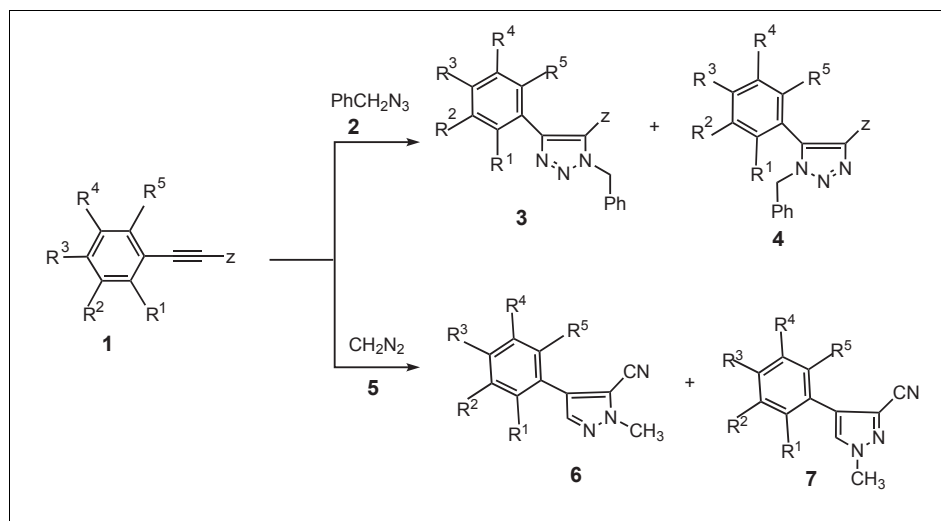


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1, 3-Dipolar-cycloaddition reaction of fluoro substituted 3-aryl-propynenitriles **1** with benzyl azide **2** afforded the expected 3-benzyl-5-aryl-3*H*-[1,2,3]triazole-4-carbonitrile **3** and 1-benzyl-5-aryl-1*H*-[1,2,3]triazole-4-carbonitrile **4** in good yield. However, 1,3-dipolar cycloaddition of diazomethane **5** with 3-aryl-propynenitriles **1** resulted in the exclusive formation of *N*-methyl-pyrazole derivatives **6** and **7**.

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Introduction.

1,2,3-Triazoles are an important class of potential organic molecules as agrochemicals, pharmaceuticals, dyestuffs and fluorescent whiteners [1]. They have been used as fungicides, herbicides [2], light stabilizers [3], optical brightening agents and corrosion retardants [4]. Fluoro-triazoles are effective in the treatment of neuropathic pain and attention disorders [5]. Similarly, pyrazole ring is the basic moiety in a number of agrochemicals, dyes, drugs and anesthetics. They are being used as psycho-pharmacological agents [6-8], pain relief agent (*e.g.*, *Celecoxib*) and cholesterol lowering agent [9]. Amino- and hydroxy-pyrazoles have been used as choline esterase inhibitors [10]. Fluorine containing pyrazole derivatives are reported to possess anticancer and antiviral activity [11].

A number of methods have been reported for the synthesis of 1,2,3-triazoles and pyrazoles [12,13]. 1,3-Dipolar-cycloaddition with alkynic dipolarophiles represent a versatile method for the synthesis of 1,2,3-triazoles and pyrazoles [14-20]. As part of our ongoing research on the synthesis of fluorine containing

conjugated alkynes and their use in the synthesis of biologically important class of heterocyclic compounds [21-23], we wish to report here, the synthesis of fluoro substituted 1,2,3-triazoles and *N*-methyl-pyrazoles *via* 1,3-dipolar-cycloaddition reactions of disubstituted alkynes with benzyl azide and diazomethane, respectively.

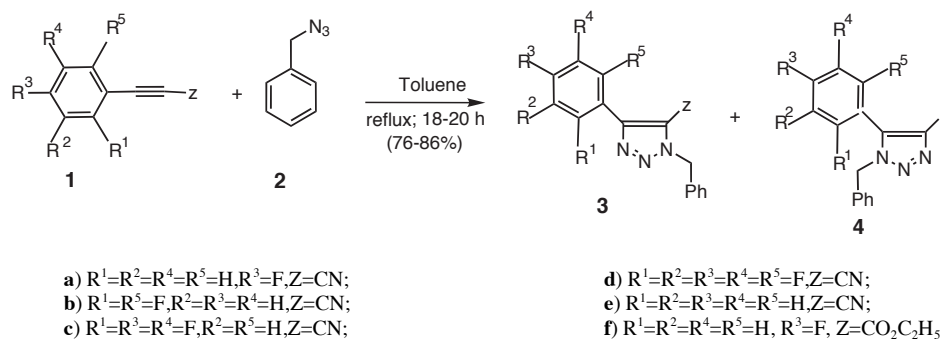
Results and Discussion.

