

SUPPORTING INFORMATION

for

Expeditious Microwave Assisted Thionation with the System $\text{PSCl}_3/\text{H}_2\text{O}/\text{Et}_3\text{N}$ under Solvent Free Condition

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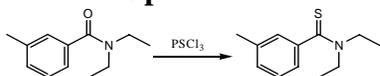
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General Information: Reagents were obtained from commercial supplier and used without further purification. Solvents were purified by the usual method and stored over molecular sieves. Freshly distilled thiophosphoryl chloride was used. Melting points were determined in an open capillary and are uncorrected. All reactions were carried out using a domestic microwave oven Samsung CE2977N operating at 2450 MHz with operator selectable power output from 100W to 900W. TLC is performed using precoated aluminium sheets with silica gel 60F₂₅₄.

Table 1. Optimization of Thionation Condition



Entry	Condition	Time	Conversion [Yield](%)
1.	Anhydrous toluene, rt.	-	No reaction
2.	Anhydrous toluene, reflux	36 hrs.	15
3.	Anhydrous toluene, 1.1 mol of H ₂ O, reflux	36 hrs.	40
4.	Anhydrous toluene, 1.1 mol of H ₂ O, 1.5 mole of Et ₃ N	5 hrs.	98
5.	Solvent Free, μ W, 180 W, 1.1 mol of H ₂ O, 1.5 mole of TEA	4-5 min.	99[89]
6.	Solvent Free, μ W, 180 W, 1.1 mol of H ₂ O, 1.5 mole of Py	5-6 min	97
7.	Solvent Free, μ W, 180 W, 1.1 mol of H ₂ O, 1.5 mole of DIPEA	4-5 min	97

Table 2. Thionation of carbonyl compounds with different organic bases

Entry	Substrate	Condition (SF, μ W, 180 W,)	Time	Conversion (%)
1.	Dimethyl thioformamide	TEA	1 min.	99
2.	Dimethyl thioformamide	Py	1 min.	99
3.	Dimethyl thioformamide	DIPEA	1 min.	99
4.	N-methyl thiopyrrolidinone	TEA	3 min.	99
5.	N-methyl thiopyrrolidinone	Py	3 min.	97
6.	N-methyl thiopyrrolidinone	DIPEA	3 min.	98
7.	Thio nicotinamide	TEA	6 min.	94
8.	Thio nicotinamide	Py	6 min.	93
9.	Thio nicotinamide	DIPEA	7 min.	94
10.	Thiobenzophenone	TEA	3 min.	97
11.	Thiobenzophenone	Py	2 min.	98
12.	Thiobenzophenone	DIPEA	4 min.	94
13.	4, 4-Dimethoxy thiobenzophenone	TEA	3 min.	98
14.	4, 4-Dimethoxy thiobenzophenone	Py	4 min.	93
15.	4, 4-Dimethoxy thiobenzophenone	DIPEA	3 min.	94
16.	(+)-1, 3, 3-Trimethyl-bicyclo [2.2.1] heptane-2-thione	TEA	1.5 min.	79
17.	(+)-1, 3, 3-Trimethyl-bicyclo [2.2.1] heptane-2-thione	Py	1.5 min.	75
18.	(+)-1, 3, 3-Trimethyl-bicyclo [2.2.1] heptane-2-thione	DIPEA	1.5 min	74

TEA=Triethyl amine, Py=Pyridine, DIPEA=Diisopropyl ethyl amine,

N, N-Dimethyl-thioformamide (2): Yellow liquid, ^1H NMR (400 MHz, CDCl_3) δ 9.21 (s, 1H), 3.33 (s, 3H), 3.29 (s, 3H); ^{13}C NMR (100.6 MHz, CDCl_3): 187.91, 45.36, 37.20; EIMS: 89 (M^+), 74, 72, 59, 56. Anal. Calc for $\text{C}_3\text{H}_7\text{NS}$. C, 40.41; H, 7.91; N, 15.71; S, 35.96. Found C, 40.53; H, 8.07; N, 15.78; S, 35.60.

N-Phenyl-thioacetamide (4): Yellow solid, mp 76-78 $^\circ\text{C}$ (Lit. 75-76 $^\circ\text{C}$), ^1H NMR (400 MHz, CDCl_3)^{2d} δ 9.71 (br, s, 1H, NH), 8.87 (br, s, 1.3H, NH), 7.67-7.65 (m, 1.4H), 7.45-7.26 (m, 3H), 7.17-7.15 (m, 2.0H), 2.73 (s, 2.6H), 2.51 (s, 2H). EIMS: 151 (M^+), 150, 118, 110, 93, 77, 59. Anal. Calc for $\text{C}_8\text{H}_9\text{NS}$. C, 63.54; H, 6.00; N, 9.26; S, 21.20. Found C, 63.64; H, 5.85; N, 9.20; S, 21.30.

Thiobenzamide (5): Yellow solid, mp 114-116 $^\circ\text{C}$ (Lit. 113-117 $^\circ\text{C}$), ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.86 (m, 2H), 7.53 (br, s, 1H, NH), 7.51-7.49 (m, 1H), 7.43-7.39 (m, 2H), 7.26 (br, s, 1H, NH). EIMS: 137 (M^+), 121, 109, 104, 77, 60, 51. Anal. Calc for $\text{C}_7\text{H}_7\text{NS}$. C, 61.28; H, 5.14; N, 10.21; S, 23.37. Found C, 61.40; H, 5.34; N, 10.28; S, 22.97.

1-Methyl-pyrrolidine-2-thione (7): Yellow liquid, ^1H NMR (400 MHz, CDCl_3) δ 3.76 (t, 2H, $J=7.3\text{Hz}$), 3.27 (s, 3H), 3.04 (t, 2H, $J=7.9\text{Hz}$), 2.11-2.04 (m, 2H); ^{13}C NMR (100.6 MHz, CDCl_3): 200.54, 56.99, 44.46, 35.24, 19.14; EIMS: 115 (M^+), 87, 82, 73, 58, 55. Anal. Calc for $\text{C}_5\text{H}_9\text{NS}$. C, 52.13; H, 7.87; N, 12.16; S, 27.84. Found C, 52.27; H, 7.96; N, 12.25; S, 27.50.

1-Vinyl-pyrrolidine-2-thione (10): White solid, mp 65-66 $^\circ\text{C}$, (Lit. 66-67 $^\circ\text{C}$) ^1H NMR (400 MHz, CDCl_3): δ 7.76-7.70 (m, 1H), 4.83-4.77 (m, 2H), 3.85-3.82 (m, 2H), 3.12 (t, 2H, $J=8.0\text{Hz}$), 2.15 (t, 2H, $J=7.6\text{Hz}$); ^{13}C NMR (100.6 MHz, CDCl_3): 201.90, 132.35, 100.84, 51.74, 45.66, 19.60; EIMS: 127(M^+), 126, 98, 85, 71, 59. Anal. Calc for $\text{C}_6\text{H}_9\text{NS}$. C, 56.65; H, 7.13; N, 11.01; S, 25.21. Found C, 56.80; H, 7.25; N, 11.06; S, 24.88.

Thionicotinamide (11): Yellow crystalline solid, mp. 190-192 $^\circ\text{C}$ (Lit. 190-191 $^\circ\text{C}$), ^1H NMR (400 MHz, DMSO): $\delta=10.1$ (br, 1H, NH_2), 9.7 (br, 1H, NH_2), 9.05 (d, $J=2.4$ Hz, 1H), 8.72-8.70 (m, 1H), 8.26-8.23 (m, 1H), 7.5 (dd, $J=4.8$ Hz, 3.2 Hz, 1H); ^{13}C NMR (100.6 MHz, CD_3OD): 200.74, 152.13, 148.62, 137.80, 136.87, 124.77; MS: m/z 138[M^+], 122, 104, 77, 51. Anal. Calcd for $\text{C}_6\text{H}_6\text{N}_2\text{S}$. C, 52.15; H, 4.38; N, 20.27; S, 23.20. Found: C, 52.29; H, 4.49; N, 20.18, S, 22.94.

Thiobenzophenone (12): Dark Blue solid, mp 50-52 $^\circ\text{C}$ (Lit. 53 $^\circ\text{C}$), ^1H NMR (400 MHz, CDCl_3): δ 7.73-7.71 (m, 4H), 7.59-7.52 (m, 2H), 7.40-7.26 (m, 4H); ^{13}C NMR (100.6 MHz, CDCl_3): 237.56, 147.55, 131.59, 129.83, 128.17; EIMS: 198(M^+), 182, 165, 152, 121, 105, 77, 51. Anal. Calc for $\text{C}_{13}\text{H}_{10}\text{S}$. C, 78.74; H, 5.08; S, 16.17. Found C, 78.88; H, 5.20; S, 15.90.

4, 4'-Dimethoxy-thiobenzophenone (14): Dark blue solid, mp 116-117 $^\circ\text{C}$ (Lit. 115 $^\circ\text{C}$), ^1H NMR (400 MHz, CDCl_3): δ 7.75-7.71 (m, 4H), 6.90-6.86 (m, 4H) 3.88 (s, 6H); ^{13}C NMR (100.6 MHz, CDCl_3): 233.60, 163.35, 141.00, 132.39, 113.39, 55.78; EIMS: 258

(M⁺), 242, 225, 210, 199, 171, 151, 135, 129, 108, 92, 77, 63. Anal. Calc for C₁₅H₁₄O₂S. C, 69.74; H, 5.46; S, 12.41. Found C, 69.86; H, 5.61; S, 12.10.

10H-Acridine-9-thione (17): Red Needles, mp 274-276 °C (Lit. 275°C), ¹H NMR (400 MHz, DMSO): δ 12.75 (s, 1H NH), 8.86 (d, 2H, J=8.4Hz), 7.83-7.79 (m, 2H), 7.67 (d, 2H, J=8.4Hz), 7.37 (m, 2H); ¹³C NMR (100.6 MHz, DMSO): 197.43, 136.01, 133.90, 129.84, 129.14, 123.20, 118.60; ESI: 212 (M+H⁺). Anal. Calc for C₁₃H₉NS. C, 73.90; H, 4.29; N, 6.63; S, 15.18. Found C, 74.04; H, 4.55; N, 6.59; S, 14.80.

Xanthene-9-thione (18): Red Needles, mp 156-157°C (Lit. 157-158°C), ¹H NMR (400 MHz, CDCl₃): δ 8.63-8.61 (m, 2H), 7.62-7.57 (m, 4H), 7.51-7.48 (m, 2H); ¹³C NMR (100.6 MHz, CDCl₃): 205.21, 150.73, 135.13, 130.10, 129.26, 124.98, 118.50; EIMS: 212(M⁺), 168, 139, 106, 79, 69. Anal. Calc for C₁₃H₈OS. C, 73.56; H, 3.80; S, 15.11. Found C, 73.70; H, 3.92; S, 14.83.

