Nano-$NiFe_2O_4$ as a Versatile and Recyclable Catalyst: An Efficient Protocol for the Synthesis of Aryl-1,2,4-triazolidine-3-thiones under Ball Milling Conditions

Pankaj V. Ledade,[1,3] Trimurti L. Lambat,[2*] Jitendra K. Gunjate,[3] Pooja M. Kadu, [4] Utpal J. Dongre, [4] Amitkumar V. Bhute,[5] Twinkle S. Wankhede,[6] Sami H. Mahmood,[7,*] and Subhash Banerjee[8,*]

Supporting Information

SI 1: **General information**

The chemicals needed were sourced from SRL, TCI, and ANCOTT, and they were all used without further purification. We used a Retsch Agate Grinding Jar (250 mL capacity) with the Planetary Ball Mill 100. The model number is 01.462.0220. All of the identified products showed physical and chemical properties that were almost identical to the real materials, including ^{1}H NMR, 13C NMR, FT-IR, and mass spectra. Using a melting point B-540 instrument, the melting points were determined. The ^{1}H NMR and ^{13}C NMR data were collected at SAIF, Punjab University, Chandigarh, India, using Bruker Avance Neo, 500 MHz NMR spectrometers, and HRMS. This FT-IR data was acquired by using SHIMADU at RTM, Nagpur University.

SI2: **The experimental procedure for the preparation of $NiFe_2O_4$ nanoparticles:**

The $NiFe_2O_4$ nanoparticles were synthesised via a straightforward sol-gel method[61] using readily available precursors: ferric chloride ($FeCl_3.6H_2O$), nickel chloride ($NiCl_2.6H_2O$), distilled water, and sodium hydroxide. In the typical procedure, a 0.2 M ferric chloride solution (20 mL) and a 0.1 M nickel chloride solution (20 mL) were prepared and mixed under vigorous stirring for 2 hours at 80 °C. Subsequently, 0.3 M NaOH was incrementally added until the pH reached 12, resulting in the formation of brown precipitates. The precipitates were then isolated through centrifugation and dried in a hot air oven for 4 hours at 100 °C, followed by calcination at 550 °C for 6 hours.

SI3: **The experimental procedure for the preparation of $CuFe_2O_4$ nanoparticles:**

The synthesis of $CuFe_2O_4$ nanoparticles was conducted in accordance with established methodologies as documented in the literature[62].A solution comprising $Cu(NO_3)_2$ (0.001 mol) and $FeCl_3 \cdot 6H_2O$ (0.002 mol) was prepared, maintaining a stoichiometric molar ratio of Cu^{2+}/Fe^{3+} at 1:2. The mixture was subjected to vigorous stirring for a duration of 2 hours at a temperature of 80 °C. Subsequently, a 0.3 M NaOH solution was incrementally added to the solutions until a pH of 12 was attained, resulting in the formation of a black precipitate. The sample was subsequently subjected to centrifugation, followed by washing with distilled water, and then placed in a hot air oven for drying at 100 °C for a duration of 4 hours. Then the resulting powder was calcinated at 550° C in a furnace for 2 hours.

SI4: **The experimental procedure for the preparation of $CoFe_2O_4$ nanoparticles:**

$CoFe_2O_4$ nanoparticles were synthesized in accordance with established methodologies documented in the literature[63].Initially, a homogeneous solution of 2.0 g of anhydrous sodium acetate was prepared in 30 mL of ethylene glycol through vigorous stirring at room temperature. Subsequently, 1.5 mmol of $CoCl_2 \cdot 6H_2O$ and 3.0 mmol of $FeCl_3 \cdot 6H_2O$ were added slowly to the homogeneous sodium acetate solution, maintaining a stoichiometric molar ratio of Co^{2+}/Fe^{3+} of 1:2. The mixture was subjected to vigorous stirring at a temperature of 70 °C for a duration of 2 hours to achieve a homogeneous solution. The solution was subsequently subjected to centrifugation, followed by washing with distilled water and drying in an open atmospheric environment. The resultant powder underwent calcination at a temperature of 550° C within a furnace for a duration of 2 hours.

SI5: **The experimental procedure for the preparation of $ZnFe_2O_4$ nanoparticles:**

$ZnFe_2O_4$ nanoparticles were synthesized utilizing a previously established methodology[64]. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 M) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.2 M) was prepared, maintaining a stoichiometric molar ratio of Zn^{2+}/Fe^{3+} of 1:2, in 50 mL of distilled water. Gelation was achieved through the addition of 0.1 M urea solution (300 mL). The resultant solution was subjected to vigorous mixing under stirring conditions at 55 °C until gel formation occurred. This gel was subsequently dried at 100 °C for a duration of 1 hour in a hot air oven. The resultant dried gel underwent calcination at a temperature of 550° C within a furnace for a duration of 2 hours.

SI6: **General Procedure for synthesis of 5-aryl-1,2,4- triazolidine-3-thione scaffolds**

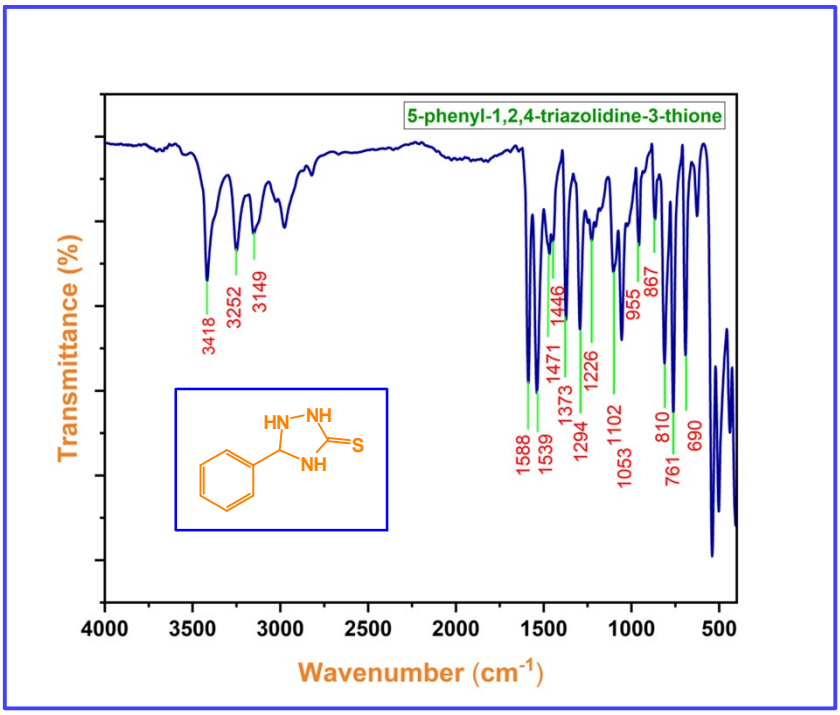
Representative procedure for the: 5-phenyl-1,2,4- triazolidine-3-thione (3a)

Ball-milling of a 25 mL stainless steel beaker at a rotation rate of 600 rpm took place during 30 minutes using six milling balls with nominal diameter (1/4 10 mm). In this process, Nano $NiFe_2O_4$ (10 mol%, 23.44 mg) as a catalyst was added to benzaldehyde 1a (1.0 mmol 106.12mg), thiosemicarbazide (1 mmol 91.14mg) / 4-methylthiosemicarbazide (1 mmol 105.17mg). The operation of ball-milling was carried out by reversing directions of rotation, with a 30-second pause between consecutive sessions of milling. After the reaction was complete, an external magnet was used to collect the $NiFe_2O_4$ nanoparticles out of the reaction medium. The crude product (3a) was then recrystallized using ethanol. The recovered nano $NiFe_2O_4$ was washed with a solution of ethanol and water, 1:1, after which it was dried in a hot-air oven at 60 ° C for 1 hour duration. The catalyst was dried and reused in subsequent cycles of reaction.

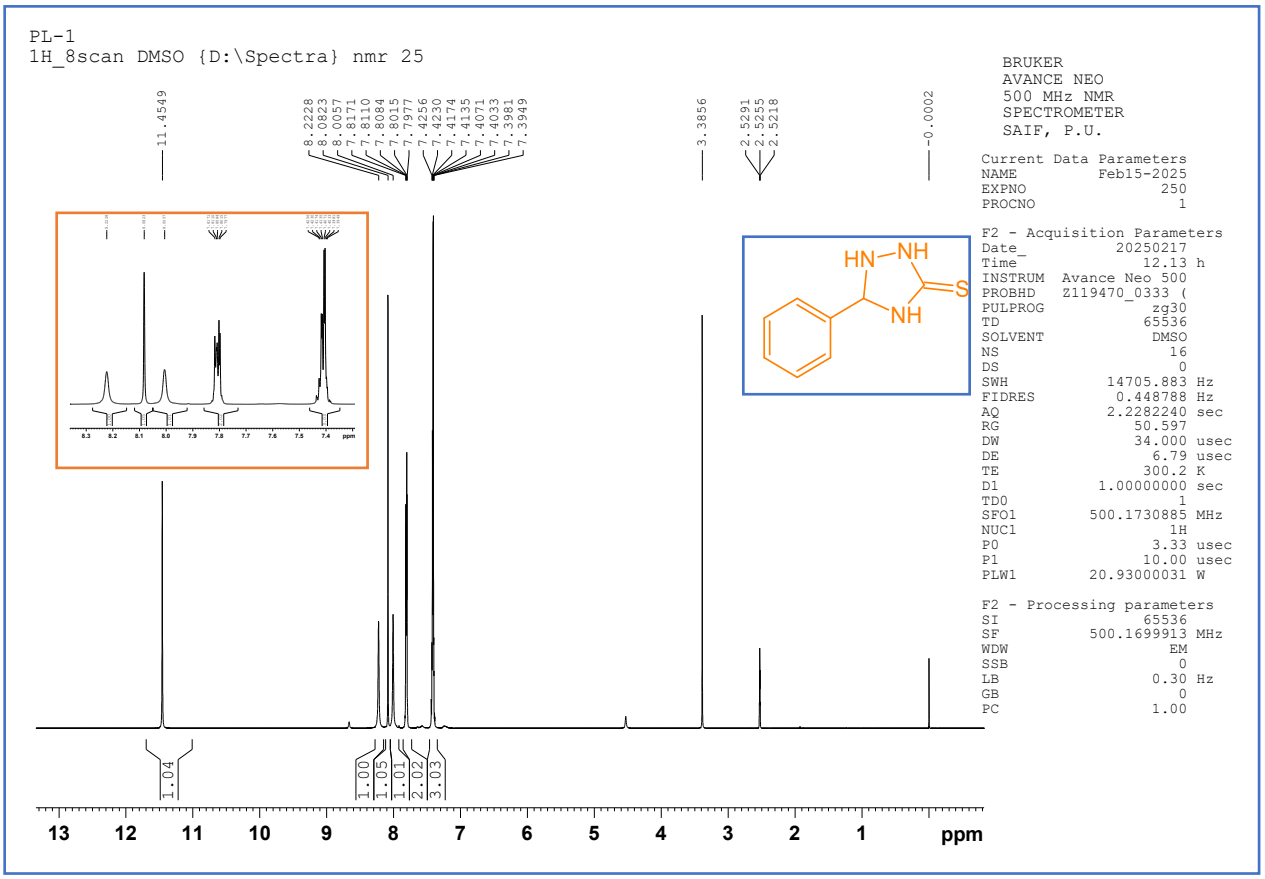
SI7: **FTIR,^{1}H NMR,^{13}C NMR Spectra of 5-aryl-1,2,4- triazolidine-3-thione scaffolds (3a-3n)**

5-phenyl-1,2,4-triazolidine-3-thione (3a)

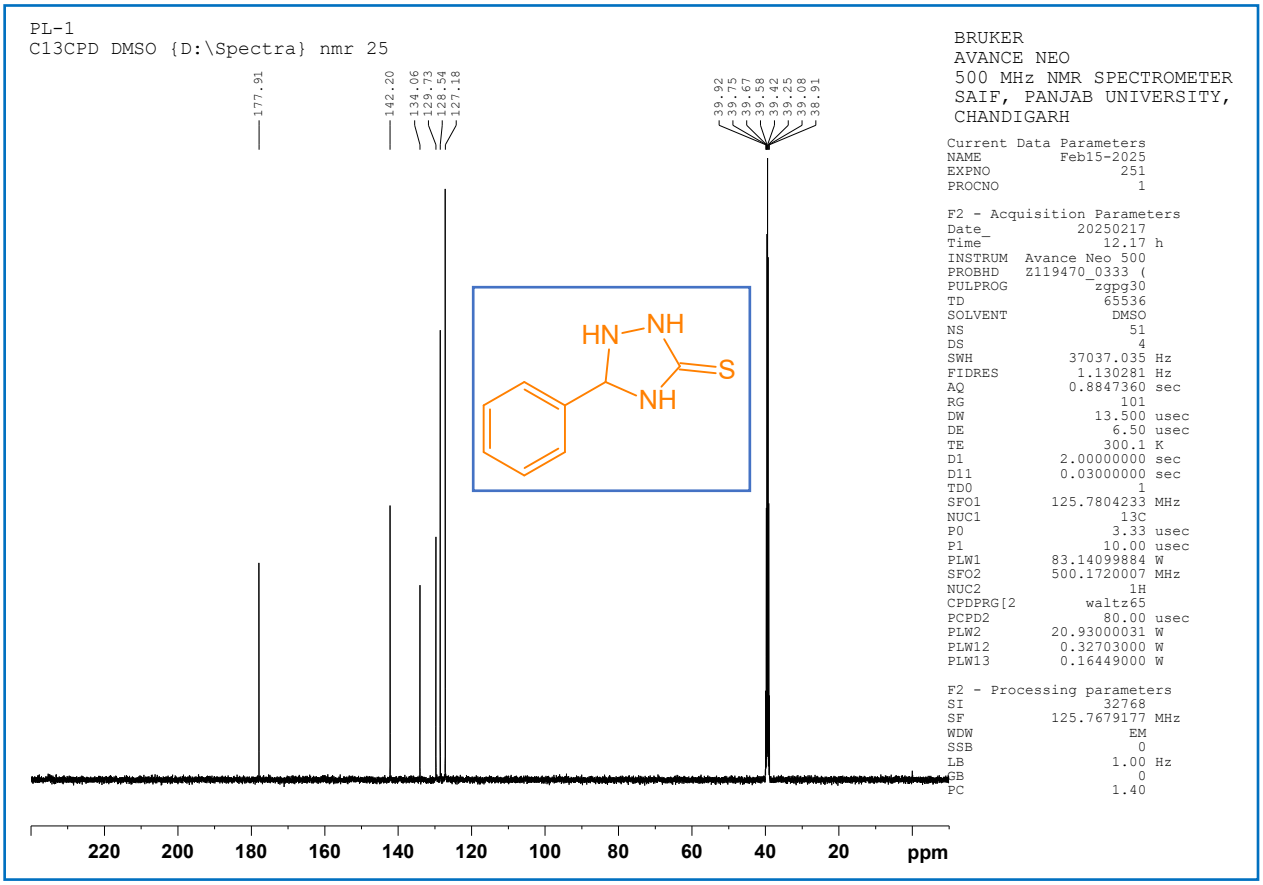
White solid; M.P. 153-154 ^{0}C; IR (KBr): 3418, 3252, 3149, 1588, 1539, 1471, 1446, 1373, 1294,1226, 1102, 1053, 955, 867, 810, 761, 690 cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d6) : δ 7.3949-7.4256 (t, 3H, *J*=15.5Hz), 7.7977-7.8171 (q, 2H, *J*=10Hz), 8.0057 (s, 1H, -NH), 8.0823 (s, 1H), 8.2228 (s, 1H, -NH), 11.4549 (s, 1H, -NH). ^{13}C-NMR (500 MHz, DMSO-d6): 127.18, 128.54, 129.73, 134.06, 142.20, 177.91; HRMS {observed [M+1] peak: 180.05 (m/z)} {calculated [M] peak: 179.25 (m/z)}



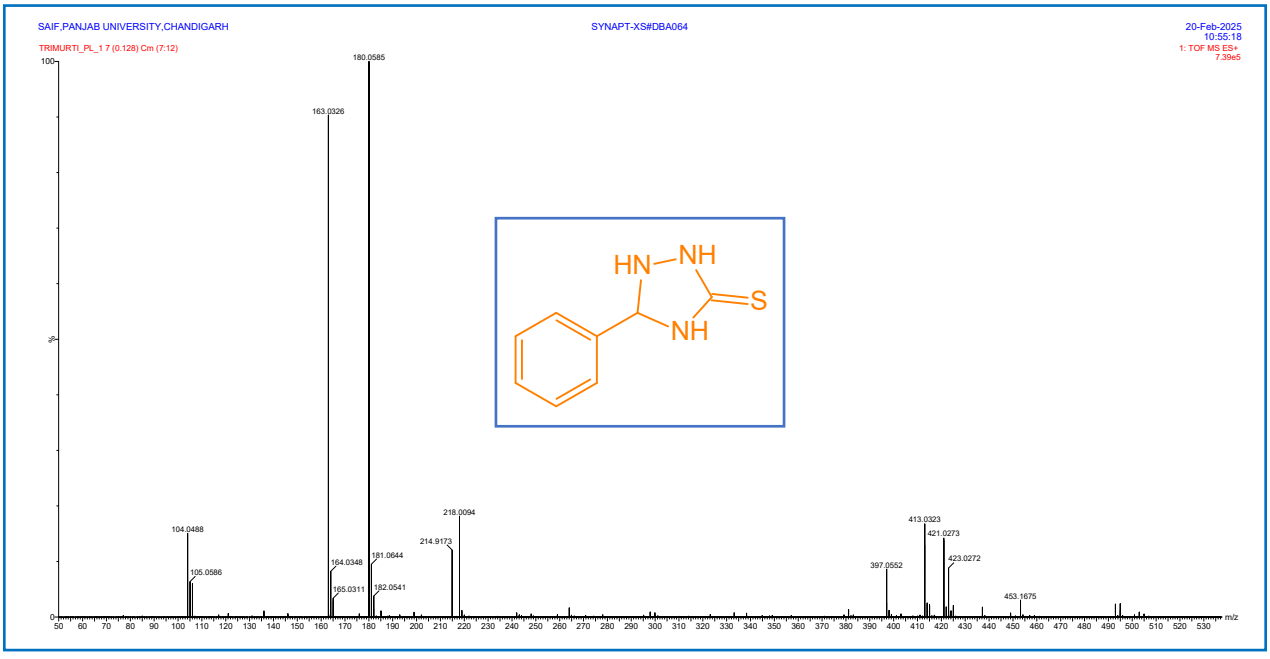
FTIR of 5-phenyl-1,2,4-triazolidine-3-thione (3a)



[1]HNMR of 5-phenyl-1,2,4-triazolidine-3-thione (3a)



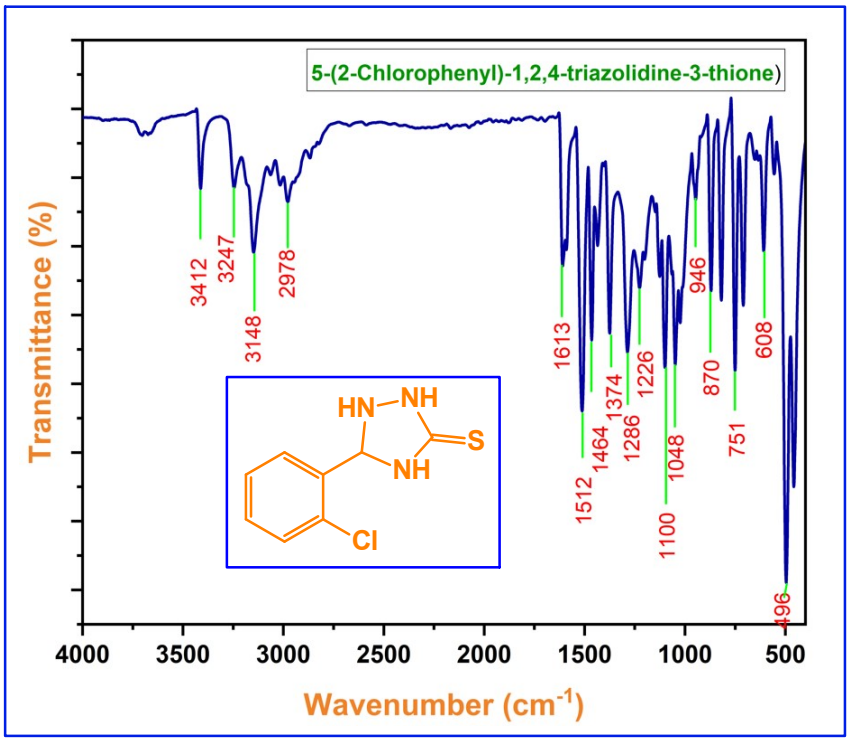
^{13}C-NMR of 5- phenyl-1,2,4-triazolidine-3-thione (3a)



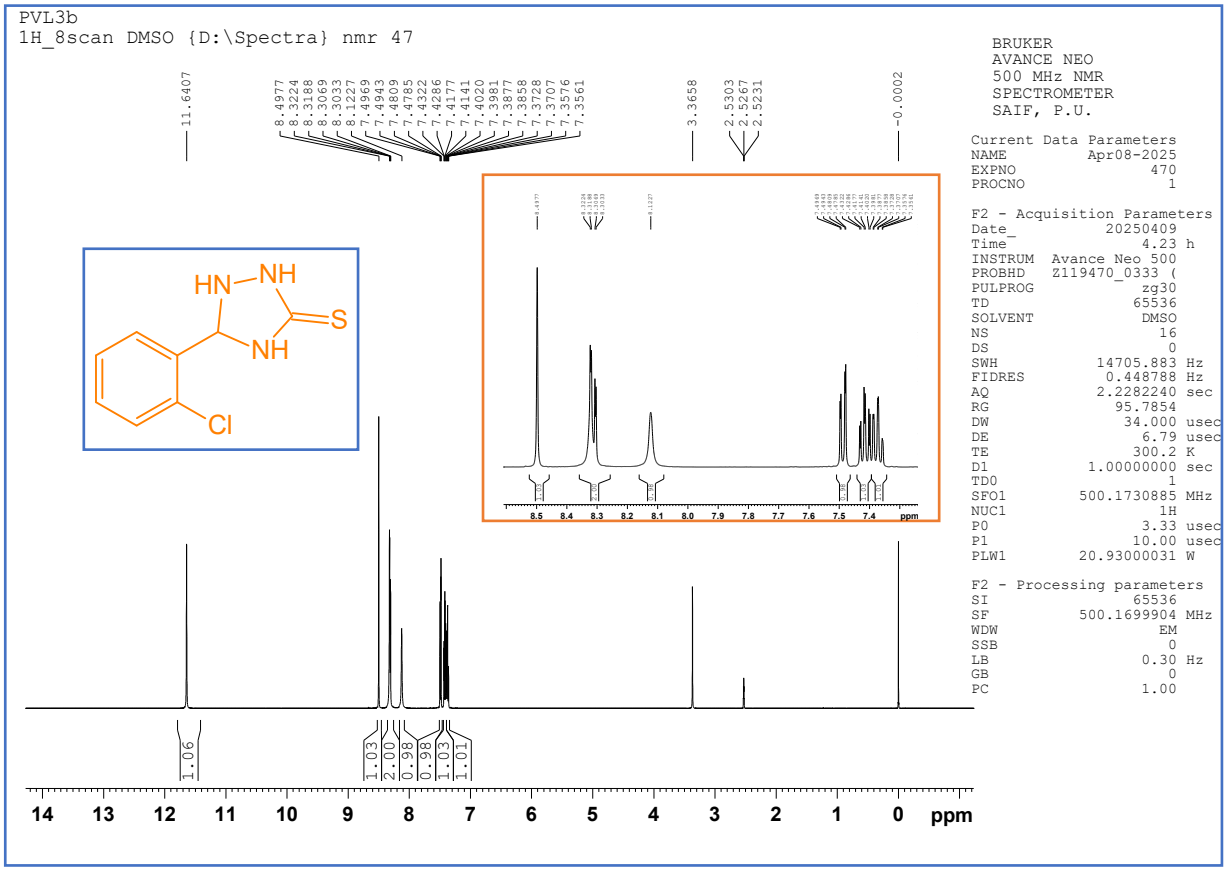
HRMS of 5-phenyl-1,2,4-triazolidine-3-thione (3a)

5-(2-chlorophenyl)-1,2,4-triazolidine-3-thione (3b)

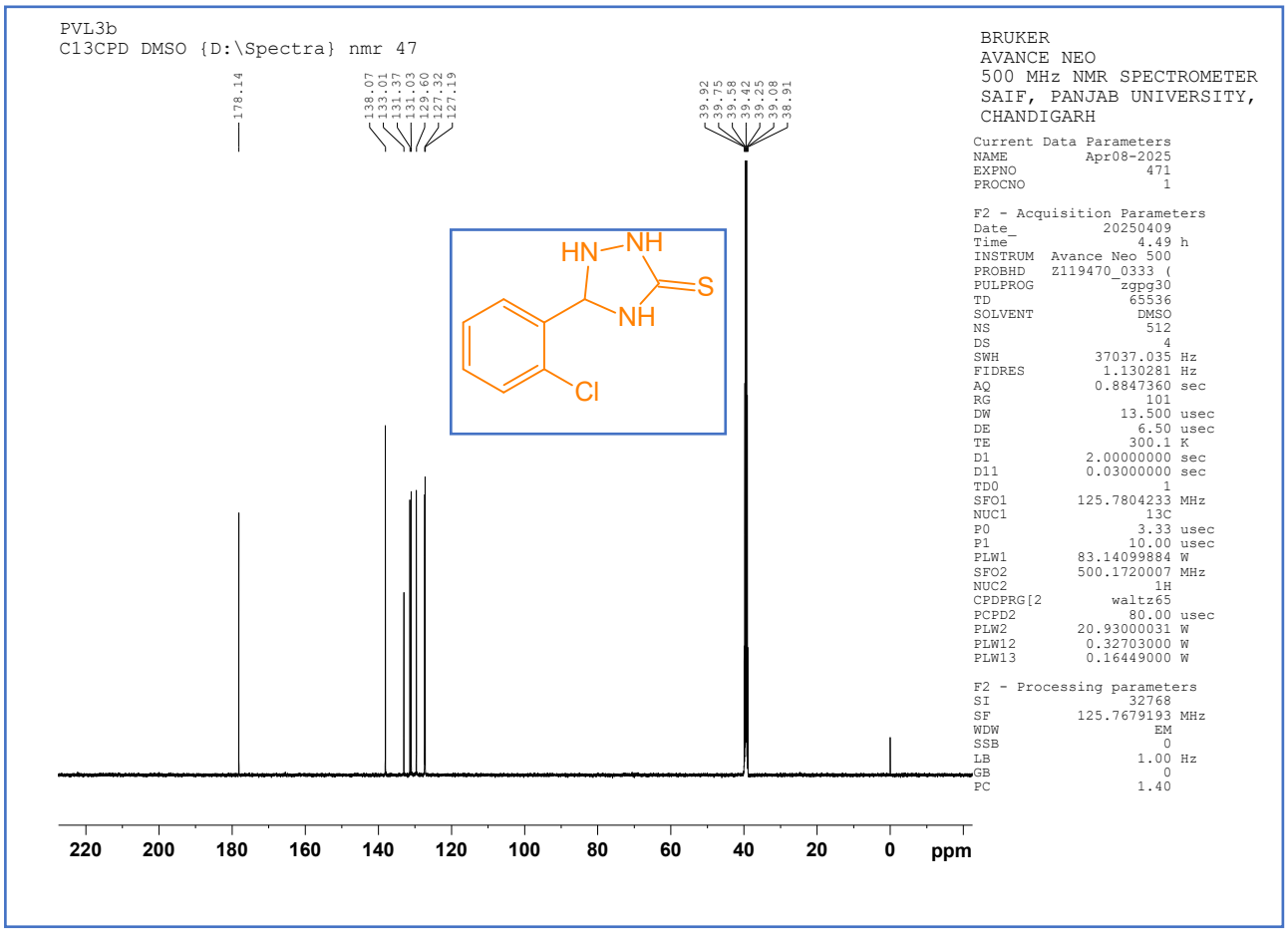
White crystal, Mp. 200-201 ˚C; IR (KBr): 3412, 3247, 3148, 2978, 1613, 1512, 1464, 1374, 1286, 1226, 1100, 1048, 946, 870, 751, 608, 496 cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d6): δ 7.3561-7.4322 (m, 2H, ArH, *J*=38.45Hz), 7.4785-7.496 (m, 1H, ArH, *J*=9Hz), 8.122 (s, 1H, CH), 8.303-8.322 (m, 1H, ArH, *J*=9.5Hz), 8.28 (s, 1H, NH), 8.4977 (s, 1H, NH), 11.6407 (s, 1H, NH); ^{13}C-NMR (500 MHz, DMSO-d6): 127.19, 127.32, 129.60, 131.03, 131.37, 133.01, 138.07, 178.14; HRMS {observed [M+1] peak: 214.02 (m/z)} {calculated [M] peak: 213.69 (m/z)}



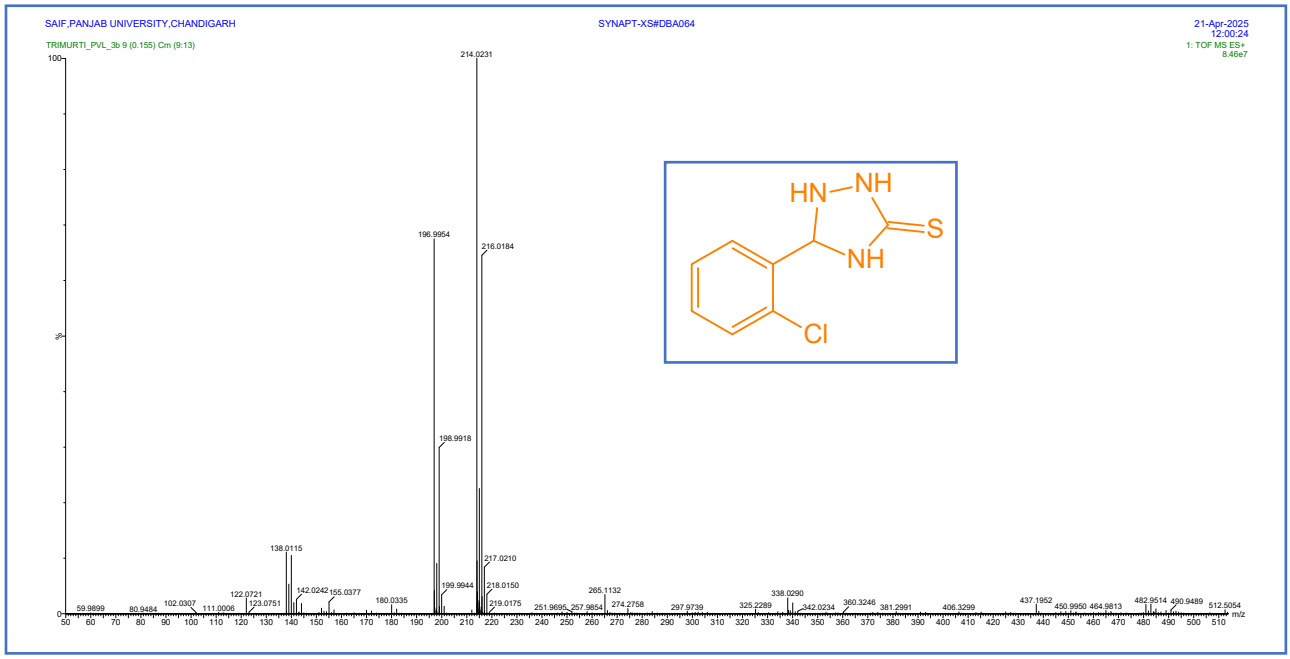
FTIR of 5-(2-chlorophenyl)-1,2,4-triazolidine-3-thione (3b)



[1]HNMR of 5-(2-chlorophenyl)-1,2,4-triazolidine-3-thione (3b)



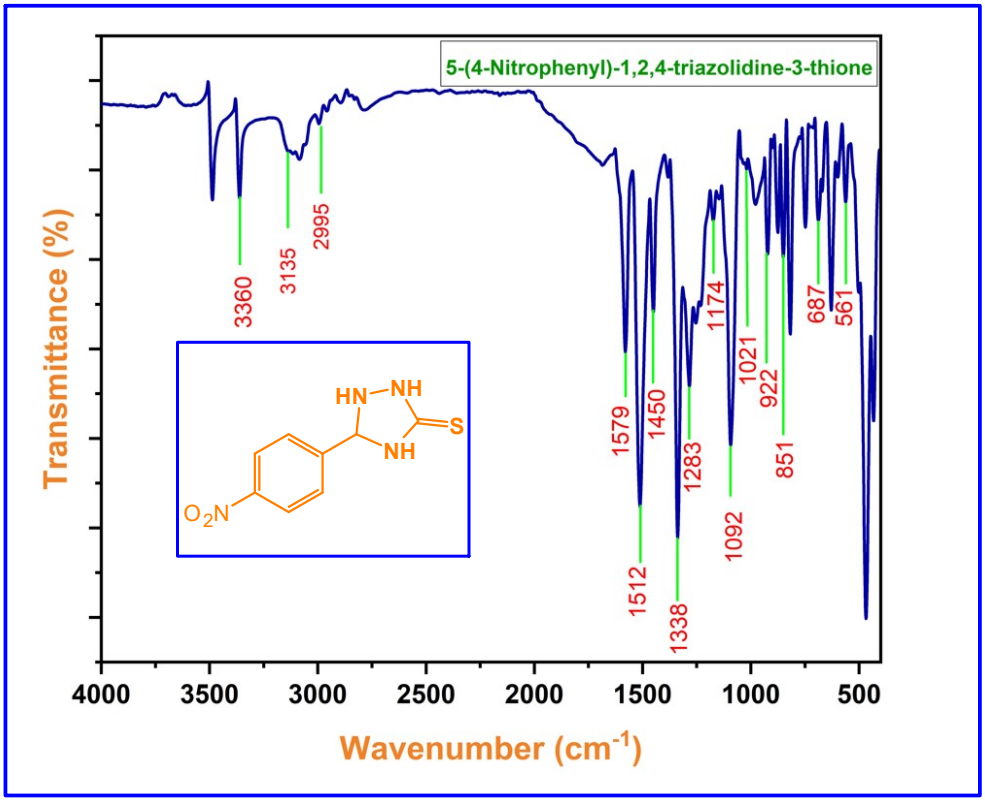
^{13}C-NMR of 5-(2-chlorophenyl)-1,2,4-triazolidine-3-thione (3b)



