Supporting Information

Electrochemically driven α-thiocarbamylation via a dehydrocoupling strategy of β-ketoesters with amines and CS2

Qian Wang,[a] Xiu-Jin Meng,[b] Hai-Tao Tang,[b] Ying-Ming Pan,*[b] Wen-Gui Duan*[a] and Mu-Xue He*[c]

[a]School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, People's Republic of China.
*E-mail: wgduan@gxu.edu.cn
[b]State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, People's Republic of China.
*E-mail: panym@mailbox.gxnu.edu.cn
[c]Guangxi Key Laboratory of Environmental Exposomics and Entire Lifecycle Health, School of Public Health of Guilin Medical University, Guilin 541199, People's Republic of China.
*E-mail: hemuxue@126.com

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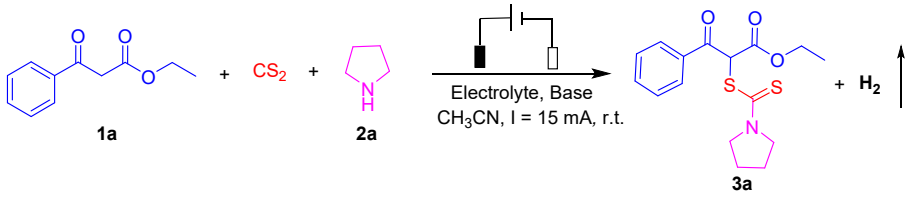
1. General Information

Without special instructions, all reagents and solvents were commercially available and were not further purified. Column chromatography was carried out using silica gel (300-400 mesh). NMR spectroscopy was performed on Bruker AV-400 or Bruker AV-600 instruments. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00) and relative to the signal of chloroform-*d* (δ 7.26, singlet). The abbreviations used to explain the multiplicities were as follows: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00) and relative to the signal of chloroform-d (δ 77.00, triplet). The HRMS spectrum was measured by micromass QTOF2 Quadrupole/Time of Flight Tandem mass spectrometer with electron spray ionization. Cyclic voltammograms were recorded on a CHI 660E potentiostat.

2. Additional Optimization of Reaction Conditions

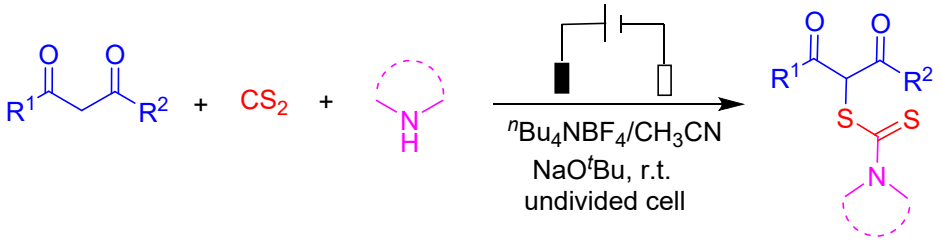
Table S1. Optimization of reaction conditions.[a]



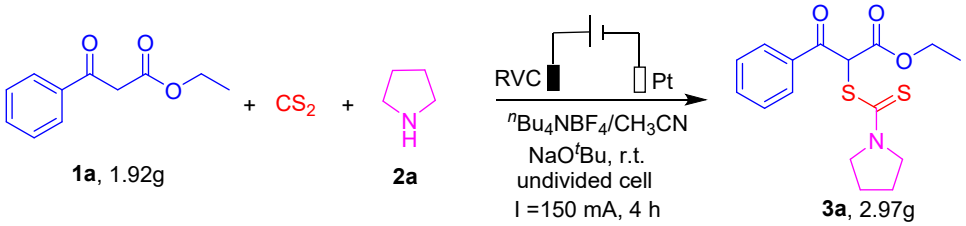
Entry	Base	Electrolyte	Yield (%)[b]
1	—	$^{n}Bu_4NBF_4$	0
2	EtONa (2 eq.)	$^{n}Bu_4NBF_4$	59
3	Cs_2CO_3 (2 eq.)	$^{n}Bu_4NBF_4$	52
4	CsF (2 eq.)	$^{n}Bu_4NBF_4$	56
5	K_2CO_3 (2 eq.)	$^{n}Bu_4NBF_4$	50
6	DBU (2 eq.)	$^{n}Bu_4NBF_4$	57
7	^{t}BuOK (2 eq.)	$^{n}Bu_4NBF_4$	48
8	DABCO (2 eq.)	$^{n}Bu_4NBF_4$	0
9	NaO^{t}Bu (1 eq.)	$^{n}Bu_4NBF_4$	63
10	NaO^{t}Bu (3 eq.)	$^{n}Bu_4NBF_4$	61
11	NaO^{t}Bu	$^{n}Bu_4NI$	54
12	NaO^{t}Bu	$^{n}Bu_4NPF_6$	60
13	NaO^{t}Bu	Et_4NBF_4	61
14	NaO^{t}Bu	Et_4NPF_6	60

[a]Reaction conditions: graphite rod anode (Φ 6 mm), Pt cathode (1 cm × 1 cm), undivided cell, constant current = 15 mA, **1a** (0.3 mmol, 1.0 equiv), CS_2 (0.36 mmol, 1.2 equiv), **2a** (0.3 mmol, 1.0 equiv), electrolyte (0.3 mmol, 1.0 equiv), base (0.3 mmol, 1.0 equiv), and CH_3CN (8 mL) under air at room temperature for 1 h. [b]Isolated yield.

3. **Procedures for the Electrolysis**



A 10 mL three-necked round-bottomed flask was charged with CS_2 (0.36 mmol, 1.2 equiv), amines (0.3 mmol, 1.0 equiv), $^{n}Bu_4NBF_4$ (0.3 mmol, 1.0 equiv), NaO^{t}Bu (0.3 mmol, 1.0 equiv) and CH_3CN (8 mL). The flask was equipped with a reticulated vitreous carbon (RVC) anode (100 PPI, 1 cm × 1 cm × 1.2 cm) and a platinum plate (1 cm x 1 cm) cathode, *β*-ketoesters (0.3 mmol, 1.0 equiv) were added, the distance between the two electrodes was 2.8 cm. Electrolysis was carried out at room temperature under air atmosphere, which using a constant current of 15 mA until the substrate was completely consumed (monitored by TLC, about 1 hour). After the reaction was completed, the solvent was concentrated under reduced pressure. Purification with silica gel column chromatography using petroleum ether/ethyl acetate to afford the desired products.



1a, 1.92g　　**2a**　　**3a**, 2.97g

A single-chamber electrolytic cell was charged with pyrrolidine **2a** (10 mmol, 0.71 g), CS_2 (12 mmol, 0.91 g), $^{n}Bu_4NBF_4$ (10 mmol, 3.29 g), NaO^{t}Bu (10 mmol, 0.96 g) and CH_3CN (0.04 M). The flask was equipped with a reticulated vitreous carbon (RVC) anode (100 PPI, 3 cm x 3 cm x 1.5 cm) and a platinum plate (3 cm x 3 cm x 0.1 cm) cathode, ethyl 3-oxo-3-phenylpropanoate **1a** (10 mmol, 1.92 g) were added. Electrolysis was carried out at room temperature under air atmosphere, which using a constant current of 150 mA until the substrate was completely consumed (monitored by TLC, about 4 hour). After the reaction was completed, the solvent was concentrated under reduced pressure. Purification with silica gel column chromatography using petroleum ether/ethyl acetate to afford the desired product **3a**. The yield of **3a** was 88% (2.97 g).

4. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded in an electrolyte solution of 0.1 M $^{n}Bu_4NBF_4$, 10 mM NaO^{t}Bu in CH_3CN (10 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 100 mV/s.

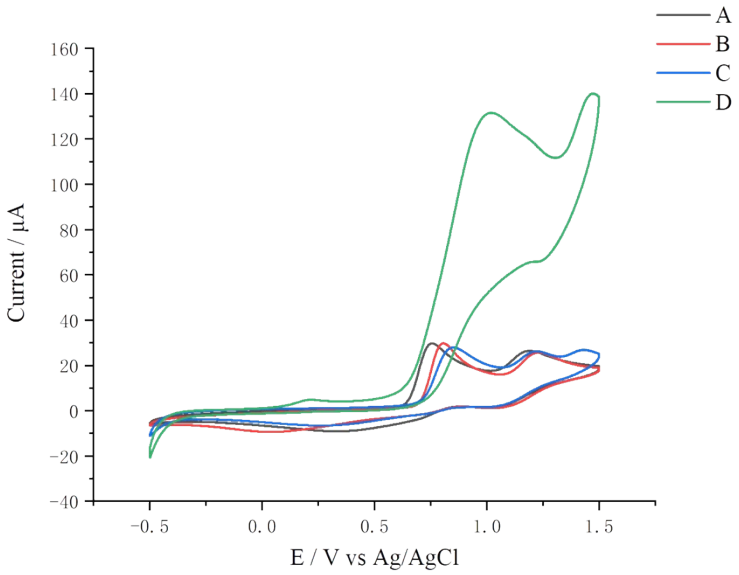


Figure S1. Cyclic voltammogram of reactants, A: background; B: CS_2 (10 mM)， $E_{p/2}$ = 0.81 V; C: **2a** (10 mM), $E_{p/2}$ = 0.86 V; D: CS_2 (10 mM) and **2a** (10 mM), $E_{p/2}$ = 0.93 V, which showed that a reaction occurred when the CS_2 and **2a** were mixed.

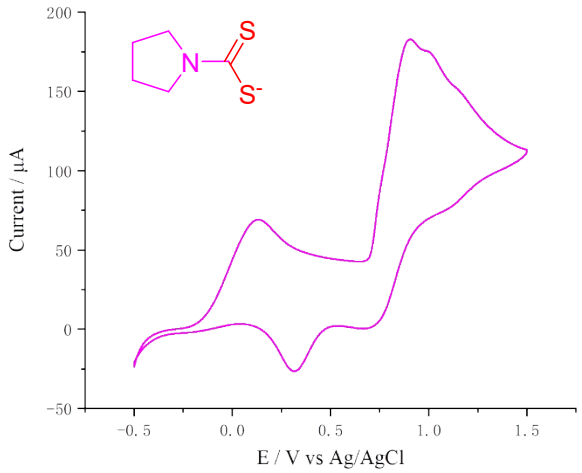
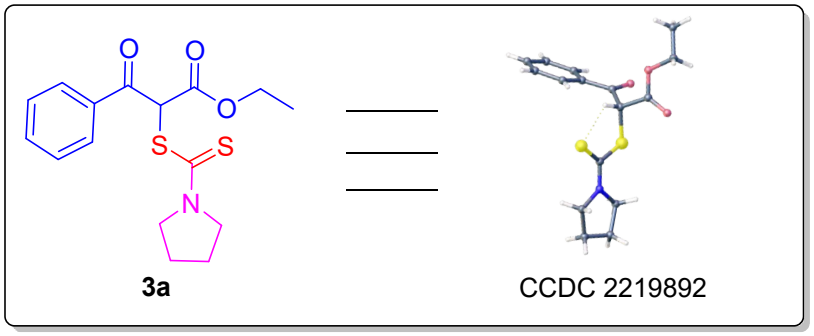


Figure S2. Cyclic voltammogram of sodium pyrrolidine-1-carbodithioate (10 mM). $E_{p/2}$ = 0.60 V.

5. The X-ray Crystal Structure of 3a



Bond precision: C-C = 0.0042 A Wavelength = 1.54184

Cell: a = 11.6432 (2) b = 16.4149 (2) c = 9.6857 (2)
Alpha = 90 beta = 113.866 (2) gamma = 90
Temperature: 295 K

	Calculated	Reported
Volume	1692.87 (6)	1692.87 (6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	$C_{16}H_{19}NO_3S_2$	$C_{16}H_{19}NO_3S_2$
Sum formula	$C_{16}H_{19}NO_3S_2$	$C_{16}H_{19}NO_3S_2$
Mr	337.44	337.44
Dx,g cm-3	1.324	1.324
Z	4	4
Mu (mm-1)	2.948	2.948
F000	712.0	712.0
F000’	716.47	
h, k, lmax	14, 20, 12	14, 20, 11
Nref	3509	3473
Tmin, Tmax	0.782, 0.863	0.342, 1.000
Tmin’	0.709	

Correction method = # Reported T Limits: Tmin = 0.342 Tmax = 1.000
AbsCorr = MULTI-SCAN

Data completeness = 0.990 Theta(max) = 75.424

R(reflections) = 0.0618 (3274) wR2(reflections) = 0.1736 (3473)

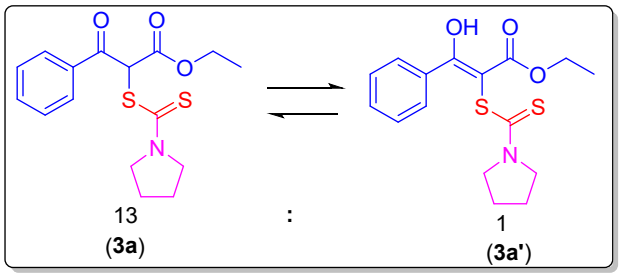
S = 0.911 Npar = 200

Table S2 Crystal data and structure refinement for 3a.

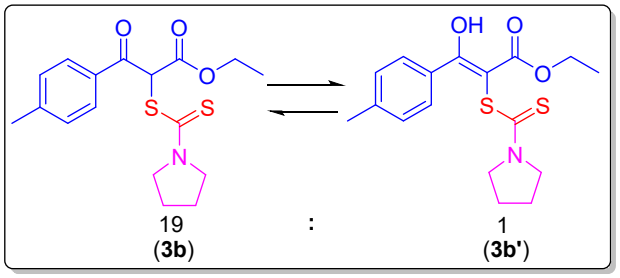
Empirical formula	$C_{16}H_{19}NO_3S_2$
Formula weight	337.44
Temperature/K	294.5(3)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.6432(2)
b/Å	16.4149(2)
c/Å	9.6857(2)
α/°	90
β/°	113.866(2)
γ/°	90
Volume/Å^3	1692.87(6)
Z	4
ρ_{calcg}/cm^3	1.324
μ/mm^{-1}	2.948
F(000)	712
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.304 to 150.848
Index ranges	-14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -9 ≤ l ≤ 11
Reflections collected	21971
Independent reflections	3473 [R_{int} = 0.0979, R_{sigma} = 0.0382]
Data/restraints/parameters	3473/0/200
Goodness-of-fit on F^2	0.911
Final R indexes [I>=2σ (I)]	R_1 = 0.0618, wR_2 = 0.1713
Final R indexes [all data]	R_1 = 0.0636, wR_2 = 0.1736
Largest diff. peak/hole / e Å^{-3}	0.58/-0.46

Crystal Data for $C_{16}H_{19}NO_3S_2$ (M =337.44 g/mol): monoclinic, space group $P2_1/c$ (no.14), a = 11.6432(2) Å, b = 16.4149(2) Å, c = 9.6857(2) Å, β = 113.866(2)°, V = 1692.87(6) Å^3, Z = 4, T = 294.5(3) K, μ(MoKα) = 2.948 mm^{-1}, *Dcalc* = 1.324 g/cm^3, 21971 reflections measured (8.304° ≤ 2Θ ≤ 150.848°), 3473 unique (R_{int} = 0.0979, R_{sigma} = 0.0382) which were used in all calculations. The final R_1 was 0.0618 (I > 2σ(I)) and wR_2 was 0.1736 (all data).

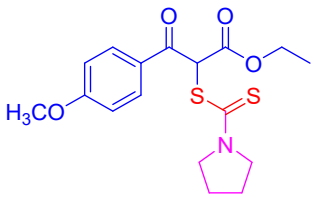
6. Characterization Data for the Electrolysis Products



Ethyl 3-oxo-3-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)propanoate (3a). Brown solid (90%, 91.1 mg). mp: 97-99 ℃. Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 - 8.06 (m, 2H), 7.60 - 7.56 (m, 1H), 7.48 - 7.44 (m, 2H), 6.88 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.91 - 3.87 (m, 2H), 3.75 - 3.61 (m, 2H), 2.08 - 1.94 (m, 4H), 1.20 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.2, 188.7, 166.8, 134.9, 134.0, 129.3, 128.8, 62.7, 60.7, 56.0, 50.8, 26.1, 24.3, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{16}H_{19}NO_3S_2Na^+$ $[M+Na]^+$: 360.0699, found 360.0693.

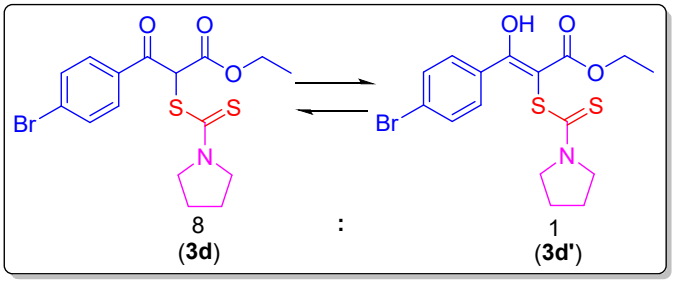


Ethyl 3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)-3-(*p*-tolyl)propanoate (3b). Yellow oil (78%, 82.2 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 - 7.93 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.82 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.88 - 3.84 (m, 2H), 3.72 - 3.56 (m, 2H), 2.36 (s, 3H), 2.06 - 1.91 (m, 4H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 190.7, 188.7, 166.9, 145.2, 132.4, 129.5, 129.4, 62.6, 60.6, 56.0, 50.8, 26.1, 24.3, 21.8, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{17}H_{21}NO_3S_2Na^+$ $[M+Na]^+$: 374.0855, found 374.0854.

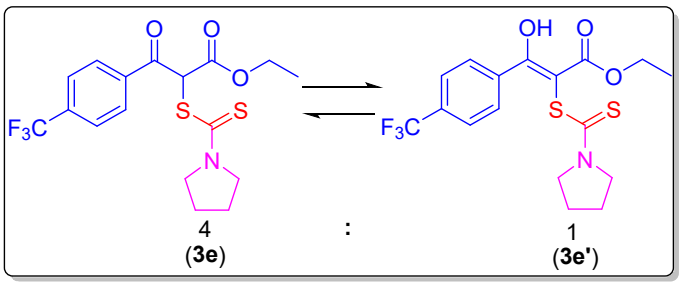


Ethyl 3-(4-methoxyphenyl)-3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)propanoate (3c). Yellow oil (85%, 93.7 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.49- 8.46 (m, 2H), 7.36 - 7.33 (m, 2H), 7.22 (s, 1H), 4.62 (q, *J* = 7.1 Hz, 2H), 4.30 (t, *J* = 7.1 Hz, 2H), 4.25 (s, 3H), 4.17 - 4.12 (m, 1H), 4.06 - 4.00 (m, 1H), 2.49 - 2.43 (m, 2H), 2.40 - 2.35 (m, 2H), 1.62 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 189.6, 188.9, 167.0, 164.3, 131.8, 127.7, 114.0, 62.6, 60.5, 55.9, 55.6,

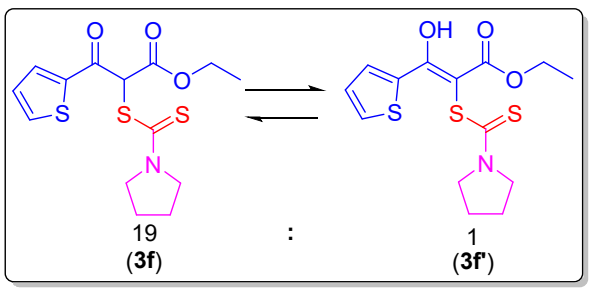
50.8, 26.1, 24.3, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{17}H_{21}NO_4S_2Na^+$ $[M+Na]^+$: 390.0804, found 390.0804.



Ethyl 3-(4-bromophenyl)-3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)propanoate (3d). Yellow oil (70%, 87.4 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 - 7.95 (m, 2H), 7.64 - 7.60 (m, 2H), 6.86 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.93 - 3.89 (m, 2H), 3.79 - 3.73 (m, 1H), 3.70 - 3.64 (m, 1H), 2.11 - 2.06 (m, 2H), 2.02 - 1.97 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 190.5, 188.5, 166.5, 133.8, 132.1, 130.8, 129.4, 62.8, 60.7, 56.1, 50.8, 26.2, 24.3, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{16}H_{18}BrNO_3S_2Na^+$ $[M+Na]^+$: 437.9804, found 437.9805.

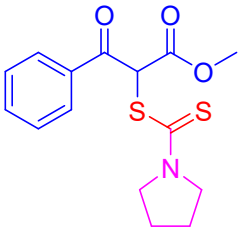


Ethyl 3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)-3-(4-(trifluoromethyl)phenyl)propanoate (3e). Yellow oil (52%, 63.2 mg). mp: 123-125 °C. Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.22 - 8.18 (m, 2H), 7.76 - 7.72 (m, 2H), 6.93 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.95 - 3.87 (m, 2H), 3.78 - 3.65 (m, 2H), 2.13 - 2.07 (m, 2H), 2.03 - 1.97 (m, 2H), 1.25 - 1.22 (m, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 190.6, 188.3, 166.3, 137.9, 135.1, 134.8, 129.6, 125.8 (q, *J* = 3.7 Hz), 122.2, 62.9, 60.8, 56.1, 50.8, 26.2, 24.3, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{17}H_{18}F_3NO_3S_2Na^+$ $[M+Na]^+$: 428.0572, found 428.0570.

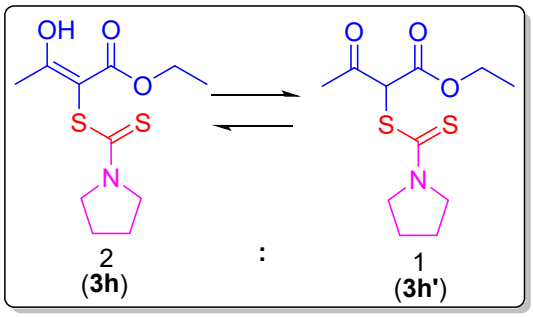


Ethyl 3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)-3-(thiophen-2-yl)propanoate (3f). Colorless oil (60%, 61.8 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.70 (dd, *J*

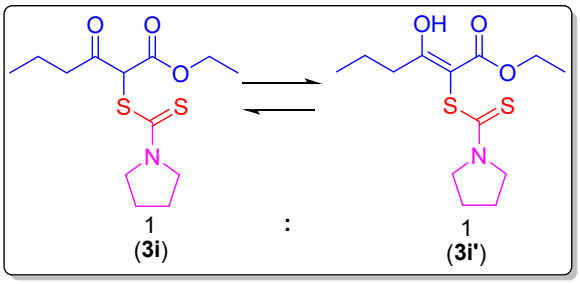
= 4.9, 1.2 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.9 Hz, 1H), 6.75 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.86 (t, *J* = 7.0 Hz, 2H), 3.75 - 3.59 (m, 2H), 2.06 - 1.92 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 188.6, 183.7, 166.4, 142.0, 135.9, 134.6, 128.6, 62.8, 61.4, 56.1, 50.8, 26.1, 24.3, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{14}H_{17}NO_3S_3Na^+$ $[M+Na]^+$: 366.0263, found 366.0259.



Methyl 3-oxo-3-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)propanoate (3g). Yellow oil (78%, 75.7 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 - 8.05 (m, 2H), 7.60 - 7.56 (m, 1H), 7.48 - 7.44 (m, 2H), 6.91 (s, 1H), 3.93 - 3.88 (m, 2H), 3.76 - 3.70 (m, 4H), 3.65 - 3.58 (m, 1H), 2.06 - 1.93 (m, 4H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.2, 188.5, 167.4, 134.8, 134.2, 129.3, 128.8, 60.4, 56.1, 53.5, 50.8, 26.1, 24.3. **HRMS** (*m/z*) (ESI): calcd for $C_{15}H_{18}NO_3S_2^+$ $[M+H]^+$: 324.0723, found 324.0724.

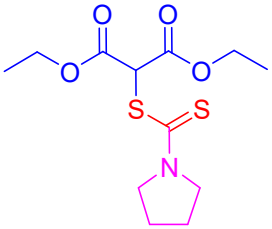


Ethyl (*E*)-3-hydroxy-2-((pyrrolidine-1-carbonothioyl)thio)but-2-enoate (3h). Yellow oil (60%, 49.6 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 14.07 (s, 0.6H), 4.27 - 4.20 (m, 2H), 3.91 - 3.87 (m, 2H), 3.76 - 3.70 (m, 2H), 2.42 (s, 1H), 2.19 (s, 2H), 2.14 - 2.07 (m, 2H), 2.02 - 1.94 (m, 2H), 1.30 - 1.24 (m, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 198.8, 186.0, 172.5, 93.8, 64.6, 61.6, 55.4, 50.5, 26.3, 24.3, 14.2. **HRMS** (*m/z*) (ESI): calcd for $C_{11}H_{18}NO_3S_2^+$ $[M+H]^+$: 276.0723, found 276.0724.

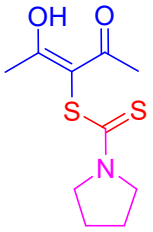


Ethyl 3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)hexanoate (3i). Yellow oil (55%, 50.1 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.99 (s, 0.5H), 4.23 - 4.17 (m, 2H), 3.86 (t, *J* = 7.0 Hz, 2H), 3.74 - 3.68

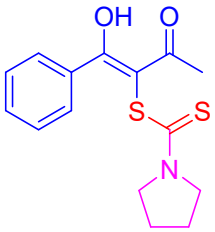
(m, 2H), 2.77 - 2.63 (m, 1H), 2.54 - 2.42 (m, 1H), 2.12 - 2.04 (m, 2H), 1.99 - 1.92 (m, 2H), 1.67 - 1.56 (m, 2H), 1.27 - 1.21 (m, 3H), 0.92 - 0.87 (m, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 192.9, 188.3, 166.3, 64.0, 61.6, 55.9, 50.8, 35.7, 26.2, 24.3, 17.2, 14.0, 13.5. **HRMS** (*m/z*) (ESI): calcd for $C_{13}H_{22}NO_3S_2^+$ $[M+H]^+$: 304.1036, found 304.1035.



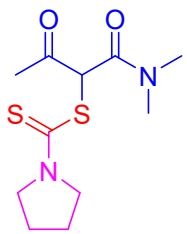
Diethyl 2-((pyrrolidine-1-carbonothioyl)thio)malonate (3j). Yellow oil (57%, 52.2 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 5.87 (d, *J* = 4.3 Hz, 1H), 4.25 - 4.21 (m, 4H), 3.88 - 3.86 (m, 2H), 3.70 - 3.67 (m, 2H), 2.09 - 2.05 (m, 2H), 1.98 - 1.93 (m, 2H), 1.28 - 1.25 (m, 6H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 188.7, 166.1, 62.7, 58.0, 55.8, 50.7, 26.2, 24.3, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{12}H_{19}NO_4S_2Na^+$ $[M+Na]^+$: 328.0648, found 328.0647.



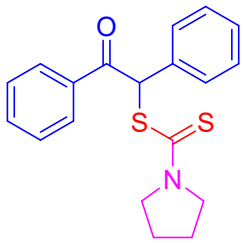
(*E*)-2-hydroxy-4-oxopent-2-en-3-yl pyrrolidine-1-carbodithioate (3k). Brown solid (47%, 34.6 mg). mp: 116-118 °C. Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.90 (t, *J* = 7.0 Hz, 2H), 3.76 (t, *J* = 6.9 Hz, 2H), 2.22 (s, 6H), 2.16 - 2.09 (m, 2H), 2.03 - 1.96 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 198.4, 192.1, 103.6, 55.7, 50.7, 26.3, 24.3. **HRMS** (*m/z*) (ESI): calcd for $C_{10}H_{16}NO_2S_2^+$ $[M+H]^+$: 246.0617, found 246.0616.



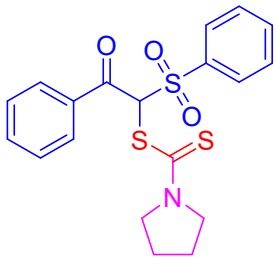
(*E*)-1-hydroxy-3-oxo-1-phenylbut-1-en-2-yl pyrrolidine-1-carbodithioate (3l). Yellow oil (50%, 46.1 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.04 - 8.01 (m, 0.7H), 7.60 - 7.54 (m, 2H), 7.50 - 7.39 (m, 2H), 3.80 - 3.57 (m, 4H), 2.33 (d, *J* = 16.9 Hz, 3H), 2.05 - 1.86 (m, 4H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 200.3, 192.9, 187.6, 135.5, 134.7, 129.6, 128.2, 67.0, 56.0, 51.1, 29.6, 26.2, 24.2. **HRMS** (*m/z*) (ESI): calcd for $C_{15}H_{18}NO_2S_2^+$ $[M+H]^+$: 308.0774, found 308.0767.



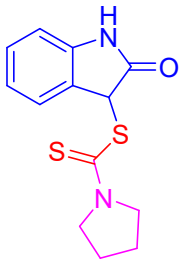
1-(Dimethylamino)-1,3-dioxobutan-2-yl pyrrolidine-1-carbodithioate (3m). Colorless oil (53%, 43.6 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.19 (s, 1H), 3.87 - 3.84 (m, 2H), 3.75 - 3.65 (m, 2H), 3.12 (s, 3H), 2.95 (s, 3H), 2.30 (s, 3H), 2.09 - 2.04 (m, 2H), 1.99 - 1.92 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 199.9, 189.5, 166.2, 63.4, 56.0, 50.9, 38.3, 36.1, 28.2, 26.1, 24.3. **HRMS** (*m/z*) (ESI): calcd for $C_{11}H_{18}N_2O_2S_2Na^+$ $[M+Na]^+$: 297.0702, found 297.0700.



