Supplementary Information

Metal-free visible-light-induced multi-component reaction of α-diazoesters leading to S-alkyl dithiocarbamates

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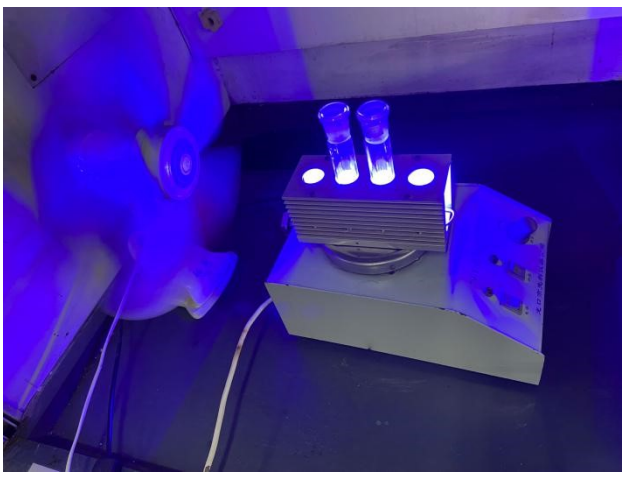
Contents

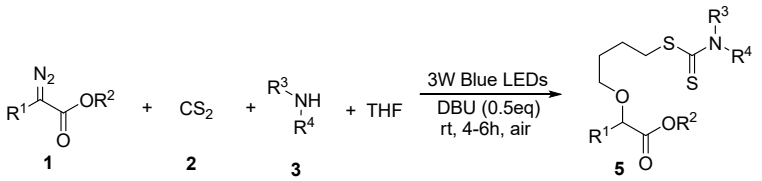
1. General information

All commercially available reagent grade chemicals were purchased from Adamas, Strem, MERYER, Alfa Aesar and Energy Chemical Company and used as received without further purification unless otherwise stated. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ on a Bruker Avance III 500MHz spectrometer with TMS as internal standard at room temperature, the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). High-resolution mass spectra (HRMS) were obtained on an LTQ Orbitrap XL mass spectrometry equipped with an ESI source. Column chromatography was performed on silica gel (200-300 mesh). There is 3.0 cm distance between the reactor and LEDs.



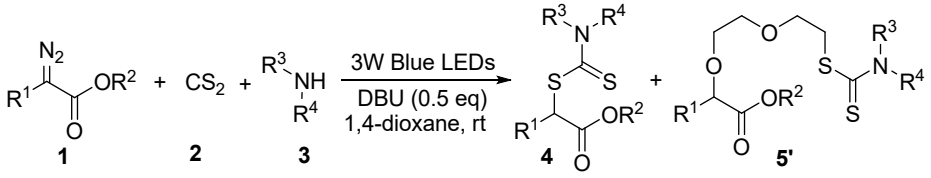
Picture of reaction setup

2. General procedure for visible-light-induced multi-component reaction of α-diazoesters leading to S-alkyl dithiocarbamates.



1 2 3 5

To a mixture of α-diazoesters **1** (0.4 mmol), CS_2 **2** (0.4 mmol), amine **3** (0.2 mmol) and DBU (0.1 mmol) was added THF (2 mL). The reaction mixture was open to air and stirred under the irradiation of 3W blue LEDs at room temperature for 4-6 h. After completion of the reaction, the reaction mixture was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired four-component product **5**.

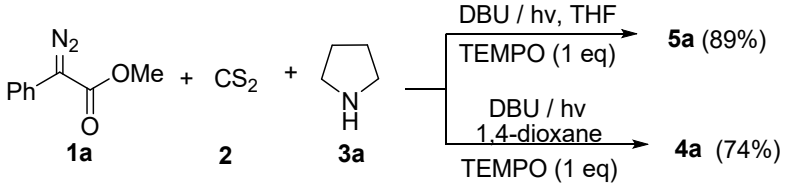


1 2 3 4 5'

To a mixture of α-diazoesters **1** (0.4 mmol), CS_2 **2** (0.4 mmol), amine **3**(0.2 mmol) and DBU (0.1 mmol) was added 1,4-dioxane (2 mL). The reaction mixture was open to air and stirred under the irradiation of 3W blue LEDs at room temperature for 6 h. After completion of the reaction, the reaction mixture was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **4** and **5'**.

3. Preliminary mechanistic studies

3.1 The addition of TEMPO in the model reaction system.



1a 2 3a

To a solution of α-diazoester **1a** (0.4 mmol), CS_2 **2** (0.4 mmol), pyrrolidine **3a**(0.2

mmol), and DBU (0.1 mmol) in THF (2 mL) or 1,4-dioxane (2 mL) was added TEMPO (0.2 mmol). The reaction mixture was stirred in air under the irradiation of 3W blue LED at room temperature for 4h. After completion of the reaction, the solution was concentrated in vacuum, the desired product **5a** and **4a** was obtained in 89% and 74% yields, respectively. This result indicated that a radical process might not be involved in the present transformations.

3.2. The procedures for Light On/off experiments.

In a 20 mL tube, to a mixture of α-diazoester **1a** (0.4 mmol), CS_2 **2** (0.4 mmol), pyrrolidine **3a** (0.2 mmol), and DBU (0.1 mmol) was added THF (2 mL). The reaction mixture was separately stirred and irradiated by 3 W Blue LEDs at room temperature for 1h and 2h. The desired product **5a** was isolated in 53% and 70%, respectively. Additionally, the reaction mixture was stirred and irradiated by 3 W Blue LEDs at room temperature for 1h, then the reaction mixture was continuously stirred in the dark for 1h, the corresponding product **5a** was obtained in 53.1% yield. Additionally, when the reaction mixture was stirred and irradiated by 3 W blue LEDs at room temperature for 2h, then the reaction mixture was continuously stirred in the dark for 1h, the corresponding product **5a** was obtained in 70% yield. Additionally, when the reaction mixture was stirred and irradiated by 3 W blue LEDs at room temperature for 3h, the corresponding product **5a** was obtained in 89% yield. The above results suggested that the continuous visible light irradiation is necessary for promoting this transformation.

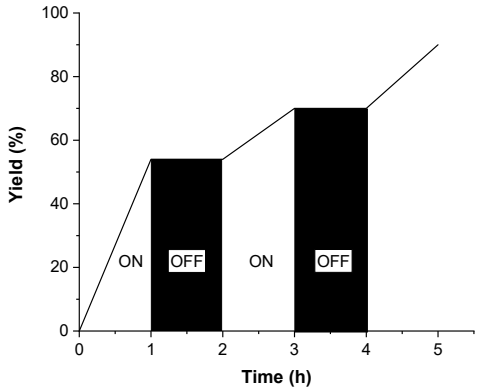
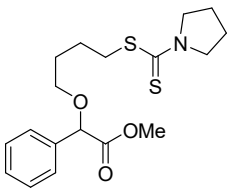
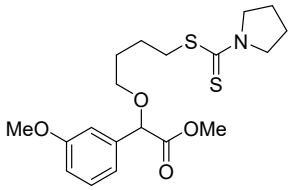


Fig S1. On/off experiments.

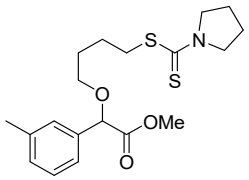
4. Characterization data of products



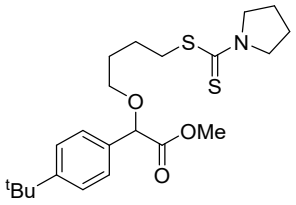
methyl 2-phenyl-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5a** was obtained in 98% yield (79.0mg) according to the general procedure (4h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.37-7.32 (m, 3H), 4.87 (s, 1H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.71 (s, 3H), 3.63 (t, *J* = 6.9 Hz, 2H), 3.58 - 3.56 (m, 1H), 3.48 – 3.46 (m, 1H), 3.33 (t, *J* = 6.9 Hz, 2H), 2.09 – 2.03 (m, 2H), 1.99 – 1.94 (m, 2H), 1.82 – 1.79 (m, 4H); ^{13}C NMR (125 MHz,$CDCl_3$) 13C NMR (125 MHz, $CDCl_3$) δ 193.0, 171.4, 136.6, 128.6, 128.6, 127.2, 81.1, 69.4, 54.9, 52.2, 50.6, 36.1, 28.8, 26.0, 25.6, 24.3. ESI HRMS: calculated for $C_{18}H_{26}NO_3S_2$, $[M+H]^+$: 368.1354; found 368.1353.



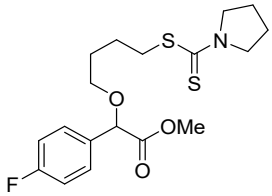
methyl2-(3-methoxyphenyl)-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)aceta te, Compound **5b** was obtained in 88% yield (69.6mg) according to the genera l procedure (4h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 1 H), 7.02–7.00 (m, 2H), 6.88–6.86 (m, 1H), 4.85 (s, 1H), 3.92 (t, *J* = 6.9 Hz, 2H), 3.81 (s, 3H), 3.71 (s, 3H), 3.63 (t, *J* = 6.9 Hz, 2H), 3.58–3.54 (m, 1H), 3.49 –3.46 (m, 1H), 3.33 (t, *J* = 6.9 Hz, 2H), 2.08–2.04 (m, 2H), 2.00–1.94 (m, 2 H), 1.83–1.78 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 171.3, 159.8, 13 8.1, 129.6, 119.6, 114.5, 112.3, 81.0, 69.4, 55.3, 54.9, 52.3, 50.6, 36.1, 28.7, 2 6.0, 25.6, 24.3. ESI HRMS: calculated for $C_{19}H_{28}NO_4S_2$, $[M+H]^+$: 398.1460; fo und 398.1457.



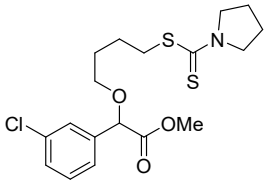
methyl 2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)-2-(m-tolyl)acetate, Compound **5c** was obtained in 92% yield (72.3mg) according to the general procedure (4h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 3H), 7.14 – 7.13 (m, 1H), 4.83 (s, 1H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.70 (s, 3H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.58 – 3.54 (m, 1H), 3.49 – 3.44 (m, 1H), 3.33 (t, *J* = 6.9 Hz, 2H), 2.35 (s, 3H), 2.09 – 2.03 (m, 2H), 1.99 – 1.94 (m, 2H), 1.82 – 1.79 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 171.5, 138.3, 136.5, 129.4, 128.5, 127.8, 124.3, 81.2, 69.3, 54.9, 52.2, 50.6, 36.1, 28.8, 26.0, 25.6, 24.3, 21.4. ESI HRMS: calculated for $C_{19}H_{28}NO_3S_2$, $[M+H]^+$: 382.1511; found 382.1510.



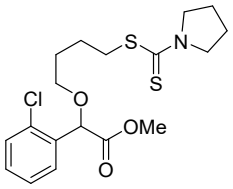
methyl 2-(4-(tert-butyl)phenyl)-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5d** was obtained in 81% yield (68.2mg) according to the general procedure (4h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 4H), 4.85 (s, 1H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.71 (s, 3H), 3.64 (t, *J* = 6.8 Hz, 2H), 3.57 – 3.55 (m, 1H), 3.48 – 3.46 (m, 1H), 3.32 (t, *J* = 6.7 Hz, 2H), 2.09 – 2.04 (m, 2H), 2.00 – 1.94 (m, 2H), 1.83 – 1.77 (m, 4H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 171.6, 151.6, 133.5, 126.9, 125.6, 80.9, 69.3, 54.9, 52.2, 50.6, 36.2, 34.6, 31.3, 28.8, 26.0, 25.6, 24.3. ESI HRMS: calculated for $C_{22}H_{34}NO_3S_2$, $[M+H]^+$: 424.1980; found 424.1979.



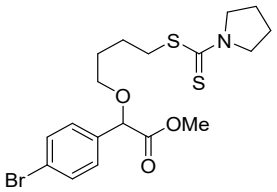
methyl 2-(4-fluorophenyl)-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5e** was obtained in 95% yield (83.4mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 4.85 (s, 1H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.71 (s, 3H), 3.64 (t, *J* = 6.8 Hz, 2H), 3.59 – 3.57 (m, 1H), 3.49 – 3.46 (m, 1H), 3.33 (t, *J* = 6.9 Hz, 2H), 2.08 – 2.04 (m, 2H), 2.00 – 1.96 (m, 2H), 1.83 – 1.77 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 171.3, 162.9 (d, *J* = 245.6 Hz), 132.5 (d, *J* = 3.1 Hz), 128.91 (d, *J* = 8.2 Hz), 115.6 (d, *J* = 21.5 Hz), 80.4, 69.4, 54.9, 52.3, 50.6, 36.1, 28.7, 26.0, 25.6, 24.3. ^{19}F NMR ($CDCl_3$, 500 MHz): -113.3; ESI HRMS: calculated for $C_{18}H_{25}FNO_3S_2$, $[M+H]^+$: 386.1260; found 386.1258.



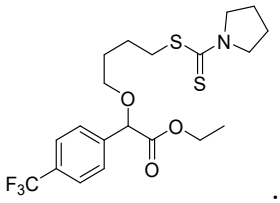
methyl 2-(3-chlorophenyl)-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5f** was obtained in 97% yield (77.8mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.34 - 7.29 (m, 3H), 4.84 (s, 1H), 3.93 (t, *J* = 6.9 Hz, 2H), 3.72 (s, 3H), 3.64 (t, *J* = 6.8 Hz, 2H), 3.61 – 3.57 (m, 1H), 3.50 – 3.46 (m, 1H), 3.33 (t, *J* = 6.8 Hz, 2H), 2.10 – 2.04 (m, 2H), 2.00 – 1.94 (m, 2H), 1.86 – 1.78 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 170.9, 138.6, 134.5, 129.9, 128.8, 127.2, 125.2, 80.4, 69.6, 54.9, 52.4, 50.6, 36.1, 28.7, 26.0, 25.6, 24.3. ESI HRMS: calculated for $C_{18}H_{25}ClNO_3S_2$, $[M+H]^+$: 402.0964; found 402.0947.



methyl 2-(2-chlorophenyl)-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5g** was obtained in 95% yield (76.2mg) according to the general procedure (6h). Yellow oil.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 1H), 7.39 -7.37 (m, 1H), 7.31 – 7.26 (m, 2H), 5.35 (s, 1H), 3.92 (t, *J* = 7.0 Hz, 2 H), 3.73 (s, 3H), 3.63 (t, *J* = 7.0 Hz, 3H), 3.52 – 3.48 (m, 1H), 3.32 (t, *J* = 6.7 Hz, 2H), 2.09 – 2.04 (m, 2H), 2.00 – 1.94 (m, 2H), 1.82 – 1.76 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 170.8, 134.7, 133.7, 129.8, 129.6, 128.8, 127.3, 77.3, 69.8, 54.9, 52.4, 50.6, 36.1, 28.8, 26.0, 25.6, 24.3. ESI HRMS: calculated for $C_{18}H_{25}ClNO_3S_2$, $[M+H]^+$: 402.0964; found 402.0960.



methyl 2-(4-bromophenyl)-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5h** was obtained in 89% yield (77.8mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.49 (m, 2H), 7.34 – 7.33 (m, 2H), 4.83 (s, 1H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.71 (s, 3H), 3.64 (t, *J* = 6.9 Hz, 2H), 3.60 – 3.56 (m, 1H), 3.49 – 3.44 (m, 1H), 3.33 (t, *J* = 7.0 Hz, 2H), 2.10 – 2.04 (m, 2H), 2.00 – 1.95 (m, 2H), 1.82 – 1.76 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 171.0, 135.7, 131.7, 128.8, 122.7, 80.4, 69.5, 54.9, 52.4, 50.6, 36.1, 28.7, 26.0, 25.6, 24.3. ESI HRMS: calculated for $C_{18}H_{25}BrNO_3S_2$, $[M+H]^+$: 446.0459; found 446.0430.



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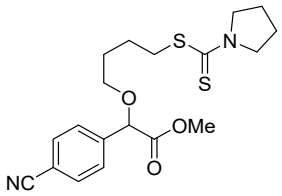
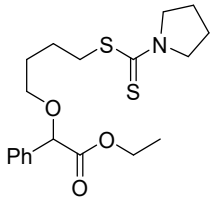
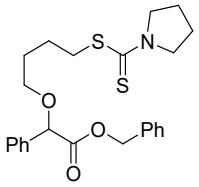
methyl 2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)-2-(4-(trifluoromethyl)phenyl)acetate, Compound **5i** was obtained in 66% yield (57.2mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.58 (m, 4H), 4.91 (s, 1H), 4.22 – 4.14 (m, 2H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.64 (t, *J* = 6.9 Hz, 3H), 3.52 – 3.48 (m, 1H), 3.34 (t, *J* = 6.6 Hz, 2H), 2.10 – 2.04 (m, 2H), 2.00 – 1.95 (m, 2H), 1.85– 1.79 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 170.3, 140.7, 130.6 (d, *J* = 32.3 Hz), 127.3, 125.49 (q, *J* = 3.7 Hz), 80.6, 69.7, 61.5, 54.9, 50.6, 36.1, 28.8, 26.1, 25.7, 24.3, 14.1. ^{19}F NMR ($CDCl_3$, 500 MHz): -62.6; ESI HRMS: calculated for $C_{20}H_{27}F_3NO_3S_2$, $[M+H]^+$: 450.1384; found 450.1389.



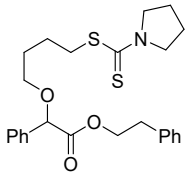
methyl 2-(4-cyanophenyl)-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5j** was obtained in 69% yield (53.8mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 4.93 (s, 1H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.73 (s,3H), 3.63 (t, *J* = 7.2 Hz, 3H), 3.52 – 3.49 (m, 1H), 3.33 (t, *J* = 7.0 Hz, 2H), 2.10 – 2.04 (m, 2H), 2.00 – 1.96 (m, 2H), 1.84 – 1.79 (m, 4H). ^{13}C NMR (125 MHz,$CDCl_3$) δ 192.8, 170.4, 141.8, 132.4, 127.7, 118.5, 112.4, 80.4, 69.9, 55.0, 52.6, 50.6, 36.0, 28.7, 26.0, 25.7, 24.3. ESI HRMS: calculated for $C_{19}H_{25}N_2O_3S_2$, $[M+H]^+$: 393.1307; found 393.1306.



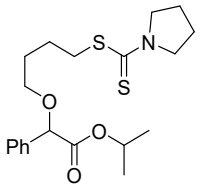
ethyl 2-phenyl-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5k** was obtained in 98% yield (74.4mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.37 – 7.30 (m, 3H), 4.85 (s, 1H), 4.21 – 4.11 (m, 2H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.63 (t, *J* = 6.9 Hz, 2H), 3.60 – 3.56 (m, 1H), 3.50 – 3.46 (m, 1H), 3.33 (t, *J* = 7.0 Hz, 2H), 2.10 – 2.04 (m, 2H), 1.99 – 1.94 (m, 2H), 1.85 – 1.76 (m, 4H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.1, 171.0, 136.7, 128.5, 128.5, 127.1, 81.2, 69.3, 61.2, 54.9, 50.6, 36.2, 28.8, 26.0, 25.6, 24.3, 14.1. ESI HRMS: calculated for $C_{19}H_{28}NO_3S_2$, $[M+H]^+$: 382.1511; found 382.1510.



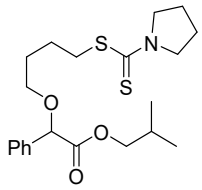
benzyl 2-phenyl-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5l** was obtained in 97% yield (74.4mg) according to the general procedure (4h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.36 – 7.32 (m, 3H), 7.31 – 7.28 (m, 3H), 7.22 – 7.20 (m, 2H), 5.18-5.10 (m, 2H), 4.91 (s, 1H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.62 (t, *J* = 6.8 Hz, 2H), 3.58 – 3.55 (m, 1H), 3.50 – 3.46 (m, 1H), 3.31 (t, *J* = 6.9 Hz, 2H), 2.07 -2.03 (m, 2H), 1.98 – 1.94 (m, 2H), 1.82 – 1.76(m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 170.8, 136.5, 135.5, 128.6, 128.6, 128.5, 128.2, 128.0, 127.2, 81.2, 69.4, 66.7, 54.9, 50.6, 36.2, 28.8, 26.0, 25.6, 24.3. ESI HRMS: calculated for $C_{24}H_{30}NO_3S_2$, $[M+H]^+$: 444.1667; found 444.1668.



phenethyl 2-phenyl-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5m** was obtained in 94% yield (86.3mg) according to the general procedure (4h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 2H), 7.34 – 7.31 (m, 3H), 7.25 – 7.19 (m, 3H), 7.10 – 7.08 (m, 2H), 4.82 (s, 1H), 4.35 – 4.31 (m, 2H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.63 (t, *J* = 6.9 Hz, 2H), 3.54 – 3.50 (m, 1H), 3.46 -3.41 (m, 1H), 3.32 (t, *J* = 6.9 Hz, 2H), 2.90 -2.86 (m, 2H), 2.07 – 2.03 (m, 2H), 1.99 – 1.95 (m, 2H), 1.81 – 1.76(m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 170.9, 137.5, 136.6, 128.9, 128.6, 128.5, 127.2, 126.5, 81.1, 69.3, 65.5, 54.9, 50.6, 36.2, 34.9, 28.8, 26.0, 25.6, 24.3. ESI HRMS: calculated for $C_{25}H_{32}NO_3S_2$, $[M+H]^+$: 458.1824; found 458.1814.

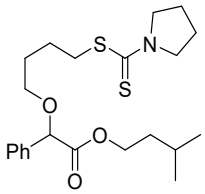


isopropyl 2-phenyl-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate Compound **5n** was obtained in 88% yield (68.8mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 -7.44 (m, 2H), 7.36 – 7.31 (m, 3H), 5.06 – 5.01 (m, 1H), 4.81 (s, 1H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.64 (t, *J* = 6.9 Hz, 2H), 3.61 – 3.56 (m, 1H), 3.50 – 3.46 (m, 1H), 3.34 (t, *J* = 6.9 Hz, 2H), 2.10 – 2.03 (m, 2H), 1.99 – 1.94 (m, 2H), 1.84 – 1.78 (m, 4H), 1.24 (d, *J* = 6.3 Hz, 3H), 1.12 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 170.6, 136.8, 128.5, 128.4, 127.1, 81.3, 69.3, 68.7, 54.9, 50.6, 36.2, 28.8, 26.0, 25.7, 24.3, 21.8, 21.5. ESI HRMS: calculated for $C_{20}H_{30}NO_3S_2$, $[M+H]^+$: 396.1667; found 396.1667.

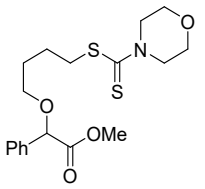


isobutyl 2-phenyl-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate ,Compound **5o** was obtained in 85% yield (69.7mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.45 (m, 2H), 7.37 – 7.31 (m, 3H), 4.86 (s, 1H), 3.94 – 3.87 (m, 4H), 3.64 (t, *J* = 7.0 Hz, 2H), 3.61 – 3.58 (m, 1H), 3.51 – 3.48 (m, 1H), 3.33 (t, *J* = 6.9 Hz, 2H), 2.08 – 2.04 (m, 2H), 1.99 – 1.95 (m, 2H), 1.90 – 1.86 (m, 1H), 1.84 – 1.78 (m, 4H), 0.83 (d, *J* = 1.7 Hz, 3H), 0.82 (d, *J* = 1.7 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 171.1, 136.9, 128.5, 127.1, 81.2, 71.1, 69.3, 54.9, 50.6, 36.2, 28.

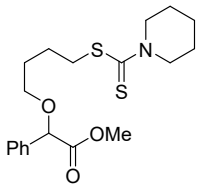
8, 27.7, 26.0, 25.6, 24.3, 18.9. ESI HRMS: calculated for $C_{21}H_{32}NO_3S_2$, $[M+H]^+$: 410.1824; found 410.1823.



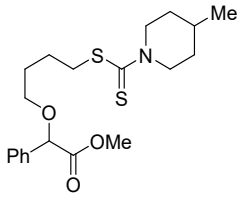
isopentyl 2-phenyl-2-(4-((pyrrolidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5p** was obtained in 97% yield (82mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.43(m, 2H), 7.36 – 7.30 (m, 3H), 4.84 (s, 1H), 4.16-4.11 (m, 2H), 3.92 (t, J = 6.9 Hz, 2H), 3.63 (t, J = 6.9 Hz, 2H), 3.60 – 3.56 (m, 1H), 3.50 – 3.46 (m, 1H), 3.33 (t, J = 7.0 Hz, 2H), 2.09 – 2.04 (m, 2H), 1.99 – 1.94 (m, 2H), 1.84 – 1.78 (m, 4H), 1.58 – 1.51 (m, 1H), 1.48 – 1.44 (m, 2H), 0.85 (d, J = 1.7 Hz, 3H), 0.83 (d, J = 1.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.2, 171.1, 136.8, 128.5, 127.1, 81.2, 69.3, 63.8, 54.9, 50.6, 37.1, 36.2, 28.8, 26.0, 25.6, 25.0, 24.3, 22.4, 22.3. ESI HRMS: calculated for $C_{22}H_{34}NO_3S_2$, $[M+H]^+$: 424.1980; found 424.1979.



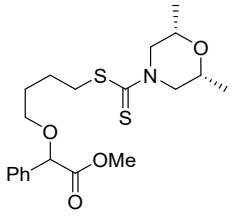
methyl 2-(4-((morpholine-4-carbonothioyl)thio)butoxy)-2-phenylacetate, Compound **5q** was obtained in72% yield (55.4mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.44 (m, 2H), 7.38 – 7.31 (m, 3H), 4.87 (s, 1H), 4.31 (brs, 2H), 3.98 (brs, 2H), 3.76 – 3.75 (m, 4H), 3.71 (s, 3H), 3.60 – 3.55 (m, 1H), 3.50 – 3.47 (m, 1H), 3.35 (t, J = 7.1 Hz, 2H), 1.84 – 1.77(m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.9, 171.4, 136.6, 128.7, 128.6, 127.2, 81.1, 69.3, 66.3, 52.3, 50.9, 36.7, 28.8, 25.4. ESI HRMS: calculated for $C_{18}H_{26}NO_4S_2$, $[M+H]^+$: 384.1303; found 384.1301.



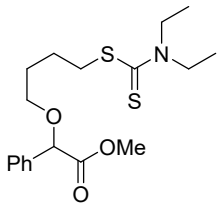
methyl 2-phenyl-2-(4-((piperidine-1-carbonothioyl)thio)butoxy)acetate, Compound **5r** was obtained in 93% yield (70.9mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.37 – 7.33 (m, 3H), 4.87 (s, 1H), 4.28 (brs, 2H), 3.91 – 3.84 (m, 2H), 3.71 (s, 3H), 3.60 – 3.55 (m, 1H), 3.50 -3.45 (m, 1H), 3.33 (t, J = 6.9 Hz, 2H), 1.83 – 1.78 (m, 4H), 1.71 – 1.65 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.9, 171.4, 136.6, 128.8, 128.6, 128.6, 128.4, 127.2, 81.1, 69.4, 52.3, 36.9, 28.9, 25.4, 24.3. ESI HRMS: calculated for $C_{19}H_{28}NO_3S_2$, $[M+H]^+$: 382.1511; found 382.1497.



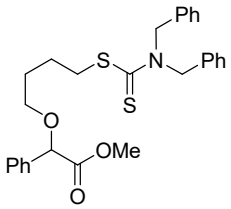
methyl 2-(4-((4-methylpiperidine-1-carbonothioyl)thio)butoxy)-2-phenylacetate, Compound **5s** was obtained in 75% yield (59.3mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.38 – 7.31 (m, 3H), 5.52 (s, 1H), 4.87 (brs, 1H), 4.60 (brs, 1H), 3.71 (s, 3H), 3.59 – 3.55 (m, 1H), 3.50 – 3.45 (m, 1H), 3.33 (brs, 2H), 3.11 (brs, 2H), 1.84 – 1.71 (m, 7H), 1.26 (brs, 2H), 0.97 (d, J = 6.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.0, 171.4, 136.6, 128.6, 128.6, 127.2, 81.1, 69.4, 52.3, 36.9, 31.0, 28.9, 25.4, 21.3. ESI HRMS: calculated for $C_{20}H_{30}NO_3S_2$, $[M+H]^+$: 396.1667; found 396.1671.



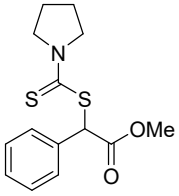
methyl2-(4-(((2R,6S)-2,6-dimethylmorpholine-4-carbonothioyl)thio)butoxy)-2-phenylacetate, Compound **5t** was obtained in 62% yield (51.0mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.44 (m, 2H), 7.38 – 7.32 (m, 3H), 5.48 (brs, 1H), 4.87 (s, 1H), 4.47 (brs, 1H), 3.71 (s, 3H), 3.64 (brs, 2H), 3.60 – 3.55 (m, 1H), 3.50 - 3.47 (m, 1H), 3.35 (t, J = 6.9 Hz, 2H), 2.85 – 2.73 (m, 2H), 1.84 – 1.77 (m, 4H), 1.24 (d, J = 6.3 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.3, 171.4, 136.6, 128.7, 128.6, 127.2, 81.1, 71.4, 69.3, 56.1, 55.2, 52.3, 36.7, 28.8, 25.4, 18.6. ESI HRMS: calculated for $C_{20}H_{30}NO_4S_2$, $[M+H]^+$: 412.1616; found 412.1620.



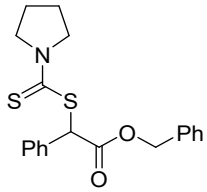
methyl 2-(4-((diethylcarbamothioyl)thio)butoxy)-2-phenylacetate, Compound **5u** was obtained in 79% yield (58.3mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 - 7.43 (m, 2H), 7.37 – 7.32 (m, 3H), 4.87 (s, 1H), 4.06 – 4.01 (m, 2H), 3.76 – 3.73 (m, 2H), 3.71 (s, 3H), 3.60 – 3.56 (m, 1H), 3.50 – 3.45 (m, 1H), 3.31 (t, J = 6.8 Hz, 2H), 1.83 – 1.78 (m, 4H), 1.29 – 1.25 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.8, 171.4, 136.6, 128.6, 128.6, 127.2, 81.1, 69.4, 52.3, 49.4, 46.7, 36.8, 28.9, 25.4, 12.4, 11.6. ESI HRMS: calculated for $C_{18}H_{28}NO_3S_2$, $[M+H]^+$: 370.1511; found 370.1513.



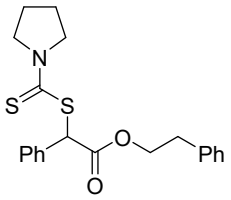
methyl 2-(4-((dibenzylcarbamothioyl)thio)butoxy)-2-phenylacetate, Compound **5v** was obtained in 85% yield (81.4mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.37 – 7.29 (m, 11H), 7.22 – 7.18 (m, 2H), 5.32 (s, 2H), 4.90 (s, 2H), 4.88 (s, 1H), 3.70 (s, 3H), 3.61 – 3.57(m, 1H), 3.51 – 3.47 (s, 1H), 3.40 (t, *J* = 7.1 Hz, 2H), 1.87 – 1.79 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.9, 171.4, 136.6, 128.9, 128.8, 128.7, 128.6, 127.9, 127.8, 127.2, 81.1, 69.3, 55.9, 53.8, 52.3, 37.7, 28.9, 25.3. ESI HRMS: calculated for $C_{28}H_{32}NO_3S_2$, $[M+H]^+$: 494.1824; found 494.1814.



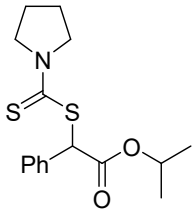
methyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate, Compound **4a** was obtained in 74% yield (42.6 mg) according to the general procedure (4h). White solid. 112-113^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.37 – 7.32 (m, 3H), 5.86 (s, 1H), 3.93 – 3.87 (m, 2H), 3.76 (s, 3H), 3.73 – 3.68 (m, 1H), 3.60 – 3.55 (m, 1H), 2.09 – 2.03 (m, 2H), 1.99 – 1.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 170.7, 134.1, 129.0, 128.8, 128.6, 58.2, 55.0, 53.1, 50.6, 26.2, 24.3. ESI HRMS: calculated for $C_{14}H_{18}NO_2S_2$, $[M+H]^+$: 296.0779; found 296.0770.



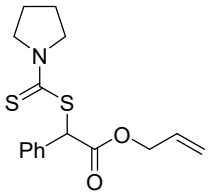
benzyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate, Compound **4b** was obtained in 67% yield (49.6mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.41 (m, 2H), 7.35 – 7.28 (m, 6H), 5.90 (s, 1H), 5.26 -5.24 (m, 1H), 5.14 -5.12 (m, 1H), 3.92 – 3.85 (m, 2H), 3.72 – 3.67 (m, 1H), 3.59 – 3.54 (m, 1H), 2.06 – 2.02 (m, 2H), 1.97 – 1.93 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 170.1, 135.6, 133.9, 128.9, 128.9, 128.6, 128.4, 128.1, 128.1, 67.6, 58.4, 55.0, 50.6, 26.2, 24.3. ESI HRMS: calculated for $C_{20}H_{22}NO_2S_2$, $[M+H]^+$: 372.1092; found 372.1085.



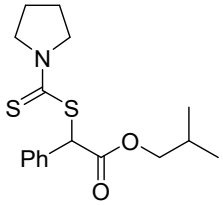
phenethyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate, Compound **4c** was obtained in 73% yield (56.4mg) according to the general procedure (6h). White solid. Mp: 93-94°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.35– 7.31 (m, 3H), 7.24 – 7.16 (m, 3H), 7.12 – 7.11 (m, 2H), 5.84 (s, 1H), 4.42 – 4.32 (m, 2H), 3.94 – 3.86 (m, 2H), 3.72 – 3.67 (m, 1H), 3.59 – 3.54 (m, 1H), 2.93 (t, J = 7.1 Hz, 2H), 2.07 – 2.03 (m, 2H), 1.99 – 1.93 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 170.1, 137.7, 134.1, 129.0, 129.0, 128.9, 128.7, 128.6, 126.4, 66.5, 58.4, 55.0, 50.6, 34.9, 26.2, 24.3. ESI HRMS: calculated for $C_{21}H_{24}NO_2S_2$, $[M+H]^+$: 386.1248; found 386.1238.



isopropyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate, Compound **4d** was obtained in 66% yield (42.6mg) according to the general procedure (6h). White solid. Mp: 145-146°C.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.44 (m, 2H), 7.35 – 7.31 (m, 3H), 5.80 (s, 1H), 5.10 – 5.05 (m, 1H), 3.81 -3.86 (m, 2H), 3.74 – 3.69 (m, 1H), 3.60 – 3.55 (m, 1H), 2.07 – 2.03 (m, 2H), 1.99 – 1.94 (m, 2H), 1.30 (d, J = 6.3 Hz, 3H), 1.14 (d, J = 6.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 169.6, 134.4, 128.8, 128.8, 128.4, 69.7, 58.6, 54.9, 50.6, 26.2, 24.3, 21.7, 21.5. ESI HRMS: calculated for $C_{16}H_{22}NO_2S_2$, $[M+H]^+$: 324.1092; found 324.1089.

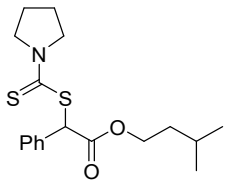


allyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate, Compound **4e** was obtained in 61% yield (42.6mg) according to the general procedure (6h). White solid.102-103°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.36 – 7.32 (m, 3H), 5.88 (s, 1H), 5.91 – 5.85 (m, 1H), 5.28 – 5.24 (m, 1H), 5.20– 5.17 (m, 1H), 4.72– 4.68 (m, 1H), 4.64 – 4.60 (m, 1H), 3.92 – 3.88 (m, 2H), 3.73 – 3.68 (m, 1H), 3.60 – 3.55 (m, 1H), 2.08 – 2.04 (m, 2H), 1.99 -1.95 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.3, 169.9, 134.1, 131.8, 128.9, 128.9, 128.6, 118.4, 66.5, 58.3, 55.0, 50.6, 26.2, 24.3. ESI HRMS: calculated for $C_{16}H_{20}NO_2S_2$, $[M+H]^+$: 322.0935; found 322.0924.

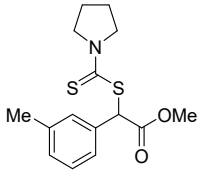


isobutyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate, Compound **4f** was obtained in 66% yield (42.6mg) according to the general procedure (6h). White solid. 82-83°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.35 – 7.31 (m, 3H), 5.87 (s, 1H), 4.00 – 3.96 (m, 1H), 3.92 – 3.86 (m, 3H), 3.74 – 3.69 (m, 1H), 3.61 – 3.56 (m,

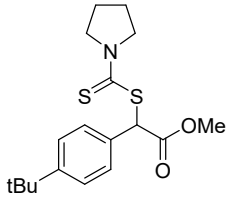
1H), 2.08 – 2.04 (m, 2H), 1.99 – 1.92 (m, 3H), 0.86 (d, J = 6.7 Hz, 3H), 0.85 (d, J = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.4, 170.2, 134.4, 128.9, 128.8, 128.5, 72.0, 58.5, 54.9, 50.6, 27.7, 26.2, 24.3, 19.0, 18.9. ESI HRMS: calculated for $C_{17}H_{24}NO_2S_2$, $[M+H]^+$: 338.1248; found 338.1250.



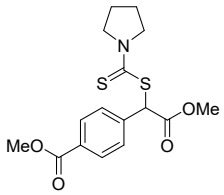
isopentyl 2-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)acetate, Compound **4g** was obtained in 68% yield (42.6mg) according to the general procedure (6h).White solid.103-104°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.36 – 7.31 (m, 3H), 5.83 (s, 1H), 4.27 – 4.22 (m, 1H), 4.16 – 4.12 (m, 1H), 3.93 – 3.86 (m, 2H), 3.74 – 3.69 (m, 1H), 3.60 – 3.55 (m, 1H), 2.08 – 2.03 (m, 2H), 1.99 – 1.95(m, 2H), 1.64 – 1.60 (m, 1H), 1.53 – 1.50 (m, 2H), 0.86 (d, J = 6.7 Hz, 3H), 0.85 (d, J = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 170.2, 134.2, 128.9, 128.8, 128.5, 64.7, 58.4, 54.9, 50.6, 37.1, 26.2, 24.9, 24.3, 22.4, 22.4. ESI HRMS: calculated for $C_{18}H_{26}NO_2S_2$, $[M+H]^+$: 352.1405; found 352.1403.



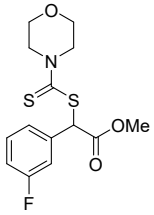
methyl 2-((pyrrolidine-1-carbonothioyl)thio)-2-(m-tolyl)acetate, Compound **4h** was obtained in 64% yield (42.6mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.23 (m, 3H), 7.14 – 7.12 (m, 1H), 5.81 (s, 1H), 3.94 – 3.85 (m, 2H), 3.76 (s, 3H), 3.74 – 3.68 (m, 1H), 3.61- 3.55 (m, 1H), 2.34 (s, 3H), 2.09 – 2.03 (m, 2H), 1.99 – 1.93 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 170.8, 138.8, 133.7, 129.5, 129.4, 128.9, 125.9, 58.2, 55.0, 53.1, 50.6, 26.2, 24.3, 21.4. ESI HRMS: calculated for $C_{15}H_{20}NO_2S_2$, $[M+H]^+$: 310.0935; found 310.0929.



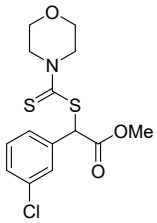
methyl 2-(4-(tert-butyl)phenyl)-2-((pyrrolidine-1-carbonothioyl)thio)acetate, Compound **4i** was obtained in 67% yield (42.6mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 4H), 5.81 (s, 1H), 3.93 – 3.88 (m, 2H), 3.76 (s, 3H), 3.72 – 3.68 (m, 1H), 3.60 – 3.56 (m, 1H), 2.08 – 2.04 (m, 2H), 1.99 – 1.94 (m, 2H), 1.30 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.6, 170.8, 151.7, 130.7, 128.4, 126.0, 57.8, 54.9, 53.1, 50.6, 34.6, 31.3, 26.2, 24.3. ESI HRMS: calculated for $C_{18}H_{26}NO_2S_2$, $[M+H]^+$: 352.1405; found 352.1406.



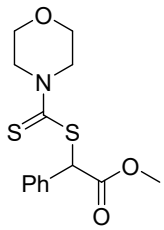
methyl 4-(2-methoxy-2-oxo-1-((pyrrolidine-1-carbonothioyl)thio)ethyl)benzoate, Compound **4j** was obtained in 56% yield (42.6mg) according to the general procedure (6h). White solid.109 – 110°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.7.53 (d, *J* = 8.4 Hz, 2H), 6.00 (s, 1H), 3.90 (s, 3H), 3.93-3.87 (m, 2H), 3.76 (s, 3H), 3.73 – 3.68 (m, 1H), 3.62 – 3.57 (m, 1H), 2.10 – 2.04 (m, 2H), 2.00 – 1.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.6, 170.2, 166.5, 139.6, 130.3, 130.1, 128.9, 57.8, 55.2, 53.3, 52.2, 50.7, 26.2, 24.3. ESI HRMS: calculated for $C_{16}H_{20}NO_2S_2$, $[M+H]^+$: 354.0834; found 354.0826.



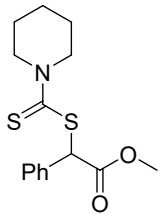
methyl 2-(3-fluorophenyl)-2-((morpholine-4-carbonothioyl)thio)acetate, Compound **4k** was obtained in 64% yield (42.6mg) according to the general procedure (6h). White solid. 97-98°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.18 – 7.15 (m, 1H), 7.05 – 7.01 (m, 1H), 5.85 (s, 1H), 4.27 (brs, 2H), 3.91 (brs, 2H), 3.79 – 3.76 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.5, 170.0, 163.8 (d, *J* = 246.2 Hz), 136.0 (d, *J* = 7.7 Hz), 130.5 (d, *J* = 8.3 Hz), 124.7 (d, *J* = 3.1 Hz), 116.19, 115.8 (d, *J* = 20.5 Hz), 66.3, 58.1, 53.3, 51.1. ^{19}F NMR ($CDCl_3$, 500 MHz): -111.6; ESI HRMS: calculated for $C_{14}H_{17}FNO_3S_2$, $[M+H]^+$: 330.0634; found 330.0621.



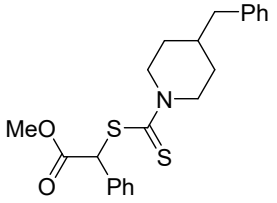
methyl 2-(3-chlorophenyl)-2-((morpholine-4-carbonothioyl)thio)acetate, Compound **4l** was obtained in 61% yield (42.6mg) according to the general procedure (6h). White solid.129-130°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.44 (m, 1H), 7.34 – 7.28 (m, 3H), 5.83 (s, 1H), 4.27 (brs, 2H), 3.91 (brs, 2H), 3.78 – 3.76 (m, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.4, 169.9, 135.7, 134.8, 130.2, 129.0, 127.1, 66.0, 58.0, 53.3, 50.8. ESI HRMS: calculated for $C_{14}H_{17}ClNO_3S_2$, $[M+H]^+$: 346.0338; found 346.0323.



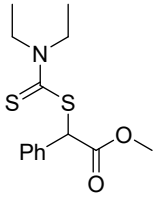
methyl 2-((morpholine-4-carbonothioyl)thio)-2-phenylacetate, Compound **4m** was obtained in 75% yield (42.6mg) according to the general procedure (6h). White solid. 99-100°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.37-7.34 (m, 3H), 5.80 (s, 1H), 4.26 (brs, 2H), 3.91 (brs, 2H), 3.76 (brs, 7H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.1, 170.4, 133.4, 129.1, 128.9, 128.8, 66.2, 58.7, 53.2, 50.8. ESI HRMS: calculated for $C_{14}H_{18}NO_3S_2$, $[M+H]^+$: 312.0728; found 312.0715.



