

Electrosynthesis of *S*-thiocarbamates with disulfides as a sulfur source

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1. Typical Experimental Procedure

(a) General

All reactions were carried out in Aqueous solvent and commercially available reagents were used as received unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated aluminium-backed silica gel 60 F₂₅₄ plates (EMD Millipore, 200 μ m thickness). TLC plates were visualized with ultraviolet light. Flash column chromatography was performed using Tsingtao silica gel (200-300). ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker Avance DRX - 400 spectrometers; chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference (CDCl₃: δ_{H} = 7.26 ppm and δ_{C} = 77.16 ppm). Data for ¹H NMR, ¹⁹F NMR and ¹³C NMR are reported as follows: chemical shift (δ , ppm), multiplicity, integration, and coupling constant (Hz). Melting points are uncorrected. The instrument for electrolysis is IKA ElectraSyn 2.0. Cyclic voltammograms were obtained on a Autolab83943 potentiostat. In the characterization data of products of supporting information, the new compounds have been marked with “*”.

(b) General procedure for synthesis of compound 3a

Disulfides **1** (0.2 mmol), isocyanides **2** (0.4 mmol), NH₄I (0.1 M) were placed in a 10 mL vial. The vial was equipped with a condenser, a GC plate (1 cm \times 1 cm) anode and a platinum plate (1 cm \times 1 cm) cathode. 2-MeTHF (3.0 mL) and H₂O (2.0 mL) were added. The electrolysis was carried out under air atmosphere at rt using a constant current of 7.3 mA until complete consumption of the substrate (monitored by TLC, about 3 h). The mixture was cooled and diluted with brine, and the product was extracted with ethyl acetate (3 \times 10 mL). The organic layer was dried with anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether to give the desired products **3**.

(c) Experimental device



Figure S1. Pictures of the IKA ElectraSyn 2.0 pro Package



Figure S2. Pictures of Autolab83943 potentiostat. for Cyclic voltammograms

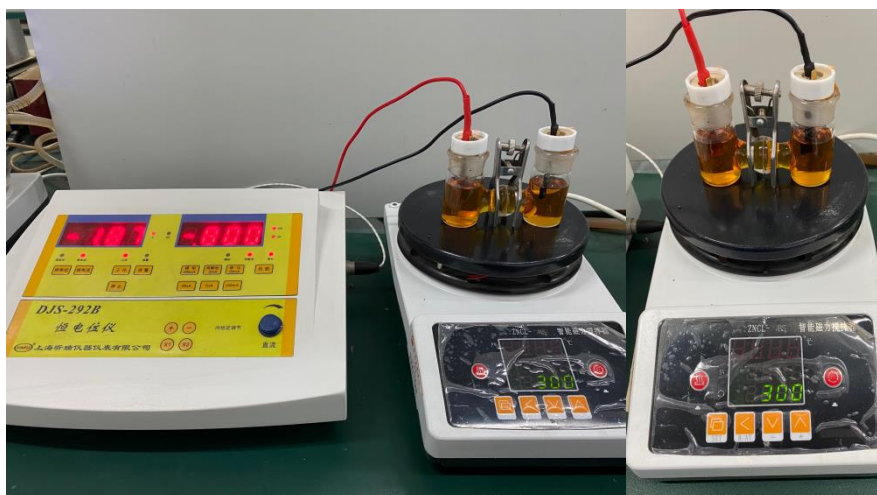


Figure S3. Pictures of the divided cell system

(d) Cyclic Voltammogram Curve

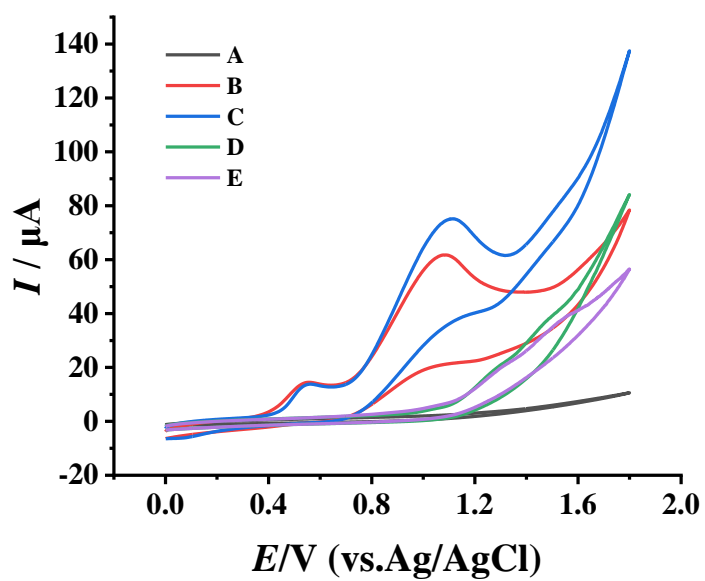
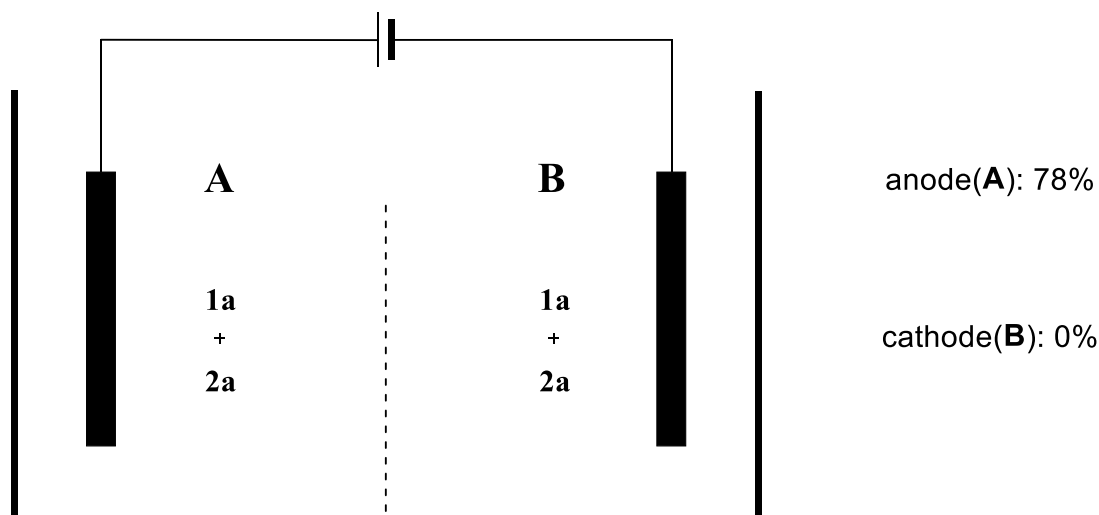


Figure S4. Cyclic voltammograms of reactants and their mixtures in 0.1 M LiClO₄/ 2-MeTHF/H₂O (3/2 v/v) using a glassy carbon disk working electrode (diameter, 3 mm), Pt disk and Ag/AgCl (0.1 M in CH₃CN) as counter and reference electrode at 50 mV/s scan rate: A) background, B) NH₄I (10 mmol/L), C) **1a** (10 mmol/L) and **2a** (20 mmol/L) and NH₄I (10 mmol/L), D) **1a** (10 mmol/L), E) **2a** (20 mmol/L).

(e) divided cell experiment



divided cell, GC(+)/Pt(-)
0.1 M NH₄I, 2-MeTHF/H₂O(5 mL, v/v 3:2)
constant current (8 mA)

The reaction was conducted using an H-type divided cell, and the yields were determined by ¹H NMR.

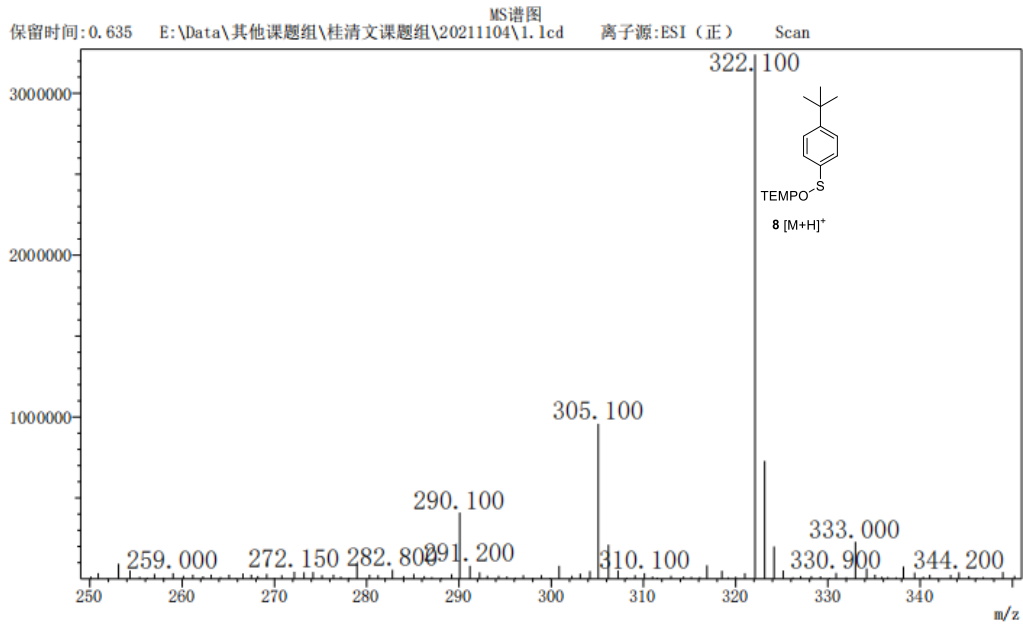
(f) The addition of TEMPO in the model reaction system

Bis[4-(1,1-dimethylethyl)phenyl] disulfide **1a** (0.2 mmol), ethyl isocyanoacetate **2a** (0.4 mmol), NH₄I (0.1 M) and TEMPO (1.0 equiv.) were placed in a 10 mL vial. The vial was equipped with a condenser, a GC plate (1 cm × 1 cm) anode and a platinum plate (1 cm × 1 cm) cathode. 2-MeTHF (3.0 mL) and H₂O (2.0 mL) were added. The electrolysis was carried out under air atmosphere at rt using a constant current of 7.3 mA until complete consumption of the substrate (monitored by TLC, about 3 h). The reaction was inhibited, and TEMPO-trapped complex **8** was detected by MS and NMR analysis.

样品信息

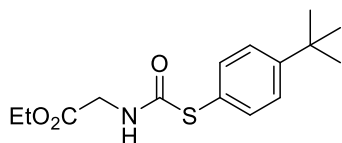
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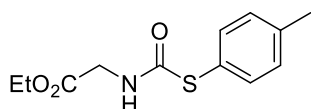
2. Characterization data of products

*ethyl (((4-(tert-butyl)phenyl)thio)carbonyl)glycinate (3a)**



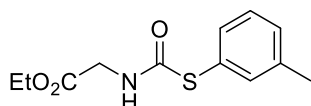
yellow solid, Mp: 60-61 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 5.94 (s, 1 H), 4.22 – 4.16 (m, 2 H), 4.02 (d, *J* = 5.2 Hz, 2 H), 1.32 (s, 9 H), 1.26 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 169.4, 167.4, 153.3, 135.3, 126.8, 124.5, 61.7, 42.7, 34.9, 31.2, 14.2; HRMS (ESI) *m/z* calcd. for C₁₅H₂₁NO₃S [M+H]⁺: 296.1315, found 296.1322.

ethyl ((p-tolylthio)carbonyl)glycinate (3b)¹



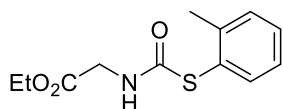
yellow solid, Mp: 60-61 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.44 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 7.6 Hz, 2 H), 6.07 (s, 1 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 3.98 (d, *J* = 5.2 Hz, 2 H), 2.35 (s, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 169.4, 167.4, 140.4, 135.6, 130.4, 124.5, 61.7, 42.7, 21.4, 14.3. MS:*m/z* 253 (M⁺).

ethyl ((m-tolylthio)carbonyl)glycinate (3c)¹



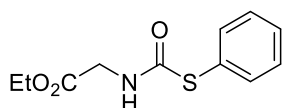
light yellow solid, Mp: 96-97 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.40 – 7.38 (m, 2 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.26 – 7.24 (m, 1 H), 5.95 (s, 1 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 4.02 (d, *J* = 5.2 Hz, 2 H), 2.37 (s, 3 H), 1.26 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 169.4, 167.2, 139.7, 136.3, 132.7, 130.9, 129.5, 127.7, 61.8, 42.8, 21.4, 14.2. MS:*m/z* 253 (M⁺).

ethyl ((o-tolylthio)carbonyl)glycinate (3d)¹



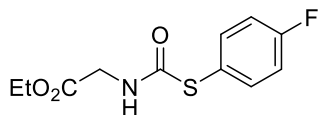
light yellow solid, Mp: 87-88 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 7.6 Hz, 1 H), 7.39 – 7.34 (m, 2 H), 7.27 – 7.23 (m, 1 H), 5.85 (s, 1 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 4.00 (d, *J* = 5.2 Hz, 2 H), 2.49 (s, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 169.4, 166.8, 143.2, 137.2, 131.3, 130.9, 127.5, 127.3, 61.8, 42.7, 21.2, 14.2. MS:*m/z* 253 (M⁺).

ethyl ((phenylthio)carbonyl)glycinate (3e)¹



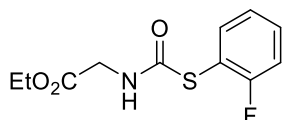
yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.60 – 7.58 (m, 2 H), 7.45 – 7.42 (m, 3 H), 5.90 (s, 1 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 4.03 (d, *J* = 4.8 Hz, 2 H), 1.26 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 169.4, 167.0, 135.7, 130.1, 129.7, 128.1, 61.9, 42.8, 14.2. MS:*m/z* 239 (M⁺).

ethyl (((4-fluorophenyl)thio)carbonyl)glycinate (3f)¹



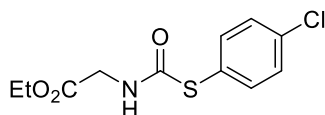
yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.56 – 7.52 (m, 2 H), 7.11 (t, $J = 8.8$ Hz, 2 H), 5.96 (s, 1 H), 4.21 (q, $J = 7.2$ Hz, 2 H), 4.03 (d, $J = 5.2$ Hz, 2 H), 1.27 (t, $J = 6.8$ Hz, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.4, 166.7, 163.8 (d, $J = 250$ Hz), 137.8 (d, $J = 8$ Hz), 123.3, 116.8 (d, $J = 21$ Hz), 61.9, 42.8, 14.2; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -110.45. MS:m/z 257 (M^+).

ethyl (((2-fluorophenyl)thio)carbonylglycinate (3g)*



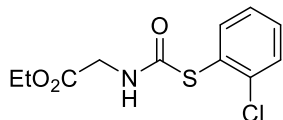
yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.57 – 7.53 (m, 1 H), 7.48 – 7.42 (m, 1 H), 7.21 – 7.16 (m, 2 H), 6.05 (s, 1 H), 4.22 (q, $J = 7.2$ Hz, 2 H), 4.05 (d, $J = 4.8$ Hz, 2 H), 1.28 (t, $J = 8.2$ Hz, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.3, 164.9, 162.7 (d, $J = 249$ Hz), 137.7, 132.6 (d, $J = 8$ Hz), 124.9 (d, $J = 4$ Hz), 116.5 (d, $J = 23$ Hz), 61.9, 43.0, 29.8, 14.2; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -105.39; HRMS (ESI) m/z calcd. for $\text{C}_{11}\text{H}_{12}\text{FNO}_3\text{S}$ [$\text{M}+\text{H}$] $^+$: 258.0595, found 258.0599.

ethyl (((4-chlorophenyl)thio)carbonylglycinate (3h)¹



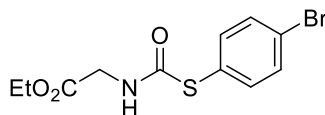
yellow solid, Mp: 72-73 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.48 (d, $J = 8.4$ Hz, 2 H), 7.38 (d, $J = 8.8$ Hz, 2 H), 5.98 (s, 1 H), 4.21 (q, $J = 7.2$ Hz, 2 H), 4.04 (d, $J = 4.8$ Hz, 2 H), 1.28 (t, $J = 6.8$ Hz, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.4, 166.2, 136.8, 136.4, 129.8, 126.4, 62.0, 42.9, 14.2. MS:m/z 273 (M^+).

ethyl (((2-chlorophenyl)thio)carbonylglycinate (3i)¹



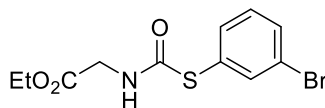
yellow solid, Mp: 77-78 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.65 (dd, $J = 7.6, 1.6$ Hz, 1 H), 7.50 (dd, $J = 8.0, 1.2$ Hz, 1 H), 7.36 (td, $J = 7.6, 1.6$ Hz, 1 H), 7.31 – 7.27 (m, 1 H), 6.22 (s, 1 H), 4.27 (q, $J = 7.2$ Hz, 2 H), 4.03 (d, $J = 5.2$ Hz, 2 H), 1.30 (t, $J = 6.8$ Hz, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.3, 164.0, 139.4, 138.0, 131.4, 130.4, 127.6, 127.5, 61.8, 40.9, 14.2. MS:m/z 273 (M^+).

ethyl (((4-bromophenyl)thio)carbonylglycinate (3j)¹



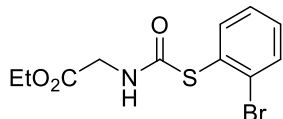
yellow solid, Mp: 54-55 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.54 (d, $J = 8.4$ Hz, 2 H), 7.41 (d, $J = 8.4$ Hz, 2 H), 5.99 (s, 1 H), 4.21 (q, $J = 7.2$ Hz, 2 H), 4.04 (d, $J = 5.2$ Hz, 2 H), 1.27 (t, $J = 7.2$ Hz, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.4, 166.0, 137.0, 132.7, 127.0, 124.6, 62.0, 42.9, 14.2. MS:m/z 317 (M^+).

ethyl (((3-bromophenyl)thio)carbonylglycinate (3k)*



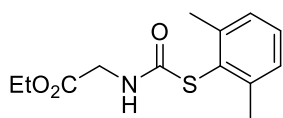
dark black solid, Mp: 51-52 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.71 (s, 1 H), 7.54 (d, *J* = 7.6 Hz, 1 H), 7.49 (d, *J* = 8.0 Hz, 1 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 6.06 (s, 1 H), 4.21 (q, *J* = 7.6 Hz, 2 H), 4.04 (d, *J* = 4.8 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 169.3, 165.8, 137.9, 134.0, 132.9, 130.7, 129.9, 122.9, 61.9, 42.9, 14.2; HRMS (ESI) *m/z* calcd. for C₁₁H₁₂BrNO₃S [M+H]⁺: 317.9794, found 317.9787.

ethyl (((2-bromophenyl)thio)carbonyl)glycinate (3l)*



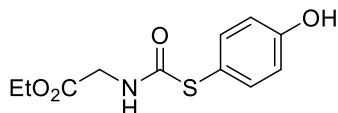
white solid, Mp: 83-84 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.72 – 7.69 (m, 2 H), 7.36 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.28 (td, *J* = 7.6, 1.6 Hz, 1 H), 6.01 (s, 1 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 4.06 (d, *J* = 5.2 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 169.3, 165.0, 138.0, 133.9, 131.5, 130.5, 129.7, 128.3, 61.9, 43.0, 14.2; HRMS (ESI) *m/z* calcd. for C₁₁H₁₂BrNO₃S [M+H]⁺: 317.9794, found 317.9788.

ethyl (((2,6-dimethylphenyl)thio)carbonyl)glycinate (3m)*



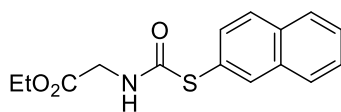
yellow solid, Mp: 67-68 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.28 – 7.24 (m, 1 H), 7.20 – 7.18 (m, 2 H), 5.78 (s, 1 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 3.97 (d, *J* = 5.2 Hz, 2 H), 2.50 (s, 6 H), 1.24 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 169.4, 166.6, 144.0, 130.6, 128.9, 127.4, 61.7, 42.6, 22.2, 14.2; HRMS (ESI) *m/z* calcd. for C₁₃H₁₇NO₃S [M+H]⁺: 268.1002, found 268.1015.

ethyl (((4-hydroxyphenyl)thio)carbonyl)glycinate (3n)*



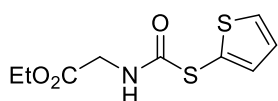
yellow solid, Mp: 83-84 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.46 (s, 1 H), 7.35 (d, *J* = 7.6 Hz, 2 H), 6.71 (d, *J* = 7.2 Hz, 2 H), 6.21 (s, 1 H), 4.20 (q, *J* = 6.8 Hz, 2 H), 4.05 (d, *J* = 4.8 Hz, 2 H), 1.27 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 169.8, 169.8, 158.6, 137.7, 117.1, 116.9, 62.1, 42.9, 14.2; HRMS (ESI) *m/z* calcd. for C₁₁H₁₃NO₄S [M+H]⁺: 256.0638, found 256.0644.

ethyl (((naphthalen-2-ylthio)carbonyl)glycinate (3o)²



light green solid, Mp: 95-96 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.12 (s, 1 H), 7.91 – 7.84 (m, 3 H), 7.63 – 7.60 (m, 1 H), 7.58 – 7.51 (m, 2 H), 5.93 (s, 1 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 4.04 (d, *J* = 5.2 Hz, 2 H), 1.25 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 169.3, 167.0, 135.8, 133.7, 133.6, 131.8, 129.5, 128.2, 128.0, 127.6, 127.0, 125.3, 61.9, 42.8, 14.2. MS:*m/z* 289 (M⁺).

