

Supporting Information

[C₁₆ MPy]AlCl₃Br : An efficient novel ionic liquid for synthesis of novel 1,2,4-triazolidine-3-thiones in water

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Table of content:

Page No.

A	General information	1
B	Typical procedure	1
C	Spectral data of [C₁₆ MPy]AlCl₃Br ionic liquid	2
D	Spectral data of 1,2,4-triazolidine-3-thione derivatives	2-24

A. General:

IR spectra were recorded on a Perkin–Elmer FT-IR 783 spectrophotometer. NMR spectra were recorded on a BrukerAC-300 MHz spectrometer in DMSO-d₆ using tetramethylsilane as internal standard. Mass spectra were recorded on a Shimadzu QP2010 GCMS. The absorption spectrum was recorded at room temperature on a UV 3600 Shimadzu UV–VIS–NIR spectrophotometer with the use of a 1.0 cm quartz cell.

B. Typical procedure:

In a 50 mL round-bottom flask, to a mixture of aldehyde or ketone (1 mmol) and thio semicarbazide (1 mmol) in water (5 mL), [C₁₆ MPy]AlCl₃Br ionic liquid (10 mol %). The reaction mixture was stirred at room temperature for the time specified in Table 2. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was filtered to yield corresponding product. These products were characterized by usual spectral techniques. (i.e. IR, ¹H; ¹³C NMR and MS).

Synthesis of the ionic liquids

N-Methyl Pyrrolidinium bromide: A solution of N-Methyl Pyrrolidine (5 g, 0.058 mol) and 1-bromohexadecane (17.69 g, 0.058 mol) in acetone (40 mL) was refluxed for 12hrs. The white crystalline precipitate was filtered after cooling, and washed with diethyl ether (22 g, 96% yield).

[C₁₆MPy]AlCl₃Br was synthesized by mixing [C₁₆MPy][Br] (3 g, 0.0076 mol) with aluminium (III) chloride (1.02 g, 0.0076 mol) and stirring in methanol for 4 hrs.

Spectral data of [C₁₆MPy]AlCl₃Br ionic liquid: ¹H-NMR (300 MHz, CDCl₃): δ 0.81-0.85 (t, 3H, *J*=12 Hz), 1.21(s,24H), 1.70-1.73(s,2H), 2.55(s,2H), 3.24(s,3H), 3.53-3.59(t,2H,*J*=18Hz),3.75-3.82(s, 4H); ¹³C-NMR (75 MHz, CDCl₃): δ 64.67, 64.20, 48.77, 31.87, 29.65, 29.61, 29.57, 29.46, 29.37, 29.31, 29.22, 26.40, 24.06, 22.64, 21.68, 14.08.

Spectral data of synthesized compounds:

Entry a, Table 2: 5-(4-methoxyphenyl)-1, 2, 4-triazolidine-3-thione

White solid; M.P. 162 °C; IR (ZnSe): 3394, 3283, 3126, 2829, 1594, 1530, 1508, 1471, 1223, 1170, 1082, 1054, 1011, 949, 930, 832, 811, 718 cm⁻¹; ¹H-NMR (300 MHz, DMSO-d₆) : δ 3.78 (s, 3H), 6.94-6.97(d, 2H, *J* = 9 Hz), 7.91 (s, 1H, -NH, D₂O exchangeable), 7.99 (s, 1H), 8.10 (s, 1H, -NH, D₂O exchangeable), 11.31 (s, 1H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, DMSO-d₆): 55.73, 114.61, 127.16, 129.38, 142.76, 161.14, 178.02.;MS (EI): 209 (m/z).

Entry b, Table2: 5-cyclohexyl-1, 2, 4-triazolidine-3-thione

White solid; M.P. 70 °C; IR (ZnSe): 3396, 3191, 3154, 2922, 2849, 1592, 1528, 1465, 1445, 1075, 939, 844, 781 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) : δ 1.16-1.31 (m, 5H), 1.65-1.82 (m, 5H), 2.20-2.26 (s, 1H), 6.63 (s, 1H, -NH, D₂O exchangeable), 7.07 (s, 1H, -NH, D₂O exchangeable), 7.27-7.29 (t, 1H, *J*=6 Hz), 10.17 (s, 1H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, CDCl₃): 25.37, 25.83, 28.90, 29.83, 40.52, 152.47, 177.99; MS (EI): 185 (m/z).

Entry c, Table2: 5-phenyl-1, 2, 4-triazolidine-3-thione

White solid; M.P. 154 °C; IR (ZnSe): 3388, 3232, 3149, 1597, 1532, 1460, 1444, 1368, 1289, 1226, 1098, 1059, 943, 870, 843, 759, 752 cm⁻¹; ¹H-NMR (300 MHz, DMSO-d₆) : δ 7.39-7.41 (t, 3H, *J*=6Hz), 7.78-7.81 (q, 2H, *J*=6Hz), 8.00 (s, 1H, -NH, D₂O exchangeable), 8.04 (s, 1H), 8.21 (s, 1H, -NH, D₂O exchangeable), 11.49 (s, 1H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, DMSO-d₆): 127.75, 129.11, 130.28, 134.64, 142.71, 178.45; MS (EI): 179 (m/z).

Entry d, Table2: 5-(4-chlorophenyl)-1, 2, 4-triazolidine-3-thione

White solid; M.P. 206 °C; IR (ZnSe): 3276, 3161, 2983, 1598, 1523, 1489, 1466, 1400, 1366, 1280, 1224, 1168, 1105, 1089, 1016, 924, 814, 696 cm⁻¹; ¹H-NMR (300 MHz, DMSO-d₆) : δ 7.44-7.47 (d, 2H, *J*=9Hz), 7.82-7.85 (d, 2H, *J*= 9Hz), 8.02 (s, 1H), 8.08 (s, 1H, -NH, D₂O exchangeable), 8.24 (s, 1H, -NH, D₂O exchangeable), 11.49 (s, 1H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, DMSO-d₆): 129.15, 129.40, 133.64, 134.69, 141.32, 178.54. MS (EI): 213 (m/z).

Entry e, Table2: 5, 5'-benzene-1, 3-diylbis (1, 2, 4-triazolidine-3-thione)

White solid; M.P. 150 °C; IR (ZnSe): 3471, 3288, 3195, 1682, 1647, 1594, 1513, 1432, 1355, 1181, 1142, 1086, 943, 760, 686 cm⁻¹; ¹H-NMR (300 MHz, DMSO-d₆) : δ 7.40-7.45 (t, 1H, *J*=15Hz), 7.78-7.81 (dd, 2H, *J*= 3,3Hz), 8.06 (s, 2H), 8.10 (s, 2H, -NH, D₂O exchangeable), 8.16 (s, 1H), 8.33 (s, 2H, -NH, D₂O exchangeable), 11.53 (s, 2H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, DMSO-d₆): 125.94, 129.17, 129.51, 130.00, 135.15, 142.20, 178.49. MS (EI): 280 (m/z).

Entry f, Table2: 5-ferrocenyl-1, 2, 4-triazolidine-3-thione

Brown solid; M.P.174 °C; IR (ZnSe): 3429, 3378, 3123, 1600, 1585, 1530, 1462, 1381, 1329, 1247, 1211, 1102, 1060, 1039, 1023, 938, 839, 820, 758, 705, 642 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) : δ 4.22 (s, 5H), 4.44 (s, 2H), 4.59- 4.60 (s, 2H), 6.34 (s, 1H, -NH, D₂O exchangeable), 7.12 (s, 1H, -NH, D₂O exchangeable), 7.80 (s, 1H), 9.67 (s, 1H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, CDCl₃): 67.97, 69.42, 69.82, 70.90, 71.27, 145.52. MS (EI): 287 (m/z).

Entry g, Table2: 4-methyl-5-(3, 4, 5-trimethoxyphenyl)-1, 2, 4-triazolidine-3-thione

White solid; M.P. 102 °C; IR (ZnSe): 3511, 3379, 3054, 2940, 1670, 1573, 1498, 1410, 1358, 1323, 1233, 1161, 1117, 993, 922, 827, 753, 658 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) : δ 3.27-3.28 (d, 3H, *J*=3Hz), 3.88-3.90 (s, 3H), 3.93-3.94 (s, 6H), 6.85 (s, 1H), 7.47-7.48 (s, 1H, -NH, D₂O exchangeable), 7.83 (s, 1H), 10.27 (s, 1H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, CDCl₃): 31.22, 56.32, 60.96, 104.53, 106.78, 128.68, 131.69, 140.28, 142.95, 153.56, 153.64, 177.73. MS (EI): 283 (m/z).

Entry h, Table2: 5, 5'-benzene-1,4-diylbis(1,2,4-triazolidine-3-thione)

White solid; M.P. >300 °C; ¹H-NMR (300 MHz, DMSO-d₆) : δ 7.82 (s, 4H), 8.04 (s, 2H), 8.09 (s, 2H, -NH, D₂O exchangeable), 8.25 (s, 2H, -NH, D₂O exchangeable), 11.50 (s, 2H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, DMSO-d₆): 127.98, 135.84, 142.12, 178.44. MS (EI): 280 (m/z).

Entry i, Table2: 4-phenyl-5-(2-thienyl)-1, 2, 4-triazolidine-3-thione

White solid; M.P. 158 °C; ¹H-NMR (300 MHz, CDCl₃) : δ 7.09 (s, 1H), 7.29-7.32 (d, 2H, *J*=9Hz), 7.42-7.47 (t, 3H, *J*=15Hz), 7.65-7.68 (d, 2H, *J*=9Hz), 8.19 (s, 1H, -NH, D₂O exchangeable), 9.12 (s, 1H, -NH, D₂O exchangeable), 10.61 (s, 1H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, CDCl₃): 124.79, 126.40, 127.89, 128.46, 131.32, 137.72, 137.87, 175.36. MS (EI): 261 (m/z).

Entry j, Table2: 5-[4-(dimethylamino)phenyl]-4-phenyl-1,2,4-triazolidine-3-thione

Pale yellow solid; M.P. 164 °C; IR (ZnSe): 3329, 3283, 1590, 1517, 1484, 1442, 1367, 1256, 1181, 1069, 947, 824 cm⁻¹; ¹H-NMR (300 MHz, DMSO-d₆) : δ 2.97 (s, 6H), 6.70-6.73 (d, 2H, *J*=9Hz), 7.16-7.20 (t, 1H, *J*=6Hz), 7.33-7.38 (t, 2H, *J*=9Hz), 7.58-7.61 (d, 2H, *J*= 6Hz), 7.67-7.70 (d, 2H, *J*= 6Hz), 8.04 (s, 1H, -NH), 9.92 (s, 1H, -NH, D₂O exchangeable), 11.58 (s, 1H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, DMSO-d₆): 40.00, 112.14, 121.69, 125.47, 125.94, 128.45, 129.25, 129.31, 129.49, 129.82, 139.65, 144.45, 151.95, 175.37. MS (EI): 298 (m/z).

