Summary Report
Minor Research Project

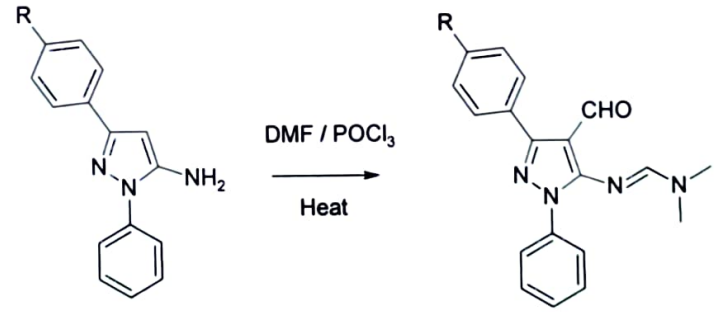
Synthesis of Pyrazolo[3, 4-*b*][1, 8]naphthyridines and study of their photophysical properties

Pyrazolo pyridines and pyrazolo naphthyridines compounds emerge as an attractive class of nitrogen heterocycles for the researchers due to their antimicrobial and fluorescence properties. These compounds also showed the pharmaceutical properties of anticancer agents, anticonvulsant agents, antiproliferative agents, CNS depressants and anti-inflammatory agents. In recent years scientist showed an increasing interest in synthesizing compounds having good fluorescent properties and good quantum yield. Literature study showed that pyrazolo naphthyridines derivatives showed significant fluorescence properties and can be used for synthesis of many electroluminescence devises. In this work we have synthesized new pyrazolo naphthyridine compounds and studied for their photophysical properties.

I) Synthesis of N'-[3-aryl-4-formyl-1-phenyl-1*H*-pyrazol-5-yl]-N,N-dimethylmethanimidamide 2

Vilsmeier-Haack formylation of 1,3 disubstituted 5-amino pyrazole with DMF and $POCl_3$ furnished compound **2** in good yield. (Scheme-1).

Scheme-1



1 2

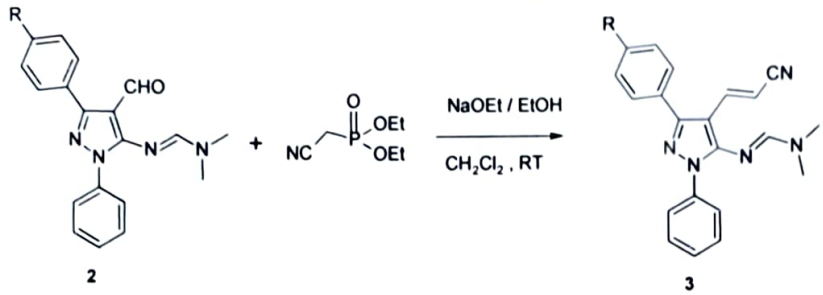
2	R
a	Cl
b	Br
c	CH_3

The IR spectrum of compound **2a** showed bands at 1620 cm^{-1} for N=CH stretching. Absorption bands at 2720 cm^{-1} and 1710 cm^{-1} confirmed the presence of aldehyde group. The ^1H NMR spectrum showed two singlets at δ 2.87 and at δ 2.98 for two CH_3 groups. Signal for aldehyde proton appear at δ 9.53 while all other aromatic protons appear in between δ 7.32 to δ 8.50.

II) Synthesis of N'-[3-aryl-4-(2-cyanoethenyl)-1-phenyl-1H-pyrazol-5-yl]-N,N-dimethylmethanimidamide 3

Reaction of N'-[3-aryl-4-formyl-1-phenyl-1*H*-pyrazol-5-yl]-N,N-dimethylmethanimidamide **2** with diethyl cyanomethyl phosphonate using NaOMe or NaOEt in dichloromethane produce compound **3** in good yield.

Scheme-2



2 3

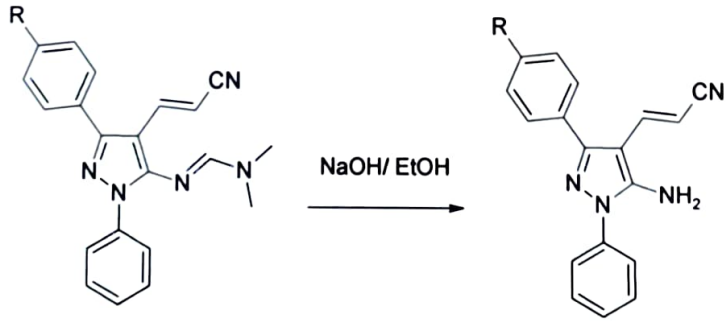
3	R
a	Cl
b	Br
c	CH_3

Compound **3a** showed IR band at 2210 cm^{-1} which confirmed the presence of CN group. PMR spectrum showed two doublets one at δ 5.69 and δ 7.24 for two olefinic protons. HRMS spectrum showed M+1 peak at 376.13 which confirmed the molecular mass of the compound **3a**.

III) Synthesis of (2*E*)-3-[5-amino-3-aryl-1-phenyl-1*H*-pyrazol-4-yl]prop-2-enenitrile 4

Compound **3** on refluxing with sodium hydroxide in ethanol furnished compound **4** in good yield. Compound **4** was characterized by spectral and analytical methods.

Scheme-3



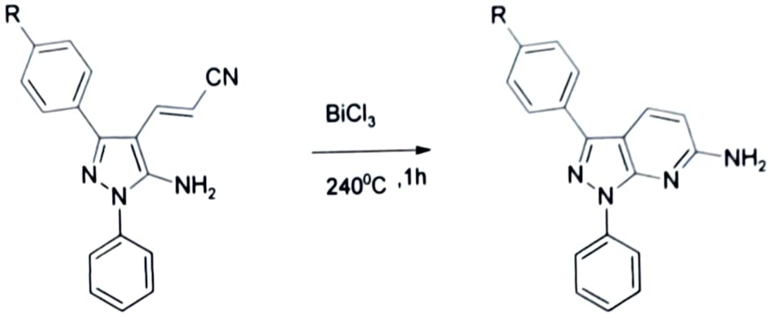
3 4

4	R
a	Cl
b	Br
c	CH_3

IV) Synthesis of 3-aryl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridin-6-amine 5

Compound **4** on heating with $ZnCl_2$ or $BiCl_3$ undergo cyclisation and furnished compound **5** in 60-70% yield. IR band at 3388 and 3338 cm^{-1} and PMR signal at δ 4.82 confirmed the presence of NH_2 group. M+1 peak in HRMS at *m/z* 301.14 matched with the calculated molecular mass of compound **5c**.

Scheme-4



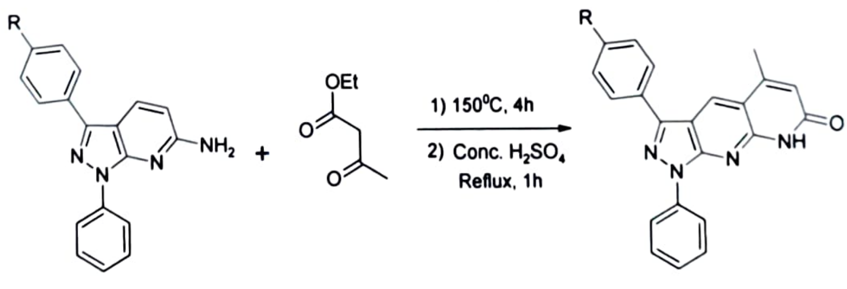
4 **5**

5	R
a	Cl
b	Br
c	CH_3

V) 3-Aryl- 5-methyl-1-phenyl-1,8-dihydro-7*H*-pyrazolo[3,4-*b*][1,8]naphthyridin-7-one 6

Compound **4** was heated with ethyl acetoacetate at 150^0C for 4 hrs, after cooling 4ml concentrated sulfuric acid was added and resulting solution was heated at 110^0C for one hour. Compound **5** showed IR bands at 3260 cm^{-1} (for NH) and 1668 cm^{-1} (for C=O). ^1H NMR spectrum showed NH singlet at δ 8.86 and aromatic protons appear in between δ 6.36 to δ 8.36. HRMS showed M+1 peak at 387.10 *(m/z)* which confirm the molecular mass of **6a**

Scheme-5



5 **6**

65	R
a	Cl
b	Br
c	CH_3

Study of the Photophysical Properties of 3-Aryl-5-methyl-1-phenyl-1,8-dihydro- pyrazolo[3,4-b][1,8] naphthyridin-7- one 6

Newly synthesized naphthyridine derivatives showed emission of blue light hence we decided to undertake the study of fluorescent properties. Different solvents were used to find out the effect of solvent on fluorescence. The absorption and emission spectra were studied by using quinine sulphate as reference standard and dichloromethane, methanol and acetonitrile as solvent.

Conclusion

We have developed an efficient method for synthesis of 3-Aryl- 5-methyl-1-phenyl-1,8-dihydro-7H-pyrazolo[3,4-b][1,8]naphthyridin-7-one. Results showed that fluorescence properties of newly synthesized naphthyridine derivatives greatly affect by solvent and substituents present at C3 position of pyrazole ring.

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