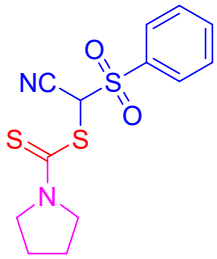
2-Oxo-1,2-diphenylethyl pyrrolidine-1-carbodithioate (3n). Yellow solid (58%, 59.4 mg). mp: 151-153 ℃.Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.7 Hz, 2H), 7.51 - 7.48 (m, 3H), 7.42 - 7.39 (m, 2H), 7.33 - 7.24 (m, 3H), 7.05 (s, 1H), 3.91 - 3.81 (m, 2H), 3.76 - 3.70 (m, 1H), 3.63 - 3.57 (m, 1H), 2.06 - 2.00 (m, 2H), 1.96 - 1.90 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 194.7, 190.7, 136.2, 134.3, 133.2, 129.4, 129.2, 129.2, 128.7, 128.5, 61.5, 55.2, 50.8, 26.3, 24.4. HRMS (m/z) (ESI): calcd for $C_{19}H_{20}NOS_2^+$ $[M+H]^+$: 342.0980, found 342.0985.



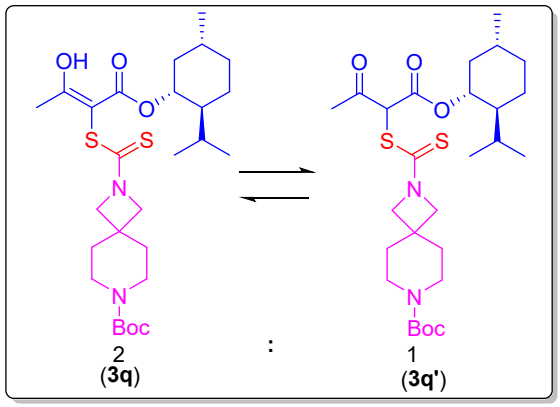
2-Oxo-2-phenyl-1-(phenylsulfonyl)ethyl pyrrolidine-1-carbodithioate (3o). Yellow oil (52%, 63.3 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 - 8.06 (m, 2H), 7.96 (s, 1H), 7.93 - 7.91 (m, 2H), 7.63 - 7.56 (m, 2H), 7.50 - 7.42 (m, 4H), 3.89 - 3.82 (m, 2H), 3.78 - 3.64 (m, 2H), 2.12 - 1.94 (m, 4H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 189.5, 187.0, 137.2, 135.5, 134.4, 130.0, 129.7, 128.8, 76.3, 56.5, 50.9, 26.1, 24.2. **HRMS** (*m/z*) (ESI): calcd for $C_{19}H_{19}NO_3S_3Na^+$ $[M+Na]^+$: 428.0419, found 428.0417.



2-Oxoindolin-3-yl pyrrolidine-1-carbodithioate (3p). Yellow oil (48%, 40.1 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.89 (s, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.25 - 7.21 (m, 1H), 7.04 - 7.00 (m, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.55 (s, 1H), 4.03 - 4.00 (m, 2H), 3.81 - 3.69 (m, 2H), 2.14 - 2.10 (m, 2H), 2.06 - 2.01 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 190.2, 176.3, 141.0, 128.9, 127.2, 125.0, 122.9, 110.2, 56.5, 52.0, 50.8, 26.2, 24.4. **HRMS** (m/z) (ESI): calcd for $C_{13}H_{14}N_2OS_2Na^+$ $[M+Na]^+$: 301.0440, found 301.0443.

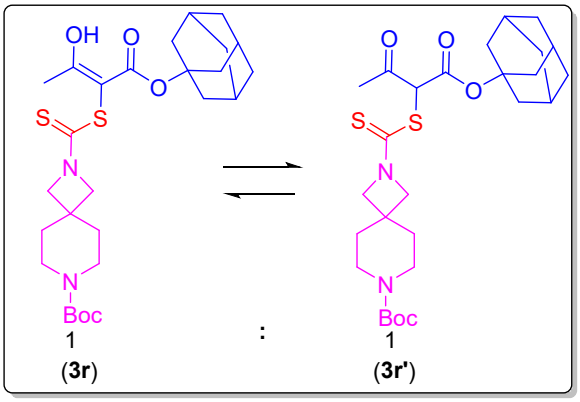


Cyano(phenylsulfonyl)methyl pyrrolidine-1-carbodithioate (3q). Yellow solid (49%, 48.0 mg). mp: 124-126 ℃. Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 - 8.06 (m, 2H), 7.80 - 7.76 (m, 1H), 7.67 - 7.63 (m, 2H), 7.43 (s, 1H), 3.95 - 3.92 (m, 2H), 3.80 - 3.69 (m, 2H), 2.17 - 2.12 (m, 2H), 2.07 - 2.02 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 184.2, 135.6, 135.5, 129.9, 129.7, 112.4, 61.8, 57.4, 51.0, 26.1, 24.2. **HRMS** (m/z) (ESI): calcd for $C_{13}H_{15}N_2O_2S_3^+$ $[M+H]^+$: 327.0290, found 327.0293.

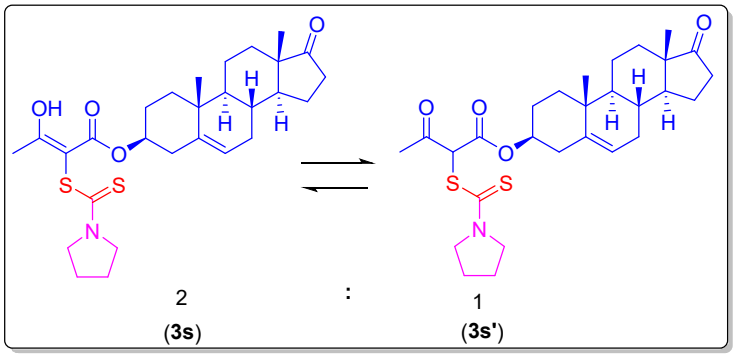


***Tert*-butyl 2-((((*E*)-3-hydroxy-1-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-1-oxobut-2-en-2-yl)thio)carbonothioyl)-2,7-diazaspiro[3.5]nonane-7-carboxylate (3r).** Yellow oil (35%, 56.8 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 14.16 (s, 0.5H), 4.78 - 4.67 (m, 1H), 4.01 - 3.94 (m, 3H), 3.47 -

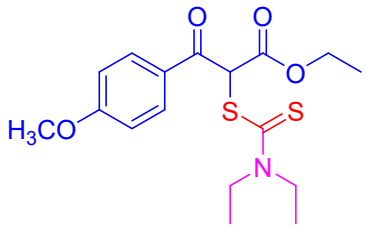
3.32 (m, 4H), 2.42 (s, 1H), 2.20 (s, 2H), 2.07 - 1.99 (m, 1H), 1.92 - 1.85 (m, 1H), 1.80 - 1.74 (m, 4H), 1.70 - 1.60 (m, 3H), 1.45 (d, J = 2.1 Hz, 9H), 1.25 (s, 2H), 1.07 - 0.95 (m, 2H), 0.91 - 0.84 (m, 7H), 0.75 - 0.71 (m, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 200.6, 166.7, 90.0, 75.4, 50.5, 46.8, 40.7, 34.1, 31.4, 30.0, 26.1, 23.2, 21.9, 20.7, 20.7, 16.1. **HRMS** (*m/z*) (ESI): calcd for $C_{27}H_{45}N_2O_5S_2^+$ $[M+H]^+$: 541.2764, found 541.2763.



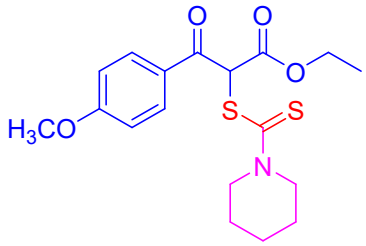
***Tert*-butyl (*E*)-2-(((1-(adamantan-1-yloxy)-3-hydroxy-1-oxobut-2-en-2-yl)thio)carbonothioyl) -2,7-diazaspiro[3.5]nonane-7-carboxylate (3s).** Yellow oil (41%, 66.0 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 14.15 (s, 0.5H), 3.99 - 3.95 (m, 4H), 3.46 - 3.30 (m, 4H), 2.42 (s, 1H), 2.17 - 2.10 (m, 11H), 1.77 - 1.72 (m, 4H), 1.64 (s, 6H), 1.44 (d, J = 2.1 Hz, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 198.8, 191.9, 171.5, 154.7, 93.2, 84.2, 82.8, 79.9, 65.7, 64.4, 62.8, 41.1, 36.1, 34.5, 30.9, 28.4, 21.1. **HRMS** (*m/z*) (ESI): calcd for $C_{27}H_{41}N_2O_5S_2^+$ $[M+H]^+$: 537.2451, found 537.2460.



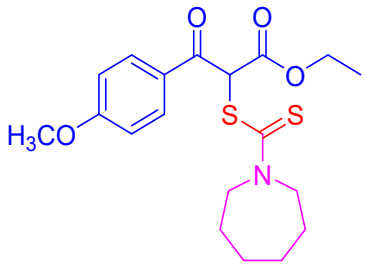
(3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (*E*)-3-hydroxy-2-((pyrrolidine-1-carbonothioyl)thio) but-2-enoate (3t). Yellow oil (40%, 62.1 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 14.09 (s, 1H), 5.38 (d, J = 5.0 Hz, 1H), 4.71 - 4.60 (m, 1H), 3.94 - 3.85 (m, 2H), 3.75 - 3.69 (m, 2H), 2.46 - 2.16 (m, 6H), 2.12 - 1.78 (m, 10H), 1.67 - 1.40 (m, 6H), 1.30 - 1.22 (m, 2H), 1.15 - 1.07 (m, 1H), 1.03 - 0.96 (m, 4H), 0.85 (d, J = 1.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 221.1, 198.8, 192.6, 185.8, 172.0, 139.5, 122.0, 94.0, 76.2, 75.1, 64.9, 55.3, 51.7, 50.9, 50.1, 47.5, 36.8, 35.9, 31.4, 30.8, 29.2, 27.5, 26.3, 24.3, 21.9, 21.0, 20.3, 19.5, 13.5. **HRMS** (*m/z*) (ESI): calcd for $C_{28}H_{39}NO_4S_2Na^+$ $[M+Na]^+$: 540.2213, found 540.2211.



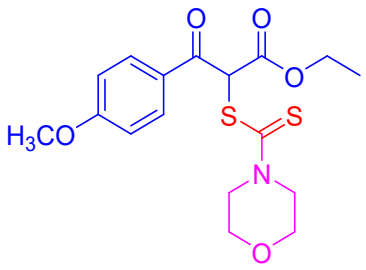
Ethyl 2-((diethylcarbamothioyl)thio)-3-(4-methoxyphenyl)-3-oxopropanoate (4a). Yellow oil (68%, 75.4 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.80 (s, 1H), 4.25 - 4.20 (m, 2H), 4.04 - 3.93 (m, 2H), 3.87 (s, 3H), 3.83 - 3.71 (m, 2H), 1.31 - 1.21 (m, 9H) **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 192.0, 189.7, 167.0, 164.3, 131.8, 127.9, 114.0, 62.5, 61.2, 55.6, 50.6, 47.2, 14.0, 12.7, 11.5. **HRMS** (*m/z*) (ESI): calcd for $C_{17}H_{24}NO_4S_2^+$ $[M+H]^+$: 370.1141, found 370.1140.



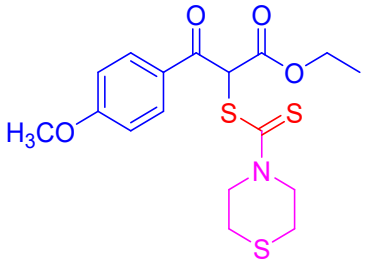
Ethyl 3-(4-methoxyphenyl)-3-oxo-2-((piperidine-1-carbonothioyl)thio)propanoate (4b). Yellow oil (80%, 91.6 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.81 (s, 1H), 4.25 - 4.18 (m, 4H), 3.88 - 3.85 (m, 5H), 1.67 (s, 6H), 1.20 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.8, 189.6, 166.9, 164.3, 131.8, 127.9, 114.0, 62.5, 61.2, 55.6, 24.1, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{18}H_{23}NO_4S_2Na^+$ $[M+Na]^+$: 404.0961, found 404.0955.



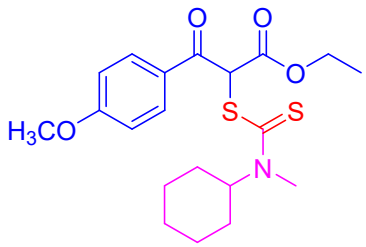
Ethyl 2-((azepane-1-carbonothioyl)thio)-3-(4-methoxyphenyl)-3-oxopropanoate (4c). Yellow oil (82%, 97.3 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.79 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.12 (t, *J* = 6.1 Hz, 2H), 3.88 (t, *J* = 6.1 Hz, 2H), 3.83 (s, 3H), 1.87 - 1.78 (m, 4H), 1.56 - 1.52 (m, 4H), 1.21 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 192.6, 189.7, 167.0, 164.3, 131.8, 127.9, 114.0, 62.5, 61.1, 56.7, 55.6, 53.2, 27.4, 26.6, 26.4, 26.0, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{19}H_{25}NO_4S_2Na^+$ $[M+Na]^+$: 418.1117, found 418.1113.



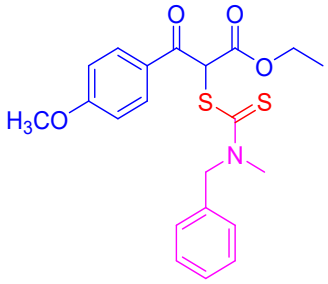
Ethyl 3-(4-methoxyphenyl)-2-((morpholine-4-carbonothioyl)thio)-3-oxopropanoate (4d). Yellow oil (76%, 87.4 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 - 8.04 (m, 2H), 6.97 - 6.93 (m, 2H), 6.79 (s, 1H), 4.33 - 3.98 (m, 6H), 3.87 (s, 3H), 3.77 - 3.74 (m, 4H), 1.24 - 1.20 (m, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 193.9, 189.2, 166.6, 164.4, 131.8, 127.8, 114.0, 62.7, 60.9, 55.6, 29.7, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{17}H_{21}NO_5S_2Na^+$ $[M+Na]^+$: 406.0753, found 406.0759.



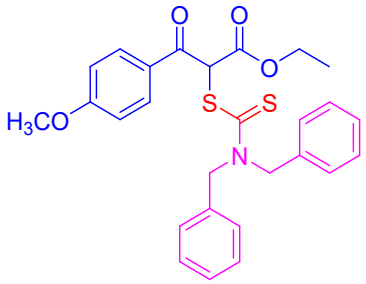
Ethyl 3-(4-methoxyphenyl)-3-oxo-2-((thiomorpholine-4-carbonothioyl)thio)propanoate (4e). Yellow oil (77%, 92.3 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 - 8.03 (m, 2H), 6.96 - 6.92 (m, 2H), 6.75 (s, 1H), 4.54 - 4.18 (m, 6H), 3.86 (s, 3H), 2.75 - 2.72 (m, 4H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 193.2, 189.2, 166.6, 164.4, 131.8, 127.8, 114.0, 62.7, 61.2, 55.6, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{17}H_{21}NO_4S_3Na^+$ $[M+Na]^+$: 422.0525, found 422.0523.



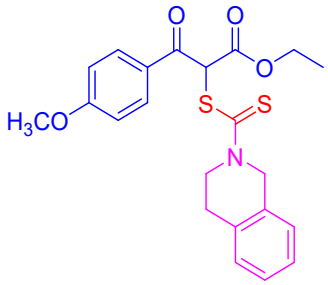
Ethyl 2-((cyclohexyl(methyl)carbamothioyl)thio)-3-(4-methoxyphenyl)-3-oxopropanoate (4f). Yellow oil (61%, 74.9 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 9.1 Hz, 2H), 6.87 (d, *J* = 7.7 Hz, 1H), 5.38 - 5.31 (m, 0.5H), 4.42 - 4.35 (m, 0.5H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 3.37 (s, 1.5H), 3.19 (s, 1.5H), 1.85 - 1.76 (m, 4H), 1.66 (d, *J* = 13.3 Hz, 1H), 1.54 - 1.47 (m, 1H), 1.42 - 1.34 (m, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.12 - 1.06 (m, 1H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 193.3, 192.5, 189.7, 167.0, 164.3, 131.8, 127.9, 114.0, 64.0, 60.8, 55.6, 38.4, 34.2, 30.3, 29.3, 25.4, 25.1, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{20}H_{28}NO_4S_2^+$ $[M+H]^+$: 410.1454, found 410.1451.



Ethyl 2-((benzyl(methyl)carbamothioyl)thio)-3-(4-methoxyphenyl)-3-oxopropanoate (4g). Yellow oil (60%, 75.2 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 - 8.06 (m, 2H), 7.34 - 7.19 (m, 5H), 6.97 - 6.94 (m, 2H), 6.82 (d, *J* = 14.1 Hz, 1H), 5.36 - 5.27 (m, 1H), 4.99 (s, 1H), 4.27 - 4.20 (m, 2H), 3.85 (s, 3H), 3.42 (s, 1H), 3.28 (s, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 195.2, 193.9, 189.4, 166.8, 164.4, 135.1, 134.2, 131.8, 130.7, 129.0, 128.9, 128.3, 128.0, 127.8, 127.3, 114.1, 62.7, 62.0, 60.5, 58.0, 55.7, 44.0, 39.1, 14.1. **HRMS** (*m/z*) (ESI): calcd for $C_{21}H_{24}NO_4S_2^+$ $[M+H]^+$: 418.1141, found 418.1142.

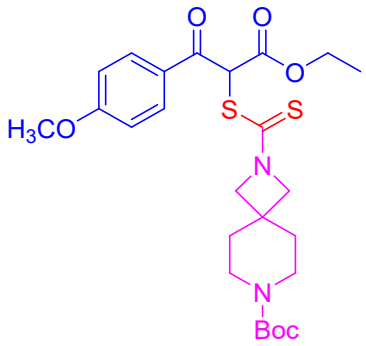


Ethyl 2-((dibenzylcarbamothioyl)thio)-3-(4-methoxyphenyl)-3-oxopropanoate (4h). Yellow oil (57%, 84.4 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.10 - 8.08 (m, 2H), 7.34 - 7.28 (m, 6H), 7.23 - 7.18 (m, 4H), 6.97 - 6.93 (m, 2H), 6.84 (s, 1H), 5.32 - 5.19 (m, 2H), 4.95 - 4.86 (m, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.24 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.1, 189.4, 166.7, 164.4, 135.0, 134.0, 131.9, 130.7, 129.0, 128.2, 127.9, 127.4, 114.0, 113.0, 62.7, 62.2, 57.0, 55.6, 54.4, 29.7, 14.1. **HRMS** (*m/z*) (ESI): calcd for $C_{27}H_{27}NO_4S_2Na^+$ $[M+Na]^+$: 516.1274, found 516.1278.

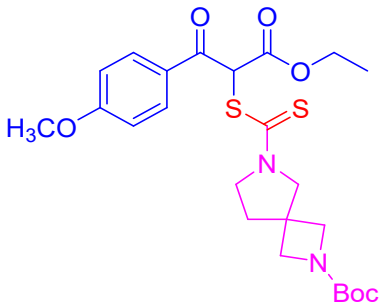


Ethyl 3-(4-methoxyphenyl)-3-oxo-2-((1,2,3,4-tetrahydroisoquinoline-2-carbonothioyl)thio)propanoate (4i). Yellow oil (66%, 85.0 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.6 Hz, 2H), 7.26 - 7.17 (m, 4H), 6.98 - 6.94 (m, 2H), 6.88 (s, 1H), 5.29 (d, *J* = 6.9 Hz, 1H), 5.04 (q, *J* = 16.0 Hz, 1H), 4.40 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.15 - 4.05 (m, 1H), 3.87 (s, 3H), 3.01 - 2.97 (m, 2H), 1.26 -

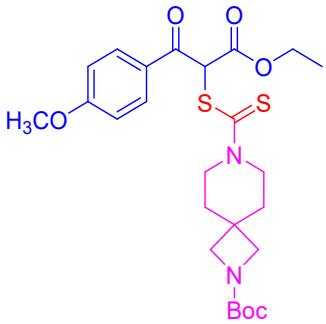
1.23 (m, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 192.8, 189.5, 166.8, 164.4, 134.9, 134.2, 132.5, 131.9, 131.2, 130.7, 128.2, 127.8, 127.6, 127.4, 127.0, 126.6, 126.3, 114.0, 62.7, 60.7, 55.6, 54.8, 51.5, 51.1, 48.3, 29.7, 29.1, 28.5, 14.1. **HRMS** (*m/z*) (ESI): calcd for $C_{22}H_{23}NO_4S_2Na^+$ $[M+Na]^+$: 452.0961, found 452.0962.



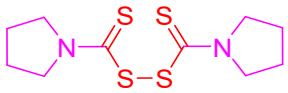
***Tert*-butyl 2-(((1-ethoxy-3-(4-methoxyphenyl)-1,3-dioxopropan-2-yl)thio)carbonothioyl)-2,7-diazaspiro[3.5]nonane-7-carboxylate (4j).** Yellow oil (56%, 87.8 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 - 8.05 (m, 2H), 6.97 - 6.93 (m, 2H), 6.63 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.02 - 3.96 (m, 3H), 3.91 - 3.87 (m, 4H), 3.42 - 3.31 (m, 4H), 1.76 - 1.71 (m, 4H), 1.44 (s, 9H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.5, 189.4, 166.8, 164.4, 154.6, 131.9, 127.6, 114.0, 79.9, 64.5, 62.7, 62.5, 60.3, 55.6, 34.9, 34.7, 28.4, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{25}H_{34}N_2O_6S_2Na^+$ $[M+Na]^+$: 545.1751, found 545.1752.



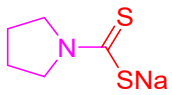
***Tert*-butyl 6-(((1-ethoxy-3-(4-methoxyphenyl)-1,3-dioxopropan-2-yl)thio)carbonothioyl)-2,6-diazaspiro[3.4]octane-2-carboxylate (4k).** Yellow oil (54%, 82.4 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.06 - 8.03 (m, 2H), 6.95 - 6.91 (m, 2H), 6.74 (d, *J* = 4.2 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.04 (s, 1H), 3.95 - 3.78 (m, 10H), 2.26 (t, *J* = 7.4 Hz, 1H), 2.16 (t, *J* = 7.1 Hz, 1H), 1.41 (s, 9H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 190.2, 189.3, 166.8, 164.4, 156.1, 131.8, 127.7, 114.0, 79.9, 64.0, 62.7, 60.6, 59.2, 55.6, 54.1, 49.3, 40.3, 38.3, 36.3, 34.6, 28.3, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{24}H_{33}N_2O_6S_2^+$ $[M+H]^+$: 509.1775, found 509.1785.



***Tert*-butyl 7-(((1-ethoxy-3-(4-methoxyphenyl)-1,3-dioxopropan-2-yl)thio)carbonothioyl)-2,7-diazaspiro[3.5]nonane-2-carboxylate (4l).** Yellow oil (50%, 78.4 mg). Petroleum ether/ethyl acetate = 20/1–5/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 - 8.04 (m, 2H), 6.96 - 6.93 (m, 2H), 6.75 (s, 1H), 4.25 - 4.19 (m, 2H), 3.87 (s, 3H), 3.68 (s, 4H), 1.88 - 1.85 (m, 4H), 1.43 (s, 9H), 1.24 - 1.20 (m, 7H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 193.0, 189.4, 166.7, 164.4, 156.3, 131.8, 127.8, 114.0, 79.8, 62.7, 61.4, 55.6, 33.6, 29.7, 28.4, 14.0. **HRMS** (*m/z*) (ESI): calcd for $C_{25}H_{34}N_2O_6S_2Na^+$ $[M+Na]^+$: 545.1751, found 545.1752.



Pyrrolidine-1-carbothioic dithioperoxyanhydride (5). White solid. mp: 140-142 ℃. Petroleum ether/ethyl acetate = 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.01 - 3.93 (m, 8H), 2.20 - 2.12 (m, 4H), 2.05 - 1.99 (m, 4H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 189.2, 57.0, 51.0, 26.6, 24.3. **HRMS** (*m/z*) (ESI): calcd for $C_{10}H_{17}N_2S_4^+$ $[M+H]^+$: 293.0269, found 293.0269.



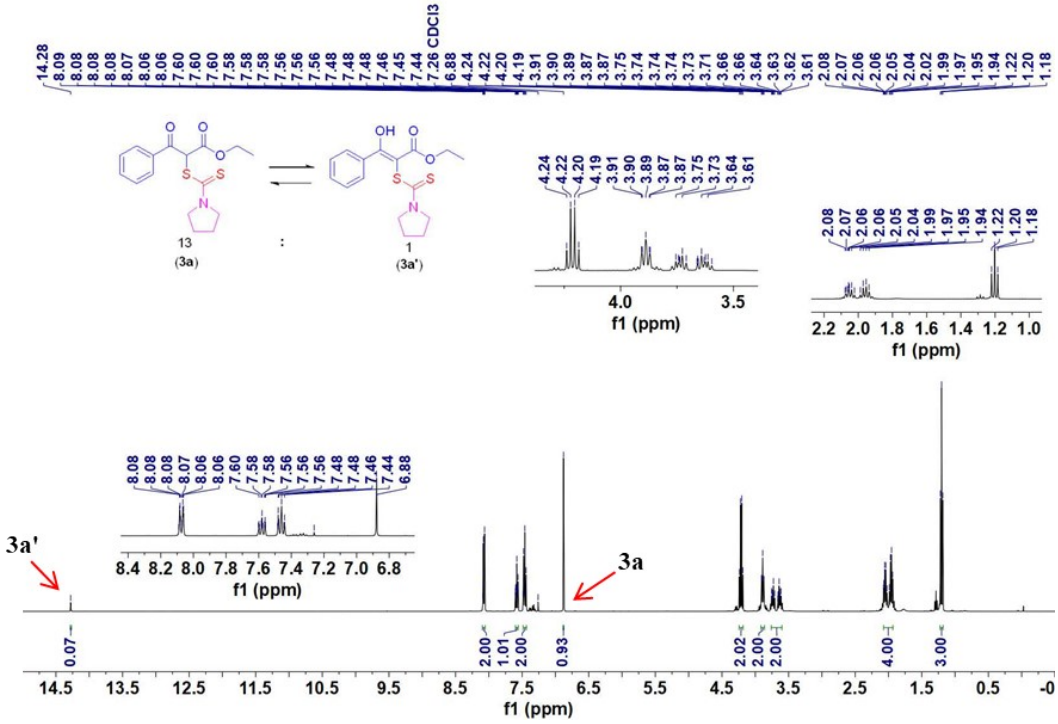
Sodium pyrrolidine-1-carbodithioate (6)[1]**.** White solid. mp: > 300 ℃. Ethyl acetate as eluent for column chromatography. **^{1}H NMR** (400 MHz, Methanol-d_4) δ 3.87 - 3.77 (m, 4H), 1.99 - 1.93 (m, 4H). **^{13}C NMR** (100 MHz, Methanol-d_4) δ 207.9, 55.2, 27.1.

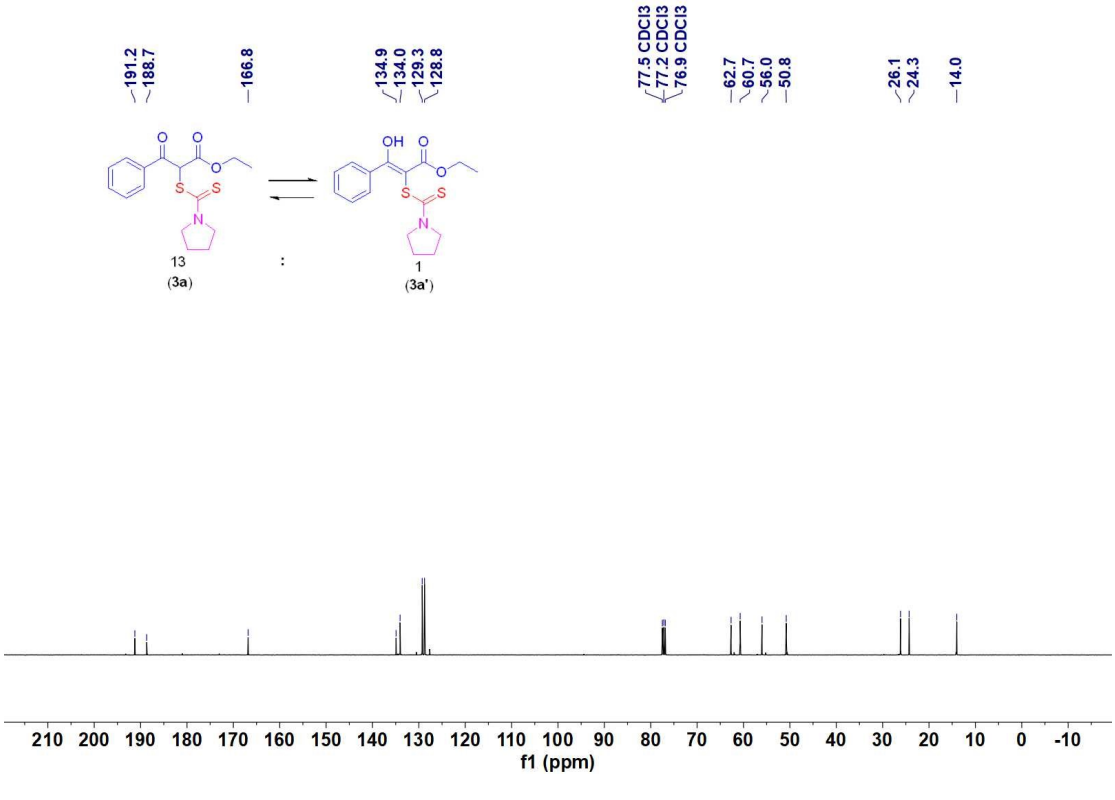
References

[1] M. M. Wang, W. C. Chu,Y. Yang, Q. Q. Yang, S. S. Qin, E. Zhang, *Bioorg. Med. Chem. Lett*., 2018, **28**, 3436-3440.

