Supporting Information

An easy access to thiazolines and thiazines *via* tandem *S*-alkylation-cyclodeamination of thioamides/haloamines

Uma Pathak,* Shubhankar Bhattacharyya, Vishwanath Dhruwansh, Lokesh Kumar Pandey, Rekha Tank and M. V. S. Suryanarayana

Synthetic Chemistry Division, Defence R & D Establishment, Jhansi Road, Gwalior-474002 (M. P.) India.

Contents

1. General details

Reagents were obtained from commercial supplier, and used without further purification. Thioamide for Entry No. 4–12, 14 were prepared by thionation of corresponding amide by reported method.[1] Melting point were measured by scientific-MP-DS melting point apparatus. Column chromatographic purification of products was performed on silica gel (60-120 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE II 400 MHz. Chemical shifts were expressed in parts per millions (**δ)** downfield from the internal standard tetramethylsilane and were reported as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Mass spectra was obtained in Agilent 5975C GC-MS and Elemental analysis was performed on Elementar vario MICRO cube CHNS analyser.

1- U. Pathak, L. K. Pandey and R. Tank, *J. Org. Chem.*, 2008, 73, 2890.

2. Experimental procedure

(1) General experimental procedure- 250 µl of water was added to 2/3-haloalkylamine salt (5.5 mmol) and mixed thoroughly. To this thioamide (5 mmol) was added and the reaction mixture was heated at 60-70 °C till the reaction is complete. Contents were cooled and neutralized with cold 5% sodium carbonate solution. Yellow oil gets separated which was extracted with ethyl acetate. Solvent removal under vacuum yielded the pure thazoline/thiazine. If required the compound can be further purified by column chromatography.

(2) Procedure for the preparation of 2-substituted thiazolines and thiazines from electronically deficient thioamides. Water (10-20µl per mmol) was added to an equimolar mixture of thioamide and and 2/3-haloalkylamine salt, and mixed thoroughly. Contents were then heated on an oil bath at 90-100°C with constant stirring till the reaction is complete. On completion of the reaction product isolation and purification is done similar to the general experimental procedure.

3. Spectroscopic characterization data

2-Phenyl-5, 6-dihydro-4H-[1, 3]-thiazine (2): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.75 (m, 2H), 7.42-7.34 (m, 3H), 3.91 (t, 2H, J_1=5.6 Hz, J_2=5.2 Hz), 3.15 (t, 3H, J=6.0 Hz), 1.93-1.89 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 158.00, 139.48, 130.19, 128.19, 126.17, 47.93, 26.45, 19.05; EIMS: m/z 177 [M^+], 130, 121 104, 74; Anal. Calcd for $C_{10}H_{11}NS$. C, 67.75; H, 6.25; N, 7.90; S, 18.09. Found C, 67.87; H, 6.31; N, 7.94; S, 17.86.

2-(4-Tolyl)-4, 5-dihydro-[1, 3]-thiazole (4): Yellow solid (m.p: 41-42°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, 2H, J=8.0 Hz), 7.17 (d, 2H, J=8.0 Hz), 4.41 (t, 2H, J=8.4 Hz), 3.36 (t, 2H, J=8.4 Hz), 2.35 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 168.81, 141.66, 130.43, 129.23, 128.37, 64.95, 33.56, 21.53; EIMS: m/z 177 [M^+], 118, 60; Anal. Calcd for $C_{10}H_{11}NS$. C, 67.75; H, 6.25; N, 7.90; S, 18.09. Found C, 67.86; H, 6.37; N, 7.72; S, 18.03.

2-(4-Methoxy-phenyl)-4, 5-dihydro- [1, 3]-thiazole (5): Pale yellow solid (m.p.: 43-44 °C)**;** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, 2H, J_1=6.8 Hz, J_2=2.0 Hz), 6.91 (dd, 2H, J_1=6.8 Hz, J_2=2.0 Hz), 4.42 (t, 2H, J=8.4), 3.84 (s, 3H), 3.39 (t, 2H, J_1=8.0, J_2=8.4); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 167.99, 161.94, 130.05, 125.77, 113.74, 64.78, 55.30, 33.55; EIMS: m/z 193 [M^+], 147, 133, 103, 60; Anal. Calcd for $C_{10}H_{11}NOS$. C, 62.15; H, 5.74; N, 7.25; S, 16.59. Found C, 62.23; H, 5.80; N, 7.15; S, 16.54.

