

# Supporting Information

## Electrochemical one-pot cascade synthesis of thio(seleno)cyanato-substituted thiazolidine-2-imines without external electrolyte

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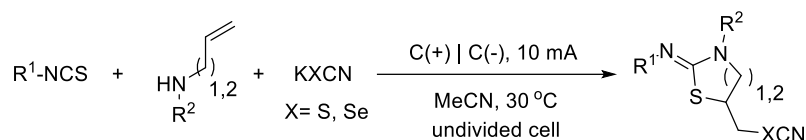
## 1. General Experimental Information

$^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (101 MHz),  $^{19}\text{F}$  NMR (377 MHz), and  $^{31}\text{P}$  NMR (162 MHz) spectra were recorded on a Bruker Ascend 400 spectrometer using  $\text{CDCl}_3$  as the solvents. Chemical shifts are given in ppm and coupling constants in Hz.  $^1\text{H}$  NMR spectra were calibrated in relation to the reference measurement of TMS (0.000 ppm). The following abbreviations were used for  $^1\text{H}$  NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), h (hexatruplet), and m (multiplet) as well as combinations of them. Flash chromatography was performed on silica gel 300–400 mesh (purchased from Qingdao Haiyang Chemical, China). HRMS were measured on a Xevo G2/TOF MS (ESI) and QSTAR Pulsar I LC/TOF MS (EI) mass spectrometer. The instrument for electrolysis was dual display potentiostat (DP3010MF) (Made in China). Cyclic voltammograms were obtained on a CHI 660E potentiostat. Both anodic and cathodic electrode were graphite rods ( $\Phi$  6 mm, hard). These electrodes were commercially available from Shang Hai Ci Yue, China. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Below is the setup for the electrochemical reaction.



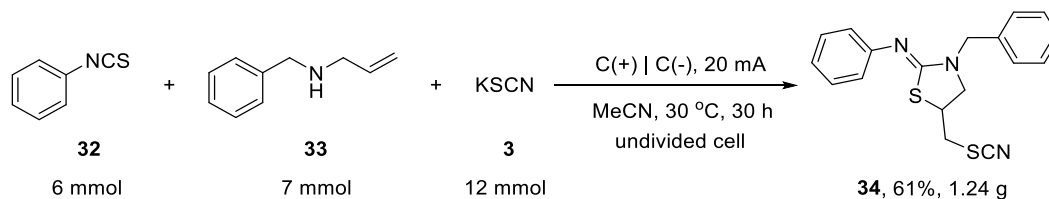
## 2. General Procedure

### 2.1 General procedure for synthesis of 4–31:



A mixture of isothiocyanates (0.2 mmol), *N*-2-en-1-amines (0.2 mmol), KXCN (0.4 mmol) in 3 mL MeCN was added to an oven-dried undivided three-necked bottle (5 mL). The electrolytic cell was equipped with graphite rods ( $\Phi$  6 mm, hard) as anode and cathode, and the distance between the two electrodes is 3 cm. The solution was electrolyzed at 30 °C under a constant current (10 mA) and the stir bar rotation speed (600 r) for 2 h. After completion of the reaction, the solvent was removed under reduced pressure to afford the residue, which was purified by flash column chromatography on a silica gel give the products 4–31.

### 2.2 Gram-scale experiment for synthesis of (*Z*)-3-benzyl-*N*-phenyl-5-(thiocyanatomethyl)thiazolidin-2-imine (**34**):



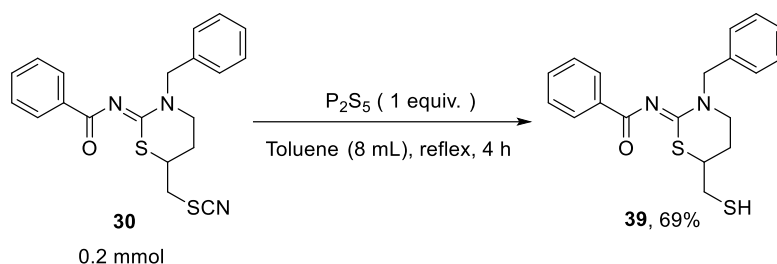
To an oven-dried undivided three-necked bottle (100 mL) with a magnetic bar was added KSCN (1.2 g, 12 mmol). The bottle was equipped with two graphite rods ( $\Phi$  20 mm, hard) as anode and cathode, and the distance between the two electrodes is 6 cm. To the bottle was successively added CH<sub>3</sub>CN (50 mL), isothiocyanatobenzene (0.8 g, 6 mmol) and *N*-benzylprop-2-en-1-amine (1.0 g, 7 mmol). The reaction mixture was stirred and electrolyzed at a constant current of 20 mA and the stir bar rotation speed (800 r) at 30 °C for 30 hours. After completion of the reaction, the solvent was removed under reduced pressure to afford the residue, which was purified by flash column chromatography on a silica gel using a mixture of petroleum ether and ethyl acetate to give the product (*Z*)-3-benzyl-*N*-phenyl-5-(thiocyanatomethyl)thiazolidin-2-imine (**34**, 1.24 g, 61%).

Current efficiency (*c.e.*) is defined as the percentage that represents the ratio of the Coulombs consumed in the formation of chemical products to the total number of Coulombs passed through the cell. It is calculated using the following formula for product **34**:

$$c.e. = \frac{z * N_p * F}{I * t} \times 100\% = \frac{2 * 3.66 * 10^{-3} \text{ mol} * 96485 \text{ s} \cdot \text{A} \cdot \text{mol}^{-1}}{20 * 10^{-3} \text{ A} * 108000 \text{ s}} \times 100\% = 32.7\%$$

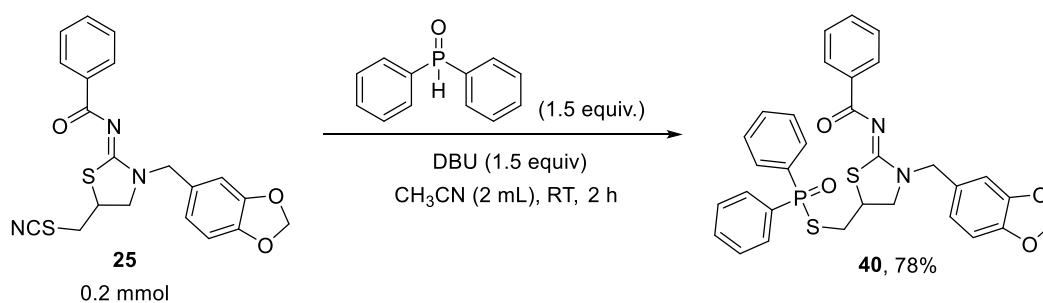
$z$ : the number of electrons added to or removed from one product molecule [-];  $N_p$ : number of mols of the product [mol];  $F$ : Faraday constant [ $96485 \text{ s} \cdot \text{A} \cdot \text{mol}^{-1}$ ];  $I$ : the current [A];  $t$ : the time [s].

### 2.3 General procedure for synthesis of (Z)-((3-(benzo[d][1,3]dioxol-5-ylmethyl)-2-(benzoylimino)thiazolidin-5-yl)methyl) diphenylphosphinothioate (**39**):



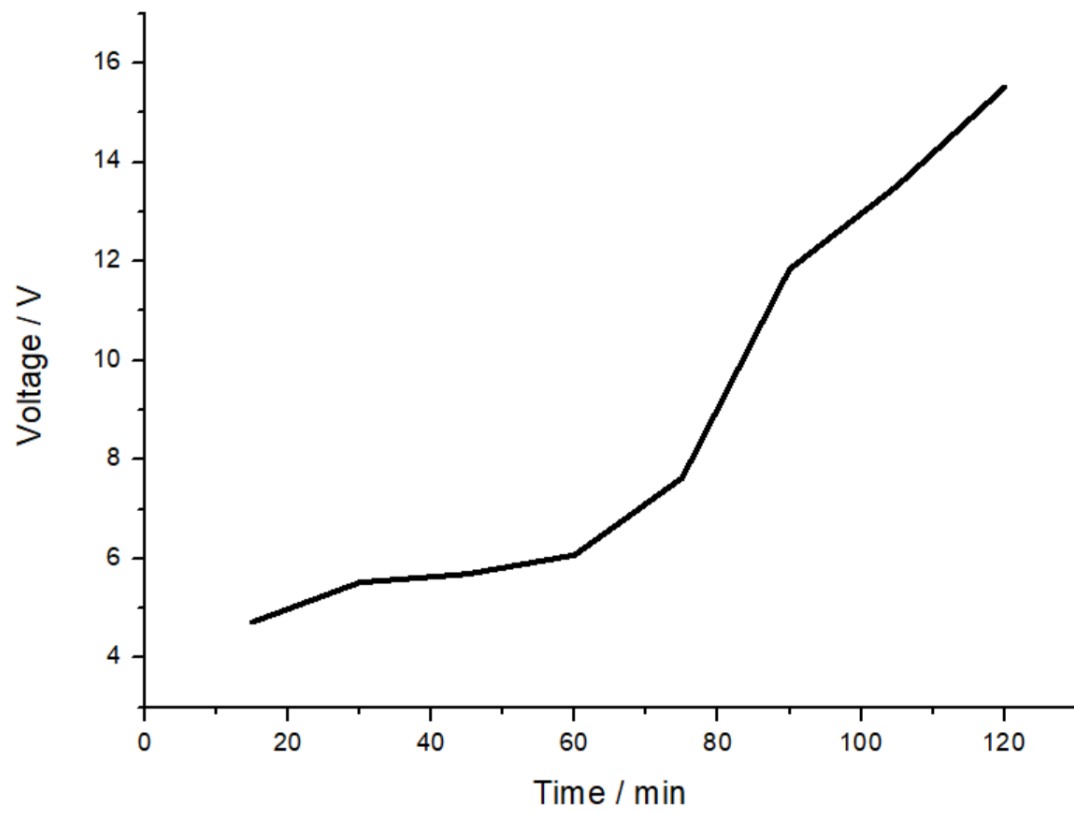
To a three-neck round bottom flask (25 mL) was added **30** (76.2 mg, 0.2 mmol),  $\text{P}_2\text{S}_5$  (90.0 mg, 0.2 mmol), and toluene (8 mL). The resulting mixture was refluxed for 4 h. After the reaction was complete, the reaction mixture was quenched by careful addition of water (10 mL), extracted with ethyl acetate ( $3 \times 10 \text{ mL}$ ), the organic phase was dried over sodium sulfate and evaporated under reduced pressure to get the crude product. Residue obtained was purified by a column chromatography on silica-gel using petroleum ether/ethyl acetate mixture ( $v/v = 1:1$ ) to afford (Z)-N-(3-benzyl-6-(mercaptomethyl)-1,3-thiazinan-2-ylidene)benzamide (**39**, 49.1 mg, 69%).

### 2.4 General procedure for synthesis of (Z)-((3-(benzo[d][1,3]dioxol-5-ylmethyl)-2-(benzoylimino)thiazolidin-5-yl)methyl) diphenylphosphinothioate (**40**):



To an oven-dried Schlenk-tube (10 mL) was added **25** (82.2 mg, 0.2 mmol), diphenylphosphine oxide (60.6 mg, 0.3 mmol), DBU (45.7 mg, 0.3 mmol) and  $\text{CH}_3\text{CN}$  (2 mL). The resulting mixture was stirred for 2 h at room temperature and the solvents were removed under reduced pressure. Residue obtained was purified by a column chromatography on silica-gel using petroleum ether/ethyl acetate mixture ( $v/v = 1:1.5$ ) to afford (Z)-((3-(benzo[d][1,3]dioxol-5-ylmethyl)-2-(benzoylimino)thiazolidin-5-yl)methyl) diphenylphosphinothioate (**40**, 91.4 mg, 78%).

### 2.5 Voltage-Time Line Chart:

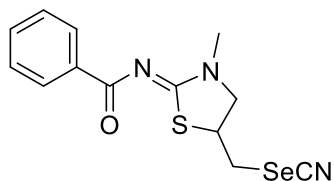


From this graph, voltage is positively correlated with time.

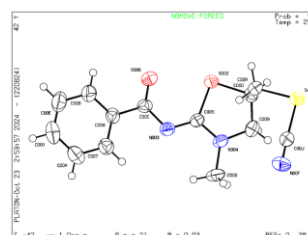
### 3. Crystal Data of compound 31

#### 3.1 Method of crystal growth and X-ray structure of compound 31:

In a 5 mL vial, 50 mg of the pure isolated compound was dissolved in minimum volume of trichloromethane at room temperature. The mixture was shaken well to obtain a homogenous and clear solution. Then, the solution was covered with a porous cap and allowed to stand undisturbed at room temperature for 5 days until the crystal was formed *via* slow evaporation method.



31

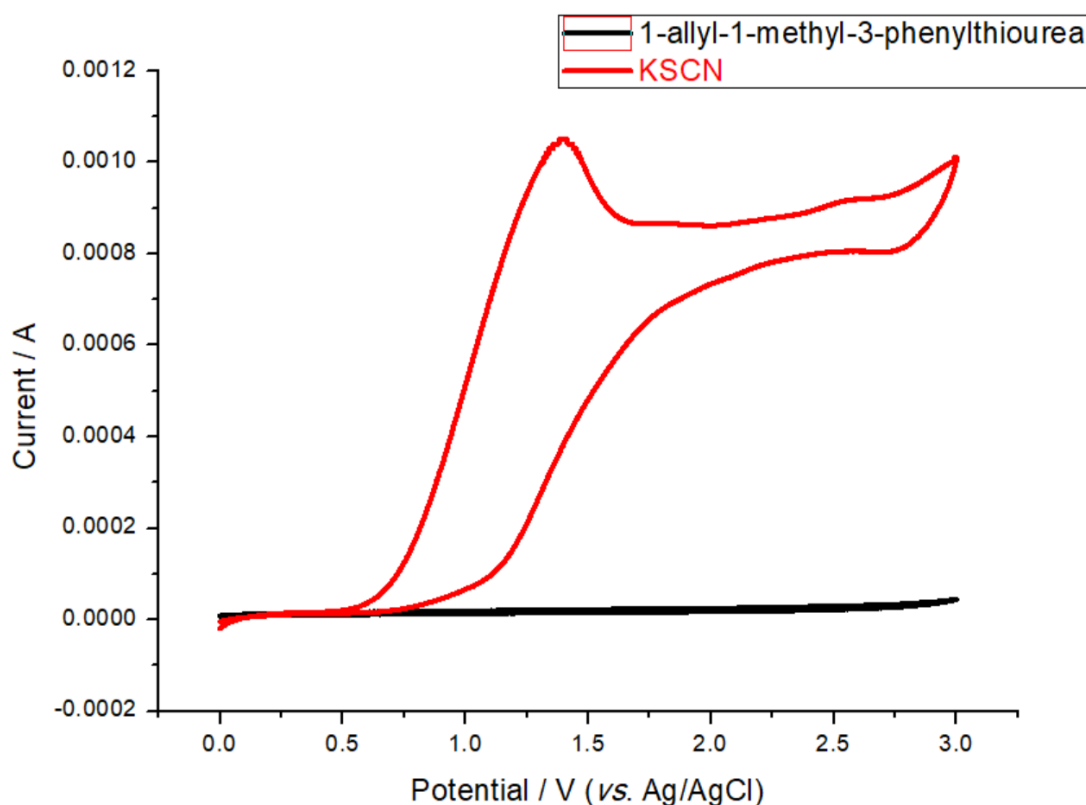


X-ray structure of 31  
CCDC 2393134

Empirical formula	C <sub>13</sub> H <sub>13</sub> N <sub>3</sub> OSse
Formula weight	338.28
Temperature/K	297.00
Crystal system	orthorhombic
Space group	Pna2 <sub>1</sub>
a/Å	23.722(3)
b/Å	7.1939(8)
c/Å	8.2904(8)
α/°	90
β/°	90
γ/°	90
Volume/Å <sup>3</sup>	1414.8(3)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.588
μ/mm <sup>-1</sup>	4.939
F(000)	680.0
Crystal size/mm <sup>3</sup>	0.41 × 0.28 × 0.18
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	7.454 to 136.478
Index ranges	-28 ≤ h ≤ 28, -8 ≤ k ≤ 8, -9 ≤ l ≤ 9
Reflections collected	28958
Independent reflections	2492 [R <sub>int</sub> = 0.0650, R <sub>sigma</sub> = 0.0506]
Data/restraints/parameters	2492/1/173
Goodness-of-fit on F <sup>2</sup>	1.108
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0314, wR <sub>2</sub> = 0.0804
Final R indexes [all data]	R <sub>1</sub> = 0.0351, wR <sub>2</sub> = 0.0810
Largest diff. peak/hole / e Å <sup>-3</sup>	0.34/-0.78
Flack parameter	0.201(12)

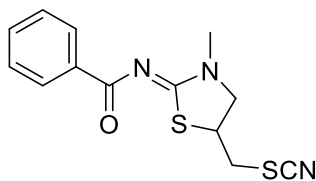
## 4. Cyclic Voltammetry Studies

Cyclic voltammetry was performed in a three-electrode cell connected to a Schlenk line under nitrogen at room temperature. The working electrode was a glassy carbon electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. MeCN (10 mL) containing 0.01 M  $n\text{Bu}_4\text{NBF}_4$  were poured into the electrochemical cell in all experiments. The scan rate is 0.05 V/s, ranging from 0 V to 3 V. The peak potentials vs. Ag/AgCl for used. 1-allyl-1-methyl-3-phenylthiourea **39** was not observed obvious oxidation peak. The oxidation peak of KSCN **3** was observed at 1.40 V (vs. Ag/AgCl).



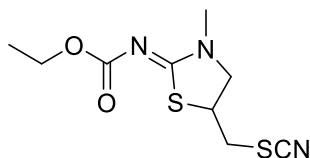
## 5. Characterization Data for Products

### (Z)-N-(3-methyl-5-(thiocyanatomethyl)thiazolidin-2-ylidene)benzamide (4)



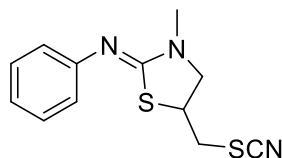
**Eluent:** petroleum ether/ethyl acetate (v/v = 3:1). Colorless and transparent liquid: 91% yield (52.9 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.27 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 3.83 (dd, *J* = 10.2, 4.0 Hz, 2H), 3.74–3.66 (m, 1H), 3.32–3.24 (m, 4H), 3.10 (dd, *J* = 13.7, 8.4 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  175.8, 169.4, 136.1, 132.2, 129.6, 128.1, 111.4, 54.3, 41.7, 37.9, 34.8. **HRMS** (EI-TOF): *m/z* [*M*]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>OS<sub>2</sub><sup>+</sup>: 291.0500; found: 291.0502.

### (Z)-N-(3-methyl-5-(thiocyanatomethyl)thiazolidin-2-ylidene)propionamide (5)



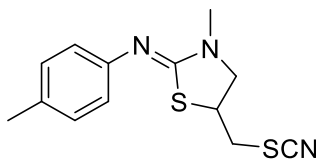
**Eluent:** petroleum ether/ethyl acetate (v/v = 1:1). Colorless and transparent liquid: 80% yield (41.4 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  4.21 (q, *J* = 7.2 Hz, 2H), 3.92–3.82 (m, 2H), 3.72 (d, *J* = 8.7 Hz, 1H), 3.29 (dd, *J* = 13.7, 5.1 Hz, 1H), 3.18 (s, 3H), 3.10 (dd, *J* = 13.7, 8.8 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  170.6, 163.1, 111.0, 62.0, 55.1, 41.4, 37.9, 34.7, 14.4. **HRMS** (EI-TOF): *m/z* [*M*]<sup>+</sup> calcd. for C<sub>9</sub>H<sub>13</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>: 259.0449; found: 259.0446.

### (Z)-3-methyl-N-phenyl-5-(thiocyanatomethyl)thiazolidin-2-imine (6)



**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Yellow liquid: 78% yield (41.0 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.32–7.25 (m, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 2H), 3.86–3.81 (m, 1H), 3.76 (dd, *J* = 10.4, 6.2 Hz, 1H), 3.61 (dd, *J* = 10.4, 2.6 Hz, 1H), 3.28–3.14 (m, 2H), 3.07 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  156.6, 151.3, 128.9, 123.5, 121.8, 111.1, 55.9, 42.0, 38.0, 33.9. **HRMS** (EI-TOF): *m/z* [*M*]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>S<sub>2</sub><sup>+</sup>: 263.0551; found: 263.0549.

### (Z)-3-methyl-5-(thiocyanatomethyl)-N-(*p*-tolyl)thiazolidin-2-imine (7)

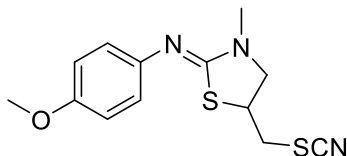


**Eluent:** petroleum ether/ethyl acetate (v/v = 3:1). Yellow liquid: 69% yield (38.2 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.08 (d, *J* = 7.5 Hz, 2H), 6.82 (d, *J* = 7.0 Hz, 2H), 3.87–3.79 (m, 1H), 3.79–3.72



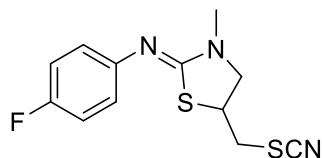
(m, 1H), 3.61 (d,  $J = 10.3$  Hz, 1H), 3.26–3.15 (m, 2H), 3.06 (s, 3H), 2.31 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  156.6, 148.8, 132.9, 129.5, 121.6, 111.2, 55.9, 41.9, 38.0, 33.9, 20.9. HRMS (EI-TOF):  $m/z$   $[\text{M}]^+$  calcd. for  $\text{C}_{13}\text{H}_{15}\text{N}_3\text{S}_2^+$ : 277.0707; found: 277.0710.

**(Z)-N-(4-methoxyphenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (8)**



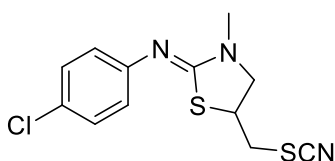
**Eluent:** petroleum ether/ethyl acetate ( $v/v = 2:1$ ). Yellow liquid: 61% yield (35.7 mg).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  6.91–6.76 (m, 4H), 3.85–3.75 (m, 5H), 3.62 (d,  $J = 10.3$  Hz, 1H), 3.27–3.17 (m, 2H), 3.07 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  157.5, 156.2, 144.0, 122.9, 114.2, 111.2, 56.2, 55.4, 42.0, 38.0, 34.1. HRMS (EI-TOF):  $m/z$   $[\text{M}]^+$  calcd. for  $\text{C}_{13}\text{H}_{15}\text{N}_3\text{OS}_2^+$ : 293.0657; found: 293.0659.

**(Z)-N-(4-fluorophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidine-2-imine (9)**



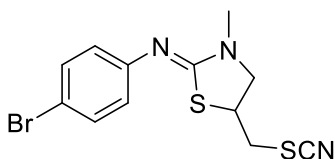
**Eluent:** petroleum ether/ethyl acetate ( $v/v = 3:1$ ). Yellow liquid: 77% yield (43.2 mg).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.00–6.92 (m, 2H), 6.89–6.82 (m, 2H), 3.88–3.84 (m, 1H), 3.77 (dd,  $J = 10.4$ , 6.2 Hz, 1H), 3.62 (dd,  $J = 10.4$ , 2.7 Hz, 1H), 3.30–3.14 (m, 2H), 3.05 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  159.3 (d,  $J = 241.6$  Hz), 157.0, 147.5 (d,  $J = 2.8$  Hz), 123.0 (d,  $J = 8.0$  Hz), 115.5 (d,  $J = 22.0$  Hz), 111.1, 55.9, 42.0, 38.0, 33.8.  $^{19}\text{F}$  NMR (377 MHz, Chloroform- $d$ )  $\delta$  -120.48. HRMS (EI-TOF):  $m/z$   $[\text{M}]^+$  calcd. for  $\text{C}_{12}\text{H}_{12}\text{FN}_3\text{S}_2^+$ : 281.0457; found: 281.0455.

**(Z)-N-(4-chlorophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (10)**



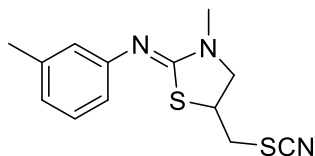
**Eluent:** petroleum ether/ethyl acetate ( $v/v = 2:1$ ). Yellow liquid: 75% yield (44.5 mg).  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.23 (d,  $J = 8.6$  Hz, 2H), 6.84 (d,  $J = 8.6$  Hz, 2H), 3.91–3.75 (m, 2H), 3.63 (dd,  $J = 10.4$ , 2.7 Hz, 1H), 3.29–3.14 (m, 2H), 3.06 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  156.8, 150.1, 129.0, 128.6, 123.2, 111.1, 55.9, 42.0, 38.0, 33.8. HRMS (EI-TOF):  $m/z$   $[\text{M}]^+$  calcd. for  $\text{C}_{12}\text{H}_{12}\text{ClN}_3\text{S}_2^+$ : 297.0161; found: 297.0163.

**(Z)-N-(4-bromophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (11)**



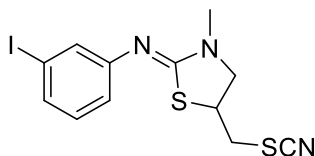
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Yellow liquid: 71% yield (48.3 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 3.86 (dtd, *J* = 8.5, 6.1, 2.6 Hz, 1H), 3.78 (dd, *J* = 10.4, 6.3 Hz, 1H), 3.62 (dd, *J* = 10.4, 2.6 Hz, 1H), 3.28–3.14 (m, 2H), 3.05 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 156.8, 150.4, 131.9, 123.6, 116.3, 111.1, 55.9, 42.0, 38.0, 33.8. **HRMS** (EI-TOF): *m/z* [M]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>12</sub>BrN<sub>3</sub>S<sub>2</sub><sup>+</sup>: 340.9656; found: 340.9653.

**(Z)-3-methyl-5-(thiocyanatomethyl)-N-(m-tolyl)thiazolidin-2-imine (13)**



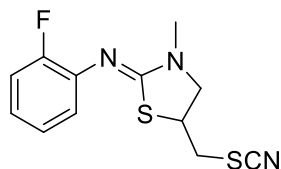
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Yellow liquid: 53% yield (29.4 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.16 (t, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.76–6.69 (m, 2H), 3.83 (dtd, *J* = 8.6, 6.0, 2.7 Hz, 1H), 3.75 (dd, *J* = 10.4, 6.2 Hz, 1H), 3.60 (dd, *J* = 10.3, 2.7 Hz, 1H), 3.28–3.14 (m, 2H), 3.06 (s, 3H), 2.32 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 156.6, 151.1, 138.7, 128.7, 124.4, 122.6, 118.6, 111.2, 55.9, 41.9, 38.0, 33.9, 21.4. **HRMS** (EI-TOF): *m/z* [M]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>S<sub>2</sub><sup>+</sup>: 277.0707; found: 277.0709.

**(Z)-N-(3-iodophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (14)**



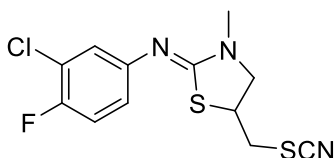
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Yellow liquid: 76% yield (59.1 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.37 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.29 (t, *J* = 1.9 Hz, 1H), 6.99 (t, *J* = 7.9 Hz, 1H), 6.91–6.85 (m, 1H), 3.89–3.84 (m, 1H), 3.80–3.76 (m, 1H), 3.62 (dd, *J* = 10.5, 2.7 Hz, 1H), 3.27–3.15 (m, 2H), 3.04 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 157.0, 152.7, 132.2, 130.9, 130.4, 121.2, 111.1, 94.3, 55.8, 42.0, 37.9, 33.8. **HRMS** (EI-TOF): *m/z* [M]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>12</sub>IN<sub>3</sub>S<sub>2</sub><sup>+</sup>: 388.9517; found: 388.9520.

**(Z)-N-(2-fluorophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (15)**



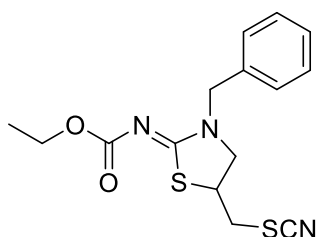
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Yellow liquid: 75% yield (42.1 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.09–6.98 (m, 3H), 6.96–6.90 (m, 1H), 3.95–3.73 (m, 2H), 3.73–3.59 (m, 1H), 3.22 (h, *J* = 8.0 Hz, 2H), 3.10 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 157.1 (d, *J* = 246.1 Hz), 153.4, 139.2 (d, *J* = 11.9 Hz), 124.4 (d, *J* = 7.6 Hz), 124.2 (d, *J* = 3.8 Hz), 123.9 (d, *J* = 1.8 Hz), 115.9 (d, *J* = 20.3 Hz), 111.1, 56.2, 42.0, 38.0, 33.8. **<sup>19</sup>F NMR** (377 MHz, Chloroform-*d*) δ -126.1. **HRMS** (EI-TOF): *m/z* [M]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>12</sub>FN<sub>3</sub>S<sub>2</sub><sup>+</sup>: 281.0457; found: 281.0460.

