

Synthesis of Thiocarbamoyl Fluorides and Isothiocyanates Using Amines with $\text{CF}_3\text{SO}_2\text{Cl}$ Jingjing Wei,[†] Shuaishuai Liang,[†] Lvqi Jiang,* and Wenbin Yi*Cite This: *J. Org. Chem.* 2020, 85, 12374–12381

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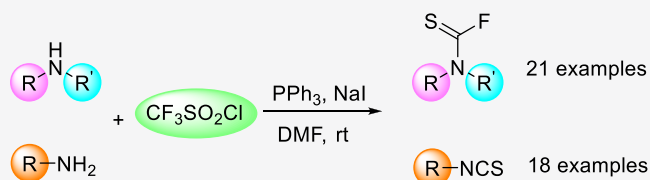
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ABSTRACT: A practical and efficient method to synthesize thiocarbamoyl fluorides and isothiocyanates from amines with trifluoromethanesulfonyl chloride was developed. In the presence of the reducing agent triphenylphosphine and sodium iodide, thiocarbamoyl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

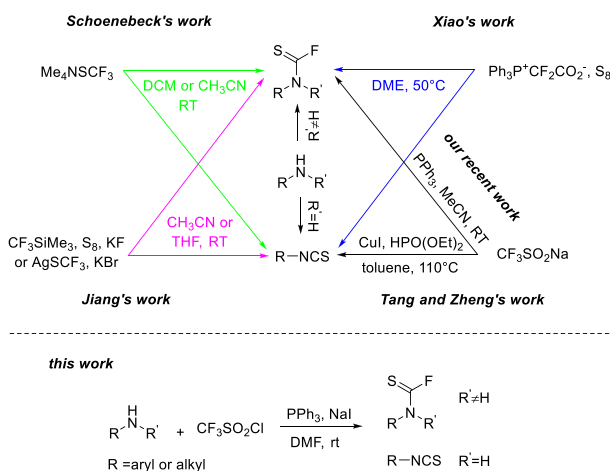


INTRODUCTION

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, making 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 these compounds under mild conditions is highly desired.

In the last years, several strategies have been reported for the synthesis of thiocarbamoyl fluorides and/or isothiocyanates from secondary amines and/or primary amines. Until now, there are about five reagents that have been developed 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 (Scheme 1).⁵ Afterward, the group of Xiao reported the 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 isothiocyanates using CF_3SiMe_3 , S_8 , and KF or AgSCF_3 and KBr (Scheme 1). Although Zheng's group⁸ has reported that the 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 synthesis of thiocarbamoyl fluorides using $\text{CF}_3\text{SO}_2\text{Na}$ and

Scheme 1. Synthetic Strategies for Thiocarbamoyl Fluorides/Isothiocyanates



triphenylphosphine has recently been reported by our group (Scheme 1).⁹ With our continuous interest in exploring the construction of $\text{N}-\text{C}$ bonds, we thought that the development of efficient methods using cheap materials would constitute an attractive option for the access of thiocarbamoyl fluorides and isothiocyanates.

Trifluoromethanesulfonyl chloride ($\text{CF}_3\text{SO}_2\text{Cl}$), as an easy-to-handle and commercially available cheap material, has been widely used in the formation of sulfonamides and sulfonic

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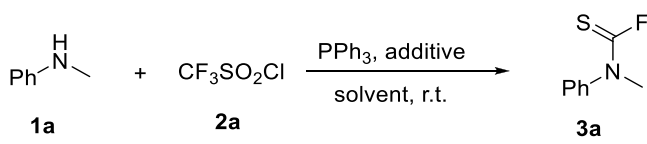


esters¹⁰ and also in electrophilic chlorination,¹¹ trifluoromethylation or trifluoromethyl-chlorosulfonylation, and so forth.¹² Our group has reported its application in the electrophilic trifluoromethylthiolation of indoles, pyrroles, enamines, and chloro-trifluoromethylthiolation of alkenes and alkynes.¹³ In this context, we envisioned that straightforward synthesis of thiocarbamoyl fluorides and isothiocyanates using CF₃SO₂Cl can be achieved under suitable reductive conditions; we herein disclose a novel use of trifluoromethanesulfonyl chloride to prepare thiocarbamoyl fluorides and isothiocyanates.

