

Supporting Information

Access to SCN-containing thiazolines via electrochemical regioselective thiocyanothiocyclization of N-allylthioamides

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Molecular structure and crystallographic data of **3ab**

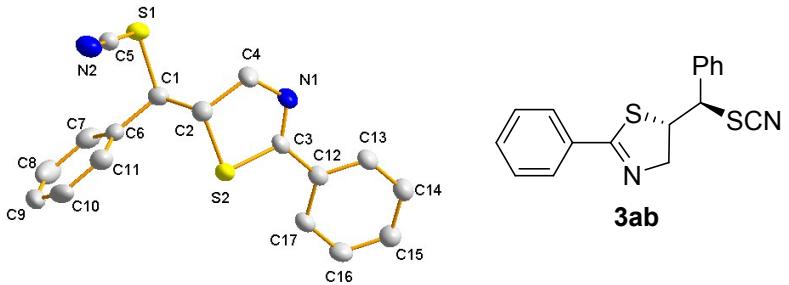


Figure S1. X-ray crystal structure of **3ab**

Table S1. Crystal data and structure refinement for **3ab**

Empirical formula	C ₁₇ H ₁₄ N ₂ S ₂
CCDC number	1960652
Formula weight	310.42
Temperature/K	170.00(10)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	7.3669(2)
b/Å	5.94050(10)
c/Å	17.4582(4)
α/°	90
β/°	91.628(2)
γ/°	90
Volume/Å ^d	763.72(3)
Z	2
ρcalcg/cm ³	1.350
μ/mm ⁻¹	0.342
F(000)	324.0
Crystal size/mm ³	0.4 × 0.15 × 0.05
Radiation	MoKα ($\lambda = 0.71073$)
2Θ range for data collection/°	4.668 to 60.728
Index ranges	-9 ≤ h ≤ 10, -8 ≤ k ≤ 8, -24 ≤ l ≤ 24
Reflections collected	21477
Independent reflections	4069 [$R_{\text{int}} = 0.0433$, $R_{\text{sigma}} = 0.0284$]
Data/restraints/parameters	4069/1/190
Goodness-of-fit on F ²	1.063
Final R indexes [I>=2σ (I)]	$R_1 = 0.0446$, $wR_2 = 0.1175$
Final R indexes [all data]	$R_1 = 0.0480$, $wR_2 = 0.1198$
Largest diff. peak/hole / e Å ⁻³	1.01/-0.52
Flack parameter	H-0.02(4)

Molecular structure and crystallographic data of **4b**

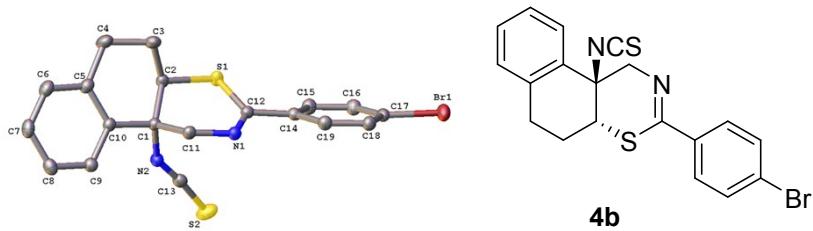


Figure S2. X-ray crystal structure of **4b**

Table S2. Crystal data and structure refinement for **4b**

Empirical formula	C ₁₉ H ₁₅ BrN ₂ S ₂
CCDC number	1960653
Formula weight	415.36
Temperature/K	169.99(11)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	9.8886(2)
b/Å	16.8537(2)
c/Å	11.1408(2)
α/°	90
β/°	108.661(2)
γ/°	90
Volume/Å ³	1759.11(6)
Z	4
ρcalcg/cm ³	1.568
μ/mm ⁻¹	5.413
F(000)	840.0
Crystal size/mm ³	0.18 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	9.888 to 152.018
Index ranges	-12 ≤ h ≤ 12, -20 ≤ k ≤ 20, -13 ≤ l ≤ 13
Reflections collected	32094
Independent reflections	3544 [R _{int} = 0.0469, R _{sigma} = 0.0200]
Data/restraints/parameters	3544/0/217
Goodness-of-fit on F ²	1.048
Final R indexes [I>=2σ (I)]	R ₁ = 0.0326, wR ₂ = 0.0852
Final R indexes [all data]	R ₁ = 0.0365, wR ₂ = 0.0890
Largest diff. peak/hole / e Å ⁻³	0.58/-0.48

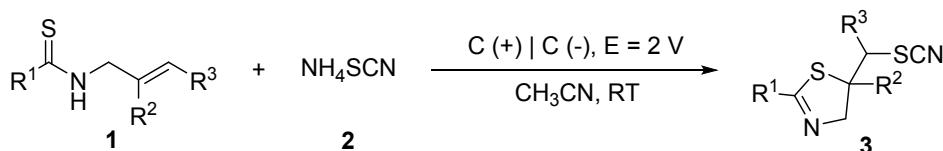
General information

All the reactions were carried out under an air atmosphere using glassware without being predried. Acetonitrile, ammonium thiocyanate, ammonium tetrabutyl hexafluorophosphonate, graphite rod, platinum sheet, graphite felt were obtained from commercial sources. The electrochemical instrument is HONGSHENGFENG DPS-305BM. Column chromatography was performed on silica gel (200-300 mesh) using analytical pure ethyl acetate, and petroleum ether. NMR spectra were recorded in CDCl_3 on 500 MHz spectrometers. ^1H NMR chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (0 ppm) or residual CHCl_3 (7.26 ppm). ^{13}C NMR chemical shifts are reported relative to the center line signal of the CDCl_3 triplet at 77.0 ppm. The following abbreviations are used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and dt = doublet of triplets, ddd = doublet of doublet of doublets m = multiplet. HRMS were obtained on an Ultima Global spectrometer with an ESI source. The X-ray single crystal diffraction was performed on Saturn 724+ instrument. Melting points are uncorrected.

Preparation of starting materials 1

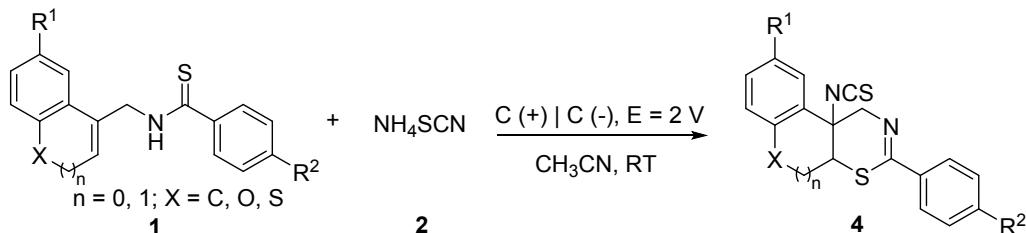
The starting materials **1a-1i¹**, **1j²**, **1k-1o¹**, **1p-1am²** were prepared according to literature procedure.

General procedure for the synthesis of 3



To a 10 mL three-necked flask was added thioamide **1** (0.2 mmol), ammonium thiocyanate **2** (0.4 mmol, 2.0 equiv.) and CH_3CN (4 mL). The flask was equipped with two graphite rods (Φ 5 mm, 1.5 cm depth) as anode and cathode. The whole cell was undivided cell. The reaction mixture was stirred and electrolyzed at a constant voltage of 2 V at room temperature for 5 h. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The pure product **3** were obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

General procedure for the synthesis of 4



To a 10 mL three-necked flask was added thioamide **1** (0.2 mmol), ammonium thiocyanate **2** (0.4 mmol, 2.0 equiv.) and CH_3CN (4 mL). The flask was equipped with two graphite rods (Φ 5 mm, 1.5 cm depth) as anode and cathode. The whole cell was undivided cell. The reaction mixture was stirred and electrolyzed at a constant voltage of 2 V at room temperature for 8 h.

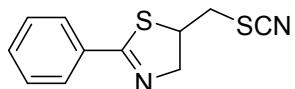
After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The pure product **4** were obtained by flash chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.



Figure S3 Reaction equipment

Characterization data for products **3** and **4**

2-phenyl-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3a)



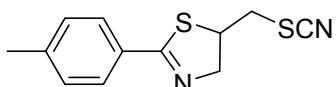
Following the general procedure, **3a** was isolated as a light yellow oil from *N*-allylbenzothioamide **1a** (36 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.2 (PE: EA = 8: 1 v/v); 39 mg, 85% yield.

¹H NMR (CDCl₃, 500 MHz): δ 7.85–7.78 (m, 2H), 7.46 (m, 3H), 4.64 (dd, *J* = 16.4, 2.2, 1H), 4.41 (dd, *J* = 16.5, 7.8, 1H), 4.27–4.18 (m, 1H), 3.16 (dd, *J* = 13.4, 6.5, 1H), 3.05 (dd, *J* = 13.4, 8.2, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 166.8, 132.6, 131.7, 128.7, 128.4, 111.3, 68.5, 50.1, 38.9.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₁H₁₁N₂S₂, 235.0364, found 235.0369.