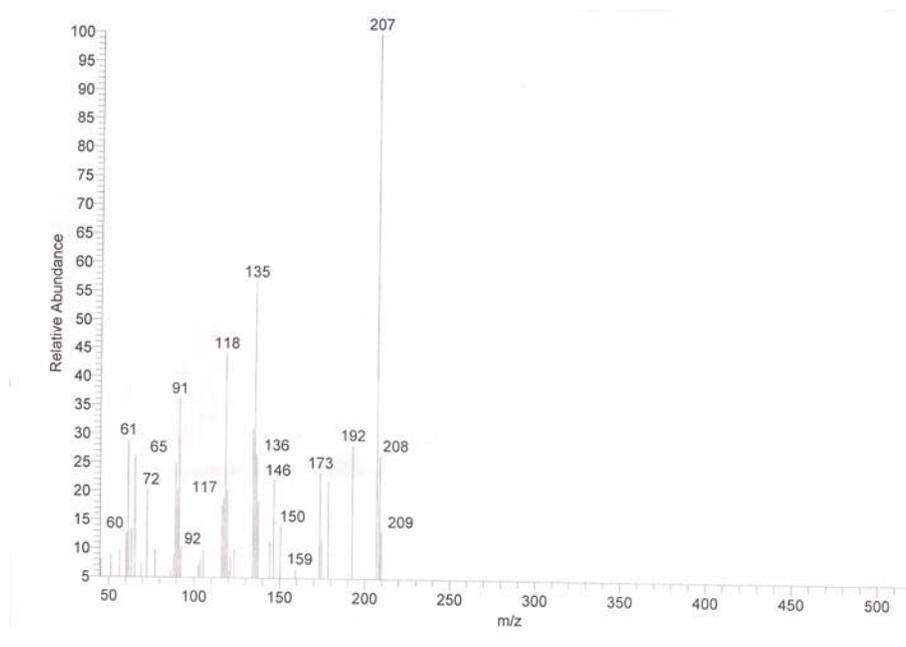
Thioxanthene-9-thione (19): Brownish-green, mp 169-170°C (Lit. 168°C), ¹H NMR (400 MHz, CDCl₃): δ 9.01-8.99 (m, 2H), 7.61-7.58 (m, 4H), 7.46-7.43 (m, 2H); ¹³C NMR (100.6 MHz, CDCl₃): 211.32, 137.69, 133.46, 132.07, 131.84, 127.15, 126.11; EIMS: 228(M⁺), 227, 212, 195, 184, 152, 139, 114, 92, 69. Anal. Calc for C₁₃H₈S₂. C, 68.38; H, 3.53; S, 28.09. Found C, 68.51; H, 3.67; S, 27.81.

(+)-1, 3, 3-Trimethyl-bicyclo [2.2.1] heptane-2-thione(20): Deep orange liquid: bp 92 °C (at 5mm Hg) (Lit. bp105 °C at 15 mmHg), [α]_D²⁰ = +46.3° (c, 1.2 in EtOAc), ¹H NMR (CDCl₃/TMS-400 MHz): δ 1.13 (s, 3H), 1.16 (s, 3H), 1.21-1.28 (m, 1H), 1.32 (s, 3H), 1.60-1.67 (m, 2H), 1.73-1.78 (m, 2H), 1.81-1.84 (d, 1H), 2.31 (br, s, 1H), ¹³C NMR (CDCl₃/TMS-100.6 MHz): δ 18.87, 24.71, 26.13, 28.32, 35.07, 43.33, 46.52, 57.37, 65.939, 271.43; EIMS m/z 168 (M⁺), 153, 135, 125, 112, 81, 71, 53; Anal. Calcd for C₁₀H₁₆S. C, 71.36; H, 9.58; S, 19.05; Found C, 71.50; H, 9.69; S, 18.79.

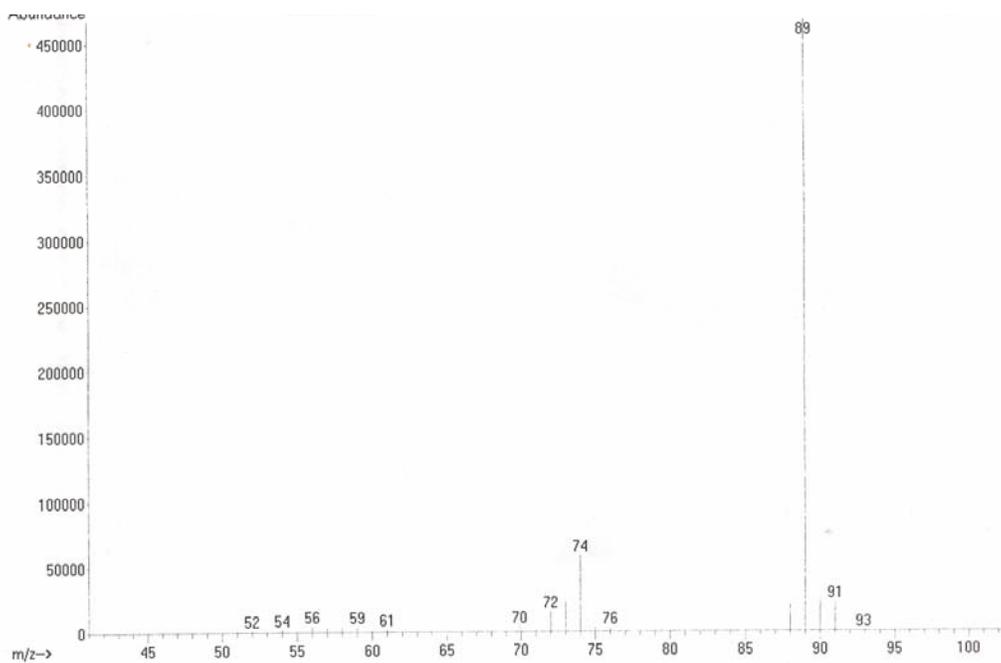
(-)-1, 7, 7-Trimethyl-bicyclo [2.2.1] heptane-2-thione: Orange solid: mp138-140°C (Lit.^{4c} 146 °C), [α]_D²⁰ = -24° (c, 3.0 in EtOAc), ¹H NMR (CDCl₃/TMS-400 MHz): δ 0.80 (s, 3H), 1.05 (s, 3H), 1.11 (s, 3H), 1.27-1.422 (m, 2H), 1.74-1.81 (m, 1H), 1.97-2.05 (m, 1H), 2.18 (t, 1H, J=4.4Hz), 2.40-2.45(d, 1H), 2.77-2.82 (br, d, 1H), ¹³C NMR (CDCl₃/TMS-100.6 MHz): δ 12.83, 19.29, 19.49, 26.84, 33.53, 44.73, 48.65, 55.20, 68.99, 271.75; EIMS m/z 168 (M⁺), 153, 125, 113, 85, 79, 67; Anal. Calcd for C₁₀H₁₆S. C, 71.36; H, 9.58; S, 19.05; Found C, 71.48; H, 9.72; S, 18.78.

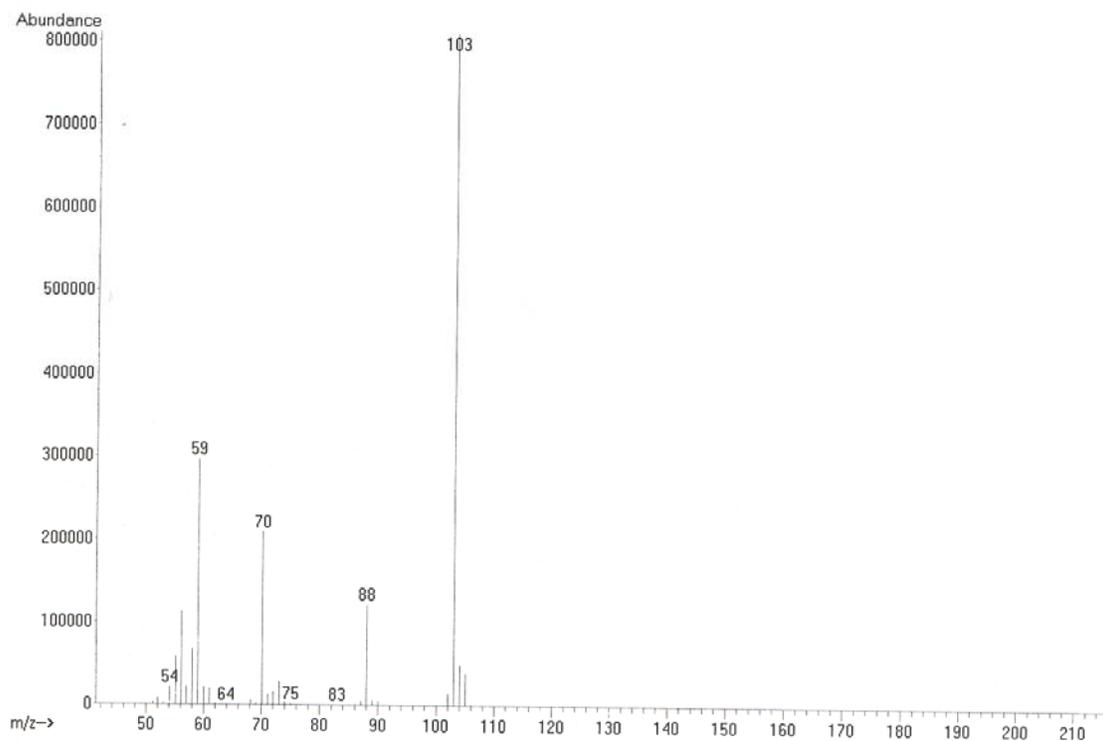
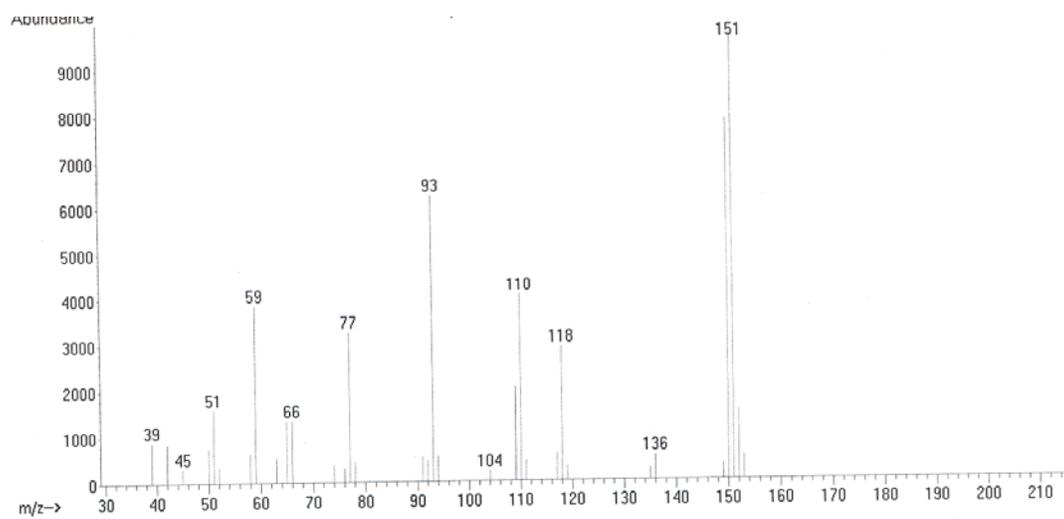
Mass Spectra of *N,N*-Diethyl-*m*-thiotoluamide (1)

