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# A Greener and Rapid Approach for Synthesis of Pyranopyrroles using Nano ZnO as an efficient Catalyst

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**Abstract:** Synthesis of pyranopyrrole derivatives by using nano ZnO as an efficient catalyst has been reported. The reactions proceed through a one-pot, three component cyclo condensation of 3-hydroxypyrrole, malononitrile and various aromatic aldehydes in the presence of nano Zinc Oxide to afford pyranopyrrole derivatives. The process presented here is operationally simple, environmentally benign and has good yield. Furthermore, the catalyst can be recovered conveniently and reused efficiently.

**Keywords:** Pyranopyrrole; One-pot multi component reaction; Nano ZnO as an efficient catalyst.

## I. INTRODUCTION

In the past decades multi component reactions plays an important role in the field of synthetic organic chemistry as they increase the efficiency of the reaction and decrease the number of laboratory operations and minimizes the chemicals used and waste produced, as well as the reaction time consumed. As a result, great attention has been paid to the development of cascade reactions. Multi component reactions (MCRs) involving a cascade process with more than two different substrates to generate complex molecular frameworks have emerged as a powerful synthetic strategy. The development of efficient and eco-friendly synthetic methodologies for the rapid construction of potentially bioactive compounds became a major task for chemists in organic synthesis[1-6]. Among the multi-component reactions [7]. It is well-known that pyrans are important core units in a number of biological products and photo chromic materials[8,9]. Compounds with pyran ring system have many pharmacological properties and play important roles in biochemical process[10].

Therefore, preparation of this heterocyclic species has attracted great importance in organic synthesis. The 4H-pyran derivatives are of the immense interests in the area of synthesizing various drugs due to their pharmacological and biological activities, such as anti-proliferative[11], anti-microbial[12], sex pheromone[13], mutagenicity[14,15], anti-tumour[16] and central nervous system activity[17]. Therefore, the synthesis of such compounds is an interesting challenge. Recently, number of transition metal or metal oxide nano particles used as heterogeneous as well as homogeneous catalyst in organic transformations because due to its ability to participate in both acid-base and redox reactions.

They are also used as catalysts in chemical industries for various types of chemical reactions. The Metal oxide nano particles exhibit unique chemical and physical properties due to their high density and limited size of corner or edge on the surface sites. In order to display mechanical stability, nano particles must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures.

In the recent years, Pyranopyrrole derivatives have been reported by using various catalysts, such as melamine trisulfonic acid (MTSA)[18], Fe(HSO<sub>4</sub>)<sub>3</sub> [19], Zirconium(IV) dichloride[20], [pmim]HSO<sub>4</sub>-SiO<sub>2</sub>[21], ZrOCl<sub>2</sub>·8H<sub>2</sub>O[22]. However, these methods suffer from drawbacks, such as low yields of products, tedious workup procedures, the requirement of longer reaction time and high temperature.

Thus, the search for new reagents and methods is still of growing importance. Recently, the use of nano Zinc Oxide as a catalyst in organic synthesis has increased considerably. Nano ZnO can be easily prepared. It is effectively used as a catalyst in organic reactions, thus development of a facile, atom-efficient, and environmentally benign method is highly acceptable. As part of our efforts to develop new synthetic methods in biologically active molecules like pyranopyrrole derivatives by one-pot synthesis, we became interested in developing one-pot synthesis of 5-amino-7-aryl-6-cyano-4H-pyrano[3,2-b]pyrrole derivatives catalyzed by nano ZnO(Scheme 1).

## II. EXPERIMENTAL

### A. Chemicals and Apparatus

All chemicals used in this process are of AR grade fine chemicals, without any further purification. The synthesized 5-amino-7-aryl-6-cyano-4H-pyrano[3,2-b]pyrrole derivatives were characterized by  $^1\text{H}$  NMR(400MHz)spectra were obtained using Bruker-Advance spectrophotometer in  $\text{CDCl}_3$ . FT-IR spectra were recorded on Bruker Alpha FT-IR with Opus 6.1 version, MASS spectra were determined on Perkin- Elmer PESCIEX-API 2000, equipped with ESI source used online with a HPLC system after the UV detector. XRD spectra were recorded on PANanalytical-Xpertpro diffracto meter and the average crystallite size was determined from the corresponding XRD data. The micro structural morphology was studied with a scanning electron microscope(SEM) JEOL-JSM 6610 LV. Magnetization measurements were made using a commercial vibrating sample magnetometer(VSM) model BHU-50 of Riken Denshi Co. Ltd. Japan.

