Supplementary material

Immobilized Cu(0) Nanoparticles on Montmorillonite-Modified with Benzalkonium Chloride (MMT-BAC@Cu(0)): As an Eco-Friendly and Proficient Heterogeneous Nano-Catalyst for Green Synthesis of 5-Substituted 1*H*-Tetrazoles

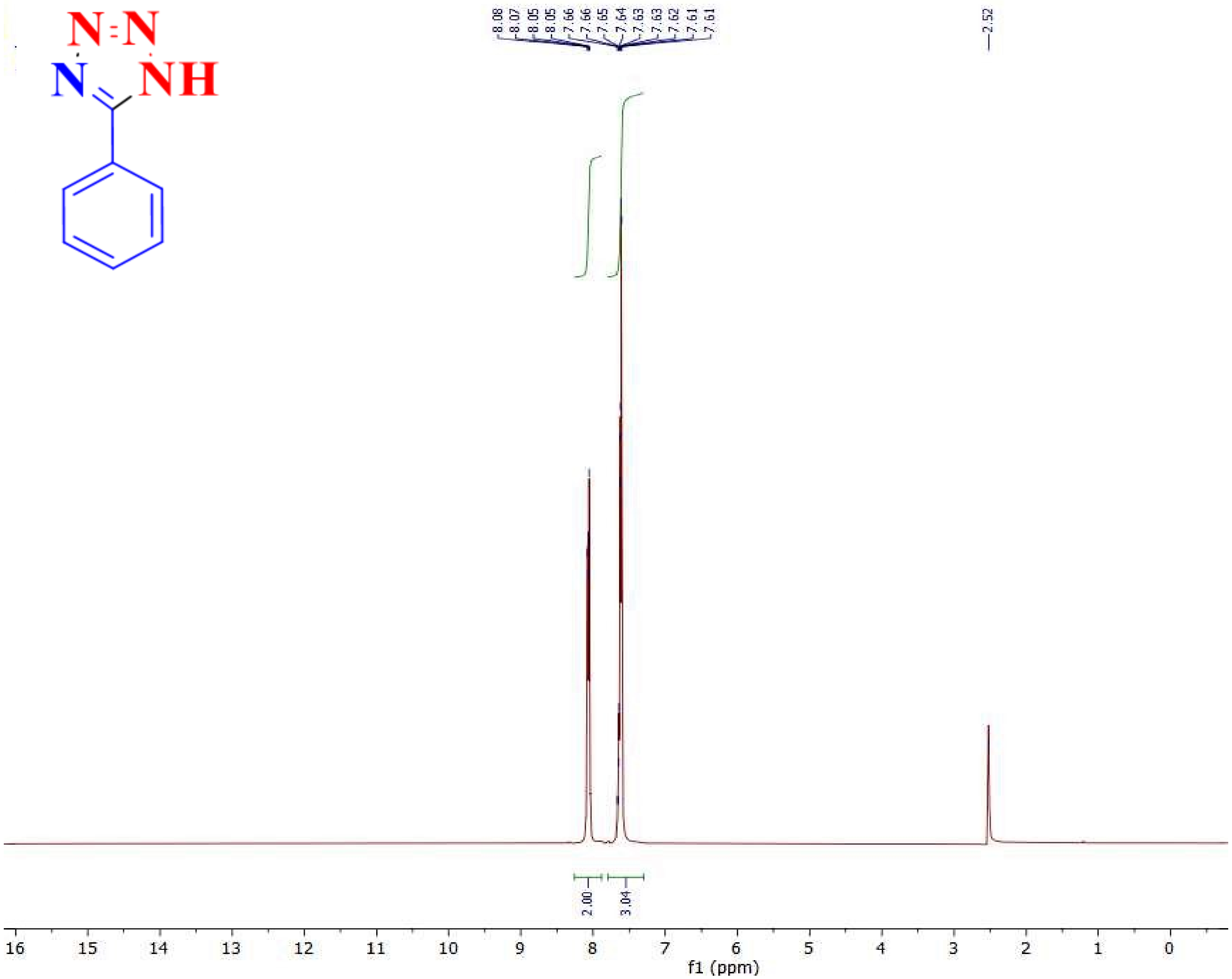
Fatemeh Pirani [a], **Hossein Eshghi** [a*] **and S. Amin Rounaghi** [b]
[a] *Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, Mashhad 91775-1436, Iran*
[b] *Research and Development Laboratory, Nano Parmin Khavaran Company, Birjand, Iran*

*Corresponding author: e-mail: heshghi@um.ac.ir

E**xperimental**

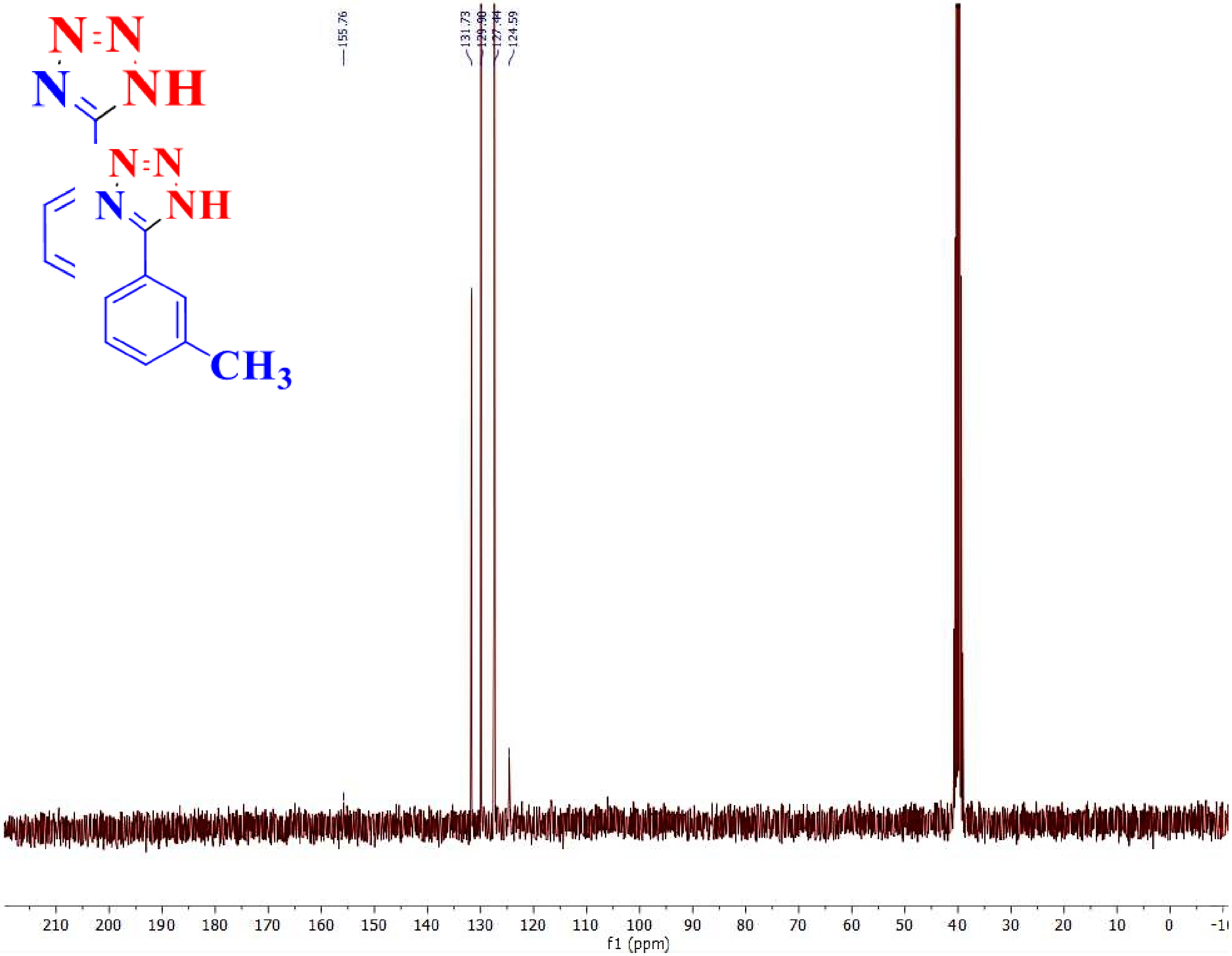
---

^{1}H NMR spectrum of compound (**5a**)

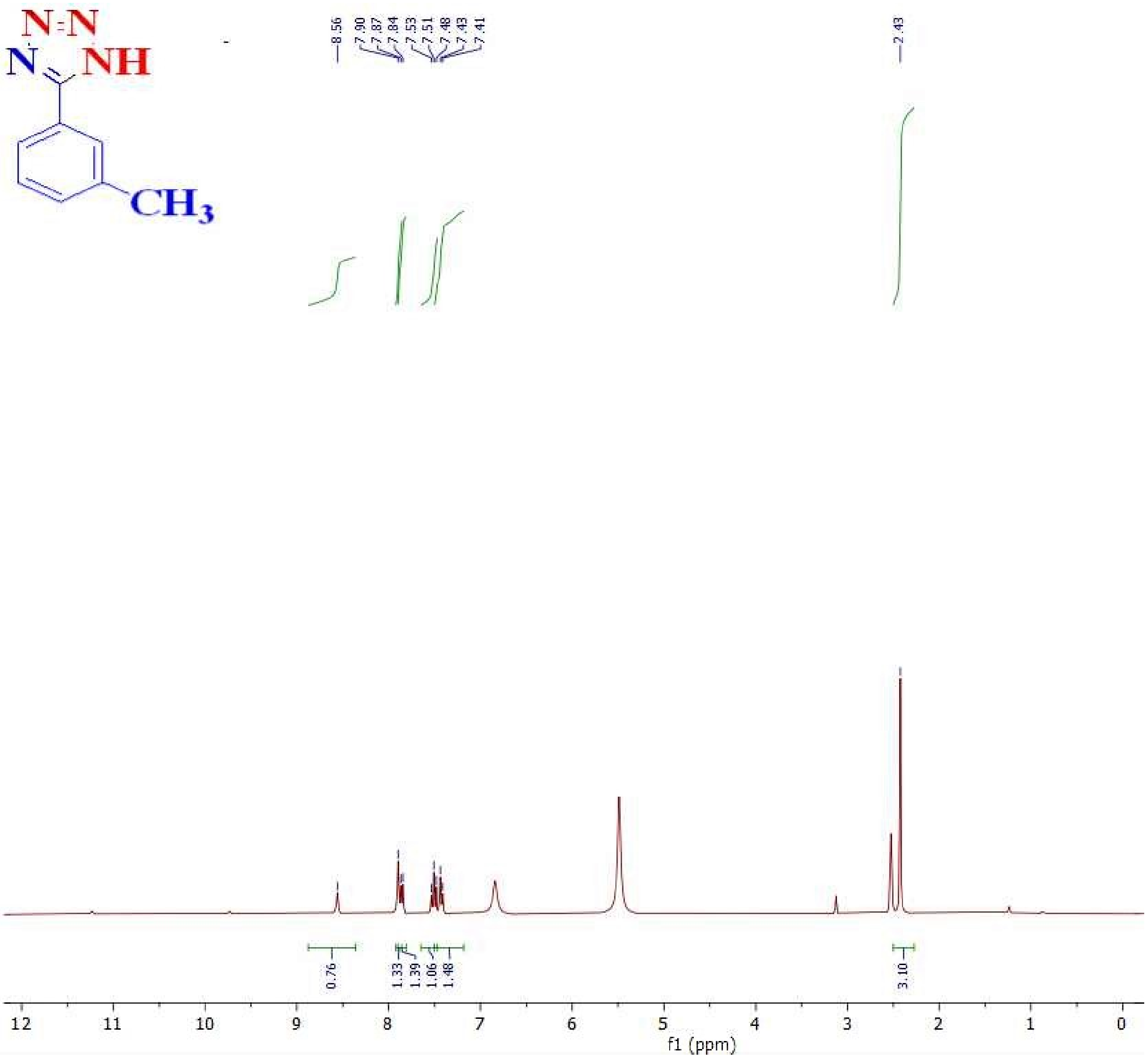


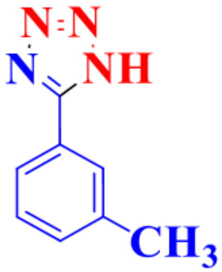
^{13}C NMR spectrum of compound (**5a**)

^{1}H NMR spectrum

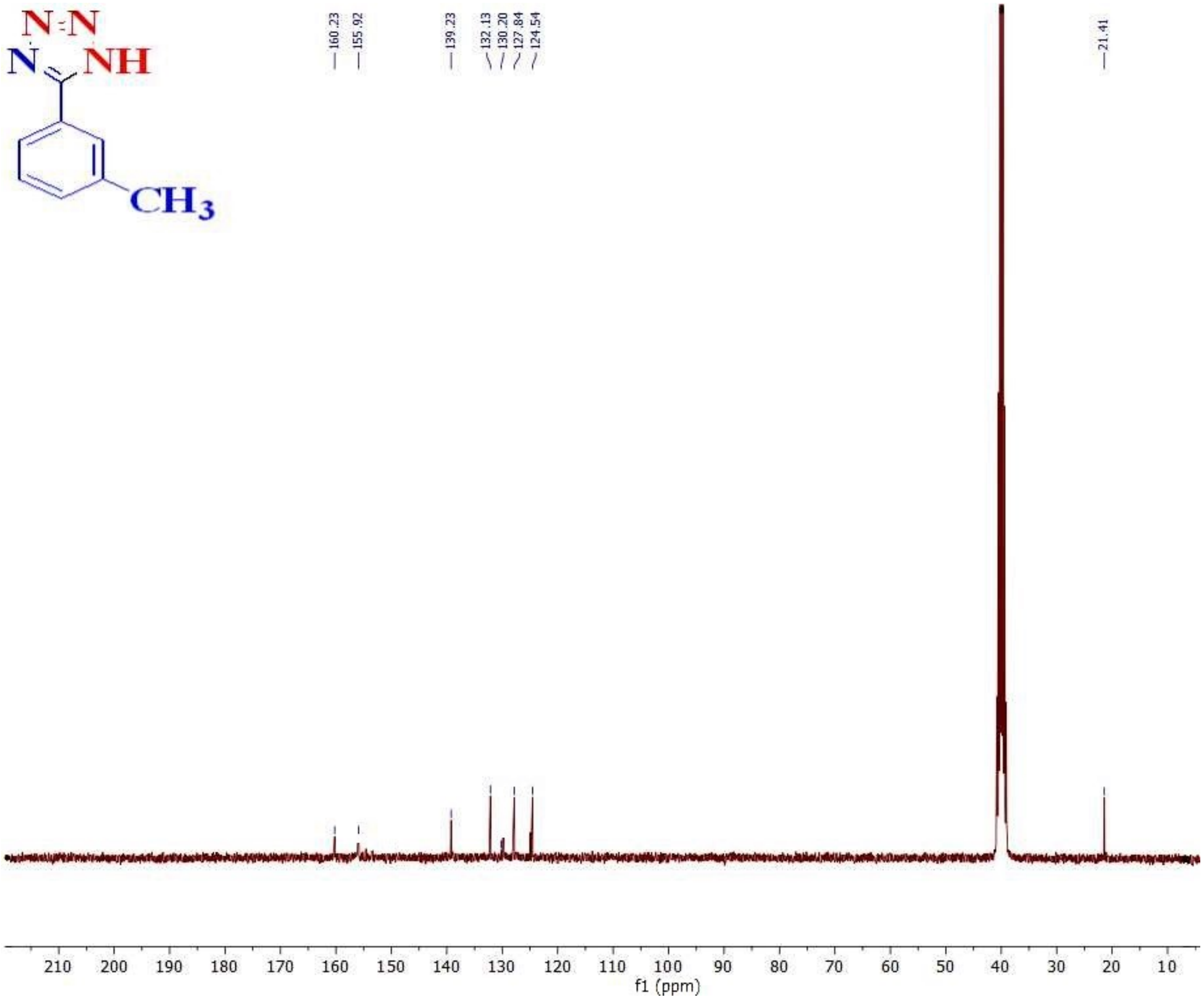


of compound (**5b**)