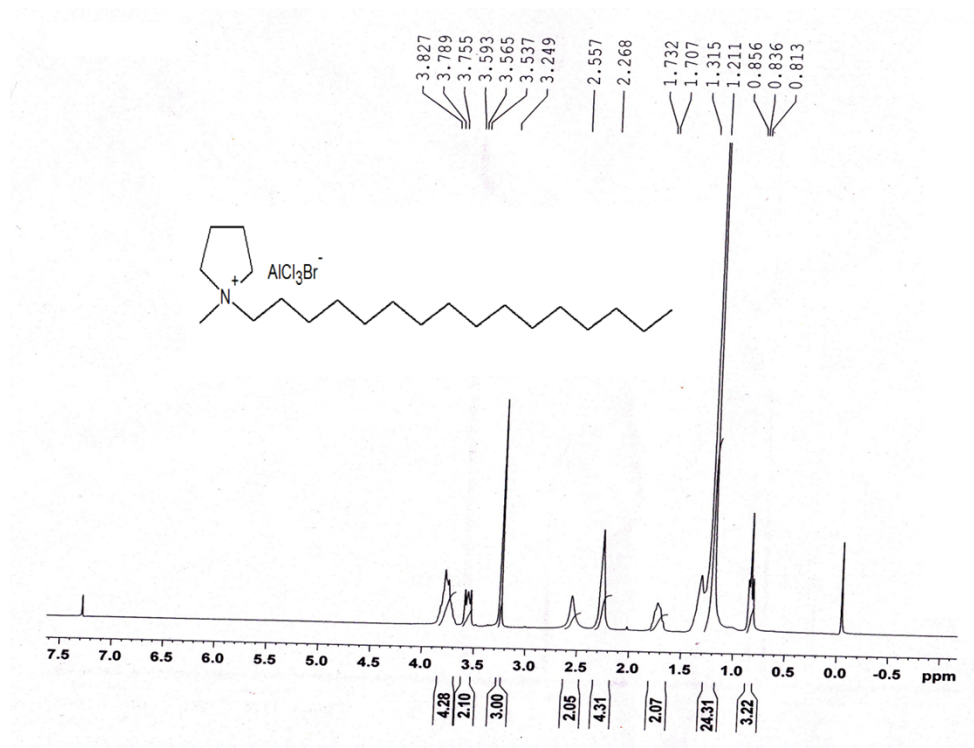
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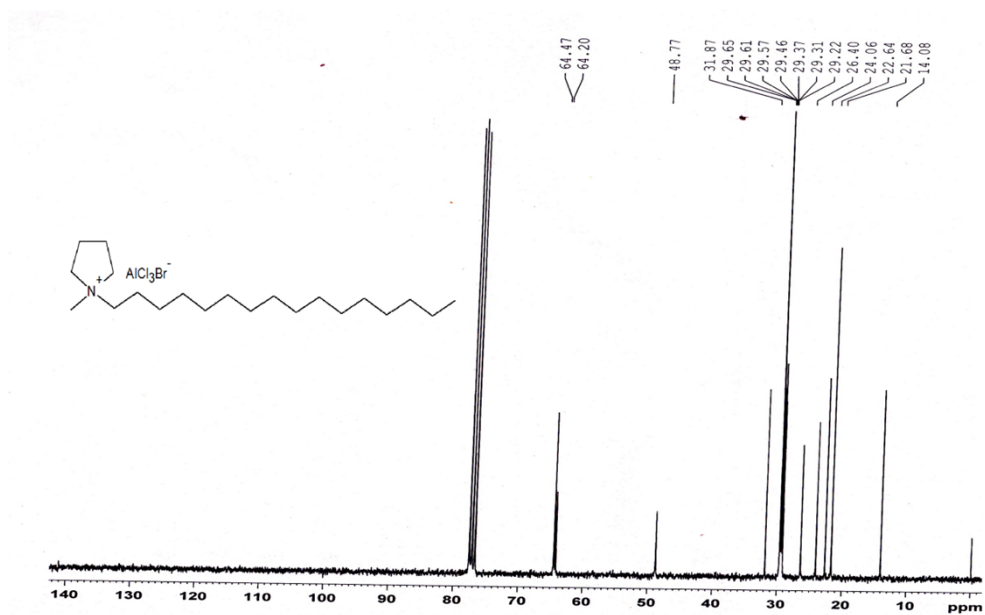
White solid; M.P. 172 °C; IR (ZnSe): 3348, 3156, 3003, 1595, 1525, 1487, 1400, 1260, 1081, 1033, 944, 925, 826 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) : δ 3.27-3.28 (d, 3H, *J*= 3Hz), 7.36-7.39

(d, 2H, $J=9$ Hz), 7.49 (s, 1H, -NH, D₂O exchangeable), 7.58-7.61 (d, 2H, $J=9$ Hz), 7.92 (s, 1H), 10.34 (s, 1H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, CDCl₃): 31.20, 128.44, 129.12, 131.86, 136.32, 141.29, 178.17. MS (EI): 227m/z).

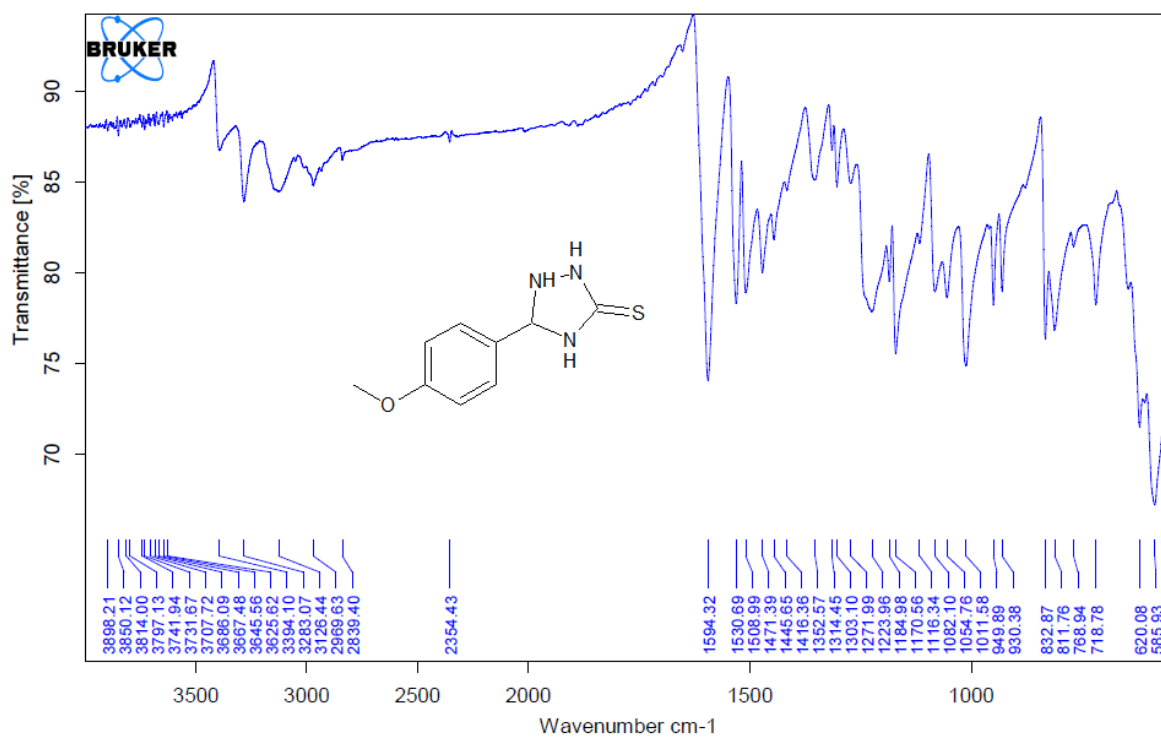
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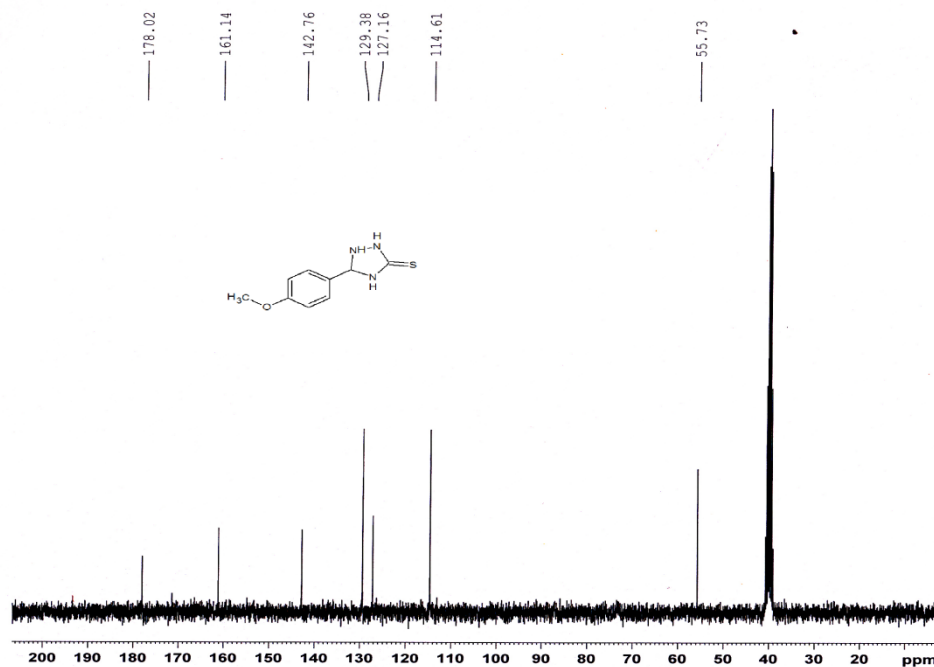
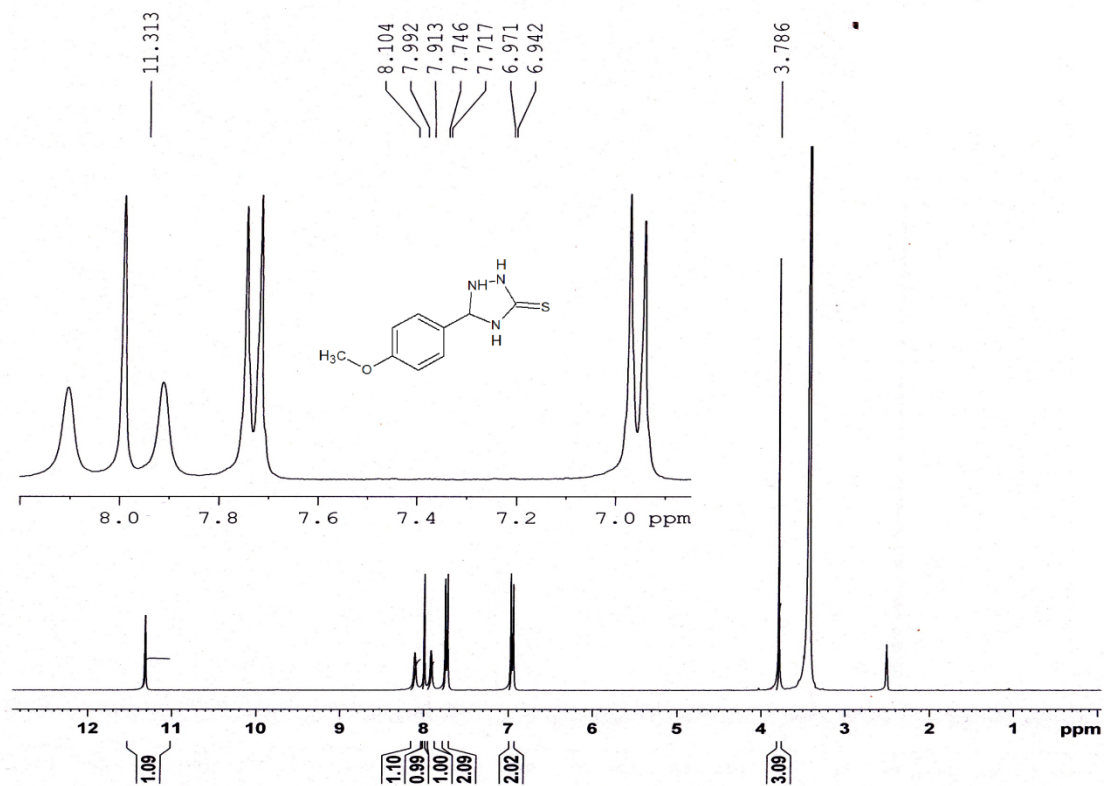
White solid; M.P. 142 °C; IR (ZnSe): 3337, 3167, 3001, 1521, 1448, 1385, 1306, 1258, 1090, 1067, 1034, 943, 881, 756 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) : δ 3.28-3.29 (d, 3H, $J=3$ Hz), 7.42 (s, 3H), 7.52 (s, 1H, -NH, D₂O exchangeable), 7.66 (s, 2H), 7.90 (s, 1H), 9.97 (s, 1H, -NH, D₂O exchangeable). ¹³C-NMR (75 MHz, CDCl₃): 31.20, 128.44, 129.12, 131.86, 136.32, 141.29, 178.17. MS (EI): 193 (m/z).



