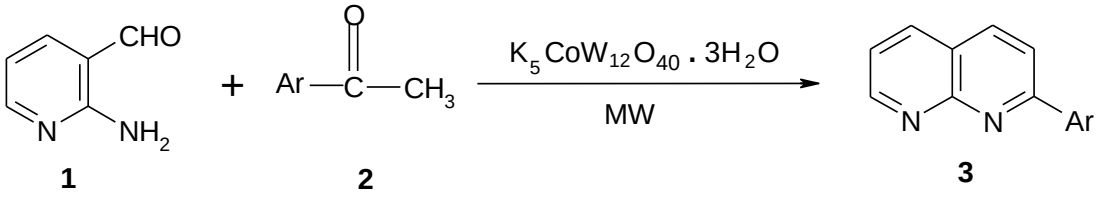
International Journal of Research in Advent Technology, Vol.6, No.6, June 2018
E-ISSN: 2321-9637
Available online at www.ijrat.org

Potassium dodecatangestocobaltate trihydrate ($K_5CoW_{12}O_{40}.3H_2O$): a mild and efficient catalyst for the synthesis of 2-aryl-1,8-naphthyridines under microwave irradiation

Mallaram Aruna[1], Pradeep Kumar Challa[2] & Gade Dayakar[3]*
[1,2,3*]*Department of Chemistry, Kakatiya University, Warangal Urban ,Telangana-506009.*

Abstract- A mild and efficient solvent-free method has been developed for the synthesis of 2-aryl-1,8-naphthyridines **3** by Friedlander reaction between 2-aminonicotinaldehyde **1** and various aryl methyl ketones **2** using stable and effective catalyst potassium dodecatangestocobaltate trihydrate ($K_5CoW_{12}O_{40}.3H_2O$) under microwave irradiation in high yields. (**Scheme I**) and **Table-1.** The structures of the compounds were elucidated by spectral analysis.



1 **2** **3**

Keywords- Potassium dodecatangestocobaltate trihydrate ($K_5CoW_{12}O_{40}.3H_2O$), Friedlander condensation, 2-Aminonicotinaldehyde , Aryl methyl ketones , 2-Aryl-1,8-naphthyridines, MWI.

1. INTRODUCTION

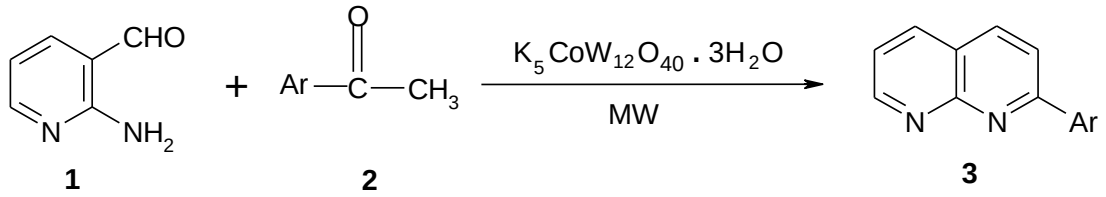
The importance of 1,8-naphthyridines in biological systems has attracted great interest due to their diverse pharmacological and microbial activities.[1-3] A brief survey of literature revealed that the most common approach towards the synthesis of 1,8-naphthyridines constitutes the Friedlander condensation between 2-aminonicotinaldehydes and carbonyl compound containing a reactive α-methylene or methyl group in the presence of base (piperidine)[4] or acid (CH_3COOH/H_2SO_4)[5] catalyst. However these methods are not very satisfactory due to drawbacks such as low yields, toxic reagents, longer reaction time at high reaction temp and tedious work-up procedures. Therefore, it was considered worthwhile to carry out the synthesis of 1,8-naphthyridines under mild conditions.

The MW induced organic reactions are becoming popular because of their simplicity and operational convenience[6-8]. Solvent–free MW assisted chemical reactions[7] are gaining importance due to the advantages and environmentally friendly processes they offer, as compared to conventional reactions. In view of this and in continuation of our ongoing program to develop environmentally benign protocols[9-11], herein, we report an efficient solvent-free synthesis of 1,8-naphthyridines using potassium dodecatangestocobaltatetrihydrate($K_5CoW_{12}O_{40}.3H_2O$) as catalyst and clean energy source, microwave irradiation**.**

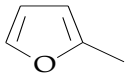
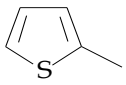
2. EXPERIMENTAL SECTION

Melting points were determined on a Cintex melting point apparatus and are uncorrected. The ^1H NMR spectra were recorded on a BRUKER Spectrometer (400 MHz). Chemical shifts were reported in parts per million using tetramethylsilane as an internal standard and were given in δ units. The solvent for NMR spectra was DMSO. Infrared spectra were takenon SHIMADZU-FTIR-8400 Spectrophotometer instrument in the frequency range of 4000-400 cm-1 by KBr powder method. The Mass spectra were recorded by MS-SHIMADZU-QP2010. All reactions

were monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60F254 (Merck) plates using UV light for detection. Common reagent grade chemicals are either commercially available and were used without further purification.



