Development of Novel Guanidine Iron (III) Complexes as a Powerful Catalyst for the Synthesis of Tetrazolo[1,5-*a*]pyrimidine by Green Protocol

Mahmoud Abd El Aleem Ali Ali El-Remaily[1,*], O. Elhady[1], Thomas Nady A. Eskander[1], Shaaban K Mohamed[3,4], Ahmed M. Abu- Dief[1,2]

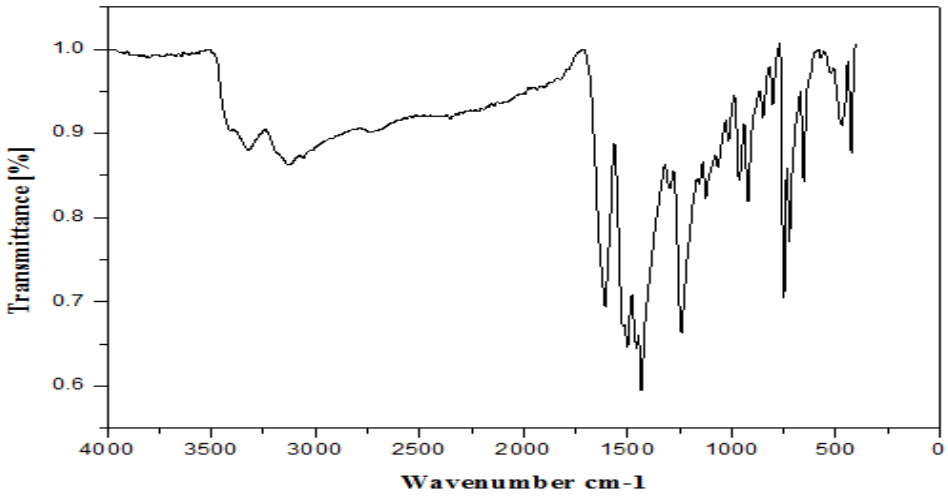
[1] *Department of Chemistry, Faculty of Science, Sohag University, Sohag 82524 Egypt*
[2] *Chemistry Department, College of Science, Taibah University, P.O. Box 344, Madinah, Saudi Arabia*
[3] *Chemistry and Environmental Division, Manchester Metropolitan University, Manchester, United Kingdom*
[4] *Chemistry Department, Faculty of Science, Minia University, El-Minia, Egypt*
**E-mail:* mahmoud_ali@science.sohag.edu.eg

2.1 | Reagents, Instrumentation and methods

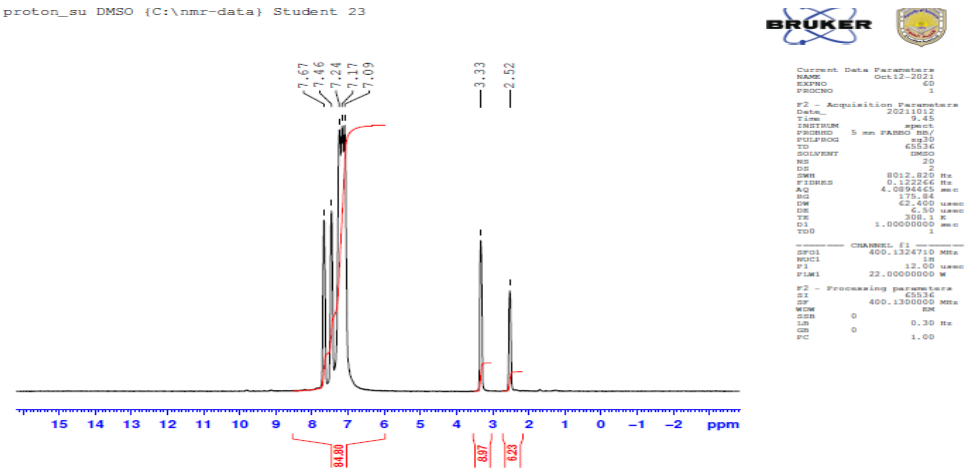
Chemicals such as (starting material "Orthoamino thiophenol, cyanoguanidine, ethyl bromoacetate, acetyl acetone, $Fe(NO_3)_3.9H_2O$, aromatic aldehyde, 5-aminotetrazole and malononitrile" solvents "glacial acetic acid,ethanol, DMF, pipredine and reagents) were used acquired from Fluka, and Sigma-Aldrich, All melting points are uncorrected and were recorded on Melt-Temp II melting point apparatus. IR spectra were measured as KBr pellets on a Shimadzu DR-8001 spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini at 400 MHz using TMS as an internal reference and DMSO-d6 as a solvent. The Mass spectroscopy system was used to confirm the purity of the compounds as well as explore the characteristic fragmentation and the expected molecular weight. The elemental analysis was carried out on a Perkin-Elmer 240C Microanalyzer. All compounds were checked for their purity on TLC plates. pH meter (model LI-127) equipped with a CL-51B combined electrode was used for pH measurements and calibrated against standard buffers (pH 4.02 and 9.18) before measurements. Thermogravimetric analysis (TGA) was conducted using a Shimadzu 60H analyser under air at a heating rate of 10°C min^{-1} from ambient temperature to 750°C at the Department of Chemistry, Faculty of Science, Thermal Analysis Unit, Cairo University, Egypt.

2.2 | Synthesis of ligands

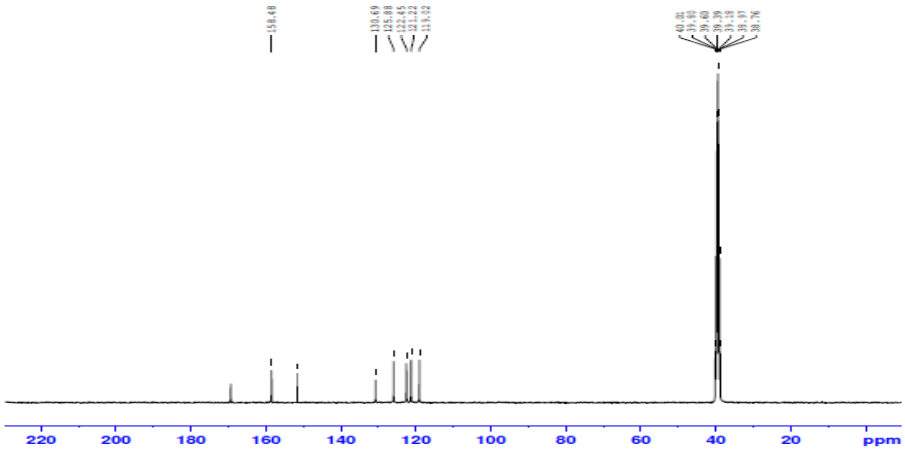
[1] IR, ^{1}H NMR and ^{13}C NMR of L_1 ligand Spectrum



