

Supporting Information

Visible-light-promoted deaminative strategy for the synthesis of S-alkyl dithiocarbamates using water as the green solvent

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I. General considerations

All reagents and solvents were obtained from commercial suppliers and used without further purification. Flash chromatography was performed on silica gel (200~300 mesh). ^1H and ^{13}C NMR data were recorded at 500 and 125 MHz on a BRUKER 500 spectrometer. Proton and carbon magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded using tetramethylsilane (TMS) as the internal standard in CDCl_3 . Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: CHCl_3 ($\delta = 7.26$ for ^1H NMR and $\delta = 77.0$ for ^{13}C NMR), $\text{DMSO}-d_6$ ($\delta = 2.50$ and 3.30 for ^1H NMR and $\delta = 39.50$ for ^{13}C NMR). Data are reported as follows: chemical shift δ/ppm , integration (^1H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet or combinations thereof; ^{13}C signals are singlets unless otherwise stated), coupling constants J in Hz, assignment.

UV-visible spectroscopy was recorded on a UV-2600 UV-visible spectrophotometer. The reactor was 3.0 cm from 10 W blue LED.

The spectrum of our lamp and the visible-light irradiation instrument

All reactions have been studied in borosilicate glass vessels irradiated by a blue light LED manufactured by Xuzhou Ai Jia Electronic Technology Co., Ltd. without using filters.

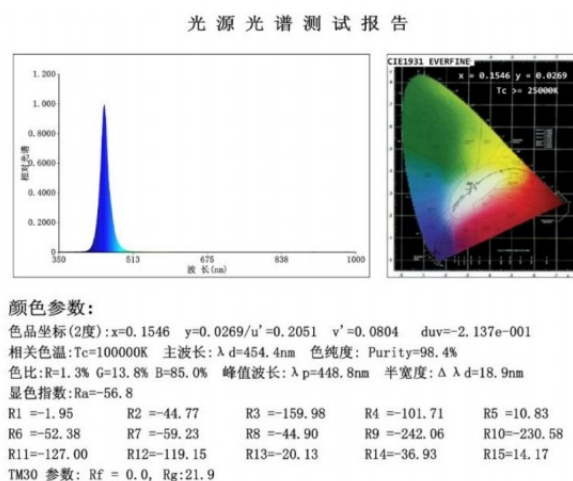


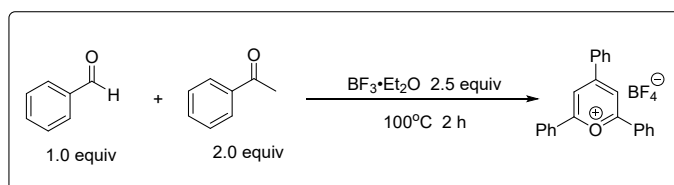
Figure S1. The spectrum of our lamp (blue LED)



Figure S2. The blue light LED

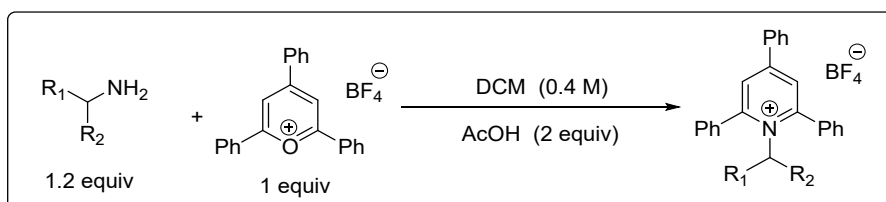
II. Experimental procedures

1. General Procedure A: Synthesis of 2,4,6-triphenylpyrylium tetrafluoroborate.^{[1] [2]}



According to the modified procedure, $\text{BF}_3 \cdot \text{OEt}_2$ (2.5 equiv) is slowly added to a mixture of aldehyde (3 mL, 30 mmol) and ketone (7 mL, 60 mmol). The reaction mixture was refluxed for 2 h at 100°C . After 2 h, the reaction mixture was allowed to attain room temperature, the thus formed diethyl ether was evaporated and delivered the oily product. Then the crude reaction mixture was dissolved in acetone and added diethyl ether to obtain bright yellow precipitate. The precipitate is then filtered using Buchner funnel to obtain 2,4,6-triphenylpyrylium tetrafluoroborate (4g, 33%).

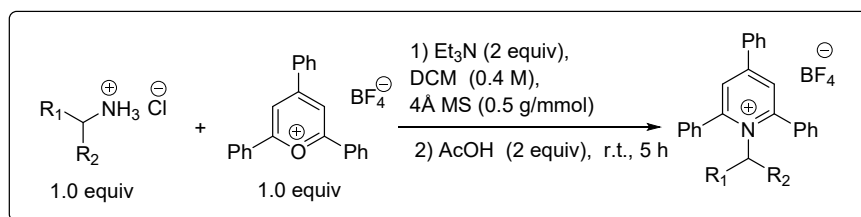
2. General Procedure B: Preparation of Pyridinium Salts from Amines^[2]



The benzylic amine (1.2 equiv) was added to a suspension of 2,4,6-triphenylpyrylium tetrafluoroborate (1.0 equiv) and DCM (0.4 M) in round bottom flask. After 20 min, acetic acid (2 equiv) was added. This mixture was allowed to stir overnight or till the consumption of the starting material. Once the starting material was consumed the solution was poured into diethyl ether and vigorously stirred to induce trituration. The

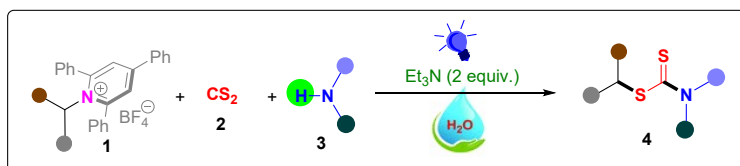
resulting solid pyridinium salt was filtered and washed with diethyl ether to obtain white solid. If the product failed to precipitate after addition of Et₂O, the resulting mixture was stored overnight at -20 °C to induce precipitation. Subsequently the precipitate was quickly filtered off, washed with cold Et₂O, and dried under vacuum.

2. General Procedure C: Preparation of Pyridinium Salts from Ammonium Salts^[2-5]



The molecular sieves (4 Å) was added in round bottom flask and heated to activate. Then the ammonium salts (1.0 equiv) was added to a suspension of 2,4,6-triphenylpyridinium tetrafluoroborate (1.0 equiv), powdered activated molecular sieves (4 Å) and DCM (0.5 M). To this solution Et₃N (2.0 equiv) was added. After stirring for 20 min acetic acid (2.0 equiv) was added. The mixture was stirred for 5 h at room temperature. The filtrate was then washed with HCl (1 M, 4 × 60 mL), sat. NaHCO₃ (4 × 60 mL), and sat. NaCl (1 × 60 mL). The organic layer was dried (Na₂SO₄), filtered, and concentrated. Small amount of diethyl ether was added and scratched at the glass surface to obtain the precipitate of the pyridinium salt, which was then filtered and concentrated.

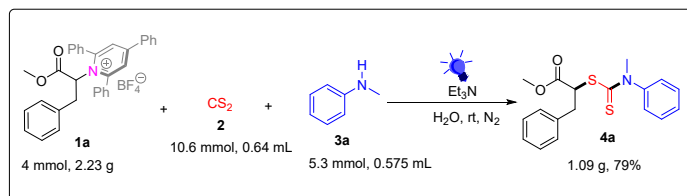
3. General procedure for the synthesis of S-Alkyl Dithiocarbamates^[6]



Katritzky salt **1** (0.3 mmol) was added to an oven dried 25 mL Schlenk tube. The tube was evacuated twice and backfilled with nitrogen. 2.0 mL H₂O (degassed), carbon disulfide **2** (0.8 mmol), amines **3** (0.4 mmol) and Et₃N (0.6 mmol) were mixed and then added to the Schlenk tube of a flow of nitrogen. Then the mixture was stirred and irradiated by the 10W blue LED at room temperature for 24 h. After completion of the

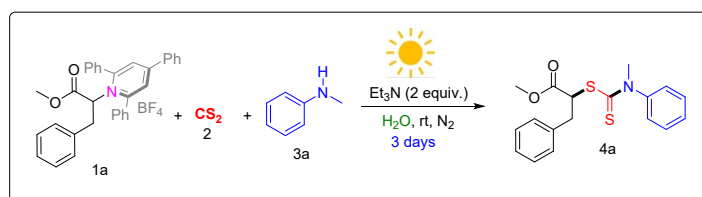
reaction (TLC), the residue was extracted with ethyl acetate (5 mL \times 3). The combined organic phase was dried over Na₂SO₄, concentrated in vacuo. The resulting crude residue was purified via column chromatography on silica gel to afford the desired products.

4. Gram scale reaction



To a 100 mL Three-necked flask equipped with a magnetic stir bar, added Katritzky salt **1a** (4 mmol, 2.23 g), carbon disulfide **2** (10.6 mmol, 0.64 mL), amines **3a** (5.3 mmol, 0.575 mL) and Et₃N (8 mmol, 1.1 mL) in H₂O (25 mL). The tube was evacuated and backfilled with nitrogen (three times). Then the mixture was stirred and irradiated by the 10W blue LED at room temperature for 24 h. After completion of the reaction (TLC), the residue was extracted with ethyl acetate (25 mL \times 3), washed with brine, dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) to afford the product **4a** (1.09 g, 79%).

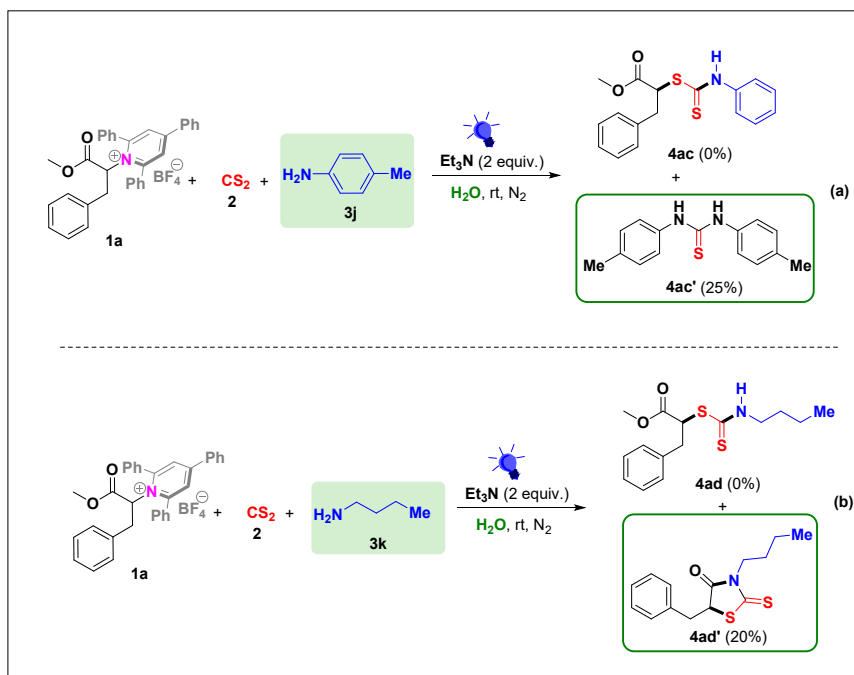
5. Irradiation with natural sunlight



Katritzky salt **1** (0.3 mmol) was added to an oven dried 25 mL Schlenk tube. The tube was evacuated twice and backfilled with nitrogen. 2.0 mL H₂O, carbon disulfide **2** (0.8 mmol), amines **3** (0.4 mmol) and Et₃N (0.6 mmol) were mixed and then added to the Schlenk tube under a positive nitrogen pressure. The solution was stirred under solar light for three days (A total of 24 hours of sunlight irradiation, Location: 36°8'54" N, 120°23'3" E). Afterward, the residue was extracted with ethyl acetate (5 mL \times 3). The combined organic phase was dried over Na₂SO₄, filtered and the filtrate

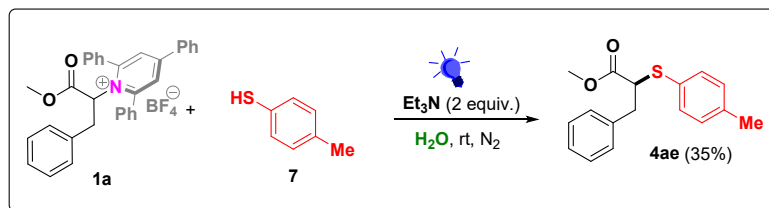
was concentrated in vacuo. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20/1, v/v) to afford the product **4a** in 71% yield.

6. Investigation of primary amines in the reaction.



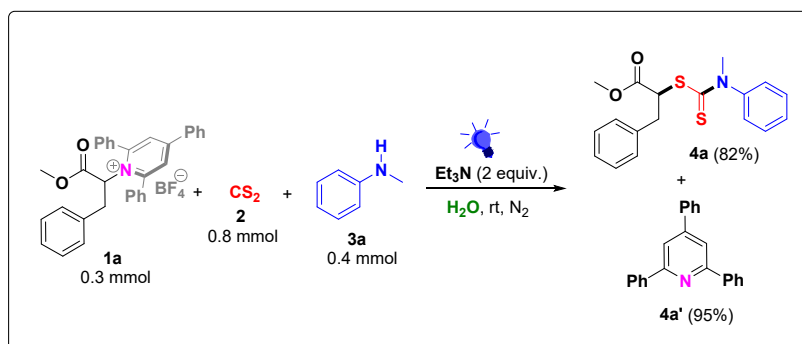
Katritzky salt **1** (0.3 mmol) was added to an oven dried 25 mL Schlenk tube. The tube was evacuated twice and backfilled with nitrogen. 2.0 mL H_2O (degassed), carbon disulfide **2** (0.8 mmol), amines **3j** or **3k** (0.4 mmol) and Et_3N (0.6 mmol) were mixed and then added to the Schlenk tube of a flow of nitrogen. Then the mixture was stirred and irradiated by the 10W blue LED at room temperature for 24 h. After completion of the reaction (TLC), the residue was extracted with ethyl acetate (5 mL \times 3). The combined organic phase was dried over Na_2SO_4 , concentrated in vacuo. The resulting crude residue was purified via column chromatography on silica gel to afford **4ac'** in 25% yield, and **4ad'** in 20% yield.

7. Investigation of aryl thiol



Katritzky salt **1** (0.3 mmol) was added to an oven dried 25 mL Schlenk tube. The tube was evacuated twice and backfilled with nitrogen. 2.0 mL H₂O (degassed), 4-methylbenzenethiol **7** (0.4 mmol), and Et₃N (0.6 mmol) were mixed and then added to the Schlenk tube of a flow of nitrogen. Then the mixture was stirred and irradiated by the 10W blue LED at room temperature for 24 h. After completion of the reaction (TLC), the residue was extracted with ethyl acetate (5 mL × 3). The combined organic phase was dried over Na₂SO₄, concentrated in vacuo. The resulting crude residue was purified via column chromatography on silica gel to afford **4ae** in 35% yield.