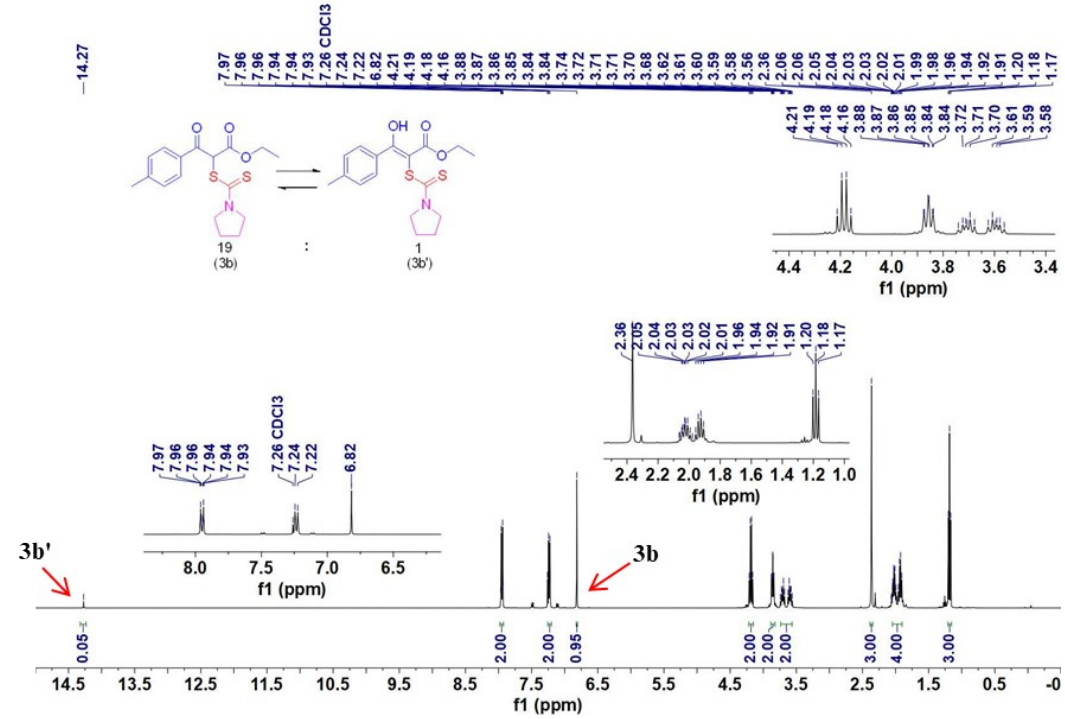
7. Copies of ^{1}H NMR and ^{13}C NMR for the Products

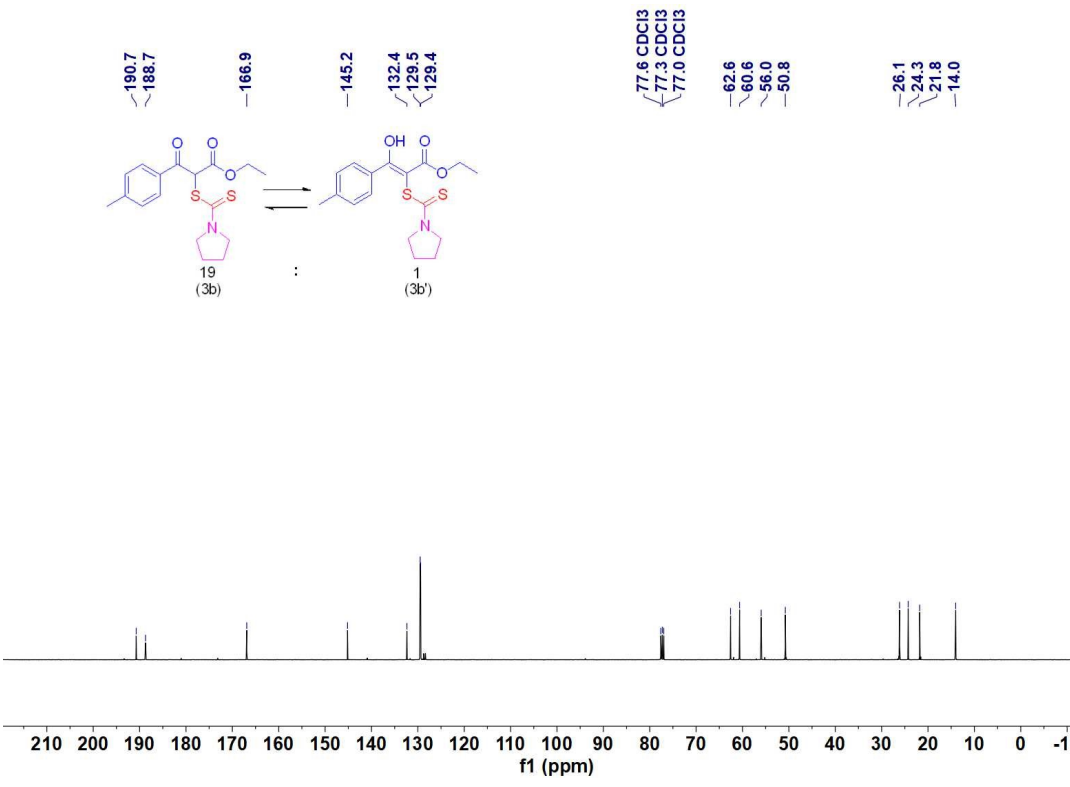
Ethyl 3-oxo-3-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)propanoate (3a)



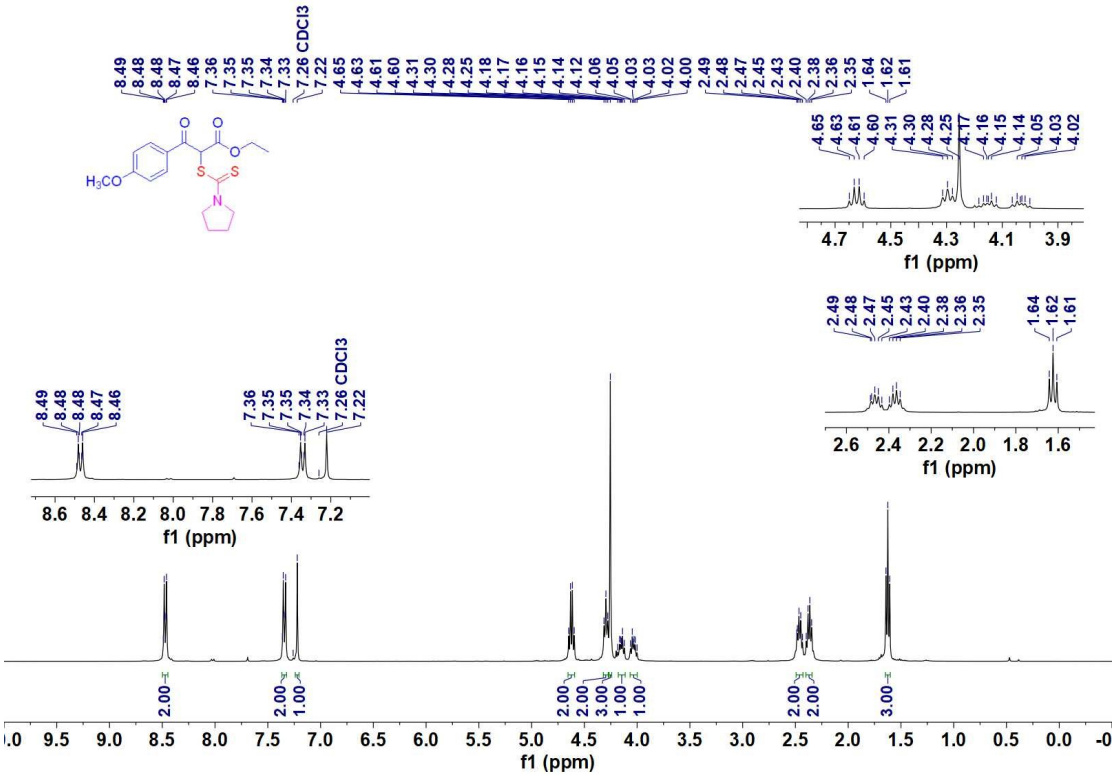


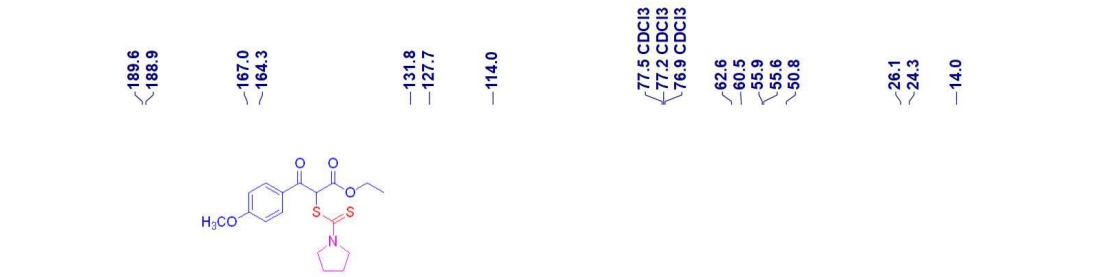
Ethyl 3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)-3-(*p*-tolyl)propanoate (3b).



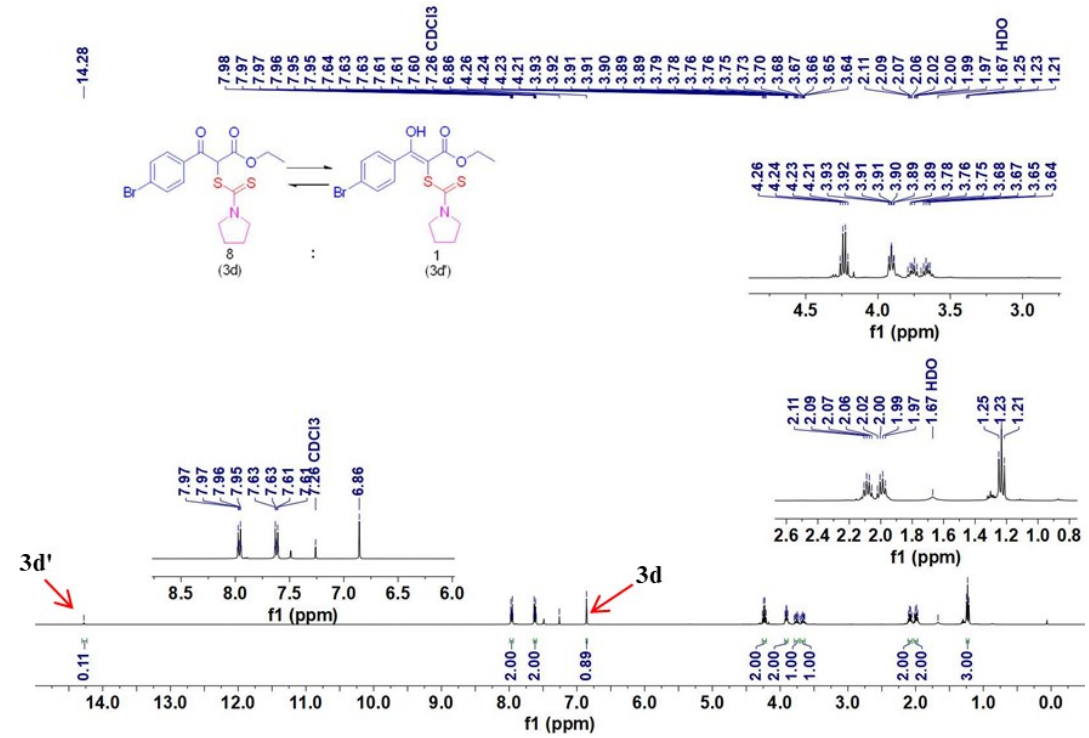


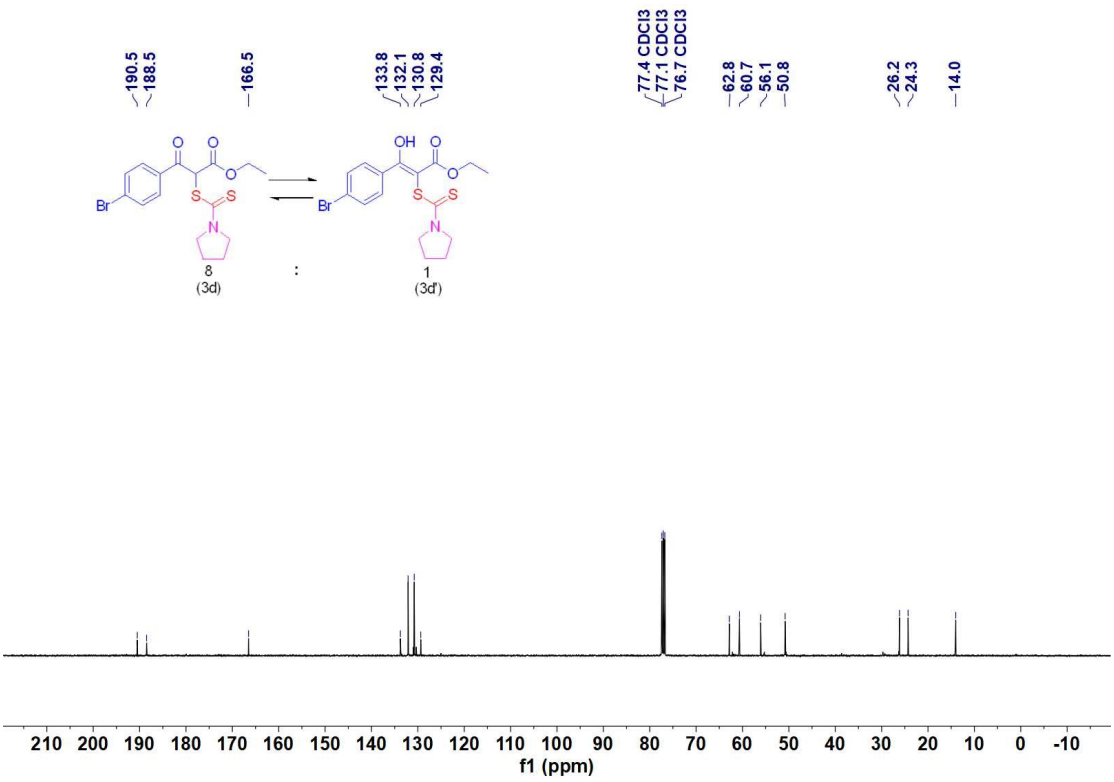
Ethyl 3-(4-methoxyphenyl)-3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)propanoate (3c)



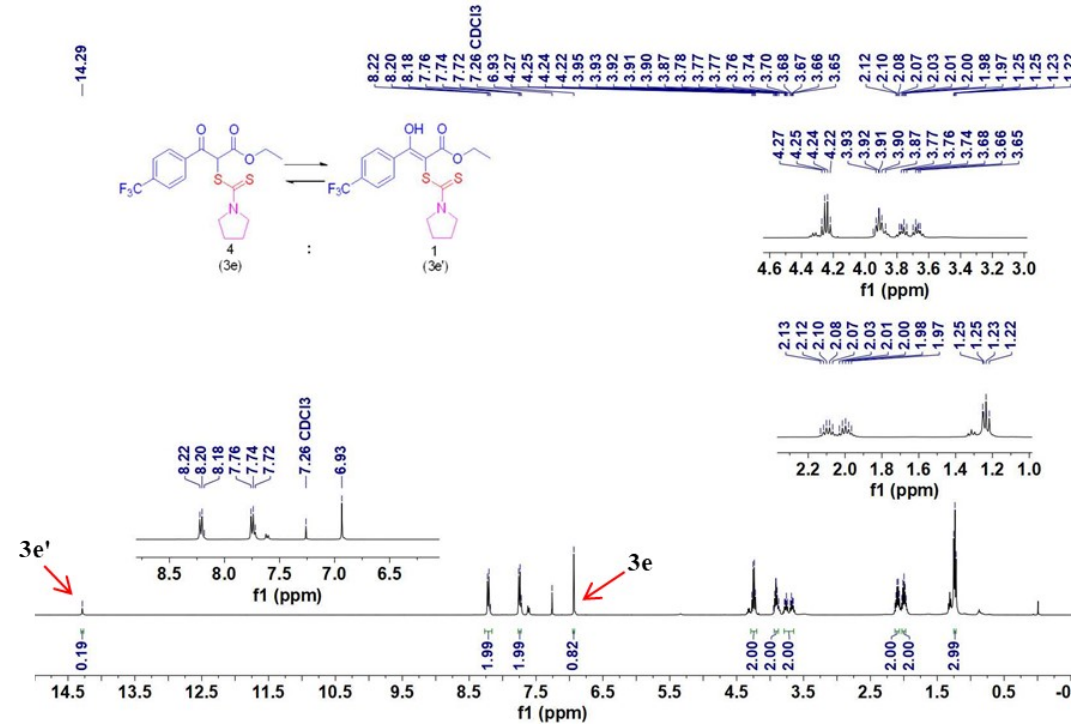


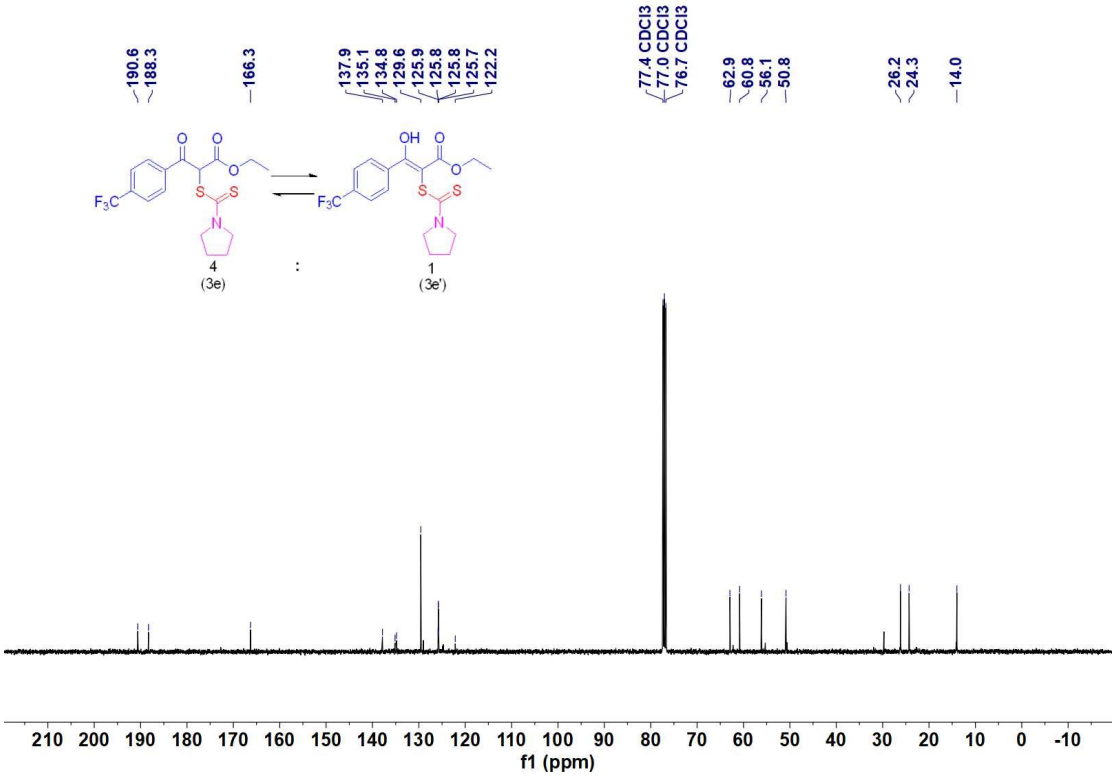
Ethyl 3-(4-bromophenyl)-3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)propanoate (3d)



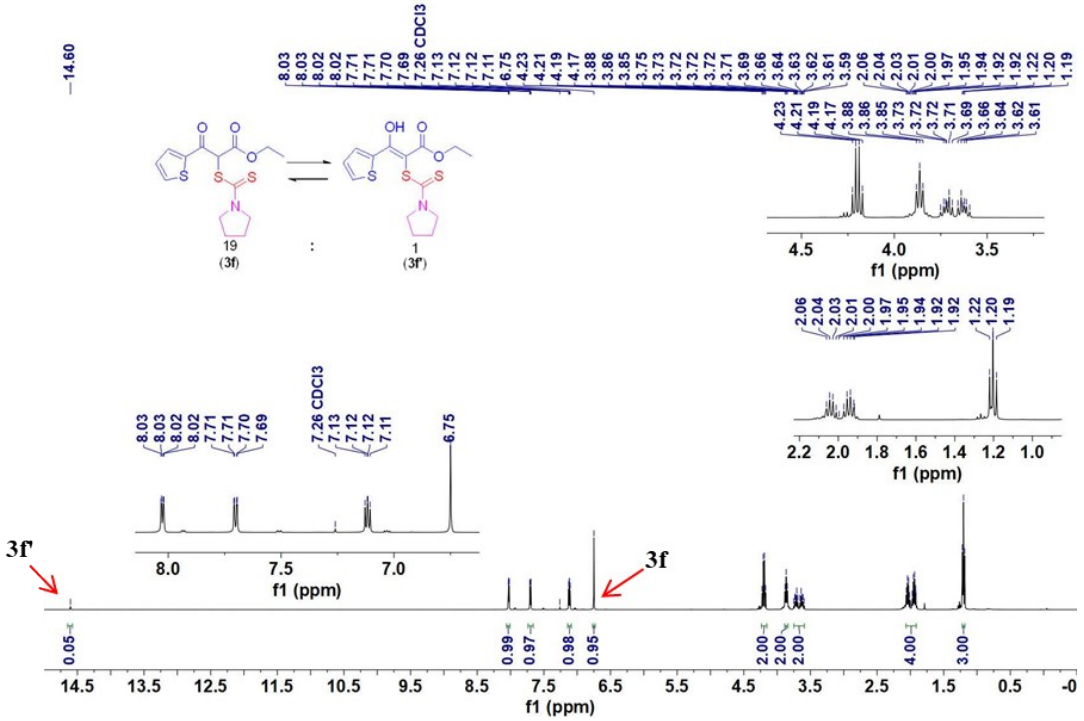


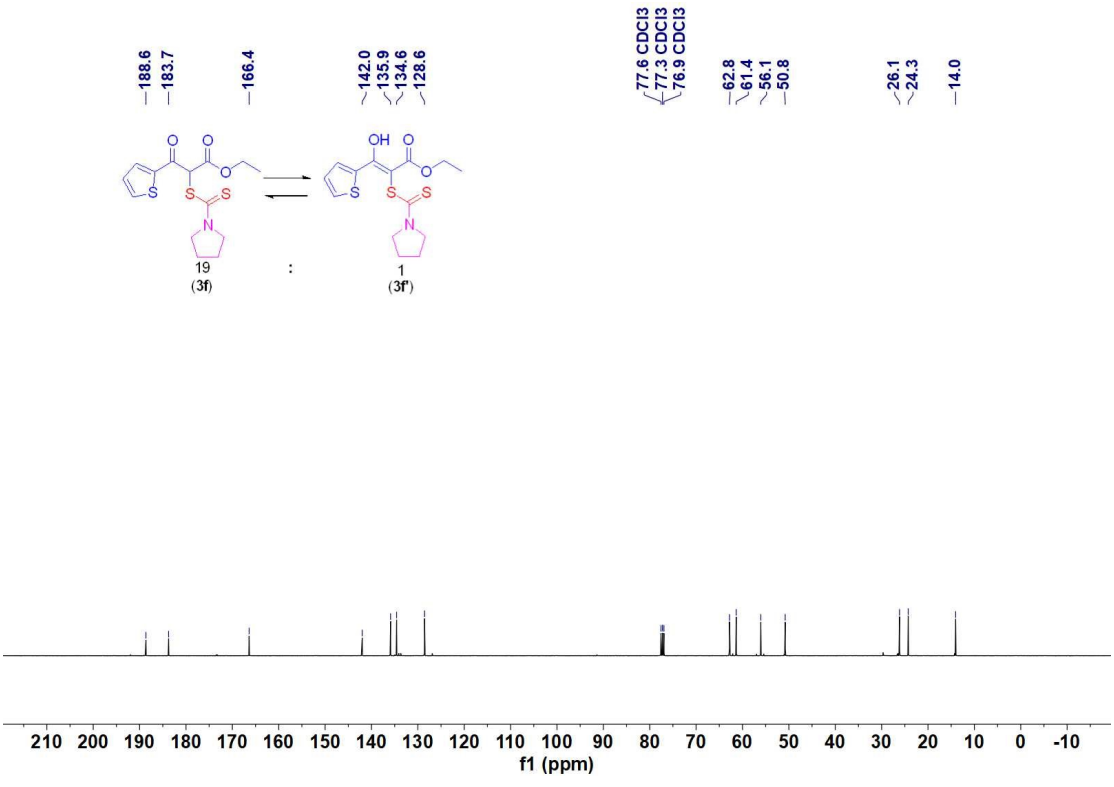
Ethyl 3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)-3-(4-(trifluoromethyl)phenyl)propanoate (3e)



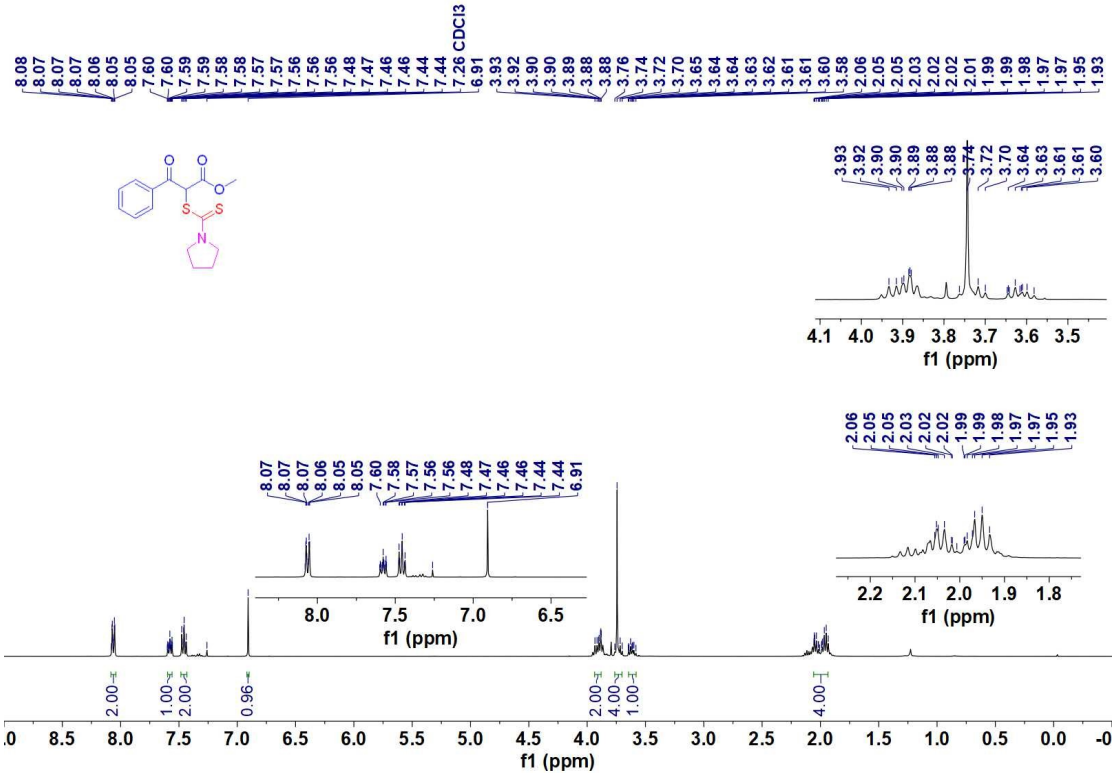


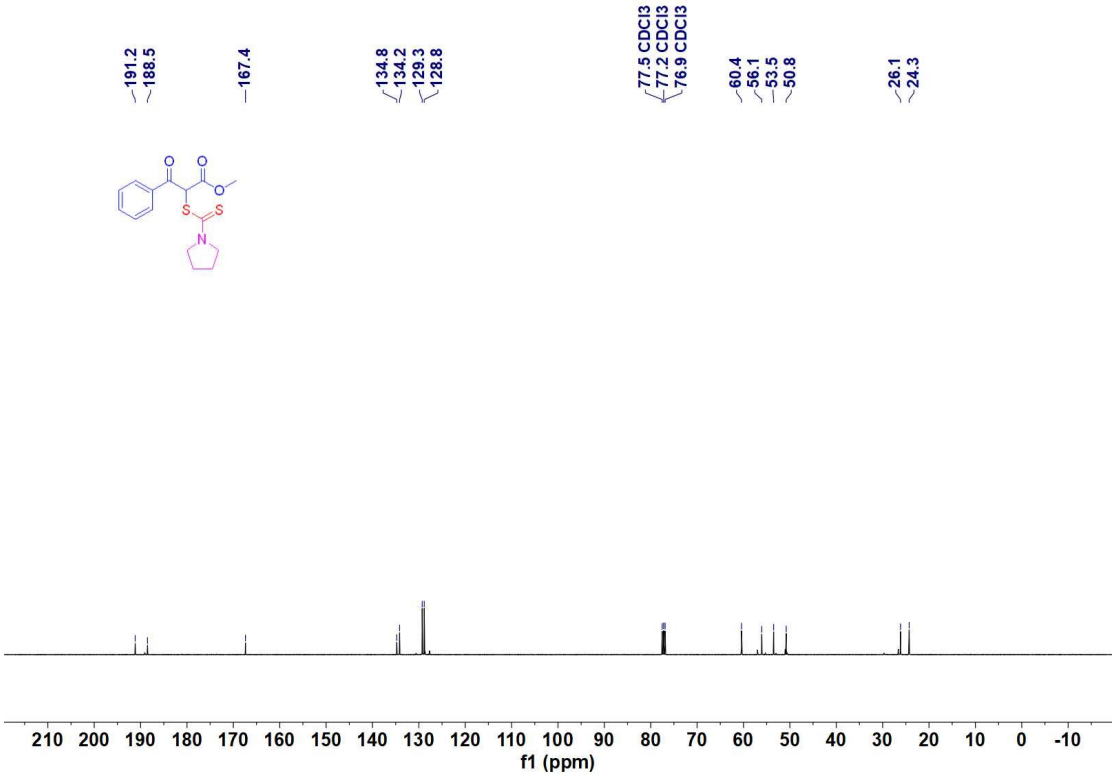
Ethyl 3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)-3-(thiophen-2-yl)propanoate (3f)