RESULTS AND DISCUSSION

We initially investigated the treatment of *N*-methylaniline **1a** with CF₃SO₂Cl **2a** (1.5 equiv) in the presence of PPh₃ (3.0 equiv) in dimethylformamide (DMF) at r.t. to yield the thiocarbamoyl fluoride product **3a** in 18% yield (Table 1, entry

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

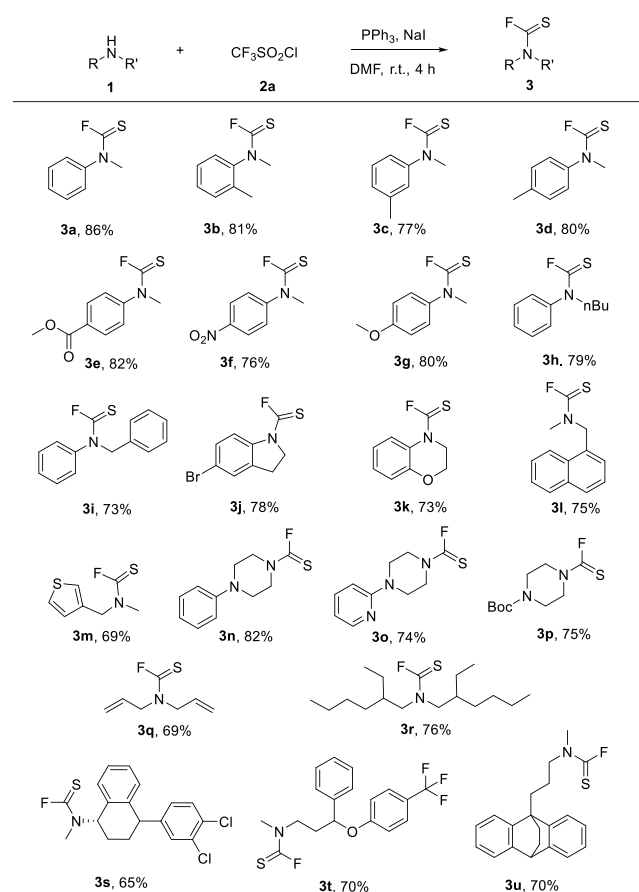
^aReaction conditions: *N*-methylaniline (0.5 mmol), CF₃SO₂Cl (0.75 mmol), and PPh₃ (1.5 mmol) in DMF (2.5 mL) at r.t. for 4 h. ^bYield determined by ¹⁹F NMR using *p*-fluorotoluene as an internal standard on crude products. ^cCF₃SO₂Cl (0.6 mmol) and PPh₃ (1.2 mmol) were used. ^dYield was obtained at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

1). Encouraged by this result, optimization of the reaction conditions was then carried out. Considering that an iodide anion can promote the reduction of sulfonyl chloride,¹⁴ a series of iodide sources including KI, NH₄I, NaI, and I₂ were tested (Table 1, entries 2–6), and among them, NaI gave the highest yield (47%, Table 1, entry 4). When KI and NH₄I were used as the catalyst, the product **3a** was obtained in 40 and 35% yield, respectively (Table 1, entries 2, 3); I₂ did not increase the yield obviously (Table 1, entry 5). Increasing the loadings of NaI to 1.5 equiv increases 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, tetrahydrofuran (THF), and 1,2-dichloroethane were less effective for this kind of reaction (Table 1, entries 8–12). When the amount of CF₃SO₂Cl **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/CF₃SO₂Cl/PPh₃/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).

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).

Scheme 2. Scope of Secondary Amines^a



^aReaction conditions: secondary amine (0.5 mmol), CF₃SO₂Cl (0.75 mmol), PPh₃ (1.5 mmol), and NaI (0.75 mmol) in DMF (2.5 mL) at r.t. for 4 h; isolated yields.

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 derivatives were also successfully employed to provide the corresponding products in 71–83% yields (**3m–3p**). Alkyl amines (**3q** and **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, were 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.

EXPERIMENTAL SECTION

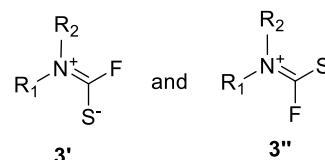
General Information. All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are identified using appropriate techniques such as ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, and ^{19}F NMR and compared with previously reported data. All unknown 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 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) and carbon (chloroform δ 77.0). Chemical shifts are reported in ppm. GC–MS data were recorded on an 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 a Waters Micromass GCT Premier spectrometer (electron ionization: EI) and Waters Q-ToF micro (electrospray ionization: ESI).

