Supporting Information

Electrochemical Synthesis of Carbamo(dithioperoxo)thioates through the Dehydrogenation Coupling of Thiols and Amines and the Insertion of CS_2

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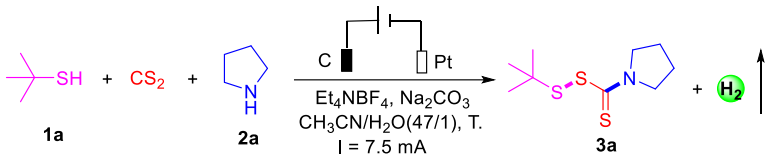
1. General Information

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]

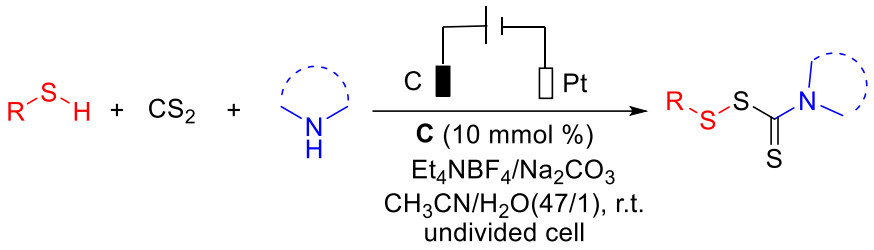


1a 2a 3a

Entry	Deviation from standard conditions	Yield (%)[b]
1	Cs_2CO_3 as base	40
2	K_2CO_3 as base	42
3	$NaHCO_3$ as base	40
4	DABCO as base	20
5	DMAP as base	22
6	DMF as solvent	38
7	CH_3CN as solvent	41
8	H_2O as solvent	20
9	I = 3 mA	41
10	I = 5 mA	43
11	I = 10 mA	40
12	Reaction at -10 °C	20
13	Reaction at 10 °C	35
14[c]	CH_3CN (5.50 mL), H_2O (1.50 mL) as the solvent	85
15[c]	CH_3CN (6.50 mL), H_2O (0.50 mL) as the solvent	87
16[c]	CH_3CN (6.70 mL), H_2O (0.30 mL) as the solvent	89
17[c]	CH_3CN (6.90 mL), H_2O (0.10 mL) as the solvent	92
18[c]	under Ar	94
19[c]	**1a** = 0.45 mmol (1.5 eq.), under Ar	81
20[c]	**1a** = 0.30 mmol (1.0 eq.), under Ar	65

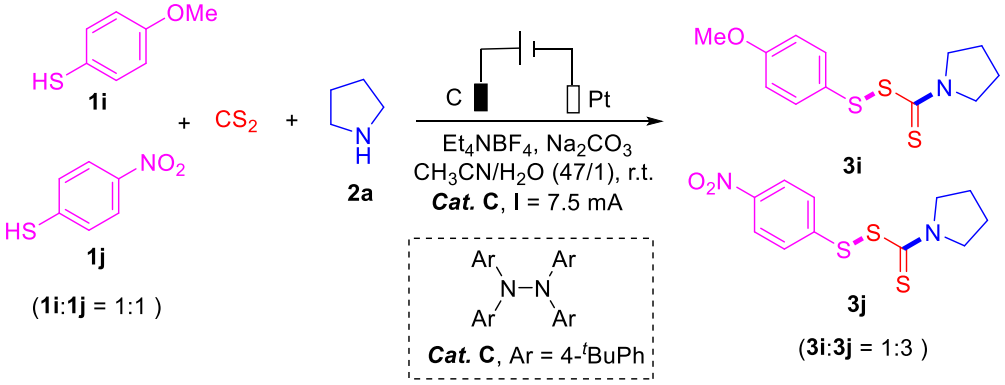
[a]Reaction conditions: graphite rod anode (*Φ* 6 mm), Pt cathode (1 cm x 1 cm), undivided cell, constant current = 7.5 mA, **1a** (0.6 mmol, 2.0 equiv.), CS_2 (0.36 mmol, 1.2 equiv.), **2a** (0.3 mmol, 1.0 equiv.), Et_4NBF_4 (0.3 mmol, 1.0 equiv.), Na_2CO_3 (0.6 mmol, 2.0 equiv.) and CH_3CN (6.85 mL), H_2O (0.15 mL) under air atmosphere at room temperature for 2 h. [b]Isolated yields. [c]catalyst **C** (10 mmol %).

3. **Procedures for the Electrolysis**

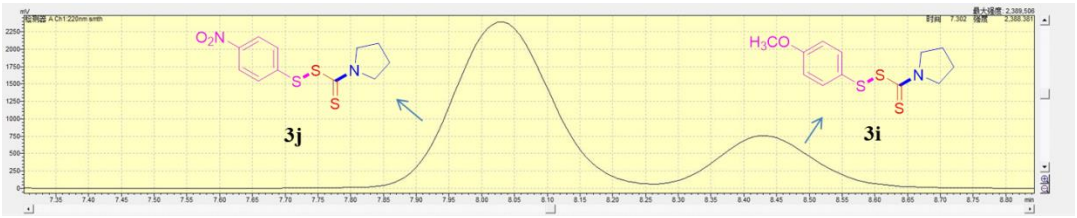


A 10 mL three-necked round-bottomed flask was charged with CS_2 (0.36 mmol, 1.2 equiv), amine compound (0.3 mmol, 1.0 equiv), catalyst **C** (0.03 mmol, 10 mmol %), Et_4NBF_4 (0.3 mmol, 1.0 equiv), Na_2CO_3 (0.6 mmol, 2.0 equiv), CH_3CN (6.85 mL) and H_2O (0.15 mL). The flask was equipped with a graphite rod anode (*Φ* 6 mm) and a platinum plate (1 cm x 1 cm) cathode, the distance between the two electrodes was 3 cm. Thiol compound (0.6 mmol, 2.0 equiv) were added. Electrolysis was carried out at room temperature under air atmosphere, which using a constant current of 7.5 mA until the substrate was completely consumed (monitored by TLC, about 2 hours). 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.

HPLC analysis of cross reaction:

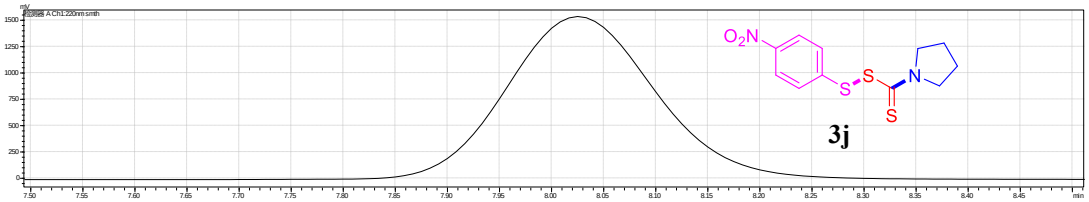


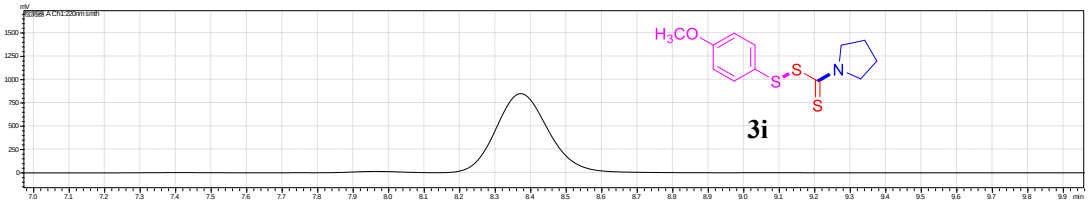
The HPLC chromatogram of the two compounds (3i and 3j) is shown below:



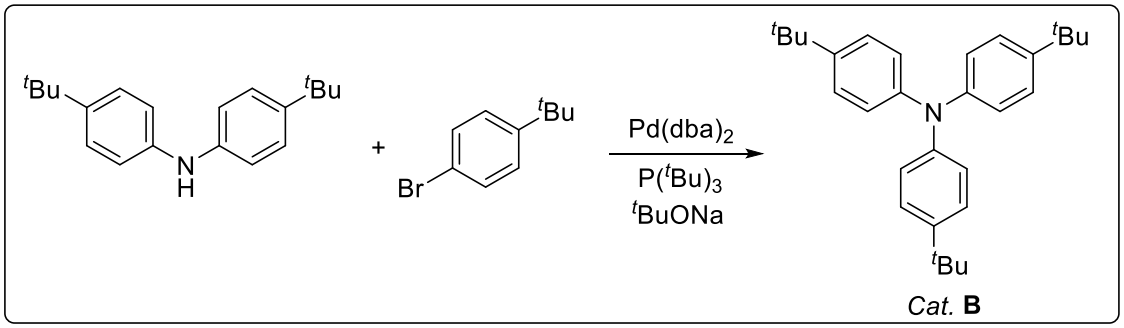
Entry	Retention time/min	Peak area
1	8.025	24805173
2	8.426	8054552

The HPLC chromatogram for each compound (3i or 3j) is shown below:



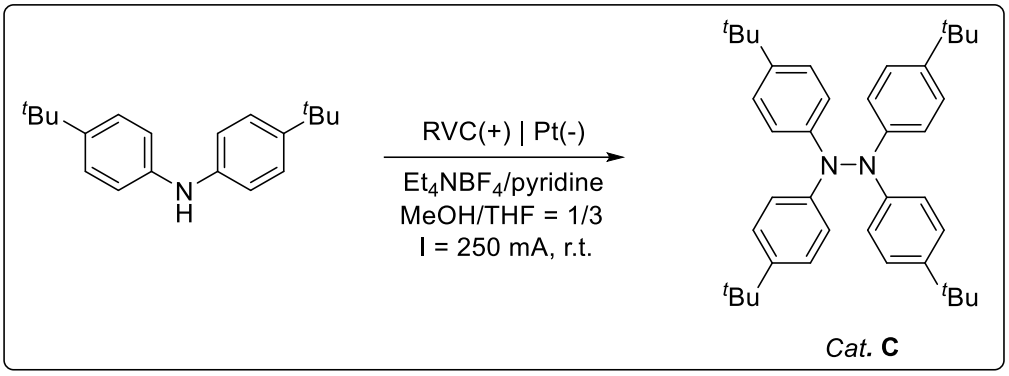


4. Typical procedure for the synthesis of Catalyst B[1]



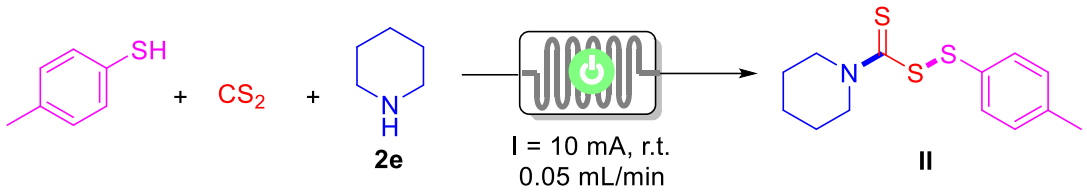
Tris(4-(*tert*-butyl)phenyl)amine (*Cat*. **B**). Bis(4-(t*ert*-butyl)phenyl)amine (5.0 g, 17.8 mmol), $Pd(dba)_2$ (511 mg, 0.9 mmol), and ^{t}BuONa (5.1 g, 53.4 mmol) were added to a dried three-necked round bottom flask. The flask was evacuated and filled with argon for three times. Dry toluene (50 mL) was added under argon atmosphere, followed by 1-bromo-4-(*tert*-butyl)benzene (7.9 g, 37.3 mmol), $P(^tBu)_3$ (360 mg, 1.8 mmol). The flask was refluxed for 12 h. The solution was allowed to cool to room temperature and concentrated under reduced pressure. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with H_2O (3 x 20 mL), dried over Na_2SO_4, collected the organic layers and recrystallized with CH_3OH to afford the desired products.

5. Typical procedure for the synthesis of Catalyst C[2]



1,1,2,2-Tetrakis(4-(*tert*-butyl)phenyl)hydrazine (*Cat*. **C**). Bis(4-(t*ert*-butyl)phenyl)amine (1.69 g, 6 mmol), Pyridine (0.5 mL, 6 mmol), Et_4NBF_4 (1.3 g, 6 mmol), MeOH (30 mL) and THF (90 mL) was added to a 500 mL beaker-type cell at room temperature for 3.5 h using a RVC plate (5.8 cm x 5.8 cm x 1.2 cm) as anode, a Pt plate cathode (3 cm x 3 cm) and a constant current of 250 mA. The RVC plate was about 2.4 cm from the Pt plate. The electrolysis was carried out until complete consumption of the substrate (monitored by TLC), the reaction mixture was concentrated under reduced pressure and recrystallized with CH_2Cl_2/CH_3OH to afford the desired products.

6. Procedures for the Flow Electrolysis



The electrolysis was conducted with a constant current of 10 mA using a flow electrolytic cell equipped with a graphite anode anode and a Pt cathode with the electrode surface of 8 cm × 6 cm. **2e** (5 mmol, 0.49 mL), CS_2 (6 mmol, 0.36 mL), *p*-toluenethiol (5 mmol, 0.62 g), *Cat.* **C** (10 mmol %, 0.28 g), DABCO (10 mmol, 1.12 g) in CH_3CN (67 mL) at room temperature were pushed via peristatic pump to pass through the flow electrolytic cell with a flow rate of 0.05 mL/min. After 22.3 h, the combined organic solution was concentrated under reduced pressure. Purification with silica gel column chromatography using ethyl acetate/petroleum ether to give **II** in 65% yield (0.92 g).

7. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded in an electrolyte solution of 0.1 M Et_4NBF_4, 10 mM Na_2CO_3 in CH_3CN (9.78 mL) and H_2O (0.22 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.

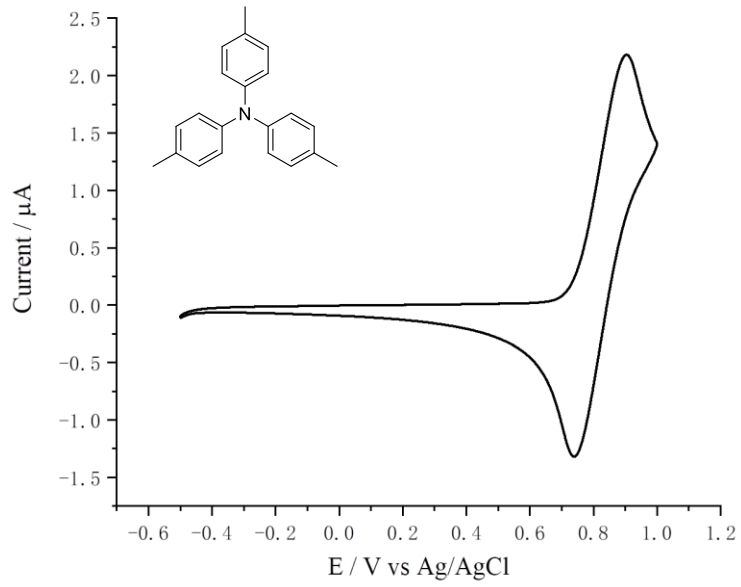


Figure S1. Cyclic voltammogram of catalyst **A** (10 mM). $E_{p/2}$ = 0.82 V.

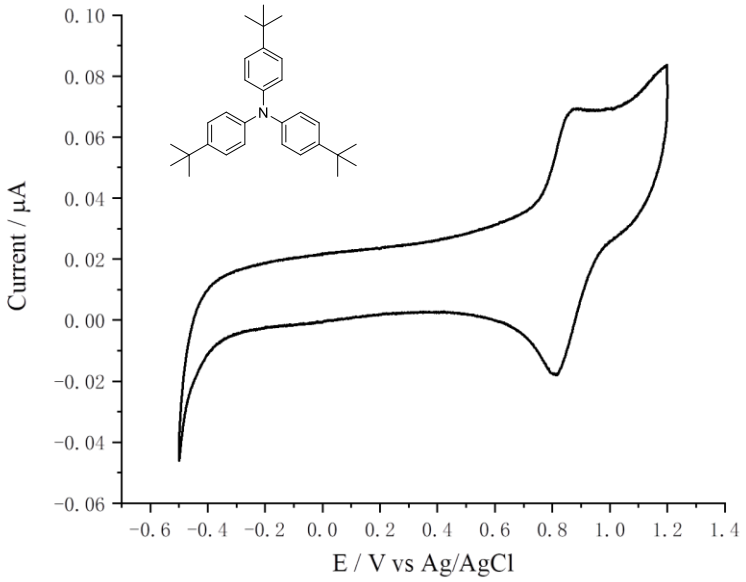


Figure S2. Cyclic voltammogram of catalyst **B** (10 mM). $E_{p/2}$ = 0.85 V.

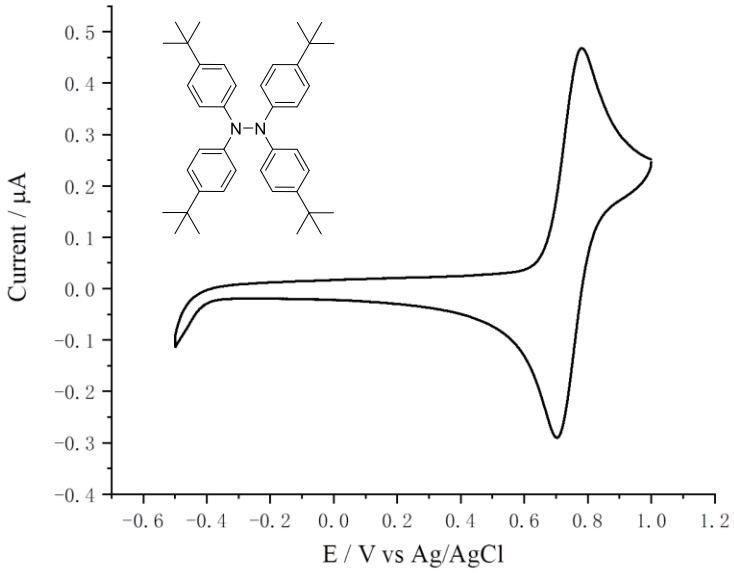


Figure S3. Cyclic voltammogram of catalyst **C** (10 mM). $E_{p/2}$ = 0.74 V.

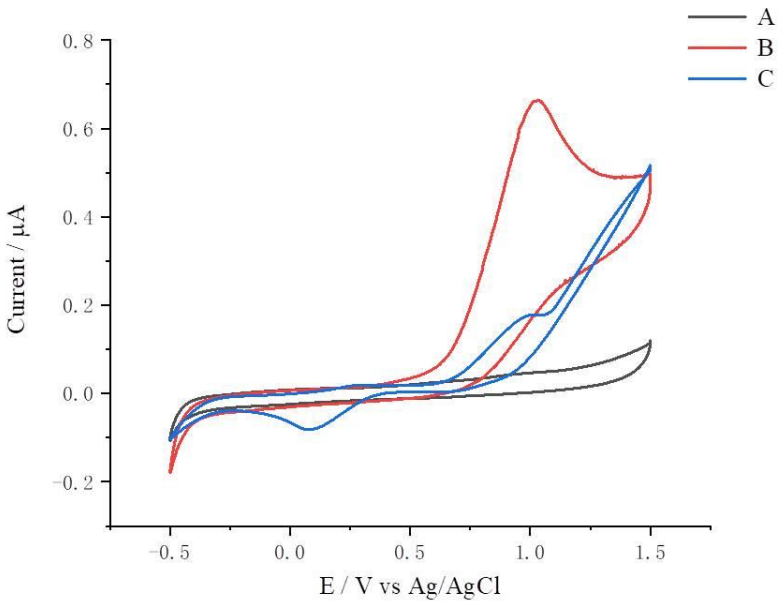


Figure S4. Cyclic voltammogram of reactants, A: CS_2 (10 mM); B: **2a** (10 mM), $E_{p/2}$ = 1.03 V; C: CS_2 (10 mM) and **2a** (10 mM), $E_{p/2}$ = 0.97 V, which showed that a reaction occurred when the CS_2 and **2a** were mixed.

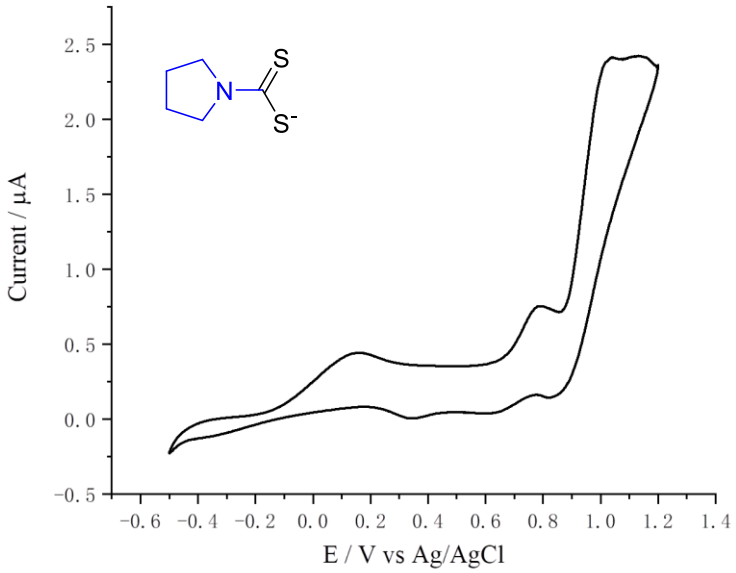
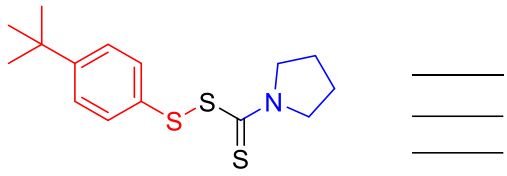
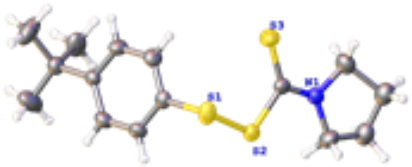


Figure S5. Cyclic voltammogram of sodium pyrrolidine-1-carbodithioate (10 mM). $E_{p/2}$ = 0.60 V.

8. The X-ray Crystal Structure of 3h



3h



CCDC 2161645

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Bond precision:   C-C = 0.0050 A          Wavelength=0.71073

Cell:             a=7.4909(10)     b=25.840(4)        c=8.5571(12)
                  alpha=90         beta=93.901(3)     gamma=90
Temperature:      296 K

                  Calculated                  Reported
Volume            1652.5(4)                   1652.5(4)
Space group       P 21/c                      P 1 21/c 1
Hall group        -P 2ybc                     -P 2ybc
Moiety formula    C15 H21 N S3                C15 H21 N S3
Sum formula       C15 H21 N S3                C15 H21 N S3
Mr                311.51                      311.51
Dx,g cm-3         1.252                       1.252
Z                 4                           4
Mu (mm-1)         0.436                       0.436
F000              664.0                       664.0
F000'             665.64
h,k,lmax          8,30,10                     8,30,10
Nref              2930                        2923
Tmin,Tmax         0.941,0.953                 0.941,0.954
Tmin'             0.941

Correction method= # Reported T Limits: Tmin=0.941 Tmax=0.954
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 25.077