2.1. 1,3-Dipolar-cycloaddition Reaction of Alkynes and Benzyl Azide.

3-Aryl-propynenitriles (**1**; *z* = CN) and ethyl 3-(4-fluorophenyl)-propionate (**1**; *z* = COOEt) are synthesized from their corresponding β -oxo-alkylidene-triphenylphosphoranes **8** [21] in good yield. The conjugated alkynes on reacting with benzyl azide in refluxing benzene/toluene furnished a mixture of two products (Scheme 1). They are separated by column chromatography and identified as triazole isomers based on their spectral data. A higher combined yield (76-86%) of the triazoles is obtained in toluene than in benzene (2-3%). All the products are new and the isomers are well characterized by IR, ¹H NMR, ¹³C

NMR and mass spectroscopy and the structure of one of the ppm. The downfield shift of methylene protons in **3a-f**

Scheme 1



products **3e** is confirmed by single crystal X-ray analysis.

Table 1
Synthesis of 1,2,3-Triazoles

Alkyne 1	Time (h)	Yield (%)	
		3	4
1a	18	51	32
1b	18	53	27
1c	18.5	55	25
1d	18.5	60	17
1e	18	47	38
1f	20	52	23

The triazole positional isomers are distinguished by IR and NMR spectroscopy. The IR spectra of compounds **3a-e** revealed the $-CN$ stretching absorption in the region $2230-2236\text{ cm}^{-1}$, whereas in compounds **4a-e**, it appeared in the region $2241-2245\text{ cm}^{-1}$. The proton nmr spectra of compounds **3a-f** and **4a-f** showed characteristic difference in the signal for benzylic protons. The signal for methylene protons of the benzyl group in compounds **3a-f** appeared in the region $\delta\ 5.69-5.75\text{ ppm}$, whereas, in compounds **4a-f**, it appeared in the region $\delta\ 5.52-5.54$

may be explained by the presence of nitrile function at *ortho* position. This is also reflected in the CMR spectra of compounds **3a** and **4a**. The methylene carbon of the benzyl group appeared slightly down field at $\delta\ 54.3\text{ ppm}$ for **3a**, when compared to its position at $\delta\ 52.5\text{ ppm}$ in the case of **4a**. Based on spectral data the compounds **3a-f** are characterized as 5-aryl-3-benzyl-3*H*-[1,2,3]-triazole-4-carbonitrile/4-carboxylic acid ethyl ester and **4a-f** as 5-aryl-1-benzyl-1*H*-[1,2,3]triazole-4-carbonitrile/4-carboxylic acid ethyl ester. This structural assignment is further evidenced by single crystal X-ray analysis (Diagram-1) of compound **3e**.

2.2 1,3-Dipolar Cycloaddition of Alkynes and Diazomethane.

The 1,3-dipolar cycloaddition of diazomethane and acetylenes was first reported by Pechman [24]. Subsequently, many groups have reported this reaction with symmetrical and unsymmetrical acetylenic compounds resulting in pyrazole derivatives. However, the structural assignments of the resultant pyrazoles were

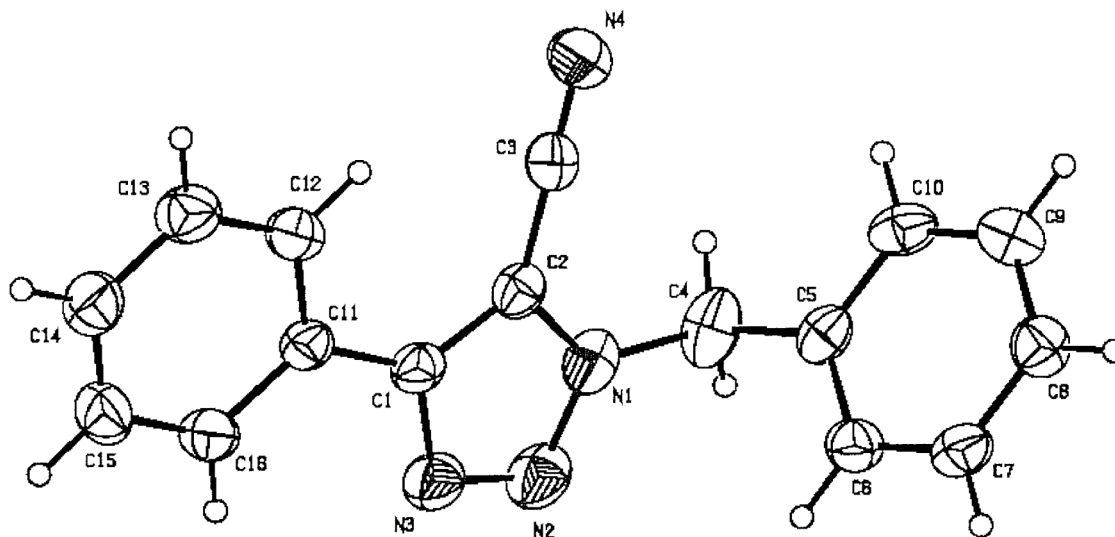


Diagram-1. X-ray crystallography of **3e**

a challenging problem with unsymmetrical acetylenic compounds [25-27].

