Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Aqueous MCRs of quaternary ammoniums, *N*-substituted formamides and sodium disulfide towards aryl thioamides

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1. General Information

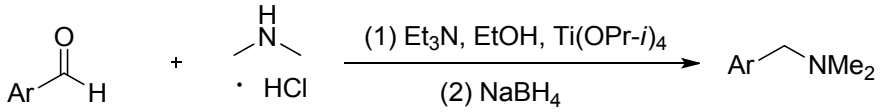
^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on 300 MHz or 400 MHz NMR spectrometer (75 MHz or 100 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants *J* are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mod.

2. Experimental Procedures

1) Synthesis of Aqueous Sodium Disulfide

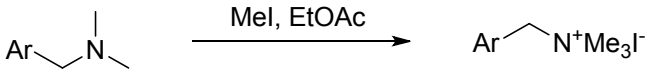
Sodium sulfide hydrate (5.07 g, 65 mmol, 1 equiv) was added to water (50 mL) and the mixture was allowed to stir at 55 °C for 30 min. Subsequently, to the reaction mixture was added the sulfur (2.50 g, 78 mmol, 1.2 equiv) and stirred for another one hour at 55 °C. Then, the reaction mixture was cooled to room temperature and was filtered to afford aqueous sodium disulfide without further purification.

2) General Procedure for the Reductive Alkylation of Dimethylamine[1]



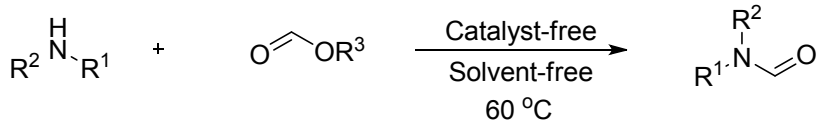
To a solution of triethylamine (2.0 g, 20 mmol) in absolute ethanol (15 mL) were added dimethylamine hydrochloride (1.65 g, 20 mmol), titanium isopropoxide (5.7 g, 20 mmol), and the starting aldehyde (10 mmol). The reaction mixture was stirred at 25 ^{o}C for 9-10 h, after which sodium borohydride (0.57 g, 15 mmol) was added and the resulting mixture was further stirred for a period of 10 h at 25 ^{o}C. The reaction was then quenched by pouring the mixture into aqueous ammonia (30 mL, 2 N), the resulting inorganic precipitate was filtered and washed with dichloromethane (50 mL), and the aqueous filtrate was extracted with dichloromethane (50 mL×2). The combined dichloromethane extracts were dried (K_2CO_3) and concentrated in vacuo to give pure *N,N*-dimethylated tertiary amines.

3) General Procedure for the Synthesis of Quaternary Ammonium Salts



Methyl iodide (3.2 mL, 50 mmol, 5 equiv) was added to a solution of corresponding alkylated dimethylamine (10 mmol, 1 equiv) in ethyl acetate (10 mL) at room temperature and the resulting mixture was stirred for several minutes. The formed solid was filtered, washed with ethyl acetate and dried under reduced pressure, affording pure quaternary ammonium salt.

4) General Procedure for the *N*-Formylated Products[2]

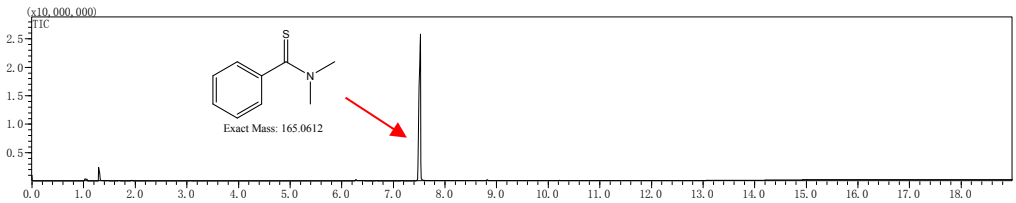


R^1 = aryl, alkyl R^3 = H, ethyl
R^2 = aryl, alkyl, H

In a typical experimental procedure, corresponding amine (1 mmol) and formic acid (1.2 mmol) or ethyl formate (3 mmol) were carefully added to a sealed glass vial without any additional solvent or catalyst and were magnetically stirred at 60 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted by using DCM or EtOAc. The obtained organic mixture was then washed with water (10 mL ×2) and a saturated solution of $NaHCO_3$ and was then dried over anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the residue obtained was then subjected to recrystallization with a suitable solvent or was isolated through column chromatography to obtain pure *N*-formylated products.

3. Mechanistic Studies

3.1 GCMS results under standard conditions



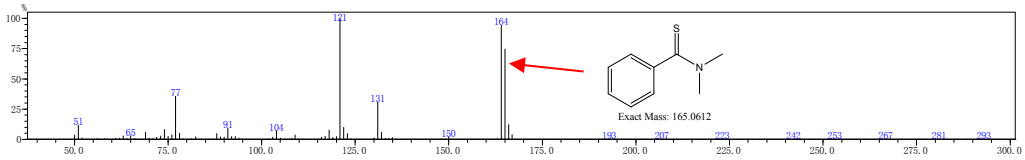


Fig. S1 GCMS spectra of compound **4**

3.2 Free radical capture experiments

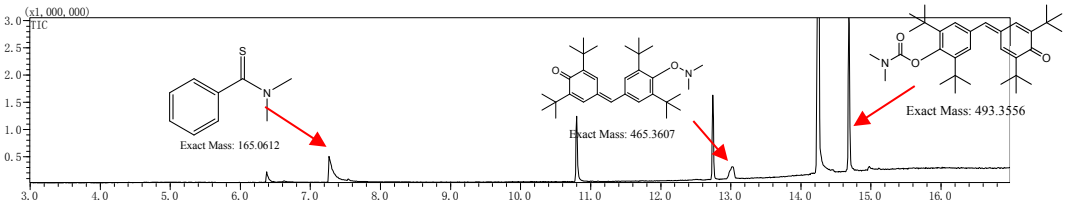


Fig. S2 GC spectrum after 3 equivalent of Galvinoxyl free radical was added

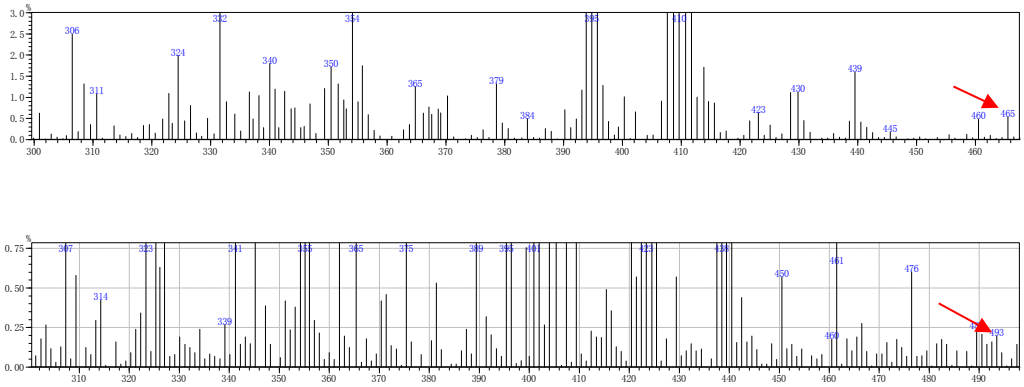


Fig. S3 MS spectra of adducts formed by Galvinoxyl free radical with dimethyl carbamic radical and dimethyiamino radical

3.3 GCMS results of $HSNMe_2$ under standard conditions

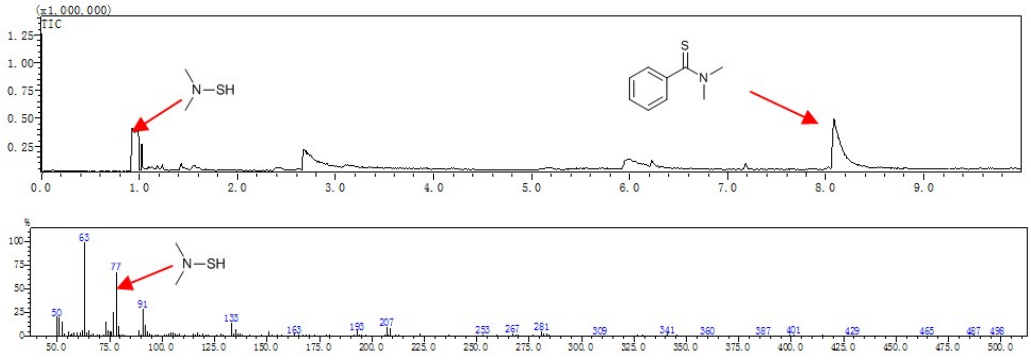
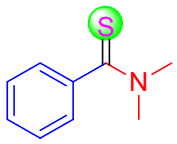


Fig. S4 GCMS spectra of $HSNMe_2$

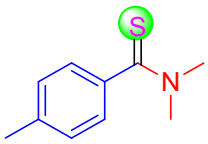
4. Characterization Data for the Products

N,N-Dimethylbenzothioamide 4[3]



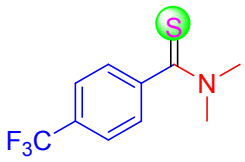
To a sealed tube were added *N,N,N*-trimethyl-1-phenylmethanamonium iodide (0.1 mmol, 27.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N,N*-Dimethylbenzothioamide (14.0 mg, 85%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39-7.26 (m, 5H), 3.60 (s, 3H), 3.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.2, 143.3, 128.5, 128.3, 125.7, 44.1, 43.2.

N,N,4-Trimethylbenzothioamide 5[3]



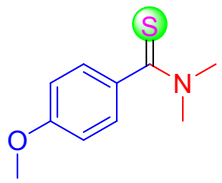
To a sealed tube were added *N,N,N*-trimethyl-1-(*p*-tolyl)methanamonium iodide (0.1 mmol, 29.1 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N,N*,4-Trimethylbenzothioamide (13.8 mg, 77%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow solid. Mp. 49-50 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 3.59 (s, 3H), 3.17 (s, 3H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.6, 140.5, 138.6, 128.8, 125.8, 44.1, 43.3, 21.2.

N,N-Dimethyl-4-(trifluoromethyl)benzothioamide 6[3]



To a sealed tube were added *N,N,N*-trimethyl-1-(4-(trifluoromethyl)phenyl)methanamonium iodide (0.1 mmol, 34.5 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N,N*-Dimethyl-4-(trifluoromethyl)benzothioamide (16.1 mg, 69%) was obtained through column chromatography (PE: EA = 5: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 3.60 (s, 3H), 3.15 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.2, 146.5, 130.2, 126.0, 125.5 (q, J = 3.8 Hz), 123.8 (q, J = 270.5 Hz), 44.0, 43.0.

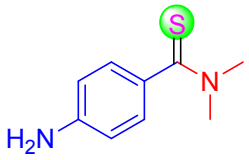
4-Methoxy-*N,N*-dimethylbenzothioamide 7[3]



To a sealed tube were added 1-(4-methoxyphenyl)-*N,N,N*-

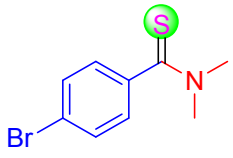
trimethylmethanamonium iodide (0.1 mmol, 30.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. 4-Methoxy-*N,N*-dimethylbenzothioamide (12.9 mg, 66%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.57 (s, 3H), 3.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.2, 159.9, 135.7, 127.8, 113.4, 55.3, 44.3, 43.5.

4-Amino-*N,N*-dimethylbenzothioamide 8[4]



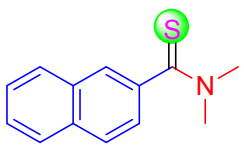
To a sealed tube were added 1-(4-aminophenyl)-*N,N,N*-trimethylmethanaminium iodide (0.1 mmol, 29.2 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. 4-Amino-*N,N*-dimethylbenzothioamide (16.6 mg, 87%) was obtained through column chromatography (PE: EA = 5: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 2H), 3.56 (s, 3H), 3.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.8, 147.4, 133.1, 128.2, 113.9, 44.4, 43.6. HRMS (ESI) *m/z* calcd for $C_{21}H_{15}NNaO_5(M+H)^+$ 181.0794, found 181.0794.

4-Bromo-*N,N*-dimethylbenzothioamide 9[3]



To a sealed tube were added 1-(4-bromophenyl)-*N,N,N*-trimethylmethanamonium iodide (0.1 mmol, 35.6 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. 4-Bromo-*N,N*-dimethylbenzothioamide (17.1 mg, 70%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow solid. Mp. 120-121 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 3.57 (s, 3H), 3.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.8, 142.0, 131.5, 127.4, 122.7, 44.1, 43.2.

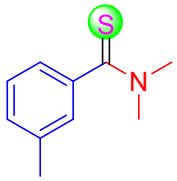
***N,N*-Dimethylnaphthalene-2-carbothioamide 10**[3]



To a sealed tube were added *N,N,N*-trimethyl-1-(naphthalen-2-

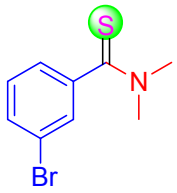
yl)methanamonium iodide (0.1 mmol, 32.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N,N*-Dimethylnaphthalene-2-carbothioamide (24.7 mg, 87%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83-7.77 (m, 4H), 7.52-7.48 (m, 2H), 7.44-7.41 (m, 1H), 3.65 (s, 3H), 3.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.1, 140.5, 133.0, 132.6, 128.3, 128.1, 127.6, 126.7, 126.6, 124.6, 123.8, 44.2, 43.2.

_N,N_,3-Trimethylbenzothioamide 11[3]



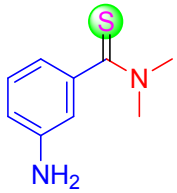
To a sealed tube were added *N,N,N*-trimethyl-1-(*m*-tolyl)methanamonium iodide (0.1 mmol, 29.1 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N,N*,3-Trimethylbenzothioamide (13.2 mg, 74%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28-7.22 (m, 1H), 7.15-7.14 (m, 2H), 7.08 (d, *J* = 7.6, 1H), 3.61 (s, 3H), 3.17 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.5, 143.3, 138.1, 129.2, 128.1, 126.3, 122.5, 44.1, 43.1, 21.3.

3-Bromo-*N,N*-dimethylbenzothioamide 12[3]



To a sealed tube were added 1-(3-bromophenyl)-*N,N,N*-trimethylmethanamonium iodide (0.1 mmol, 35.6 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. 3-Bromo-*N,N*-dimethylbenzothioamide (19.8 mg, 81%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46-7.44 (m, 2H), 7.24-7.21 (m, 2H), 3.58 (s, 3H), 3.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.0, 144.9, 144.8, 131.5, 129.9, 128.6, 124.2, 44.1, 43.1.

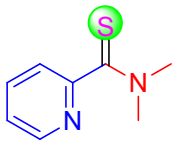
3-Amino-*N,N*-dimethylbenzothioamide 13[5]



To a sealed tube were added 1-(3-Aminophenyl)-*N,N,N*-trimethylmethanaminium iodide (0.1 mmol, 29.2 mg), aqueous

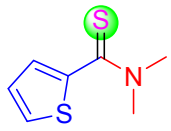
sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. 3-Amino-*N,N*-dimethylbenzothioamide (14.1 mg, 78%) was obtained through column chromatography (PE: EA = 2: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.12-7.08 (m, 1H), 6.62-6.60 (m, 3H), 3.73 (s, 2H), 3.57 (s, 3H), 3.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.4, 146.4, 144.4, 129.2, 115.4, 115.2, 112.4, 44.0, 43.0. HRMS (ESI) *m/z* calcd for $C_{21}H_{15}NNaO_5(M+H)^+$ 181.0794, found 181.0794.

_N,N_-Dimethylpyridine-2-carbothioamide 14[3]



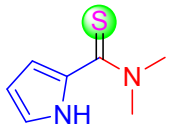
To a sealed tube were added *N,N,N*-trimethyl-1-(pyridin-2-yl)methanamonium iodide (0.1 mmol, 27.8 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N,N*-Dimethylpyridine-2-carbothioamide (12.1 mg, 73%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.52 (d, *J* = 4.6 Hz, 1H), 7.74 (t, *J* = 8.6 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.28-7.24 (m, 1H), 3.61 (s, 3H), 3.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.9, 159.4, 148.0, 136.9, 123.1, 123.1, 43.7, 43.2.

_N,N_-Dimethylthiophene-2-carbothioamide 15[3]



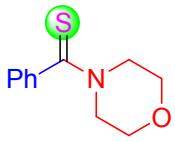
To a sealed tube were added *N,N,N*-trimethyl-1-(thiophen-2-yl)methanamonium iodide (0.1 mmol, 28.3 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N,N*-Dimethylbenzothioamide (9.7 mg, 57%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, *J* = 5.1 Hz, 1H), 7.10 (d, *J* = 3.6 Hz, 1H), 6.96 (t, *J* = 4.4 Hz, 1H), 3.56 (s, 3H), 3.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.6, 145.1, 129.2, 126.4, 126.4, 44.6.

_N,N_-Dimethyl-1*H*-pyrrole-2-carbothioamide 16[6]



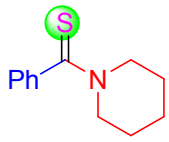
To a sealed tube were added 2-(pyrrolyl)methyltrimethylammonium iodide (0.1 mmol, 26.6 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), DMF (77 μL, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N,N*-Dimethyl-1*H*-pyrrole-2-carbothioamide (6.2 mg, 40%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.93 (s, 1H), 6.98-6.95 (m, 1H), 6.52-6.49 (m, 1H), 6.30-6.27 (m, 1H), 3.60 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 186.7, 130.1, 122.9, 111.7, 110.5, 45.1, 44.5.

Morpholino(phenyl)methanethione 17[3]



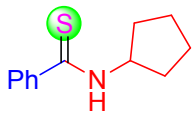
To a sealed tube were added *N,N,N*-trimethyl-1-phenylmethanamonium iodide (0.1 mmol, 27.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), morpholine-4-carbaldehyde (115.1 mg, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. Morpholino(phenyl)methanethione (16.1 mg, 78%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow solid. Mp. 137-138 °C . ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37-7.27 (m, 5H), 4.56-4.43 (m, 2H), 3.90-3.88 (m, 2H), 3.66-3.59 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.0, 142.5, 128.8, 128.5, 125.8, 66.7, 66.5, 52.5, 49.5.

Phenyl(piperidin-1-yl)methanethione 18[3]



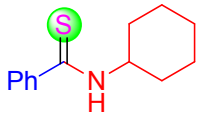
To a sealed tube were added *N,N,N*-trimethyl-1-phenylmethanamonium iodide (0.1 mmol, 27.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), piperidine-1-carbaldehyde (113.2 mg, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. Phenyl(piperidin-1-yl)methanethione (17.4 mg, 85%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.26 (m, 5H), 4.37 (t, *J* = 5.5 Hz, 2H), 3.52 (t, *J* = 4.0 Hz, 2H), 1.86-1.80 (m, 2H), 1.78-1.72 (m, 2H), 1.60-1.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.5, 143.3, 128.3, 128.3, 125.3, 53.1, 50.5, 26.8, 25.4, 24.1.

