



Co-Ni Nanomaterial Mediated Synthesis of Various 2-amino-4-phenyl-6-Pyridine 3,5 Dicarbonitrile.

Report of a project carried out as a part of curriculum for the
Degree of Master of Science in Organic Chemistry

CHO-453

Submitted by

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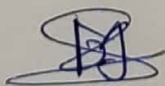
2021-2022

DECLARATION BY THE CANDIDATE

I hereby declare that this project entitled "**Co-Ni Nanomaterial Mediated Synthesis of Various 2-amino-4-phenyl-6-Pyridine 3,5 Dicarbonitrile**" is a confident and genuine project work carried out by us under supervision of **Dr. Amol Haridas Kategaonkar**, Assistant Professor, P.G. Department of Organic Chemistry, M.V.P. Samaj's K.S.K.W. Arts, Commerce and Science College CIDCO Uttamnagar, Dist. Nashik Maharashtra.

Date- 22.06.2022

Place- Nashik



MR. MINDE MANOJ PANDURANG

CERTIFICATE BY THE SUPERVISOR

This is to certify that entitled "Co-Ni Nanomaterial Mediated Synthesis Of Various 2-amino-4-phenyl-6-Pyridine 3,5 Dicarbonitrile." is a bonafide and genuine project work done by **MR. MINDE MANOJ PANDURANG** fulfilment of the requirement for degree of Master of Science (Organic Chemistry)

Date: - 22.06.2022

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ACKNOWLEDGEMENT

CERTIFICATE

This is to certify that projected entitled “**Co-Ni Nanomaterial Mediated Synthesis Of Various 2-amino-4-phenyl-6-Pyridine 3,5 Dicarbonitrile**” is a bonafide projected work done **Mr. MANOJ PANDURANG MINDE** supervision of **Dr. Amol Haridas Kategaonkar**.

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Date: -

Place: CIDCO Nashik

MR. MINDE MANOJ PANDURANG

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1. INTRODUCTION

Transition metal oxides (TMOs) are widely used as hetero-Generous catalysts or catalysis supports in the chemical Industry. [1-2] Nanometer-sized metal particles, from several to a few hundred nanometers, have attracted intensive Attention in recent Years due to their wide application in batteries, hard alloys, Catalysts, and electronics. Nickel particles have been conventionally used in many industrial and consumer products Including Magnets, stainless steel, special alloys, coinage, Plating and glasses.

Due to the increased specific surface Area And reactivity, nanometer sized nickel particles could significantly improve the properties of Conventional products and Promote new applications, such as catalysis for hydrogenation and for Controlled grow [3-5]

Cobalt accommodates a variety of oxidation states such as 0, +1, +2 and +3. The low-valent cobalt Species (-1 and 0) are frequently found in some well-known organometallic complexes and starting Materials and starting materials [6-7]

This metal oxide is very important role on organic synthesis reactions such as Multicomponent Reactions. As we are the developed this catalyst by green chemistry methods .Multicomponent reactions (MCRs) have drawn high efforts In recent years owing to exceptional synthetic efficiency, High selectivity, and procedural simplicity [8-13]. One-pot Multicomponent reactions are a new method to construct Heterocyclic compounds with bond making and/or bond Breaking in one step with high atom economy, and the Diversity can be achieved by varying the reacting components. A large number of organic reactions which were carried out afforded higher yields, shorter reaction time, and milder conditions [14-16]. Substituted pyridines were used as medical scaffolds Because they are part of many natural product structures [17-18]. Pyridine derivatives have also showed a broad Spectrum of biological activities such as antimitotic agents [19], anti-inflammatory substances [20], and anticonvulsants

[21]. In addition, they also regulate arterial pressure [22] and Cholesterol level in blood [23]. Furthermore, they were Utilized as electrical materials [24] and chelating agents [25].

