CHAPTER- III

SECTION-B

One-pot Synthesis of 5-substituted-1H-tetrazole from aldehydes Catalyzed by $TiCl_3$

III.B. Present Investigation

III.B.1. Background of the present investigation

Tetrazoles are a class of heterocycles which are receiving considerable attention due to wide range of applications associated with it and the literature having tetrazole chemistry are growing rapidly[1] .Tetrazoles are reported to possess a huge biological activities such as antifungal[2], antibacterial [3], analgesic[4], antiviral, anti-inflammatory, antiulcer [5], and antihypertensive activities[6].Synthetic tetrazole derivatives have also been reported to possess antidiabetic [7], anti-HIV[8] activities and used for treatment of asthma[9]. 5-substituted-1H-tetrazoles can act as lipophilic spacer and carboxylic acid surrogates[10] and used in explosives[11], function as ligands in coordination chemistry[12].In addition, some famous drugs , Pamiroplast, candesartan, valsartan, losartan, and zolarsartan [13] contain tetrazolyl moieties. Traditional synthesis of 5-substituted 1H-tetrazole has been reported to proceed via [3+2] cycloaddition of azide ion with nitrile [14].This procedure suffers from a few drawbacks, e.g. expensive and toxic metal organic azide and nitrile and probability of forming hydrazoic acid which is explosive.There are several catalyst in literature ,e.g. $BF_3.OEt_2$[15], $Pd(OAc)_2/ZnBr_2$[16], $AlCl_3$[17], $Yb(OTf)_3$[18] etc,but there are still a few drawbacks, e.g, tedious separation and recovery of the catalysts.Recently several heterogeneous catalytic system such as nanocrystalline ZnO, Zn/Al HT[19], $FeCl_3/SiO_2$, [20], Cu_2O[21], $CdCl_2$ [22], And metal-modified montmorillonites and zeolite were extensively reported[23]. Many metals, such as Fe, Cu, Mo, V, Zn, Al, Mn, Co were used to improve the effectiveness of montmorillonites[24-31]. These methods also have some drawbacks, such as , these require excess amount of sodium azide, long reaction time, in spite of that , the cycloaddition is too

slow to be practically useful except strong electron withdrawing groups activate the nitrile group. Due to the wide applications of the tetrazole-embedded structures, easy and economical synthetic protocols are still worth exploring[32]. One-pot protocols are particularly important as they get off the isolation of intermediate products[33].One-pot protocols for the synthesis of tetrazole have already been reported in literature using ammonia and iodine[34]. But this methodology should be avoided because this could result in the formation of hydrazoic acid and triiodide monoamine, which are explosive [35]. In view of the availability, lower toxicity and ease of handling of aldehydes as compared to nitriles, the application of aldehydes for the synthesis of tetrazole derivatives are highly attractive and advantageous strategy. Direct transformation of aldehydes to the corresponding tetrazoles via [3+2] cycloaddition is well documented in literature[36-38].Titanium, a very abundant, inexpensive and nontoxic element, has been rarely utilized in organic synthesis. Out of several titanium compounds, a few of them ($TiCl_4$, $TiCl_3$, $TiCl_2(OR)_2$, Cp_2TiCl_2, etc.) are widely used [39]. To the best of our knowledge, $TiCl_3$ has been not yet used for the synthesis of 5-substituted-1H-tetrazole.

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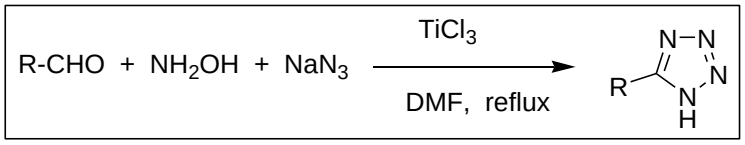
III.B.2. Result and discussion

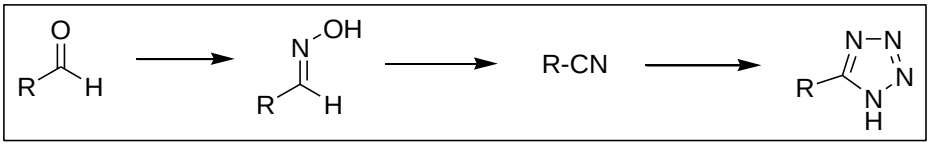
In this connection, herein, we report the protocol, where we used less expensive and easily available starting material aldehydes along with hydroxylamine hydrochloride and sodium azide catalysed by Titanium trichloride resulting in the formation of a number of tetrazole derivatives (1-16) from moderate to excellent yield (**Table. III.B. 1.**). Water solubility of catalyst, non-toxicity, easy work-up, low duration and excellent yield of the products are special feature of this methodology.

The synthesis of tetrazoles (1-16) was achieved by the addition of hydroxylamine hydrochloride, sodium azide, Titanium tri chloride in DMF to various aldehydes and heating at reflux condition to afford the corresponding tetrazoles **(Scheme. III.B. 1.)** after work-up under acidic condition**.** The effect of temperature (Table1), solvent (Table 2) and amount of catalyst (Table3) were monitored. It

was found that DMF was the best solvent (**entry 4, Table. III.B. 2**.). We also optimized the amount of catalyst and it was found to be 20mol% (**entry 4, Table. III.B. 3**.). For the generalization of the reaction, we applied optimized condition i.e. Hydroxylamine hydrochloride (1.2mmol), sodium azide (1.5mmol) and $TiCl_3$ catalyst (20 mol%) under reflux condition to different aldehyde (1mmol) and got 42-95% yield at 3.5-6h (**Table. III.B. 4**.). This strategy applies to all types of aldehydes (aliphatic, aromatic and heterocyclic). The best result was found for aldehydes having electron withdrawing groups.The direct transformation of aldehydes into nitriles is well documented in literature with different reaction conditions [40-42]. Spectroscopic data confirmed the formation of the expected products. The intermediate nitrile is formed first (**Scheme. III.B. 2.**) and then [3+2] cycloaddition reaction takes place between nitrile and azide ion. $TiCl_3$ facilitate the cycloaddition reaction because in absence of $TiCl_3$, only oxime is formed (**Table. III.B. 3., entry 6**).completion of reaction was tested by TLC and after acidic work-up, the desired products were achieved by column chromatography using pet ether and ethyl acetate mixture as eluent.