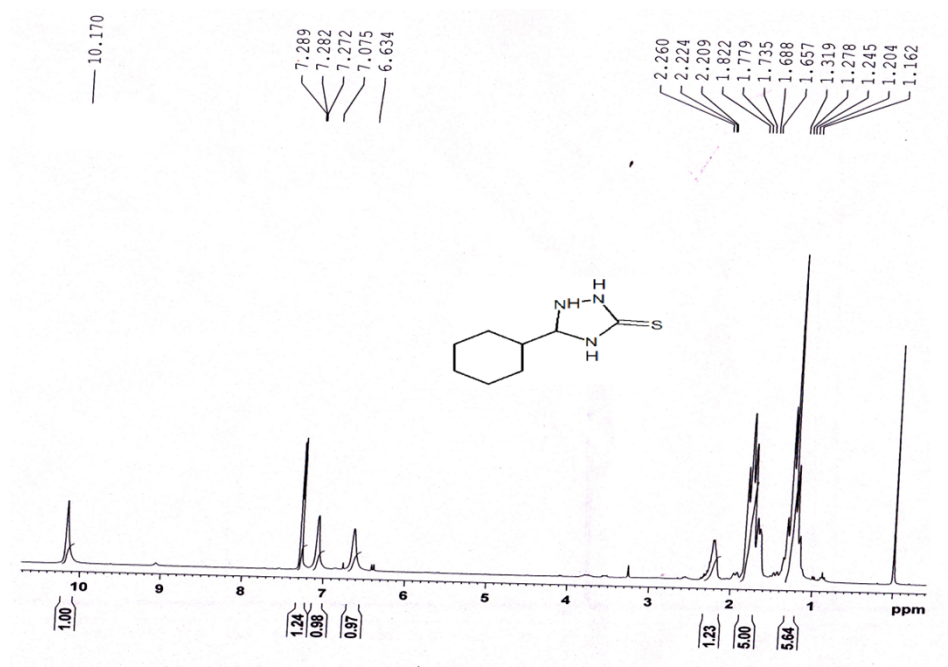
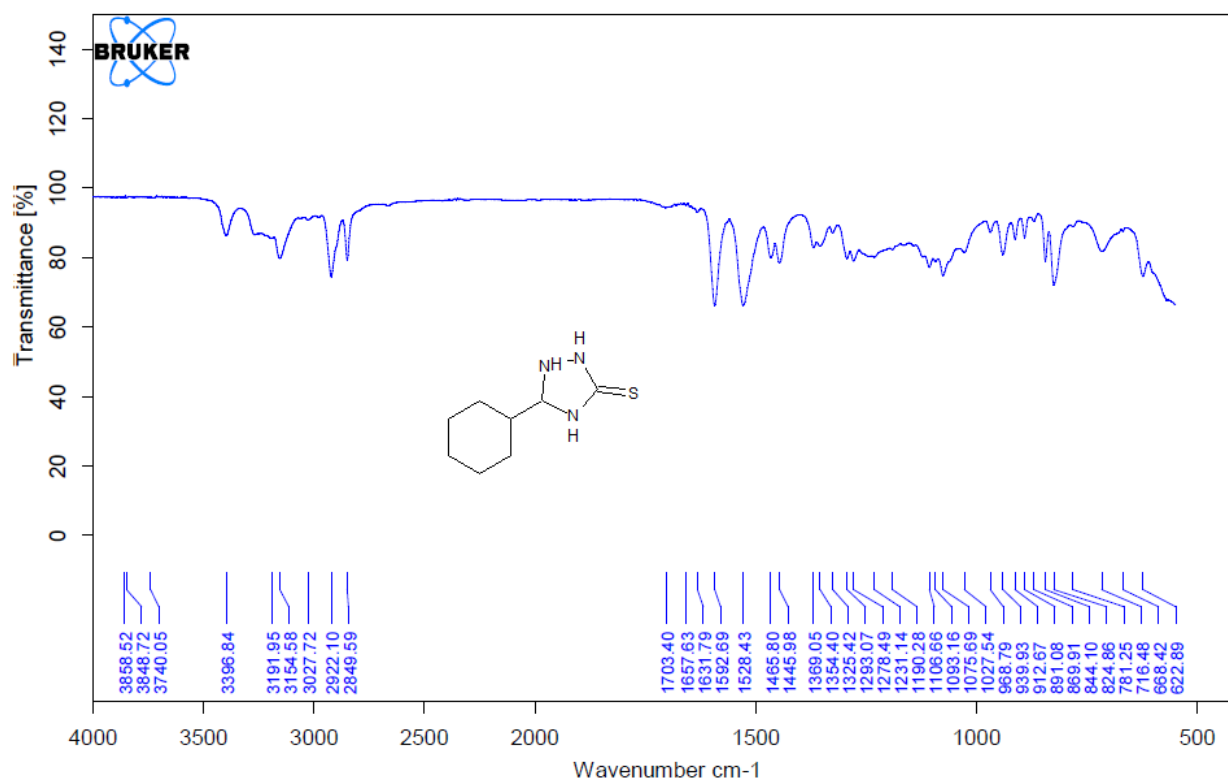


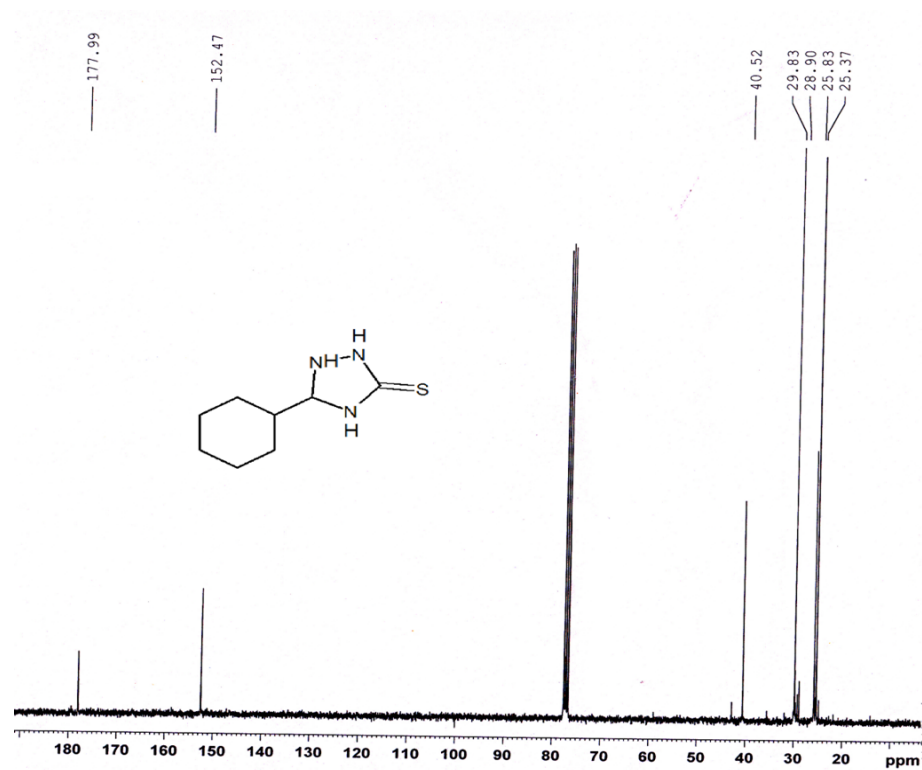
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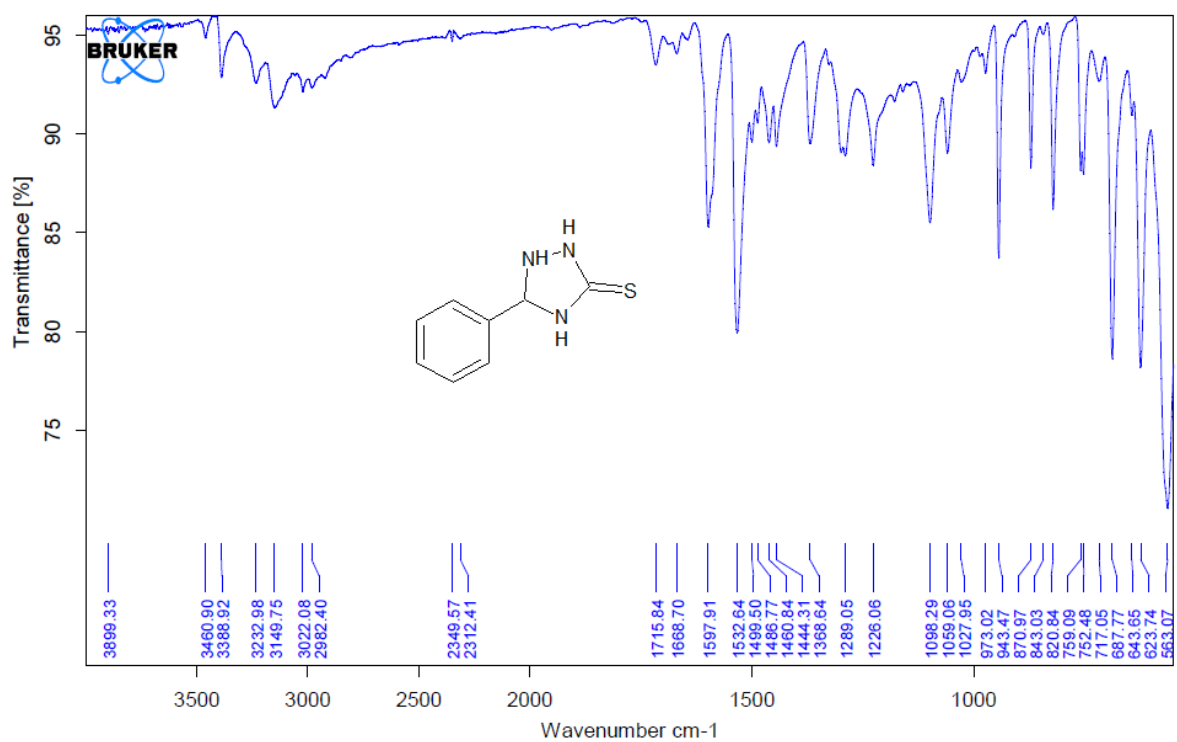


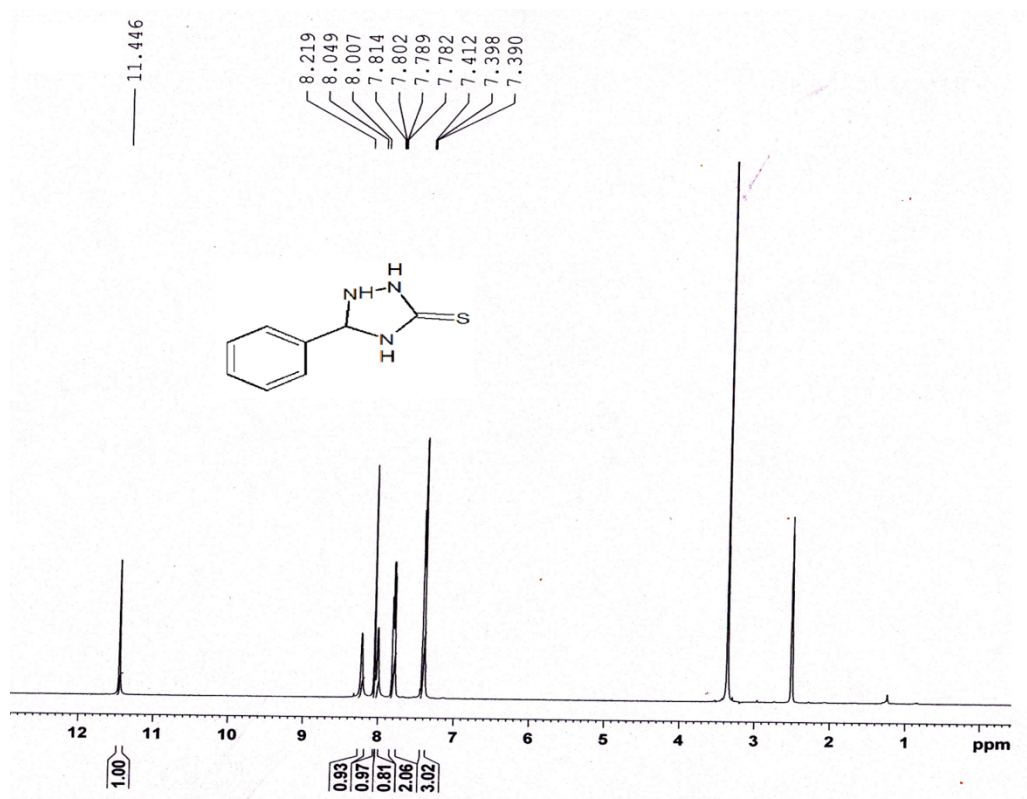
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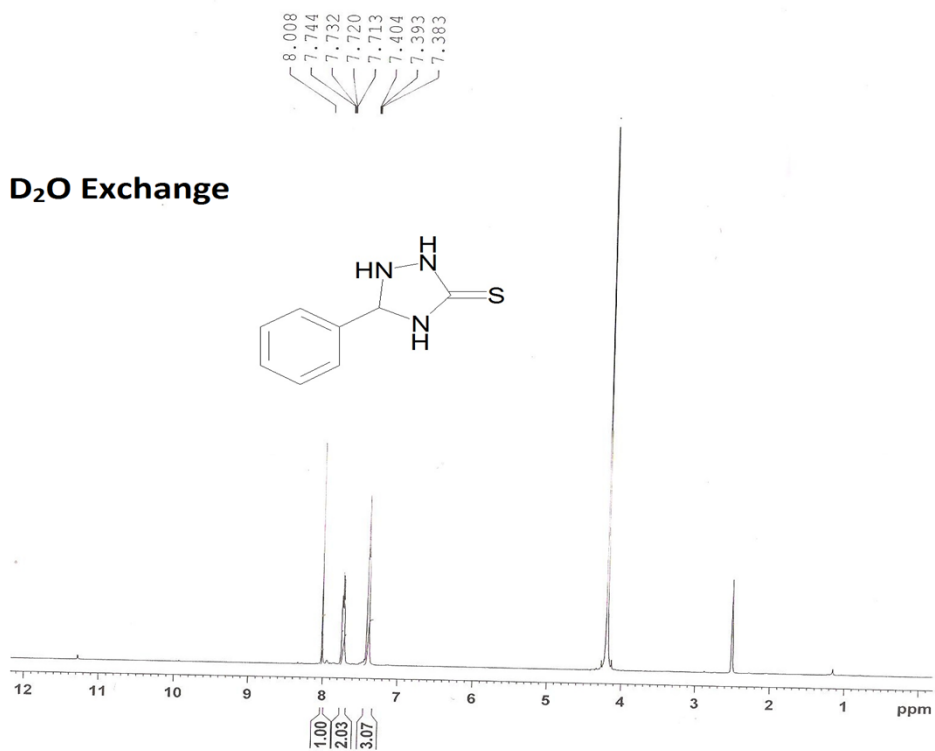