R(reflections)= 0.0539( 1588)                wR2(reflections)=
                                             0.1412( 2923)
S = 1.002                 Npar= 224
```

Table S2 Crystal data and structure refinement for 3h.

Empirical formula	$C_{15}H_{21}NS_3$
Formula weight	311.51
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.4909(10)
b/Å	25.840(4)
c/Å	8.5571(12)
α/°	90
β/°	93.901(3)
γ/°	90
Volume/Å^3	1652.5(4)
Z	4
ρ_{calc}g/cm^3	1.252
μ/mm^{-1}	0.436
F(000)	664.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.026 to 50.154
Index ranges	$-7 \le h \le 8$, $-30 \le k \le 30$, $-10 \le l \le 10$
Reflections collected	25315
Independent reflections	2923 [R_{int} = 0.1012, R_{sigma} = 0.0768]
Data/restraints/parameters	2923/67/224
Goodness-of-fit on F^2	1.002
Final R indexes [I>=2σ (I)]	R_1 = 0.0539, wR_2 = 0.1098
Final R indexes [all data]	R_1 = 0.1322, wR_2 = 0.1412
Largest diff. peak/hole / e Å^{-3}	0.19/-0.27

Crystal Data for $C_{15}H_{21}NS_3$ (M =311.51 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 7.4909(10) Å, b = 25.840(4) Å, c = 8.5571(12) Å, β = 93.901(3)°, V = 1652.5(4) Å^3, Z = 4, T = 296.15 K, μ(MoKα) = 0.436 mm^{-1}, *Dcalc* = 1.252 g/cm^3, 25315 reflections measured (5.026° ≤ 2Θ ≤ 50.154°), 2923 unique (R_{int} = 0.1012, R_{sigma} = 0.0768) which were used in all calculations. The final R_1 was 0.0539 (I > 2σ(I)) and wR_2 was 0.1412 (all data).

Table S3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 3h. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S2	4502.6(12)	3770.3(4)	3737.6(11)	59.3(3)
S1	6350.9(14)	3223.9(4)	3327.0(12)	68.3(4)
S3	7276.2(14)	4419.1(5)	2203.2(15)	84.3(4)
N1	4086(4)	4731.0(12)	2919(3)	54.3(8)
C1	10236(5)	3268.3(12)	7711(4)	47.3(8)
C4	7842(5)	3243.0(13)	5034(4)	51.1(9)
C7	5295(5)	4359.4(14)	2894(4)	50.2(9)
C6	8557(5)	3047.1(14)	7733(4)	59.3(10)
C2	10679(5)	3470.2(15)	6286(4)	60.9(10)
C3	9507(5)	3461.6(15)	4966(4)	61.6(11)
C12	11523(5)	3299.8(15)	9158(4)	59.6(9)
C5	7386(5)	3029.6(14)	6420(5)	59.0(10)
C11	2277(5)	4689.7(17)	3453(5)	72.1(12)
C8	4399(6)	5254.8(16)	2307(5)	73.8(12)
C9	2390(20)	5474(8)	2180(20)	79(3)
C15	10910(40)	3056(8)	10600(20)	105(6)
C16	1490(20)	5224(6)	3461(19)	79(3)
C14	11651(19)	3898(3)	9598(17)	86(4)
C13	13396(14)	3144(9)	8826(15)	114(5)
C14B	12750(20)	3748(6)	9160(18)	119(6)
C13B	12620(20)	2791(5)	9172(17)	106(4)
C15B	10530(30)	3266(10)	10640(20)	116(6)
C17	2920(20)	5566(6)	2637(18)	75(5)
C10	1370(18)	5161(5)	2530(20)	79(4)

Table S4 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3h. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S2	51.8(6)	58.2(7)	67.1(7)	7.9(5)	-1.5(5)	-3.6(5)
S1	79.6(8)	57.5(7)	64.9(7)	-13.5(5)	-16.1(6)	6.9(5)
S3	60.1(7)	97.0(9)	97.9(9)	28.9(7)	20.9(6)	3.5(6)
N1	56(2)	48(2)	59(2)	1.9(15)	2.5(15)	-5.3(16)
C1	50(2)	41(2)	50.7(19)	1.7(16)	5.5(15)	1.2(17)
C4	57(3)	42(2)	54(2)	-5.0(18)	-2.4(19)	5.2(18)
C7	47(2)	59(2)	44(2)	-0.3(17)	-2.1(17)	-6.0(19)
C6	68(3)	60(3)	50(2)	12.7(19)	10(2)	-6(2)
C2	52(2)	81(3)	51(2)	6(2)	10.7(19)	-8(2)
C3	64(3)	77(3)	44(2)	3(2)	7(2)	1(2)
C12	59(2)	67(2)	51.7(18)	4.8(17)	-2.6(14)	-1.1(16)
C5	58(2)	51(2)	67(3)	7(2)	3(2)	-10.4(19)
C11	53(3)	76(3)	88(3)	1(2)	13(2)	5(2)
C8	85(3)	57(3)	79(3)	4(2)	0(2)	-6(2)
C9	76(7)	71(7)	89(8)	-4(7)	-5(6)	10(5)
C15	123(14)	127(11)	64(5)	27(7)	-8(5)	-46(10)
C16	77(7)	71(7)	89(8)	-4(7)	-5(6)	10(5)
C14	89(8)	76(3)	86(8)	-9(4)	-37(7)	-13(4)
C13	66(4)	188(15)	85(8)	-19(9)	-13(4)	36(7)
C14B	136(11)	121(7)	92(10)	39(8)	-50(8)	-66(8)
C13B	96(8)	107(5)	108(9)	-6(6)	-45(7)	40(6)
C15B	89(9)	210(20)	46(4)	-12(8)	2(5)	-13(11)
C17	80(10)	48(7)	92(10)	-7(6)	-18(7)	6(6)
C10	63(6)	65(7)	108(11)	-11(9)	-10(8)	14(6)

Table S5 Bond Lengths for 3h.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S2	S1	2.0249(14)	C2	C3	1.382(5)
S2	C7	1.803(4)	C12	C15	1.487(11)
S1	C4	1.778(4)	C12	C14	1.592(9)
S3	C7	1.641(4)	C12	C13	1.506(9)
N1	C7	1.321(4)	C12	C14B	1.478(9)
N1	C11	1.463(5)	C12	C13B	1.550(9)
N1	C8	1.476(5)	C12	C15B	1.514(10)
C1	C6	1.383(5)	C11	C16	1.501(14)
C1	C2	1.387(5)	C11	C10	1.580(14)
C1	C12	1.519(5)	C8	C9	1.601(18)
C4	C3	1.374(5)	C8	C17	1.414(17)
C4	C5	1.372(5)	C9	C16	1.47(3)
C6	C5	1.378(5)	C17	C10	1.56(3)

Table S6 Bond Angles for 3h.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	S2	S1	105.76(13)	C15	C12	C1	116.2(12)
