Supporting Information

Transition metal-free α-Csp3-H oxidative sulfuration of benzyl thiosulfates with anilines to form N-aryl thioamides

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1. General Information

$^1$H NMR, $^{13}$C NMR and $^{19}$F NMR were recorded in CDCl$_3$ or DMSO-d$_6$ at room temperature on the Bruker DPX-400 spectrometer (400 MHz, 100 MHz and 377 MHz). The chemical-shifts scale is based on internal TMS. For spectra, chemical shifts were reported in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constant (Hz). Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. High resolution mass spectra were ensured on a MALDI-FTMS. The structures of known compounds were further corroborated by comparing their $^1$H NMR, $^{13}$C NMR data and MS data with those of literature.

All reactions were monitored and post-processing by TLC with Qingdao GF254 silica gel coated plates. Most reagents were obtained from commercial suppliers such as J&K Scientific and used without further purification unless otherwise noted.

2. General procedure for Bunte salts synthesis

A flask was charged with aryl halides (21.2 mmol, 1.0 eq), anhydrate sodium thiosulfate (31.8 mmol, 1.5 eq) and CuI (2.12 mmol, 10 mmol%). The flask was evacuated and filled with nitrogen. DMSO (21 mL) was charged via syringe followed by DMEDA (0.46 mL, 4.24 mmol, 20 mmol%). The mixture was heated at 80 °C for 3 h. Then the reaction mixture was cooled to room temperature which followed by crystallization on addition of saturate aqueous NaCl (60 mL). The mixture was filtered and the solid was washed with saturate aqueous NaCl and hexanes. The solid was dissolved in 50 mL MeOH and stirred for 1 h at room temperature. The mixture was filtered and the filtrate was concentrated on a rotovap at 40–45 °C. The resulted solid was dried under vacuum$^{[1]}$.

3. General procedure for N-aryl aryl thioamides synthesis

$$\begin{align*}
\text{Cul (10 mmol%), MeHN} &\rightarrow \text{NMe (20 mmol%)}, \\
\text{Na}_2\text{S}_2\text{O}_3 (1.5 equiv), DMSO, 80^\circ C, 6h} &\rightarrow \text{S-} \text{S-O-Na}
\end{align*}$$

3. General procedure for N-aryl aryl thioamides synthesis

$$\begin{align*}
\text{R}^1 &\text{O-} \text{S-} \text{S-} \text{ONa} + \text{R}^2 \text{NH}_2 &\rightarrow \text{R}^1 \text{N} \text{H} \text{S} \text{R}^2 \\
\text{Imidazole (2.0 equiv)} &\rightarrow \text{R}^1 \text{N} \text{H} \text{S} \text{R}^2 \\
\text{Na}_2\text{CO}_3 (2.0 equiv) \quad \text{N}_2, 135^\circ C, 48h} &\rightarrow \text{R}^1 \text{N} \text{H} \text{S} \text{R}^2
\end{align*}$$

S-2
To a solution of the Bunte salts (0.75 mmol) in Dimethyl sulfoxide (2.0 mL) was added aniline (0.25 mmol), imidazole (34 mg, 0.5 mmol), and Na$_2$CO$_3$ (53 mg, 0.50 mmol) under nitrogen atmosphere in a screw-cap Schlenk test tube. The reaction mixture was stirred at 135 °C for 48 h. After the reaction was finished, the reaction mixture was cooled to room temperature and quenched with water. The mixture was extracted with dichloromethane (3.0 mL × 3), the combined organic phases were dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated under vacuum. The residue was purified by column chromatography to give the corresponding products (Petroleum ether / dichloromethane = 3:2-1:1; Petroleum ether / ethyl acetate = 4:1-7:1) (42%-99 %).

4. The Single Crystal X-ray Diffraction Study of 3af, 3ea and intermediate VI

4.1 The Single Crystal X-ray Diffraction Study of 3af

CCDC 1838715 (3af) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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Crystal size/mm$^3$ 0.28 × 0.12 × 0.09
Radiation CuK$\alpha$ ($\lambda = 1.54184$)
2$\Theta$ range for data collection/° 7.448 to 134.312
Index ranges -14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -6 ≤ l ≤ 9
Reflections collected 3928
Independent reflections 3928 [R$_{int}$ = ?; R$_{sigma} = 0.0428$]
Data/restraints/parameters 3928/0/156
Goodness-of-fit on F$^2$ 1.004
Final R indexes [I$>=$2$\sigma$ (I)] R$_1$ = 0.0431, wR$_2$ = 0.0969
Final R indexes [all data] R$_1$ = 0.0652, wR$_2$ = 0.1015
Largest diff. peak/hole / e Å$^{-3}$ 0.29/-0.15

4.2 The Single Crystal X-ray Diffraction Study of 3ea

CCDC 1838811 (3ea) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Identification code 201803177
Empirical formula C$_{14}$H$_{10}$F$_{3}$NS
Formula weight 281.29
Temperature/K 293(2)
Crystal system monoclinic
Space group P2$_1$/c
a/Å 13.5721(6)
b/Å 12.8938(8)
c/Å 7.9189(4)
$\alpha$/° 90
$\beta$/° 106.101(5)
$\gamma$/° 90
Volume/Å$^3$ 1331.42(13)
Z 4
$\rho_{calc}$/g/cm$^3$ 1.403
$\mu$/mm$^{-1}$ 2.374
F(000) 576.0
Crystal size/mm$^3$ 0.19 × 0.13 × 0.07
Radiation: CuKα (λ = 1.54184)

2θ range for data collection/°: 6.778 to 134.15

Index ranges: -16 ≤ h ≤ 10, -12 ≤ k ≤ 15, -8 ≤ l ≤ 9

Reflections collected: 4928

Independent reflections: 2380 [Rint = 0.0290, Rsigma = 0.0392]

Data/restraints/parameters: 2380/42/186

Goodness-of-fit on F²: 1.047

Final R indexes [I>=2σ (I)]: R₁ = 0.0610, wR₂ = 0.1697

Final R indexes [all data]: R₁ = 0.0764, wR₂ = 0.1865

Largest diff. peak/hole / e Å⁻³: 0.40/-0.28

4.3 The Single Crystal X-ray Diffraction Study of intermediate VI

CCDC 1865343(VI) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Identification code: 201806280

Empirical formula: C₁₅H₁₂S₄

Formula weight: 320.49

Temperature/K: 293(2)

Crystal system: orthorhombic

Space group: P₂₁₂₁₂

a/Å: 14.6712(15)

b/Å: 11.6039(10)

c/Å: 4.3268(5)

α/°: 90

β/°: 90
γ° 90
Volume/Å³ 736.61(13)
Z 2
ρcalc g/cm³ 1.445
μ/mm⁻¹ 5.766
F(000) 332.0
Crystal size/mm³ 0.25 × 0.15 × 0.13
Radiation CuKα (λ = 1.54184)
2Θ range for data collection/° 9.718 to 134.006
Index ranges -14 ≤ h ≤ 17, -12 ≤ k ≤ 13, -2 ≤ l ≤ 5
Reflections collected 1698
Independent reflections 1136 [Rint = 0.0322, Rσ = 0.0489]
Data/restraints/parameters 1136/0/75
Goodness-of-fit on F² 1.081
Final R indexes [I > 2σ (I)] R₁ = 0.0569, wR₂ = 0.1594
Final R indexes [all data] R₁ = 0.0646, wR₂ = 0.1709
Largest diff. peak/hole / e Å⁻³ 0.32/-0.34
Flack parameter 0.00(5)