(Fig.1S) IR (cm^{-1}) of L_1

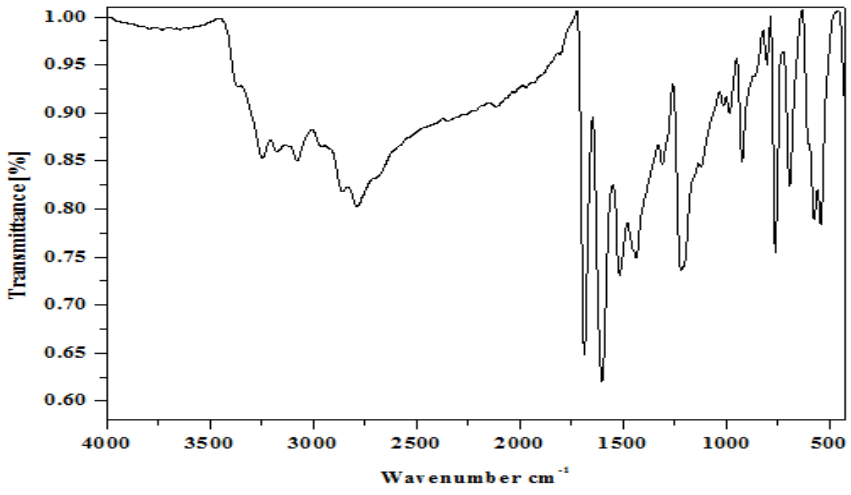


(Fig.2S) ^{1}H NMR of L_1 ligand

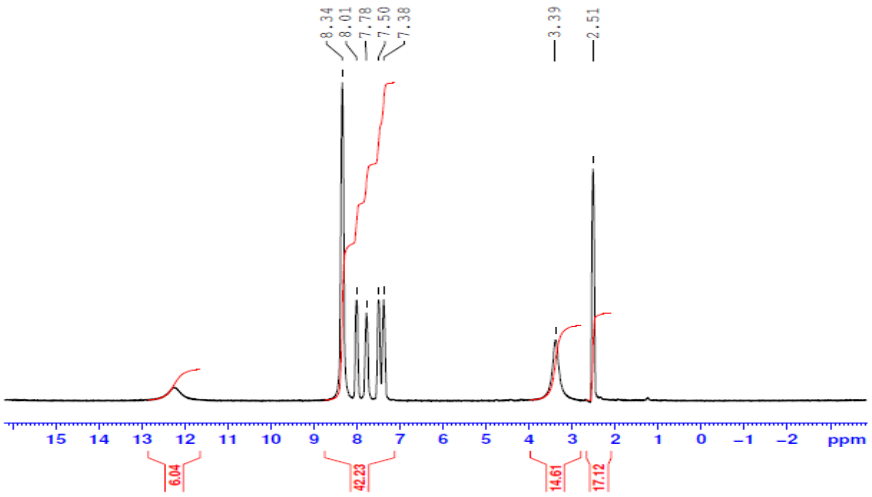


(Fig.3S) ^{13}C-NMR of L_1 ligand

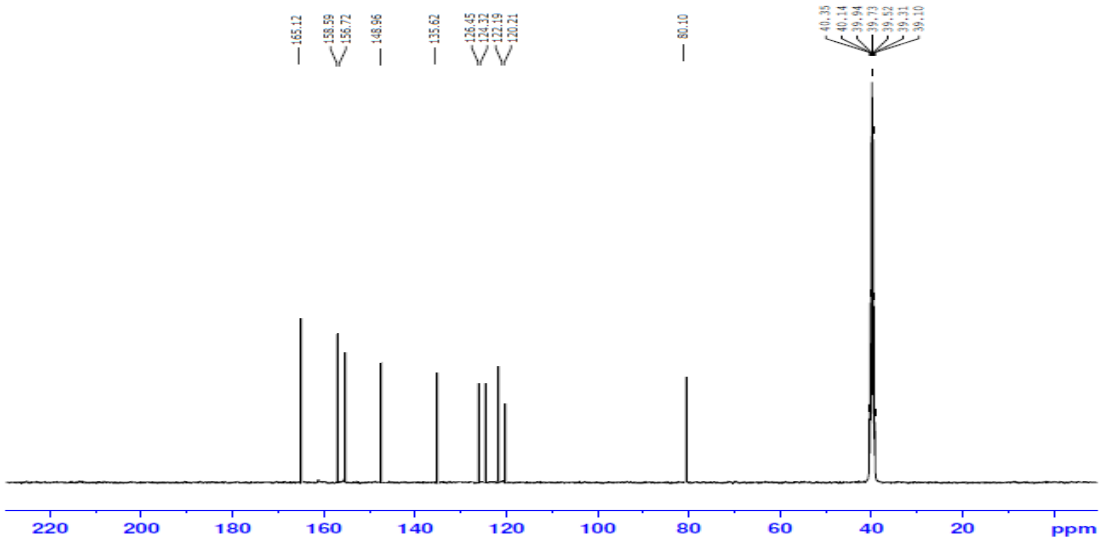
[2] IR, ^{1}H NMR and ^{13}C NMR of L_2 ligand Spectrum



(Fig.4S) IR (cm^{-1}) of L_2

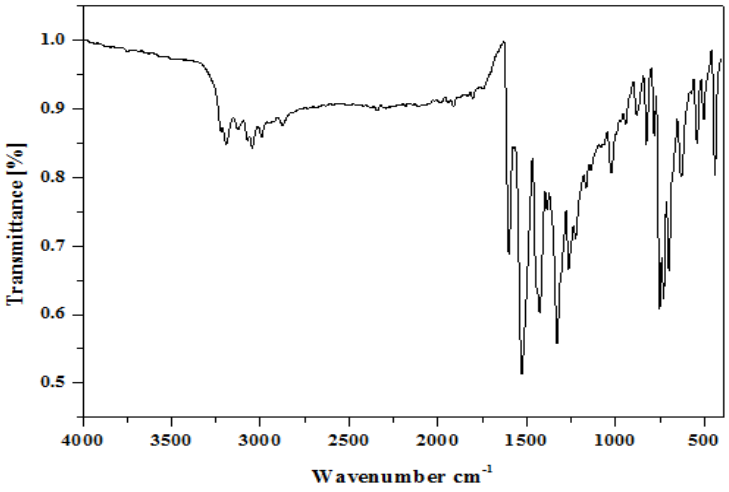


(Fig.5S) ^{1}H-NMR of L_2 ligand

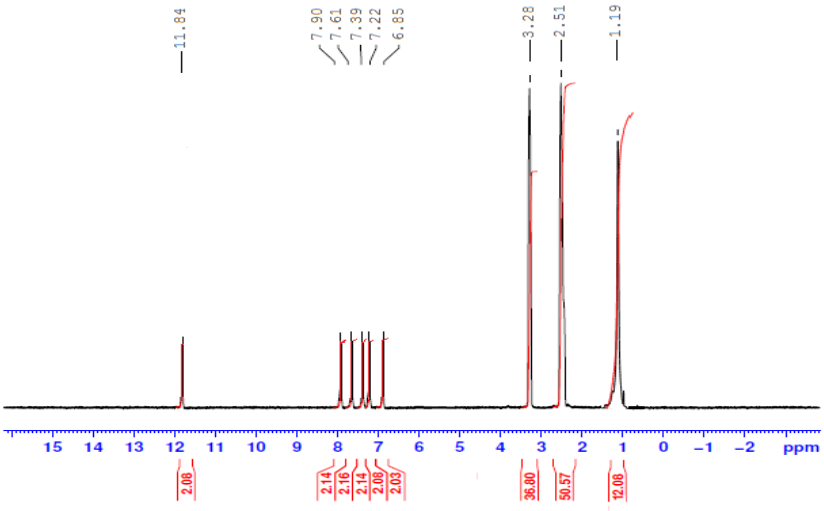


(Fig.6S) ^{13}C-NMR of L_2 ligand

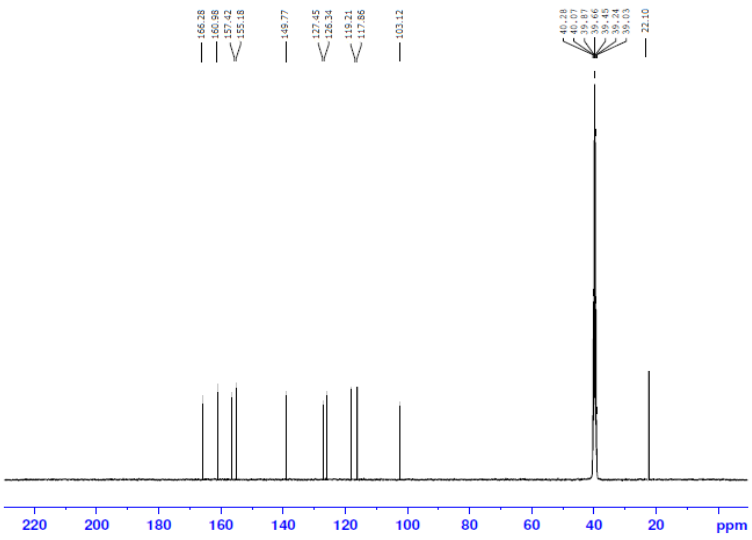
[3] IR, ^{1}H NMR and ^{13}C NMR of L_3 ligand Spectrum