**(Z)-N-(3-chloro-4-fluorophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (17)**



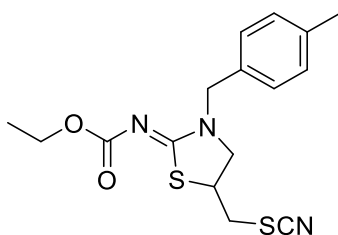
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Yellow liquid: 68% yield (42.8 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.03 (td,  $J$  = 8.8, 1.0 Hz, 1H), 6.96 (dd,  $J$  = 6.5, 2.1 Hz, 1H), 6.76 (dt,  $J$  = 7.8, 3.0 Hz, 1H), 3.88 (m, 1H), 3.79 (dd,  $J$  = 10.4, 6.4 Hz, 1H), 3.64 (dd,  $J$  = 10.5, 2.2 Hz, 1H), 3.23 (m, 2H), 3.05 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  157.4, 154.6 (d,  $J$  = 244.1 Hz), 148.2 (d,  $J$  = 3.0 Hz), 123.7, 121.3 (d,  $J$  = 6.6 Hz), 120.7 (d,  $J$  = 18.3 Hz), 116.5 (d,  $J$  = 21.8 Hz), 111.0, 55.9, 42.1, 38.0, 33.8. **<sup>19</sup>F NMR** (377 MHz, Chloroform-*d*)  $\delta$  -123.22. **HRMS** (EI-TOF):  $m/z$  [M]<sup>+</sup> calcd. For C<sub>12</sub>H<sub>11</sub>ClFN<sub>3</sub>S<sub>2</sub><sup>+</sup>: 315.0067; found: 315.0070.

**ethyl (Z)-(3-benzyl-5-(thiocyanatomethyl)thiazolidin-2-ylidene)carbamate (20)**



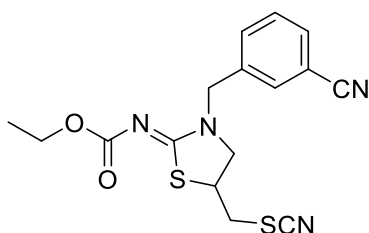
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Colorless and transparent liquid: 77% yield (51.6 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.39–7.32 (m, 3H), 7.29–7.23 (m, 2H), 4.89 (d,  $J$  = 14.6 Hz, 1H), 4.79 (d,  $J$  = 14.6 Hz, 1H), 4.24 (q,  $J$  = 7.1 Hz, 2H), 3.83–3.66 (m, 2H), 3.55 (dd,  $J$  = 11.0, 1.7 Hz, 1H), 3.20 (dd,  $J$  = 13.6, 5.3 Hz, 1H), 2.91 (dd,  $J$  = 13.6, 8.9 Hz, 1H), 1.35 (t,  $J$  = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  170.7, 163.3, 134.8, 129.0, 128.3, 128.3, 110.8, 62.0, 52.3, 50.9, 41.2, 37.7, 14.5. **HRMS** (EI-TOF):  $m/z$  [M]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>: 335.0762; found: 335.0760.

**ethyl (Z)-(3-(4-methylbenzyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene)carbamate (21)**



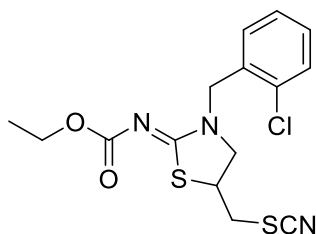
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Colorless and transparent liquid: 74% yield (51.6 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.15 (s, 4H), 4.87 (d,  $J$  = 14.5 Hz, 1H), 4.74 (d,  $J$  = 14.5 Hz, 1H), 4.24 (q,  $J$  = 7.1 Hz, 2H), 3.81–3.65 (m, 2H), 3.54 (d,  $J$  = 9.3 Hz, 1H), 3.19 (dd,  $J$  = 13.6, 5.4 Hz, 1H), 2.90 (dd,  $J$  = 13.6, 8.8 Hz, 1H), 2.35 (s, 3H), 1.35 (t,  $J$  = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  163.2, 138.2, 131.7, 129.7, 128.3, 110.8, 62.1, 52.3, 50.8, 41.2, 37.7, 21.1, 14.5. **HRMS** (EI-TOF):  $m/z$  [M]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>: 349.0919; found: 349.0921.

**ethyl (Z)-(3-(3-cyanobenzyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene)carbamate (22)**



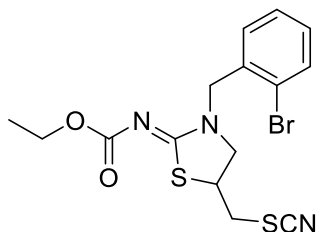
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Colorless and transparent liquid: 79% yield (56.9 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (dt, *J* = 7.3, 1.6 Hz, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.56–7.47 (m, 2H), 4.98 (d, *J* = 15.0 Hz, 1H), 4.79 (d, *J* = 15.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.92–3.78 (m, 1H), 3.76 (dd, *J* = 11.3, 7.3 Hz, 1H), 3.60 (dd, *J* = 11.3, 2.9 Hz, 1H), 3.25 (dd, *J* = 13.7, 5.2 Hz, 1H), 3.02 (dd, *J* = 13.8, 9.1 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 171.1, 163.1, 136.5, 132.6, 132.0, 131.6, 129.9, 118.2, 113.2, 110.8, 62.3, 52.5, 50.1, 41.5, 37.7, 14.4. **HRMS** (EI-TOF): *m/z* [M]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>: 360.0715; found: 360.0713.

**ethyl (Z)-3-(2-chlorobenzyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene)carbamate (23)**



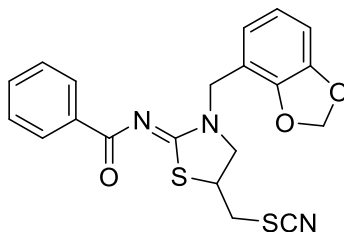
**Eluent:** petroleum ether/ethyl acetate (v/v = 3:1). Light yellow liquid: 60% yield (44.3 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.44–7.39 (m, 1H), 7.36–7.27 (m, 3H), 5.07 (d, *J* = 15.0 Hz, 1H), 4.86 (d, *J* = 15.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.82–3.69 (m, 2H), 3.63–3.55 (m, 1H), 3.23 (dd, *J* = 13.5, 5.6 Hz, 1H), 2.99 (dd, *J* = 13.6, 8.9 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 170.7, 163.2, 133.8, 132.4, 130.5, 130.0, 129.8, 127.5, 110.7, 62.1, 52.4, 48.4, 41.3, 37.8, 14.4. **HRMS** (EI-TOF): *m/z* [M]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>16</sub>ClN<sub>3</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>: 369.0372; found: 369.0375.

**ethyl (Z)-3-(2-bromobenzyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene)carbamate (24)**



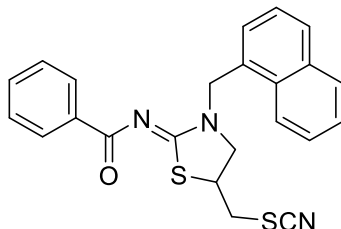
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Light yellow liquid: 67% yield (55.3 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.37–7.29 (m, 2H), 7.21 (ddd, *J* = 8.0, 6.2, 2.9 Hz, 1H), 5.06 (d, *J* = 15.0 Hz, 1H), 4.85 (d, *J* = 15.0 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.83–3.67 (m, 2H), 3.58 (dd, *J* = 11.1, 2.1 Hz, 1H), 3.23 (dd, *J* = 13.4, 5.5 Hz, 1H), 3.01 (dd, *J* = 13.5, 8.8 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 170.8, 163.2, 134.1, 133.3, 130.5, 130.0, 128.1, 123.9, 110.7, 62.1, 52.3, 50.8, 41.3, 37.8, 14.4. **HRMS** (EI-TOF): *m/z* [M]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>16</sub>BrN<sub>3</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup>: 412.9867; found: 412.9869.

**(Z)-N-(3-(benzo[d][1,3]dioxol-4-ylmethyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene)benzamide (25)**



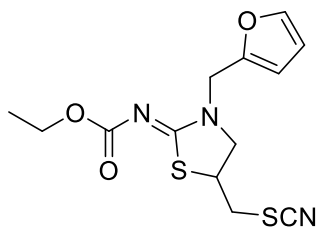
**Eluent:** petroleum ether/ethyl acetate (v/v = 3:1). Colorless and transparent liquid: 90% yield (73.9 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.34–8.27 (m, 2H), 7.56–7.49 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 6.84 (s, 1H), 6.83–6.76 (m, 2H), 5.96 (s, 2H), 4.91 (s, 2H), 3.82–3.71 (m, 2H), 3.66–3.58 (m, 1H), 3.22 (dd, *J* = 13.7, 5.1 Hz, 1H), 2.95 (dd, *J* = 13.6, 9.0 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 175.9, 169.4, 148.3, 147.7, 136.0, 132.3, 129.7, 128.9, 128.2, 122.0, 111.1, 108.7, 108.5, 101.3, 51.7, 51.2, 41.6, 37.8. **HRMS** (EI-TOF): *m/z* [M]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub><sup>+</sup>: 411.0711; found: 411.0708.

**(Z)-N-(3-(naphthalen-1-ylmethyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene)benzamide (26)**



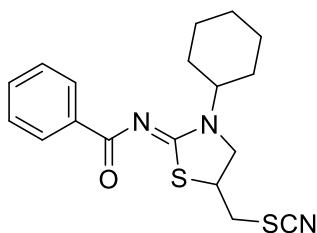
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Colorless and transparent liquid: 87% yield (72.5 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 8.43–8.37 (m, 2H), 8.19–8.11 (m, 1H), 7.91 (ddd, *J* = 6.6, 4.8, 1.6 Hz, 2H), 7.60–7.40 (m, 7H), 5.86 (d, *J* = 14.6 Hz, 1H), 5.05 (d, *J* = 14.6 Hz, 1H), 3.69–3.54 (m, 2H), 3.54–3.39 (m, 1H), 3.01 (dd, *J* = 13.2, 5.1 Hz, 1H), 2.55 (dd, *J* = 13.6, 9.1 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 176.1, 168.8, 136.1, 133.9, 132.3, 131.3, 130.9, 129.7, 129.7, 129.0, 128.4, 128.2, 127.1, 126.4, 125.3, 123.3, 110.8, 51.0, 50.0, 41.3, 37.5. **HRMS** (EI-TOF): *m/z* [M]<sup>+</sup> calcd. for C<sub>23</sub>H<sub>19</sub>N<sub>3</sub>OS<sub>2</sub><sup>+</sup>: 417.0970; found: 417.0972.

**ethyl (Z)-3-(furan-2-ylmethyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene)carbamate (27)**



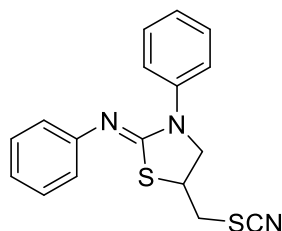
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Colorless and transparent liquid: 76% yield (49.4 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*) δ 7.39 (t, *J* = 1.3 Hz, 1H), 6.36 (d, *J* = 1.4 Hz, 2H), 4.92 (d, *J* = 15.4 Hz, 1H), 4.72 (d, *J* = 15.4 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.85–3.63 (m, 3H), 3.23 (dd, *J* = 13.7, 5.7 Hz, 1H), 2.97 (dd, *J* = 13.6, 9.0 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*) δ 170.4, 163.1, 148.4, 143.0, 110.8, 110.7, 109.8, 62.1, 52.5, 43.5, 41.4, 37.5, 14.4. **HRMS** (EI-TOF): *m/z* [M]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub><sup>+</sup>: 325.0555; found: 325.0558.

**(Z)-N-(3-cyclohexyl-5-(thiocyanatomethyl)thiazolidin-2-ylidene)benzamide (28)**



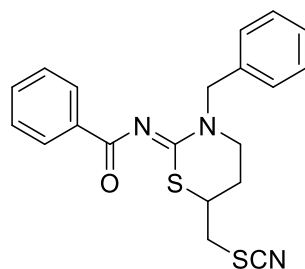
**Eluent:** petroleum ether/ethyl acetate (v/v = 3:1). Colorless and transparent liquid: 88% yield (63.2 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.27–8.22 (m, 2H), 7.55–7.47 (m, 1H), 7.43 (dd,  $J$  = 8.2, 6.6 Hz, 2H), 4.72–4.58 (m, 1H), 3.86–3.71 (m, 3H), 3.24 (dd,  $J$  = 13.8, 4.6 Hz, 1H), 3.04 (dd,  $J$  = 13.7, 8.9 Hz, 1H), 1.97–1.86 (m, 4H), 1.75 (d,  $J$  = 13.1 Hz, 1H), 1.61–1.40 (m, 4H), 1.20 (ddd,  $J$  = 21.5, 12.5, 8.2 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  175.9, 168.5, 136.2, 132.1, 129.6, 128.0, 111.2, 56.8, 48.4, 41.5, 37.4, 30.6, 29.8, 25.6, 25.3. **HRMS** (EI-TOF):  $m/z$  [M]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>21</sub>N<sub>3</sub>OS<sub>2</sub><sup>+</sup>: 359.1126; found: 359.1129.

**(Z)-N,3-diphenyl-5-(thiocyanatomethyl)thiazolidin-2-imine (29)**



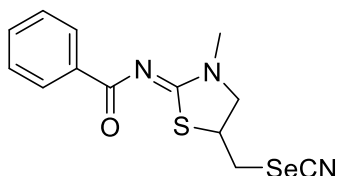
**Eluent:** petroleum ether/ethyl acetate (v/v = 3:1). Yellow liquid: 65% yield (42.2 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.55 (d,  $J$  = 8.0 Hz, 2H), 7.41 (t,  $J$  = 7.8 Hz, 2H), 7.29 (t,  $J$  = 7.7 Hz, 2H), 7.19 (t,  $J$  = 7.4 Hz, 1H), 7.08 (t,  $J$  = 7.4 Hz, 1H), 6.94 (d,  $J$  = 7.6 Hz, 2H), 4.37 (dd,  $J$  = 10.6, 6.1 Hz, 1H), 4.09 (dd,  $J$  = 10.6, 2.7 Hz, 1H), 3.98–3.89 (m, 1H), 3.29 (qd,  $J$  = 13.6, 7.3 Hz, 2H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  150.9, 145.9, 140.5, 129.0, 129.0, 125.2, 123.9, 122.9, 121.6, 111.9, 55.8, 41.4, 37.8. **HRMS** (EI-TOF):  $m/z$  [M]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>S<sub>2</sub><sup>+</sup>: 325.0707; found: 325.0704.

**(Z)-N-(3-benzyl-6-(thiocyanatomethyl)-1,3-thiazinan-2-ylidene)benzamide (30)**



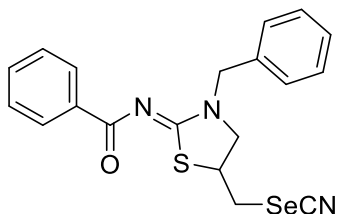
**Eluent:** petroleum ether/ethyl acetate (v/v = 3:1). Colorless and transparent liquid: 87% yield (66.3 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.20–8.11 (m, 2H), 7.50–7.42 (m, 1H), 7.41–7.29 (m, 7H), 5.23 (d,  $J$  = 14.5 Hz, 1H), 5.05 (d,  $J$  = 14.5 Hz, 1H), 3.68–3.57 (m, 1H), 3.56–3.48 (m, 2H), 3.24 (dd,  $J$  = 13.7, 5.7 Hz, 1H), 3.11 (dd,  $J$  = 13.7, 8.7 Hz, 1H), 2.58–2.42 (m, 1H), 2.11–1.93 (m, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  174.5, 164.0, 136.9, 135.9, 131.7, 129.6, 128.9, 128.0, 128.0, 111.1, 56.1, 46.2, 40.8, 38.2, 27.8. **HRMS** (EI-TOF):  $m/z$  [M]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>OS<sub>2</sub><sup>+</sup>: 381.0970; found: 381.0974.

**(Z)-N-(3-methyl-5-(selenocyanatomethyl)thiazolidin-2-ylidene)benzamide (31)**



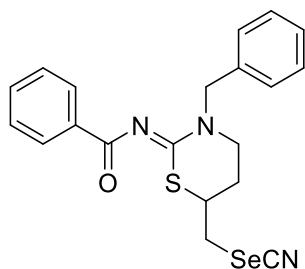
**Eluent:** petroleum ether/ethyl acetate (v/v = 2:1). Colorless and transparent solid: 82% yield (55.6 mg). mp 117-118 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 3.97–3.84 (m, 2H), 3.74 (d, *J* = 9.1 Hz, 1H), 3.39 (dd, *J* = 12.7, 4.9 Hz, 1H), 3.35 (s, 3H), 3.24 (dd, *J* = 12.7, 8.6 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 175.8, 169.4, 136.0, 132.2, 129.6, 128.1, 100.7, 55.2, 42.3, 34.9, 33.3. **HRMS** (ESI-TOF): *m/z* [M+Na]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>13</sub>N<sub>3</sub>NaOSSe<sup>+</sup>: 361.9842; found: 361.9840.

**(Z)-N-(3-benzyl-5-(selenocyanatomethyl)thiazolidin-2-ylidene)benzamide (32)**



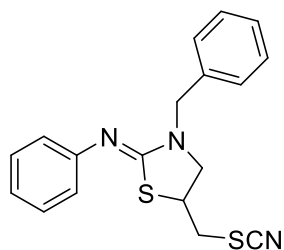
**Eluent:** petroleum ether/ethyl acetate (v/v = 3:1). Colorless and transparent solid: 80% yield (66.4 mg). mp 135-136 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.35–8.27 (m, 2H), 7.56–7.48 (m, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.41–7.30 (m, 5H), 5.03 (s, 2H), 3.90–3.73 (m, 2H), 3.62 (dd, *J* = 11.5, 2.6 Hz, 1H), 3.31 (dd, *J* = 12.7, 5.3 Hz, 1H), 3.05 (dd, *J* = 12.7, 9.0 Hz, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 175.9, 169.5, 136.0, 135.2, 132.3, 129.7, 129.1, 128.4, 128.4, 128.1, 100.4, 52.6, 51.4, 42.2, 33.1. **HRMS** (ESI-TOF): *m/z* [M+Na]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>17</sub>N<sub>3</sub>NaOSSe<sup>+</sup>: 438.0155; found: 438.0151.

**(Z)-N-(3-benzyl-6-(selenocyanatomethyl)-1,3-thiazinan-2-ylidene)benzamide (33)**



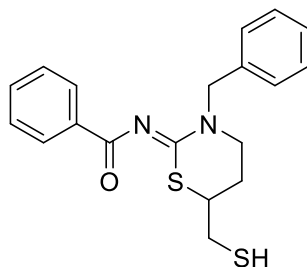
**Eluent:** petroleum ether/ethyl acetate (v/v = 1.5:1). Colorless and transparent solid: 87% yield (74.4 mg). mp 159-160 °C. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.20–8.11 (m, 2H), 7.50–7.43 (m, 1H), 7.43–7.27 (m, 7H), 5.21 (d, *J* = 14.6 Hz, 1H), 5.06 (d, *J* = 14.6 Hz, 1H), 3.72 – 3.59 (m, 1H), 3.59–3.44 (m, 2H), 3.34 (dd, *J* = 12.8, 5.4 Hz, 1H), 3.24 (dd, *J* = 12.8, 8.8 Hz, 1H), 2.61–2.37 (m, 1H), 2.12–1.93 (m, 1H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 174.5, 164.1, 137.0, 136.0, 131.7, 129.5, 128.9, 128.1, 128.0, 128.0, 101.2, 56.0, 46.2, 41.4, 33.4, 28.5. **HRMS** (ESI-TOF): *m/z* [M+Na]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>NaOSSe<sup>+</sup>: 452.0312; found: 452.0313.

**(Z)-3-benzyl-N-phenyl-5-(thiocyanatomethyl)thiazolidin-2-imine (38)**



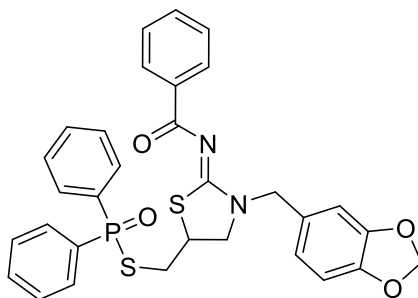
**Eluent:** petroleum ether/ethyl acetate (v/v = 3:1). Light yellow liquid: 61% yield (1.24 g). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.41–7.20 (m, 7H), 7.07 (t,  $J$  = 7.2 Hz, 1H), 6.96 (d,  $J$  = 7.5 Hz, 2H), 4.81 (d,  $J$  = 14.7 Hz, 1H), 4.65 (d,  $J$  = 14.6 Hz, 1H), 3.77–3.65 (m, 2H), 3.47 (d,  $J$  = 10.3 Hz, 1H), 3.18–3.00 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  156.0, 151.1, 136.5, 129.0, 128.8, 128.3, 127.8, 123.5, 121.8, 111.0, 53.0, 50.1, 41.9, 38.0. **HRMS** (EI-TOF):  $m/z$  [M]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>S<sub>2</sub><sup>+</sup>: 339.0864; found: 339.0867.

**(Z)-N-(3-benzyl-6-(mercaptomethyl)-1,3-thiazinan-2-ylidene)benzamide (39)**



**Eluent:** petroleum ether/ethyl acetate (v/v = 1:1). Colorless and transparent liquid: 69% yield (49.1 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.15 (d,  $J$  = 7.7 Hz, 2H), 7.45 (t,  $J$  = 7.2 Hz, 1H), 7.40–7.28 (m, 7H), 5.27 (dd,  $J$  = 14.6, 3.0 Hz, 1H), 4.96 (dd,  $J$  = 14.6, 4.2 Hz, 1H), 3.57–3.36 (m, 3H), 2.91–2.68 (m, 2H), 2.40 (dt,  $J$  = 13.6, 4.4 Hz, 1H), 2.09 (s, 1H), 1.92 (dtd,  $J$  = 14.0, 9.1, 4.9 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  174.2, 165.3, 137.2, 136.2, 131.5, 129.6, 128.9, 128.0, 127.9, 55.9, 46.8, 41.1, 38.0, 28.7. **HRMS** (EI-TOF):  $m/z$  [M]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>OS<sub>2</sub><sup>+</sup>: 356.1017; found: 356.1014.

**(Z)-((3-(benzo[d][1,3]dioxol-5-ylmethyl)-2-(benzoylimino)thiazolidin-5-yl)methyl) diphenylphosphinothioate (40)**

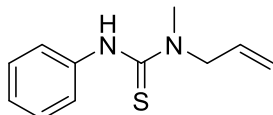


**Eluent:** petroleum ether/ethyl acetate (v/v = 1:1.5). Colorless and transparent liquid: 78% yield (91.4 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.34–8.25 (m, 2H), 7.93–7.78 (m, 4H), 7.64–7.37 (m, 9H), 6.84 (s, 1H), 6.82–6.71 (m, 2H), 5.95 (s, 2H), 5.02 (d,  $J$  = 14.2 Hz, 1H), 4.77 (d,  $J$  = 14.2 Hz, 1H), 3.72 (d,  $J$  = 9.5 Hz, 2H), 3.61 (dd,  $J$  = 11.8, 7.8 Hz, 1H), 3.02–2.86 (m, 2H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  175.8, 170.1, 147.4, 136.4, 133.2, 133.0, 132.7, 132.1, 131.9, 131.5, 131.4, 131.3,



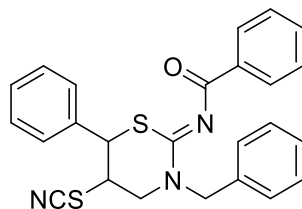
129.6, 129.3, 128.9, 128.8, 128.0, 122.0, 108.8, 108.4, 101.18, 52.4, 51.0, 42.5, 33.7. **<sup>31</sup>P NMR** (162 MHz, Chloroform-*d*)  $\delta$  43.9. **HRMS** (ESI-TOF):  $m/z$   $[M+H]^+$  calcd. for  $C_{31}H_{28}N_2O_4PS_2^+$ : 587.1228; found: 587.1223.

**1-allyl-1-methyl-3-phenylthiourea (41)**



**Eluent:** petroleum ether/ethyl acetate (v/v = 5:1). Colorless and transparent liquid: 92% yield (37.9 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.37 – 7.26 (m, 4H), 7.18 (tt,  $J$  = 6.7, 1.5 Hz, 2H), 5.89 (ddt,  $J$  = 17.2, 10.5, 5.3 Hz, 1H), 5.36 – 5.20 (m, 2H), 4.38 (d,  $J$  = 5.4 Hz, 2H), 3.24 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  182.3, 139.7, 131.8, 128.7, 125.7, 125.3, 117.9, 56.0, 39.0. **HRMS** (EI-TOF):  $m/z$   $[M]^+$  calcd. for  $C_{11}H_{14}N_2S^+$ : 206.0878; found: 206.0876.