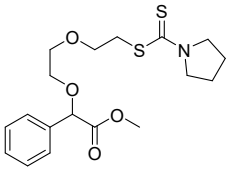
methyl 2-phenyl-2-((piperidine-1-carbonothioyl)thio)acetate, Compound **4n** was obtained in 46% yield (42.6mg) according to the general procedure (6h). White solid. 71-72°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 2H), 7.36 – 7.32 (m, 3H), 5.81 (s, 1H), 4.35 (brs, 1H), 4.10 (brs, 1H), 3.90 (brs, 1H), 3.82 (s, 1H), 3.76 (s, 3H), 1.69 (brs, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.2, 170.7, 133.7, 129.0, 128.9, 128.7, 58.9, 53.1, 51.6, 26.0, 25.4, 24.2. ESI HRMS: calculated for $C_{15}H_{20}NO_2S_2$, $[M+H]^+$: 310.0935; found 310.0923.



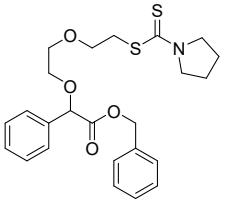
methyl 2-((4-benzylpiperidine-1-carbonothioyl)thio)-2-phenylacetate, Compound **4o** was obtained in 43% yield (42.6mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.38 – 7.31 (m, 3H), 7.30 – 7.26 (m, 2H), 7.21 – 7.18 (m, 1H), 7.14 – 7.09 (m, 2H), 5.82 – 5.77 (m, 1H), 5.47 (brs, 1H), 4.53 – 4.51 (m, 1H), 3.75 (s, 3H), 3.14 – 2.97 (m, 2H), 2.54 (brs, 2H), 1.89 – 1.84 (m, 1H), 1.76 -1.74 (m, 2H), 1.36 – 1.24 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 170.7, 139.6, 129.7, 129.0, 129.0, 128.9, 128.7, 128.4, 126.2, 58.9, 53.1, 51.9, 50.8, 42.5, 38.0, 32.0, 31.5. ESI HRMS: calculated for $C_{22}H_{26}NO_2S_2$, $[M+H]^+$: 400.1405; found 400.1389.



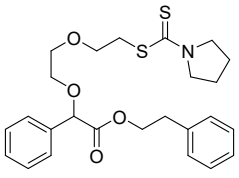
methyl 2-((diethylcarbamothioyl)thio)-2-phenylacetate, Compound **4p** was obtained in 68% yield (42.6mg) according to the general procedure (6h). White solid. 77-78°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.44 (m, 2H), 7.36 – 7.32 (m, 3H), 5.79 (s, 1H), 4.01 – 3.97 (m, 2H), 3.81 – 3.76 (m, 1H), 3.76 (s, 3H), 3.70 – 3.65 (m, 1H), 1.30 – 1.25 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.3, 170.7, 133.8, 129.0, 128.9, 128.6, 58.8, 53.1, 49.5, 47.0, 12.6, 11.6. ESI HRMS: calculated for $C_{14}H_{20}NO_2S_2$, $[M+H]^+$: 298.0935; found 298.0923.



methyl2-phenyl-2-(2-(2-((pyrrolidine-1-carbonothioyl)thio)ethoxy)ethoxy)acetate, Compound **5a'** was obtained in 16% yield (12.3mg) according to the general procedure (4h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.38 – 7.32 (m, 3H), 5.04 (s, 1H), 3.93 (t, *J* = 6.9 Hz, 2H), 3.75 – 3.72 (m, 4H), 3.71 (s, 3H), 3.70 – 3.69 (m, 1H), 3.67- 3.64 (m, 3H), 3.57 – 3.54 (m, 2H), 2.08 – 2.04 (m, 2H), 2.00 – 1.96 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 171.3, 136.5, 128.7, 128.6, 127.3, 81.3, 70.4, 69.6, 68.8, 55.1, 52.3, 50.6, 36.0, 26.1, 24.3. ESI HRMS: calculated for $C_{18}H_{26}NO_4S_2$, $[M+H]^+$: 384.1303; found 384.1293.

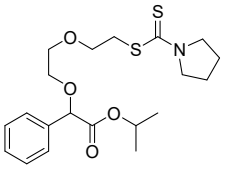


benzyl 2-phenyl-2-(2-(2-((pyrrolidine-1-carbonothioyl)thio)ethoxy)ethoxy)acetate, Compound **5b'** was obtained in 27% yield (24.7mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.34 – 7.28 (m, 6H), 7.22 – 7.21(m, 2H), 5.18 – 5.11 (m, 2H), 5.08 (s, 1H), 3.92 (t, *J* = 6.9 Hz, 2H), 3.74 – 3.69 (m, 5H), 3.68 – 3.65 (m, 1H), 3.64 – 3.61 (m, 2H), 3.55 – 3.52 (m, 2H), 2.05 – 2.01 (m, 2H), 1.98 – 1.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 170.7, 136.4, 135.5, 128.6, 128.6, 128.5, 128.2, 127.9, 127.4, 81.3, 70.4, 69.6, 68.9, 66.7, 55.1, 50.6, 36.0, 26.0, 24.3. ESI HRMS: calculated for $C_{24}H_{30}NO_4S_2$, $[M+H]^+$: 460.1616; found 460.1610.

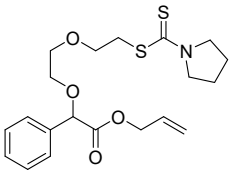


Phenethyl 2-phenyl-2-(2-(2-((pyrrolidine-1-carbonothioyl)thio)ethoxy)ethoxy)acetate, Compound **5c'** was obtained in 21% yield (19.8 mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42– 7.39 (m 2H), 7.35 – 7.31 (m, 3H), 7.24 – 7.17 (m, 3H), 7.09 – 7.07 (m, 2H), 4.98 (s, 1H), 4.36 – 4.29 (m, 2H), 3.91 (t, *J* = 6.9 Hz, 2H), 3.74 – 3.62 (m, 8H),

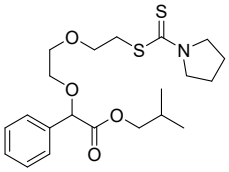
3.54 (t, *J* = 6.3 Hz, 2H), 2.89-2.86 (m, 2H), 2.06 – 2.02 (m, 2H), 1.99 – 1.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 170.8, 137.5, 136.5, 128.9, 128.6, 128.5, 127.3, 126.5, 81.3, 70.4, 69.6, 68.8, 65.5, 55.1, 50.6, 36.0, 35.0, 26.0, 24.3. ESI HRMS: calculated for $C_{25}H_{32}NO_4S_2$, $[M+H]^+$: 474.1773; found 474.1764.



isopropyl 2-phenyl-2-(2-(2-((pyrrolidine-1-carbonothioyl)thio)ethoxy)ethoxy)acetate, Compound **5d'** was obtained in 28% yield (23.0mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1Hz, 2H), 7.36 – 7.31 (m, 3H), 5.06-5.01 (m, 1H), 4.97 (s, 1H), 3.92 (t, *J* = 7.0Hz, 2H), 3.76 – 3.71 (m, 5H), 3.67 – 3.63 (m, 3H), 3.56 (t, *J* = 6.3Hz, 2H), 2.09 – 2.04 (m, 2H), 1.99-1.94 (m, 2H), 1.24 (d, *J* = 6.7 Hz, 3H), 1.12 (d, *J* = 6.7Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 170.4, 136.7, 128.5, 127.2, 81.4, 70.3, 69.6, 68.8, 68.7, 55.1, 50.6, 36.0, 26.0, 24.3 21.8, 21.5. ESI HRMS: calculated for $C_{20}H_{30}NO_4S_2$, $[M+H]^+$: 412.1616; found 412.1621.

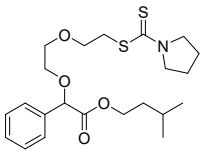


allyl 2-phenyl-2-(2-(2-((pyrrolidine-1-carbonothioyl)thio)ethoxy)ethoxy)acetate, Compound **5e'** was obtained in 32% yield (26.2mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 2H), 7.37 – 7.32(m, 3H), 5.88 – 5.80 (m, 1H), 5.21 – 5.15 (m, 2H), 5.06 (s, 1H), 4.63 – 4.59 (m, 2H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.76 – 3.71 (m, 5H), 3.70 – 3.63 (m, 3H), 3.56(t, *J* = 6.3 Hz, 2H), 2.08 – 2.04 (m, 2H), 2.00 – 1.96 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 170.5, 136.5, 131.7, 128.6, 128.6, 127.3, 118.4, 81.3, 70.4, 69.6, 68.9, 65.6, 55.1, 50.6, 36.0, 26.0, 24.3. ESI HRMS: calculated for $C_{20}H_{28}NO_4S_2$, $[M+H]^+$: 410.1460; found 410.1448.

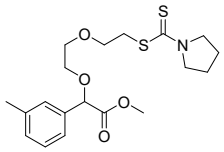


isobutyl 2-phenyl-2-(2-(2-((pyrrolidine-1-carbonothioyl)thio)ethoxy)ethoxy)acetate, Compound **5f'** was obtained in 26% yield (22.1mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.35 – 7.31 (m, 3H), 5.02 (s, 1H), 3.94 - 3.87(m, 4H), 3.75 – 3.71 (m, 5H), 3.67 – 3.63 (m, 3H), 3.55 (t, *J* = 6.3 Hz, 2H), 2.08 – 2.04 (m, 2H), 1.99 – 1.91 (m, 2H), 1.90-1.84 (m, 1H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 170.9, 136.7, 128.5, 128.5, 127.3, 81.3,

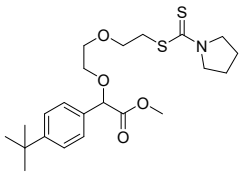
71.1, 70.4, 69.6, 68.8, 55.1, 50.6, 36.0, 27.7, 26.0, 24.3, 18.9. ESI HRMS: calculated for $C_{21}H_{32}NO_4S_2$, $[M+H]^+$: 426.1773; found 426.1764.



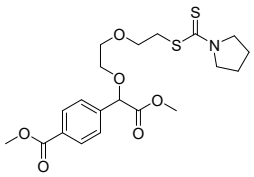
isopentyl 2-phenyl-2-(2-(2-((pyrrolidine-1-carbonothioyl)thio)ethoxy)ethoxy)acetate, Compound **5g'** was obtained in 28% yield (24.6mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.36 – 7.31 (m, 3H), 5.00 (s, 1H), 4.15 – 4.12 (m, 2H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.76 – 3.71 (m, 5H), 3.67-3.63 (m, 3H), 3.56 (t, *J* = 6.2 Hz, 2H), 2.08 – 2.04 (m, 2H), 2.00 – 1.94 (m, 2H), 1.57 – 1.52 (m, 1H), 1.48 – 1.44 (m, 2H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 171.0, 136.7, 128.5, 128.5, 127.3, 81.3, 70.4, 69.6, 68.8, 63.8, 55.1, 50.6, 37.2, 36.0, 26.0, 25.0, 24.3, 22.4, 22.3. ESI HRMS: calculated for $C_{22}H_{34}NO_4S_2$, $[M+H]^+$: 440.1929; found 440.1925.



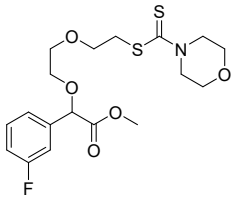
methyl 2-(2-(2-((pyrrolidine-1-carbonothioyl)thio)ethoxy)ethoxy)-2-(m-tolyl)acetate, Compound **5h'** was obtained in 31% yield (24.6mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.25 – 7.23 (m, 2H), 7.14 – 7.13 (m, 1H), 5.00 (s, 1H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.74 – 3.69 (m, 8H), 3.67 – 3.62 (m, 3H), 3.57 – 3.54 (m, 2H), 2.35 (s, 3H), 2.08 – 2.04 (m, 2H), 2.00 – 1.96 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 171.4, 138.4, 136.4, 129.5, 128.5, 127.9, 124.5, 81.3, 70.4, 69.6, 68.8, 55.1, 52.3, 50.6, 36.0, 26.1, 24.3, 21.4. ESI HRMS: calculated for $C_{19}H_{28}NO_4S_2$, $[M+H]^+$: 398.1460; found 398.1451.



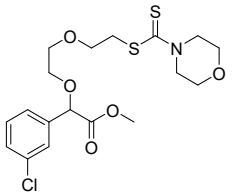
methyl 2-(4-(tert-butyl)phenyl)-2-(2-(2-((pyrrolidine-1-carbonothioyl)thio)ethoxy)ethoxy)acetate, Compound **5i'** was obtained in 30% yield (26.3mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (s, 4H), 5.02 (s, 1H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.74 – 3.69 (m, 8H), 3.68 – 3.65 (m, 3H), 3.56 (t, *J* = 6.3 Hz, 2H), 2.10 – 2.05 (m, 2H), 2.00 – 1.96 (m, 2H), 1.31 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 171.5, 151.6, 133.4, 127.1, 125.6, 81.1, 70.4, 69.6, 68.7, 55.1, 52.2, 50.6, 36.0, 34.6, 31.3, 26.1, 24.3. ESI HRMS: calculated for $C_{22}H_{34}NO_4S_2$, $[M+H]^+$: 440.1929; found 440.1926.



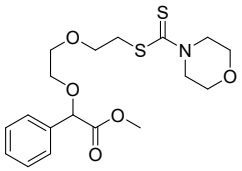
methyl 4-(3-oxo-12-(pyrrolidin-1-yl)-12-thioxo-2,5,8-trioxa-11-thiadodecan-4-yl)benzoate, Compound **5j'** was obtained in 32% yield (28.2mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 5.12 (s, 1H), 3.94 – 3.91 (m, 5H), 3.77 – 3.71 (m, 8H), 3.69 – 3.63 (m, 3H), 3.57 – 3.53 (m, 2H), 2.08 – 2.04 (m, 2H), 2.00 – 1.96 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.4, 170.8, 166.7, 141.4, 130.3, 129.8, 127.2, 80.9, 70.4, 69.6, 69.2, 55.1, 52.4, 52.2, 50.6, 35.9, 26.0, 24.3. ESI HRMS: calculated for $C_{20}H_{28}NO_6S_2$, $[M+H]^+$: 442.1358; found 442.1360.



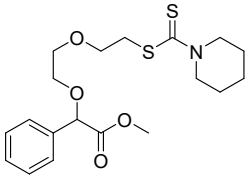
methyl 2-(3-fluorophenyl)-2-(2-(2-((morpholine-4-carbonothioyl)thio)ethoxy)ethoxy)acetate, Compound **5k'** was obtained in 33% yield (27.5mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 1H), 7.24 – 7.20 (m, 2H), 7.04 – 7.00 (m, 1H), 5.04 (s, 1H), 4.32 (brs, 2H), 3.99 (brs, 2H), 3.77 – 3.74 (m, 6H), 3.73 – 3.71 (m, 6H), 3.67 – 3.64 (m, 1H), 3.60 – 3.58 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.3, 170.8, 162.8 (d, *J* = 245.1 Hz), 138.9 (d, *J* = 7.3 Hz), 130.1 (d, *J* = 8.1 Hz), 122.9 (d, *J* = 2.9 Hz), 115.6 (d, *J* = 21.0 Hz), 114.3 (d, *J* = 22.0 Hz), 80.6 (d, *J* = 1.8 Hz), 70.4, 69.4, 69.0, 66.3, 52.4, 51.4, 36.5. ^{19}F NMR ($CDCl_3$, 500 MHz): -112.4; ESI HRMS: calculated for $C_{18}H_{25}FNO_5S_2$, $[M+H]^+$: 418.1158; found 418.1142.



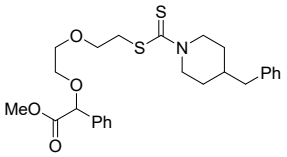
methyl 2-(3-chlorophenyl)-2-(2-(2-((morpholine-4-carbonothioyl)thio)ethoxy)ethoxy)acetate, Compound **5l'** was obtained in 35% yield (30.3mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.35 – 7.34 (m, 1H), 7.31 – 7.28 (m, 2H), 5.02 (s, 1H), 4.31 (brs, 2H), 3.97(brs, 2H), 3.76 – 3.74 (m, 6H), 3.73 – 3.71 (m, 6H), 3.67 – 3.64 (m, 1H), 3.60 – 3.57 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.3, 170.8, 138.5, 134.5, 129.9, 128.8, 127.4, 125.4, 80.6, 70.4, 69.4, 69.1, 66.2, 52.5, 51.0, 36.5. ESI HRMS: calculated for $C_{18}H_{25}ClNO_5S_2$, $[M+H]^+$: 434.0863; found 434.0845.



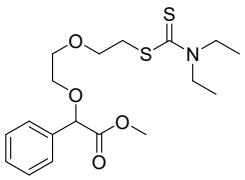
methyl 2-(2-(2-((morpholine-4-carbonothioyl)thio)ethoxy)ethoxy)-2-phenylacetate, Compound **5m'** was obtained in 21% yield (16.8mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.45 (m, 2H), 7.38 – 7.33 (m, 3H), 5.03 (s, 1H), 4.31 (brs, 2H), 3.97(brs, 2H), 3.77 – 3.73(m, 6H), 3.72 – 3.69 (m, 6H), 3.67 – 3.63(m, 1H), 3.60 – 3.57(m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.4, 171.3, 136.4, 128.7, 128.6, 127.3, 81.3, 70.4, 69.3, 68.8, 66.3, 52.3, 50.7, 36.6. ESI HRMS: calculated for $C_{18}H_{26}NO_5S_2$, $[M+H]^+$: 400.1252; found 400.1253.



methyl 2-phenyl-2-(2-(2-((piperidine-1-carbonothioyl)thio)ethoxy)ethoxy)acetate, Compound **5n'** was obtained in 34% yield (27.0mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.38 – 7.32 (m, 3H), 5.04 (s, 1H), 4.28 (brs, 2H), 3.89 (brs, 2H), 3.75 – 3.70 (m, 8H), 3.67 – 3.63 (m, 1H), 3.58 – 3.52 (m, 2H), 1.71 – 1.67 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.3, 171.3, 136.5, 128.7, 128.6, 127.3, 81.3, 70.4, 69.6, 68.8, 53.1, 52.3, 51.4, 36.6, 26.0, 25.4, 24.3. ESI HRMS: calculated for $C_{19}H_{28}NO_4S_2$, $[M+H]^+$: 398.1460; found 398.1448.

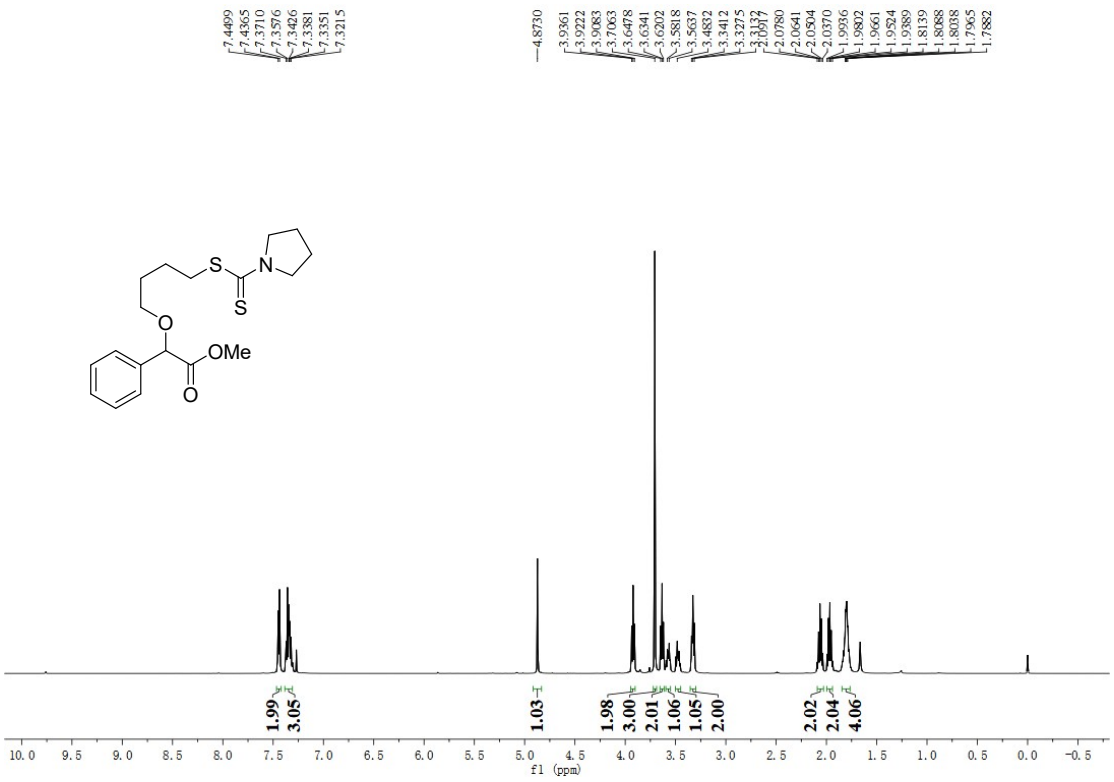


methyl 2-(2-(2-((4-benzylpiperidine-1-carbonothioyl)thio)ethoxy)ethoxy)-2-phenylacetate, Compound **5o'** was obtained in 31% yield (30.1mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.45 (m, 2H), 7.37 – 7.32 (m, 3H), 7.30 – 7. 27 (m, 2H), 7.22 – 7.19 (m, 1H), 7.14 – 7.12 (m, 2H), 5.57 (brs, 1H), 5.50 (s, 1H), 4.63 (brs, 1H), 3.75 – 3.70 (m, 8H), 3.67 – 3.63 (m, 1H), 3.59 – 3.53 (m, 2H), 3.13 – 2.96 (m, 2H), 2.56 (brs, 2H), 1.91 – 1.85 (m, 1H), 1.78 – 1.73 (m, 2H), 1.31 – 1.28 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.5, 171.3, 139.7, 136.5, 129.1, 128.7, 128.6, 128.4, 127.3, 126.2, 81.3, 70.4, 69.6, 68.8, 52.3, 50.4, 42.6, 38.2, 36.7, 32.0, 31.7. ESI HRMS: calculated for $C_{26}H_{34}NO_4S_2$, $[M+H]^+$:488.1929; found 488.1921.

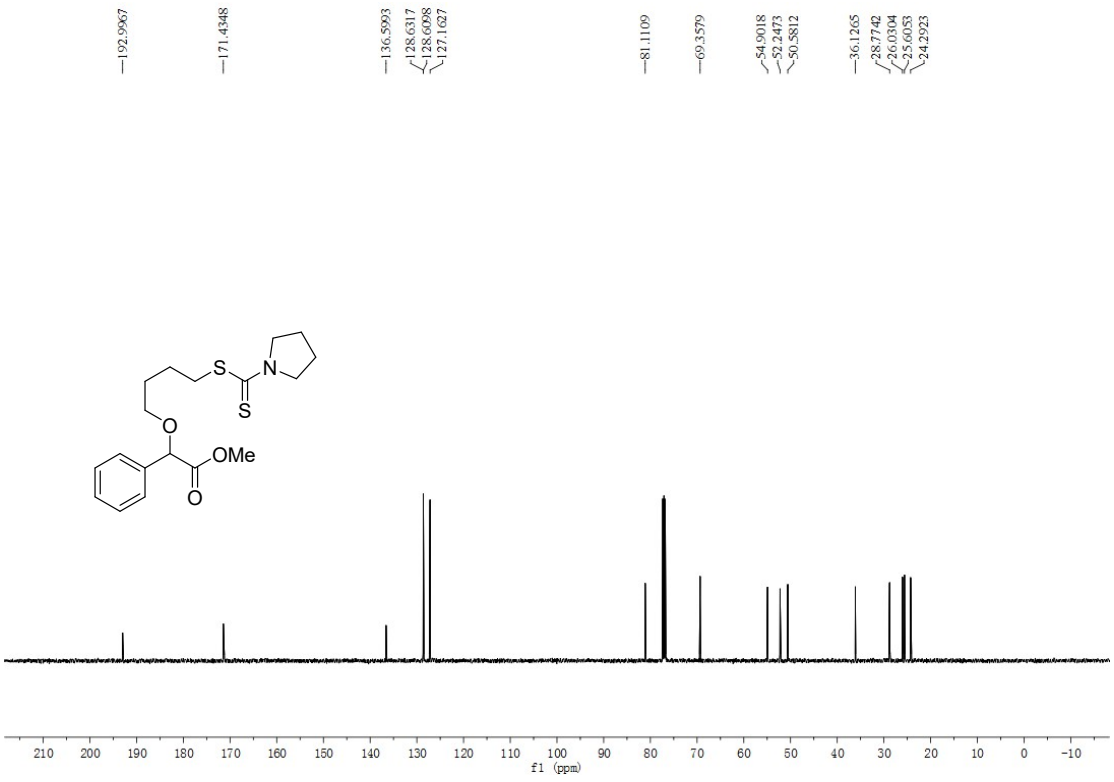


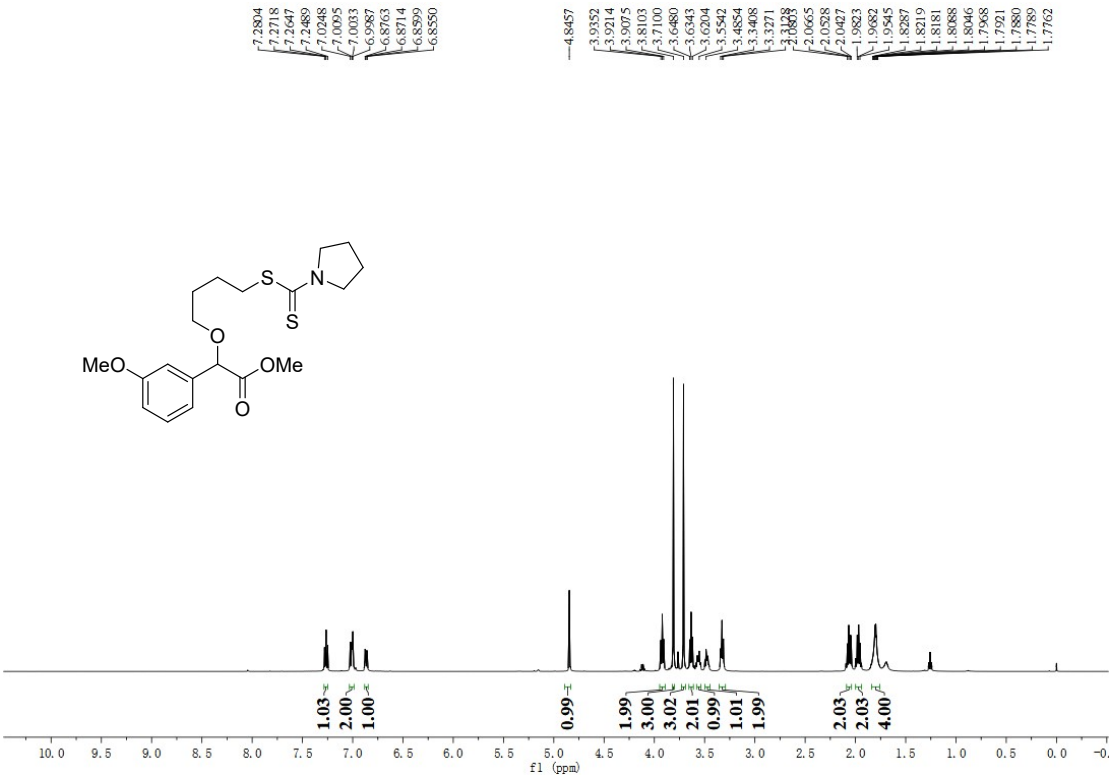
methyl 3-ethyl-12-phenyl-4-thioxo-8,11-dioxa-5-thia-3-azatridecan-13-oate, Compound **5p'** was obtained in 30% yield (23.1mg) according to the general procedure (6h). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.37 – 7.33 (m, 3H), 5.04 (s, 1H), 4.05 – 4.01 (m, 2H), 3.76 – 3.72 (m, 5H), 3.72 – 3.70 (m, 5H), 3.67 – 3.63 (m, 1H), 3.56 – 3.53 (m, 2H), 1.30 – 1.25 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.3, 171.3, 136.5, 128.7, 128.6, 127.3, 81.3, 70.4, 69.6, 68.8, 52.3, 49.6, 46.7, 36.6, 12.5, 11.6. ESI HRMS: calculated for $C_{18}H_{28}NO_4S_2$, $[M+H]^+$: 386.1460; found 386.1443.

5.Copies of NMR spectra for products

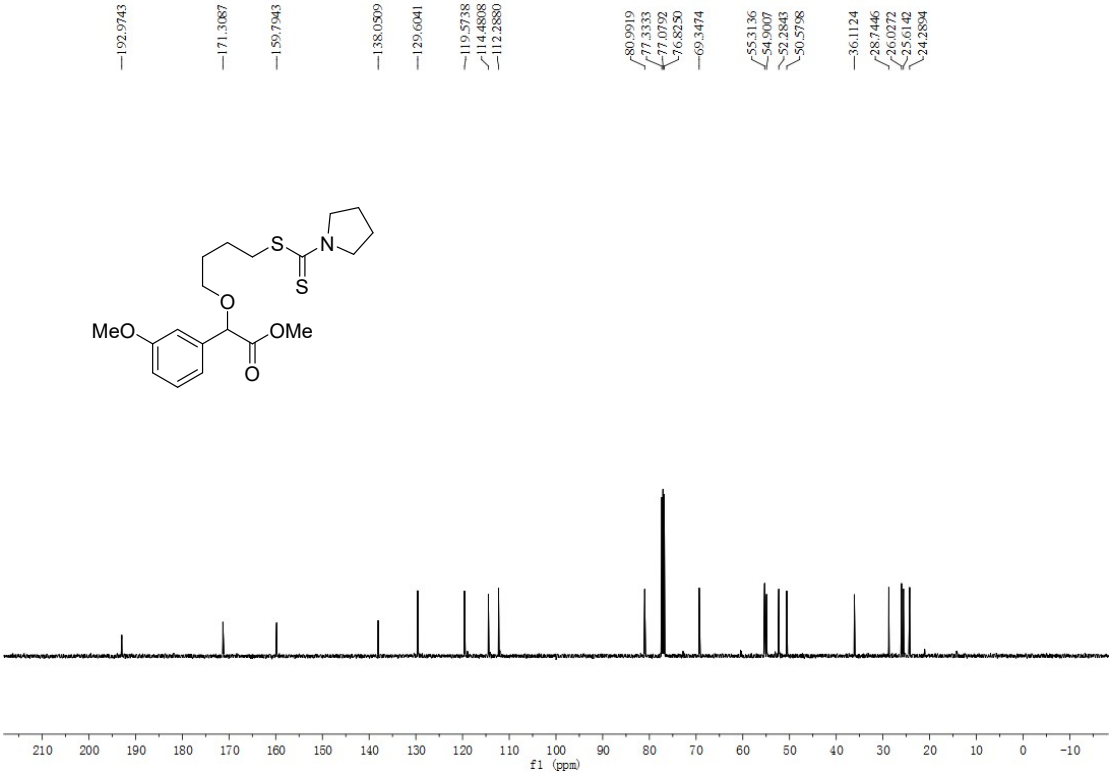


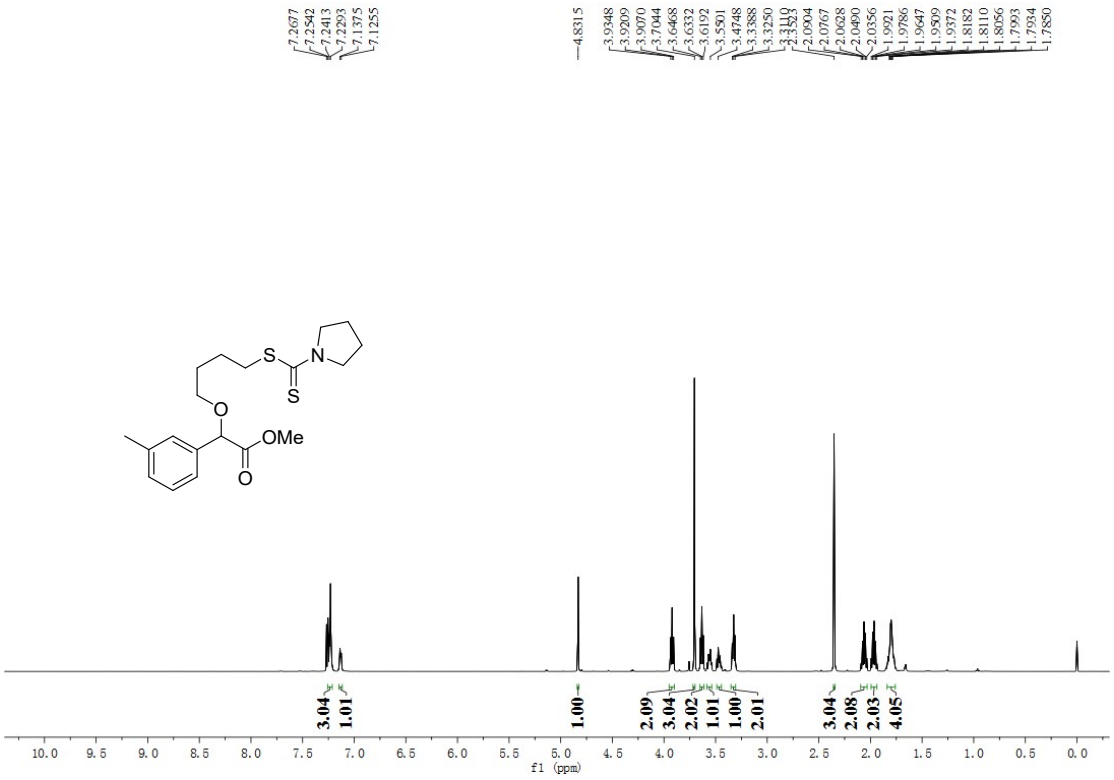
5a (500 MHz NMR, $CDCl_3$)



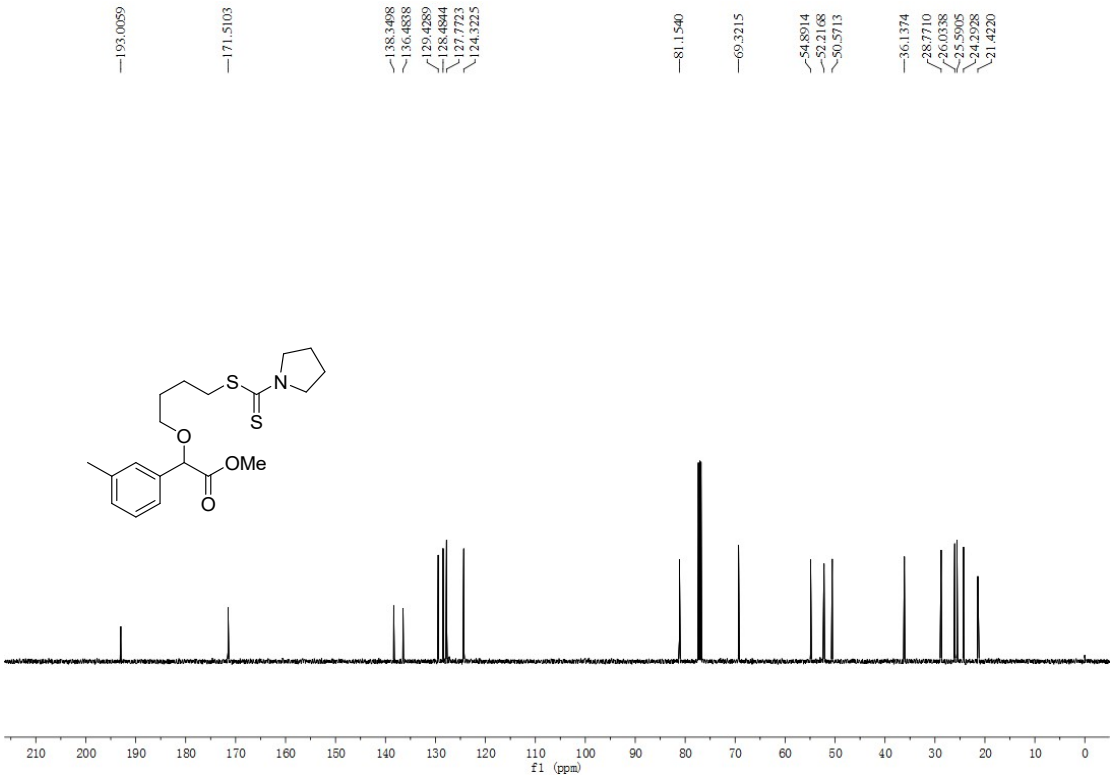


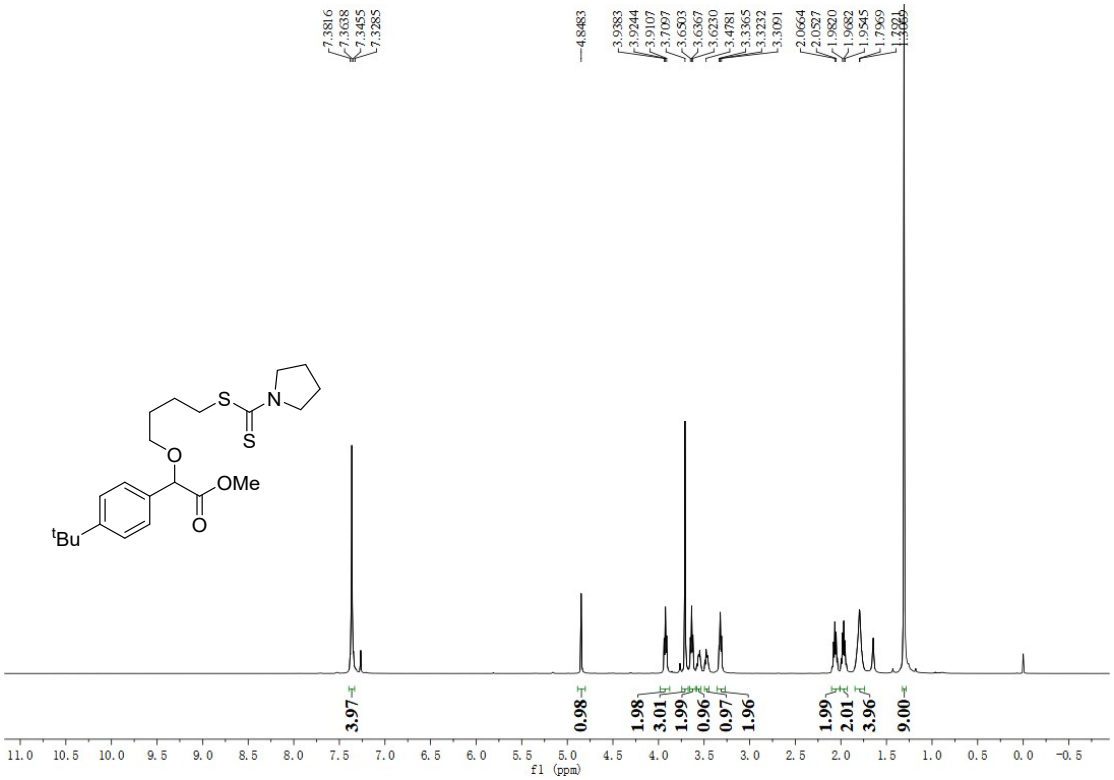
5b (500 MHz NMR, $CDCl_3$)



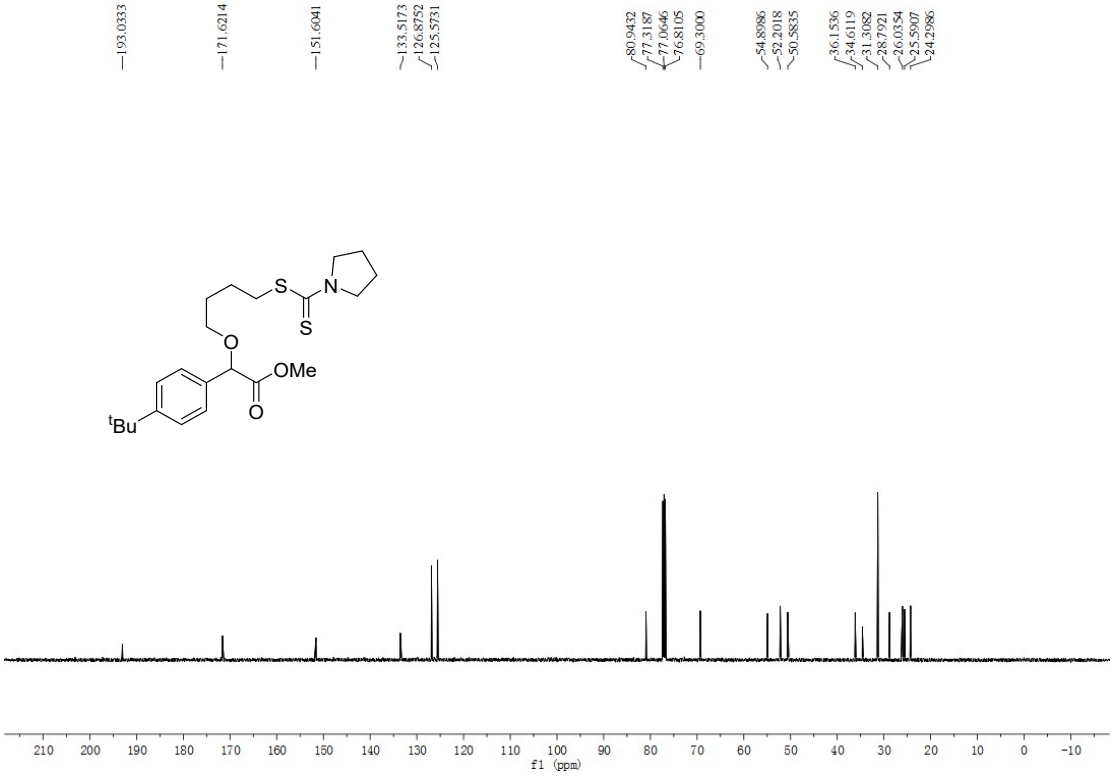


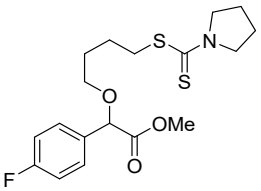
5c (500 MHz NMR, $CDCl_3$)

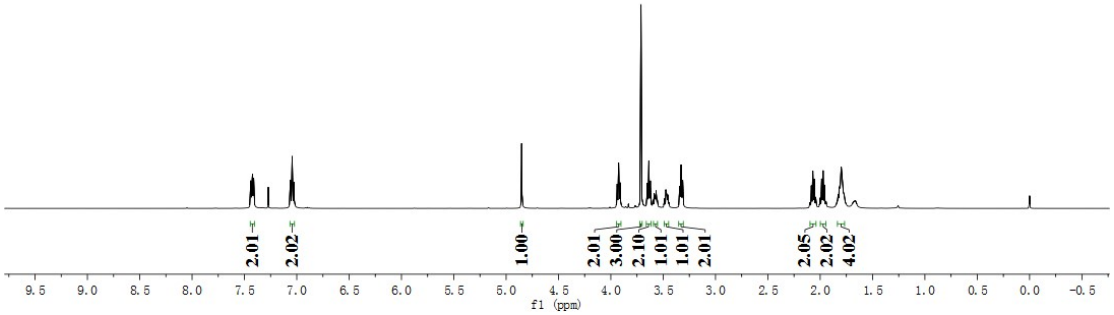




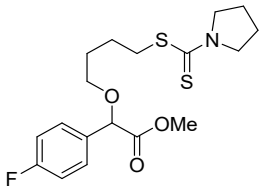
5d (500 MHz NMR, $CDCl_3$)

