



# Development of novel pyrazolones by using SiO<sub>2</sub>/ZnCl<sub>2</sub> – green approach

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**Abstract.** The present research work deals with the green synthesis of substituted pyrazolone derivatives **4(a–f)** from 2,4-dinitrophenylhydrazine with various substituted aromatic aldehyde and ethyl acetoacetate in the presence of silica-supported zinc chloride (SiO<sub>2</sub>/ZnCl<sub>2</sub>) as a recyclable Lewis acid catalyst. The synthesized compounds were structurally characterized with IR, <sup>1</sup>H NMR, Mass spectra and elemental analysis. All these compounds were tested for their antioxidant activity by using the DPPH radical scavenging method.

**Keywords.** Pyrazolone; silica-supported zinc chloride catalyst; green synthesis; anti-oxidant activity.

## 1. Introduction

Green chemistry is “the utilization of a set of principle that eliminates or reduces the generation or use of hazardous substances in the design, manufacture, and application of chemical products”.<sup>1</sup> One of the principles of green chemistry reveals that selective catalytic reagents are higher to stoichiometric reagents in chemical synthesis. In recent years, the magic of catalysis has prompted significant ways to accelerate the conversion of reactants into appropriate products and give a variety of pharmaceutical compounds. This will reduce the burden of by-product and save energy. The usage of catalysts is favoured because it gives 100% atom economy. Catalysts are fully recovered without any change in their chemical and physical properties. The catalyzed reactions are faster, reaction yields are better, and there is minimal production of waste material and maximum utilization of the reactants. Green synthesis is mainly designed with the intention to provide computational efficiency in mind, in addition, it also contributes a new formulation by molecular level to achieve sustainability and materials suitable for convenience. This is both effective and efficient, and

inherently safer design of molecules, materials, products, and process.<sup>2</sup> In heterocyclic compounds, the pyrazolone and its derivatives are having numerous medications. It represents wide biological actions including analgesic, antipyretic, anti-inflammatory,<sup>3</sup> antioxidant,<sup>4</sup> antibacterial, antifungal,<sup>5</sup> anticancer,<sup>6</sup> uricosuric and antitubercular activities.<sup>7</sup> Various synthetic pyrazolone compounds have potential core active moiety like *analgesic and antipyretic* – antipyrine, propyphenazone, *anti-inflammatory* – metamizole, *uricosuric* – sulfinpyrazone (Figure 1).

Besides, it has been observed that some synthetic heterocyclic compounds with a pyrazolone ring have antioxidant activity.

The condensation of hydrazine hydrate and ethylacetoacetate is a recognized way to synthesize pyrazolone derivatives. Methanol,<sup>8</sup> ethanol,<sup>9</sup> dimethylformamide<sup>10</sup> and dioxane<sup>11</sup> can be used as a solvent for this transformation. Consequently, the research of several substituted pyrazolone derivatives has been investigated by different methods, using ionic liquids, especially based on the [HMIM]HSO<sub>4</sub>,<sup>4,12</sup> reusable catalysts, CuI nanoparticles,<sup>13</sup> and tungstophosphoric acid.<sup>14</sup> Besides, a variety of other catalysts are also used for the synthesis of these

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pyrazolone derivatives through a condensation reaction. In recent years, a few catalysts have been comprised as 3-aminopropylated silica gel,<sup>15</sup> silica sulphuric acid,<sup>16</sup> N-(3-silicapropyl)-N-methyl imidazolium hydrogen sulphate,<sup>17</sup> sodium dodecyl sulphate,<sup>18</sup> xanthan sulfuric acid,<sup>19</sup> 1,3-disulfonic acid imidazolium tetrachloroaluminate,<sup>20</sup> silica-bonded N-propylpiperazine sulfamic acid,<sup>21</sup> as reusable solid catalysts. Almost all these methods had several limitations such as more reaction times, less percentage yields, tiresome work-up procedures, usage of various toxic solvents and catalysts. Therefore, it is needed to overcome these difficulties and develop a new way for the synthesis of pyrazolone derivatives.