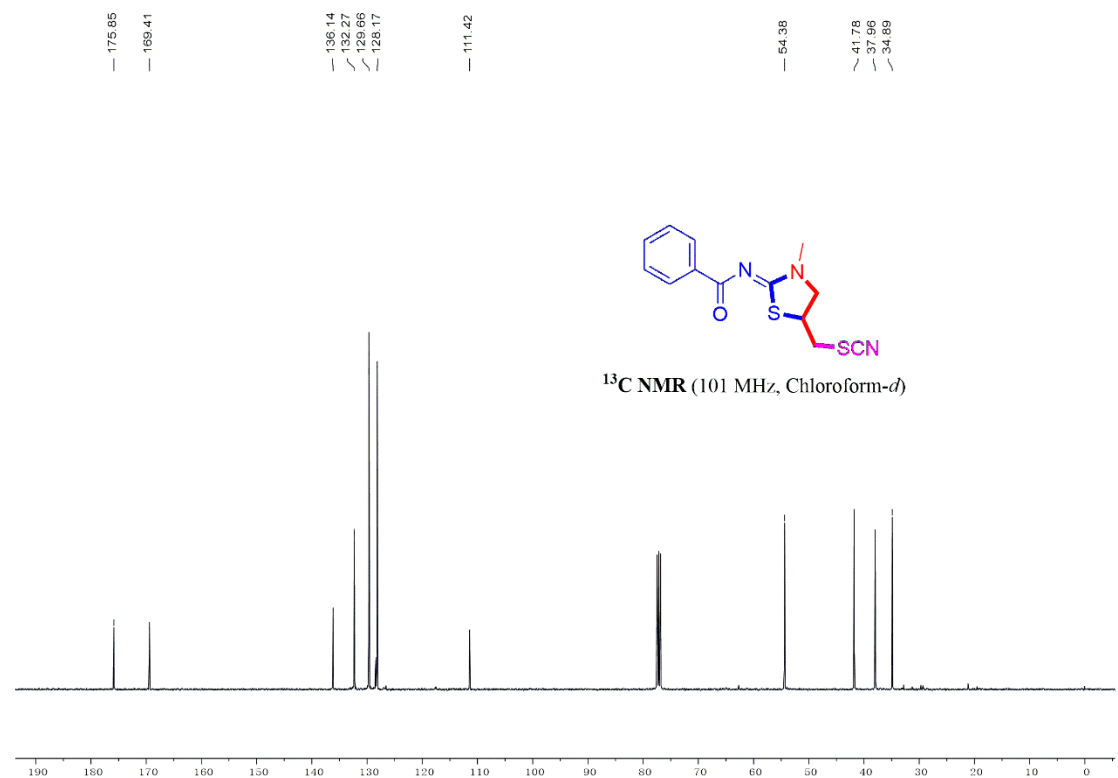
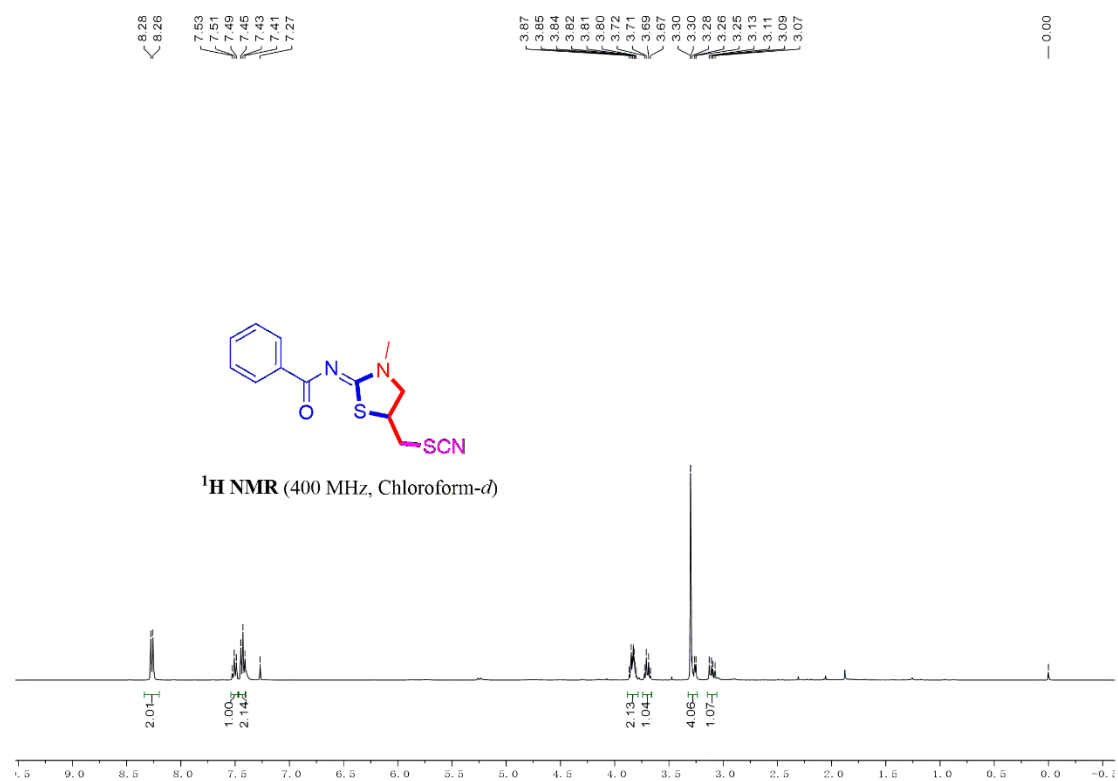
**(Z)-N-(3-benzyl-6-phenyl-5-thiocyanato-1,3-thiazinan-2-ylidene)benzamide (43)**



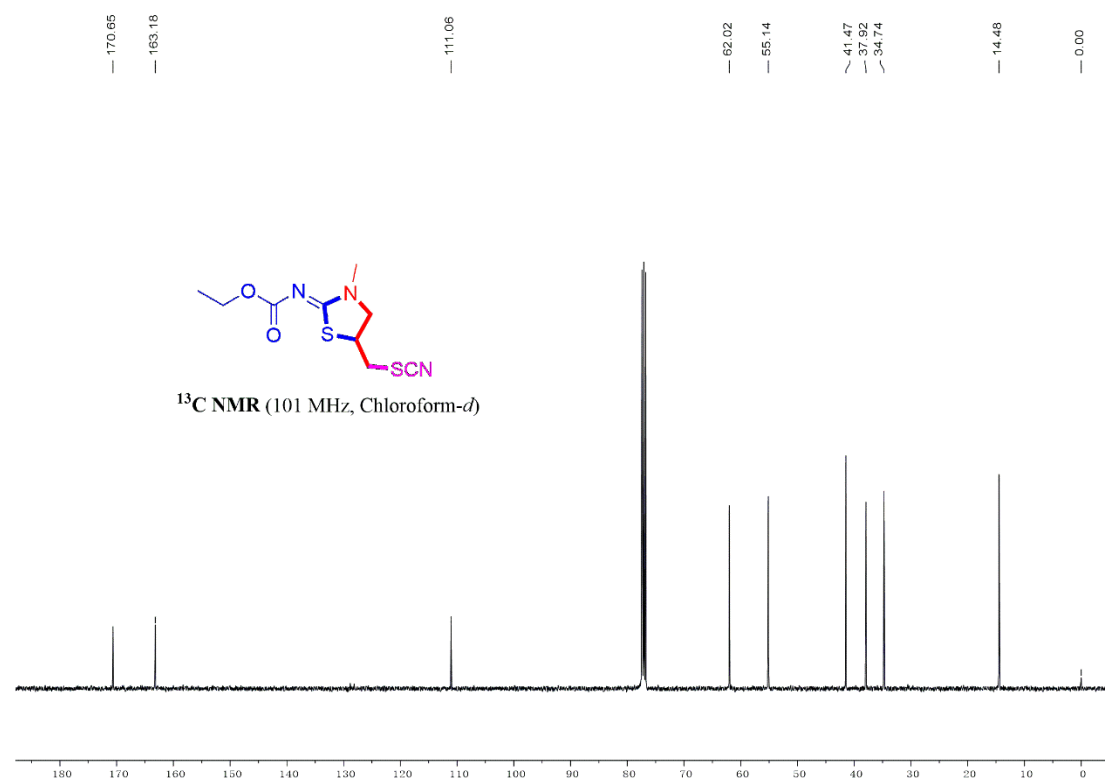
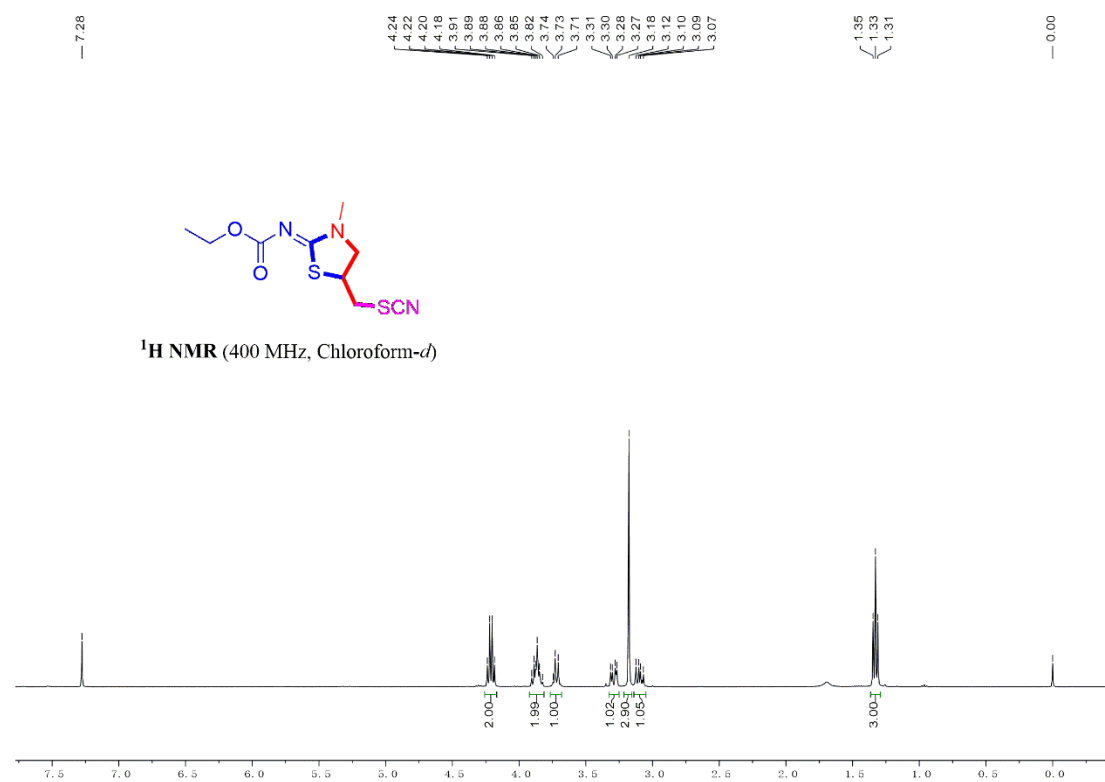
**Eluent:** petroleum ether/ethyl acetate (v/v = 4:1). Colorless and transparent liquid: 76% yield (67.3 mg). **<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  8.29–8.22 (m, 2H), 7.53–7.47 (m, 1H), 7.45–7.33 (m, 10H), 7.30 (dd,  $J$  = 6.7, 3.0 Hz, 2H), 5.00 (q,  $J$  = 14.5 Hz, 2H), 4.41–4.22 (m, 2H), 3.92 (dd,  $J$  = 11.6, 7.3 Hz, 1H), 3.74 (dd,  $J$  = 11.6, 5.8 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, Chloroform-*d*)  $\delta$  175.8, 136.0, 136.0, 135.1, 132.2, 129.8, 129.7, 129.5, 129.1, 128.4, 128.3, 128.1, 127.5, 56.1, 52.6, 51.4, 46.5. **HRMS** (EI-TOF):  $m/z$   $[M]^+$  calcd. for  $C_{25}H_{21}N_3OS_2^+$ : 443.1126; found: 443.1128.

## 6. Copies of NMR Spectra

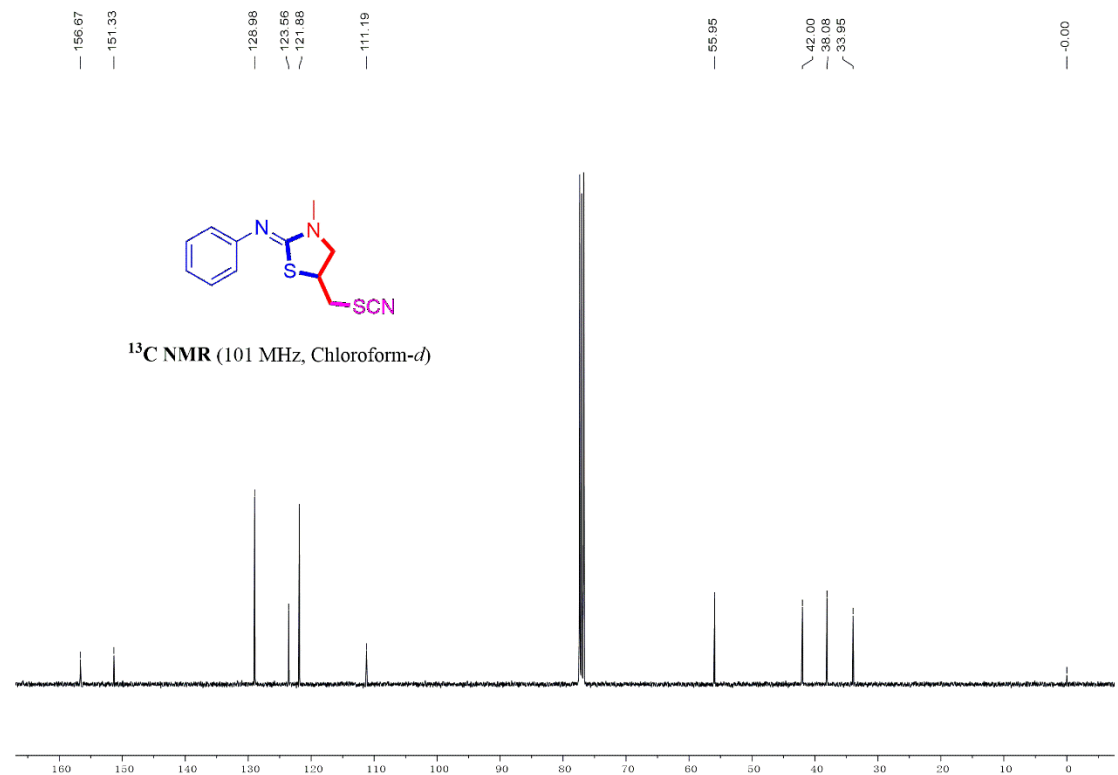
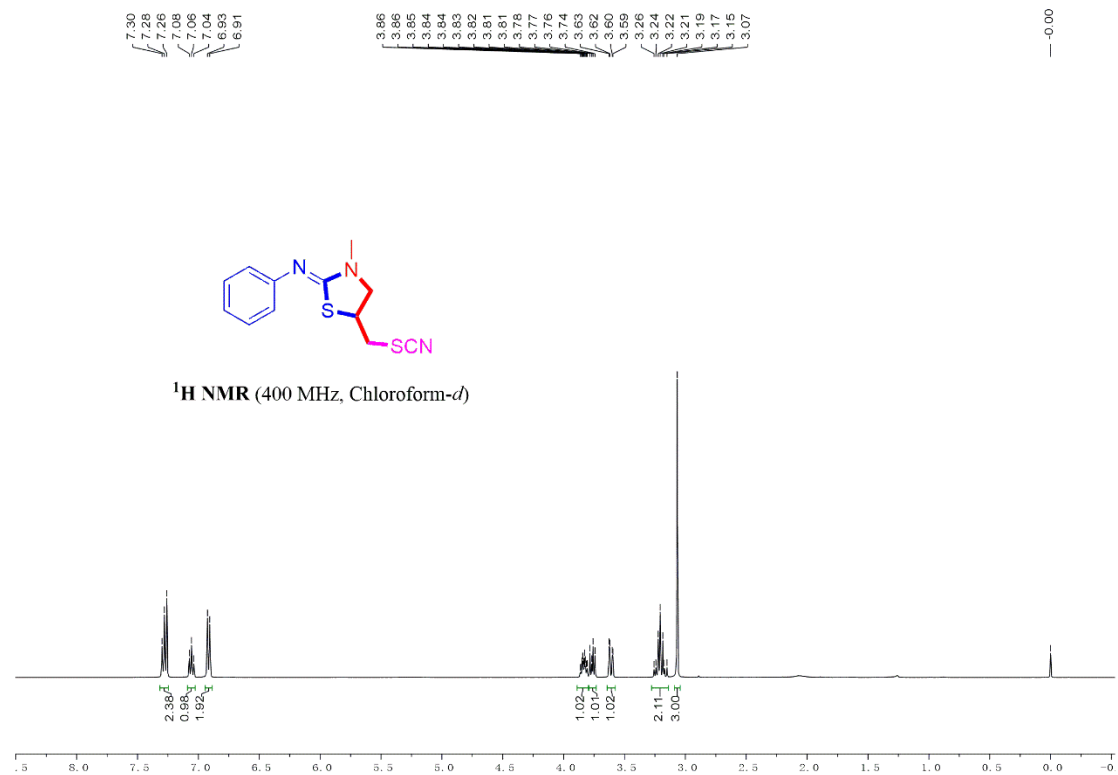
### (Z)-N-(3-methyl-5-(thiocyanatomethyl)thiazolidin-2-ylidene)benzamide (4)



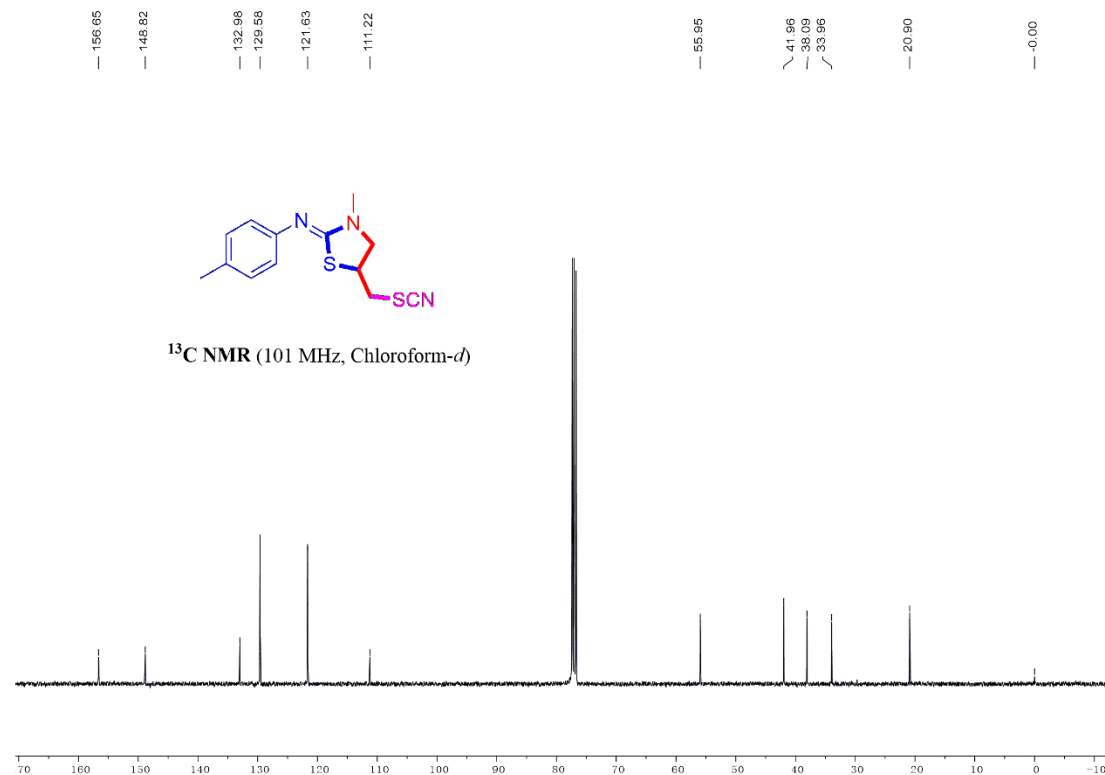
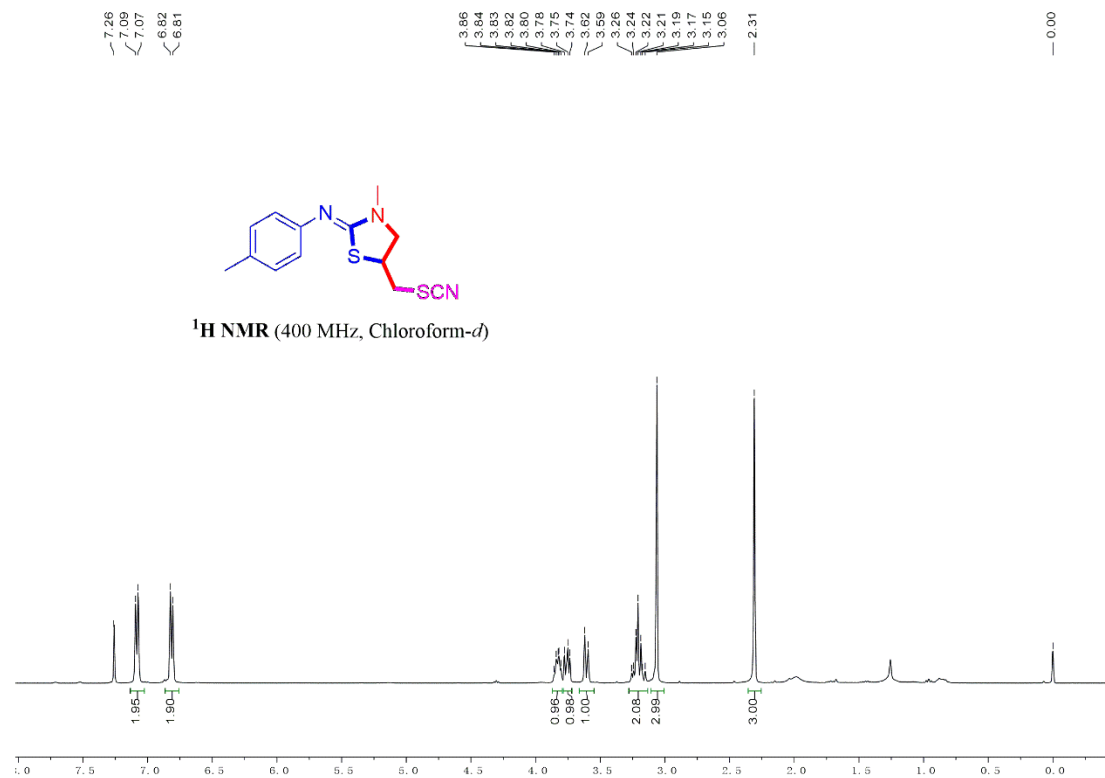
**(Z)-N-(3-methyl-5-(thiocyanatomethyl)thiazolidin-2-ylidene)propionamide (5)**



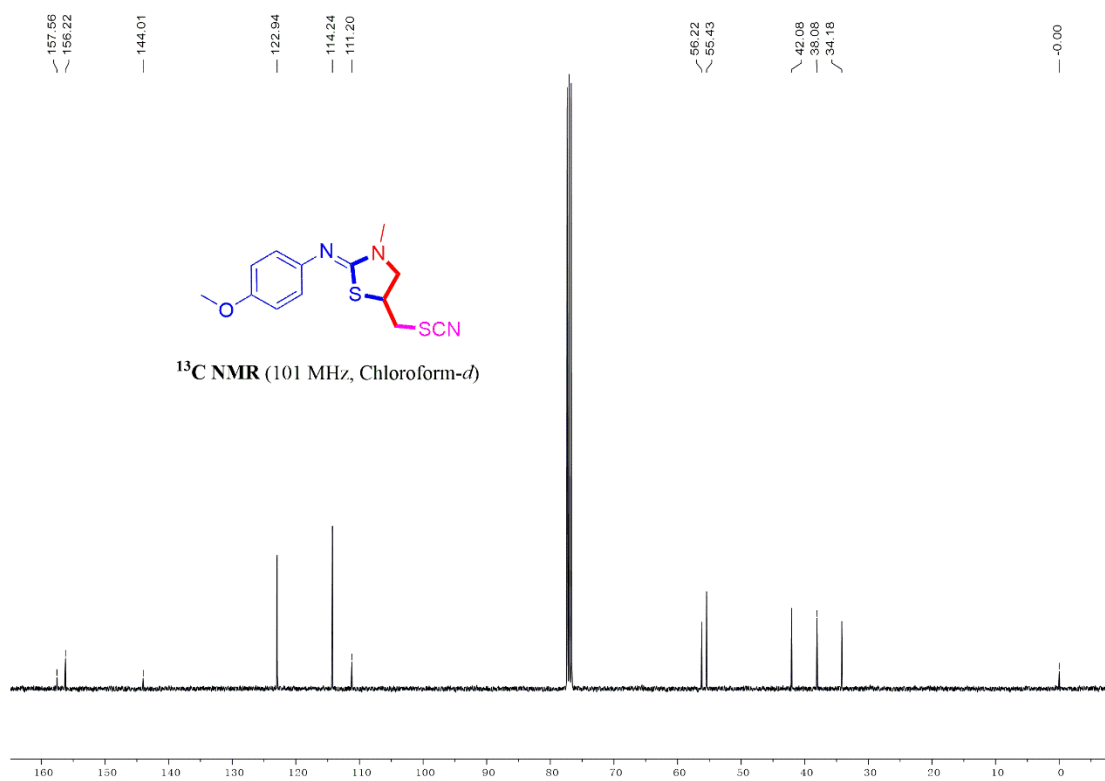
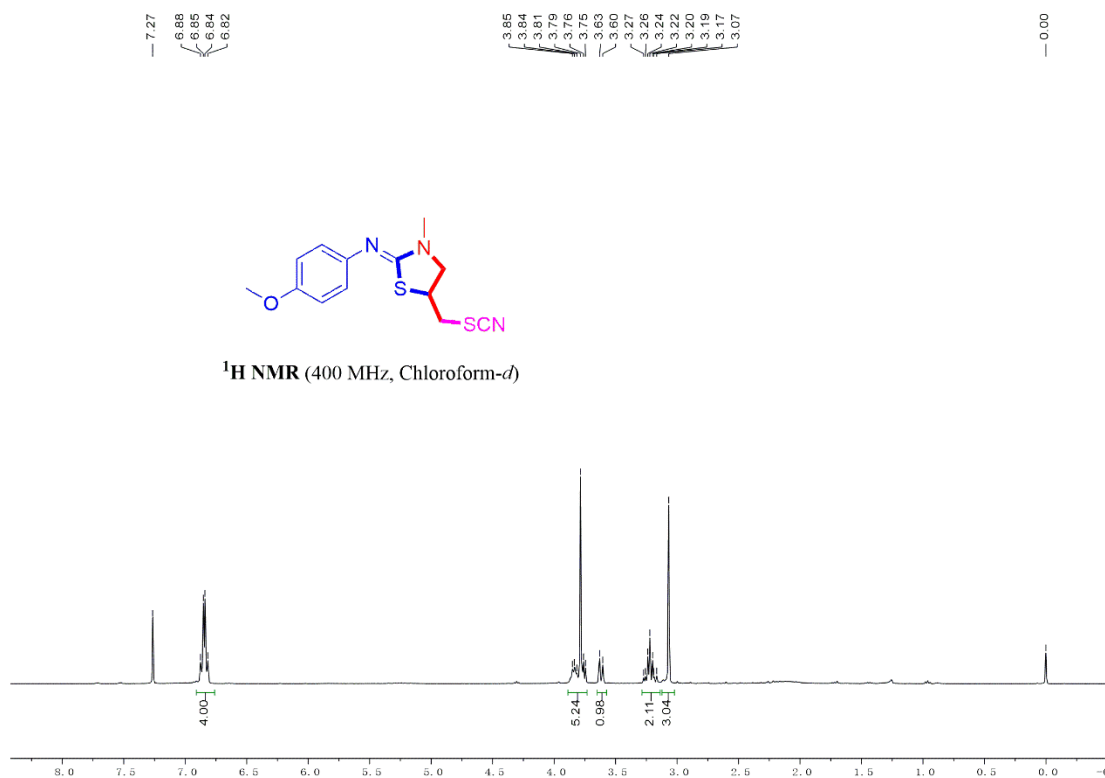
**(Z)-3-methyl-N-phenyl-5-(thiocyanatomethyl)thiazolidin-2-imine (6)**



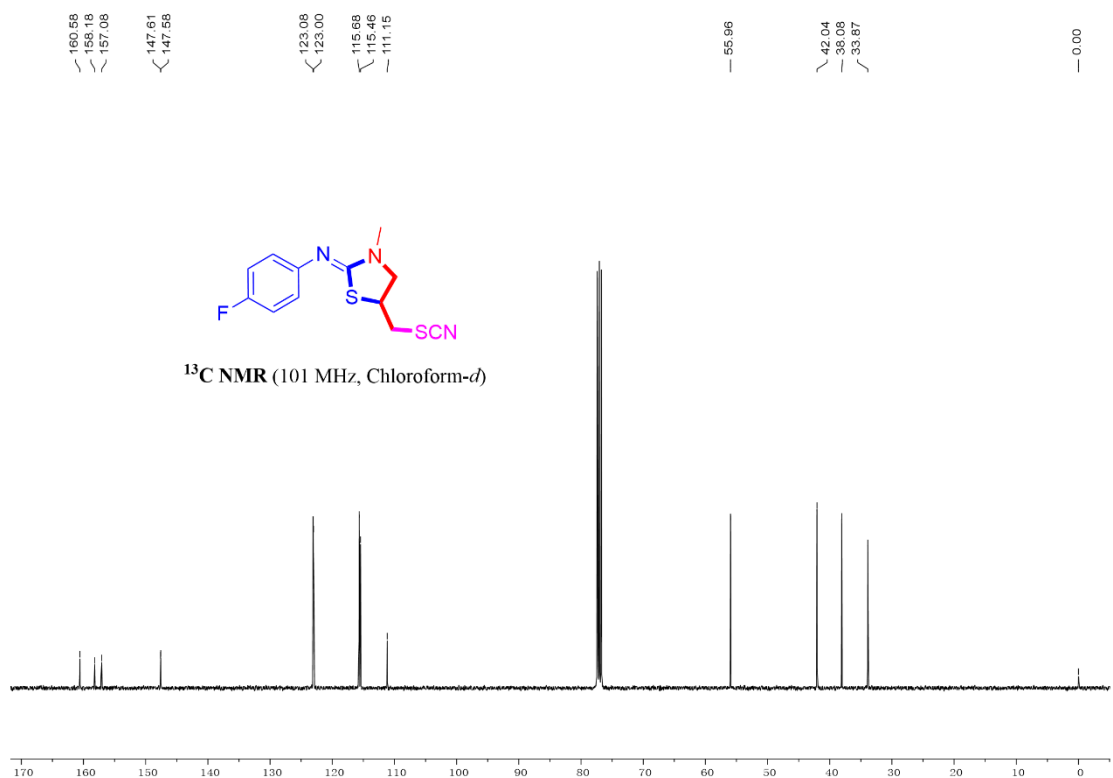
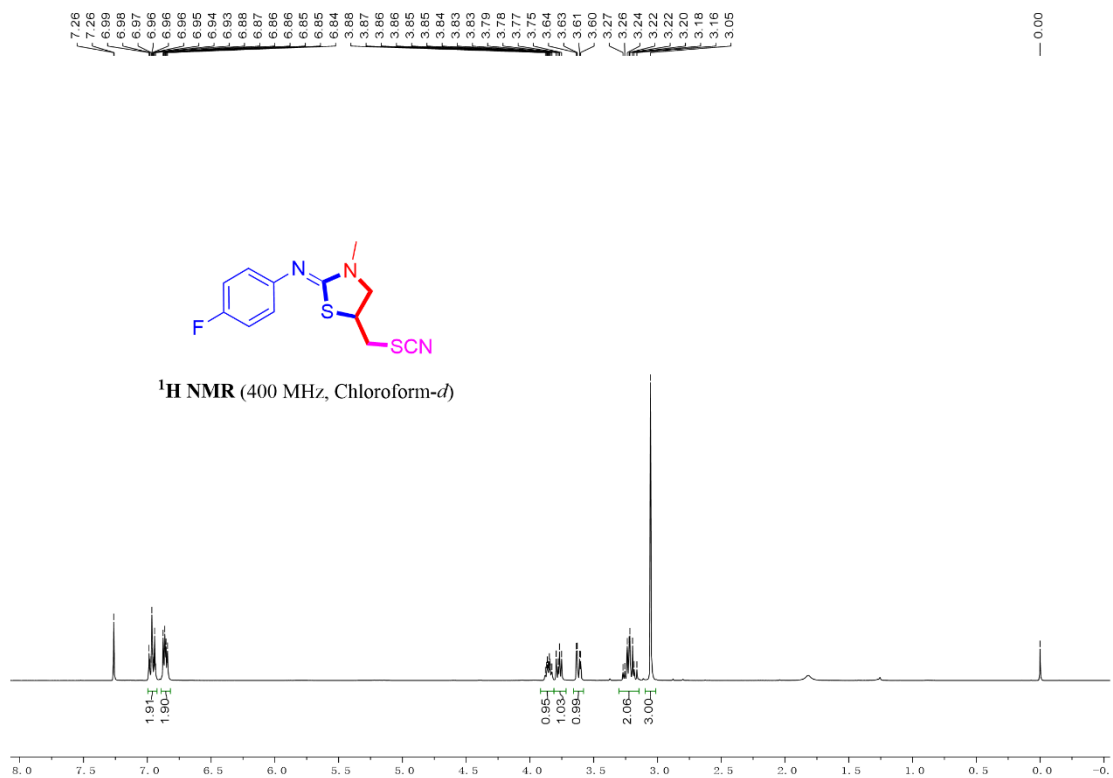
**(Z)-3-methyl-5-(thiocyanatomethyl)-N-(p-tolyl)thiazolidin-2-imine (7)**