C4	S1	S2	103.70(12)	C15	C12	C14	103.4(10)
C7	N1	C11	127.1(3)	C15	C12	C13	112.8(10)
C7	N1	C8	122.4(3)	C13	C12	C1	112.3(5)
C11	N1	C8	110.5(3)	C13	C12	C14	105.2(7)
C6	C1	C2	116.1(3)	C14B	C12	C1	113.8(6)
C6	C1	C12	122.6(3)	C14B	C12	C13B	109.5(7)
C2	C1	C12	121.4(3)	C14B	C12	C15B	112.8(11)
C3	C4	S1	119.9(3)	C15B	C12	C1	110.8(11)
C5	C4	S1	121.3(3)	C15B	C12	C13B	103.6(9)
C5	C4	C3	118.8(3)	C4	C5	C6	120.6(3)
S3	C7	S2	123.6(2)	N1	C11	C16	107.8(7)
N1	C7	S2	111.2(3)	N1	C11	C10	99.4(7)
N1	C7	S3	125.1(3)	N1	C8	C9	100.2(8)
C5	C6	C1	122.1(3)	C17	C8	N1	107.8(7)
C3	C2	C1	122.4(4)	C16	C9	C8	105.6(14)
C4	C3	C2	120.0(3)	C9	C16	C11	101.5(13)
C1	C12	C14	105.6(5)	C8	C17	C10	101.3(12)
C1	C12	C13B	105.5(5)	C17	C10	C11	101.3(10)

Table S7 Torsion Angles for 3h.

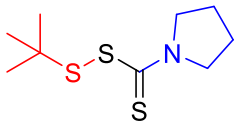
A	B	C	D	Angle/°	A	B	C	D	Angle/°
S2	S1	C4	C3	-106.3(3)	C6	C1	C12	C15B	-22.4(11)
S2	S1	C4	C5	75.6(3)	C2	C1	C6	C5	-0.3(5)
S1	S2	C7	S3	-8.2(2)	C2	C1	C12	C15	-178.4(10)
S1	S2	C7	N1	172.2(2)	C2	C1	C12	C14	67.7(7)
S1	C4	C3	C2	-179.1(3)	C2	C1	C12	C13	-46.4(11)
S1	C4	C5	C6	179.9(3)	C2	C1	C12	C14B	28.1(11)
N1	C11	C16	C9	30.3(16)	C2	C1	C12	C13B	-92.0(9)
N1	C11	C10	C17	-37.9(12)	C2	C1	C12	C15B	156.5(10)
N1	C8	C9	C16	31.9(16)	C3	C4	C5	C6	1.8(5)
N1	C8	C17	C10	-32.2(13)	C12	C1	C6	C5	178.7(3)
C1	C6	C5	C4	-1.2(6)	C12	C1	C2	C3	-177.8(3)
C1	C2	C3	C4	-0.6(6)	C5	C4	C3	C2	-0.9(5)
C7	N1	C11	C16	172.6(7)	C11	N1	C7	S2	-3.5(4)
C7	N1	C11	C10	-157.3(7)	C11	N1	C7	S3	176.9(3)
C7	N1	C8	C9	164.6(7)	C11	N1	C8	C9	-12.7(8)
C7	N1	C8	C17	-174.8(7)	C11	N1	C8	C17	7.9(7)
C6	C1	C2	C3	1.2(6)	C8	N1	C7	S2	179.7(3)
C6	C1	C12	C15	2.7(10)	C8	N1	C7	S3	0.1(5)
C6	C1	C12	C14	-111.2(7)	C8	N1	C11	C16	-10.2(8)
C6	C1	C12	C13	134.7(10)	C8	N1	C11	C10	19.9(7)
C6	C1	C12	C14B	-150.8(10)	C8	C9	C16	C11	-38.0(18)
C6	C1	C12	C13B	89.1(9)	C8	C17	C10	C11	43.8(15)

Table S8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3h.

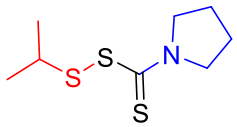
Atom	*x*	*y*	*z*	U(eq)
H6	8206.97	2905.66	8663.17	71
H2	11804.36	3616.61	6215.34	73
H3	9845.62	3603.86	4032.79	74
H5	6276.14	2871.71	6474.62	71
H11A	2317.81	4542.45	4497.55	87
H11B	1548.58	4467.28	2754.41	87
H11C	2265.05	4733.4	4578.12	87
H11D	1715.77	4363.37	3147.89	87
H8AA	4902.49	5243.25	1292.54	89
H8AB	5172.56	5456.79	3027.78	89
H8BC	5491.38	5398.21	2803.31	89
H8BD	4516.43	5240.88	1185.49	89
H9A	2393.28	5847.03	2299.11	95
H9B	1797.2	5386.43	1172.58	95
H15A	10766.68	2690.58	10439.38	158
H15B	9790.34	3205.02	10845.96	158
H15C	11786.7	3115.39	11457.79	158
H16A	205.85	5217.37	3245.14	95
H16B	1776.54	5397.3	4453.33	95
H14A	12535.1	3946.05	10451.81	129
H14B	10510.6	4016.47	9901.44	129
H14C	11985.56	4091.64	8706.58	129
H13A	13455.73	2774.77	8718.68	171
H13B	14214.1	3253.39	9674.19	171
H13C	13714.22	3304.84	7871.98	171
H14D	13478.03	3755.17	10128.47	179
H14E	12067.85	4061.43	9052.47	179
H14F	13505.26	3717.13	8301.84	179
H13D	13259.08	2771.04	8238.32	159
H13E	11824.92	2500.51	9211.21	159
H13F	13455.39	2785.98	10073.43	159
H15D	9841.09	2951.28	10622.96	174
H15E	9735.43	3556.75	10687.12	174
H15F	11366.73	3267.05	11533.36	174
H17A	2716.09	5839.17	1867.45	89
H17B	3074.2	5718.04	3674.52	89
H10A	1023.43	5070.97	1453.5	95

H10B	331.12	5286.67	3034.31	95

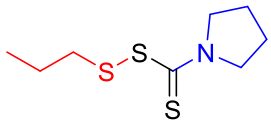
9. Characterization Data for the Electrolysis Products



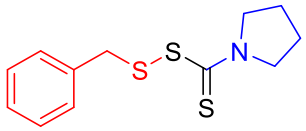
***Tert*-butyl pyrrolidine-1-carbo(dithioperoxo)thioate (3a).** White solid (96%, 67.7 mg). mp: 97-99 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.91 (t, *J* = 7.2 Hz, 2H), 3.80 (t, *J* = 6.8 Hz, 2H), 2.12 - 2.05 (m, 2H), 1.99 - 1.92 (m, 2H), 1.31 (s, 9H). **^{13}C NMR** (100 M Hz, Chloroform-*d*) δ 193.7, 56.9, 50.7, 50.0, 30.0, 26.6, 24.2. **HRMS** (*m/z*) (ESI): calcd for $C_9H_{18}NS_3^+$ $[M+H]^+$: 236.0596, found 236.0596.



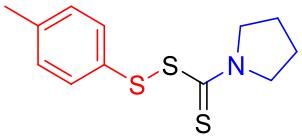
Isopropyl pyrrolidine-1-carbo(dithioperoxo)thioate (3b). White brown solid (80%, 53.0 mg). mp: 71-73 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 3.95 (t, *J* = 7.2 Hz, 2H), 3.77 (t, *J* = 7.2 Hz, 2H), 3.31 - 3.24 (m, 1H), 2.13 - 2.08 (m, 2H), 2.01 - 1.96 (m, 2H), 1.31 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 193.3, 56.7, 50.6, 41.1, 26.5, 24.2, 22.1. **HRMS** (*m/z*) (ESI): calcd for $C_8H_{15}NS_3Na^+$ $[M+Na]^+$: 244.0259, found 244.0255.