5-(thiocyanatomethyl)-2-(p-tolyl)-4,5-dihydrothiazole (3b)



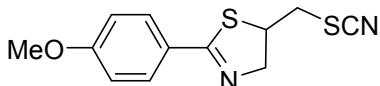
Following the general procedure, **3b** was isolated as a light yellow oil from *N*-allyl-4-methylbenzothioamide **1b** (39 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.3$ (PE: EA = 4: 1 v/v); 34 mg, 70% yield.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.70 (d, $J = 8.2$, 2H), 7.23 (d, $J = 7.9$, 2H), 4.62 (dd, $J = 16.4$, 2.1, 1H), 4.39 (dd, $J = 16.4$, 7.8, 1H), 4.20 (m, 1H), 3.15 (dd, $J = 13.4$, 6.5, 1H), 3.04 (dd, $J = 13.4$, 8.2, 1H), 2.40 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 166.7, 142.2, 129.9, 129.4, 128.4, 111.4, 68.4, 49.9, 38.9, 21.5.

HRMS (ESI-TOF, [M + H⁺]): calcd for $\text{C}_{12}\text{H}_{13}\text{N}_2\text{S}_2$, 249.0520, found 249.0524.

2-(4-methoxyphenyl)-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3c)



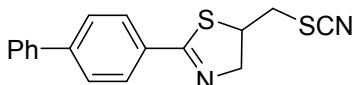
Following the general procedure, **3c** was isolated as a light yellow solid from *N*-allyl-4-methoxybenzothioamide **1c** (42 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.3$ (PE: EA = 8: 1 v/v); 38 mg, 72% yield. Mp: 78–80 °C.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.76 (d, $J = 8.8$, 2H), 6.92 (d, $J = 8.8$, 2H), 4.60 (dd, $J = 16.3$, 2.1, 1H), 4.37 (dd, $J = 16.2$, 7.7, 1H), 4.20 (m, 1H), 3.85 (s, 3H), 3.16 (dd, $J = 13.4$, 6.5, 1H), 3.04 (dd, $J = 13.4$, 8.2, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 166.0, 162.3, 130.1, 125.3, 114.0, 111.3, 68.3, 55.4, 50.1, 38.9.

HRMS (ESI-TOF, [M + H⁺]): calcd for $\text{C}_{12}\text{H}_{13}\text{N}_2\text{OS}_2$, 265.0469, found 265.0475.

2-([1,1'-biphenyl]-4-yl)-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3d)



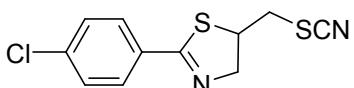
Following the general procedure, **3d** was isolated as a light yellow solid from *N*-allyl-[1,1'-biphenyl]-4-carbothioamide **1d** (51 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.4$ (PE: EA = 4: 1 v/v); 46 mg, 74% yield. Mp: 80–82 °C.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.80 (d, $J = 8.3$, 2H), 7.57 (d, $J = 8.3$, 2H), 7.50–7.51 (m, 2H), 7.38 (t, $J = 7.6$, 2H), 7.33–7.28 (m, 1H), 4.56 (dd, $J = 16.4$, 2.2, 1H), 4.33 (dd, $J = 16.4$, 7.8, 1H), 4.15 (m, 1H), 3.08 (dd, $J = 13.4$, 6.5, 1H), 2.96 (dd, $J = 13.4$, 8.2, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 166.4, 144.4, 139.9, 131.4, 129.0, 128.9, 128.1, 127.3, 127.2, 111.4, 68.5, 50.1, 38.9.

HRMS (ESI-TOF, [M + Na⁺]): calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{NaS}_2$, 333.0496, found 333.0499.

2-(4-chlorophenyl)-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3e)



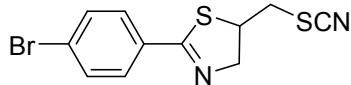
Following the general procedure, **3e** was isolated as a light yellow oil from *N*-allyl-4-chlorobenzothioamide **1e** (42 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4

mmol). $R_f = 0.4$ (PE: EA = 4: 1 v/v); 43 mg, 81% yield.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.75 (d, $J = 8.4$, 2H), 7.40 (d, $J = 8.4$, 2H), 4.63 (dd, $J = 16.5$, 2.1, 1H), 4.40 (dd, $J = 16.5$, 7.9, 1H), 4.29–4.21 (m, 1H), 3.16 (dd, $J = 13.4$, 6.5, 1H), 3.05 (dd, $J = 13.4$, 8.1, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 165.6, 137.8, 131.0, 129.7, 128.9, 111.2, 68.5, 50.4, 38.8.
HRMS (ESI-TOF, [M + H $^+$]): calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{S}_2\text{Cl}$, 268.9974, found 268.9977.

2-(4-bromophenyl)-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3f)

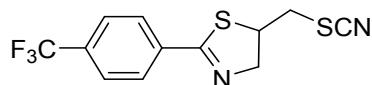


Following the general procedure, **3f** was isolated as a light yellow solid from *N*-allyl-4-bromobenzothioamide **1f** (51 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.2$ (PE: EA = 8: 1 v/v); 51 mg, 82% yield. Mp: 98–100 °C.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.75 (d, $J = 8.5$, 2H), 7.63 (d, $J = 8.5$, 2H), 4.69 (dd, $J = 16.5$, 2.2, 1H), 4.46 (dd, $J = 16.6$, 7.9, 1H), 4.32 (m, 1H), 3.23 (dd, $J = 13.4$, 6.5, 1H), 3.12 (dd, $J = 13.5$, 8.1, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 165.7, 131.9, 131.5, 129.8, 126.3, 111.1, 68.5, 50.4, 38.8.
HRMS (ESI-TOF, [M + H $^+$]): calcd for $\text{C}_{11}\text{H}_{10}\text{N}_2\text{S}_2\text{Br}$, 312.9469, found 312.9474.

5-(thiocyanatomethyl)-2-(4-(trifluoromethyl)phenyl)-4,5-dihydrothiazole (3g)



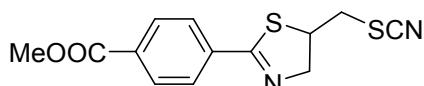
Following the general procedure, **3g** was isolated as a light yellow oil from *N*-allyl-4-(trifluoromethyl)benzothioamide **1g** (50 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.3$ (PE: EA = 8:1 v/v); 48 mg, 80% yield.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.93 (d, $J = 8.1$, 2H), 7.69 (d, $J = 8.2$, 2H), 4.67 (dd, $J = 16.7$, 2.3, 1H), 4.45 (dd, $J = 16.7$, 7.9, 1H), 4.30 (m, 1H), 3.18 (dd, $J = 13.5$, 6.6, 1H), 3.07 (dd, $J = 13.5$, 8.0, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 165.5, 135.7, 133.2 (q, $J = 32.9$), 128.7, 125.6, 125.6, 123.6 (q, $J = 272.6$), 111.1, 68.7, 50.5, 38.8.

HRMS (ESI-TOF, [M + H $^+$]): calcd for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{F}_3\text{S}_2$, 303.0237, found 303.0244.

Methyl 4-(5-(thiocyanatomethyl)-4,5-dihydrothiazol-2-yl)benzoate (3h)



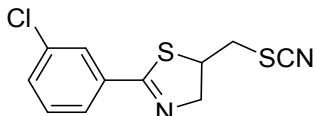
Following the general procedure, **3h** was isolated as a light yellow solid from methyl 4-(allylcaramothioly)benzoate **1h** (47 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.4$ (PE: EA = 4: 1 v/v); 49 mg, 84% yield. Mp: 89–91 °C.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.08 (d, $J = 8.4$, 2H), 7.87 (d, $J = 8.4$, 2H), 4.67 (dd, $J = 16.7$, 2.2, 1H), 4.44 (dd, $J = 16.7$, 7.9, 1H), 4.27 (m, 1H), 3.94 (s, 3H), 3.17 (dd, $J = 13.5$, 6.5, 1H), 3.06 (dd, $J = 13.5$, 8.1, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 166.3, 166.1, 136.3, 132.8, 129.8, 128.4, 111.2, 68.6, 52.4, 50.4, 38.8.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₃H₁₃N₂O₂S₂, 293.0418, found 293.0425.

2-(3-chlorophenyl)-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3i)



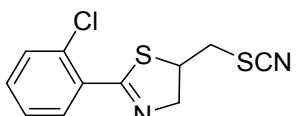
Following the general procedure, **3i** was isolated as a light yellow oil from *N*-allyl-3-chlorobenzothioamide **1i** (42 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.4 (PE: EA = 4: 1 v/v); 45 mg, 84% yield.

¹H NMR (CDCl₃, 500 MHz): δ 7.76 (t, J = 1.9, 1H), 7.60 (dt, J = 7.7, 1.3, 1H), 7.39 (dt, J = 8.2, 1.4, 1H), 7.29 (t, J = 7.9, 1H), 4.56 (dd, J = 16.5, 2.2, 1H), 4.34 (dd, J = 16.6, 7.9, 1H), 4.18 (m, 1H), 3.08 (dd, J = 13.5, 6.5, 1H), 2.98 (dd, J = 13.5, 8.1, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 165.5, 134.8, 134.2, 131.6, 129.9, 128.3, 126.6, 111.2, 68.5, 50.4, 38.8.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₁H₁₀N₂S₂Cl, 268.9974, found 268.9977.