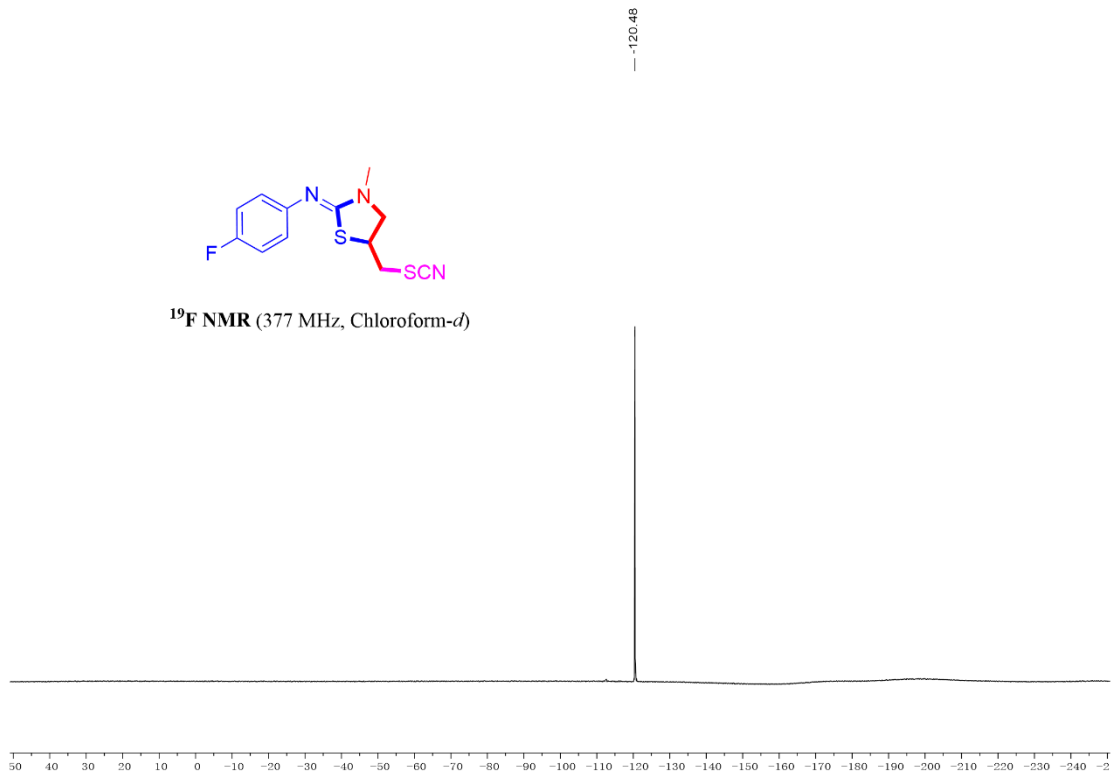


**(Z)-N-(4-methoxyphenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (8)**

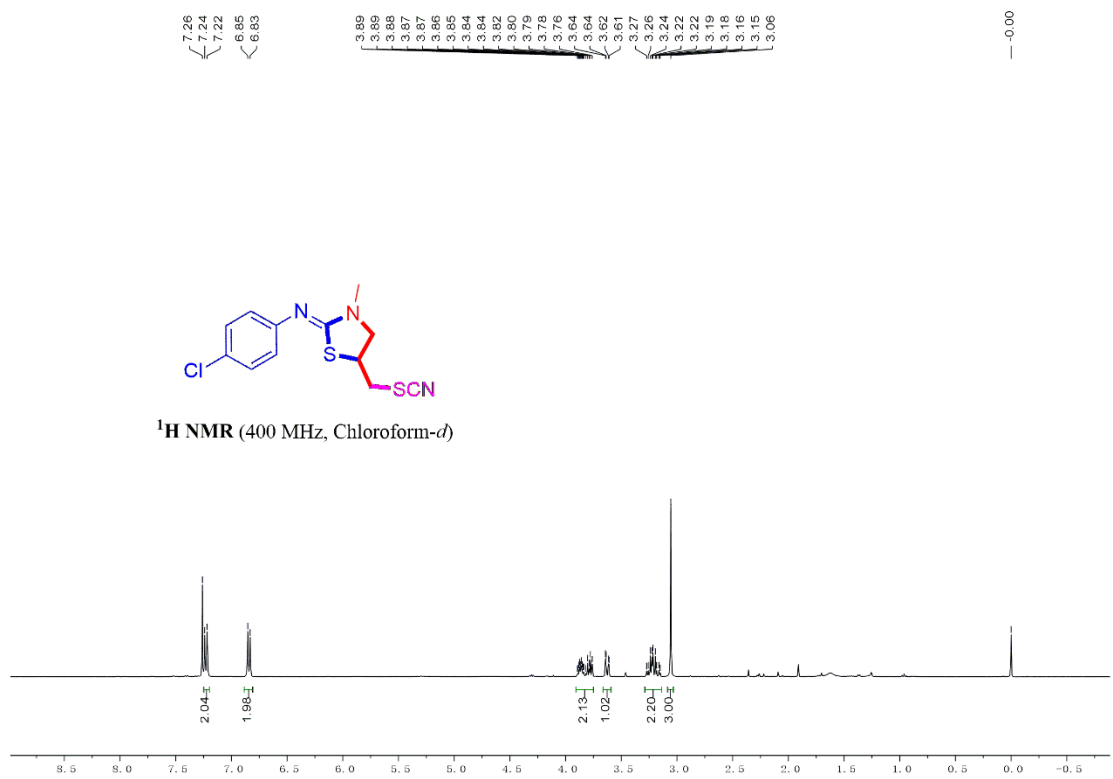


**(Z)-N-(4-fluorophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidine-2-imine (9)**

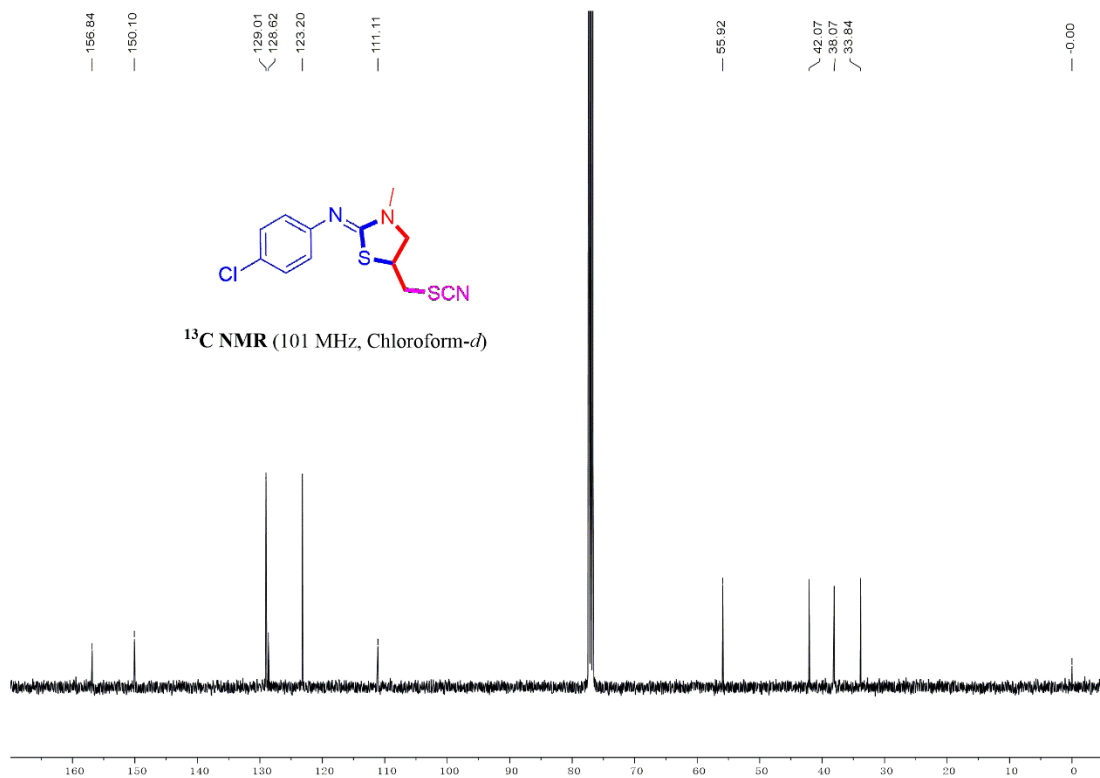




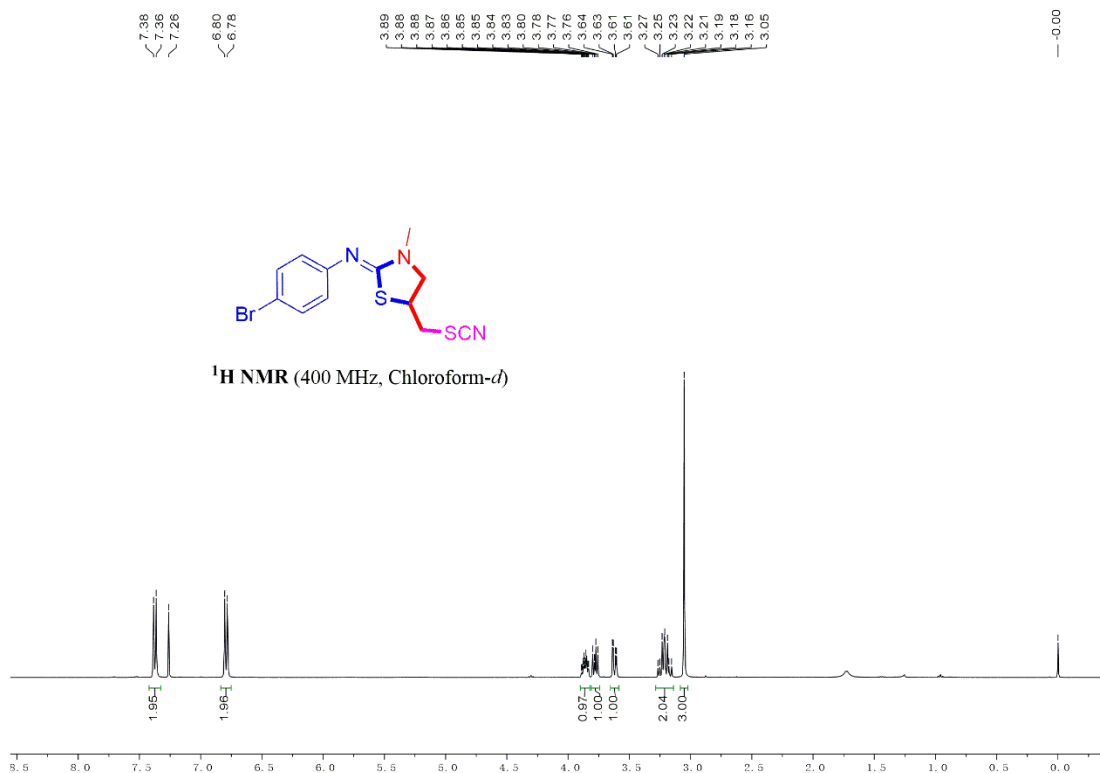
**(Z)-N-(4-chlorophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (10)**

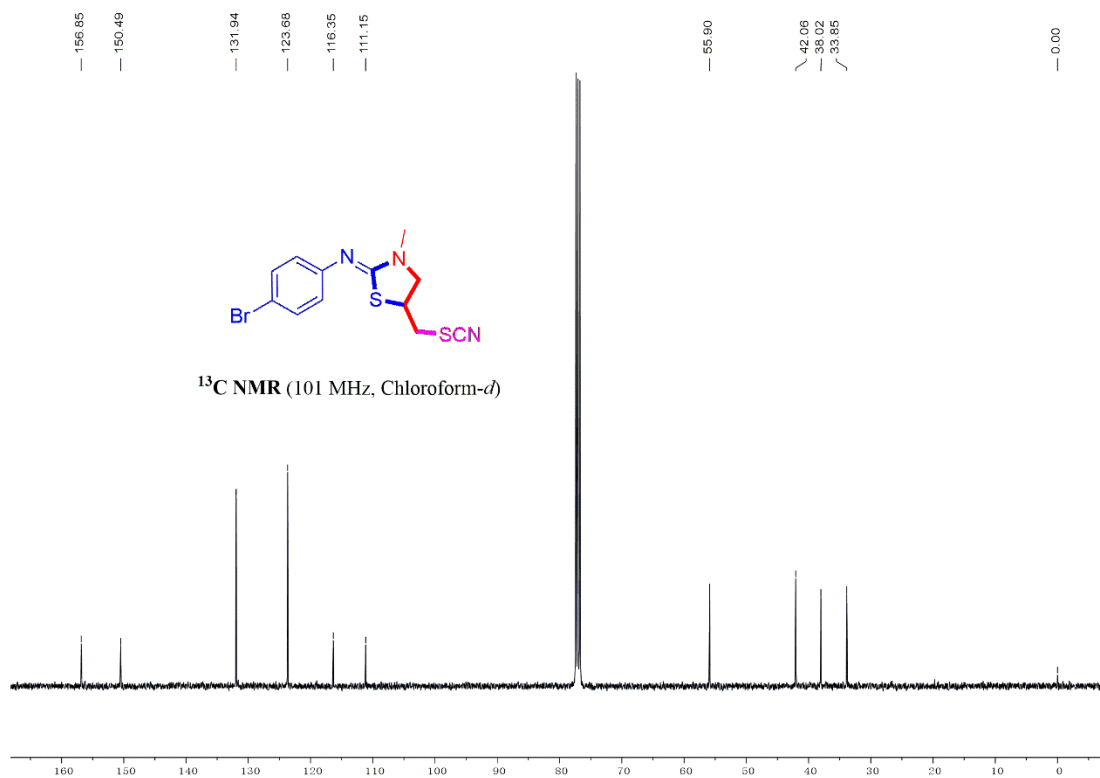




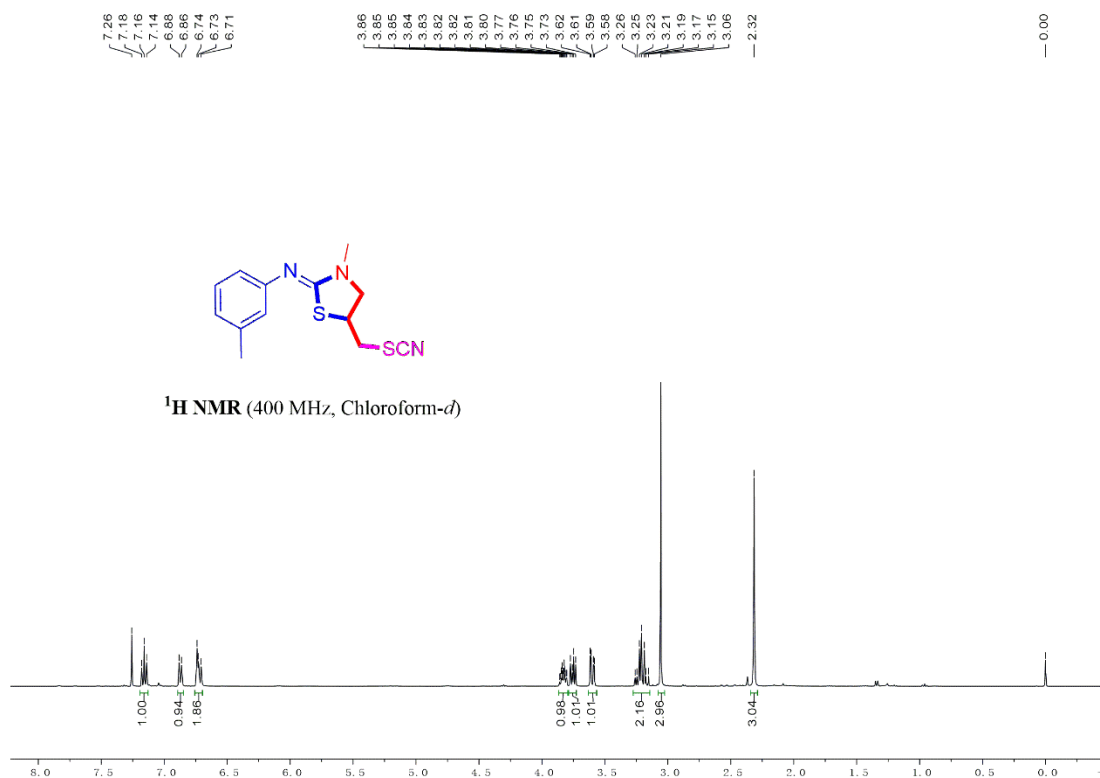


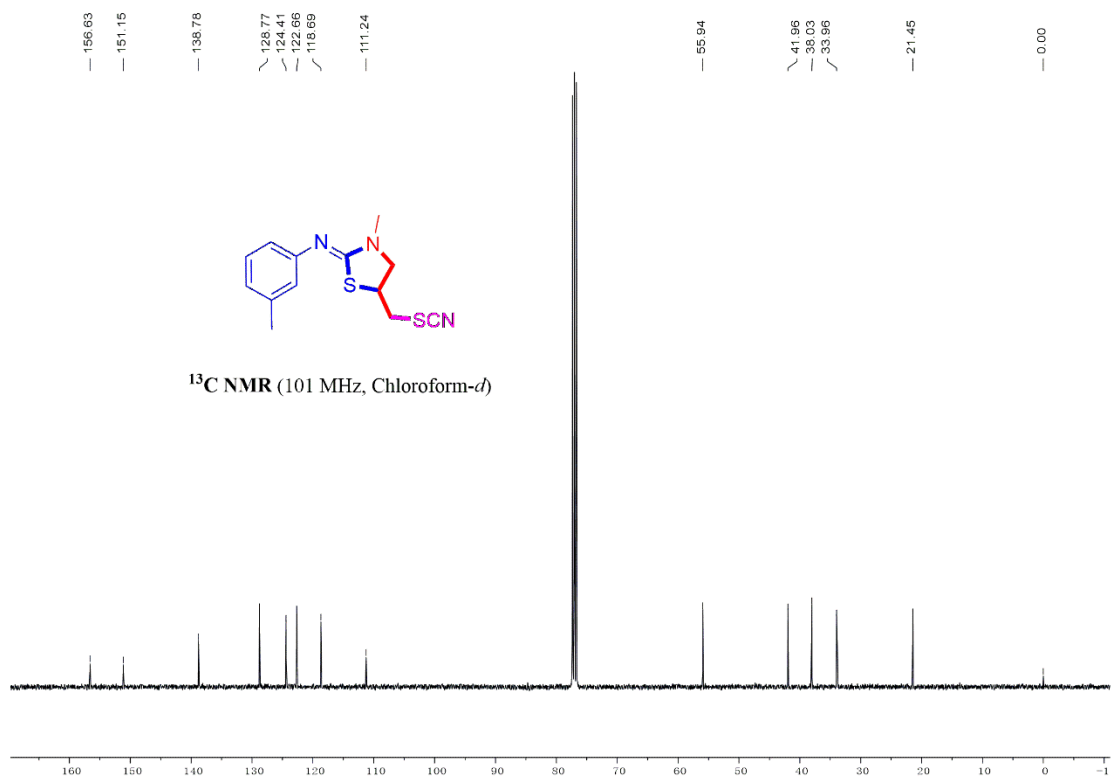
**(Z)-N-(4-bromophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (11)**



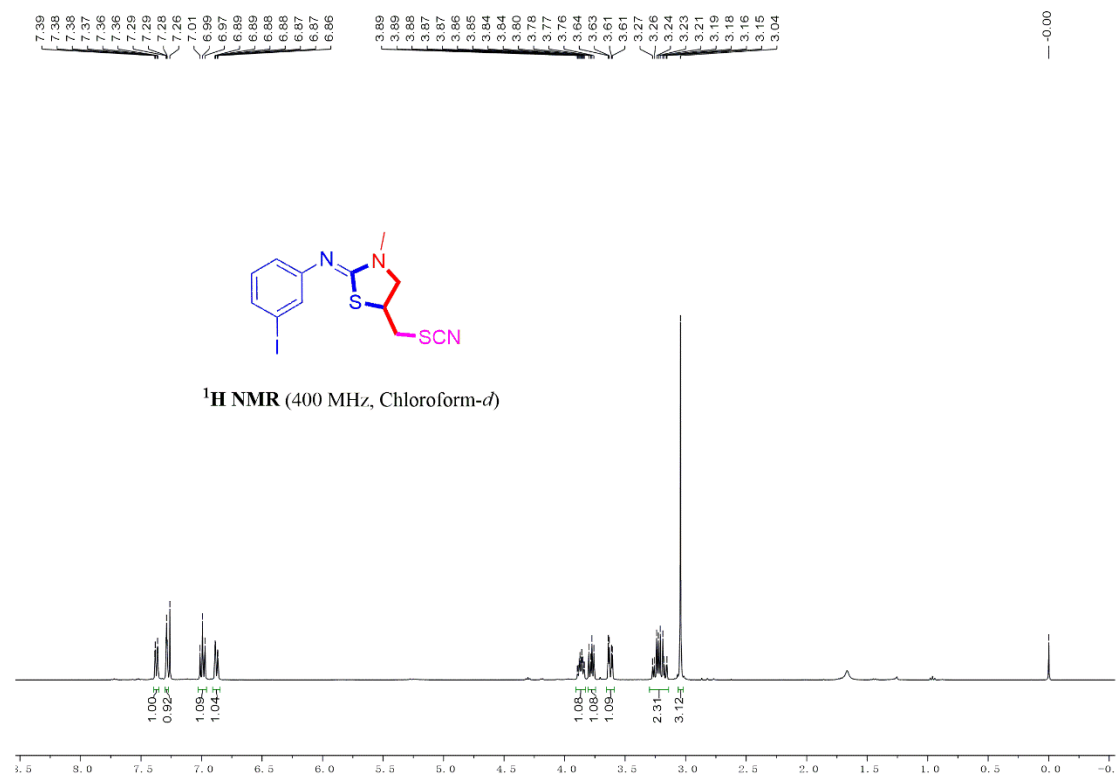


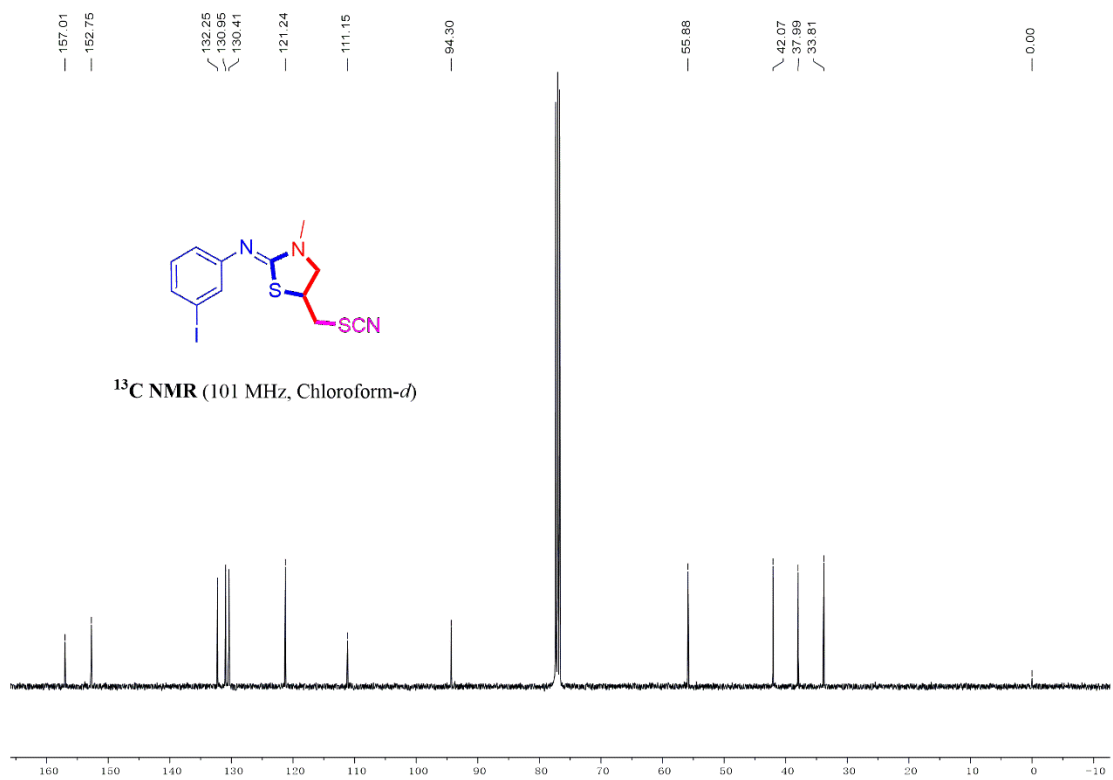
**(Z)-3-methyl-5-(thiocyanatomethyl)-N-(m-tolyl)thiazolidin-2-imine (13)**