Conjugated acetylenic nitrile **1** and freshly prepared diazomethane **5** are reacted at -5°C temperature for 12 h under constant stirring. The crude reaction mixture is passed through a silica column to isolate two new products along with a small quantity of unreacted acetylenic nitrile **1**. The mass spectra of these two products revealed same molecular ion indicating that they are positional isomers of pyrazoles. The proton nmr spectra revealed the presence of methyl protons in the region δ 3.91-4.16 ppm indicating that they are *N*-methylated pyrazoles **6** and **7**.

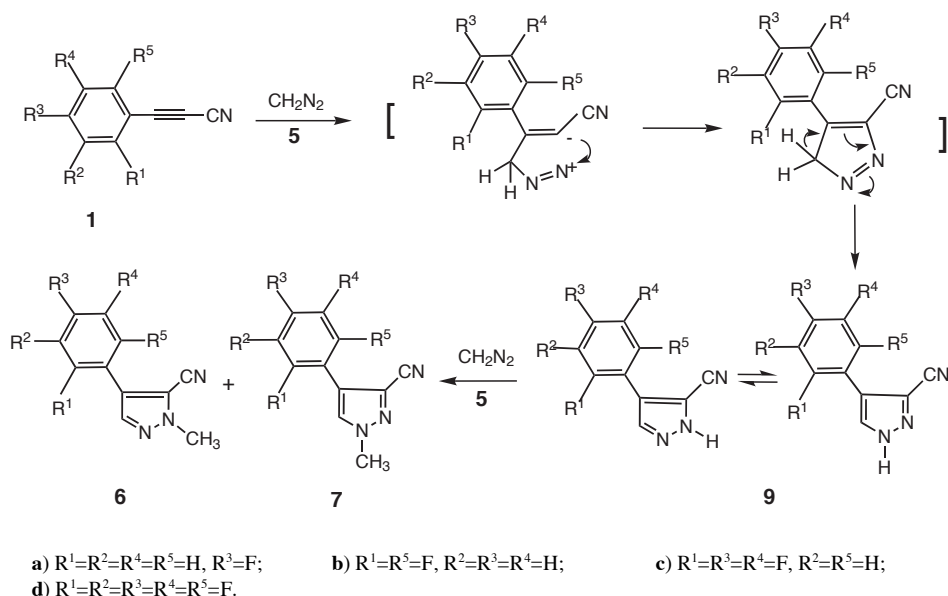
It is presumed that the pyrazole ring is formed by the 1,3-dipolar cycloaddition of diazomethane **5** onto the

Table 2
Synthesis of *N*-Methyl-pyrazoles

Alkyne	Time (h)	Yield (%)	
		6	7
1a	8.5	26	52
1b	8.5	16	59
1c	9	19	58
1d	9	13	60

overlapping with aromatic protons. The significant difference in ^1H NMR spectra of **6** and **7** is in the position of the lone pyrazole ring proton appearing at δ 7.74 ppm in compound **6** and at δ 7.51 ppm in **7**. The downfield shift in **6** is due to the proton being attached to the $\text{C}-\text{C}=\text{N}$

Scheme 2



acetylene **1**. The diazomethane **5** present in the reaction medium acts as a methylating agent [28-30] resulting exclusively in the *N*-methyl-pyrazole derivatives **6** and **7** (Scheme 2). The steps involved in the formation of the isomeric *N*-methyl-pyrazole derivatives **6** and **7** from the alkynenitriles **1** and diazomethane **5** are depicted in Scheme 2.

The IR spectra of the regioisomers of pyrazoles showed characteristic strong nitrile absorption in the region $2230\text{--}2239\text{ cm}^{-1}$. The ^1H NMR spectra of compound **6** showed a signal at δ 4.06-4.16 ppm for methyl protons and the olefinic proton of pyrazole ring appeared as singlet at δ 7.74-7.94 ppm. In the case of compound **7**, the *N*-methyl protons appeared at δ 3.91-4.08 ppm and the lone proton present on the pyrazole ring is seen at δ 7.51-7.82 ppm

function, where as in **7**, it is attached to $\text{C}=\text{C}-\text{N}$ part of the ring. The compounds **6a-d** and **7a-d** are tentatively characterized as 4-aryl-2-methyl-2*H*-pyrazole-3-carbonitrile and 4-aryl-1-methyl-1*H*-pyrazole-3-carbonitrile respectively. They are further confirmed by NOED studies.

