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# One-pot synthesis of 2-amino-3-cyanopyridine derivatives catalyzed by zinc zirconium phosphate in solvent-free conditions

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ABSTRACT

A simple and efficient procedure for the synthesis of 2-amino-3-cyanopyridines from aldehydes, ketones, malononitrile, and ammonium acetate via one-pot reaction is reported. Zinc zirconium phosphate (ZPZn) nanoparticles were used as a convenient and efficient catalyst for this multicomponent reaction (MCR) under solvent-free conditions, and fair to excellent yields were achieved. The catalyst was characterized by ICP-OES, XRD, $NH_3$-TPD, Py-FTIR, $N_2$ adsorption-desorption, SEM, and TEM. The steric and electronic properties of the different substrates had a significant influence on the reaction conditions. The catalyst was recovered and reused at least six times without any discernible decrease in its catalytic activity. This procedure tolerates most of the substrates and has the advantages of short reaction times, high yields, and environmentally friendly.

***Keywords**: Zinc zirconium phosphate, Nanoparticles, Multi-component reactions, Solvent-free, Solid catalyst.*

## 1. Introduction

Multi-component reactions (MCRs) are those reactions in which three or more reactants come together in a single reaction vessel to form a new product which contains portions of all the components. They have been known for over 150 years [1]. MCRs are by far the richest class of strategies resulting in high structural diversity and molecular complexity via a single one-pot transformation. MCRs are an area of considerable interest because the products are produced in a single step, and also the variety could be formed by changing the reaction components [2-4]. Nowadays, there is an increasing number of new three- and four-component reactions, which can produce some of the important classes of pharmaceutical compounds biological activities, such as anticonvulsant [5], cardiotonic [6] and vasorelaxant [7]. Also, several examples of "higher-order" MCRs where five or even more components are involved in a one-pot reaction can also be found in the literature [8,9].

The N-heteroaromatic pyridine is prevalent in numerous natural products, pharmaceuticals, and functional materials and is extremely important in the chemistry of biological systems.

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Among these compounds, 2-amino-3-cyanopyridine derivatives have been reported to possess remarkable pharmacological properties and activities such as antiviral, anticancer, antitubercular, antimicrobial, $A_{2A}$ adenosine receptor antagonists, and fungicidal activities [7-10]. Therefore, the synthesis of these compounds continues to attract interest in organic chemistry. Various preparation methods for the synthesis of 2-Amino-3-cyanopyridines have been reported such as $[EtNH_3]NO_3$ [7], MWI [10,11], $Yb(PFO)_3$ [12], $FePO_4$ [13], TBBDA [14], $Ti(dpm)(NMe_2)_2$ [15], $[Bmim][BF_4]$ [16], Cellulose–$SO_3H$ [17], Ultrasonic irradiation [18,19], SBTETASA [20], Trifluoroethanol [21] and also a multiple step procedure using amino acid and refluxing [22].

Layered zirconium hydrogen phosphate with a α-type structure, $Zr(HPO_4)_2{\cdot}H_2O$, is one of the most important inorganic materials as it shows several advantages such as extreme insolubility in water and organic solvents, high water tolerance ability, high thermal stability, and easy sedimentation. These properties made α-zirconium phosphate (ZrP) a suitable heterogeneous catalyst and catalyst support [23,24], excellent ion exchanger [25], an interesting intercalating agent [26], which also has been used in nanocomposite [27], proton conductor for fuel cells, drug delivery and immobilization of biological materials [28,29].

To satisfy the requirements for application in different fields, it has been prepared by different methods in a wide variety of sizes from 2 nm to up to 2 μm [30-32]. The crystal structure of ZrP is built up by covalent bonds between atoms in layers, hydrogen bonds and van der Waals forces between layers [32]. It consists of layers made of planes of zirconium atoms bonded, on both sides of each plane, to mono-hydrogen phosphate groups. Water molecules are placed in the interlayer region, forming a hydrogen-bonding network with the phosphate groups. The crystalline ZrP possesses weak and strong Brönsted and Lewis acid centers, which are attributed to P-OH groups and the $Zr^{4+}$, respectively. Due to the presence of high hydroxyl group density on ZrP surface, which can be assumed as hooks, various organic functional groups could adsorb on, allowing to control both the reactivity and selectivity of the reaction. The $H^+$ of the P–OH moiety in ZP can be exchanged for various other ions, which results in the enlargement of the interlayer distance [33-35]. Several studies about the successful exchange of the $H^+$ of the P–OH group in ZP with various divalent and trivalent cations have been reported [36-41]. It has been reported that ZP possesses excellent selectivity towards $Pb^{2+}$, $Zn^{2+}$, and $Fe^{3+}$ as an ion exchanger [42-44]. Furthermore, ZP has been reported to exhibit antibacterial activities when it was loaded with $Cu^{2+}$, $Zn^{2+}$, or $Ce^{3+}$ [39-41]. Several reports have also appeared in the literature concerning the catalytic activities of ion exchanged materials of this type, including the use of zirconium phosphate-ferric chloride complex and potassium iron zirconium phosphate as a catalyst in Friedel-Crafts reaction [45-48].

