Supplementary Information

Cu(II) immobilized on aminated epichlorohydrin activated silica (CAES): as a new, green and efficient nanocatalyst for preparation of 5-substituted-1*H*-tetrazoles

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Experimental

General

The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra were provided on Brucker Avance 100 and 400 MHz instruments in acetone-d_6, DMSO-d_6 and CD_3CN. Mass spectra were recorded with Agilent Technologies (HP) 5973 Network Mass Selective Detector and Shimadzu GC-MS-QP5050 instruments at 70 eV. Thermogravimetric analysis (TGA) was performed on a Shimadzu Thermogavimetric Analyzer (TG-50) under air atmosphere. BET surface area and pore size distribution were measured on a Belsorp mini II system at −196 ˚C using N_2 as adsorbate. Inductively coupled plasma (ICP) was carried out on a Varian, VISTA-PRO, CCD, Australia. All of the products were known compounds and characterized by the FT-IR and comparison of their melting points with known compounds. The structure of selected products was further confirmed by ^{1}HNMR, ^{13}CNMR spectroscopy, and mass spectrometry.

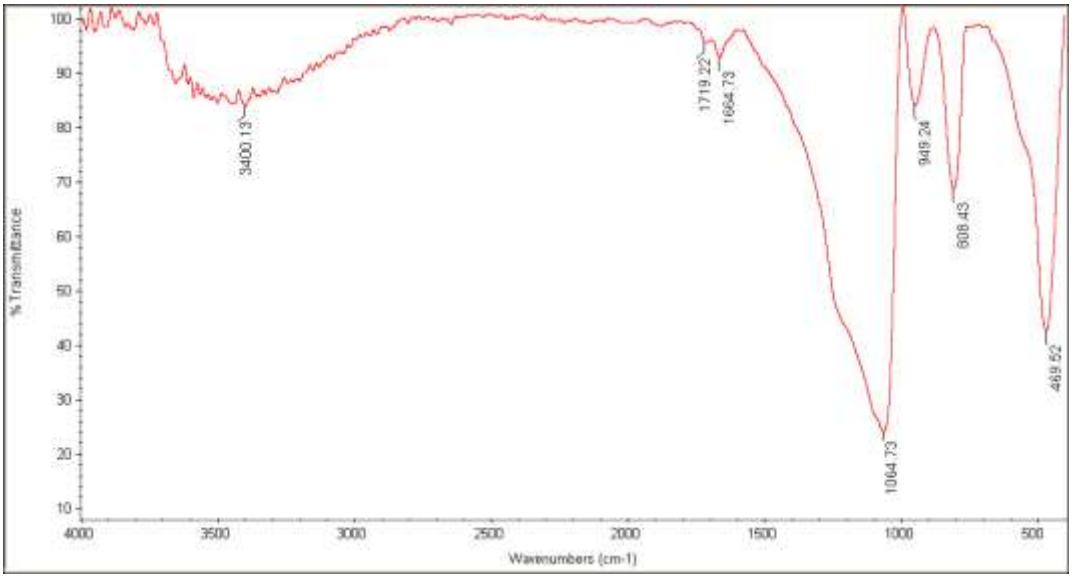

Figure 1: FT-IR (KBr) of activated silica with HCl.

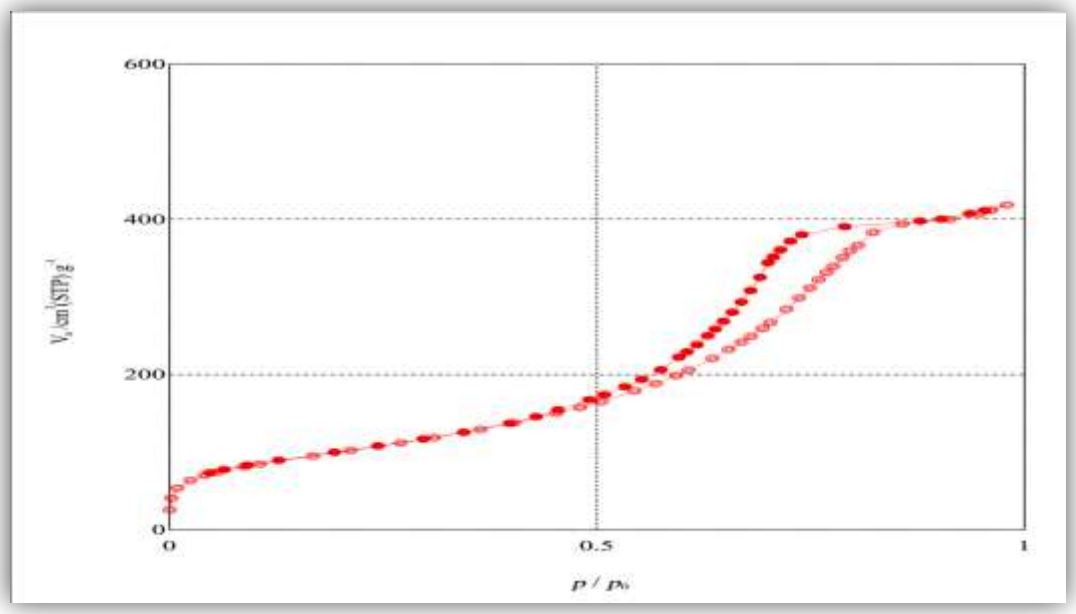

Figure 2: Adsorption/desorption isotherm of activated silica with HCl.

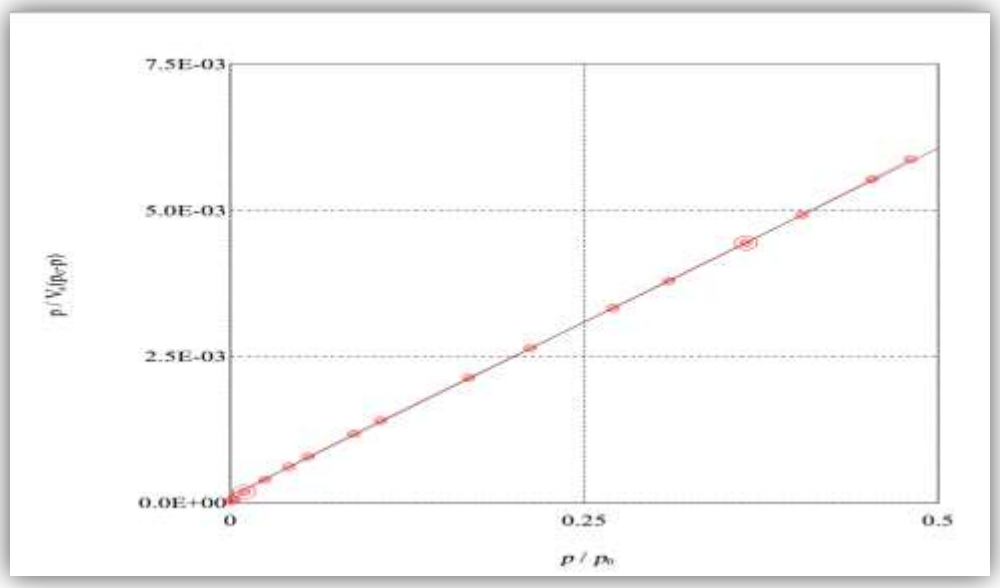

Figure 3: BET-Plot of activated silica with HCl.

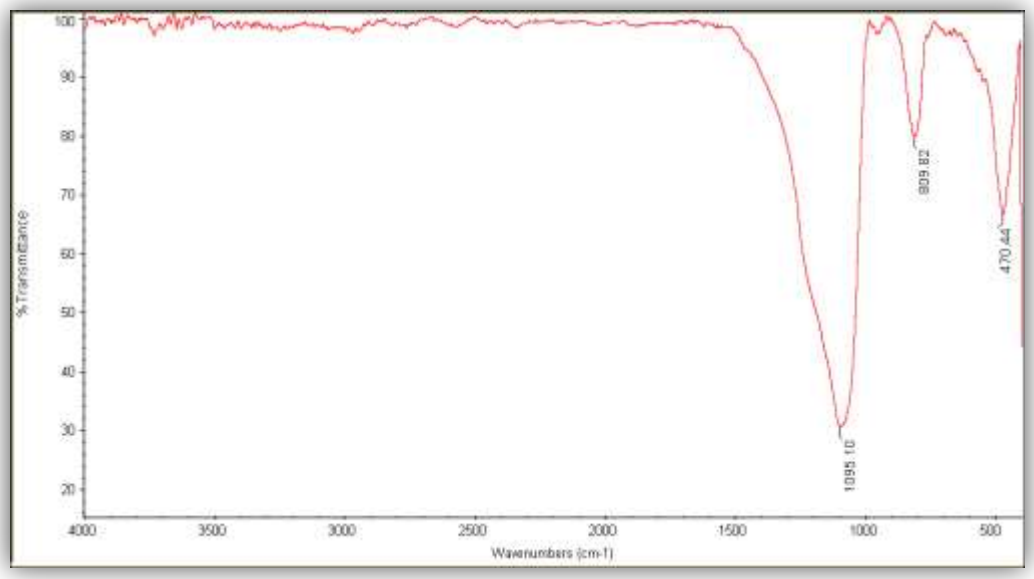

Figure 4: FT-IR (KBr) of activated silica with NaOH solution.

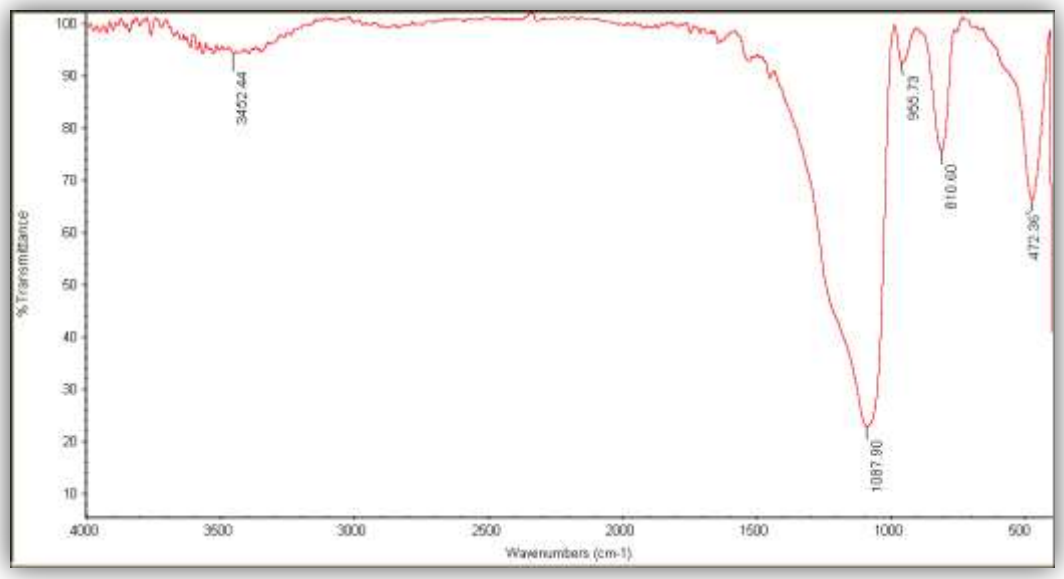

Figure 5: FT-IR (KBr) of epichlorohydrin-SiO_2.

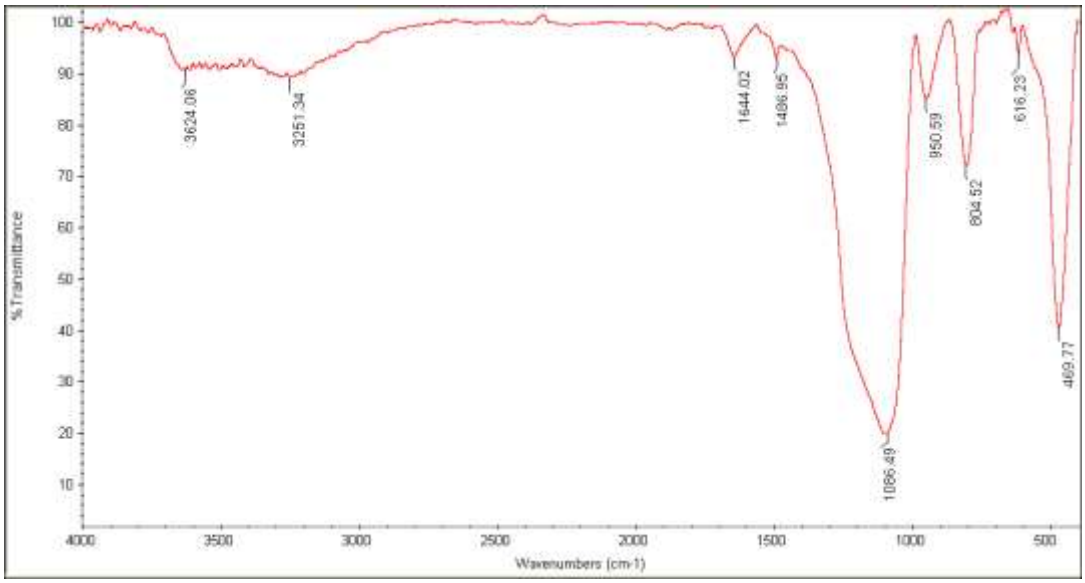

Figure 6: FT-IR (KBr) of aminated epichlorohydrin-SiO_2.

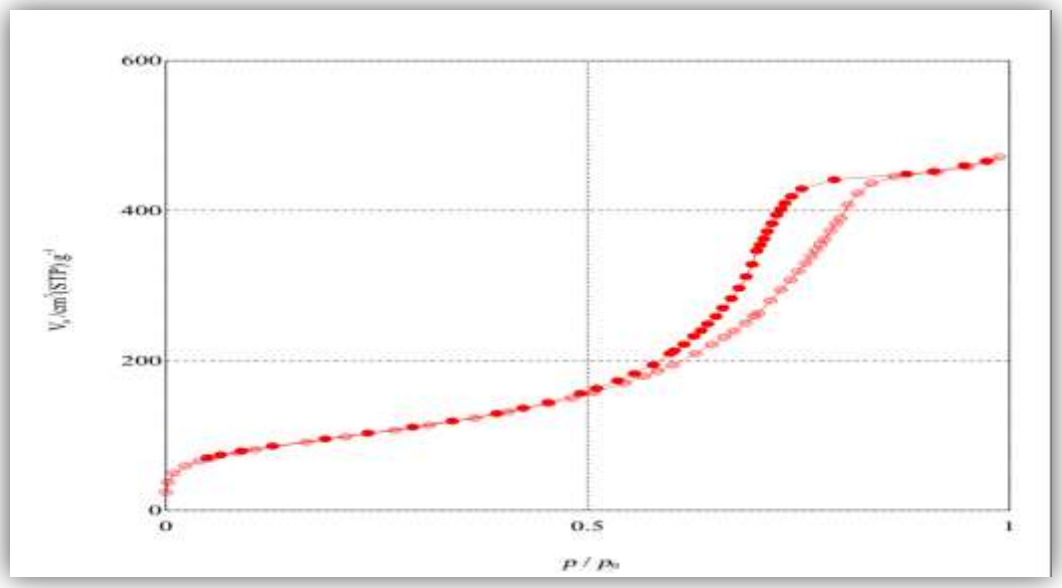

Figure 7: Adsorption/desorption isotherm of aminated epichlorohydrin-SiO_2.

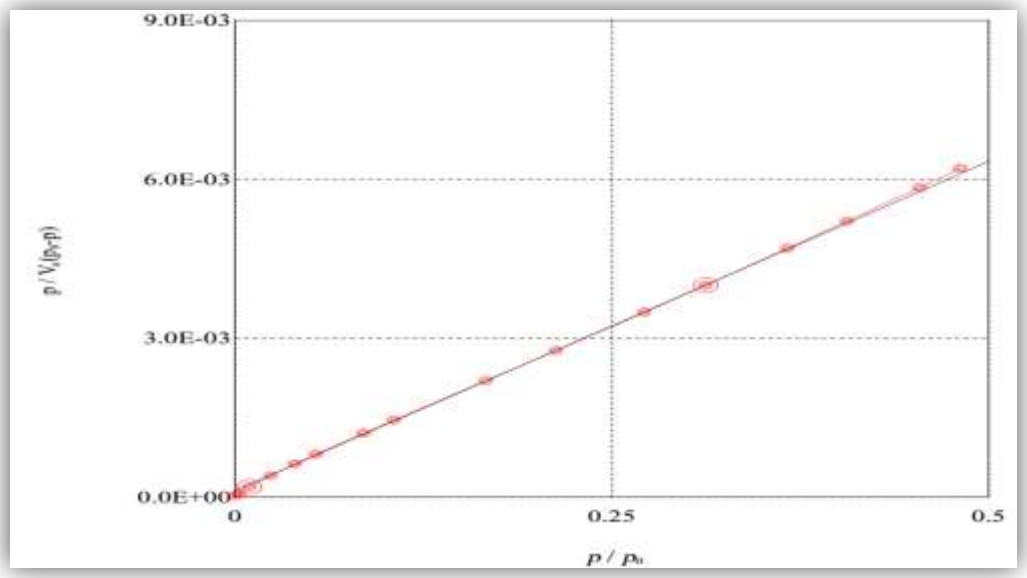

Figure 8: BET-Plot of aminated epichlorohydrin-SiO_2.