5. The experiment of trapping the intermediate V'

\[
\begin{align*}
\text{1a} + \text{2a} \rightarrow \text{V}', \text{detected by MS(ESI⁺)} \\
[M+H]^+: \text{Calcd. 340.04} \\
\text{Found: 340.15}
\end{align*}
\]
6. Exploring the mechanism by tracking experiments

To a solution of the Bunte salts 1d (0.75 mmol) in Dimethyl sulfoxide (2.0 mL) was added aniline 2a (0.25 mmol), imidazole (34 mg, 0.5 mmol), and Na₂CO₃ (53 mg, 0.50 mmol) under nitrogen atmosphere in five screw-cap Schlenk test tube. The reaction mixture was stirred at 135 °C. The reaction in sequence for 2.5h, 15h, 21h, 27h and 38h. After the reaction was finished, the reaction mixture was cooled to room temperature. The mixture was extracted with dichloromethane (3.0 mL × 3), the combined organic phases were dried over anhydrous Na₂SO₄ and the solvent was evaporated under vacuum. The processed samples were separately passed through mass spectrometry and nuclear magnetic detection. The test results are as follows.
6.1 Nuclear magnetic tracking results

![NMR Spectra](image)

- **2.5 h**
- **15 h**
- **21 h**
- **27 h**
- **38 h**

**Chemical Structures**

- **a:**
  - ![Chemical Structure a](image)
  - **b:**
    - ![Chemical Structure b](image)
  - **c:**
    - ![Chemical Structure c](image)
  - **d:**
    - ![Chemical Structure d](image)
  - **e:**
    - ![Chemical Structure e](image)
  - **f:**
    - ![Chemical Structure f](image)
6.2 Mass spectrometry tracking results

2.5 h

$$m/z : [M+H]^+ \text{ Calcd. 157.0}$$

Found: 157.1

$$m/z : [M-\text{H}]^- \text{ Calcd. 246.0}$$

Found: 245.8

15 h

$$m/z : [M+H]^+ \text{ Calcd. 157.0}$$

Found: 157.2

$$m/z : [M-\text{H}]^- \text{ Calcd. 246.0}$$

Found: 245.9
7. Characterization data of products

**N-phenylbenzothioamide (3aa).** Prepared according to the general procedure to afford a yellow solid in 98% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.12 (s, 1H), 7.77 (d, J = 7.40 Hz, 2H), 7.67 (d, J = 7.68 Hz, 2H), 7.46 (q, J = 8.19 Hz, 1H), 7.37 (d, J = 6.4 Hz, 4H), 7.26 (d, J = 7.2 Hz, 1H); 13C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.41, 142.87, 138.91, 131.25, 128.94, 128.53, 126.95, 126.73, 123.81. The analytical data correspond with those reported in the literature\(^2\).

**N-(m-tolyl)benzothioamide (3ab).** Prepared according to the general procedure to afford a yellow solid in 91% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.90 (s, 1H), 7.86 (d, J = 7.4 Hz, 2H), 7.52-7.45 (m, 2H), 7.41 (t, J = 7.52 Hz, 2H), 7.27 (t, J = 4.58 Hz, 3H), 2.29 (s, 3H); 13C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 199.62, 142.06, 137.56, 134.34, 131.49, 131.07, 128.69, 128.24, 126.89, 126.83, 126.81, 18.01. The analytical data correspond with those reported in the literature\(^3\).

**N-(m-tolyl)benzothioamide (3ac).** Prepared according to the general procedure to afford a yellow solid in 87% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.02 (s, 1H), 7.40 (t, J = 7.18 Hz, 2H), 7.30 (t, J = 7.48 Hz, 2H), 7.26 (d, J = 7.2 Hz, 1H); 13C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 199.62, 142.06, 137.56, 134.34, 131.49, 131.07, 128.69, 128.24, 126.89, 126.83, 126.81, 18.01. The analytical data correspond with those reported in the literature\(^3\).
N-(p-toly)benzothioamide (3ad). Prepared according to the general procedure to afford a yellow solid in 78% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.98 (s, 1H), 7.84 (d, \(J = 7.48\) Hz, 2H), 7.61 (d, \(J = 8.08\) Hz, 2H), 7.50 (t, \(J = 6.86\) Hz, 1H), 7.43 (t, \(J = 7.44\) Hz, 2H), 7.24 (t, \(J = 7.32\) Hz, 2H), 2.38 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.41, 143.15, 139.10, 138.95, 131.28, 128.88, 128.65, 127.89, 126.76, 124.36, 120.97, 21.48. The analytical data correspond with those reported in the literature\(^4\).

N-(3-methoxyphenyl)benzothioamide (3ae). Prepared according to the general procedure to afford a yellow solid in 82% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.05 (s, 1H), 7.81 (d, \(J = 6.92\) Hz, 2H), 7.59 (s, 1H), 7.48 (d, \(J = 6.84\) Hz, 1H), 7.42 (d, \(J = 7.04\) Hz, 2H), 7.31 (t, \(J = 7.84\) Hz, 1H), 7.20 (d, \(J = 7.08\) Hz, 1H), 6.83 (d, \(J = 7.44\) Hz, 1H), 3.81 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.30, 159.99, 143.30, 140.13, 131.32, 129.80, 128.68, 126.73, 115.71, 112.83, 109.09, 55.49. The analytical data correspond with those reported in the literature\(^3\).

N-(4-methoxyphenyl)benzothioamide (3af). Prepared according to the general procedure to afford a yellow solid in 53% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.02 (s, 1H), 7.81 (t, \(J = 7.88\) Hz, 2H), 7.58 (d, \(J = 8.92\) Hz, 2H), 7.46 (t, \(J = 7.34\) Hz, 1H), 7.40 (t, \(J = 7.48\) Hz, 2H), 6.93 (d, \(J = 8.92\) Hz, 2H), 3.81 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.38, 158.23, 142.81, 132.02, 131.28, 128.64, 126.79, 125.73, 114.18, 55.54. The analytical data correspond with those reported in the literature\(^2\).

N-(2,5-dimethylylphenyl)benzothioamide (3ag). Prepared according to the general procedure to afford a yellow solid in 70% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.80 (s, 1H), 7.89 (d, \(J = 7.44\) Hz, 2H), 7.52 (t, \(J = 7.22\) Hz, 1H), 7.44 (t, \(J = 7.44\) Hz, 2H), 7.34 (s, 1H), 7.20 (d, \(J = 7.72\) Hz, 1H), 7.10 (d, \(J = 7.56\) Hz, 1H), 2.36 (s, 3H), 2.28 (s, 3H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.45, 141.18, 136.24, 135.62, 130.35, 130.05, 129.82, 128.01, 127.63, 126.03, 125.75, 19.94, 16.50. The analytical data correspond with those reported in the literature\(^5\).