With growing environmental concerns, there is more demand for the use of green and insoluble catalysts or eco-friendly solvent-free conditions. When an insoluble catalyst is used, it can be easily recovered from the reaction mixture by simple filtration and then recycled and reused several times, making the process more economically and environmentally viable. Furthermore, the reported examples have demonstrated that heterogeneous catalysts typically require easier work-up procedures. With this in mind, and as part of ongoing work towards the development of efficient green catalysts for organic transformations [25], we report herein the use of zinc zirconium phosphate (ZPZn) as an efficient catalyst for the mild and convenient MCRs, which is characterized by ICP-OES, XRD, BET, $NH_3$-TPD, Py-FTIR, SEM and TEM.

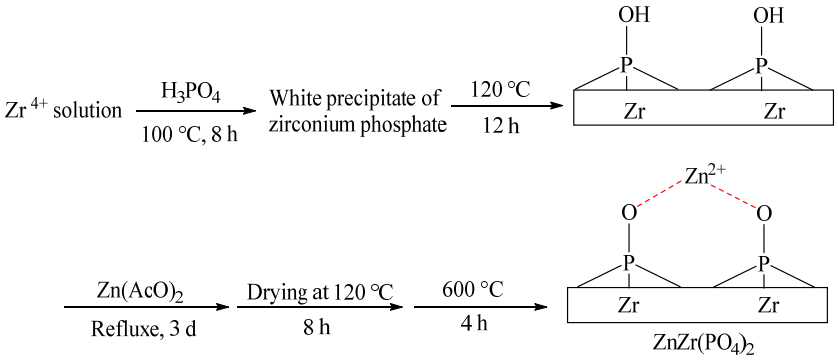
## 2. Experimental

### *2.1. Catalyst synthesis*

All the reagents and solvents used in the current study were purchased from the Merck Chemical Company and used without further purification. The catalyst was prepared according to previously published procedures, with some modifications [25]. ZP was prepared according to the following procedure. $ZrOCl_2 \cdot 8H_2O$ (5 g) was heated at reflux in a solution of $H_3PO_4$ (50 ml, 12 mol/L) for 8 h. The resulting mixture was cooled to ambient temperature to give a suspension, which was filtered, then the filter cake was washed with a solution of $H_3PO_4$ (0.1 mol/L) until the filtrate was free of chloride ions. To determine the presence of any chlorine ion in the filtrate, the silver nitrate test was used. The filter cake was then washed several times with distilled water until the pH of the filtrate was neutral. The solid was then collected and dried in an oven at 120°C for 12 h. ZPZn was prepared through an ion-exchange reaction. Briefly, ZP (3 g) was dispersed in deionized water (50 ml) at 60°C, and the resulting suspension was treated with a solution of $Zn(OAc)_2$ (100 ml, 0.1 mol/L) in water (excess amount of $Zn^{2+}$). This mixture was then heated at reflux for 3 d. It is noteworthy that the acetate ion performed effectively as a base to keep the hydrogen ion concentration in the solution sufficiently low to achieve high loadings of the catalyst [45]. A complete exchange between the cations and the hydrogen ions of the P–OH groups could not be achieved in less than 3 d or at temperatures below 80°C [40]. The resulting slurry was filtered hot to give a light white solid, which was washed with distilled water until no $Zn^{2+}$ ions could be detected in the filtrate (i.e., until the filtrate was colorless). The product was then dried at 120°C for 8 h before being calcined at 600°C for 4 h to give the final product, ZPZn, as a white solid (Scheme 1).

### *2.2. General procedure for the preparation of 2-amino-3-cyanopyridines*

A mixture of aldehyde (1 mmol), ketone (1 mmol), malononitrile (1 mmol), ammonium acetate (2 mmol) and the catalyst (1.5 mol%) was stirred in one-pot at 60ºC for the appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was washed with EtOH and the catalyst was removed. The corresponding pure solid product was obtained by being recrystallized from hot EtOH affording the 2-amino-3-cyanopyridine derivatives.




**Scheme 1.** Procedure for the preparation of ZPZn.

### *2.3. Recyclability studies of catalyst*

To examine the recyclability of the catalyst, the used ZPZn was recovered from the reaction media and re-used. For recycling, after the first use, the catalyst was separated from the reaction mixture by centrifugation, washed sequentially with ethanol and water before being dried at 110 °C for 2h, and then activated at 450°C for 2 h.

