Indian Journal of Heterocyclic Chemistry
Vol. 27 - Number 02 (Apr-Jun 2017) 157-164

ISSN (Print) : 0971-1627
ISSN (Online) : 2456-4311

MULTICOMPONENT, ONE-POT SYNTHESIS OF HIGHLY SUBSTITUTED PYRIDINES WITH ZINC OXIDE NANOPARTICLES AS CATALYST

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ABSTRACT ZnO nanoparticles were used for a highly efficient one-pot synthesis of highly substituted pyridines by the three component condensation reaction of aromatic aldehydes, malononitrile, and ammonium acetate in the mixture of methanol and water as solvent under classical heating. Using microwave heating, reaction times were shortened from 3 hr to 3 min. The advantage of this method includes the use of green catalyst, short reaction time, easy work up, and excellent yields.

KEYWORDS ZnO Nanoparticles, Microwave irradiation, Multicomponent reaction, Pyridine derivatives.

INTRODUCTION

Multicomponent reactions (MCR) have received more importance for the rapid and highly efficient synthesis of diverse and complex heterocyclic molecules. Multicomponent reactions constitute a very powerful tool to synthesize more classical drug-like, heterocyclic core structures.[1] The pyridine ring system has an important structural motif in naturally occurring compounds as well as in many heterocyclic compounds of pharmaceutical interest.[2] Nitrogen-containing heterocyclic compounds have been widespread in nature, and their applications to pharmaceuticals and agrochemicals field are becoming more and more important.[3] MCR strategy has emerged as a new synthetic tool for the construction of functionalized N-heterocycles. Nitrogen-containing heterocycles show a vast abundance in numerous natural products and several biologically active pharmaceuticals.[4] The attractive heterocyclic scaffolds prepared by MCR pathways are specifically important for the diverse chemical library foundation of drug-like compounds, in which combination of small molecular building blocks in a one-step process leads to greater efficiency in generating diversity.[5] These pyridine skeletons are the most predominant due to their broad spectrum of potential biological activities as antimitotic agents, anti-inflammatory agents, and anticonvulsants.[6-8] Substituted pyridines are building blocks for many pharmaceuticals, agrochemicals, organic intermediates, supramolecules, nanoparticles, OLED, solar cells, and polymers.[9] Furthermore, the preparation of pyridines has been also achieved in the presence of Au/MgO,[10] Montmorillonite K-10,[11] NaOH,[12] $SnCl_2 \cdot 2H_2O$,[13] FeF_3.[14] [bmim]OH,[15] KF/alumina,[16] DBU,[17] TBAH,[18] $ZnCl_2$,[19] microporous molecular sieves,[20] boric acid,[21]

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silica nanoparticles,[22] and Silver(I)–N- heterocyclic carbine.[23]

Microwave synthesis represents a major breakthrough in synthetic chemistry methodology, a dramatic change in the way chemical synthesis is performed and in the way it is perceived in the scientific community. Microwave provides a powerful way to do synthetic chemistry in green approach.[16] Nanochemistry is an up growing research area due to their unique properties,[25] the usage of nanomaterials such as heterogeneous catalyst has gained a significant role in organic synthesis due to simple work up procedure, environmentally benign nature, reusability, low cost, and ease of isolation. Zinc oxide nanoparticles (ZnO-NPs) were heterogeneous catalysts and they are inexpensive, nontoxic, easy to handle, recyclable, and eco-friendly which can be widely used in many organic transformations, cosmetics, paints, and fibers. It can also play a role of Lewis acid in various organic transformations.[26-30]

We have prepared ZnO nanoparticles which have smallest particle size; due to this, it provides larger surface area, so reaction proceeds faster. Although the use of ZnO nanoparticles for the synthesis of pyridines has been reported earlier, the use of microwave in such case has not been explored because current class of substituted pyridines is different from that reported earlier. We herein report a rapid and green approach to achieve highly substituted pyridines in excellent yields in the presence of ZnO nanoparticles as catalyst under controlled MW irradiation **(Scheme 1)**.