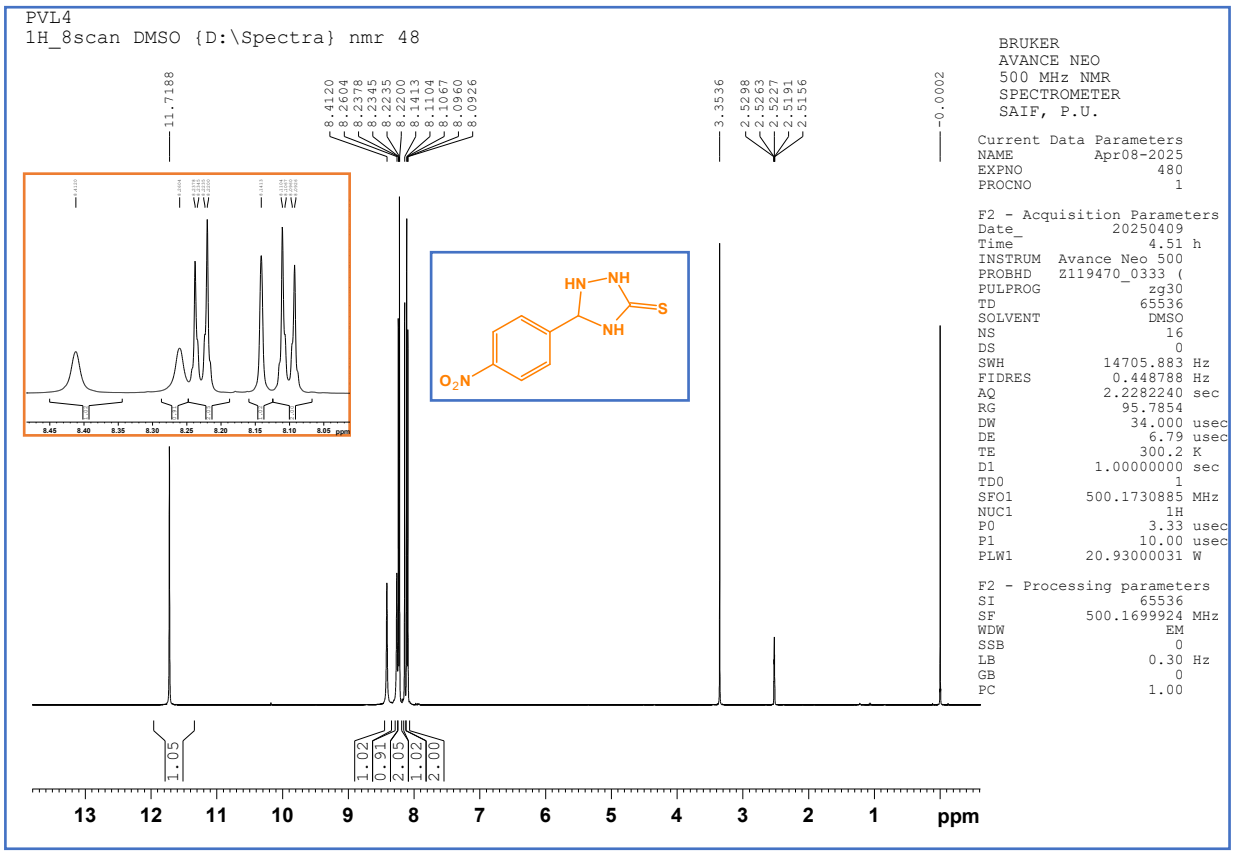
HRMS of 5-(2-chlorophenyl)-1,2,4-triazolidine-3-thione (3b)

5-(4-Nitrophenyl)-1,2,4-triazolidine-3-thione (3c)

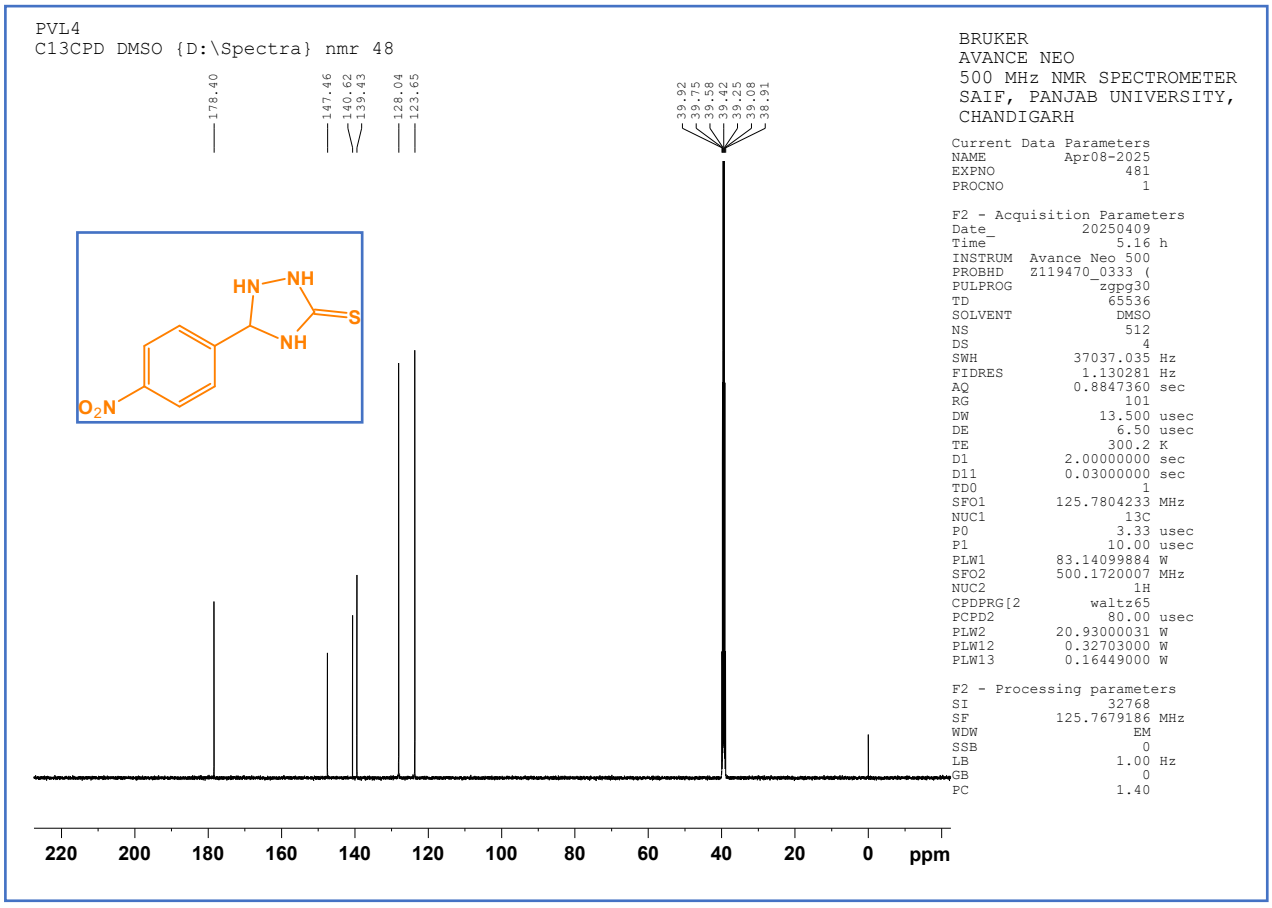
Yellow solid, Mp. 227-228 ^{o}C; IR (KBr): 3360, 2995, 1579, 1512, 1450, 1338, 1283, 1174, 1092, 1021, 922, 851, 687, 561 cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d6): δ 8.0926-8.1104 (d, 2H, ArH, J = 9 Hz), 8.2200-8.2378 (d, 2H, ArH, J = 8.5 Hz), 8.1413 (s, 1H, CH), 8.2604 (s, 1H, NH), 8.4120 (s, 1H, NH), 11.7188 (s, 1H, NH); ^{13}C-NMR (500 MHz, DMSO-d6): 123.65, 128.04, 139.43, 140.62, 147.46, 178.40; HRMS {observed [M+1] peak: 225.04 (m/z)} {calculated [M] peak: 224.24 (m/z)}.



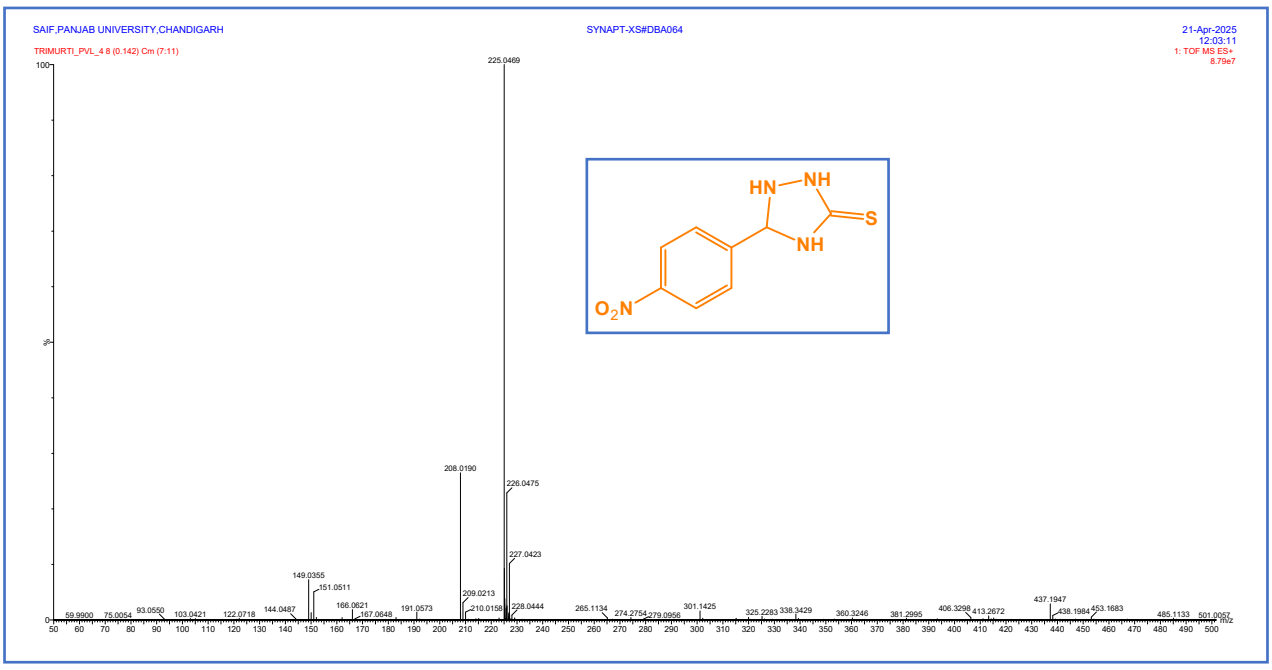
FTIR of 5-(4-Nitrophenyl)-1,2,4-triazolidine-3-thione (3c)



[1]HNMR of 5-(4-Nitrophenyl)-1,2,4-triazolidine-3-thione (3c)



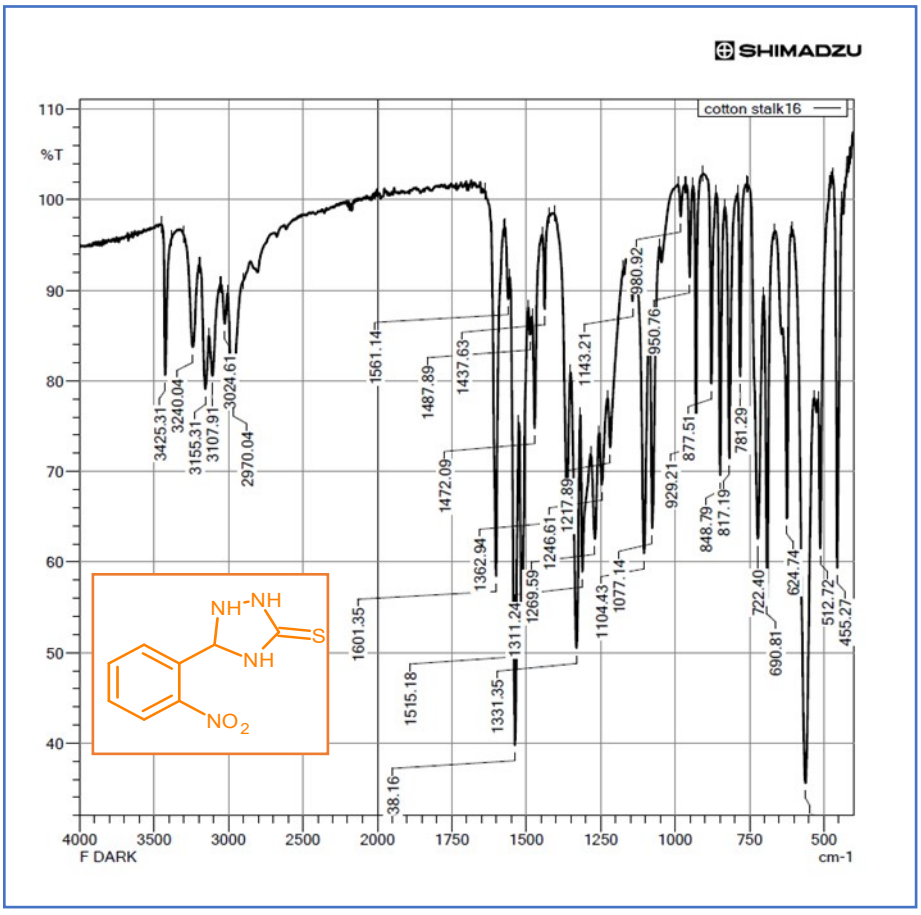
^{13}C-NMR of 5-(4-Nitrophenyl)-1,2,4-triazolidine-3-thione (3c)



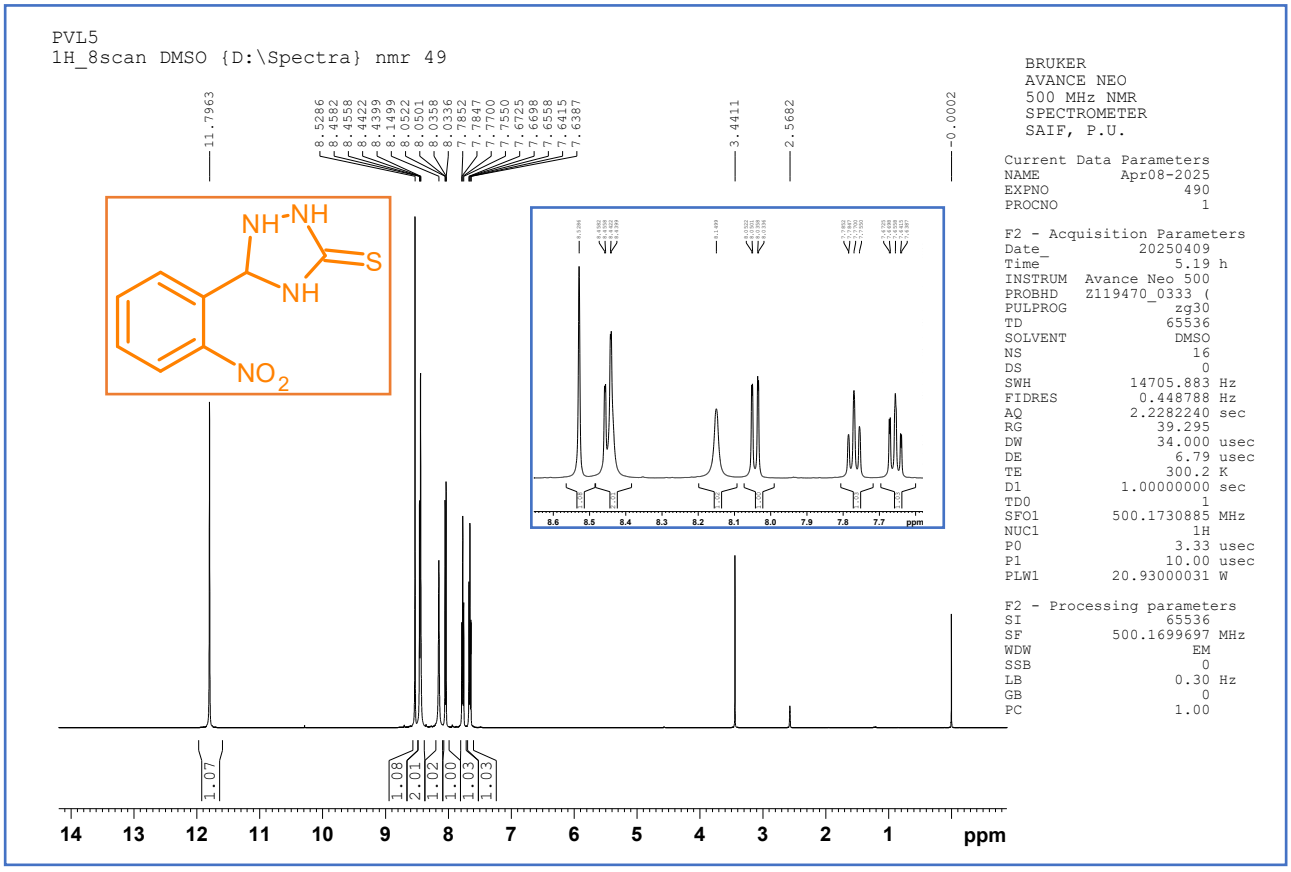
HRMS of 5-(4-Nitrophenyl)-1,2,4-triazolidine-3-thione (3c)

5-(2-Nitrophenyl)-1,2,4-triazolidine-3-thione (3d)

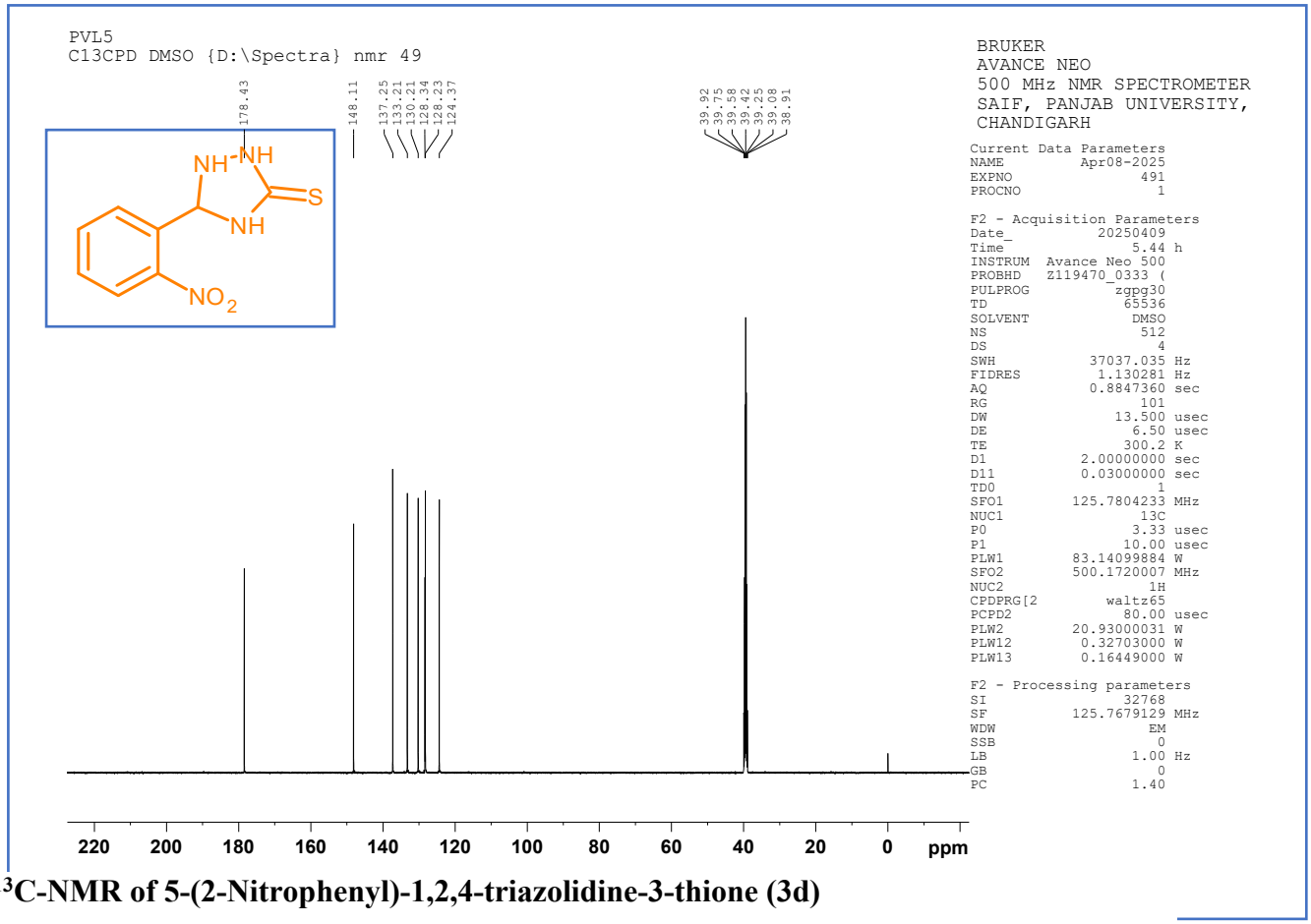
Yellow solid, Mp. 199-200 ˚C; IR (KBr): 3425,3107,3024,2970,1601,1515,1437,1331,1246,929,848,722,690,512 cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d6): δ 7.6387-7.6725 (m, 1H,ArH, *J* = 17 Hz), 7.7550-7.7852 (t, 1H, ArH, J = 15 Hz), 8.0336-8.0522 (dd, 1H, *J* = 9.5 Hz), 8.1499 (s, 1H, NH), 8.4399-8.4582 (dd, 2H, *J* = 9.5 Hz), 8.5286 (s, 1H,NH), 11.7963 (s, 1H, NH); 13C-NMR (500 MHz, DMSO-d6): 124.37, 128.23, 128.34, 130.21, 133.21, 137.25,148.11,178.43; HRMS {observed [M+1] peak: 225.04 (m/z)} {calculated [M] peak: 224.24 (m/z)}.



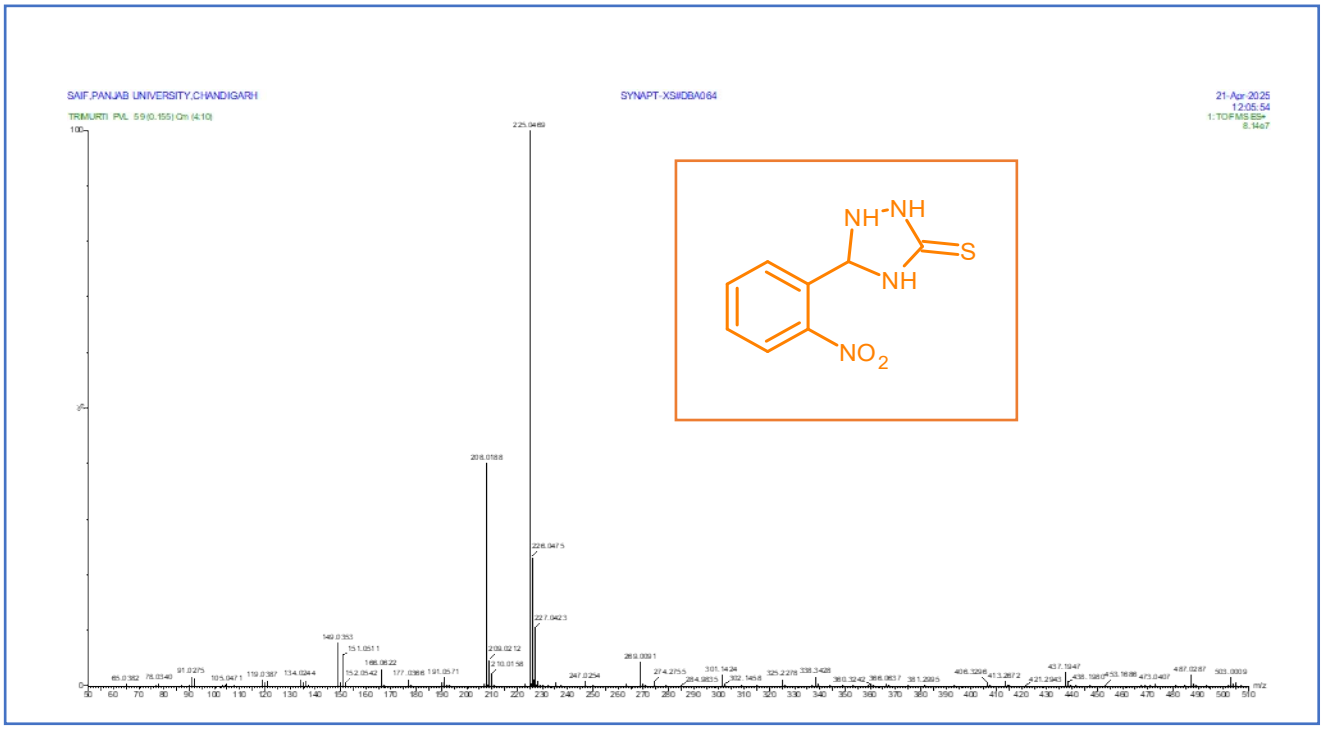
FTIR of 5-(2-Nitrophenyl)-1,2,4-triazolidine-3-thione (3d)



[1]HNMR of 5-(2-Nitrophenyl)-1,2,4-triazolidine-3-thione (3d)



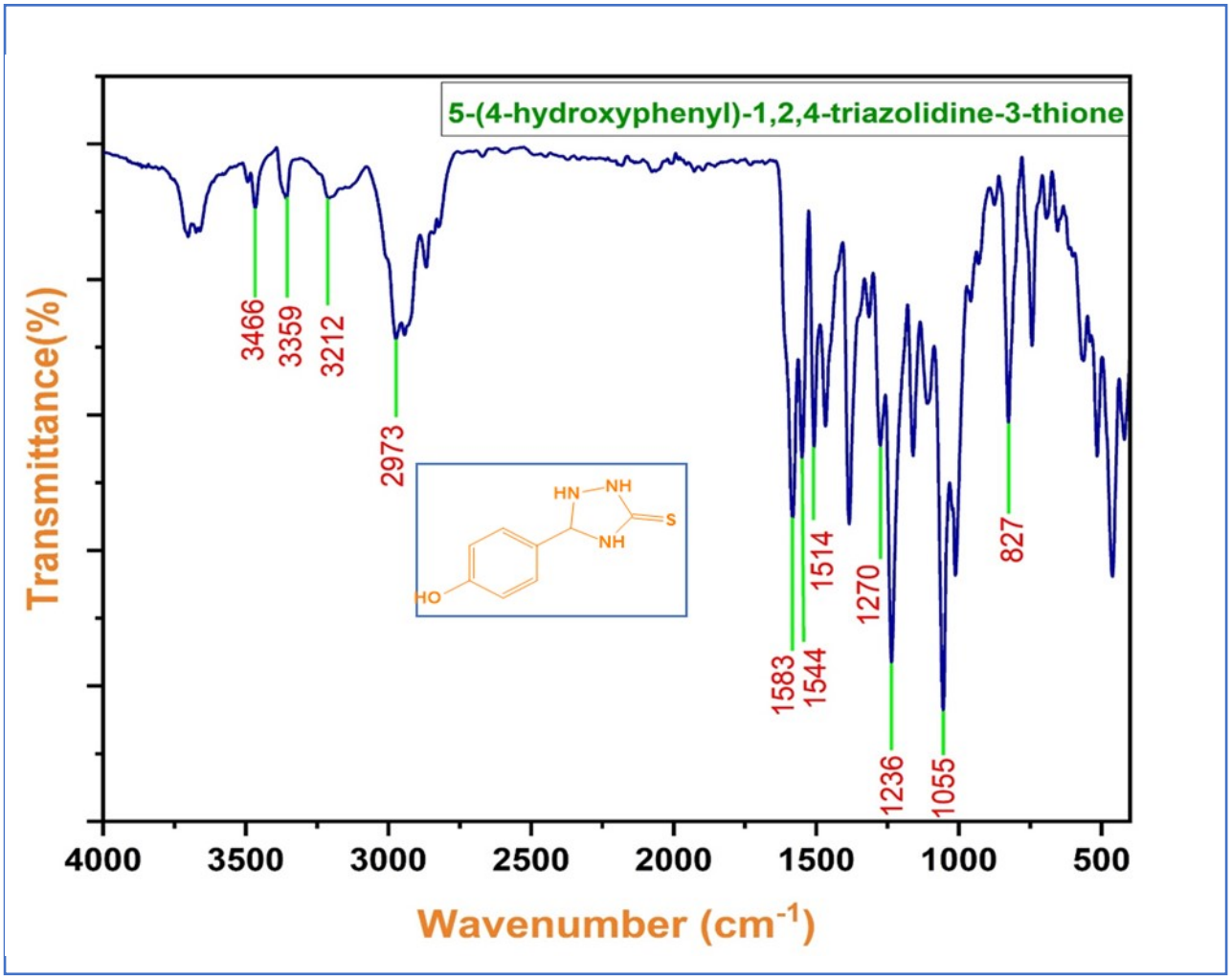
^{13}C-NMR of 5-(2-Nitrophenyl)-1,2,4-triazolidine-3-thione (3d)



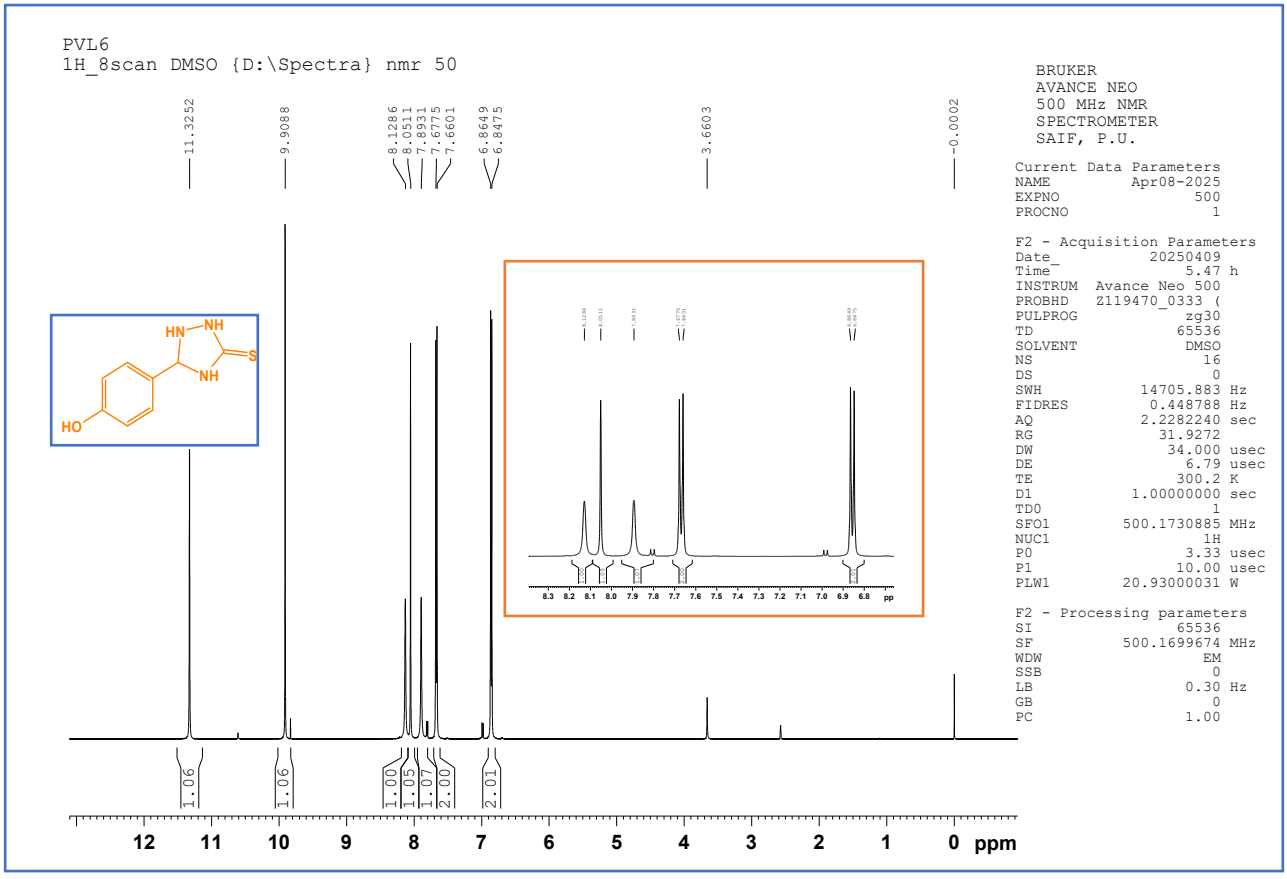
HRMS of 5-(2-Nitrophenyl)-1,2,4-triazolidine-3-thione (3d)

5-(4-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3e)

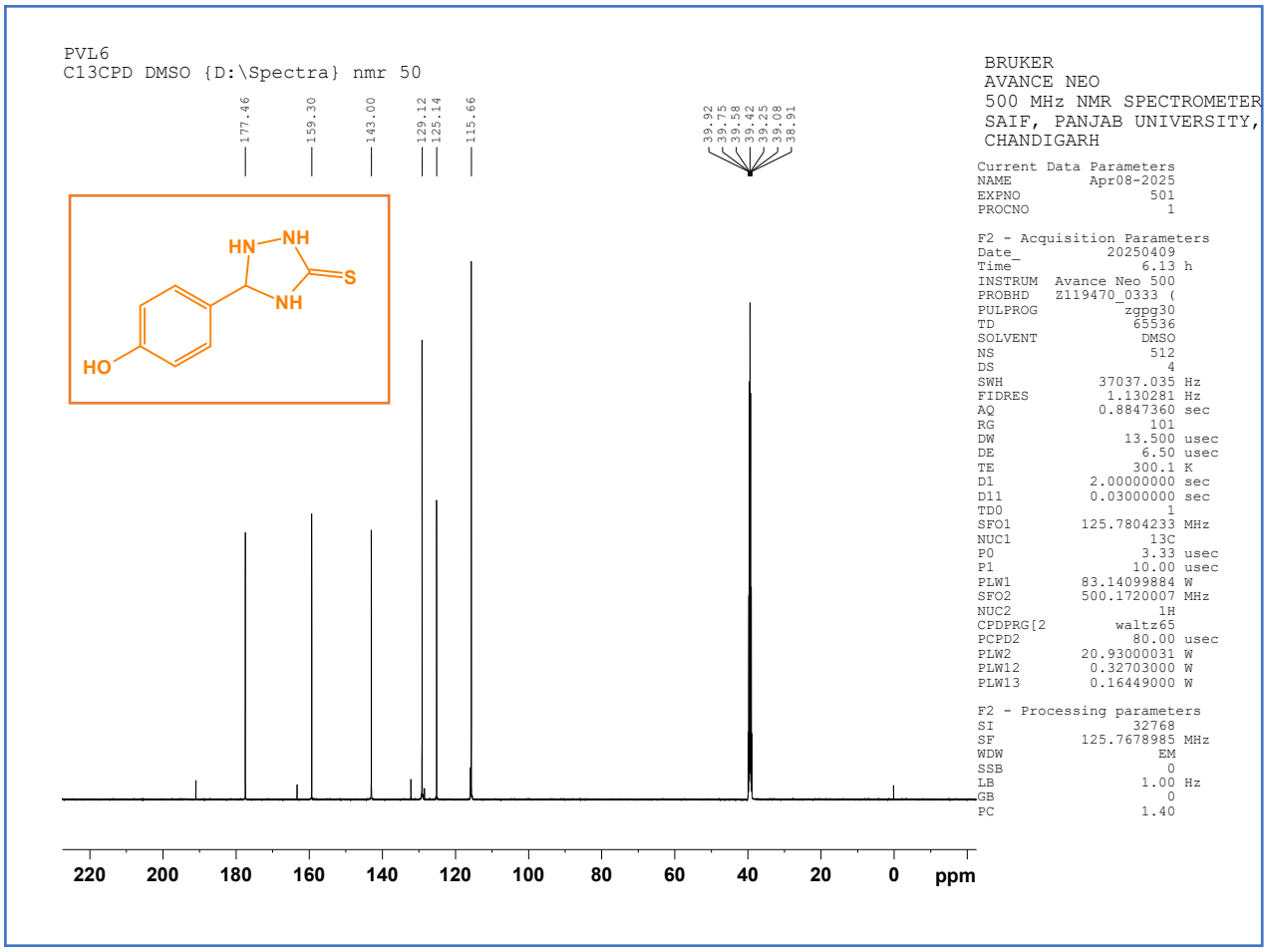
White crystal, Mp. 221-223 ˚C; IR (KBr): 3466, 3359, 3212, 2973, 1583, 1544, 1514, 1270, 1236, 1055, 827, 1048, 946, 870, 751, 608, 496 cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d6): δ 6.8475-6.8649 (d, 2H, ArH, *J*=8.5Hz), 7.6601-7.6775 (d, 2H, ArH, *J*= 8.5Hz), 7.8931 (s, 1H, CH), 8.0511 (s, 1H, Ar-OH,), 8.1286 (s, 1H, NH), 9.9088 (s, 1H, NH), 11.3252 (s, 1H, NH); ^{13}C-NMR (500 MHz, DMSO-d6): 115.66, 125.14, 129.12, 143.00, 159.30, 177.46 ; HRMS {observed [M+1] peak: 196.05 (m/z)} {calculated [M] peak: 195.24 (m/z)}.