1 **2** **3**

	Ar		**Ar**
a:	C_6H_5	i:	4-$NO_2C_6H_4$
b:	4-$CH_3C_6H_4$	j:	4-C_6H_5-C_6H_4
c:	4-$CH_3OC_6H_4$	k:	2-$C_{10}H_7$
d,	4-ClC_6H_4	l:	2-C_5H_4N
e:	4-BrC_6H_4	m:	3-C_5H_4N
f:	2-HOC_6H_4	n:	4-C_5H_4N
g:	4-HOC_6H_4	o:	
h:	3-$NO_2C_6H_4$	p:	

Scheme I

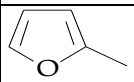
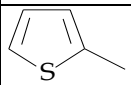
3. RESULTS AND DISCUSSION

The Friedlander condensation of 2-aminonicotinaldehyde **1** with various aryl methyl ketones **2** in the presence of potassium dodecatangestocobaltatetrihydrate($K_5CoW_{12}O_{40}.3H_2O$) in solvent-free conditions under microwave irradiation furnished the corresponding 2-aryl-1,8-naphthyridines **3** (Scheme-1).This method provides an easy access to 1,8-naphthyridines in fairly good yields, avoids pollution problems, reduces reaction time and is completed in a few minutes.

In a typical experiment, a mixture of 2-aminonicotinaldehyde **1** acetophenone **2a** (Ar=C_6H_5) and $K_5CoW_{12}O_{40}.3H_2O$ was exposed to microwave irradiation at 600 watts for 6.0 min. Work-up of the reaction mixture afforded 2-phenyl-1,8-naphthyridine **3a** (Ar=C_6H_5) in 88% yield, m.p. 116 ^oC(lit[12]. m.p. 116 ^oC); IR (KBr); 1605 (C=N); ^1H NMR ($CDCl_3$); 8.22 (m, 1H, C_3-H), 8.35 (m, 1H, C_4-H), 8.63 (m, 1H, C_5-H), 8.87(m, 1H, C_7-H) 7.40-7.75 (m, 6H, C_6-H, 5ArH); Mass (ESI): m/z 207$[M+H]^+$. The reaction is of general applicability and the different 1,8-naphthyridines **3b-p** synthesized are presented in Table-1.

To the best of our knowledge, this is the first report on rapid Friedlander synthesis of 1,8-naphthyridines using potassium dodecatangestocobaltate trihydrate ($K_5CoW_{12}O_{40}.3H_2O$) as reusable catalyst under microwave irradiation in solvent-free conditions.

Table 1 : Physical data of 2-Aryl-1,8-naphthyridines 3

Compd	Ar	Reaction period (min)	Yield (%)	M.P. (^{o}C)	
				Found	Reported[12]
3a	C_6H_5	6.0	88	116	116
3b	4-$CH_3C_6H_4$	5.5	92	146	147
3c	4-$CH_3OC_6H_4$	5.5	90	147	148
3d	4-ClC_6H_4	6.5	93	202	202
3e	4-BrC_6H_4	7.0	92	218	217
3f	2-HOC_6H_4	5.5	88	187	188
3g	4-HOC_6H_4	6.0	90	255	254
3h	3-$NO_2C_6H_4$	7.0	90	218	219
3i	4-$NO_2C_6H_4$	6.5	92	264	263
3j	4-C_6H_5-C_6H_4	6.5	90	186	186
3k	2-$C_{10}H_7$	7.0	88	164	165
3l	2-C_5H_4N	5.5	90	149	148
3m	3-C_5H_4N	6.0	88	142	142
3n	4-C_5H_4N	5.5	92	167	168
3o		5.0	88	146	146
3p		5.5	90	134	133

4. CONCLUSION

The reported procedure is an attractive methodology for the Friedlander synthesis of 1,8-naphthyridines. The mild conditions, good yields, high purity, short reaction time and non-toxic reusable catalyst are some of the major advantages of this method.

ACKNOWLEDGEMENT
The authors are thankful to the Director, IICT, Hyderabad for providing. ^{1}H NMR and mass spectra. One of them(P K Ch) is grateful to UGC, New Delhi for the award of Senior Research Fellowship.

REFERENCES

[1] Qi-Dong You, Zhi-Yu Li, Chiung-Hua Huang, Qian Yang, Xiao-Jian Wang, Qing-Long Guo, Xiao-Guang Chen, Xun-Gui He, Tsai-Kun Li and Ji-Wang Chern, *J. Med. Chem.*, 2009, **52 ,**5649.
[2] Madsen-Duggan C. B. Debenham ., J.S,. Shen C, Stribing D.S, Shearaman L.P, Strack A.M, Goulet M.T and Hale J.J, *Bioorg Med Chem. Lett.*, 2010, **20,** 3750.
[3]Roma G., Braccio M.D, Grossi G, Piras D, Ballabeni V, Tognolini M, Bertini S and Barocelli E, *Eur. J. Med. Chem.*, 2010, **45,**352.
[4] Hawes E.M. and. Wibberley D.G, *J. Chem.Soc. (C)*, (1966), 315.
[5] Thummel R.P and Kohli D.K *J. Heterocycl. Chem.*, 1977**, 14 ,**124.
[6] Caddick S, *Tetrahedron*, **51**(1995), 10403.
[7]Loupy A, Petit,J. hamelin, F.T. Boullet,.Jacquault P and Mathe D., *Synthesis*, 1998, 1213.
[8] Lidstrom P Tiernery J, Wathey B and Westman J, *Tetrahedron*, 2001, **57,**9225.
[9] Mogilaiah K, Hari Prasad D and Nageswara Rao A, *Indian J. Heterocyclic Chem*, 2013, **22,** 329.
[10].Mogilaiah K, Nageswara Rao A. and Koteswara Rao P, *Indian J. Chem.*, 2015, **54B,**1280.
[11]Mogilaiah K, Praveena D, Jyothi S and Nageswara Rao , *Indian J. Heterocyclic Chem*, 2015, **24 ,**315.
[12] Reddy K. V, Mogilaiah K and Sreenivasulu B,*J.Indian Chem. Soc.*, 1986, **63,**443.