***N*-Cyclopentylbenzothioamide 19**[7]



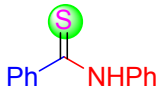
To a sealed tube were added *N,N,N*-trimethyl-1-phenylmethanamonium iodide (0.1 mmol, 27.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), *N*-cyclopentylformamide (113.2 mg, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N*-Cyclopentylbenzothioamide (17.0 mg, 83%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70-7.68 (m, 2H), 7.53 (s, 1H), 7.46-7.35 (m, 3H), 4.92-4.84 (m, 1H), 2.26-2.19 (m, 2H), 1.77-1.56 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.3, 142.2, 130.8, 128.4, 126.5, 57.9, 32.4, 24.1.

***N*-Cyclohexylbenzothioamide 20**[8]



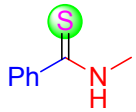
To a sealed tube were added *N,N,N*-trimethyl-1-phenylmethanaminium iodide (0.1 mmol, 27.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), *N*-cyclohexanylformamide (127.2 mg, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N*-Cyclohexanylbenzothioamide (19.7 mg, 90%) was obtained through column chromatography (PE: EA = 10: 1) as a yellow solid. Mp. 91-92 °C .^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70-7.68 (m, 2H), 7.45-7.34 (m, 4H), 4.56-4.49 (m, 1H), 2.20-2.16 (m, 2H), 1.80-1.67 (m, 3H), 1.52-1.19 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.6, 142.3, 130.8, 128.4, 126.5, 54.8, 31.6, 25.4, 24.6.

***N*-phenylbenzothioamide 21**[9]



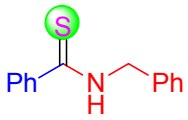
To a sealed tube were added *N,N,N*-trimethyl-1-phenylmethanamonium iodide (0.1 mmol, 27.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), *N*-phenylformamide (121.1 mg, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N*-Benzylbenzothioamide (16.4 mg, 77%) was obtained through column chromatography (PE: EA = 5: 1) as a yellow solid. Mp. 101-102 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.10 (s, 1H), 7.85-7.74 (m, 4H), 7.52-7.27 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.4, 143.1, 139.0, 131.2, 129.0, 128.6, 126.9, 126.7, 123.7.

_N_-Methylbenzothioamide 22[10]



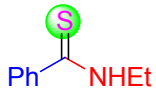
To a sealed tube were added *N,N,N*-trimethyl-1-phenylmethanamonium iodide (0.1 mmol, 27.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), *N*-cyclopentylformamide (59.1 mg, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N*-Methylbenzothioamide (8.0 mg, 53%) was obtained through column chromatography (PE: EA = 5: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (s, 1H), 7.71-7.69 (m, 2H), 7.45-7.41 (m, 1H), 7.36-7.33 (m, 2H), 3.29 (d, *J* = 4.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.0, 141.5, 131.0, 128.4, 126.5, 33.6.

_N_-Benzylbenzothioamide 23[3]



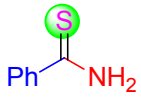
To a Schlenk tube were added *N,N,N*-trimethyl-1-phenylmethanamonium iodide (0.1 mmol, 27.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), *N*-benzylformamide (135.2 mg, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N*-Benzylbenzothioamide (19.1 mg, 84%) was obtained through column chromatography (PE: EA = 5: 1) as a yellow solid. Mp. 84-85 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82-7.73 (m, 3H), 7.47-7.42 (m, 1H), 7.40-7.33 (m, 7H), 4.98 (d, *J* = 5.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.0, 141.5, 136.1, 131.1, 128.9, 128.4, 128.3, 128.1, 126.6, 50.9.

_N_-Ethylbenzothioamide 24[10]



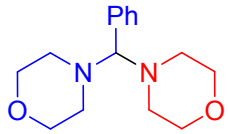
To a sealed tube were added *N,N,N*-trimethyl-1-phenylmethanamonium iodide (0.1 mmol, 27.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), *N*-benzylformamide (73.1 mg, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. *N*-Ethylbenzothioamide (14.2 mg, 86%) was obtained through column chromatography (PE: EA = 5: 1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73-7.71 (m, 2H), 7.57 (s, 1H), 7.46-7.43 (m, 1H), 7.39-7.35 (m, 2H), 3.88-3.81 (m, 2H), 1.36 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.0, 141.9, 130.9, 128.4, 126.5, 41.7, 13.3.

Benzothioamide 25[4]



To a sealed tube were added *N,N,N*-trimethyl-1-phenylmethanamonium iodide (0.1 mmol, 27.7 mg), aqueous sodium disulfide (1.3 mmol, 1.3 M, 1 mL), formamide (45.0 mg, 10 equiv). The mixture was stirred at 130 °C for 12 h under N_2. Benzothioamide (4.0 mg, 29%) was obtained through column chromatography (PE: EA = 5: 1) as a yellow solid. Mp. 115-116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (s, 1H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.51-7.48 (m, 1H), 7.40-7.37 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.7, 139.0, 132.0, 128.4, 126.8.

Benzaldehyde bis(morpholino) aminal 26[11]



Flash column chromatography on silica gel (PE: EA = 10: 1) gave a yellow solid (8.8 mg, 43%). Mp. 101-102 oC. 1H NMR (CDCl3, 400 MHz) δ 7.35-7.24 (m, 3H), 7.19-7.17 (m, 2H), 3.67-3.62 (m, 9H), 2.43-2.37 (m, 8H); 13C NMR (CDCl3, 100 MHz) δ 133.8, 128.6, 127.6, 127.6, 88.9, 67.0, 49.3.

5. References

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8 T. Guntreddi, R. Vanjari and K. H. Singh, *Org. Lett.*, 2014, **16**, 3624.

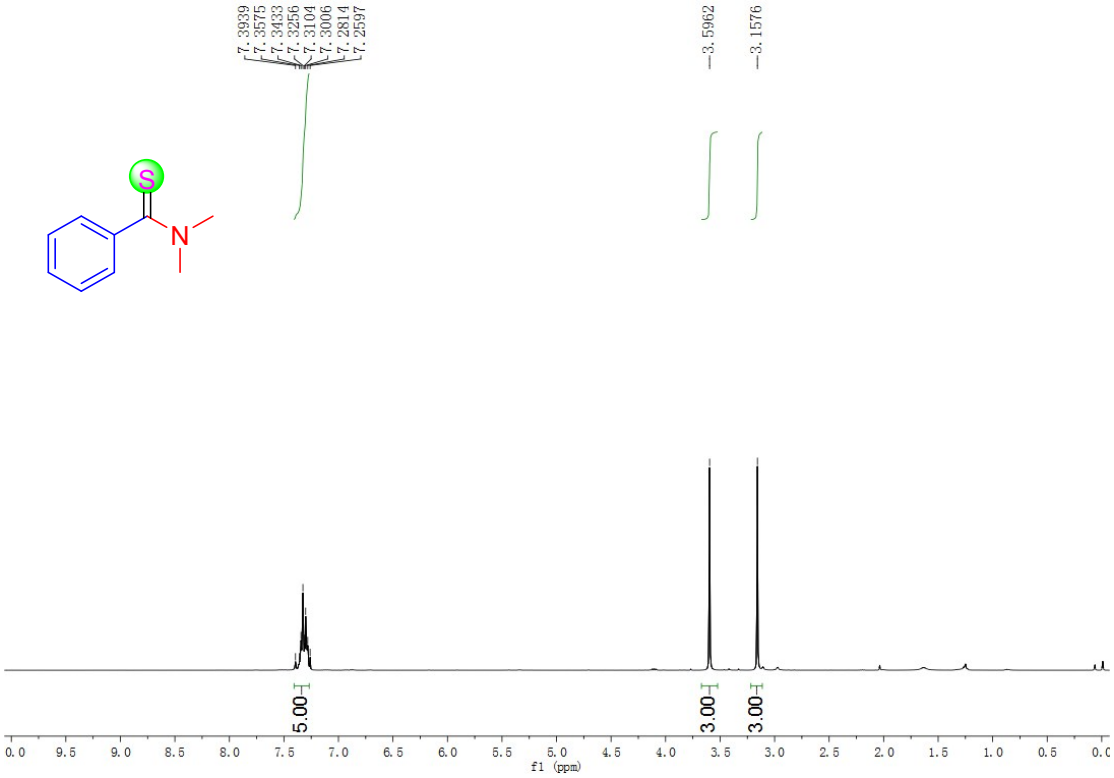
9 N. Xu, X.-J. Jin, K. Suzuki, K. Yamaguchi and N. Mizuno, *New J. Chem.*, 2016, **40**, 4865.

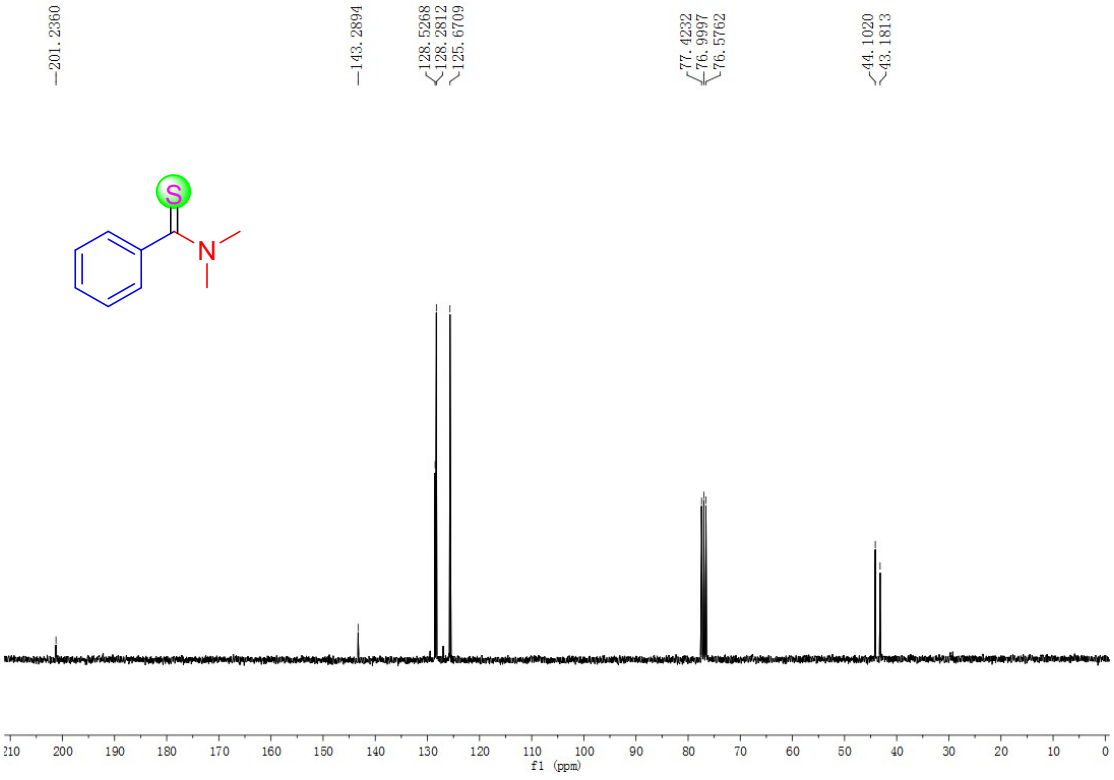
10 H.-Z. Li, W.-J. Xue, G.-D. Yin and A.-X. Wu, *Tetrahedron Lett.*, 2015, **56**, 5843.

11 N. Sakai, H. Hori, Y. Yoshida, T. Konakahara and Y. Ogiwara, Tetrahedron, 2015, 71, 4722.

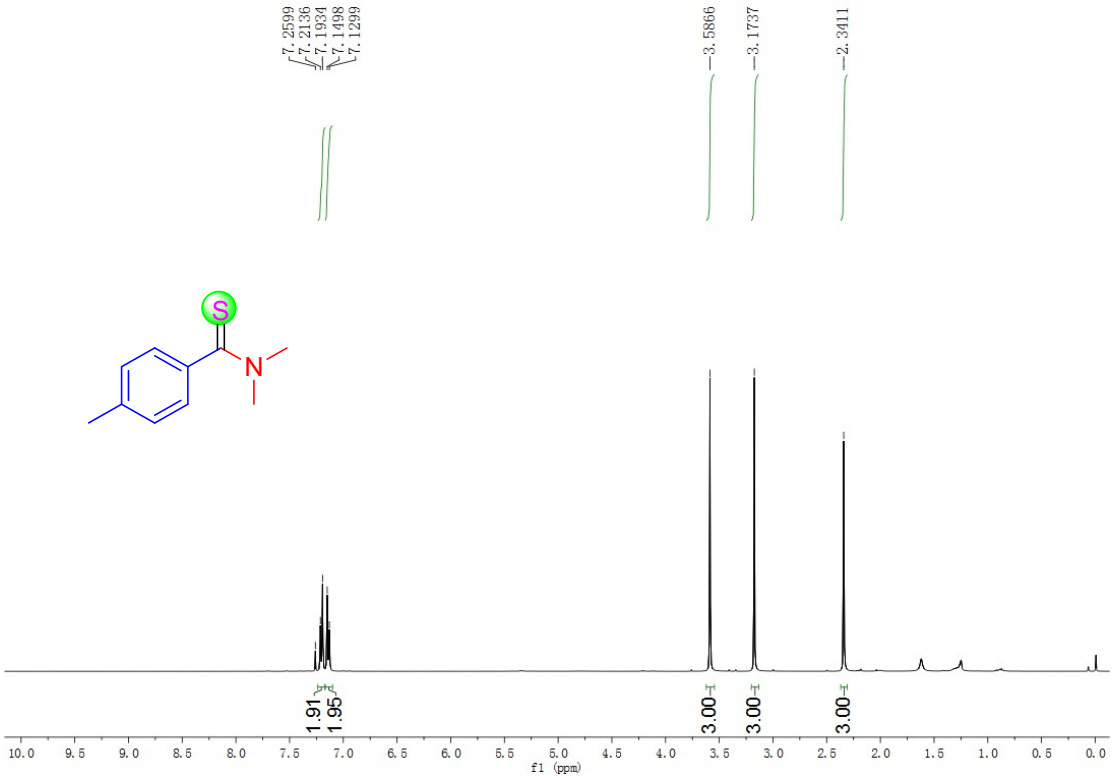
6. Copies of the ^{1}H NMR and ^{13}C NMR Spectra

Compound 4:





Compound 5: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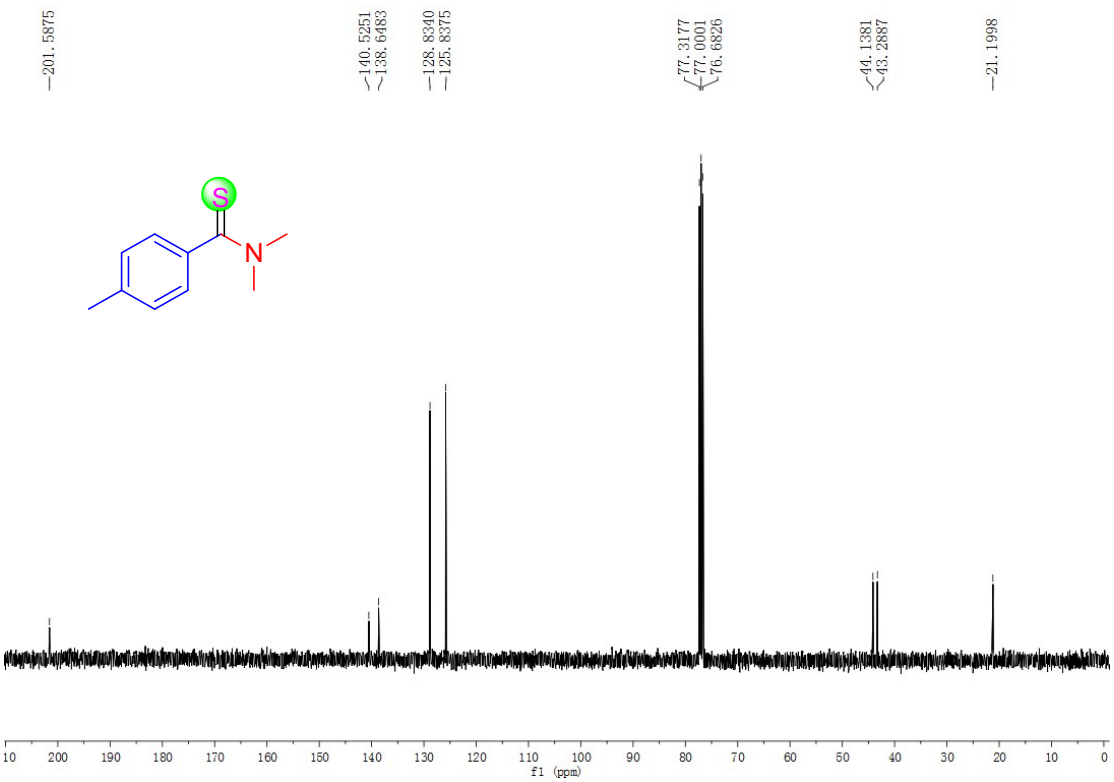
7.2136
7.1934
7.1498
7.1299
3.5866
3.1737
2.3411
1.91
1.95
3.00
3.00
3.00
f1 (ppm)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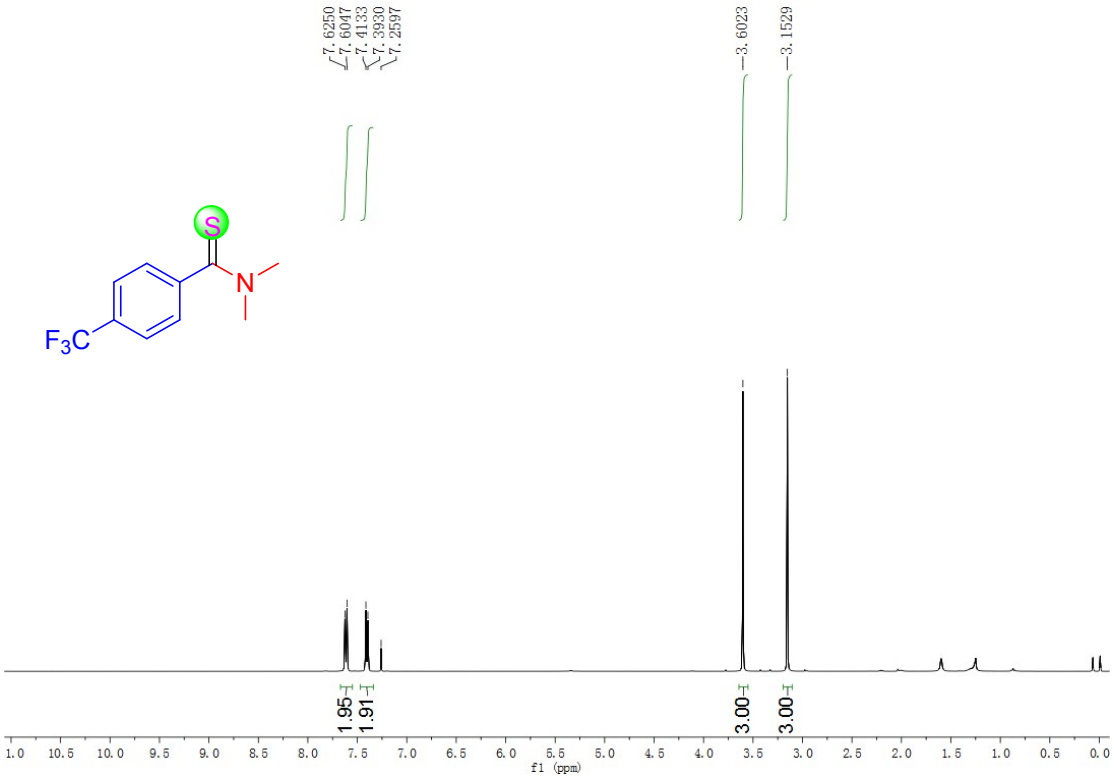
21.1998
f1 (ppm)