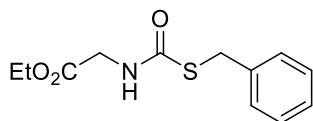
ethyl (((thiophen-2-ylthio)carbonyl)glycinate (3p)²



dark and brown oil; ¹H NMR (400 MHz, CDCl₃): δ 7.60 – 7.58 (m, 1 H), 7.33 – 7.32 (m, 1 H), 7.12 (dd, *J* = 5.2, 3.6 Hz, 1 H), 6.11 (s, 1 H), 4.18 (q, *J* = 7.2 Hz, 2 H), 4.00 (d, *J* = 5.2 Hz, 2 H), 1.25 (t, *J* = 7.2

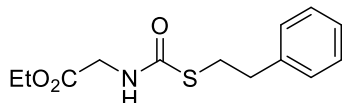
Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.2, 166.5, 137.9, 133.4, 128.5, 125.5, 61.9, 42.7, 14.2. MS:m/z 245 (M^+).

ethyl ((benzylthio)carbonyl)glycinate (3q)¹



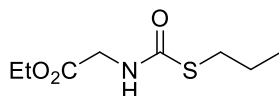
yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.27 (m, 4 H), 7.25 – 7.22 (m, 1 H), 5.99 (s, 1 H), 4.22 (q, $J = 7.2$ Hz, 2 H), 4.17 (s, 2 H), 4.07 (d, $J = 5.2$ Hz, 2 H), 1.28 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.5, 167.5, 138.1, 128.9, 128.7, 127.4, 61.9, 42.9, 34.3, 14.3. MS:m/z 253 (M^+).

ethyl ((phenethylthio)carbonyl)glycinate (3r)¹



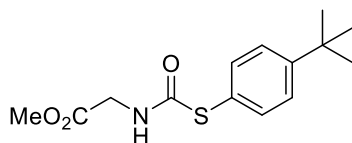
yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.32 – 7.28 (m, 2 H), 7.23 – 7.20 (m, 3 H), 5.95 (s, 1 H), 4.23 (q, $J = 7.2$ Hz, 2 H), 4.07 (d, $J = 5.2$ Hz, 2 H), 3.16 (t, $J = 7.2$ Hz, 2 H), 2.92 (t, $J = 8.4$ Hz, 2 H), 1.29 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.6, 167.8, 140.2, 128.8, 128.6, 126.6, 61.9, 42.8, 36.8, 31.5, 14.3. MS:m/z 267 (M^+).

ethyl ((propylthio)carbonyl)glycinate (3s)*



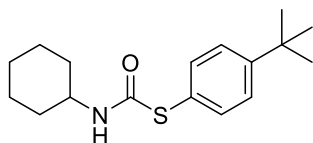
dark and brown oil; ^1H NMR (400 MHz, CDCl_3): δ 6.20 (s, 1 H), 4.17 (q, $J = 7.2$ Hz, 2 H), 4.05 (d, $J = 5.2$ Hz, 2 H), 2.84 (t, $J = 7.2$ Hz, 2 H), 1.58 (q, $J = 7.2$ Hz, 2 H), 1.23 (t, $J = 7.2$ Hz, 3 H), 0.918 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.7, 168.3, 61.7, 42.7, 31.9, 23.7, 14.1, 13.2; HRMS (ESI) m/z calcd. for $\text{C}_8\text{H}_{15}\text{NO}_3\text{S}$ [$\text{M}+\text{H}$] $^+$: 206.0845, found 206.0852.

methyl (((4-(tert-butyl)phenyl)thio)carbonyl)glycinate (3t)*



Light yellow solid, Mp: 76-77 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.51 – 7.49 (m, 2 H), 7.45 – 7.43 (m, 2 H), 5.90 (s, 1 H), 4.04 (d, $J = 5.2$ Hz, 2 H), 3.74 (s, 3 H), 1.33 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.9, 167.5, 153.5, 135.4, 126.9, 124.5, 54.6, 42.6, 35.0, 31.3; HRMS (ESI) m/z calcd. for $\text{C}_{14}\text{H}_{19}\text{NO}_3\text{S}$ [$\text{M}+\text{H}$] $^+$: 282.1158, found 282.1165.

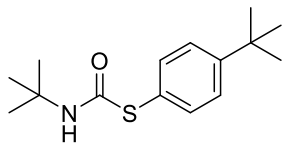
S-(4-(tert-butyl)phenyl) cyclohexylcarbamothioate (3u)⁴



yellow solid, Mp: 53-54 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.47 (d, $J = 8.4$ Hz, 2 H), 7.42 (d, $J = 8.4$ Hz, 2 H), 5.26 (s, 1 H), 3.73 (s, 1 H), 1.88 – 1.86 (m, 2 H), 1.67 – 1.54 (m, 4 H), 1.32 (s, 9 H), 1.17 –

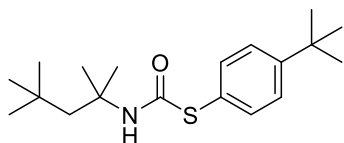
1.09 (m, 4 H); ^{13}C NMR (100 MHz, CDCl_3): δ 165.5, 153.0, 135.2, 126.6, 50.5, 34.9, 32.9, 31.4, 31.3, 25.5, 24.6. MS:m/z 291 (M^+).

***S*-(4-(*tert*-butyl)phenyl) *tert*-butylcarbamothioate (3v)³**



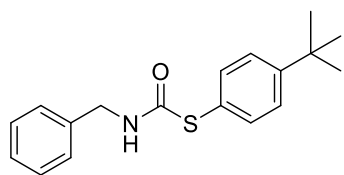
Light yellow solid, Mp: 99-100 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.44 (dd, $J = 16.0, 8.8$ Hz, 4 H), 5.20 (s, 1 H), 1.32 (s, 9 H), 1.31 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.6, 152.7, 135.2, 126.5, 125.6, 53.5, 34.9, 31.3, 29.0. MS:m/z 265 (M^+).

S*-(4-(*tert*-butyl)phenyl) (2,4,4-trimethylpentan-2-yl)carbamothioate (3w)



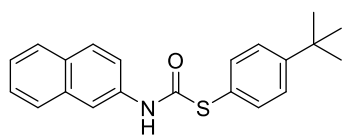
light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.44 (q, $J = 8.8$ Hz, 4 H), 5.20 (s, 1 H), 1.61 (s, 2 H), 1.36 (s, 6 H), 1.31 (s, 9 H), 0.92 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.4, 151.8, 134.3, 125.5, 124.7, 56.2, 51.1, 33.7, 30.5, 30.3, 30.2, 28.0; HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{31}\text{NOS}$ [$\text{M}+\text{H}$]⁺: 322.2199, found 322.2204.

S*-(4-(*tert*-butyl)phenyl) benzylcarbamothioate (3x)



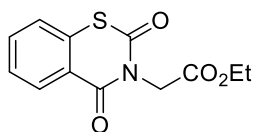
light yellow oil; ^1H NMR (500 MHz, CDCl_3): δ 7.48 (d, $J = 8.5$ Hz, 2 H), 7.41 (d, $J = 8.5$ Hz, 2 H), 7.33 – 7.30 (m, 2 H), 7.27 – 7.25 (m, 1 H), 7.22 – 7.21 (m, 2 H), 5.65 (s, 1 H), 4.44 (d, $J = 6.0$ Hz, 2 H), 1.30 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3): δ 166.9, 153.3, 137.8, 135.4, 128.9, 127.8, 127.7, 126.8, 125.0, 45.4, 34.9, 31.3; HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{31}\text{NOS}$ [$\text{M}+\text{H}$]⁺: 300.1344, found 300.1352.

S*-(4-(*tert*-butyl)phenyl) naphthalen-2-ylcarbamothioate (3y)



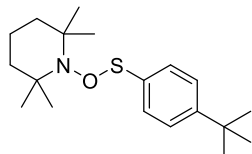
light yellow oil; ^1H NMR (500 MHz, CDCl_3): δ 8.05 (s, 1 H), 7.76 – 7.71 (m, 3 H), 7.55 (d, $J = 8.0$ Hz, 2 H), 7.48 (d, $J = 8.0$ Hz, 2 H), 7.45 – 7.37 (m, 2 H), 7.30 – 7.25 (m, 2 H), 1.34 (s, 9 H); ^{13}C NMR (125 MHz, CDCl_3): δ 165.1, 153.6, 135.5, 135.1, 133.9, 130.8, 129.0, 127.8, 127.7, 126.9, 126.8, 125.3, 124.6, 119.5, 116.6, 35.0, 31.3; HRMS (ESI) m/z calcd. for $\text{C}_{19}\text{H}_{31}\text{NOS}$ [$\text{M}+\text{H}$]⁺: 336.1334, found 336.1341.

ethyl* 2-(2,4-dioxo-2*H*-benzo[e][1,3]thiazin-3(4*H*)-yl)acetate (7)



red oil; ^1H NMR (400 MHz, CDCl_3): δ 8.37 (d, $J = 8.8$ Hz, 1 H), 7.63 (t, $J = 6.8$ Hz, 1 H), 7.44 (t, $J = 8.0$ Hz, 1 H), 7.33 (d, $J = 8.0$ Hz, 1 H), 4.88 (s, 2 H), 4.23 (q, $J = 7.2$ Hz, 2 H), 1.28 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.4, 164.5, 163.0, 134.4, 132.3, 131.9, 127.6, 124.8, 122.4, 61.9, 43.0, 14.2; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{11}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$: 266.0482, found 266.0495.

1-(((4-(tert-butyl)phenyl)thio)oxy)-2,2,6,6-tetramethylpiperidine (8)⁵



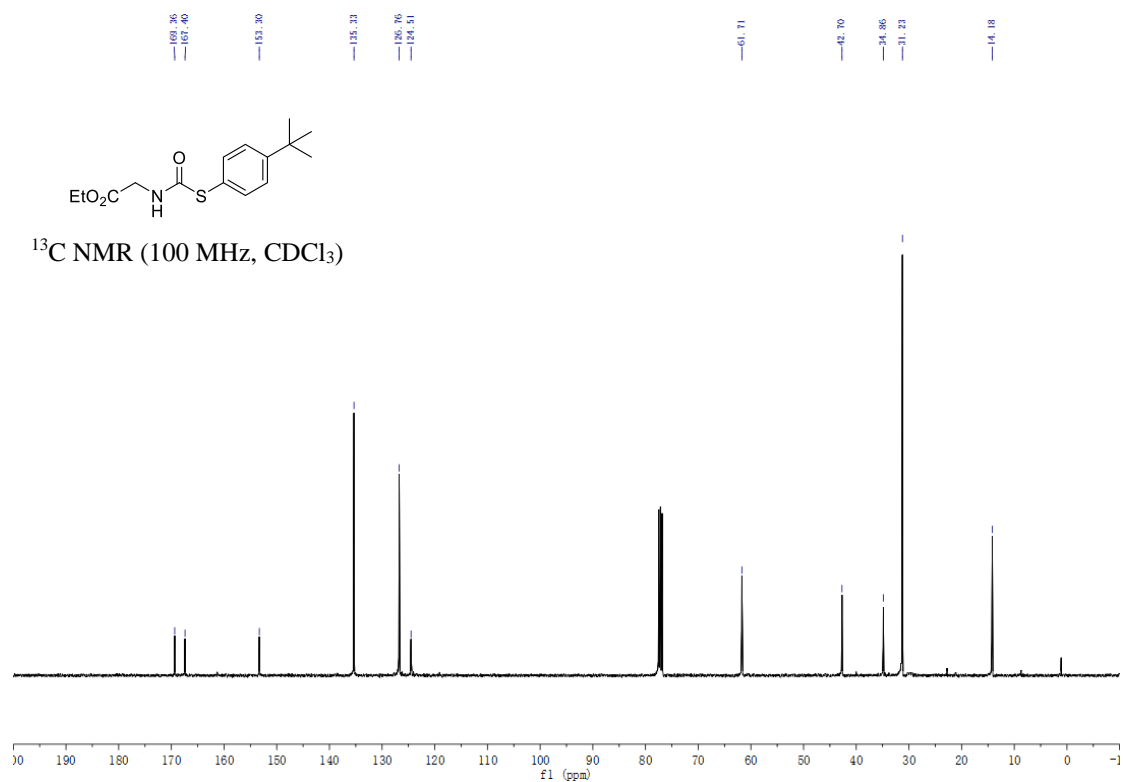
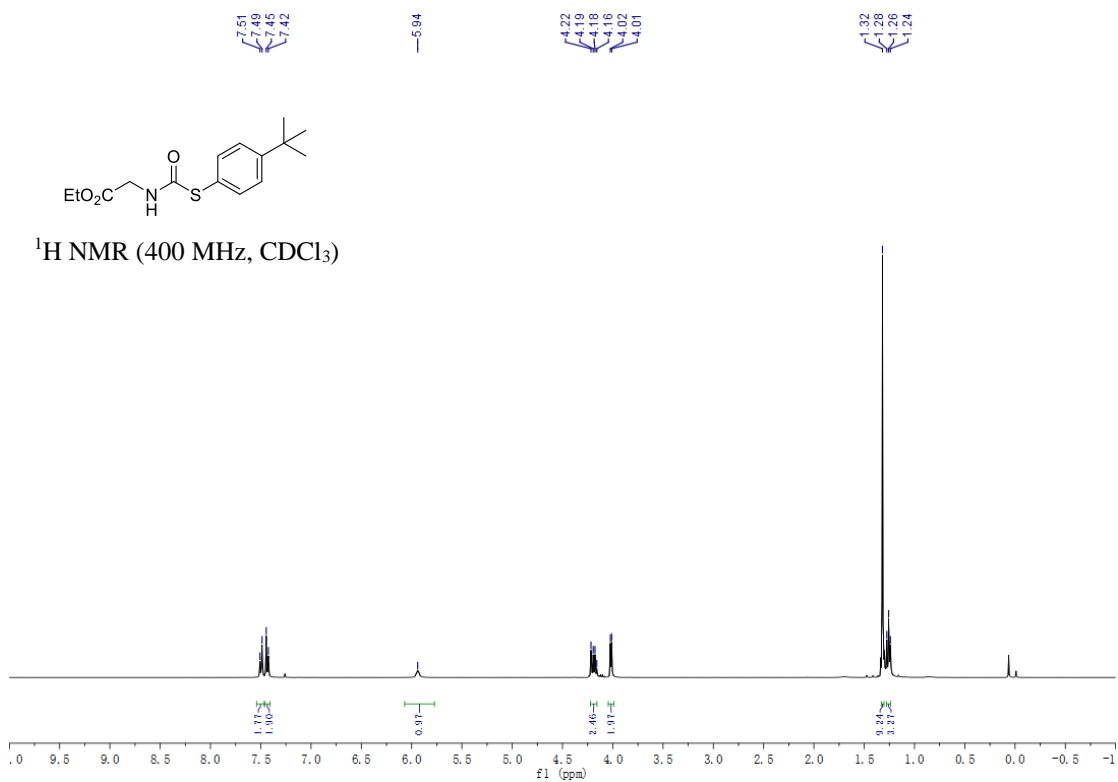
red oil; ^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, $J = 8.4$ Hz, 2 H), 7.47 (d, $J = 8.4$ Hz, 2 H), 1.67 – 1.51 (m, 15 H), 1.35 (s, 9 H), 0.99 – 0.91 (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.4, 146.8, 125.5, 125.3, 60.9, 58.4, 43.3, 41.2, 35.1, 34.5, 32.3, 31.1, 28.5, 27.74, 17.1.

3. References

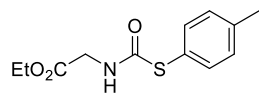
1. W. Wei.; P.-L. Bao.; H.-L. Yue.; S.-T. Liu.; L.-L. Wang.; Y.-D. Li.; D.-S. Yang., *Org. Lett.* **2018**, *20*, 5291–5295.
2. P.-L. Bao.; L.-L. Wang.; H.-L. Yue.; Y. Shao.; J.-W. Wen.; D.-S. Yang.; X.-H. Zhao.; H. Wang.; W. Wei., *J. Org. Chem.* **2019**, *84*, 2976–2983.
3. W.-H. Bao.; Z. Wang.; X. Tang.; Y.-F. Zhang.; J.-X. Tan.; Q. Zhu.; Z. Cao.; Y.-W. Lin.; W.-M. He., *Chin. Chem. Lett.* **2019**, *30*, 2259-2262.
4. W.-H. Bao.; C. Wu.; J.-T. Wang.; W. Xia.; P. Chen.; Z.-L. Tang.; X.-H. Xu.; W.-M. He., *Org. Biomol. Chem.* **2018**, *16*, 7025.
5. W.-K. Yuan.; J. Huang.; X. Xu.; L. Wang.; X.-Y. Tang., *Org. Lett.* **2021**, *23*, 18, 7139-7143.

4. ^1H , ^{13}C and ^{19}F NMR spectra of products

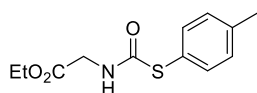
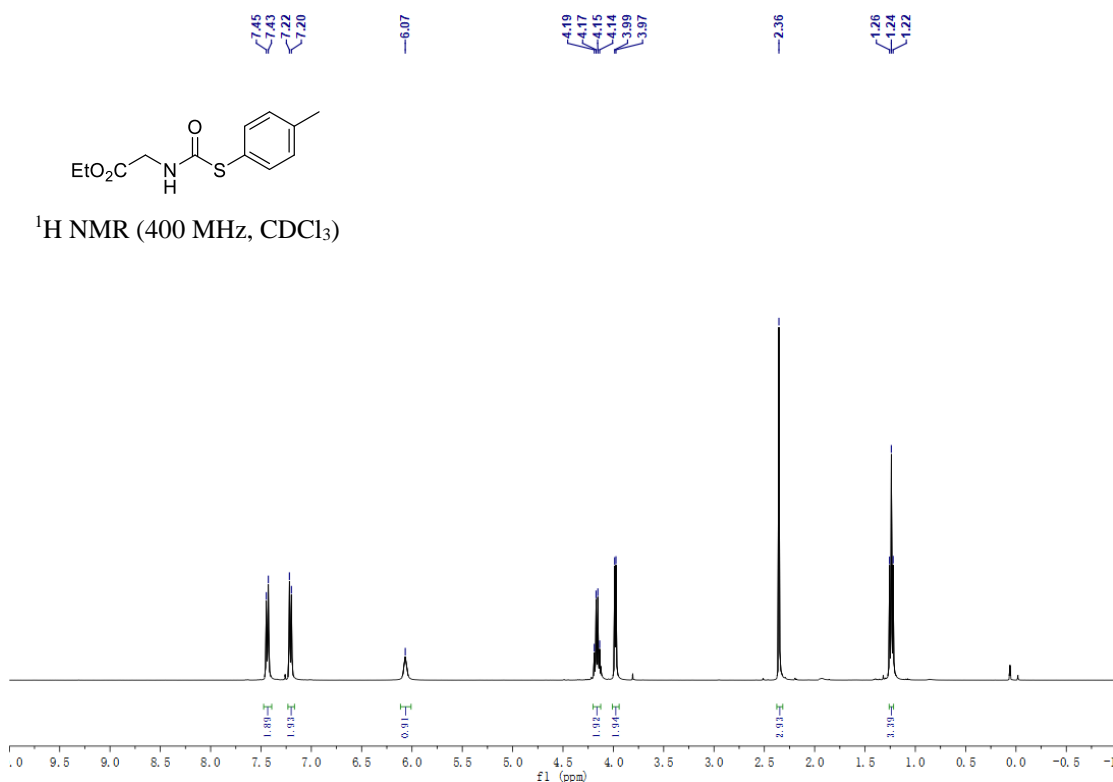
ethyl ((4-(tert-butyl)phenyl)thio)carbonyl)glycinate (3a)



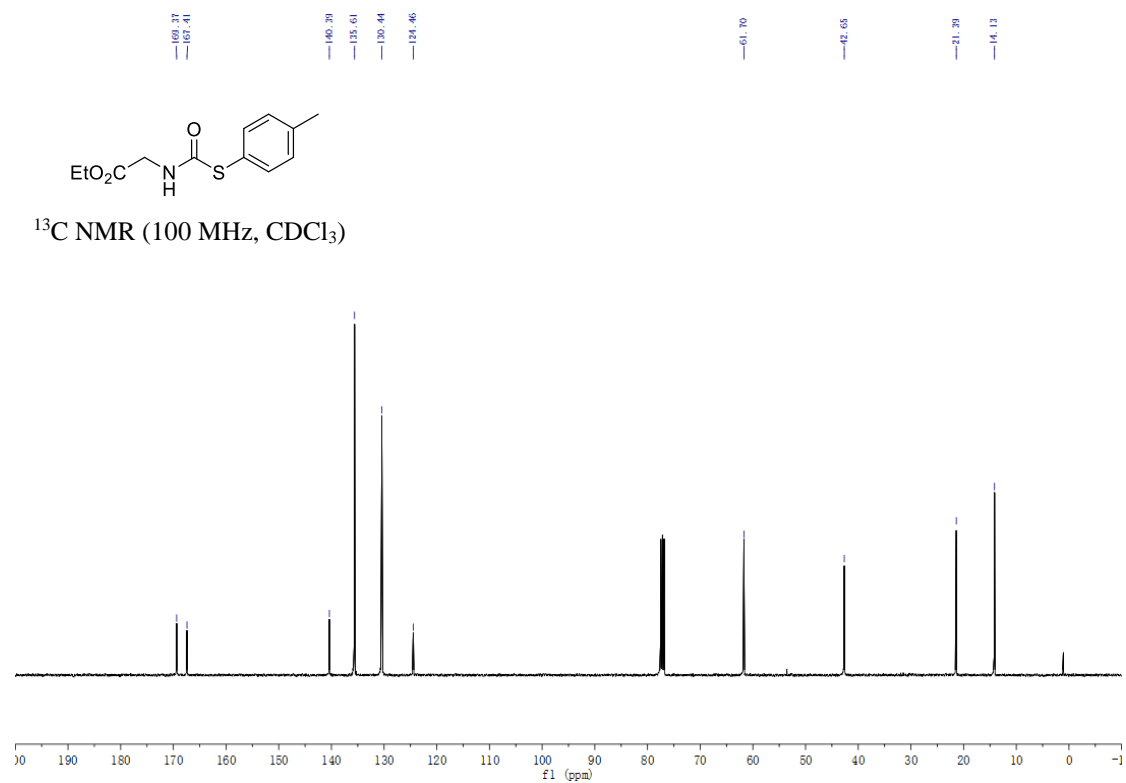
ethyl ((p-tolylthio)carbonyl)glycinate (3b)



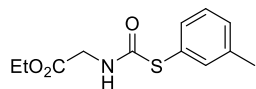
^1H NMR (400 MHz, CDCl_3)