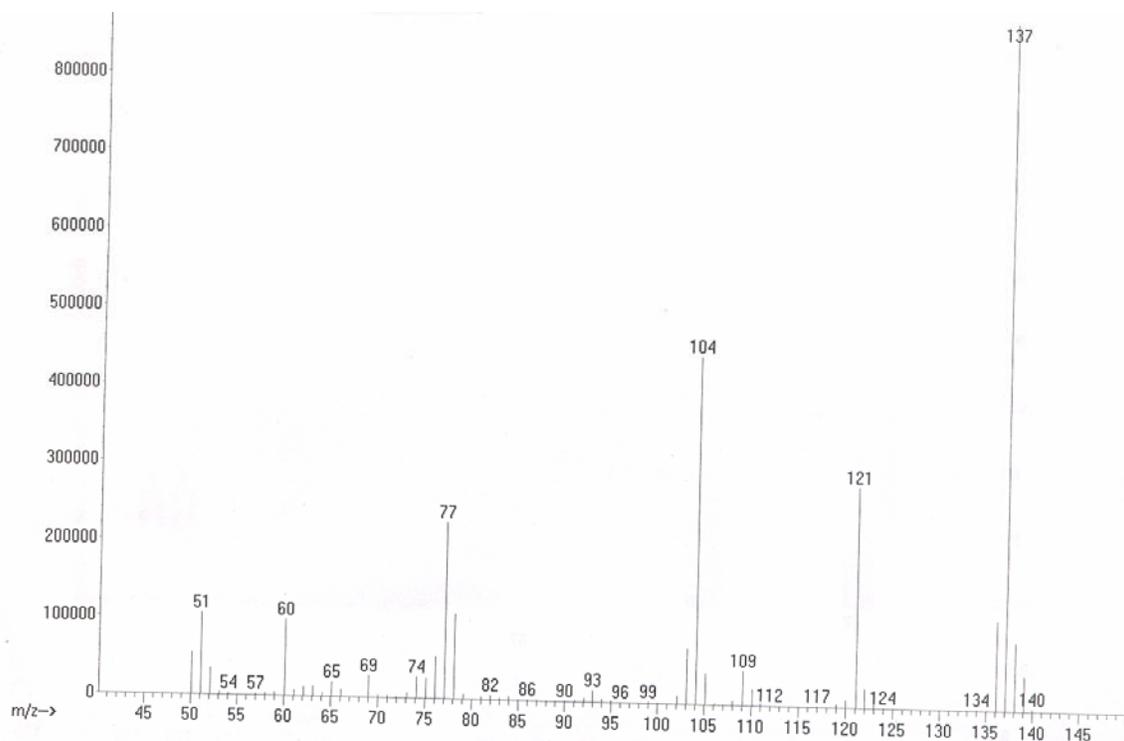
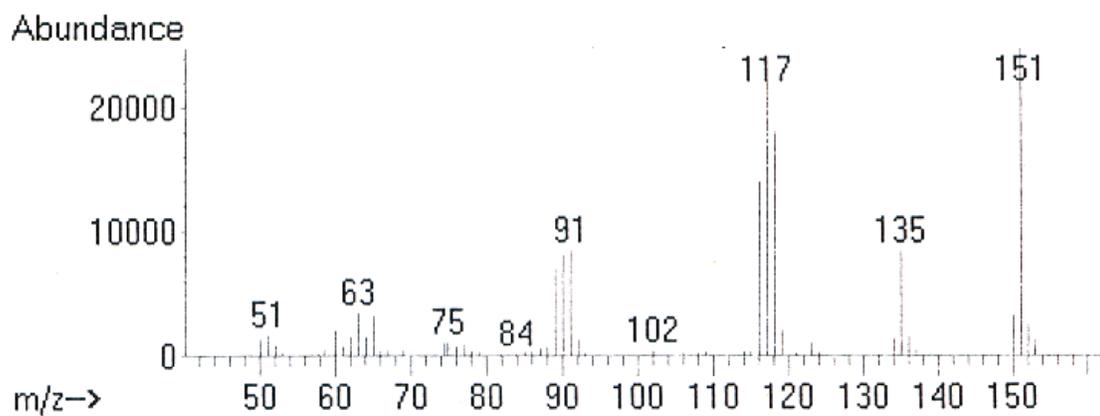
S6

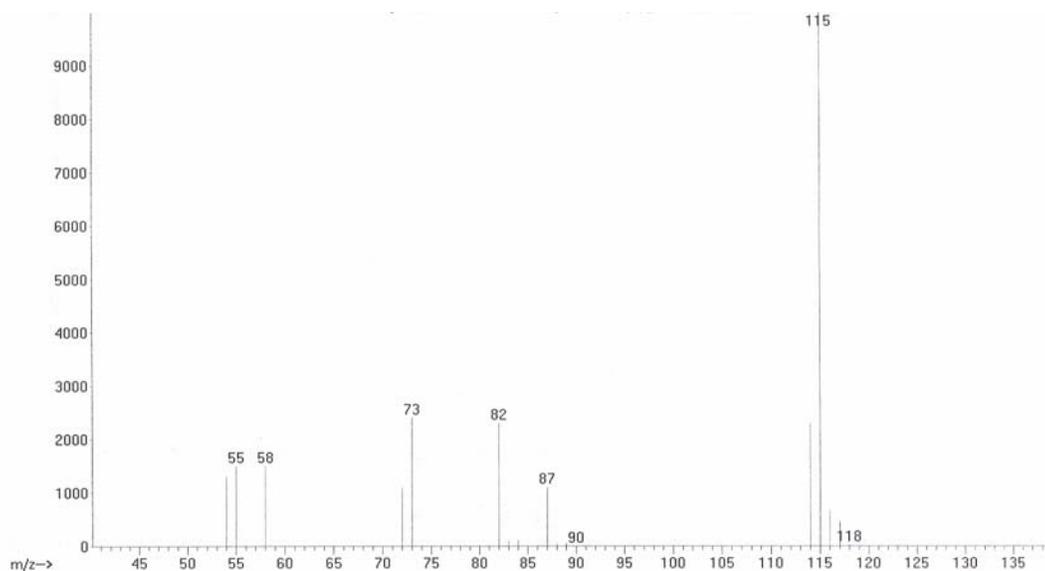
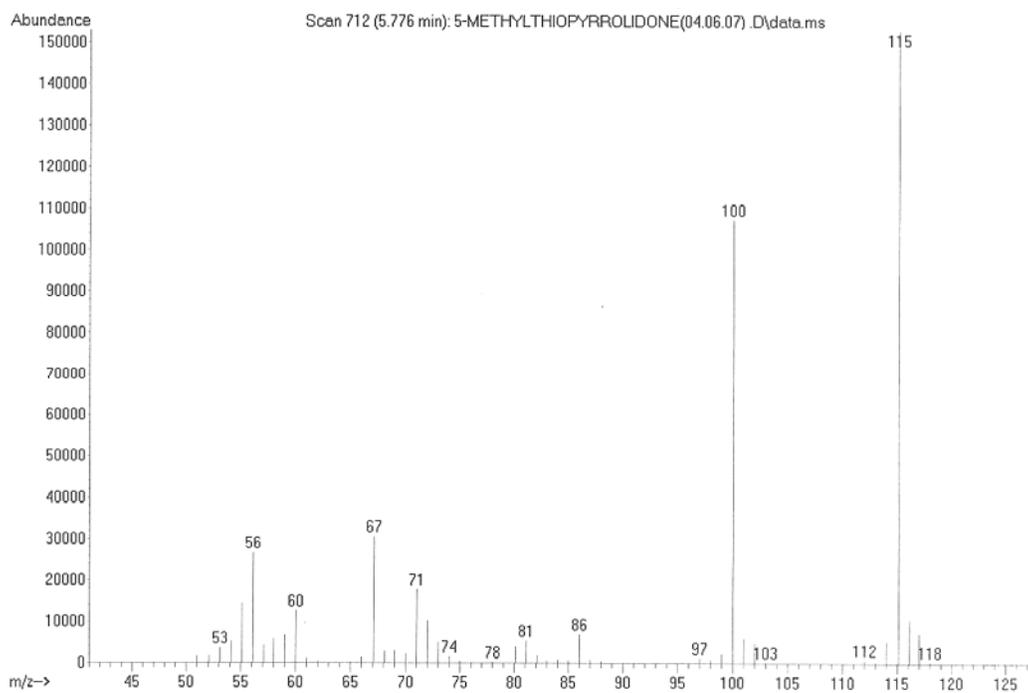


Mass Spectra of *N,N*-Dimethyl-thioformamide (2)



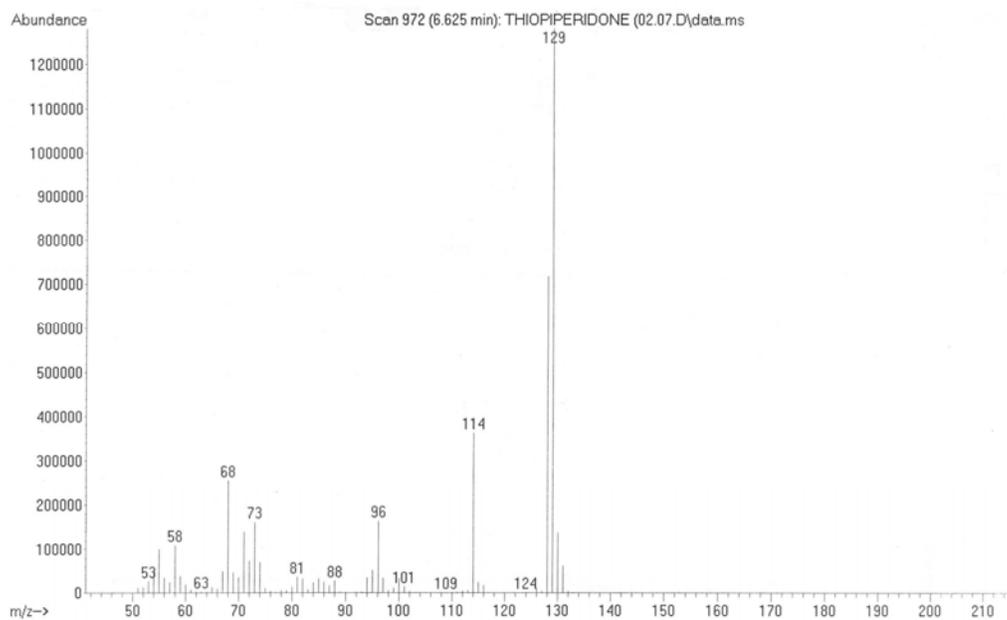
Mass Spectra of *N,N*-Dimethyl-thioacetamide (3)**Mass Spectra of *N*-Phenyl-thioacetamide (4)**