Compound 6:


7.6250
7.6047
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7.3930
7.2597
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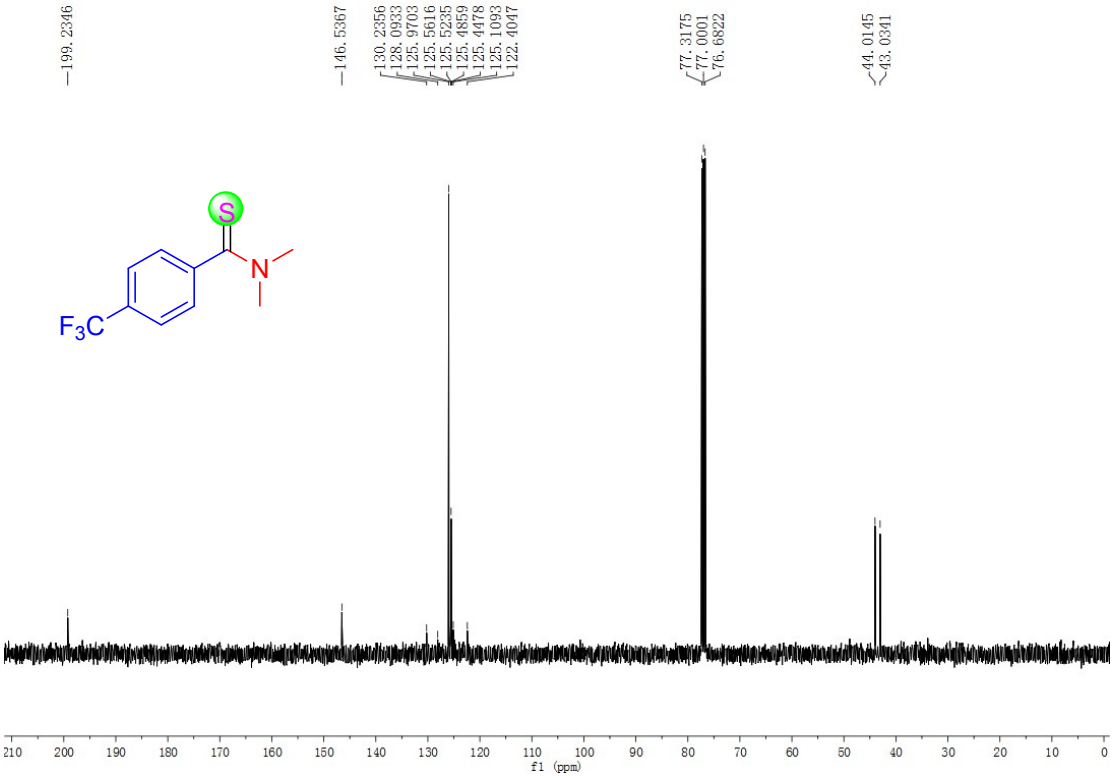
3.1529
1.95
1.91
3.00
3.00
f1 (ppm)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146.5367
130.2356
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125.5616
125.5235
125.4859
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125.1093
122.4047
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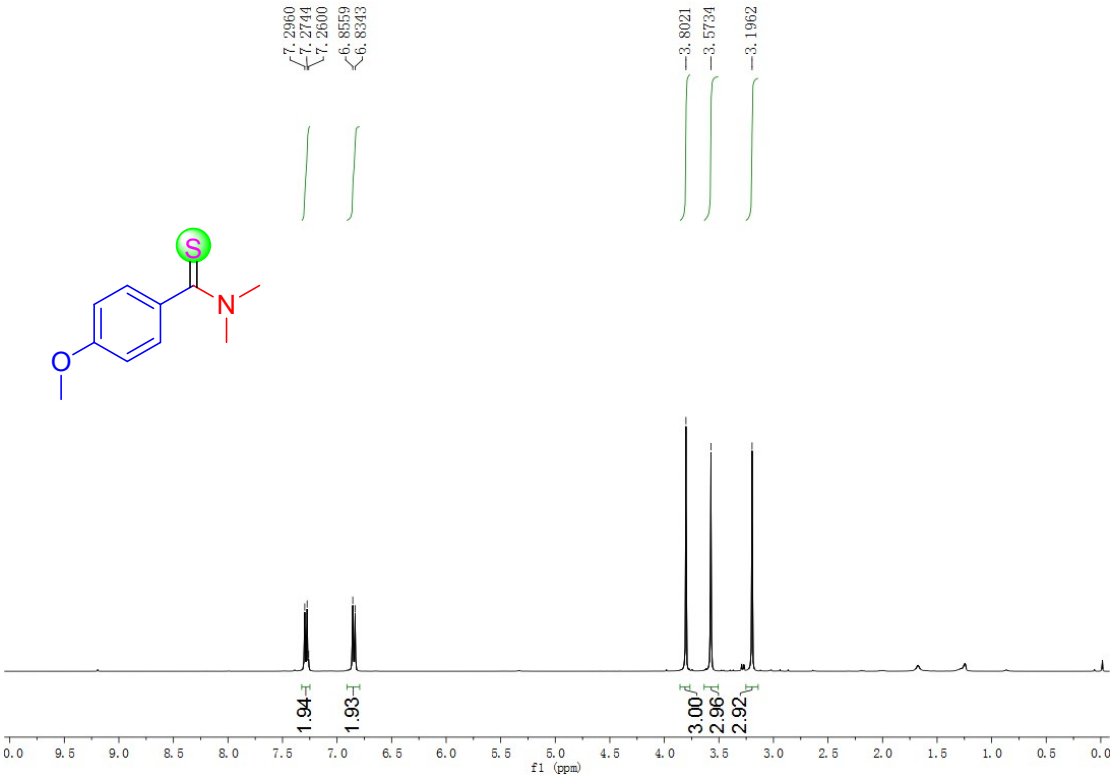
77.0001
76.6822
44.0145
43.0341
f1 (ppm)

Compound 7: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7.2600
6.8559
6.8343
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3.5734
3.1962
S
N
O
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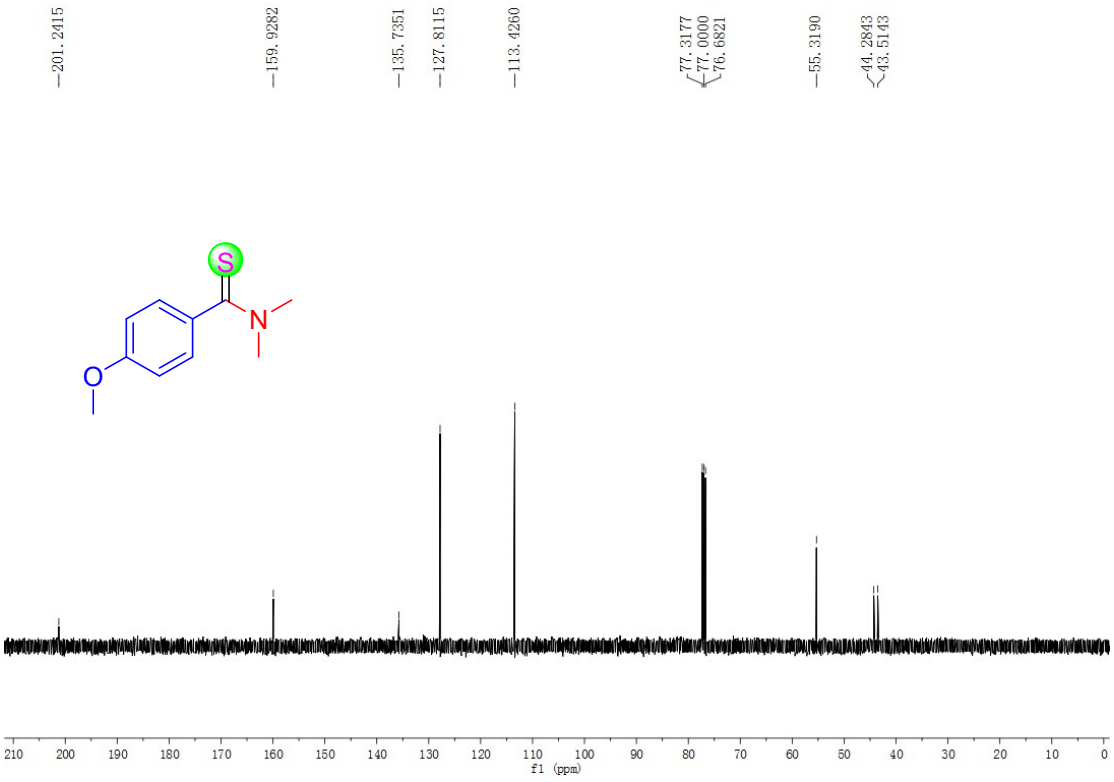
1.93
3.00
2.96
2.92
f1 (ppm)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77.0000
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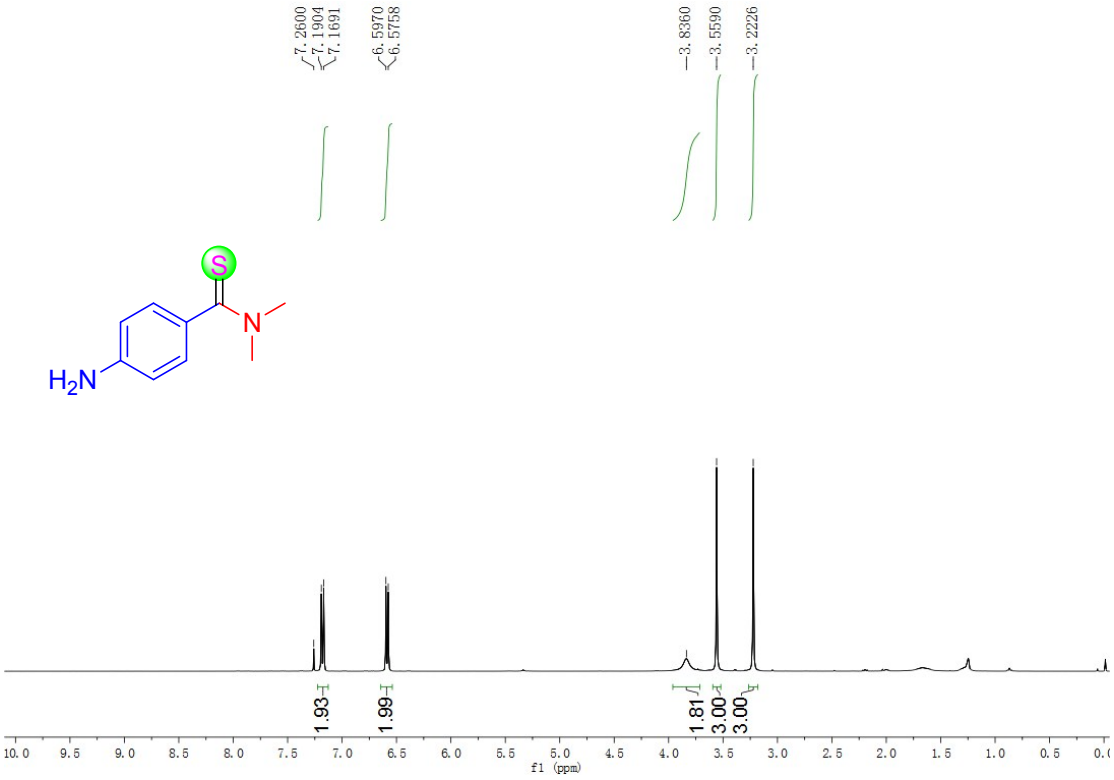
N
O
f1 (ppm)

Compound 8: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7.1904
7.1691
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6.5758
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3.5590
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N
H2N
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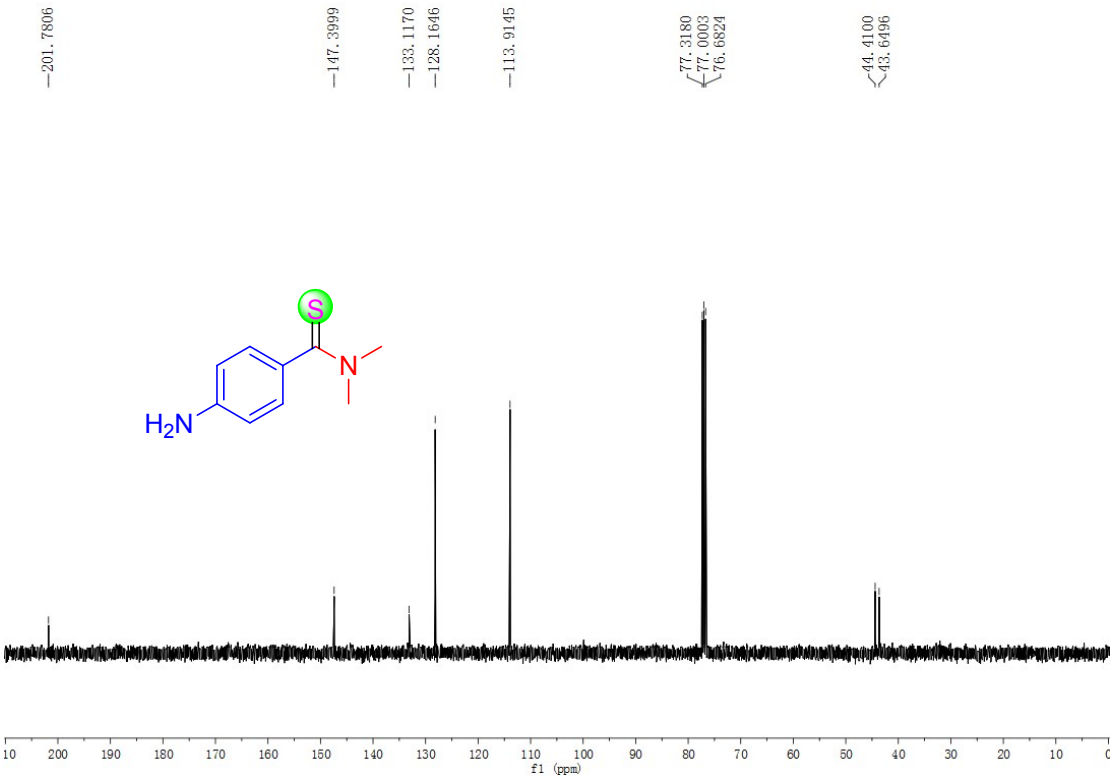
1.99
1.81
3.00
3.00
f1 (ppm)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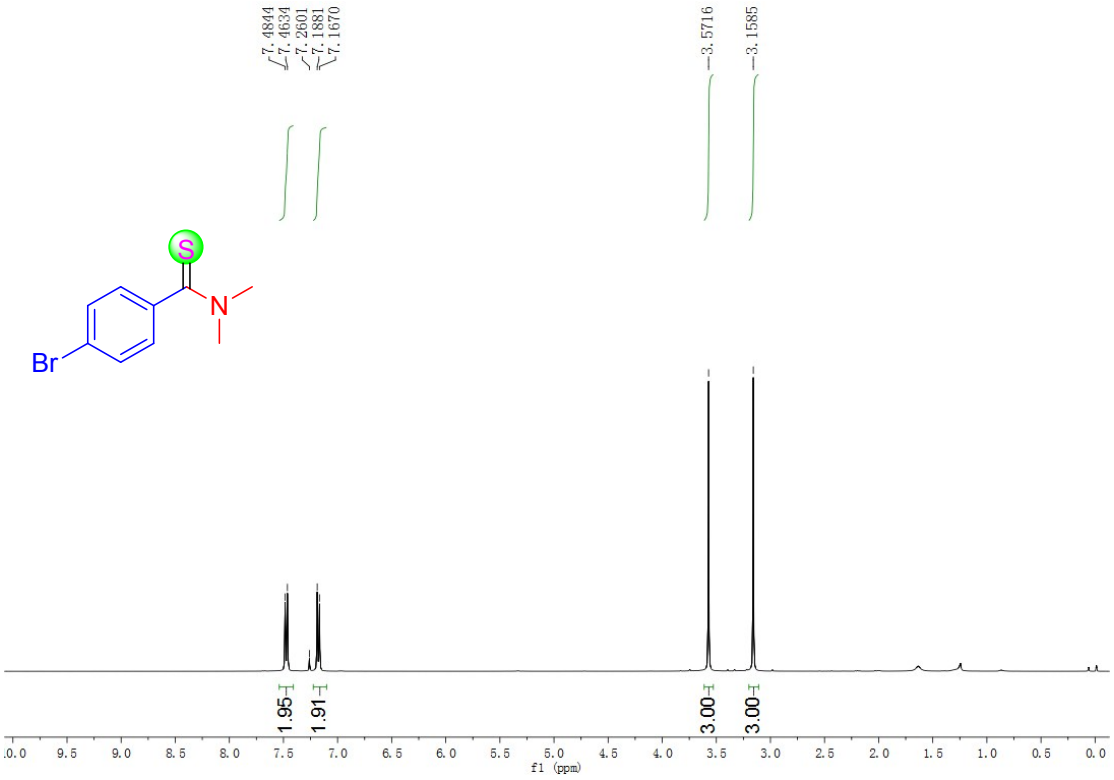
N
H2N
f1 (ppm)