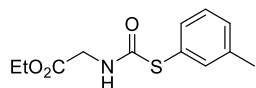
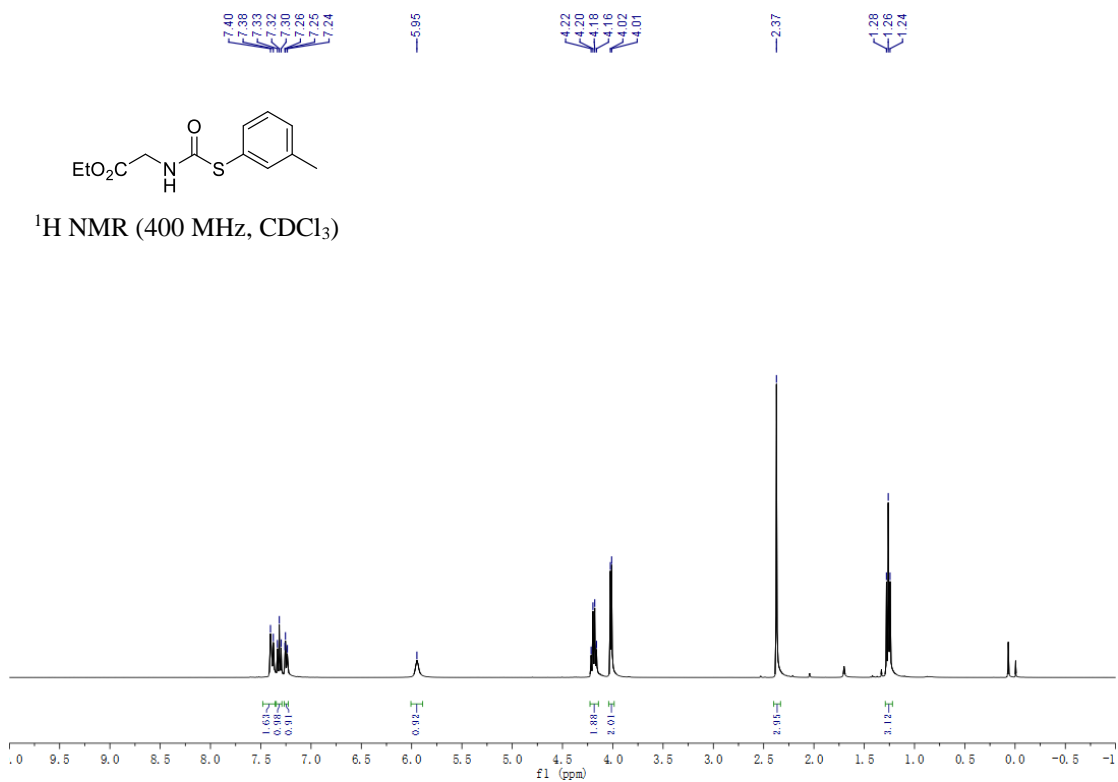
^{13}C NMR (100 MHz, CDCl_3)



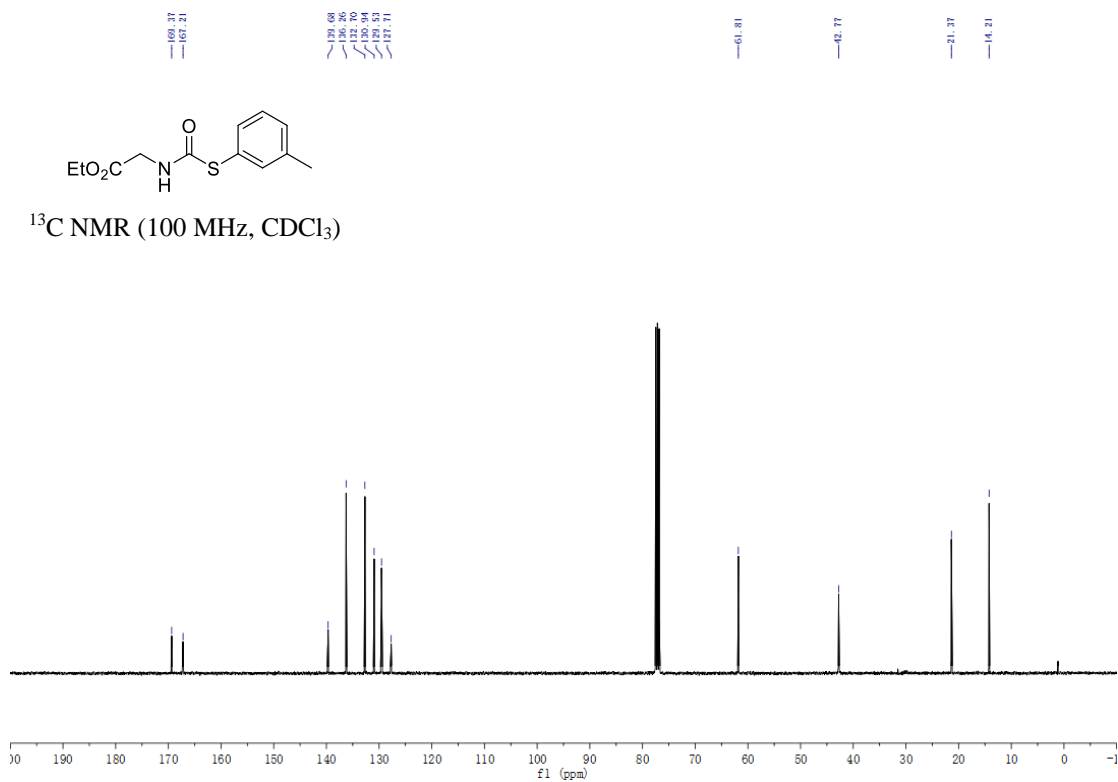
ethyl ((*m*-tolylthio)carbonyl)glycinate (3c)



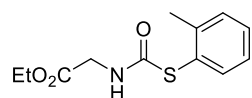
¹H NMR (400 MHz, CDCl₃)



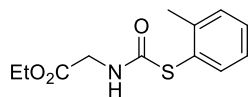
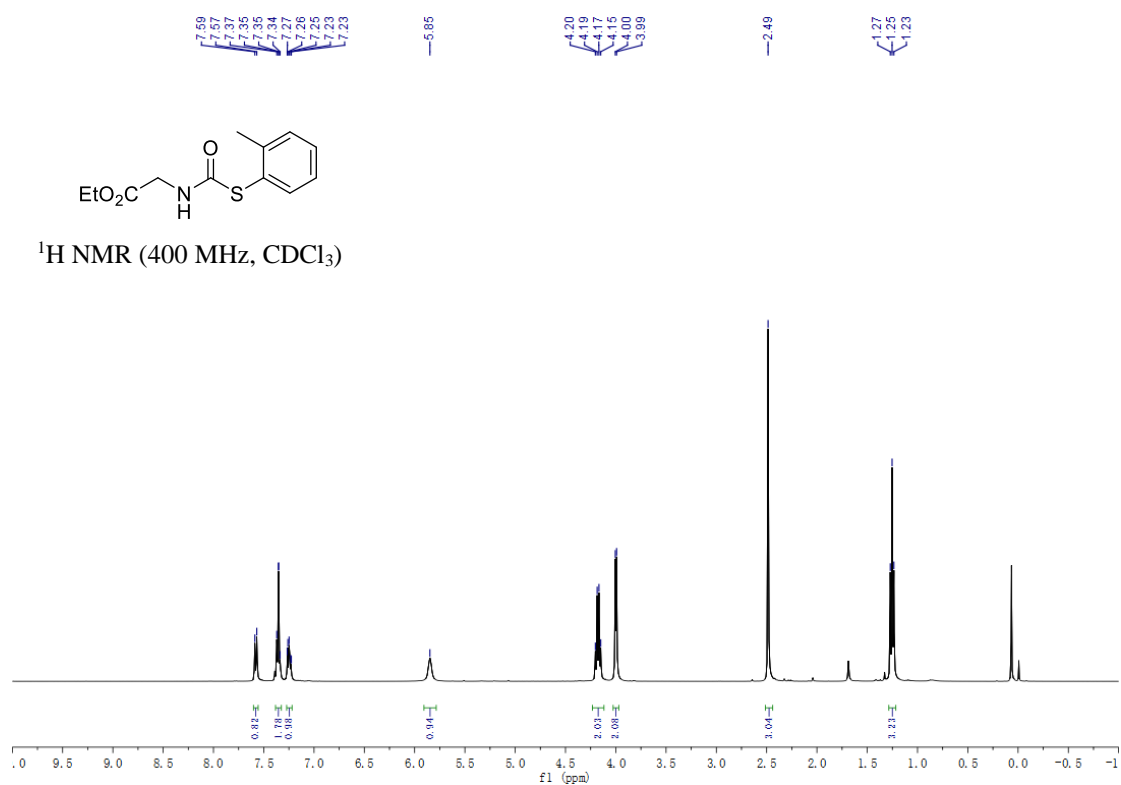
¹³C NMR (100 MHz, CDCl₃)



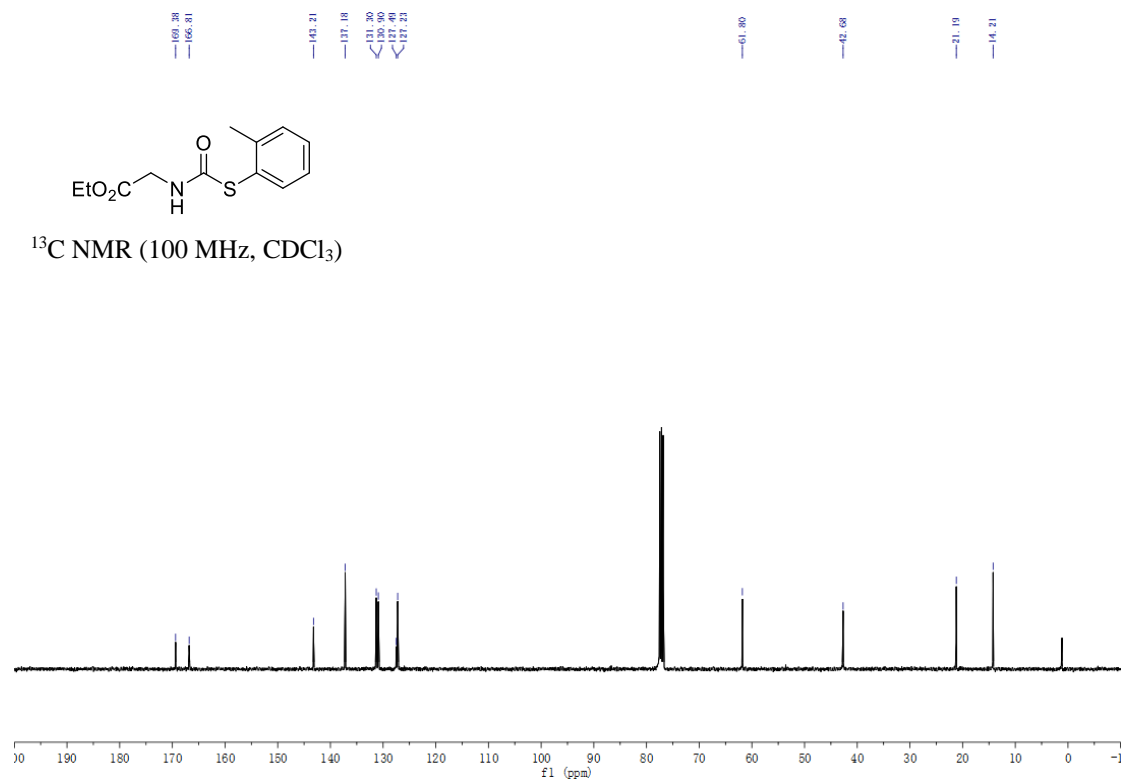
ethyl ((*o*-tolylthio)carbonyl)glycinate (3d)



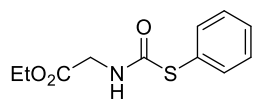
¹H NMR (400 MHz, CDCl₃)



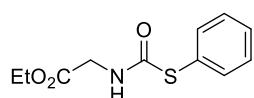
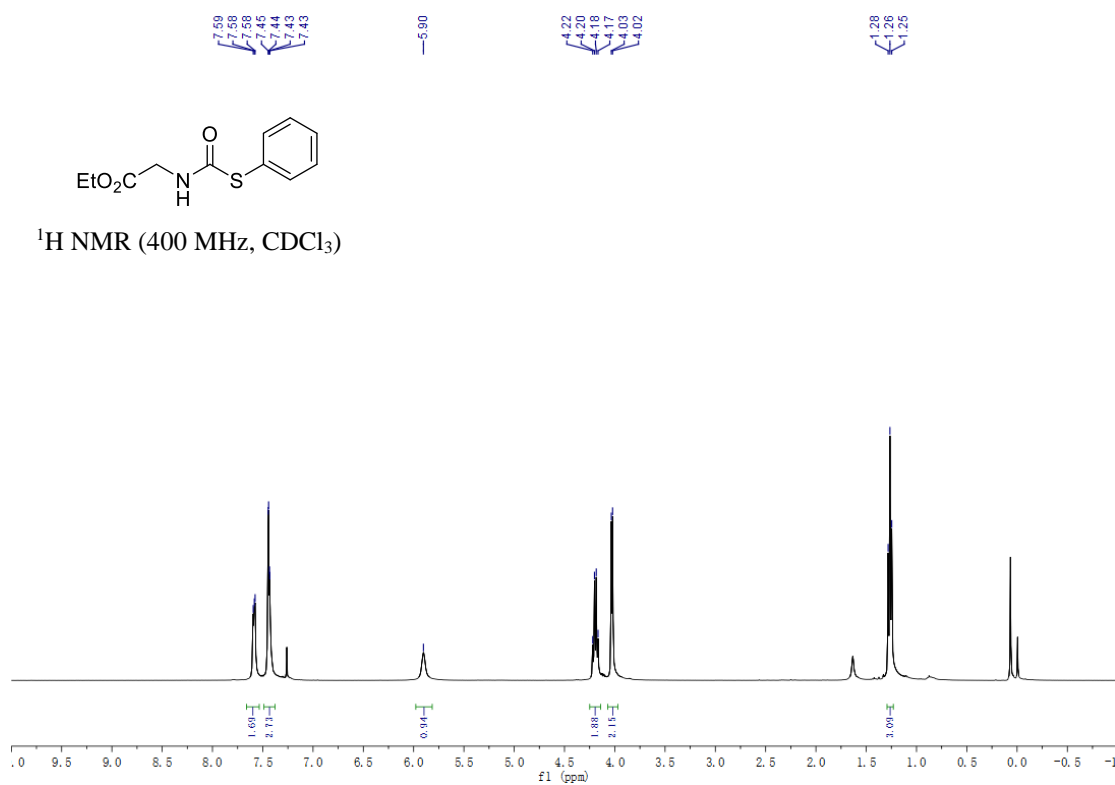
¹³C NMR (100 MHz, CDCl₃)



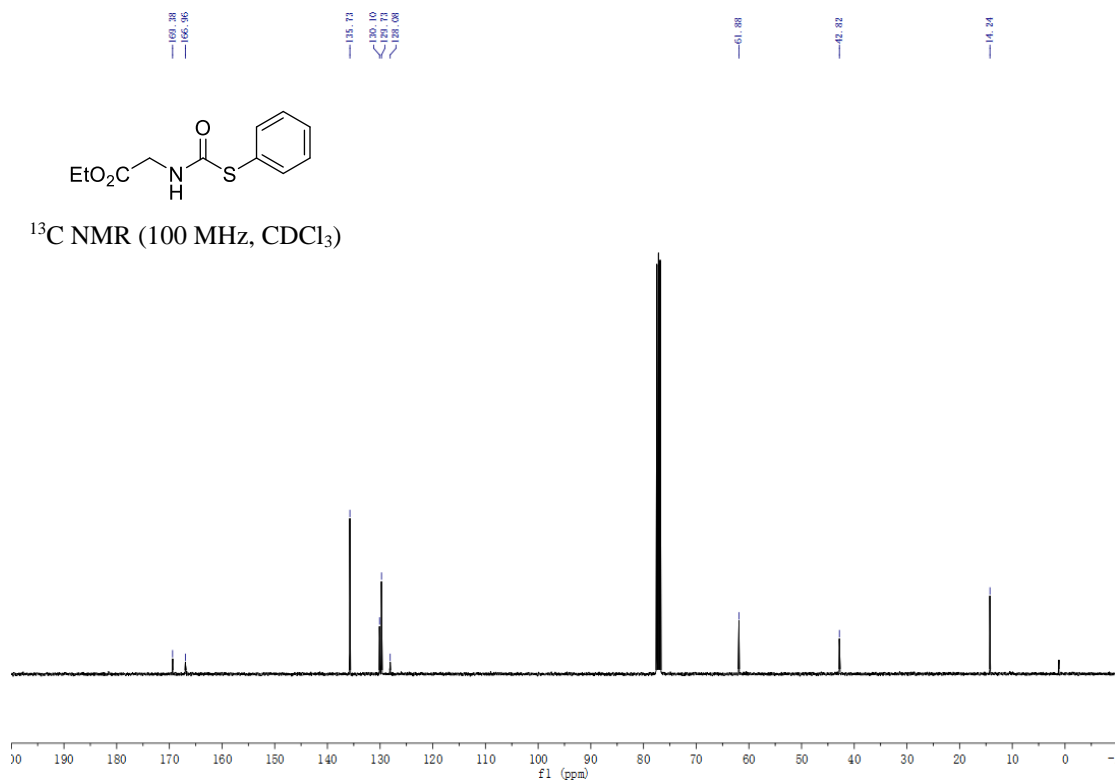
ethyl ((phenylthio)carbonyl)glycinate (3e)



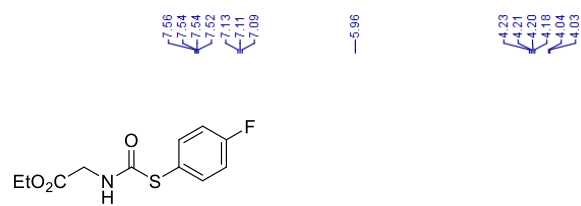
^1H NMR (400 MHz, CDCl_3)



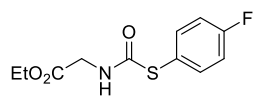
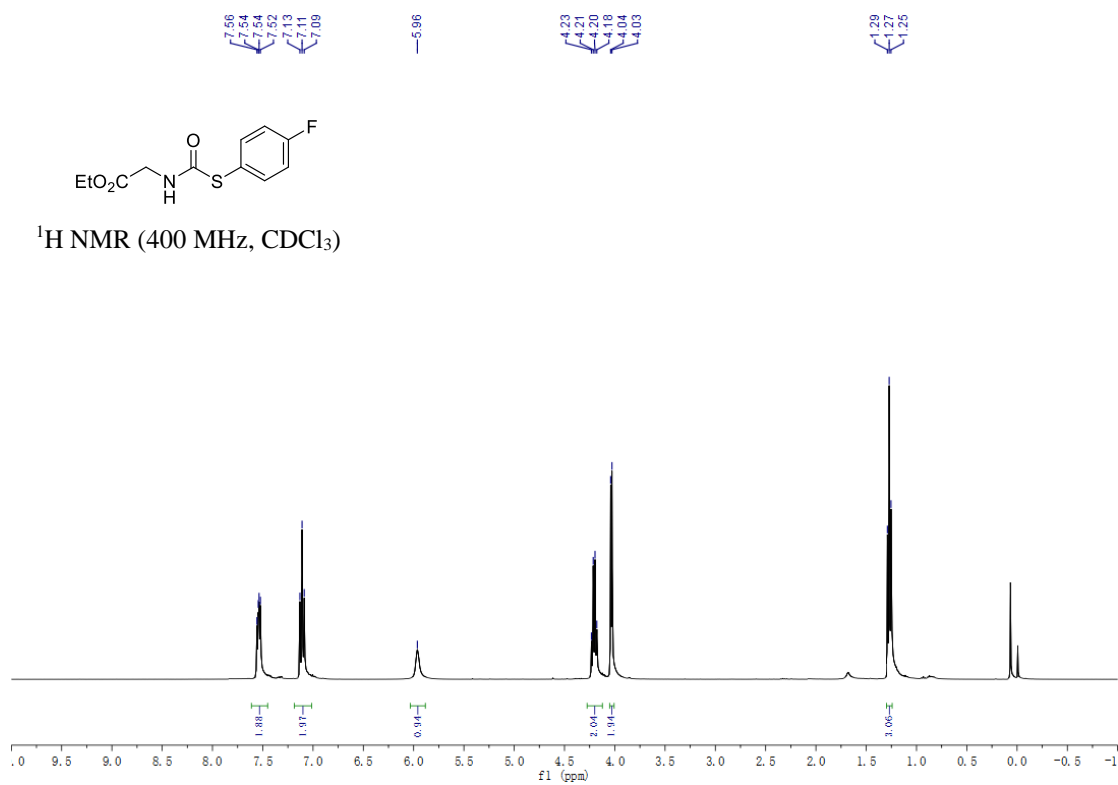
^{13}C NMR (100 MHz, CDCl_3)



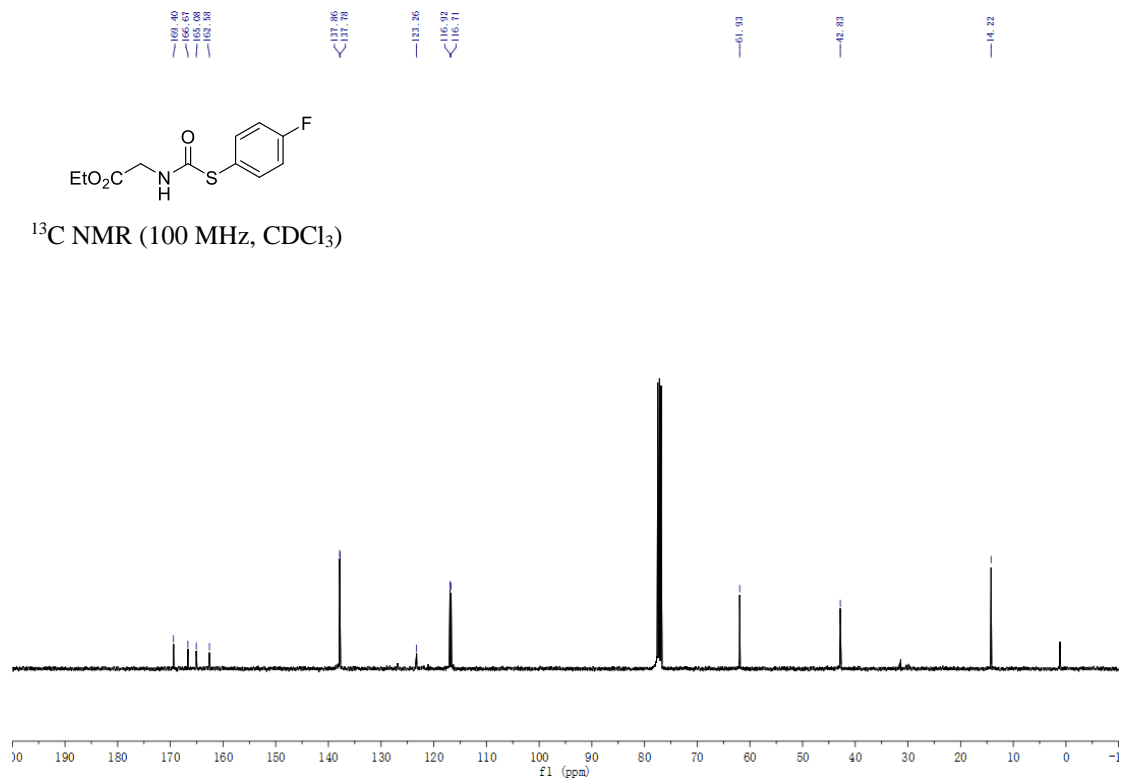
ethyl ((4-fluorophenyl)thio)carbonyl)glycinate (3f)