2-(4-Bromo-phenyl)-4, 5-dihydro-[1, 3]-thiazole (6): Colourless solid (m.p.: 90-92 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.68 (m, 2H), 7.56-7.52 (m, 2H), 4.45 (t, 2H, J=8.4 Hz), 3.43 (t, 2H, J=8.4 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 167.67, 131.85, 129.98, 125.83, 65.39, 34.09; EIMS: m/z 243 [M^++2], 241 [M^+], 102, 75, 60; Anal. Calcd for C_9H_8BrNS. C, 44.64; H, 3.33; N, 5.78; S, 13.24. Found C, 44.71; H, 3.41; N, 5.63; S, 13.23.

2-(4-Hydroxy-phenyl)-4, 5-dihydro-[1, 3]-thiazole (7): Light yellow solid (m.p.: 198-199 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.94 (s, 1H, OH), 7.64-7.58 (m, 2H), 6.85-6.80 (m, 2H), 4.30 (t, 2H, J=8.0 Hz), 3.36 (t, 2H, J=8.0 Hz); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 165.42, 160.16, 129.84, 124.06, 115.21, 64.54, 33.06.; EIMS: 179 [M^+], 119, 91, 60.; Anal calc. for C_9H_9NOS. C, 60.31; H, 5.06; N, 7.81; S, 17.89. Found C, 60.43; H, 4.96; N, 7.75; S, 17.91.

2-(3-Nitro-phenyl)-4, 5-dihydro-[1, 3]-thiazole (8): Yellow solid (m.p.: 135-137 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 8.31 (d, 1H, J=6.8 Hz), 8.15 (d, 1H, J=7.2 Hz), 7.60 (t, 1H, J=8.0 Hz), 4.51 (t, 2H, J=8.4 Hz), 3.50 (t, 2H, J=8.4 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 166.36, 148.24, 134.84, 134.03, 129.59, 125.55, 123.27, 65.37, 34.30; EIMS: m/z 208 [M^+], 178, 118, 60; Anal. Calcd for $C_9H_8N_2O_2S$, C, 51.91; H, 3.87; N, 13.45; S, 15.40. Found C, 51.98; H, 3.98; N, 13.58; S, 15.07.

2-(4-Nitro-phenyl)-4, 5-dihydro-[1, 3]-thiazole (9): Yellow solid (m.p.: 150-152 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (dd, 2H, J_1=7.2 Hz, J_2=1.6 Hz), 8.00-7.98 (m, 2H), 4.51 (t, 2H, J=8.4 Hz), 3.50 (t, 2H, J=8.4 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 166.61, 149.22, 138.72, 129.27, 123.71, 65.54, 34.28; EIMS: m/z 208 [M^+],

178, 118, 60; Anal. Calcd for $C_9H_8N_2O_2S$. C, 51.91; H, 3.87; N, 13.45; S, 15.40. Found C, 51.96; H, 3.97; N, 13.35; S, 15.34.

2-(2, 6-Dichloro-phenyl)-4, 5-dihydro-[1, 3]-thiazole (10): Yellow solid (m.p.: 71-72 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.16 (m, 3H), 4.42 (d, 2H, *J*=8 Hz), 3.48 (d, 2H, *J*=8 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 163.65, 133.49, 132.40, 130.56, 127.80, 64.86, 34.97; EIMS: 231 [M^+], 185, 171, 150, 136, 123, 109, 100, 75, 60.; Anal calc. for $C_9H_7Cl_2NS$. C, 46.57; H, 3.04; N, 6.03; S, 13.81. Found C, 46.68; H, 2.91; N, 5.93; S, 13.91.