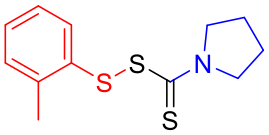
Propyl pyrrolidine-1-carbo(dithioperoxo)thioate (3c). Yellow oil (70%, 46.4 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.96 (t, *J* = 6.9 Hz, 2H), 3.74 (t, *J* = 6.9 Hz, 2H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.14 - 2.08 (m, 2H), 2.02 - 1.97 (m, 2H), 1.73 - 1.67 (m, 3H), 1.02 - 0.99 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 193.0, 56.7, 50.5, 40.5, 26.5, 24.2, 22.0, 13.2. **HRMS** (*m/z*) (ESI): calcd for $C_8H_{16}NS_3^+$ $[M+H]^+$: 222.0439, found 222.0438.



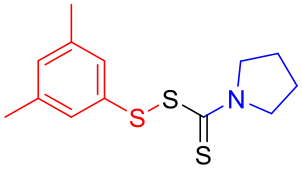
Benzyl pyrrolidine-1-carbo(dithioperoxo)thioate (3d). Brown solid (50%, 40.4 mg). mp: 96-98 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 - 7.35 (m, 2H), 7.34 - 7.27 (m, 3H), 4.11 (s, 2H), 3.98 (t, *J* = 7.0 Hz, 2H), 3.70 (t, *J* = 6.8 Hz, 2H), 2.13 - 2.07 (m, 2H), 2.04 - 1.98 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 192.4, 136.1, 129.7, 128.5, 127.7, 56.6, 50.6, 42.8, 26.5, 24.2. **HRMS** (*m/z*) (ESI): calcd for $C_{12}H_{16}NS_3^+$ $[M+H]^+$: 270.0439, found 270.0436.



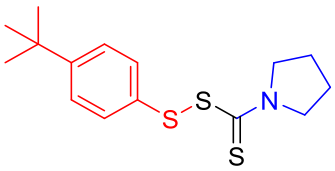
***P*-tolyl pyrrolidine-1-carbo(dithioperoxo)thioate (3e).** White brown solid (76%, 61.3 mg). mp: 123-125 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 3.94 (t, *J* = 7.0 Hz, 2H), 3.72 (t, *J* = 6.9 Hz, 2H), 2.30 (s, 3H), 2.11 - 2.05 (m, 2H), 1.99 - 1.93 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.7, 138.5, 132.8, 130.5, 129.7, 56.9, 50.6, 26.6, 24.2, 21.2. **HRMS** (*m/z*) (ESI): calcd for $C_{12}H_{16}NS_3^+$ $[M+H]^+$: 270.0439, found 270.0438.



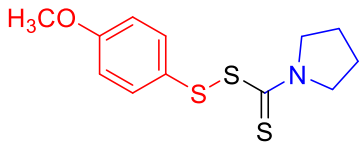
***O*-tolyl pyrrolidine-1-carbo(dithioperoxo)thioate (3f).** White solid (77%, 62.1 mg). mp: 129-131 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 - 7.62 (m, 1H), 7.15 (d, 3H), 3.95 (t, *J* = 7.0 Hz, 2H), 3.77 (t, *J* = 6.9 Hz, 2H), 2.54 (s, 3H), 2.14 - 2.08 (m, 2H), 2.01 - 1.96 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.3, 138.0, 134.7, 130.3, 130.0, 127.9, 126.6, 56.9, 50.7, 26.7, 24.2, 20.4. **HRMS** (*m/z*) (ESI): calcd for $C_{12}H_{16}NS_3^+$ $[M+H]^+$: 270.0439, found 270.0438.



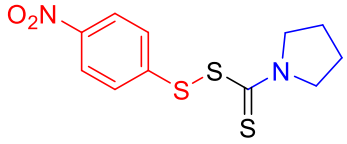
3,5-Dimethylphenyl pyrrolidine-1-carbo(dithioperoxo)thioate (3g). White brown solid (74%, 62.8 mg). mp: 63-65 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 - 7.55 (m, 3H), 4.36 - 4.33 (m, 2H), 4.17 - 4.14 (m, 2H), 2.66 (s, 6H), 2.51 - 2.48 (m, 2H), 2.39 - 2.36 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.6, 138.7, 135.5, 130.0, 127.2, 56.9, 50.6, 26.6, 24.2, 21.3. **HRMS** (*m/z*) (ESI): calcd for $C_{13}H_{18}NS_3^+$ $[M+H]^+$: 284.0596, found 284.0596.



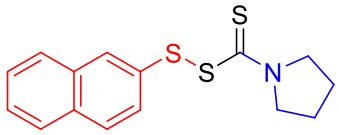
4-(*Tert*-butyl)phenyl pyrrolidine-1-carbo(dithioperoxo)thioate (3h). White solid (80%, 74.7 mg). mp: 111-113 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 - 7.47 (m, 2H), 7.35 - 7.27 (m, 2H), 3.96 (t, *J* = 7.0 Hz, 2H), 3.75 (t, *J* = 6.9 Hz, 2H), 2.14 - 2.06 (m, 2H), 2.01 - 1.94 (m, 2H), 1.28 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.8, 151.5, 132.7, 130.1, 126.1, 57.0, 50.6, 34.6, 31.3, 26.6, 24.2. **HRMS** (*m/z*) (ESI): calcd for $C_{15}H_{22}NS_3^+$ $[M+H]^+$: 312.0909, found 312.0908.



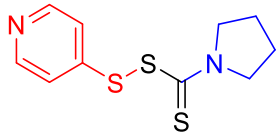
4-Methoxyphenyl pyrrolidine-1-carbo(dithioperoxo)thioate (3i). White solid (65%, 55.6 mg). mp: 61-63 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.69 - 7.64 (m, 2H), 6.84 - 6.80 (m, 2H), 3.95 (t, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.70 (t, *J* = 6.9 Hz, 2H), 2.11 - 2.06 (m, 2H), 1.99 - 1.95 (m, 2H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 192.1, 160.4, 134.0, 127.0, 114.5, 56.8, 55.4, 50.5, 26.6, 24.2. **HRMS** (*m/z*) (ESI): calcd for $C_{12}H_{15}NOS_3Na^+$ $[M+Na]^+$: 308.0208, found 308.0208.



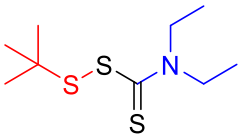
4-Nitrophenyl pyrrolidine-1-carbo(dithioperoxo)thioate (3j). Yellow solid (87%, 78.3 mg). mp: 108-110 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 - 8.08 (m, 2H), 7.61 - 7.56 (m, 2H), 3.95 (t, *J* = 7.0 Hz, 2H), 3.83 (t, *J* = 6.9 Hz, 2H), 2.20 - 2.13 (m, 2H), 2.07 - 2.00 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 188.8, 146.7, 145.0, 127.4, 126.4, 124.5, 123.9, 57.3, 50.9, 26.7, 24.3. **HRMS** (*m/z*) (ESI): calcd for $C_{11}H_{13}N_2O_2S_3^+$ $[M+H]^+$: 301.0134, found 301.0133.