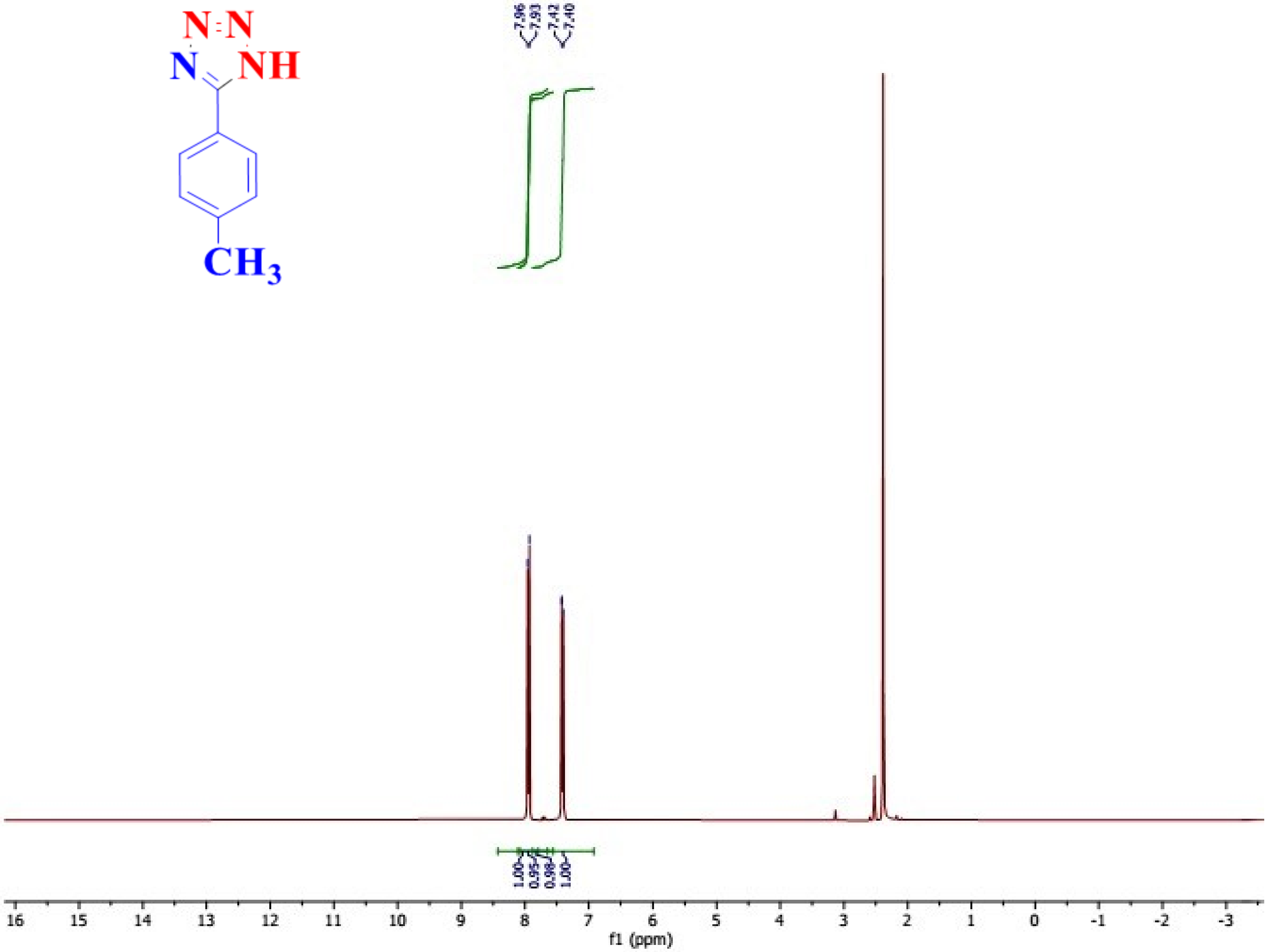

N=N
N
NH
CH3
8.56
7.90
7.87
7.84
7.53
7.51
7.48
7.43
7.41
2.43
0.76
1.33
1.39
1.06
1.48
3.10
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)



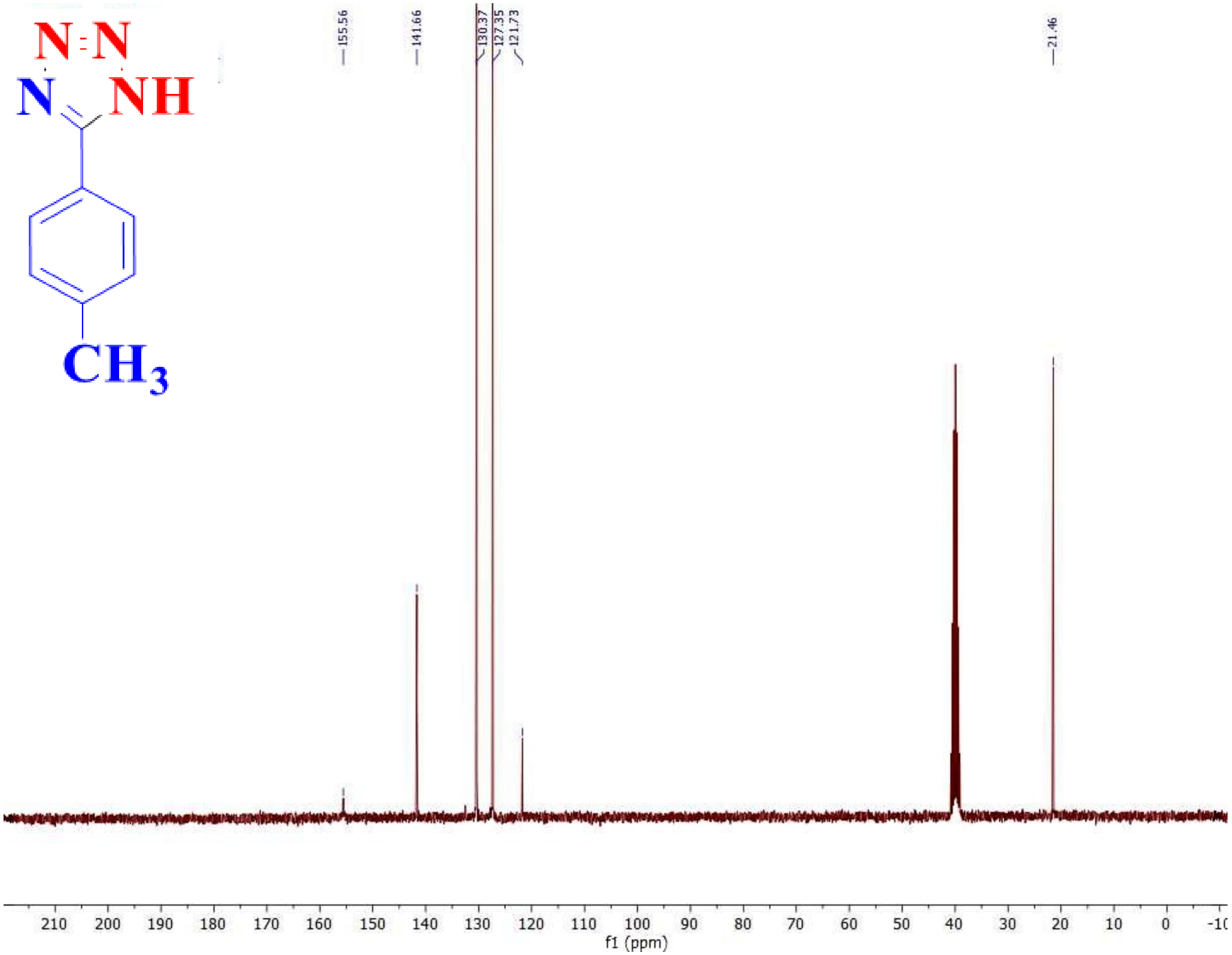
^{13}C NMR spectrum of compound (**5b**)


N=N
N
NH
CH3
160.23
155.92
139.23
132.13
130.20
127.84
124.54
21.41
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

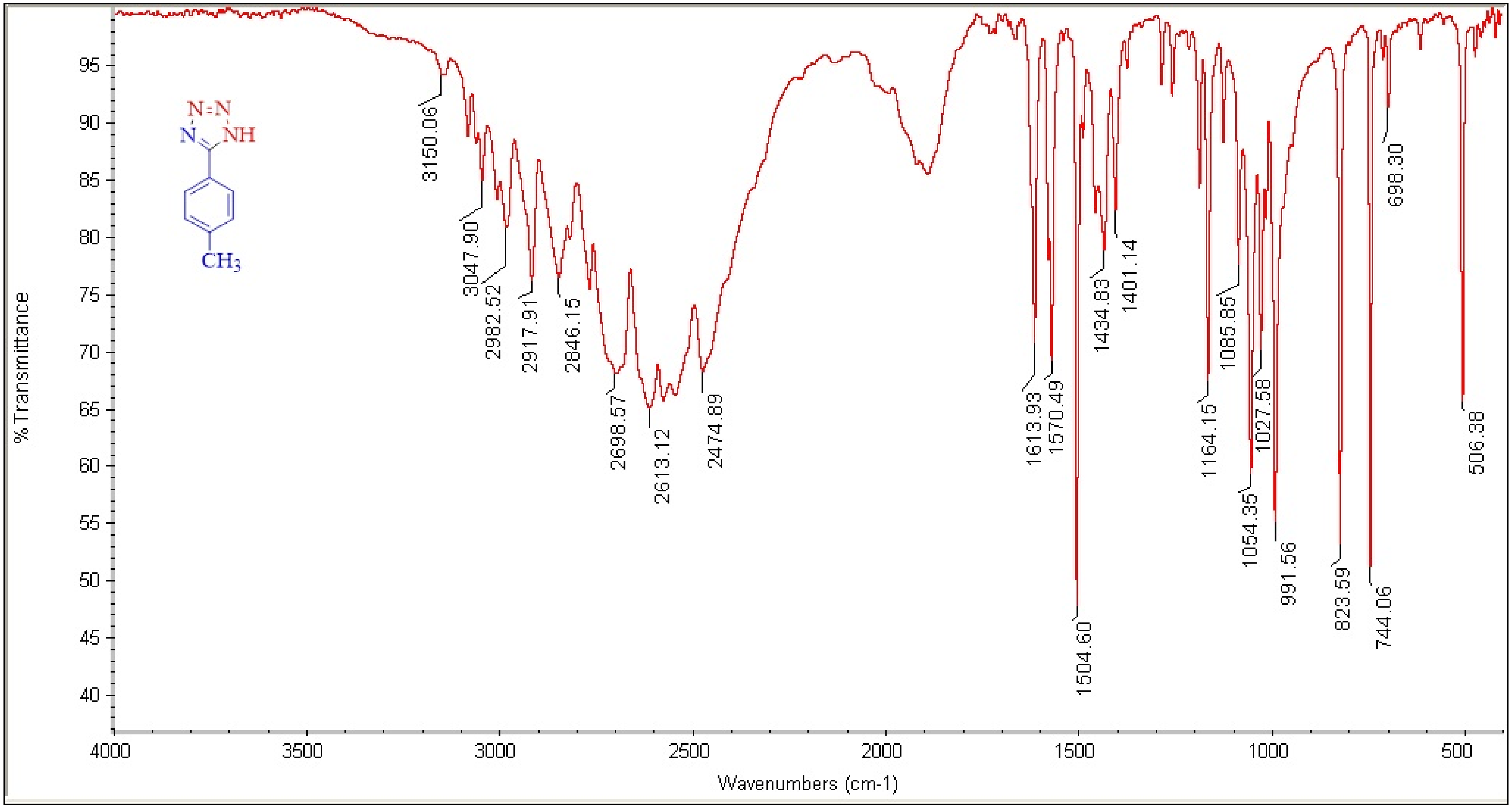
^{1}H NMR spectrum of compound (**5c**)

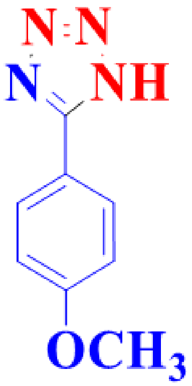


^{13}C NMR spectrum of compound (**5c**)