Within the framework of green chemistry, solvents and catalysts are Recognized to play a key role. They are recognized as the most deliberated of the twelve principles of green chemistry [26-28]. To be considered as green elements, solvents and catalysts should fulfil various requirements, notably biodegradability, non-toxicity and recyclability, as well as cost-effectiveness.

Pyridine derivatives have played a very important role in the improvement of heterocyclic chemistry and are ordinarily used in organic synthesis.[29]. Pyridine derivatives have been reported to possess anti-fungal, antibacterial activities. Amino acids have a unique bifunctional, structure that serves to conveniently from peptides, peptidomimetics, and proteins. Due to its numerous biological activities reported.

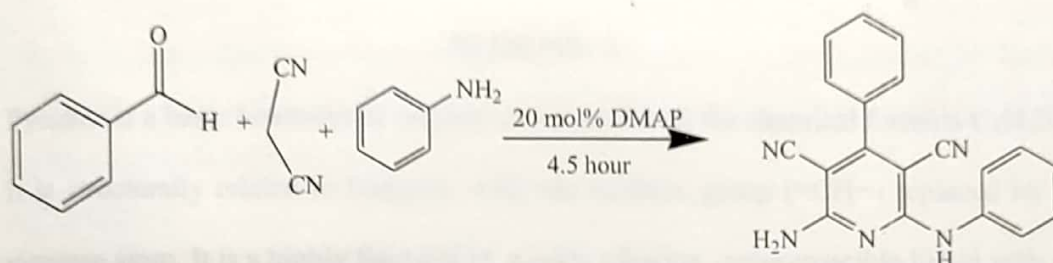


This reaction performed using an equivalent of benzene, chlorides, two equivalents of acetonitrile, and the equivalent of sulfur dioxide in the presence of ZnO nano particles. Catalyst, NaOH, under reflux conditions in EtOH for 12h.

2. LITERATURE REVIEW

Naglaa F.H.Mahmoud and Ahmed EL-Sewedy

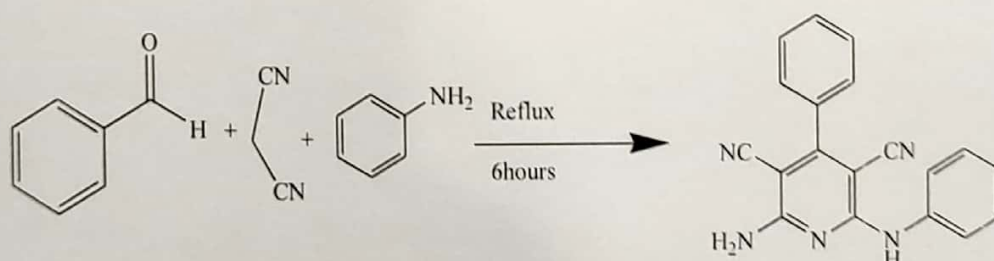
An efficient and convenient synthesis of substituted pyridine derivatives has been achieved by the one-pot, multicomponent condensation of using Benzaldehyde, malenonitrile, aniline, and the catalyst is 20 mol % DMAP, solvent is Methanol and reaction time is 4.5 hour