2-Thiophen-3-yl-4, 5-dihydro-[1, 3]-thiazole (11): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.41(m, 2H), 7.07-7.05 (m, 1H), 4.40 (t, 2H, *J*=8.4 Hz), 3.44 (t, 2H, *J*=8.0 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 161.61, 137.04, 130.75, 129.66, 127.54, 64.70, 34.44; EIMS: m/z 169 [M^+], 123, 108, 60; Anal. Calcd for $C_7H_7NS_2$, C, 49.67; H, 4.17; N, 8.27; S, 37.89. Found C, 49.81; H, 4.67; N, 8.34; S, 37.16

2-Thiophen-3-yl-5,6-dihydro-4H-[1, 3]-thiazine (12): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, 1H, *J*=3.6 Hz), 7.35 (d, 1H, *J*=5.2 Hz), 7.02-7.00 (m, 1H), 3.86 (t, 2H, *J*=5.6 Hz), 3.14 (t, 2H, *J*=6.0 Hz), 1.95-1.89 (m, 2H), ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 152.01, 144.30, 128.00, 127.12, 126.12, 47.69, 26.36, 19.61; EIMS: m/z 183 [M^+], 136, 127, 110, 74; Anal. Calcd for $C_8H_9NS_2$, C, 52.42; H, 4.95; N, 7.64; S, 34.99. Found C, 52.54; H, 5.07; N, 7.77; S, 34.61

3-(4, 5-Dihydrothiazol-2-yl)-pyridine (13) : Yellow solid (m.p.: 111-113 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.04 (s, 1H), 8.68 (d, 1H, *J*=4.4 Hz), 8.13 (dt, 1H, J_1=8.0 Hz, J_2=1.6 Hz), 7.38 (dd, 1H, J_1=8.0 Hz, J_2=4.8 Hz), 4.48 (t, 2H, *J*=8.4 Hz), 3.46 (t, 2H, *J*=8.4 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 165.67, 151.30, 148.87, 135.96, 129.24, 123.57, 65.11, 33.91; EIMS: m/z 164 [M^+], 118, 105, 60; Anal. Calcd for $C_8H_8N_2S$, C, 58.51; H, 4.91; N, 17.06; S, 19.53. Found C, 58.59; H, 4.95; N, 17.09; S, 19.36.

2-Cyclohexyl-5, 6-dihydro-4H-[1, 3]-thiazine (14): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.64 (t, 2H, *J*=4.0 Hz), 3.00 (t, 2H, *J*=8.0 Hz), 2.17-2.09 (m, 1H), 1.88-1.80 (m, 2H), 1.79-1.76 (m, 4H), 1.47-1.33 (m, 2H), 1.31-1.21 (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 165.74, 50.49, 47.23, 31.20, 26.33, 26.23, 25.92, 19.45; EIMS: 183 [M^+], 155, 142, 128, 115, 100, 83, 74, 55.; Anal calc. for $C_{10}H_{17}NS$. C, 65.52; H, 9.35; N, 7.64; S, 17.49. Found C, 65.63; H, 9.26; N, 7.55; S, 17.54.

2-amino-4, 5-dihydro-[1, 3]-thiazole (15): Yellow solid (m.p.: 80-82 ^{o}C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.22 (s, br, 2H, NH_2), 3.77 (t, 2H, *J*=7.6 Hz), 3.21 (t, 2H, *J*=7.6 Hz); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 159.84, 60.07, 35.04. EIMS: 102 [M^+], 74, 60. Anal calc. for $C_3H_6N_2S$. C, 35.27; H, 5.92; N, 27.42; S, 31.39. Found C, 35.35; H, 5.80; N, 27.51; S, 31.32.

4. Selected copies of ^{1}H NMR and ^{13}C NMR

(i) **^{1}H NMR spectra of 2-Thiophen-3-yl-4, 5-dihydro-[1, 3]-thiazole (11)**

(ii) **^{13}C NMR spectra of 2-Thiophen-3-yl-4, 5-dihydro-[1, 3]-thiazole (11)**

(iii) **Mass spectra of 2-Thiophen-3-yl-4, 5-dihydro-[1, 3]-thiazole (11)**

(iv) **^{1}H NMR spectra of 2-Thiophen-3-yl-5, 6-dihydro-4H-[1, 3]-thiazine (12)**