2-(2-chlorophenyl)-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3j)



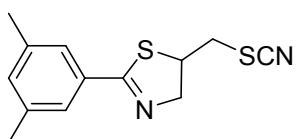
Following the general procedure, **3j** was isolated as a light yellow oil from *N*-allyl-2-chlorobenzothioamide **1j** (42 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.4 (PE: EA = 4: 1 v/v); 48 mg, 88% yield.

¹H NMR (CDCl₃, 500 MHz): δ 7.60 (dd, J = 7.6, 1.8, 1H), 7.44 (dd, J = 8.0, 1.3, 1H), 7.37 (td, J = 7.7, 1.8, 1H), 7.31 (td, J = 7.5, 1.4, 1H), 4.64 (dd, J = 16.5, 2.1, 1H), 4.40 (dd, J = 16.5, 7.8, 1H), 4.25 (m, 1H), 3.20 (dd, J = 13.4, 6.4, 1H), 3.09 (dd, J = 13.4, 8.2, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 164.7, 132.5, 132.2, 131.5, 130.6, 126.9, 111.3, 68.1, 51.1, 38.7.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₁H₁₀N₂S₂Cl, 268.9974, found 268.9979.

2-(3,5-dimethylphenyl)-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3k)



Following the general procedure, **3k** was isolated as a light yellow oil from *N*-allyl-2-chlorobenzothioamide **1k** (41 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.5 (PE: EA = 4: 1 v/v); 36 mg, 68% yield.

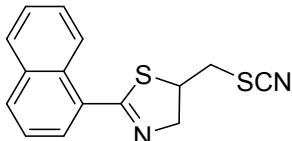
¹H NMR (CDCl₃, 500 MHz): δ 7.43 (s, 1H), 7.43 (s, 1H), 7.12 (s, 1H), 4.62 (dd, J = 16.4, 2.1, 1H), 4.39 (dd, J = 16.4, 7.8, 1H), 4.20 (m, 1H), 3.15 (dd, J = 13.4, 6.5, 1H), 3.04 (dd, J =

13.4, 8.2, 1H), 2.35 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): δ 167.2, 138.4, 133.4, 132.4, 126.2, 111.3, 68.3, 49.9, 38.9, 21.1.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₃H₁₅N₂S₂, 263.0677, found 263.0683.

2-(naphthalen-1-yl)-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3l)



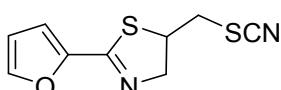
Following the general procedure, **3l** was isolated as a light yellow oil from *N*-allylnaphthalene-1-carbothioamide **1l** (46 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.4 (PE: EA = 4: 1 v/v); 35 mg, 63% yield.

¹H NMR (CDCl₃, 500 MHz): δ 8.82 (d, J = 8.5, 1H), 7.96–7.81 (m, 3H), 7.62–7.45 (m, 3H), 4.80 (dd, J = 16.4, 2.2, 1H), 4.60 (dd, J = 16.4, 7.9, 1H), 4.23 (m, 1H), 3.23 (dd, J = 13.4, 6.4, 1H), 3.12 (dd, J = 13.4, 8.1, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 166.3, 133.8, 131.7, 130.4, 129.6, 129.3, 128.5, 127.6, 126.5, 125.7, 124.7, 111.4, 69.6, 49.6, 39.0.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₅H₁₃N₂S₂, 285.0520, found 285.0524.

2-(furan-2-yl)-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3m)



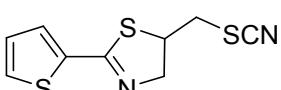
Following the general procedure, **3m** was isolated as a yellow oil from *N*-allylfuran-2-carbothioamide **1m** (34 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol), and electrolyzed for 8 hours. R_f = 0.3 (PE: EA = 4: 1 v/v); 28 mg, 63% yield.

¹H NMR (CDCl₃, 500 MHz): δ 7.56 (d, J = 1.6, 1H), 6.94 (d, J = 3.5, 1H), 6.52 (dd, J = 3.6, 1.8, 1H), 4.61 (dd, J = 16.4, 2.0, 1H), 4.37 (dd, J = 16.5, 7.7, 1H), 4.26 – 4.18 (m, 1H), 3.14 (dd, J = 13.5, 6.6, 1H), 3.04 (dd, J = 13.5, 8.1, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 156.2, 147.3, 145.4, 114.5, 112.1, 111.2, 68.2, 50.1, 38.7.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₉H₉N₂O₂S₂, 225.0156, found 225.0161.

5-(thiocyanatomethyl)-2-(thiophen-2-yl)-4,5-dihydrothiazole (3n)



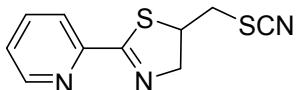
Following the general procedure, **3n** was isolated as a yellow oil from *N*-allyltiophene-2-carbothioamide **1n** (37 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.5 (PE: EA = 4: 1 v/v); 36 mg, 76% yield.

¹H NMR (CDCl₃, 500 MHz): δ 7.51 (dd, J = 5.2, 1.1, 1H), 7.45 (dd, J = 3.8, 1.1, 1H), 7.11 (dd, J = 5.1, 3.7, 1H), 4.59 (dd, J = 16.3, 2.0, 1H), 4.38 (dd, J = 16.3, 7.6, 1H), 4.27 (m, 1H), 3.18 (dd, J = 13.4, 6.6, 1H), 3.08 (dd, J = 13.4, 8.1, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 159.9, 136.2, 131.3, 130.5, 127.7, 111.2, 67.9, 51.0, 38.7.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₉H₉N₂S₂, 240.9928, found 240.9931.

2-(pyridin-2-yl)-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3o)



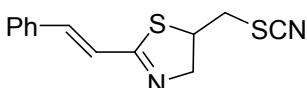
Following the general procedure, **3o** was isolated as a yellow oil from *N*-allylpyridine-2-carbothioamide **1o** (36 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.5 (PE: EA = 1: 1 v/v); 37 mg, 79% yield.

¹H NMR (CDCl₃, 500 MHz): δ 8.64 (m, 1H), 8.05 (dd, J = 7.9, 1.2, 1H), 7.78 (m, 1H), 7.38 (m, 1H), 4.71 (dd, J = 16.9, 2.3, 1H), 4.49 (dd, J = 16.9, 8.1, 1H), 4.16 (m, 1H), 3.18 (dd, J = 13.4, 6.3, 1H), 3.04 (dd, J = 13.4, 8.4, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 169.4, 150.5, 149.4, 136.7, 125.8, 121.6, 111.4, 68.9, 48.5, 39.0.

HRMS (ESI-TOF, [M + Na⁺]): calcd for C₁₀H₉N₃NaS₂, 258.0136, found 258.0139.

(E)-2-styryl-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3p)



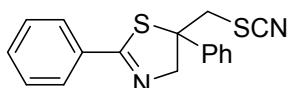
Following the general procedure, **3p** was isolated as a yellow solid from (E)-*N*-allyl-3-phenylprop-2-enethioamide **1p** (41 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.2 (PE: EA = 2: 1 v/v); 23 mg, 44% yield. Mp: 118–120 °C.

¹H NMR (CDCl₃, 500 MHz): δ 7.54–7.36 (m, 5H), 7.11 (d, J = 16.2, 1H), 7.01 (d, J = 16.2, 1H), 4.55 (dd, J = 16.7, 2.2, 1H), 4.34 (dd, J = 16.7, 7.7, 1H), 4.22–4.12 (m, 1H), 3.13 (dd, J = 13.4, 6.6, 1H), 3.02 (dd, J = 13.4, 8.1, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 166.2, 142.2, 134.9, 129.8, 128.9, 127.6, 122.1, 111.3, 68.1, 49.5, 38.9.

HRMS (ESI-TOF, [M + Na⁺]): calcd for C₁₃H₁₃N₂S₂, 261.0520, found 261.0526.

2,5-diphenyl-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3q)



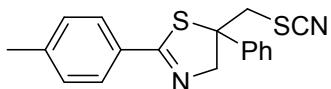
Following the general procedure, **3q** was isolated as a yellow oil from *N*-(2-phenylallyl)benzothioamide **1q** (48 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.4 (PE: EA = 4: 1 v/v); 38 mg, 61% yield.

¹H NMR (CDCl₃, 500 MHz): δ 7.89–7.77 (m, 2H), 7.51 (t, J = 7.4, 1H), 7.48–7.41 (m, 4H), 7.41–7.35 (m, 3H), 4.92 (d, J = 16.1, 1H), 4.56 (d, J = 16.1, 1H), 3.70 (d, J = 13.3, 1H), 3.65 (d, J = 13.3, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 167.4, 138.8, 132.7, 131.8, 129.2, 128.7, 128.6, 128.3, 127.1, 111.6, 73.4, 69.3, 46.9.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₇H₁₅N₂S₂, 311.0677, found 311.0683.