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 N_2 ; *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 using a syringe; $\text{CF}_3\text{SO}_2\text{Cl}$ (0.75 mmol, 126 mg, 1.5 equiv) was dissolved in DMF (1.25 mL) and the solution was added to the vessel using a syringe. The resulting solution was stirred at room temperature for 4 h. After that, the reaction mixture was diluted with water and extracted with CH_2Cl_2 ; 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.

Typical Procedure of Gram-scale Synthesis for Thiocarbamoyl Fluorides. In a 150 mL oven-dried reaction vessel, PPh_3 (30 mmol, 7.86 g, 3 equiv) and NaI (15 mmol, 2.25 g, 1.5 equiv) were consecutively placed under N_2 ; *N*-methylaniline **1a** (1.07 g, 10 mmol, 1 equiv) dissolved in DMF (40 mL) was added to the sealed reaction vessel using a syringe; then, the mixture was cooled to 0 °C under stirring. $\text{CF}_3\text{SO}_2\text{Cl}$ (15 mmol, 2.52 g, 1.5 equiv) dissolved in DMF (10 mL) was then slowly added via a syringe. The resulting mixture was then allowed to warm to room temperature and stirred for 5 h. Upon completion, the reaction mixture was diluted with water (300 mL) and extracted with CH_2Cl_2 (300 mL); the organic layers were washed with brine (300 mL) 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).

Typical Procedure of Gram-scale Synthesis for Isothiocyanates. In a 150 mL oven-dried reaction vessel, PPh_3 (30 mmol, 7.86 g, 3 equiv) and NaI (15 mmol, 2.25 g, 1.5 equiv) were consecutively placed under N_2 ; aniline **1a** (0.93 g, 10 mmol, 1 equiv) dissolved in DMF (40 mL) was added to the sealed reaction vessel using a syringe; then, the mixture was cooled to 0 °C under stirring. $\text{CF}_3\text{SO}_2\text{Cl}$ (15 mmol, 2.52 g, 1.5 equiv) dissolved in DMF (10 mL) was then slowly added via a syringe. The resulting mixture was then allowed to warm to room temperature and stirred for 5 h. Upon completion, the reaction mixture was diluted with water (300 mL) and extracted with CH_2Cl_2 (300 mL); the organic layers were washed with brine (300 mL) 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''**.** $3a':3a'' = 5:1$, 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''**). ^{19}F NMR (470 MHz, chloroform-*d*): δ 21.57 (**3a'**), 20.05 (**3a''**). $^{13}\text{C}\{^1\text{H}\}$ 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''**.** $3b':3b'' = 4:1$, 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'**). ^{19}F NMR (470 MHz, chloroform-*d*): δ 21.32 (**3b'**), 17.25 (**3b''**). $^{13}\text{C}\{^1\text{H}\}$ 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''**.** $3c':3c'' = 6:1$, 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''**.** $3d':3d'' = 5:1$, 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'**), 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) (methylamino)benzoate **3e' and **3e''**.** $3e':3e'' = 6:1$, white solid, mp 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''**.** $3f':3f'' = 4:1$, 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''. 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''. 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 $\text{C}_{11}\text{H}_{14}\text{FNS}$, 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''). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{14}\text{H}_{12}\text{FNS}$, 245.0674; found, 245.0669.

5-Bromindoline-1-carbothioyl Fluoride 3j' and 3j''. 3j':3j'' = 1:4, yellow solid, mp 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''). $^{13}\text{C}\{^1\text{H}\}$ 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. Because of 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 $\text{C}_9\text{H}_7\text{BrFNS}$, 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''). $^{13}\text{C}\{^1\text{H}\}$ 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). Because of 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 $\text{C}_9\text{H}_8\text{FNOS}$, 197.0311; found, 197.0317.

Methyl(naphthalen-1-ylmethyl)carbamothioic Fluoride 3l' and 3l''. 3l':3l'' = 10:7, yellow solid, mp 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. $^{13}\text{C}\{^1\text{H}\}$ 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). Because of 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 $\text{C}_{13}\text{H}_{12}\text{FNS}$, 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''). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_7\text{H}_8\text{FNS}_2$, 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). ^{19}F NMR (470 MHz, chloroform-*d*): δ 13.34. $^{13}\text{C}\{^1\text{H}\}$ 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, mp 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). ^{19}F NMR (470 MHz, chloroform-*d*): δ 13.91. $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{10}\text{H}_{12}\text{FN}_3\text{S}$, 225.0736; found, 225.0745.