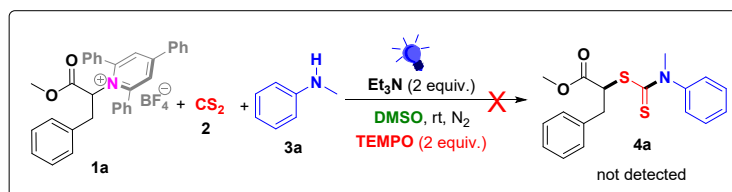
8. The experiment of the recovery of 2,4,6-triphenylpyridine



Katritzky salt **1** (0.3 mmol) was added to an oven dried 25 mL Schlenk tube. The tube was evacuated twice and backfilled with nitrogen. 2.0 mL H₂O (degassed), carbon disulfide **2** (0.8 mmol), N-methylaniline **3a** (0.4 mmol) and Et₃N (0.6 mmol) were mixed and then added to the Schlenk tube of a flow of nitrogen. Then the mixture was stirred and irradiated by the 10W blue LED at room temperature for 24 h. After completion of the reaction (TLC), the residue was extracted with ethyl acetate (5 mL × 3). The combined organic phase was dried over Na₂SO₄, concentrated in vacuo. The resulting crude residue was purified via column chromatography on silica gel to afford the **4a** in 82% isolated yield, and 2,4,6-triphenylpyridine in 95% yield.

III. Experiments of investigations on the mechanism

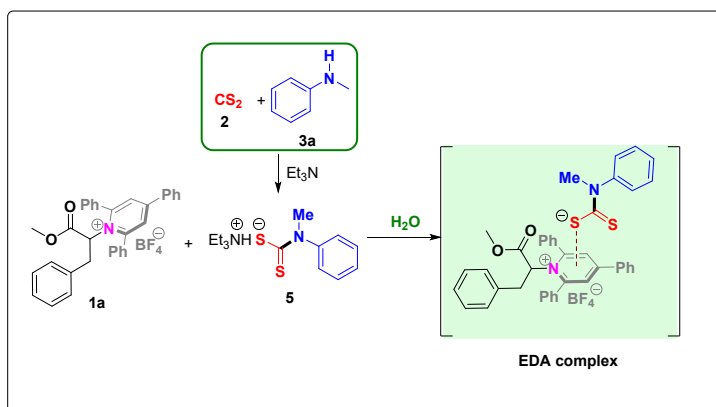
1. Control experiment using radical inhibitors



Katritzky salt **1** (0.3 mmol) and TEMPO (2.0 equiv) was added to an oven dried 25 mL Schlenk tube. The tube was evacuated twice and backfilled with nitrogen. 2.0 mL H_2O , carbon disulfide **2** (0.8 mmol), amines **3** (0.4 mmol) and Et_3N (0.6 mmol) were mixed and then added to the Schlenk tube of a flow of nitrogen. Then the mixture was stirred and irradiated by the 10 W blue LED at room temperature for 24 h. No desired product **4a** was detected.

2. UV-vis absorption spectra

The UV/Vis absorption spectra of Katritzky salt **1a** (10^{-5} M), carbon disulfide **2** (2.66×10^{-5} M) with and *N*-methylaniline **3a** (1.33×10^{-5} M) in DMSO and H_2O were recorded in 1 cm path quartz cuvettes by using the UV-2600 UV-Vis spectrophotometer, respectively.



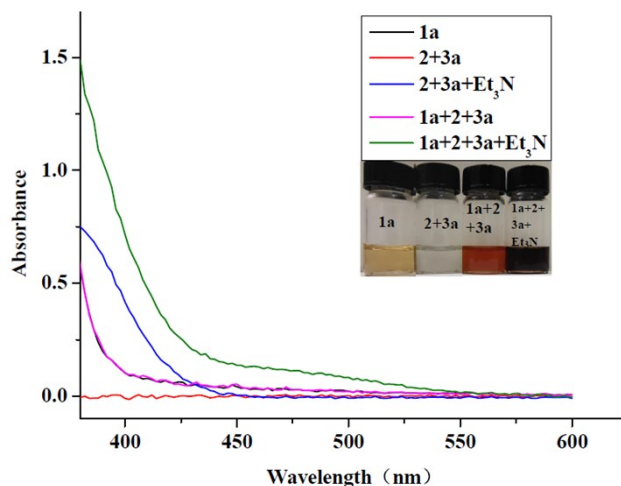


Figure S3. UV-vis absorption spectra of various combinations of **1a**, **2**, **3a** and Et_3N in DMSO/ H_2O ($v_1/v_2 = 1:1$)

A Job's plot was drawn to evaluate the stoichiometry of the EDA complex (**A**) with Katritzky salt (**1a**) and **5**, where **5** was formed through reaction of CS_2 and **3a**. The Job's plot was calculated measuring the absorption of DMSO and H_2O solutions at 315 nm with different donor/acceptor ratios with constant concentration (2.33×10^{-5} M) of the two components. The absorbance values were plotted against the molar fraction (%) of Katritzky salt (**1a**) and **5**. The maximum absorbance was obtained with a 1:1 mixture, indicating that it is the stoichiometry of the EDA complex in solution (Figure S4).

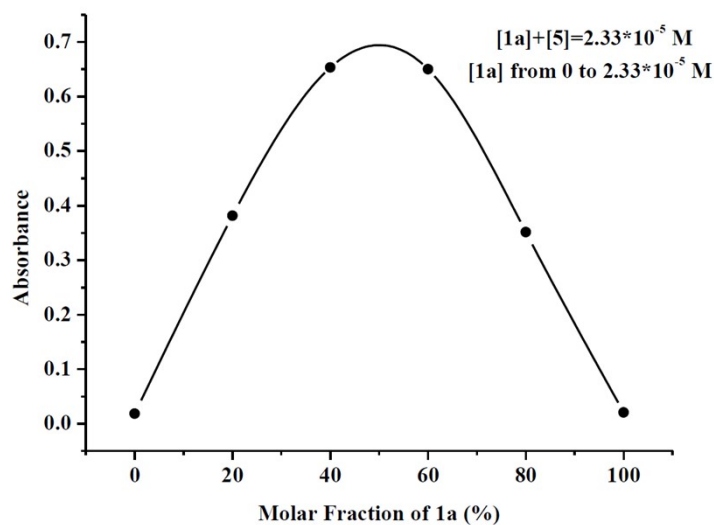
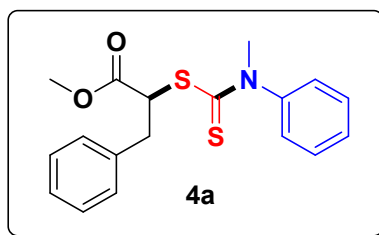


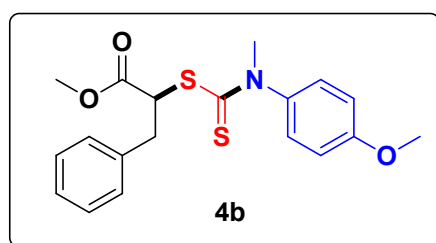
Figure S4. Jot's plot for ratio between **1a** and **5**

IV. Characterization of products



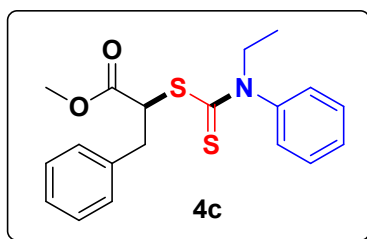
Methyl (S)-2-((methyl(phenyl)carbamothioyl)thio)-3-phenylpropanoate (4a).

Eluent petroleum ether/ethyl acetate (20:1). Yellow oil, 85 mg, 82% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.44 (d, $J = 7.4$ Hz, 3H), 7.25–7.21 (m, 7H), 4.97 (t, $J = 7.0$ Hz, 1H), 3.75 (s, 3H), 3.57 (s, 3H), 3.15 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 196.5, 171.4, 144.2, 137.5, 129.8, 129.1, 128.3, 126.8, 126.8, 55.8, 52.3, 46.3, 38.2. HRMS calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_2\text{S}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 368.0749; found 368.0752.

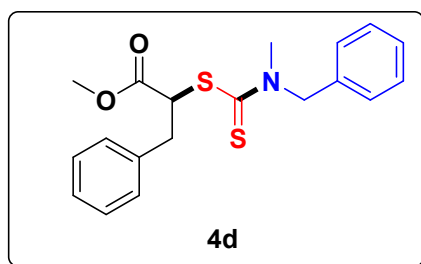


Methyl (S)-2-(((4-methoxyphenyl)(methyl)carbamothioyl)thio)-3-phenylpropanoate (4b). Eluent petroleum ether/ethyl acetate (10:1). Brown oil, 95 mg, 85% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.32–7.24 (m, 5H), 7.17 (d, $J = 8.4$ Hz, 2H), 6.98 (d,

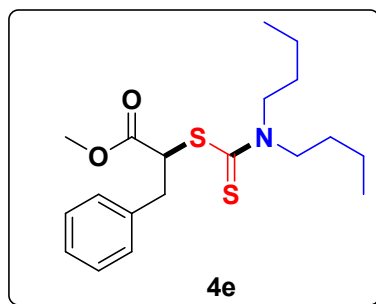
$J = 8.8$ Hz, 2H), 4.99 (t, $J = 5.0$ Hz, 1H), 3.88 (s, 3H), 3.76 (s, 3H), 3.61 (s, 3H), 3.18–3.12(m, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 197.1, 171.6, 160.0, 137.6, 136.97, 129.2, 128.3, 128.1, 126.8, 115.0, 56.0, 55.5, 52.4, 46.61, 38.3. HRMS calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_3\text{S}_2^+$ $[\text{M}+\text{H}]^+$: 376.1036; found 376.1035.



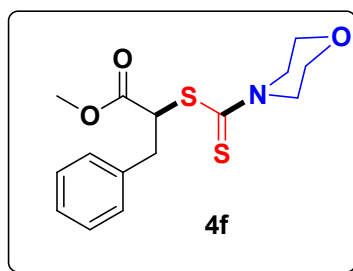
Methyl (*S*)-2-((ethyl(phenyl)carbamothioyl)thio)-3-phenylpropanoate (4c). Eluent petroleum ether/ethyl acetate (20:1). Yellow oil, 82 mg, 76% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.42–7.46 (m, 3H), 7.25–7.17 (m, 7H), 5.97 (t, $J = 6.5$ Hz, 1H), 4.35–4.25 (m, 2H), 3.55 (s, 3H), 3.15 – 3.06 (m, 2H), 1.28 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 196.0, 171.5, 137.6, 129.8, 129.7, 129.3, 129.2, 128.3, 127.9, 126.8, 55.5, 53.0, 52.3, 38.3, 11.7. HRMS calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_2\text{S}_2^+$ $[\text{M}+\text{H}]^+$: 360.1086; found 360.1084.



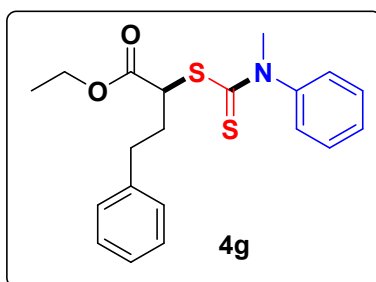
Methyl (*S*)-2-((benzyl(methyl)carbamothioyl)thio)-3-phenylpropanoate (4d). Eluent petroleum ether/ethyl acetate (20:1). Yellow oil, 95 mg, 88% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.34–7.28 (m, 6H), 7.26–7.18 (m, 4H), 5.40–5.27 (m, 1H), 5.12 (t, $J = 7.6$ Hz, 1H), 5.04–4.90(m, 1H), 3.68 (s, 3H), 3.43 (s, 1H), 3.32–3.28 (m, 2H), 3.25 (s, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 196.2, 171.4, 137.3, 129.2, 128.9, 128.7, 128.4, 127.7, 127.2, 126.9, 59.6, 55.9, 52.5, 43.4, 38.1. HRMS calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_2\text{S}_2^+$ $[\text{M}+\text{H}]^+$: 360.1086; found 360.1083.



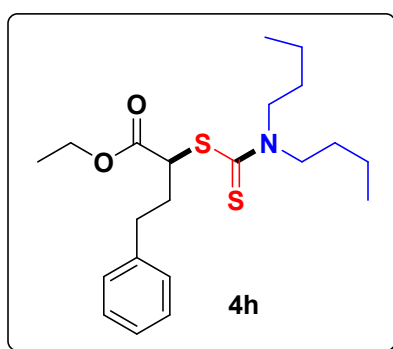
Methyl (S)-2-((dibutylcarbamothioyl)thio)-3-phenylpropanoate (4e). Eluent petroleum ether/ethyl acetate (20:1). Yellow oil, 79 mg, 72% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.31–7.26 (m, 4H), 7.24–7.20 (m, 1H), 5.08 (t, $J = 7.0$ Hz, 1H), 3.93–3.89 (m, 2H), 3.69–3.59 (m, 5H), 3.29–3.22 (m, 2H), 1.72–1.64 (m, 4H), 1.37–1.32 (m, 4H), 0.95 (dd, $J = 12.1, 7.2$ Hz, 6H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 193.2, 171.7, 137.6, 129.2, 128.3, 126.9, 55.3, 52.7, 52.4, 38.3, 29.4, 28.3, 20.1, 20.0, 13.8, 13.7. HRMS calcd for $\text{C}_{19}\text{H}_{30}\text{NO}_2\text{S}_2^+$ $[\text{M}+\text{H}]^+$: 368.1712; found 368.1708.



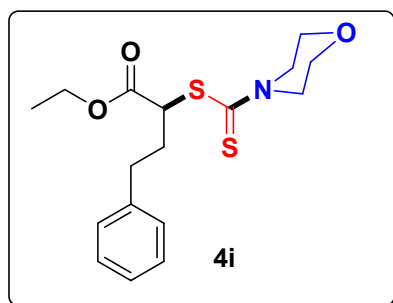
Methyl (S)-2-((morpholine-4-carbonothioyl)thio)-3-phenylpropanoate (4f). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 65 mg, 67% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.34–7.28 (m, 4H), 7.27–7.24 (m, 1H), 5.11 (t, $J=7.6$ Hz, 1H), 4.29 (s, 2H), 3.97 (s, 2H), 3.77 (s, 4H), 3.69 (s, 3H), 3.29 (d, $J = 7.6$ Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 194.8, 171.4, 137.2, 129.1, 128.4, 127.0, 66.1, 55.1, 52.6, 50.9, 38.0. HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{NO}_3\text{S}_2^+$ $[\text{M}+\text{H}]^+$: 326.0879; found 326.0884.



Ethyl (*S*)-2-((methyl(phenyl)carbamothioyl)thio)-4-phenylbutanoate (4g). Eluent petroleum ether/ethyl acetate (20:1). Yellow oil, 80 mg, 71% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.49–7.42 (m, 3H), 7.26 (t, $J=7.4$ Hz, 4H), 7.19–7.14 (m, 3H), 4.73 (t, $J=7.1$ Hz, 1H), 4.21–4.15 (m, 2H), 3.74 (d, $J=15.1$ Hz, 3H), 2.75–2.62 (m, 2H), 2.25–2.08 (m, 2H), 1.28 (t, $J=7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 197.1, 171.5, 140.8, 129.9, 129.2, 128.4, 126.9, 126.1, 61.5, 54.9, 46.3, 33.5, 33.5, 14.2. HRMS calcd for $\text{C}_{20}\text{H}_{24}\text{NO}_2\text{S}_2^+ [\text{M}+\text{H}]^+$: 374.1243; found 374.1242.