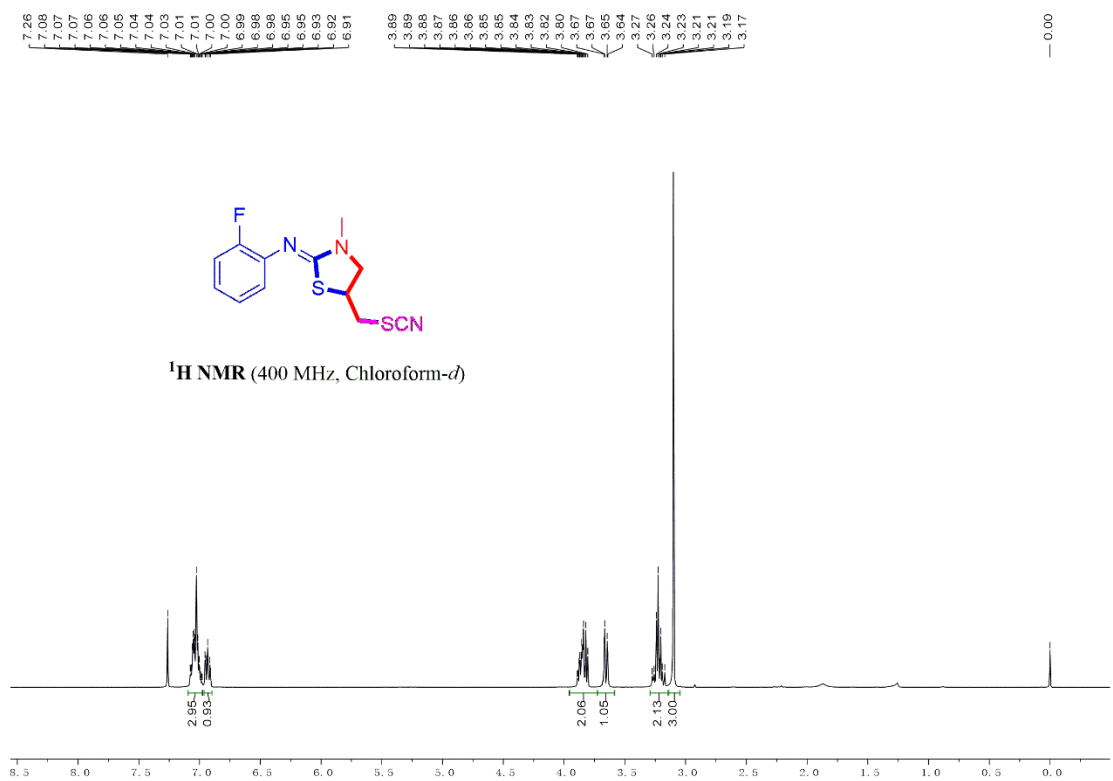


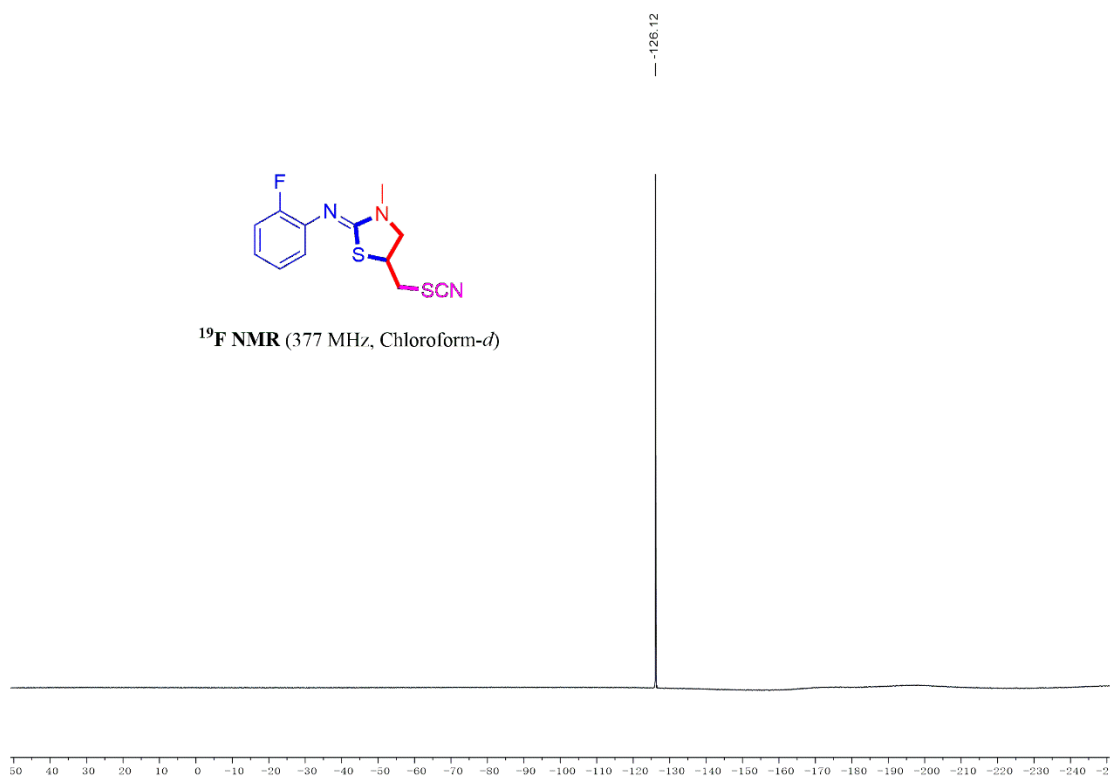
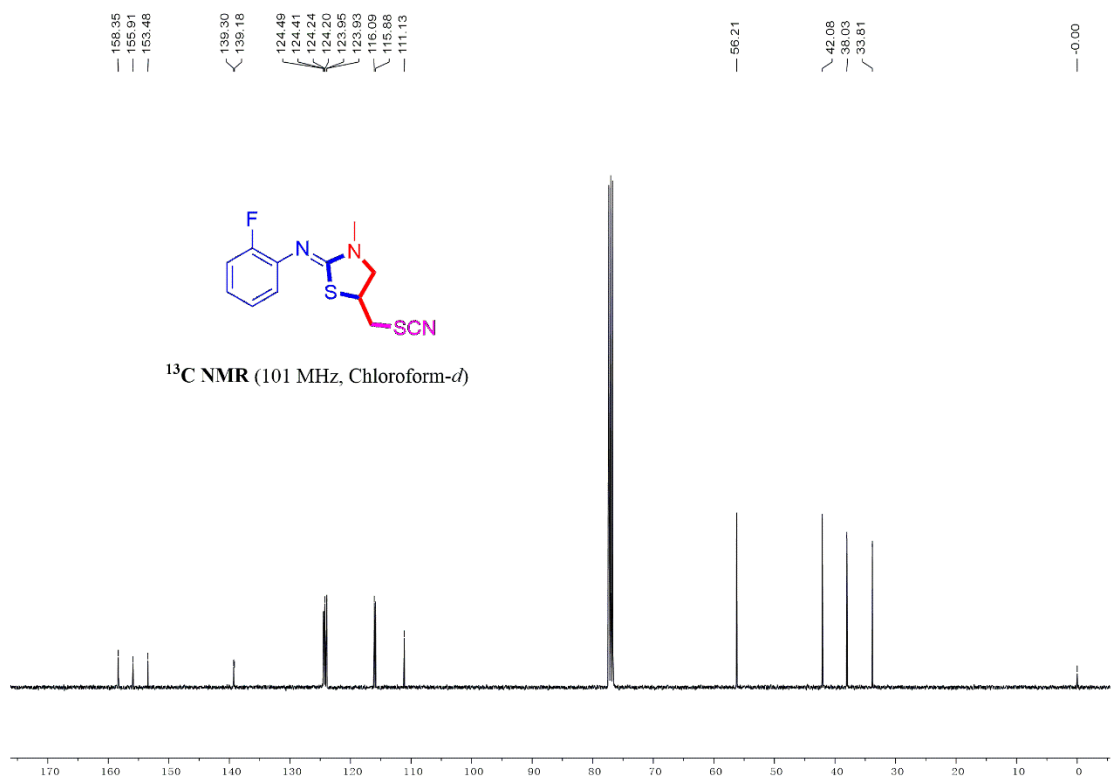
**(Z)-N-(3-iodophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (14)**



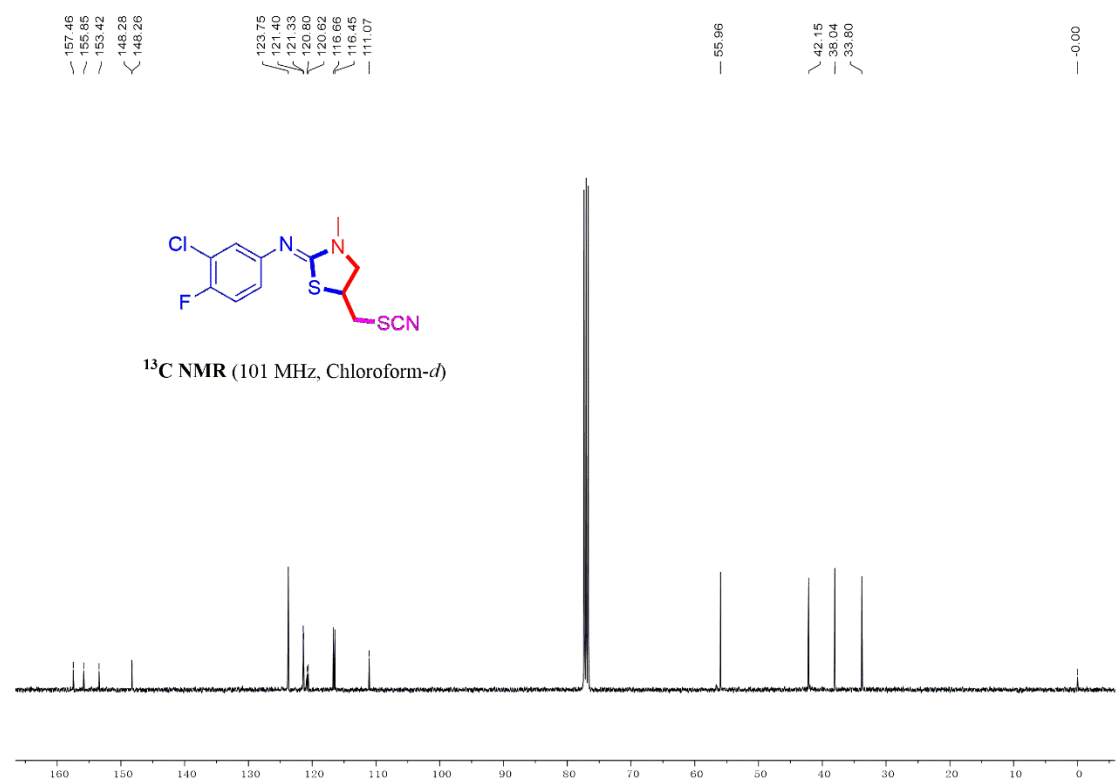
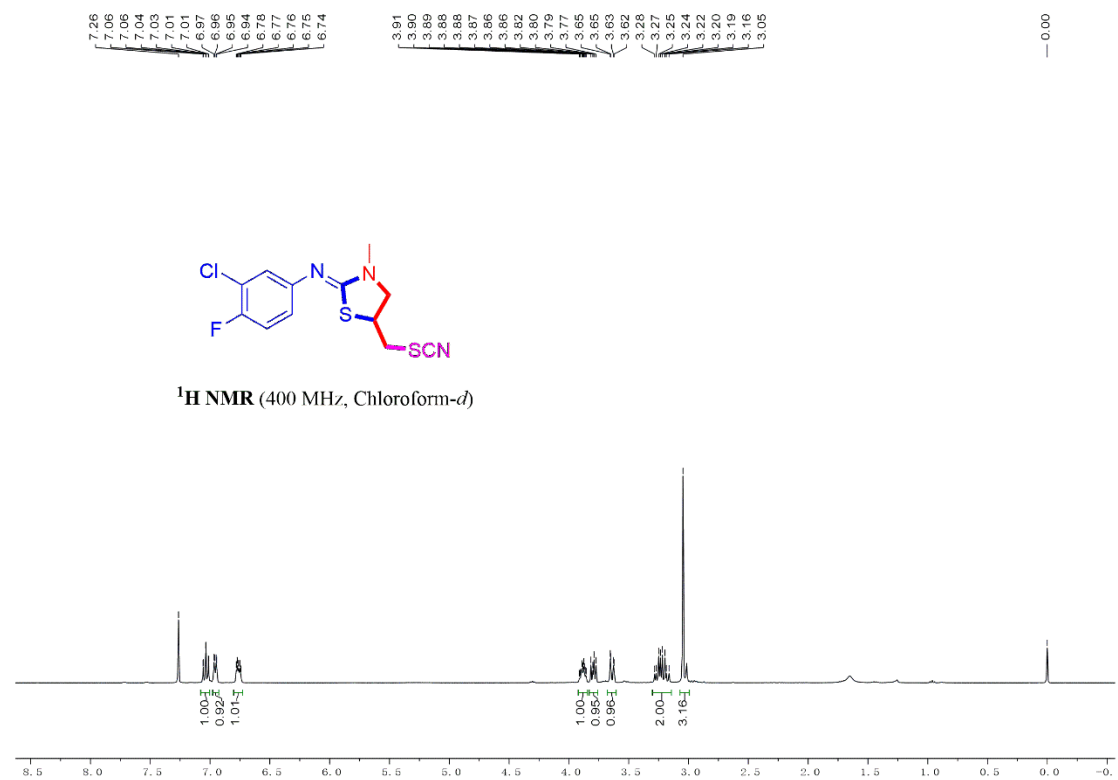


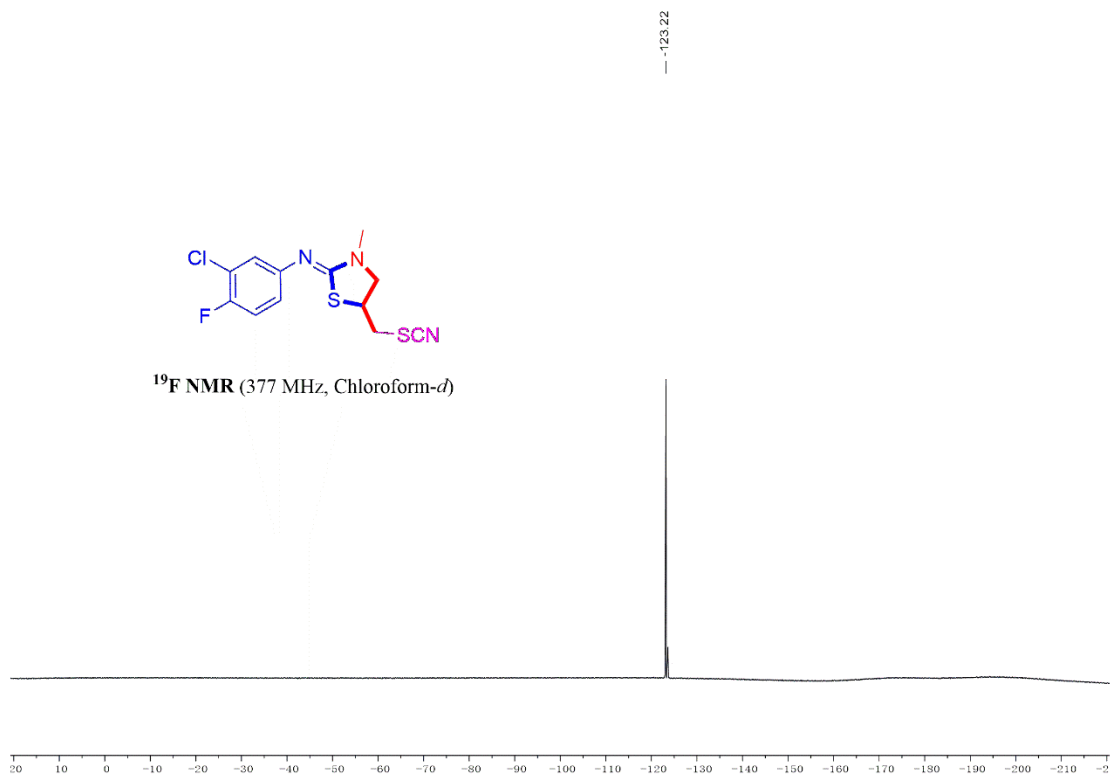
**(Z)-N-(2-fluorophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (15)**



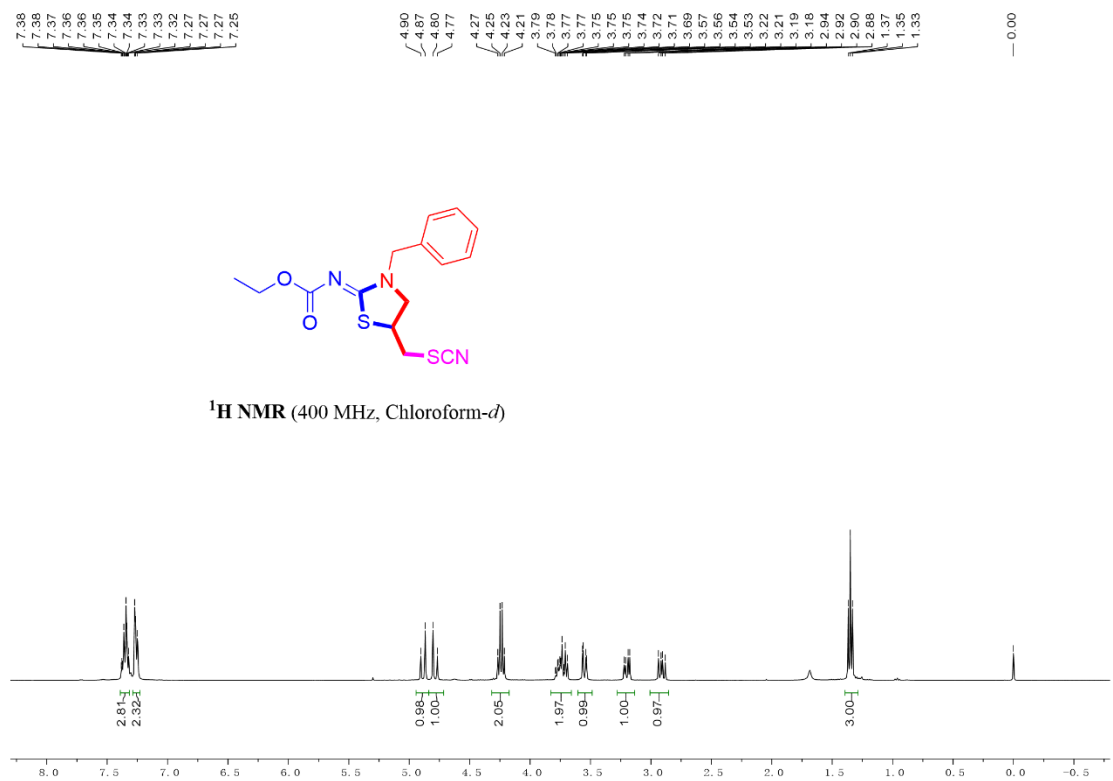


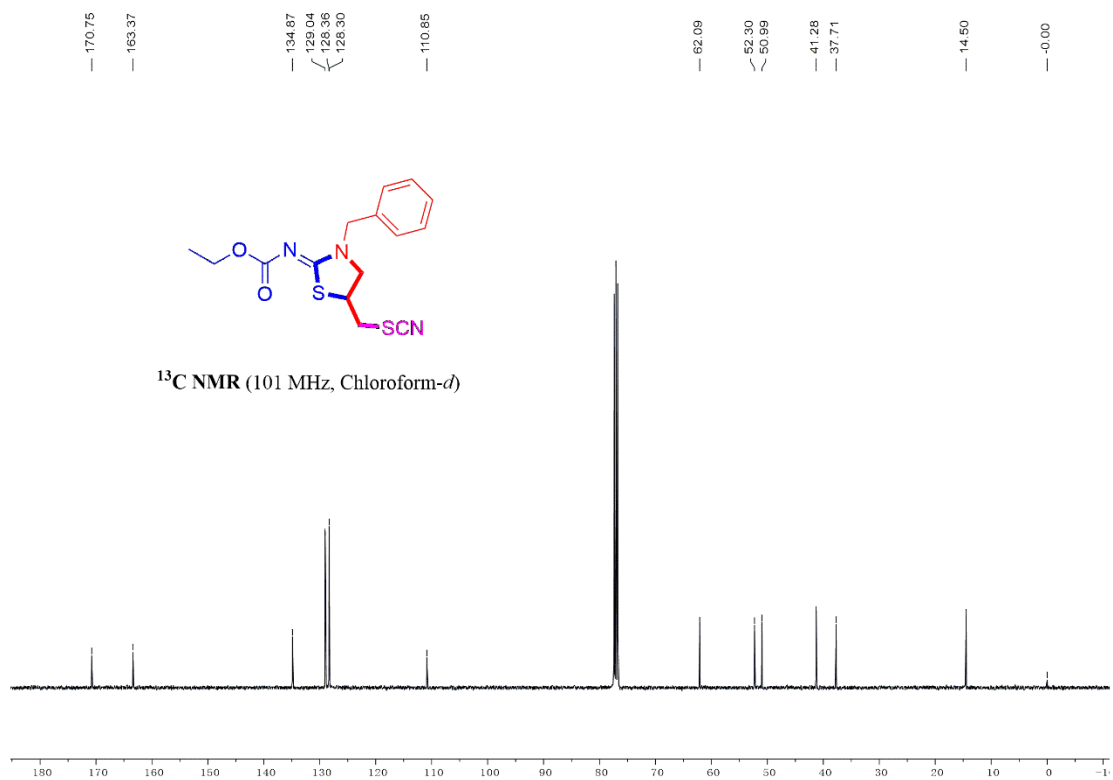
**(Z)-N-(3-chloro-4-fluorophenyl)-3-methyl-5-(thiocyanatomethyl)thiazolidin-2-imine (17)**



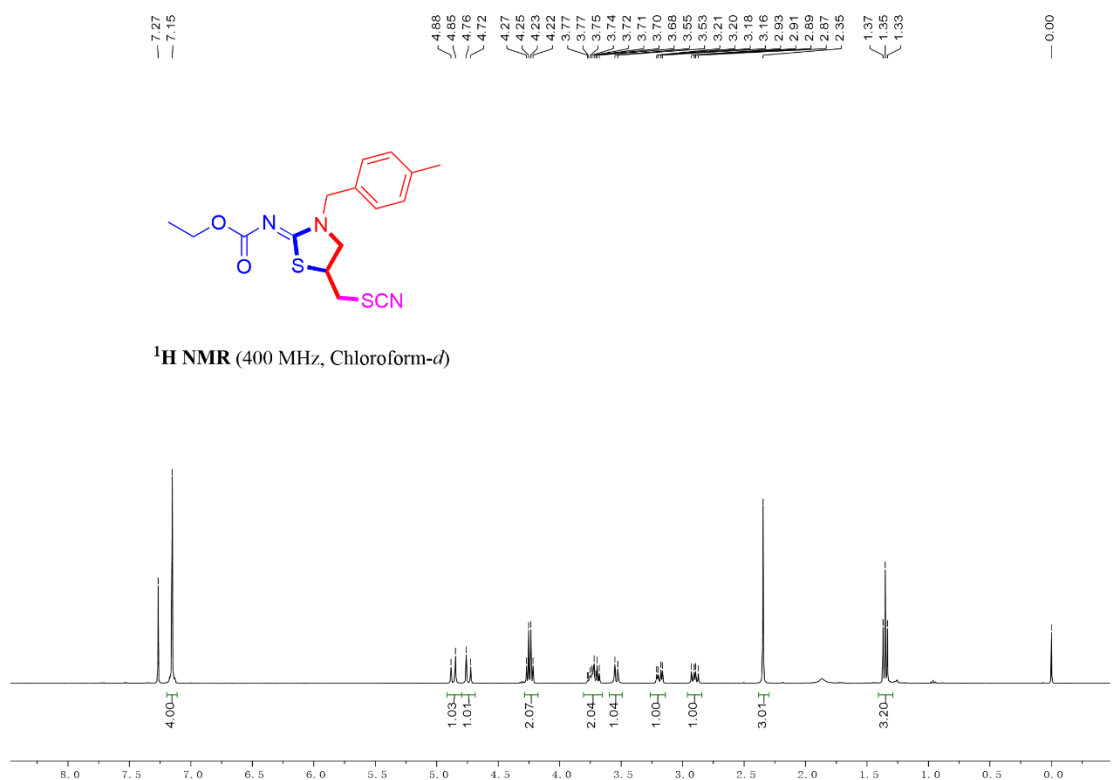


**ethyl (Z)-3-benzyl-5-(thiocyanatomethyl)thiazolidin-2-ylidene carbamate (20)**

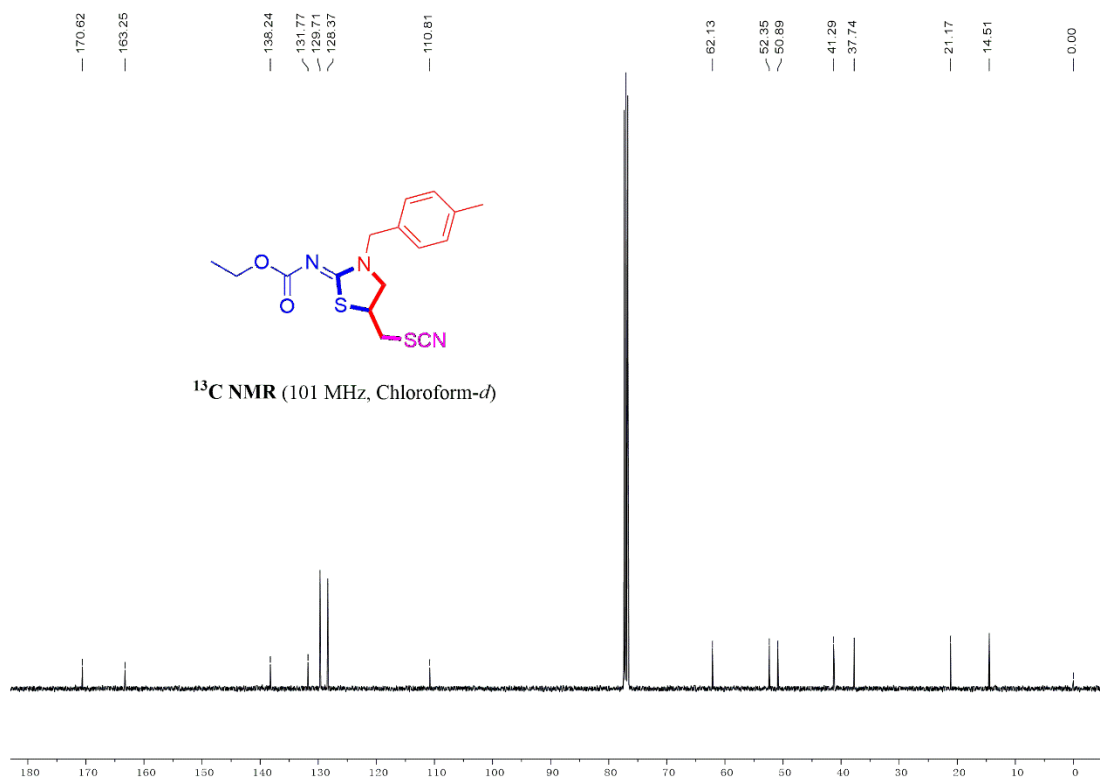




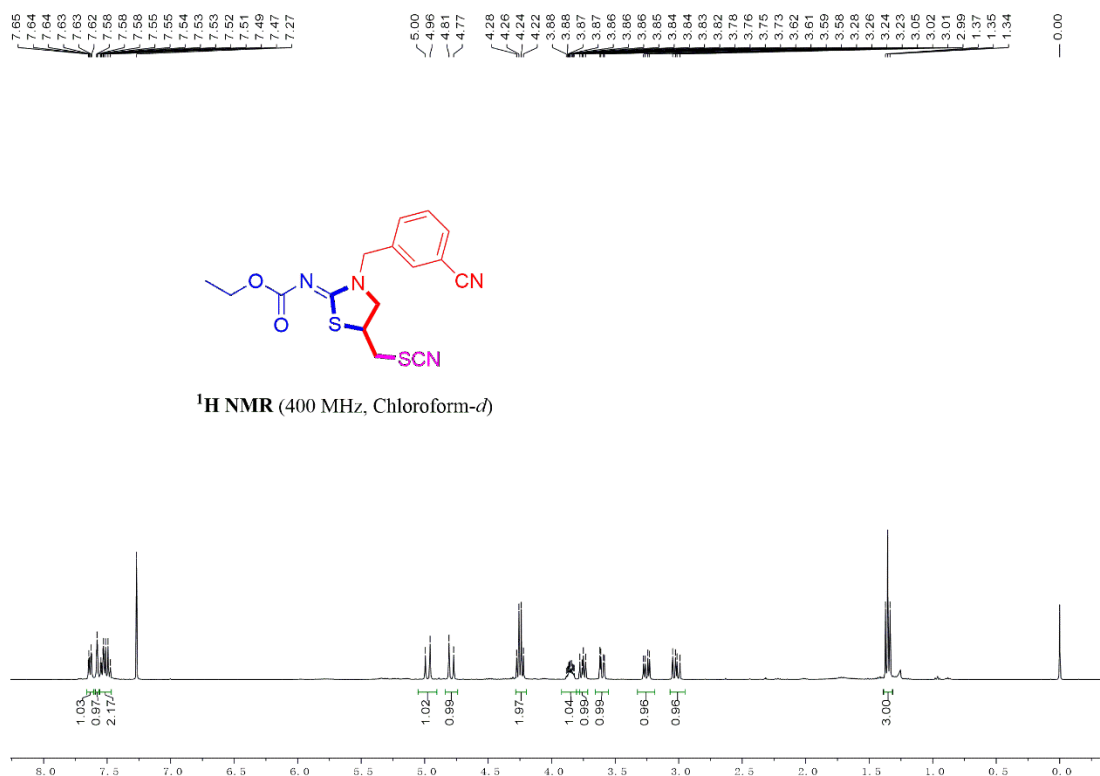
**ethyl (Z)-3-(4-methylbenzyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene carbamate (21)**