RESULTS AND DISCUSSION

Catalyst characterization

The transmission electron microscopy (TEM) image was determined for the pure ZnO nanoparticles and the morphology, particle size of ZnO nanoparticles was investigated by scanning electron microscopy (SEM) **Figure 1**. The TEM and SEM images show particles with diameters in the range of nanometers. The X-ray diffraction (XRD) pattern of the ZnO nanoparticles was shown in **Figure 2.**

The XRD pattern of ZnO nanoparticles was crystalline with hexagonal wurtzite structure, and their XRD peaks at 2θ angle 31.9, 34.6, and 36.2° were corresponding to diffraction from planes (100), (002), and (101), respectively [JCPDS: 36-1451] (**Figure 2**). The XRD of ZnO shows the average particle size in the range of 60 to 70 nm which was determined using Debye-Scherrer formula as,

$$d = K\lambda/\beta\cos\theta$$

Where d is the average particle size perpendicular to the reflecting planes, K is a grain shape dependent constant (0.9), λ is the X-ray wavelength, β FWHM is the full width at half maximum, and θ is the Bragg angle.

Optimization of reaction conditions

Optimization of catalyst loading

To find optimal loading of catalyst and reaction condition, a mixture of 4-chlorobenzaldehyde (1 mmol), malononitrile (2 mmol), ammonium acetate (1.5 mmol), and ZnO nanoparticles as catalyst (0.4 mmol) in methanol:water (6:1) as solvent was irradiated in microwave synthesizer system at 560W (65°C-70°C) for 180 s as model reaction. In the absence of a catalyst, the yield of the product was very low which indicates crucial role of catalyst. 0.4 mmol of ZnO nanoparticles as catalyst was suitable to catalyze the reaction smoothly, and results are summarized in **Table 1.**

The effect of different solvents on the yield of model reaction was studied, and results are summarized in **Table 2**.

Table 1: Optimization of catalyst loading to synthesize substituted pyridine derivatives[a]

Entry	Catalyst mmol	Time (sec)	Yield[b] (%)
1	0	180	30
2	0.1	180	60
3	0.25	180	70
4	0.4	180	88
5	0.7	180	80

[a]Reaction conditions: Aromatic aldehyde (1 mmol), malononitrile (2 mmol), ammonium acetate (1.5 mmol), [b]isolated yield

Table 2: Effect of various solvent on the synthesis of substituted pyridine derivatives[a]

Entry	Solvent	Time (sec)	Yield[b] (%)
1	H_2O	180	15
2	MeOH	180	70
3	CH3CN	180	50
4	DMF	180	45
5	EtOH	180	60
6	MeOH: H_2O (6:1)	180	88

[a]Reaction conditions: Aromatic aldehyde (1 mmol), malononitrile (2 mmol), ammonium acetate (1.5 mmol), catalyst (0.4 mmol), [b]isolated yield

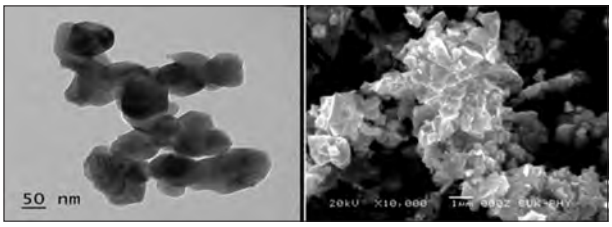


Figure 1: Transmission electron microscopy and scanning electron microscopy images of ZnO NPs

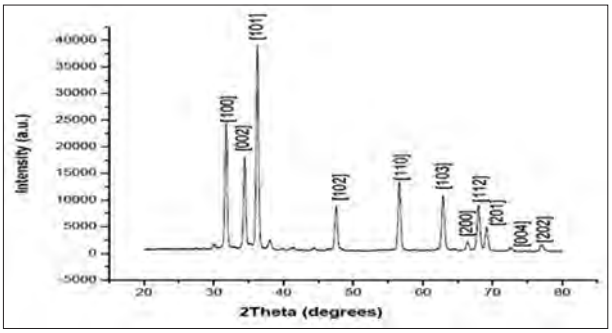


Figure 2: X-ray diffraction patterns of the prepared ZnO nanoparticles

It was found that among all five solvents, a mixture of methanol and water was effective solvent to carry out this transformation with high yield. Therefore, mixture of methanol and water was selected for the synthesis of substituted pyridine derivatives.

