Supporting information

Chemospecific and Ligand Free CuI Catalysed Heterogeneous N-Arylation of amines with diheteroaryl halides at Room Temperature.

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Contents

General information:

All the starting materials were obtained from commercial supplies and used as received. Ethanol and chloroform was distilled before use and used as such. Triple distilled water was used for the reaction. The reactions were performed in air atmosphere without any specific precautions. Column chromatography was performed with silica gel 200-400 mesh using chloroform and methanol as eluents. All the products of **table** 2 and 3 are known compounds[1-11].

Synthesis of Benzothiazol-2-yl-diethyl-amine (General Procedure 1).

In a round bottom flask 0.95 gm (0.013 mol) of diethyl amine and 0.19gm (0.001 mol) of CuI was stirred for half hour. A blue colour solution was formed. To this add 0.56 gm (0.01mol) of KOH dissolved in minimum 5ml of water. Stirred it for anotherr half hour. Orange coloured precipitate was formed. After stirring for another 30 min, 0.274 gm (0.001 mol) of tributylbenzyl ammonium choride was added followed by the addition of 1.69 gm (0.01 mol) diheteroaryl halide in 45ml chloroform. The reaction mixture was stirred for 6h at room temperature. The progress of reaction was monitored by the consumption of aryl halide. The organic layer was collected and the aqueous layer was washed with chloroform (3 x 25ml). The combined organic layer is dried over anhydrous Na_2SO_4 and solvent was evaporated at reduced pressure. Products were purified either by crystallizing or by flash chromatography.

2-Piperazin-1-yl-benzothiazole (General Procedure 2)

In a round bottom flask 1.12 gm (0.013 mol) of piperazine and 0.19gm (0.001 mole) CuI in water (5ml) was stirred for 30 min. 0.56 gm (0.01mol) of KOH was added in it and stirred for another 30 min. After stirring 0.274 gm (0.001 mol) of tributylbenzyl ammonium choride was added. The reaction mixture was stirred for 30 min and then 1.69 gm (0.01 mol) diheteroaryl halide in 45ml ethanol was added in reaction mixture. The reaction mixture was stirred for 6h at room temperature. The progress of reaction was monitored by the consumption of aryl halide. After completion of the reaction the ethanol was evaporated in vacuum and the aqueous layer was washed with chloroform (3 x

25ml). The combined organic layer is dried over anhydrous Na_2SO_4 and solvent was evaporated at reduced pressure. Products were purified either by crystallizing or by flash chromatography.

Benzothiazol-2-yl-dimethyl-amine[1,2]

White crystalline solid; mp 84-86 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 3.192 (s, 6H), 7.06 (t, 1H), 7.28 (t, 1H), 7.57 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.19, 118.80,120.6,120.9, 125.93, 131.51, 153.28, 168.79 HRMS (ESI, MeOH): *m*/*z* 179 $[M+H]^+$;

Benzothiazol-2-yl-diethyl-amine[3]

Colourless liquid**;** ^1H NMR (400 MHz, $CDCl_3$): δ 1.275 (t, 6H), 3.57 (t, 4H), 7.01 (t, 1H), 7.25 (t, 1H), 7.57 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.89, 45.39, 118.53, 120.53, 125.81, 153.34, 167.34; HRMS (ESI, MeOH): *m*/*z* 206$[M+H]^+$;

2-Pyrrolidin-1-yl-benzothiazole[4,5]

White crystalline solid; mp 96-98 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 2.07 (p, 4H), 3.59 (t, 4H), 7.04 (t, 1H), 7.3 (t, 1H)7.5(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.02, 49.48, 118.70, 120.65, 125.90, 130.77, 152.2, 164.22 ; HRMS (ESI, MeOH): *m*/*z* 204. $[M+H]^+$;

2-Morpholin-4-yl-benzothiazole[6]

White crystalline solid; mp 118-120 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 3.63.(t, 4H), 3.85 (t, 4H), 7.12 (t, 1H), 7.31 (t, 1H), 7.61(t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.12, 66.26, 119.34, 120.79, 121.71, 126.12, 129.07, 129.33, 130.56, 150.12, 168.20; HRMS (ESI, MeOH): *m*/*z* 221 $[M+H]^+$;

2-Morpholin-6-chloro-4-yl-benzothiazole[6]

White crystalline solid; mp 110-112 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 3.61 (t 4), 3.84 (t, 4H), 7.27 (m, 1H), 7.45(d, 2H), 7.58(d, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$):δ 48.47,

66.19,119.95,120.46,126.58, 126.78, 131.77, 151.18, 169.04; HRMS (ESI, MeOH): *m*/*z* 255.5 $[M+H]^+$;

2-Morpholin-6-nitro-4-yl-benzothiazole[6]

Yellow Solid; mp decompose after 200°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (t 4), 3.88 (t, 4H), 7.50 (d, 1H), 8,2 (d,d, 1H), 8.54 (d, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$):δ 48.69, 65.90,118.30,118.69, 122.85, 131.279, 141.34, 158.34, 172.91; HRMS (ESI, MeOH): *m*/*z* 265 $[M+H]^+$.

2-Morpholin-4-yl-1H-benzoimidazole[6]

White crystalline solid; mp 117-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.17 s, 1H, NH), 3.61 (t, 4H), 3.84 (t, 4H), 7.25 (m, 2H), 7.45(d, 1H) 7.58(d, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.75, 119.00, 124.31, 129.82, 139.62, 155.31, 170.12; HRMS (ESI, MeOH): *m*/*z* 204 $[M+H]^+$.

4-Thiazol-2-yl-morpholine[6]

Pale yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.46 (t 4), 3.83 (t, 4H), 6.61 (d, 1H), 7.22 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 48.73, 66.16, 107.72, 139.41; HRMS (ESI, MeOH): *m*/*z* 171 $[M+H]^+$.

Benzothiazol-2-yl-benzyl-amine[7]

White crystalline solid; mp 176-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 4.79(s, 2H), 7.08(t, 1H), 7.28-7.42 (m, 6H), 7.55 (m, 2H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.34, 25.44, 30.88, 47.20, 50.94, 155.90, 171.01; HRMS(ESI, MeOH): m/z calcd. 241$[M+H]^+$.

(4-Amino-benzyl)-benzothiazol-2-yl-amine[7]

White crystalline solid; mp decompose after 230 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.37 (d, 2H, NH_2), 5.0 (s, 2H), 6.52 (d, 2H) 7.03(d, 2H), 7.2(t, 1H), 7.4(d, 1H) 7.6(d, 1H), 8.3(t, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ; HRMS (ESI, MeOH): *m*/*z* 256 $[M+H]^+$.

2-Piperazin-1-yl-benzothiazole[9-11]

White crystalline solid; mp 54 ^{o}C, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68 (S, 1H, NH), 2.1 (p, 4H), 3.6 (t, 4H), 7.02 (t, 3H), 7.28 (t, 3H), 7.57(d-d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.65, 49.66, 119.22, 120.81, 121.51, 126.12, 130.74, 152.86, 169.21; HRMS (ESI, MeOH): m/z. 220 $[M+H]^+$.

6-Chloro-2-piperazin-1-yl-benzothiazole[9,10]

White crystalline solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (s, 1H, NH), 3.0 (t, 4H), 3.59 (t, 4H), 7.2 (d-d, 1H), 7.4(d, 1H), 7.56(d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 38.99, 45.49, 119.70, 120.36, 126.43, 126.44, 131.81, 151.40, 169.12; HRMS(ESI, MeOH): m/z 254 [M +H]+;

1-Thiazol-2-yl-piperazine [9]

Colourless Liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97(s, 1H, NH), 2.9 (t, 4H), 3.45 (t, 4H), 6.58 (d 1H), 7.19 (d, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.01, 47.22, 108.12, 141,02, 174 HRMS(ESI, MeOH): m/z 170 $[M+H]^+$.

2-Piperazin-1-yl-1H-benzoimidazole[12, 13.]

White crystalline solid; ^{1}H NMR (400 MHz, DMSO-d6): δ 2.4-3.1 (b, 8H), 6.9 (m, 2H), 7.16 (m 2H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.34, 25.44, 30.88, 47.20, 50.94, 155.90, 171.01; HRMS(ESI, MeOH): m/z 203 $[M+H]^+$.