### B. General Procedure for the Synthesis of Catalyst

For the preparation of Nano Zinc Oxide catalyst by wet chemical method, 0.2 M solution of  $\text{Zn}(\text{NO}_3)_2$  and 0.4M NaOH were used. Zinc nitrate was dissolved in water to which sodium hydroxide was added drop-wise with continuous stirring at room temperature leading to generation of metal hydroxides. The stirring was continued for 6 hrs at  $85^\circ\text{C}$ .The reaction mixture was then filtered and dried in oven at  $60^\circ\text{C}$ . The as-synthesized powder, thus obtained was calcined in a Muffle furnace at  $600^\circ\text{C}$  for 2 hours and furnace cooled. The product was characterised by SEM, EDAX and XRD.

### C. Characterizations of Catalyst

Characterization of nano ZnO was done based on JCPDS values. For all doped and un-doped ZnO samples the absorption peaks in the range of  $600 - 700 \text{ cm}^{-1}$  could be attributed to the ZnO stretching modes [23,24]. In our FT-IR spectra the main peaks observed were: absorption peaks in the range of  $1100 - 1600 \text{ cm}^{-1}$  corresponding to the Zn-OH bending mode [24], and this band could be normally reduced by calcinations process at higher temperature [25,26], a broad band in the  $2900 - 3700 \text{ cm}^{-1}$  region which can be explained as overlapping O-H stretching modes and C-H stretching modes(Figure 1)

X-ray diffraction pattern of ZnO nanoparticles show sharp and well defined peaks. It indicates. the good crystallinity of synthesized material. The observed  $2\theta$  values are consistent with the standard JCPDS values(JCPDS No.80-0075) which specify the wurtzite structure of ZnO nano particles d-values were compared with standard JCPDS files and showed presence of pure oxides(Figure 2).SEM image shows the surface morphology of the oxide nano particles. Zinc oxide nano particles are fine with spherical shape and average grain size is below 70 nm(Figure 3). EDAX confirms the presence of metals Zn and oxygen in expected atomic percentage(Figure 4).

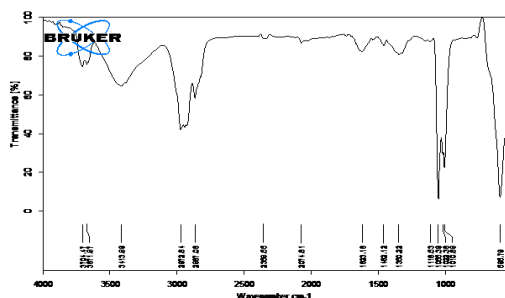


Figure 1 (FT-IR of nano ZnO)

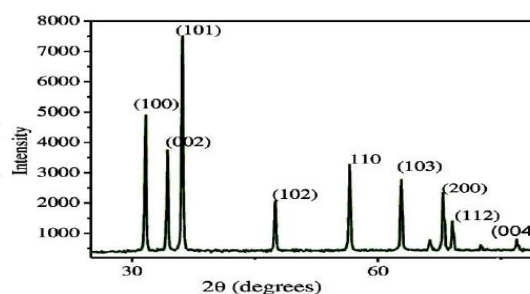


Figure 2 (XRD of nano ZnO)

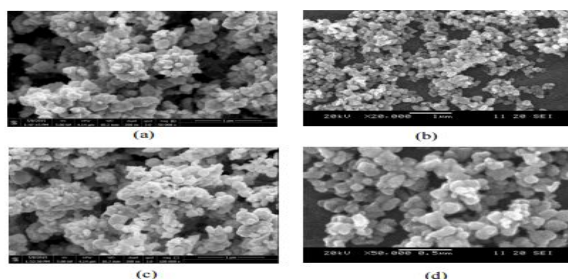


Figure 3 (SEM of nano ZnO)