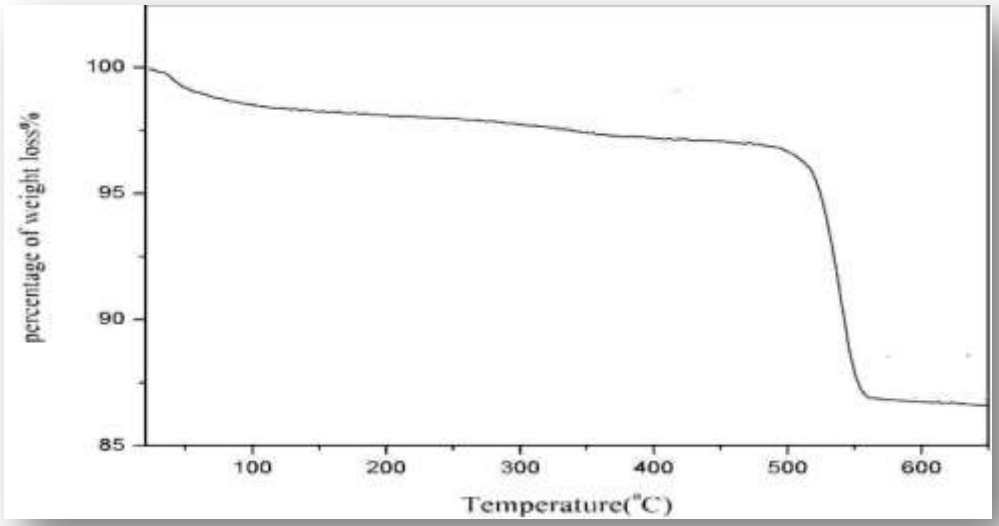

Figure 9: Thermogravimetric analysis (TGA) of aminated epichlorohydrin-SiO_2.

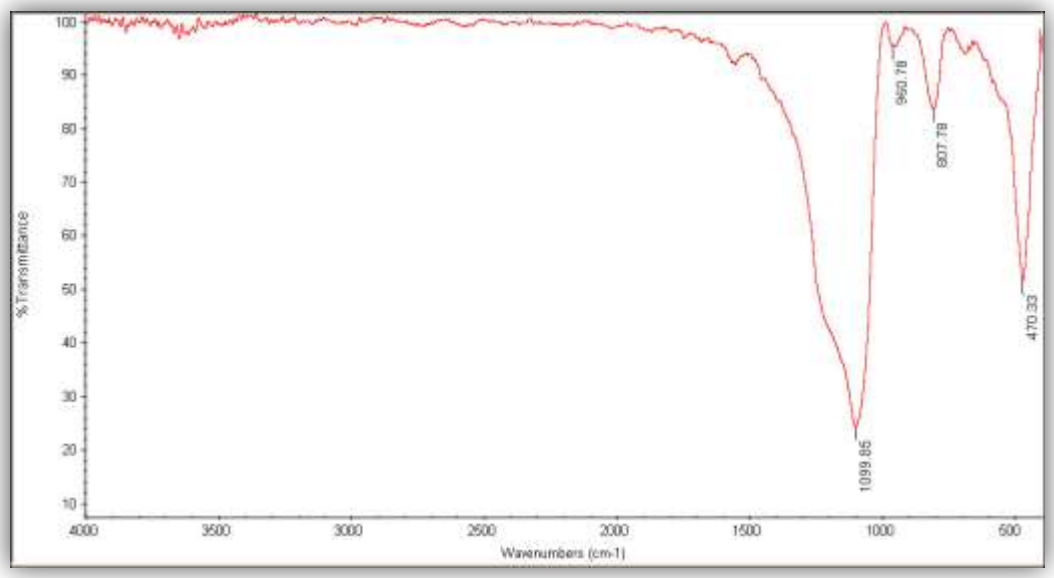

Figure 10: FT-IR (KBr) of Cu supported on aminated epichlorohydrin-SiO_2.

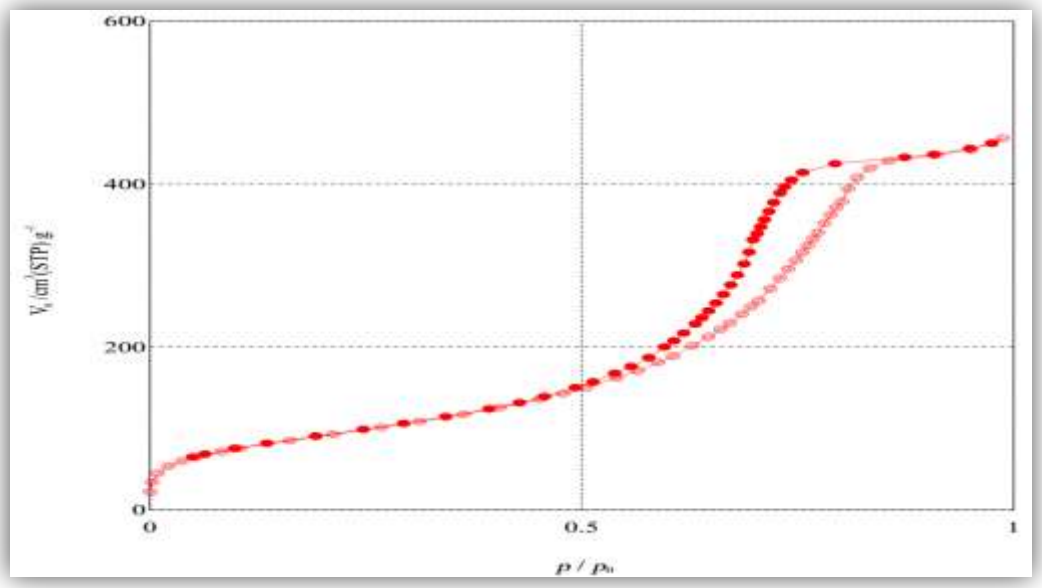

Figure 11: Adsorption/desorption isotherm of Cu supported on aminated epichlorohydrin-SiO_2.

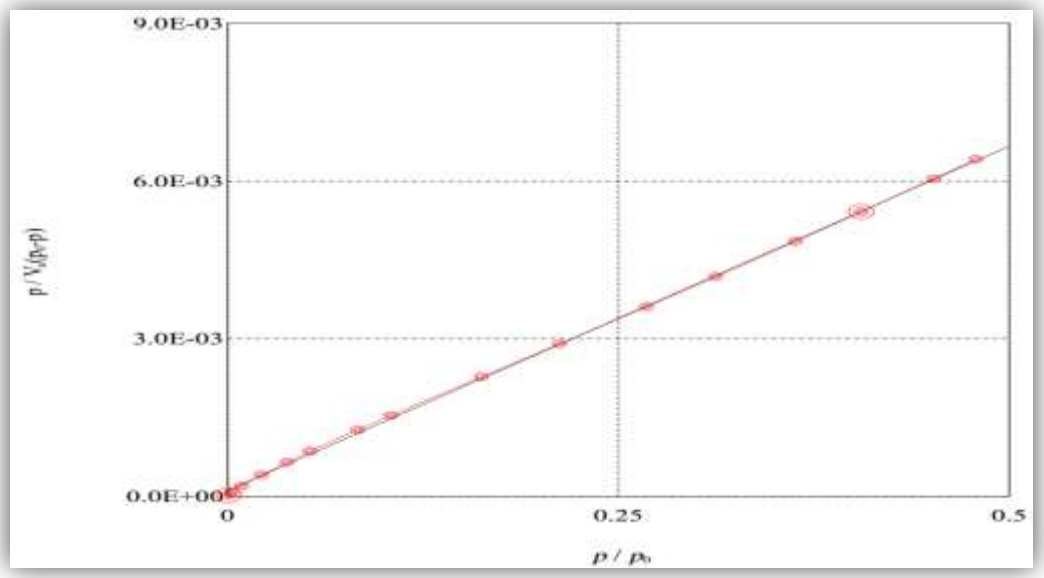

Figure 12: BET-Plot of Cu supported on aminated epichlorohydrin-SiO_2.

Sample (Samp) **12/31/2014, 9:12:09 AM** **Tube 61**

Weight: 0.0617 Volume: 25 Dilution: 1

El	Wavelen.	Sol'n Conc.	Units	SD	%RSD	Int. (c/s)	Calc Conc.
Cu	324.754	39.716	ppm	0.21826	0.5	104924	16092 ppm

Figure 13: ICP of Cu supported on aminated epichlorohydrin-SiO_2.

Cu (Samp) **2/21/2015, 5:33:15 AM** **Tube 33**

Weight: 0.0444 Volume: 20 Dilution: 5

El	Wavelen.	Sol'n Conc.	Units	SD	%RSD	Int. (c/s)	Calc Conc.
Cu	324.754	4.6406	ppm	0.016139	0.3	11199	12452 ppm

Figure 14: ICP of fifth reused Cu supported on aminated epichlorohydrin-SiO_2.

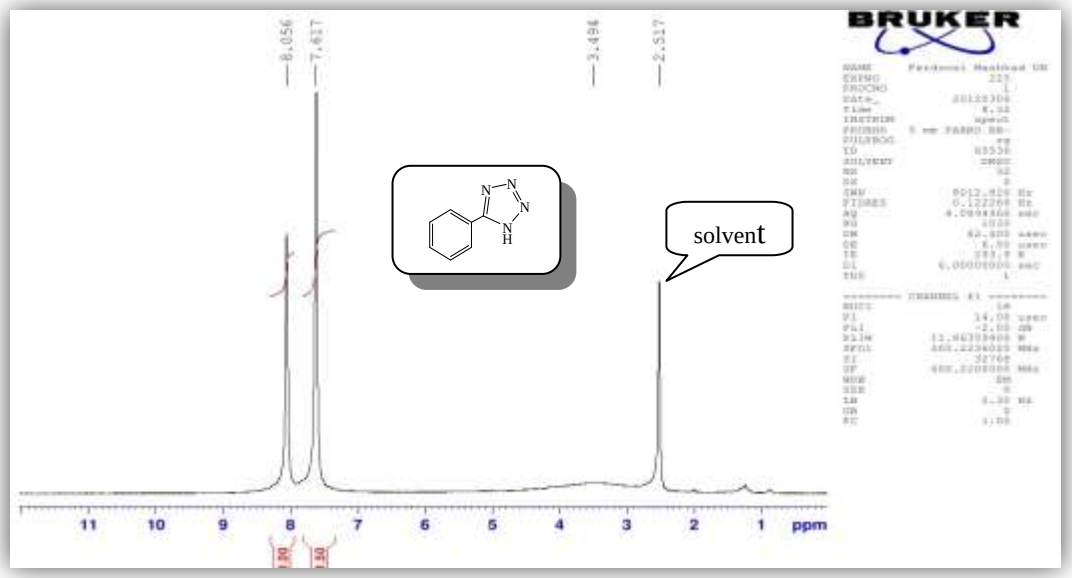

Figure 15: ^{1}H NMR (400 MHz, DMSO-d_6) of 5-Phenyl-1*H*-tetrazole (Table 2, entry 1).

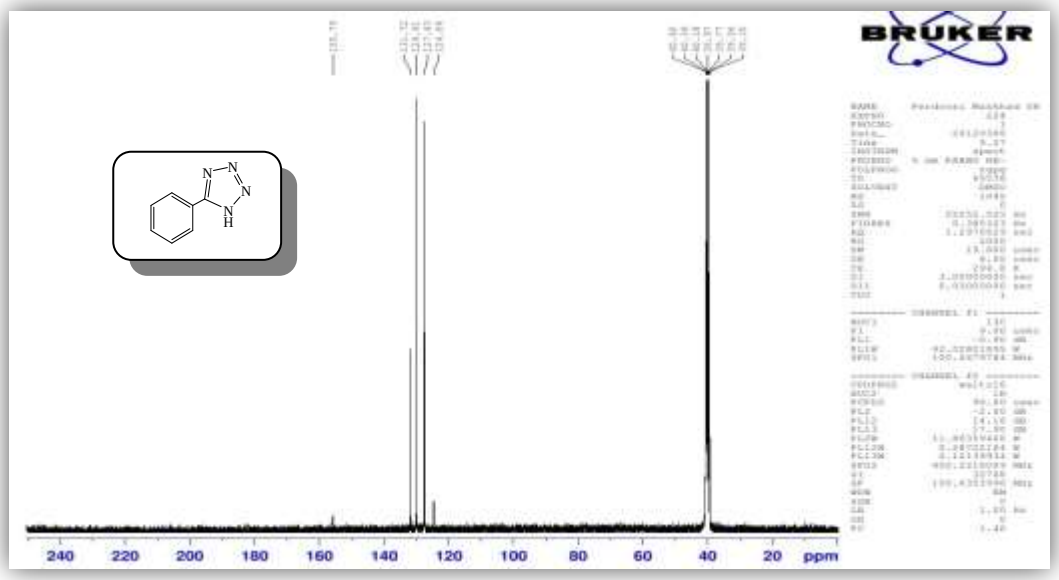

Figure 16: ^{13}C NMR (100 MHz, DMSO-d_6) of 5-Phenyl-1*H*-tetrazole (Table 2, entry 1).

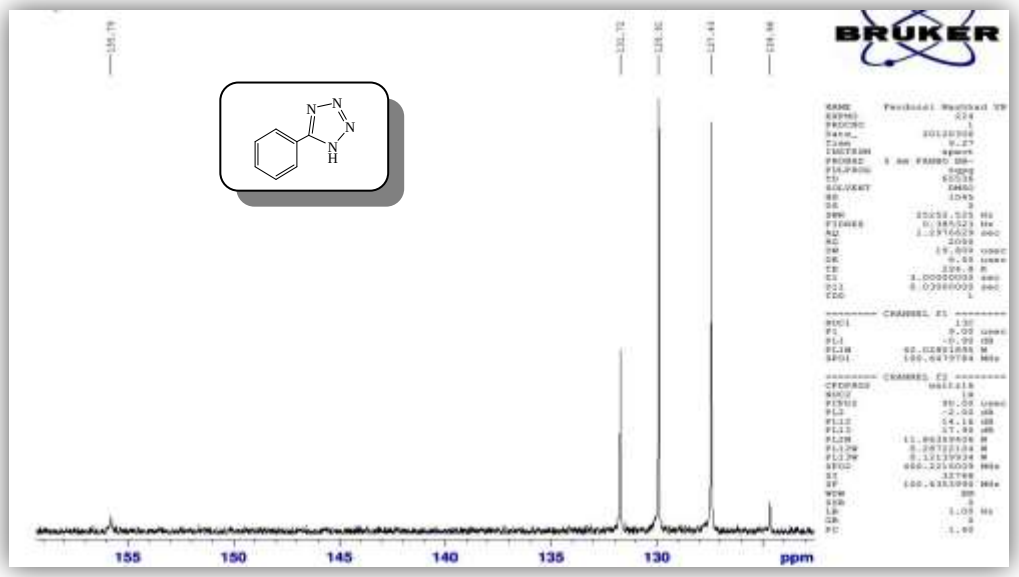

Figure 17: ^{13}C NMR (100 MHz, DMSO-d_6) of 5-Phenyl-1*H*-tetrazole (Table 2, entry 1) expanded.

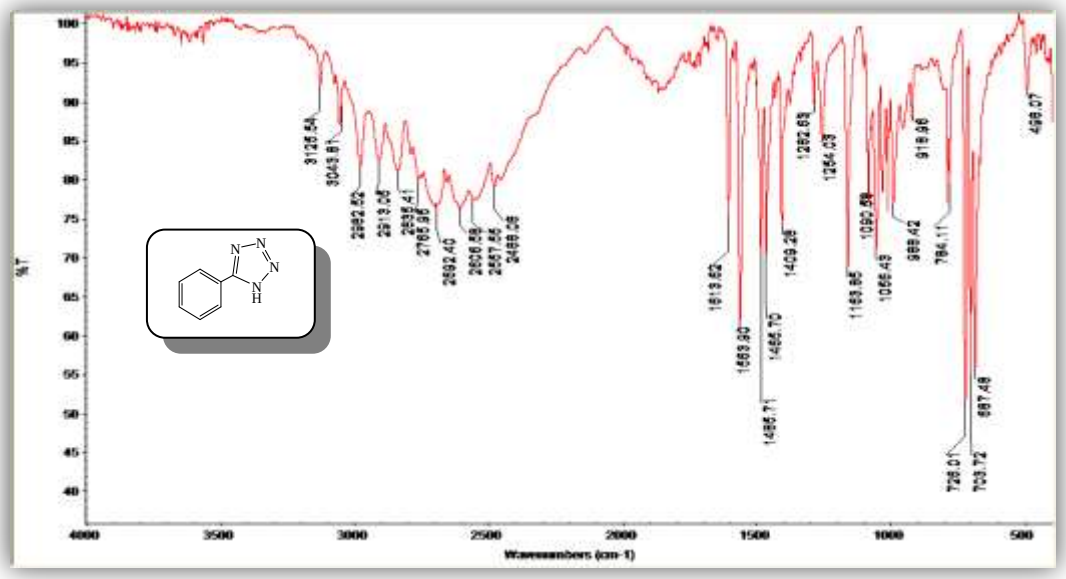

Figure 18: FT-IR (KBr) of 5-Phenyl-1*H*-tetrazole (Table 2, entry 1).