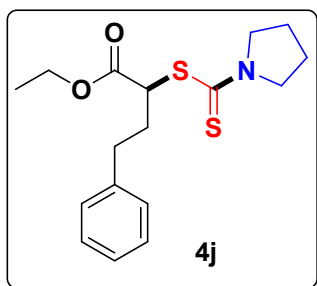


Ethyl (*S*)-2-((dibutylcarbamothioyl)thio)-4-phenylbutanoate (4h). Eluent petroleum ether/ethyl acetate (50:1). Colorless oil, 107 mg, 90% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.24 (d, $J=7.4$ Hz, 2H), 7.18–7.13 (m, 3H), 4.83 (t, $J=7.0$ Hz, 1H), 4.17 (q, $J=7.1$ Hz, 2H), 3.94–3.82 (m, 2H), 3.70–3.56 (m, 2H), 2.31–2.17 (m, 2H), 2.30–2.18 (m, 2H), 1.71–1.63 (m, 4H), 1.39–1.29 (m, 4H), 1.26 (t, $J=7.1$ Hz, 3H), 0.96–0.90 (m, 6H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 193.6, 171.6, 140.9, 128.4, 128.4, 126.0, 61.5, 55.2, 54.3, 52.6, 33.7, 33.5, 29.4, 28.3, 20.1, 14.1, 13.8, 13.7. HRMS calcd for $\text{C}_{21}\text{H}_{34}\text{NO}_2\text{S}_2^+ [\text{M}+\text{H}]^+$: 396.2025; found 396.2024.

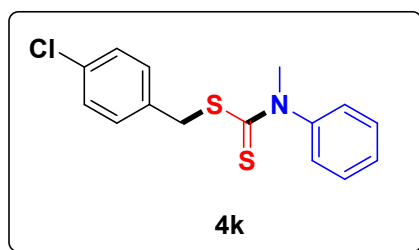


Methyl (*S*)-2-((morpholine-4-carbonothioyl)thio)-4-phenylbutanoate (4i). Eluent petroleum ether/ethyl acetate (5:1). Yellow oil, 73 mg, 69% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.26–7.22 (m, 2H), 7.16 (t, $J=6.6$ Hz, 3H), 4.82 (t, $J=7.0$ Hz, 1H),

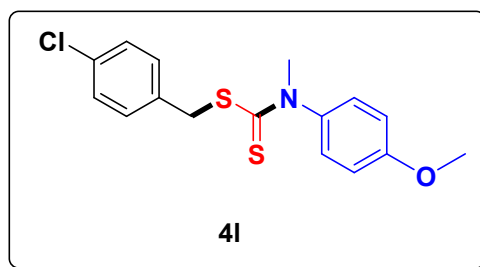
4.35–4.13 (m, 4H), 3.97 (s, 2H), 3.75–3.69 (m, 4H), 2.79–2.69 (m, 2H), 2.31–2.18 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 195.2, 171.3, 140.6, 128.4, 128.4, 126.2, 66.1, 61.7, 54.1, 50.9, 33.6, 33.5, 14.2. HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{NO}_3\text{S}_2^+ [\text{M}+\text{H}]^+$: 354.1192; found 354.1190.



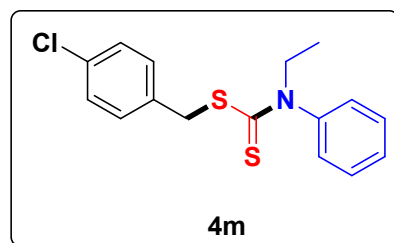
Ethyl (S)-4-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)butanoate (4j). Eluent petroleum ether/ethyl acetate (15:1). Yellow oil, 63 mg, 62% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.29–7.26 (m, 2H), 7.21–7.17 (m, 3H), 4.90 (t, $J = 7.0$ Hz, 1H), 4.23–4.19 (m, 2H), 3.91 (t, $J = 6.9$ Hz, 2H), 3.74–3.61 (m, 2H), 2.83–2.72 (m, 2H), 2.35–2.21 (m, 2H), 2.11–2.05 (m, 2H), 2.00–1.95 (m, 2H), 1.30 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 190.4, 171.5, 140.8, 128.4, 128.3, 126.0, 61.6, 55.1, 53.6, 50.5, 33.8, 33.4, 26.0, 24.2, 14.1. HRMS calcd for $\text{C}_{17}\text{H}_{24}\text{NO}_2\text{S}_2^+ [\text{M}+\text{H}]^+$: 338.1243; found 338.1246.



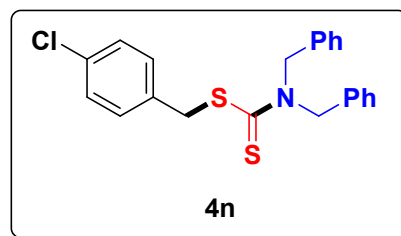
4-Chlorobenzyl methyl(phenyl)carbamodithioate (4k). Eluent petroleum ether/ethyl acetate (20:1). Brown oil, 63 mg, 68% yield. ^1H NMR ($\text{DMSO}-d_6$, 500 MHz, ppm) δ 7.50 (t, $J = 5.8$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.31–7.28 (m, 2H), 7.22 (t, $J = 8.6$ Hz, 4H), 4.63 (d, $J = 5.8$ Hz, 2H), 3.46 (s, 3H). ^{13}C NMR ($\text{DMSO}-d_6$, 125 MHz, ppm) δ 182.1, 144.1, 138.8, 130.9, 130.0, 128.9, 127.9, 127.6, 127.2, 47.6, 43.0. HRMS calcd for $\text{C}_{15}\text{H}_{15}\text{ClNS}_2^+ [\text{M}+\text{H}]^+$: 308.0329; found 308.0334.



4-Chlorobenzyl (4-methoxyphenyl)(methyl)carbamodithioate (4l). Eluent petroleum ether/ethyl acetate (5:1). Brown solid, 82 mg, 81% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.22 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.9$ Hz, 4H), 6.94 (d, $J = 8.8$ Hz, 2H), 4.75 (d, $J = 5.6$ Hz, 2H), 3.79 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 182.4, 159.3, 136.8, 134.8, 132.9, 128.6, 128.6, 128.0, 115.7, 55.4, 48.7, 43.7. HRMS calcd for $\text{C}_{16}\text{H}_{17}\text{ClNOS}_2^+ [\text{M}+\text{H}]^+$: 338.0435; found 338.0429.

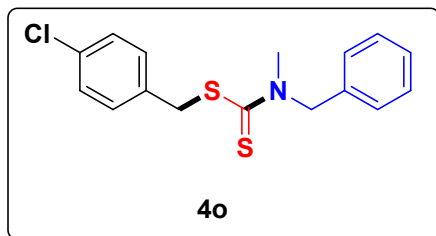


4-Chlorobenzyl ethyl(phenyl)carbamodithioate (4m). Eluent petroleum ether/ethyl acetate (20:1). Yellow oil, 60 mg, 59% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.47 (t, $J = 7.4$ Hz, 2H), 7.39 (t, $J = 7.1$ Hz, 1H), 7.21 (dd, $J = 15.9, 7.8$ Hz, 4H), 7.11 (d, $J = 8.0$ Hz, 2H), 4.77 (d, $J = 5.2$ Hz, 2H), 4.27 (q, $J = 6.9$ Hz, 2H), 1.21 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 181.6, 140.7, 136.7, 132.9, 130.6, 128.8, 128.6, 128.6, 128.1, 50.0, 48.6, 12.9. HRMS calcd for $\text{C}_{16}\text{H}_{17}\text{ClNS}_2^+ [\text{M}+\text{H}]^+$: 322.0485; found 322.0481.

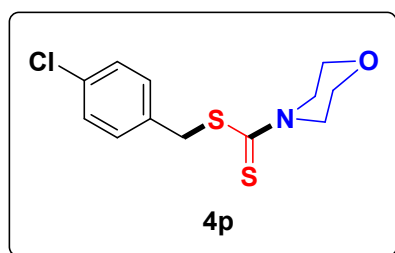


4-Chlorobenzyl dibenzylcarbamodithioate (4n). Eluent petroleum ether/ethyl acetate (5:1). Yellow solid, 103 mg, 86% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.34–7.27 (m, 6H), 7.23 (d, $J = 7.0$ Hz, 4H), 7.14 (d, $J = 8.3$ Hz, 2H), 6.91 (d, $J = 8.3$

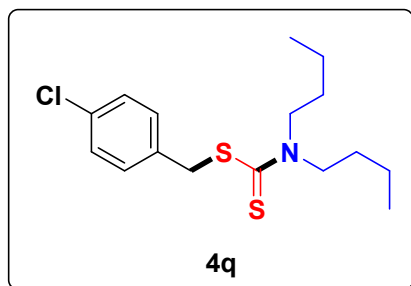
Hz, 2H), 4.96 (s, 4H), 4.75 (d, $J = 5.1$ Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 183.0, 136.3, 135.8, 133.008, 129.0, 128.7, 128.6, 127.9, 126.9, 54.2, 49.5. HRMS calcd for $\text{C}_{22}\text{H}_{20}\text{ClNS}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 420.0618; found 420.0612.



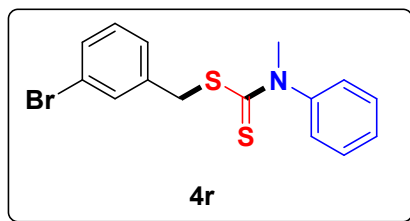
4-Chlorobenzyl benzyl(methyl)carbamodithioate (4o). Eluent petroleum ether/ethyl acetate (5:1). Yellow solid, 80 mg, 83% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.33 (t, $J = 7.2$ Hz, 2H), 7.28 (d, $J = 6.9$ Hz, 1H), 7.24 (d, $J = 5.1$ Hz, 4H), 7.18 (d, $J = 8.2$ Hz, 2H), 5.04 (s, 2H), 4.83 (d, $J = 5.1$ Hz, 2H), 3.16 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 182.6, 136.7, 136.3, 133.3, 129.1, 128.9, 128.8, 127.8, 127.1, 56.8, 49.5, 38.0. HRMS calcd for $\text{C}_{16}\text{H}_{16}\text{ClNS}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 344.0305; found 344.0301.



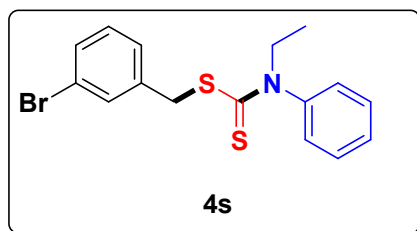
4-Chlorobenzyl morpholine-4-carbodithioate (4p).^[7] Eluent petroleum ether/ethyl acetate (10:1). White solid, 63 mg, 73% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.3–7.27 (m, 4H), 4.56 (s, 2H), 4.32 (s, 2H), 3.94 (s, 2H), 3.75 (s, 4H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 196.7, 134.6, 133.4, 130.7, 128.7, 66.2, 50.5, 40.9. HRMS calcd for $\text{C}_{12}\text{H}_{14}\text{ClNOS}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 310.0098; found 310.0103.



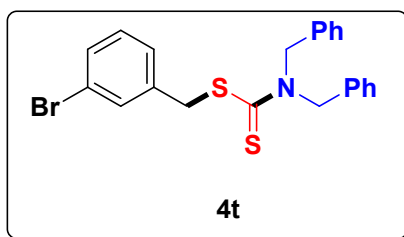
4-Chlorobenzyl dibutylcarbamodithioate (4q). Eluent petroleum ether/ethyl acetate (10:1). Yellow oil, 73 mg, 74% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.28 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 4.84 (d, $J = 5.1$ Hz, 2H), 3.62–3.50 (m, 4H), 1.64 – 1.57 (m, 4H), 1.36–1.28 (m, 4H), 0.91 (t, $J = 7.3$ Hz, 6H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 180.9, 137.0, 133.2, 129.0, 128.7, 51.1, 49.2, 29.5, 20.1, 13.8. HRMS calcd for $\text{C}_{16}\text{H}_{25}\text{ClNS}_2^+ [\text{M}+\text{H}]^+$: 330.1111; found 330.1108.



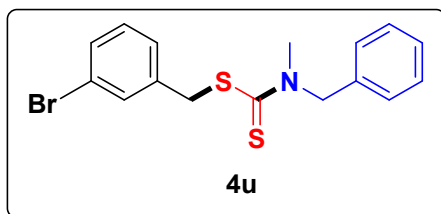
3-Bromobenzyl methyl(phenyl)carbamodithioate (4r). Eluent petroleum ether/ethyl acetate (20:1). Yellow oil, 83 mg, 79% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.48 (t, $J = 7.7$ Hz, 2H), 7.40–7.30 (m, 3H), 7.24 (d, $J = 7.8$ Hz, 2H), 7.17–7.11 (m, 2H), 4.80 (d, $J = 5.7$ Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 182.4, 142.6, 140.6, 130.7, 130.4, 130.2, 130.1, 128.7, 127.0, 125.8, 122.6, 48.8, 43.6. HRMS calcd for $\text{C}_{15}\text{H}_{15}\text{BrNS}_2^+ [\text{M}+\text{H}]^+$: 351.9824; found 351.9827.



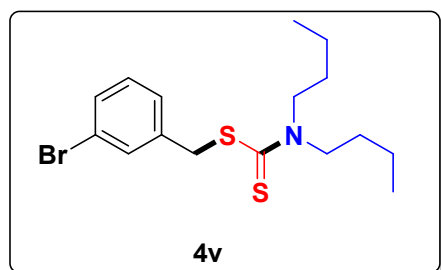
3-Bromobenzyl ethyl(phenyl)carbamodithioate (4s). Eluent petroleum ether/ethyl acetate (20:1). Brown oil, 63 mg, 57% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.49 (t, $J = 7.7$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.35–7.31 (m, 1H), 7.29 (s, 1H), 7.21 (d, $J = 7.5$ Hz, 2H), 7.15–7.09 (m, 2H), 4.79 (d, $J = 5.7$ Hz, 2H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 181.7, 140.7, 140.6, 130.6, 130.3, 130.2, 130.1, 128.9, 128.2, 125.8, 122.5, 50.0, 48.6, 12.9. HRMS calcd for $\text{C}_{16}\text{H}_{17}\text{BrNS}_2^+ [\text{M}+\text{H}]^+$: 365.9980; found 365.9984.



3-Bromobenzyl dibenzylcarbamodithioate (4t). Eluent petroleum ether/ethyl acetate (10:1). Yellow oil, 106 mg, 80% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.35 (d, $J = 7.6$ Hz, 4H), 7.31 (d, $J = 7.3$ Hz, 3H), 7.27 (d, $J = 7.1$ Hz, 4H), 7.14 (s, 1H), 7.09 (t, $J = 7.8$ Hz, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 5.00 (s, 4H), 4.81 (d, $J = 5.1$ Hz, 2H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 183.1, 140.2, 135.7, 130.5, 130.2, 130.0, 129.0, 128.0, 127.0, 126.0, 122.6, 54.3, 49.6. HRMS calcd for $\text{C}_{22}\text{H}_{21}\text{BrNS}_2^+$ $[\text{M}+\text{H}]^+$: 442.0293; found 442.0299.