Compound 9: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7.4634
7.2601
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N
Br
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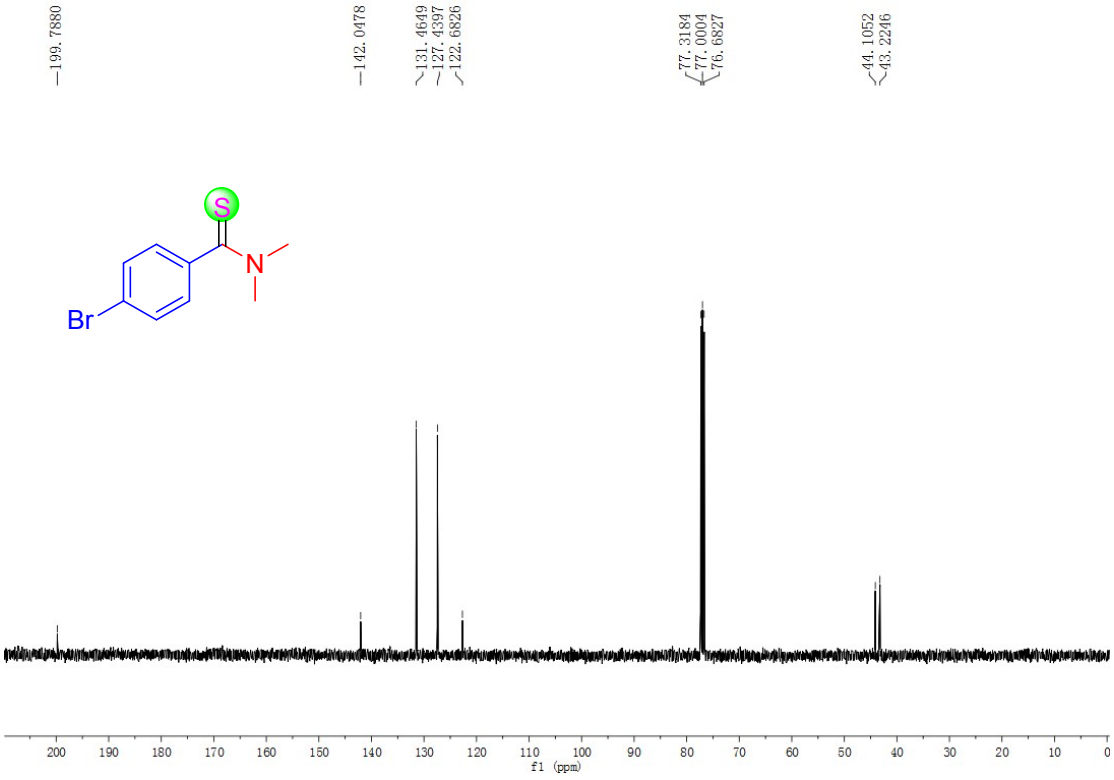
1.91
3.00
3.00
f1 (ppm)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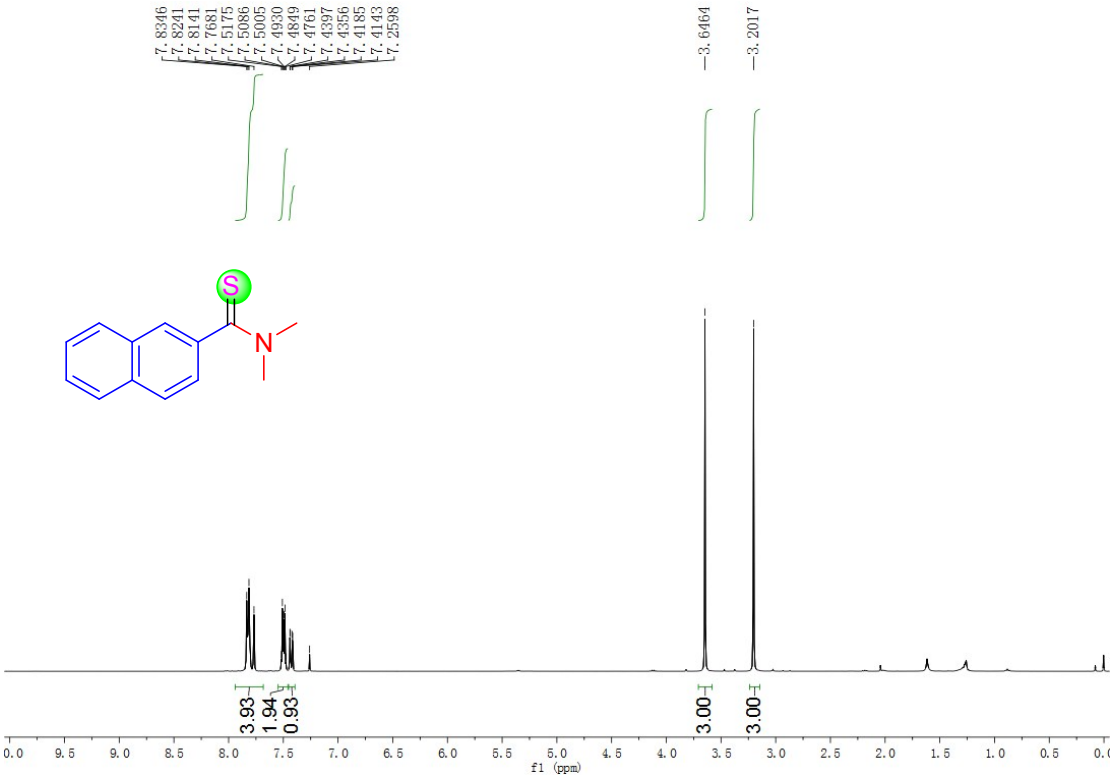
S
N
Br
f1 (ppm)

Compound 10: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7.8241
7.8141
7.7681
7.5175
7.5086
7.5005
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7.4849
7.4761
7.4397
7.4356
7.4185
7.4143
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S
N
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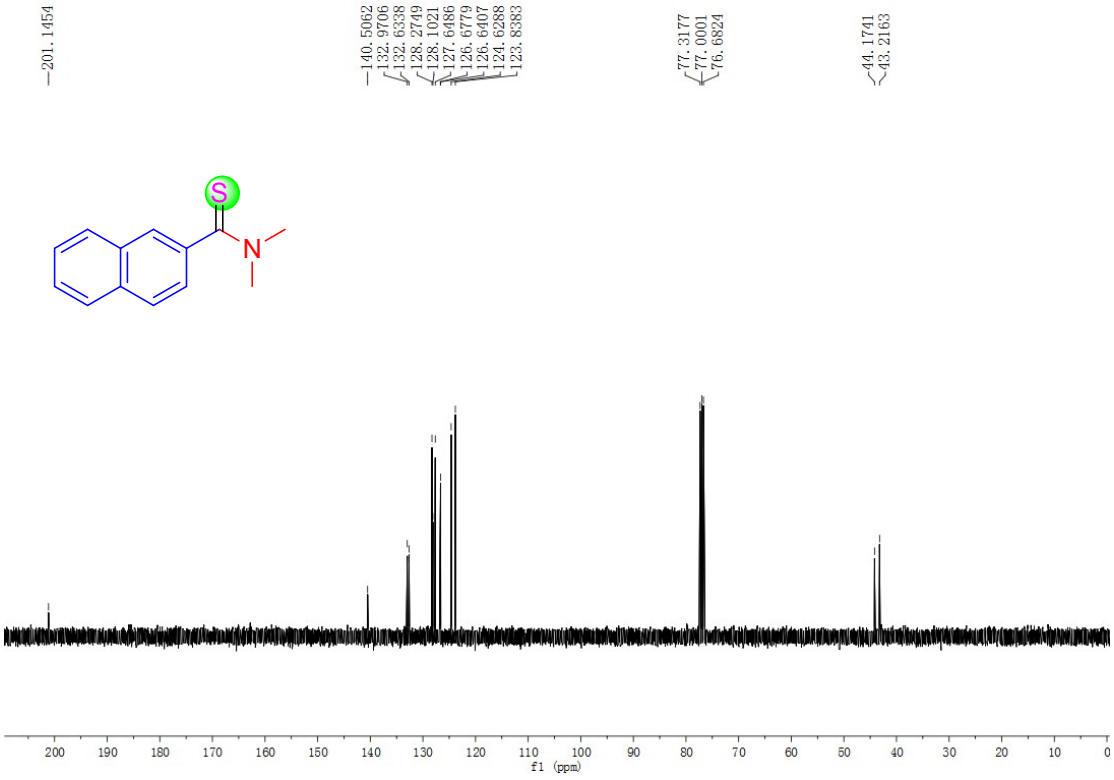
0.93
3.00
3.00
f1 (ppm)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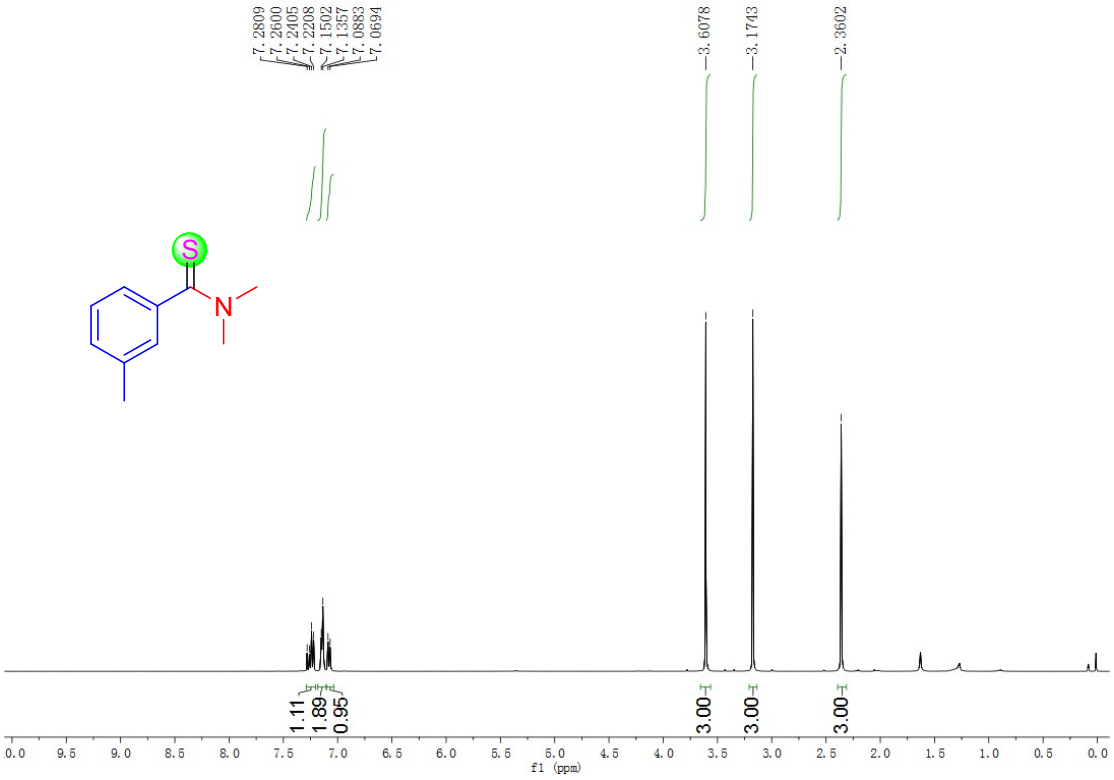
N
f1 (ppm)

Compound 11: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7.2405
7.2208
7.1502
7.1357
7.0883
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N
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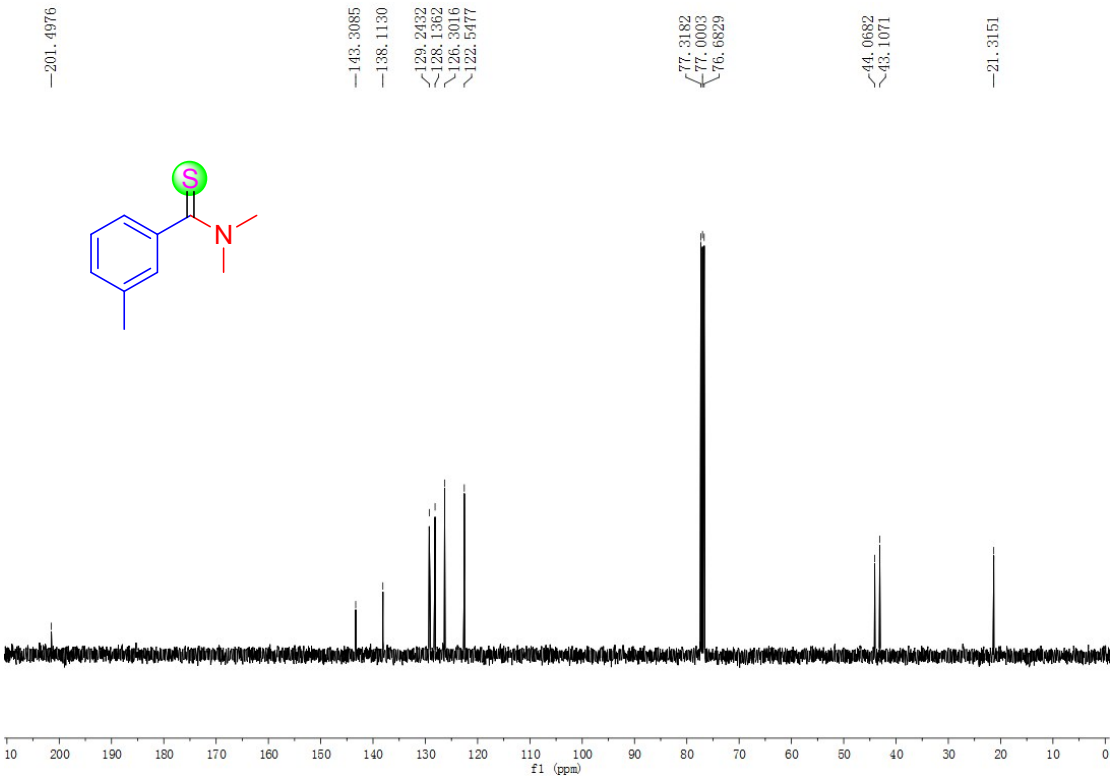
3.00
f1 (ppm)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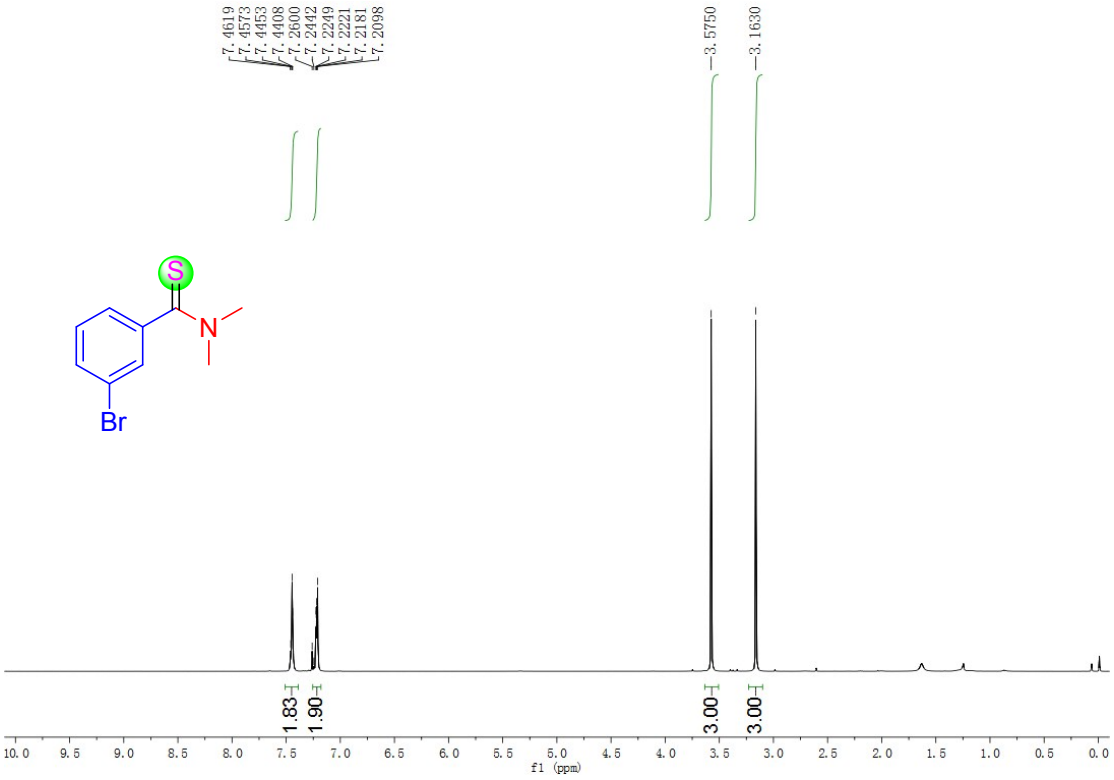
S
N
f1 (ppm)

Compound 12: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N
Br
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1.90
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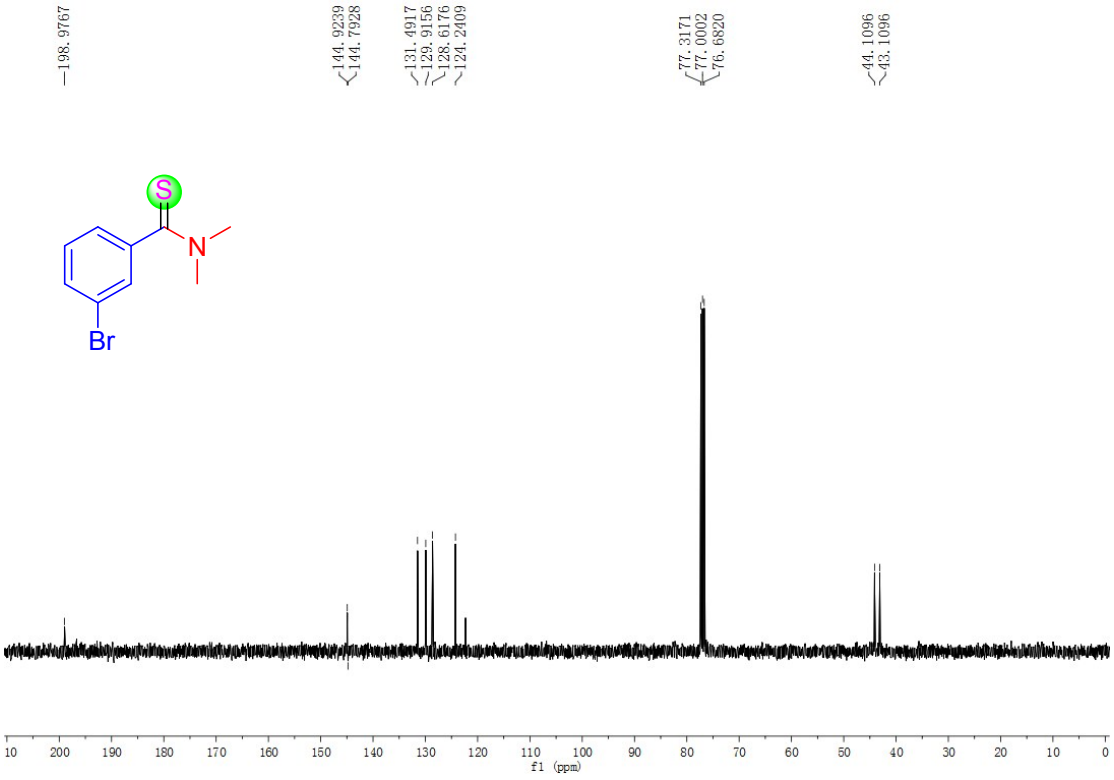
3.00
f1 (ppm)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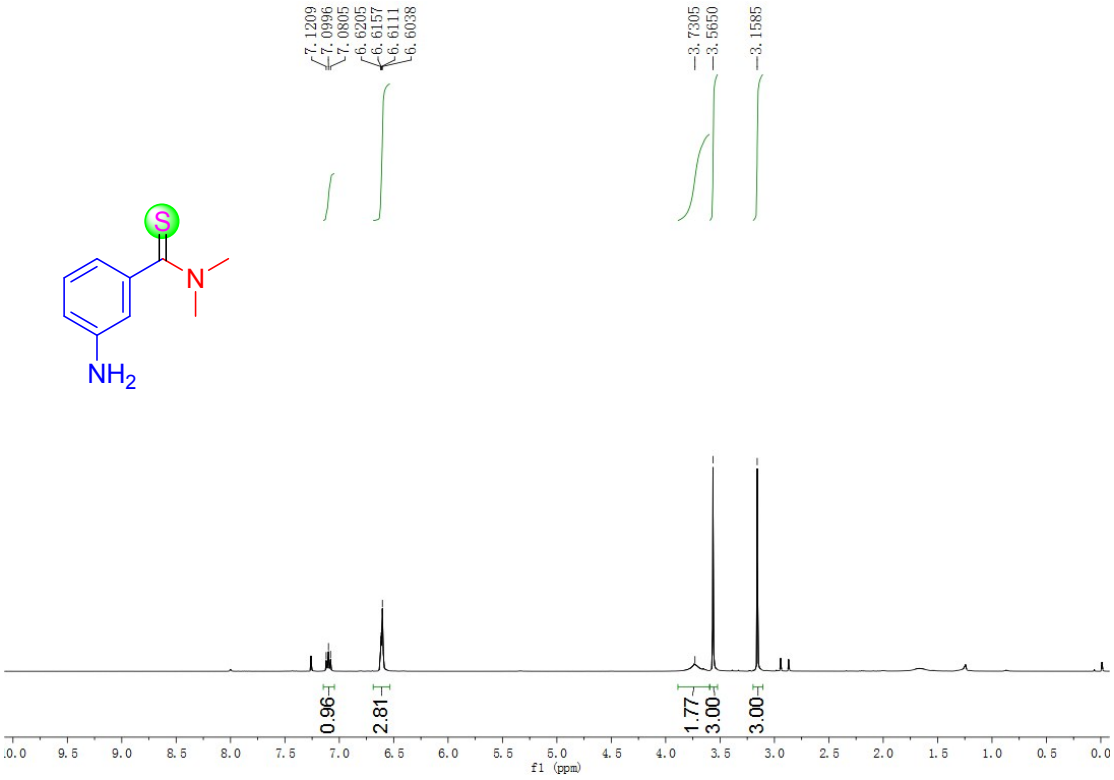
S
N
Br
f1 (ppm)