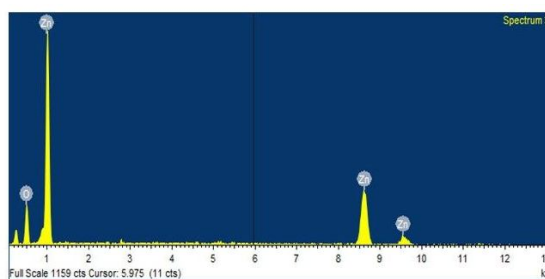
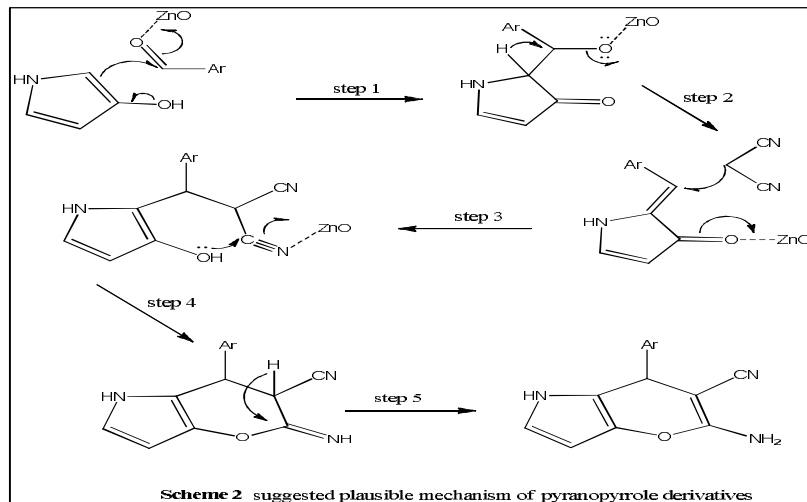
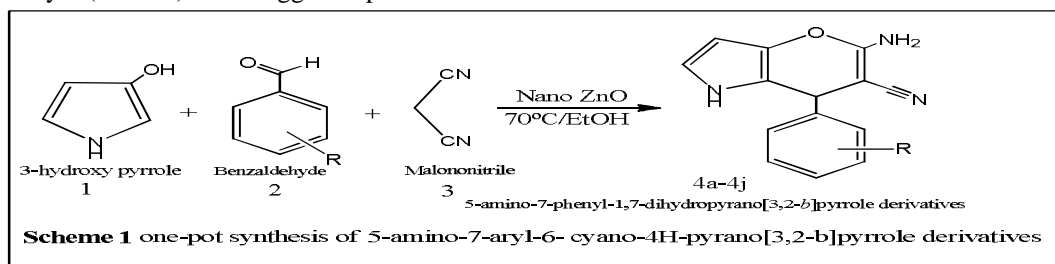


Figure 4 (EDAX of nano ZnO)

#### D. General Procedure for Synthesis of Pyrano Pyrrole Derivatives

A mixture of Aldehyde (10 mmol), 3-hydroxypyrrrole (10 mmol), malononitrile (11 mmol) and nano Zinc Oxide catalyst (500mg) (which is activated previously in microwave oven for 2 minutes) were taken in a 50 ml round bottomed flask and 5ml of Ethanol was added as solvent. Then the reaction mixture was refluxed at 70°C for 30 minutes. The progress of the reaction was monitored by thin layer chromatography (n-Hexane, Ethyl acetate 3:1). The catalyst was simply recovered by filtration and washed by dichloromethane. Then the reaction mixture was concentrated under rotary evaporator and then the solid product was recrystallised from hot ethanol for several times to get pure product. The corresponding products were confirmed by FT-IR, <sup>1</sup>H-NMR, MASS spectral analysis (Table 1). The suggested plausible mechanism was showed in scheme 2.