Scheme. III.B.1. $TiCl_3$ catalyzed one-pot protocol for the conversion of aldehydes into 5-substituted 1H- tetrazole



Scheme. III.B. 2. Proposed reaction intermediate for the synthesis of 5-substituted 1H-tetrazole

Table. III.B. 1: Effect of temperature on the synthesis of 5-substituted 1H-tetrazole[a]

Entry	**Temperature(^{0}C)**	**Yield(%)[b]**
1	Room temp	Nil
2	60	25
3	100	62
4	130	95
5	**reflux**	**95[c]**

[a]Reaction condition: benzaldehyde (1mmol), hydroxylamine hydrochloride (1.2 mmol), sodium azide (1.5mmol), DMF (5ml), $TiCl_3$ catalyst (20mol%) at reflux condition for 4h

[b]Isolated Yield

[c]Optimized condition

Table. III.B. 2: Effect of solvent on the synthesis of 5-substituted 1H-tetrazole[a]

Entry	**Solvent**	**Yield(%)[b]**
1	None	Nil
2	DMSO	60
3	H_2O	20
4	**DMF**	**95[c]**
5	Acetonitrile	30
6	Toluene	Nil
7	THF	Nil

[a]Reaction condition: benzaldehyde (1mmol), Hydroxylamine hydrochloride (1.2mmol), sodium azide(1.5mmol), DMF(5ml), $TiCl_3$ catalyst (20mol%) at reflux condition for 4h

[b]Isolated yield of product

[c]Optimized condition

Table. III.B. 3: Effect of catalyst loading for the synthesis of 5-substituted 1H-tetrazole[a]

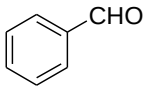
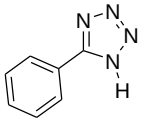
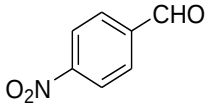
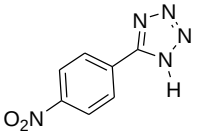
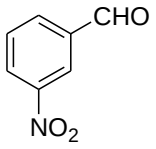
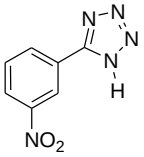
Entry	Catalyst(mol%)	Yield(%)[b]
1	5	40
2	10	67
3	15	95
4	**20**	**95[c]**
5	30	96
6	none	Oxime

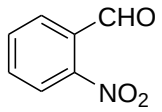
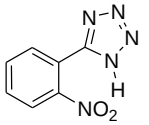
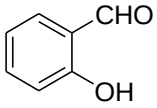
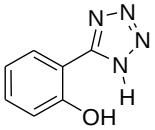
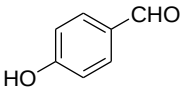
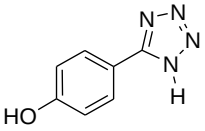
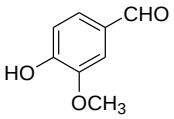
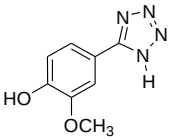
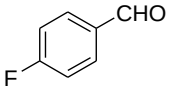
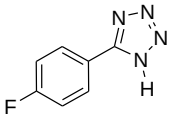
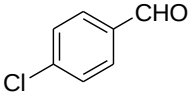
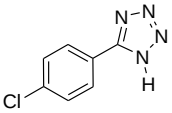
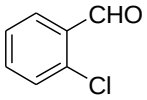
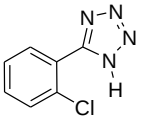
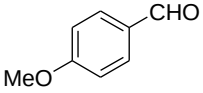
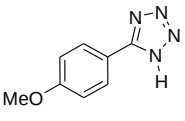
[a]Reaction condition: benzaldehyde (1mmol), Hydroxylamine hydrochloride (1.2mmol), sodium azide (1.5mmol), DMF (5ml), $TiCl_3$ catalyst at reflux condition for 4h

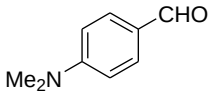
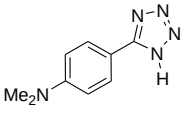
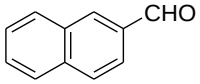
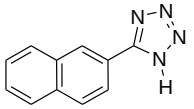
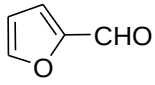
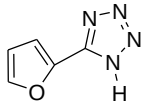
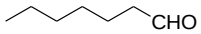
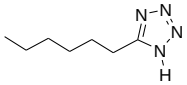
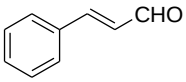
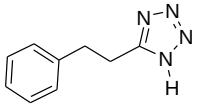
[b]Isolated Yield of Product

[c]Optimized condition

Table. III.B. 4: Synthesis of 5-substituted 1H-tetrazole derivatives[a]

Entry	Reactant	Time(h)	Product	Yield(%)[b]
1		4		86
2		3.5		84
3		3		95

4		4		61
5		5		74
6		4		76
7		5		71
8		3.5		92
9		3		89
10		5		52
11		5		75

12		5.5		82
13		3.5		85
14		3		79
15		6		42
16		4		81

[a]Aldehyde (1mmol), hydroxylamine hydrochloride (1.2 mmol), sodium azide (1.5 mmol) and Titanium trichloride (20mol%) in DMF(5ml) under reflux condition.

[b]Isolated yield

III.B.3. Experimental

III.B.3.1. Chemicals

All the chemicals used for the present investigation are mentioned in **table .III.B.5.**

The source of the chemicals and their purity are listed in **table. III.B.5.**

Table. III.B.5.

Chemicals required for present investigation

Entry	Chemical	Source	Purity(%)
1	Benzaldehyde	Sigma-Aldrich	98
2	4-Nitrobenzaldehyde	LOBA Chemie	98
3	3-Nitrobenzaldehyde	LOBA Chemie	98
4	2-Nitrobenzaldehyde	LOBA Chemie	98
5	2-hydroxybenzaldehyde	S.D. Fine	99
6	4-Hydroxybenzaldehyde	S.D. Fine	98
7	3-Methoxy-4-hydroxy benzaldehyde	S.D Fine	99
8	4-Fluoro benzaldehyde	Fisher Scientific	98
9	4-Chlorobenzaldehyde	S.D.Fine	98
10	2-Chlorobenzaldehyde	S.D.Fine	97
11	4-Methoxybenzaldehyde	S.D.Fine	98
12	N, N-dimethyl-4-aminobenzaldehyde	Sigma-Aldrich	99
13	2-Napthaldehyde	Sigma-Aldrich	98
14	Furfural	Sigma-Aldrich	99
15	Heptaldehyde	Spectrochem	97
16	Cinnamaldehyde	Sigma-Aldrich	98
17	Hydroxylamine hydrochloride	Fisher Scientific	96
18	Sodium azide	LOBA Chemie	99
19	Titanium trichloride	LOBA Chemie	15% solution
20	DMF	Merk	99
21	Sodium sulphate anhydrous	SRL	99.5
22	Petrolium ether	T.B	98
23	Ethylacetate	T.B	99
24	Silica-gel 60-120 mesh for column	SRL	-
25	Silica gel for TLC	SRL	-
26	Potassium bromide for IR	Merk	99
27	DMSO-d_6 for NMR	ACROS	99.8

28	$CDCl_3$ for NMR	ACROS	99.8

III.B.3.2. Reaction procedure and purification

Aldehyde (1mmol), hydroxylamine hydrochloride (1.2mmol), sodium azide (1.5mmol) and titanium trichloride (20 mol%) were added to 5ml DMF and the mixture was kept on reflux for requisite time (Table 4). The progress of reaction was monitored by TLC and after completion of reaction, the mixture was treated with HCl (5ml dil.HCl), thereafter the mixture was added to 100ml water and extracted with ethylacetate, washed by water a few times. The extract was dried over anhydrous Na_2SO_4, purified by column chromatography on silica-gel (60-120 mesh) by pet-ether and ethyl acetate (75:25) as eluent.