5-phenyl-5-(thiocyanatomethyl)-2-(p-tolyl)-4,5-dihydrothiazole (3r)



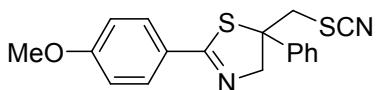
Following the general procedure, **3r** was isolated as a yellow solid from 4-methyl-N-(2-phenylallyl)benzothioamide **1r** (54 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.2$ (PE: EA = 8: 1 v/v); 44 mg, 65% yield. Mp: 108–110 °C.

^1H NMR (CDCl₃, 500 MHz): δ 7.78–7.70 (m, 2H), 7.44–7.34 (m, 5H), 7.24 (d, $J = 8.0$, 2H), 4.88 (d, $J = 16.0$, 1H), 4.53 (d, $J = 16.0$, 1H), 3.68 (d, $J = 13.3$, 1H), 3.62 (d, $J = 13.2$, 1H), 2.40 (s, 3H).

^{13}C NMR (CDCl₃, 125 MHz): δ 167.3, 142.4, 138.9, 130.0, 129.4, 129.2, 128.6, 128.2, 127.2, 111.7, 73.3, 69.1, 46.9, 21.6.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₈H₁₇N₂S₂, 325.0833, found 325.0834.

2-(4-methoxyphenyl)-5-phenyl-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3s)



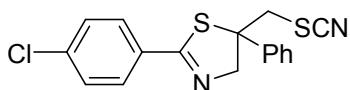
Following the general procedure, **3s** was isolated as a yellow solid from 4-methoxy-N-(2-phenylallyl)benzothioamide **1s** (57 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.2$ (PE: EA = 4: 1 v/v); 45 mg, 67% yield. Mp: 110–112 °C.

^1H NMR (CDCl₃, 500 MHz): δ 7.84–7.76 (m, 2H), 7.45–7.32 (m, 5H), 6.96–6.91 (m, 2H), 4.86 (d, $J = 15.8$, 1H), 4.50 (d, $J = 15.9$, 1H), 3.85 (s, 3H), 3.68 (d, $J = 13.3$, 1H), 3.62 (d, $J = 13.2$, 1H).

^{13}C NMR (CDCl₃, 125 MHz): δ 166.7, 162.5, 138.9, 130.0, 129.2, 128.6, 127.2, 125.4, 114.0, 111.7, 73.2, 69.2, 55.5, 46.9.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₄H₁₅N₂OS₂, 341.0782, found 341.0782.

2-(4-chlorophenyl)-5-phenyl-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3t)



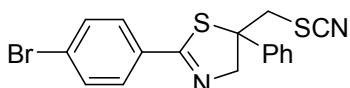
Following the general procedure, **3t** was isolated as a yellow solid from 4-chlor-N-(2-phenylallyl)benzothioamide **1t** (57 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.5$ (PE: EA = 4: 1 v/v); 47 mg, 69% yield. Mp: 118–120 °C.

^1H NMR (CDCl₃, 500 MHz): δ 7.85–7.71 (m, 2H), 7.50–7.30 (m, 7H), 4.90 (d, $J = 16.2$, 1H), 4.54 (d, $J = 16.2$, 1H), 3.68 (d, $J = 13.4$, 1H), 3.62 (d, $J = 13.3$, 1H).

^{13}C NMR (CDCl₃, 125 MHz): δ 166.2, 138.7, 138.0, 131.1, 129.5, 129.3, 129.0, 128.7, 127.1, 111.6, 73.4, 69.8, 46.9.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₇H₁₄N₂S₂Cl, 345.0287, found 345.0295.

2-(4-bromophenyl)-5-phenyl-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3u)



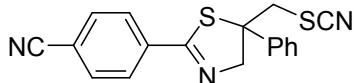
Following the general procedure, **3u** was isolated as a yellow solid from 4-bromo-N-(2-phenylallyl)benzothioamide **1u** (67 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.4$ (PE: EA = 4: 1 v/v); 53 mg, 68% yield. Mp: 120–122 °C.

^1H NMR (CDCl₃, 500 MHz): δ 7.74–7.65 (m, 2H), 7.61–7.54 (m, 2H), 7.46–7.32 (m, 5H), 4.90 (d, $J = 16.2$, 1H), 4.54 (d, $J = 16.2$, 1H), 3.68 (d, $J = 13.4$, 1H), 3.63 (d, $J = 13.3$, 1H).

^{13}C NMR (CDCl₃, 125 MHz): δ 166.3, 138.7, 131.9, 131.6, 129.7, 129.2, 128.7, 127.1, 126.5, 111.5, 73.5, 69.8, 46.9.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₇H₁₄N₂S₂Br, 388.9782, found 388.9778.

4-(5-phenyl-5-(thiocyanatomethyl)-4,5-dihydrothiazol-2-yl)benzonitrile (**3v**)



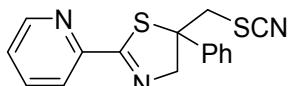
Following the general procedure, **3v** was isolated as a yellow solid from 4-cyano-N-(2-phenylallyl)benzothioamide **1v** (56 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.3$ (PE: EA = 4: 1 v/v); 41 mg, 62% yield. Mp: 114–116 °C.

^1H NMR (CDCl₃, 500 MHz): δ 7.96 (d, $J = 8.3$, 2H), 7.74 (d, $J = 8.4$, 2H), 7.46–7.33 (m, 5H), 4.96 (d, $J = 16.5$, 1H), 4.60 (d, $J = 16.5$, 1H), 3.68 (d, $J = 13.5$, 1H), 3.64 (d, $J = 13.5$, 1H).

^{13}C NMR (CDCl₃, 125 MHz): δ 165.8, 138.5, 136.4, 132.5, 129.3, 128.9, 128.8, 127.0, 118.0, 115.2, 111.5, 73.6, 70.3, 46.8.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₈H₁₄N₃S₂, 336.0629, found 336.0628.

5-phenyl-2-(pyridin-2-yl)-5-(thiocyanatomethyl)-4,5-dihydrothiazole (**3w**)



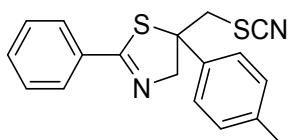
Following the general procedure, **3w** was isolated as a yellow oil from N-(2-phenylallyl)pyridine-2-carbothioamide **1w** (51 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.5$ (PE: EA = 1: 1 v/v); 41 mg, 67% yield.

^1H NMR (CDCl₃, 500 MHz): δ 8.71 (dt, $J = 4.9, 1.3$, 1H), 8.14 (d, $J = 7.9$, 1H), 7.85 (td, $J = 7.7, 1.8$, 1H), 7.51–7.37 (m, 6H), 5.06 (d, $J = 16.5$, 1H), 4.70 (d, $J = 16.5$, 1H), 3.74 (d, $J = 13.3$, 1H), 3.70 (d, $J = 13.3$, 1H).

^{13}C NMR (CDCl₃, 125 MHz): δ 169.9, 150.5, 149.4, 139.2, 136.8, 129.2, 128.5, 127.1, 125.9, 121.4, 111.7, 73.7, 67.2, 47.2.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₆H₁₄N₃S₂, 312.0629, found 312.0633.

2-phenyl-5-(thiocyanatomethyl)-5-(p-tolyl)-4,5-dihydrothiazole (**3x**)



Following the general procedure, **3x** was isolated as a yellow oil from 4-methyl-N-(2-phenylallyl)benzothioamide **1x** (54 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4

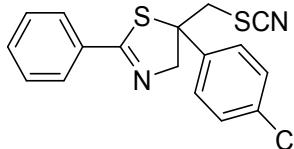
mmol). $R_f = 0.4$ (PE: EA = 8: 1 v/v); 39 mg, 60% yield.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.78–7.70 (m, 2H), 7.44–7.34 (m, 5H), 7.25–7.23 (m, 2H), 4.88 (d, $J = 16.0$, 1H), 4.53 (d, $J = 16.0$, 1H), 3.68 (d, $J = 13.3$, 1H), 3.62 (d, $J = 13.2$, 1H), 2.40 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 167.3, 142.4, 138.9, 130.0, 129.4, 129.2, 128.6, 128.2, 127.2, 111.7, 73.3, 69.1, 46.9, 21.6.

HRMS (ESI-TOF, [M + H $^+$]): calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{S}_2$, 325.0833, found 325.0836.

5-(4-chlorophenyl)-2-phenyl-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3y)



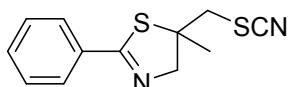
Following the general procedure, **3y** was isolated as a yellow oil from *N*-(2-(4-chlorophenyl)allyl)benzothioamide **1y** (57 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.4$ (PE: EA = 4: 1 v/v); 42 mg, 62% yield.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.86–7.82 (m, 2H), 7.53–7.39 (m, 5H), 7.34–7.30 (m, 2H), 4.88 (d, $J = 16.1$, 1H), 4.52 (d, $J = 16.1$, 1H), 3.68 (d, $J = 13.4$, 1H), 3.63 (d, $J = 13.4$, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 167.3, 137.4, 134.7, 132.5, 132.0, 129.4, 128.8, 128.5, 128.3, 111.5, 73.5, 68.8, 46.5.

