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Multicomponent synthesis of di-aryl dithiocarbamates via electron donor–acceptor photoactivation with thianthrenium salts.

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Table of contents

I. General informations. **2**
II. Optimization of reaction conditions. **4**
III. Experimental procedures. **7**
General procedure for the synthesis of S-Aryl Dithiocarbamates. **7**
Gram-scale reaction **8**
IV. Experiments of investigations on the mechanism. **10**
UV-vis absorption spectra **10**
Job's plot **10**
Light on/off experiment **12**
Radical Clock Cyclization Experimet **13**
V. Characterization of products **14**
VI. Reference **31**
VII. NMR spectra **32**

I. General informations.

All reagents were obtained from commercial suppliers and used without further purification. Aryl thianthrenium Salts **2** were prepared from the previous procedures.[1, 4] Yields for all compounds were determined by the column chromatography which was generally performed on silica gel (200-300 mesh) using petroleum ether 40-60 (PE)/EtOAc as eluent, and reactions were monitored by thin layer chromatography (TLC) on a glass pate coated with silica gel with fluorescent indicator (GF254) using UV light. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ADNANCE III 500 MHz using $CDCl_3$ as solvent with TMS as internal standard. Chemical shifts are given in ppm (δ) referenced to $CDCl_3$ with 7.26 for ^{1}H and 77.16 for ^{13}C, and to DMSO-d_6 with 2.50 for ^{1}H and 39.52 for ^{13}C. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, or combinations thereof, and coupling constants are expressed in hertz. Melting points were measured on a SGW® X-4B apparatus and uncorrected. HRMS were recorded on Agilent 6210TOF LC/MS mass spectrometer. UV-visible spectroscopy was recorded on a Shimadzu UV-2250 UV-visible spectrophotometer.

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

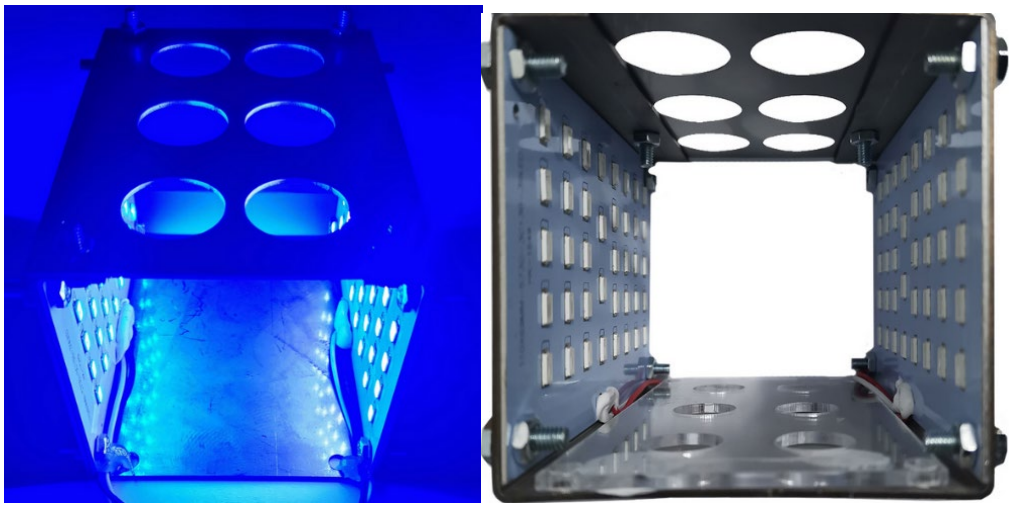
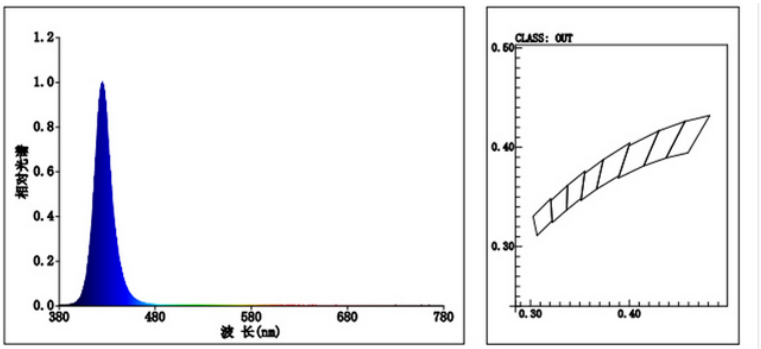


Figure S1. The blue LED lamp.



颜色参数:

色品坐标:x=0.1678 y=0.0129/u'=0.2381 v'=0.0411 duv=-2.453e-001

相关色温:Tc=100000K 主波长:λd=436.9nm 色纯度: Purity=98.9%

色比:R=2.3% G=25.7% B=72.0% 峰值波长:λp=424.6nm 半宽度:Δλd=18.8nm

显色指数:Ra=-64.8

R1 =14 R2 =-39 R3 =-186 R4 =-142 R5 =18 R6 =-39 R7 =-77

R8 =-68 R9 =-206 R10=-254 R11=-152 R12=-121 R13=10 R14=-46 R15=47

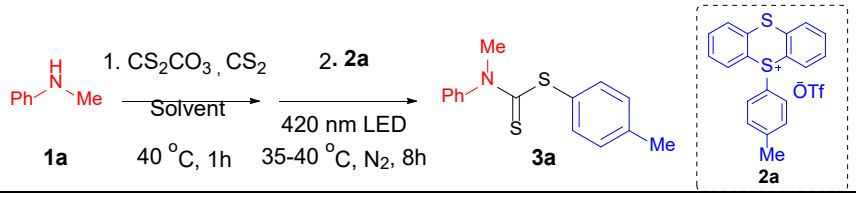
光度参数:

光通量 Φ = 0.9319 lm 光效 : 4.37 lm/W Φe = 82.20 mW

Figure S2. The spectrum of our lamp

II. Optimization of reaction conditions.

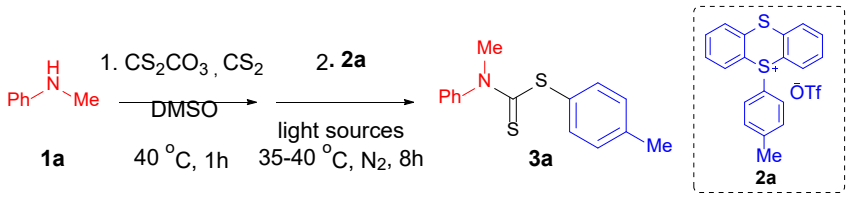
Table S1: Screening of solvents.



Entry [a]	Solvent	Yield of **3a** [b]	Entry [a]	Solvent	Yield of **3a** [b]
1	DMF	52%	5	Acetone	N.D.[c]
2	MeCN	messy	6	PhMe	Trace
3	DCE	N.D. [c]	7	H_2O	44%
4	MeOH	messy	8	DMSO	80%

[a] **1a** (1.0 eq.), CS_2 (2.0 eq.) and CS_2CO_3 (2.0 eq.) were dissolved in solvent (2 mL), stirred for 1h at 40 °C; then **2a** (0.2 mmol) was added, irradiation with 10w blue LED (420 nm) at room temperature (~35-40 °C) under N_2 for 8h. [b] Isolated yield. [c] N.D. = No detected.

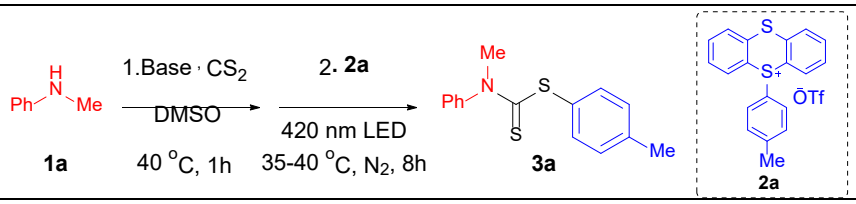
Table S2: Screening of light sources.



Entry [a]	Light source	Yield of **3a** [b]
1	420 nm (10 W)	80%
2	460 nm (10 W)	70%
3	395 nm (10 W)	44%
4	White CFL	48%
5	Dark	0%

[a] **1a** (1.0 eq.), CS_2 (2.0 eq.) and CS_2CO_3 (2.0 eq.) were dissolved in DMSO (2 mL), stirred for 1h at 40 °C; then **2a** (0.2 mmol) was added, irradiation with different lights at room temperature (~35-40 °C) under N_2 for 8h. [b] Isolated yield.

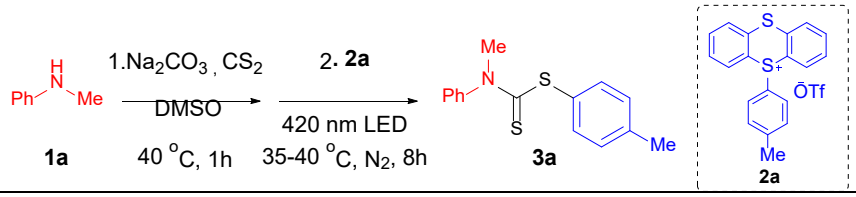
Table S3: Screening of bases.



Entry [a]	Base	Yield of **3a** [b]	Entry [a]	Base	Yield of **3a** [b]
1	NaOH	N. D. [c]	5	CsF	75%
2	K_2CO_3	63%	6	KOH	59%
3	Na_2CO_3	80%	7	Et_3N	55%
4	K_3PO_4	messy	8	none	N. R. [d]

[a] **1a** (1.0 eq.), CS_2 (2.0 eq.) and base (2.0 eq.) were dissolved in DMSO (2 mL), stirred for 1h at 40 °C; then **2a** (0.2 mmol) was added, irradiation with10w blue LED (420 nm) at room temperature (~35-40 °C) under N_2 for 8h. [b] Isolated yield. [c] N.D. = No detected. [d] N.R. = No reaction.

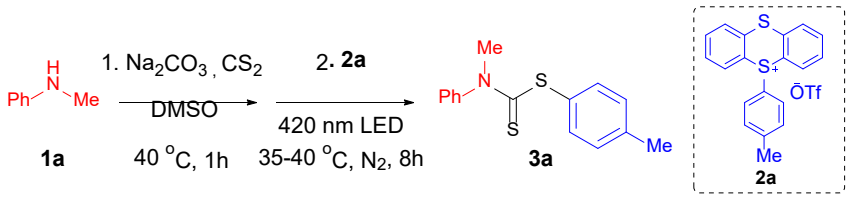
Table S4: Screening of the amount of CS_2 and Na_2CO_3



Entry [a]	CS_2 (X eq.)	Na_2CO_3 (X eq.)	Yield of **3a** [b]	Entry [a]	CS_2 (X eq.)	Na_2CO_3 (X eq.)	Yield of **3a** [b]
1	1.0	2.0	37%	4	1.5	2.0	52%
2	1.0	1.1	40%	5	2.5	2.0	70%
3[c]	2.0	2.0	74%	6	2.0	1.1	80%

[a] **1a** (1.0 eq.), CS_2 (X eq.) and Na_2CO_3 (X eq.) were dissolved in DMSO (2 mL), stirred for 1h at 40 °C; then **2a** (0.2 mmol) was added, irradiation with 10w blue LED (420 nm) at room temperature (~35-40 °C) under N_2 for 8h. [b] Isolated yield. [c] **1a** (1.0 eq.), CS_2 (2 eq.), Na_2CO_3 (2.0 eq.) and **2a** (0.2 mmol) were dissolved in solvent. irradiation with 10w blue LED (420 nm) at room temperature (~35-40 °C) under N_2 for 8h.

Table S5: Screening of the mixture solvents and others

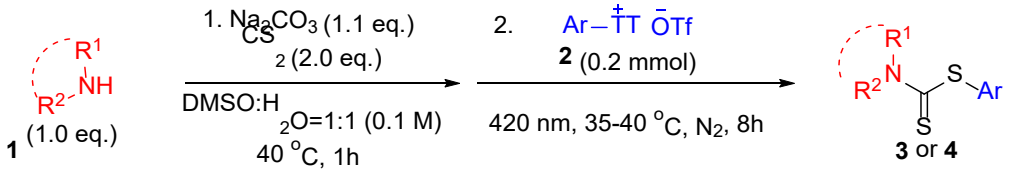


Entry [a]	Solvent	Yield of **3a** [b]
1	DMSO (1 mL)	59%
2	DMSO (4 mL)	45%
3	DMSO : H_2O (0.4 mL : 1.6 mL)	55%
4	DMSO : H_2O (1.0 mL : 1.0 mL)	81%
5	DMSO : H_2O (0.5 mL : 0.5 mL)	74%
6[c]	DMSO : H_2O (1.0 mL : 1.0 mL)	50%
7[d]	DMSO : H_2O (1.0 mL : 1.0 mL)	60%
8[d]	DMSO (2 mL)	56%

[a] **1a** (1.0 eq.), CS_2 (2 eq.) and Na_2CO_3 (1.1 eq.) were dissolved in solvent (X mL), stirred for 1h at 40 °C; then **2a** (0.2 mmol) was added, irradiation with 10w blue LED (420 nm) at room temperature (~35-40 °C) under N_2 for 8h. [b] Isolated yield. [c] air atmosphere. [d] **1a** (1.0 eq.), CS_2 (2 eq.), Na_2CO_3 (1.1 eq.) and **2a** (0.2 mmol) were dissolved in solvent. irradiation with 10w blue LED (420 nm) at room temperature (~35-40 °C) under N_2 for 8h.

III. Experimental procedures.

General procedure for the synthesis of S-Aryl Dithiocarbamates.



General procedure A: To a 5 mL glass tube was charged with secondary aromatic or aliphatic amine (1.0 equiv), CS_2 (25 μL, 0.4 mmol, 2.0 eq.), and Na_2CO_3 (23.3 mg, 0.22 mmol, 1.1 equiv) in 2 mL mixture solvent (DMSO : H_2O = 1 mL : 1 mL) for 1h at 40 °C, then aryl thianthrenium salt **2** (0.2 mmol) was added, the tube was sealed with a rubber plug and purged with N_2 for three times. The reaction was stirred and irradiated with a 420 nm blue LEDs (approximately 2 cm away from the light source) at room temperature (the actual reaction temperature is about 35~40 °C) for 8 h. The reaction mixture was diluted with 25.0 mL of dichloromethane, followed by washing with 5 mL of H_2O. The dichloromethane layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography (eluent: PE/AcOEt) to provide the products **3** or **4**.

General procedure B: To a 5 mL glass tube was charged with secondary aromatic or aliphatic amine (1.0 equiv), CS_2 (25 μL, 0.4 mmol, 2.0 eq.), and Cs_2CO_3 (130.4 mg, 0.4 mmol, 2.0 equiv) in 2 mL mixture solvent (DMSO : H_2O = 1 mL : 1 mL) for 5h at 40 °C, then aryl thianthrenium salt **2** (0.2 mmol) was added, the tube was sealed with a rubber plug and purged with N_2 for three times. The reaction was stirred and irradiated with a 420 nm blue LEDs (approximately 2 cm away from the light source) at room temperature (the actual reaction temperature is about 35~40 °C) for 12 h. The reaction mixture was diluted with 25.0 mL of dichloromethane, followed by washing with 5 mL x 2 of H_2O. The dichloromethane layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography (eluent: PE/AcOEt) to provide the products **3m-q**.

General procedure C: To a 5 mL glass tube was charged with secondary aromatic or aliphatic amine (1.0 equiv) and CS_2 (25 μL, 0.4 mmol, 2.0 eq.) in 1.5 mL anhydrous DMSO at 0 °C, the tube was sealed with a rubber plug and purged with N_2 for three times. Then ^{n}-BuLi (0.27 mL, 1.5 M in THF, 0.4 mmol, 2.0 equiv) was added slowly, and warm to 40 °C gradually, stirred for 5h. Finally, aryl thianthrenium salt **2** (0.2 mmol) was added, the reaction was stirred and irradiated with a 420 nm blue LEDs (approximately 2 cm away from the light source) at room temperature (the actual reaction temperature is about 35~40 °C) for 8 h. The reaction mixture quenched with aqueous NH_4Cl solution, followed by diluting with 25.0 mL of dichloromethane and washing with 5.0 mL x 2 of H_2O. The dichloromethane layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography (eluent: PE/AcOEt) to provide the products **3h** and **3j**.

Gram-scale reaction

To a 100 mL Three-necked flask equipped with a magnetic stir bar, added *N*-methylaniline **1a** (0.55 mL, 5 mmol), CS_2 (0.63 mL, 10 mmol), and Na_2CO_3 (0.59 g, 5.5 mmol) in DMSO (50 mL). The mixture was stirred for 1h at 40 °C before the aryl thianthrenium salt **2a** (2.28 g, 5 mmol) was added. Then the Three-necked flask was connected to a peristaltic pump with teflon catheters as shown in **Figure S3**. And the whole unit was purged with N_2 for three times. The reaction was initiated by the peristaltic pump with a flow rate 10.0 mL min^{-1} under 420 nm blue LEDs for 5h at room temperature. The reaction mixture was diluted with 300 mL of dichloromethane, followed by washing with 50 mL X 2 of H_2O. The dichloromethane layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography (PE/AcOEt = 70 : 1) to provide the product **3a** as a yellow solid (0.90 g, 66%)**.** Additionally, the thianthrenium (TT) **2a'** was recovered as a white solid (0.97 g, 90%).

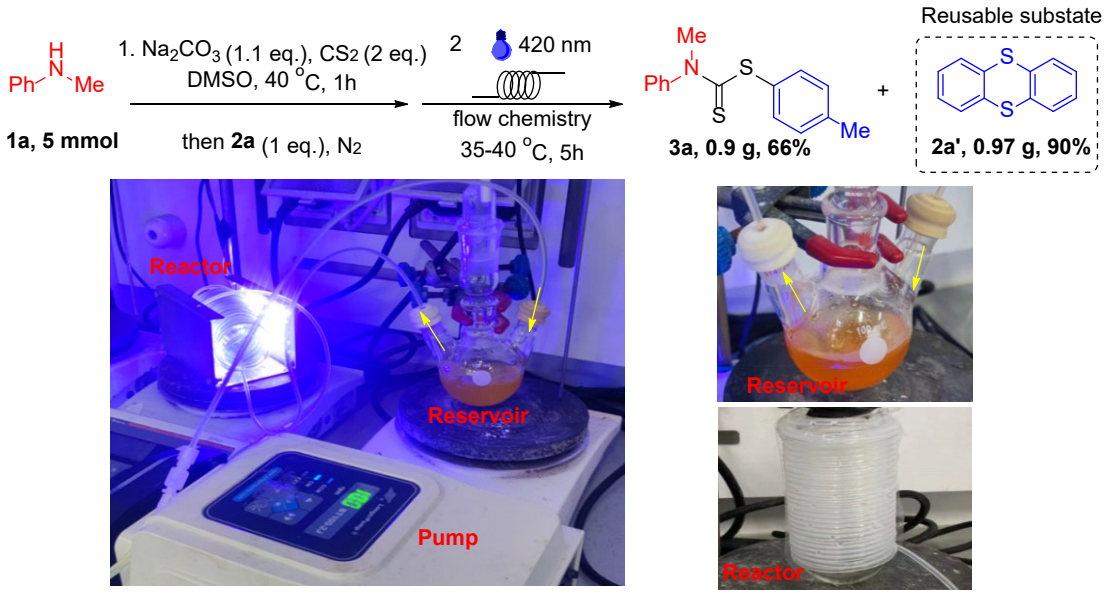


Figure S3. Gram-scale experiment

IV. Experiments of investigations on the mechanism.

UV-vis absorption spectra

UV/vis absorption spectra were measured in a 1 cm quartz cuvette using a Shimadzu UV-2250 UV/Visible spectrophotometer. Absorption spectra of individual reaction components and mixtures thereof were recorded as shown in **Figure S4**. A bathochromic shift was observed for a mixture of 0.05 M [**1a** + thianthrenium salt **2a** + CS2 + Et_3N] in DMSO, which was a visibly intense yellow in color. This indicates the formation of an electron donor-acceptor (EDA) complex (red line 3).

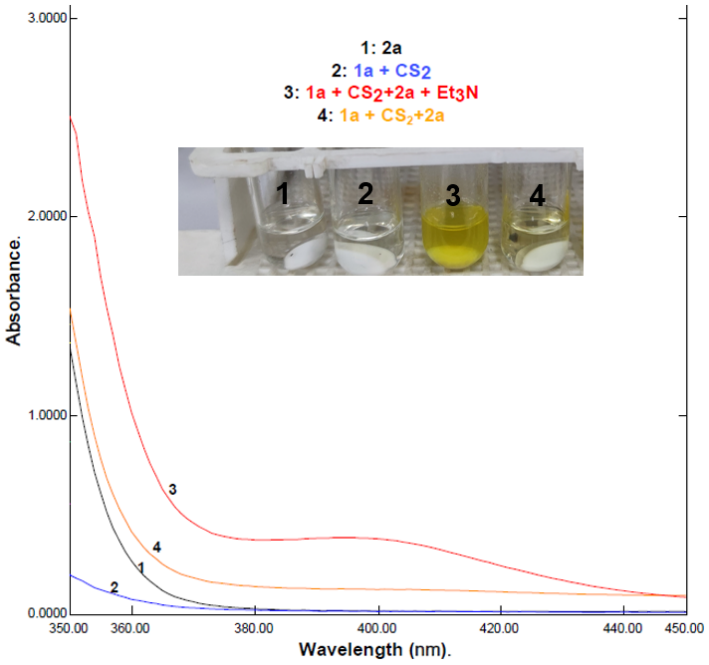


Figure S4. UV-vis absorption spectra of various combinations

Job's plot

Two equimolar (0.02 M) solution of **2a** and **5a (**where **5a** was generated [2] through the reaction of CS_2 and **1a** in the presence of Et_3N) in DMSO were prepared. Then 7 samples were prepared with specific volumes of the two stock solutions to give a total volume of 4 mL and were analysed by UV/vis spectroscopy. The absorbance values at 420 nm (corresponding to the EDA complex's absorption) were measured (**Table S6**)

and plotted as a function of the molar fraction of thiolate **5a** by using UV/vis spectroscopy (**Figure S5**). A parabolic curve with a maximum absorbance value at 50% mol fraction of thianthrenium salt **2a** was obtained, indicating a 1:1 EDA complex between **2a** and the conjugated base of **5a**.