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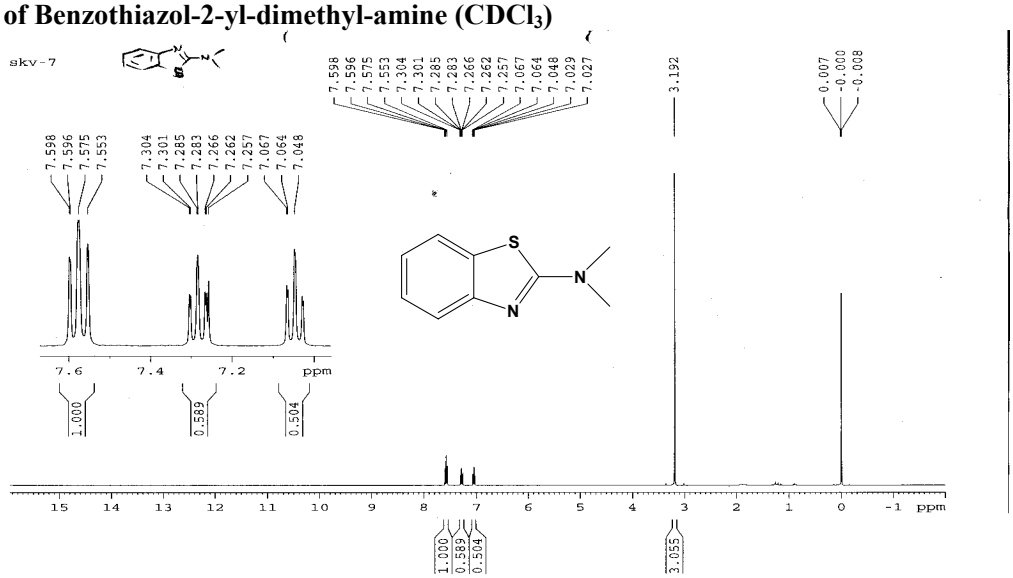
^{1}H NMR of Benzothiazol-2-yl-dimethyl-amine ($CDCl_3$)



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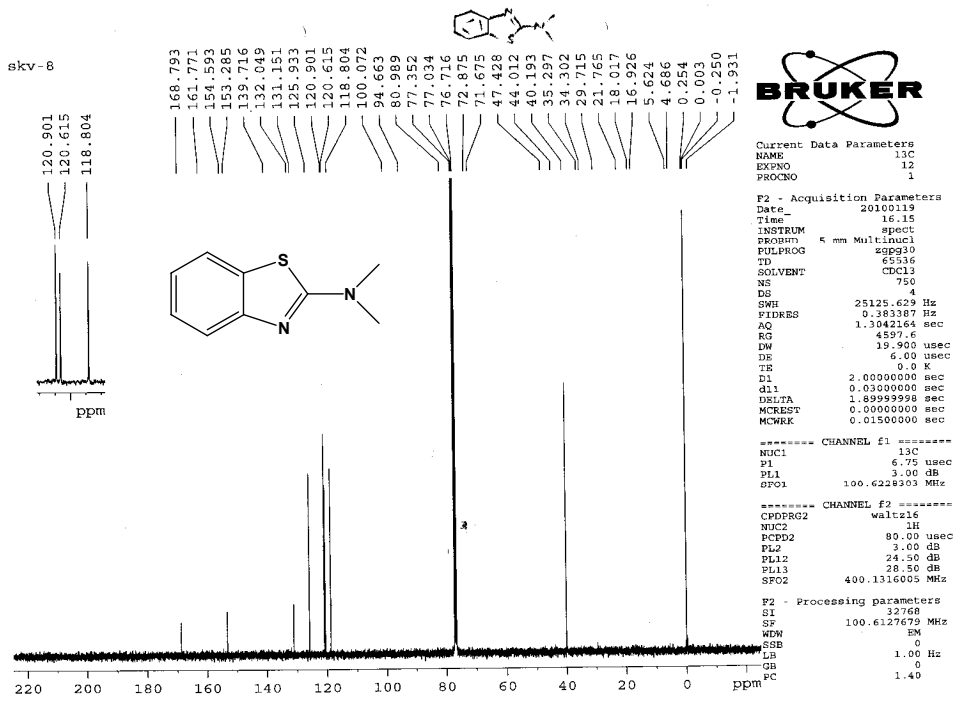

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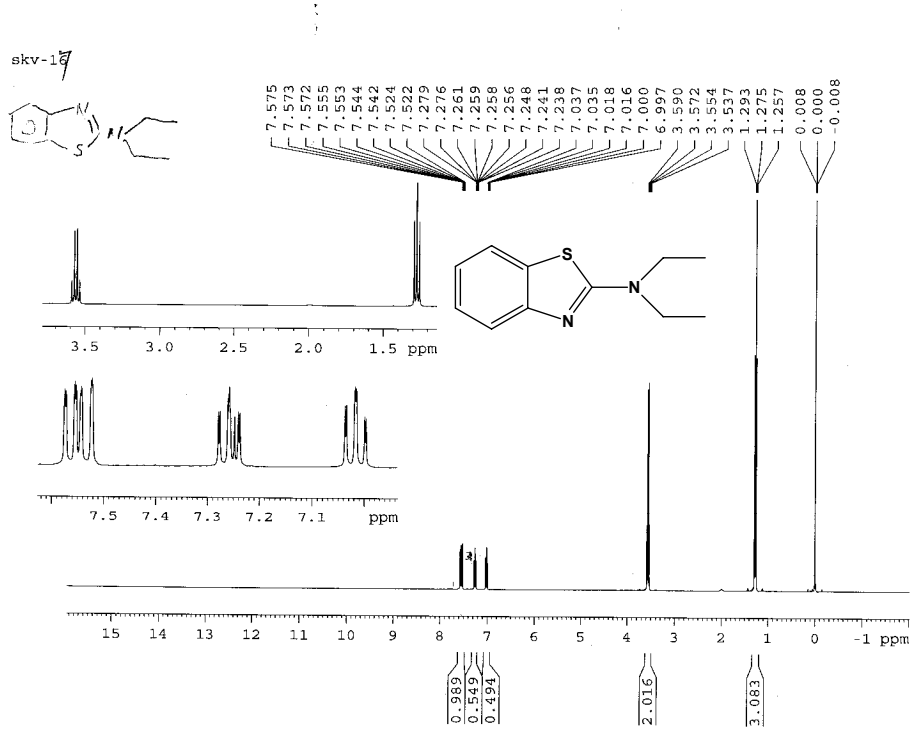

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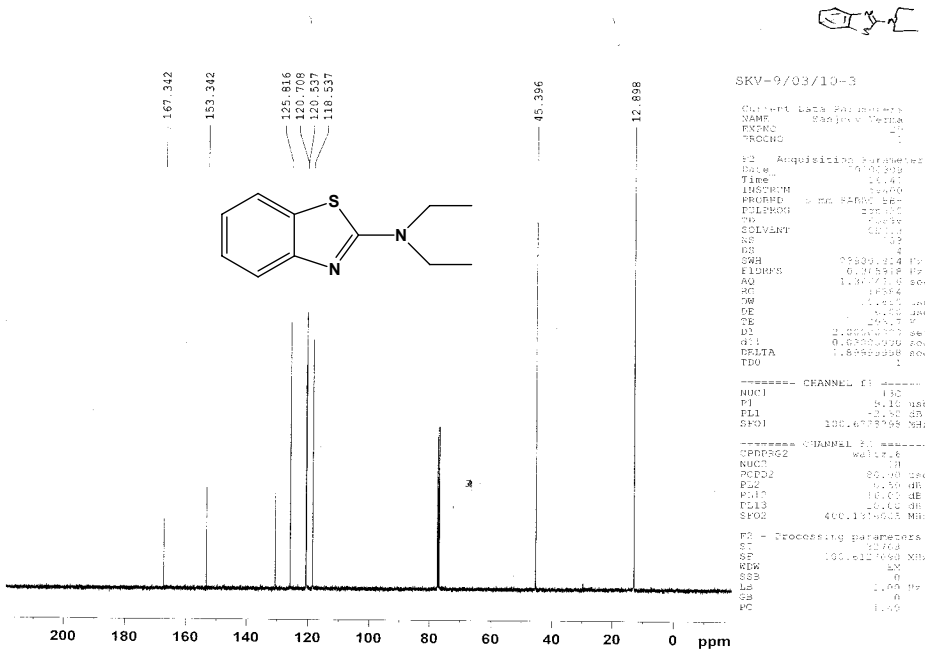

