 1H+3H, **3c'+3c''**), 7.04 – 6.96 (m, 2H, **3c'**), 3.62 (s, 3H, **3c'**), 3.45 (d, $J = 2.5$ Hz, 3H, **3c''**), 2.37 (d, $J = 5.4$ Hz, 3H+3H, **3c''+3c'**). ^{19}F NMR (470 MHz, Chloroform-*d*) δ 21.32 (**3c'**), 19.76 (**3c''**). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 183.2 (d, $J = 323.9$ Hz, **3c''**), 181.6 (d, $J = 319.2$ Hz, **3c'**), 145.1 (**3c''**), 142.1 (**3c'**), 141.1 (**3c''**), 140.8 (**3c'**), 130.7 (**3c''**), 130.4 (**3c'**), 130.3 (**3c'**), 128.3 (**3c''**), 127.4 (**3c''**), 126.4 (**3c'**), 123.9 (d, $J = 1.9$ Hz, **3c''**), 122.9 (**3c'**), 45.9 (d, $J = 7.2$ Hz, **3c'**), 42.0 (d, $J = 4.4$ Hz, **3c''**), 22.4 (**3c''**), 22.3 (**3c'**).

methyl(p-tolyl)carbamothioic fluoride 3d' and 3d''. $^7\text{3d':3d''}=5:1$, yellow oil, yield 80% (73.2 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.26 (d, $J = 7.3$ Hz, 2H, **3d''**), 7.22 (d, $J = 8.4$ Hz, 2H+2H, **3d'+3d''**), 7.08 (d, $J = 8.0$ Hz, 2H, **3d'**), 3.62 (s, 3H, **3d'**), 3.46 (d, $J = 2.5$ Hz, 3H, **3d''**), 2.37 (d, $J = 5.6$ Hz, 3H+3H, **3d''+3d'**). ^{19}F NMR (470 MHz, Chloroform-*d*) δ 21.14 (**3d'**), 19.76 (**3d''**). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 183.4 (d, $J = 324.0$ Hz, **3d''**), 181.7 (d, $J = 319.1$ Hz, **3d'**), 142.7 (**3d''**), 139.7 (**3d''**), 139.6 (**3d'**), 139.6 (**3d'**), 131.5 (**3d''**), 131.2 (**3d'**), 126.6 (d, $J = 2.0$ Hz, **3d''**), 125.6 (**3d'**), 46.0 (d, $J = 7.1$ Hz, **3d'**), 42.0 (d, $J = 4.7$ Hz, **3d''**), 22.3 (**3d''**), 22.1 (**3d'**).

methyl 4-((fluorocarbonothioyl)(methyl)amino)benzoate 3e' and 3e''. $^7\text{3e':3e''}=6:1$, White solid, M.p. 66.8–68.2 °C, yield 82% (93.1 mg). Eluent: ethyl acetate/petroleum ether (10:90). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.07 (d, $J = 8.3$ Hz, 2H+2H, **3e''+3e'**), 7.43 (d, $J = 8.2$ Hz, 2H, **3e''**), 7.33 – 7.25 (m, 2H, **3e'**), 3.90 (s, 3H+3H, **3e''+3e'**), 3.64 (s, 3H, **3e'**), 3.49 (d, $J = 4.3$ Hz, 3H, **3e''**). ^{19}F NMR (470 MHz, Chloroform-*d*) δ 22.07 (**3e'**), 21.21 (**3e''**). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 181.1 (d, $J = 320.6$ Hz, **3e'**), 166.8 (**3e'**), 145.7 (**3e'**), 132.0 (**3e'**), 131.0 (**3e'**), 127.2 (**3e'**), 126.0 (**3e'**), 53.5 (**3e'**), 45.6 (d, $J = 7.1$ Hz, **3e'**), 41.7 (**3e'**). HR-MS (EI) m/z : M^+ Calcd. For $\text{C}_{10}\text{H}_{10}\text{FNO}_2\text{S}$ 227.0416; found 227.0415.

methyl(4-nitrophenyl)carbamothioic fluoride 3f' and 3f''. $^7\text{3f':3f''}=4:1$, yellow solid, yield 76% (81.3 mg). Eluent: ethyl acetate/petroleum ether (10:90). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.33 (d, $J = 8.5$ Hz, 2H, **3f'**), 7.47 (d, $J = 8.6$ Hz, 2H, **3f'**), 3.71 (s, 3H, **3f'**). ^{19}F NMR (470 MHz, Chloroform-*d*) δ 23.03 (**3f'**), 22.46 (**3f''**). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 180.7 (d, $J = 317.0$ Hz, **3f'**), 147.9 (**3f'**), 147.2 (**3f'**), 127.0 (**3f'**), 126.1 (**3f'**), 45.6 (**3f'**).