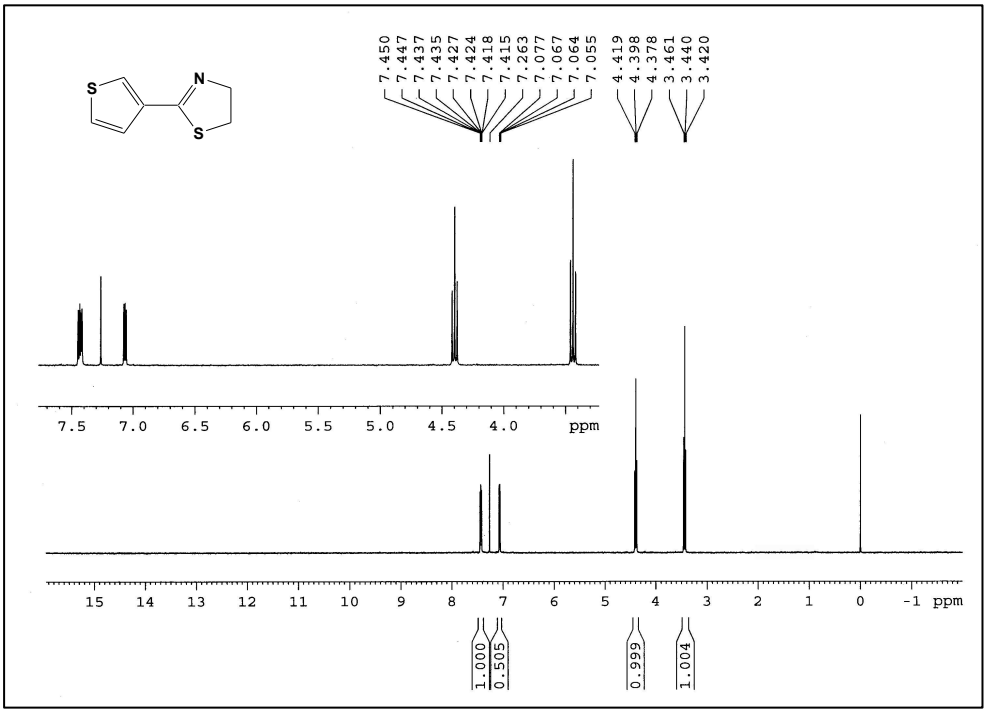
(v) **^{13}C NMR spectra of 2-Thiophen-3-yl-5, 6-dihydro-4H-[1, 3]-thiazine (12)**

(vi) **Mass spectra of 2-Thiophen-3-yl-5, 6-dihydro-4H-[1, 3]-thiazine (12)**

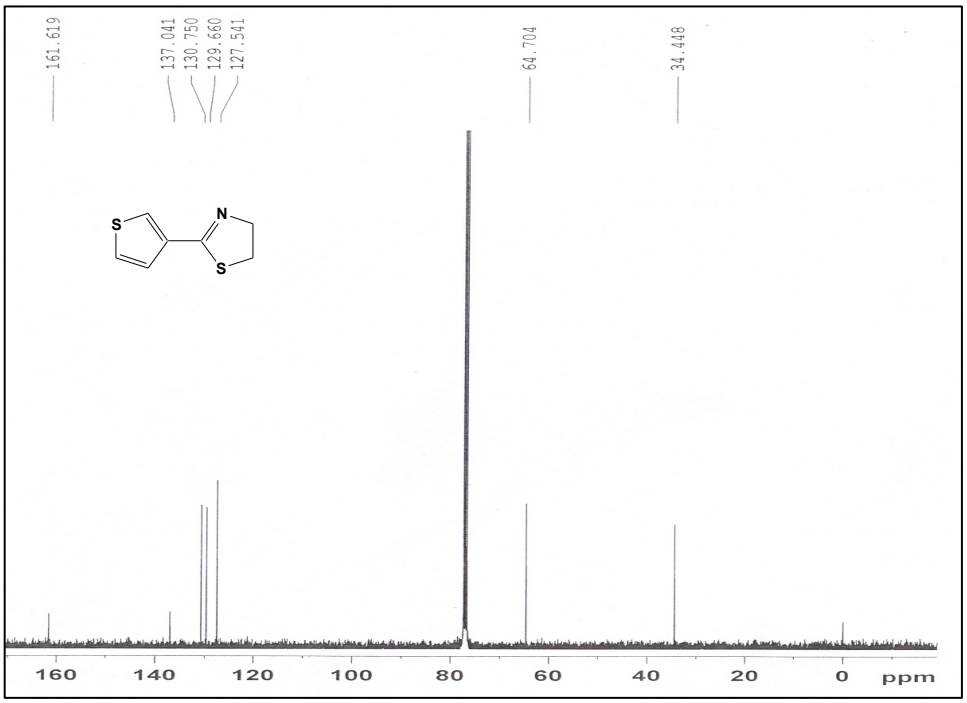
(vii) **^{1}H NMR spectra of 2-Cyclohexyl-5, 6-dihydro-4H-[1, 3]-thiazine (14)**