#### E. Spectral data for the Synthesized Pyranopyrrole Derivatives

- 1) 5-amino-7-phenyl-1,7-dihydropyrano[3,2-b]pyrrole (4a): IR (KBr,  $\nu_{\max}, \text{cm}^{-1}$ ): 3442, 3285 (asym. and sym. str. of  $-\text{NH}_2$ ), 3388 (NH), 2172 ( $-\text{CN}$  str.), 1281 (asym. str. of cyclic Ar C-O-C ether). <sup>1</sup>H-NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.37 (s, 3H, OCH<sub>3</sub>), 5.43 (s, 1H, pyran H<sub>4</sub>), 6.11 (d, 1H, pyrrole H<sub>3</sub>), 6.63 (d, 2H, Ar-H), 6.68 (d, 1H, pyrrole H<sub>2</sub>), 6.89 (s, 2H, D<sub>2</sub>O exch., NH<sub>2</sub>), 7.05 (d, 2H, Ar-H), 7.54 (s, 1H, pyrrole NH). ESI-MS m/z(%): 237 ([M+H]<sup>+</sup> 100).
- 2) 5-amino-7-(p-tolyl)-1,7-dihydropyrano[3,2-b]pyrrole (4b): IR (KBr,  $\nu_{\max}, \text{cm}^{-1}$ ): 3442, 3285 (asym. and sym. str. of  $-\text{NH}_2$ ), 3388 (NH), 2172 ( $-\text{CN}$  str.), 1281 (asym. str. of cyclic Ar C-O-C ether). <sup>1</sup>H-NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.83 (s, 3H, -CH<sub>3</sub> Str), 3.37 (s, 3H, OCH<sub>3</sub>), 5.43 (s, 1H, pyran H<sub>4</sub>), 6.11 (d, 1H, pyrrole H<sub>3</sub>), 6.63 (d, 2H, Ar-H), 6.68 (d, 1H, pyrrole H<sub>2</sub>), 6.89 (s, 2H, D<sub>2</sub>O exch., NH<sub>2</sub>), 7.05 (d, 2H, Ar-H), 7.54 (s, 1H, pyrrole NH). ESI-MS m/z(%): 251 ([M+H]<sup>+</sup> 100).
- 3) 5-amino-7-(4-chlorophenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4c): IR (KBr,  $\nu_{\max}, \text{cm}^{-1}$ ): 3442, 3285 (asym. and sym. str. of  $-\text{NH}_2$ ), 3388 (NH), 2172 ( $-\text{CN}$  str.), 1281 (asym. str. of cyclic Ar C-O-C ether). <sup>1</sup>H-NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.37 (s, 3H, OCH<sub>3</sub>), 5.43 (s, 1H, pyran H<sub>4</sub>), 6.11 (d, 1H, pyrrole H<sub>3</sub>), 6.63 (d, 2H, Ar-H), 6.68 (d, 1H, pyrrole H<sub>2</sub>), 6.89 (s, 2H, D<sub>2</sub>O exch., NH<sub>2</sub>), 7.05 (d, 2H, Ar-H), 7.54 (s, 1H, pyrrole NH). ESI-MS m/z(%): 271 ([M+H]<sup>+</sup> 100).
- 4) 5-amino-7-(2-chlorophenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4d): IR (KBr,  $\nu_{\max}, \text{cm}^{-1}$ ): 3442, 3285 (asym. and sym. str. of  $-\text{NH}_2$ ), 3388 (NH), 2172 ( $-\text{CN}$  str.), 1281 (asym. str. of cyclic Ar C-O-C ether). <sup>1</sup>H-NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.37 (s, 3H, OCH<sub>3</sub>), 5.43 (s, 1H, pyran H<sub>4</sub>), 6.11 (d, 1H, pyrrole H<sub>3</sub>), 6.63 (d, 2H, Ar-H), 6.68 (d, 1H, pyrrole H<sub>2</sub>), 6.89 (s, 2H, D<sub>2</sub>O exch., NH<sub>2</sub>), 7.05 (d, 2H, Ar-H), 7.54 (s, 1H, pyrrole NH). ESI-MS m/z(%): 271 ([M+H]<sup>+</sup> 100).