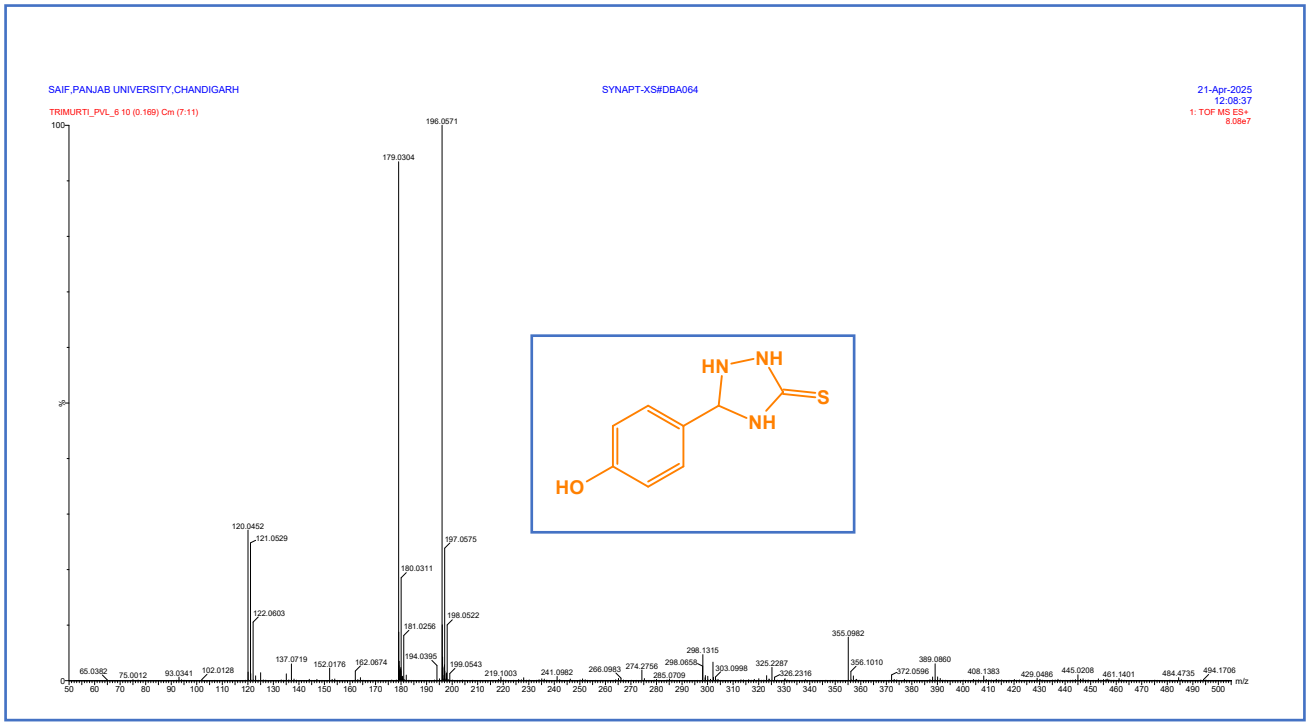
FTIR of 5-(4-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3e)



[1]HNMR of 5-(4-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3e)



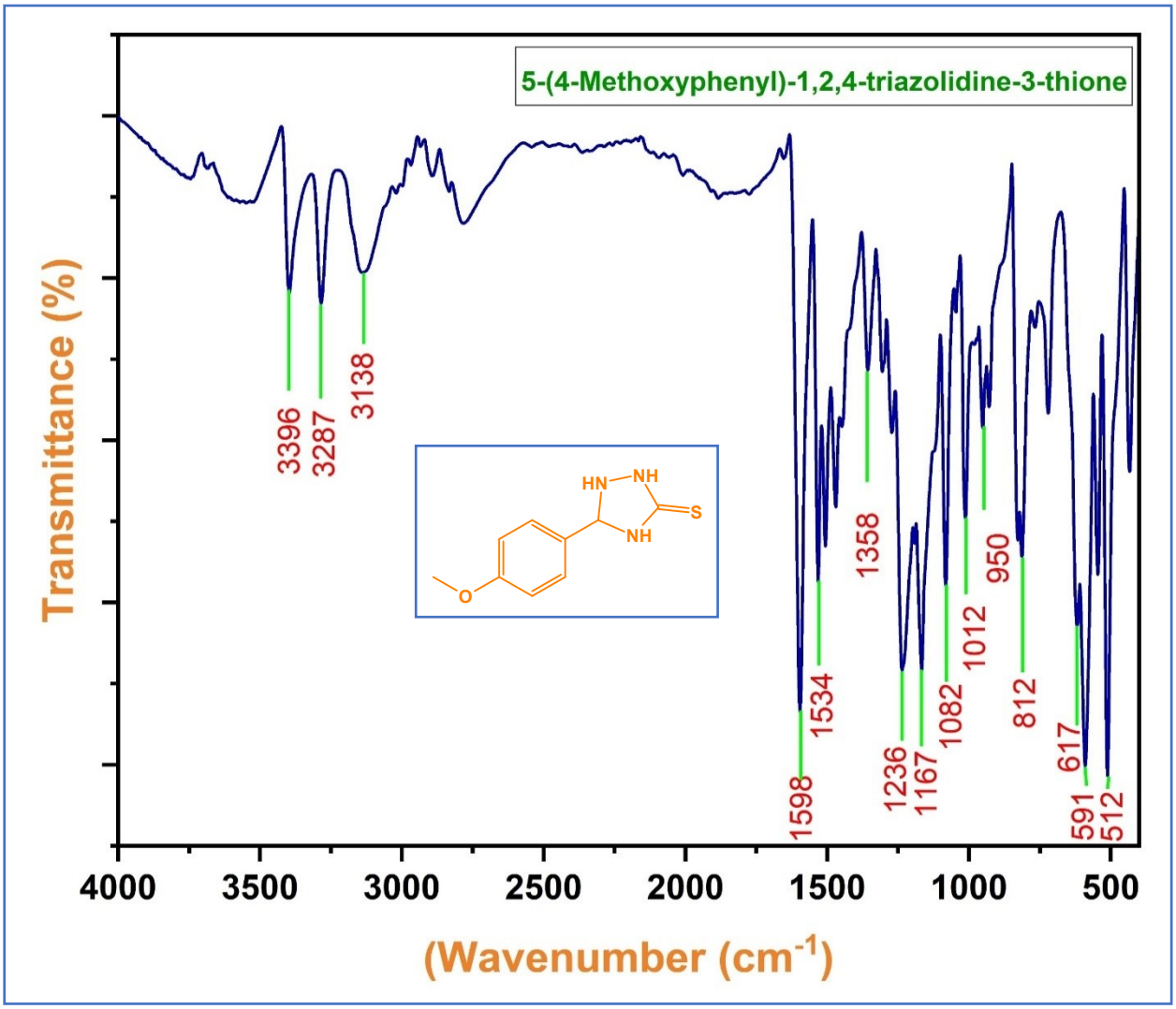
^{13}C-NMR of 5-(4-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3e)



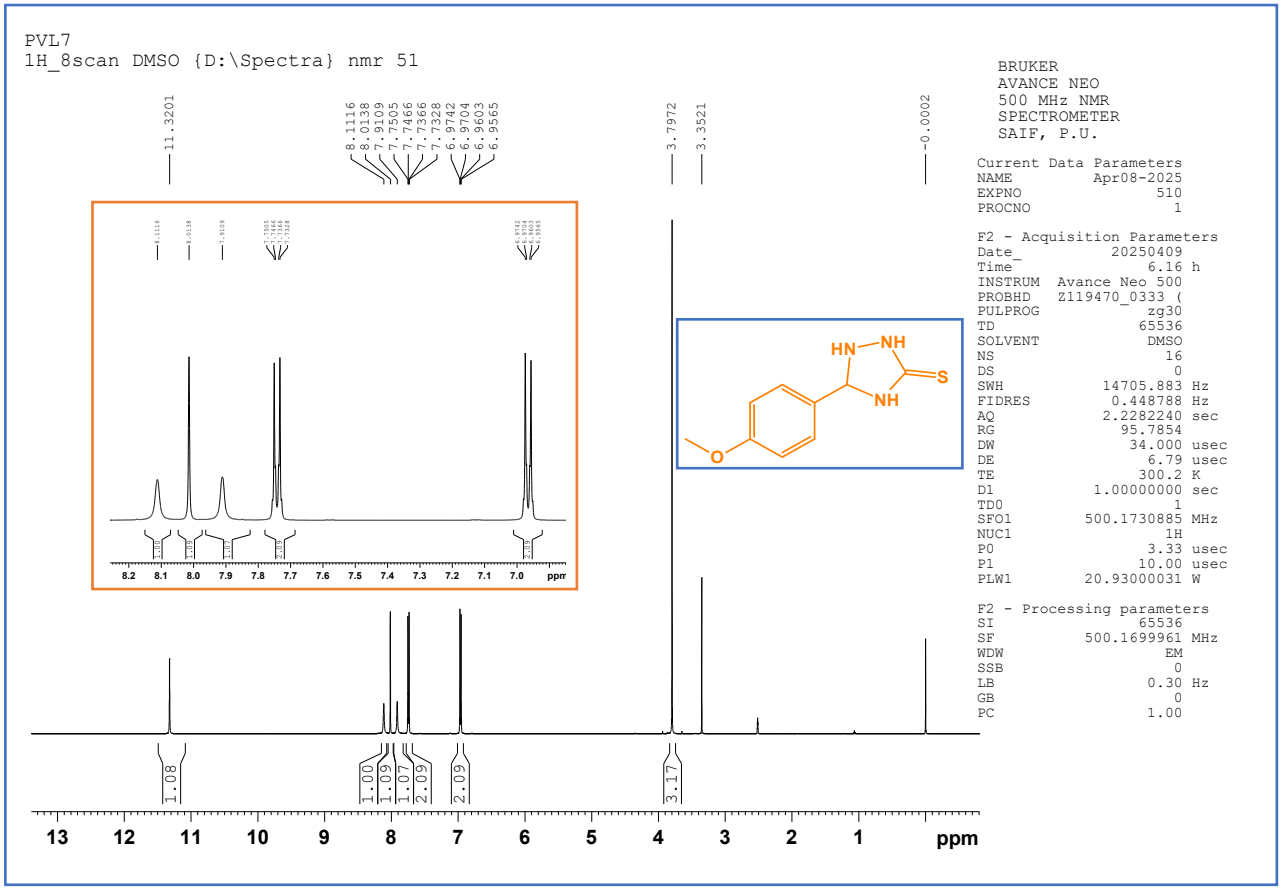
HRMS of 5-(4-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3e)

5-(4-Methoxyphenyl)-1,2,4-triazolidine-3-thione (3f)

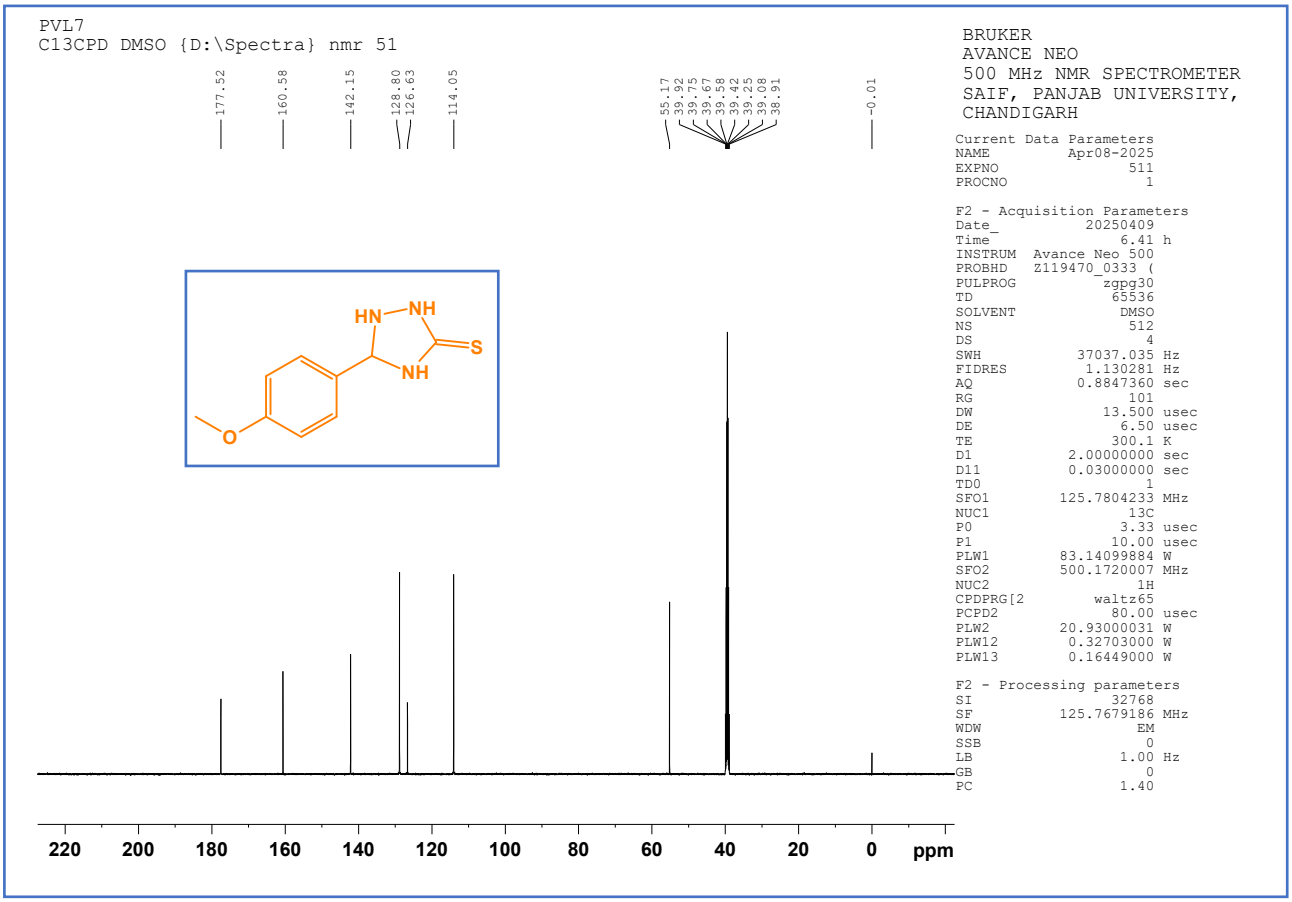
White crystal, Mp. 155-157 ˚C; IR (KBr):3396, 3287, 3138, 1598, 1534, 1358, 1236, 1167, 1082, 1012, 950, 812, 617, 512 cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d6): δ 3.7972 (s, 3H, OCH3), 6.9565-6.9742 (d, 2H, ArH, J = 9 Hz), 7.7328-7.7505 (d, 2H, ArH, J = 9 Hz), 7.9109 (s, 1H, CH), 8.0138 (s, 1H, NH), 8.1116 (s, 1H, NH), 11.3201 (s, 1H, NH); ^{13}C-NMR (500 MHz, DMSO-d6): 55.2, 114.05, 126.63, 128.80, 142.15, 160.58, 177.52; HRMS{observed [M+1] peak: 210.07 (m/z)} {calculated [M] peak: 209.27 (m/z)}.



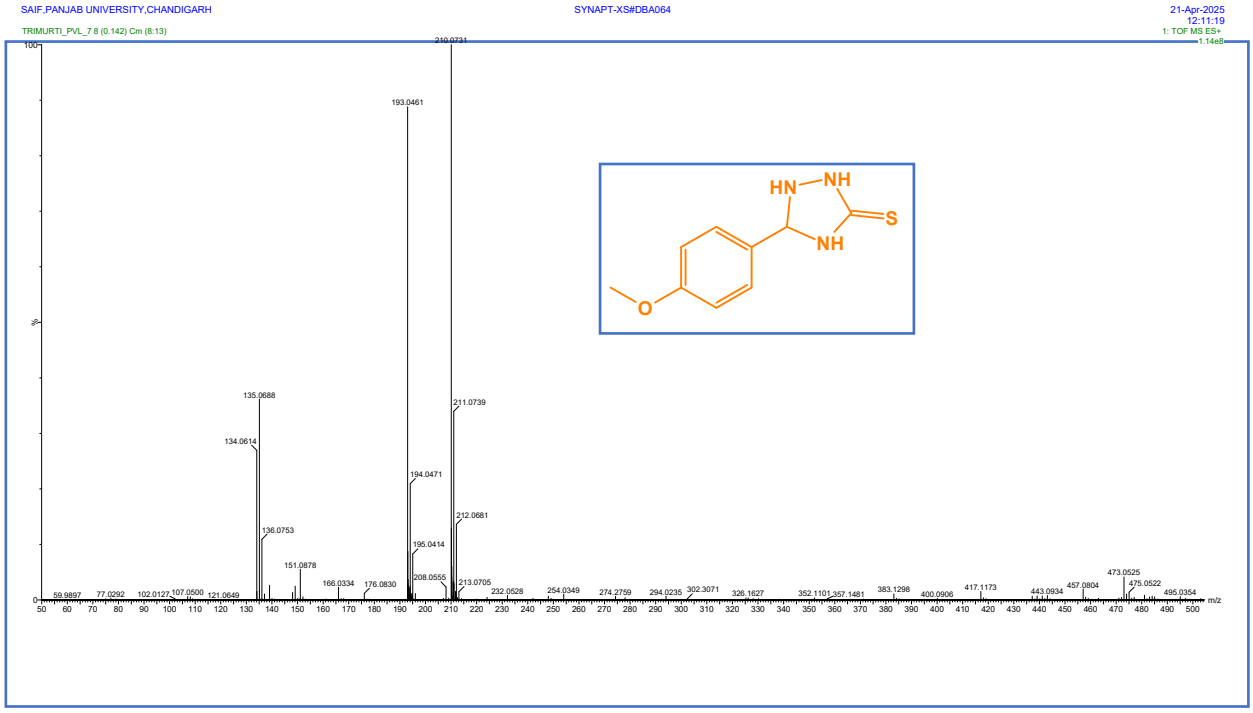
FTIR of 5-(4-Methoxyphenyl)-1,2,4-triazolidine-3-thione (3f)



[1]HNMR of 5-(4-Methoxyphenyl)-1,2,4-triazolidine-3-thione (3f)



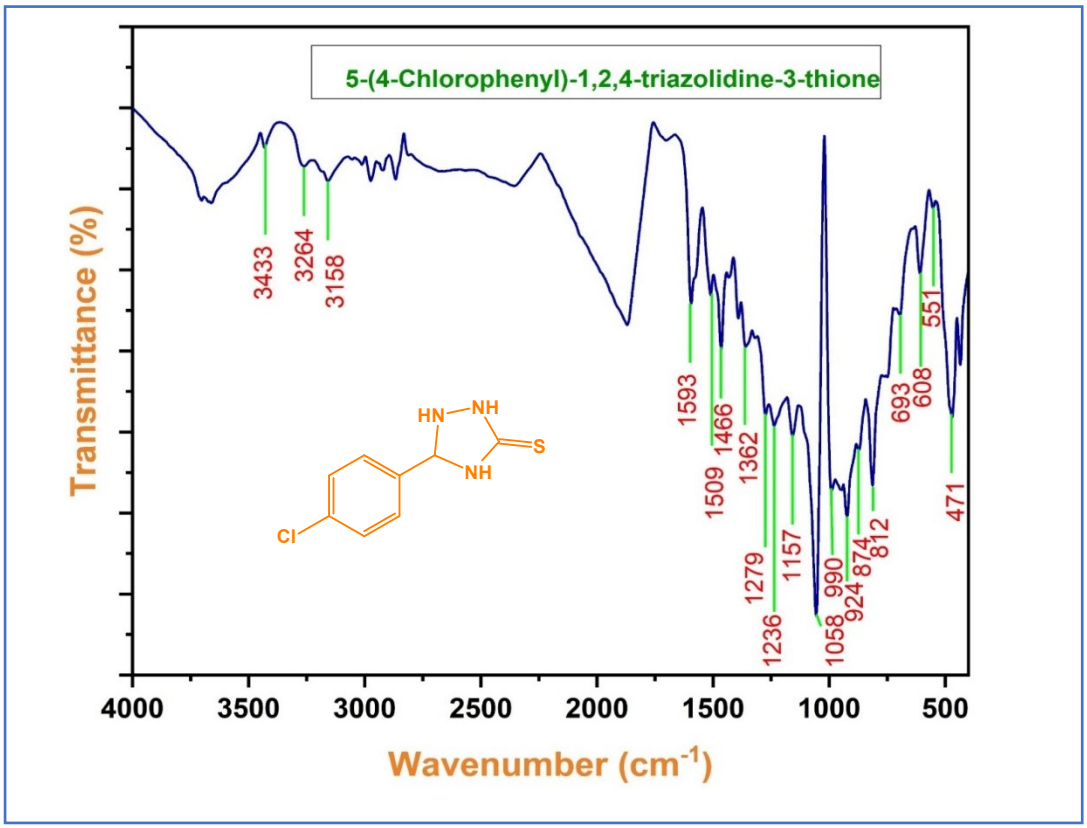
^{13}C-NMR of 5-(4-Methoxyphenyl)-1,2,4-triazolidine-3-thione (3f)



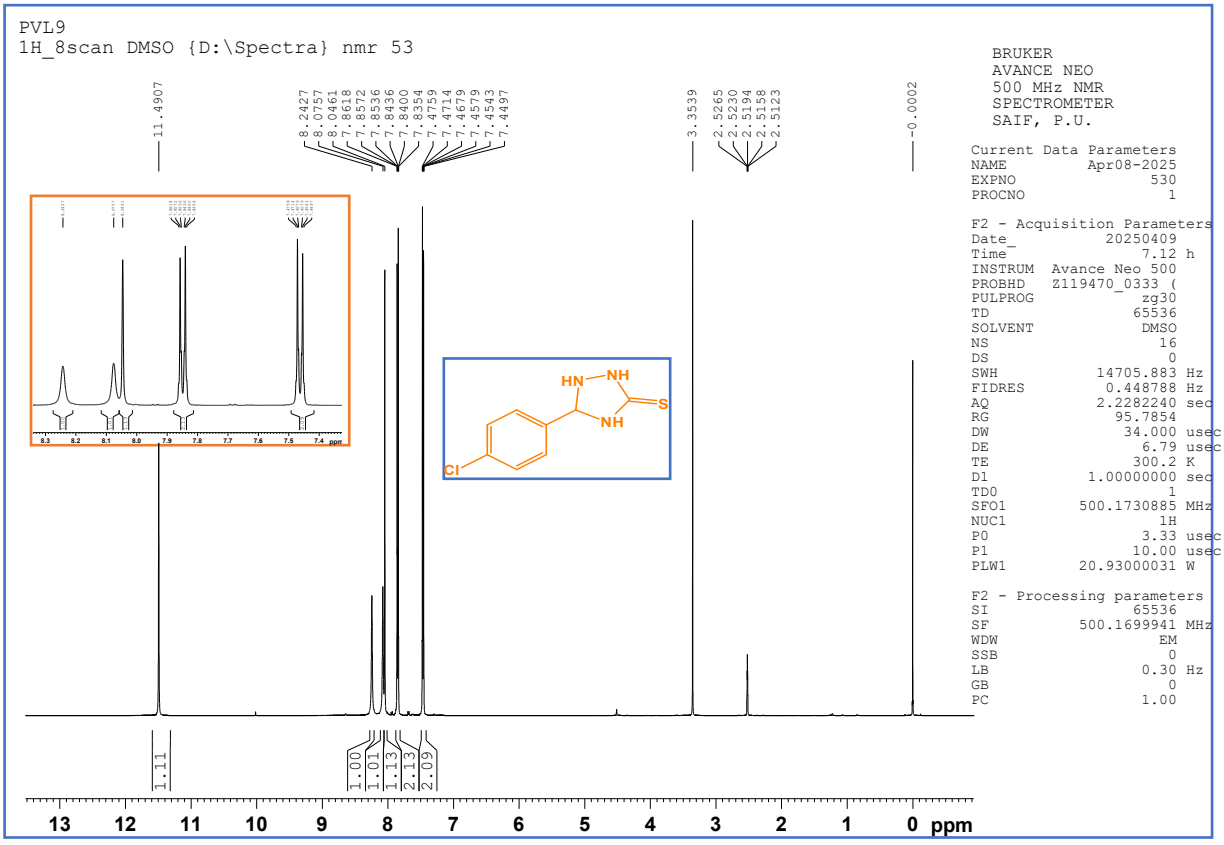
HRMS of 5-(4-Methoxyphenyl)-1,2,4-triazolidine-3-thione (3f)

5-(4-Chlorophenyl)-1,2,4-triazolidine-3-thione (3g)

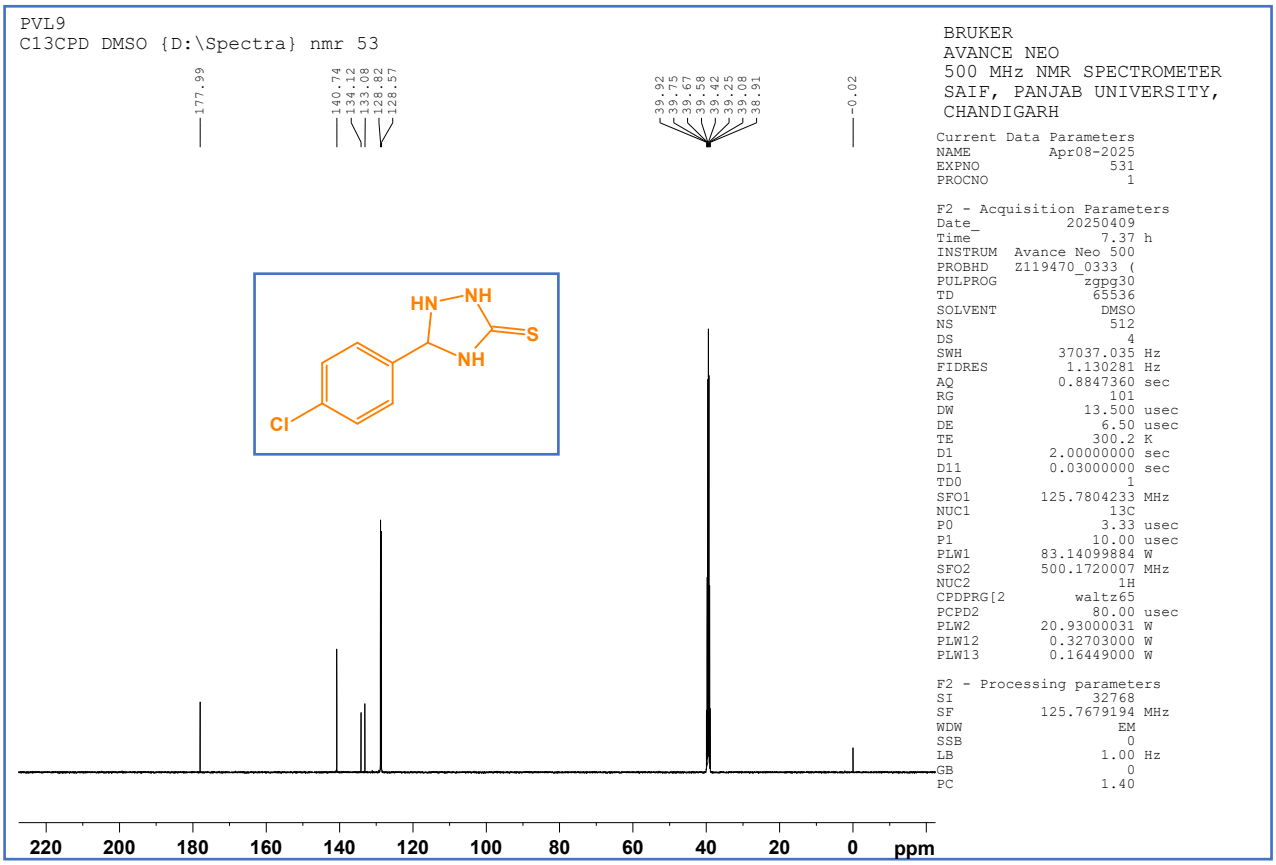
White crystal, Mp. 206-208 ˚C; IR (KBr): 3433, 3264, 3158, 1593, 1509, 1466, 1362, 1279, 1236, 1157, 1058, 990, 924, 874, 693, 551 cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d6): δ 7.4497-7.4759 (d, 2H, ArH, J = 13 Hz), 7.8354-7.8618 (d, 2H, ArH, J = 13 Hz), 8.0461 (s, 1H, CH), 8.0757 (s, 1H, NH), 8.2427 (s, 1H, NH), 11.4907 (s, 1H, NH). ^{13}C-NMR (500 MHz, DMSOd6): 128.57, 128.82, 133.08, 134.12, 140.74, 177.99; HRMS{observed [M+1] peak: 214.02 (m/z)} {calculated [M] peak: 213.69 (m/z)}.