(Fig.7S) IR (cm^{-1}) of L_3

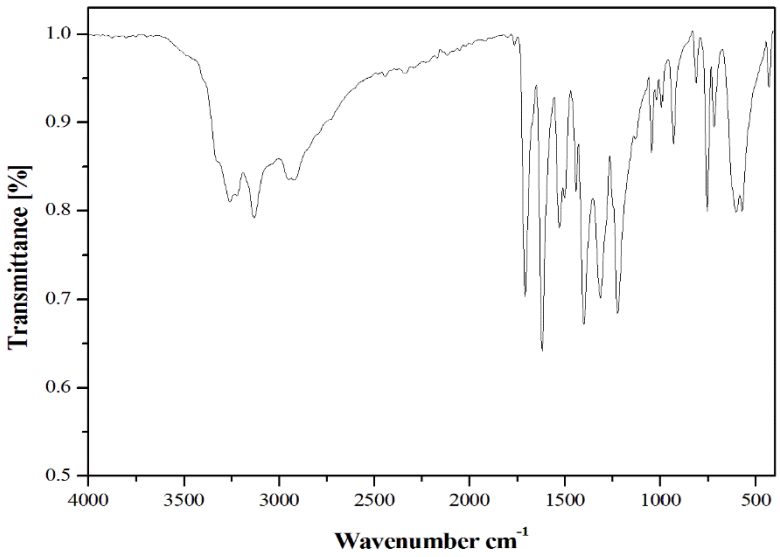


(Fig.8S) ^{1}H NMR of L_3 ligand

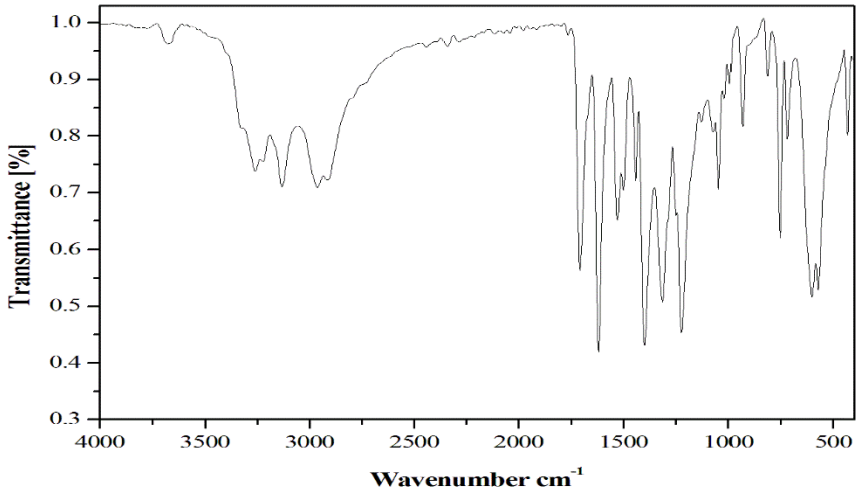


(Fig.9S) ^{13}C NMR of L_3 ligand

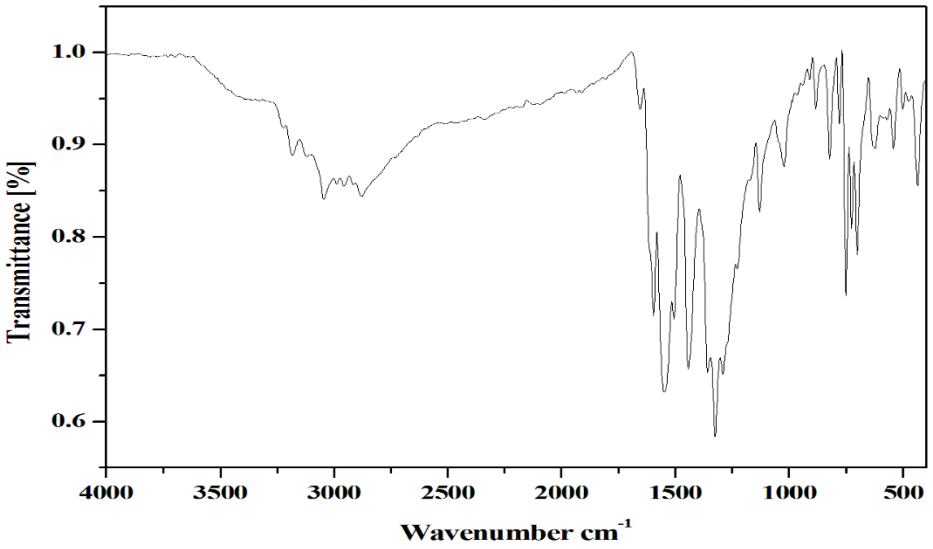
3.2 | IR of FeL_1, FeL_2 and FeL_3



(Fig.10S) IR spectrum of FeL_1

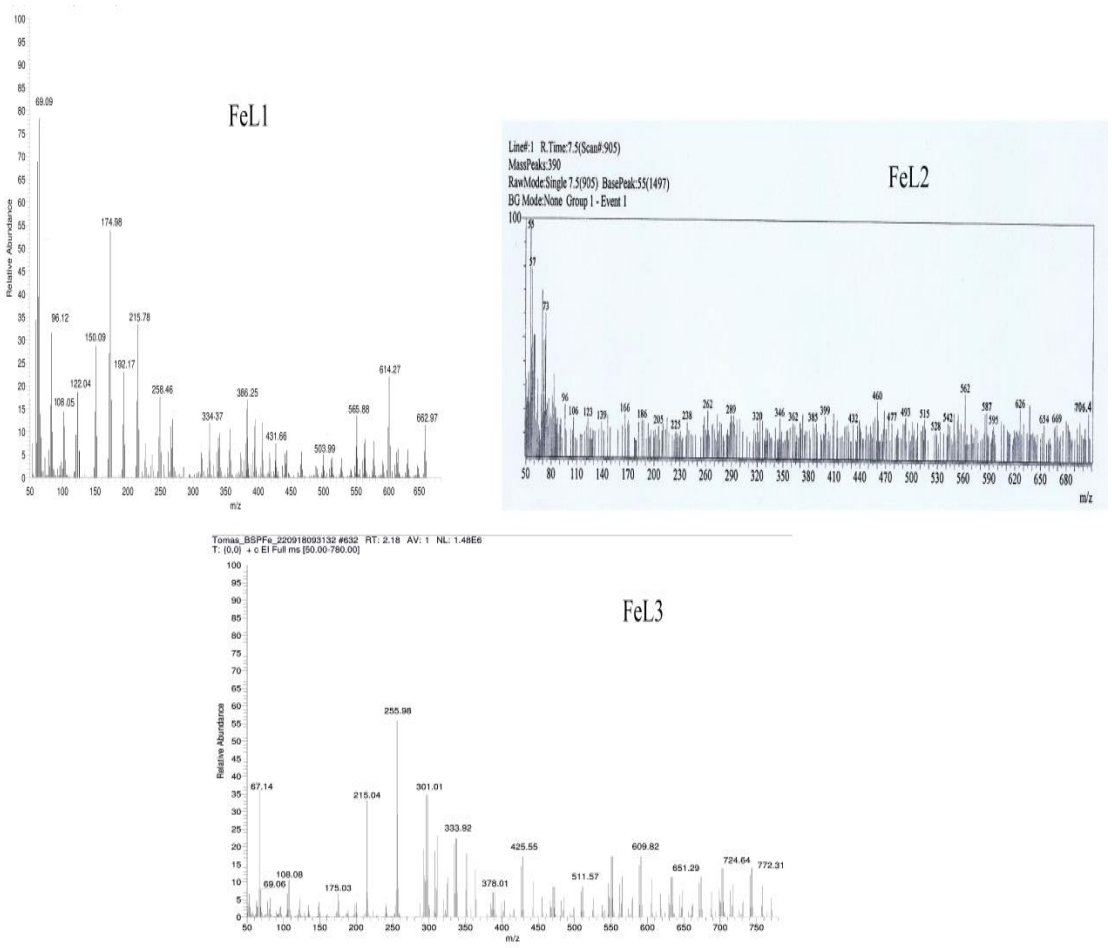


(Fig.11S) IR spectrum of FeL_2



(Fig.12S) IR spectrum of FeL_3

3.4 | Mass Spectrometry



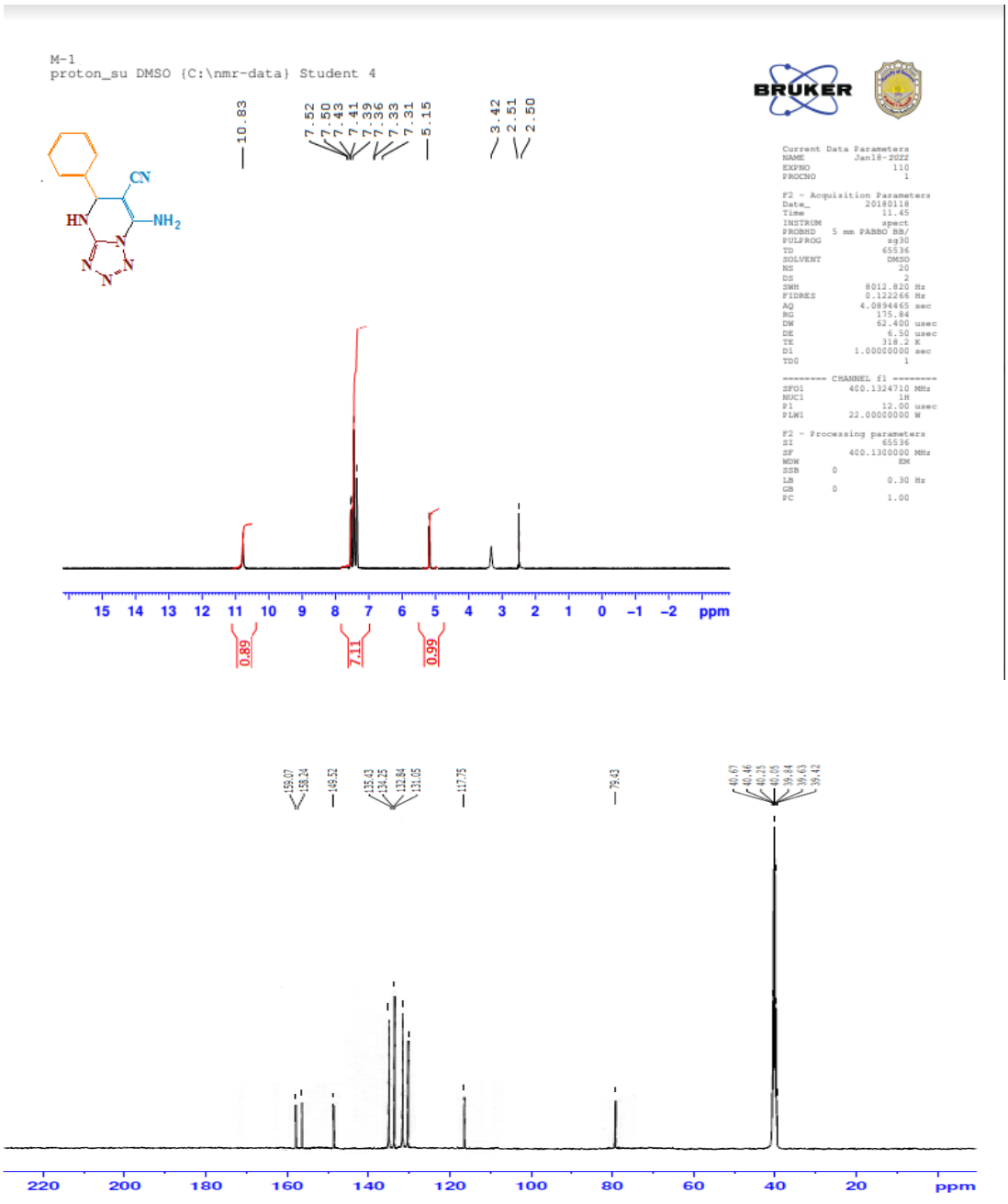
(Fig.S13) mass spectroscopy of FeL_1, FeL_2 and FeL_3

3.6 | Thermal Analysis (Table S1)

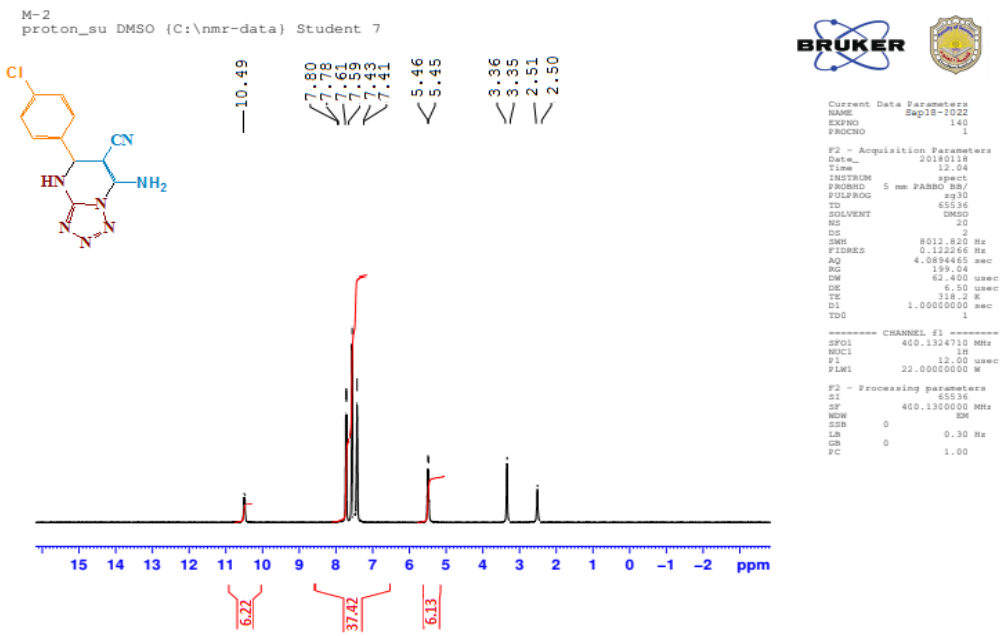
Complexes	Temperature °C	Fragment loss %		Weight loss %		E^* (KJmol^{-1})	A (S^{-1})	ΔH^* KJmol^{-1})	ΔG^* (KJmol^{-1})	ΔS^* (Jmol^{-1}K^{-1})
		Molecular formula	M. Wt.	Found	Calc.					
FeL_1	47- 172	$2H_2O + NO_3$	98	14.7	(14.8)	31.29	0.004	30.39	61.06	281.71