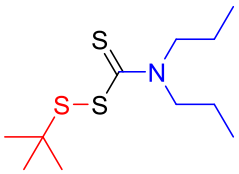
Naphthalen-2-yl pyrrolidine-1-carbo(dithioperoxo)thioate (3k). White solid (78%, 71.4 mg). mp: 76-78 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.80 - 7.76 (m, 3H), 7.69 - 7.66 (m 1H), 7.49 - 7.43 (m, 2H), 3.96 (t, *J* = 7.0 Hz, 2H), 3.75 (t, *J* = 6.9 Hz, 2H), 2.11 - 2.05 (m, 2H), 1.99 - 1.93 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.3, 133.3, 132.9, 129.0, 128.9, 127.8, 127.1, 126.7, 126.5, 57.0, 50.7, 26.6, 24.2. **HRMS** (*m/z*) (ESI): calcd for $C_{15}H_{16}NS_3^+$ $[M+H]^+$: 306.0439, found 306.0438.



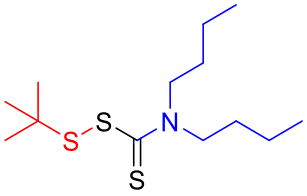
Pyridin-4-yl pyrrolidine-1-carbo(dithioperoxo)thioate (3l). Yellow oil (70%, 53.8 mg). mp: 170-172 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 - 8.42 (m, 2H), 7.36 - 7.32 (m, 2H), 3.94 (t, *J* = 7.0 Hz, 2H), 3.83 (t, *J* = 6.8 Hz, 2H), 2.18 - 2.12 (m, 2H), 2.05 - 1.98 (m, 2H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 188.7, 149.9, 149.3, 147.3, 120.8, 120.0, 57.2, 50.9, 26.7, 24.3. **HRMS** (*m/z*) (ESI): calcd for $C_{10}H_{13}N_2S_3^+$ $[M+H]^+$: 257.0235, found 257.0234.



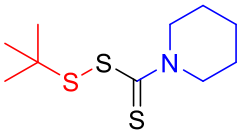
***Tert*-butyl diethylcarbamo(dithioperoxo)thioate (4a).** Colorless oil (89%, 63.3 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.11 - 3.82 (m, 4H), 1.38 - 1.33 (m, 3H), 1.33 - 1.30 (m, 9H), 1.29 - 1.23 (m, 3H) **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.9, 51.8, 50.0, 47.0, 30.0, 13.3, 11.4. **HRMS** (*m/z*) (ESI): calcd for $C_9H_{20}NS_3^+$ $[M+H]^+$: 238.0752, found 238.0752.



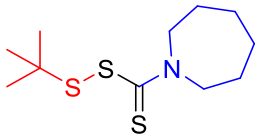
***Tert*-butyl dipropylcarbamo(dithioperoxo)thioate (4b).** Yellow oil (91%, 72.4 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.89 (t, *J* = 7.6 Hz, 2H), 3.75 (t, *J* = 8.0 Hz, 2H), 1.81 - 1.68 (m, 4H), 1.28 (s, 9H), 0.98 - 0.85 (m, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 197.4, 58.9, 54.5, 50.0, 30.0, 21.6, 19.5, 11.2. **HRMS** (*m/z*) (ESI): calcd for $C_{11}H_{24}NS_3^+$ $[M+H]^+$: 266.1065, found 266.1065.



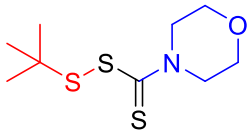
***Tert*-butyl dibutylcarbamo(dithioperoxo)thioate (4c).** Colorless oil (90%, 79.1 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.94 (t, *J* = 7.9 Hz, 2H), 3.79 (t, *J* = 8.0 Hz, 2H), 1.77 - 1.65 (m, 4H), 1.44 - 1.32 (m, 4H), 1.30 (s, 9H), 0.98 - 0.88 (m, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 197.2, 57.2, 52.7, 50.0, 30.2, 30.0, 28.2, 20.1, 13.9. **HRMS** (*m/z*) (ESI): calcd for $C_{13}H_{28}NS_3^+$ $[M+H]^+$: 294.1378, found 294.1378.



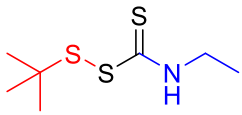
***Tert*-butyl piperidine-1-carbo(dithioperoxo)thioate (4d).** Yellow solid (82%, 61.3 mg). mp: 57-59 °C. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.33 - 4.05 (m, 4H), 1.73 (s, 6H), 1.34 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 197.2, 55.5, 50.1, 30.0, 24.3. **HRMS** (*m/z*) (ESI): calcd for $C_{10}H_{20}NS_3^+$ $[M+H]^+$: 250.0752, found 250.0752.



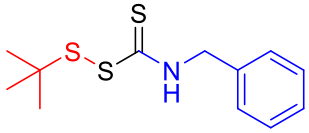
***Tert*-butyl azepane-1-carbo(dithioperoxo)thioate (4e).** Yellow oil (85%, 67.1 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 4.16 (t, *J* = 6.2 Hz, 2H), 4.03 (t, *J* = 6.1 Hz, 2H), 1.89 - 1.83 (m, 4H), 1.58 - 1.52 (m, 4H), 1.29 (s, 9H). **^{13}C NMR** (150 MHz, Chloroform-*d*) δ 196.5, 57.2, 52.1, 48.9, 29.0, 27.0, 25.5, 25.4, 24.8. **HRMS** (*m/z*) (ESI): calcd for $C_{11}H_{22}NS_3^+$ $[M+H]^+$: 264.0909, found 264.0907.



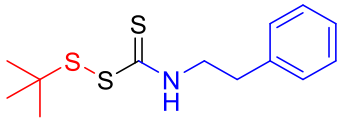
***Tert*-butyl morpholine-4-carbo(dithioperoxo)thioate (4f).** Brown solid (71%, 53.5 mg). mp: 63-65 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.22 (s, 4H), 3.79 - 3.73 (m, 4H), 1.31 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 199.0, 66.4, 53.3, 51.8, 50.4, 30.0. **HRMS** (*m/z*) (ESI): calcd for $C_9H_{18}NOS_3^+$ $[M+H]^+$: 252.0545, found 252.0546.



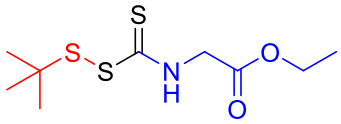
***Tert*-butyl ethylcarbamo(dithioperoxo)thioate (4g).** Brown oil (53%, 33.2 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.83 - 3.75 (m, 2H), 1.35 (s, 9H), 1.30 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.3, 50.9, 41.1, 29.8, 13.4. **HRMS** (*m/z*) (ESI): calcd for $C_7H_{16}NS_3^+$ $[M+H]^+$: 210.0439, found 210.0439.



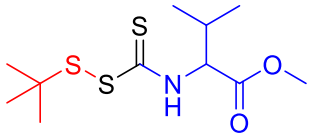