HRMS (ESI-TOF, [M + H $^+$]): calcd for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{S}_2\text{Cl}$, 345.0287, found 345.0290.

5-methyl-2-phenyl-5-(thiocyanatomethyl)-4,5-dihydrothiazole (3z)



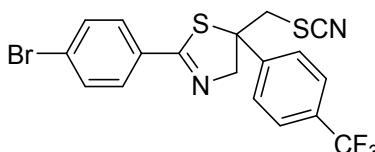
Following the general procedure, **3z** was isolated as a yellow oil from *N*-(2-methylallyl)benzothioamide **1z** (38 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.4$ (PE: EA = 4: 1 v/v); 38 mg, 76% yield.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.73–7.67 (m, 2H), 7.43–7.37 (m, 1H), 7.37–7.32 (m, 2H), 4.38 (d, $J = 16.2$, 1H), 4.07 (d, $J = 16.2$, 1H), 3.34 (d, $J = 13.5$, 1H), 3.28 (d, $J = 13.4$, 1H), 1.70 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 167.5, 132.8, 131.6, 128.6, 128.2, 112.5, 74.5, 62.4, 45.5, 24.6.

HRMS (ESI-TOF, [M + H $^+$]): calcd for $\text{C}_{12}\text{H}_{13}\text{N}_2\text{S}_2$, 249.0520, found 249.0525.

2-(4-bromophenyl)-5-(thiocyanatomethyl)-5-(4-(trifluoromethyl)phenyl)-4,5-dihydrothiazole (3aa)



Following the general procedure, **3aa** was isolated as a yellow oil from 4-bromo-*N*-(2-(4-(trifluoromethyl)phenyl)allyl)benzothioamide **1aa** (80 mg, 0.2 mmol) and ammonium

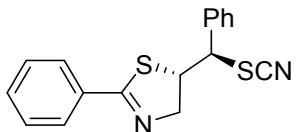
thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.5$ (PE: EA = 4: 1 v/v); 65 mg, 72% yield.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.74–7.67 (m, 4H), 7.63–7.56 (m, 2H), 7.51 (d, J = 8.2, 2H), 4.91 (d, J = 16.2, 1H), 4.53 (d, J = 16.3, 1H), 3.70 (d, J = 13.6, 1H), 3.66 (d, J = 13.5, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 166.0, 142.8, 132.0, 131.3, 131.0 (q, J = 33.0), 129.7, 127.6, 126.7, 126.2 (q, J = 3.7), 123.7 (q, J = 272.3), 111.2, 73.7, 69.5, 46.3.

HRMS (ESI-TOF, [M + H⁺]): calcd for $\text{C}_{18}\text{H}_{13}\text{N}_2\text{F}_3\text{S}_2\text{Br}$, 456.9654, found 456.9656.

(S)-2-phenyl-5-((R)-phenyl(thiocyanato)methyl)-4,5-dihydrothiazole (3ab)



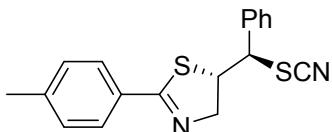
Following the general procedure, **3ab** was isolated as a yellow solid from *N*-cinnamylbenzothioamide **1ab** (48 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.3$ (PE: EA = 8: 1 v/v); 40 mg, 66% yield. Mp: 85–87 °C.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.82–7.76 (m, 2H), 7.55–7.51 (m, 1H), 7.50–7.42 (m, 7H), 4.91 (dd, J = 16.3, 3.6, 1H), 4.79 (ddd, J = 10.7, 8.1, 3.6, 1H), 4.68 (dd, J = 16.3, 8.1, 1H), 4.36 (d, J = 10.5, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 166.9, 137.8, 132.5, 131.6, 129.4, 129.2, 128.6, 128.3, 127.7, 110.2, 68.4, 56.5, 54.6.

HRMS (ESI-TOF, [M + H⁺]): calcd for $\text{C}_{17}\text{H}_{15}\text{N}_2\text{S}_2$, 311.0677, found 311.0680.

(S)-5-((R)-phenyl(thiocyanato)methyl)-2-(p-tolyl)-4,5-dihydrothiazole (3ac)



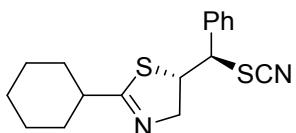
Following the general procedure, **3ac** was isolated as a yellow solid from *N*-cinnamyl-4-methylbenzothioamide **1ac** (54 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.5$ (PE: EA = 4: 1 v/v); 40 mg, 63% yield. Mp: 88–90 °C

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.61 (d, J = 8.0, 2H), 7.42–7.33 (m, 5H), 7.18 (d, J = 7.9, 2H), 4.82 (dd, J = 16.2, 3.6, 1H), 4.69 (ddd, J = 11.0, 8.1, 3.6, 1H), 4.59 (dd, J = 16.3, 8.1, 1H), 4.28 (d, J = 10.6, 1H), 2.37 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 166.8, 142.1, 137.9, 129.9, 129.4, 129.3, 129.2, 128.2, 127.7, 110.2, 68.3, 56.5, 54.5, 21.5.

HRMS (ESI-TOF, [M + H⁺]): calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{S}_2$, 325.0833, found 325.0836.

(S)-2-cyclohexyl-5-((R)-phenyl(thiocyanato)methyl)-4,5-dihydrothiazole (3ad)



Following the general procedure, **3ad** was isolated as a yellow oil from *N*-(3-phenylallyl)cyclohexanecarbothioamide **1ad** (52 mg, 0.2 mmol) and ammonium thiocyanate **2**

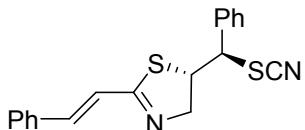
(30 mg, 0.4 mmol). R_f = 0.2 (PE: EA = 8: 1 v/v); 20 mg, 32% yield.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.39 (d, J = 7.0, 3H), 7.31 (dd, J = 7.5, 2.1, 2H), 4.66–4.45 (m, 2H), 4.43–4.29 (m, 1H), 4.18 (d, J = 10.0, 1H), 2.40 (td, J = 11.3, 9.4, 5.5, 1H), 1.88–1.63 (m, 5H), 1.37–1.17 (m, 5H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 175.0, 137.8, 129.3, 129.1, 127.7, 110.3, 67.6, 56.7, 54.0, 43.3, 31.3, 31.2, 25.7.

HRMS (ESI-TOF, [M + H⁺]): calcd for $\text{C}_{17}\text{H}_{21}\text{N}_2\text{S}_2$, 317.1146, found 317.1151.

(S)-5-((R)-phenyl(thiocyanato)methyl)-2-((E)-styryl)-4,5-dihydrothiazole (3ae)



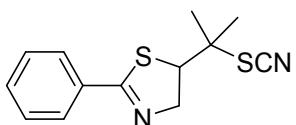
Following the general procedure, **3ae** was isolated as a yellow solid from (E)-*N*-cinnamyl-3-phenylprop-2-enethioamide **1ae** (56 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.3 (PE: EA = 2: 1 v/v); 24 mg, 36% yield. Mp: 128–130 °C.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.44–7.40 (m, 5H), 7.38–7.34 (m, 5H), 6.94 (d, J = 4.3, 2H), 4.74 (dd, J = 16.5, 3.8, 1H), 4.70–4.63 (m, 1H), 4.56 (dd, J = 16.5, 7.9, 1H), 4.26 (d, J = 10.5, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 166.3, 141.8, 137.8, 134.9, 129.7, 129.4, 129.2, 128.9, 127.7, 127.5, 122.0, 110.1, 68.1, 56.5, 54.0.

HRMS (ESI-TOF, [M + H⁺]): calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{S}_2$, 337.0833, found 337.0837.

2-phenyl-5-(2-thiocyanatopropan-2-yl)-4,5-dihydrothiazole (3af)



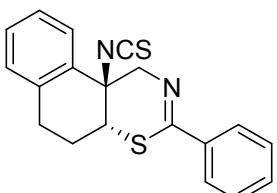
Following the general procedure, **3af** was isolated as a yellow oil from *N*-(3-methylbut-2-en-1-yl)benzothioamide **1af** (41 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.2 (PE: EA = 15: 1 v/v); 30 mg, 58% yield.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.84–7.77 (m, 2H), 7.50–7.39 (m, 3H), 4.69 (dd, J = 17.0, 3.2, 1H), 4.46 (dd, J = 17.0, 9.1, 1H), 4.32 (dd, J = 9.1, 3.2, 1H), 1.61 (s, 3H), 1.45 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 166.9, 132.5, 131.6, 128.6, 128.3, 110.7, 67.0, 60.5, 58.4, 27.0, 23.6.

HRMS (ESI-TOF, [M + H⁺]): calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{S}_2$, 263.0677, found 263.0681.