	173- 284	$N_7O_6H_7$	201	30.35	(30.36)			29.39	95.32	-287.87
	285- 354	CH	13	1.97	(1.96)			28.64	121.37	-290.64
	354- 520	$C_8N_3S_2$	202	30.45	(30.50)			27.67	155.52	-293.23
	523- 710	C_5H_8	68	10.2	(10.2)			26.17	208.87	-296.12
Residue	> 710	Fe+C_2	80.5	12.2	(12.16)					
FeL_2	43- 158	NO_3	62	8.7	(8.8)	33.92	0.02	33.08	60.19	268.48
	159- 207	$C_4H_6N_3O_3$	144	20.38	(20.4)			32.39	82.43	273.42
	208- 299	$C_6H_4N_5O_5$	226	31.99	(32)			31.81	101.67	-276.11
	300- 543	$C_9H_5N_2S_2$	205	29	(28.99)			30.41	148.44	-280.35
Residue	>550	Fe+CH	69.5	9.83	(9.81)					
FeL_3	53-214	H_2O	18	2.3	(2.3)	71.22	0.007	70.11	110.13	-298.70
	215- 358	$C_{13}H_{16}N_9O_9S_2$	506	65.45	(65.5)			68.85	156.08	-305.01
	359- 560	$C_4H_6N_2$	82	10.6	(10.6)			67.41	209.21	-308.94
	563- 741	C_5H_2	62	8.03	(8.03)			65.80	269.45	-311.87
Residue	> 742	Fe+C_4	104.5	13.6	(13.5)					