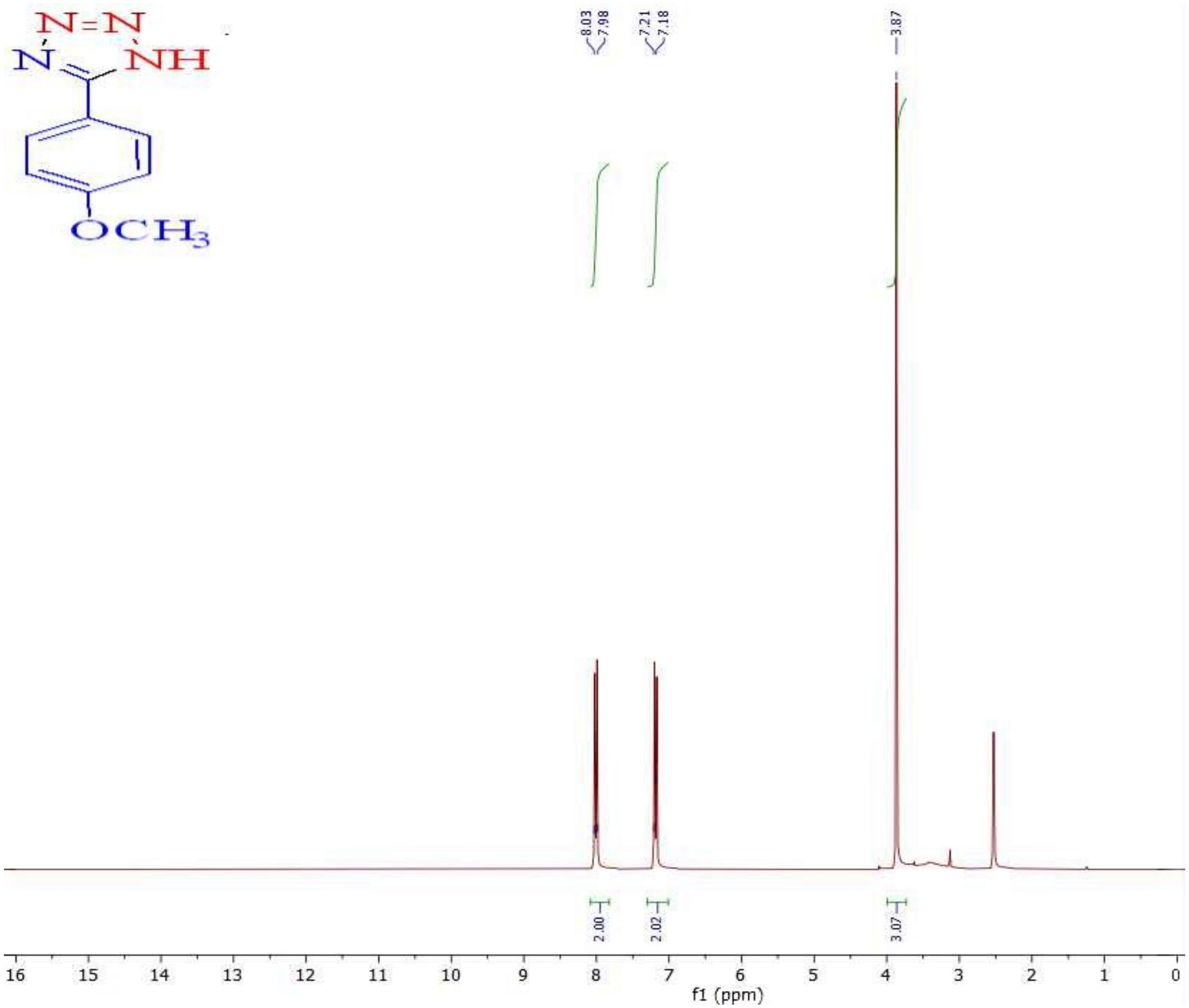


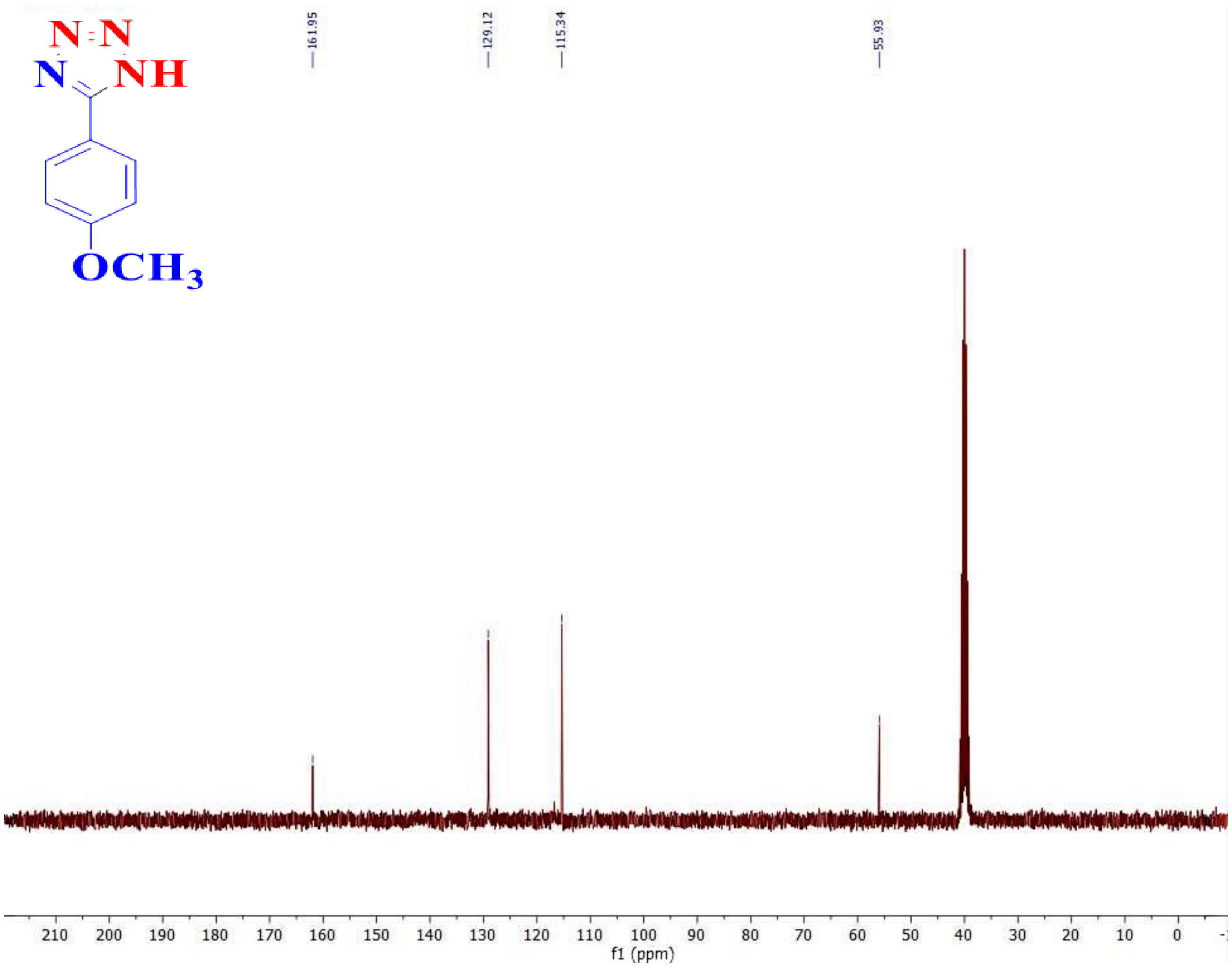
FT-IR spectrum of compound (**5c**)





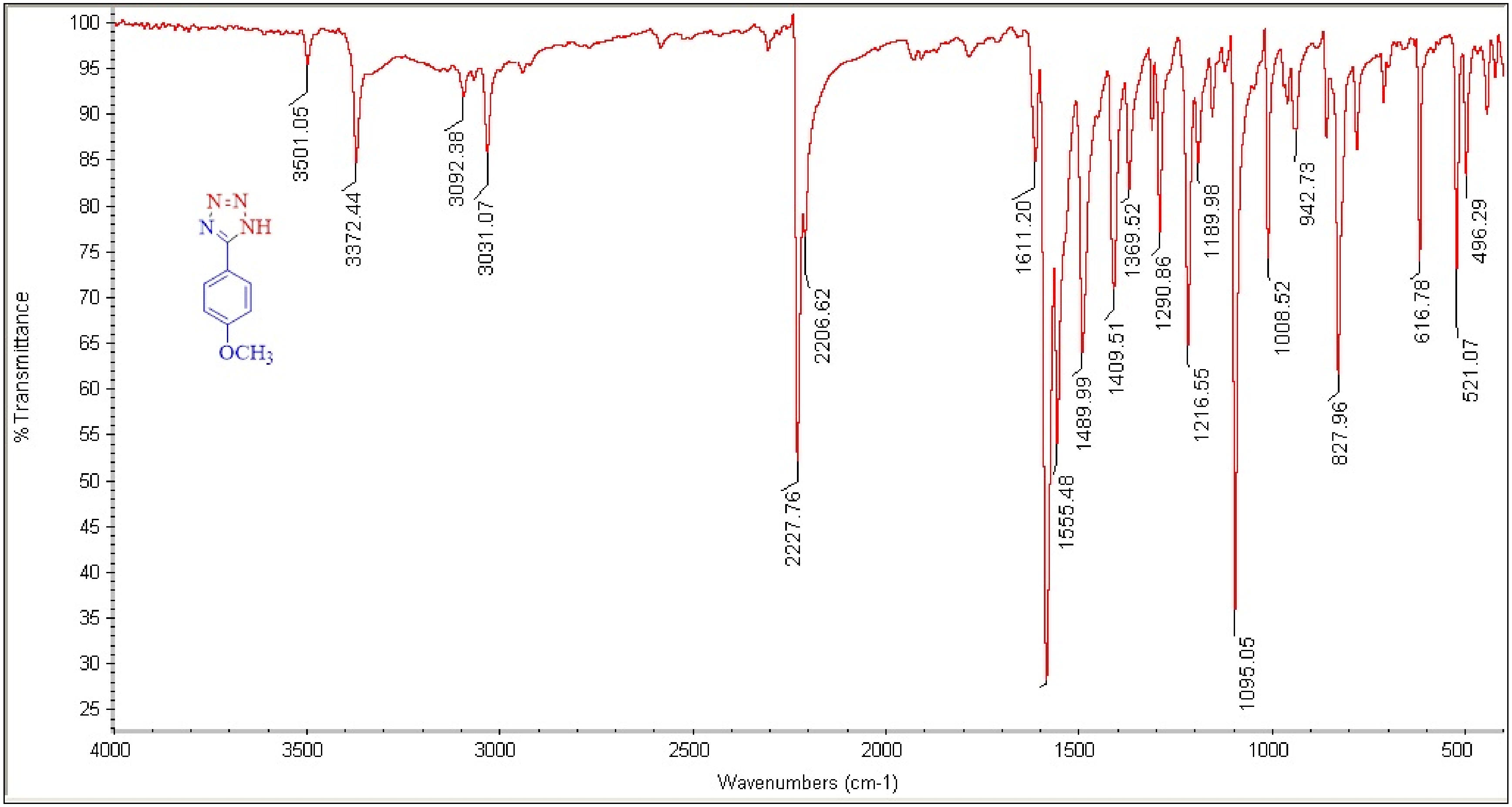
^{1}H NMR spectrum of compound (**5d**)


N=N
N
NH
OCH3
8.03
7.98
7.21
7.18
3.87
2.00
2.02
3.07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

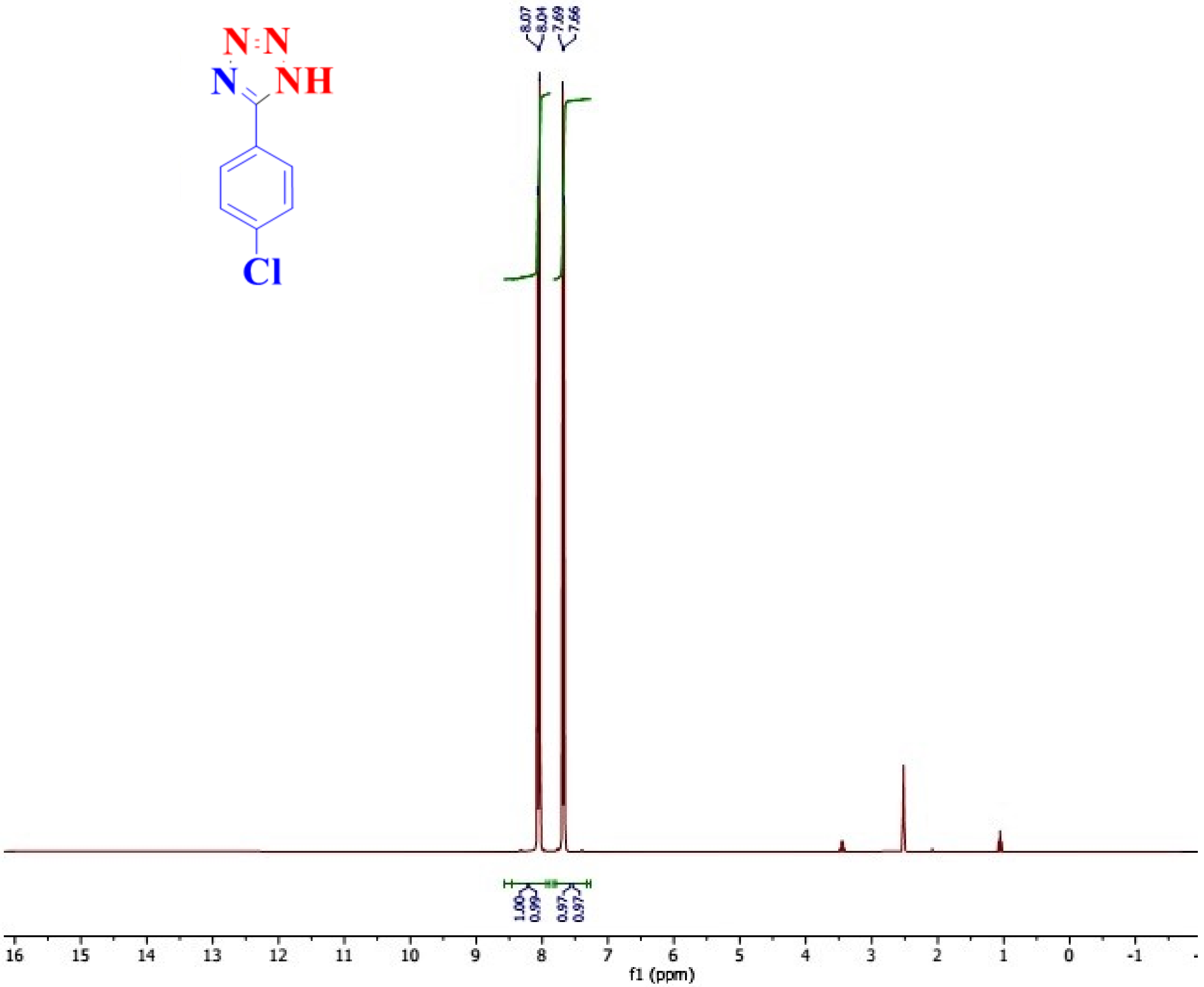


^{13}C NMR spectrum of compound (**5d**)

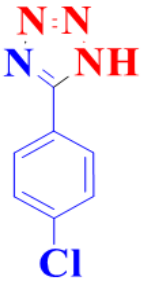
FT-IR spectrum of compound (**5d**)

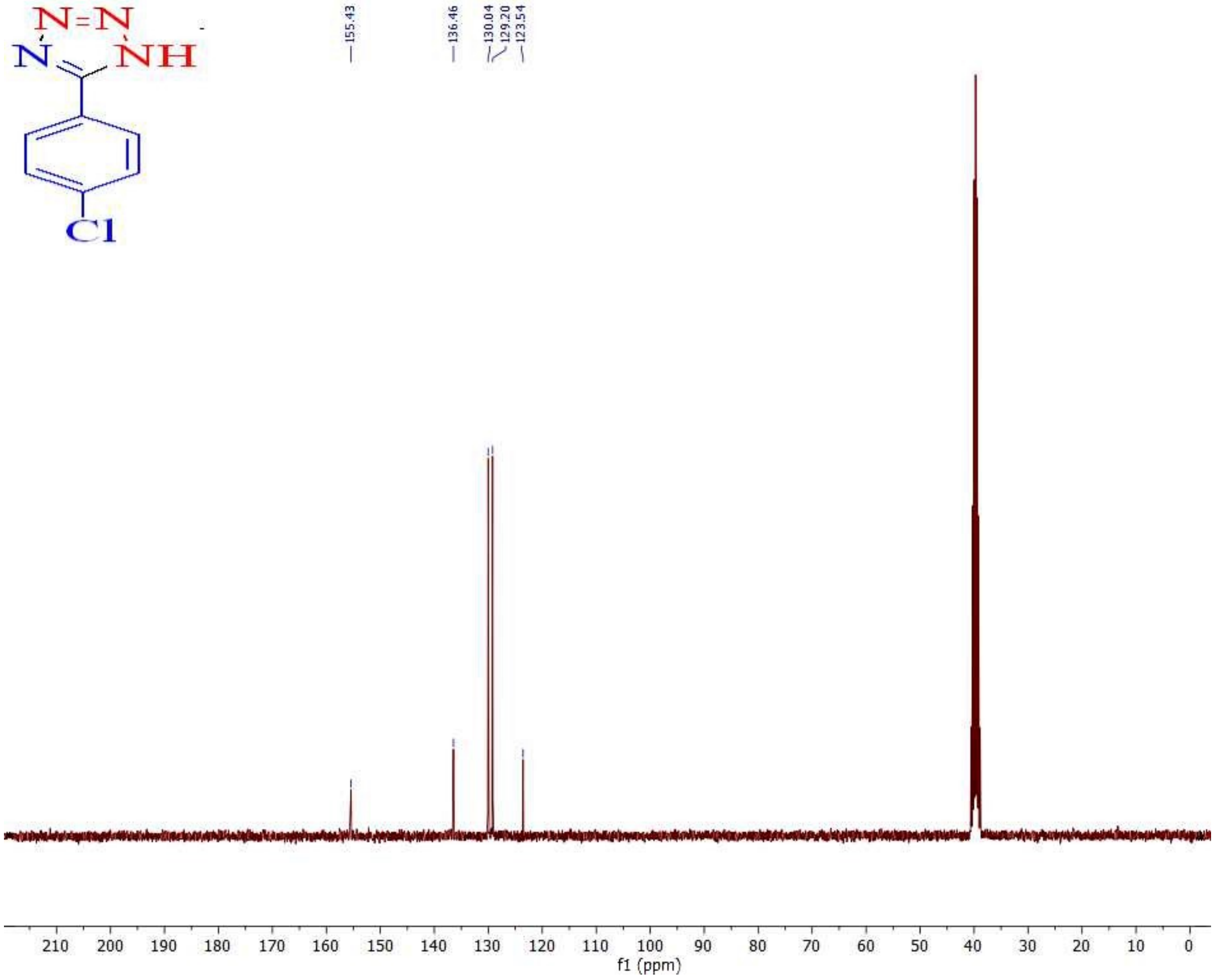


^{1}H NMR spectrum of compound (**5e**)