(4aR,10bS)-10b-isothiocyanato-3-phenyl-4a,5,6,10b-tetrahydro-1H-naphtho[1,2-e][1,3]thiazine (4a)



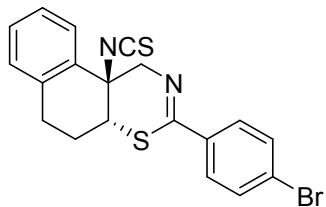
Following the general procedure, **4a** was isolated as a yellow solid from *N*-(*(3,4-dihydronaphthalen-1-yl)methyl*)benzothioamide **1ah** (56 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.5$ (PE: EA = 4: 1 v/v); 36 mg, 44% yield, Mp: 112–114 °C.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.87–7.83 (m, 2H), 7.63 (dd, $J = 7.6, 1.6$, 1H), 7.52–7.41 (m, 3H), 7.34 (m, 2H), 7.20–7.14 (m, 1H), 4.39 (dd, $J = 17.5, 2.2$, 1H), 4.09 (d, $J = 17.5$, 1H), 3.85 (ddd, $J = 12.6, 3.4, 2.1$, 1H), 3.15–2.90 (m, 2H), 2.52 (ddt, $J = 14.3, 6.0, 3.1$, 1H), 2.18 (m, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 158.5, 138.5, 137.2, 134.4, 130.8, 129.2, 128.6, 128.4, 127.3, 127.1, 126.6, 57.9, 57.3, 46.2, 31.2, 28.3.

HRMS (ESI-TOF, [M + H⁺]): calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{S}_2$, 337.0833, found 337.0833.

(4aR,10bS)-3-(4-bromophenyl)-10b-isothiocyanato-4a,5,6,10b-tetrahydro-1H-naphtho[1,2-e][1,3]thiazine (4b)



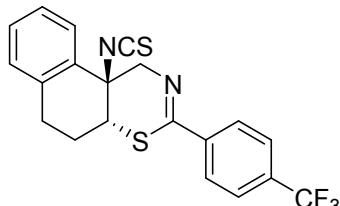
Following the general procedure, **4b** was isolated as a yellow solid from 4-bromo-*N*-(*(3,4-dihydronaphthalen-1-yl)methyl*)benzothioamide **1ai** (71 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.4$ (PE: EA = 10: 1 v/v); 43 mg, 52% yield, Mp: 115–117 °C.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.70 (d, $J = 8.5$, 2H), 7.58 (dd, $J = 7.7, 1.6$, 1H), 7.57–7.52 (m, 2H), 7.35–7.27 (m, 2H), 7.13 (d, $J = 7.3$, 1H), 4.35 (dd, $J = 17.6, 2.3$, 1H), 4.03 (d, $J = 17.6$, 1H), 3.82 (dt, $J = 12.5, 2.8$, 1H), 2.99 (m, 2H), 2.48 (ddt, $J = 14.3, 6.0, 3.1$, 1H), 2.20–2.05 (m, 1H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 157.4, 137.6, 135.3, 134.3, 131.6, 129.2, 128.7, 128.1, 127.3, 127.1, 57.8, 57.3, 46.3, 31.3, 28.3.

HRMS (ESI-TOF, [M + H⁺]): calcd for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{S}_2\text{Br}$, 414.9938, found 414.9931.

(4aR,10bS)-10b-isothiocyanato-3-(4-(trifluoromethyl)phenyl)-4a,5,6,10b-tetrahydro-1H-naphtho[1,2-e][1,3]thiazine (4c)



Following the general procedure, **4c** was isolated as a yellow solid from *N*-(*(3,4-dihydronaphthalen-1-yl)methyl*)-4-(trifluoromethyl)benzothioamide **1aj** (69 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.4$ (PE: EA = 10: 1 v/v); 44 mg, 54%

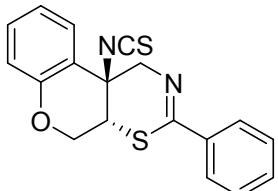
yield, Mp: 114–116 °C.

¹H NMR (CDCl₃, 500 MHz): δ 7.94 (d, *J* = 8.1, 2H), 7.68 (d, *J* = 8.2, 2H), 7.60 (dd, *J* = 7.5, 1.6, 1H), 7.39–7.27 (m, 2H), 7.20–7.10 (m, 1H), 4.40 (dd, *J* = 17.7, 2.2, 1H), 4.07 (d, *J* = 17.7, 1H), 3.85 (dt, *J* = 12.5, 2.8, 1H), 3.01 (m, 2H), 2.50 (ddt, *J* = 14.2, 5.9, 3.0, 1H), 2.21–2.10 (m, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 157.4, 141.5, 137.7, 135.2, 134.3, 132.5 (d, *J* = 32.5), 129.2, 128.8, 127.3, 127.2, 127.0, 125.4, 123.9 (d, *J* = 272.3), 57.7, 57.4, 46.4, 31.3, 28.3.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₂₀H₁₆N₂S₂F₃, 405.0707, found 405.0705.

(4aS,10bS)-10b-isothiocyanato-3-phenyl-1,4a,5,10b-tetrahydrochromeno[4,3-e][1,3]thiazine (4d)



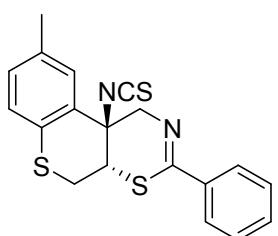
Following the general procedure, **4d** was isolated as a yellow oil from *N*-(2H-chromen-4-yl)methyl)benzothioamide **1ak** (56 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.4 (PE: EA = 10: 1 v/v); 39 mg, 58% yield.

¹H NMR (CDCl₃, 500 MHz): δ 7.80 (dd, *J* = 7.2, 1.8, 2H), 7.57–7.35 (m, 4H), 7.29–7.25 (m, 1H), 7.05 (td, *J* = 7.6, 1.1, 1H), 6.86 (dd, *J* = 8.3, 1.1, 1H), 4.51–4.43 (m, 2H), 4.26 (t, *J* = 11.7, 1H), 4.17 (d, *J* = 17.3, 1H), 4.10 (ddd, *J* = 11.3, 4.1, 2.2, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 157.8, 152.8, 139.5, 138.0, 131.1, 130.5, 128.5, 127.3, 126.6, 121.9, 121.3, 117.3, 67.9, 56.9, 53.8, 43.0.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₈H₁₄N₂OS₂, 338.0548, found 338.0550.

(4aS,10bS)-10b-isothiocyanato-9-methyl-3-phenyl-1,4a,5,10b-tetrahydrothiochromeno[4,3-e][1,3]thiazine (4e)



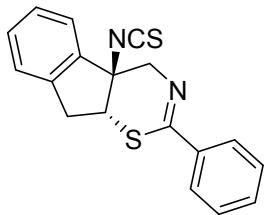
Following the general procedure, **4e** was isolated as a yellow solid from *N*-(6-methyl-2H-thiochromen-4-yl)methyl)benzothioamide **1al** (62 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). R_f = 0.4 (PE: EA = 10: 1 v/v); 44 mg, 60% yield, Mp: 120–122 °C.

¹H NMR (CDCl₃, 500 MHz): δ 7.80 (d, *J* = 7.5, 2H), 7.51–7.33 (m, 4H), 7.08–6.94 (m, 2H), 4.35–4.21 (m, 2H), 4.06 (ddd, *J* = 12.1, 3.9, 1.8, 1H), 3.46 (dd, *J* = 13.7, 12.0, 1H), 3.30 (dd, *J* = 13.7, 3.7, 1H), 2.35 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): δ 156.8, 138.4, 138.1, 135.1, 131.7, 131.0, 130.0, 129.0, 128.5, 127.1, 126.6, 126.3, 57.6, 56.7, 44.9, 31.0, 21.0.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₉H₁₇N₂S₃, 369.0554, found 369.0555.

(4aS,9aR)-4a-isothiocyanato-2-phenyl-4,4a,9,9a-tetrahydroindeno[1,2-e][1,3]thiazine (4f)



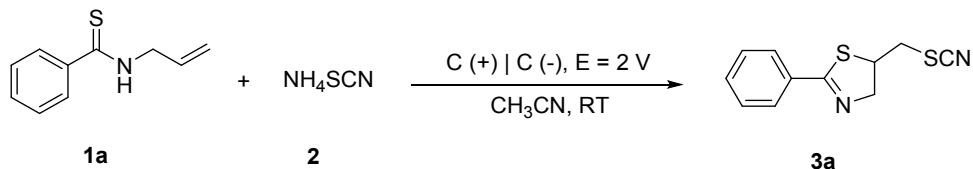
Following the general procedure, **4f** was isolated as a yellow solid from *N*-(1*H*-inden-3-yl)methylbenzothioamide **1am** (53 mg, 0.2 mmol) and ammonium thiocyanate **2** (30 mg, 0.4 mmol). $R_f = 0.4$ (PE: EA = 10: 1 v/v); 24 mg, 38% yield, Mp: 109–111 °C.

^1H NMR (CDCl₃, 500 MHz): δ 7.92–7.87 (m, 2H), 7.57–7.27 (m, 7H), 4.50 (dd, $J = 14.5, 2.3, 1\text{H}$), 4.04 (dd, $J = 9.1, 7.9, 2.6, 1.0, 1\text{H}$), 3.63 (dd, $J = 16.0, 7.9, 1\text{H}$), 3.42 (dd, $J = 14.5, 1.0, 1\text{H}$), 3.02 (dd, $J = 15.9, 9.3, 1\text{H}$).