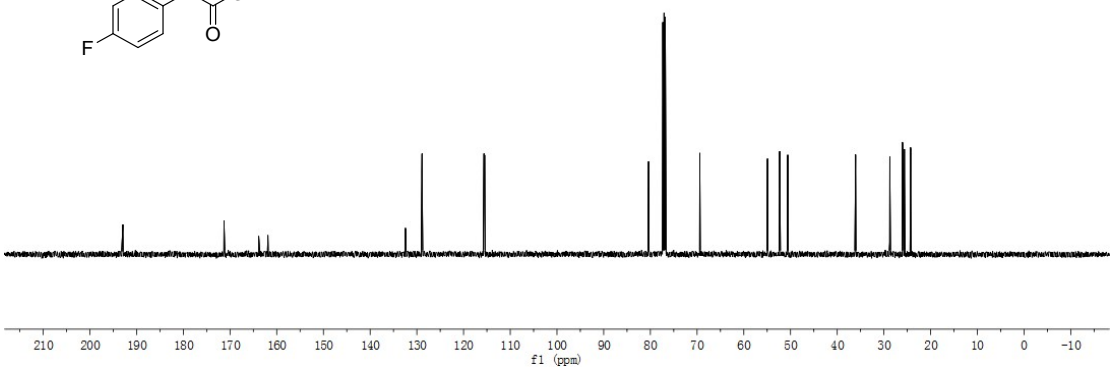


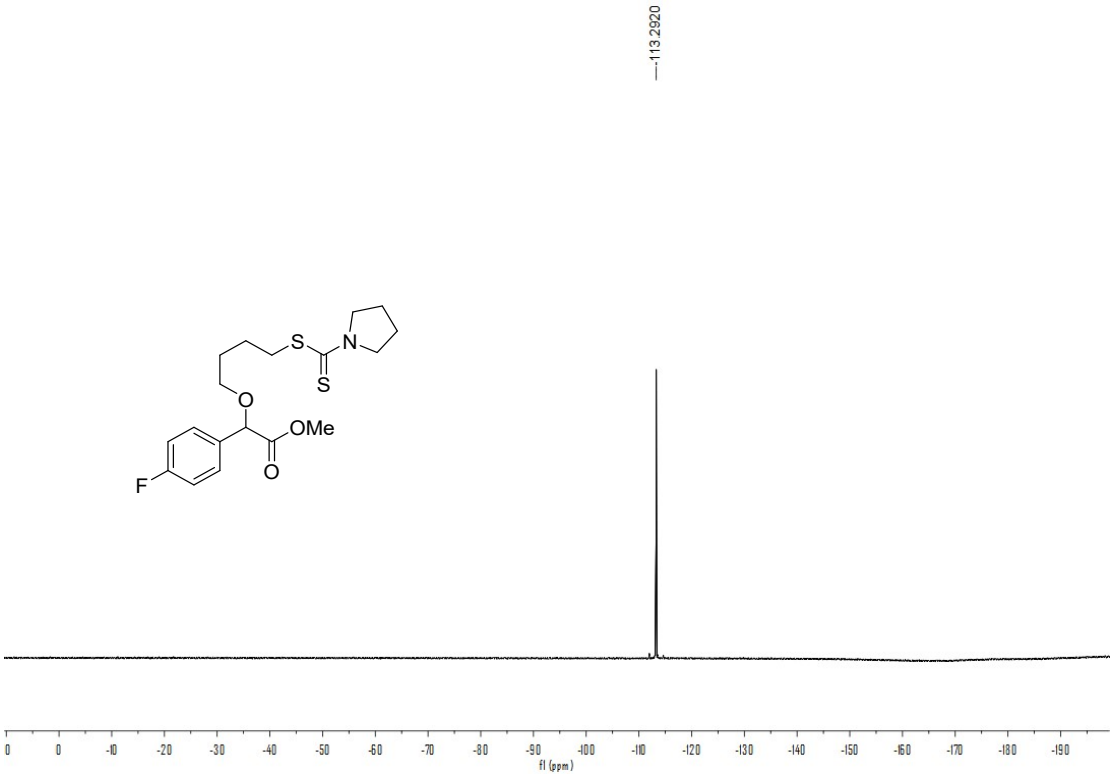




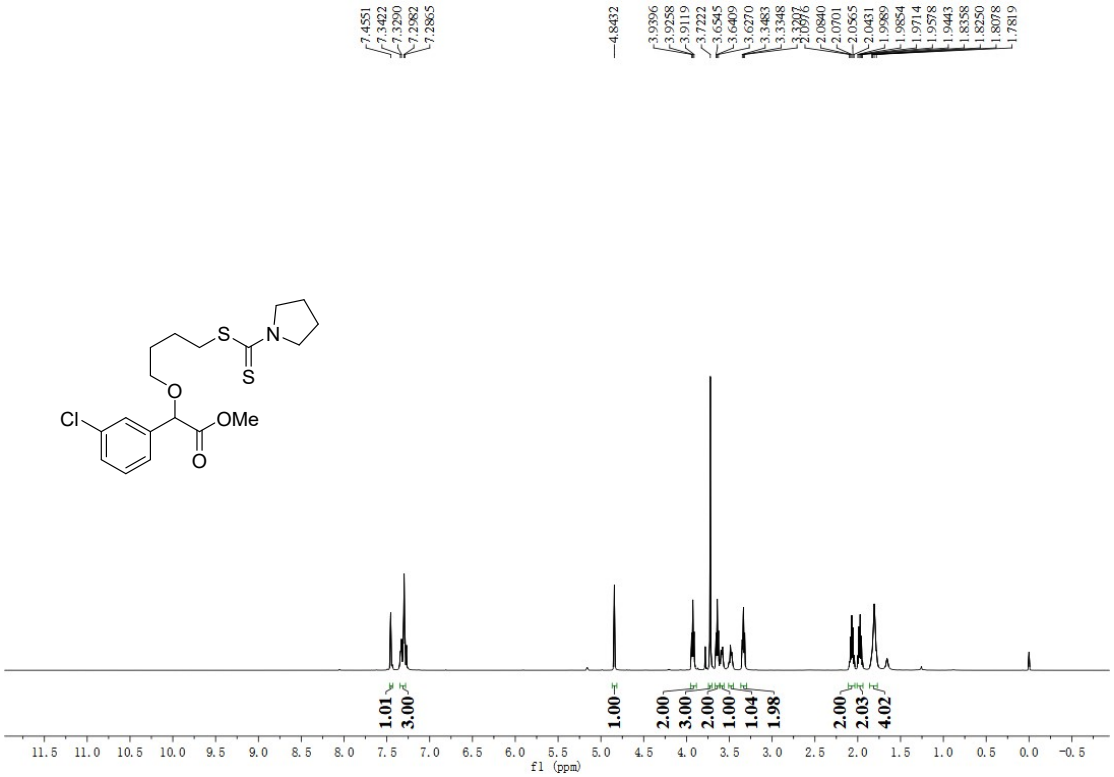
5e (500 MHz NMR, $CDCl_3$)



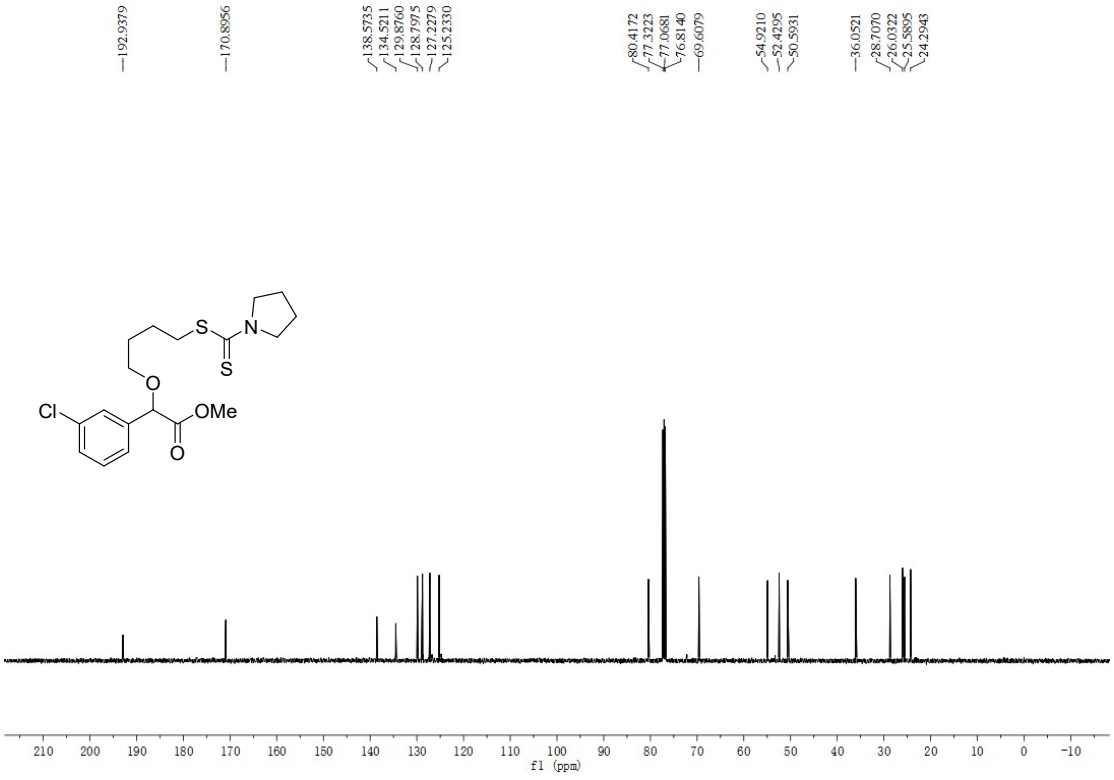


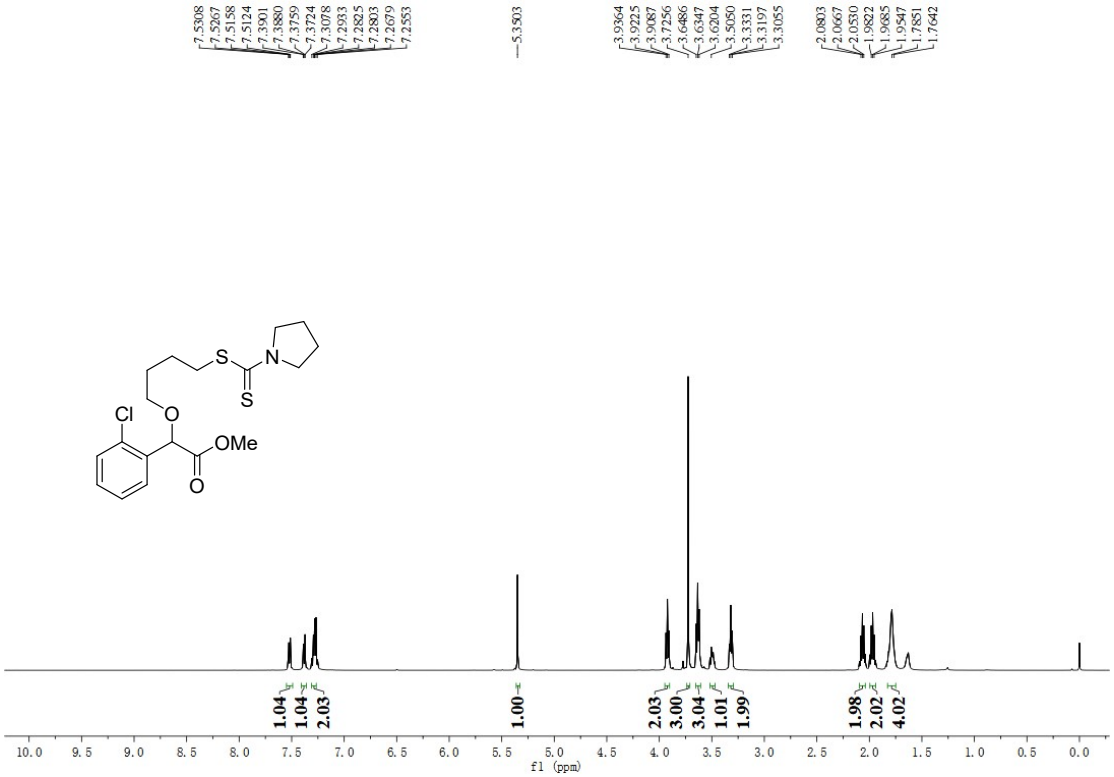


5e (500 MHz ^{19}F NMR, $CDCl_3$)

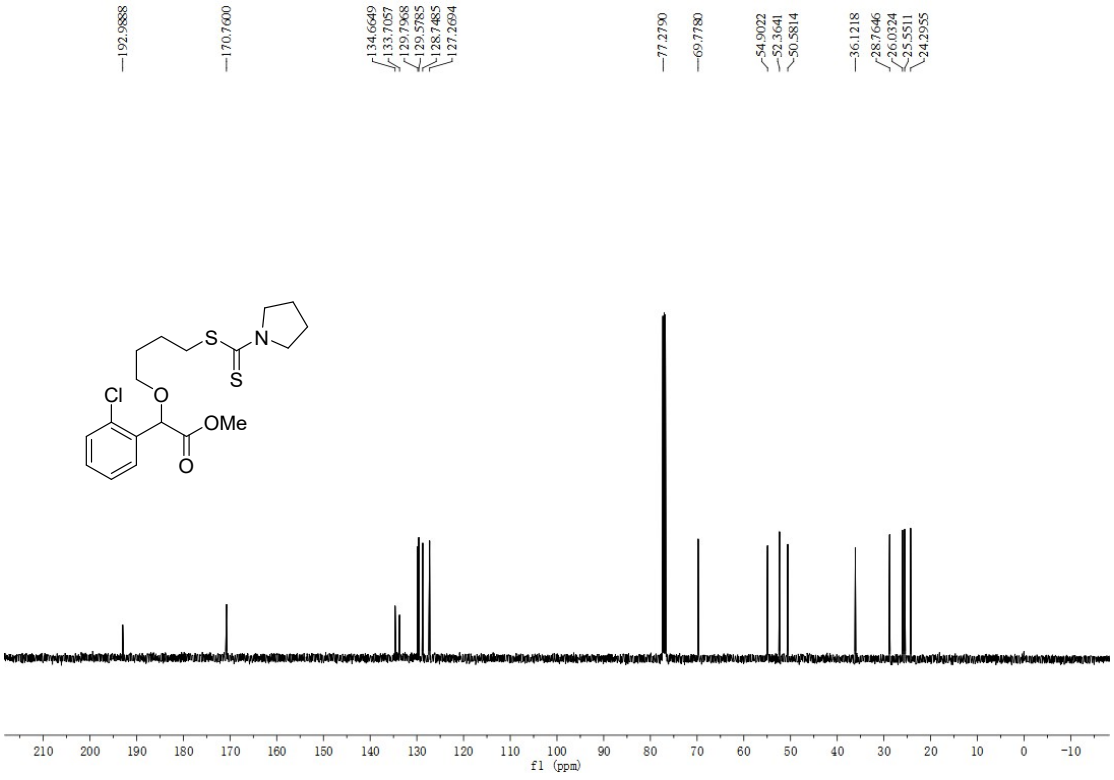


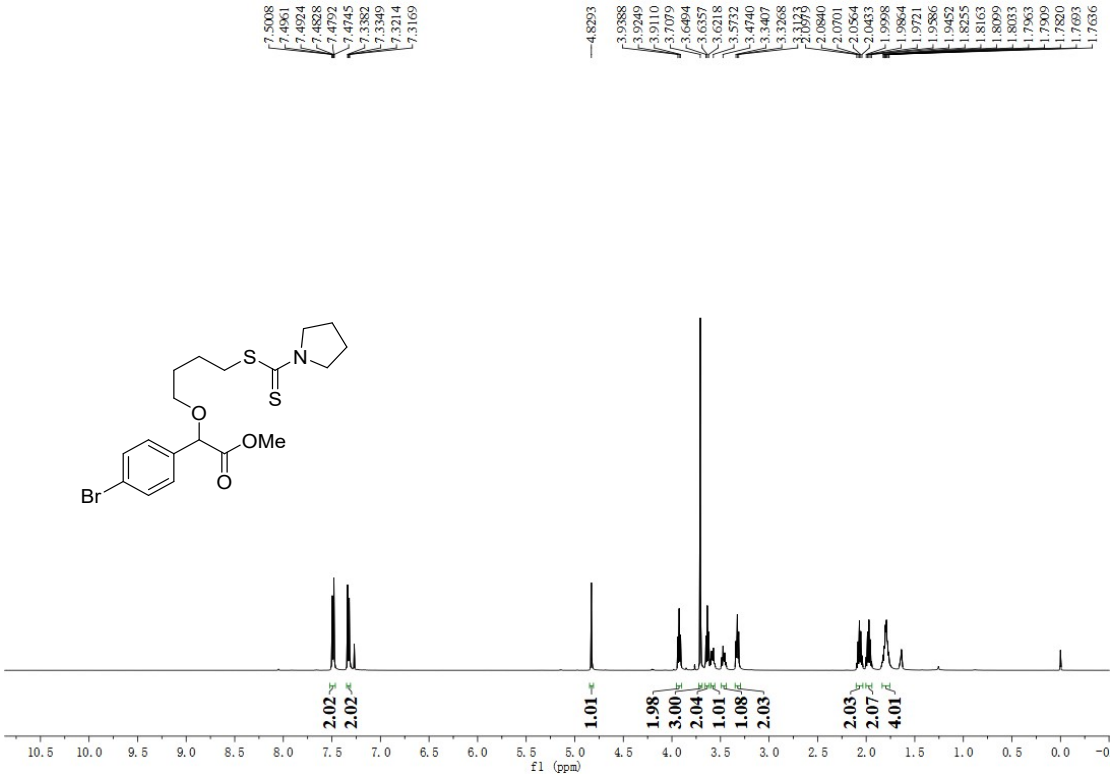
5f (500 MHz NMR, $CDCl_3$)



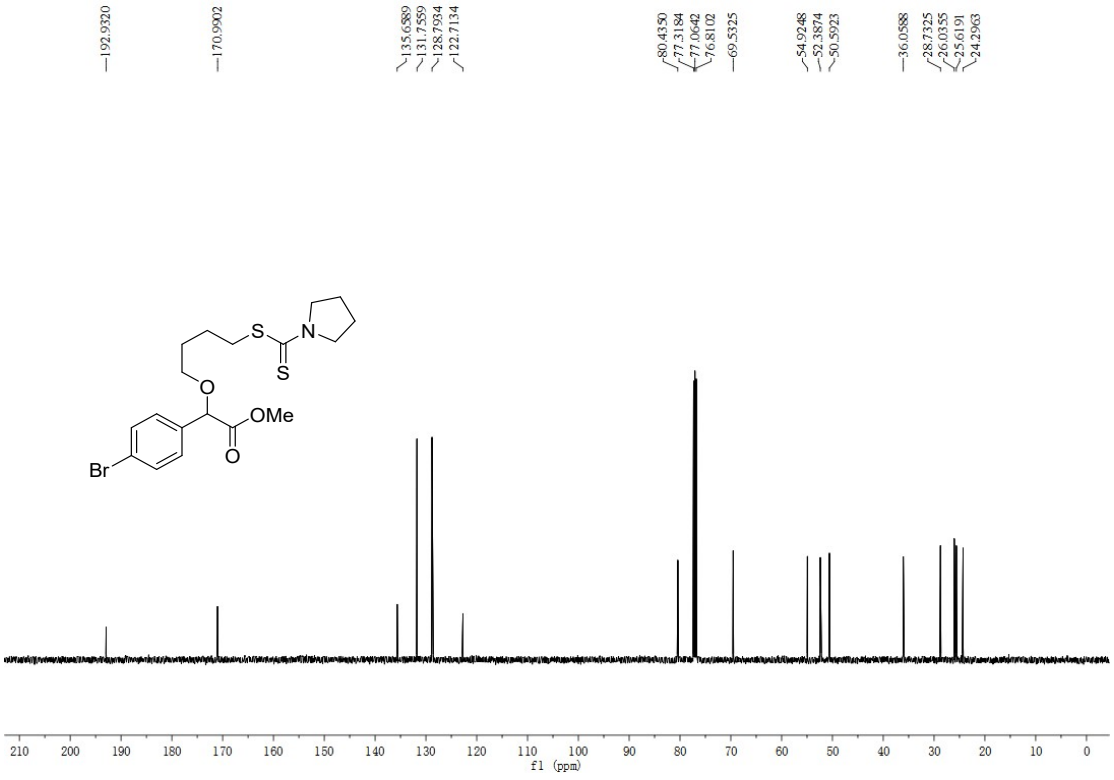


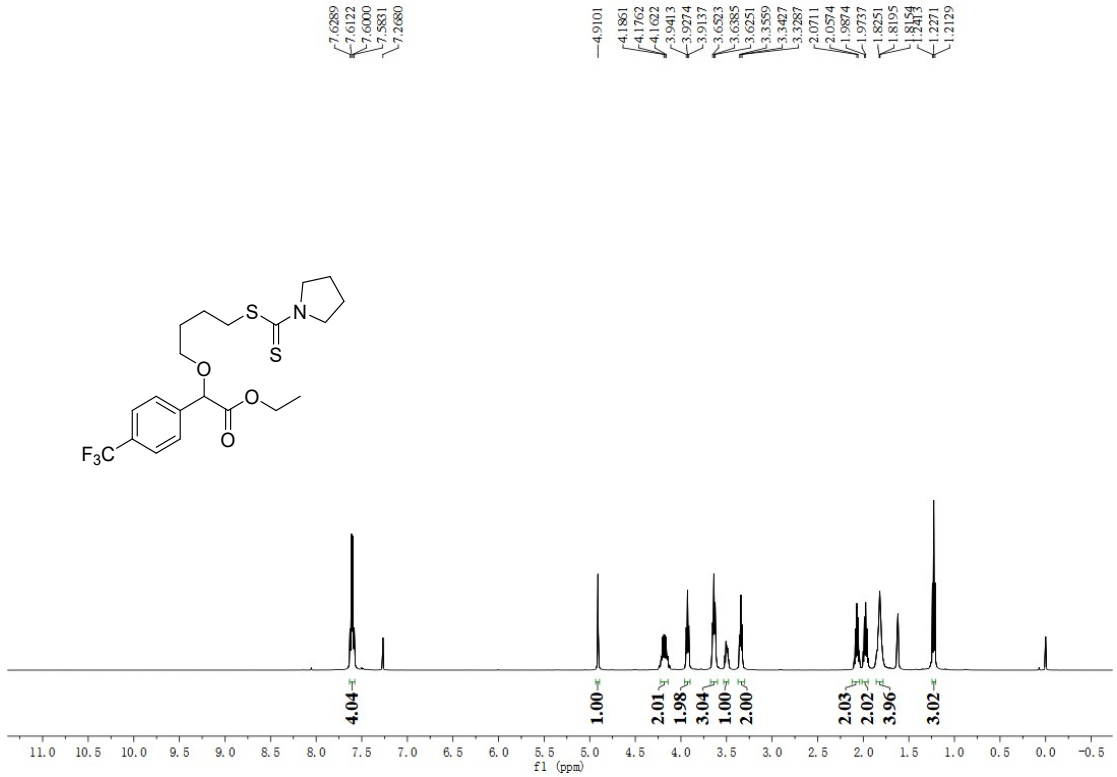
5g (500 MHz NMR, $CDCl_3$)



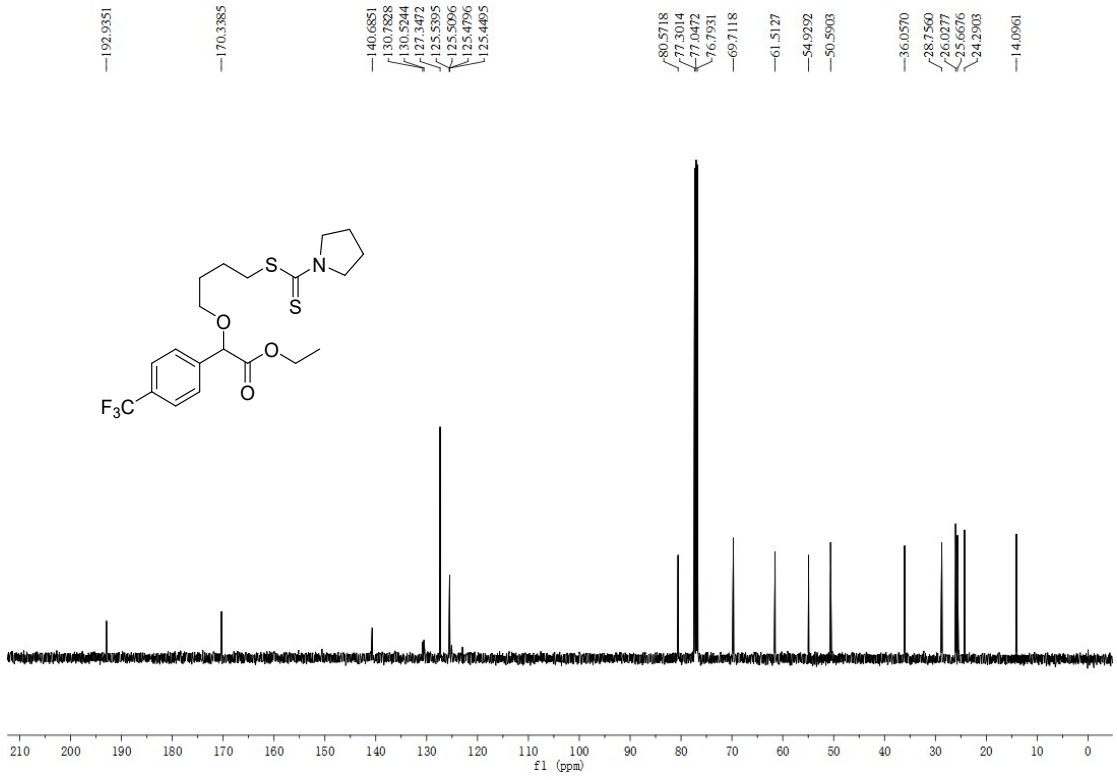


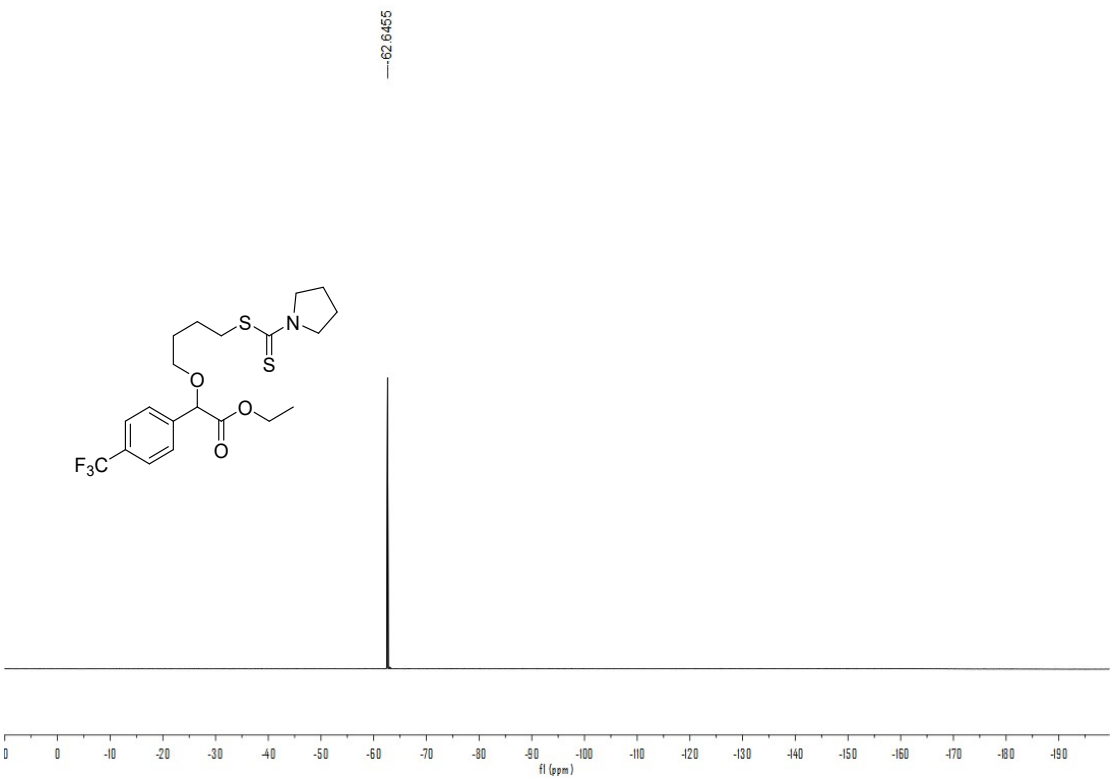
5h (500 MHz NMR, $CDCl_3$)



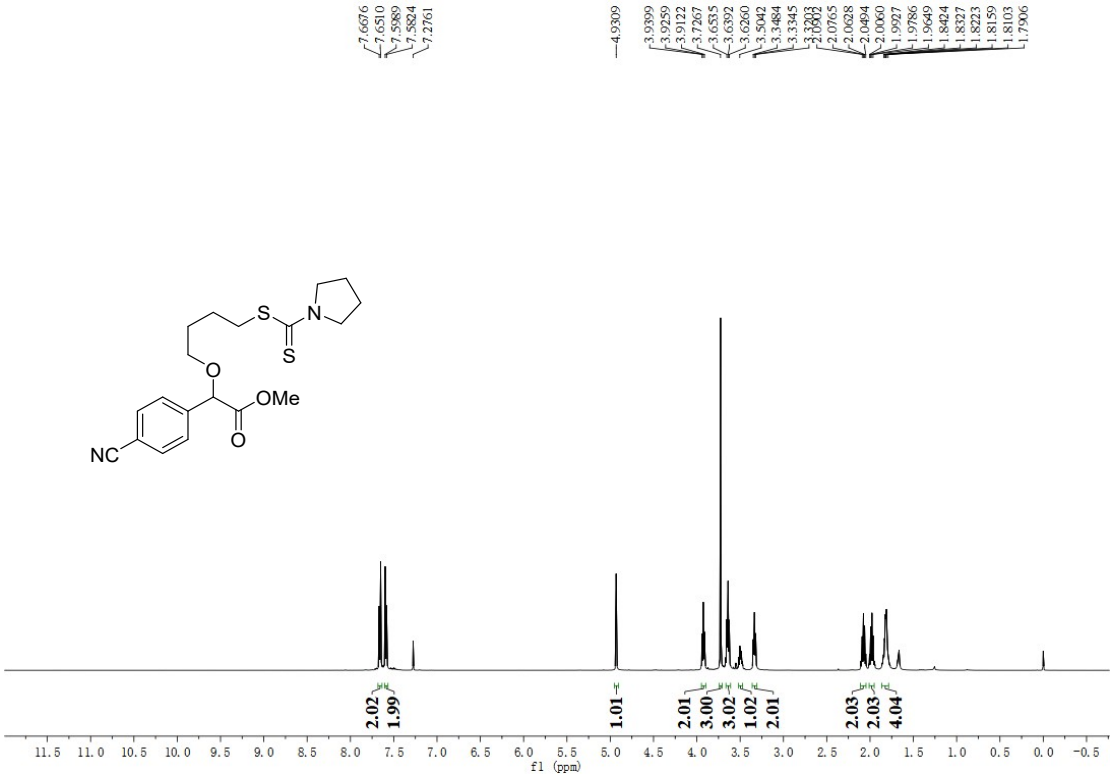


5i (500 MHz NMR, $CDCl_3$)

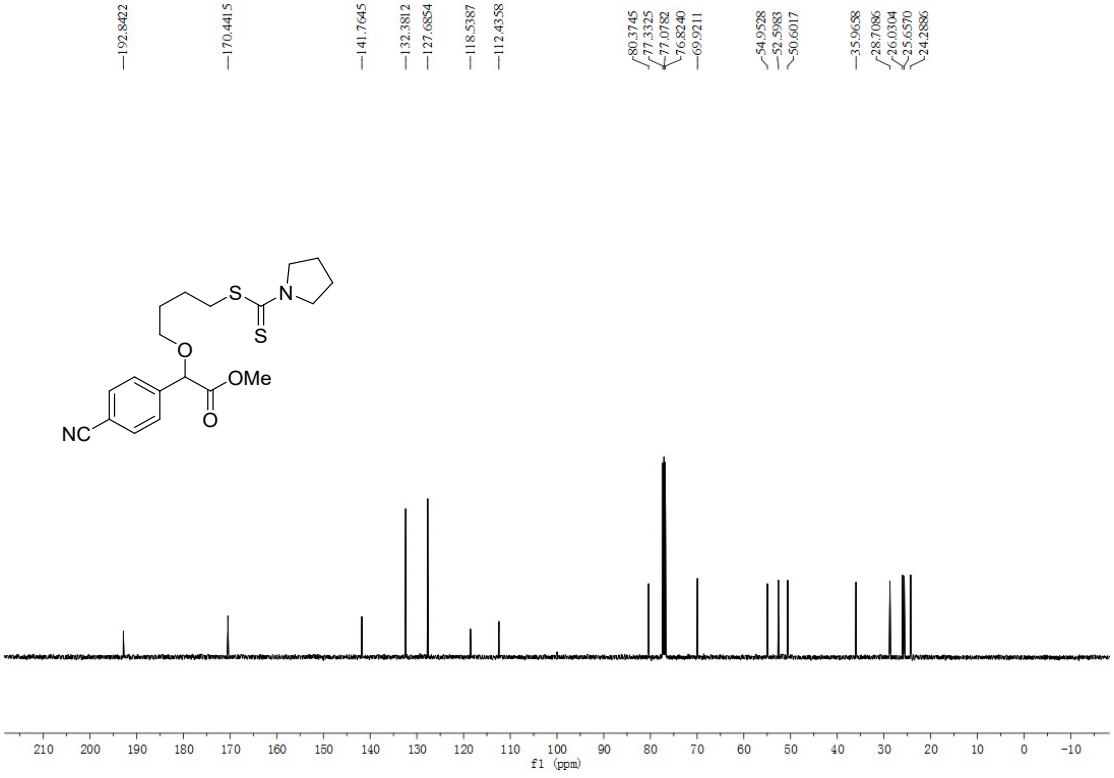


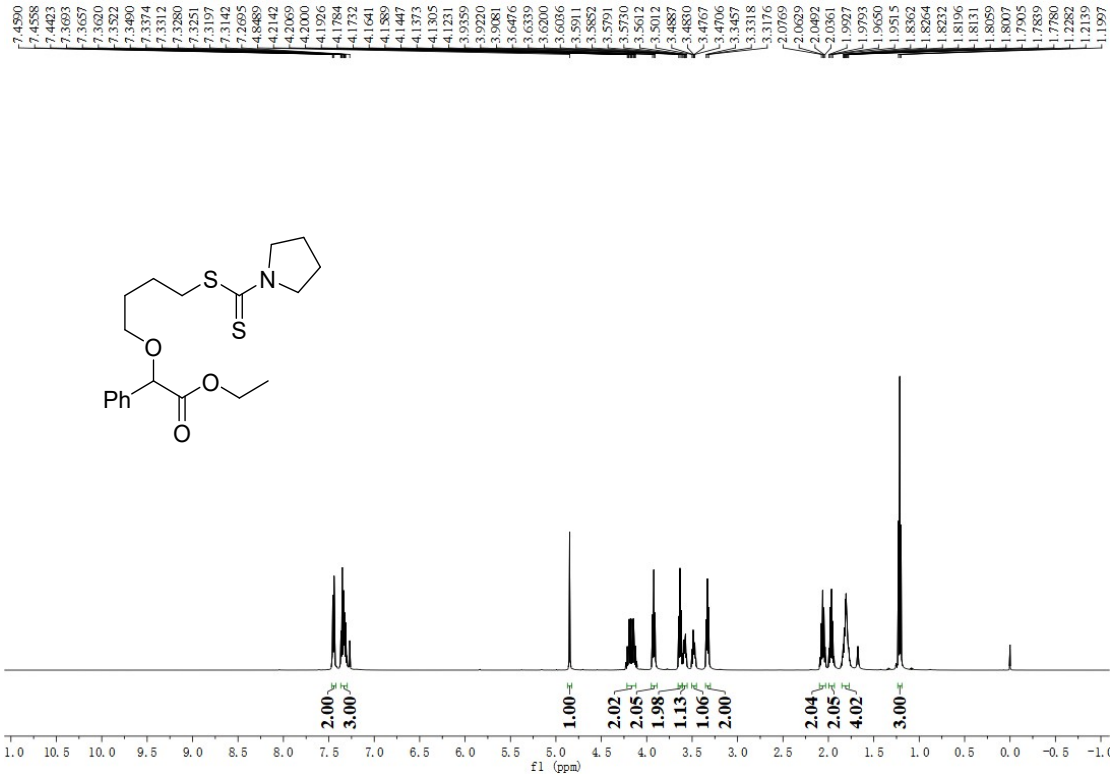


5i (500 MHz ^{19}FNMR, $CDCl_3$)

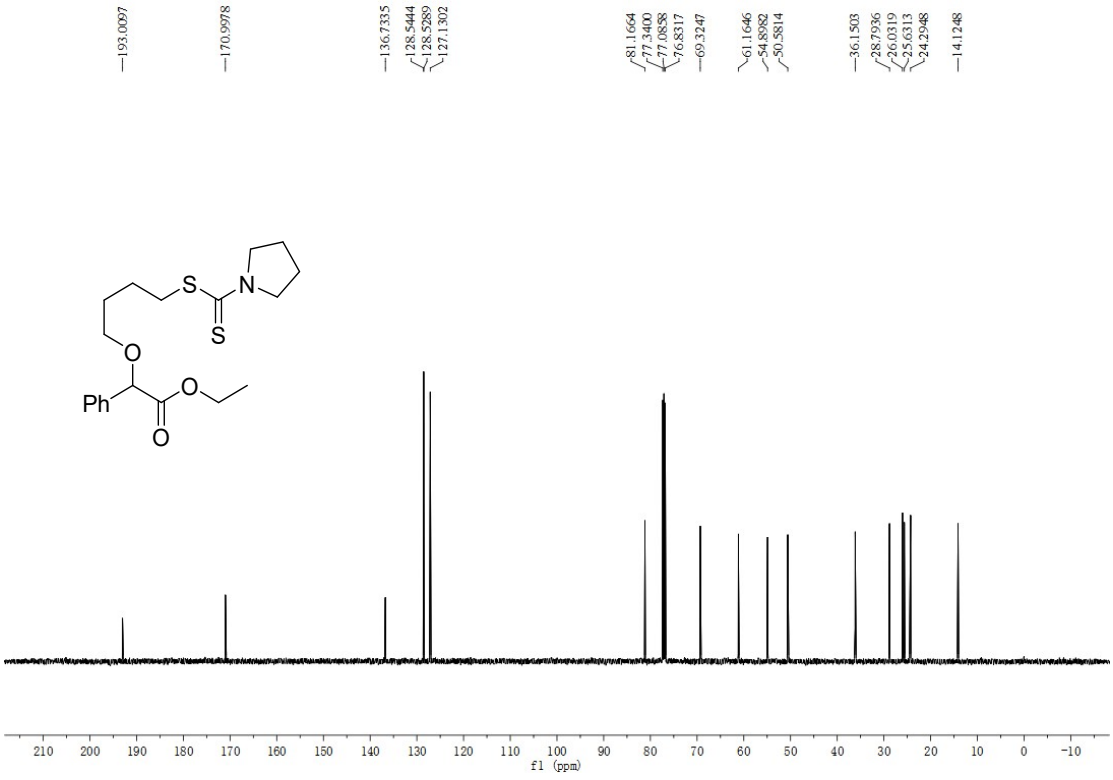


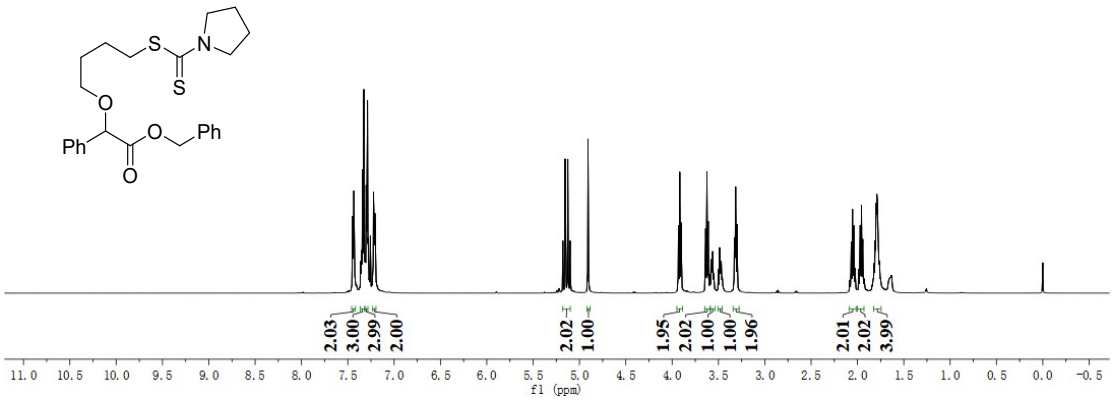
5j (500 MHz NMR, $CDCl_3$)



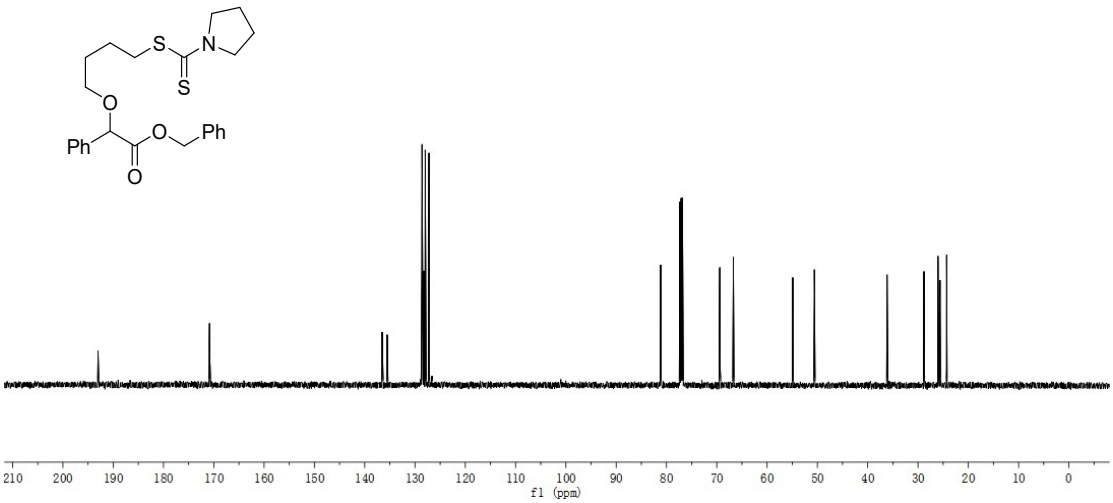


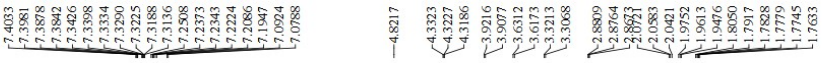
5k (500 MHz NMR, $CDCl_3$)

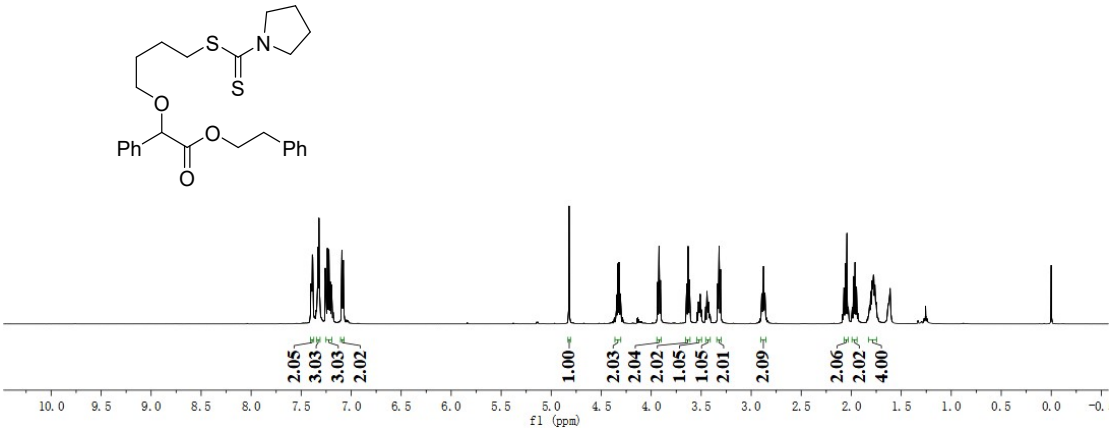




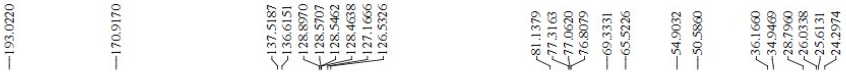
5l (500 MHz NMR, $CDCl_3$)