(viii) **^{13}C NMR spectra of 2-Cyclohexyl-5, 6-dihydro-4H-[1, 3]-thiazine (14)**

(ix) **Mass spectra of 2-Cyclohexyl-5, 6-dihydro-4H-[1, 3]-thiazine (14)**



^{1}H NMR spectra of 2-Thiophen-3-yl-4, 5-dihydro-[1, 3]-thiazole (11)



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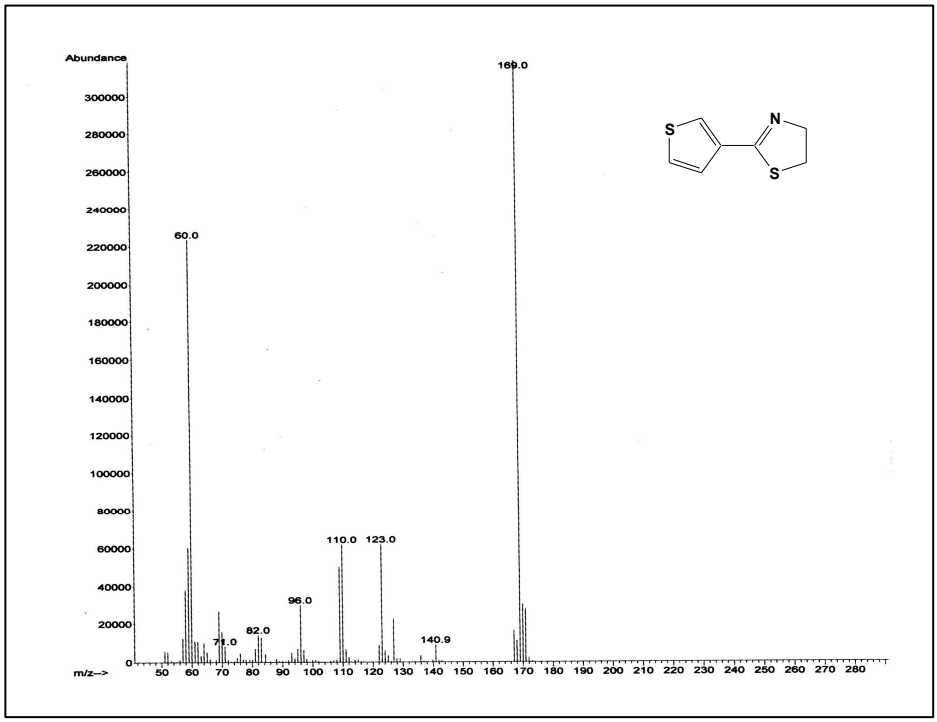