III.B.3.3. Spectroscopic measurements

All melting points were determined by open capillary method. IR spectra were recorded on KBr disks on Shimadzu 8300 spectrometer. ^{1}H and ^{13}C NMR were recorded on 300 MHz Bruker Avance FT NMR spectrometer using TMS as internal standard.

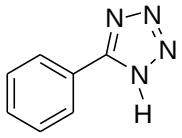
III.B.4. Conclusion

In conclusion, we have explored a lewis-acid, titanium trichloride catalyzed one-pot facile synthesis of 5-substituted 1H-tetrazole from easily available aldehyde (aromatic, aliphatic, heterocyclic), hydroxylamine hydrochloride and sodium azide under reflux condition. Advantages of this methodology are, no use of harmful organic solvent and toxic catalyst, which causes environmental pollution, easy work-up process and excellent yield of products.

III.B.5. Characterization data

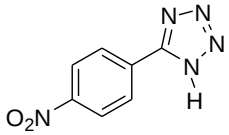
Spectroscopic data of 5-substituted 1H-tetrazole derivatives

1. 5-phenyl-1H-tetrazole



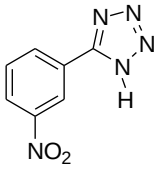
White solid; M.P: 211 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.59–7.65 (m, 3H), 8.04–8.08 (m, 2H).[1] ^{13}C NMR (75 MHz, DMSO-d_6): δ= 126.92, 127.40, 128.15, 129.38, 131.19, 134.23, 155.14

2. 5-(4-nitrophenyl)-1H-tetrazole



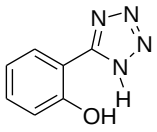
Yellow solid; M.P: 215 ^{o}C. ^{1}H NMR (400MHz, DMSO-d_6): δ = 8.46 (d, J = 8.84 Hz, 2H), 8.32 (d, J = 8.92 Hz, 2H); ^{13}C NMR (75MHz, DMSO-d_6): δ = 123.74, 124.82, 128.43, 129.28, 148.94, 156.02 (C=N), 162.76

3. 5-(3-nitrophenyl)-1H-tetrazole



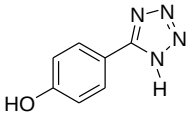
Yellow solid, M.P: 107 ^{o}C. ^{1}H NMR (400MHz, DMSO-d_6): δ = 8.85 (s, 1H), 8.43–8.50 (m, 2H), 7.90–7.94 (m, 1H).[1] ^{13}C NMR (75MHz, DMSO-d_6): δ = 125.05, 129.14, 129.76, 134.79, 136.59, 151.82, 158.64.

4. 2-(1H-tetrazol-5-yl) phenol



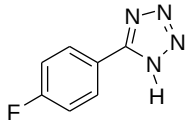
White solid powder; M.P: 217 ^{o}C. ^{1}H NMR (300MHz, DMSO-d_6): δ =7.18 (q, J = 10.2, 2H), 7.54 (s, 1H), 8.14 (d, J = 7.2, 1H). ^{13}C NMR (75MHz, DMSO-d_6): δ = 110.94, 116.81, 120.16, 129.50, 133.08, 152.10, 155.76.

5. 4-(1H-tetrazol-5-yl) phenol



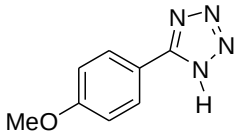
Yellow solid; M.P: 230 ^{o}C. ^{1}H NMR (300MHz, DMSO-d_6): δ = 6.95 (d, J = 6.8, 2H), 7.62 (d, J = 7.8, 2H). ^{13}C NMR (75MHz, DMSO-d_6): δ =115.16, 116.61, 129.22, 130.82, 155.45 (C=N), 160.55.

6. 5-(4-fluorophenyl)-1H-tetrazole



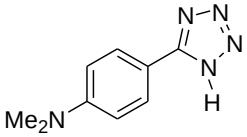
Yellow solid; M.P: 185 ^{o}C.^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.90-8.02 (m, 2H), 7.15-7.33 (m, 2H). ^{13}C NMR (75MHz, DMSO-d_6): δ = 116.64, 121.22, 130.47, 155.14, 165.68

7. 5-(4-methoxyphenyl)-1H-tetrazole



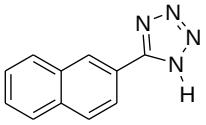
Yellow solid; M.P: 225 ^{o}C. ^{1}H NMR (400MHz, DMSO-d_6): δ = 3.85 (s, 3H), 7.97–8.01 (m, 2H), 7.16–7.19 (m, 2H).[1] ^{13}C NMR (75MHz, DMSO-d_6): δ = 55.70, 113.84, 114.79, 126.76, 128.48, 129.82, 162.11, 162.95.

8. 5-(N, N-dimethyl-4-phenyl)-1H-tetrazole



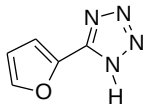
Brownish solid, ^{1}H NMR (300MHz, DMSO-d_6): δ = 3.03 (s, 6H), 6.81 (d, J = 8.4, 2H), 7.83 (m, 2H). ^{13}C NMR (75MHz, DMSO-d_6): δ = 111.14, 121.22, 128.48, 152.36, 155.42.

9. 15-(naphthalene-3-yl)-1H-tetrazole



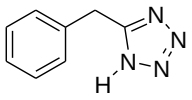
Yellow solid; M.P: 209 ^{o}C ^{1}H NMR (300MHz, DMSO-d_6): δ = 7.65 (d, 2H), 8.03-8.26 (m, 2H), 8.67 (s, 1H); ^{13}C NMR (75MHz, DMSO-d_6): δ = 122.19, 124.27, 127.81, 128.44, 129.22, 129.76, 133.25, 134.48, 155.14