(4-methoxyphenyl)(methyl)carbamothioic fluoride 3g' and 3g''. $^7\text{3g':3g''}=5:1$, yellow oil, yield 80% (79.6 mg). Eluent: ethyl acetate/petroleum ether (5:95). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.24 (d, $J = 8.9$ Hz, 2H, **3g''**), 7.14 – 7.09 (m, 2H, **3g'**), 6.97 – 6.89 (m, 2H+2H, **3g''+3g'**), 3.80 (d, $J = 2.8$ Hz, 3H+3H, **3g''+3g'**), 3.61 (s, 3H, **3g'**), 3.45 (d, $J = 2.5$ Hz, 3H, **3g''**). ^{19}F NMR (470 MHz, Chloroform-*d*) δ 21.11 (**3g'**), 19.76 (**3g''**). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 183.6 (d, $J = 324.3$ Hz, **3g''**), 181.8 (d, $J = 318.7$ Hz, **3g'**), 160.3 (**3g''+3g'**), 138.0 (**3g''**), 134.9 (**3g'**), 128.0 (d, $J = 2.0$ Hz, **3g''**), 127.0 (**3g'**), 116.0 (**3g''**), 115.8 (**3g'**), 56.6 (**3g'**), 56.6 (**3g''**), 46.1 (d, $J = 7.3$ Hz, **3g'**), 42.1 (d, $J = 4.6$ Hz, **3g''**).

butyl(phenyl)carbamothioic fluoride 3h' and 3h''. $^7\text{3h':3h''}=4:1$, yellow oil, yield 79% (83.3 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.49 – 7.39 (m, 3H+2H, **3h''+3h'**), 7.39 – 7.34 (m, 1H, **3h'**), 7.30 (dd, $J = 7.6, 1.9$ Hz, 2H, **3h''**), 7.17 (dd, $J = 7.7, 2.0$ Hz, 2H, **3h'**), 4.09 – 4.01 (m, 2H, **3h'**), 3.80 (td, $J = 7.5, 1.6$ Hz, 2H, **3h''**), 1.71 – 1.57 (m, 2H+2H, **3h'+3h''**), 1.34 (hd, $J = 7.4, 2.5$ Hz, 2H+2H, **3h'+3h''**), 0.91 (td, $J = 7.4, 2.5$ Hz, 3H+3H, **3h''+3h'**). ^{19}F NMR (470 MHz, Chloroform-*d*) δ 24.40 (**3h'**), 16.74 (**3h''**). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 183.4 (d, $J = 324.3$ Hz, **3h''**), 181.5 (d, $J = 319.5$ Hz, **3h'**), 143.8 (**3h''**), 140.6 (**3h'**), 130.9 (**3h''**), 130.7 (**3h'**), 129.7 (**3h''+3h'**), 127.9 (**3h''**), 126.9

(**3h'**), 57.9 (d, $J = 7.3$ Hz, **3h'**), 54.9 (d, $J = 3.3$ Hz, **3h''**), 31.1 (**3h''**), 29.1 (**3h'**), 20.9 (**3h'**), 20.8 (**3h''**), 14.7 (**3h'**), 14.6 (**3h''**). HR-MS (EI) m/z : M^+ Calcd. For $C_{11}H_{14}FNS$ 211.0831; found 211.0825.

benzyl(phenyl)carbamothioic fluoride 3i' and 3i''. **3i':3i''**=4:1, yellow oil, yield 73% (89.4 mg). Eluent: ethyl acetate/petroleum ether (3:97). 1H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.23 (m, 6H+8H, **3i''+3i'**), 7.17 – 7.11 (m, 4H, **3i''**), 6.98 (dd, $J = 7.5, 2.3$ Hz, 2H, **3i'**), 5.28 (s, 2H, **3i'**), 4.94 (s, 2H, **3i''**). ^{19}F NMR (470 MHz, Chloroform-*d*) δ 24.43 (**3i'**), 18.31 (**3i''**). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 183.0 (d, $J = 324.3$ Hz, **3i''**), 182.6 (d, $J = 319.8$ Hz, **3i'**), 143.8 (**3i''**), 140.4 (**3i'**), 135.4 (**3i''**), 135.3 (**3i'**), 130.8 (**3i'**), 130.6 (**3i''**), 130.0 (**3i'**), 129.8 (**3i''**), 129.7 (**3i'**), 129.5 (**3i''**), 129.5 (**3i'**), 128.0 (**3i''**), 127.1 (**3i'**), 61.7 (d, $J = 6.9$ Hz, **3i'**), 58.7 (d, $J = 3.4$ Hz, **3i''**). HR-MS (EI) m/z : M^+ Calcd. For $C_{14}H_{12}FNS$ 245.0674; found 245.0669.