Mass Spectra of Thiobenzamide (5)**Mass Spectra of 4-Methyl-thiobenzamide (6)**

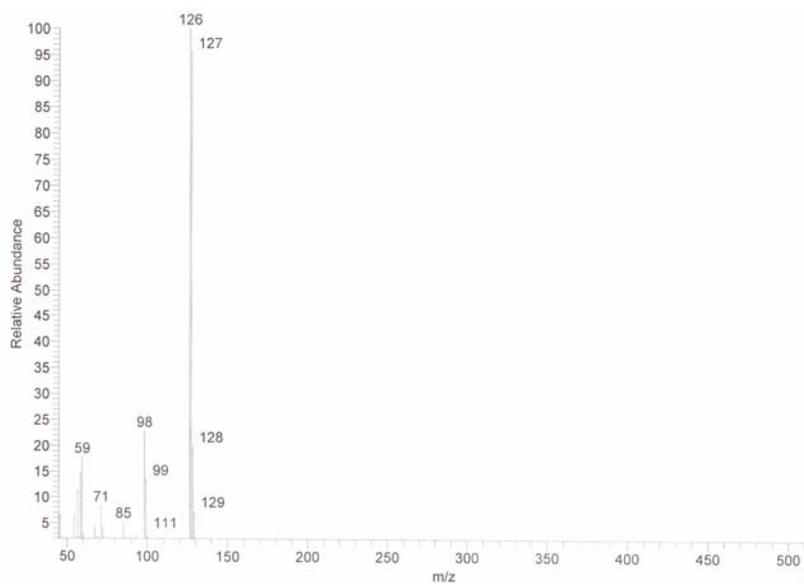
Mass Spectra of compound 1-Methyl-pyrrolidine-2-thione (7)**Mass Spectra of compound 5-Methyl-pyrrolidine-2-thione (8)**

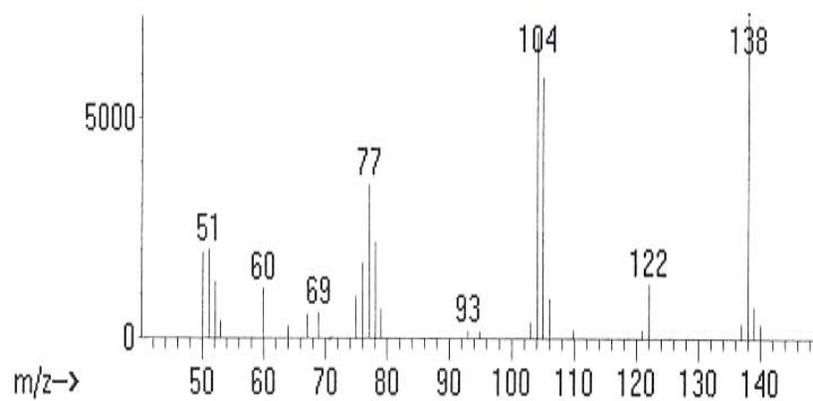
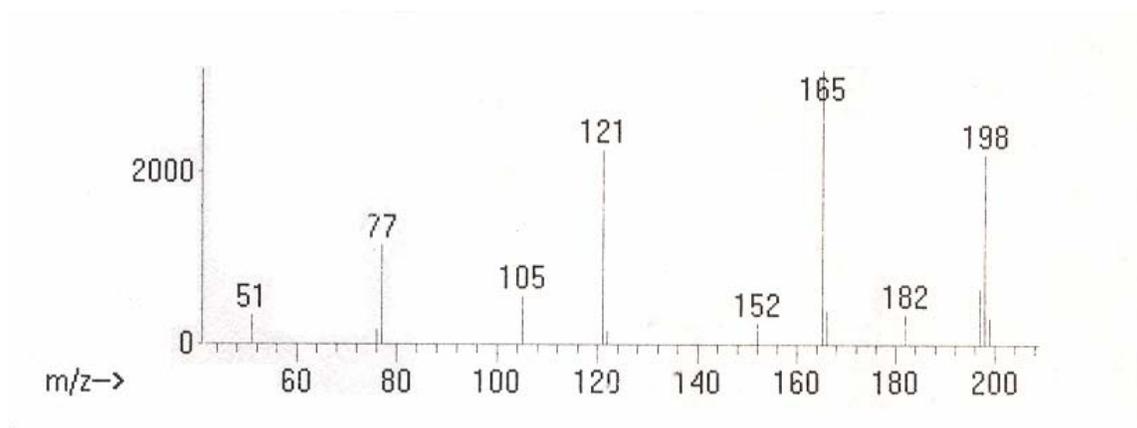
Mass Spectra of compound 1-Methyl-piperidine-2-thione (9)

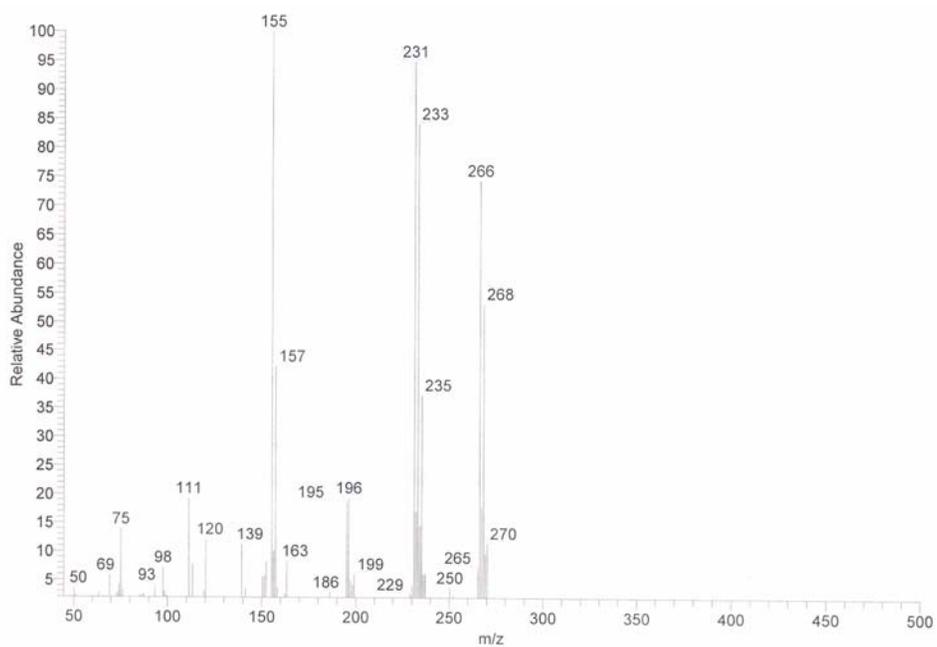
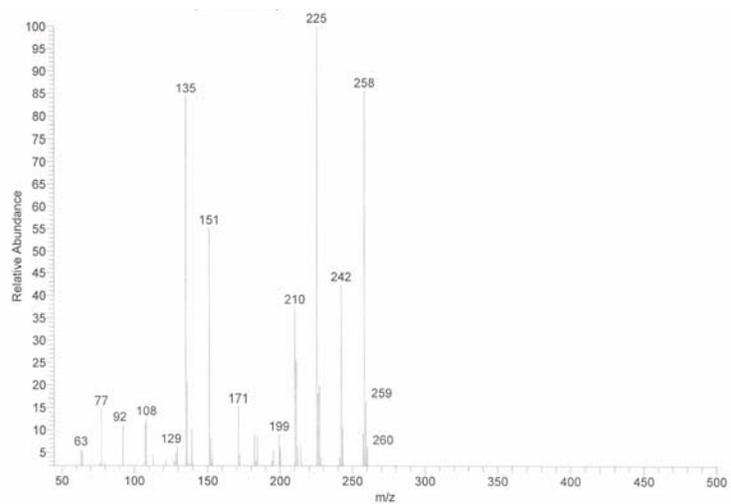
S10

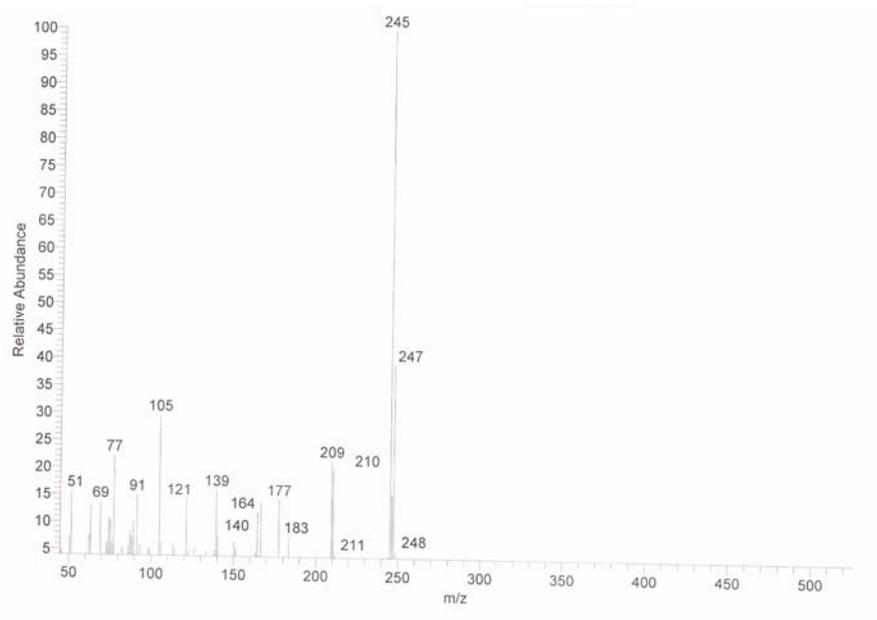
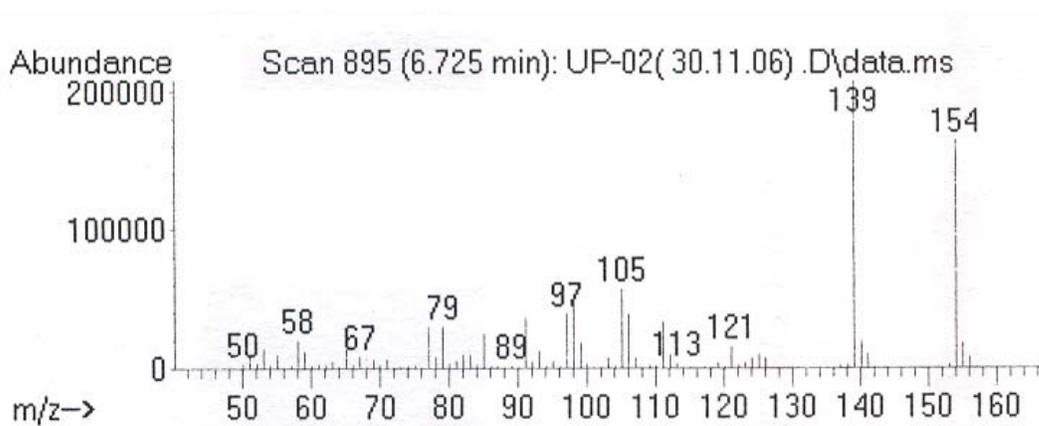