Compound 13: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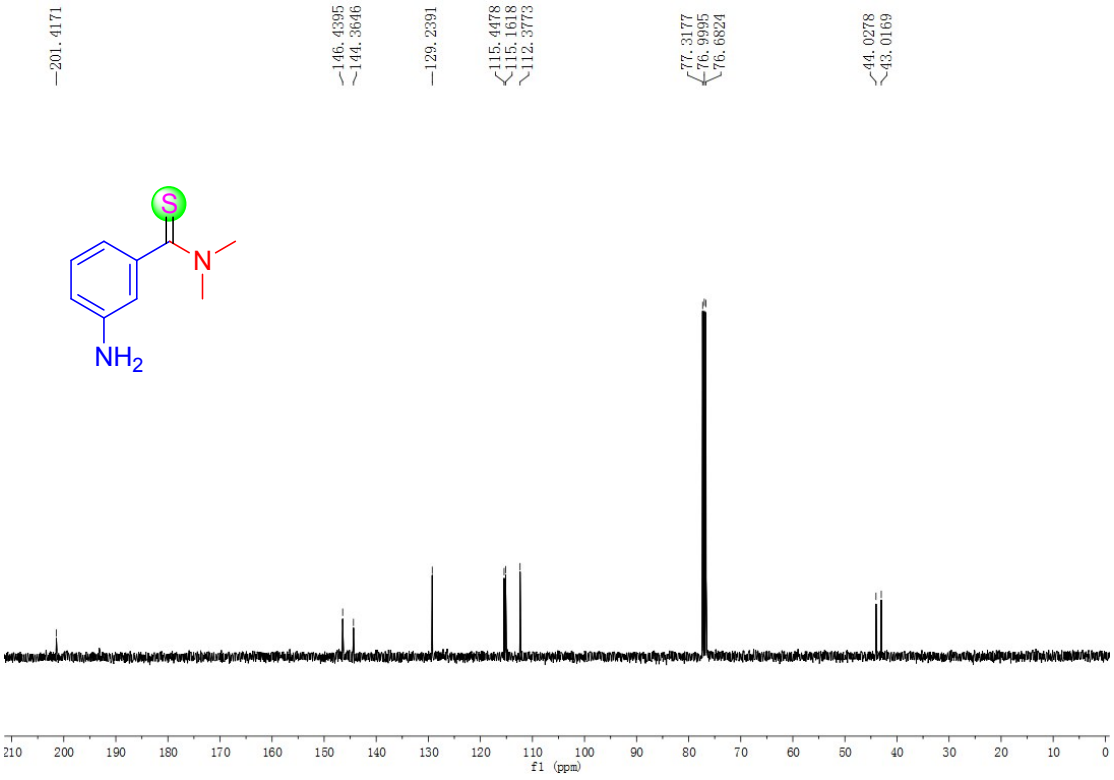
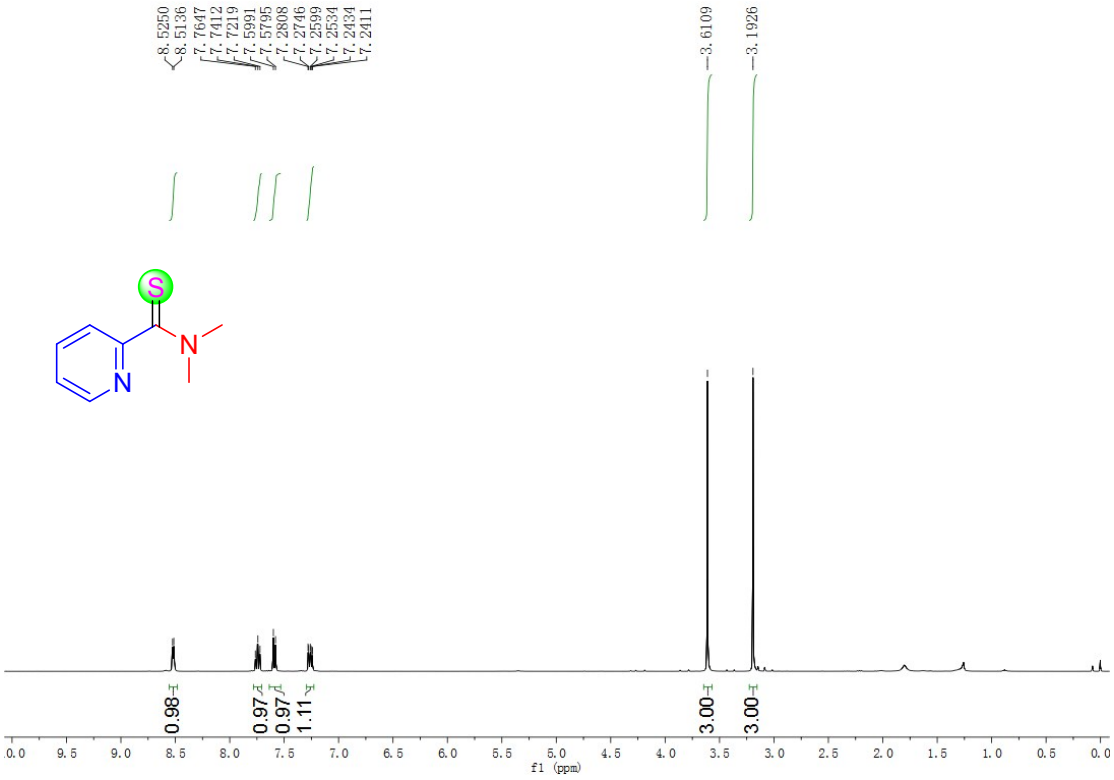
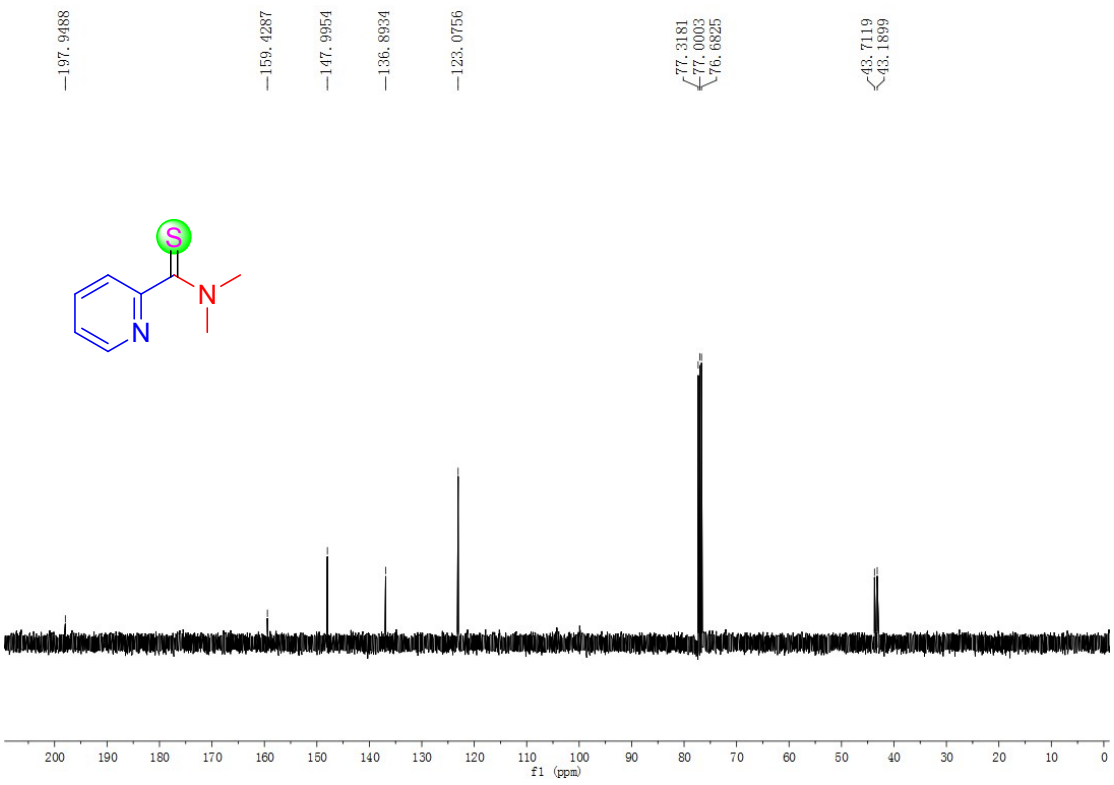
S
N
NH2
0.96
2.81
1.77
3.00
3.00
f1 (ppm)

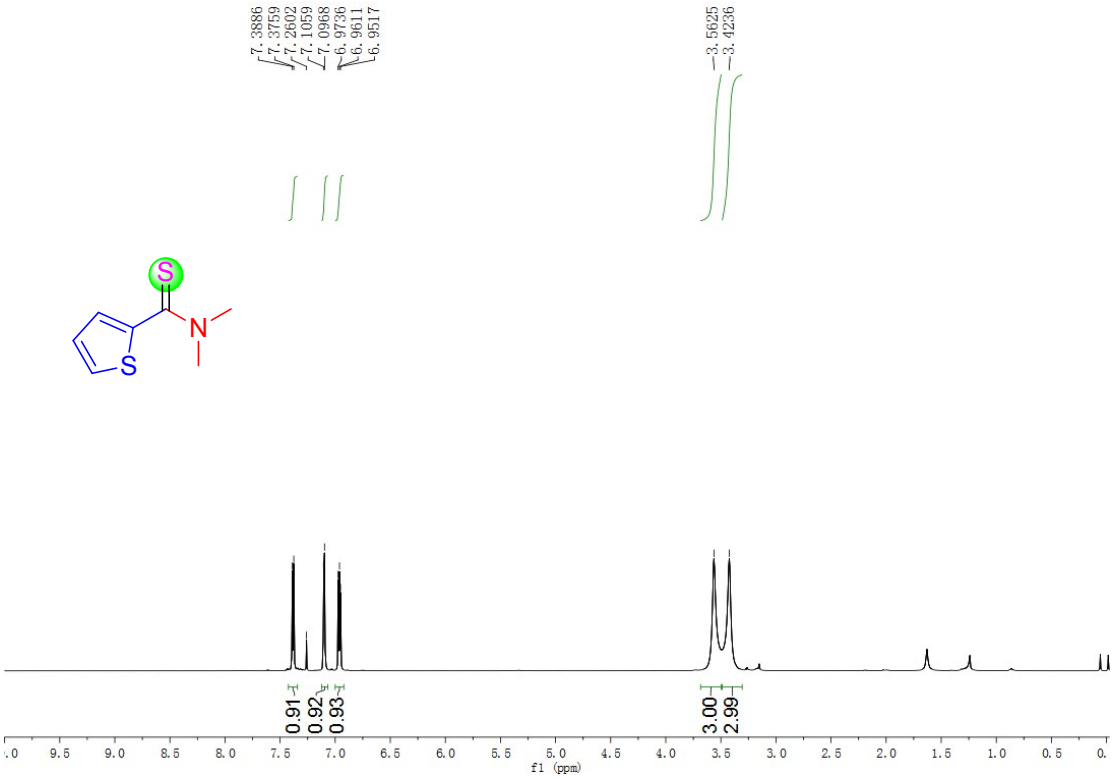

201.4171
146.4395
144.3646
129.2391
115.4478
115.1618
112.3773
77.3177
76.9995
76.6824
44.0278
43.0169
S
N
NH2
f1 (ppm)

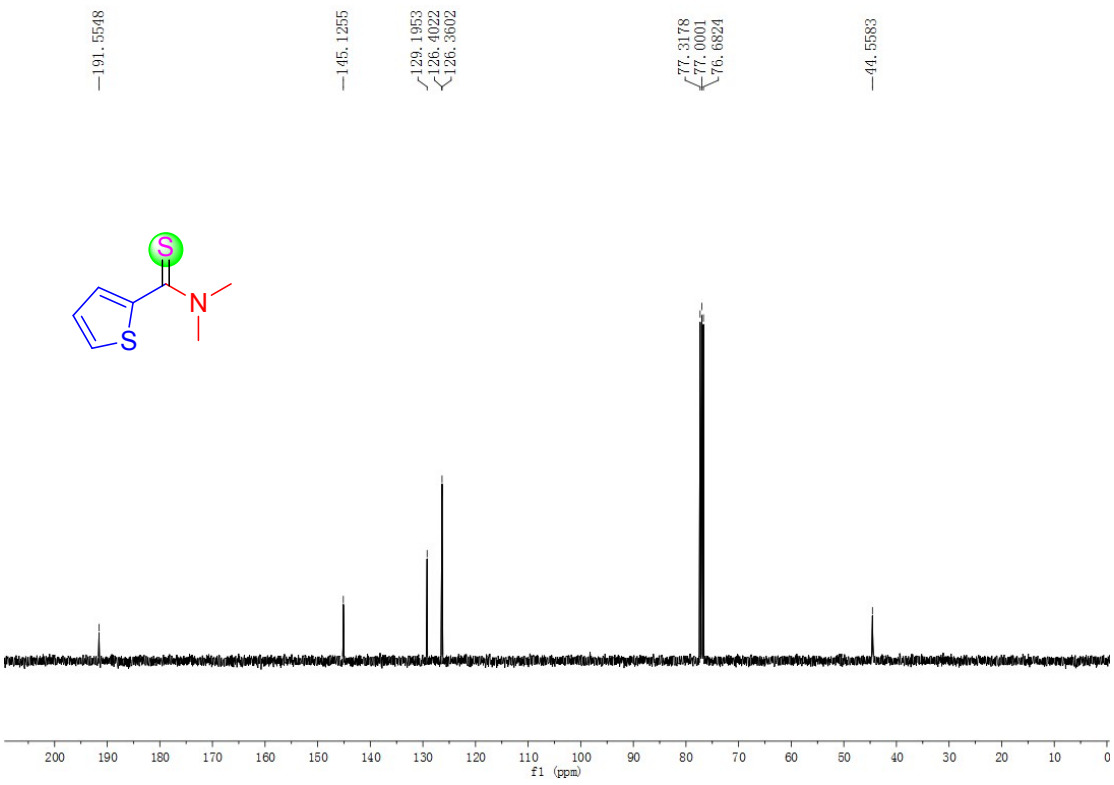
Compound 14:


8.5250
8.5136
7.7647
7.7412
7.7219
7.5991
7.5795
7.2808
7.2746
7.2599
7.2534
7.2434
7.2411
3.6109
3.1926
S
N
N
0.98
0.97
0.97
1.11
3.00
3.00
f1 (ppm)

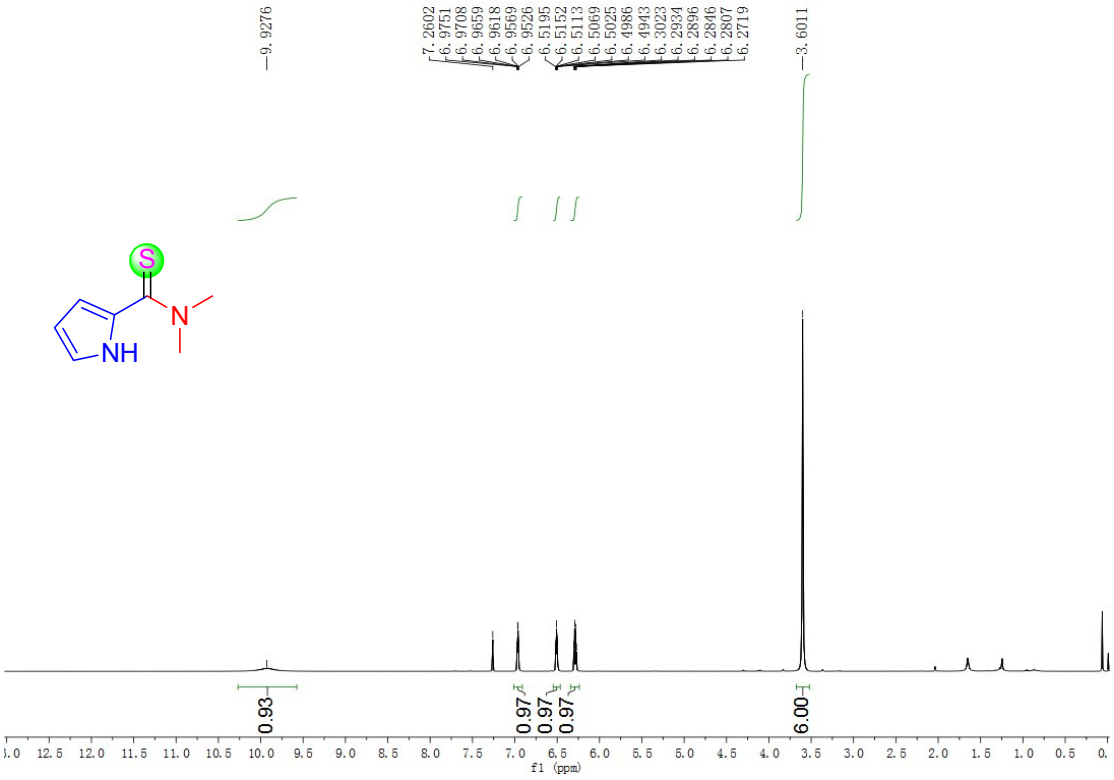

197.9488
159.4287
147.9954
136.8934
123.0756
77.3181
77.0003
76.6825
43.7119
43.1899
S
N
N
f1 (ppm)