N-(2,6-diisopropylphenyl)benzothioamide (3ah). Prepared according to the general procedure to afford a yellow solid in 72% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.63 (s, 1H), 7.93 (s, 1H), 7.91 (d, \(J = 1.4\) Hz, 1H), 7.56-7.50 (m, 1H), 7.48-7.38 (m, 3H), 7.27 (d, \(J = 7.72\) Hz, 2H), 3.07 (m, 2H), 1.28 (d, \(J = 6.84\) Hz, 6H), 1.20 (d, \(J = 6.92\) Hz, 6H); \(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.22, 191.45, 159.99, 143.30, 140.13, 131.32, 129.80, 128.68, 126.73, 115.71, 112.83, 109.09, 55.49. The analytical data correspond with those reported in the literature\(^6\).
N-(3-chlorophenyl)benzothioamide (3ai). Prepared according to the general procedure to afford a yellow solid in 83% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.03 (s, 1H), 7.86 (s, 1H), 7.79 (s, 2H), 7.60 (s, 1H), 7.50 (t, \(J = 6.90\) Hz, 1H), 7.41 (t, \(J = 7.34\) Hz, 2H), 7.34 (t, \(J = 7.78\) Hz, 1H), 7.24 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.81, 142.85, 139.98, 134.56, 131.48, 129.00, 128.68, 126.96, 126.70, 123.70, 121.81. The analytical data correspond with those reported in the literature\(^2\).

N-(4-chlorophenyl)benzothioamide (3aj). Prepared according to the general procedure to afford a yellow solid in 92% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.94 (s, 1H), 7.74 (d, \(J = 6.99\) Hz, 2H), 7.62 (d, \(J = 7.68\) Hz, 2H), 7.42 (d, \(J = 6.96\) Hz, 1H), 7.33 (q, \(J = 8.77\) Hz, 4H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 197.65, 141.80, 136.42, 131.08, 130.45, 128.13, 127.65, 125.66, 124.03, 113.59. The analytical data correspond with those reported in the literature\(^2\).

N-(3-bromophenyl)benzothioamide (3ak). Prepared according to the general procedure to afford a yellow solid in 52% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.00 (s, 1H), 7.99 (s, 1H), 7.80 (s, 2H), 7.68 (d, \(J = 4.00\) Hz, 1H), 7.50 (t, \(J = 6.86\) Hz, 1H), 7.42 (d, \(J = 7.34\) Hz, 3H), 7.29 (d, \(J = 7.12\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.79, 142.84, 140.06, 131.50, 130.27, 129.88, 128.69, 126.68, 125.52, 122.39, 122.30. The analytical data correspond with those reported in the literature\(^3\).

N-(4-bromophenyl)benzothioamide (3al). Prepared according to the general procedure to afford a yellow solid in 69% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.99 (s, 1H), 7.81 (d, \(J = 6.28\) Hz, 2H), 7.66 (d, \(J = 7.28\) Hz, 2H), 7.56-7.47 (m, 3H), 7.43 (d, \(J = 6.96\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.60, 142.89, 137.96, 132.12, 131.47, 128.69, 126.67, 125.25, 119.93. The analytical data correspond with those reported in the literature\(^3\).

N-(4-fluorophenyl)benzothioamide (3am). Prepared according to the general procedure to afford a yellow solid in 98% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.06 (s, 1H), 7.79 (d, \(J = 7.44\) Hz, 2H), 7.63 (q, \(J = 4.51\) Hz, 2H), 7.49 (t, \(J = 3.34\) Hz, 1H), 7.40 (t, \(J = 7.56\) Hz, 2H), 7.08 (t, \(J = 8.54\) Hz, 2H); \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -113.59. The analytical data correspond with those reported in the literature\(^2\).
N-(4-bromo-3-fluorophenyl)benzothioamide (3an). Prepared according to the general procedure to afford a yellow solid in 62% yield; mp 140 °C; \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.02 (s, 1H), 7.94 (s, 1H), 7.79 (d, \(J = 5.52\) Hz, 2H), 7.59-7.49 (m, 2H), 7.43 (t, \(J = 7.52\) Hz, 2H), 7.33 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.91, 158.85 (d, \(J_{C-F} = 246.11\) Hz), 139.48 (d, \(J_{C-F} = 9.30\) Hz), 133.50, 131.62, 128.77, 126.67, 120.00 (d, \(J_{C-F} = 3.57\) Hz), 111.79, 111.52, 106.30 (d, \(J_{C-F} = 20.60\)Hz); \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -114.27; HR-MS (ESI\(^{+}\)): calcd. for C\(_{13}\)H\(_9\)BrFNS [M+H]\(^{+}\): 309.9696, Found: 309.9697.

N-(3-bromophenyl)benzothioamide (3ao). Prepared according to the general procedure to afford a yellow solid in 35% yield; \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.20 (s, 1H), 7.99 (d, \(J = 7.56\) Hz, 2H), 7.94-7.84 (m, 3H), 7.75 (d, \(J = 7.12\) Hz, 1H), 7.57-7.43 (m, 6H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 200.58, 142.04, 134.90, 134.28, 131.57, 128.78, 128.72, 128.56, 126.94, 126.88, 126.50, 125.45, 124.76, 121.86. The analytical data correspond with those reported in the literature\(^{[7]}\).

N-(naphthalen-2-yl)benzothioamide (3ap). Prepared according to the general procedure to afford a yellow solid in 47% yield; \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.18 (s, 1H), 8.39 (s, 1H), 7.87 (d, \(J = 7.80\) Hz, 2H), 7.83 (t, \(J = 3.66\) Hz, 2H), 7.71 (d, \(J = 8.12\) Hz, 1H), 7.50 (q, \(J = 3.03\) Hz, 3H), 7.45 (d, \(J = 7.36\)Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.42, 143.12, 136.45, 133.34, 131.99, 131.35, 128.81, 128.69, 127.99, 127.73, 126.70, 126.28, 122.66, 121.24. The analytical data correspond with those reported in the literature\(^{[8]}\).

3-fluoro-N-phenylbenzothioamide (3ba). Prepared according to the general procedure to afford a yellow solid in 92% yield; \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.02 (s, 1H), 7.74 (d, \(J = 7.76\) Hz, 2H), 7.58 (d, \(J = 7.92\) Hz, 2H), 7.48-7.38 (m, 3H), 7.31 (t, \(J = 7.26\) Hz, 1H), 7.20 (t, \(J = 7.94\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 195.57, 161.50 (d, \(J_{C-F} = 246.84\) Hz), 144.11, 137.74, 129.24 (d, \(J_{C-F} = 7.87\) Hz), 126.89, 126.18, 122.67, 120.80, 117.70 (d, \(J_{C-F} = 3.57\) Hz), 113.50 (d, \(J_{C-F} = 23.31\) Hz); \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -111.50. The analytical data correspond with those reported in the literature\(^{[10]}\).

3-fluoro-N-(p-tolyl)benzothioamide (3bd). Prepared according to the general procedure to afford a yellow solid in 83% yield; \(^{1}H\) NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.97 (s, 1H), 7.59 (t, \(J = 7.56\) Hz, 4H), 7.39 (q, \(J = 7.16\) Hz, 1H), 7.24 (d, \(J = 7.00\) Hz, 2H), 7.18 (dq, \(J = 9.48\) Hz, 2.24 Hz, 1H), 2.38 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 195.45, 161.50 (d, \(J_{C-F} = 246.81\) Hz), 144.01 (d, \(J_{C-F} = 6.72\) Hz), 136.25, 135.22, 129.21 (d, \(J_{C-F} = 8.18\) Hz),
128.66, 122.76, 120.79 (d, J_C-F = 2.57 Hz), 117.04 (d, J_C-F = 21.28 Hz), 113.49 (d, J_C-F = 23.52 Hz), 20.17; ^19_F NMR (377 MHz, CDCl_3) δ -111.59. The analytical data correspond with those reported in the literature^{10}.

