Supporting Information

Electrochemical Oxidative Thioetheration of Aldehyde Hydrazones

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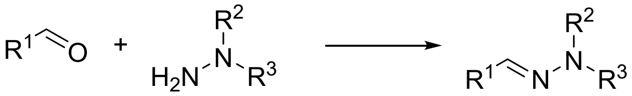
A. Instrumentation and Chemicals

All purchased reagents and solvents were used without further purification unless otherwise noted. All the electrochemical reactions were performed in an undivided cell unless otherwise noted. The electrolysis instrument used is an adjustable DC regulated power supply (PGD-2303S) (Taiwan Gwinstek Electronic Technology Co, Ltd.). Cyclic voltammograms were obtained on a CHI 760E potentiostat (CH Instruments, Inc.). All the reagents were purchased from WuXi AppTec. TecAnalytical thin-layer chromatography was performed by using commercially prepared 100-400 mesh silica gel plates (GF_{254}) and visualization was effected at 254 nm. All the Arylaldehyde Hydrazones derivatives were prepared according to known procedures. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.16 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). Melting points were determined with a Büchi Melting Point B-545 instrumen.

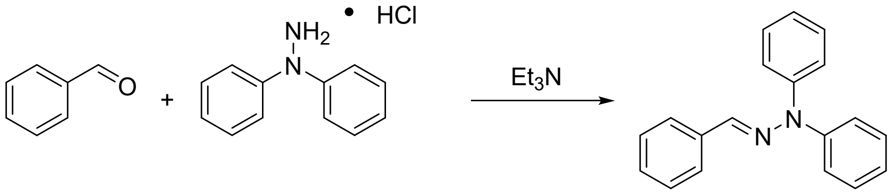
B. Experimental Procedure

B1. General procedures for the synthesis of aldehyde hydrazones



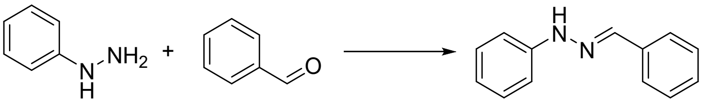
A mixture of hydrazine (2.4 mmol), aldehyde (2.0 mmol) and anhydrous $MgSO_4$ (0.5 g) in CH_2Cl_2 (10 mL) was stirred overnight at room temperature. After filtration of $MgSO_4$, CH_2Cl_2 was removed under reduced pressure and the residue was subjected to column chromatography to give the desired product with almost quantitative yields.

B2. General procedures for the synthesis of (*E*)-2-benzylidene-1,1-diphenylhydrazine



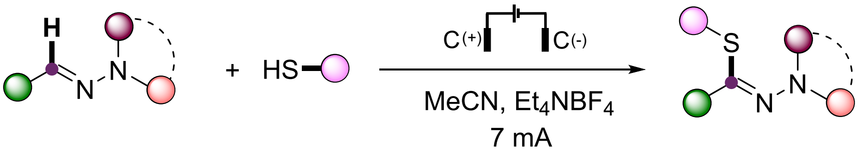
A mixture of hydrazine hydrochloride (2.4 mmol), aldehyde (2.0 mmol), Et_3N (3.0 equiv) and anhydrous $MgSO_4$ (0.5 g) in CH_2Cl_2 (10 mL) was stirred overnight at room temperature. After filtration of $MgSO_4$, CH_2Cl_2 was removed under reduced pressure and the residue was subjected to column chromatography to give the desired product with almost quantitative yields.

B3. General procedures for the synthesis of (*E*)-1-benzylidene-2-phenylhydrazine



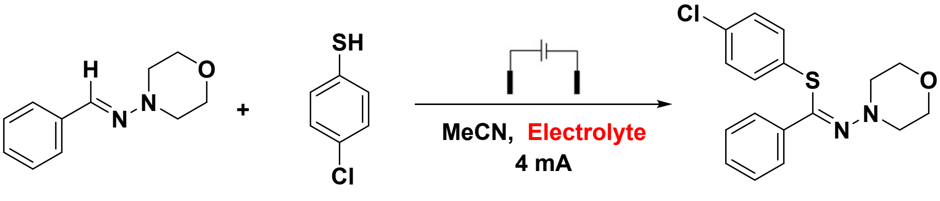
A 250 mL three-necked flask was charged with 50 mL anhydrous ethanol, aldehyde (20 mmol), hydrazine (25 mmol) and acetic acid (114.4 μL, 2 mmol). The reaction mixture was then refluxed for 2-4 h (monitored by TLC). After removal of ethanol, the residue was dissolved in ethyl acetate (100 mL), washed with a mixture of acetic acid (100 mL) and water (100 mL), and the organic phase was dried over Na_2SO_4 and concentrated under vacuum. The residue was subjected to column chromatography to give the desired product with almost quantitative yields.

B4. Electrochemical C-H thioetherification of hydrazones with thiophenols



In an oven-dried undivided three-necked flask (10 mL) equipped with a stir bar, aldehyde hydrazone compounds (0.1 mmol), thiophenol (7.0 equiv, 0.7 mmol), Et_4NBF_4 (1.0 equiv), MeCN (4.0 mL) were combined and added. The flask was equipped with stone grinding rods electrodes (∅ 6 mm) as both the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA under room temperature for 5 h. After the condensation was completed (monitored by TLC), the resulting mixture was extracted with ethyl acetate (30 mL ∅ 3), dried over anhydrous $MgSO_4$, filtered and evaporated in vacuo. The thioetheration products were obtained after being purified by column chromatography on silica gel with petroleum ether-ethyl acetate (15:1).

Table S1. Optimization of electrolyte[a]



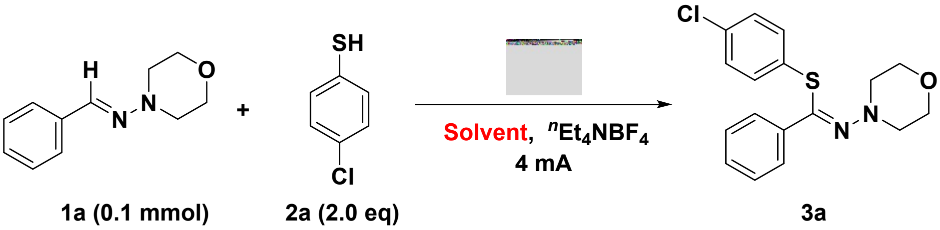
1a (0.1 mmol) **2a (2.0 eq)** **3a**

Entry	Electrolyte	Yield[b](%)
1	**Et_4NBF_4**	**15**
2	$^nBu_4NBF_4$	10
3	$^nBu_4NClO_4$	trace
4	$^nBu_4NCl$	trace
5	NH_4ClO_4	trace
6	$^nBu_4NPF_6$	n.r.
7	KI	n.r.

[a]Reaction conditions: C as anode (∅ 6 mm), Pt as cathode (10∅10∅0.2 mm), constant

current 4 mA, **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), Electrolyte (0.1 mmol, 1.0 equiv), MeCN (4 mL), room temperature, under air, 5 h, undivided cell. [b]Isolated yield based on **1a**, n.r. = no reaction.

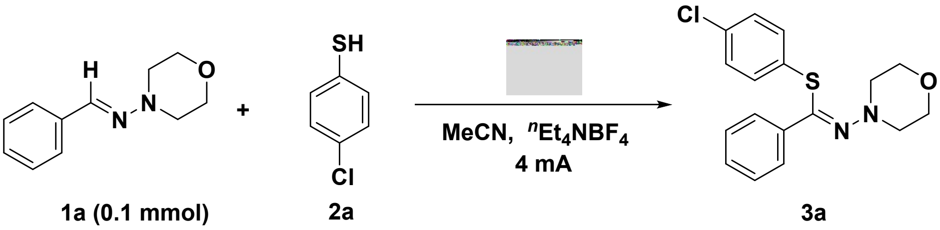
Table S2. Optimization of solvent[a]



Entry	Solvent	Yield[b](%)
1	MeOH	n.r.
2	DMSO	trace
3	DCE	trace
4	DMF	trace
5	THF	n.r.
6	DMA	trace
7	1,4-Dioxane	n.r.

[a]Reaction conditions: C as anode (⌀ 6 mm), Pt as cathode (10×10×0.2 mm), constant current 4 mA, **1a** (0.1 mmol), **2a** (0.2 mmol, 2.0 equiv), Et_4NBF_4 (0.1 mmol, 1.0 equiv), Solvent (4 mL), room temperature, under air, 5 h, undivided cell. [b]Isolated yield based on **1a**, n.r. = no reaction.

Table S3. Optimization of 2a equivalents [a]

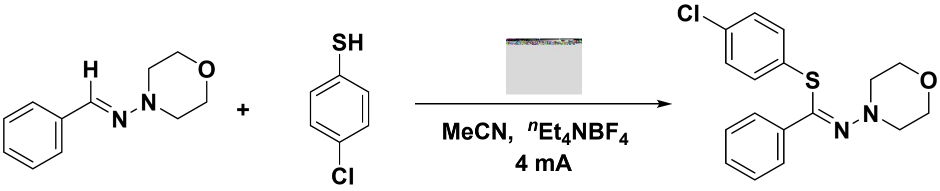


Entry	**2a**	Yield[b](%)
1	1.0 equiv	12

2	3.0 equiv	20
2	4.0 equiv	39
3	5.0 equiv	43
4	6.0 equiv	51
5	**7.0 equiv**	**60**
6	8.0 equiv	56

[a]Reaction conditions: C as anode (∅ 6 mm), Pt as cathode (10∅10∅0.2 mm), constant current 4 mA, **1a** (0.1 mmol), **2a**, Et_4NBF_4 (0.1 mmol, 1.0 equiv), MeCN (4 mL), room temperature, under air, 5 h, undivided cell. [b]Isolated yield based on **1a**.

Table S4. Optimization of electrodes[a]



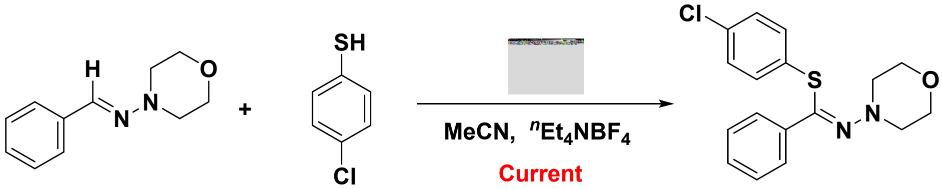
1a (0.1 mmol) **2a (7.0 eq)** **3a**

Entry	anode/cathode	Yield^b(%)
1	C | GF	trace
2	**C | C**	**65**
3	C | SS	n.r.
4	C | Mg	26
5	C | Zn	52
6	C | Ni	trace
7	C | Al	58
10	GF | C	17
11	Ni | C	n.r.
13	Pt | Pt	n.r

14	RVC | Pt	n.r.

[a]Reaction conditions: electrodes, constant current 4 mA, **1a** (0.1 mmol), **2a** (0.7 mmol, 7.0 equiv), Et_4NBF_4 (0.1 mmol, 1.0 equiv), MeCN (4 mL), room temperature, under air, 5 h, undivided cell. [b]Isolated yield based on **1a**, n.r. = no reaction.

Table S5. Optimization of current[a]



1a (0.1 mmol) **2a (7.0 eq)** **3a**

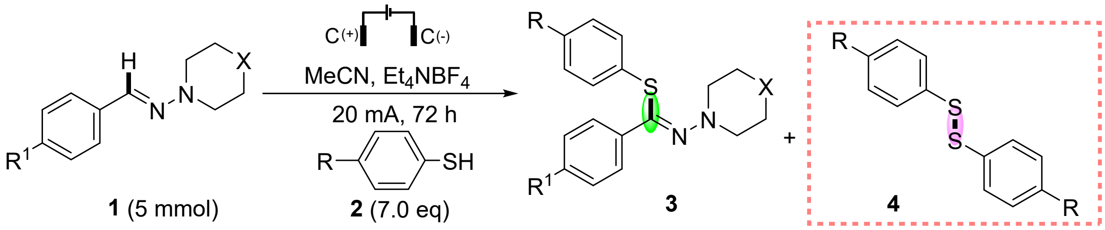
Entry	Current	Yield[b](%)
1	1 mA	33
2	3 mA	58
3	5 mA	67
4	**7 mA**	**73**
4	8 mA	49
5	10 mA	trace

[a]Reaction conditions: C as anode and cathode (∅ 6 mm), constant current, **1a** (0.1 mmol), **2a** (0.7 mmol, 7.0 equiv), Et_4NBF_4 (0.1 mmol, 1.0 equiv), MeCN (4 mL), room temperature, under air, 5 h, undivided cell. [b]Isolated yield based on **1a**.

B5. Gram-scale experiments

In an oven-dried undivided three-necked flask (100 mL) equipped with a stir bar, aldehyde hydrazone compounds (5 mmol), thiophenol (7.0 equiv), Et_4NBF_4 (1.0 equiv), MeCN (20 mL) were combined and added. The flask was equipped with stone grinding rods electrodes (∅ 6 mm) as both the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA under room temperature for 72 h. After the condensation was completed (monitored by TLC), the resulting mixture was extracted with ethyl acetate (30 mL × 3), dried over anhydrous $MgSO_4$, filtered and evaporated in vacuo. The thioetheration products were obtained after being purified by column chromatography on silica gel with petroleum ether-ethyl acetate (15:1).

Scheme S1 Gram-Scale Experiments



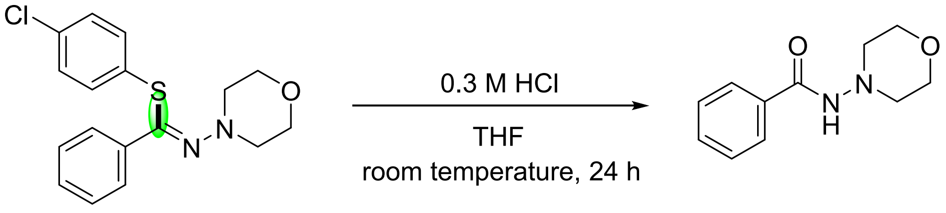
1 (5 mmol) **2** (7.0 eq) **3** **4**

R^1	R	X	the yield of **3**	the yield of **4**
R^1 = H	R = Cl	X = O	**3a**, 49%, 0.813 g	**4a**, 93%, 3.988 g
R^1 = H	R = Cl	X = C	**3ad**, 61%, 1.007 g	**4a**, 91%, 3.903 g
R^1 = H	R = CF$_3$	X = O	**3d**, 54%, 0.988 g	**4d**, 90%, 4.779 g
R^1 = CF$_3$	R = Cl	X = O	**3w**, 47%, 0.940 g	**4a**, 97%, 4.160 g

B6. Hydrolysis reaction of hydrazone

3a (0.2569 mmol) was added to a 7.5 mL 1/1 mixture of HCl (0.3 N) / THF. The resulting solution was stirred at room temperature and monitored by TLC. After 24 h, the solution was extracted by DCM and washed with aq NaHCO$_3$. The organic layer was dried over MgSO$_4$ and concentrated. The residue was purified by flash chromatography to afford **6a**.

Scheme S2 Hydrolysis reaction of hydrazone



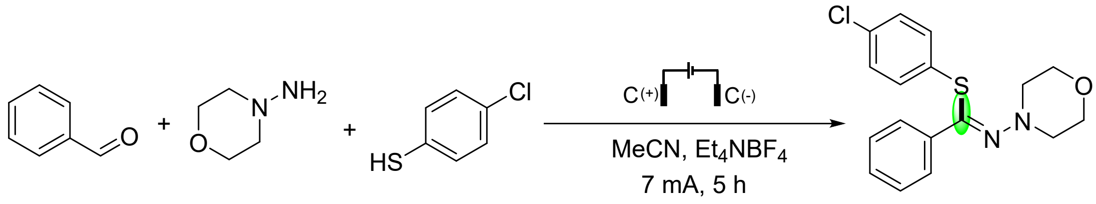
3a, 0.2569 mmol **6a**, 92%

B7. Electroredox three-component coupling reaction

In an oven-dried undivided three-necked flask (10 mL) equipped with a stir bar, benzaldehyde (0.2 mmol), hydrazine (1.2 equiv), *p*-chlorophenylthiophenol (7.0 equiv), MeCN (4.0 mL) were combined and added. The flask was equipped with stone grinding rods electrodes (∅ 6 mm) as both the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA under room temperature for 5 h.

After the condensation was completed (monitored by TLC), the resulting mixture was extracted with ethyl acetate (30 mL × 3), dried over anhydrous $MgSO_4$, filtered and evaporated in vacuo. The thioetheration products were obtained after being purified by column chromatography on silica gel with petroleum ether-ethyl acetate (15:1).

Scheme S3 Electroredox three-component coupling reaction

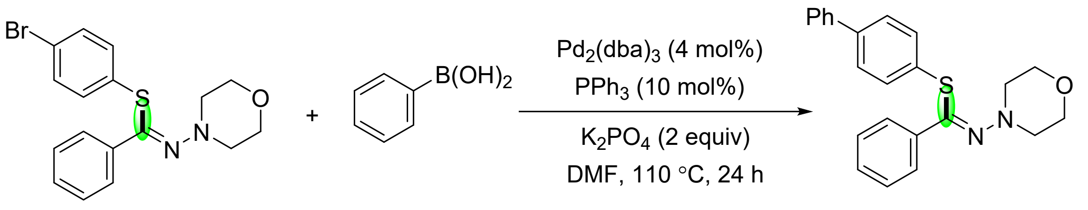


7a (0.1 mmol) **8a** (1.2 equiv) **2a** (7.0 equiv) **3a**, 30%

B8. Suzuki cross-coupling reaction

4-Bromophenyl (*Z*)-*N*-morpholinobenzimidothioate (0.2 mmol), phenylboronic acid (0.4 mmol, 2.0 equiv), $Pd(dba)_3$ (4 mol%), PPh_3 (10 mol%), K_2PO_4 (2.0 equiv), and DMF (2 mL) were added sequentially to the sealed tube, The reaction mixture was kept stirring at 110 °C for 24 h under a nitrogen atmosphere. After completion of the reaction (monitored by TLC), the resulting mixture was extracted with ethyl acetate (30 mL × 3), dried over anhydrous $MgSO_4$, filtered and evaporated in vacuo. The desired products were obtained after being purified by column chromatography on silica gel with petroleum ether-ethyl acetate (10:1).

Scheme S4 Suzuki cross-coupling reaction



3c (0.2 mmol) **9a** (2.0 equiv) **10a**, 54%

B9. Oxidation reaction of 3a[1]

(a) In a Schlenk flask (25 mL), **3a** (0.3 mmol), mCPBA (0.9 mmol) and DCM (5 mL) were added in sequence. After stirring for 3 h at 0 °C, the mixture was quenched with water, and extracted with ethyl acetate, and the combined organic phases were dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo. Finally, the product **12a** was analyzed by high-resolution mass spectrometry.

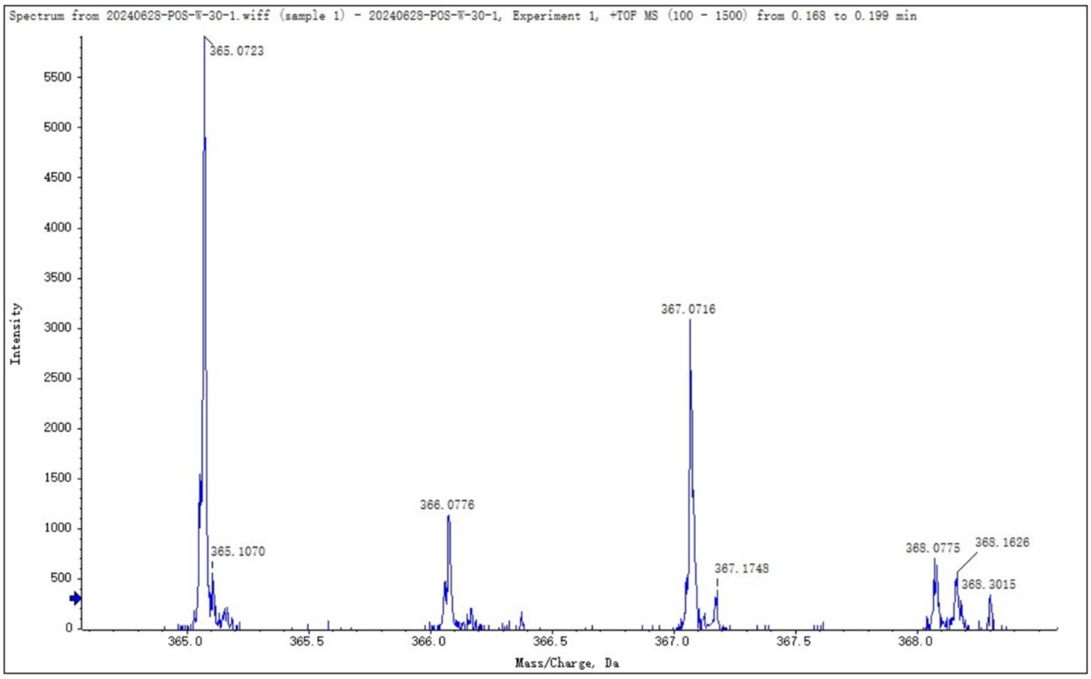


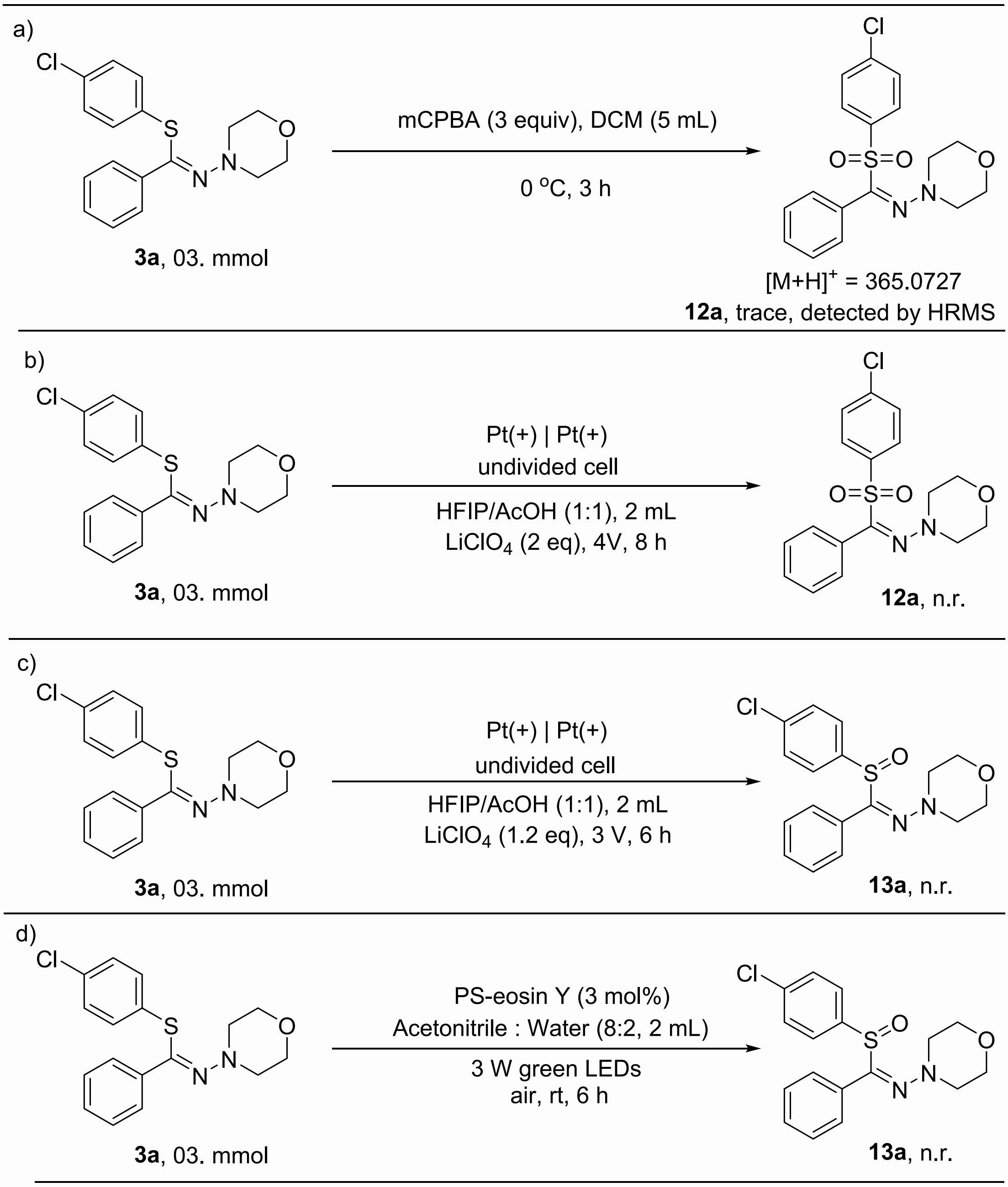
Figure S1 HRMS of product **12a**

(b) The reaction was carried out in an undivided cell equipped with two platinum electrodes (15 mm × 10 mm × 0.2 mm). **3a** (0.3 mmol), $LiClO_4$ (0. 6 mmol), HFIP (1 mL) and HOAc (1 mL) were added to the electrochemical cell and and the mixture was stirred under an air atmosphere. The reaction was performed at rt with a constant voltage of 4 V maintained for 8 h. TLC analysis was used to monitor the reaction progress. However, the reaction did not proceed, and extending the reaction time did not yield better results.

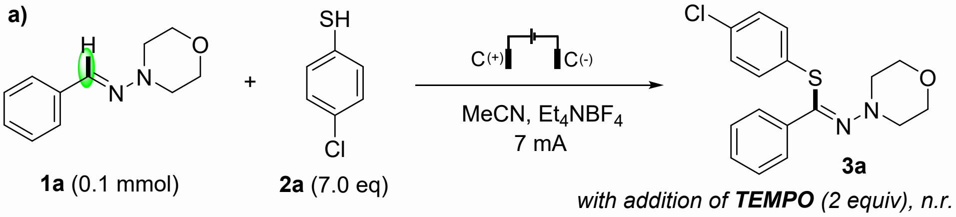
(c) The reaction was carried out in an undivided cell equipped with two platinum electrodes (15 mm × 10 mm × 0.2 mm). **3a** (0.3 mmol), $LiClO_4$ (0.36 mmol), HFIP (1 mL) and HOAc (1 mL) were added to the electrochemical cell and and the mixture was stirred under an air atmosphere. The reaction was performed at rt with a constant voltage of 3 V maintained for 6 h. TLC analysis was used to monitor the reaction progress. However, the reaction did not proceed, and extending the reaction time did not yield better results.

(d) A mixture of **3a** (1 mmol) and polymer-supported eosin Y (3 mol%) was taken in an oven dried round bottom flask containing 2 mL of acetonitrile: water (8:2) and irradiated with green LEDs (2 x 3 W) at room temperature under an open air atmosphere. The completion of the photoreaction was monitored by TLC.

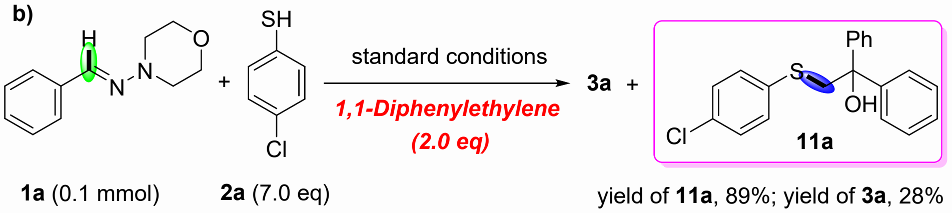
Scheme S5 Oxidation reaction of 3a



B10. Control experiments

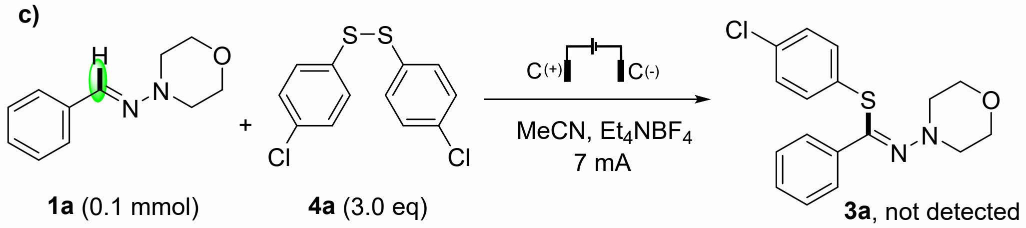


with addition of ***TEMPO*** *(2 equiv), n.r.*
with addition of ***BHT*** *(2 equiv), 31%*



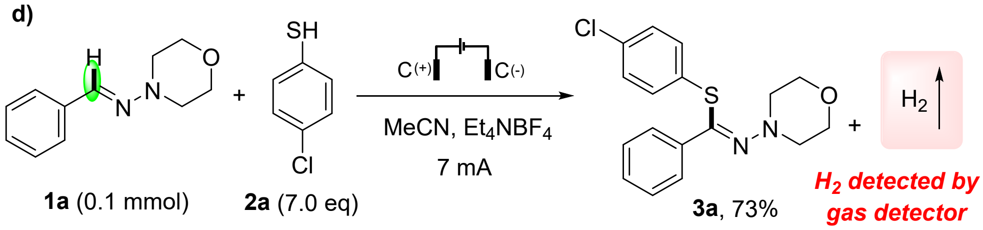
yield of **11a**, 89%; yield of **3a**, 28%

In an oven-dried undivided three-necked flask (10 mL) equipped with a stir bar, (*E*)-*N*-morpholino-1-phenylmethanimine (0.1 mmol), *p*-chlorophenylthiophenol (7.0 equiv, 0.7 mmol), Et_4NBF_4 (1.0 equiv), added BHT (2.0 equiv), TEMPO (2.0 equiv), 1,1-diphenylethylene (2.0 equiv), respectively. MeCN (4.0 mL) were combined and added. The flask was equipped with stone grinding rods electrodes (∅ 6 mm) as both the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA under room temperature for 5 h. (monitored by TLC).



In an oven-dried undivided three-necked flask (10 mL) equipped with a stir bar, (*E*)-*N*-morpholino-1-phenylmethanimine (0.1 mmol), 1,2-bis(4-chlorophenyl) disulfide (3.5 equiv, 0.35 mmol), Et_4NBF_4 (1.0 equiv), MeCN (4.0 mL) were combined and added. The flask was equipped with stone grinding rods electrodes (∅ 6 mm) as both the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA under room temperature for 5 h. (monitored by TLC).

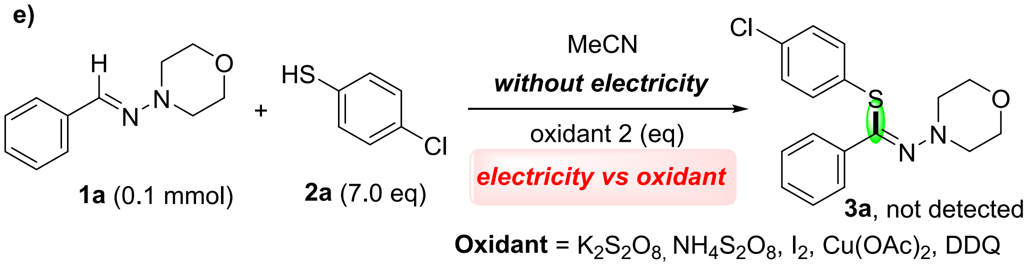
d)



In order to demonstrate the release of H_2 during the thioetherification reaction, the model reaction of aldehyde hydrazone compound (**1**), thiophenol (**2**) were monitored by a H_2 detector under standard conditions. As the thioetherification reaction proceeded, the H_2 was observed clearly and the concentration increased gradually. (Figure S2)

Figure S2. H_2 Detection Experiment

e)



In an oven-dried undivided three-necked flask (10 mL) equipped with a stir bar, (*E*)-*N*-morpholino-1-phenylmethanimine (0.1 mmol), *p*-chlorophenylthiophenol (7.0 equiv, 0.7 mmol), MeCN (4.0 mL) oxidants ($K_2S_2O_8$, $NH_4S_2O_8$, I_2, $Cu(OAc)_2$, DDQ) were combined and added. The reaction mixture was stirred under room temperature for 5 h. After the condensation was completed (monitored by TLC).

B11. Cyclic voltammetry experiments

CV was carried out using a computer controlled potentiostat (CHI760E) and a standard three electrode arrangement. The tested compound (0.1 M), glassy carbon (φ=4 × 45 mm) as the working electrode, Pt wire (*φ*=0.5×37 mm) as the auxiliary electrode, and Ag/AgCl (saturated aqueous KCl, *φ*=4×45 mm) as the reference electrode. All the electrochemical measurements were carried out in MeOH solvent with Et_4NBF_4 (0.05 M) as the supporting electrolyte. The scan rate for the measurements were typically 50 mv/s. The potential ranges investigated were 0 V to + 2.0 V vs Ag/AgCl (saturated aqueous KCl).

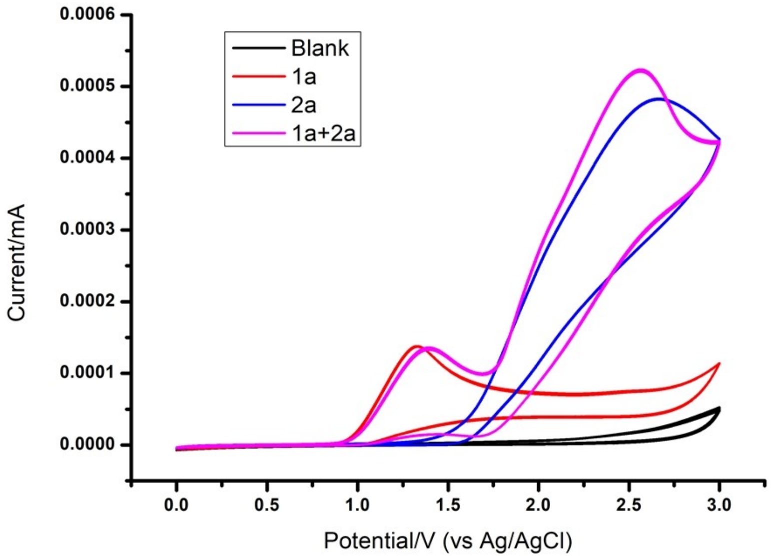


Figure S3. Cyclic Voltammetry. Cyclic voltammograms of 0.05 M $^{n}Et_4NBF_4$ in the solvent of MeCN at room temperature. (a) Blank; (b) **1a** (1 mM); (c) **2a** (1 mM); (d) **1a** (1 mM) and **2a** (1 mM). The CV plotting convention was IUPAC. CV analysis was performed at a 50 mV/s scan rate by using a glassy carbon electrode (GCE) (d = 4 mm) as a working electrode, a Pt wire as a counter electrode, and a silver chloride electrode as a reference electrode. The starting point was 0.00 V, and the direction of the initial scan was oxidativ.

B12. On/off current experiment.

To the 10 mL three-necked round bottom flask with a magnetic stir bar was added aldehyde hydrazone compound (0.1 mmol), thiophenol (7.0 equiv, 0.7 mmol), Et_4NBF_4 (1.0 equiv), MeCN (4.0 mL) were combined and added. The flask was equipped with stone grinding rods electrodes (∅ 6 mm) as both the anode and cathode. The electrolysis was carried out at room temperature using a constant current of 7 mA. The reaction mixture was stirred and electrolyzed for 0, 1.66, 3.33 and 5 h respectively. Meanwhile, the setting time span for 1 h, and only stirred without electrolyzed. The yield of the product was determined by GC and dodecane as internal standard.

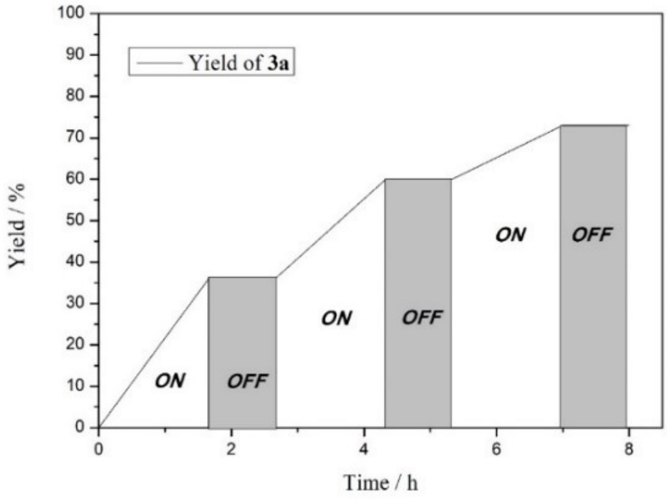
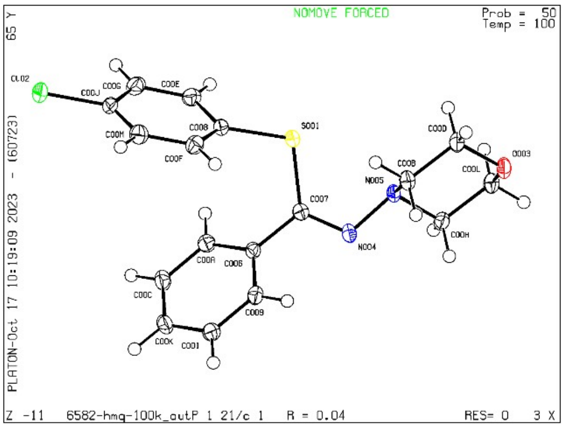


Figure S4. On/off current experiments.

C. X-ray Crystallographic Analysis for Product 3a

The X-ray crystallographic structures for **3a**. ORTEP representation with 86% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 2303390.