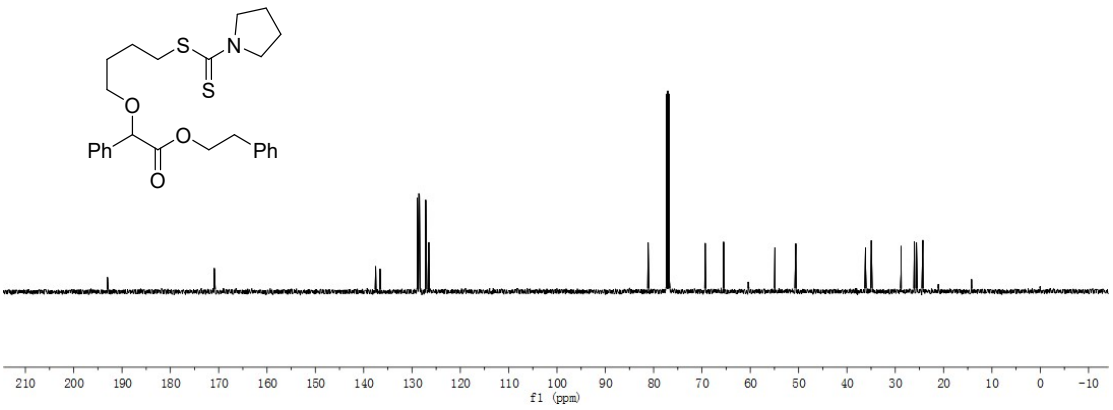


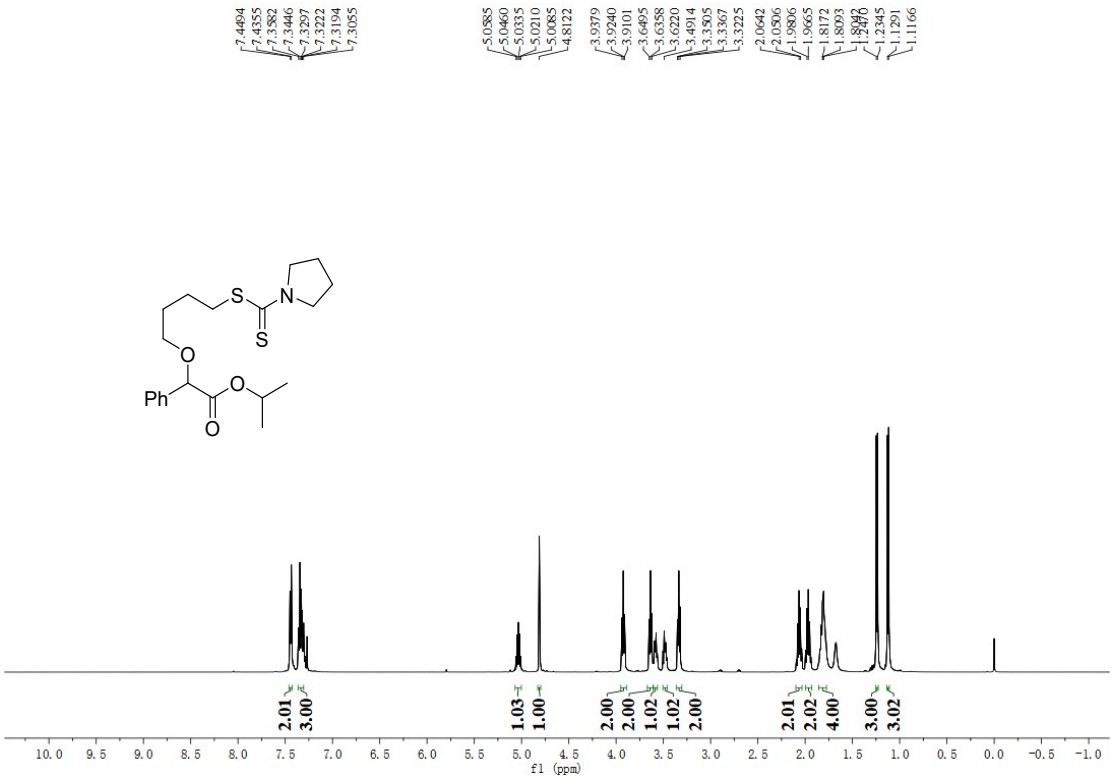




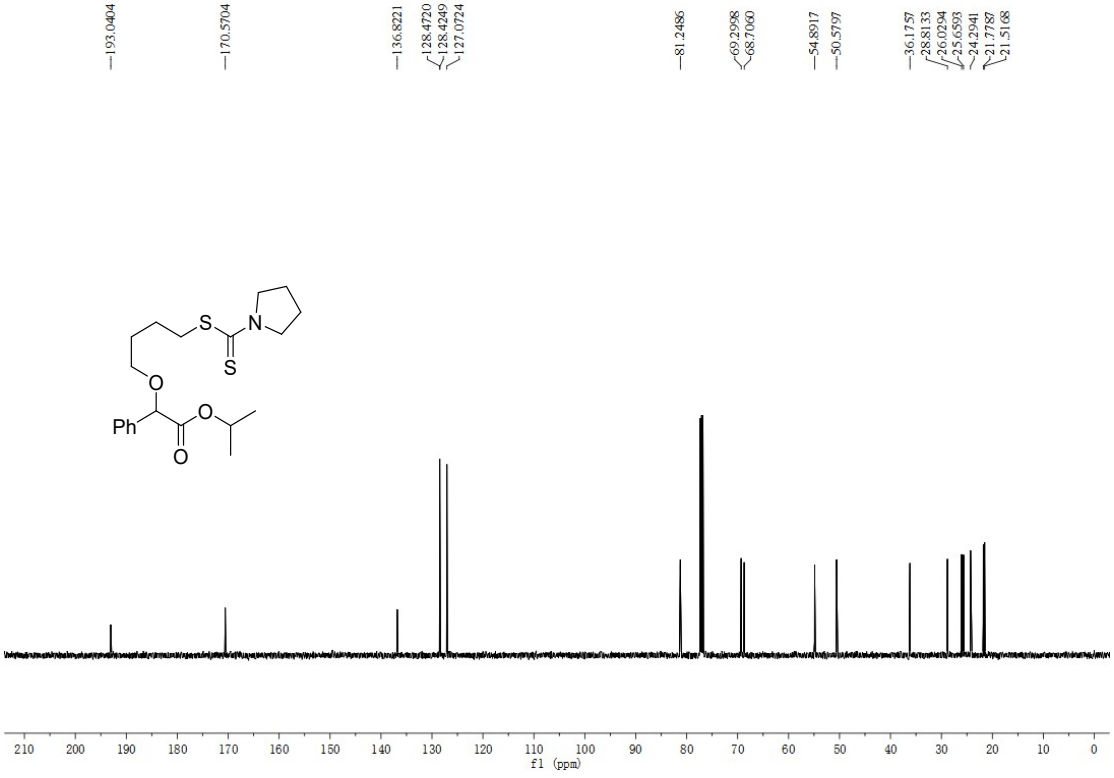
5m (500 MHz NMR, $CDCl_3$)

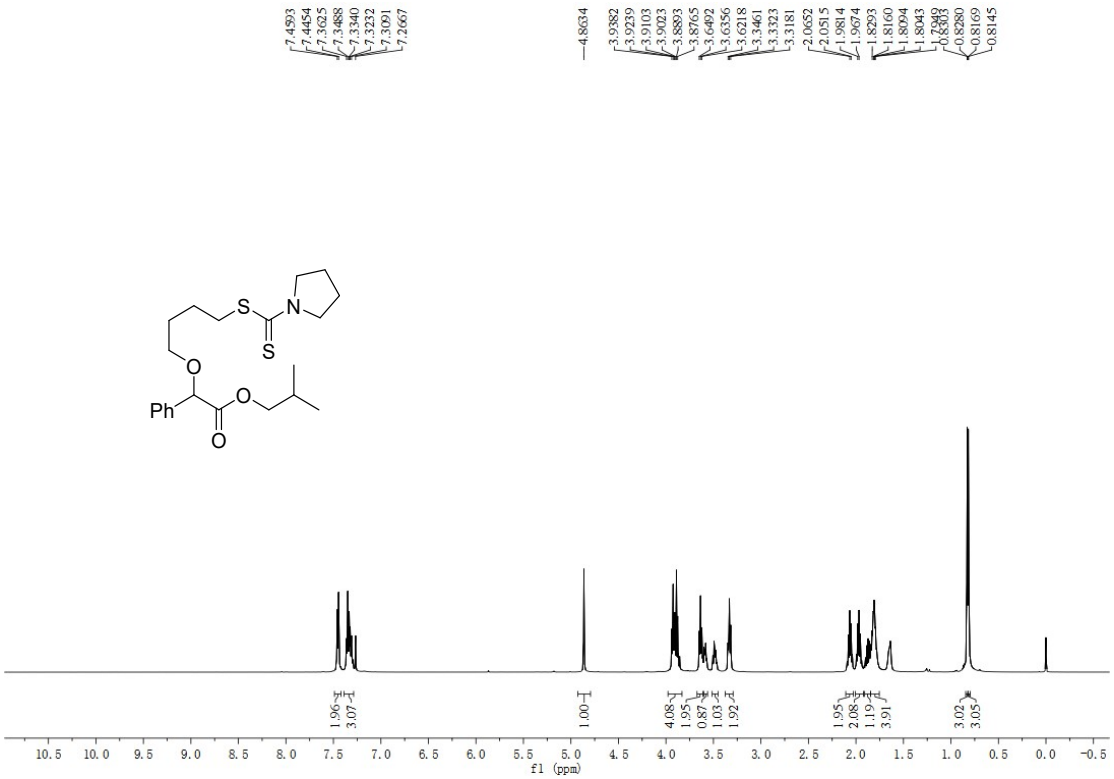




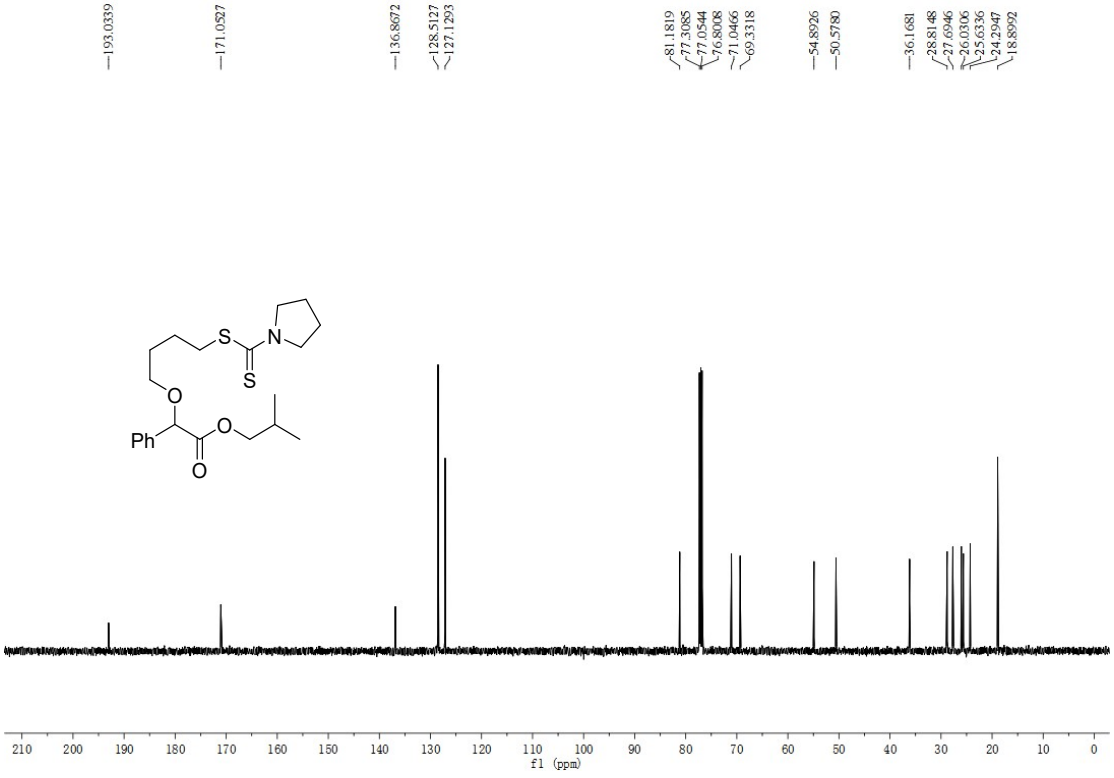


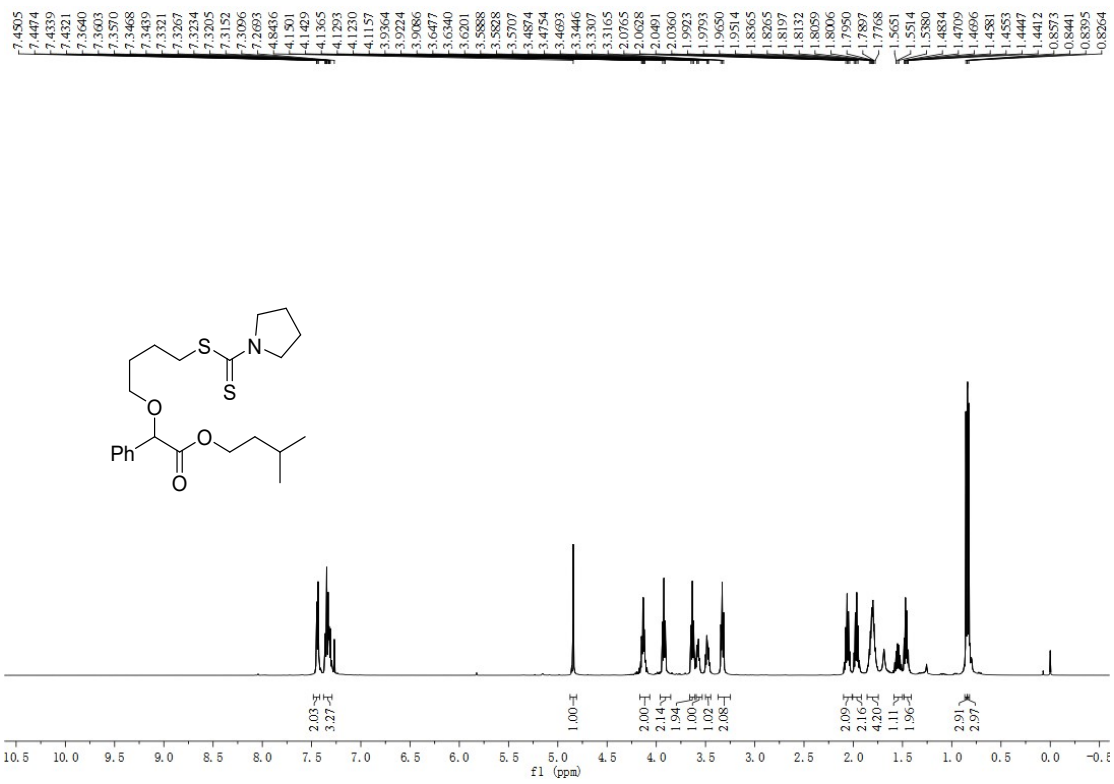
5n (500 MHz NMR, $CDCl_3$)



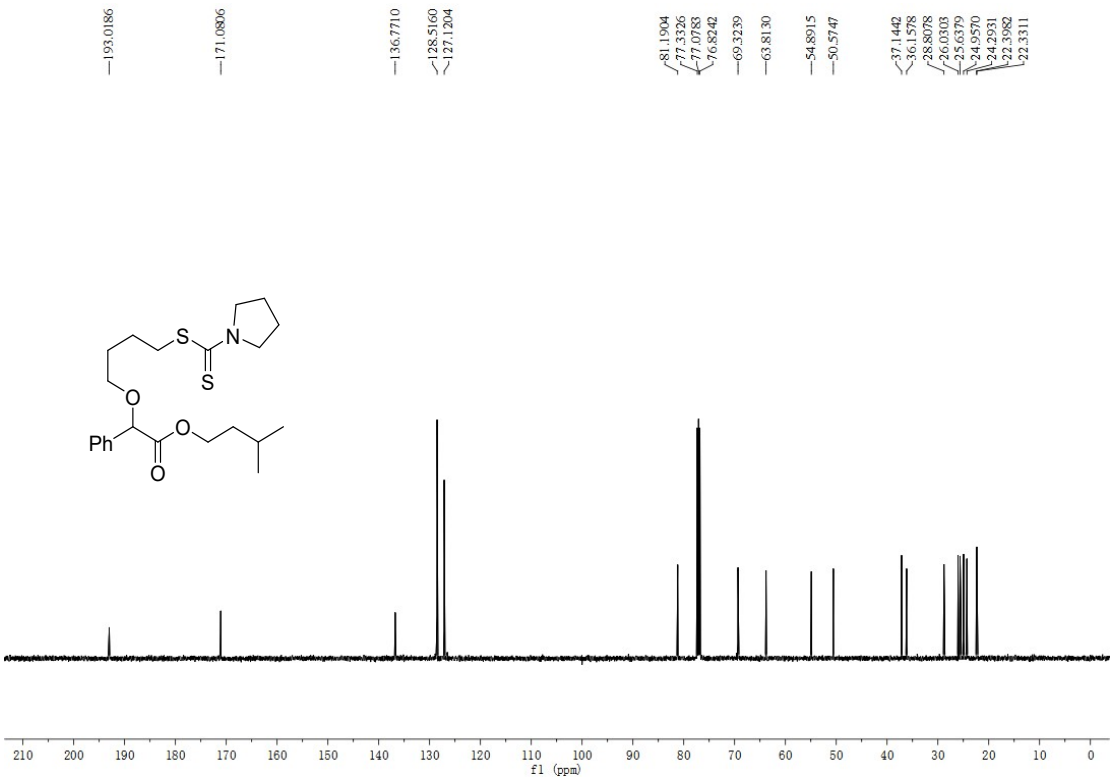


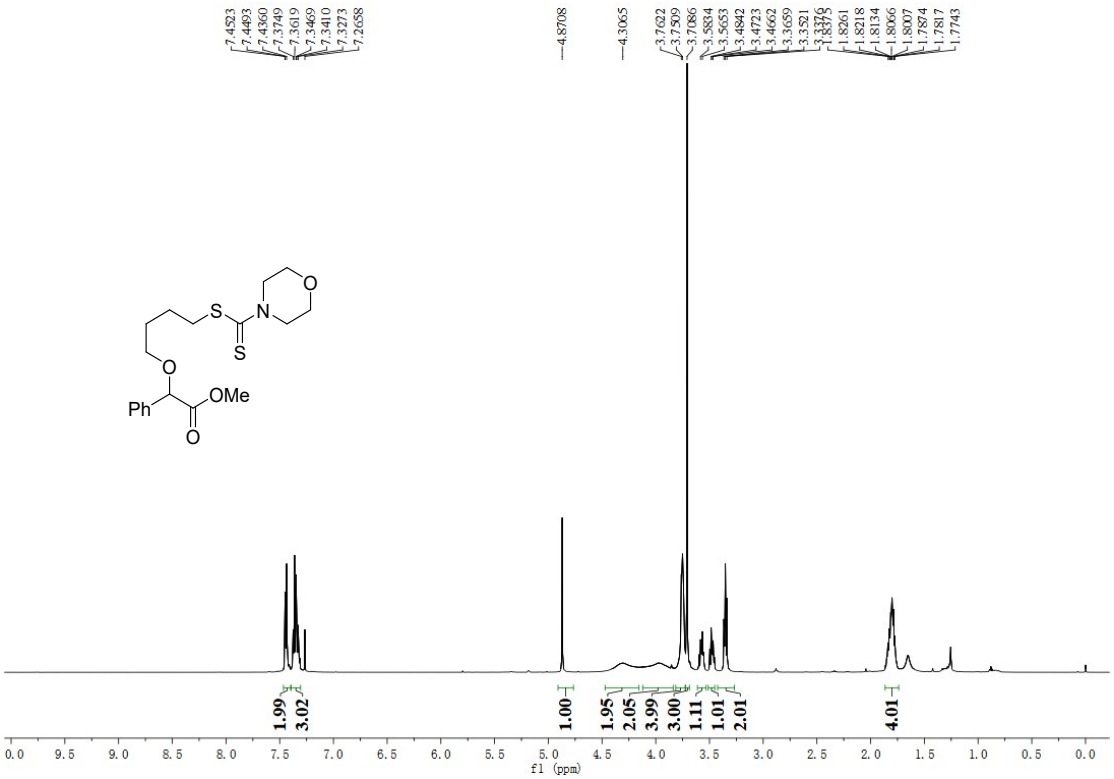
5o (500 MHz NMR, $CDCl_3$)



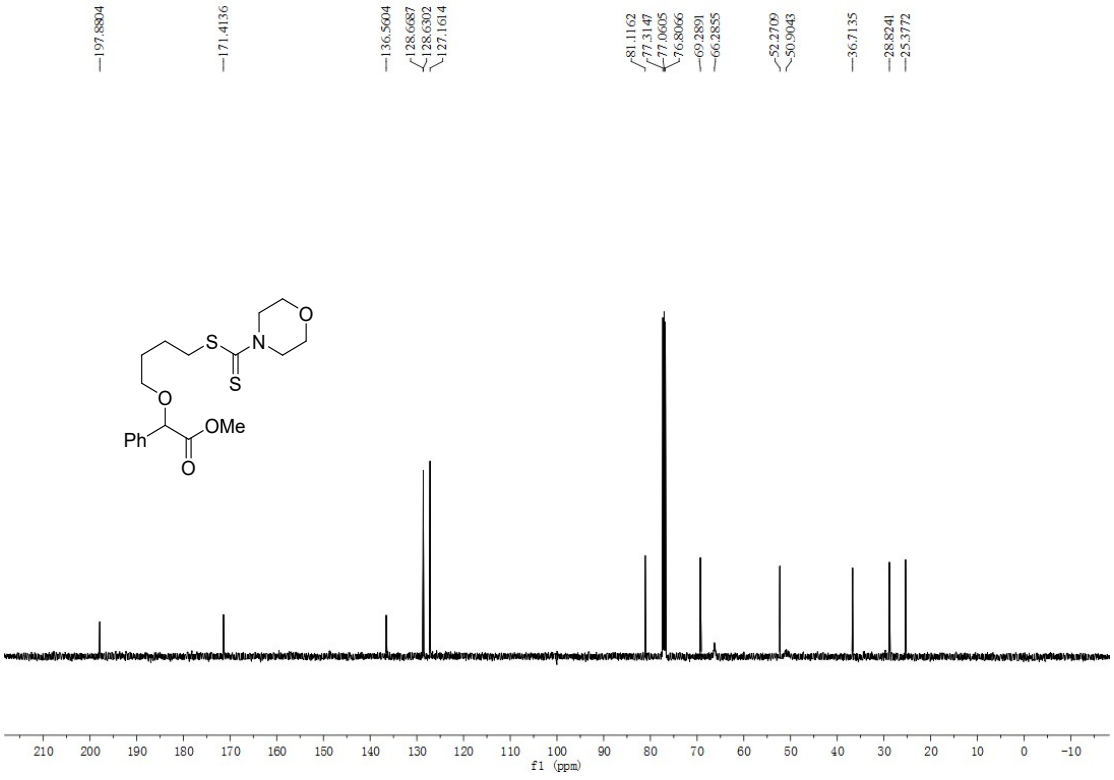


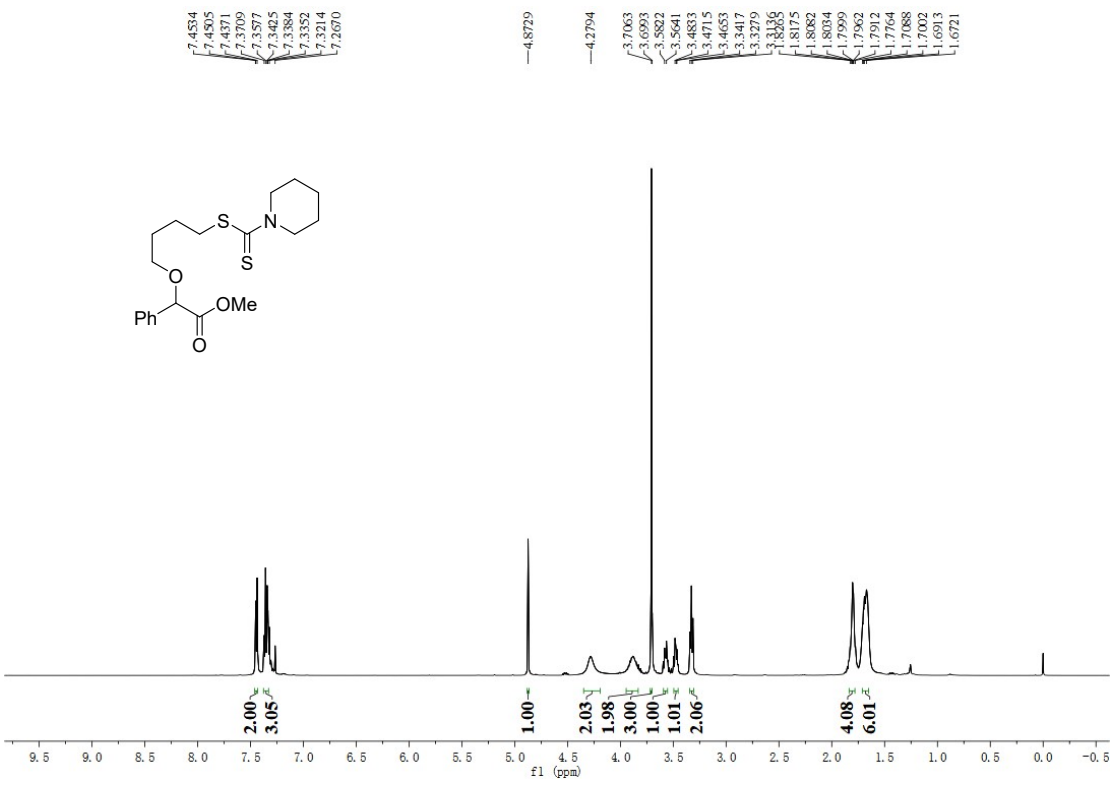
5p (500 MHz NMR, $CDCl_3$)



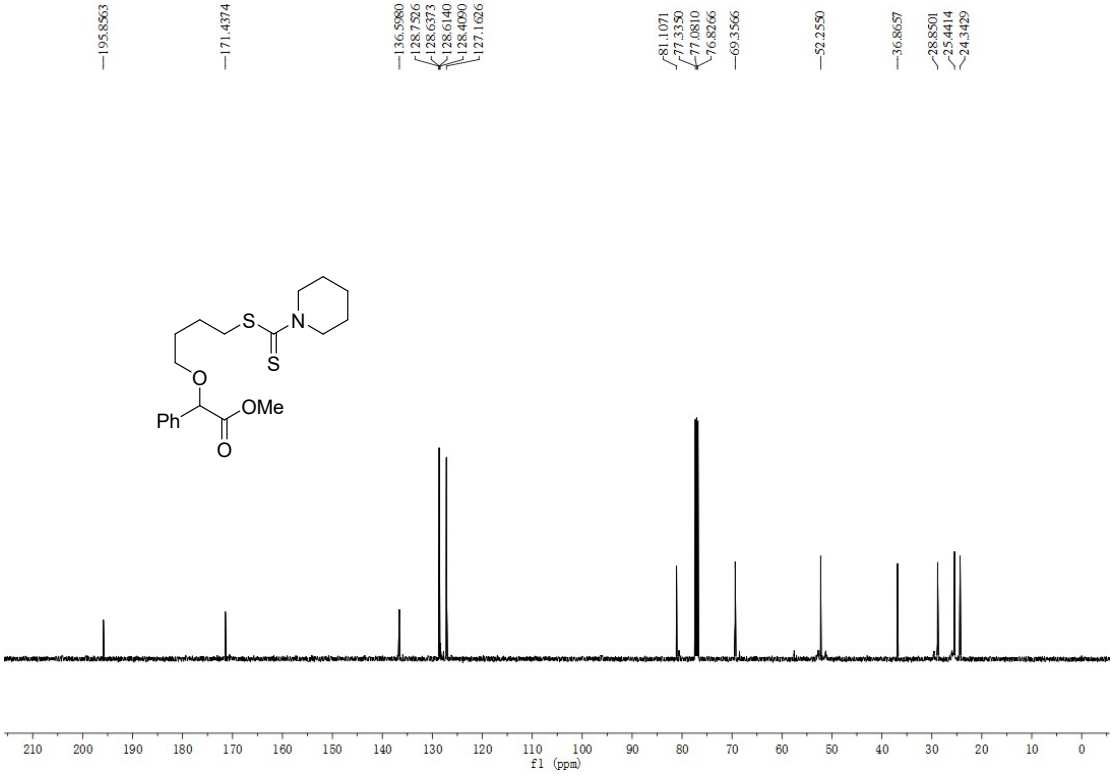


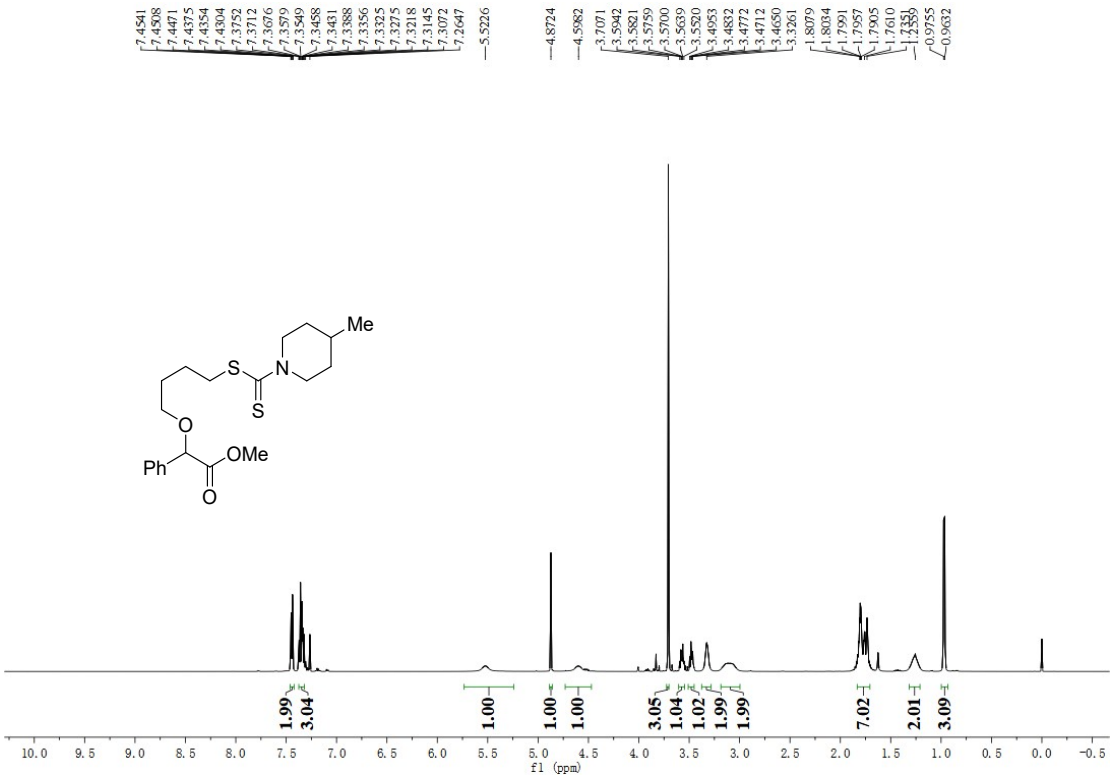
5q (500 MHz NMR, $CDCl_3$)



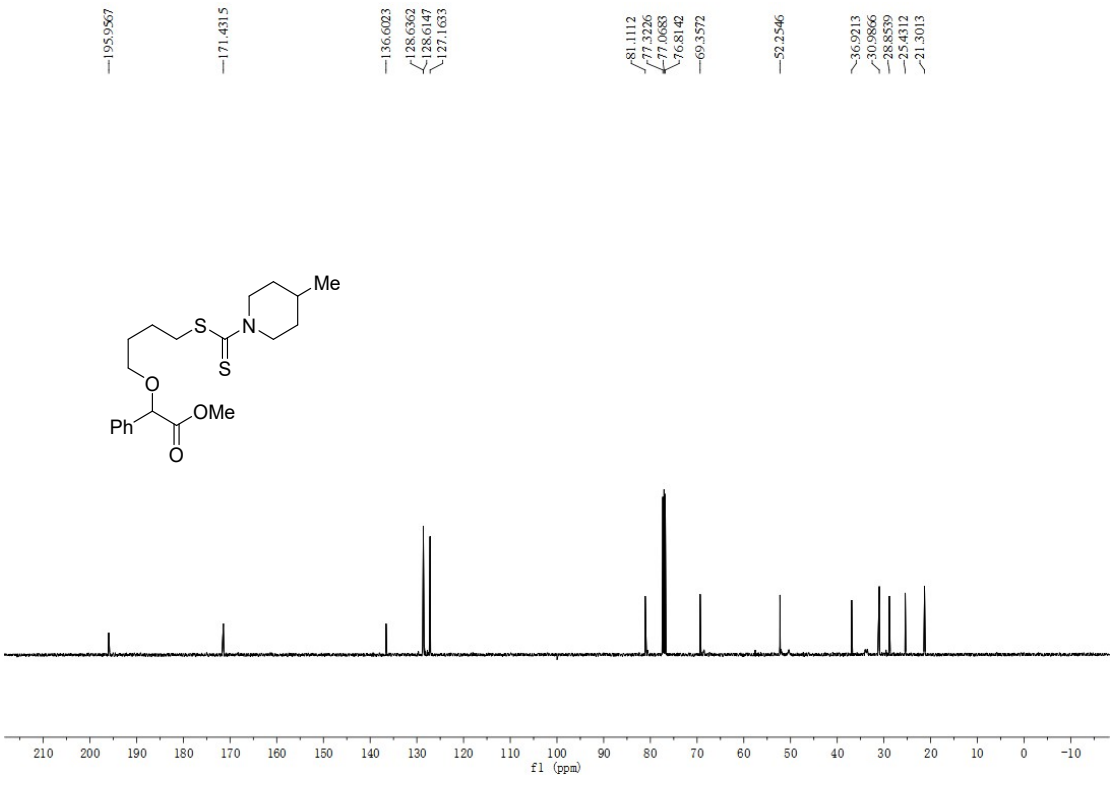


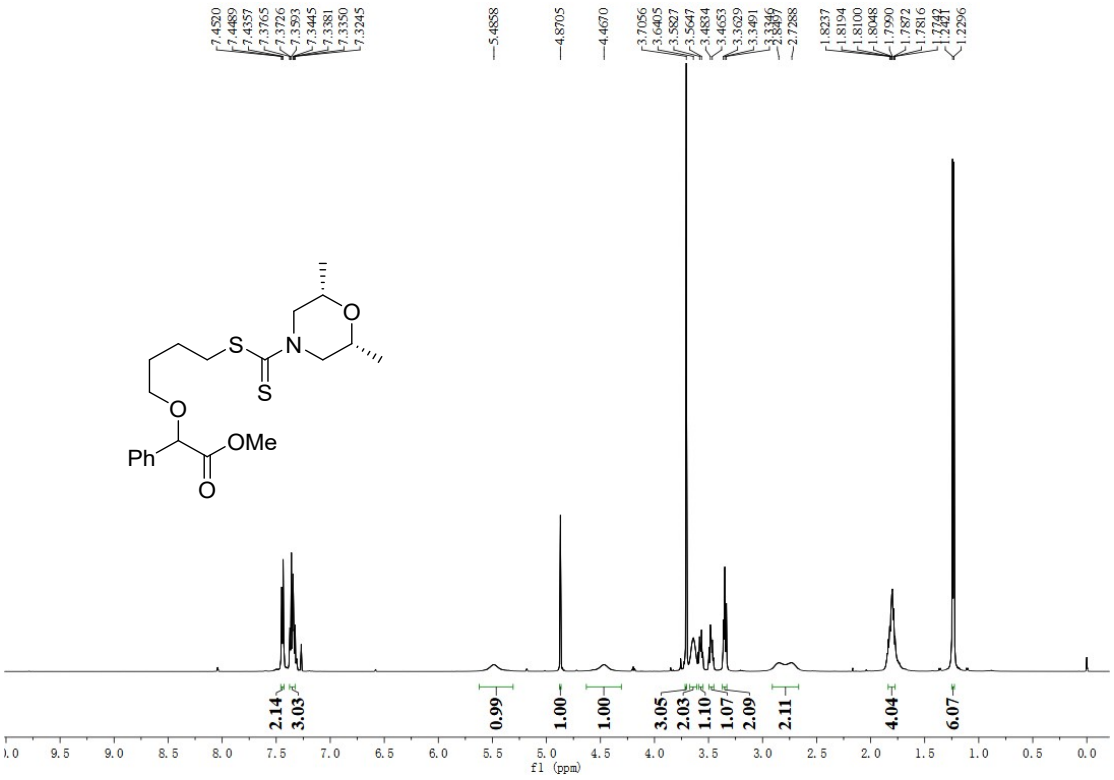
5r (500 MHz NMR, $CDCl_3$)



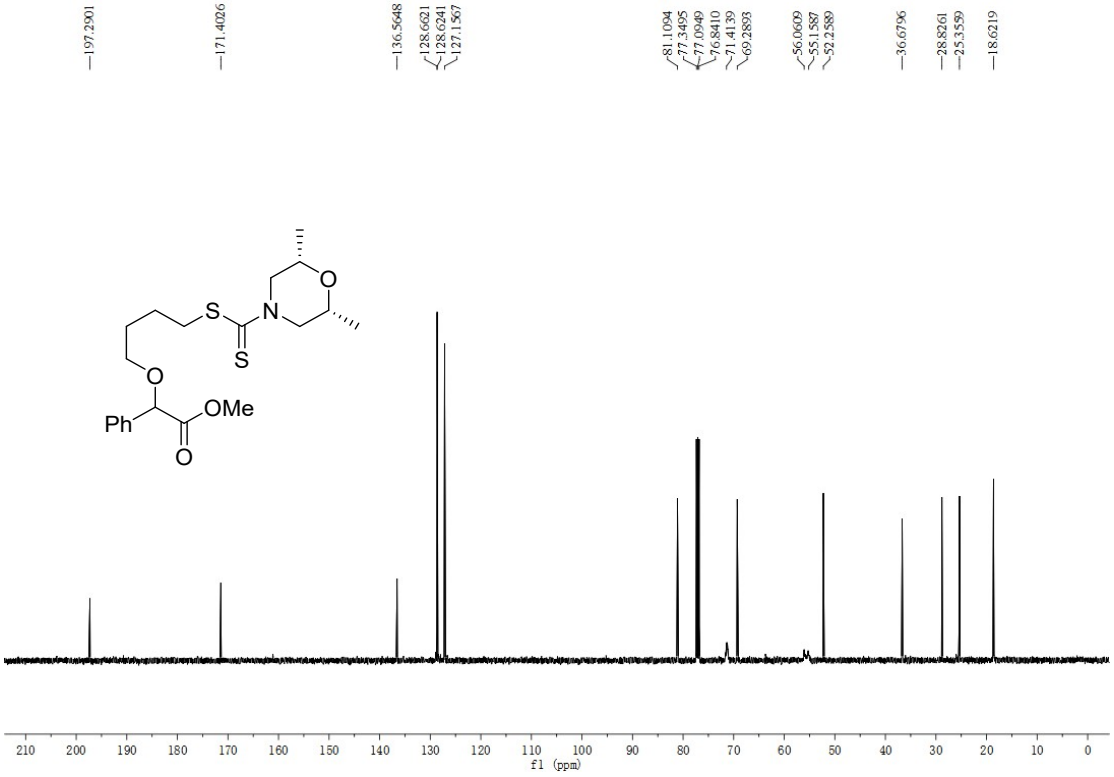


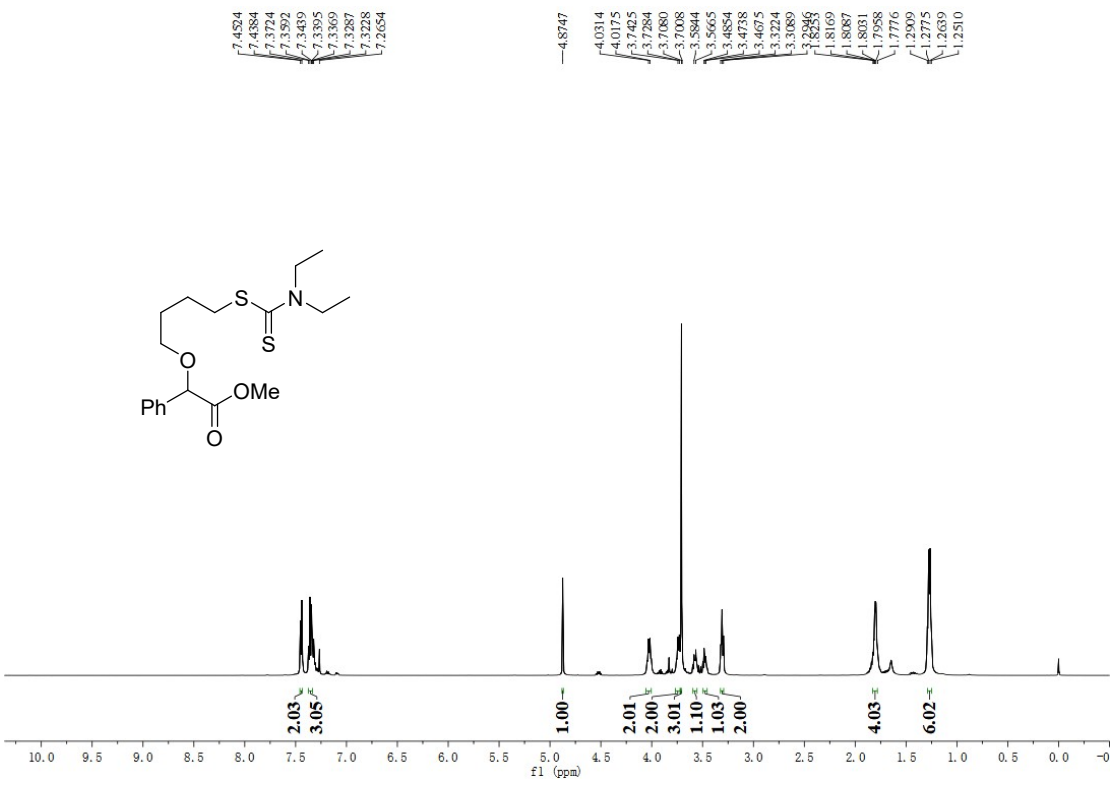
5s (500 MHz NMR, $CDCl_3$)