10. 5-(furan-2-yl)-1H-tetrazole



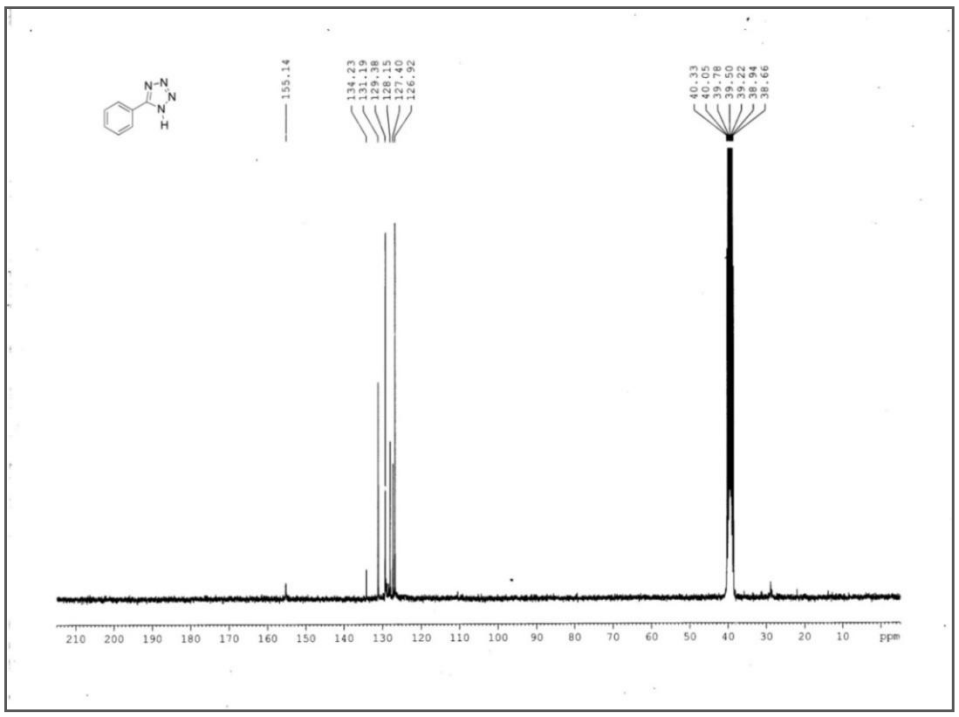
Yellow solid; M.P: 201 ^{o}C. ^{1}H NMR (300MHz, DMSO-d_6): δ = 6.33-7.10 (m, 1H), 7.20-7.34 (m, 1H), 7.52-8.07 (m, 1H); ^{13}C NMR (75MHz, DMSO-d_6): δ = 112.86, 113.42, 140.30, 146.40, 148.70

11. 5-benzyl-1H-tetrazole

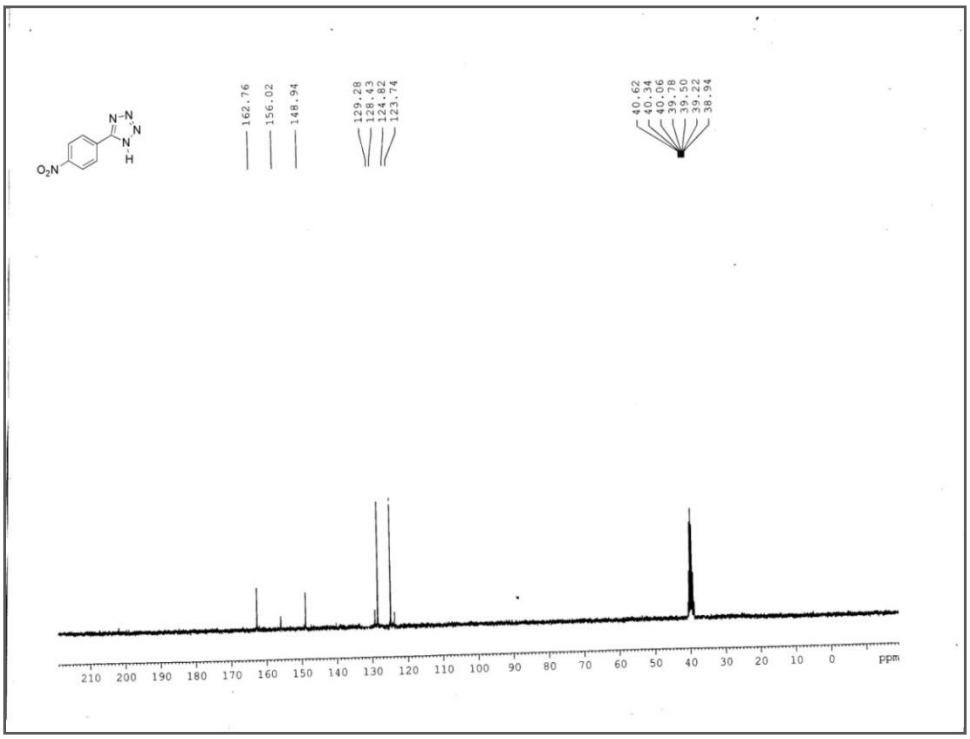


White solid; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 4.34 (s, 2H), 7.33-7.38. ^{13}C NMR (75MHz, DMSO-d_6): δ = 29.33, 127.47, 129.11, 129.18, 155.68.