5-bromoindoline-1-carbothioyl fluoride 3j' and 3j''. **3j':3j''**=1:4, yellow solid, M.p. 117.7-121.5 °C, yield 78% (101.0 mg). Eluent: ethyl acetate/petroleum ether (5:95). 1H NMR (500 MHz, Chloroform-*d*) δ 8.66 (dd, $J = 8.7, 2.2$ Hz, 1H, **3j'**), 7.40 (td, $J = 7.9, 7.2, 2.0$ Hz, 3H+1H, **3j''+3j'**), 7.27 (s, 1H, **3j'**), 4.41 – 4.30 (m, 2H+2H, **3j'+3j''**), 3.21 (dt, $J = 16.7, 8.3$ Hz, 2H+2H, **3j''+3j'**). ^{19}F NMR (470 MHz, Chloroform-*d*) δ 39.56 (**3j'**), 16.86 (**3j''**). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 177.2 (d, $J = 326.5$ Hz), 140.1, 140.1, 137.0, 136.2, 132.3 (d, $J = 3.6$ Hz), 131.4, 130.0, 129.2, 120.3, 119.9 (d, $J = 2.1$ Hz), 119.7, 119.5, 55.2 (d, $J = 6.8$ Hz), 52.3, 27.7, 27.3. Due to difficulty to assign peaks in ^{13}C NMR to **3j'** and **3j''** only chemical shifts are indicated. HR-MS (EI) m/z : M^+ Calcd. For C_9H_7BrFNS 258.9467; found 258.9471.

2,3-dihydro-4H-benzo[b][1,4]oxazine-4-carbothioyl fluoride 3k' and 3k''. **3k':3k''**=1:25, yellow oil, yield 73% (71.9 mg). Eluent: ethyl acetate/petroleum ether (5:95). 1H NMR (500 MHz, Chloroform-*d*) δ 7.41 (t, $J = 7.5$ Hz, 1H, **3k''**), 7.16 (t, $J = 7.9$ Hz, 1H, **3k''**), 6.93 (t, $J = 7.7$ Hz, 2H, **3k''**), 4.38 (dp, $J = 9.7, 4.7$ Hz, 4H, **3k''**). ^{19}F NMR (470 MHz, Chloroform-*d*) δ 25.58 (**3k'**), 18.11 (**3k''**). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 180.5 (d, $J = 324.6$ Hz), 147.0, 129.2, 125.3, 125.2, 124.7, 121.8, 118.9, 66.2, 49.7 (d, $J = 6.4$ Hz). Due to difficulty to assign peaks in ^{13}C NMR to **3k'** and **3k''** only chemical shifts are indicated. HR-MS (EI) m/z : M^+ Calcd. For C_9H_8FNOS 197.0311; found 197.0317.

methyl(naphthalen-1-ylmethyl)carbamothioic fluoride 3l' and 3l''. **3l':3l''**=10:7, yellow solid, M.p. 69.6-71.3 °C, yield 75% (87.1 mg). Eluent: ethyl acetate/petroleum ether (5:95). 1H NMR (500 MHz, Chloroform-*d*) δ 8.05(d, $J = 8.3$ Hz, 1H, **3l'**), 7.95 – 7.91 (m, 1H+1H, **3l''+3l'**), 7.91 – 7.84 (m, 1H+2H, **3l'+3l''**), 7.63 – 7.54 (m, 2H+2H, **3l'+3l''**), 7.49 (td, $J = 7.6, 2.8$ Hz, 1H+1H, **3l'+3l''**), 7.42 (d, $J = 6.9$ Hz, 1H, **3l'**), 7.30 (d, $J = 7.1$ Hz, 1H, **3l''**), 5.43 (s, 2H, **3l'**), 5.17 (s, 2H, **3l''**), 3.28 (s, 3H, **3l''**), 2.96 (d, $J = 2.3$ Hz, 3H, **3l'**). ^{19}F NMR (470 MHz, Chloroform-*d*) δ 17.58, 13.79. $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 183.1 (d, $J = 321.1$ Hz), 182.5 (d, $J = 320.6$ Hz), 135.0, 134.9, 133.3 (d, $J = 10.9$ Hz), 132.6, 131.9, 130.6, 130.5, 130.4, 130.3, 130.2, 130.0, 129.6 (d, $J = 12.7$ Hz), 128.3, 128.2 (d, $J = 2.5$ Hz), 127.4 (d, $J = 4.1$ Hz), 126.6, 126.5, 126.4, 124.5, 123.2, 58.0 (d, $J = 6.4$ Hz), 53.7 (d, $J = 6.1$ Hz), 42.0 (d, $J = 6.2$ Hz), 36.1 (d, $J = 6.5$ Hz). Due to difficulty to assign peaks in ^{13}C NMR to **3l'** and **3l''** only chemical shifts are indicated. HR-MS (EI) m/z : M^+ Calcd. For $C_{13}H_{12}FNS$ 233.0674; found 233.0680.