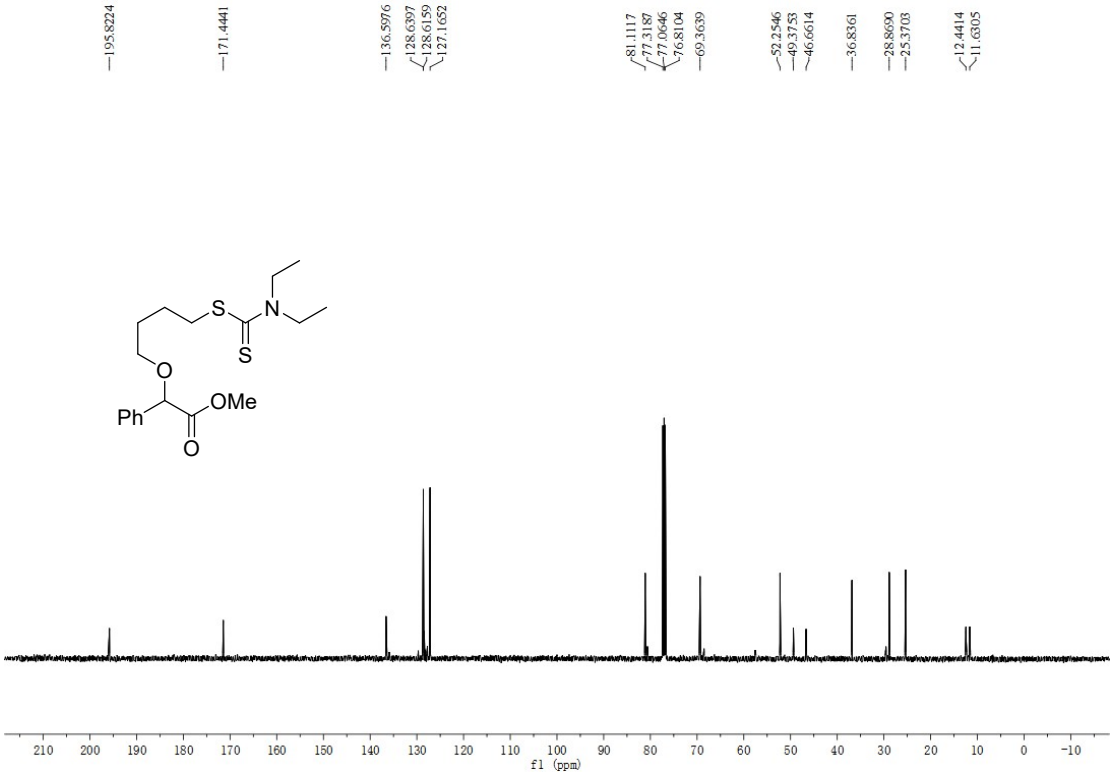


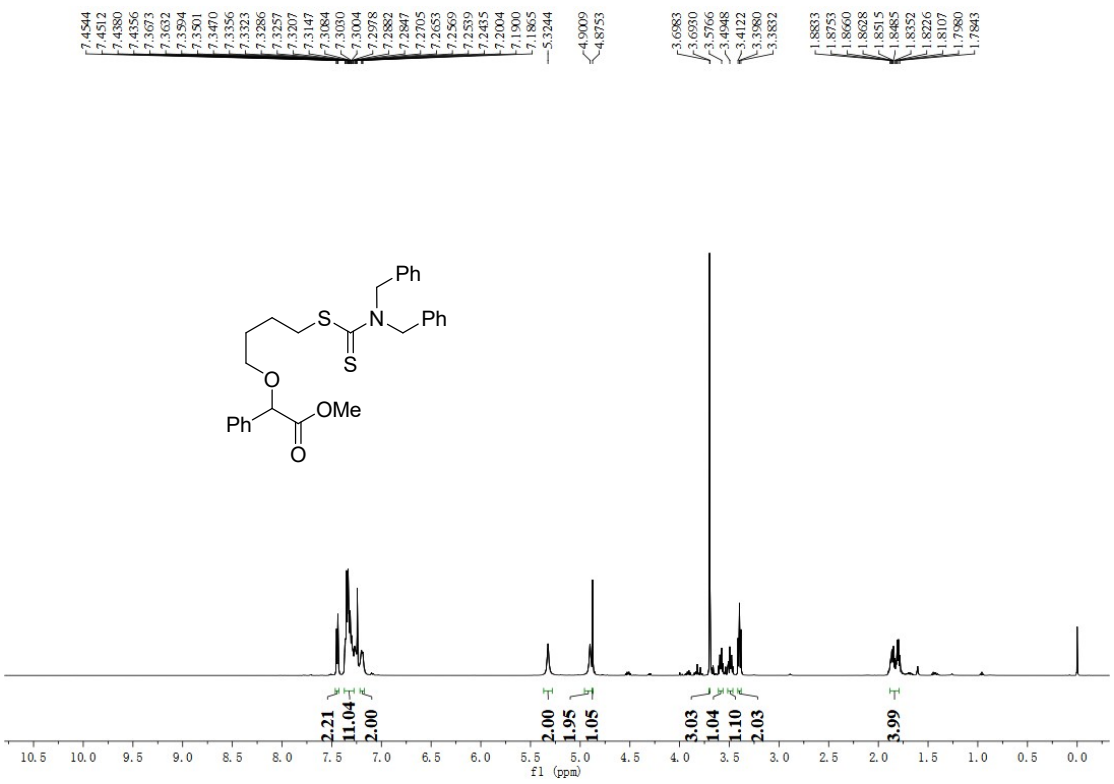
5t (500 MHz NMR, $CDCl_3$)



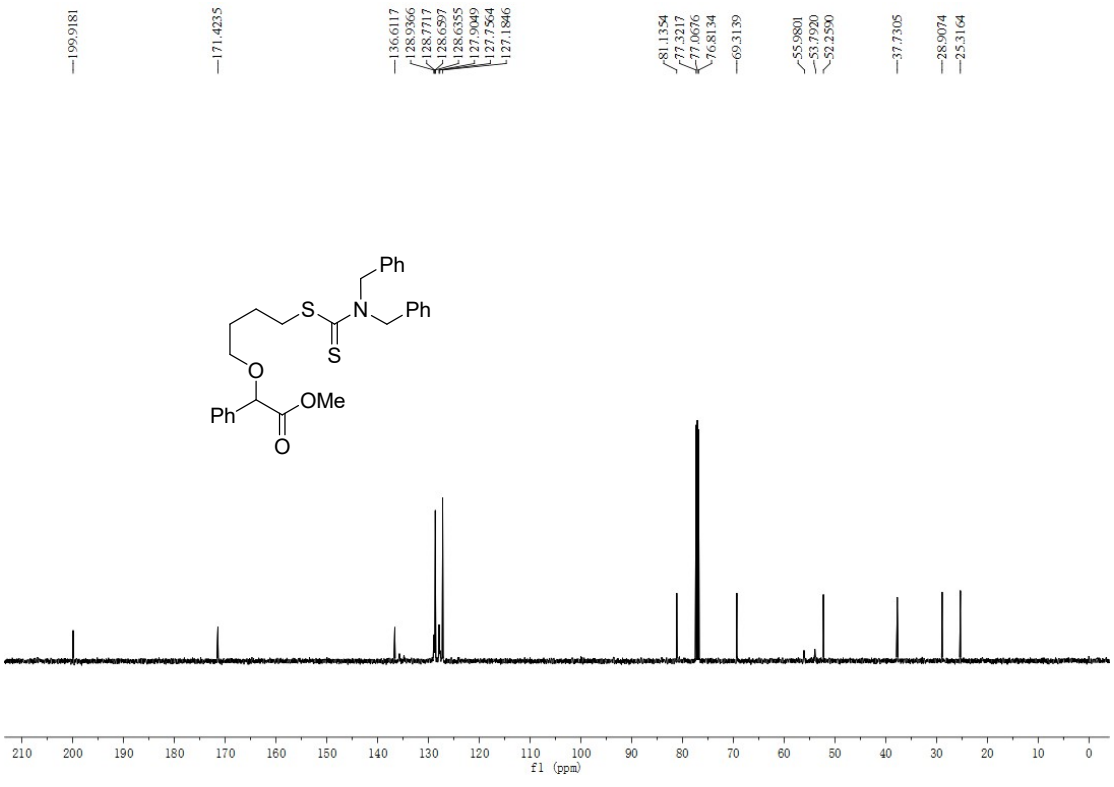


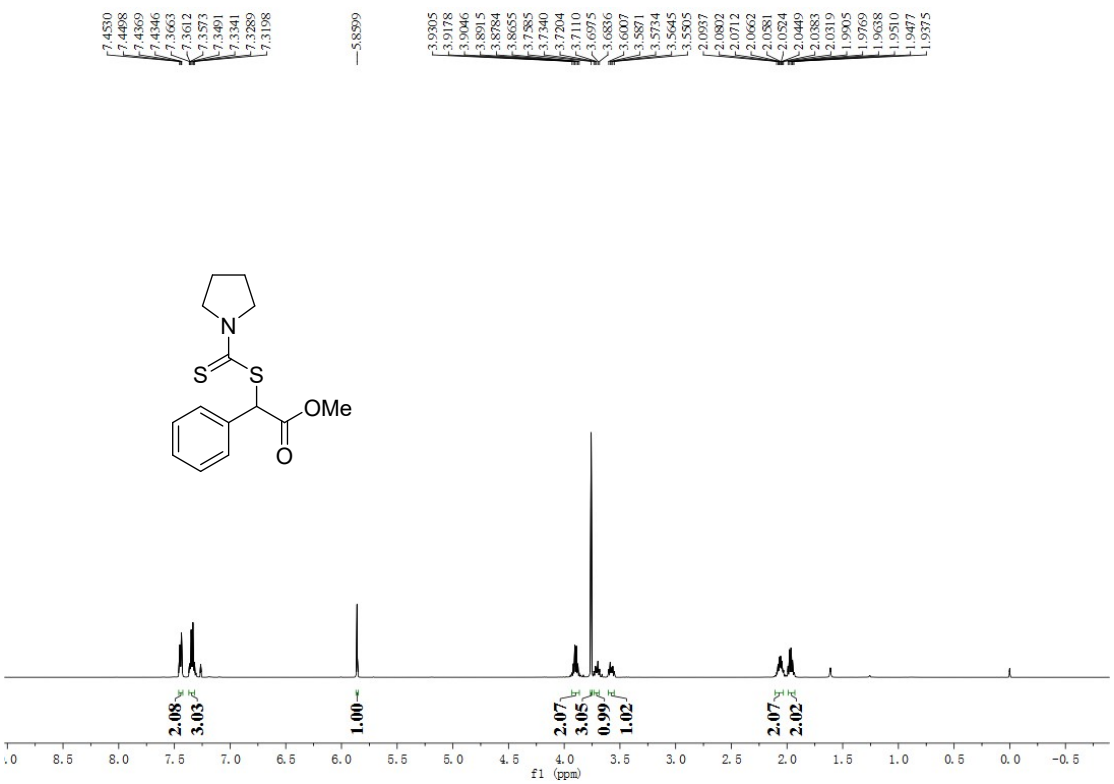
5u (500 MHz NMR, $CDCl_3$)



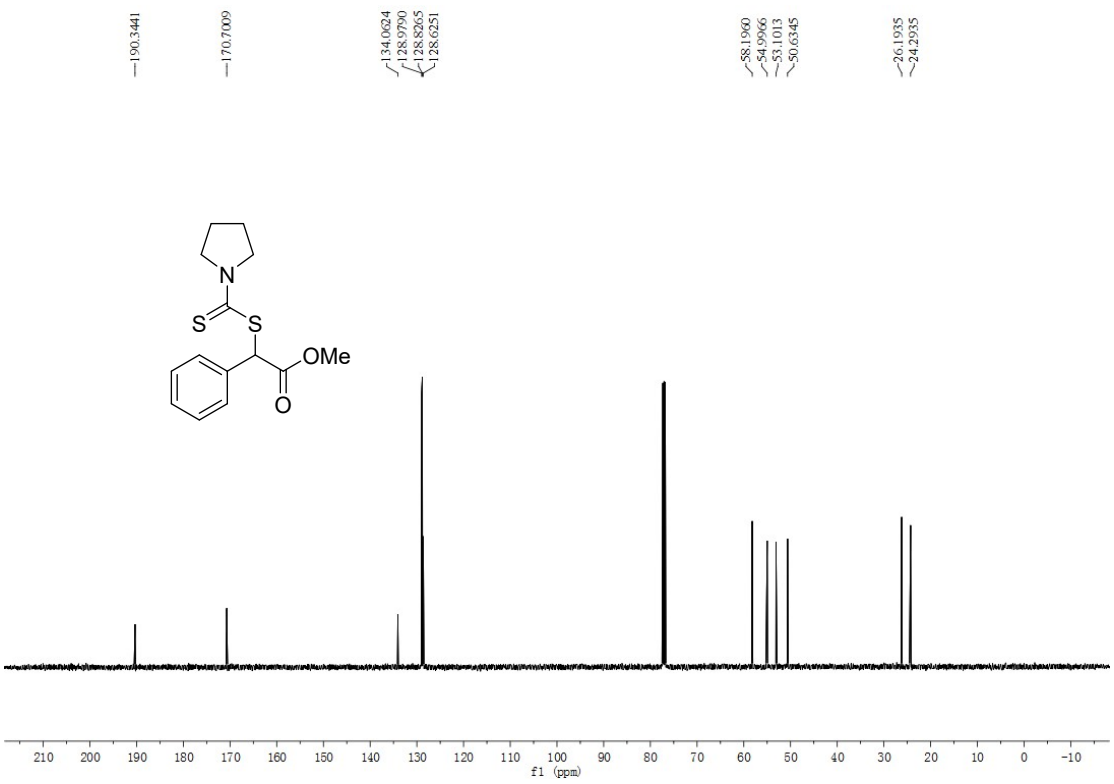


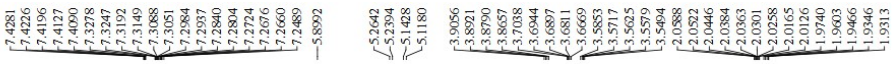
5v (500 MHz NMR, $CDCl_3$)

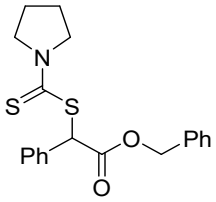


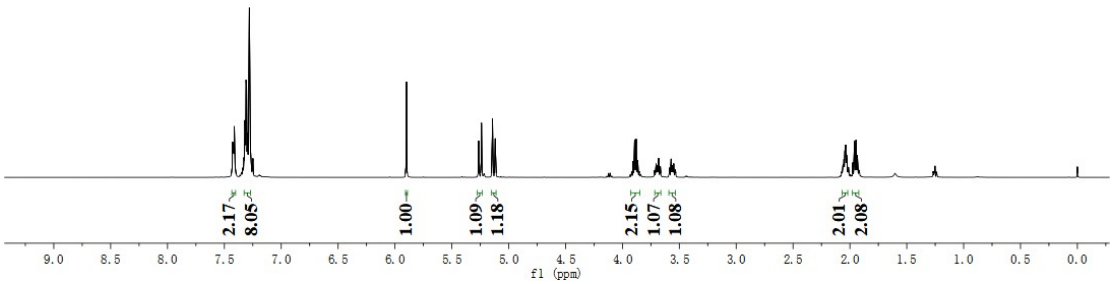


4a (500 MHz NMR, $CDCl_3$)

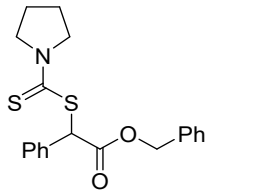


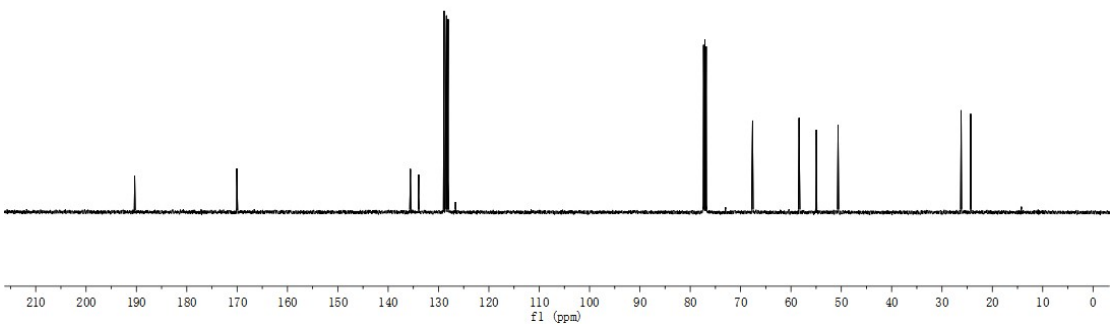


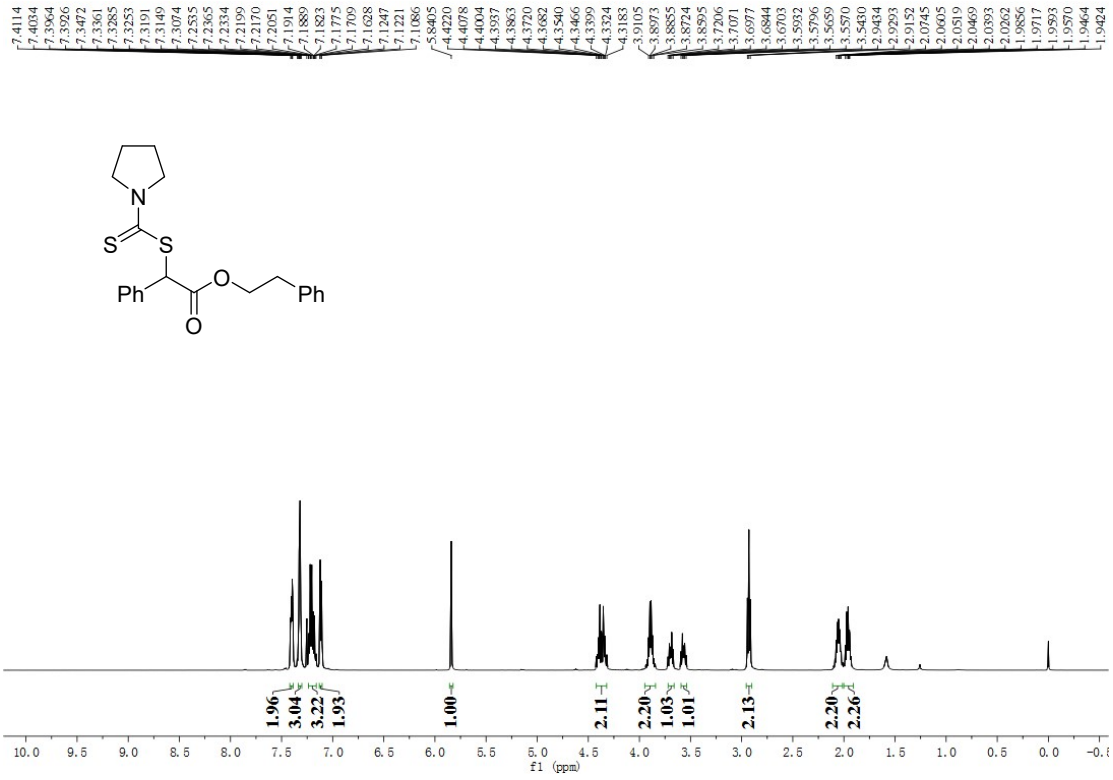




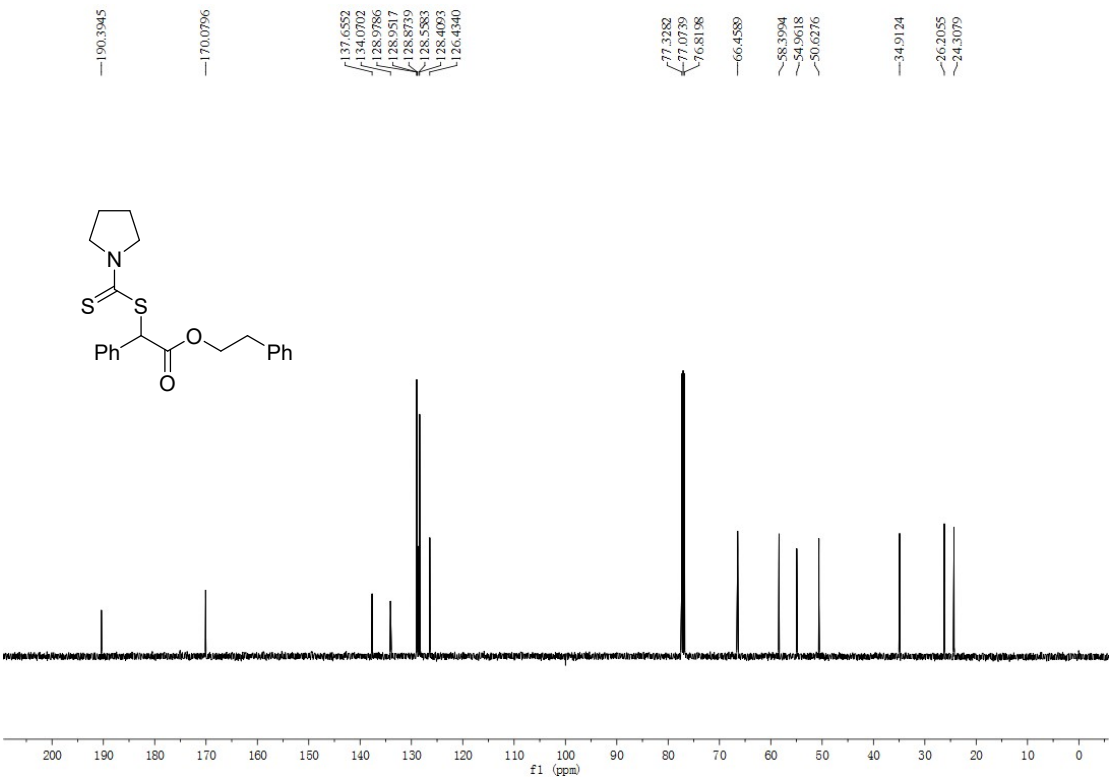
4b (500 MHz NMR, $CDCl_3$)

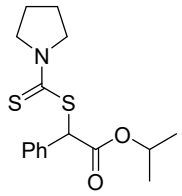


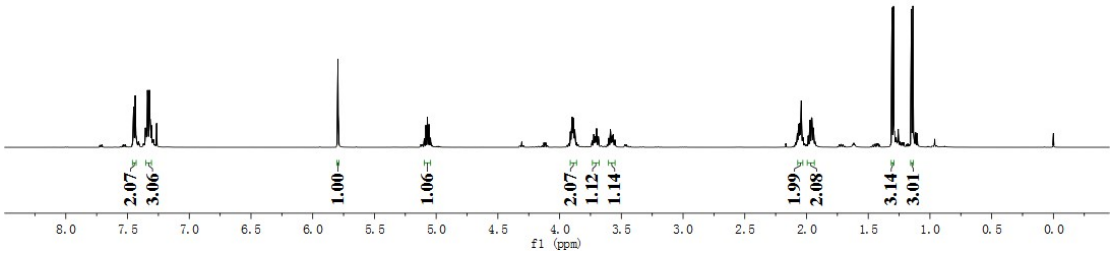




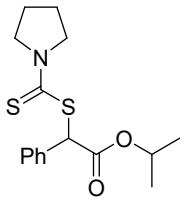
4c (500 MHz NMR, $CDCl_3$)

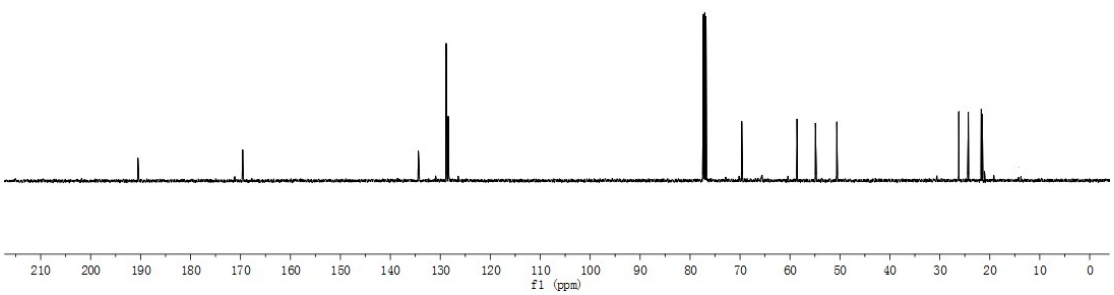


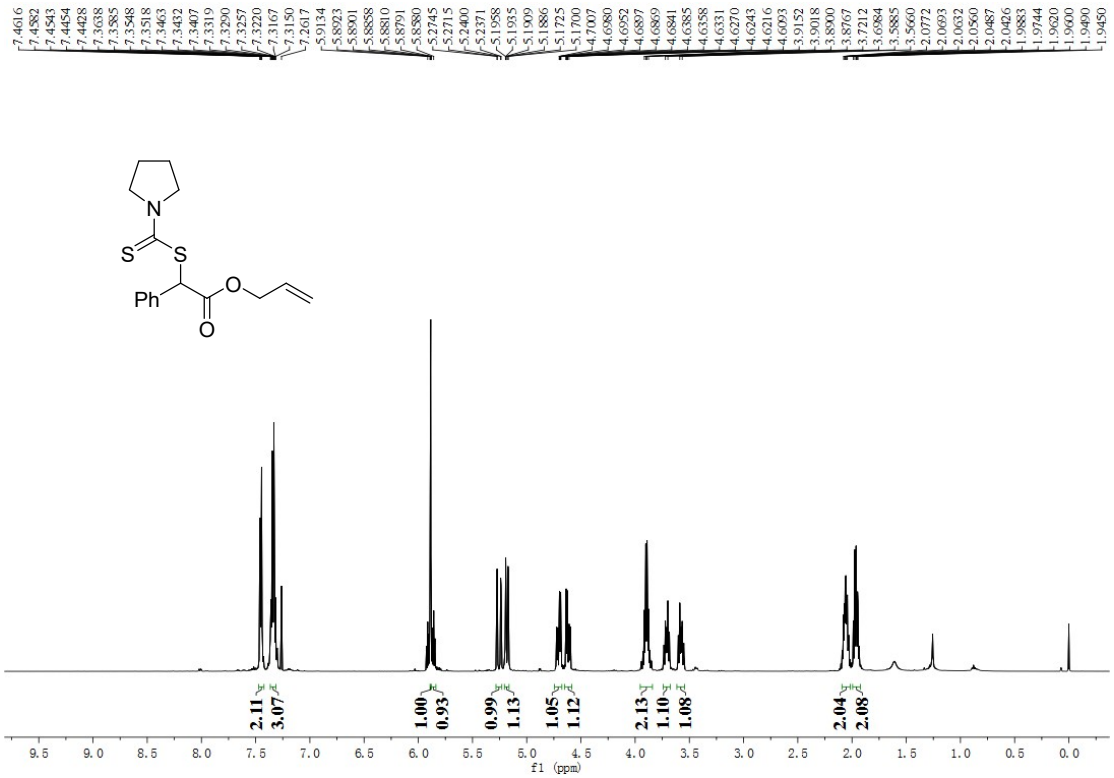




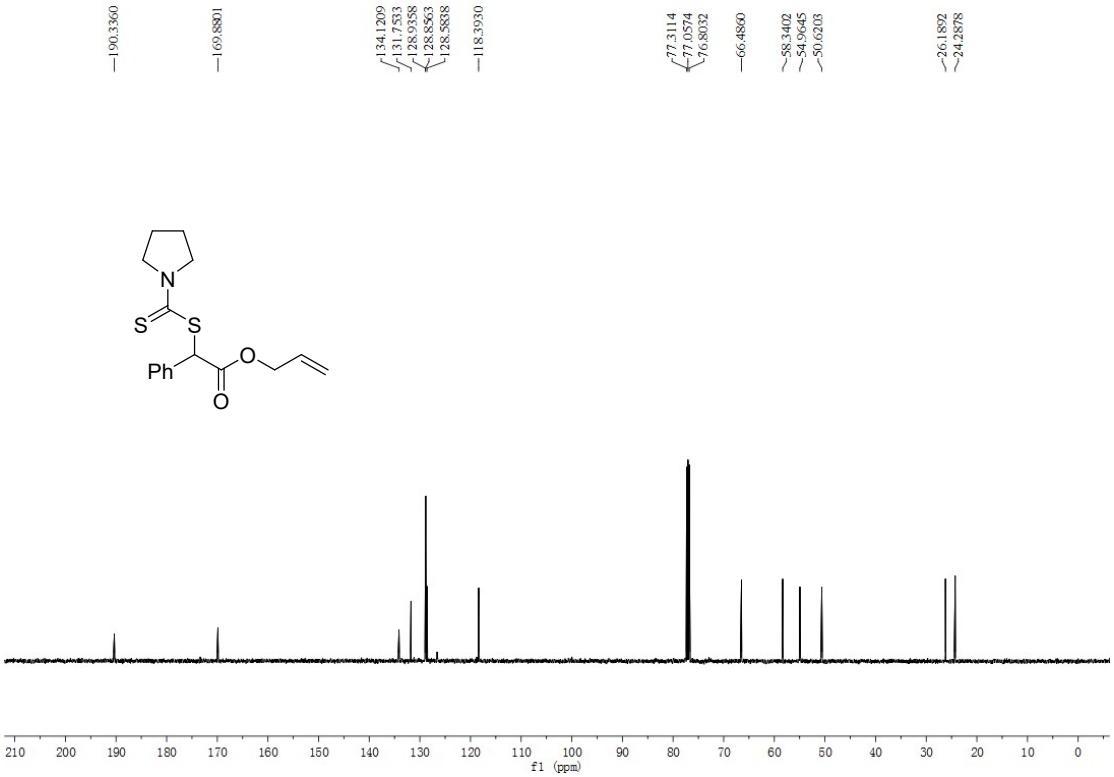
4d (500 MHz NMR, $CDCl_3$)

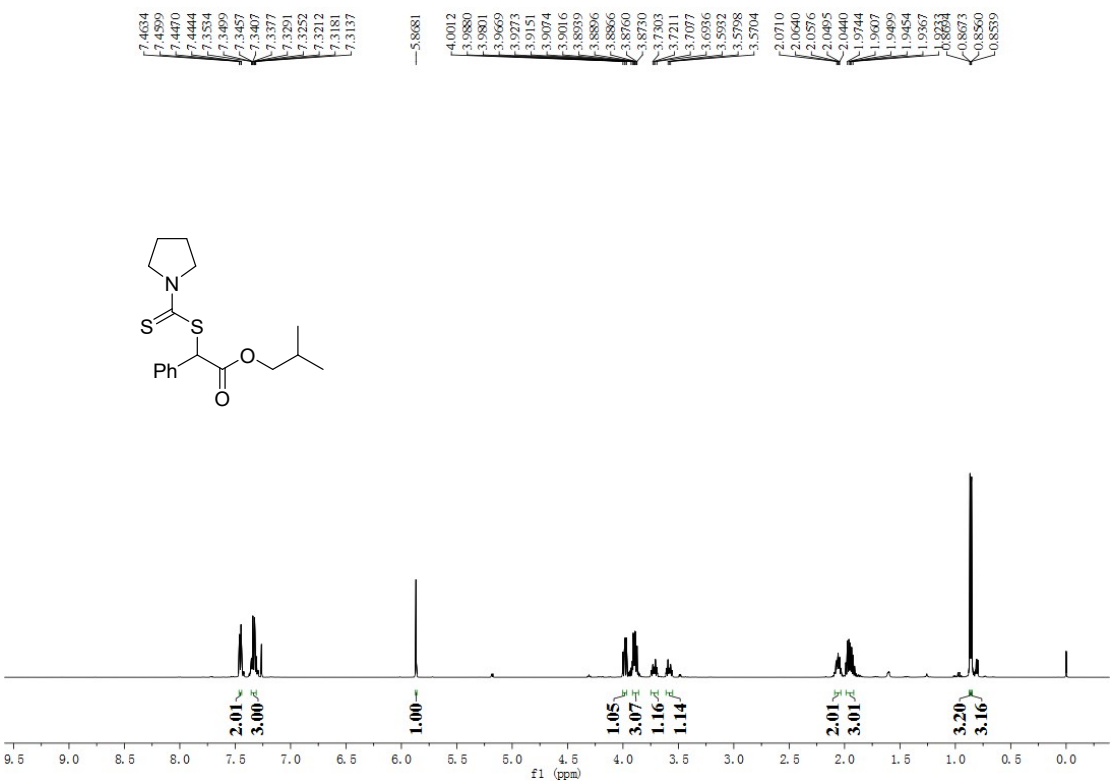




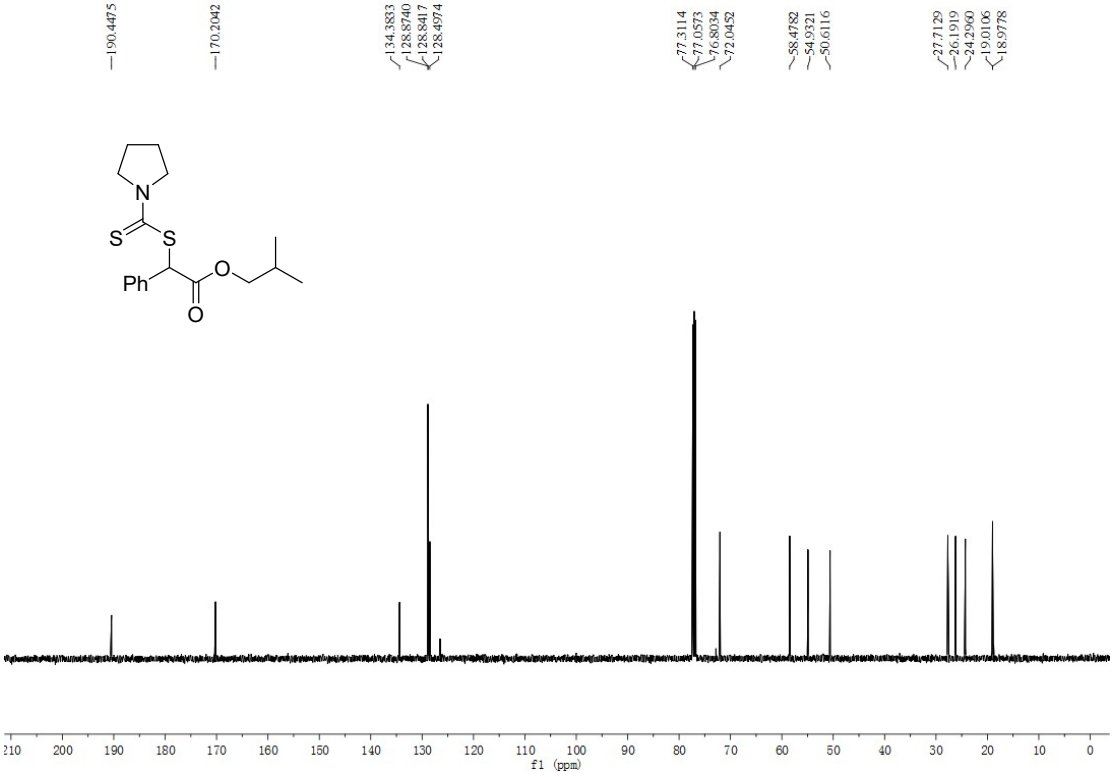


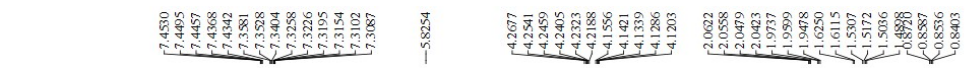
4e (500 MHz NMR, $CDCl_3$)

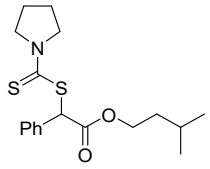


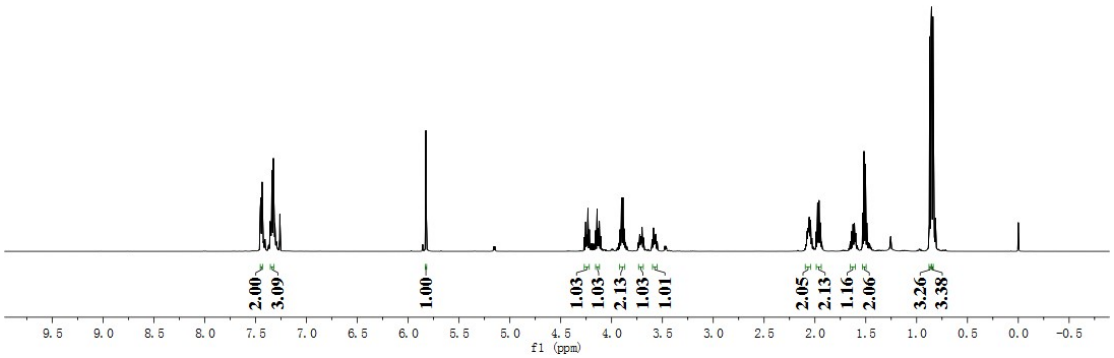


4f (500 MHz NMR, $CDCl_3$)

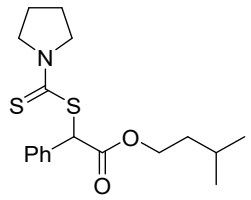


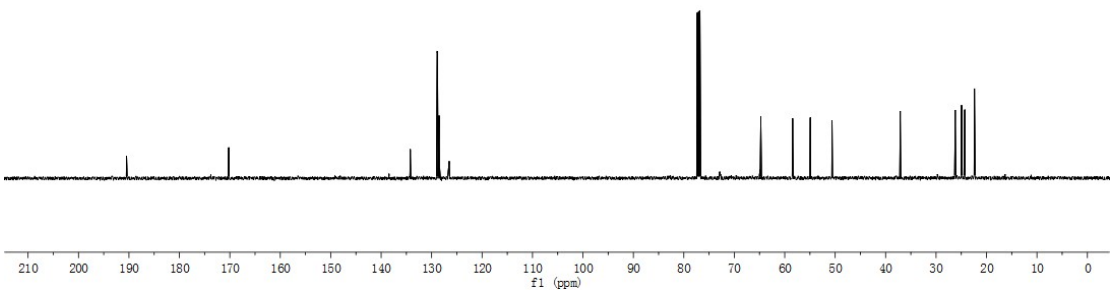


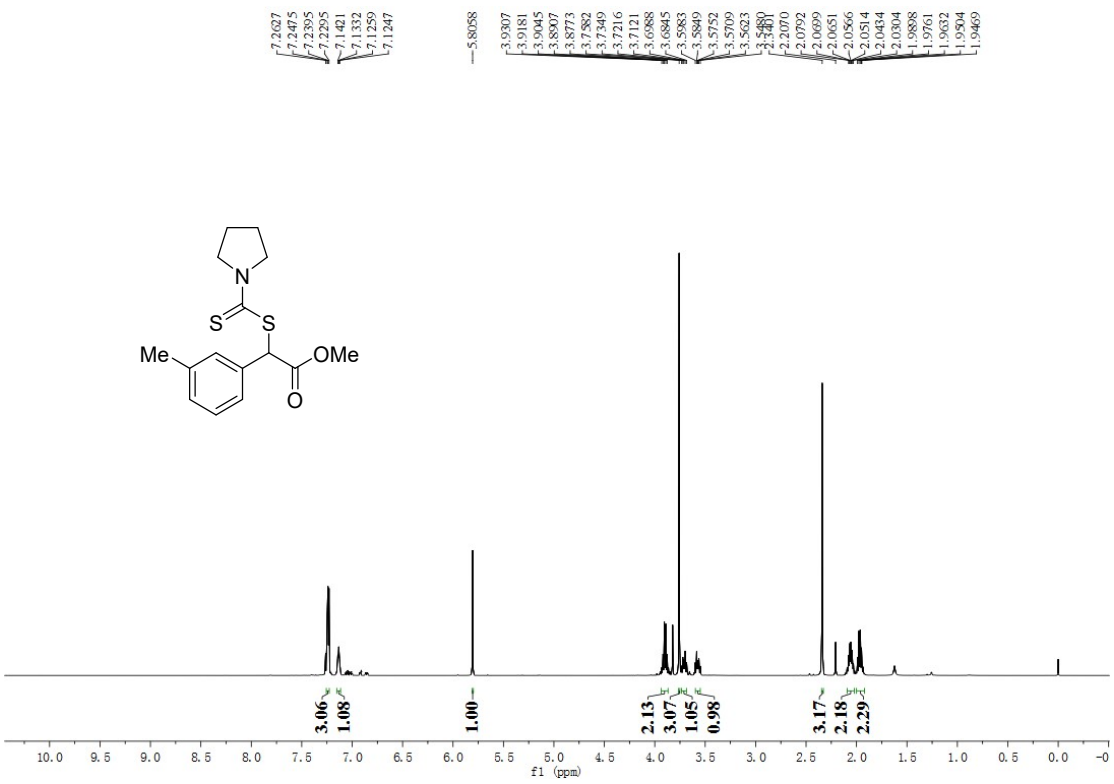




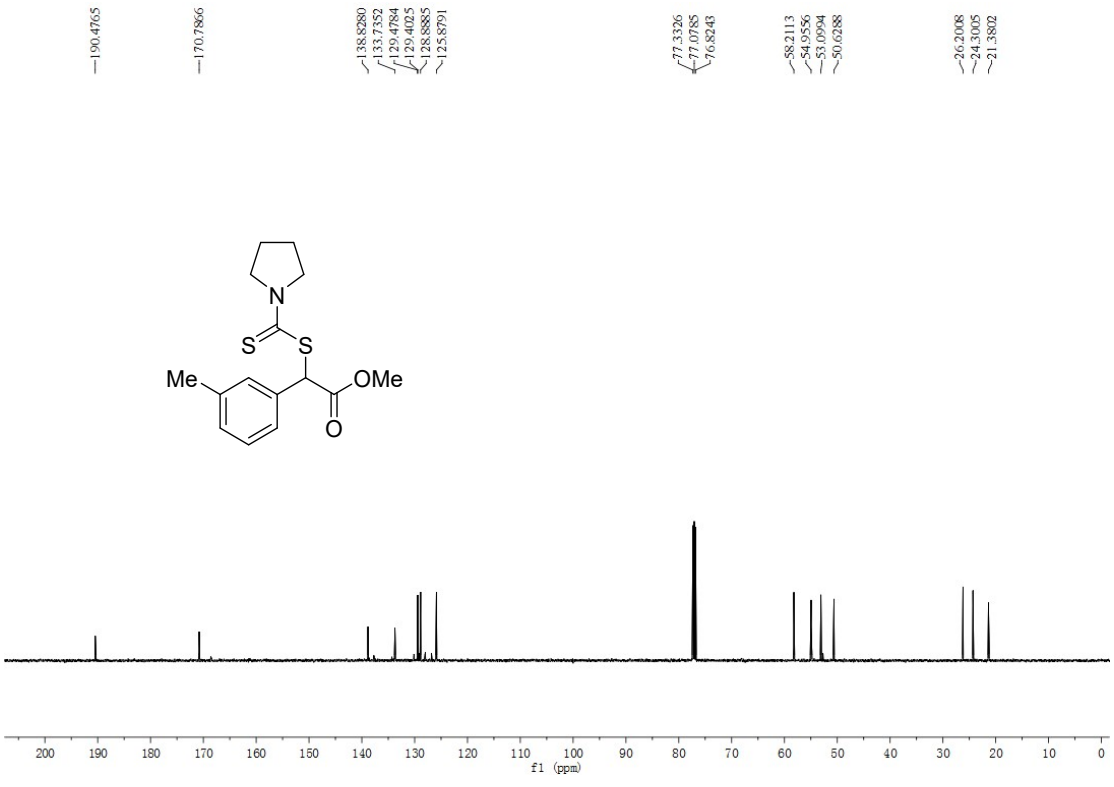
4g (500 MHz NMR, $CDCl_3$)