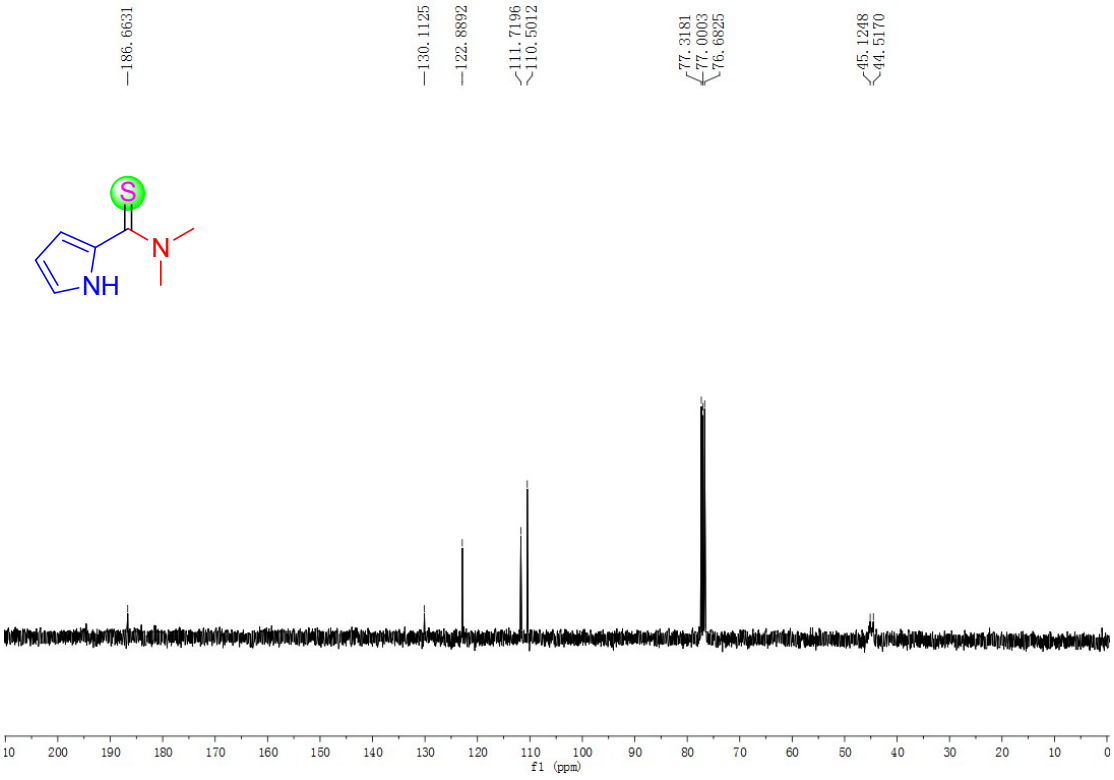
Compound 15:


7.3886
7.3759
7.2602
7.1059
7.0968
6.9736
6.9611
6.9517
3.5625
3.4236
0.91
0.92
0.93
3.00
2.99
f1 (ppm)

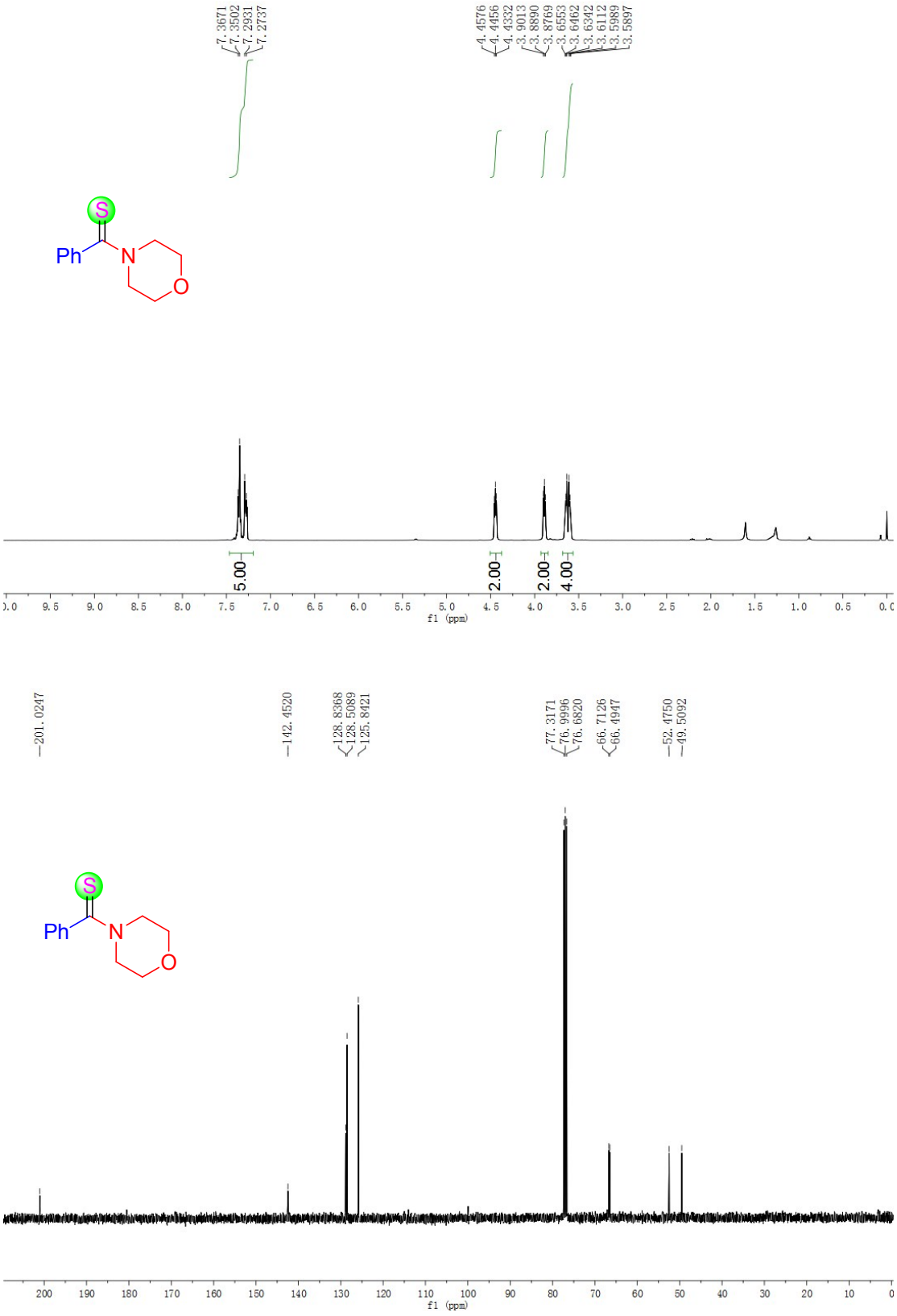

191.5548
145.1255
129.1953
126.4022
126.3602
77.3178
77.0001
76.6824
44.5583
f1 (ppm)

Compound 16:

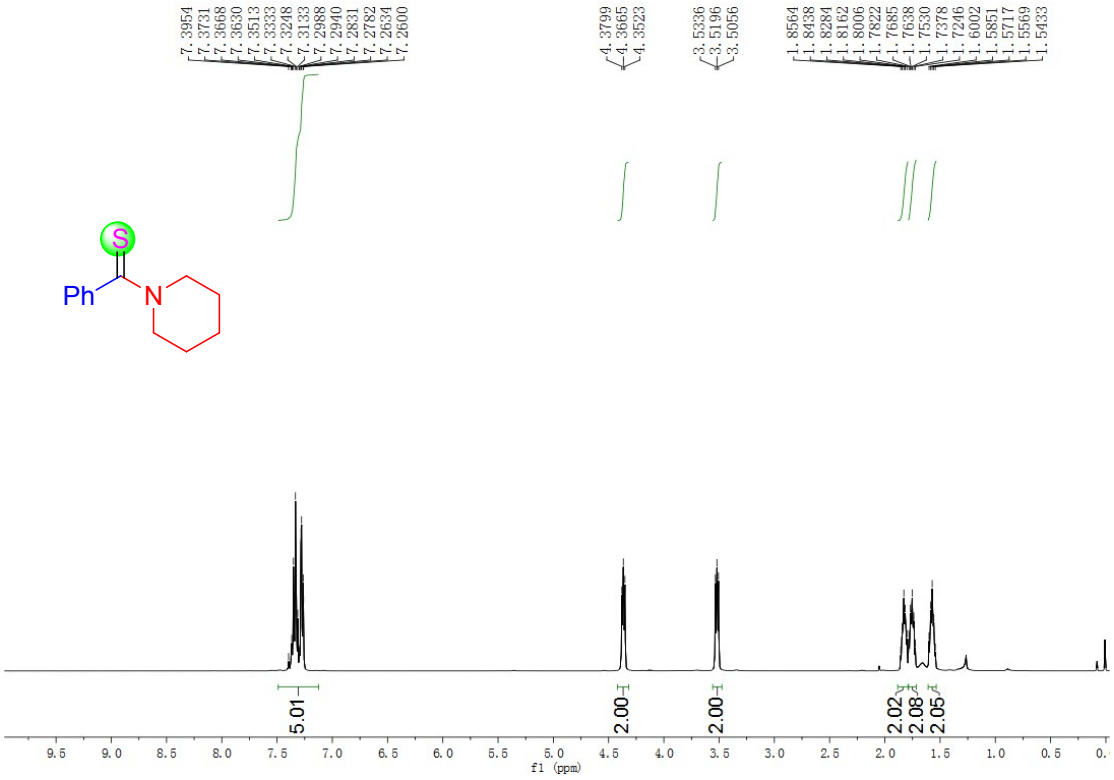

9.9276
7.2602
6.9751
6.9708
6.9659
6.9618
6.9569
6.9526
6.5195
6.5152
6.5113
6.5069
6.5025
6.4986
6.4943
6.3023
6.2934
6.2896
6.2846
6.2807
6.2719
3.6011
S
N
NH
0.93
0.97
0.97
0.97
6.00
f1 (ppm)

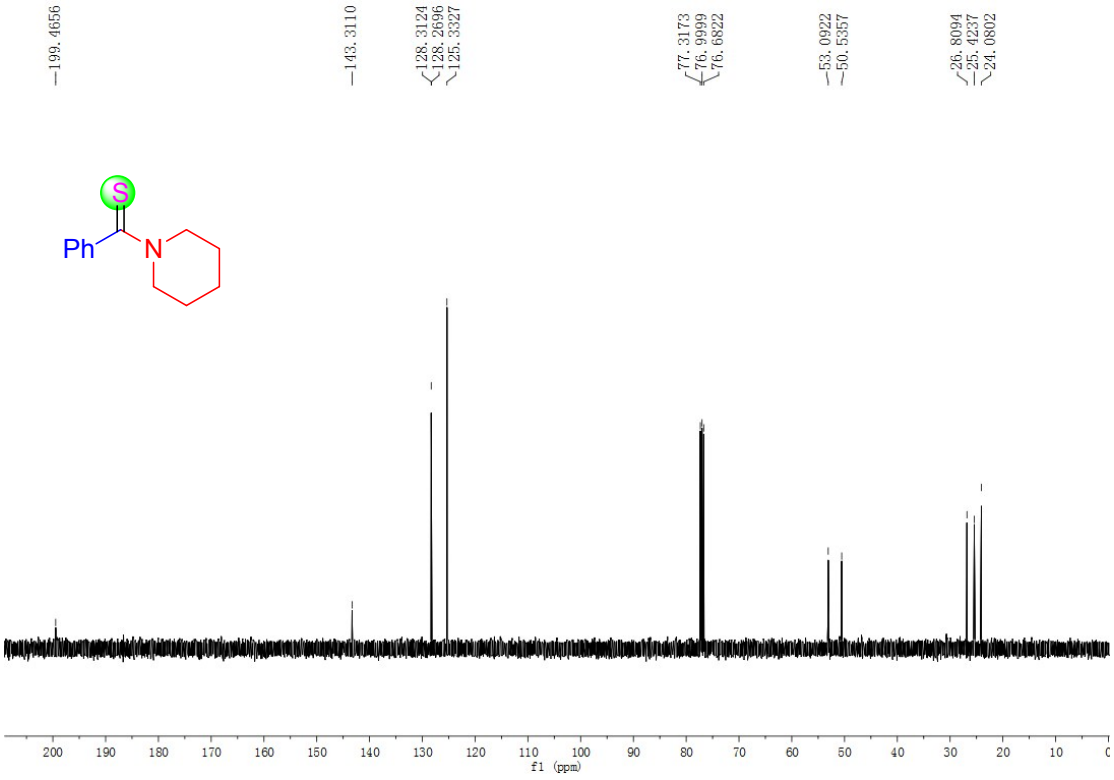

186.6631
130.1125
122.8892
111.7196
110.5012
77.3181
77.0003
76.6825
45.1248
44.5170
S
N
NH
f1 (ppm)

Compound 17:

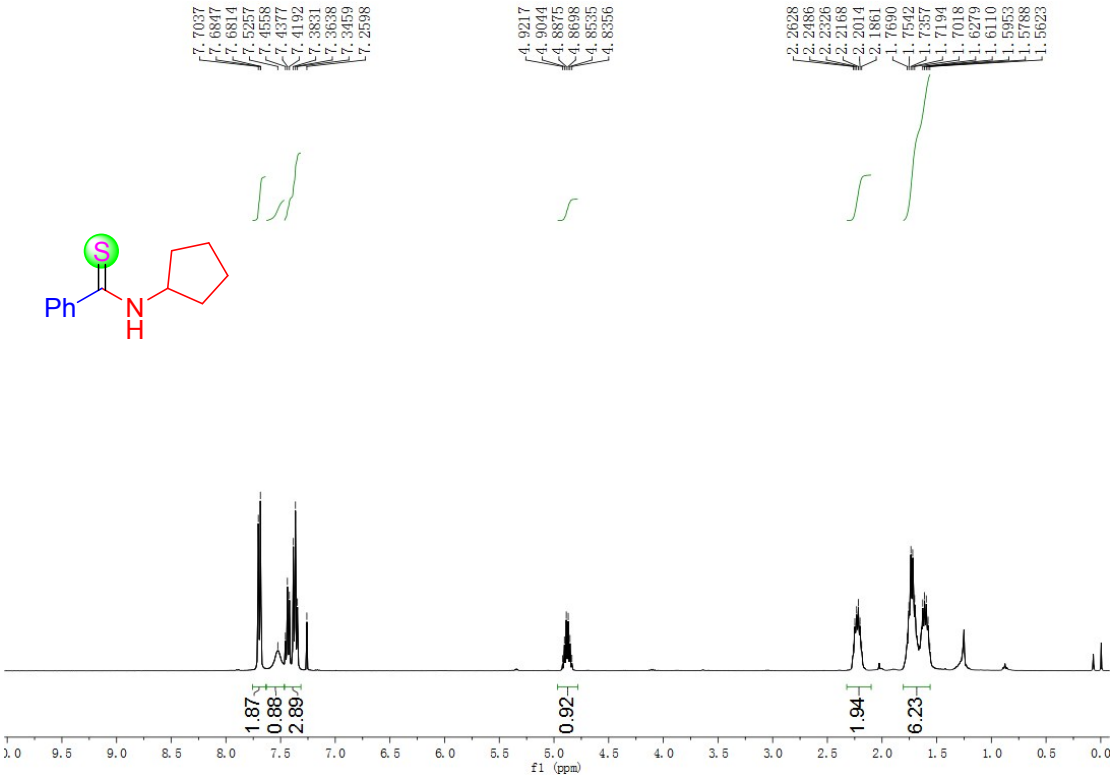

7.3671
7.3502
7.2931
7.2737
4.4576
4.4456
4.4332
3.9013
3.8890
3.8769
3.6553
3.6462
3.6342
3.6112
3.5989
3.5897
S
Ph
N
O
5.00
2.00
2.00
4.00
f1 (ppm)
201.0247
142.4520
128.8368
128.5089
125.8421
77.3171
76.9996
76.6820
66.7126
66.4947
52.4750
49.5092
S
Ph
N
O
f1 (ppm)

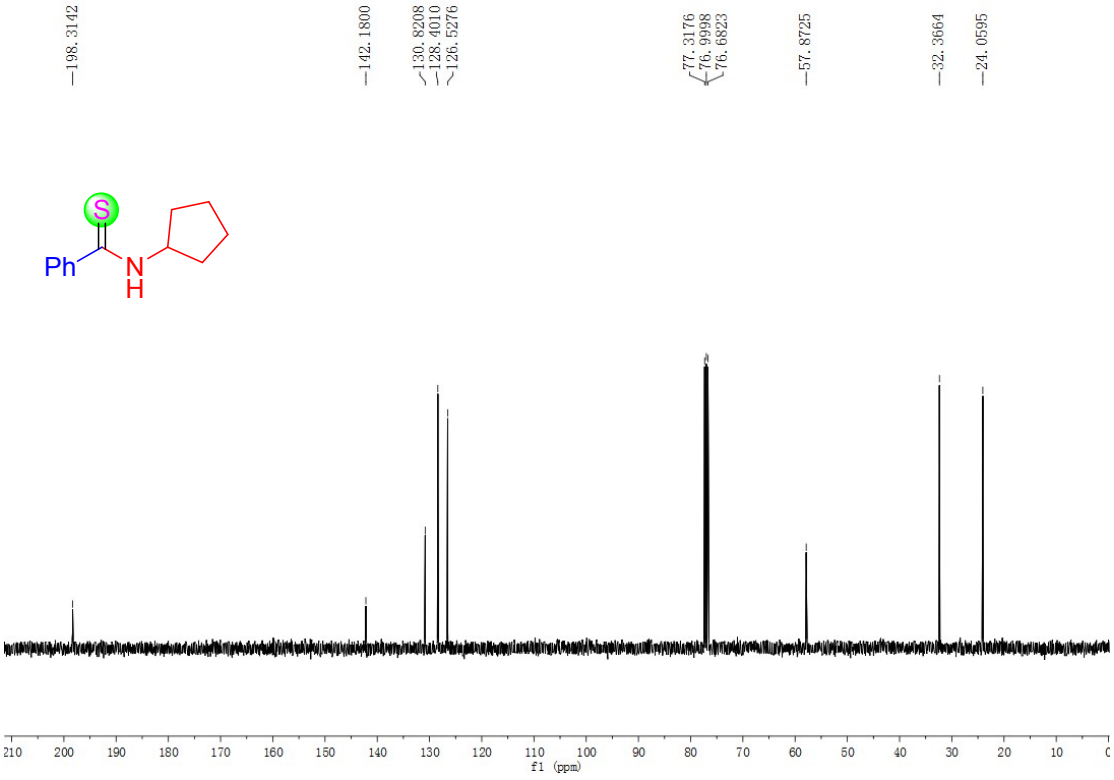
Compound 18:


7.3954
7.3731
7.3668
7.3630
7.3513
7.3333
7.3248
7.3133
7.2988
7.2940
7.2831
7.2782
7.2634
7.2600
4.3799
4.3665
4.3523
3.5336
3.5196
3.5056
1.8564
1.8438
1.8284
1.8162
1.8006
1.7822
1.7685
1.7638
1.7530
1.7378
1.7246
1.6002
1.5851
1.5717
1.5569
1.5433
S
Ph
N
5.01
2.00
2.00
2.02
2.08
2.05
f1 (ppm)