Table S6. The absorbance values of various combinations of **2a** and **5a**

V_{2a} (mL)	V_{5a} (mL)	Xi_{2a}	Xi_{5a}	δA_{2a}^{420}	$\Delta(\delta A_{2a}^{420}) * Xi_{2a}$
3.5	0.5	0.875	0.125	0.1851	0.1620
3.0	1.0	0.750	0.250	0.3000	0.2250
2.5	1.5	0.625	0.375	0.5034	0.3146
2.0	2.0	0.500	0.500	0.6678	0.3339
1.5	2.5	0.375	0.625	0.7836	0.2939
1.0	3.0	0.250	0.750	0.9800	0.2450
0.5	3.5	0.125	0.875	1.0847	0.1356

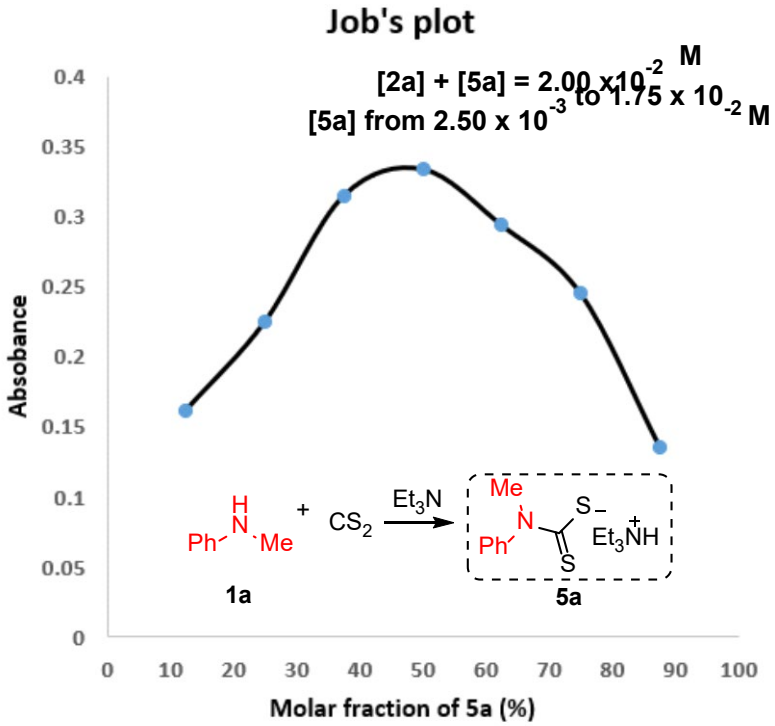


Figure S5. Job's plot for ratio between **2a** and **5a**

Light on/off experiment

To a 5 mL glass tube was charged with *N*-methylaniline **1a** (55 μL, 0.5 mmol), CS_2 (63 μL, 1.0 mmol), and Na_2CO_3 (58.3 mg, 0.55 mmol) in 5 mL DMSO for 1h at 40 °C, then aryl thianthrenium (TT) salt **2a** (228 mg, 0.5 mmol) was added, the tube was sealed with a rubber plug and purged with N_2 for three times. The reaction was stirred and irradiated with a 420 nm blue LEDs (approximately 2 cm away from the light source) at room temperature (the actual reaction temperature is about 35~40 °C) for 1h at which point a reaction aliquot (0.5 mL) was taken, and diluted with $CDCl_3$ and analysed by ^1H NMR spectroscopy with anisole as an internal standard. The light was switched off and the mixture was stirred in the dark for 1h at which point a reaction aliquot (0.5 mL) was taken, and diluted with $CDCl_3$ and analysed by ^1H NMR spectroscopy with anisole as an internal standard. Repeat the above operations until 7th hour. (**Figure S6**)

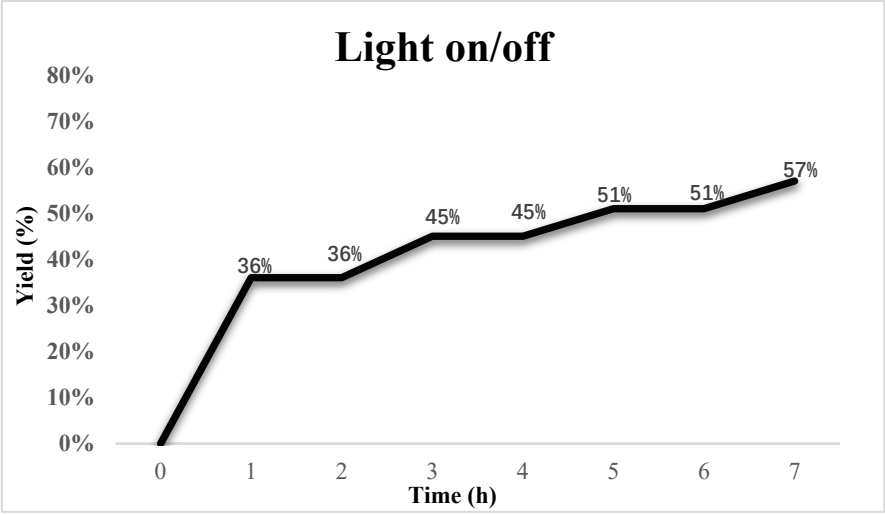
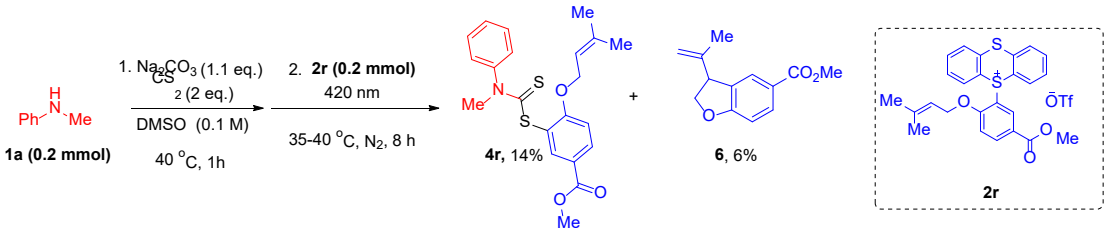


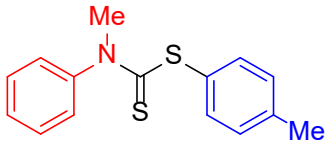
Figure S6. Light on/off experiment

Radical Clock Cyclization Experimet



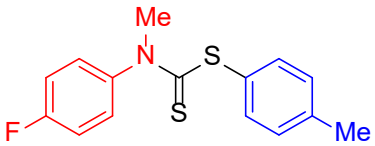
To a 5 mL glass tube was charged with *N*-methylaniline (0.2 mmol), CS_2 (25 μL, 0.4 mmol, 2.0 eq.), and Na_2CO_3 (23.3 mg, 0.22 mmol, 1.1 equiv.) in DMSO (2 mL) for 1h at 40 °C, then aryl thianthrenium salt **2r** (0.2 mmol) was added, the tube was sealed with a rubber plug and purged with N_2 for three times. The reaction was stirred and irradiated with a 420 nm blue LEDs (approximately 2 cm away from the light source) at room temperature (the actual reaction temperature is about 35~40 °C) for 8 h. The reaction mixture was diluted with 25.0 mL of dichloromethane, followed by washing with 5 mL of H_2O. The dichloromethane layer was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography eluenting with PE/AcOEt (100:1 to 50:1, v/v) to provide the products **4r** (11.3 mg, 14%) as a brown solid, and **6** (2.6 mg, 6%) as a colorless oil.

V. Characterization of products



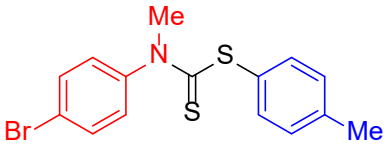
3a

***p*-Tolyl methyl(phenyl)carbamodithioate. (3a)** Following the general **procedure A**, **3a** which was purified by PE/EtOAc (70:1) and obtained as a yellow solid (44 mg, 80%). **Mp** = 119-120 °C. **R_f** = 0.25 (PE/EtOAc = 50:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 – 7.44 (m, 3H), 7.40 – 7.34 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 3.78 (s, 3H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 200.20, 145.03, 140.20, 136.63 (2C), 129.93 (2C), 129.81 (2C), 129.19, 129.11, 126.97 (2C), 46.57, 21.52. **HRMS m/z** (ESI) calcd for $C_{15}H_{15}NNaS_2$ $[M + Na]^+$ 296.0538 ; found 296.0528.



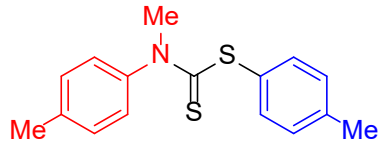
3b

***p*-Tolyl (4-fluorophenyl) (methyl) carbamodithioate. (3b)** Following the general **procedure A**, **3b** which was purified by PE/EtOAc (70:1) and obtained as a yellow solid (40 mg, 69%). **Mp** = 114-115 °C. **R_f** = 0.25 (PE/EtOAc = 50:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.18 (m, 4H), 3.79 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 200.64, 162.49 (d, *J* = 249.6 Hz), 140.91, 140.34, 136.59 (2C), 130.00 (2C), 128.92 (d, *J* = 9.1 Hz, 3C), 116.82 (d, *J* = 22.9 Hz, 2C), 46.59, 21.53. **HRMS m/z** (ESI) calcd for $C_{15}H_{14}FNNaS_2$ $[M + Na]^+$ 314.0444 ; found 314.0444.



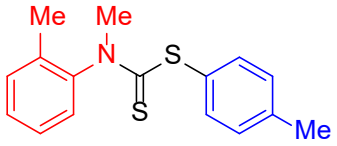
3c

***p*-Tolyl (4-bromophenyl) (methyl) carbamodithioate. (3c)** Following the general **procedure A**, **3c** which was purified by PE/EtOAc (70:1) and obtained as a yellow solid (39 mg, 55%). **Mp** = 127-128 °C. $\mathbf{R_f}$ = 0.20 (PE/EtOAc = 50:1).^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.72 – 7.61 (m, 2H), 7.34 – 7.21 (m, 6H), 3.78 (s, 3H), 2.41 (s, 3H).^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 200.31, 143.94, 140.39, 136.58 (2C), 133.08 (2C), 130.02 (2C), 128.83, 128.74 (2C), 123.08, 46.35, 21.53. **HRMS m/z** (ESI) calcd for $C_{15}H_{15}BrNS_2$ $[M + H]^+$ 351.9824 ; found 351.9824.



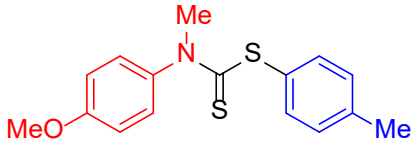
3d

***p*-Tolyl methyl (*p*-tolyl) carbamodithioate. (3d)** Following the general **procedure A**, **3d** which was purified by PE/EtOAc (70:1) and obtained as a yellow solid (40 mg, 70%). **Mp** = 129-130 °C. $\mathbf{R_f}$ = 0.20 (PE/EtOAc = 50:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.30 (m, 4H), 7.26 (m, 4H), 3.79 (s, 3H), 2.46 (s, 3H), 2.41 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 200.22, 142.46, 140.15, 139.28, 136.64 (2C), 130.41 (2C), 129.91 (2C), 129.31, 126.63 (2C), 46.66, 21.53, 21.33. **HRMS m/z** (ESI) calcd for $C_{16}H_{17}NNaS_2$ $[M + Na]^+$ 310.0695 ; found 310.0688.



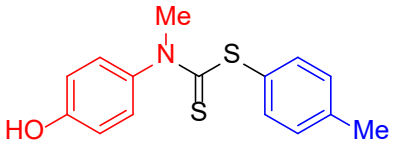
3e

***p*-Tolyl methyl (*o*-tolyl) carbamodithioate. (3e)** Following the general **procedure A**, **3e** which was purified by PE/EtOAc (70:1) and obtained as a yellow solid (30 mg, 52%). **Mp** = 131-132 °C. **R_f** = 0.25 (PE/EtOAc = 50:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.27 (m, 6H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.74 (s, 3H), 2.41 (s, 3H), 2.37 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 200.13, 143.73, 140.19, 136.60 (2C), 135.26, 131.60, 129.94 (2C), 129.62, 129.05, 127.52, 127.19, 45.08, 21.55, 17.49. **HRMS m/z** (ESI) calcd for $C_{16}H_{17}NNaS_2$ $[M + Na]^+$ 310.0695 ; found 310.0691.



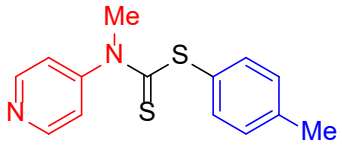
3f

***p*-Tolyl (4-methoxyphenyl) (methyl) carbamodithioate. (3f)** Following the general **procedure A**, **3f** which was purified by PE/EtOAc (30:1) and obtained as a yellow solid (36 mg, 59%). **Mp** = 107-108 °C. **R_f** = 0.35 (PE/EtOAc = 10:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.29 (m, 4H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.79 (s, 3H), 2.41 (s, 3H).^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 200.66, 159.84, 140.14, 137.72, 136.62 (2C), 129.92 (2C), 129.44, 128.07 (2C), 114.85 (2C), 55.57, 46.78, 21.53. **HRMS m/z** (ESI) calcd for $C_{16}H_{17}NNaOS_2$ $[M + Na]^+$ 326.0644 ; found 326.0643.



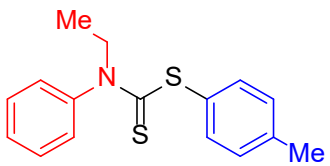
3g

***p*-Tolyl (4-hydroxyphenyl) (methyl) carbamodithioate. (3g)** Following the general **procedure A**, **3g** which was purified by PE/EtOAc (20:1) and obtained as a yellow solid (31 mg, 54%). **Mp** = 170-171 °C. $\mathbf{R_f}$ = 0.10 (PE/EtOAc = 10:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.36 – 7.18 (m, 6H), 6.95 (d, *J* = 8.4 Hz, 2H), 5.43 (s, 1H), 3.78 (s, 3H), 2.40 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 200.83, 156.13, 140.22, 136.61 (2C), 129.96 (2C), 128.76, 128.26 (2C), 127.71, 116.46 (2C), 46.82, 21.54. **HRMS m/z** (ESI) calcd for $C_{15}H_{16}NOS_2$ $[M + H]^+$ 290.0688 ; found 299.0664.



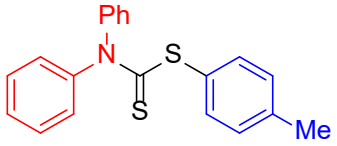
3h

***p*-Tolyl methyl (pyridin-4-yl) carbamodithioate. (3h)** Following the general **procedure C**, **3h** which was purified by PE/EtOAc (2:1) and obtained as a yellow solid (27 mg, 50%). **Mp** = 155-157 °C. $\mathbf{R_f}$ = 0.20 (PE/EtOAc = 2:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 5.3 Hz, 2H), 7.38 (d, *J* = 5.1 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 3.79 (s, 3H), 2.41 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 200.00, 152.40, 151.58 (2C), 140.68, 136.55 (2C), 130.15 (2C), 128.18, 121.89 (2C), 45.80, 21.56. **HRMS m/z** (ESI) calcd for $C_{14}H_{14}N_2NaS_2$ $[M + Na]^+$ 297.0491 ; found 297.0500.



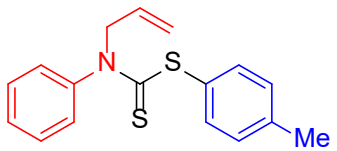
3i

***p*-Tolyl ethyl (phenyl) carbamodithioate. (3i)** Following the general **procedure A**, **3i** which was purified by PE/EtOAc (70:1) and obtained as a yellow solid (35 mg, 61%). **Mp** = 128-129 °C. **R_f** = 0.25 (PE/EtOAc = 50:1).^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.58 – 7.47 (m, 3H), 7.39 – 7.35 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 199.71, 143.18, 140.14, 136.69 (2C), 129.89 (2C), 129.74 (2C), 129.20, 129.15, 128.05 (2C), 53.09, 21.53, 11.92. **HRMS m/z** (ESI) calcd for $C_{16}H_{18}NS_2$ $[M + H]^+$ 288.0875 ; found 288.0868.



3j

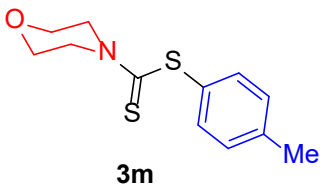
***p*-Tolyl diphenylcarbamodithioate. (3j)** Following the general **procedure C**, **3j** which was purified by PE/EtOAc (70:1) and obtained as a yellow solid (17 mg, 25%). **Mp** = 204-205 °C. **R_f** = 0.30 (PE/EtOAc = 50:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.54 – 7.48 (m, 4H), 7.46 (t, *J* = 7.6 Hz, 4H), 7.41 – 7.33 (m, 4H), 7.25 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 202.49, 145.44 (2C), 140.28, 136.53 (2C), 130.00 (2C), 129.62 (4C), 128.90, 128.32 (2C), 128.01 (4C), 21.56. **HRMS m/z** (ESI) calcd for $C_{20}H_{18}NS_2$ $[M + H]^+$ 336.0875 ; found 336.0885.



3k

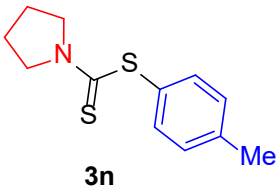
***p*-Tolyl allyl (phenyl) carbamodithioate. (3k)** Following the general **procedure A**, **3k** which was purified by PE/EtOAc (70:1) and obtained as a yellow solid (21 mg,

35%). **Mp** = 154-155 °C. **R_f** = 0.25 (PE/EtOAc = 50:1).^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.56 – 7.46 (m, 3H), 7.39 – 7.29 (m, 4H), 7.24 (d, *J* = 7.9 Hz, 2H), 6.05 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.20 – 5.11 (m, 1H), 4.94 (d, *J* = 6.4 Hz, 2H), 2.41 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 200.59, 140.22, 136.64 (2C), 131.01, 129.92 (2C), 129.61 (2C), 129.31, 129.24, 129.09, 128.08 (2C), 119.54, 60.70, 21.53. **HRMS m/z** (ESI) calcd for $C_{17}H_{18}NS_2$ $[M+H]^+$ 300.0875 ; found 300.0876.



3m

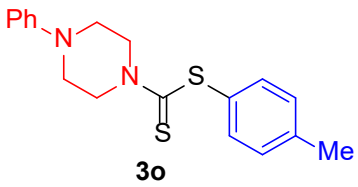
***p*-Tolyl morpholine-4-carbodithioate. (3m)** Following the general **procedure B**, **3m** which was purified by PE/EtOAc (10:1) and obtained as a yellow solid (36 mg, 71%). **Mp** = 136-137 °C. **R_f** = 0.15 (PE/EtOAc = 10:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.46 – 3.98 (m, 4H), 3.90 – 3.79 (m, 4H), 2.44 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 198.57, 140.63, 136.92 (2C), 130.10 (2C), 127.41, 66.32 (br, 2C), 51.26 (br, 2C), 21.57. The spectra data are matched with those reported. [3]



3n

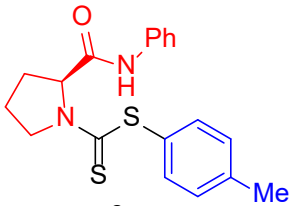
***p*-Tolyl pyrrolidine-1-carbodithioate. (3n)** Following the general **procedure B**, **3n** which was purified by PE/EtOAc (10:1) and obtained as a yellow solid (31 mg, 65%). **Mp** = 115-116 °C. **R_f** = 0.30 (PE/EtOAc = 10:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 3.96 (t, *J* = 7.0 Hz, 2H), 3.82 (t, *J*

= 6.9 Hz, 2H), 2.43 (s, 3H), 2.15 (m, 2H), 2.02 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 193.58, 140.40, 136.77 (2C), 130.03 (2C), 127.70, 55.37, 51.04, 26.38, 24.42, 21.58. The spectra data are matched with those reported [3]



3o

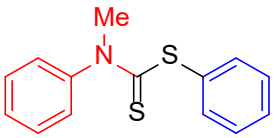
***p*-Tolyl 4-phenylpiperazine-1-carbodithioate. (3o)** Following the general **procedure B**, **3o** which was purified by PE/EtOAc (15:1) and obtained as a yellow solid (30 mg, 46%). **Mp** = 168-169 °C. **R_f** = 0.4 (PE/EtOAc = 10:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.27 (m, 4H), 6.98 (d, *J* = 7.5 Hz, 3H), 4.40 (d, *J* = 105.2 Hz, 4H), 3.38 (s, 4H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 198.16, 150.31, 140.60, 136.95 (2C), 130.11 (2C), 129.38 (2C), 127.61, 120.64, 116.40 (2C), 51.21(br), 50.24 (br), 48.84, 21.59. **HRMS m/z** (ESI) calcd for $C_{18}H_{21}N_2S_2$ $[M + H]^+$ 329.1141 ; found 329.1150.



3p

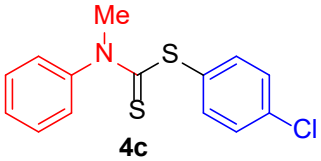
***p*-Tolyl (S)-2- (phenylcarbamoyl) pyrrolidine-1-carbodithioate. (3p)** Following the general **procedure B**, **3p** which was purified by PE/EtOAc (4:1) and obtained as a yellow solid (23 mg, 32%). **Mp** = 310-312 °C. **R_f** = 0.2 (PE/EtOAc = 4:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 9.52 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.35 – 7.26 (m, 4H), 7.11 (t, *J* = 7.4 Hz, 1H), 5.50 (d, *J* = 7.6 Hz, 1H), 3.95 (d, *J*

= 9.5 Hz, 2H), 2.63 (dd, *J* = 12.5, 6.8 Hz, 1H), 2.45 (m, 4H), 2.25 (m, 1H), 2.07 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 198.01, 167.32, 140.89, 137.93, 136.70 (2C), 130.19 (2C), 128.94 (2C), 127.19, 124.32, 120.12 (2C), 68.13, 51.77, 27.67, 25.21, 21.60. **HRMS m/z** (ESI) calcd for $C_{19}H_{21}N_2OS_2$ $[M + H]^+$ 357.1090 ; found 357.1095.



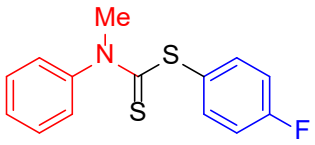
4b

Phenyl methyl(phenyl)carbamodithioate. (4b) Following the general **procedure A**, **4b** which was purified by PE/EtOAc (70:1) and obtained as a yellow solid (31 mg, 60%). **Mp** = 90-91 °C. **R_f** = 0.3 (PE/EtOAc = 50:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 – 7.37 (m, 10H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 199.66, 144.94, 136.82 (2C), 132.60, 129.95, 129.87 (2C), 129.20, 129.06 (2C), 126.97 (2C), 46.59. **HRMS m/z** (ESI) calcd for $C_{14}H_{14}NS_2$ $[M + H]^+$ 260.0562 ; found 260.0554.



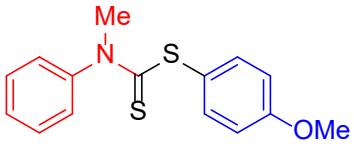
4c

4-Chlorophenyl methyl(phenyl)carbamodithioate. (4c) Following the general **procedure A**, **4c** which was purified by PE/EtOAc (50:1) and obtained as a yellow solid (33 mg, 57%). **Mp** = 129-130 °C. **R_f** = 0.4 (PE/EtOAc = 10:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 – 7.49 (m, 3H), 7.42 – 7.32 (m, 6H), 3.81 (s, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 198.77, 144.78, 138.01 (2C), 136.42, 131.04, 129.89 (2C), 129.33 (2C), 129.30, 126.93 (2C), 46.60. **HRMS m/z** (ESI) calcd for $C_{14}H_{13}NClS_2$ $[M + H]^+$ 294.0172 ; found 294.0166.