3-fluoro-N-(4-fluorophenyl)benzothioamide (3bm).
Prepared according to the general procedure to afford a yellow solid in 64% yield, mp 110 °C; ^1H NMR (CDCl_3, 400 MHz) δ 8.98 (s, 1H), 7.67 (q, J = 4.49 Hz, 2H), 7.57 (d, J = 7.64 Hz, 2H), 7.40 (q, J = 7.17 Hz, 1H), 7.20 (q, J = 7.36 Hz, 1H); ^13_C NMR (CDCl_3, 100 MHz) δ 197.08, 162.51 (d, J_C-F = 246.55 Hz), 160.94 (d, J_C-F = 246.33 Hz), 144.62 (d, J_C-F = 7.06 Hz), 134.67, 130.31 (d, J_C-F = 8.09 Hz), 126.03 (d, J_C-F = 8.31 Hz), 121.81 (d, J_C-F = 2.52 Hz), 118.30 (d, J_C-F = 21.27 Hz), 116.04 (d, J_C-F = 22.74 Hz), 114.52 (d, J_C-F = 23.55 Hz); ^19_F NMR (377 MHz, CDCl_3) δ -111.42, -113.27; HR-MS (ESI^+): calcd. for C_{13}H_{9}F_{2}NS [M+H]^+: 250.0497, Found: 250.0496.

N-(3-bromophenyl)benzothioamide (3ca).
Prepared according to the general procedure to afford a yellow solid in 65% yield; ^1H NMR (CDCl_3, 400 MHz) δ 9.02 (s, 1H), 7.77 (d, J = 7.84 Hz, 2H), 7.45 (t, J = 7.04 Hz, 3H), 7.33 (m, 3H), 7.04 (d, J = 7.36 Hz, 1H); ^13_C NMR (CDCl_3, 100 MHz) δ 198.12, 159.66, 144.62, 138.90, 129.68, 129.08, 127.03, 123.66, 118.07, 117.40, 112.61, 55.51. The analytical data correspond with those reported in the literature^{11}.

3-chloro-N-phenylbenzothioamide (3da).
Prepared according to the general procedure to afford a yellow solid in 81% yield; ^1H NMR (CDCl_3, 400 MHz) δ 8.90 (s, 1H), 7.83 (s, 1H), 7.75 (d, J = 7.20 Hz, 2H), 7.70 (d, J = 7.36 Hz, 1H), 7.44 (d, J = 7.88 Hz, 3H), 7.37 (t, J = 7.92 Hz, 1H), 7.31 (t, J = 7.06 Hz, 1H); ^13_C NMR (CDCl_3, 100 MHz) δ 195.52, 143.70, 137.71, 133.70, 130.10, 128.89, 128.12, 126.20, 125.96, 123.71, 122.64. The analytical data correspond with those reported in the literature^{5}.

N-phenyl-3-(trifluoromethyl)benzothioamide (3ea).
Prepared according to the general procedure to afford a yellow solid in 77% yield, mp 130 °C; ^1H NMR (CDCl_3, 400 MHz) δ 9.03 (s, 1H), 8.08 (s, 1H), 8.02 (d, J = 7.48 Hz, 1H), 7.75 (d, J = 7.48 Hz, 3H), 7.57 (t, J = 7.56 Hz, 1H), 7.46 (t, J = 7.42 Hz, 2H), 7.33 (t, J = 7.06 Hz, 1H); ^13_C NMR (CDCl_3, 100 MHz) δ 196.61, 143.72, 138.64, 131.09 (q, J = 32.72 Hz), 130.02, 129.31, 129.18, 127.67, 127.36, 123.75, 123.60 (q, J = 271.32 Hz), 123.52 (q, J = 3.83 Hz); ^19_F NMR (377 MHz, CDCl_3) δ -62.65; HR-MS (ESI^+): calcd. for C_{14}H_{10}F_{3}NS [M+H]^+: 282.0559, Found: 282.0558.
4-methyl-N-phenylbenzothioamide (3fa). Prepared according to the general procedure to afford a yellow solid in 44% yield; \(^1\)H NMR (CDCl\(_3\) 400 MHz) \(\delta\) 8.98 (s, 1H), 7.77 (s, 4H), 7.44 (s, 2H), 7.29 (s, 1H), 7.23 (s, 2H), 2.40 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.28, 141.95, 140.41, 139.11, 129.27, 129.06, 126.91, 126.70, 123.77, 21.40. The analytical data correspond with those reported in the literature\(^9\).

4-cyano-N-phenylbenzothioamide (3ga). Prepared according to the general procedure to afford a yellow solid in 87% yield; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.11 (s, 1H), 7.90 (d, \(J = 8.12\) Hz, 2H), 7.76 (d, \(J = 7.84\) Hz, 2H), 7.70 (d, \(J = 8.16\) Hz, 2H), 7.47 (t, \(J = 7.70\) Hz, 2H), 7.34 (t, \(J = 6.86\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 195.89, 146.62, 138.52, 132.46, 129.20, 127.46, 127.37, 123.53, 118.10, 114.31. The analytical data correspond with those reported in the literature\(^3\).

N-phenyl-4-(trifluoromethyl)benzothioamide (3ha). Prepared according to the general procedure to afford a yellow solid in 99% yield, mp 190°C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.95 (s, 1H), 7.86 (d, \(J = 7.44\) Hz, 2H), 7.70 (d, \(J = 7.32\) Hz, 2H), 7.63 (d, \(J = 7.48\) Hz, 2H), 7.40 (t, \(J = 6.98\) Hz, 2H), 7.26 (t, \(J = 6.98\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 195.70, 145.20, 137.62, 131.73 (q, \(J = 34.76\) Hz), 128.17, 126.33, 126.03, 124.70 (q, \(J = 3.83\) Hz), 122.62 (q, \(J = 270.60\) Hz), 122.57; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -62.89; HR-MS (ESI\(^+\)): calcd. for C\(_{14}\)H\(_{10}\)F\(_3\)NS [M+H\(^+\)]: 282.0559, Found: 282.0557.

N-(m-tolyl)-3-(trifluoromethyl)benzothioamide (3eb). Prepared according to the general procedure to afford a yellow solid in 99% yield, mp 82°C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 8.88 (s, 1H), 8.12 (s, 1H), 8.05 (d, \(J = 7.68\) Hz, 1H), 7.76 (d, \(J = 7.64\) Hz, 1H), 7.57 (t, \(J = 7.76\) Hz, 3H), 7.49 (t, \(J = 4.12\) Hz, 1H), 7.30 (d, \(J = 9.24\) Hz, 3H), 2.32 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 196.76, 141.60, 136.13, 133.25, 130.11, 130.05 (q, \(J = 32.64\) Hz), 128.96, 128.26, 127.45, 126.80 (q, \(J = 6.90\) Hz), 125.88, 125.62, 122.71 (q, \(J = 3.80\) Hz), 122.58 (q, \(J = 270.80\) Hz), 16.91; \(^{19}\)F NMR (377 MHz, CDCl\(_3\)) \(\delta\) -62.61; HR-MS (ESI\(^+\)): calcd. for C\(_{15}\)H\(_{12}\)F\(_3\)NS [M+H\(^+\)]: 296.0715, Found: 296.0716.