## 3. Results and Discussion

### *3.1. Catalyst characterization*

The ICP-OES analyses of ZP and ZPZn are shown in Table 1. The results obtained in the current study for ZPZn were compared with those reported previously in the literature [39-41]. Our results revealed that there was a negligible leach of zinc ions into the reaction media after the reaction (i.e., following the first use of the catalyst).

Pyridine has been verified to be an excellent FTIR spectroscopy probe to characterize the nature of the acid sites of the catalyst and the resulting IR spectrum is shown in Fig. 1. The main bands observed over the samples are assigned according to the literature data [24]. The origin of Brönsted acidity of the samples is due to the presence of P–OH groups. The pyridine-desorbed FTIR spectra of ZrP showed characteristic strong bands about 1446 $cm^{-1}$ , which are assigned to the coordinated pyridine in Lewis acid sites. The pyridinium ions are formed by the transfer of protons from the P-OH groups in the ZrP to the organic base. The absorption peak about 1630 and 1541 $cm^{-1}$ are caused by pyridine adsorbed on Brönsted acid sites [23, 24]. Additionally, the band at 1488 $cm^{-1}$ indicates the combination band between those adjacent Lewis and Brönsted acid sites at 1541 and 1446 $cm^{-1}$ respectively [23].

It is obvious from the figure that the prepared ZrP shows a higher number of Brønsted acid sites accompanied by low amounts of Lewis acid sites.

The surface morphology of the ZP and ZPZn was studied by SEM (Fig. 2). The SEM image of ZP (Fig. 2(a)) revealed the presence of hexagonal plates with well-defined shapes and very smooth surfaces. Fig. 2(b) and (c) show the SEM images of ZPZn. These images revealed that the structure of ZPZn was less ordered than that of ZP and that the ZPZn particles had aggregated to form both sheets and spheres of different shapes and sizes [39,40,45].

Fig. 3 shows the TEM images of ZPZn. It shows that ZPZn catalyst retained the original morphology of ZP (layered structure) and that the particles were approximately 150 nm in size. These images also showed nanoparticles of different sizes on the smooth surface of the ZP.

**Table 1.** Element contents of ZPZn (atm.%) and physical properties of the catalysts before and after the reaction.

| Entry | Sample | Zn | O | Zr | P | BET ($m^2/g$) | Total acidity (mmol $NH_3/g$) |
|---|---|---|---|---|---|---|---|
| 1 | ZP | - | 65.3 | 12.4 | 22.3 | 118.2 | 2.5 |
| 2 | ZPZn | 12.1 | 54.1 | 12.3 | 21.5 | 102.4 | 1.6 |
| 3 | ZPZn [a] | 11.9 | 54.2 | 12.3 | 21.6 | 102.1 | 1.52 |
| 4 | ZPZn [b] | 4.5 | 63.6 | 12 | 19.9 | 86.4 | 0.78 |

[a]After the first cycle.
[b]After the 7th cycle.