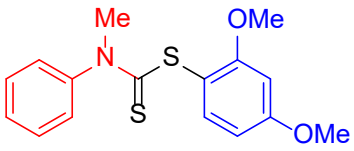
4d

4-Fluorophenyl methyl(phenyl)carbamodithioate. (4d) Following the general **procedure A**, **4d** which was purified by PE/EtOAc (50:1) and obtained as a yellow solid (32 mg, 58%). **Mp** = 102-103 °C. **R_f** = 0.3 (PE/EtOAc = 50:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.59 – 7.47 (m, 3H), 7.44 – 7.36 (m, 4H), 7.12 (t, *J* = 8.7 Hz, 2H), 3.81 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 199.44 (d, *J* = 2.1 Hz), 163.85 (d, *J* = 250.9 Hz), 144.77, 138.87 (d, *J* = 8.7 Hz, 2C), 129.89 (2C), 129.29, 128.04 (d, *J* = 3.3 Hz), 126.94 (2C), 116.32 (d, *J* = 22.1 Hz, 2C), 46.68. **HRMS m/z** (ESI) calcd for $C_{14}H_{13}FNS_2$ $[M + H]^+$ 278.0468 ; found 278.0471.



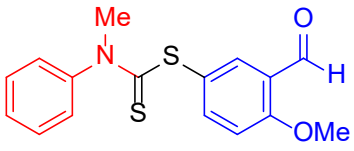
4e

4-Methoxyphenyl methyl(phenyl)carbamodithioate. (4e) Following the general **procedure A**, **4e** which was purified by PE/EtOAc (20:1) and obtained as a yellow solid (35 mg, 60%). **Mp** = 125-126 °C. **R_f** = 0.3 (PE/EtOAc = 10:1).^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.59 – 7.46 (m, 3H), 7.42 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 6.99 – 6.90 (m, 2H), 3.85 (s, 3H), 3.81 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 200.80, 160.98, 144.99 (2C), 138.25, 129.81 (2C), 129.11, 126.96 (2C), 123.48, 114.63 (2C), 55.28, 46.63. **HRMS m/z** (ESI) calcd for $C_{15}H_{16}NOS_2$ $[M + H]^+$ 290.0668 ; found 290.0661.



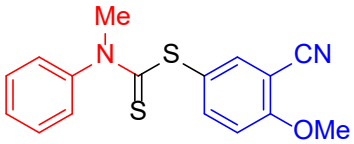
4f

2, 4-Dimethoxyphenyl methyl(phenyl)carbamodithioate. (4f) Following the general **procedure A**, **4f** which was purified by PE/EtOAc (10:1) and obtained as a yellow solid (35 mg, 55%). **Mp** = 142-143 °C. **R_f** = 0.2 (PE/EtOAc = 10:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.56 – 7.49 (m, 2H), 7.49 – 7.40 (m, 3H), 7.27 (dd, *J* = 9.2, 1.5 Hz, 1H), 6.59 – 6.52 (m, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 200.09, 163.18, 161.49, 145.22, 139.36, 129.79 (2C), 128.95, 126.98 (2C), 112.23, 105.32, 99.38, 56.18, 55.41, 46.66. **HRMS m/z** (ESI) calcd for $C_{16}H_{18}NO_2S_2$ $[M + H]^+$ 320.0773 ; found 320.0778.



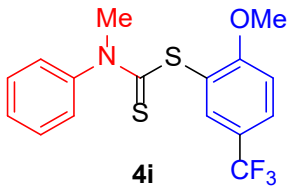
4g

3-Formyl-4-methoxyphenyl methyl(phenyl)carbamodithioate. (4g) Following the general **procedure A**, **4g** which was purified by PE/EtOAc (10:1) and obtained as a yellow solid (34 mg, 54%). **Mp** = 139-141 °C. **R_f** = 0.1 (PE/EtOAc = 10:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 10.44 (s, 1H), 7.85 (d, *J* = 2.4 Hz, 1H), 7.60 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.57 – 7.46 (m, 3H), 7.39 (d, *J* = 6.8 Hz, 2H), 7.06 (d, *J* = 8.7 Hz, 1H), 3.99 (s, 3H), 3.80 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 199.45, 188.77, 162.76, 144.77, 144.43, 137.11, 129.88 (2C), 129.28, 126.93 (2C), 125.27, 124.61, 112.42, 55.90, 46.66. **HRMS m/z** (ESI) calcd for $C_{16}H_{16}NO_2S_2$ $[M + H]^+$ 318.0617 ; found 318.0612.



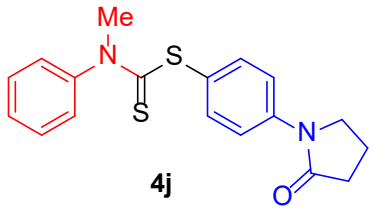
4h

3-Cyano-4-methoxyphenyl methyl(phenyl)carbamodithioate. (4h) Following the general **procedure A**, **4h** which was purified by PE/EtOAc (10:1) and obtained as a yellow solid (40 mg, 64%). **Mp** = 145-146 °C. **R_f** = 0.1 (PE/EtOAc = 10:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.61 – 7.48 (m, 5H), 7.41 – 7.35 (m, 2H), 7.02 (d, *J* = 8.7 Hz, 1H), 3.99 (s, 3H), 3.80 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 198.64, 162.28, 144.54, 143.17, 142.00, 129.95 (2C), 129.44, 126.89 (2C), 124.64, 115.61, 111.82, 102.76, 56.31, 46.75. **HRMS m/z** (ESI) calcd for $C_{16}H_{15}N_2OS_2$ $[M + H]^+$ 315.0620 ; found 315.0622.



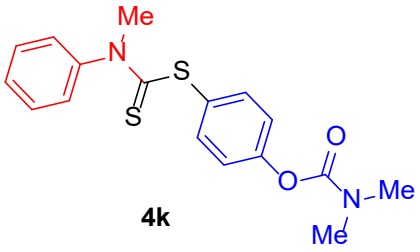
4i

2-Methoxy-5-(trifluoromethyl)phenyl methyl(phenyl)carbamodithioate. (4i) Following the general **procedure A**, **4i** which was purified by PE/EtOAc (10:1) and obtained as a yellow solid (30 mg, 42%). **Mp** = 121-122 °C. **R_f** = 0.15 (PE/EtOAc = 10:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.63 (d, *J* = 2.4 Hz, 1H), 7.58 – 7.40 (m, 5H), 7.04 (d, *J* = 8.7 Hz, 1H), 3.92 (s, 3H), 3.81 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 197.31, 162.72, 144.95, 135.63 (q, *J* = 3.7 Hz), 129.88 (2C), 129.44 (q, *J* = 3.6 Hz), 129.22, 126.92 (2C), 123.37 (q, *J* = 287.1 Hz),123.15 (d, *J* = 33.2 Hz), 121.71, 111.47, 56.45, 46.56. **HRMS m/z** (ESI) calcd for $C_{16}H_{15}F_3NOS_2$ $[M + H]^+$ 358.0542 ; found 358.0545.



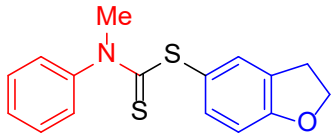
4j

4-(2-Oxopyrrolidin-1-yl)phenyl methyl(phenyl)carbamodithioate. (4j) Following the general **procedure A**, **4j** which was purified by PE/EtOAc (3:1) and obtained as a yellow solid (40 mg, 59%). **Mp** = 175-176 °C. **R_f** = 0.1 (PE/EtOAc = 4:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.70 (m, 2H), 7.58 – 7.46 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 4H), 3.90 (t, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 2.63 (t, *J* = 8.1 Hz, 2H), 2.24 – 2.12 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 199.92, 174.46, 144.93, 140.89, 137.37 (2C), 129.84 (2C), 129.18, 127.43, 126.95 (2C), 119.59 (2C), 48.50, 46.58, 32.95, 17.96. **HRMS m/z** (ESI) calcd for $C_{18}H_{19}N_2OS_2$ $[M + H]^+$ 343.0933 ; found 343.0935.



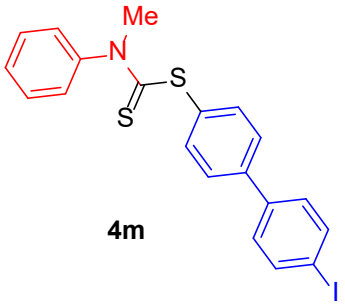
4k

4-((Methyl(phenyl)carbamothioyl)thio)phenyl dimethylcarbamate. (4k) Following the general **procedure A**, **4k** which was purified by PE/EtOAc (5:1) and obtained as a yellow solid (46 mg, 67%). **Mp** = 144-146 °C. **R_f** = 0.3 (PE/EtOAc = 4:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 – 7.44 (m, 3H), 7.44 – 7.35 (m, 4H), 7.19 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.11 (s, 3H), 3.03 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 199.66, 154.32, 152.91, 144.88, 137.87 (2C), 129.86 (2C), 129.20, 128.86, 126.93 (2C), 122.29 (2C), 46.60, 36.72, 36.50. **HRMS m/z** (ESI) calcd for $C_{17}H_{18}N_2NaO_2S_2$ $[M + Na]^+$ 369.0702 ; found 369.0705.



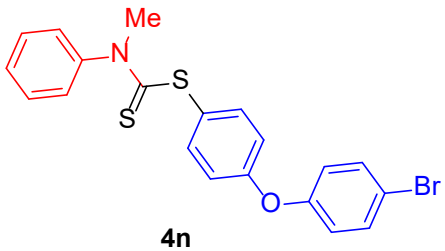
4l

2, 3-Dihydrobenzofuran-5-yl methyl(phenyl)carbamodithioate. (4l) Following the general **procedure A**, **4l** which was purified by PE/EtOAc (50:1) and obtained as a yellow solid (40 mg, 66%). **Mp** = 158-159 °C. $\mathbf{R_f}$ = 0.1 (PE/EtOAc = 50:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.57 – 7.45 (m, 3H), 7.38 (dd, *J* = 7.0, 1.7 Hz, 2H), 7.22 (s, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 4.64 (t, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.25 (t, *J* = 8.7 Hz, 2H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 201.26, 161.83, 145.01, 137.27, 133.52, 129.80 (2C), 129.08, 128.20, 126.94 (2C), 122.92, 110.03, 71.77, 46.65, 29.41. **HRMS m/z** (ESI) calcd for $C_{16}H_{16}NOS_2$ $[M + H]^+$ 302.0668 ; found 302.0660.



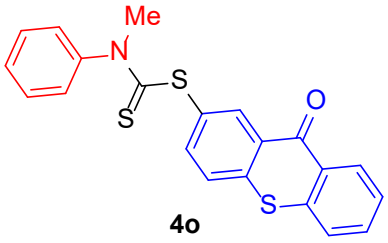
4m

4'-Iodo-[1,1'-biphenyl]-4-yl methyl(phenyl)carbamodithioate. (4m) Following the general **procedure A**, **4m** which was purified by PE/EtOAc (50:1) and obtained as a yellow solid (61 mg, 66%). **Mp** = 160-161 °C. $\mathbf{R_f}$ = 0.3 (PE/EtOAc = 50:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.47 (m, 5H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 199.26, 144.94, 141.41, 139.69, 137.92 (2C), 137.21 (2C), 131.94, 129.88 (2C), 129.25, 129.07 (2C), 127.43 (2C), 126.96 (2C), 93.74, 46.60. **HRMS m/z** (ESI) calcd for $C_{20}H_{17}INS_2$ $[M + H]^+$ 461.9842 ; found 461.9851.



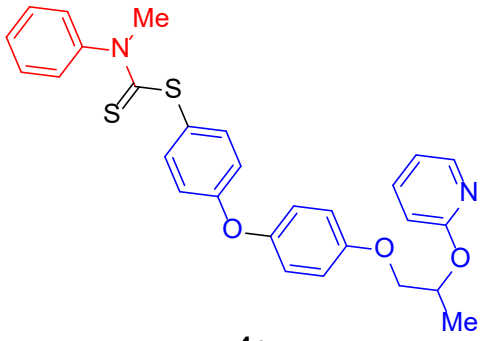
4n

4-(4-Bromophenoxy)phenyl methyl(phenyl)carbamodithioate. (4n) Following the general **procedure A**, **4n** which was purified by PE/EtOAc (50:1) and obtained as a yellow solid (43 mg, 50%). **Mp** = 140-141 °C. $\mathbf{R_f}$ = 0.3 (PE/EtOAc = 50:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 7.61 – 7.45 (m, 5H), 7.39 (dd, *J* = 10.8, 8.0 Hz, 4H), 7.00 (dd, *J* = 8.8, 7.1 Hz, 4H), 3.82 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 199.86, 158.73, 155.24, 144.86, 138.56 (2C), 132.93 (2C), 129.88 (2C), 129.23, 126.96 (2C), 126.59, 121.63 (2C), 118.53 (2C), 116.74, 46.69. **HRMS m/z** (ESI) calcd for $C_{20}H_{17}BrNOS_2$ $[M + H]^+$ 429.9929 ; found 429.9933.



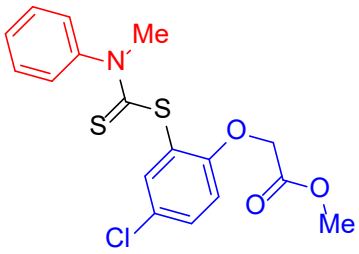
4o

9-Oxo-9H-thioxanthen-2-yl methyl(phenyl)carbamodithioate. (4o) Following the general **procedure A**, **4o** which was purified by PE/EtOAc (10:1) and obtained as a yellow solid (25 mg, 32%). **Mp** = 206-207 °C. $\mathbf{R_f}$ = 0.3 (PE/EtOAc = 10:1). ^{1}**H NMR** (400 MHz, Chloroform-*d*) δ 8.65 – 8.58 (m, 2H), 7.70 – 7.46 (m, 8H), 7.45 – 7.41 (m, 2H), 3.82 (s, 3H). ^{13}**C NMR** (101 MHz, Chloroform-*d*) δ 198.48, 179.18, 144.78, 140.13, 139.20, 137.68, 136.78, 132.46, 131.01, 129.94, 129.92 (2C), 129.61, 129.35, 129.22, 126.97 (2C), 126.61, 126.53, 126.08, 46.56. **HRMS m/z** (ESI) calcd for $C_{21}H_{16}NOS_3$ $[M + H]^+$ 394.0389 ; found 394.0390.



4p

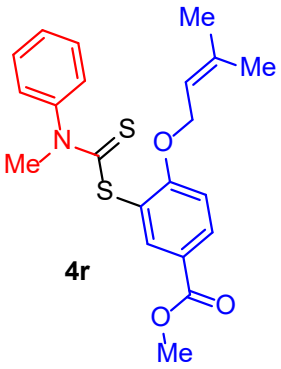
4-(4-(2-(Pyridin-2-yloxy)propoxy)phenoxy)phenyl methyl(phenyl) carbamodithioate. (4p) Following the general **procedure A**, **4p** which was purified by PE/EtOAc (20:1) and obtained as a yellow solid (53 mg, 53%). **Mp** = 115-116 °C. **R_f** = 0.3 (PE/EtOAc = 10:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.18 (dd, *J* = 5.2, 1.9 Hz, 1H), 7.59 (m, 1H), 7.56 – 7.45 (m, 3H), 7.39 (d, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 6.96 (dd, *J* = 11.3, 8.9 Hz, 4H), 6.91 – 6.86 (m, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 5.62 (q, *J* = 5.7 Hz, 1H), 4.22 (dd, *J* = 9.9, 5.3 Hz, 1H), 4.11 (dd, *J* = 9.9, 4.8 Hz, 1H), 3.81 (s, 3H), 1.52 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 200.26, 163.15, 160.35, 155.78, 149.03, 146.80, 144.94, 138.76, 138.32 (2C), 129.84 (2C), 129.15, 126.96 (2C), 125.13, 121.65 (2C), 117.37 (2C), 116.82, 115.89 (2C), 111.71, 71.02, 69.27, 46.65, 17.05. **HRMS m/z** (ESI) calcd for $C_{28}H_{27}N_2O_3S_2$ $[M + H]^+$ 503.1459 ; found 503.1465.



4q

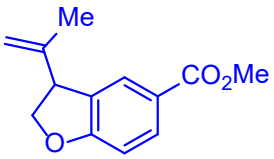
Methyl 2-(4-chloro-2-((methyl(phenyl)carbamothioyl)thio)phenoxy)acetate. (4q) Following the general **procedure A**, **4q** which was purified by PE/EtOAc (10:1) and obtained as a yellow solid (34 mg, 45%). **Mp** = 85-86 °C. **R_f** = 0.2 (PE/EtOAc = 10:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.50 (m, 2H), 7.50 – 7.43 (m, 3H), 7.38 (d, *J* = 7.4 Hz, 2H), 6.82 (dt, *J* = 8.4, 1.0 Hz, 1H), 4.66 (s, 2H), 3.83 (s, 3H), 3.80 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 197.48, 168.74, 157.47, 145.06, 137.58, 131.73, 129.88 (2C), 129.19, 126.93 (2C), 126.79, 123.98, 114.59, 66.73, 52.28, 46.56. **HRMS m/z** (ESI) calcd for $C_{17}H_{17}ClNO_3S_2$ $[M + H]^+$ 382.0333 ; found 382.0333.



4r

methyl 3-((methyl(phenyl)carbamothioyl)thio)-4-((3-methylbut-2-en-1-yl) oxy) benzoate. (4r) R_f = 0.2 (PE/EtOAc = 50:1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.04 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.83 (d, *J* = 2.2 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.53 – 7.47 (m, 3H), 7.21 (d, *J* = 8.8 Hz, 1H), 5.44 – 5.39 (m, 1H), 4.64 (d, *J* = 6.6 Hz, 2H), 3.83 (s, 3H), 3.70 (s, 3H), 1.78 (s, 4H), 1.73 (s, 4H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 196.79, 165.80, 163.23, 145.28, 139.76, 138.69, 133.95, 130.32 (2C), 129.62, 127.33 (2C), 122.38, 121.71, 119.56, 113.72, 66.17, 52.52, 46.78, 25.99, 18.71. **HRMS m/z** (ESI) calcd for $C_{21}H_{24}NO_3S_2$ $[M + H]^+$ 402.1198 ; found 402.1186.



6

methyl 3-(prop-1-en-2-yl)-2,3-dihydrobenzofuran-5-carboxylate. (6)

R_f = 0.6 (PE/EtOAc = 50:1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.80 (t, *J* = 1.5 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 4.92 (d, *J* = 0.9 Hz, 1H), 4.90 – 4.88 (m, 1H), 4.74 (t, *J* = 9.5 Hz, 1H), 4.44 (dd, *J* = 9.2, 6.7 Hz, 1H), 4.19 (dd, *J* = 9.8, 6.7 Hz, 1H), 3.87 (s, 2H), 1.64 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.98, 164.34, 143.82, 131.55, 129.34, 126.95, 122.85, 113.64, 109.32, 76.32, 51.91,

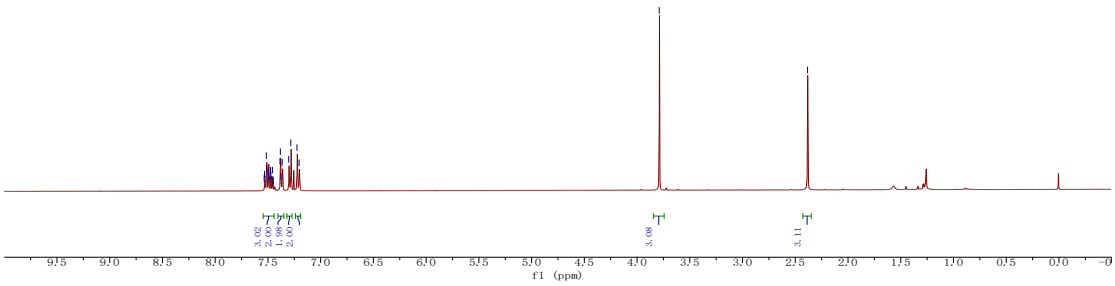
49.60, 18.71. **HRMS m/z** (EI) calcd for $C_{13}H_{14}O_3$ $[M]^+$ 218.0943 ; found 218.0939. The spectra data are matched with those reported [4]

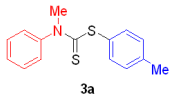
VI. Reference

1. Z. Y. Tian, Z. H. Lin and C. P. Zhang, *Org. Lett.*, 2021, **23**, 4400-4405.
2. X. Li, W. Cui, Q. Deng, X. Song, J. Lv and D. Yang, *Green Chem.*, 2022, **24**, 1302-1307.
3. S. K. Parida, S. Jaiswal, P. Singh and S. Murarka, *Org. Lett.,* 2021, **23**, 6401-6406.
4. J. Li, J. Chen, R. Sang, W. S. Ham, M. B. Plutschack, F. Berger, S. Chabbra, A. Schnegg, C. Genicot and T. Ritter, *Nat. Chem.*, 2020, **12**, 56-62.