- 5) *5-amino-7-(4-bromophenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4e)*: IR (KBr,  $\nu_{\max}, \text{cm}^{-1}$ ): 3442, 3285 (asym. and sym. str. of -NH<sub>2</sub>), 3388 (NH), 2172 (-CN str.), 1281 (asym. str. of cyclic Ar C-O-C ether). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.37 (s, 3H, OCH<sub>3</sub>), 5.43 (s, 1H, pyran H<sub>4</sub>), 6.11(d, 1H, pyrrole H<sub>3</sub>), 6.63 (d, 2H, Ar-H), 6.68 (d, 1H, pyrrole H<sub>2</sub>), 6.89 (s, 2H, D<sub>2</sub>O exch., NH<sub>2</sub>), 7.05 (d, 2H, Ar-H), 7.54 (s, 1H, pyrrole NH). ESI-MS m/z(%) : 316 ([M+H]<sup>+</sup> 100).
- 6) *5-amino-7-(2-nitrophenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4f)*: IR (KBr,  $\nu_{\max}, \text{cm}^{-1}$ ): 3442, 3285 (asym. and sym. str. of -NH<sub>2</sub>), 3388 (NH), 2172 (-CN str.), 1281 (asym. str. of cyclic Ar C-O-C ether). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.37 (s, 3H, OCH<sub>3</sub>), 5.43 (s, 1H, pyran H<sub>4</sub>), 6.11(d, 1H, pyrrole H<sub>3</sub>), 6.63 (d, 2H, Ar-H), 6.68 (d, 1H, pyrrole H<sub>2</sub>), 6.89 (s, 2H, D<sub>2</sub>O exch., NH<sub>2</sub>), 7.05 (d, 2H, Ar-H), 7.54 (s, 1H, pyrrole NH). ESI-MS m/z(%) : 282 ([M+H]<sup>+</sup> 100).
- 7) *5-amino-7-(2-hydroxyphenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4g)*: IR (KBr,  $\nu_{\max}, \text{cm}^{-1}$ ): 3442, 3285 (asym. and sym. str. of -NH<sub>2</sub>), 3388 (NH), 2172 (-CN str.), 1281 (asym. str. of cyclic Ar C-O-C ether). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.37 (s, 3H, OCH<sub>3</sub>), 5.32(m, 1H, -OH), 5.43 (s, 1H, pyran H<sub>4</sub>), 6.11(d, 1H, pyrrole H<sub>3</sub>), 6.63 (d, 2H, Ar-H), 6.68 (d, 1H, pyrrole H<sub>2</sub>), 6.89 (s, 2H, D<sub>2</sub>O exch., NH<sub>2</sub>), 7.05 (d, 2H, Ar-H), 7.54 (s, 1H, pyrrole NH). ESI-MS m/z(%) : 253 ([M+H]<sup>+</sup> 100).
- 8) *5-amino-7-(4-nitrophenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4h)*: IR (KBr,  $\nu_{\max}, \text{cm}^{-1}$ ): 3442, 3285 (asym. and sym. str. of -NH<sub>2</sub>), 3388 (NH), 2172 (-CN str.), 1281 (asym. str. of cyclic Ar C-O-C ether). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.37 (s, 3H, OCH<sub>3</sub>), 5.43 (s, 1H, pyran H<sub>4</sub>), 6.11(d, 1H, pyrrole H<sub>3</sub>), 6.63 (d, 2H, Ar-H), 6.68 (d, 1H, pyrrole H<sub>2</sub>), 6.89 (s, 2H, D<sub>2</sub>O exch., NH<sub>2</sub>), 7.05 (d, 2H, Ar-H), 7.54 (s, 1H, pyrrole NH). ESI-MS m/z(%) : 282 ([M+H]<sup>+</sup> 100).
- 9) *5-amino-7-(4-hydroxyphenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4i)*: IR (KBr,  $\nu_{\max}, \text{cm}^{-1}$ ): 3442, 3285 (asym. and sym. str. of -NH<sub>2</sub>), 3388 (NH), 2172 (-CN str.), 1281 (asym. str. of cyclic Ar C-O-C ether). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.37 (s, 3H, OCH<sub>3</sub>), 5.32(m, 1H, -OH), 5.43 (s, 1H, pyran H<sub>4</sub>), 6.11(d, 1H, pyrrole H<sub>3</sub>), 6.63 (d, 2H, Ar-H), 6.68 (d, 1H, pyrrole H<sub>2</sub>), 6.89 (s, 2H, D<sub>2</sub>O exch., NH<sub>2</sub>), 7.05 (d, 2H, Ar-H), 7.54 (s, 1H, pyrrole NH). ESI-MS m/z(%) : 253 ([M+H]<sup>+</sup> 100).
- 10) *5-amino-7-(4-methoxyphenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4j)*: IR (KBr,  $\nu_{\max}, \text{cm}^{-1}$ ): 3442, 3285 (asym. and sym. str. of -NH<sub>2</sub>), 3388 (NH), 2172 (-CN str.), 1281 (asym. str. of cyclic Ar C-O-C ether). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.37 (s, 3H, OCH<sub>3</sub>), 5.43 (s, 1H, pyran H<sub>4</sub>), 6.11(d, 1H, pyrrole H<sub>3</sub>), 6.63 (d, 2H, Ar-H), 6.68 (d, 1H, pyrrole H<sub>2</sub>), 6.89 (s, 2H, D<sub>2</sub>O exch., NH<sub>2</sub>), 7.05 (d, 2H, Ar-H), 7.54 (s, 1H, pyrrole NH). ESI-MS m/z(%) : 267 ([M+H]<sup>+</sup> 100).