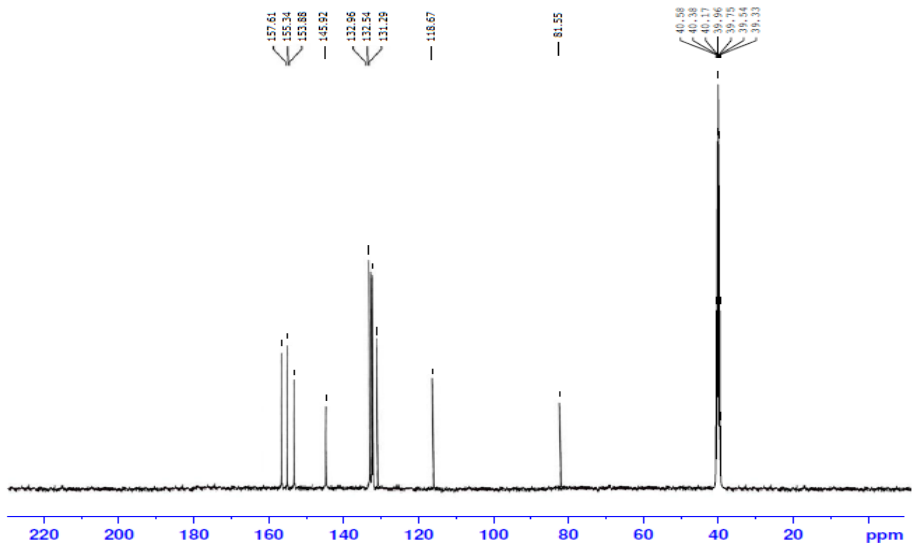
Scanned copies of ^{1}H-NMR and ^{13}C-NMR spectra of the 7-amino-4,5-dihydro-tetrazolo[1,5-*a*]pyrimidine-6-carbonitrile derivatives

(Fig.S14) ^{1}HNMR and ^{13}C 7-Amino-5-phenyl-4,5-dihydro-tetrazolo[1,5-a]pyrimidine-6-carbonitrile (4a)

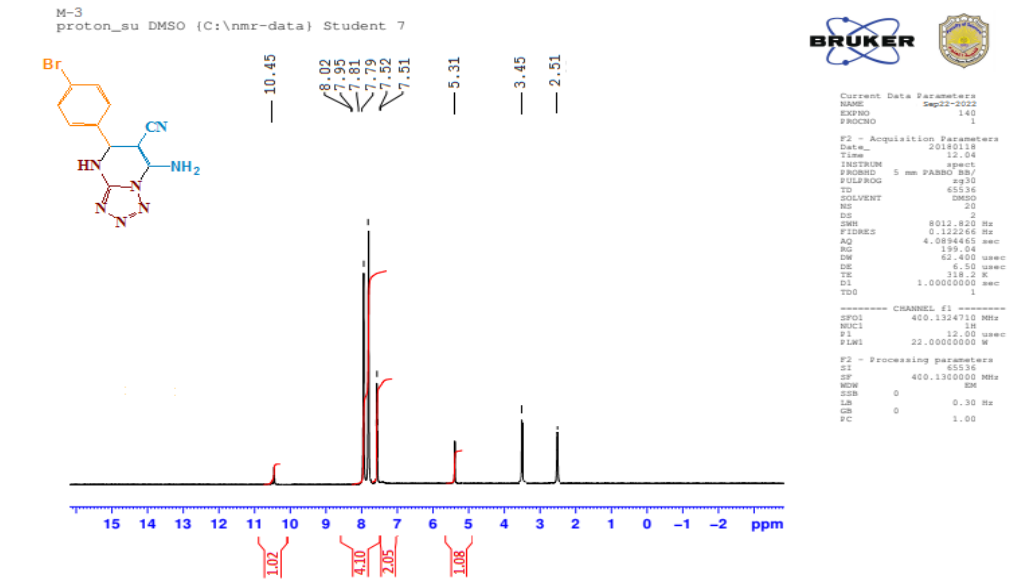


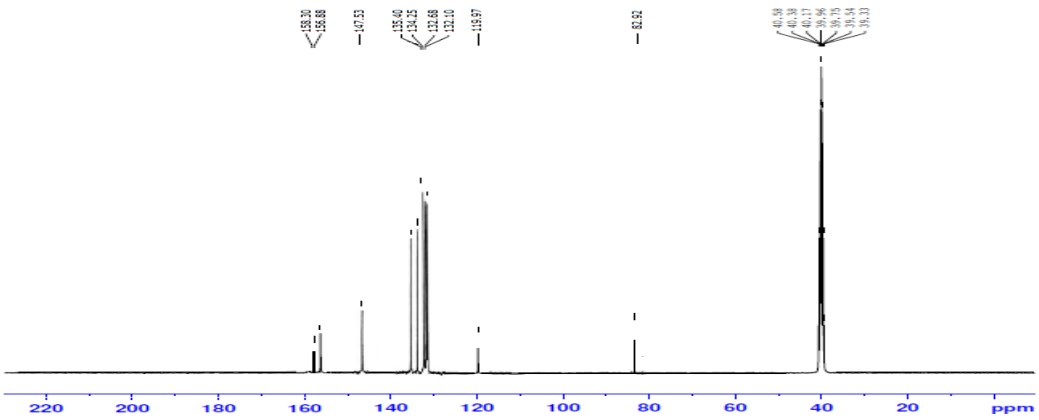
(Fig.S15) ^{1}HNMR and ^{13}C 7-amino-5-(4-chloro-phenyl)-4,5-dihydro-tetrazolo[1,5-*a*]pyrimidine-6-carbonitrile (4b)