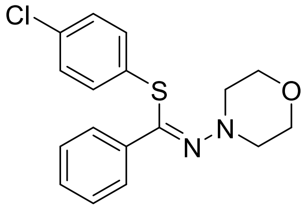


Empirical formula	$C_{17}H_{18}ClN_2OS$
Formula weight	333.84
Temperature	99.98 (10) K
Wavelength	0.71073 *Å*
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	a = 5.3567 (2) *Å* alpha = 90 deg. b = 14.2027 (5) *Å* beta = 90.995 (4) deg. c = 21.0025 (8) *Å* gamma = 90 deg.
Volume	1597.62 (10) $Å^3$
Z, Calculated density	4, 1.388 Mg/m^3
Absorption coefficient	0.373 mm^{-1}
F(000)	700
Crystal size	1 × 1 × 1 mm
Theta range for data collection	3.462 to 58.23 deg.
Limiting indices	$-6 \leq h \leq 4$, $-12 \leq k \leq 18$, $-21 \leq l \leq 25$
Reflections collected /	9512 / 3476 [R_{int} = 0.0266, R_{sigma} =

unique	0.0375]
Data / restraints / parameters	3476/0/199
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	$R_1 = 0.0390$, $wR_2 = 0.0970$
R indices (all data)	$R_1 = 0.0510$, $wR_2 = 0.1042$

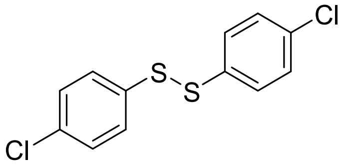
D. Characterization Data of Products

4-Chlorophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3a**)



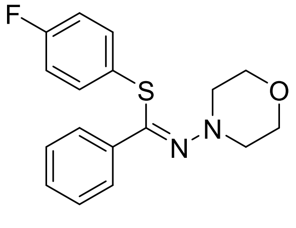
Yield: 73%, 24.2 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow solid; mp: 92.1-92.7 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.23 (d, J = 7.2 Hz, 2H), 7.19 (d, J = 7.1 Hz, 1H), 7.16 – 7.12 (m, 2H), 7.10 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 3.91 – 3.85 (m, 4H), 3.05 (s, 4H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 163.8, 135.3, 134.6, 134.3, 130.3, 129.3, 128.9, 128.8, 128.0, 66.3, 54.5. HRMS (ESI) m/z: calcd for $C_{17}H_{17}N_2OSCl$ [M+H]+ 333.0828; found 333.0830.

1,2-Bis(4-chlorophenyl)disulfane (**4a**)[2]



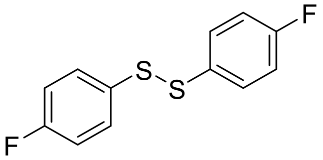
Yield: 94%, 80.6 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 – 7.41 (m, 4H), 7.32 – 7.28 (m, 4H).

4-Fluorophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3b**)



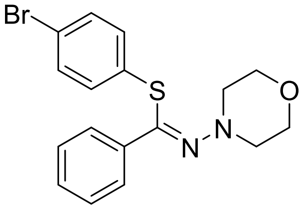
Yield: 62%, 19.6 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.16 (ddd, J = 17.9, 10.4, 4.3 Hz, 7H), 6.78 (t, J = 8.6 Hz, 2H), 3.92 – 3.87 (m, 4H), 3.08 – 3.03 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.9, 136.4, 136.4, 134.6, 129.1, 128.9, 127.9, 126.9, 115.9, 115.7, 66.3, 54.5; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -112.27 – -112.89 (m), -113.43. HRMS (ESI) m/z: calcd for $C_{17}H_{17}N_2OSF$ [M+H]+ 317.1124; found 317.1125.

1,2-Bis(4-fluorophenyl)disulfane (**4b**)[2]



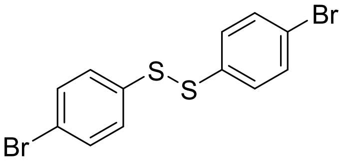
Yield: 96%, 73.2 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 – 7.45 (m, 4H), 7.08 – 7.01 (m, 4H).

4-Bromophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3c**)



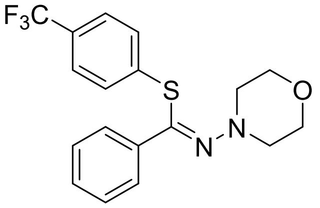
Yield: 60%, 22.6 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 (td, *J* = 8.5, 4.9 Hz, 4H), 7.20 – 7.15 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 3.95 – 3.88 (m, 4H), 3.12 – 3.04 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.5, 134.6, 131.7, 130.9, 129.4, 128.9, 128.00, 122.5, 66.3, 54.5; HRMS (ESI) m/z: calcd for $C_{17}H_{17}N_2OSBr$ [M+H]+ 377.0323; found 377.0327.

1,2-Bis(4-bromophenyl)disulfane (**4c**)[2]



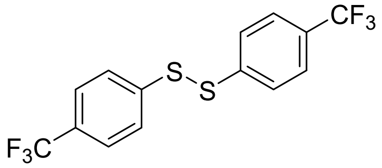
Yield: 96%, 108.2 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.4 Hz, 4H), 7.36 (d, *J* = 8.5 Hz, 4H).

4-(trifluoromethyl)phenyl (*Z*)-*N*-morpholinobenzimidothioate (**3d**)



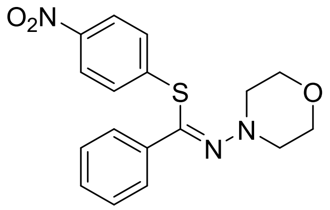
Yield: 93%, 34.0 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow solid; mp: 80.2-80.6 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 4H), 7.23 (d, *J* = 6.3 Hz, 1H), 7.20 – 7.15 (m, 2H), 3.92 – 3.87 (m, 4H), 3.12 – 3.07 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 162.0, 137.0, 134.6, 133.6, 129.6, 128.9, 128.1, 125.3, 125.3, 125.2, 66.2, 54.5; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.81. HRMS (ESI) m/z: calcd for $C_{18}H_{17}N_2OSF_3$ [M+H]+ 367.1092; found 367.1093.

1,2-Bis(4-(trifluoromethyl)phenyl)disulfane (**4d**)[5]



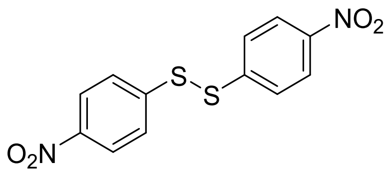
Yield: 96%, 101.9 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.60 (d, *J* = 9.6 Hz, 8H).

4-Nitrophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3e**)



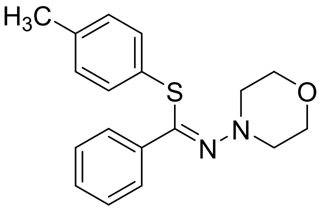
Yield: 67%, 30.0 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.43 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.34 (d, *J* = 7.0 Hz, 2H), 7.20 – 7.18 (m, 1H), 7.16 – 7.12 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.03 – 6.99 (m, 1H), 3.94 – 3.88 (m, 4H), 3.15 – 3.09 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 164.0, 136.8, 134.6, 133.1, 132.1, 129.9, 129.3, 128.9, 127.6, uh66.3, 54.4. HRMS (ESI) m/z: calcd for $C_{17}H_{17}N_3O_3S$ [M+H]+ 344.1069; found 344.1064.

1,2-Di-p-tolyldisulfane (**4e**)[2]



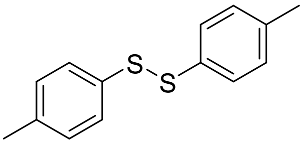
Yield: 97%, 89.3 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 8.22 (d, *J* = 8.4 Hz, 4H), 7.65 (s, 4H).

p-tolyl (*Z*)-*N*-morpholinobenzimidothioate (**3f**)



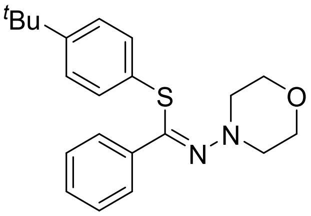
Yield: 47%, 14.7 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Green oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 (d, J = 7.1 Hz, 2H), 7.17 (d, J = 7.2 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.09 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 7.5 Hz, 2H), 3.94 – 3.90 (m, 4H), 3.12 – 3.07 (m, 4H), 2.23 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.0, 138.1, 135.0, 134.3, 129.4, 128.94, 128.92, 127.9, 127.7, 66.3, 54.5, 21.1. HRMS (ESI) m/z: calcd for $C_{17}H_{20}N_2OS$ [M+H]+ 313.1375; found 313.1376

1,2-Di-p-tolyldisulfane (**4f**)[2]



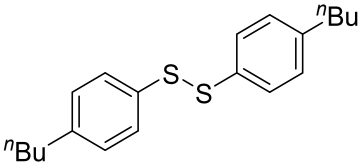
Yield: 95%, 70.1 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, J = 7.9 Hz, 4H), 7.18 (d, J = 7.6 Hz, 4H), 2.40 (s, 6H).

4-(tert-butyl)phenyl (*Z*)-*N*-morpholinobenzimidothioate (**3g**)



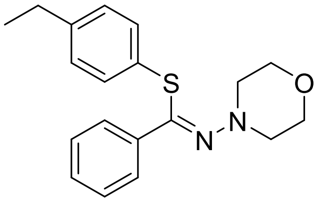
Yield: 41%, 14.5 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown solid; mp: 72.7-73.8 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.18 (d, J = 7.5 Hz, 2H), 7.13 – 7.05 (m, 7H), 3.92 – 3.86 (m, 4H), 3.10 – 3.04 (m, 4H), 1.19 (s, 9H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.2, 151.5, 134.9, 134.2, 128.9, 128.8, 127.8, 127.6 125.5, 66.3, 54.5, 34.5, 31.1. HRMS (ESI) m/z: calcd for $C_{21}H_{26}N_2OS$ [M+H]+ 355.1844; found 355.1848.

1,2-Bis(4-butylphenyl)disulfane (**4g**)[3]



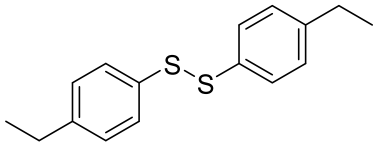
Yield: 97%, 96.0 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.59 (d, *J* = 8.2 Hz, 4H), 7.45 (d, *J* = 8.1 Hz, 4H), 1.45 – 1.41 (m, 18H).

4-Ethylphenyl (*Z*)-*N*-morpholinobenzimidothioate (**3h**)



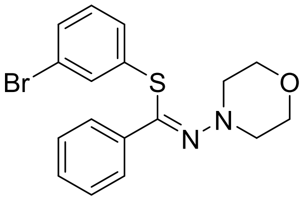
Yield: 43%, 14.0 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown oil; ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.23 (d, *J* = 7.3 Hz, 2H), 7.17 (d, *J* = 6.4 Hz, 1H), 7.14 – 7.09 (m, 4H), 6.93 (d, *J* = 7.6 Hz, 2H), 3.95 – 3.91 (m, 4H), 3.11 (s, 4H), 2.52 (q, *J* = 7.4 Hz, 2H), 1.13 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 144.6, 134.5, 129.0, 128.2, 127.7, 66.3, 15.4; HRMS (ESI) m/z: calcd for $C_{19}H_{22}N_2OS$ [M+H]+ 327.1531; found 327.1533.

1,2-Bis(4-ethylphenyl)disulfane (**4h**)[5]



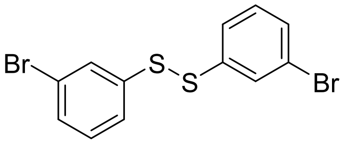
Yield: 97%, 79.7 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.47 (t, *J* = 9.1 Hz, 4H), 7.19 (d, *J* = 7.5 Hz, 4H), 2.67 (q, *J* = 7.2 Hz, 4H), 1.28 – 1.25 (m, 6H).

3-Bromophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3i**)



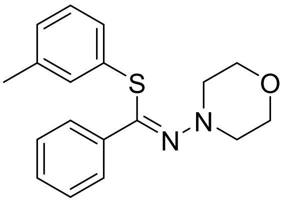
Yield: 64%, 24.1 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow liquid; ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.36 (s, 1H), 7.30 – 7.23 (m, 3H), 7.19 (td, *J* = 13.9, 7.0 Hz, 3H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 3.93 – 3.85 (m, 4H), 3.11 – 3.03 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 163.1, 136.5, 134.6, 134.0, 132.4, 130.9, 129.8, 129.4, 128.9, 128.0, 122.1, 66.3, 54.5. HRMS (ESI) m/z: calcd for $C_{17}H_{17}N_2OSBr$ [M+H]+ 377.0323; found 377.0327.

1,2-Bis(3-bromophenyl)disulfane (**4i**)[8]



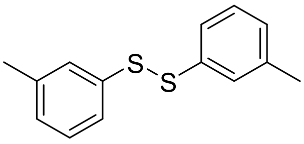
Yield: 98%, 109.9 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.69 – 7.65 (m, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H).

m-tolyl (*Z*)-*N*-morpholinobenzimidothioate (**3j**)



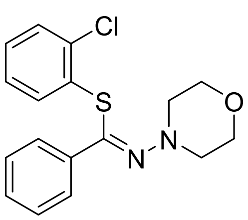
Yield: 50%, 15.6 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown liquid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 6.8 Hz, 2H), 7.20 – 7.16 (m, 1H), 7.13 (dd, *J* = 9.8, 4.4 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 3H), 6.93 (d, *J* = 6.2 Hz, 1H), 3.94 – 3.90 (m, 4H), 3.10 (s, 4H), 2.17 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.3, 135.0, 134.9, 131.2, 129.0, 128.9, 128.7, 128.3, 127.7, 66.4, 54.5, 21.0; HRMS (ESI) m/z: calcd for $C_{18}H_{20}N_2OS$ [M+H]+ 313.1375; found 313.1374.

1,2-Di-o-tolyldisulfane (**4j**)[6]



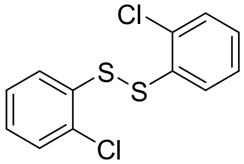
Yield: 96%, 70.8 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.55 (s, 4H), 7.40 – 7.35 (m, 2H), 7.21 (d, *J* = 7.3 Hz, 2H), 2.50 (s, 6H).

2-Chlorophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3k**)



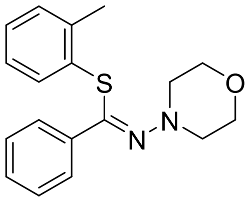
Yield: 67%, 22.2 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow oil; ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.36 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 6.8 Hz, 1H), 7.10 (dd, *J* = 13.4, 6.3 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 3.88 (t, *J* = 4.7 Hz, 4H), 3.08 (t, *J* = 4.7 Hz, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 163.9, 138.1, 136.8, 134.7, 131.4, 129.9, 129.8, 129.3, 128.82, 127.6, 126.8, 66.3, 54.4. HRMS (ESI) m/z: calcd for $C_{17}H_{17}N_2OSCl$ [M+H]+ 333.0828; found 333.0828.

1,2-Bis(2-chlorophenyl)disulfane (**4k**)[8]



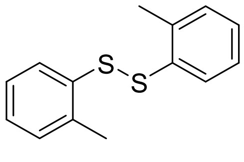
Yield: 94%, 80.6 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.61 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H).

o-tolyl (*Z*)-*N*-morpholinobenzimidothioate (**3l**)



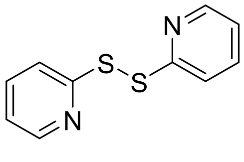
Yield: 33%, 10.3 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown solid; mp: 75.1-75.6 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.29 – 7.25 (m, 3H), 7.17 (d, *J* = 7.0 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.96 (t, *J* = 7.3 Hz, 1H), 3.94 – 3.87 (m, 4H), 3.14 – 3.06 (m, 4H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 164.2, 141.1, 135.9, 135.1, 131.0, 130.3, 129.1, 128.8, 128.7, 127.6, 126.1, 66.3, 54.5, 21.2. HRMS (ESI) m/z: calcd for $C_{18}H_{20}N_2OS$ [M+H]+ 313.1375; found 313.1377.

1,2-Di-o-tolyldisulfane (**4l**)[6]



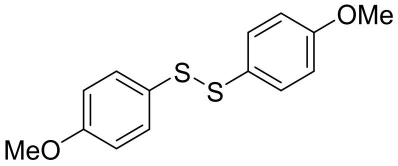
Yield: 96%, 70.8 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.62 – 7.54 (m, 2H), 7.20 (q, *J* = 8.3, 6.6 Hz, 6H), 2.53 – 2.46 (m, 6H).

1,2-Di(pyridin-2-yl)-1λ^6,2λ^6-disulfane-1,1,2,2-tetraone (**4m**)[8]



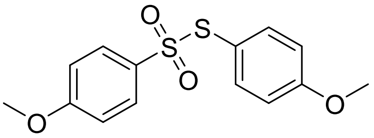
Yield: 94%, 72.4 mg (petroleum ether /ethyl acetate as eluent, 5:1 v/v); Yellow liquid; ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 8.43 (d, *J* = 4.1 Hz, 2H), 7.61 – 7.55 (m, 4H), 7.11 – 7.05 (m, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 158.9, 149.6, 137.5, 121.2, 119.7.

1,2-Bis(4-methoxyphenyl)disulfane (**4n**)[3]



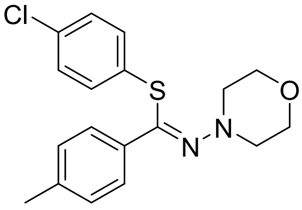
Yield: 53%, 51.6 mg (ligroin as eluent); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.43 (m, 4H), 6.89 – 6.86 (m, 4H), 3.82 (d, *J* = 2.0 Hz, 6H).

S-(4-methoxyphenyl) 4-methoxybenzenesulfonothioate (**5n**)[4]



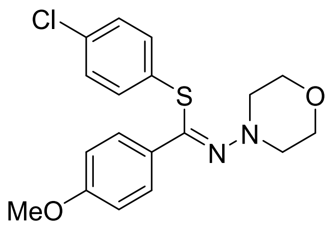
Yield: 44%, 47.7 mg (petroleum ether /ethyl acetate as eluent, 5:1 v/v); ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.53 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 6.88 (dd, *J* = 13.8, 8.7 Hz, 4H), 3.89 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 162.3, 138.4, 135.0, 129.9, 119.0, 114.9, 113.9, 55.7, 55.5.

4-Chlorophenyl (*Z*)-4-methyl-*N*-morpholinobenzimidothioate (**3o**)



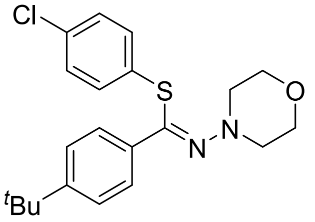
Yield: 67%, 23.2 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow solid; mp: 106.3-107.1 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.12 (dd, *J* = 12.9, 8.2 Hz, 4H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 7.7 Hz, 2H), 3.90 – 3.86 (m, 4H), 3.06 – 3.02 (m, 4H), 2.24 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 163.7, 139.5, 135.1, 134.1, 131.8, 130.6, 128.0, 128.8, 128.7, 66.3, 21.3. HRMS (ESI) m/z: calcd for $C_{18}H_{19}N_2OSCl$ [M+H]+ 347.0985; found 347.0984.

4-Chlorophenyl (*Z*)-4-methoxy-*N*-morpholinobenzimidothioate (**3p**)



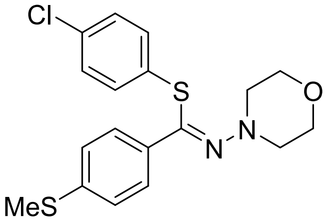
Yield: 60%, 21.7 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown solid; mp: 112.8-113.9 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 3.7 Hz, 4H), 6.69 (d, J = 8.4 Hz, 2H), 3.89 (s, 4H), 3.75 (s, 3H), 3.05 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.2, 160.5, 135.0, 134.1, 130.8, 130.5, 128.8, 127.1, 113.4, 66.3, 55.3, 54.6. HRMS (ESI) m/z: calcd for $C_{18}H_{19}N_2O_2SCl$ [M+H]+ 363.0934; found 363.0938.

4-Chlorophenyl (*Z*)-4-(tert-butyl)-*N*-morpholinobenzimidothioate (**3q**)



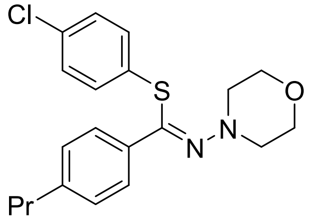
Yield: 72%, 27.9 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow solid; mp: 110.8-111.9 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.17 (t, J = 14.1 Hz, 4H), 7.11 (d, J = 8.2 Hz, 2H), 7.08 (s, 2H), 3.90 (s, 4H), 3.07 (s, 4H), 1.25 (d, J = 17.7 Hz, 9H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.7, 135.2, 134.1, 130.5, 128.6, 124.985, 66.3, 54.5, 34.7, 31.1; HRMS (ESI) m/z: calcd for $C_{21}H_{25}N_2OSCl$ [M+H]+ 389.1454; found 389.1456.

4-Chlorophenyl (*Z*)-4-(methylthio)-*N*-morpholinobenzimidothioate (**3r**)



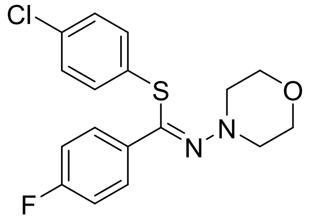
Yield: 58%, 21.9 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown solid; mp: 135.5-135.9 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.23 – 7.18 (m, 2H), 7.16 – 7.09 (m, 4H), 7.07 – 7.00 (m, 2H), 3.89 (dt, J = 15.5, 5.3 Hz, 4H), 3.06 (dt, J = 15.5, 5.2 Hz, 4H), 2.47 – 2.38 (m, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.5, 140.7, 134.9, 134.2, 131.3, 130.5, 129.3, 128.9, 125.4, 66.3, 54.6, 15.4. HRMS (ESI) m/z: calcd for $C_{18}H_{19}N_2OS_2Cl$ [M+H]+ 379.0706; found 379.0708.

4-Chlorophenyl (*Z*)-*N*-morpholino-4-propylbenzimidothioate (**3s**)



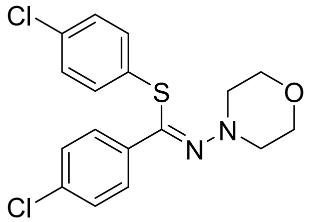
Yield: 45%, 16.8 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow liquid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.16 – 7.09 (m, 4H), 7.07 (d, J = 7.9 Hz, 2H), 6.96 (d, J = 7.5 Hz, 2H), 3.91 (s, 4H), 3.07 (s, 4H), 2.49 (t, J = 7.2 Hz, 2H), 1.53 (q, J = 7.2 Hz, 2H), 0.84 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.1, 144.1, 135.3, 134.2, 131.9, 130.5, 128.8, 128.7, 128.1, 66.3, 54.5, 37.6, 24.3, 13.4. HRMS (ESI) m/z: calcd for $C_{20}H_{23}N_2OSCl$ [M+H]+ 375.1298; found 375.1301.

4-Chlorophenyl (*Z*)-4-fluoro-*N*-morpholinobenzimidothioate (**3t**)



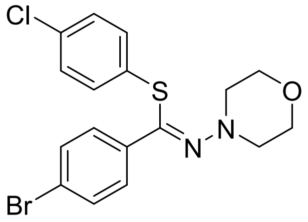
Yield: 61%, 21.4 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow solid; mp: 105.8-106.5 °C;^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 – 7.24 (m, 2H), 7.12 (s, 4H), 6.87 (t, J = 8.5 Hz, 2H), 3.92 – 3.88 (m, 4H), 3.08 – 3.04 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.6, 135.2, 134.5, 130.9, 130.9, 130.1, 129.0, 115.2, 115.0, 66.3, 54.5; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -110.77. HRMS (ESI) m/z: calcd for $C_{17}H_{16}N_2OSClF$ [M+H]+ 351.0734; found 351.0738.

4-Chlorophenyl (*Z*)-4-chloro-*N*-morpholinobenzimidothioate (**3u**)



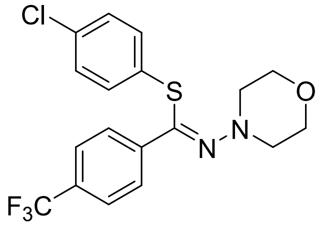
Yield: 70%, 25.6 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown solid; mp: 94.1-94.9 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 7.13 (s, 4H), 3.92 – 3.87 (m, 4H), 3.09 – 3.05 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 161.8, 135.5, 135.1, 134.6, 133.3, 130.2, 130.0, 129.1, 128.3, 66.2, 54.5. HRMS (ESI) m/z: calcd for $C_{17}H_{16}N_2OSCl_2$ [M+H]+ 367.0439; found 367.0442.

4-Chlorophenyl (*Z*)-4-bromo-*N*-morpholinobenzimidothioate (**3v**)



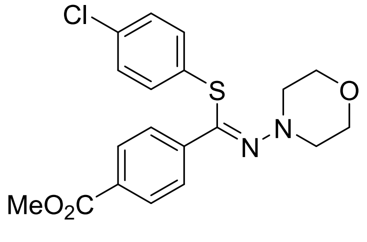
Yield: 62%, 25.4 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); White solid; mp: 126.8-127.4 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.33 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.13 (s, 4H), 3.92 – 3.87 (m, 4H), 3.10 – 3.04 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 161.64, 134.99, 134.59, 133.82, 131.22, 130.44, 129.94, 129.07, 123.85, 66.19, 54.54. HRMS (ESI) m/z: calcd for $C_{17}H_{16}N_2OSClBr$ [M+H]+ 410.9933; found 410.9937.

4-Chlorophenyl (*Z*)-*N*-morpholino-4-(trifluoromethyl)benzimidothioate (**3w**)



Yield: 82%, 32.0 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Pale yellow solid; mp: 117.8-118.1 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.44 (q, *J* = 7.8, 7.3 Hz, 4H), 7.17 – 7.08 (m, 4H), 3.93 – 3.87 (m, 4H), 3.13 – 3.06 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 160.8, 138.4, 135.0, 134.8, 129.5, 129.2, 129.1, 125.02, 124.99, 124.96, 124.94, 66.2, 54.5. ^{19}F NMR (471 MHz, Chloroform-*d*) *δ* -62.86. HRMS (ESI) m/z: calcd for $C_{18}H_{16}N_2OSClF_3$ [M+H]+ 401.0702; found 401.0705.

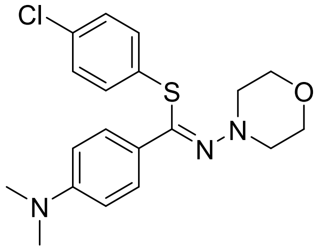
Methyl (*Z*)-4-(((4-chlorophenyl)thio)(morpholinoimino)methyl)benzoate (**3x**)



Yield: 76%, 29.6 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown solid; mp: 73.3-74.1 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2

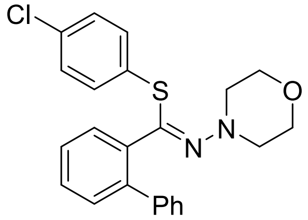
Hz, 2H), 7.15 – 7.11 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 7H), 3.12 – 3.07 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.41, 161.77, 139.16, 135.13, 134.66, 130.58, 129.67, 129.22, 129.04, 128.93, 66.23, 54.57, 52.28. HRMS (ESI) m/z: calcd for $C_{19}H_{19}N_2O_3SCl$ [M+H]+ 391.0883; found 391.0887.

4-Chlorophenyl (*Z*)-4-(dimethylamino)-*N*-morpholinobenzimidothioate (**3y**)



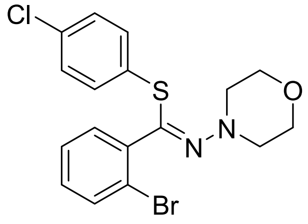
Yield: 62%, 23.3 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown liquid; ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.51 (d, *J* = 8.2 Hz, 1H), 7.44 (s, 1H), 7.31 (s, 4H), 7.20 (s, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 3.87 (s, 4H), 3.12 (s, 4H), 2.83 (s, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 152.6, 133.5, 133.3, 133.2, 130.4, 129.4, 125.1, 119.6, 66.4, 52,0, 44.3. HRMS (ESI) m/z: calcd for $C_{19}H_{22}N_3OSCl$ [M+H]+ 376.1250; found 376.1254.

4-Chlorophenyl (*Z*)-*N*-morpholino-[1,1'-biphenyl]-2-carbimidothioate (**3z**)



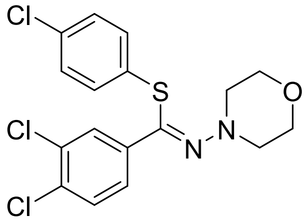
Yield: 54%, 22.0 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow liquid; ^{1}H NMR (500 MHz, Chloroform-*d*) *δ* 7.38 – 7.33 (m, 4H), 7.29 – 7.24 (m, 4H), 7.11 (d, *J* = 6.6 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.75 – 6.69 (m, 2H), 3.91 (s, 4H), 3.04 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) *δ* 140.1, 139.6, 136.4, 134.7, 132.6, 130.6, 130.0, 129.80, 129.76, 128.5, 128.1, 127.8, 127.6, 126.8, 66.3, 54.1; HRMS (ESI) m/z: calcd for $C_{23}H_{21}N_2OSCl$ [M+H]+ 409.1141; found 409.1143.

4-Chlorophenyl (*Z*)-2-bromo-*N*-morpholinobenzimidothioate (**3aa**)



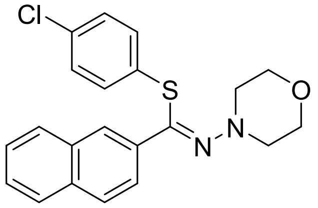
Yield: 64%, 26.2 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow solid; mp: 119.5-120.4 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 6.9 Hz, 3H), 7.11 (d, J = 7.8 Hz, 2H), 7.07 – 7.02 (m, 3H), 3.96 (s, 4H), 3.12 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.9, 136.9, 135.1, 132.6, 130.7, 130.4, 128.6, 128.3, 126.7, 122.3, 66.2, 54.3. HRMS (ESI) m/z: calcd for $C_{17}H_{17}N_2OSClBr$ [M+H]+ 410.9933; found 410.9937.

4-Chlorophenyl (*Z*)-3,4-dichloro-*N*-morpholinobenzimidothioate (**3ab**)



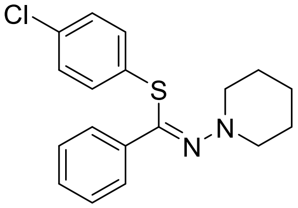
Yield: 66%, 22.4 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow liquid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (s, 1H), 7.24 (d, J = 8.3 Hz, 1H), 7.15 (d, J = 11.7 Hz, 5H), 3.89 – 3.85 (m, 4H), 3.09 – 3.05 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.2, 134.9, 134.8, 133.7, 132.4, 130.7, 129.9, 129.5, 129.2, 128.1, 66.2, 54.5. HRMS (ESI) m/z: calcd for $C_{17}H_{16}N_2OSCl_3$ [M+H]+ 401.0049; found 401.0051.

4-Chlorophenyl (*Z*)-*N*-morpholinoquinoline-6-carbimidothioate (**3ac**)



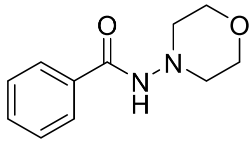
Yield: 69%, 26.4 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Brown solid; mp: 119.2-119.6 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.75 (t, J = 7.2 Hz, 2H), 7.60 (d, J = 8.5 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.33 (d, J = 8.4 Hz, 1H), 7.18 (d, J = 7.5 Hz, 2H), 7.03 (d, J = 7.5 Hz, 2H), 3.93 (s, 4H), 3.13 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.1, 135.0, 134.2, 133.4, 132.6, 132.3, 130.3, 129.0, 128.9, 128.4, 127.7, 127.6, 127.0, 126.4, 125.8, 66.3, 54.6. HRMS (ESI) m/z: calcd for $C_{21}H_{19}N_2OSCl$ [M+H]+ 383.0985; found 383.0988.

4-Chlorophenyl (*Z*)-*N*-(piperidin-1-yl)benzimidothioate (**3ad**)



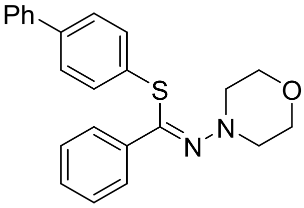
Yield: 78%, 25.7 mg (petroleum ether /ethyl acetate as eluent, 15:1 v/v); Yellow solid; mp: 64.9-66.2 °C;^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.30 – 7.20 (m, 3H), 7.20 – 7.08 (m, 5H), 7.07 – 7.03 (m, 1H), 3.08 – 2.92 (m, 4H), 1.86 – 1.73 (m, 4H), 1.54 (s, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.8, 135.4, 134.8, 134.0, 130.9, 129.01, 128.97, 128.6, 127.9, 55.7, 25.3, 23.9. HRMS (ESI) m/z: calcd for $C_{18}H_{19}N_2SCl$ [M+H]+ 331.1036; found 331.1039.

N-morpholinobenzamide (**6a**)[7]



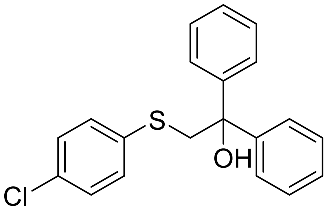
Yield: 92%, 19.0 mg (petroleum ether /ethyl acetate as eluent, 2:1 v/v); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 6.9 Hz, 2H), 7.52 (d, *J* = 6.8 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.10 (s, 1H), 3.91 – 3.82 (m, 4H), 2.98 (d, *J* = 6.2 Hz, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.6, 133.6, 131.8, 128.7, 127.1, 66.4.

[1,1'-biphenyl]-4-yl (*Z*)-*N*-morpholinobenzimidodothioate (**10a**)



Yield: 54%, 51.9 mg (petroleum ether /ethyl acetate as eluent, 20:1 v/v); Yellow liquid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 7.2, 3.1 Hz, 1H), 7.58 (q, *J* = 8.5, 7.8 Hz, 3H), 7.51 (dd, *J* = 14.7, 5.8 Hz, 3H), 7.47 (d, *J* = 6.1 Hz, 2H), 7.44 – 7.39 (m, 3H), 7.38 – 7.33 (m, 2H), 3.70 – 3.64 (m, 4H), 2.93 – 2.85 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 131.8, 130.3, 129.7, 129.0, 128.9, 128.8, 128.21, 128.18, 128.1, 127.11, 127.08, 126.8, 126.8, 66.3, 54.8. HRMS (ESI) m/z: calcd for $C_{23}H_{22}N_2OS$ [M+H]+ 375.1531; found 375.1537.

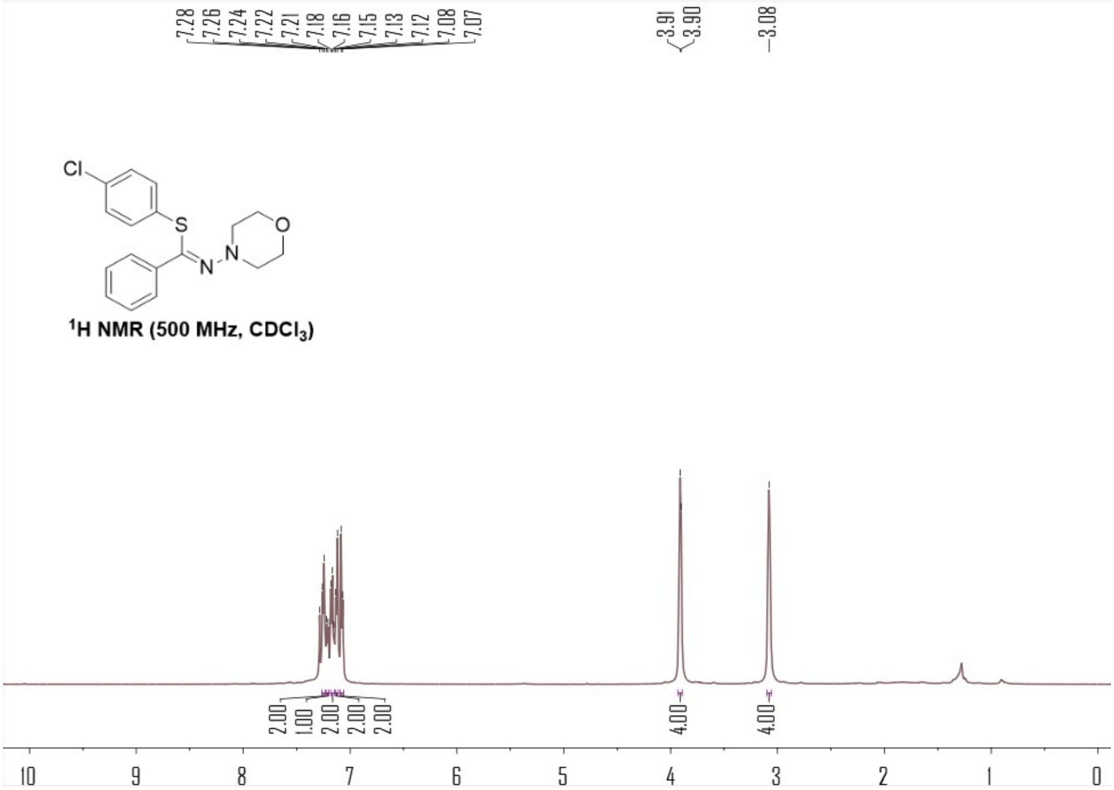
2-((4-chlorophenyl)thio)-1,1-diphenylethan-1-ol (**11a**)[9]

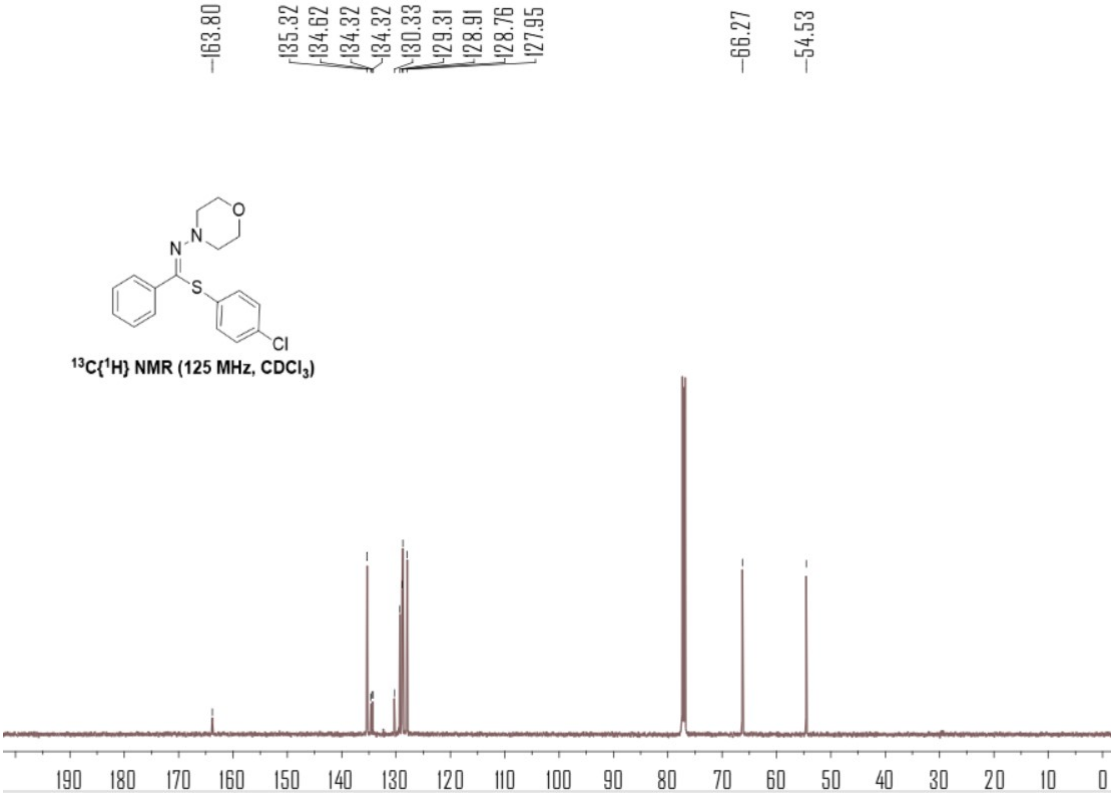


Yield: 89%, 30.3 mg (petroleum ether /ethyl acetate as eluent, 2:1 v/v); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.3 Hz, 4H), 7.35 (t, *J* = 7.5 Hz, 4H), 7.30 (t, *J* = 7.8 Hz, 4H), 7.24 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 2H), 3.51 (s, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.0, 135.1, 132.8, 131.7, 129.2, 128.4, 127.5, 126.2, 49.3.