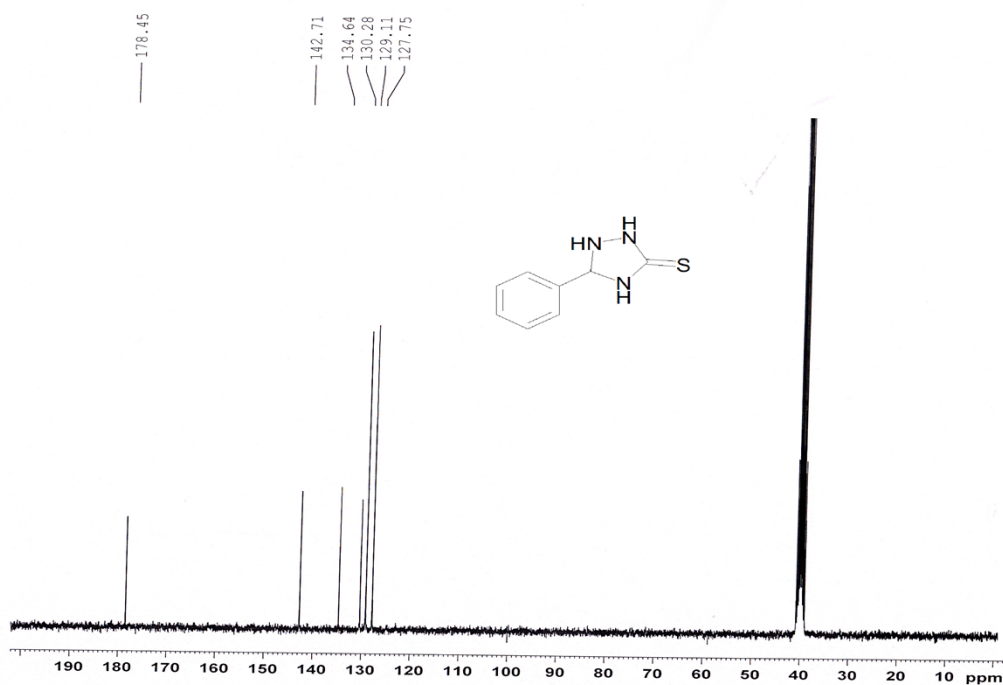
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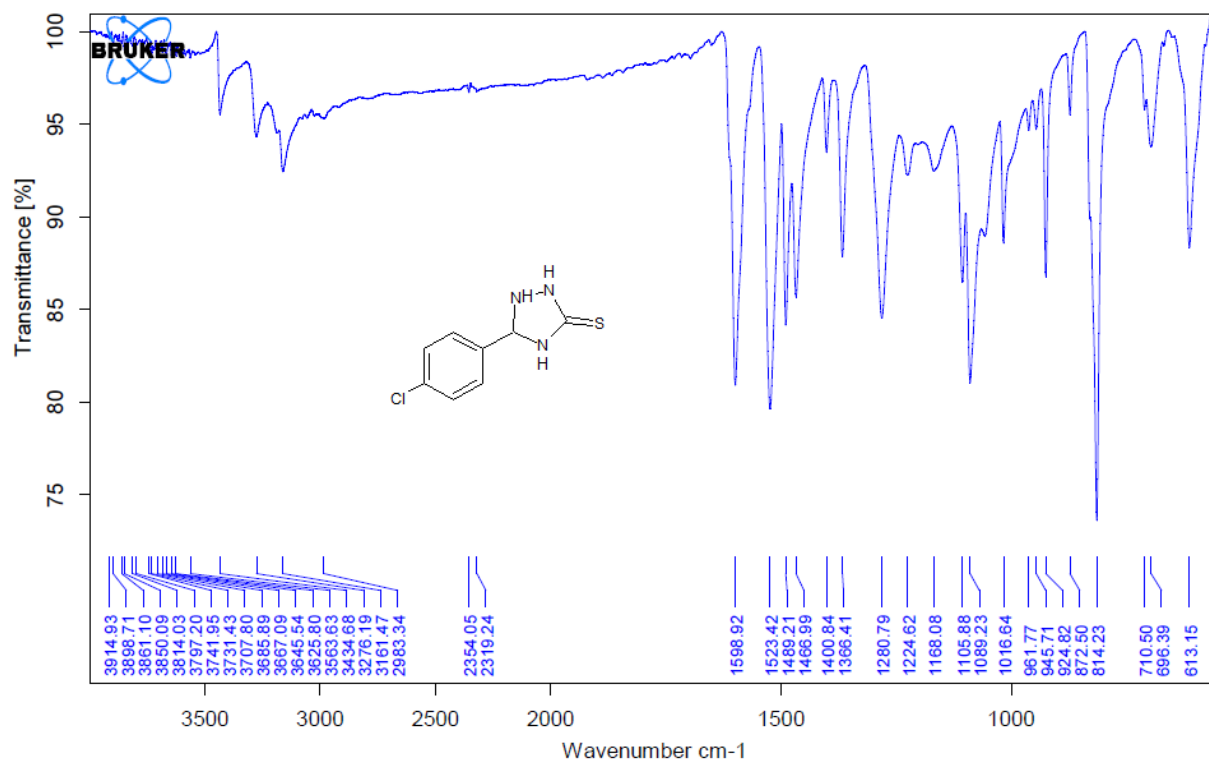


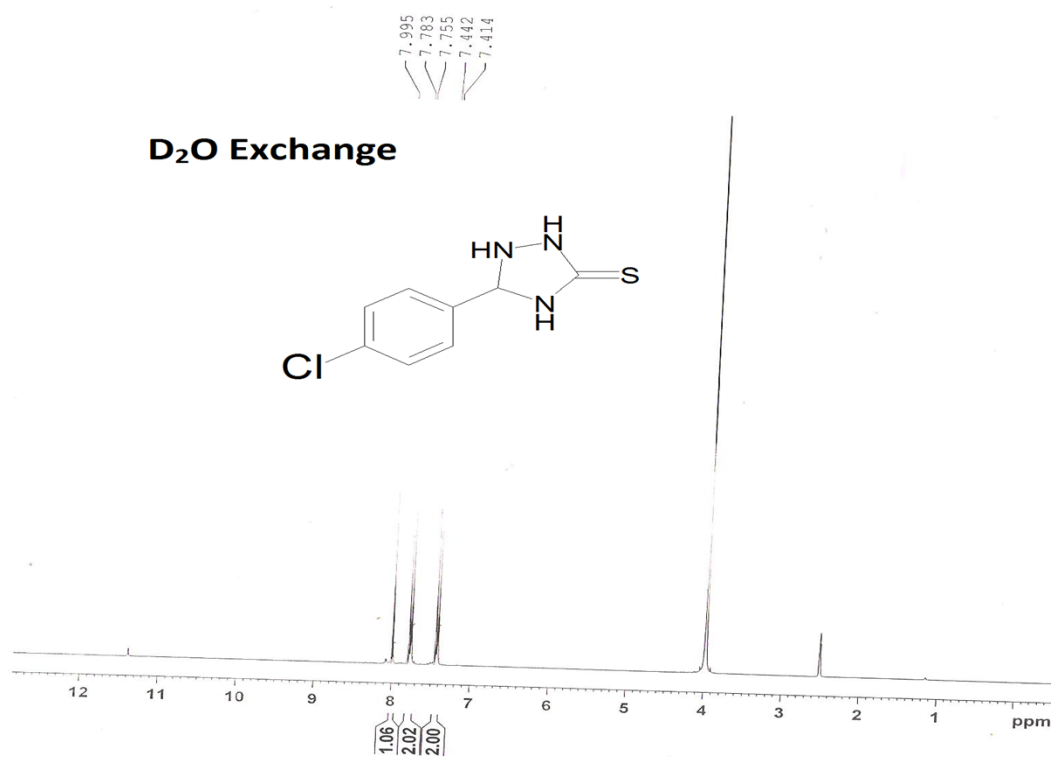
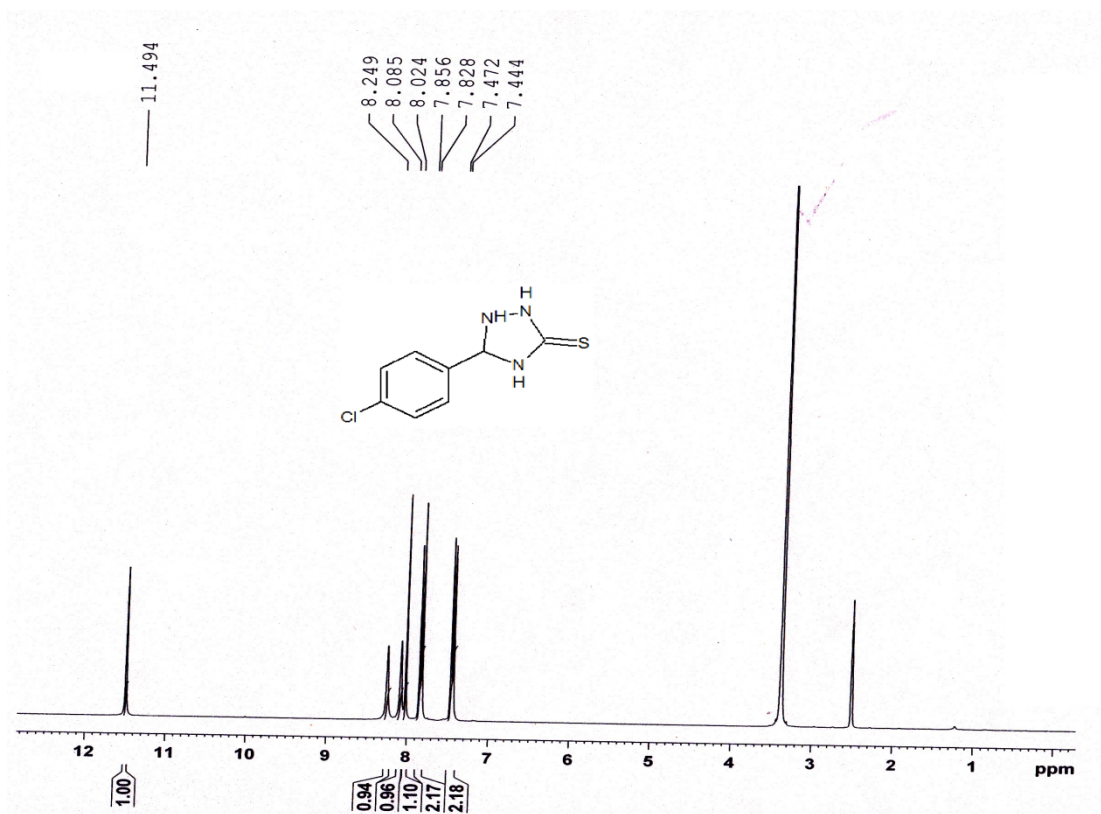
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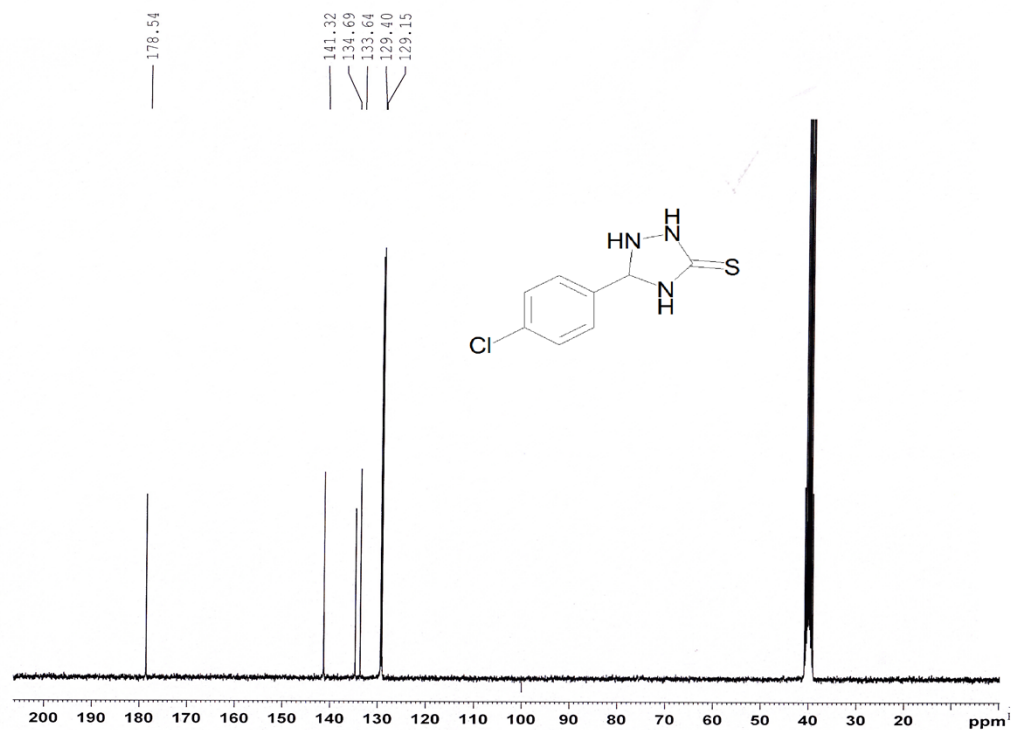