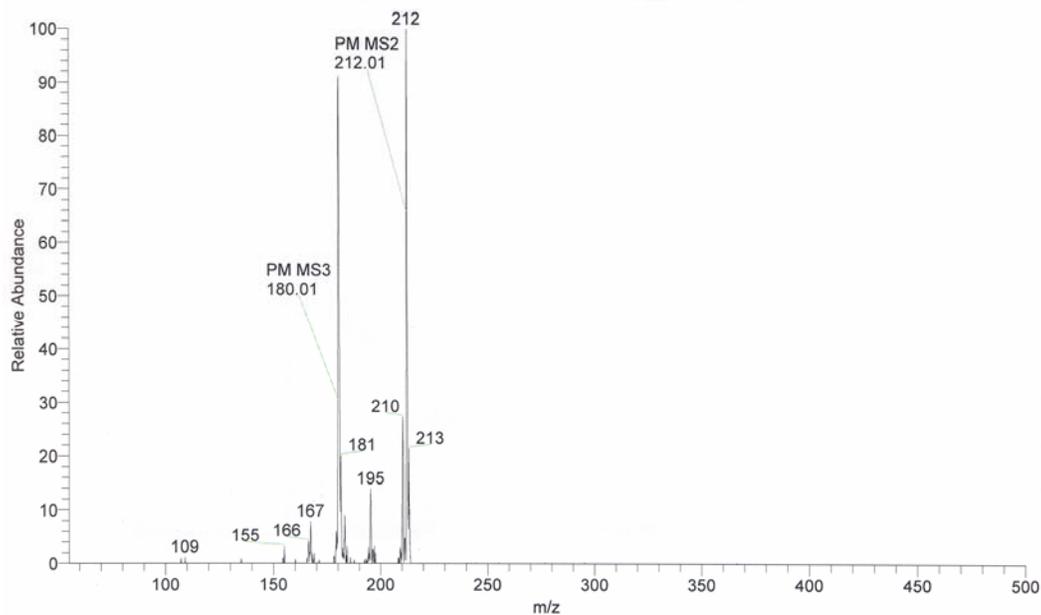
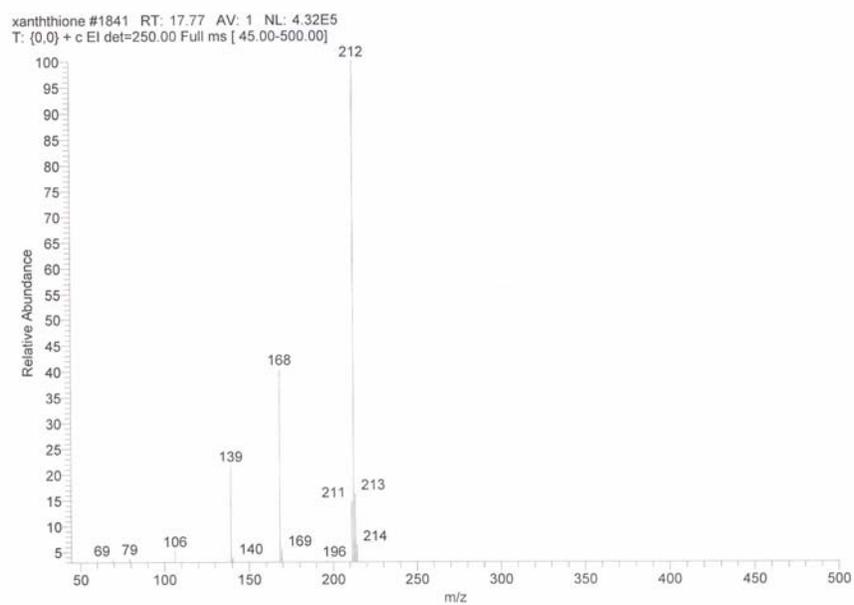
Mass Spectra of 1-Vinyl- pyrrolidine-2-thione (10)

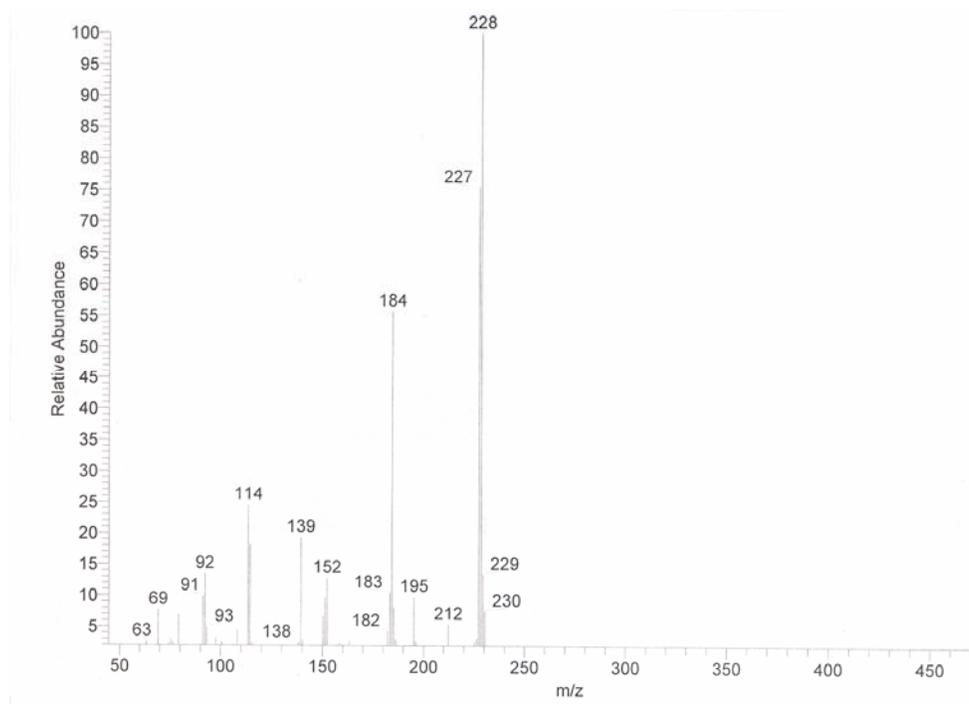
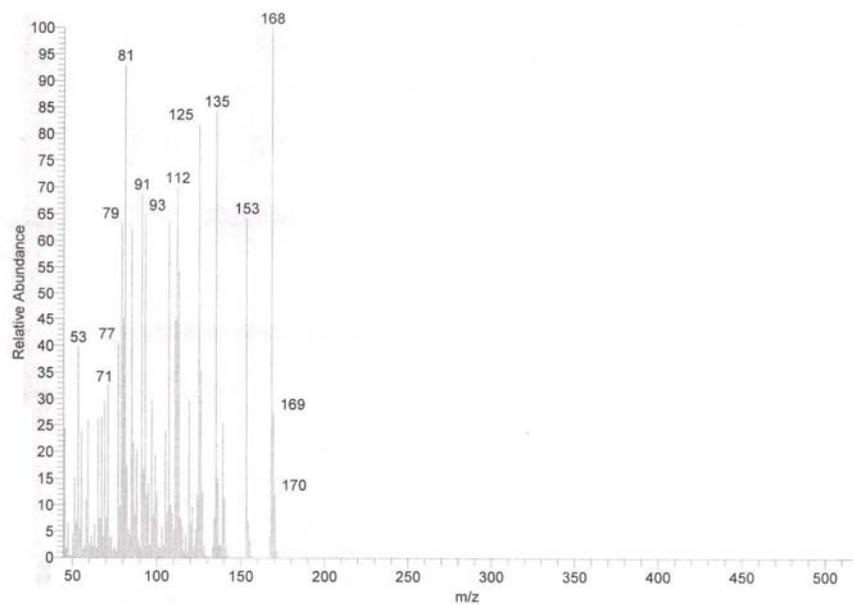


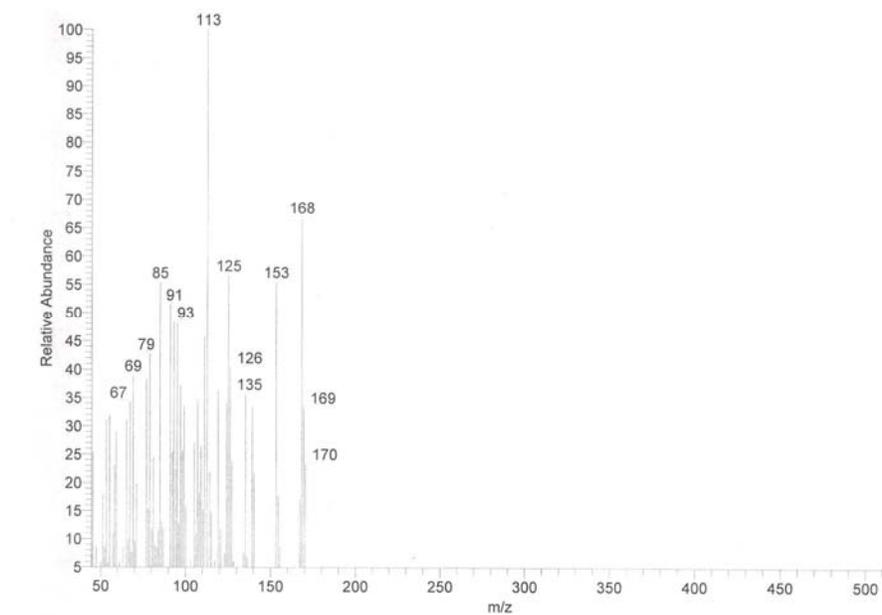
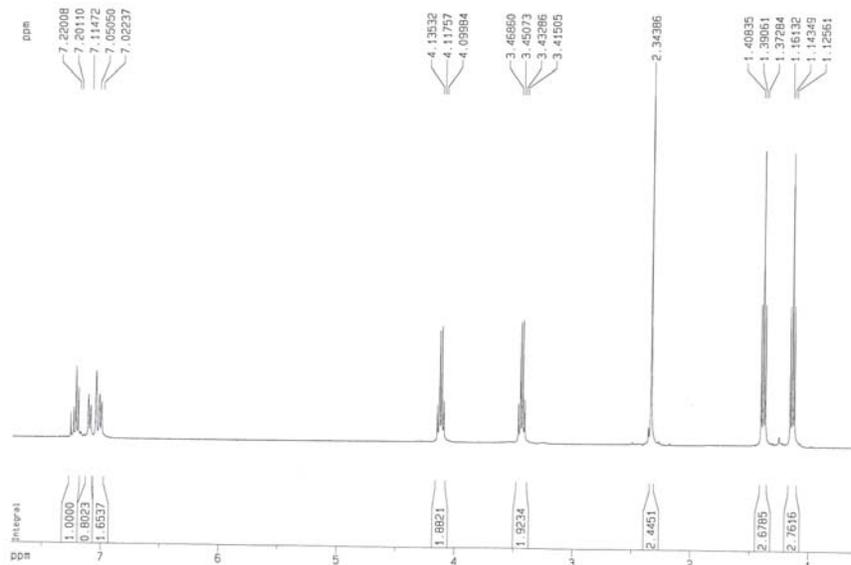
Mass Spectra of Thionicotinamide (11)**Mass Spectra of Thiobenzophenone (12)**