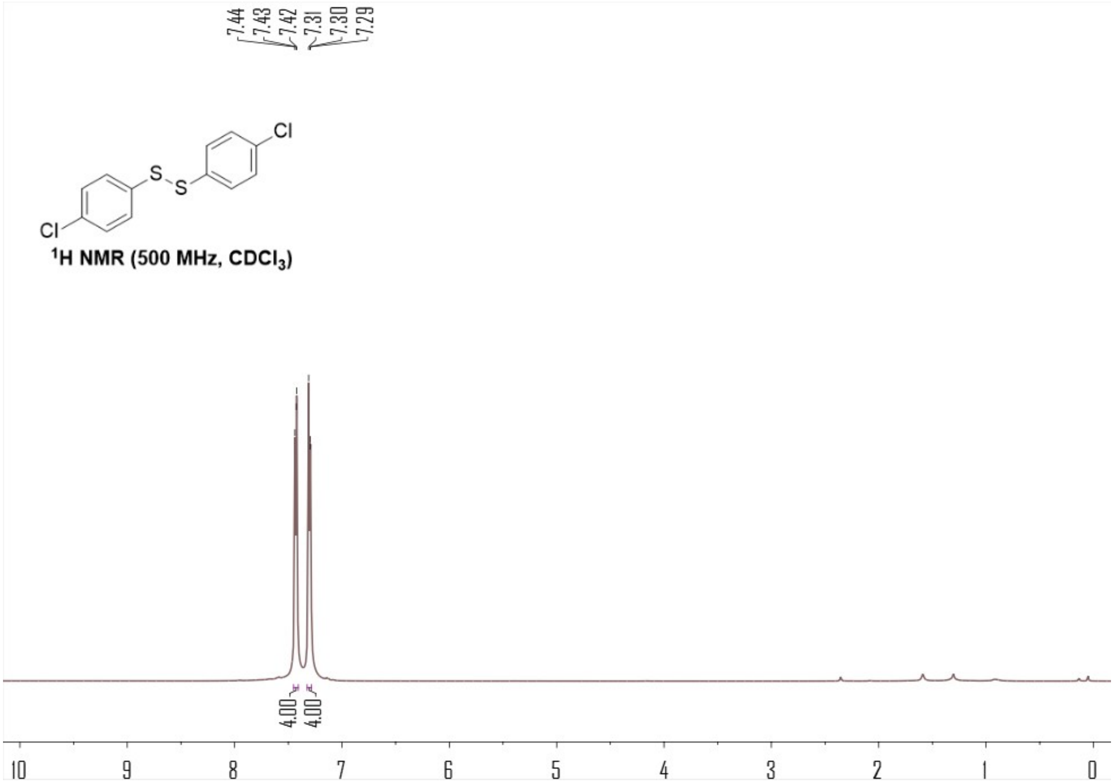
E. Copies of ^{1}H , ^{13}C and ^{19}F NMR spectra

4-Chlorophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3a**)

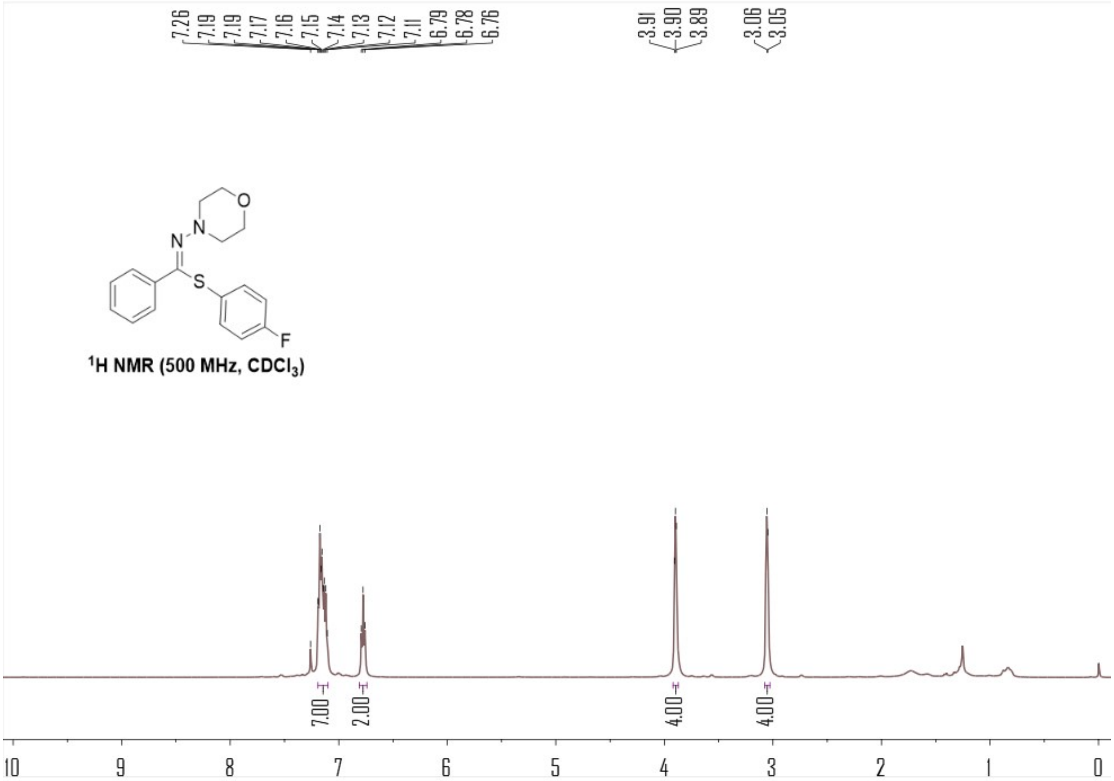


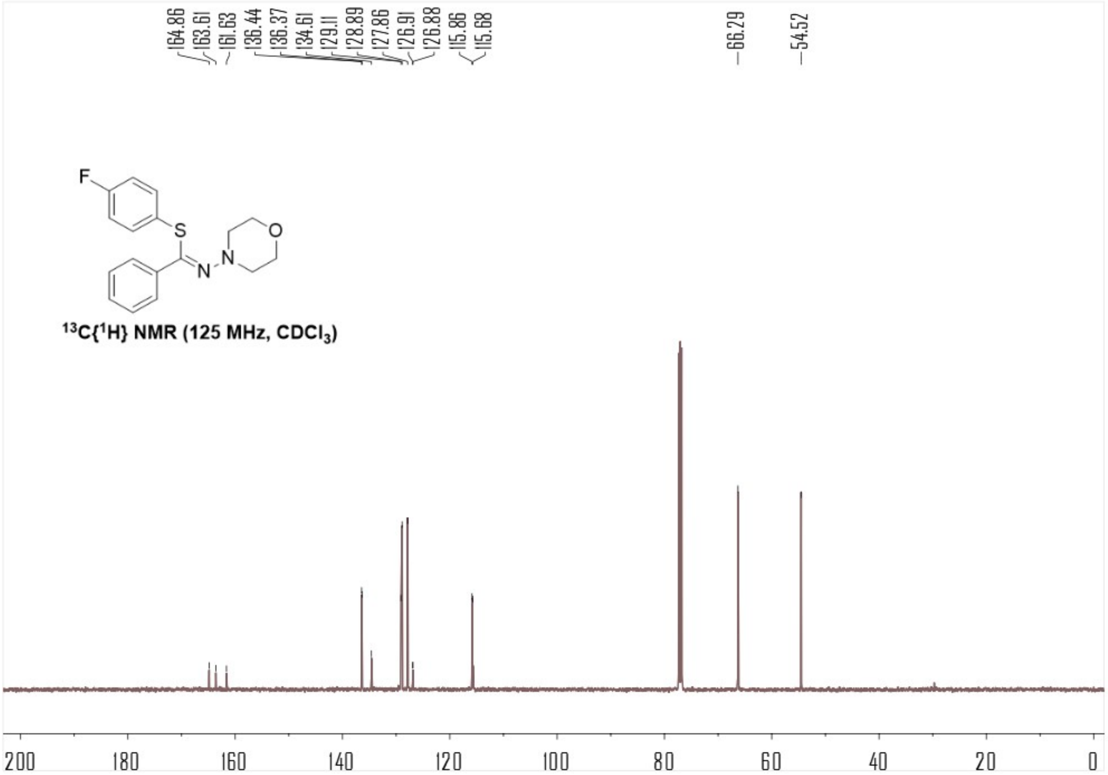


1,2-Bis(4-chlorophenyl)disulfane (**4a**)



4-Fluorophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3b**)

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136.44
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134.61
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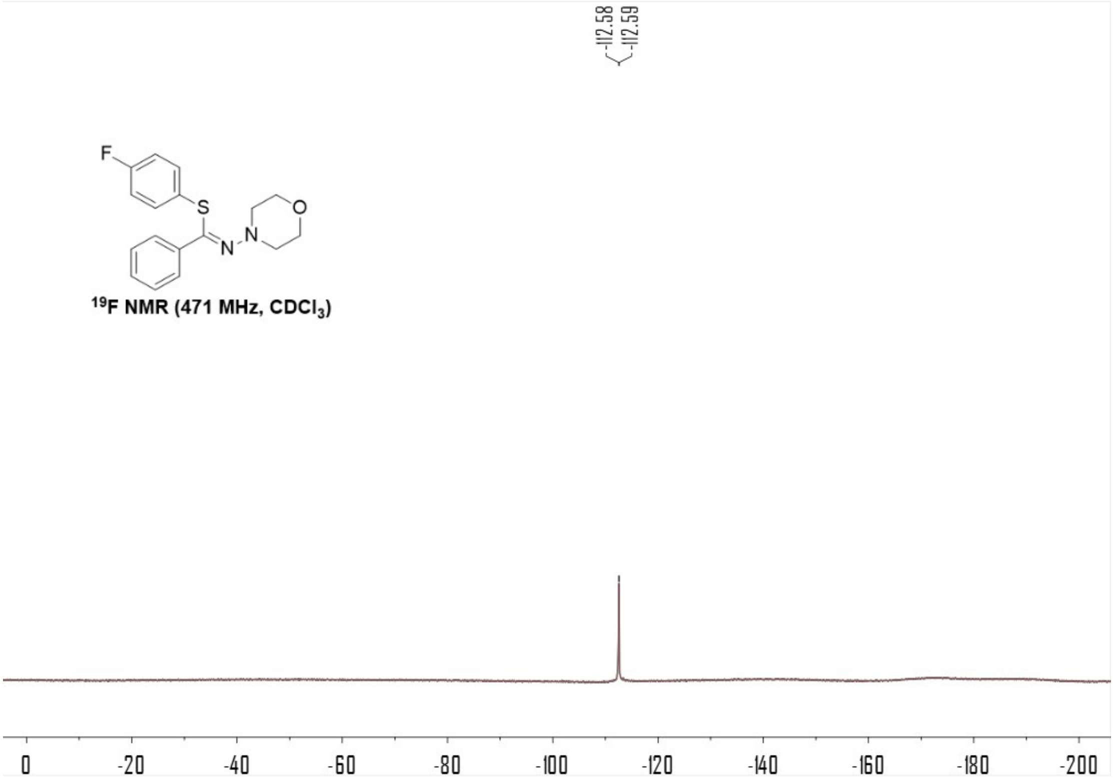
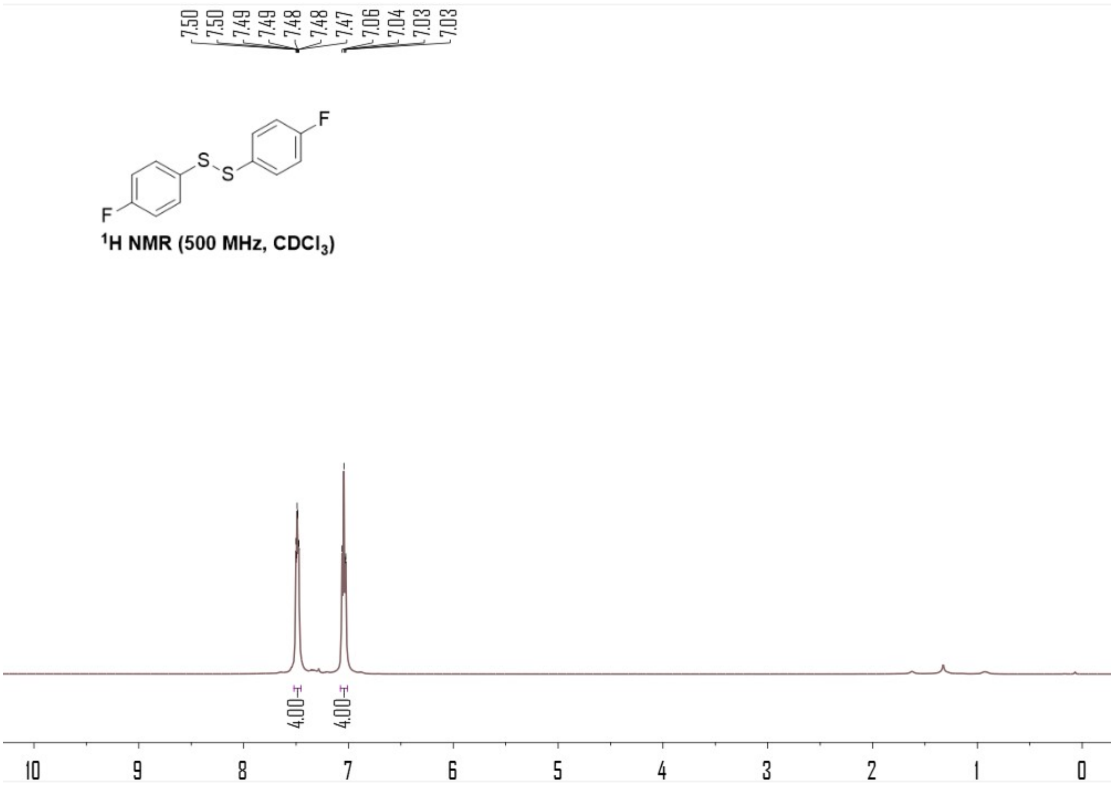
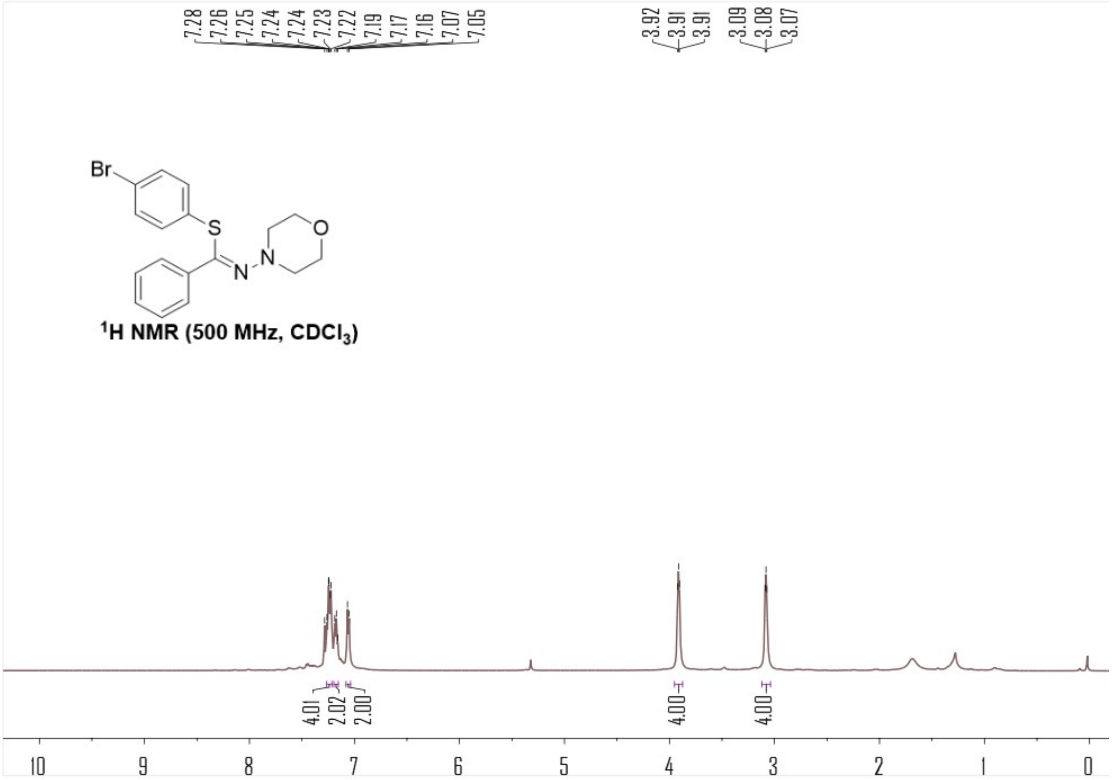
128.89
127.86
126.91
126.88
115.86
115.68
66.29
54.52
F
S
N
N
O
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
200
180
160
140
120
100
80
60
40
20
0

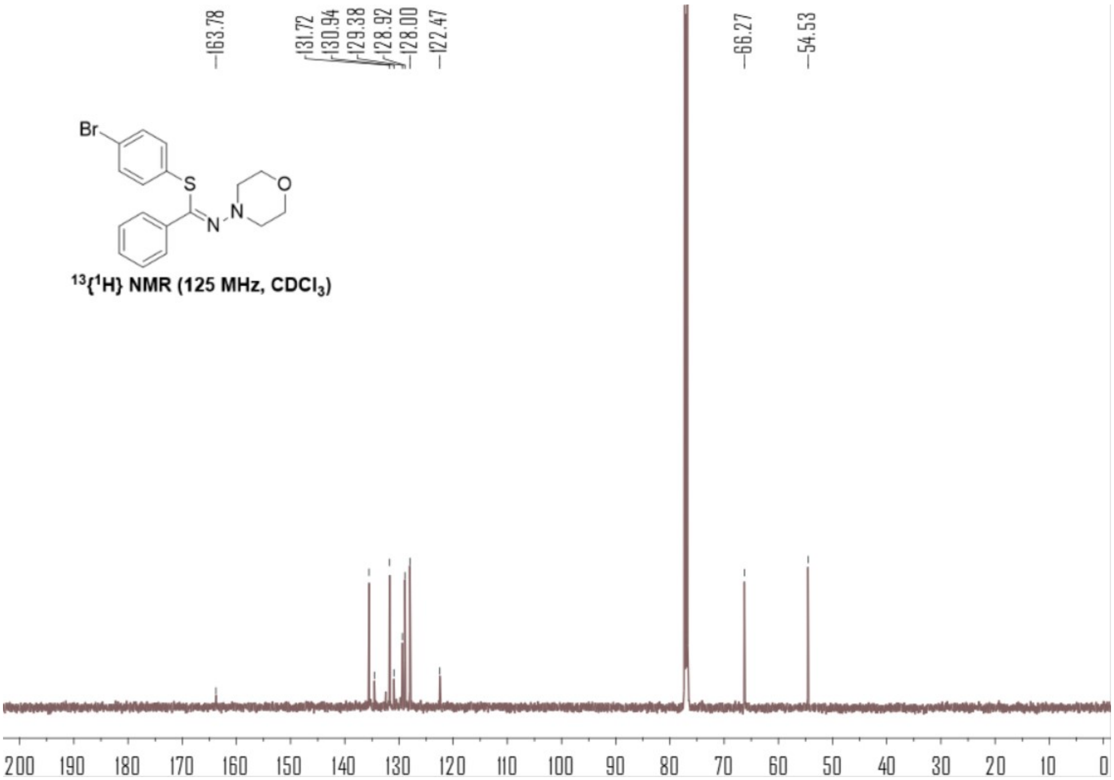

-112.58
-112.59
F
S
N
N
O
^{19}F NMR (471 MHz, $CDCl_3$)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

1,2-Bis(4-fluorophenyl)disulfane (**4b**)

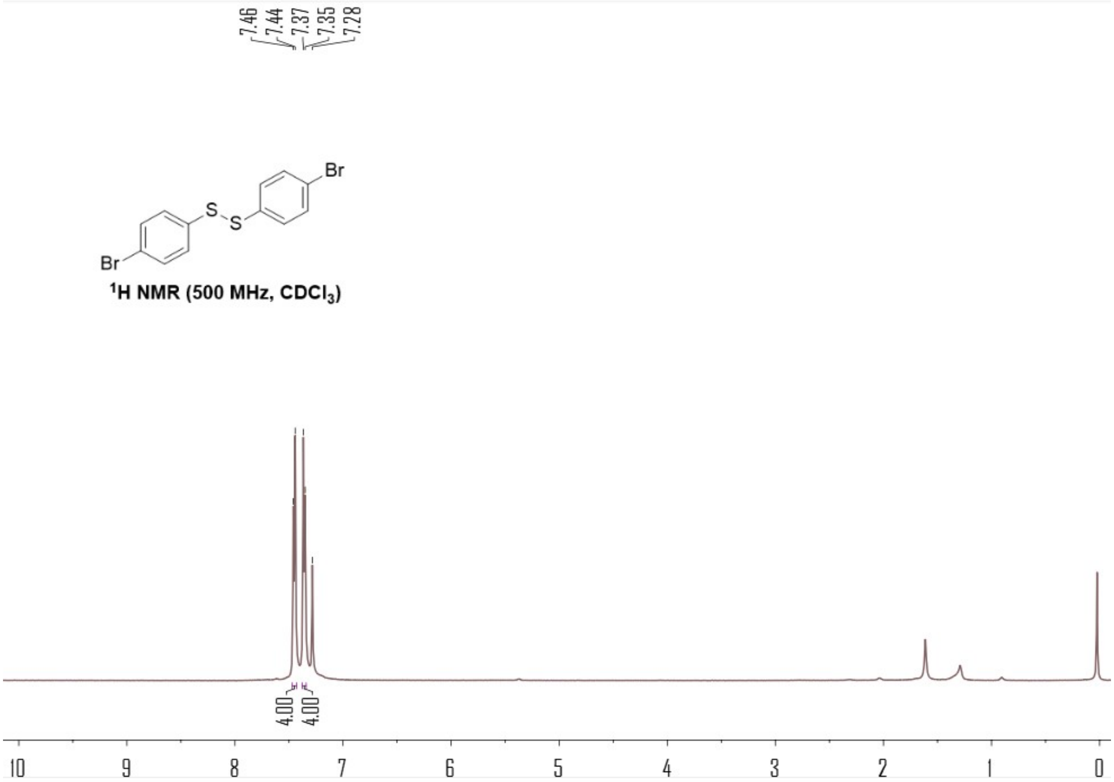


4-Bromophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3c**)

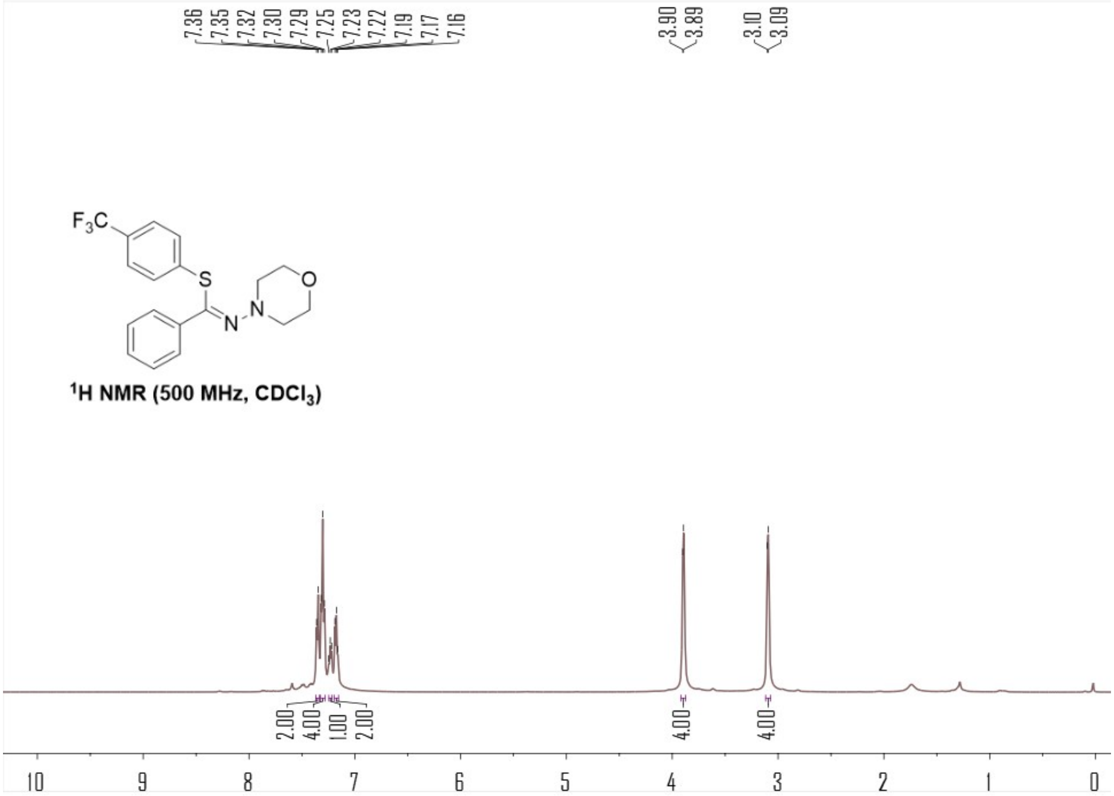


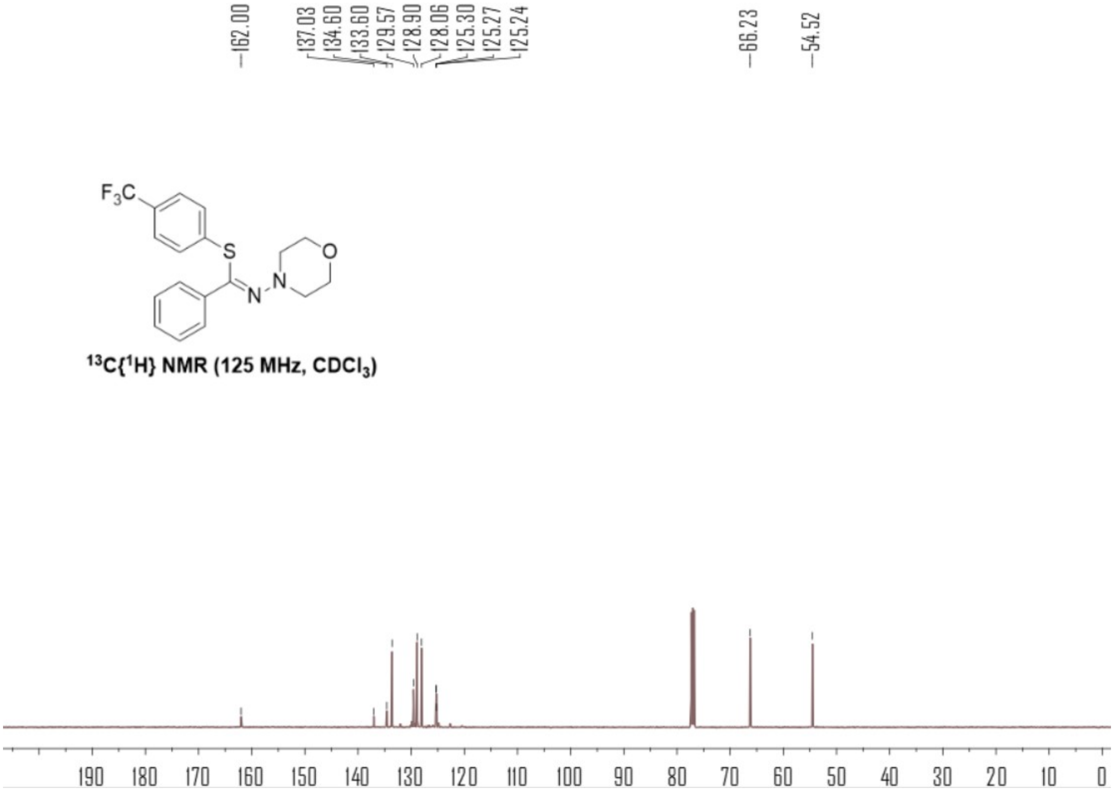


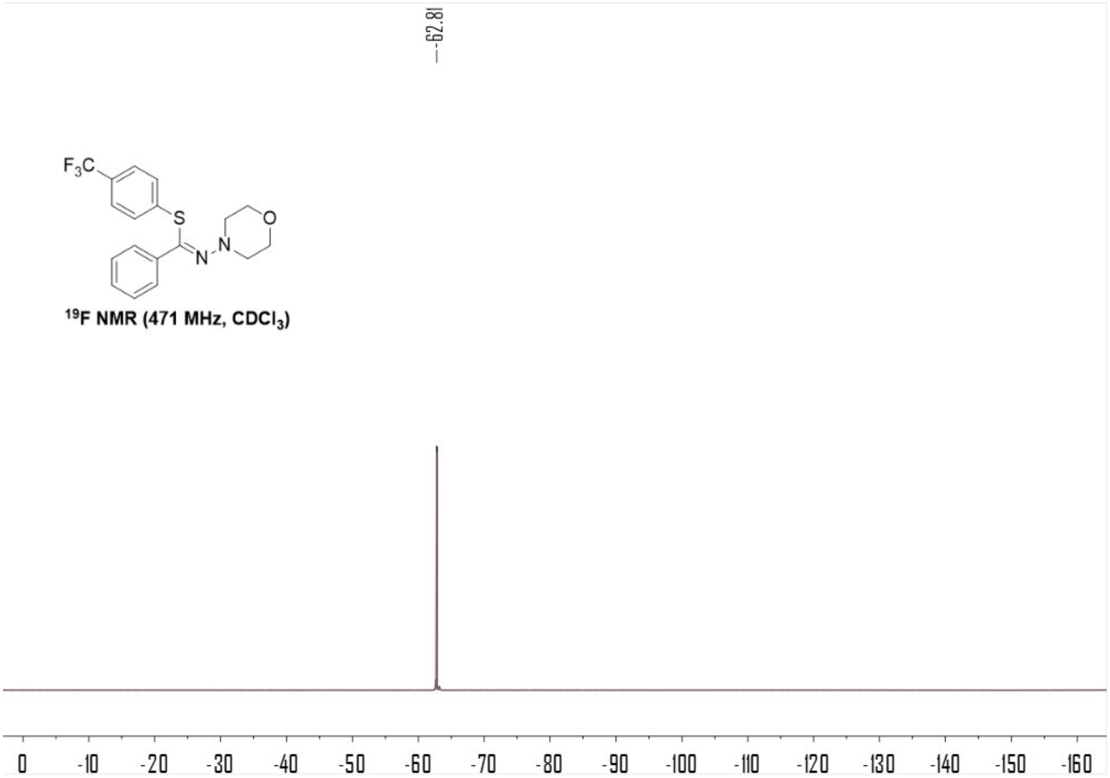
1,2-Bis(4-bromophenyl)disulfane (**4c**)



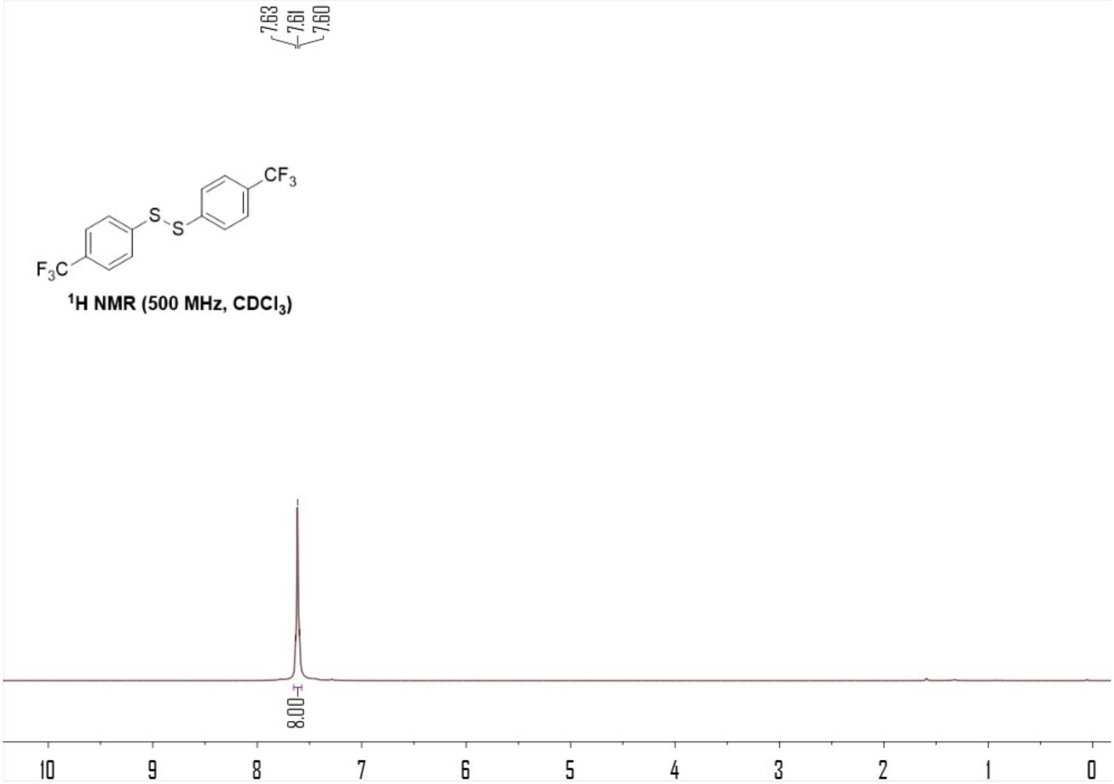
4-(Trifluoromethyl)phenyl (*Z*)-*N*-morpholinobenzimidothioate (**3d**)



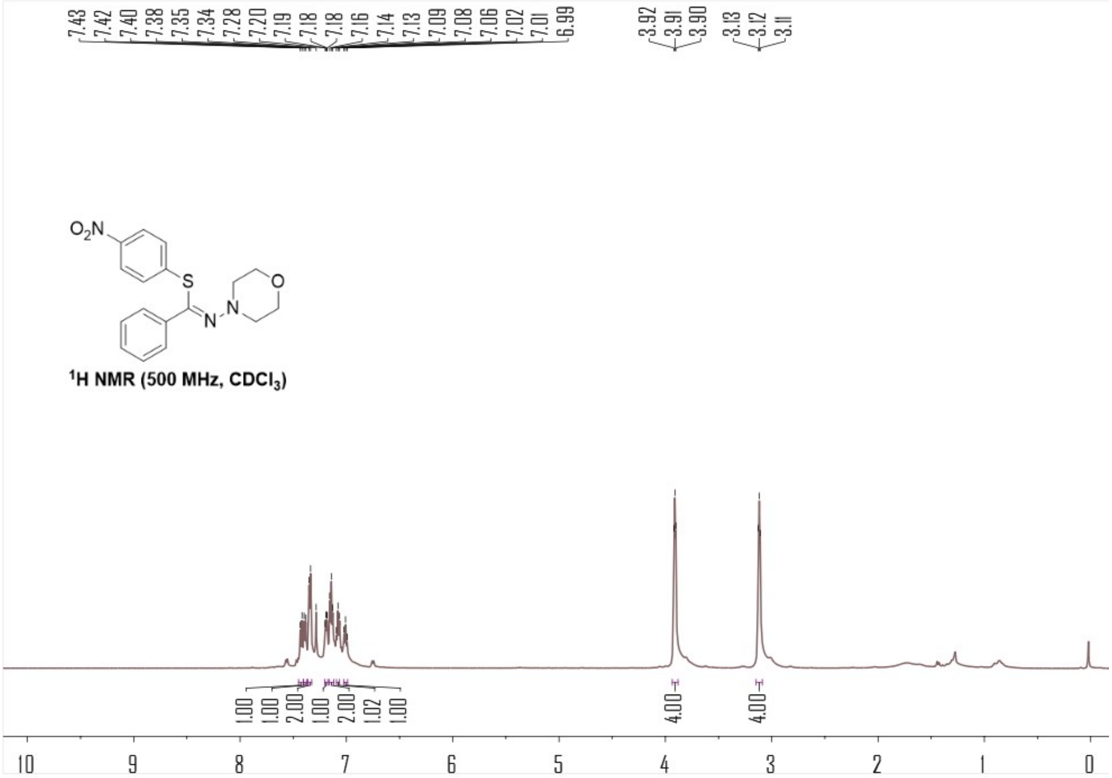


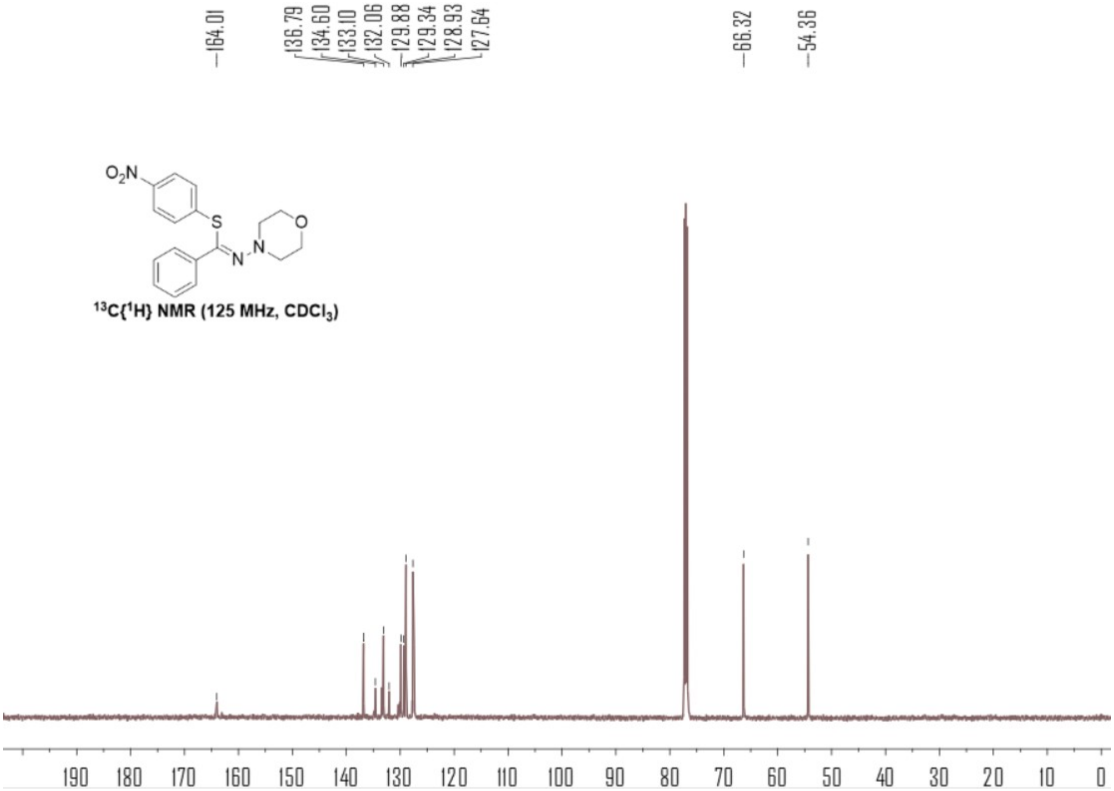


1,2-Bis(4-(trifluoromethyl)phenyl)disulfane (**4d**)