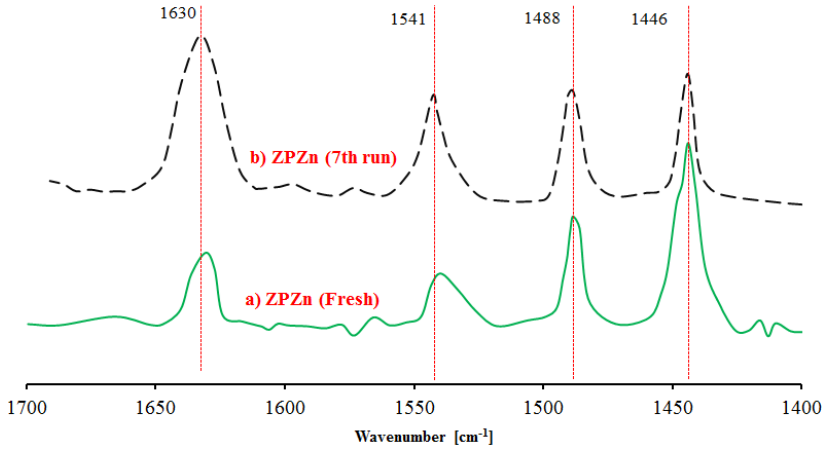



**Fig. 1.** Pyridine-desorbed FTIR spectra of ZPZn (Fresh and after the 7th run).

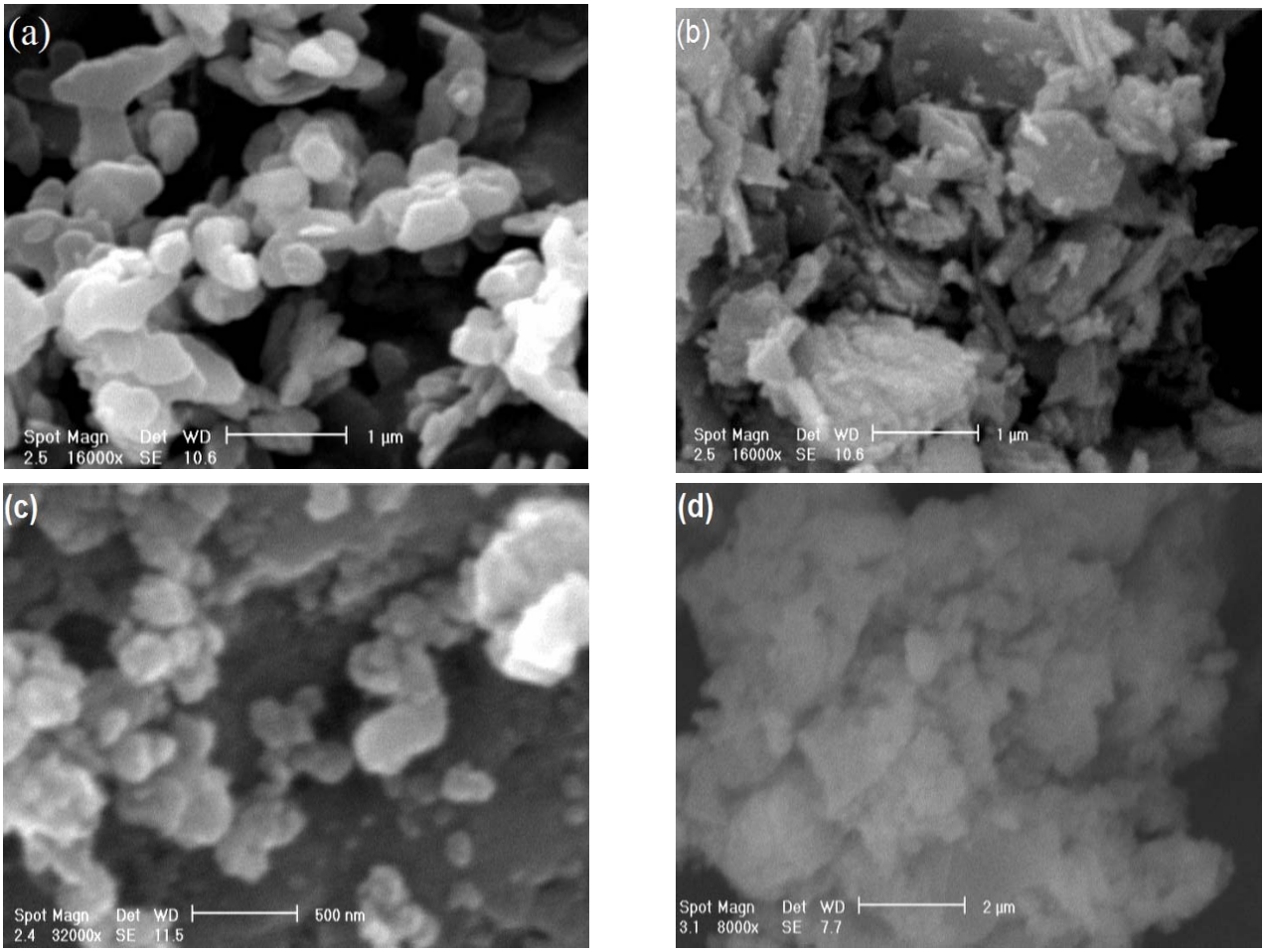



**Fig. 2.** SEM images of the regular morphology of prepared ZP (a), ZPZn fresh (b, c) and after the 7th run (d).

The presence of metallic crystal nanoparticles on the surface of ZP indicated that the zinc deposited on the surface of the ZP had agglomerated. Similar observations have also been reported for copper, zinc, and cerium with ZP [40,41]. Fig. 2(d) and 3(d) show the SEM and TEM images of the catalyst after several regenerations, respectively. All these images showed that the sheets and particles had conglomerated to a much greater extent following the 7th run because of the process used to regenerate the catalyst. A detailed discussion about XRD, BET, and TPD-$NH_3$ of the catalyst is presented in the supplementary information (Pages S2-S6).