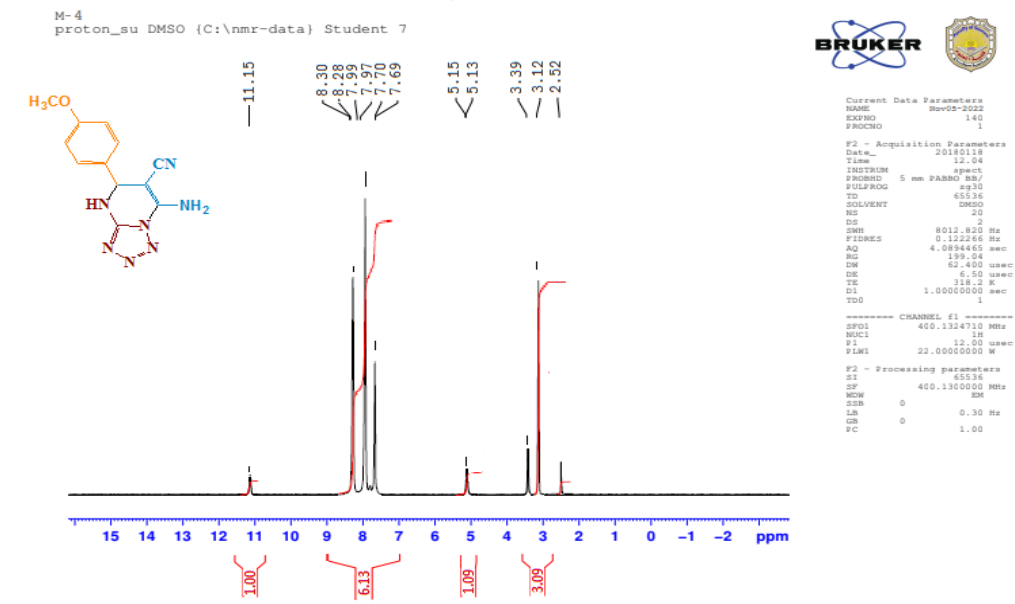


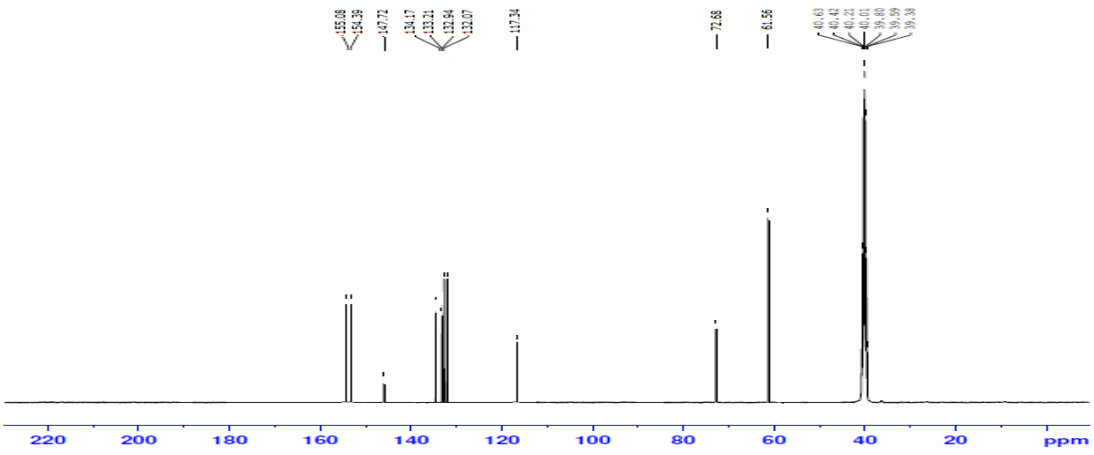
(Fig.S16) ^{1}HNMR and ^{13}C-NMR of 7-amino-5-(4-bromo-phenyl)-4,5-dihydro-tetrazolo[1,5-*a*]pyrimidine-6-carbonitrile (4c)



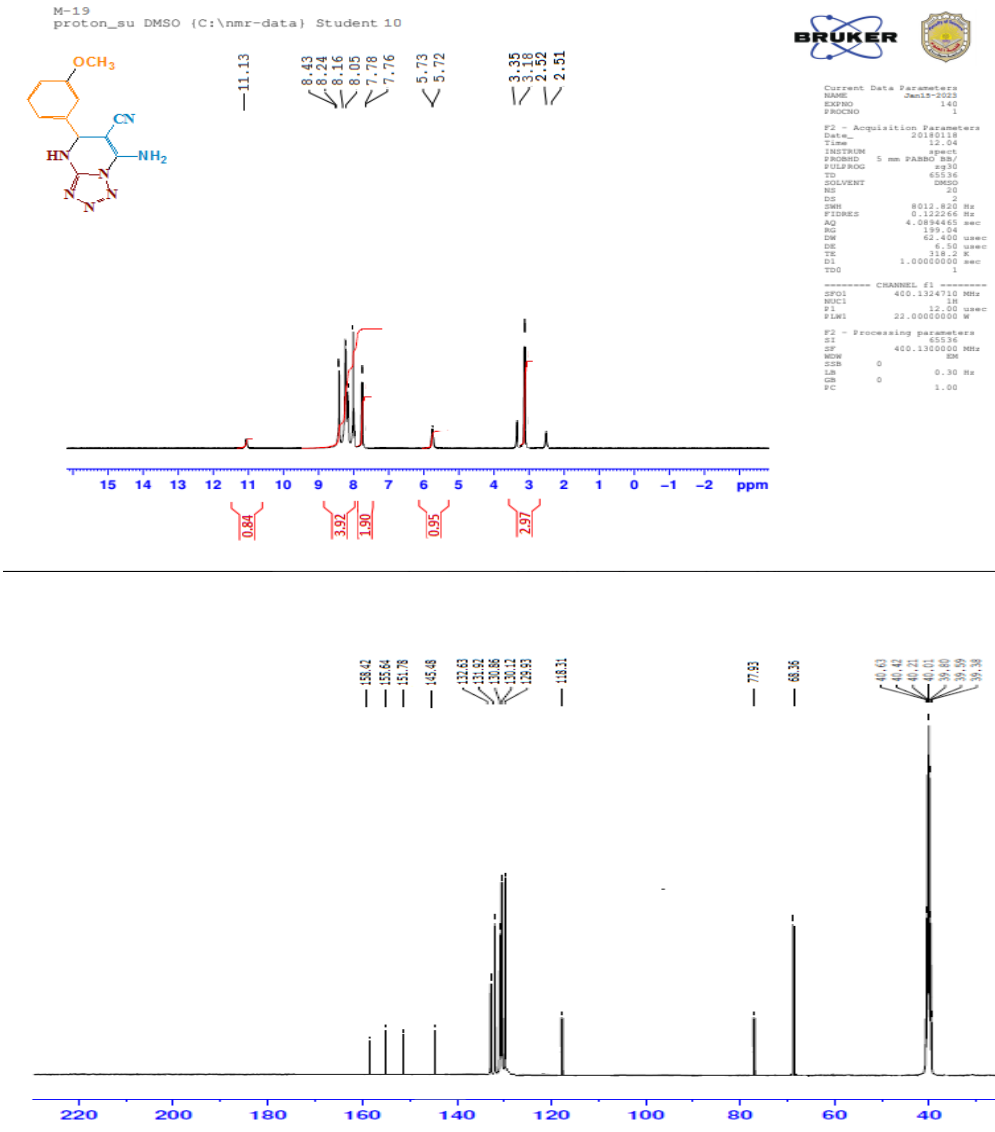


(Fig.S17) ^{1}HNMR and ^{13}C-NMR of 7-amino-5-(4-methoxy-phenyl)-4,5-dihydro-tetrazolo[1,5-*a*]pyrimidine-6-carbonitrile (4d)