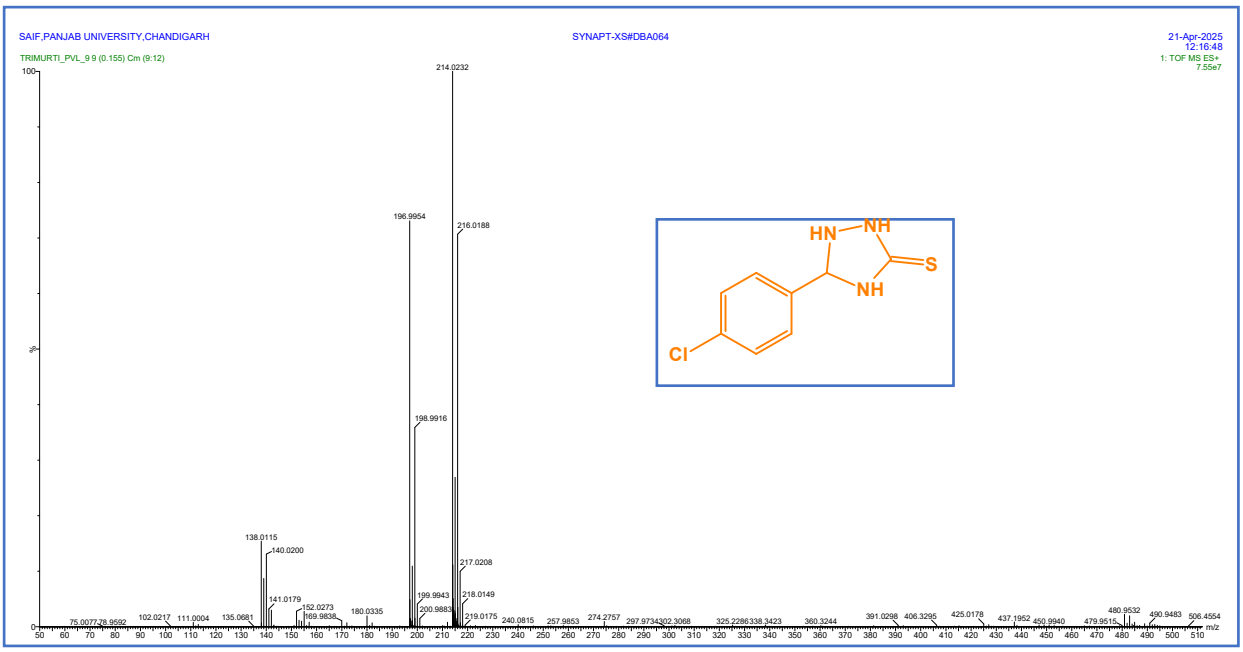
FTIR of 5-(4-Chlorophenyl)-1,2,4-triazolidine-3-thione (3g)



[1]HNMR of 5-(4-Chlorophenyl)-1,2,4-triazolidine-3-thione (3g)



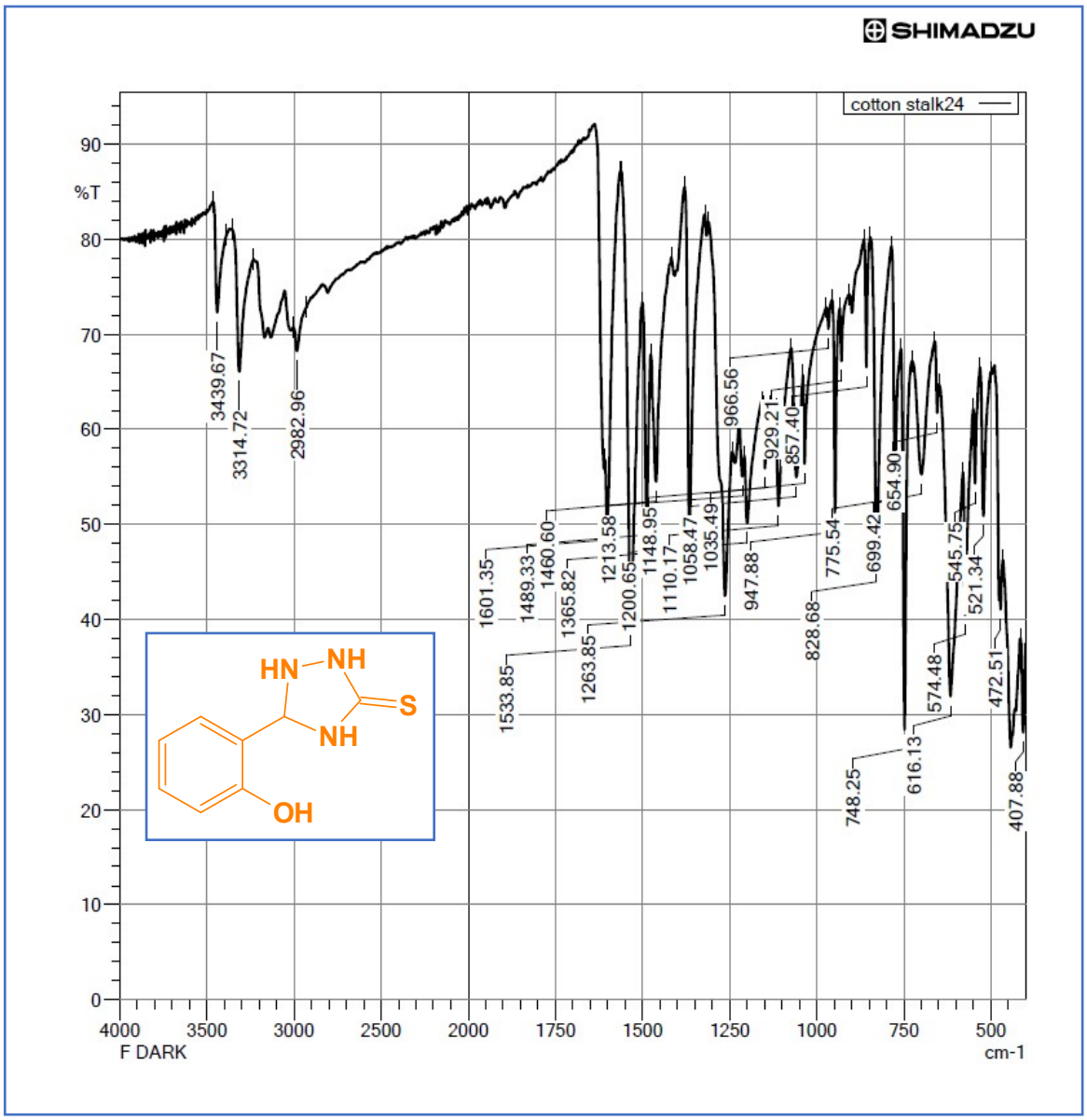
^{13}C-NMR of 5-(4-Chlorophenyl)-1,2,4-triazolidine-3-thione (3g)



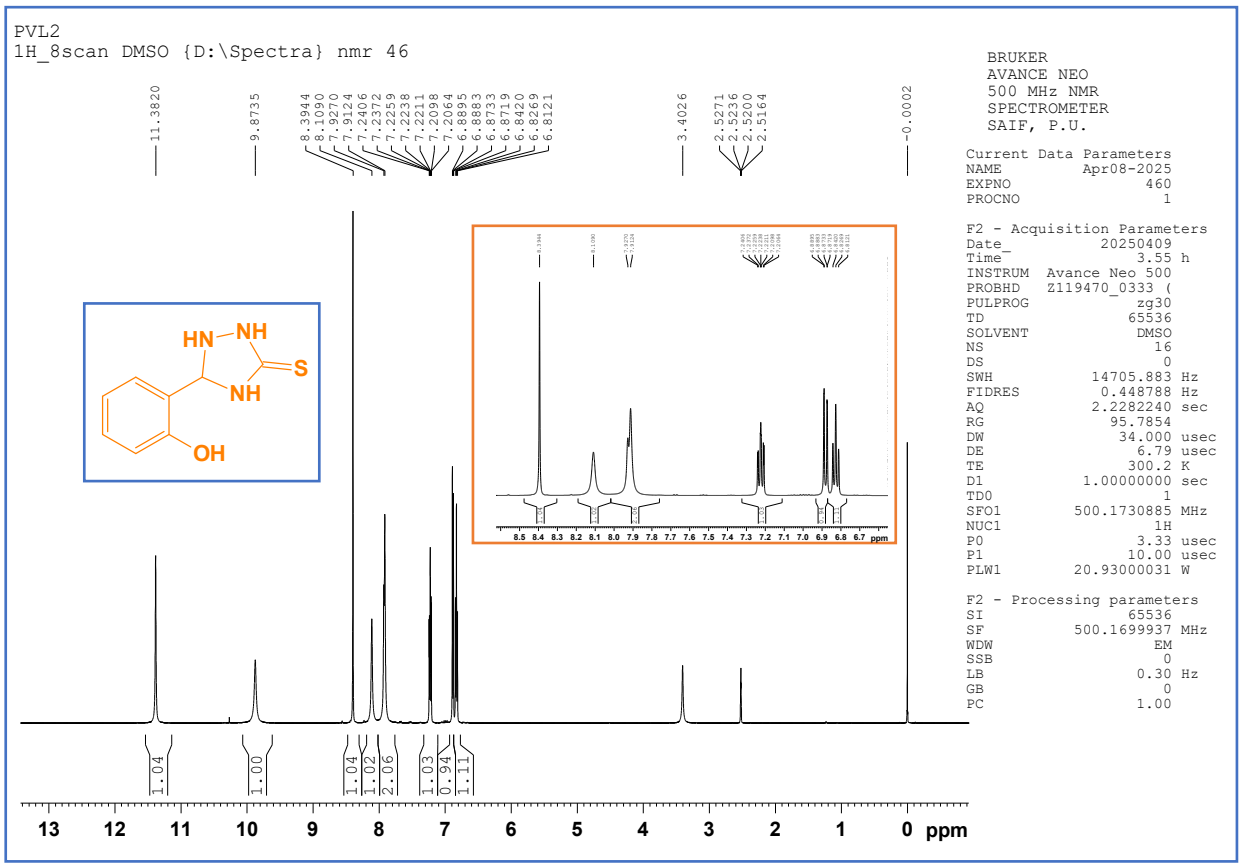
HRMS of 5-(4-Chlorophenyl)-1,2,4-triazolidine-3-thione (3g)

5-(2-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3h)

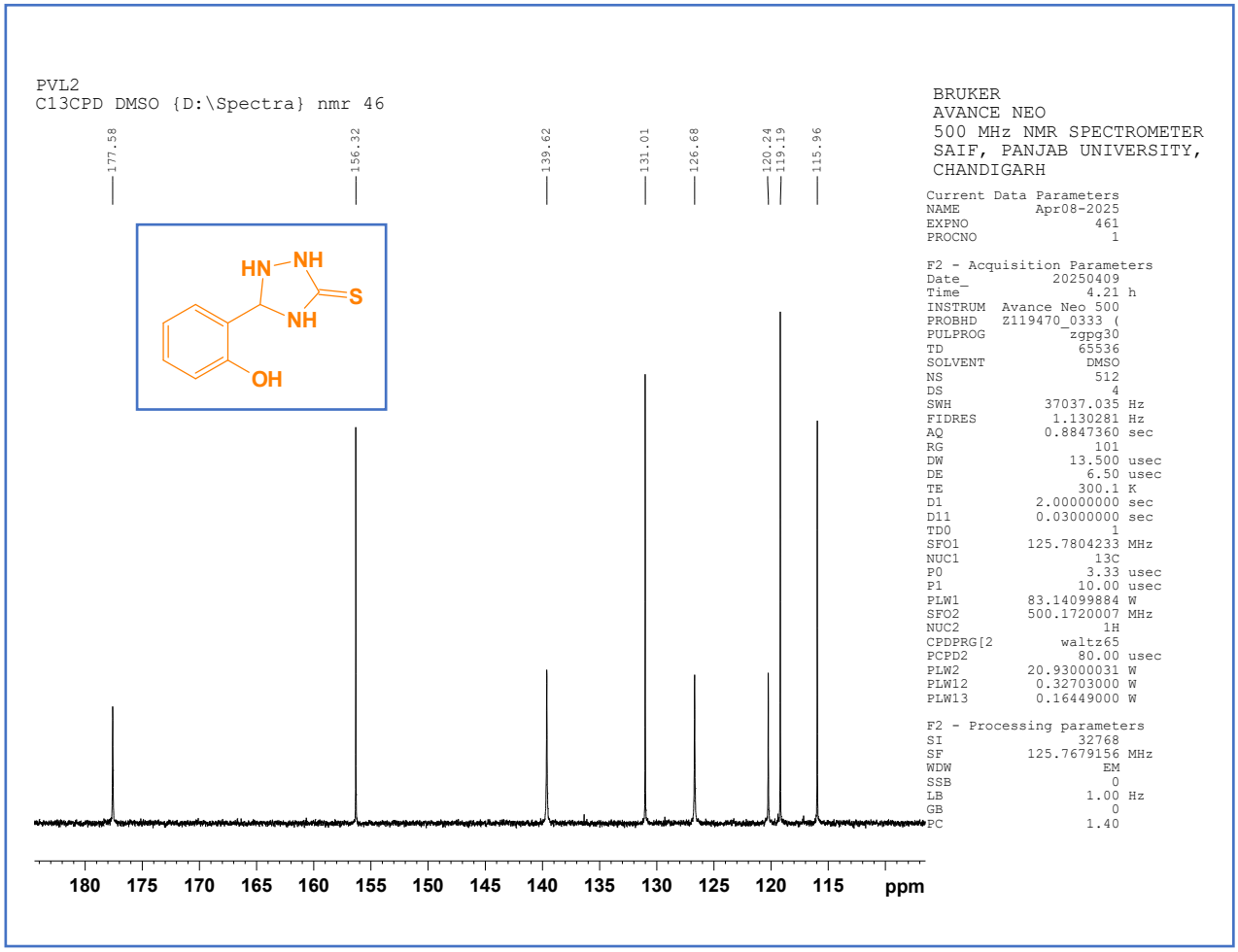
White crystal, Mp. 217-219˚C; IR (KBr): 3439, 3314, 3170, 2982, 1601, 1533, 1489, 1365, 1263, 1213, 1110, 1058, 947, 828, 748, 616, 521 cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d6): δ 6.8121-6.8420 (t, 1H, ArH, J = 15 Hz), 6.8719-6.8895 (d, 1H, ArH, J = 9 Hz), 7.2064-7.2406 (m, 1H, ArH, J = 7.5Hz), 7.9124-7.9270 (d, 2H, J = 7.5Hz), 8.1090 (s, 1H, CH), 8.11 (s, 1H, NH), 8.3944 (s, 1H, NH), 9.8735 (s, 1H, OH), 11.3820 (s, 1H, NH); ^{13}C-NMR (500 MHz, DMSO-d6): 115.96, 119.19, 120.24, 126.68, 131.01, 139.62, 156.32, 177.58; HRMS{observed [M+1] peak: 196.03 (m/z)} {calculated [M] peak: 195.24 (m/z)}.



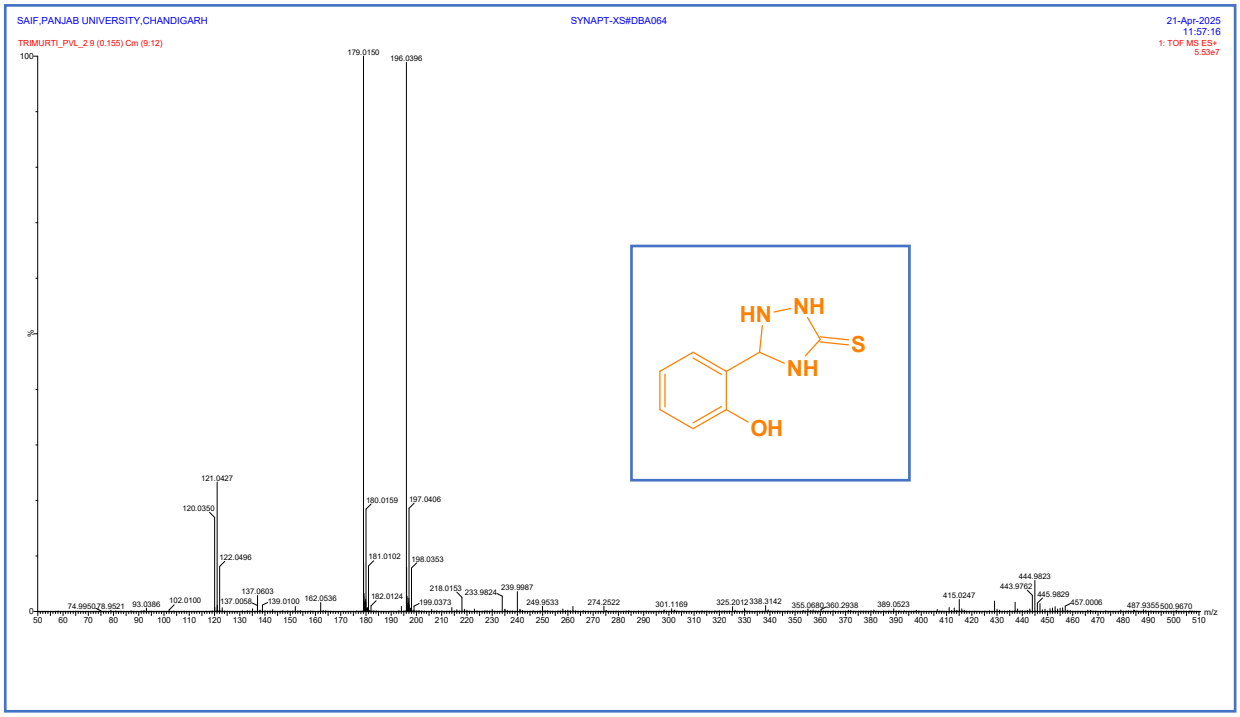
FTIR of 5-(2-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3h)



[1]HNMR of 5-(2-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3h)



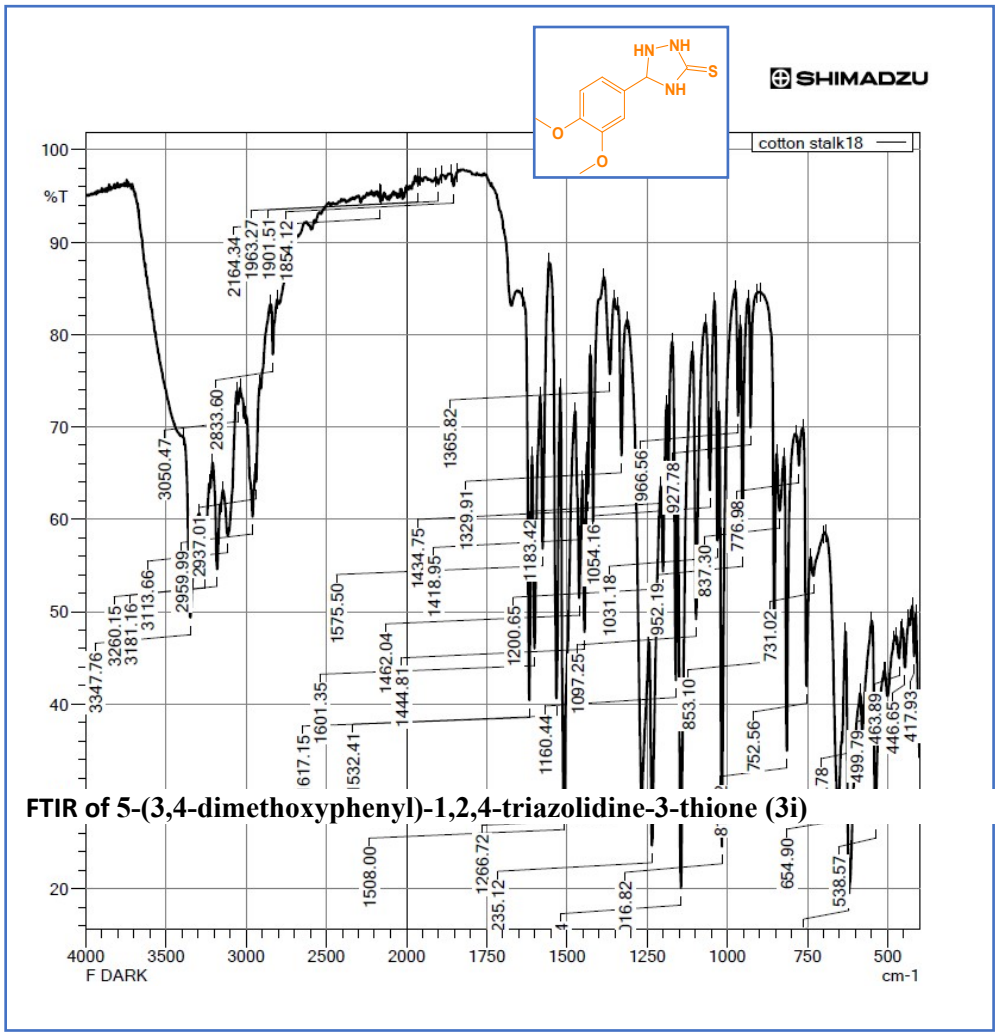
^{13}C-NMR of 5-(2-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3h)



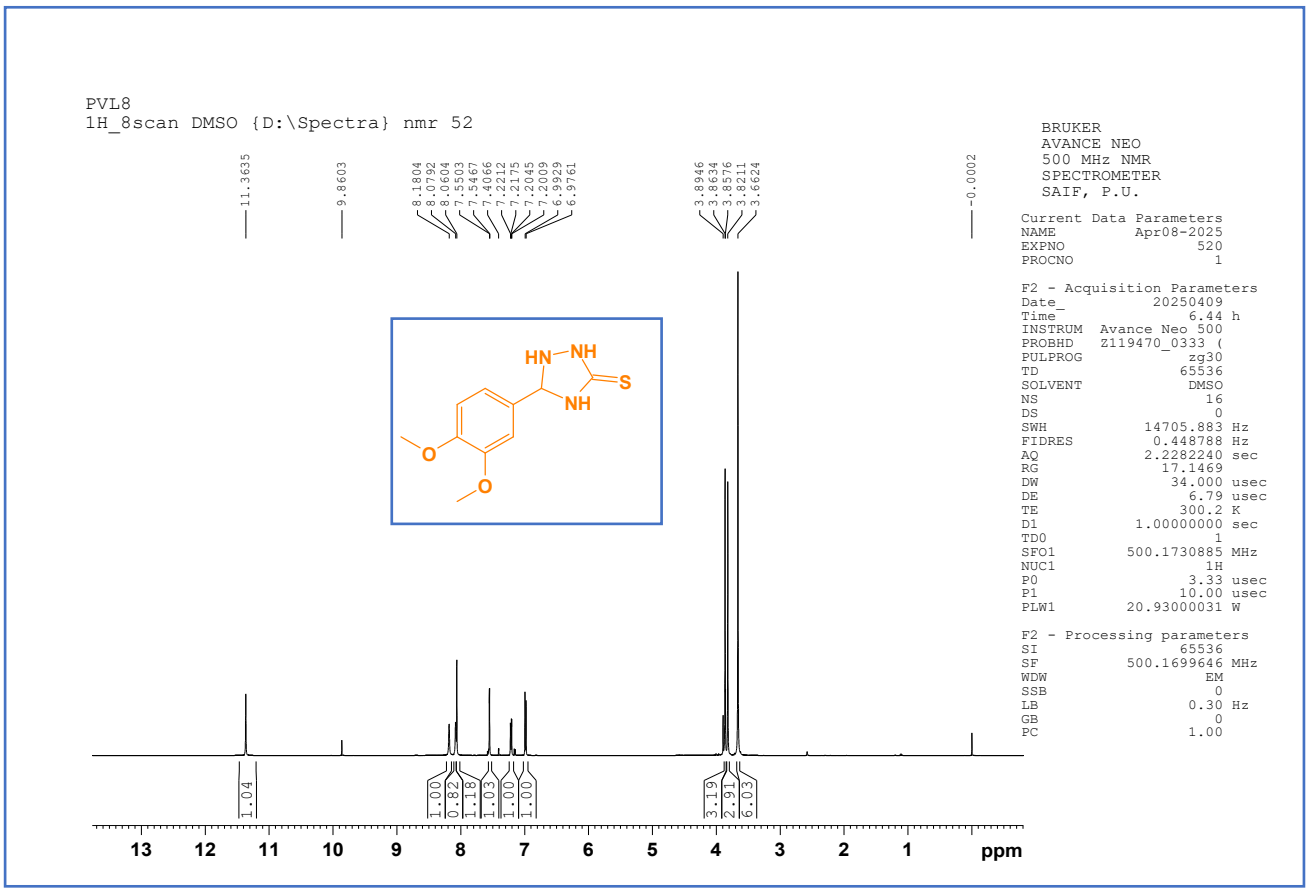
HRMS of 5-(2-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3h)

5-(3,4-dimethoxyphenyl)-1,2,4-triazolidine-3-thione (3i)

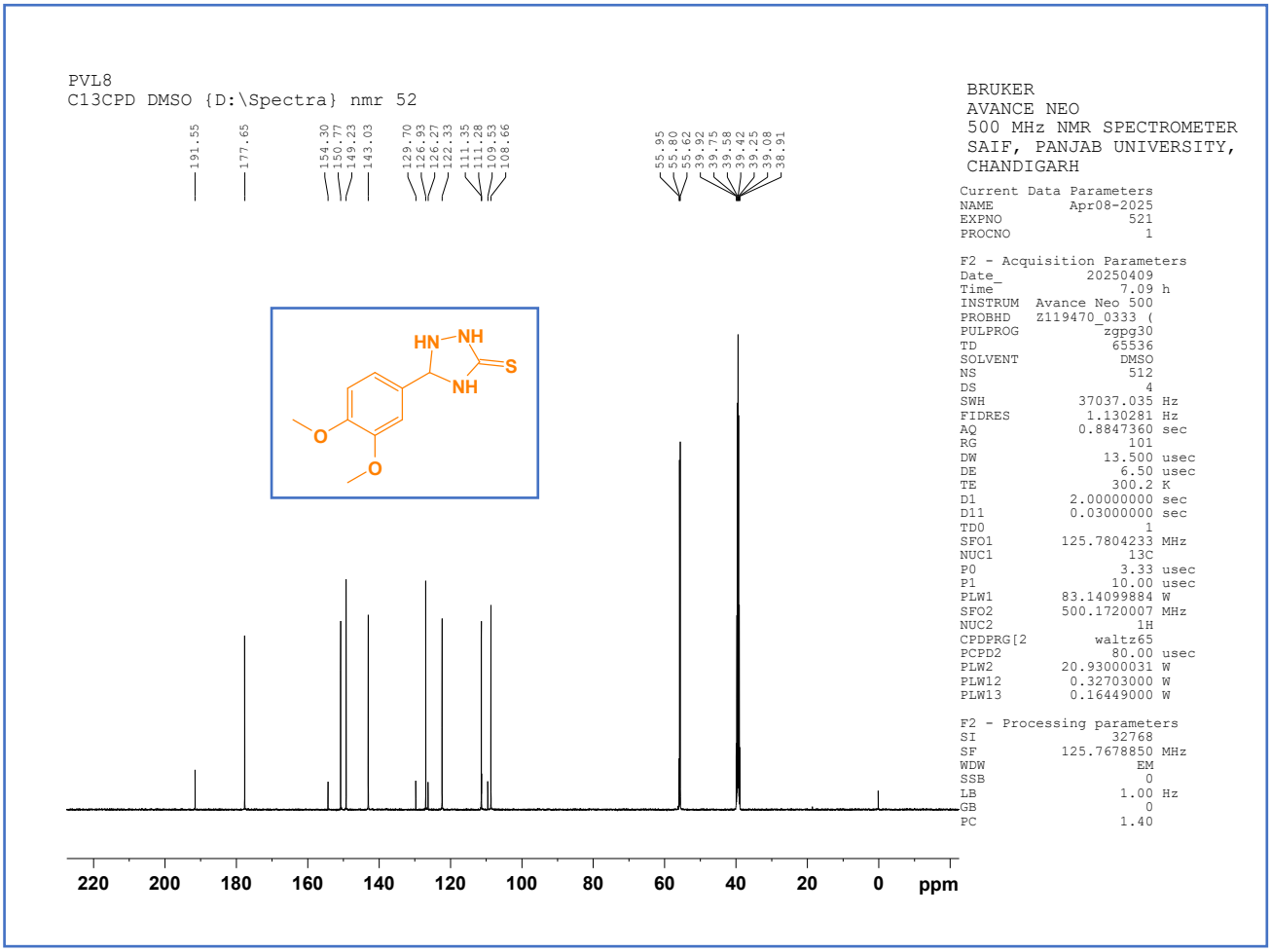
White Crystalline solid; M.P. 221-223^{o}C; IR (KBr): 3347, 3260, 3181, 2959, 1617, 1532, 1462, 1365, 1266, 1200, 1160, 1054, 952, 837, 752, 654, 538 cm^{-1};^{1}H-NMR (500 MHz, DMSO-d6): δ 3.8211 (s, 3H, OCH_3), 3.8576-3.8634 (s, 3H, J = 3Hz) 6.976-6.992 (d, 1H, J = 8 Hz) 7.200-7.221 (dd, 1H, J= 10.5 Hz),7.546-7.550 (d, 1Hz, J = 2Hz), 8.060 (s, 1H), 8.079 (s, 1H), 8.180 (s, 1H), 11.363 (s, 1H); ^{13}C-NMR (500 MHz, DMSO-d6):; HRMS{observed [M+1] peak: 240.08 (m/z)} {calculated [M] peak: 239.29 (m/z)}



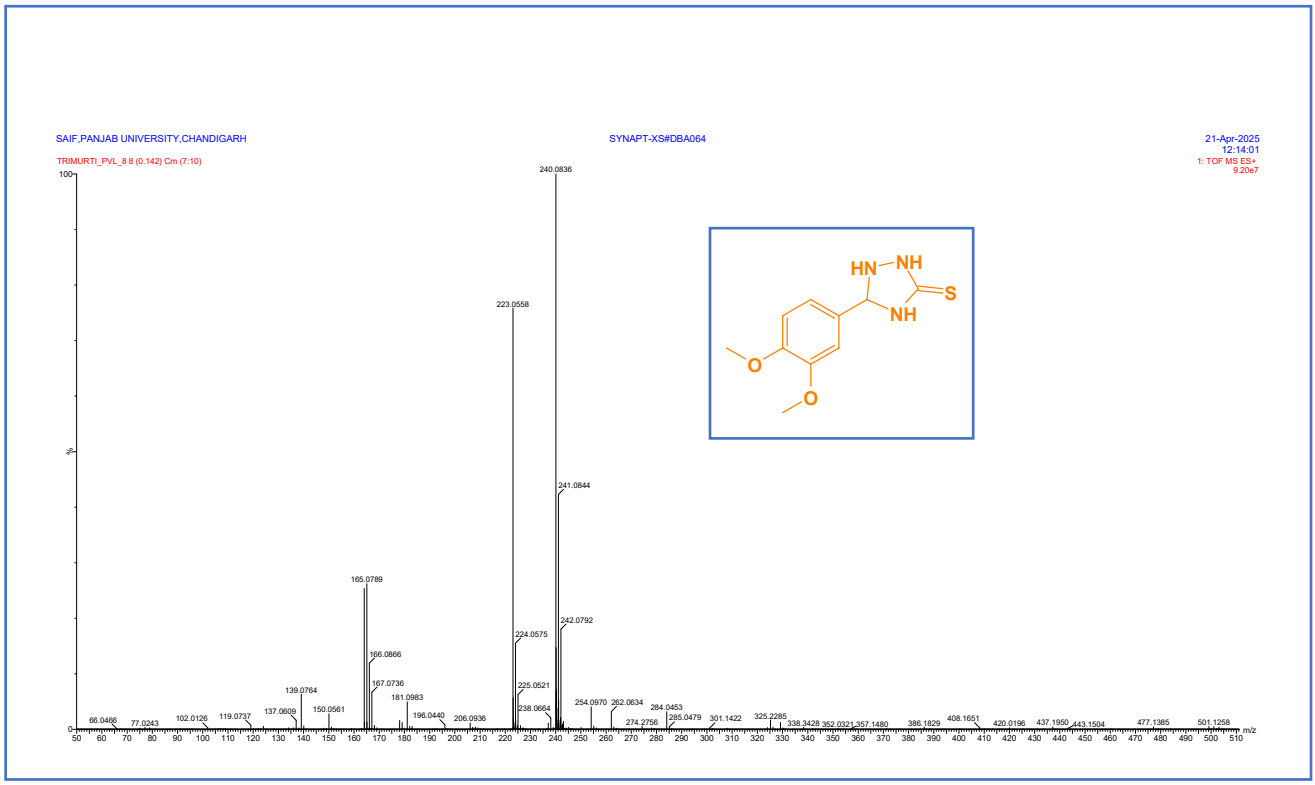
FTIR of 5-(3,4-dimethoxyphenyl)-1,2,4-triazolidine-3-thione (3i)



[1]HNMR of 5-(3,4-dimethoxyphenyl)-1,2,4-triazolidine-3-thione (3i)



