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# Nanocrystalline Cu–ZnO as an Green Catalyst for One Pot Synthesis of 4,4'-((phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) Derivatives

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Synthesis of 4.4'-((phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) derivatives was successively carried out using Cu doped ZnO nanomaterials. The nanocrystalline Cu-ZnO was obtained by decomposing as-synthesized copper-zinc oxalate intermediate at 520 °C. The prepared Cu-ZnO nanostructured catalyst was characterized with FTIR, X-ray diffraction, field emission scanning electron microscope and electron diffraction techniques. XRD analysis indicates the formation of highly crystalline hexagonal phase of ZnO along with the presence of monoclinic CuO. FESEM photographs shows the existence of plate like structures made up of small spherical shaped particles having size in the range of 30-50 nm. As-synthesized Cu-ZnO was used as heterogeneous catalyst for one pot synthesis of 4,4'-((phenyl)methylene)bis(3-methyl-1-phenyl-1Hpyrazol-5-ol) derivatives using phenyl hydrazine, ethyl acetoacetate and aromatic aldehydes. The 3-methyl-1-phenyl-1H-pyrazol-5-ol was obtained as in-situ precursor to the series of bis-pyrazolone derivatives. The progress of reaction was monitored by thin layer chromatography. The obtained organic product was further characterized and confirmed by FT-IR. <sup>1</sup>H-NMR. <sup>13</sup>C-NMR and HRMS spectroscopic techniques. The Cu-ZnO catalyst confers upto 96% yield of pyrazolone derivatives in ethanol solvent at refluxing condition. The Cu-ZnO catalyst was used successfully up to 5 cycles without much loss of catalytic activity. Overall, the use of environmental friendly Cu-ZnO nanostructures as a heterogeneous catalyst shows higher yield and lower reaction time towards the synthesis of bispyrazolone derivatives by Tandem Knoevenagel/Michael reaction.

**Keywords:** Heterogeneous Catalyst, Nanocrystalline Cu–ZnO, Bispyrazolone, One Pot Synthesis, Tandem Knoevenagel/Michael Reaction.

# **1. INTRODUCTION**

The role of pyrazolone compounds has been increasing day by day in pharmaceutical industries due to its nitrogen containing five membered heterocyclic moieties. Consequently, nowadays the researchers are actively involved in the synthesis of pyrazolone derivatives due to its enormous applications as drug molecules.<sup>1</sup> The pyrazolone moiety containing compounds exhibits biological activities such as antioxidant, antidepressant, gastric secretion stimulatory, anti-inflammatory<sup>2</sup> etc. Furthermore, these compounds have been efficiently used as herbicidal, analgesic, antimicrobial, antifungal and antipyretic drugs.<sup>3</sup> These compounds have unique electrical and optical properties<sup>4</sup> too. The 4,4'-((aryl)methylene)bis(3-methyl-1-phenyl-1Hpyrazol-5-ol) derivatives are routinely applied as pesticides, fungicides, insecticides in the pesticide industries<sup>5, 6</sup> and used as chelating agent for the extraction of different metal ions.<sup>7</sup>

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In view of such intrinsic merits, the synthesis of 4,4'-((aryl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) derivatives have been carried out using several homogenous as well as heterogeneous catalysts such as 1,3,5tris(hydrogensulfato) benzene,8 lanthanum (III) triflate on graphene oxide,9 LiOH,10 1-(carboxymethyl) pyridinium chloride,<sup>11</sup> NH<sub>4</sub>OAc,<sup>12</sup> CsF,<sup>13</sup> PEG-SO<sub>3</sub>H,<sup>14</sup> Bronsted acidic ionic liquid supported on nanoporous Na<sup>+</sup>-montmorillonite,<sup>15</sup> Ce(SO<sub>4</sub>)<sub>2</sub>  $\cdot$  4H<sub>2</sub>O, Fe(SO<sub>4</sub>)<sub>2</sub>  $\cdot$  $(NH_4)_2 \cdot 6(H_2O)$ ,<sup>16</sup> Cu-isatin schiff base complex,<sup>17</sup> diammonium hydrogen phosphate,<sup>18</sup> xanthan sulfuric acid,<sup>19</sup> 3-aminopropylated silica gel,<sup>20</sup> 4-(succinimido)-1butane sulfonic acid,<sup>21</sup> 1,3-disulfonic acid imidazolium tetrachloroaluminate,<sup>22</sup> 1-sulfopyridinium chloride<sup>23</sup> and 2-hydroxy ethyl ammonium propionate.<sup>24</sup> Present, the homogenous catalysis in organic synthesis becomes an environmental issue. Hence, the development of heterogeneous cost effective and easy to scale up method for the synthesis of bispyrazolones has become an important area of research.