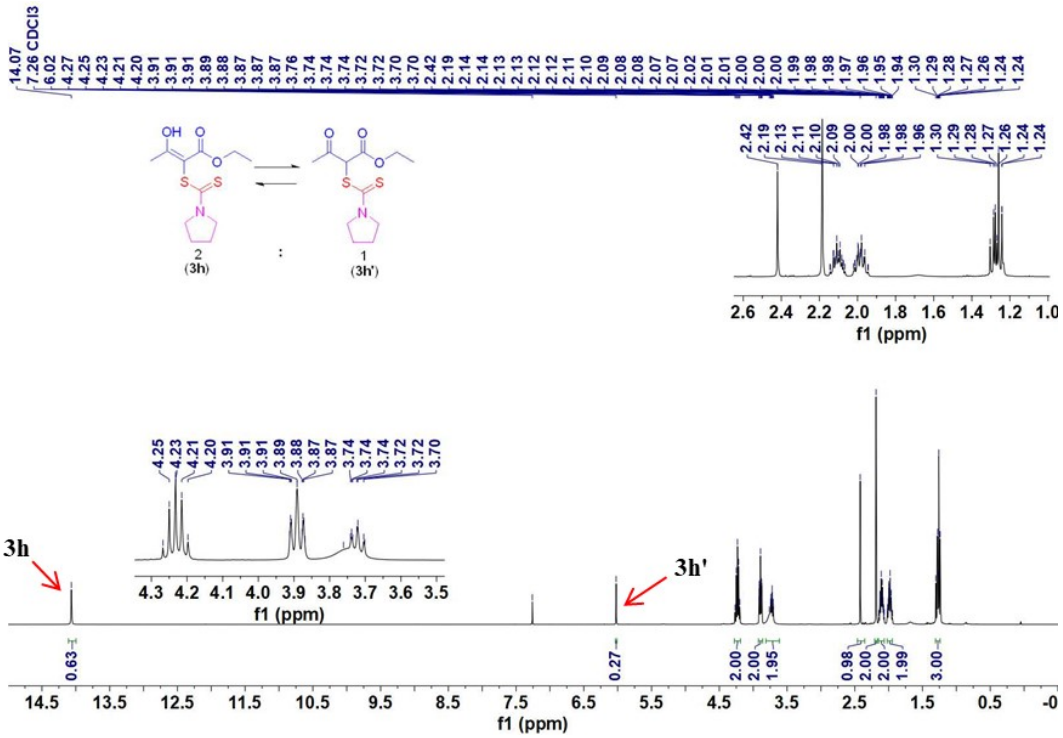


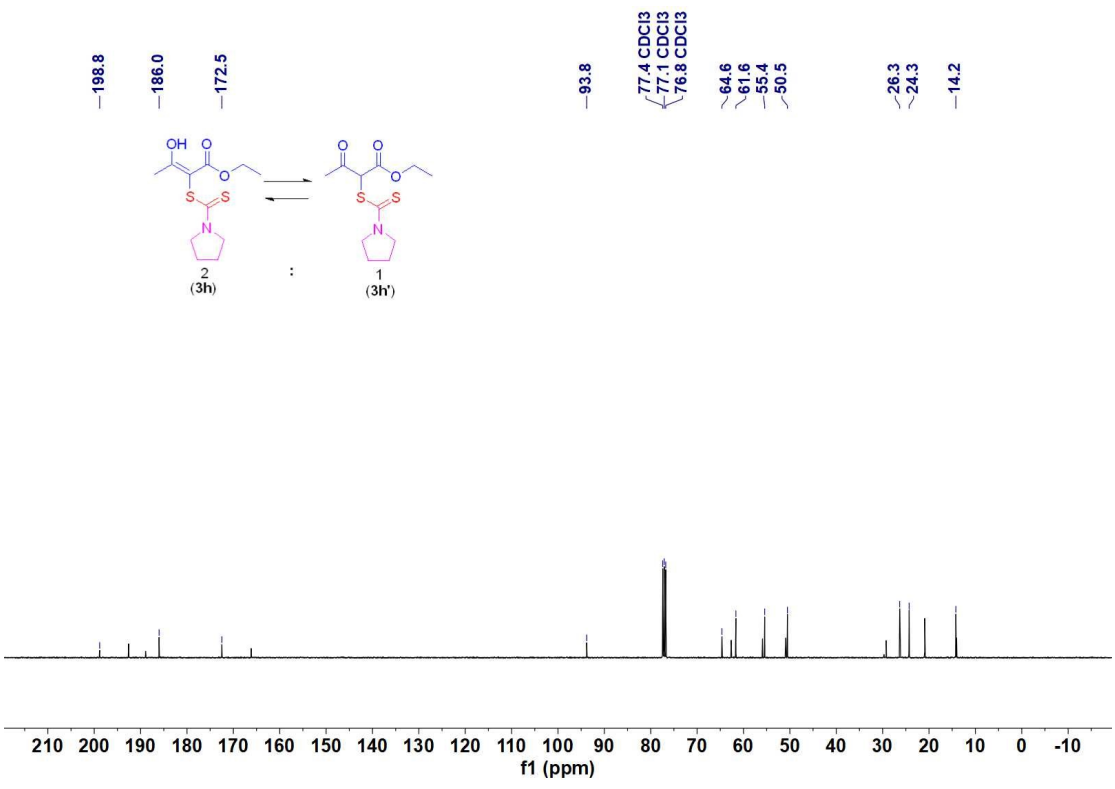
Methyl 3-oxo-3-phenyl-2-((pyrrolidine-1-carbonothioyl)thio)propanoate (3g)



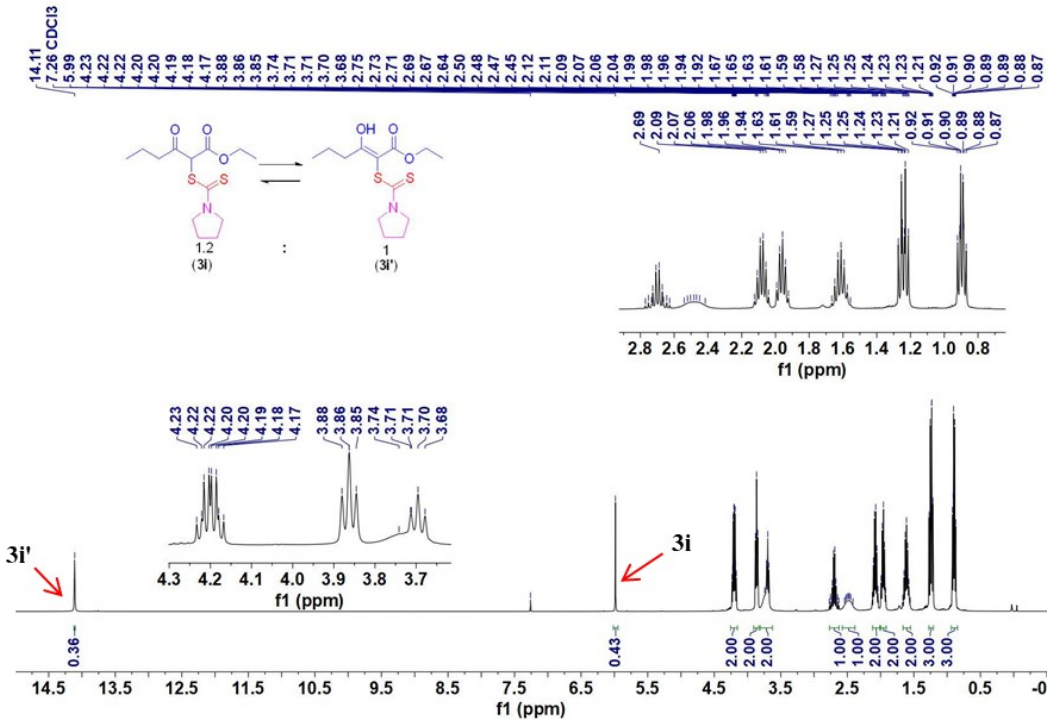


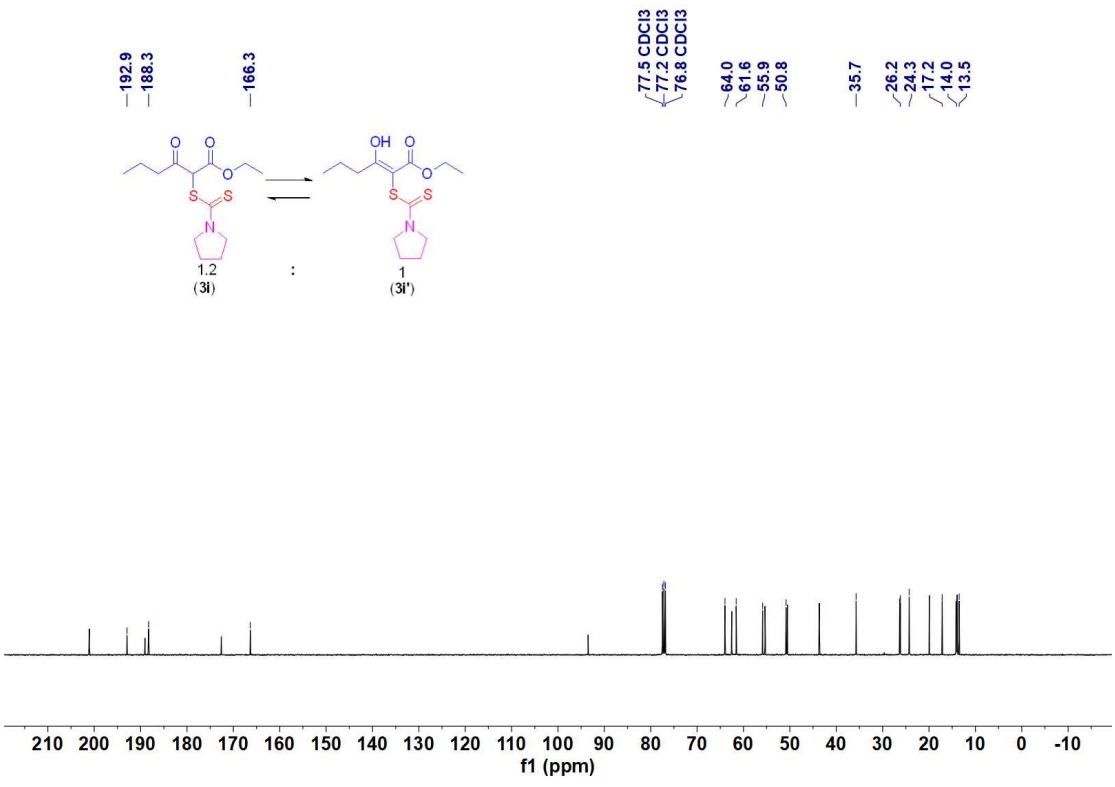
Ethyl (*E*)-3-hydroxy-2-((pyrrolidine-1-carbonothioyl)thio)but-2-enoate (3h).



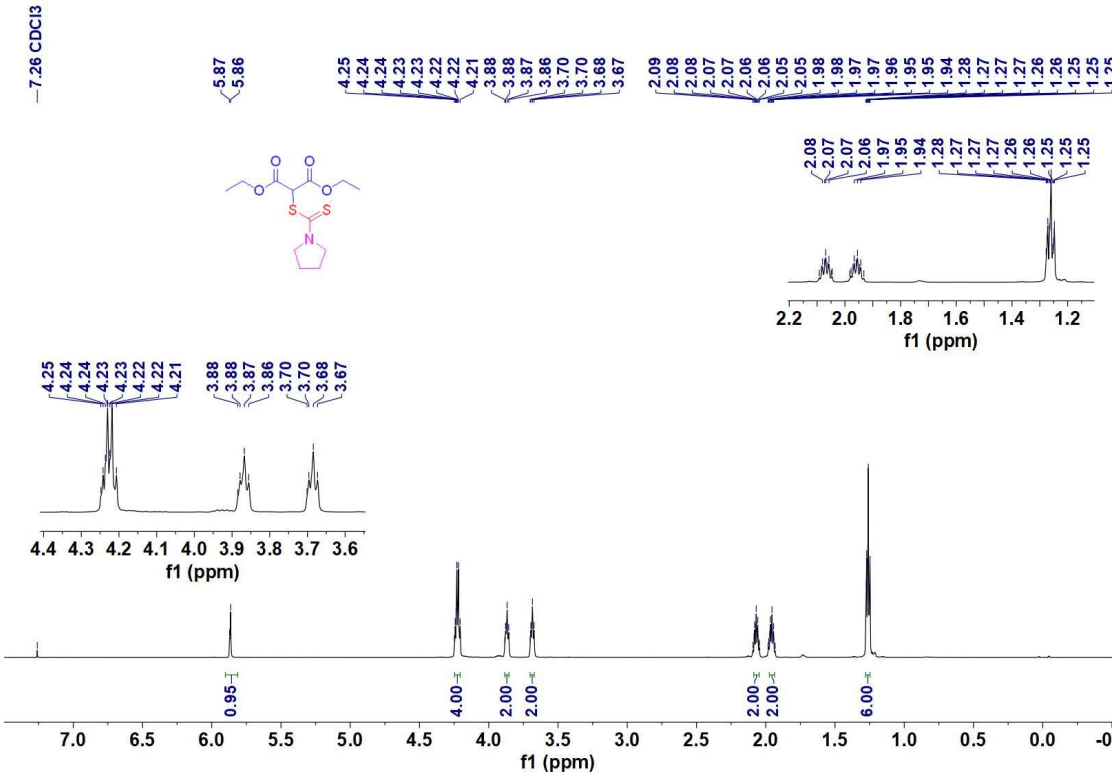


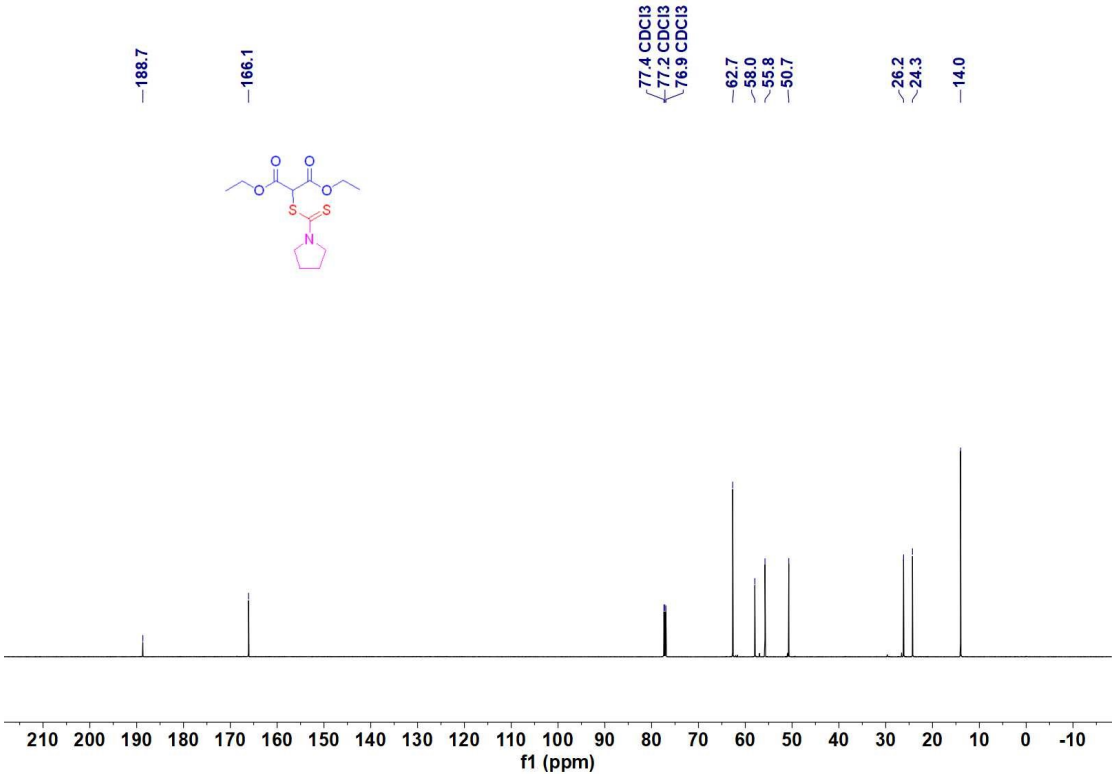
Ethyl 3-oxo-2-((pyrrolidine-1-carbonothioyl)thio)hexanoate (3i)



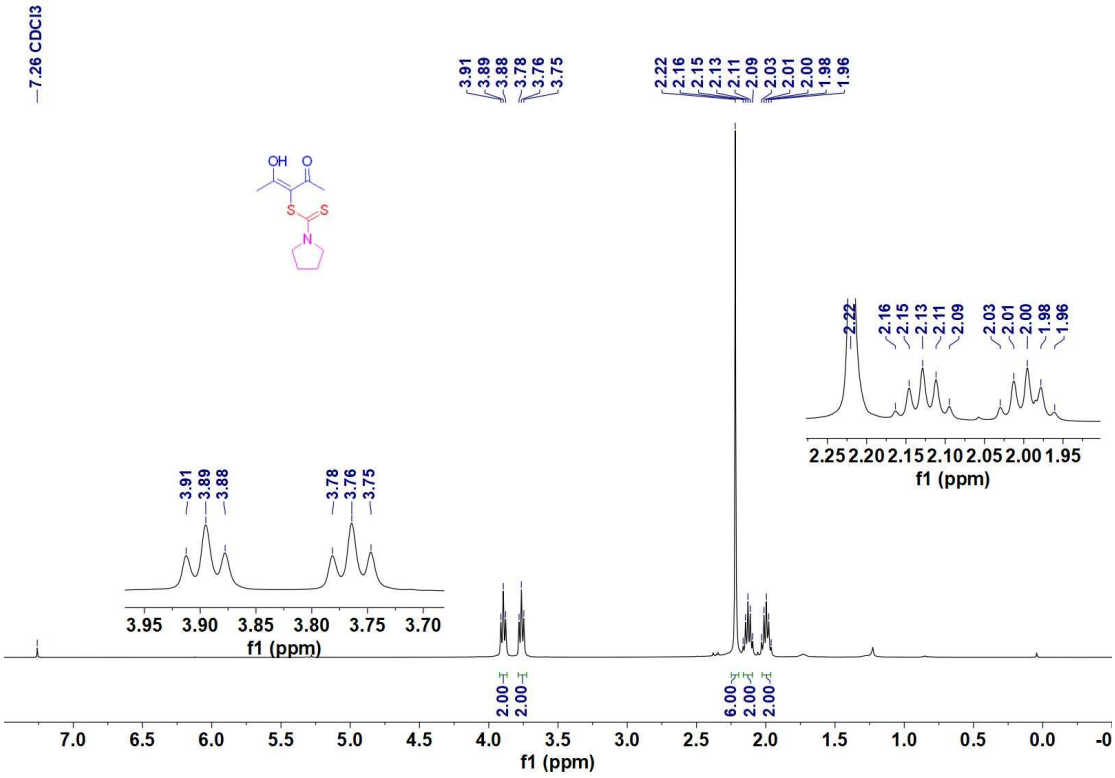


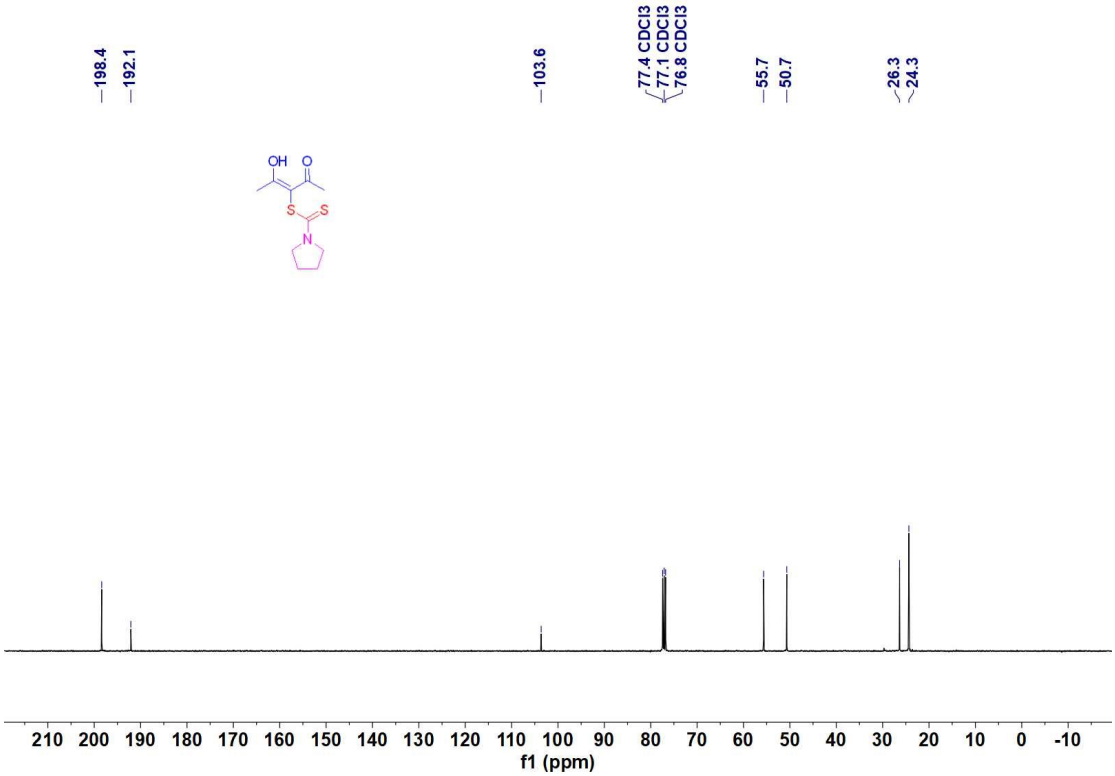
Diethyl 2-((pyrrolidine-1-carbonothioyl)thio)malonate (3j)



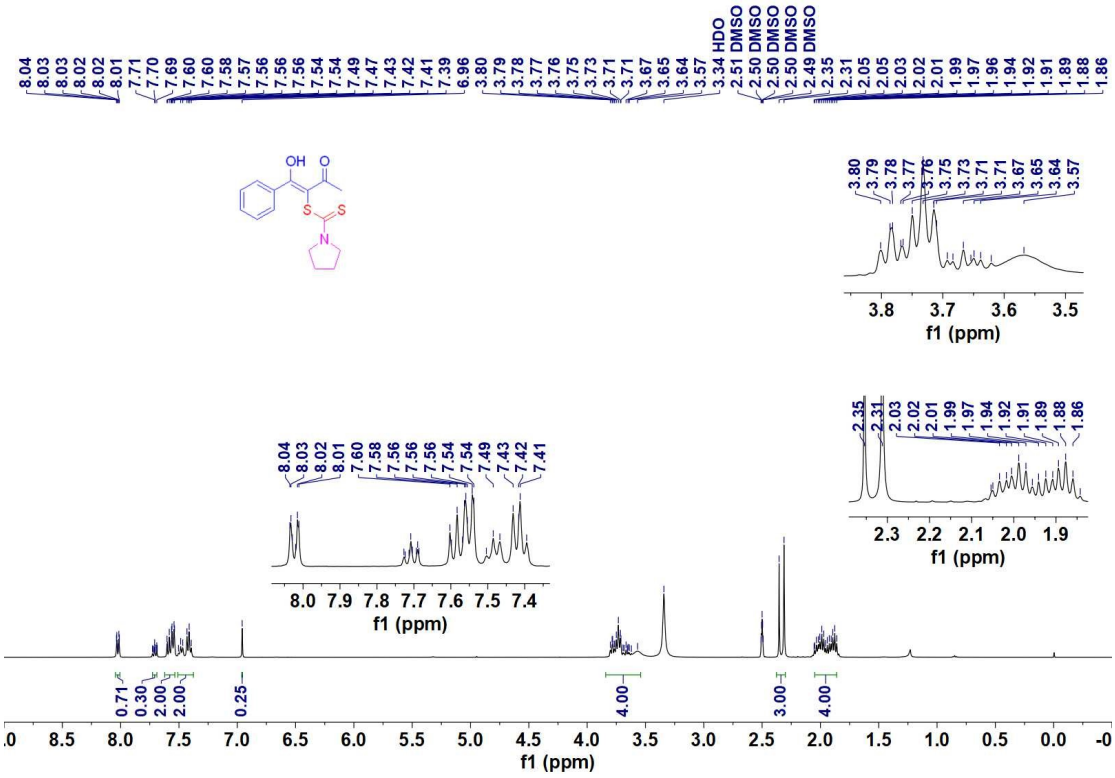


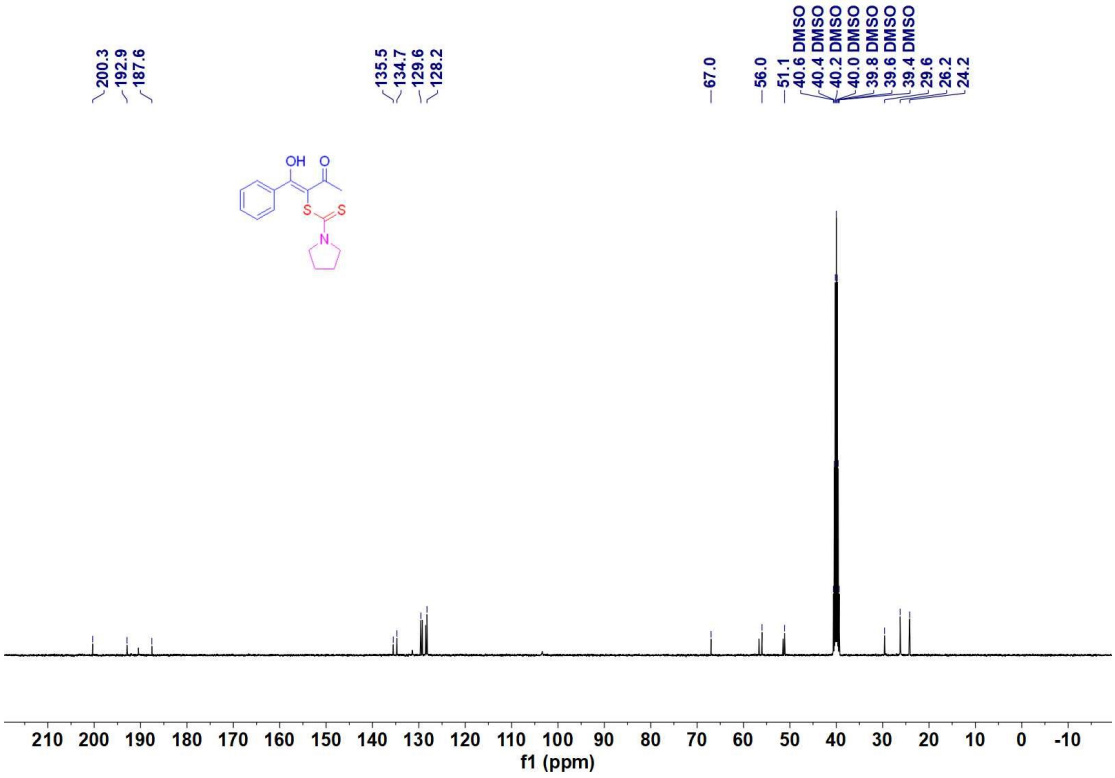
(*E*)-2-hydroxy-4-oxopent-2-en-3-yl pyrrolidine-1-carbodithioate (3k)