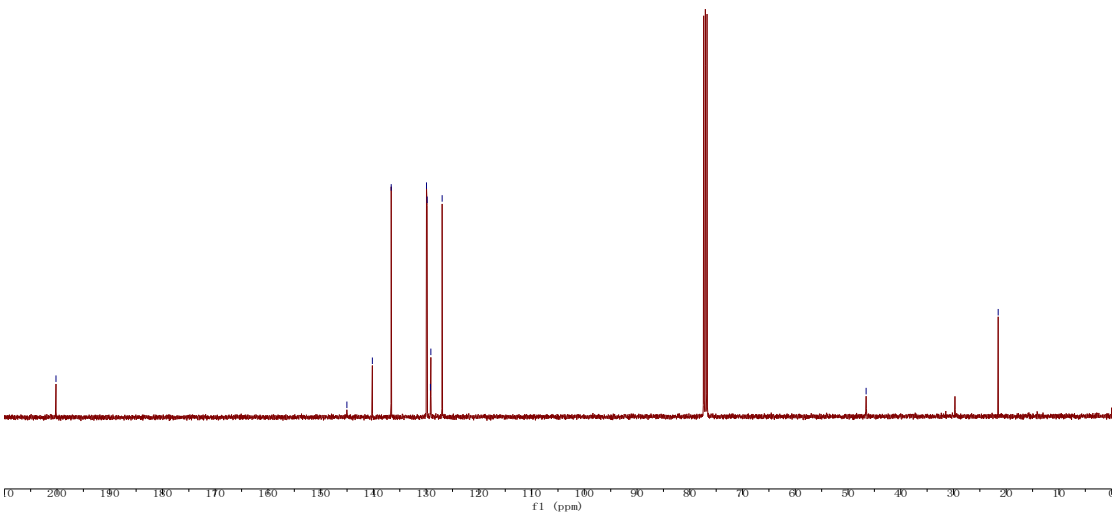
VII. NMR spectra

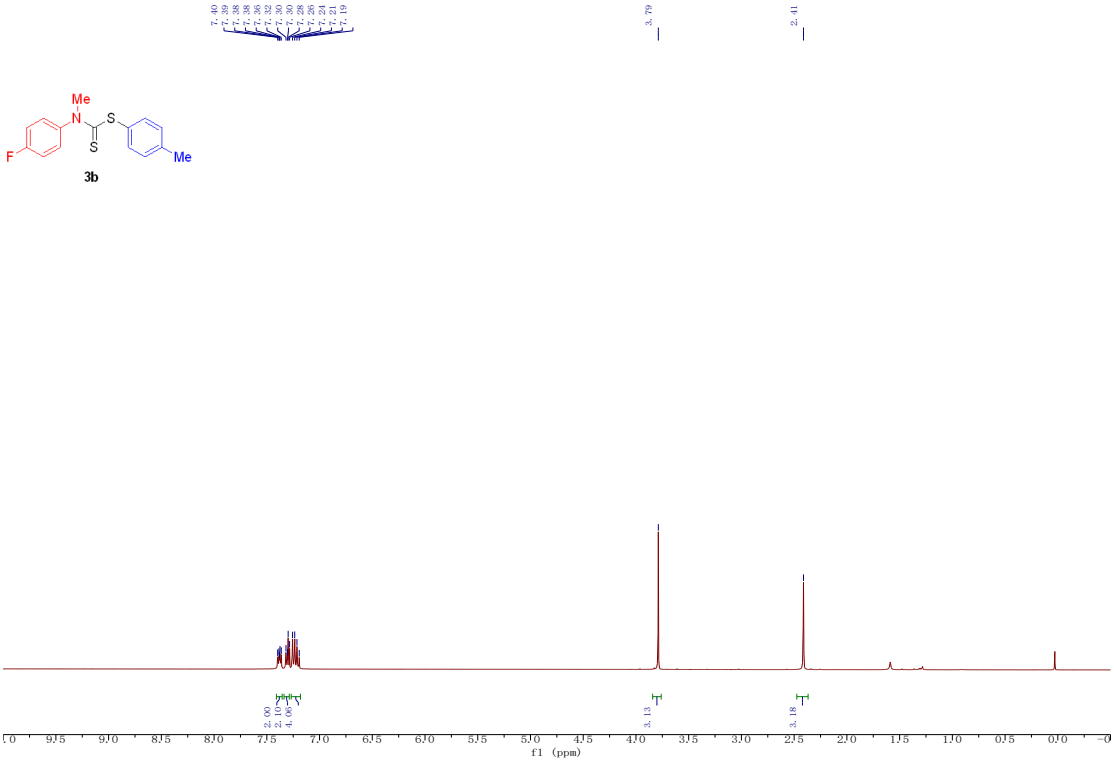
3a





3a

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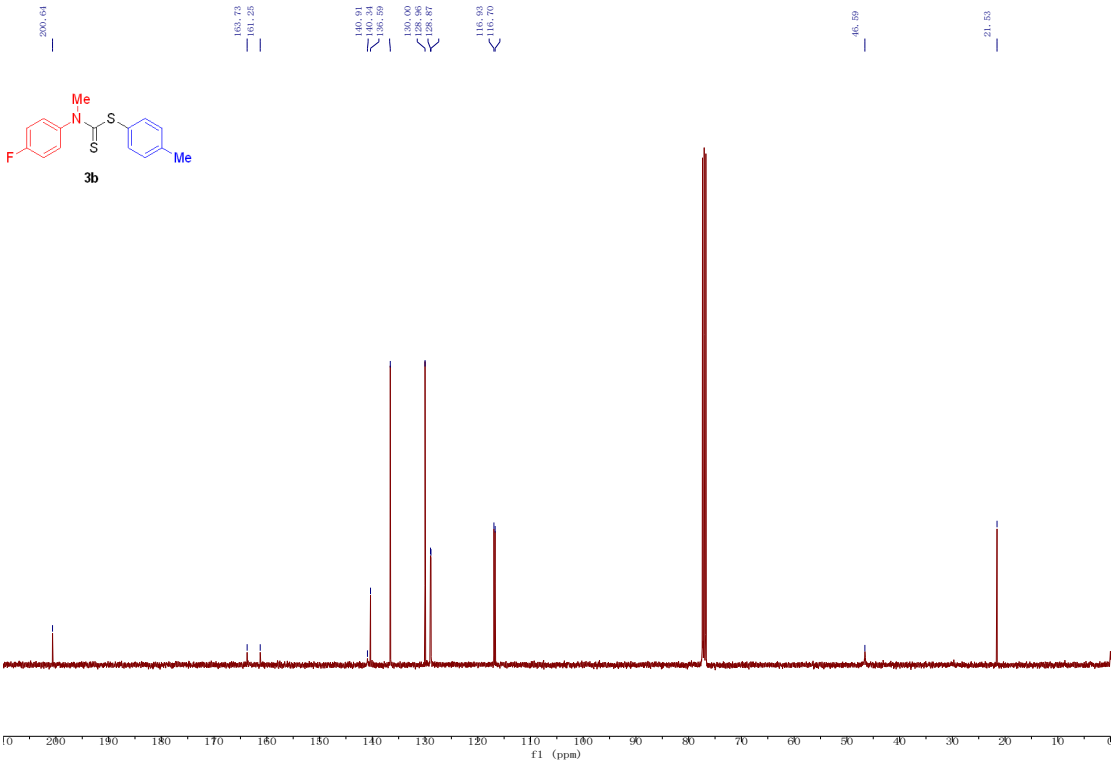
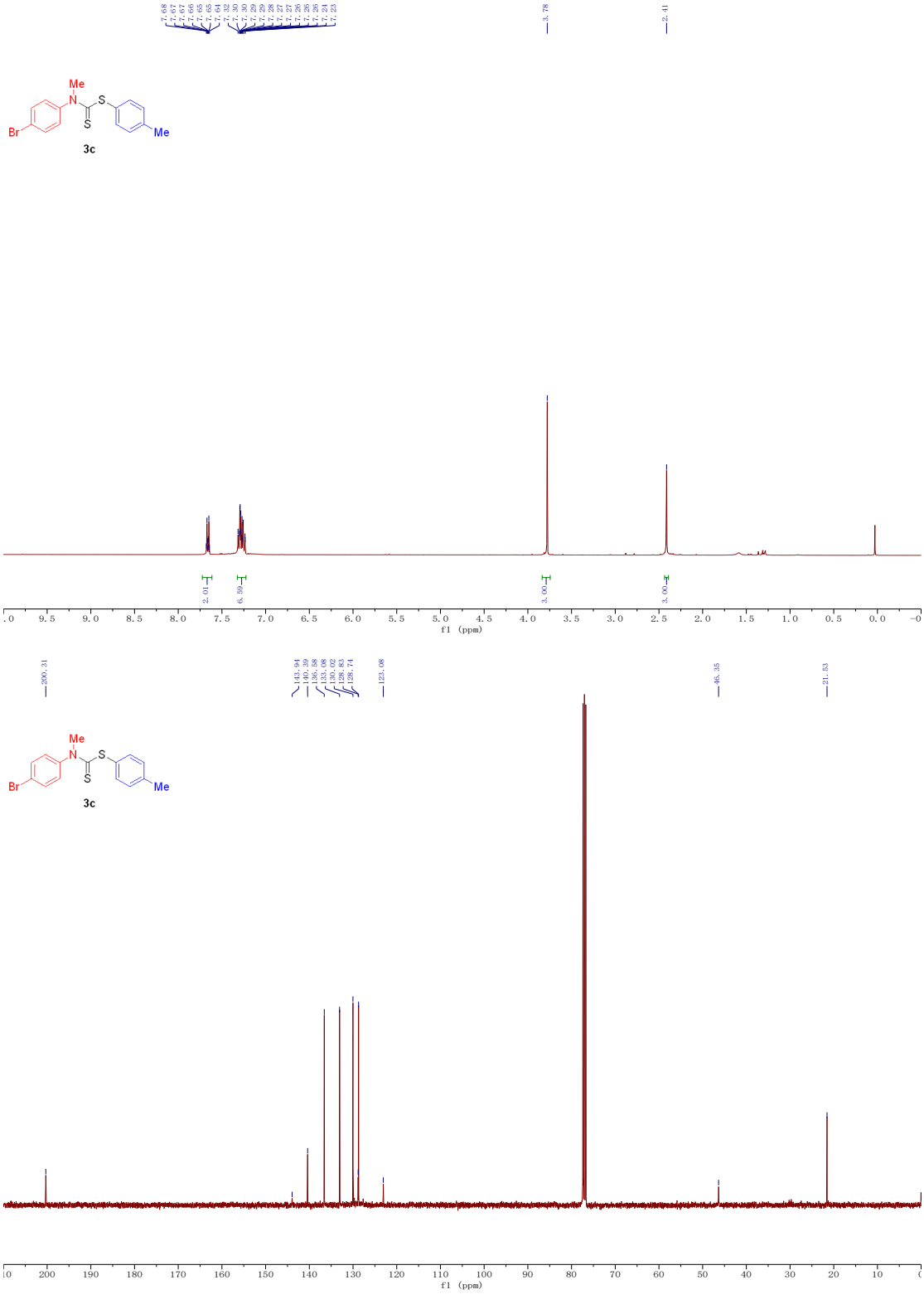
7.39
7.38
7.36
7.32
7.30
7.28
7.25
7.24
7.21
7.19
3.79
2.41
Me
N
S
S
F
Me
3b
2.00
2.10
4.06
3.13
3.18
f1 (ppm)


200.64
163.73
161.25
140.91
140.34
136.39
130.99
128.96
128.87
116.93
116.70
46.89
21.83
Me
N
S
S
F
Me
3b
f1 (ppm)


7.68
7.67
7.67
7.66
7.65
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7.28
7.27
7.27
7.26
7.26
7.24
7.23
3.78
2.41
Me
N
S
S
Br
Me
3c
2.01
6.89
3.00
3.00
f1 (ppm)
200.31
143.94
140.39
136.84
133.08
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N
S
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Br
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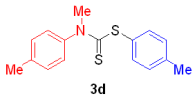
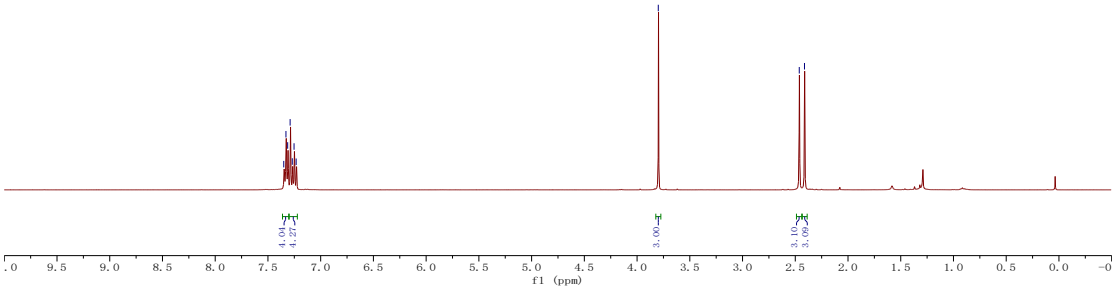
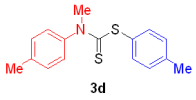
3c
f1 (ppm)

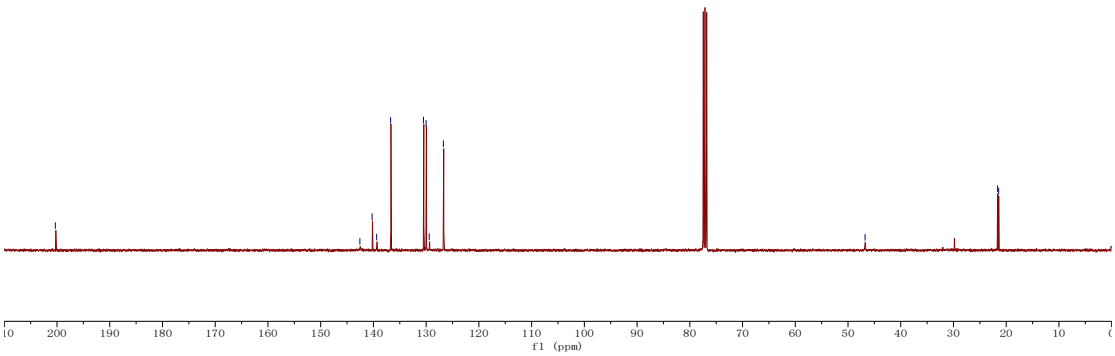


3d





3d




7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.35
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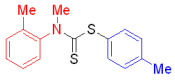
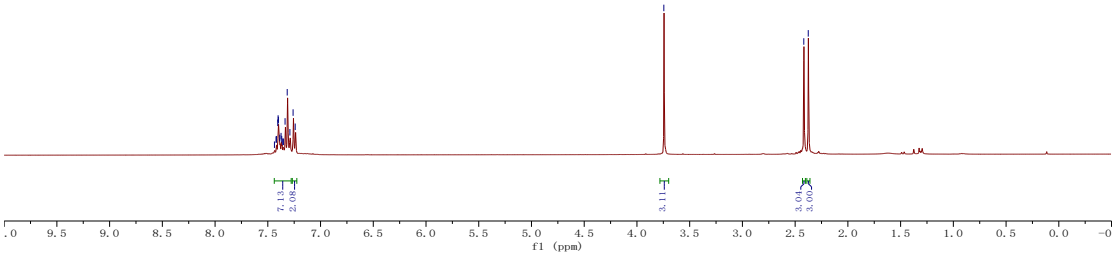
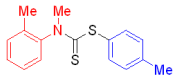
7.29
7.26
7.24
3.74
2.41
2.37


Me
Me
N
S
S
Me

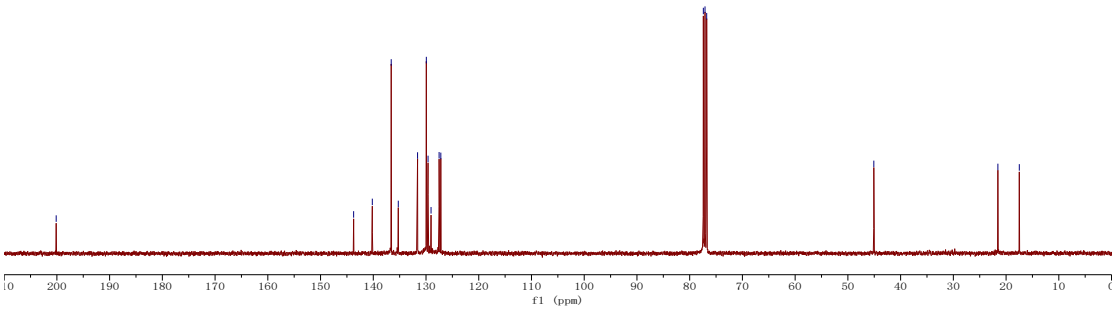
3e


7.13
2.08
3.11
3.04
3.00
f1 (ppm)

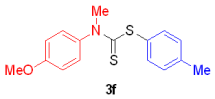

200.13
143.73
140.19
136.60
135.36
131.60
129.94
129.62
129.05
127.52
127.19
77.41
77.09
76.77
45.08
21.55
17.49


Me
Me
N
S
S
Me

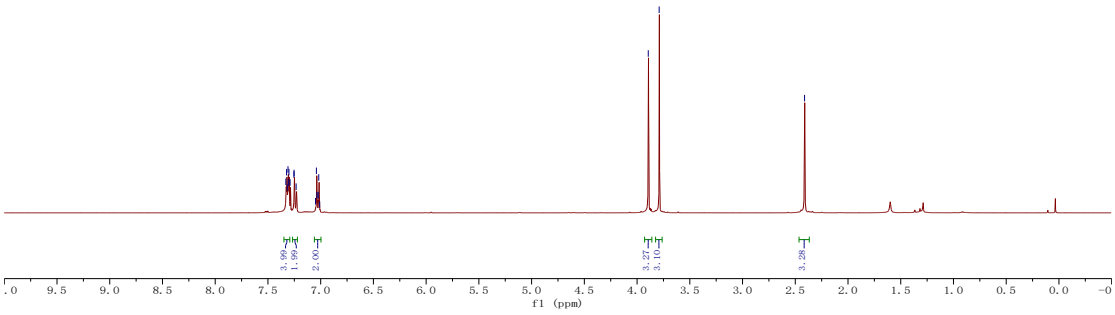
3e


f1 (ppm)


7.33
7.32
7.31
7.30
7.30
7.30
7.28
7.25
7.25
7.23
7.04
7.04
7.03
7.02
7.01
7.00
3.89
3.79
2.41


Me
N
S
S
MeO
Me

3f


3.99
1.96
2.00
3.27
3.10
3.28
f1 (ppm)


200.66
159.84
140.14
137.72
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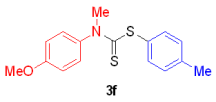
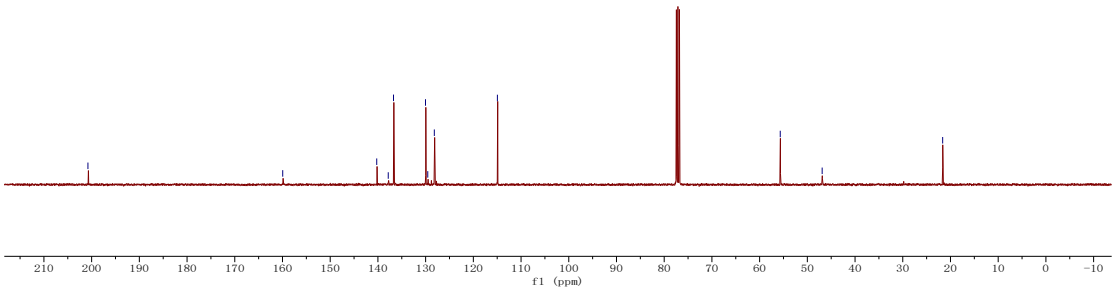
129.92
129.44
128.07
114.85
55.57
46.78
21.83


Me
N
S
S
MeO
Me

3f


f1 (ppm)


7.32
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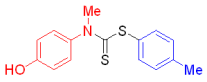
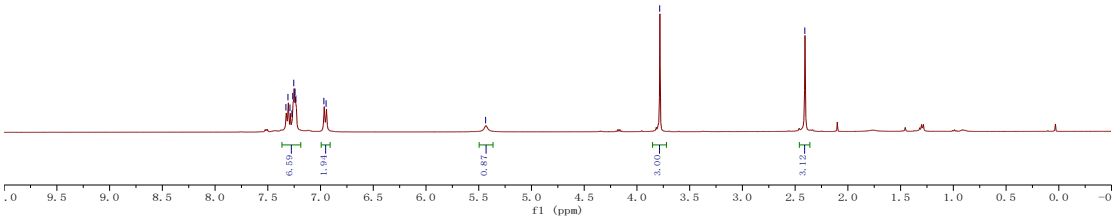
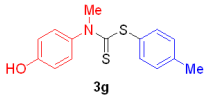
7.28
7.27
7.26
7.25
7.24
7.23
6.96
6.94
5.43
3.78
2.40


Me
N
S
S
HO
Me

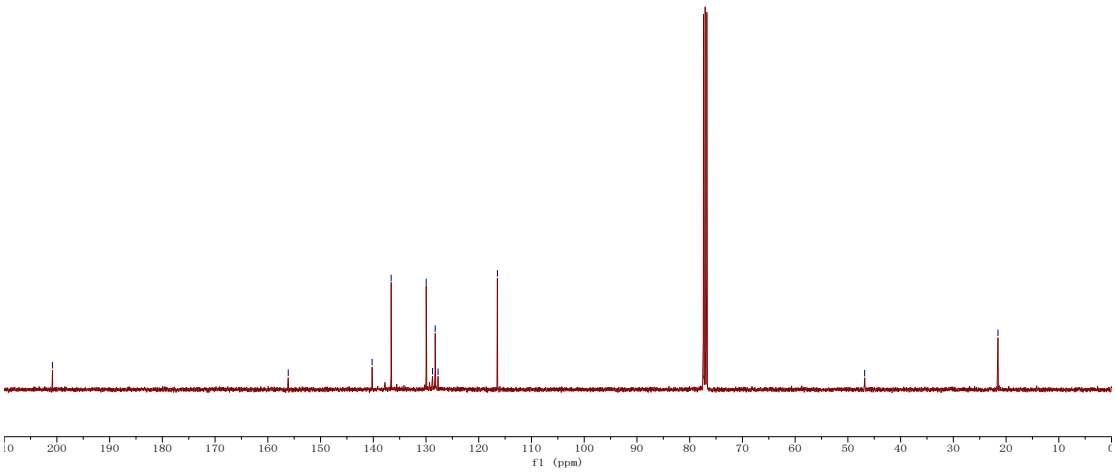
3g

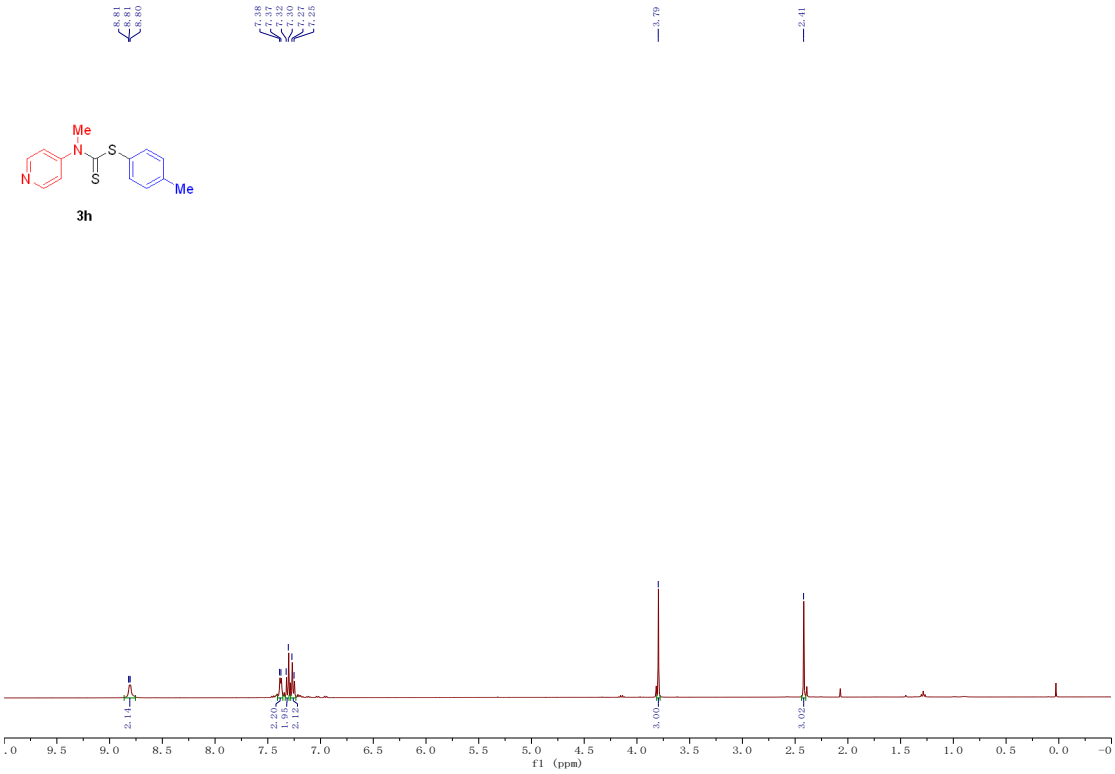

6.59
1.94
0.87
3.00
3.12
f1 (ppm)