N-(m-tolyl)-3-(trifluoromethyl)benzothioamide (3ec). Prepared according to the general procedure to afford a yellow solid in 99% yield, mp 126°C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.03 (s, 1H), 8.05 (s, 1H), 7.98 (d, \(J = 7.64\) Hz, 1H), 7.73 (d, \(J = 7.59\) Hz, 1H), 7.54 (t, \(J = 7.44\) Hz,
N-(p-tolyl)-3-(trifluoromethyl)benzothioamide (3ed). Prepared according to the general procedure to afford a yellow solid in 72% yield, mp 128°C; \( ^1H \) NMR (CDCl\(_3\), 400 MHz) \( \delta \) 9.03 (s, 1H), 8.06 (s, 1H), 8.00 (d, \( J = 7.80 \) Hz, 1H), 7.73 (d, \( J = 7.72 \) Hz, 1H), 7.56 (q, \( J = 8.60 \) Hz, 4H), 7.23 (s, 1H), 2.38 (s, 3H); \( ^{13}C \) NMR (CDCl\(_3\), 100 MHz) \( \delta \) 196.49, 143.59, 137.43, 136.13, 131.02 (q, \( J_{C-F} = 32.78 \) Hz), 130.02, 129.72, 129.24, 127.53 (q, \( J_{C-F} = 3.38 \) Hz), 123.85, 123.67 (q, \( J_{C-F} = 275.68 \) Hz), 123.57 (q, \( J_{C-F} = 3.76 \) Hz), 21.21; \( ^{19}F \) NMR (377 MHz, CDCl\(_3\)) \( \delta \) -62.62; HR-MS (ESI\(^+\)): calcd. for C\(_{15}\)H\(_{12}\)F\(_3\)NS [M+H]\(^+\): 296.0715, Found: 296.0720.

N-(3-methoxyphenyl)-3-(trifluoromethyl)benzothioamide (3ee). Prepared according to the general procedure to afford a yellow solid in 57% yield, mp 102-103°C; \( ^1H \) NMR (CDCl\(_3\), 400 MHz) \( \delta \) 9.05 (s, 1H), 8.05 (s, 1H), 7.99 (d, \( J = 6.44 \) Hz, 1H), 7.74 (d, \( J = 7.36 \) Hz, 1H), 7.56 (s, 2H), 7.34 (t, \( J = 8.34 \) Hz, 1H), 7.20 (t, \( J = 6.90 \) Hz, 1H), 6.85 (d, \( J = 7.6 \) Hz, 1H), 3.83 (s, 3H); \( ^{13}C \) NMR (CDCl\(_3\), 100 MHz) \( \delta \) 196.39, 160.05, 143.85, 139.77, 131.06 (q, \( J_{C-F} = 33.76 \) Hz), 129.98, 129.89, 129.29, 127.65, 123.64 (q, \( J_{C-F} = 276.00 \) Hz), 123.54, 115.67, 113.06, 109.13, 55.47; \( ^{19}F \) NMR (377 MHz, CDCl\(_3\)) \( \delta \) -62.62; HR-MS (ESI\(^+\)): calcd. for C\(_{15}\)H\(_{12}\)F\(_3\)NOS [M+H]\(^+\): 312.0664, Found: 312.0663.

N-(4-methoxyphenyl)-3-(trifluoromethyl)benzothioamide (3ef). Prepared according to the general procedure to afford a yellow solid in 83% yield, mp 121°C; \( ^1H \) NMR (CDCl\(_3\), 400 MHz) \( \delta \) 9.04 (s, 1H), 8.05 (s, 1H), 7.99 (d, \( J = 7.84 \) Hz, 1H), 7.73 (d, \( J = 7.76 \) Hz, 1H), 7.61-7.52 (m, 3H), 6.96-6.93 (m, 2H), 3.83 (s, 3H); \( ^{13}C \) NMR (CDCl\(_3\), 100 MHz) \( \delta \) 196.48, 158.42, 143.40, 131.64, 130.99 (q, \( J_{C-F} = 32.60 \) Hz), 130.05, 129.23, 127.60 (q, \( J_{C-F} = 36.53 \) Hz), 125.63, 123.64 (q, \( J_{C-F} = 270.96 \) Hz), 123.58 (q, \( J_{C-F} = 3.87 \) Hz), 114.24, 55.50; \( ^{19}F \) NMR (377 MHz, CDCl\(_3\)) \( \delta \) -62.60; HR-MS (ESI\(^+\)): calcd. for C\(_{15}\)H\(_{12}\)F\(_3\)NOS [M+H]\(^+\): 312.0664, Found: 312.0661.

N-(2,5-dimethylphenyl)-3-(trifluoromethyl)benzothioamide (3eg). Prepared according to the general procedure to afford a
yellow solid in 94% yield, mp 101 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.80 (s, 1H), 8.04 (s, 1H), 7.95 (d, $J = 7.68$ Hz, 1H), 7.67 (d, $J = 7.64$ Hz, 1H), 7.48 (t, $J = 7.76$ Hz, 1H), 7.20 (s, 1H), 7.11 (d, $J = 7.72$ Hz, 1H), 7.02 (d, $J = 7.56$ Hz, 1H), 2.27 (s, 3H), 2.19 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 196.66, 141.68, 135.94, 135.72, 130.99 (q, $J_{C-F}$ = 25.76 Hz), 130.20, 130.10, 129.90, 128.94, 128.24 (d, $J_{C-F}$ = 4.93 Hz), 126.71 (q, $J_{C-F}$ = 3.63 Hz), 125.96, 122.72 (q, $J_{C-F}$ = 4.04 Hz), 122.58 (q, $J_{C-F}$ = 267.37 Hz), 19.91, 16.47; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -62.62; HR-MS (ESI$^+$): calcd. for C$_{16}$H$_{14}$F$_3$NS [M+H]$^+$: 310.0872, Found: 310.0872.

N-(3-chlorophenyl)-3-(trifluoromethyl)benzothioamide (3ei). Prepared according to the general procedure to afford a yellow solid in 86% yield, mp 125 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.02 (s, 1H), 8.04 (s, 1H), 7.98 (s, 1H), 7.86 (s, 1H), 7.75 (d, $J = 7.44$ Hz, 1H), 7.61 (s, 1H), 7.56 (t, $J = 7.30$ Hz, 1H), 7.37 (t, $J = 7.36$ Hz, 1H), 7.28 (d, $J = 7.60$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 195.91, 142.41, 138.66, 133.69, 130.09 (q, $J = 32.70$ Hz), 129.11, 129.04, 128.31, 126.81, 126.30, 122.74, 122.54 (q, $J = 271.03$ Hz), 122.50, 120.02; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -62.65; HR-MS (ESI$^+$): calcd. for C$_{14}$H$_9$ClF$_3$NS [M+H]$^+$: 316.0169, Found: 316.0172.