SCHEME-1

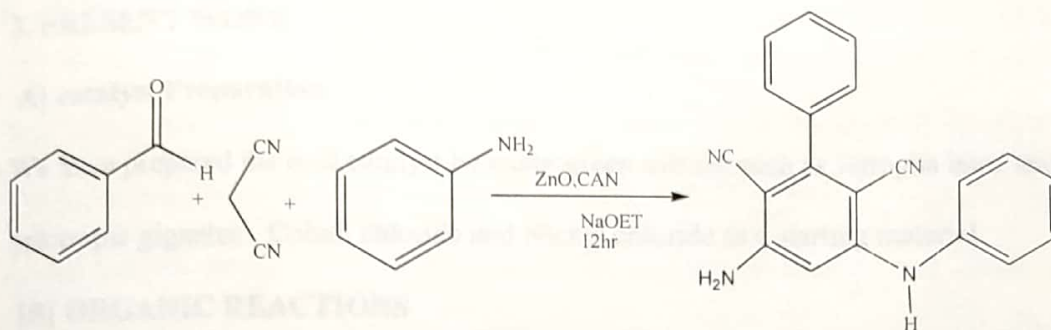
Naglaa F.H.Mahmoud and Ahmed EL-Sewedy

This reaction using ethanolic solutions of aromatic aldehydes, malononitrile, and Aniline in the presence of Lewis acids as catalysts such as $AlCl_3$, $ZnCl_2$, and $FeCl_3$. The reaction mixture was refluxed for 6 h using different molar ratios 1 : 2 : 1, 1 : 2 : 2, and 1 : 2 : 3 (aromatic aldehydes: malononitrile: Aniline), respectively.



SCHEME- 2

This reaction performed using one equivalent of aromatic aldehydes, two equivalents of malononitrile, and One equivalent of aniline the presence of ZnO (nano particles), CAN, NaOEt, and/or H_3PO_4 as catalysts in Refluxing ethanol for 12h.



SCHEME- 3

Pyridine is a basic heterocyclic organic compound with the chemical formula C_5H_5N . It is structurally related to benzene, with one methine group ($=CH-$) replaced by a nitrogen atom. It is a highly flammable, weakly alkaline, water-miscible liquid with a distinctive, unpleasant fish-like smell. Pyridine is colorless, but older or impure samples can appear yellow. The pyridine ring occurs in many important compounds, including agrochemicals, pharmaceuticals, and vitamins. Pyridine heterocycles have special interest due to its important class of natural and non-natural products and show high biological activities in pharmaceutical and biological fields.

3. PRESENT WORK

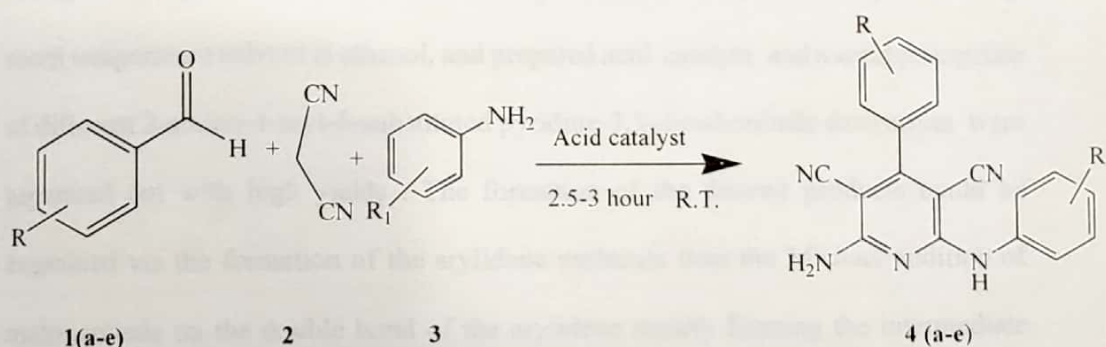
A) catalyst Preparation

We have prepared the acid catalyst by using green solvent such as Jatropha latex and calotropic gigantea . Cobalt chloride and Nickel chloride as a starting material.

[B] ORGANIC REACTIONS

We have demonstrated the Synthesis 2- amino - 4 -phenyl- 6-(phenylamino)pyridine-3,5 dicarbonitrile structure derivative in acidic medium of substituent benzaldehyde, Aniline and malenonitrile in the presence of acids catalyst

SCHEME -4



4. RESULTS AND DISCUSSION

According to literature 2-amino-4-phenyl-6-substituted pyridine-3,5-dicarbonitrile derivatives were synthesized by a multistep pathway in the presence of 20 Mol% DMAP as the catalyst and reaction time is 4.5 hour with 81% yield.