Free radicals play a vital role in human cell protection as immortality development and breakthrough of diseases. Free radicals also called as reactive oxygen species (ROS), which contain hydroxyl radicals ( $\text{OH}^\cdot$ ), superoxide anions ( $\text{O}_2^\cdot$ ), nitric oxide ( $\text{NO}^\cdot$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and lipid peroxidation. As antioxidants can act as a defence mechanism against exposure to free damage cells further decisive during the air pollution, smoke of tobacco, alcohols, pesticides, drug addiction, fried groceries, and many more can enhance the radical exposure.<sup>22</sup>

The present work focused on developing efficient and green methods for the synthesis of pharmacologically active heterocyclic compounds. Nowadays, multi-component reactions (MCRs) play a vital role in the improvement of cost-effective and eco-friendly protocols in organic synthesis in a single-step reaction. In persistence of interest in the synthesis of heterocyclic compounds, consequently, the synthesis of pyrazolone moiety was performed by using a heterogeneous catalyst in water/ethanol, including their spectroscopy data, and statistical analysis of their antioxidant potential.

## 2. Experimental

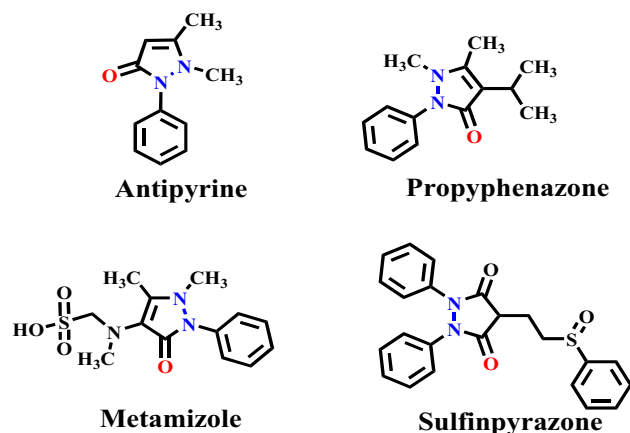
### 2.1 Materials and physical measurements

All the chemicals and reagents used were obtained from Avra, Merck and Sigma-Aldrich Co. and were used without additional purification. Melting points were determined in open capillaries in Elico melting point apparatus and were uncorrected. The reactions were monitored by thin layer chromatography (TLC) using silica gel-G UV 254 plates using 10% and 20% ethyl acetate and hexane as mobile phase. The final products were characterized by Fourier-transform infrared (FT-IR),  $^1\text{H}$  nuclear magnetic resonance (NMR), elemental

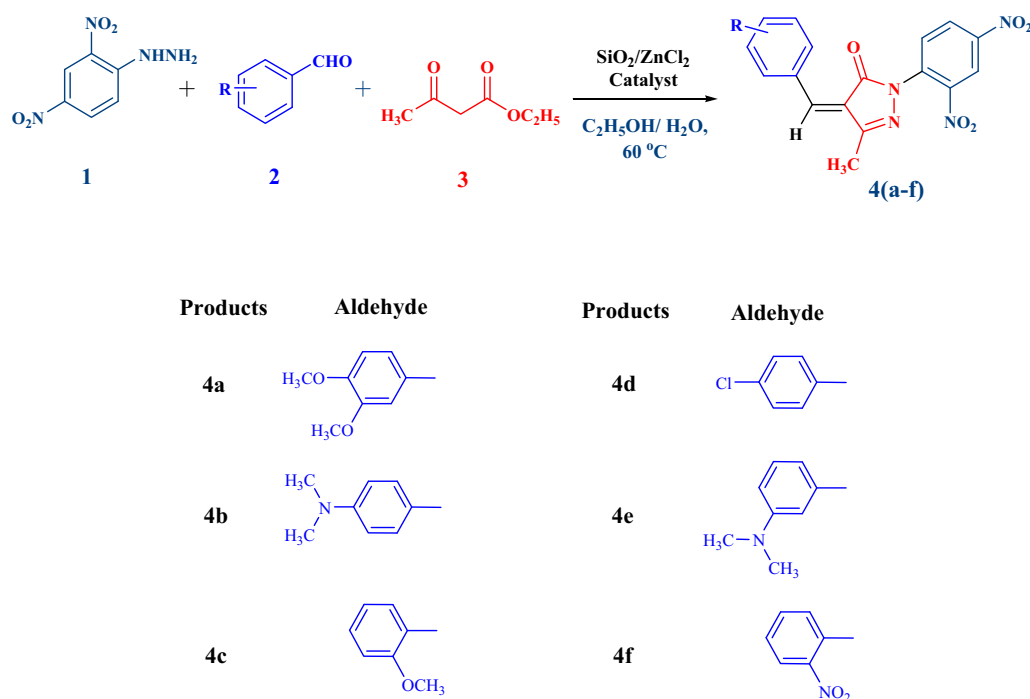
analysis (CHN) and melting points. IR spectra (KBr pellet) were recorded on Bruker Tensor 27 FT-IR spectrometer at Sri Venkateswara College of Pharmacy, Chittoor.  $^1\text{H}$  NMR spectra were recorded on a Bruker DRX400 spectrometer and the elemental analysis was performed using a Heraeus CHN-O-Rapid analyzer at Sophisticated Instrumentation Facility, VIT University, Vellore. NMR spectra were recorded in  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$ . Chemical shifts ( $\delta$ ) are reported in ppm relative to tetramethylsilane (TMS) as an internal standard. *J* values are given in Hz. High-resolution mass spectrometry (HRMS) spectra were recorded on a JEOL TMS-HX 110 mass spectrometer.