### III. RESULTS AND DISCUSSION

#### A. Effect of loading of Catalyst on the Synthesis of Pyranopyrrole Derivatives

The present reaction observed under different amounts of catalyst. The result reveals that 500mg of catalyst is enough to get the good yield of product. On further increment of catalyst quantity will not lead appreciable change in the yield of product. Hence 500mg of catalyst was taken to perform the reaction. The results are as tabulated in Table 2.

#### B. Comparative Catalytic activity of nano ZnO with other Catalysts for the Synthesis of Pyranopyrrole Derivatives

Reaction times for the formation of 5-amino-7-aryl-6- cyano-4H-pyrano[3,2-b]pyrrole derivatives with various catalysts are presented in Table 3. It is observed that with other catalysts and particularly under reflux conditions the reaction times are very much higher. Under reflux conditions, synthesis of 5-amino-7-aryl-6- cyano-4H-pyrano[3,2-b]pyrrole derivatives catalyzed by (MTSA)[18], ZrOCl<sub>2</sub>·8H<sub>2</sub>O [22] have been reported shorter reaction times, the present method offers a comparatively very low cost and easily producible nano Zinc Oxide for effective results.(Table 3)

#### C. Effect of Solvent on Synthesis of Pyranopyrrole Derivatives

Investigation of reaction medium for the process revealed that solvents playing a major role in the reaction. The results are summarized in Table 4. It was found that polar solvents such as acetic acid, CH<sub>3</sub>CN and C<sub>2</sub>H<sub>5</sub>OH were much better than non-polar solvents. Trace amount of yield observed when H<sub>2</sub>O was used as solvent, presumably due to the aggregation of the hydrophobic catalyst. Although CH<sub>3</sub>COOH is effective, low yield was obtained when the catalyst was reused, therefore we selected C<sub>2</sub>H<sub>5</sub>OH as solvent.

#### D. Effect of Temperature on Synthesis of Pyranopyrrole Derivatives

The reaction temperature for the formation of 5-amino-7-aryl-6- cyano-4H-pyrano[3,2-b]pyrrole derivatives with nano Zinc Oxide catalyst is 70°C is presented in table 5. It is observed that at below 70°C temperature yield of the product is low and reaction time is high. So we have confirmed 70°C is suitable temperature for this reaction.