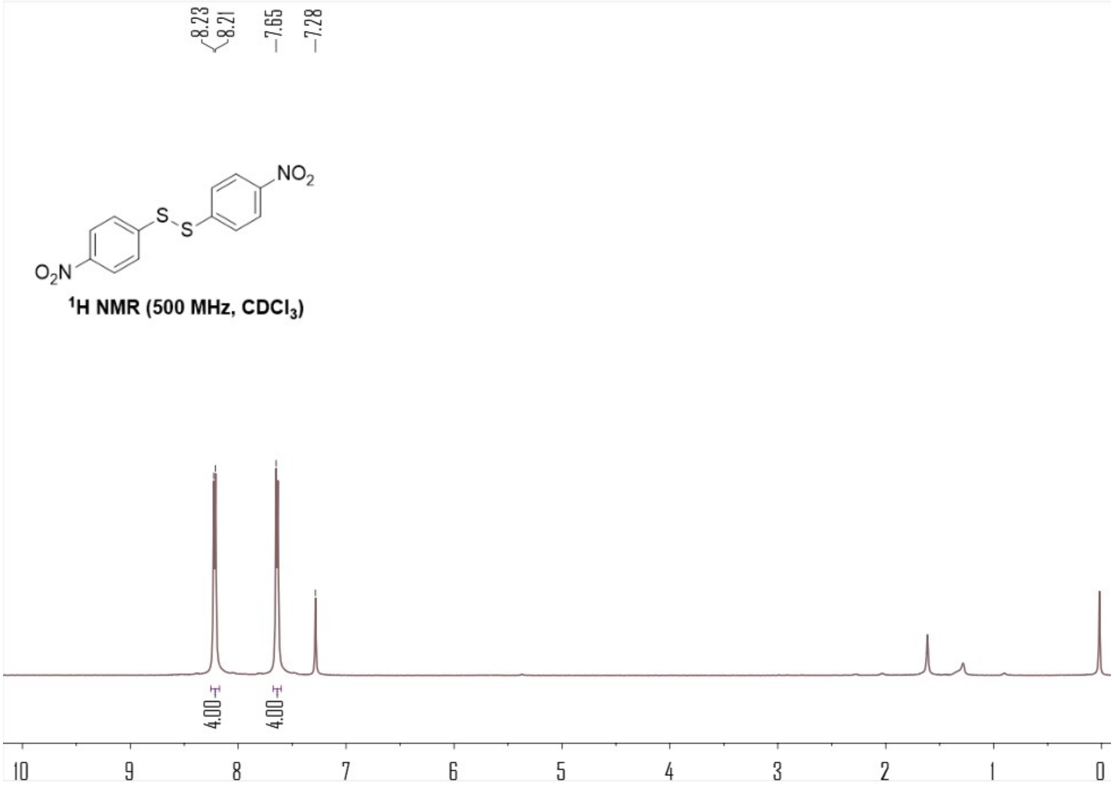


4-Nitrophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3e**)

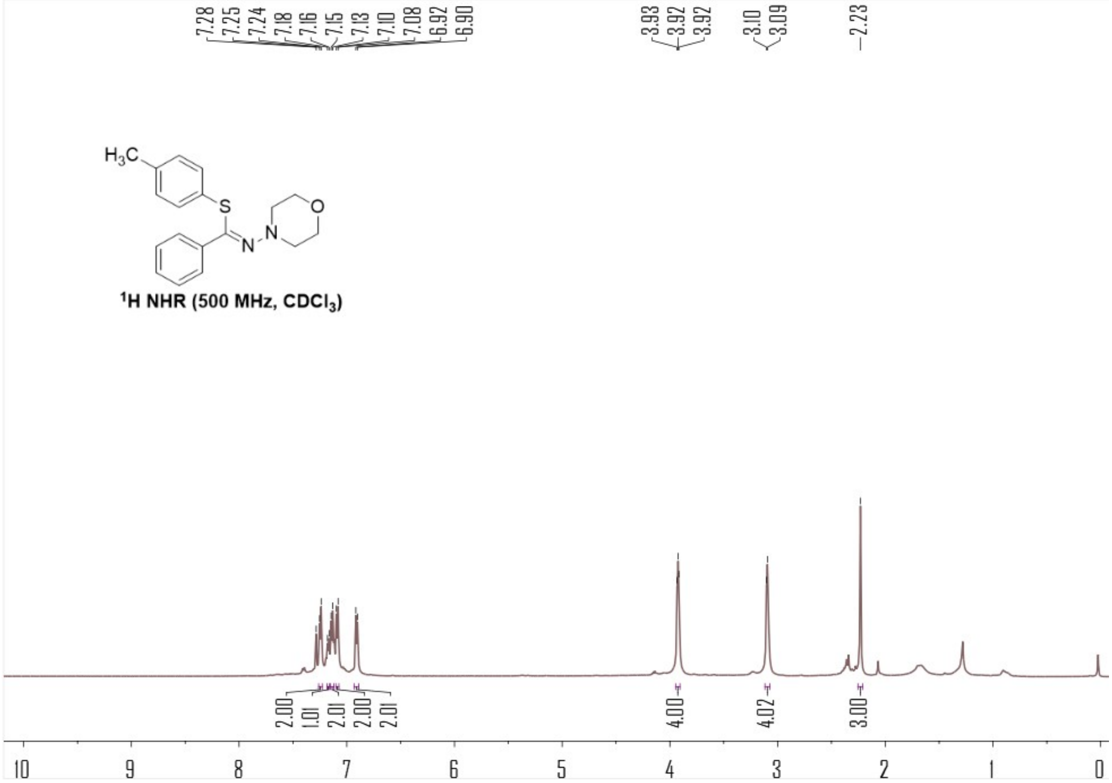


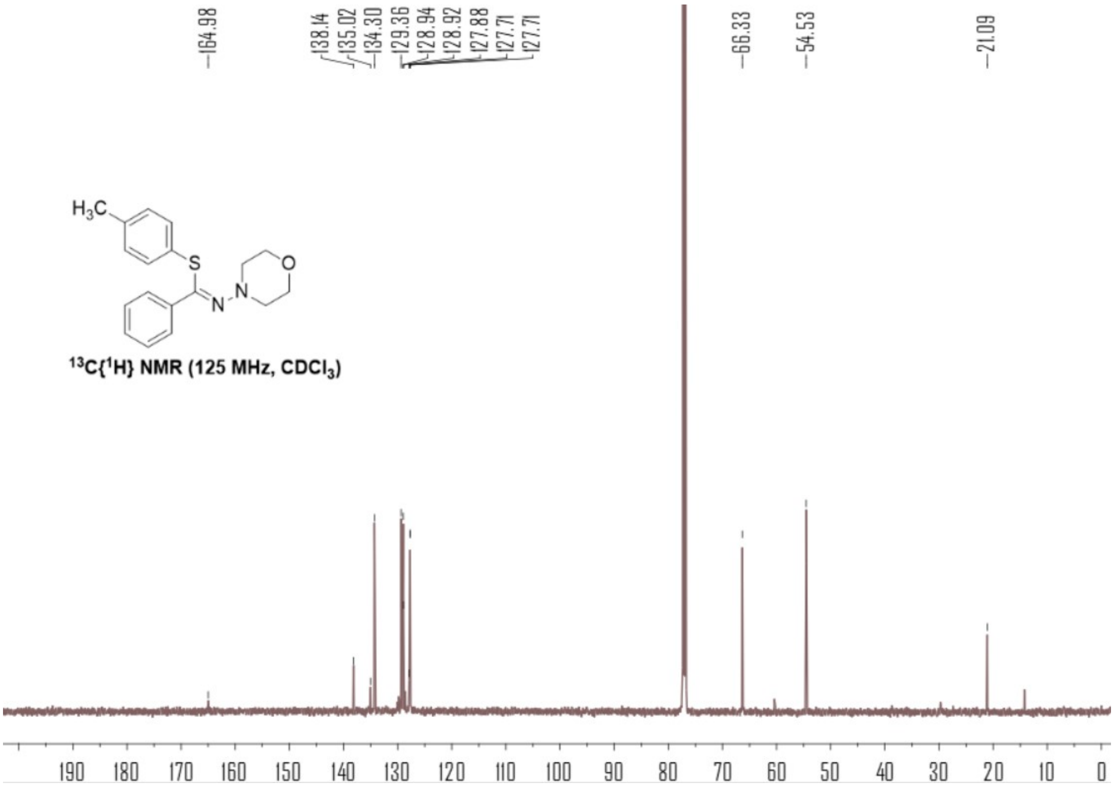


1,2-Di-p-tolyldisulfane (**4e**)

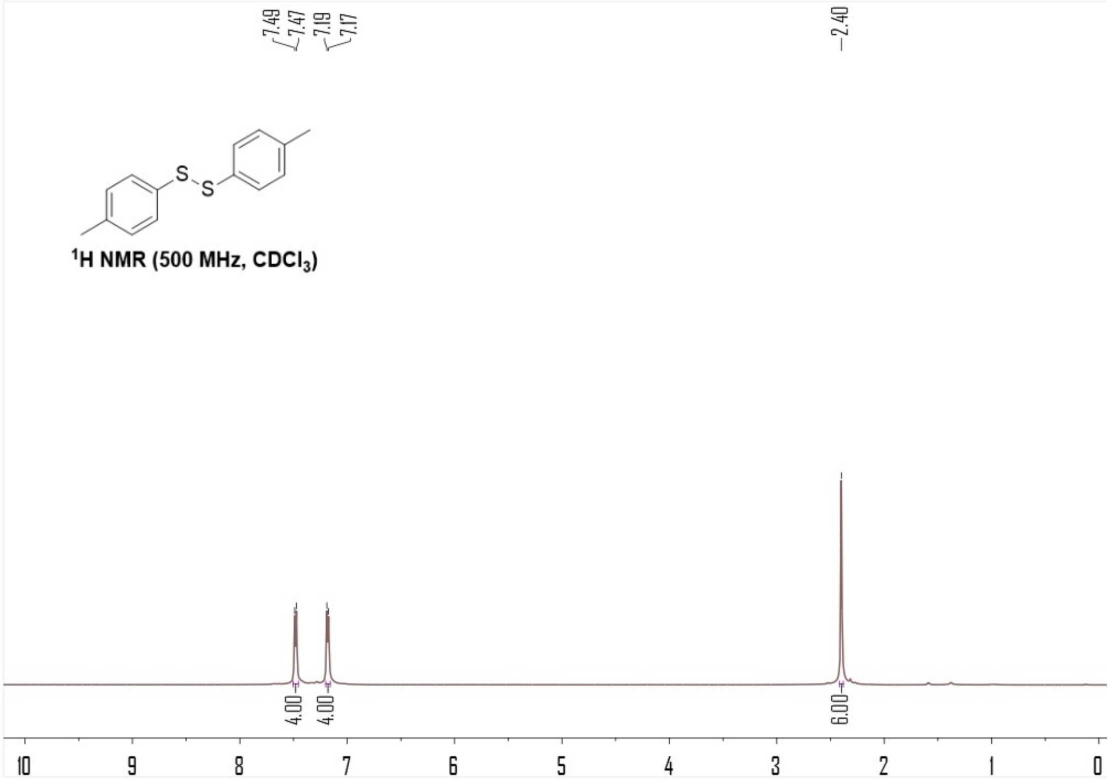


p-Tolyl (*Z*)-*N*-morpholinobenzimidothioate (**3f**)

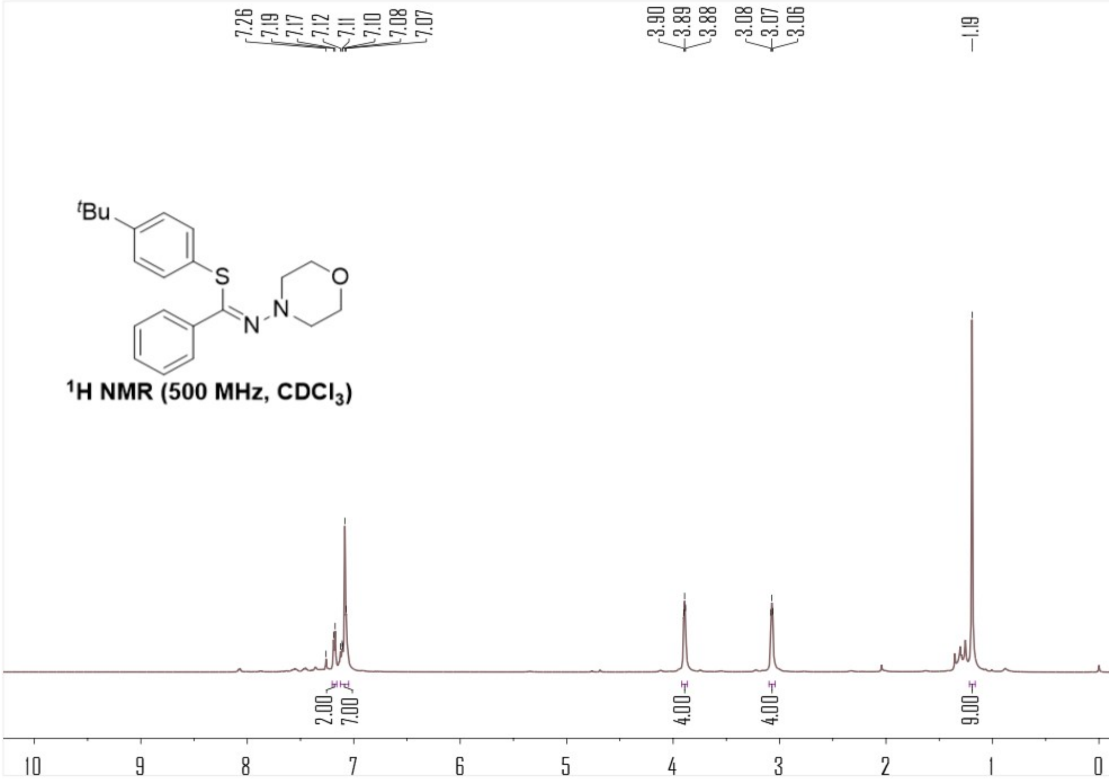


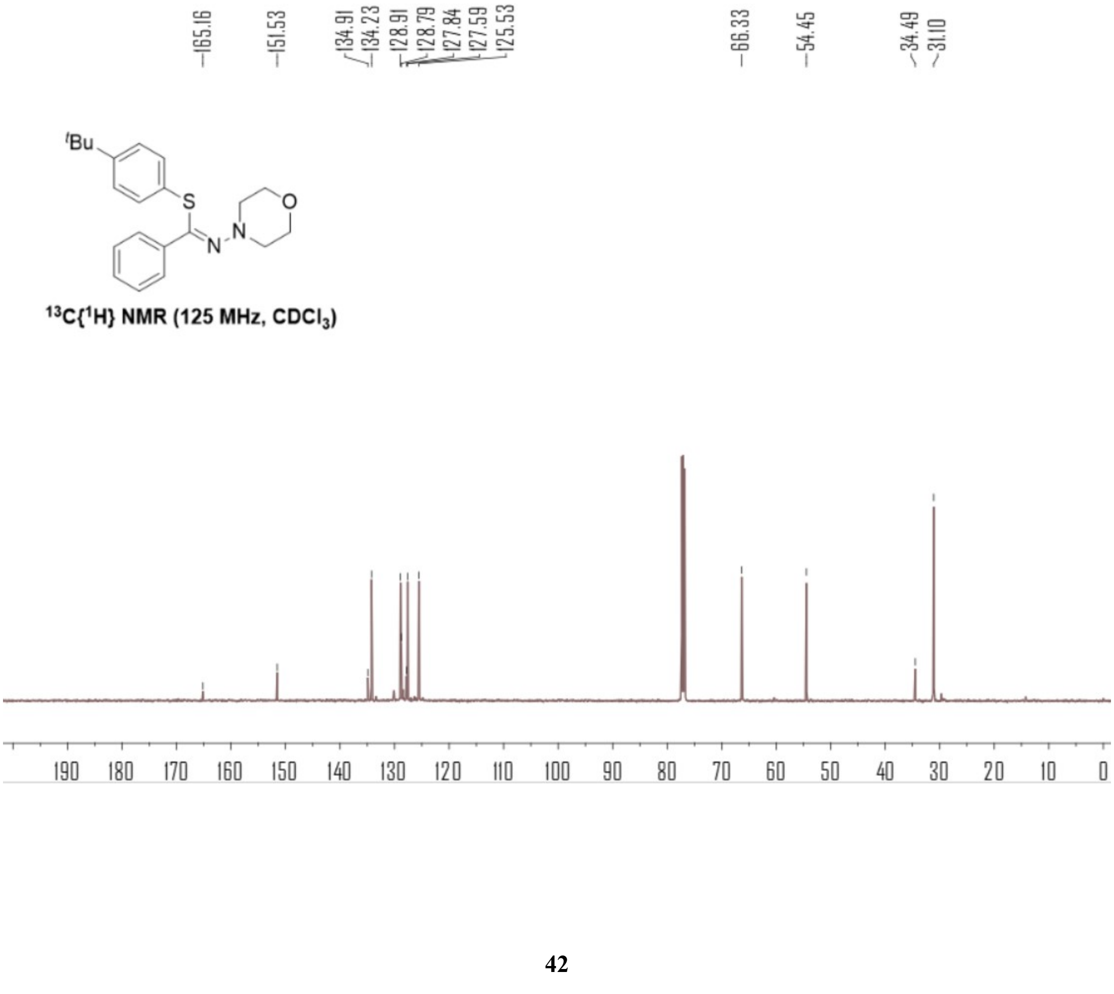


1,2-Di-p-tolyldisulfane (**4f**)

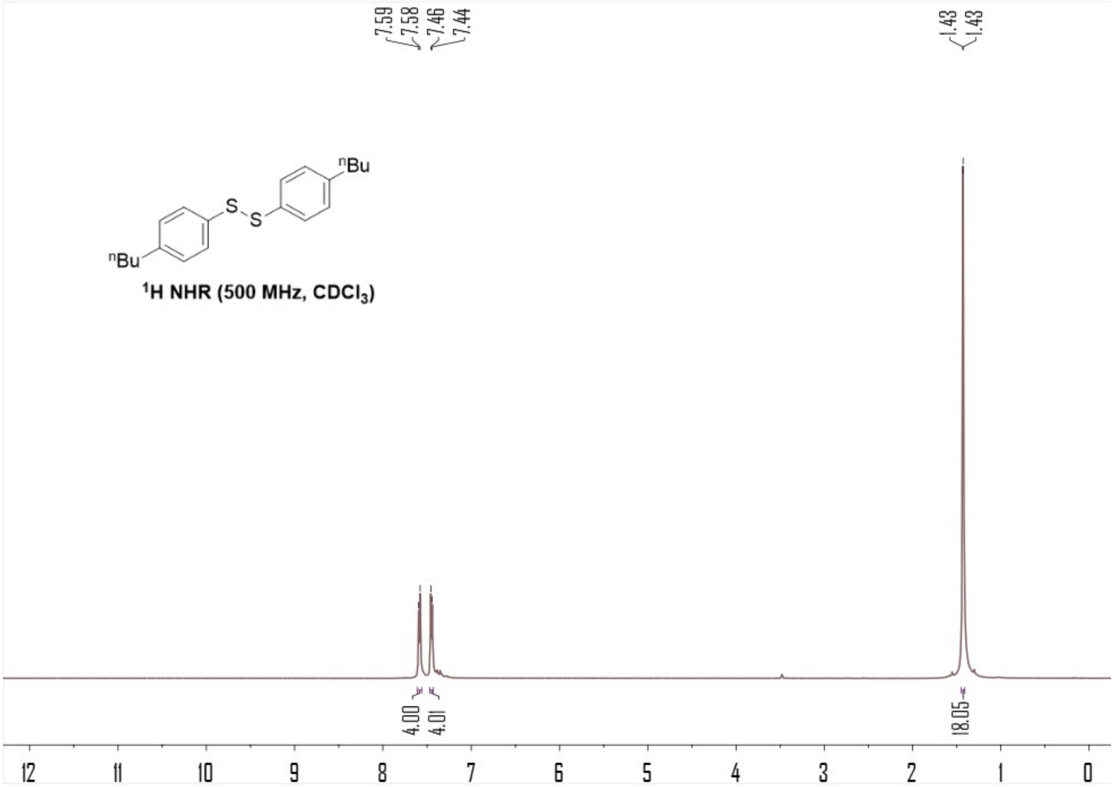


4-(Tert-butyl)phenyl (*Z*)-*N*-morpholinobenzimidothioate (**3g**)

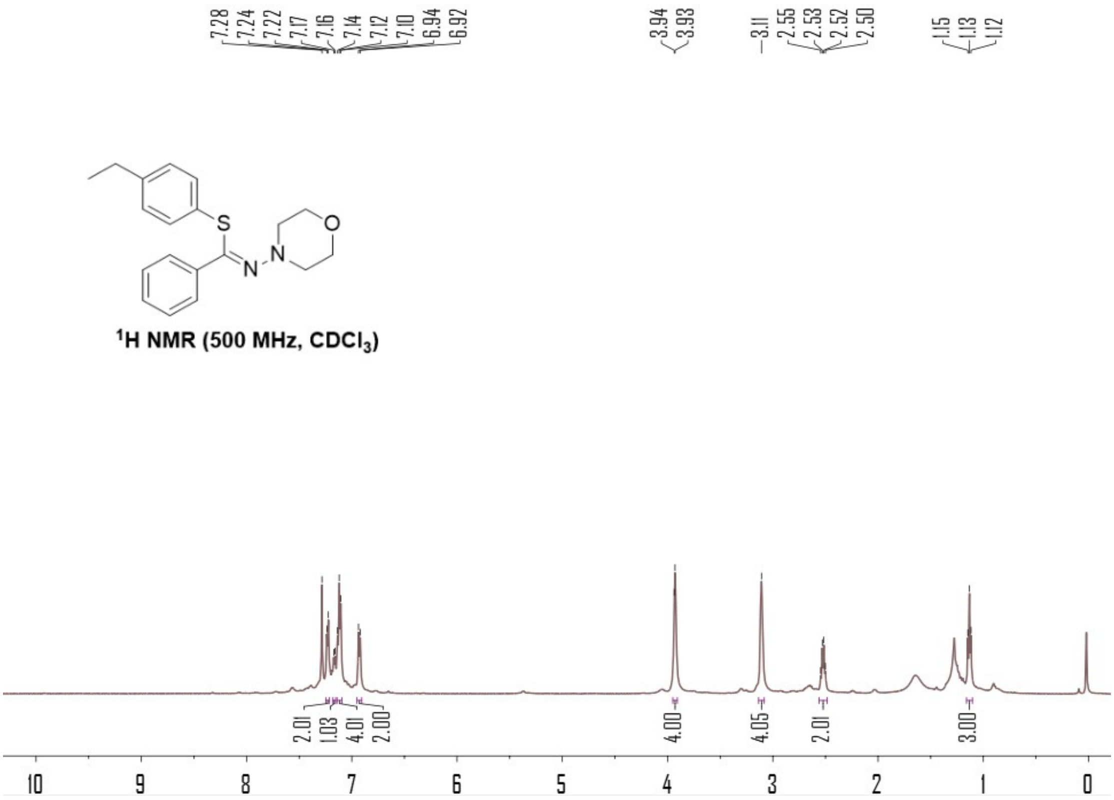


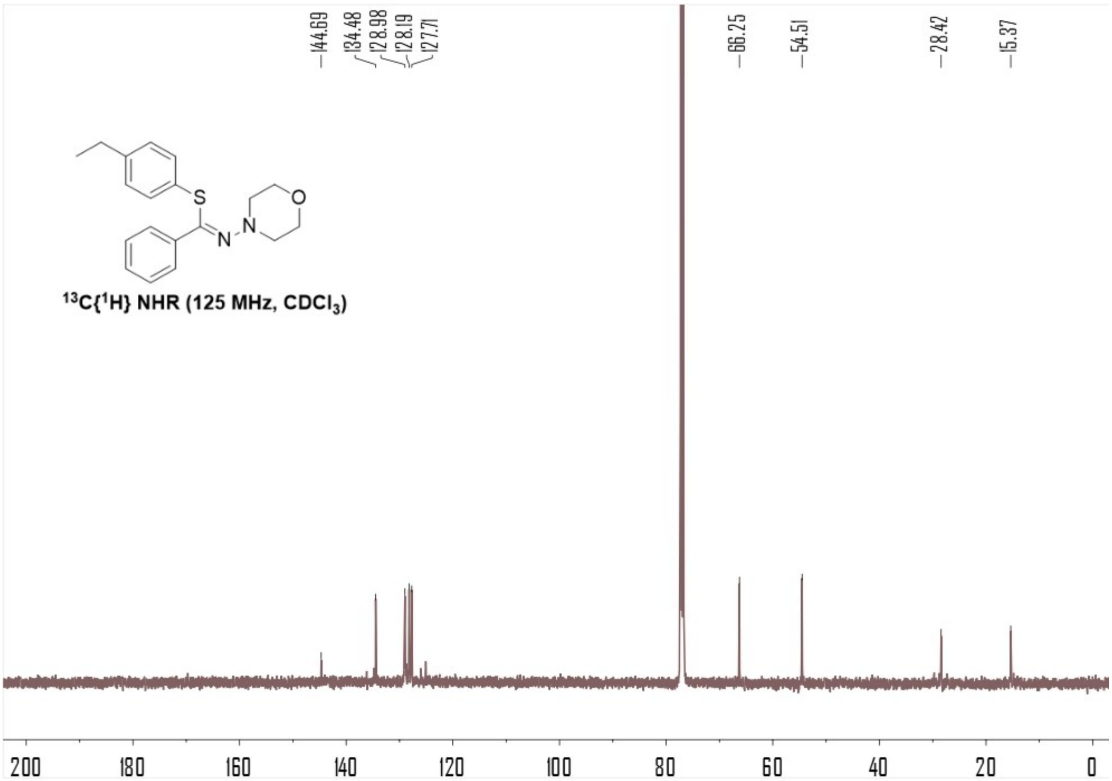


1,2-Bis(4-butylphenyl)disulfane (**4g**)

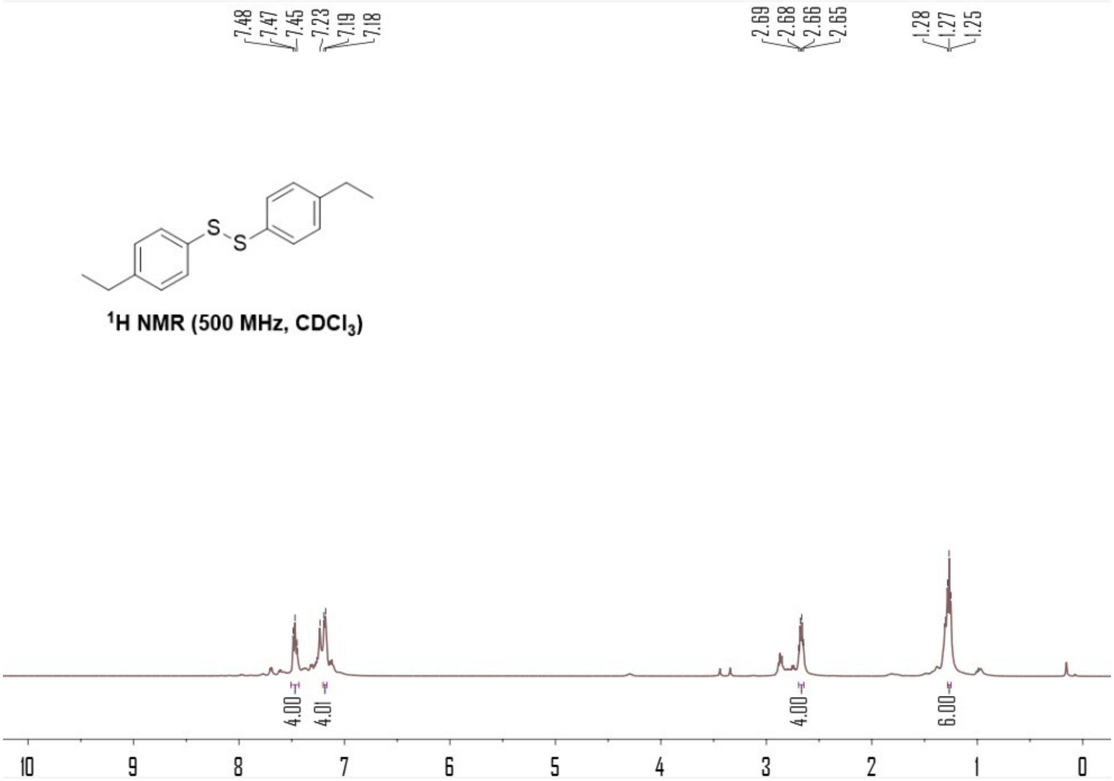


4-Ethylphenyl (*Z*)-*N*-morpholinobenzimidothioate (**3h**)

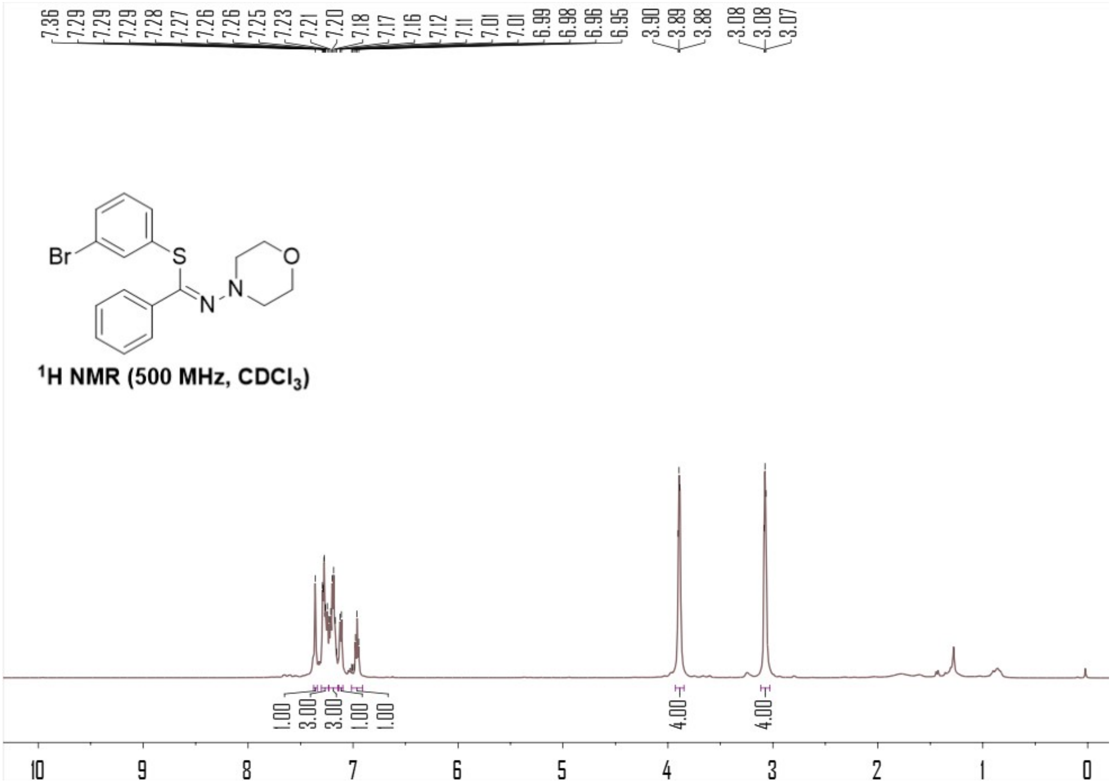


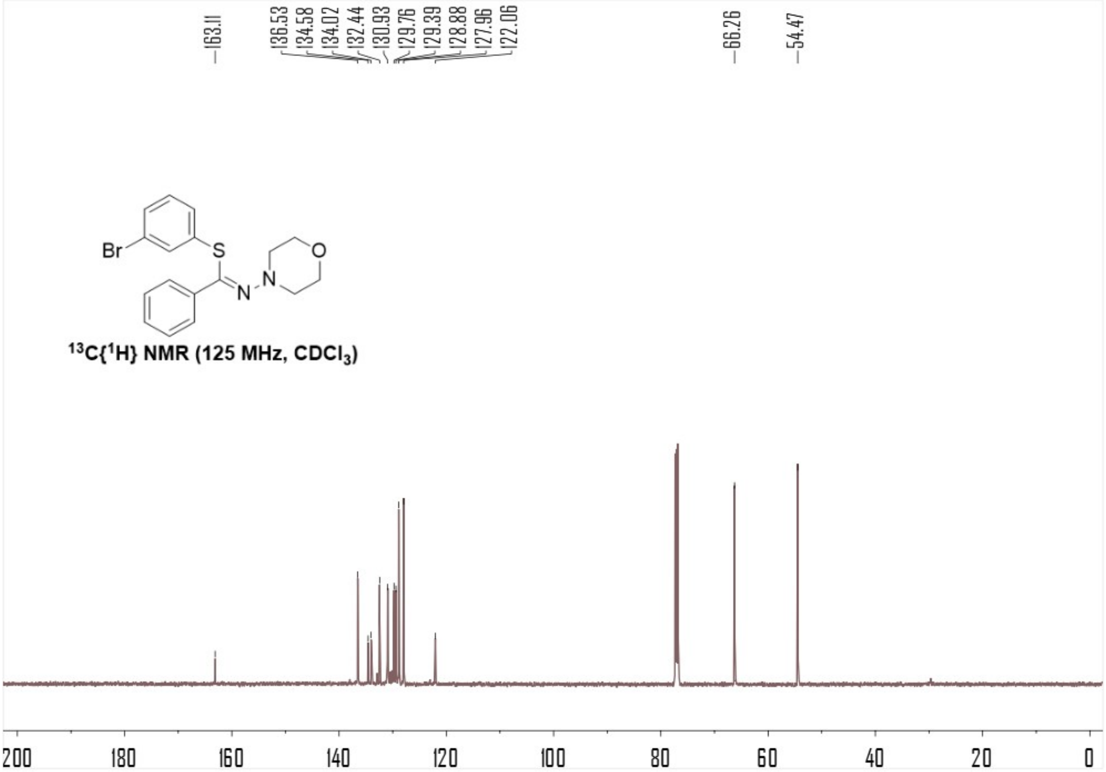


1,2-Bis(4-ethylphenyl)disulfane (**4h**)

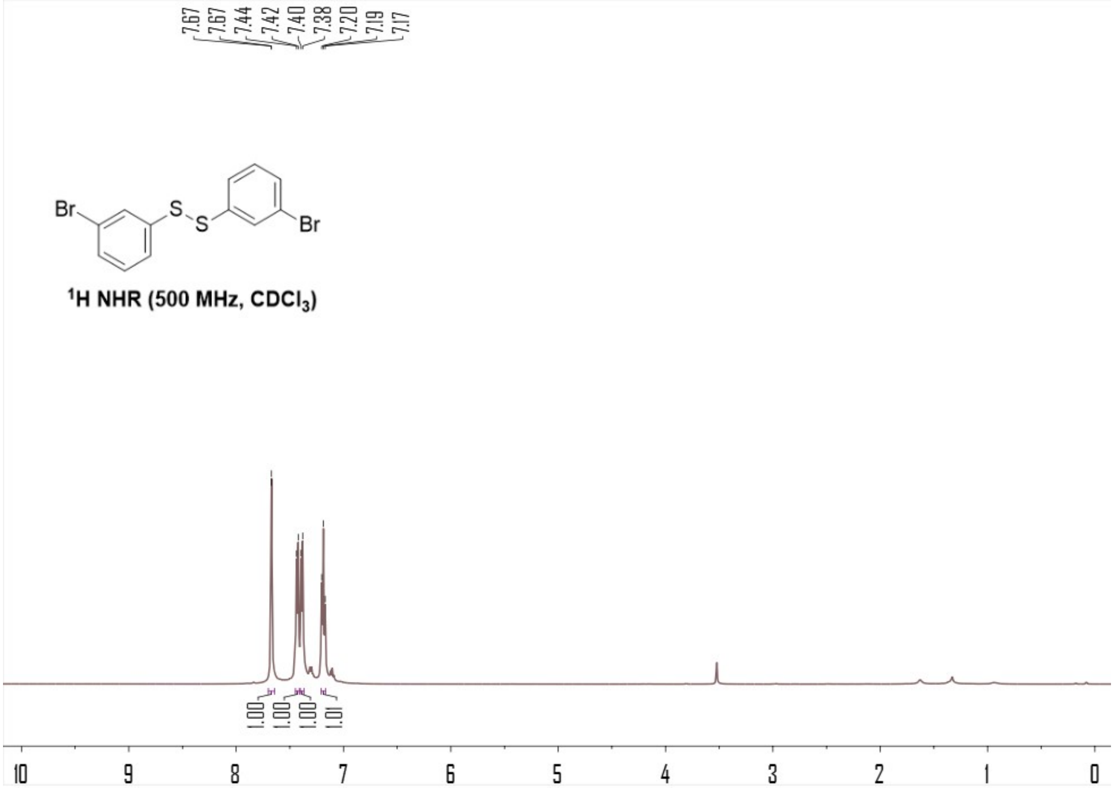


3-Bromophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3i**)