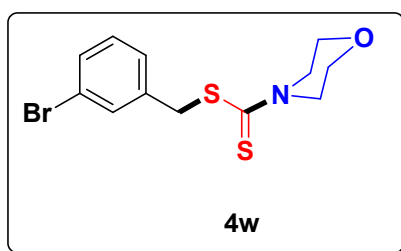


3-Bromobenzyl benzyl(methyl)carbamodithioate (4u). Eluent petroleum ether/ethyl acetate (10:1). Colorless oil, 64 mg, 58% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.39–7.35 (m, 2H), 7.33 (d, $J = 7.5$ Hz, 2H), 7.28 (d, $J = 7.1$ Hz, 1H), 7.25–7.23 (m, 2H), 7.16 (dd, $J = 12.7, 4.7$ Hz, 2H), 5.04 (s, 2H), 4.84 (d, $J = 5.3$ Hz, 2H), 3.17 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 182.6, 140.5, 136.1, 130.6, 130.6, 130.2, 128.9, 127.8, 127.0, 126.3, 122.6, 56.7, 49.5, 38.0. HRMS calcd for $\text{C}_{16}\text{H}_{17}\text{BrNS}_2^+$ $[\text{M}+\text{H}]^+$: 365.9980; found 365.9982.

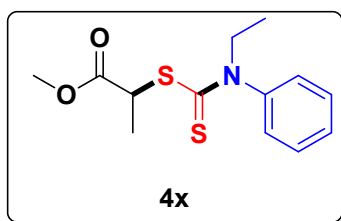


3-Bromobenzyl dibutylcarbamodithioate (4v). Eluent petroleum ether/ethyl acetate (10:1). Colorless oil, 76 mg, 68% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.45 (s,

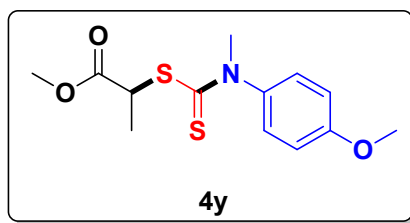
1H), 7.40 (d, $J = 7.8$ Hz, 1H), 7.27–7.25 (m, 1H), 7.20 (t, $J = 7.8$ Hz, 1H), 4.88 (d, $J = 5.2$ Hz, 2H), 3.62–3.55 (m, 4H), 1.65–1.59 (m, 4H), 1.34 (dd, $J = 15.1, 7.5$ Hz, 4H), 0.94 (t, $J = 7.3$ Hz, 6H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 181.1, 140.9, 130.7, 130.6, 130.3, 126.3, 122.7, 51.2, 49.4, 29.6, 20.2, 13.8. HRMS calcd for $\text{C}_{16}\text{H}_{25}\text{BrNS}_2^+ [\text{M}+\text{H}]^+$: 374.0606; found 374.0601.



3-Bromobenzyl morpholine-4-carbodithioate (4w). Eluent petroleum ether/ethyl acetate (10:1). Colorless oil, 71 mg, 71% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.53 (s, 1H), 7.39 (d, $J = 7.9$ Hz, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.17 (t, $J = 7.8$ Hz, 1H), 4.56 (s, 2H), 4.33 (s, 2H), 3.95 (s, 2H), 3.76 (s, 4H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 196.5, 138.5, 132.2, 130.6, 130.0, 128.0, 122.5, 66.2, 51.1, 40.9. HRMS calcd for $\text{C}_{12}\text{H}_{15}\text{BrNOS}_2^+ [\text{M}+\text{H}]^+$: 331.9773; found 331.9782.

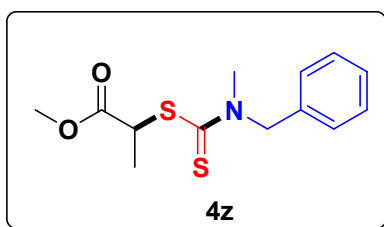


Methyl (S)-2-((ethyl(phenyl)carbamothioyl)thio)propanoate (4x). Eluent petroleum ether/ethyl acetate (20:1). Yellow oil, 42 mg, 49% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.47 (m, 3H), 7.23 (d, $J = 6.7$ Hz, 2H), 4.69 (q, $J = 7.4$ Hz, 1H), 4.34–4.27 (m, 2H), 3.71 (s, 3H), 1.47 (d, $J = 7.3$ Hz, 3H), 1.25 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 196.7, 172.8, 129.8, 129.3, 128.0, 100.0, 52.8, 52.6, 49.3, 17.1, 11.1. HRMS calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_2\text{S}_2^+ [\text{M}+\text{H}]^+$: 284.0773; found 284.0779.



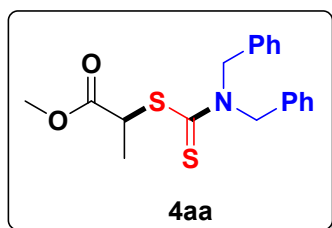
Methyl (S)-2-(((4-methoxyphenyl)(methyl)carbamothioyl)thio)propanoate (4y).

Eluent petroleum ether/ethyl acetate (20:1). Brown oil, 49 mg, 55% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 4.65 (q, *J* = 7.3 Hz, 1H), 3.84 (s, 3H), 3.71 (d, *J* = 5.0 Hz, 6H), 1.48 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 197.6, 172.8, 159.9, 137.0, 128.0, 114.9, 55.5, 52.6, 49.5, 46.4, 17.1. HRMS calcd for C₁₃H₁₈NO₃S₂⁺ [M+H]⁺: 300.0723; found 300.0728.



Methyl (S)-2-((benzyl(methyl)carbamothioyl)thio)propanoate (4z).

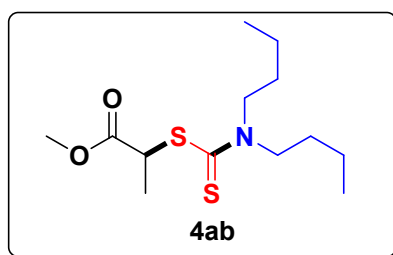
Eluent petroleum ether/ethyl acetate (20:1). Yellow oil, 52 mg, 61% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.40–7.27 (m, 4H), 7.22 (d, *J* = 6.4 Hz, 1H), 5.42–4.89 (m, 2H), 4.85–4.78 (m, 1H), 3.43 (s, 1H), 3.26 (s, 2H), 1.63 (t, *J* = 10.0 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 196.6, 172.6, 135.3, 128.7, 127.7, 127.1, 59.5, 57.8, 52.7, 49.7, 17.3. HRMS calcd for C₁₃H₁₈NO₂S₂⁺ [M+H]⁺: 284.0773; found 284.0776.



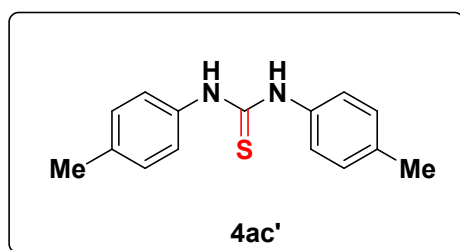
Methyl (S)-2-((dibenzylcarbamothioyl)thio)propanoate (4aa).

Eluent petroleum ether/ethyl acetate (10:1). Yellow oil, 78 mg, 72% yield. ¹H NMR (CDCl₃, 500 MHz, ppm) δ 7.38–7.33 (m, 6H), 7.26–7.24 (m, 4H), 5.35–5.22 (m, 2H), 4.95–4.85 (m, 3H), 3.78 (s, 3H), 1.65 (d, *J* = 7.4 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz, ppm) δ 197.4,

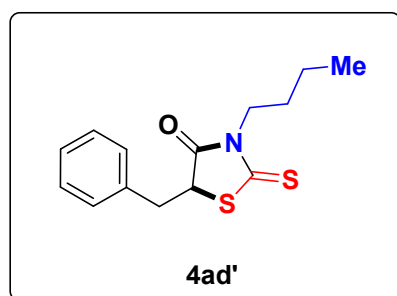
172.6, 135.3, 134.3, 129.0, 128.8, 128.0, 127.9, 127.8, 127.2, 56.1, 54.1, 52.8, 49.8, 17.2. HRMS calcd for $C_{19}H_{22}NO_2S_2^+$ $[M+H]^+$: 360.1086; found 360.1090.



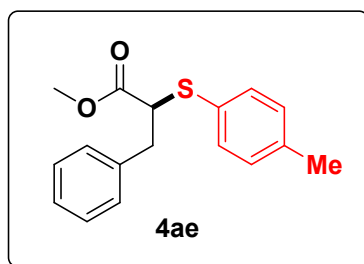
Methyl (S)-2-((dibutylcarbamothioyl)thio)propanoate (4ab). Eluent petroleum ether/ethyl acetate (15:1). Yellow oil, 60 mg, 69% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 4.80 (q, $J = 7.4$ Hz, 1H), 3.93–3.89 (m, 2H), 3.75 (s, 3H), 3.71–3.57 (m, 2H), 1.74–1.65 (m, 4H), 1.59 (d, $J = 7.4$ Hz, 3H), 1.39–1.32 (m, 4H), 0.98–0.92 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.7, 173.0, 55.2, 52.7, 49.1, 29.3, 28.3, 20.1, 17.4, 13.8, 13.7. HRMS calcd for $C_{13}H_{26}NO_2S_2^+$ $[M+H]^+$: 292.1399; found 292.1400.



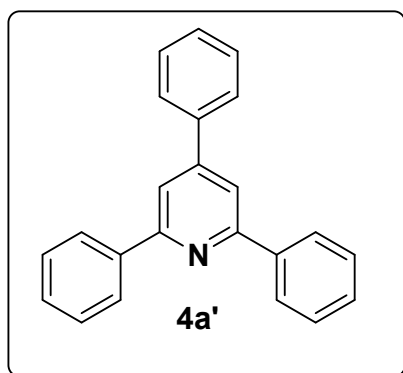
1,3-di-*p*-tolylthiourea (4ac'). Eluent petroleum ether/ethyl acetate (10:1). Yellow oil, 20 mg, 25% yield. 1H NMR ($CDCl_3$, 500 MHz, ppm) δ 7.80 (s, 2H), 7.25 (d, $J = 8.3$ Hz, 4H), 7.20 (d, $J = 8.2$ Hz, 4H), 2.35 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm) δ 180.2, 137.1, 134.4, 130.1, 125.5, 21.0. HRMS calcd for $C_{15}H_{17}N_2S^+$ $[M+H]^+$: 257.1107; found 257.1110.



5-Benzyl-3-butyl-2-thioxothiazolidin-4-one (4ad'). Eluent petroleum ether/ethyl acetate (10:1). Yellow oil, 18 mg, 20% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.33 – 7.27 (m, 3H), 7.22 (d, $J = 7.2$ Hz, 2H), 4.42 (dd, $J = 9.5, 3.8$ Hz, 1H), 3.96 – 3.89 (m, 2H), 3.54 – 3.50 (m, 1H), 3.14 – 3.09 (m, 1H), 1.55 – 1.47 (m, 2H), 1.33 – 1.26 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 200.4, 175.8, 135.6, 129.2, 128.8, 127.6, 52.4, 44.5, 38.4, 28.7, 19.9, 13.6. HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{NOS}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 302.0644; found 302.0646.



Methyl 3-phenyl-2-(*p*-tolylthio)propanoate (4ae). Eluent petroleum ether/ethyl acetate (20:1). Colorless oil, 30 mg, 35% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 7.33 (d, $J = 8.0$ Hz, 2H), 7.28 (t, $J = 7.4$ Hz, 2H), 7.22 (t, $J = 7.1$ Hz, 1H), 7.18 (d, $J = 7.3$ Hz, 2H), 7.12 (d, $J = 7.9$ Hz, 2H), 3.83 (dd, $J = 9.3, 6.3$ Hz, 1H), 3.59 (s, 3H), 3.17 (dd, $J = 13.9, 9.3$ Hz, 1H), 3.04 (dd, $J = 13.9, 6.2$ Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 172.1, 138.6, 137.8, 133.9, 129.8, 129.1, 129.0, 128.5, 126.8, 52.4, 52.1, 37.9, 21.2. HRMS calcd for $\text{C}_{17}\text{H}_{19}\text{O}_2\text{S}^+ [\text{M}+\text{H}]^+$: 287.1100; found 287.1114.