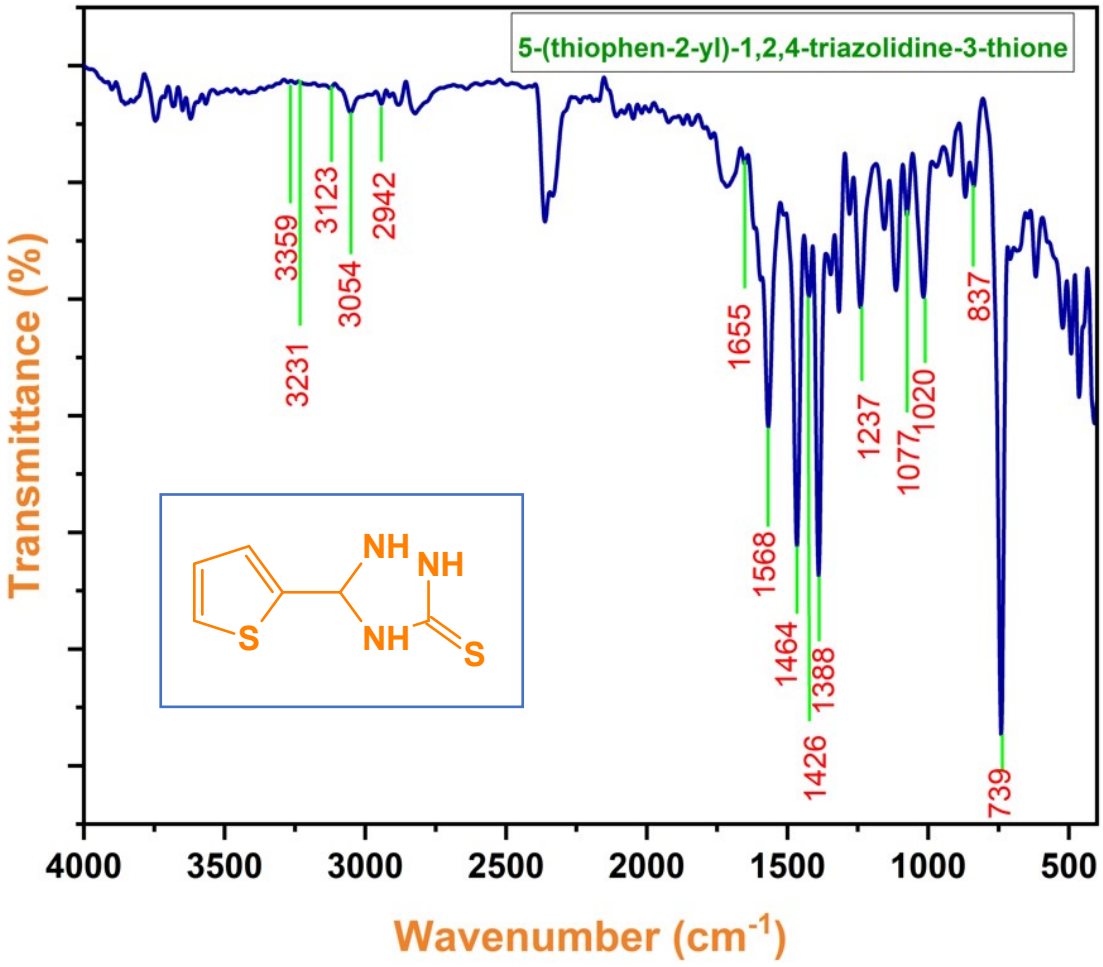
^{13}C-NMR of 5-(3,4-dimethoxyphenyl)-1,2,4-triazolidine-3-thione (3i)



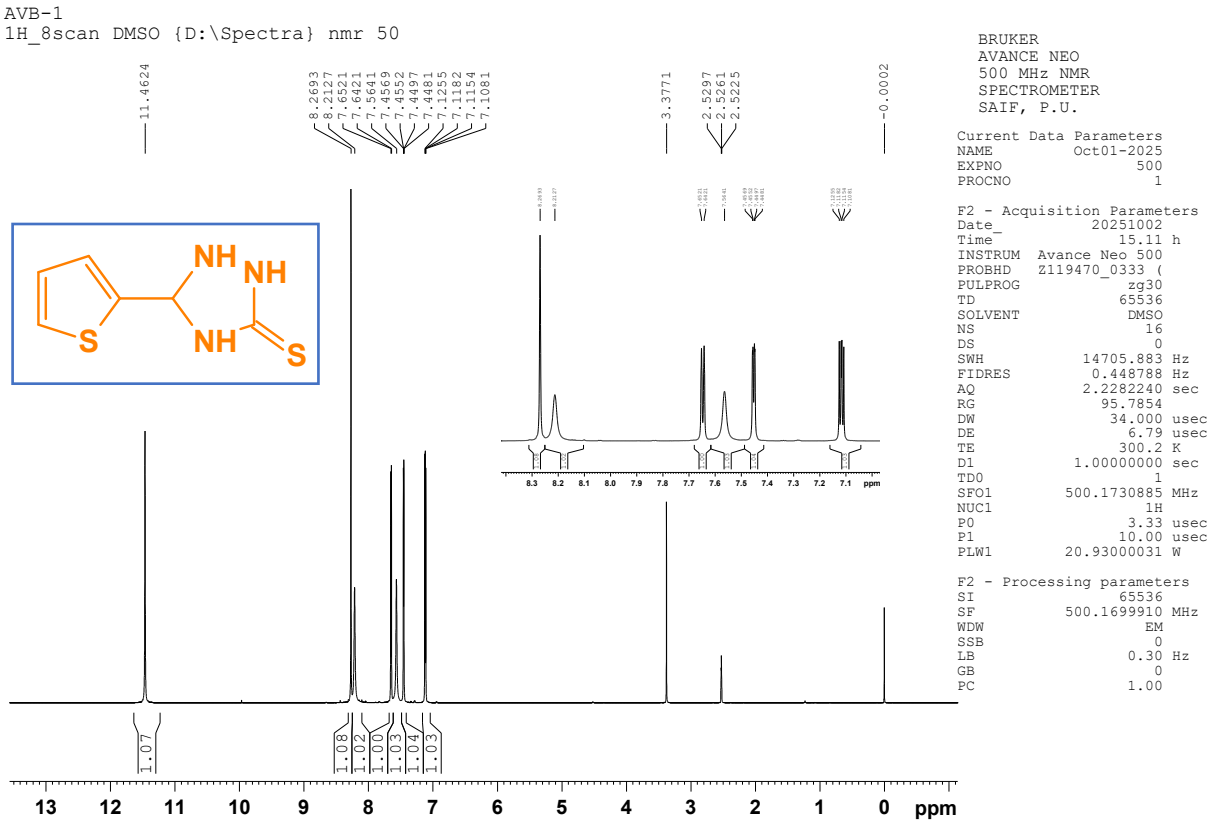
HRMS of 5-(3,4-dimethoxyphenyl)-1,2,4-triazolidine-3-thione (3i)

5-(thiophen-2-yl)-1,2,4-triazolidine-3-thione (3j)

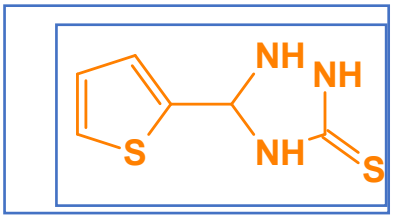
Yellow solid; M.pt. 219-221^{o}C ; IR (KBr): 3359, 3231, 3123, 2942, 1655, 1568, 1464, 1426, 1388, 1237, 1077, 1020, 837, 739cm^{-1} ^{1}H-NMR (500 MHz, DMSO-d6): δ 71081-7.1255 (m, 1H, J = 8.5Hz), 7.4481-7.4569 (d, 1H, J = 4Hz), 7.5641 (s, 1H), 7.6421-7.6521 (d, 1H, J = 5 Hz), 8.2127 (s, 1H), 8.2693 (s, 1H), 11.4624 (s, 1H); ^{13}C-NMR (500 MHz, DMSO-d6):127.83, 128.74, 130.46, 137.54, 138.51, 177.46 ; HRMS{observed [M+1] peak: 186.01 (m/z)} {calculated [M] peak: 185.27 (m/z)}



FTIR of 5-(thiophen-2-yl)-1,2,4-triazolidine-3-thione (3j)



^{1}H NMR of 5-(thiophen-2-yl)-1,2,4-triazolidine-3-thione (3j)

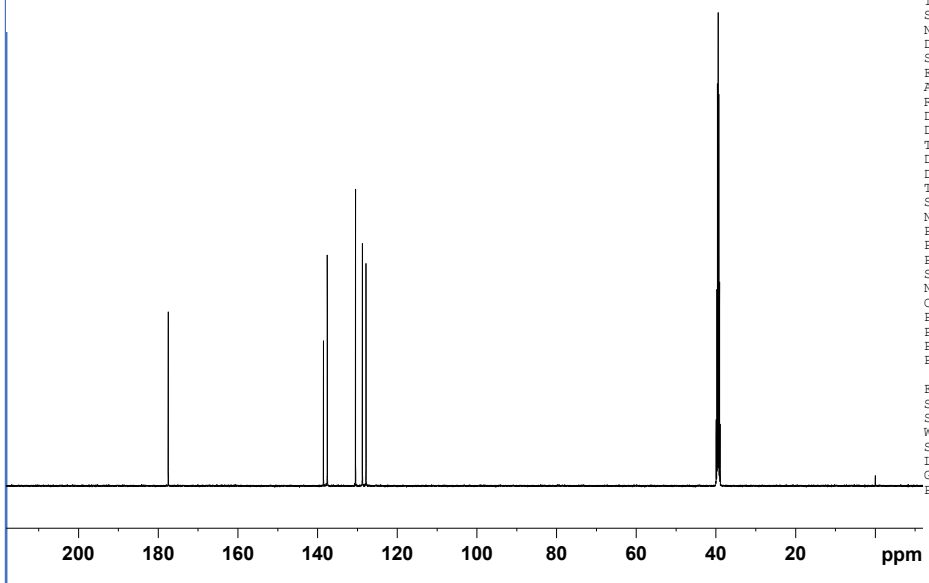


AVB-1
C13CPD DMSO {D:\Spectra} nmr 50

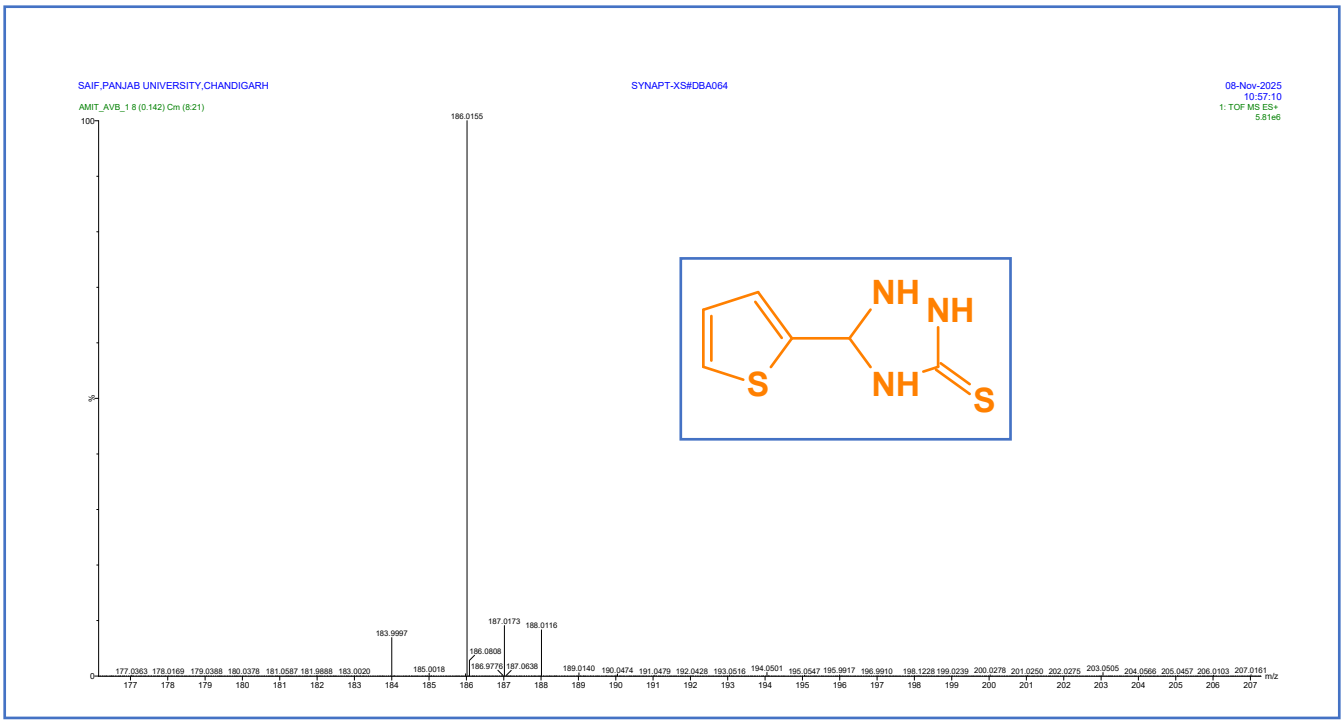
177.46
138.51
137.54
130.46
128.74
127.83
39.92
39.75
39.58
39.42
39.25
39.08
38.91
0.02

BRUKER
AVANCE NEO
500 MHz NMR SPECTROMETER
SAIF, PANJAB UNIVERSITY,
CHANDIGARH

^{13}C-NMR of 5-(thiophen-2-yl)-1,2,4-triazolidine-3-thione (3j)



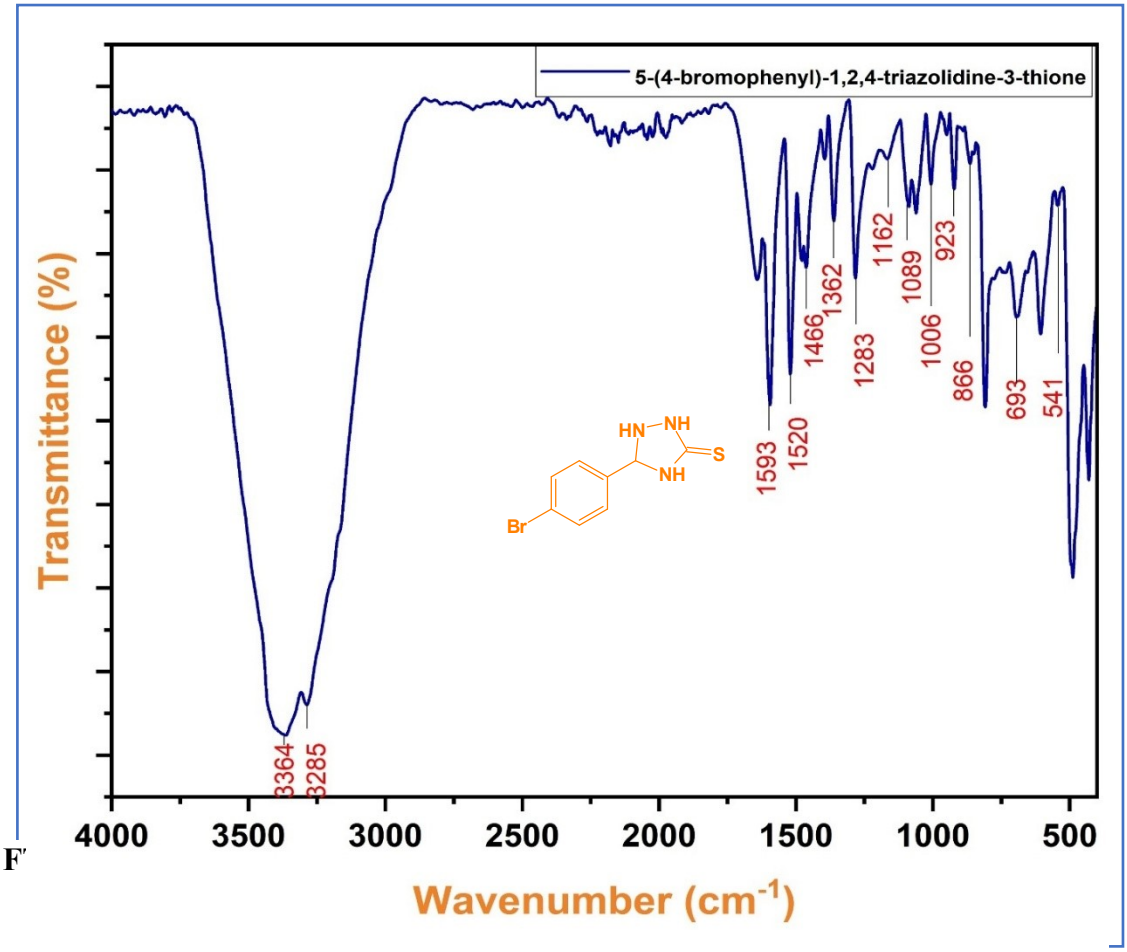

```
Current Data Parameters
NAME          Oct01-2025
EXPNO                501
PROCNO                 1

F2 - Acquisition Parameters
Date_           20251002
Time              15.37 h
INSTRUM  Avance Neo 500
PROBHD   Z119470_0333 (
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                   512
DS                     4
SWH           37037.035 Hz
FIDRES         1.130281 Hz
AQ            0.8847360 sec
RG                   101
DW               13.500 usec
DE                6.50 usec
TE               300.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1        125.7804233 MHz
NUC1                13C
P0                 3.33 usec
P1                10.00 usec
PLW1        83.14099884 W
SFO2        500.1720007 MHz
NUC2                1H
CPDPRG[2         waltz65
PCPD2             80.00 usec
PLW2        20.93000031 W
PLW12        0.32703000 W
PLW13        0.16449000 W

F2 - Processing parameters
SI                 32768
SF          125.7679177 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



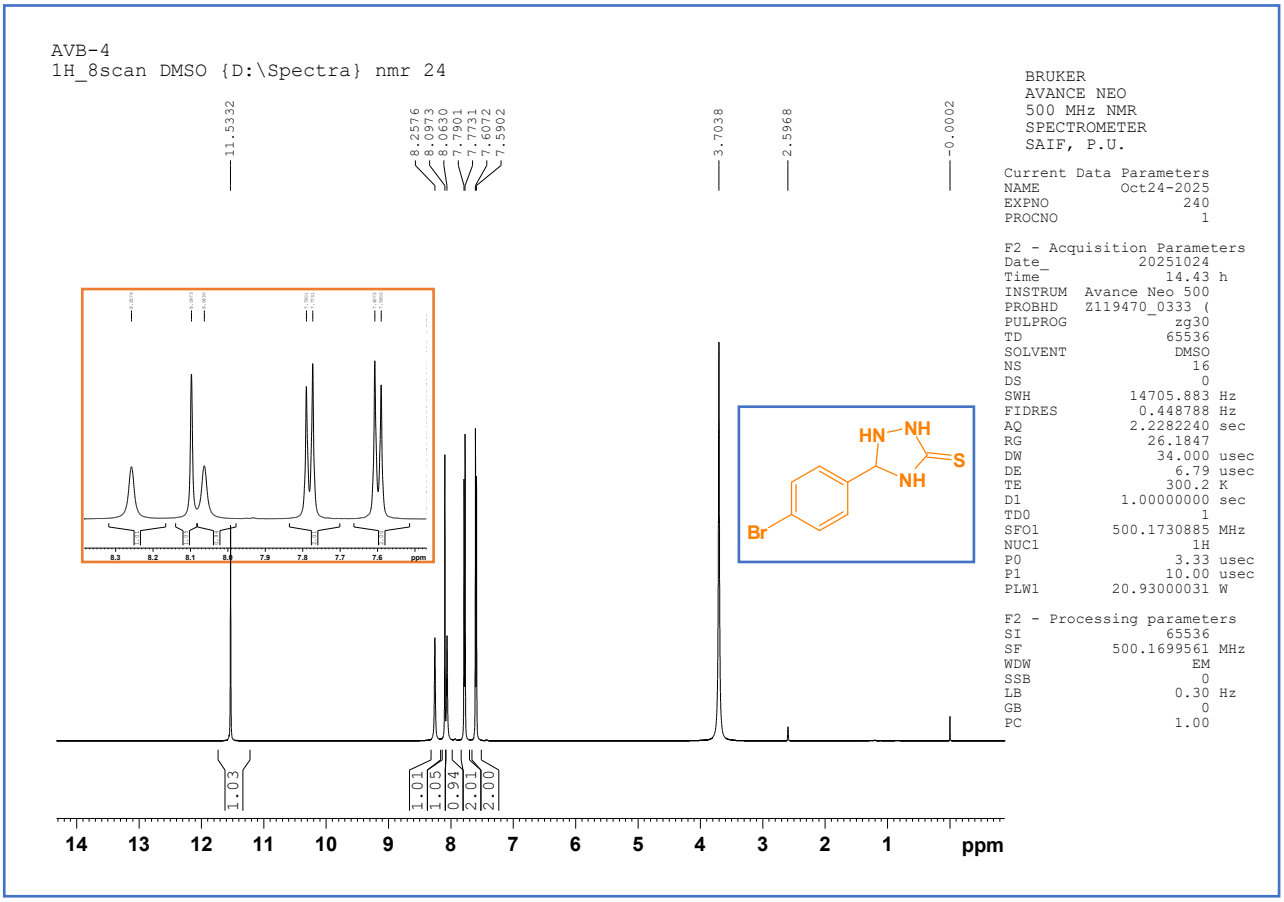
HRMS of 5-(thiophen-2-yl)-1,2,4-triazolidine-3-thione (3j)

5-(4-bromophenyl)-1,2,4-triazolidine-3-thione (3k)

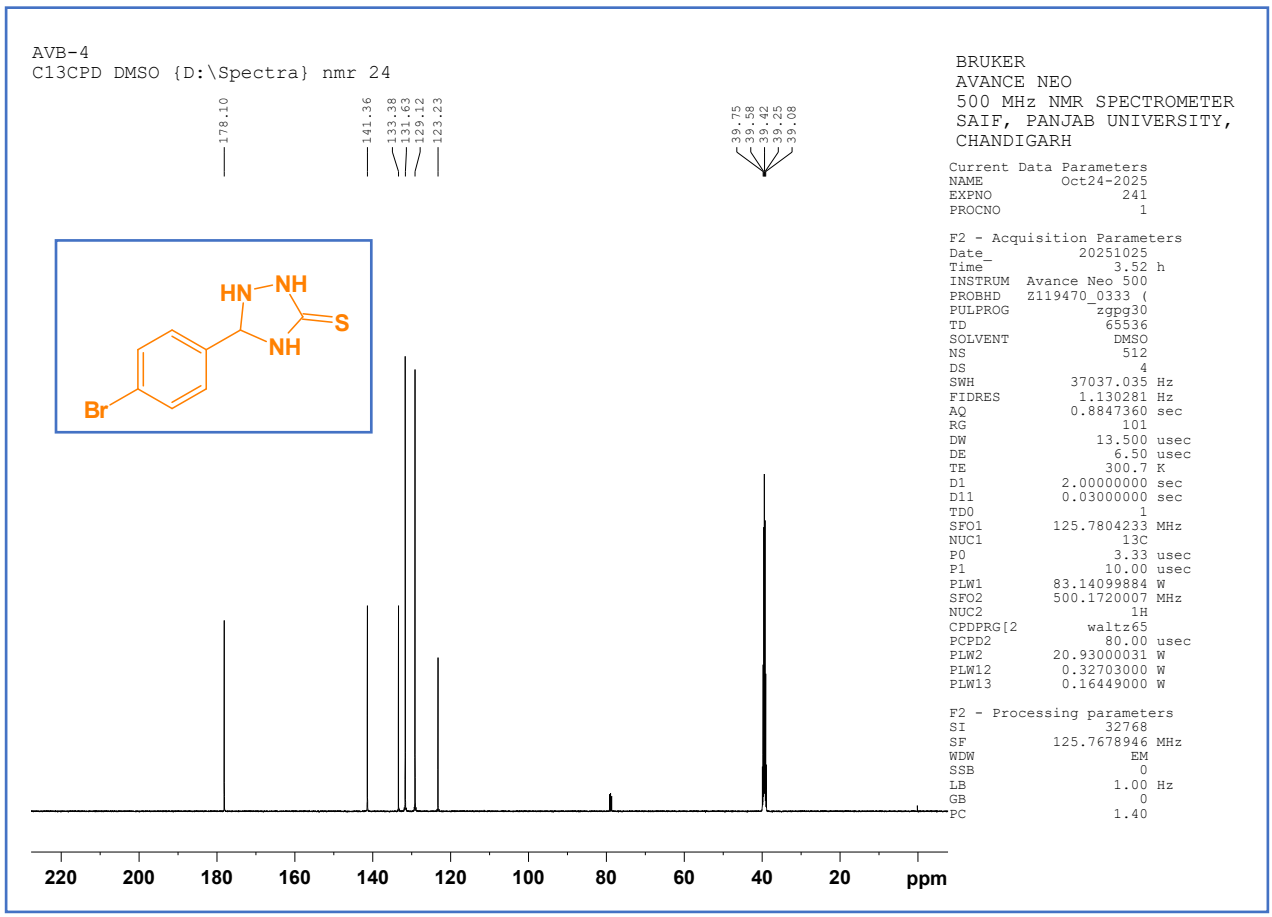
White crystal, Mp. 201-203 ˚C; IR (KBr): 3364, 3285, 1593, 1520, 1466, 1362, 1283, 1162, 1089, 1006, 923, 866, 693, 541 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d6): δ 7.5902-7.6072 (d, 2H, ArH, J = 8.5 Hz), 7.7731-7.7901(d, 2H, ArH, J = 8.5 Hz), 8.0630 (s,1H, CH), 8.0973 (s, 1H, NH), 8.2576 (s, 1H, NH), 11.5332 (s, 1H, NH); ^{13}C-NMR (500 MHz, DMSO-d6): 123.23, 129.12, 131.63, 133.38, 141.36, 178.10; HRMS{observed [M+1] peak: 259.99 (m/z)} {calculated [M] peak: 258.14 (m/z)}



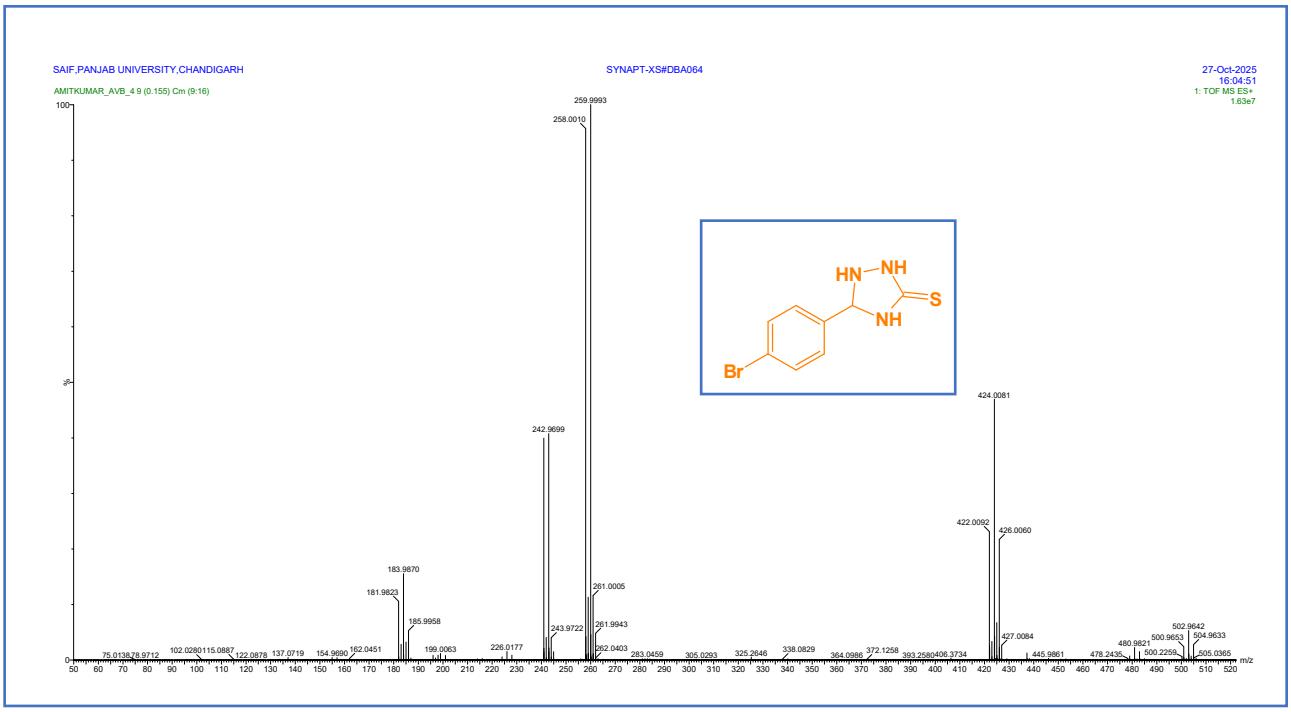
F'



[1]HNMR of 5-(4-bromophenyl)-1,2,4-triazolidine-3-thione (3k)



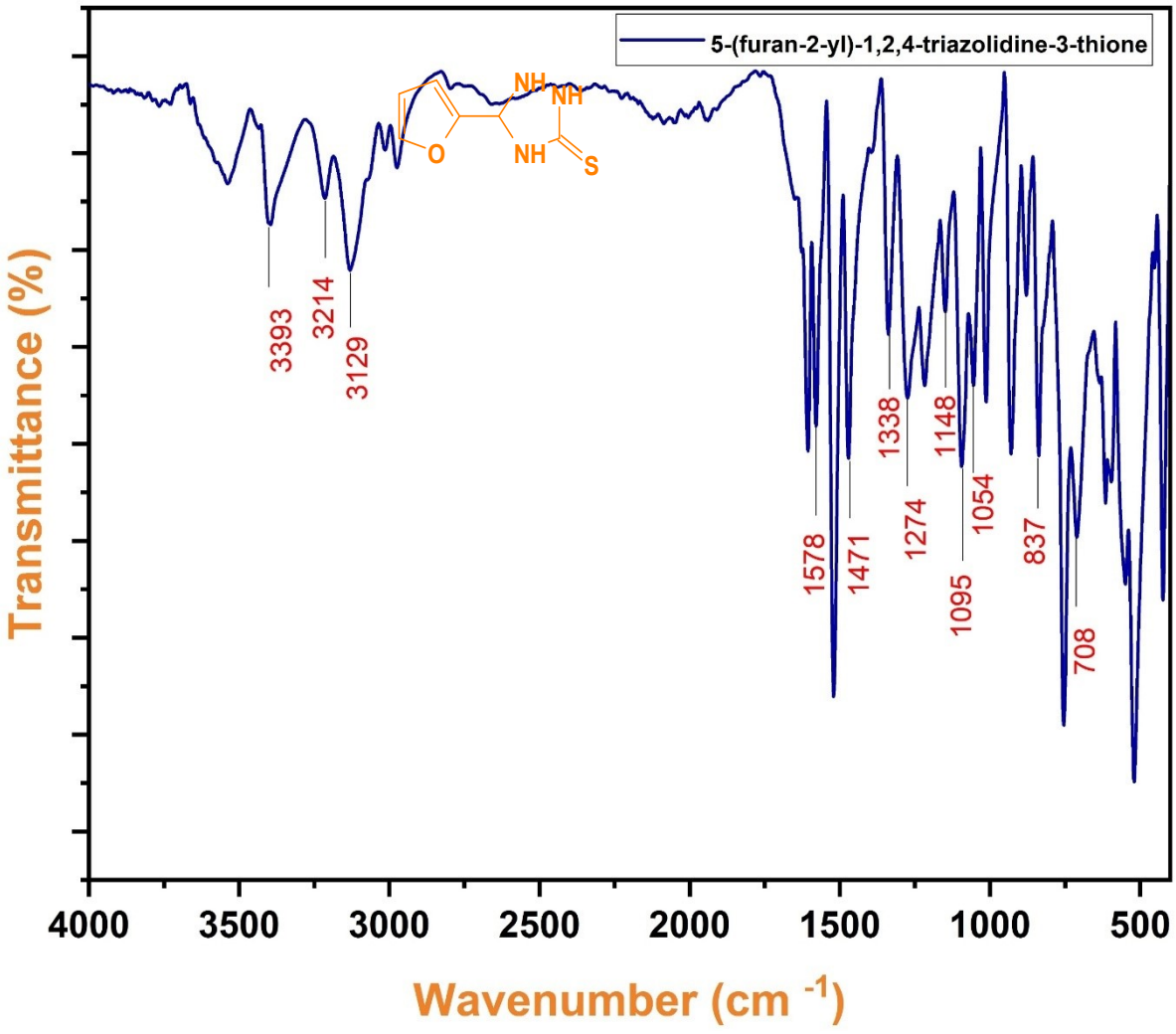
^{13}C-NMR of 5-(4-bromophenyl)-1,2,4-triazolidine-3-thione (3k)



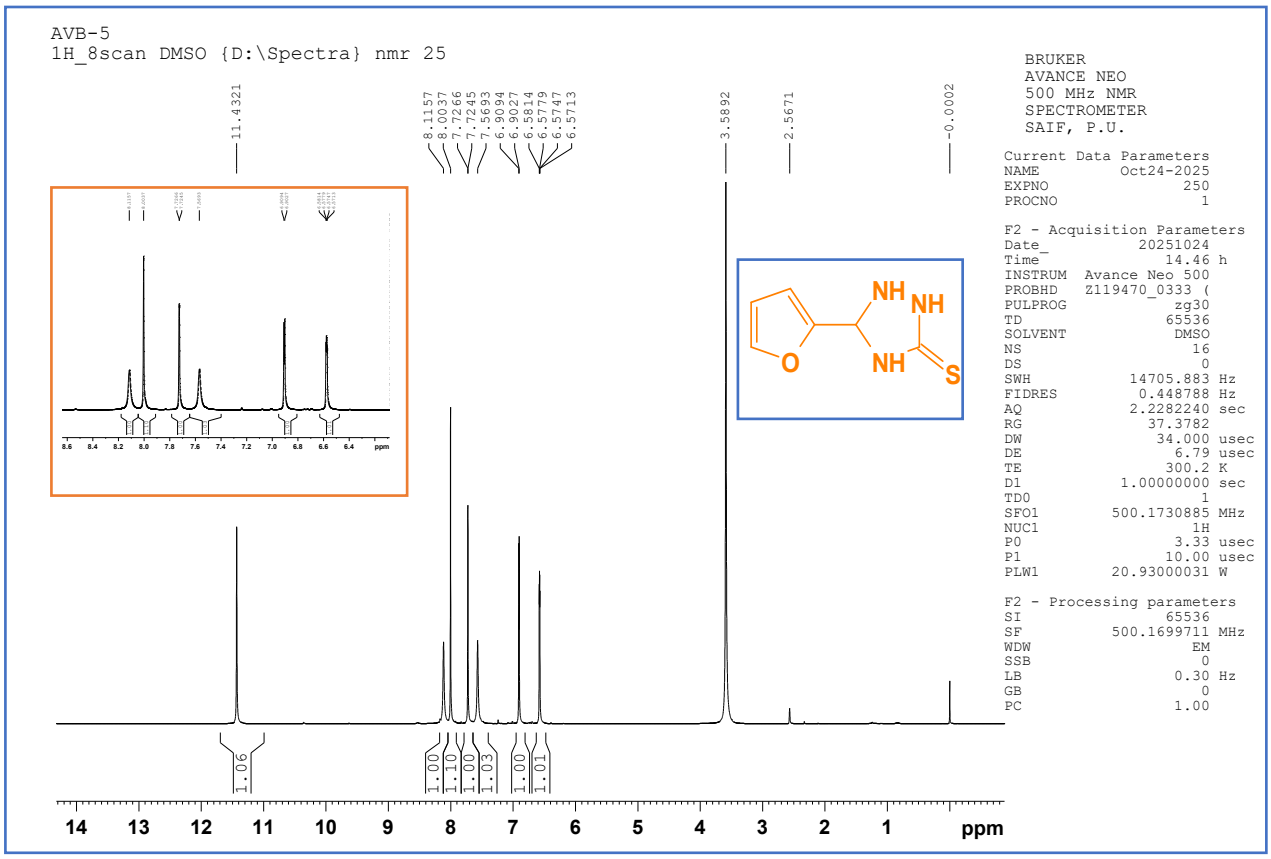
HRMS of 5-(4-bromophenyl)-1,2,4-triazolidine-3-thione (3k)

5-(furan-2-yl)-1,2,4-triazolidine-3-thione (3l)

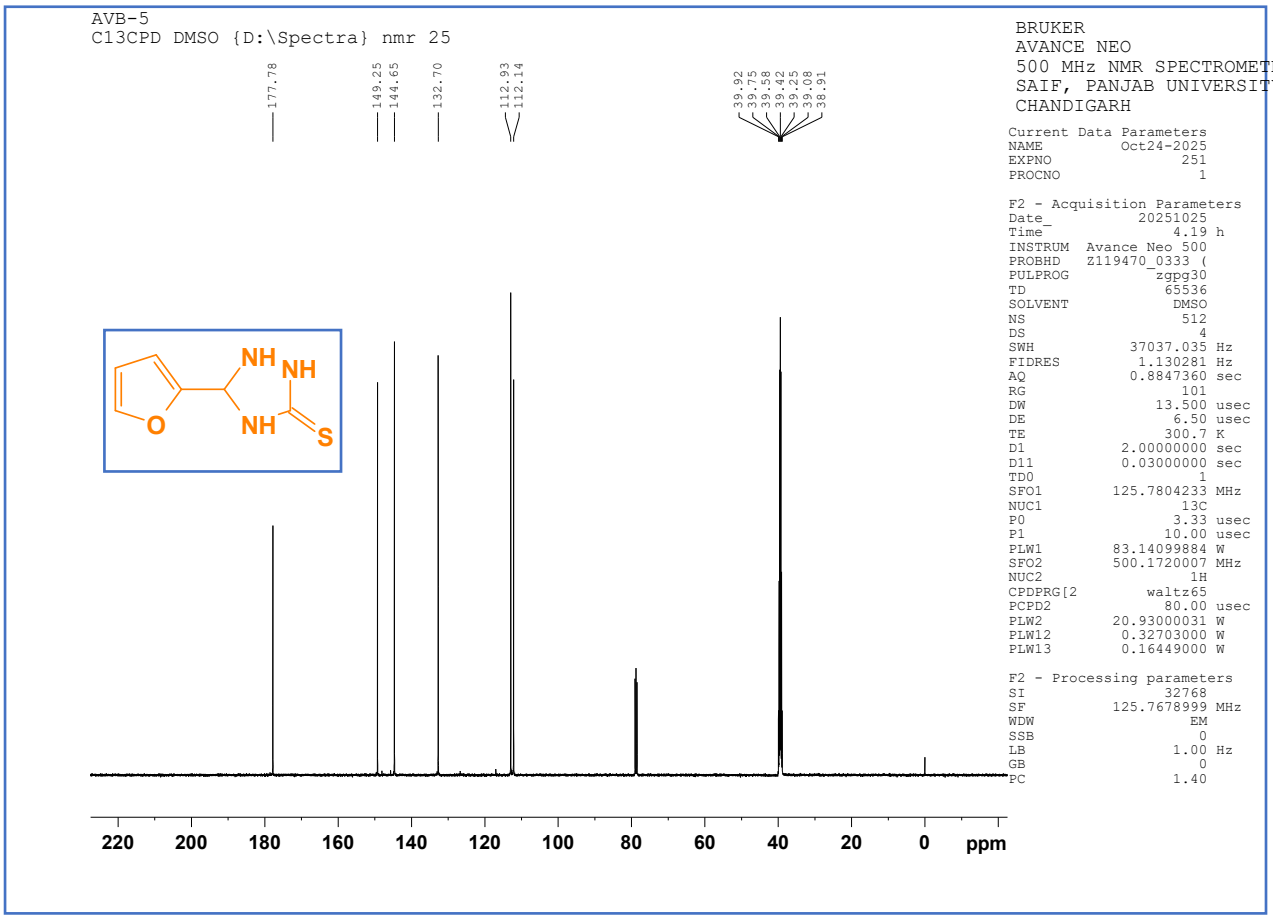
Pale yellow solid, Mp. 187-189 ˚C; IR (KBr): 3393, 3214, 3129, 1578, 1471, 1338, 1274, 1148, 1095, 1054, 923, 837, 708, 541 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d6): δ 6.5713-6.5814 (q, 1H, ArH, J = 5 Hz), 6.9027-6.9094(d, 1H, ArH, J = 3.5 Hz), 7.5693 (s,1H, CH),7.7245-7.7266 (d, 1H, ArH, J=1Hz), 8.0037 (s, 1H, NH), 8.1157 (s, 1H, NH), 11.4321 (s, 1H, NH); ^{13}C-NMR (500 MHz, DMSO-d6): 112.14, 112.93, 132.70, 144.65, 149.25, 177.78; HRMS{observed [M+1] peak: 170.05 (m/z)} {calculated [M] peak: 169.20 (m/z)}



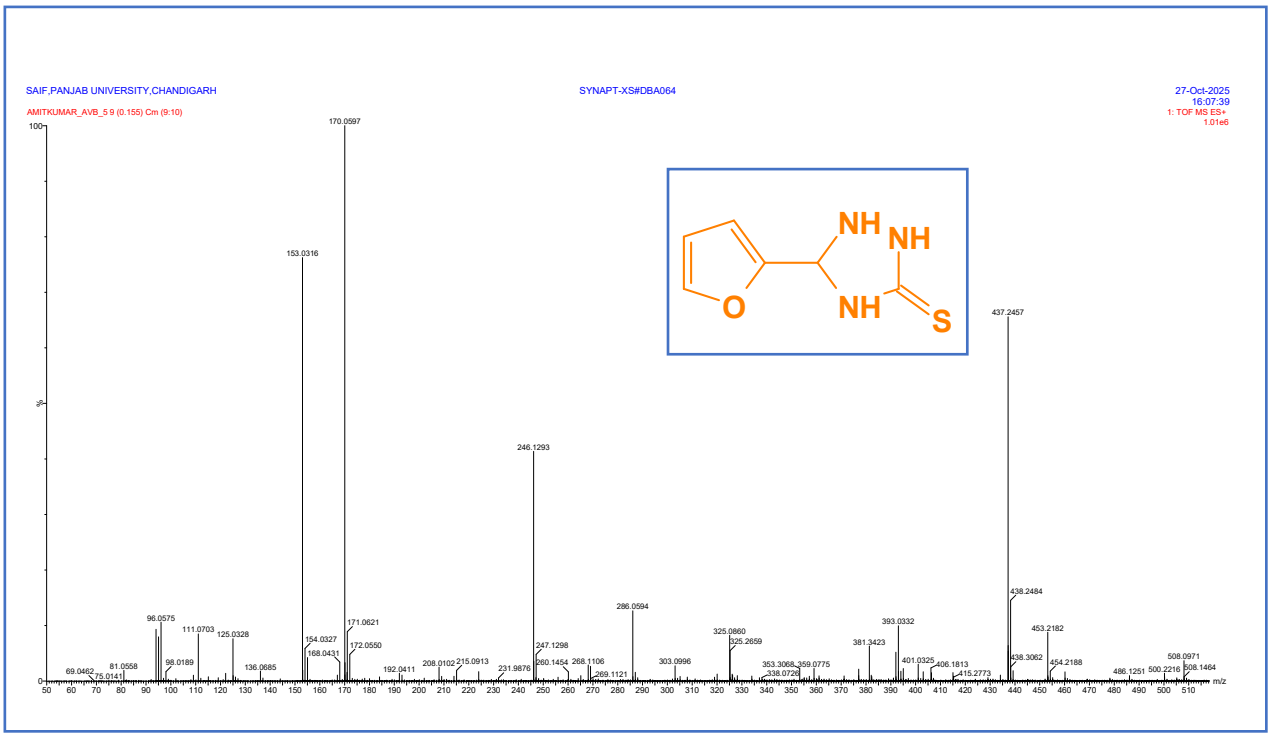
FTIR of 5-(furan-2-yl)-1,2,4-triazolidine-3-thione (3l)



[1]HNMR of 5-(furan-2-yl)-1,2,4-triazolidine-3-thione (3l)



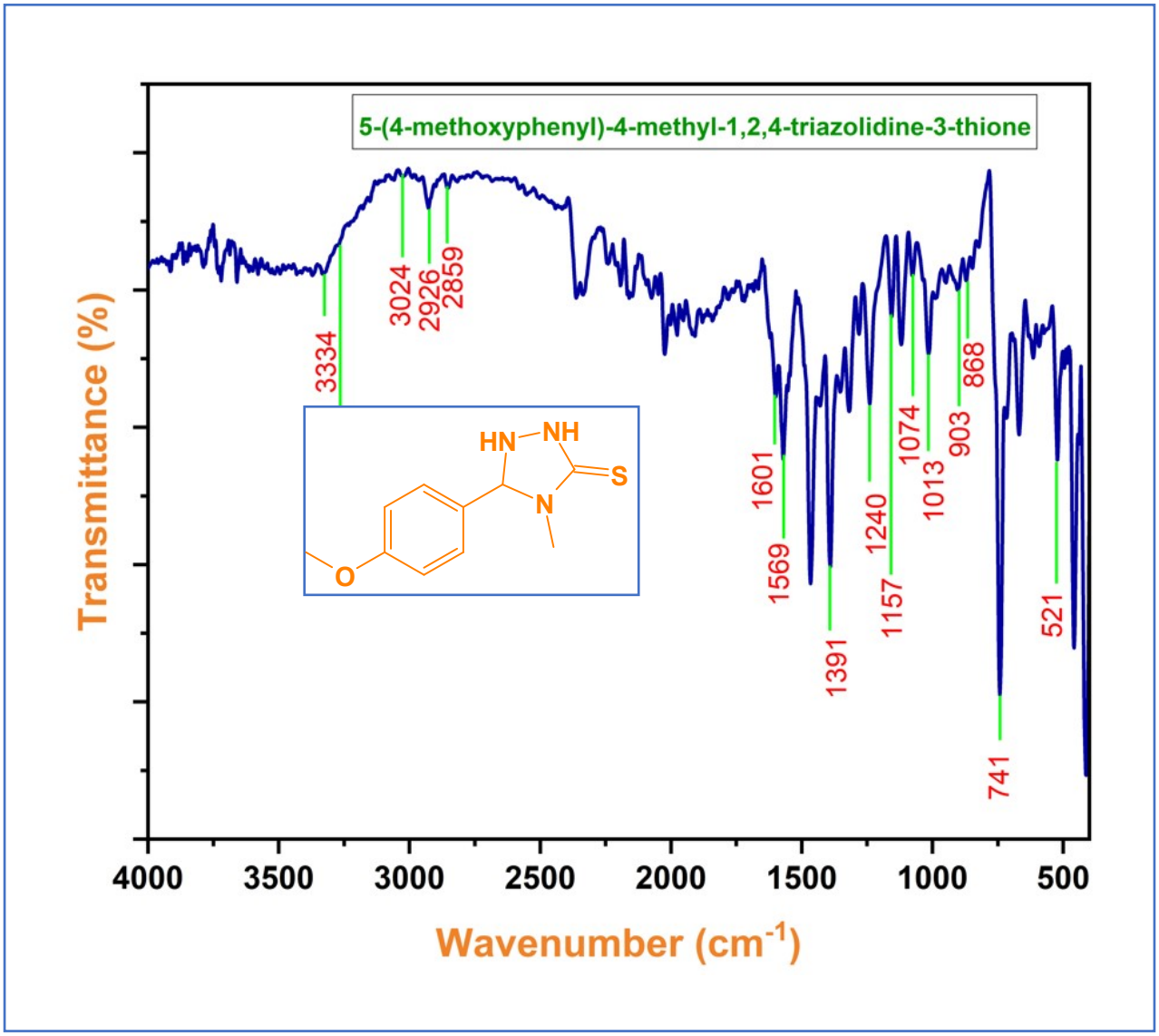
^{13}C-NMR of 5-(furan-2-yl)-1,2,4-triazolidine-3-thione (3l)



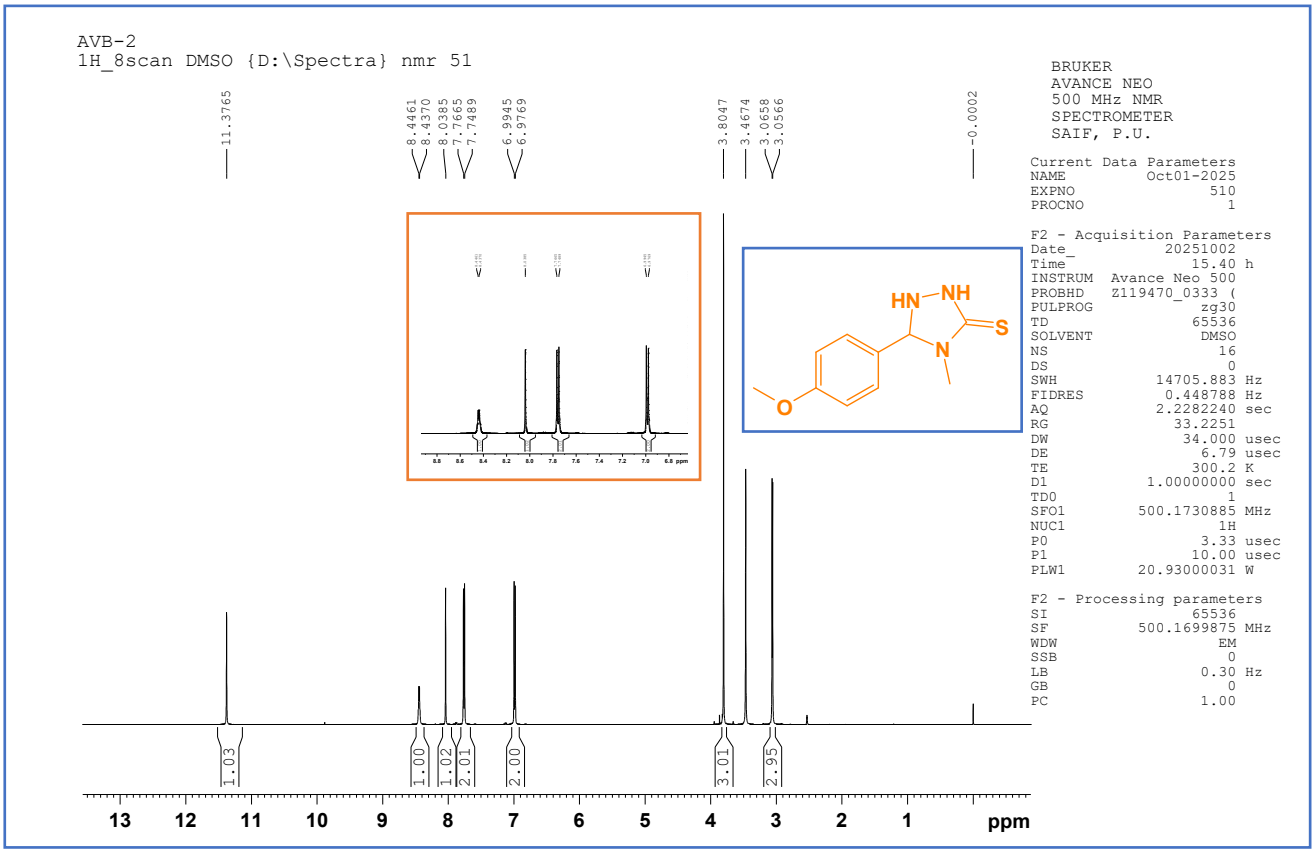
HRMS of 5-(furan-2-yl)-1,2,4-triazolidine-3-thione (3l)

5-(4-methoxyphenyl)-4-methyl-1,2,4-triazolidine-3-thione (3m)

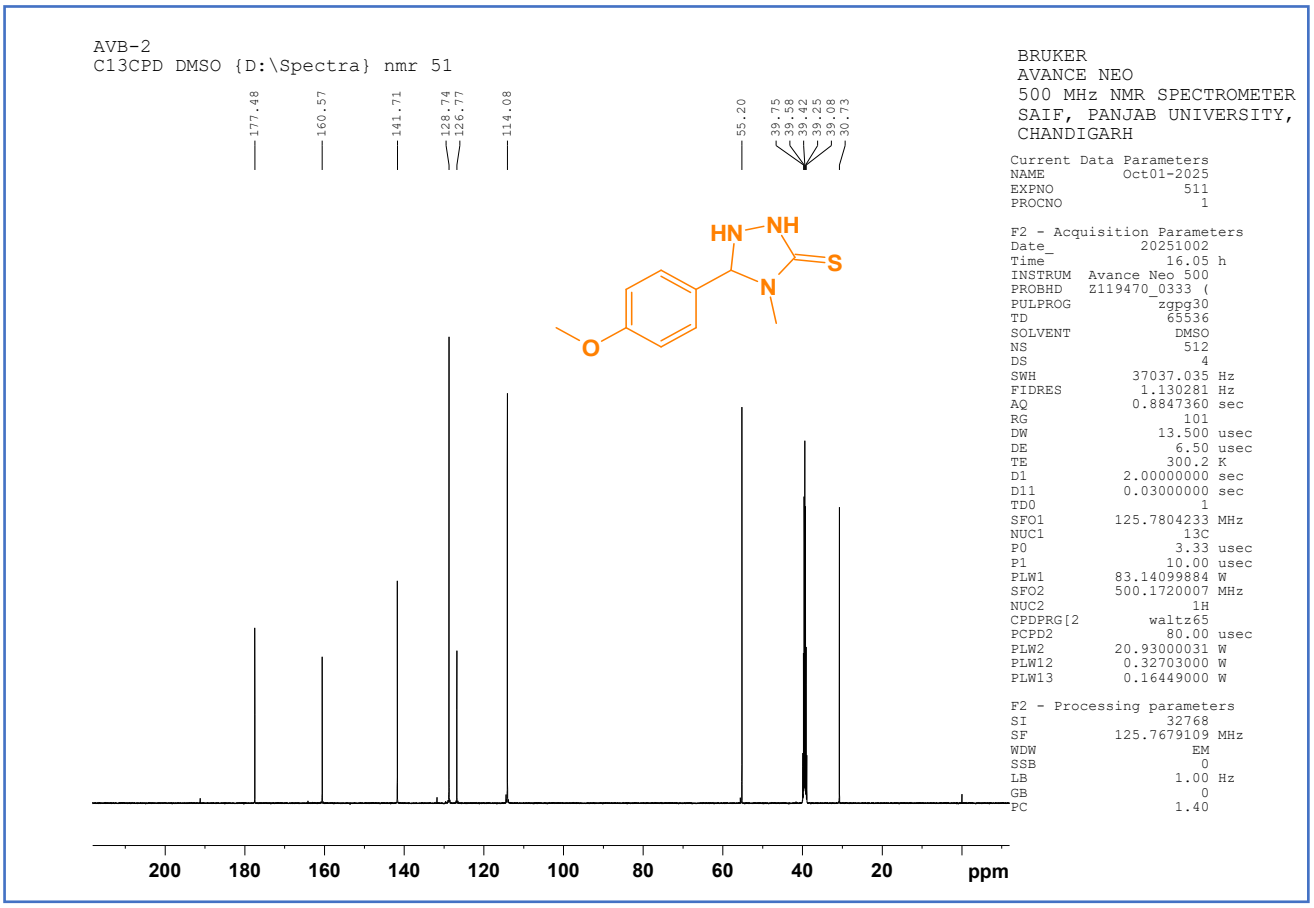
White crystal, Mp. 203-204 ˚C; IR (KBr): 3334,3265, 3024, 2926, 2859, 1601, 1569, 1391, 1240, 1157, 1074, 1013, 903, 868, 741, 521 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d6): δ 3.0566-3.0658 (br s, 3H, (N-CH_3), J = 4.5 Hz),3.8047 (s, 3H, (O-CH_3), 6.9769-6.9945 (d, 2H, ArH, J = 9 Hz), 7.7489-7.7665 (d, 2H, ArH), 8.0385 (s,1H, CH),8.4370-8.4461 (br s, 1H, NH), 11.3765 (s, 1H, NH); ^{13}C-NMR (500 MHz, DMSO-d6): 30.73, 55.20, 114.08, 126.77, 128.74, 141.71, 160.57, 177.48; HRMS{observed [M+1] peak: 224.08 (m/z)} {calculated [M] peak: 223.29 (m/z)}.



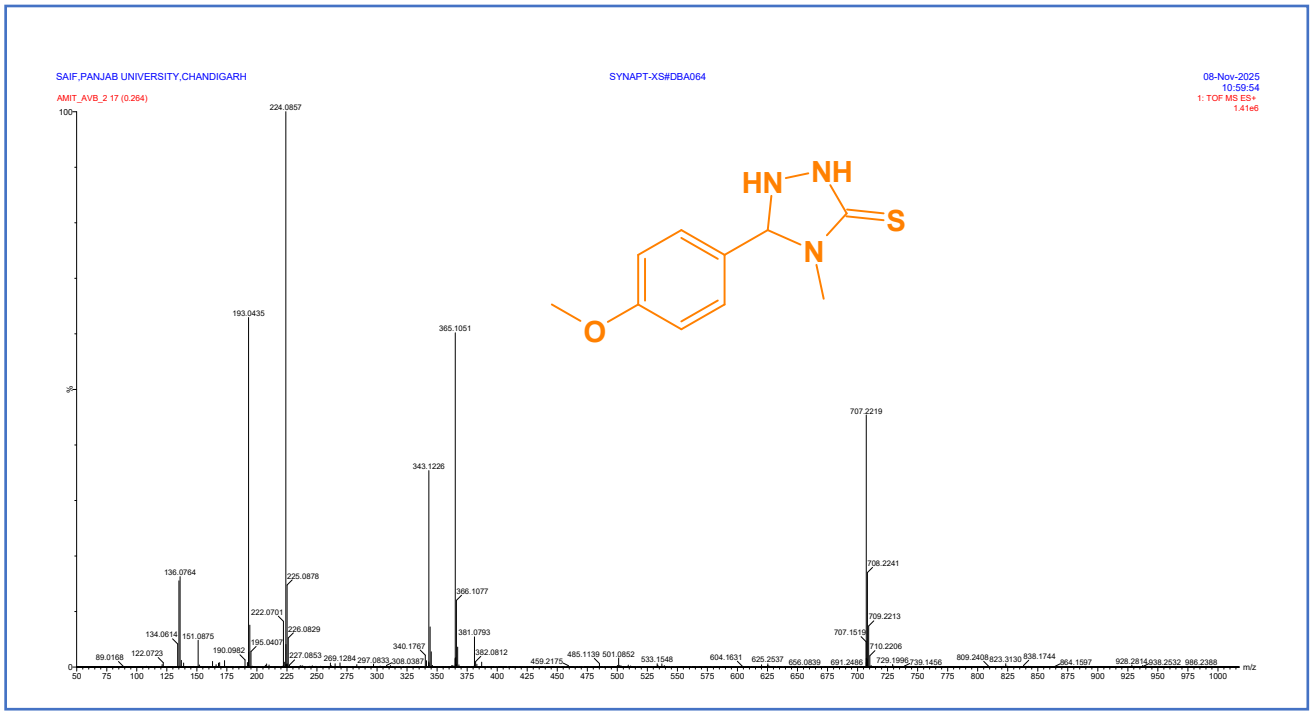
FTIR of 5-(4-methoxyphenyl)-4-methyl-1,2,4-triazolidine-3-thione (3m)



[1]HNMR of 5-(4-methoxyphenyl)-4-methyl-1,2,4-triazolidine-3-thione (3m)



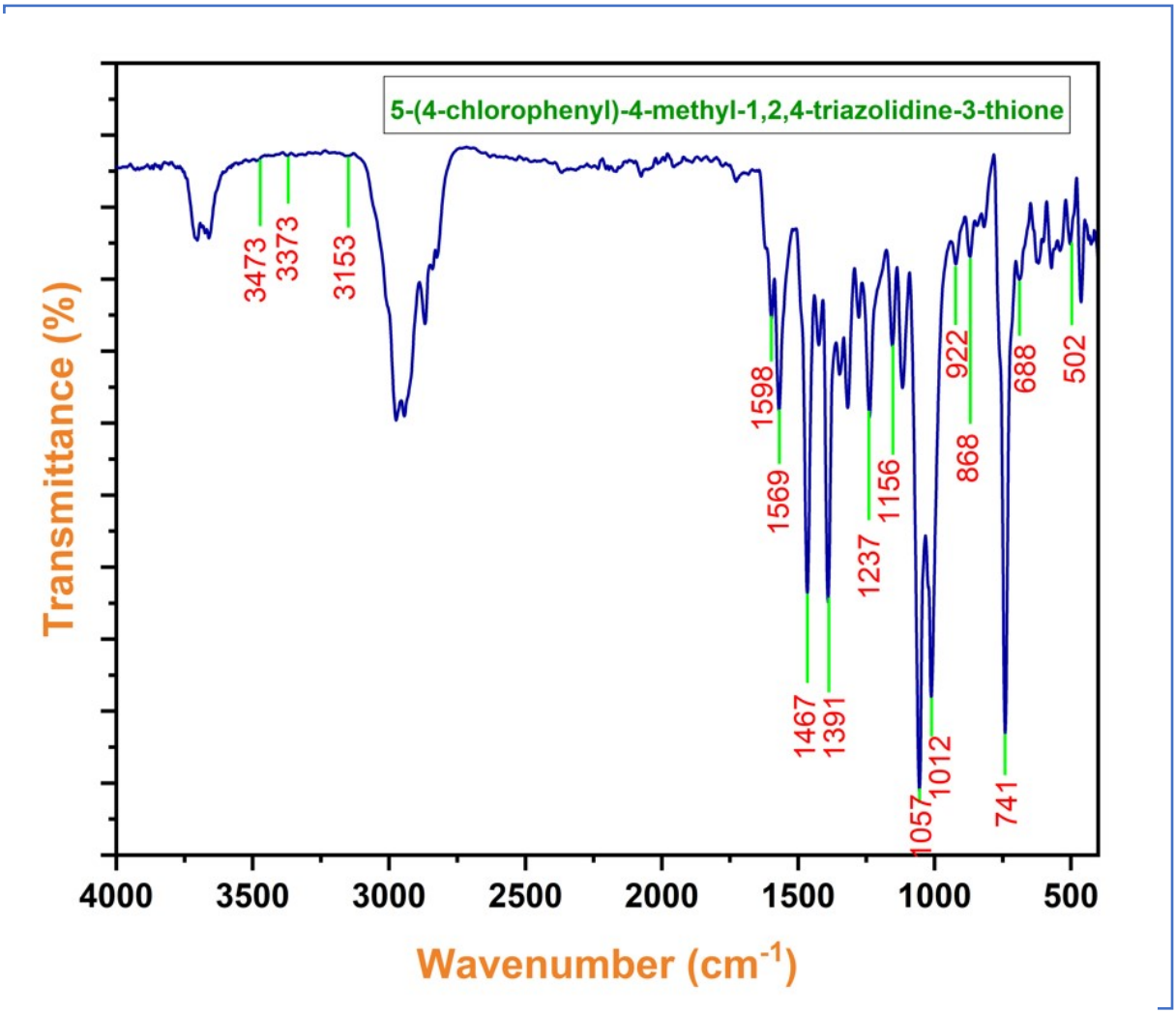
^{13}C-NMR of 5-(4-methoxyphenyl)-4-methyl-1,2,4-triazolidine-3-thione (3m)



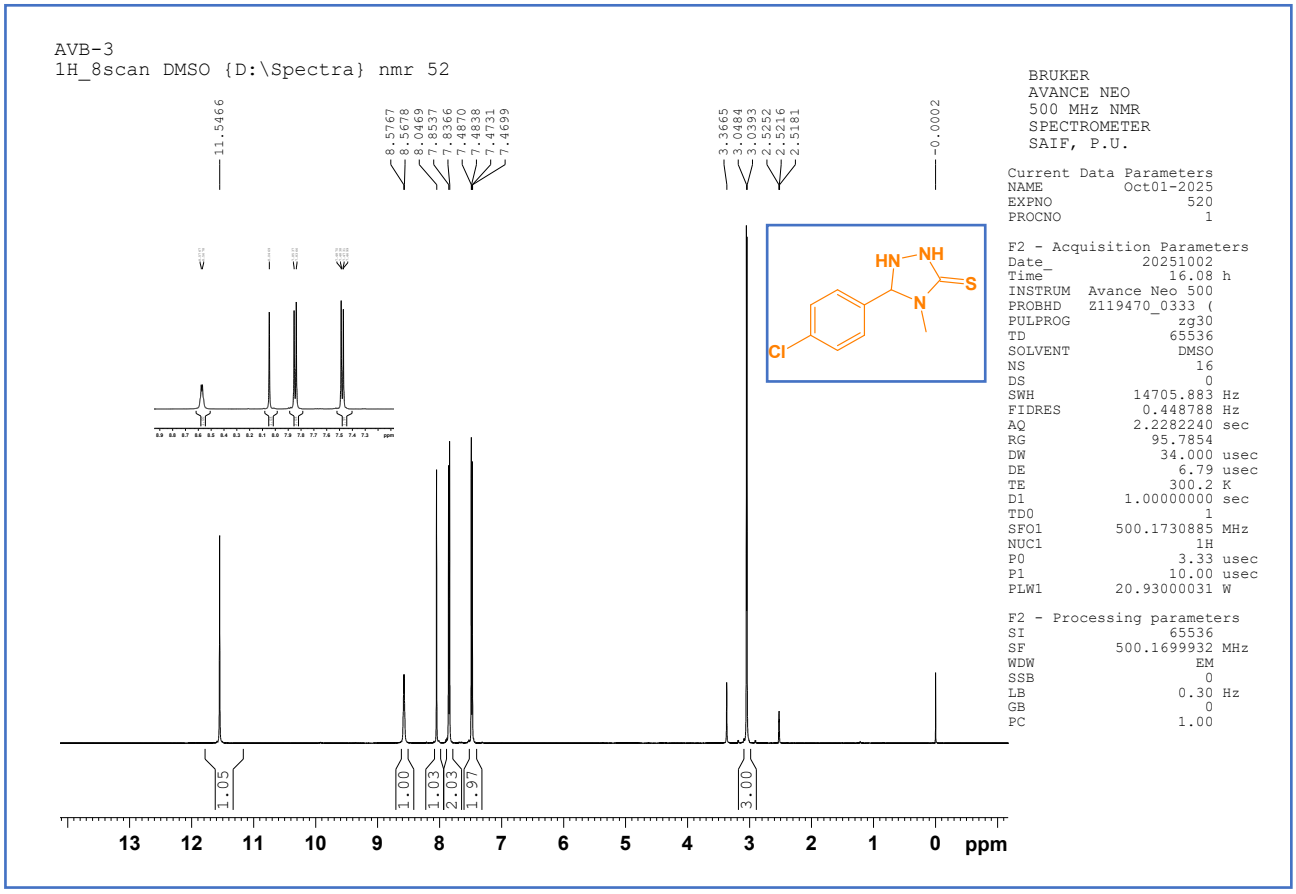
HRMS of 5-(4-methoxyphenyl)-4-methyl-1,2,4-triazolidine-3-thione (3m)

5-(4-chlorophenyl)-4-methyl-1,2,4-triazolidine-3-thione (3n)

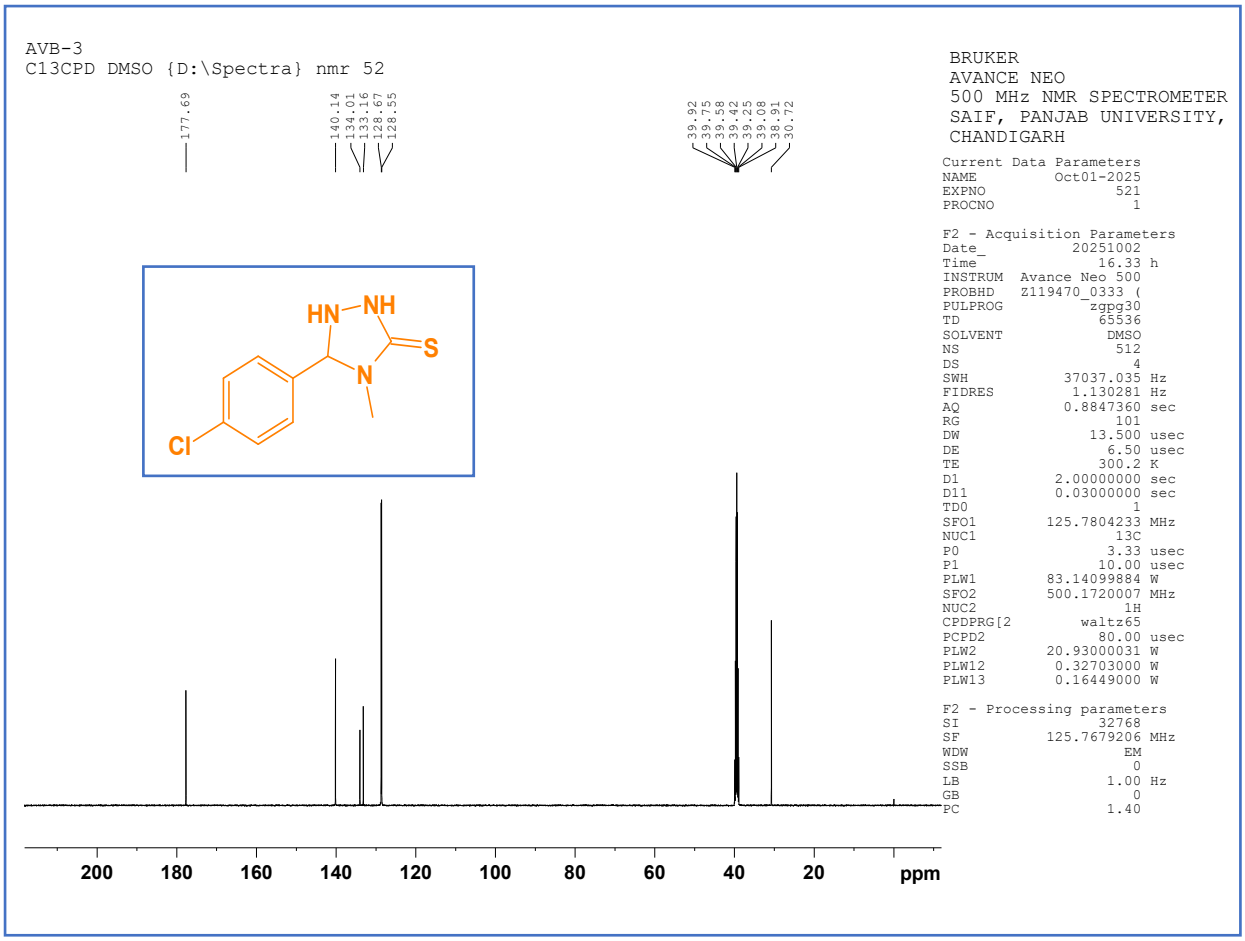
White crystal, Mp. 178-181 ˚C; IR (KBr): 3473, 3373, 3153, 1598, 1569, 1467, 1391, 1237, 1156, 1057, 1012, 922, 868, 741, 688,502 cm^{-1}; ^{1}H-NMR (500 MHz, DMSO-d_6): δ 3.0393-3.0484 (br s, 3H, N-CH3), 7.4699-7.4870 (d, 2H, ArH), 7.8366-7.8537 (d, 2H, ArH),8.0469 (s, 1H, CH), 8.5678-8.5767 (br s, 1H, NH), 11.5466 (s, 1H, NH); ^{13}C-NMR (500 MHz, DMSO-d6):30.72, 128.55, 128.67, 133.16, 134.01, 140.14, 177.69 ; HRMS{observed [M+1] peak: 224.08 (m/z)} {calculated [M] peak: 223.29 (m/z)}.



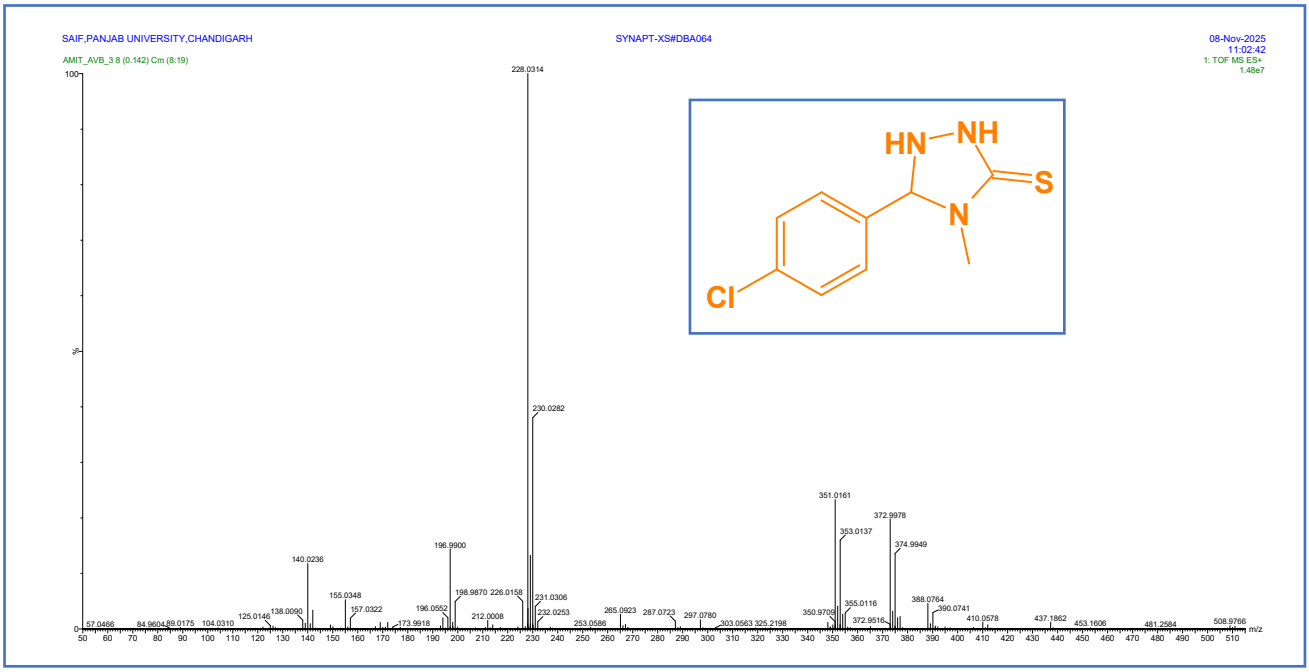
FTIR of 5-(4-chlorophenyl)-4-methyl-1,2,4-triazolidine-3-thione (3n)



[1]HNMR of 5-(4-chlorophenyl)-4-methyl-1,2,4-triazolidine-3-thione (3n)



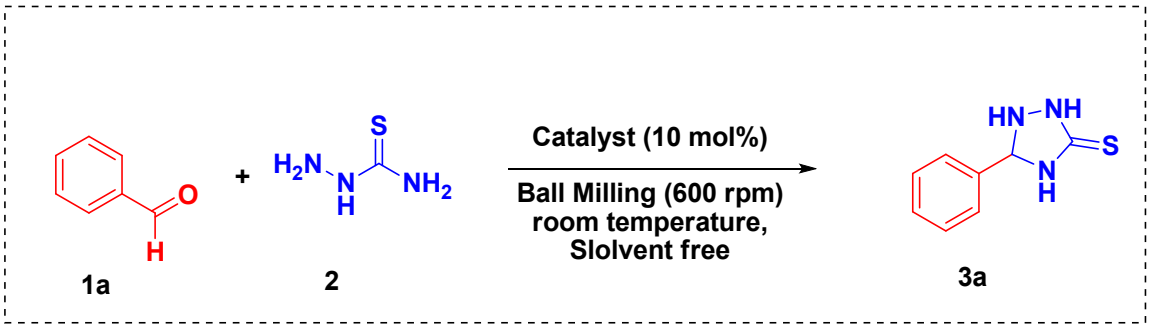
^{13}C-NMR of 5-(4-chlorophenyl)-4-methyl-1,2,4-triazolidine-3-thione (3n)



HRMS of 5-(4-chlorophenyl)-4-methyl-1,2,4-triazolidine-3-thione (3n)

SI8:

Table 1: Optimisation of reaction conditions [a]



Entry	Products (3a)	Catalyst / Additives	Time (min)	Catalyst (mol %)	Yield (%)[b]
1	Assembly (I)	$NiFe_2O_4$ NPs	15 min	5	35
2		$NiFe_2O_4$ NPs	20 min	5	41
3		$NiFe_2O_4$ NPs	25 min	5	44
4		$NiFe_2O_4$ NPs	30 min	5	57
5		$NiFe_2O_4$ NPs	35 min	5	59
6		$NiFe_2O_4$ NPs	40 min	5	63
7		$NiFe_2O_4$ NPs	45 min	5	66
8	**Assembly (II)**	$NiFe_2O_4$ NPs	15 min	10	78
9		$NiFe_2O_4$ NPs	20 min	10	81
10		$NiFe_2O_4$ NPs	25 min	10	88
11		**$NiFe_2O_4$ NPs**	**30 min**	**10**	**97**
12		$NiFe_2O_4$ NPs	35 min	10	94
13		$NiFe_2O_4$ NPs	40 min	10	91
14		$NiFe_2O_4$ NPs	45 min	10	90
15	Assembly (III)	$NiFe_2O_4$ NPs	15 min	15	74
16		$NiFe_2O_4$ NPs	20 min	15	80
17		$NiFe_2O_4$ NPs	25 min	15	82
18		$NiFe_2O_4$ NPs	30 min	15	86
19		$NiFe_2O_4$ NPs	35 min	15	85
20		$NiFe_2O_4$ NPs	40 min	15	83
21		$NiFe_2O_4$ NPs	45 min	15	81
22	Assembly (IV)	$NiFe_2O_4$ NPs	50 min	10	88
23		$NiFe_2O_4$ NPs	55 min	10	85
24		$NiFe_2O_4$ NPs	60 min	10	83
25		$NiFe_2O_4$ NPs	60 min	15	87
26	Assembly (V)	$CoFe_2O_4$ NPs	30 min	10	22
27		$CuFe_2O_4$ NPs	30 min	10	25
28		Fe_3O_4 NPs	30 min	10	10
29		$ZnFe_2O_4$ NPs	30 min	10	22
30		No catalyst	30 min	-	NR

[a] Reaction Conditions: Benzaldehyde (1mmol), Thiosemicarbazide (1mmol), Solvent free, room temperature under ball-milling condition (600 rpm), NR: Not recovered, [b] isolated yield.

SI 9:

Table 2 Effect of reaction conditions on the yield of (3a).

Entry	Catalyst	Catalyst (Mole%)	Time (min)	Rotation (rpm)	Yield (%) [b]
1	$NiFe_2O_4$ NPs	5	30	400	51
2	$NiFe_2O_4$ NPs	5	30	500	54
3	$NiFe_2O_4$ NPs	5	30	600	57
4	$NiFe_2O_4$ NPs	10	30	400	95
5	$NiFe_2O_4$ NPs	10	30	500	96
6	**$NiFe_2O_4$ NPs**	**10**	**30**	**600**	**97**
7	$NiFe_2O_4$ NPs	15	30	400	83
8	$NiFe_2O_4$ NPs	15	30	500	84
9	$NiFe_2O_4$ NPs	15	30	600	86
10	$NiFe_2O_4$ NPs	20	30	400	88
11	$NiFe_2O_4$ NPs	20	30	500	91
12	$NiFe_2O_4$ NPs	20	30	600	93

[b] Isolated yield, Model reaction (3a): benzaldehyde (1.0 mmol), thiosemicarbazide (1.0 mmol) under ball milling condition.

SI 10:

Table 3: Comparison of Nano $NiFe_2O_4$-catalyzed conventional methodologies for the synthesis of (3a).

Entry	Catalyst	Catalyst (mol%)	Reaction Condition	Time (min)	Yield (%) [b]
1	$NiFe_2O_4$ NPs	5	Reflux/ EtOH: H_2O (1:1)	30	22
2	$NiFe_2O_4$ NPs	5	Reflux/ EtOH: H_2O (1:1)	60	30
3	$NiFe_2O_4$ NPs	5	Reflux/ EtOH: H_2O (1:1)	90	38
4	$NiFe_2O_4$ NPs	5	Reflux/ EtOH: H_2O (1:1)	120	43
5	$NiFe_2O_4$ NPs	10	Reflux/ EtOH: H_2O (1:1)	30	50
6	$NiFe_2O_4$ NPs	10	Reflux/ EtOH: H_2O (1:1)	60	55
7	$NiFe_2O_4$ NPs	10	Reflux/ EtOH: H_2O (1:1)	90	57
8	$NiFe_2O_4$ NPs	10	Reflux/ EtOH: H_2O (1:1)	120	56
9	$NiFe_2O_4$ NPs	15	Reflux/ EtOH: H_2O (1:1)	30	52
10	$NiFe_2O_4$ NPs	15	Reflux/ EtOH: H_2O (1:1)	60	54
11	$NiFe_2O_4$ NPs	15	Reflux/ EtOH: H_2O (1:1)	90	56
12	$NiFe_2O_4$ NPs	15	Reflux/ EtOH: H_2O (1:1)	120	55
13	$NiFe_2O_4$ NPs	20	Reflux/ EtOH: H_2O (1:1)	30	50
14	$NiFe_2O_4$ NPs	20	Reflux/ EtOH: H_2O (1:1)	60	51
15	$NiFe_2O_4$ NPs	20	Reflux/ EtOH: H_2O (1:1)	90	49
16	$NiFe_2O_4$ NPs	20	Reflux/ EtOH: H_2O (1:1)	120	52
17	No Catalyst	--	Reflux/ EtOH: H_2O (1:1)	90	NR

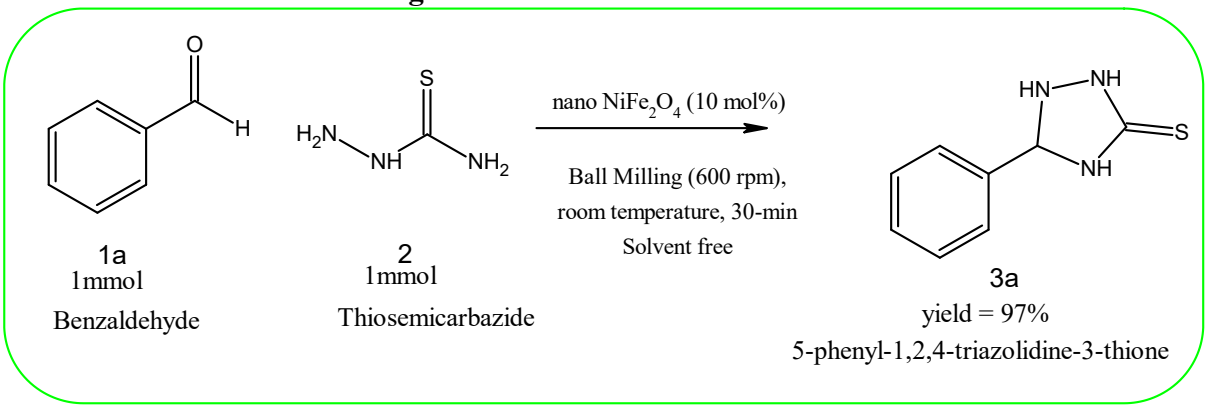
[b] Isolated yield, Model reaction (3a): benzaldehyde (1.0 mmol), thiosemicarbazide (1.0 mmol) under conventional condition, NR: Not recovered.

SI 11:

Table 4: (A) Calculation of Green Chemistry Metrics (EcoScale and E-factor & atom economy)

(A) Calculation of Ecoscale:

1. **EcoScale Score for the synthesis of 5-phenyl-1,2,4-triazolidine-3-thione (3a) under the ball-milling conditions:**



1a
1mmol
Benzaldehyde

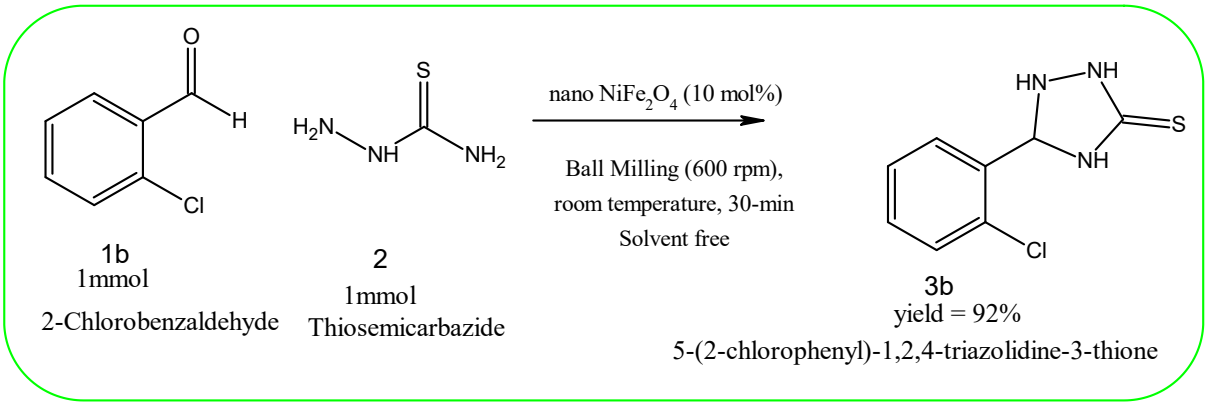
2
1mmol
Thiosemicarbazide

3a
yield = 97%
5-phenyl-1,2,4-triazolidine-3-thione

Parameter	Penalty
1. Yield 97%	1.5
2. Price of reaction components	
Benzaldehyde: **cheap**	0
Thiosemicarbazide: **inexpensive**	0
nano $NiFe_2O_4$: **recyclable, low cost**	0
3. **Safety**	
Benzaldehyde: **mild irritant**	
Thiosemicarbazide: **toxic if swallowed, irritant**	3
Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	
4. Technical setup	
Unconventional activation technique	**2**
5. Temperature/time	**0**
Room temperature < 1 h	
6. Workup & Purification	
None	**0**
Total Penalty Points	**6.5**

EcoScale Score = 100- Total Penalty Points = 93.5

2. EcoScale Score for the synthesis of 5-(2-chlorophenyl)-1,2,4-triazolidine-3-thione (3b) under the ball-milling conditions:



1b
1mmol
2-Chlorobenzaldehyde

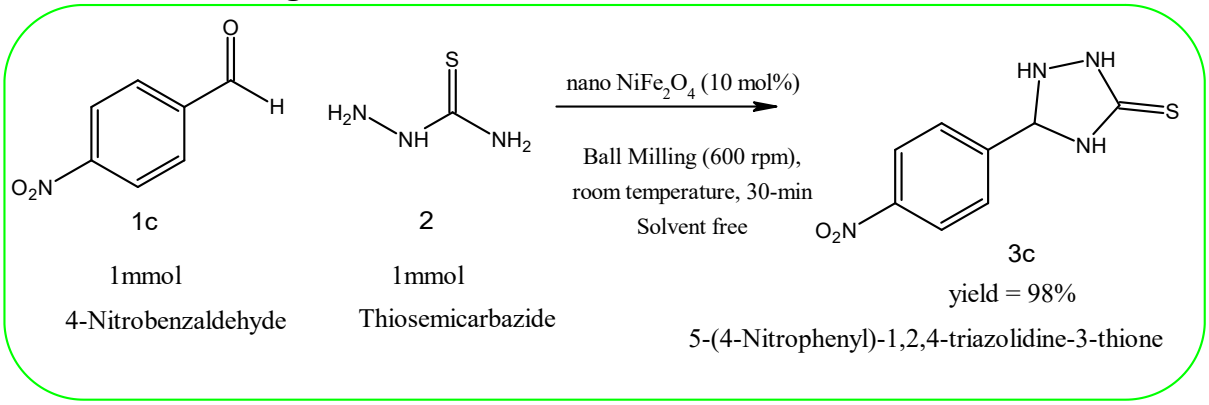
2
1mmol
Thiosemicarbazide

3b
yield = 92%
5-(2-chlorophenyl)-1,2,4-triazolidine-3-thione

Parameter	Penalty
1. Yield 92%	4
2. Price of reaction components 2-Chlorobenzaldehyde: **cheap** Thiosemicarbazide: **inexpensive** nano $NiFe_2O_4$: **recyclable, low cost**	 0 0 0
3. **Safety** 2-Chlorobenzaldehyde: **irritant, lachrymator, harmful if swallowed** Thiosemicarbazide: **toxic if swallowed, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	3
4. Technical setup Unconventional activation technique	2
5. Temperature/time Room temperature < 1 h	0
6. Workup & Purification None	0
Total Penalty Points	**9**

EcoScale Score = 100- Total Penalty Points = 91

3. EcoScale Score for the synthesis of 5-(4-Nitrophenyl)-1,2,4-triazolidine-3-thione (3c) under the ball-milling conditions:

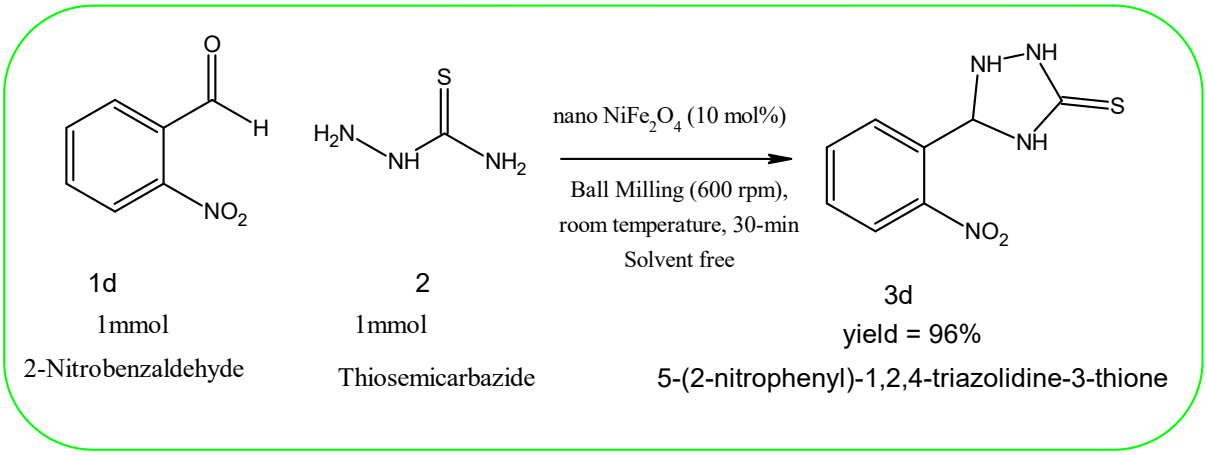


1mmol 4-Nitrobenzaldehyde + 1mmol Thiosemicarbazide → yield = 98% 5-(4-Nitrophenyl)-1,2,4-triazolidine-3-thione

Parameter	Penalty
1. Yield 98%	1
2. Price of reaction components	
4-Nitrobenzaldehyde: **cheap**	0
Thiosemicarbazide: **inexpensive**	0
nano $NiFe_2O_4$: **recyclable, low cost**	0
3. **Safety**	
4-Nitrobenzaldehyde: **harmful, irritant, possible mutagenic concerns**	3
Thiosemicarbazide: **toxic if swallowed, irritant**	
Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	
4. Technical setup	
Unconventional activation technique	2
5. Temperature/time	0
Room temperature < 1 h	
6. Workup & Purification	
None	0
Total Penalty Points	**6**

EcoScale Score = 100- Total Penalty Points = 94

4. EcoScale Score for the synthesis of 5-(2-Nitrophenyl)-1,2,4-triazolidine-3-thione (3d) under the ball-milling conditions:



1d
1mmol
2-Nitrobenzaldehyde

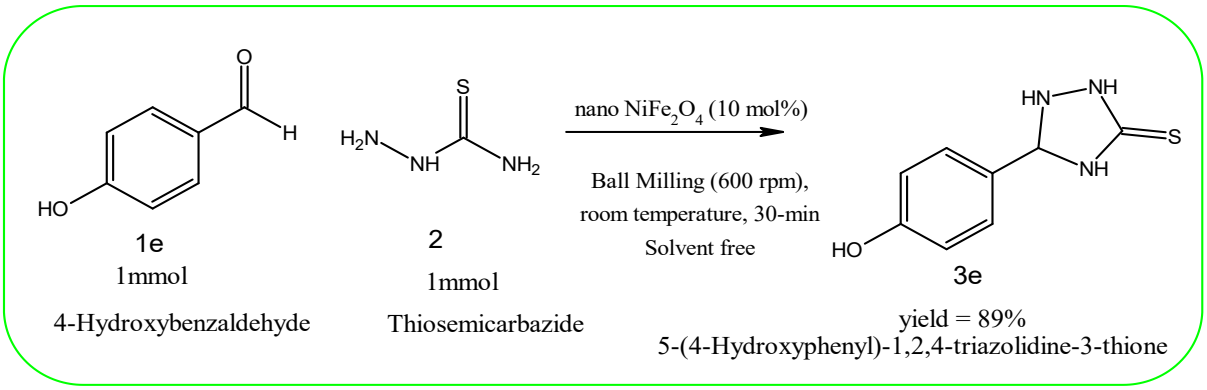
2
1mmol
Thiosemicarbazide

3d
yield = 96%
5-(2-nitrophenyl)-1,2,4-triazolidine-3-thione

Parameter	Penalty
1. Yield 96%	2
2. Price of reaction components	
2-Nitrobenzaldehyde: **inexpensive**	0
Thiosemicarbazide: **inexpensive**	0
nano $NiFe_2O_4$: **recyclable, low cost**	0
3. **Safety**	
2-Nitrobenzaldehyde: **harmful if swallowed, irritant**	
Thiosemicarbazide: **toxic if swallowed, irritant**	3
Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	
4. Technical setup	
Unconventional activation technique	2
5. Temperature/time	0
Room temperature < 1 h	
6. Workup & Purification	
None	0
Total Penalty Points	**7**

EcoScale Score = 100- Total Penalty Points = 93