N-(4-chlorophenyl)-3-(trifluoromethyl)benzothioamide (3ej). Prepared according to the general procedure to afford a yellow solid in 66% yield, mp 102°C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.02 (s, 1H), 8.04 (s, 1H), 7.99 (d, $J = 7.44$ Hz, 1H), 7.75 (d, $J = 7.40$ Hz, 1H), 7.69 (d, $J = 7.40$ Hz, 1H), 7.56 (t, $J = 7.36$ Hz, 1H), 7.37 (t, $J = 7.36$ Hz, 1H), 7.28 (d, $J = 7.60$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 195.78, 142.33, 136.07, 131.48, 130.07 (q, $J = 32.37$ Hz), 129.11, 129.02, 128.31, 128.25, 126.84, 124.08, 122.55 (q, $J = 270.97$ Hz), 122.47; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -62.63; HR-MS (ESI$^+$): calcd. for C$_{14}$H$_9$ClF$_3$NS [M+H]$^+$: 316.0169, Found: 316.0171.

N-(3-bromophenyl)-3-(trifluoromethyl)benzothioamide (3ek). Prepared according to the general procedure to afford a yellow solid in 62% yield, mp 103 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.03 (s, 1H), 8.03 (s, 1H), 7.97 (s, 1H), 7.75 (d, $J = 7.44$ Hz, 1H), 7.67 (s, 1H), 7.56 (t, $J = 7.40$ Hz, 1H), 7.43 (d, $J = 7.64$ Hz, 1H), 7.30 (t, $J = 7.44$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 196.93, 143.38, 139.76, 131.13 (q, $J_{C-F} = 32.78$ Hz), 130.40, 130.25, 130.03, 129.35, 127.86, 126.64, 123.56 (q, $J_{C-F} = 270.76$ Hz), 123.54, 122.37, 122.37; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -62.64; HR-MS (ESI$^+$): calcd. for C$_{14}$H$_9$BrF$_3$NS [M+H]$^+$: 359.9664, Found: 359.9689.

N-(4-bromophenyl)-3-(trifluoromethyl)benzothioamide S-18
(3e). Prepared according to the general procedure to afford a yellow solid in 42% yield, mp 100°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 9.00 (s, 1H), 8.05 (s, 1H), 8.01 (d, J = 7.44 Hz, 1H), 7.76 (d, J = 7.32 Hz, 1H), 7.66 (d, J = 8.04 Hz, 2H), 7.56 (t, J = 7.80 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 195.71, 142.42, 136.63, 131.22, 130.05 (q, J = 32.69 Hz), 129.07, 128.31, 126.82, 124.27, 122.53 (q, J = 270.93 Hz), 122.45, 119.31; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -62.63; HR-MS (ESI$^+$): calcd. for C$_{14}$H$_9$BrF$_3$NS [M+H]$^+$: 359.9664, Found: 359.9660.

N-(4-fluorophenyl)-3-(trifluoromethyl)benzothioamide (3em). Prepared according to the general procedure to afford a yellow solid in 93% yield, mp 89°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 9.06 (s, 1H), 8.05 (s, 1H), 7.99 (d, J = 7.80 Hz, 1H), 7.74 (d, J = 7.68 Hz, 1H), 7.66 (m, 2H), 7.56 (t, J = 7.78 Hz, 1H), 7.13 (t, J = 8.52 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 197.10, 161.04 (d, J$_{C-F}$ = 246.61 Hz), 143.31, 134.68 (d, J$_{C-F}$ = 2.98 Hz), 135.13, 129.32, 127.79 (q, J$_{C-F}$ = 3.56 Hz), 126.10 (d, J = 8.02 Hz), 123.61 (q, J$_{C-F}$ = 270.90 Hz), 123.51 (d, J$_{C-F}$ = 3.63 Hz), 116.06 (d, J$_{C-F}$ = 22.60 Hz); $^{19}$F NMR (377 MHz, CDCl$_3$) δ -62.62, -113.09; HR-MS (ESI$^+$): calcd. for C$_{14}$H$_9$F$_4$NS [M+H]$^+$: 300.0465, Found: 300.0467.

N-(4-bromo-3-fluorophenyl)-3-(trifluoromethyl)benzothioamide (3en). Prepared according to the general procedure to afford a yellow solid in 42% yield, mp 70°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.97 (s, 1H), 7.96 (s, 1H), 7.91 (d, J = 5.32 Hz, 1H), 7.85 (s, 1H), 7.69 (d, J = 7.68 Hz, 1H), 7.51 (q, J = 8.51 Hz, 2H), 7.28 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 195.80, 157.89 (d, J$_{C-F}$ = 246.45 Hz), 142.38, 138.13 (d, J$_{C-F}$ = 9.23 Hz), 132.64, 130.20 (q, J$_{C-F}$ = 32.75 Hz), 129.01, 128.39, 126.93 (q, J$_{C-F}$ = 3.47 Hz), 122.51 (q, J$_{C-F}$ = 271.06 Hz), 122.46, 119.04 (d, J$_{C-F}$ = 3.63 Hz), 116.06 (d, J$_{C-F}$ = 22.60 Hz); $^{19}$F NMR (377 MHz, CDCl$_3$) δ -62.62, -113.09; HR-MS (ESI$^+$): calcd. for C$_{14}$H$_9$BrF$_3$NS [M+H]$^+$: 377.9570, Found: 377.9567.

N-(naphthalen-1-yl)benzothioamide (3eo). Prepared according to the general procedure to afford a yellow solid in 98% yield, mp 120°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 9.23 (s, 1H), 8.25 (s, 1H), 8.17 (d, J = 7.64 Hz, 1H), 7.95-7.89 (m, 2H), 7.86 (q, J = 2.97 Hz, 1H), 7.80 (d, J = 7.84 Hz, 1H), 7.76 (d, J = 7.28 Hz, 1H), 7.62 (t, J = 7.86 Hz, 1H), 7.59-7.53 (m, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 198.76, 142.69, 134.61, 134.13, 131.21 (q, J$_{C-F}$ = 32.72 Hz), 130.07, 129.37, 128.88, 128.73, 127.94, 127.10, 125.63, 125.46, 124.79, 123.82, 123.67 (q, J$_{C-F}$ = 273.57 Hz), 121.70, 105.32; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -62.56; HR-MS (ESI$^+$): calcd. for C$_{14}$H$_9$BrF$_3$NS [M+H]$^+$: 332.0715, Found: 332.0715.
N-(naphthalen-2-yl)-3-(trifluoromethyl)benzothioamide (3ep). Prepared according to the general procedure to afford a yellow solid in 49% yield, mp 106 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 9.14 (s, 1H), 8.29 (s, 1H), 8.03 (s, 1H), 7.96 (d, J = 7.52 Hz, 1H), 7.81 (d, J = 8.80 Hz, 1H), 7.76 (d, J = 2.36 Hz, 2H), 7.68 (d, J = 7.48 Hz, 1H), 7.62 (d, J = 8.40 Hz, 2H), 7.49 (t, J = 7.72 Hz, 1H), 7.43 (q, J = 3.11 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 195.52, 142.62, 135.10, 132.27, 131.09, 130.05 (q, J$_{C-F}$ = 32.82 Hz), 129.05, 128.27, 127.93, 126.99, 126.75, 126.67, 125.80, 125.47, 122.60 (q, J$_{C-F}$ = 271.06 Hz), 122.57, 121.47, 120.42; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -62.56; HR-MS (ESI$^+$): calcd. for C$_{18}$H$_{12}$F$_3$NS [M+H]$^+$: 332.0715, Found: 332.0718.