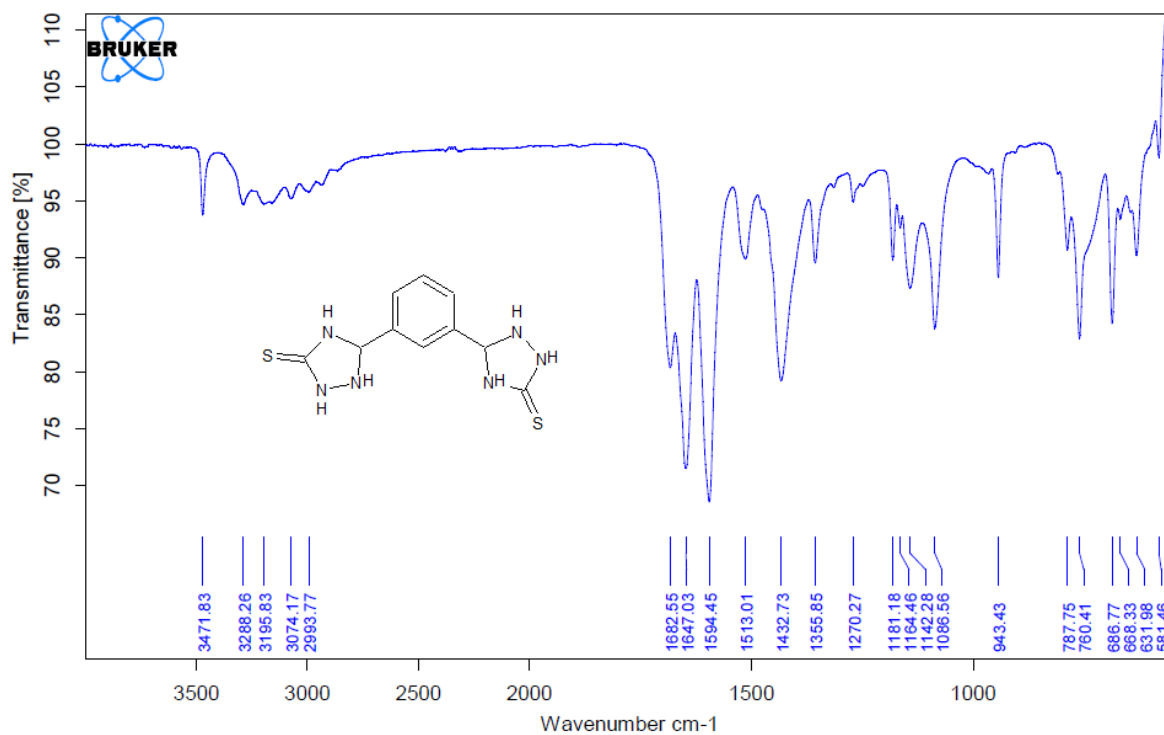
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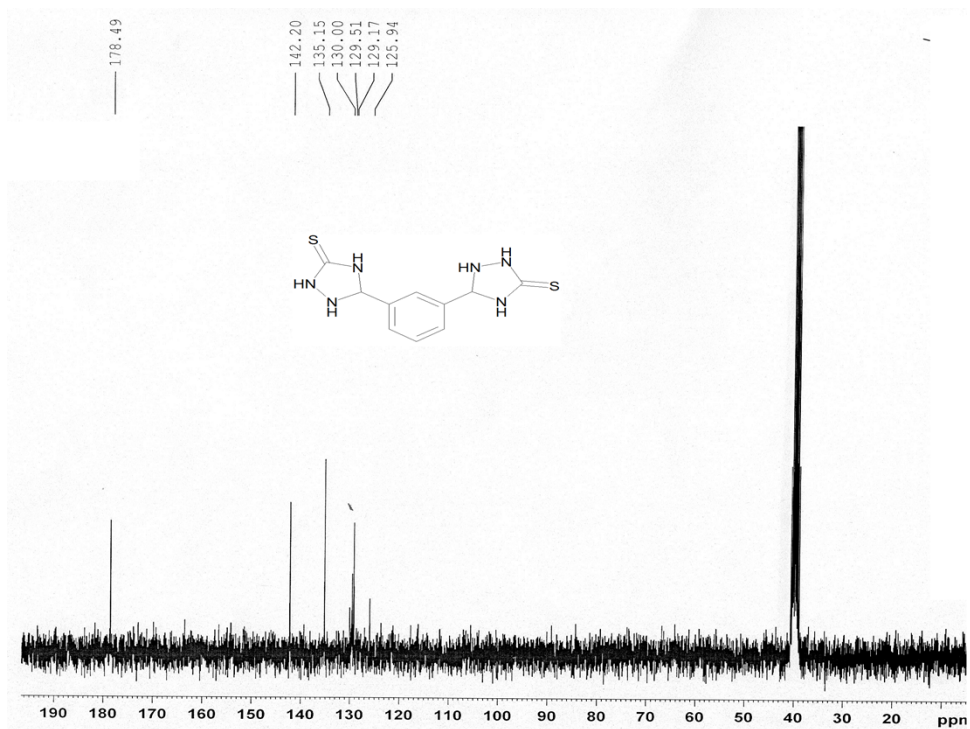
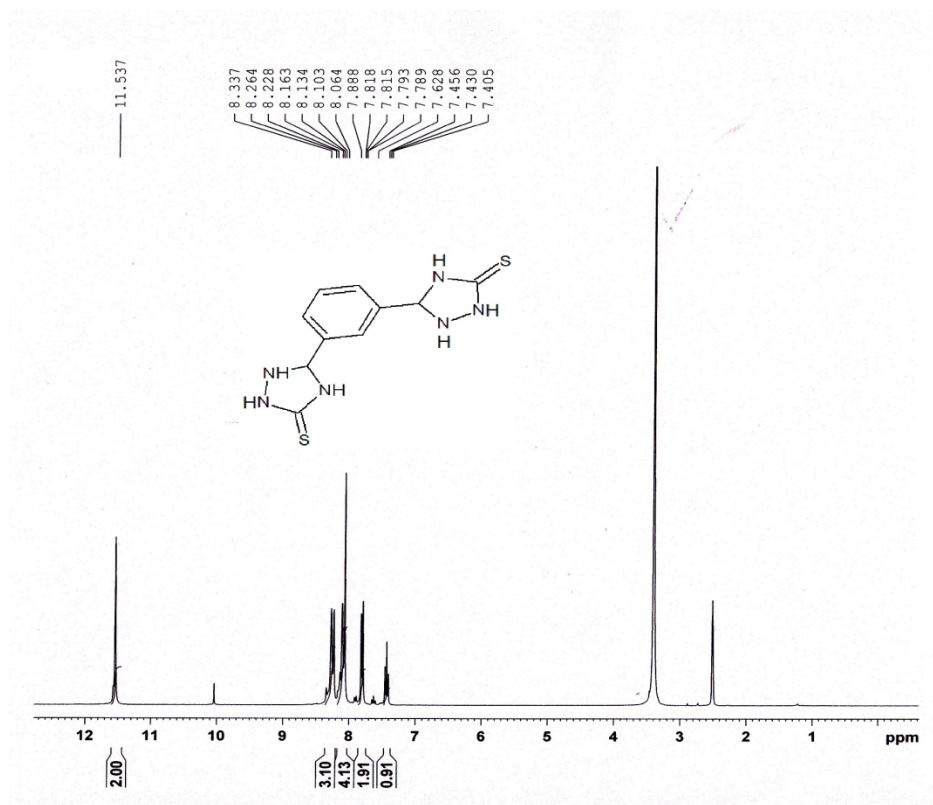




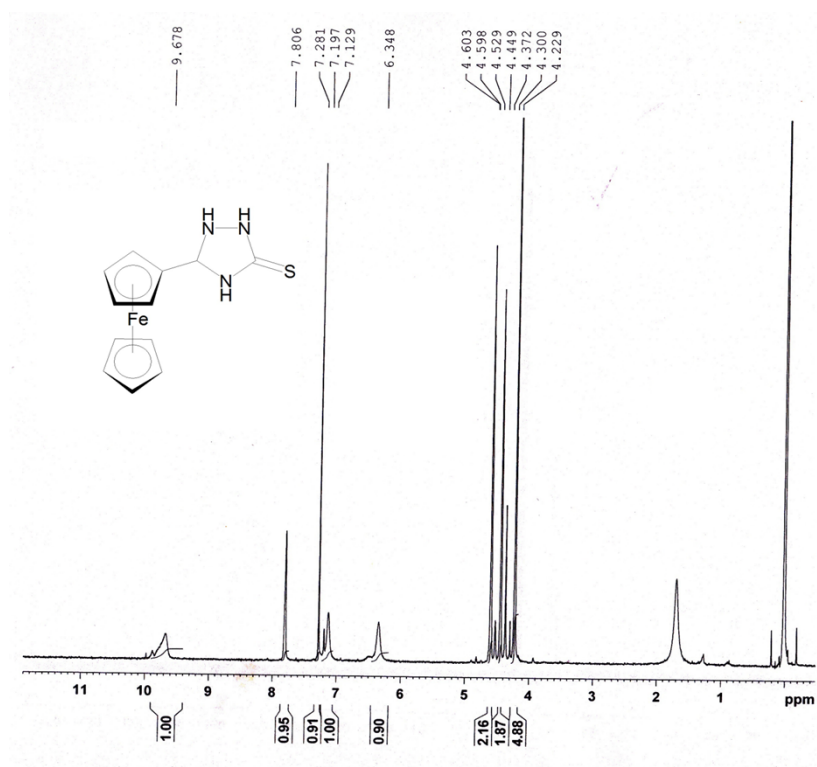
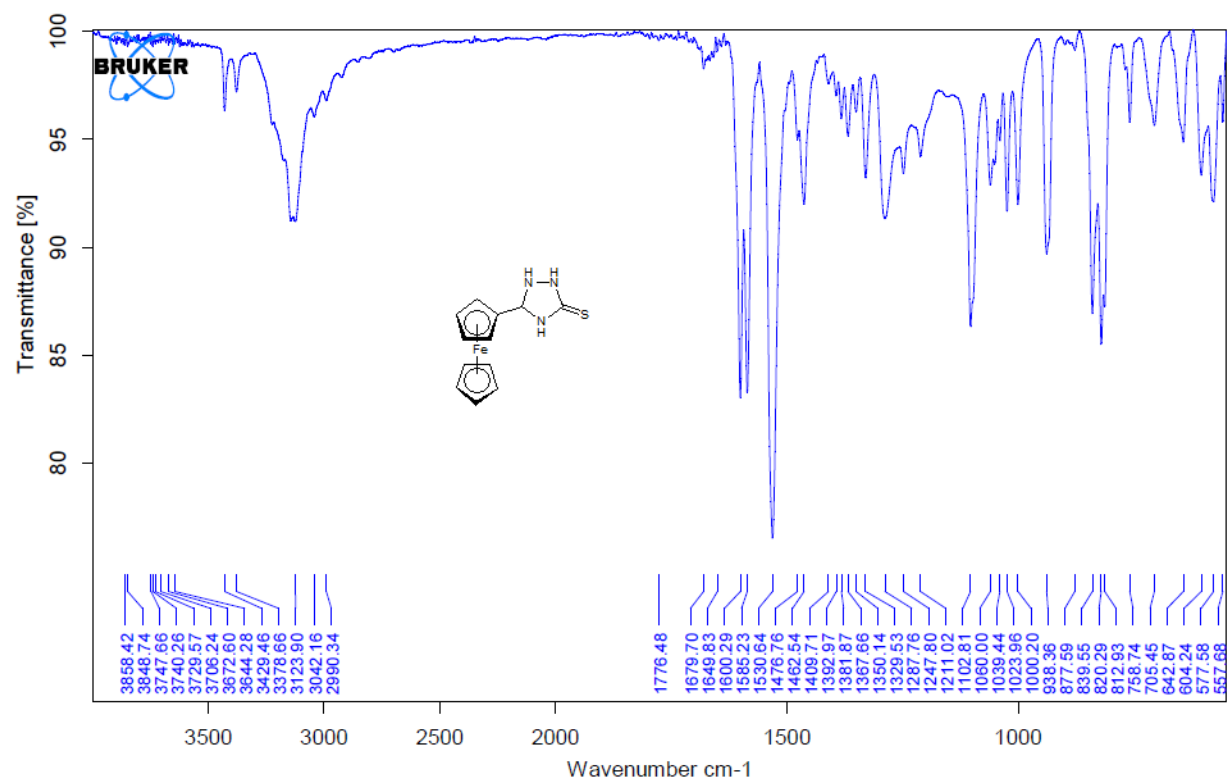