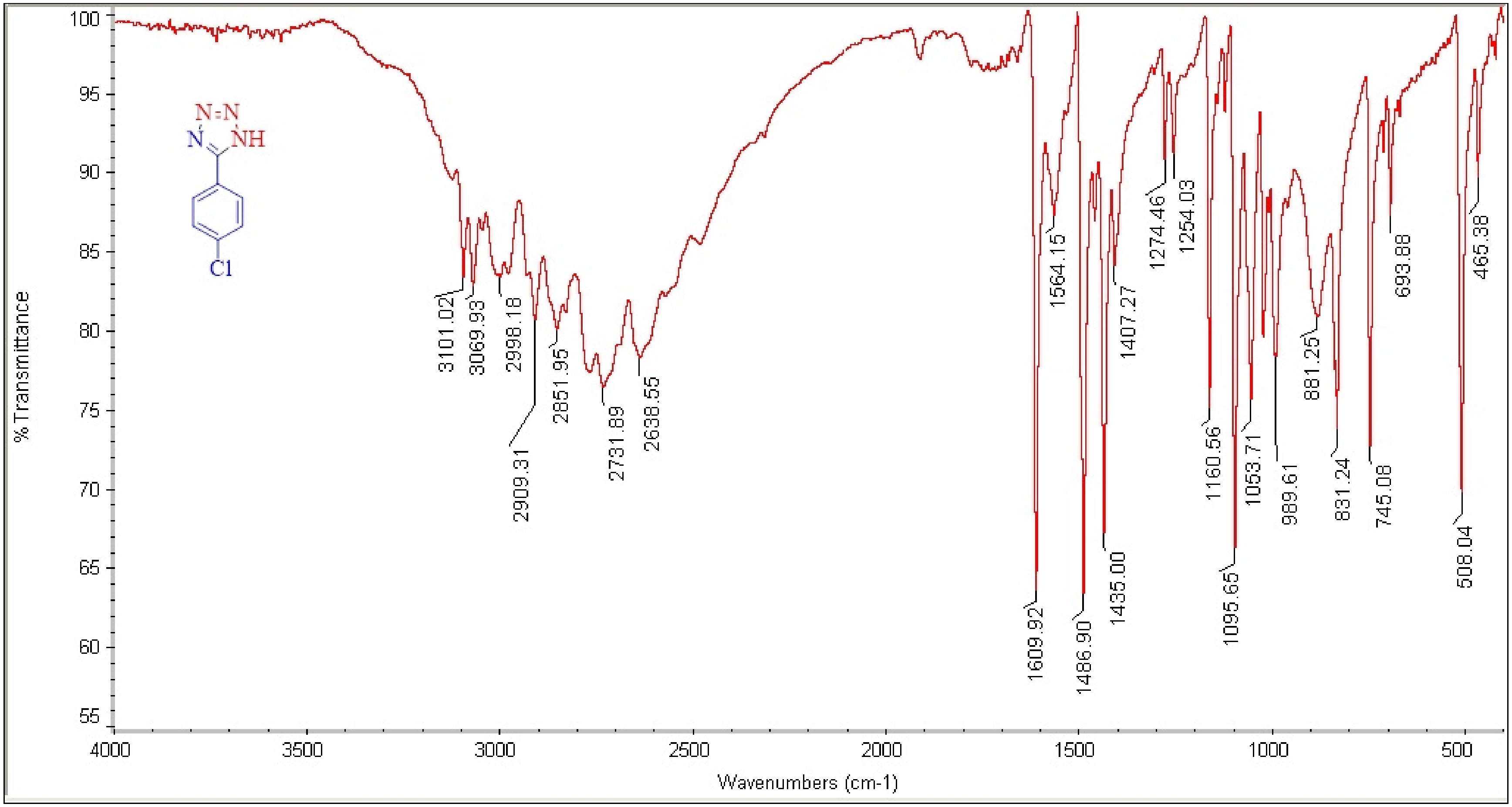


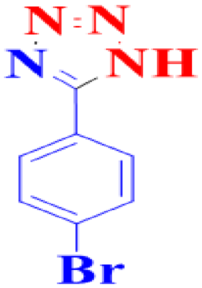
^{13}C NMR spectrum of compound (**5e**)



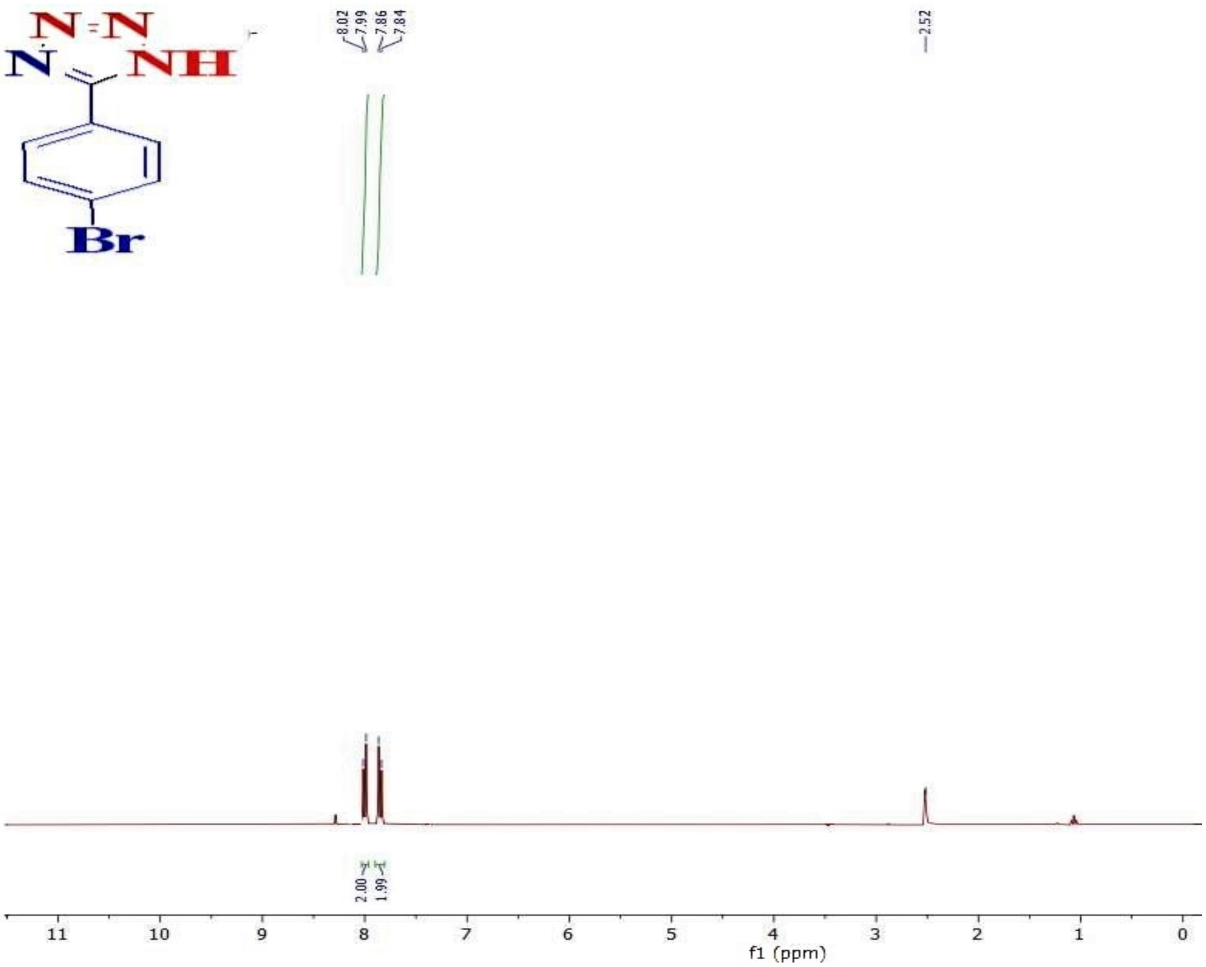


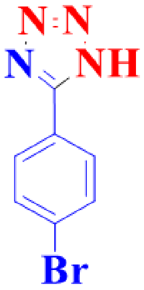
FT-IR spectrum of compound (**5e**)


% Transmittance
100
95
90
85
80
75
70
65
60
55
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
N=N
N
NH
Cl
3101.02
3069.93
2998.18
2909.31
2851.95
2731.89
2638.55
1609.92
1564.15
1486.90
1435.00
1407.27
1274.46
1254.03
1160.56
1095.65
1053.71
989.61
881.25
831.24
745.08
693.88
508.04
465.38

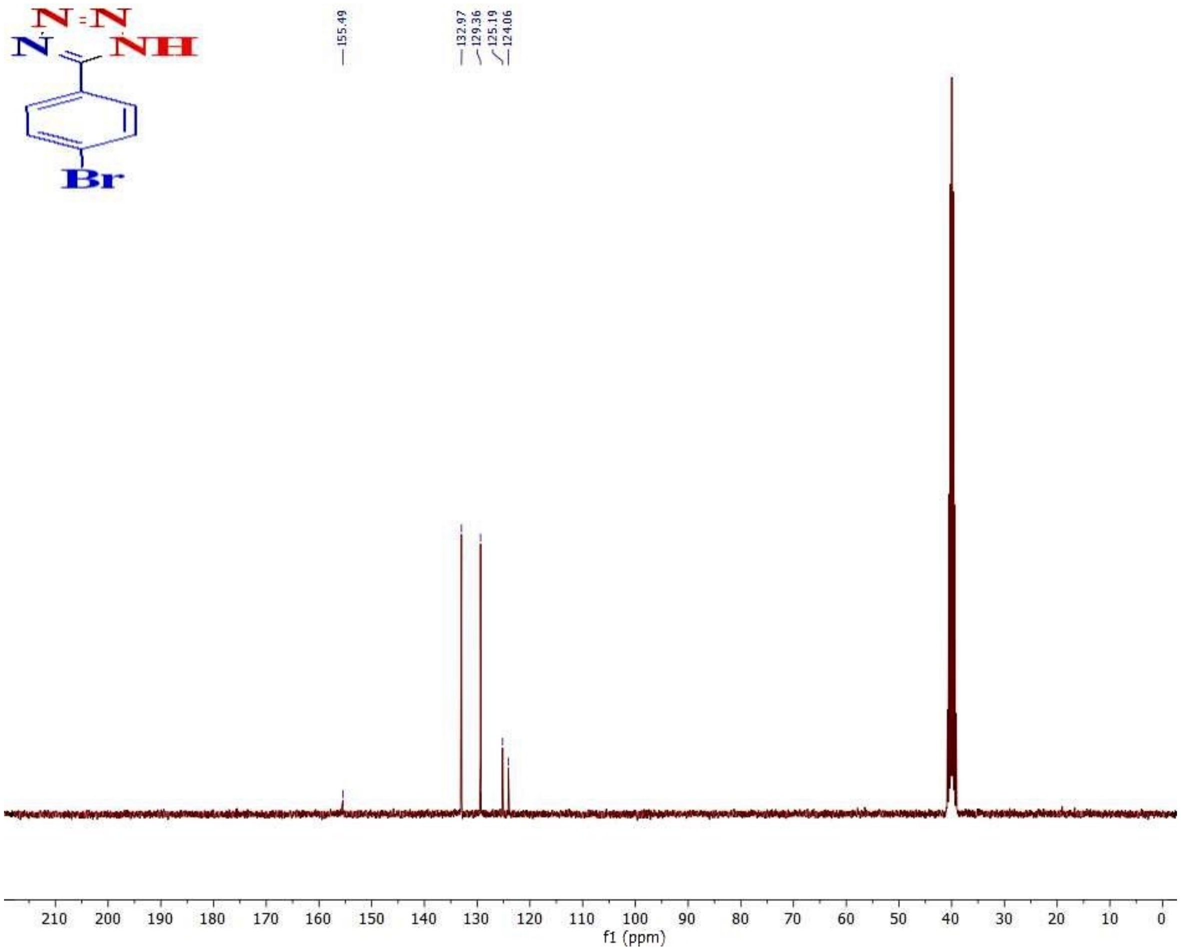


^{1}H NMR spectrum of compound (**5f**)

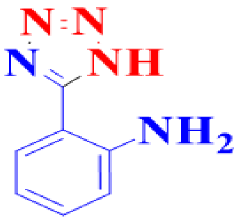

N=N
N
NH
Br
8.02
7.99
7.86
7.84
2.52
2.00
1.99
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

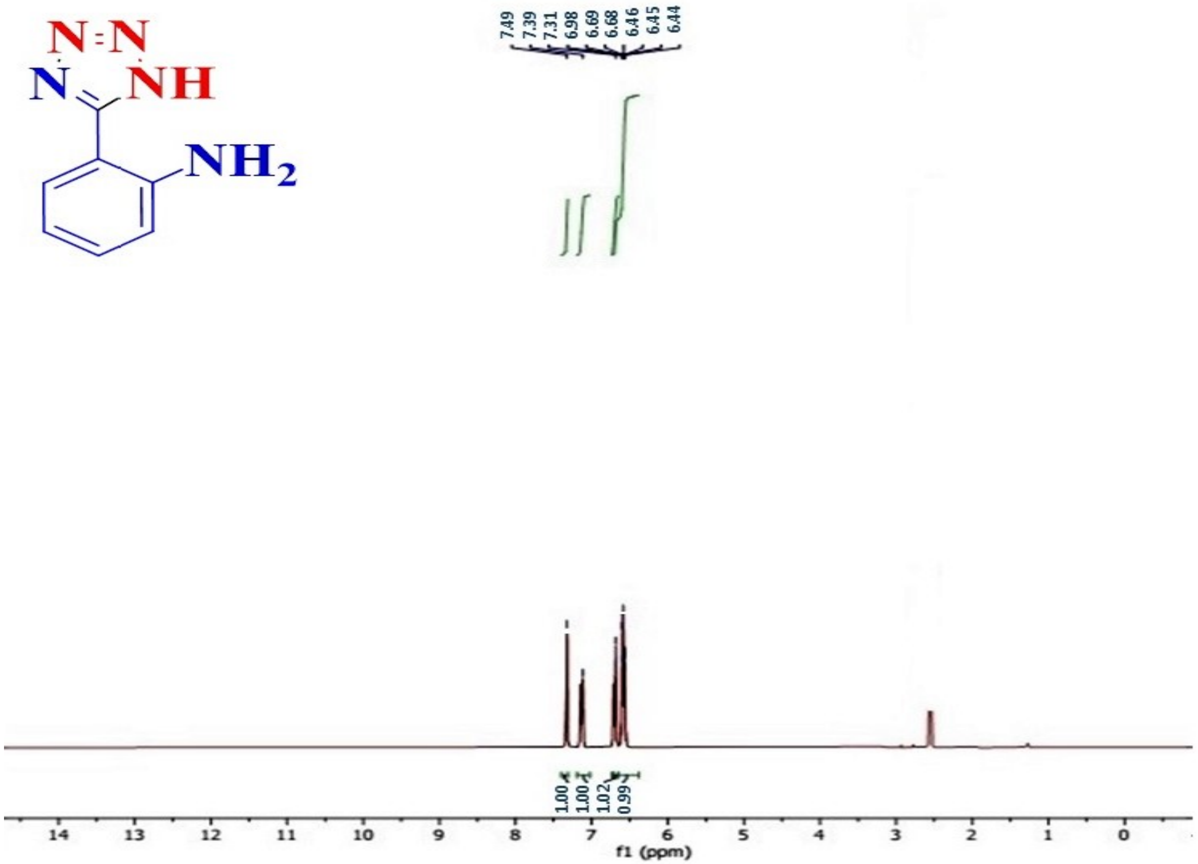


^{13}C NMR spectrum of compound (**5f**)

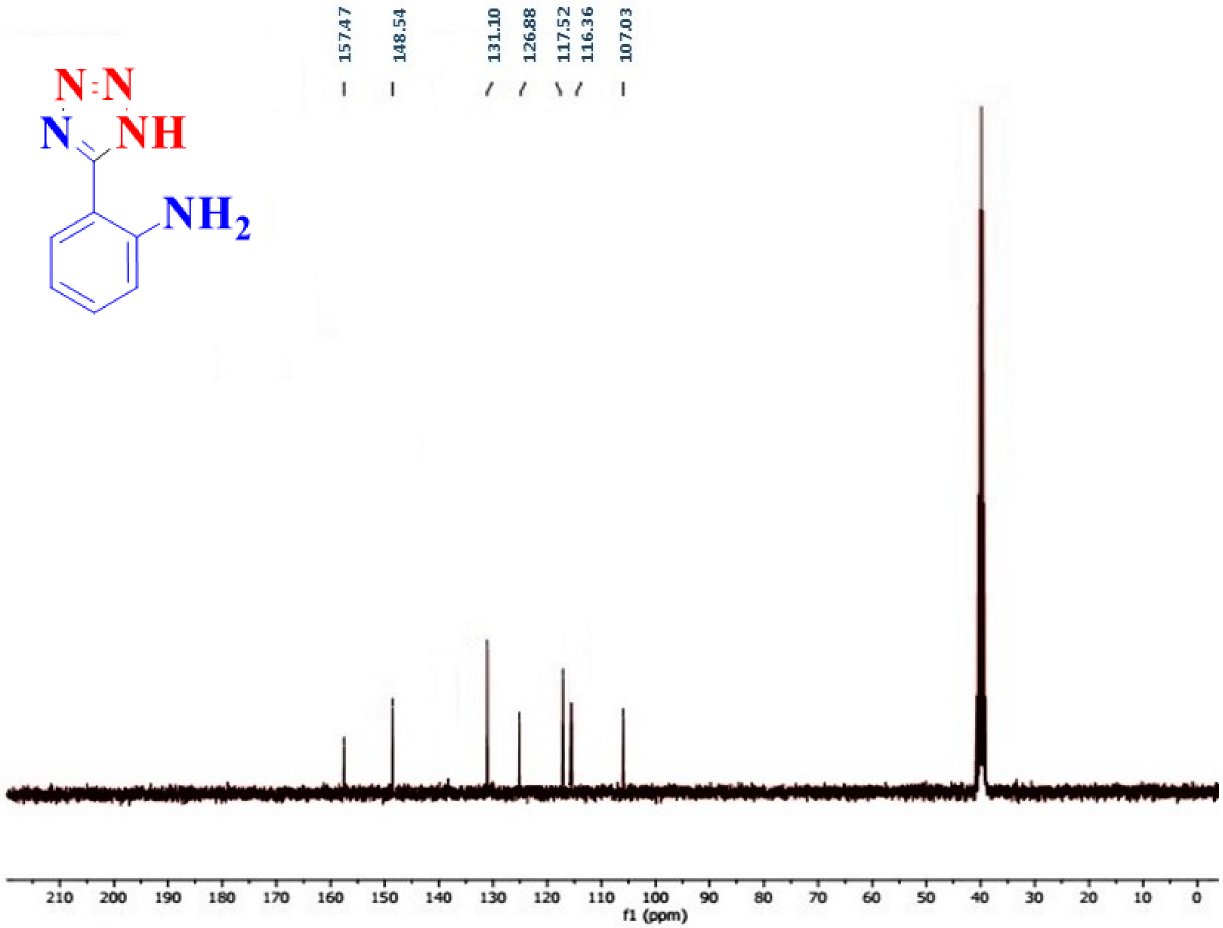


^{1}H NMR spectrum of compound (**5g**)