200.83
156.13
140.22
136.61
129.96
128.76
128.36
127.71
116.46
46.82
21.54

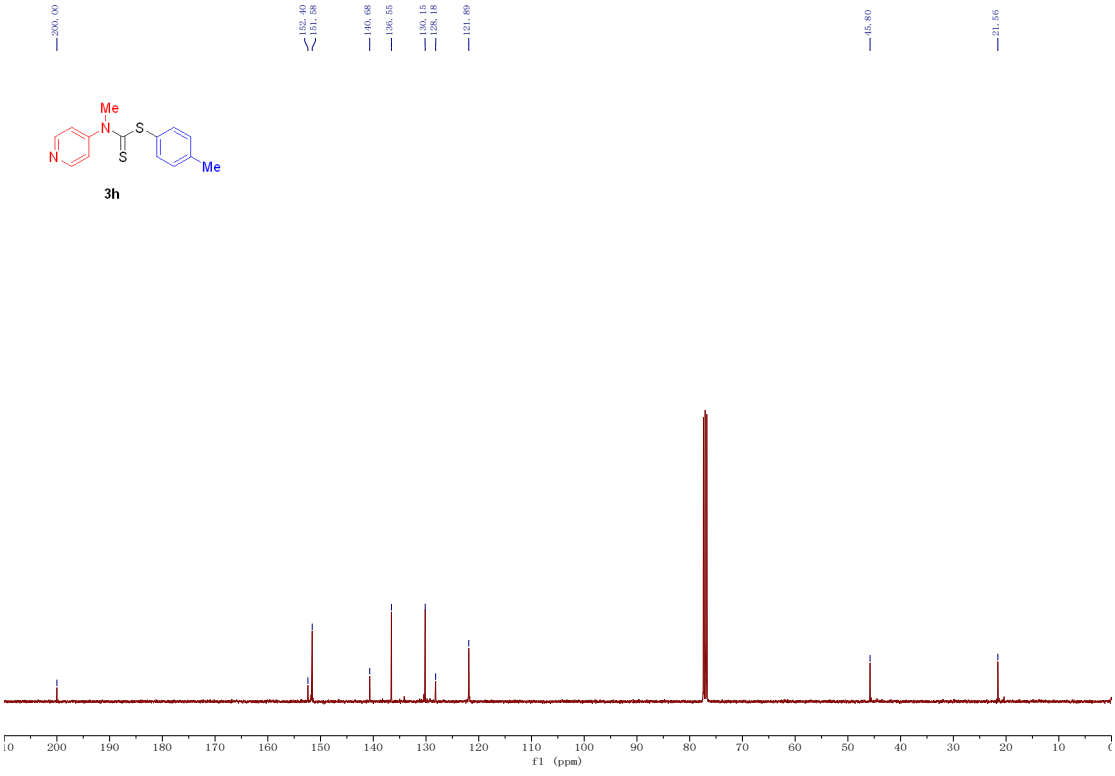

Me
N
S
S
HO
Me

3g


f1 (ppm)

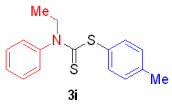

8.81
8.81
8.80
7.38
7.37
7.32
7.30
7.27
7.25
3.79
2.41
Me
N
S
S
N
Me
2.14
2.20
1.95
2.12
3.00
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3h

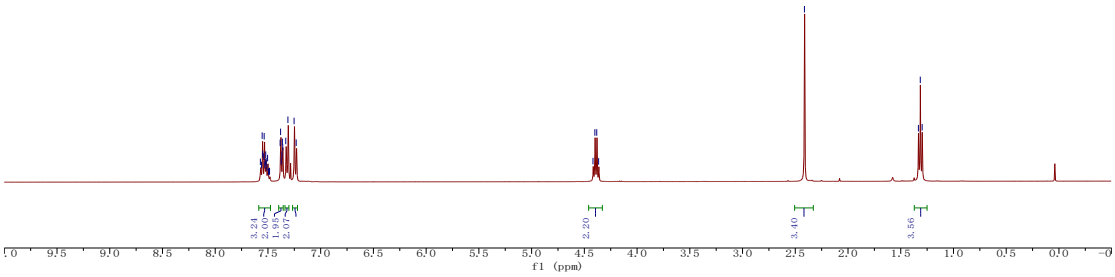

200.00
162.40
151.58
140.68
136.55
130.15
128.18
121.89
45.80
21.56
Me
N
S
S
N
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3h


7.57
7.56
7.55
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.50
7.50
7.49
7.48
7.48
7.38
7.37
7.37
7.36
7.36
7.35
7.33
7.31
7.25
7.23
4.41
4.40
4.38
4.36
2.41
1.33
1.31
1.29


Me
N
S
S
Me

3i


3.24
2.00
1.95
2.07
2.20
3.40
3.56
f1 (ppm)


199.71
143.18
140.14
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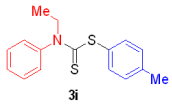
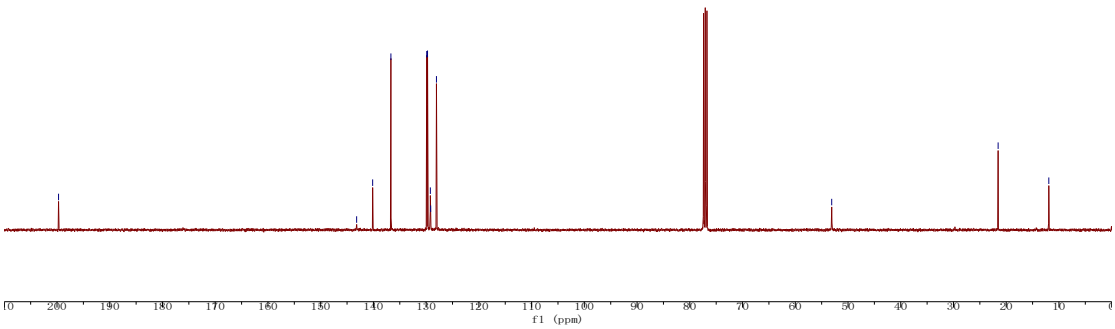
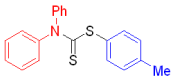
129.74
129.30
128.15
128.05
53.09
21.53
11.92

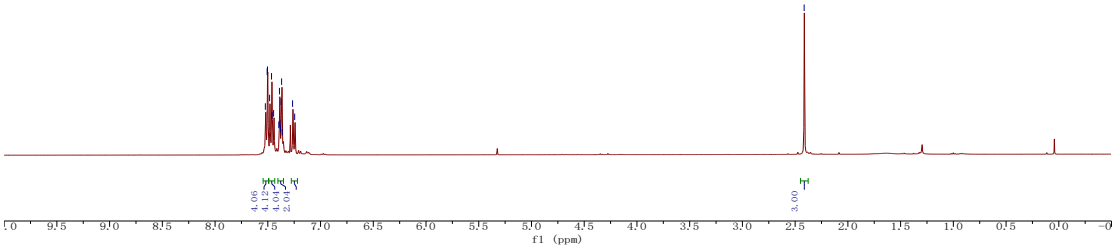

Me
N
S
S
Me

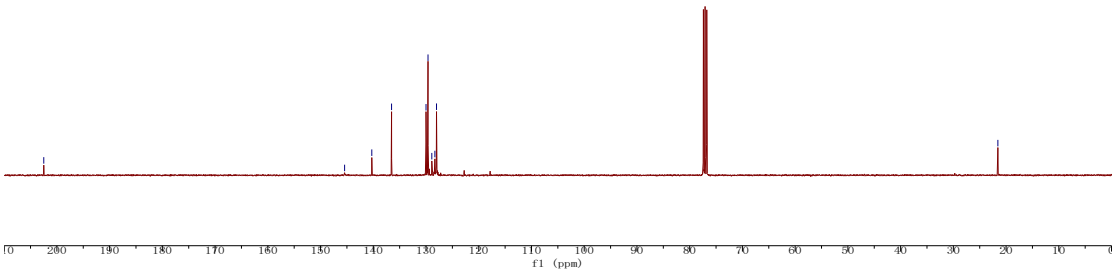
3i

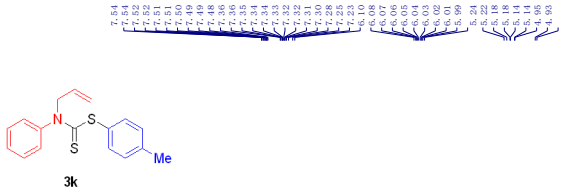

f1 (ppm)



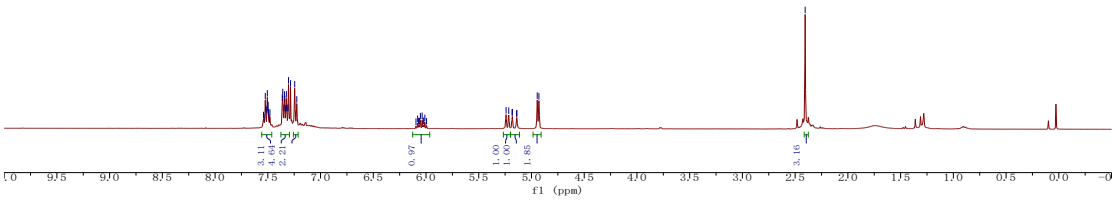
3j

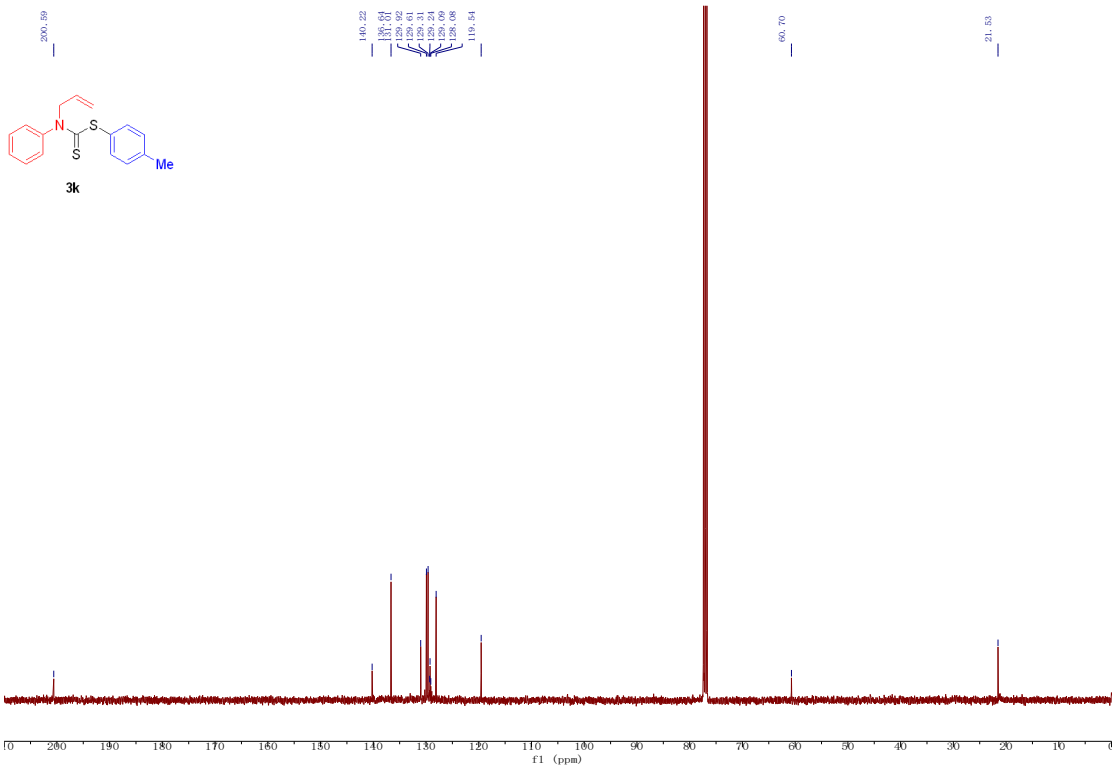






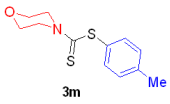
3k



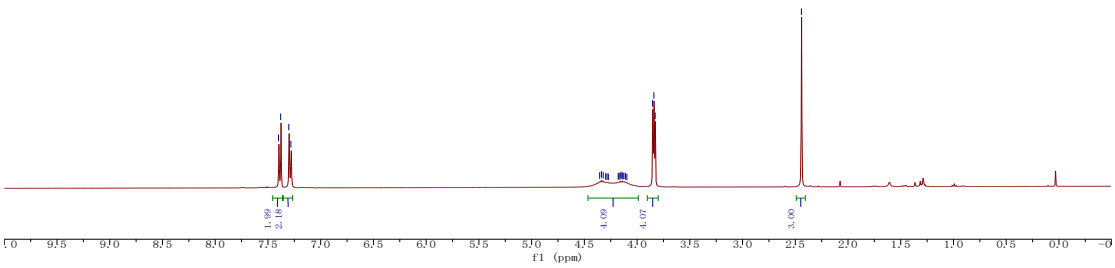


3k

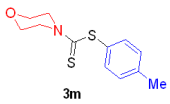

7.39
7.37
7.30
7.28
4.35
4.33
4.32
4.29
4.28
4.27
4.17
4.17
4.16
4.15
4.14
4.13
4.12
4.11
4.09
3.85
3.84
3.82
2.44


O
N
S
S
Me

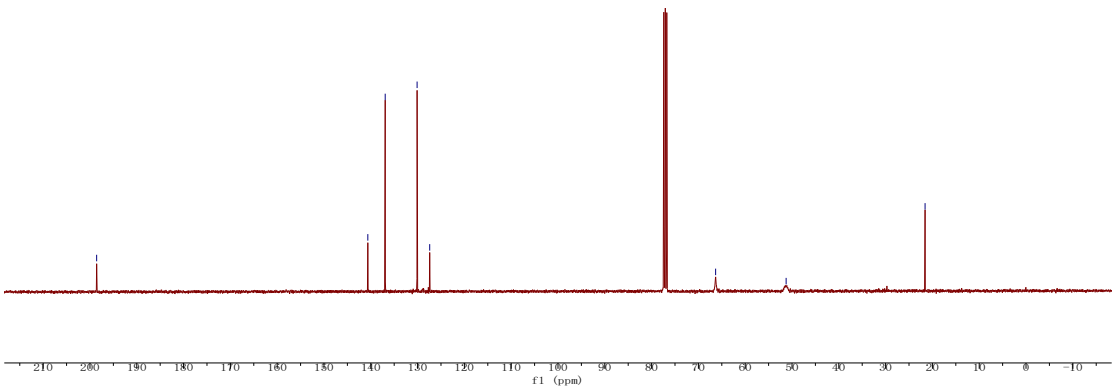
3m

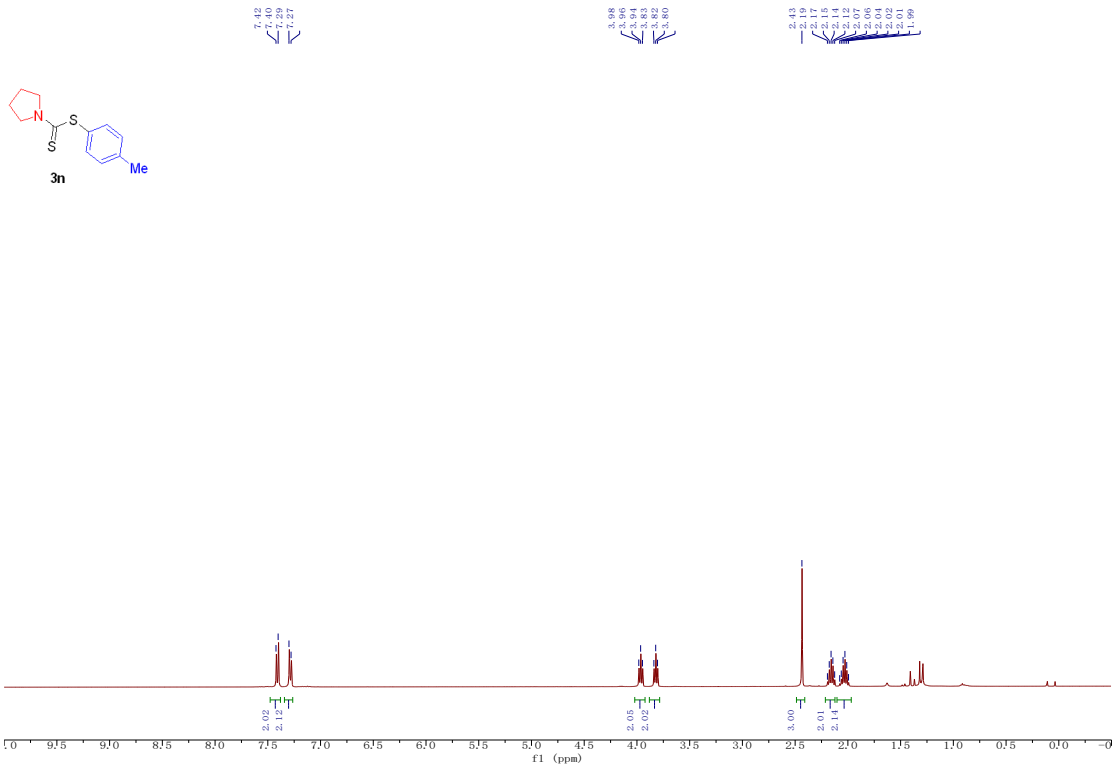

1.99
2.18
4.09
4.07
3.00
f1 (ppm)