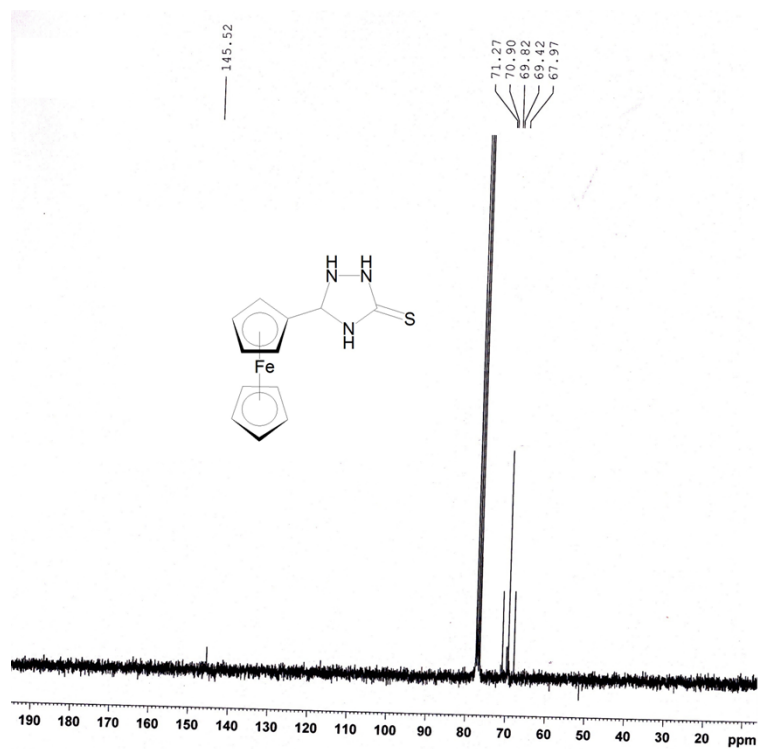
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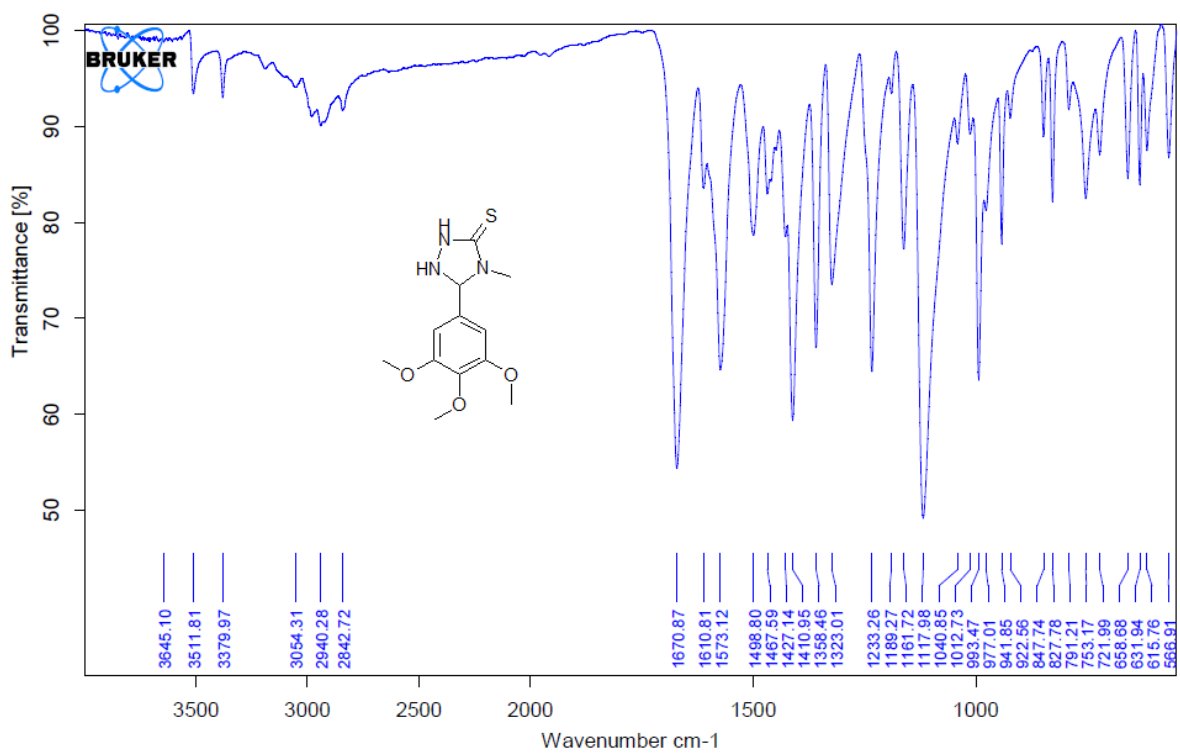


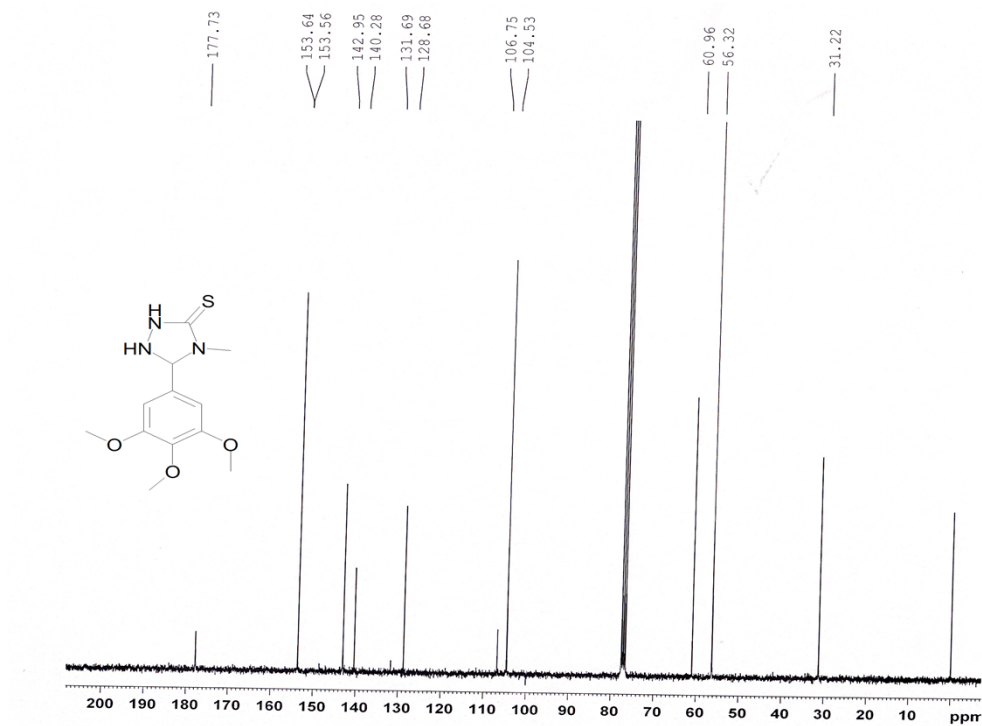
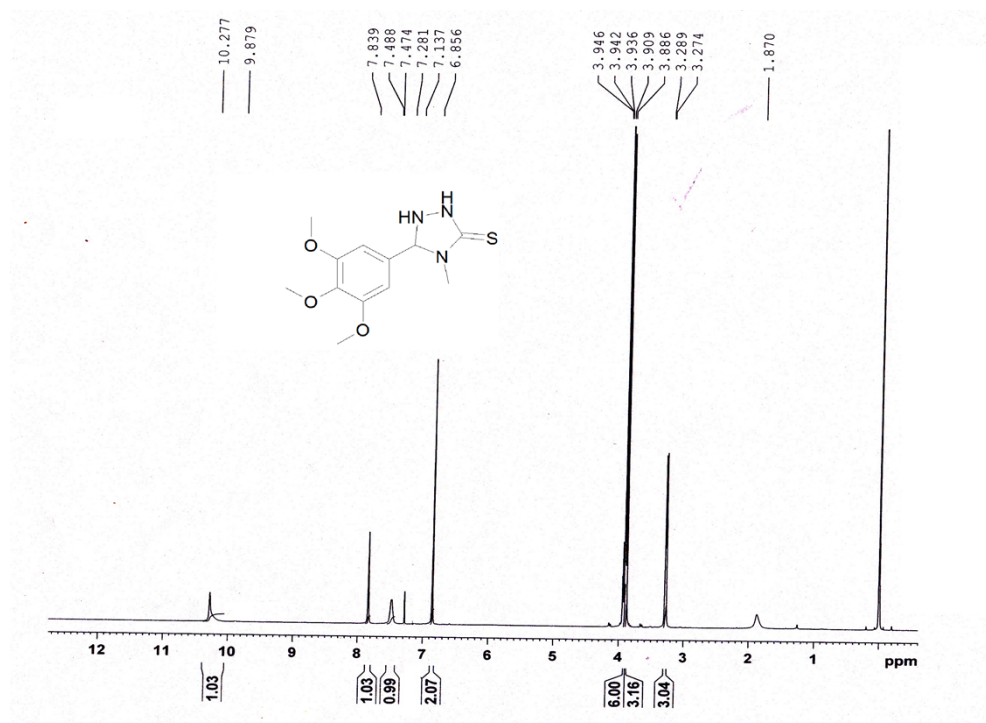
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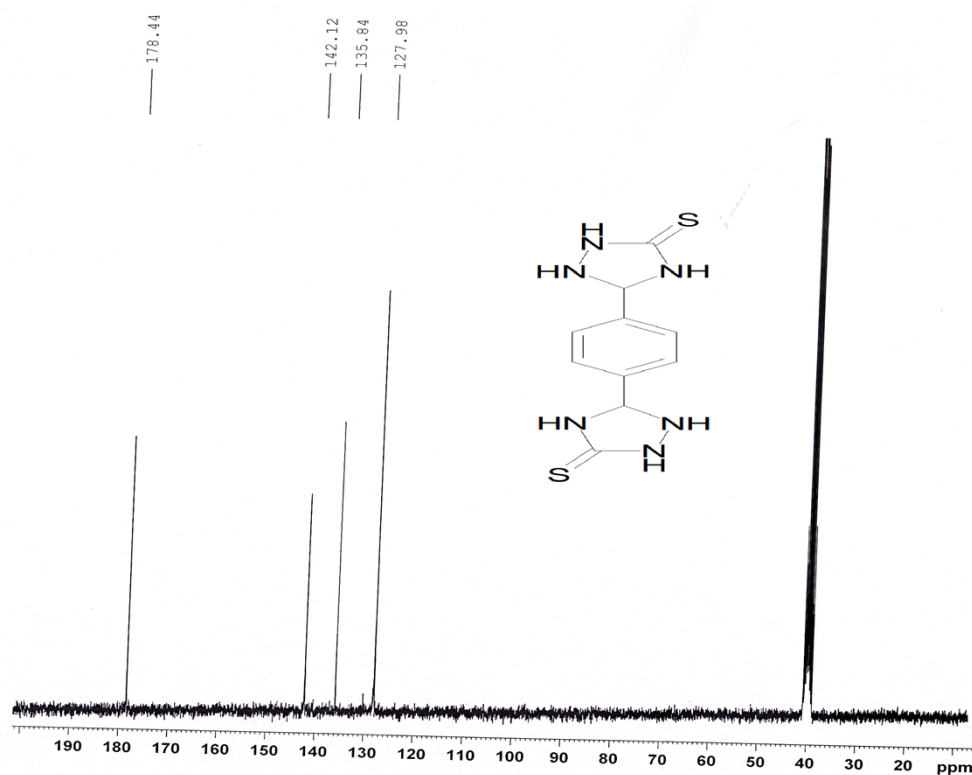
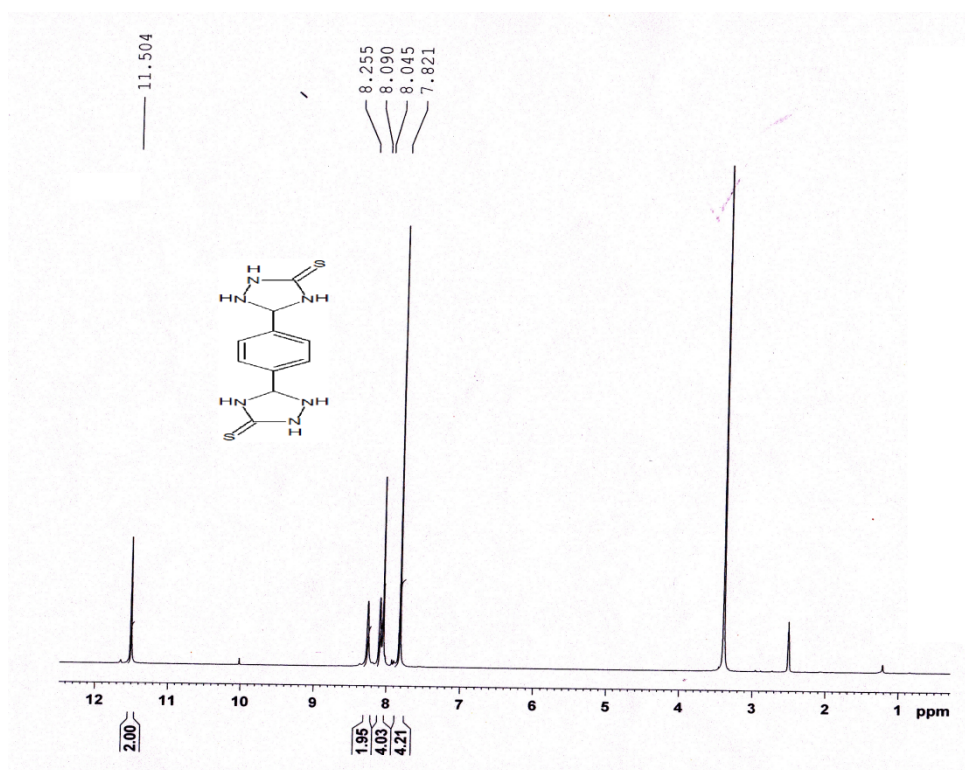