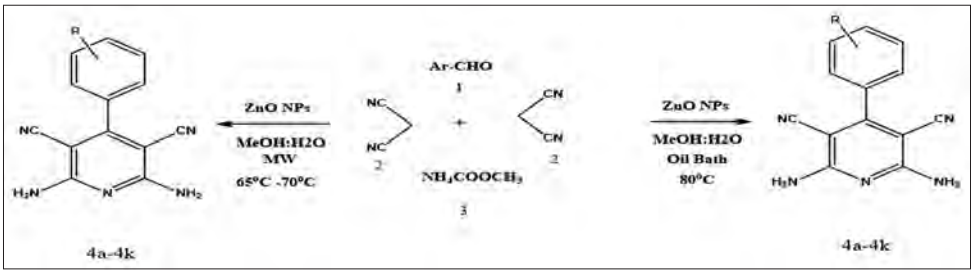
From the green chemistry point of view, efficient recovery and reuse of the catalyst were highly desirable. The recovery and reusability of ZnO-NPs was investigated. After the reaction completed, hot EtOH was added until the solid crude product dissolved. Then, ZnO-NPs as the catalysts were isolated from the mixture of reaction by simple filtration and reused again after washing with EtOH. The reusability of ZnO-NPs was examined efficiently (without any activation) using 4-chlorobenzaldehyde as a model substrate. The recovered ZnO-NPs were reused directly for four consecutive cycles, and all the results are summarized in **Table 3.**

The results obtained from microwave irradiation were compared with conventional heating in **Table 4.** The yields

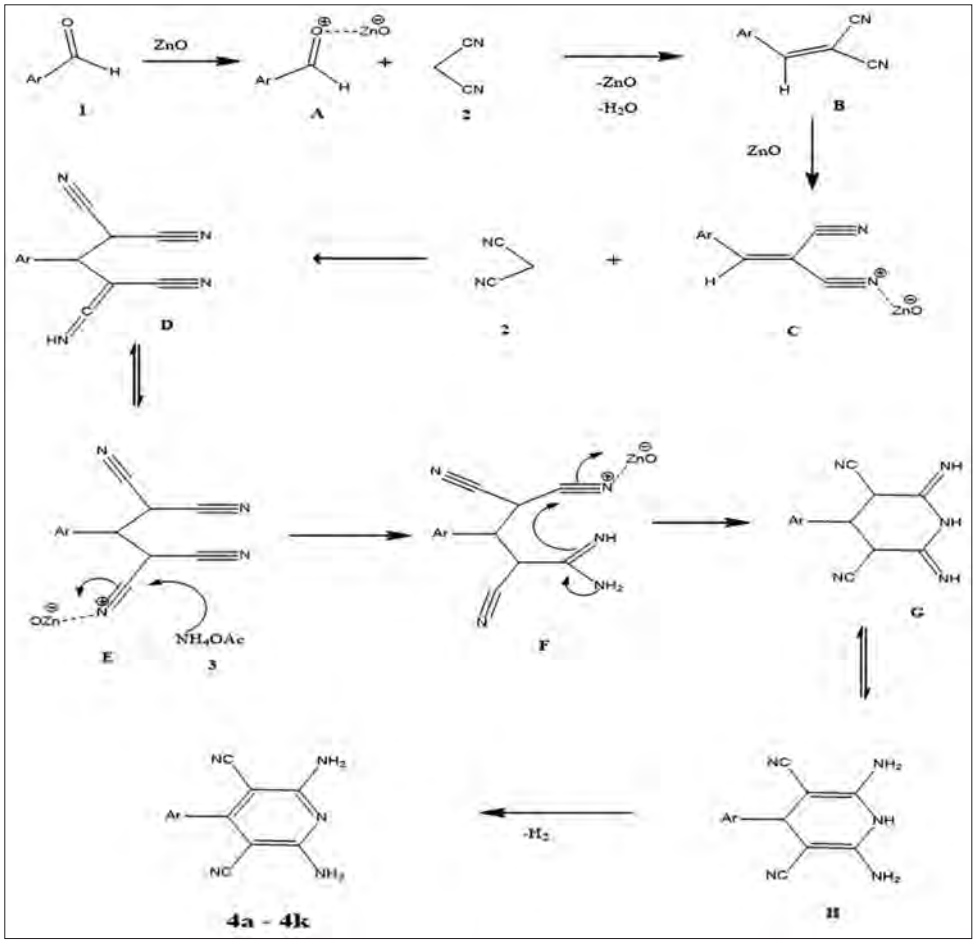
Table 3: Catalyst reusability for synthesis of substituted pyridine derivatives[a]