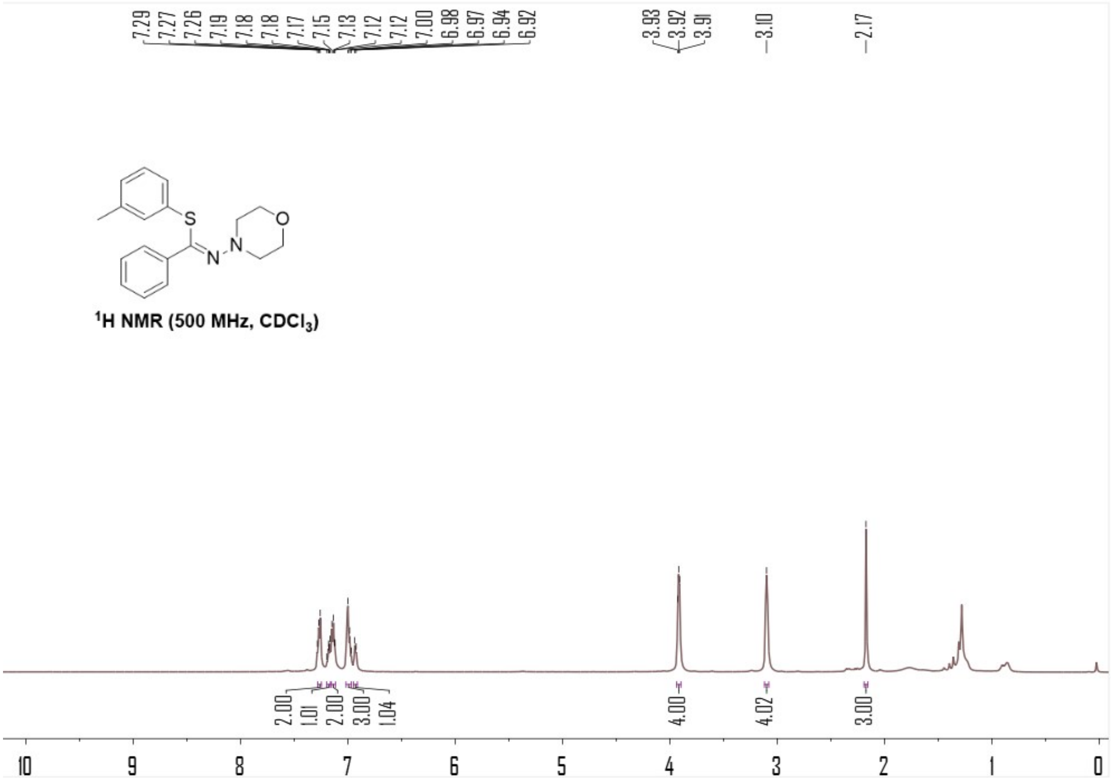


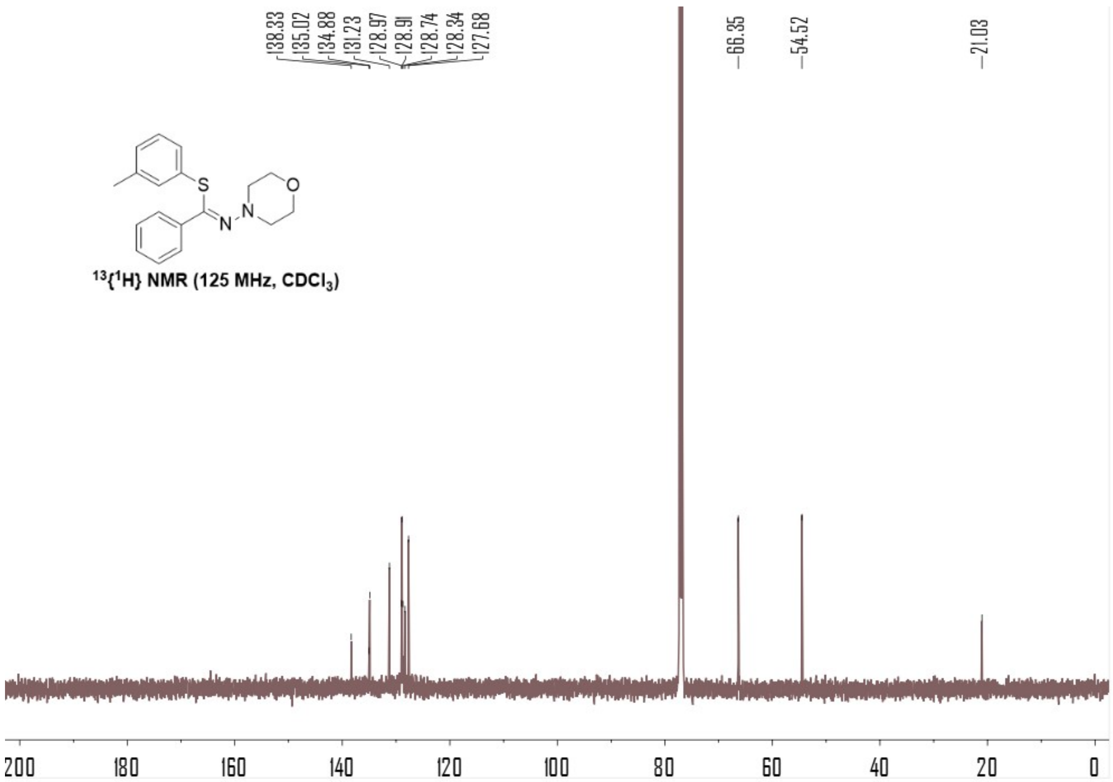


1,2-Bis(3-bromophenyl)disulfane (**4i**)

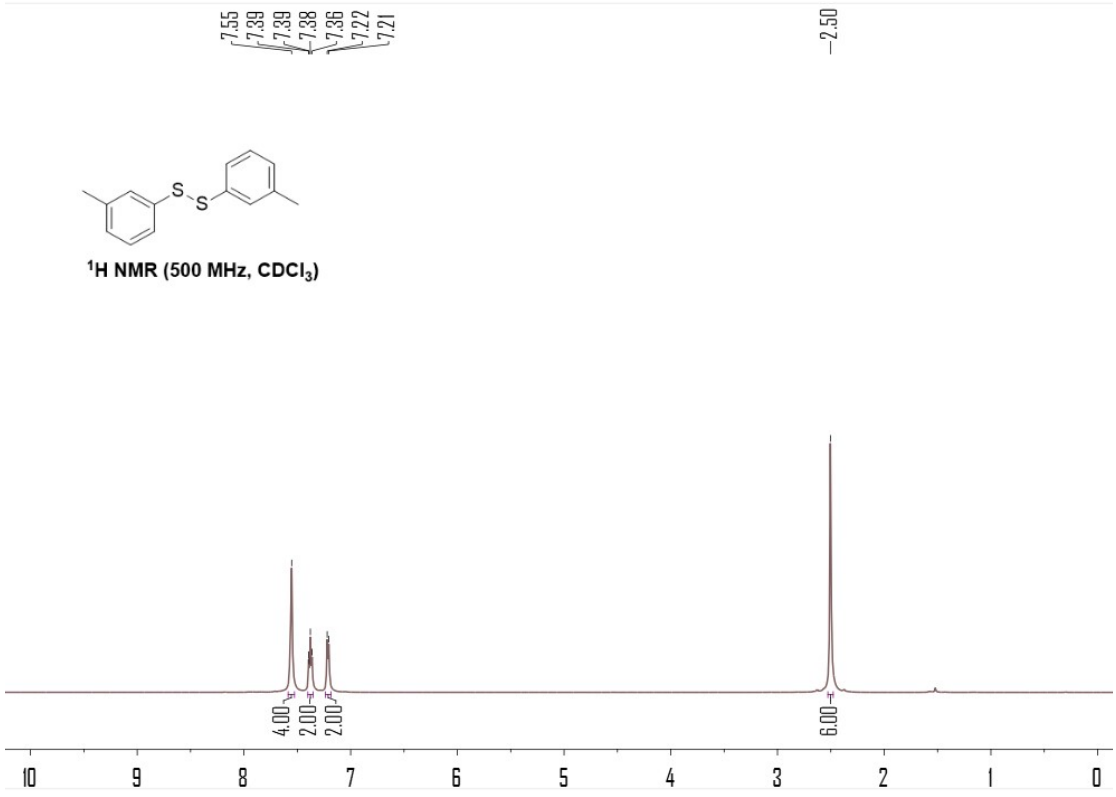


m-Tolyl (*Z*)-*N*-morpholinobenzimidothioate (**3j**)

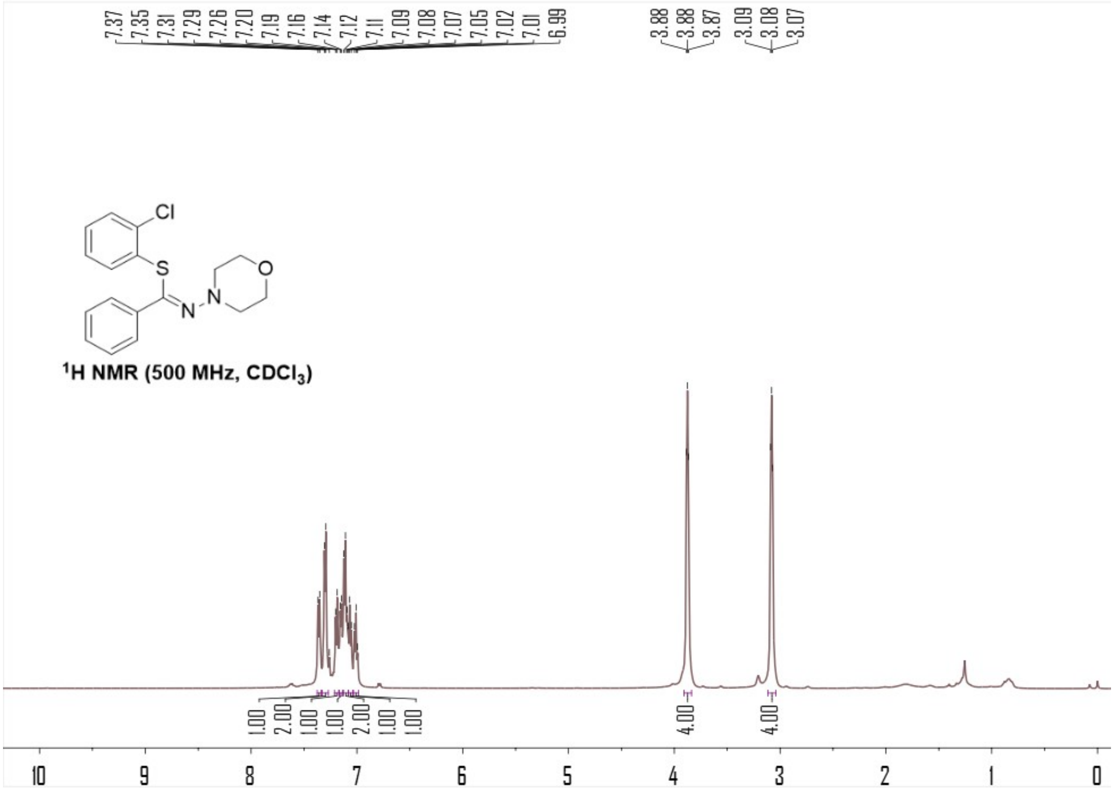


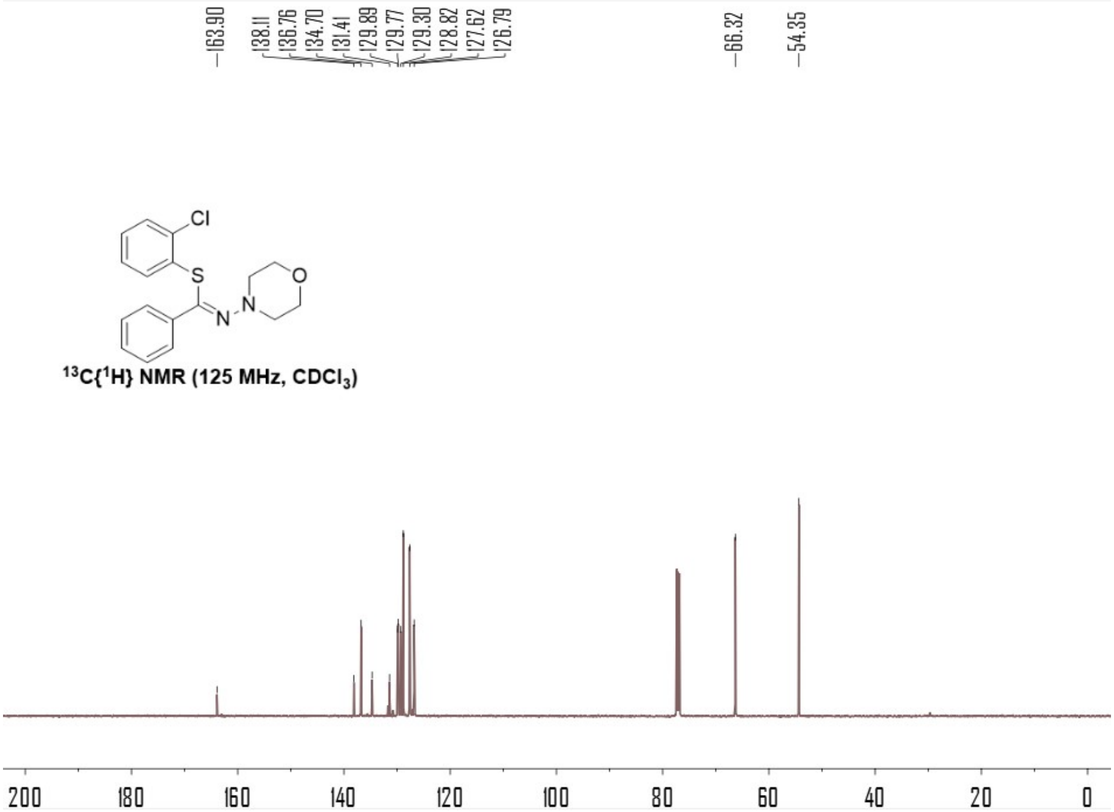


1,2-Di-o-tolyldisulfane (**4j**)

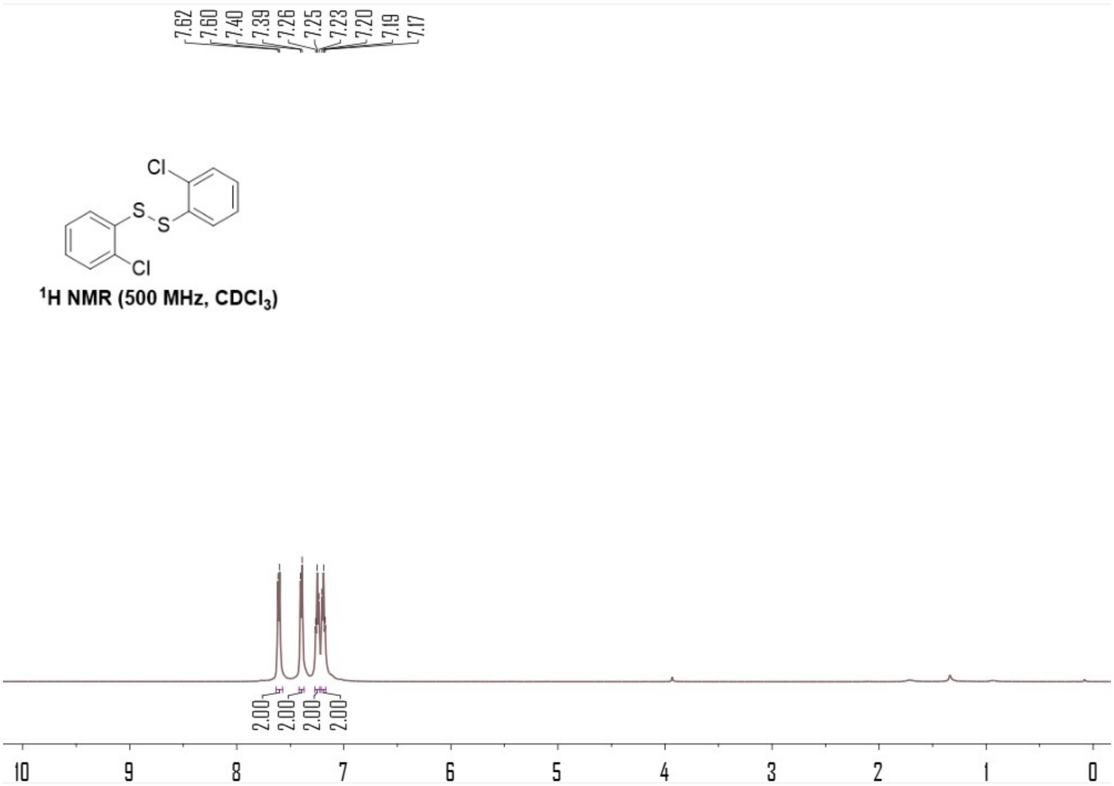


2-Chlorophenyl (*Z*)-*N*-morpholinobenzimidothioate (**3k**)

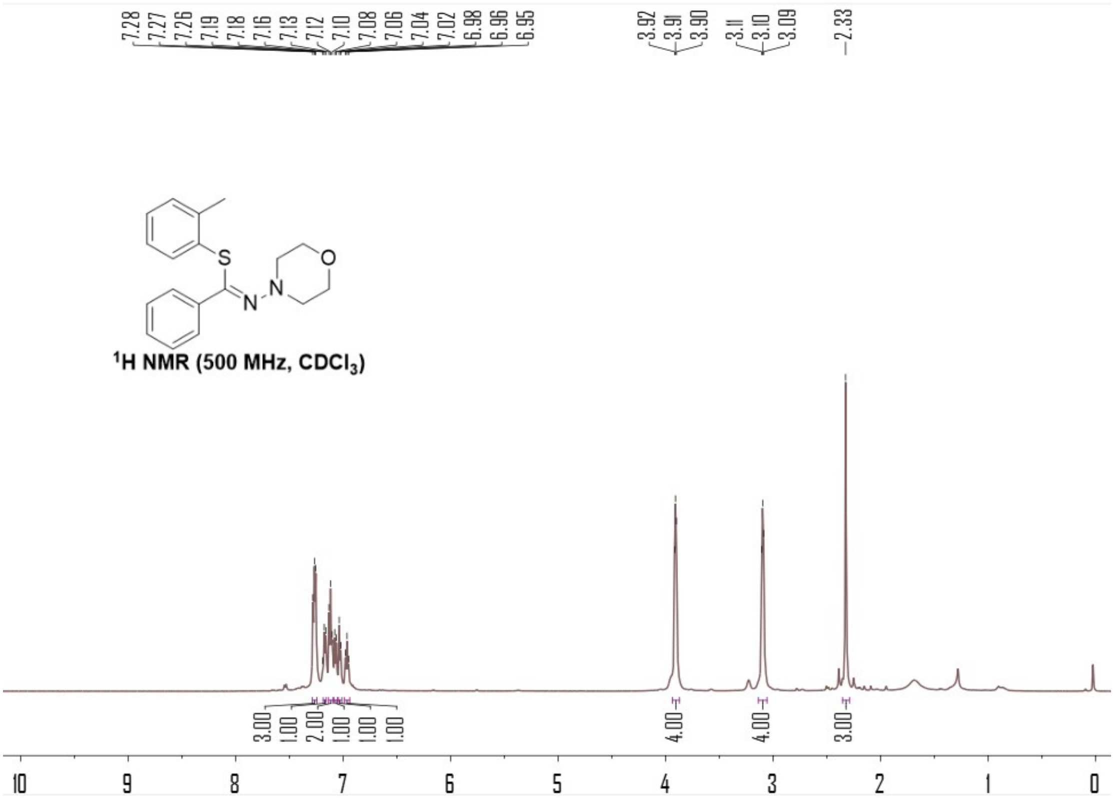


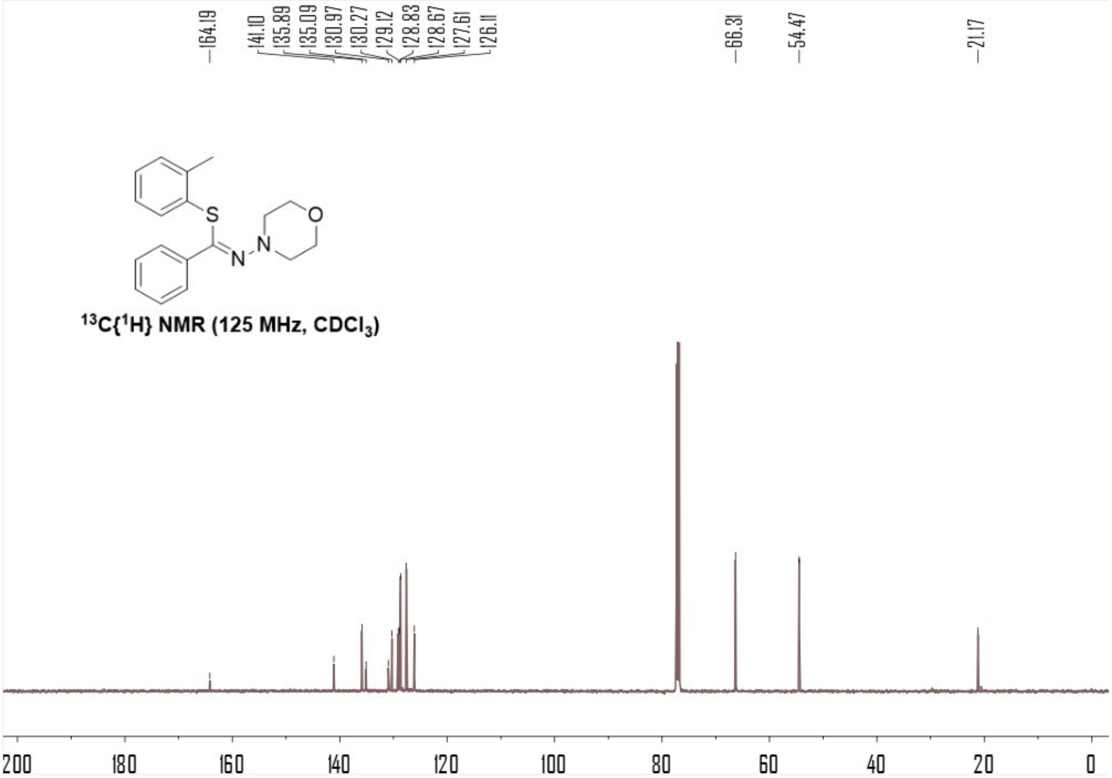


1,2-Bis(2-chlorophenyl)disulfane (**4k**)

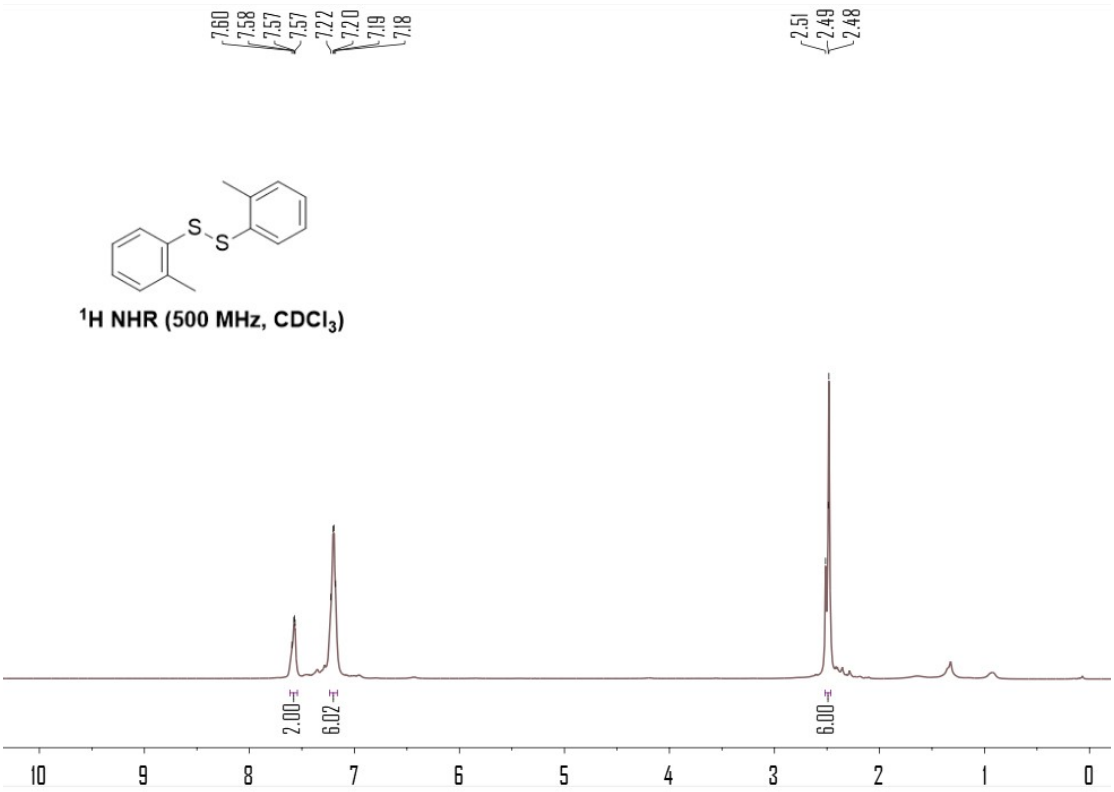


o-Tolyl (*Z*)-*N*-morpholinobenzimidothioate (**3l**)

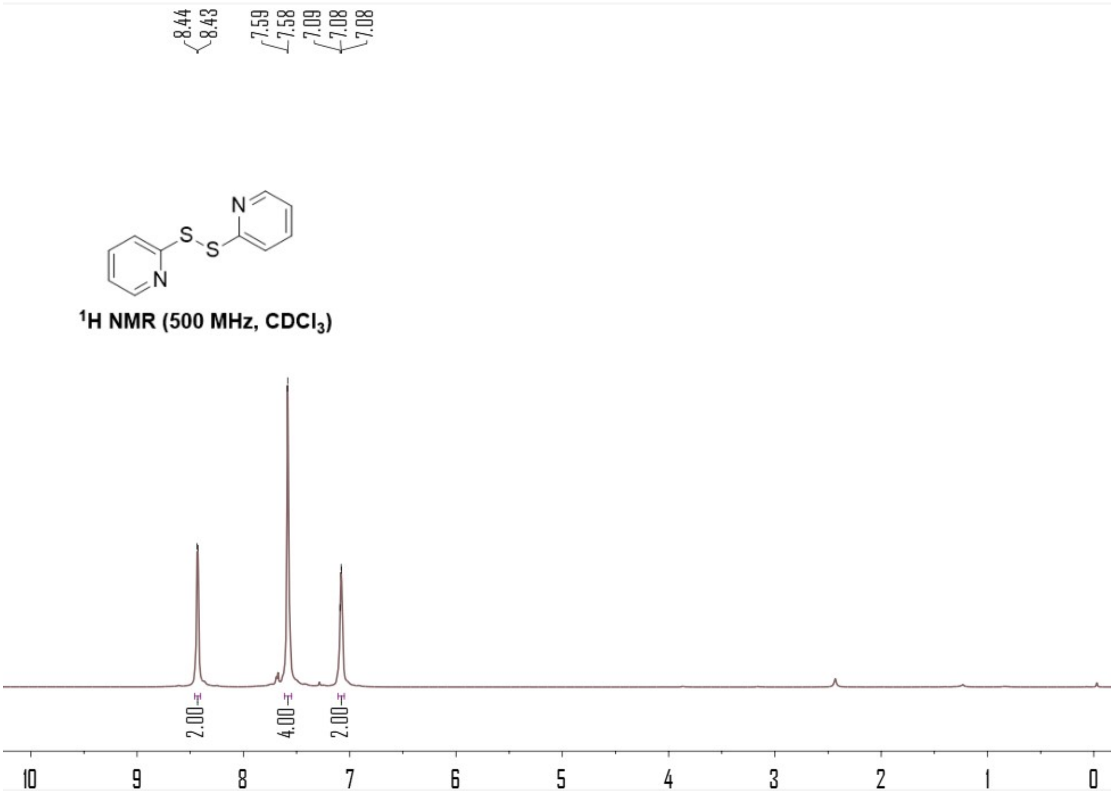


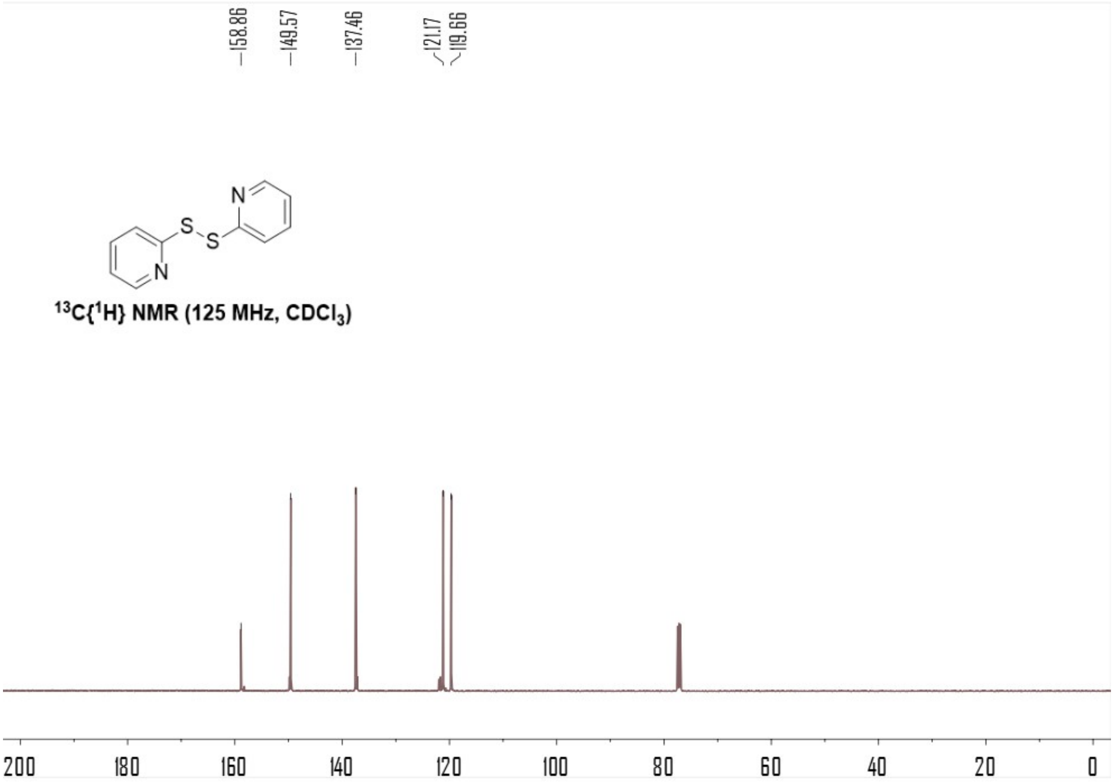


1,2-Di-o-tolyldisulfane (**4l**)

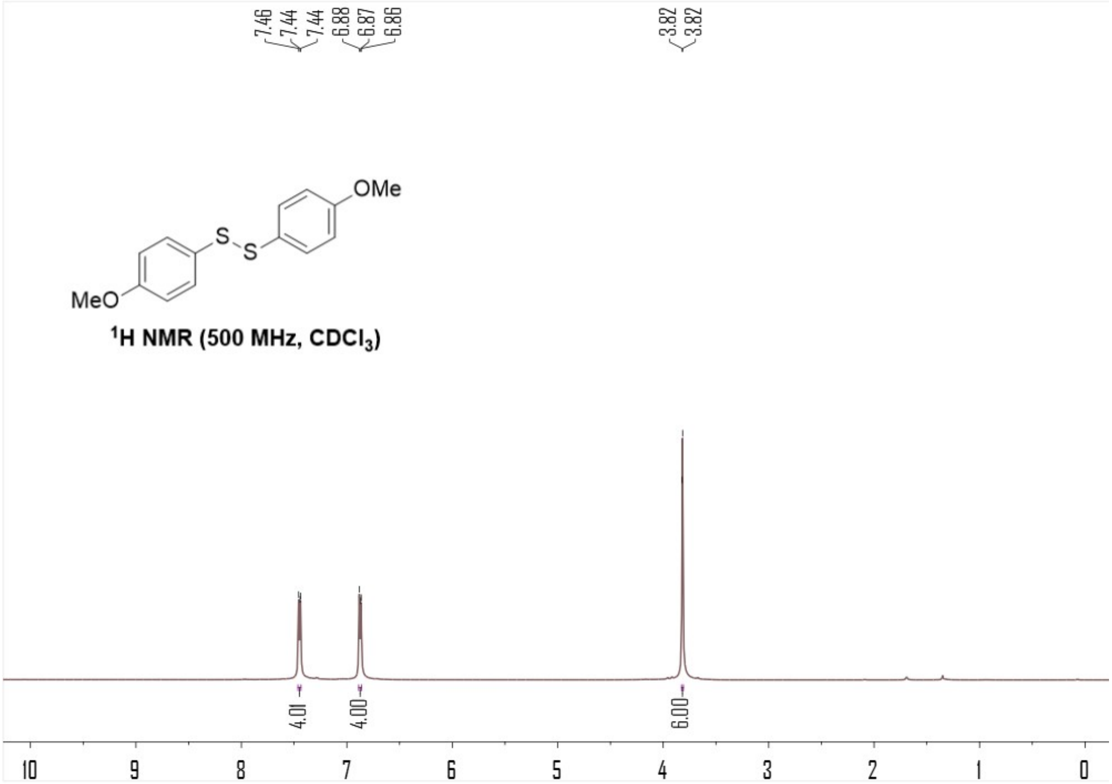


1,2-Di(pyridin-2-yl)-1λ^6,2λ^6-disulfane-1,1,2,2-tetraone (**4m**)

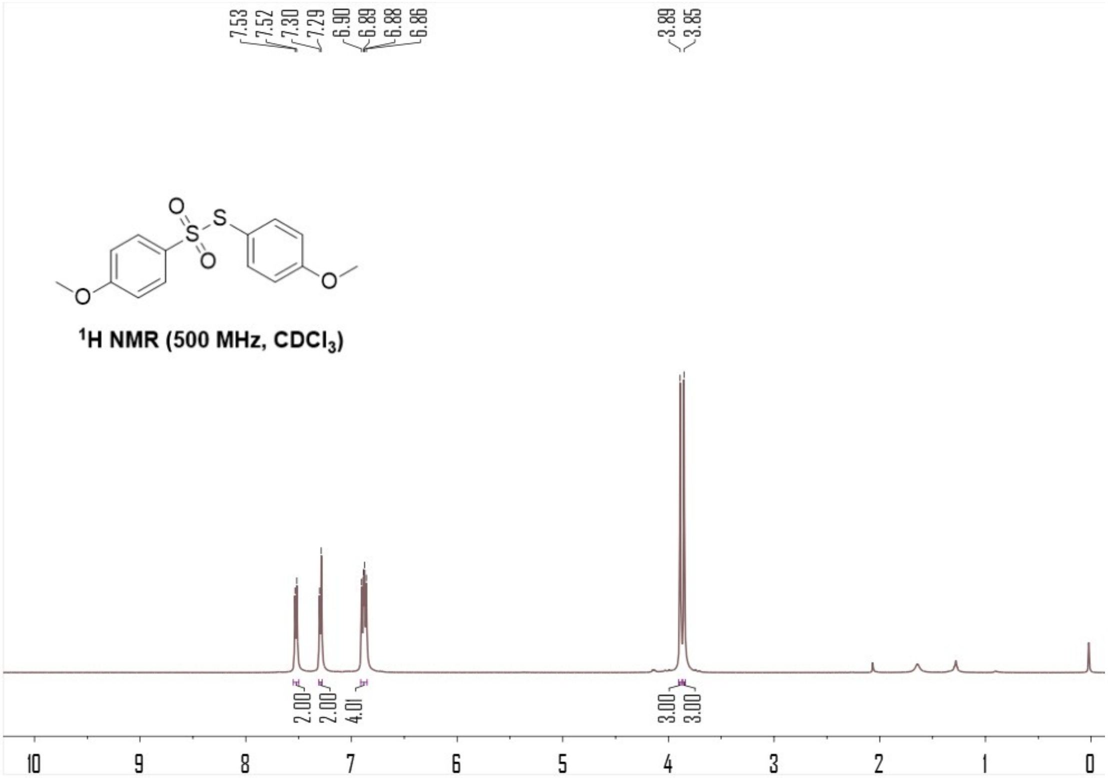


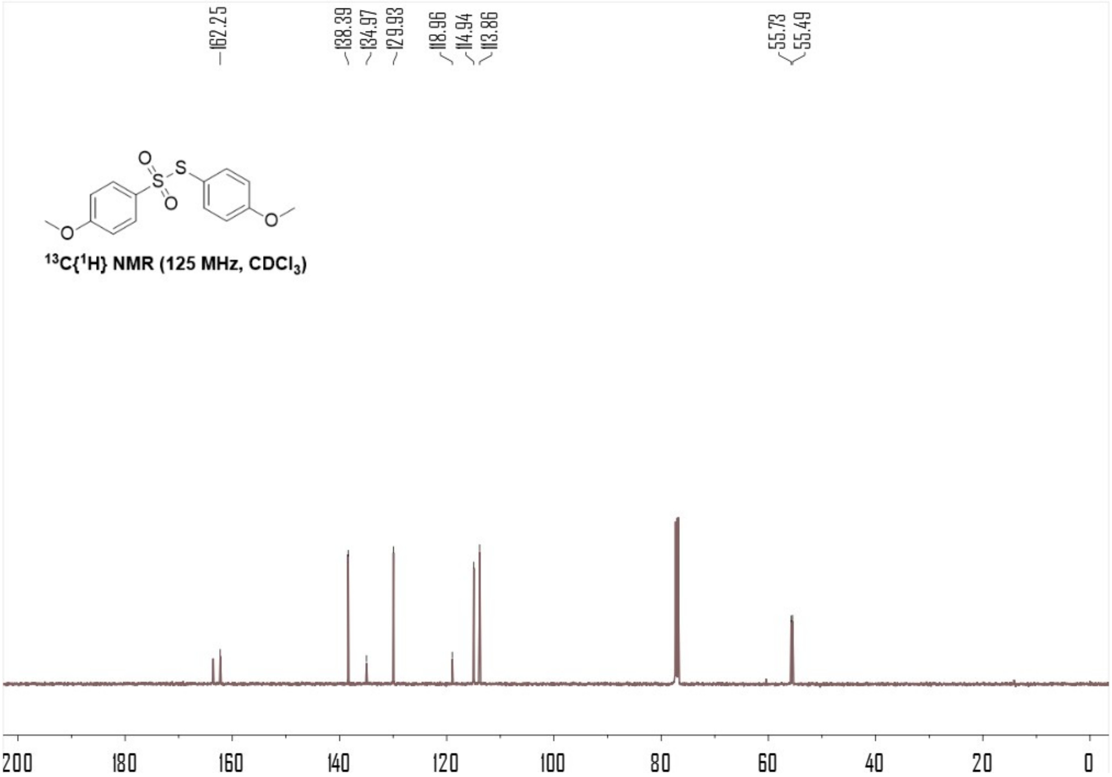


1,2-Bis(4-methoxyphenyl)disulfane (**4n**)