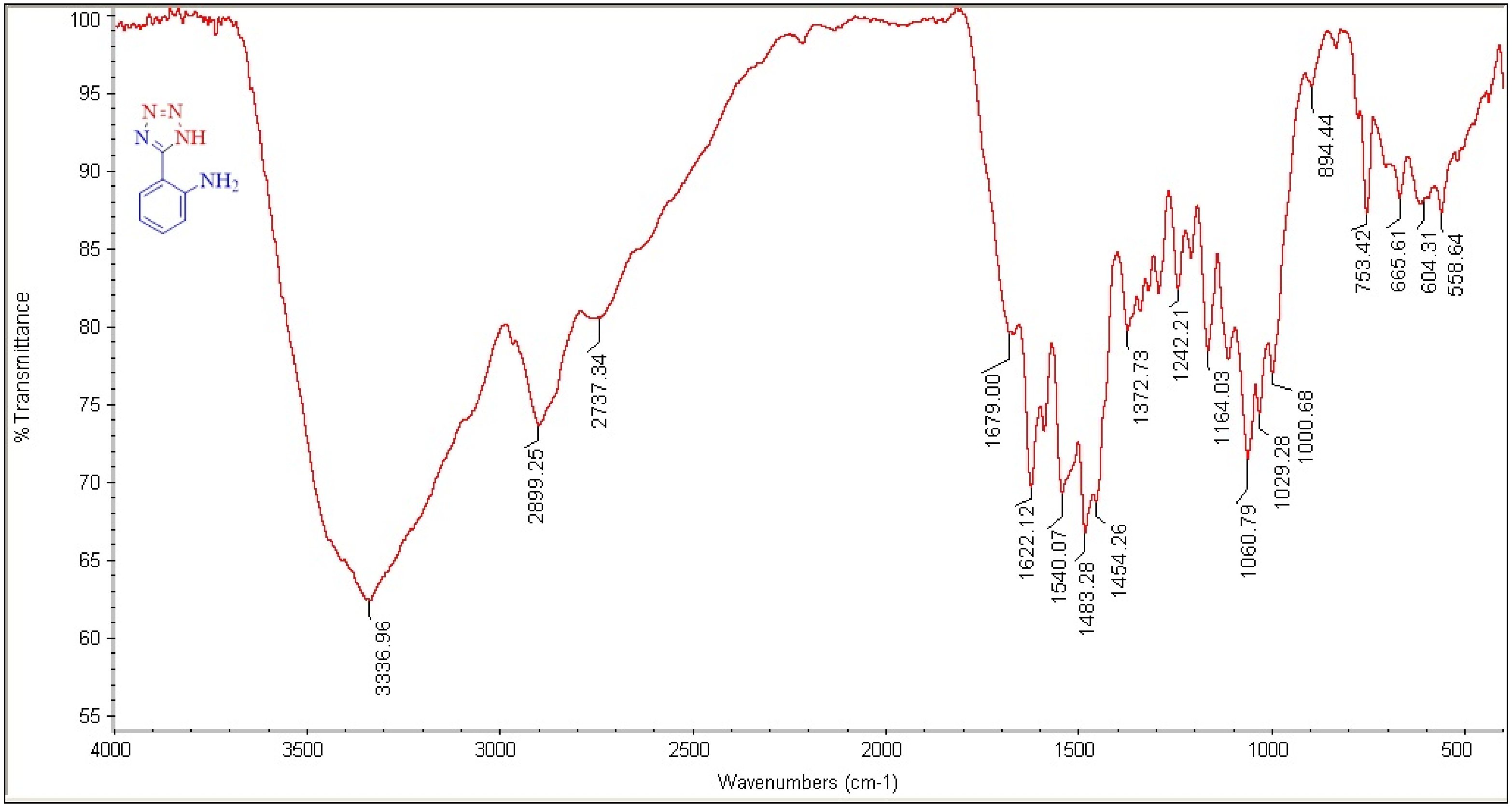



N=N
N
NH
NH2
7.49
7.39
7.31
6.98
6.69
6.68
6.46
6.45
6.44
1.00
1.00
1.02
0.99
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

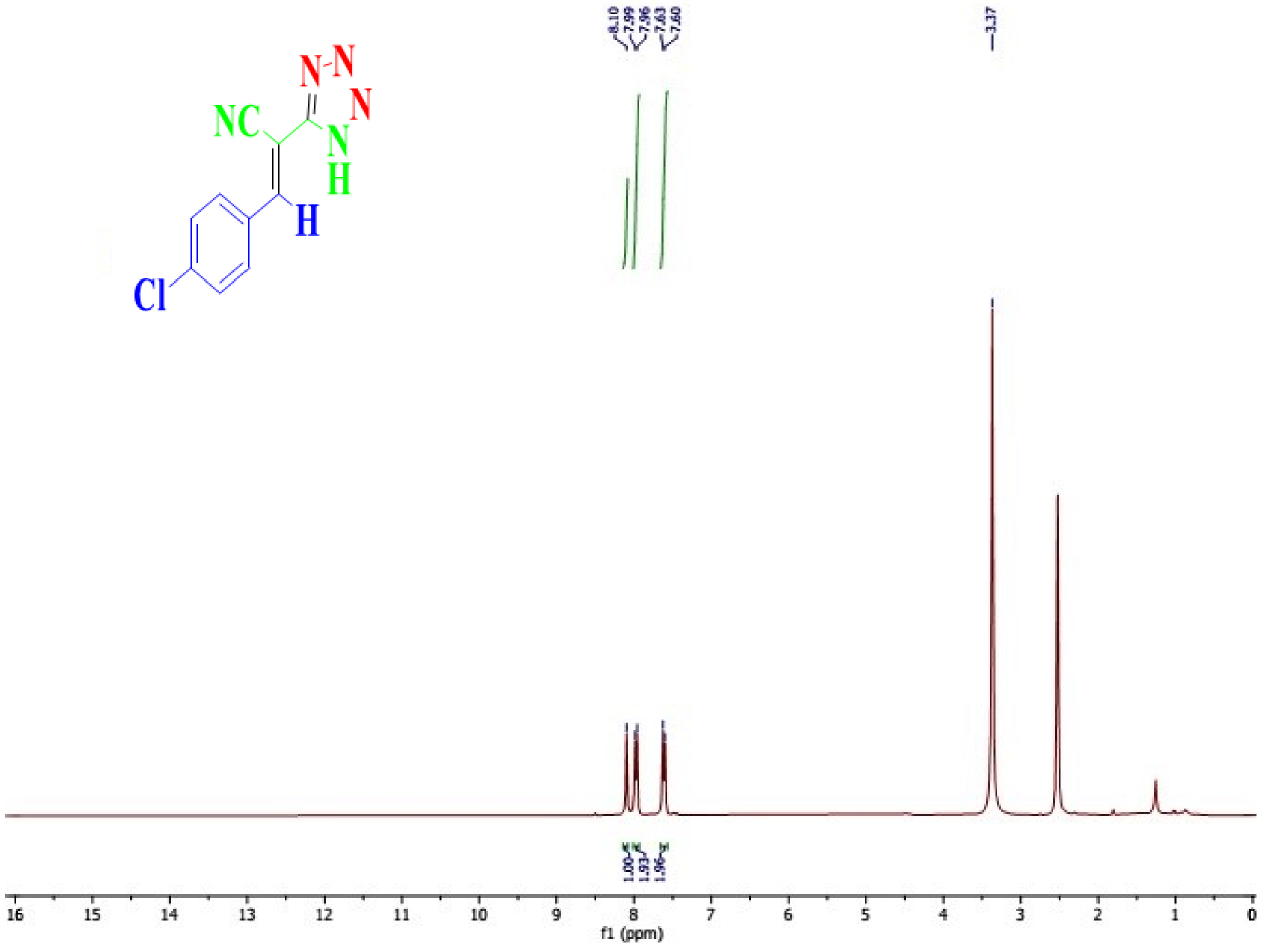
^{13}C NMR spectrum of compound (**5g**)



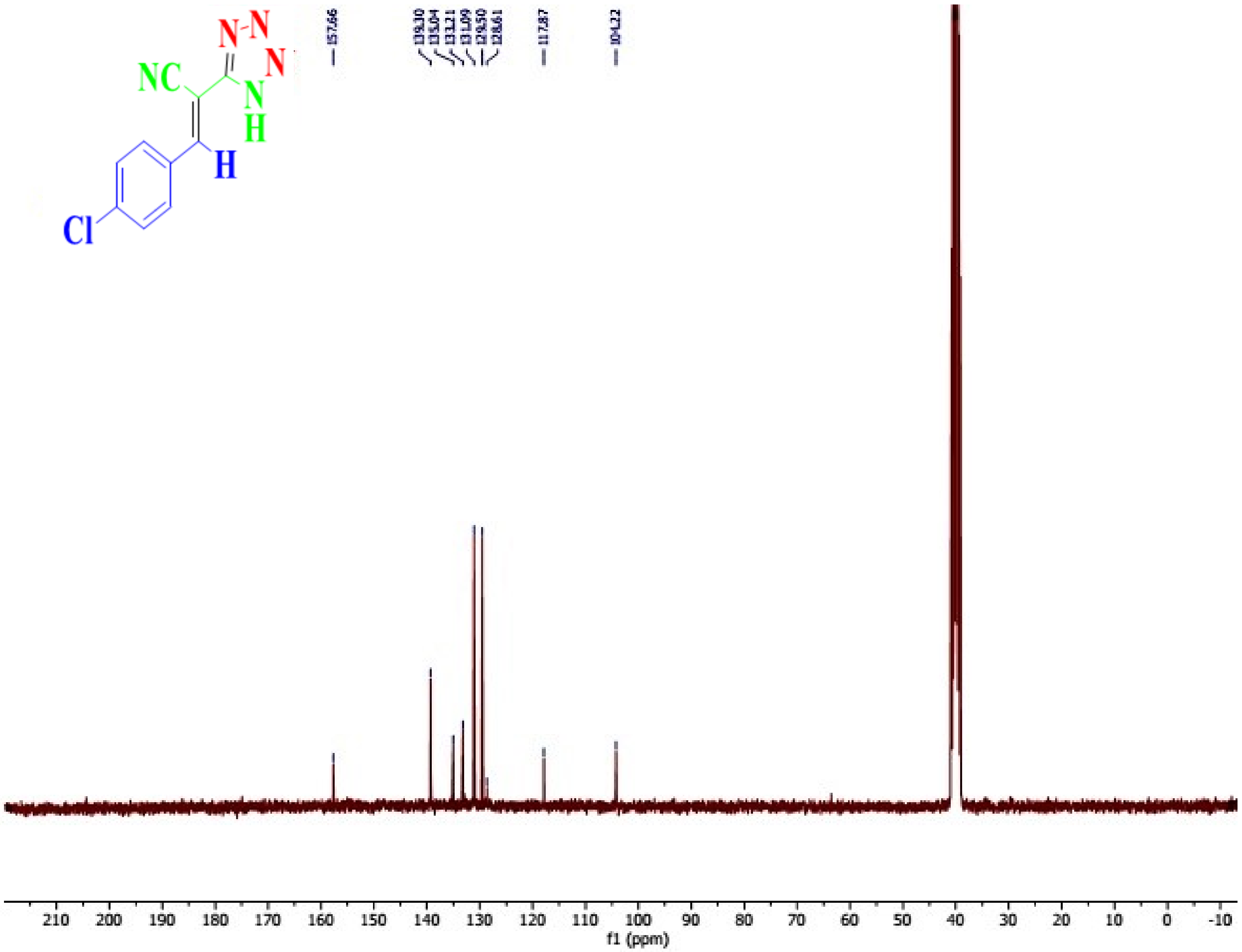
FT-IR spectrum of compound (**5g**)



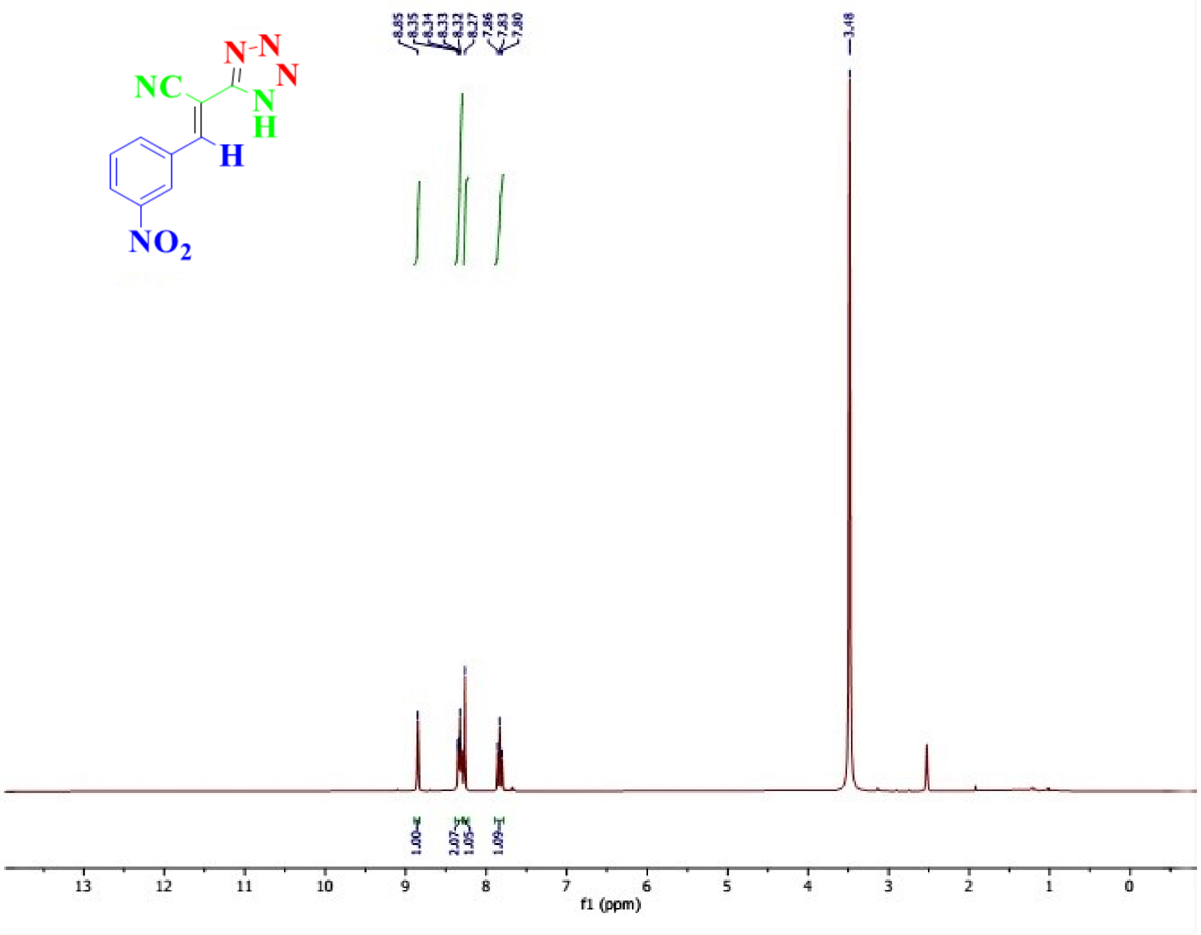
^{1}H NMR spectrum of compound (**6a**)