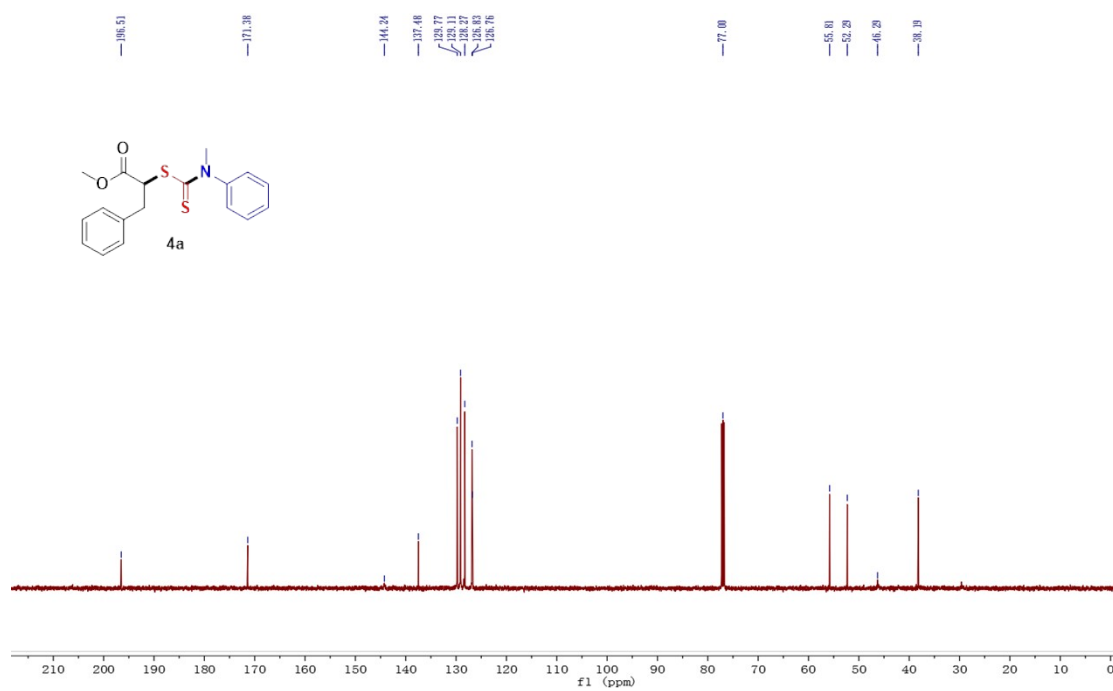
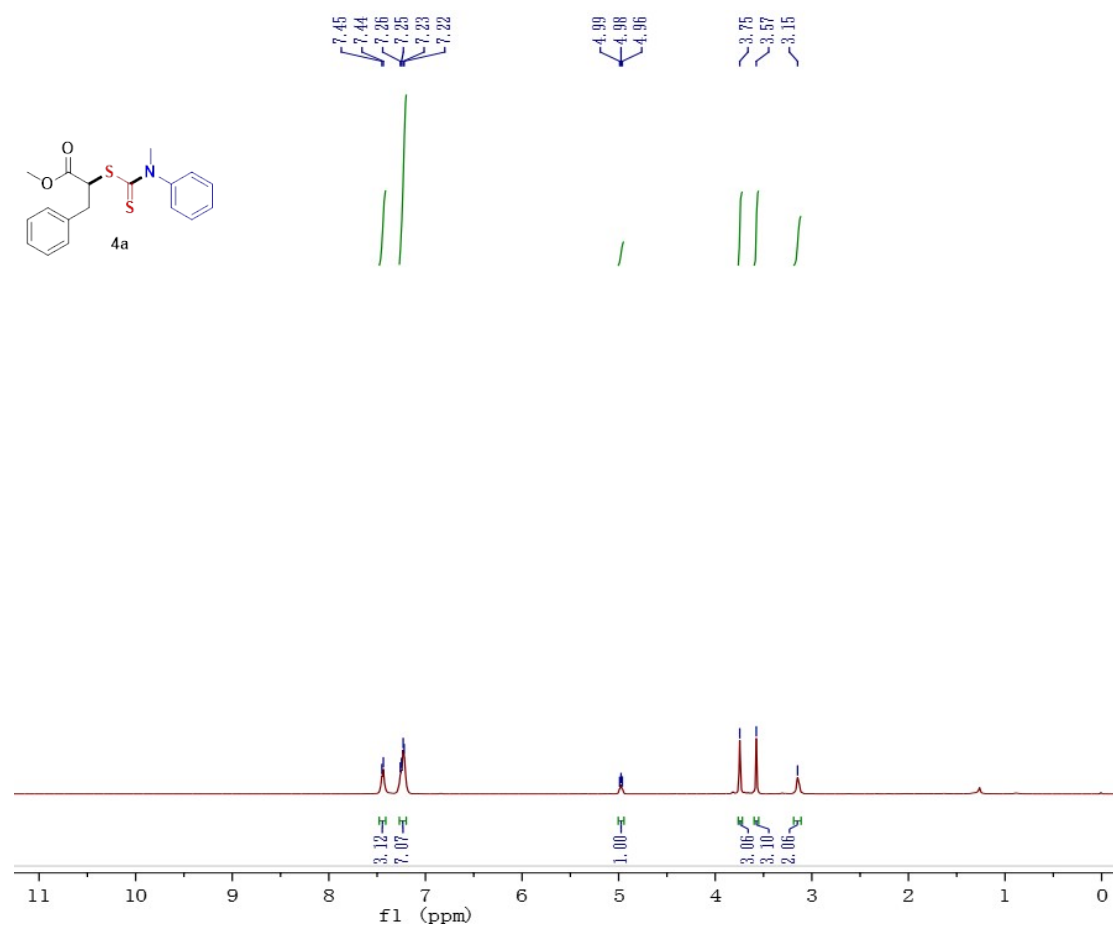
2,4,6-Triphenylpyridine (4a').⁸ Eluent petroleum ether/ethyl acetate (100:1). White solid, 88 mg, 95% yield. ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 8.23 (d, $J = 7.5$ Hz, 4H),

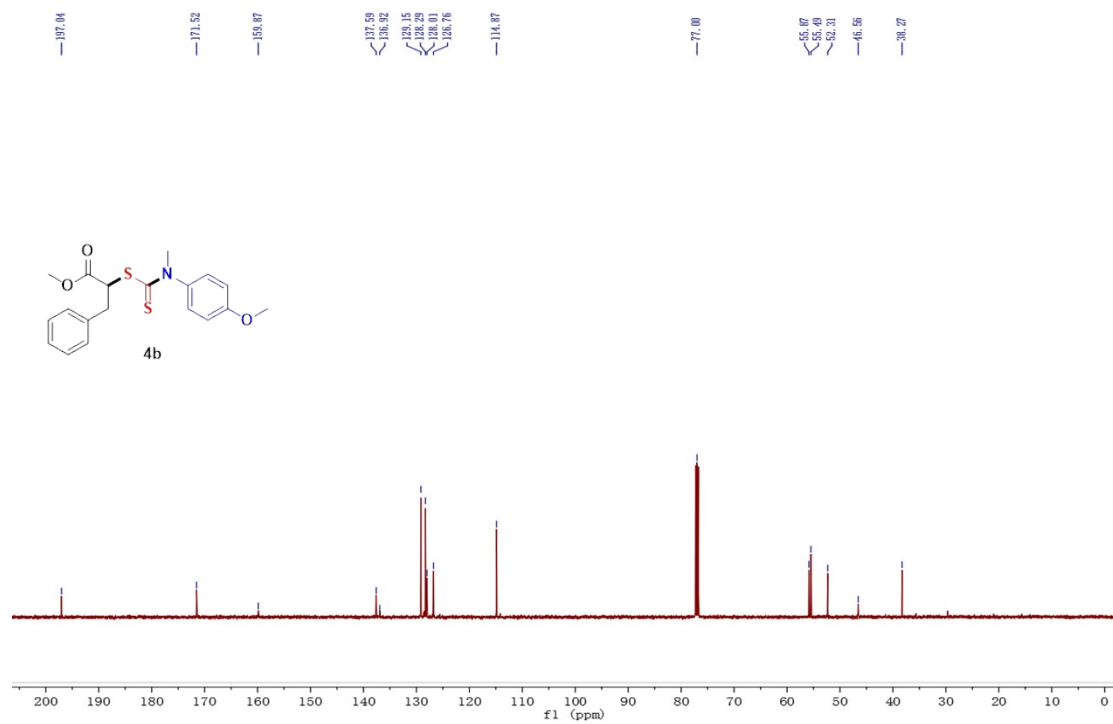
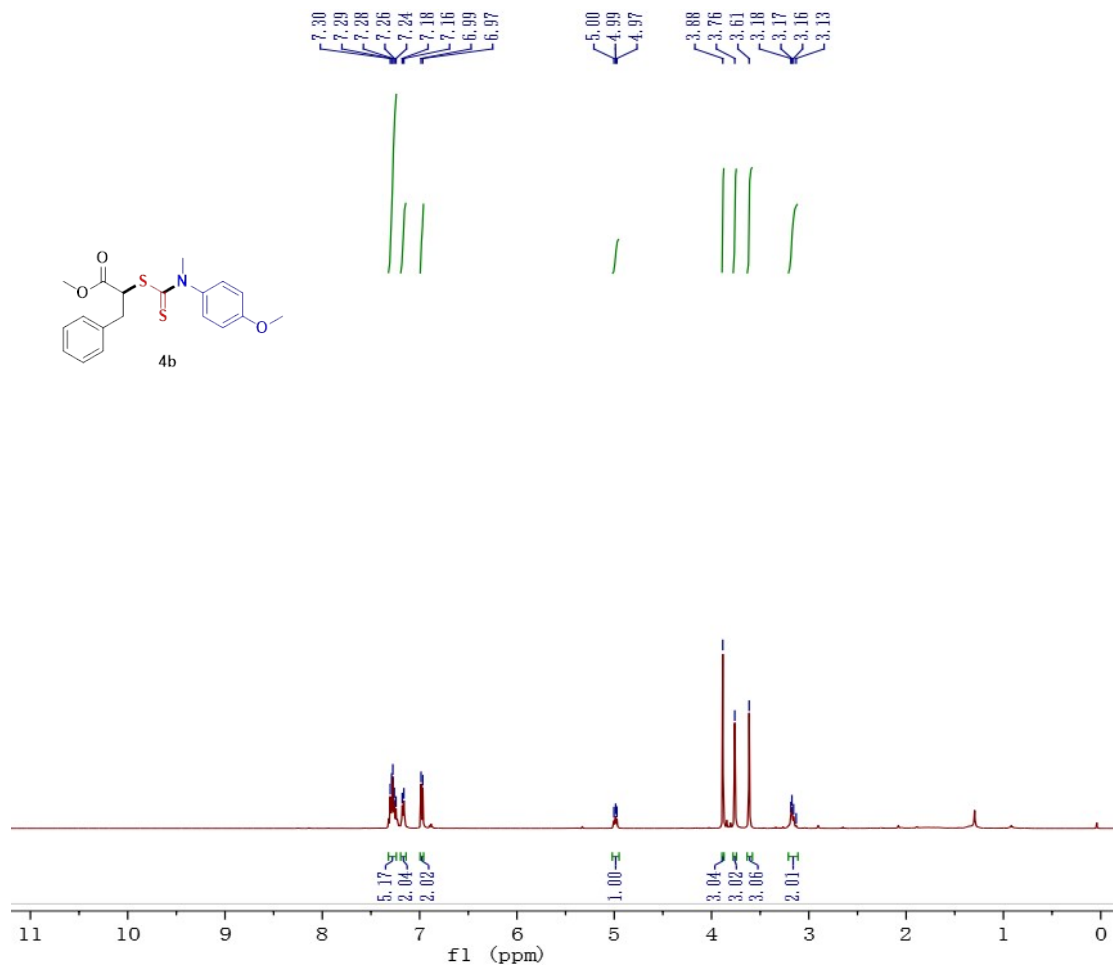
7.91 (s, 2H), 7.77 (d, $J = 7.3$ Hz, 2H), 7.57 – 7.52 (m, 6H), 7.51 – 7.45 (m, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 157.5, 150.2, 139.6, 139.0, 129.1, 129.0, 128.9, 128.7, 127.2, 127.1, 117.1. HRMS calcd for $\text{C}_{23}\text{H}_{18}\text{N}^+$ $[\text{M}+\text{H}]^+$: 308.1434; found 308.1436.

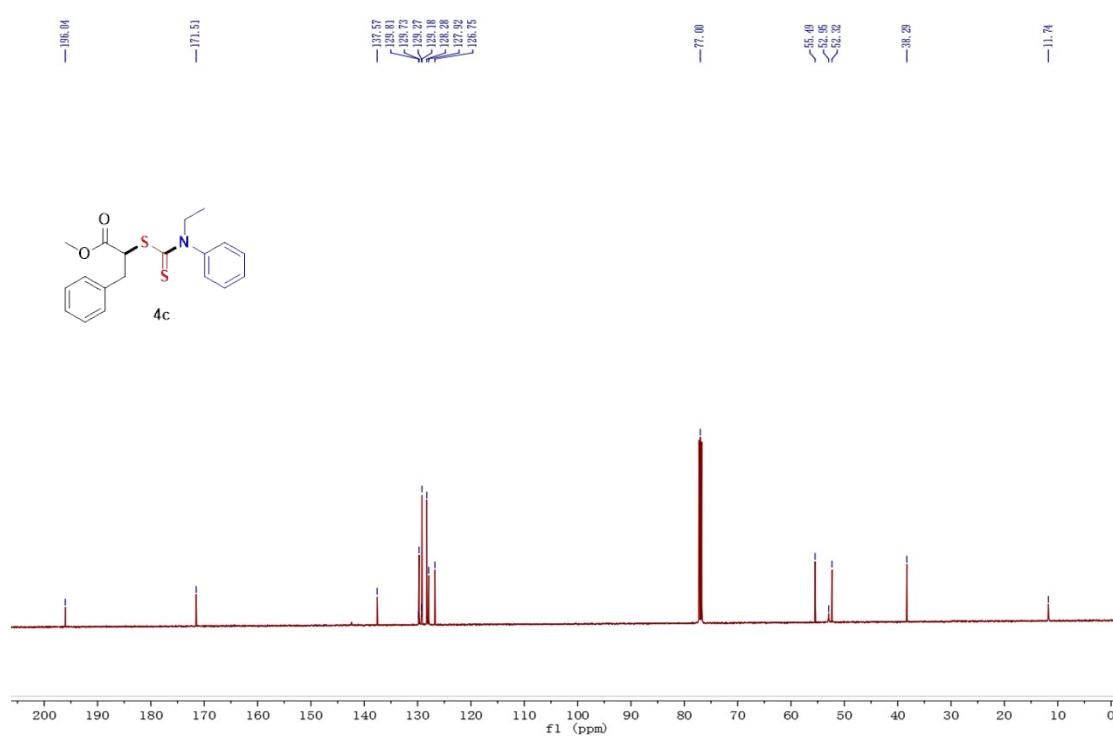
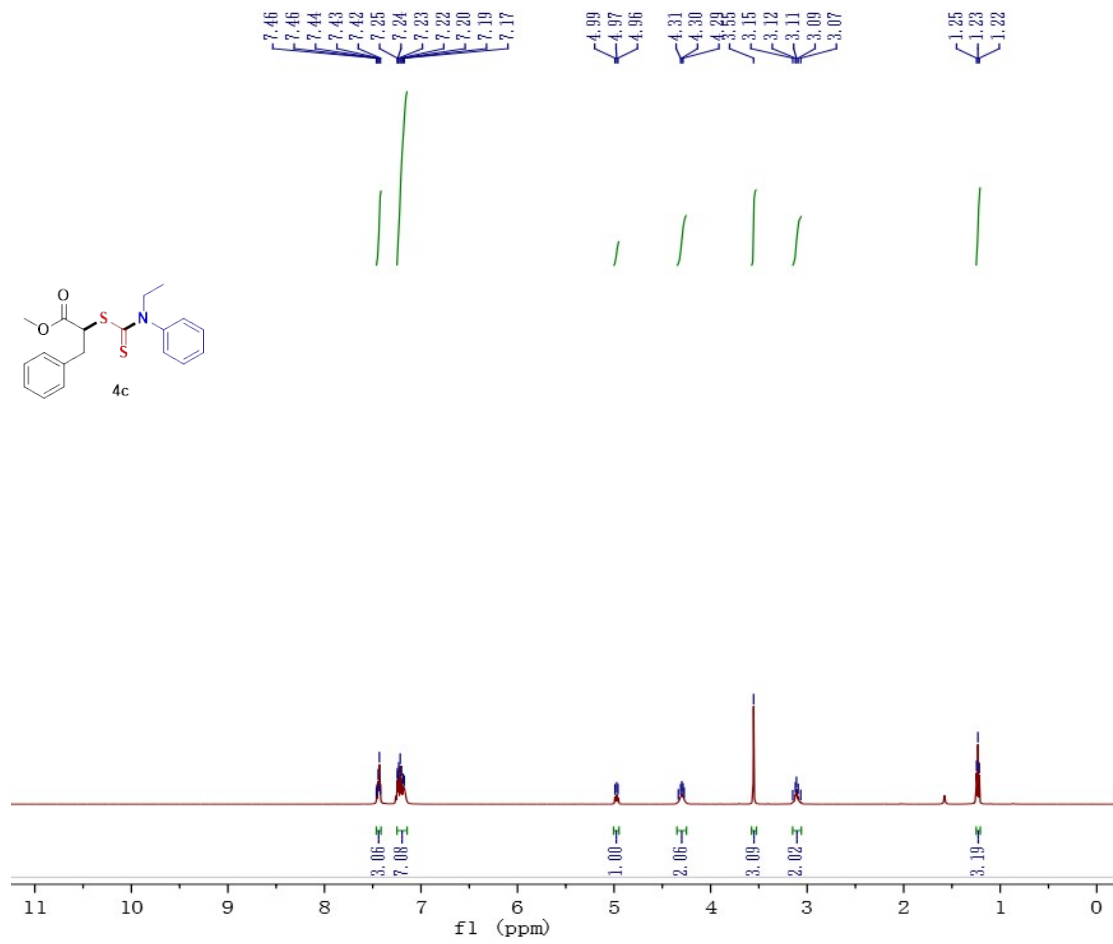
V. References