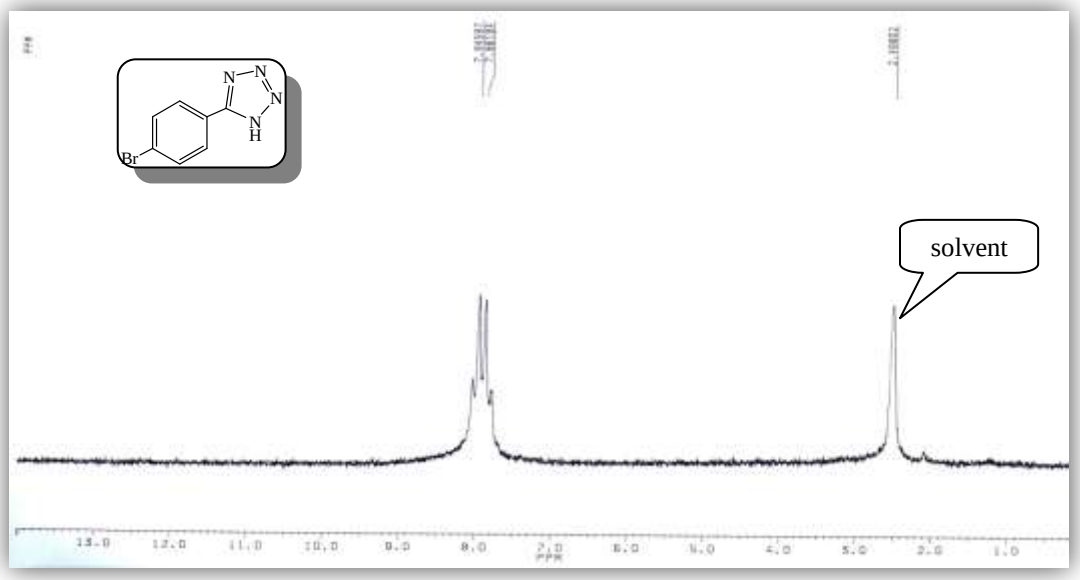

Figure 19: ^{1}H NMR (100 MHz, DMSO-d_6) of 5-(4-Boromophenyl)-1*H*-tetrazole (Table 2, entry 2).

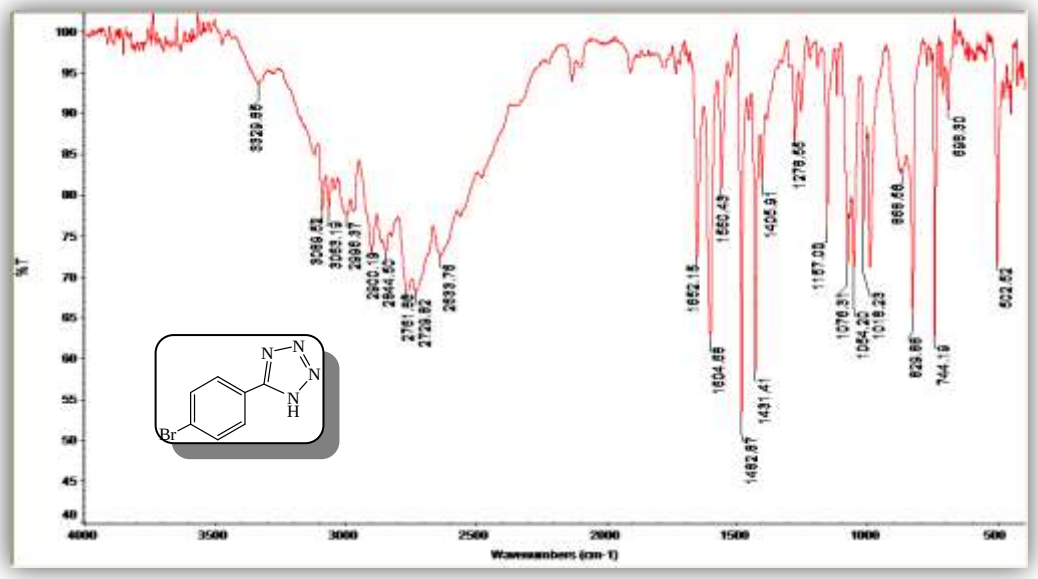

Figure 20: FT-IR (KBr) of 5-(4-Boromophenyl)-1*H*-tetrazole (Table 2, entry 2).

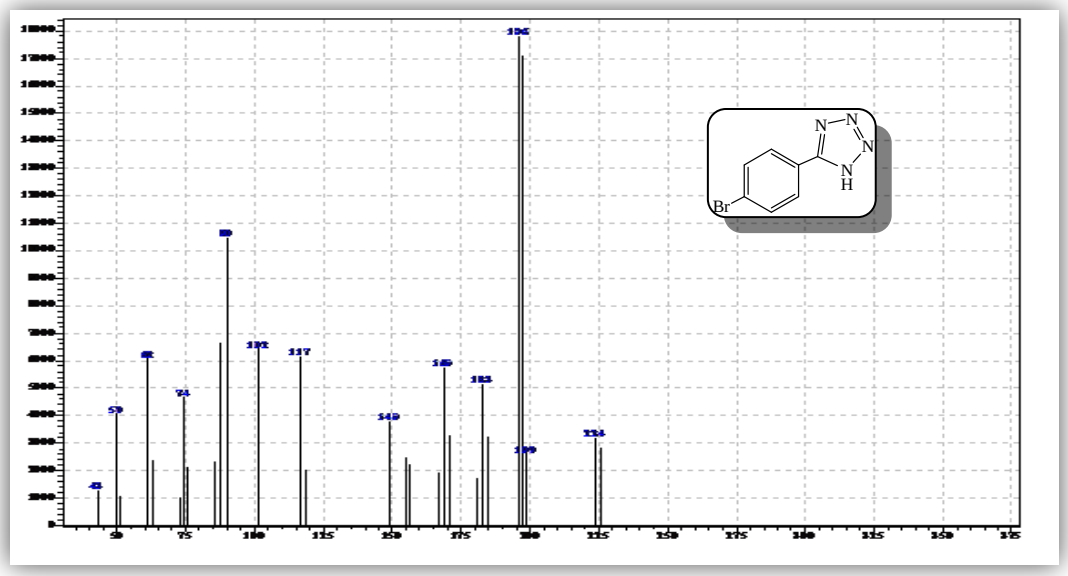

Figure 21: Mass spectrum of 5-(4-Boromophenyl)-1*H*-tetrazole (Table 2, entry 2).

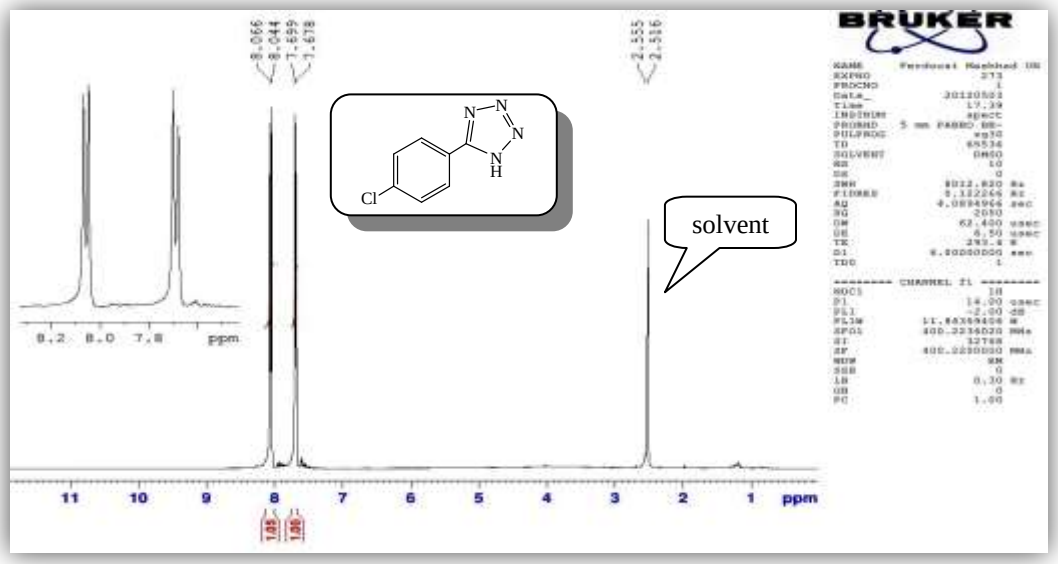

Figure 22: ^{1}H NMR (400 MHz, DMSO-d_6) of 5-(4-Chlorophenyl)-1*H*-tetrazole (Table 2, entry 3).

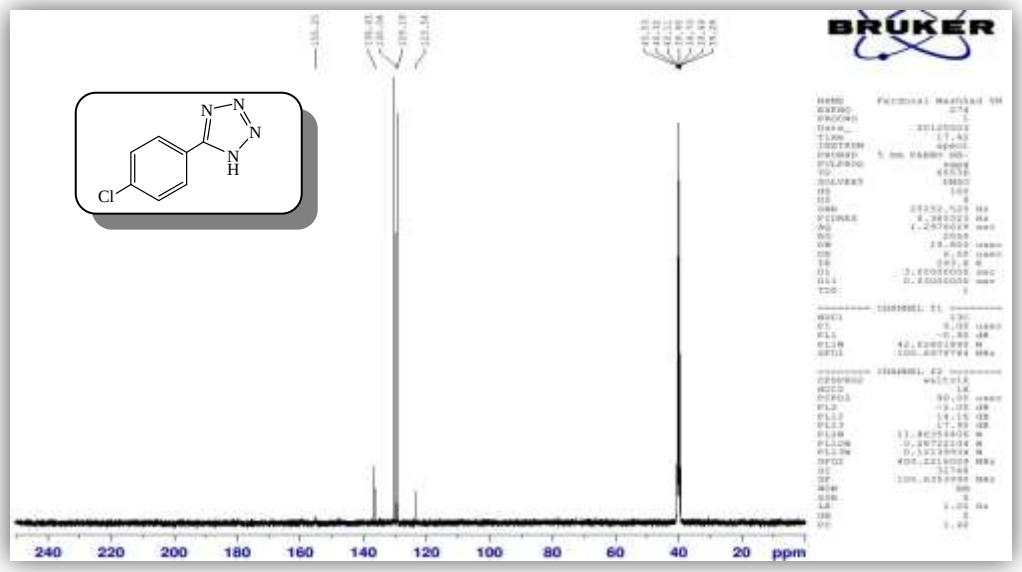

Figure 23: ^{13}C NMR (100 MHz, DMSO-d_6) of 5-(4-Chlorophenyl)-1*H*-tetrazole (Table 2, entry 3).

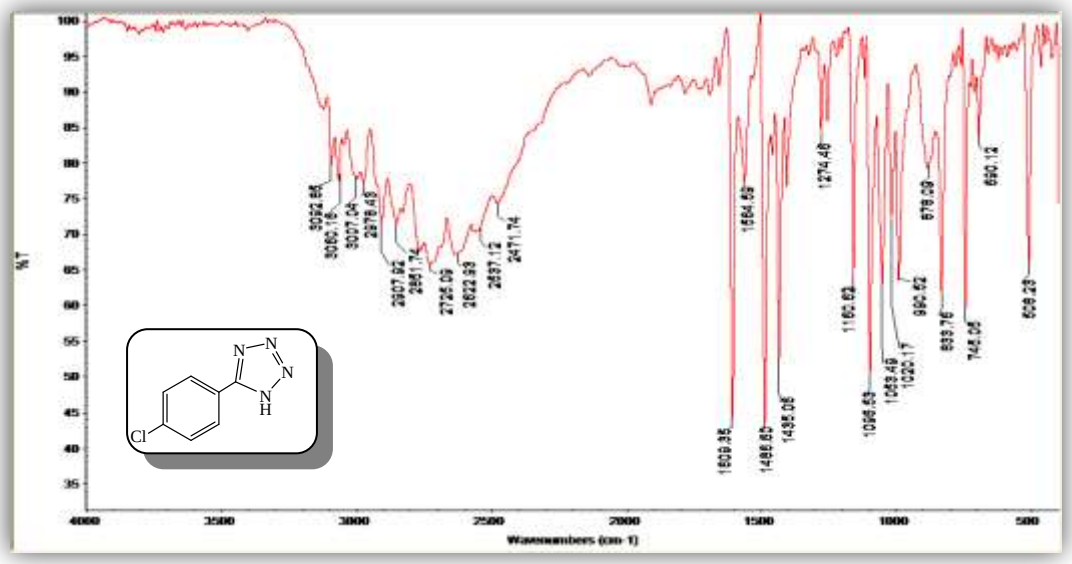

Figure 24: FT-IR (KBr) of 5-(4-Chlorohenyl)-1*H*-tetrazole (Table 2, entry 3).

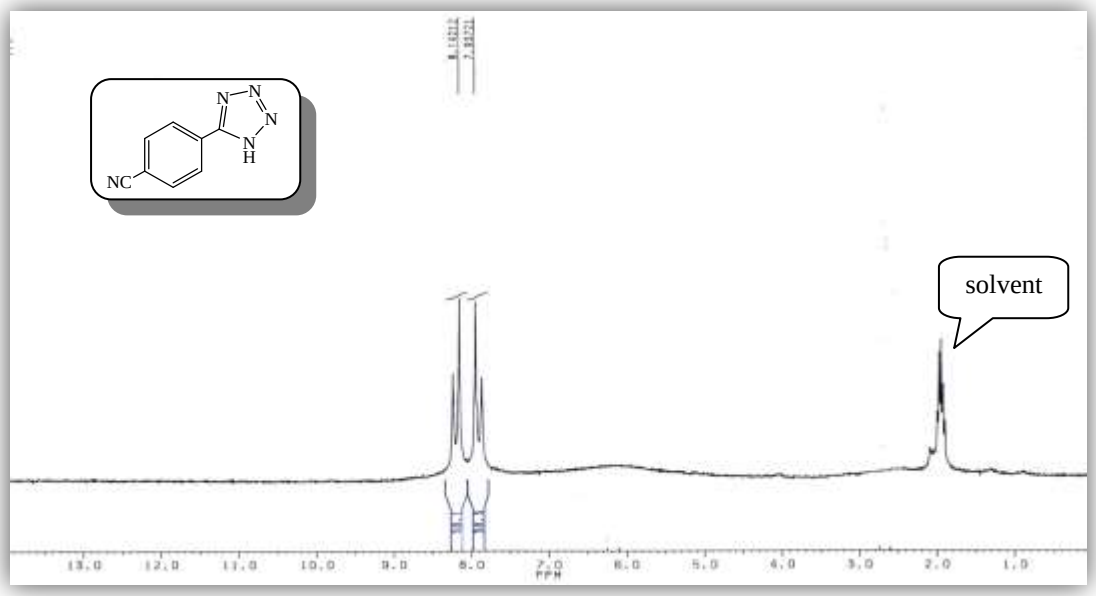

Figure 25: ^{1}H NMR (100 MHz, CD_3CN) of 4-(1*H*-tetrazol-5-yl)benzonitrile (Table 2, entry 4).

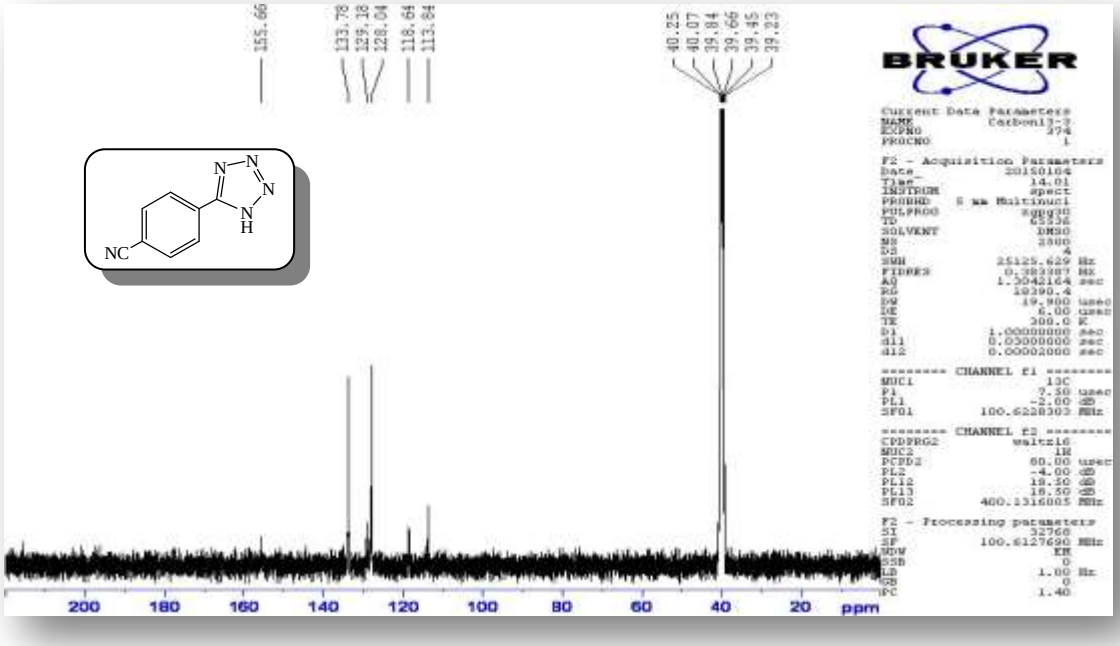

Figure 26: ^{13}C NMR (400 MHz, DMSO-d_6) of 4-(1*H*-tetrazol-5-yl)benzonitrile (Table 2, entry 4).