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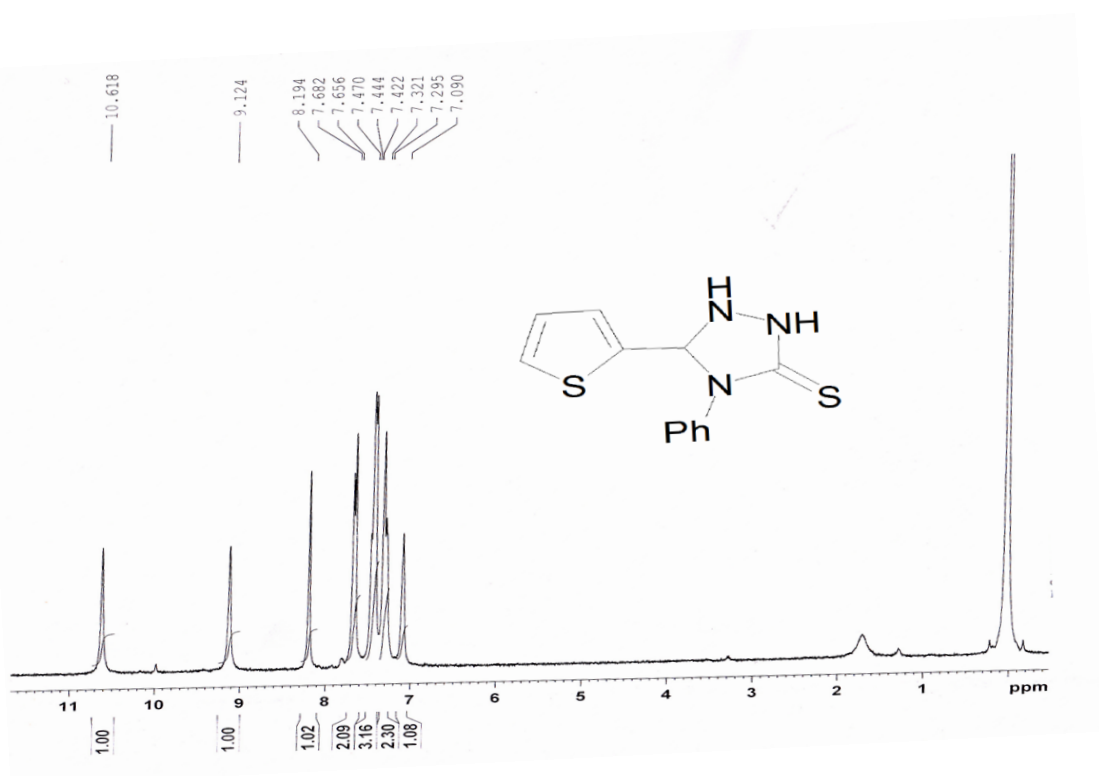
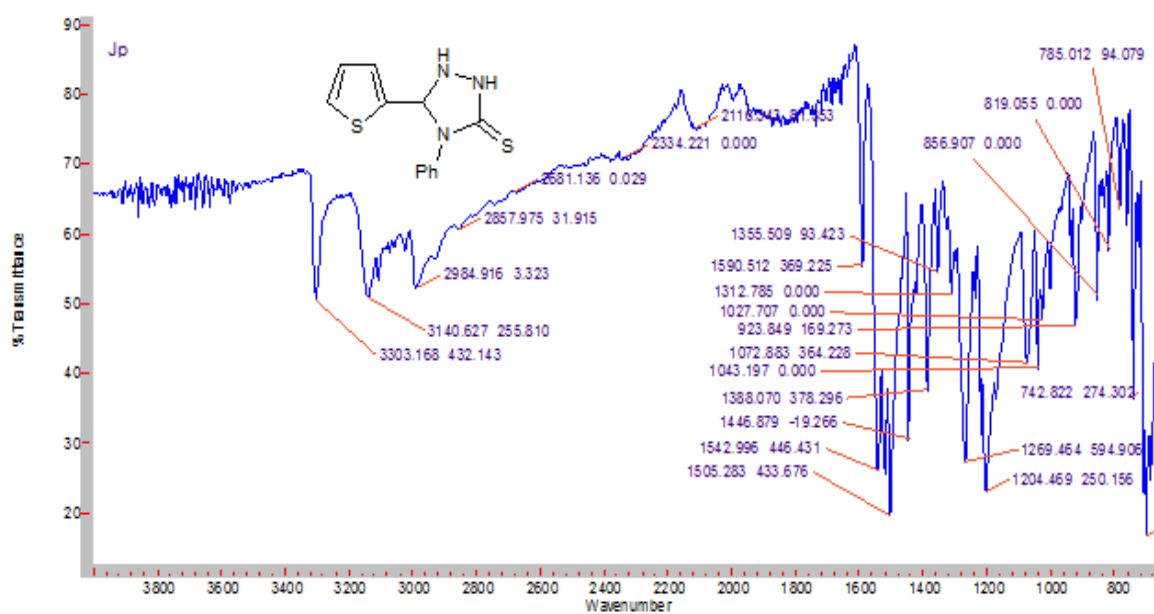


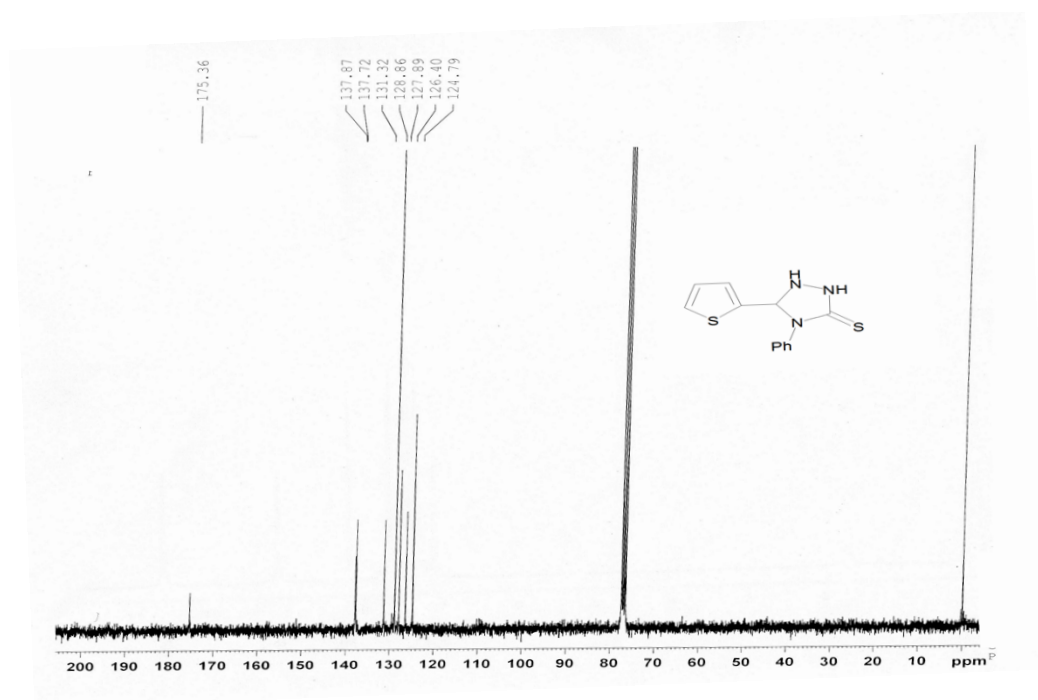


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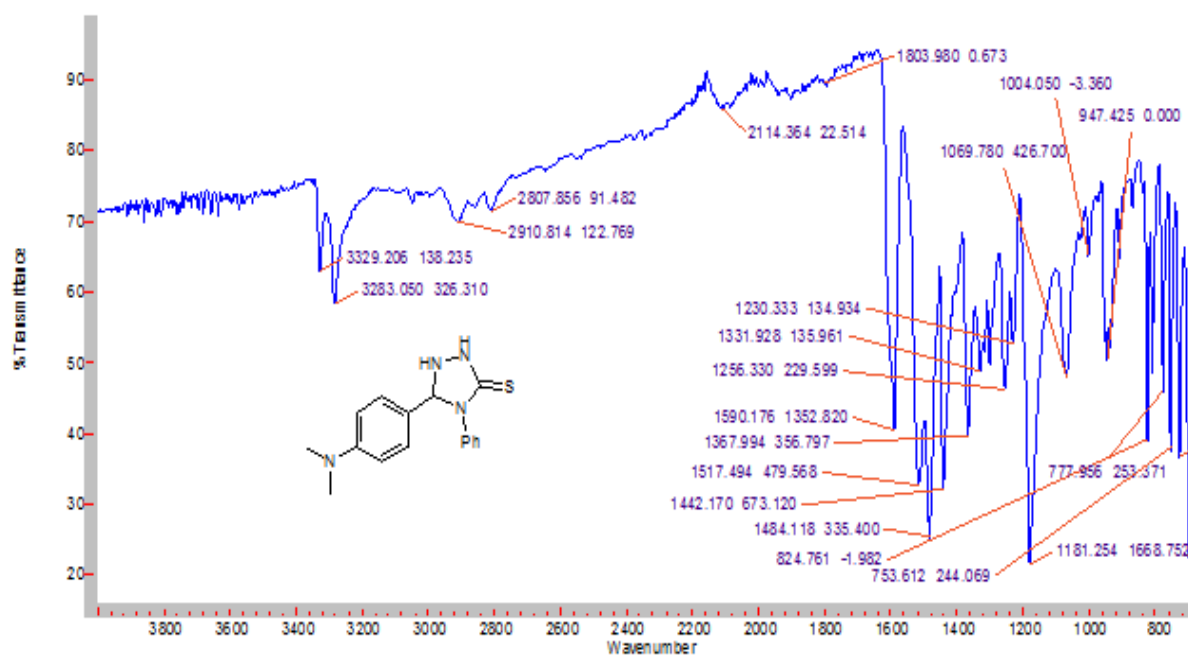