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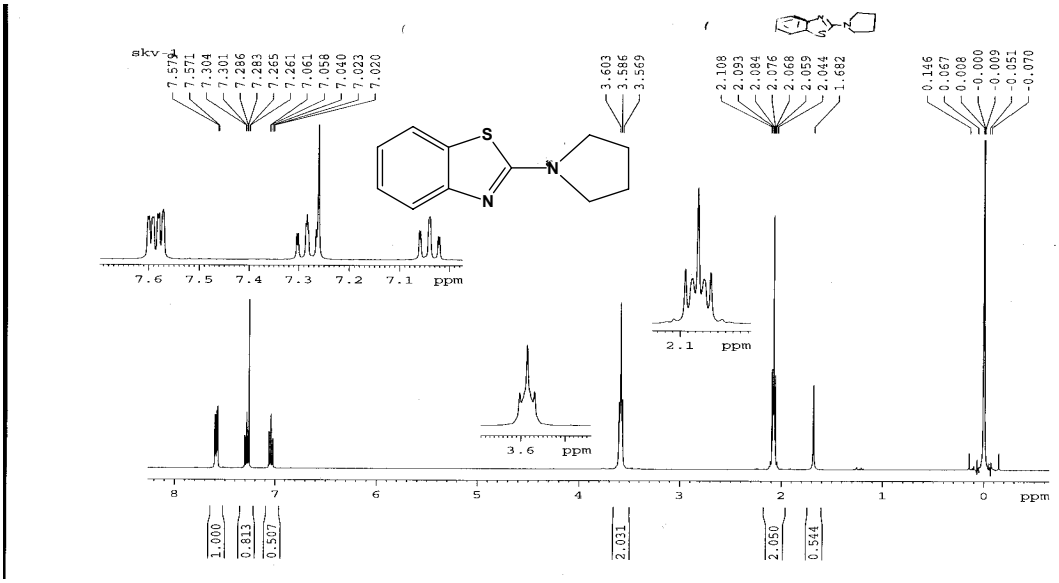

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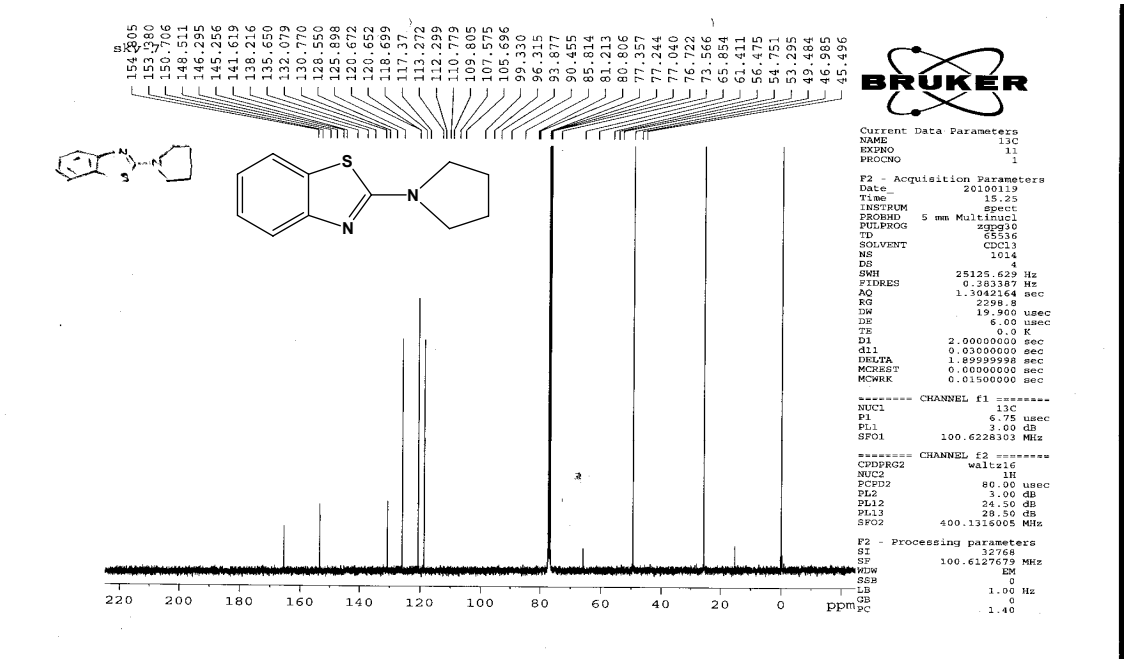

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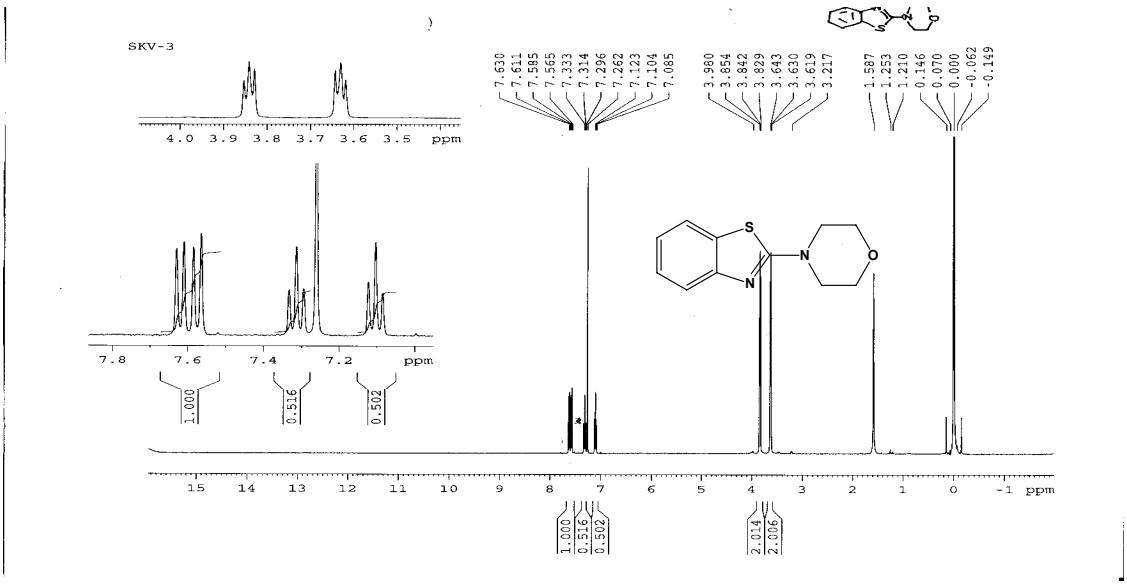

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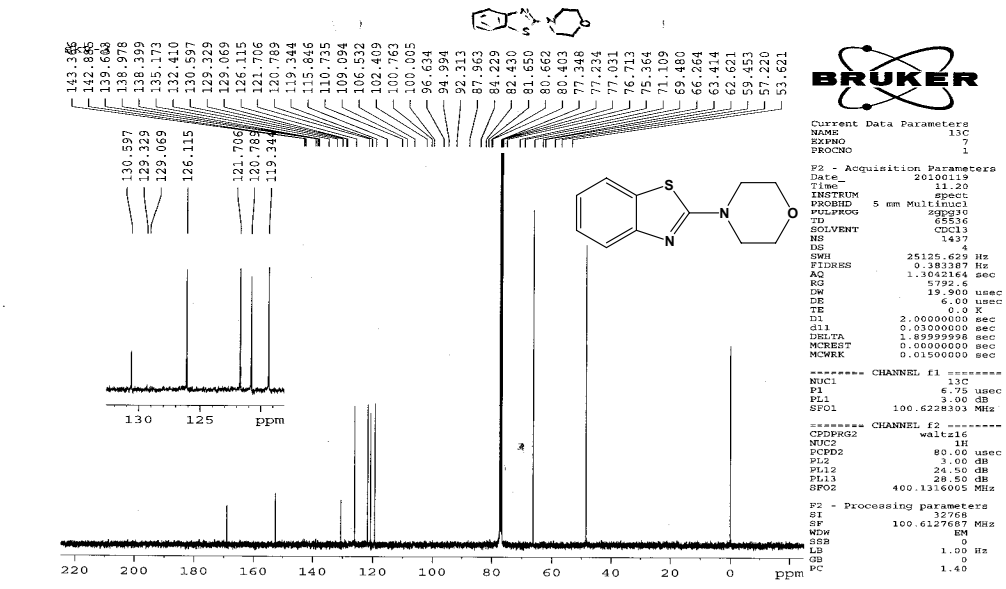

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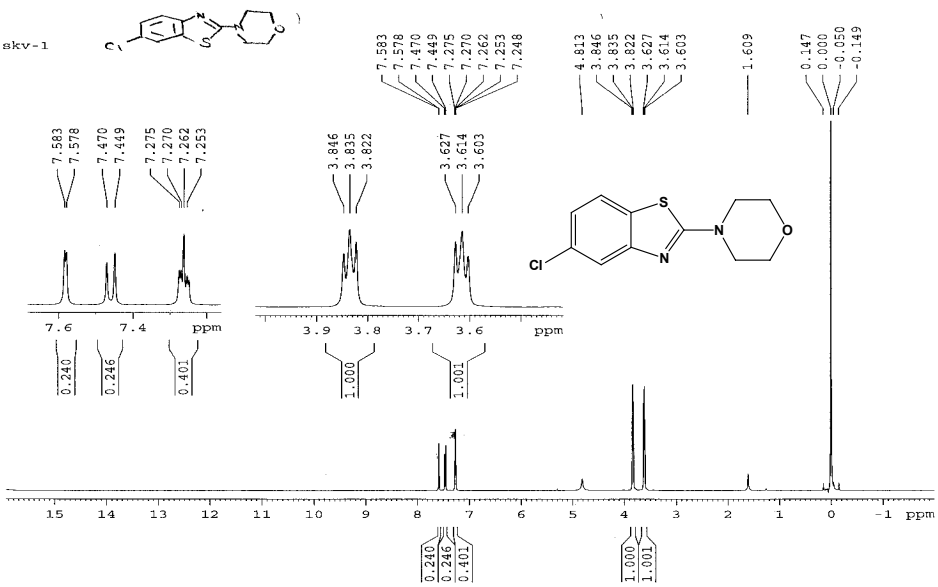