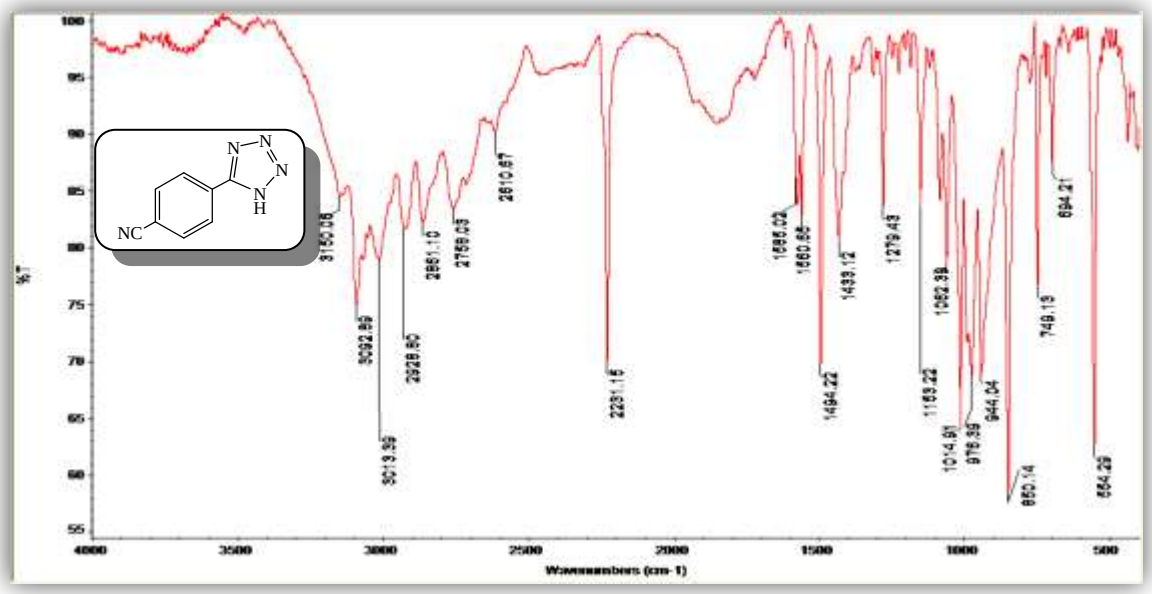

Figure 27: FT-IR (KBr) of 4-(1*H*-tetrazol-5-yl)benzonitrile (Table 2, entry 4).

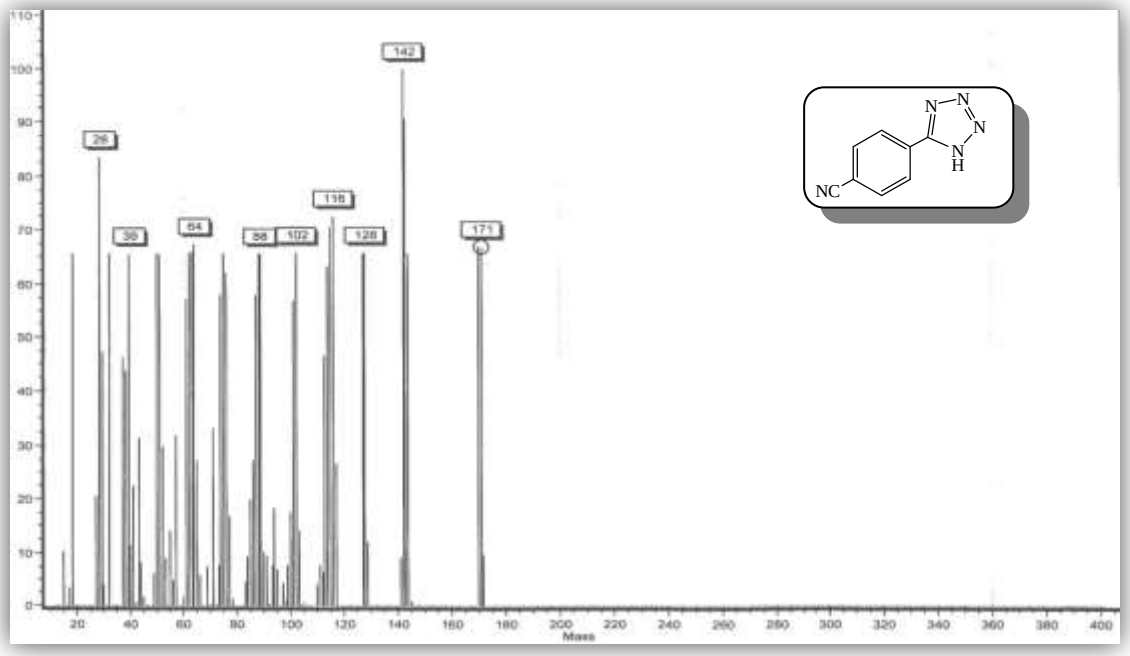

Figure 28: Mass spectrum of 4-(1*H*-tetrazol-5-yl)benzonitrile (Table 2, entry 4).

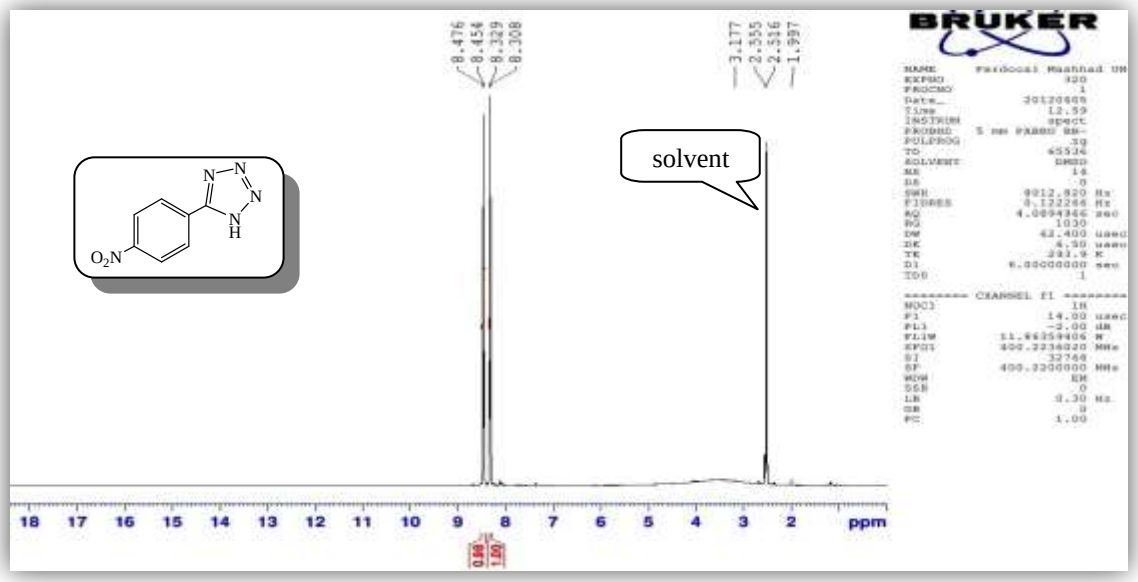

Figure 29: ^{1}H NMR (400 MHz, DMSO-d_6) of 5-(4-Nitrophenyl)-1*H*-tetrazole (Table 2, entry 5).

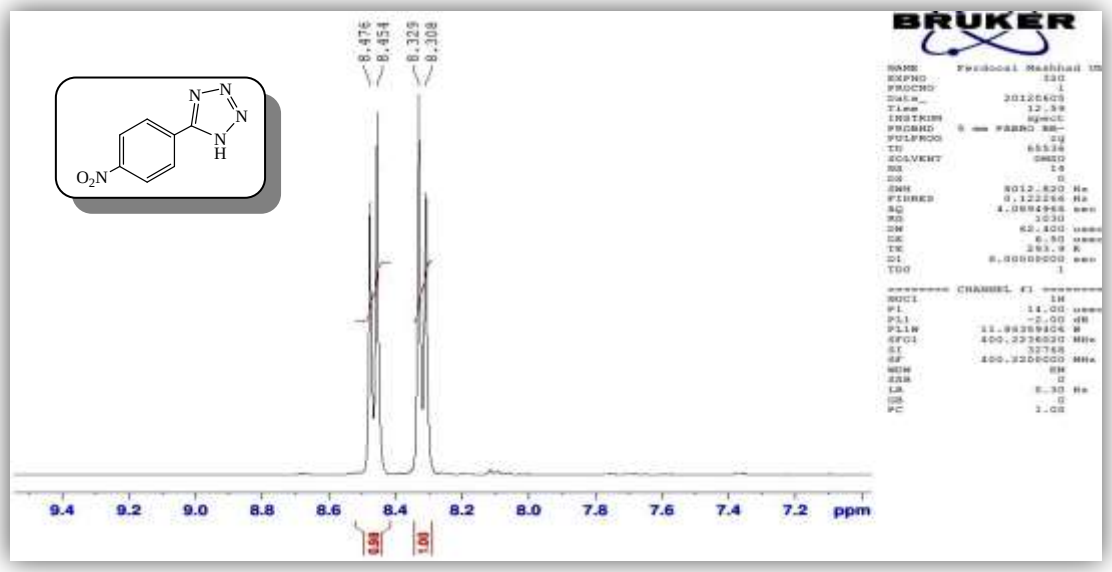

Figure 30: ^{1}H NMR (400 MHz, DMSO-d_6) of 5-(4-Nitrophenyl)-1*H*-tetrazole (Table 2, entry 5) expanded.

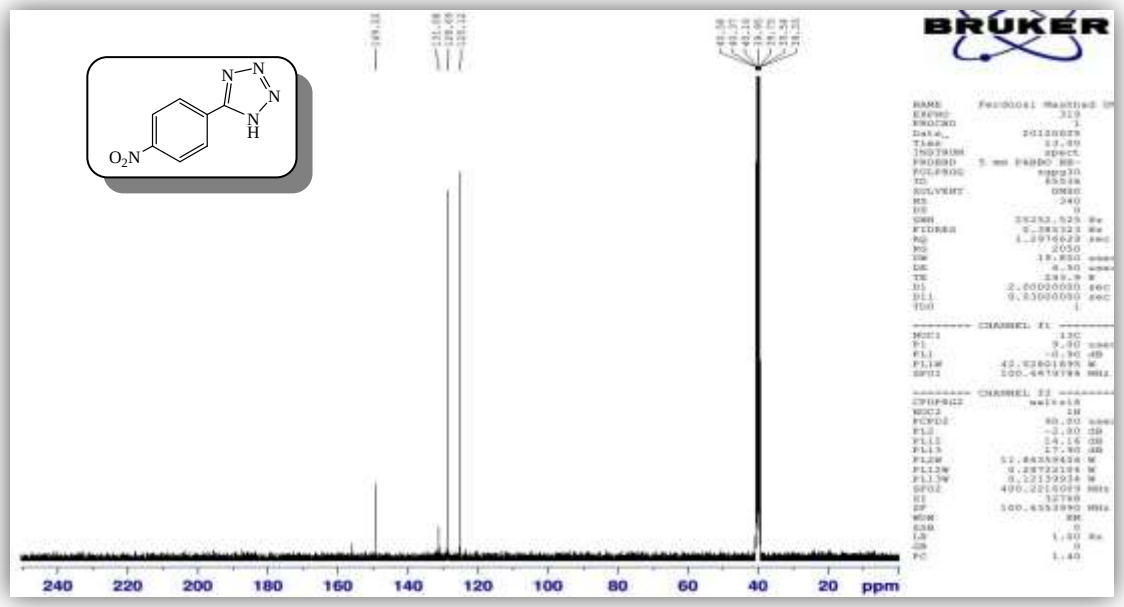

Figure 31: ^{13}C NMR (100 MHz, DMSO-d_6) of 5-(4-Nitrophenyl)-1*H*-tetrazole (Table 2, entry 5).

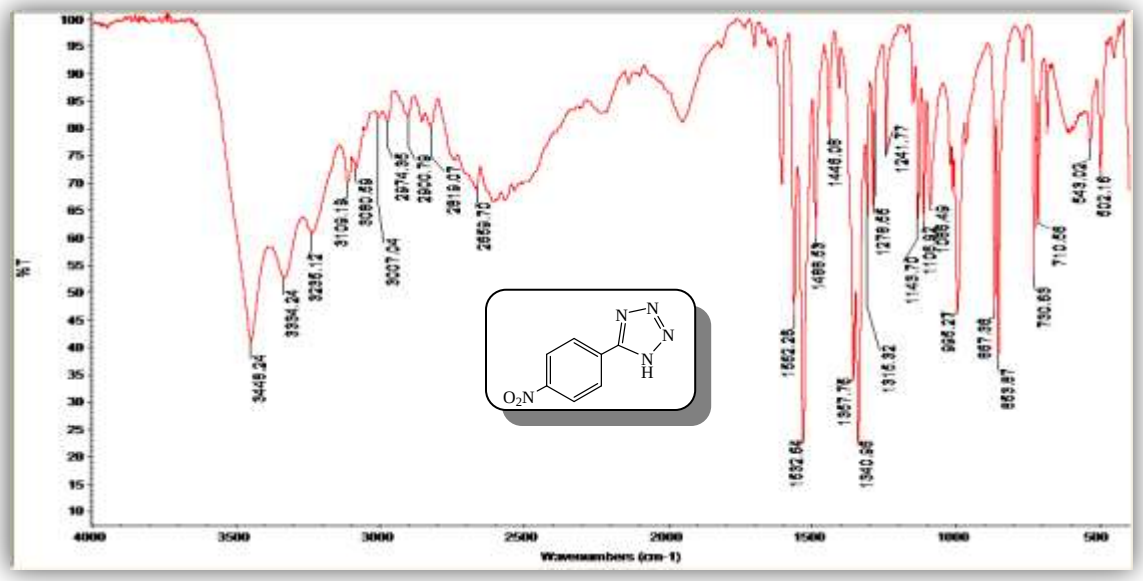

Figure 32: FT-IR (KBr) of 5-(4-Nitrophenyl)-1*H*-tetrazole (Table 2, entry 5).

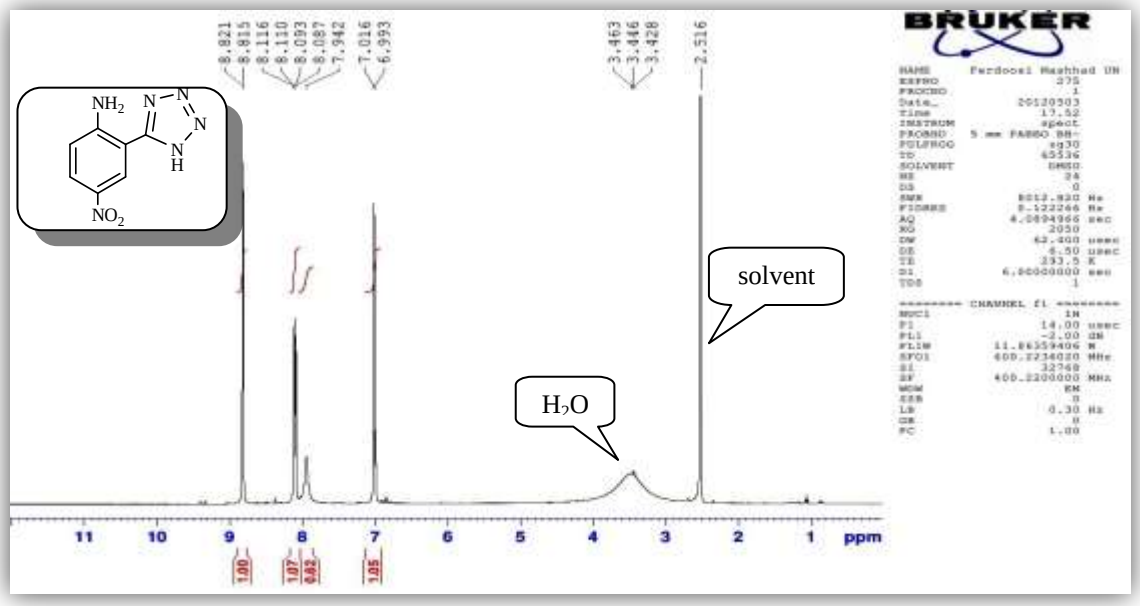

Figure 33: ^{1}H NMR (400 MHz, DMSO-d_6) of 4-Nitro-2-(1*H*-tetrazol-5-yl)benzenamine (Table 2, entry 6).