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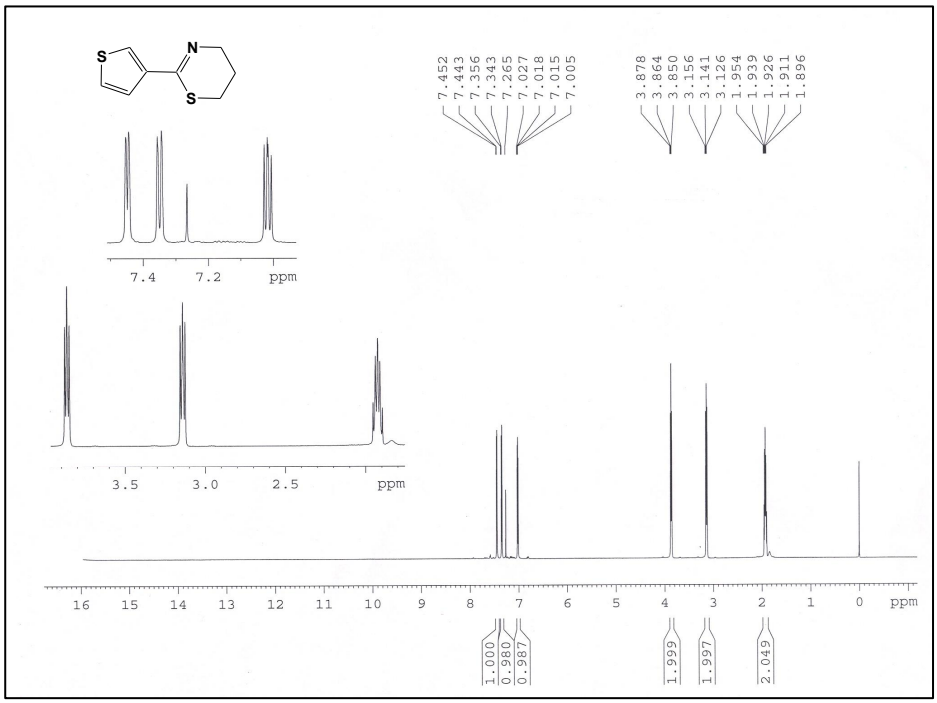

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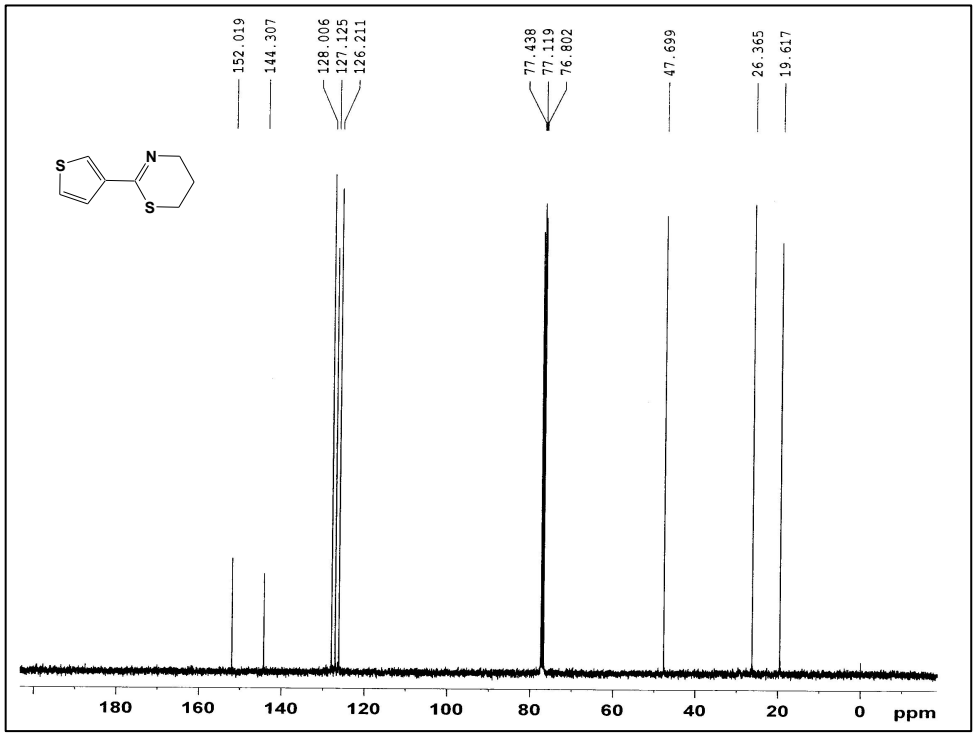