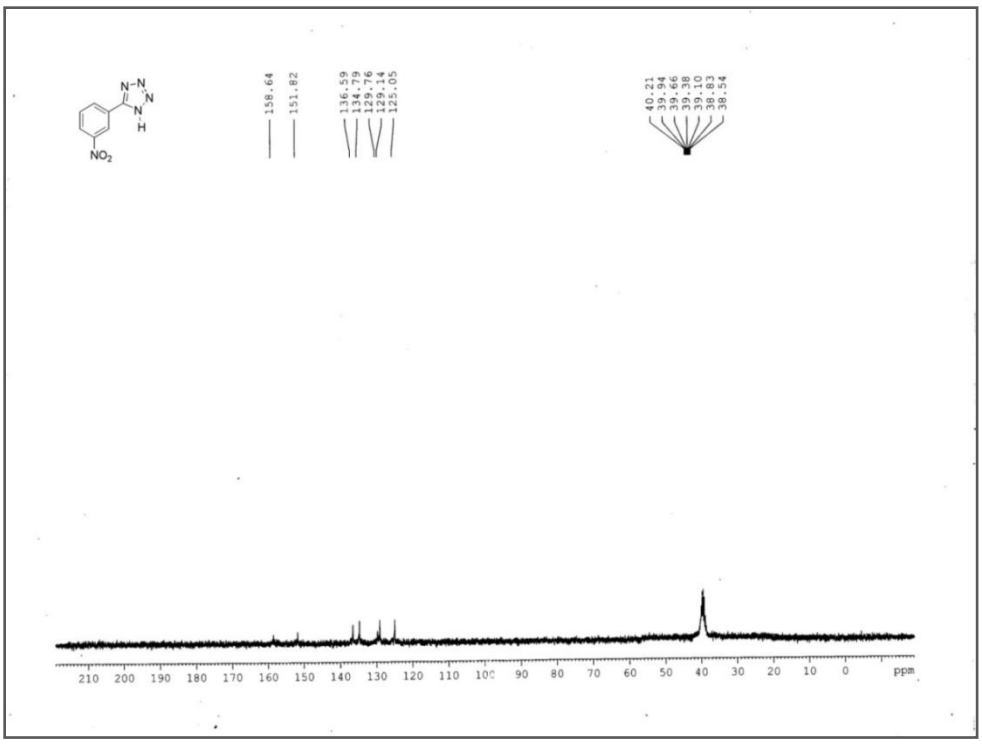
III .B.6. Supporting Spectra



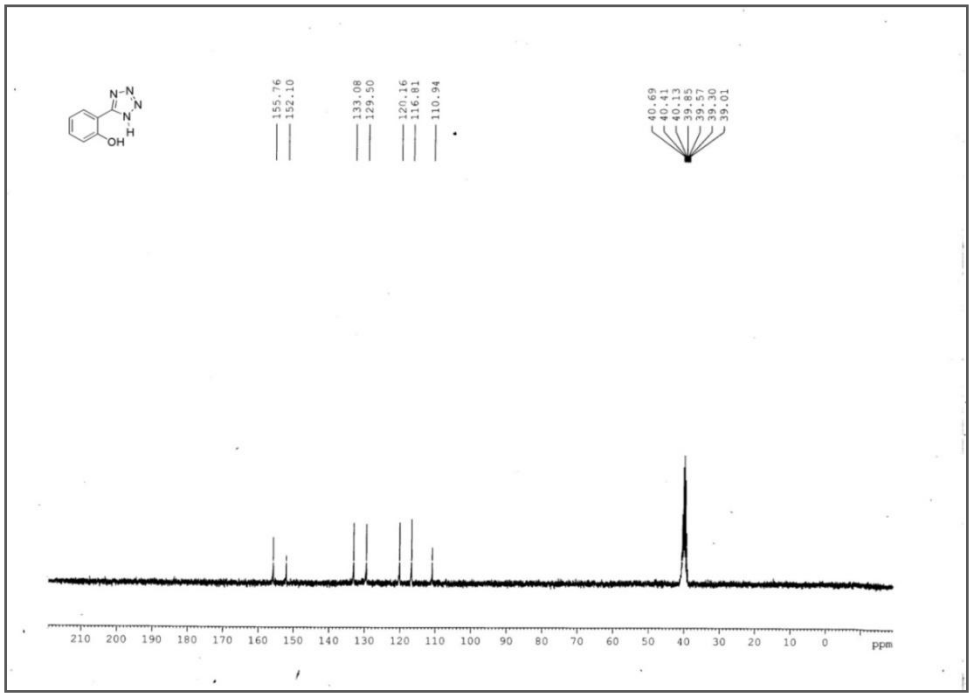
III.B.6.1. ^{13}C NMR spectrum of 5-phenyl-1H-tetrazole



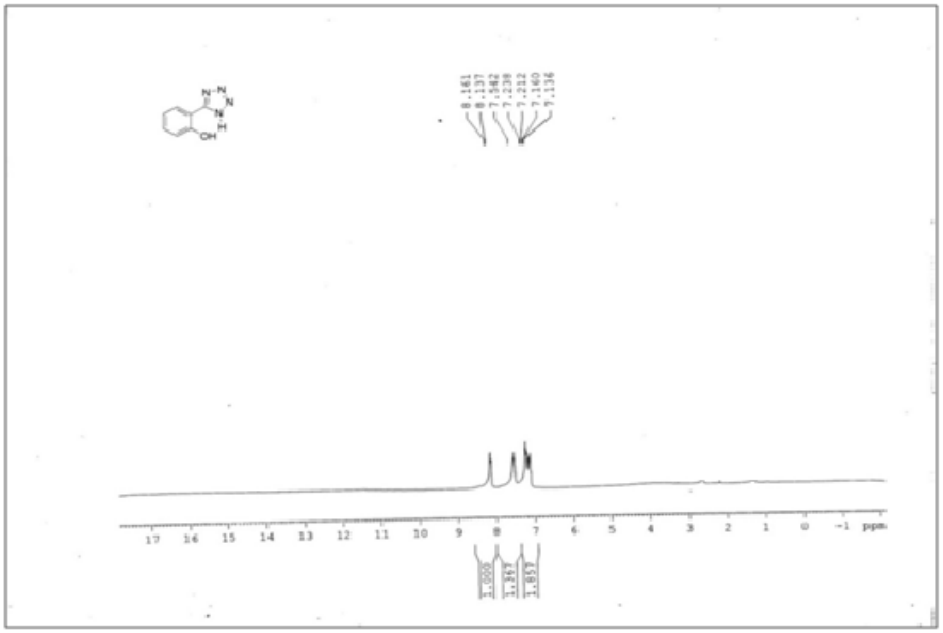
III.B.6.2. ^{13}C NMR spectrum of 5-(4-nitrophenyl)-1H-tetrazole



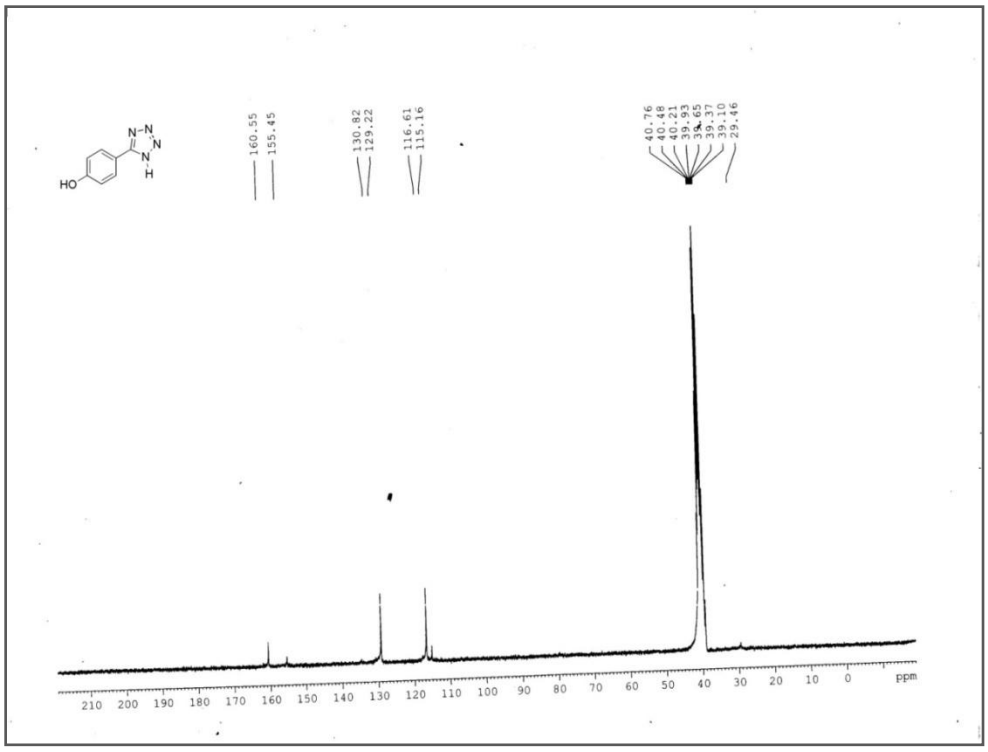
III.B.6.3. ^{13}C NMR spectrum of 5-(3-nitrophenyl)-1H-tetrazole