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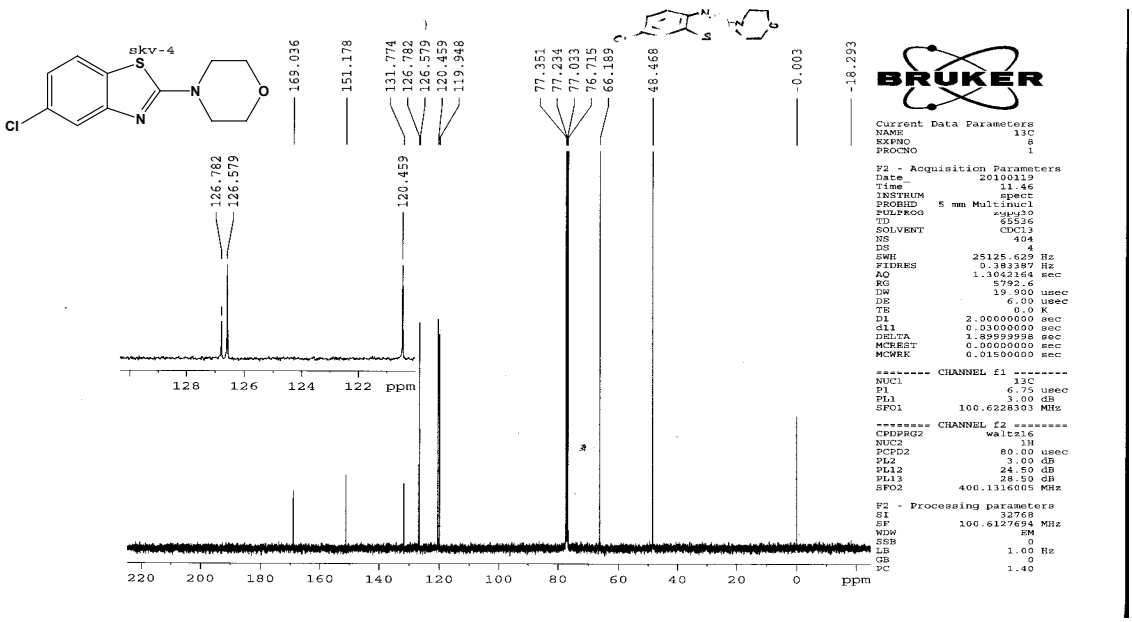

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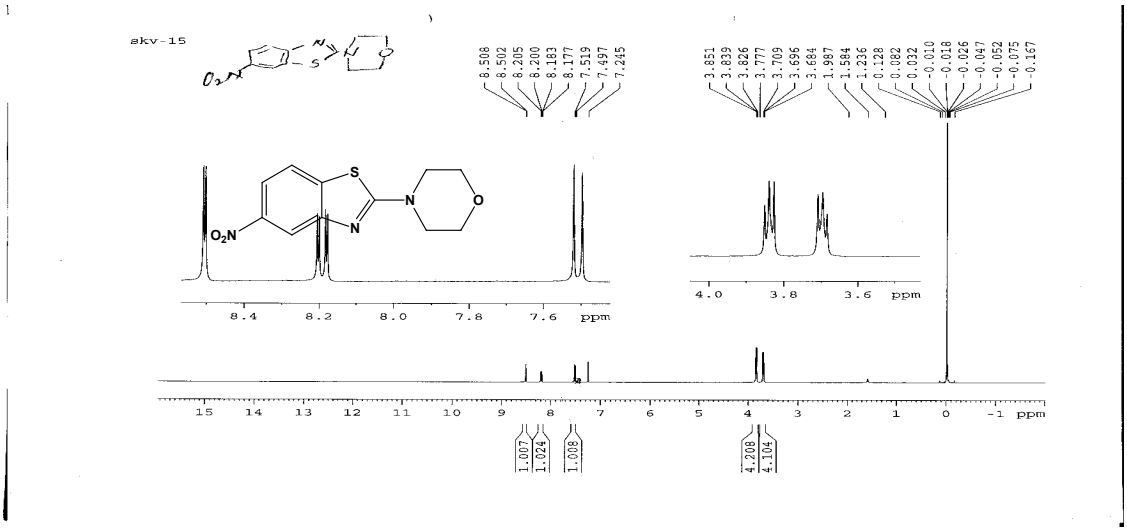

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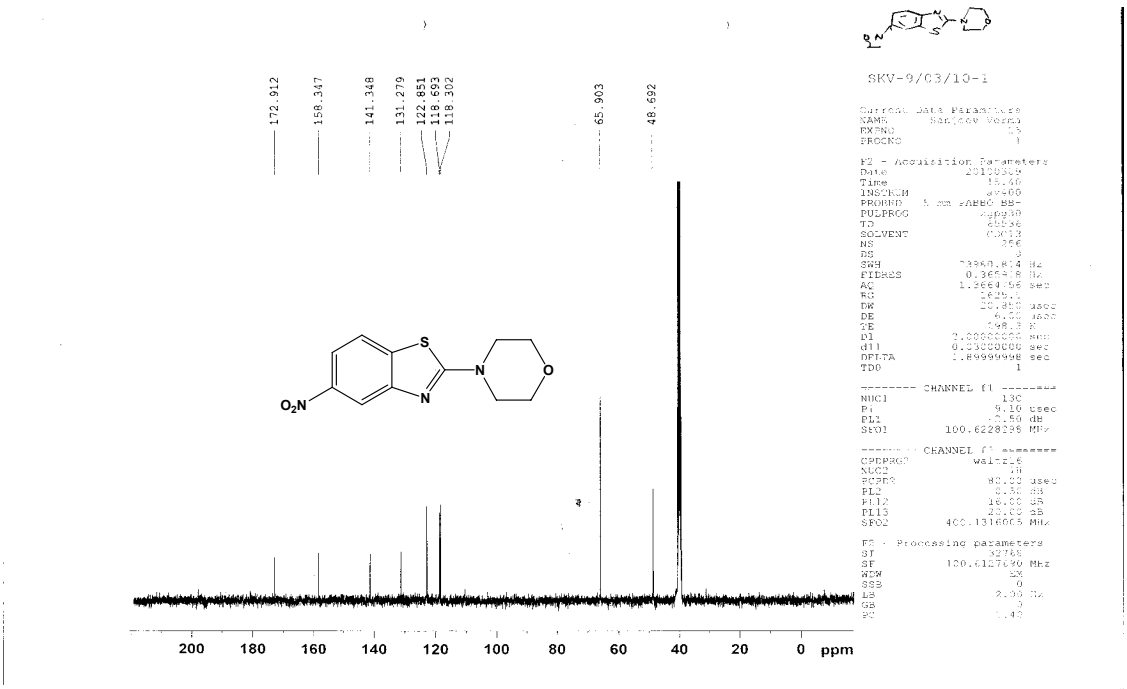

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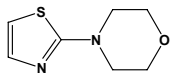

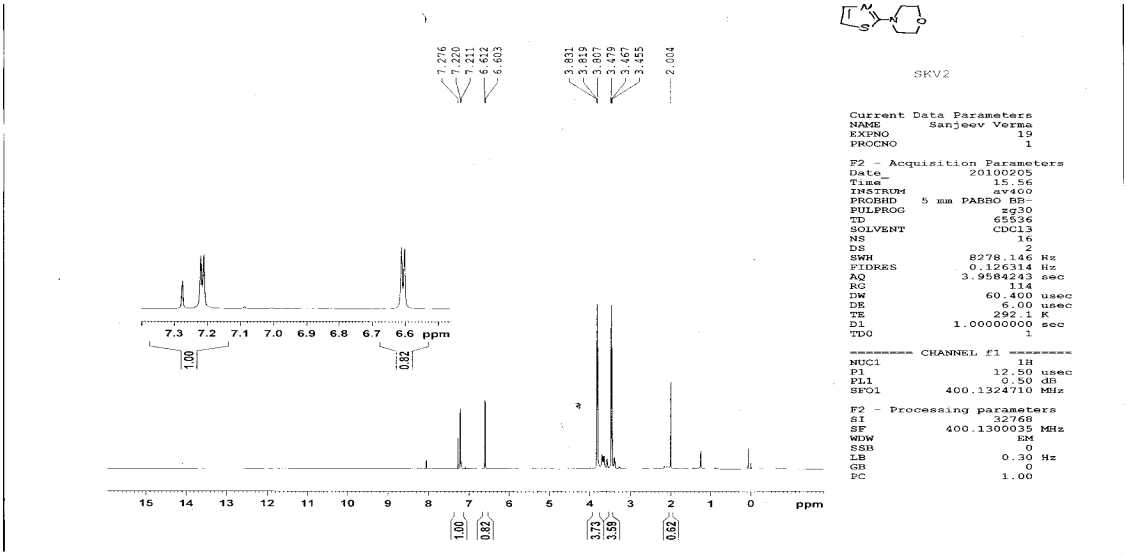

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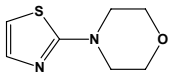