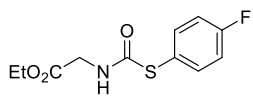


^1H NMR (400 MHz, CDCl_3)

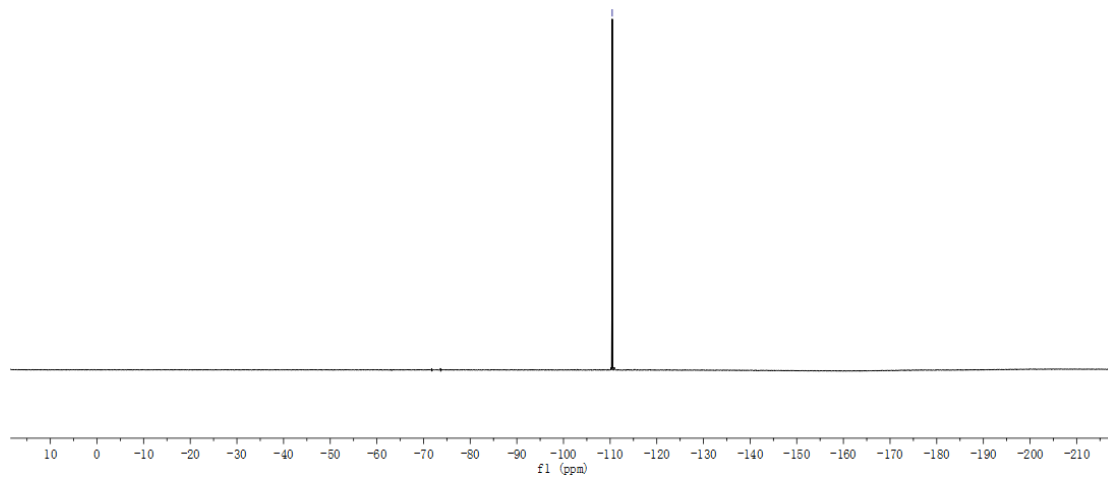


^{13}C NMR (100 MHz, CDCl_3)

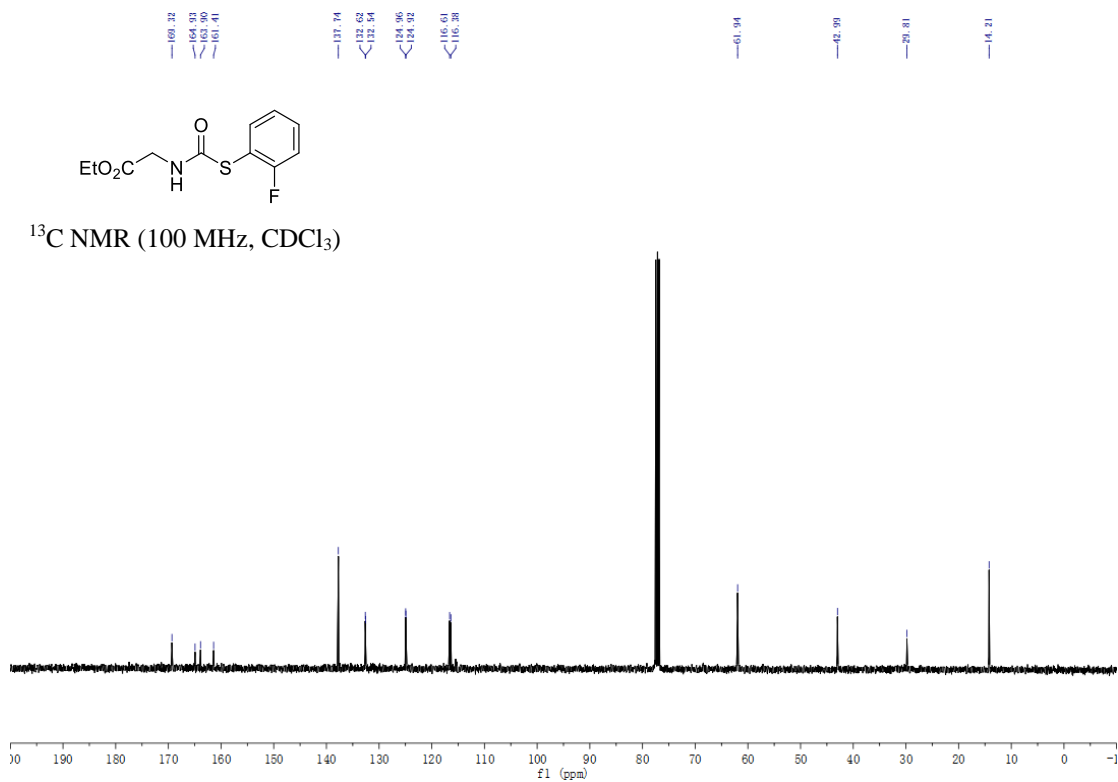
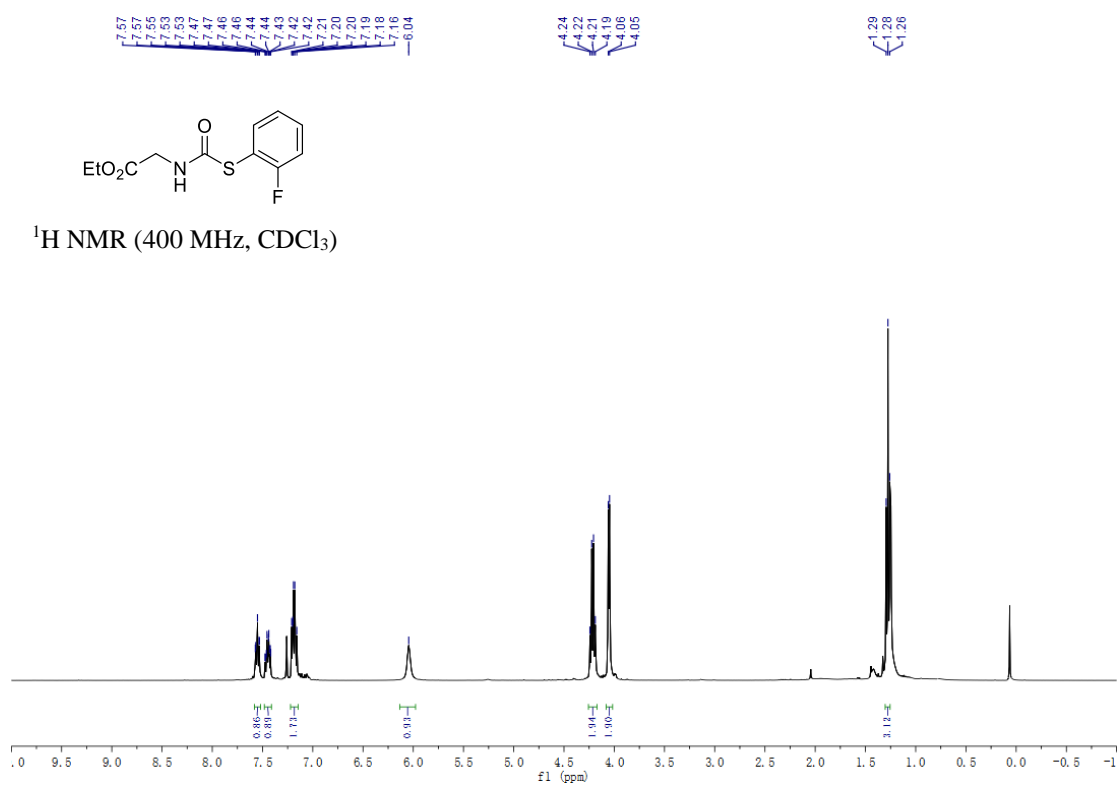


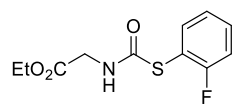


^{19}F NMR (376 MHz, CDCl_3)

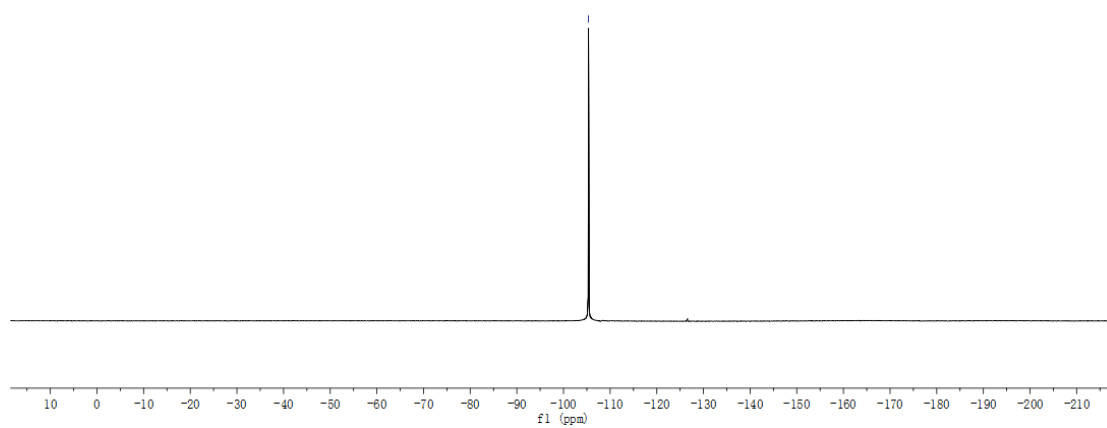


ethyl ((2-fluorophenyl)thio)carbonylglycinate (3g)

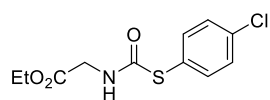




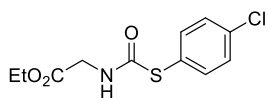
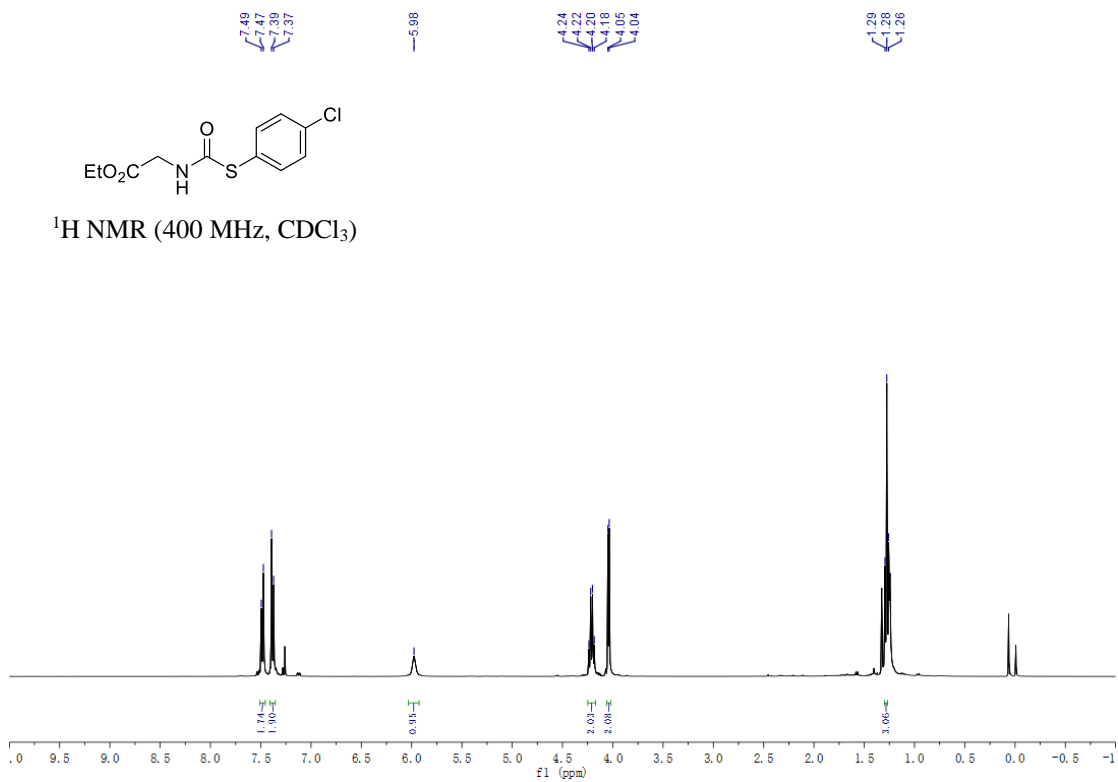
^{19}F NMR (376 MHz, CDCl_3)



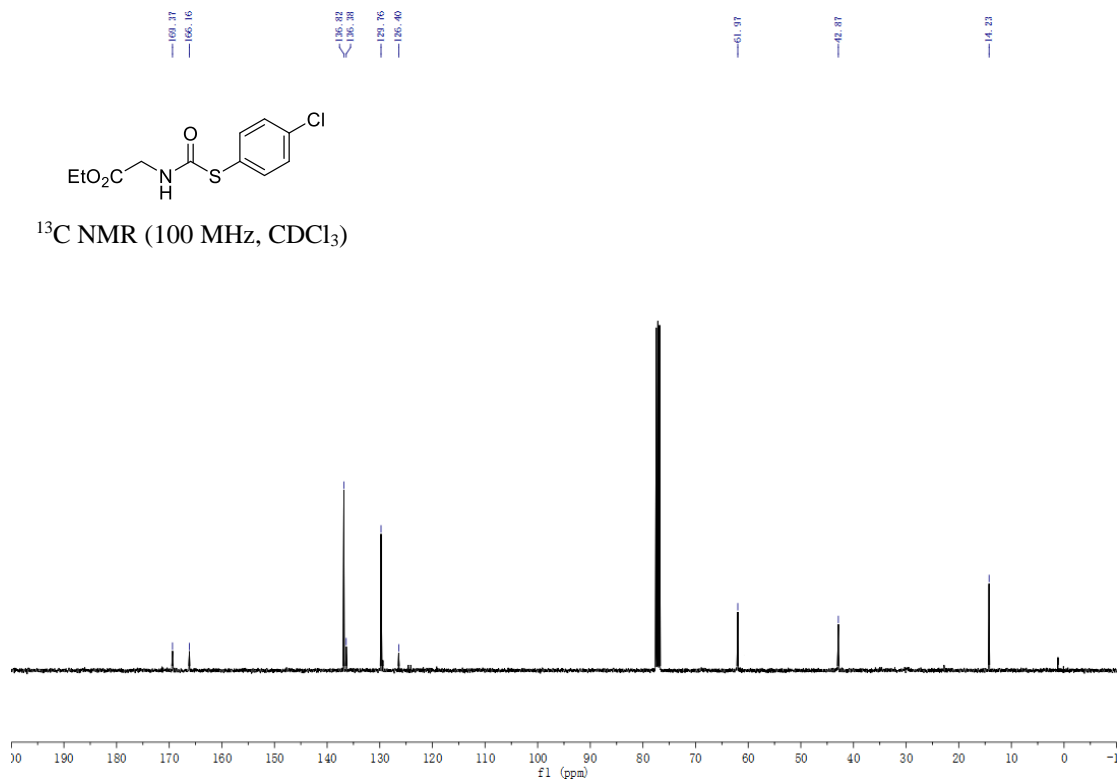
ethyl (((4-chlorophenyl)thio)carbonyl)glycinate (3h)



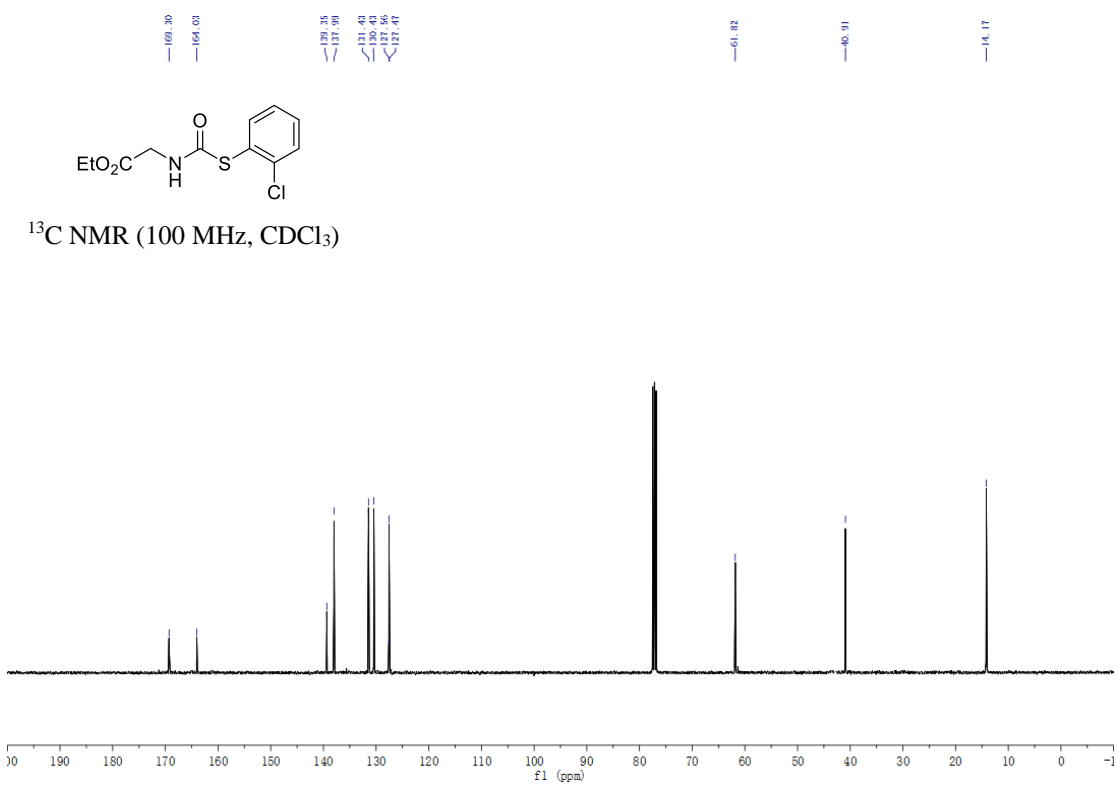
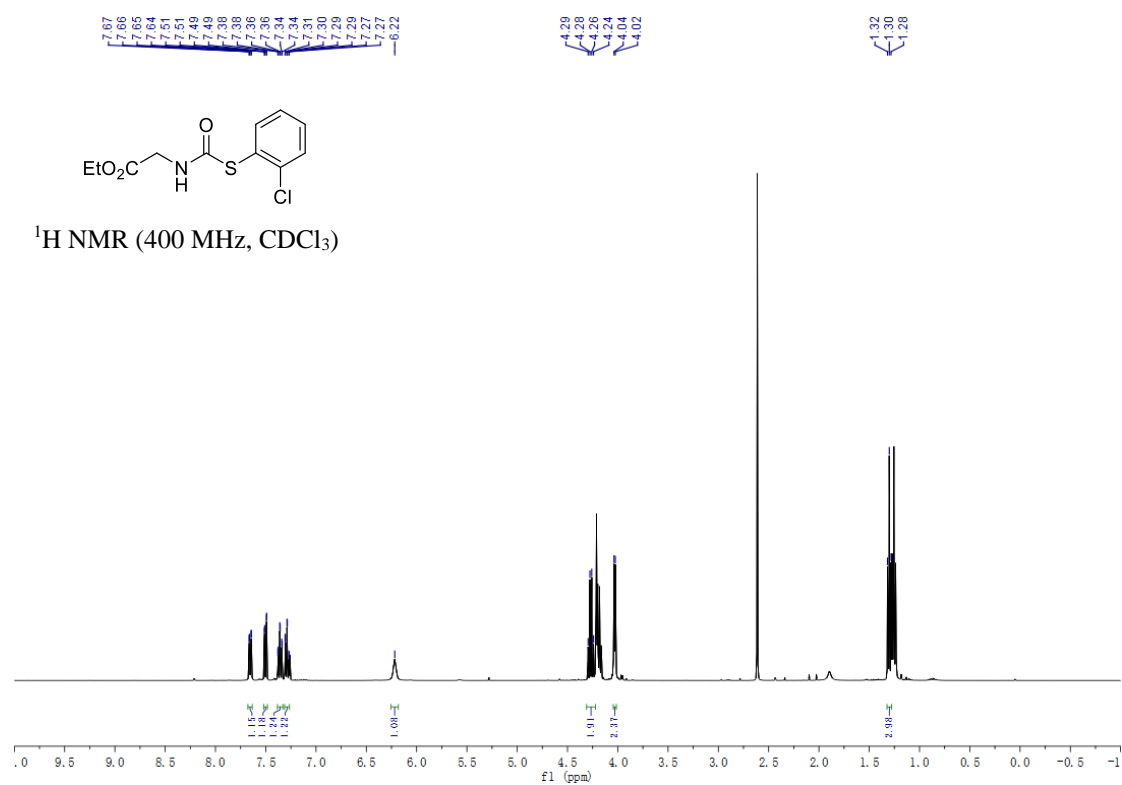
^1H NMR (400 MHz, CDCl_3)



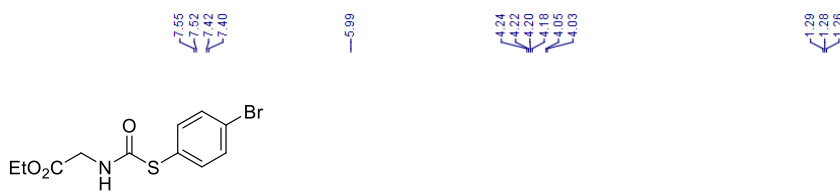
^{13}C NMR (100 MHz, CDCl_3)