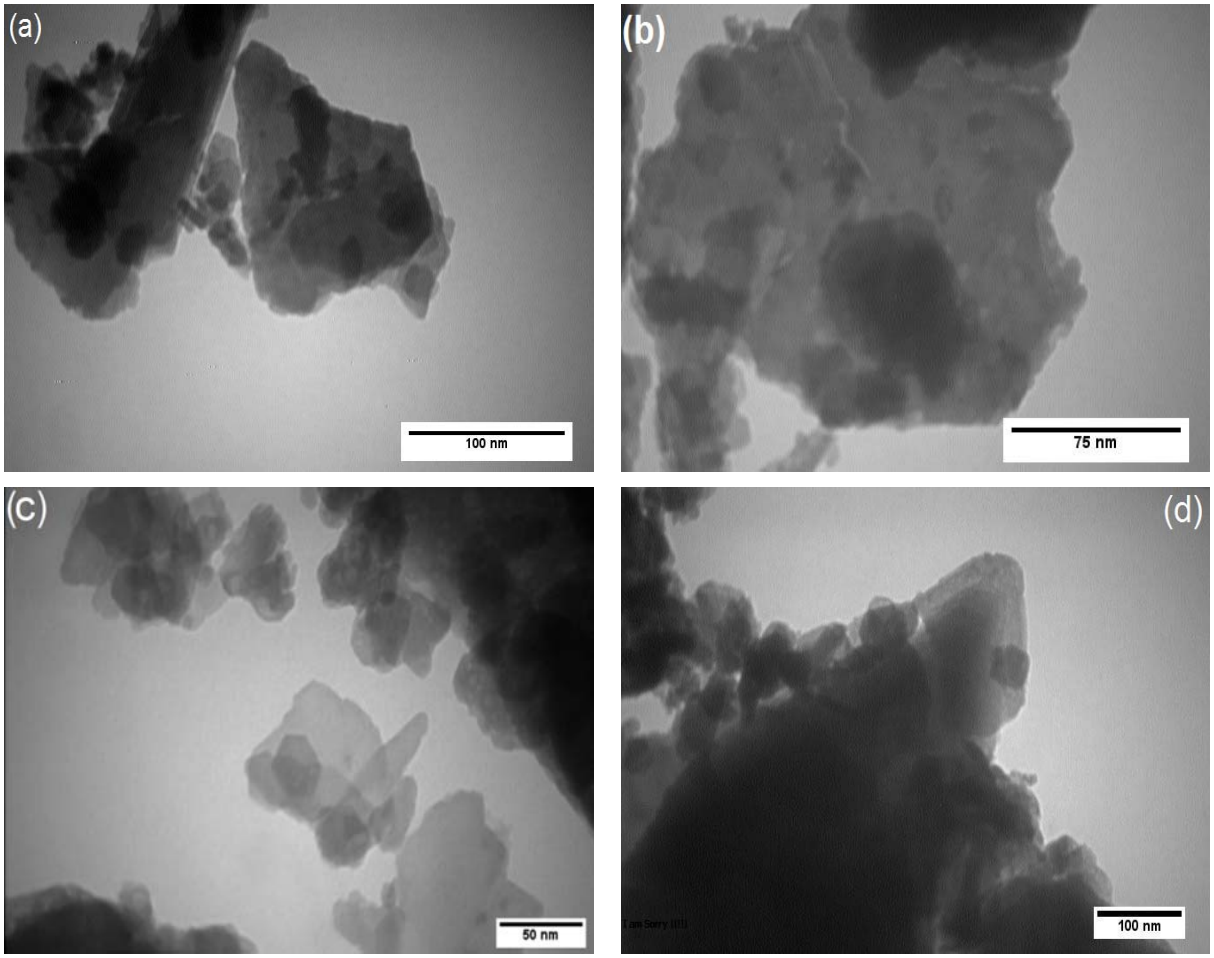
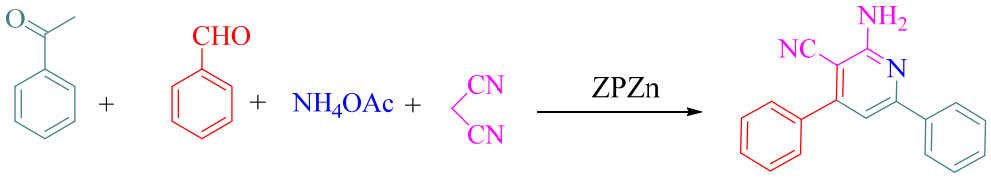



**Fig. 3.** TEM images of the regular morphology of prepared ZPZn fresh (a-c) (different magnification) and after the 7th run (d).