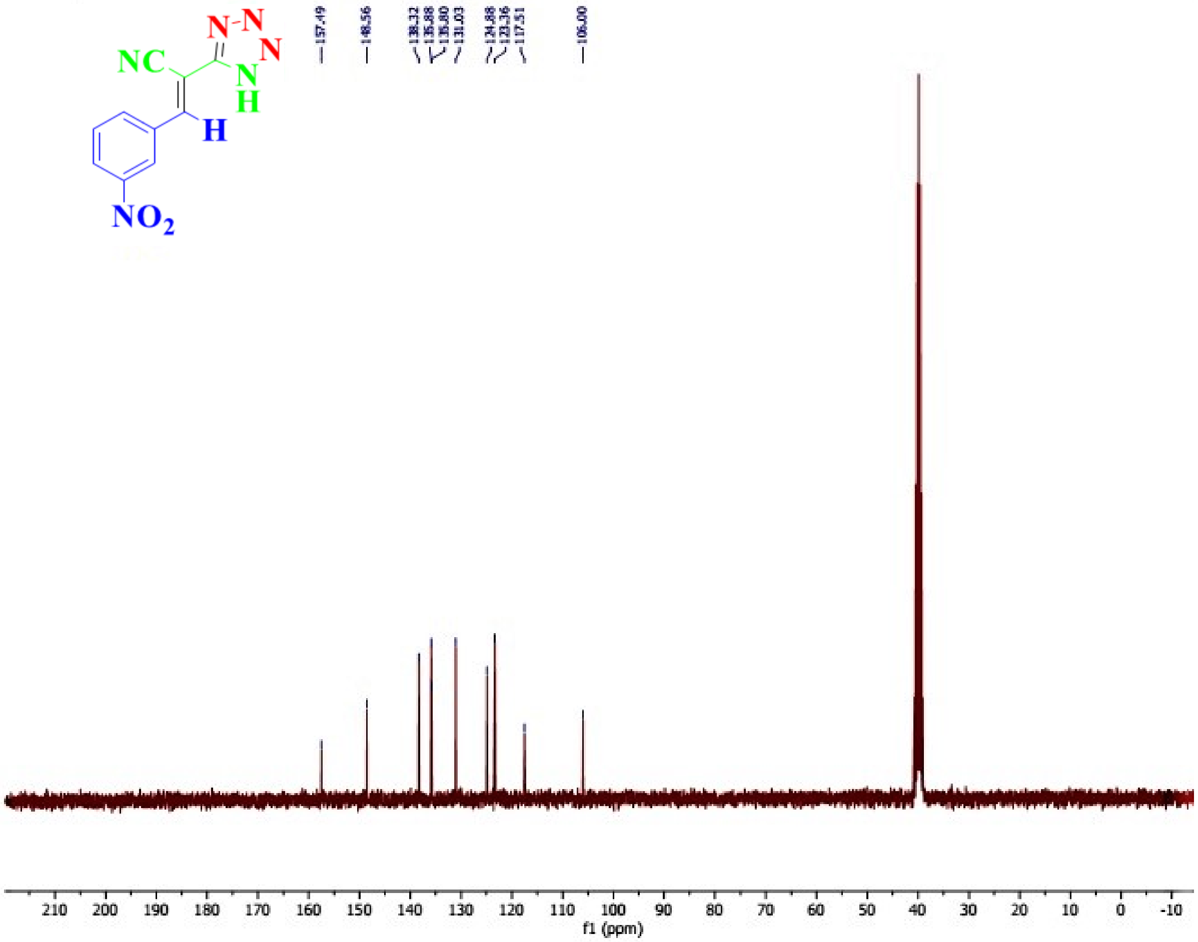
^{13}C NMR spectrum of compound (**6a**)



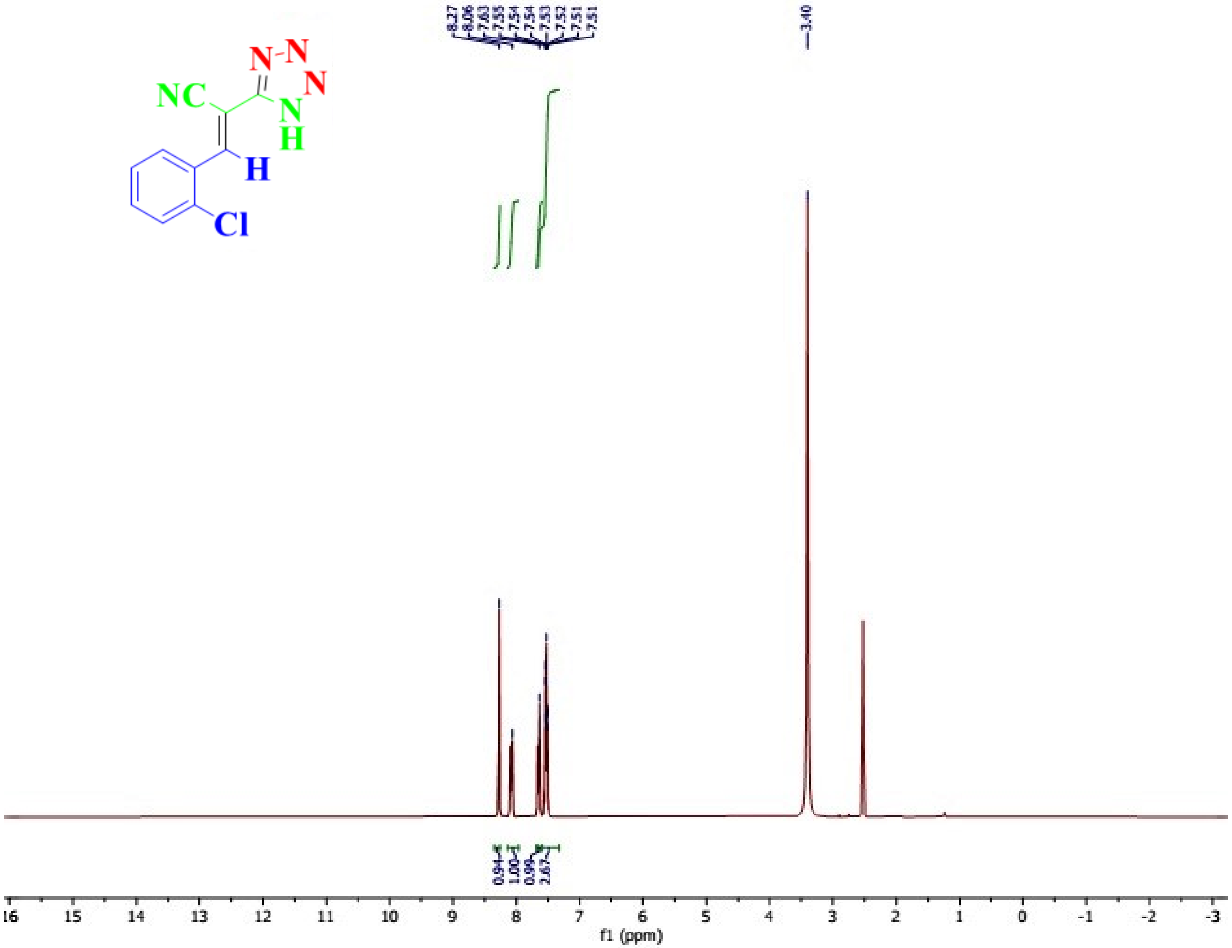
^{1}H NMR spectrum of compound (**6b**)


NC
N
N
N
N
H
H
NO2
8.85
8.35
8.34
8.33
8.32
8.27
7.86
7.83
7.80
3.48
1.00
2.07
1.05
1.09
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

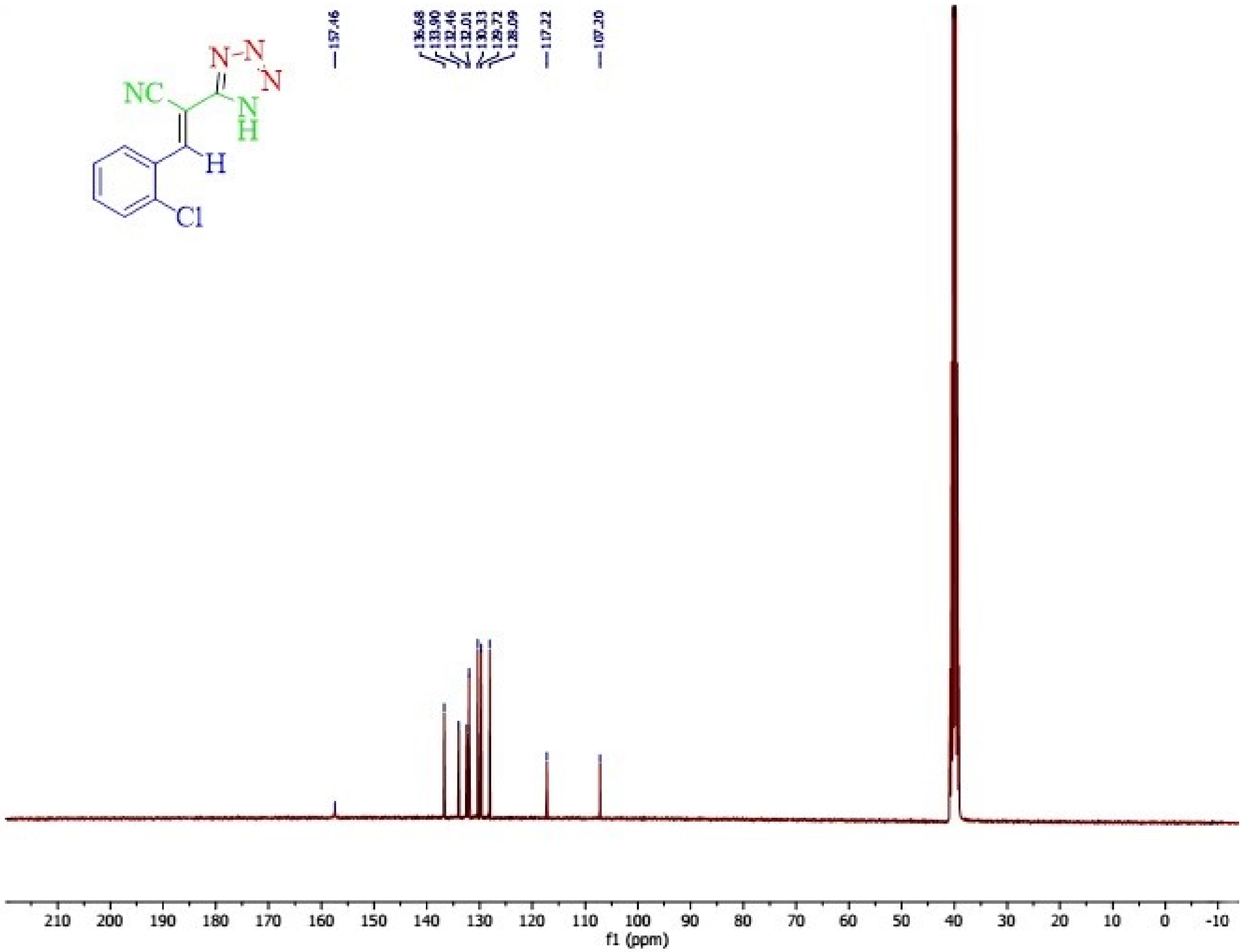
^{13}C NMR spectrum of compound (**6b**)



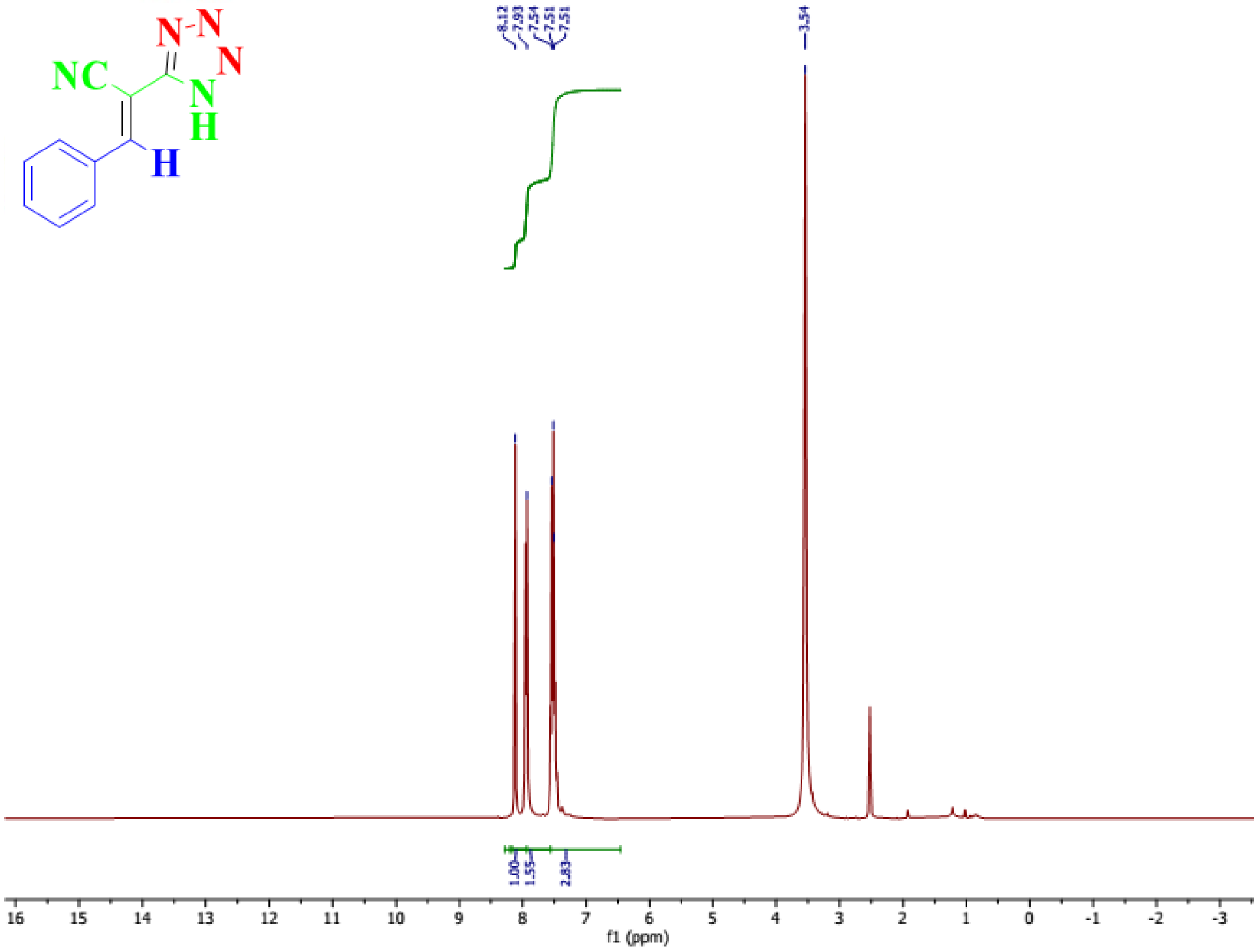
^{1}H NMR spectrum of compound**(6c)**



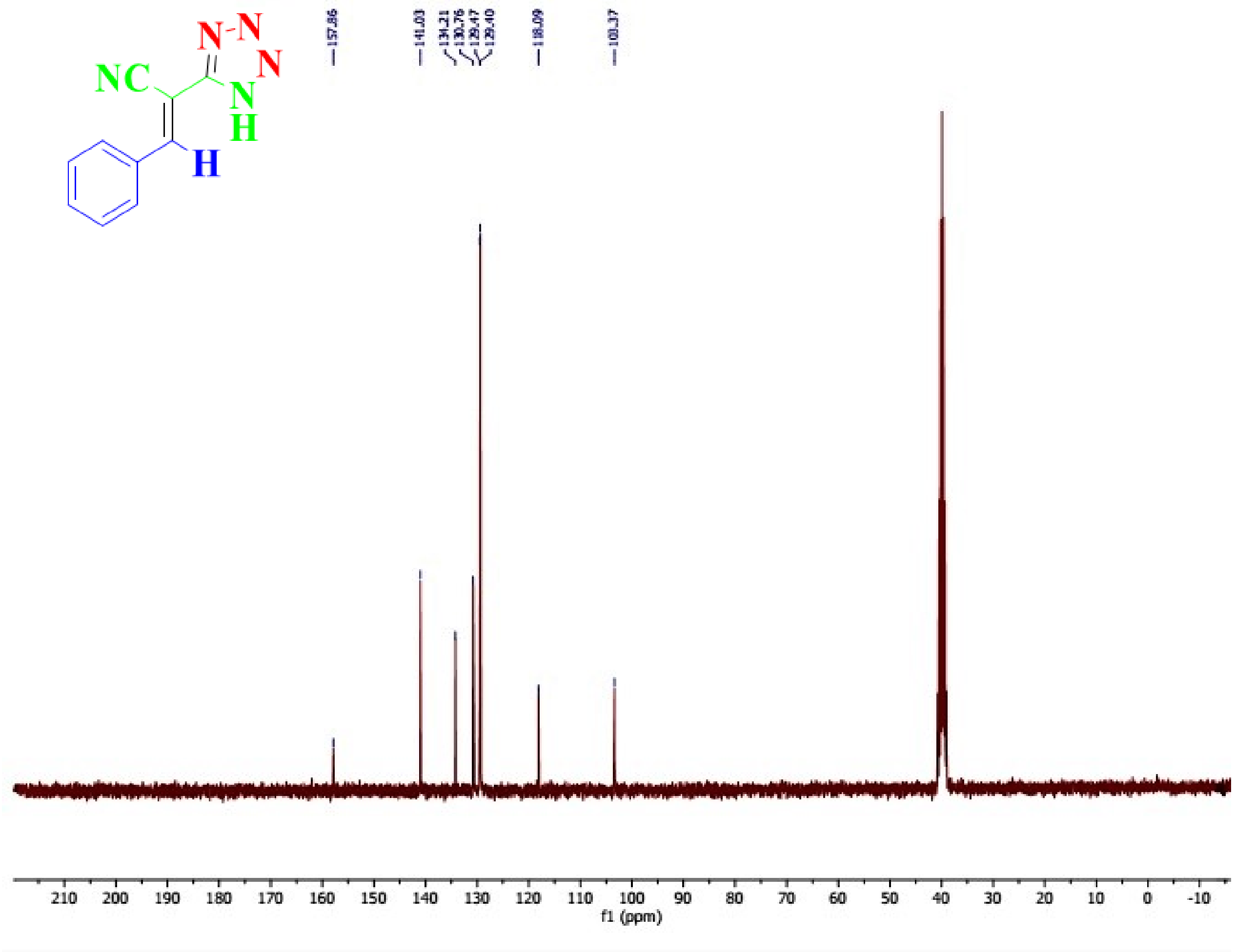
^{13}C NMR spectrum of compound (**6c**)