***Tert*-butyl benzylcarbamo(dithioperoxo)thioate (4h).** White solid (67%, 54.5 mg). mp: 87-89 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 - 7.31 (m, 5H), 4.92 (d, *J* = 5.5 Hz, 2H), 1.27 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.9, 135.4, 129.0, 128.4, 128.3, 50.8, 50.2, 29.8. **HRMS** (*m/z*) (ESI): calcd for $C_{12}H_{18}NS_3^+$ $[M+H]^+$: 272.0596, found 272.0592.



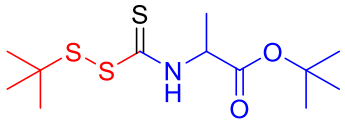
***Tert*-butyl phenethylcarbamo(dithioperoxo)thioate (4i).** Brown oil (73%, 62.4 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 - 7.28 (m, 2H), 7.24 - 7.19 (m, 3H), 3.97 - 3.90 (m, 2H), 2.94 (t, *J* = 6.9 Hz, 2H), 1.48 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.9, 138.1, 128.9, 128.8, 126.9, 50.5, 46.8, 34.0, 30.2. **HRMS** (*m/z*) (ESI): calcd for $C_{13}H_{20}NS_3^+$ $[M+H]^+$: 286.0752, found 286.0753.



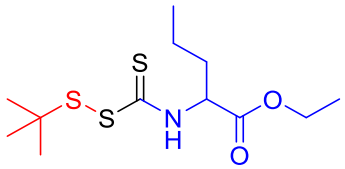
Ethyl (*tert*-butyldisulfannecarbonothioyl)glycinate (4j). Brown solid (60%, 48.1 mg). mp: 50-52 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.44 (d, *J* = 4.6 Hz, 2H), 4.31 - 4.25 (m, 2H), 1.38 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 193.0, 168.4, 62.2, 51.0, 47.3, 29.8, 14.2. **HRMS** (*m/z*) (ESI): calcd for $C_9H_{18}NO_2S_3^+$ $[M+H]^+$: 268.0494, found 268.0492.



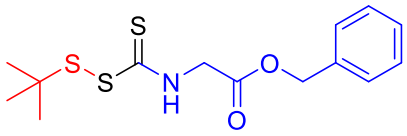
Methyl (*tert*-butyldisulfannecarbonothioyl)valinate (4k). Brown solid (65%, 57.5 mg). mp: 35-37 ℃. Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.24 - 5.18 (m, 1H), 3.77 (s, 3H), 2.40 - 2.32 (m, 1H), 1.59 (s, 9H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 197.6, 171.5, 62.5, 52.4, 50.7, 31.4, 30.2, 18.7, 18.4. **HRMS** (*m/z*) (ESI): calcd for $C_{11}H_{22}NO_2S_3^+$ $[M+H]^+$: 296.0807, found 296.0805.



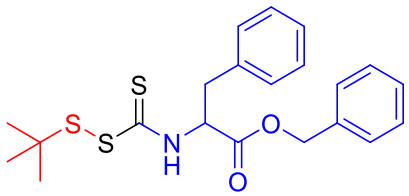
***Tert*-butyl (*tert*-butyldisulfannecarbonothioyl)alaninate (4l).** Blue oil (80%, 74.2 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.96 - 4.90 (m, 1H), 1.51 (s, 3H), 1.49 (s, 9H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.7, 170.8, 83.1, 54.4, 50.9, 29.8, 28.0, 17.6. **HRMS** (*m/z*) (ESI): calcd for $C_{12}H_{24}NO_2S_3^+$ $[M+H]^+$: 310.0964, found 310.0963.



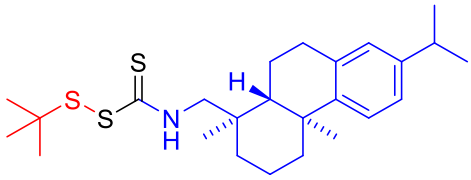
Ethyl 2-((*tert*-butyldisulfannecarbonothioyl)amino)pentanoate (4m). Brown oil (70%, 64.9 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.15 - 5.09 (m, 1H), 4.27 - 4.21 (m, 2H), 2.05 - 1.96 (m, 1H), 1.89 - 1.80 (m, 1H), 1.37 (s, 9H), 1.35 - 1.32 (m, 1H), 1.32 - 1.28 (m, 3H), 1.27 - 1.20 (m, 1H), 0.95 - 0.91 (m, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 192.2, 171.1, 61.9, 57.9, 50.9, 33.8, 29.9, 18.4, 14.2, 13.8. **HRMS** (*m/z*) (ESI): calcd for $C_{12}H_{24}NO_2S_3^+$ $[M+H]^+$: 310.0964, found 310.0963.



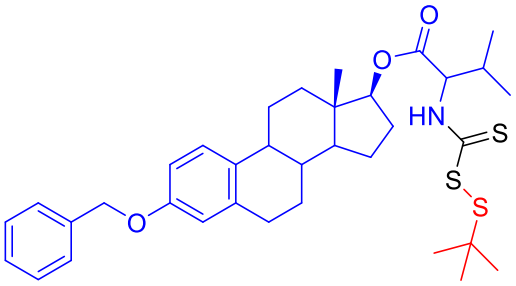
Benzyl (*tert*-butyldisulfannecarbonothioyl)glycinate (4n). Brown oil (72%, 71.1 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 - 7.34 (m, 5H), 5.25 (s, 2H), 4.51 (d, *J* = 4.7 Hz, 2H), 1.36 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 193.2, 168.2, 134.7, 128.8, 128.8, 128.6, 67.8, 51.0, 47.3, 29.8. **HRMS** (*m/z*) (ESI): calcd for $C_{14}H_{20}NO_2S_3^+$ $[M+H]^+$: 330.0651, found 330.0647.



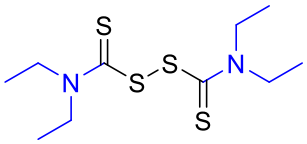
Benzyl (*tert*-butyldisulfannecarbonothioyl)phenylalaninate (4o). Brown oil (70%, 88.0 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.99 (d, *J* = 7.4 Hz, 1H), 7.40 - 7.36 (m, 3H), 7.31 - 7.29 (m, 2H), 7.25 - 7.24 (m, 3H), 7.04 – 7.01 (m, 2H), 5.40 - 5.35 (m, 1H), 5.18 (d, *J* = 3.7 Hz, 2H), 3.40 - 3.28 (m, 2H), 1.18 (s, 9H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 192.7, 169.9, 134.8, 134.7, 129.5, 128.9, 128.8, 128.8, 128.7, 127.5, 67.7, 58.8, 50.8, 36.7, 29.7. **HRMS** (*m/z*) (ESI): calcd for $C_{21}H_{26}NO_2S_3^+$ $[M+H]^+$: 420.1120, found 420.1116.



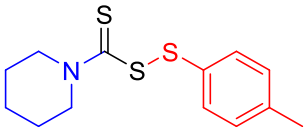