In the NOED experiments of compound **6a**, the irradiation of signal at δ 7.74 ppm (s, 1H, $\text{C}_5\text{-H}$ on pyrazole ring) caused enhancement of the signal of phenyl ring proton at δ 7.60 ppm (ddd, 1H, *meta* to $-\text{F}$ atom), while the irradiation of signal at δ 4.09 ppm (s, 3H, $\text{N}-\text{CH}_3$) caused no enhancement of the peak at δ 7.74 ppm. The above information indicates that, in compound **6a**, *N*-methyl group at δ 4.07 ppm was not close enough with the olefinic proton of pyrazole ring, while the olefinic

proton at δ 7.74 ppm is spatially close enough to the aryl proton appearing at δ 7.60 ppm (Diagram 2).

In the NOED experiments of compound **7a**, the irradiation of signal at δ 3.94 ppm (s, 3H, N-CH₃) caused enhancement of the peak at δ 7.51 ppm. The irradiation of signal at δ 7.51 ppm (s, 1H, C₅-H of pyrazole ring) caused enhancement of the peaks at δ 7.49 ppm (ddd, 1H, *meta* to -F atom) and δ 3.94 ppm (s, 3H, N-CH₃). These results indicate that, in compound **7a**, the olefinic proton at δ 7.51 ppm was close enough to cause the enhancement of N-methyl group signal at δ 3.94 ppm and spatially close enough to give the enhancement of the aryl proton signal at δ 7.49 ppm (Diagram 2).

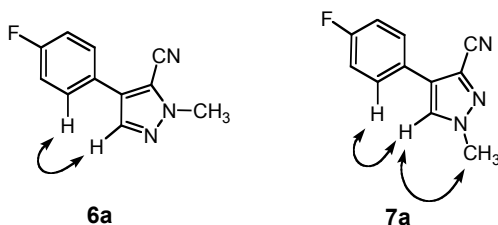


Diagram-2. Spatial interactions observed by NOED experiments

EXPERIMENTAL

3.1. General.

Melting points were determined in open glass capillaries on a Fisher Johnes melting point apparatus and are uncorrected. IR spectra were recorded on FT-IR Shimadzu Perkin-Elmer 1310 infrared spectrophotometer. ¹H NMR (200 MHz) and ¹³C NMR (50 MHz) spectra were recorded on Varian Gemini spectrometer in CDCl₃ solvent using TMS as internal standard. Mass spectra were recorded on a VG-micro mass 7070H instrument at 70eV. Elemental analyses were carried out on EI Elemental Vario EL (Germany) apparatus. Single crystal analysis was carried out on Bruker SMART Apex CCD diffractometer.

3.2. General procedure for the Preparation of 1,2,3-Triazoles (**3a-f** and **4a-f**).

Azidomethylbenzene **2** (1 mmol) and alkynenitrile/ ester **1** (1 mmol) were taken in dry toluene (5 mL) and refluxed for 18-20 h under nitrogen atmosphere. The reaction mixture was cooled, adsorbed on silica gel (100-200 mesh) and passed through a silica column for purification and isolation of the products. An initial fraction of hexane contains toluene and unreacted azide. Later fractions eluted with ethyl acetate and pet ether (1:9) afforded the isomer **3a-f** first followed by the second isomer **4a-f** which was eluted with a 3:7 mixture of ethyl acetate and pet ether.

3.2.1. 3-Benzyl-5-(4-fluorophenyl)-3H-[1,2,3]triazole-4-carbonitrile (**3a**).

Compound **3** (0.14 g, 51.2%) was obtained as white colour solid, mp 89 °C. IR (KBr): 3070, 2930, 2234, 1495, 1128 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 5.69 (s, 2H), 7.15-7.22 (m, 3H), 7.37-7.49 (m, 5H) and 8.00-8.09 ppm (m, 2H). ¹³C NMR (50

MHz, CDCl₃): δ 54.3 (s, -CH₂-Ph), 106.4 (s), 109.7 (s), 116.2 (d, ²J_{C-F}=22.0 Hz, *ortho* to-F), 123.9 (d, ⁴J_{C-F}=3.0 Hz, *para* to -F), 128.3 (s), 128.4 (d, ³J_{C-F}=9.0 Hz, *meta* to -F), 129.1 (s), 129.3 (s), 132.8 (s), 151.5 (s) and 163.7 ppm (d, ¹J_{C-F}=251.1 Hz, directly attached to -F). EIMS: *m/z* (relative intensity) 278 (M⁺, 11), 249 (6), 91 (100%).