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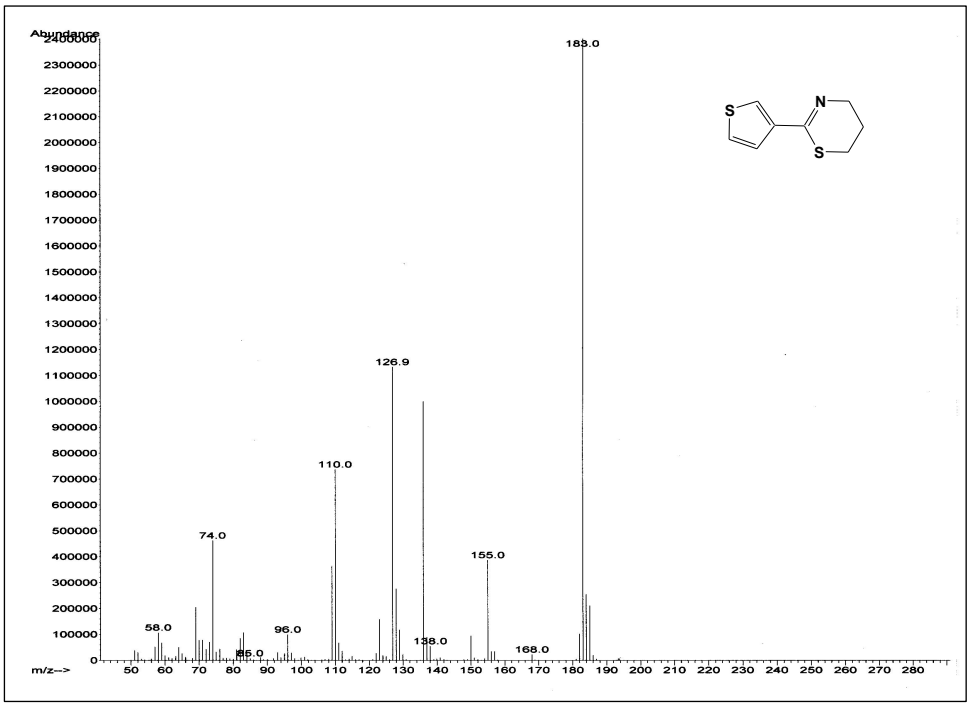

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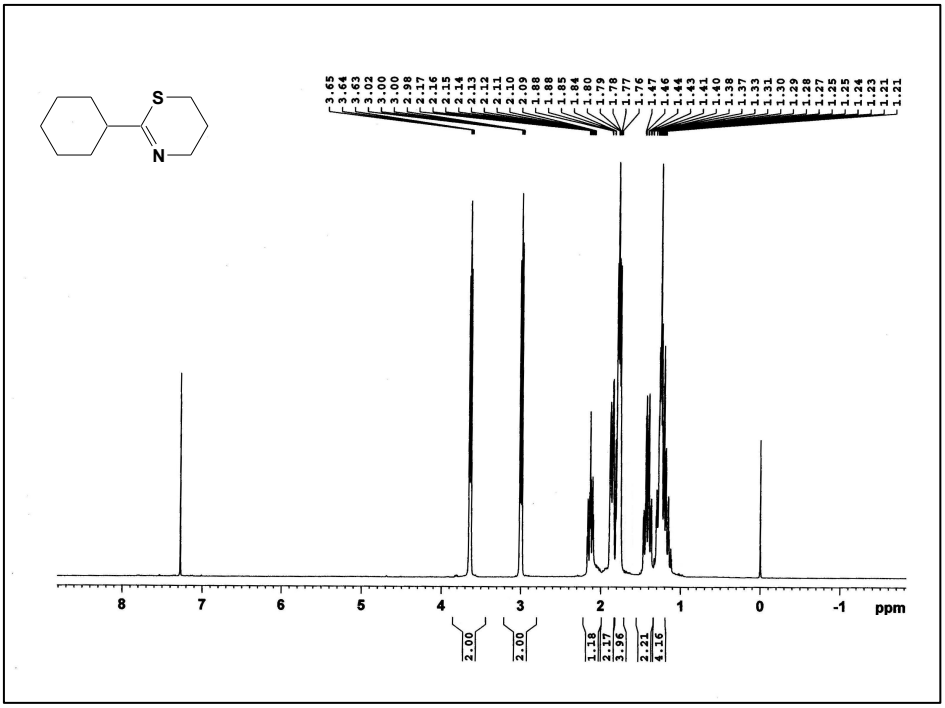