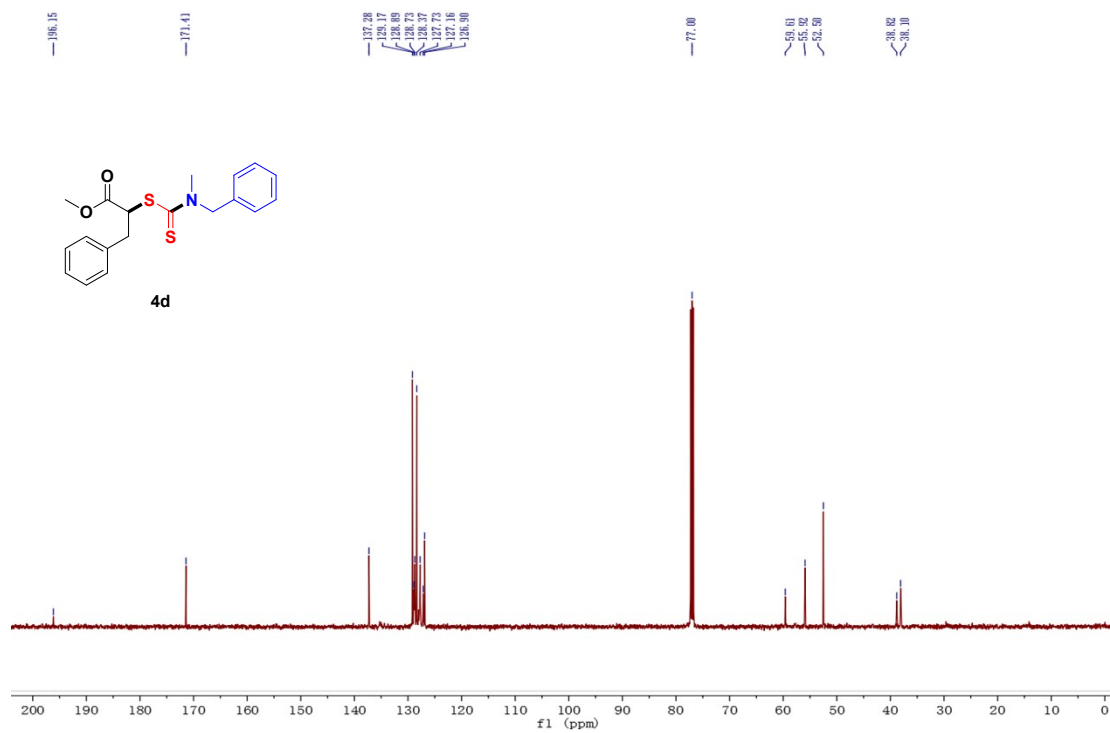
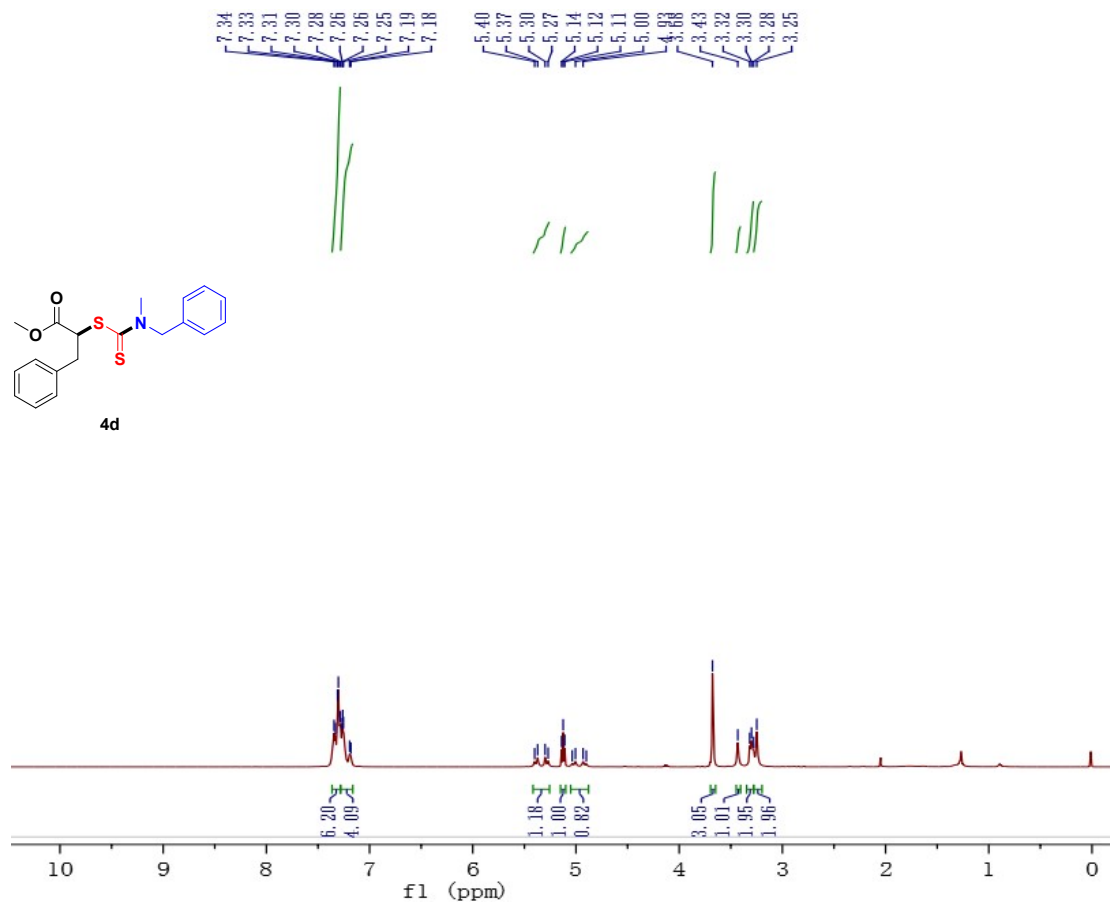
- [1] L. Habert and K. Cariou, *Angew. Chem. Int. Ed.*, **2021**, 60, 171–175.
- [2] F. T. Pulikottil, R. Pilli, R. V. Suku and R. Rasappan, *Org. Lett.*, **2020**, 22, 2902–2907.
- [3] M. E. Hoerrner, K. M. Baker, C. H. Basch, E. M. Bampo, and M. P. Watson, *Org. Lett.*, **2019**, 21, 7356-7360.
- [4] F. J. R. Klauck, H. Yoon, M. J. James, M. Lautens and F. Glorius, *ACS Catal.*, **2019**, 9, 236–241.
- [5] M. Ociepa, J. Turkowska and Dorota Gryko, *ACS Catal.*, **2018**, 8, 11362–11367.
- [6] L. Pitzer, F. Schäfers and F. Glorius, *Angew. Chem., Int. Ed.*, **2019**, 58, 8572-8576.
- [7] K. Biswas, S. Ghosh, P. Ghosh and B. Basu, *J. Sulfur. Chem.*, **2016**, 37, 361–376.
- [8] W. Tan, Y. J. Ong, N. Yoshikai, *Angew. Chem., Int. Ed.*, **2017**, 56, 8240-8244.

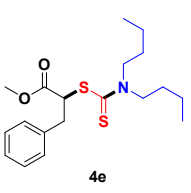
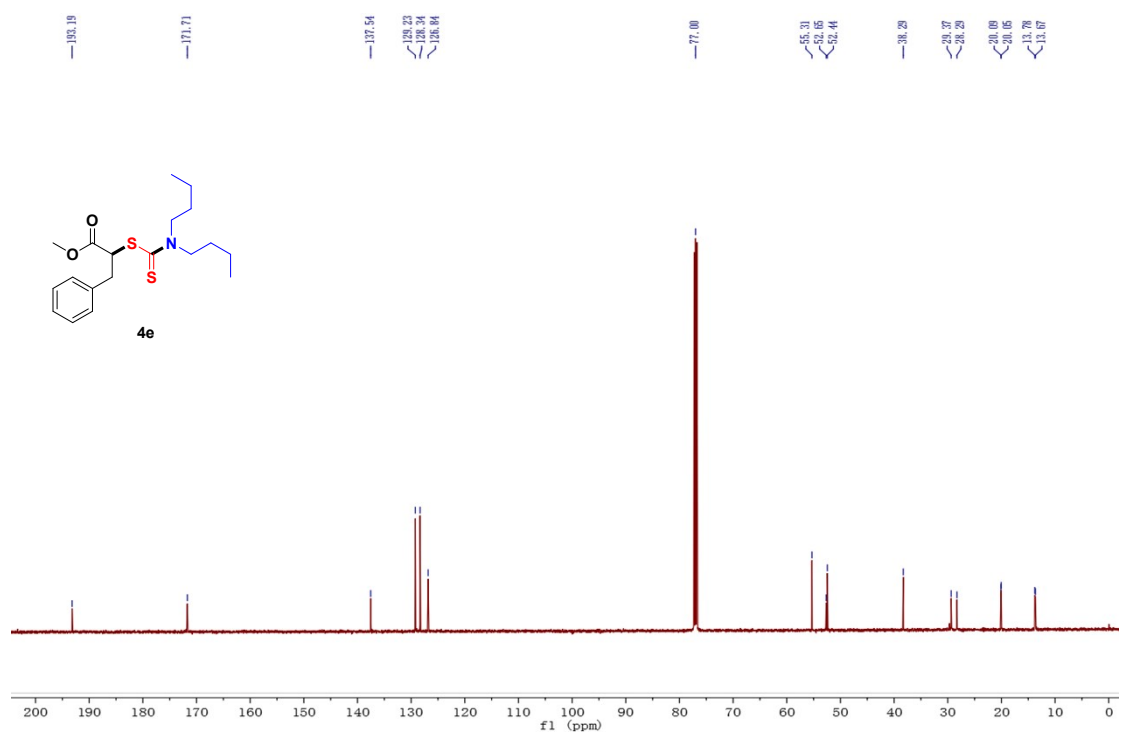
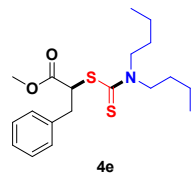
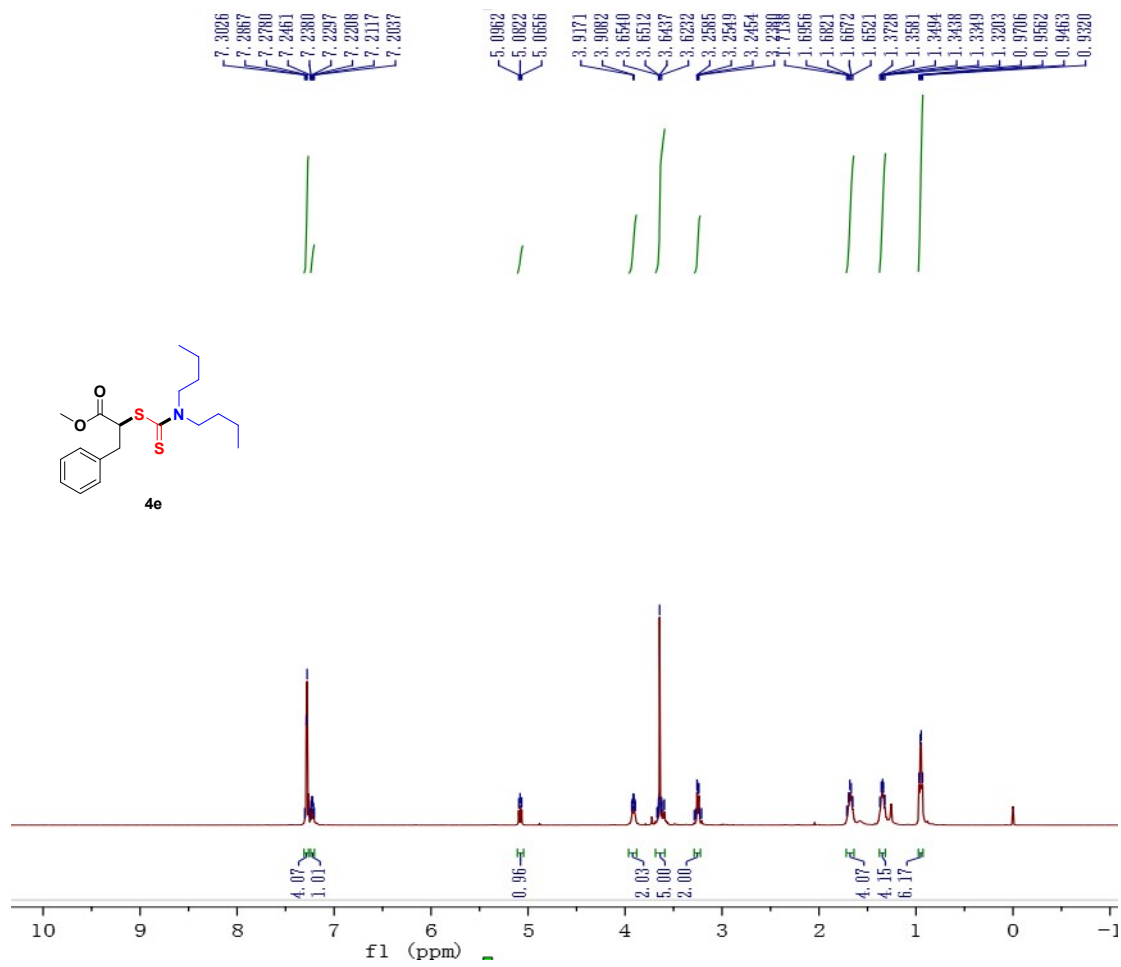
VI. NMR spectra of the products