***Tert*-butyl(((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)carbamo(dithioperoxo)thioate (4p).** Colorless oil (50%, 67.4 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.02 - 6.97 (m, 1H), 6.89 (d, *J* = 2.0 Hz, 1H), 3.81 - 3.75 (m, 1H), 3.62 - 3.54 (m, 1H), 2.99 - 2.79 (m, 3H), 2.36 - 2.28 (m, 1H), 1.96 - 1.68 (m, 5H), 1.60 - 1.56 (m, 1H), 1.50 - 1.46 (m, 1H), 1.42 - 1.38 (m, 1H), 1.26 (s, 9H), 1.24 (s, 3H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.03 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 191.8, 146.8, 145.9, 134.5, 126.9, 124.2, 124.0, 50.7, 46.1, 38.4, 37.6, 36.9, 33.5, 30.2, 30.0, 25.2, 24.1, 24.1, 19.3, 18.8, 18.6. **HRMS** (*m/z*) (ESI): calcd for $C_{25}H_{40}NS_3^+$ $[M+H]^+$: 450.2317, found 450.2314.



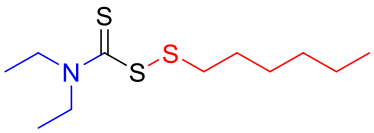
(13*S*,17*S*)-3-(Benzyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl (*tert*-butyldisulfannecarbonothioyl)valinate (4q). Colorless oil (58%, 108.8 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.17 (d, *J* = 8.1 Hz, 1H), 7.45 - 7.33 (m, 5H), 7.21 - 7.19 (m, 1H), 6.80 - 6.78 (m, 1H), 6.73 (d, *J* = 2.7 Hz, 1H), 5.11 - 5.08 (m, 1H), 5.04 (s, 2H), 4.82 - 4.78 (m, 1H), 2.89 - 2.83 (m, 2H), 2.48 - 2.40 (m, 1H), 2.33 - 2.19 (m, 3H), 1.92 - 1.87 (m, 2H), 1.82 - 1.74 (m, 1H), 1.66 - 1.59 (m, 1H), 1.41 (s, 15H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 192.8, 170.2, 156.8, 137.9, 137.3, 132.6, 128.6, 127.9, 127.5, 126.4, 114.9, 112.4, 84.5, 77.4, 77.3, 77.1, 76.8, 70.0, 63.2, 50.9, 49.6, 43.8, 43.0, 38.5, 36.9, 31.7, 30.0, 29.8, 27.5, 27.2, 26.2, 23.3, 18.8, 18.6, 12.4. **HRMS** (*m/z*) (ESI): calcd for $C_{35}H_{48}NO_3S_3^+$ $[M+H]^+$: 626.2791, found 626.2786.



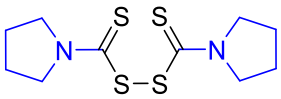
Disulfiram (I)[3]. White solid (50%, 44.4 mg). mp: 69-71 °C. Petroleum ether/ethyl acetate = 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.06 - 3.98 (m, 8H), 1.48 (t, *J* = 8.0 Hz, 6H), 1.29 (t, *J* = 8.0 Hz, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 192.7, 52.1, 47.6, 13.5, 11.5.



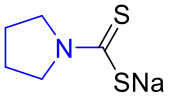
***p*-Tolyl piperidine-1-carbo(dithioperoxo)thioate (II)[4].** Yellow oil (70%, 59.4 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 - 7.46 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.29 (s, 2H), 3.96 (s, 2H), 2.31 (s, 3H), 1.70 (s, 6H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 194.8, 138.3, 132.8, 130.2, 129.7, 55.6, 52.0, 26.3, 25.5, 24.1, 21.2.



Hexyl diethylcarbamo(dithioperoxo)thioate (III)[5]. Yellow oil (44%, 35.0 mg). Petroleum ether/ethyl acetate = 80/1–20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.01 (m, 2H), 3.78 (m, 2H), 2.85 - 2.76 (m, 2H), 1.62 (m, 2H), 1.40 - 1.24 (m, 12H), 0.84 (t, *J* = 8.0 Hz, 3H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 196.1, 51.6, 47.0, 38.6, 31.4, 28.5, 28.2, 22.5, 14.1, 13.1, 11.5.



Pyrrolidine-1-carbothioic dithioperoxyanhydride (5). White solid (96%, 84.1 mg). 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)[6]. 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] J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy, L. M. *J. Org. Chem*., 1999, **64**, 5575-5580.

[2] Z. W. Hou, Z. Y. Mao, Y. Y. Melcamu, X. Lu, H. C. Xu, *Angew. Chem. Int. Ed*., 2018, **57**, 1636 -1639.

[3] C. N. Kapanda, G. G. Muccioli, G. Labar, J. H. Poupaert, D. M. Lambert, *J. Med. Chem*., 2009, **52**, 7310-7314.

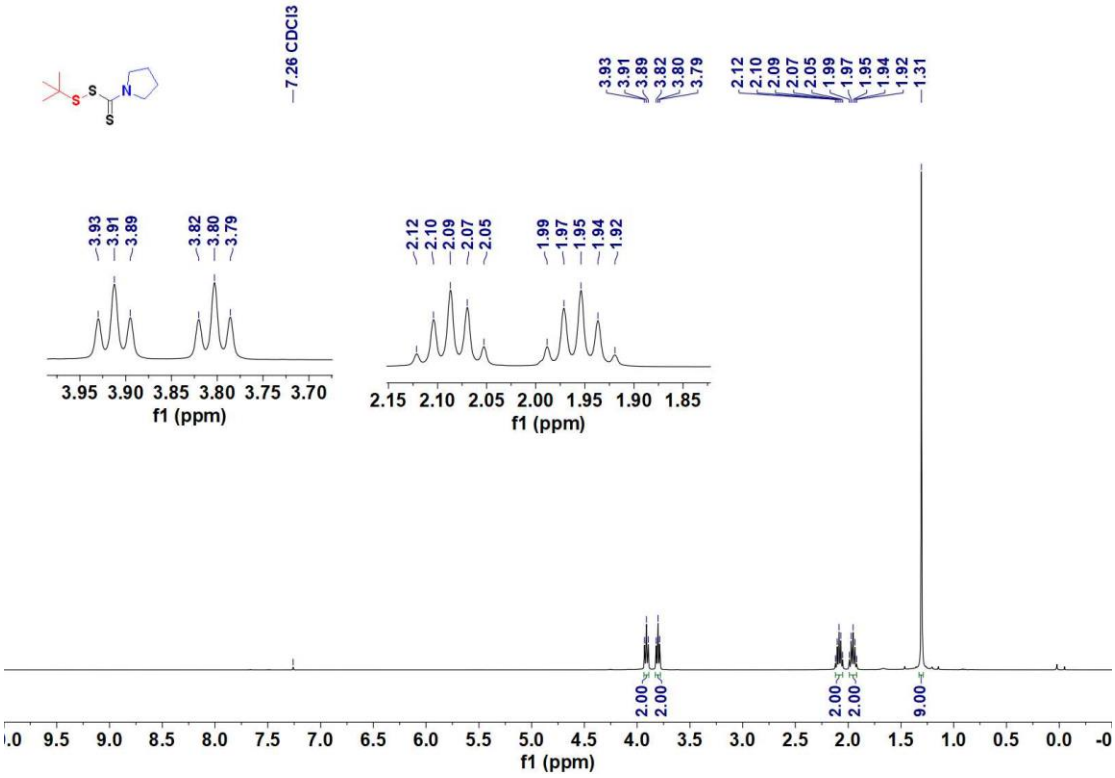
[4] A. Gucchait, N. Joardar, P. K. Parida, P. Roy, N. Mukherjee, A. Dutta, R. Yesuvadian, S. P. SinhaBabu, K. Jana, A. K. Misra, *Eur. J. Med. Chem*., 2018, **143**, 598-610.

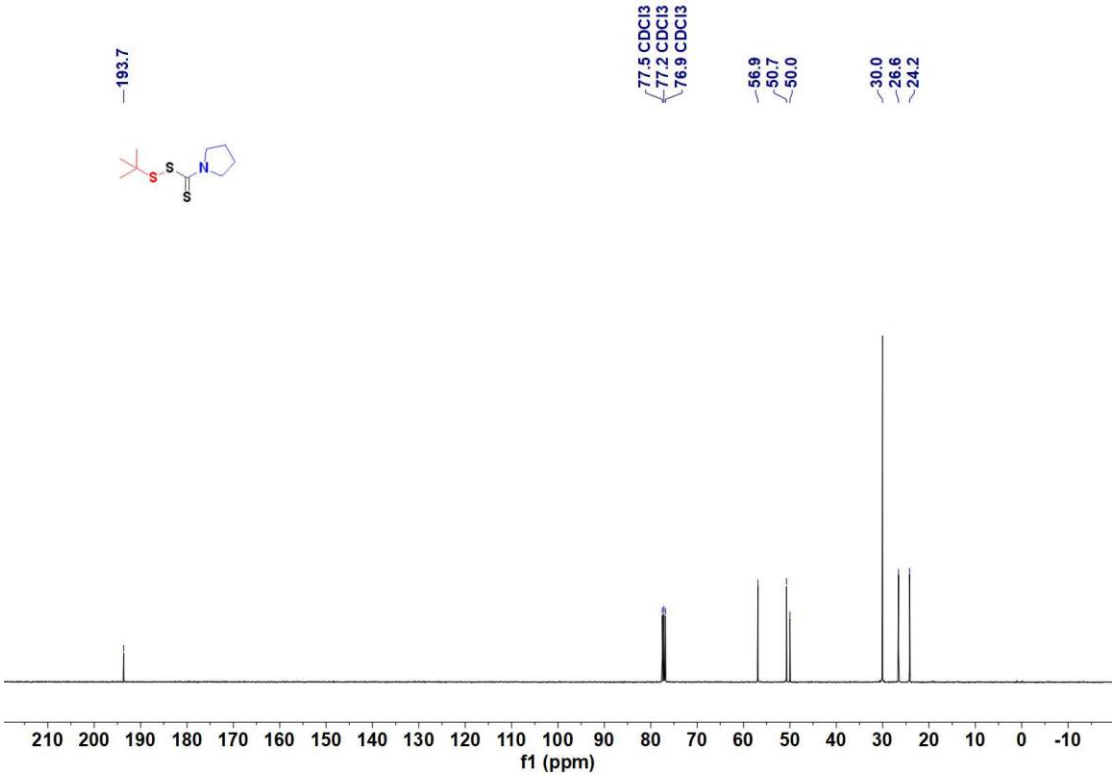
[5] V. Cilibrasi, K. Tsang, M. Morelli, F. Solfa, H. L. Wiggins, A. T. Jones, A. D. Westwell, *Tetrahedron Lett.*, 2015, **56**, 2583-2585.

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

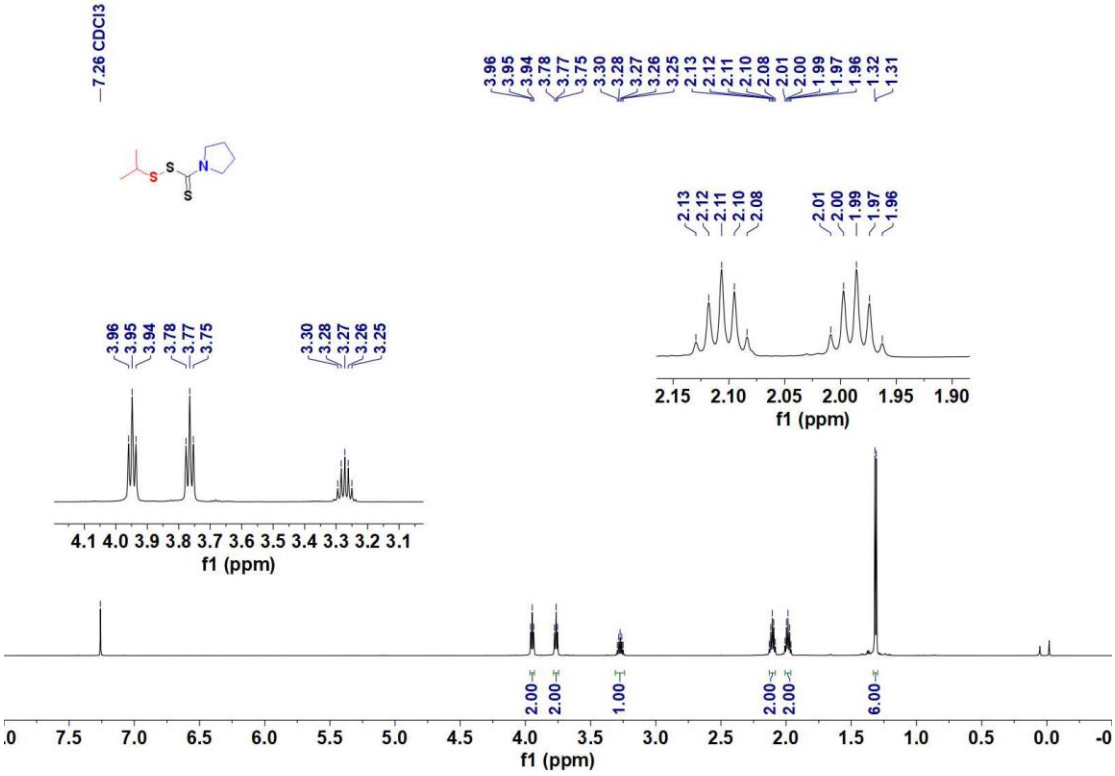
10. Copies of ^{1}H NMR and ^{13}C NMR for the Products

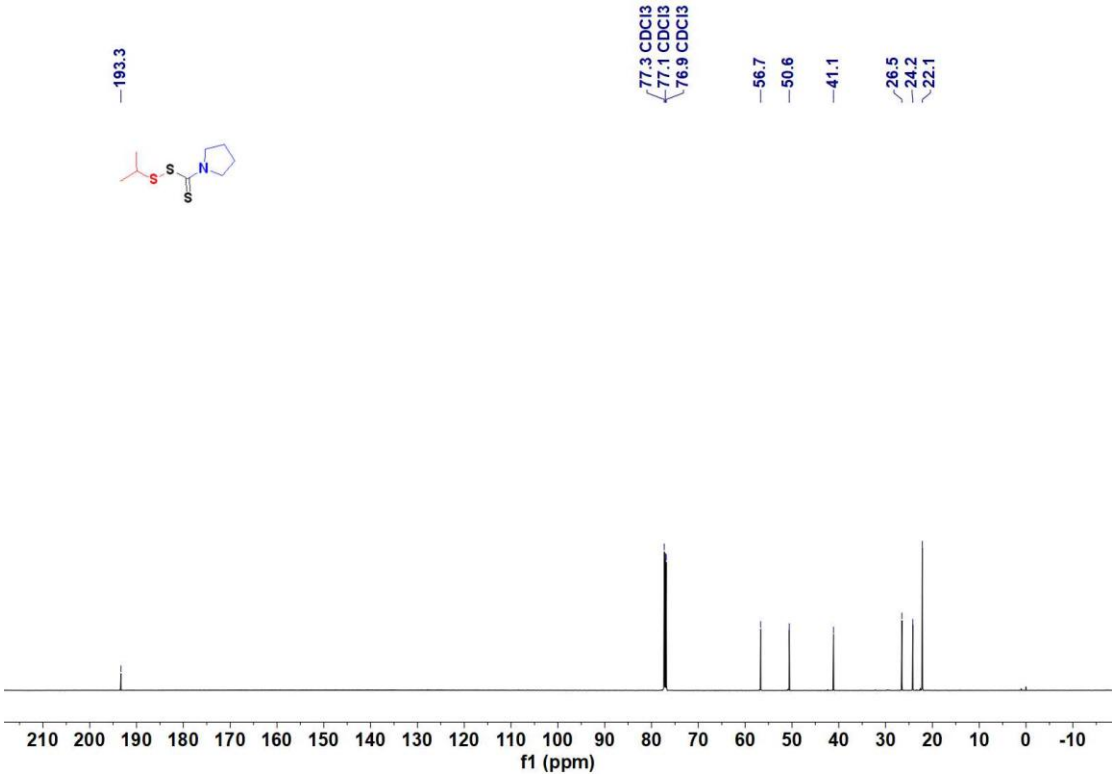
***Tert*-butyl pyrrolidine-1-carbo(dithioperoxo)thioate (3a)**



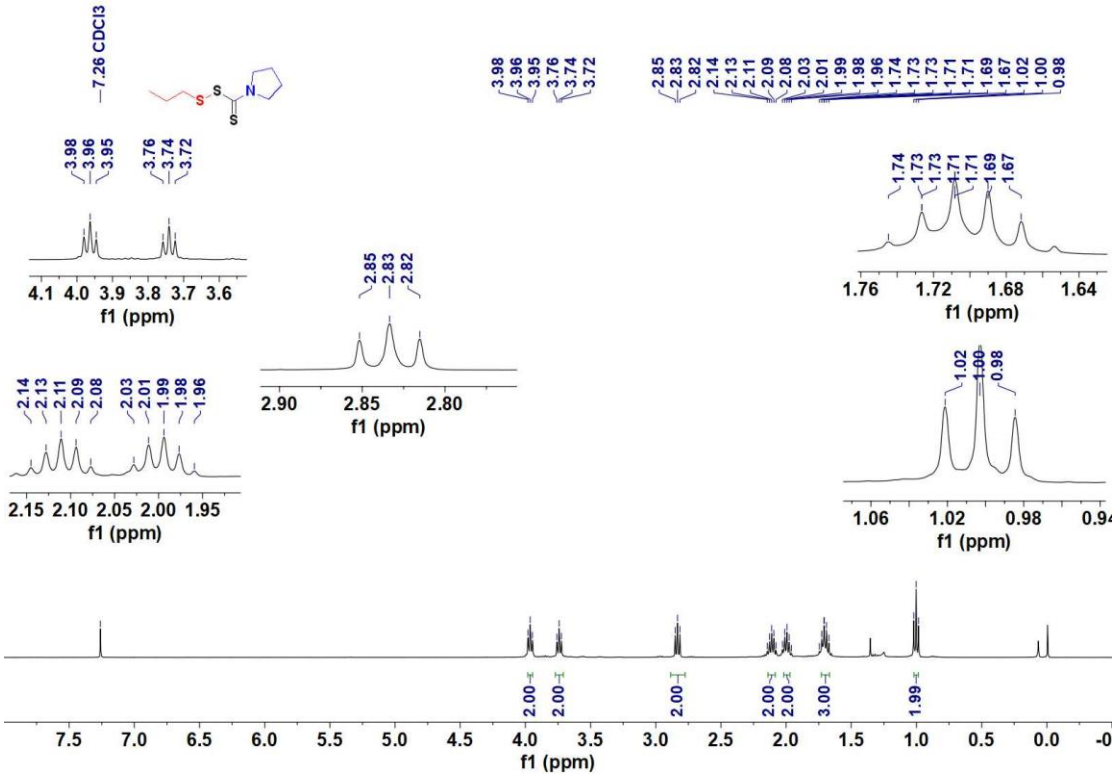


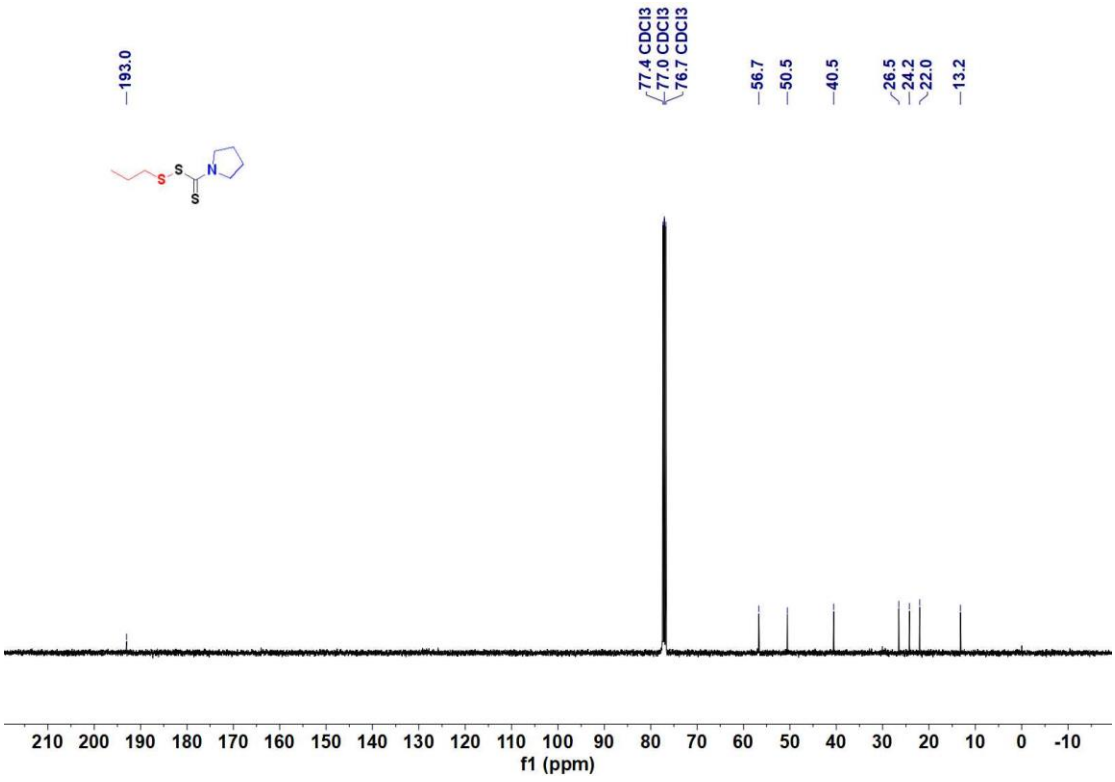
Isopropyl pyrrolidine-1-carbo(dithioperoxo)thioate (3b)



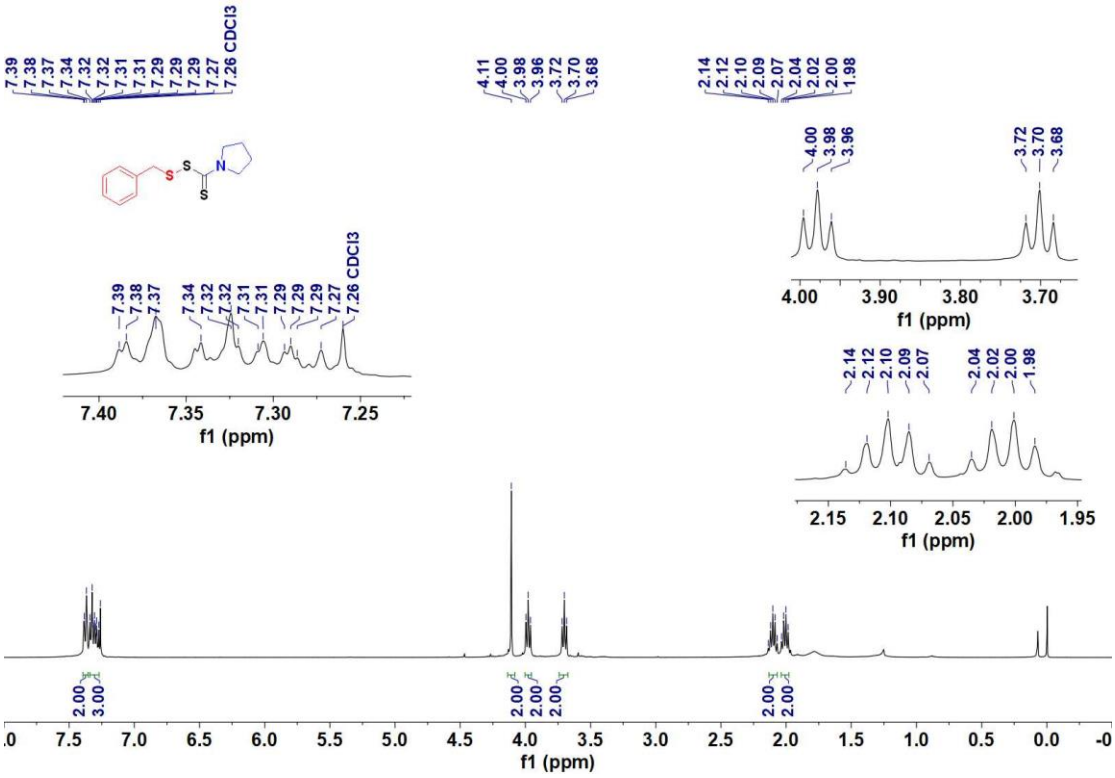


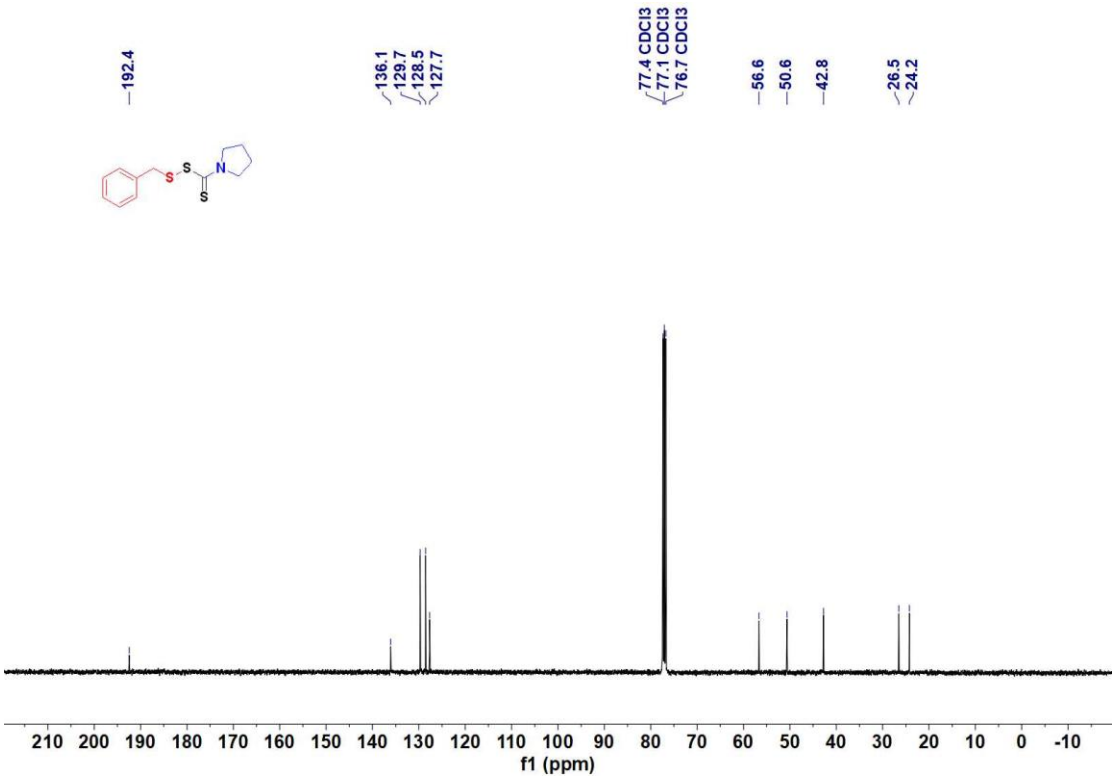
Propyl pyrrolidine-1-carbo(dithioperoxo)thioate (3c)



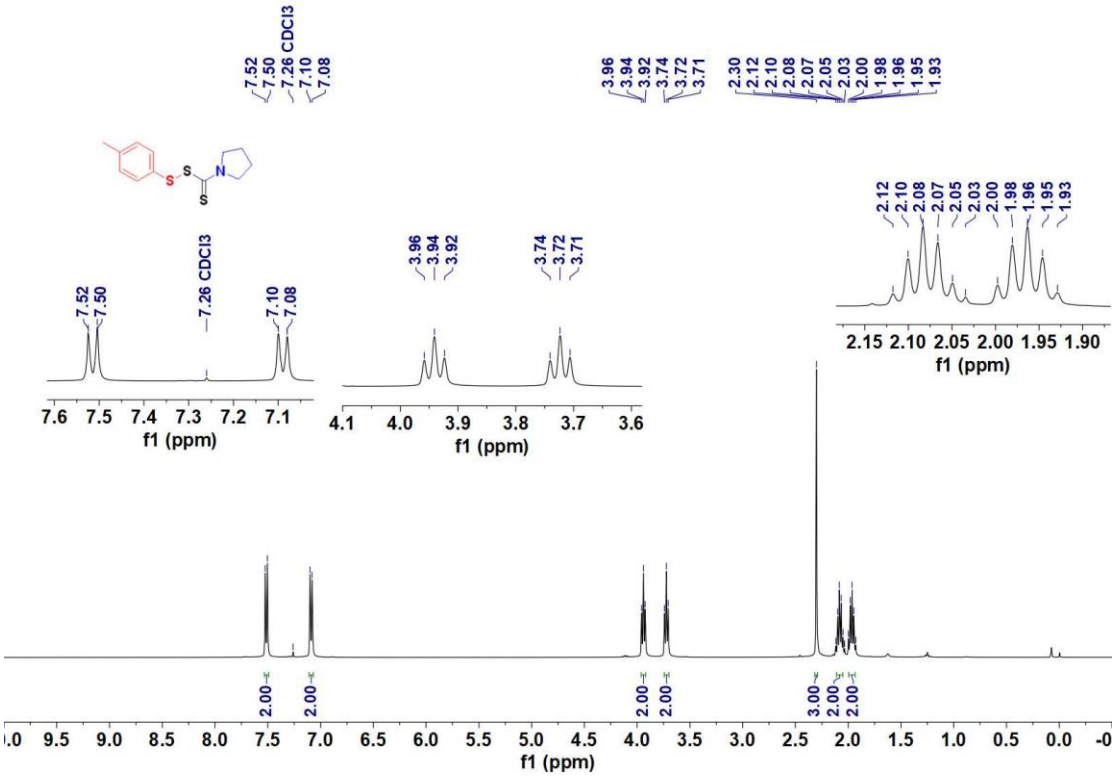


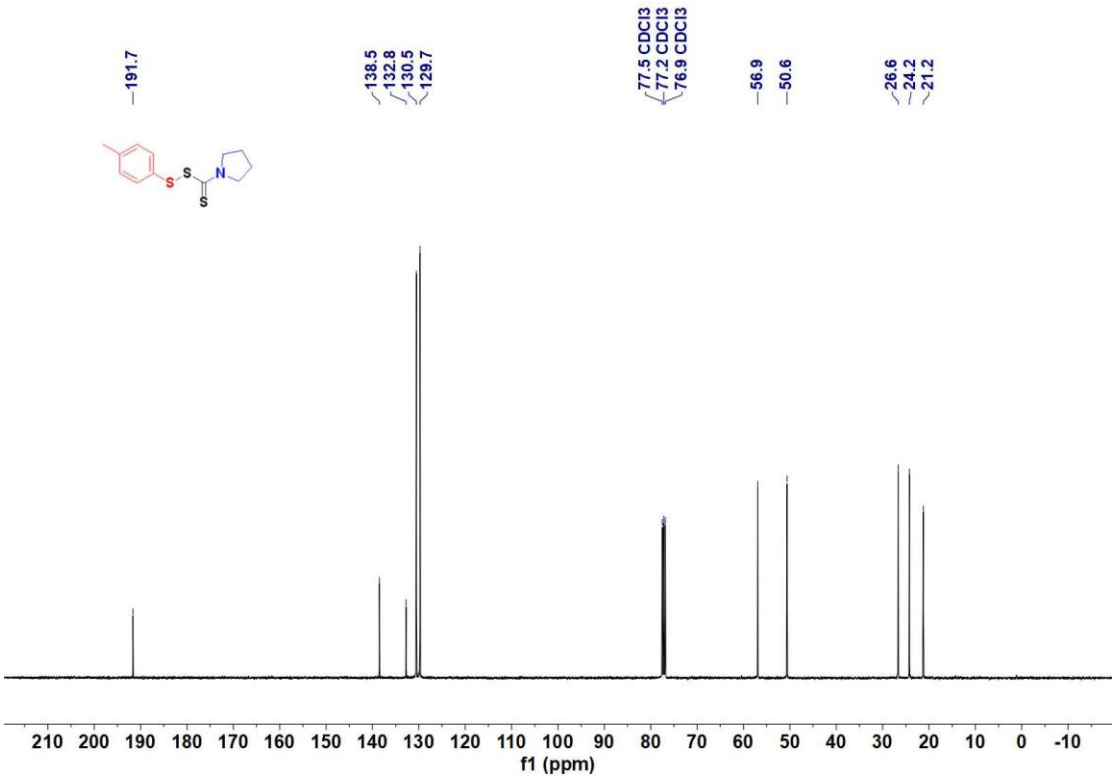
Benzyl pyrrolidine-1-carbo(dithioperoxo)thioate (3d)