methyl(thiophen-3-ylmethyl)carbamothioic fluoride 3m' and 3m''. **3m':3m''**=10:7, yellow oil, yield 69% (65.1 mg). Eluent: ethyl acetate/petroleum ether (1:99). 1H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.26 (m, 1H+1H, **3m'+3m''**), 7.16 – 7.12 (m, 1H, **3m'**), 7.05 – 6.97 (m, 1H+2H, **3m'+3m''**), 5.09 (s, 2H, **3m'**), 4.81 (s, 2H, **3m''**), 3.31 (d, $J = 1.7$ Hz, 3H, **3m''**), 3.12 (d, $J = 2.2$ Hz, 3H, **3m'**). ^{19}F NMR (470 MHz, Chloroform-*d*) δ 16.52 (**3m'**), 14.02 (**3m''**). $^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*) δ 182.9 (d, $J = 321.4$ Hz, **3m'**), 182.0 (d, $J = 320.6$ Hz, **3m''**), 136.9 (**3m''**), 136.4 (**3m'**), 129.4 (**3m'**), 128.9 (**3m''**), 128.3 (**3m''**), 127.9 (**3m'**), 127.7 (**3m'**), 127.7 (**3m''**), 54.6 (d, $J = 5.6$ Hz, **3m'**), 50.5 (d, $J = 6.4$ Hz, **3m''**), 41.9 (d, $J = 6.2$ Hz, **3m''**), 36.7 (d, $J = 6.4$ Hz, **3m'**). HR-MS (EI) m/z : M^+ Calcd. For $C_7H_8FNS_2$ 189.0082; found 189.0079.

4-phenylpiperazine-1-carbothioyl fluoride 3n. ¹⁸ Off-white solid, yield 82% (91.8 mg). Eluent: ethyl acetate/petroleum ether (5:95). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.7 Hz, 2H), 6.92 (t, *J* = 7.0 Hz, 3H), 4.11 (t, *J* = 5.2 Hz, 2H), 3.91 – 3.79 (m, 2H), 3.24 (dt, *J* = 40.8, 5.2 Hz, 4H). ¹⁹F NMR (470 MHz, Chloroform-*d*) δ 13.34. ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ 181.1 (d, *J* = 320.3 Hz), 151.2, 130.5, 122.2, 118.0, 51.4 (d, *J* = 6.2 Hz), 50.1, 49.6, 47.6 (d, *J* = 5.3 Hz).

4-(pyridin-2-yl)piperazine-1-carbothioyl fluoride 3o. Yellow solid, M.p. 80.0-83.1 °C, yield 74% (83.3 mg). Eluent: ethyl acetate/petroleum ether (10:90). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.56 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 6.81 – 6.64 (m, 2H), 4.19 – 4.07 (m, 2H), 3.93 – 3.83 (m, 2H), 3.71 (ddd, *J* = 19.2, 6.8, 4.8 Hz, 4H). ¹⁹F NMR (470 MHz, Chloroform-*d*) δ 13.91. ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ 181.2 (d, *J* = 320.8 Hz), 159.2, 148.8, 139.2, 115.5, 108.5, 51.0 (d, *J* = 6.2 Hz), 47.2 (d, *J* = 5.1 Hz), 45.6, 45.2. HR-MS (EI) *m/z*: M⁺ Calcd. For C₁₀H₁₂FN₃S 225.0736; found 225.0745.

tert-butyl 4-(fluorocarbothioyl)piperazine-1-carboxylate 3p. ¹⁸ Off-white solid, yield 75% (93.0 mg). Eluent: ethyl acetate/petroleum ether (5:95). ¹H NMR (500 MHz, Chloroform-*d*) δ 3.97 (dd, *J* = 6.4, 4.4 Hz, 2H), 3.72 (t, *J* = 5.3 Hz, 2H), 3.59 (t, *J* = 5.4 Hz, 2H), 3.56 – 3.49 (m, 2H), 1.48 (s, 9H). ¹⁹F NMR (470 MHz, Chloroform-*d*) δ 14.43. ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ 181.1 (d, *J* = 320.3 Hz), 155.2, 81.9, 51.3 (d, *J* = 6.0 Hz), 47.5, 29.3.