N-(o-tolyl)-4-(trifluoromethyl)benzothioamide (3hb). Prepared according to the general procedure to afford a yellow solid in 99% yield, mp 124 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.81 (s, 1H), 7.88 (d, J = 7.84 Hz, 2H), 7.61 (d, J = 8.00 Hz, 2H), 7.23 (d, J = 3.16 Hz, 3H), 2.24 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 196.92, 144.06, 136.11, 133.14, 130.12, 127.43, 126.16, 126.87, 125.56, 124.64 (q, J = 3.65 Hz), 122.65 (q, J = 270.56 Hz), 16.86; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -62.88; HR-MS (ESI$^+$): calcd. for C$_{15}$H$_{11}$F$_3$NS [M+H]$^+$: 296.0715, Found: 296.0719.

N-(m-tolyl)-4-(trifluoromethyl)benzothioamide (3hc). Prepared according to the general procedure to afford a yellow solid in 99% yield, mp 129 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.99 (s, 1H), 7.91 (d, J = 7.52 Hz, 1H), 7.56 (d, J = 7.48 Hz, 2H), 7.34 (t, J = 7.62 Hz, 1H), 7.13 (d, J = 7.84 Hz, 2H), 7.23 (d, J = 3.16 Hz, 3H), 2.40 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 196.61, 146.18, 139.26, 138.54, 132.67 (q, J = 30.58 Hz), 128.99, 128.19, 127.05, 125.69 (q, J = 3.77 Hz), 124.14, 123.65 (q, J = 270.75 Hz), 120.74, 21.44; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -62.86; HR-MS (ESI$^+$): calcd. for C$_{15}$H$_{11}$F$_3$NS [M+H]$^+$: 296.0715, Found: 296.0719.

N-(3-methoxyphenyl)-4-(trifluoromethyl)benzothioamide (3hd). Prepared according to the general procedure to afford a yellow solid in 48% yield, mp 122 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.98 (s, 1H), 7.81 (d, J = 7.20 Hz, 2H), 7.59 (d, J = 7.40 Hz, 2H), 7.51 (s, 1H), 7.26 (t, J = 7.76 Hz, 1H), 7.13 (d, J = 7.48 Hz, 1H), 6.78 (d, J = 7.40 Hz, 1H), 3.75 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 195.48, 159.06, 145.28, 138.78, 131.65 (q, J$_{C-F}$ = 32.78 Hz), 128.87, 126.04, 124.66, 122.64 (q, J$_{C-F}$ = 271.09 Hz), 114.51, 112.00, 108.01, 54.46; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -62.88; HR-MS (ESI$^+$): calcd. for C$_{15}$H$_{12}$F$_3$NS [M+H]$^+$: 332.0715, Found: 332.0718.
N-(4-methoxyphenyl)-4-(trifluoromethyl)benzothioamide (3he). Prepared according to the general procedure to afford a yellow solid in 61% yield, mp 125 °C; $^1$H NMR (DMSO-d$_6$, 400 MHz) $\delta$ 11.89 (s, 1H), 7.97 (d, $J = 8.12$ Hz, 2H), 7.83 (d, $J = 8.24$ Hz, 2H), 7.79 - 7.74 (m, 2H), 7.03 - 6.99 (m, 2H), 3.79 (s, 3H); $^{13}$C NMR (DMSO-d$_6$, 100 MHz) $\delta$ 195.20, 157.63, 146.45, 132.96, 130.43 (q, $J = 31.74$ Hz), 128.34, 125.59, 125.26 (q, $J = 3.68$ Hz), 124.25 (q, $J = 271.98$ Hz), 113.87, 55.51; $^{19}$F NMR (377 MHz, DMSO-d$_6$) $\delta$ -61.23; HR-MS (ESI$^+$): calcd. for C$_{15}$H$_{12}$F$_3$NOS [M+H]$^+$: 312.0664, Found: 312.0662.

N-(2,5-dimethylphenyl)-4-(trifluoromethyl)benzothioamide (3hf). Prepared according to the general procedure to afford a yellow solid in 94% yield, mp 95 °C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.76 (s, 1H), 7.89 (d, $J = 7.92$ Hz, 2H), 7.62 (d, $J = 8.04$ Hz, 2H), 7.25 (s, 1H), 7.13 (d, $J = 7.76$ Hz, 1H), 7.04 (d, $J = 7.60$ Hz, 1H), 2.29 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 196.80, 144.18, 135.88, 131.78 (q, $J_{C,F} = 32.74$ Hz), 129.96, 129.93, 128.27, 126.13, 125.87, 124.66 (q, $J_{C,F} = 3.70$ Hz), 122.65 (q, $J_{C,F} = 270.73$ Hz), 19.92, 16.45; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -62.89; HR-MS (ESI$^+$): calcd. for C$_{16}$H$_{14}$F$_3$NS [M+H]$^+$: 310.0872, Found: 310.0877.

N-(3-chlorophenyl)-4-(trifluoromethyl)benzothioamide (3hi). Prepared according to the general procedure to afford a yellow solid in 90% yield, mp 113°C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 9.01 (s, 1H), 7.87 (s, 3H), 7.67 (d, $J = 7.20$ Hz, 1H), 7.61 (d, $J = 5.20$ Hz, 1H), 7.35 (d, $J = 6.84$ Hz, 1H), 7.28 (d, $J = 7.44$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 197.04, 145.86, 139.61, 134.74, 132.90 (q, $J_{C,F} = 32.66$ Hz), 130.17, 127.35, 127.07, 125.75, 123.63, 123.59 (q, $J_{C,F} = 270.96$ Hz), 121.72; $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -62.90; HR-MS (ESI$^+$): calcd. for C$_{14}$H$_9$ClF$_3$NS [M+H]$^+$: 316.0169, Found: 316.0167.

N-(4-chlorophenyl)-4-(trifluoromethyl)benzothioamide (3hj). Prepared according to the general procedure to afford a yellow solid in 71% yield, mp 173°C; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.99 (s, 1H), 7.92 (d, $J = 7.88$ Hz, 2H), 7.72 (dq, $J = 8.68$ Hz, $J = 4.92$ Hz, 4H), 7.43 (d, $J = 8.40$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 195.89, 144.89, 136.09, 131.87 (q, $J = 35.84$ Hz), 131.45, 128.28, 126.05, 124.73, 123.89, 122.56 (q, $J = 271.56$ Hz); $^{19}$F NMR (377 MHz, CDCl$_3$) $\delta$ -62.88; HR-MS (ESI$^+$):
N-(3-bromophenyl)-4-(trifluoromethyl)benzothioamide (3hk). Prepared according to the general procedure to afford a yellow solid in 50% yield, mp 98°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 9.05 (s, 1H), 7.99 (s, 1H), 7.88 (d, J = 6.60 Hz, 2H), 7.67 (d, J = 7.00 Hz, 3H), 7.43 (d, J = 7.60 Hz, 1H), 7.30 (t, J = 7.34 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 196.03, 144.77, 138.72, 131.85 (q, J = 32.12 Hz), 129.37, 129.22, 126.06, 125.47, 124.70 (q, J = 3.92 Hz), 122.58 (q, J = 270.96 Hz), 121.50, 121.23; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -62.88; HR-MS (ESI$^+$): calcd. for C$_{14}$H$_9$BrF$_3$NS [M+H]$^+$: 359.9664, Found: 359.9666.