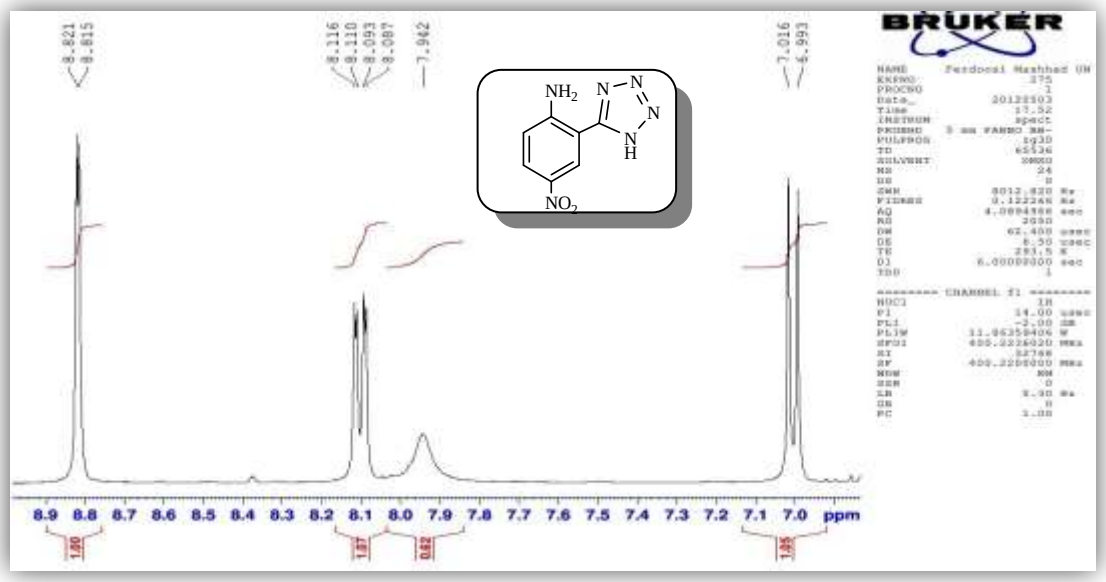

Figure 34: ^{1}H NMR (400 MHz, DMSO-d_6) of 4-Nitro-2-(1*H*-tetrazol-5-yl)benzenamine (Table 2, entry 6) expanded.

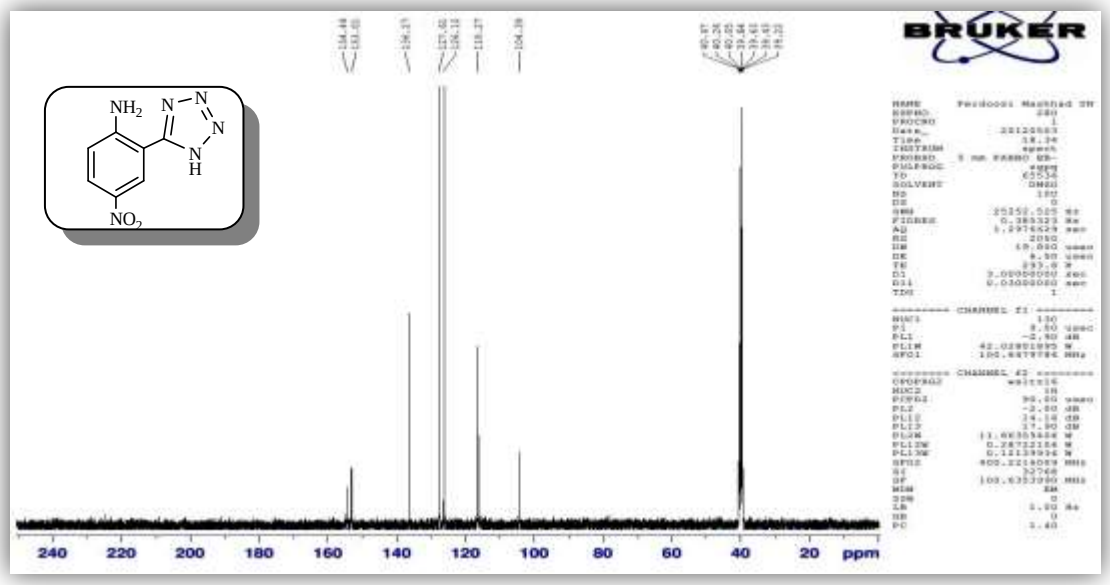

Figure 35: ^{13}C NMR (100 MHz, DMSO-d_6) of 4-Nitro-2-(1*H*-tetrazol-5-yl)benzenamine (Table 2, entry 6).

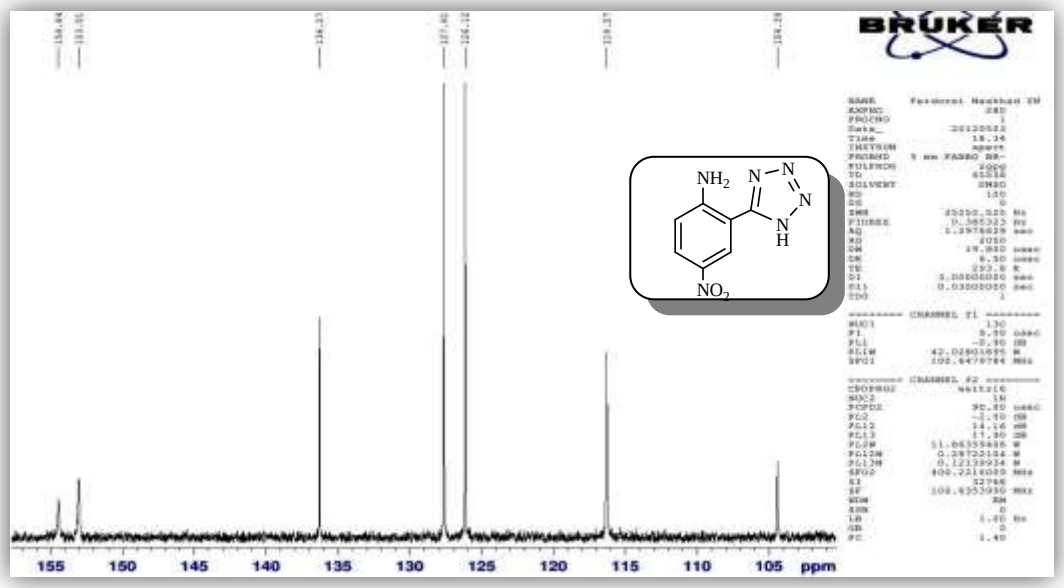

Figure 36: ^{13}C NMR (100 MHz, DMSO-d_6) of 4-Nitro-2-(1*H*-tetrazol-5-yl)benzenamine (Table 2, entry 6) expanded.

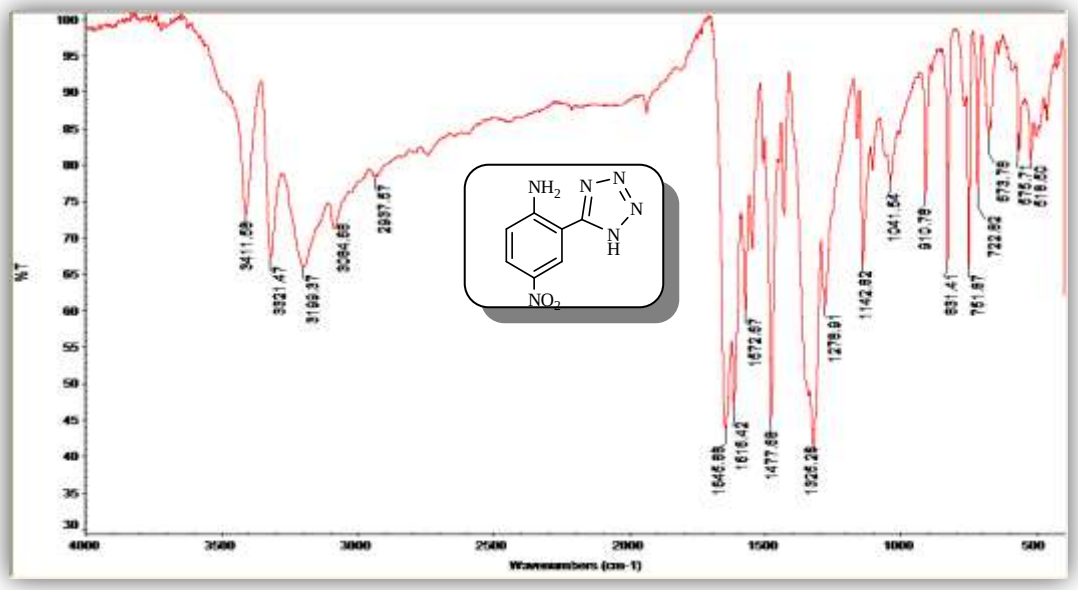

Figure 37: FT-IR (KBr) of 4-Nitro-2-(1*H*-tetrazol-5-yl)benzenamine (Table 2, entry 6).

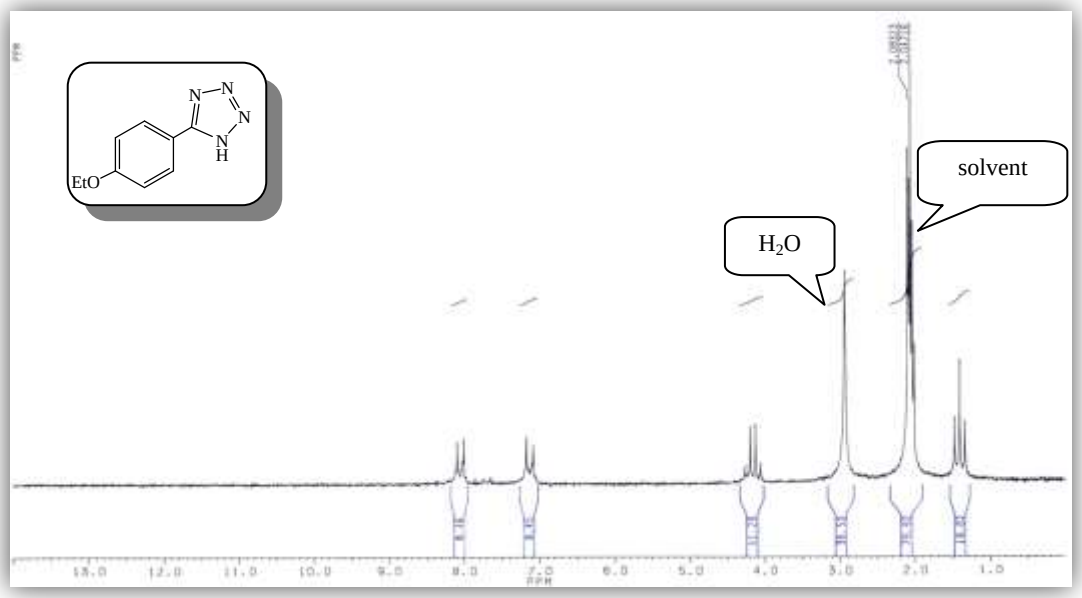

Figure 38: ^{1}H NMR (100 MHz, acetone-d_6) of 5-(4-Ethoxyphenyl)-1*H*-tetrazole (Table 2, entry 7).

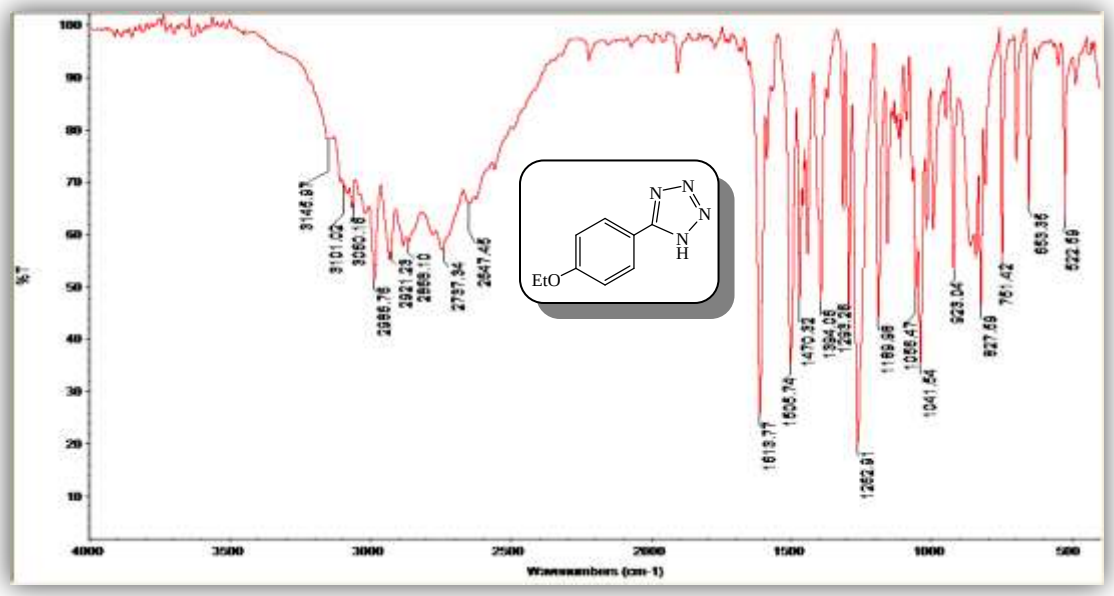

Figure 39: FT-IR (KBr) of 5-(4-Ethoxyphenyl)-1*H*-tetrazole (Table 2, entry 7).

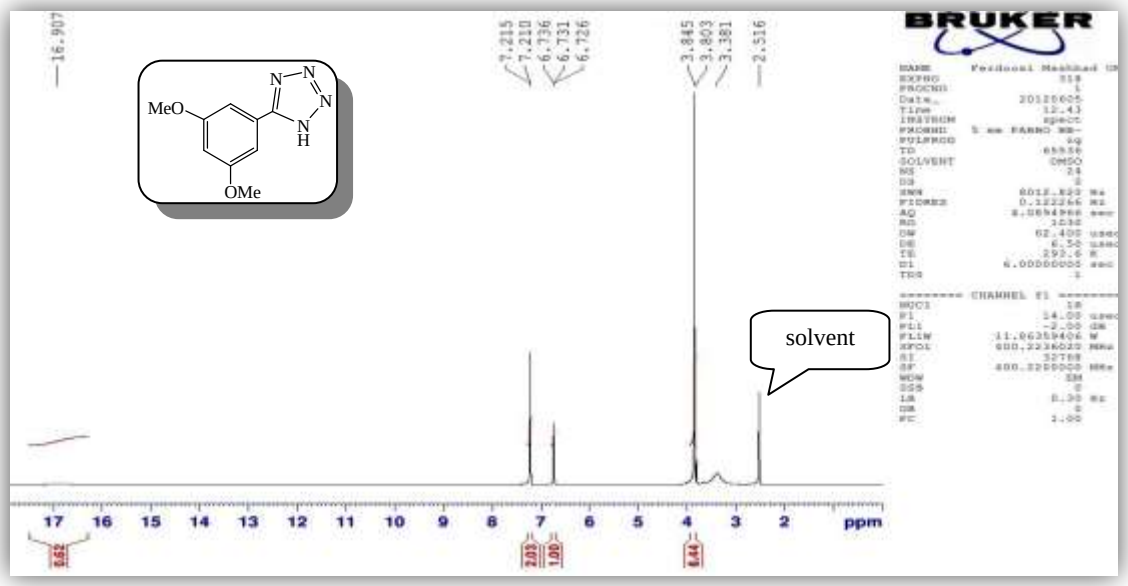

Figure 40: ^{1}H NMR (400 MHz, DMSO-d_6) of 5-(3, 5-Dimethoxyphenyl)-1*H*-tetrazole (Table 2, entry 8).

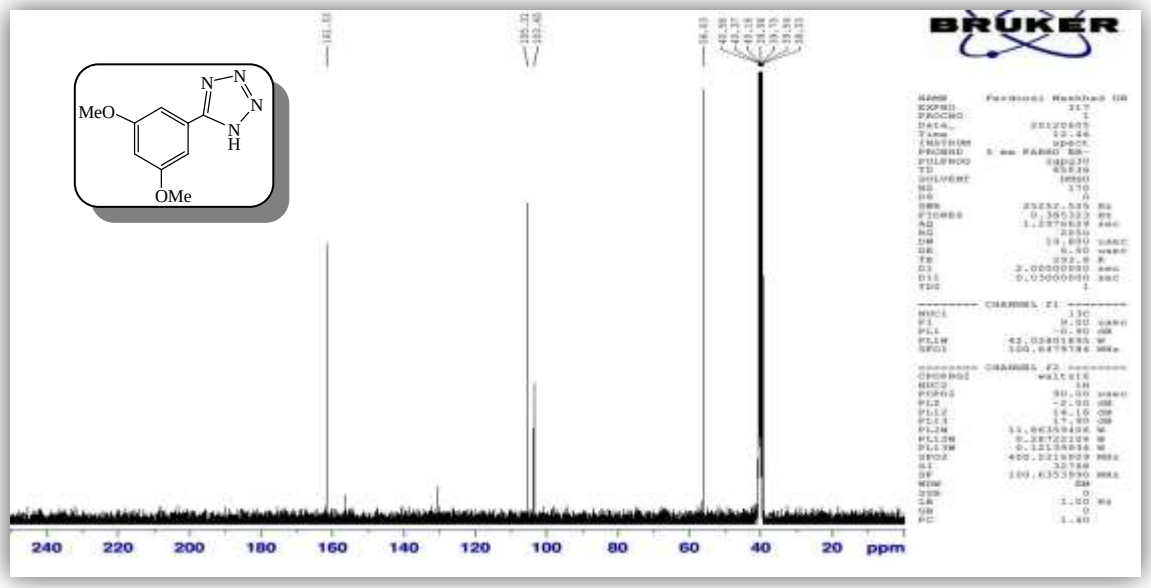

Figure 41: ^{13}C NMR (100 MHz, DMSO-d_6) of 5-(3,5-Dimethoxyphenyl)-1*H*-tetrazole (Table 2, entry 8).