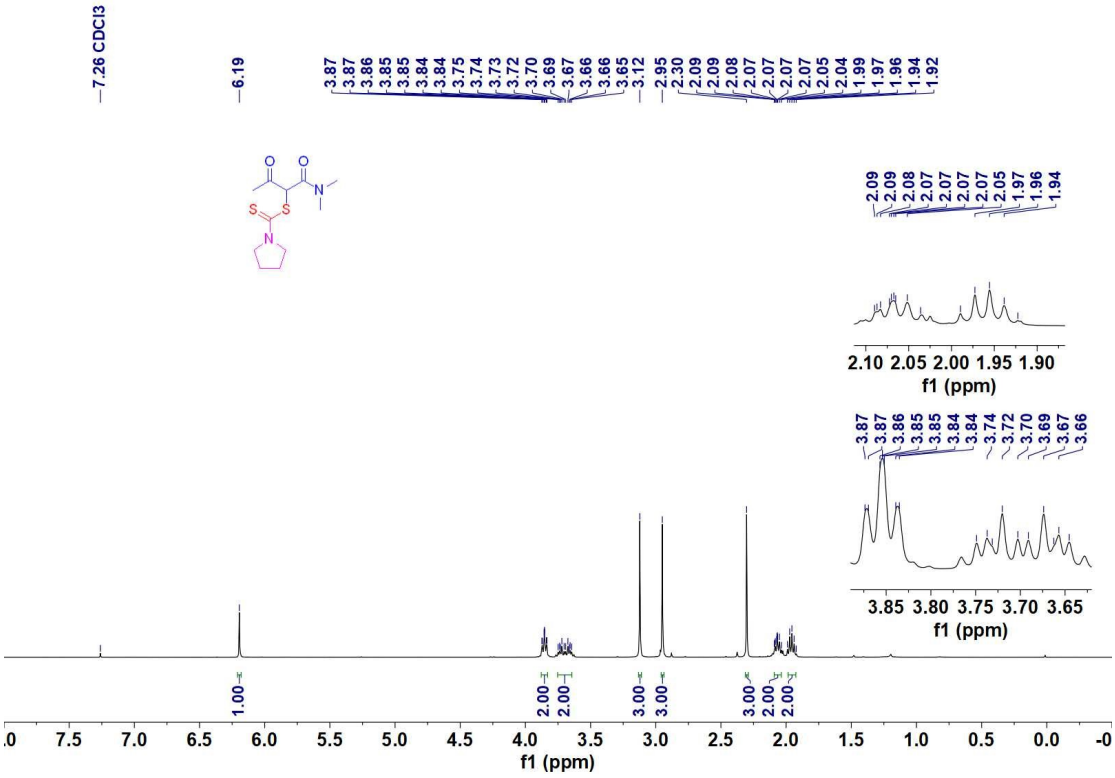


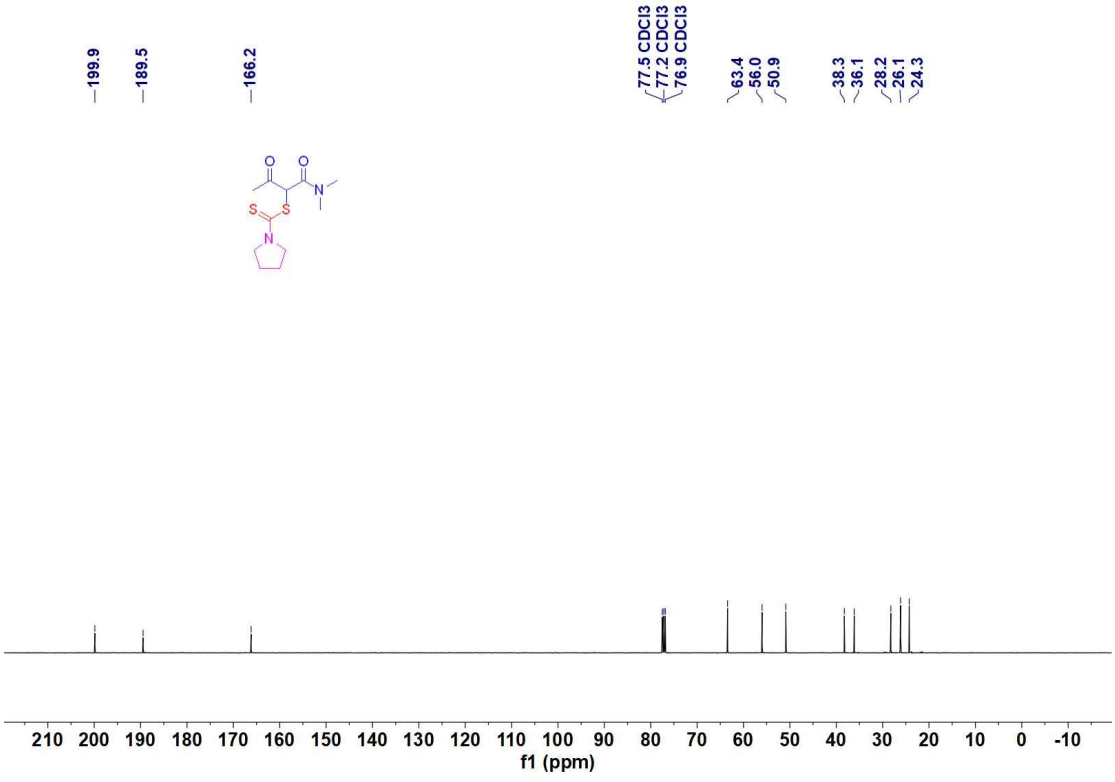
(*E*)-1-hydroxy-3-oxo-1-phenylbut-1-en-2-yl pyrrolidine-1-carbodithioate (3l)



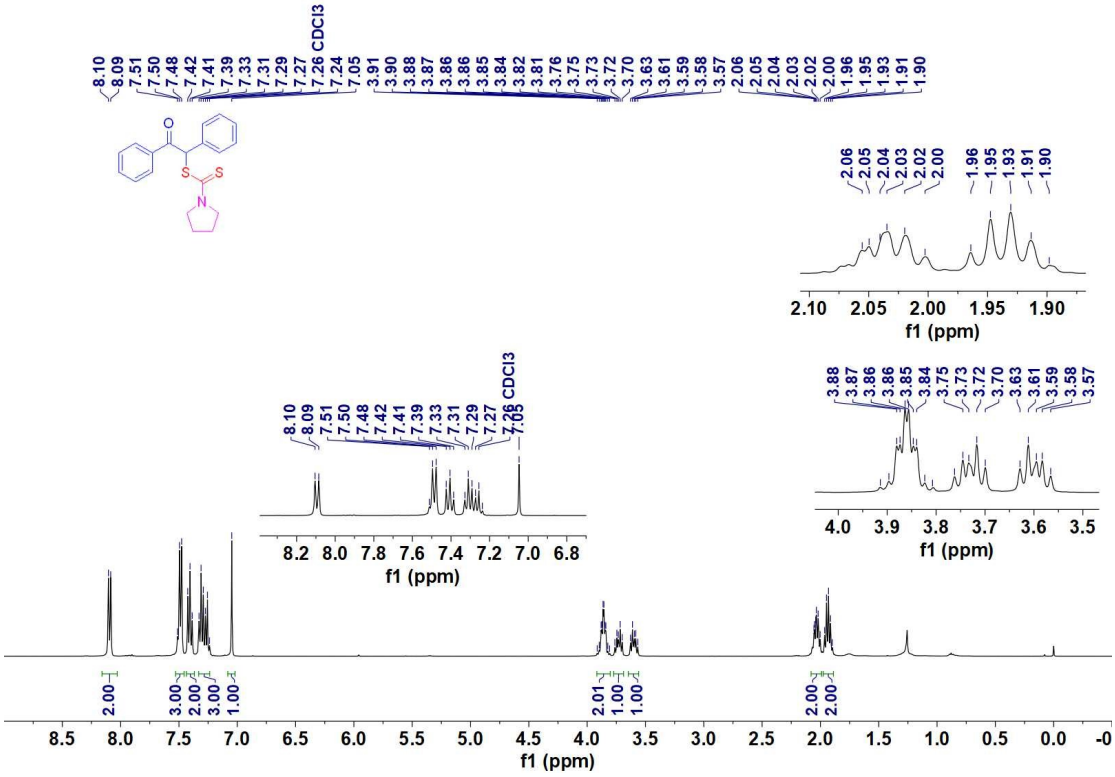


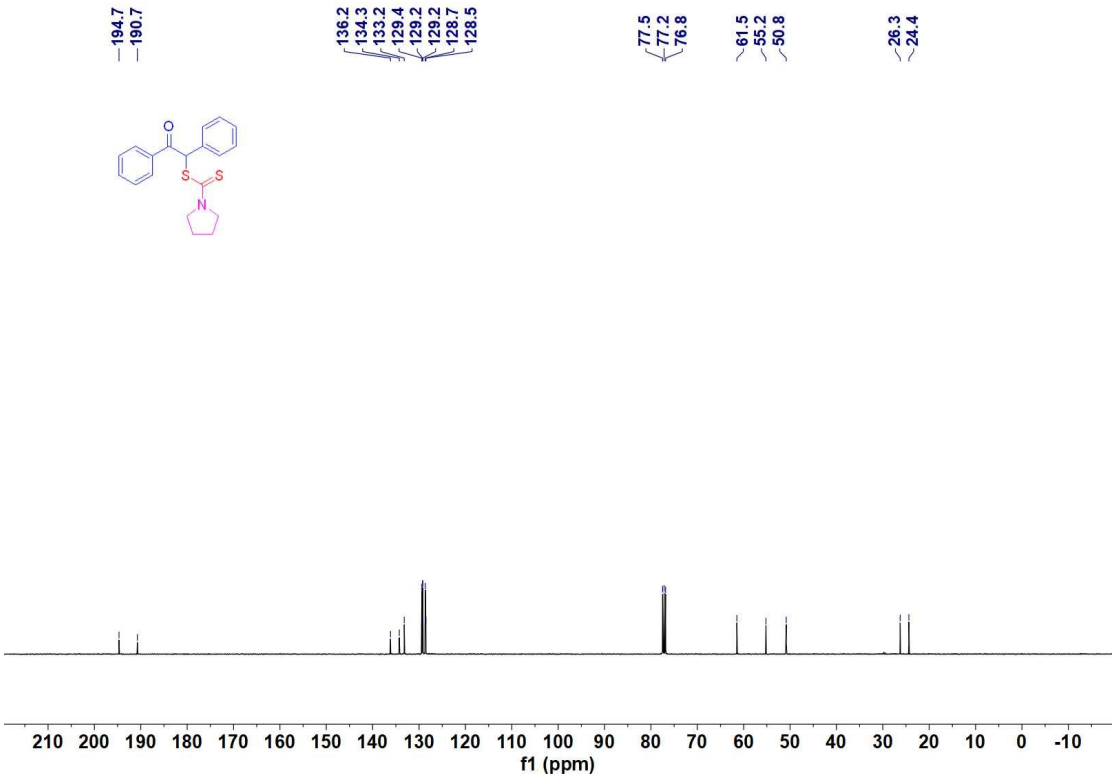
1-(Dimethylamino)-1,3-dioxobutan-2-yl pyrrolidine-1-carbodithioate (3m)



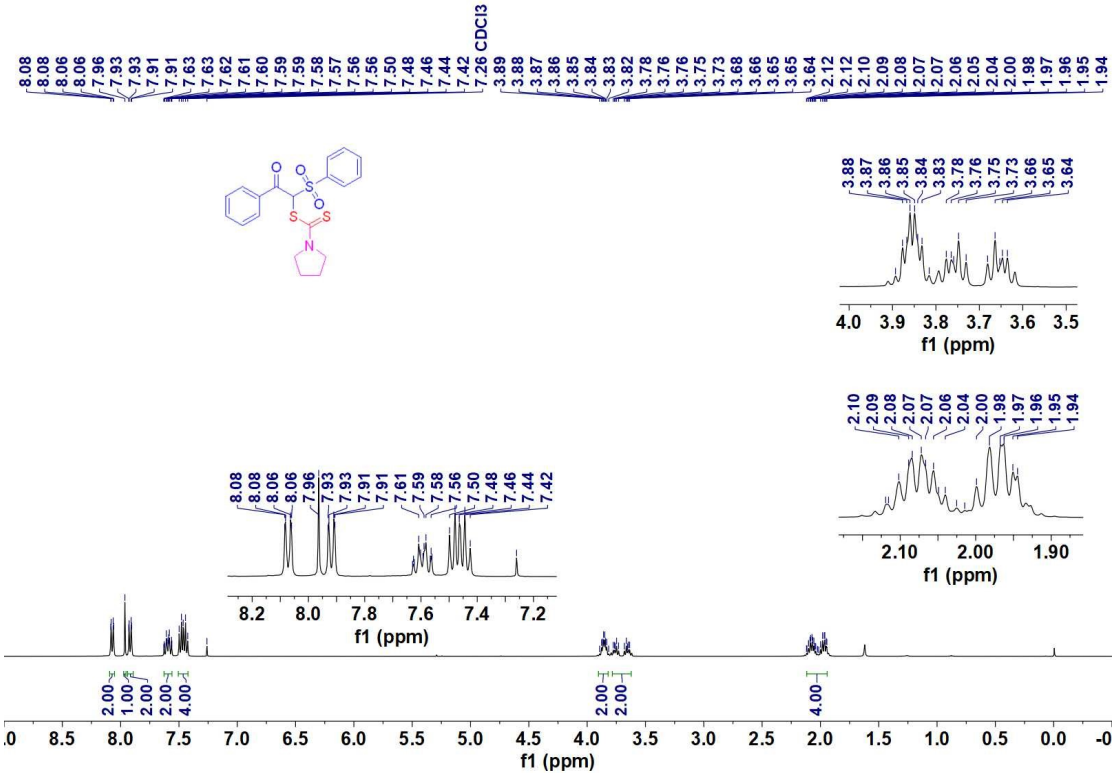


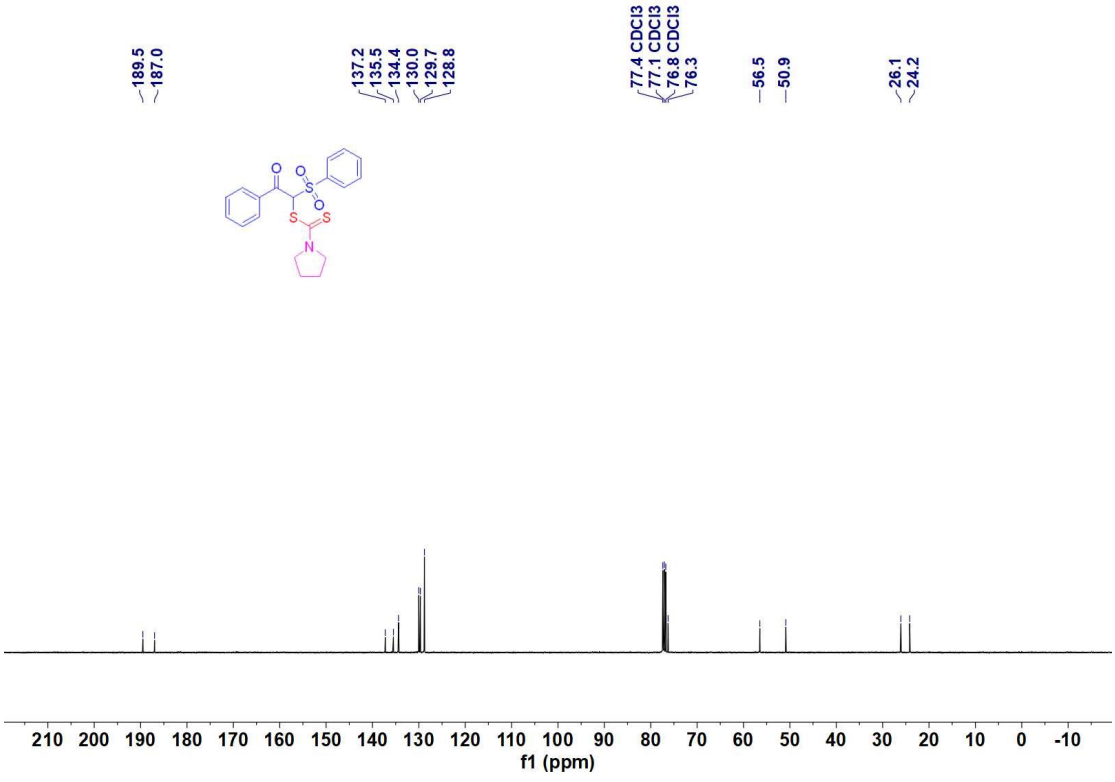
2-Oxo-1,2-diphenylethyl pyrrolidine-1-carbodithioate (3n)



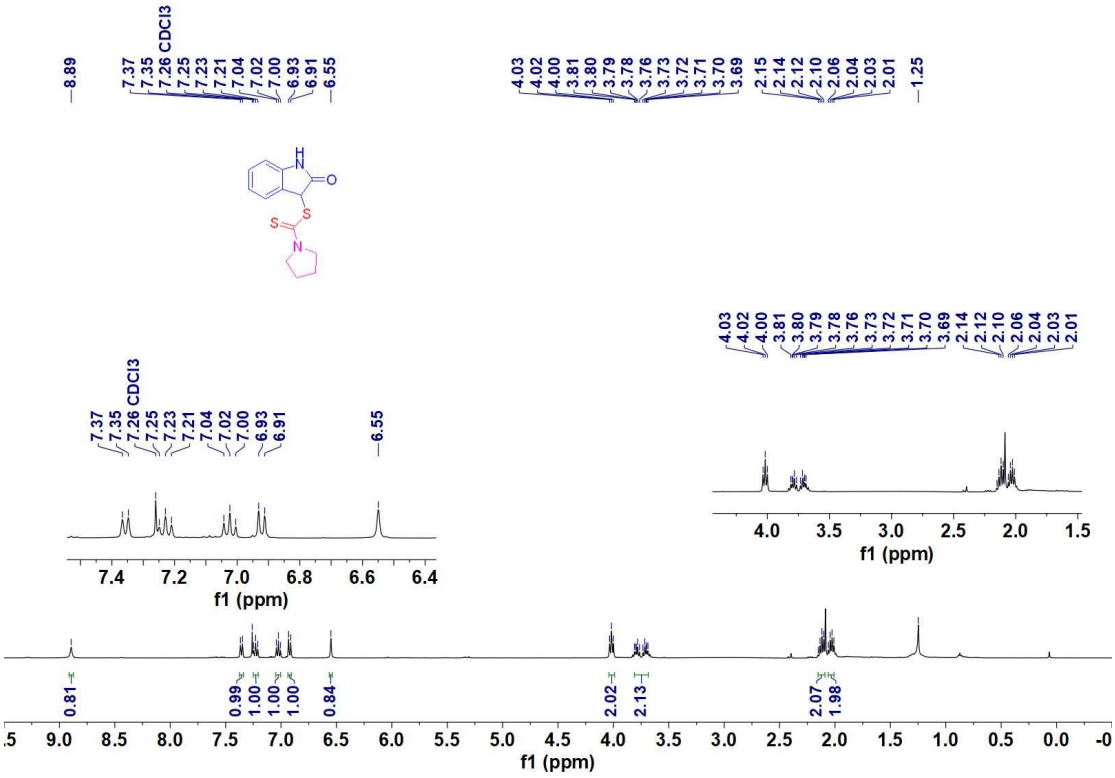


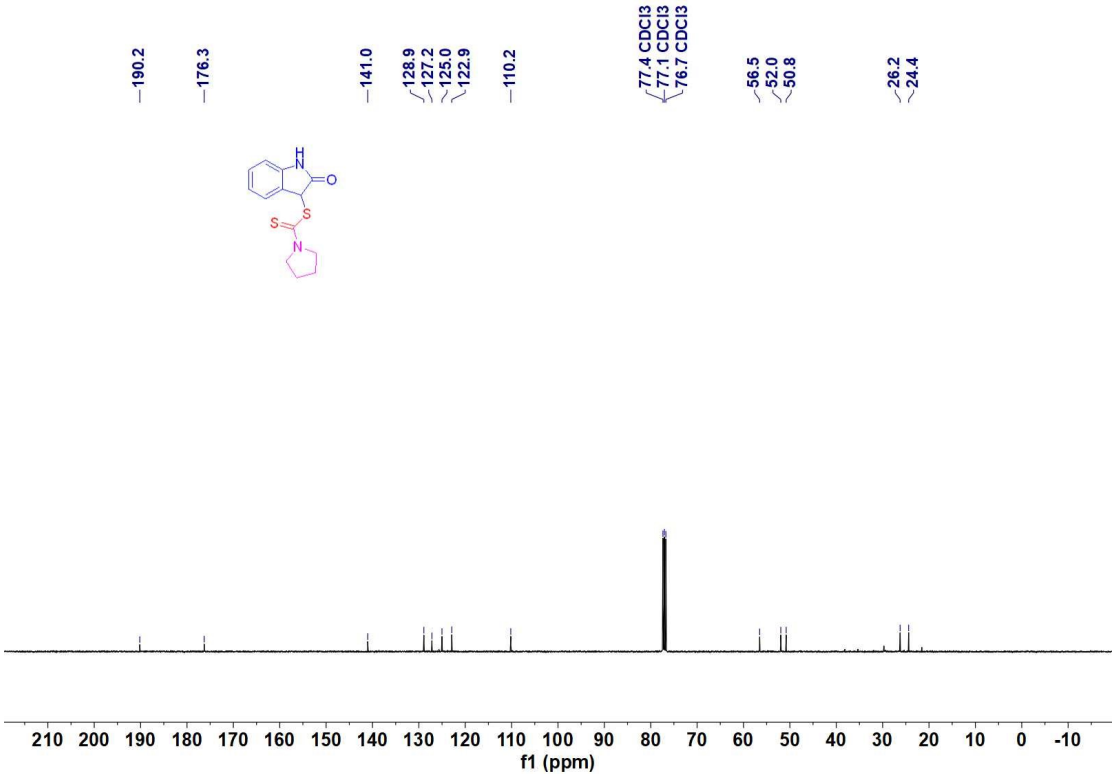
2-Oxo-2-phenyl-1-(phenylsulfonyl)ethyl pyrrolidine-1-carbodithioate (3o)



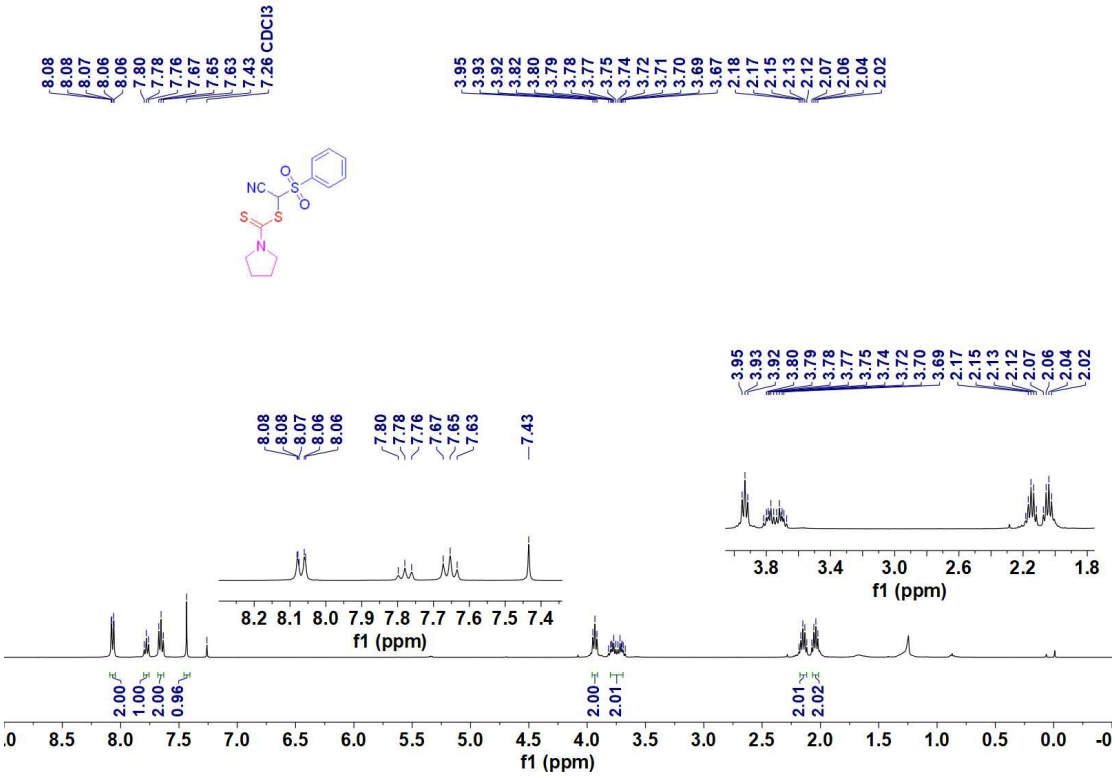


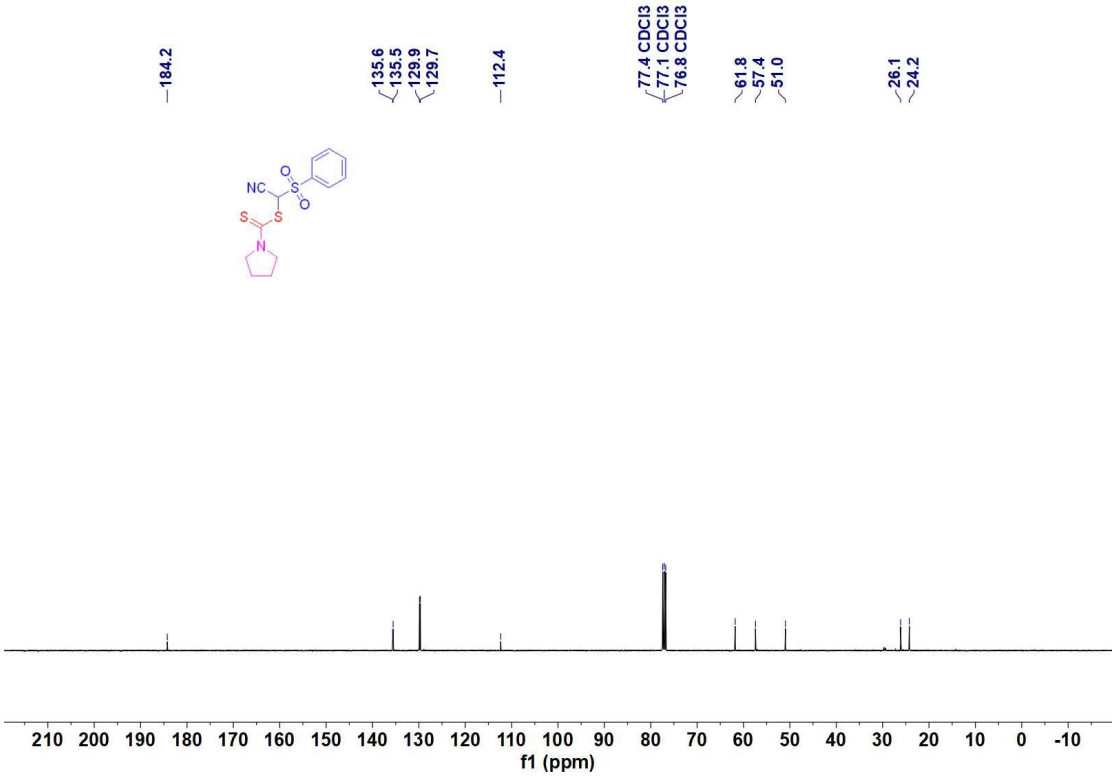
2-Oxoindolin-3-yl pyrrolidine-1-carbodithioate (3p)



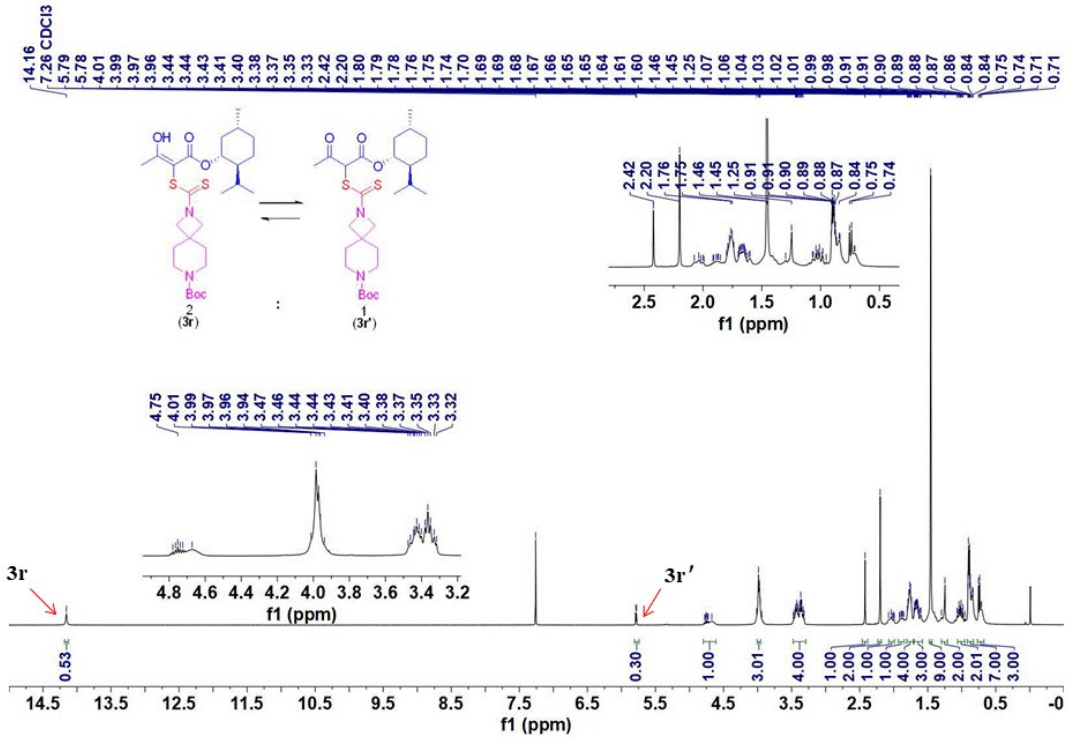


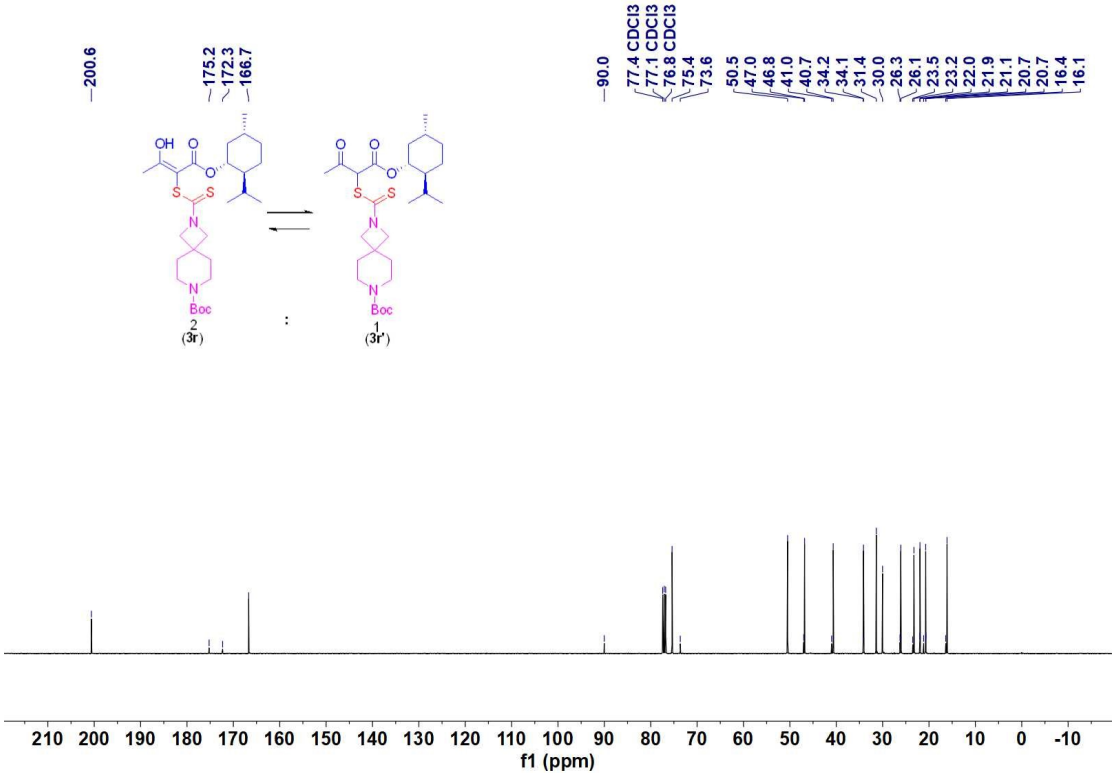
Cyano(phenylsulfonyl)methyl pyrrolidine-1-carbodithioate (3q)