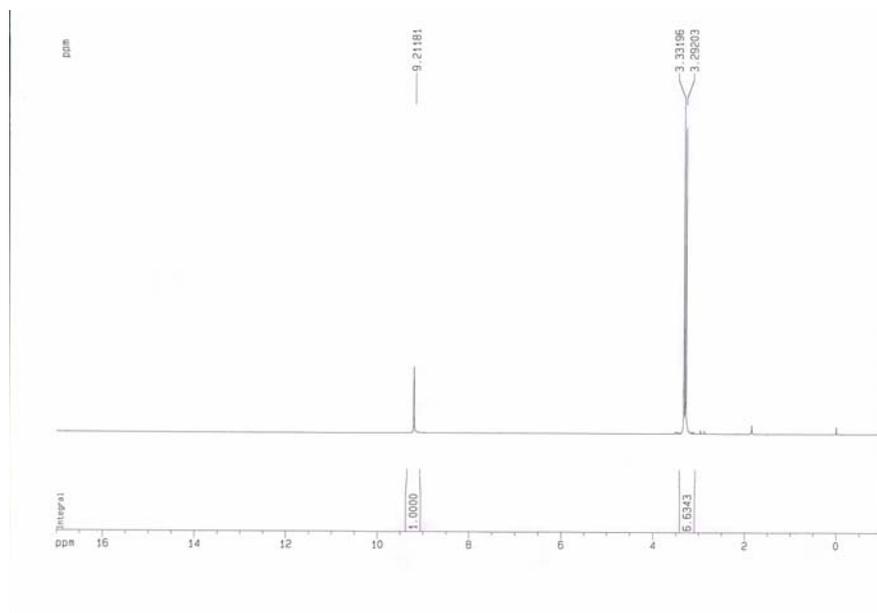
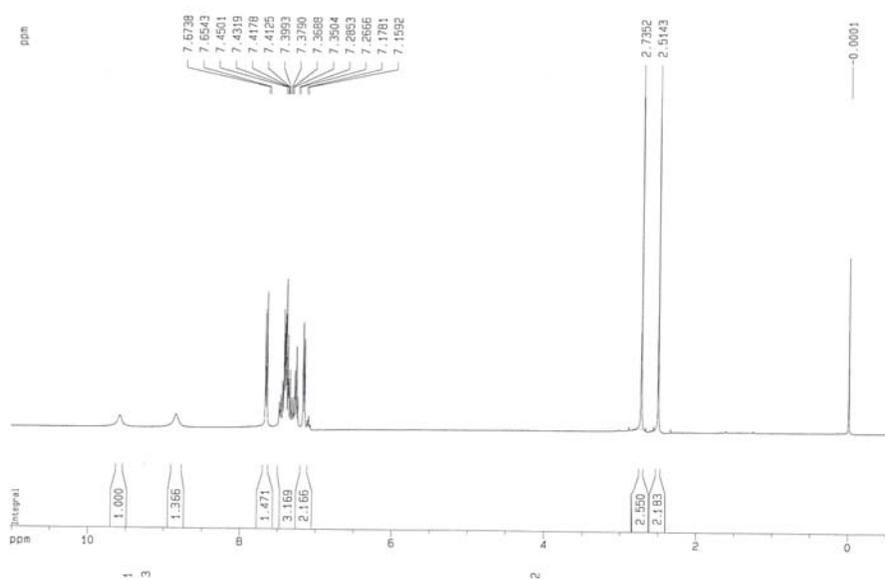
Mass Spectra of 4, 4'-Dichlorothiobenzophenone (13)**Mass Spectra of 4, 4'-Dimethoxythiobenzophenone (14)**

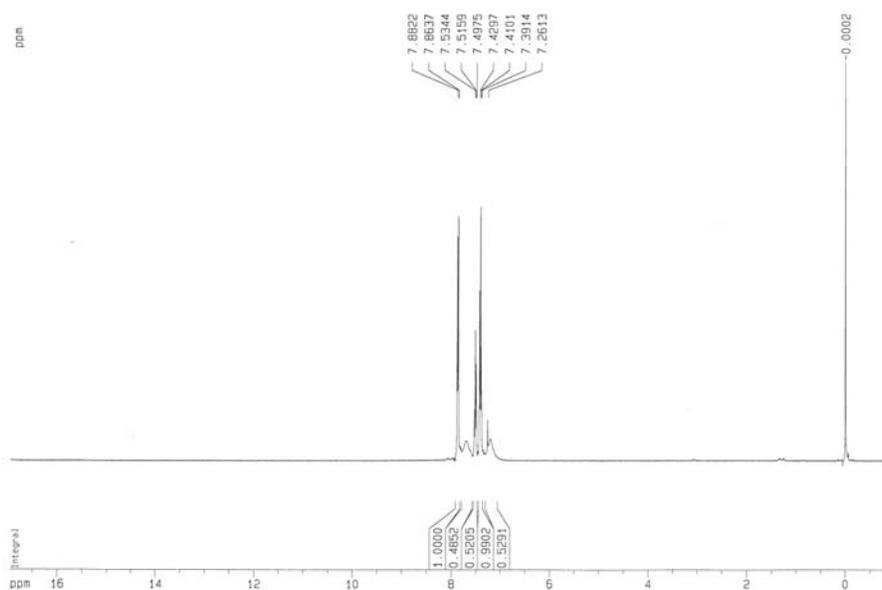
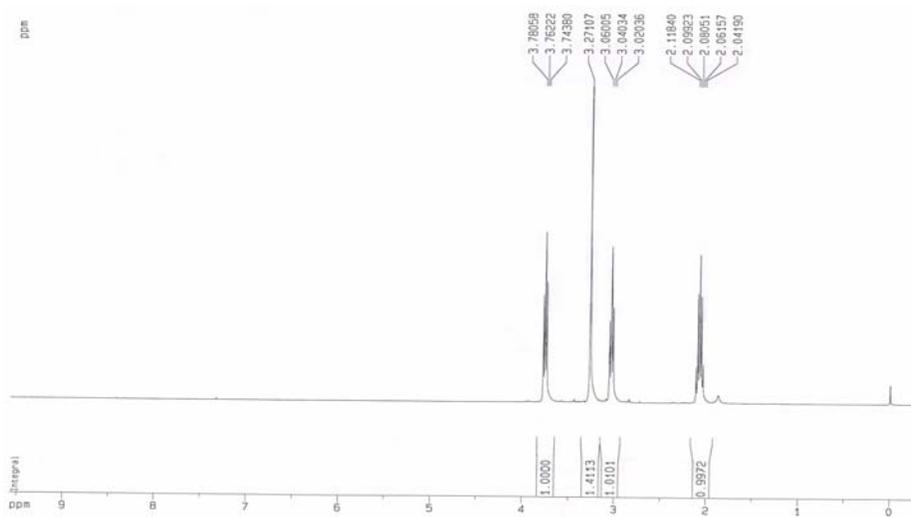
Mass Spectra of 2-Chloro-5-aminothiobenzophenone (15)**Mass Spectra of 3, 5, 5-Trimethyl-cyclohex-2-enethione (16)**

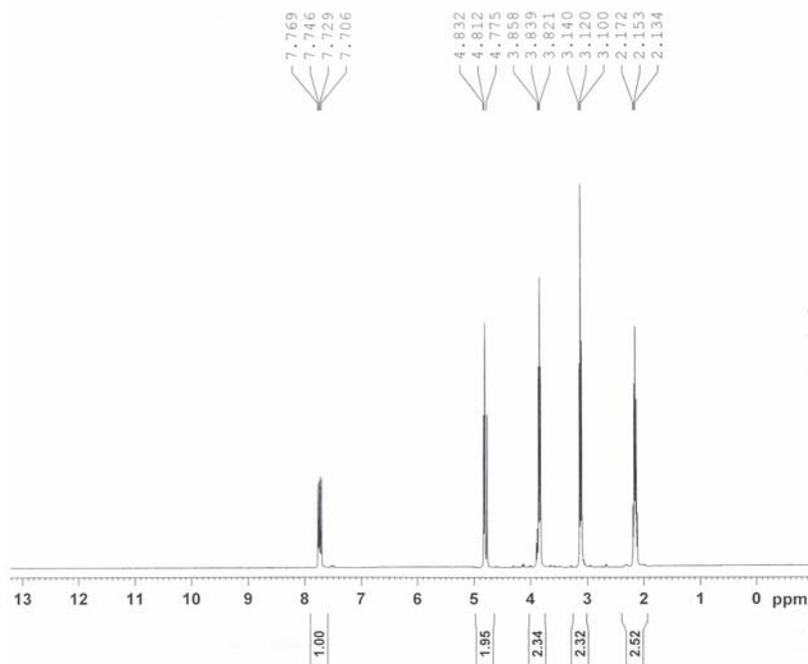
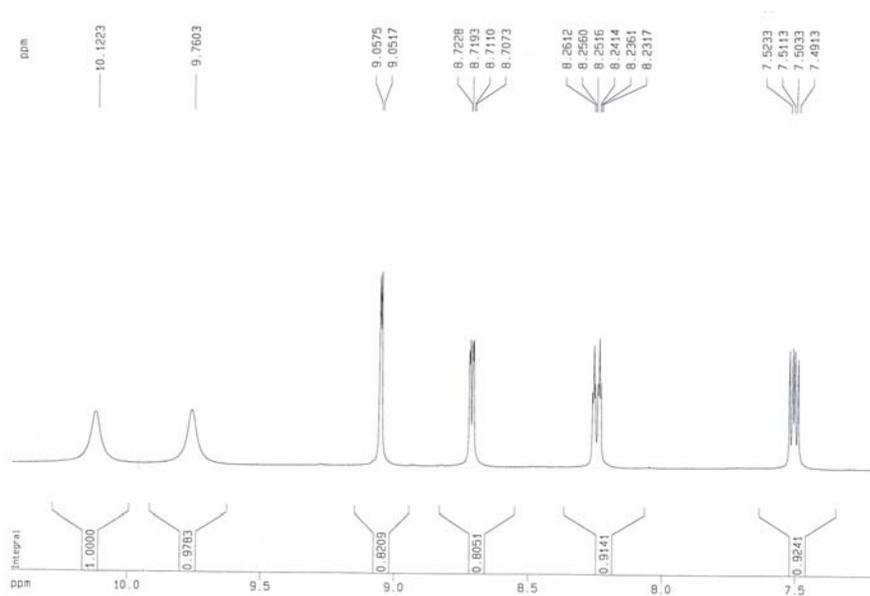
Mass Spectra of 10H-Thioacridone (17)**Mass Spectra of Xanthene-9-thione (18)**

Mass Spectra of Thioxanthene-9-thione (19)**Mass Spectra of (+)-1, 3, 3-Trimethyl-bicyclo [2.2.1] heptane-2-thione (20)**

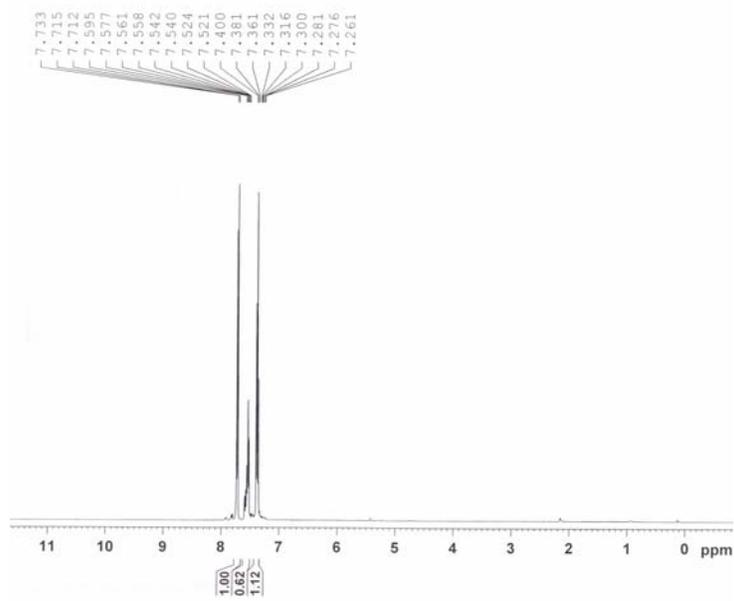
Mass Spectra of (-)-1, 7, 7-Trimethyl-bicyclo [2.2.1] heptane-2-thione (21)**¹H NMR of compound N, N-Diethyl-*m*-thiotoluamide (1)**