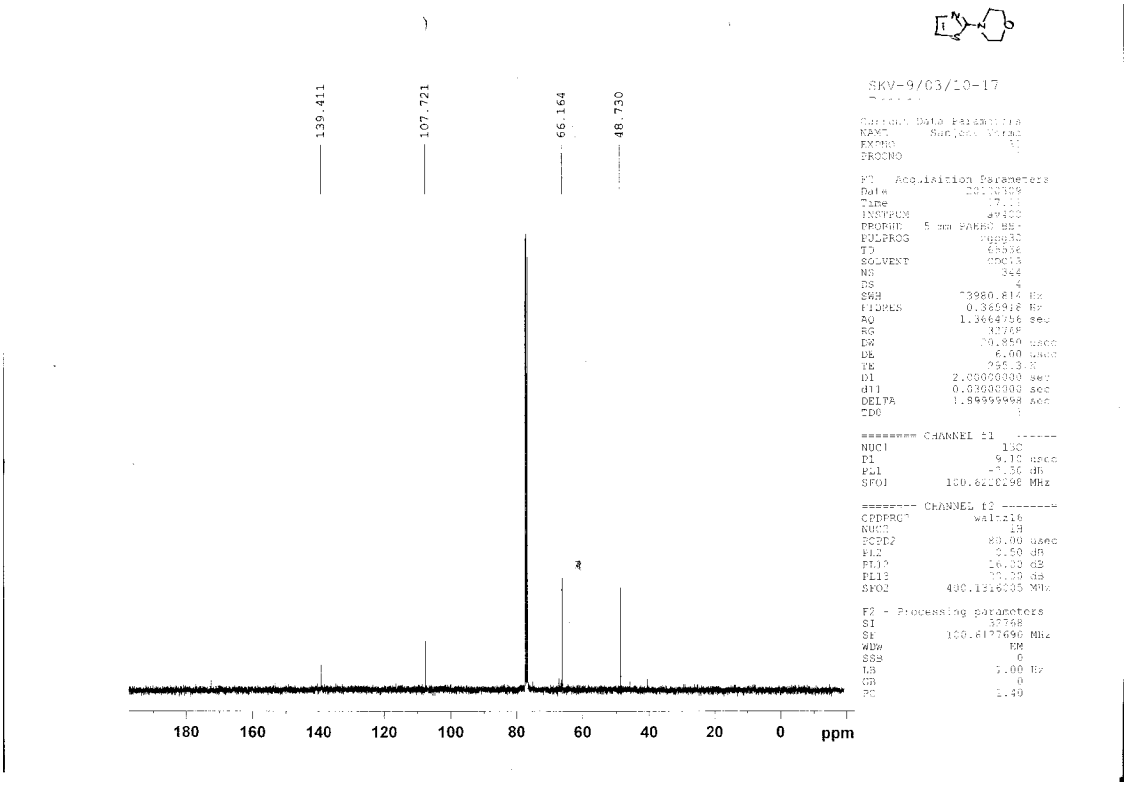

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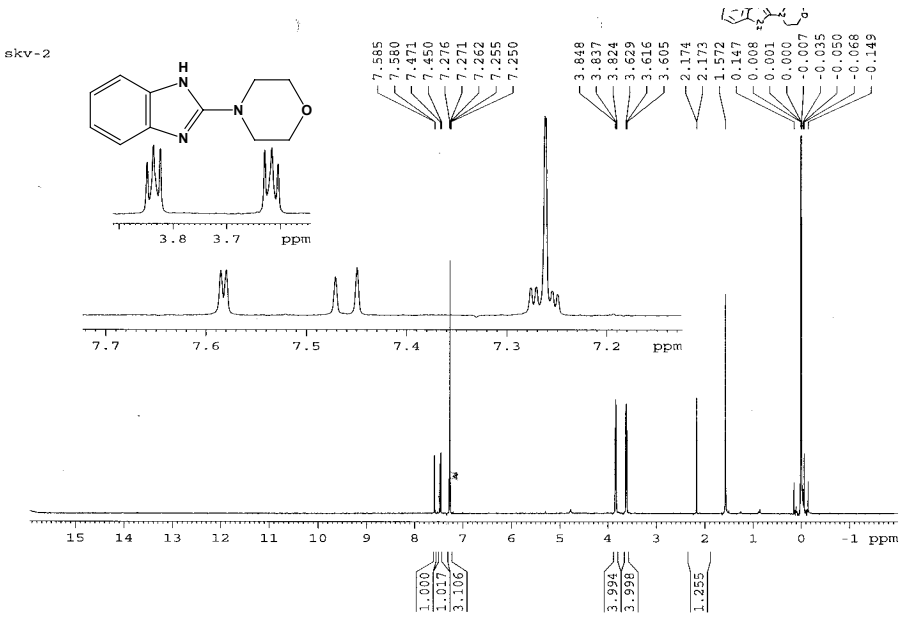

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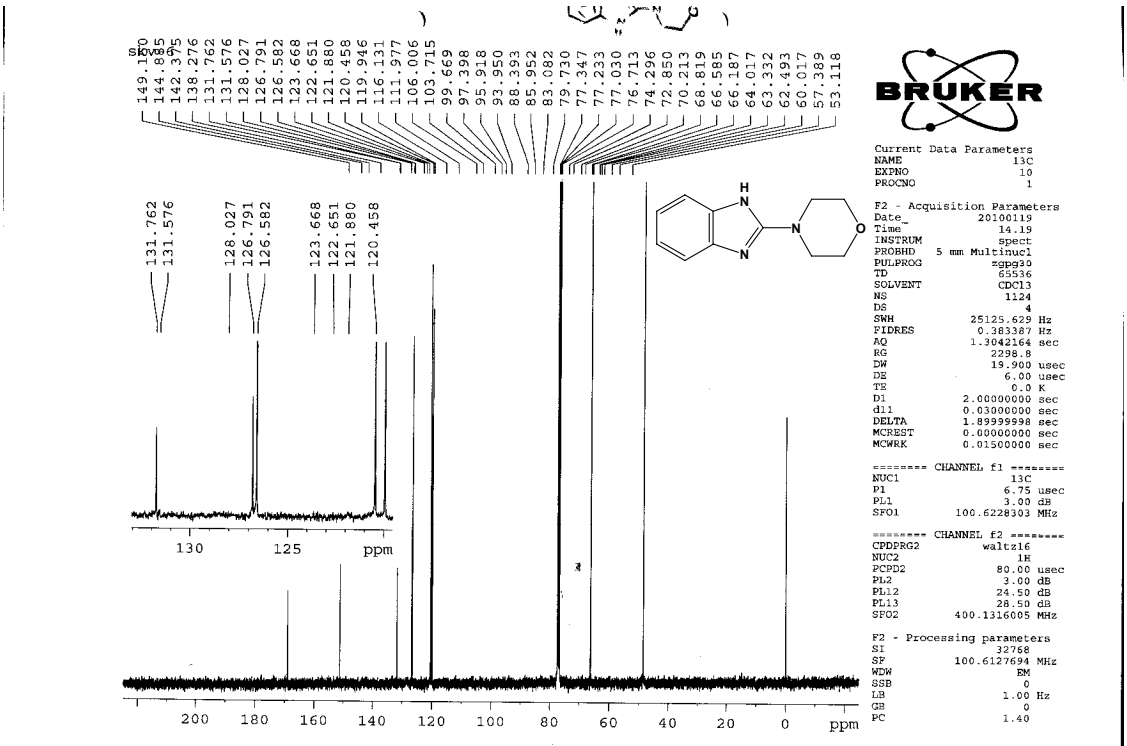