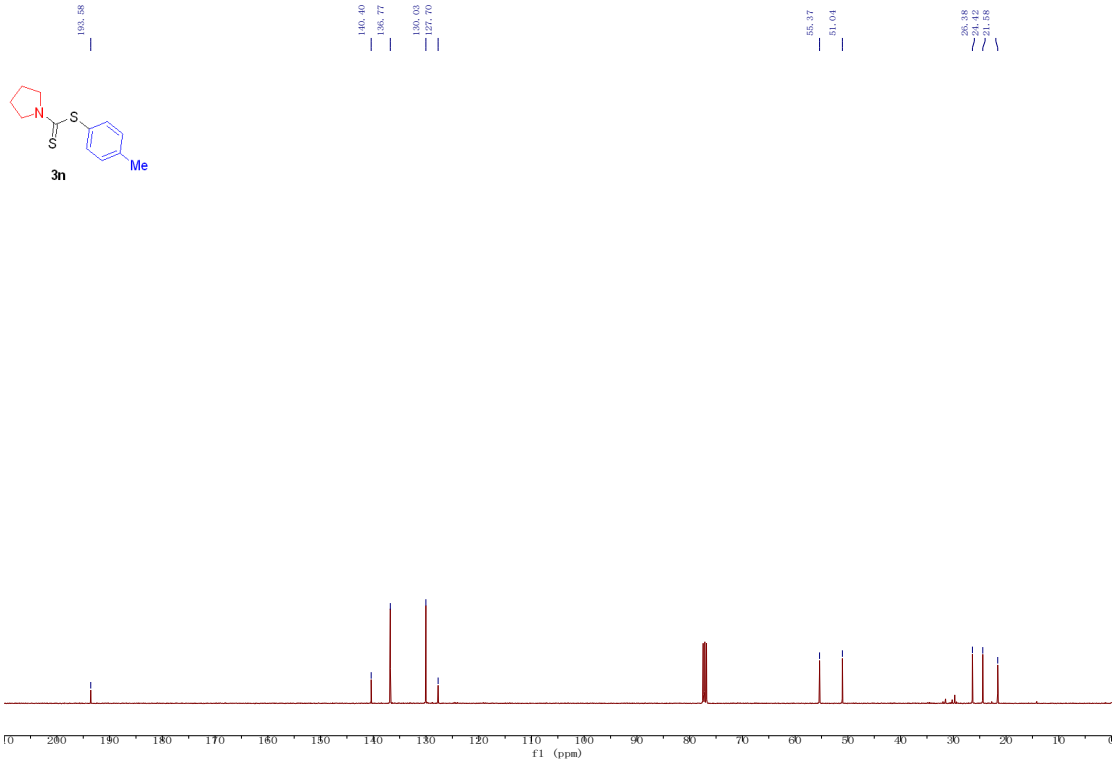

198.57
140.63
136.92
130.10
127.41
66.32
51.26
21.67

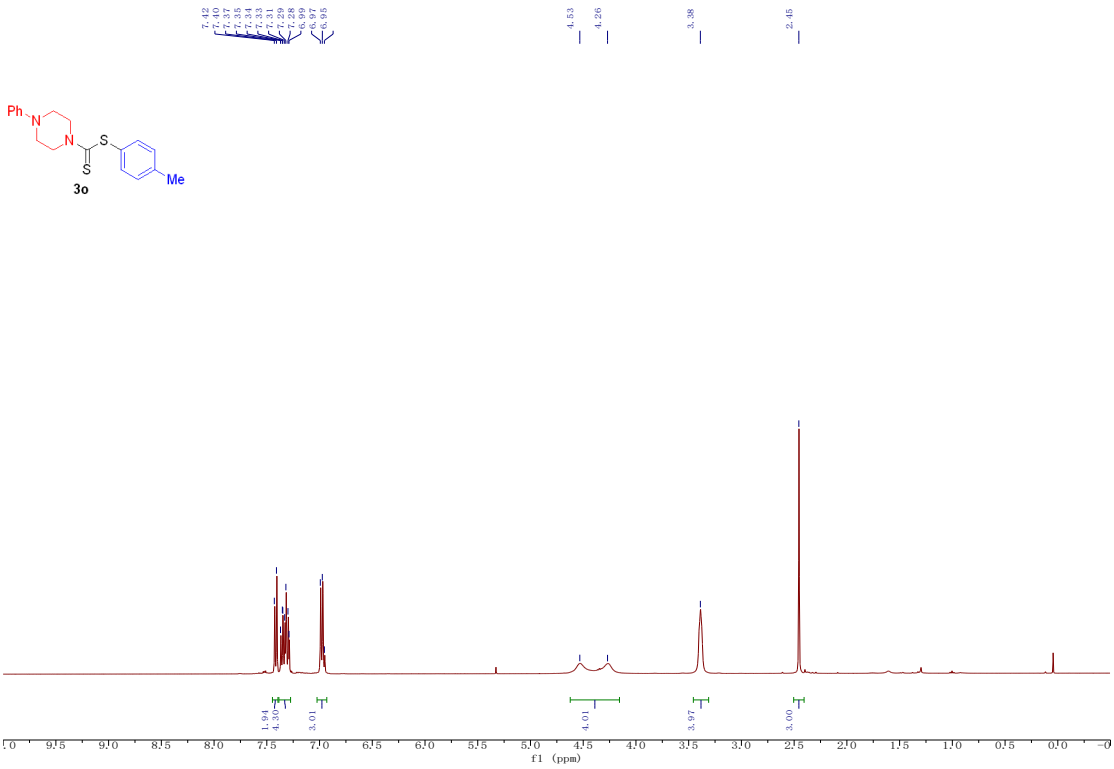

O
N
S
S
Me

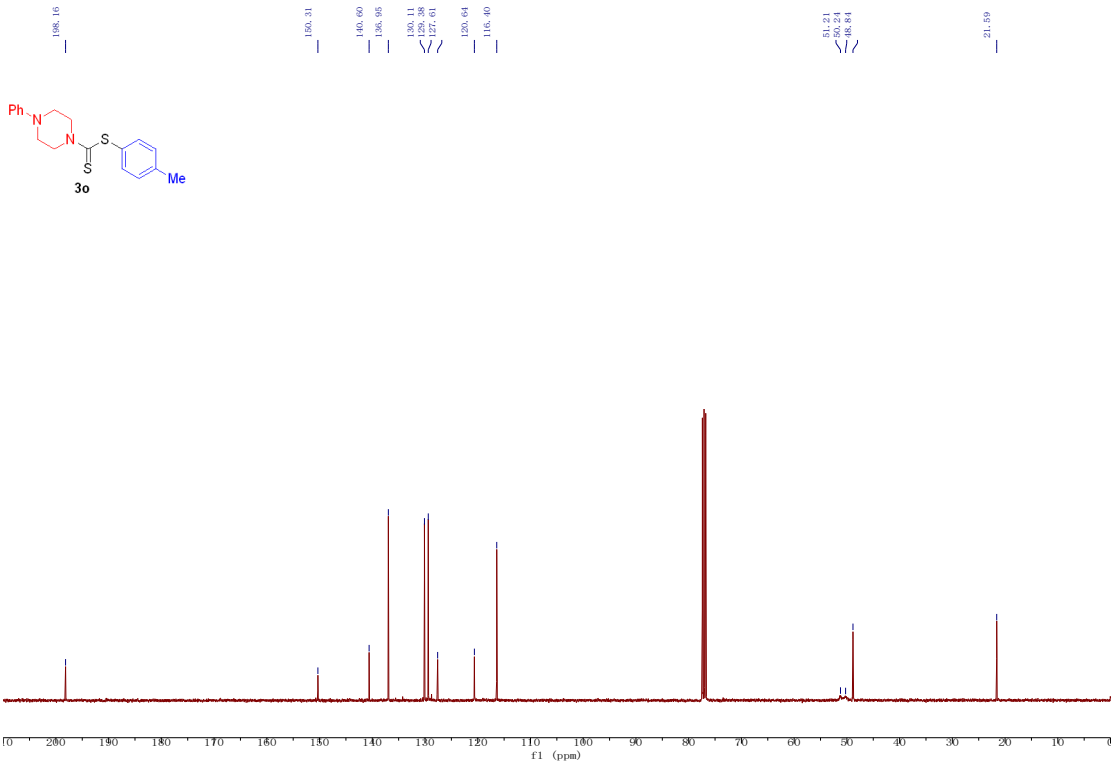
3m

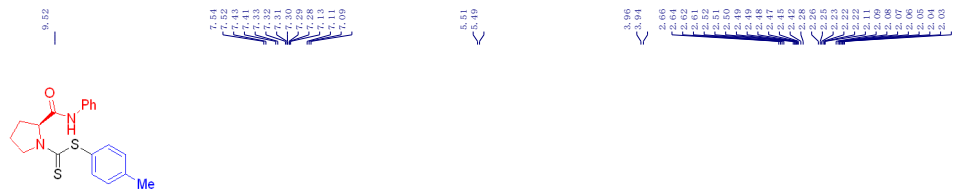

f1 (ppm)


7.42
7.40
7.29
7.27
3.98
3.96
3.84
3.83
3.82
3.80
2.43
2.19
2.17
2.15
2.14
2.12
2.07
2.06
2.04
2.02
2.01
1.99
N
S
S
Me
3n
2.02
2.12
2.05
2.02
3.00
2.01
2.14
f1 (ppm)

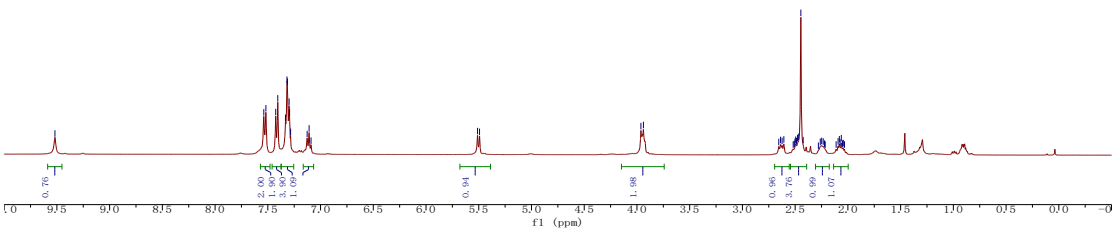

193.58
140.40
136.77
130.03
127.70
55.37
51.04
28.38
24.42
21.58
N
S
S
Me
3n
f1 (ppm)


7.42
7.40
7.37
7.35
7.34
7.33
7.31
7.29
7.28
6.99
6.97
6.95
4.53
4.26
3.38
2.45
Ph
N
N
S
S
Me
3o
1.94
4.30
3.01
4.01
3.97
3.00
f1 (ppm)

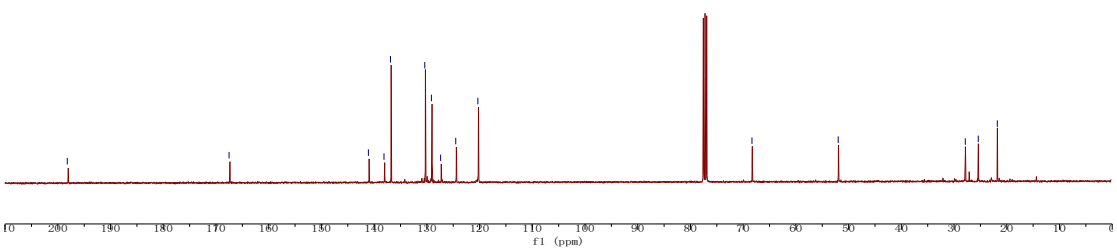

198.16
150.31
140.60
136.95
130.11
129.98
127.61
120.64
116.40
51.21
50.24
48.84
21.59
Ph
N
N
S
S
Me
3o
f1 (ppm)



3p



3p




7.57
7.55
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.48
7.48
7.48
7.47
7.47
7.46
7.46
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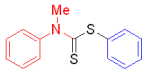
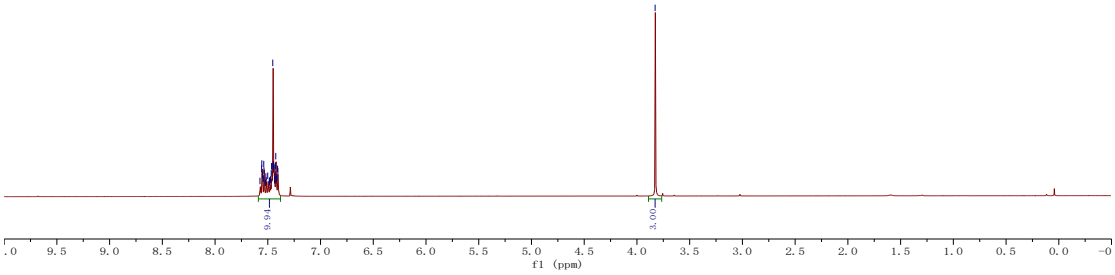
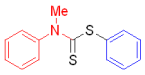
7.42
7.42
7.41
7.40
7.40
3.82


Me
N
S
S

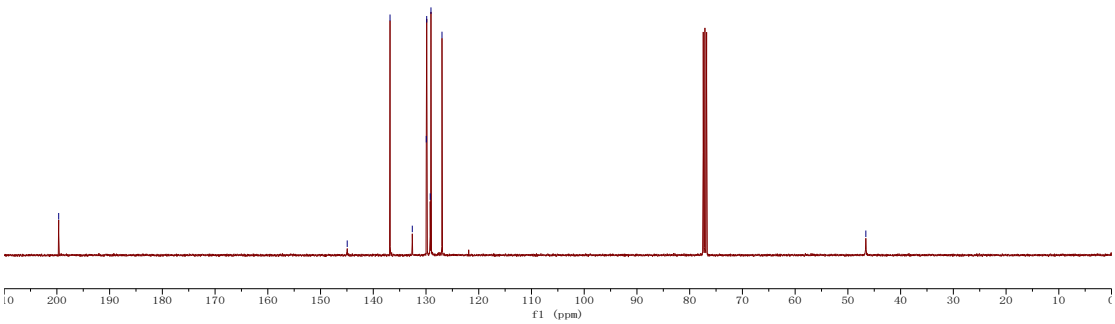
4b


9.94
3.00
f1 (ppm)

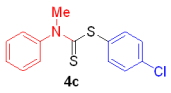

199.66
144.94
136.82
132.60
129.95
129.87
129.20
129.06
126.97
46.59


Me
N
S
S

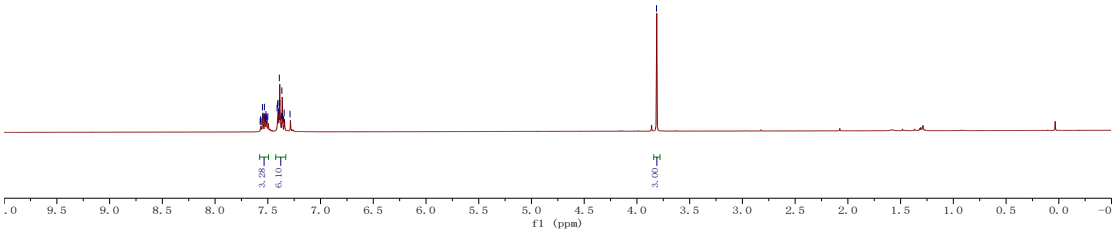
4b


f1 (ppm)


7.57
7.56
7.55
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.28
3.81


Me
N
S
S
Cl

4c


3.28
6.10
3.00
f1 (ppm)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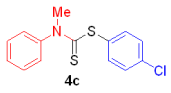
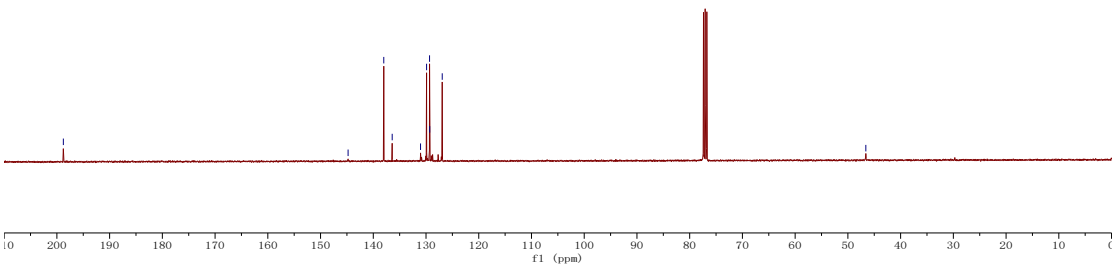
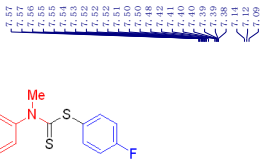
138.01
136.42
131.04
129.89
129.33
129.30
126.93
46.60

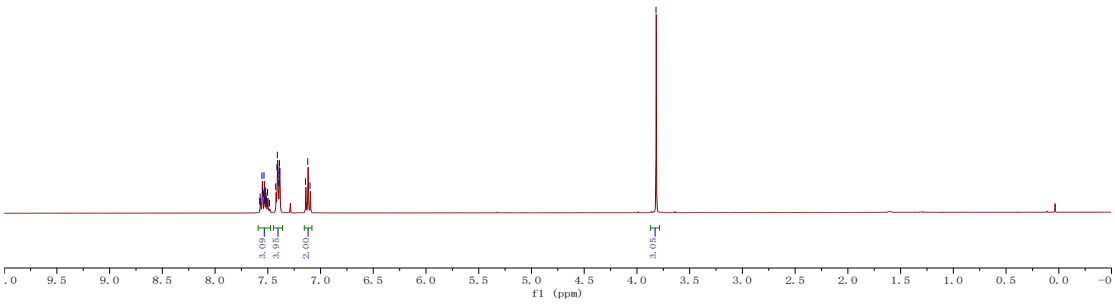

Me
N
S
S
Cl

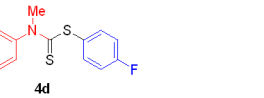
4c


f1 (ppm)



4d





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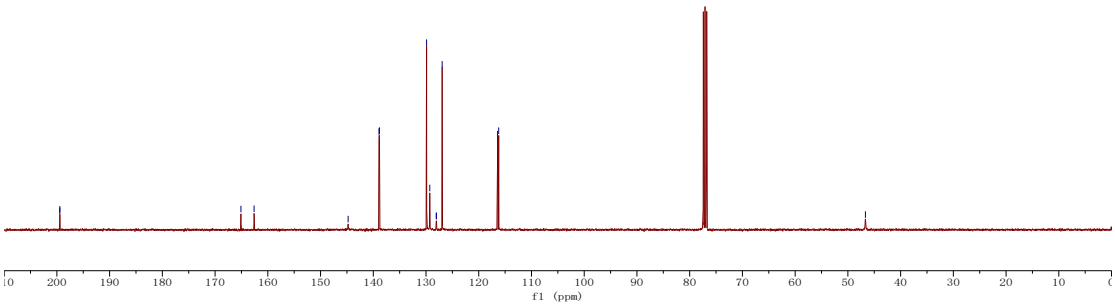
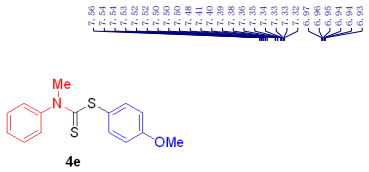
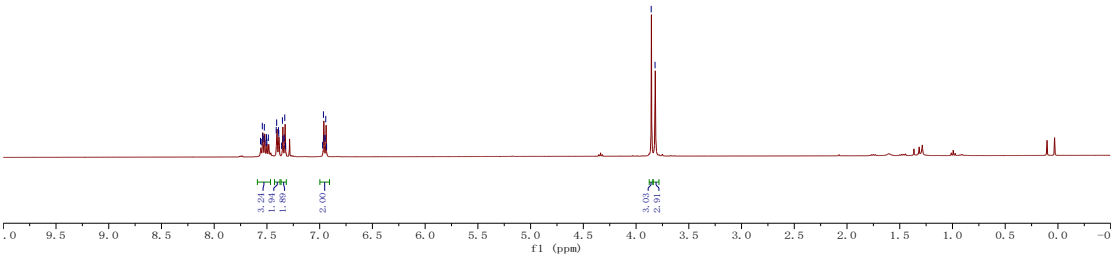
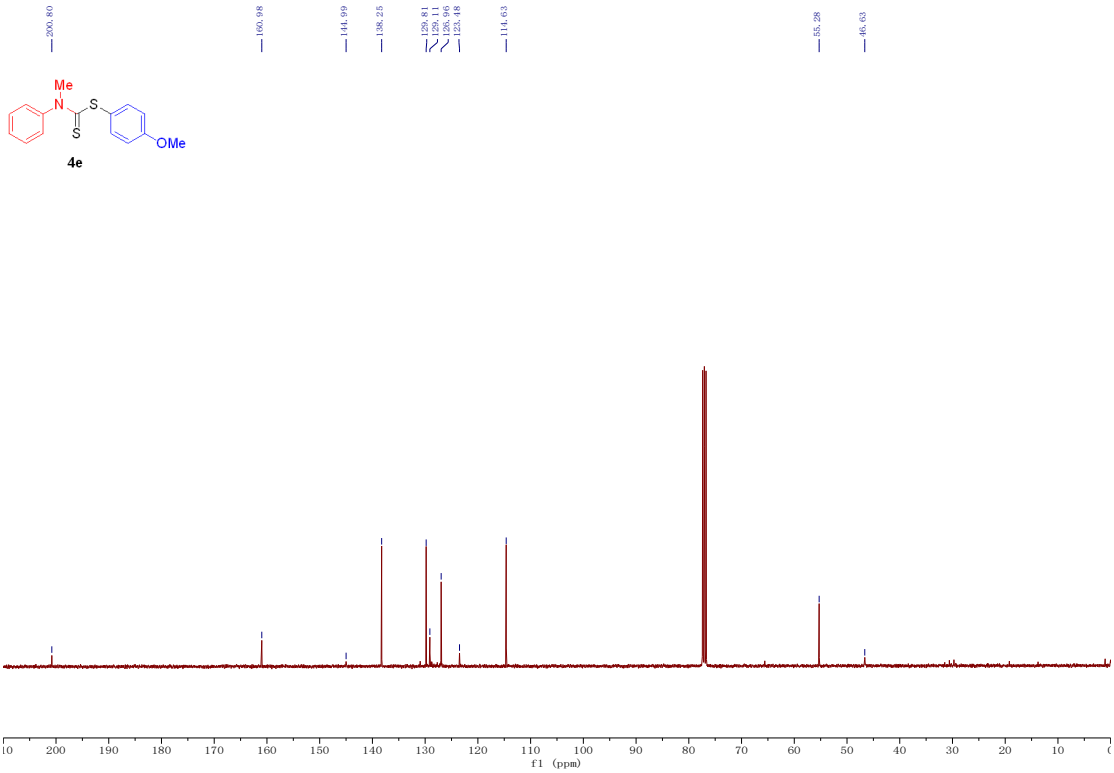




4e



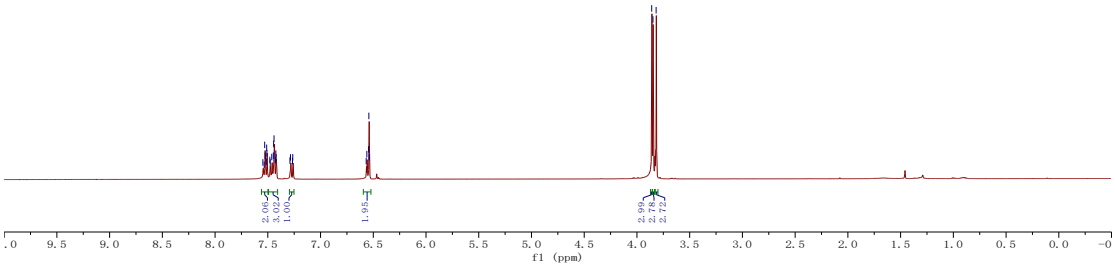


4e

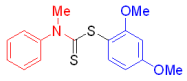

7.54
7.53
7.52
7.51
7.51
7.51
7.50
7.48
7.47
7.46
7.44
7.44
7.44
7.42
7.42
7.42
7.29
7.28
7.26
7.26
6.56
6.56
6.54
6.54
6.53
3.86
3.84
3.81


Me
N
S
S
OMe
OMe

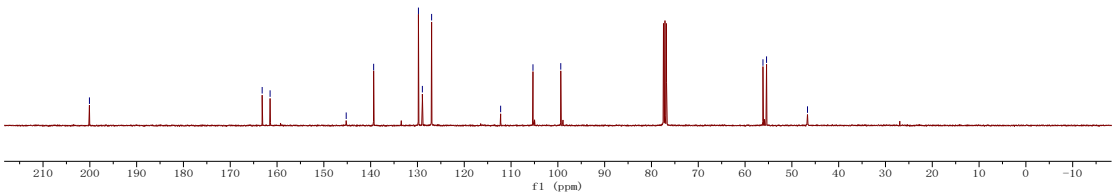
4f


2.06
3.02
1.00
1.95
2.99
2.78
2.72
f1 (ppm)


200.09
163.18
161.49
145.22
139.36
129.79
128.95
120.98
112.23
105.32
99.38
56.18
55.41
46.66


Me
N
S
S
OMe
OMe

4f


f1 (ppm)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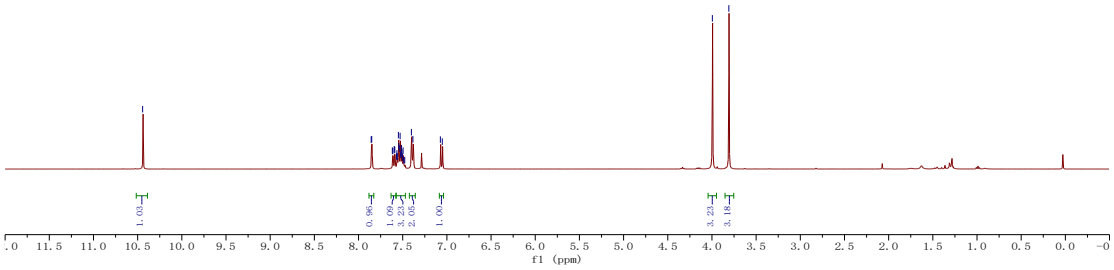
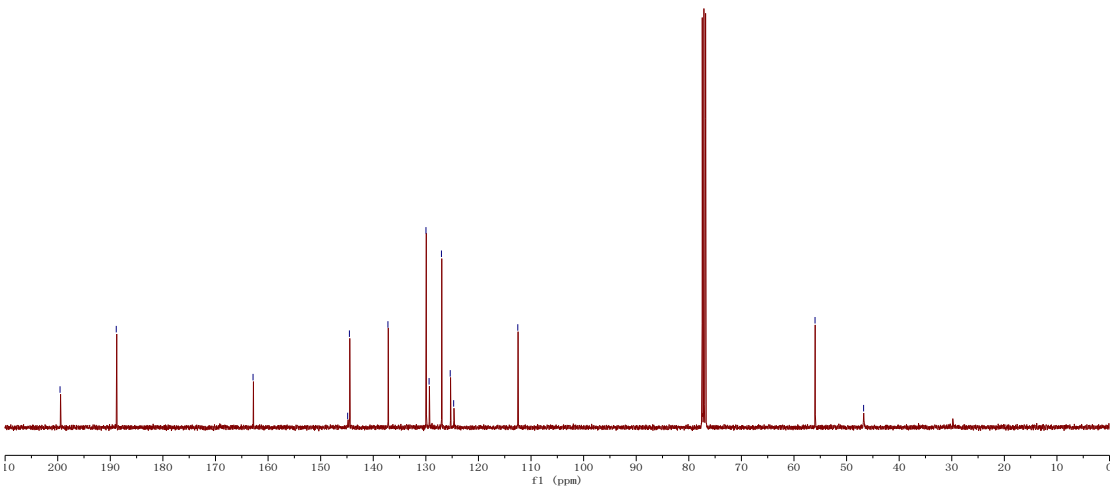
7.85
7.84
7.61
7.61
7.59
7.58
7.56
7.56
7.54
7.54
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.48
7.47
7.40
7.38
7.07
7.05
3.99
3.80
Me
N
S
S
O
H
OMe