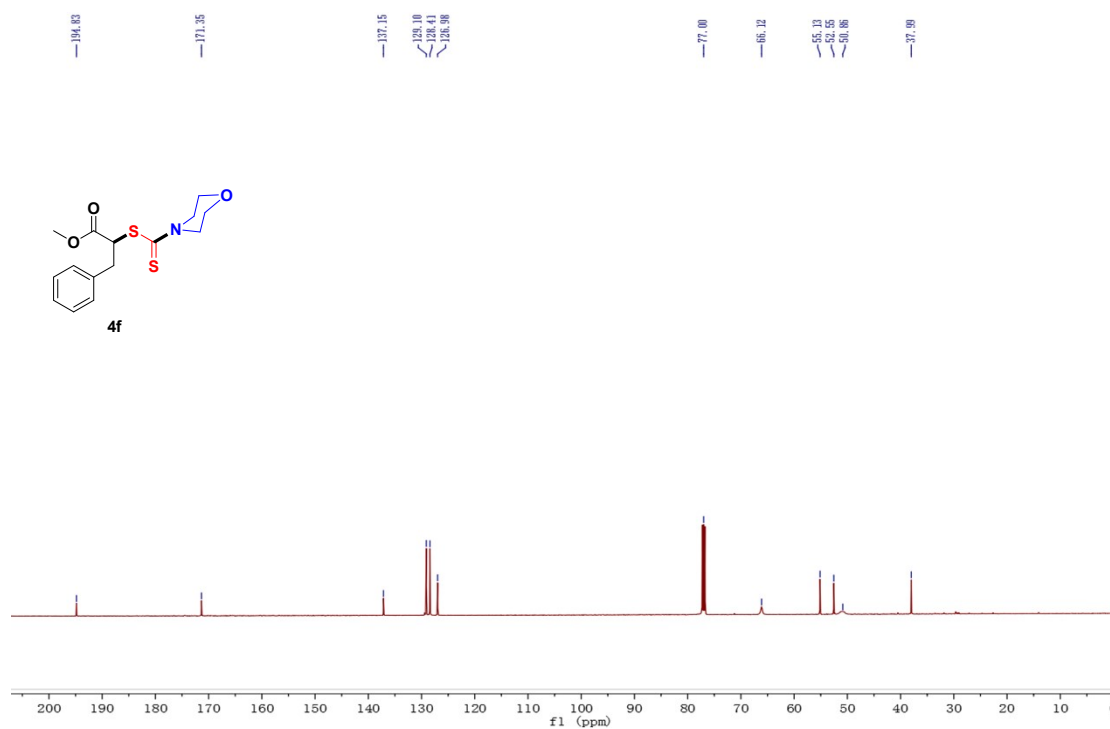
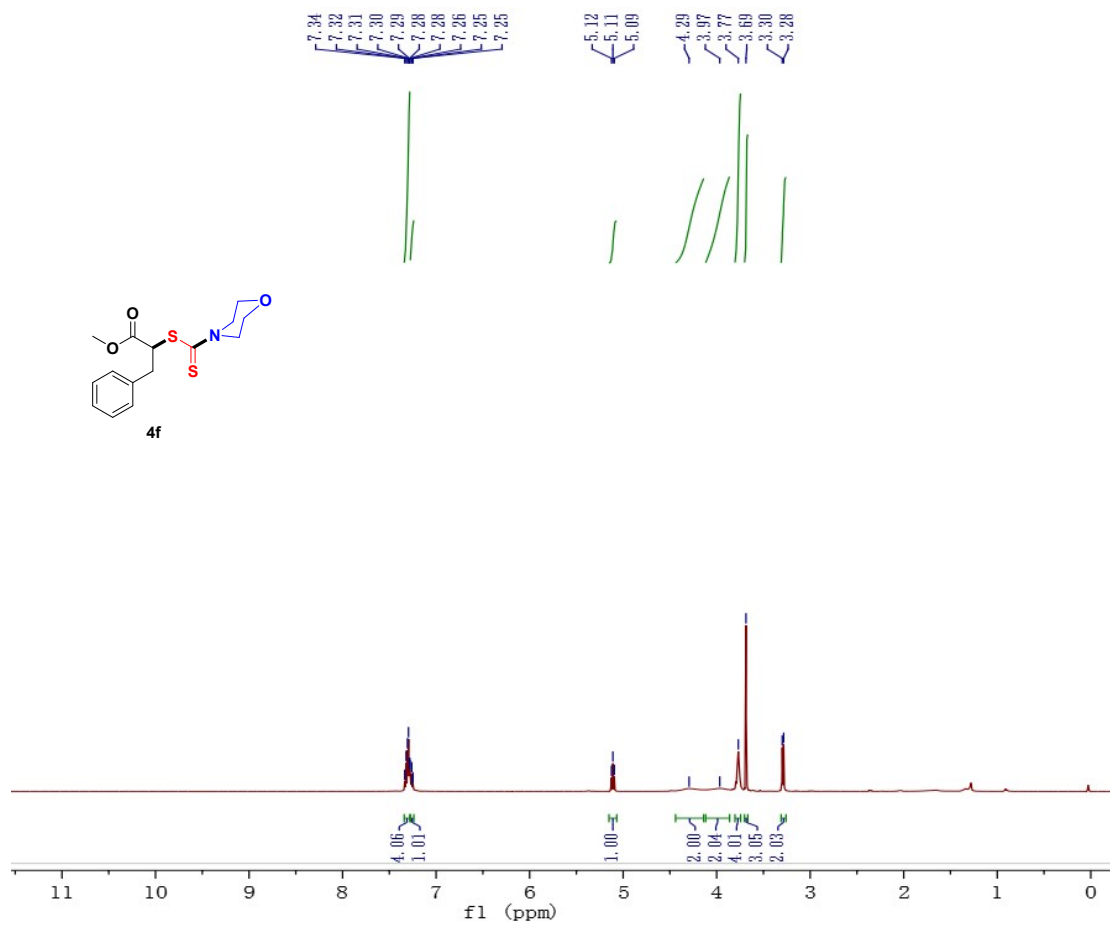


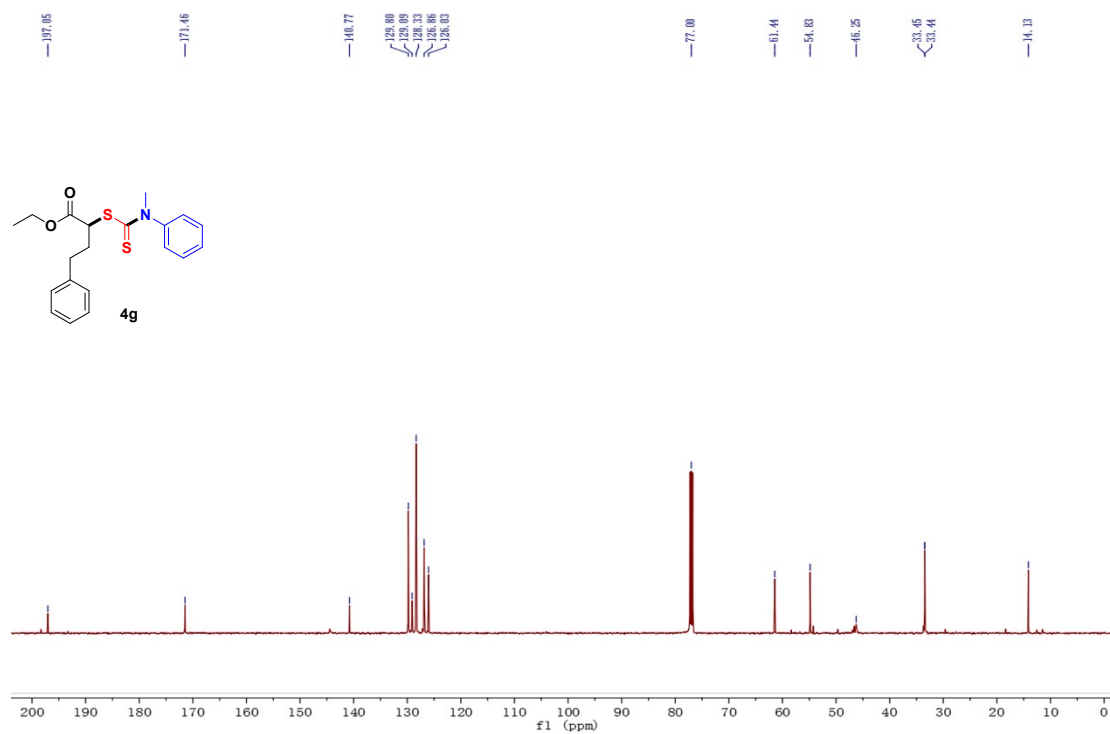
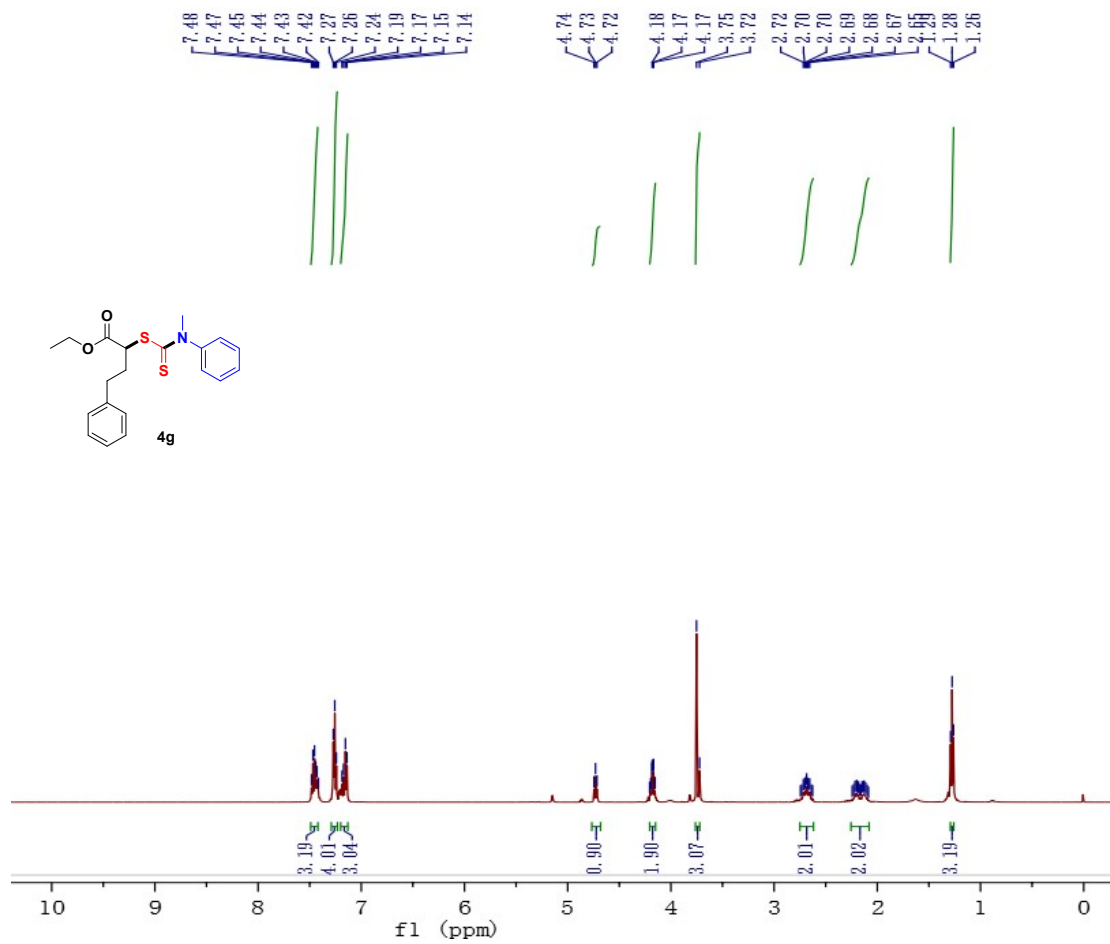


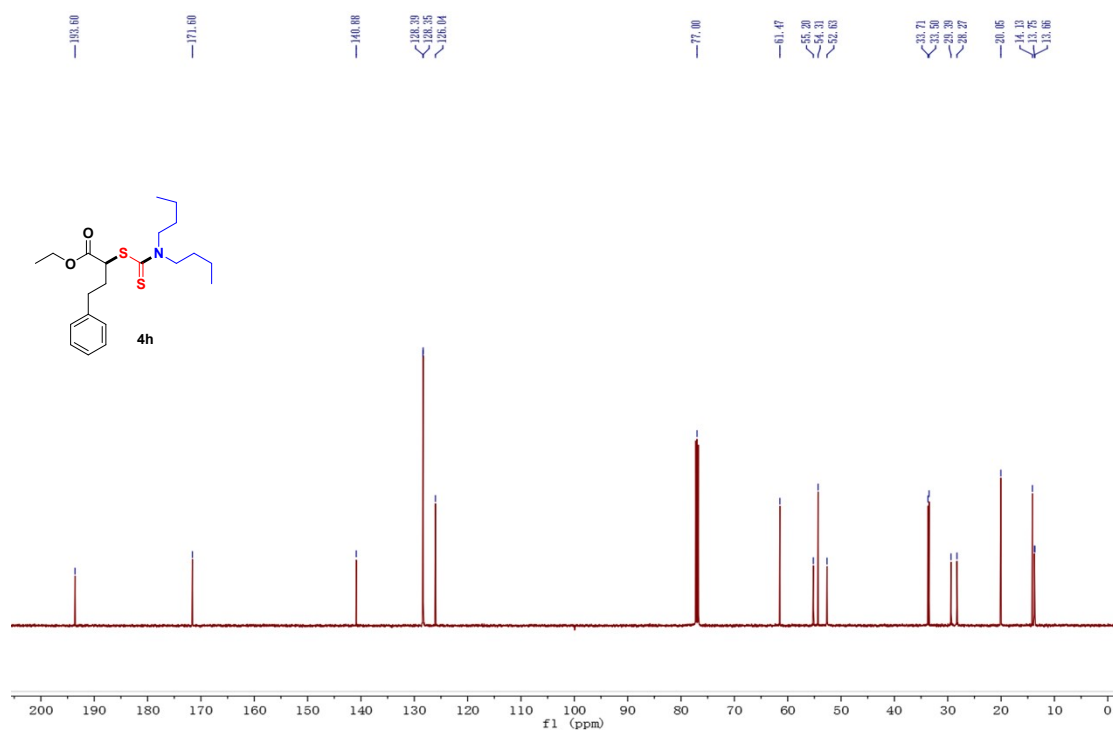
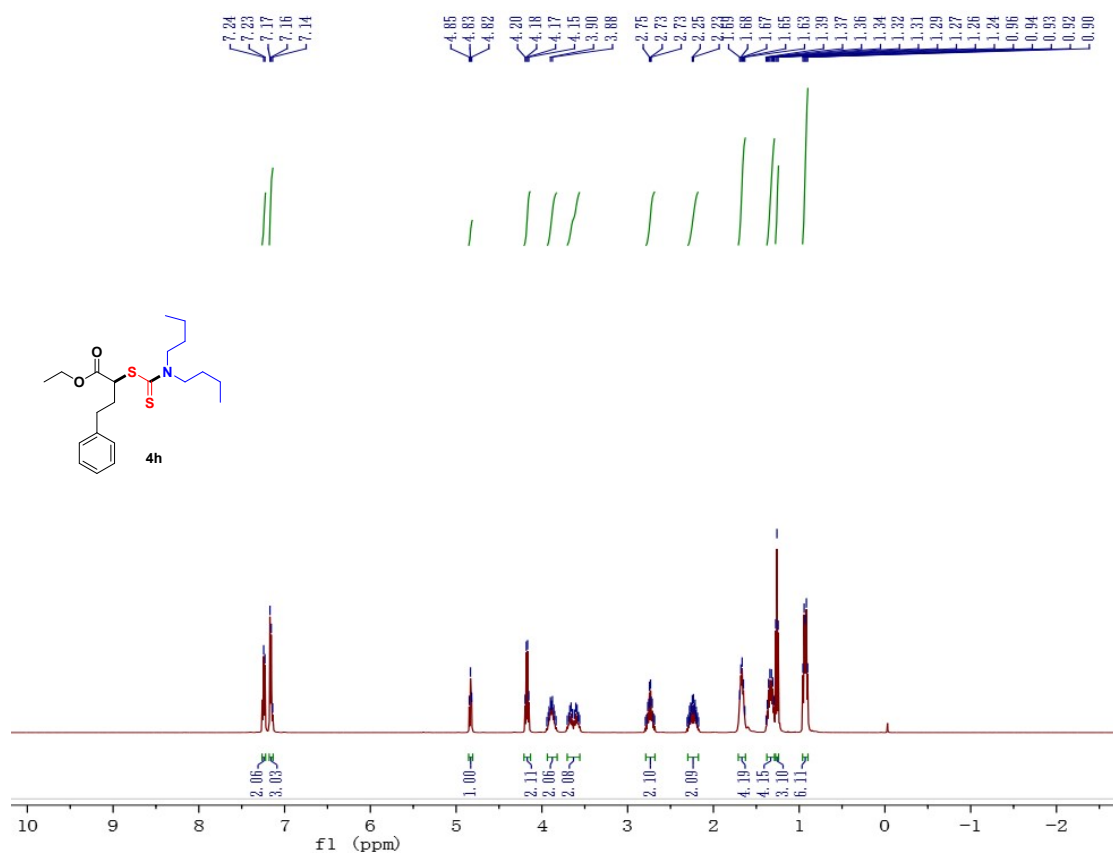