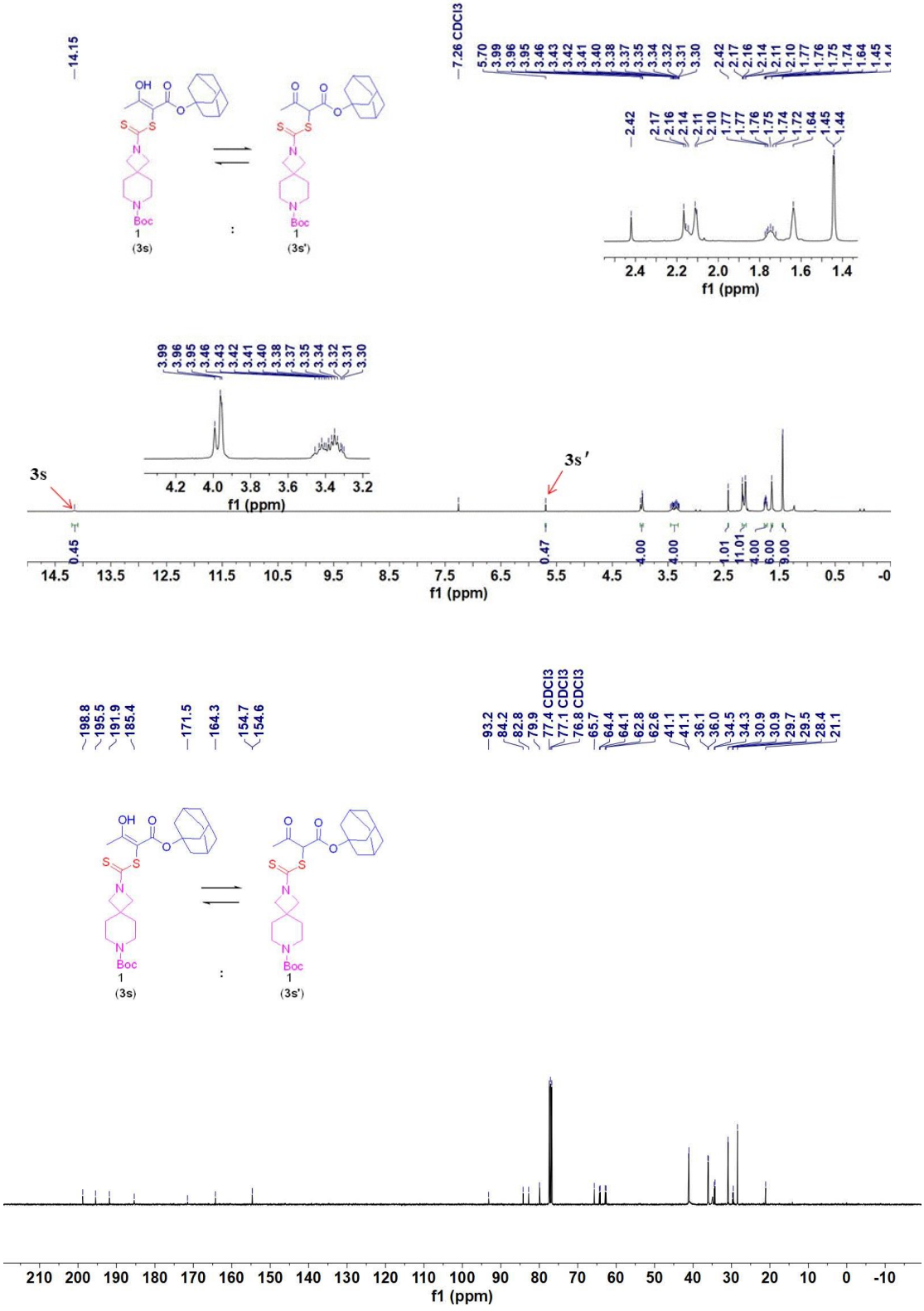


***Tert*-butyl 2-((((*E*)-3-hydroxy-1-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-1-oxobut-2-en-2-yl)thio)carbonothioyl)-2,7-diazaspiro[3.5]nonane-7-carboxylate (3r)**

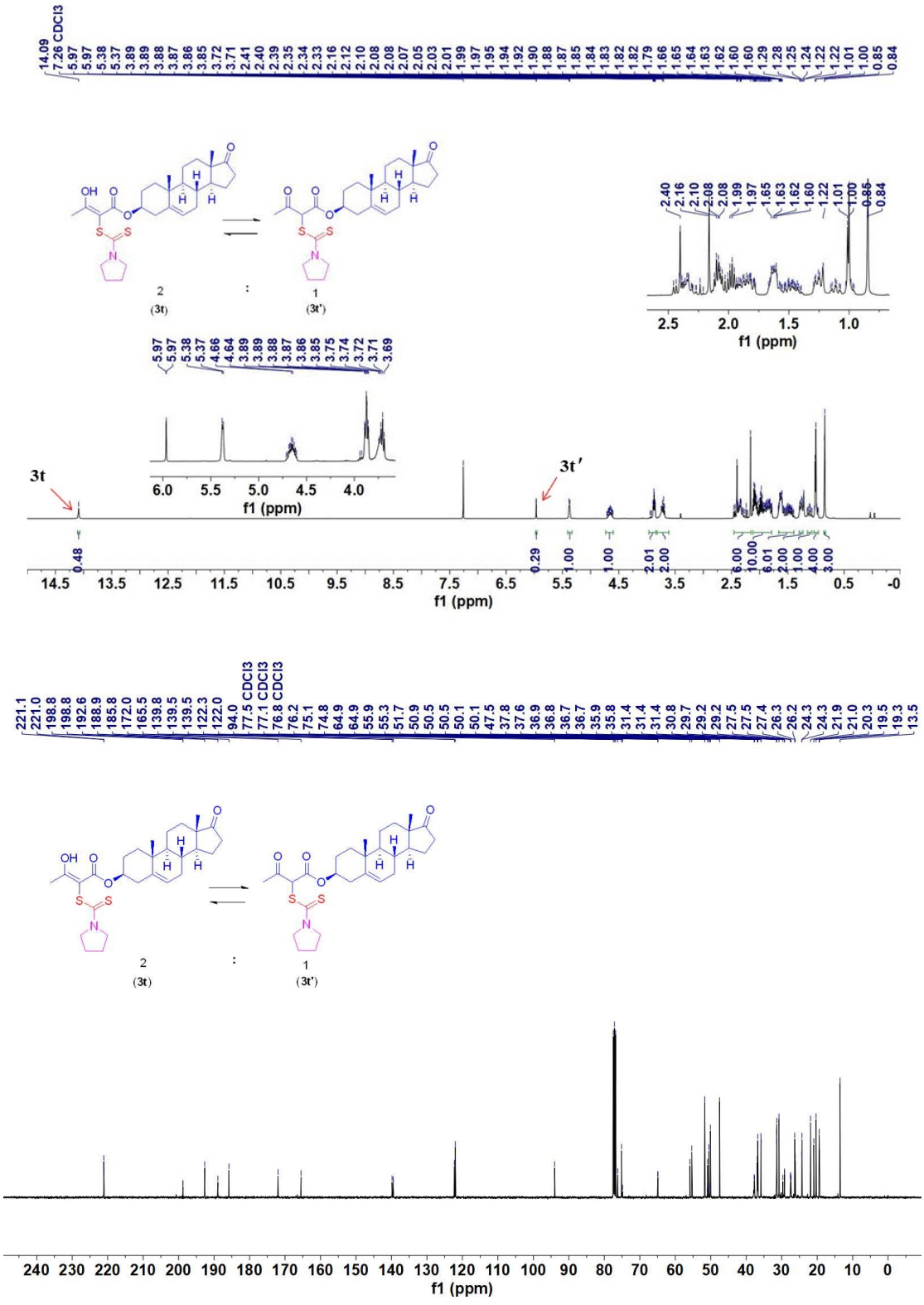




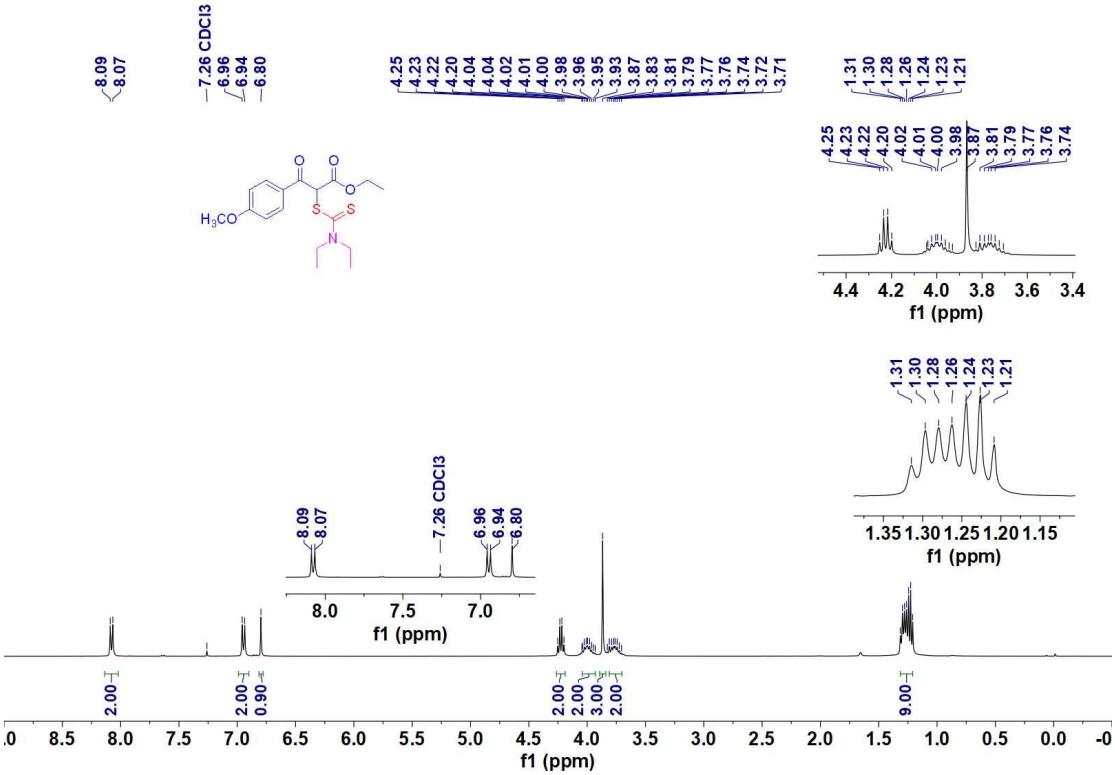
***Tert*-butyl (*E*)-2-(((1-(adamantan-1-yloxy)-3-hydroxy-1-oxobut-2-en-2-yl)thio)carbonothioyl) -2,7-diazaspiro[3.5]nonane-7-carboxylate (3s)**

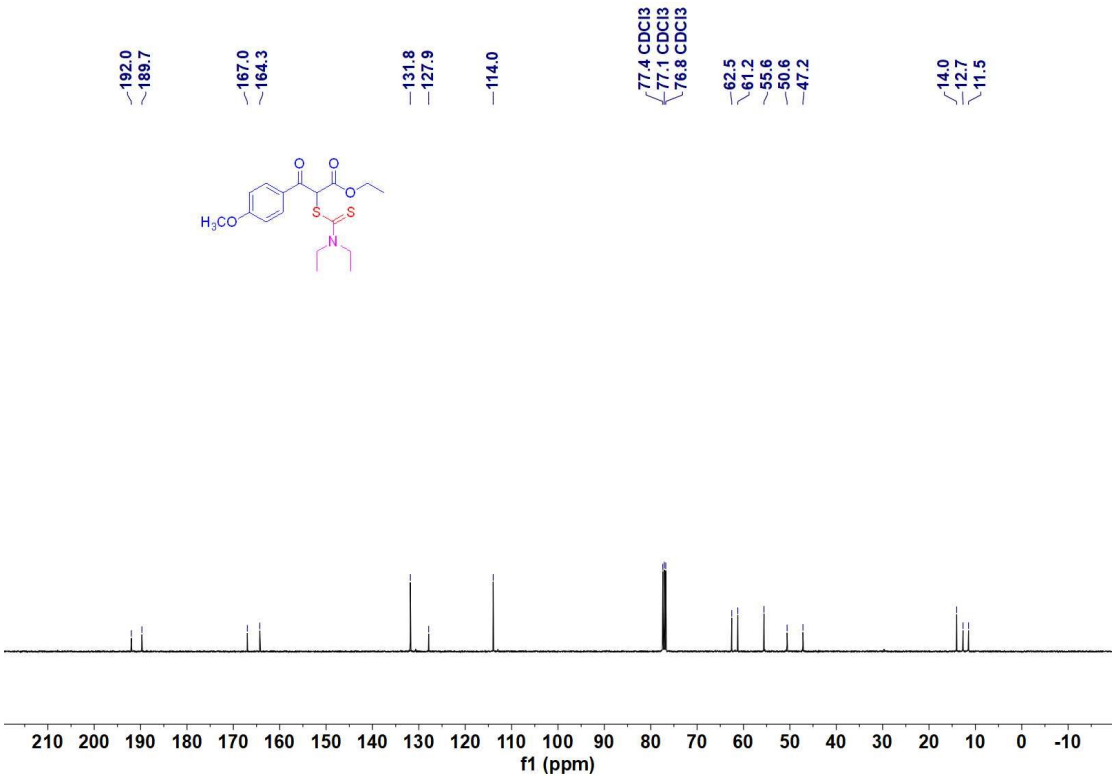


(3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (*E*)-3-hydroxy-2-((pyrrolidine-1-carbonothioyl)thio)
but-2-enoate (3t)

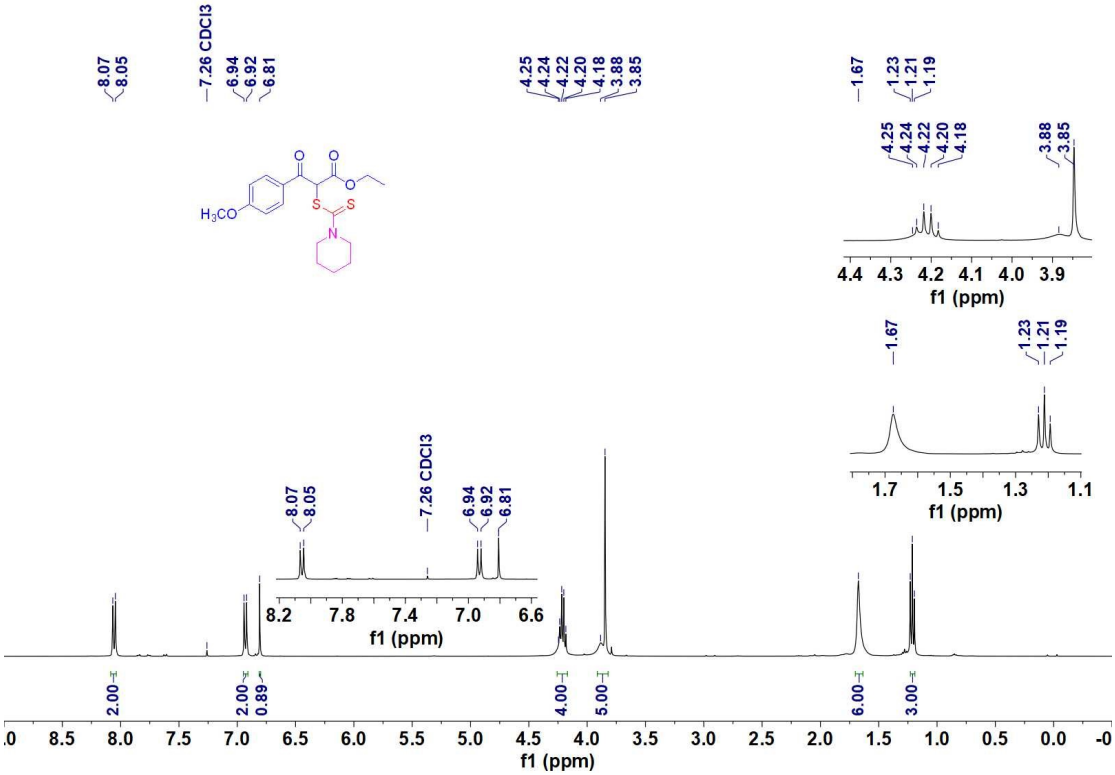


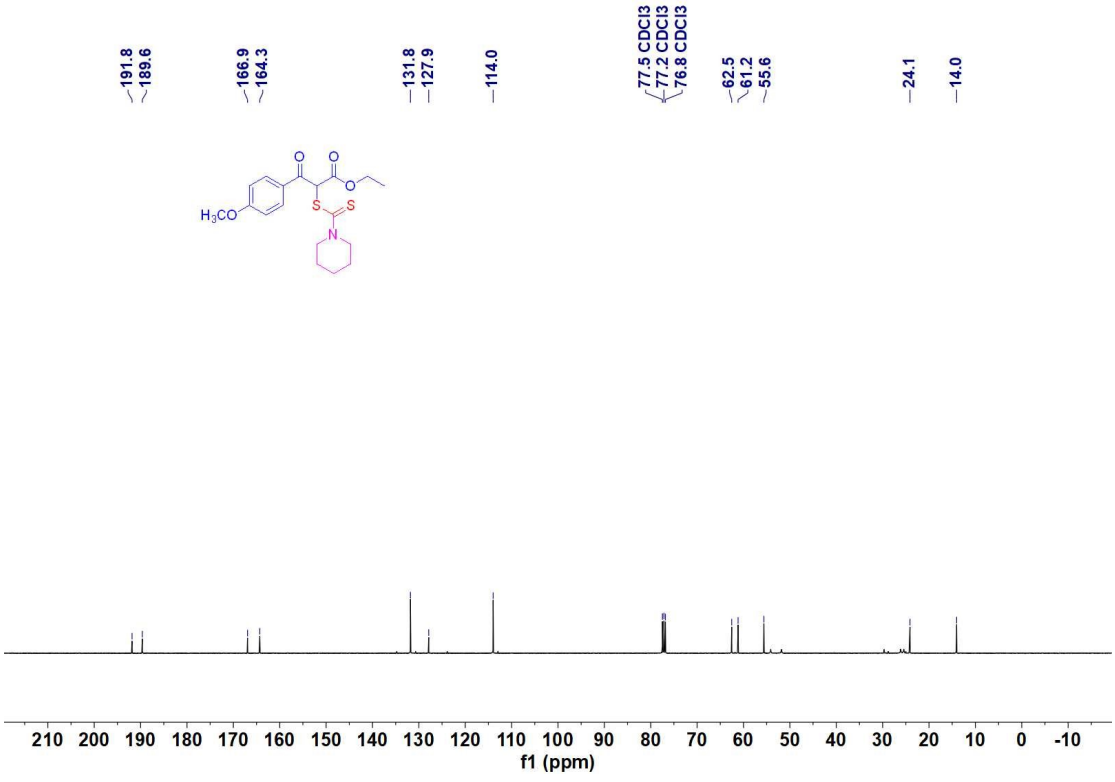
Ethyl 2-((diethylcarbamothioyl)thio)-3-(4-methoxyphenyl)-3-oxopropanoate (4a)



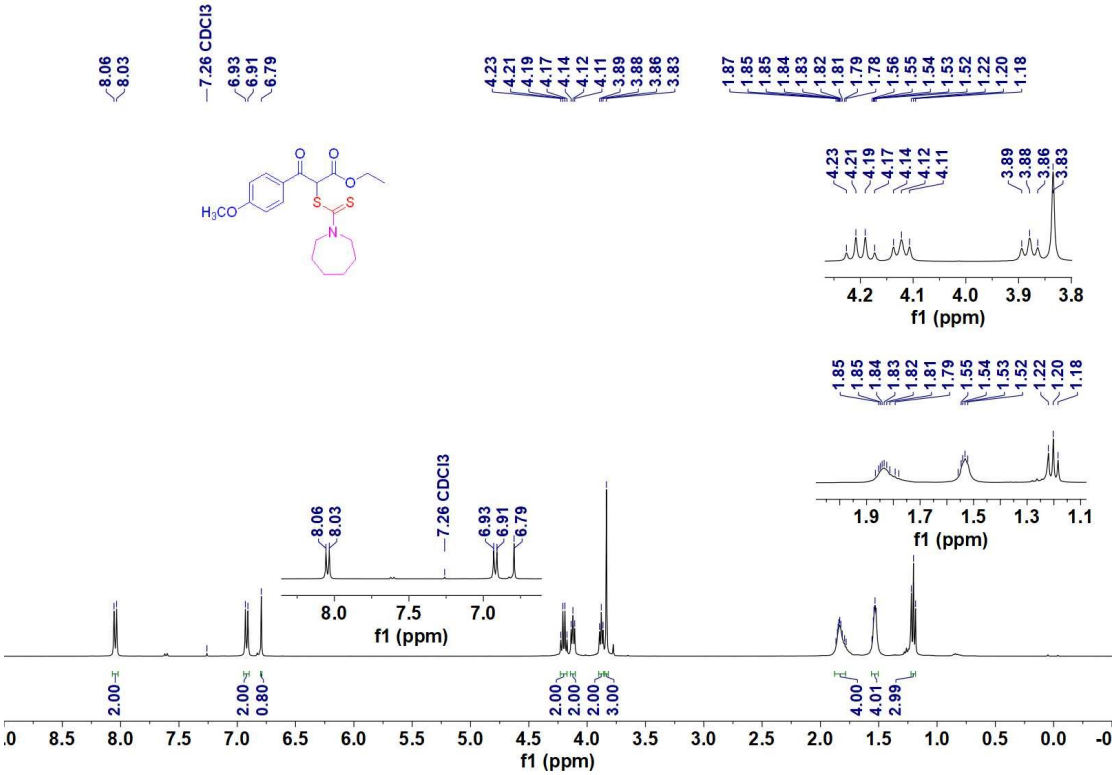


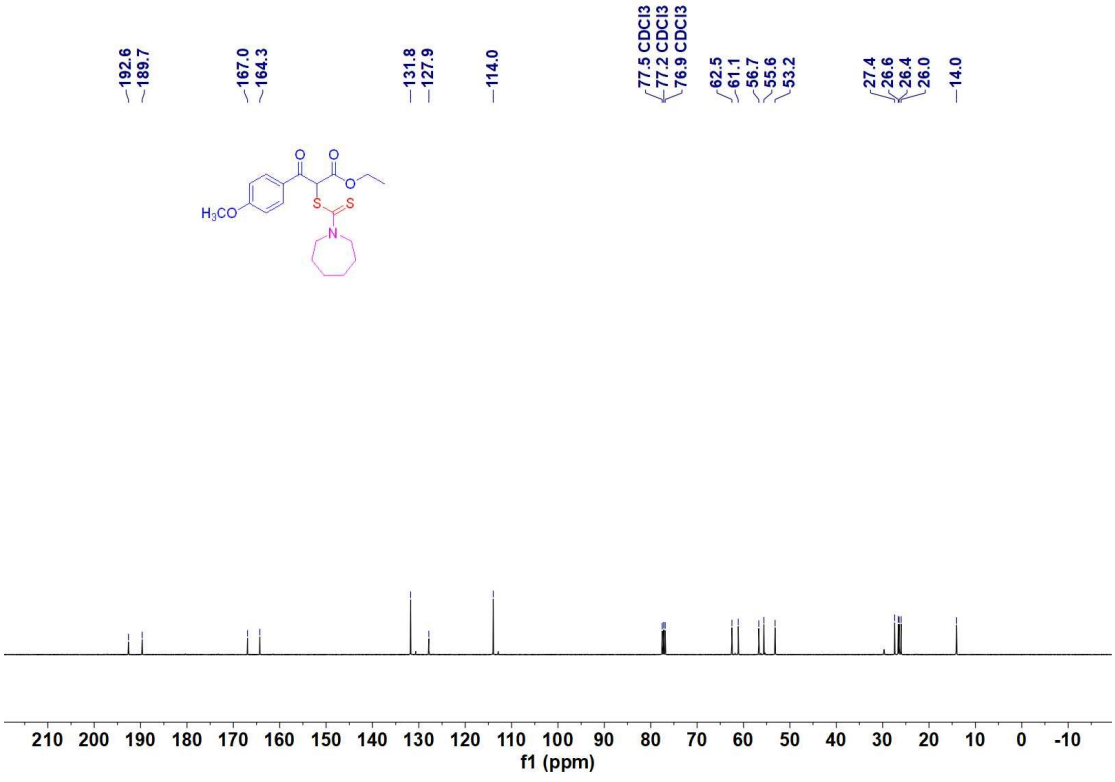
Ethyl 3-(4-methoxyphenyl)-3-oxo-2-((piperidine-1-carbonothioyl)thio)propanoate (4b)