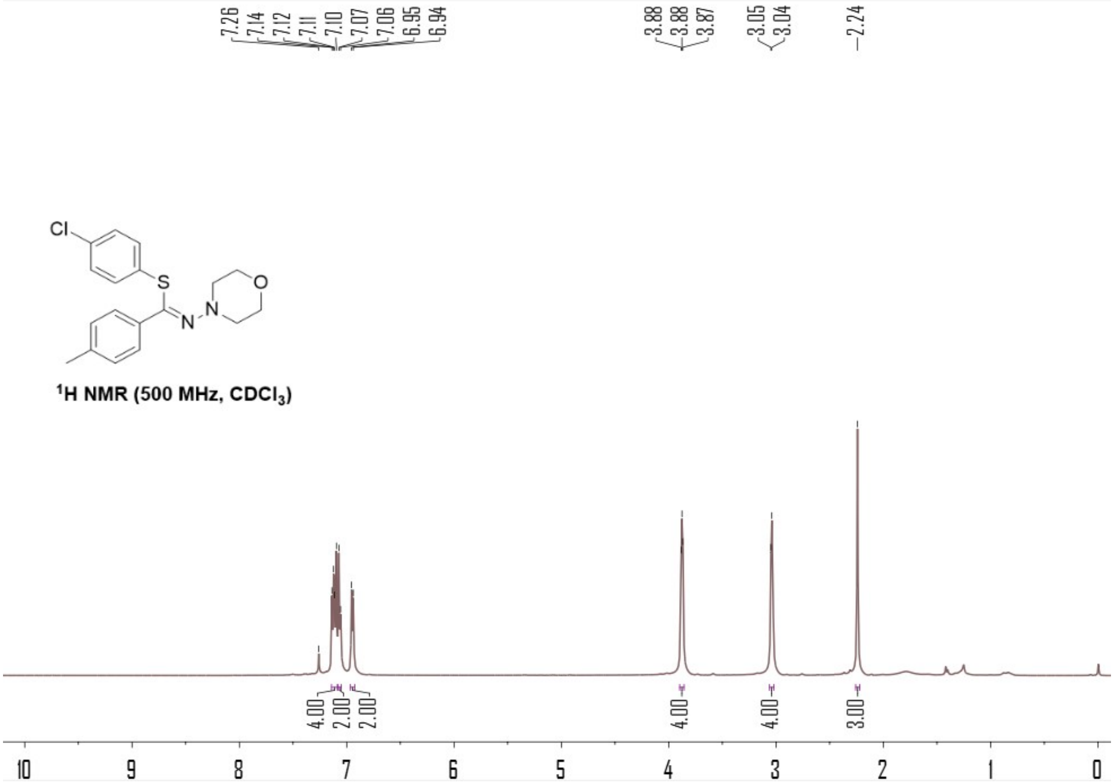


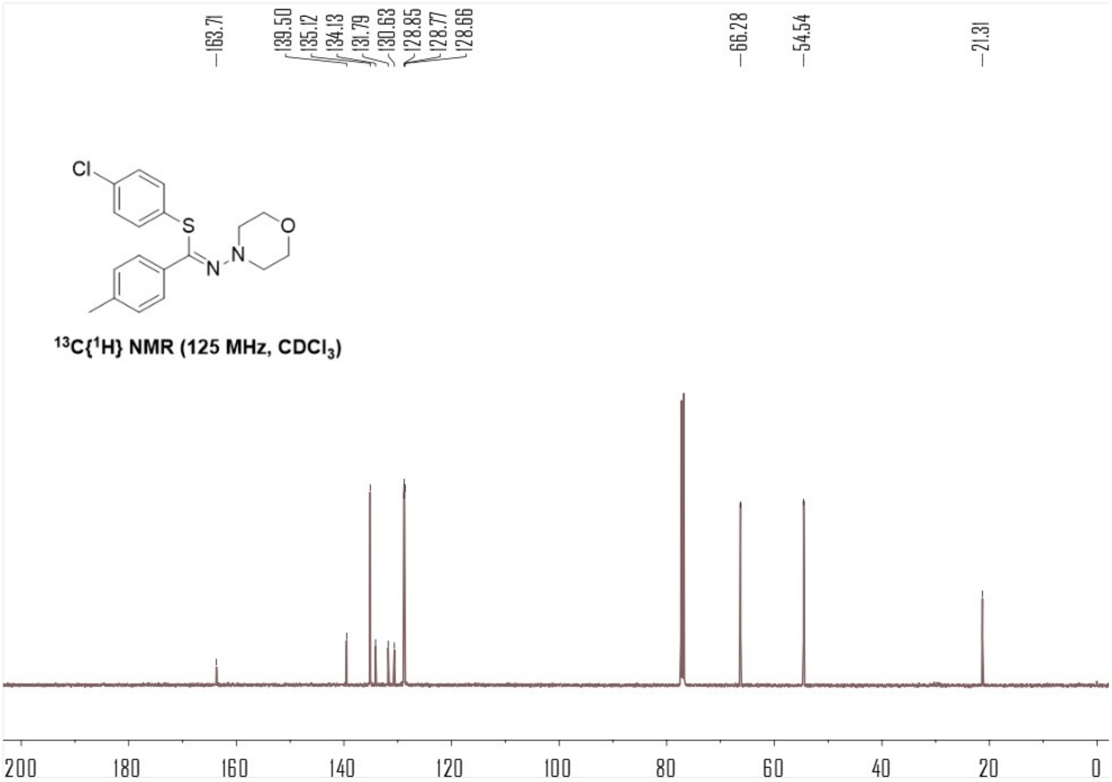
S-(4-Methoxyphenyl) 4-methoxybenzenesulfonothioate (**5n**)



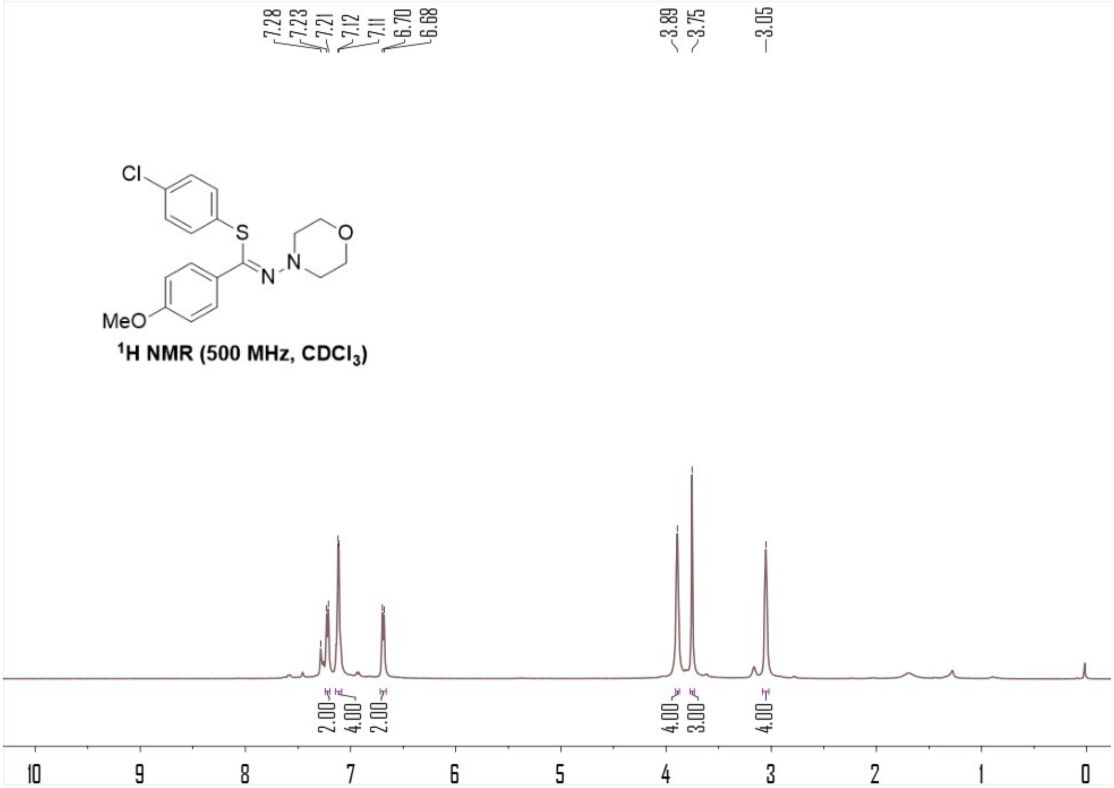


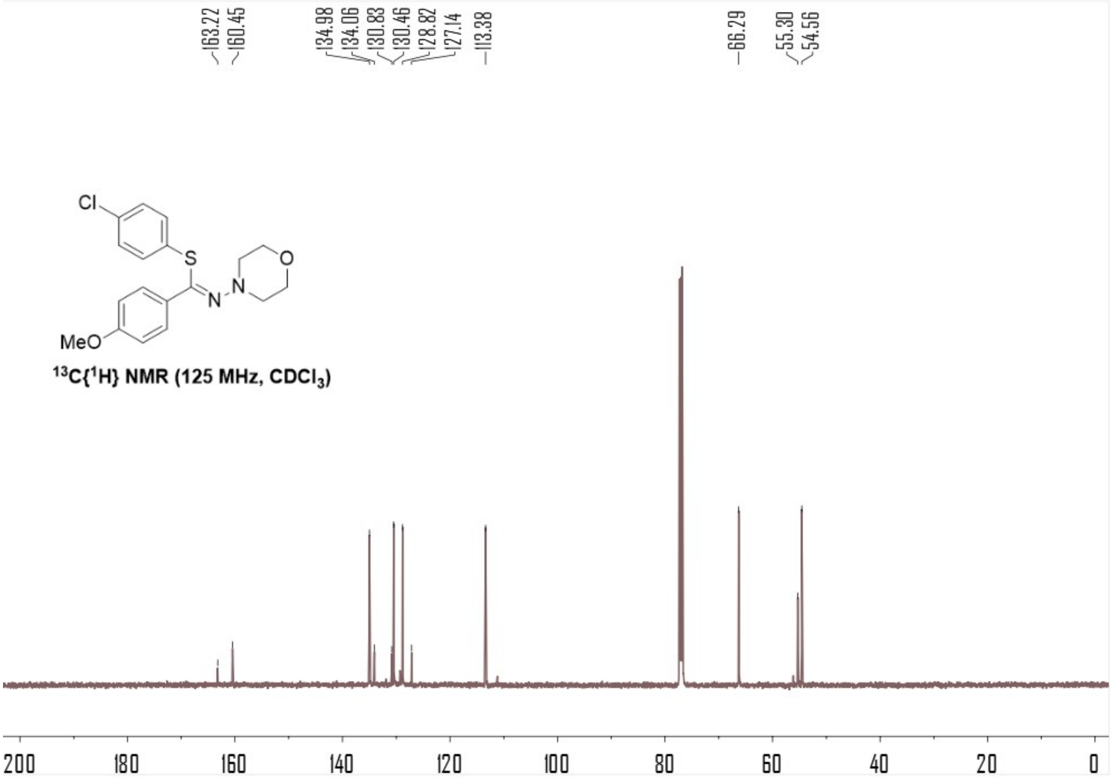
4-Chlorophenyl (*Z*)-4-methyl-*N*-morpholinobenzimidothioate (**3o**)



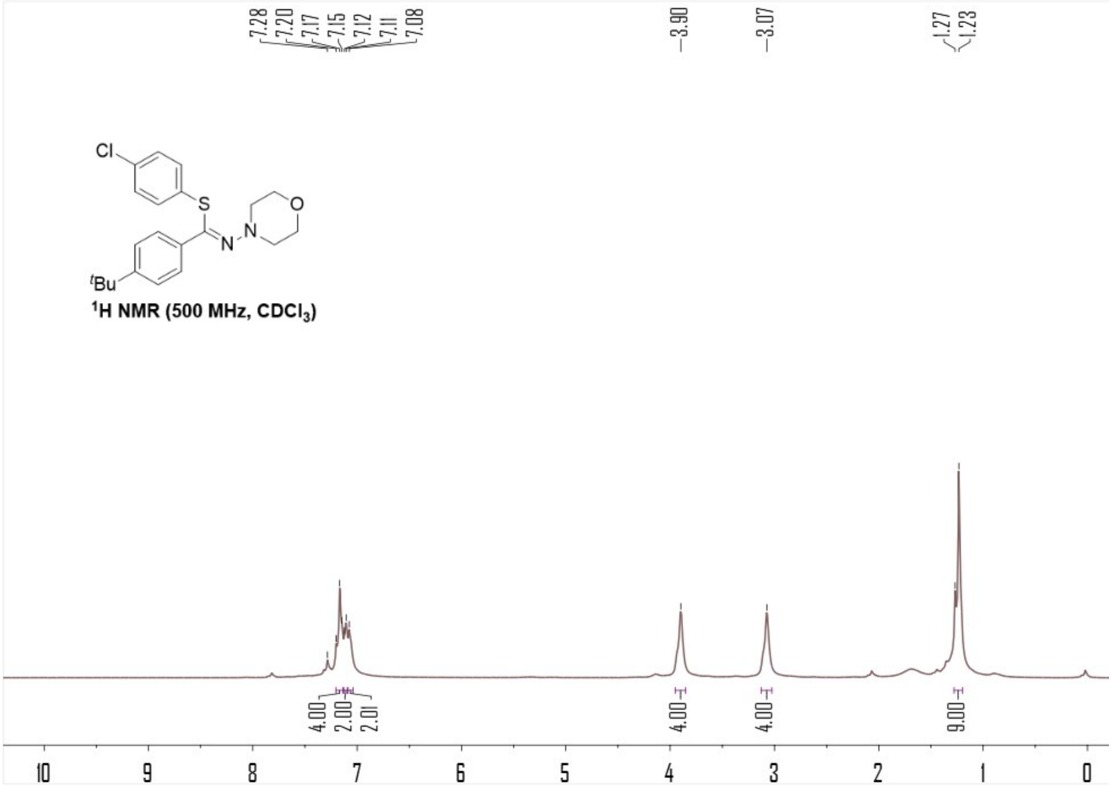


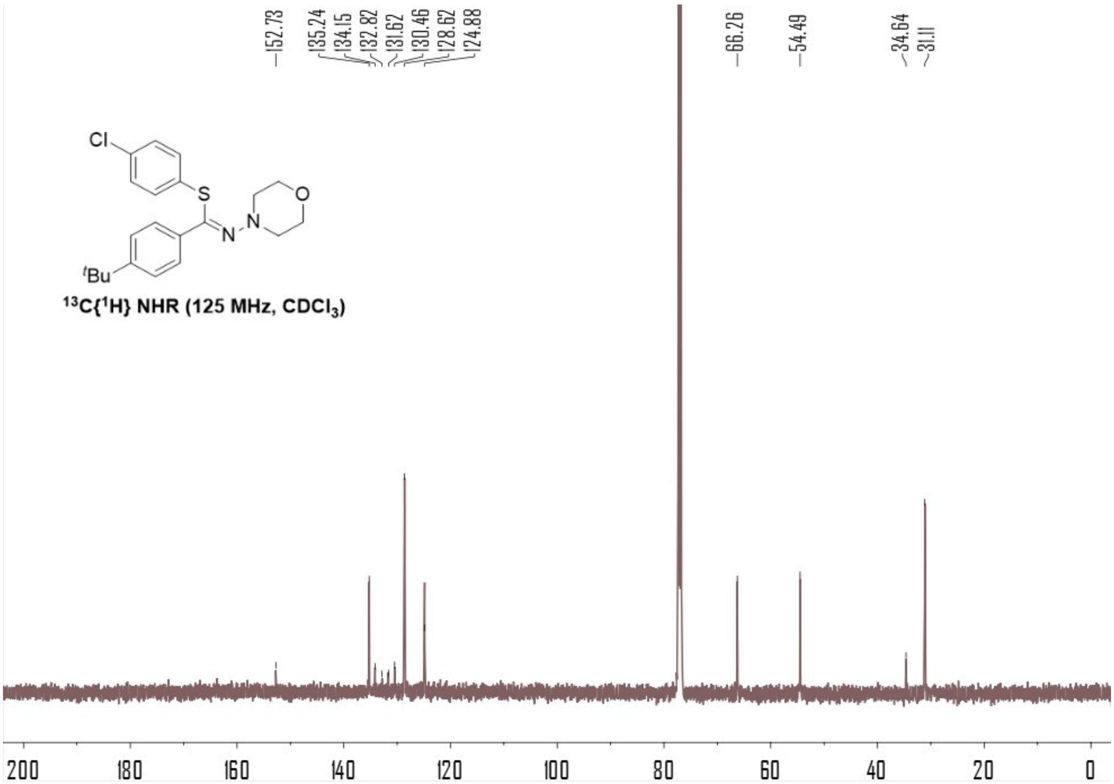
4-Chlorophenyl (*Z*)-4-methoxy-*N*-morpholinobenzimidothioate (**3p**)



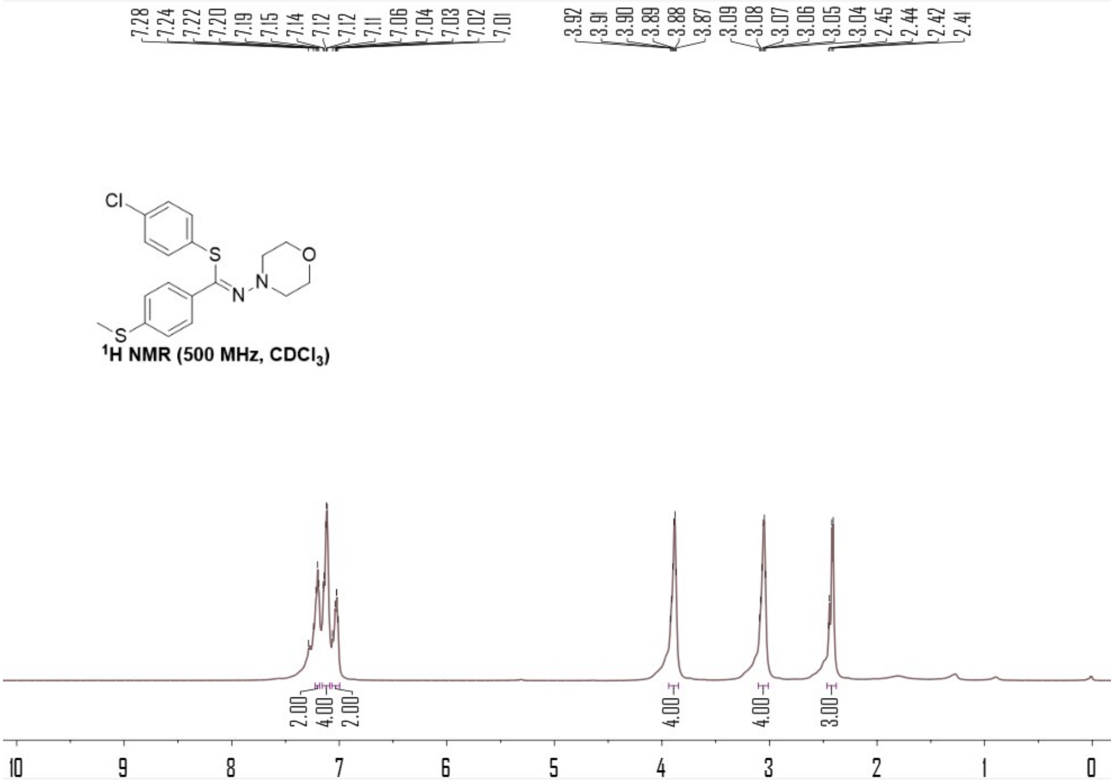


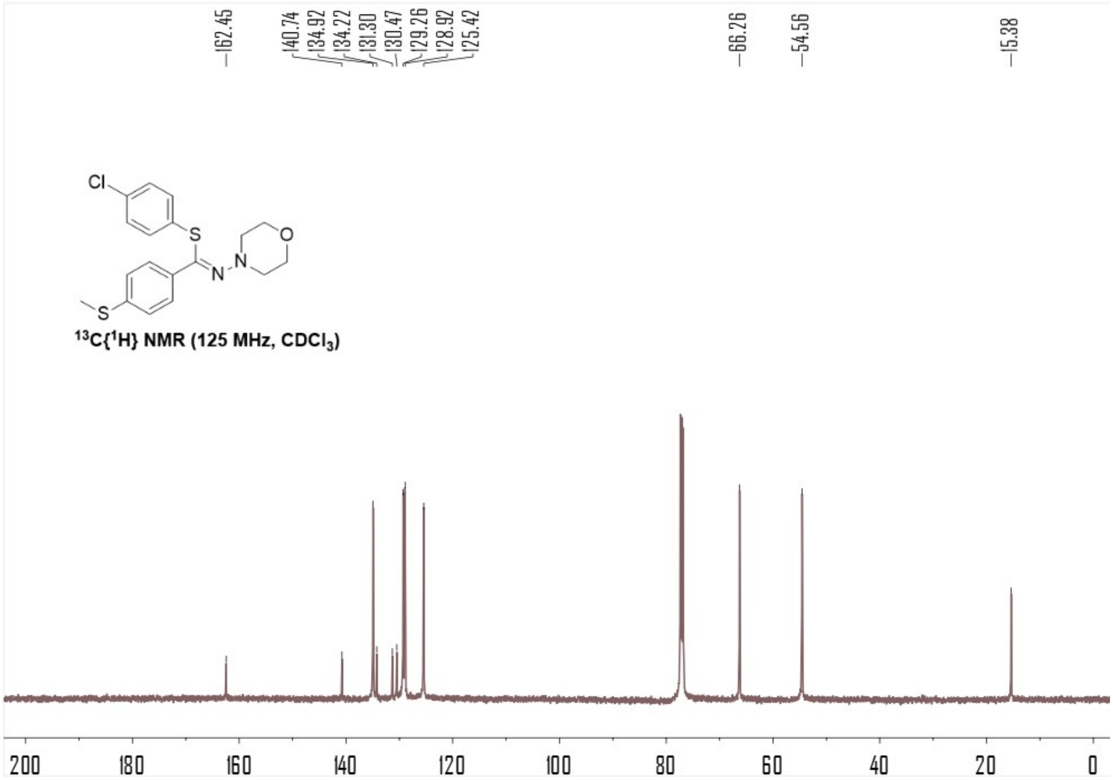
4-Chlorophenyl (*Z*)-4-(tert-butyl)-*N*-morpholinobenzimidothioate (**3q**)



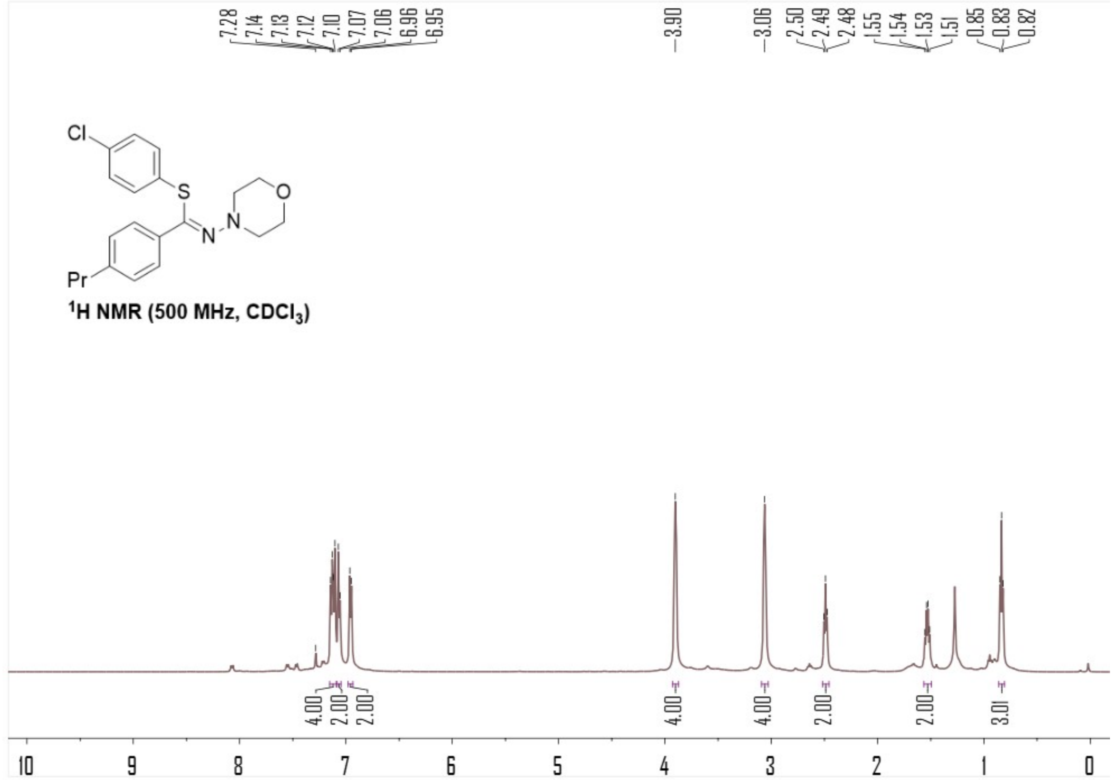


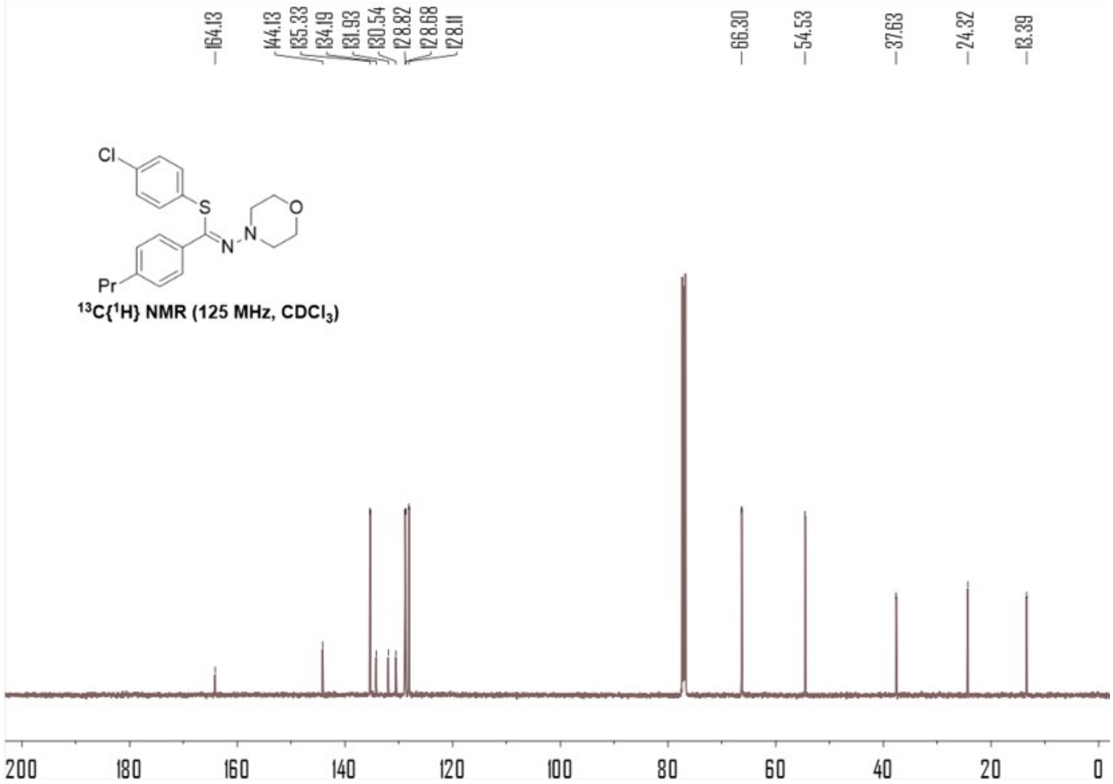
4-Chlorophenyl (*Z*)-4-(methylthio)-*N*-morpholinobenzimidothioate (**3r**)



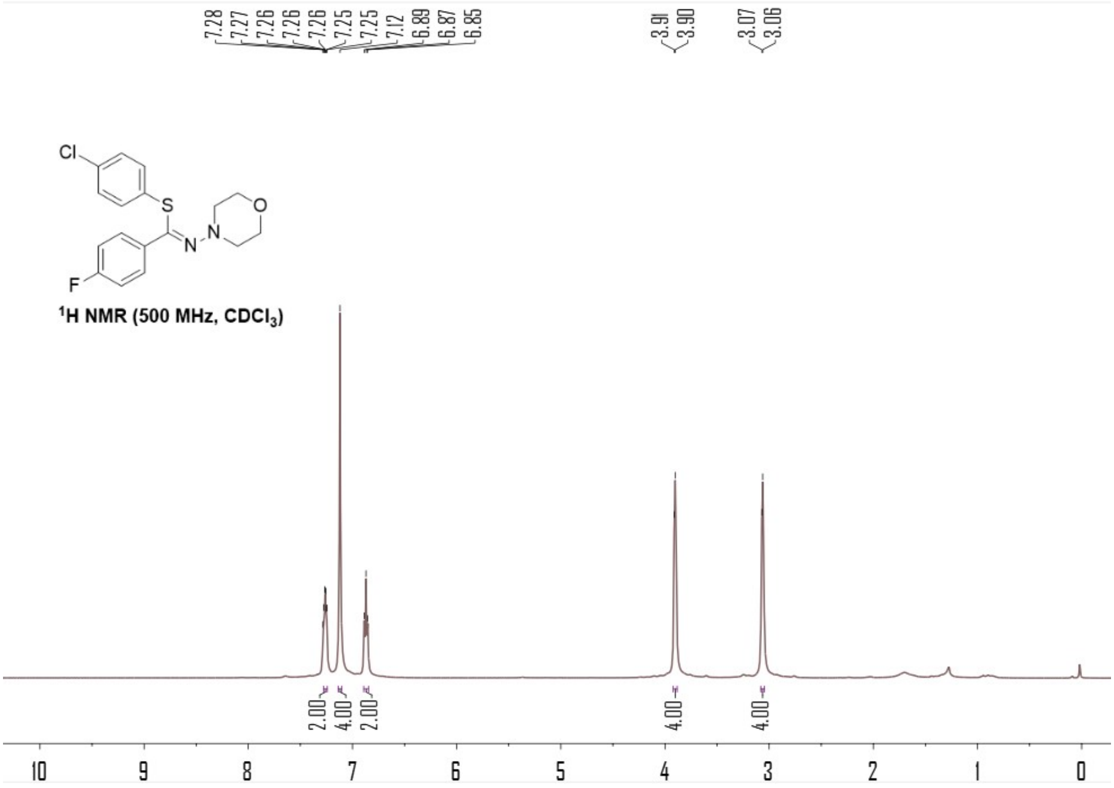


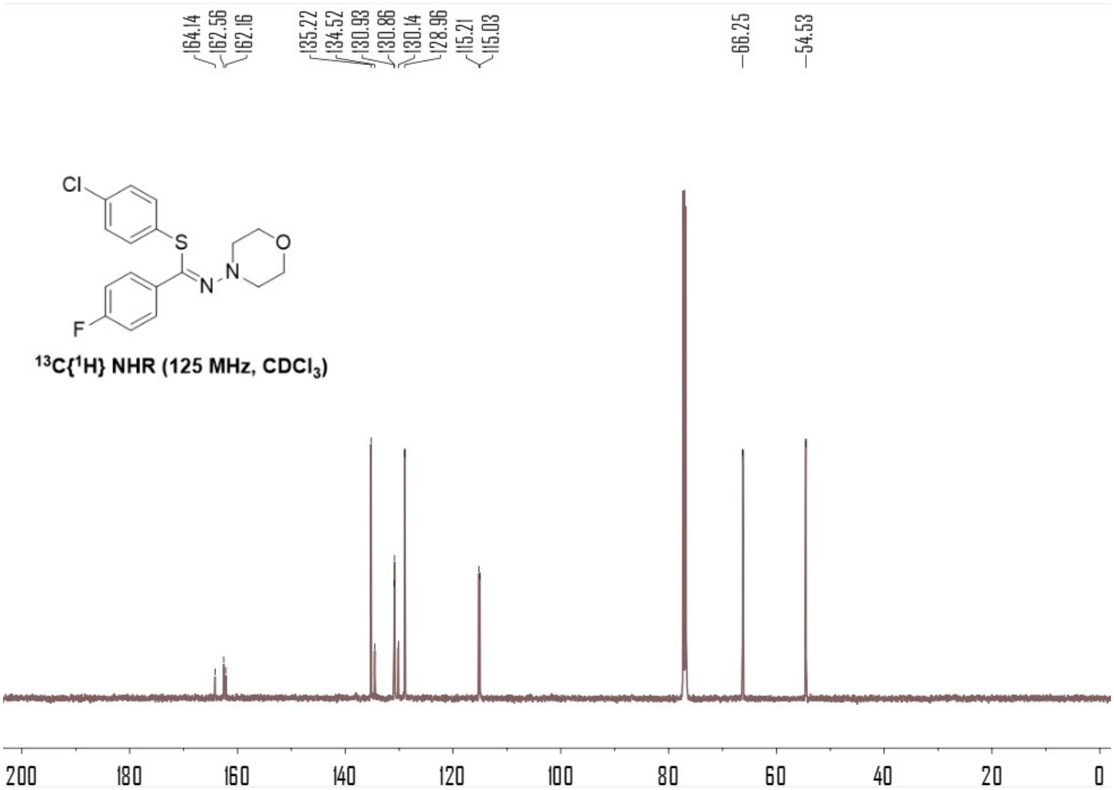
4-Chlorophenyl (*Z*)-*N*-morpholino-4-propylbenzimidothioate (**3s**)





4-Chlorophenyl (*Z*)-4-fluoro-*N*-morpholinobenzimidothioate (**3t**)