4g


1.03
0.96
1.09
3.23
2.05
1.00
3.23
3.18
f1 (ppm)


199.45
188.77
162.76
144.77
144.43
137.11
129.88
129.28
126.93
125.57
124.61
112.42
55.90
46.66
Me
N
S
S
O
H
OMe

4g


f1 (ppm)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7.59
7.57
7.57
7.57
7.56
7.55
7.55
7.55
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7.54
7.53
7.52
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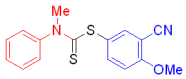
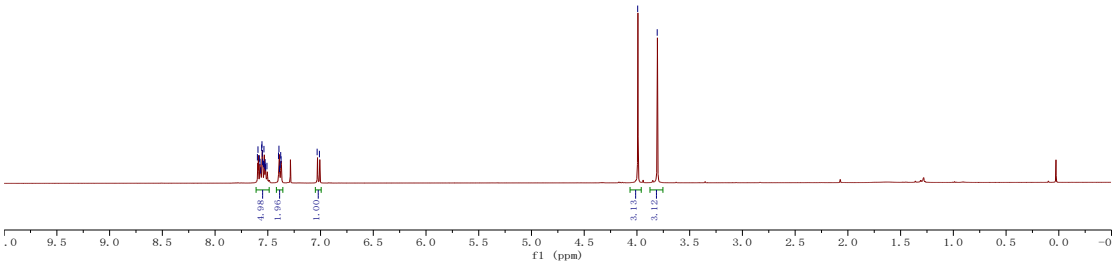
7.37
7.37
7.03
7.01


3.99
3.80


Me
N
S
S
CN
OMe

4h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1.96
1.00
3.13
3.12
f1 (ppm)


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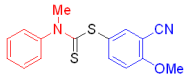
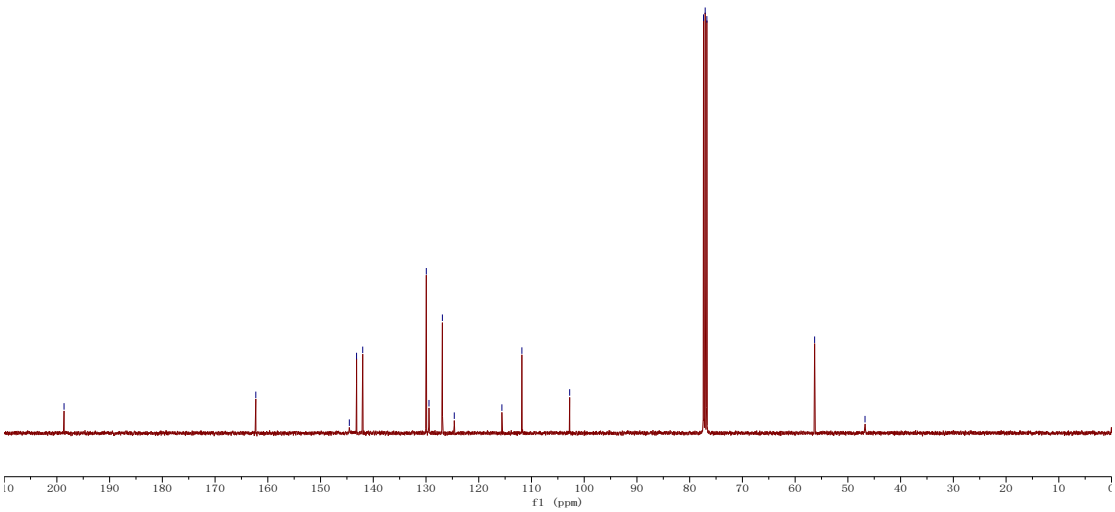
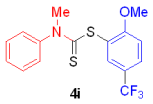
162.28
144.54
143.17
142.00
129.95
129.44
126.89
124.64
115.61
111.82
102.76
77.48
77.06
76.74
56.31
46.75


Me
N
S
S
CN
OMe

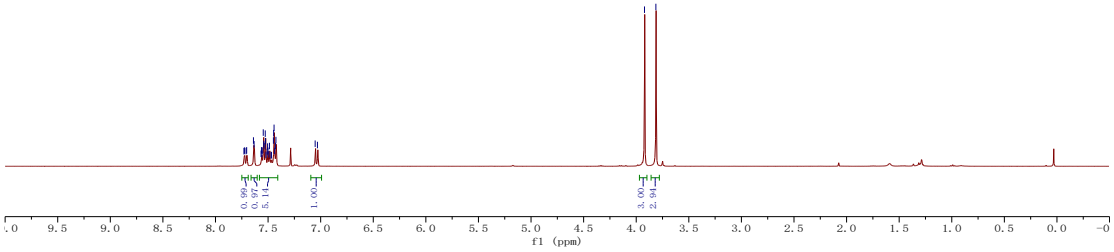
4h


f1 (ppm)


7.72
7.72
7.70
7.70
7.65
7.63
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.52
7.51
7.50
7.50
7.50
7.49
7.48
7.46
7.44
7.44
7.43
7.43
7.42
7.42
7.03
3.92
3.81


Me
N
S
S
OMe
CF3

4i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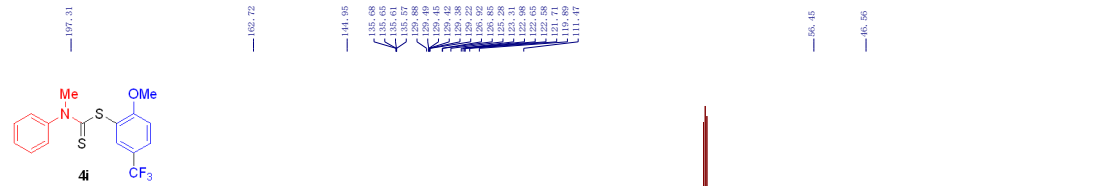
0.97
5.14
1.00
3.00
2.94
f1 (ppm)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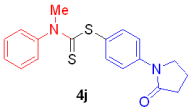
135.61
135.57
129.88
129.49
129.45
129.42
129.38
129.22
126.92
126.86
125.28
123.31
122.98
122.65
122.58
121.71
119.89
111.47
56.45
46.56

Me
N
S
S
OMe
CF3

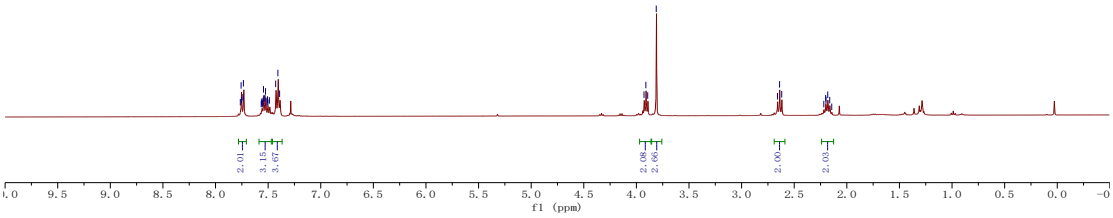
4i

f1 (ppm)


7.76
7.75
7.75
7.73
7.73
7.56
7.56
7.55
7.55
7.54
7.54
7.53
7.52
7.52
7.50
7.50
7.50
7.48
7.42
7.40
7.39
3.92
3.90
3.89
3.81
2.65
2.63
2.61
2.21
2.20
2.19
2.18
2.16
2.14


Me
N
S
S
N
O

4j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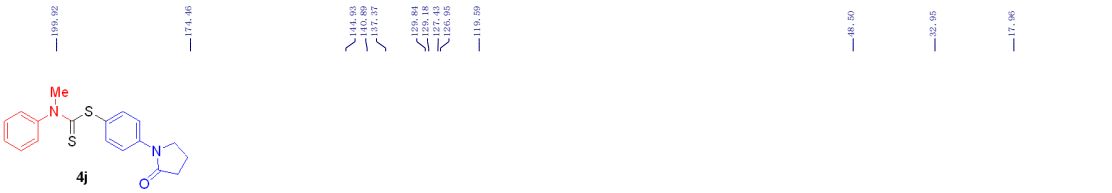
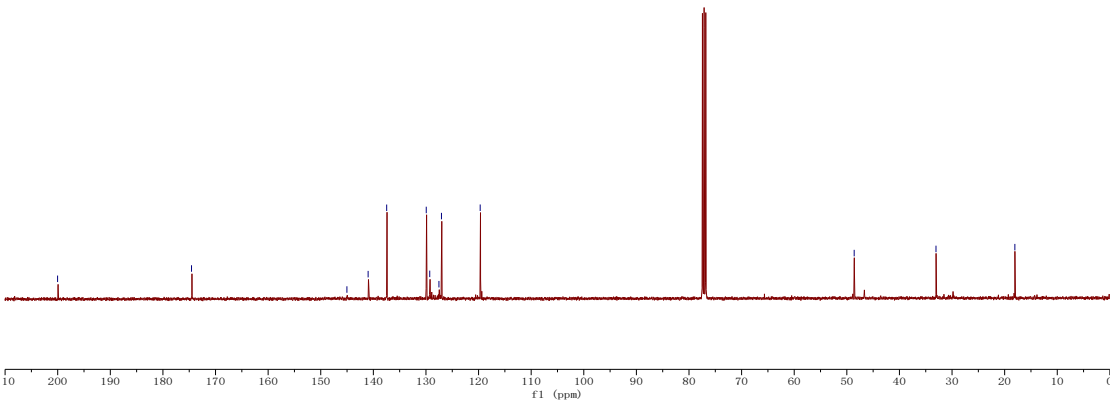
2.08
2.06
2.00
2.03
f1 (ppm)


199.92
174.46
144.93
140.89
137.37
129.84
129.18
127.43
126.95
119.59
48.50
32.95
17.96

Me
N
S
S
N
O

4j


f1 (ppm)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7.55
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7.52
7.50
7.50
7.50
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7.48
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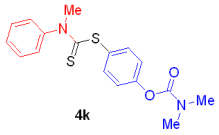
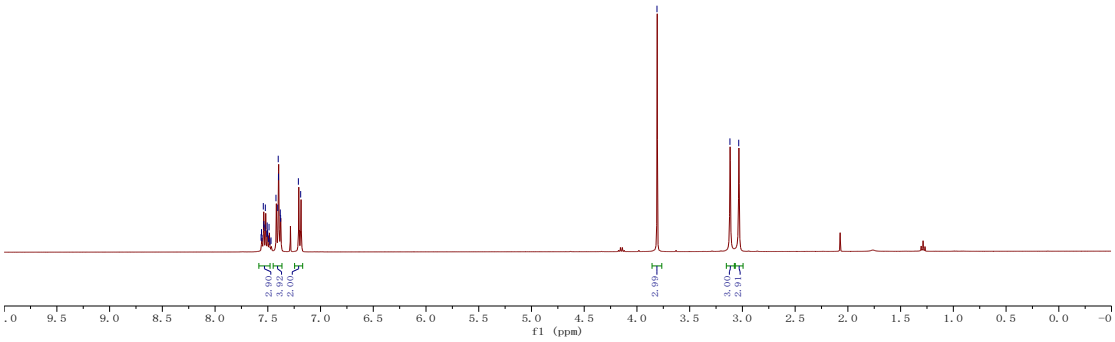
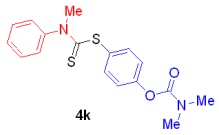
7.37
7.21
7.18
3.80
3.11
3.03


Me
N
S
S
O
O
N
Me
Me

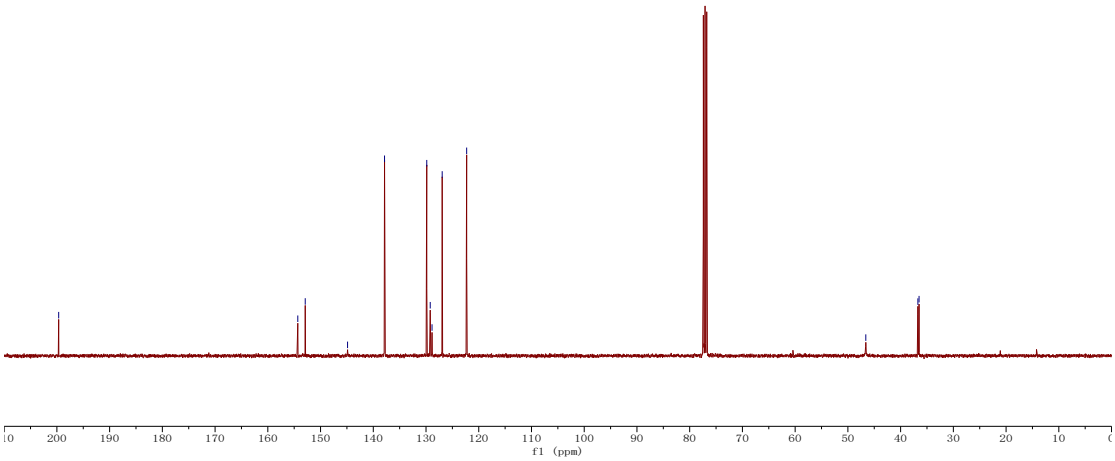
4k


2.99
3.00
2.91
f1 (ppm)

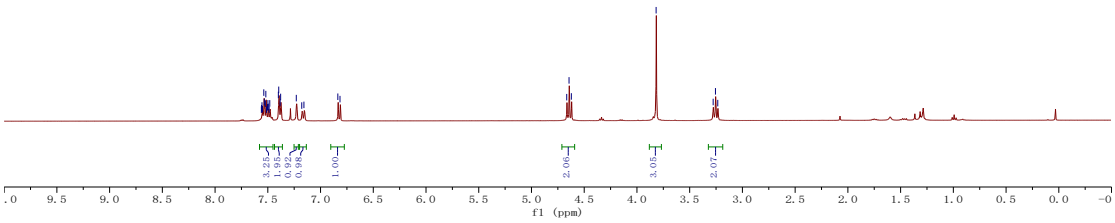

199.66
154.32
152.91
144.88
137.87
129.86
129.20
128.86
126.94
122.29
46.60
36.72
36.50

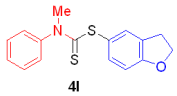

Me
N
S
S
O
O
N
Me
Me

4k

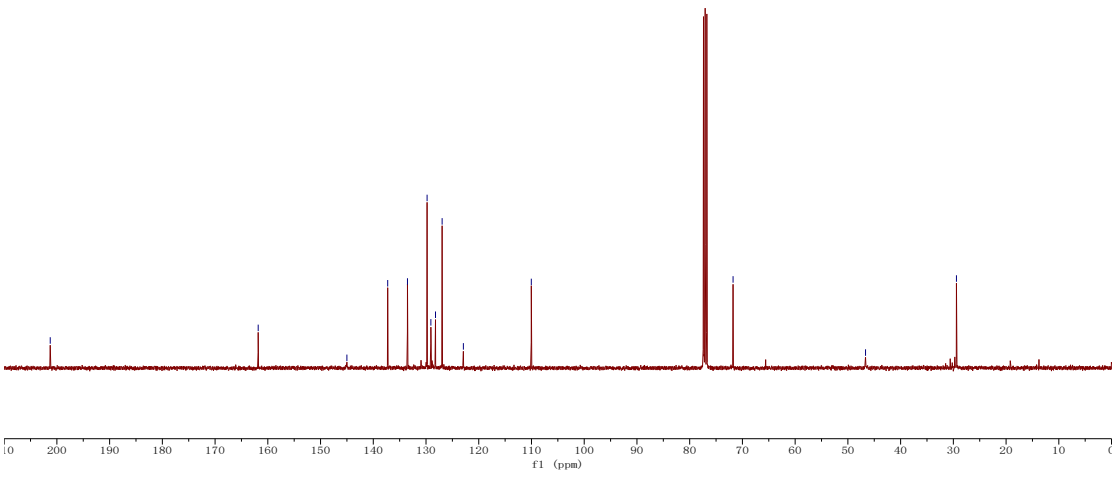

f1 (ppm)