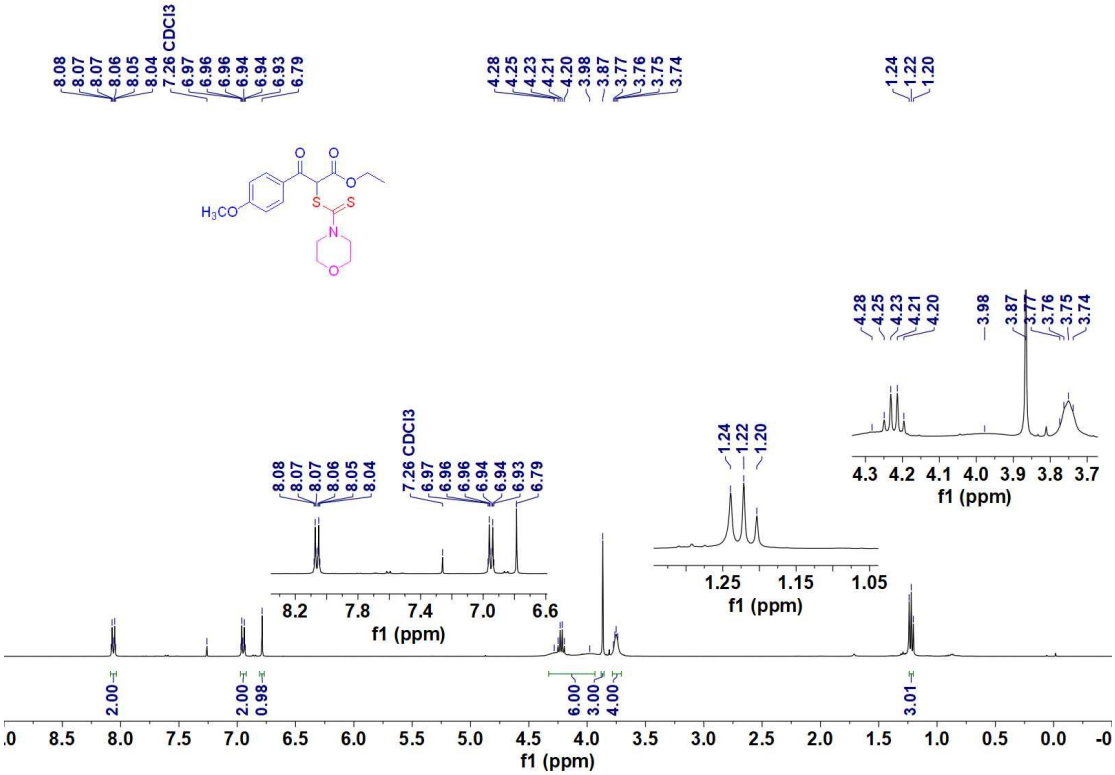


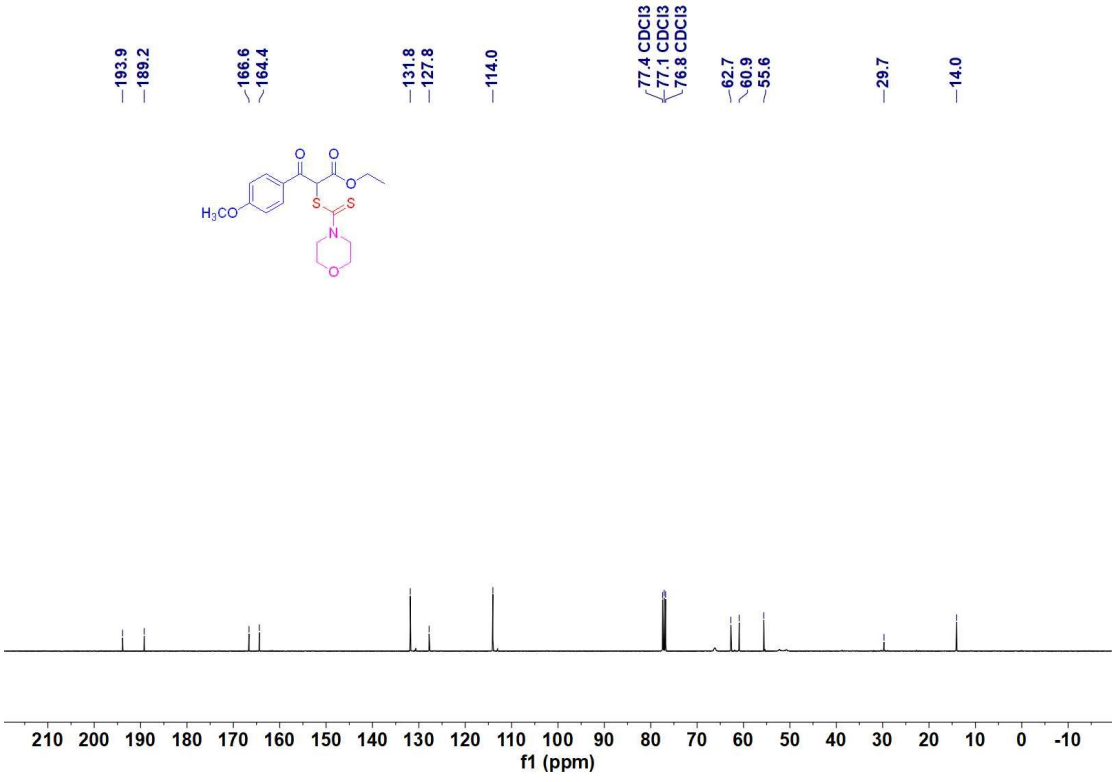
Ethyl 2-((azepane-1-carbonothioyl)thio)-3-(4-methoxyphenyl)-3-oxopropanoate (4c)



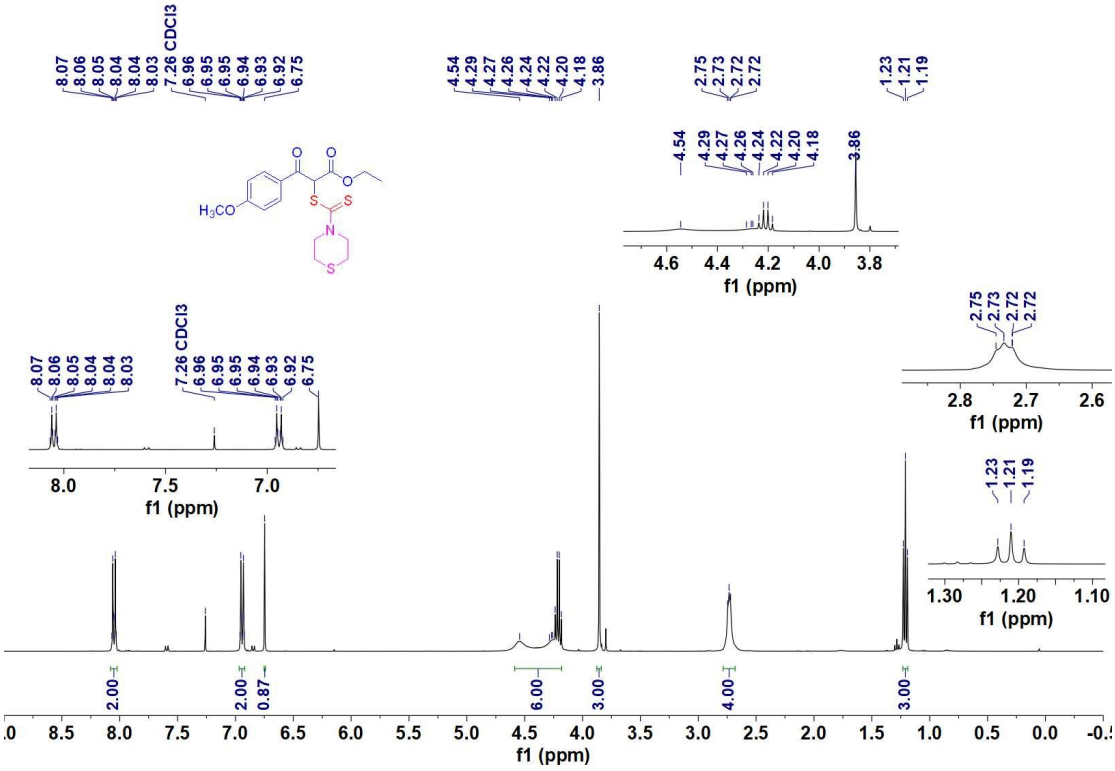


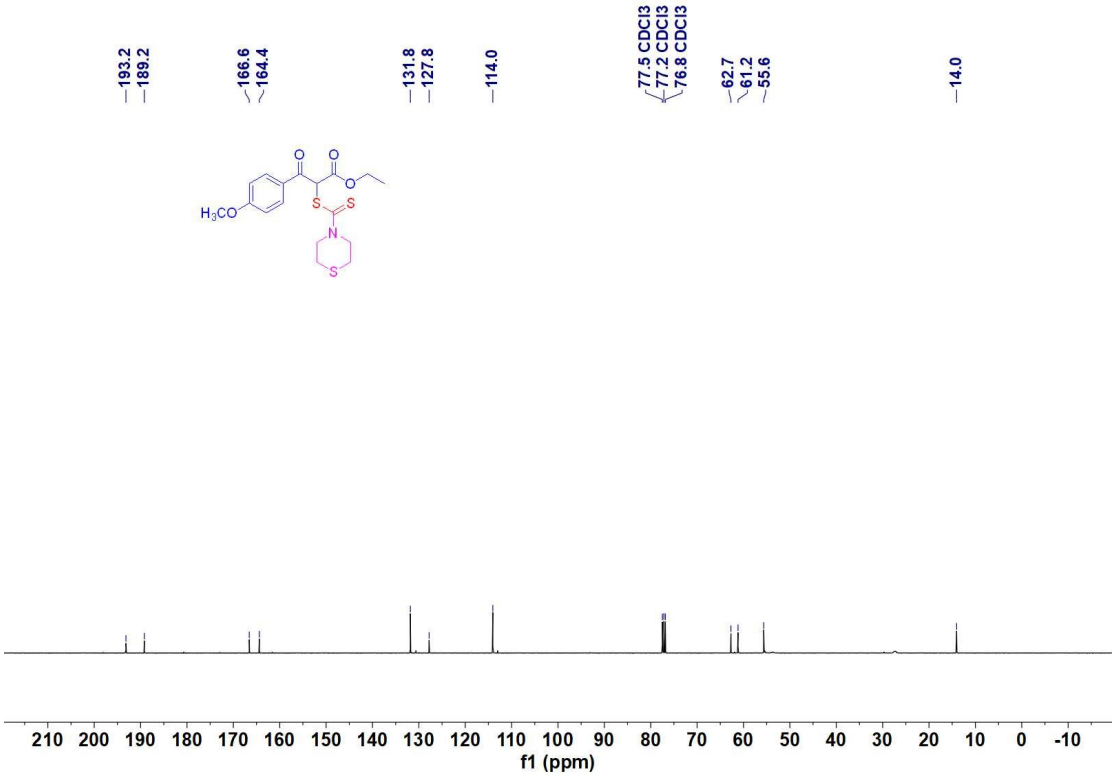
Ethyl 3-(4-methoxyphenyl)-2-((morpholine-4-carbonothioyl)thio)-3-oxopropanoate (4d)



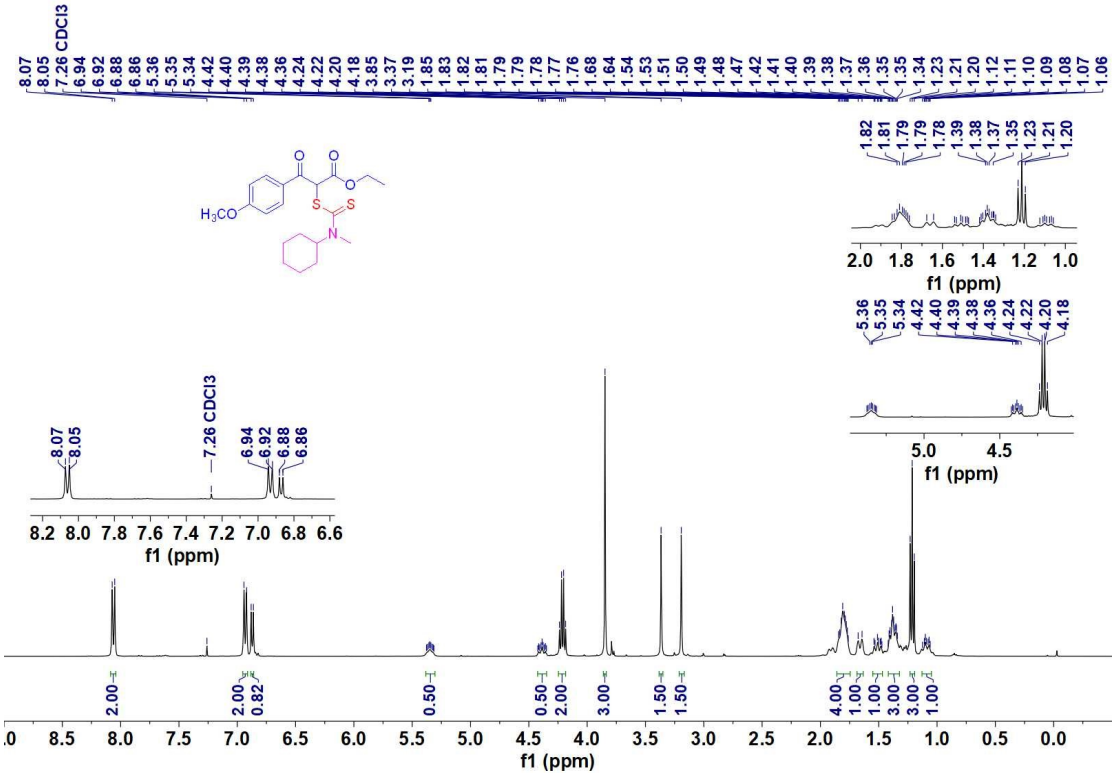


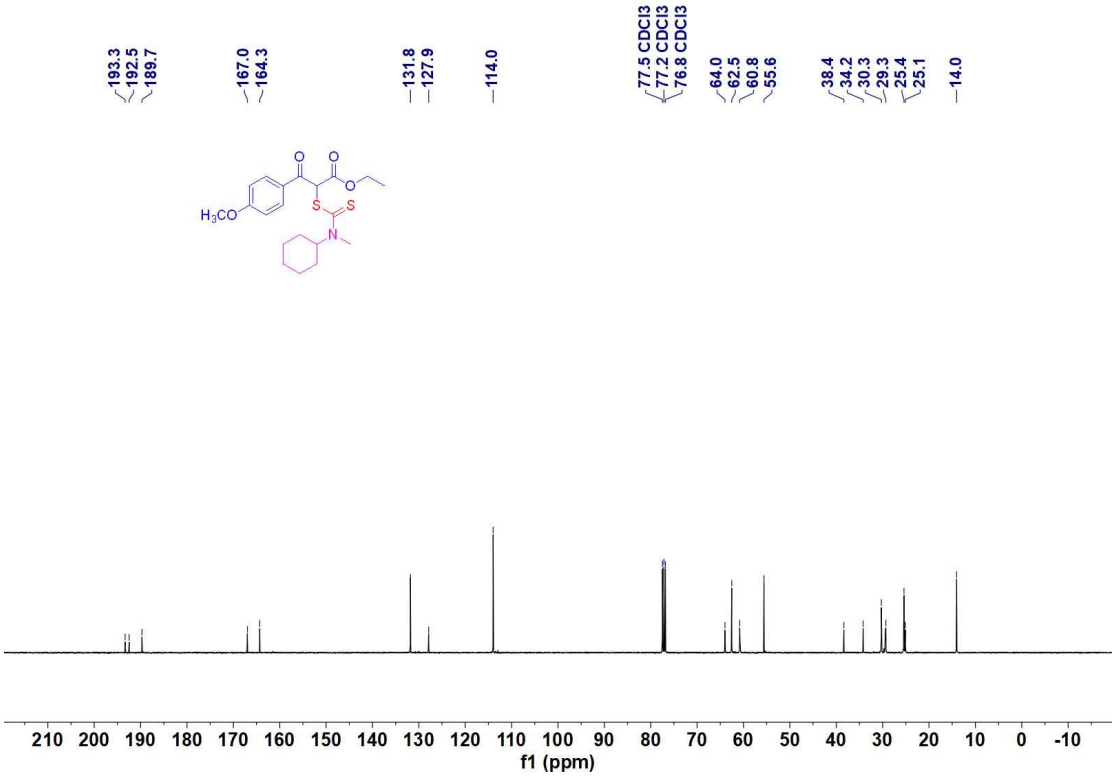
Ethyl 3-(4-methoxyphenyl)-3-oxo-2-((thiomorpholine-4-carbonothioyl)thio)propanoate (4e)



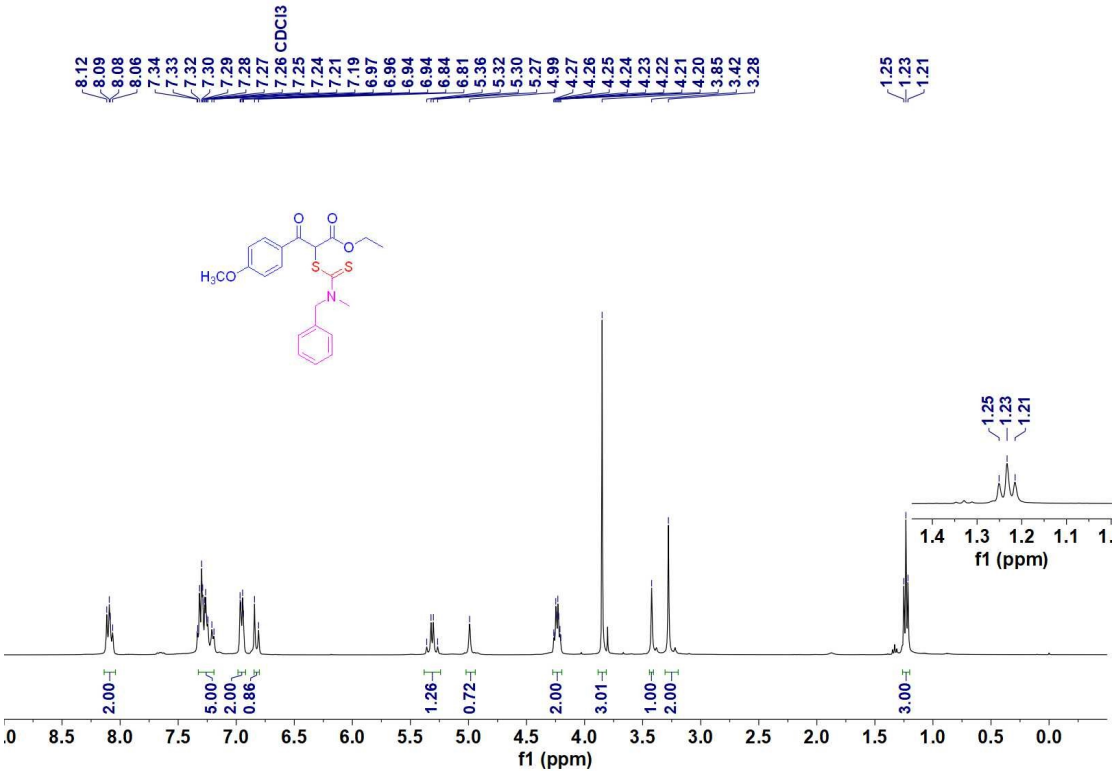


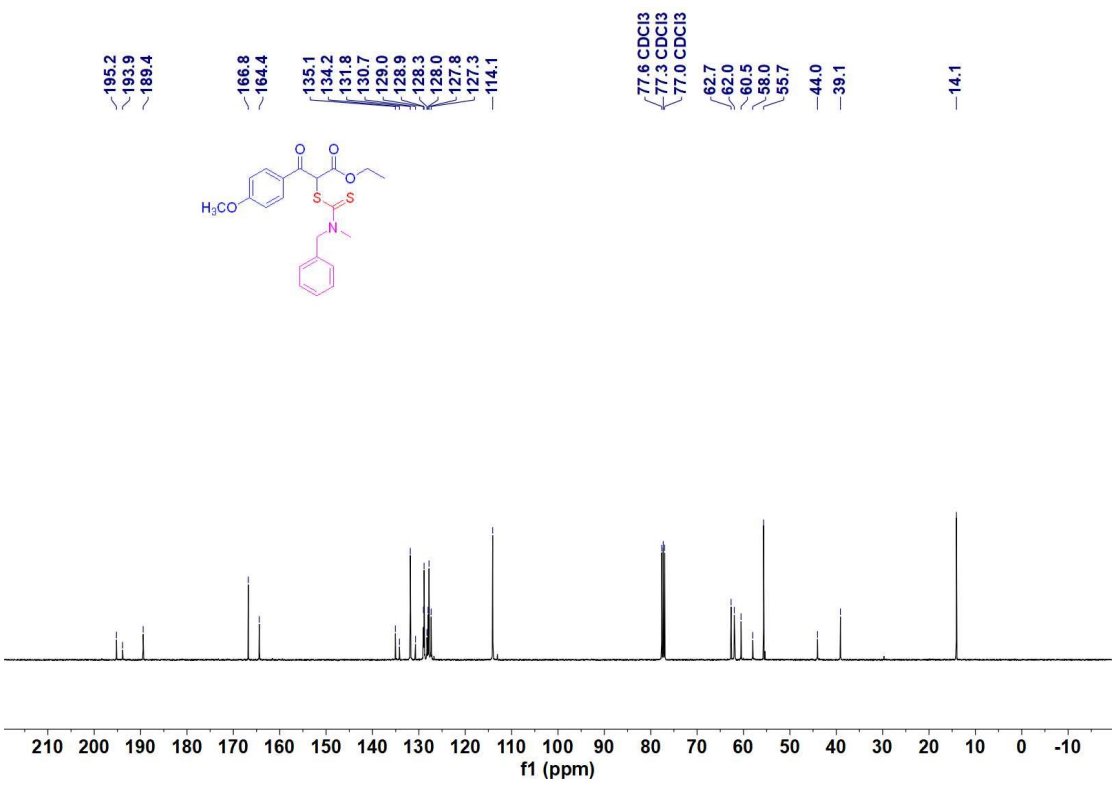
Ethyl 2-((cyclohexyl(methyl)carbamothioyl)thio)-3-(4-methoxyphenyl)-3-oxopropanoate (4f)



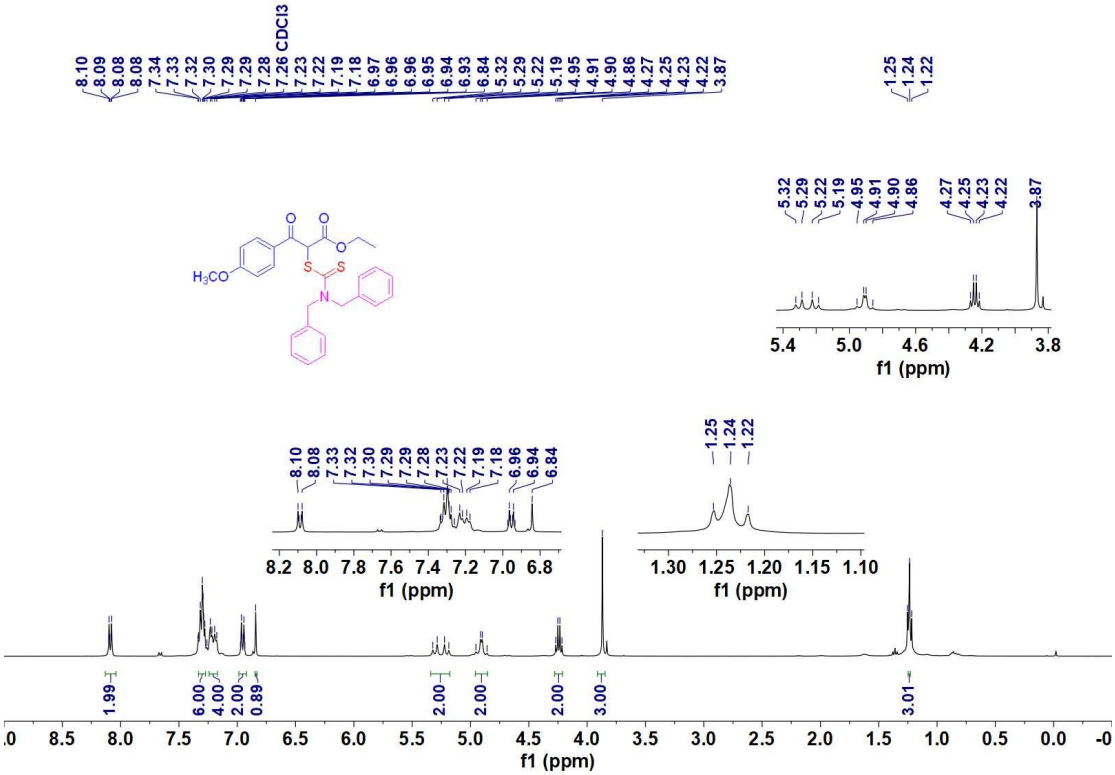


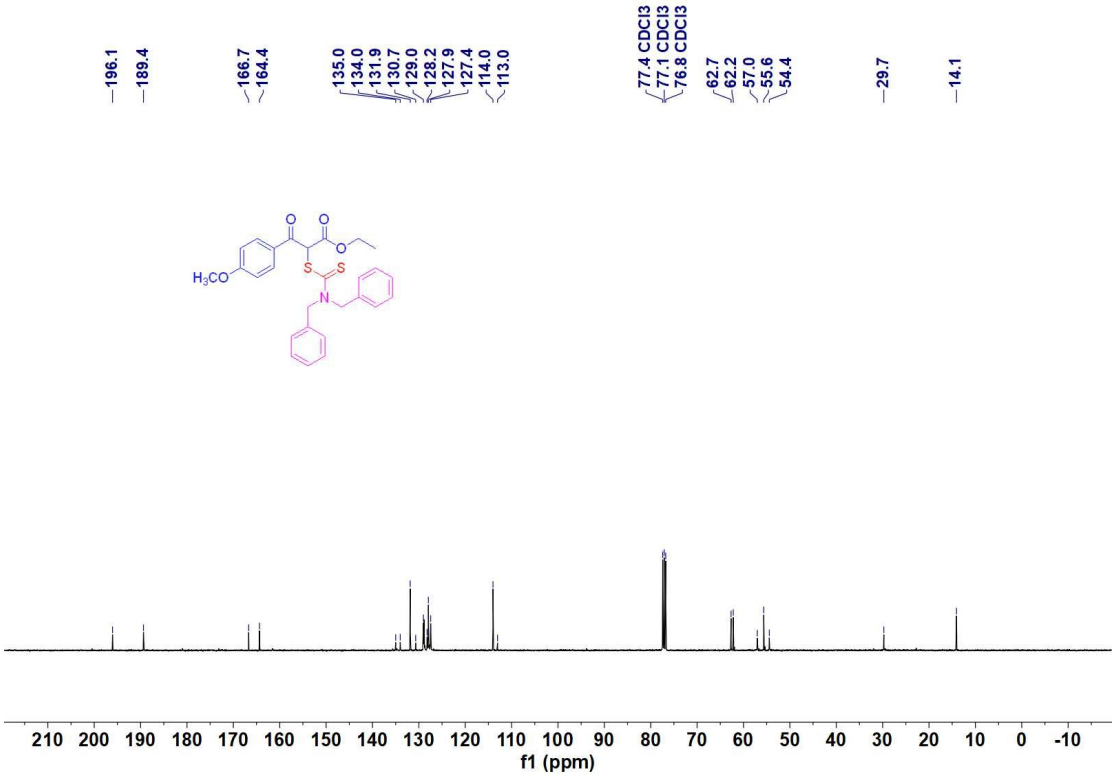
Ethyl 2-((benzyl(methyl)carbamothioyl)thio)-3-(4-methoxyphenyl)-3-oxopropanoate (4g)



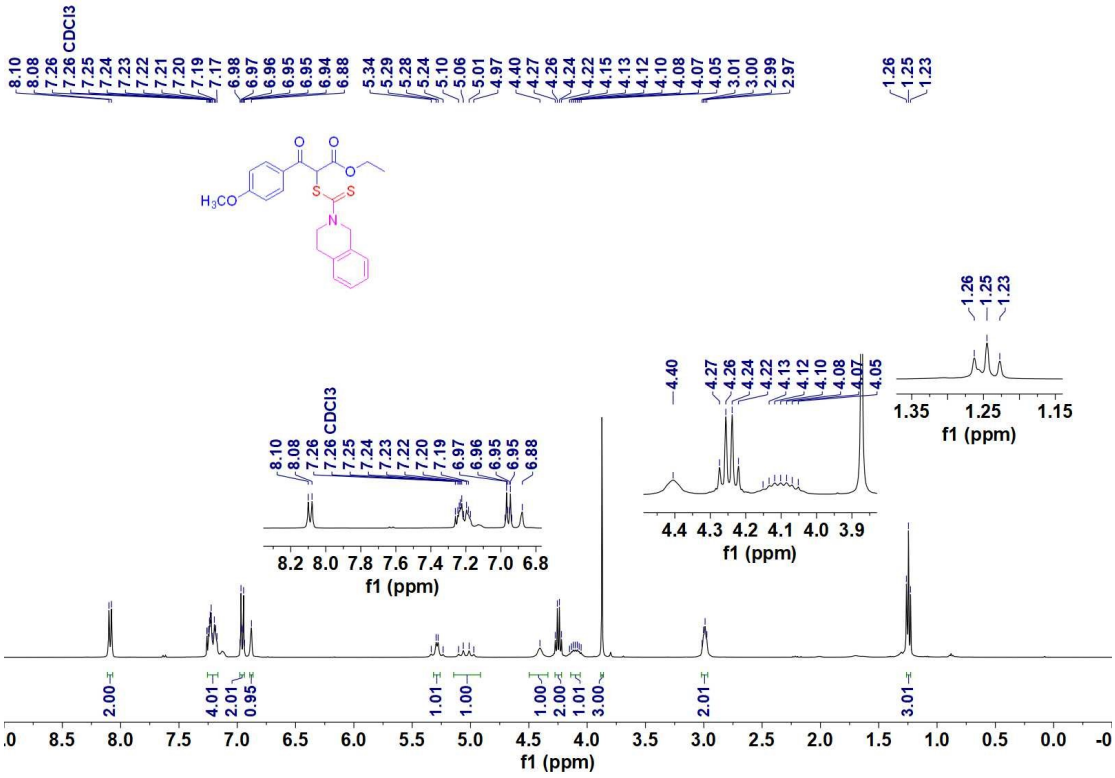


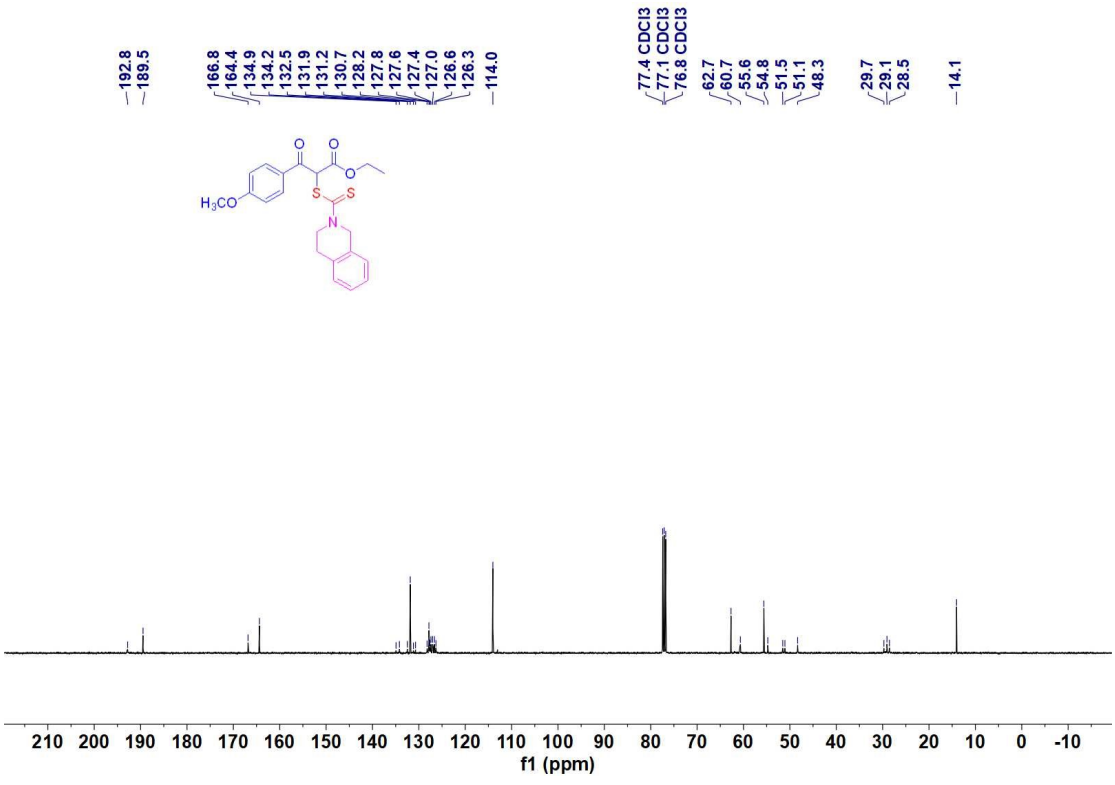
Ethyl 2-((dibenzylcarbamothioyl)thio)-3-(4-methoxyphenyl)-3-oxopropanoate (4h)