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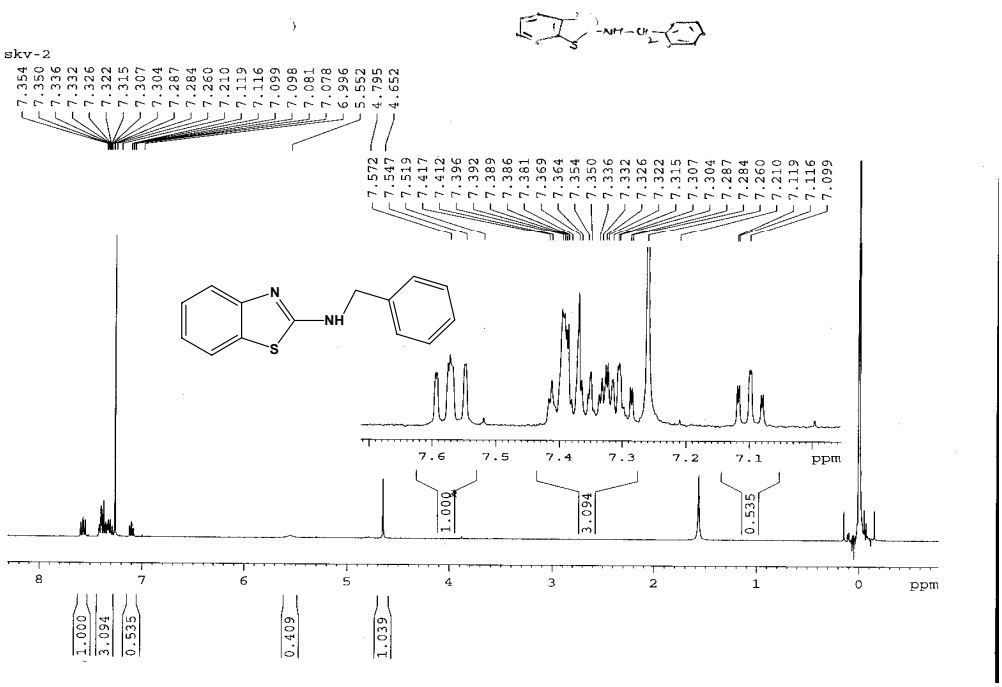

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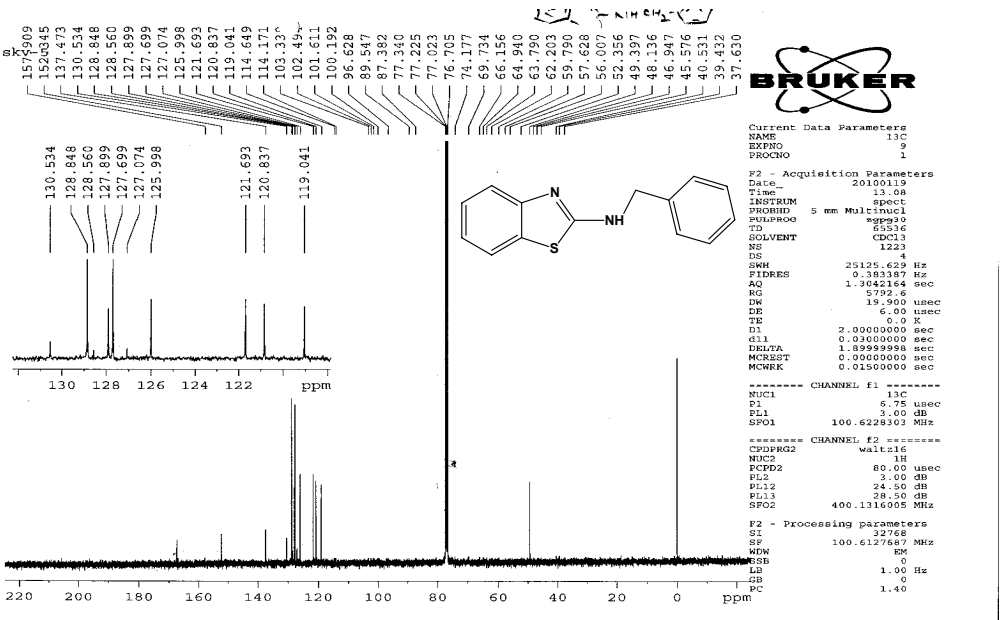

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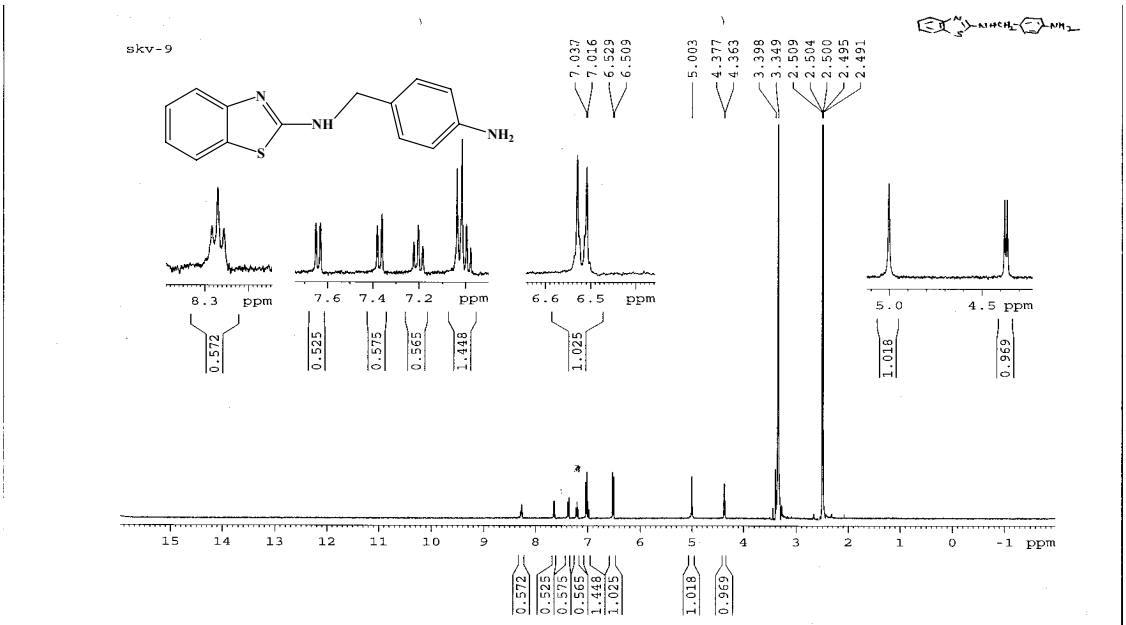

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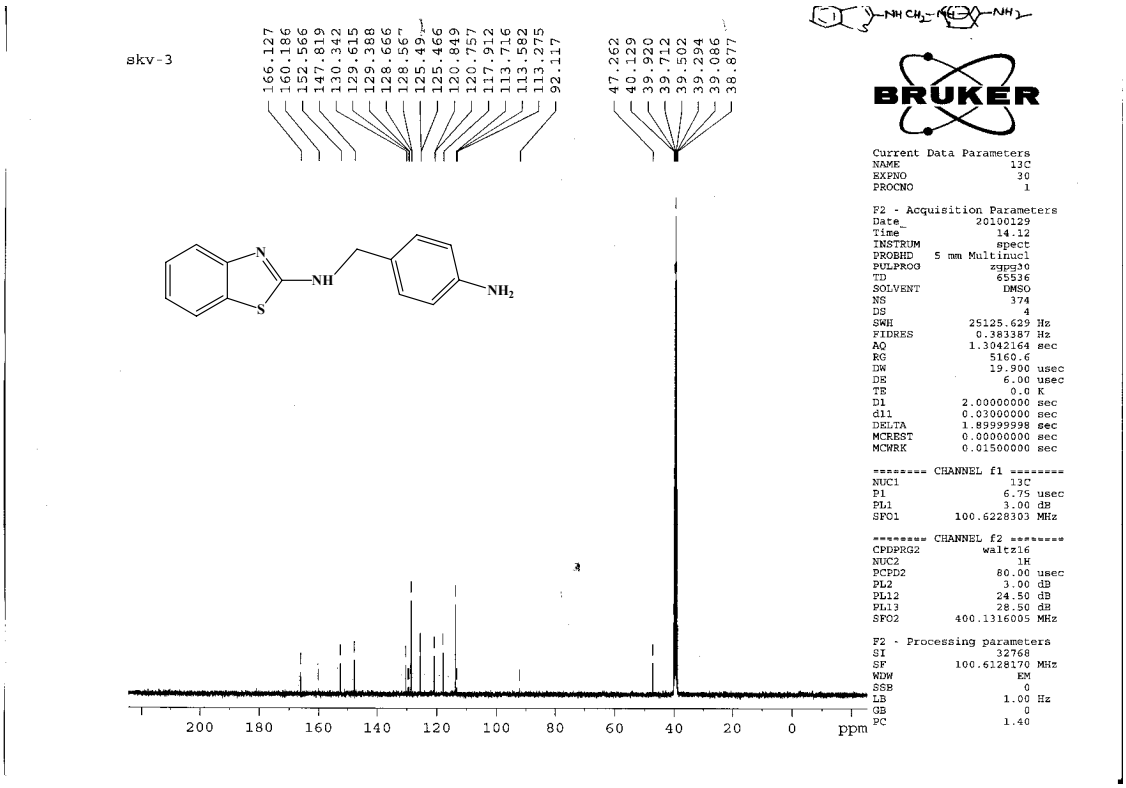