Number of cycles	Catalyst recovery	Yield[b] (%)
Cycle 1	95	88
Cycle 2	90	81
Cycle 3	85	77
Cycle 4	80	70

[a]Reaction conditions: Aromatic aldehyde (1 mmol), malononitrile (2 mmol), ammonium acetate (1.5 mmol), catalyst, [b]isolated yield

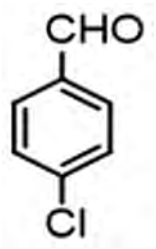
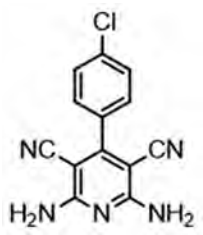
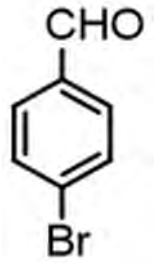
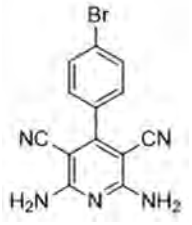
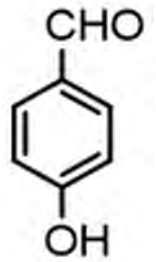
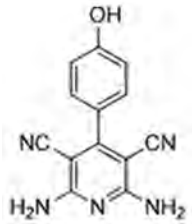
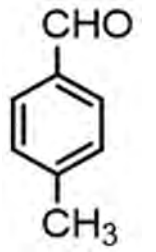
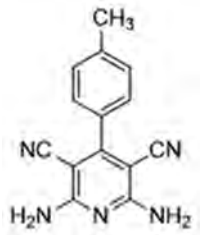
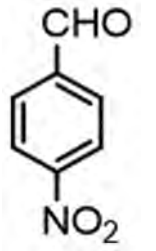
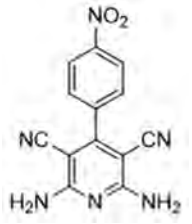
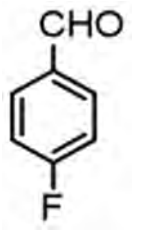
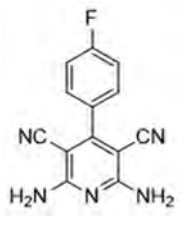


Scheme 1: Synthesis of substituted pyridine derivatives



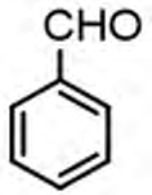
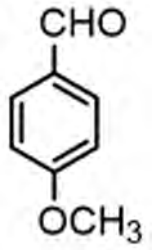
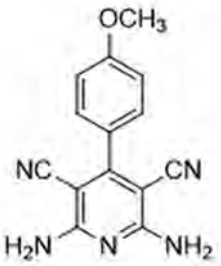
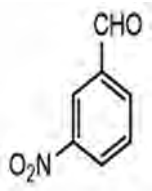
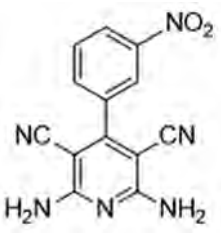
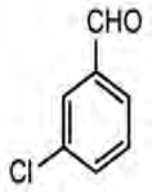
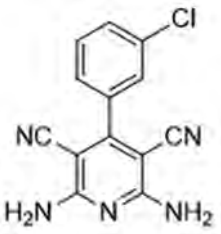
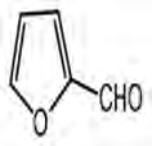
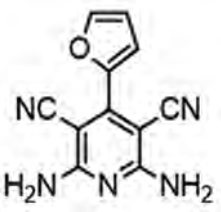
Scheme 2: (a-h) Plausible mechanism for the formation of substituted pyridine derivatives