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162.56
162.16
135.22
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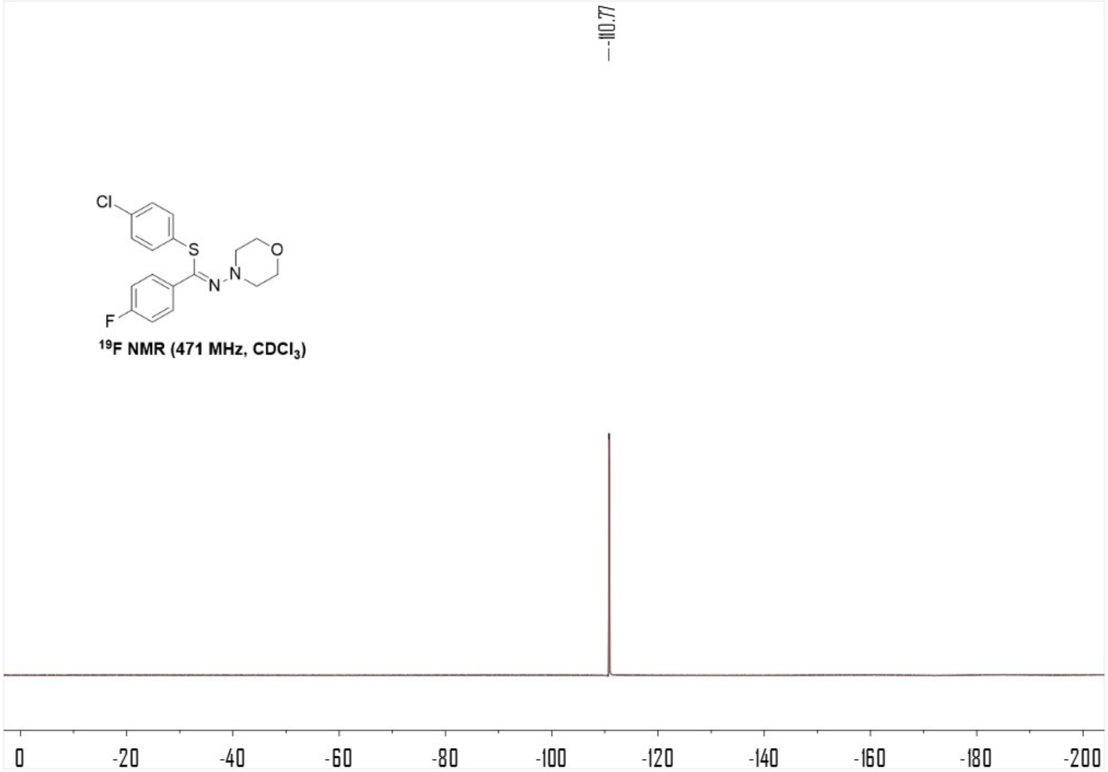
130.93
130.86
130.14
128.96
115.21
115.03
66.25
54.53
Cl
S
O
N
N
F
$^{13}C\{^{1}H\}$ NHR (125 MHz, $CDCl_3$)
200
180
160
140
120
100
80
60
40
20
0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Cl
S
O
N
N
F
^{19}F NMR (471 MHz, $CDCl_3$)
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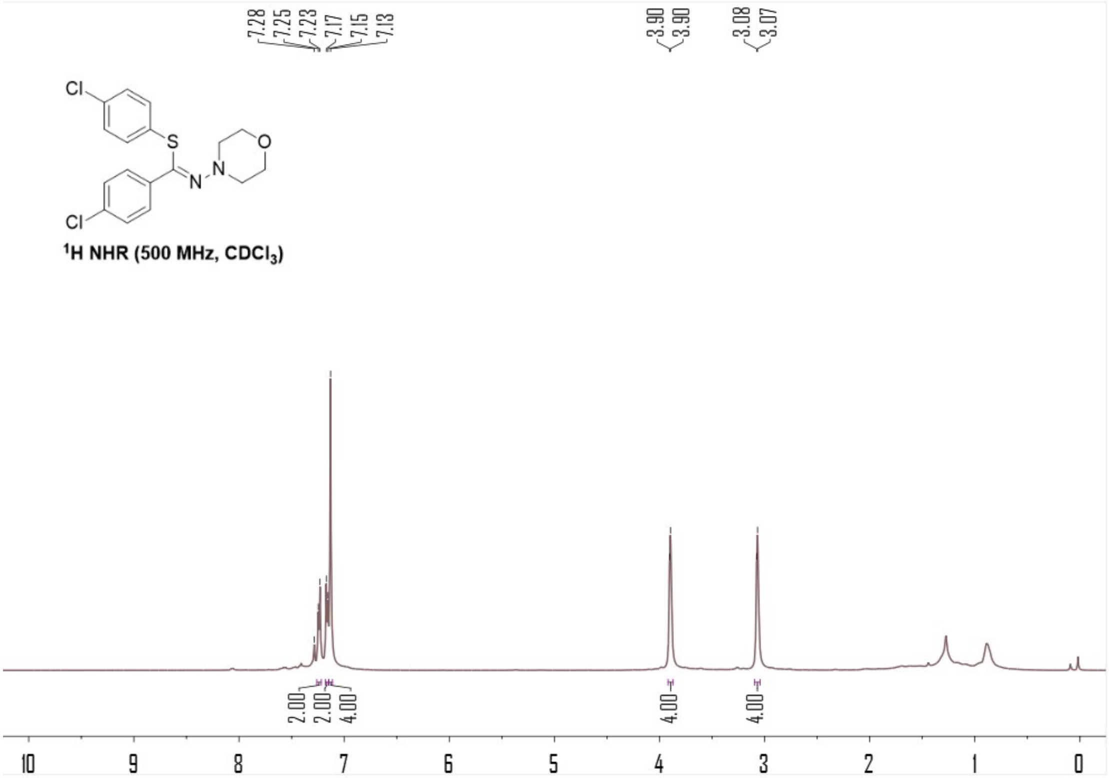
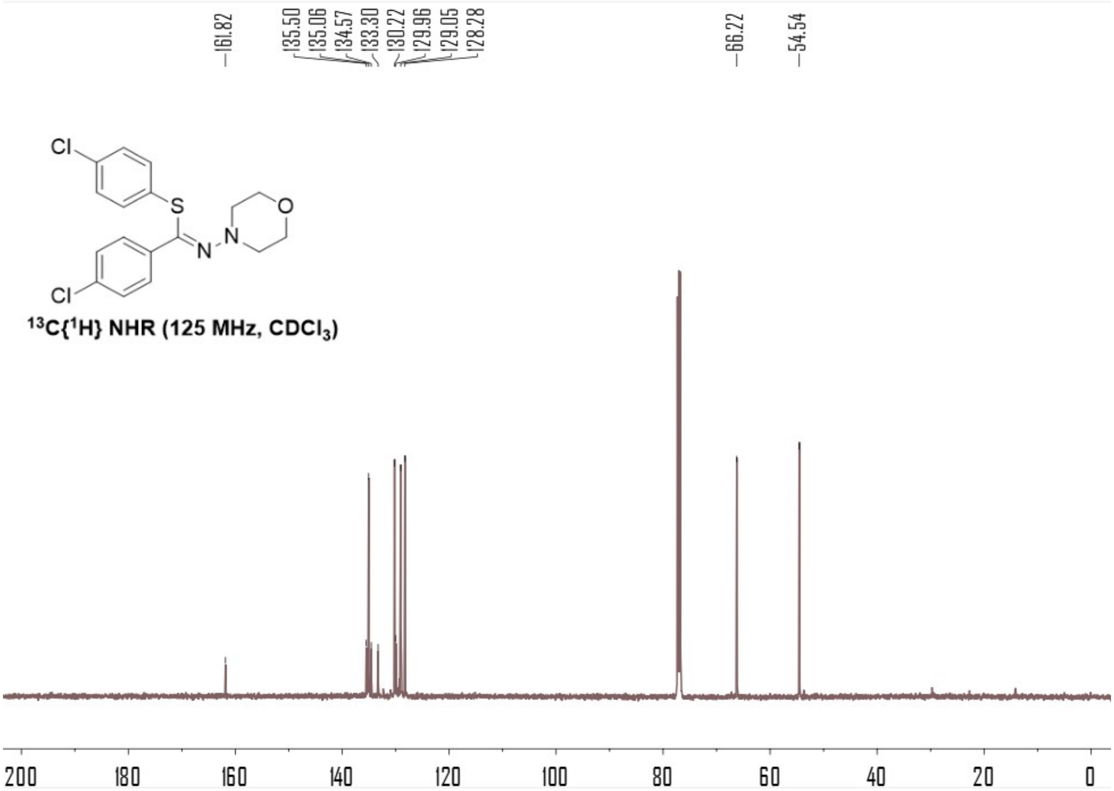
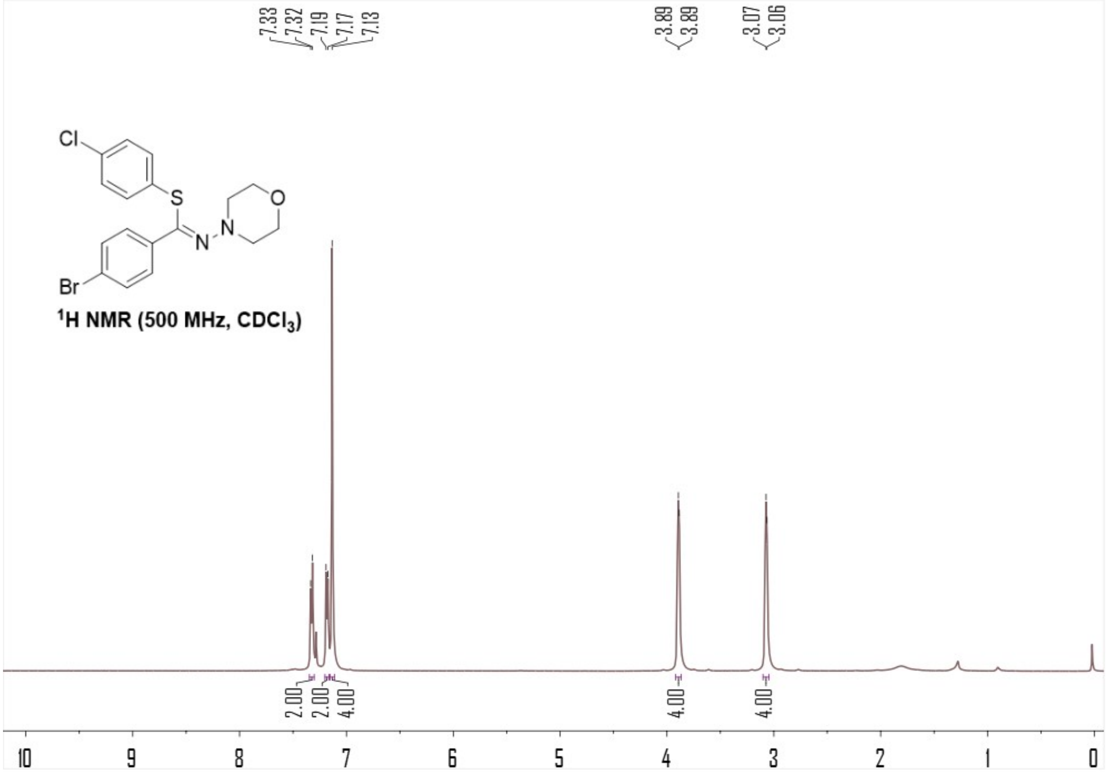
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200

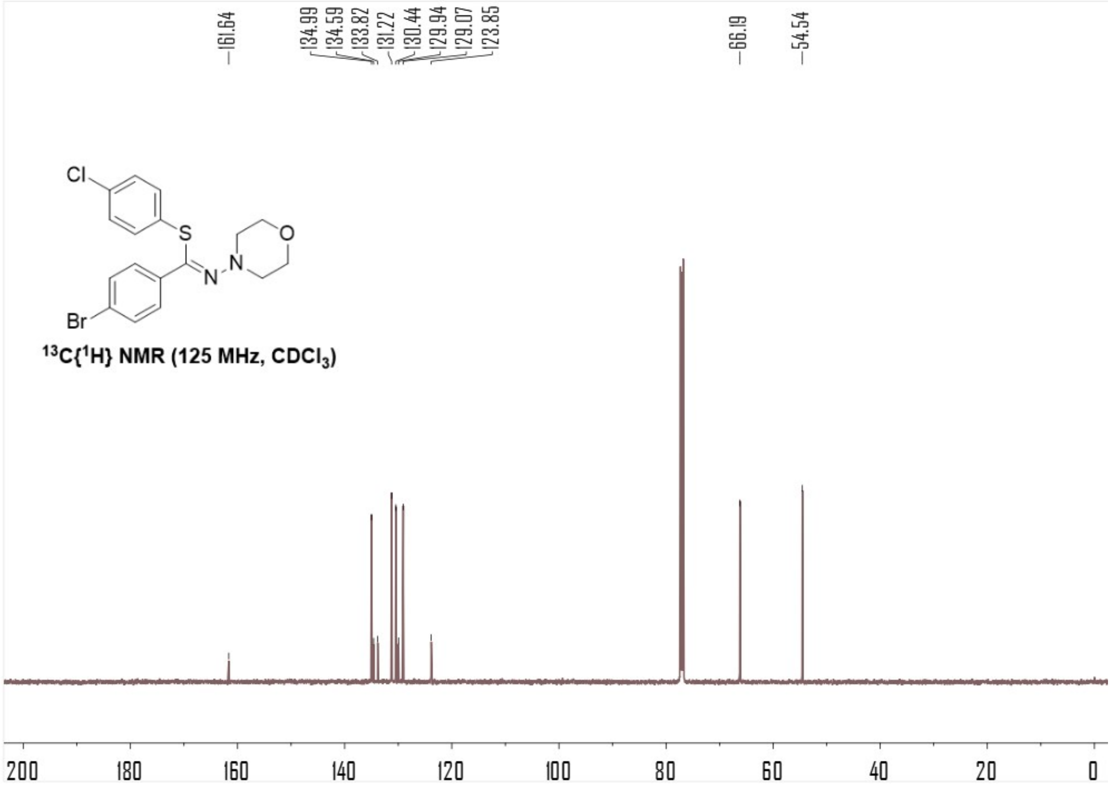
4-Chlorophenyl (*Z*)-4-chloro-*N*-morpholinobenzimidothioate (**3u**)



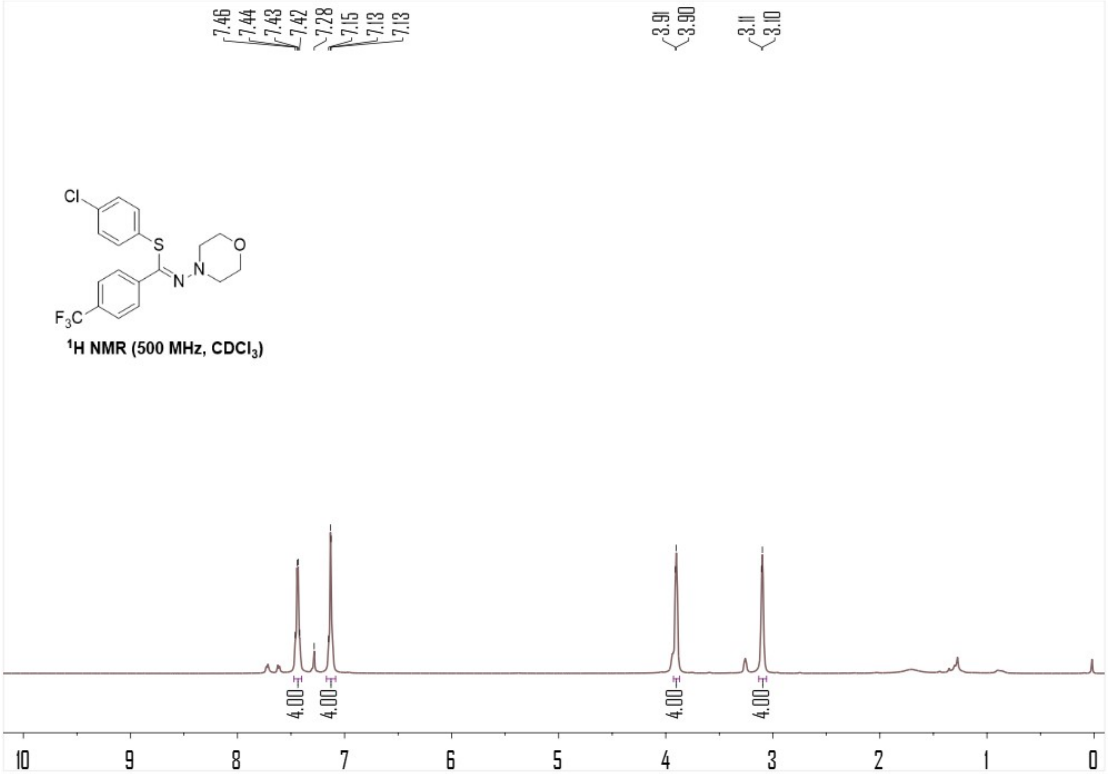


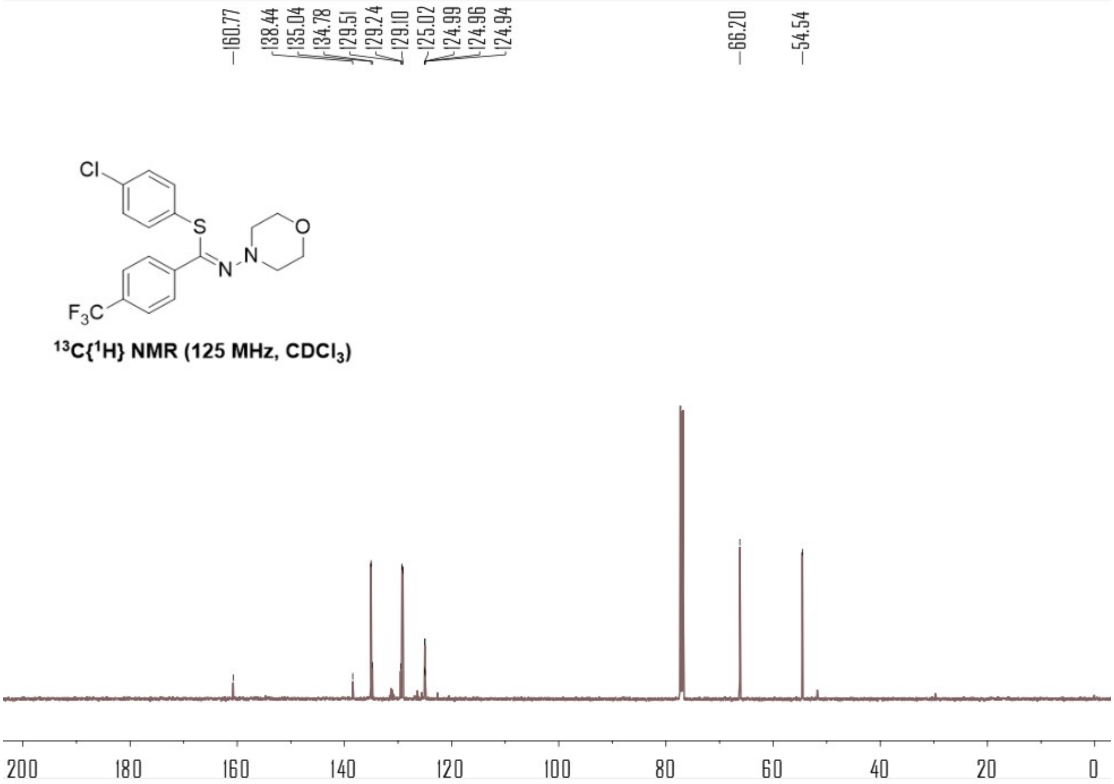
4-Chlorophenyl (*Z*)-4-bromo-*N*-morpholinobenzimidothioate (**3v**)

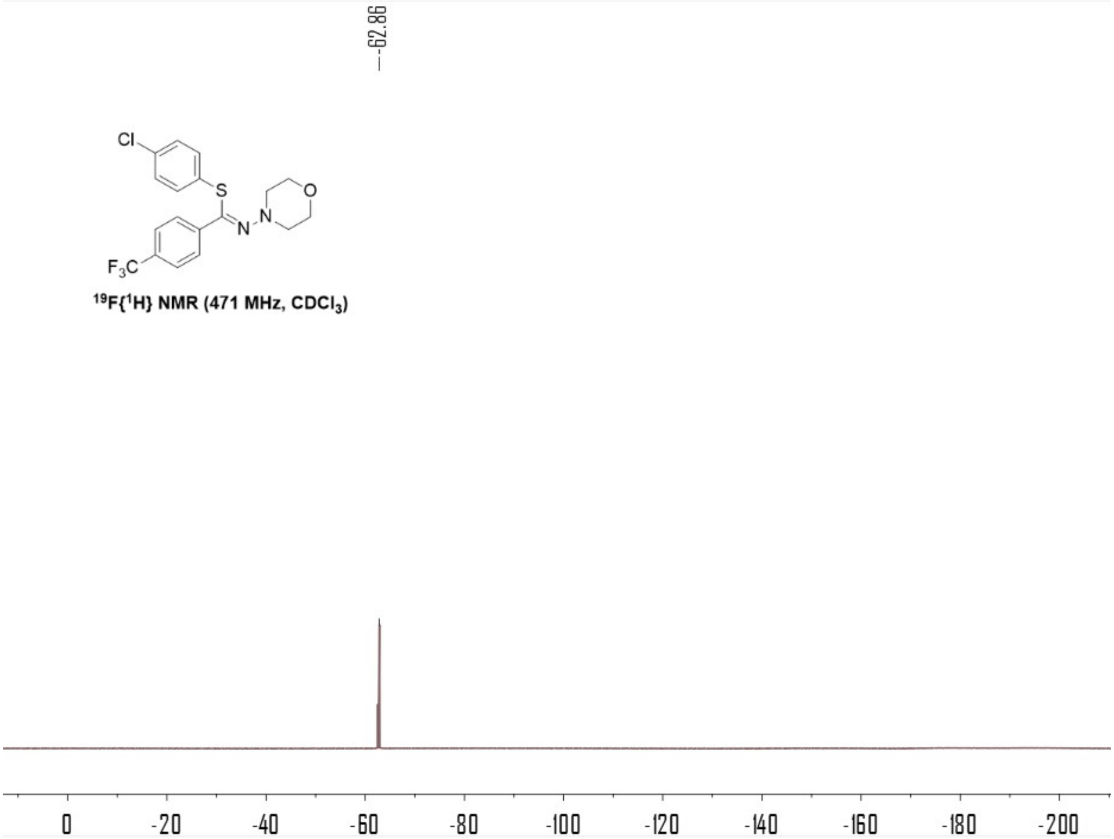




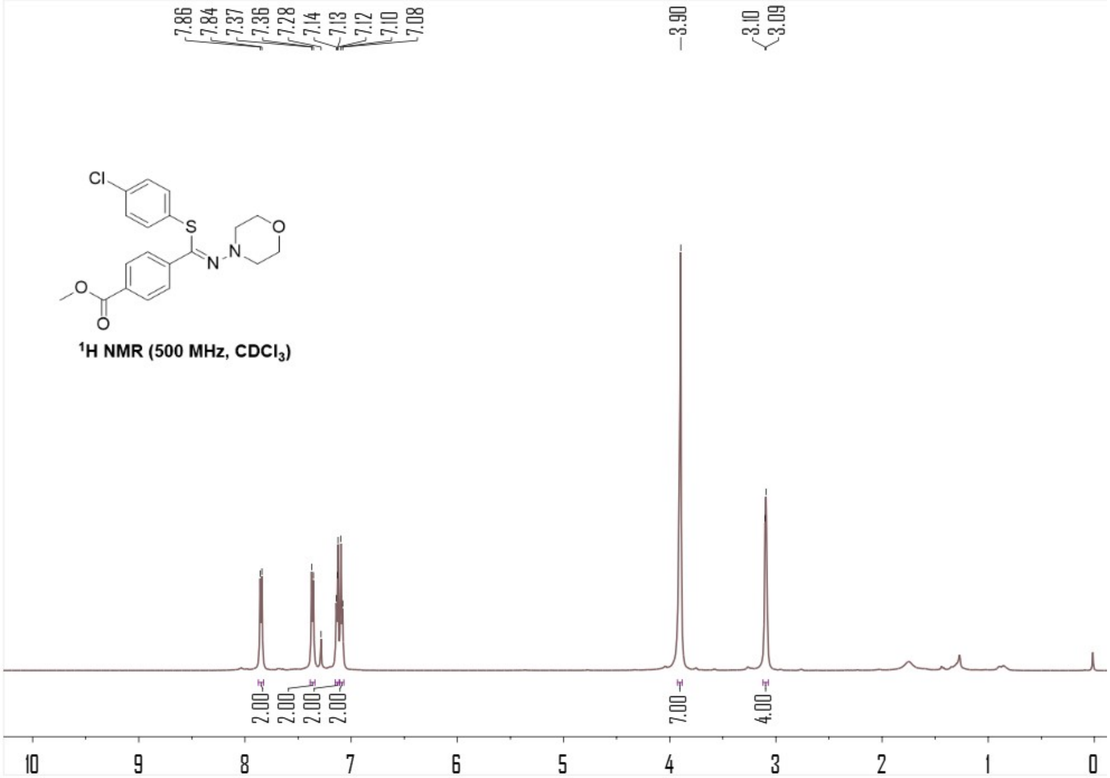
4-Chlorophenyl (*Z*)-*N*-morpholino-4-(trifluoromethyl)benzimidothioate (**3w**)

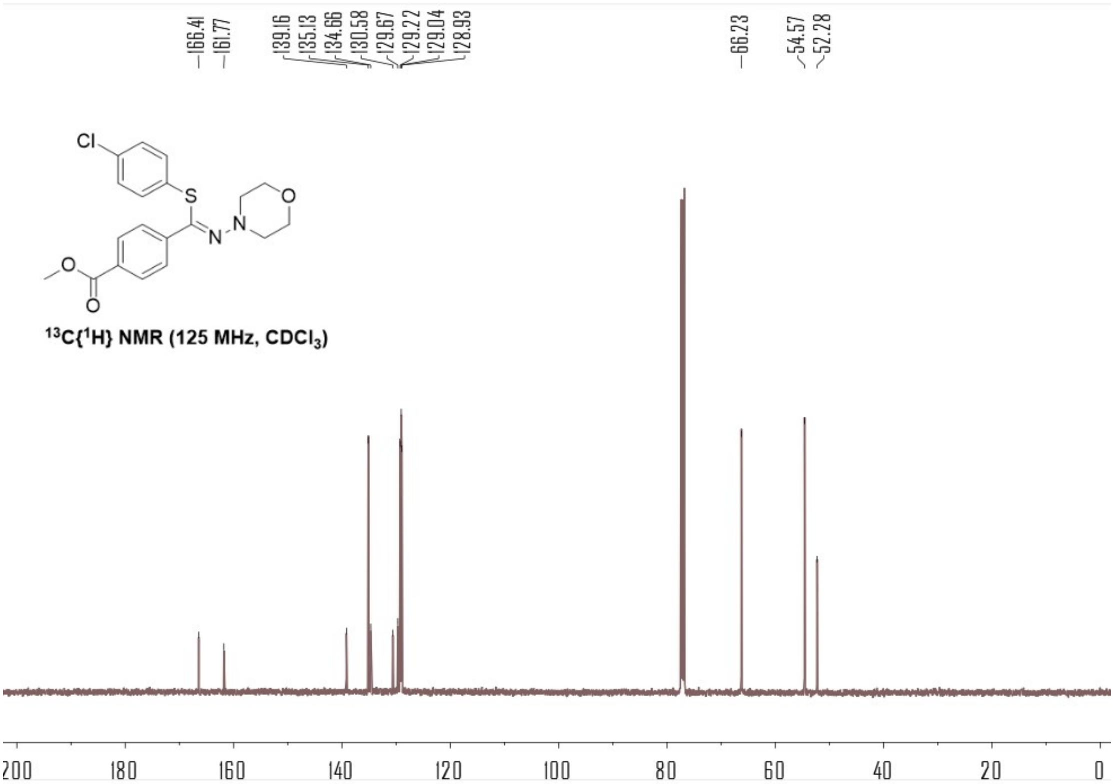




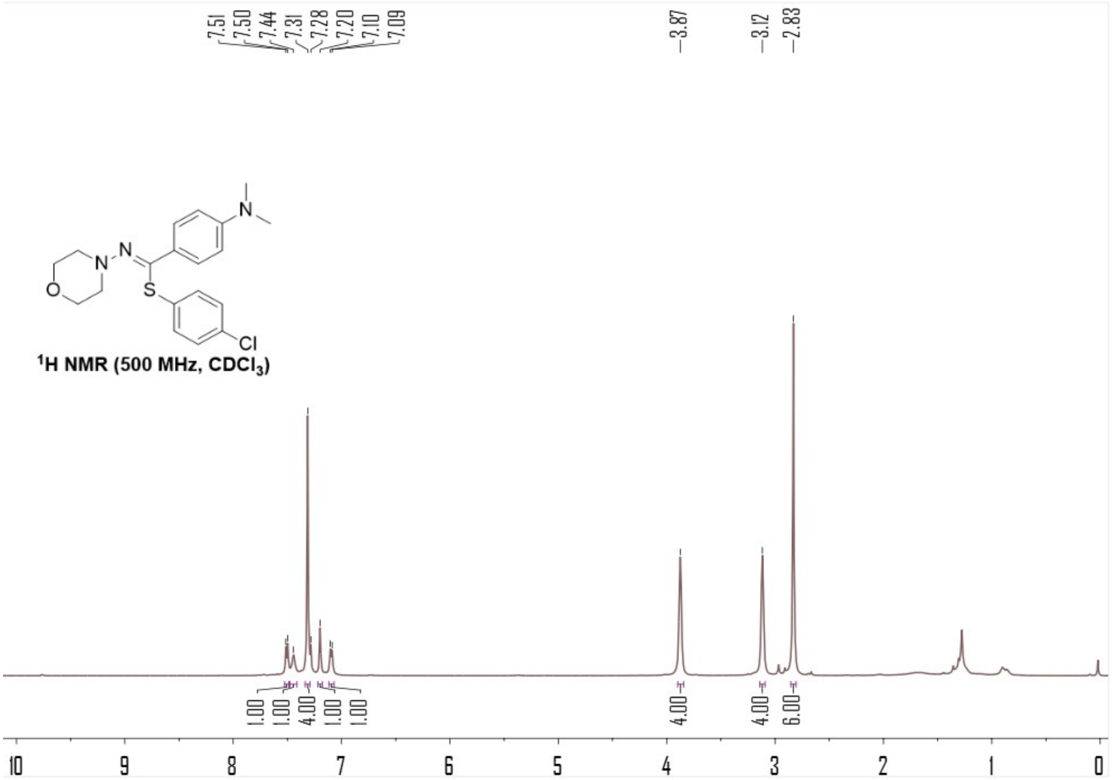


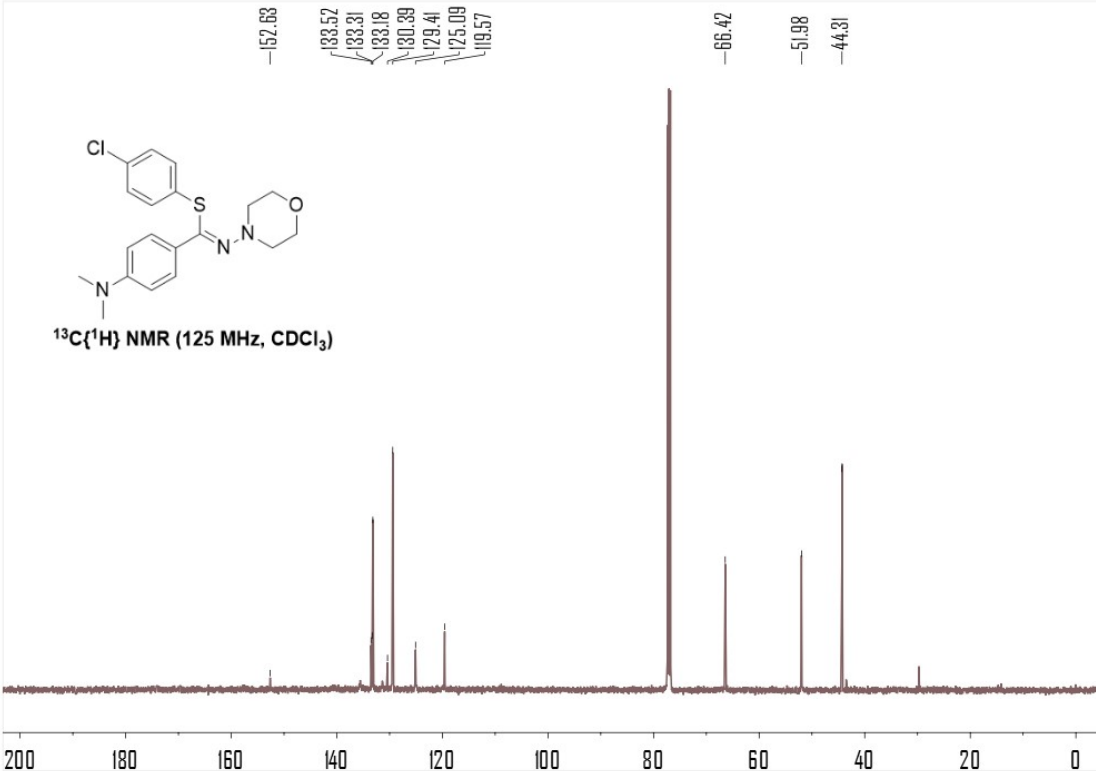
Methyl (*Z*)-4-(((4-chlorophenyl)thio)(morpholinoimino)methyl)benzoate (**3x**)



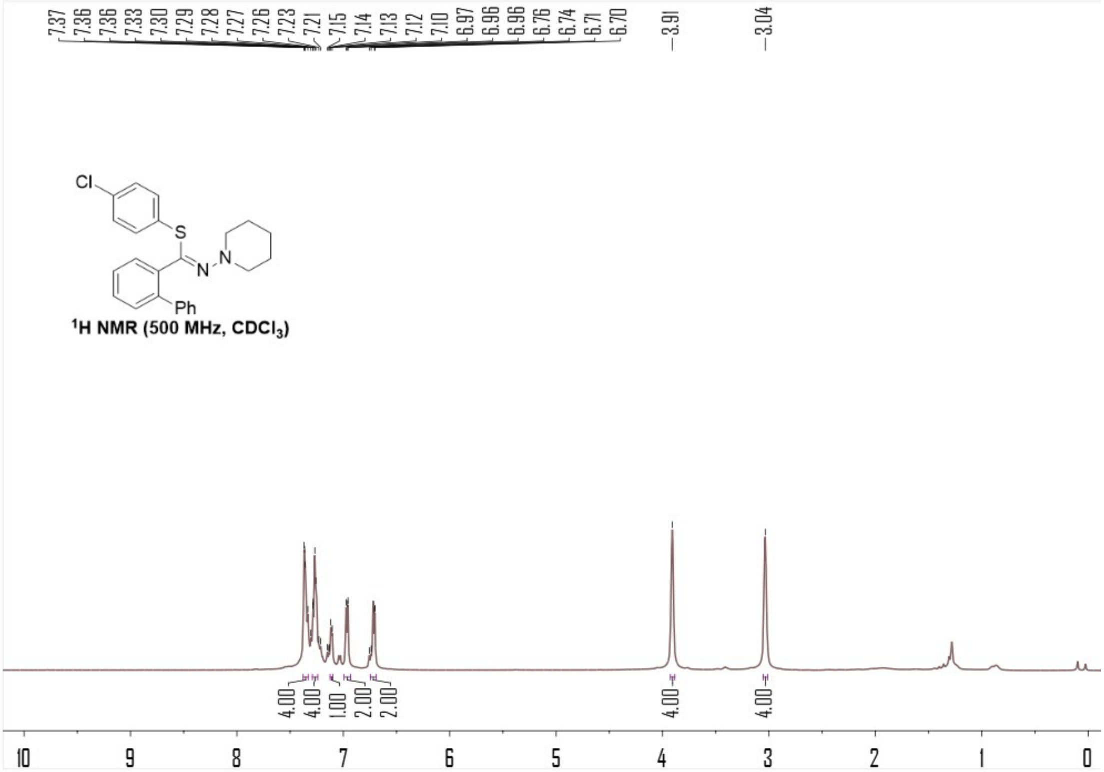


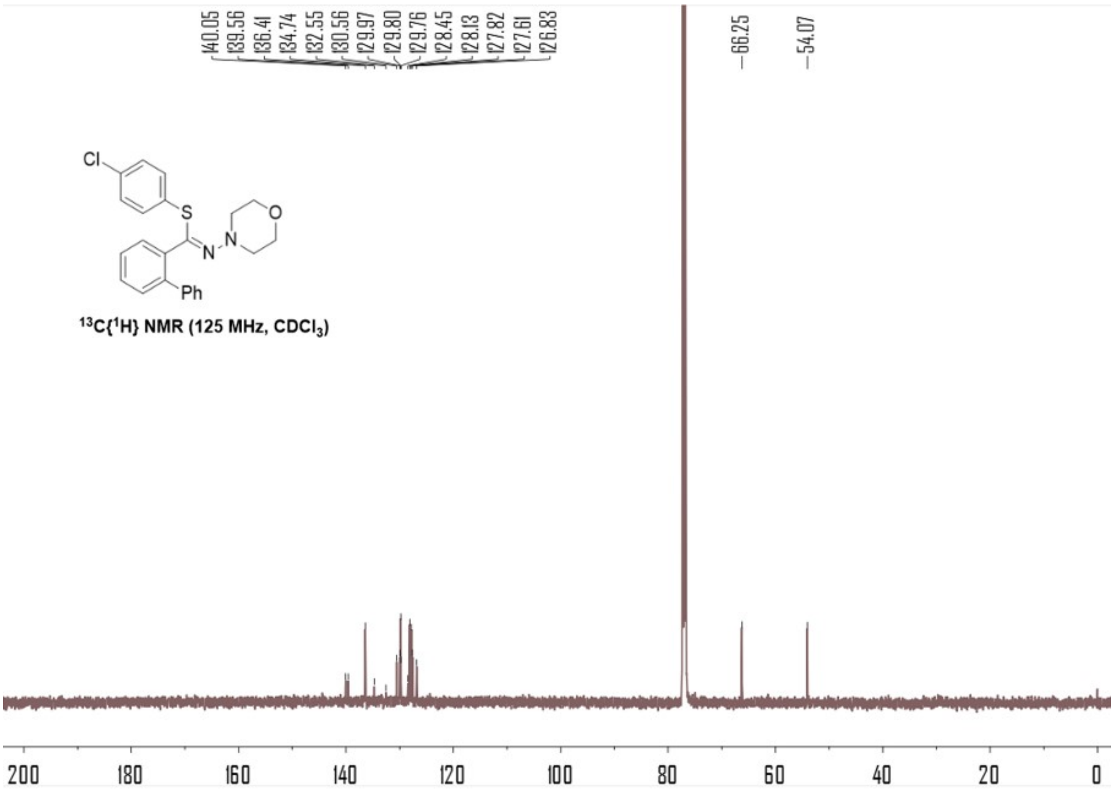
4-Chlorophenyl (*Z*)-4-(dimethylamino)-*N*-morpholinobenzimidothioate (**3y**)