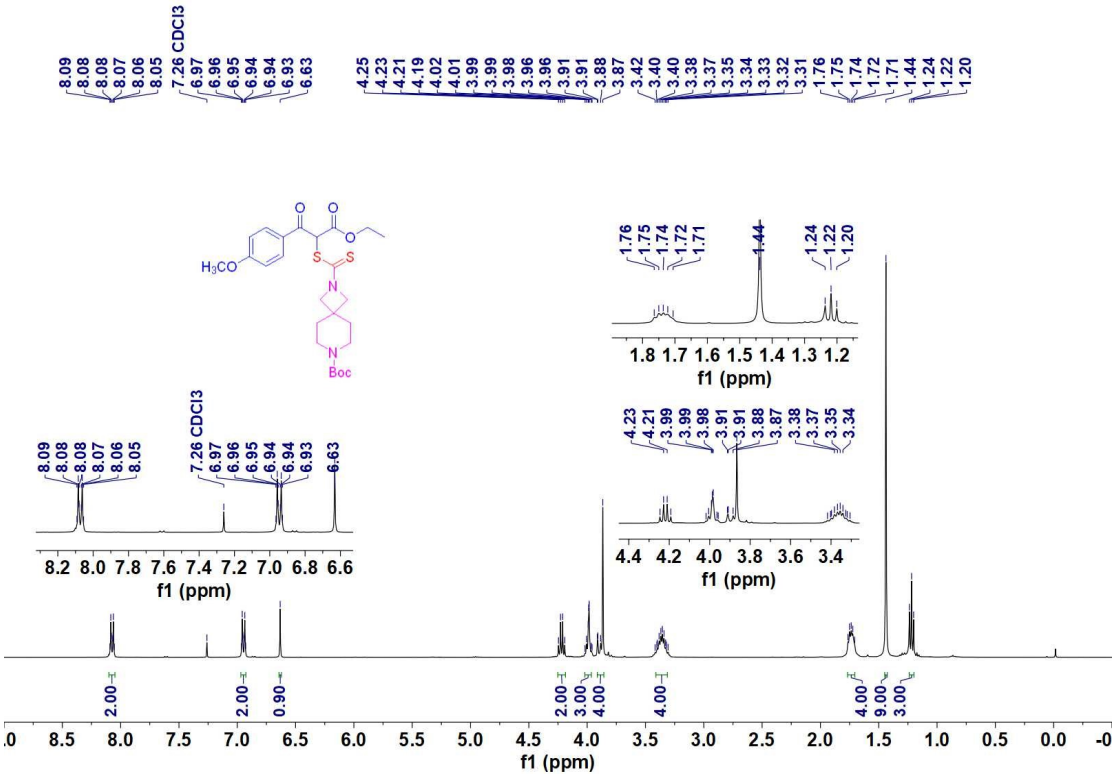


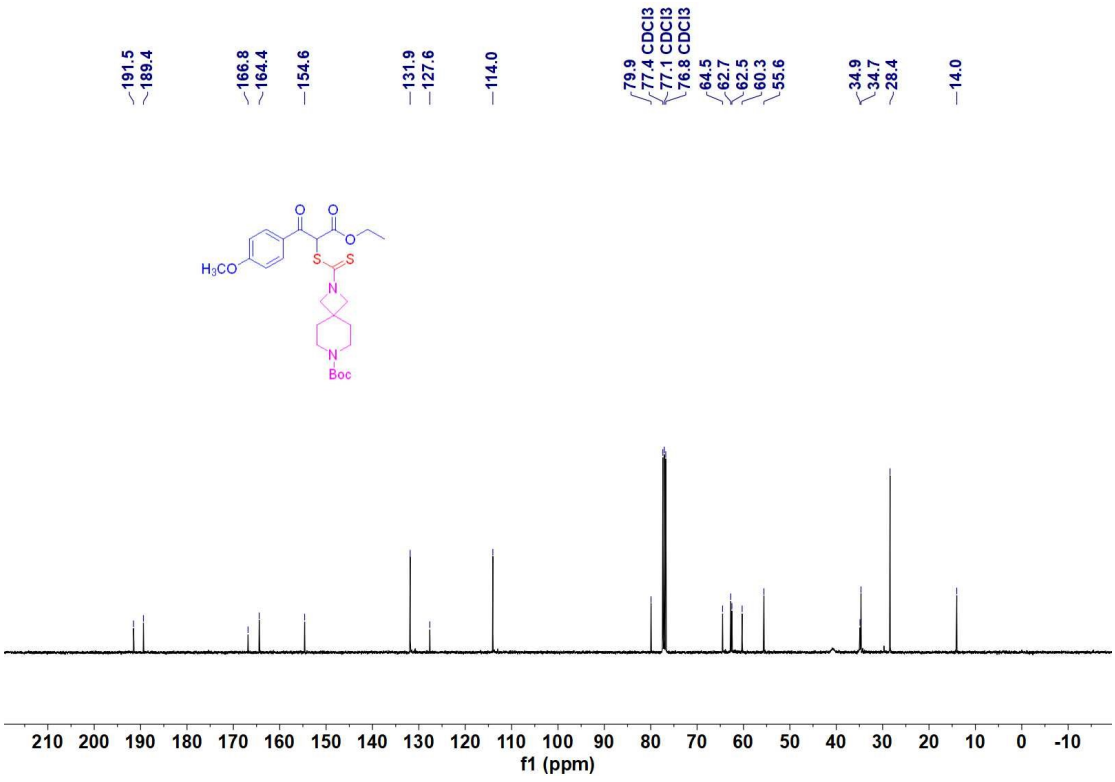
Ethyl 3-(4-methoxyphenyl)-3-oxo-2-((1,2,3,4-tetrahydroisoquinoline-2-carbonothioyl)thio)propanoate (4i)



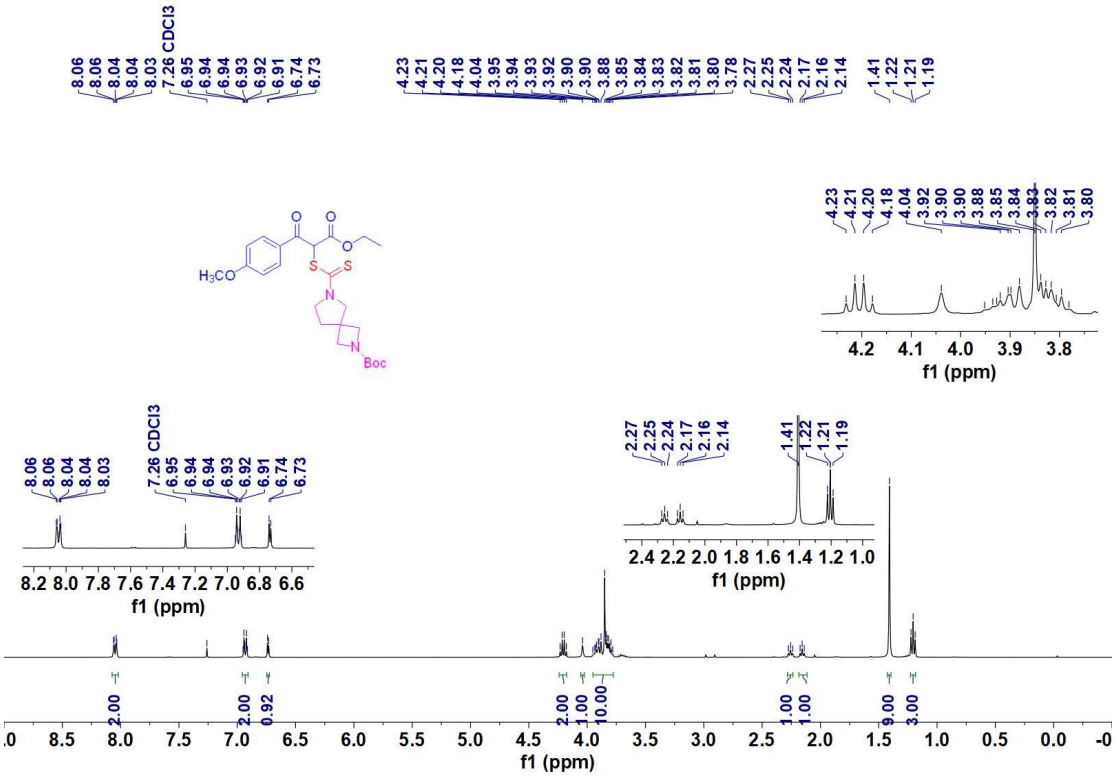


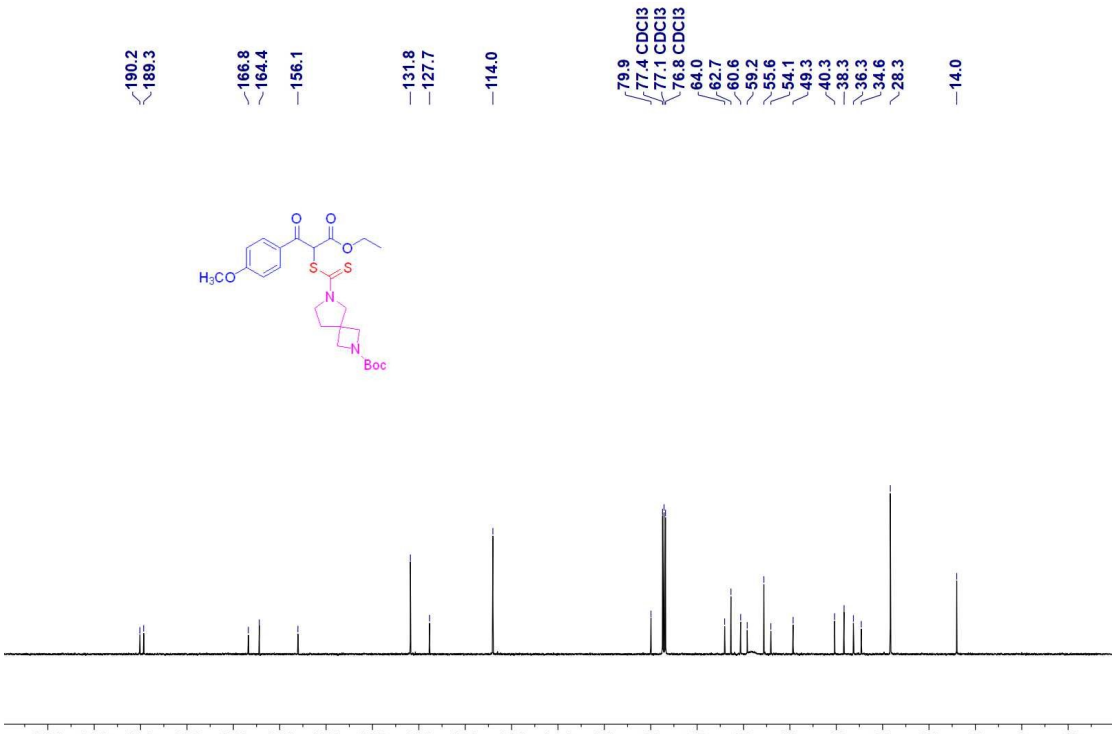
***Tert*-butyl 2-(((1-ethoxy-3-(4-methoxyphenyl)-1,3-dioxopropan-2-yl)thio)carbonothioyl)-2,7-diazaspiro[3.5]nonane-7-carboxylate (4j)**



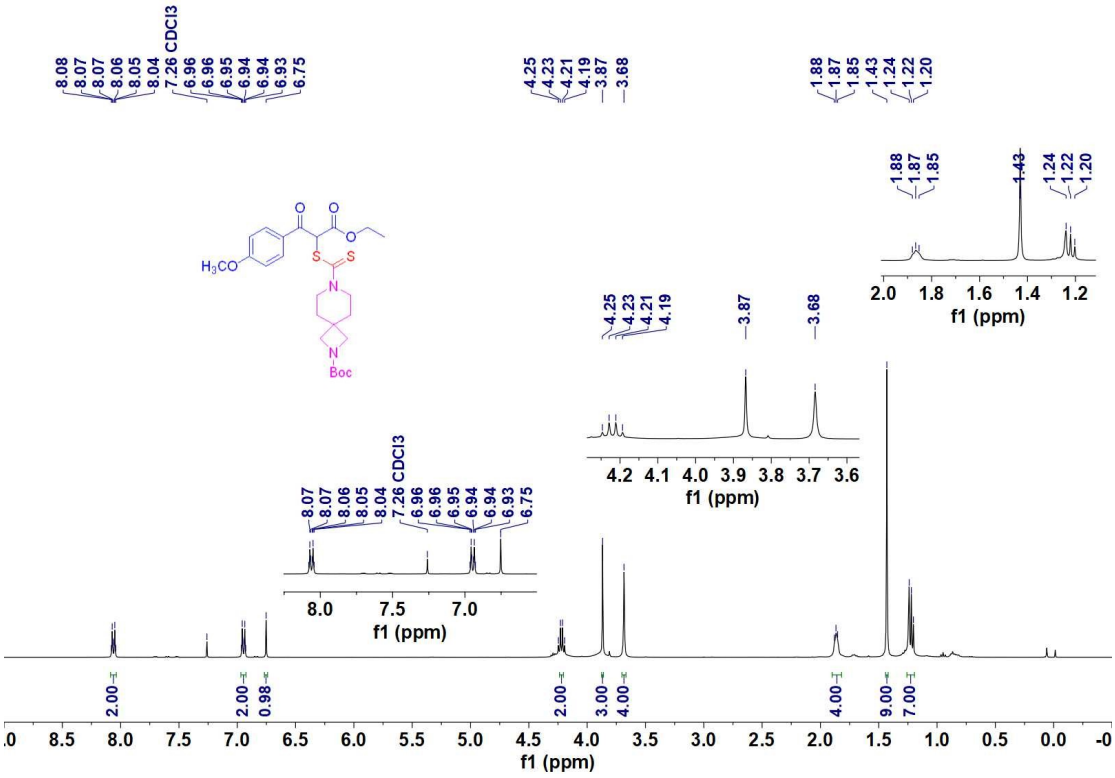


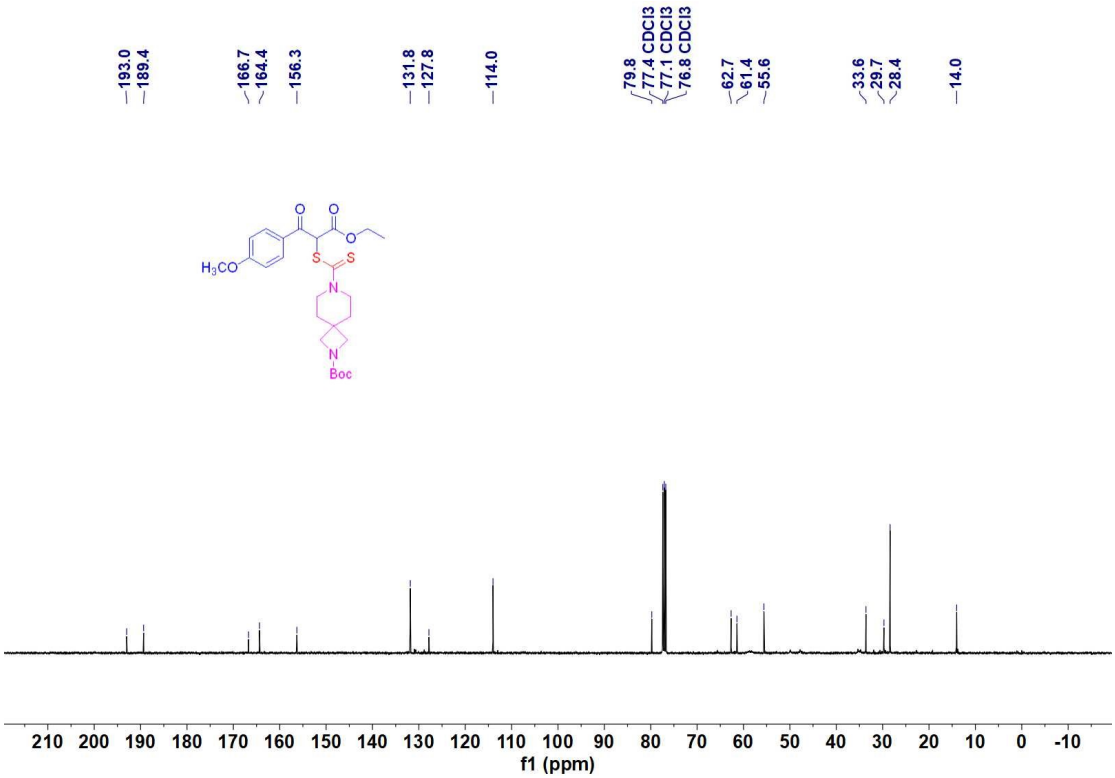
***Tert*-butyl 6-(((1-ethoxy-3-(4-methoxyphenyl)-1,3-dioxopropan-2-yl)thio)carbonothioyl)-2,6-diazaspiro[3.4]octane-2-carboxylate (4k)**



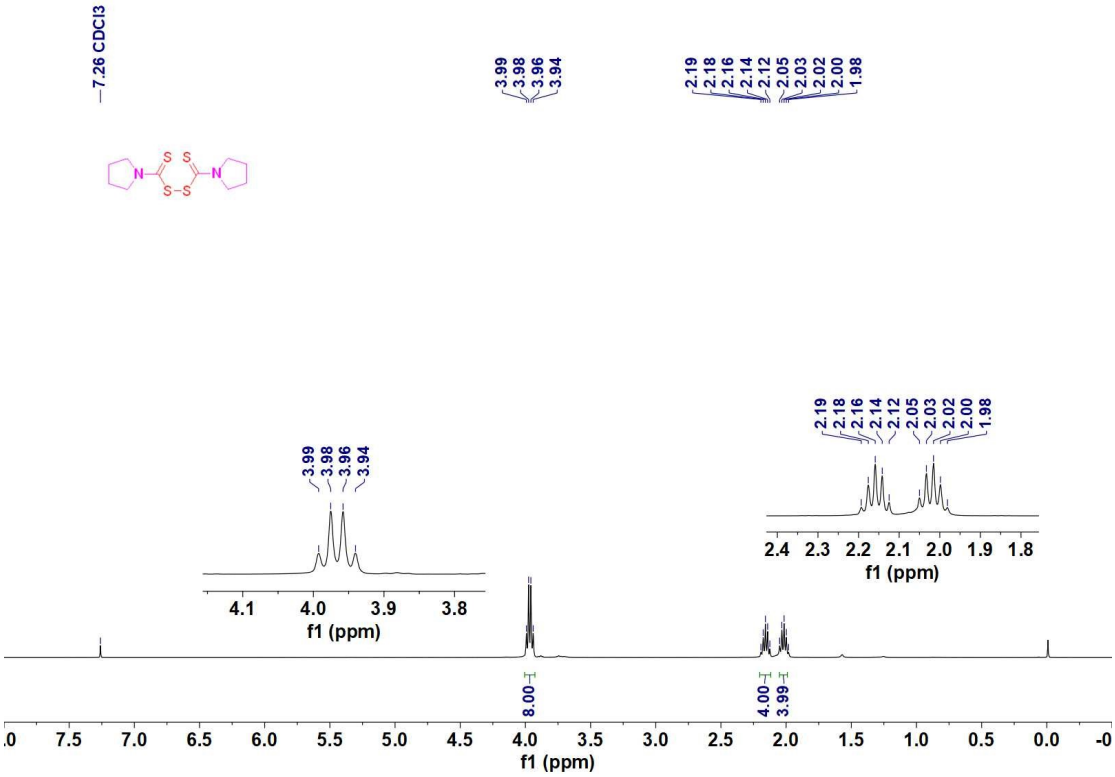


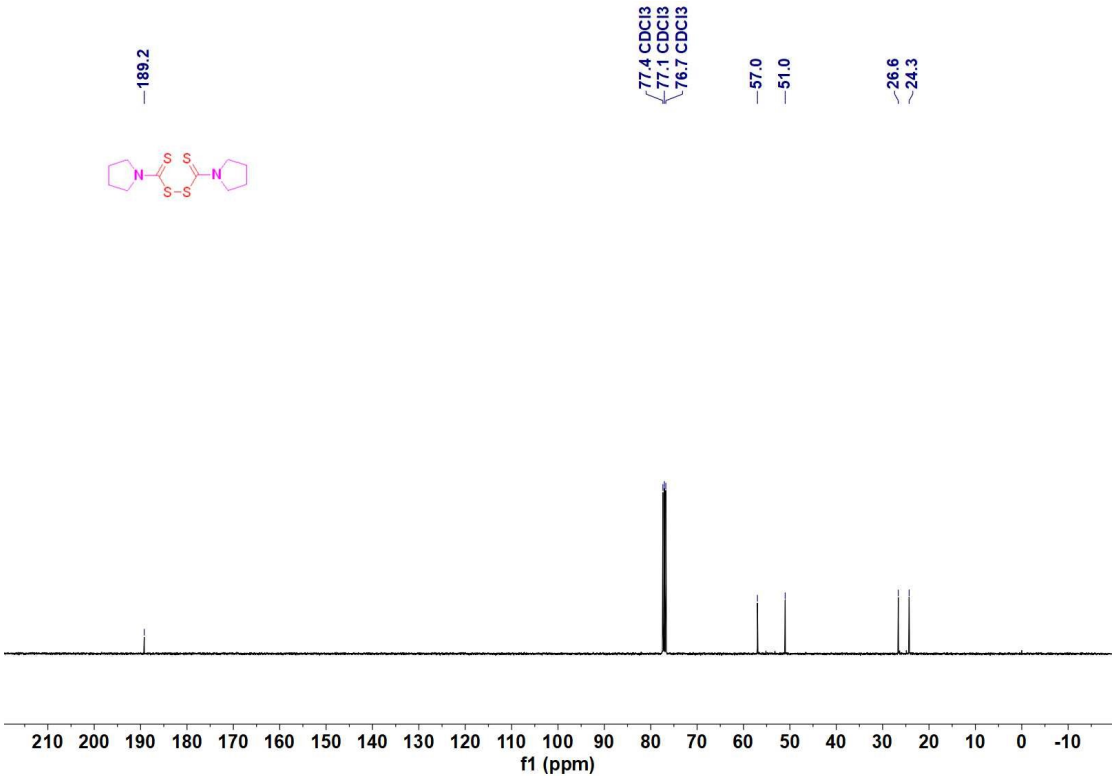
***Tert*-butyl 7-(((1-ethoxy-3-(4-methoxyphenyl)-1,3-dioxopropan-2-yl)thio)carbonothioyl)-2,7-diazaspiro[3.5]nonane-2-carboxylate (4l)**



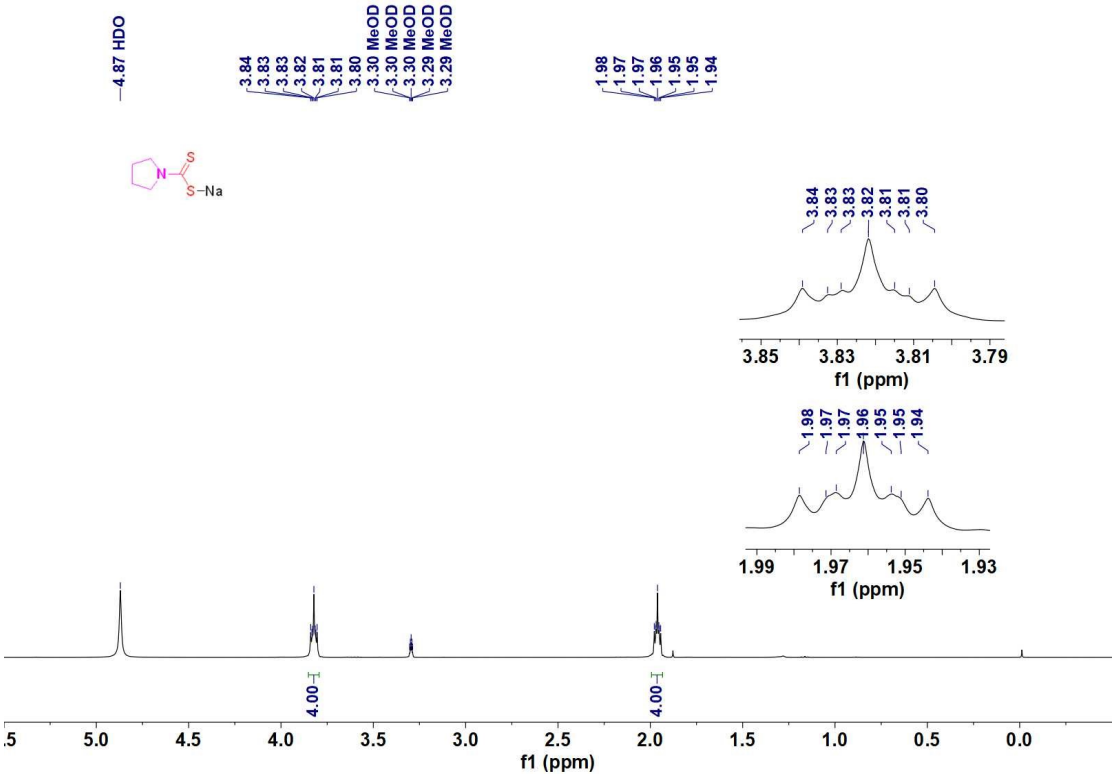


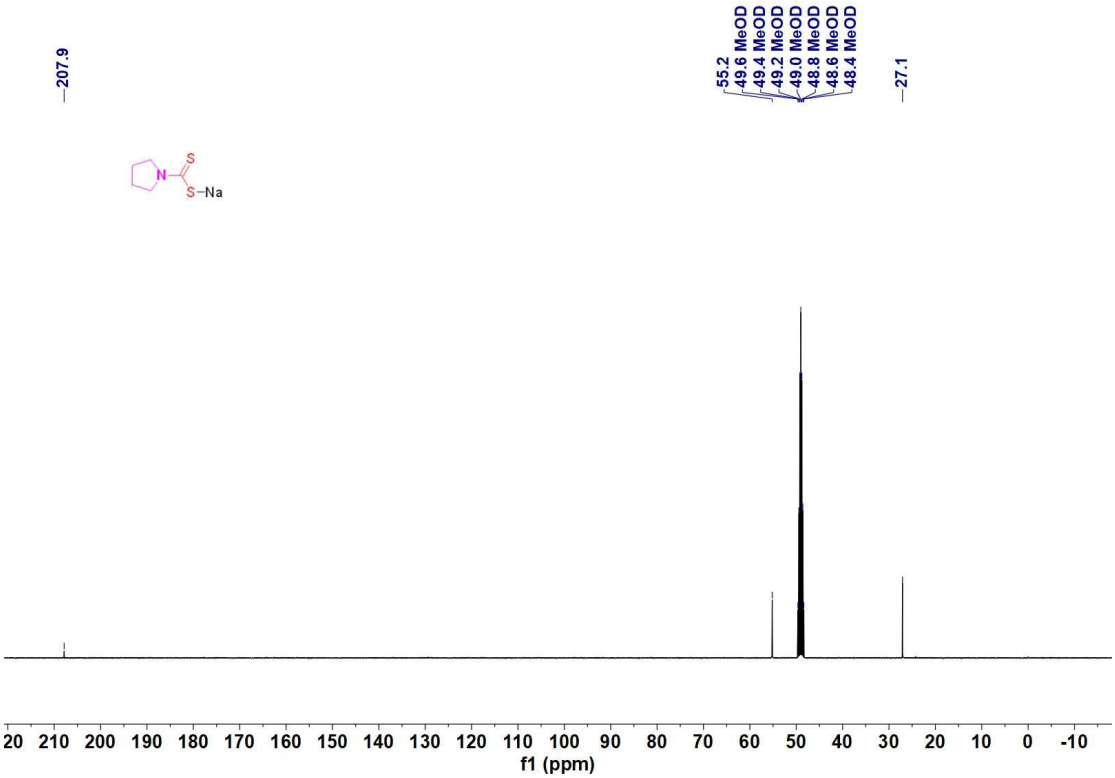
Bis(pyrrolindin-1-ylthiocarbonyl)disulfide (5)





Sodium pyrrolidine-1-carbodithioate (6)




207.9
55.2
49.6 MeOD
49.4 MeOD
49.2 MeOD
49.0 MeOD
48.8 MeOD
48.6 MeOD
48.4 MeOD
27.1
N
S
S
Na
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)