### *3.2. Synthesis of 2-amino-3-cyanopyridines*

To find out the suitable conditions for the reaction, a series of experiments were performed for the synthesis of 2-amino-4,6-diphenylnicotinonitrile (**1a**) as a model compound (Table 2). The reaction was performed in various solvents to identify the best solvent condition. Several classic solvents such as EtOH, MeOH, $CH_3CN$, $H_2O$, DMF, n-hexane, $CHCl_3$, THF, 1,4-Dioxane, toluene and also solvent-free conditions were examined. The experimental results showed that the yield of the product is higher under solvent-free conditions (Table 2, entry 11). In order to further improve the reaction yield, five experiments at different temperatures were performed (Table 2, entries 11-15). It was observed that the application of a lower temperature gave the corresponding product in lower yield. The reaction provided little amounts of product without the catalyst (Table 2 entry 20). The optimal conditions were determined as the reaction was catalyzed by 1.5 mol% of ZPZn under solvent-free conditions at 60 ºC in 60 min (Table 2 entry 11). To delineate the scope and generality of our new protocol, this methodology was examined by the reaction of several substituted aldehydes and acetophenones (Table 3). The reaction succeeded well, providing the corresponding 2-amino-4,6-diphenyl nicotinonitrile derivatives in fair to high yields, demonstrating the generality of the method and its good tolerance of both EW and ED substituents on the both aromatic rings. The electronic effect seemed to have a clear influence on the reaction since the EW groups on the different aromatic rings resulted in better yields than ED groups. We also studied this condensation reaction with 2-substituted benzaldehyde and found that the reaction time was longer and yields were somewhat lower than other aldehydes, which were possibly attributed to the steric hindrance (Table 3, entries 4,5). Surprisingly, the aliphatic aldehyde (hexanal) and the aliphatic ketone (acetone) gave no products. Obviously, the reactivity of aldehydes is the key factor for this one-pot transformation.

**Table 2.** Synthesis of 2-amino-4,6-diphenylnicotinonitrile (**1a**) under different conditions.[a]




| Entry | Solvent | Catalyst (mol%) | Temp. (ºC) | Time (min) | Yield (%)[b] |
|---|---|---|---|---|---|
| 1 | EtOH | 1.5 | Reflux | 120 | 71 |
| 2 | $H_2O$ | 1.5 | Reflux | 120 | Trace |
| 3 | MeOH | 1.5 | Reflux | 120 | 66 |
| 4 | $CHCl_3$ | 1.5 | Reflux | 120 | 41 |
| 5 | $CH_3CN$ | 1.5 | Reflux | 120 | 45 |
| 6 | THF | 1.5 | Reflux | 120 | 53 |
| 7 | DMF | 1.5 | 100 | 120 | 61 |
| 8 | n-hexane | 1.5 | Reflux | 120 | 16 |
| 9 | 1,4-Dioxane | 1.5 | Reflux | 120 | 32 |
| 10 | Toluene | 1.5 | Reflux | 120 | 22 |
| 11 | Solvent-free | 1.5 | 60 | 60 | 88 |
| 12 | Solvent-free | 1.5 | R.T. | 120 | Trace |
| 13 | Solvent-free | 1.5 | 40 | 120 | 46 |
| 14 | Solvent-free | 1.5 | 80 | 60 | 88 |
| 15 | Solvent-free | 1.5 | 100 | 60 | 89 |
| 16 | Solvent-free | 0.5 | 60 | 90 | 35 |
| 17 | Solvent-free | 1 | 60 | 60 | 58 |
| 18 | Solvent-free | 3 | 60 | 60 | 72 |
| 19 | Solvent-free | 5 | 60 | 60 | 88 |
| 20[c] | Solvent-free | - | 60 | 120 | Trace |

[a]The reaction was carried out in 5 ml of solvent.
[b]The yields refer to the isolated pure products.
[c]The reaction was carried out in the absence of ZPZn.

Based on previous research, a plausible mechanism for this condensation reaction was proposed. It is reasonable to suppose an initial activation of the carbonyl group of aldehyde by the Zn Lewis acid sites. Next, the carbonyl carbon was attacked by the nucleophilic malononitrile to form intermediate arylidene malononitrile. The subsequent Michael addition of ketone followed by cyclization afforded the desired final product (Scheme 2).