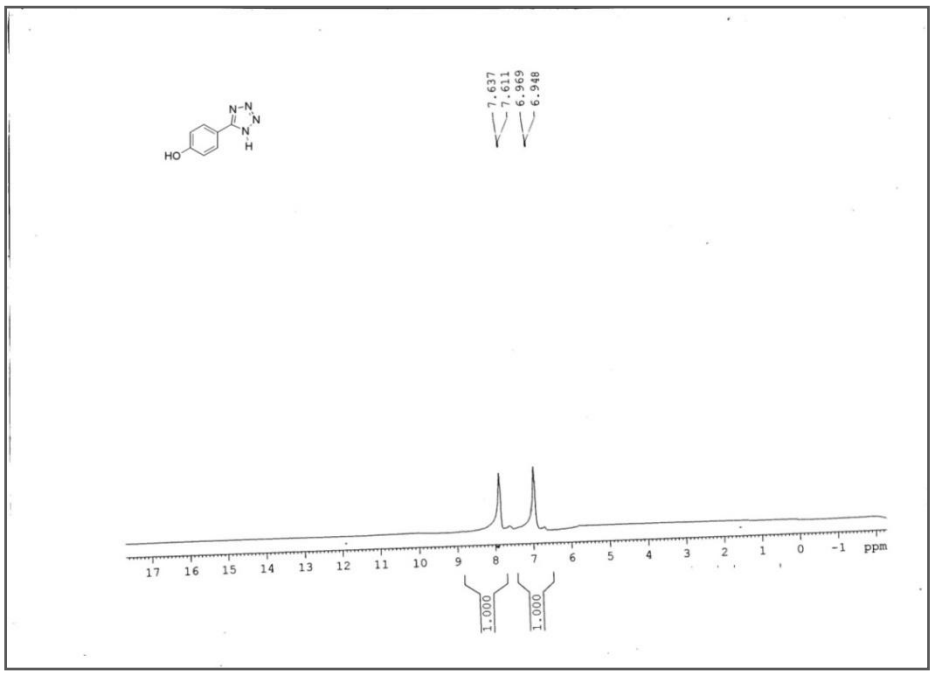
III.B.6.4. ^{13}C NMR spectrum of 2-(1H-tetrazol-5-yl) phenol



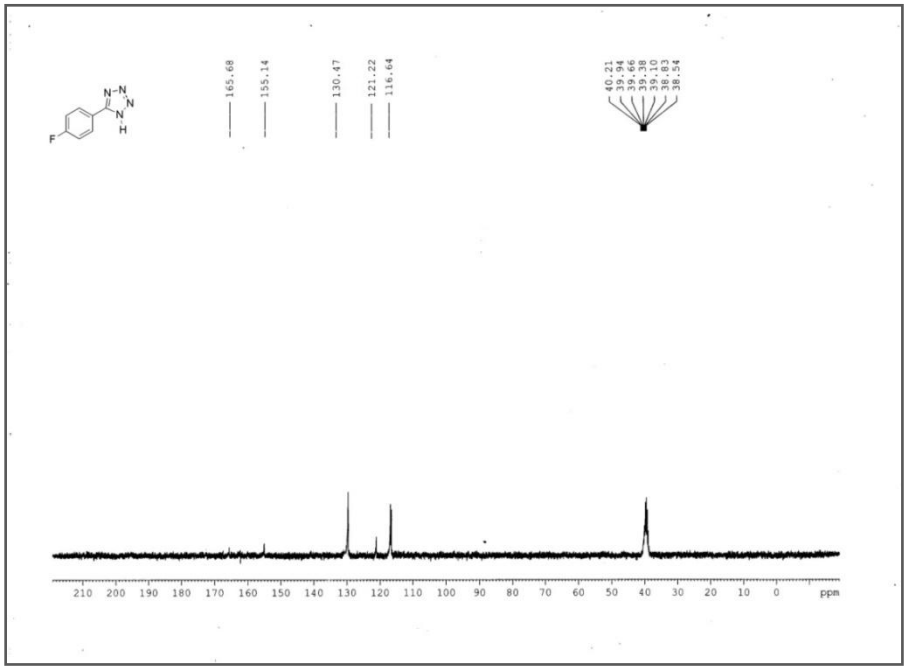
III.B.6.5. ^{1}H NMR spectrum of 2-(1H-tetrazol-5-yl) phenol



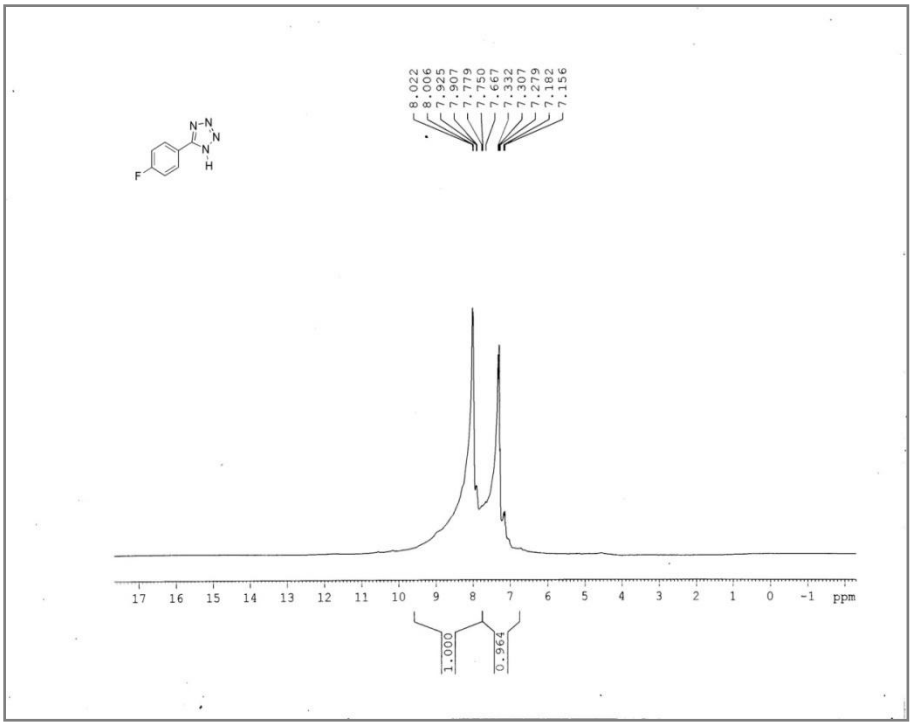
III.B.6.6. ^{13}C NMR spectrum of 4-(1H-tetrazol-5-yl) phenol



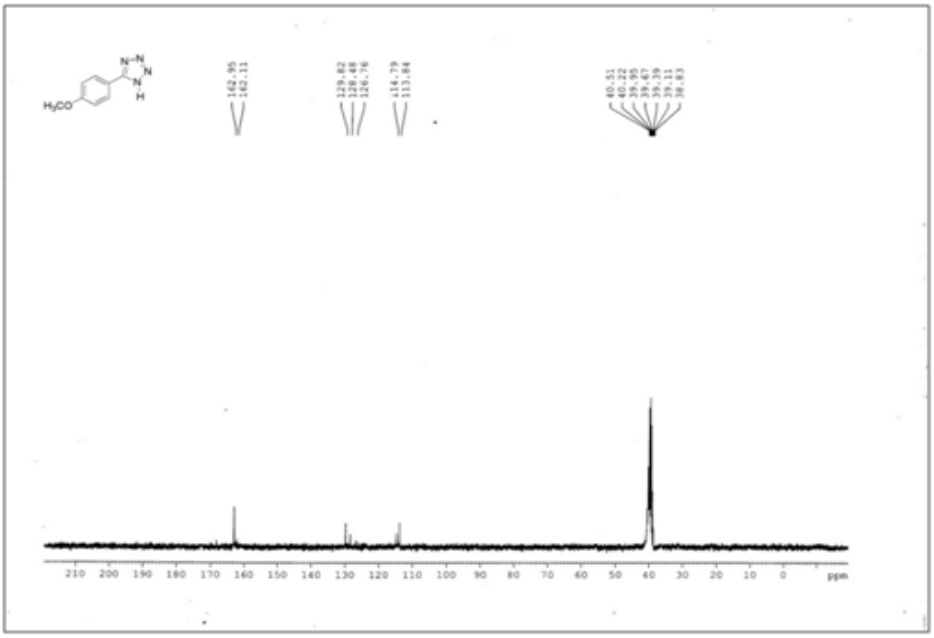
III.B.6.7. . ^{1}H NMR spectrum of 4-(1H-tetrazol-5-yl) phenol