Anal. Calcd. for C₁₆H₁₁FN₄: C, 69.04; H, 3.98; N, 20.14. Found: C, 69.07; H, 3.97; N, 20.19.

3.2.2. 3-Benzyl-5-(2,4-difluorophenyl)-3H-[1,2,3]triazole-4-carbonitrile (**3b**).

Compound **3b** (0.16 g, 53.4%) was obtained as white colour solid, mp 120 °C. IR (KBr): 3057, 2925, 2233, 1494, 1127 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 5.75 (s, 2H), 7.02-7.01 (m, 2H) and 7.37-7.50 ppm (m, 5H). EIMS: *m/z* (relative intensity) 296 (M⁺, 12), 249 (35), 267 (82), 249 (10), 197 (51) 91 (100%).

Anal. Calcd. for C₁₆H₁₀F₂N₄: C, 64.85; H, 3.40; N, 18.92. Found: C, 64.64; H, 3.51; N, 18.55.

3.2.3. 3-Benzyl-5-(2,4,5-trifluoro-phenyl)-3H-[1,2,3] triazole-4-carbonitrile (**3c**).

Compound **3c** (0.17 g, 55.1 %) was obtained as white colour solid, mp 75 °C. IR (KBr): 3059, 2926, 2236, 1491, 1130 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 5.73 (s, 2H), 7.07 (m, 1H), 7.36-7.50 (m, 5H) and 7.84 ppm (m, 2H). EIMS: *m/z* (relative intensity) 318 (M⁺, 12), 285 (18), 195 (4), 142 (4), 91 (100), 65 (55), 51 (9%).

Anal. Calcd. for C₁₆H₉F₃N₄: C, 61.13; H, 2.88; N, 17.83. Found: C, 61.19; H, 2.51; N, 17.45.

3.2.4. 3-Benzyl-5-(2,3,4,5,6-pentafluorophenyl)-3H-[1,2,3]-triazole-4-carbonitrile (**3d**).

Compound **3d** (0.21 g, 60.8%) was obtained as liquid, IR (KBr): 3061, 2924, 2233, 1486, 1131 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 5.75 (s, 2H) and 7.39-7.48 ppm (m, 5H). EIMS: *m/z* (relative intensity) 350 (M⁺, 49), 322 (35), 304 (22), 91 (100%).

Anal. Calcd. for C₁₆H₇F₅N₄: C, 54.84; H, 2.01; N, 16.00. Found: C, 54.98; H, 2.03; N, 16.05.

3.2.5. 3-Benzyl-5-phenyl-3H-[1,2,3]triazole-4-carbonitrile (**3e**).

This compound (0.12 g, 47.3%) was obtained as white solid, mp 112 °C. IR (KBr): 3070, 2930, 2231 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 5.69 (s, 2H), 7.34-7.56 (m, 7H), 7.97-8.08 ppm (m, 3H). EIMS: *m/z* (relative intensity) 260 (M⁺, 9), 231 (20), 149 (10), 141 (14), 105 (92), 91 (100), 83 (85), 77 (45), 51 (8), 43 (50%).

Anal. Calcd. for C₁₆H₁₂N₄: C, 73.81; H, 4.64; N, 21.53. Found: C, 73.84; H, 4.63; N, 21.32.

X-ray Data.

A colorless cube crystal of compound **3e** was obtained using ethanol as solvent. The crystal belongs to the monoclinic crystal system, space group C2/c with a=13.5305 (17), b=11.1770 (14), c=17.938(2) Å, β =90.386(2)°, V=2712.7(6) Å³, Z=8, λ =0.71073 Å, μ (MoK α)=0.080 mm⁻¹, F₀₀₀ = 1088, T=273(2) K. Data collection yielded 2385 reflections resulting in 1918 unique (*I*>2 σ (*I*), θ range: 0.995 – 25.0°. Full matrix least-squares refinement led to a final R=0.0397, wR=0.1035 and GOF =1.055. Intensity data were measured on Bruker Smart Apex with CCD area-detector. Crystallographic data for the structure of 3-benzyl-5-phenyl-3H-[1,2,3] triazole-4-carbonitrile **3e** has

been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC261890.

3.2.6. 3-Benzyl-5-(4-fluorophenyl)-3*H*-[1,2,3] triazole-4-carboxylic acid ethyl ester (**3f**).