In our present study, we have investigated the one-pot multicomponent reactions (MCRs) to prepare amino-pyridine derivatives using acid catalysts such as a molar ratio of 1 : 2 : 1 (aromatic aldehydes: malononitrile: aniline) where the desired products were obtained in moderate yields. The reaction was performed with aromatic aldehydes (1 equivalent), malononitrile (2 equivalents), and aniline (1 equivalent) by room temperature solvent is ethanol, and prepared acid catalyst, and a solid precipitate of different 2-amino-4-aryl-6-substituted pyridine-3,5-dicarbonitrile derivatives were separated out with high yields. The formation of the desired products could be explained via the formation of the arylidene molecule than the Michael addition of malononitrile on the double bond of the arylidene moiety forming the intermediate which underwent cyclization by the nucleophilic attack of amine on the cyanocarbon followed by aromatization to the final products.

As a conclusion, we have developed From an economical and environmental point of view, we have studied initially the three-component reaction of benzaldehyde, malenonitrile, aniline and (1:2:1) in the presence of (20 mol%) acid catalyst at room temperature for 2.5 to 3 h to obtain the desired substituted pyridine derivative in quantitative yield. However, no product formation was observed when the mixture was stirred under similar reaction conditions in the absence of acid catalyst. The catalytic activity of the recycled acid catalyst was also examined according to the typical experiment conditions.

Compound **4e** shows seven signals in ^1H NMR spectrum. In this 6.9 δ and 7.31 δ shows the singlet attached to the benzene ring 4.0 δ 2H singlet attached to the substituted pyridine ring. 7.01 δ and 6.62 δ shows to the singlet attached to benzene ring.

Compound **4e** shows seven signals in LCMS. A sharp broad peak obtained at retention time is 0.26 at this retention time 329.40 (M+2) mass obtained at base peak.

MECHANISM:

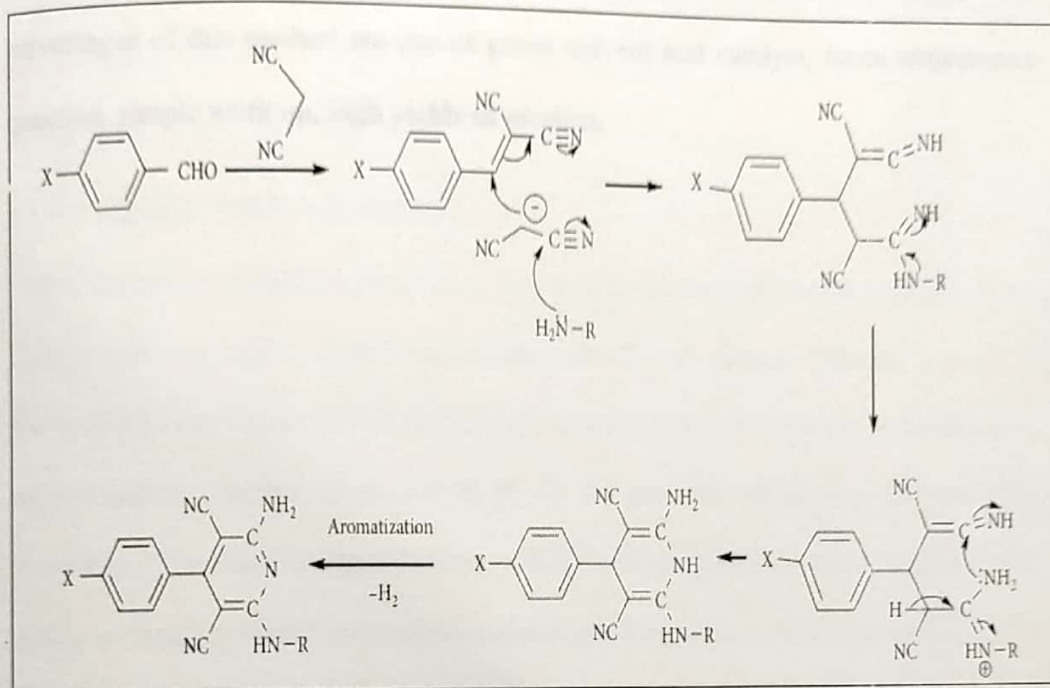


Table 1. Synthesis of 2-amino-4-phenyl-6-substituted pyridine-3,5-dicarbonitrile derivatives