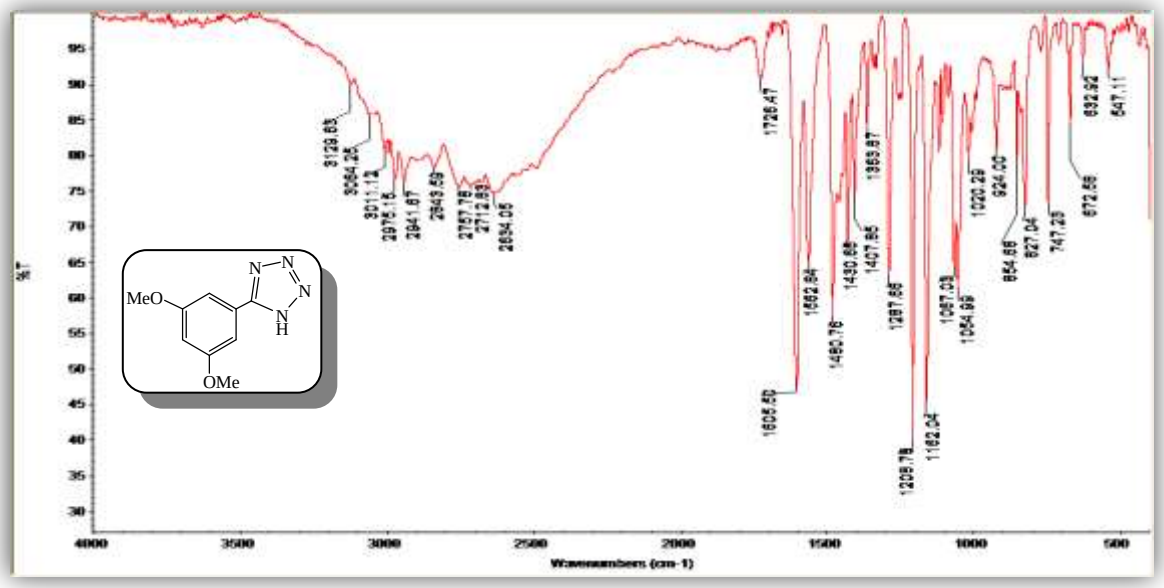

Figure 42: FT-IR (KBr) of 5-(3,5-Dimethoxyphenyl)-1*H*-tetrazole (Table 2, entry 8).

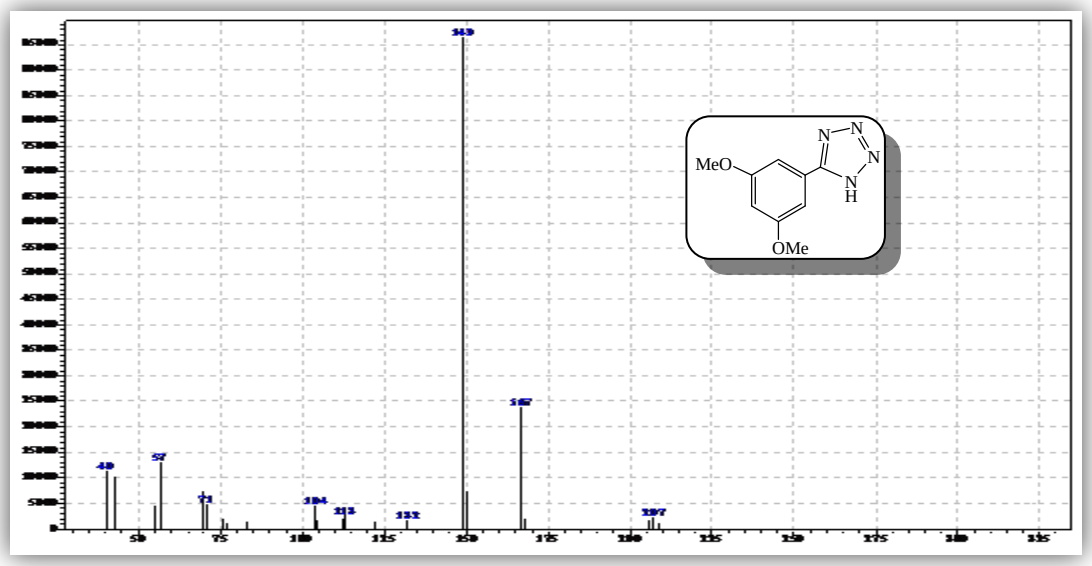

Figure 43: Mass spectrum of 5-(3, 5-Dimethoxyphenyl)-1*H*-tetrazole (Table 2, entry 8).

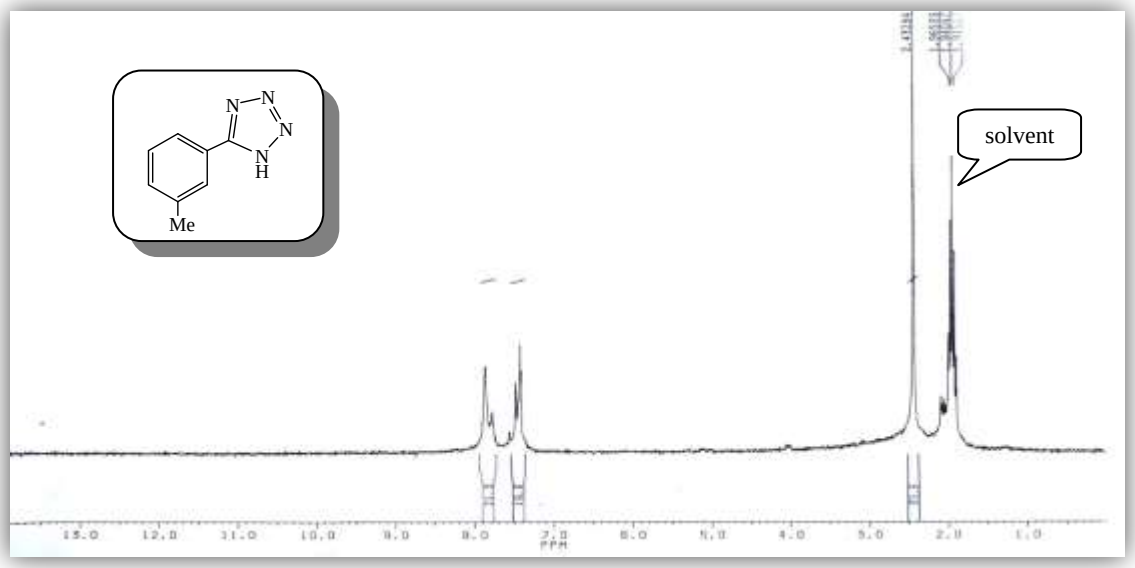

Figure 44: ^{1}H NMR (100 MHz, CD_3CN) of 5-*m*-Tolyl-1*H*-tetrazole (Table 2, entry 9).

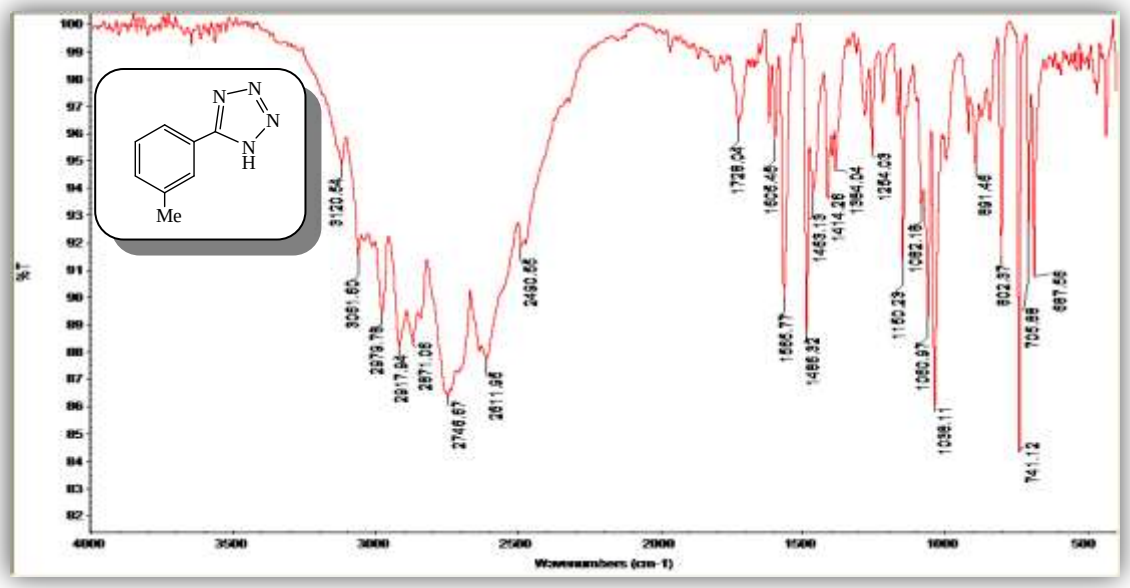

Figure 45: FT-IR (KBr) of 5-*m*-Tolyl-1*H*-tetrazole (Table 2, entry 9).

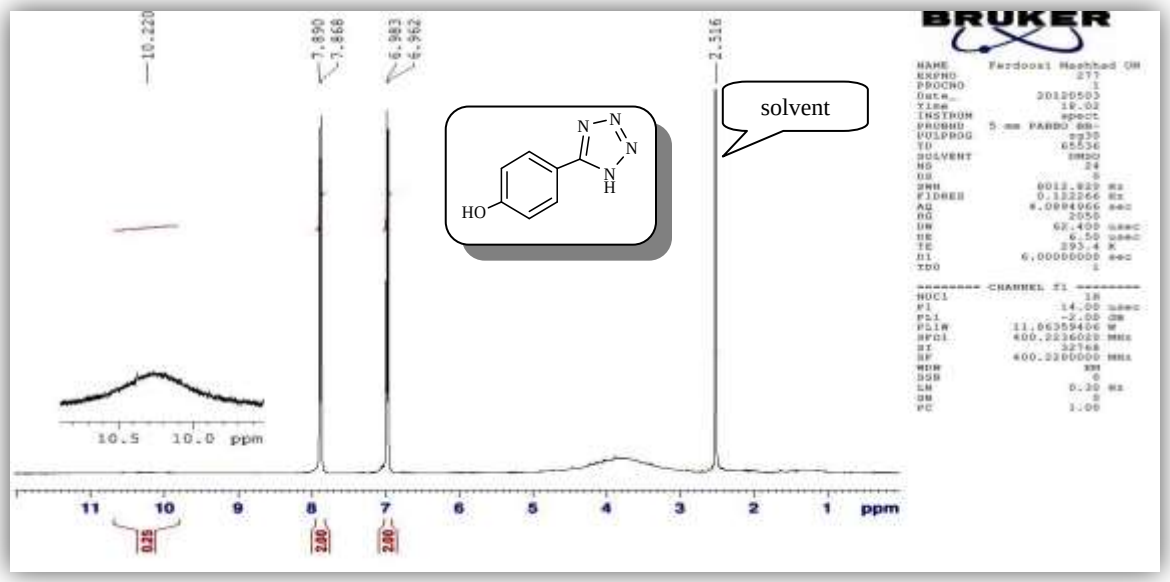

Figure 46: ^{1}H NMR (400 MHz, DMSO-d_6) of 4-(1*H*-tetrazol-5-yl) phenol (Table 2, entry 10).

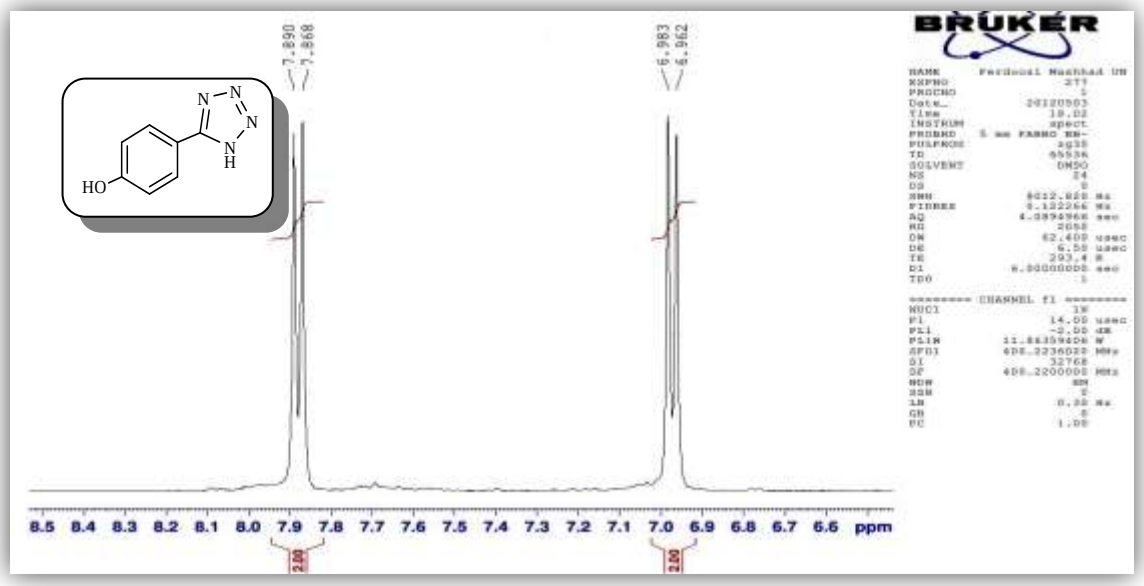

Figure 47: ^{1}H NMR (400 MHz, DMSO-d_6) of 4-(1*H*-tetrazol-5-yl)phenol (Table 2, entry 10) expanded.

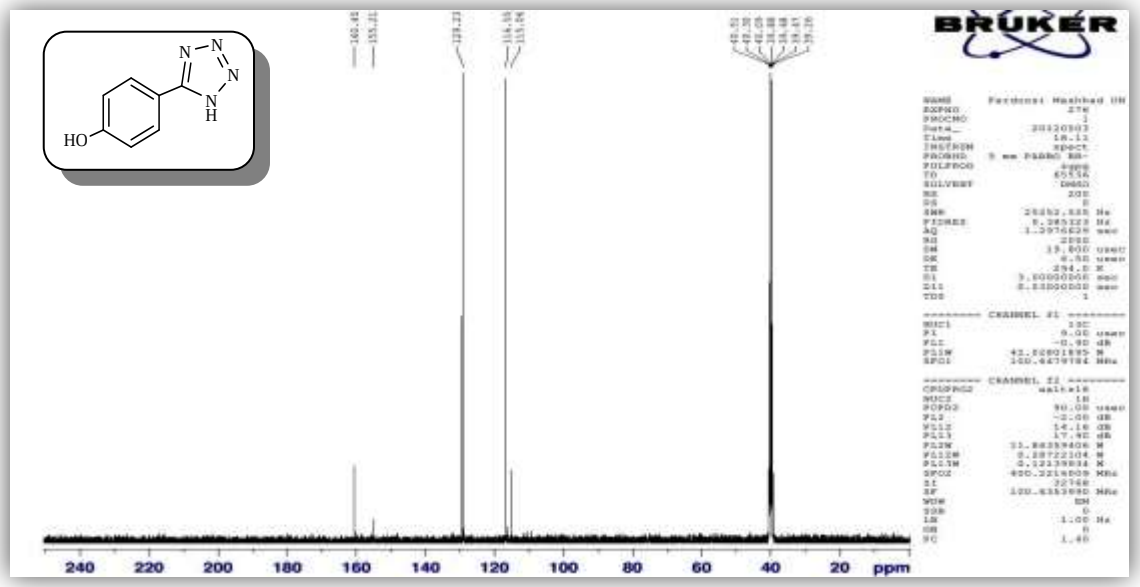

Figure 48: ^{13}C NMR (100 MHz, DMSO-d_6) of 4-(1*H*-tetrazol-5-yl) phenol (Table 2, entry 10).

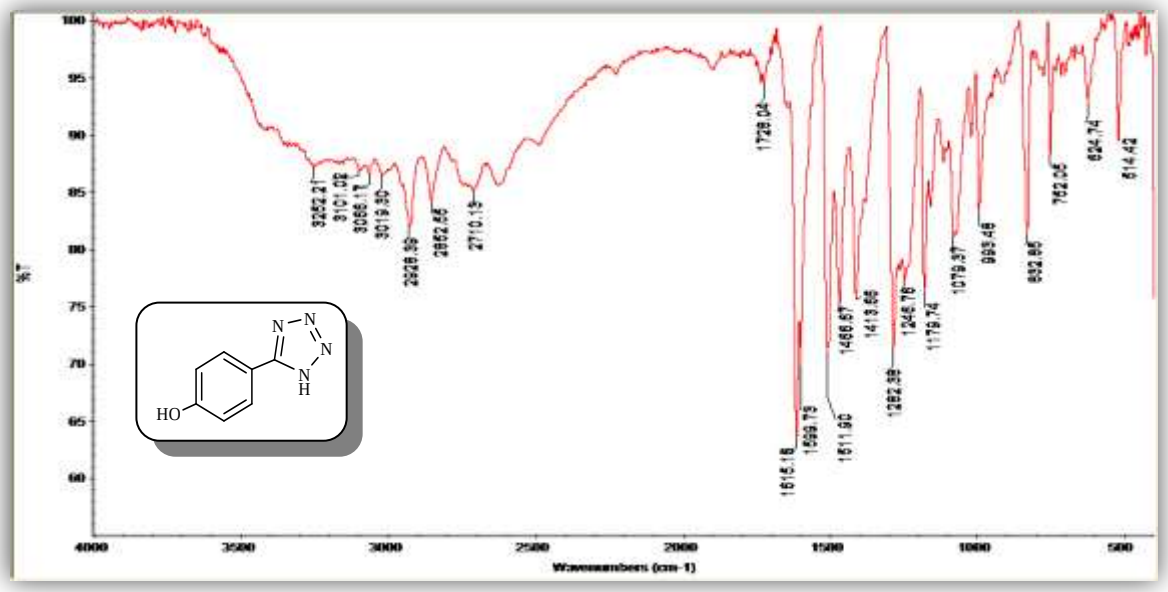

Figure 49: FT-IR (KBr) of 4-(1*H*-tetrazol-5-yl) phenol (Table 2, entry 10).