^1H NMR of compound *N,N*-Dimethyl-thioformamide (2) **^1H NMR of compound *N*-Phenyl-thioacetamide (4)**

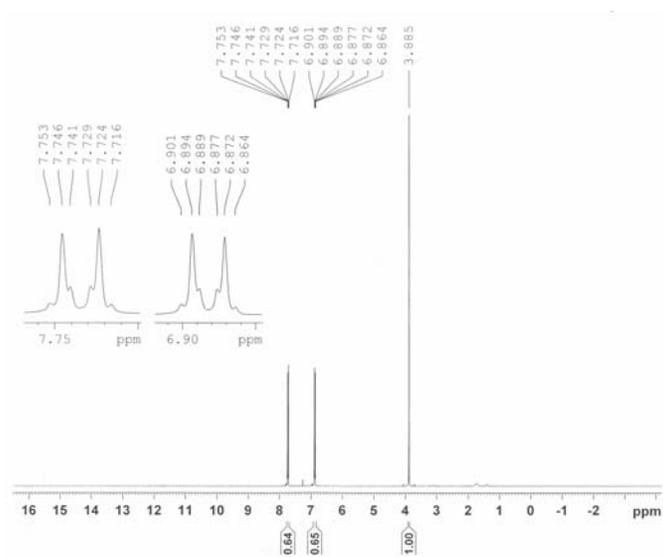
^1H NMR of compound Thiobenzamide (5) **^1H NMR of compound 1-Methyl-pyrrolidine-2-thione (7)**

^1H NMR of 1-Vinyl- pyrrolidine-2-thione (10) **^1H NMR of compound Thionicotinamide (11)**

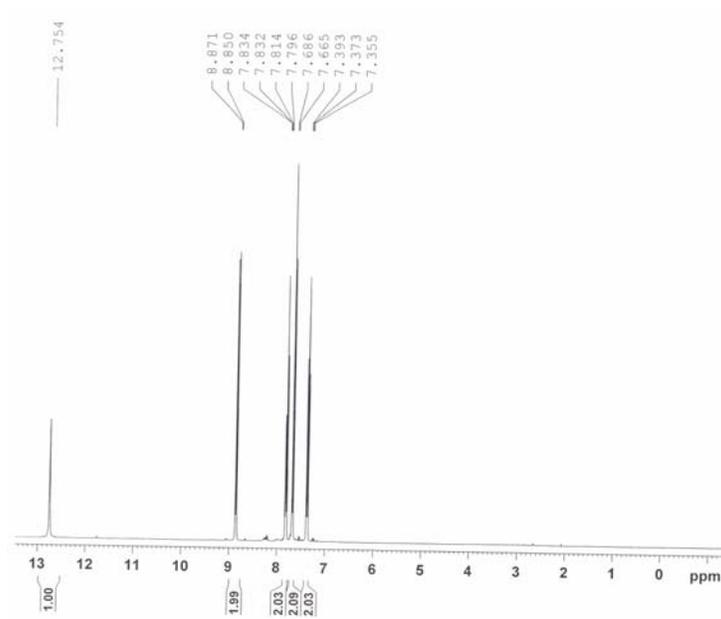
¹H NMR of Thiobenzophenone (12)



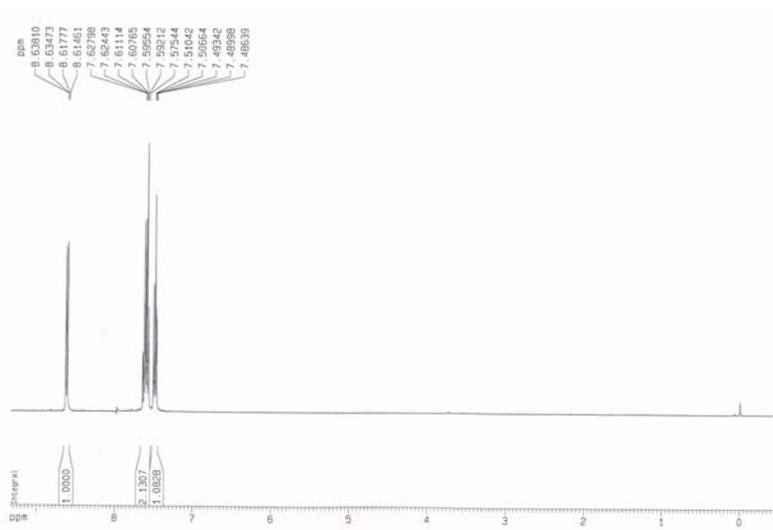
¹H NMR of 4,4'-Dimethoxythiobenzophenone (14)



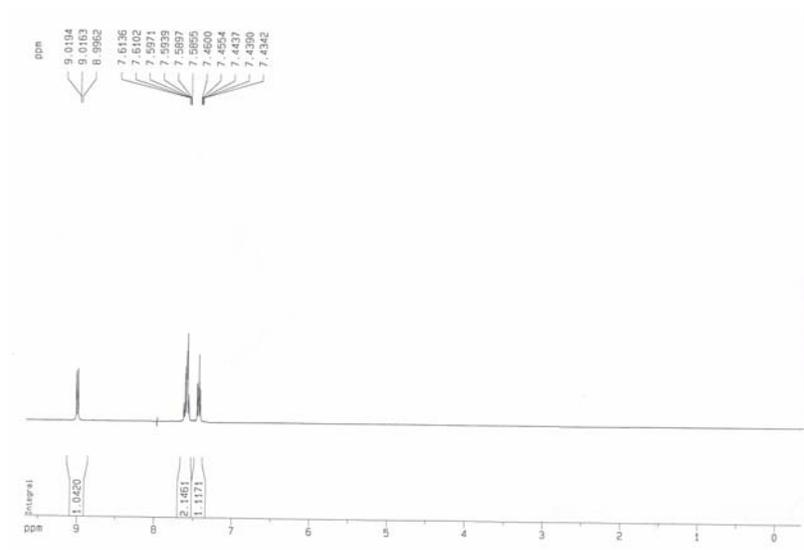
¹H NMR of 10H-Thioacridone (17)



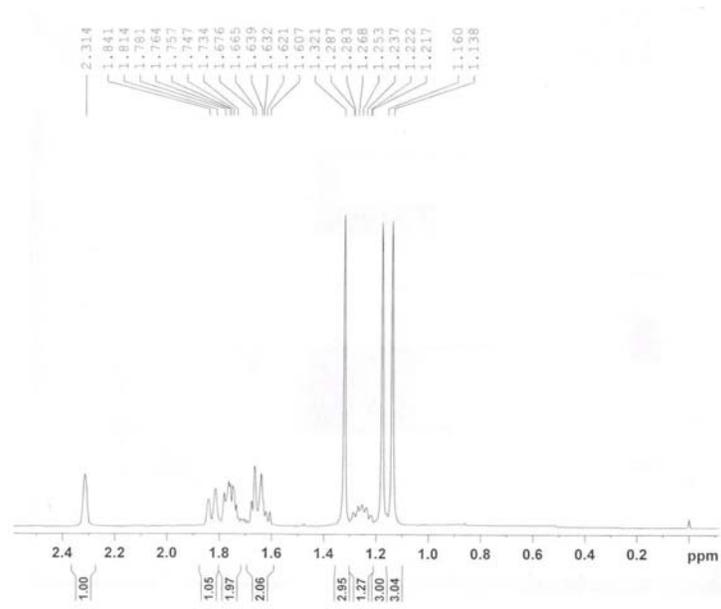
¹H NMR of Xanthene-9-thione (18)



¹H NMR of Thioxanthene-9-thione (19)

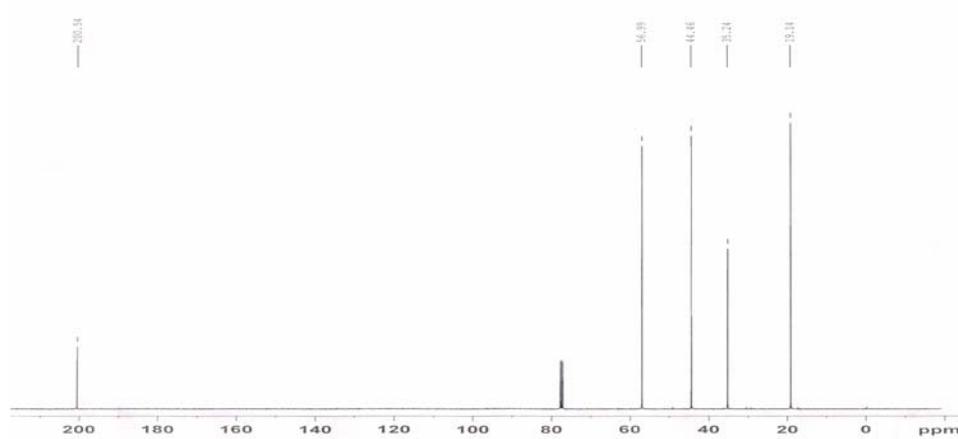


¹H NMR of (+)-1, 3, 3-Trimethyl-bicyclo [2.2.1] heptane-2-thione (20)