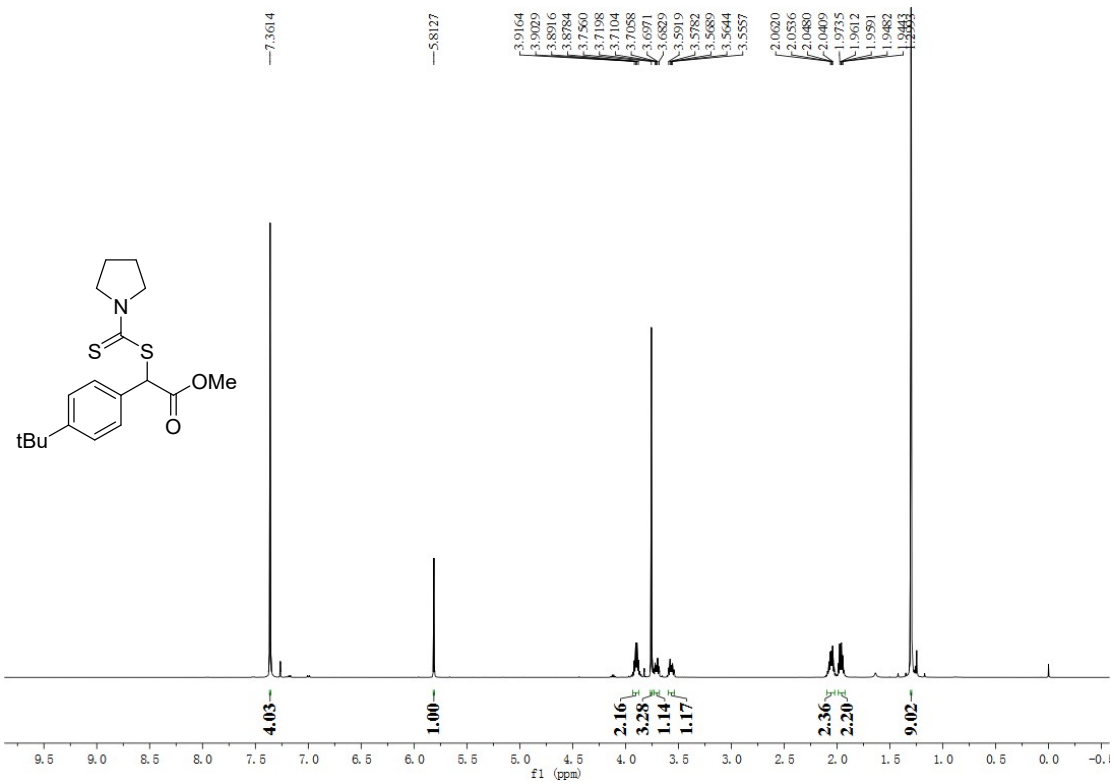




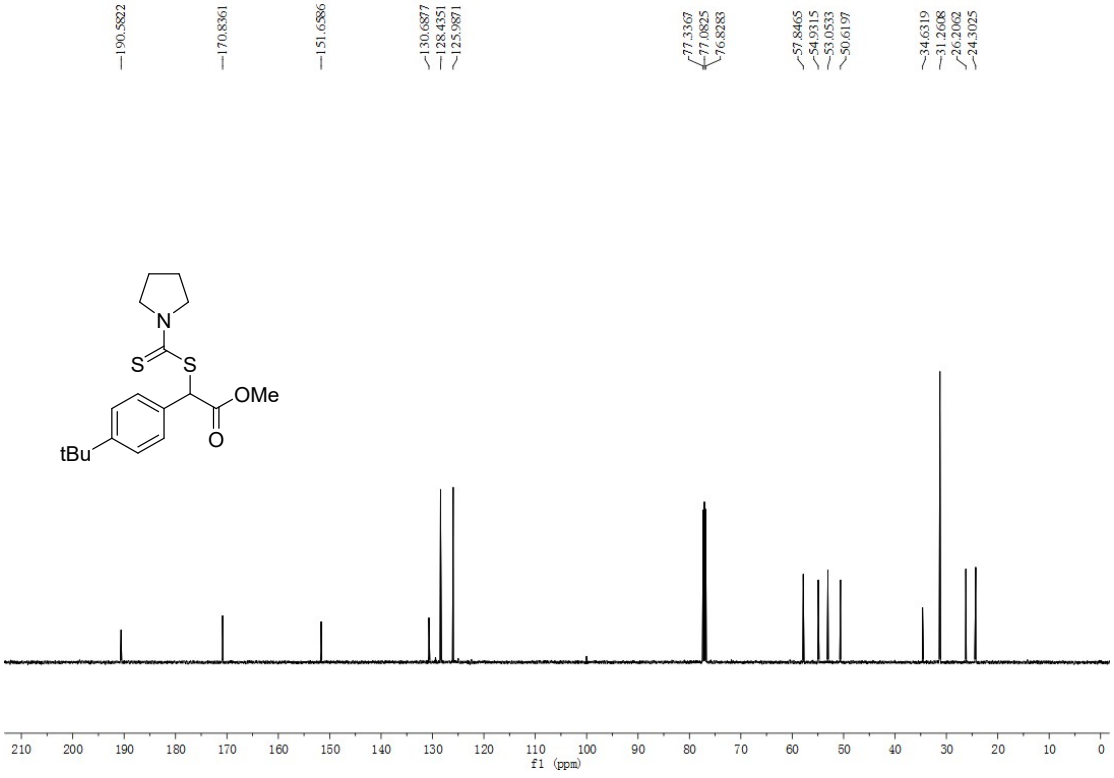


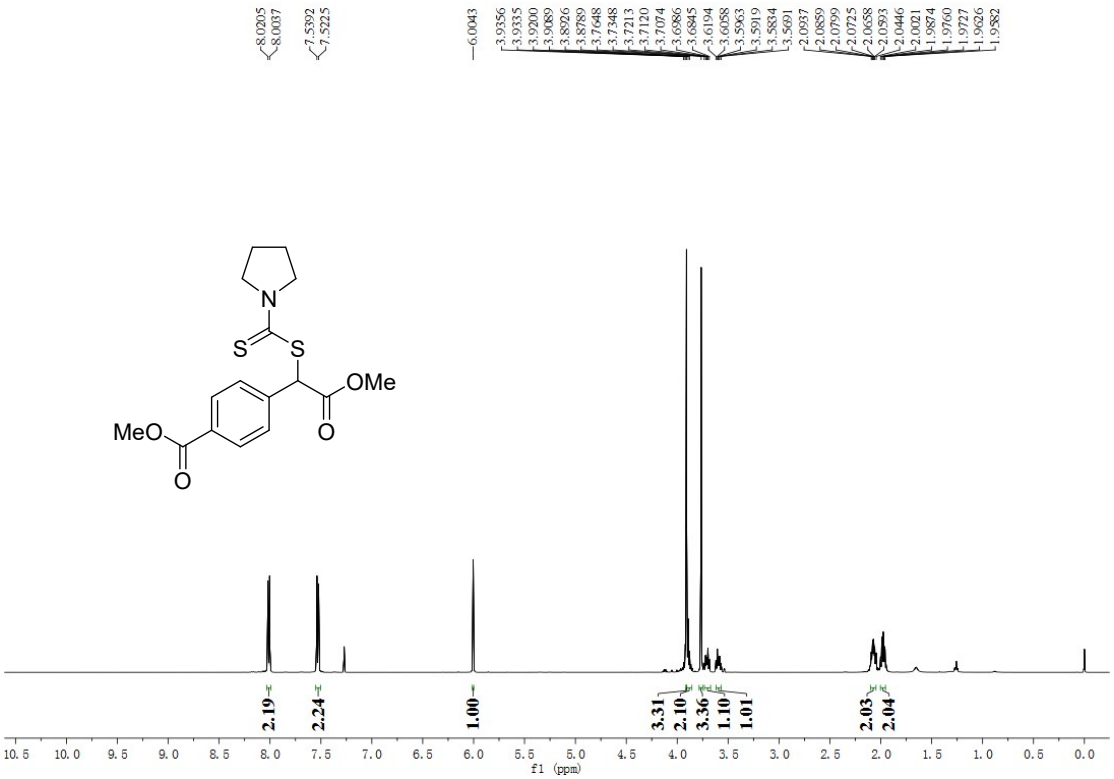
4h (500 MHz NMR, $CDCl_3$)



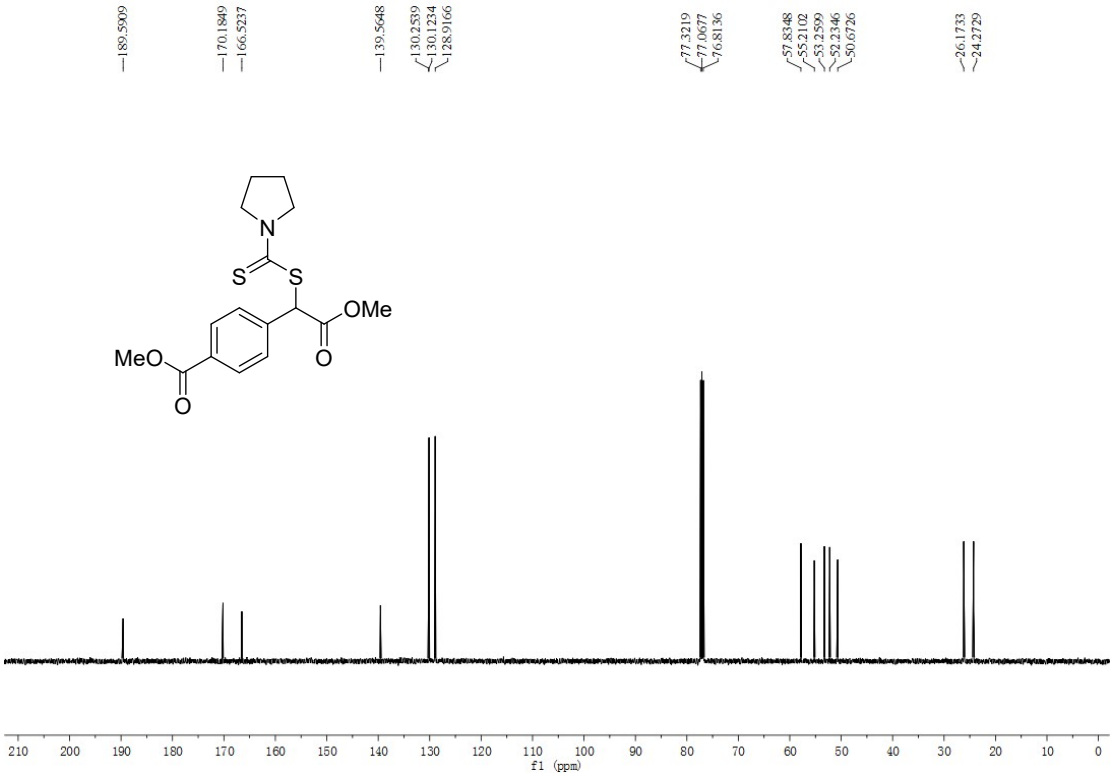


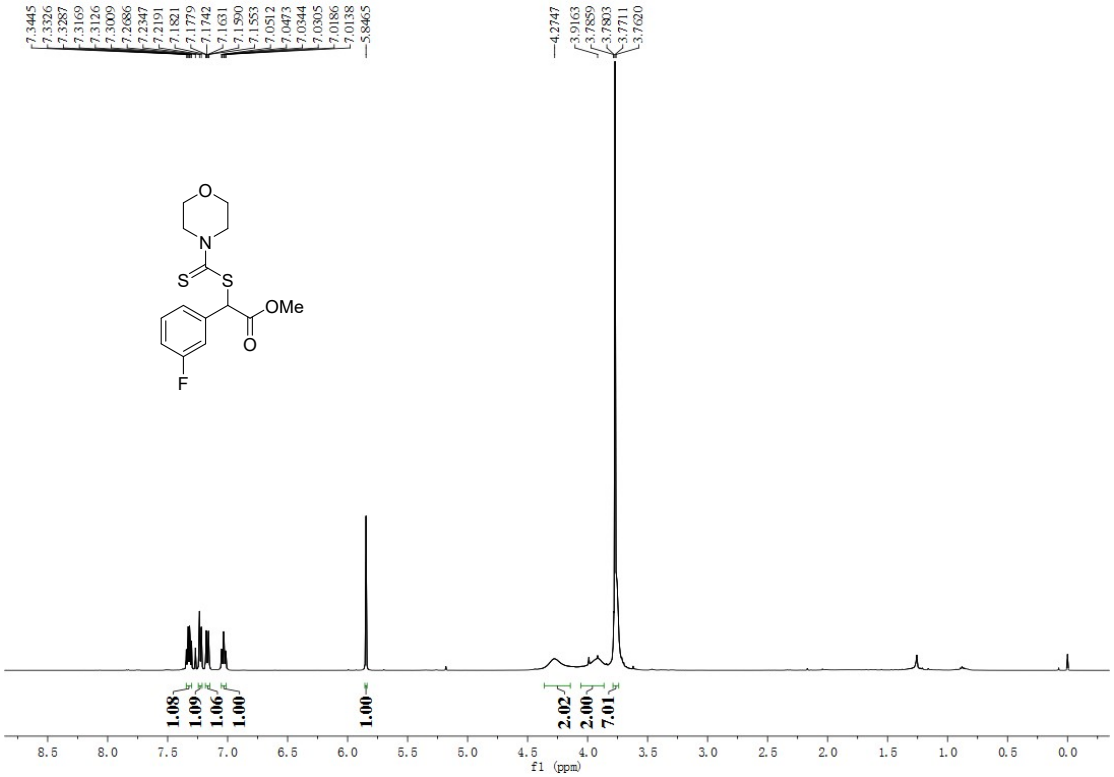
4i (500 MHz NMR, $CDCl_3$)



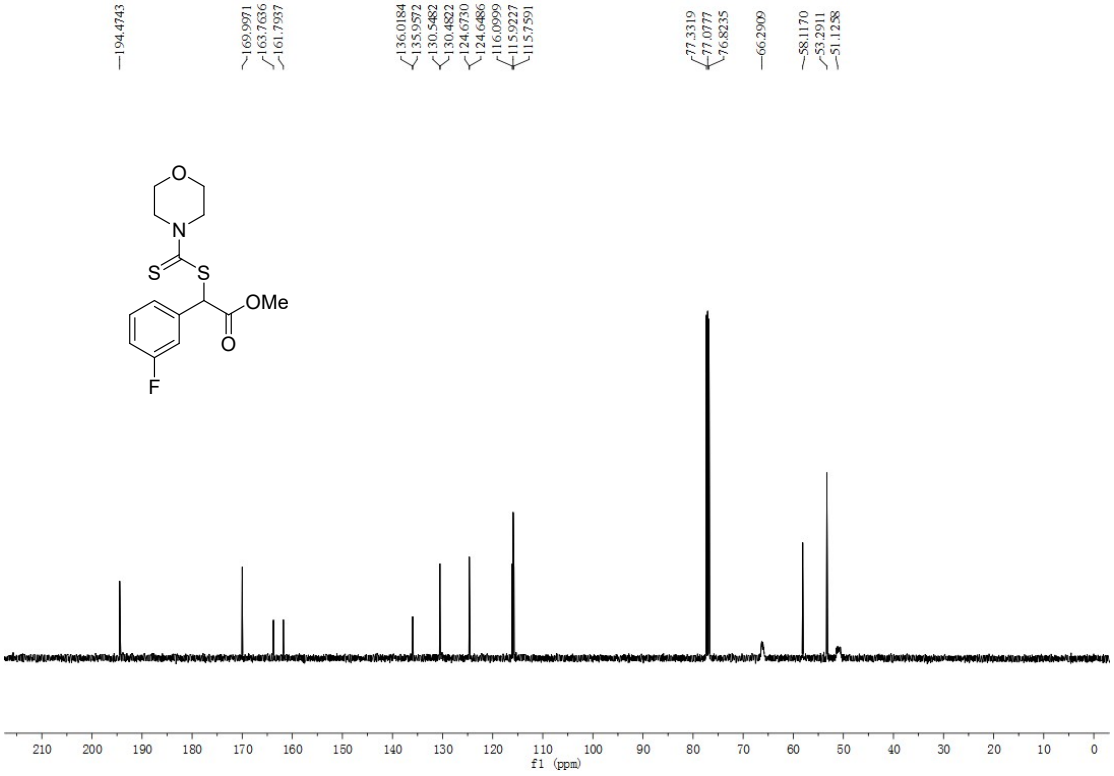


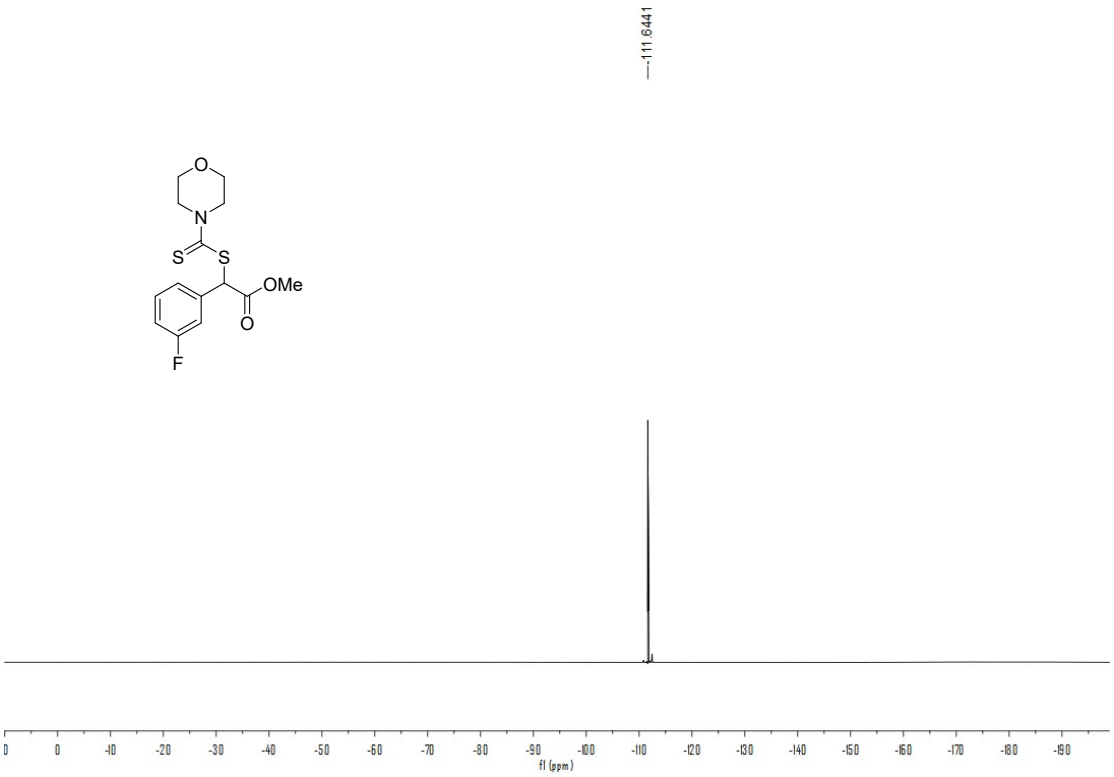
4j (500 MHz NMR, $CDCl_3$)



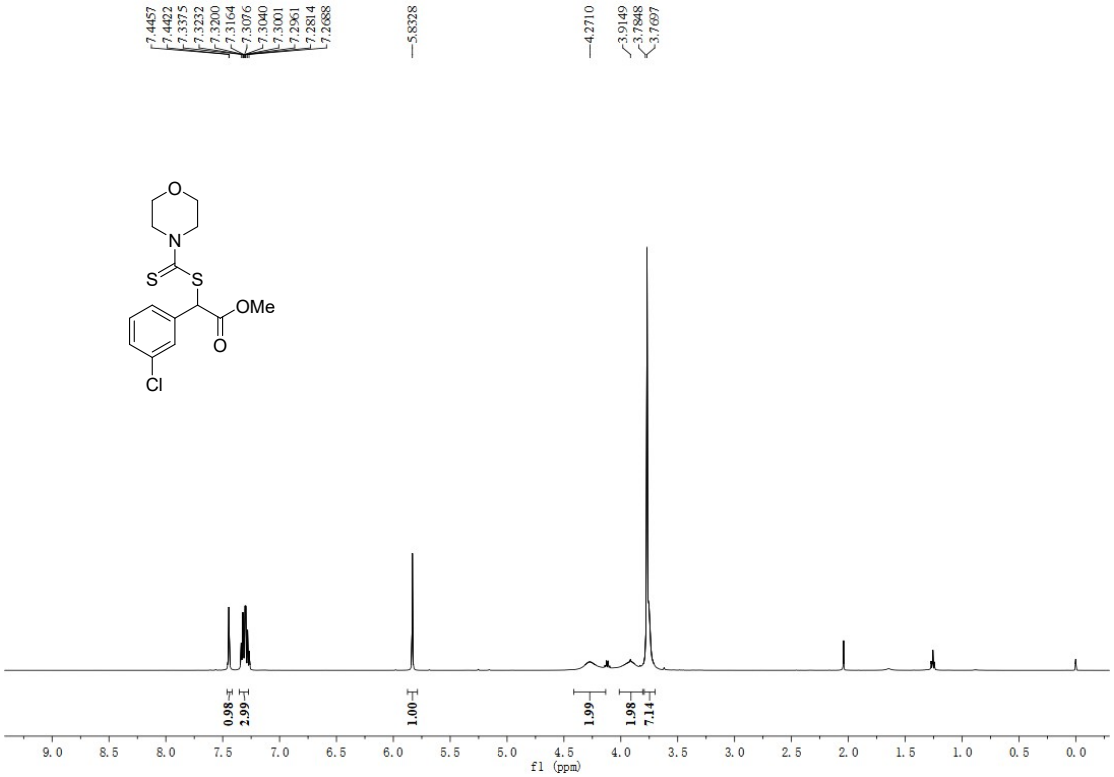


4k (500 MHz NMR, $CDCl_3$)

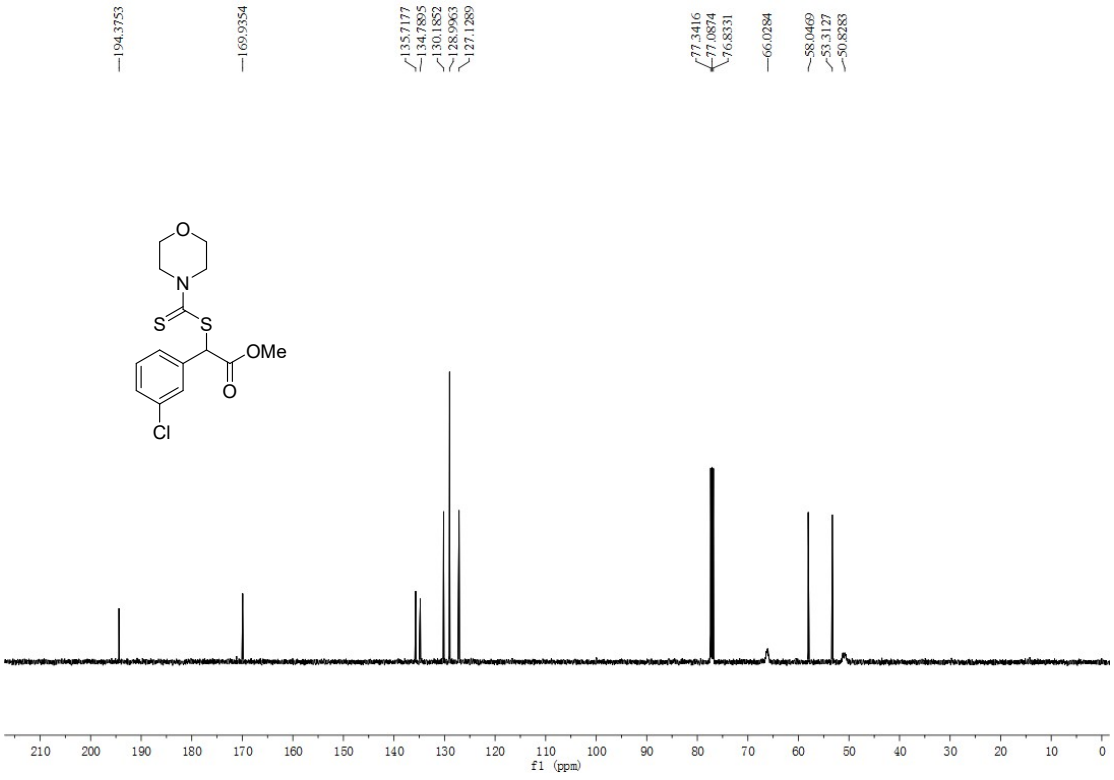


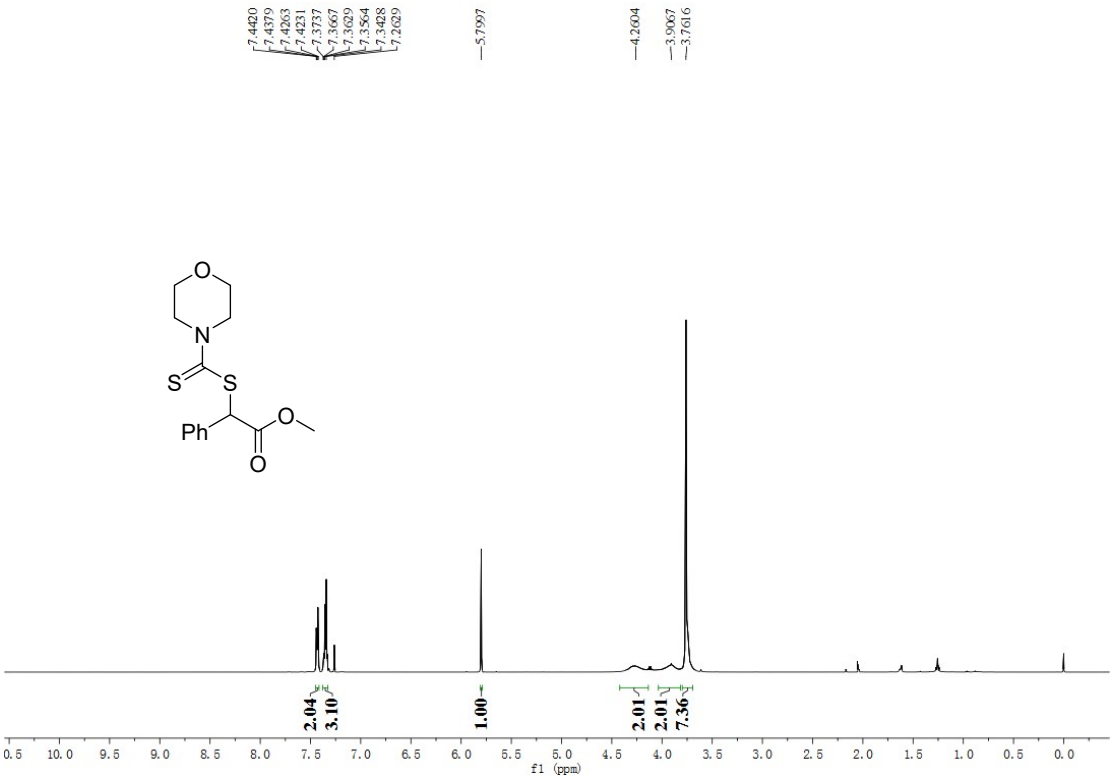


4k (500 MHz ^{19}FNMR, $CDCl_3$)

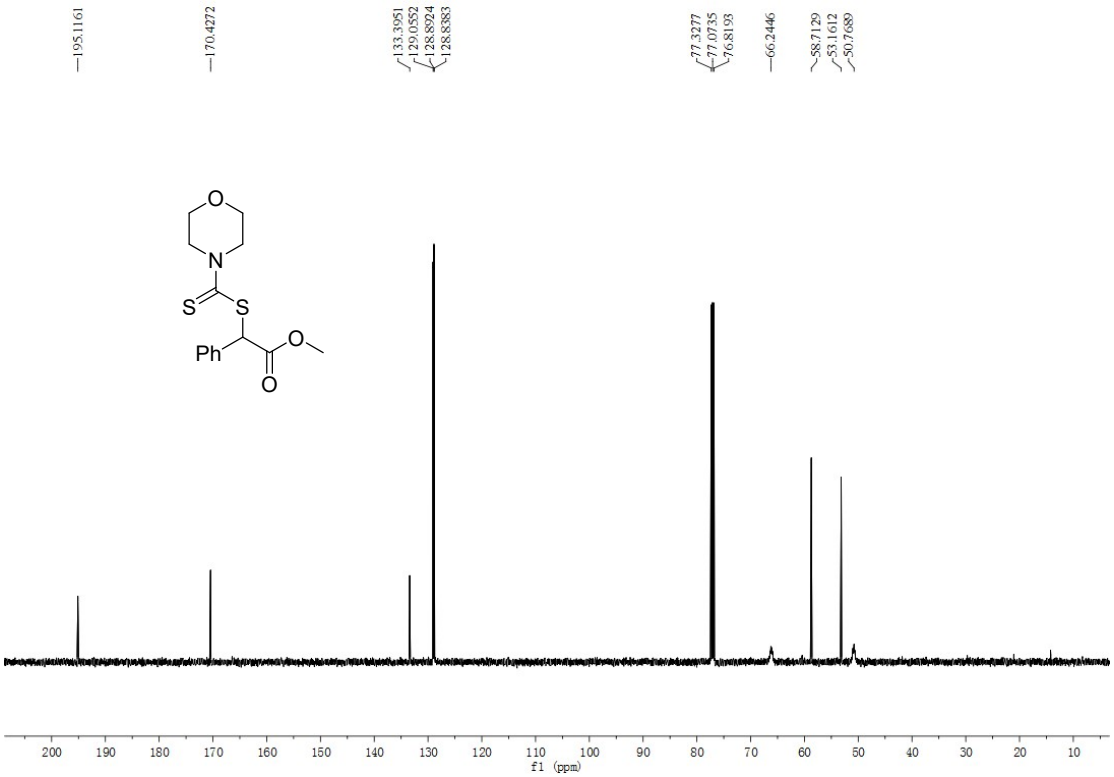


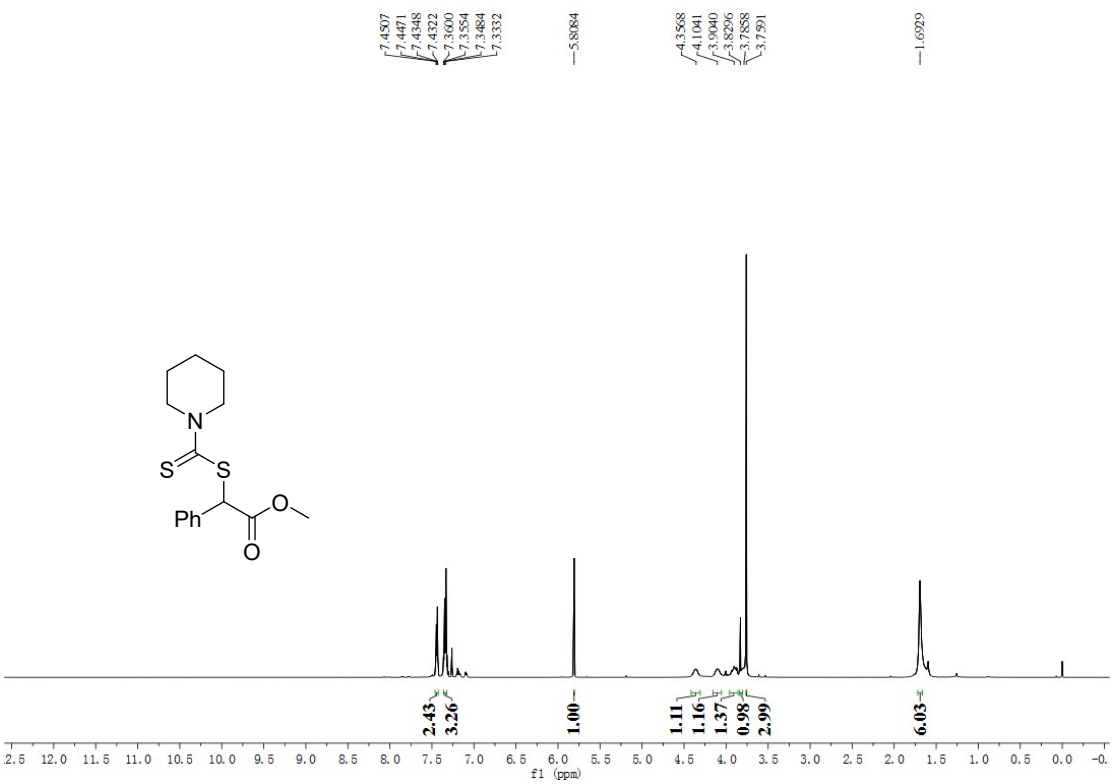
4l (500 MHz NMR, $CDCl_3$)



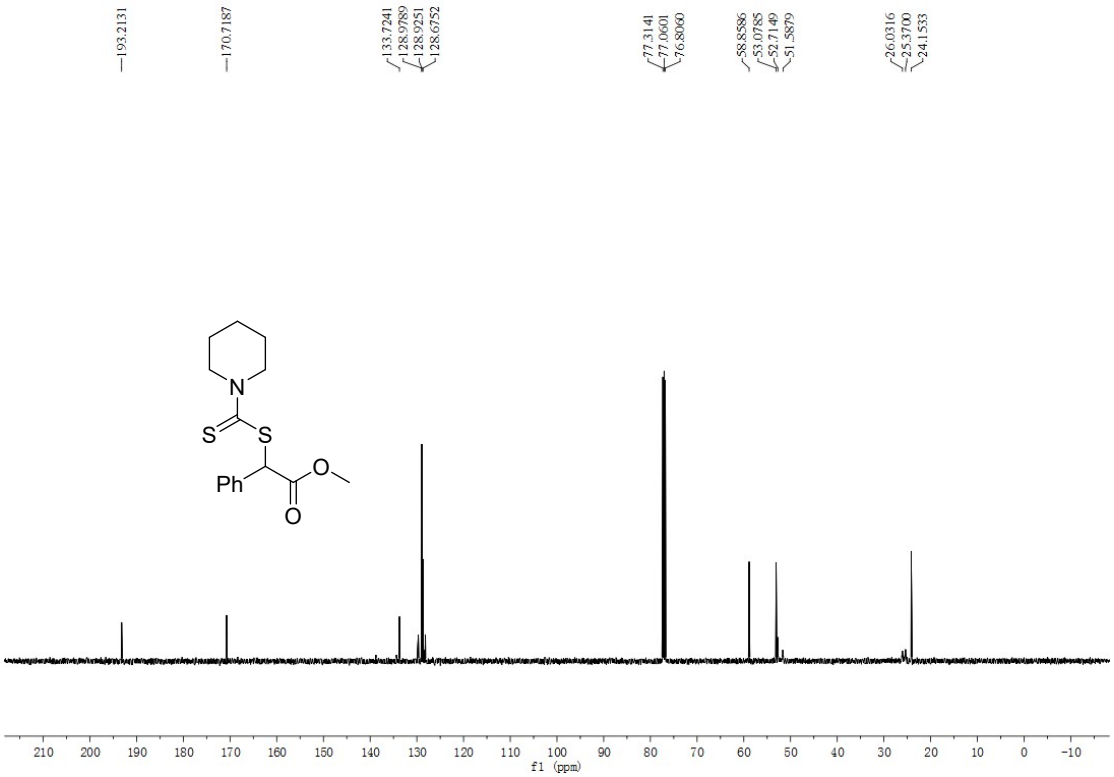


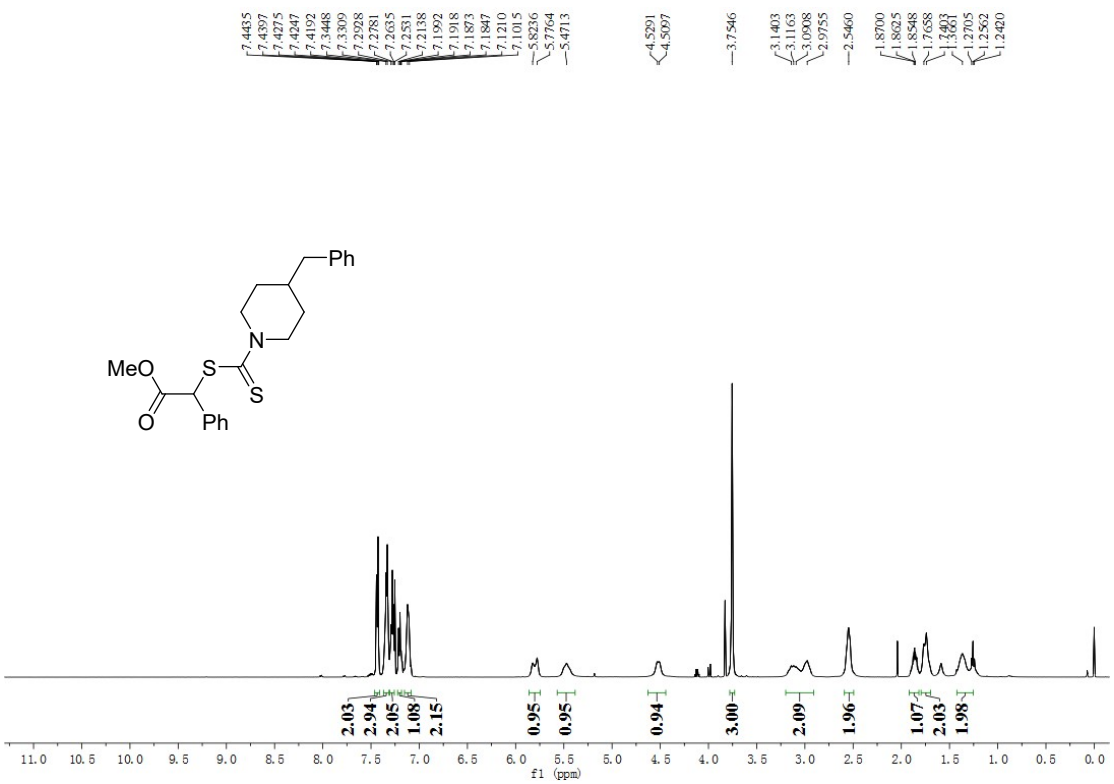
4m(500 MHz NMR, $CDCl_3$)



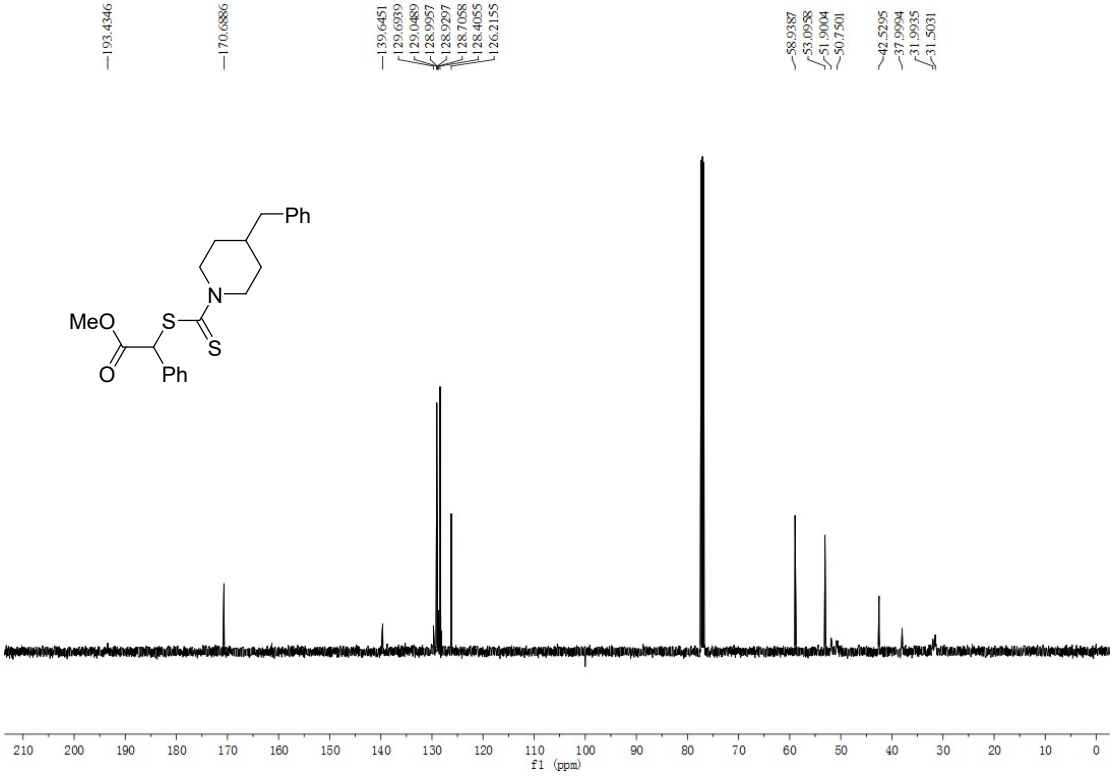


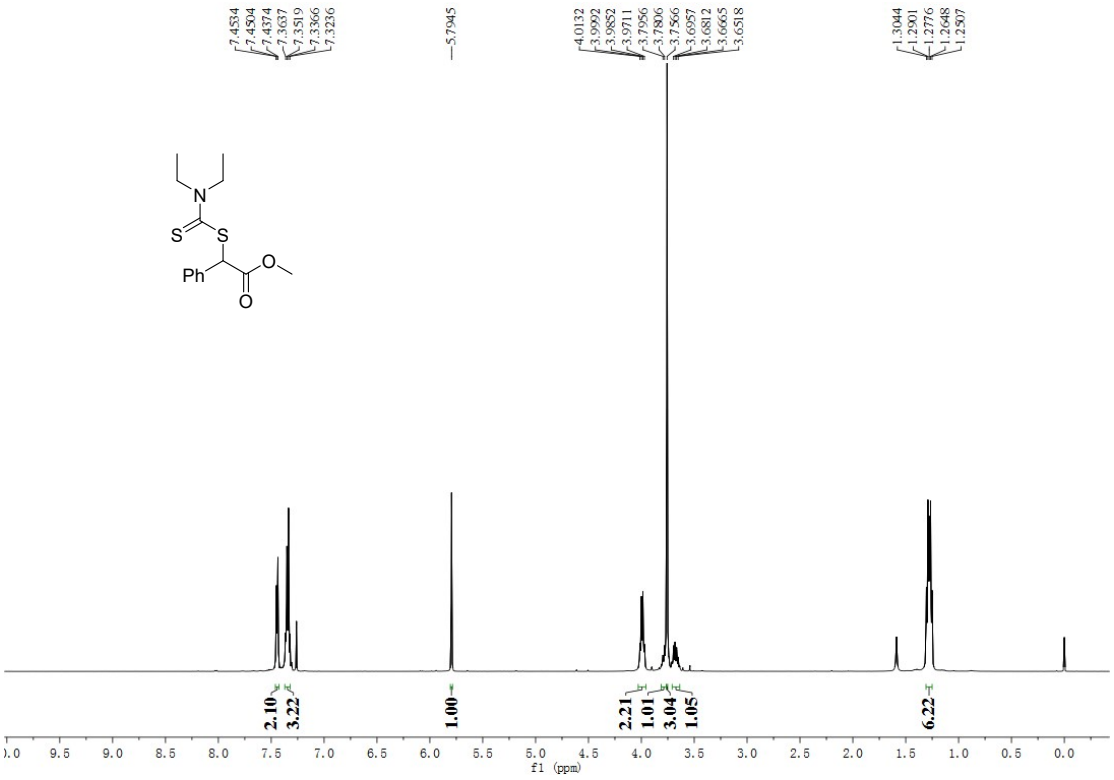
4n (500 MHz NMR, $CDCl_3$)



