

## ZnO Nanopowder: an Efficient Catalyst for the Preparation of 2,4,5-Triaryl Imidazoles under Solvent-Free Condition

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**Abstract.** ZnO nanopowder has been applied for the efficient synthesis of substituted 2,4,5-triaryl imidazoles through the three-component cyclo-condensation reaction of benzil, ammonium acetate and aldehydes under thermal solvent-free conditions.

**Keywords:** ZnO nano powder; 2,4,5-triaryl imidazoles; Solvent-free

### 1. Introduction

Compounds containing imidazole skeletons exhibit important biological activities and play important roles in biochemical process [1-2]. Also large classes of imidazole derivatives are used as ionic liquids [3-4]. Thus these properties have instituted a diverse collection of synthetic approaches to these heterocycles. A number of routes have been developed for synthesis of substituted imidazoles. For example, Brønsted and Lewis acids have been used in liquid or solid-phase synthesis [5-13]. Some of these procedures have certain limitations such as tedious process, long reaction times, harsh reaction conditions, and low yields.

Herein we report a simple and convenient method for the synthesis of 2,4,5-triaryl imidazole derivatives via one-pot three-component cyclo-condensation reaction of benzil, ammonium acetate and aldehydes in the presence of ZnO nanopowders as catalyst under thermal solvent-free conditions (Figure 1).

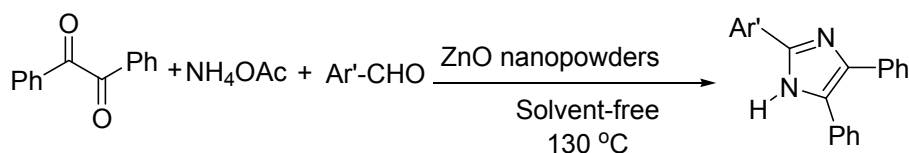


Fig. 1

### 2. Experimental

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by spectroscopic data (IR, NMR spectra) and melting points with authentic samples. The NMR spectra were recorded on a Bruker Avance DEX 400 MHz instrument. The spectra were measured in DMSO-d<sub>6</sub> relative to TMS (0.00 ppm). IR spectra were recorded on a JASCO FT-IR 460plus spectrophotometer. All of the compounds were solid and solid state IR spectra were recorded using the KBr disk technique. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on silica gel polygram SIL G/UV 254 plates.

#### 2.1. General procedure:

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To a mixture of aldehyde (1 mmol), benzil (1 mmol) and  $\text{NH}_4\text{OAc}$  (3 mmol), ZnO nanopowder (0.01 g) was added and the mixture stirred at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture dissolved in hot ethanol and filtered. Solvent was evaporated and the corresponding pure product was obtained after recrystallization in ethanol. The results are summarized in Table 2.

## 2.2. Selected data:

**2-(4-*tert*-butylphenyl)-4,5-diphenyl-1*H*-imidazole:** m.p: 290-292 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ): 1.34 (s, 9H), 7.23 (t,  $J = 7.2$  Hz, 1H), 7.32 (t,  $J = 7.6$  Hz, 2H), 7.38 (t,  $J = 7.2$  Hz, 1H), 7.45 (t,  $J = 7.2$  Hz, 2H), 7.51 (m, 4H), 7.57 (d,  $J = 7.6$  Hz, 2H), 8.03 (d,  $J = 8.4$  Hz, 2H), 12.63 (s, 1H, NH);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta = 31.5, 34.9, 125.5, 125.9, 126.9, 127.6, 128.2, 128.3, 128.4, 128.6, 128.9, 129.1, 131.6, 131.7, 135.7, 137.4, 146.0, 146.1, 151.3$  ppm; IR (KBr): 3417, 3058, 2963, 2903, 1603, 1586, 1504, 1492, 1450, 1434, 1407, 1392, 1362, 1321, 1268, 1201, 1181, 1156, 1134, 1105, 1071, 1025, 967, 946, 839, 774, 765, 720, 696  $\text{cm}^{-1}$ ; Found: C, 85.25; H, 6.93; N, 7.99  $\text{C}_{25}\text{H}_{24}\text{N}_2$ ; requires: C, 85.19; H, 6.86; N, 7.95%].

## 3. Results and discussions

At first, to improve the yield and optimize the reaction conditions, the reaction was carried out using benzil, benzaldehyde and ammonium acetate in the presence of ZnO nanopowder as catalyst (Figure 2). Initially, the effect of temperature on the reaction rate was investigated (Table 1). At 100 °C, the reaction proceeded smoothly and almost complete conversion of product was observed. Further increase in temperature to 130 °C increased the rate of the reaction. Therefore, we kept the reaction temperature as 130 °C (giving short reaction time and high yield).