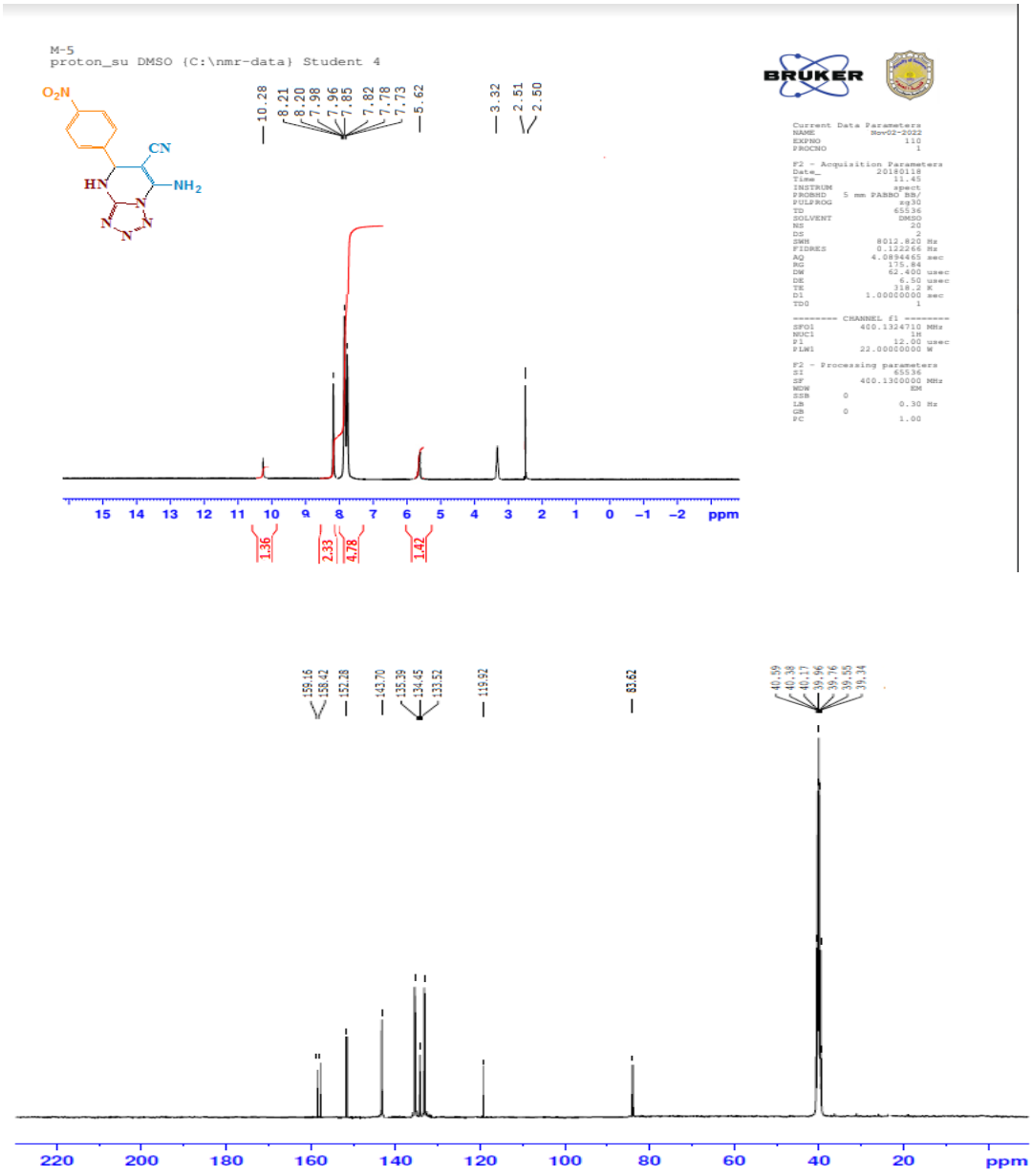




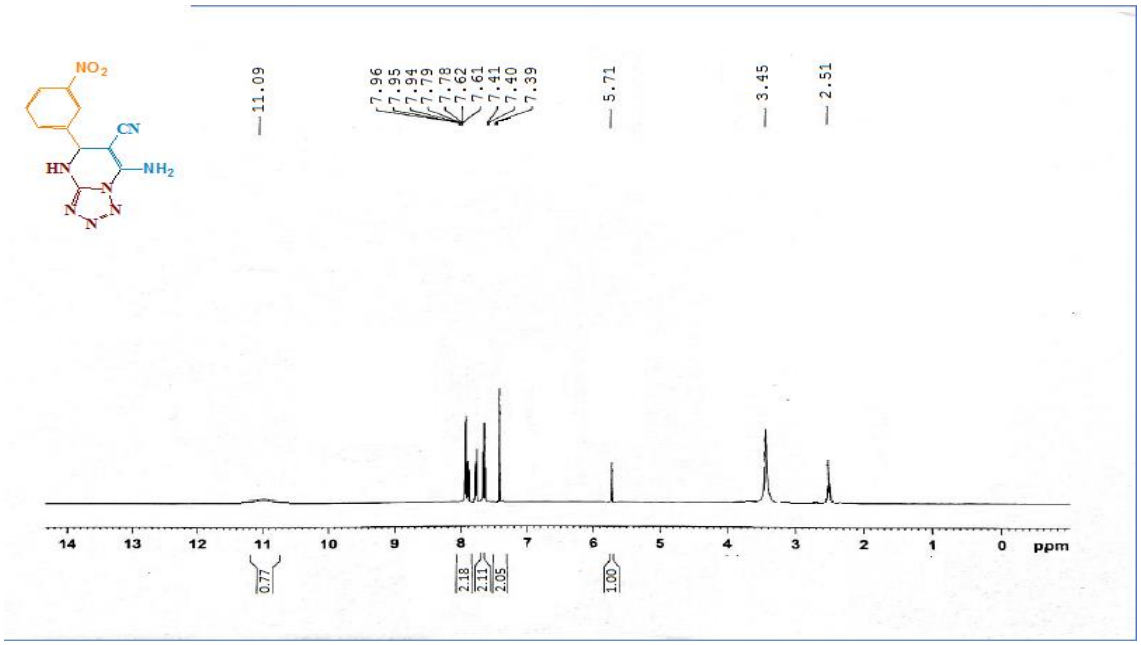
(Fig.S18) ^{1}HNMR and ^{13}C-NMR of 7-amino-5-(3-methoxy-phenyl)-4,5-dihydro-tetrazolo[1,5-*a*]pyrimidine-6-carbonitrile (4e)

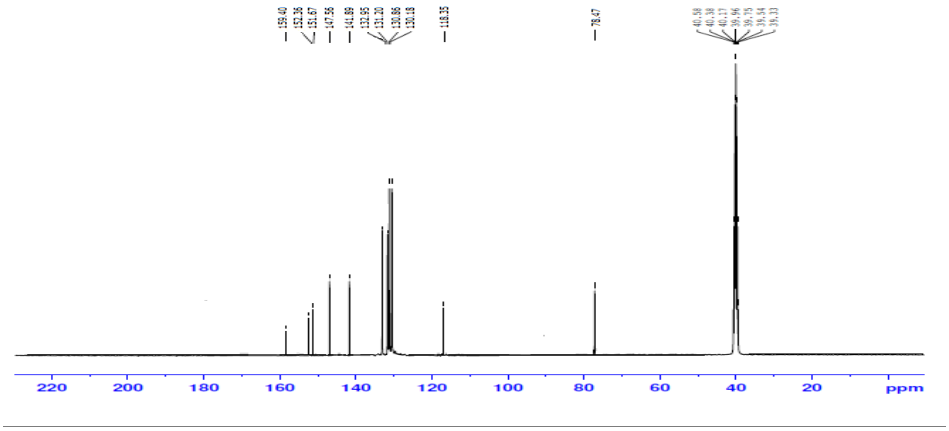


(Fig.S19) ^{1}HNMR and ^{13}C-NMR 7-amino-5-(4-nitro-phenyl)-4,5-dihydro-tetrazolo[1,5-*a*]pyrimidine-6-carbonitrile (4f)