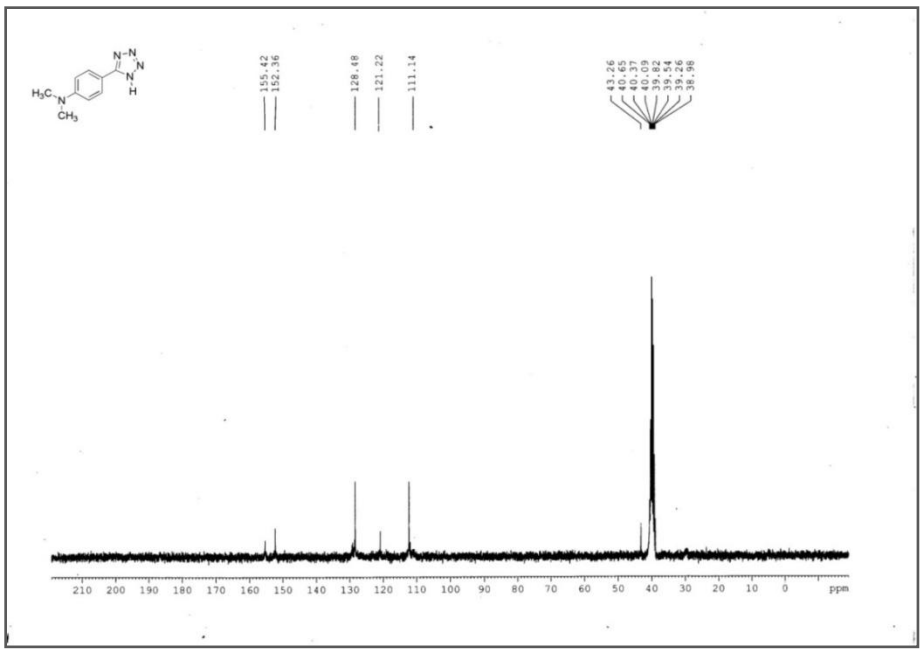
III.B.6.8. ^{13}C NMR spectrum of 5-(4-fluorophenyl)-1H-tetrazole



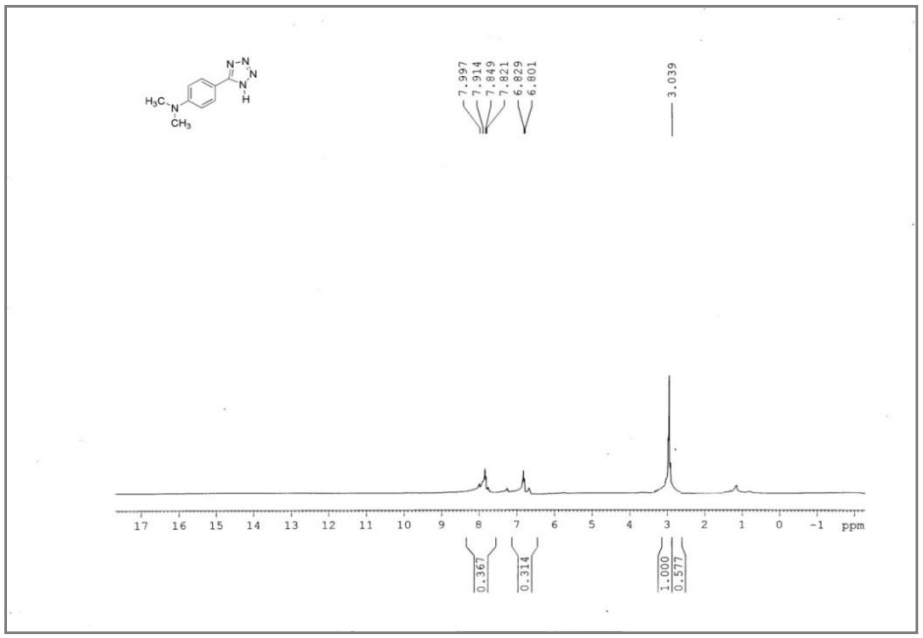
III.B.6.9. ^{1}H NMR spectrum of 5-(4-fluorophenyl)-1H-tetrazole



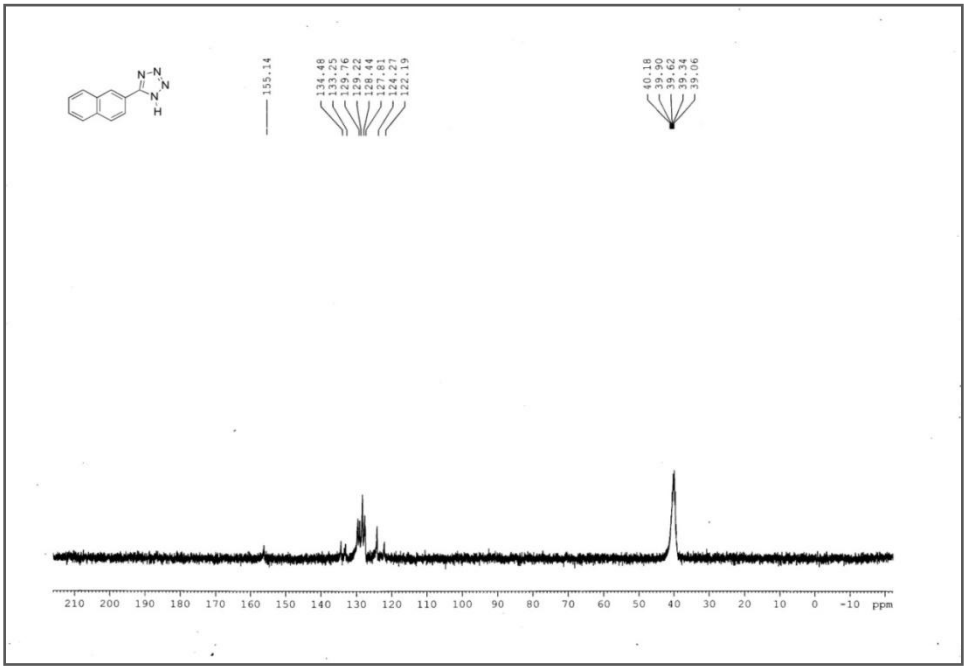
III.B.6.10. ^{13}C NMR spectrum of 5-(4-methoxyphenyl)-1H-tetrazole