### 2.2 Synthesis

In this present work, compounds were synthesized as shown in Figure 2. Substituted 4-benzylidene-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one were prepared by condensation of substituted benzaldehyde, ethyl acetoacetate and 2,4-dinitrophenylhydrazine in presence of silica-supported zinc chloride ( $\text{SiO}_2/\text{ZnCl}_2$ ) as a recyclable catalyst by multicomponent reaction (MCR). Substituted pyrazolone was prepared by the reported procedure. The most important target was to develop an effective multi-component approach for the synthesis of substituted 4-benzylidene-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one [4] through the reaction of various substituted aromatic aldehyde [1] with 2,4-dinitrophenylhydrazine [2] and ethyl acetoacetate [3] by using silica-supported zinc chloride ( $\text{SiO}_2/\text{ZnCl}_2$ ) as a recyclable Lewis acid catalyst. All the reactions were carried out by refluxing with water/ethanol and the yield of the obtained products 4(a–f) were generated in good to



**Figure 1.** Important marketed drugs containing pyrazolone ring.



**Figure 2.** The scheme for the synthesis of pyrazolone derivatives 4(a–f).

excellent yields ranged within 86–94% and results are summarized in Table S1, Supplementary Information. As mentioned in Table S1, different aryl aldehydes having electron-withdrawing and electron-donating groups were found to give favourable compounds in good yields.

### 2.3 Preparation of catalyst ( $\text{SiO}_2/\text{ZnCl}_2$ )

The catalyst  $\text{ZnCl}_2$  supported on silica gel was prepared according to the previous procedure. About 2.7 g of  $\text{ZnCl}_2$  (12 mmol) was added to 9.1 g silica gel (grade 60, 230–400 mesh) in 50 mL ethanol. The reaction mixture was stirred and refluxed for 1 h in the absence of light, filtered, washed with dry  $\text{CCl}_4$  and dried under vacuum at  $160^\circ\text{C}$  for 10 h.<sup>23</sup>

### 2.4 Synthesis of substituted 4-benzylidene-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one using $\text{SiO}_2/\text{ZnCl}_2$ catalyst

An equimolar mixture of substituted aromatic aldehyde (0.02 mol), ethyl acetoacetate (0.02 mol) and 2,4-dinitrophenylhydrazine (0.02 mol) were added to 0.10 g of supported  $\text{ZnCl}_2$  on  $\text{SiO}_2$  (15%, w/w) in 10 mL of water (or) ethanol in round bottom flask equipped with condenser at  $60^\circ\text{C}$  for the given time (Table S1, Supplementary Information). After completion of the reaction (monitored by TLC), and diluted with cold

water (5 mL) the resulting mixture was extracted with ethyl acetate ( $3 \times 10$  mL). The combined organic layers were washed with 10%  $\text{NaHCO}_3$  and water, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated under reduced pressure. The resulting crude product substituted 4-benzylidene-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one derivatives were purified by recrystallization from hot ethanol to give the desired products.