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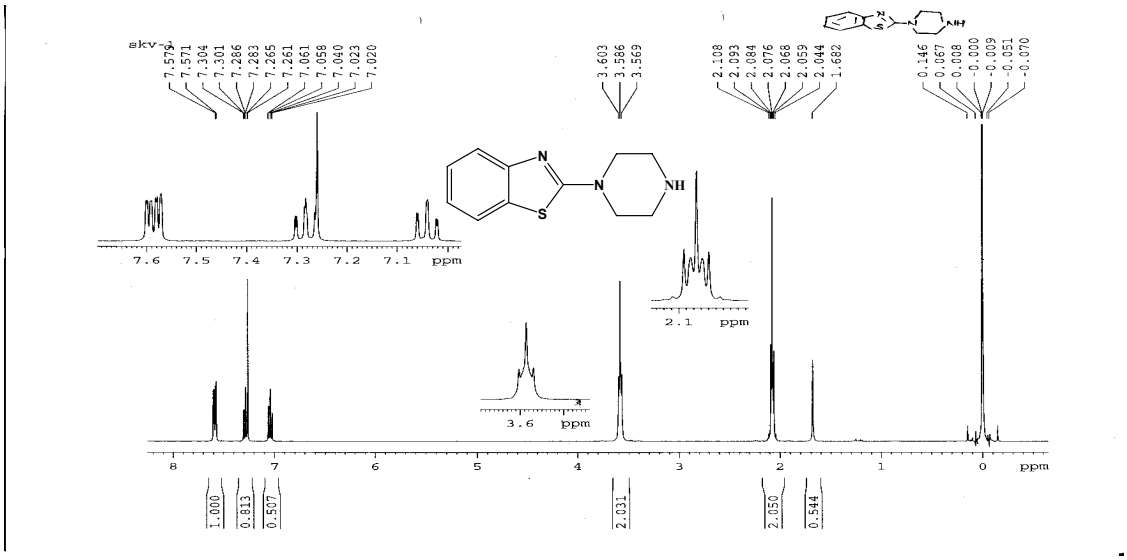
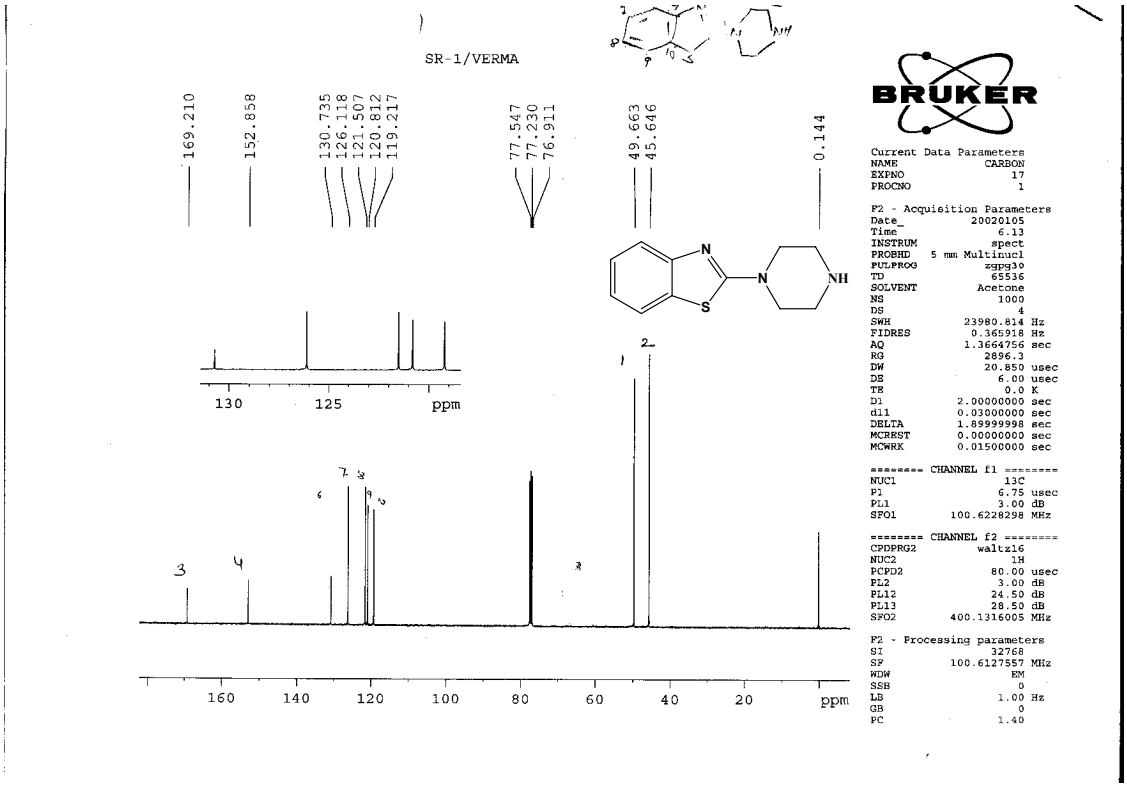
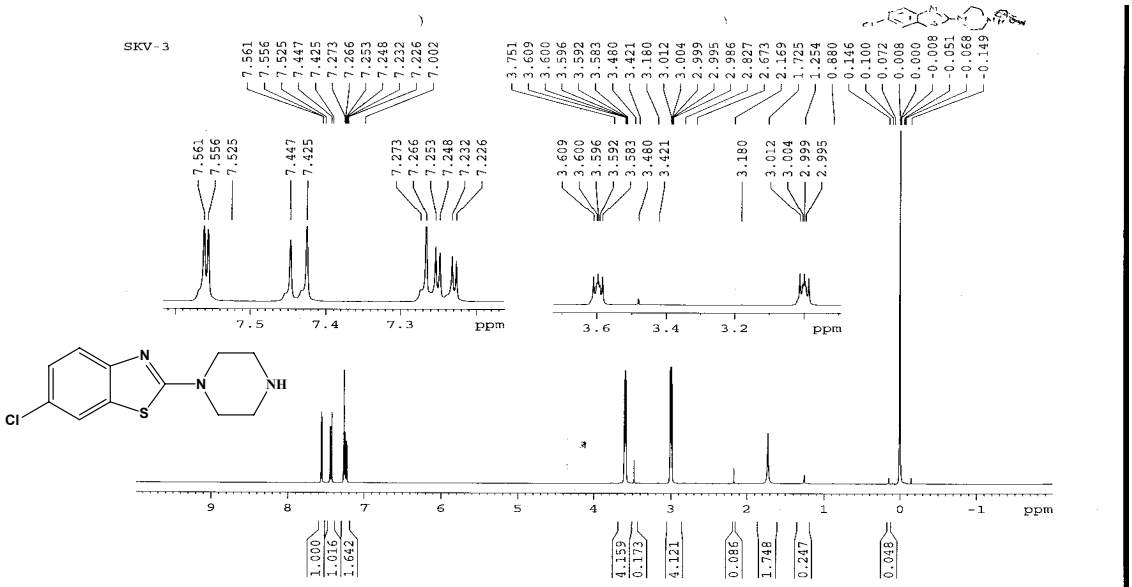