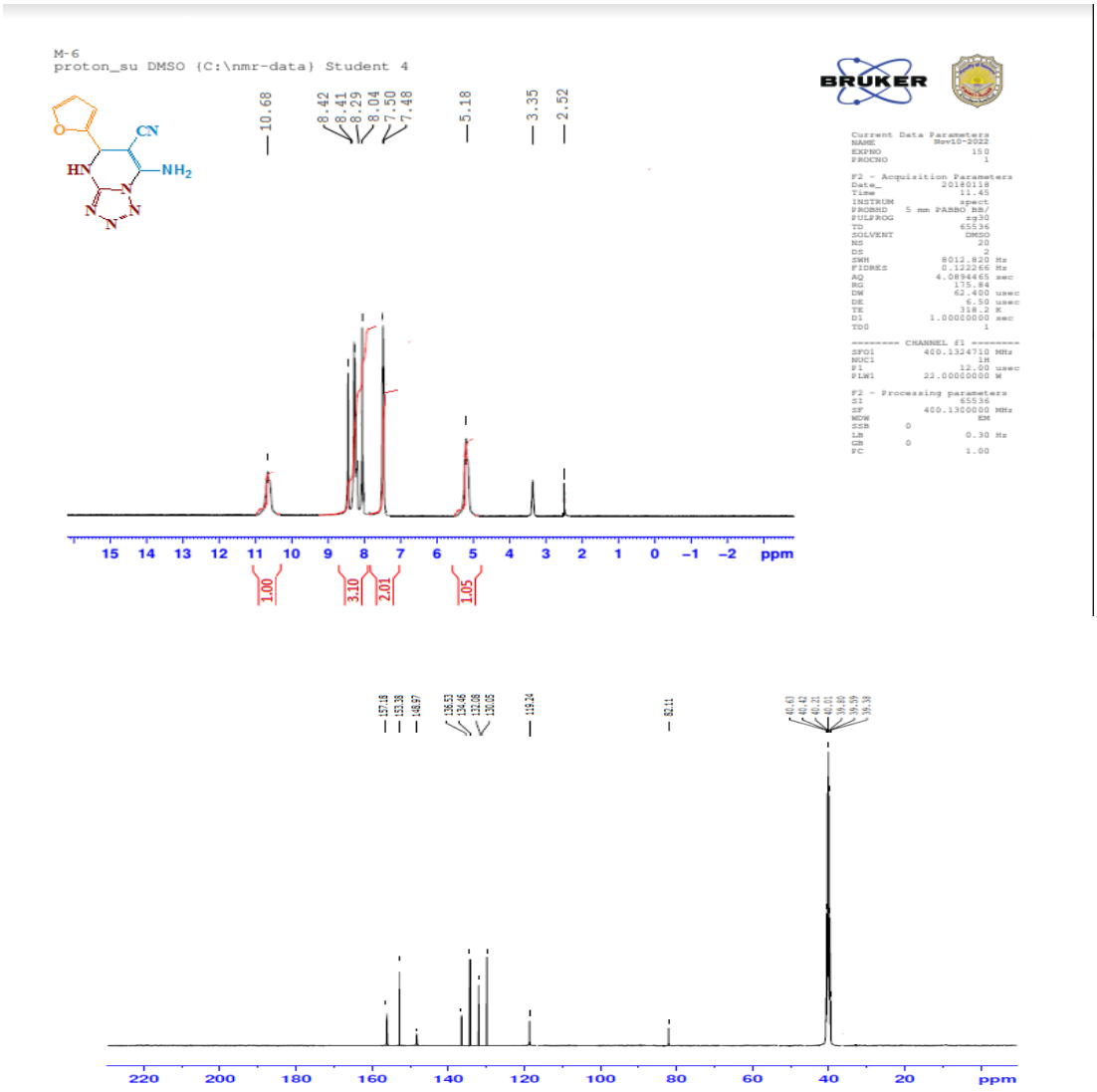


(Fig.S20) ^{1}HNMR and ^{13}C-NMR of 7-amino-5-(3-nitro-phenyl)-4,5-dihydro-tetrazolo[1,5-*a*]pyrimidine-6-carbonitrile (4g)

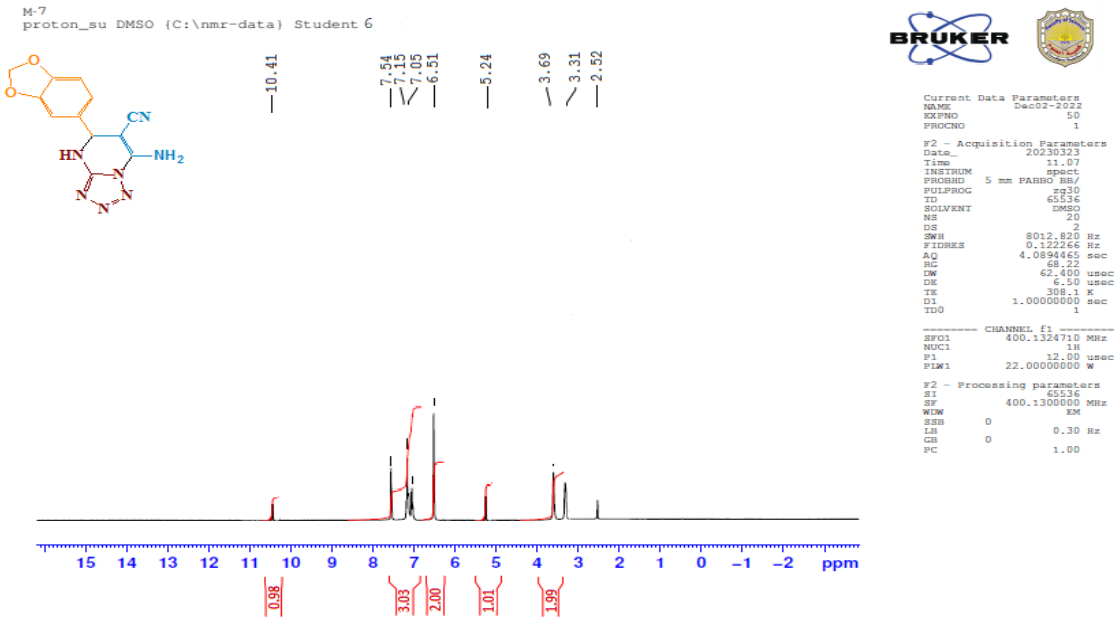


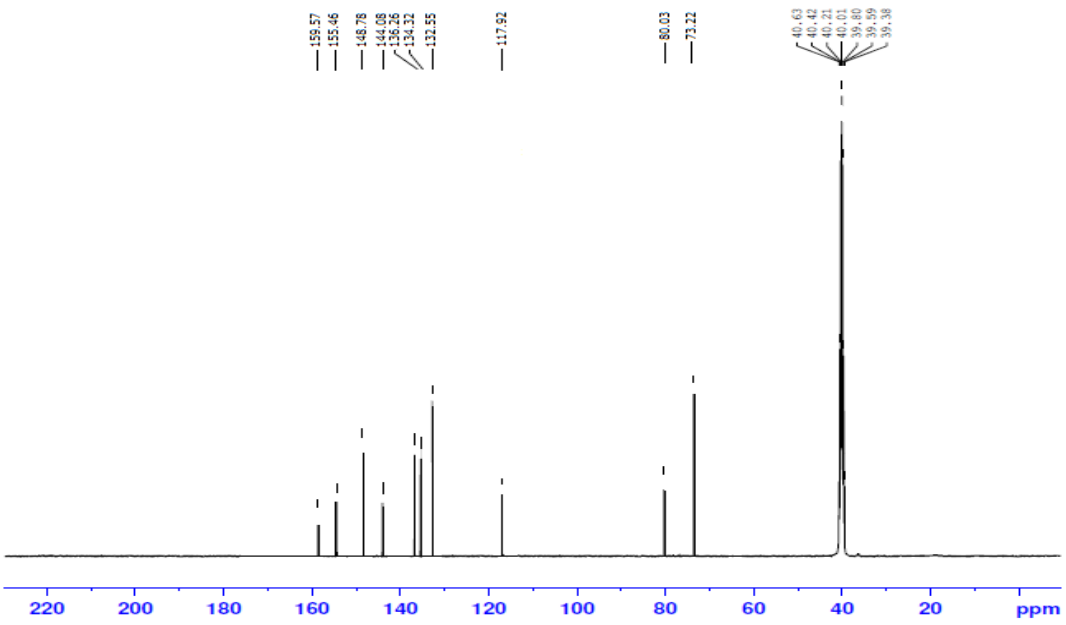


(Fig.S21) ^{1}HNMR and ^{13}CNMR of 7-amino-5-furan-2-yl-4,5-dihydro-tetrazolo[1,5-*a*]pyrimidine-6-carbonitrile (4h)



(Fig.S22) ^{1}HNMR and ^{13}C-NMR of 7-amino-5-benzo[1,3]dioxol-5-yl-4,5-dihydro-tetrazolo[1,5-*a*]pyrimidine-6-carbonitrile (4i)


M-7
proton_su DMSO (C:\nmr-data) Student 6
10.41
7.54
7.15
7.05
6.51
5.24
3.69
3.31
2.52
CN
HN
NH2
BRUKER
Current Data Parameters
NAME Dec02-2022
EXPNO 50
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230323
Time 11.07
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 20
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 68.22
DW 62.400 usec
DE 6.50 usec
TE 308.1 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
SFO1 400.1324710 MHz
NUC1 1H
P1 12.00 usec
PLW1 22.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 ppm
0.98
3.03
2.00
1.01
1.99


159.57
155.46
148.78
144.08
136.26
134.31
132.55
117.92
80.03
73.22
40.63
40.42
40.21
40.01
39.80
39.59
39.38
220 200 180 160 140 120 100 80 60 40 20 ppm