Compound	R & R1	Time (min)	Yield (%) ^a	M. P. (°C)
4a	-H & -H	155	91	248-250
4b	4-Cl & -H	165	85	300-302
4c	H & 4-Me	160	79	202-205
4d	2-Cl & H	175	81	289-291
4e	4-OH & H	170	75	312-315

5. CONCLUSION

We have developed , environmentally protocol for the Synthesis 2-amino-4-phenyl-6-(phenylamino) pyridine-3,5-dicarbonitrile derivative in acidic medium. The advantages of this method are use of green solvent and catalyst, room temperature reaction, simple work up, high yields of product.

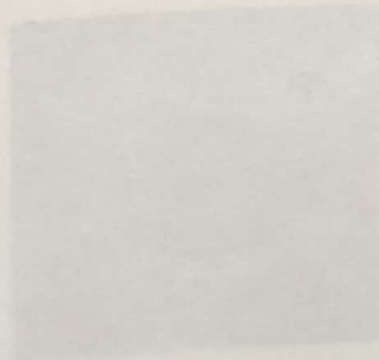
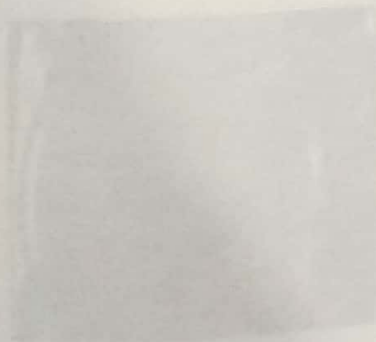
EXPERIMENTAL PREPARATION

1. We have developed a green protocol for the synthesis of 2-amino-4-phenyl-6-(phenylamino) pyridine-3,5-dicarbonitrile derivative in acidic medium. The advantages of this method are use of green solvent and catalyst, room temperature reaction, simple work up, high yields of product.

Figure 1



Figure 2



6. EXPERIMENTAL WORK

The products were identified by comparing their melting point that mentioned in a reported literature. The melting point was taken in open capillaries in a paraffin oil and are uncorrected.

GENERAL PROCEDURE

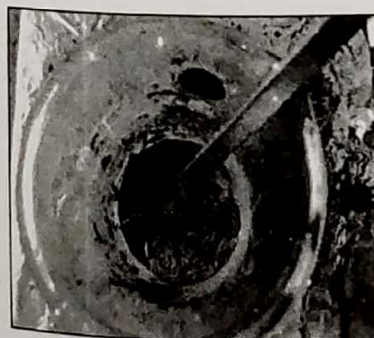
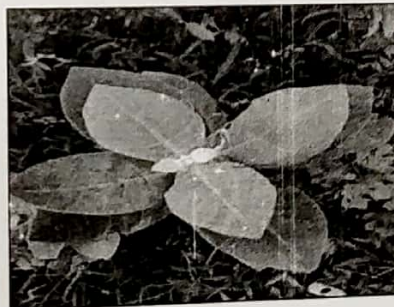
A) CATALYST PREPARATION

Firstly we have collected a plant latex such as *Jatropha* and *Calotropis gigantea* from field in glass container. Take 5 mL of latex in 100 mL beaker, then add 1 mole of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 1 mole $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in it. Stir the solution of proper dissolution of solid. Mixture is heated for 10 min at 80°C . we get solid which was first bluish in color than it converts to greenish color which indicates conversion of material and finally brownish material obtained. It was a quick and fast process for getting solid phase from latex. Then place material for calcination in temperature range of 550 to 650°C in muffle furnace.

Jatropha plant



Calotropis gigantea plant



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