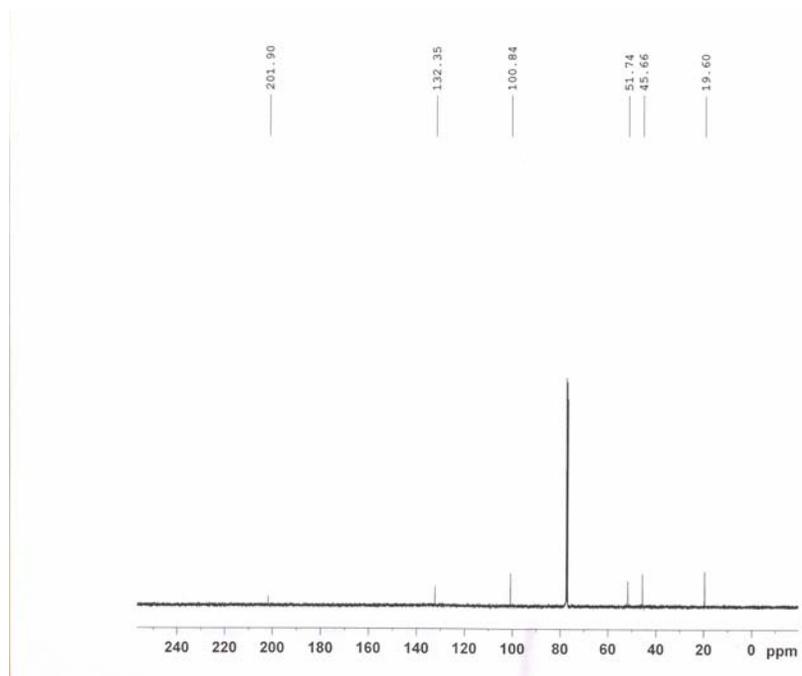


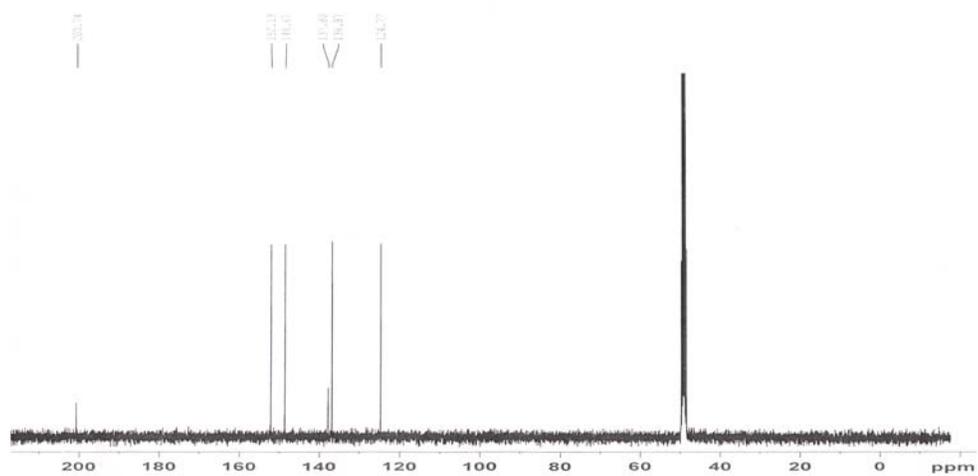
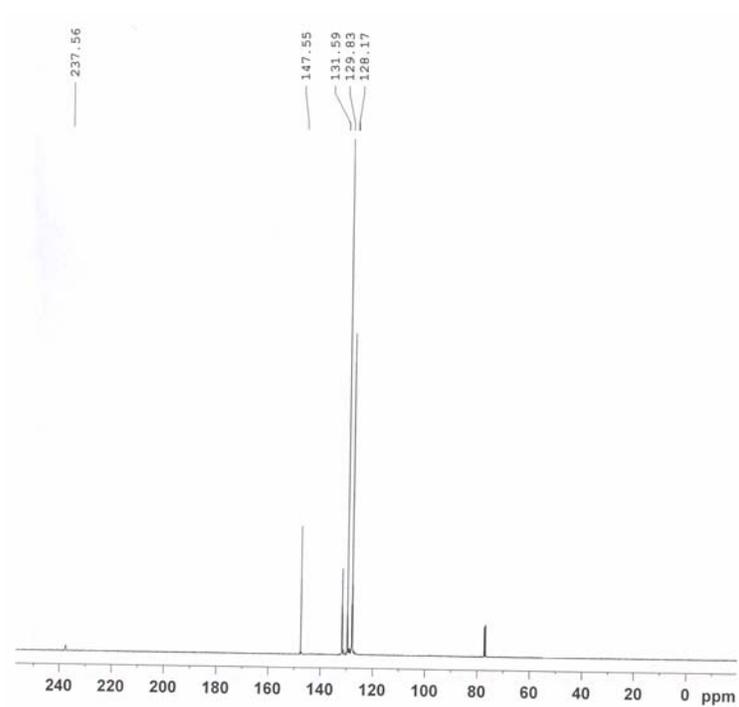
^{13}C NMR of compound 1-Methyl-pyrrolidine-2-thione (7)

S24



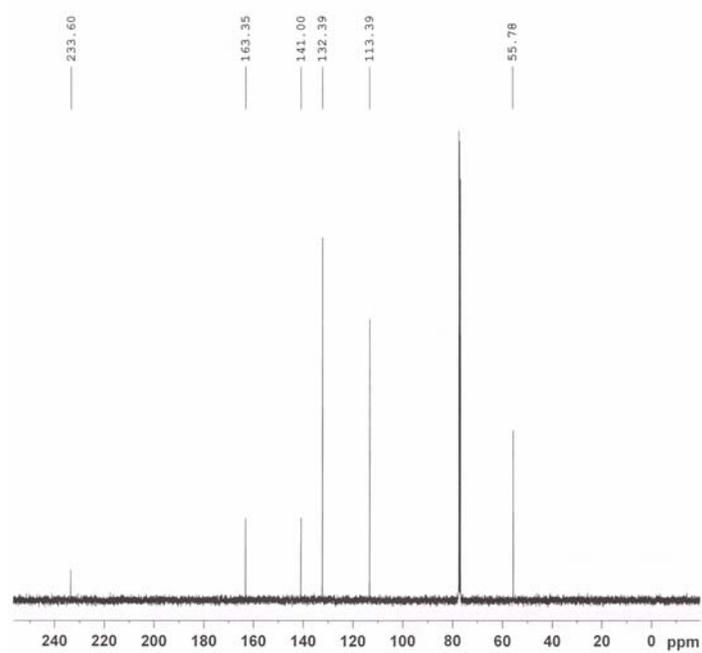
^{13}C NMR of compound 1-Vinyl- pyrrolidine-2-thione (10)



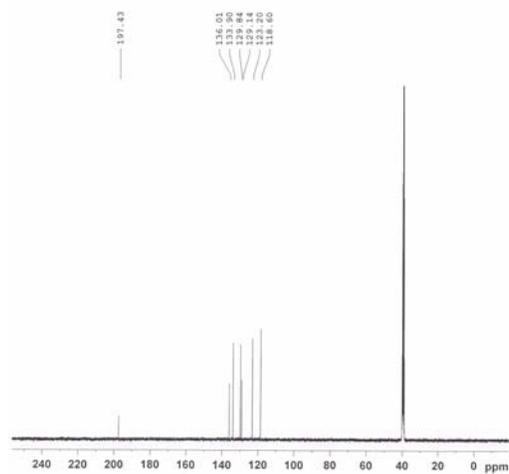
^{13}C NMR of compound Thionicotinamide (11) **^{13}C NMR of compound Thiobenzophenone (12)**

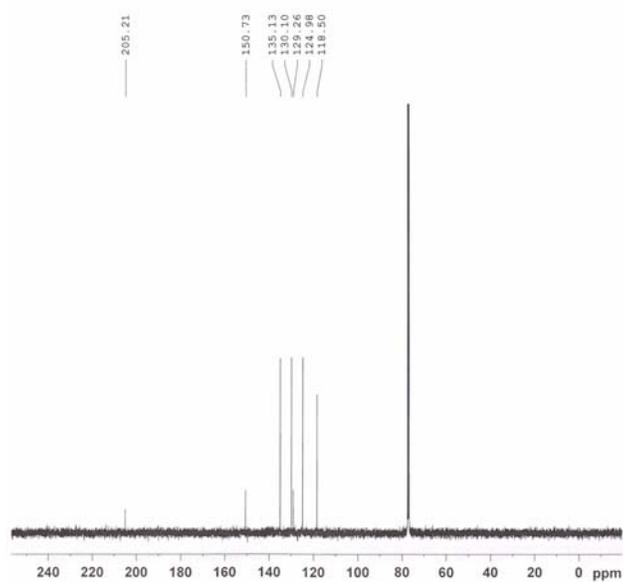
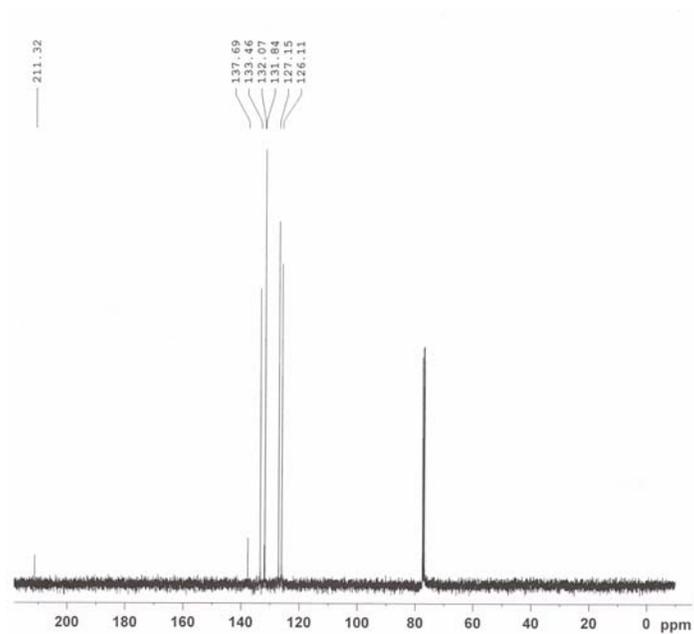
^{13}C NMR of compound 4, 4'-Dimethoxythiobenzophenone (14)

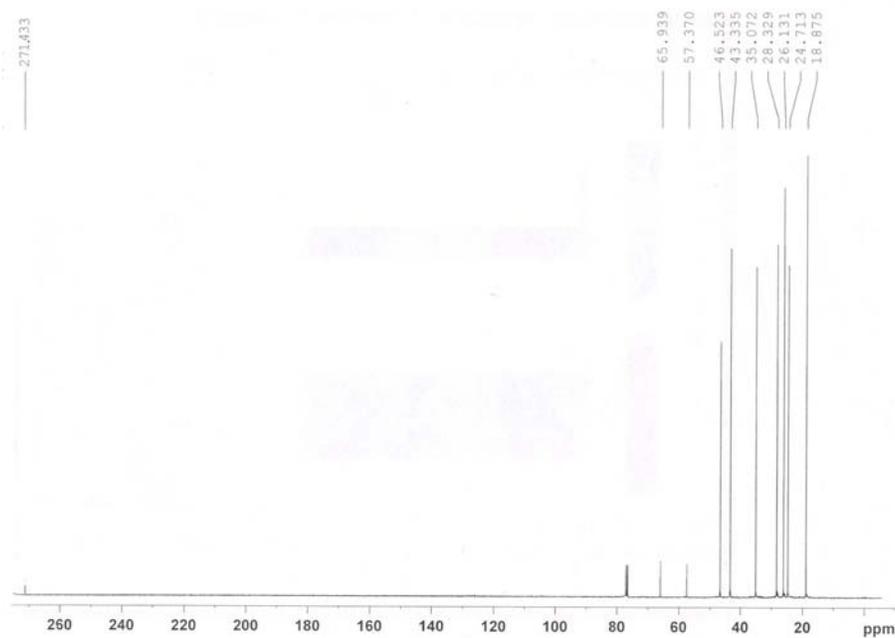
S26



^{13}C NMR of compound 10H-Thioacridone (17)



^{13}C NMR of compound Xanthene-9-thione (18) **^{13}C NMR of compound Thioxanthene-9-thione (19)**

^{13}C NMR of (+)-1, 3, 3-Trimethyl-bicyclo [2.2.1] heptane-2-thione (20) **^{13}C NMR of (-)-1, 7, 7-Trimethyl-bicyclo [2.2.1] heptane-2-thione (21)**