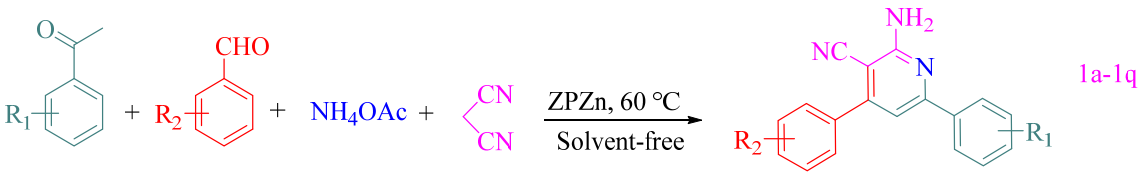
### *3.3. Reusability of the catalyst*

The reusability of the ZPZn catalyst was investigated under the optimum reaction conditions for the synthesis of **1a**. The elemental composition of the catalyst remained largely unchanged following its 7th run, although the amount of zinc in the catalyst was reduced by almost 60% compared with the first run (Table 1). The recycled ZPZn catalyst gave a similar product yield to the freshly prepared catalyst up until the sixth cycle. The yields for 7 runs were 90, 90, 90, 87, 83, 81 and 73%, respectively.

### *3.4. Comparison of activities of various catalysts*

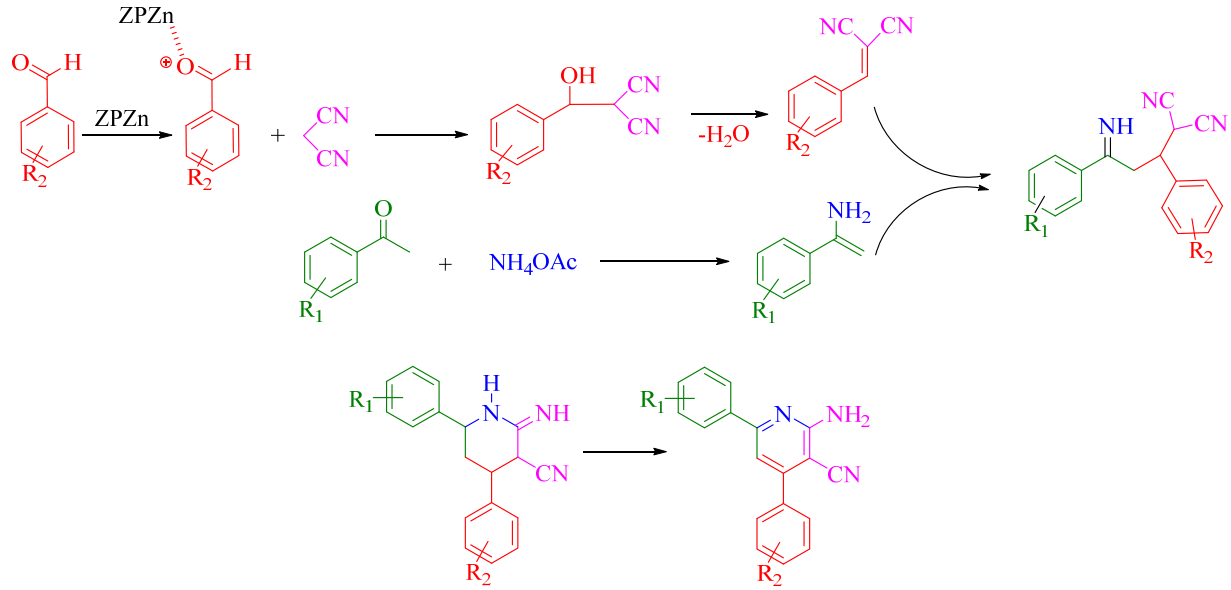
To show the value of the present work in comparison with reported results in the literature, the results of ZPZn catalyst for the synthesis of 2-amino-4,6-bis-(4-chlorophenyl)-nicotinonitrile (**1m**) was compared with results obtained by other groups (Table 4). As it can be seen from this Table, ZPZn acts as an effective catalyst with respect to reaction temperature, time, and yield.