^{13}C NMR (CDCl₃, 125 MHz): δ 162.1, 141.3, 138.5, 138.0, 131.1, 129.4, 128.5, 128.2, 127.0, 125.2, 123.3, 64.7, 55.9, 49.2, 40.8.

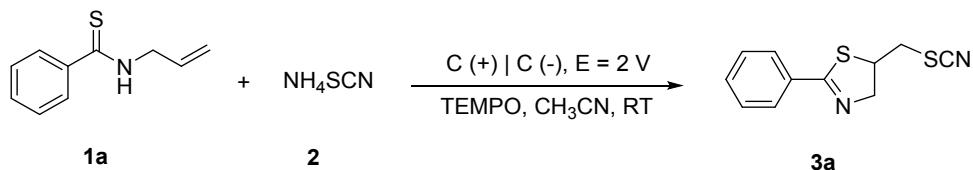
HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₈H₁₄N₂S₂, 323.0677, found 323.0682.

Procedure for gram scale synthesis

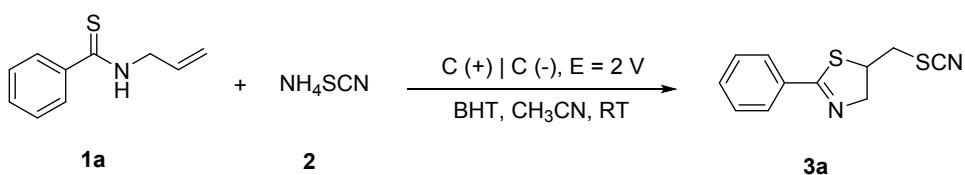


To a 250 mL three-necked flask was added *N*-allylbenzothioamide **1a** (1.77 g, 10 mmol), ammonium thiocyanate (1.52 g, 20 mmol) and CH₃CN (100 mL). The flask was equipped with two graphite rods (Φ 10 mm, 3 cm depth) as anode and cathode. The whole cell was undivided cell. The reaction mixture was stirred and electrolyzed at a constant voltage of 2 V at room temperature for 24 hours. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was purified by flash chromatography (PE: EA = 8: 1) to afford product **3a** (1.66 g, 71%).

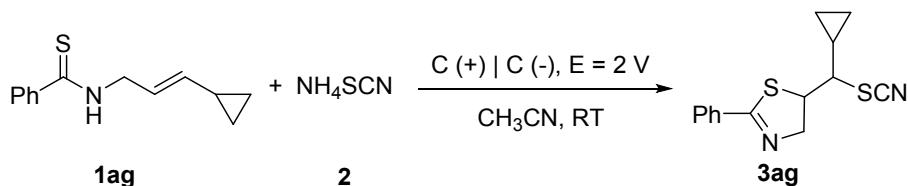
Control experiments



To a 10 mL three-necked flask was added *N*-allylbenzothioamide **1a** (36 mg, 0.2 mmol), ammonium thiocyanate (30 mg, 0.4 mmol) TEMPO (90 mg, 0.6 mmol) and CH₃CN (4 mL). The flask was equipped with two graphite rods (Φ 5 mm, 1.5 cm depth) as anode and cathode. The whole cell was undivided cell. The reaction mixture was stirred and electrolyzed at a constant voltage of 2 V at room temperature for 10 hours. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was purified by flash chromatography (PE: EA = 8: 1) to afford product **3a** (31 mg, 68%).



To a 10 mL three-necked flask was added *N*-allylbenzothioamide **1a** (36 mg, 0.2 mmol), ammonium thiocyanate (30 mg, 0.4 mmol), BHT (130 mg, 0.6 mmol) and CH₃CN (4 mL). The flask was equipped with two graphite rods (Φ 5 mm, 1.5 cm depth) as anode and cathode. The whole cell was undivided cell. The reaction mixture was stirred and electrolyzed at a constant voltage of 2 V at room temperature for 8 hours. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was purified by flash chromatography (PE: EA = 8: 1) to afford product **3a** (27 mg, 57%).



To a 10 mL three-necked flask was added (E)-*N*-(3-cyclopropylallyl)benzothioamide **1ag** (44 mg, 0.2 mmol), ammonium thiocyanate (30 mg, 0.4 mmol) and CH₃CN (4 mL). The flask was equipped with two graphite rods (Φ 5 mm, 1.5 cm depth) as anode and cathode. The whole cell was undivided cell. The reaction mixture was stirred and electrolyzed at a constant voltage of 2 V at room temperature for 10 hours. After completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was purified by flash chromatography (PE: EA = 8: 1) to afford product **3ag** (38 mg, 72%).

5-(cyclopropyl(thiocyanato)methyl)-2-phenyl-4,5-dihydrothiazole (3ag)

yellow oil, R_f = 0.4 (PE: EA = 4: 1 v/v); 38 mg, 72% yield.

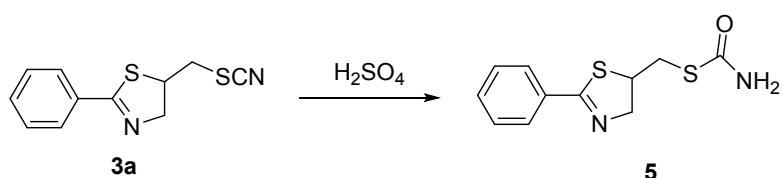
¹H NMR (CDCl₃, 500 MHz): δ 7.84–7.80 (m, 2H), 7.51–7.46 (m, 1H), 7.43 (dd, J = 8.3, 6.6, 2H), 4.61–4.48 (m, 3H), 2.74–2.65 (m, 1H), 1.26–1.18 (m, 1H), 0.94–0.88 (m, 1H), 0.83–0.78 (m, 1H), 0.72–0.67 (m 1H), 0.51–0.46 (m, 1H).

¹³C NMR (CDCl₃, 125 MHz): δ 167.1, 132.7, 131.5, 128.6, 128.3, 110.9, 68.5, 60.8, 56.4, 14.7, 9.7, 5.6.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₄H₁₅N₂S₂, 275.0677, found 275.0677.

Follow-up transformations

General procedure for the synthesis of **5**



To a 25 mL round-bottom flask was added **3a** (47 mg, 0.2 mmol) and sulfuric acid (1 mL,

95%). The reaction mixture was stirred at room temperature for 2 h. After completion of the reaction (monitored by TLC), the mixture was diluted with EtOAc (5 mL) and saturated NaHCO₃ (10 mL), then extracted with EtOAc (3 × 5 mL). The organic layer was separated, dried over MgSO₄ and concentrated under vacumm. The residue was purified by flash chromatography (PE: EA = 2: 1) to afford product **5** (44 mg, 87%).

S-((2-phenyl-4,5-dihydrothiazol-5-yl)methyl) carbamothioate (5)

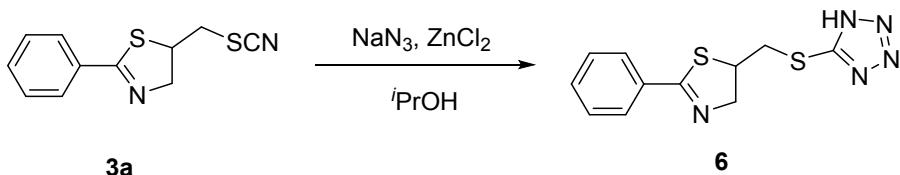
White solid, R_f = 0.4 (PE: EA = 2: 1 v/v), 44 mg, 87% yield. Mp: 138–140 °C.

¹H NMR (CDCl₃, 500 MHz): δ 7.84–7.76 (m, 2H), 7.48–7.38 (m, 3H), 5.56 (s, 2H), 4.53 (dd, J = 16.3, 2.7, 1H), 4.31 (dd, J = 16.2, 8.0, 1H), 4.13 (m, 1H), 3.21–3.00 (m, 2H).

¹³C NMR (CDCl₃, 125 MHz): δ 168.0, 167.4, 133.1, 131.3, 128.5, 128.3, 68.8, 51.0, 35.8.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₁H₁₃N₂OS₂, 253.0469, found 253.0469.

General procedure for the synthesis of 6



To a 10 mL oven-dried Schlenk-tube was added **3a** (47 mg, 0.2 mmol), ZnCl₂ (27 mg, 0.2 mmol), NaN₃ (16 mg, 0.24 mmol), and iPrOH (1 mL). The resulting mixture was heated to 50 °C and stirred vigorously for 4 h. After completion of the reaction (monitored by TLC), the mixture was diluted with EtOAc (5 mL), after the usual workup with 5% aq NaOH (10 mL), then extracted with EtOAc (3 × 5 mL). The organic layer was separated, dried over MgSO₄ and concentrated under vacumm. The residue was purified by flash chromatography (DCM: MeOH = 5: 1) to afford product **6** (50 mg, 91%).