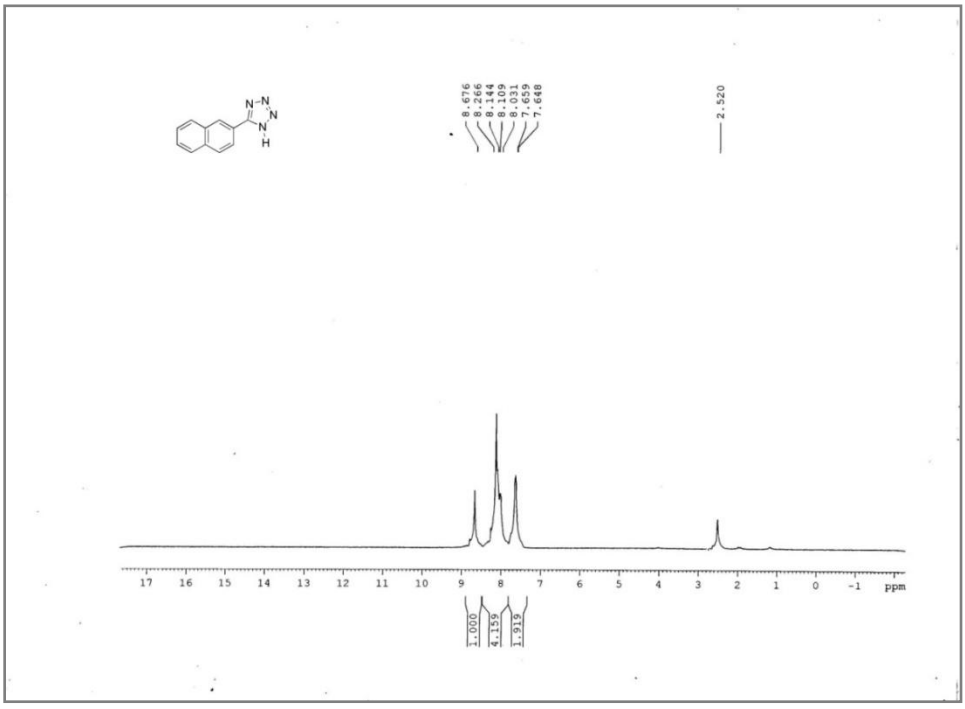
III.B.6.11. ^{13}C NMR spectrum of 5-(N, N-dimethyl-4-phenyl)-1H-tetrazole



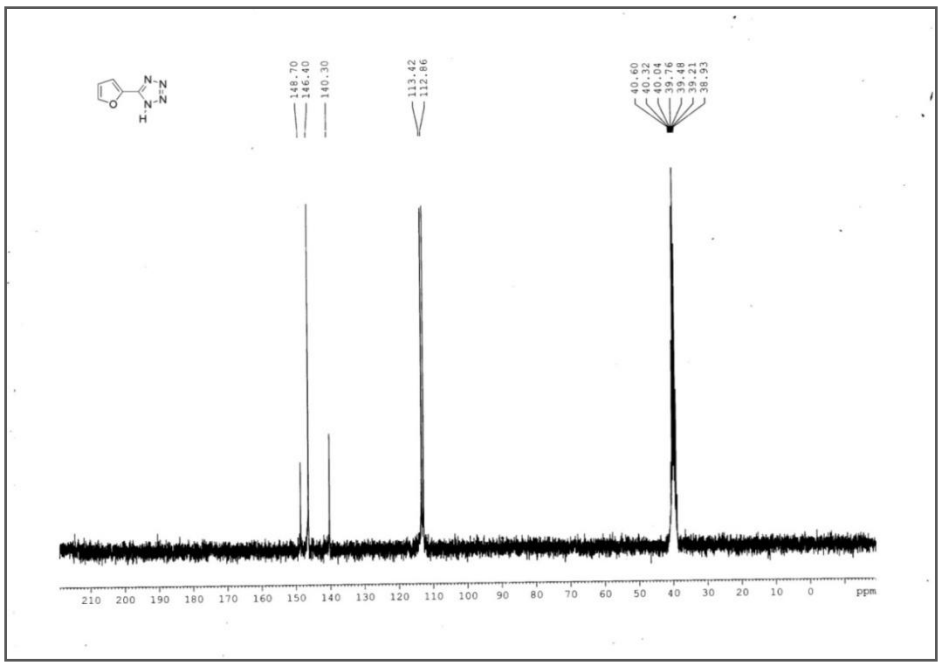
III.B.6.12. ^{1}H NMR spectrum of 5-(N, N-dimethyl-4-phenyl)-1H-tetrazole



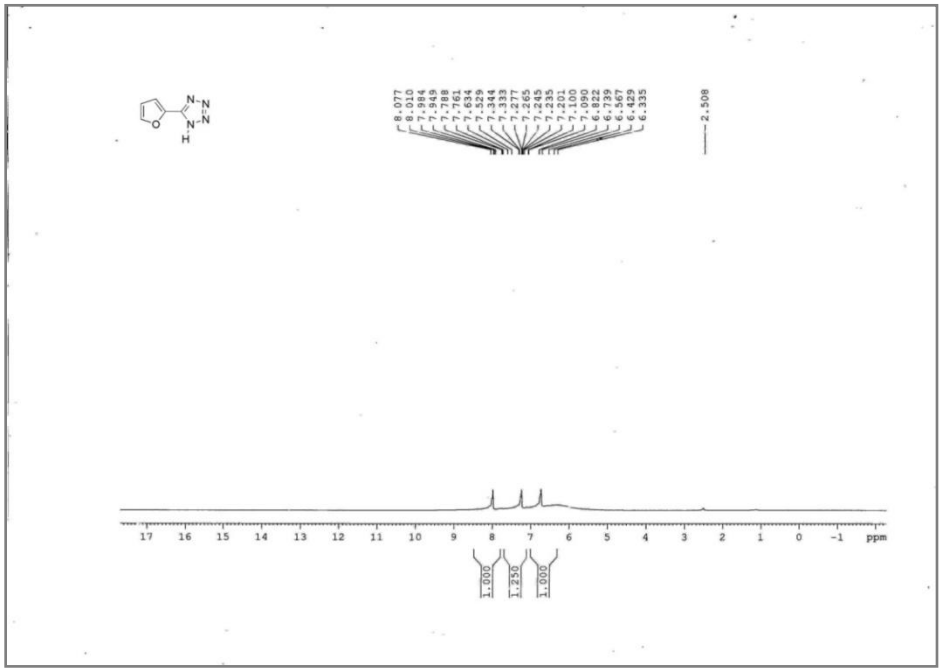
III.B.6.13. . ^{13}C NMR spectrum of 15-(naphthalene-3-yl)-1H-tetrazole



III.B.6.14. ^{1}H NMR spectrum of 15-(naphthalene-3-yl)-1H-tetrazole



III.B.6.15. ^{13}C NMR spectrum of 5-(furan-2-yl)-1H-tetrazole



III.B.6.16. ^{1}H NMR spectrum of 5-(furan-2-yl)-1H-tetrazole

III.B.7. References

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