### E. Recycling of the Catalyst

Catalyst reusability is of major task in heterogeneous catalysis. Catalyst recycling was achieved by filtration of reaction mixture the catalyst washed thrice with ethyl acetate, dried and the fresh reactants dissolved in ethyl alcohol was introduced into the round bottom flask, followed by refluxing, allowing the reaction to proceed for the next run. The catalyst was consecutively reused for five times with any noticeable loss of its catalytic activity.(Table 6)

Table 1. Synthesis of pyrano pyrrol derivatives

S.No.	Compound	R	Time (min)	Yield(%)
1	5-amino-7-phenyl-1,7-dihydropyrano[3,2-b]pyrrole (4a)	H	30	95
2	5-amino-7-(p-tolyl)-1,7-dihydropyrano[3,2-b]pyrrole (4b)	4-CH <sub>3</sub>	35	95
3	5-amino-7-(4-chlorophenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4c)	4-Cl	35	95
4	5-amino-7-(2-chlorophenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4d)	2-Cl	30	95
5	5-amino-7-(4-bromophenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4e)	4-Br	35	93
6	5-amino-7-(2-nitrophenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4f)	2-NO <sub>2</sub>	40	90
7	5-amino-7-(2-hydroxyphenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4g)	2-OH	35	93
8	5-amino-7-(4-nitrophenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4h)	4-NO <sub>2</sub>	35	90
9	5-amino-7-(4-hydroxyphenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4i)	4-OH	40	93
10	5-amino-7-(4-methoxyphenyl)-1,7-dihydropyrano[3,2-b]pyrrole (4j)	4-OCH <sub>3</sub>	45	90

Table 2. Comparison of effect of the present catalyst with other catalysts on synthesis of pyranopyrrole derivatives

S.No.	Catalyst	Reaction conditions	Time	Yield	Reference
1	melamine trisulfonic acid (MTSA)	EtOH/Reflux	1.5h	92	18
2	Fe(HSO <sub>4</sub> ) <sub>3</sub>	EtOH/Reflux	6h	86	19
3	Zirconium(IV) dichloride	CH <sub>3</sub> CN/Ultrasonic	30min.	86	20
4	[pmim]HSO <sub>4</sub> -SiO <sub>2</sub>	CH <sub>3</sub> CN/50 <sup>o</sup> C	3h	89	21
5	ZrOCl <sub>2</sub> ·8H <sub>2</sub> O	Solvent-free/70 <sup>o</sup> C	1h	94	22
6	Nano ZnO	EtOH/70 <sup>o</sup> C	30min	95	Present work

Table 3 Effect of catalyst loading on the formation of pyranopyrrole derivatives

S.No.	Catalyst loading in(mg)	Time(min)	Yield (%)
1.	200	30	42
2.	300	30	66
3.	400	30	78
4.	500	30	95
5.	600	30	95

Table 4. Effect of solvent on synthesis of pyranopyrrole derivatives

S. No.	Catalyst	Solvent	Time	Yield(%)
1	ZnO	H <sub>2</sub> O	12 h	Trace
2	ZnO	CH <sub>2</sub> Cl <sub>2</sub>	5 h	30
3	ZnO	CH <sub>3</sub> COOH	1.5 h	85
4	ZnO	CH <sub>3</sub> CN	1 h	90
5	ZnO	C <sub>2</sub> H <sub>5</sub> OH	30 min	95

Table 5. Effect of Temperature on the formation of pyranopyrrole derivatives

S.No.	Catalyst	Temperature(°C)	Time	Yield (%)
1	ZnO	R.T.	9h	20
2	ZnO	40	5h	50
3	ZnO	50	1.5h	75
4	ZnO	70	30 min	95

Table 6. Recyclability of the catalyst in synthesis of pyranopyrrole derivatives

Run no.	Yield(%)
1	95
2	93
3	91
4	88
5	86

#### IV. CONCLUSION

In conclusion, we have demonstrated that nano ZnO is an effective catalyst for the MCRs of structurally diverse aldehydes with 3-hydroxypyrrrole and malononitrile, resulting in the formation of substituted pyrano pyrroles in high yields. The catalyst can be recovered, and reused at least up to five cycles for the synthesis of pyrano pyrrole derivatives.

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