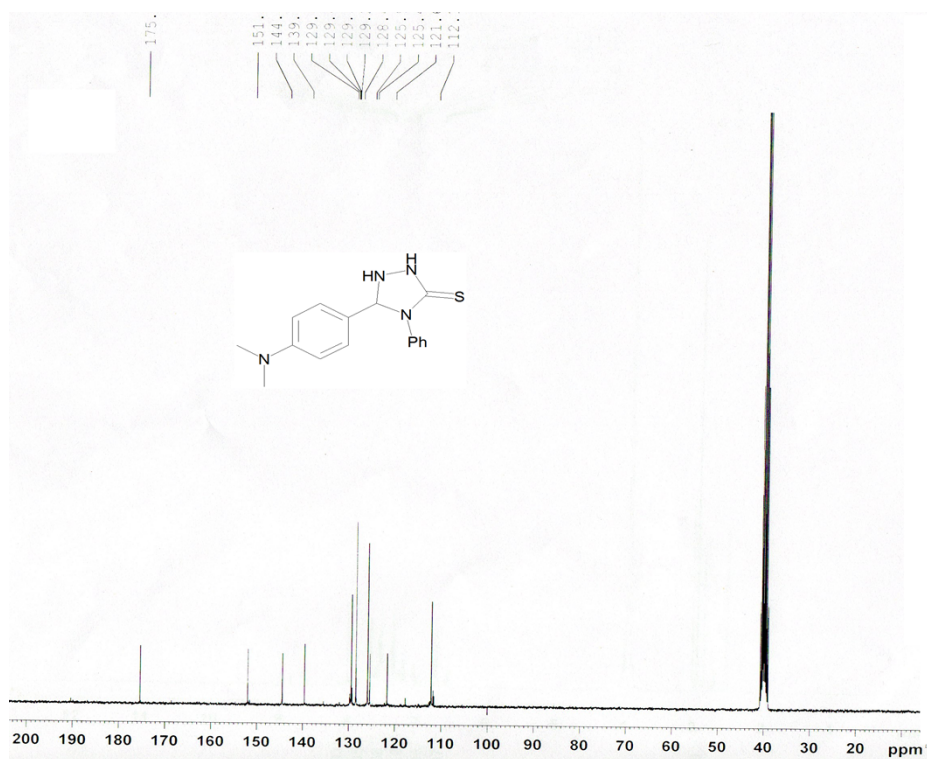
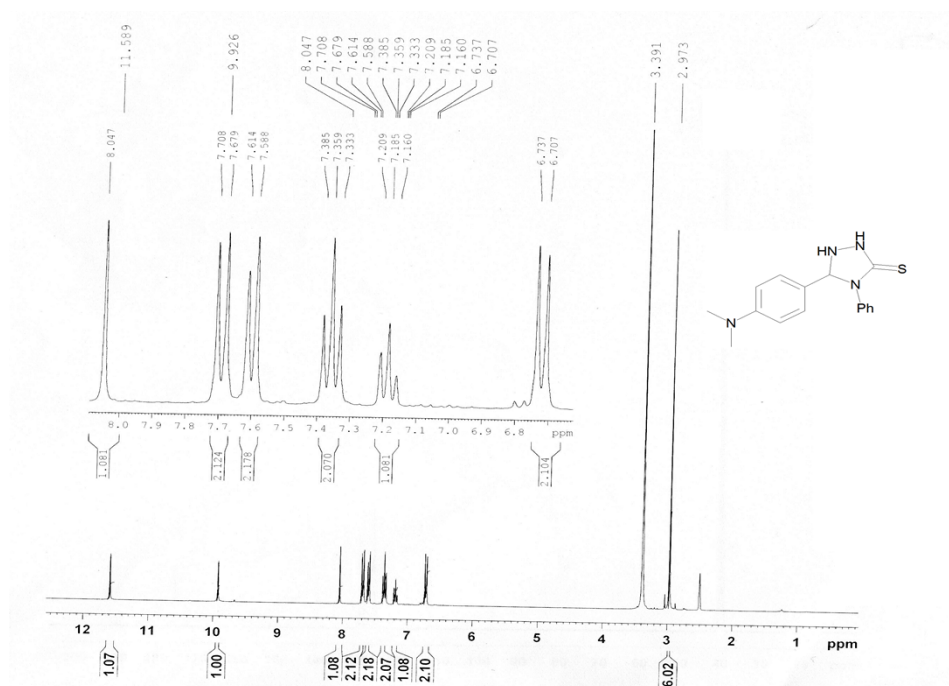
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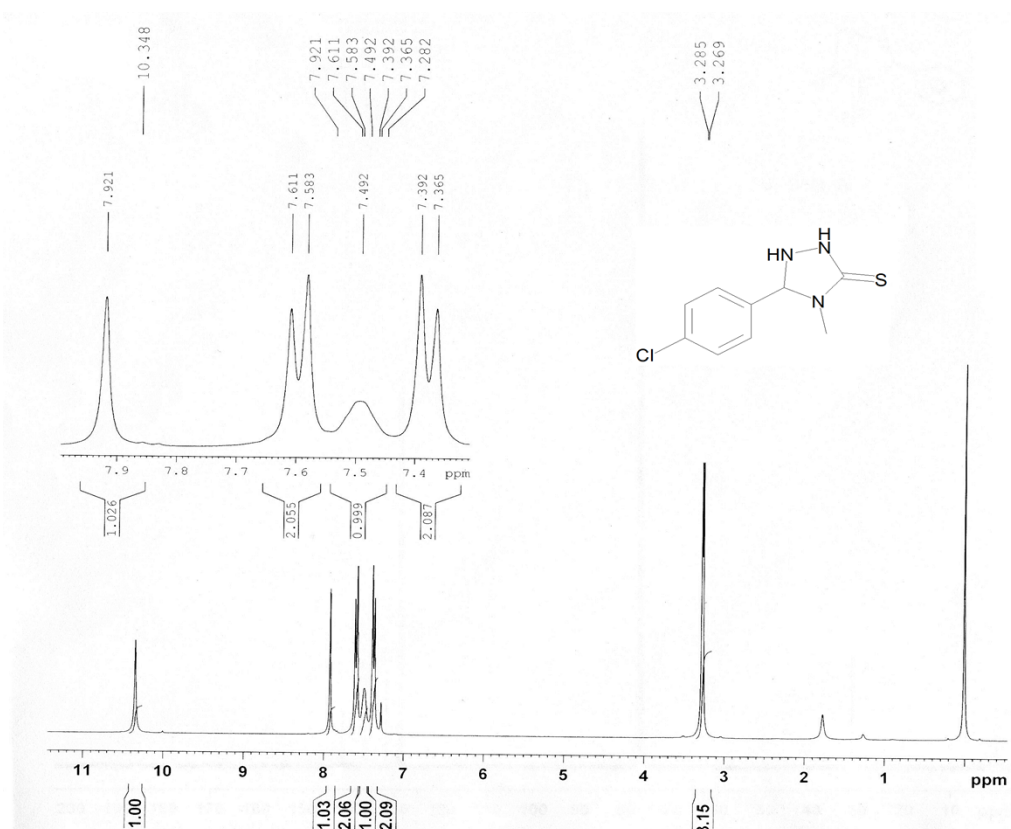
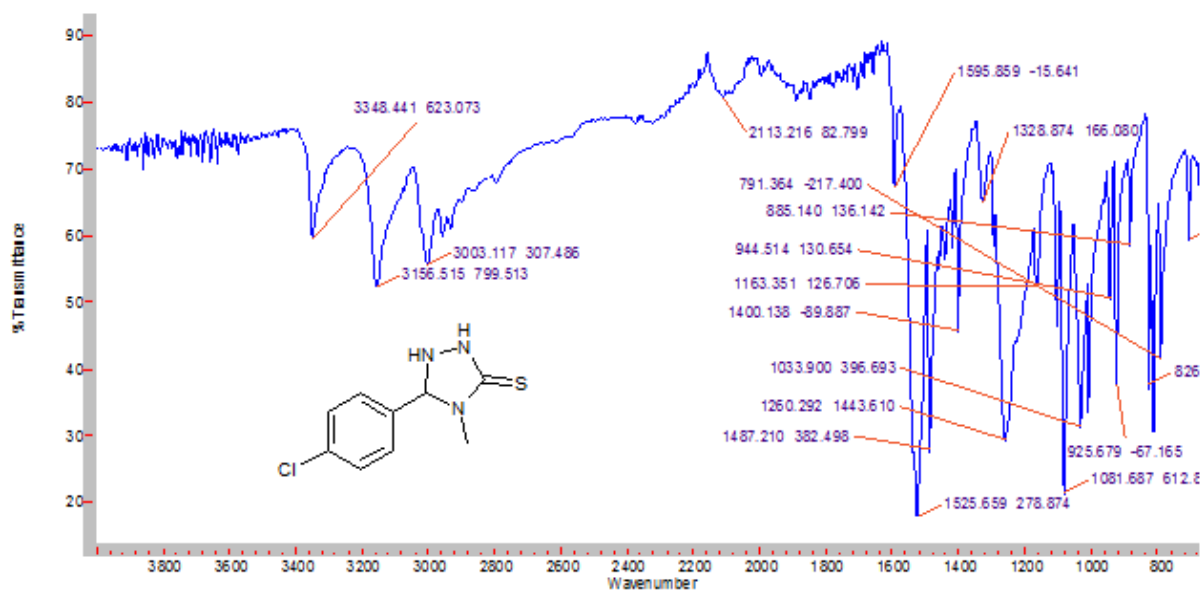


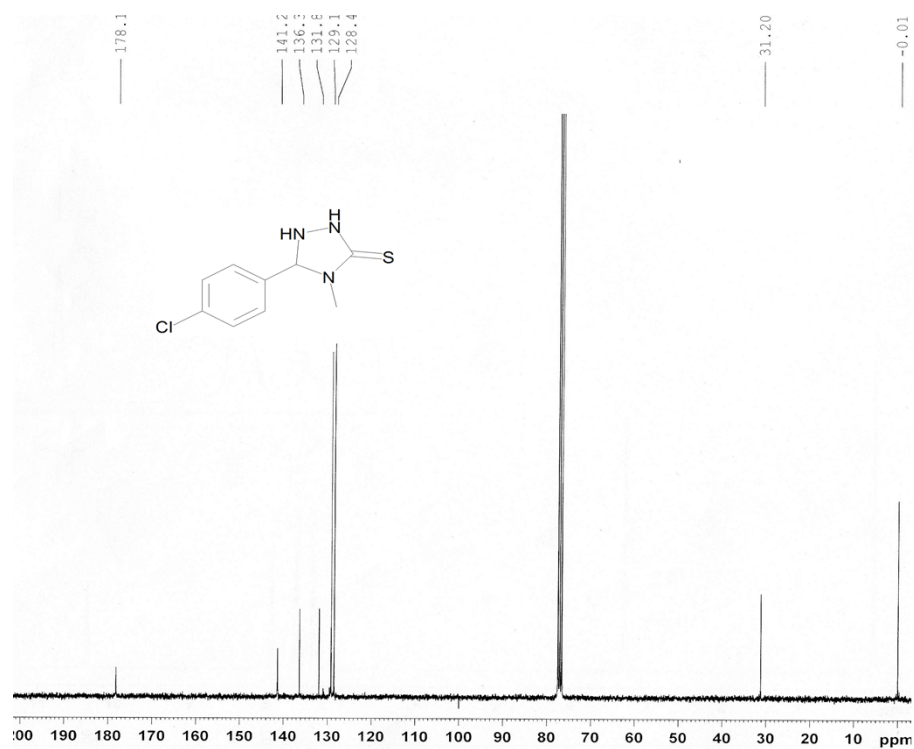
Entry j, Table 2:





Entry k, Table 2:





Entry 1, Table 2:

