Electronic Supplementary Material (ESI) for RSC Advances.

Design of a new method for one-pot synthesis of 2-amino thiazoles using trichloroisocyanuric acid in presence of a novel multi-functional and magnetically catalytic nanosystem: Ca/4-MePyr IL@ZY-Fe_3O_4

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Supporting Information

Experimental

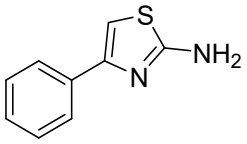
2.1. Chemicals and apparatus

Chemical substances were purchased from the Merck, Fluka and Aldrich Chemical Companies and used as received. Melting points (°C) were determined in an open-glass capillary using an electro-thermal digital melting point apparatus and are uncorrected. Progress of the catalytic process was monitored by thin layer chromatography (TLC) using silica gel plates in the solvent system (ethyl acetate/*n*-hexane, 2:1). FT-IR spectra were obtained with KBr disc on a galaxy series FT-IR 5000 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. NMR spectra were obtained in DMSO-d_6 solvent and are reported as parts per million (ppm) downfield from Me_4Si as internal standard. Nitrogen adsorption and desorption isotherms (BET analysis) were measured at 196 °C by a USA Micromeritics (MicroActive for TriStar II Plus Version 2.03, Serial # 283) system after the samples were vacuum dried at 110°C overnight. Field emission scanning electron microscopy (FESEM) images were performed on a Carl Zeiss EVO LS 10 (Germany) FE-SEM that it equipped with energy dispersive X-ray spectrometer (EDX). Nanocomposites based zeolite-Y were characterized using a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (CuK, radiation, λ= 0.154056 nm), at a scanning speed of 2°/min from 10° to 100°(2θ). The TGA/DTA measurements were carried out by using a TA-Q600 instrument (made in the USA). TGA/DTA runs were recorded at a scan rate of 10° min^{-1} up to 700 °C under pure argon atmosphere.

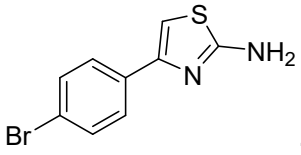
2.3. General procedure for the catalytic synthesis of 2-aminothiazoles

In 3.0 mL of EtOH, 0.5 mmol TCCA, 1.5 mmol acetophenone derivative, and 0.01 g of Ca/4-MePy-IL@ZY-Fe_3O_4 were stirred at 80 °C for 25 min. The completion of the reaction was monitored by TLC and after confirming the production of the intermediate product carbonyl alkyl halide, 1.0 mmol of thiourea was added to the reaction mixture. After the completion of the reaction within the appropriate time mentioned in Table 3, the nanocatalyst was then gathered utilizing an external magnet. To produce a neutral solution, 10% sodium bicarbonate solution is then added to the mixture. In this situation, filter paper should be used to separate thiazole precipitate. By washing the precipitate with water and ethanol and drying in an oven, the pure product of substituted 2-aminothiazole is obtained. The side product of cyanuric acid is produced by adding a few drops of diluted acid and neutralizing the solution under the filter. All 2-aminothiazole products are known and were identified by comparison of their melting point, FT-IR and ^{1}H NMR with those of authentic samples.

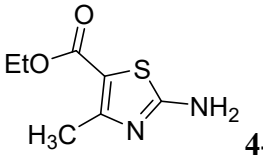
Spectroscopic data for selected compounds



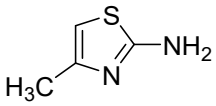
4-Phenyl-2-aminothiazole (3a): IR (KBr), υ_{max}: 3434, 3253 (NH_2), 3113 (C–H), 1598 (C=N), 1519, 1481, 1336 (C=C), 1070 (C-N), 728 (S-C=N) cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 8.96 (s, 2H, NH_2), 7.74 (d, J = 7.20 Hz, 2H, Ph-H), 7.51-7.44 (m, 3H, Ph-H), 7.27 (s, 1H, thiazole-H) ppm.



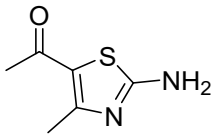
4-(4-Boromophenyl)-2-aminothiazole (3b): FT-IR (KBr), υ_{max}: 3439, 3294 (NH_2), 3108 (aromatic C–H), 1647 (C=N), 1512, 1461, 1332 (C=C), 1069 (C-N), 831 (C-Br), 716 (S-C=N) cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 7.75 (d, J = 6.81 Hz, 2H, H-Ar), 7.62 (d, J = 6.81 Hz, 2H, H-Ar), 7.08 (s, 2H, NH_2), 7.07 (s, 1H, H-thiazole) ppm.



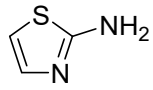
4-Methyl-5-(ethoxycarbonyl)-2-aminothiazole (3c) IR (KBr), υ_{max}: 3374, 3301 (NH_2), 2979 (C–H), 1674 (C=O), 1514 (C=N), 1373 (C=C), 1277 (C-O), 1095 (C-N), 756 (S-C=N) cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz): δ_H 7.72 (s, 2H, NH_2), 4.14 (q, J = 6.00 Hz, 2H, $\underline{CH_2}CH_3$), 2.35 (s, 3H, CH_3), 1.22 (t, J = 6.21 Hz, 3H, $CH_2\underline{CH_3}$) ppm: ^{13}C NMR (DMSO-d_6, 75 MHz): δ_C 170.7 (C=O), 162.5, 159.7, 107.9, 60.3 (O-CH_2), 17.4, 14.7 (CH_3) ppm.



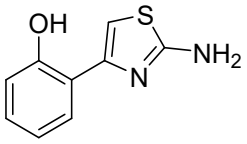
4-Methylthiazol-2-amine (3d) IR (KBr), υ_{max}: 3433, 3264 (NH_2), 3090 (C–H), 2918 (C-H), 1620 (C=N), 1504, 1373, 1318 (C=C), 1115 (C-N) cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 7.55 (s, 1H, H-thiazole), 7.17 (br, 2H, NH_2, D_2O exchangeable), 2.17 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 169.2, 153.4, 111.1, 15.7 ppm.



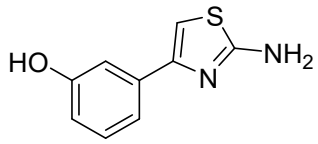
1-(2-Amino-4-methylthiazol-5-yl)ethan-1-one (3e) IR (KBr), υ_{max}: 3268 (NH_2), 3066 (C–H), 1661 (C=O), 1602 (C=N), 1496, 1310 (C=C), 1104 (C-N), 977 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 7.83 (s, 2H, NH_2), 2.40 (s, 3H, CH_3), 2.32 (s, 3H, CH_3) ppm.



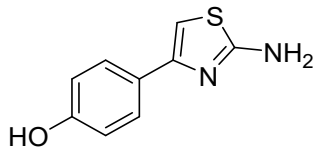
Thiazol-2-amine (3f) IR (KBr), υ_{max}: 3410, 3290 (NH_2), 3083 (aromatic C–H), 1626 (C=N), 1521, 1492, 1325 (C=C), 1199 (C-N), 1029, 696 (S-C=N), 514 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 6.93-6.88 (t br, 3H, H-thiazole and NH_2), 6.56 (d, J = 4.00 Hz, 1H, H-thiazole) ppm.



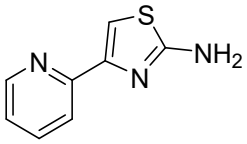
4-(2-Hydroxyphenyl)-2-aminothiazole (3g): IR (KBr), υ_{max}: 3439, 3246 (OH, NH_2), 1612 (C=N), 1505, 1449, 1332 (C=C), 1242 (C-O), 1019 (C-N), 756 (S-C=N) cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 11.17 (s, 1H, OH),7.95 (s, 2H, NH_2), 7.83 (d, J = 7.61 Hz, 1H, H-Ar), 7.70-7.49 (d br, 1H, H-Ar), 7.20 (s, 1H, thiazole), 6.83 (d, J = 7.6 Hz, 1H, H-Ar), 6.72 (t br, 1H, H-Ar) ppm.



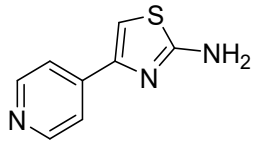
4-(3-Hydroxyphenyl)-2-aminothiazole (3h): FT-IR (KBr), υ_{max}: 3431, 3338, 3192 (NH, OH), 1598 (C=N), 1508, 1445, 1321 (C=C), 1291, 1224 (C-O), 1142 (C-N), 760 (S-C=N), 703 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 9.31 (br, 1H, OH), 7.54 (s br, 2H, H-Ar), 7.12 (s br, 4H, H-Ar, NH_2, H-thiazole), 6.73 (s, 1H, H-Ar) ppm.



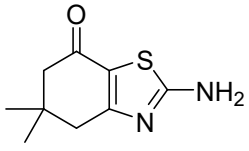
4-(4-Hydroxyphenyl)-2-aminothiazole (3i): IR (KBr), υ_{max}: 3349, 3308, 3197 (OH, NH_2), 1615 (C=N), 1502, 1434, 1338 (C=C), 1259, 1172 (C-O), 1032 (C-N), 833, 731 (S-C=N), 600 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ_H 9.66 (s, OH), 7.62 (d br, 3H, H-thiazole and H-Ar), 7.52 (s, 2H, NH_2), 6.73 (d, J = 8.51 Hz, 2H, Ar-H) ppm.



4-(Pyridin-2-yl)thiazol-2-amine (3j): FT-IR (KBr), υ_{max} 3429 (NH_2), 1635 (C=N), 1234, 1145 (C=C), 1057, 1014 (C-N), 884(S-C=N), 851, 578 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ_H 8.89 (s, 1H, H-pyridyl), 8.52 (d br, 1H, H-pyridyl), 8.05 (d, J = 7.20 Hz, 1H, H-pyridyl), 7.63 (s, 1H, H-pyridyl), 7.46 (s, 2H, NH_2), 7.35 (s, 1H, H-thiazole) ppm.

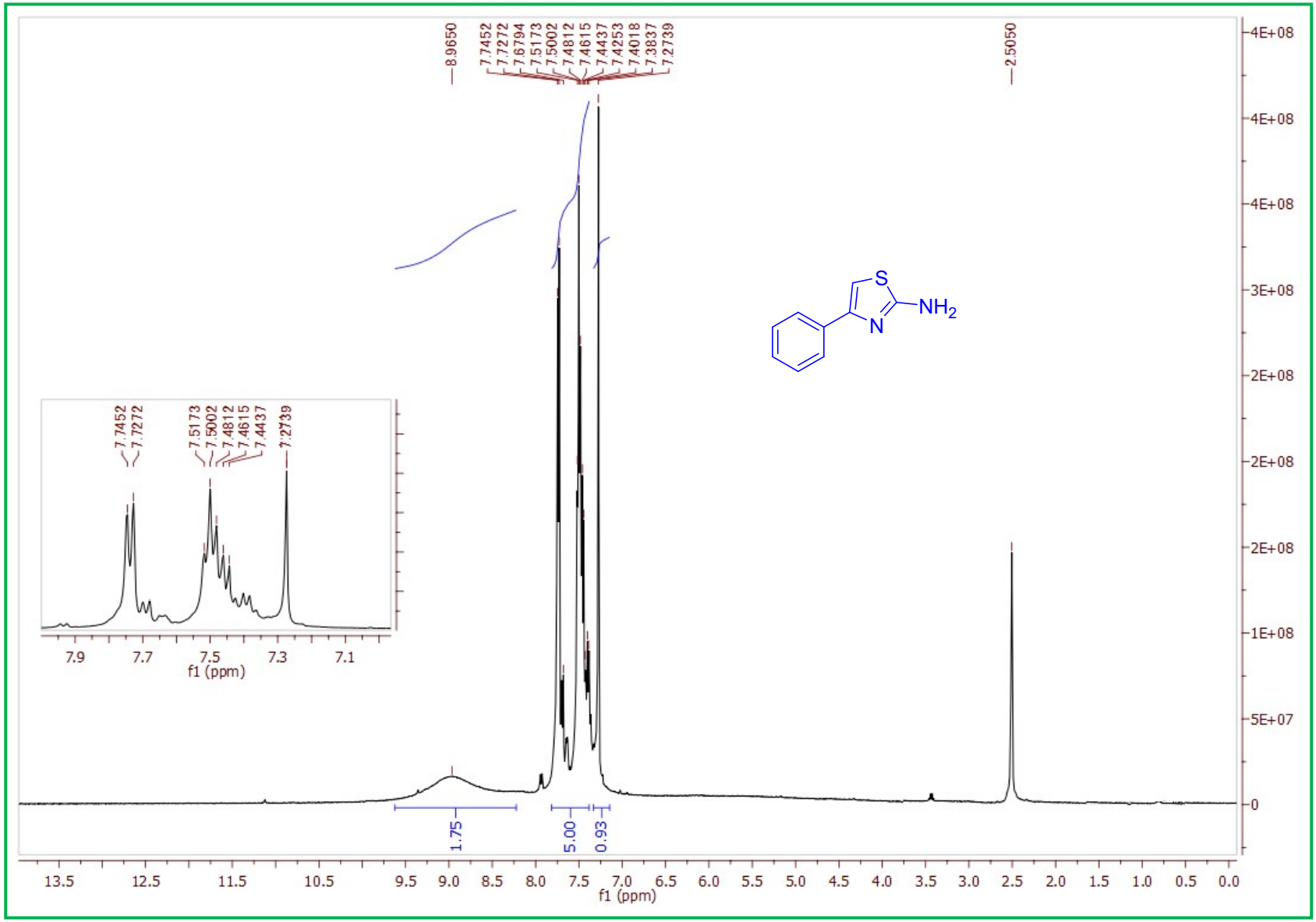


4-(Pyridin-4-yl)thiazol-2-amine (3l): FT-IR (KBr), υ_{max}: 3428(NH_2), 1633, 1612 (C=N), 1580, 1340, 1291 (C=C), 1025 (C-N), 811 (S-C=N), 703 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ_H 8.90 (s, 1H, H-pyridyl), 8.52 (d br, 1H, H-pyridyl), 7.89 (d, J = 7.20 Hz, 1H, H-pyridyl), 7.63 (s, 1H, H-pyridyl), 7.46-7.31 (t br, 3H, NH_2 and H-thiazole) ppm.

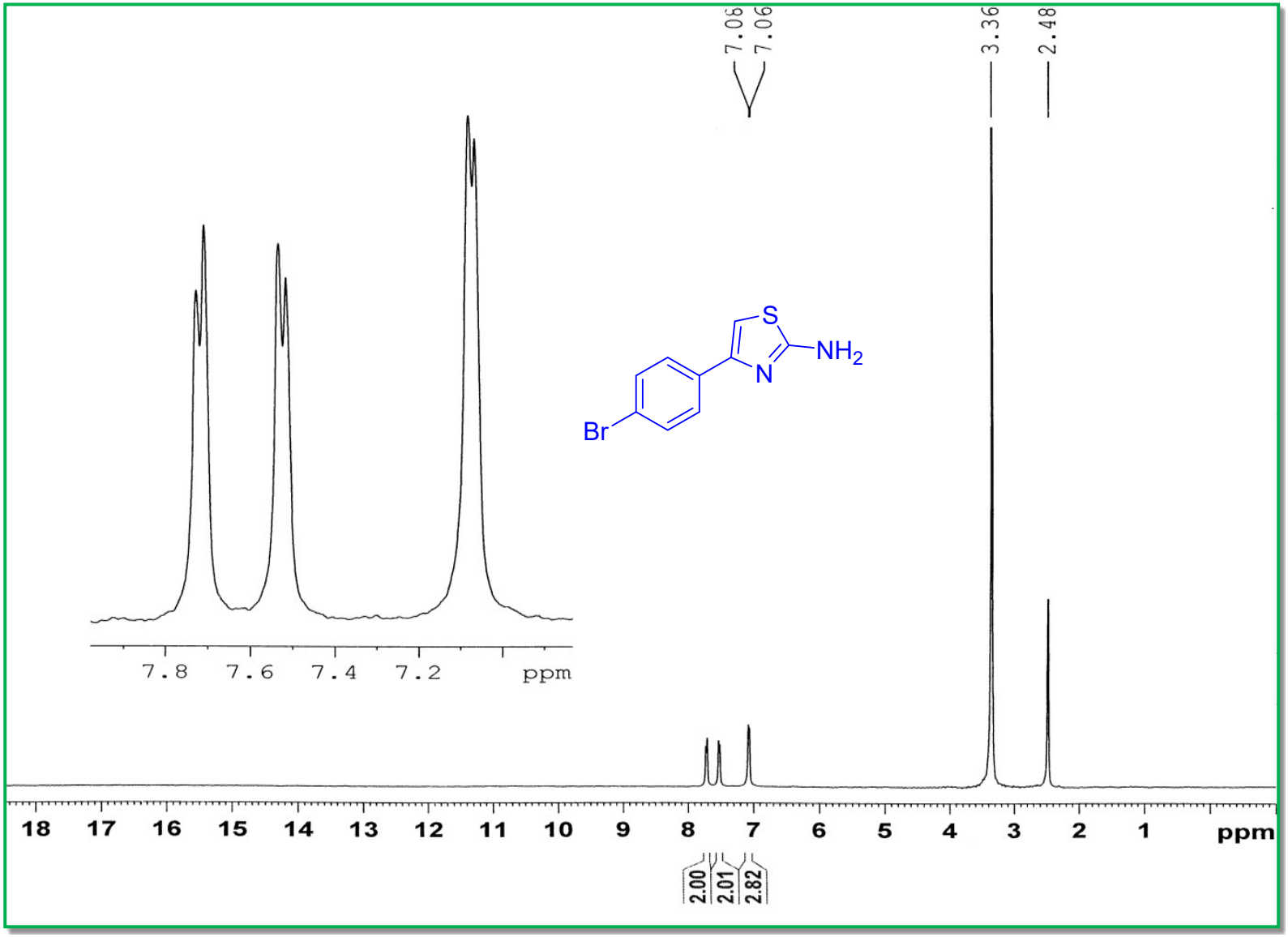


2-Amino-5,5-dimethyl-5,6-dihydrobenzo[d]thiazol-7(4*H*)-one (3m): FT-IR (KBr), υ_{max}: 3390, 3297, 3100 (NH_2), 2958 (C-H), 1644 (C=O), 1625, 1600 (C=N), 1511, 1369, 1311, 1255, (C=C) 1146, 1055 (C-N), 584 (S-C=N) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ_H 8.09 (s, 2H, NH_2), 2.58 (s, 2H, CH_2), 2.26 (s, 2H, CH_2), 1.03 (s, 3H, CH_3), 1.02 (s, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 189.3 (C=O), 174.2 (C=N), 166.9, 117.4, 51.2, 40.9, 34.2, 28.4 ppm.

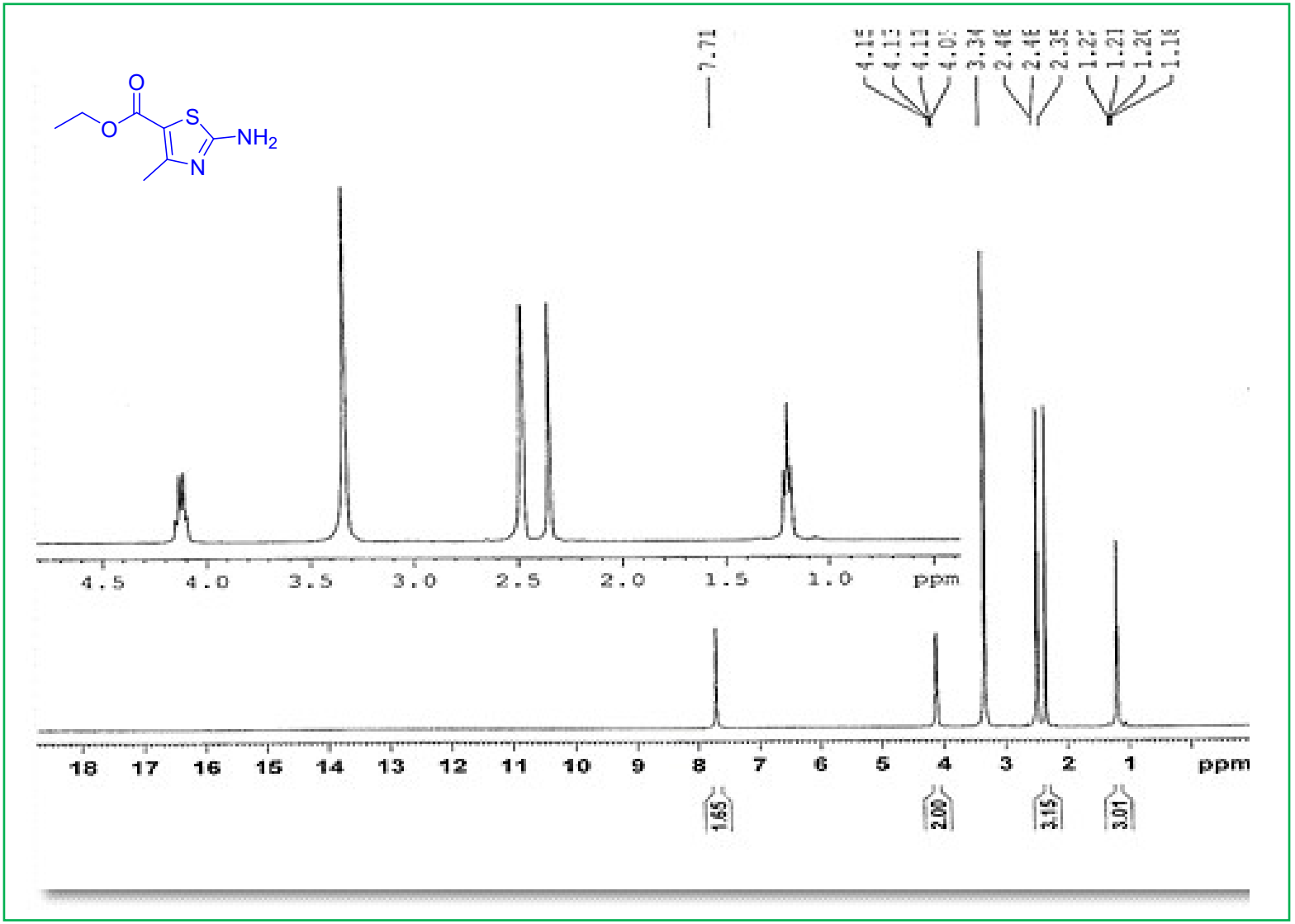
[1]H NMR spectrum of 4-Phenyl-2-aminothiazole (3a)



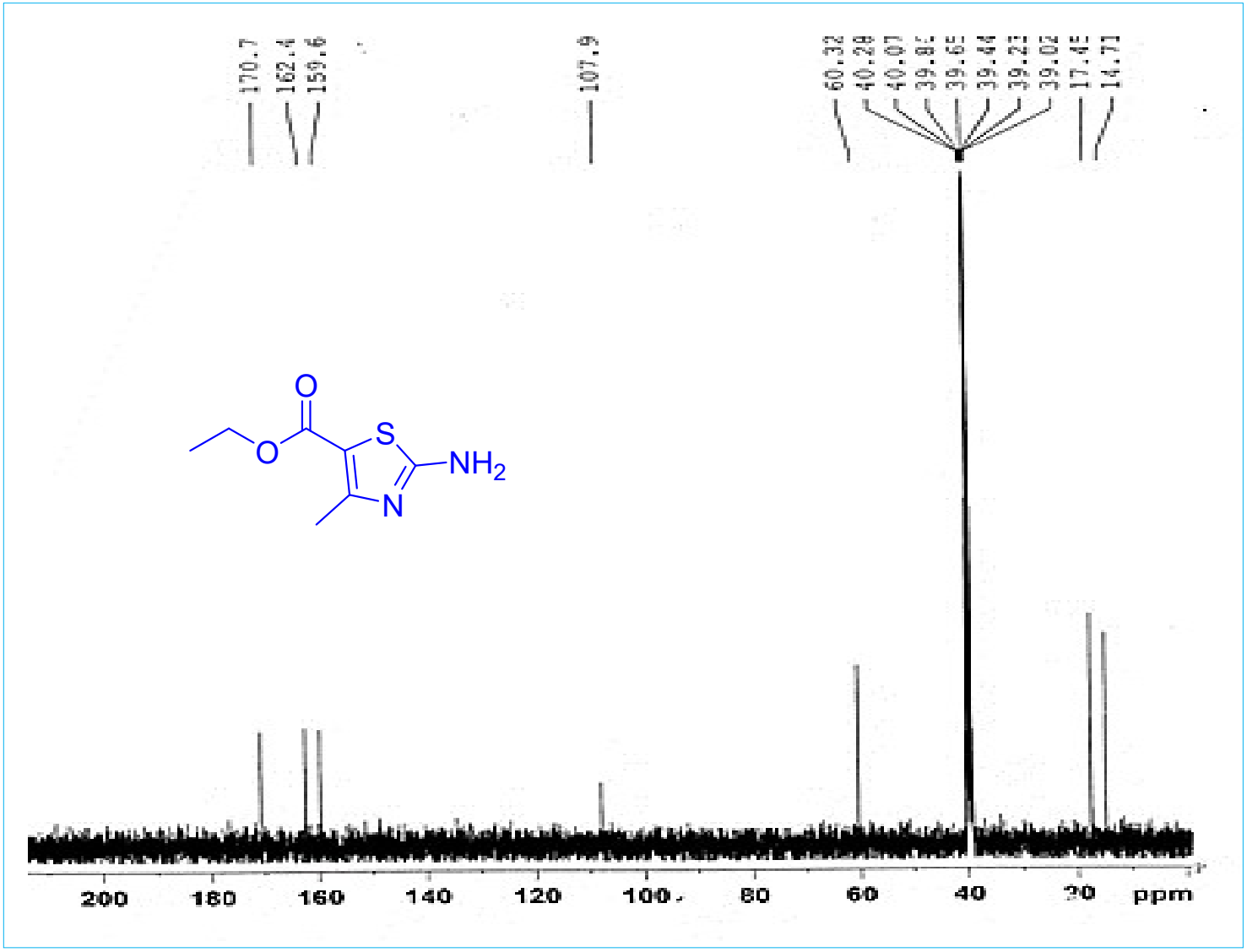
^{1}H NMR spectrum of 4-(4-Boromophenyl)-2-aminothiazole (3b)



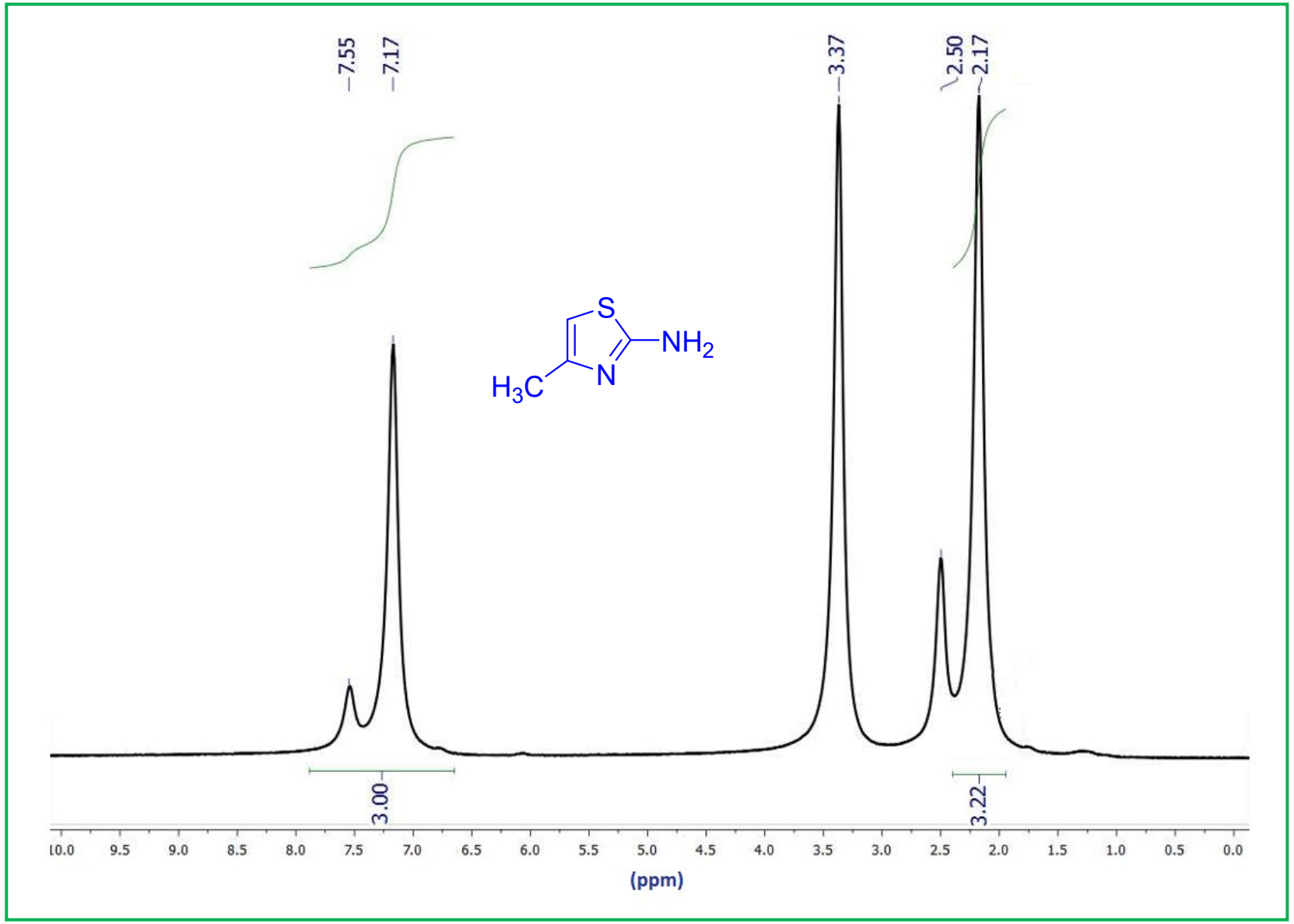
[1]H NMR spectrum of 4-Methyl-5-(ethoxycarbonyl)-2-aminothiazole (3c)



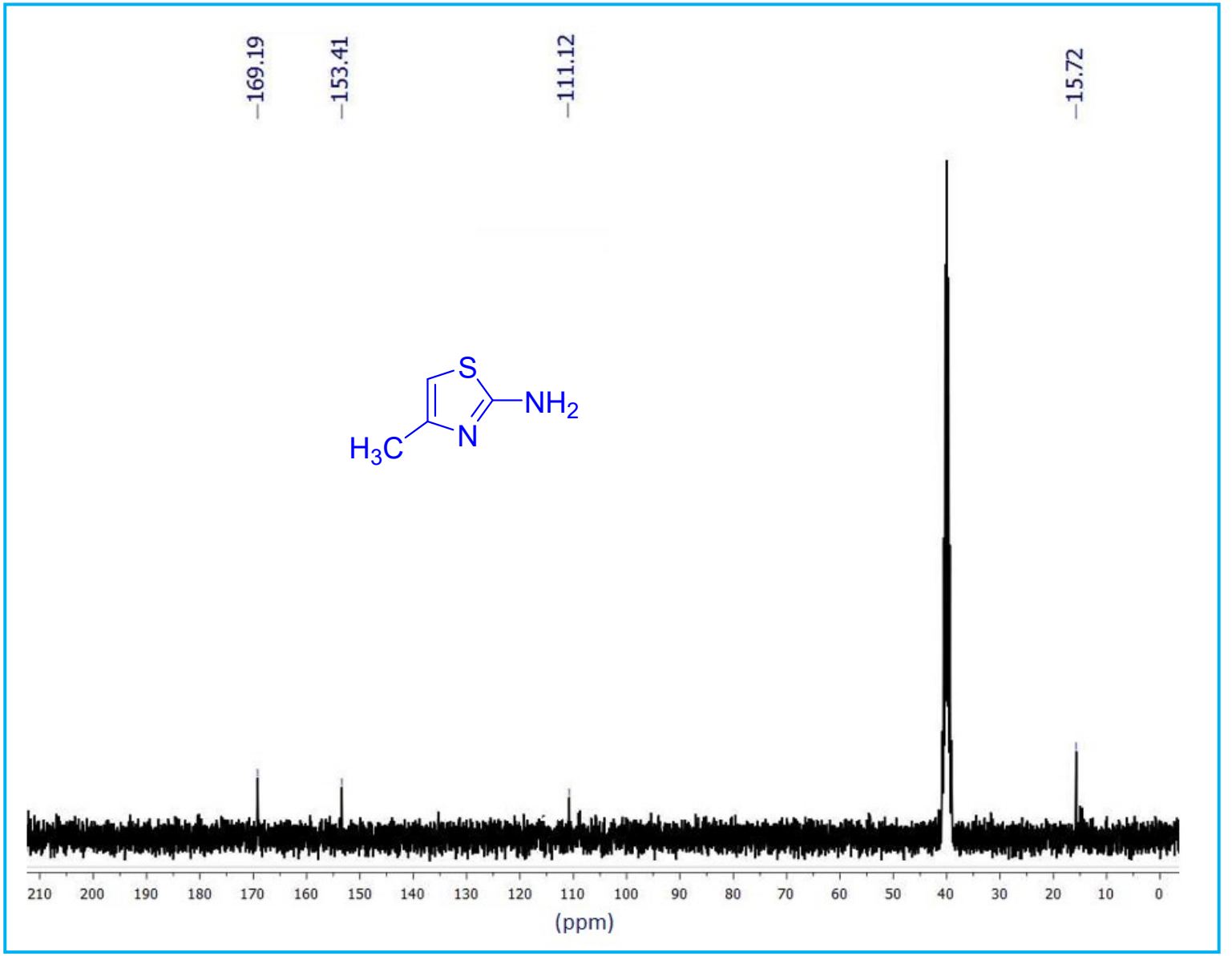
^{13}C NMR spectrum of 4-Methyl-5-(ethoxycarbonyl)-2-aminothiazole (3c)



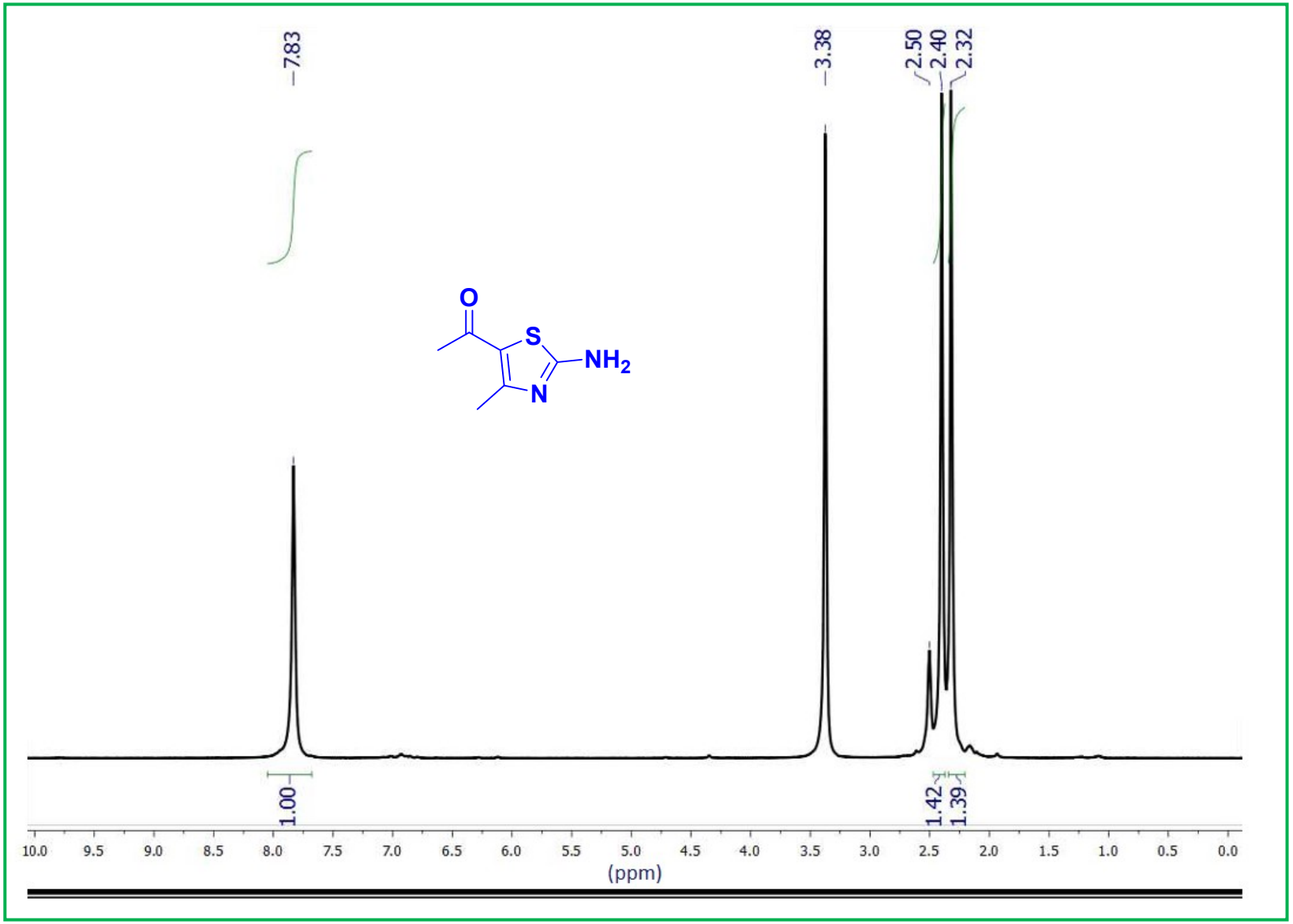
^{1}H NMR spectrum of 4-methylthiazol-2-amine (3d)



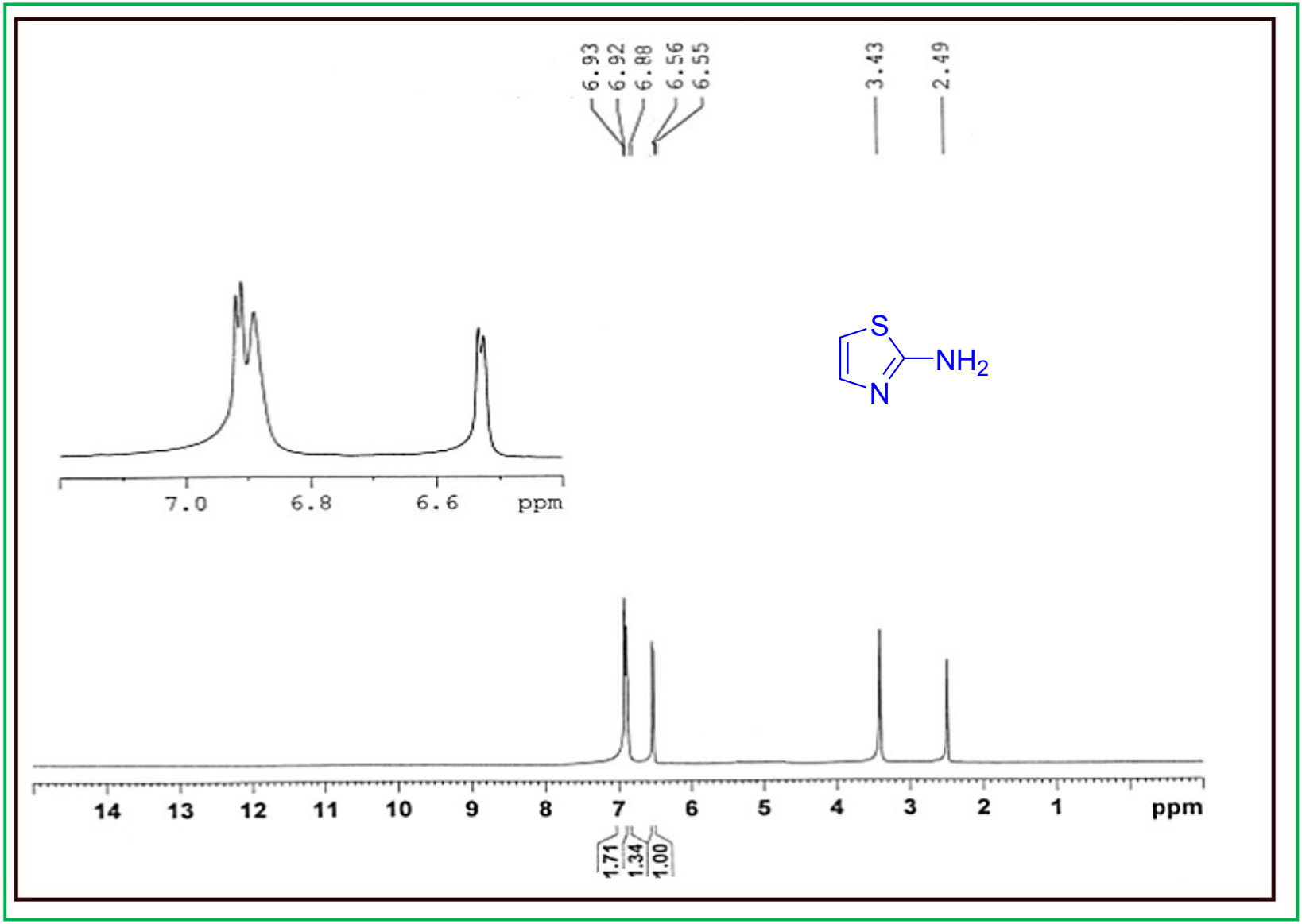
^{13}C NMR spectrum of 4-methylthiazol-2-amine (3d)



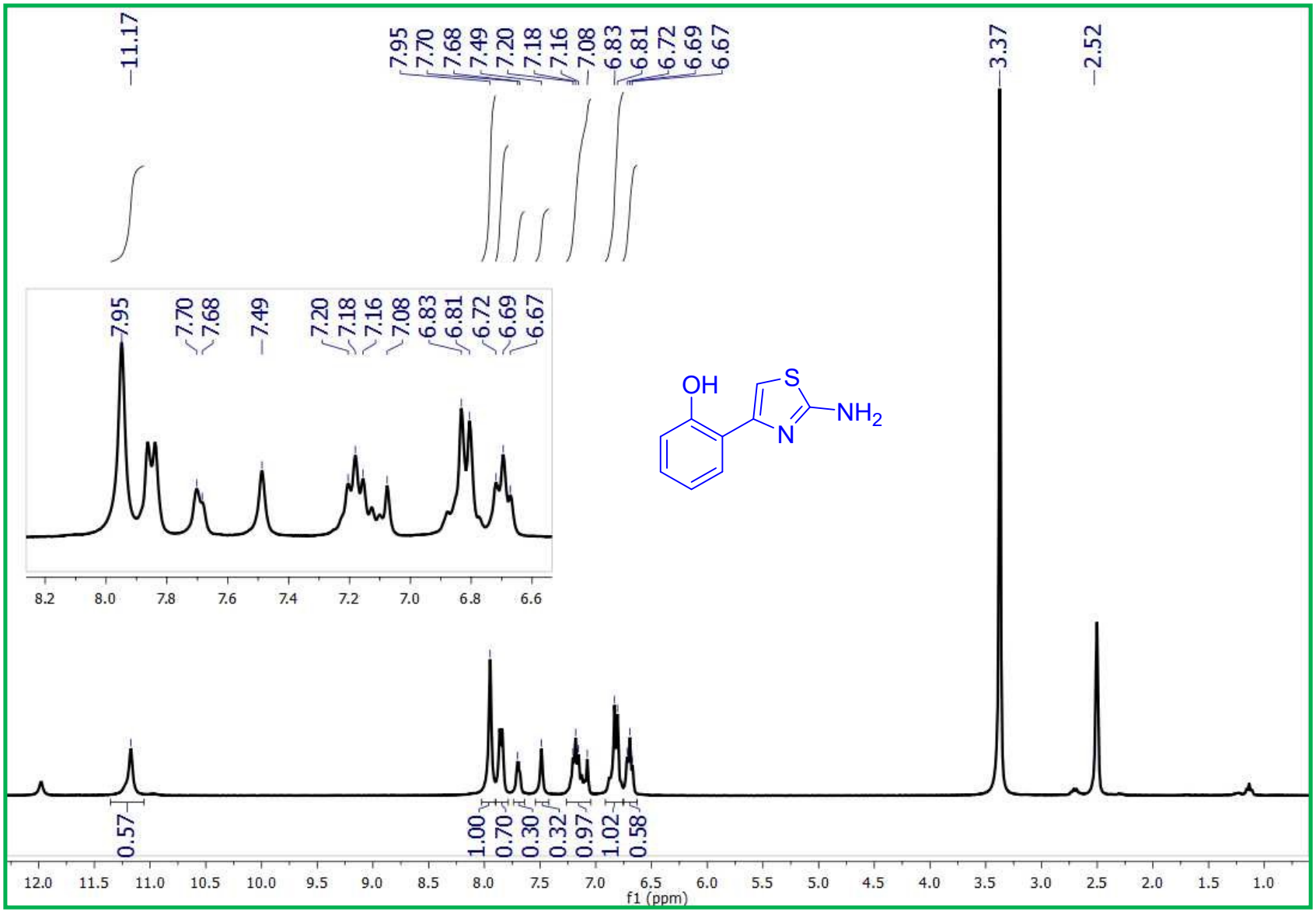
^{1}H NMR spectrum of 1-(2-amino-4-methylthiazol-5-yl)ethan-1-one (3e)



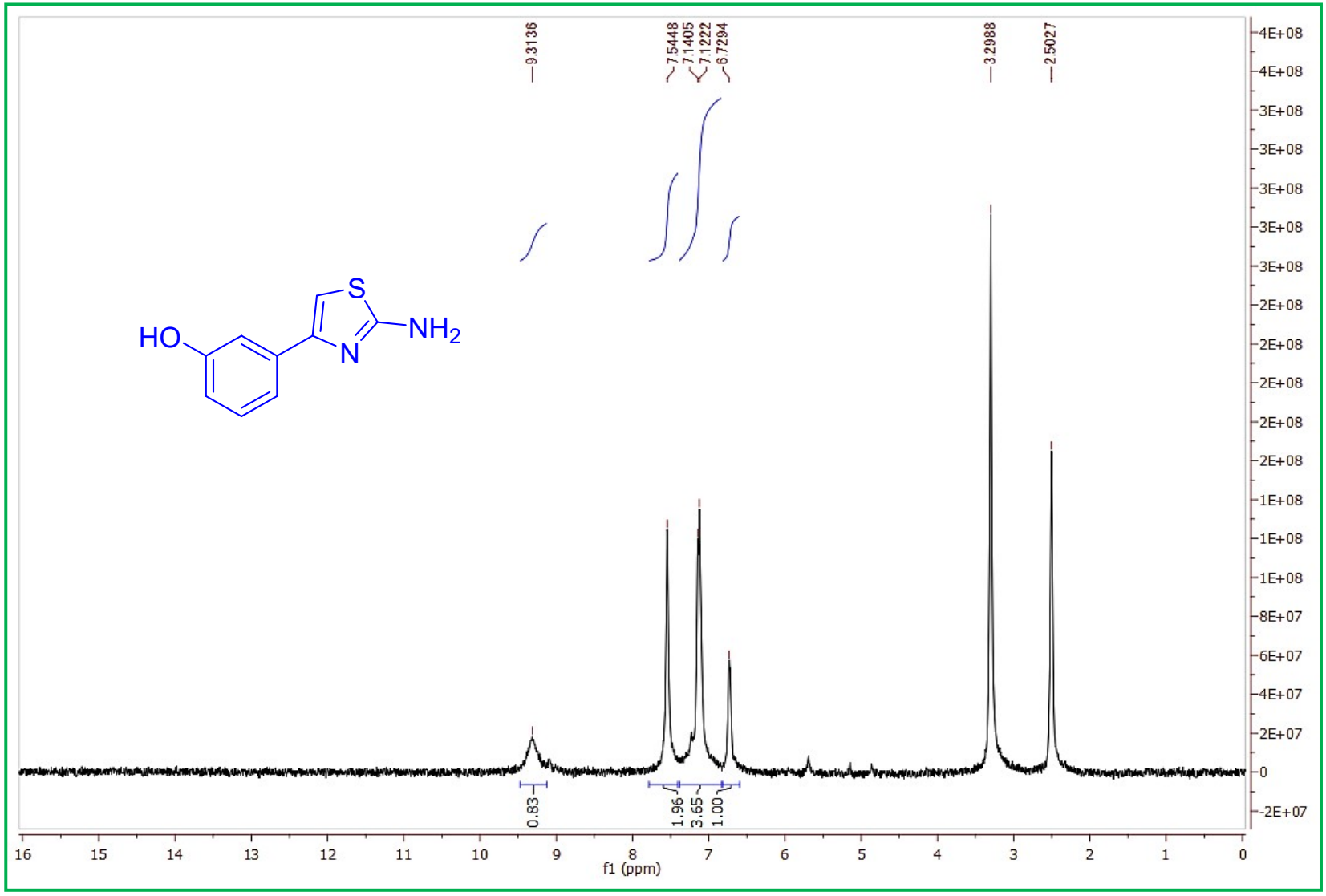
^{1}H NMR spectrum of thiazol-2-amine (3f)



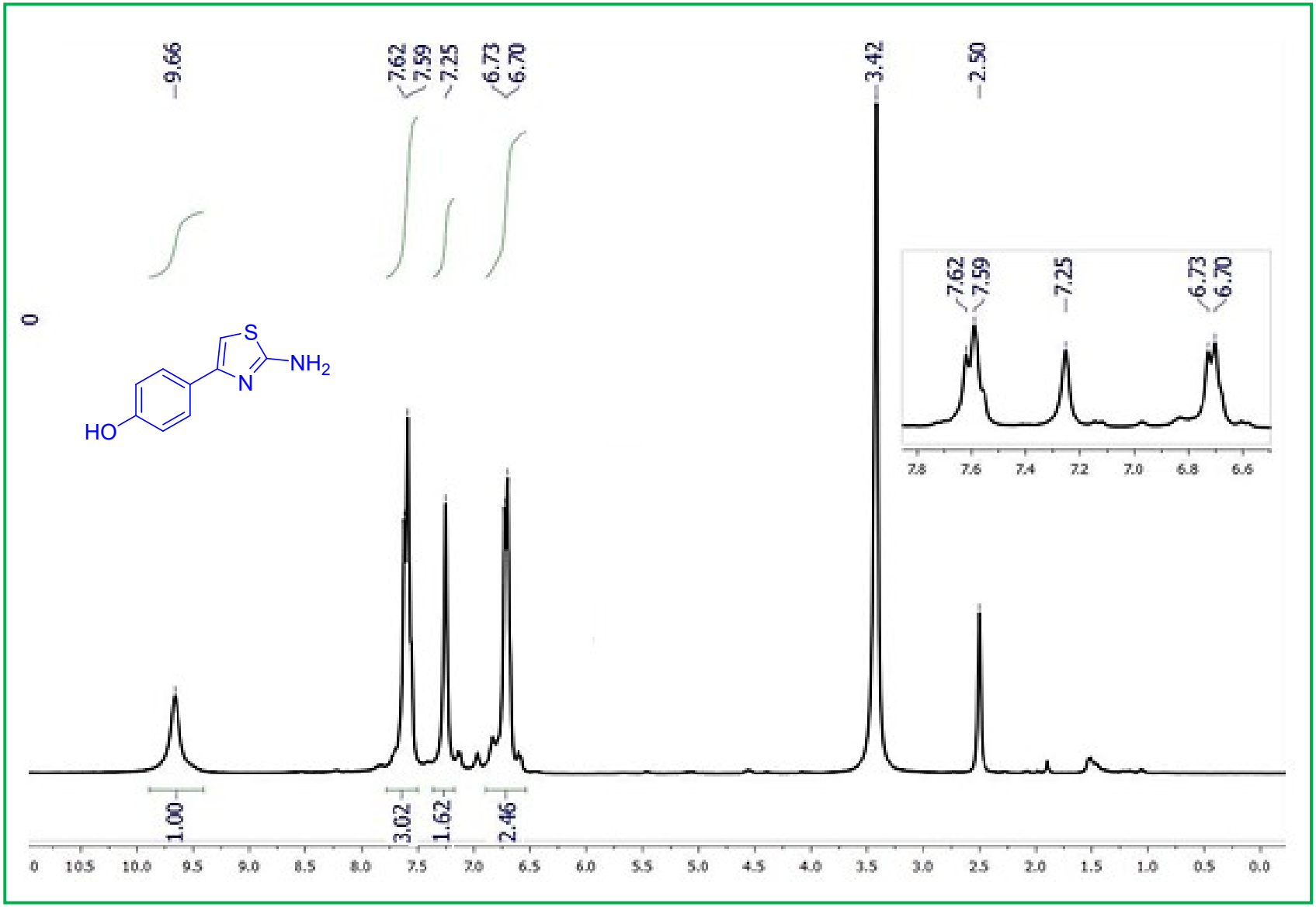
[1]H NMR spectrum of 4-(3-Hydroxyphenyl)-2-aminothiazole (3g)



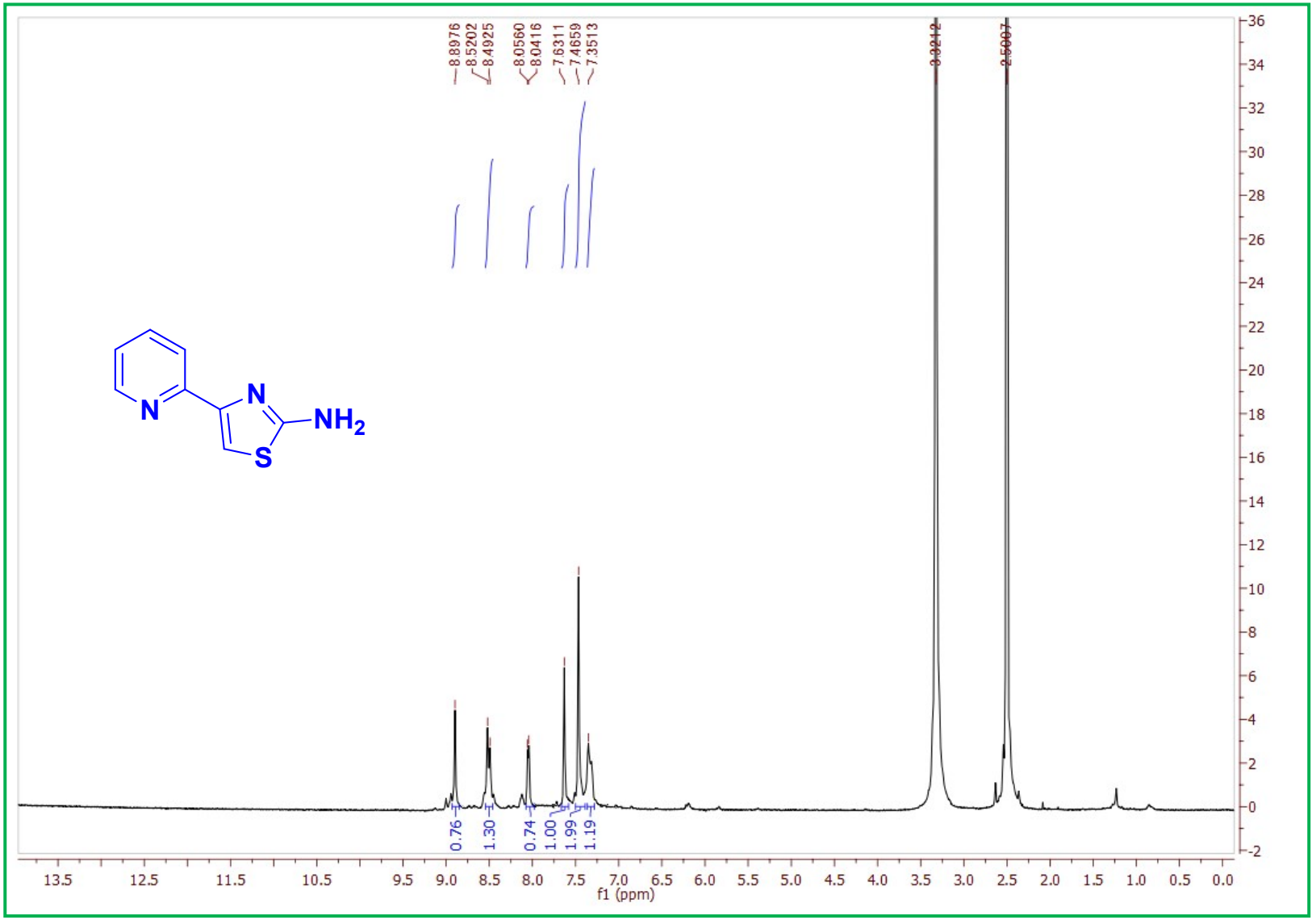
^{1}H NMR spectrum of 4-(3-Hydroxyphenyl)-2-aminothiazole (3h)



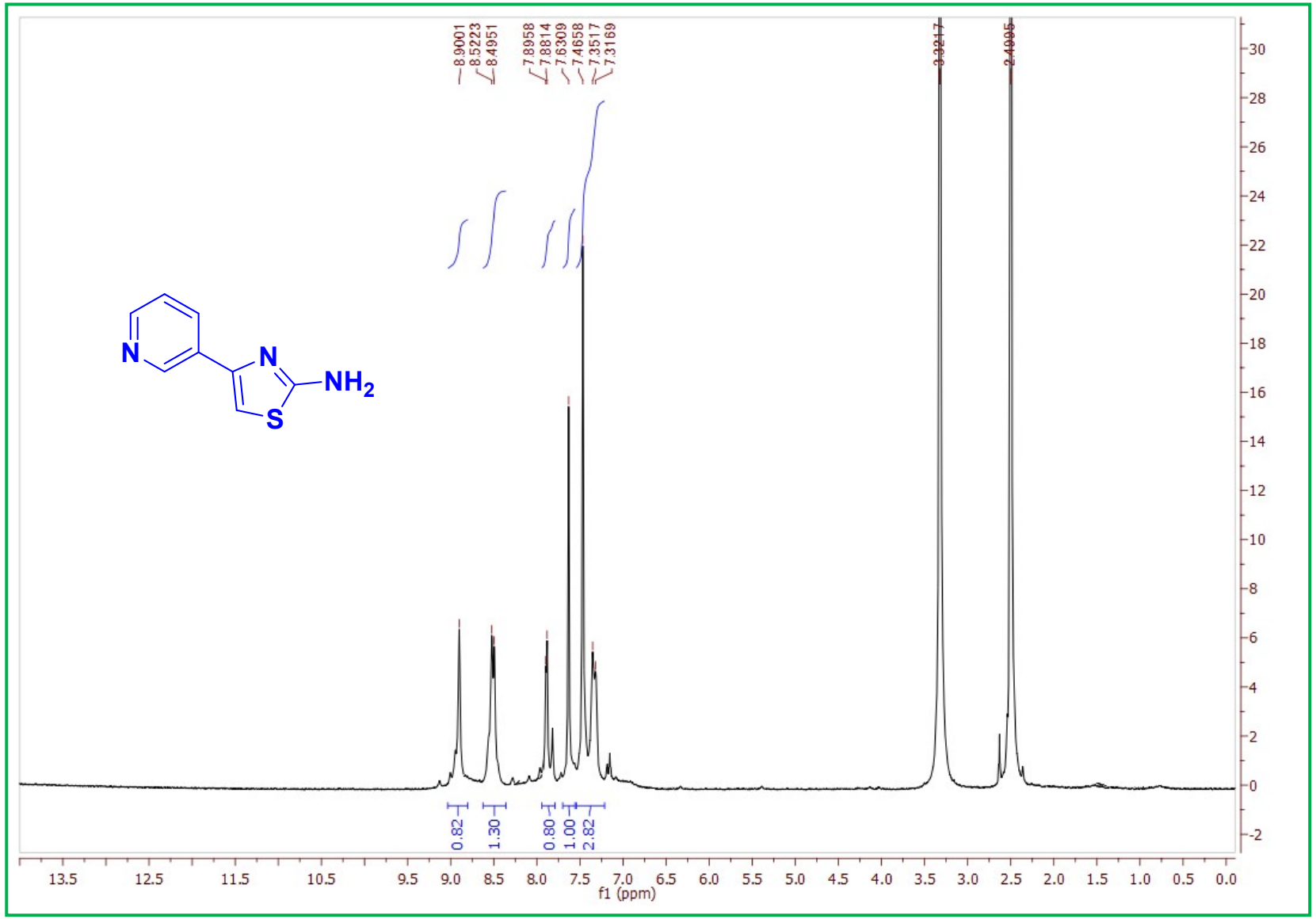
[1]H NMR spectrum of 4-(4-Hydroxyphenyl)-2-aminothiazole (3i)



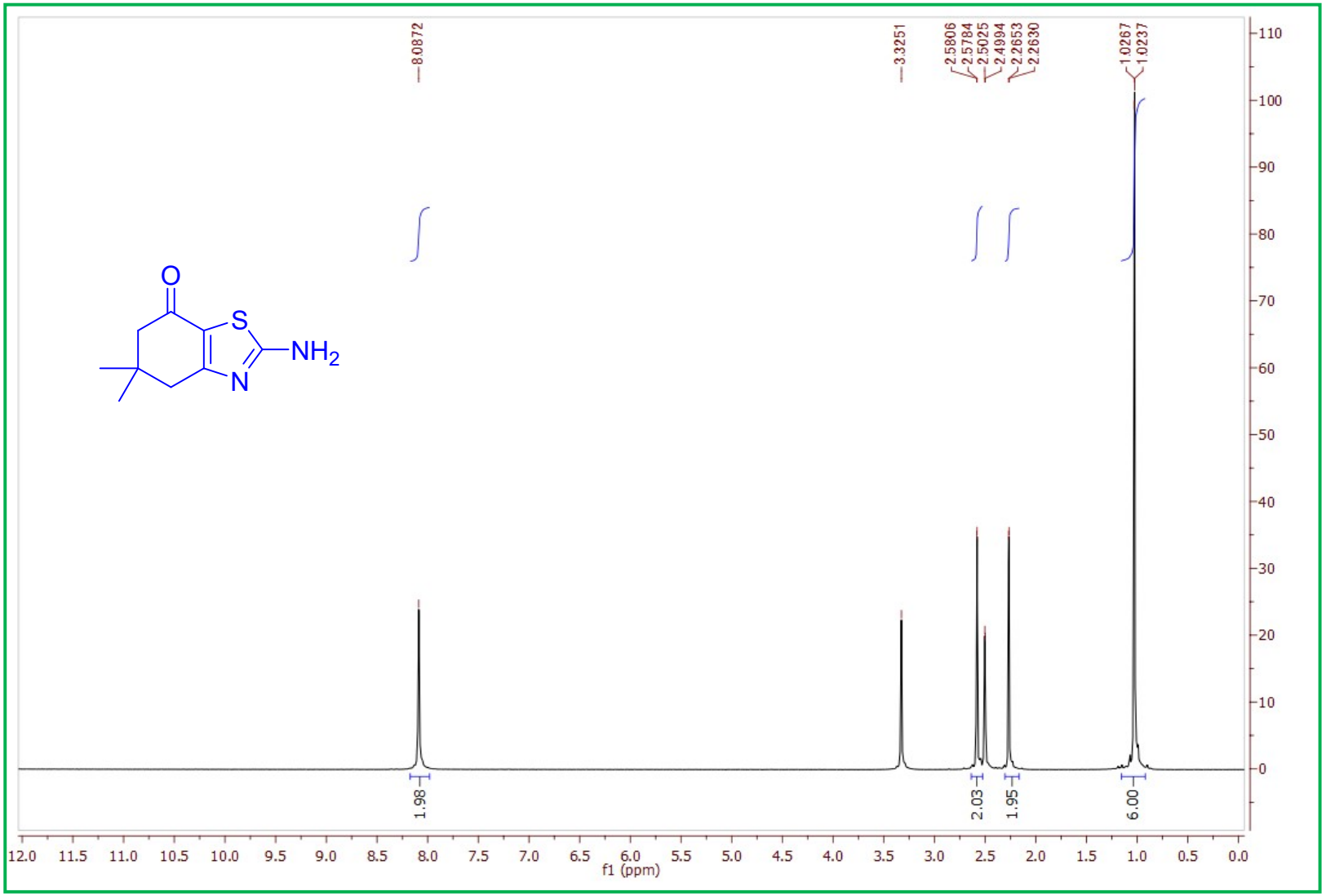
[1]H NMR spectrum of 4-(Pyridin-2-yl)thiazol-2-amine (3j)



^{1}H NMR spectrum of 4-(Pyridin-3-yl)thiazol-2-amine (3k)



^{1}H NMR spectrum of 2-Amino-5,5-dimethyl-5,6-dihydrobenzo[d]thiazol-7(4*H*)-one (3m)



^{13}C NMR spectrum of 2-Amino-5,5-dimethyl-5,6-dihydrobenzo[d]thiazol-7(4*H*)-one (3m)