5-((1H-tetrazol-5-yl)thiomethyl)-2-phenyl-4,5-dihydrothiazole (6)

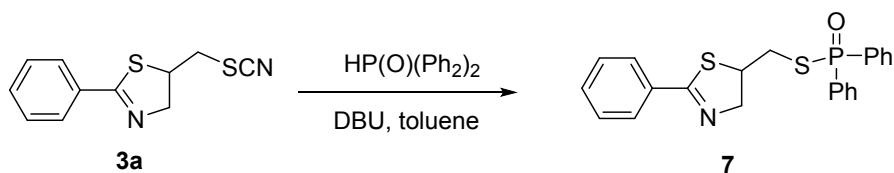
White solid, R_f = 0.4 (DCM: MeOH = 5: 1 v/v), 50 mg, 91% yield. Mp: 94–96 °C.

¹H NMR (DMSO, 500 MHz): δ 7.77–7.70 (m, 2H), 7.53–7.42 (m, 3H), 4.48 (d, J = 14.0, 1H), 4.37–4.16 (m, 2H), 3.27 (d, J = 6.9, 2H).

¹³C NMR (DMSO, 125 MHz): δ 170.2, 161.7, 137.9, 136.6, 134.0, 133.2, 73.8, 55.5, 43.1.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₁H₁₃N₅S₂, 278.0534, found 278.0535.

General procedure for the synthesis of 7



To a 25 mL round-bottom flask was added **3a** (47 mg, 0.2 mmol), HP(O)(Ph₂)₂ (60 mg, 0.3 mmol), DBU (45 mg, 0.3 mmol), and toluene (2 mL). The reaction mixture was stirred at room temperature for 3 h. After completion of the reaction (monitored by TLC), the solvents were removed under vacuum. The residue was purified by flash chromatography (PE: EA = 1: 1) to afford product **7** (67 mg, 82%).

S-((2-phenyl-4,5-dihydrothiazol-5-yl)methyl) diphenylphosphinothioate (7)

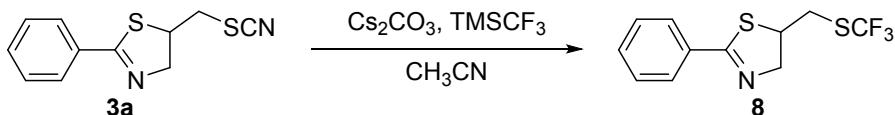
Yellow solid, $R_f = 0.3$ (PE: EA = 1: 1 v/v), 67 mg, 82% yield. Mp: 114–116 °C.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.93–7.74 (m, 6H), 7.60–7.35 (m, 9H), 4.55 (dd, $J = 16.3, 2.6, 1\text{H}$), 4.26 (dd, $J = 16.3, 8.0, 1\text{H}$), 4.15 (m, 1H), 3.00 (dt, $J = 12.6, 7.7, 2\text{H}$).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 167.0, 133.5, 133.3, 133.0, 132.6, 131.6, 131.5, 131.4, 128.8, 128.8, 128.5, 128.3, 68.9, 51.3, 34.6.

HRMS (ESI-TOF, [M + H $^+$]): calcd for $\text{C}_{22}\text{H}_{21}\text{NOS}_2\text{P}_2$, 410.0802, found 410.0800.

General procedure for the synthesis of 8



To a 25 mL round-bottom flask was added **3a** (47 mg, 0.2 mmol), Cs_2CO_3 (65 mg, 0.2 mmol), and CH_3CN (1.6 mL). Then trifluoromethyltrimethylsilane (57 mg, 0.4 mmol) was added at 0 °C. The mixture was stirred at room temperature for 8 h. After completion of the reaction (monitored by TLC), the resulting mixture was filtered through a short pad of celite and extracted with DCM (3×5 mL). The organic layer was washed with water (10 mL) and brine (10 mL), dried over MgSO_4 , and concentrated under vacuum. The residue was purified by flash chromatography (PE: EA = 15: 1) to afford product **8** (43 mg, 78%).

2-phenyl-5-(((trifluoromethyl)thio)methyl)-4,5-dihydrothiazole (8)

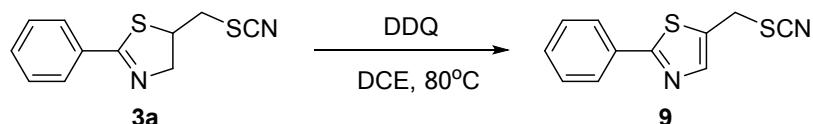
Colorless oil, $R_f = 0.3$ (PE: EA = 15: 1 v/v), 43 mg, 78% yield.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.84–7.73 (m, 2H), 7.49–7.43 (m, 1H), 7.40 (dd, $J = 8.3, 6.7, 2\text{H}$), 4.58 (dd, $J = 16.4, 2.4, 1\text{H}$), 4.34 (dd, $J = 16.3, 7.8, 1\text{H}$), 4.14–4.06 (m, 1H), 3.10 (dd, $J = 14.1, 6.7, 1\text{H}$), 3.00 (dd, $J = 14.1, 8.4, 1\text{H}$).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 166.9, 132.8, 131.5, 130.8 (q, $J = 306.6$), 128.6, 128.4, 68.7, 50.0, 35.3.

HRMS (ESI-TOF, [M + H $^+$]): calcd for $\text{C}_{11}\text{H}_{11}\text{NS}_2\text{F}_3$, 278.0285, found 278.0292.

General procedure for the synthesis of 9



To a solution of **3a** (47 mg, 0.2 mmol) in DCE (1.2 mL) was added 5 Å MS (50 mg). After 10 min, DDQ (90 mg, 0.4 mmol) was added at room temperature. The reaction mixture was stirred at 80 °C for 6 h. After completion of the reaction (monitored by TLC), the mixture was quenched with 10% NaOH (10.0 mL) and extracted with DCM (3×5 mL). The separated organic layer was dried over MgSO_4 and concentrated under vacuum. The residue was purified by flash chromatography (PE: EA = 10: 1) to afford product **9** (42 mg, 92%).

2-phenyl-5-(thiocyanatomethyl)thiazole (9)

White solid, $R_f = 0.5$ (PE: EA = 4: 1 v/v), 42 mg, 92% yield. Mp: 90–92 °C.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.96–7.86 (m, 2H), 7.80 (s, 1H), 7.48–7.41 (m, 3H), 4.43 (s, 2H).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 170.3, 144.2, 133.1, 131.3, 130.7, 129.1, 126.6, 111.0, 30.7.

HRMS (ESI-TOF, [M + H⁺]): calcd for C₁₁H₉N₂S₂, 233.0207, found 233.0207.

Cyclic voltammetry experiment

Cyclic voltammetry (CV) was taken using a CS300H in COM3 potentiostation Glass carbon as working electrode, Pt wire as counter electrode, Ag/AgCl as reference, ⁿBu₄NPF₆ (0.05 M) as electrolyte in CH₃CN (4 mL), **1a** (0.05 M), **2** (0.05 M), scan rate: 100 mV/s, ranging from -0.5 V to 2.0 V.

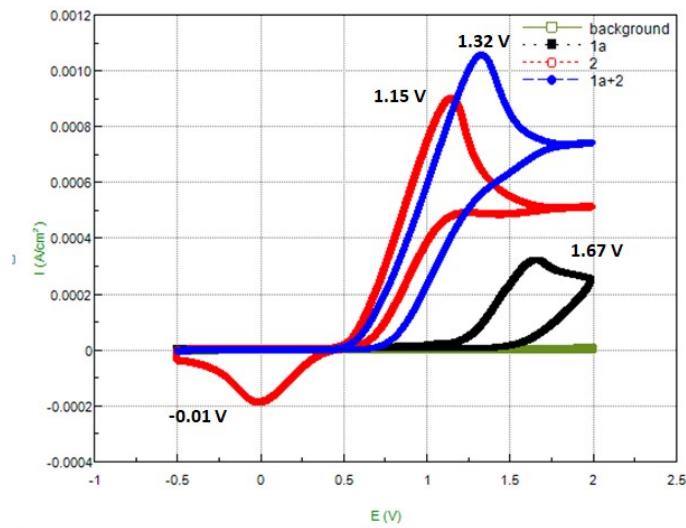


Figure S4. Cyclic voltammetry experiment

The cyclic voltammetry experiments of **1a** and **2** were performed, and the oxidation peaks were observed at 1.67 V and 1.15 V, respectively. This result indicated that NH₄SCN was easier to oxidize under electrochemical conditions. In addition, the peak of the SCN anion oxidation ($E_p^{\text{ox}} = 1.15 \text{ V}$) was non-reversible owing to the formation of (SCN)₂ fixed by its reduction peak ($E_p^{\text{red}} = -0.01 \text{ V}$). When **1a** and **2** were added to the system at the same time, the reduction peak of **2** disappeared, which indicated that the generated (SCN)₂ is consumed by **1a** as shown in the mechanism.

References

1. P. Ricci, T. Khotavivattana, L. Pfeifer, *Chem. Sci.*, 2017, **8**, 1195.
2. P. D. Morse, D. A. Nicewicz, *Chem. Sci.*, 2015, **6**, 270.