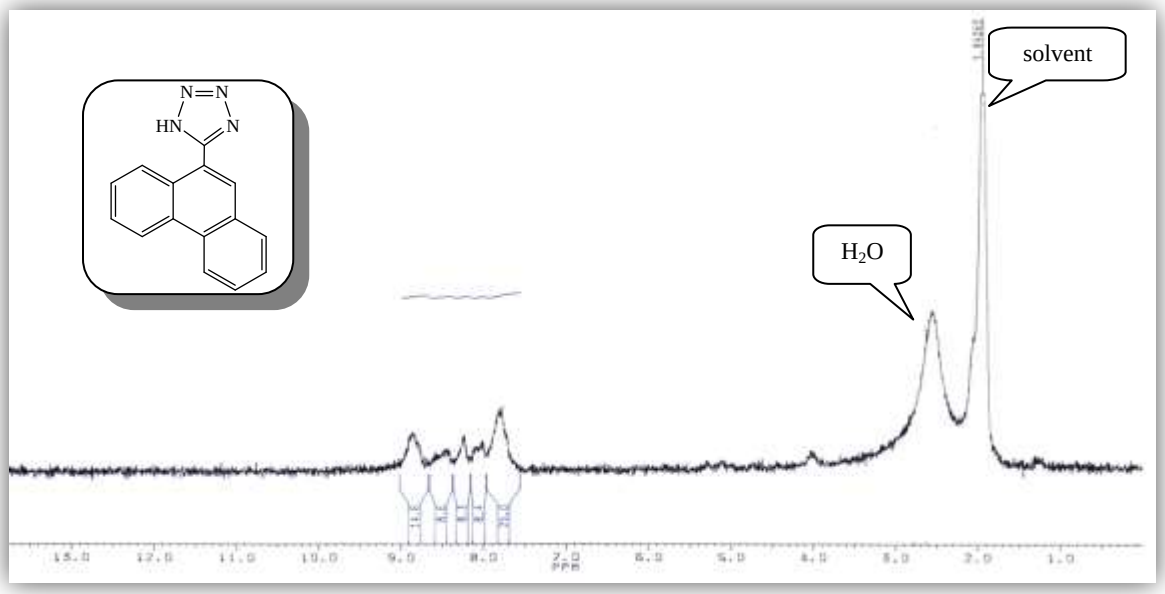

Figure 50: ^{1}H NMR (100 MHz, DMSO-d_6) of 5-(Phenanthren-9-yl)-1*H*-tetrazole (Table 2, entry 11).

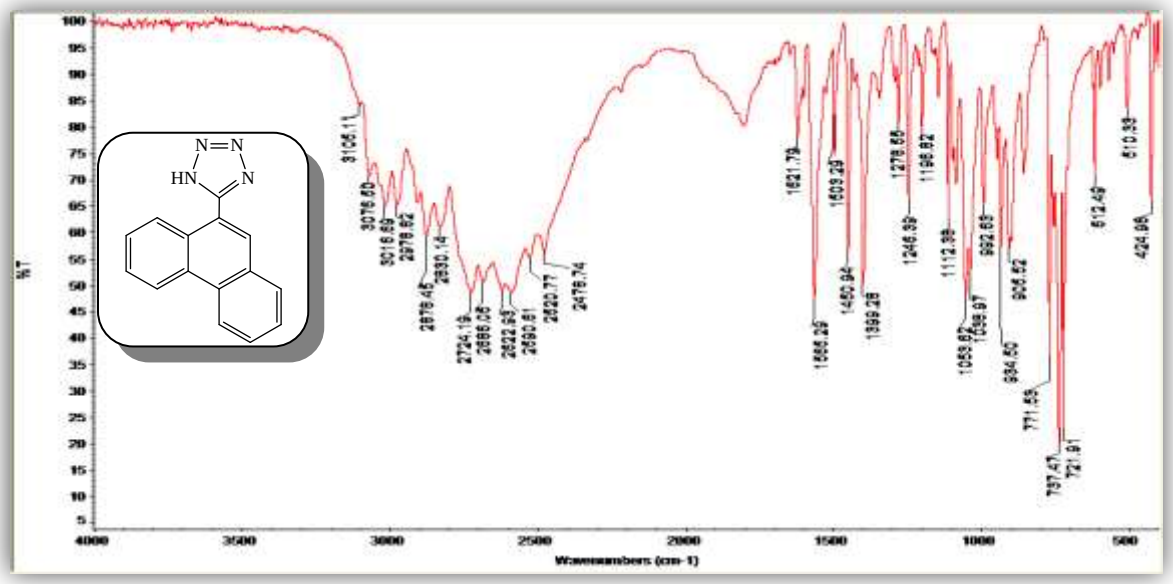

Figure 51: FT-IR (KBr) of 5-(Phenanthren-9-yl)-1*H*-tetrazole (Table 2, entry 11).

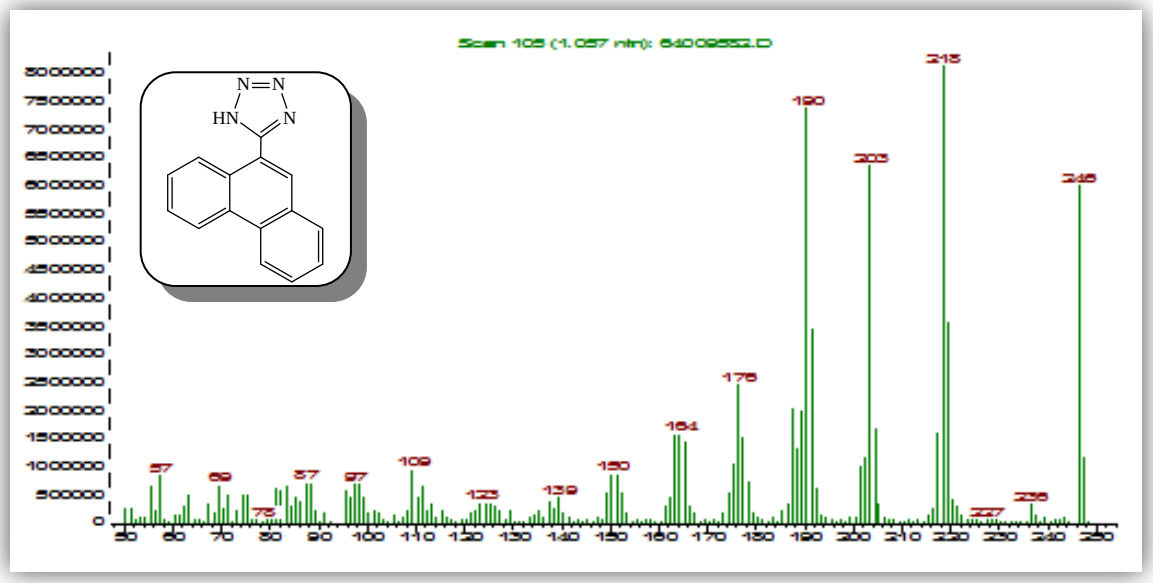

Figure 52: Mass spectrum of 5-(Phenanthren-9-yl)-1*H*-tetrazole (Table 2, entry 11).

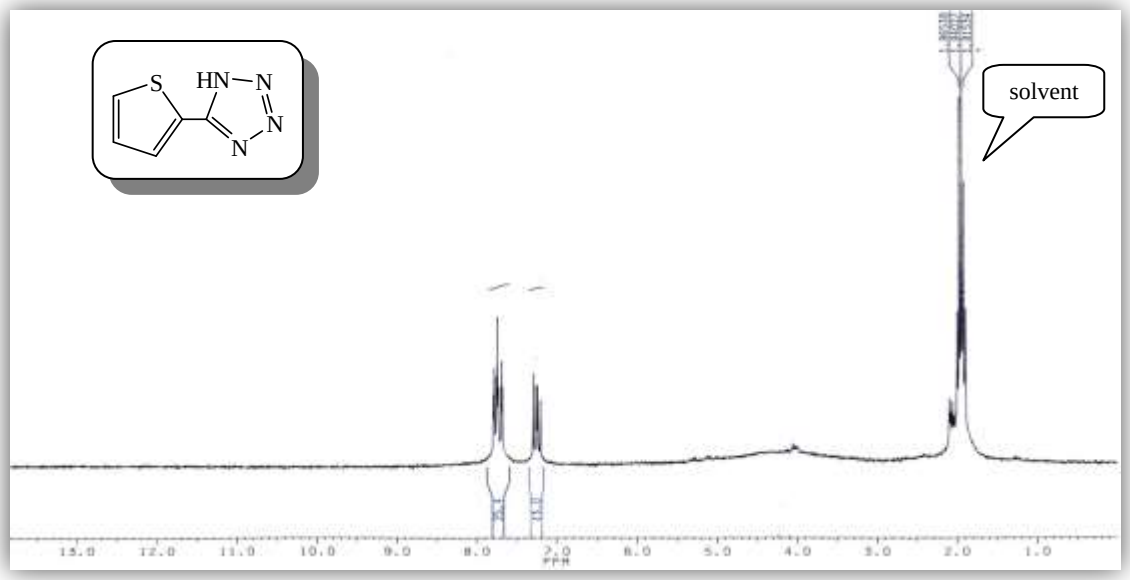

Figure 53: ^{1}H NMR (100 MHz, CD_3CN) of 5-(Thiophen-2-yl)-1*H*-tetrazole (Table 2, entry 12).

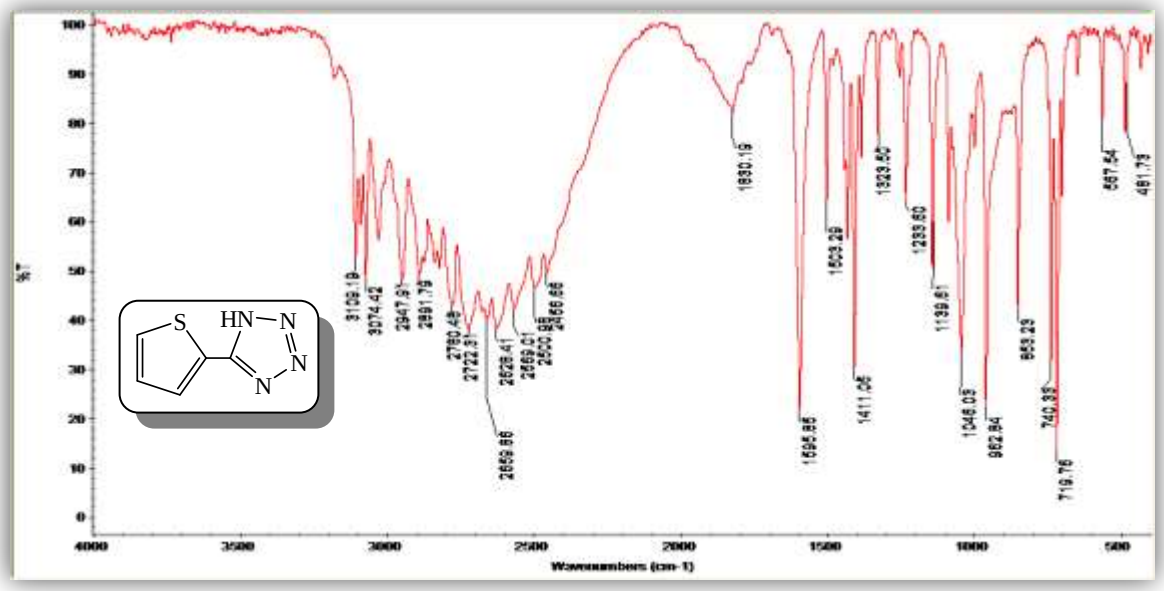

Figure 54: FT-IR (KBr) of 5-(Thiophen-2-yl)-1*H*-tetrazole (Table 2, entry 12).

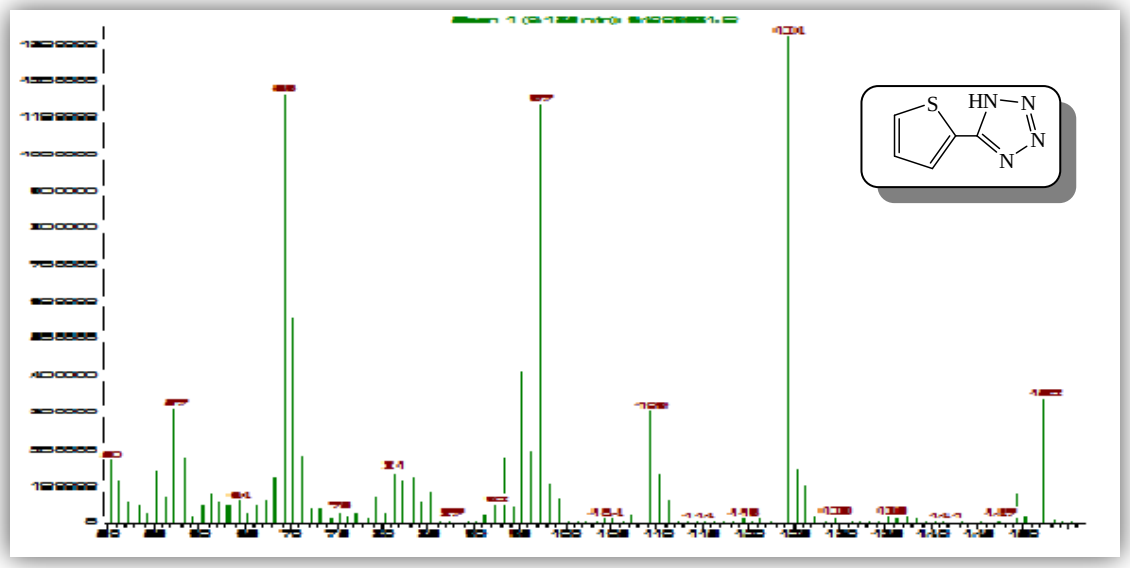

Figure 55: Mass spectrum of 5-(Thiophen-2-yl)-1*H*-tetrazole (Table 2, entry 12).

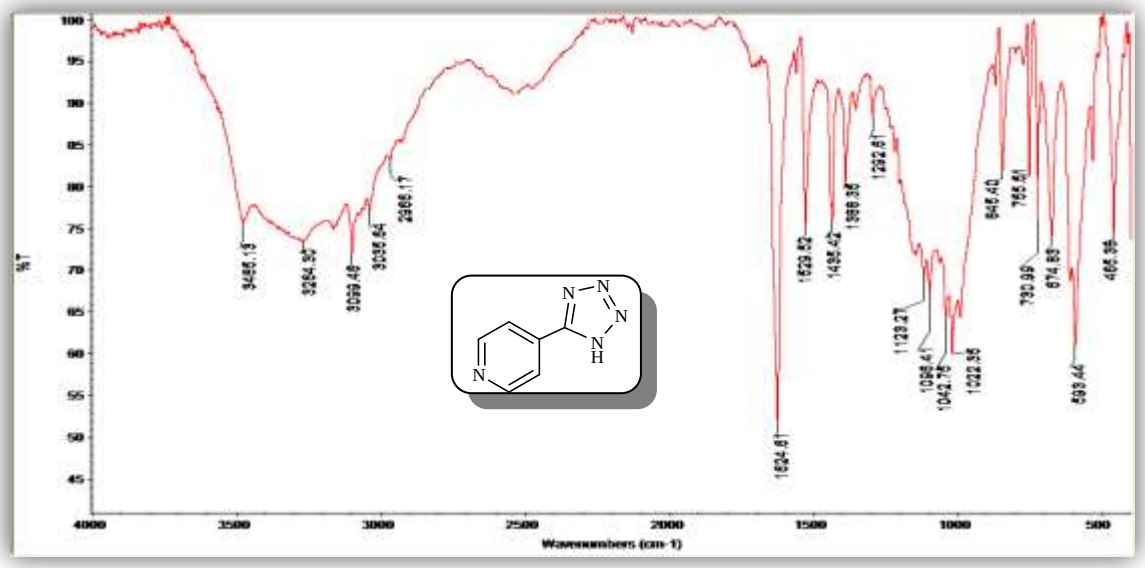

Figure 56: FT-IR (KBr) of 4-(1*H*-tetrazol-5-yl) pyridine (Table 2, entry 13).