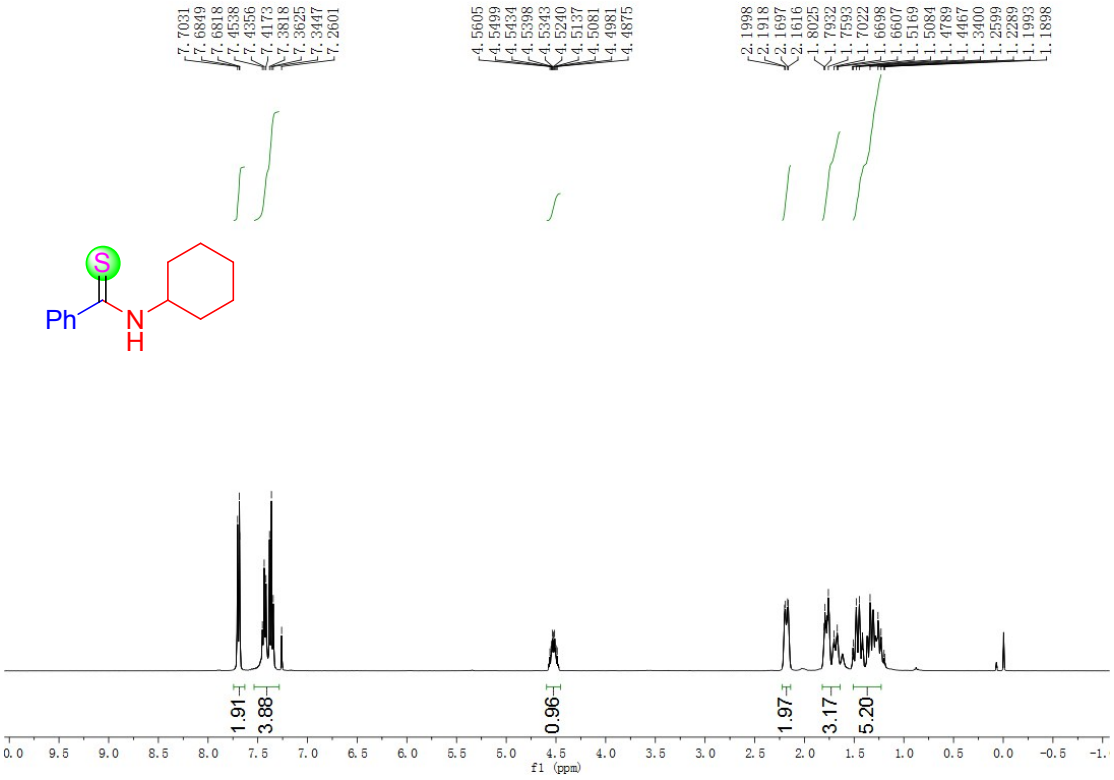

199.4656
143.3110
128.3124
128.2696
125.3327
77.3173
76.9999
76.6822
53.0922
50.5357
26.8094
25.4237
24.0802
S
Ph
N
f1 (ppm)

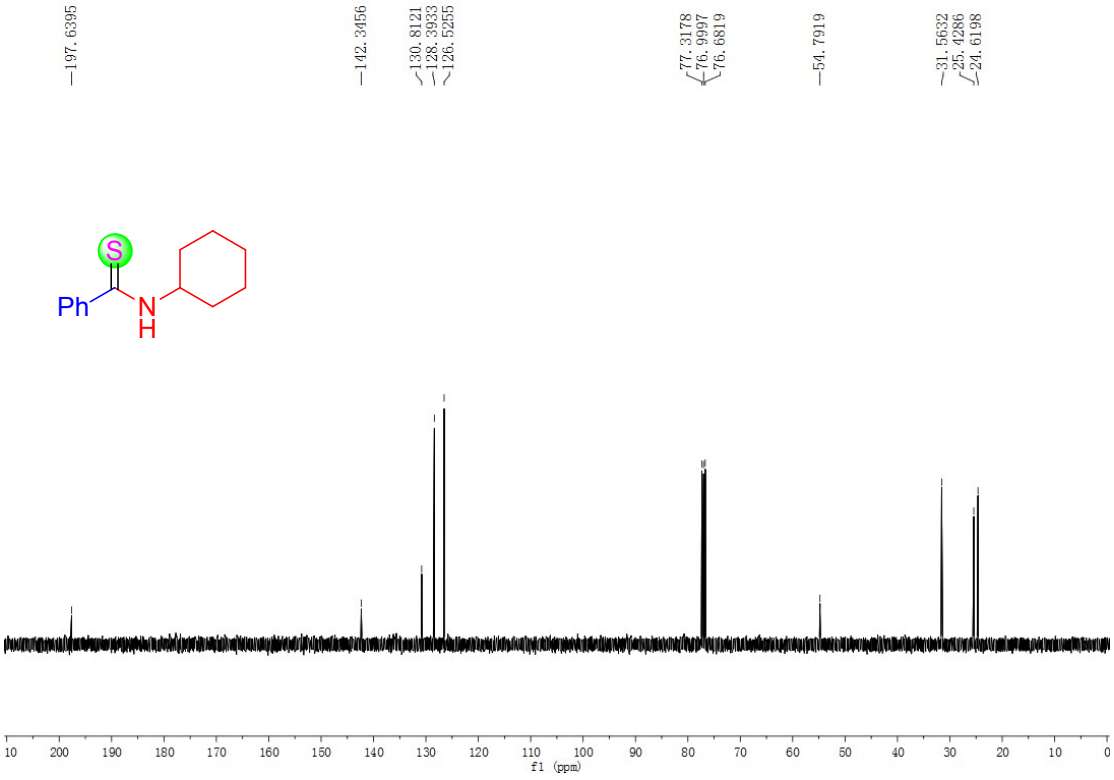
Compound 19:


7.7037
7.6847
7.6814
7.5257
7.4558
7.4377
7.4192
7.3831
7.3638
7.3459
7.2598
4.9217
4.9044
4.8875
4.8698
4.8535
4.8356
2.2628
2.2486
2.2326
2.2168
2.2014
2.1861
1.7690
1.7542
1.7357
1.7194
1.7018
1.6279
1.6110
1.5953
1.5788
1.5623
S
Ph
N
H
1.87
0.88
2.89
0.92
1.94
6.23
f1 (ppm)

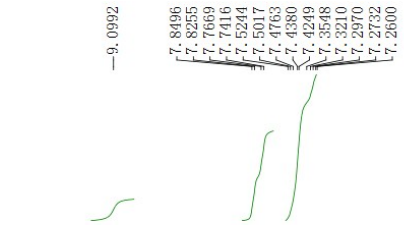

198.3142
142.1800
130.8208
128.4010
126.5276
77.3176
76.9998
76.6823
57.8725
32.3664
24.0595
S
Ph
N
H
f1 (ppm)

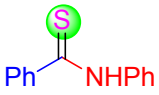
Compound 20:

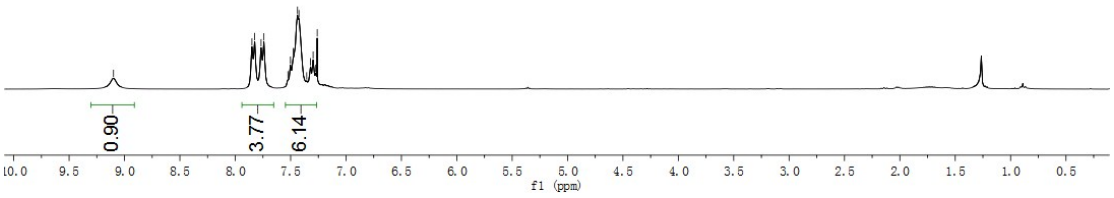

7.7031
7.6849
7.6818
7.4538
7.4356
7.4173
7.3818
7.3625
7.3447
7.2601
4.5605
4.5499
4.5434
4.5398
4.5343
4.5240
4.5137
4.5081
4.4981
4.4875
2.1998
2.1918
2.1697
2.1616
1.8025
1.7932
1.7593
1.7022
1.6698
1.6607
1.5169
1.5084
1.4789
1.4467
1.3400
1.2599
1.2289
1.1993
1.1898
S
Ph
N
H
1.91
3.88
0.96
1.97
3.17
5.20
f1 (ppm)

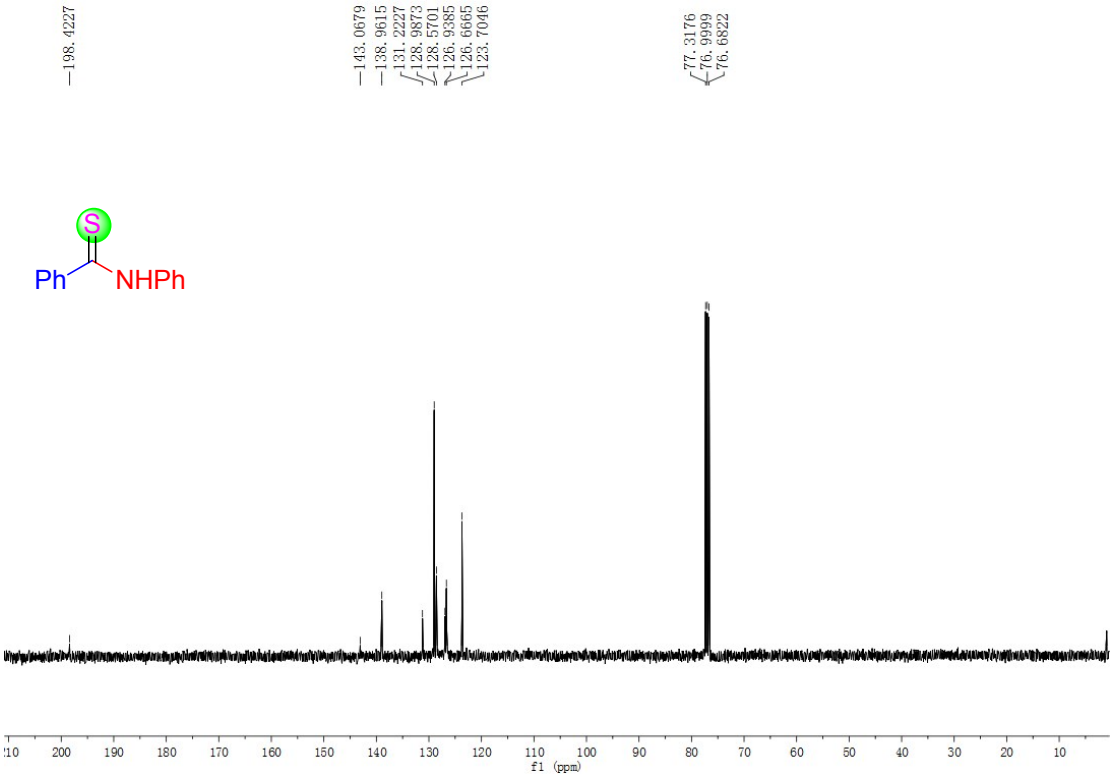

197.6395
142.3456
130.8121
128.3933
126.5255
77.3178
76.9997
76.6819
54.7919
31.5632
25.4286
24.6198
S
Ph
N
H
f1 (ppm)

Compound 21:

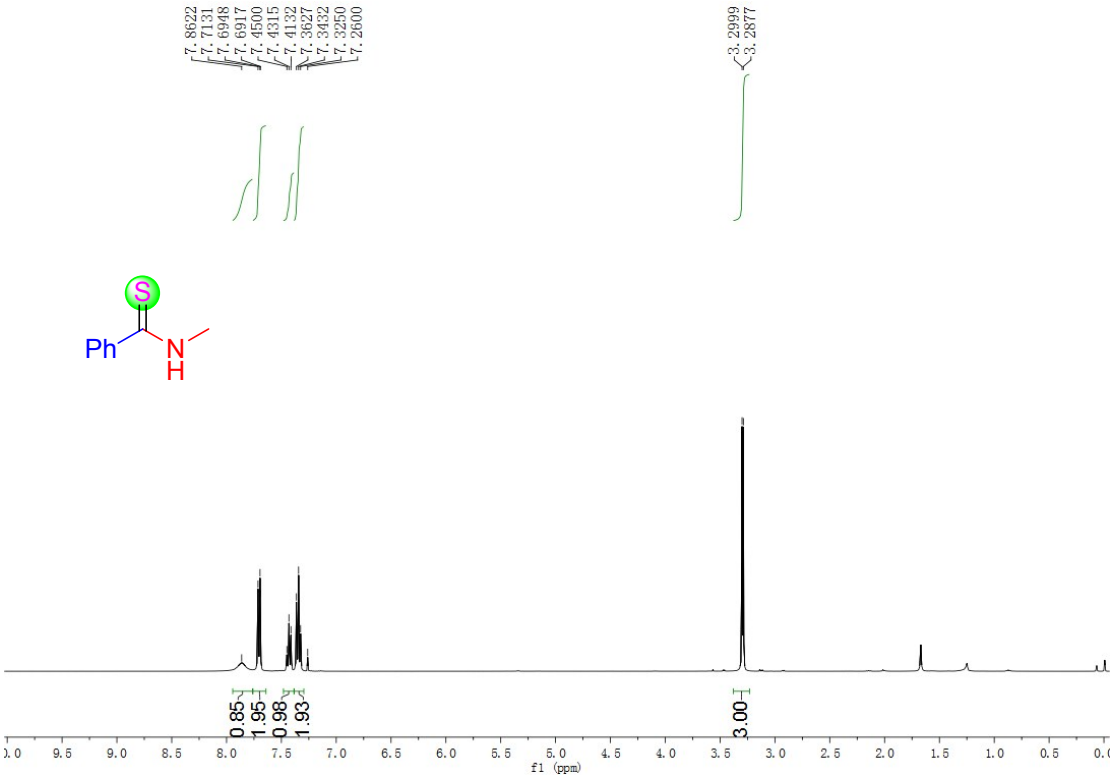

9.0992
7.8496
7.8255
7.7669
7.7416
7.5244
7.5017
7.4763
7.4380
7.4249
7.3548
7.3210
7.2970
7.2732
7.2600

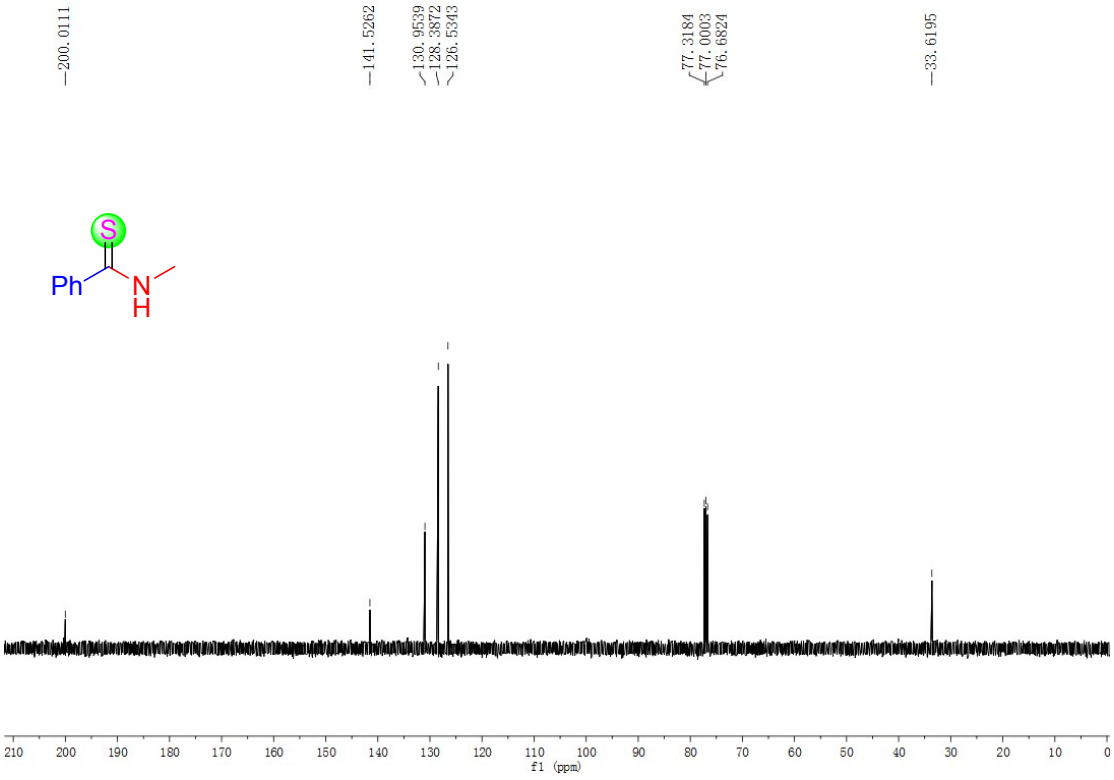

S
Ph
NHPh


0.90
3.77
6.14
f1 (ppm)

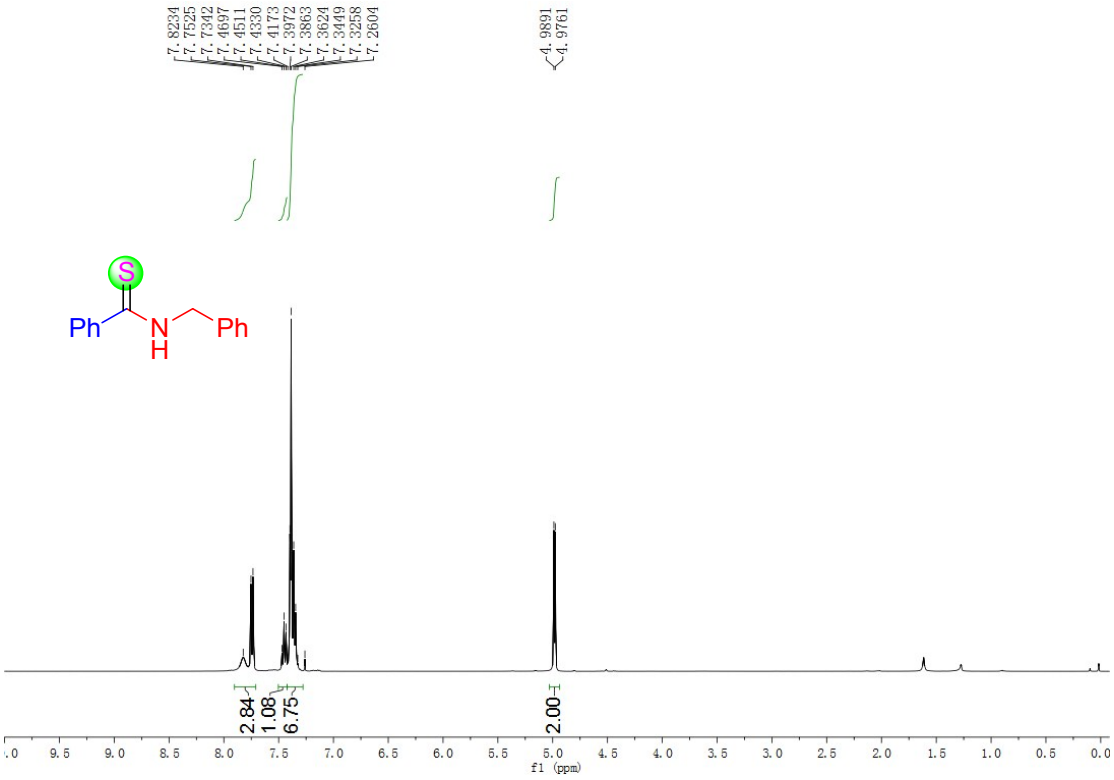

198.4227
143.0679
138.9615
131.2227
128.9873
128.5701
126.9385
126.6665
123.7046
77.3176
76.9999
76.6822
S
Ph
NHPh
f1 (ppm)