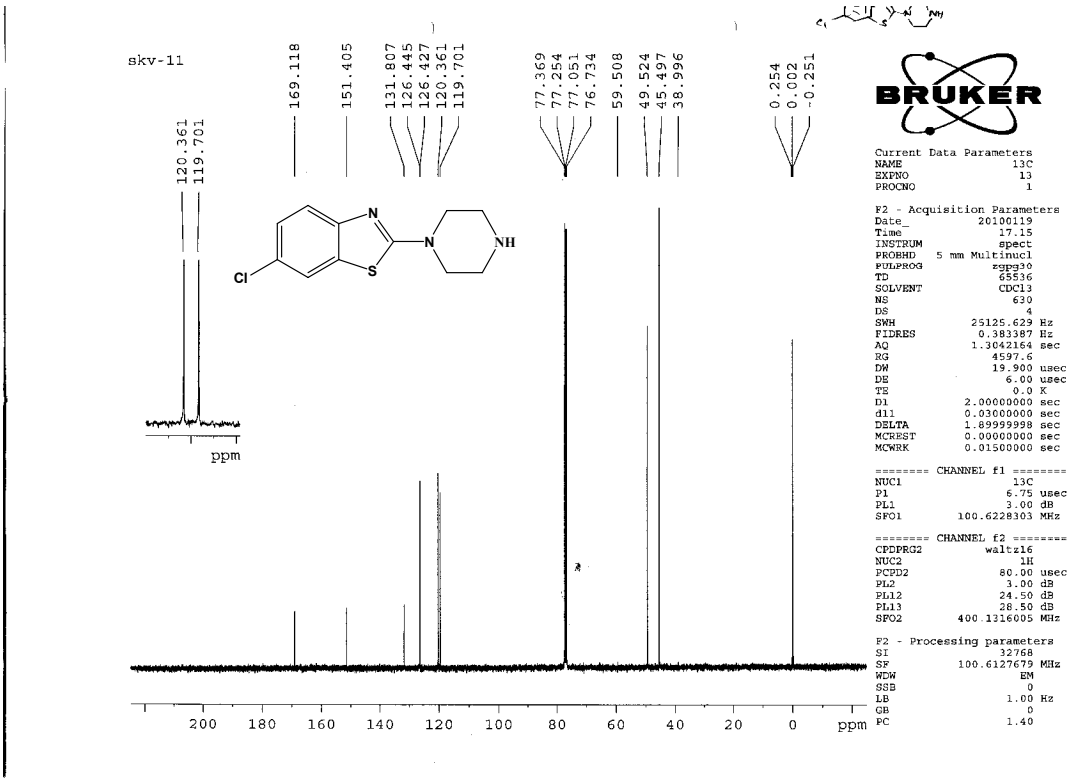
^{13}C NMR of 2-Piperazin-1-yl-benzothiazole ($CDCl_3$)



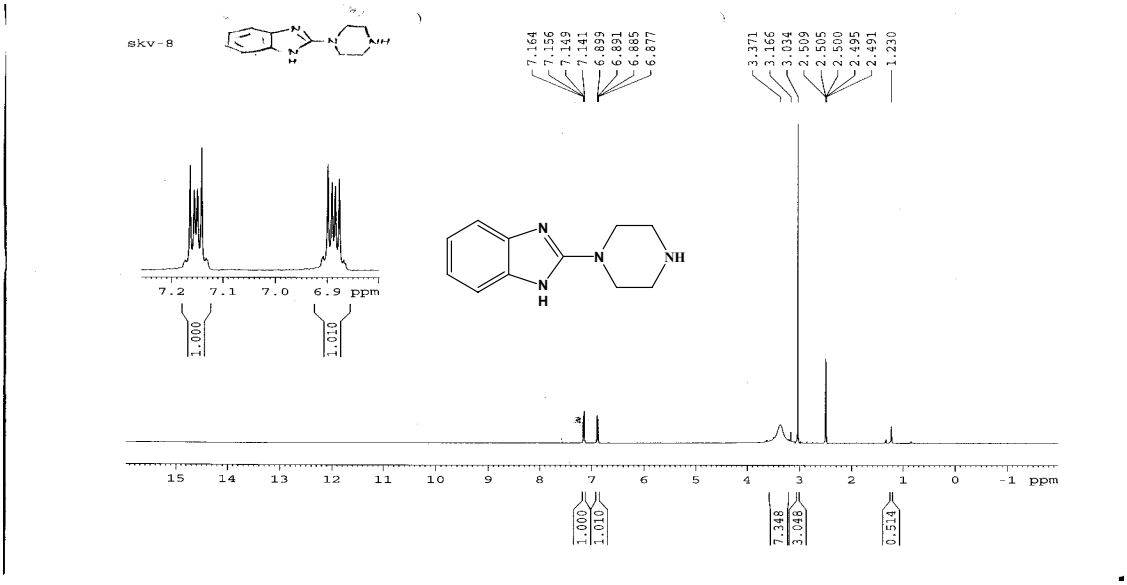
^{1}H NMR of 6-Chloro-2-piperazin-1-yl-benzothiazole ($CDCl_3$)



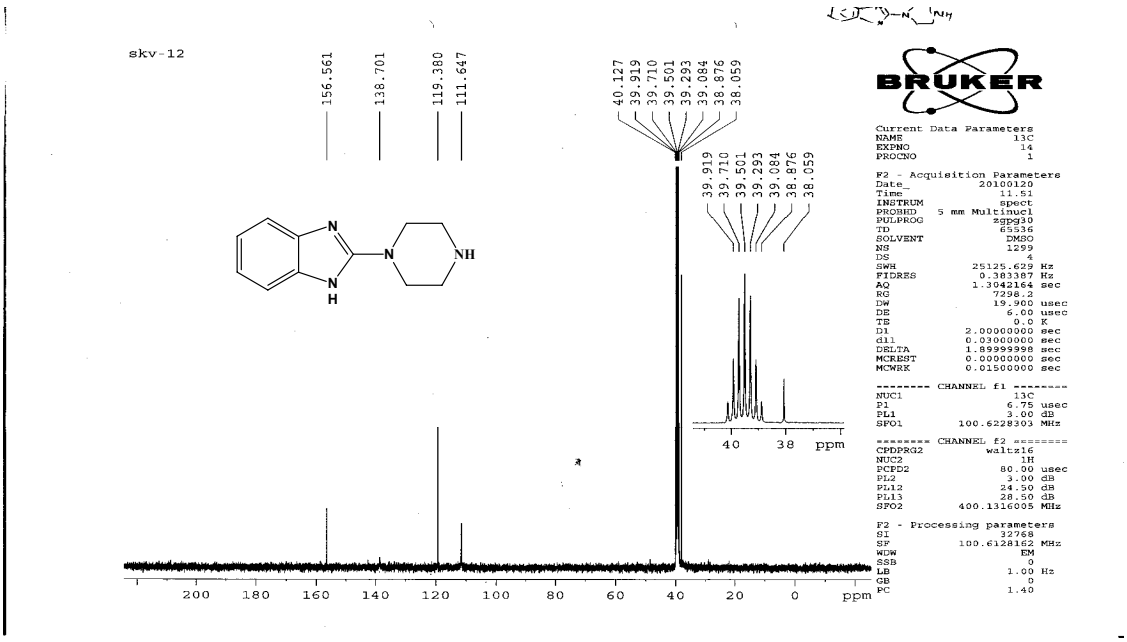
^{13}C NMR of 6-Chloro-2-piperazin-1-yl-benzothiazole ($CDCl_3$)



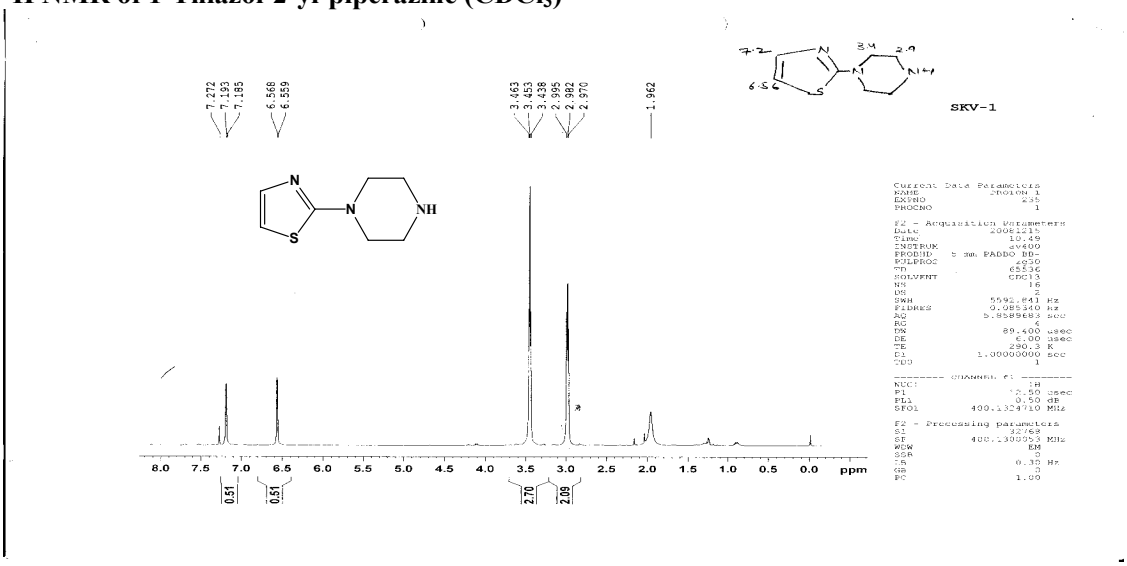
^{1}H NMR of 2-Piperazin-1-yl-1H-benzoimidazole (DMSO-d^{6})



^{13}C NMR of 2-Piperazin-1-yl-1H-benzoimidazole (DMSO-d^{6})



^{1}H NMR of 1-Thiazol-2-yl-piperazine ($CDCl_3$)



^{13}C NMR of 1-Thiazol-2-yl-piperazine ($CDCl_3$)