N-(4-bromophenyl)-4-(trifluoromethyl)benzothioamide (3hl). Prepared according to the general procedure to afford a yellow solid in 74% yield, mp 126-127°C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.98 (s, 1H), 7.91 (d, J = 7.68 Hz, 2H), 7.69 (t, J = 6.70 Hz, 4H), 7.57 (d, J = 8.32 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 195.82, 144.93, 136.62, 131.88 (q, J = 30.19 Hz), 131.24, 126.03, 124.73 (q, J = 3.59 Hz), 124.10, 121.51 (q, J = 270.83 Hz), 119.28; $^{19}$F NMR (377 MHz, CDCl$_3$) δ -62.89; HR-MS (ESI$^+$): calcd. for C$_{14}$H$_9$BrF$_3$NS [M+H]$^+$: 359.9664, Found: 359.9662.

N-(4-fluorophenyl)-4-(trifluoromethyl)benzothioamide (3hm). Prepared according to the general procedure to afford a yellow solid in 98% yield, mp 180 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.91 (s, 1H), 7.85 (d, J = 7.80 Hz, 2H), 7.62 (t, J = 7.32 Hz, 4H), 7.08 (t, J = 8.24 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 196.17, 159.99 (d, J = 246.61 Hz), 144.76, 133.57 (d, J = 2.85 Hz), 131.84 (q, J = 32.60 Hz), 126.05, 124.92 (d, J = 8.24 Hz), 124.73 (d, J = 3.55 Hz), 122.59 (q, J = 270.90 Hz), 115.06 (d, J = 22.71 Hz); $^{19}$F NMR (377 MHz, CDCl$_3$) δ -62.91, -113.02; HR-MS (ESI$^+$): calcd. for C$_{14}$H$_9$F$_4$NS [M+H]$^+$: 300.0465, Found: 300.0459.

N-(4-bromo-3-fluorophenyl)-4-(trifluoromethyl)benzothioamide (3hm). Prepared according to the general procedure to afford a yellow solid in 86% yield, mp 146 °C; $^1$H NMR (CDCl$_3$, 400 MHz) δ 9.01 (s, 1H), 7.88 (d, J = 4.8 Hz, 3H), 7.68 (d, J = 7.88 Hz, 2H), 7.59 (t, J = 7.66 Hz, 1H), 7.35 (d, J = 12.60 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 196.96, 158.90 (d, J$_{CF}$ = 246.61 Hz), 139.08 (d, J$_{CF}$ = 9.71 Hz), 133.67, 133.00 (q, J$_{CF}$ = 32.94 Hz), 127.06, 125.81 (d, J$_{CF}$ = 3.59 Hz), 123.56 (q, J$_{CF}$ = 270.97 Hz), 119.94 (d, J$_{CF}$ = 3.59 Hz), 119.89 (d, J$_{CF}$ = 3.59 Hz).
111.74, 111.47, 106.77 (d, J_C-F = 21.11 Hz); \[^{19}F\] NMR (377 MHz, CDCl\(_3\)) \(\delta\) -62.93, -103.92; HR-MS (ESI\(^+\)): calcd. for C\(_{14}\)H\(_8\)BrF\(_4\)NS [M+H]^+: 377.9570, Found: 377.9577.

\[\begin{array}{c}
\text{N-(naphthalen-1-yl)-4-(trifluoromethyl)benzothioamide (3ho). Prepared according to the general procedure to afford a yellow solid in 52\% yield, mp 150^\circ\text{C}; \text{\[^{1}H\] NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.25 (s, 1H), 8.06 (d, J = 8.00 Hz, 2H), 7.95 - 7.88 (m, 2H), 7.84 (t, J = 4.50 Hz, 1H), 7.76 (d, J = 7.28 Hz, 1H), 7.72 (d, J = 8.08 Hz, 2H), 7.55 (t, J = 7.84 Hz, 3H); \text{\[^{13}C\] NMR (CDCl\(_3\), 100 MHz) \(\delta\) 198.89, 145.07, 134.53, 134.33, 132.94 (q, J_C-F = 32.20 Hz), 128.91, 128.84, 128.66, 127.26, 127.09, 126.63, 125.75 (q, J_C-F = 3.66 Hz), 125.45, 124.71, 123.68 (q, J_C-F = 271.04 Hz), 121.63; \text{\[^{19}F\] NMR (377 MHz, CDCl\(_3\)) \(\delta\) -62.84; HR-MS (ESI\(^+\)): calcd. for C\(_{18}\)H\(_{12}\)F\(_3\)NS [M+H]^+: 332.0715, Found: 332.0720.}
\end{array}\]

\[\begin{array}{c}
\text{N-(naphthalen-1-yl)-4-(trifluoromethyl)benzothioamide (3hp). Prepared according to the general procedure to afford a yellow solid in 58\% yield, mp 185^\circ\text{C}; \text{\[^{1}H\] NMR (DMSO-d6, 400 MHz) \(\delta\) 12.21 (s, 1H), 8.56 (d, J = 1.84 Hz, 2H), 7.99 (d, J = 8.88 Hz, 1H), 7.94 (q, J = 2.57 Hz, 2H), 7.87 (dd, J = 1.72 Hz, J = 8.60 Hz, 3H), 7.56-7.53 (m, 2H); \text{\[^{13}C\] NMR (DMSO-d6, 100 MHz) \(\delta\) 196.61, 146.65, 137.86, 133.25, 131.88, 130.88 (q, J_C-F = 31.79 Hz), 129.29 (d, J_C-F = 12.41 Hz), 128.69, 128.62, 128.31, 128.07, 127.06, 126.65, 125.60 (q, J_C-F = 3.72 Hz), 124.49, 123.90; \text{\[^{19}F\] NMR (377 MHz, CDCl\(_3\)) \(\delta\) -61.21; HR-MS (ESI\(^+\)): calcd. for C\(_{18}\)H\(_{12}\)F\(_3\)NS [M+H]^+: 332.0715, Found: 332.0716.}
\end{array}\]

8. NMR spectra

Compound 3aa
Compound 3ab
Compound 3ac
Compound 3ad
Compound 3ae
Compound 3af
Compound 3ag
Compound 3ah
Compound 3ai
Compound 3aj
Compound 3ak
Compound 3al
Compound 3am
Compound 3an
Compound 3ao
Compound 3ap
Compound 3ba
Compound 3bd
Compound 3bm
Compound 3ca
Compound 3da
Compound 3ea
Compound 3fa
Compound 3ga
Compound 3ha
Compound 3eb
Compound 3ec
S-54
Compound 3ed
Compound 3ee
Compound 3ef
Compound 3eg
Compound 3ei
Compound 3ej
Compound 3ek
Compound 3el
Compound 3em
Compound 3en
Compound 3eo
Compound 3ep
Compound 3hb
Compound 3hc
Compound 3hd
Compound 3he
Compound 3hg
Compound 3hi
Compound 3hj
Compound 3hk
Compound 3hl
Compound 3hm
Compound 3hn
Compound 3ho
Compound 3hp
9. References