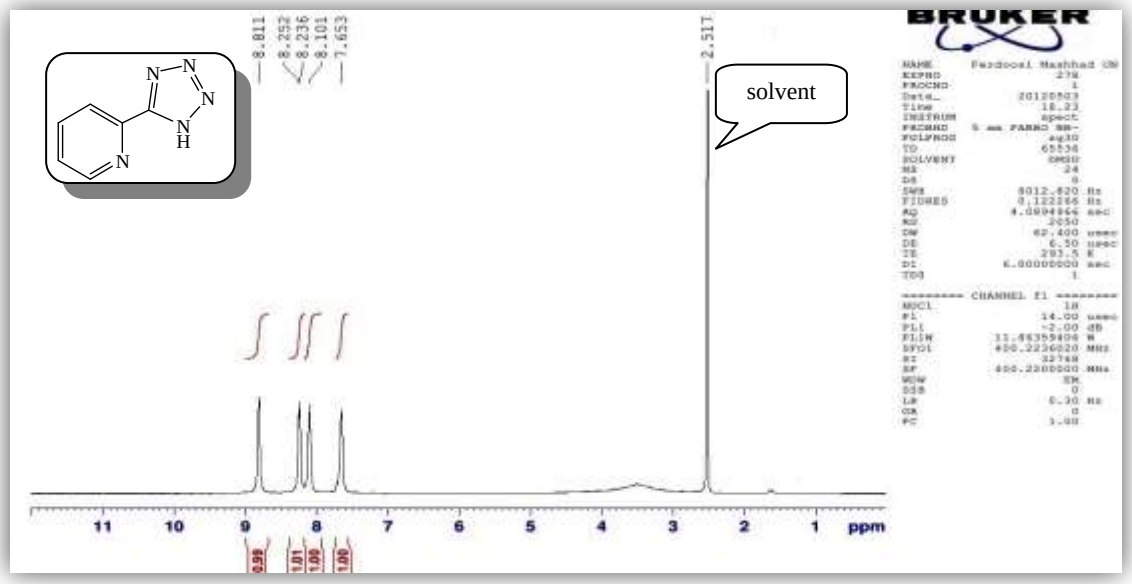

Figure 57: ^{1}H NMR (400 MHz, DMSO-d_6) of 2-(1*H*-tetrazol-5-yl)pyridine (Table 2, entry 14).

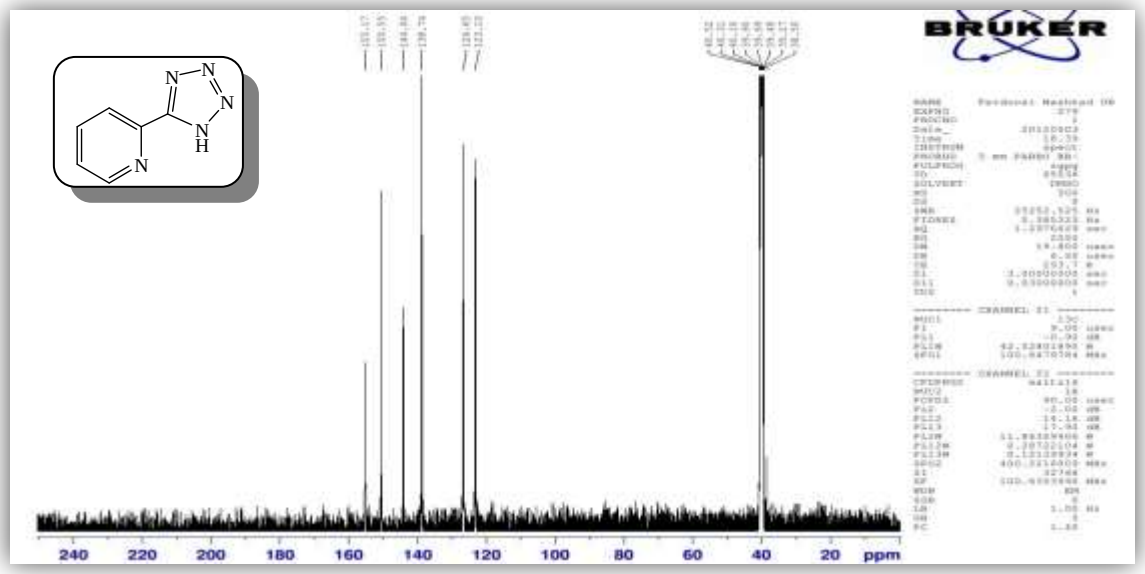

Figure 58: ^{13}C NMR (100 MHz, DMSO-d_6) of 2-(1*H*-tetrazol-5-yl) pyridine (Table 2, entry 14).

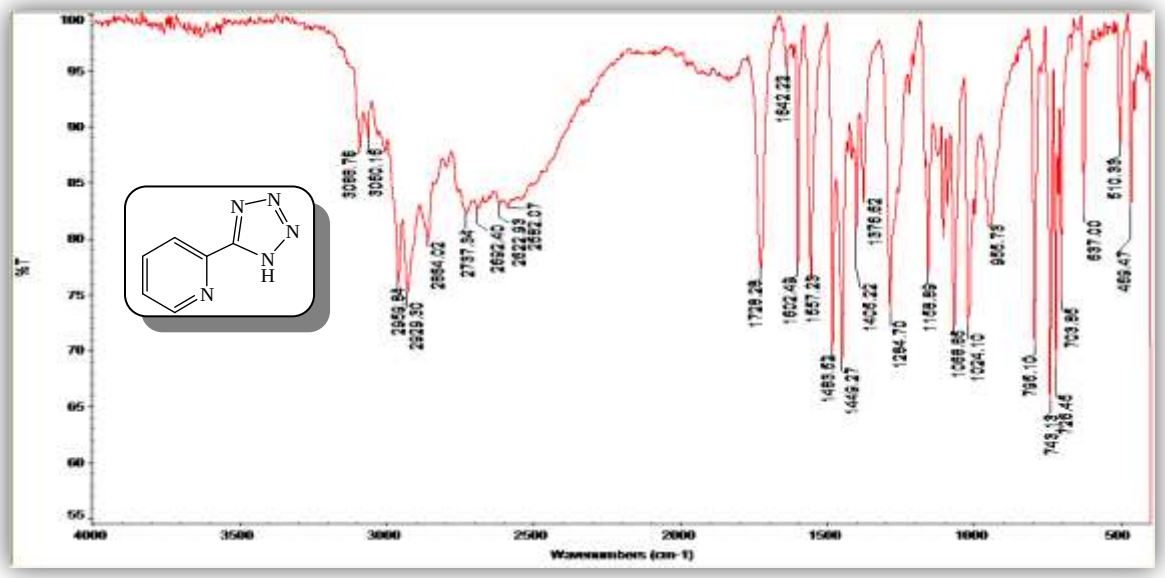

Figure 59: FT-IR of 2-(1*H*-tetrazol-5-yl) pyridine (Table 2, entry 14).

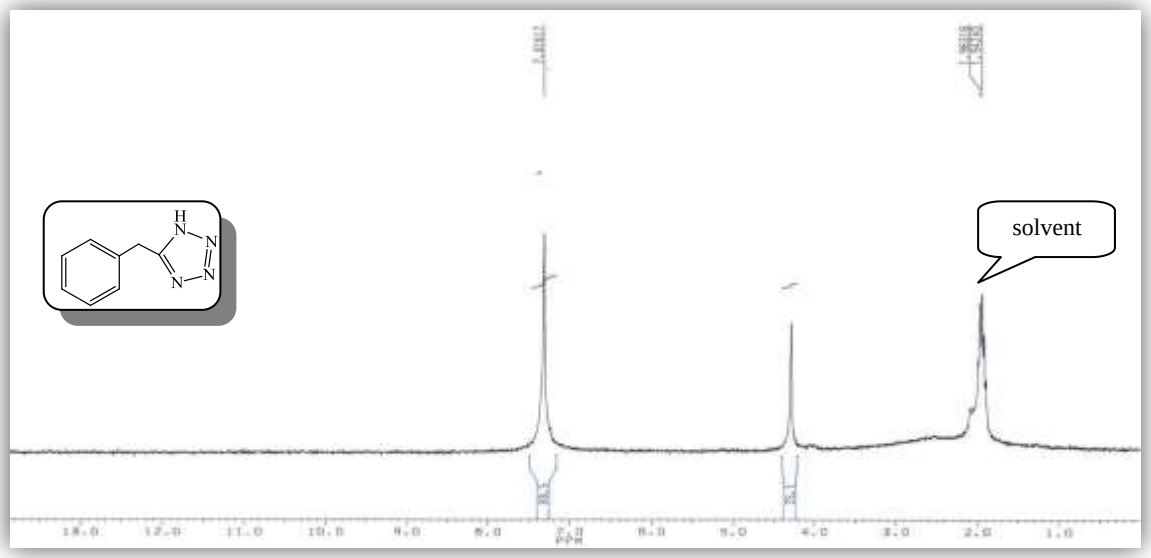

Figure 60: ^{1}H NMR (100 MHz, CD_3CN) of 5-Benzyl-1*H*-tetrazole (Table 2, entry 15).

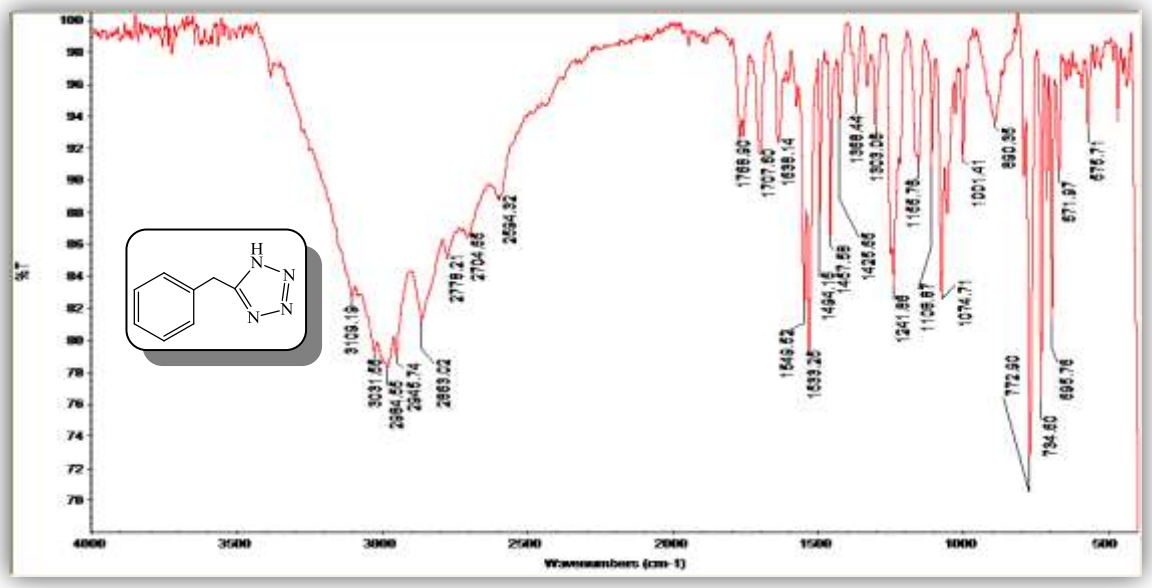

Figure 61: FT-IR of 5-Benzyl-1*H*-tetrazole (Table 2, entry 15).

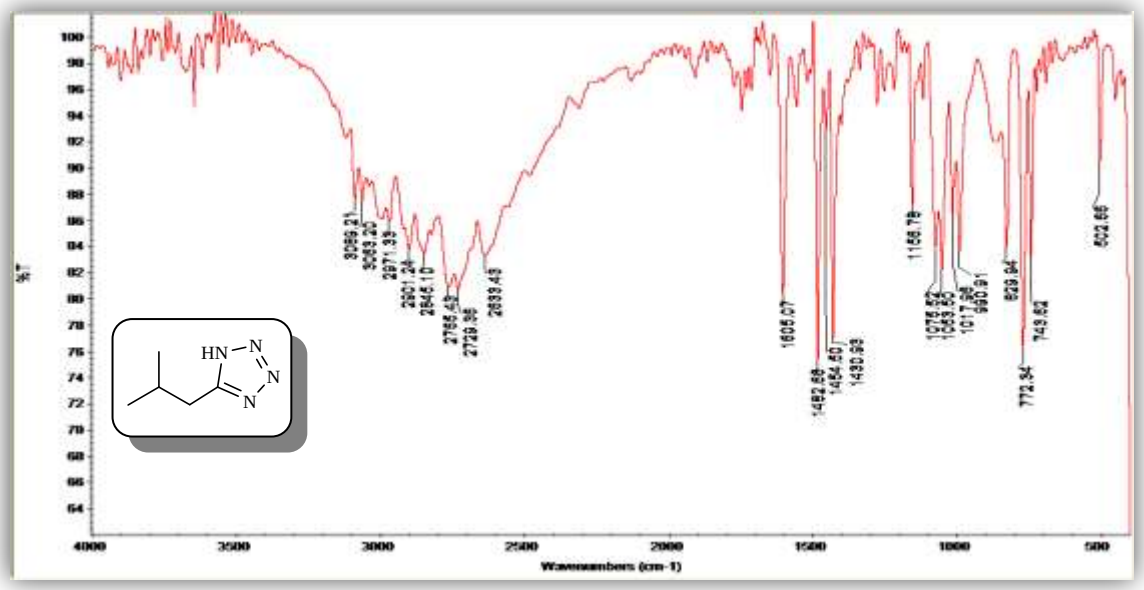

Figure 62: FT-IR of 5-Isobutyl-1*H*-tetrazole (Table 2, entry 16).

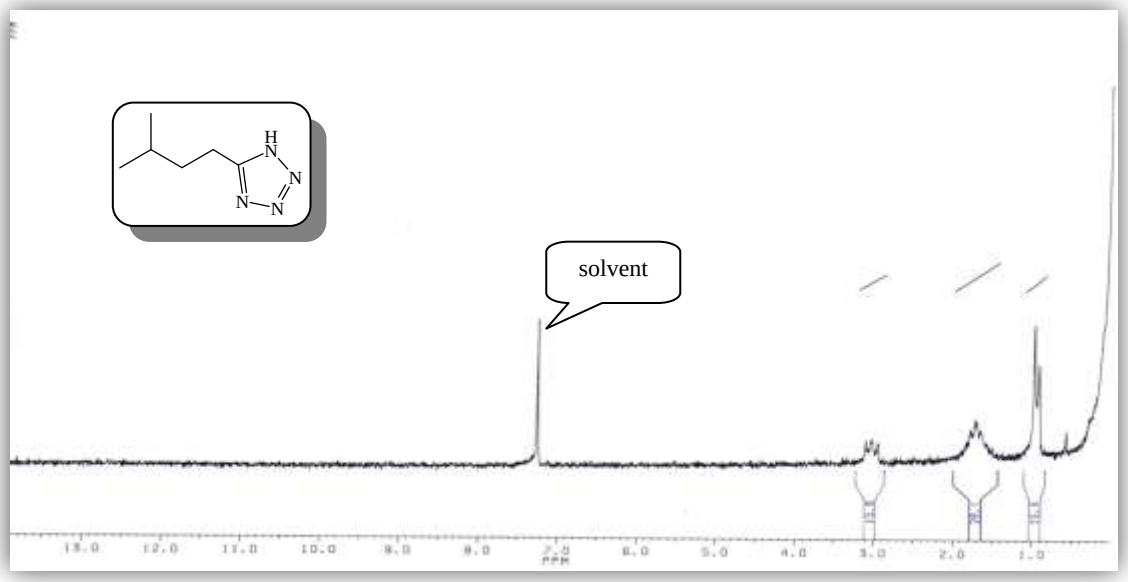

Figure 63: ^{1}H NMR (100 MHz, $CDCl_3$) of 5-Isopentyl-1*H*-tetrazole (Table 2, entry 17).

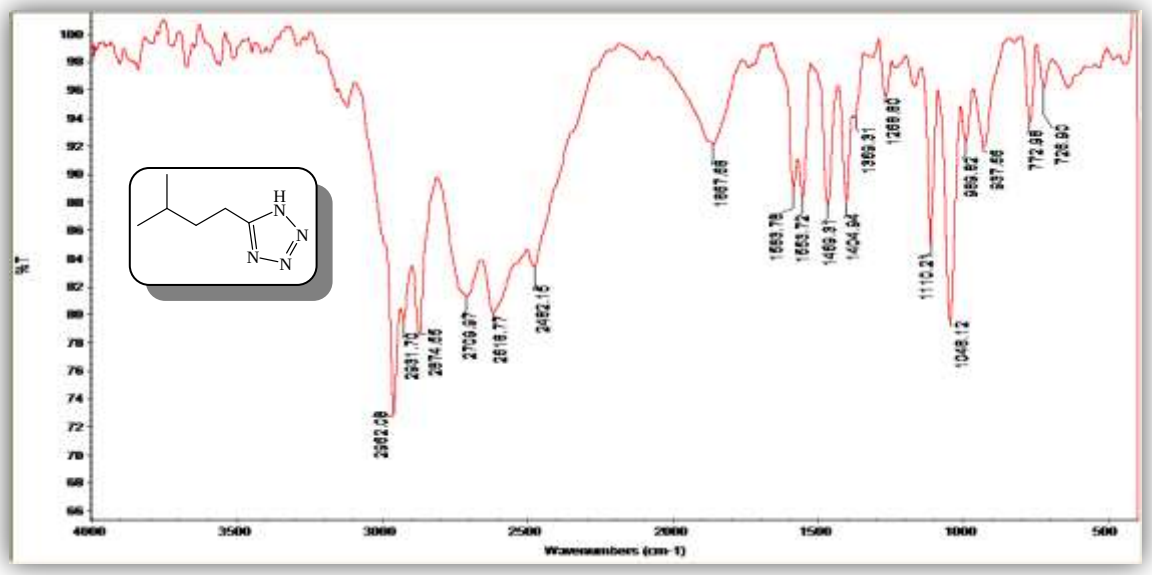

Figure 64: FT-IR of 5-Isopentyl-1*H*-tetrazole (Table 2, entry 17).