Table 4: Comparison between classical and microwave heating for synthesis of substituted pyridine derivatives[a]

Entries	Aryl aldehyde	Product	M.P. °C (References)	Classical heating		Microwave heating	
				Time/h	Yield[b] (%)	Time/sec	Yield[b] (%)
1		 (4a)	>300[5,24]	3	80	180	88
2		 (4b)	>300[5,24]	3	79	180	83
3		 (4c)	>300[5,24]	3	77	180	80
4		 (4d)	>300[5,24]	3	78	180	82
5		 (4e)	>300[5,24]	3	82	180	87
6		 (4f)	>300[5,24]	3	80	180	84

(Contd...)

Table 4: (*Continued*)

Entries	Aryl aldehyde	Product	M.P. °C (References)	Classical heating		Microwave heating	
				Time/h	Yield[b] (%)	Time/sec	Yield[b] (%)
7		 (4g)	>300[5,24]	3	77	180	82
8		 (4h)	>300[5,24]	3	72	180	75
9		 (4i)	>300[5,24]	3	81	180	85
10		 (4j)	>300[5,24]	3	75	180	83
11		 (4k)	>300[5,24]	3	78	180	84

[a]Reaction conditions: Aromatic aldehyde (1 mmol), malononitrile (2 mmol), ammonium acetate (1.5 mmol), catalyst (0.4 mmol), [b]isolated yield

obtained using microwave heating were generally higher than conventional heating and reaction times reduced from 3 h to 3 min.

Taking into consideration the reported literature (31, 32), a plausible reaction mechanism is depicted in **Scheme 2**. ZnO nanoparticles have a smallest particle size and possess Lewis and Bronsted acidity. Zn binds oxygen thereby increasing electrophilicity of carbonyl carbon of aromatic aldehyde. The first step proceeds via Knoevenagel condensation between benzaldehyde and malononitrile gives

benzilidenemalononitrile **B** as an intermediate. Michael addition of the second equivalent of the malononitrile 2 would furnish the adduct **D** with tautomeric form E. Then a nucleophilic attack of ammonium acetate 3 on cyanide group of **E** affords the intermediate F. cycloaddition of F would yield to the structure G that is in equilibration with H tautomer, this tautomer would subsequently undergo auto-oxidation by air to yield the desired product **(Table 4, entry 1-11).**

EXPERIMENTAL SECTION

All reactions were performed in the borosil round bottom flask, volume 25 mL. Analytical thin layer chromatography was performed using thin layer chromatography (TLC) pre-coated silica gel 60 F_{254} Merck (20 × 20 cm). TLC plates were visualized by exposing to ultraviolet light or by iodine vapors. Microwave reactions were carried out in a Microwave Synthesizer System (850W power; Cata R System). Melting points were taken in an open capillary and are uncorrected. The XRD patterns were recorded on Bruker D2 PHASER XRD. SEM image was obtained on JEOL JSM-6360. TEM image was obtained on JEOL JEM 2100. Mass spectra were recorded on a Perkin Elmer Clarus 600 mass spectrometer using EI ionization. ^{1}H nuclear magnetic resonance (NMR) and ^{13}C spectra were recorded with AV 400 Bruker 400 MHz NMR instrument. Chemical data for protons are reported in parts per million (ppm, scale) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent (DMSO: δ 2.5).

Preparation of ZnO nanoparticles

Synthesis of ZnO nanoparticles was done by Sol-gel method. Aqueous ammonia (1:1) was added into 0.2M Zinc acetate solution with magnetic stirring to maintain the pH in between 7 and 8 to get a gel. After 4 h continuous stirring, white gel was dried at 80°C for 6 h and the obtained dry product was calcinated at 400°C for 3 h in a muffle furnace. The size and their perfect morphology were observed under XRD, SEM, and TEM.

Thermal method for the preparation of substituted pyridine derivatives

A mixture of aromatic aldehyde (1 mmol), malononitrile (2 mmol), ammonium acetate (1.5 mmol), and ZnO nanoparticles (0.4 mmol) as catalyst in methanol:water (6:1) was mixed and magnetically stirred at 80°C for 3 h. After completion of the reaction, the reaction mixture was recrystallized from EtOH to afford the pure product.