**Table 3.** Synthesis 2-amino-3-cyanopyridines using ZPZn under solvent-free conditions.[a]



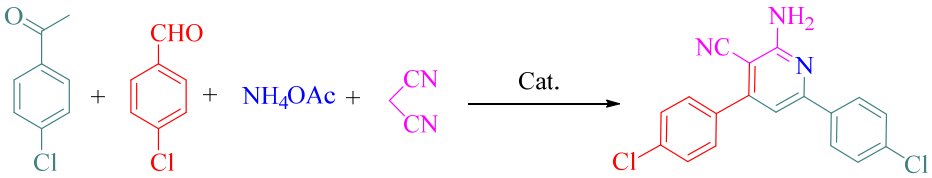

| Entry | Ketone | Aldehyde | Product | Time (min) | Yield (%) | m.p. (°C)[b] | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Found | Reported | |
| 1 | $C_6H_5$ | $C_6H_5$ | 1a | 60 | 88 | 185-187 | 184-186 | [13] |
| 2 | $C_6H_5$ | 4-Me-$C_6H_4$ | 1b | 75 | 83 | 177-179 | 176-178 | [13] |
| 3 | $C_6H_5$ | 4-MeO-$C_6H_4$ | 1c | 75 | 80 | 179-181 | 180-182 | [11] |
| 4 | $C_6H_5$ | 2-Cl-$C_6H_4$ | 1d | 45 | 90 | 191-193 | 193-195 | [12] |
| 5 | $C_6H_5$ | 4-Cl-$C_6H_4$ | 1e | 30 | 94 | 224-226 | 223-225 | [13] |
| 6 | $C_6H_5$ | 4-Br-$C_6H_4$ | 1f | 30 | 92 | 225-227 | 225-227 | [16] |
| 7 | 4-Me-$C_6H_4$ | $C_6H_5$ | 1g | 90 | 85 | 177-179 | 178 | [13] |
| 8 | 4-MeO-$C_6H_4$ | $C_6H_5$ | 1h | 90 | 82 | 179-181 | 177-179 | [13] |
| 9 | 4-Cl-$C_6H_4$ | $C_6H_5$ | 1i | 45 | 91 | 240-242 | 241-242 | [12] |
| 10 | 4-Br-$C_6H_4$ | $C_6H_5$ | 1j | 45 | 92 | 242-244 | 241-243 | [16] |
| 11 | 4-Cl-$C_6H_4$ | 4-Me-$C_6H_4$ | 1k | 60 | 89 | 216-217 | 216-218 | [11] |
| 12 | 4-Cl-$C_6H_4$ | 4-MeO-$C_6H_4$ | 1l | 60 | 86 | 203-203 | 204-205 | [12] |
| 13 | 4-Cl-$C_6H_4$ | 4-Cl-$C_6H_4$ | 1m | 20 | 94 | 231-233 | 230-231 | [13] |
| 14 | 4-Me-$C_6H_4$ | 4-Cl-$C_6H_4$ | 1n | 45 | 90 | 173-175 | 172-174 | [16] |
| 15 | 4-MeO-$C_6H_4$ | 4-Cl-$C_6H_4$ | 1O | 45 | 88 | 195-197 | 195-196 | [14] |
| 16 | 4-F-$C_6H_4$ | 4-Cl-$C_6H_4$ | 1p | 20 | 95 | 217-219 | 219-220 | [14] |
| 17 | 4-MeO-$C_6H_4$ | 4-MeO-$C_6H_4$ | 1q | 90 | 82 | 160-162 | 160-162 | [14] |

[a]All products were characterized by M.p, IR and $^1$H NMR spectral data and comparison with those of authentic samples or reported data (Supplementary information Pages S7-S11).
[b]Isolated yield.




**Scheme 2.** A plausible reaction mechanism for the synthesis of 2-amino-3-cyanopyridine derivatives.

**Table 4.** Comparison of efficiency of various catalysts in the synthesis of **1m**.




| Entry | Catalyst | Solvent | Temp. (ºC) | Time (min) | Yield (%)[a] | Ref. |
|---|---|---|---|---|---|---|
| 1 | $[EtNH_3]NO_3$ | Solvent-free | 60 | 150 | 90 | [7] |
| 2 | MWI[b] | Solvent-free | - | 8 | 83 | [11] |
| 3 | $Yb(PFO)_3$ | EtOH | Reflux | 240 | 85 | [12] |
| 4 | $FePO_4$ | EtOH | Reflux | 240 | 93 | [13] |
| 5 | TBBDA | Solvent-free | 100 | 30 | 90 | [14] |
| 6 | $[Bmim][BF_4]$ | Solvent-free | 60 | 300 | 88 | [16] |
| 7 | Cellulose–$SO_3H$ | $H_2O$ | 60 | 150 | 94 | [17] |
| 8 | SBTETASA | Solvent-free | 100 | 10 | 90 | [20] |
| 9 | Trifluoroethanol | Solvent-free | Reflux | 360 | 95 | [21] |
| 10 | α-ZrP | Solvent-free | 60 | 120 | 64 | This Work |
| 11 | ZPZn | Solvent-free | 60 | 60 | 88 | This Work |

[a]The yields refer to the isolated pure products.
[b]Microwave irradiation.

## 4. Conclusions

In summary, we have reported the catalytic performance of water-insoluble ZPZn in an MCR. The catalyst was characterized by various methods and results showed good agreement with the literature. ZPZn showed outstanding catalytic performance with fair to excellent yields for all condensation reactions. These conditions are compatible with some acid-sensitive functional groups. The attractive features of these procedures are shorter reaction times, mild reaction conditions, high yields and no side reactions, ease of preparation and handling of the catalyst, green aspects by avoiding toxic catalysts and solvents, recyclability of the catalyst, and simple experimental procedure.

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