### 2.5 Reusability of catalyst

The reusability of the catalyst was tested in the synthesis of 4-benzylidene-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one. In a typical experiment, after completion of the reaction, ( $\text{SiO}_2/\text{ZnCl}_2$ ) was isolated from the reaction mixture by filtration and washed with ethyl acetate and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . If  $\text{ZnCl}_2$  is used as a catalyst, it leaches the  $\text{Zn}^{2+}$  into the reaction. To minimize the leaching of zinc ions,  $\text{SiO}_2$  was used as a supporting agent to bind the zinc ions. However, no significant leaching of the modifier was observed under our reaction conditions. In the reaction mixture, Zn content was verified by analysing after filtering-off the catalyst. Moreover, no reaction was observed in the solvent after removing the catalyst. Using the recycled catalyst for consecutive times in the chemical reaction of benzaldehyde and 2,4-dinitrophenylhydrazine furnished the product

with no significant decrease in the reaction yield. The recovered catalyst (98%) was reused three times without any loss of activity. This reusability demonstrates the high stability of the catalyst under the operating conditions.

## 2.6 Spectral data of synthesized compounds

**2.6a Compound 4a:** (4Z)-4-(3,4-dimethoxybenzylidene)-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one Yellow solid; Yield 92%; M.p. 218 °C<sup>23</sup>; FT-IR (KBr, cm<sup>-1</sup>): 1182, 1412 (C=C<sub>aromatic</sub>), 1519 (C=N), 1695 (C=O), 1342 (NO<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.01–9.03 (dd, 3H, phenyl ring), 6.95 (s, 1H, -C=H), 6.83–7.20 (dd, 3H, phenyl ring), 2.29 (s, 3H, -CH<sub>3</sub>), 3.87 (s, 6H, 2x-OCH<sub>3</sub>); Analytical cal. C<sub>19</sub>H<sub>16</sub>N<sub>4</sub>O<sub>7</sub>: C, 55.34; H, 3.91; N, 13.59. Found: C, 55.31; H, 3.93; N, 13.60; MS (EI): (m/z) Calculated for C<sub>19</sub>H<sub>16</sub>N<sub>4</sub>O<sub>7</sub> [M+H]<sup>+</sup>: 412.3529; Found, 412.0632 (Rel. Int.100%).

**2.6b Compound 4b:** (4Z)-4-(4-(dimethylamino)benzylidene)-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one Orange crystalline solid; Yield 94%; M.p. 236 °C<sup>23</sup>; FT-IR (KBr, cm<sup>-1</sup>): 1417 (C=C<sub>aromatic</sub>), 1628 (C=N), 1713 (C=O), 1306 (NO<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.40–9.03 (dd, 4H, phenyl ring), 8.01 (d, 1H, -C=H), 6.80–6.83 (dd, 3H, phenyl ring), 2.94 (s, 3H, -CH<sub>3</sub>), 2.29 (s, 6H, 2xCH<sub>3</sub>); Analytical cal. C<sub>19</sub>H<sub>17</sub>N<sub>5</sub>O<sub>5</sub>: C, 57.72; H, 4.33; N, 17.71; Found: C, 57.68; H, 4.37; N, 17.65; MS (EI): (m/z) Calculated for C<sub>19</sub>H<sub>17</sub>N<sub>5</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 396.1263; Found, 396.1236 (Rel. Int.100%).

**2.6c Compound 4c:** (4Z)-4-(2-methoxybenzylidene)-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one Light yellow crystalline solid; Yield 91%; M.p. 228 °C<sup>24</sup>; FT-IR (KBr, cm<sup>-1</sup>): 1418 (C=C<sub>aromatic</sub>), 1701 (C=O), 1561 (C=N), 1506, 1325 (NO<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.21–9.03 (dd, 3H, phenyl ring), 8.03 (d, 1H, -C=H), 7.10–7.41 (dd, 4H, phenyl ring), 2.29 (d, 3H, -CH<sub>3</sub>), 3.84 (s, 3H, -OCH<sub>3</sub>); Analytical cal. C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>6</sub>: C, 56.55; H, 3.69; N, 14.65; Found: C, 56.68; H, 3.67; N, 14.60; MS (EI): (m/z) Calculated for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>6</sub> [M+H]<sup>+</sup>: 382.0913; Found, 382.1682 (Rel. Int.100%).