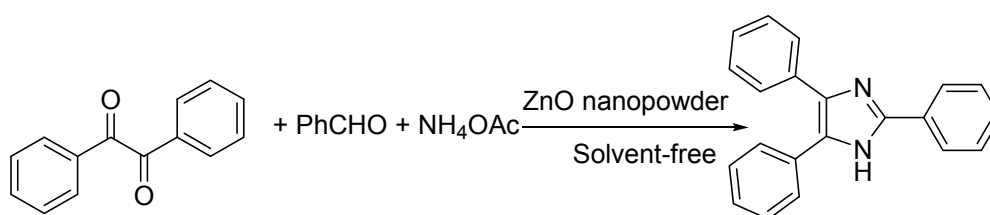


Fig. 2: preparation of 2,4,5-triphenyl-1*H*-imidazole using ZnO nanopowder as catalyst

Finally, among the tested various amount of the catalyst and temperature, the condensation of benzil, benzaldehyde and ammonium acetate was best catalyzed by 0.01 g of catalyst (Table 1). In order to improve the yields, we performed reaction using different quantities of reagents. The best results were obtained with 1:1:3 molar ratios of benzil, aryl aldehyde and ammonium acetate respectively. The results were summarized in Table 1.

Table 1: Optimization of the reaction conditions in the synthesis of 2,4,5-triphenyl-1*H*-imidazole under solvent-free condition

Entry	Catalyst	T (°C)	Time (min)	Yield (%) <sup>a</sup>
1	0.05	r.t.	300	-
2	0.05	80	250	15
3	0.05	100	100	47
4	0.05	130	15	83
5	0.1	130	12	79
6	0.075	130	12	81
7	0.025	130	21	85
8	0.01	130	31	90
9	0.005	130	85	75

<sup>a</sup>Isolated Yield

Using these optimized reaction conditions, the scope and efficiency of these procedures were explored for the synthesis of corresponding 2,4,5-triaryl imidazole derivatives.

Generally, the cyclocondensation reaction between benzil, arylaldehydes and ammonium acetate proceeded well and afforded the desired products (Table 2, Entries 1-11) in good to excellent yields. As shown in Table 2, the reaction was compatible successfully with a variety of aryl aldehydes having electron-donating and electron-withdrawing substituents.

In the all cases aromatic aldehydes containing electron-withdrawing groups (such as nitro-) gave shorter time than that with electron-donating groups (such as methoxy-). Though *meta*- and *para*- substituted aromatic aldehydes gave good results, *ortho*-substituted aromatic aldehydes (such as 2-nitrobenzaldehyde) gave lower yields and longer reaction time because of the steric effects.

The work-up procedure is very clear-cut; that is, the products were isolated and purified by simple filtration and crystallization from ethanol. Our protocol avoids the use of dry media during the reaction process, making it superior to the previous methods.

## 4. Conclusion

In conclusion, a reliable, rapid, and environmentally benign method for synthesizing 2,4,5-triaryl imidazoles has been developed. Compared to previous reported methodologies, the present protocol features simple operations, short reaction time, environmental friendliness and good yields.

Table 2: Synthesis of 2,4,5-triaryl imidazoles using ZnO nanopowder as catalyst

Entry	Aldehyde	Amine source	Time (min)	Yield (%) <sup>a</sup>
1	Benzaldehyde	NH <sub>4</sub> OAc	31	90
2	4-Hydroxybenzaldehyde	NH <sub>4</sub> OAc	300	56
3	4-Methoxybenzaldehyde	NH <sub>4</sub> OAc	290	67
4	4-Methylbenzaldehyde	NH <sub>4</sub> OAc	250	71
5	4- <i>tert</i> -Butylbenzaldehyde	NH <sub>4</sub> OAc	40	75
6	2-Methylbenzaldehyde	NH <sub>4</sub> OAc	260	77
7	4-Fluorobenzaldehyde	NH <sub>4</sub> OAc	55	80
7	2-Chlorobenzaldehyde	NH <sub>4</sub> OAc	270	81
8	4-Chlorobenzaldehyde	NH <sub>4</sub> OAc	30	86
9	2,4-Dichlorobenzaldehyde	NH <sub>4</sub> OAc	250	83
10	2-Nitrobenzaldehyde	NH <sub>4</sub> OAc	65	80
11	3-Nitrobenzaldehyde	NH <sub>4</sub> OAc	25	89

<sup>a</sup>Isolated yields. All known products have been reported previously in the literature and were characterized by comparison of IR and NMR spectra with authentic samples [5-13].

## 5. Acknowledgments

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