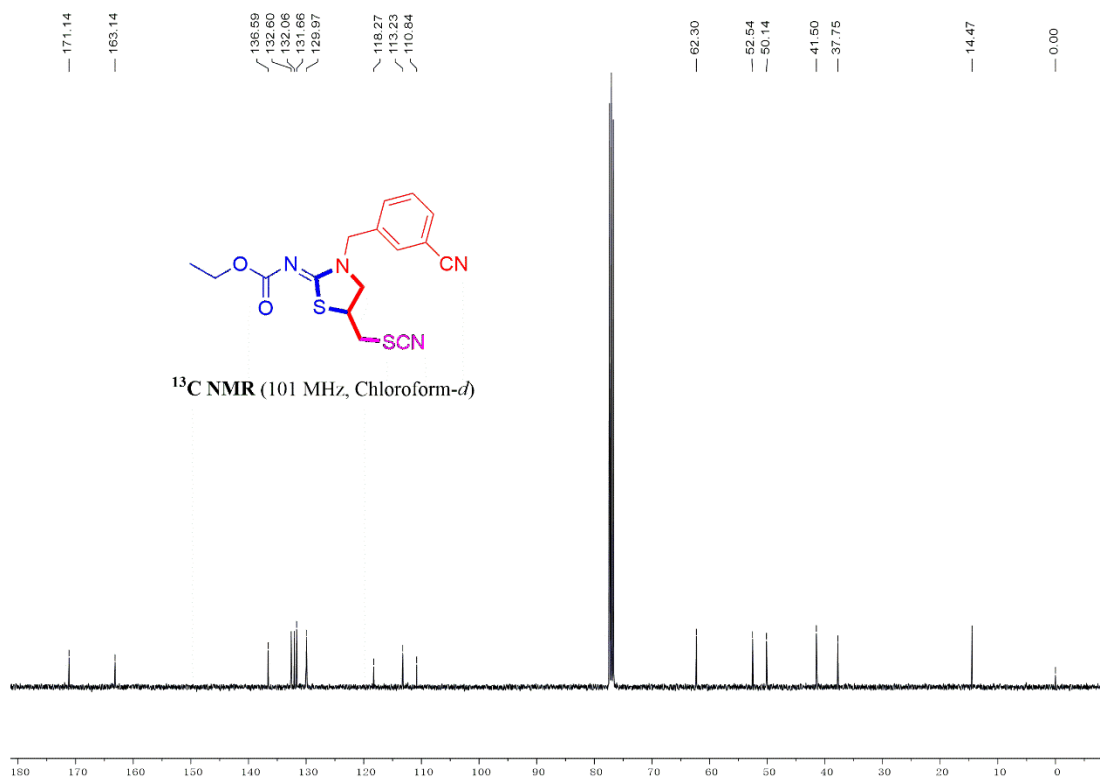




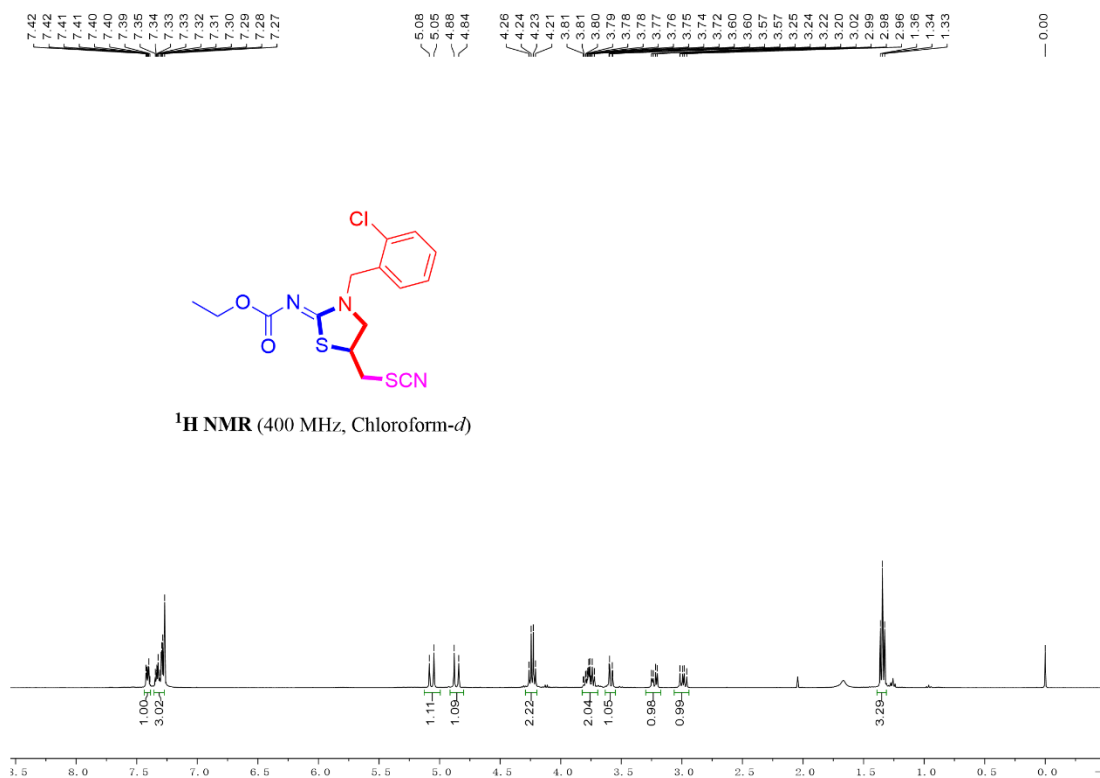


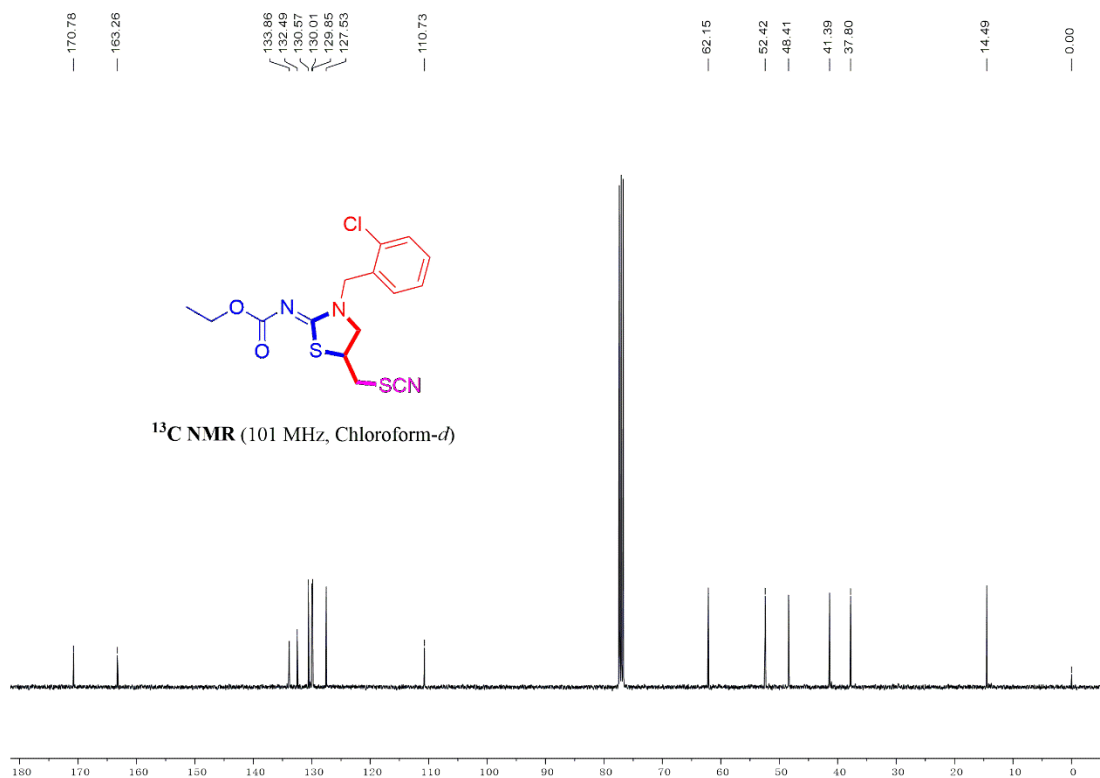
**ethyl (Z)-3-(3-cyanobenzyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene carbamate (22)**



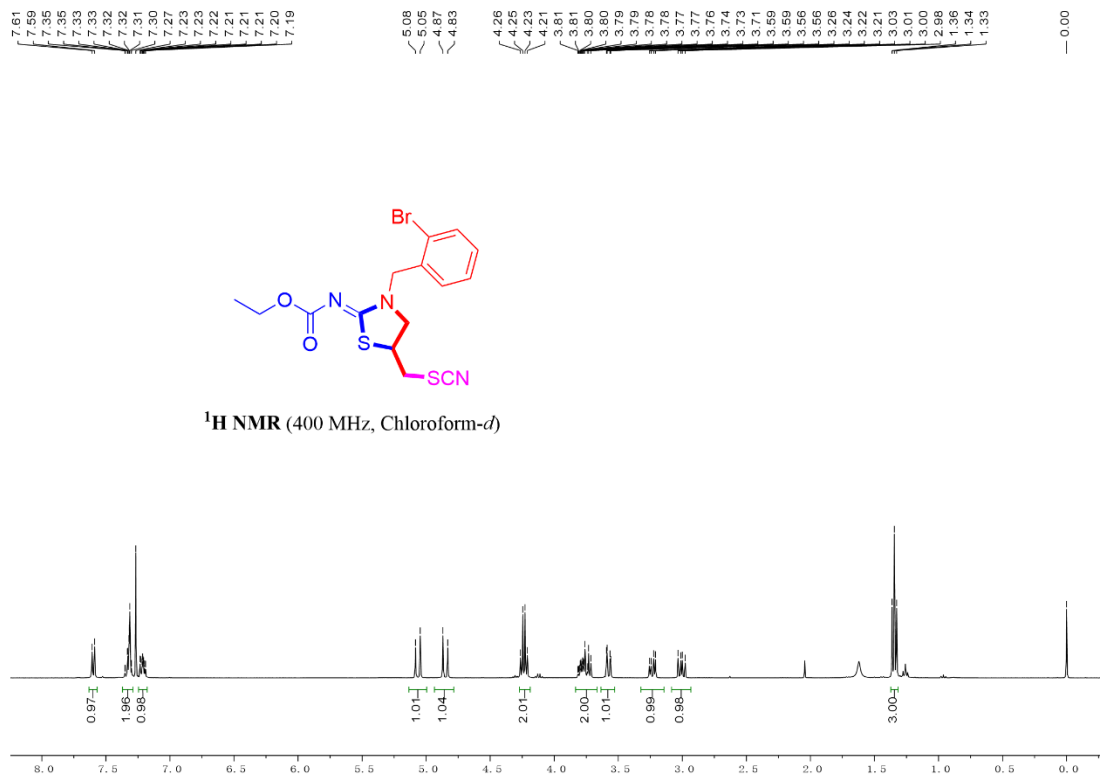


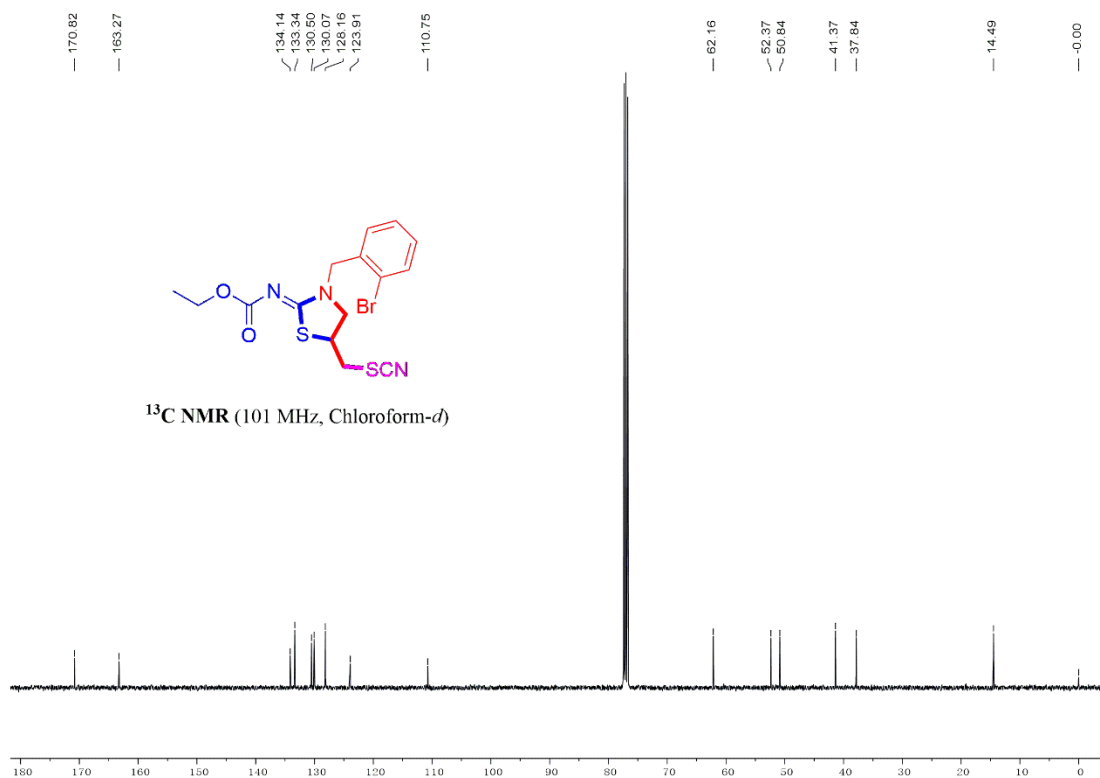
**ethyl (Z)-3-(2-chlorobenzyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene carbamate (23)**



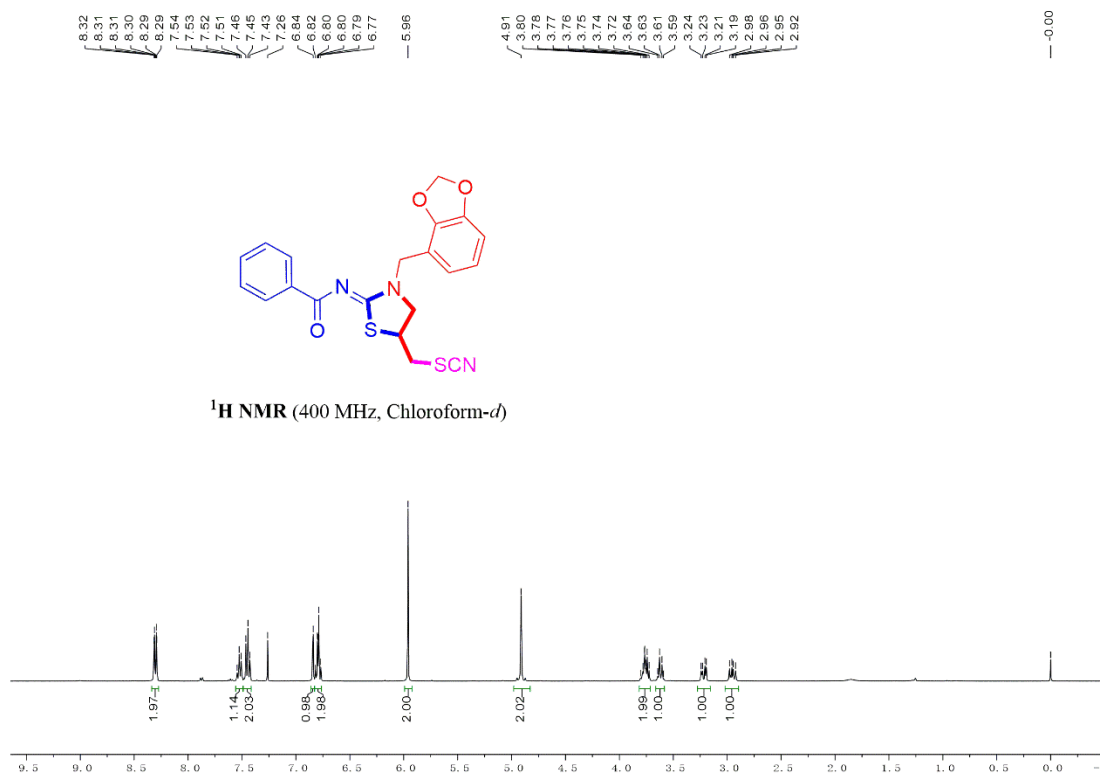


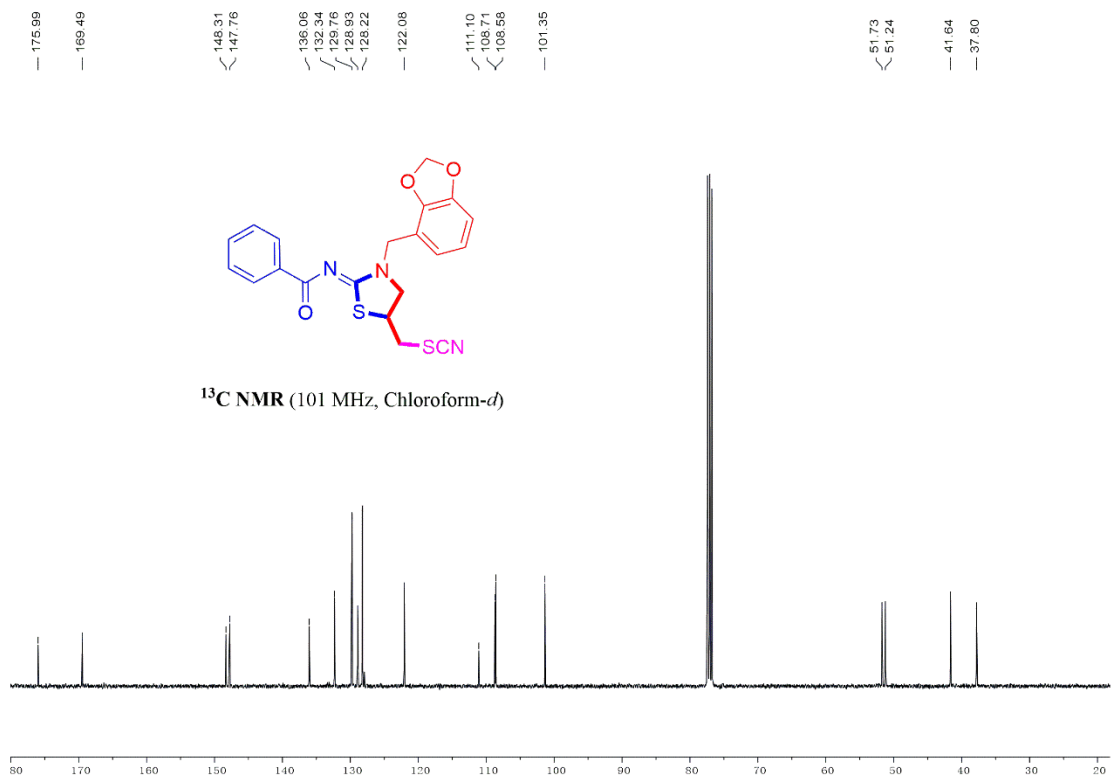
**ethyl (Z)-3-(2-bromobenzyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene carbamate (24)**



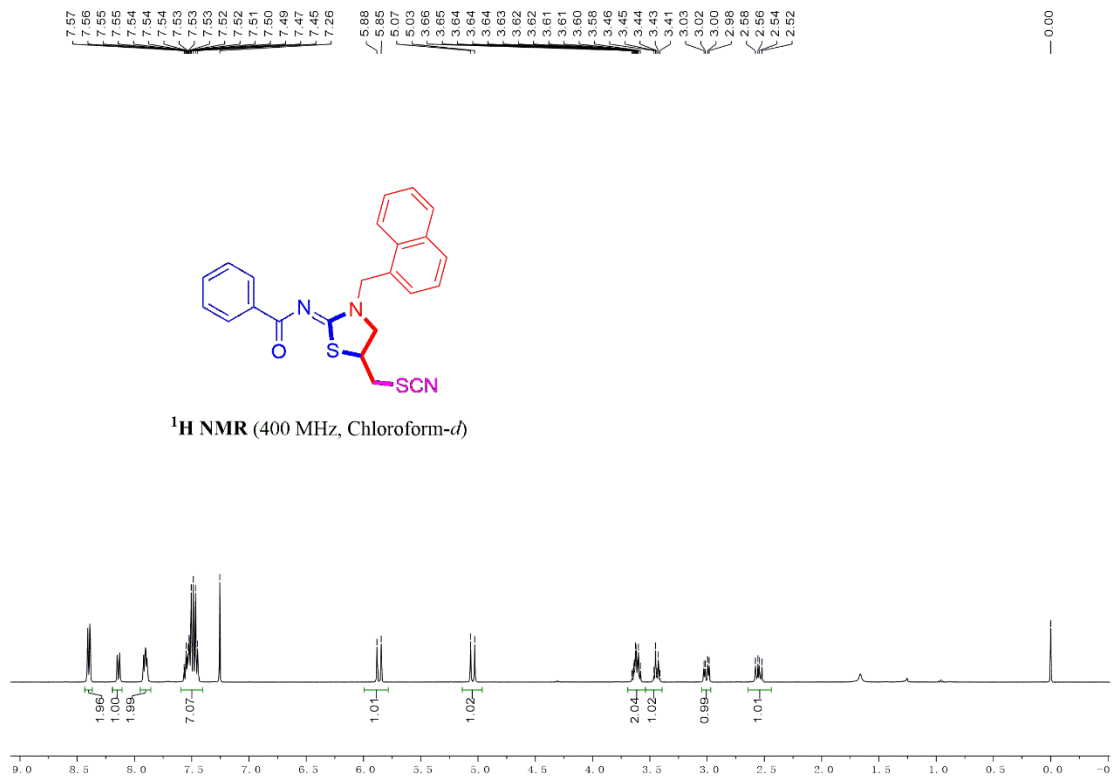


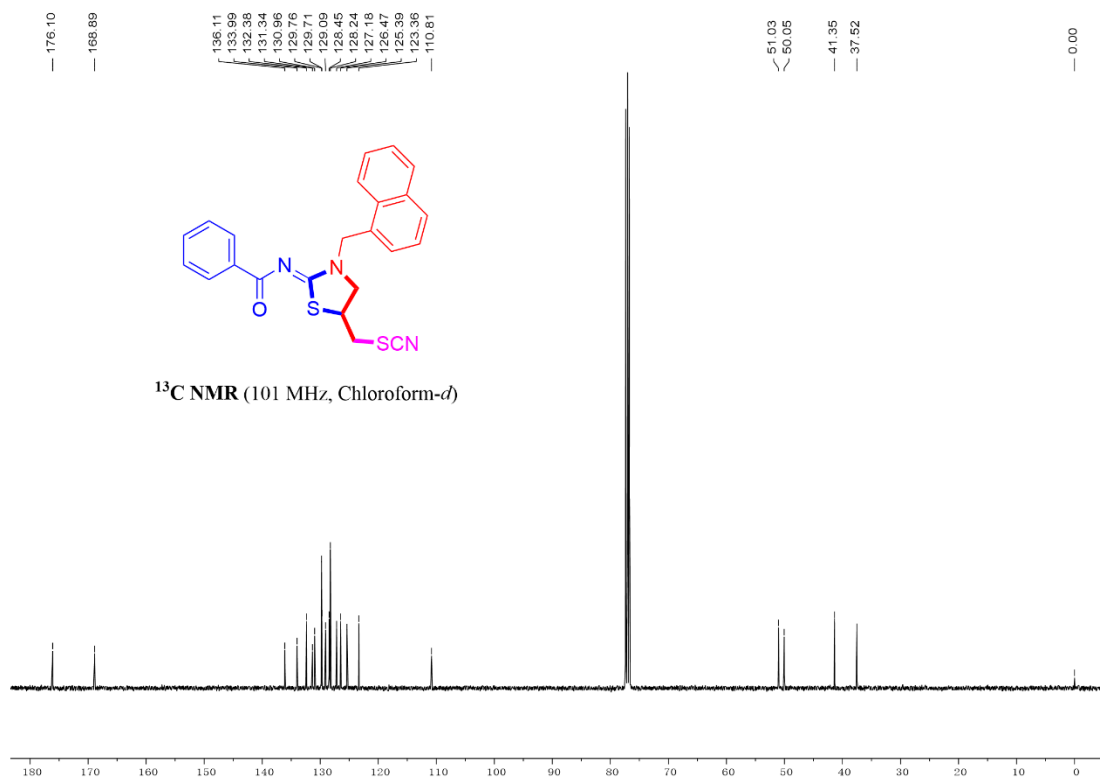
**(Z)-N-(3-(benzo[*d*][1,3]dioxol-4-ylmethyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene)benzamide (25)**



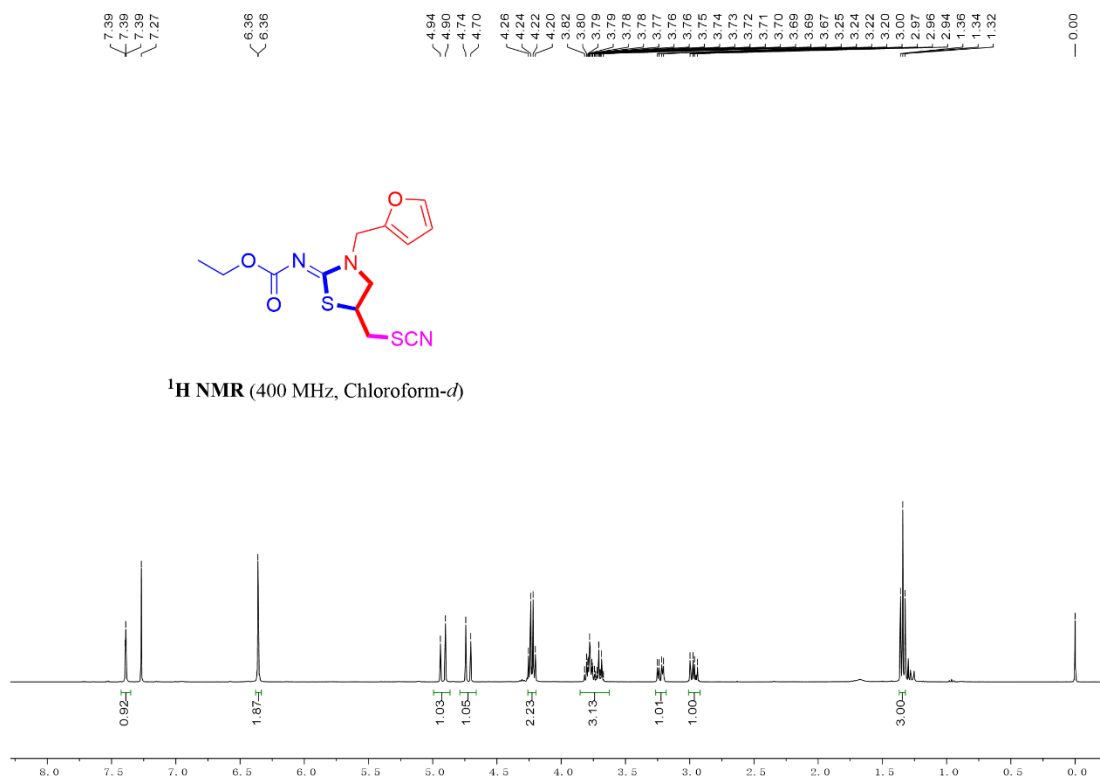


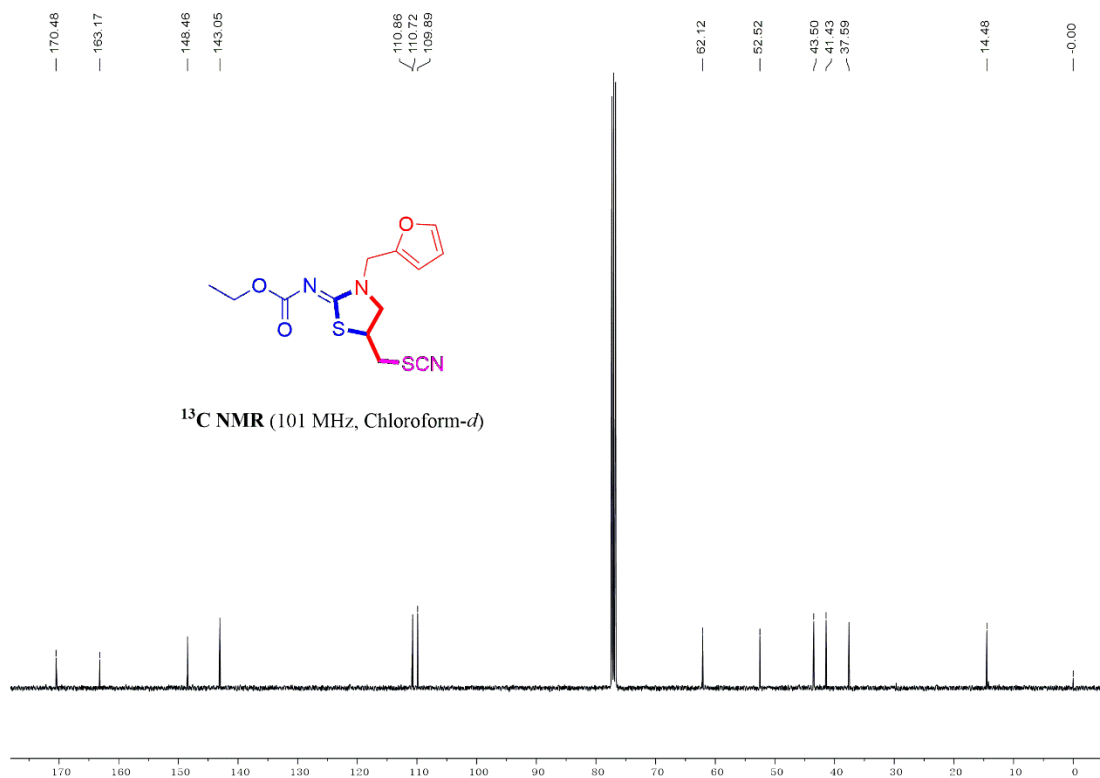
**(Z)-N-(3-(naphthalen-1-ylmethyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene)benzamide (26)**



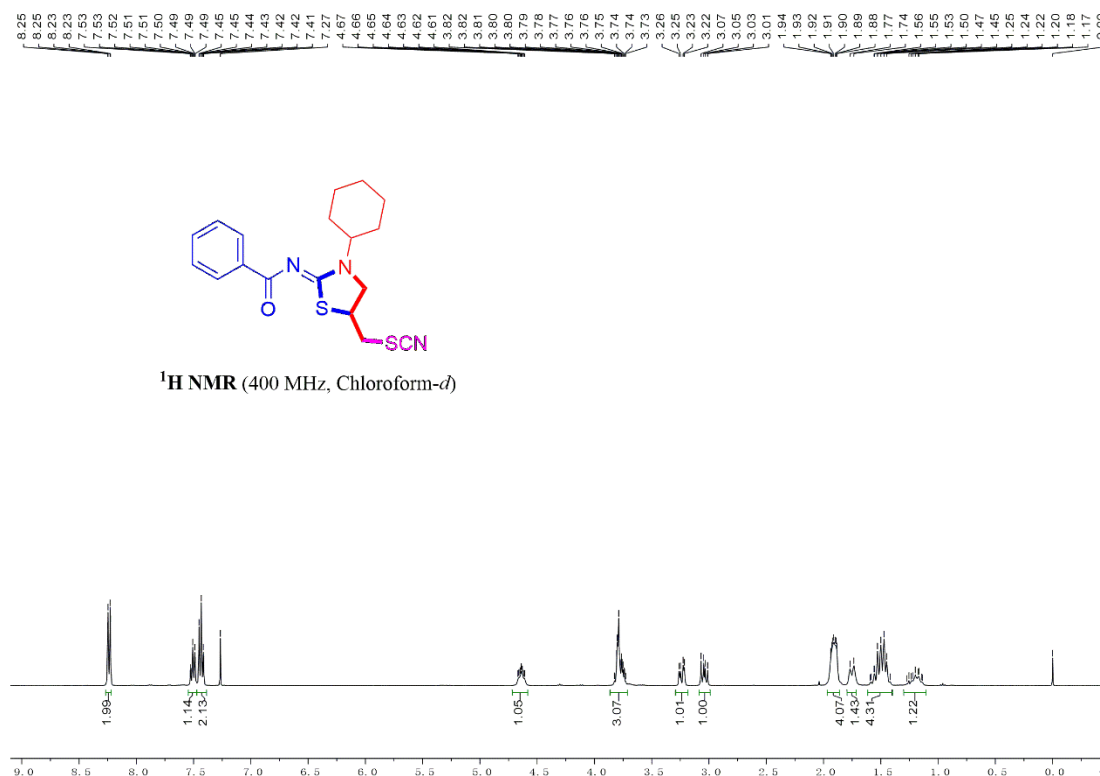


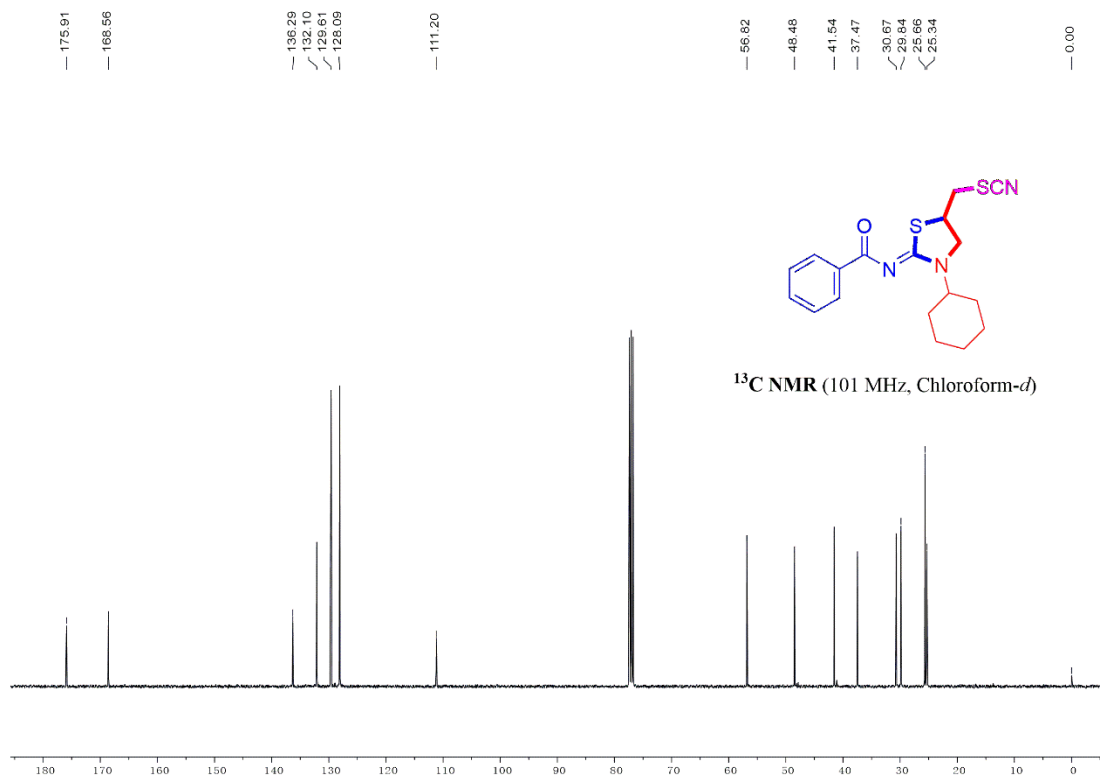
**ethyl (Z)-3-(furan-2-ylmethyl)-5-(thiocyanatomethyl)thiazolidin-2-ylidene)carbamate (27)**



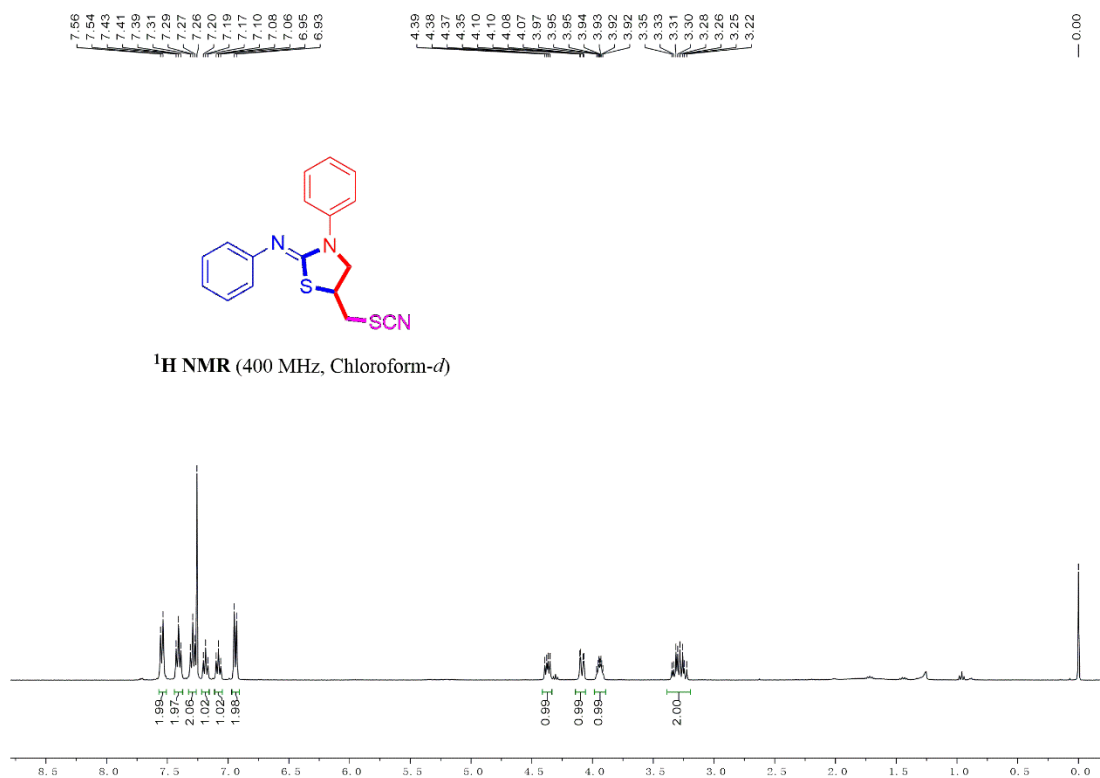


**(Z)-N-(3-cyclohexyl-5-(thiocyanatomethyl)thiazolidin-2-ylidene)benzamide (28)**

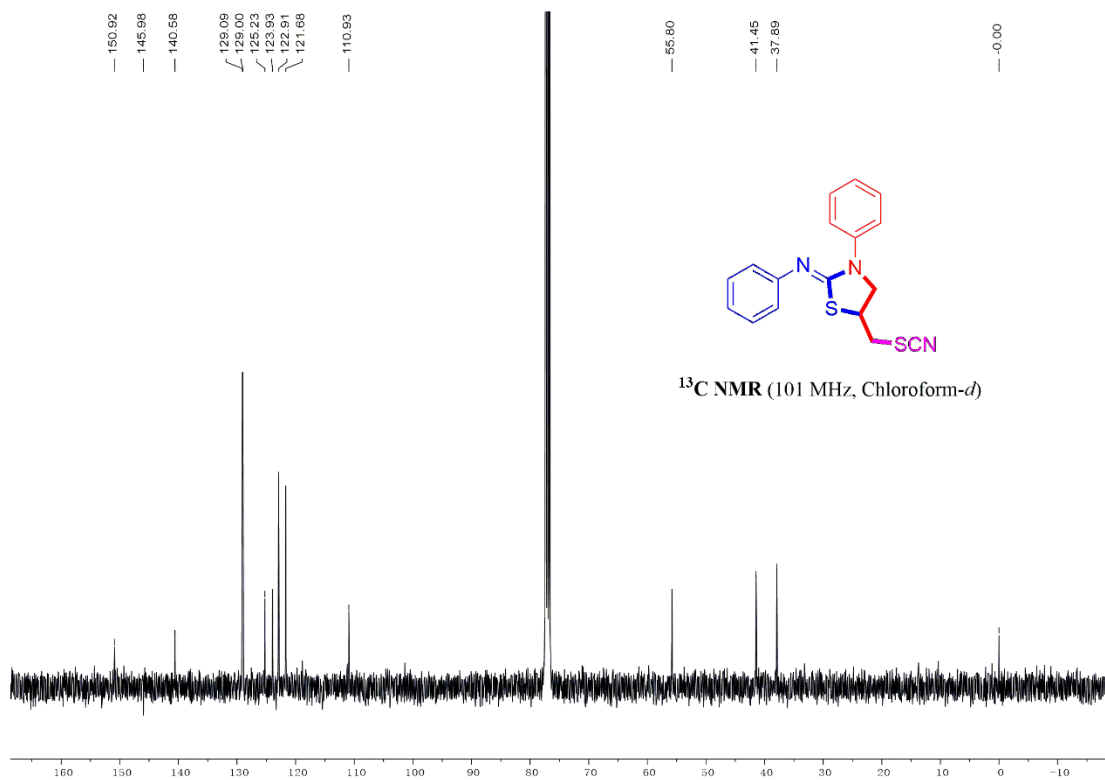




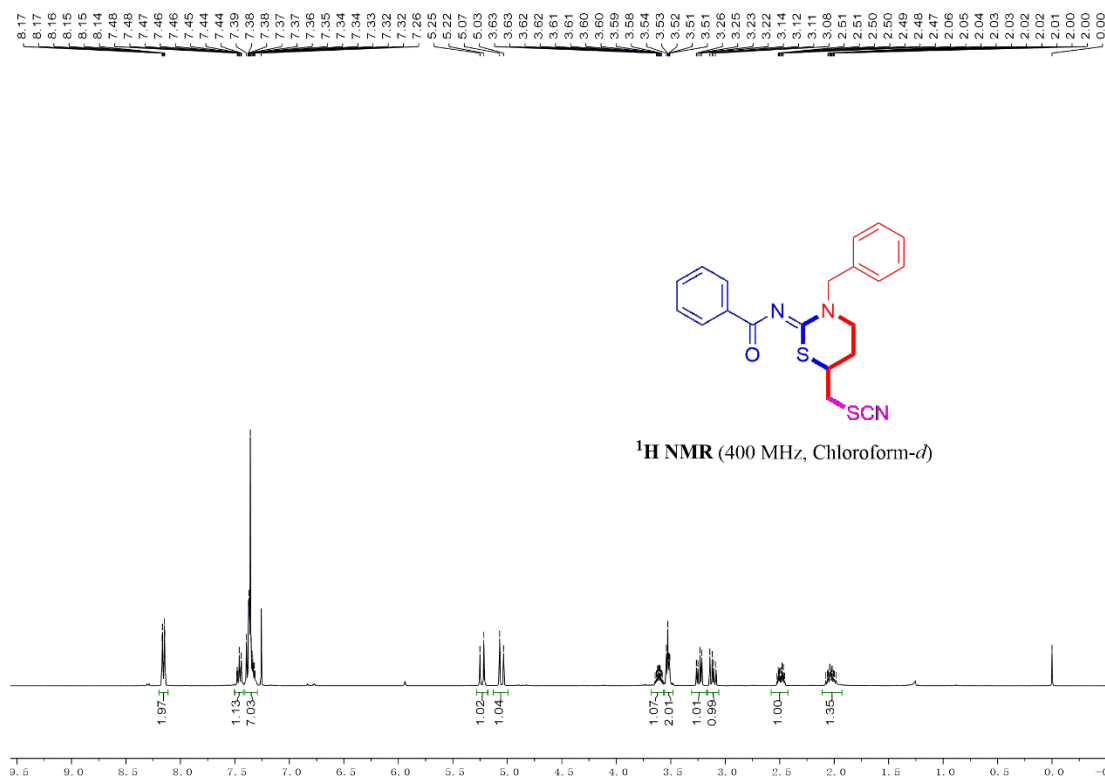
**(Z)-N,3-diphenyl-5-(thiocyanatomethyl)thiazolidin-2-imine (29)**

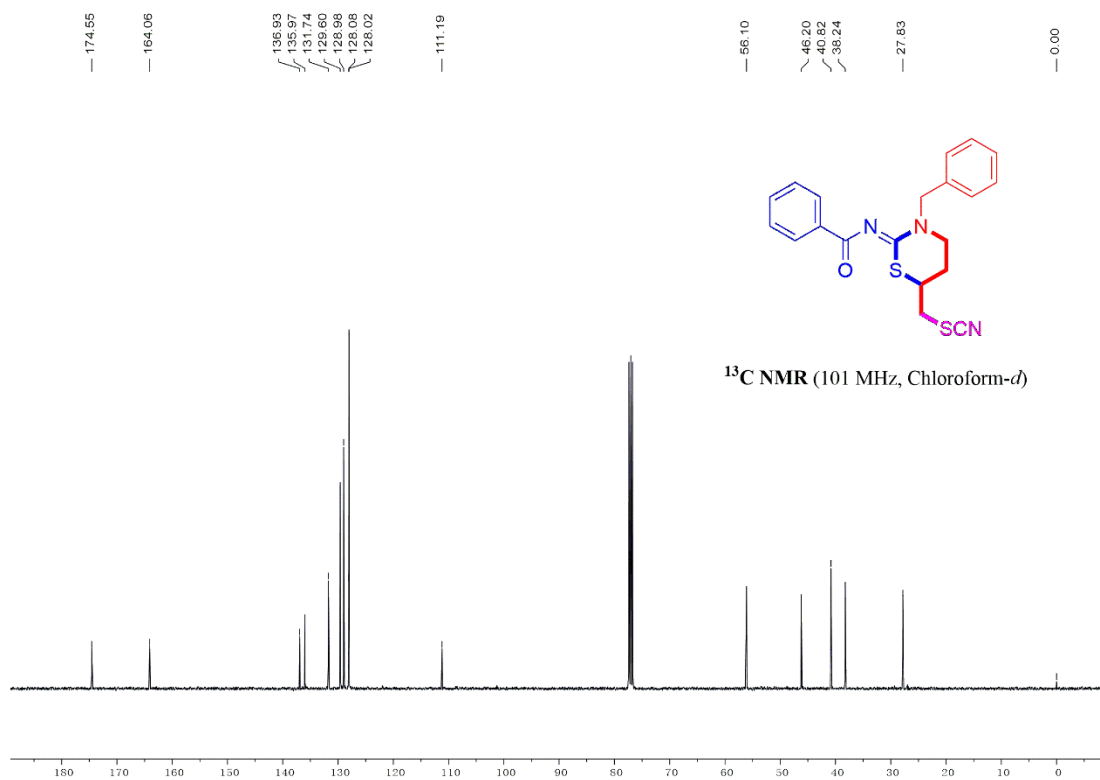




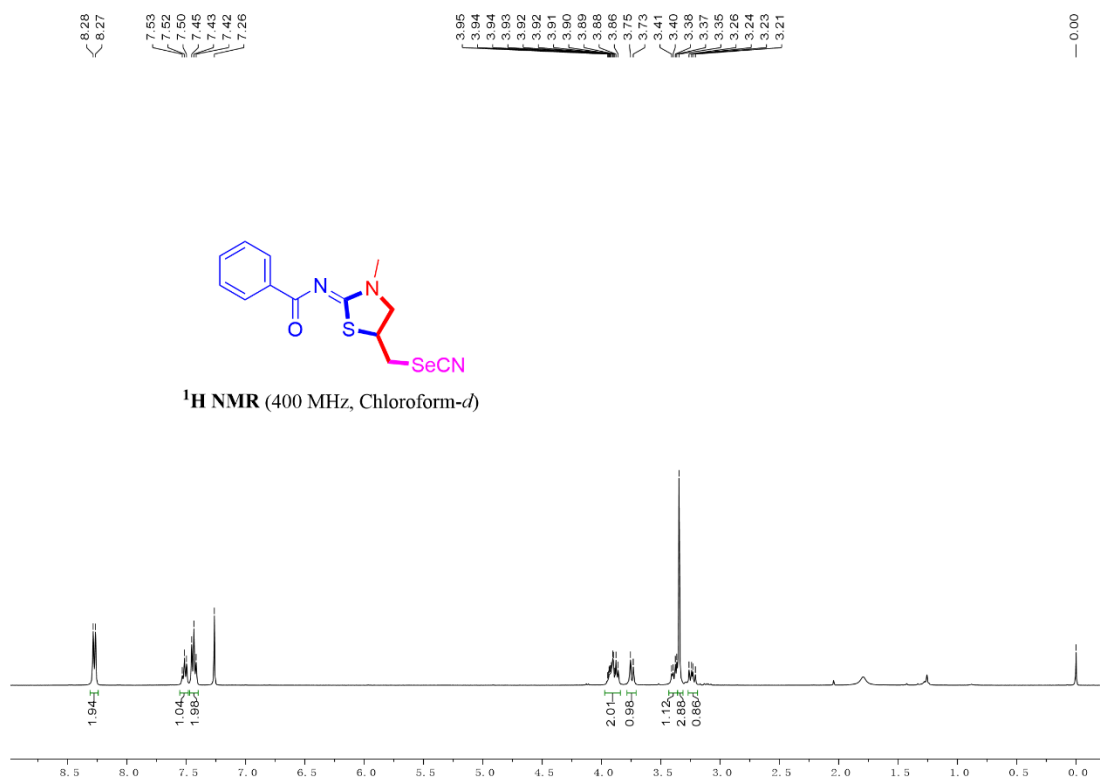


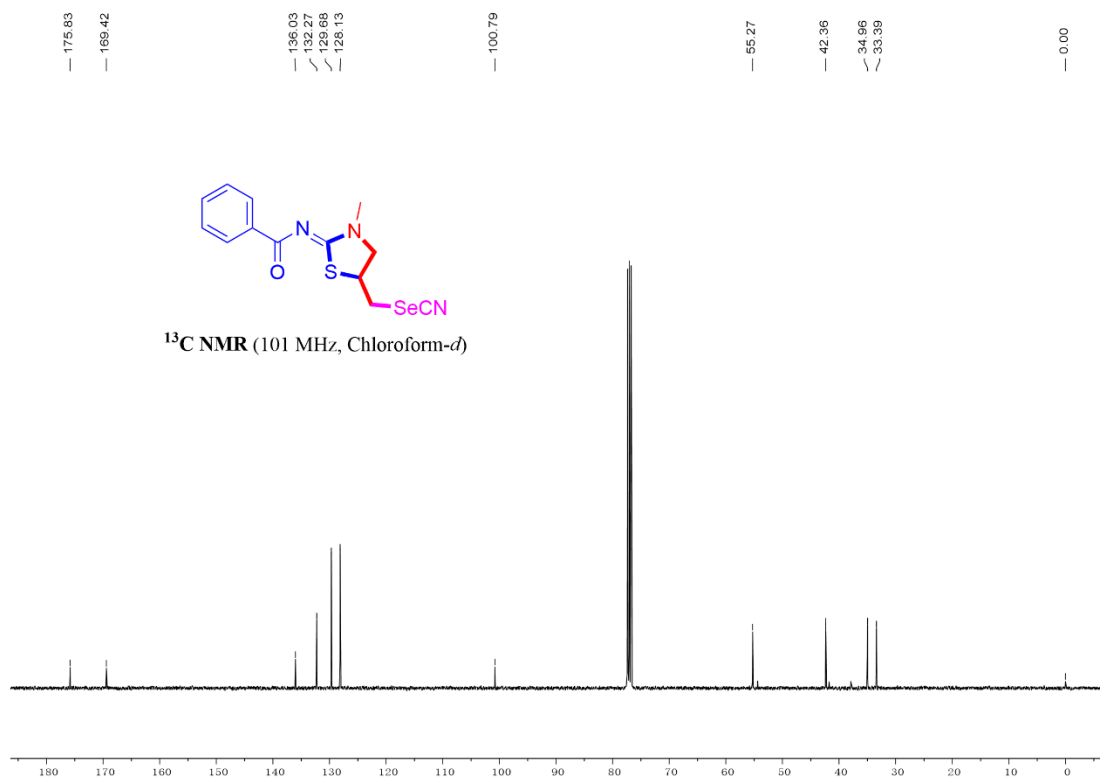
**(Z)-N-(3-benzyl-6-(thiocyanatomethyl)-1,3-thiazinan-2-ylidene)benzamide (30)**



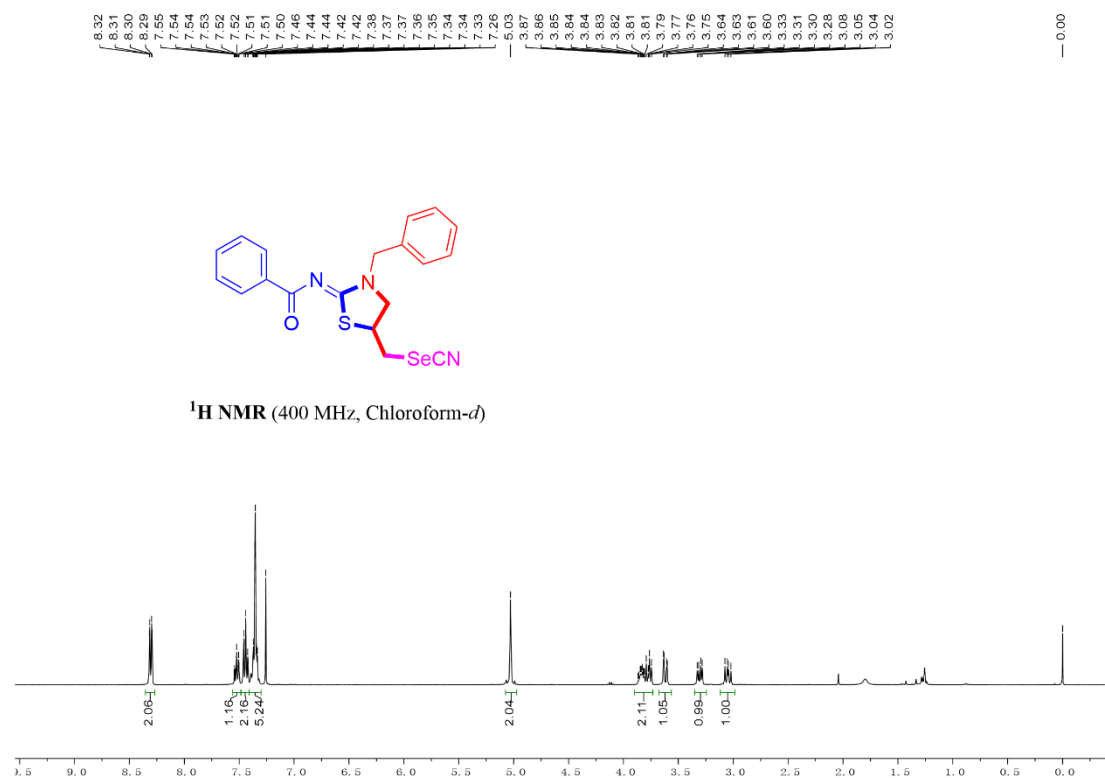


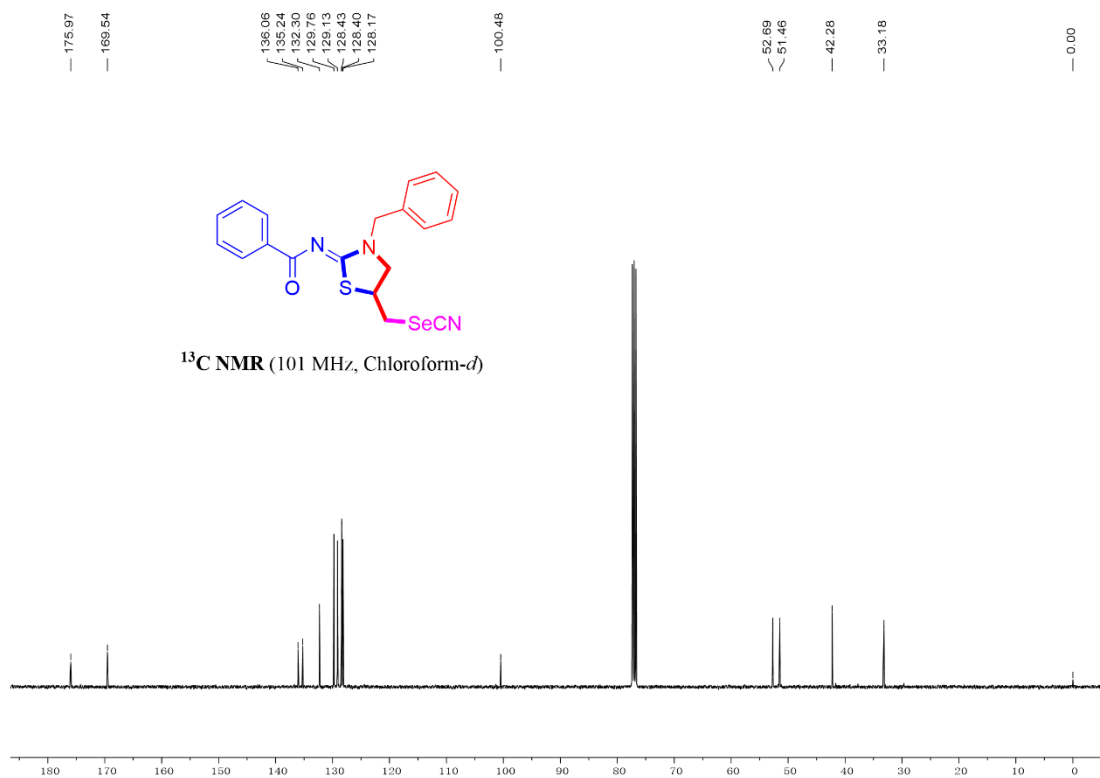
**(Z)-N-(3-methyl-5-(selenocyanatomethyl)thiazolidin-2-ylidene)benzamide (31)**