**2.6d Compound 4d:** (4Z)-4-(4-chlorobenzylidene)-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one Orange crystalline solid; Yield 86%; M.p. 178 °C; FT-IR (KBr, cm<sup>-1</sup>): 1127, 1424 (C=C<sub>aromatic</sub>), 1741 (C=O), 1512 (C=N), 1320 (NO<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.03–9.03 (dd, 3H, phenyl ring), 8.10 (m, 1H, -C=H), 6.82–7.45 (m, 4H, phenyl ring), 2.29 (s, 3H, -CH<sub>3</sub>); Analytical cal. C<sub>17</sub>H<sub>11</sub>N<sub>4</sub>O<sub>5</sub>Cl: C, 52.79; H, 2.87; N, 14.49; Found: C, 52.68; H, 2.82; N, 14.53; MS (EI): (m/z) Calculated for C<sub>17</sub>H<sub>11</sub>ClN<sub>4</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 386.0418; Found, 386.1746 (Rel. Int.100%).

**2.6e Compound 4e:** (4Z)-4-(3-(dimethylamino)benzylidene)-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one Orange crystalline solid; Yield 90%; M.p. 230 °C; FT-IR

(KBr, cm<sup>-1</sup>): 1422 (C=C<sub>aromatic</sub>), 1694 (C=O), 1332 (NO<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.40–9.73 (m, 3H, phenyl ring), 7.26 (s, 1H, -C=H), 6.71–7.74 (m, 4H, phenyl ring), 1.29 (s, 3H, -CH<sub>3</sub>), 3.44 (s, 6H, 2xN-CH<sub>3</sub>); Analytical cal. C<sub>19</sub>H<sub>17</sub>N<sub>5</sub>O<sub>5</sub>: C, 57.72; H, 4.33; N, 17.71; Found: C, 57.65; H, 4.38; N, 17.67; MS (EI): (m/z) Calculated for C<sub>19</sub>H<sub>17</sub>N<sub>5</sub>O<sub>5</sub> [M+H]<sup>+</sup>: 395.1230; Found, 395.3688 (Rel. Int.100%).

**2.6f Compound 4f:** (4Z)-4-(2-nitrobenzylidene)-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one Light yellow crystalline solid; Yield 88%; M.p. 212 °C; FT-IR (KBr, cm<sup>-1</sup>): 1608 (C=C<sub>aromatic</sub>), 1725 (C=O), 1495, 1331 (NO<sub>2</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.41–9.10 (m, 3H, phenyl ring), 7.27 (s, 1H, -C=H), 7.44–7.66 (m, 4H, phenyl ring); Analytical cal. C<sub>17</sub>H<sub>11</sub>N<sub>5</sub>O<sub>7</sub>: C, 51.39; H, 2.79; N, 17.63; Found: C, 51.30; H, 2.82; N, 17.58; MS (EI): (m/z) Calculated for C<sub>17</sub>H<sub>11</sub>N<sub>5</sub>O<sub>7</sub> [M+H]<sup>+</sup>: 397.2985; Found, 397.0658 (Rel. Int.100%).

## 2.7 Evaluation of in-vitro antioxidant activity

The activity of the synthesized compounds was quantitatively measured by diphenylpicrylhydrazyl (DPPH) radical assay method to characterize antioxidants.<sup>25</sup> When antioxidants react with stable free radical (DPPH), it gets converted into 1,1-diphenyl-2-picryl hydrazine. The stable free radical DPPH was measured by a decrease in absorbance at λ 540 nm, which is purple in colour. Ascorbic acid was used as the standard drug. The per cent scavenging activity was calculated by using the formula,

$$\text{Scavenging activity (\%)} = \frac{\text{Control} - \text{Test}}{\text{Control}} \times 100$$