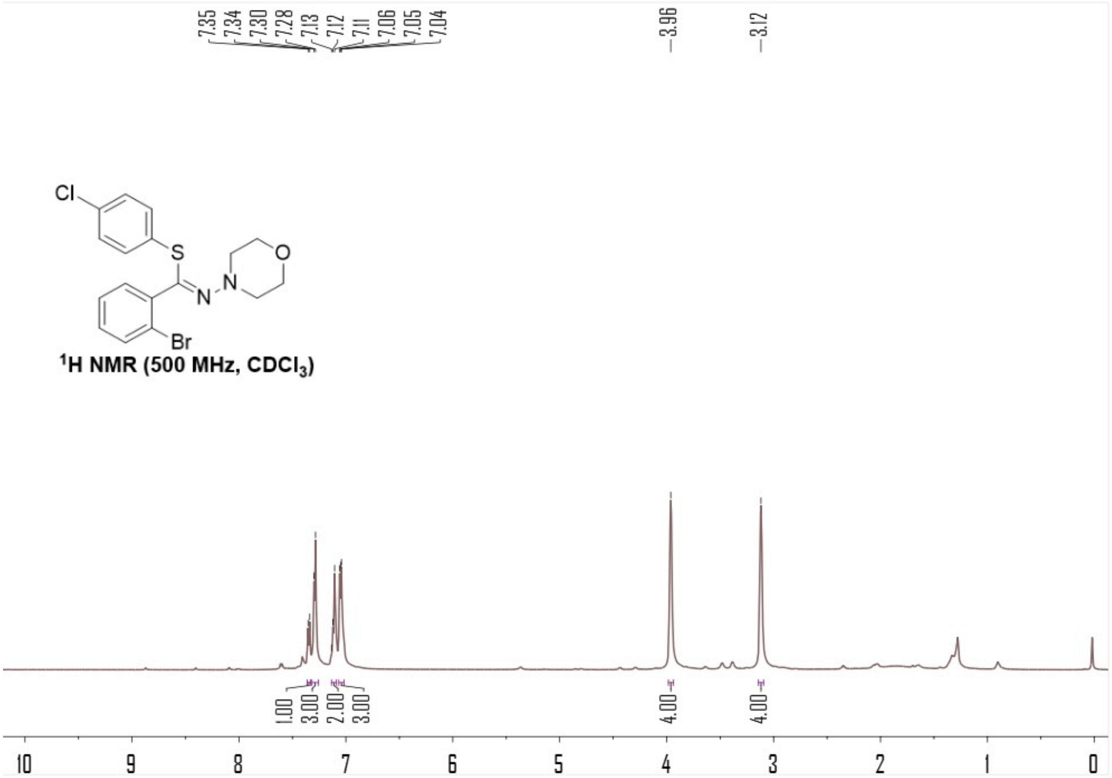


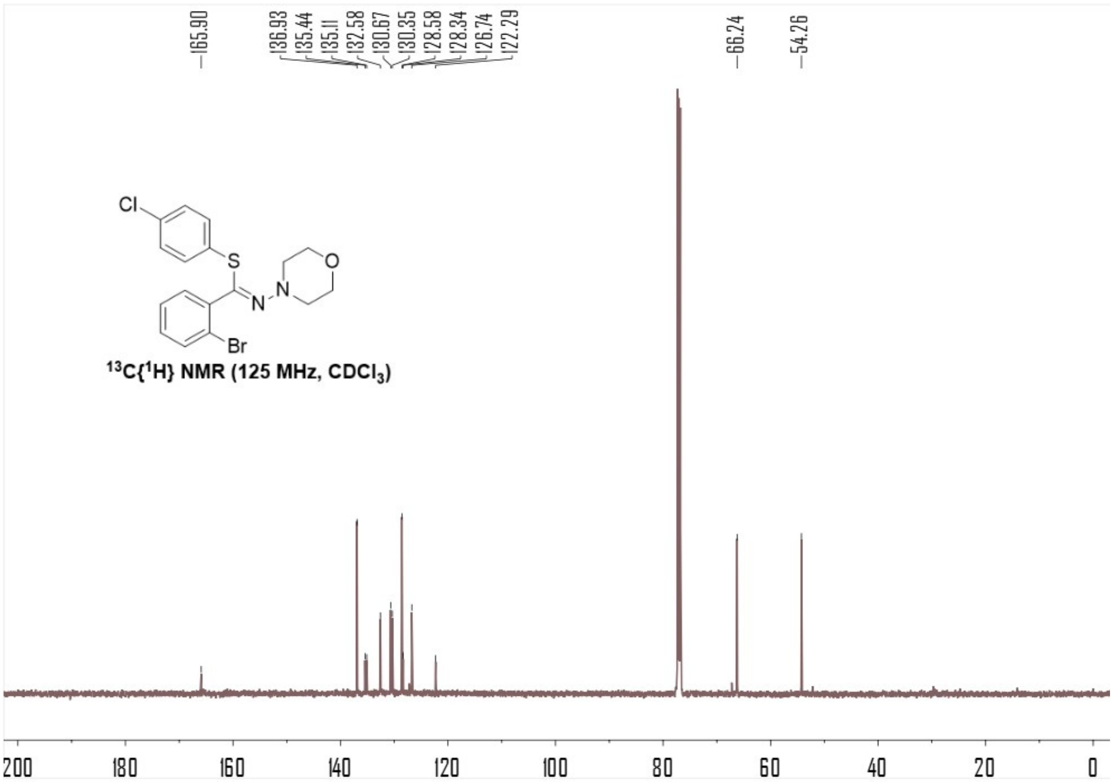
4-Chlorophenyl (*Z*)-*N*-morpholino-[1,1'-biphenyl]-2-carbimidothioate (**3z**)



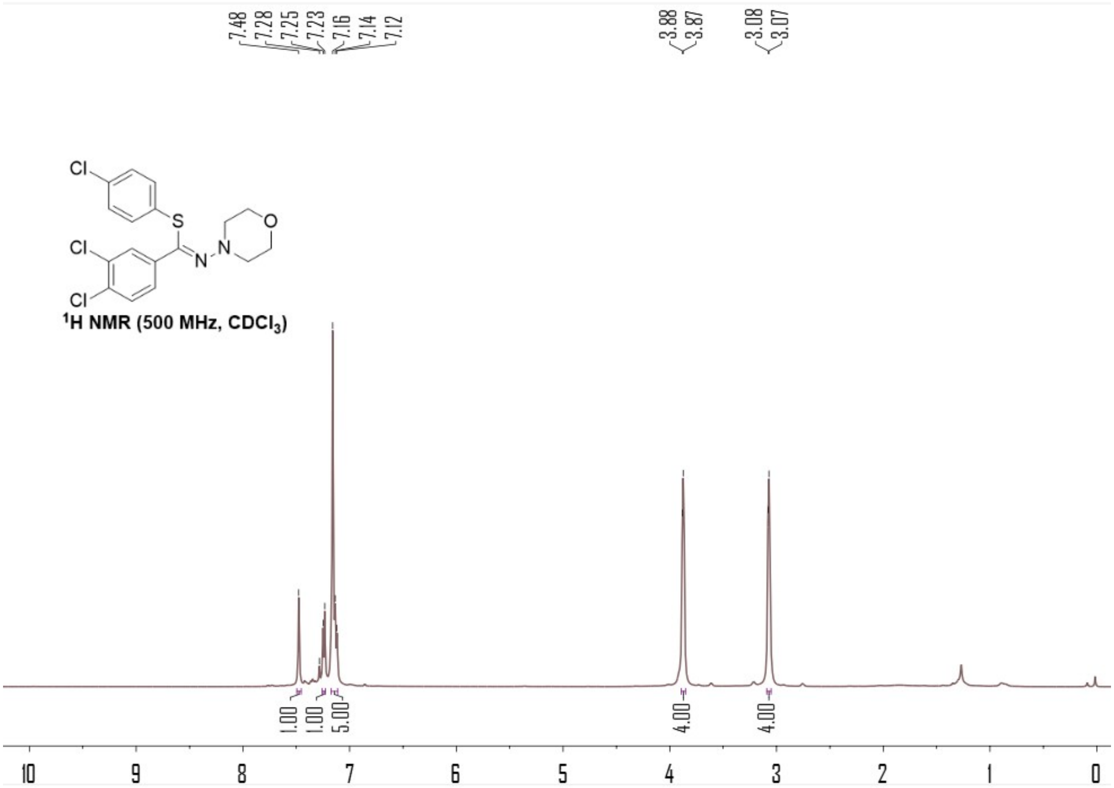


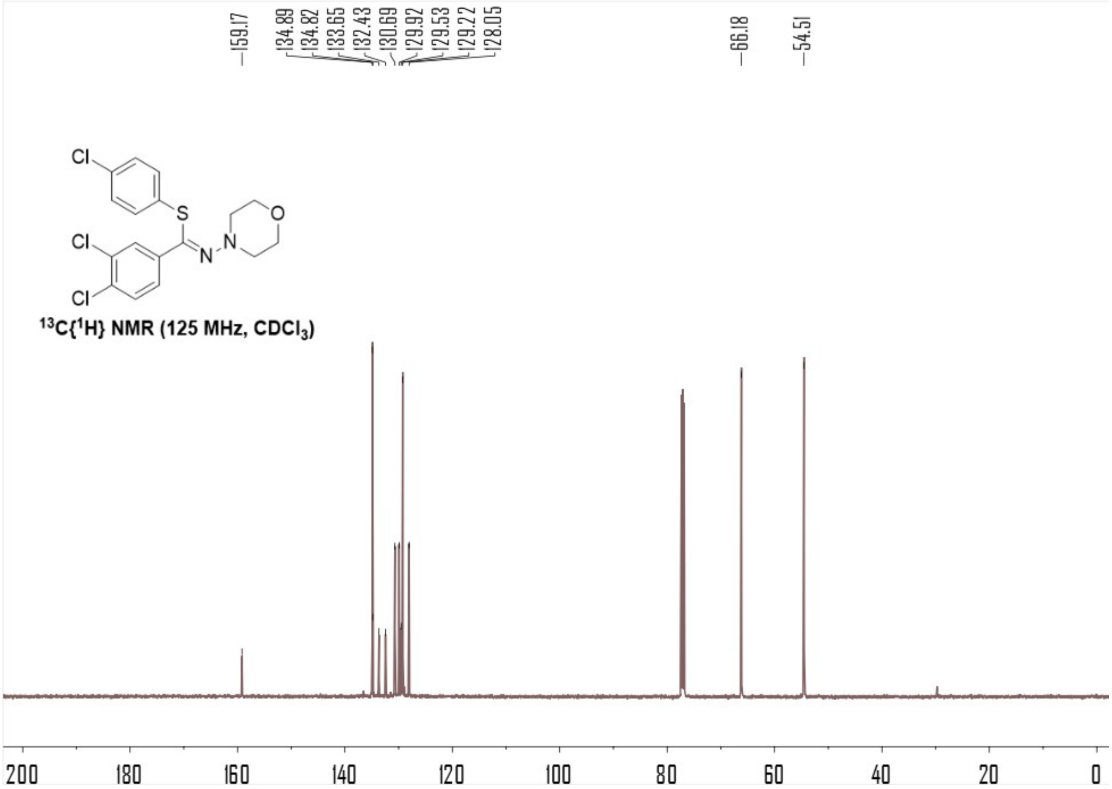
4-Chlorophenyl (*Z*)-2-bromo-*N*-morpholinobenzimidothioate (**3aa**)



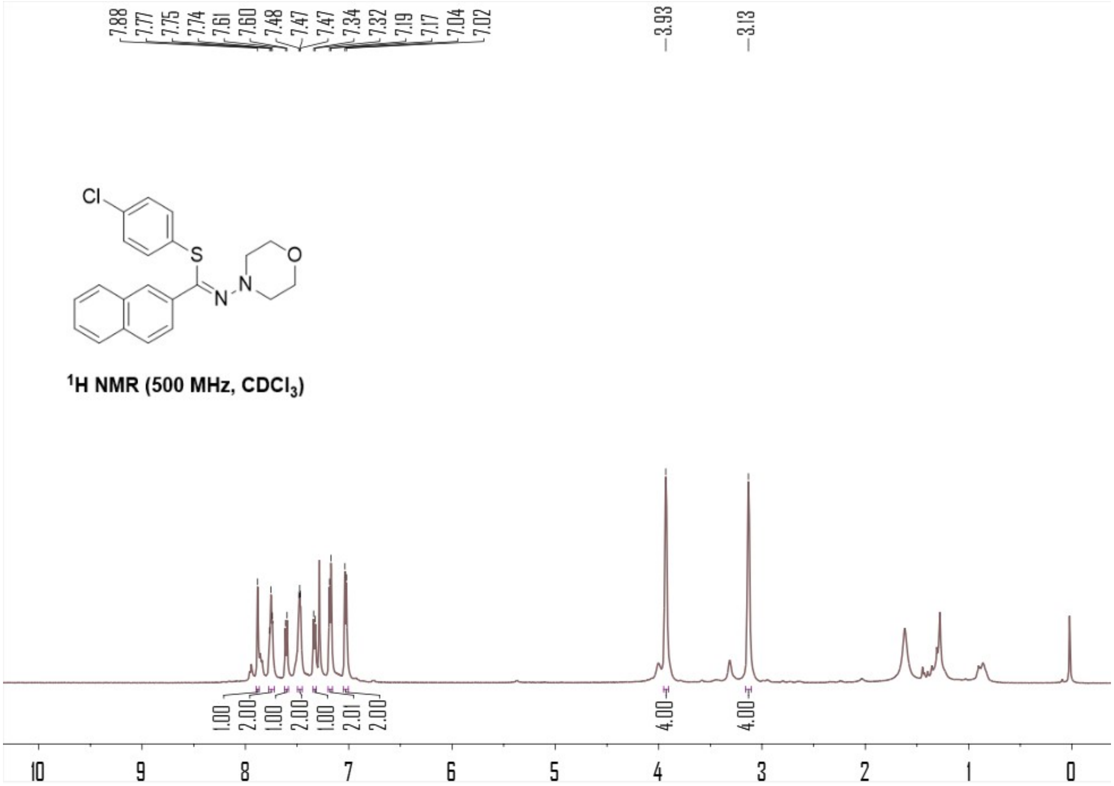


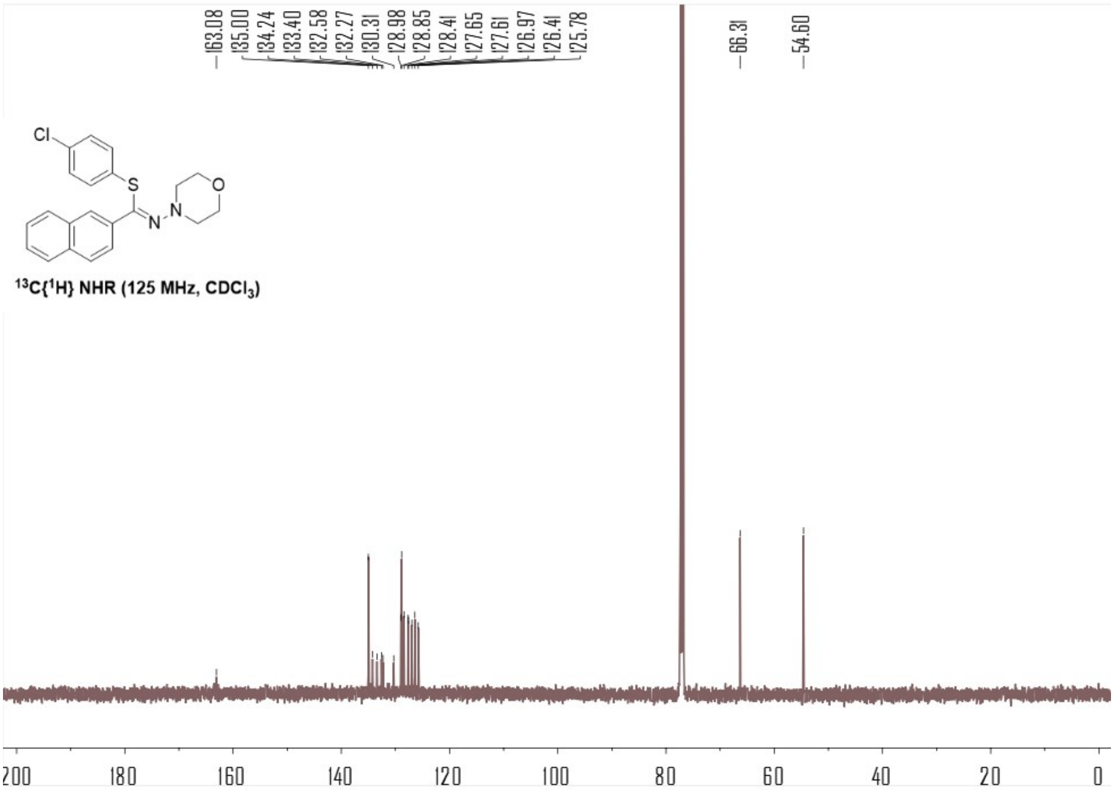
4-Chlorophenyl (*Z*)-3,4-dichloro-*N*-morpholinobenzimidothioate (**3ab**)



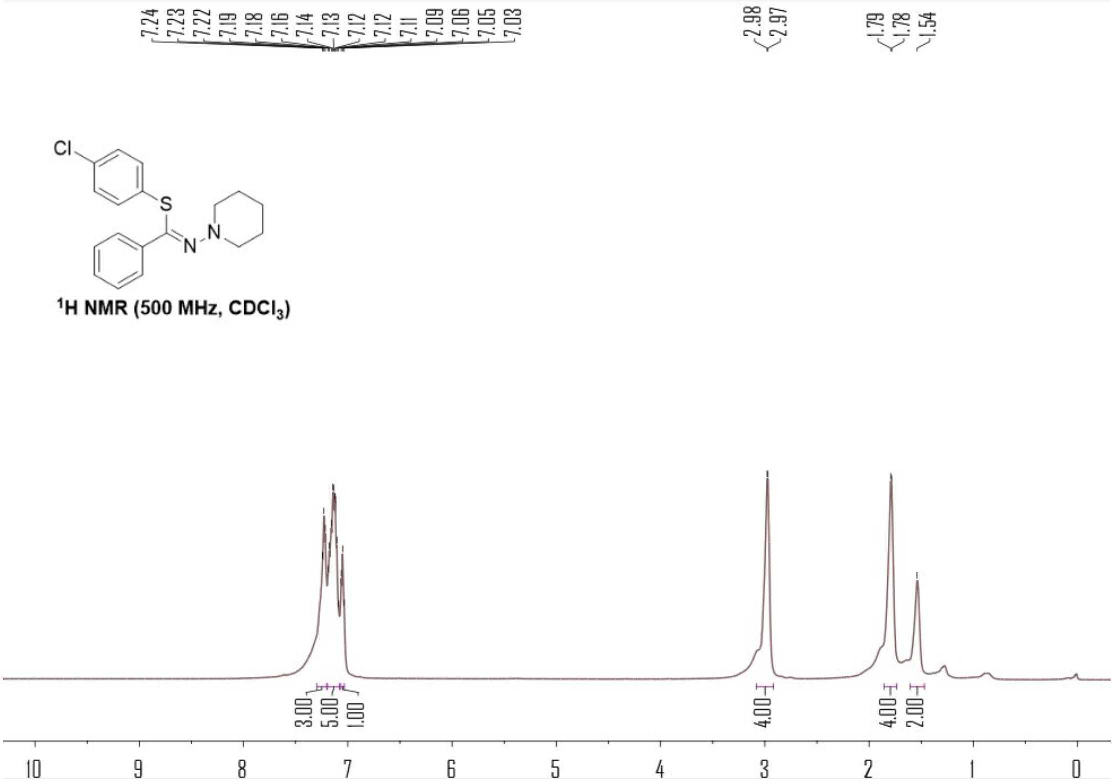


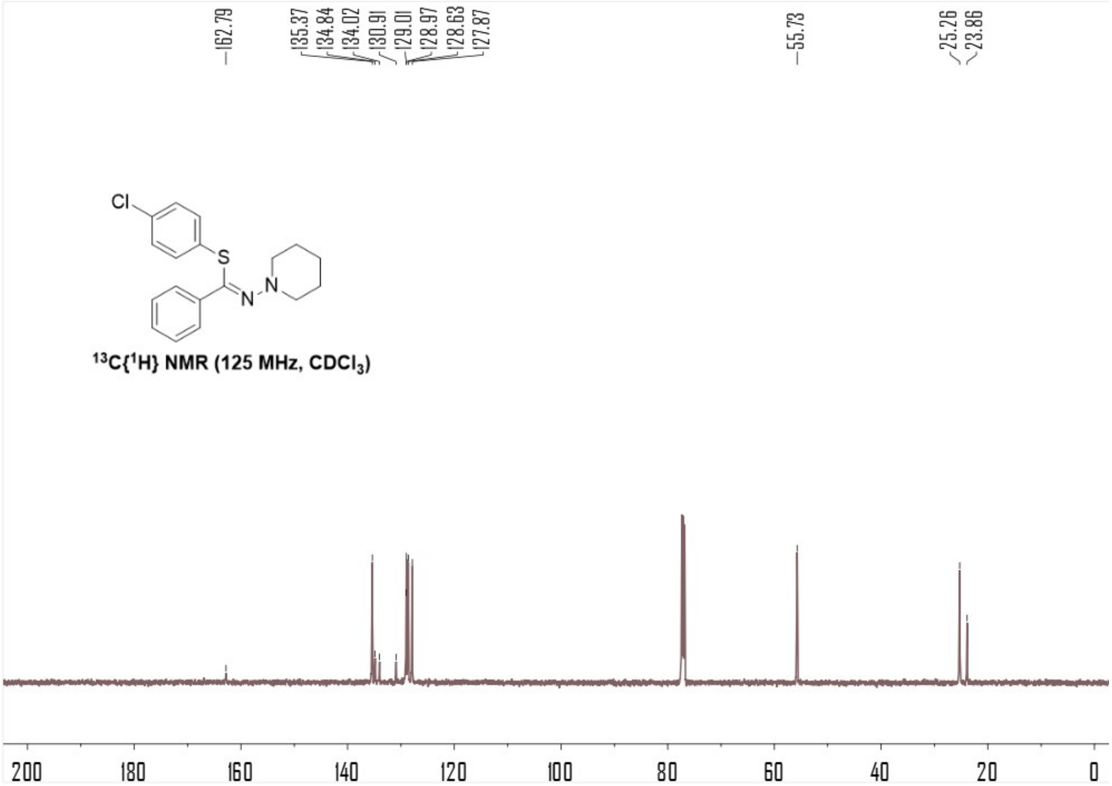
4-Chlorophenyl (*Z*)-*N*-morpholinoquinoline-6-carbimidothioate (**3ac**)



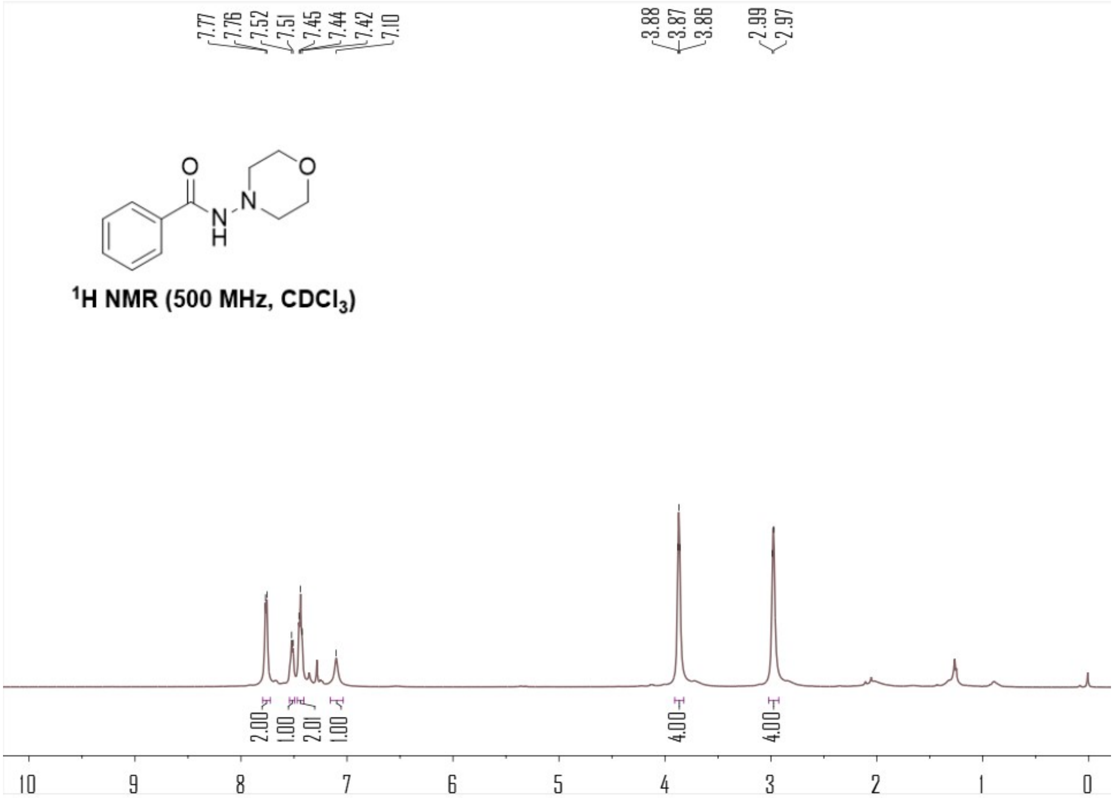


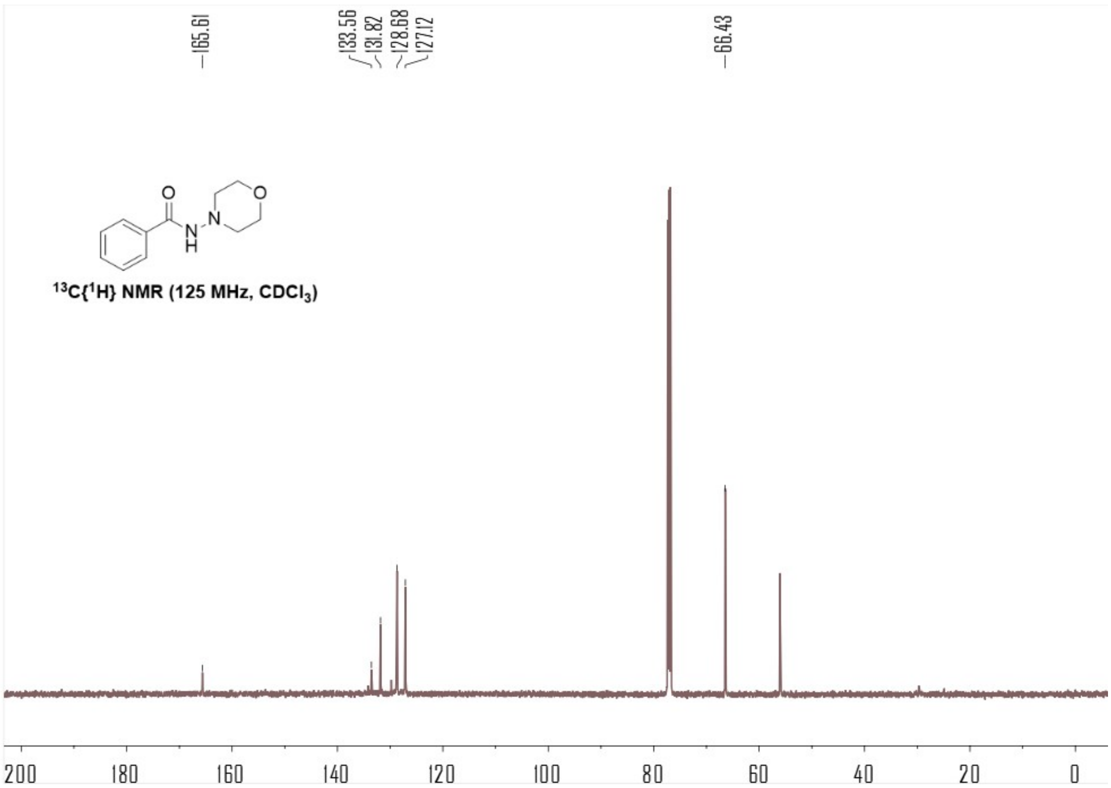
4-Chlorophenyl (*Z*)-*N*-(piperidin-1-yl)benzimidothioate (**3ad**)



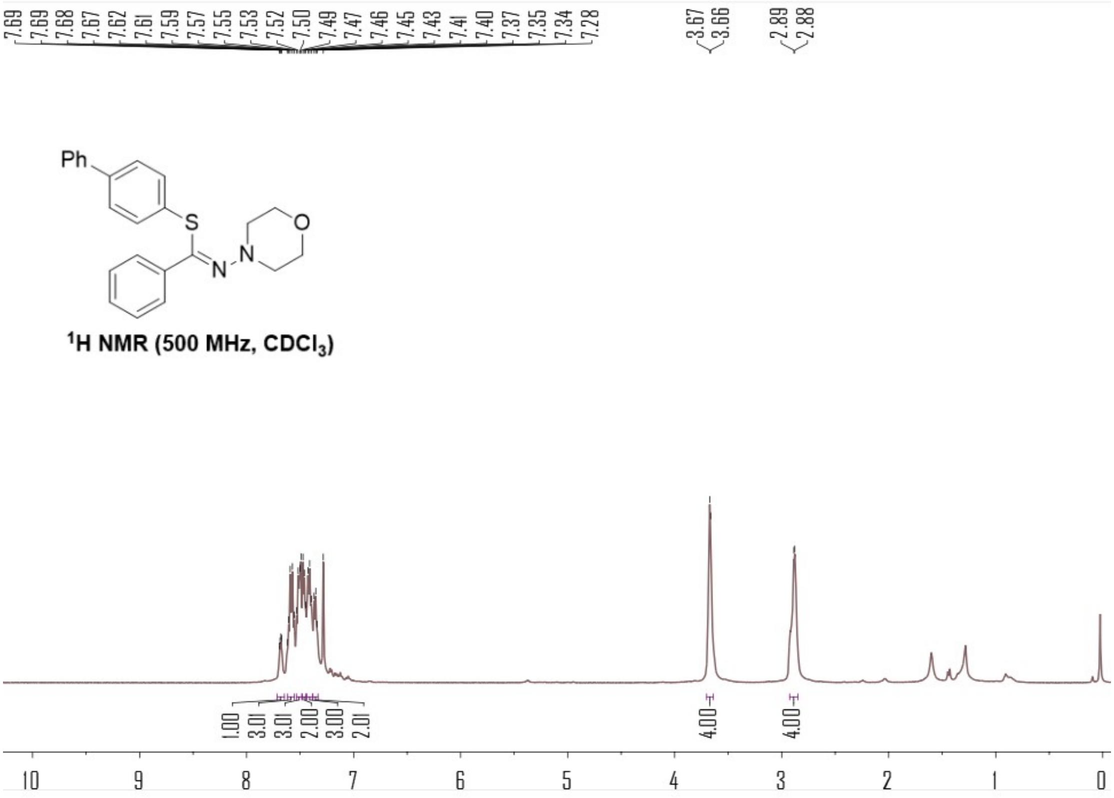


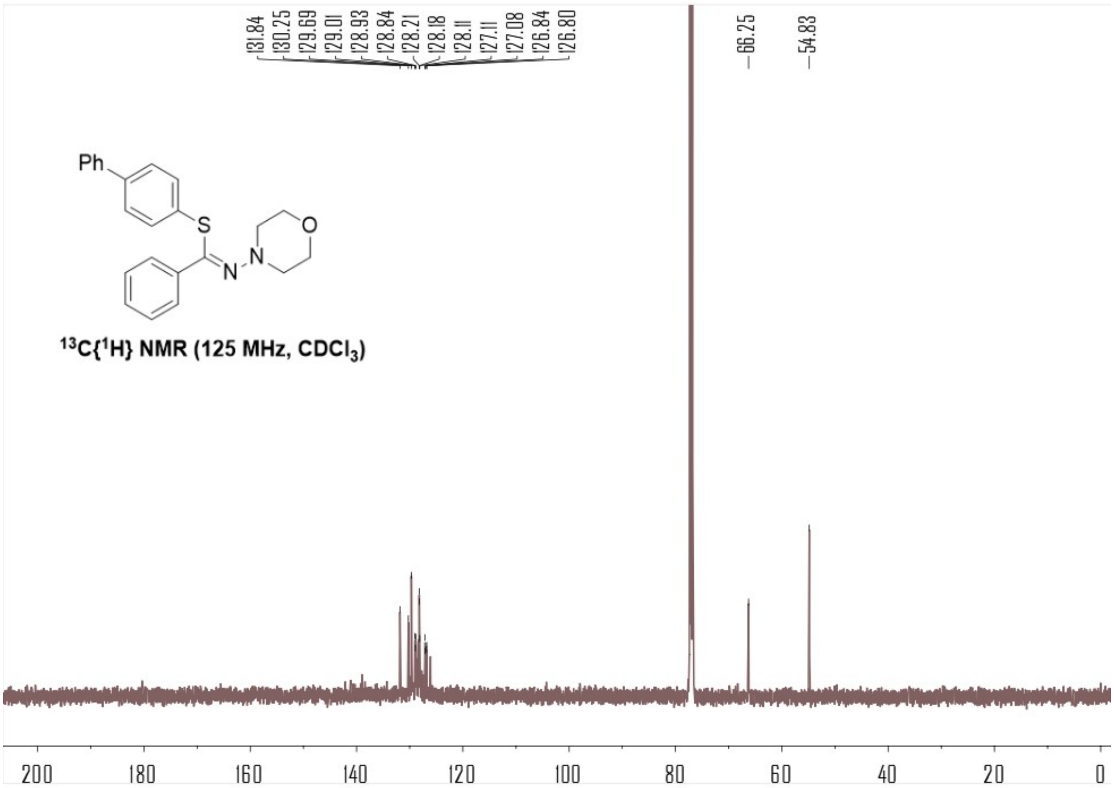
N-Morpholinobenzamide (**6a**)



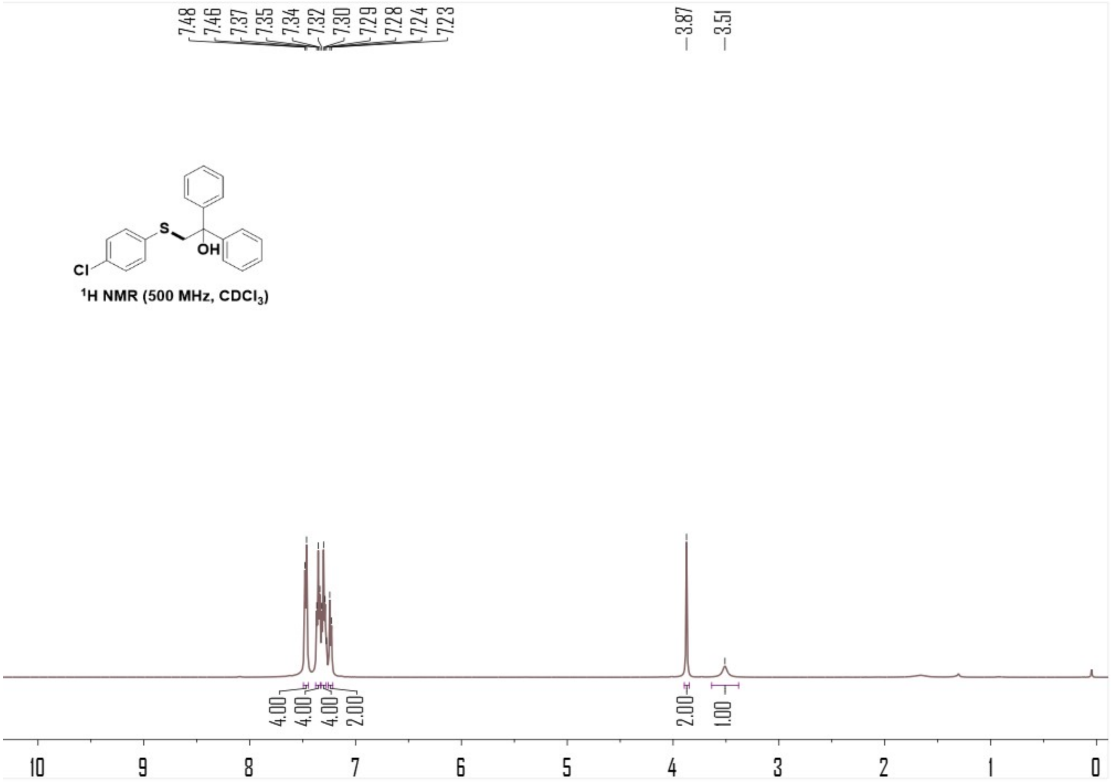


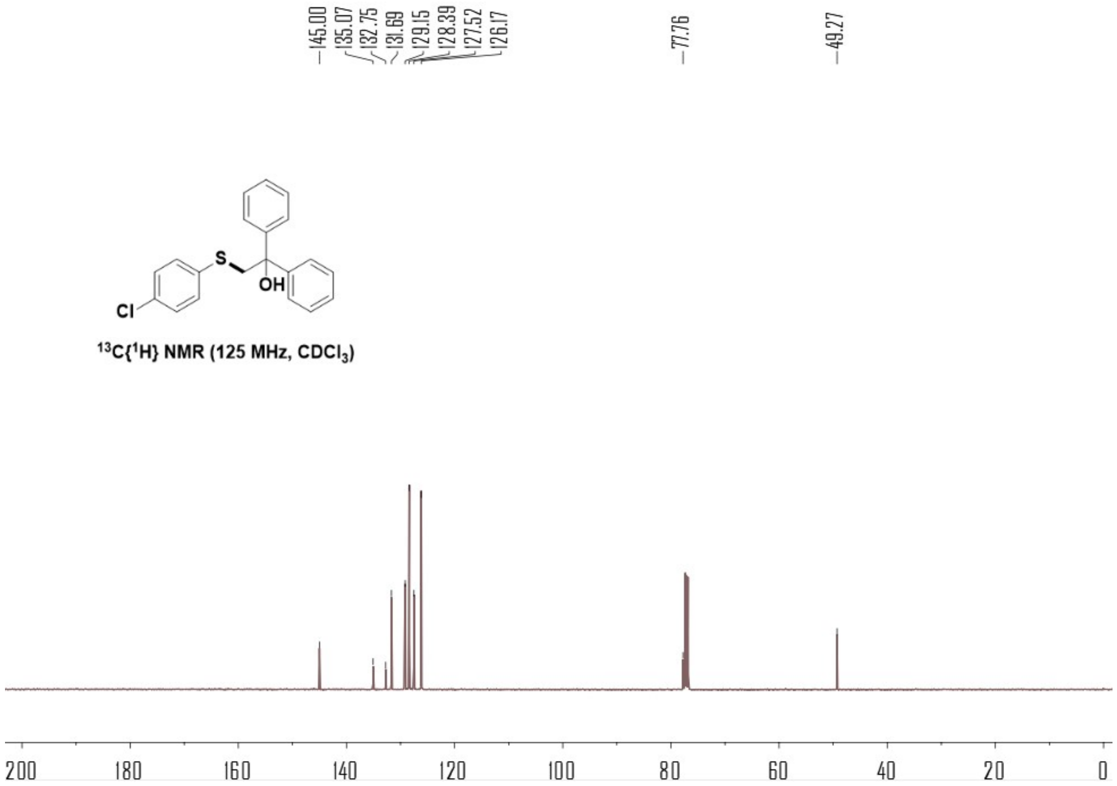
[1,1'-Biphenyl]-4-yl (*Z*)-*N*-morpholinobenzimidothioate (**10a**)





2-((4-Chlorophenyl)thio)-1,1-diphenylethan-1-ol (**11a**)





$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$)

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