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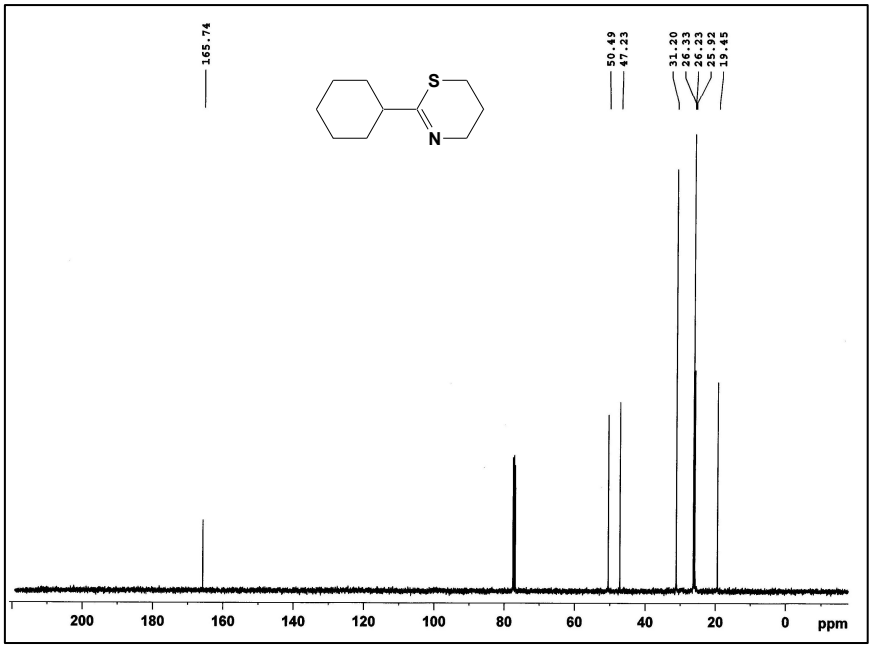

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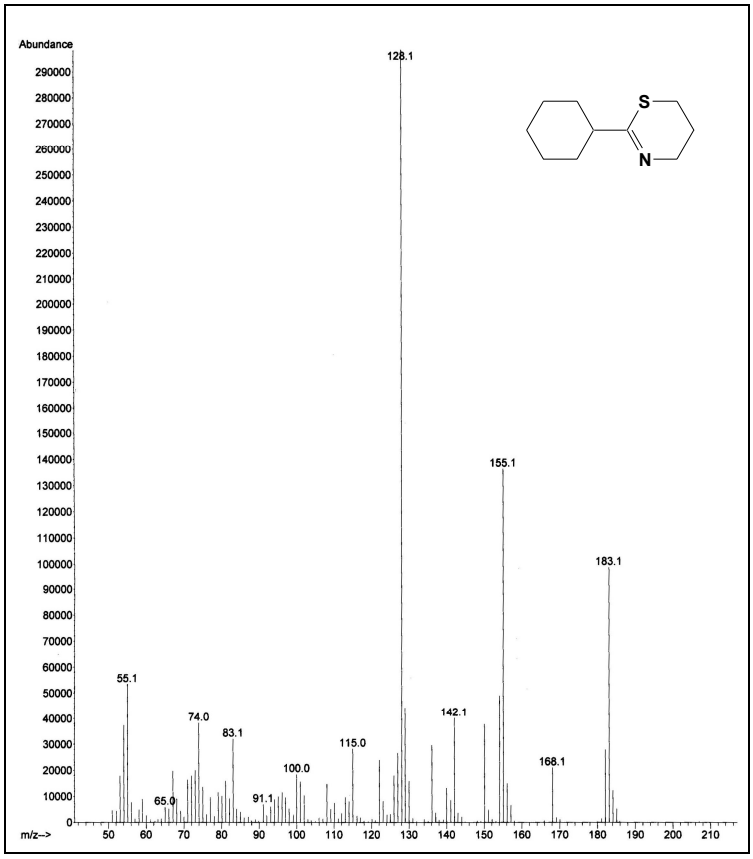

Mass spectra of 2-Cyclohexyl-5, 6-dihydro-4H-[1, 3]-thiazine (14)