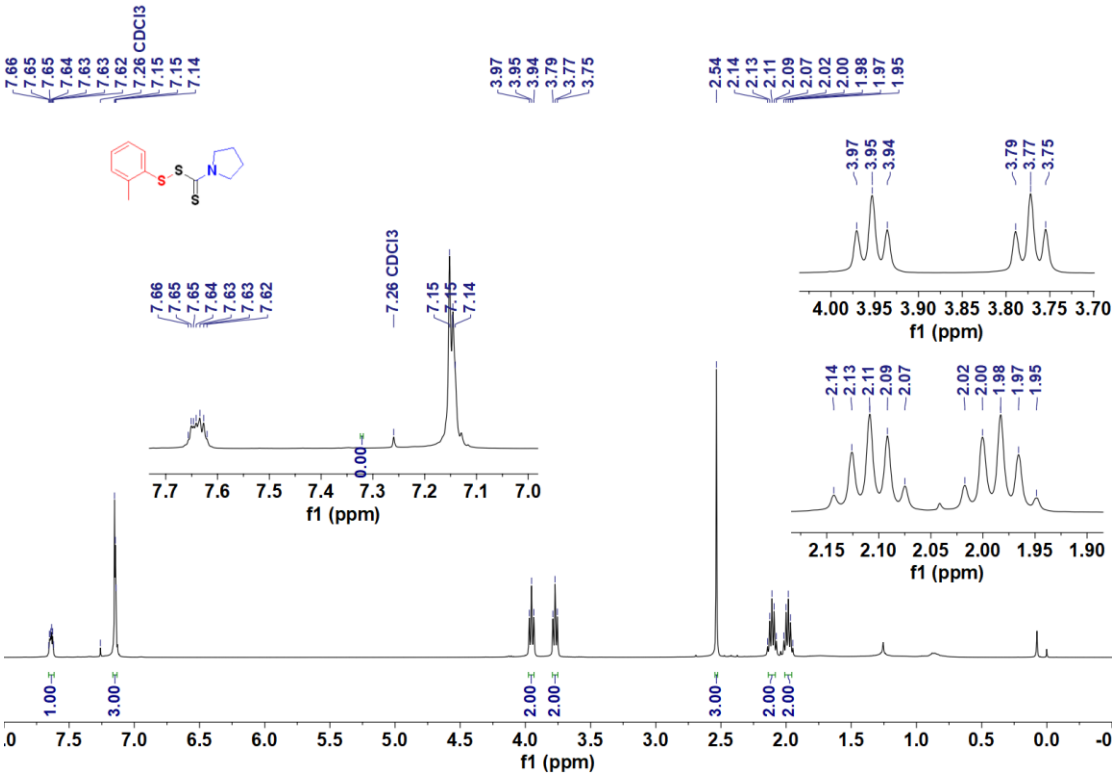


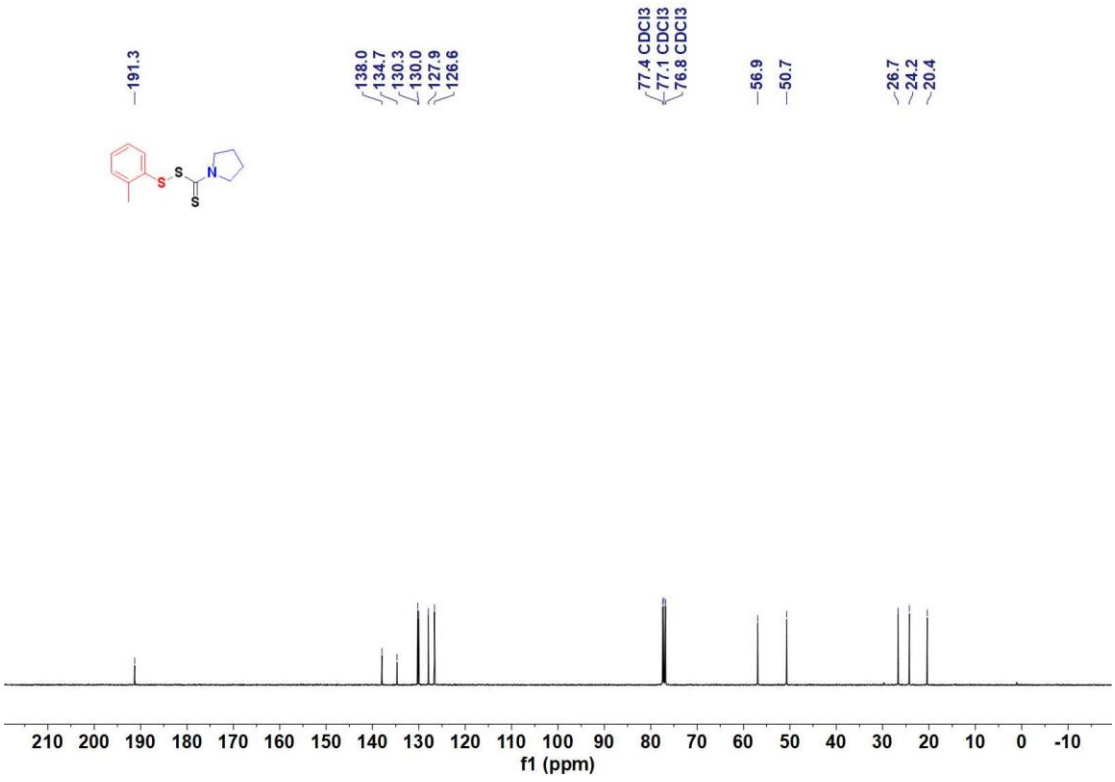
***P*-tolyl pyrrolidine-1-carbo(dithioperoxo)thioate (3e)**



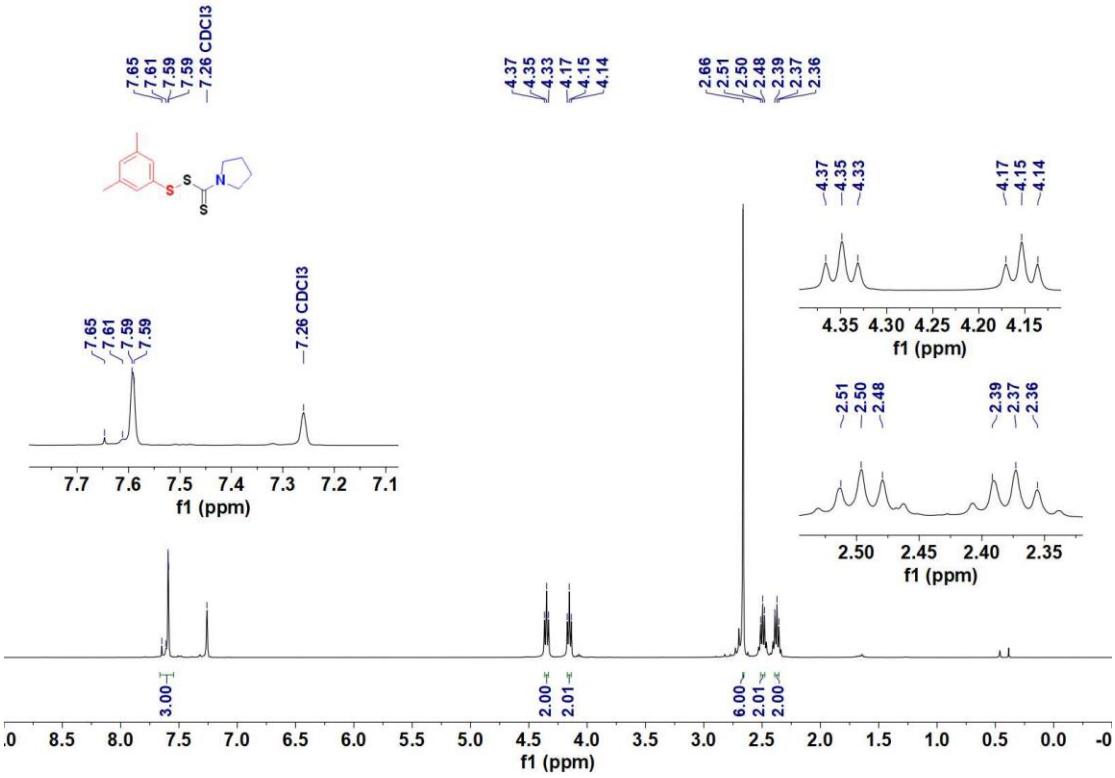


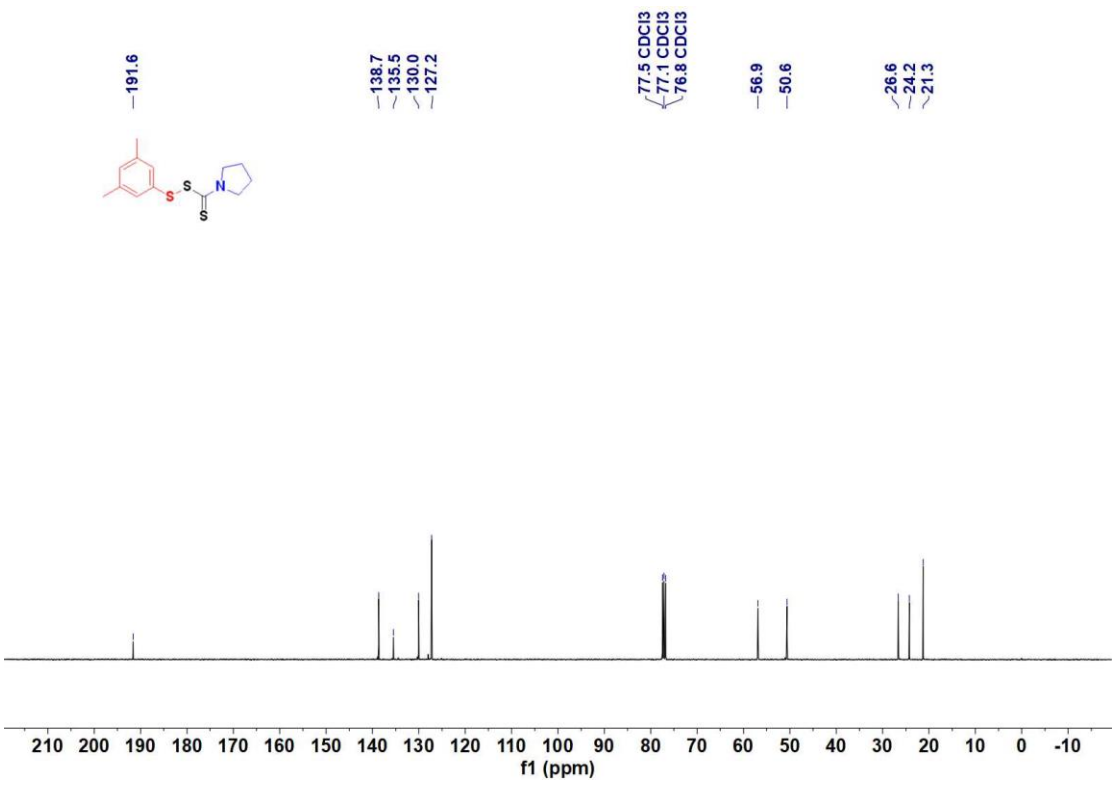
***O*-tolyl pyrrolidine-1-carbo(dithioperoxo)thioate (3f)**



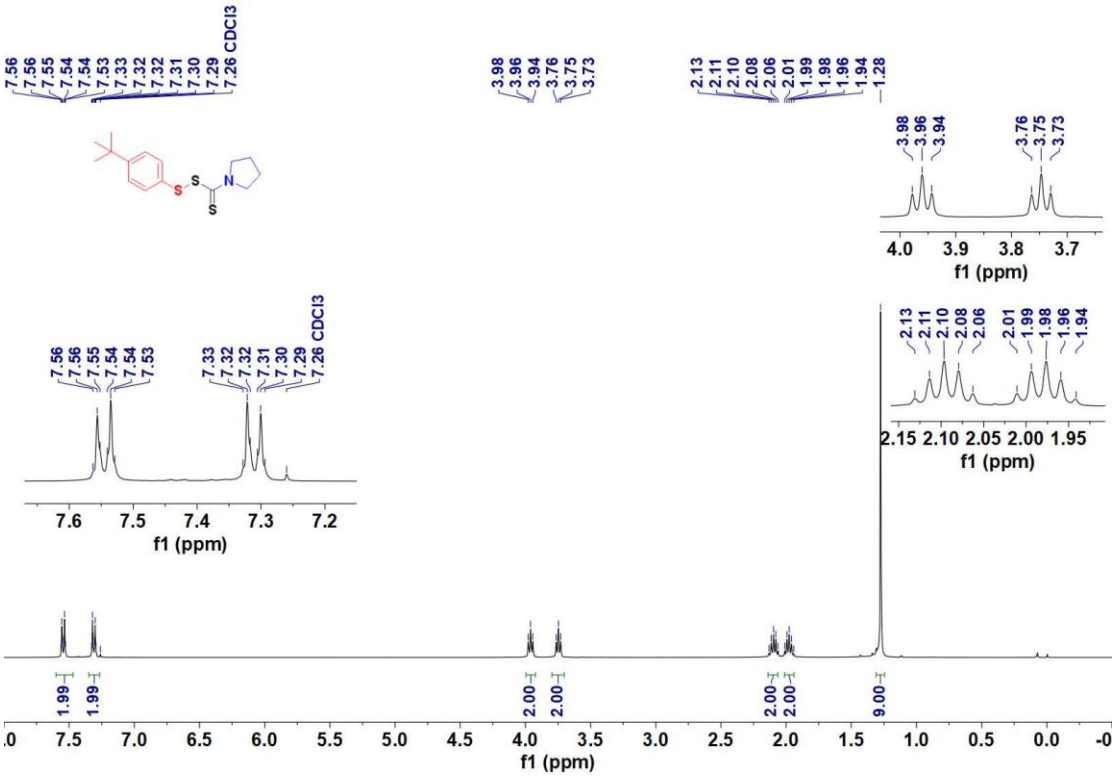


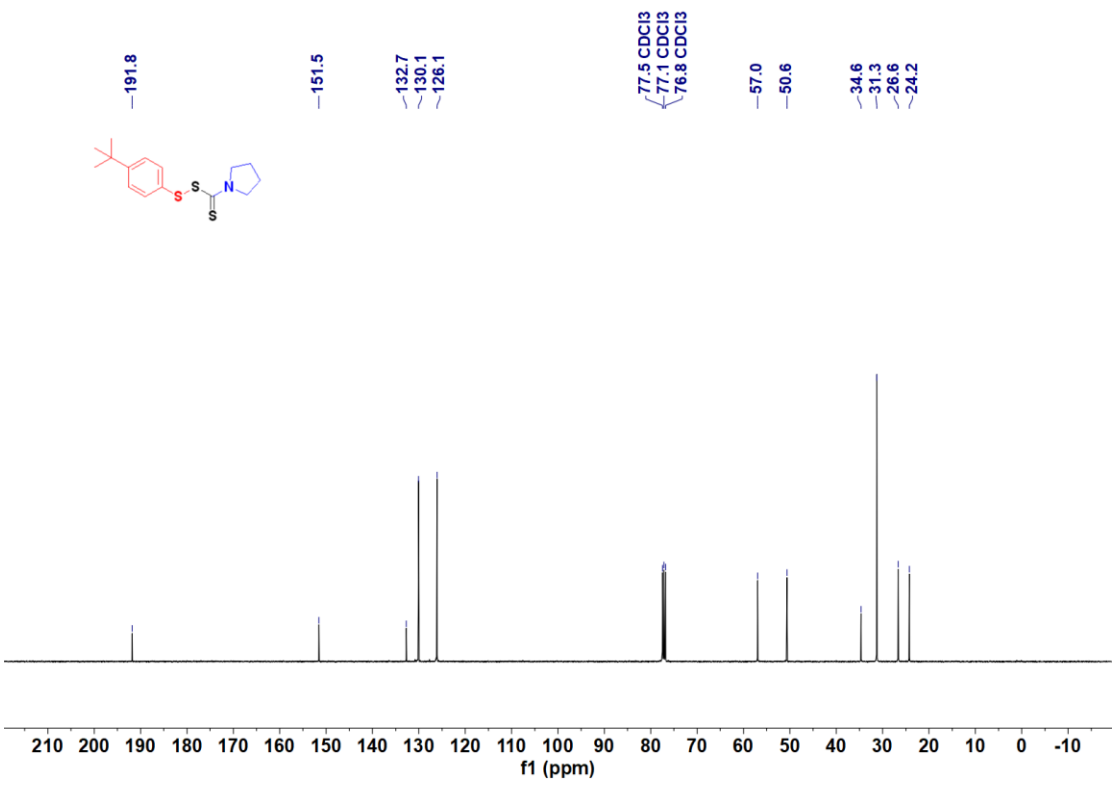
3,5-Dimethylphenyl pyrrolidine-1-carbo(dithioperoxo)thioate (3g)



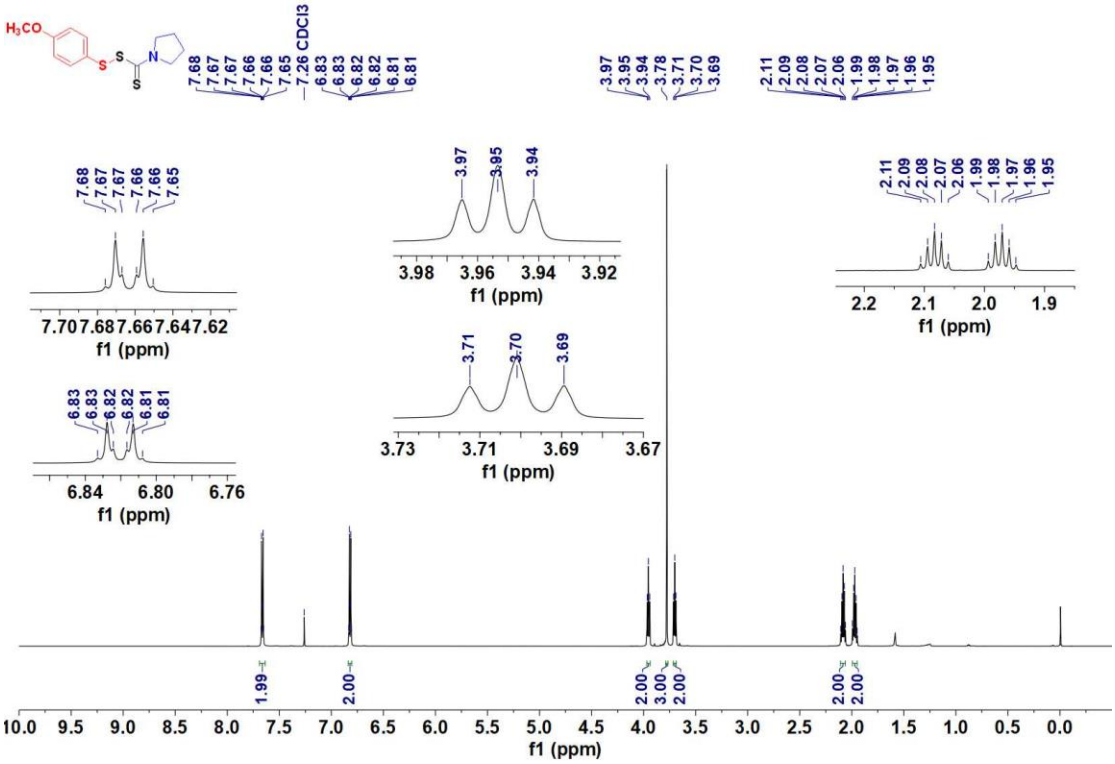


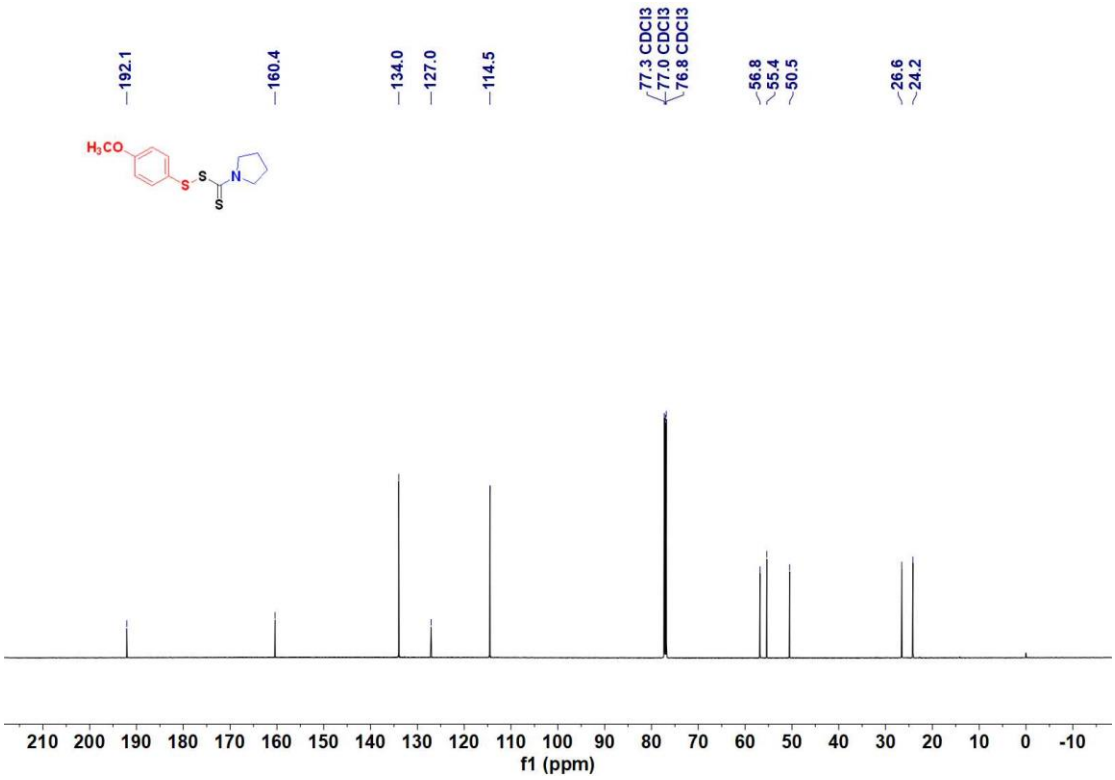
4-(*Tert*-butyl)phenyl pyrrolidine-1-carbo(dithioperoxo)thioate (3h)



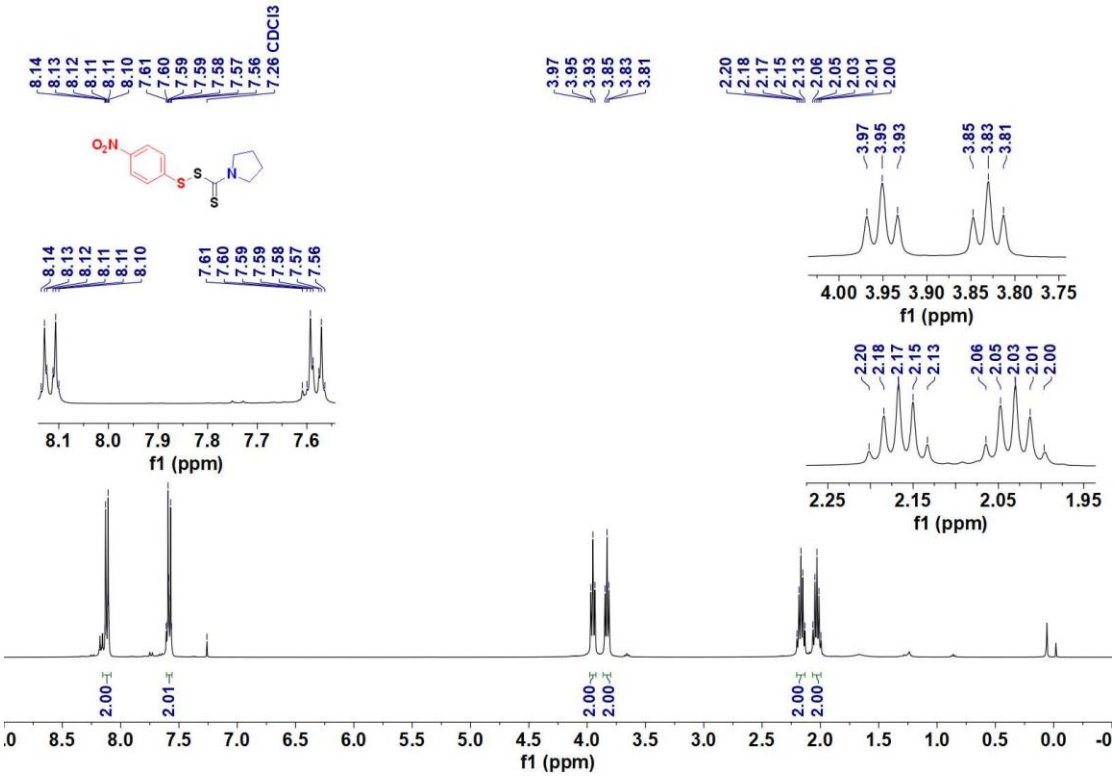


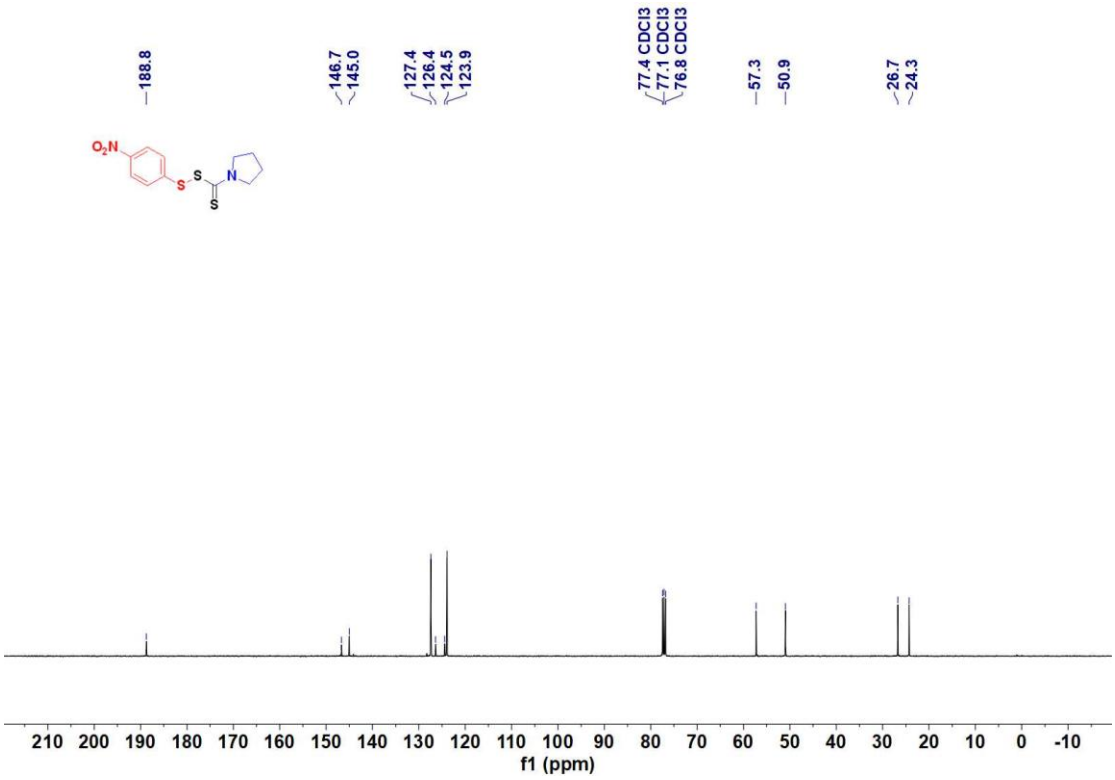
4-Methoxyphenyl pyrrolidine-1-carbo(dithioperoxo)thioate (3i)



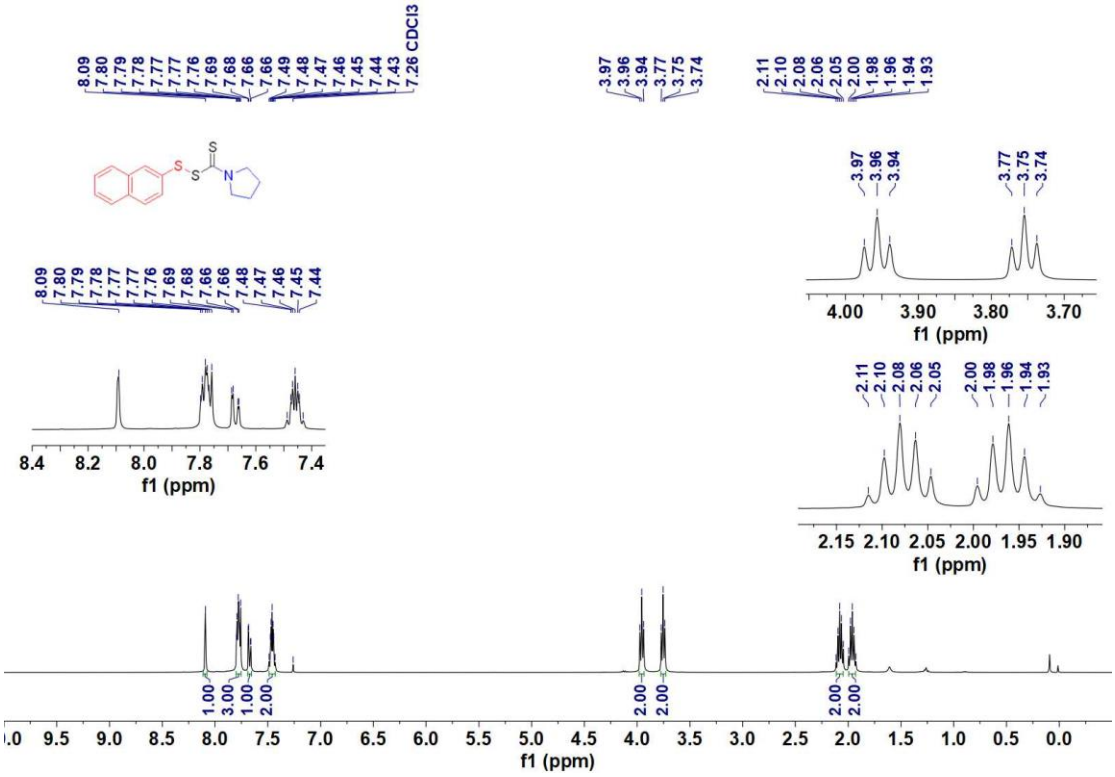


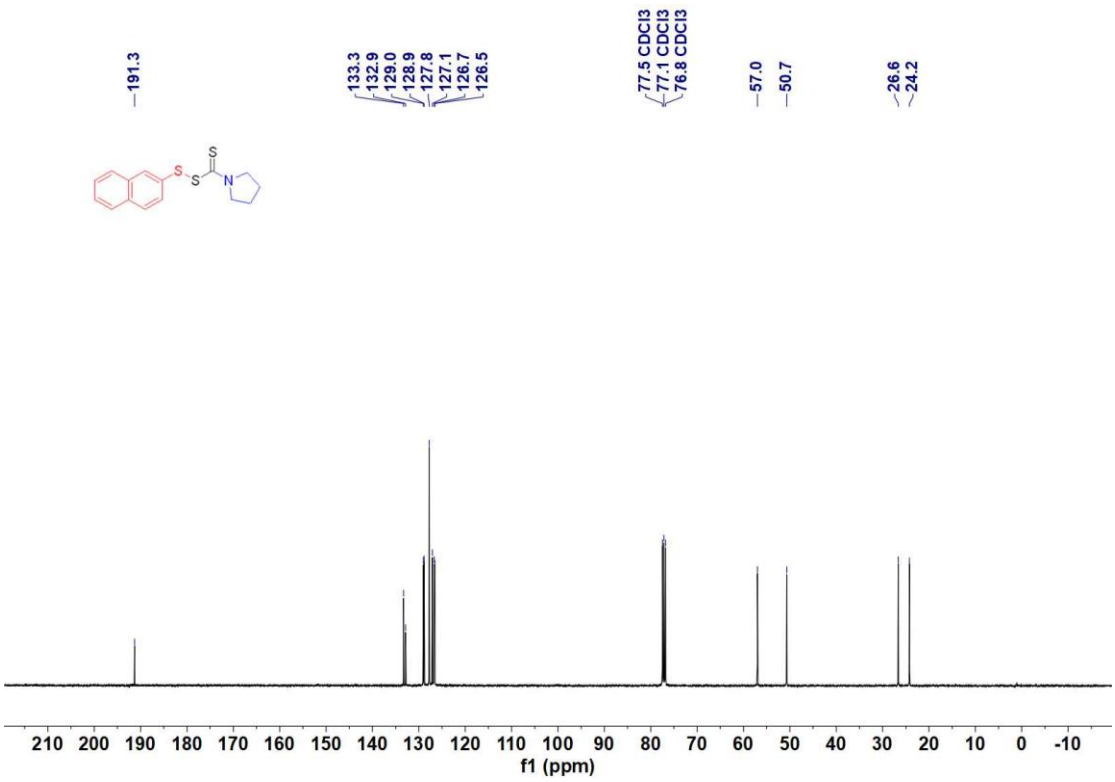
4-Nitrophenyl pyrrolidine-1-carbo(dithioperoxo)thioate (3j)



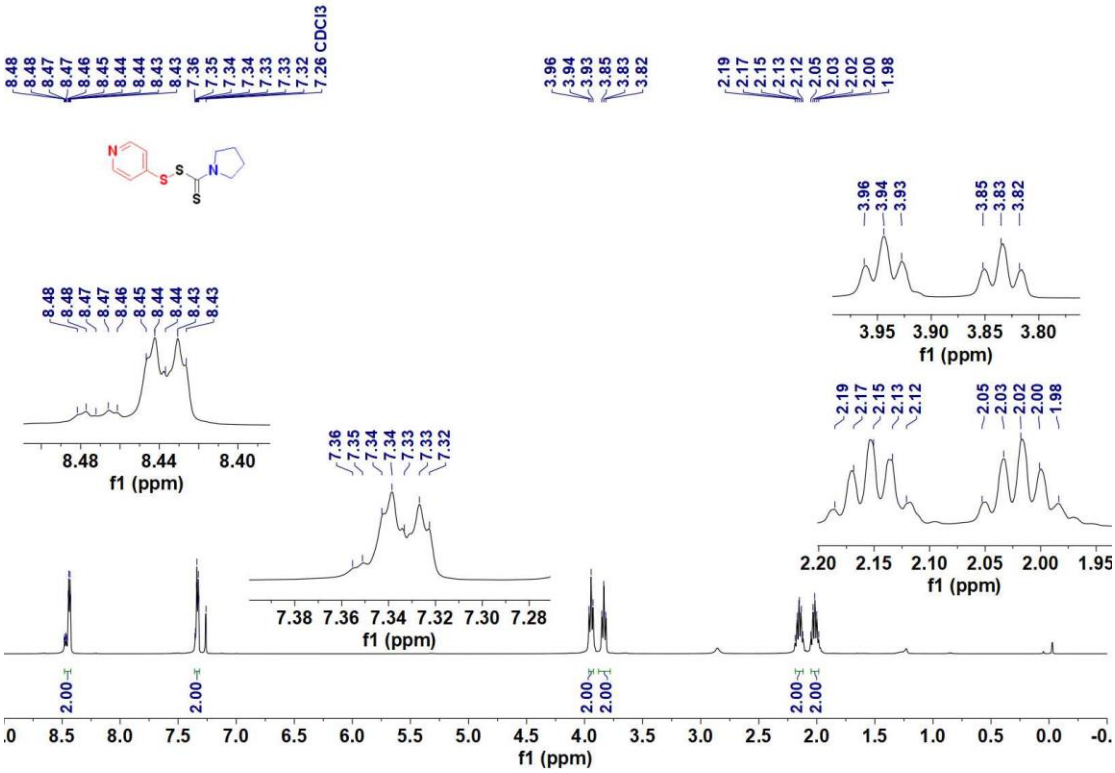


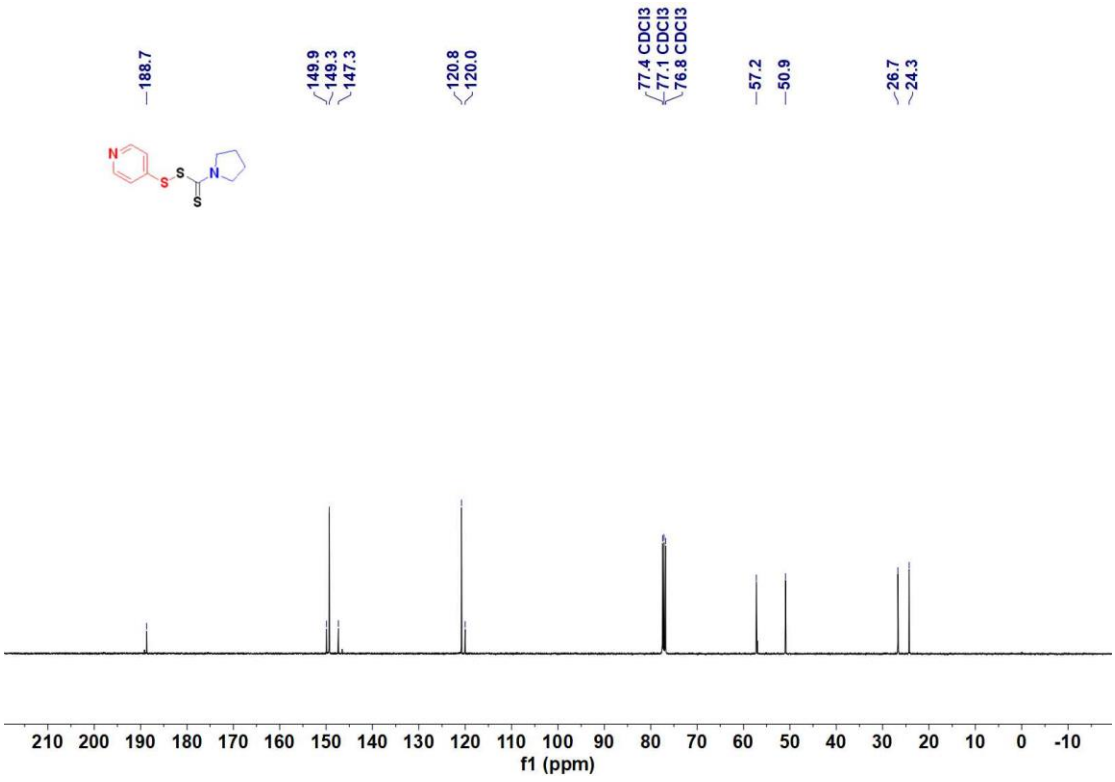
Naphthalen-2-yl pyrrolidine-1-carbo(dithioperoxo)thioate (3k)



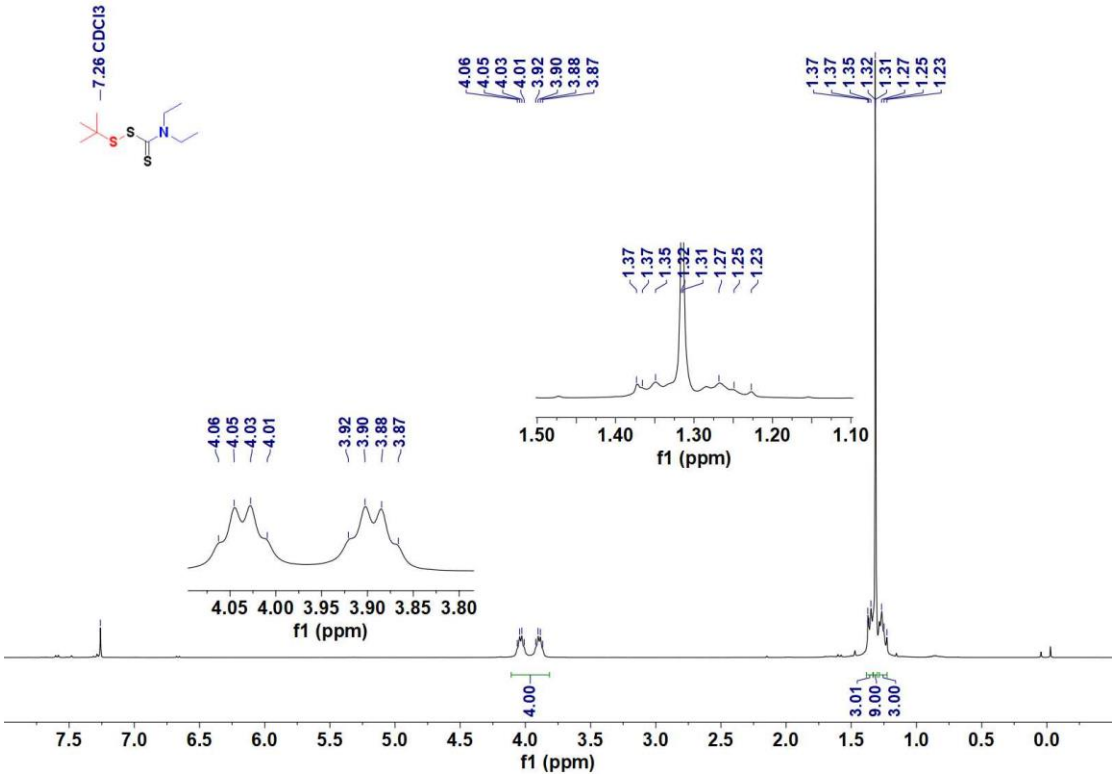


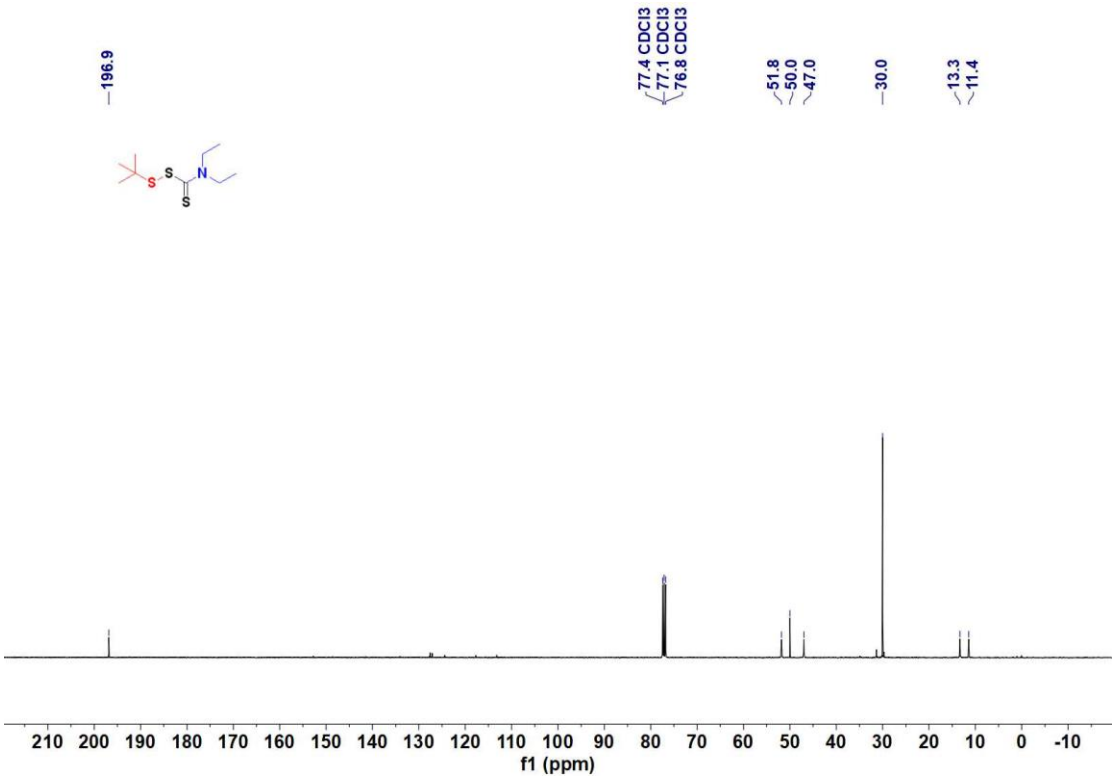
Pyridin-4-yl pyrrolidine-1-carbo(dithioperoxo)thioate (3l)



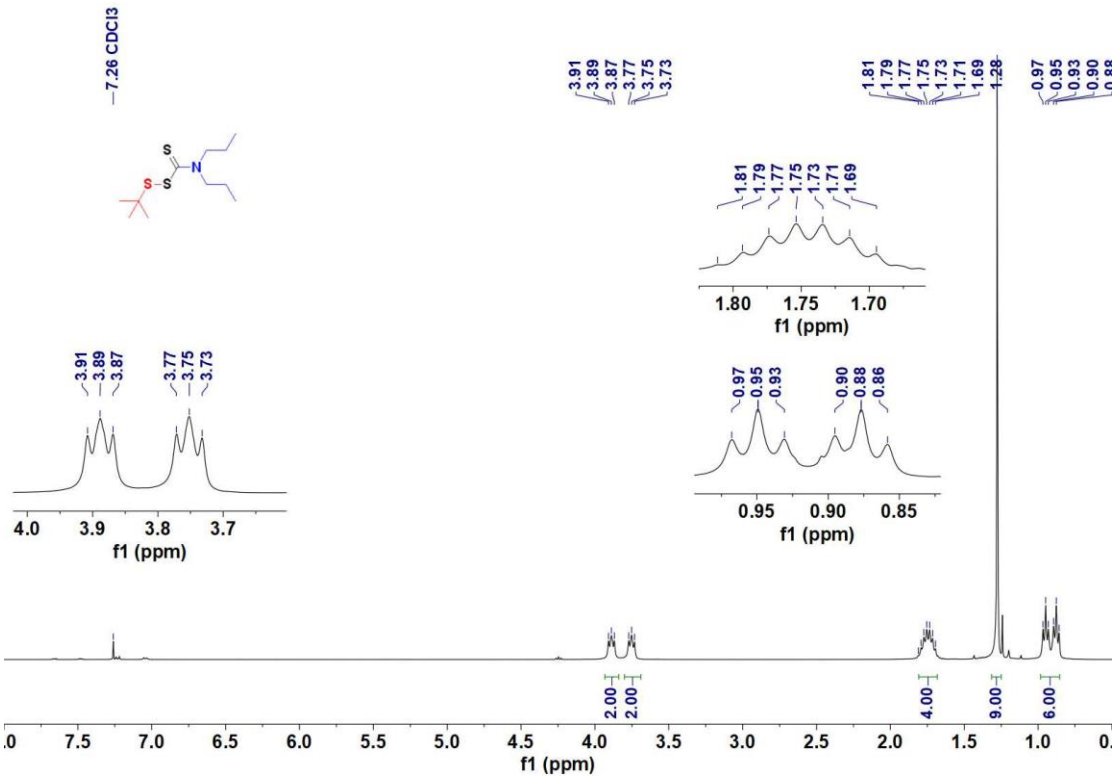


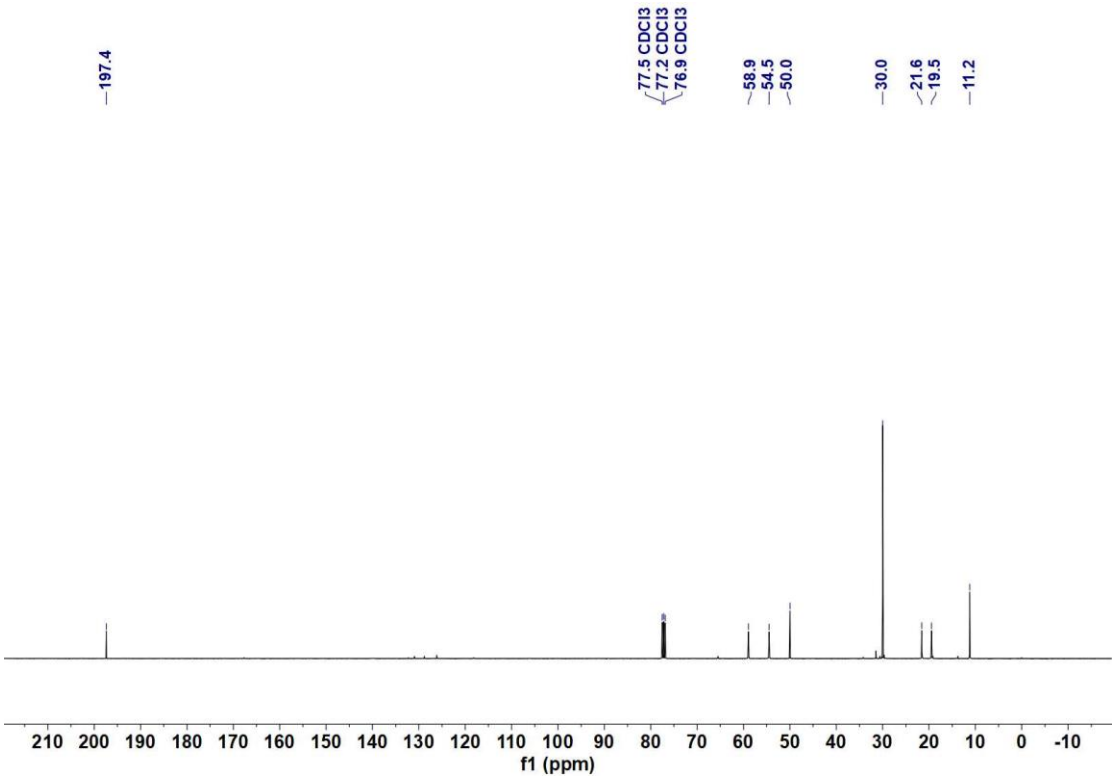
***Tert*-butyl diethylcarbamo(dithioperoxo)thioate (4a)**



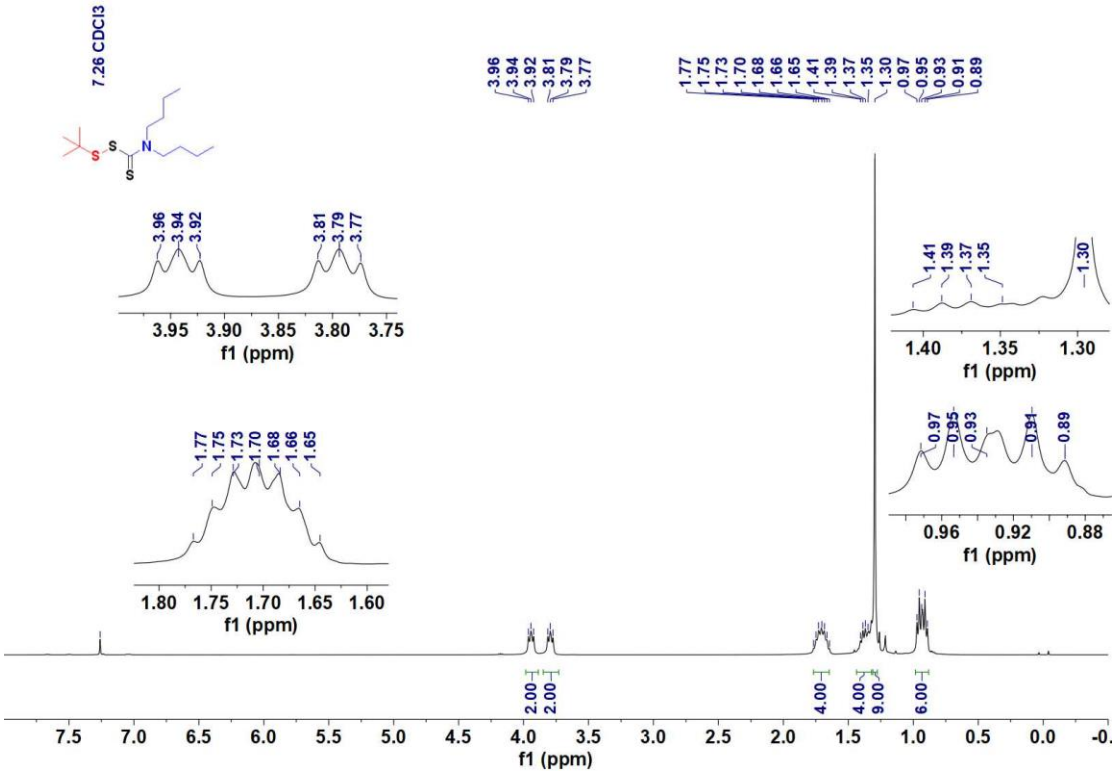


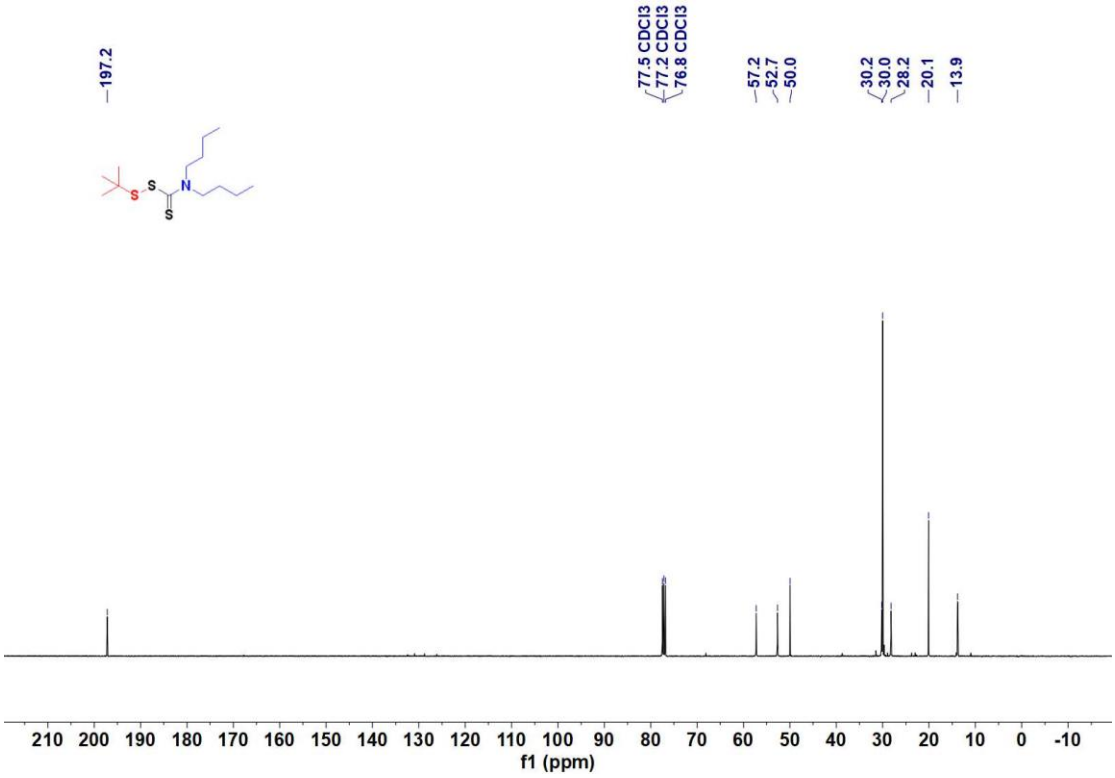
***Tert*-butyl dipropylcarbamo(dithioperoxo)thioate (4b)**



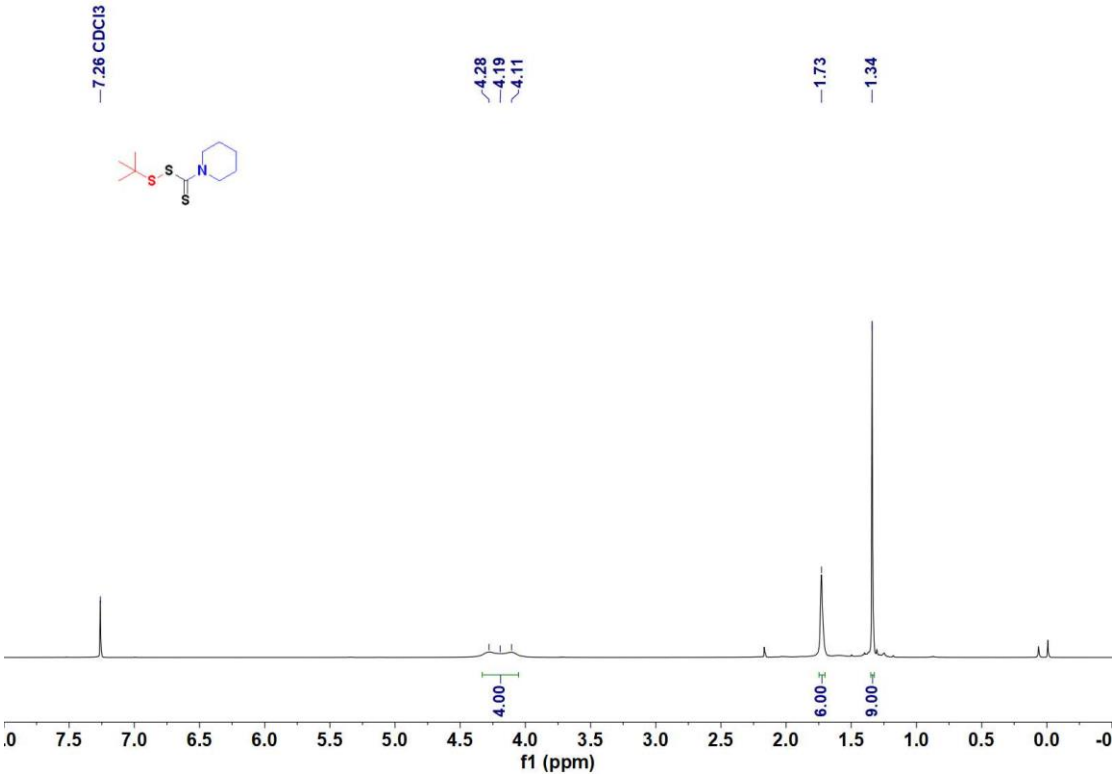


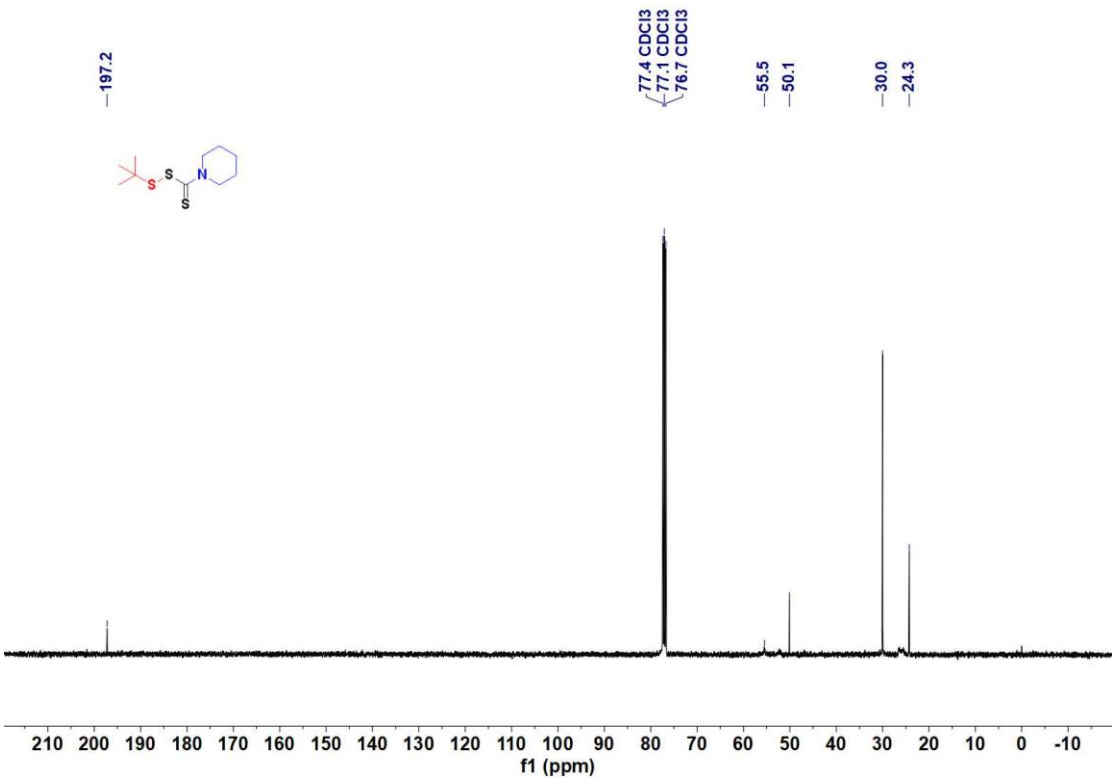
***Tert*-butyl dibutylcarbamo(dithioperoxo)thioate (4c)**



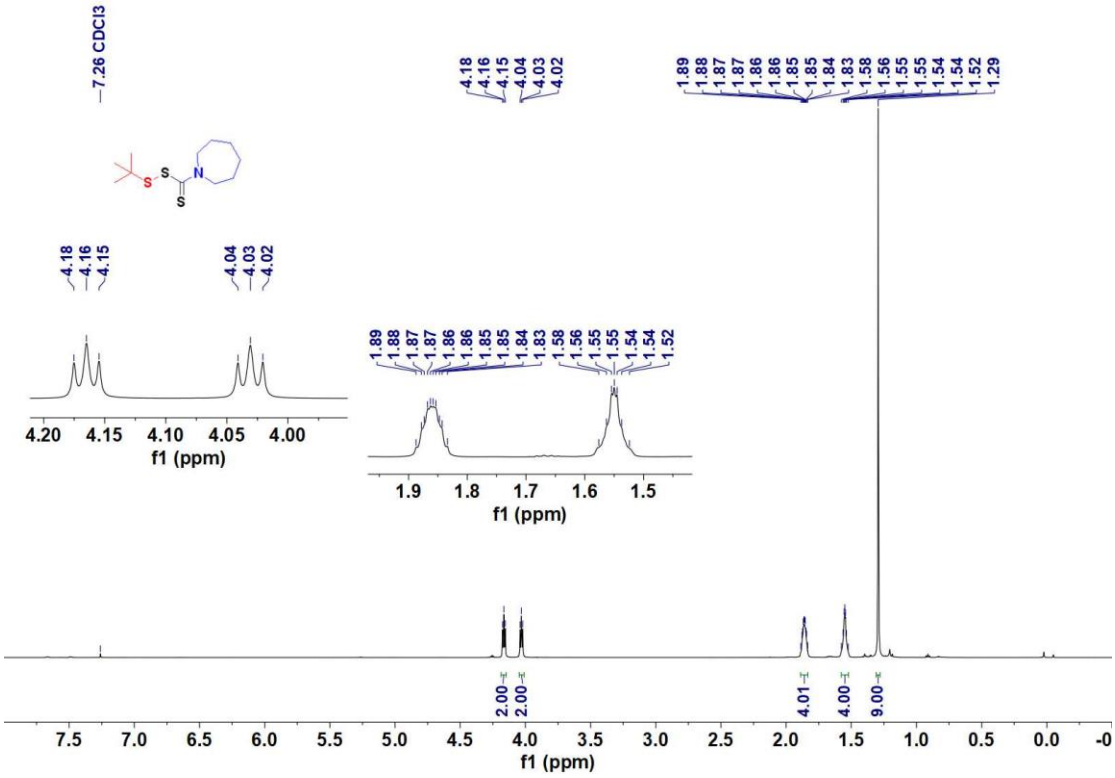


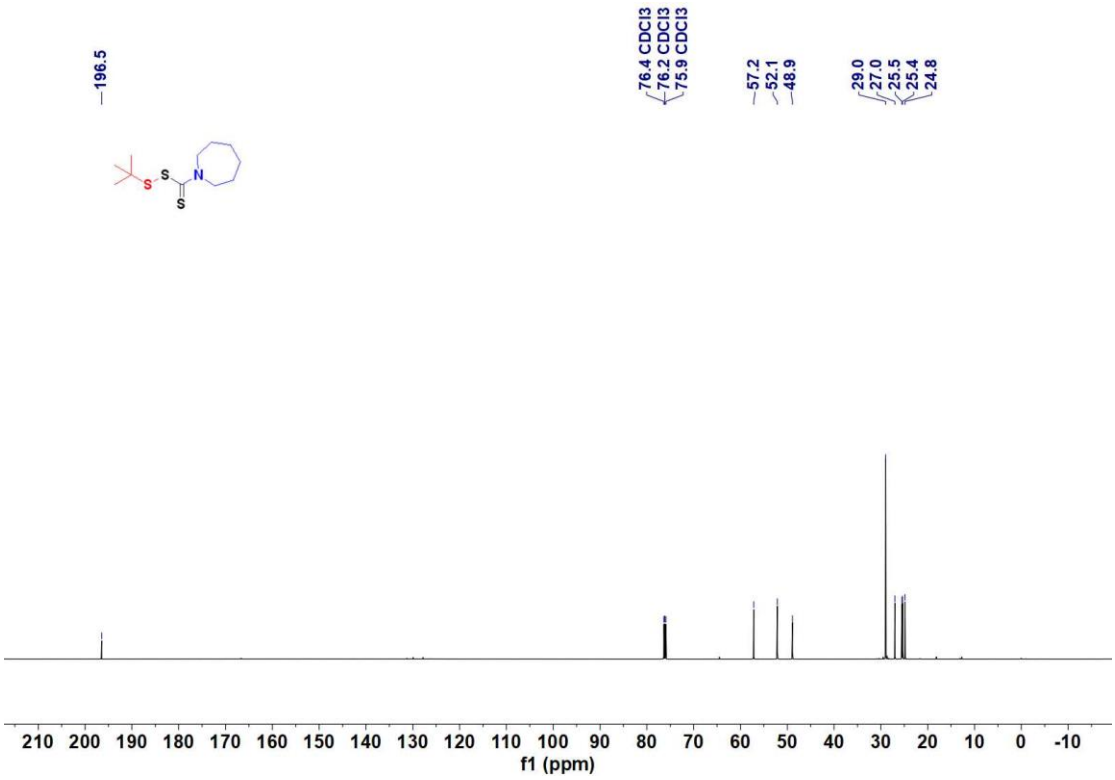
***Tert*-butyl piperidine-1-carbo(dithioperoxo)thioate (4d)**



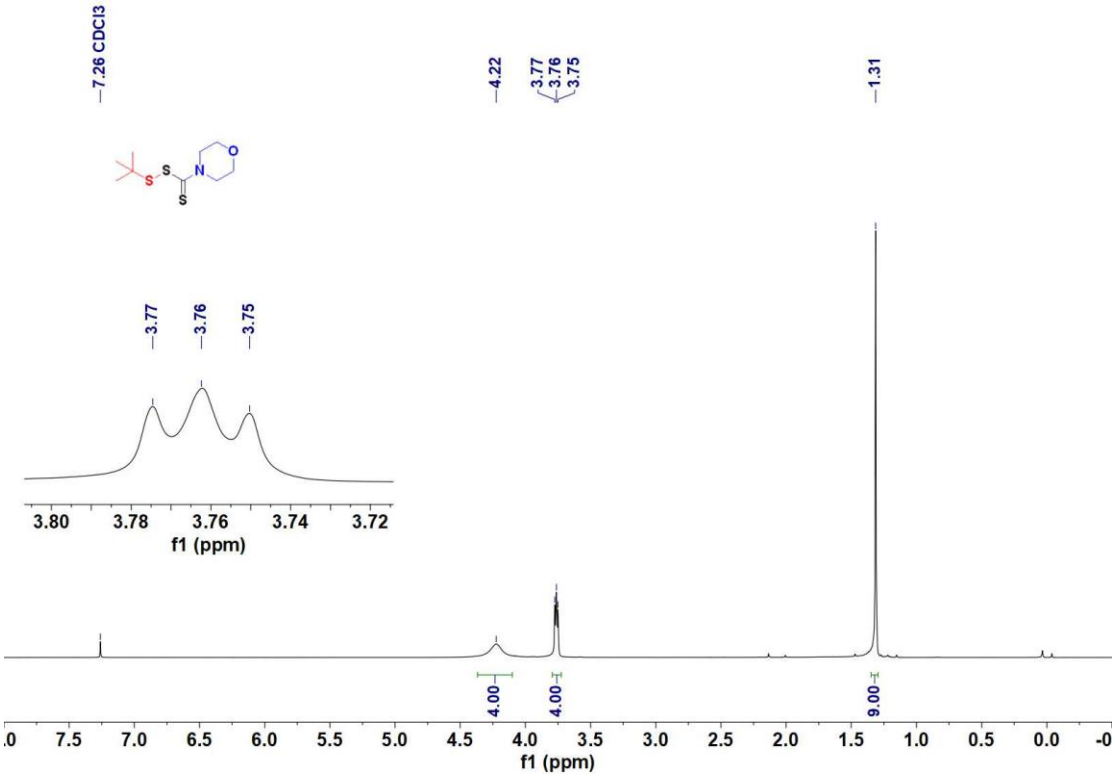


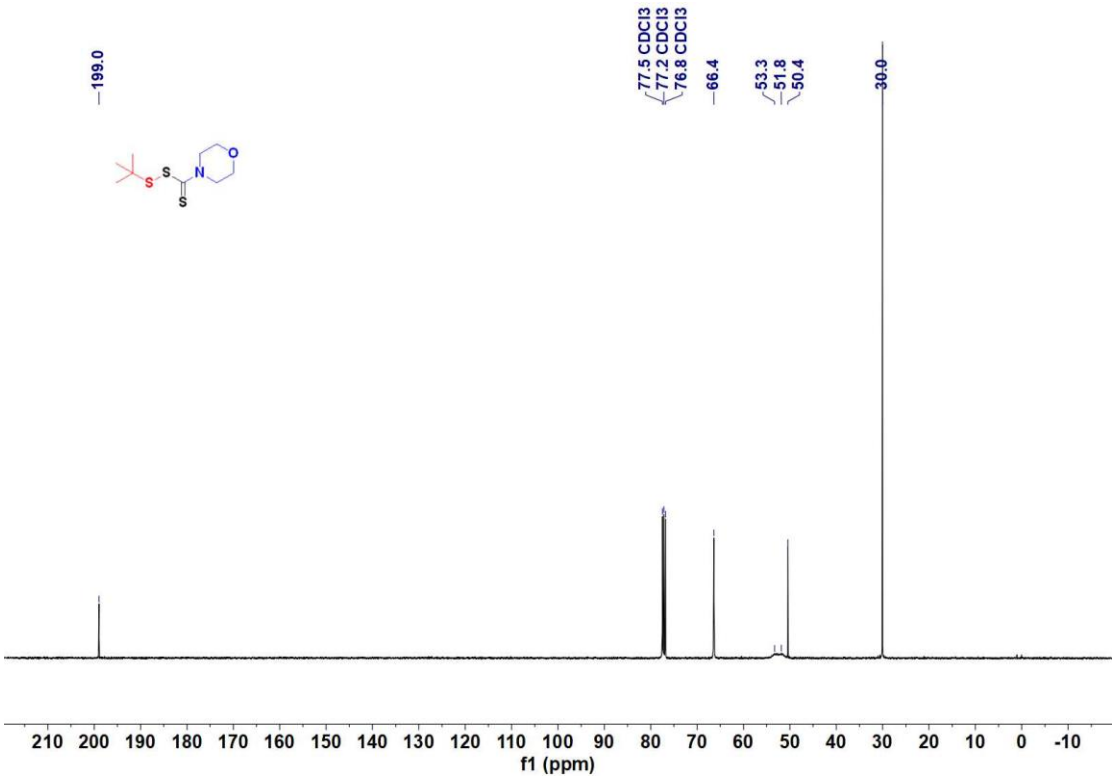
***Tert*-butyl azepane-1-carbo(dithioperoxo)thioate (4e)**



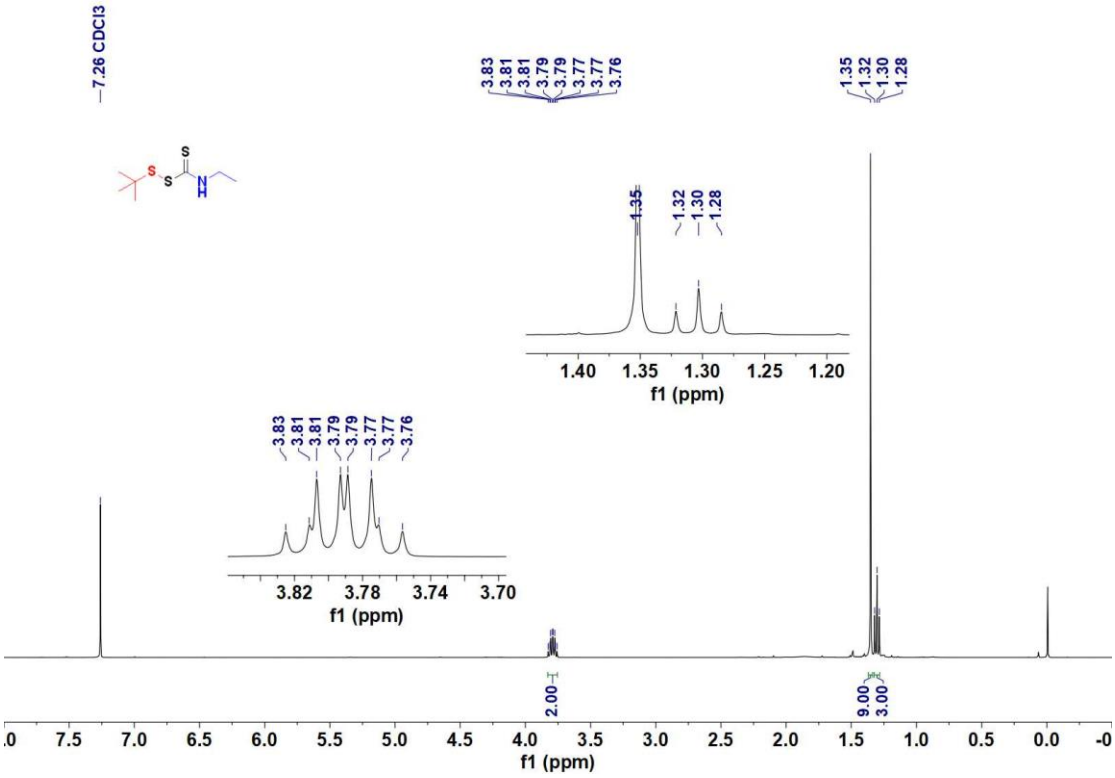


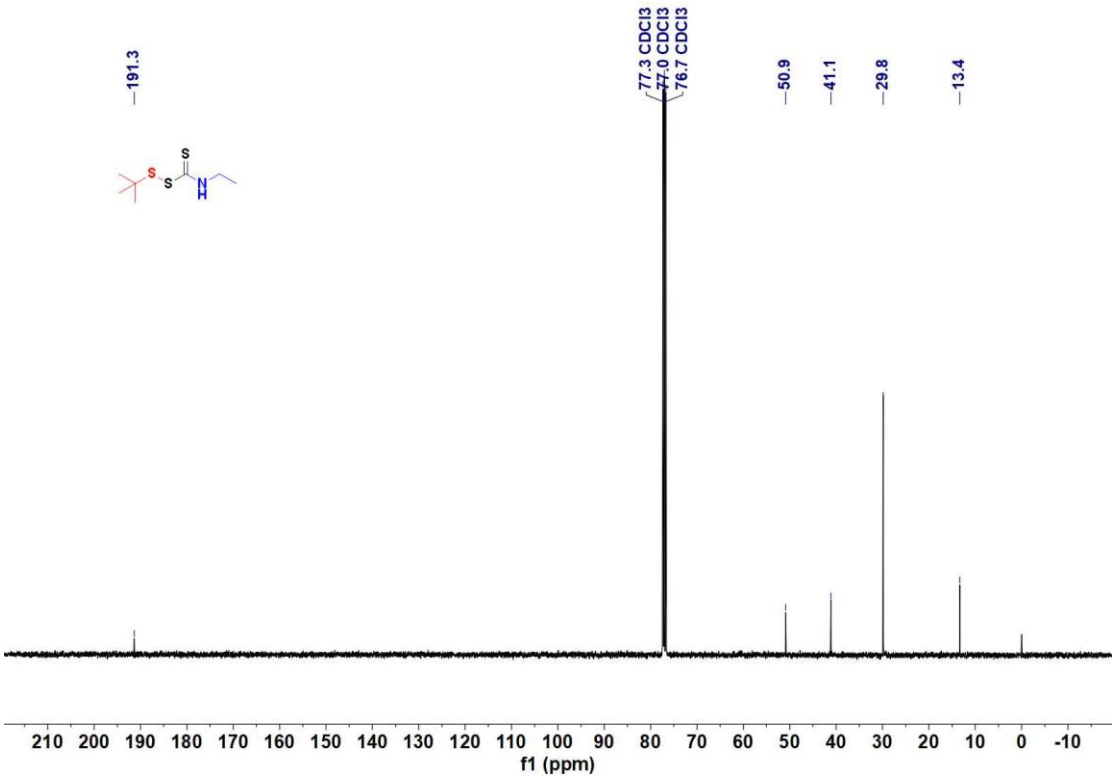
***Tert*-butyl morpholine-4-carbo(dithioperoxo)thioate (4f)**



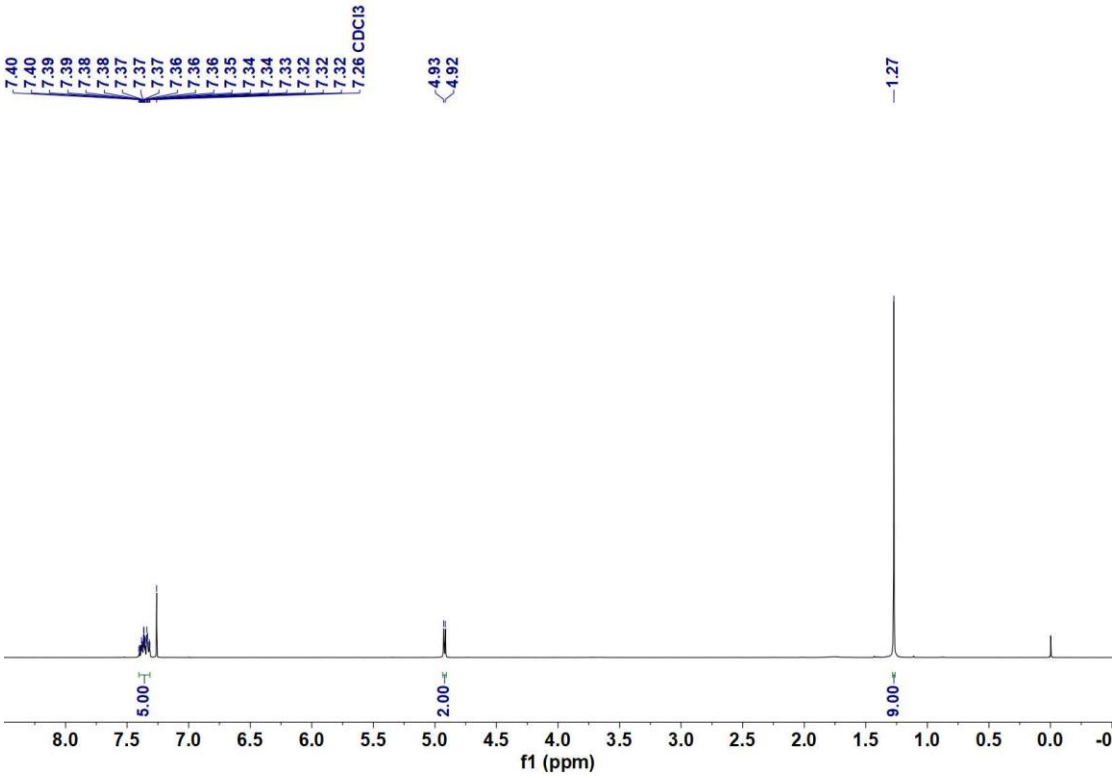


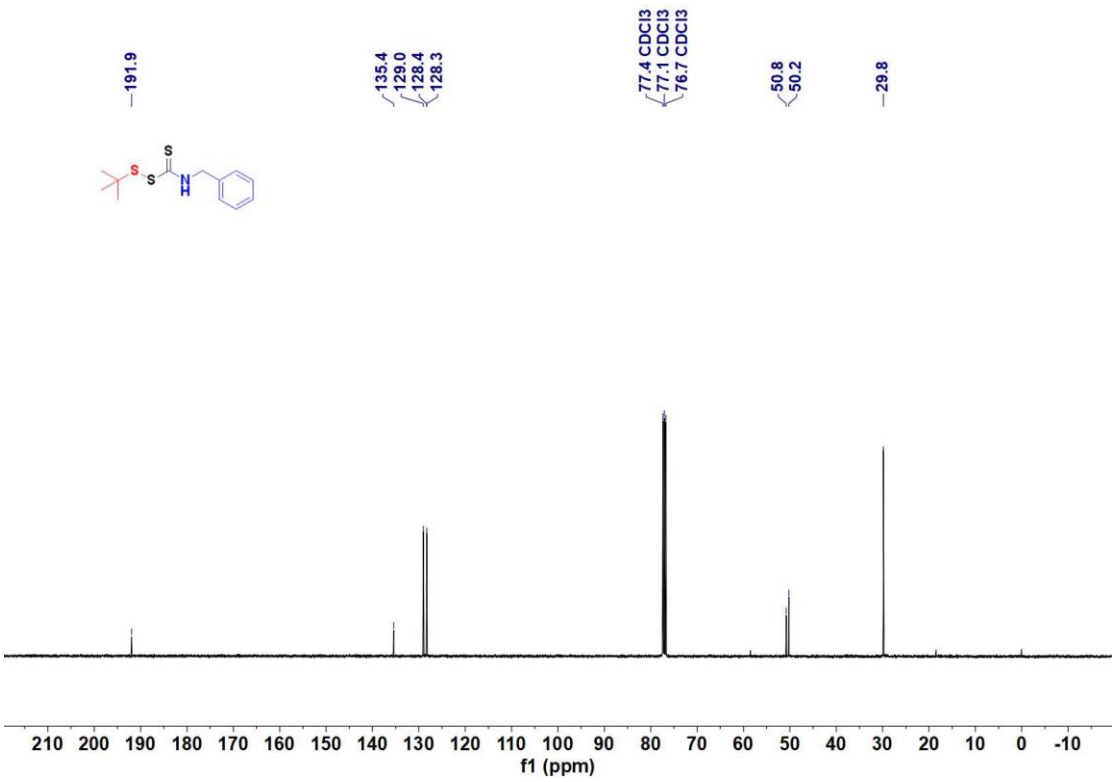
***Tert*-butyl ethylcarbamo(dithioperoxo)thioate (4g)**



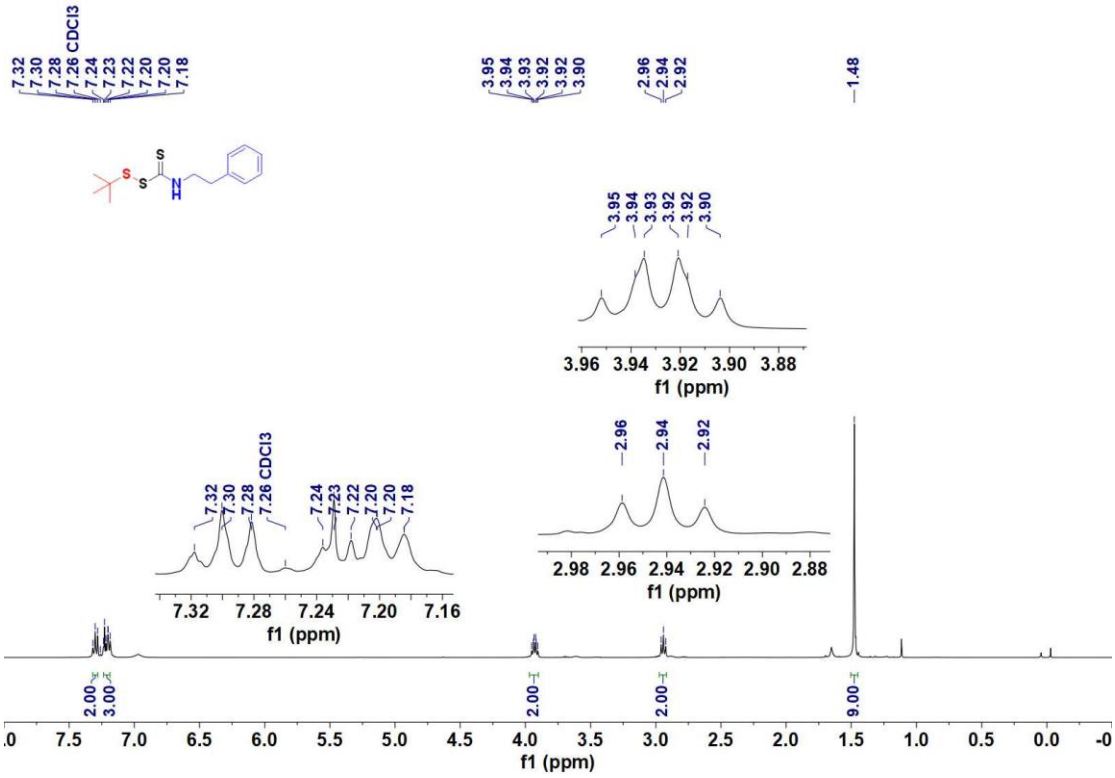


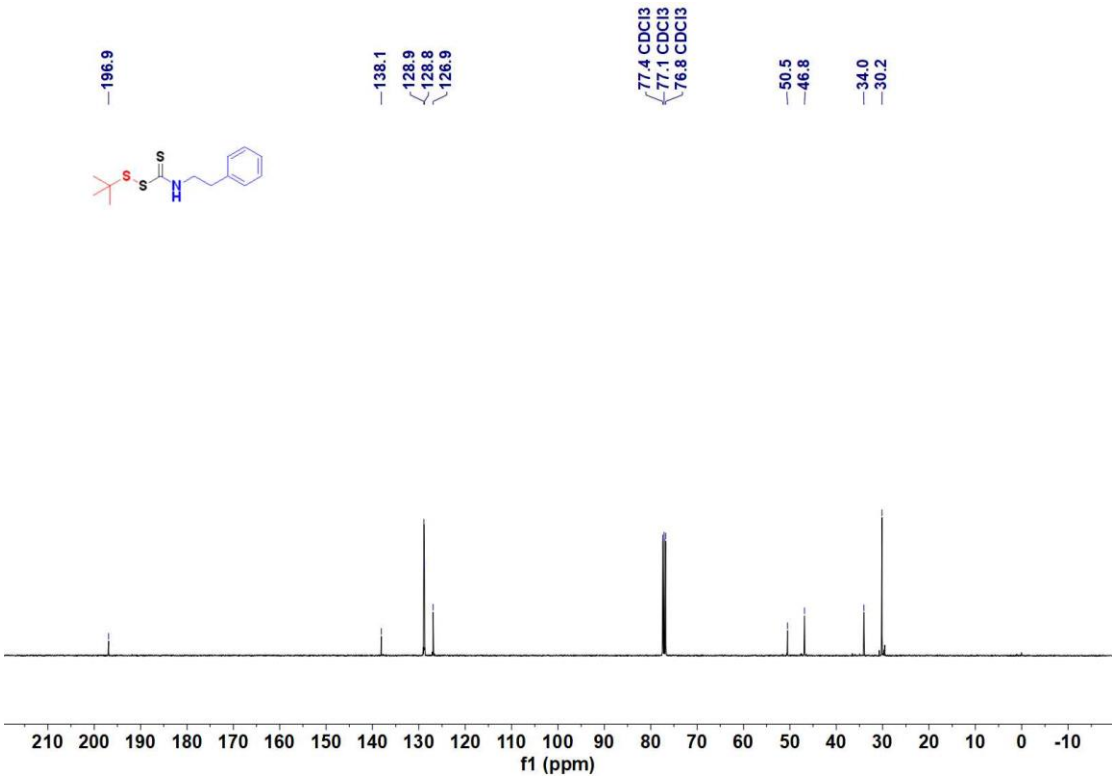
***Tert*-butyl benzylcarbamo(dithioperoxo)thioate (4h)**



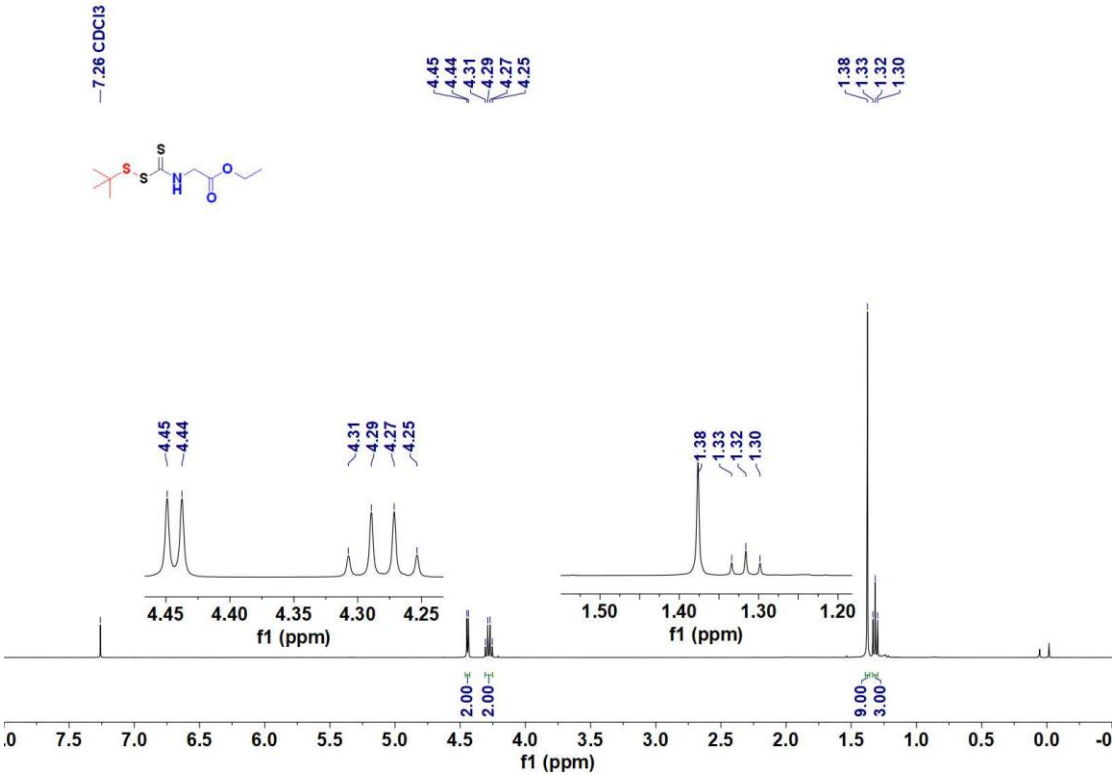


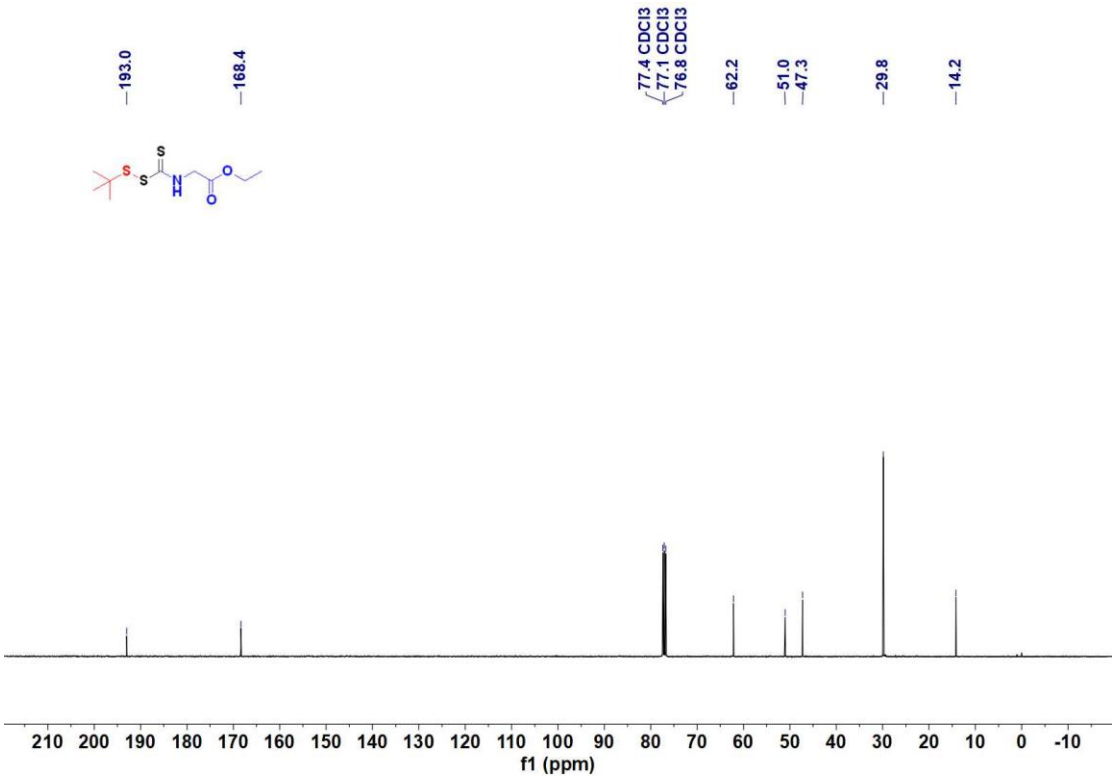
***Tert*-butyl phenethylcarbamo(dithioperoxo)thioate (4i)**



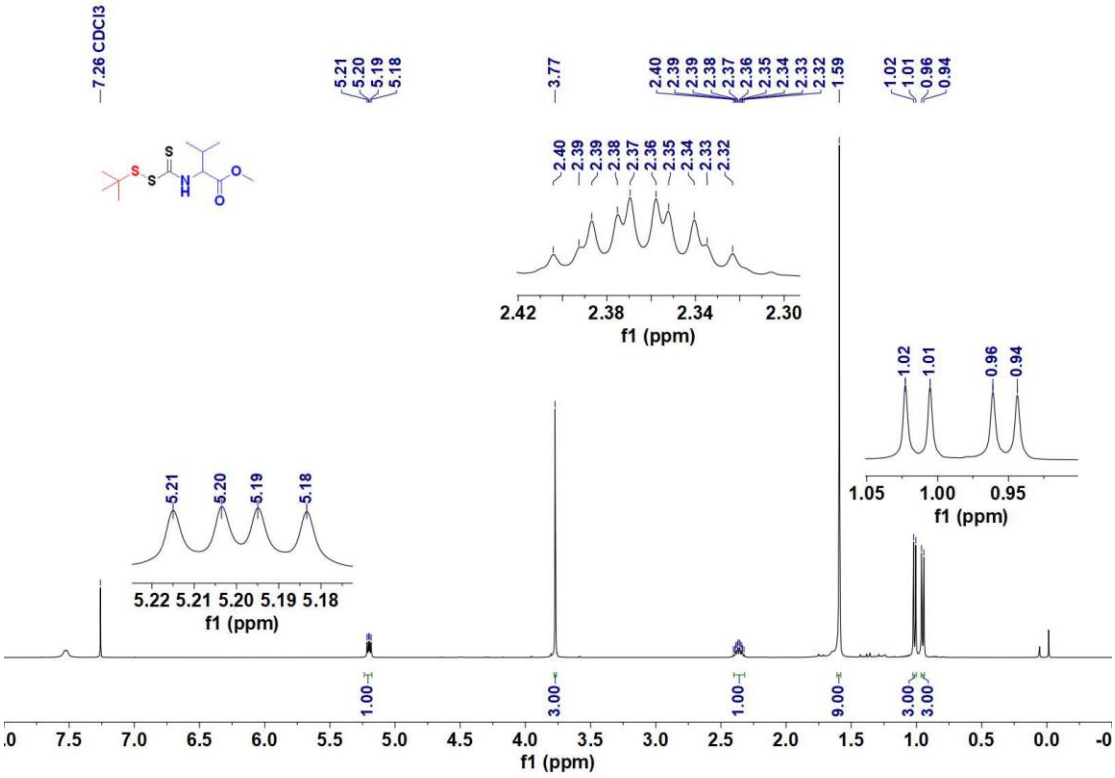


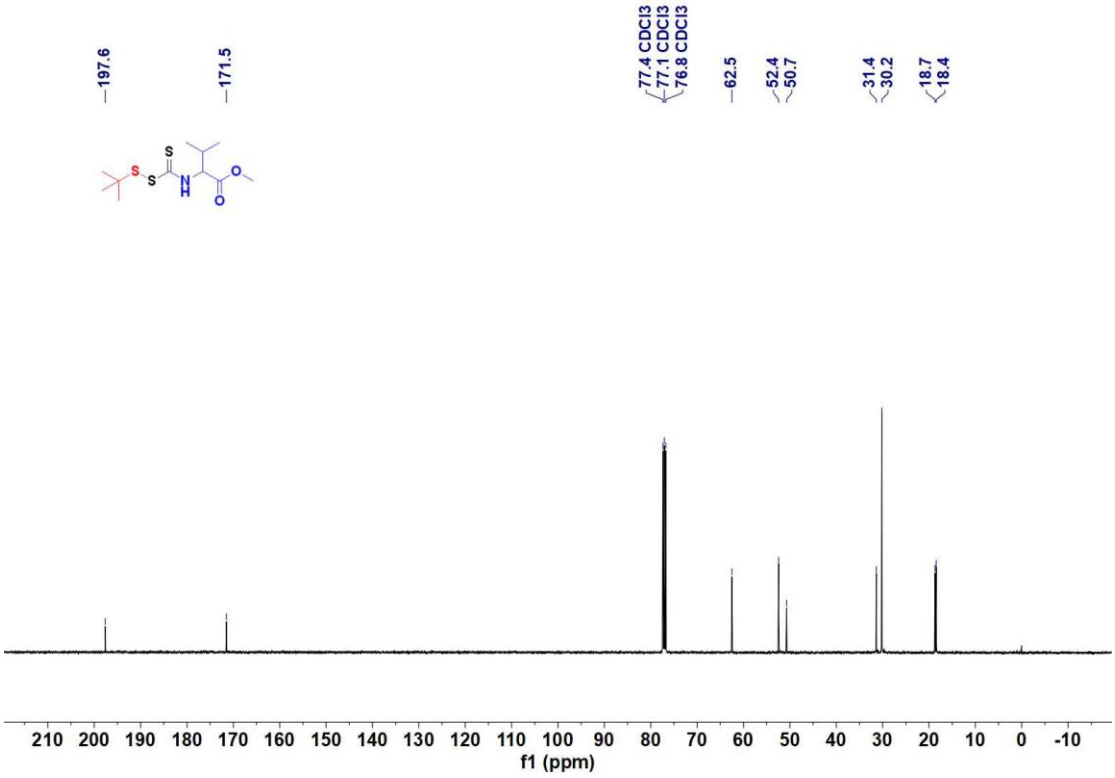
Ethyl (tert-butyldisulfannecarbonothioyl)glycinate (4j)



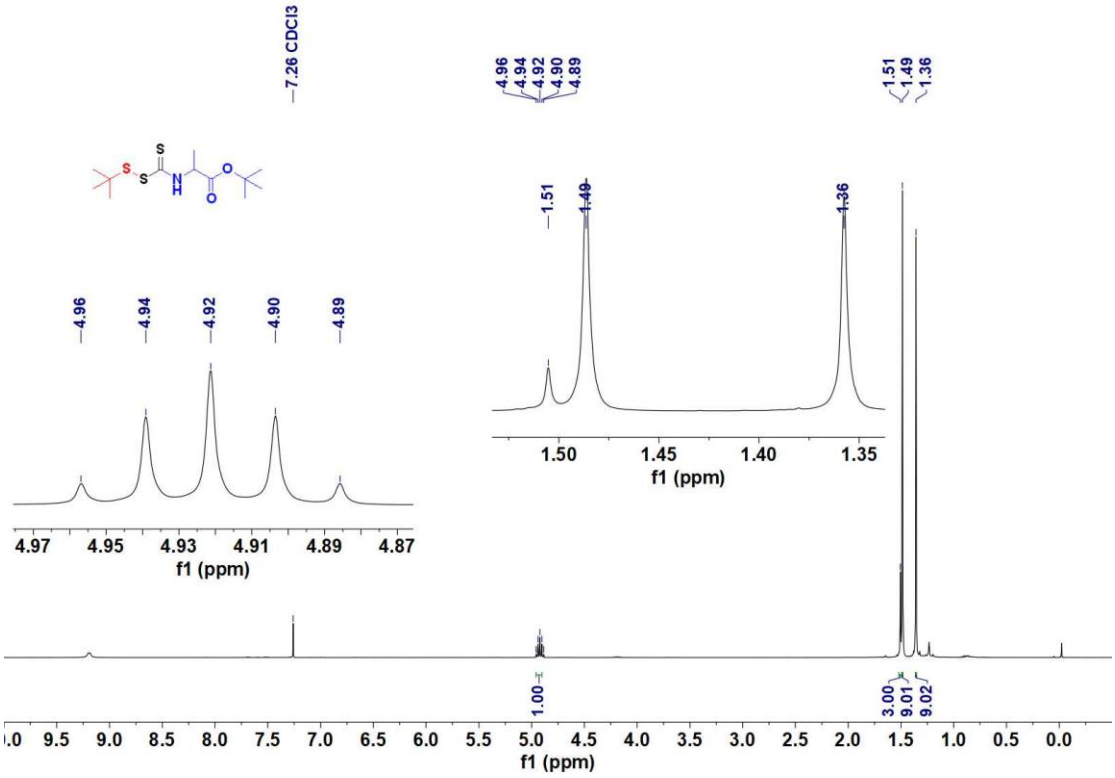


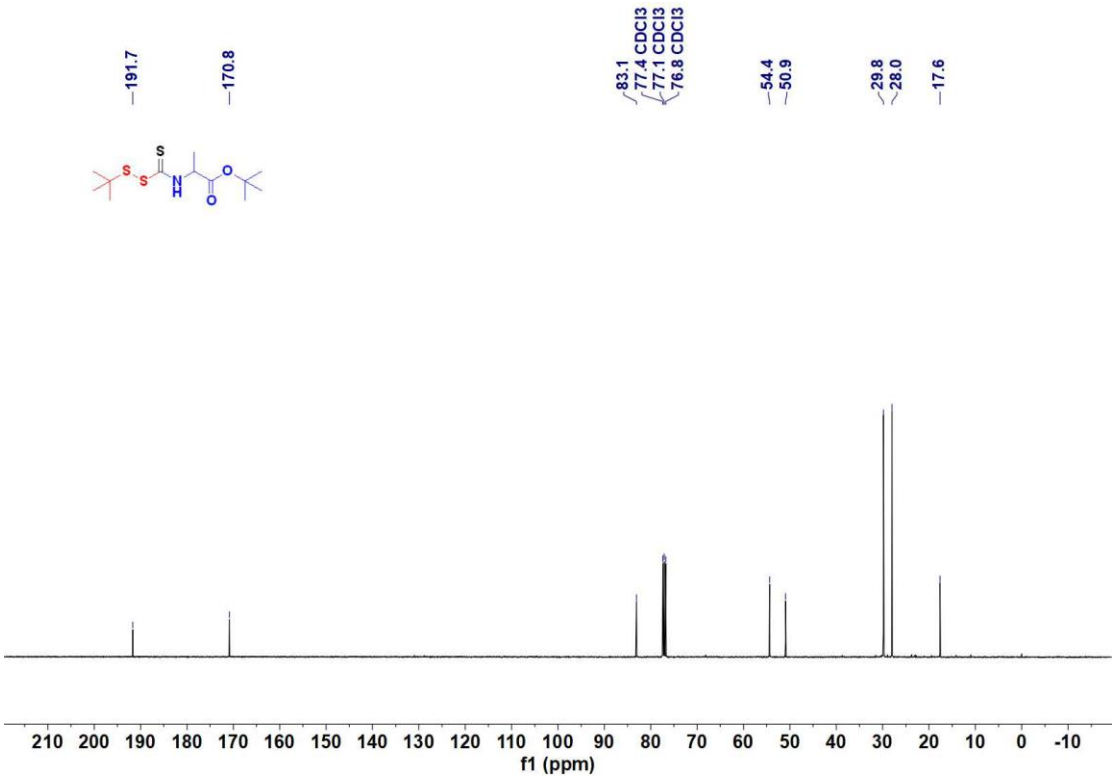
Methyl (*tert*-butyldisulfannecarbonothioyl)valinate (4k)



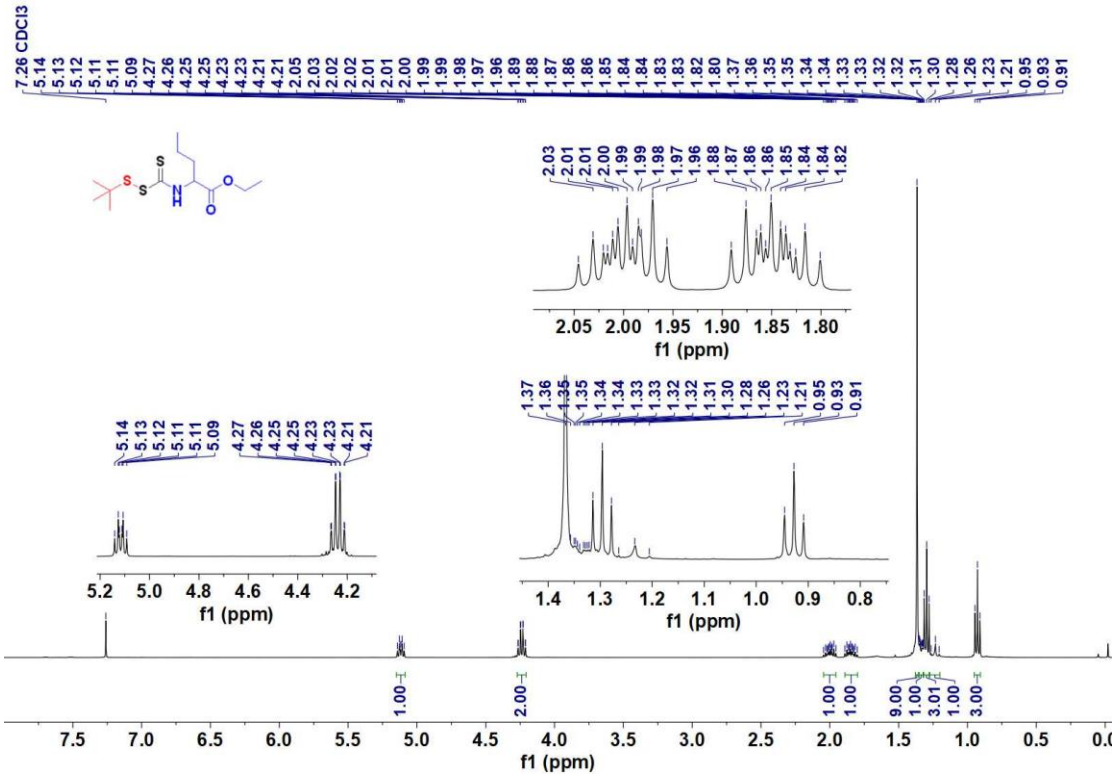


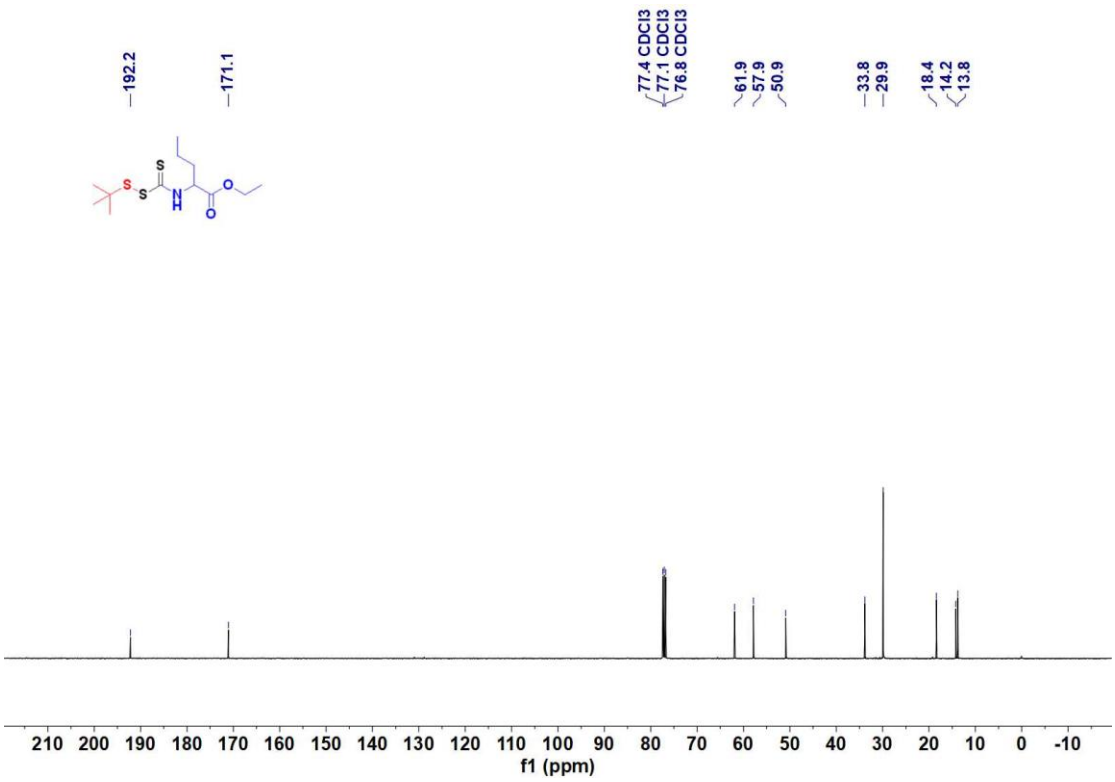
***Tert*-butyl (tert-butyldisulfannecarbonothioyl)alaninate (4l)**



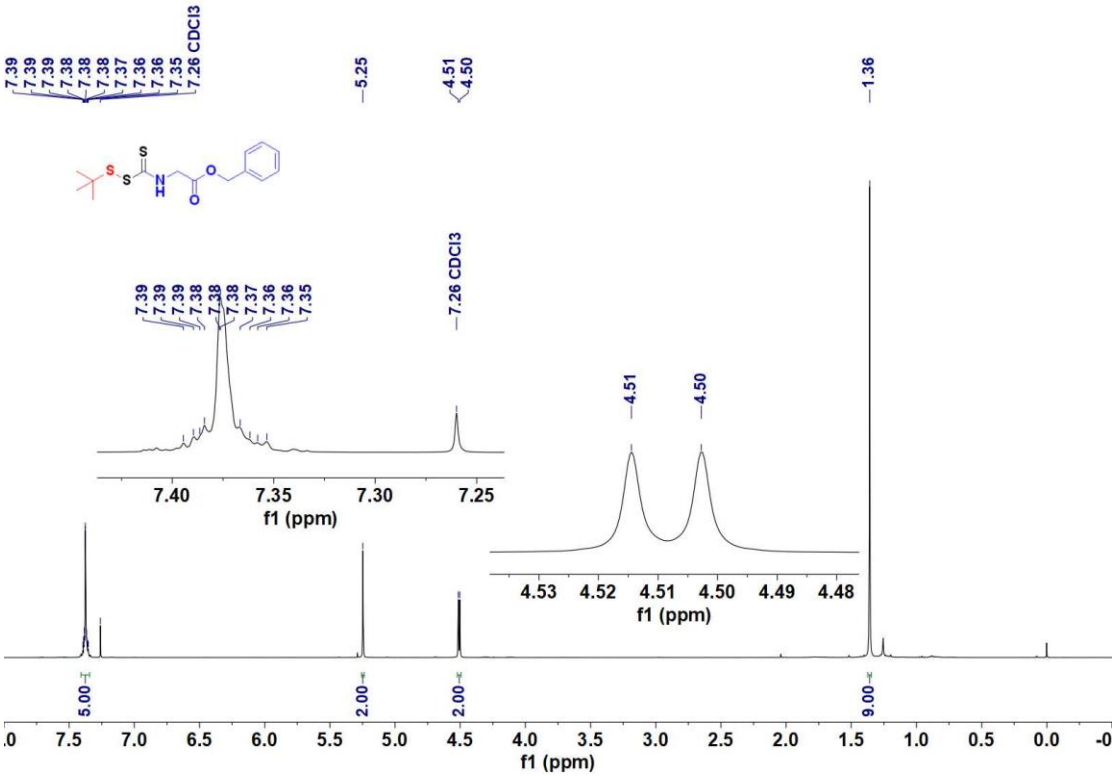


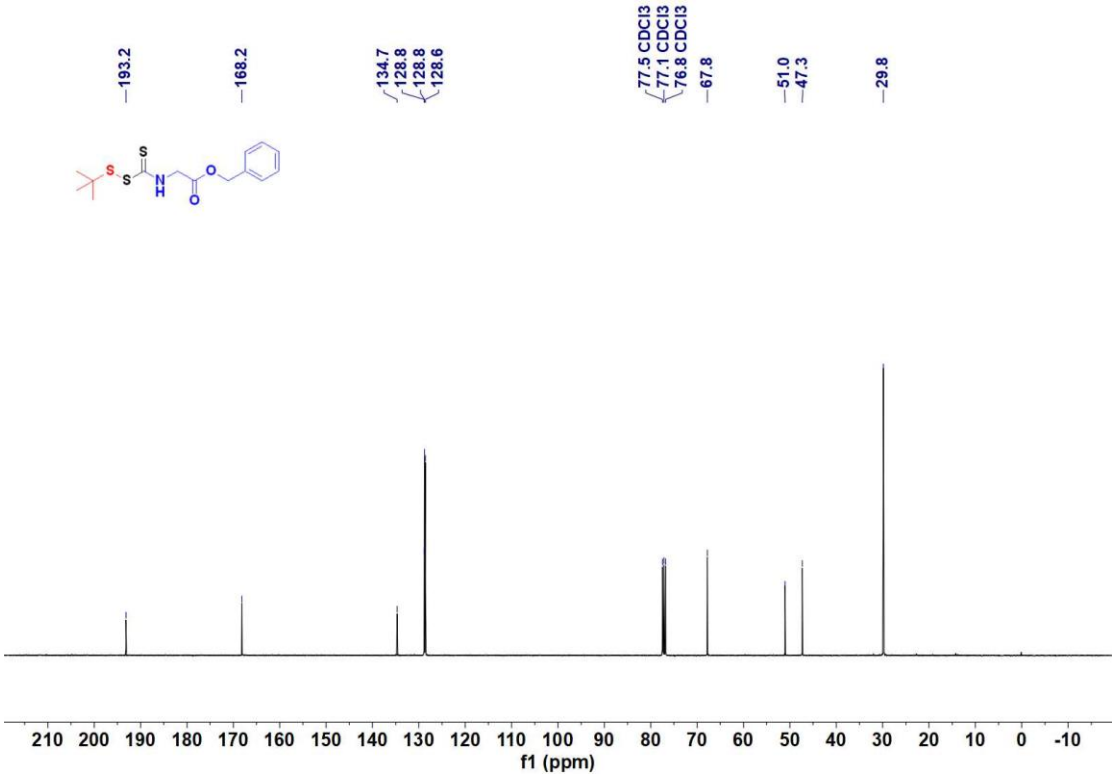
Ethyl 2-((*tert*-butyldisulfannecarbonothioyl)amino)pentanoate (4m)



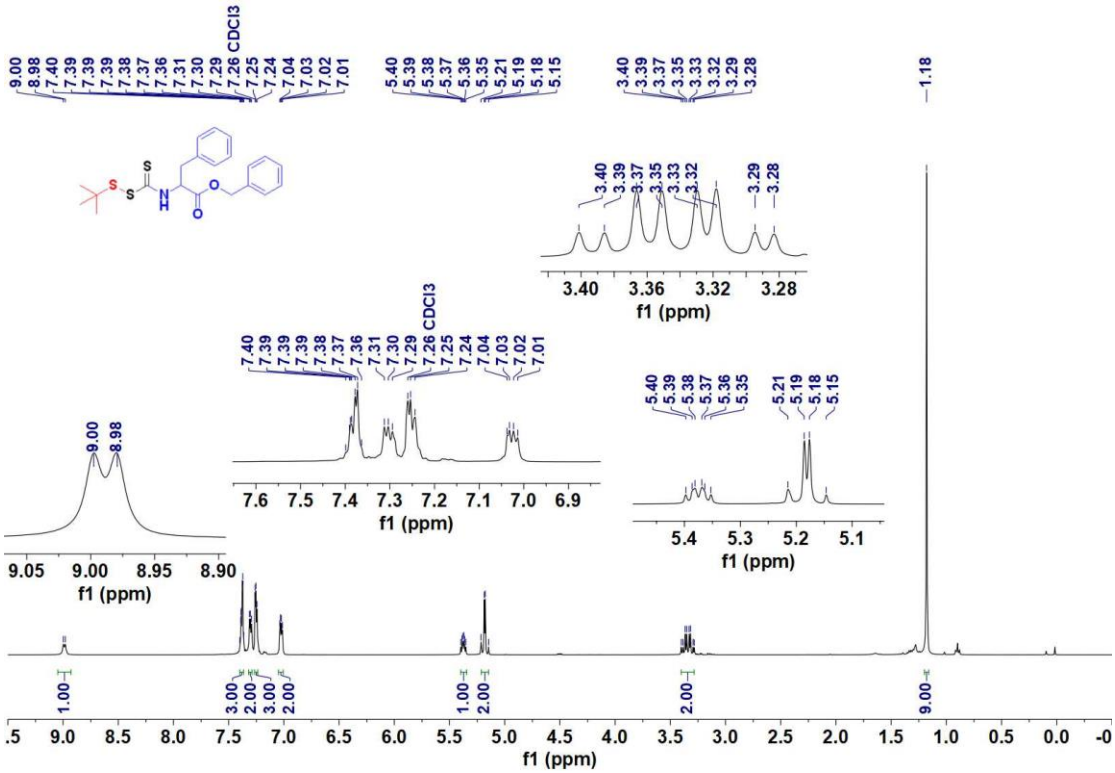


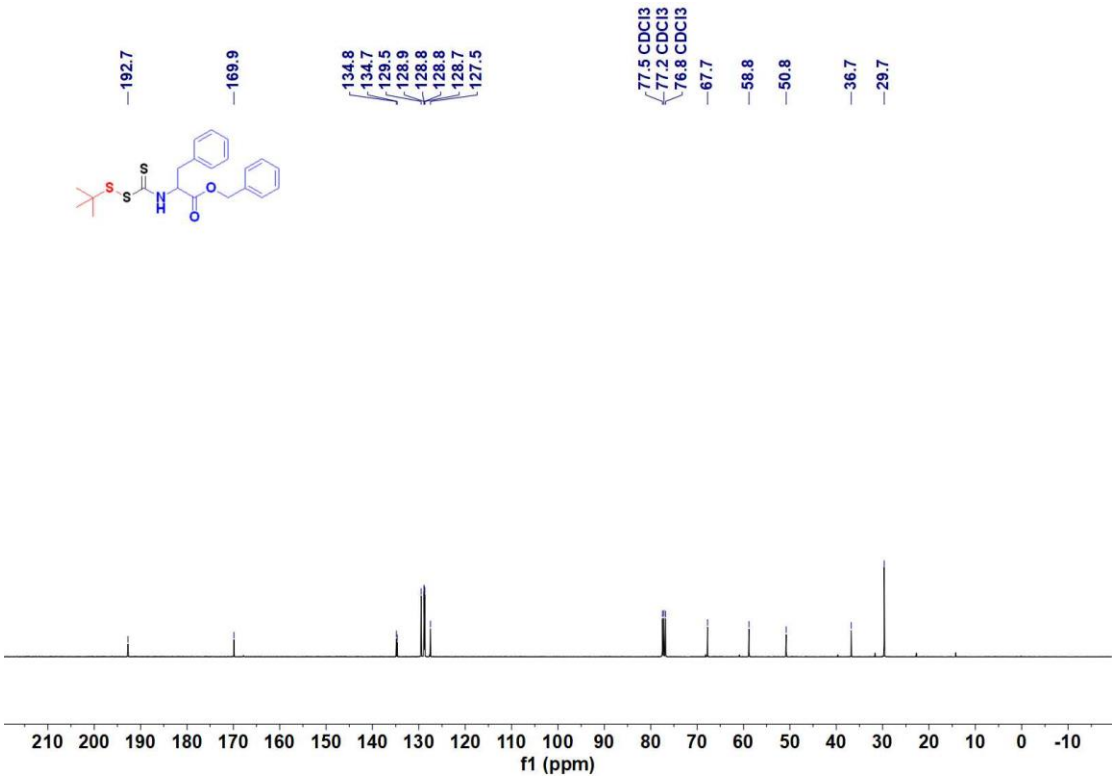
Benzyl (*tert*-butyldisulfannecarbonothioyl)glycinate (4n)



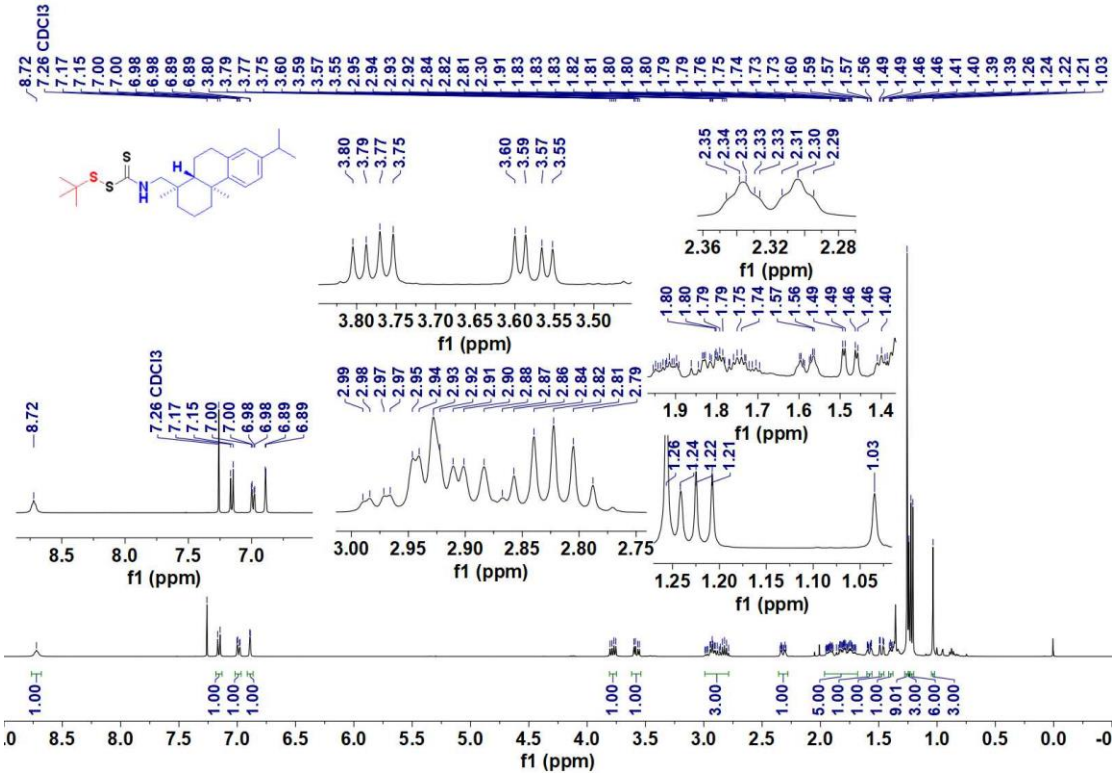


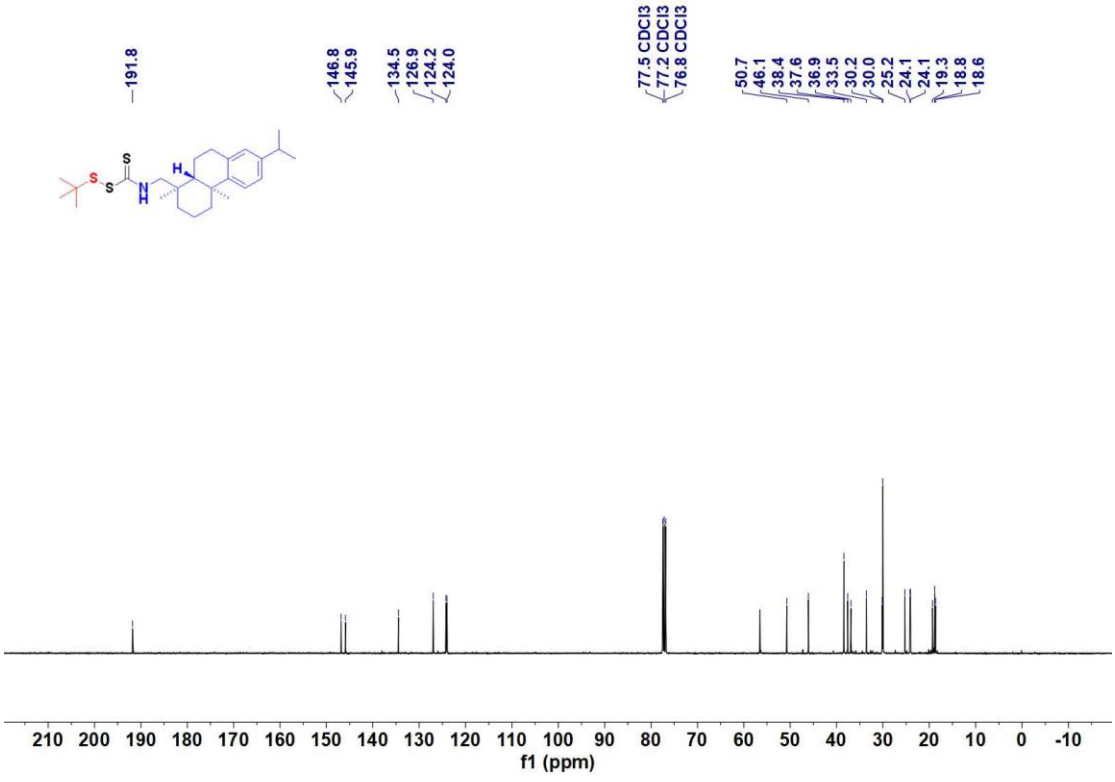
Benzyl (*tert*-butyldisulfannecarbonothioyl)phenylalaninate (4o)



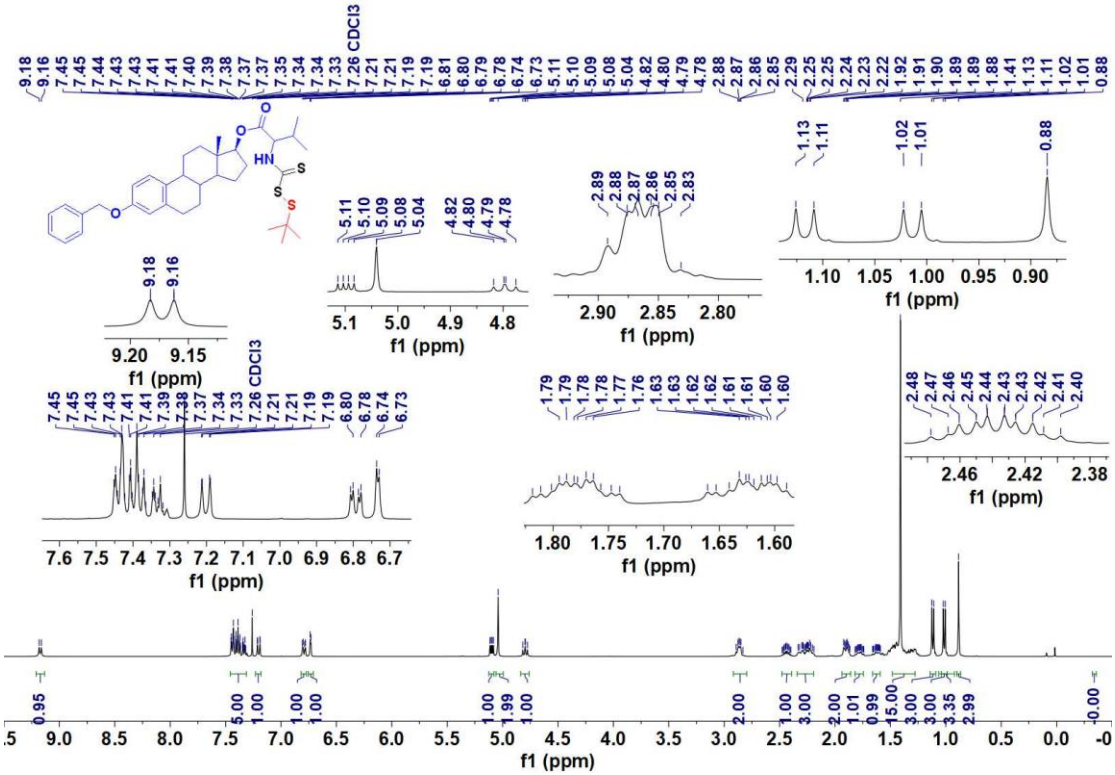


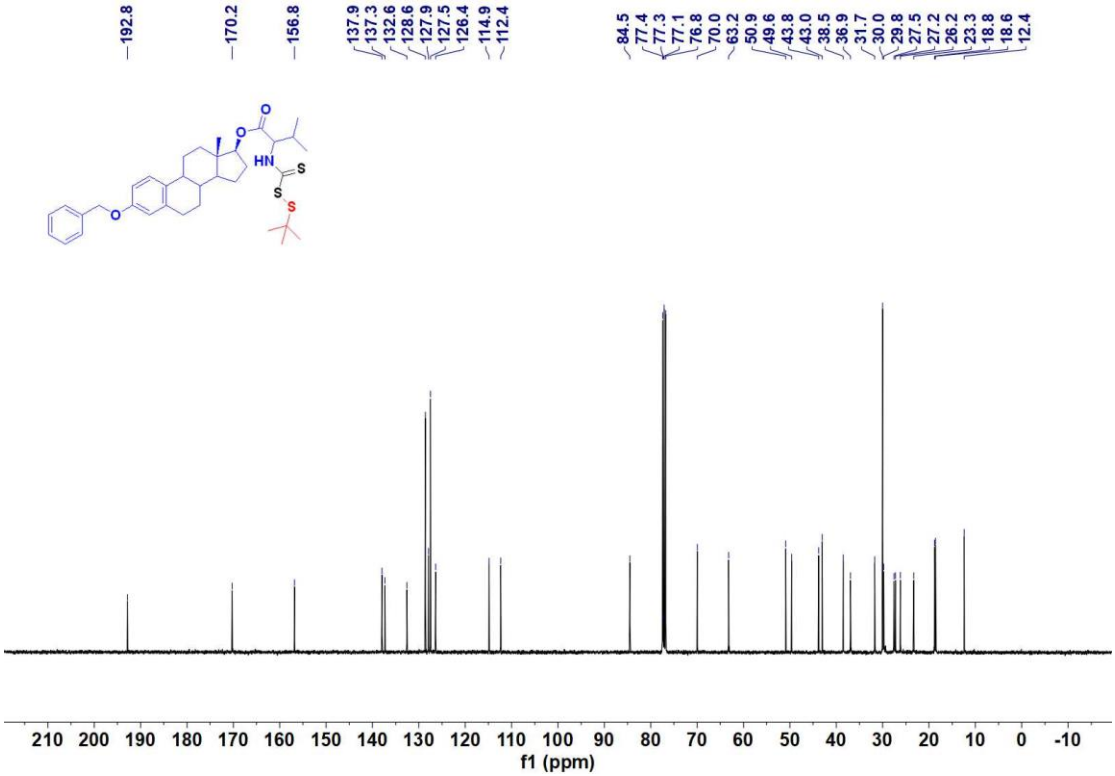
***Tert*-butyl(((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)carbamo(dithioperoxo)thioate (4p)**



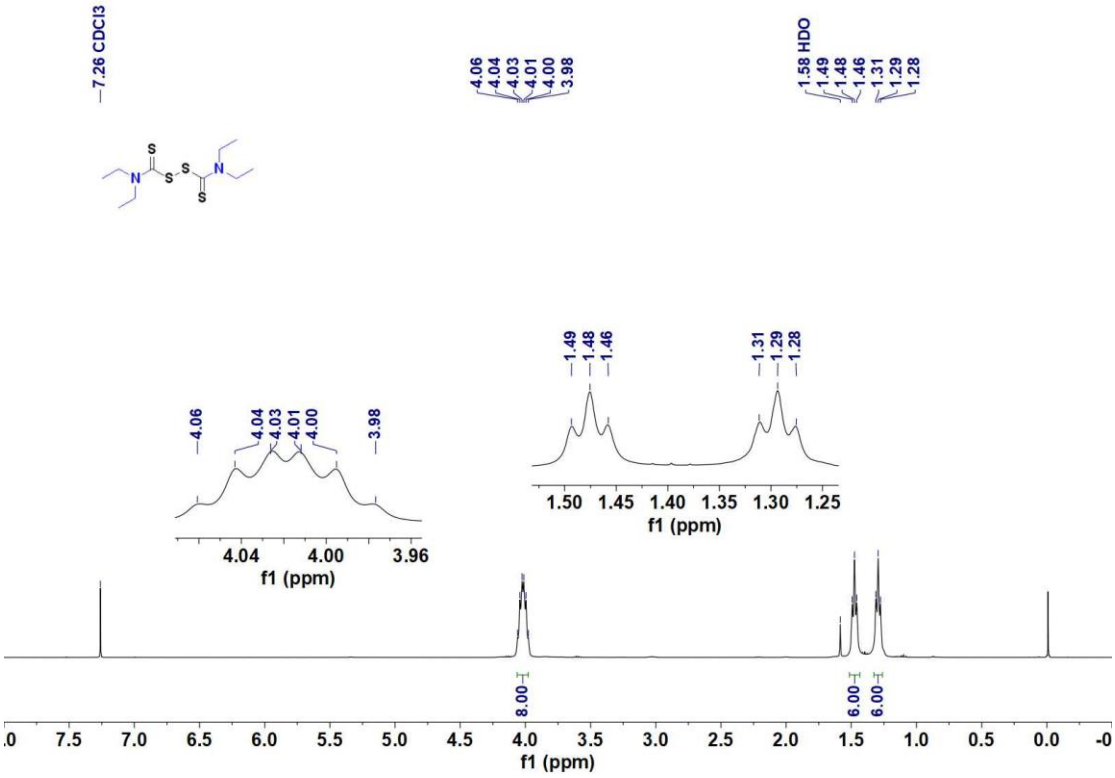


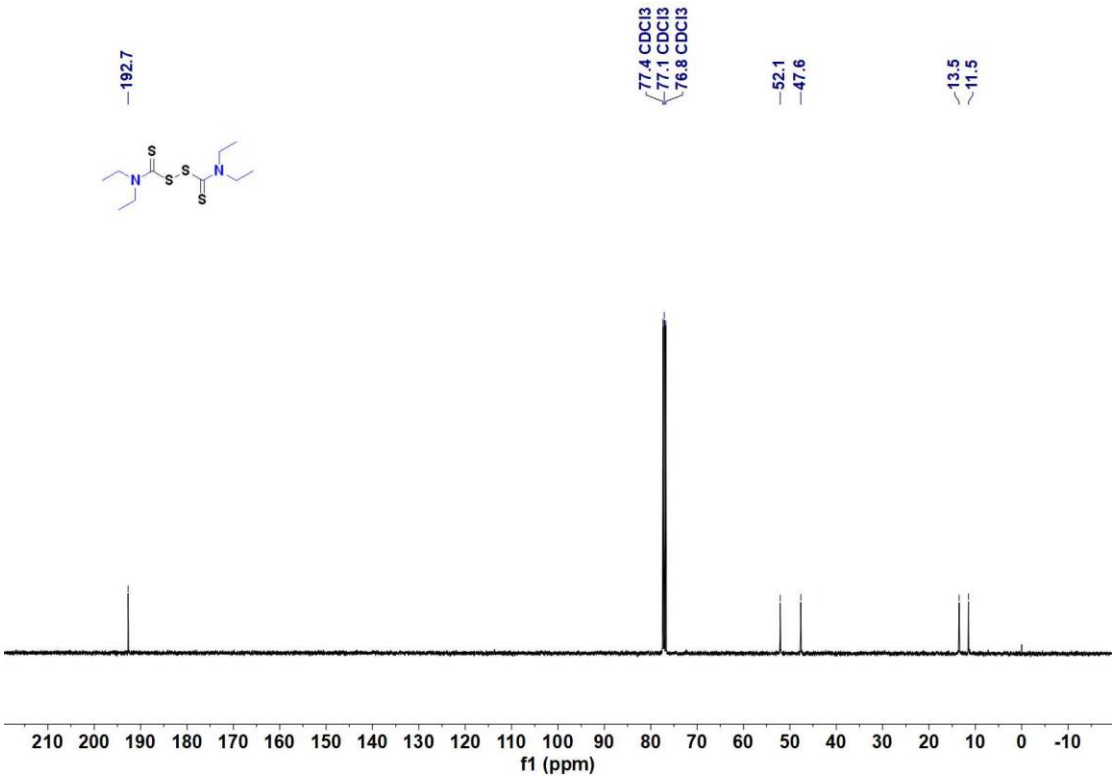
(13*S*,17*S*)-3-(Benzyloxy)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl (*tert*-butyldisulfannecarbonothioyl)valinate (4q)



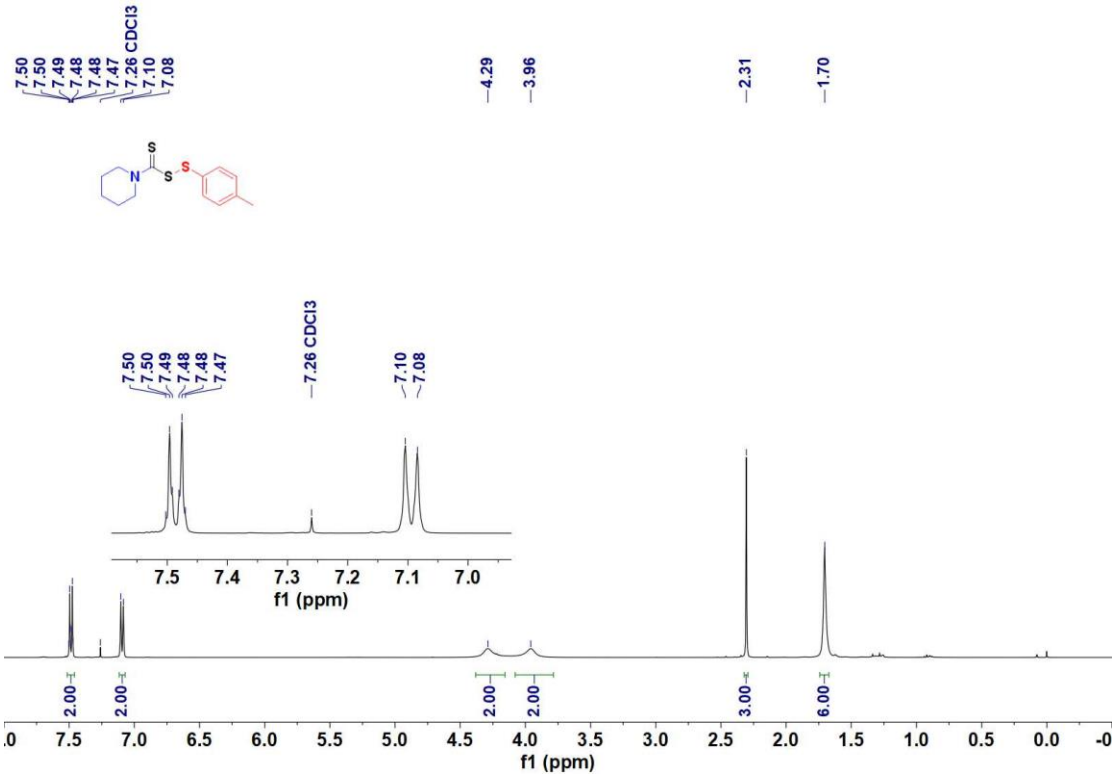


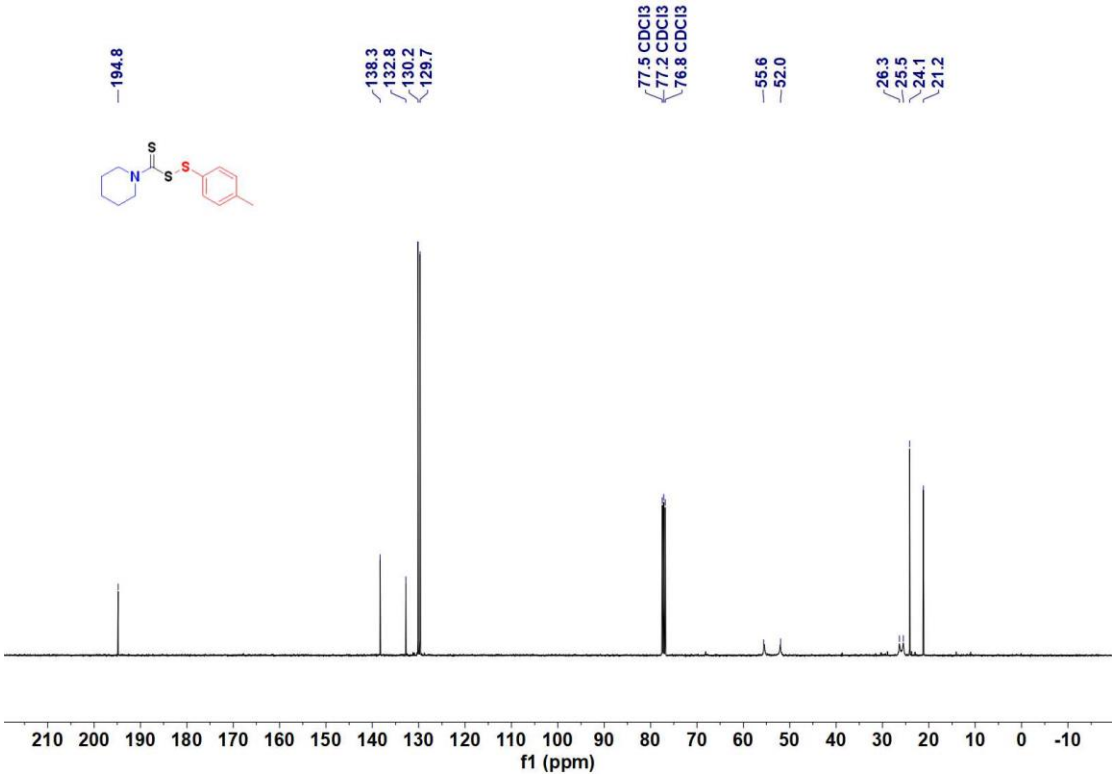
Disulfiram (I)



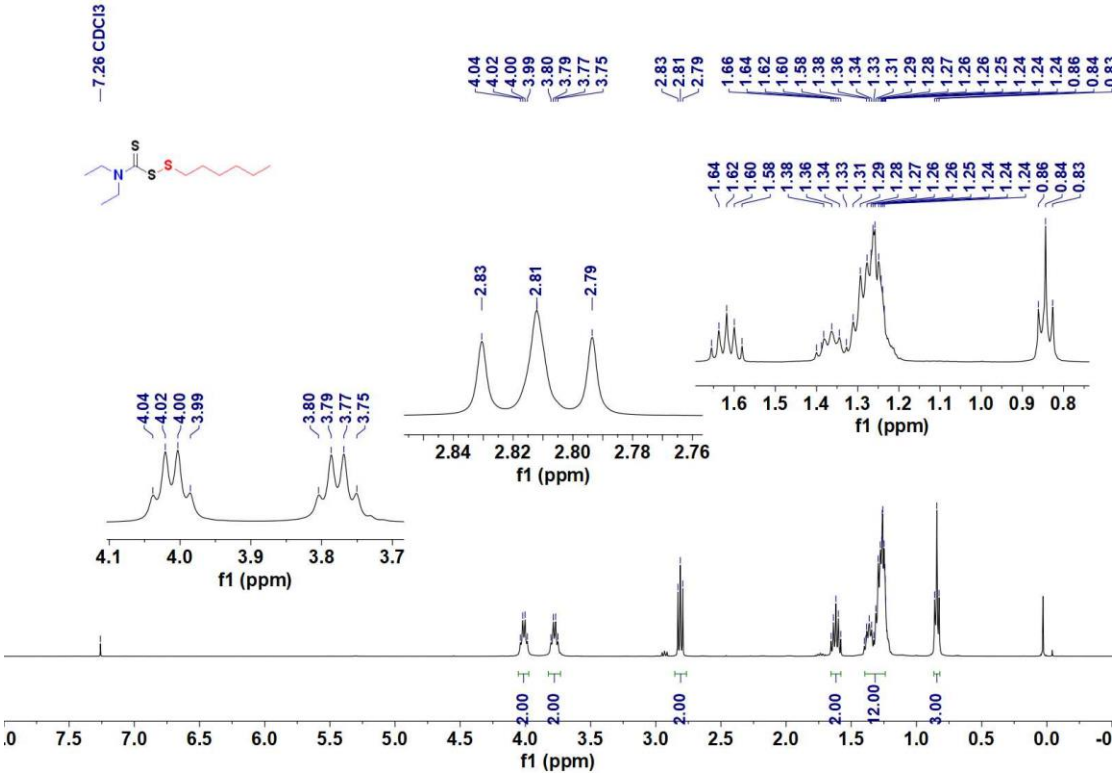


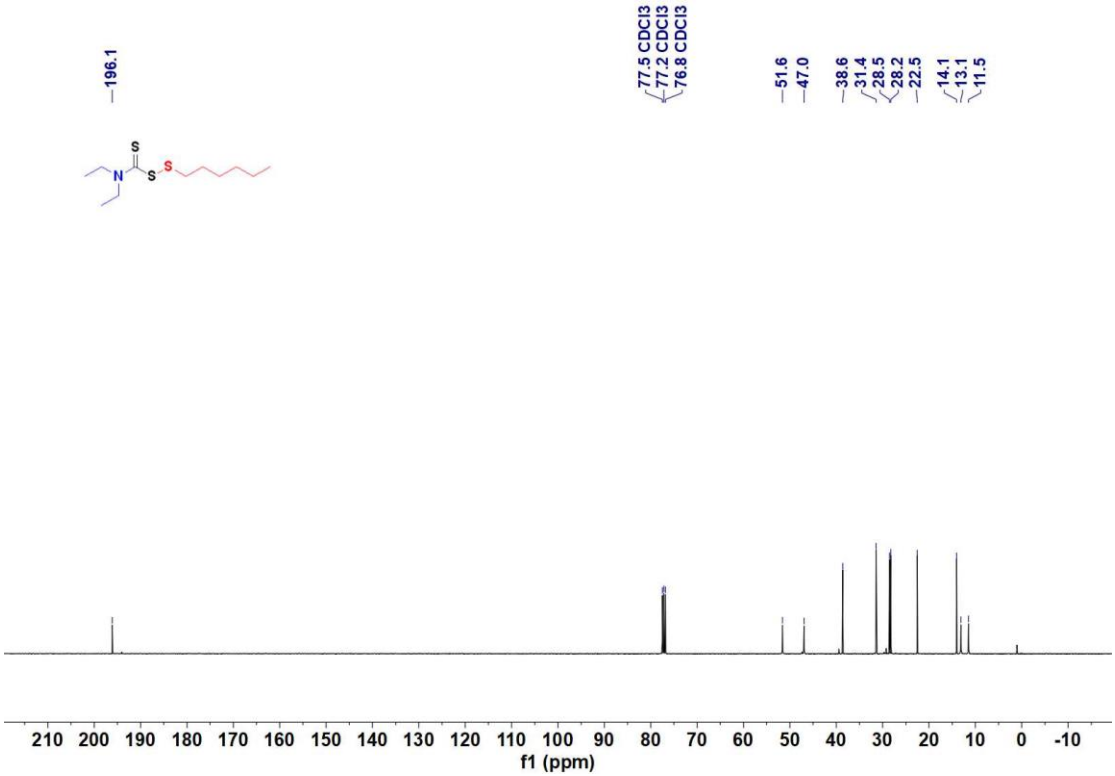
***p*-Tolyl piperidine-1-carbo(dithioperoxo)thioate (II)**



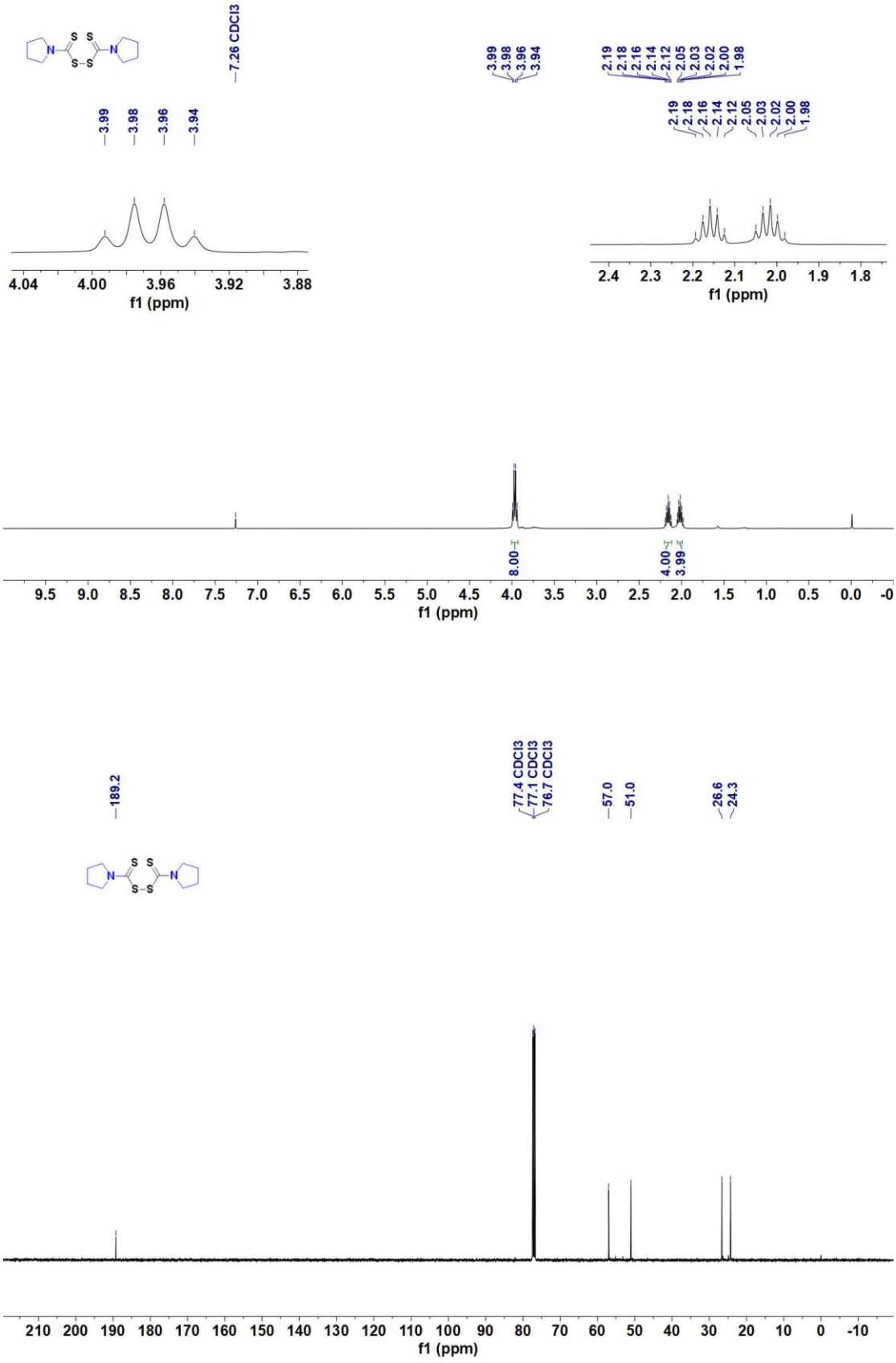


Hexyl diethylcarbamo(dithioperoxo)thioate (III)





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



Sodium pyrrolidine-1-carbodithioate (6)