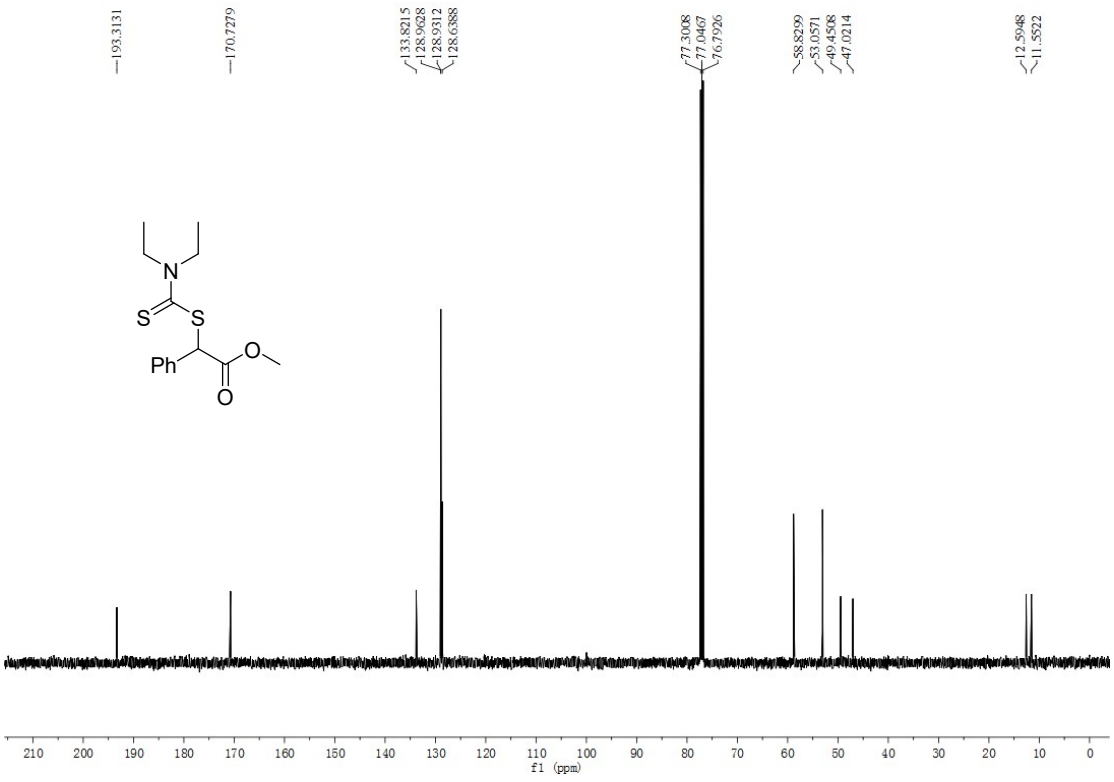


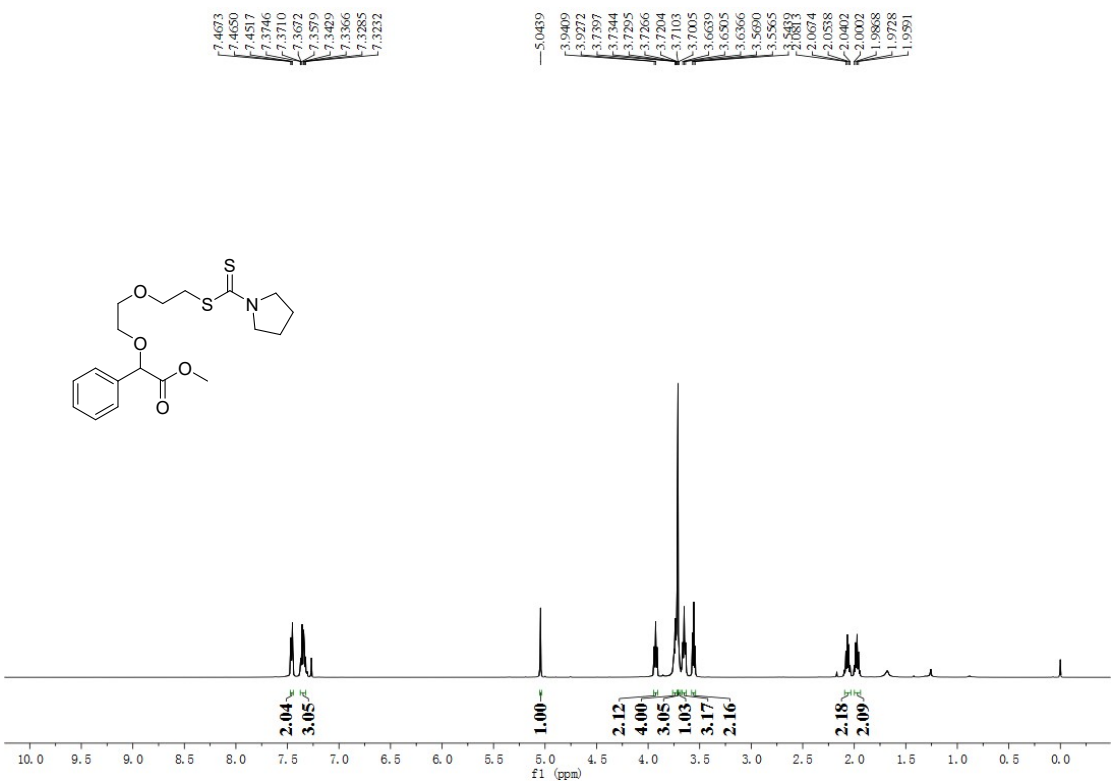
4o (500 MHz NMR, $CDCl_3$)



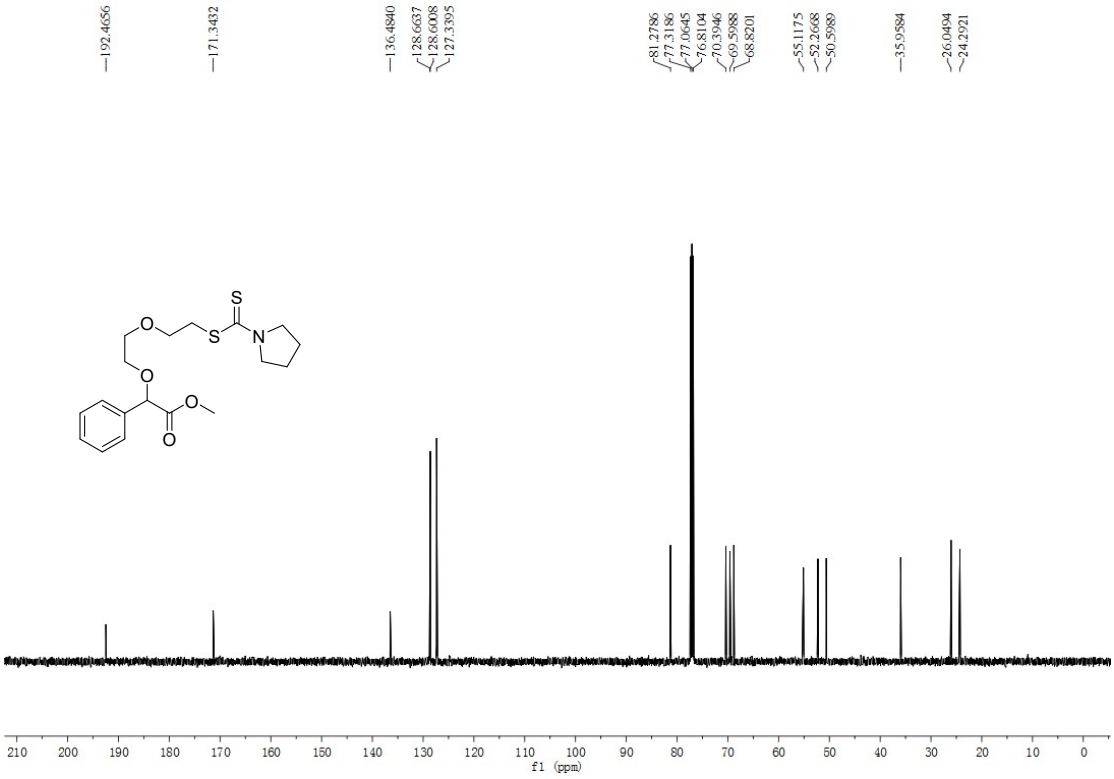


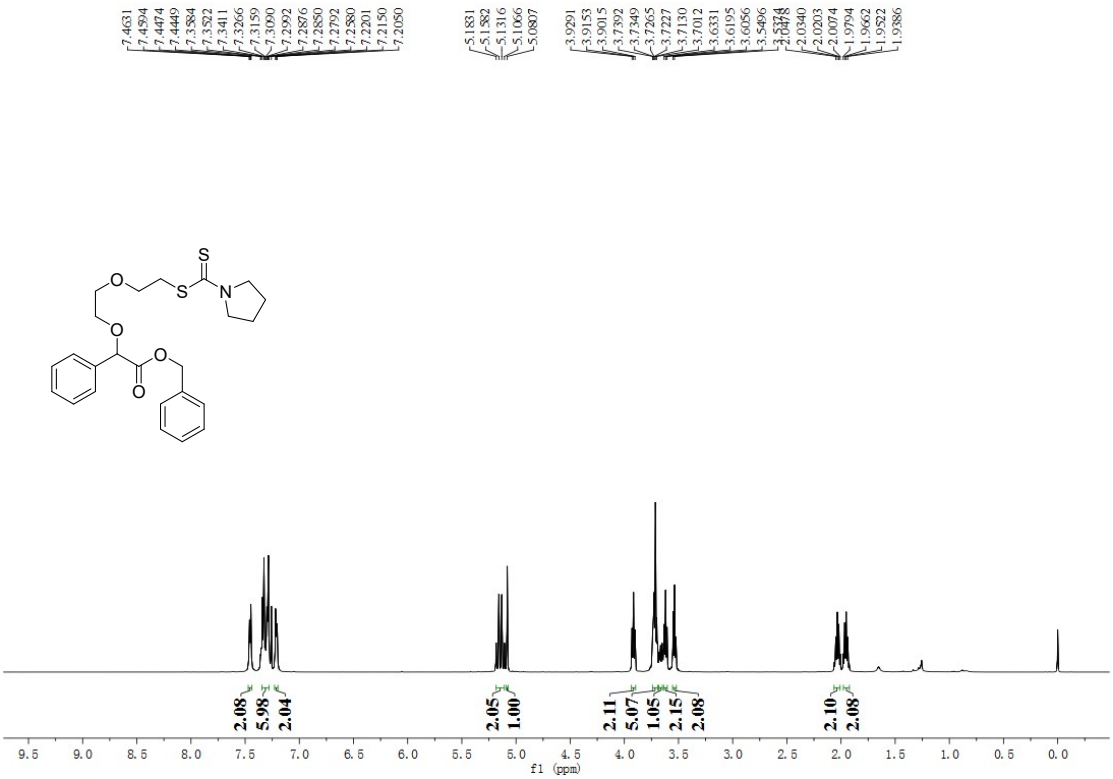
4p (500 MHz NMR, $CDCl_3$)



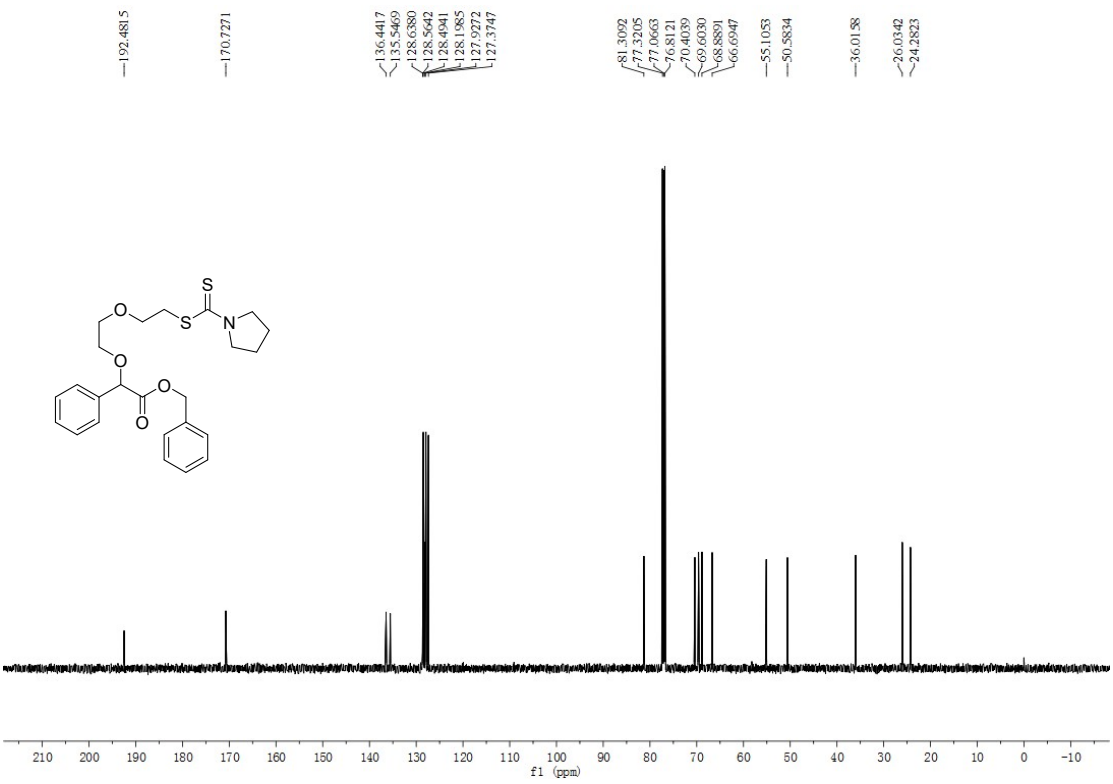


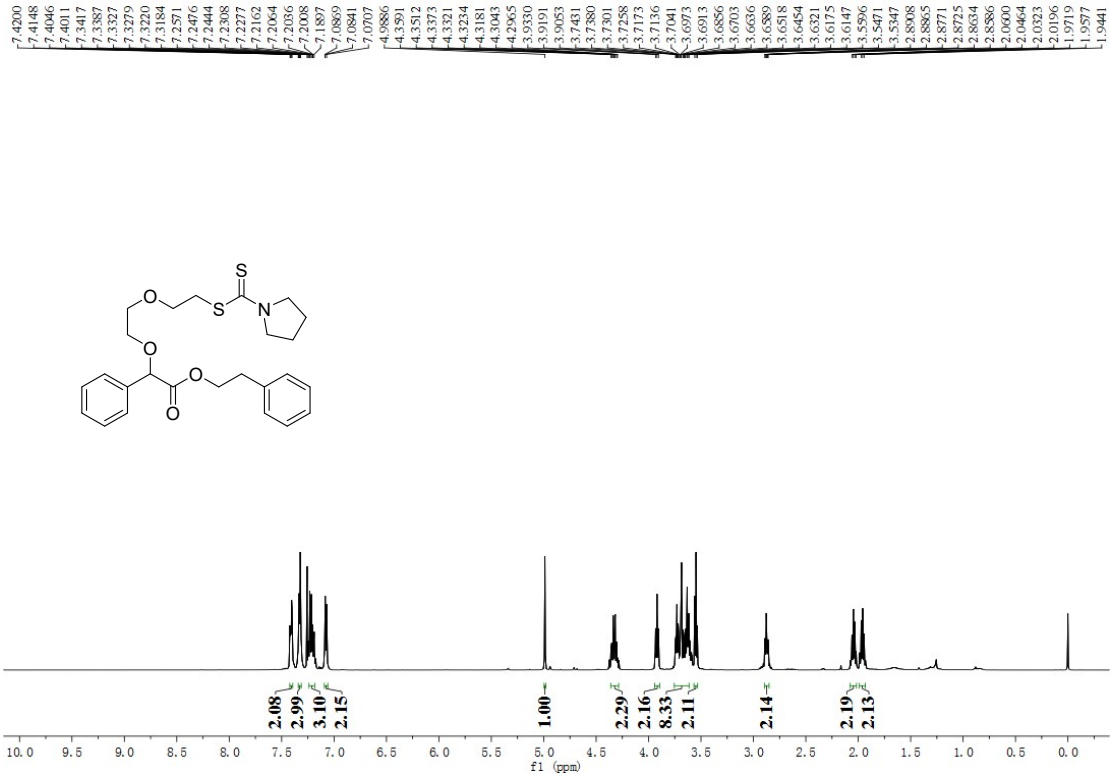
5a' (500 MHz NMR, $CDCl_3$)



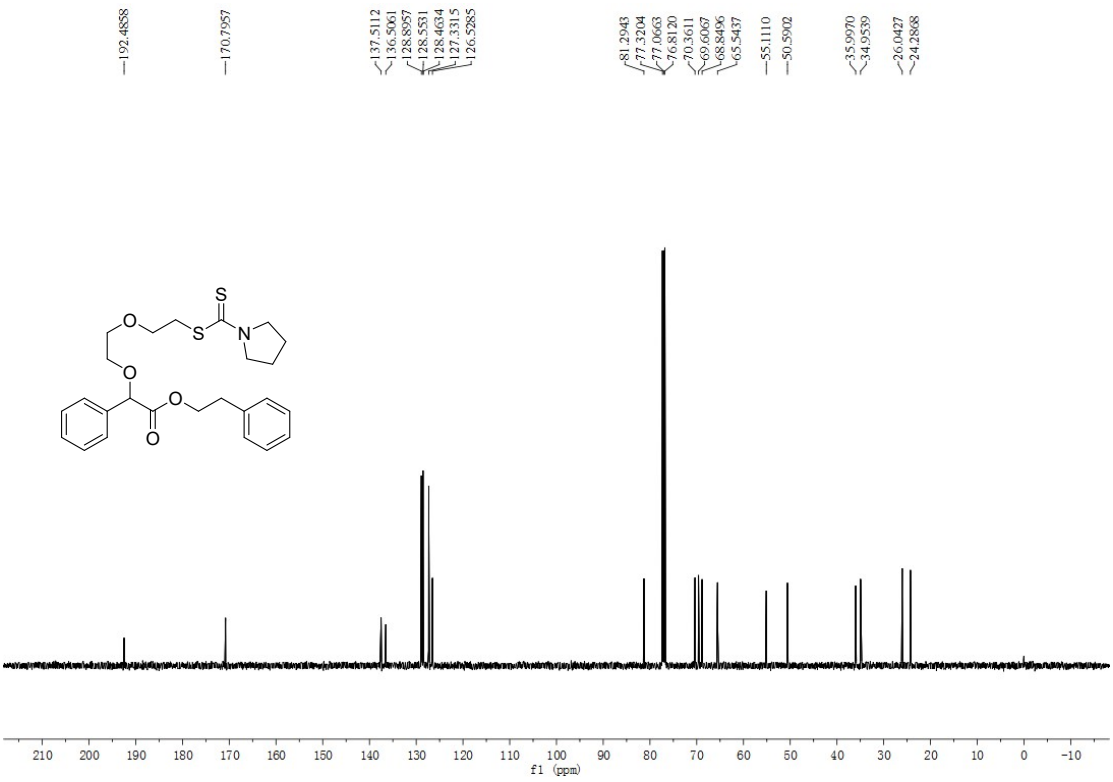


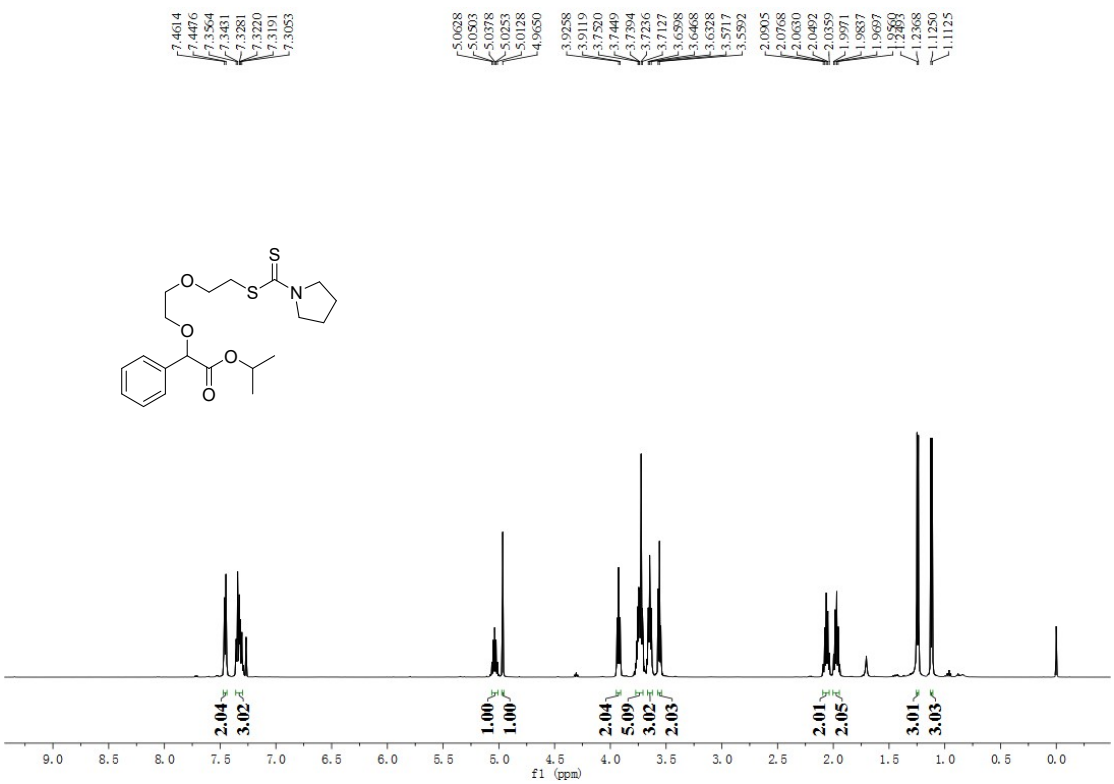
5b' (500 MHz NMR, $CDCl_3$)



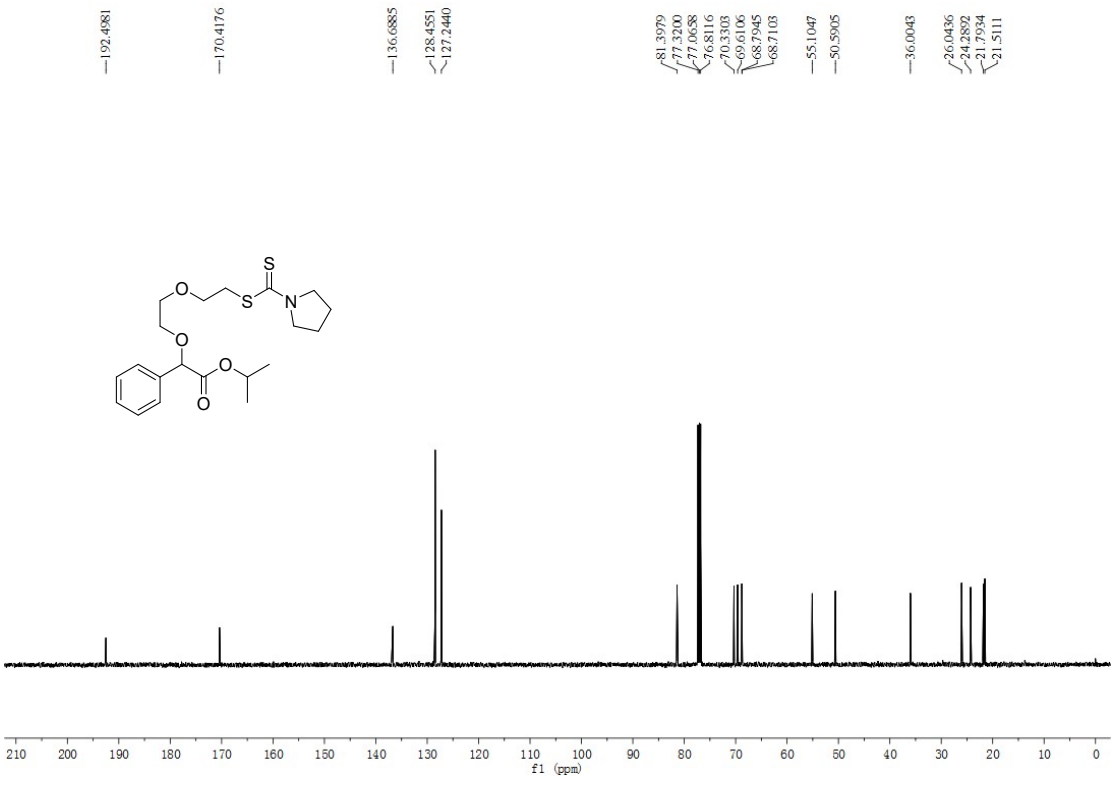


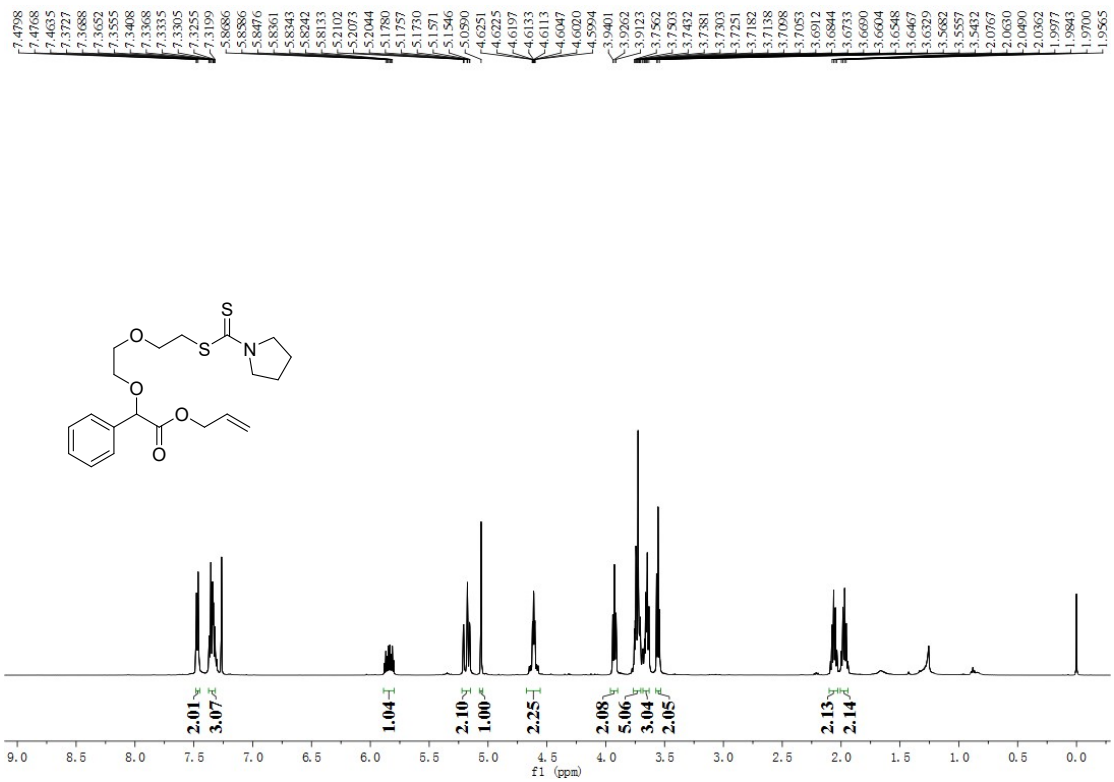
5c' (500 MHz NMR, $CDCl_3$)



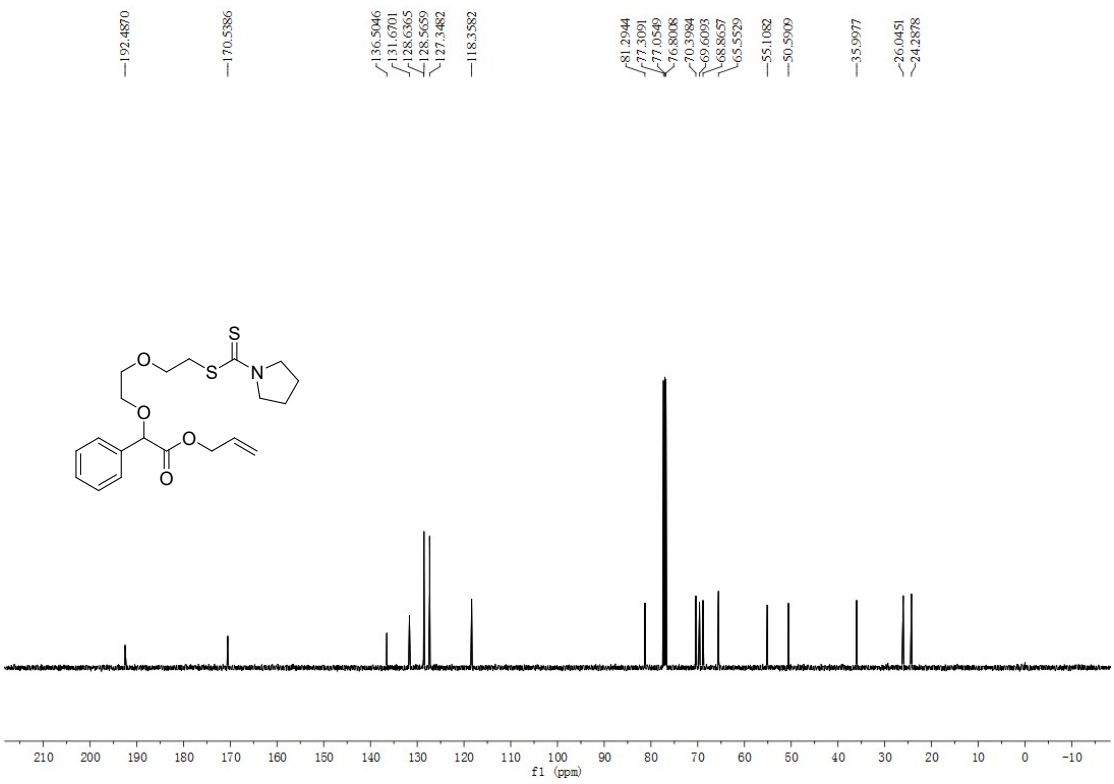


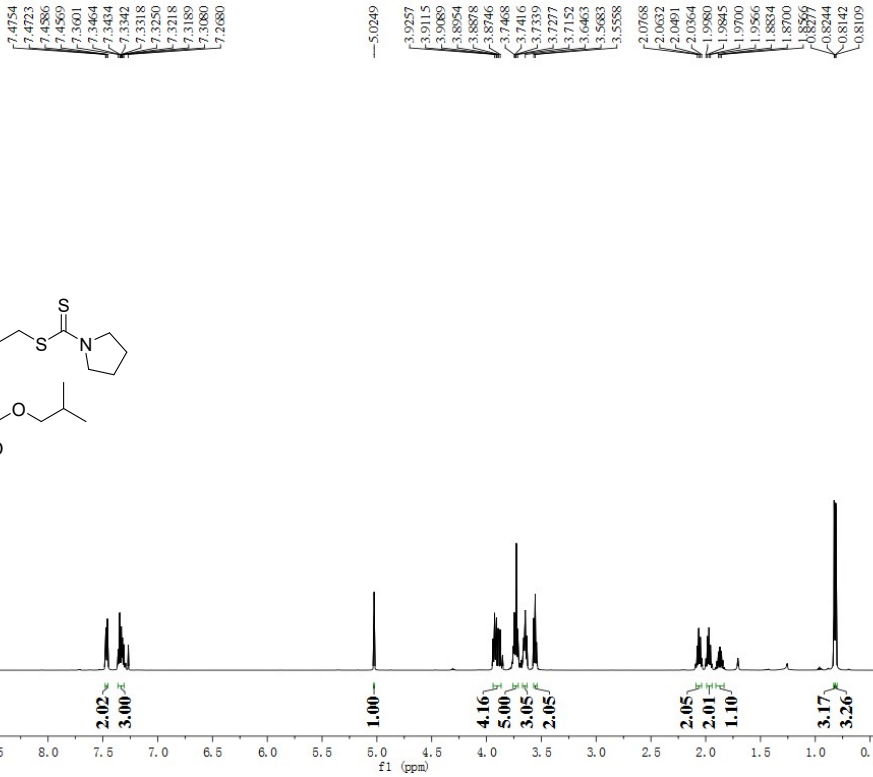
5d' (500 MHz NMR, $CDCl_3$)



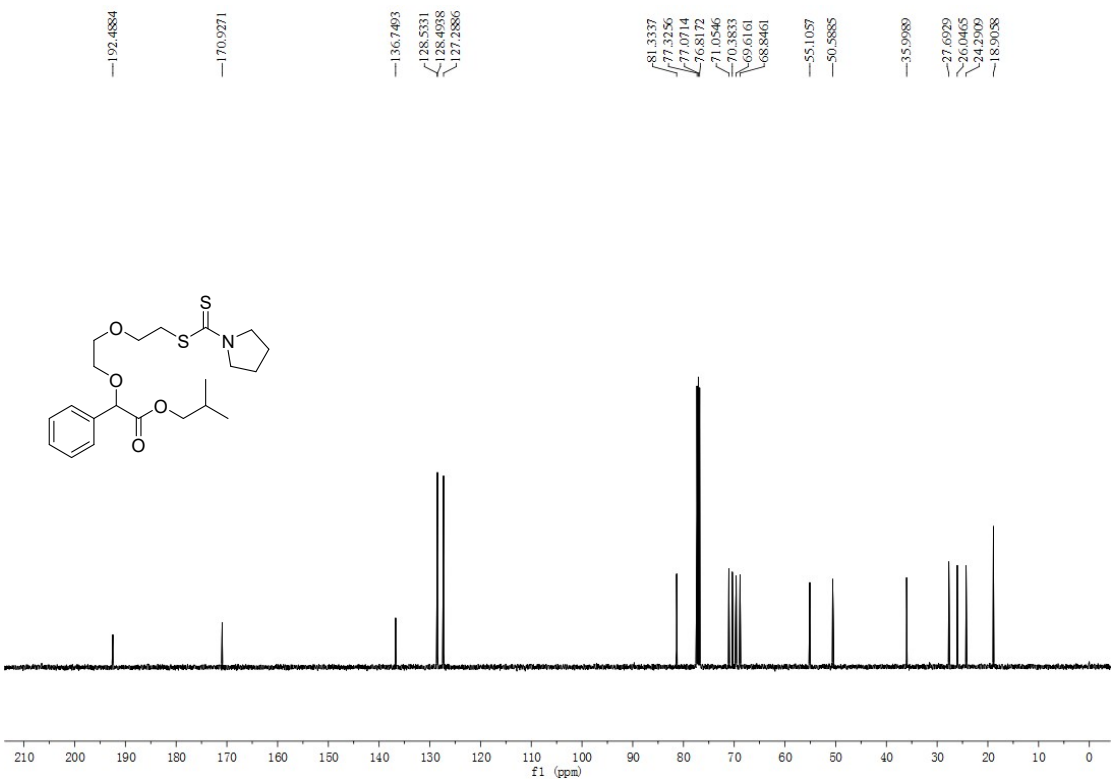


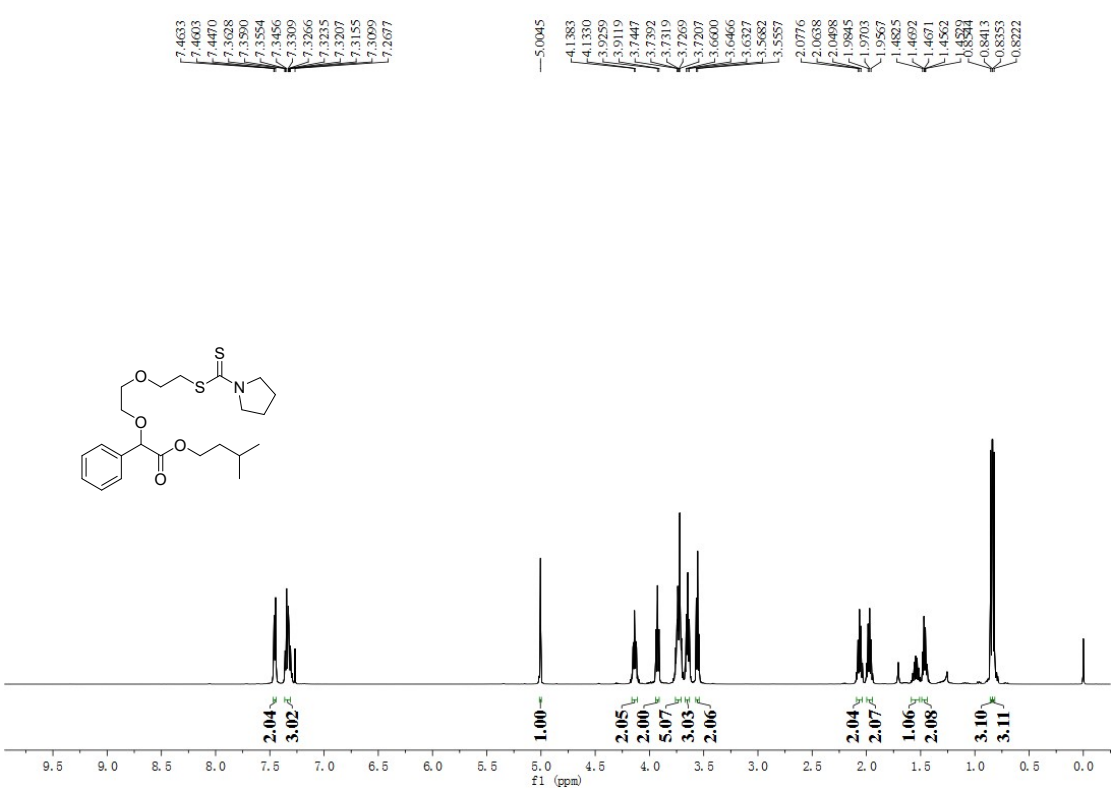
5e' (500 MHz NMR, $CDCl_3$)



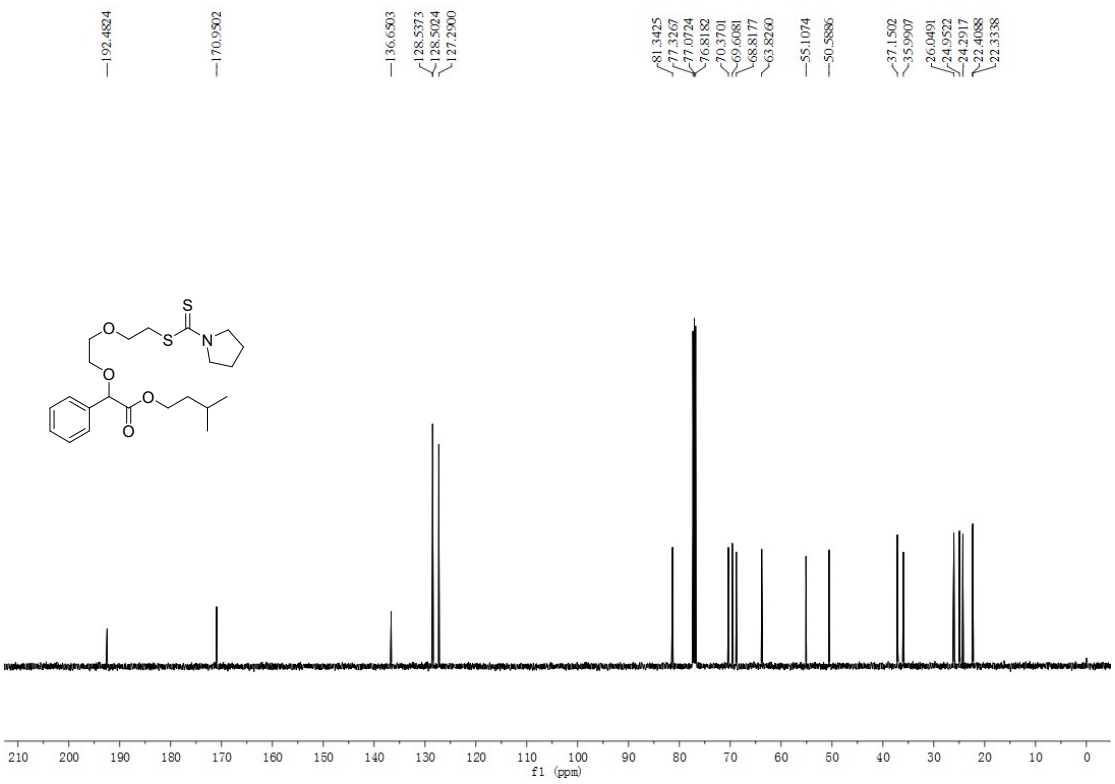


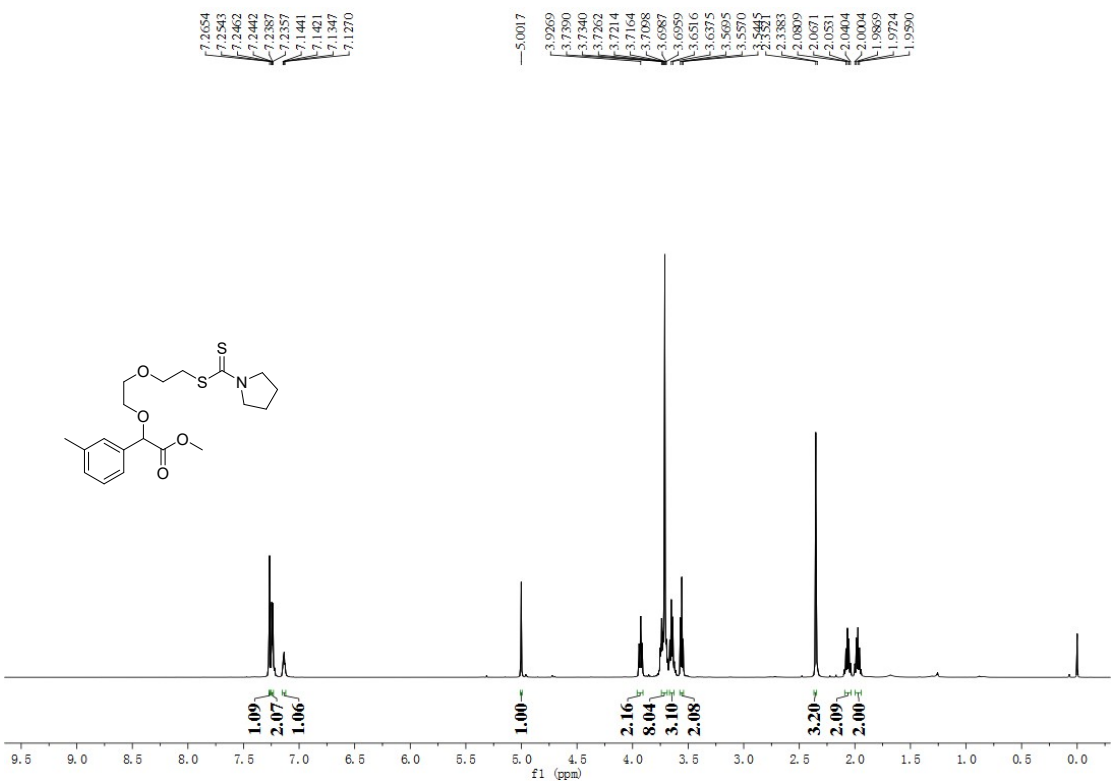
5f' (500 MHz NMR, $CDCl_3$)