**DPPH method** The stock solution was prepared by using DPPH (10 mg) dissolved in 10 mL dimethylsulfoxide (DMSO) and added at various concentrations in ethanolic solution (10 mL). Solutions of the test compounds in various concentrations (125, 250, 500 µg/mL) as well as of ascorbic acid as reference standard was prepared in ethanol. An aliquot of each of these solutions (1.0 mL) was taken in different 10 mL volumetric flasks to which the DPPH stock solution (1.0 mL) was added and volume was made to 10 mL. The plates were incubated at 37 °C for 20 min and the absorbance of each solution was measured at 540 nm and performed in triplicate.<sup>26–28</sup>

## 3. Results and Discussion

### 3.1 Spectral data and interpretation of the compounds

The products were identified by IR, <sup>1</sup>H NMR spectroscopy and elemental analysis. In <sup>1</sup>H NMR spectrum



of **4(a-f)** it revealed a multiplet for the two aromatic hydrogen's range at  $\delta$  8.41–9.79 ppm and  $\delta$  6.69–7.74 ppm. One singlet related to the ethylene hydrogen at  $\delta$  7.12–7.38 ppm and one singlet related to three hydrogen's of  $-\text{CH}_3$  group at  $\delta$  1.22–1.29 ppm.

**3.1a Characterization of Catalyst ( $\text{SiO}_2/\text{ZnCl}_2$ ):** The FT-IR spectrum of the catalyst ( $\text{SiO}_2/\text{ZnCl}_2$ ) is shown in Figure S1, Supplementary Information. The FT-IR spectrum of the catalytic system displayed a symmetrical stretching band at  $3434\text{ cm}^{-1}$  for hydroxyl group and the band resonating at  $1610\text{ cm}^{-1}$  was attributed to the bending of adsorbed water. A band appeared at  $1172\text{ cm}^{-1}$  and this can be attributed to the bending of Si-O-Si antisymmetric stretching vibrations and the band at  $817\text{ cm}^{-1}$  was also evidence of the symmetric stretching vibration of the rocking mode of Si-O-Si. The O-H stretching band around  $3434\text{ cm}^{-1}$  was also presented in the catalyst. Considering the FT-IR spectra of  $\text{SiO}_2/\text{ZnCl}_2$ , it was concluded that  $\text{ZnCl}_2$  was successfully coated with silica layer.<sup>29</sup>

### 3.2 Optimization studies

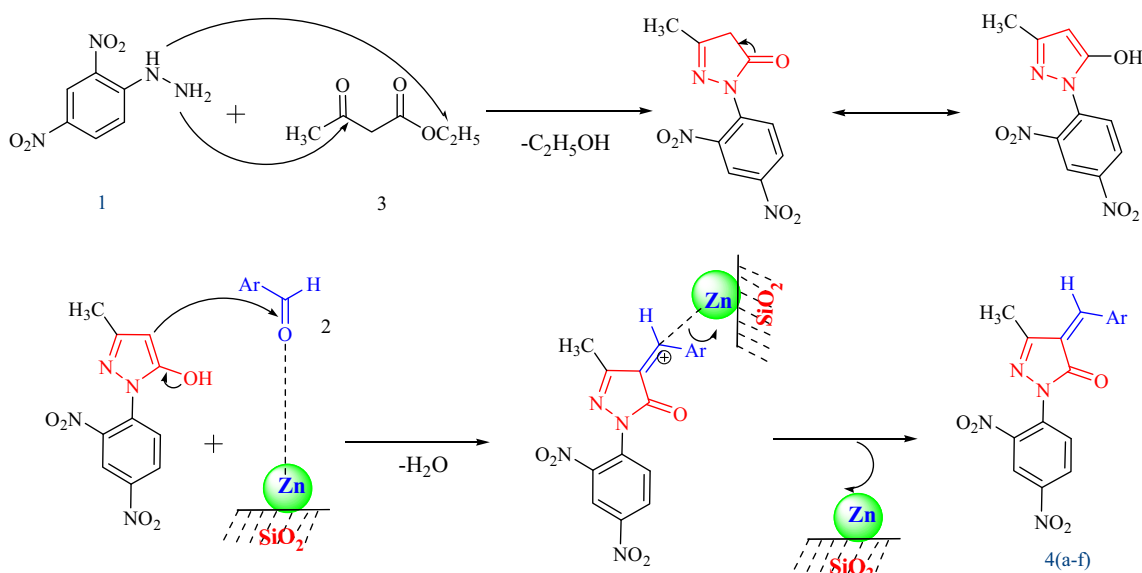
In the present study, in the first series of experiments, an investigation was done on the effect of catalyst loading, the nature of solvent, optimum reaction temperature and the time taken. Initially, the three-component reaction was conducted on 2 mmol scale of benzaldehyde, 2,4-dinitrophenylhydrazine and ethyl acetoacetate at a suitable temperature, under catalyst-