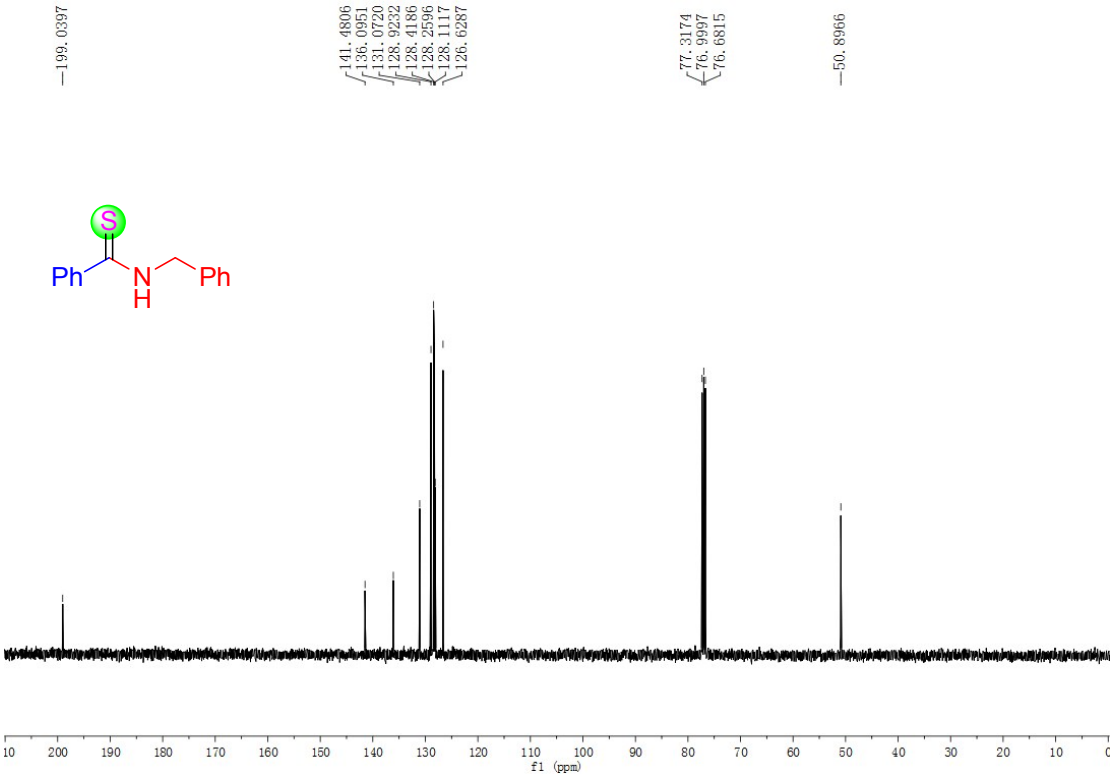
Compound 22:


7.8622
7.7131
7.6948
7.6917
7.4500
7.4315
7.4132
7.3627
7.3432
7.3250
7.2600
3.2999
3.2877
S
Ph
N
H
0.85
1.95
0.98
1.93
3.00
f1 (ppm)

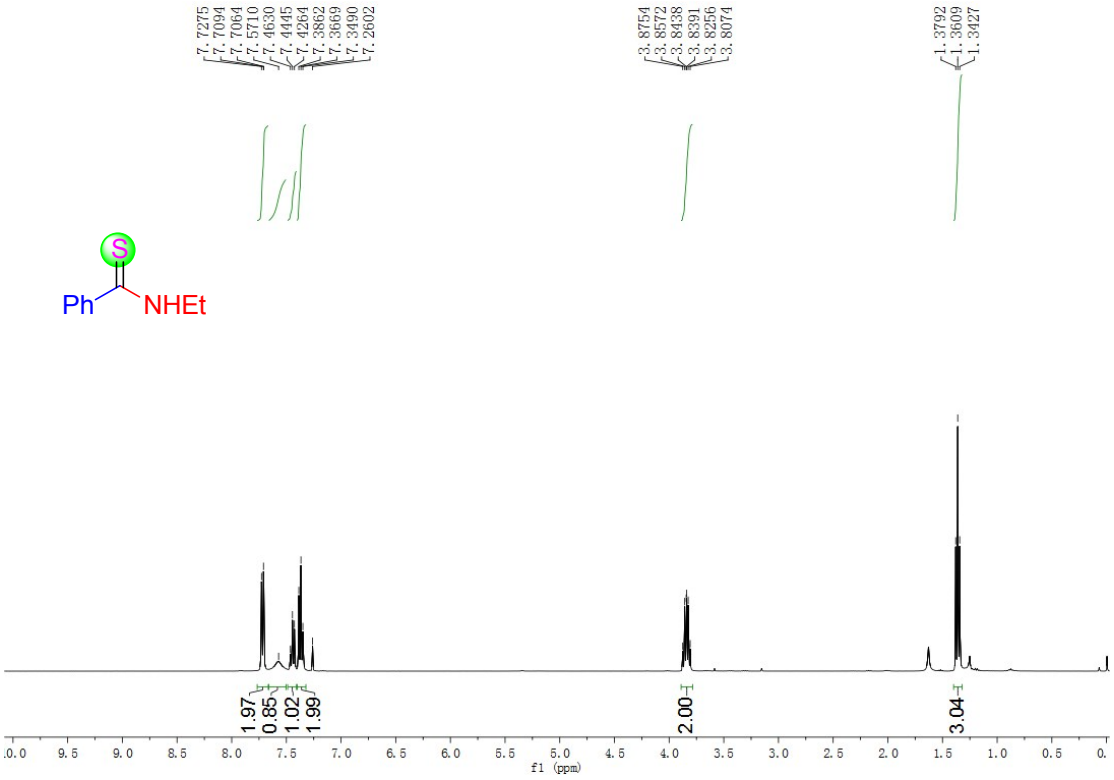

200.0111
141.5262
130.9539
128.3872
126.5343
77.3184
77.0003
76.6824
33.6195
S
Ph
N
H
f1 (ppm)

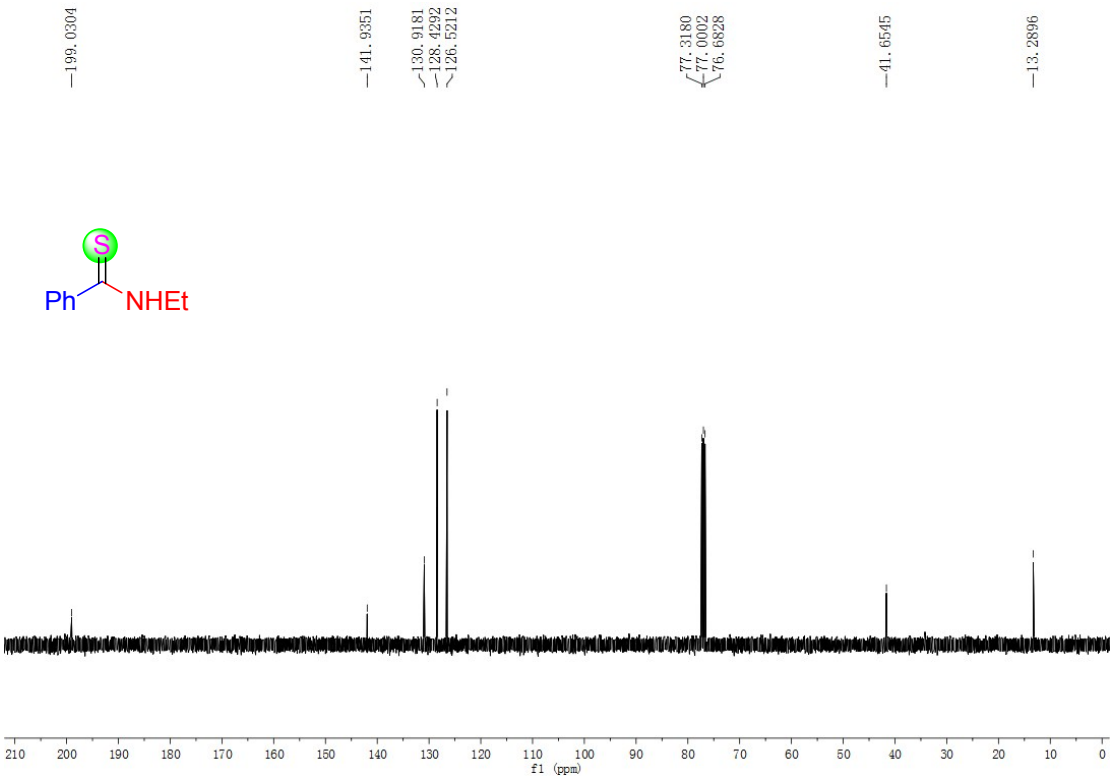
Compound 23:


7.8234
7.7525
7.7342
7.4697
7.4511
7.4330
7.4173
7.3972
7.3863
7.3624
7.3449
7.3258
7.2604
4.9891
4.9761
S
Ph
N
H
Ph
2.84
1.08
6.75
2.00
f1 (ppm)

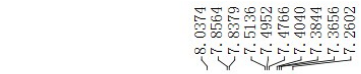

199.0397
141.4806
136.0951
131.0720
128.9232
128.4186
128.2596
128.1117
126.6287
77.3174
76.9997
76.6815
50.8966
S
Ph
N
H
Ph
f1 (ppm)

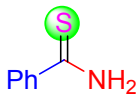
Compound 24:

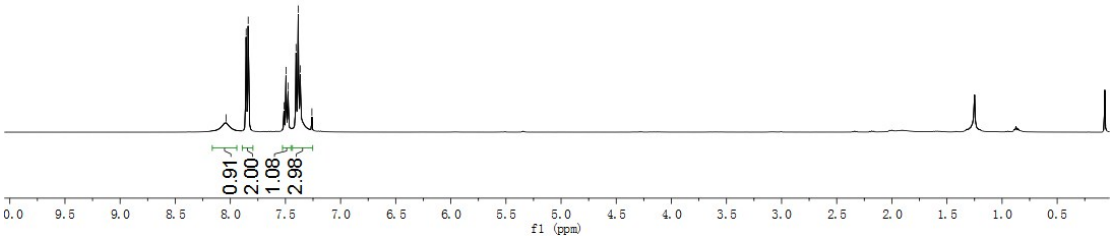

7.7275
7.7094
7.7064
7.5710
7.4630
7.4445
7.4264
7.3862
7.3669
7.3490
7.2602
3.8754
3.8572
3.8438
3.8391
3.8256
3.8074
1.3792
1.3609
1.3427
S
Ph
NHEt
1.97
0.85
1.02
1.99
2.00
3.04
f1 (ppm)


199.0304
141.9351
130.9181
128.4292
126.5212
77.3180
77.0002
76.6828
41.6545
13.2896
S
Ph
NHEt
f1 (ppm)

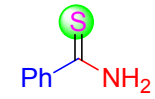
Compound 25:

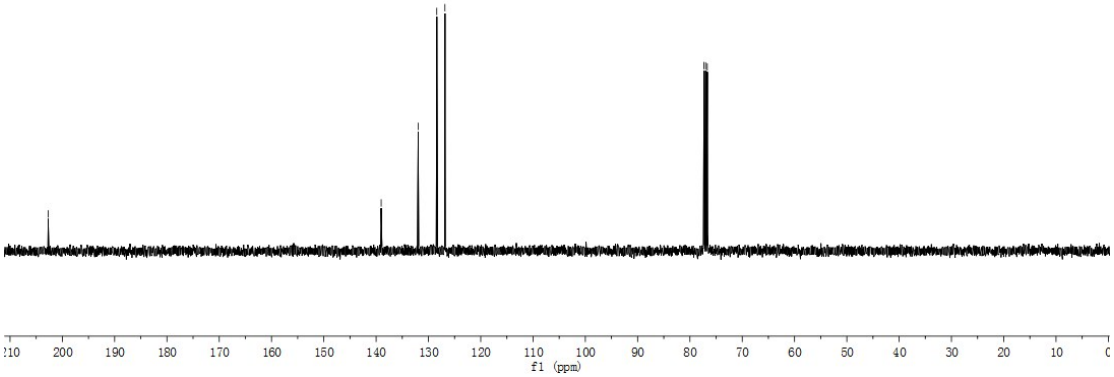

8.0374
7.8564
7.8379
7.5136
7.4952
7.4766
7.4040
7.3844
7.3656
7.2602


S
Ph
NH2

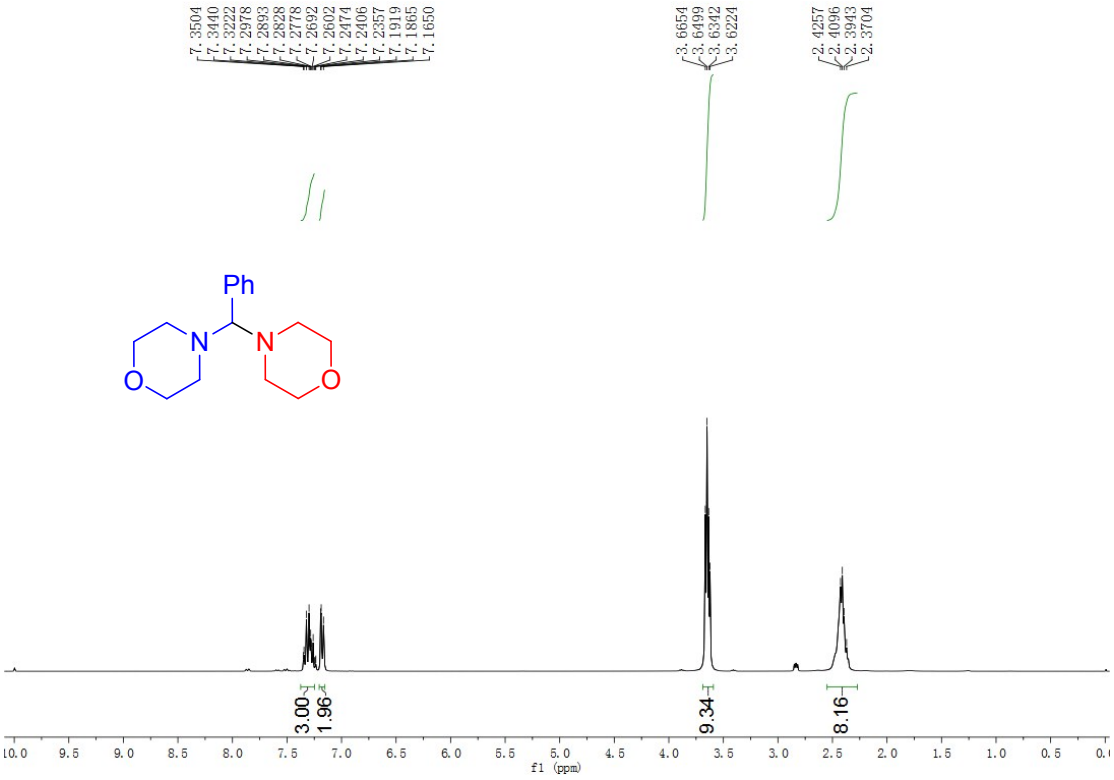

0.91
2.00
1.08
2.98
f1 (ppm)

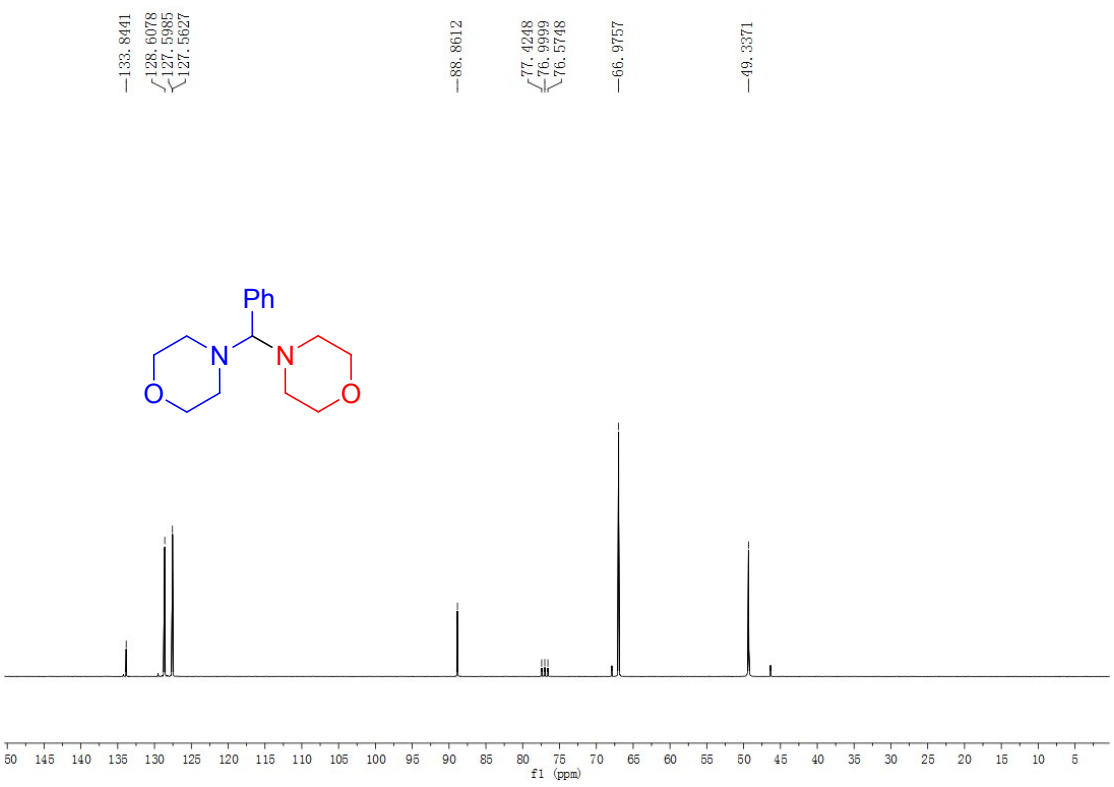

202.7058
139.0336
131.9580
128.4075
126.8475
77.3184
77.0005
76.6830


S
Ph
NH2


f1 (ppm)

Compound 26:


7.3504
7.3440
7.3222
7.2978
7.2893
7.2828
7.2778
7.2692
7.2602
7.2474
7.2406
7.2357
7.1919
7.1865
7.1650
3.6654
3.6499
3.6342
3.6224
2.4257
2.4096
2.3943
2.3704
Ph
N
N
O
O
3.00
1.96
9.34
8.16
f1 (ppm)


133.8441
128.6078
127.5985
127.5627
88.8612
77.4248
76.9999
76.5748
66.9757
49.3371
Ph
N
N
O
O
f1 (ppm)