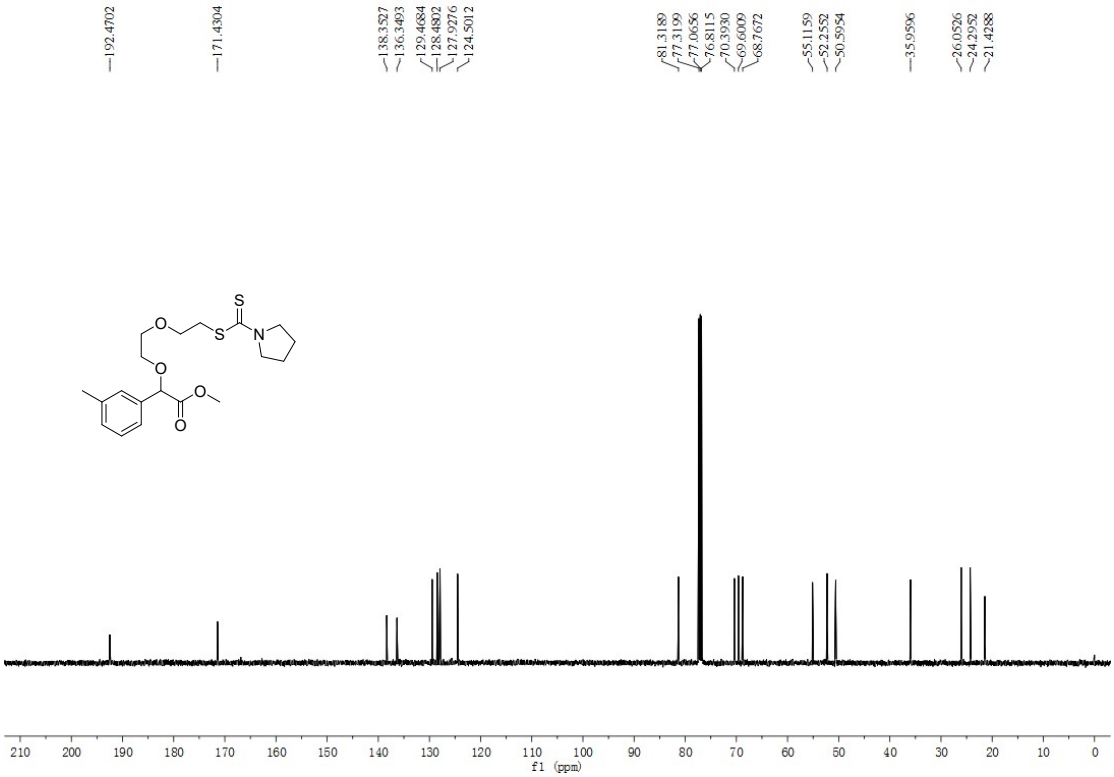


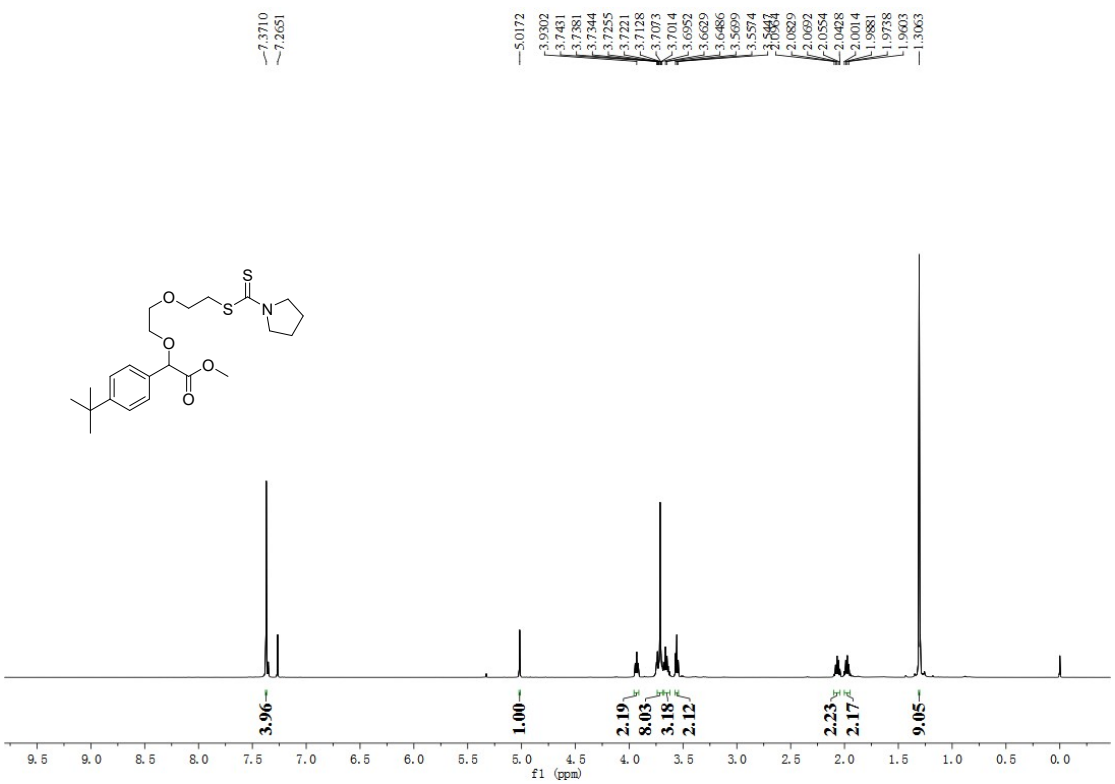
5g' (500 MHz NMR, $CDCl_3$)



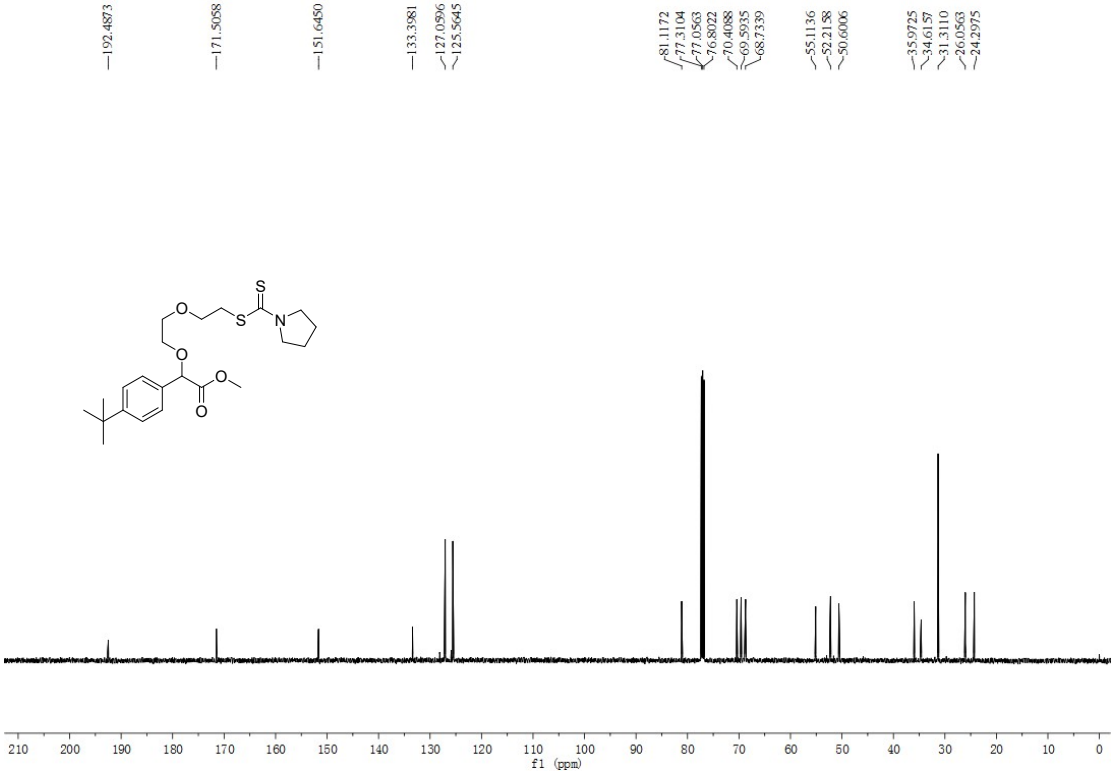


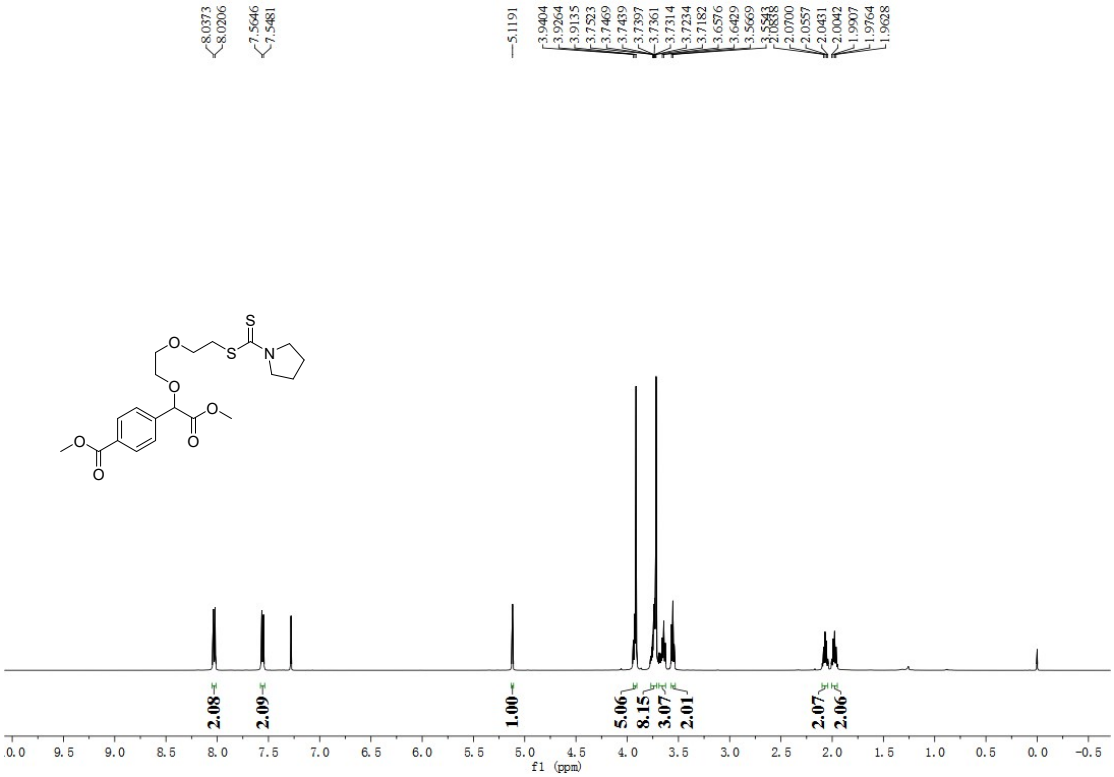
5h' (500 MHz NMR, $CDCl_3$)



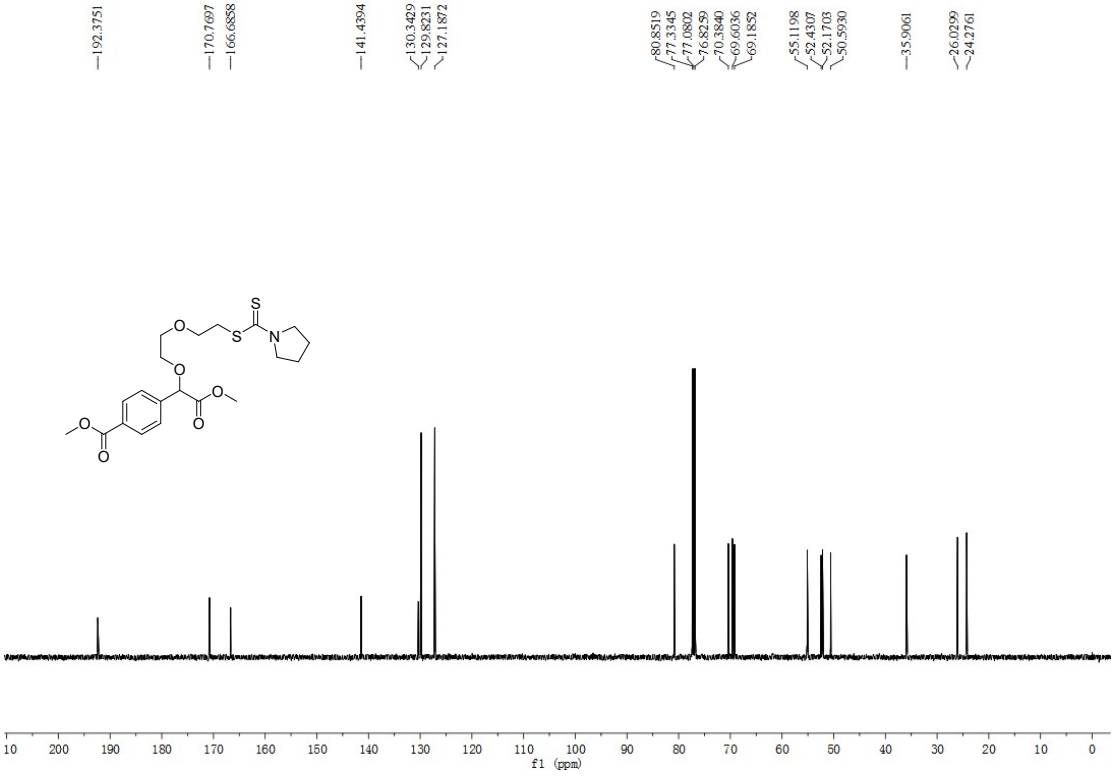


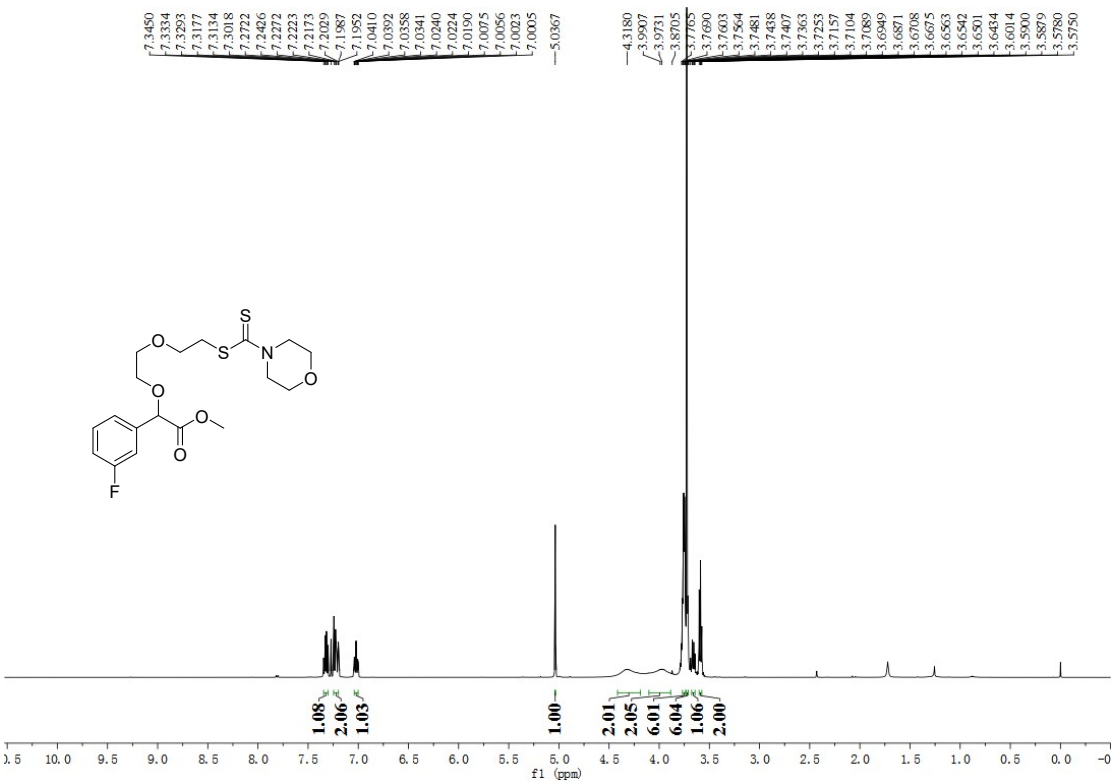
5i' (500 MHz NMR, $CDCl_3$)



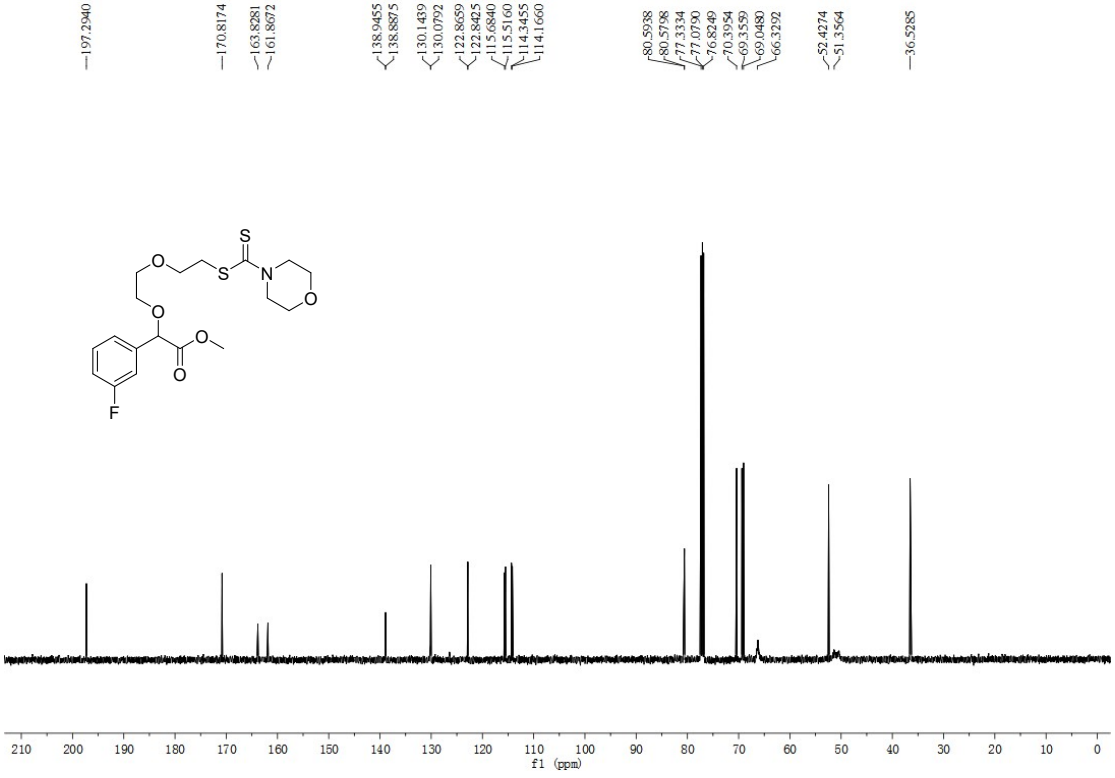


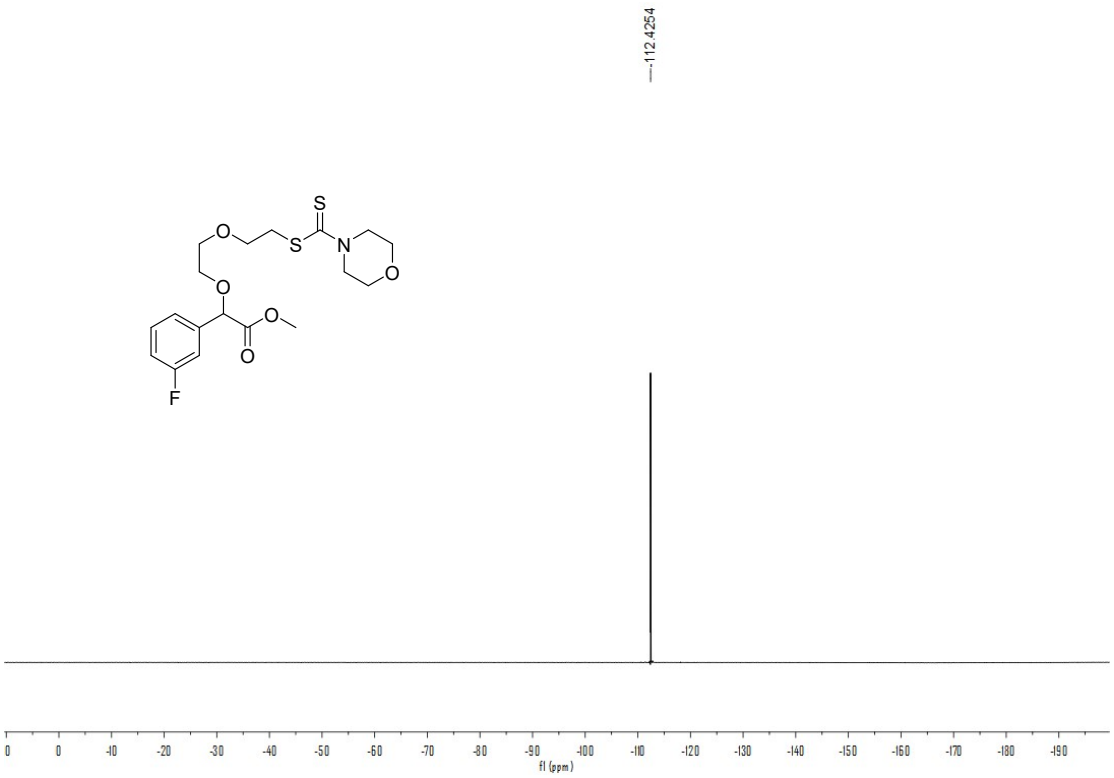
5j' (500 MHz NMR, $CDCl_3$)



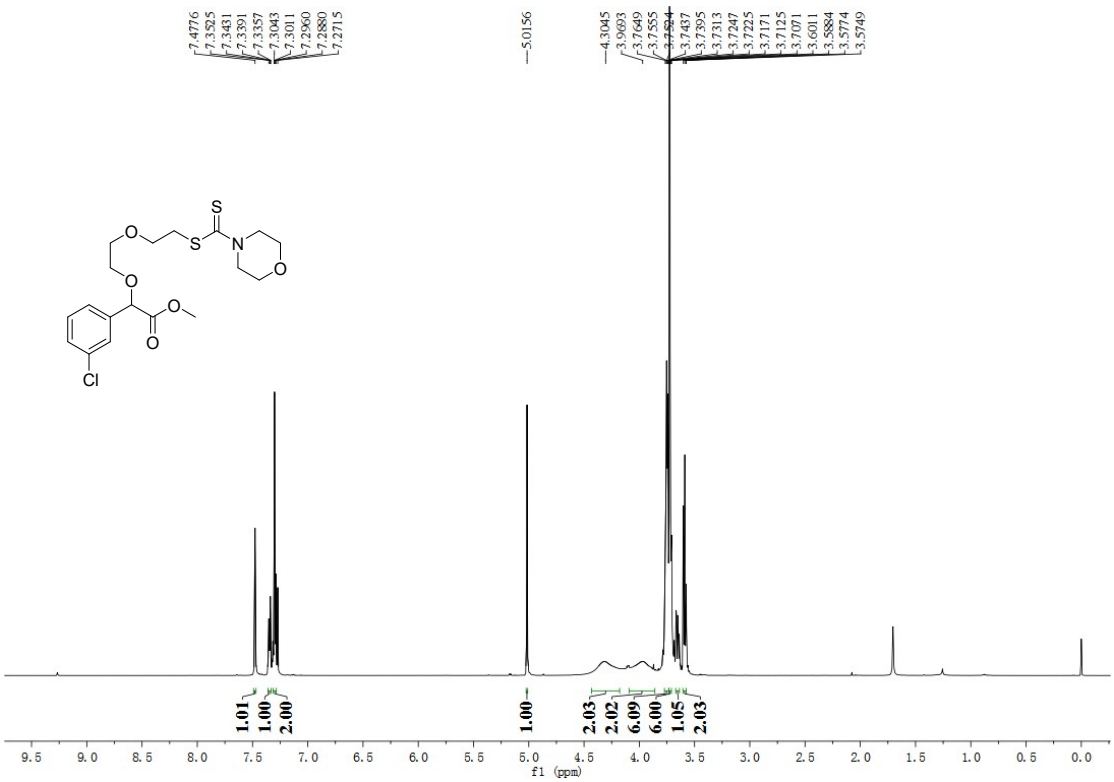


5k' (500 MHz NMR, $CDCl_3$)

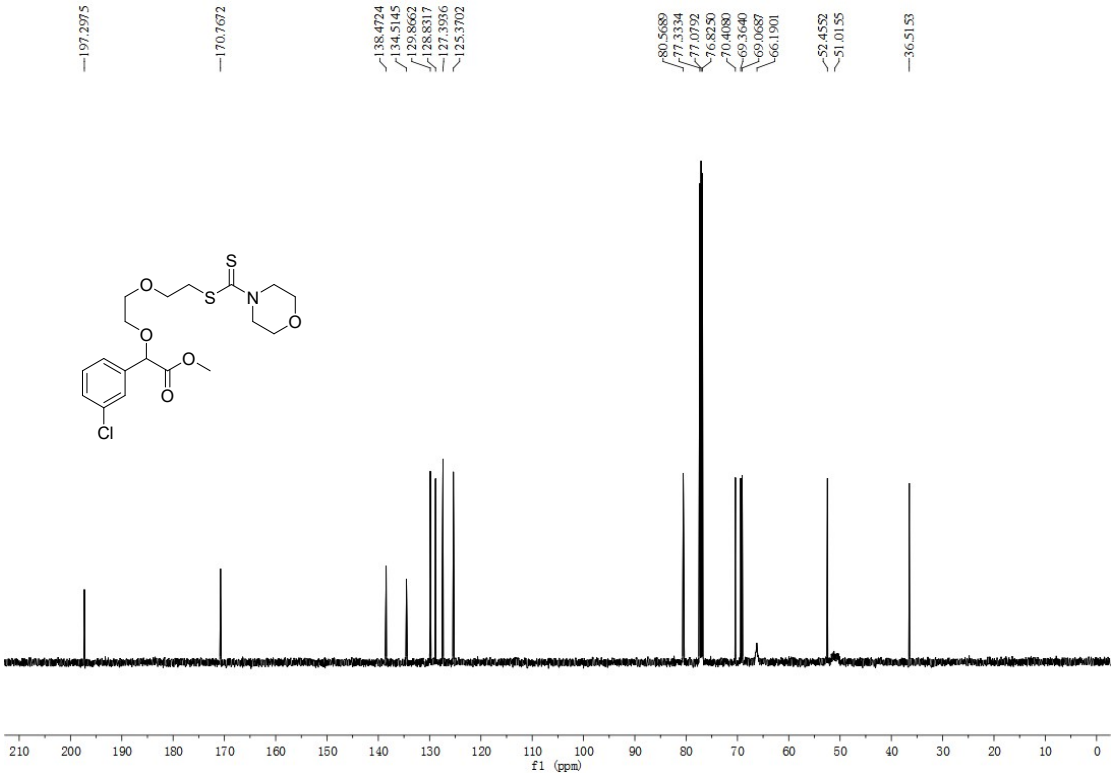


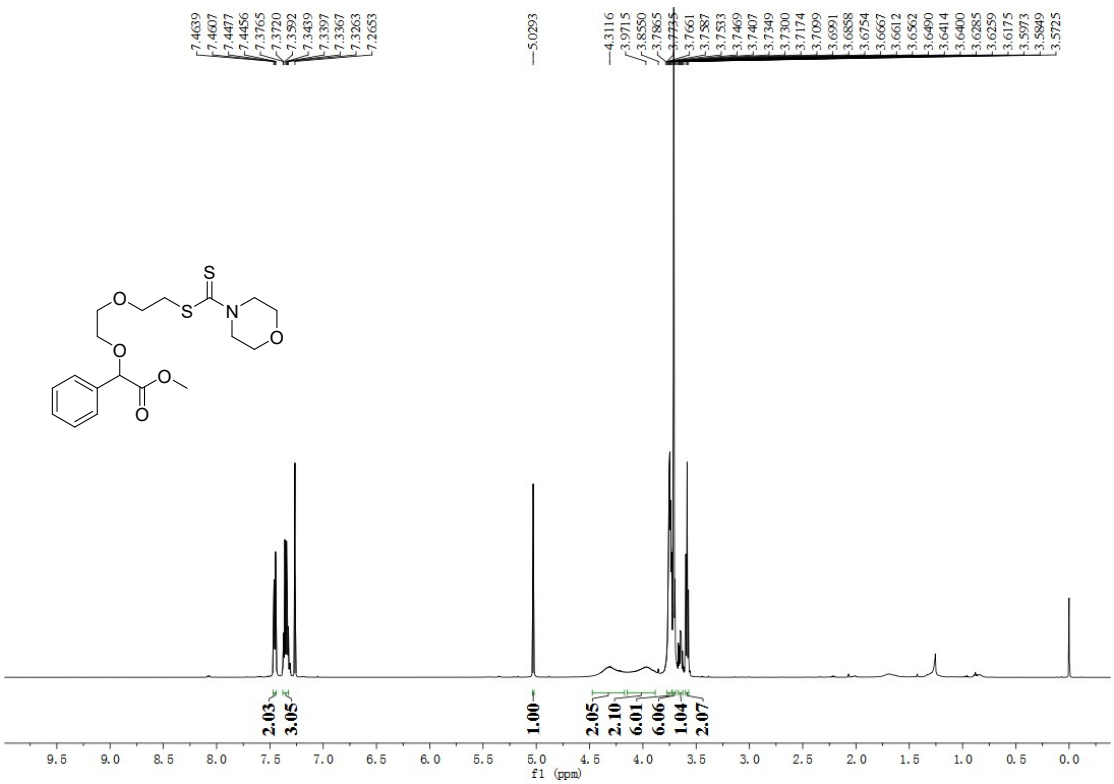


5k' (500 MHz ^{19}F NMR, $CDCl_3$)

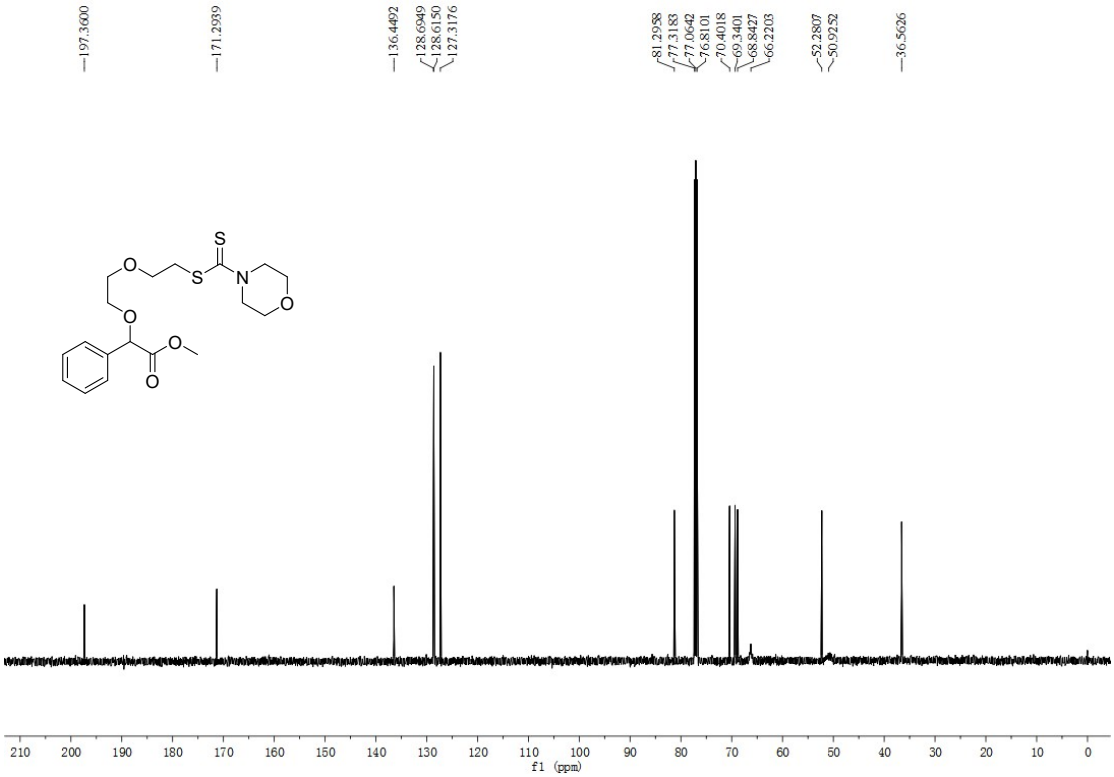


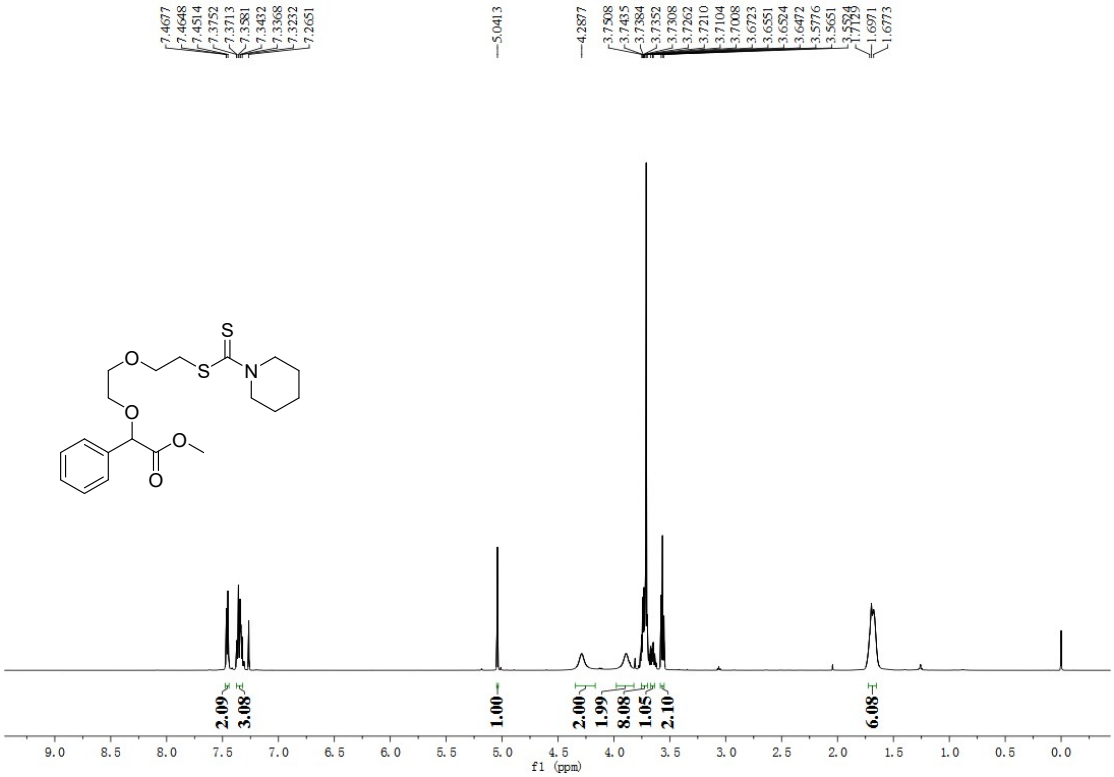
5l' (500 MHz NMR, $CDCl_3$)



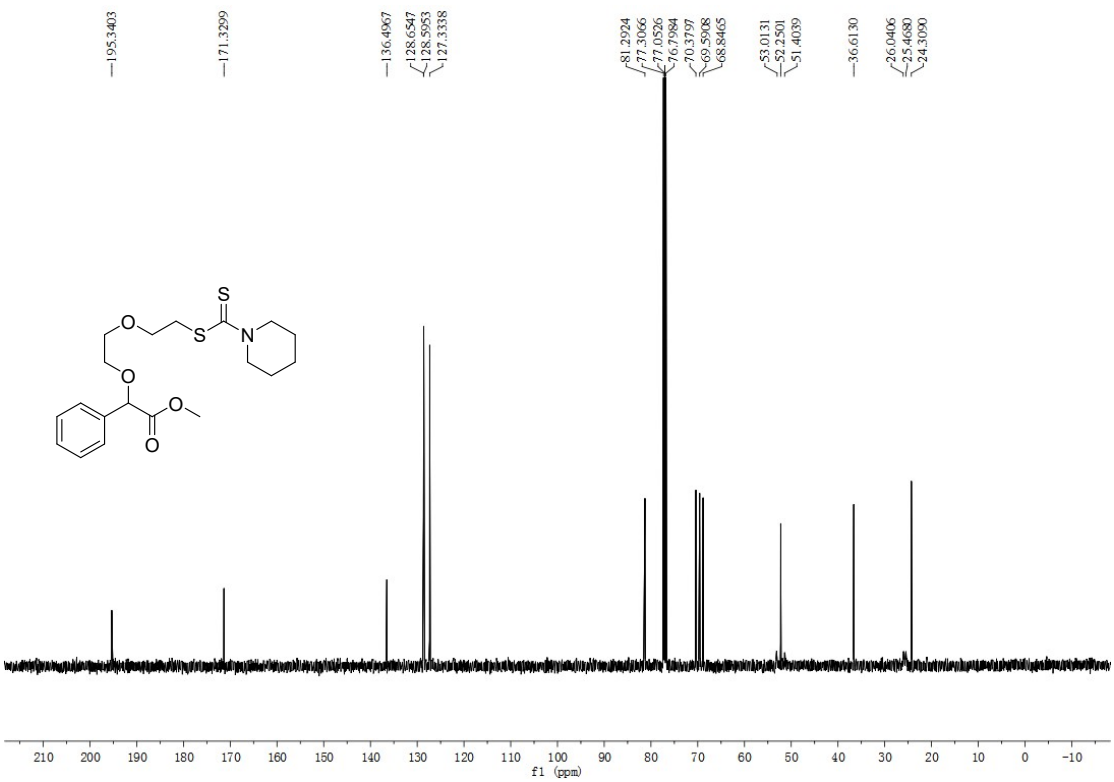


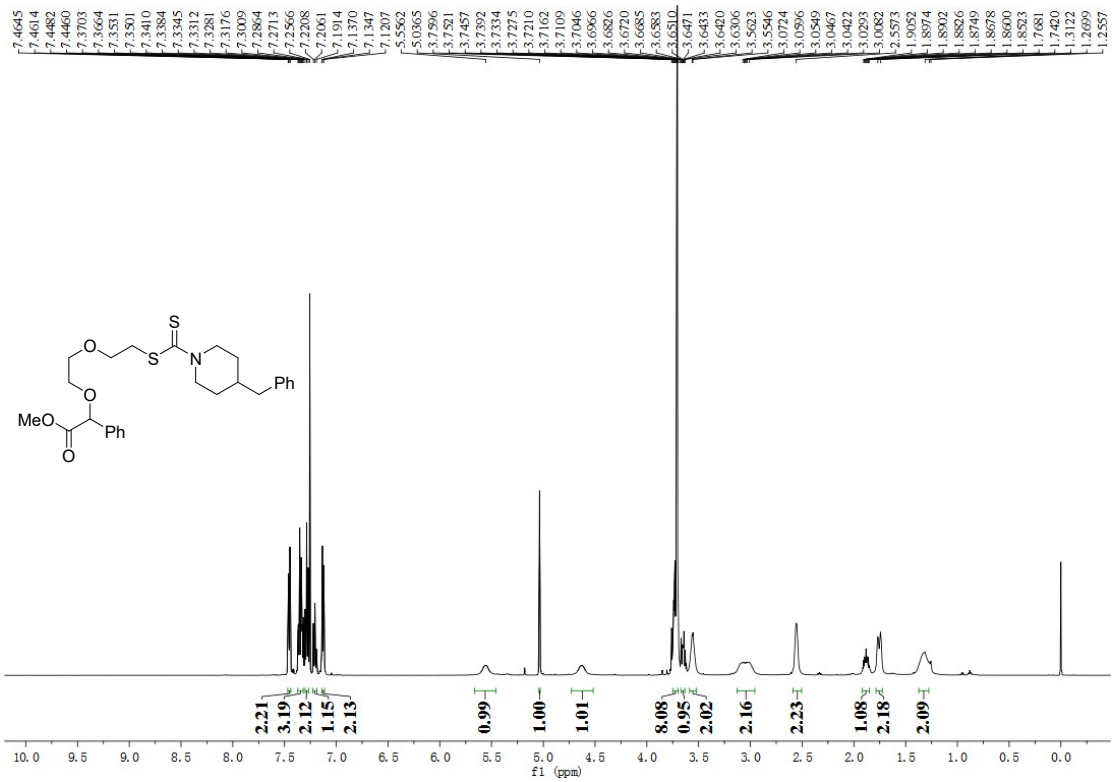
5m' (500 MHz NMR, $CDCl_3$)



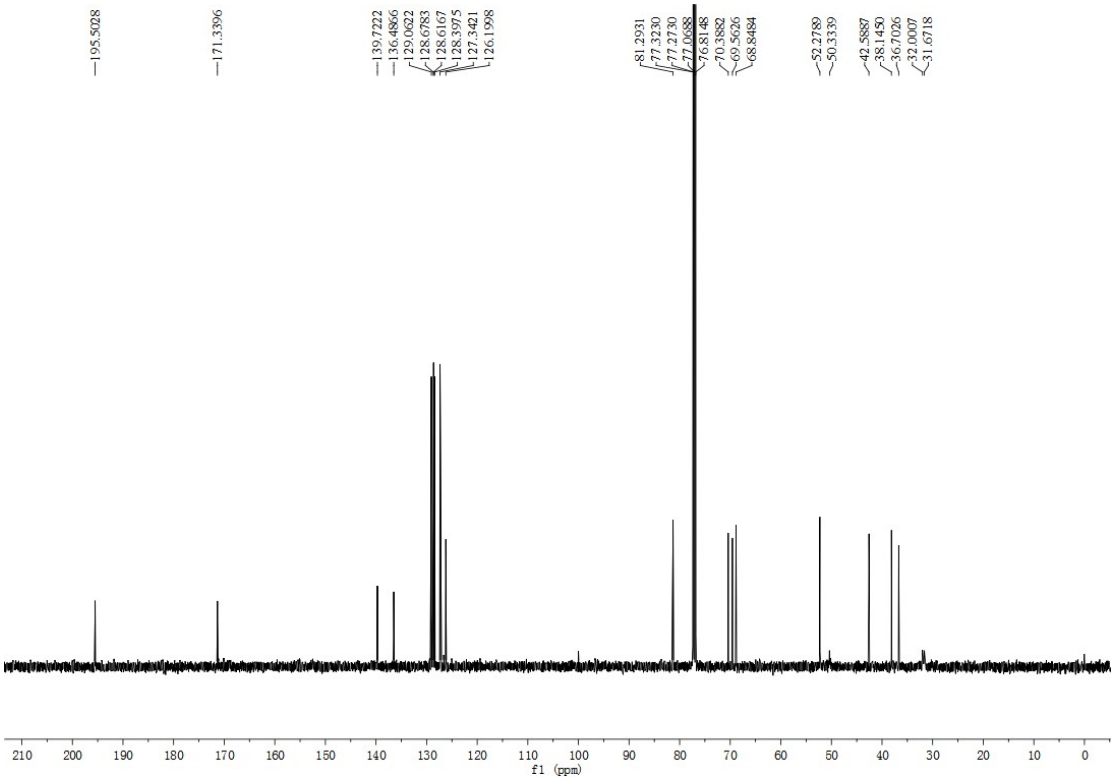


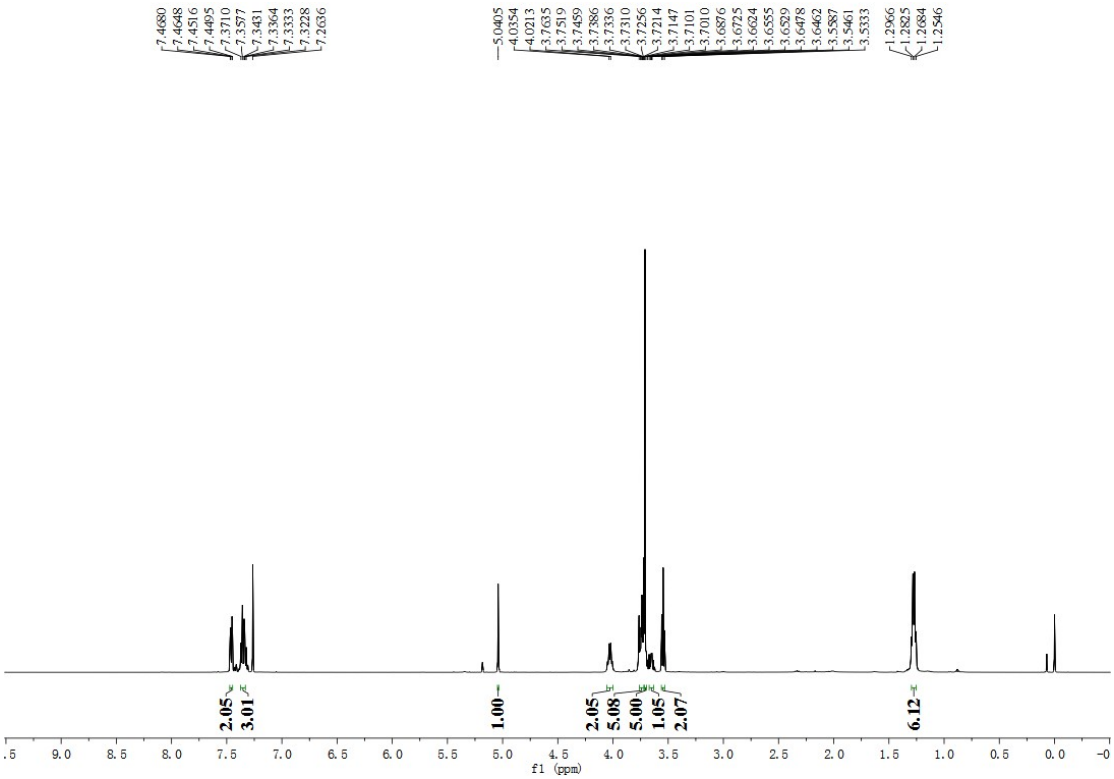
5n' (500 MHz NMR, $CDCl_3$)





5o' (500 MHz NMR, $CDCl_3$)





5p' (500 MHz NMR, $CDCl_3$)