Compound **3f** (0.17 g, 52.4%) was obtained as white solid, mp 104 °C. IR (KBr): 3050, 1715, 1480, 1284 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 1.23 (t, 3H, J=7.0 Hz), 4.23 (q, 2H, J=7.0 Hz), 5.88 (s, 2H), 7.01-7.14 (m, 2H), 7.3 (s, 5H) and 7.63-7.76 ppm (m, 2H). EIMS: *m/z* (relative intensity) 325 (M⁺, 2), 296 (16), 268 (30), 253 (55), 224 (56), 149 (9), 135 (15), 91 (100%).

Anal. Calcd. for C₁₈H₁₆FN₃O₂ C, 70.32; H, 5.25; N, 18.23. Found: C, 70.70; H, 5.75; N, 18.51.

3.2.7. 1-Benzyl-5-(4-fluorophenyl)-1*H*-[1,2,3]triazole-4-carbonitrile (**4a**).

Compound **4a** (0.09 g, 32.8%) was obtained as white solid, mp 68 °C. IR (KBr): 3070, 2927, 2243, 1498, 1238 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 5.54 (s, 2H), 7.03-7.09 (m, 2H), 7.18-7.23 (m, 2H) and 7.29-7.38 ppm (m, 5H). ¹³C NMR (50 MHz, CDCl₃): δ 52.5 (s, -CH₂-Ph), 111.6 (s), 116.6 (d, ²J_{C-F}=22.4 Hz, *ortho* to -F), 119.2 (d, ⁴J_{C-F}=3.1 Hz, *meta* to -F), 120.3 (s), 127.1 (s), 128.5 (s), 131.0 (d, ³J_{C-F}=8.9 Hz, *para* to -F), 133.6 (s), 142.7 (s) and 164.0 ppm (d, ¹J_{C-F}=253.3 Hz, directly attached to -F). EIMS: *m/z* (relative intensity) 278 (M⁺, 25), 250 (32), 91 (100%).

Anal. Calcd. for C₁₆H₁₁FN₄ C, 69.04; H, 3.98; N, 20.14. Found: C, 69.16; H, 3.89; N, 20.18.

3.2.8. 1-Benzyl-5-(2,4-difluorophenyl)-1*H*-[1,2,3]triazole-4-carbonitrile (**4b**).

Compound **4b** (0.08 g, 27.5%) was obtained as white solid, mp 84-85 °C. IR (KBr): 3073, 2929, 2245, 1595, 1466, 1260 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 5.52 (s, 2H), 6.92-7.0 (m, 2H), 6.98-7.07 (m, 2H), 7.15-7.23 (m, 3H) and 7.52 ppm (m, 1H). EIMS: *m/z* (relative intensity) 296 (M⁺, 5), 267 (7), 91 (100%).

Anal. Calcd. for C₁₆H₁₀F₂N₄ C, 64.85; H, 3.40; N, 18.92. Found: C, 64.11; H, 3.53; N, 18.64.

3.2.9. 1-Benzyl-5-(2,4,5-trifluorophenyl)-1*H*-[1,2,3] triazole-4-carbonitrile (**4c**).

Compound **4c** (0.08 g, 25.9%) was obtained as white colour solid, mp 63 °C. IR (KBr): 3055, 2925, 2241, 1490, 1131 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 5.54 (s, 2H), 6.98 (m, 1H), 7.16 (m, 1H) and 7.23-7.73 ppm (m, 5H). EIMS: *m/z* (relative intensity) 314 (M⁺, 4), 285 (2), 268 (1), 91(100), 65 (7%).

Anal. Calcd. for C₁₆H₉F₃N₄ C, 61.13; H, 2.88; N, 17.83. Found: C, 61.12; H, 2.79; N, 17.92.

3.2.10. 1-Benzyl-5-(2,3,4,5,6-pentafluorophenyl)-1*H*-[1,2,3]triazole-4-carbonitrile (**4d**).

Compound **4d** (0.06 g, 17.16%) was obtained as white colour solid, mp 72 °C. IR (KBr): 3065, 2925, 2243, 1490, 1128 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 5.53 (s, 2H), 6.85-6.92 (m, 2H) and 7.15-7.26 ppm (m, 3H). EIMS: *m/z* (relative intensity) 350 (M⁺, 30), 322 (26), 91 (100%).

Anal. Calcd. for C₁₆H₇F₅N₄ C, 54.84; H, 2.01; N, 16.00. Found: C, 54.74; H, 2.09; N, 16.09.

3.2.11. 1-Benzyl-5-phenyl-1*H*- [1,2,3] triazole-4-carbonitrile (**4e**).