diallylcarbamothioic fluoride 3q. Yellow oil, yield 69% (54.7 mg). Eluent: ethyl acetate/petroleum ether (1:99). ¹H NMR (500 MHz, Chloroform-*d*) δ 5.81 (dddd, *J* = 47.8, 16.3, 10.2, 5.9 Hz, 2H), 5.36 – 5.16 (m, 4H), 4.33 (dd, *J* = 6.2, 1.5 Hz, 2H), 4.04 (dd, *J* = 5.8, 1.7 Hz, 2H). ¹⁹F NMR (470 MHz, Chloroform-*d*) δ 15.21. ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ 182.8 (d, *J* = 321.6 Hz), 131.4, 130.6, 120.9, 120.2, 56.6 (d, *J* = 5.6 Hz), 52.1 (d, *J* = 5.5 Hz). HR-MS (EI) *m/z*: M⁺ Calcd. For C₇H₁₀FNS 159.0518; found 159.0522.

bis(2-ethylhexyl)carbamothioic fluoride 3r. Yellow oil, yield 76% (115.1 mg). Eluent: ethyl acetate/petroleum ether (1:99). ¹H NMR (500 MHz, Chloroform-*d*) δ 3.60 (d, *J* = 7.5 Hz, 2H), 3.44 – 3.30 (m, 2H), 2.01 (p, *J* = 6.8 Hz, 1H), 1.70 (p, *J* = 6.5 Hz, 1H), 1.38 – 1.21 (m, 16H), 0.95 – 0.85 (m, 12H). ¹⁹F NMR (470 MHz, Chloroform-*d*) δ 17.53. ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ 183.0 (d, *J* = 319.8 Hz), 58.1, 54.8, 39.1, 37.4, 31.4, 31.3, 29.5, 29.5, 24.8, 24.7, 24.0, 24.0, 15.1, 15.0, 11.6, 11.5. HR-MS (EI) *m/z*: M⁺ Calcd. For C₁₇H₃₄FNS 303.2396; found 303.2406.

((1S,4S)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(methyl)carbamothioic fluoride 3s' and 3s''. 3s':3s''=5:3, white solid, M.p. 92.2-95.7 °C, yield 65% (119.3 mg). Eluent: ethyl acetate/petroleum ether (5:95). ¹H NMR (500 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 3H+1H, 3s'+3s''), 7.28 (d, *J* = 2.0 Hz, 2H, 3s''), 7.21 (d, *J* = 7.7 Hz, 1H, 3s'), 7.14 (d, *J* = 7.7 Hz, 1H, 3s''), 7.09 (dd, *J* = 8.9, 2.1 Hz, 1H+1H, 3s''+3s'), 7.02 (ddd, *J* = 6.2, 5.0, 1.3 Hz, 1H+1H, 3s'+3s''), 6.82 (ddd, *J* = 11.0, 8.3, 2.1 Hz, 1H+1H, 3s'+3s''), 6.17 (dt, *J* = 11.1, 5.7 Hz, 1H, 3s'), 5.63 (t, *J* = 8.4 Hz, 1H, 3s''), 4.24 (td, *J* = 6.0, 2.9 Hz, 1H+1H, 3s'+3s''), 3.10 (s, 3H, 3s''), 2.91 (d, *J* = 2.7 Hz, 3H, 3s'), 2.31 (ddddt, *J* = 17.9, 12.4, 8.6, 5.6, 2.9 Hz, 1H+1H, 3s''+3s'), 2.08 (dtt, *J* = 13.4, 5.0, 3.0 Hz, 1H+1H, 3s'+3s''), 2.00 (dtd, *J* = 11.8, 5.8, 2.6 Hz, 1H, 3s'), 1.94 – 1.82 (m, 2H, 3s''), 1.74 (tdd, *J* = 13.1, 10.6, 2.8 Hz, 1H, 3s'). ¹⁹F NMR (470 MHz, Chloroform-*d*) δ 20.30 (3s'), 11.65 (3s''). ¹³C{¹H} NMR (126 MHz, Chloroform-*d*) δ 184.1 (d, *J* = 320.5 Hz, 3s'), 183.0 (d, *J* = 320.8 Hz, 3s''), 147.4 (3s'), 147.2 (3s''), 139.1 (3s'), 139.0 (3s''), 134.5 (3s''), 134.1 (3s'), 133.6 (3s''), 133.6 (3s'), 132.3 (3s'), 131.6 (3s''), 131.6 (3s'), 131.5 (3s'), 131.4 (3s''), 131.3 (3s'), 129.6 (3s'), 129.6 (3s''), 129.5 (3s''), 129.4 (3s'), 129.1 (3s''), 129.0 (3s'), 128.9 (3s'), 128.9 (3s''), 128.2 (3s''+3s'), 63.4 (d, *J* = 6.5 Hz, 3s'), 59.9 (3s''), 43.8 (3s'), 43.8 (3s''), 38.7 (3s''), 33.1 (3s'), 30.8 (3s''), 30.7 (3s'), 23.9 (3s''), 21.6 (3s'). HR-MS (EI) *m/z*: M⁺ Calcd. For C₁₈H₁₆Cl₂FNS 367.0365; found 367.0371.

methyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)carbamothioic fluoride 3t. 3t':3t''=5:6, yellow oil, yield 70% (129.9 mg). Eluent: ethyl acetate/petroleum ether (3:97). ¹H NMR (500 MHz, Chloroform-*d*) δ

7.43 (d, $J = 8.4$ Hz, 2H, $3t'+3t''$), 7.38 – 7.26 (m, 5H, $3t'+3t''$), 6.89 (dd, $J = 8.6, 6.1$ Hz, 2H, $3t'+3t''$), 5.23 (ddd, $J = 38.3, 8.6, 4.1$ Hz, 1H, $3t'+3t''$), 4.00 – 3.86 (m, 1H, $3t'+3t''$), 3.81 – 3.65 (m, 1H, $3t'+3t''$), 3.36 – 3.09 (m, 3H, $3t'+3t''$), 2.42 – 2.13 (m, 2H, $3t'+3t''$). ^{19}F NMR (470 MHz, Chloroform- d) δ 17.69, 13.64, -61.47. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 183.8 (d, $J = 6.5$ Hz), 181.2 (d, $J = 4.7$ Hz), 161.0 (d, $J = 21.1$ Hz), 140.8 (d, $J = 40.4$ Hz), 133.3 (d, $J = 10.6$ Hz), 130.1 (d, $J = 11.2$ Hz), 129.4 (d, $J = 13.5$ Hz), 127.9 (p, $J = 3.6$ Hz), 126.6 (d, $J = 7.3$ Hz), 124.6 – 123.7 (m), 116.8 (d, $J = 3.6$ Hz), 78.9, 53.7 (d, $J = 5.5$ Hz), 49.7 (d, $J = 4.9$ Hz), 42.8 (d, $J = 5.9$ Hz), 38.1 (d, $J = 6.5$ Hz), 37.8, 35.5. Due to difficulty to assign peaks in ^{13}C NMR to $3t'$ and $3t''$ only chemical shifts are indicated. HR-MS (EI) m/z : M^+ Calcd. For $\text{C}_{18}\text{H}_{17}\text{F}_4\text{NOS}$ 371.0967; found 371.0972.

(3-(9,10-ethanoanthracen-9(10H)-yl)propyl)(methyl)carbamothioic fluoride $3u'$ and $3u''$. $3u':3u''=1:1$, yellow oil, yield 70% (118.5 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^1H NMR (500 MHz, Chloroform- d) δ 7.37 – 7.27 (m, 3H+3H, $3u'+3u''$), 7.24 – 7.10 (m, 5H+5H, $3u'+3u''$), 4.34 (d, $J = 2.8$ Hz, 1H+1H, $3u'+3u''$), 4.02 (t, $J = 7.9$ Hz, 1H+1H, $3u'+3u''$), 3.79 (t, $J = 7.5$ Hz, 1H+1H, $3u'+3u''$), 3.49 – 3.21 (m, 3H+3H, $3u'+3u''$), 2.60 – 2.44 (m, 2H+2H, $3u'+3u''$), 2.31 – 2.20 (m, 1H+1H, $3u'+3u''$), 2.20 – 2.09 (m, 1H+1H, $3u'+3u''$), 1.93 – 1.83 (m, 2H+2H, $3u'+3u''$), 1.62 (ddd, $J = 16.5, 7.1, 3.5$ Hz, 2H+2H, $3u'+3u''$). ^{19}F NMR (470 MHz, Chloroform- d) δ 17.52 ($3u'$), 13.16 ($3u''$). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 182.7 (d, $J = 321.1$ Hz), 182.5 (d, $J = 319.7$ Hz), 146.0, 145.8, 126.6, 126.5, 124.7, 124.6, 122.2, 121.9, 57.5 (d, $J = 5.9$ Hz), 53.7 (d, $J = 4.7$ Hz), 45.8, 45.6, 45.5 (d, $J = 6.3$ Hz), 42.7 (d, $J = 6.0$ Hz), 37.8 (d, $J = 6.4$ Hz), 30.7, 28.9 (d, $J = 13.0$ Hz), 28.7 (d, $J = 8.0$ Hz), 24.7, 22.5. Due to difficulty to assign peaks in ^{13}C NMR to $3u'$ and $3u''$ only chemical shifts are indicated. HR-MS (EI) m/z : M^+ Calcd. For $\text{C}_{21}\text{H}_{22}\text{FNS}$ 339.1457; found 339.1460.