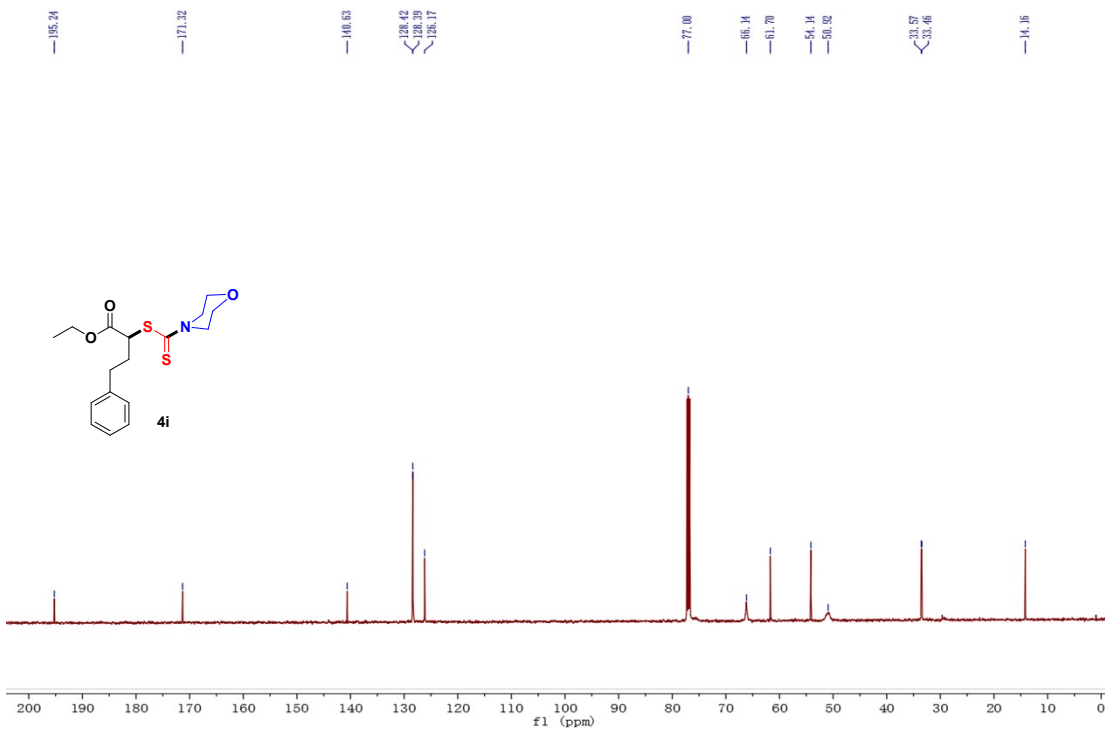
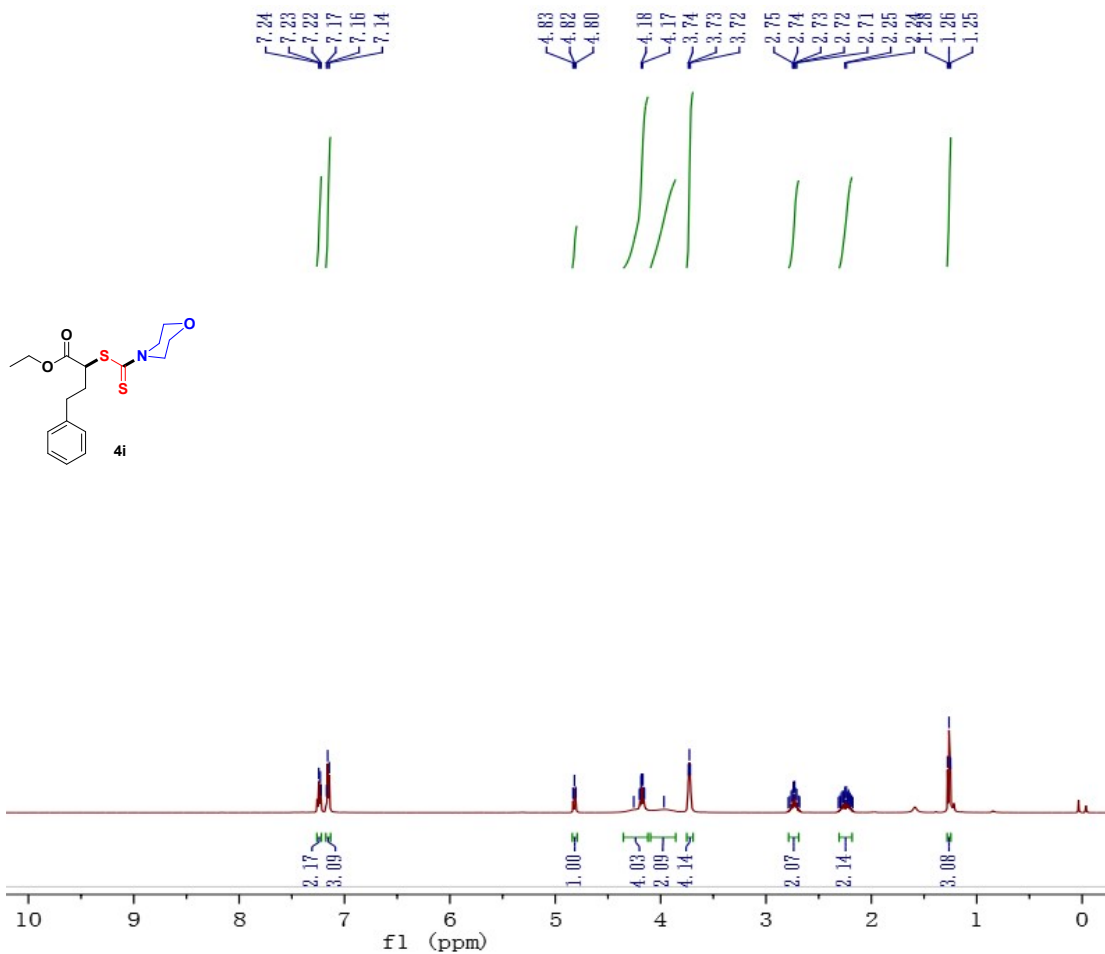


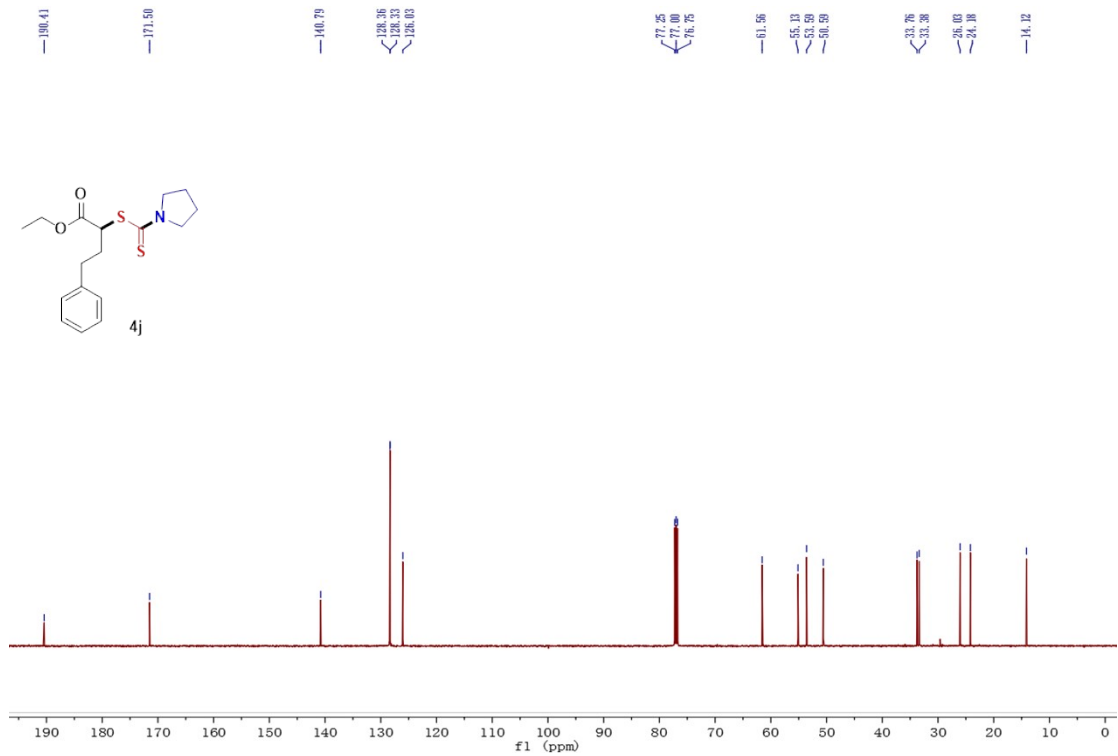
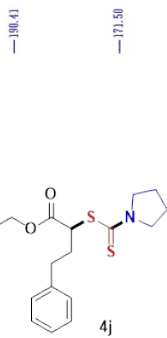
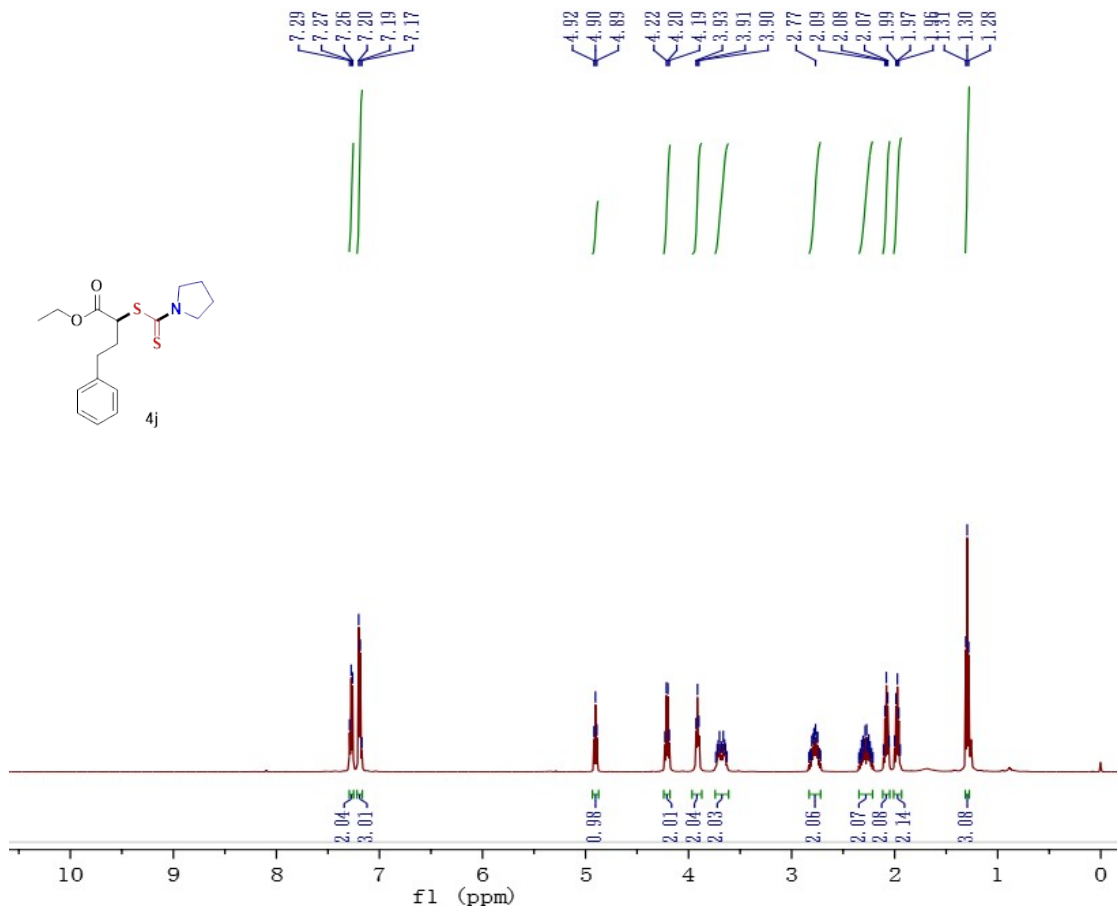
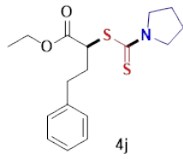


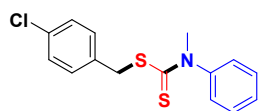
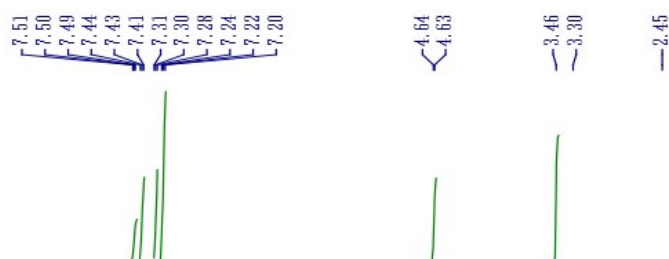




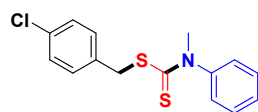
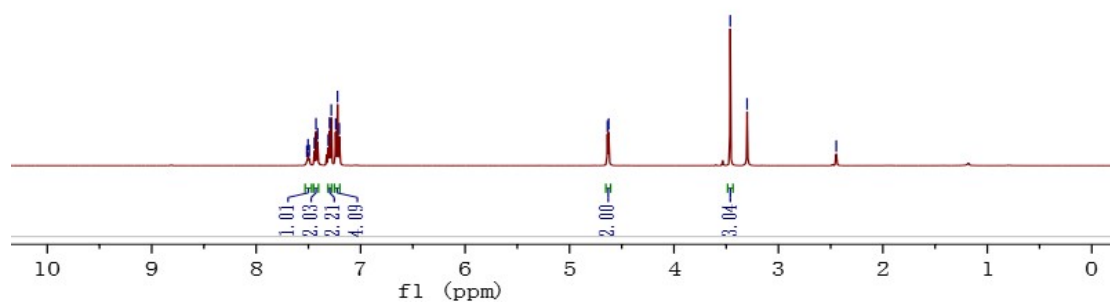








4k



4k