Compound **4e** (0.1 g, 38.7%) was obtained as white colour solid, mp 79 °C. IR (KBr): 3041, 2239, 1128 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 5.53 (s, 2H), 7.01-7.14 (m, 2H), 7.13-7.39 (m, 5H) and 7.45-7.61 ppm (m, 3H). EIMS: *m/z* (relative intensity) 260 (M⁺, 20), 231 (10), 173 (7), 91 (100), 65 (13), 51 (4%).

Anal. Calcd. for C₁₆H₁₂N₄ C, 73.81; H, 4.64; N, 21.53. Found: C, 73.73; H, 4.65; N, 21.51.

3.2.12. 1-Benzyl-5-(4-fluorophenyl)-1-[1,2,3]triazole-4-carboxylic acid ethyl ester (**4f**).

Compound **4f** (0.07 g, 23.5%) was obtained as white solid, mp 78-79 °C. IR (KBr): 3059, 1726, 1484, 1283 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 1.32 (t, 3H, J=7.0 Hz), 4.28 (q, 2H, J=7.0 Hz), 5.42 (s, 2H), 6.97-7.02 (m, 2H), 7.08-7.17 (m, 4H) and 7.23-7.30 ppm (m, 3H). EIMS: *m/z* (relative intensity) 325 (M⁺, 2), 296 (12), 268 (27), 253 (45), 224 (46), 91 (100), 65 (30%).

Anal. Calcd. for C₁₈H₁₆FN₃O₂ C, 70.32; H, 5.25; N, 18.23. Found: C, 70.73; H, 5.74; N, 18.50.

3.3. General Procedure for the Preparation of Pyrazoles, **6a-d** and **7a-d**.

Conjugated alkyne nitrile **1** (2 mmol) was dissolved in dry ether (3 mL) and cooled to -5 °C. To this, a cold ethereal solution (2.7 ml) of diazomethane **5** (0.88 g, 2 mmol) was added drop wise and stirred for 12 h. The reaction mixture was adsorbed on silica gel (100-200 mesh) and purified by column chromatography. The initial hexane fractions gave unreacted acetylene **1**. Elution with hexane and 5% chloroform solvent mixture gave compound **6**. This was followed by elution with hexane mixed with 10% ethyl acetate to isolate compound **7**.

3.3.1. 4-(4-Fluorophenyl)-2-methyl-2*H*-pyrazole-3-carbonitrile (**6a**).

Compound **6a** (0.1 g, 26%) was obtained as white solid, mp 66 °C. IR (KBr): 2944, 2230, 1611, 1557, 1362, 1162 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 4.09 (s, 3H, N-CH₃), 7.14 (ddd, 2H, ³J_{H-H}=8.8, ³J_{H-F}=6.4, ⁴J_{H-H}=2.2 Hz), 7.6 (ddd, 2H, ³J_{H-H}=8.8, ⁴J_{H-F}=5.3, ⁴J_{H-H}=2.1 Hz) and 7.74 ppm (1H, s). ¹³C NMR (50 MHz, CDCl₃): δ 38.5 (s, CH₃), 96.1 (s, C₃), 111.6 (s, CN), 116.2 (d, ²J_{C-F}=21.8 Hz, *ortho* to -F), 125.5 (s, *para* to -F), 128.3 (d, ³J_{C-F}=8.2 Hz, *meta* to -F), 129.0 (s, C₄), 137.0 (s, C₅) and 162.7 ppm (d, ¹J_{C-F}=248.7 Hz, directly attached to -F). EIMS: *m/z* (relative intensity) 201 (M⁺, 100), 200 (3), 187 (97), 158 (3), 149 (1%).

Anal. Calcd. for C₁₁H₈FN₃ C, 65.64, H, 4.00, N, 20.89. Found: C, 65.68, H, 4.03, N, 20.88.

3.3.2. 4-(2,6-Difluorophenyl)-2-methyl-2*H*-pyrazole-3-carbonitrile (**6b**).

Compound **6b** (0.07 g, 16%) was obtained as white solid, mp 74 °C. IR (KBr): 2944, 2235, 1585 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 4.16 (s, 3H, N-CH₃), 7.02 (m, 2H), 7.33 (m, 1H) and 7.74 ppm (s, 1H). EIMS: *m/z* (relative intensity) 219 (M⁺, 29), 217 (68), 176 (100), 162 (41), 140 (80%).

Anal. Calcd. for C₁₁H₇F₂N₃ C, 60.26; H, 3.22; N, 19.17. Found: C, 60.29; H, 3.24; N, 19.19.

3.3.3. 4-(2,4,5-Trifluorophenyl)-2-methyl-2*H*-pyrazole-3-carbonitrile (**6c**).