Isothiocyantobenzene $5a$. ⁷ Yellow oil, yield 84% (56.7 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^1H NMR (500 MHz, Chloroform- d) δ 7.36 (tt, $J = 9.7, 4.7$ Hz, 2H), 7.30 (td, $J = 7.2, 3.5$ Hz, 1H), 7.21 (dt, $J = 12.6, 6.3$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 136.5, 132.3, 130.6, 128.4, 126.8.

1-isothiocyanto-4-methylbenzene $5b$. ⁷ Yellow oil, yield 85% (63.3 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^1H NMR (500 MHz, Chloroform- d) δ 7.16 (d, $J = 8.3$ Hz, 2H), 7.13 – 7.09 (m, 2H), 2.36 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 138.6, 135.6, 131.2, 129.4, 126.6, 22.3.

2-isothiocyanto-1,3,5-trimethylbenzene $5c$. ⁷ White solid, yield 82% (72.6 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^1H NMR (500 MHz, Chloroform- d) δ 6.87 (s, 2H), 2.34 (s, 6H), 2.30 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 159.6, 136.0, 131.6, 131.0, 130.2, 130.0, 127.8, 114.8, 62.5, 56.2, 42.7, 42.1.

1-fluoro-4-isothiocyantobenzene $5d$. ⁷ Yellow oil, yield 79% (60.4 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^1H NMR (500 MHz, Chloroform- d) δ 7.25 – 7.18 (m, 2H), 7.11 – 7.00 (m, 2H). ^{19}F NMR (470 MHz, Chloroform- d) δ -112.00. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 162.2 (d, $J = 249.1$ Hz), 128.4, 128.4, 117.8, 117.6.

1-chloro-4-isothiocyantobenzene $5e$. ⁷ Yellow oil, yield 80% (67.6 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^1H NMR (500 MHz, Chloroform- d) δ 7.32 (dq, $J = 9.1, 2.5, 2.0$ Hz, 2H), 7.24 – 7.10 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 137.8, 134.0, 130.8, 130.2, 128.0.

1-bromo-4-isothiocyantobenzene $5f$. ⁷ Yellow oil, yield 82% (87.3 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^1H NMR (500 MHz, Chloroform- d) δ 7.70 – 7.62 (m, 2H), 7.00 – 6.90 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform- d) δ 139.7, 138.1, 132.2, 128.5, 93.1.

4-isothiocyanto-1,1'-biphenyl $5g$. ⁶ White solid, yield 86% (90.7 mg). Eluent: ethyl acetate/petroleum ether (3:97). ^1H NMR (500 MHz, Chloroform- d) δ 7.63 – 7.56 (m, 4H), 7.47 (t, $J = 7.7$ Hz, 2H), 7.42 – 7.37 (m,

1
2
3 1H), 7.34 – 7.29 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 141.3 , 140.7 , 136.6 , 131.3 , 130.0 ,
4 129.2 , 128.9 , 128.0 , 127.2 .

5
6 **1-isothiocyanato-4-methoxybenzene 5h.**⁷ Yellow oil, yield 83% (68.5 mg). Eluent: ethyl acetate/petroleum
7 ether (5:95). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.18 – 7.13 (m, 2H), 6.85 (d, $J = 9.0$ Hz, 2H), 3.80 (s, 3H).
8 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 159.6 , 134.9 , 128.0 , 124.6 , 115.9 , 56.6 .

9
10 **1-ethynyl-4-isothiocyanatobenzene 5i.**⁶ Yellow solid, yield 85% (67.6 mg). Eluent: ethyl acetate/petroleum
11 ether (3:97). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.44 (m, 2H), 7.20 – 7.14 (m, 2H), 3.18 (s, 1H).
12 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 138.0 , 134.4 , 132.6 , 126.8 , 122.2 , 83.5 , 80.3 .

13
14 **4-isothiocyanatobenzonitrile 5j.**⁷ Yellow oil, yield 79% (63.2 mg). Eluent: ethyl acetate/petroleum ether
15 (10:90). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 2H), 7.33 – 7.28 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126
16 MHz, Chloroform-*d*) δ 140.6 , 137.1 , 134.7 , 127.5 , 118.9 , 111.7 .