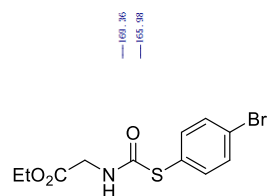
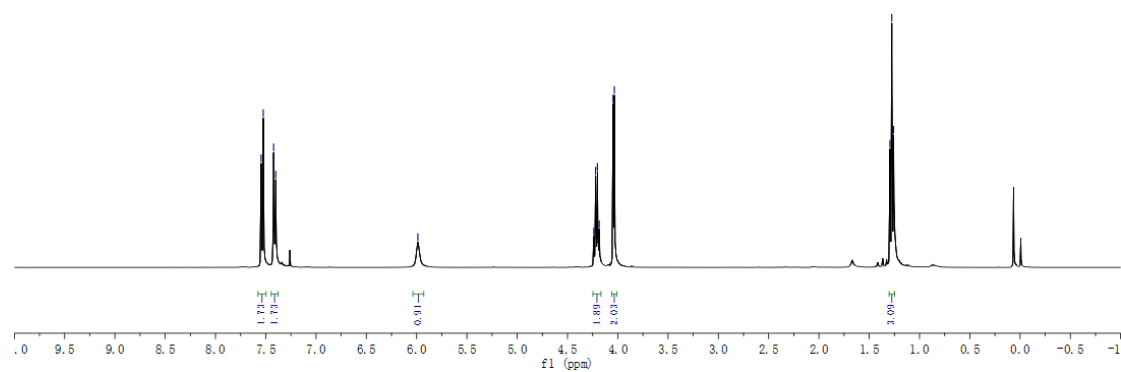
ethyl (((2-chlorophenyl)thio)carbonyl)glycinate (3i)



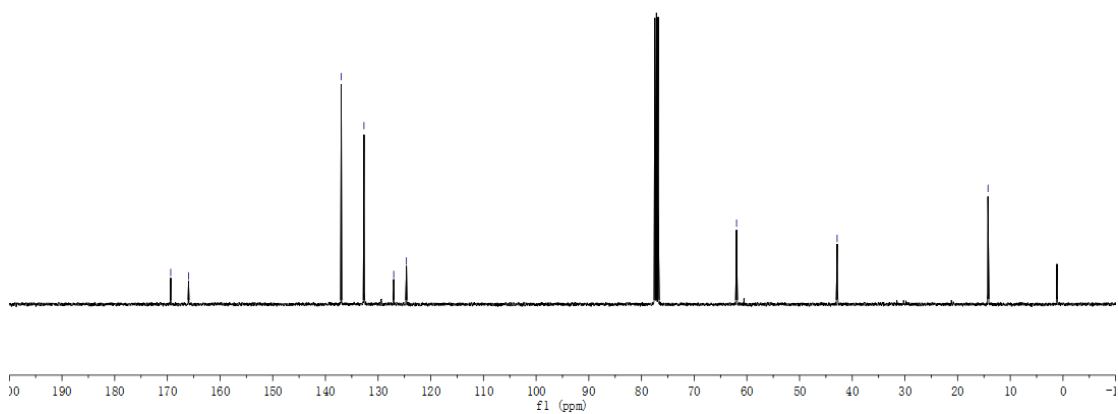
ethyl ((4-bromophenyl)thio)carbonylglycinate (3j)



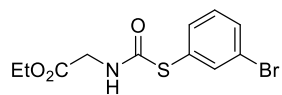
¹H NMR (400 MHz, CDCl₃)



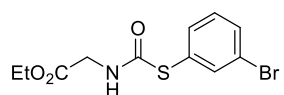
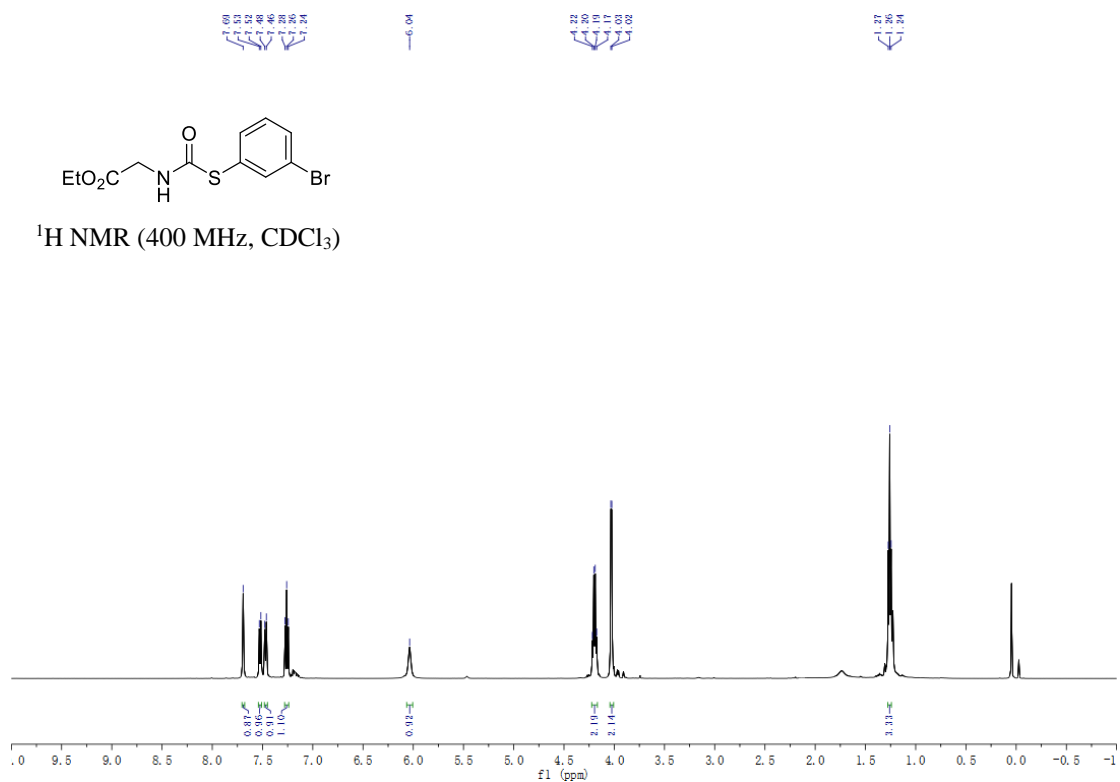
¹³C NMR (100 MHz, CDCl₃)



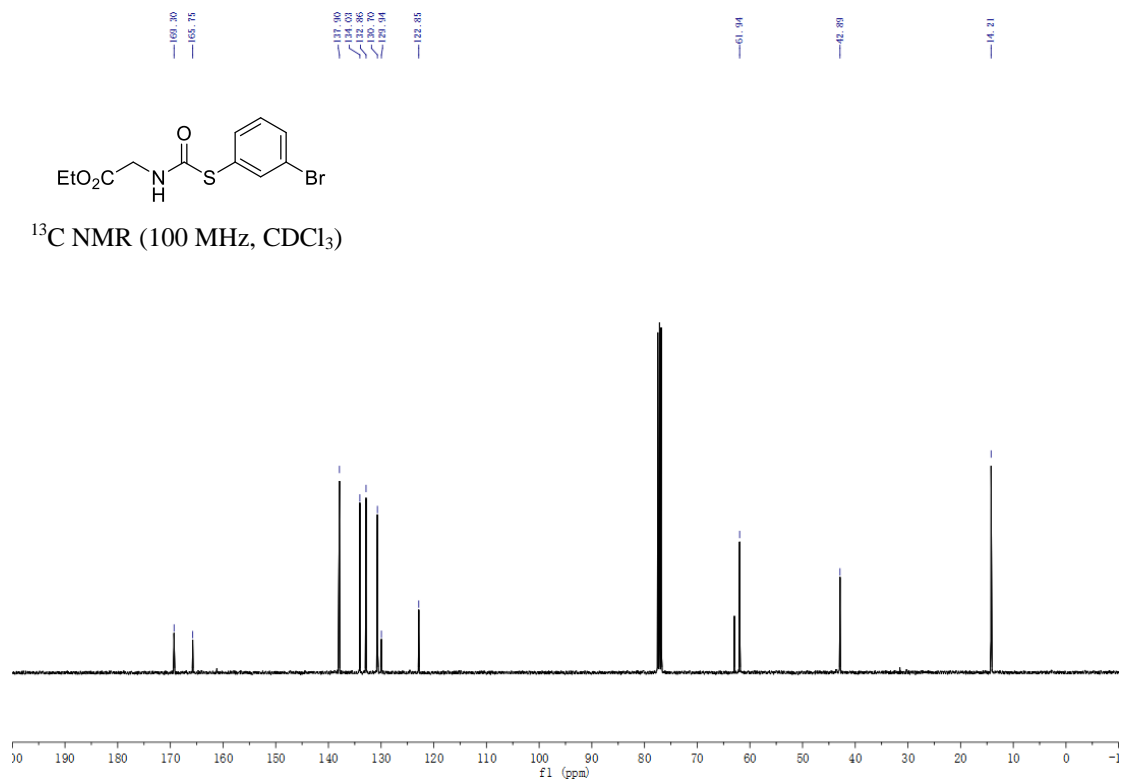
ethyl ((3-bromophenyl)thio)carbonylglycinate (3k)



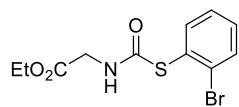
^1H NMR (400 MHz, CDCl_3)



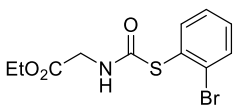
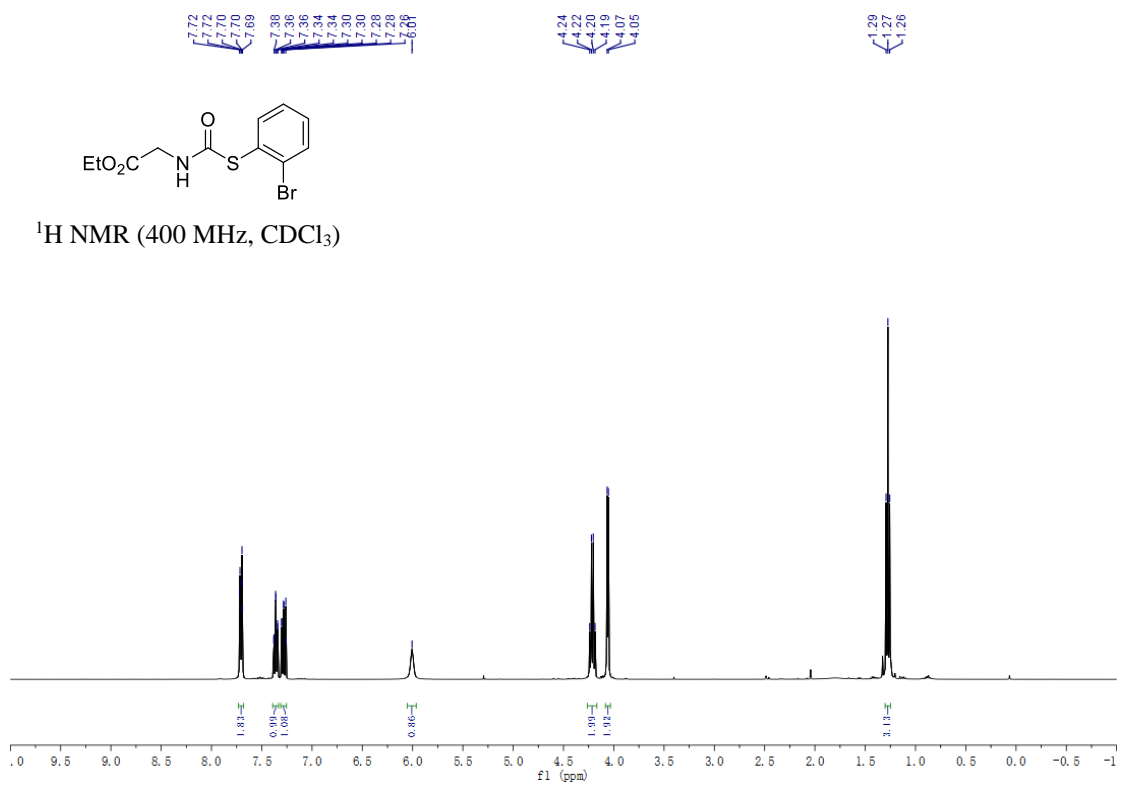
^{13}C NMR (100 MHz, CDCl_3)



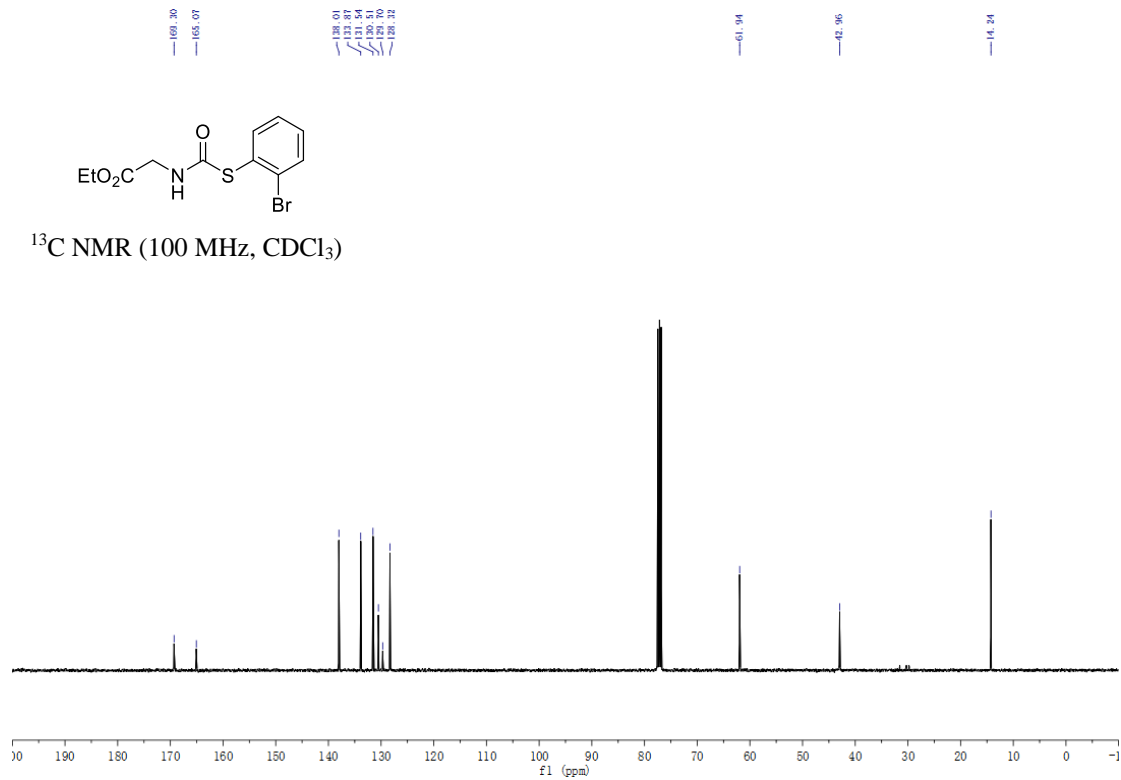
ethyl (((2-bromophenyl)thio)carbonyl)glycinate (31)



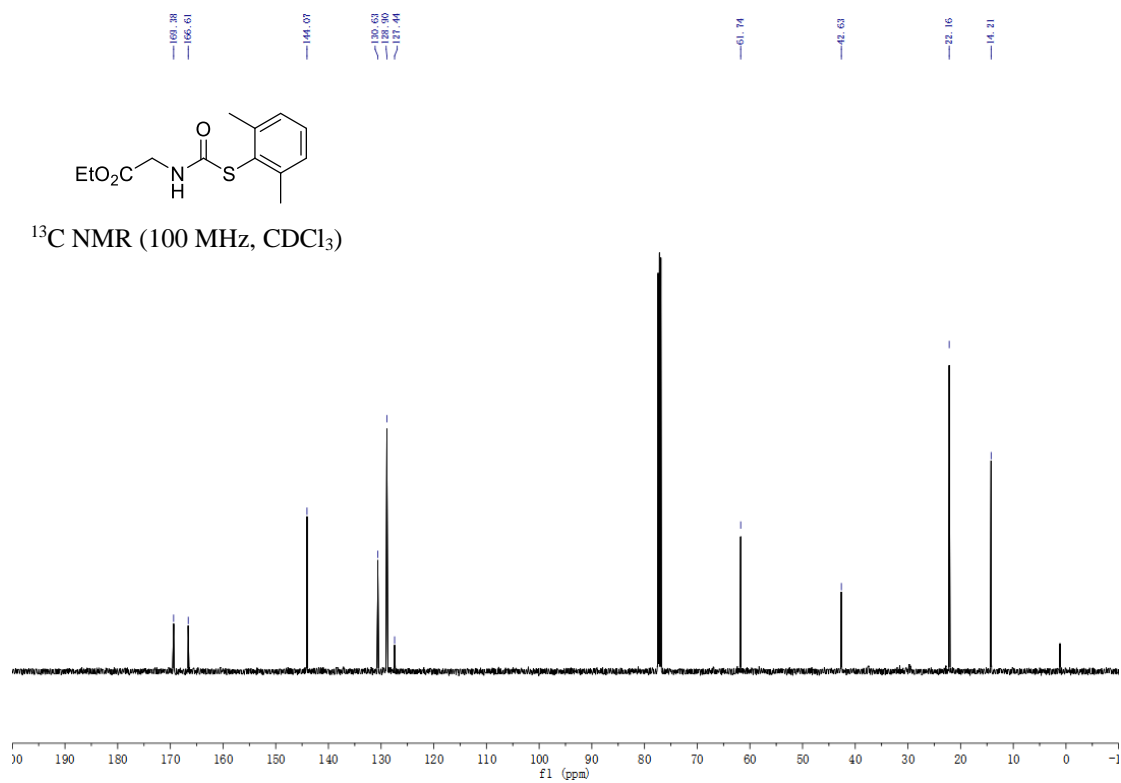
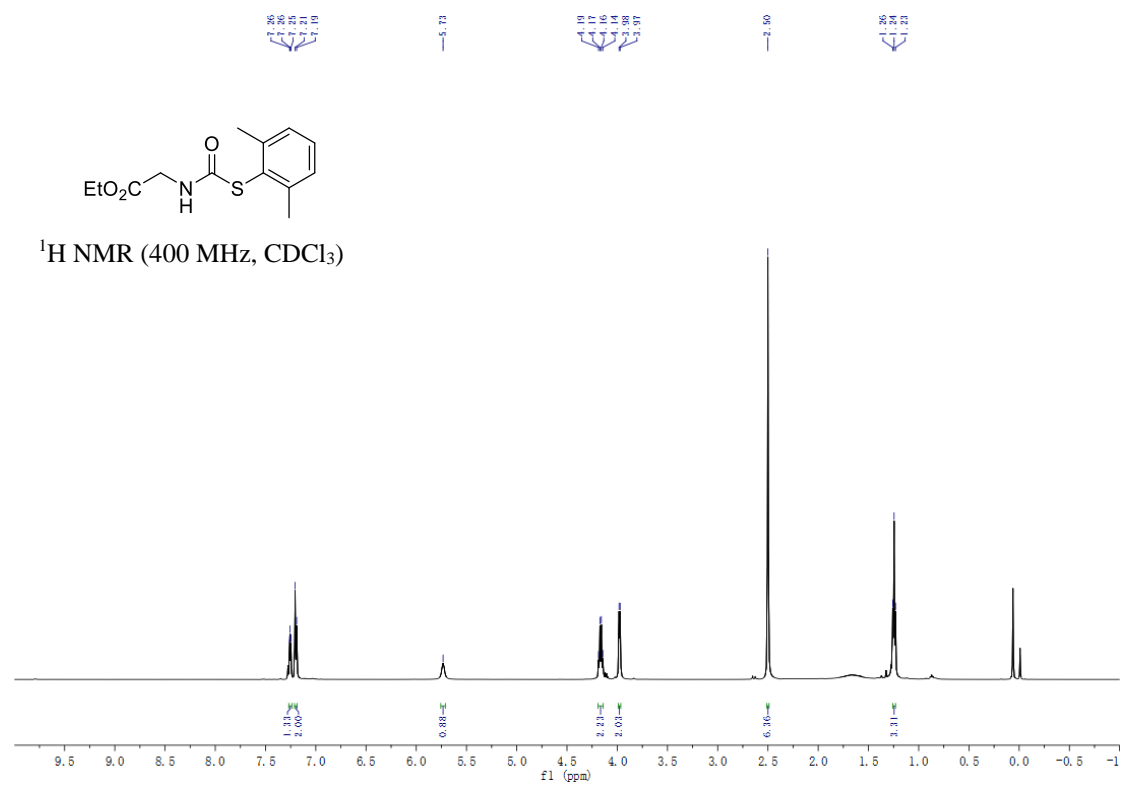
^1H NMR (400 MHz, CDCl_3)