Compound **6c** (0.09 g, 19%) was obtained as white solid, mp 74 °C. IR (KBr): 2930, 2234, 1610, 1385 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 4.12 (s, 3H), 7.09 (m, 1H), 7.47 (m, 1H) and

7.78 ppm (s, 1H). EIMS: m/z (relative intensity) 237 (M^+ , 87), 209(56), 181(45%).

Anal. Calcd. for $C_{11}H_6F_3N_3$ C, 55.68; H, 2.55; N, 17.72. Found: C, 55.72; H, 2.58; N, 17.81.

3.3.4. 4-(2,3,4,5,6-Pentafluorophenyl)-2-methyl-2H-pyrazole-3-carbonitrile (**6d**).

Compound **6d** (0.07 g, 13%) was obtained as white solid, mp. 129°C. IR (KBr): 2941, 2239, 1375 cm^{-1} ; 1H NMR (200 MHz, $CDCl_3$): δ 4.06 (s, 3H, -NCH₃) and 7.94 ppm (s, 1H). EIMS: m/z (relative intensity) 273 (M^+ , 98), 155(78), 141 (100%).

Anal. Calcd. for $C_{11}H_4F_5N_3$ C, 48.34, H, 1.51, N, 15.38. Found: C, 48.28, H, 1.50, N, 15.29.

3.3.5. 4-(4-Fluorophenyl)-1-methyl-1H-pyrazole-3-carbonitrile (**7a**).

Compound **7a** (0.2 g, 52%) was obtained as white solid, mp 135 °C. IR (KBr): 2925, 2234, 1609, 1160 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ 3.94 (s, 3H, N-CH₃), 7.06 (ddd, 2H, $^3J_{H-H}=8.8$, $^3J_{H-F}=6.4$, $^4J_{H-F}=2.1$ Hz), 7.49 (ddd, 1H, $^3J_{H-H}=8.8$, $^4J_{H-H}=5.3$, $^4J_{H-F}=2.1$ Hz) and 7.51 ppm (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 38.7 (s, CH₃), 95.1 (s, C₃), 113.5 (s, CN), 115.0 (d, $^2J_{C-F}=21.9$ Hz, *ortho* to -F), 125.5 (s, *para* to -F), 127.4 (d, $^3J_{C-F}=8.1$ Hz, *meta* to -F), 128.0 (s, C₄), 136.7 (s, C₅) and 161.3 ppm (d, $^1J_{C-F}=247.7$ Hz, directly attached to -F). EIMS: m/z (relative intensity) 201 (M^+ , 100), 200 (3), 187 (97), 158 (3%).

Anal. Calcd. for $C_{11}H_8FN_3$: C, 65.64, H, 4.00, N, 20.89. Found: C, 65.57, H, 4.02, N, 20.77.

3.3.6. 4-(2,6-Difluorophenyl)-1-methyl-1H-pyrazole-3-carbonitrile (**7b**).

Compound **7b** (0.25 g, 59%) was obtained as white solid, mp 153 °C. IR (KBr): 2236, 1378 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ 3.91 (s, 3H, -NCH₃), 6.96 (m, 1H), 7.52 (m, 1H) and 7.82 ppm (s, 1H). EIMS: m/z (relative intensity) 219 (M^+ , 32), 204 (20), 203 (100%).

Anal. Calcd. for $C_{11}H_8F_2N_3$ C, 60.26; H, 3.22; N, 19.17. Found: C, 60.30; H, 3.24; N, 19.06.

3.3.7. 4-(2,4,5-Trifluorophenyl)-1-methyl-1H-pyrazole-3-carbonitrile (**7c**).

Compound **7c** (0.27g, 58%) was obtained as white solid, mp 144-145 °C. IR (KBr): 2925, 2235, 1610, 1385 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ 3.94 (s, 3H, N-CH₃), 6.96 (m, 1H), 7.67 (m, 1H) and 7.67 ppm (s, 1H). EIMS: m/z (relative intensity) 237 (M^+ , 87), 209(58%).

Anal. Calcd. for $C_{11}H_6F_3N_3$ C, 55.68; H, 2.55; N, 17.72. Found: C, 55.71; H, 2.58; N, 17.79.

3.3.8. 4-(2,3,4,5,6-Pentafluorophenyl)-1-methyl-1H-pyrazole-3-carbonitrile (**7d**).

Compound **7d** (0.32 g, 60%) was obtained as white solid, mp 129-130 °C. IR (KBr): 2936, 2239, 1569 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ 4.08 (s, 3H, N-CH₃), 7.66 ppm (s, 1H). EIMS: m/z (relative intensity) 273 (M^+ , 85), 155(28), 141 (100).

Anal. Calcd. for $C_{11}H_4F_5N_3$ C, 48.37; H, 1.48; N, 15.38. Found: C, 48.39; H, 1.51; N, 15.37.

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