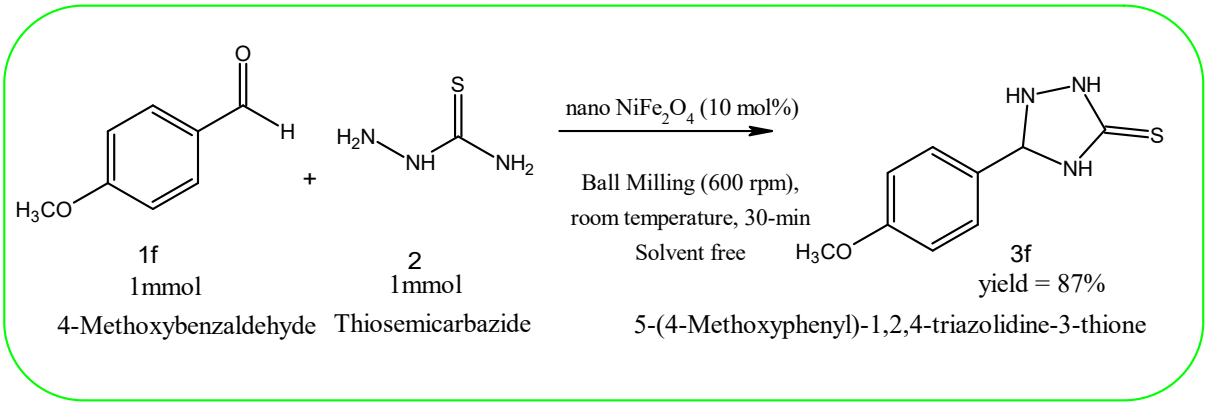
5. EcoScale Score for the synthesis of 5-(4-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3e) under the ball-milling conditions:



Parameter	Penalty
1. Yield 89%	5.5
2. Price of reaction components 4-Hydroxybenzaldehyde: **cheap** Thiosemicarbazide: **inexpensive** nano $NiFe_2O_4$: **recyclable, low cost**	 0 0 0
3. **Safety** 4-Hydroxybenzaldehyde: **mild irritant, low acute toxicity** Thiosemicarbazide: **acute oral toxicity, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	3
4. Technical setup Unconventional activation technique	2
5. Temperature/time Room temperature < 1 h	0
6. Workup & Purification None	0
Total Penalty Points	**10.5**

EcoScale Score = 100- Total Penalty Points = 89.5

6. EcoScale Score for the synthesis of 5-(4-Methoxyphenyl)-1,2,4-triazolidine-3-thione (3f) under the ball-milling conditions:



1f
1mmol
4-Methoxybenzaldehyde

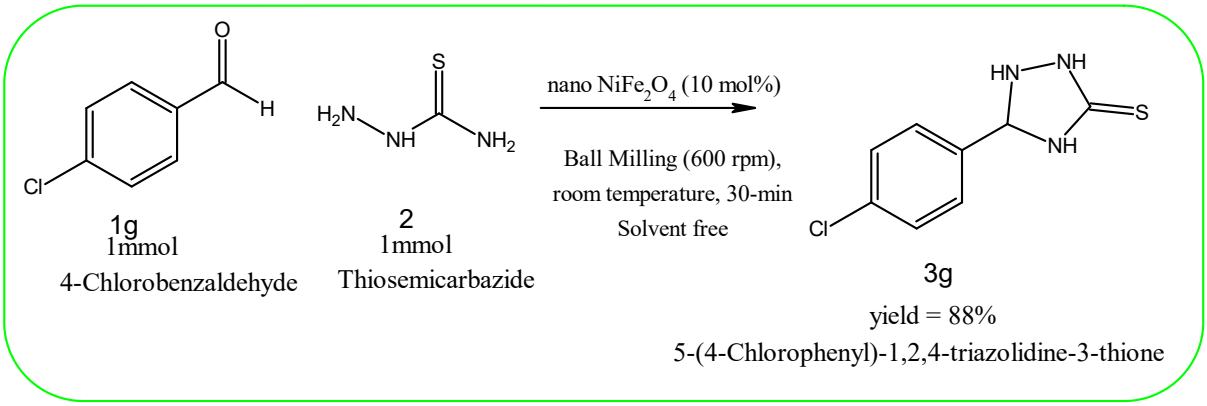
2
1mmol
Thiosemicarbazide

3f
yield = 87%
5-(4-Methoxyphenyl)-1,2,4-triazolidine-3-thione

Parameter	Penalty
1. Yield 87%	6.5
2. Price of reaction components 4-Methoxybenzaldehyde: **cheap** Thiosemicarbazide: **inexpensive** nano $NiFe_2O_4$: **recyclable, low cost**	 0 0 0
3. **Safety** 4-Methoxybenzaldehyde: **low toxicity** Thiosemicarbazide: **acute oral toxicity, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	3
4. Technical setup Unconventional activation technique	2
5. Temperature/time Room temperature < 1 h	0
6. Workup & Purification None	0
Total Penalty Points	**11.5**

EcoScale Score = 100- Total Penalty Points = 88.5

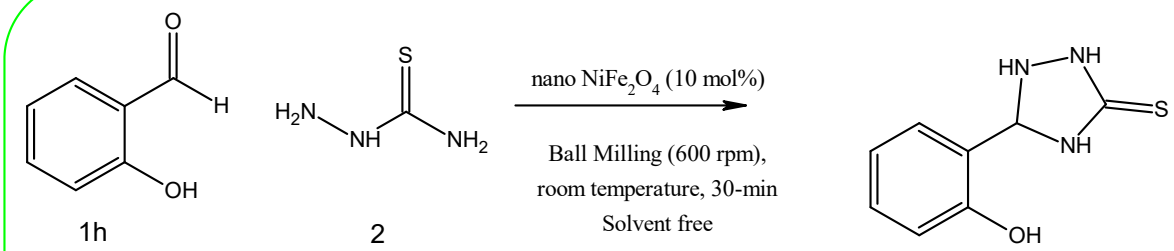
7. **EcoScale Score for the synthesis of 5-(4-Chlorophenyl)-1,2,4-triazolidine-3-thione (3g) under the ball-milling conditions:**



Parameter	Penalty
1. Yield 88%	6
2. Price of reaction components 4-Chlorobenzaldehyde: **cheap** Thiosemicarbazide: **inexpensive** nano $NiFe_2O_4$: **recyclable, low cost**	 0 0 0
3. **Safety** 4-Chlorobenzaldehyde: **irritant, harmful if swallowed** Thiosemicarbazide: **acute oral toxicity, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	3
4. Technical setup Unconventional activation technique	2
5. Temperature/time Room temperature < 1 h	0
6. Workup & Purification None	0
Total Penalty Points	**11**

EcoScale Score = 100- Total Penalty Points = 89

8. EcoScale Score for the synthesis of 5-(2-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3h) under the ball-milling conditions:



1h
1mmol
2-Hydroxybenzaldehyde

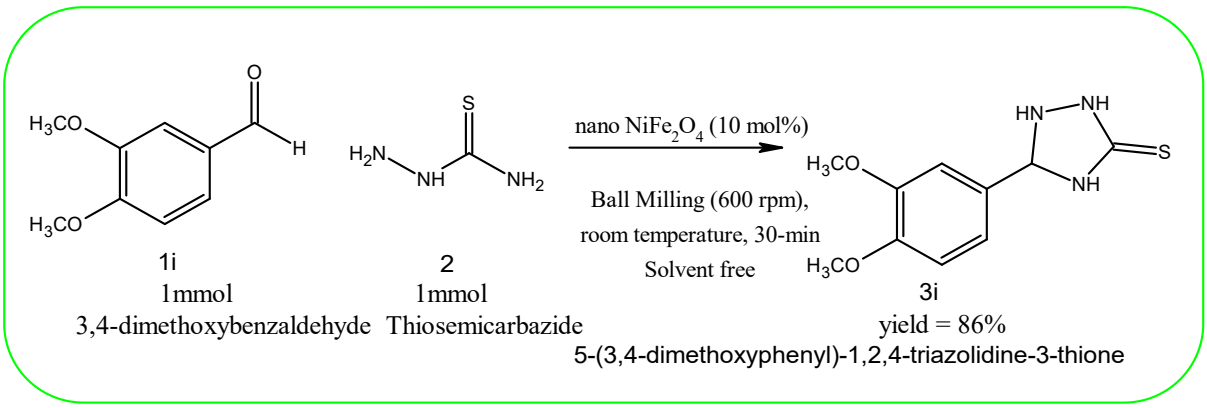
2
1mmol
Thiosemicarbazide

3h
yield = 90%
5-(2-Hydroxyphenyl)-1,2,4-triazolidine-3-thione

Parameter	Penalty
1. Yield 90%	5
2. Price of reaction components 2-Hydroxybenzaldehyde: **inexpensive and widely available** Thiosemicarbazide: **inexpensive** nano $NiFe_2O_4$: **recyclable, low cost**	 0 0 0
3. **Safety** 2-Hydroxybenzaldehyde: **mild irritant, low acute toxicity** Thiosemicarbazide: **acute oral toxicity, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	3
4. Technical setup Unconventional activation technique	2
5. Temperature/time Room temperature < 1 h	0
6. Workup & Purification None	0
Total Penalty Points	**10**

EcoScale Score = 100- Total Penalty Points = 90

9. EcoScale Score for the synthesis of 5-(3,4-dimethoxyphenyl)-1,2,4-triazolidine-3-thione (3i) under the ball-milling conditions:



1i
1mmol
3,4-dimethoxybenzaldehyde

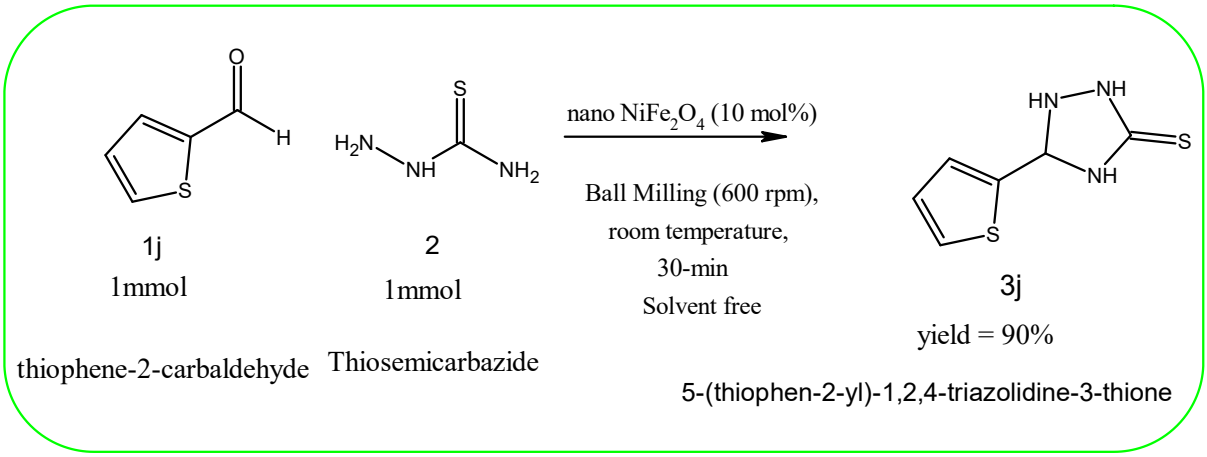
2
1mmol
Thiosemicarbazide

3i
yield = 86%
5-(3,4-dimethoxyphenyl)-1,2,4-triazolidine-3-thione

Parameter	Penalty
1. Yield 86%	7
2. Price of reaction components 3,4-dimethoxybenzaldehyde: **inexpensive and commercially available** Thiosemicarbazide: **inexpensive** nano $NiFe_2O_4$: **recyclable, low cost**	0 0 0
3. **Safety** 3,4-dimethoxybenzaldehyde: **low toxicity, mild irritant** Thiosemicarbazide: **acute oral toxicity, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	3
4. Technical setup Unconventional activation technique	2
5. Temperature/time Room temperature < 1 h	0
6. Workup & Purification None	0
Total Penalty Points	**12**

EcoScale Score = 100- Total Penalty Points = 88

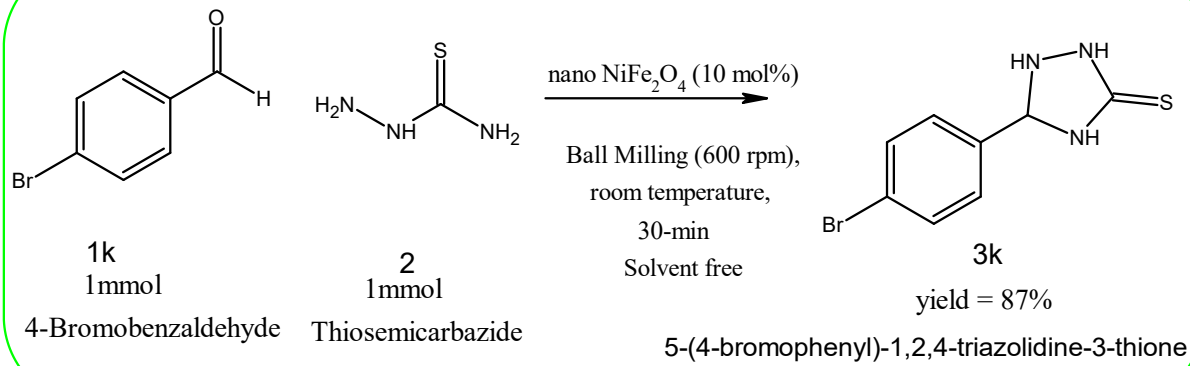
10. EcoScale Score for the synthesis of 5-(thiophen-2-yl)-1,2,4-triazolidine-3-thione (3j) under the ball-milling conditions:



Parameter	Penalty
1. Yield 90%	5
2. Price of reaction components Thiophene-2-carbaldehyde: **inexpensive and commercially available at low price** Thiosemicarbazide: **inexpensive** nano $NiFe_2O_4$: **recyclable, low cost**	0 0 0
3. **Safety** Thiophene-2-carbaldehyde: **lachrymatory, strong odor, irritant** Thiosemicarbazide: **acute oral toxicity, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	3
4. Technical setup Unconventional activation technique	2
5. Temperature/time Room temperature < 1 h	0
6. Workup & Purification None	0
Total Penalty Points	**10**

EcoScale Score = 100- Total Penalty Points = 90

11. EcoScale Score for the synthesis of 5-(4-bromophenyl)-1,2,4-triazolidine-3-thione (3k) under the ball-milling conditions:



1k
1mmol
4-Bromobenzaldehyde

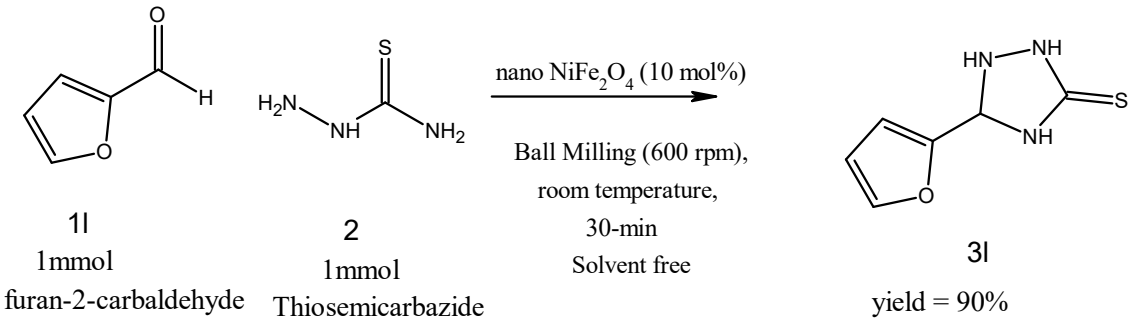
2
1mmol
Thiosemicarbazide

3k
yield = 87%
5-(4-bromophenyl)-1,2,4-triazolidine-3-thione

Parameter	Penalty
1. Yield 87%	6.5
2. Price of reaction components 4-Bromobenzaldehyde: **inexpensive commercial reagent** Thiosemicarbazide: **inexpensive** nano $NiFe_2O_4$: **recyclable, low cost**	 0 0 0
3. **Safety** 4-Bromobenzaldehyde: **irritant, harmful if swallowed** Thiosemicarbazide: **acute oral toxicity, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	3
4. Technical setup Unconventional activation technique	2
5. Temperature/time Room temperature < 1 h	0
6. Workup & Purification None	0
Total Penalty Points	**11.5**

EcoScale Score = 100- Total Penalty Points = 88.5

12. EcoScale Score for the synthesis of 5-(furan-2-yl)-1,2,4-triazolidine-3-thione (3l) under the ball-milling conditions:



1l
1mmol
furan-2-carbaldehyde

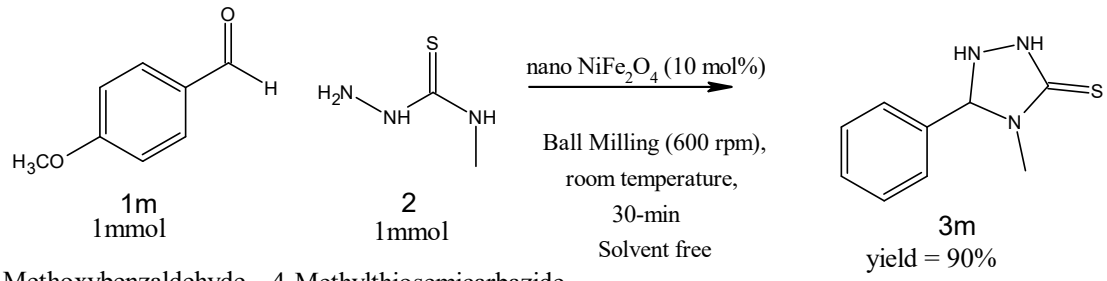
2
1mmol
Thiosemicarbazide

3l
yield = 90%
5-(furan-2-yl)-1,2,4-triazolidine-3-thione

Parameter	Penalty
1. Yield 90%	5
2. Price of reaction components furan-2-carbaldehyde: **inexpensive commercial reagent** Thiosemicarbazide: **inexpensive** nano $NiFe_2O_4$: **recyclable, low cost**	 0 0 0
3. **Safety** furan-2-carbaldehyde: **irritant, harmful, suspected carcinogen (IARC 2B)** Thiosemicarbazide: **acute oral toxicity, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	10
4. Technical setup Unconventional activation technique	2
5. Temperature/time Room temperature < 1 h	0
6. Workup & Purification None	0
Total Penalty Points	**17**

EcoScale Score = 100- Total Penalty Points = 83

13. EcoScale Score for the synthesis of 4-methyl-5-phenyl-1,2,4-triazolidine-3-thione (3m) under the ball-milling conditions:



1m, 1mmol — 4-Methoxybenzaldehyde

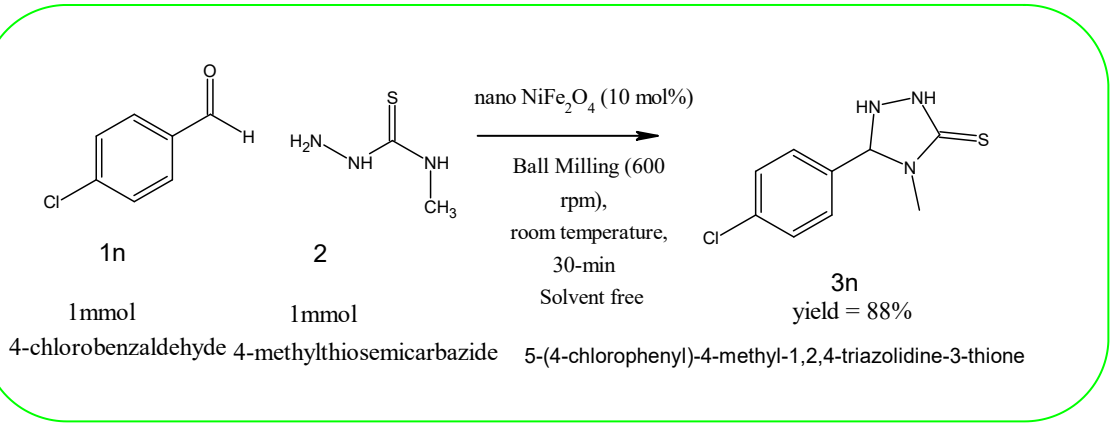
2, 1mmol — 4-Methylthiosemicarbazide

3m, yield = 90% — 4-methyl-5-phenyl-1,2,4-triazolidine-3-thione

Parameter	Penalty
1. Yield 90%	5
2. Price of reaction components 4-Methoxybenzaldehyde: **inexpensive** 4-Methylthiosemicarbazide: **slightly more expensive than unsubstituted** nano $NiFe_2O_4$: **recyclable, low cost**	 0 0 0
3. **Safety** 4-Methoxybenzaldehyde: **irritant, harmful, suspected carcinogen (IARC 2B)** 4-Methylthiosemicarbazide: **acute oral toxicity, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	3
4. Technical setup Unconventional activation technique	2
5. Temperature/time Room temperature < 1 h	0
6. Workup & Purification None	0
Total Penalty Points	**10**

EcoScale Score = 100- Total Penalty Points = 90

14. EcoScale Score for the synthesis of 5-(4-chlorophenyl)-4-methyl-1,2,4-triazolidine-3-thione (3n) under the ball-milling conditions:



1mmol 4-chlorobenzaldehyde | 1mmol 4-methylthiosemicarbazide | 5-(4-chlorophenyl)-4-methyl-1,2,4-triazolidine-3-thione

Parameter	Penalty
1. Yield 88%	6
2. Price of reaction components 2-Chlorobenzaldehyde: **cheap** 4-Methylthiosemicarbazide: **slightly more expensive than unsubstituted** nano $NiFe_2O_4$: **recyclable, low cost**	 0 0 0
3. **Safety** 2-Chlorobenzaldehyde: **irritant, lachrymator, harmful if swallowed** 4-Methylthiosemicarbazide: **acute oral toxicity, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	3
4. Technical setup Ball milling (mechanochemistry) – special equipment, but no pressure, inert gas, glovebox, or microwave required	2
5. Temperature/time Room temperature, only 30 minutes → ideal	0
6. Workup & Purification Solvent-free → simple filtration/washing, no chromatography	0
Total Penalty Points	**11**

EcoScale Score = 100- Total Penalty Points = 89

(B) Calculation of E-Factor:

1. **E-factor calculation for the synthesis of 3a under ball-milling conditions:**

Reactant 1 (1a):	Benzaldehyde	0.1061 g	1 mmol	FW 106.12
Reactant 2 (2):	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	-----
Solvent	------	------	------	----
Auxiliary (grinding):	------	------	------	------
Product (3a)	5-phenyl-1,2,4-triazolidine-3-thione	0.1741 g	0.97 mmol	179.24

Product yield = 97%

$$E - factor = \frac{0.1061 + 0.0911 - (0.1741)}{0.1741}$$

= 0.0231/0.1741= **0.13 kg waste per 1 kg**

2. **E-factor calculation for the synthesis of 3b under ball-milling conditions:**

Reactant 1 (1b):	2-Chlorobenzaldehyde	0.1406 g	1 mmol	FW 140.57
Reactant 2 (2):	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------
Product (3b)	5-(2-chlorophenyl)-1,2,4-triazolidine-3-thione	0.1966 g	0.92 mmol	213.69

Product yield = 92%

$$E - factor = \frac{0.1406 + 0.0911 - (0.1966)}{0.1966}$$

$$= \frac{0.0351}{0.1966} = 0.17 \text{ kg waste per 1 kg}$$

3. E-factor calculation for the synthesis of 3c under ball-milling conditions:

Reactant 1 (1c):	4-Nitrobenzaldehyde	0.1511 g	1 mmol	FW 151.12
Reactant 2 (2)	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------
Product (3c)	5-(4-Nitrophenyl)-1,2,4-triazolidine-3-thione	0.2199 g	0.92 mmol	224.24

Product yield = 92%

$$E - factor = \frac{0.1511 + 0.0911 - (0.2199)}{0.2199}$$

$$= \frac{0.0223}{0.2199} = 0.10 \text{ kg waste per 1 kg}$$

4. E-factor calculation for the synthesis of 3d under ball-milling conditions:

Reactant 1 (1d):	2-Nitrobenzaldehyde	0.1511 g	1 mmol	FW 151.12
Reactant 2 (2)	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------
Product (3d)	5-(2-Nitrophenyl)-1,2,4-triazolidine-3-thione	0.2153g	0.96 mmol	224.24

Product yield = 96%

$$E-factor = \frac{0.1511 + 0.0911 + - (0.2135)}{0.2135}$$
$$= \frac{0.0287}{0.2135} = 0.13 \text{ kg waste per 1 kg}$$

5. E-factor calculation for the synthesis of 3e under ball-milling conditions:

Reactant 1 (1e):	4-Hydroxybenzaldehyde	0.1221g	1 mmol	FW 122.12
Reactant 2 (2)	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------
Product (3e)	5-(4-hydroxyphenyl)-1,2,4-triazolidine-3-thione	0.1738g	0.89 mmol	195.24

Product yield = 89%

$$E-factor = \frac{0.1221 + 0.0911 - (0.1738)}{0.1738}$$
$$= \frac{0.0394}{0.1738} = 0.22 \text{ kg waste per 1 kg}$$

6. E-factor calculation for the synthesis of 3f under ball-milling conditions:

Reactant 1 (1f):	4-Methoxybenzaldehyde	0.1362 g	1 mmol	FW 136.15
Reactant 2 (2)	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------
Product (3f)	5-(4-Methoxyphenyl)-1,2,4-triazolidine-3-thione	0.1821 g	0.87 mmol	209.27

Product yield = 87%

$$E-factor = \frac{0.1362 + 0.0911 - (0.1821)}{0.1821}$$

$$= \frac{0.0452}{0.1821}$$ = 0.24 kg waste per 1 kg

7. E-factor calculation for the synthesis of 3g under ball-milling conditions:

Reactant 1 (1g):	4-Chlorobenzaldehyde	0.1406 g	1 mmol	FW 140.57
Reactant 2 (2)	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------
Product (3g)	5-(4-Chlorophenyl)-1,2,4-triazolidine-3-thione	0.1880 g	0.87 mmol	213.69

Product yield = 87%

$$E - factor = \frac{0.1406 + 0.0911 - (0.1880)}{0.1880}$$

$$= \frac{0.0437}{0.1880}$$ = 0.23 kg waste per 1 kg

8. E-factor calculation for the synthesis of 3h under ball-milling conditions:

Reactant 1 (1h):	2-Hydroxybenzaldehyde	0.1221g	1 mmol	FW 122.12
Reactant 2 (2)	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------

Product (3h)	5-(2-Hydroxyphenyl)-1,2,4-triazolidine	0.1757 g	0.90 mmol	195.24

Product yield = 90%

$$E-factor = \frac{0.1221 + 0.0911 - (0.1757)}{0.1757}$$

$$= \frac{0.0375}{0.1757}$$ = 0.21kg waste per 1 kg

9. E-factor calculation for the synthesis of 3i under ball-milling conditions:

Reactant 1 (1i):	3,4-Dimethoxybenzaldehyde	0.1662 g	1 mmol	FW 166.17
Reactant 2 (2)	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------
Product (3i)	5-(3,4-dimethoxyphenyl)-1,2,4-triazolidine-3-thione	0.2058 g	0.86 mmol	239.29

Product yield = 86%

$$E-factor = \frac{0.1662 + 0.0911 - (0.2058)}{0.2058}$$

$$= \frac{0.0515}{0.2058}$$ = 0.25kg waste per 1 kg

10. E-factor calculation for the synthesis of 3j under ball-milling conditions:

Reactant 1 (1j):	Thiophene-2-carbaldehyde	0.1122 g	1 mmol	FW 112.15
Reactant 2 (2)	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------

Product (3j)	5-(thiophen-2-yl)-1,2,4-triazolidine-3-thione	0.1667 g	0.90 mmol	185.27

Product yield = 90%

$$E-factor = \frac{0.1122 + 0.0911 - (0.1667)}{0.1667}$$

$$= \frac{0.0366}{0.1667}$$ = 0.22kg waste per 1 kg

11. E-factor calculation for the synthesis of 3k under ball-milling conditions:

Reactant 1 (1k):	4-Bromobenzaldehyde	0.1850 g	1 mmol	FW 185.02
Reactant 2 (2)	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------
Product (3k)	5-(4-bromophenyl)-1,2,4-triazolidine-3-thione	0.2246 g	0.87 mmol	258.14

Product yield = 87%

$$E-factor = \frac{0.1850 + 0.0911 - (0.2246)}{0.2246}$$

$$= \frac{0.0515}{0.2246}$$ = 0.23kg waste per 1 kg

12. E-factor calculation for the synthesis of 3l under ball-milling conditions:

Reactant 1 (1l):	Furan-2-carbaldehyde	0.0961g	1 mmol	FW 96.08
Reactant 2 (2)	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------

Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------
Product (3l)	5-(furan-2-yl)-1,2,4-triazolidine-3-thione	0.1523 g	0.90 mmol	258.14

Product yield = 90%

$$E-factor = \frac{0.0961 \ + 0.0911 - (0.1523)}{0.1523}$$
$$= \frac{0.0349}{0.1523} = 0.23 \text{ kg waste per 1 kg}$$

13. E-factor calculation for the synthesis of 3m under ball-milling conditions:

Reactant 1 (1m):	4-Methoxybenzaldehyde	0.1362 g	1 mmol	FW 136.15
Reactant 2 (2)	4-methylthiosemicarbazide	0.1052g	1 mmol	FW 105.16
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------
Product (3m)	5-(4-methoxyphenyl)-4-methyl-1,2,4-triazolidine-3-thione	0.2010 g	0.90 mmol	223.29

Product yield = 90%

$$E-factor = \frac{0.1362 + 0.1052 - (0.2010\ )}{0.2010}$$
$$= \frac{0.0404}{0.2010} = 0.20 \text{ kg waste per 1 kg}$$

14. E-factor calculation for the synthesis of 3n under ball-milling conditions:

Reactant 1 (1n):	4-Chlorobenzaldehyde	0.1406 g	1 mmol	FW 140.57

Reactant 2 (2)	4-methylthiosemicarbazide	0.1052g	1 mmol	FW 105.16
Reagent/Catalyst	------	------	------	------
Solvent	------	------	------	------
Auxiliary (grinding):	------	------	------	------
Product (3n)	5-(4-chlorophenyl)-4-methyl-1,2,4-triazolidine-3-thione	0.2004 g	0.88 mmol	227.71

Product yield = 88%

$$E - factor = \frac{0.1406 + 0.1052 - (0.2004)}{0.2004}$$

$$= \frac{0.0454}{0.2004} = 0.23 \text{ kg waste per 1 kg}$$

(C) Calculation of Atom economy

1. Atom economy for 5-phenyl-1,2,4-triazolidine-3-thione (3a)

Compound	Molecular Formula	Molar Mass (g/mol)
Benzaldehyde (1a)	C_7H_6O	106.12
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		197.25
Required Product (3a)	$C_8H_9N_3S$	179.24
By-product: - Water		18.02

mass balance Check: 106.12 + 91.13 = 197.25

179.24 + 18.02 = 197.26 → perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants} X\ 100$$

$$= \frac{179.24}{197.25} X\ 100$$

$$= 90.87\%$$

2. Atom economy for 5-(2-chlorophenyl)-1,2,4-triazolidine-3-thione (3b)

Compound	Molecular Formula	Molar Mass (g/mol)
2-Chlorobenzaldehyde (1b)	C_7H_5ClO	140.57
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		231.70
Required Product (3b)	$C_8H_8ClN_3S$	213.69
By-product: - Water		18.02

Mass balance check: 140.57 + 91.13 = 231.70

213.69 + 18.02 = 231.71 → perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants} X\ 100$$

$$= \frac{213.69}{231.70} X\ 100$$

$$= 92.21\%$$

3. Atom economy for 5-(4-Nitrophenyl)-1,2,4-triazolidine-3-thione (3c)

Compound	Molecular Formula	Molar Mass (g/mol)
4-Nitrobenzaldehyde (1c)	$C_7H_5NO_3$	151.12
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		242.25
Required Product (3c)	$C_8H_8N_4O_2S$	224.24
By-product: - Water		18.02

Mass balance check: 151.12 + 91.13 = 242.25

224.24 + 18.02 = 242.26 → perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants} X\ 100$$

$$= \frac{224.24}{242.25} X\ 100$$

$$= 92.58\%$$

4. Atom economy for 5-(2-Nitrophenyl)-1,2,4-triazolidine-3-thione (3d)

Compound	Molecular Formula	Molar Mass (g/mol)
2-Nitrobenzaldehyde (1d)	$C_7H_5NO_3$	151.12
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		242.25
Required Product (3d)	$C_8H_8N_4O_2S$	224.24
By-product: - Water		18.02

Mass balance check: 151.12 + 91.13 = 242.25

224.24 + 18.02 = 242.26 → perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants} X\ 100$$

$$= \frac{224.24}{242.25} X\ 100$$

$$= 92.58\%$$

5. Atom economy for 5-(4-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3e)

Compound	Molecular Formula	Molar Mass (g/mol)
4-Hydroxybenzaldehyde (1e)	$C_7H_6O_2$	122.12
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		213.25
Required Product (3e)	$C_8H_9N_3OS$	195.24
By-product: - Water		18.02

Mass balance check: 122.12 + 91.13 = 213.25

195.24 + 18.02 = 213.26 → perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants} X\ 100$$

$$= \frac{195.24}{213.25} X\ 100$$

$$= 91.53\%$$

6. Atom economy for 5-(4-Methoxyphenyl)-1,2,4-triazolidine-3-thione (3f)

Compound	Molecular Formula	Molar Mass (g/mol)
4-Methoxybenzaldehyde (1f)	$C_8H_8O_2$	136.15
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		227.28
Required Product (3f)	$C_9H_{11}N_3OS$	209.27
By-product: - Water		18.02

Mass balance check: 136.15 + 91.13 = 227.28

209.27 + 18.02 = 227.29 → perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants} X\ 100$$

$$= \frac{209.27}{227.28} X\ 100$$

$$= 92.07\%$$

7. Atom economy for 5-(4-Chlorophenyl)-1,2,4-triazolidine-3-thione (3g)

Compound	Molecular Formula	Molar Mass (g/mol)
4-Chlorobenzaldehyde (1g)	C_7H_5ClO	140.57
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		231.70
Required Product (3g)	$C_8H_8ClN_3S$	213.69
By-product: - Water		18.02

Mass balance check: 140.57 + 91.13 = 231.70

213.69 + 18.02 = 231.71 → perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants}\ X\ 100$$

$$= \frac{213.69}{231.69}\ X\ 100$$

$$= 92.21\%$$

8. Atom economy for 5-(2-Hydroxyphenyl)-1,2,4-triazolidine-3-thione (3h)

Compound	Molecular Formula	Molar Mass (g/mol)
2-Hydroxybenzaldehyde (1h)	$C_7H_6O_2$	122.12
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		213.25
Required Product (3h)	$C_8H_9N_3OS$	195.24
By-product: - Water		18.02

Mass balance check: 122.12 + 91.13 = 213.25

195.24 + 18.02 = 213.26 → perfect matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants}\ X\ 100$$

$$= \frac{195.24}{213.25}\ X\ 100$$

$$= 91.53\%$$

9. Atom economy for 5-(3,4-dimethoxyphenyl)-1,2,4-triazolidine-3-thione (3i)

Compound	Molecular Formula	Molar Mass (g/mol)
3,4-Dimethoxybenzaldehyde (1i)	$C_9H_{10}O_3$	166.17
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		257.30
Required Product (3i)	$C_{10}H_{13}N_3O_2S$	239.29
By-product: - Water		18.02

Mass balance check: 166.17 + 91.13 = 257.30

239.29 + 18.02 = 257.31 → perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants} X\ 100$$

$$= \frac{239.29}{257.30} X\ 100$$

$$= 93.00\%$$

10. Atom economy for 5-(thiophen-2-yl)-1,2,4-triazolidine-3-thione (3j)

Compound	Molecular Formula	Molar Mass (g/mol)
Thiophene-2-carbaldehyde (1j)	C_5H_4OS	112.15
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		203.28
Required Product (3j)	$C_6H_7N_3S_2$	185.27
By-pr**oduct:** - Water		18.02

Mass balance check: 112.15 + 91.13 = 203.28

185.27 + 18.02 = 203.29 → perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants} X\ 100$$

$$= \frac{185.27}{203.28} X\ 100$$

$$= 91.14\%$$

11. Atom economy for 5-(4-bromophenyl)-1,2,4-triazolidine-3-thione (3k)

Compound	Molecular Formula	Molar Mass (g/mol)
4-Bromobenzaldehyde (1k)	C_7H_5BrO	185.02
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		276.15
Required Product (3k)	$C_8H_8BrN_3S$	258.14
By-p**roduct:** - Water		18.02

Mass balance check: 185.02 + 91.13 = 276.15

258.14 + 18.02 = 276.16 → perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants} X\ 100$$

$$= \frac{258.14}{276.15} X\ 100$$

$$= 93.49\%$$

12. Atom economy for 5-(furan-2-yl)-1,2,4-triazolidine-3-thione (3l)

Compound	Molecular Formula	Molar Mass (g/mol)
Furan-2-carbaldehyde (1l)	$C_5H_4O_2$	96.09
Thiosemicarbazide (2)	CH_5N_3S	91.13
Sum of Reactant		187.22
Required Product (3l)	$C_6H_7N_3OS$	169.20
By-p**roduct:** - Water		18.02

Mass balance check: 96.09 + 91.13 = 187.22

169.20 + 18.02 = 187.22 → perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants} X\ 100$$

$$= \frac{169.20}{187.22} X\ 100$$

$$= 90.35\%$$

13. Atom economy for 5-(4-methoxyphenyl)-4-methyl-1,2,4-triazolidine-3-thione (3m)

Compound	Molecular Formula	Molar Mass (g/mol)
4-Methoxybenzaldehyde (1m)	$C_8H_8O_2$	136.15
4-Methylthiosemicarbazide (2a)	$C_2H_7N_3S$	105.16
Sum of Reactant		241.31
Required Product (3m)	$C_{10}H_{13}N_3OS$	223.29
By-pr**oduct:** - Water		18.02

Mass balance check: 136.15 + 105.16 = 241.31

223.29 + 18.02 = 241.31→ perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants}\ X\ 100$$

$$= \frac{223.29}{241.31}\ X\ 100$$

$$= 92.56\%$$

14. Atom economy for 5-(4-chlorophenyl)-4-methyl-1,2,4-triazolidine-3-thione (3n)

Compound	Molecular Formula	Molar Mass (g/mol)
4-Chlorobenzaldehyde (1n)	C_7H_5ClO	140.57
4-Methylthiosemicarbazide (2a)	$C_2H_7N_3S$	105.16
Sum of Reactant		245.73
Required Product (3n)	$C_9H_{10}ClN_3S$	227.71
By-pr**oduct:** - Water		18.02

Mass balance check: 140.57 + 105.16 = 245.73

227.71 + 18.02 = 245.73→ perfectly matches

$$Atom\ economy = \frac{Molecuar\ weight\ of\ required\ Product}{Sum\ of\ MW\ of\ all\ reactants}\ X\ 100$$

$$= \frac{227.71}{245.73}\ X\ 100$$

= 92.67 %

(D) Calculation of Green Chemistry Metrics (EcoScale and E-factor) for conventional method.

1. **EcoScale Score for the synthesis of 5-phenyl-1,2,4-triazolidine-3-thione (3a) under conventional method.**

Parameter	Penalty
1. Yield 57%	21.5
2. Price of reaction components Benzaldehyde: **cheap** Thiosemicarbazide: **inexpensive** nano $NiFe_2O_4$: **recyclable, low cost** Solvent (Ethanol & water): **Green**	 0 0 0 0
3. **Safety** Benzaldehyde: **mild irritant** Thiosemicarbazide: **toxic if swallowed, irritant** Nano $NiFe_2O_4$: **No highly flammable, explosive, or carcinogenic reagents**	3
4. Technical setup Unconventional activation technique	**2**
5. Temperature/time Heating > 1hour	**5**
6. Workup & Purification	**5**
Total Penalty Points	**36.5**

EcoScale Score = 100- Total Penalty Points = 63.5

2. E-factor calculation for the synthesis of 3a under conventional method:

Reactant 1 (1a):	Benzaldehyde	0.1061 g	1 mmol	FW 106.12
Reactant 2 (2):	Thiosemicarbazide	0.0911 g	1 mmol	FW 91.13
Reagent/Catalyst	------	------	------	------
Solvent	EtOH:H_2O	8.945 g	5 mL:5 mL	------
Auxiliary (grinding):	------	------	------	------
Product (3a)	5-phenyl-1,2,4-triazolidine-3-thione	0.102 g	0.57 mmol	179.24

Product yield = 57%

$$E - factor = \frac{0.1061 + 0.0911 + 8.945 - (0.102)}{0.102}$$

= 9.0402/0.102= 88.6 kg waste per 1 kg

SI12: **References**

62. K. Pradhan, S. Paul and A. R. Das, *Catalysis Science & Technology*, 2014, **4**, 822–831.

63. B. Y. Yu and S. Y. Kwak, *Dalton Transactions*, 2011, **40**, 9989–9998.

64. M. Atif, S. K. Hasanain and M. Nadeem, *Solid State Communications*, 2006, **138**, 416–421.