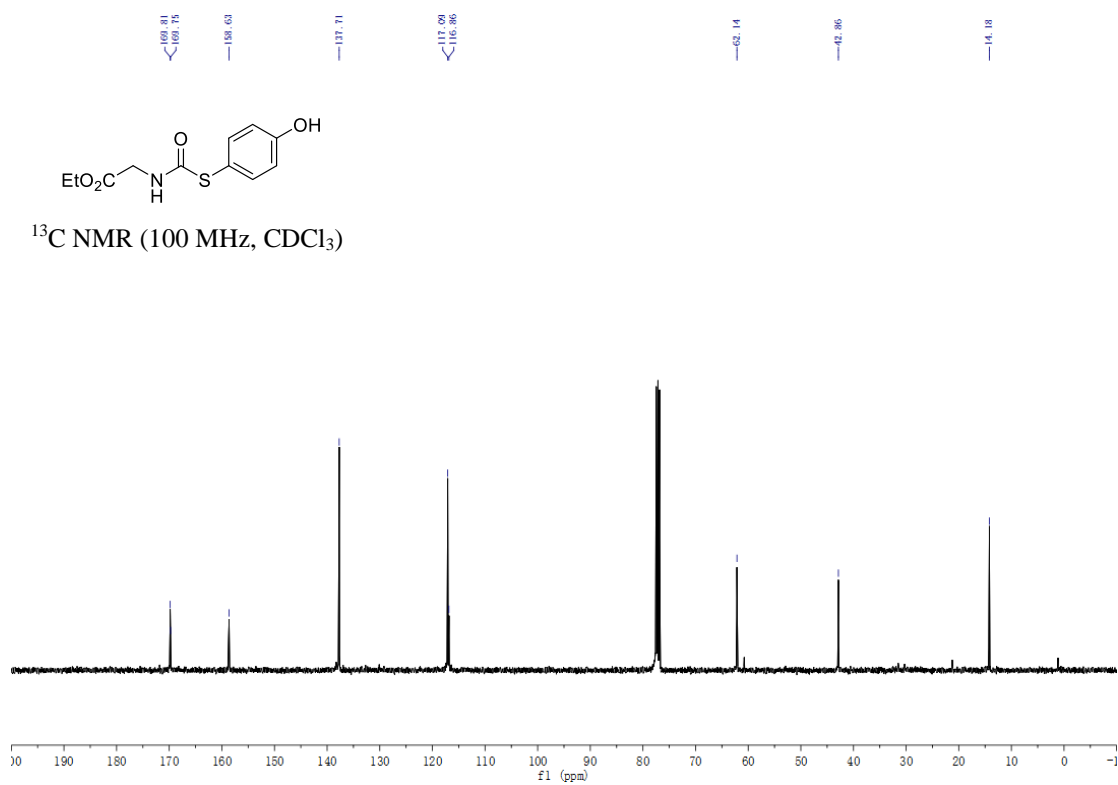
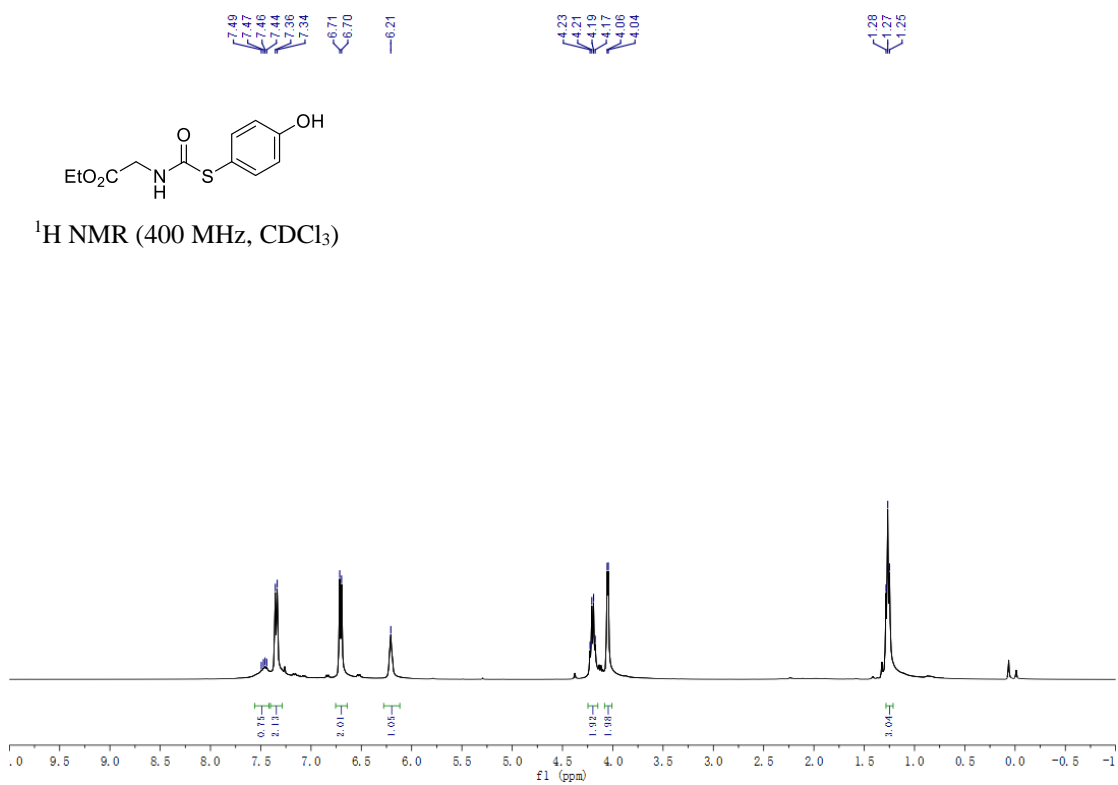
^{13}C NMR (100 MHz, CDCl_3)



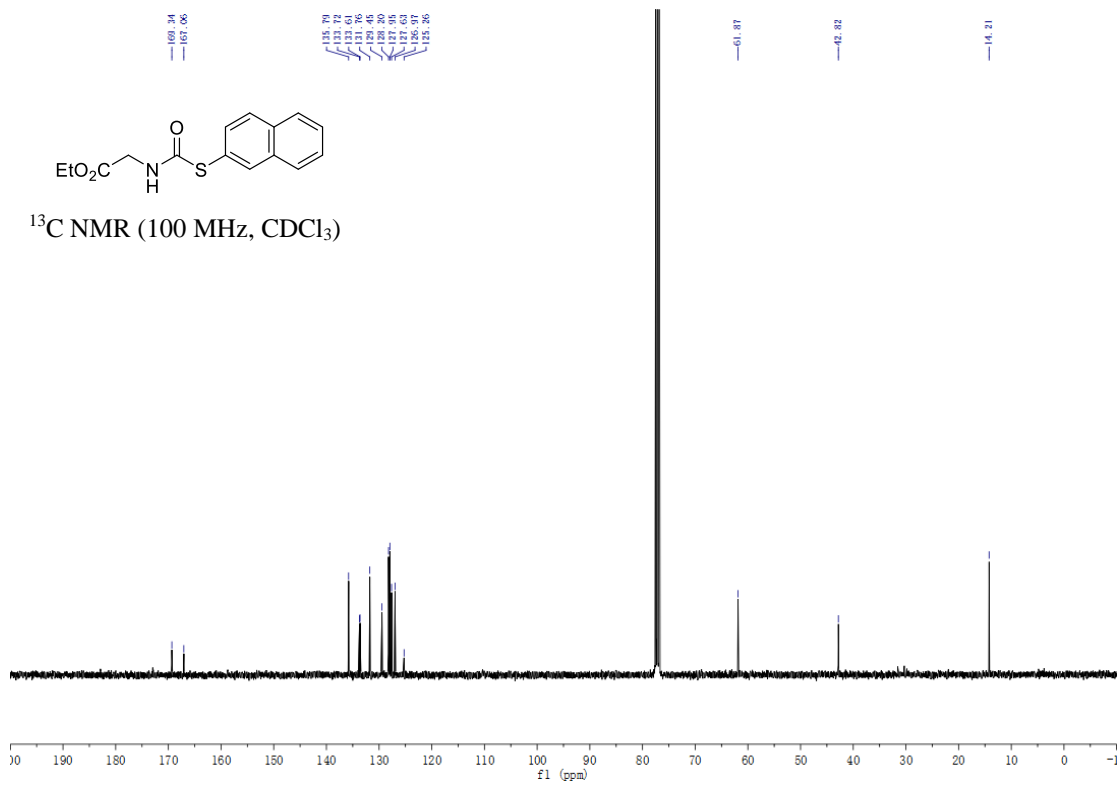
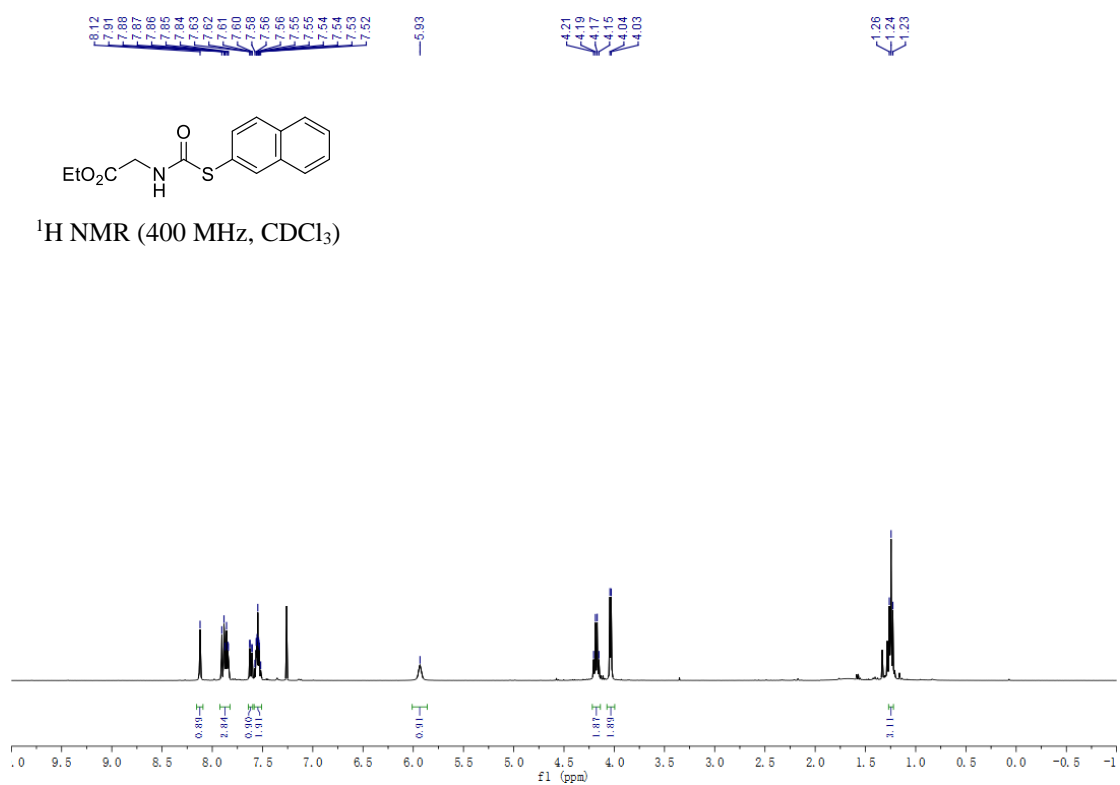
ethyl (((2,6-dimethylphenyl)thio)carbonyl)glycinate (3m)



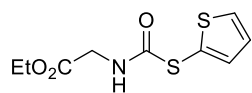
ethyl (((4-hydroxyphenyl)thio)carbonyl)glycinate (3n)



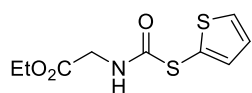
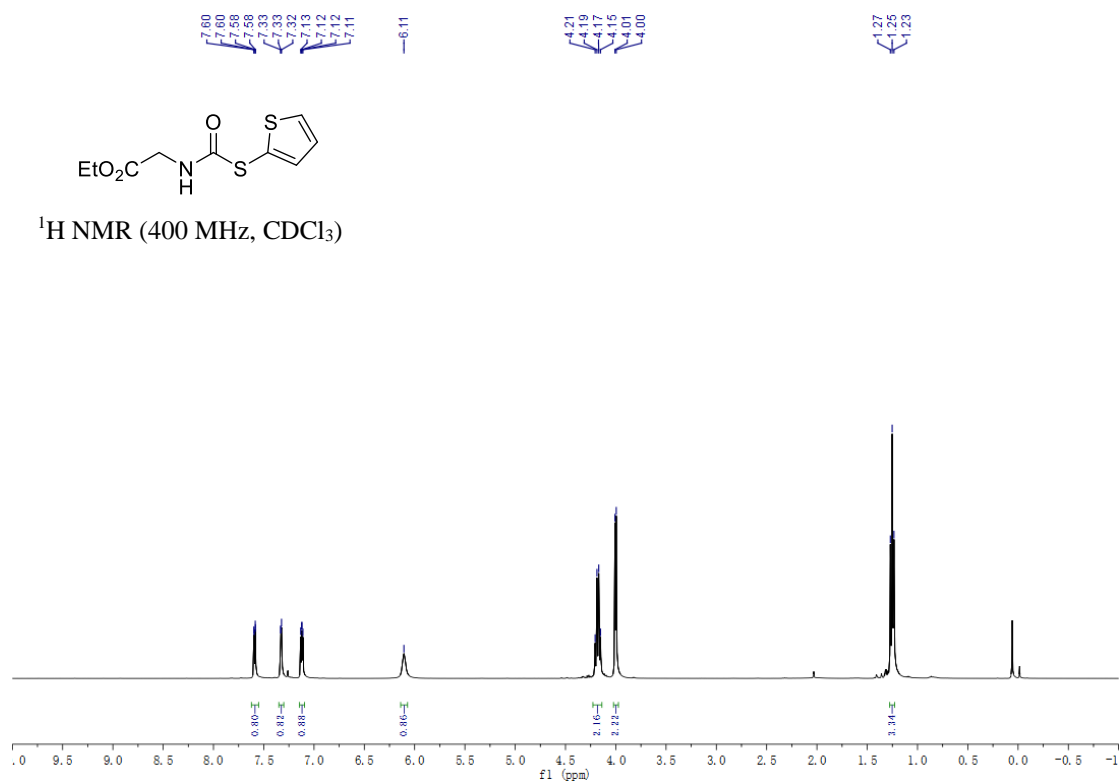
ethyl ((naphthalen-2-ylthio)carbonyl)glycinate (3o)



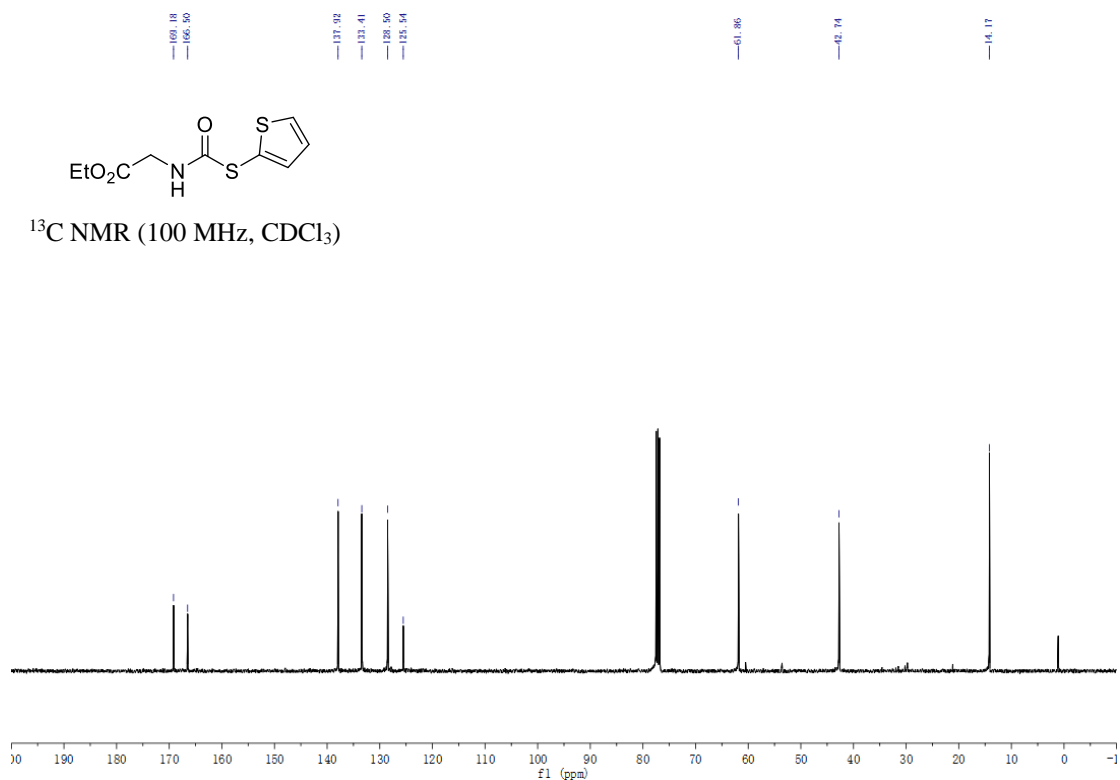
ethyl ((thiophen-2-ylthio)carbonyl)glycinate (3p)



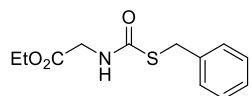
^1H NMR (400 MHz, CDCl_3)



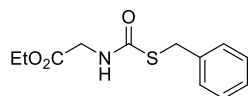
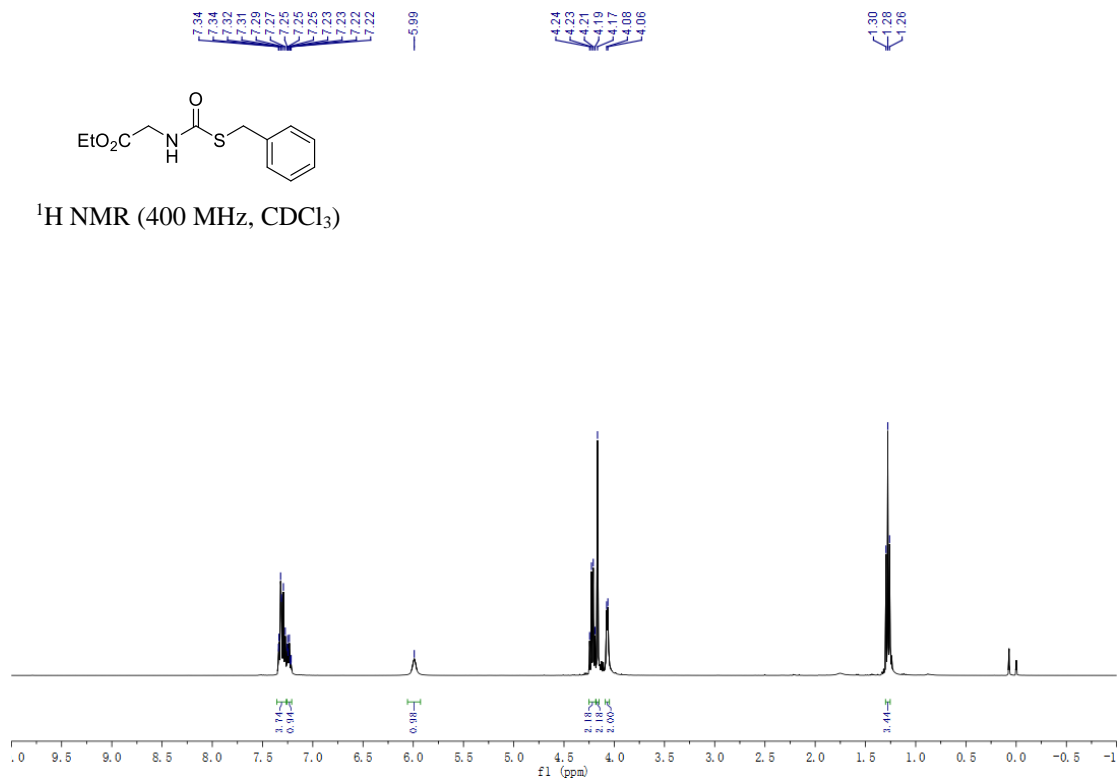
^{13}C NMR (100 MHz, CDCl_3)



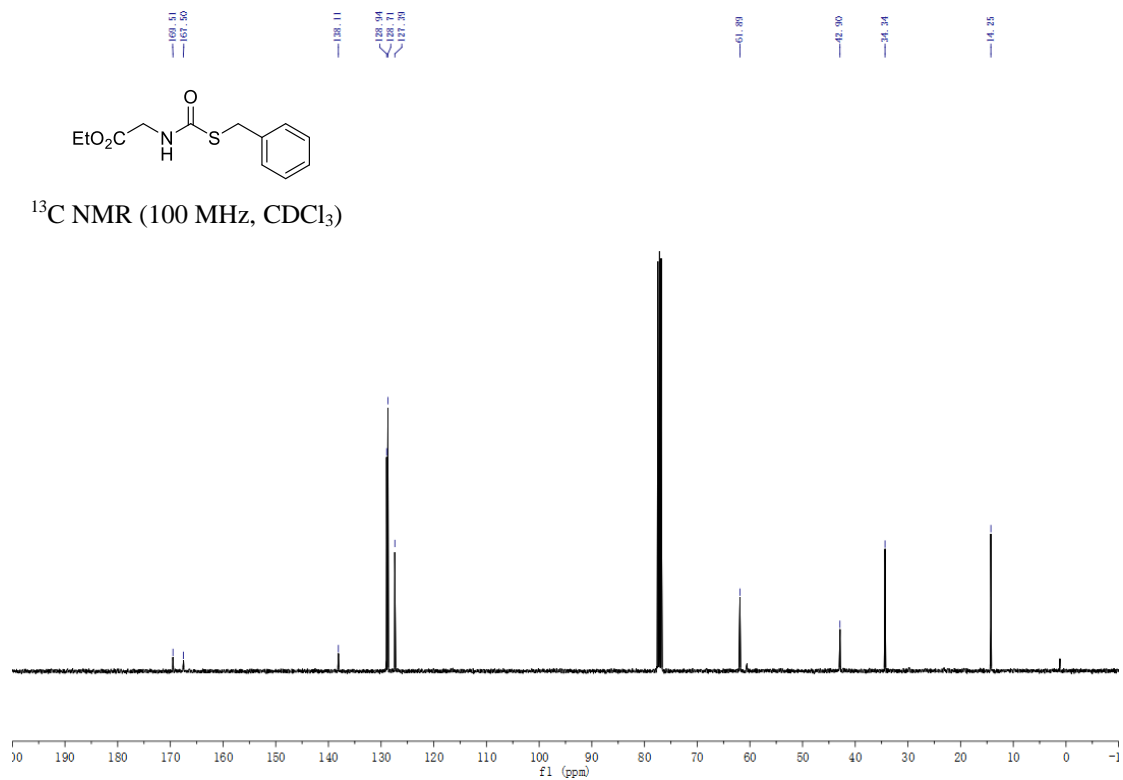
ethyl ((benzylthio)carbonyl)glycinate (3q)



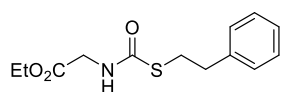
¹H NMR (400 MHz, CDCl₃)



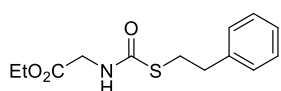
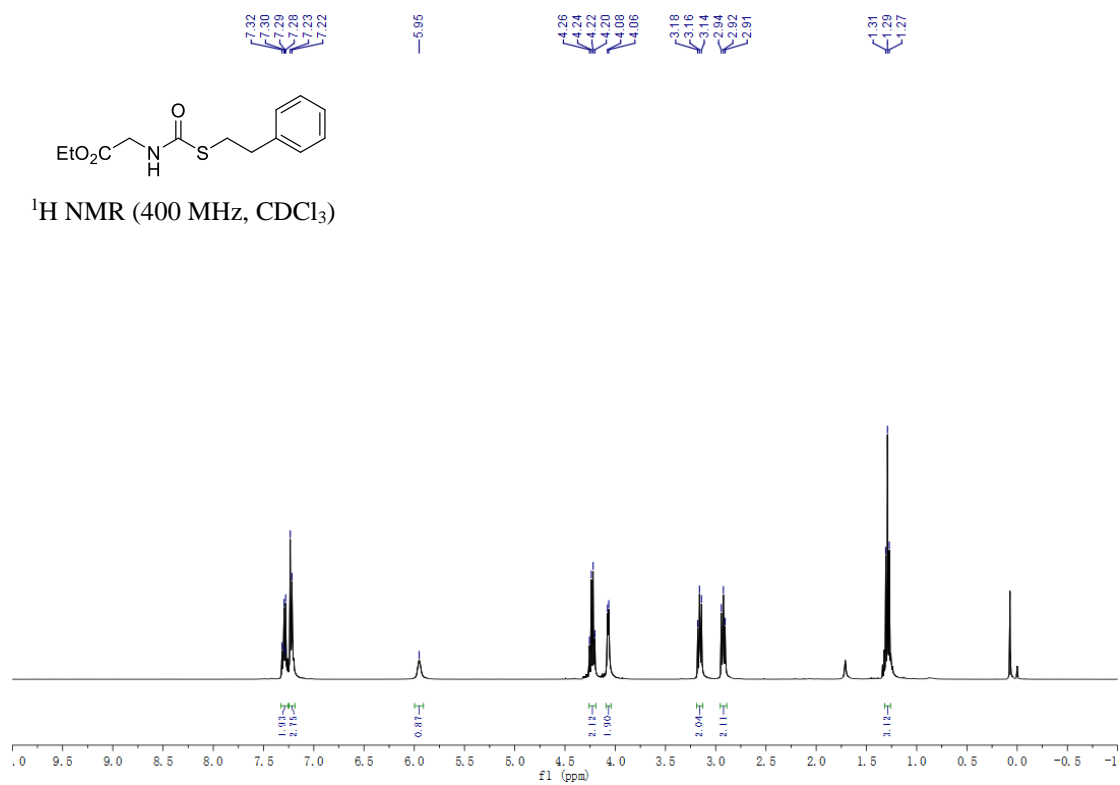
¹³C NMR (100 MHz, CDCl₃)



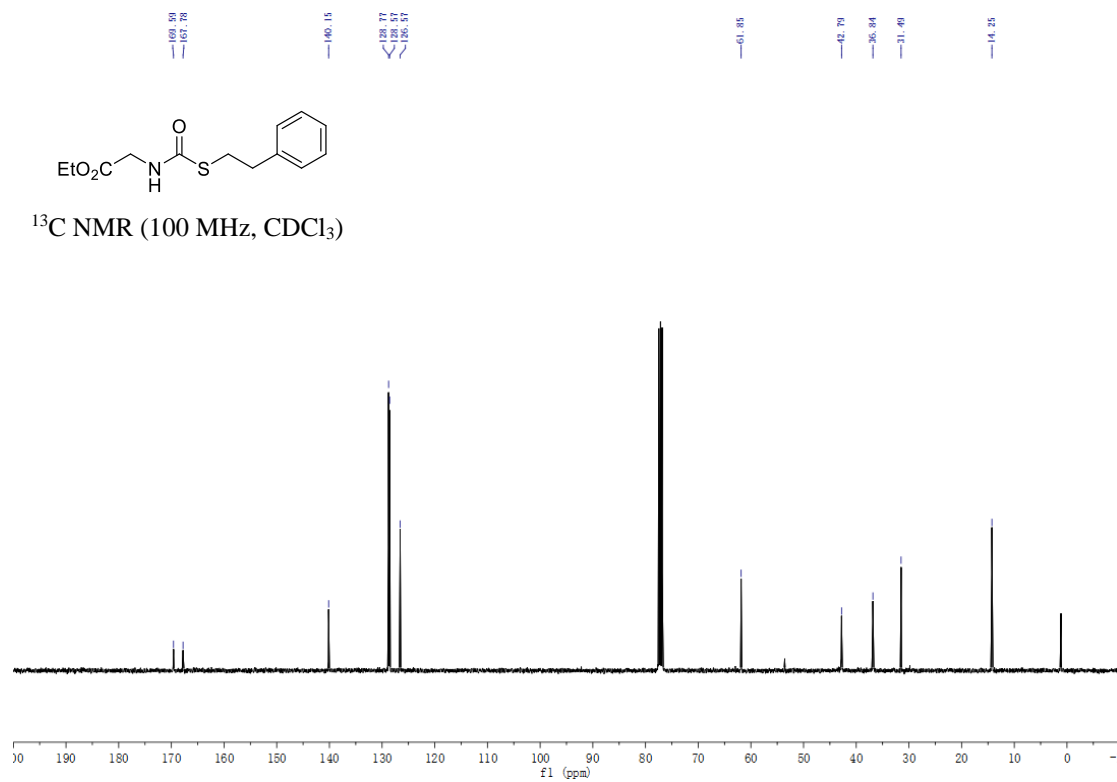
ethyl ((phenethylthio)carbonyl)glycinate (3r)



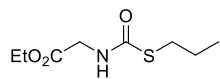
¹H NMR (400 MHz, CDCl₃)



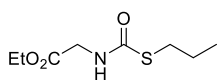
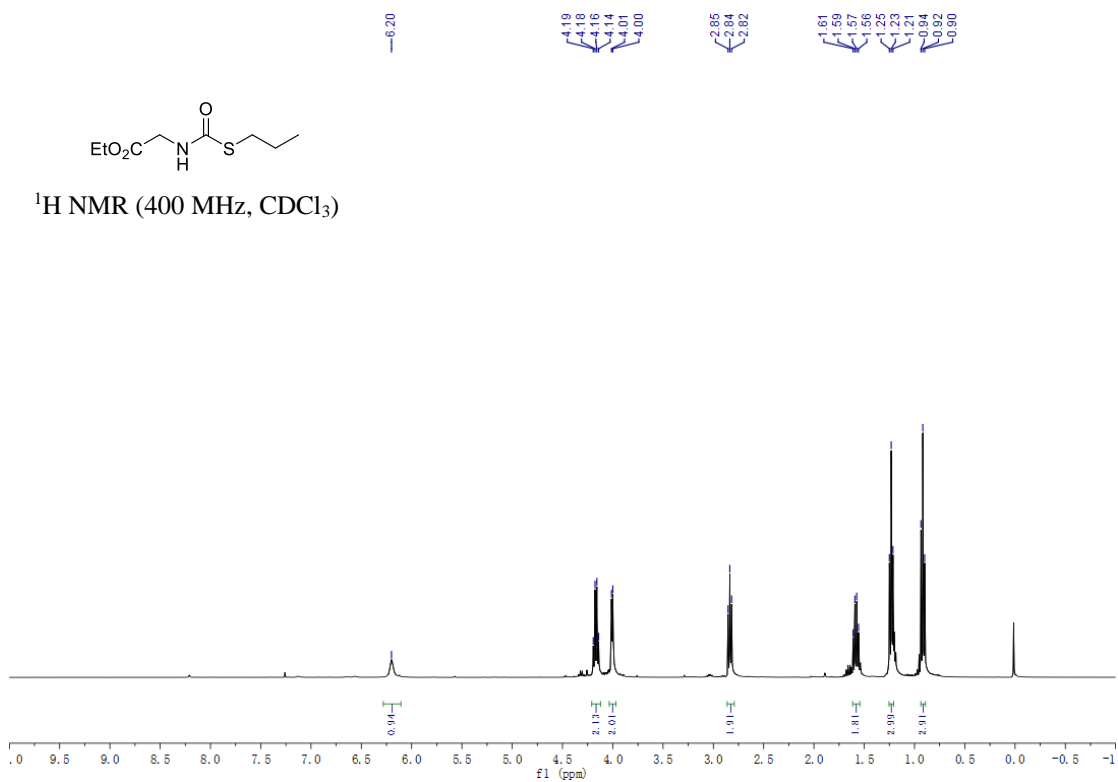
¹³C NMR (100 MHz, CDCl₃)



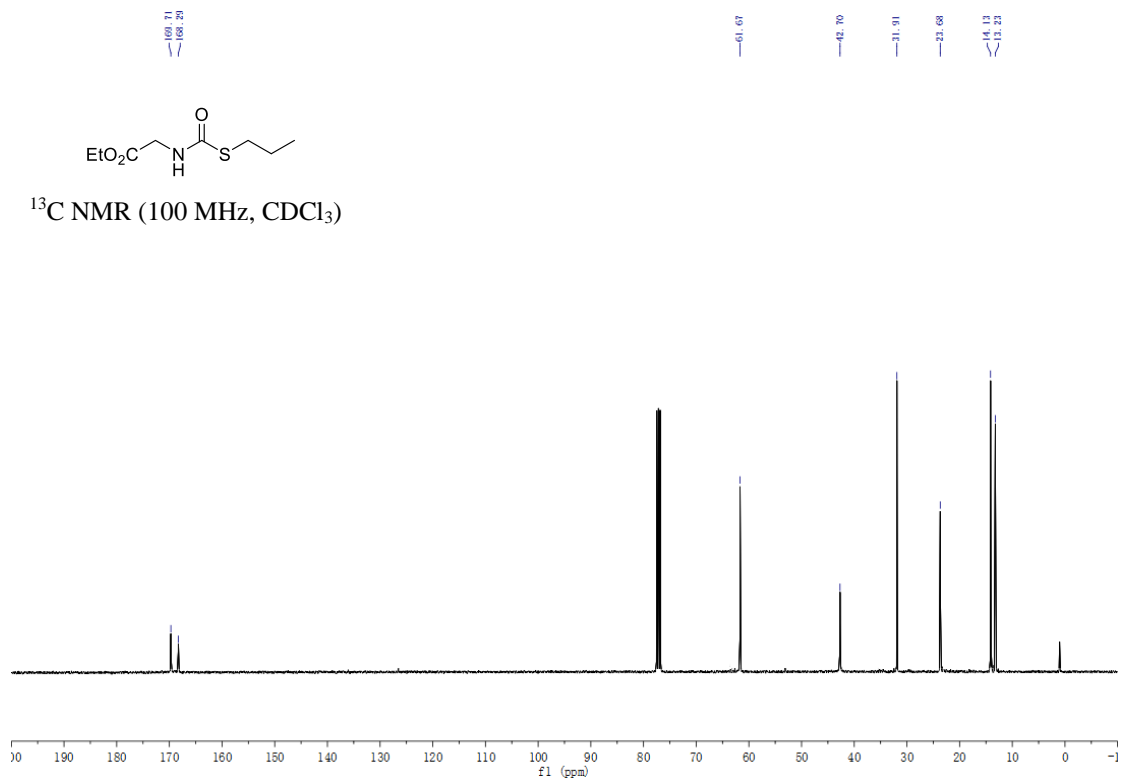
ethyl ((propylthio)carbonyl)glycinate (3s)



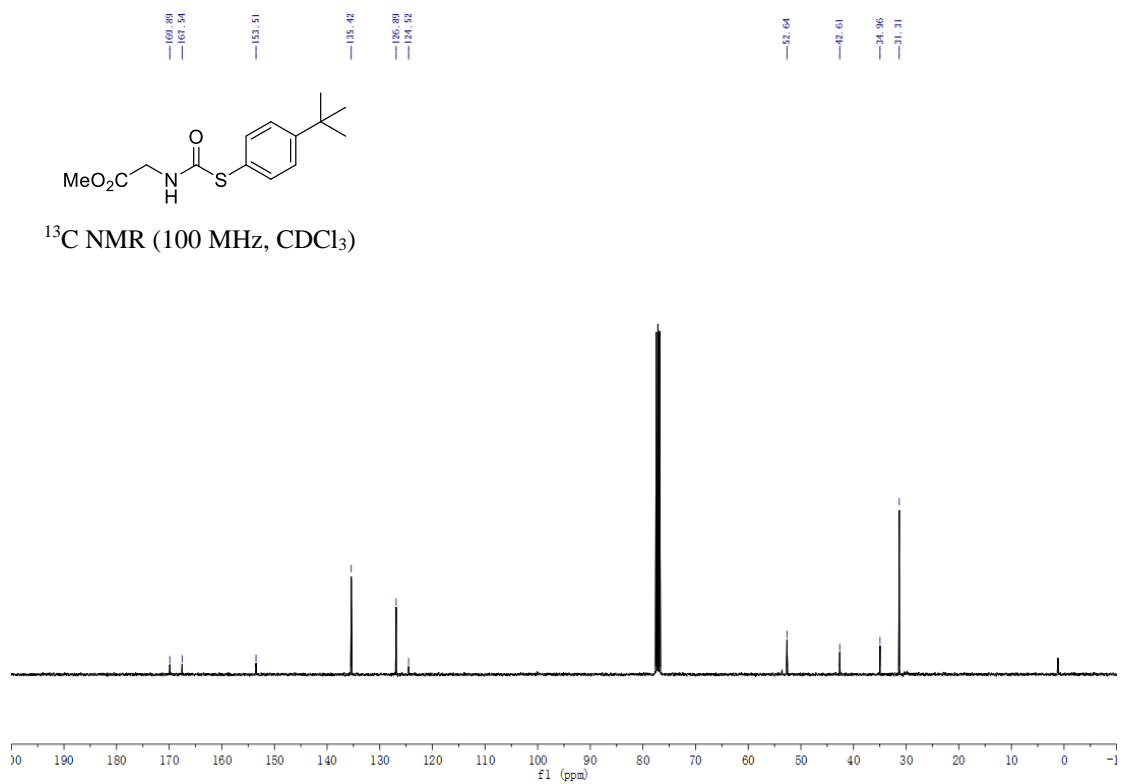
¹H NMR (400 MHz, CDCl₃)



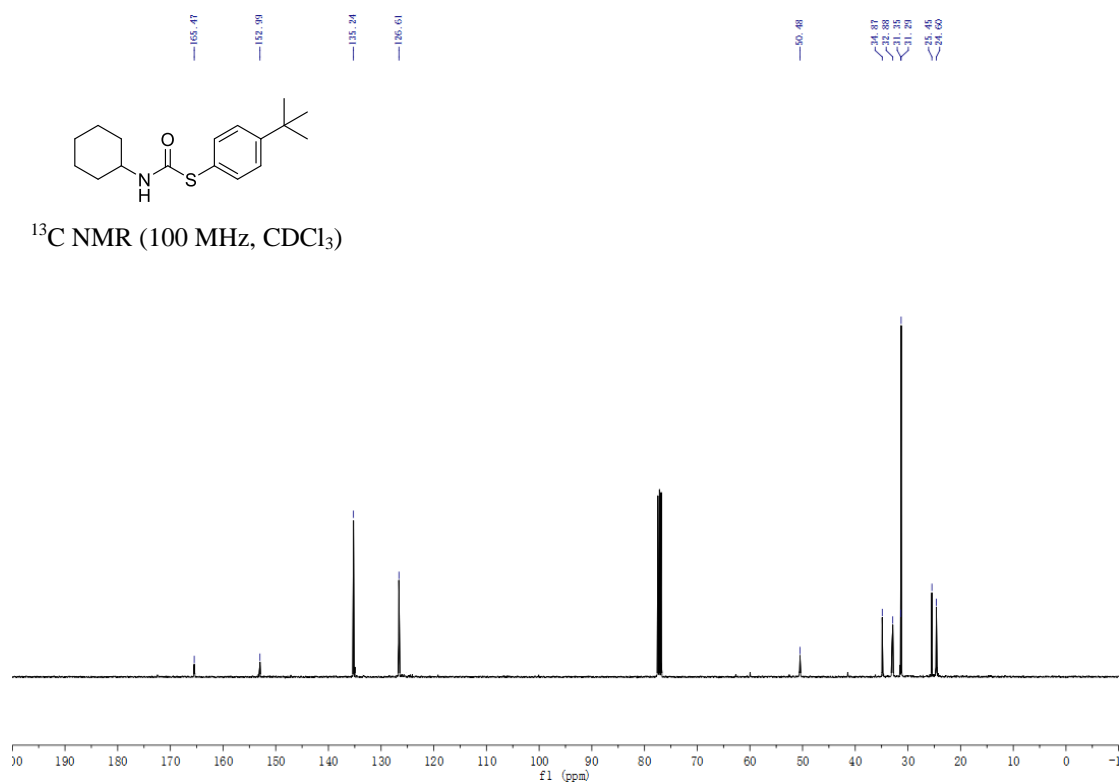
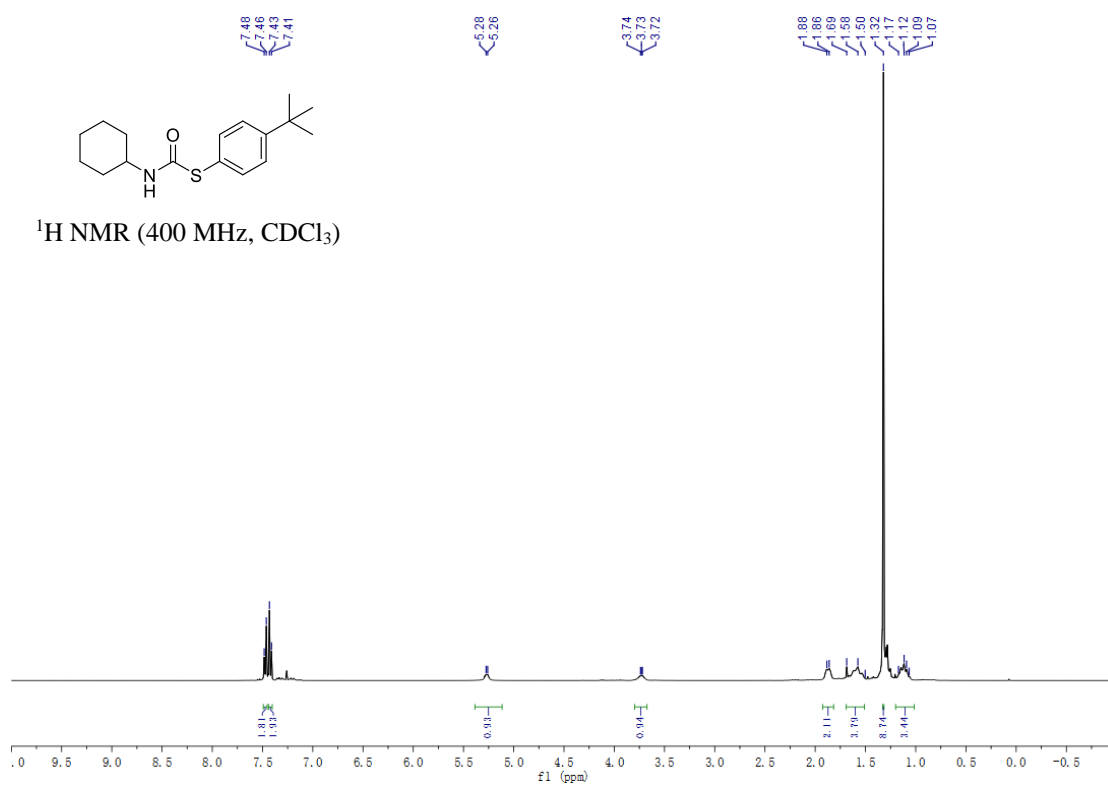
¹³C NMR (100 MHz, CDCl₃)



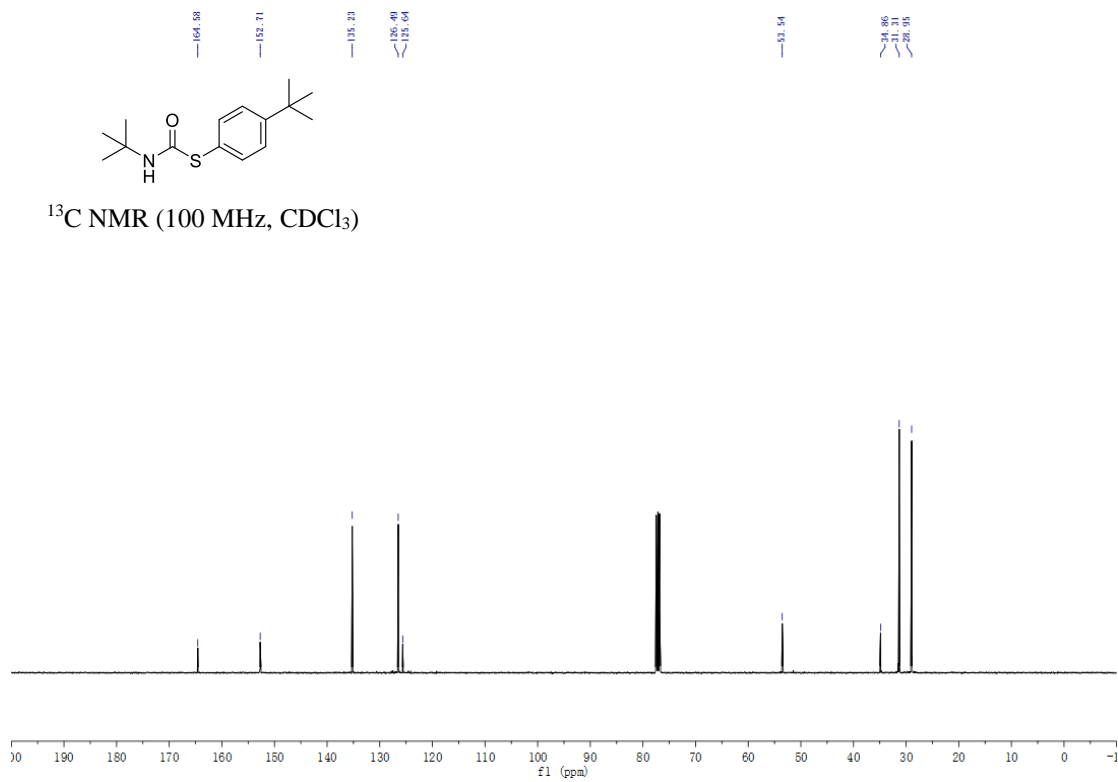
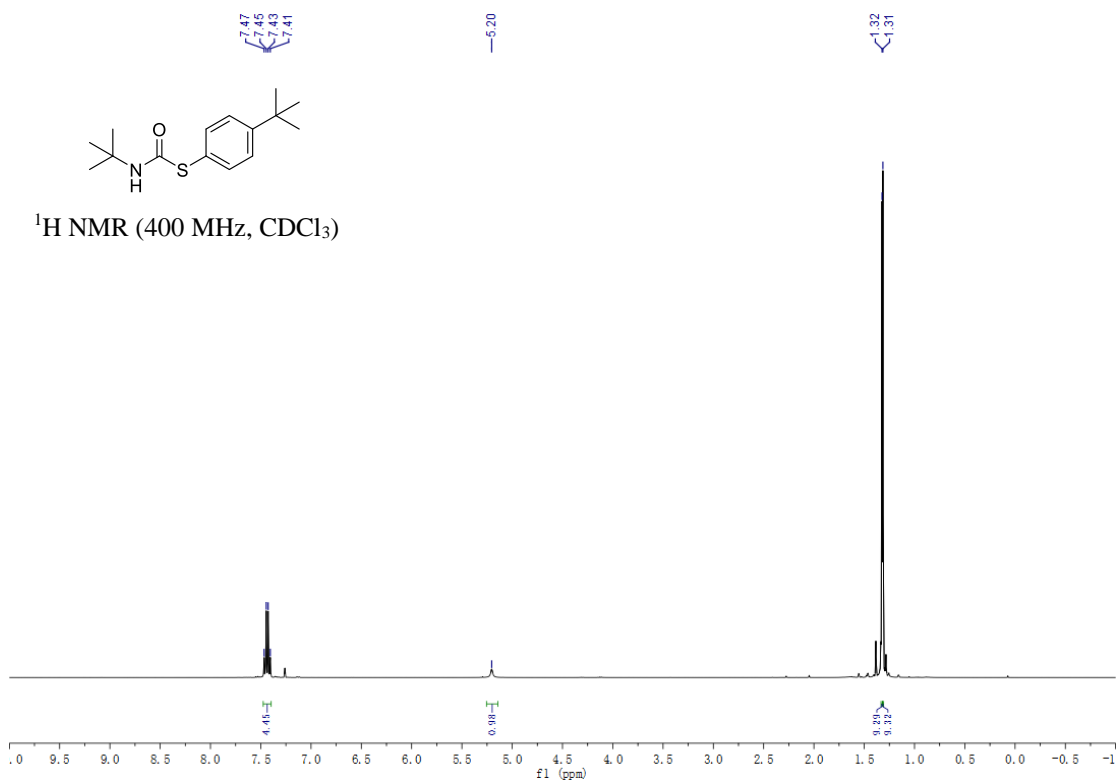
methyl ((4-(tert-butyl)phenyl)thio)carbonyl)glycinate (3t)