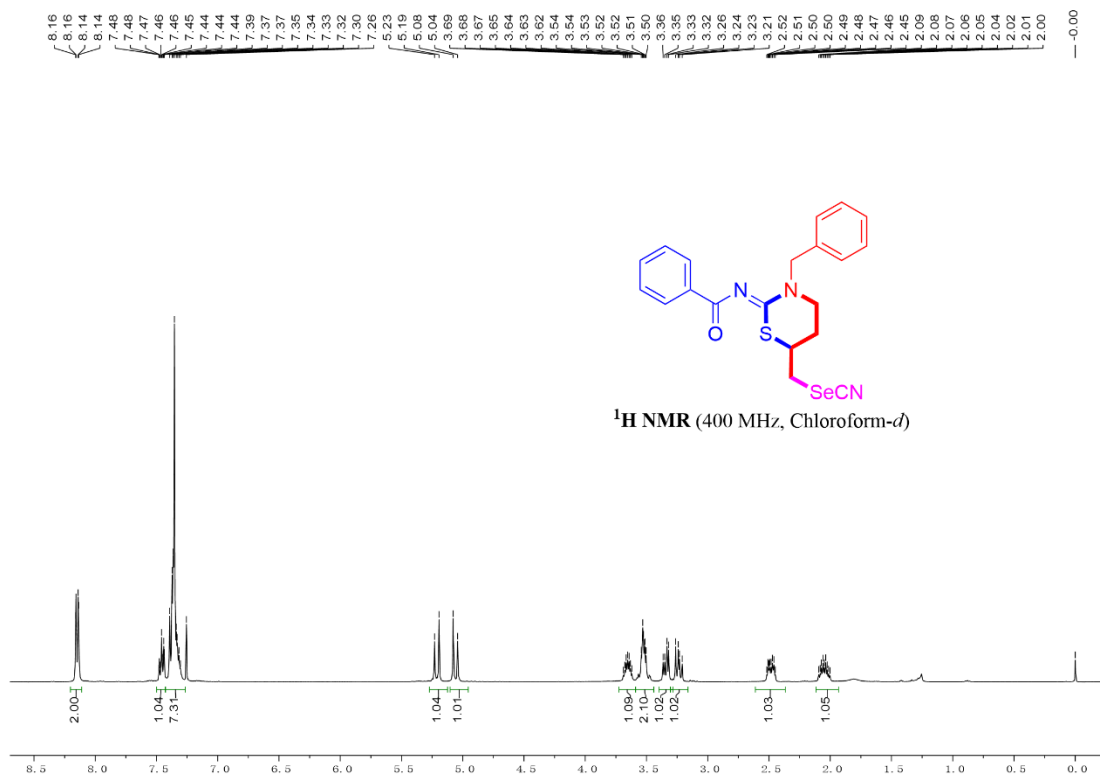


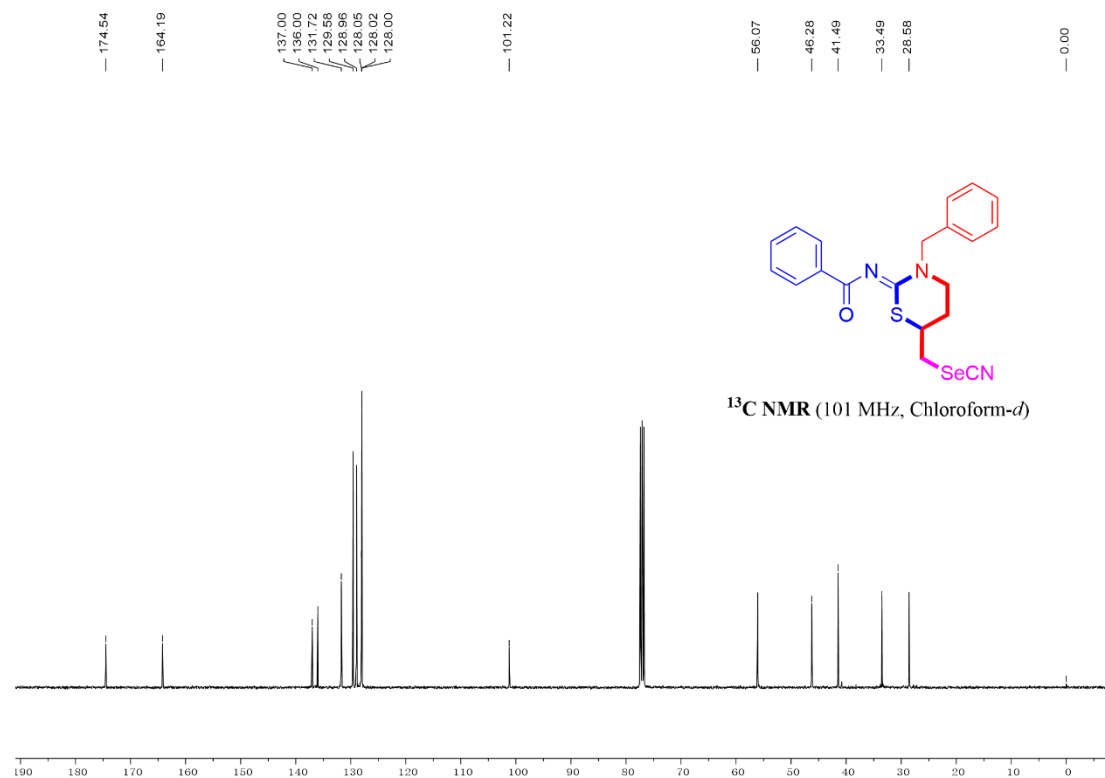
**(Z)-N-(3-benzyl-5-(selenocyanatomethyl)thiazolidin-2-ylidene)benzamide (32)**



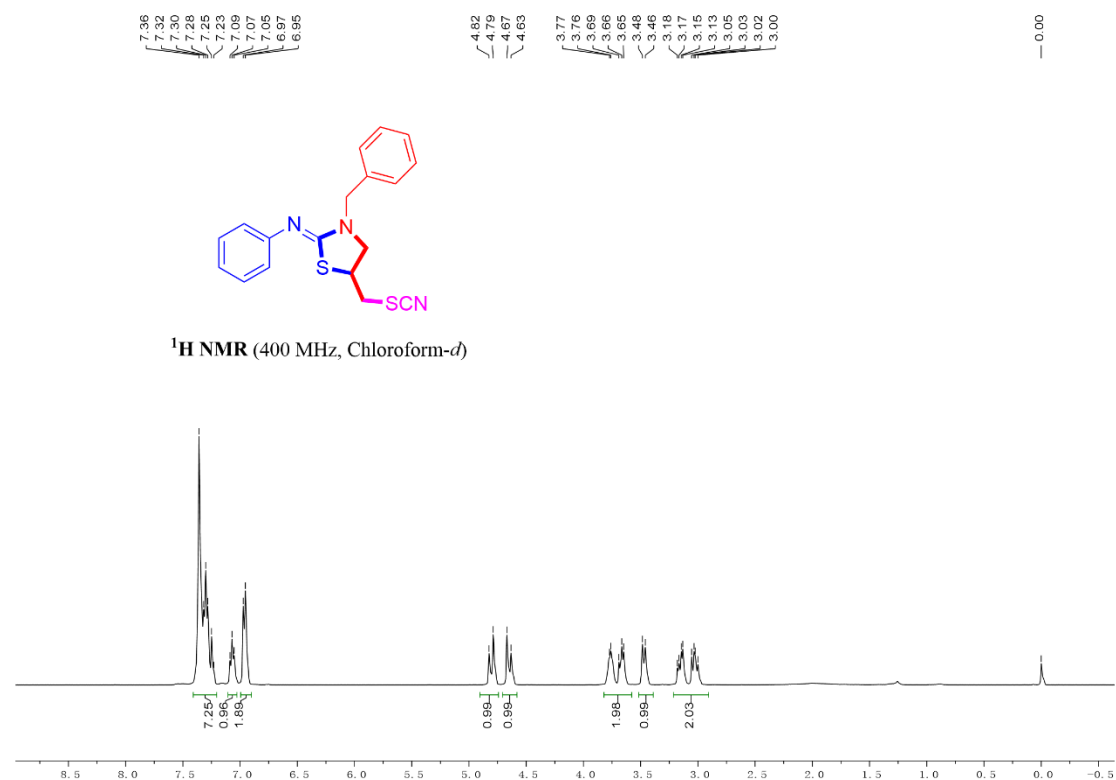


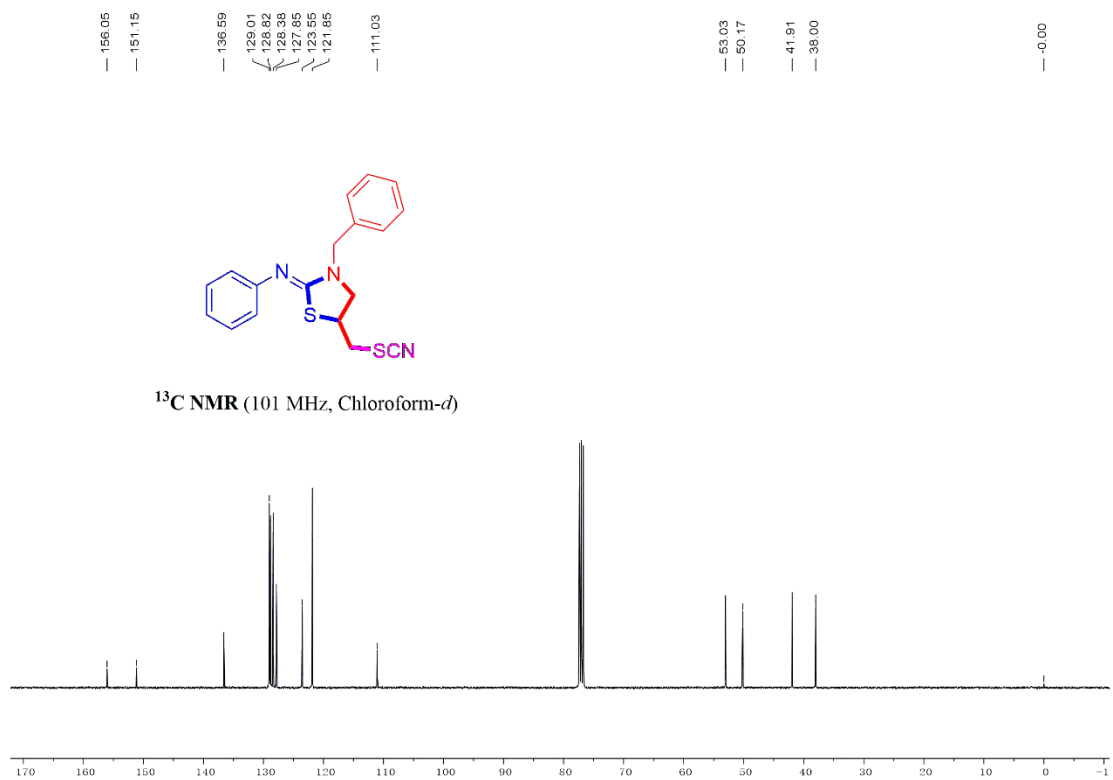
**(Z)-N-(3-benzyl-6-(selenocyanatomethyl)-1,3-thiazinan-2-ylidene)benzamide (33)**



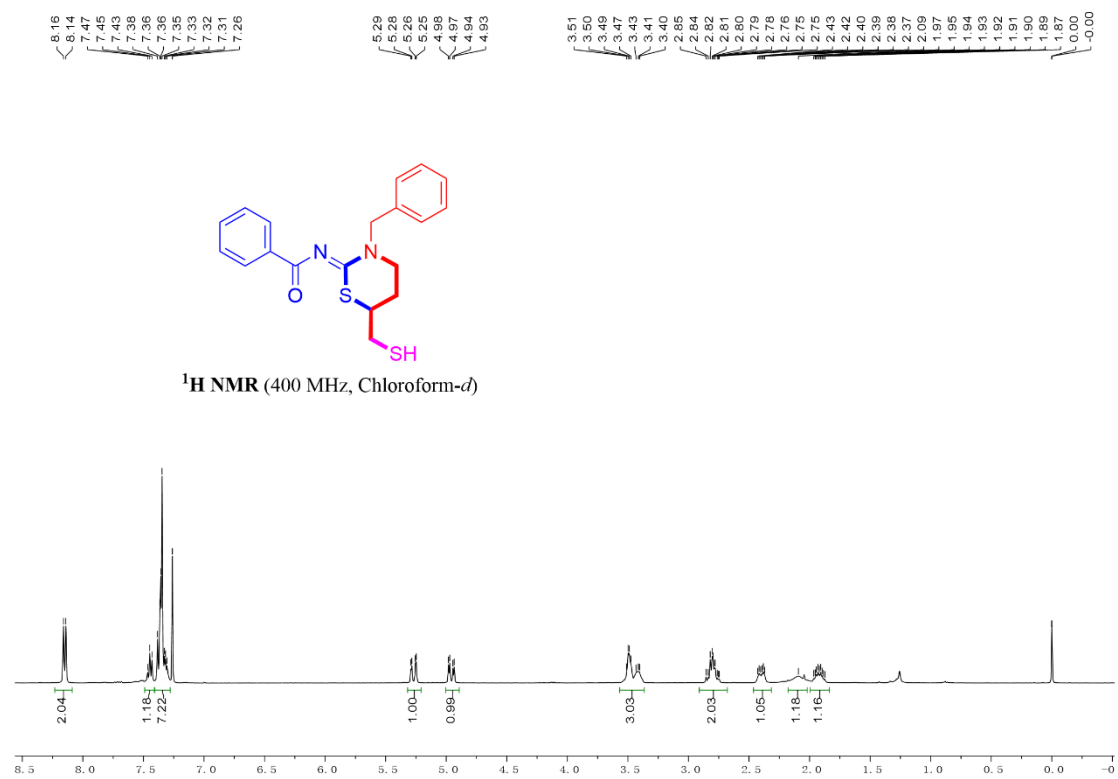


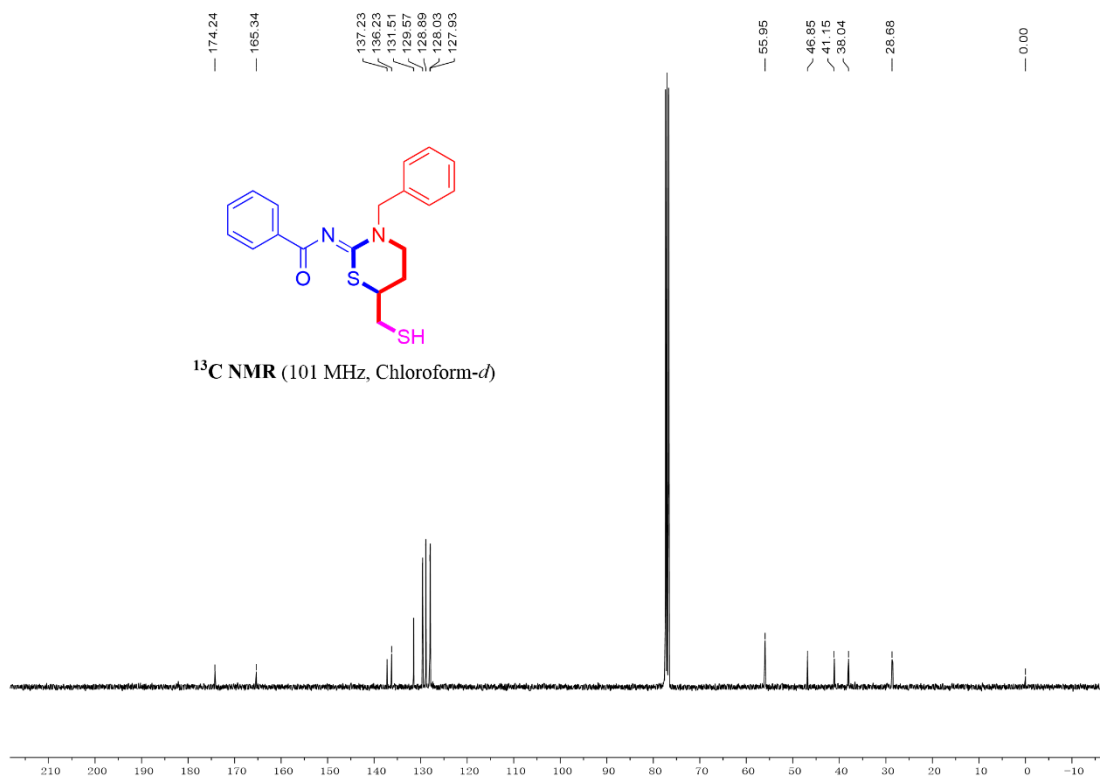
**(Z)-3-benzyl-N-phenyl-5-(thiocyanatomethyl)thiazolidin-2-imine (38)**



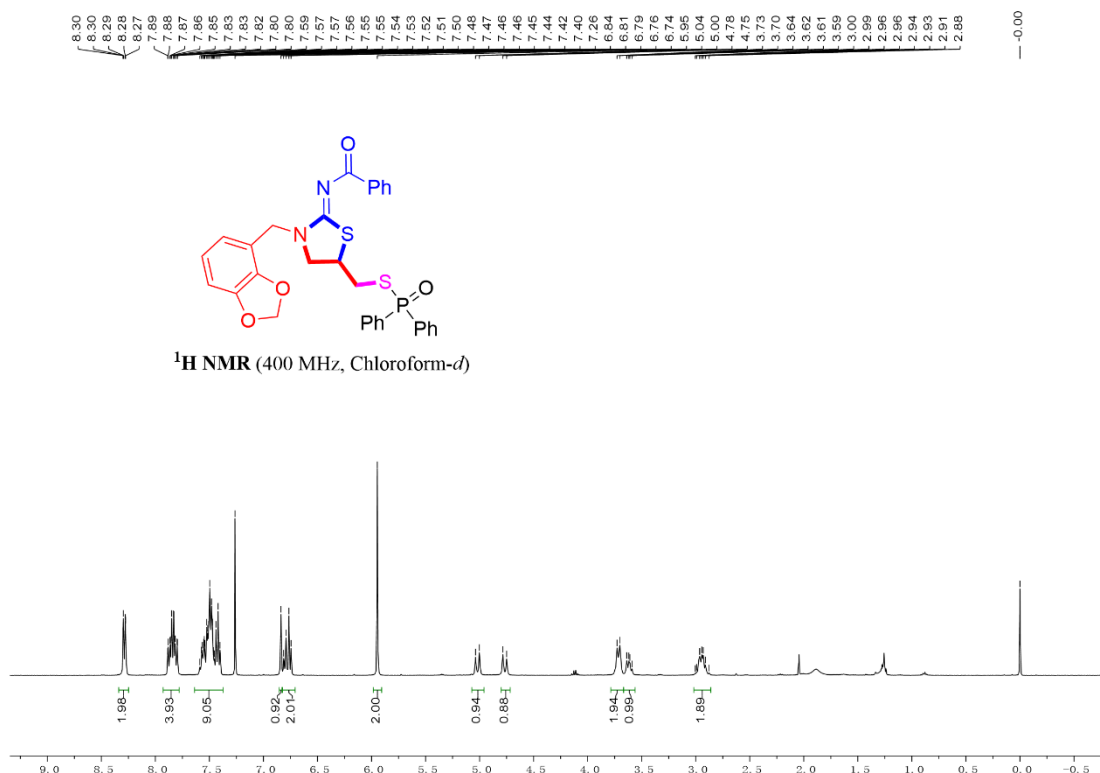


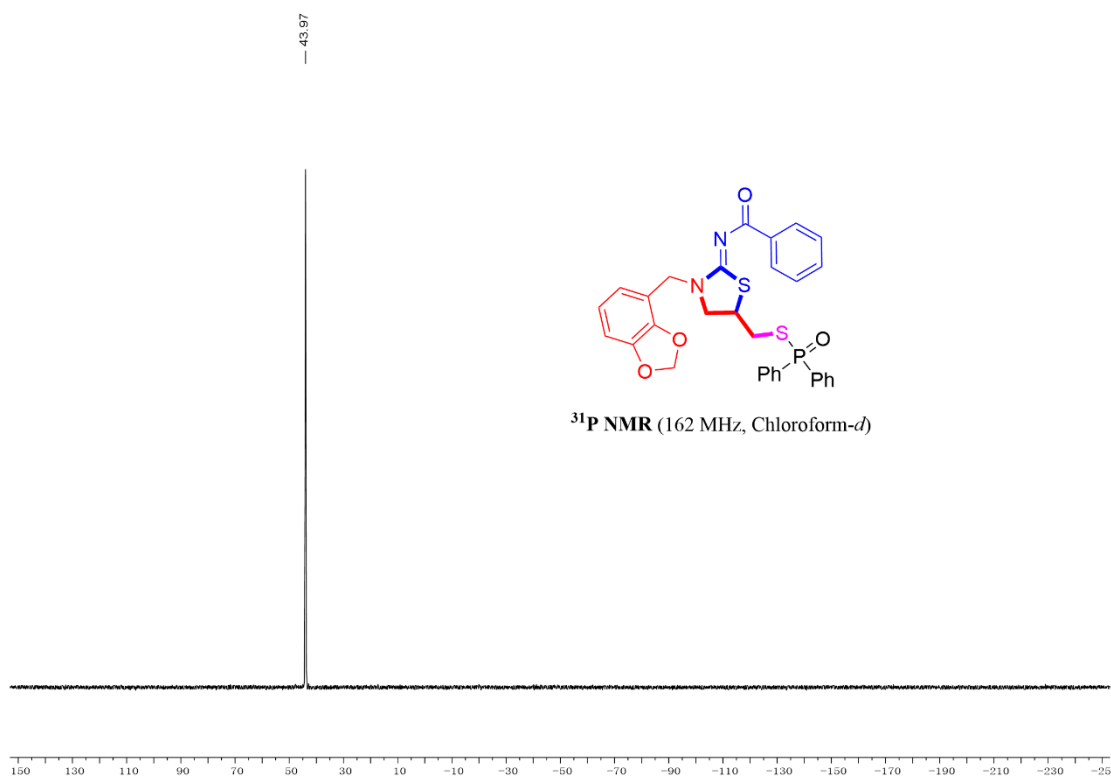
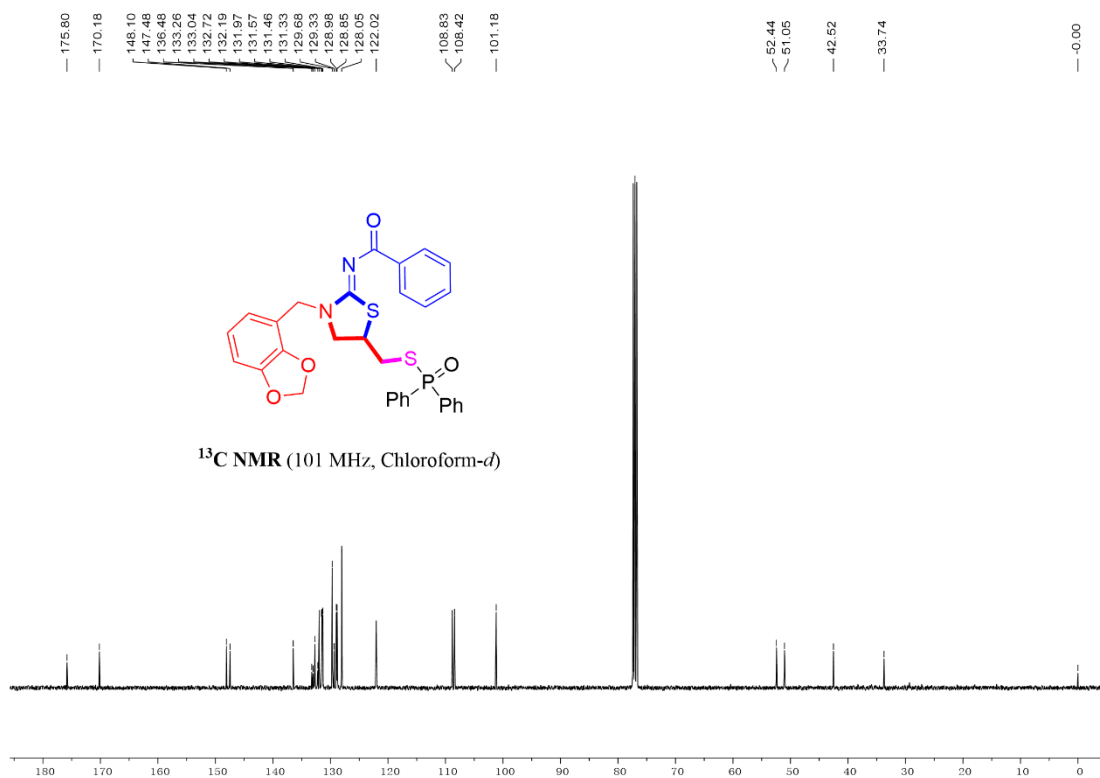
**(Z)-N-(3-benzyl-6-(mercaptomethyl)-1,3-thiazinan-2-ylidene)benzamide (39)**





**(Z)-((3-(benzo[d][1,3]dioxol-5-ylmethyl)-2-(benzoylimino)thiazolidin-5-yl)methyl)diphenylphosphinothioate (40)**



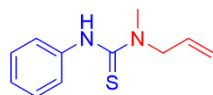




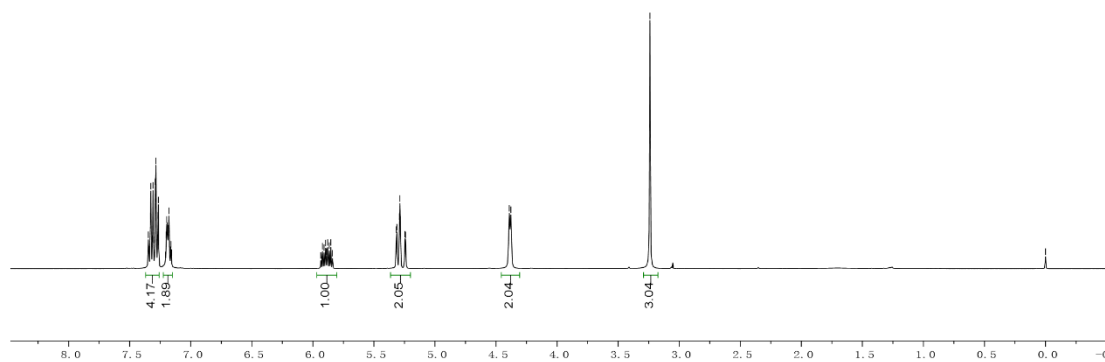
# 1-allyl-1-methyl-3-phenylthiourea (41)



0.00



<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)



182.33

139.73

131.80

128.66

125.68

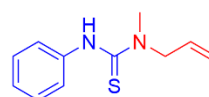
125.34

117.88

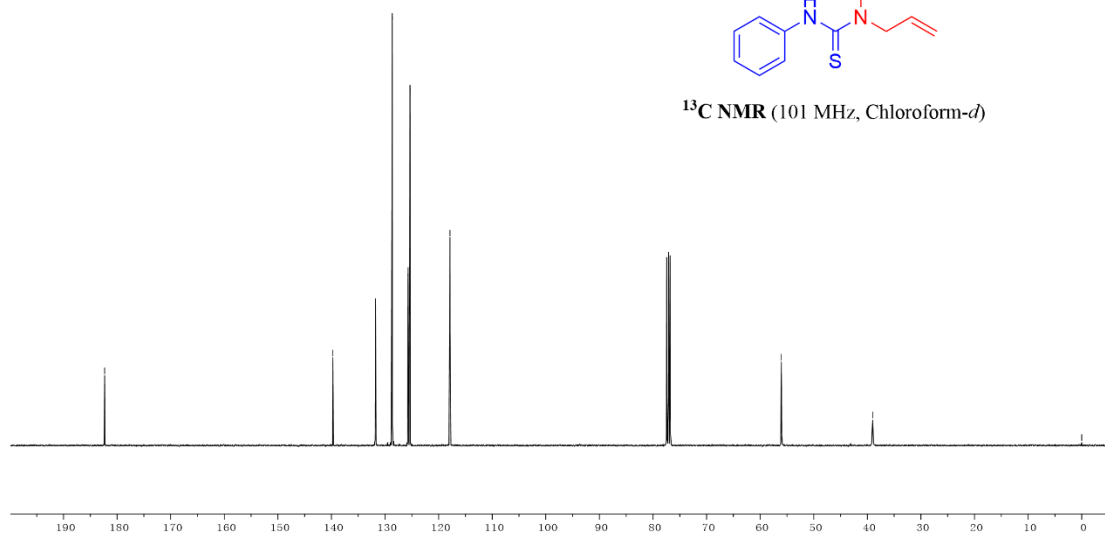
56.04

39.02

-0.00



<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)



(Z)-N-(3-benzyl-6-phenyl-5-thiocyanato-1,3-thiazinan-2-ylidene)benzamide (43)