17
18 **1-isothiocyanato-4-nitrobenzene 5k.**^{5b} Yellow solid, yield 77% (69.3 mg). Eluent: ethyl acetate/petroleum
19 ether (10:90). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.31 – 8.22 (m, 2H), 7.42 – 7.33 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR
20 (126 MHz, Chloroform-*d*) δ 146.8 , 141.3 , 139.0 , 127.4 , 126.3 .

21
22 **3-isothiocyanatopyridine 5l.**⁷ Yellow oil, yield 82% (55.8 mg). Eluent: ethyl acetate/petroleum ether (10:90).
23 ^1H NMR (500 MHz, Chloroform-*d*) δ 8.55 – 8.35 (m, 2H), 7.53 – 7.39 (m, 1H), 7.28 (dd, $J = 9.0, 3.5$ Hz, 1H).
24 $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 148.6 , 148.1 , 140.2 , 133.3 , 130.5 , 125.0 .

25
26 **(2-isothiocyanatoethyl)benzene 5m.**²⁰ Colorless oil, yield 74% (60.3 mg). Eluent: ethyl acetate/petroleum
27 ether (1:99). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.34 (dd, $J = 8.1, 6.7$ Hz, 2H), 7.30 – 7.26 (m, 1H), 7.24 –
28 7.18 (m, 2H), 3.72 (t, $J = 7.0$ Hz, 2H), 2.99 (t, $J = 7.0$ Hz, 2H).

29
30 **3-(2-isothiocyanatoethyl)-1H-indole 5n.**¹⁹ White solid, yield 75% (75.8 mg). Eluent: ethyl acetate/petroleum
31 ether (10:90). ^1H NMR (500 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.55 (d, $J = 7.9$ Hz, 1H), 7.38 (d, $J = 8.1$ Hz,
32 1H), 7.24 – 7.20 (m, 1H), 7.17 – 7.13 (m, 1H), 7.10 (d, $J = 2.3$ Hz, 1H), 3.77 (t, $J = 6.8$ Hz, 2H), 3.16 (t, $J =$
33 6.8 Hz, 2H).

34
35 **1-isothiocyanatoadamantane 5o.**⁷ White solid, yield 77% (74.3 mg). Eluent: ethyl acetate/petroleum ether
36 (1:99). ^1H NMR (500 MHz, Chloroform-*d*) δ 2.10 (q, $J = 3.2$ Hz, 3H), 1.97 (d, $J = 2.9$ Hz, 6H), 1.70 – 1.60
37 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*) δ 59.5 , 44.8 , 36.6 , 30.3 .

38
39 **1,3-dihydro-2H-benzo[d]imidazole-2-thione 5p.**²¹ White solid, yield 69% (51.8 mg). Eluent: ethyl
40 acetate/petroleum ether (10:90). ^1H NMR (500 MHz, DMSO-*d*₆) δ 12.49 (s, 2H), 7.07 (ddt, $J = 19.4, 5.8, 3.4$
41 Hz, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO-*d*₆) δ 169.6 , 133.7 , 123.8 , 110.9 .

42
43 **benzo[d]oxazole-2(3H)-thione 5q.**²¹ White solid, yield 70% (52.9 mg). Eluent: ethyl acetate/petroleum ether
44 (10:90). ^1H NMR (500 MHz, DMSO-*d*₆) δ 13.81 (s, 1H), 7.48 – 7.41 (m, 1H), 7.28 – 7.15 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$
45 NMR (126 MHz, DMSO-*d*₆) δ 181.6 , 149.6 , 132.6 , 126.6 , 125.2 , 111.9 , 111.4 .

46
47 **benzo[d]thiazole-2(3H)-thione 5r.**²² White solid, yield 67% (55.9 mg). Eluent: ethyl acetate/petroleum ether
48 (10:90). ^1H NMR (500 MHz, DMSO-*d*₆) δ 13.70 (s, 1H), 7.63 (d, $J = 7.9$ Hz, 1H), 7.38 – 7.30 (m, 1H), 7.30 –
49 7.20 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO-*d*₆) δ 191.3 , 142.7 , 130.8 , 128.6 , 125.6 , 123.2 , 113.9 .

50 51 ASSOCIATED CONTENT

52 53 Supporting Information

54 The Supporting Information is available free of charge on the ACS Publication website at DOI:

55 ^1H NMR, ^{13}C NMR, and ^{19}F NMR for products (PDF).

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Notes

The authors declare no competing financial interest.

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