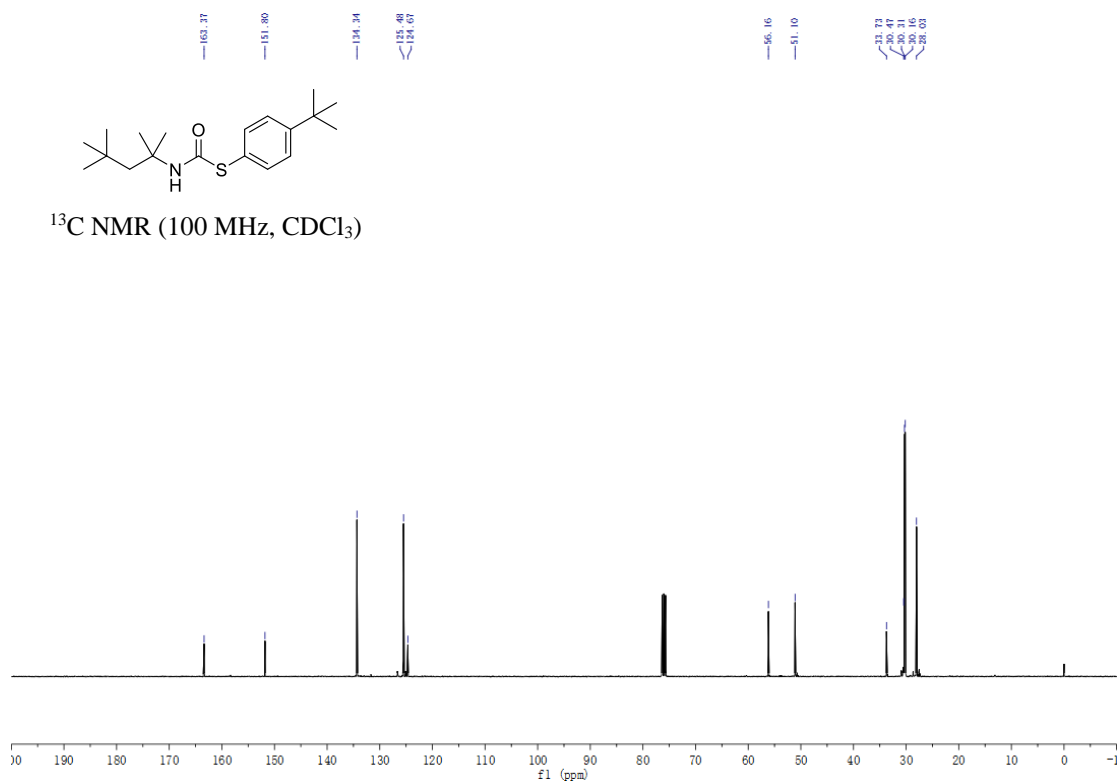
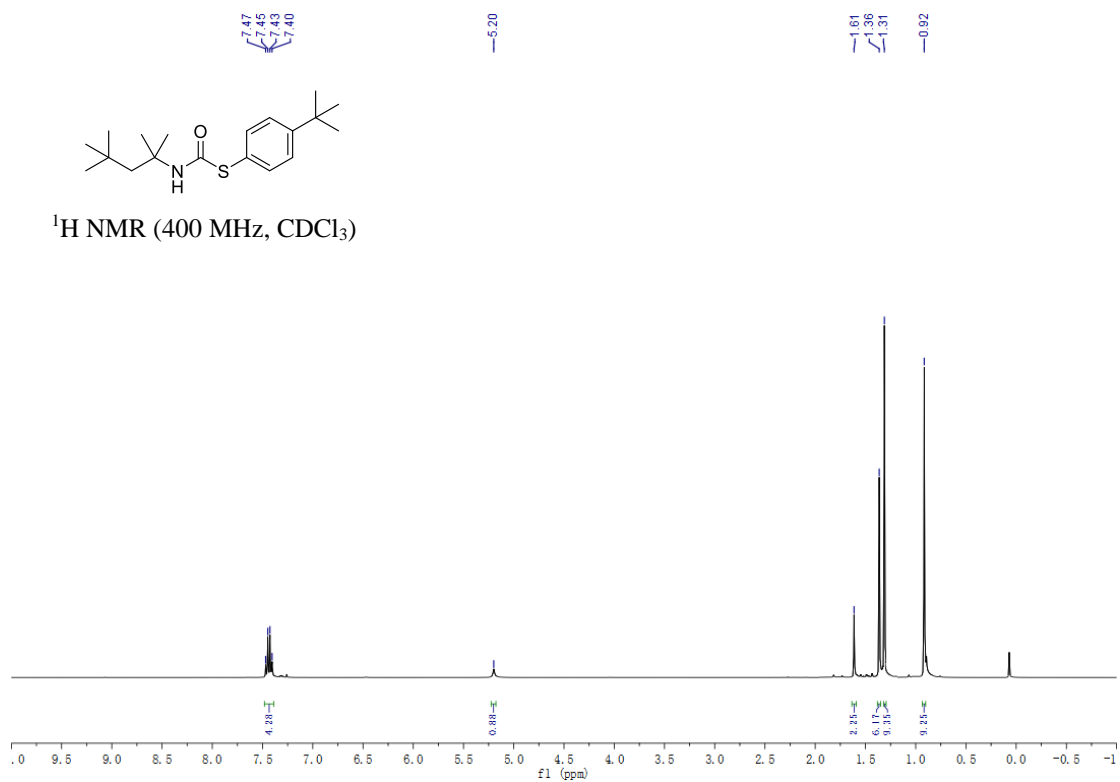
S-(4-(*tert*-butyl)phenyl) cyclohexylcarbamothioate (**3u**)



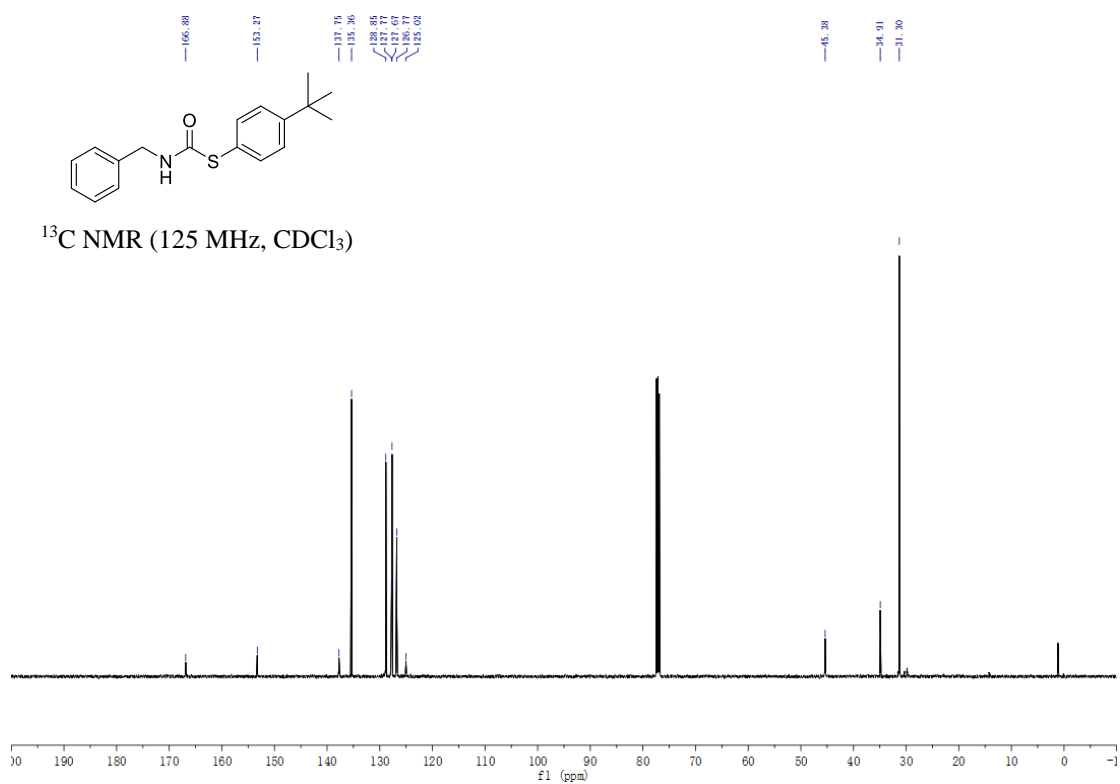
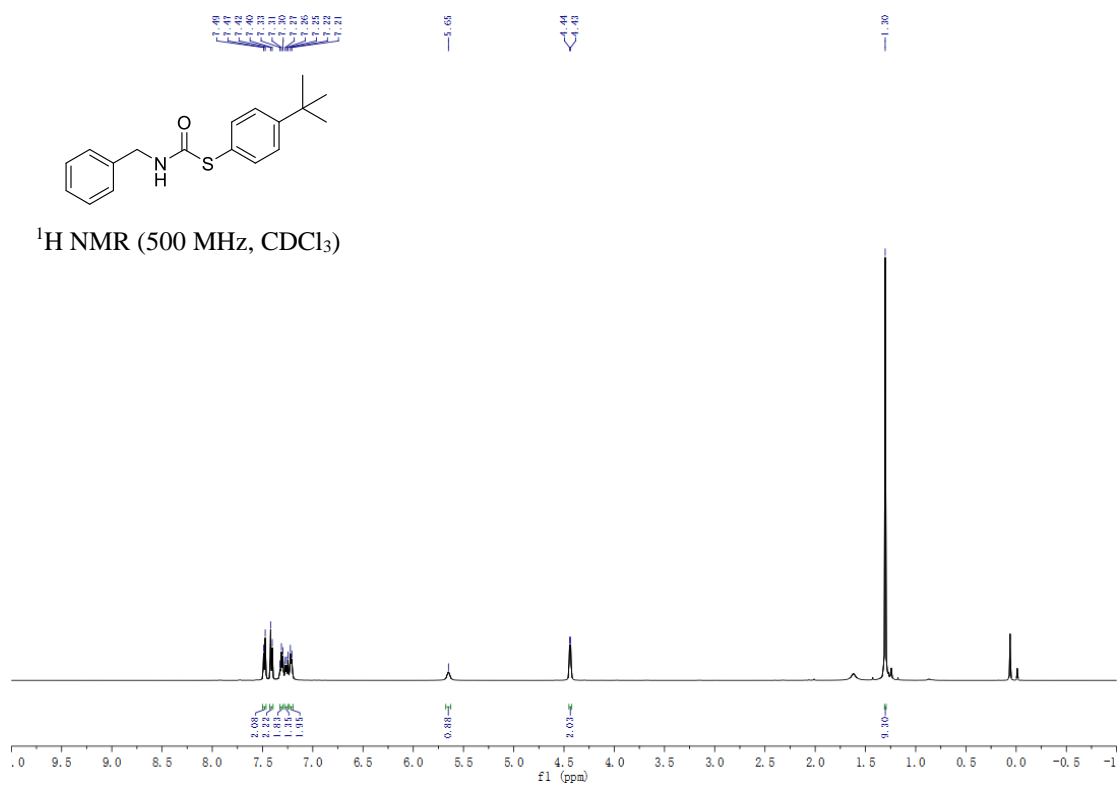
S-(4-(*tert*-butyl)phenyl) *tert*-butylcarbamothioate (**3v**)



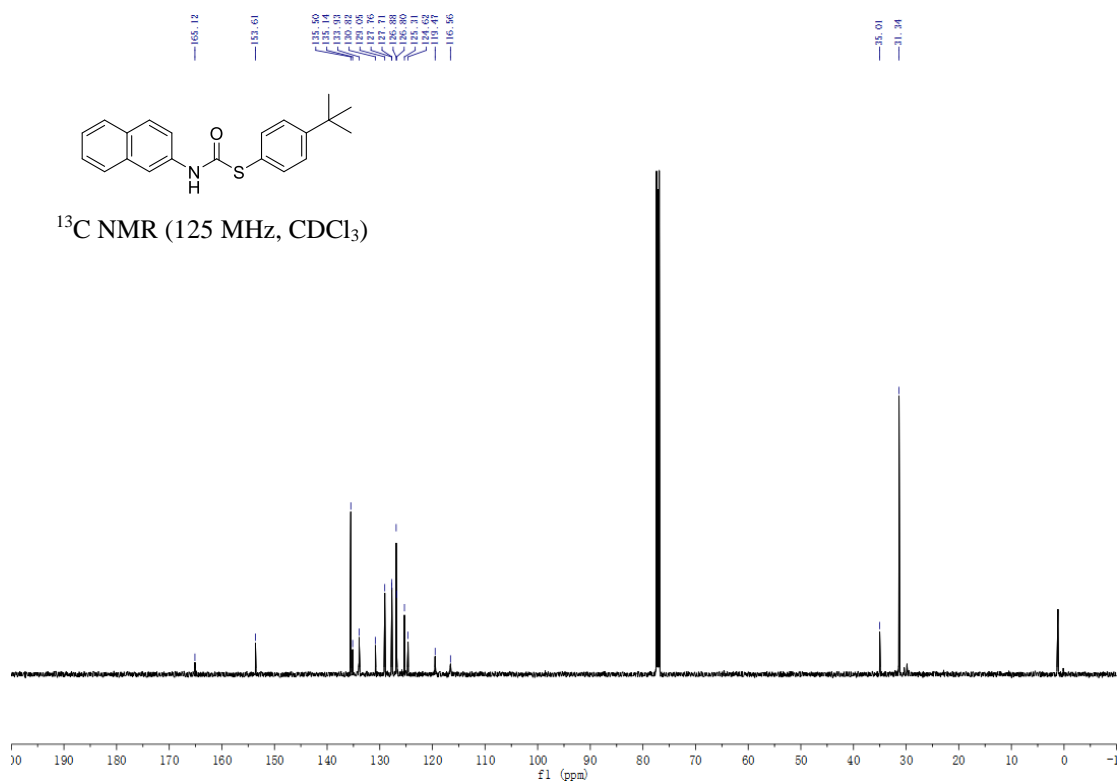
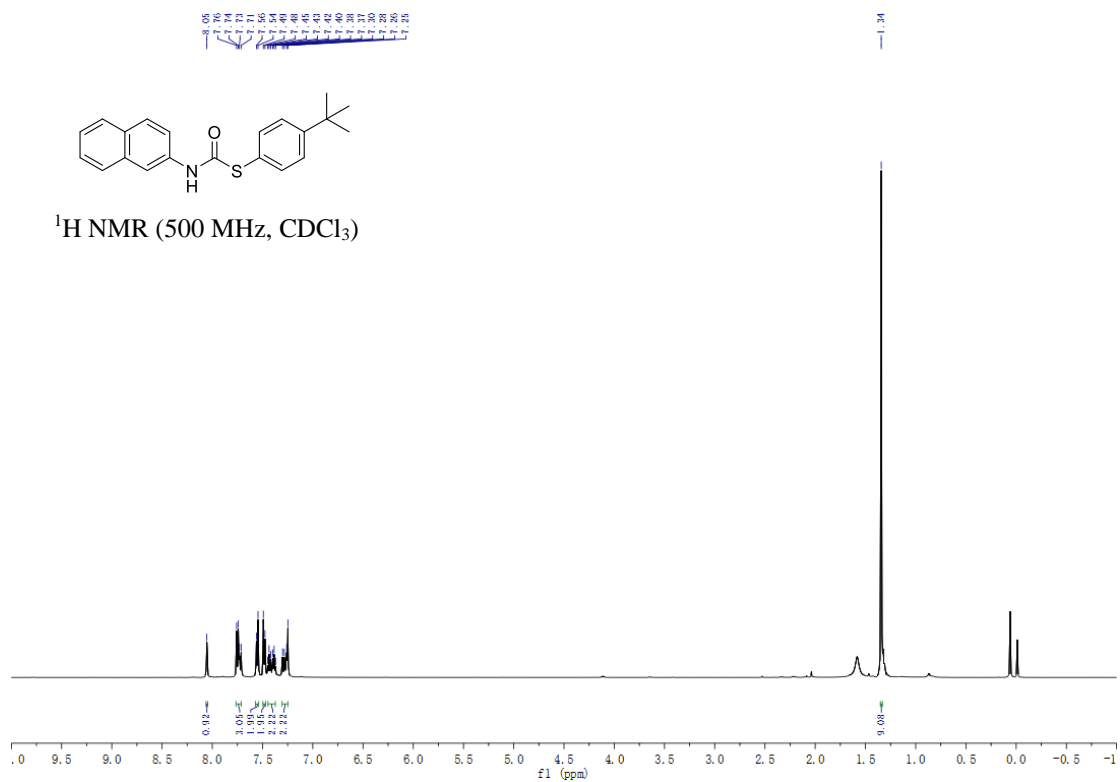
S-(4-(*tert*-butyl)phenyl) (2,4,4-trimethylpentan-2-yl)carbamothioate (**3w**)



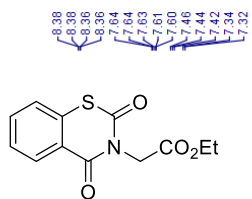
S-(4-(*tert*-butyl)phenyl) benzylcarbamothioate (3x)



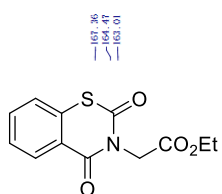
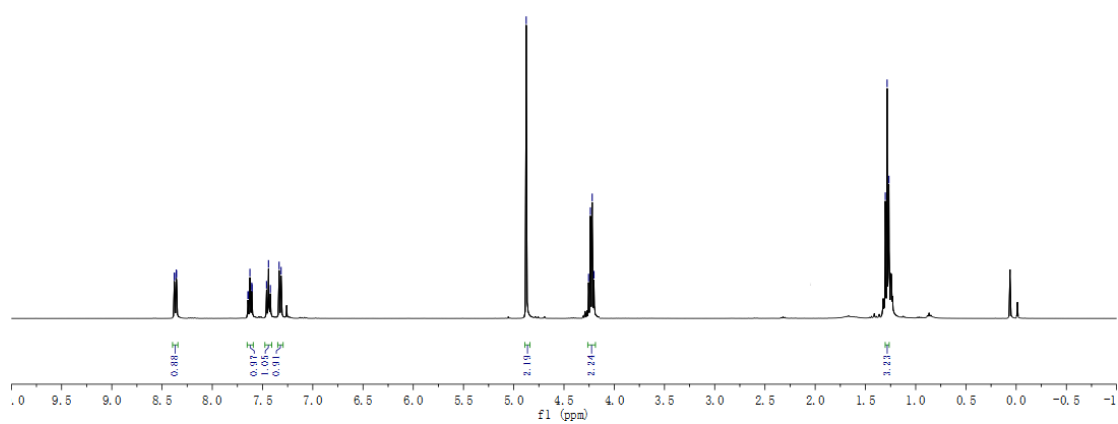
S-(4-(*tert*-butyl)phenyl) naphthalen-2-ylcarbamothioate (3y)



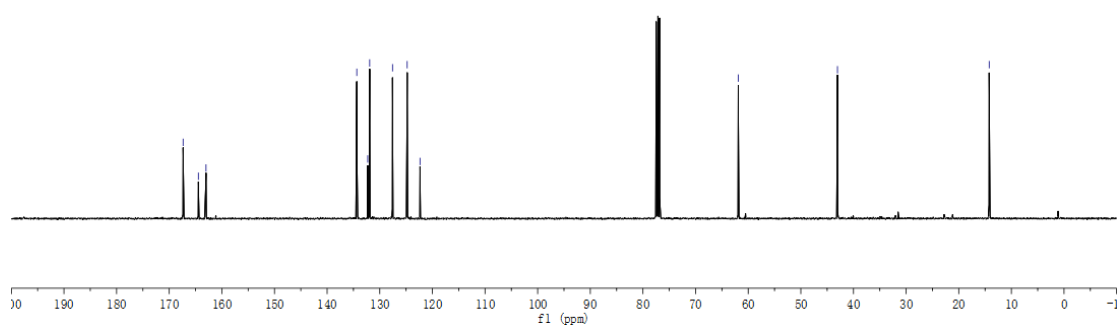
ethyl 2-(2,4-dioxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)acetate (7)



^1H NMR (400 MHz, CDCl_3)



^{13}C NMR (100 MHz, CDCl_3)



1-(((4-(tert-butyl)phenyl)thio)oxy)-2,2,6,6-tetramethylpiperidine (8)