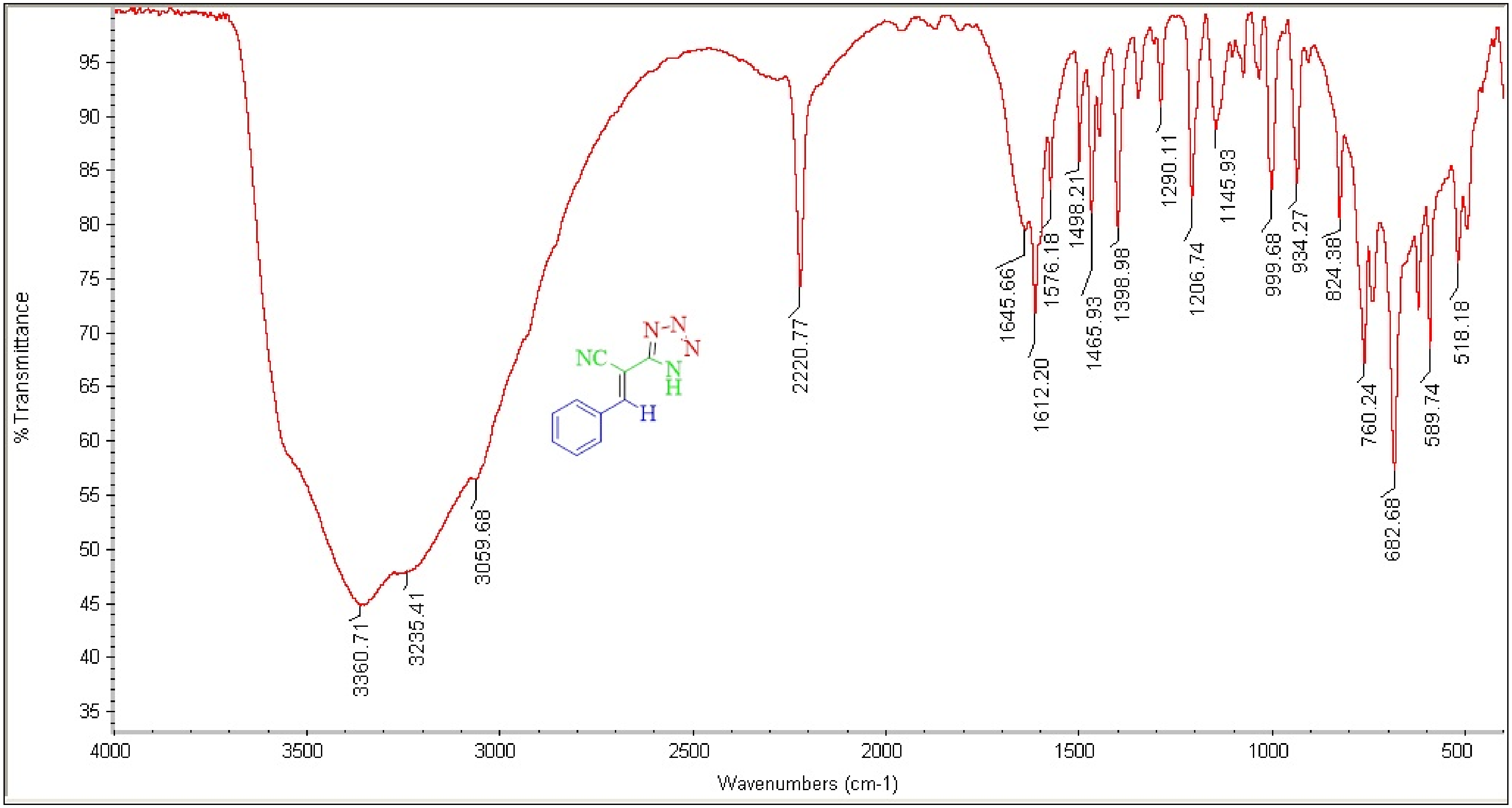
^{1}H NMR spectrum of compound (**6d**)



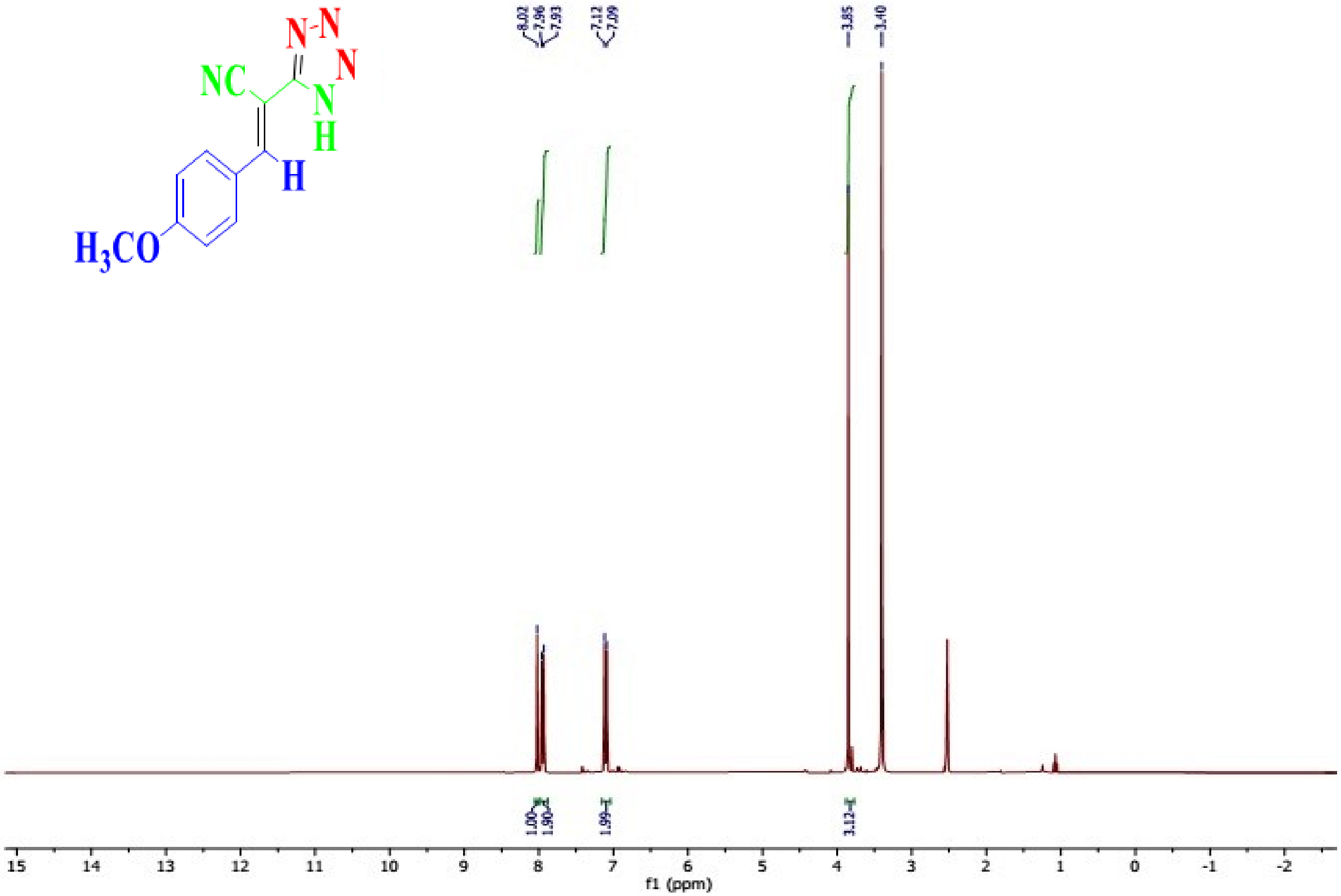
^{13}C NMR spectrum of compound (**6d**)



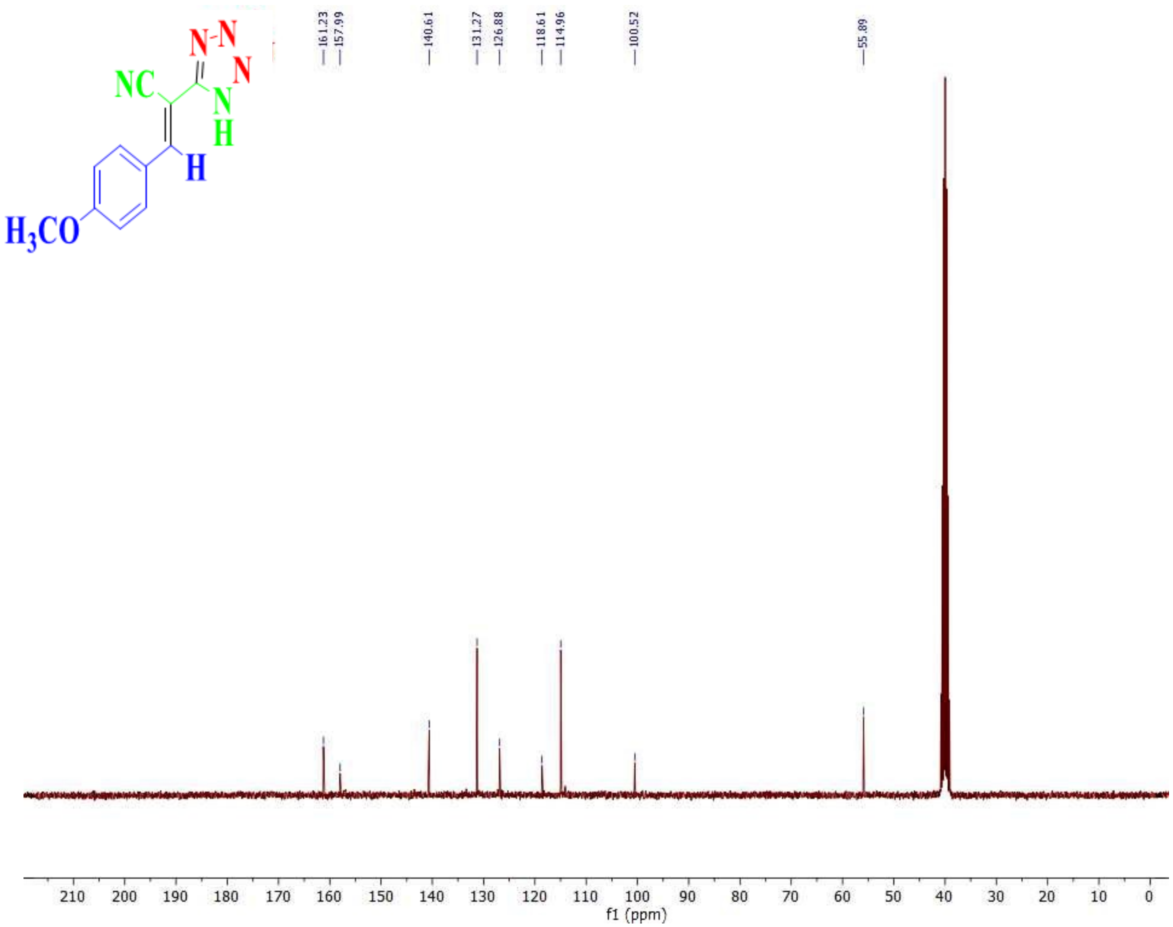
FT-IR spectrum of compound (**6d**)



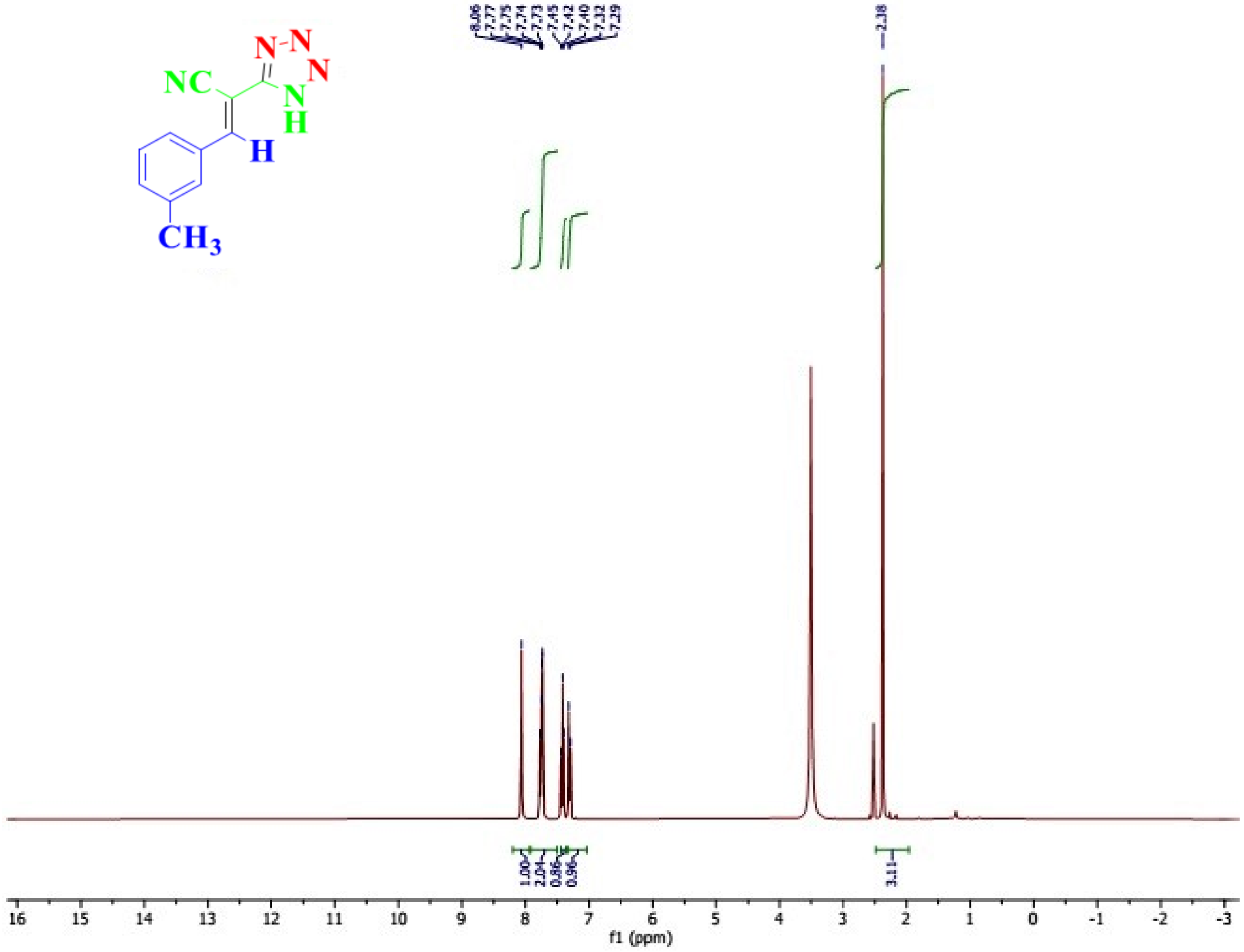
^{1}H NMR spectrum of compound (**6e**)