free conditions, where, initially a trace amount of product had formed (Table S2, entry 1, Supplementary Information), signifying the need of a catalyst. To enhance the yield of the product and to optimize the reaction conditions, it was then studied in the presence of different catalysts such as  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{SiO}_2\text{-Cl}$ ,  $\text{SiO}_2/\text{ZnCl}_2$ . Maximum yield (86%) was obtained when the reaction was carried out with 10 mol% of the  $\text{SiO}_2/\text{ZnCl}_2$  catalyst.

Our analysis revealed that the optimum amount of  $\text{SiO}_2/\text{ZnCl}_2$  was relative to the reactant. The catalyst plays a crucial role in the reaction. The results are summarized in Table S2, Supplementary Information. The reaction improved with almost the same ease with aromatic and aliphatic aldehydes. Various functional groups such as methoxy ( $\text{OCH}_3$ ), dimethylamino ( $\text{N}(\text{CH}_3)_2$ ), chloro ( $\text{Cl}$ ) and nitro ( $\text{NO}_2$ ) groups containing compounds were tolerated. However, there are no significant changes in the yield that were observed when more than one substitute was present in the phenyl ring (Table S1, entry 1). Hence, electronic and steric factors played a negligible role in this protocol.

### 3.3 A tentative mechanistic pathway for the multicomponent reaction

The plausible mechanism for the synthesis of substituted 4-benzylidene-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one has been shown in Figure 3. The first step involves the condensation of 2,4-dinitrophenylhydrazine with ethylacetoacetate for the



**Figure 3.** The mechanism for the synthesis of substituted 4-benzylidene-3-methyl-1-(2,4-dinitrophenyl)-1H-pyrazol-5(4H)-one.

synthesis of 3-methyl-1-(2,4-dinitrophenyl)-1*H*-pyrazol-5-ol. Aldehyde is activated by the catalyst  $\text{SiO}_2/\text{ZnCl}_2$ . Further, the carbonyl carbon is attacked by the nucleophilic 3-methyl-1-(2,4-dinitrophenyl)-1*H*-pyrazol-5-ol to form the subsequent products of substituted pyrazolone derivatives.

### 3.4 DPPH radical scavenging activity

All the synthesized compounds were subjected to evaluation of antioxidant profile using DPPH radical scavenging assay method and due to their hydrogen donating ability. As mentioned in Table S3 (Supplementary Information), six compounds **4(a–f)** showed radical scavenging activity. It was observed from the data that the scavenging activity order of the test compounds was  $4f > 4a > 4c > 4d > 4e > 4b$ . The physically powerful DPPH scavenging activity can be attributed in part to the nitro ( $-\text{NO}_2$ ) group present in **4f** and methoxy ( $-\text{OCH}_3$ ) groups present in **4a** and **4c**.

## 4. Conclusions

In summary, a simple, minimizing by-products, maximizing atom economy and eco-friendly synthesis of substituted pyrazolones using  $\text{SiO}_2/\text{ZnCl}_2$  as a recyclable heterogeneous catalyst was formed. The synthesized compounds were acknowledged by spectral data and compounds that illustrated significant to moderate activity for *in vitro* antioxidant activity. The most important one of this methodology is the use of mild reaction conditions, shorter reaction times and higher yields. The products were obtained with a high yield of 86–94% through multi-component reaction and may possibly be used in the synthesis of various biologically active compounds. These catalysts are fully recovered for three consecutive runs without any change in their catalytic activity.

### Supplementary Information (SI)

Characterization data and copies of  $^1\text{H}$  NMR spectra of compounds are reported and available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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