Microwave irradiation for the preparation of substituted pyridine derivatives

A mixture of aromatic aldehyde (1 mmol), malononitrile (2 mmol), ammonium acetate (1.5 mmol), and ZnO nanoparticles (0.4 mmol) as catalyst in methanol:water (6:1) was irradiated in microwave synthesizer system at 560W (65°C-70°C) for 180 s. After completion of the reaction, the reaction mixture was recrystallized from EtOH to afford the pure product.

Spectral data of a representative compounds

2,6-Diamino-4-(4-chlorophenyl) pyridine-3, 5-dicarbonitrile (4a) (Table 4, entry 1)

White solid; m.p. >300°C; ^{1}H NMR (400 MHz, DMSO-*d*6) *δ*: 7.61 (d, J=8.4 Hz, 2H), 7.51 (d, J=8.4 Hz, 2H), 7.31 (s, 4H); ^{13}C NMR (100MHz, DMSO-*d*6), δ = 160.8, 158.5, 134.6, 133.8, 130.2, 128.3, 116.2, 79.6 ppm, MS(EI): *m/z* 269.15, IR(KBr, cm^{-1}) 3472, 3422, 3373, 3220, 3116, 2204, 1672,1627,1516,1170,831,766.

2,6-Diamino-4-(4-bromophenyl) pyridine-3, 5-dicarbonitrile (4b) (Table 4,entry 2)

Cream solid; m.p. >300°C; ^{1}H NMR (400 MHz, DMSO-*d*6) *δ*: 7.74 (d, J=6.8 Hz, 2H), 7.44 (d, J=6.8 Hz, 2H), 7.26 (s, 4H) ppm; ^{13}C NMR (100MHz, DMSO-*d*6), 160.8, 158.5, 134.2, 133.5, 130.4, 123.4, 116.2, 79.5 ppm, MS(EI): *m/z* 314.93, IR(KBr, cm^{-1}) 3463, 3427, 3353, 3214, 3158, 2206,1675,1622,1534,1070,833.

*2,6-Diamino-4-(4-hydroxyphenyl) pyridine-3, 5-dicarbonitrile (4c) (*Table 4*, entry 3)*

White solid; m.p. >300°C; ^{1}H NMR (400 MHz, DMSO-*d*6) *δ*: 9.91(s, 1H, OH), 7.31 (d, J=8.8 Hz, 2H), 7.13 (s, 4H), 6.88 (d, J=8.8 Hz, 2H) ppm; ^{13}C NMR (100MHz, DMSO-*d*6), δ = 161.1, 159.6, 129.9, 125.3, 116.7, 115.1, 79.6 ppm, MS(EI): *m/z* 251.25, IR(KBr, cm^{-1}) 3466, 3412, 3363, 3224, 3161, 2202, 1672, 1627, 1516, 1170, 823,775.

2,6-Diamino-4-(p-tolyl) pyridine-3, 5-dicarbo nitrile (4d) (Table 4, entry 4)

Cream solid; m.p. >300°C; ^{1}H NMR (400 MHz, DMSO-*d*6) *δ*: 7.36-7.31 (m,4H,ArH), 7.19 (s, 4H), 2.37 (s, 3H) ppm; ^{13}C NMR (100MHz, DMSO-*d*6), δ = 160.9, 159.7, 139.5, 132.1, 129.0, 128.1, 116.4, 79.7,20.8 ppm, MS(EI): *m/z* 249.06, IR(KBr, cm^{-1}) 3477,3422,3367,3216,3157,220 6,1676,1624,1566,1370,820,766.

CONCLUSION

High surface area and recyclability of the nanocrystalline ZnO catalyst, easy preparation of the catalyst, low reaction times were the main advantages of this method. Satisfactory yield of products and easy workup make this a useful protocol for green synthesis of this class of compounds.

ACKNOWLEDGMENTS

This research was financially supported by UGC, New Delhi [File No. 47-1160/14(WRO) dated: 28th Dec. 2015]. We are grateful for analytical help of SIF, VIT university, Vellore and SAIF IISc., Bangalore.

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Received: 21 Apr 2017, Accepted: 27 May 2017