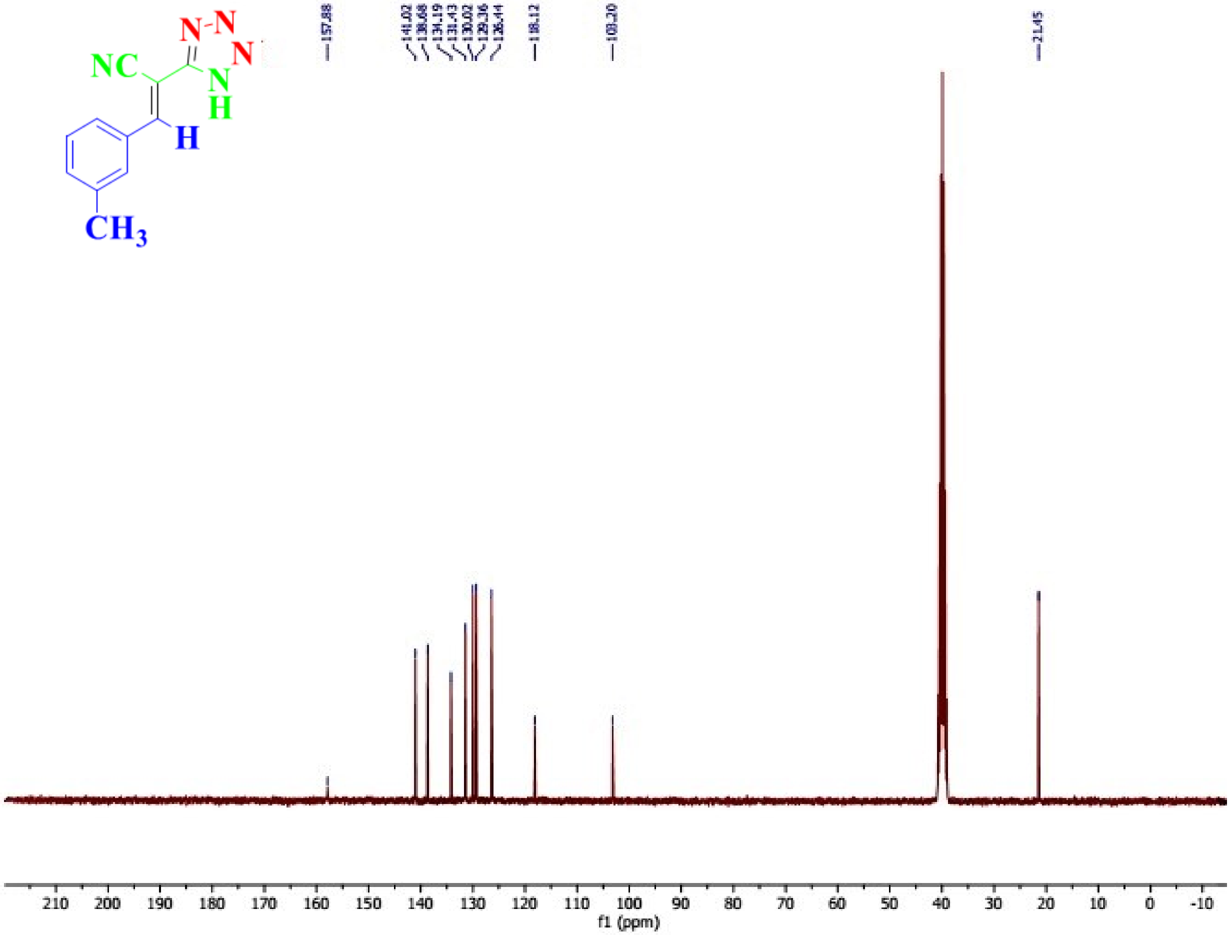
^{13}C NMR spectrum of compound (**6e**)



^{1}H NMR spectrum of compound (**6f**)



^{13}C NMR spectrum of compound (**6f**)



Experimental

General

All reagents were purchased from Merck and Fluka companies and used without further purifications. Organo-modified montmorillonite with benzalkonium chloride was supplied by Nano parmin Khavaran company. The melting points were recorded on an Electro thermal type 9100 melting point apparatus. The IR spectra were obtained on Avatar370 FT-IR Thermo Nicolet, and only noteworthy absorptions are mentioned. The ^{1}H NMR (300 MHz) and the ^{13}C NMR (75 MHz) spectra were recorded on a Brucker DRX-300Avance, using (DMSO-d6) as applied solvent and TMS as internal standard at 300 and 75 MHz, respectively; δ in ppm, J in Hz. The mass spectra were scanned on a Varian Mat CH-7at 70 eV. The size and morphology of the prepared catalysts were studied with TEM (Leo 912AB microscope operated at 120 kV) and FESEM (TESCAN BRNO-Mira3 LMU). The metal loading and leaching were evaluated with ICP-OES analyses (Avio 200 ICP Optical Emission Spectrometer).

The preparation of Immobilized Cu(0) Nanoparticles on Montmorillonite-Modified with Benzalkonium Chloride(MMT-BAC@Cu(0))

$Cu(NO_3)_2.6H_2O$ (100 mL, 0.05 M) aqueous solution was added to MMT-BAC (0.5 g) (benzalkonium has already been modified on the surface, and the MMT-BAC sample was used industrially). The resulting mixture was stirred at 80 °C for 8 hours at a high and uniform speed. Then, $NaBH_4$ (34.0 mmol, 1.32 g) was added. Finally, the resulting mixture was washed several times with deionized water and ethanol after filtering. Then, the resultant precipitation was dried for 14 hours at 50 °C in a vacuum oven, and finally, the catalyst MMT-BAC@Cu(0) was obtained.

The preparation of DES

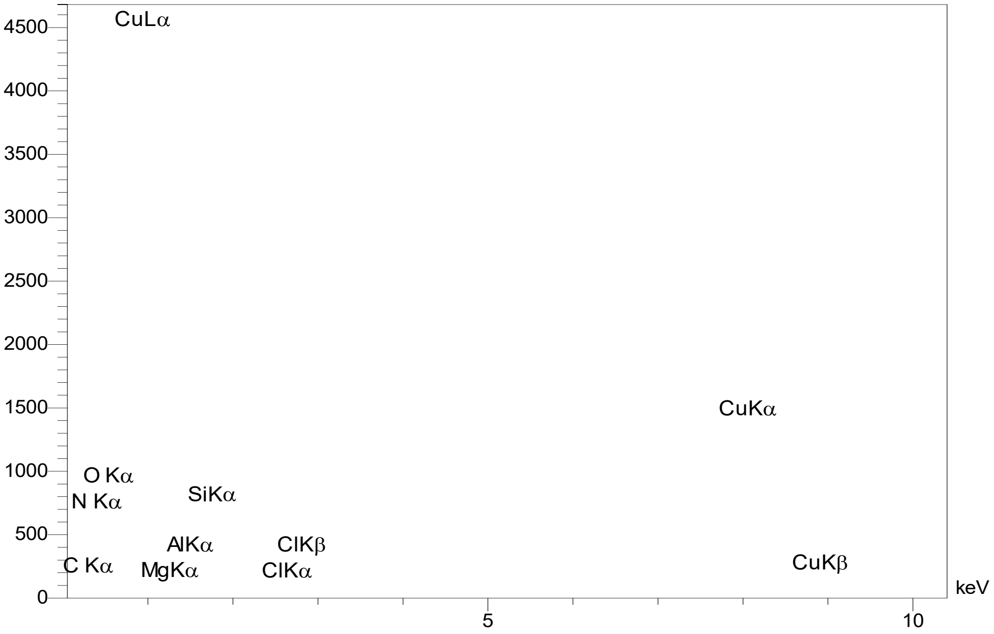
DES (ChCl:Urea) (1:2) were prepared using the method described by Abbott et al. Choline chloride (1.0 mmol, 0.139 g) and urea (2.0 mmol, 0.120 g) were mixed together and heated at 50 °C until a clear homogeneous liquid was formed.

A typical procedure for the preparation of the 5-substituted 1*H*-tetrazole derivatives (5a-g)

Benzonitriles (**2a-g**) (1.0 mmol) and sodium azide (1.0 mmol, 0.065 g), and MMT-BAC@Cu(0) nanocatalyst (0.015 g) in DES (ChCl:Urea) (1:2) (0.5 g) was magnetically stirred at 80 °C for a specifed time (see Table 3). The reaction progress was monitored by TLC. Upon completion of the reaction, the reaction mixture was cooled to ambient temperature, and deionized water (5 mL) was added and stirred for 1 hour. After the separation of the catalyst by filtration, hydrochloric acid solution (10 mL, 5 N) was added to the filterate solution, and the precipitated tetrazole were filtered and recrystallized from ethanol.

A typical procedure for the preparation of the 5-substituted 1*H*-tetrazole derivatives (6a-g)

Aldehydes (**3a-g**) (1.0 mmol), malononitrile (1.0 mmol, 0.066 g), and sodium azide (1.0 mmol, 0.065 g), and MMT-BAC@Cu(0) nanoclay (0.015 g) in DES(ChCl:Urea) (1:2) (0.5 g) was magnetically stirred at 80 °C for a specified time (see Table 3). The reaction progress was monitored by TLC. Upon completion of the reaction, the reaction mixture was cooled to ambient temperature, and deionized water (5 mL) was added and stirred for 1 hour. After the separation of the catalyst by filtration, hydrochloric acid solution (10 mL, 5 N) was added to the filterate solution, and the precipitated tetrazole were filtered and dissolved in hot ethanol. After concentration of solution, purification with column chromatography was carried out with ethyl acetate: n-hexane eluent.



EDS diagram of MMT-BAC@Cu(0) nanoclay

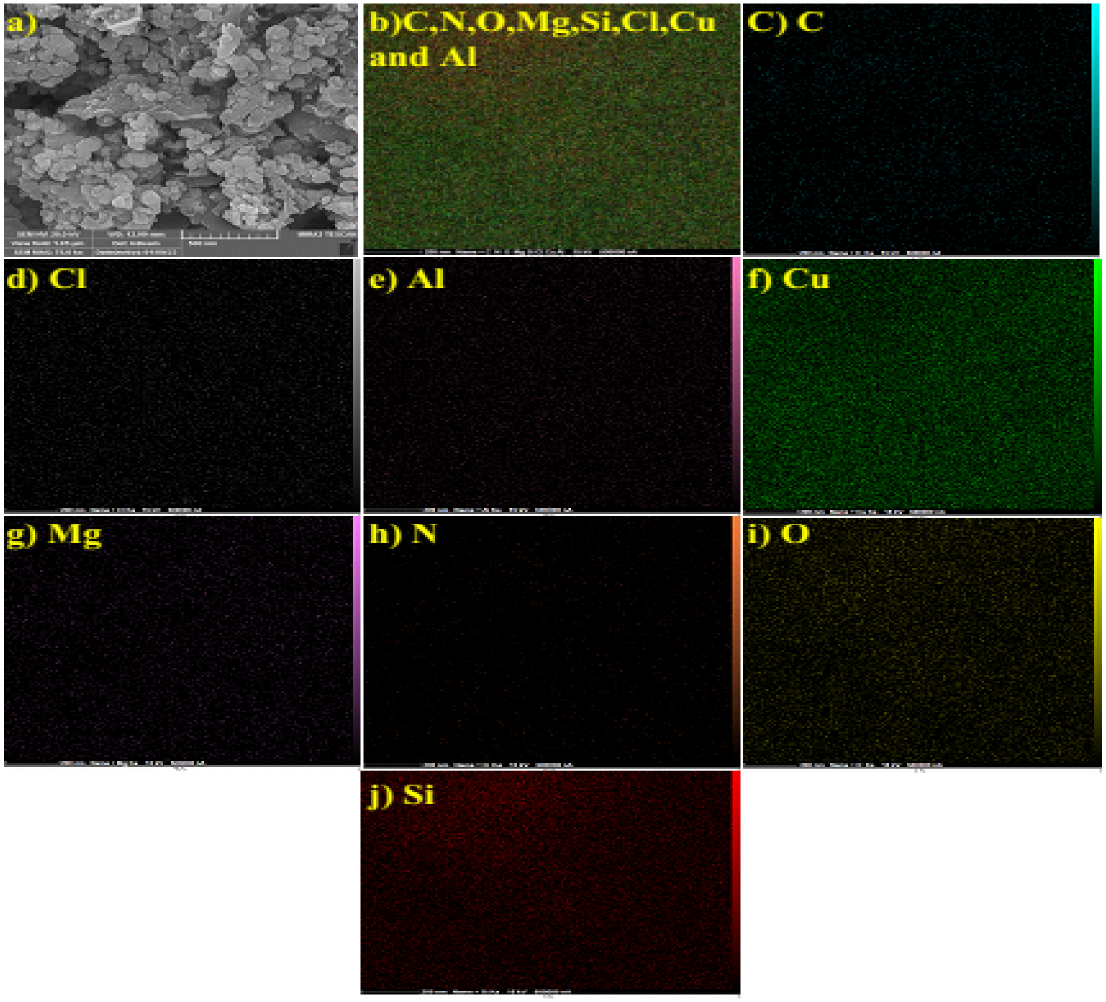
Quantitative Results

Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Pk/Bg	Class	LConf	HConf	Cat#
C	Ka	3.7	3.3661	0.0388	0.0238	10.37	21.58	0.2293		0.00	11.99	A	8.41	12.32	0.00
N	Ka	2.2	3.4218	0.0308	0.0189	6.46	11.53	0.2919		0.00	12.54	A	4.87	8.05	0.00
O	Ka	33.8	3.4774	0.1745	0.1069	27.51	42.99	0.3886		0.00	196.19	A	25.78	29.23	0.00
Mg	Ka	0.8	1.6968	0.0015	0.0009	0.25	0.25	0.3791		0.00	2.31	B	0.15	0.35	0.00
Al	Ka	3.3	1.7224	0.0059	0.0036	0.73	0.67	0.4963		0.00	2.99	B	0.58	0.87	0.00
Si	Ka	15.6	1.7479	0.0295	0.0181	2.86	2.55	0.6322		0.00	6.56	A	2.60	3.13	0.00
Cl	Ka	0.4	0.2554	0.0010	0.0006	0.07	0.05	0.8286		0.00	2.11	B	0.03	0.12	0.00
Cu	Ka	39.5	0.7271	0.7180	0.4400	51.76	20.37	0.8499		0.00	21.18	A	48.75	54.77	0.00
				1.0000	0.6127	100.00	100.00			0.00					0.00

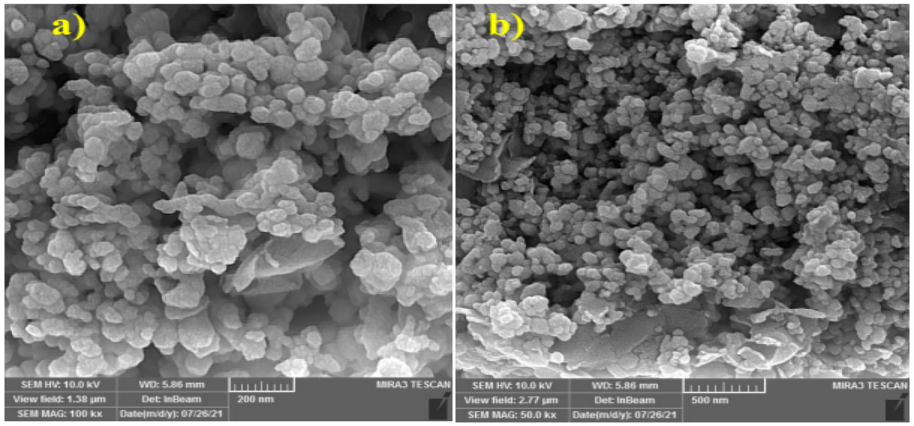
Automatic Identification Results

Elt	Line	Int	keV	Prob%
C	Ka1	9.2	0.290	100
O	Ka1	40.3	0.540	100
Cu	Ka1	36.9	8.010	100
Si	Ka1	19.1	1.740	100
Nb	La1	8.8	2.170	100
Os	La1	1.7	8.850	100
Al	Ka1	3.9	2.699	0

Elemental mapping of MMT-BAC@Cu(0) nanoclay



FE-SEM image of MMT-BAC@Cu(0) nanoclay



TEM image of MMT-BAC@Cu(0) nanoclay