tert-Butyl(4-(fluorocarbonothioyl)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). ^{19}F NMR (470 MHz, chloroform-*d*): δ 14.43. $^{13}\text{C}\{^1\text{H}\}$ 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 (dddt, *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). ^{19}F NMR (470 MHz, chloroform-*d*): δ 15.21. $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_7\text{H}_{10}\text{FNS}$, 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). ^{19}F NMR (470 MHz, chloroform-*d*): δ 17.53. $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{17}\text{H}_{34}\text{FNS}$, 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, mp 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 (dddd, 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'). ^{19}F NMR (470 MHz, chloroform-*d*): δ 20.30 (3s'), 11.65 (3s''). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{18}\text{H}_{16}\text{Cl}_2\text{FNS}$, 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. Because of 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. Because of 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.

Isothiocyanatobenzene 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-Isothiocyanato-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-Isothiocyanato-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-isothiocyanatobenzene 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-isothiocyanatobenzene 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-isothiocyanatobenzene 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-Isothiocyanato-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, 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, 129.2, 128.9, 128.0, 127.2.

1-Isothiocyanato-4-methoxybenzene 5h.⁷ Yellow oil, yield 83% (68.5 mg). Eluent: ethyl acetate/petroleum 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). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, chloroform-*d*): δ 159.6, 134.9, 128.0, 124.6, 115.9, 56.6.

1-Ethynyl-4-isothiocyanatobenzene 5i.⁶ Yellow solid, yield 85% (67.6 mg). Eluent: ethyl acetate/petroleum 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). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, chloroform-*d*): δ 138.0, 134.4, 132.6, 126.8, 122.2, 83.5, 80.3.

4-Isothiocyanatobenzonitrile 5j.⁷ Yellow oil, yield 79% (63.2 mg). Eluent: ethyl acetate/petroleum ether (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 MHz, chloroform-*d*): δ 140.6, 137.1, 134.7, 127.5, 118.9, 111.7.

1-Isothiocyanato-4-nitrobenzene 5k.^{5b} Yellow solid, yield 77% (69.3 mg). Eluent: ethyl acetate/petroleum 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 (126 MHz, chloroform-*d*): δ 146.8, 141.3, 139.0, 127.4, 126.3.

3-Isothiocyanatopyridine 5l.⁷ Yellow oil, yield 82% (55.8 mg). Eluent: ethyl acetate/petroleum ether (10:90). ^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). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, chloroform-*d*): δ 148.6, 148.1, 140.2, 133.3, 130.5, 125.0.

(2-Isothiocyanatoethyl)benzene 5m.²⁰ Colorless oil, yield 74% (60.3 mg). Eluent: ethyl acetate/petroleum 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), 7.24–7.18 (m, 2H), 3.72 (t, J = 7.0 Hz, 2H), 2.99 (t, J = 7.0 Hz, 2H).

3-(2-Isothiocyanatoethyl)-1H-indole 5n.¹⁹ White solid, yield 75% (75.8 mg). Eluent: ethyl acetate/petroleum 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, 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 = 6.8 Hz, 2H).

1-Isothiocyanatoadamantane 5o.⁷ White solid, yield 77% (74.3 mg). Eluent: ethyl acetate/petroleum ether (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 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, chloroform-*d*): δ 59.5, 44.8, 36.6, 30.3.

1,3-Dihydro-2H-benzof[d]imidazole-2-thione 5p.²¹ White solid, yield 69% (51.8 mg). Eluent: ethyl 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 Hz, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO}-d_6$): δ 169.6, 133.7, 123.8, 110.9.

Benzo[d]oxazole-2(3H)-thione 5q.²¹ White solid, yield 70% (52.9 mg). Eluent: ethyl acetate/petroleum ether (10:90). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 13.81 (s, 1H), 7.48–7.41 (m, 1H), 7.28–7.15 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO}-d_6$): δ 181.6, 149.6, 132.6, 126.6, 125.2, 111.9, 111.4.

Benzo[d]thiazole-2(3H)-thione 5r.²² White solid, yield 67% (55.9 mg). Eluent: ethyl acetate/petroleum ether (10:90). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): δ 13.70 (s, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.38–7.30 (m, 1H), 7.30–7.20 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, $\text{DMSO}-d_6$): δ 191.3, 142.7, 130.8, 128.6, 125.6, 123.2, 113.9.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.0c01634>.

^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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