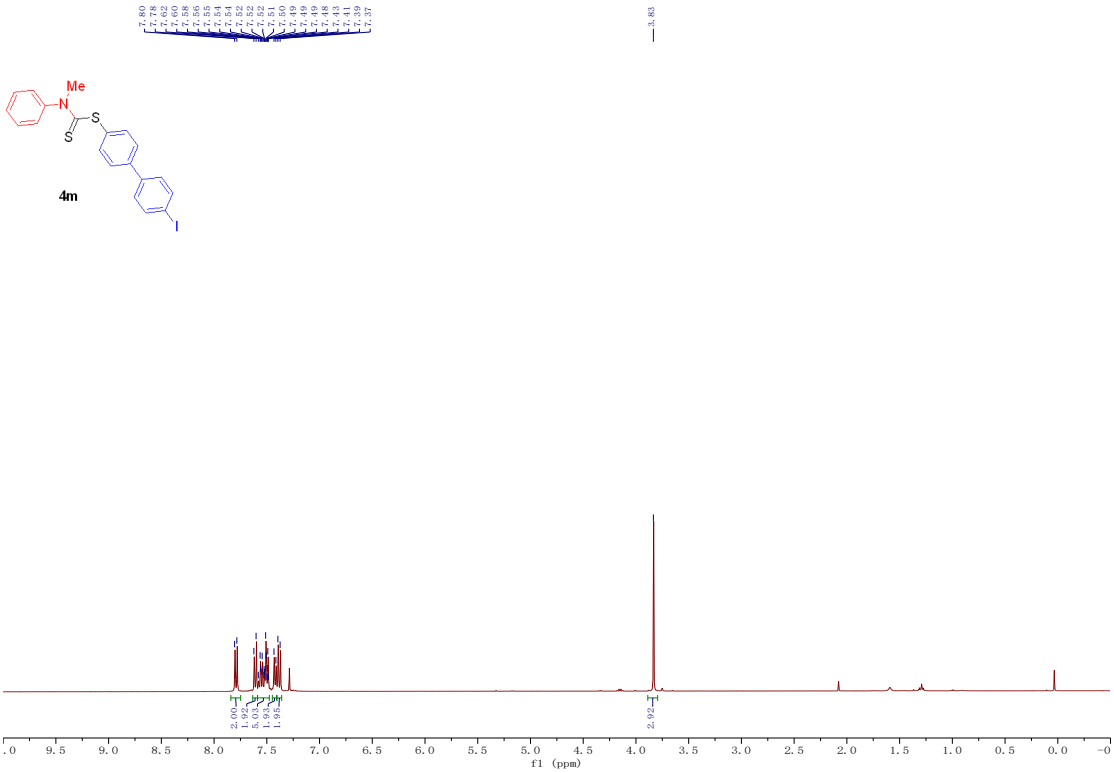
4l





4l

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7.52
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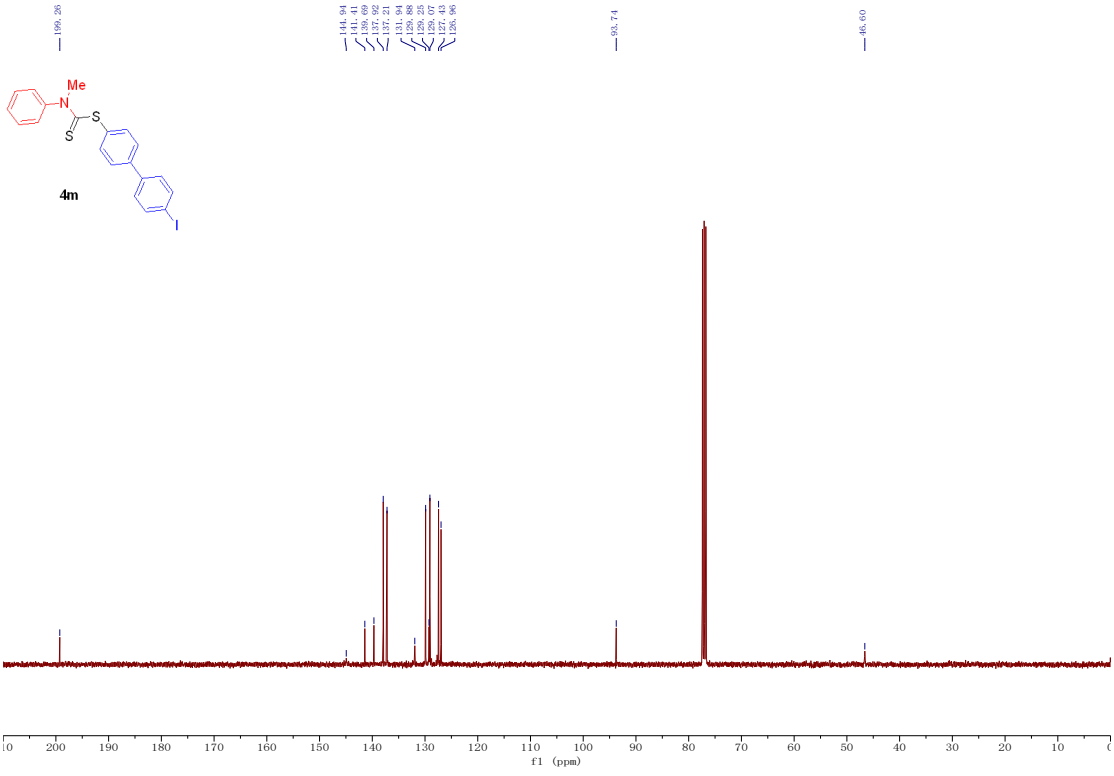
7.52
7.51
7.50
7.49
7.49
7.49
7.48
7.43
7.41
7.39
7.37
3.83
Me
N
S
S
I
4m
2.00
1.92
5.03
1.94
1.94
2.92
f1 (ppm)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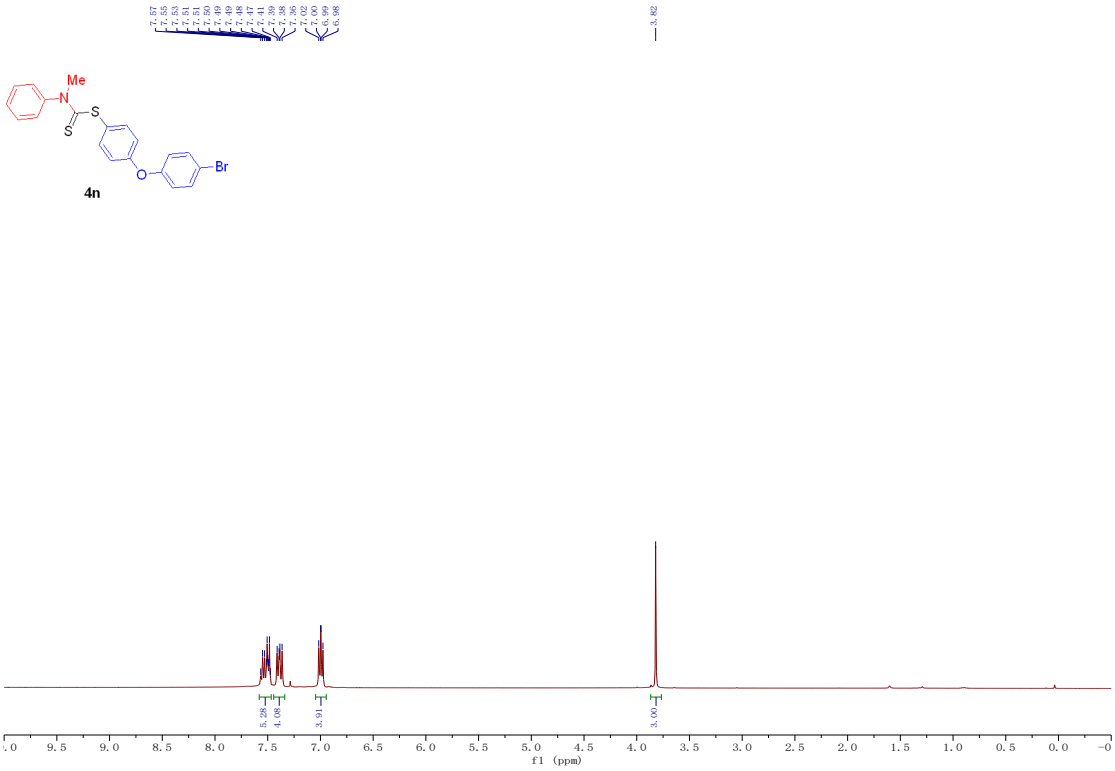
141.41
139.69
137.92
137.21
131.94
129.88
129.35
128.57
127.43
126.96
93.74
46.60
Me
N
S
S
I
4m
f1 (ppm)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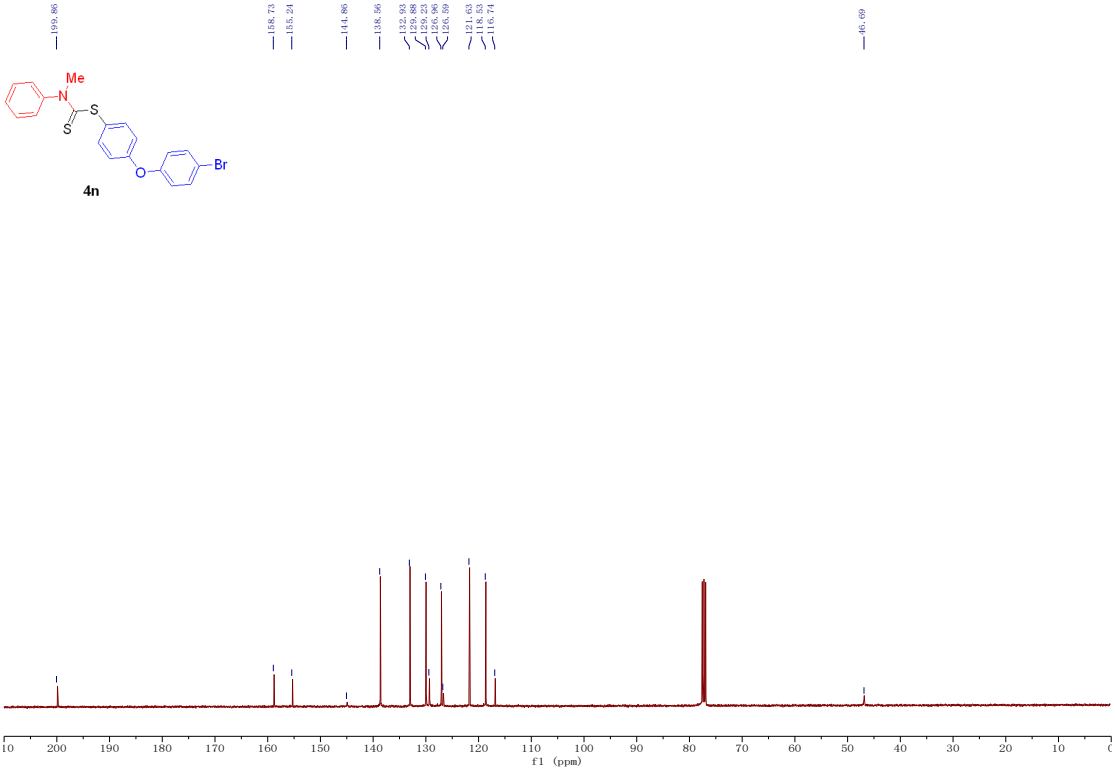
7.49
7.48
7.47
7.41
7.39
7.38
7.36
7.02
7.00
6.99
6.98
3.82
Me
N
S
S
O
Br
4n
5.28
4.08
3.91
3.00
f1 (ppm)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132.93
129.88
129.23
128.96
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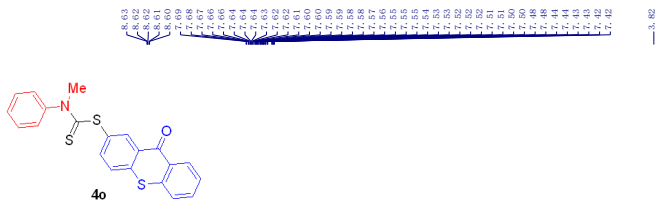
121.63
118.53
116.74
46.69
Me
N
S
S
O
Br
4n
f1 (ppm)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7.50
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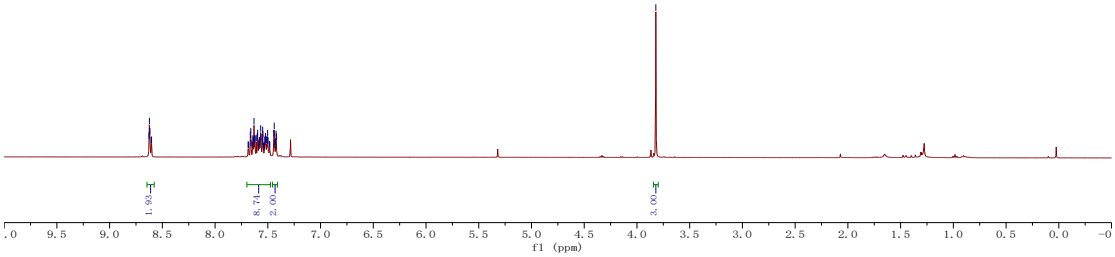
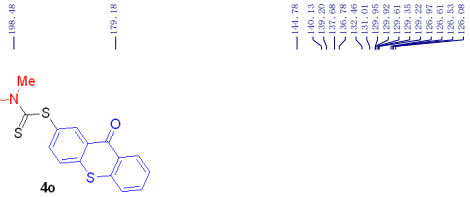
7.42
3.82

Me
N
S
S
O
S

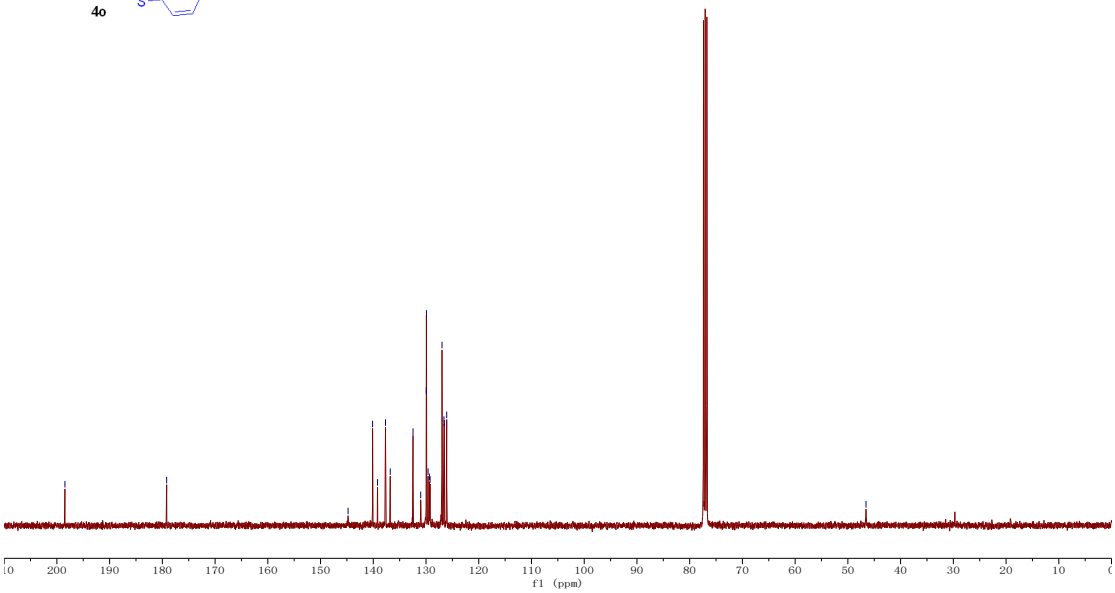
4o

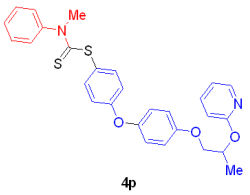

1.93
8.74
2.00
3.00
f1 (ppm)


198.48
179.18
144.78
140.13
139.20
137.68
136.78
132.46
131.01
129.95
129.92
129.61
129.35
129.22
126.97
126.61
126.53
126.08
46.56

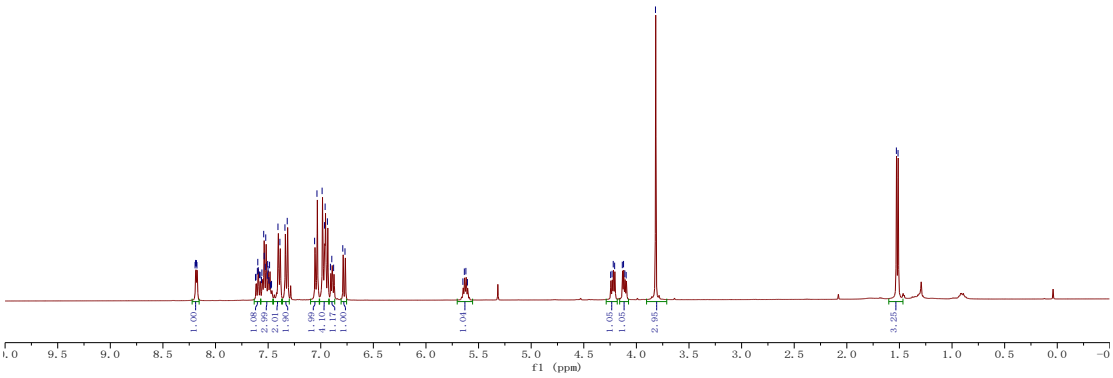
Me
N
S
S
O
S

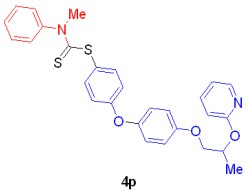
4o


f1 (ppm)

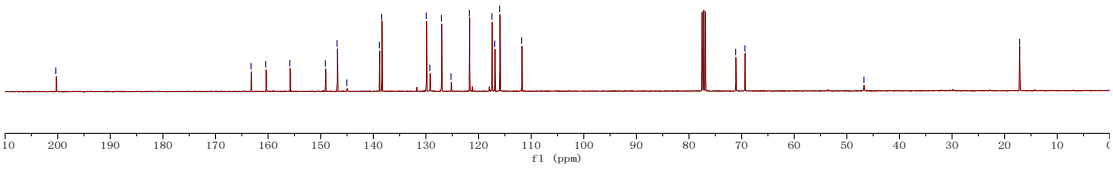


4p

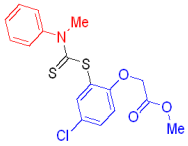




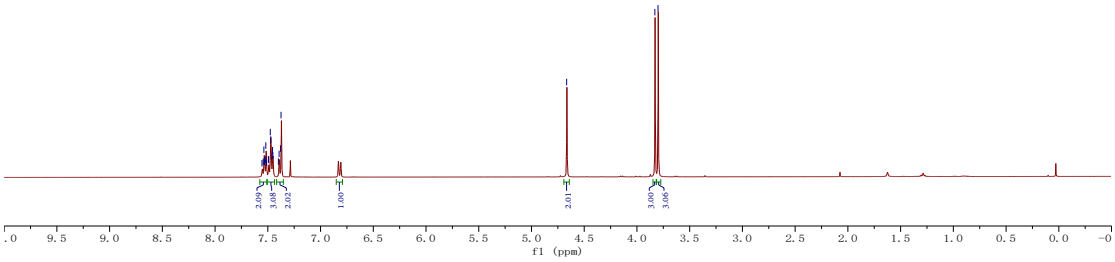
4p



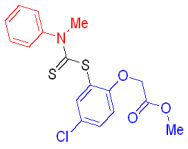

7.55
7.54
7.53
7.53
7.52
7.51
7.51
7.49
7.49
7.47
7.47
7.45
7.45
7.45
7.39
7.39
7.37
7.37
4.66
3.83
3.80


Me
N
S
S
O
O
O
Me
Cl

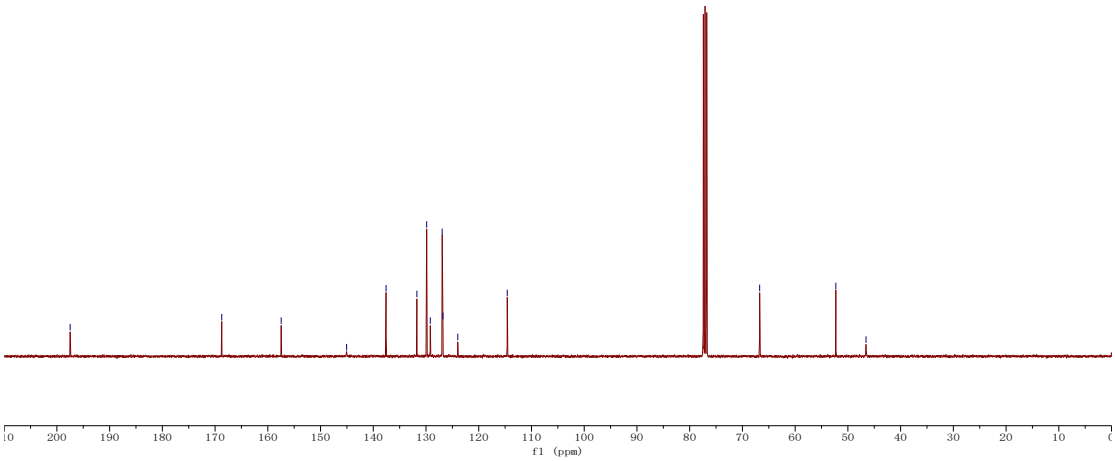
4q

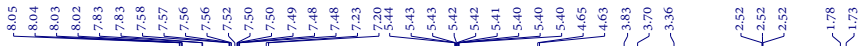

2.09
3.08
2.02
1.00
2.01
3.00
3.06
f1 (ppm)

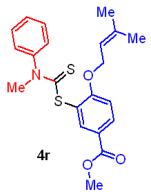

197.48
168.74
157.47
145.06
137.58
131.73
129.88
129.19
126.93
126.79
123.98
114.59
66.73
53.28
46.56


Me
N
S
S
O
O
O
Me
Cl

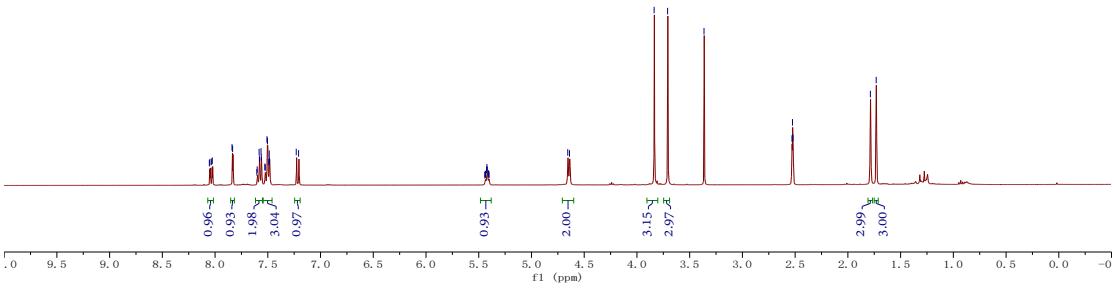
4q

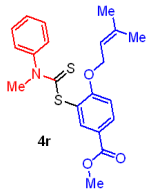

f1 (ppm)


8.05
8.04
8.03
8.02
7.83
7.83
7.58
7.57
7.56
7.56
7.52
7.50
7.50
7.49
7.48
7.48
7.23
5.44
5.43
5.43
5.42
5.42
5.41
5.40
5.40
5.40
4.65
4.63
3.83
3.70
3.36
2.52
2.52
2.52
1.78
1.73


Me
Me
N
Me
S
S
O
O
O
Me

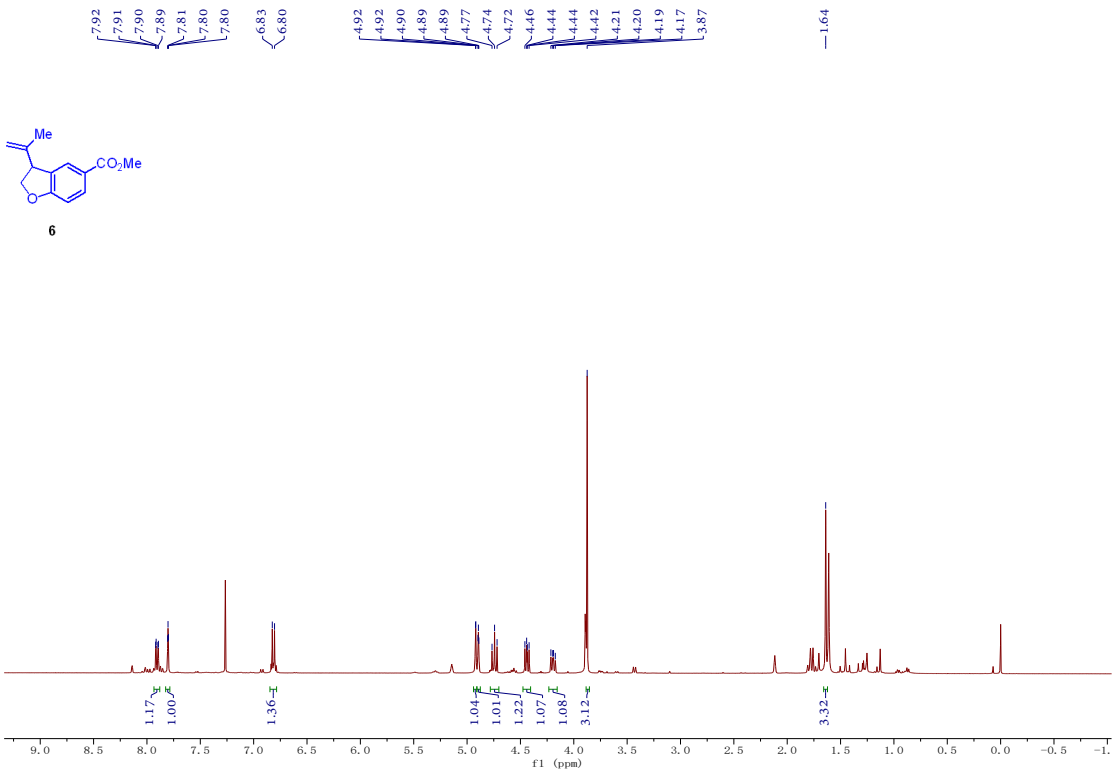
4r

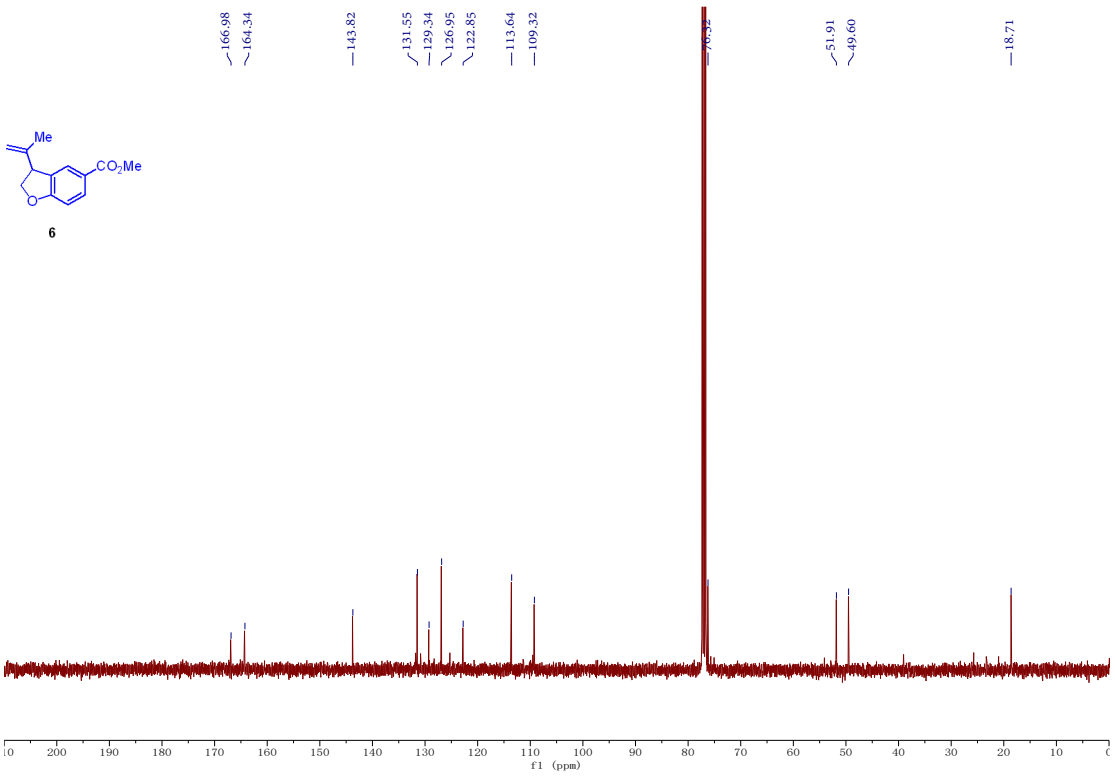

0.96
0.93
1.98
3.04
0.97
0.93
2.00
3.15
2.97
2.99
3.00
f1 (ppm)


Me
Me
N
Me
S
S
O
O
O
Me

4r

165.80
163.23
145.28
139.76
138.69
133.95
130.32
129.62
127.33
122.38
121.71
119.66
113.72
66.17
62.52
46.78
25.99
18.71
f1 (ppm)


7.92
7.91
7.90
7.89
7.81
7.80
7.80
6.83
6.80
4.92
4.92
4.90
4.89
4.89
4.77
4.74
4.72
4.46
4.44
4.44
4.42
4.21
4.20
4.19
4.17
3.87
1.64
Me
CO2Me
6
1.17
1.00
1.36
1.04
1.01
1.22
1.07
1.08
3.12
3.32
f1 (ppm)


166.98
164.34
143.82
131.55
129.34
126.95
122.85
113.64
109.32
76.32
51.91
49.60
18.71
Me
CO2Me
6
f1 (ppm)