Nowadays, the synthesis of nano materials and their utilization as an environmentally benign catalyst for organic transformation<sup>25, 26</sup> as well as degradation of organic waste<sup>27</sup> is an important area of research. Numerous physical and chemical methods routinely used for the synthesis of nanomaterial with unique morphology and uniform particle size.<sup>28</sup> It has been established that nanosized materials exhibit altogether different or superior properties than those of large particle sized materials.<sup>29, 30</sup> Due to their smaller size they have high surface to volume ratio that increases the surface energy leading to distinctively different chemical, electronic, optical, magnetic, and mechanical properties.

The enhancement of catalytic activity can be accomplished by doping nanomaterials such as nano *n*-propylsulphonated  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>,<sup>31</sup> nanosized Fe<sub>3</sub>O<sub>4</sub> based vanadic acid,<sup>32</sup> Pd(0) NPs,<sup>33</sup> sulfonated carbon/nanometal oxide composites<sup>34</sup> and ZnO NPs<sup>35</sup> for the synthesis of 4,4'-((aryl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s. Therefore, due to promising role and high environmental stability of nanomaterials as a catalyst, we have introduced Cu–ZnO nanocrystalline materials for organic transformation.

In this context, herein, we report the synthesis of nanocrystalline Cu–ZnO catalyst via solution based precipitation technique. The as-synthesized Cu–ZnO material is used as an effective heterogeneous catalyst for the synthesis of 4,4'-((aryl)methylene)bis(3-methyl-1-phenyl-1Hpyrazol-5-ol)s in ethanol solvent at reflux conditions. We observed that nanocrystalline Cu–ZnO catalyst produced better yield for the Tandem Knoevenagel/Michael reaction. The used catalyst is found environmental friendly and can be recycled almost up to five times without further loss in the product yield.

# 2. EXPERIMENTAL DETAILS

#### 2.1. Procedure for Synthesis of Cu-ZnO Catalyst

Zinc sulphate (99.9%, SD-fine), copper sulphate (99.9%, SD-fine) and oxalic acid have been used as precursor material. Oxalic acid (0.1 N) solution was added drop wise in the mixture of zinc sulphate (0.1 N) and copper sulphate (0.1 N) with constant stirring. The intermediate copperzinc oxalate was obtained and washed with distilled water (1 lit). Obtained precipitate was dried at 100 °C for 8 hrs. The dried intermediate powder was decomposed at 520 °C to generate desired nanocrystalline Cu–ZnO.

### 2.2. Synthesis of 4,4'-((phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) Derivatives Using Cu–ZnO Catalyst

Phenyl hydrazine (1 mmol) and ethyl acetoacetate (1 mmol) were taken in 10 ml ethanol in 25 ml single neck round bottom flask equipped with condenser. Then, nano Cu-ZnO catalyst was added in the reaction mixture. Then reaction mass was refluxed for 60 min. The formation of intermediate pyrazolone was confirmed by TLC technique. After completion of the reaction, different aromatic aldehydes (0.5 mmol) were added into above (same) reaction mass for the next step. Then reaction mixture was again refluxed for 30 min and completion of reaction was checked by TLC. Reaction mixture was cooled and catalyst was separated by centrifugation, washed with ethanol. The used catalyst was oven dried at 120 °C and recycled for the same organic transformation. The filtrate was concentrated to get solidified compound which was subsequently recrystallized in ethyl acetate. The obtained pure products were characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and HR-MS techniques.

# 2.3. Characterization of Powder Catalyst and Organic Compounds

Fourier Transform Infra-Red spectroscopy (FTIR) (IR Affinity-1S) in the wavelength range of 400–4000 cm<sup>-1</sup> was used to study the formation of nanocrystalline ZnO and Cu–ZnO. Powder X-ray Diffractograms were recorded on a Model Rigaku-D/MaX-2200V X-ray Diffractometer (XRD) using CuK $\alpha$ -radiation with Ni filter. The surface morphology and particle size were determined using a Field Emission Scanning Electron Microscope (FESEM Model JEOL-JSM6700F). <sup>1</sup>H and <sup>13</sup>C-NMR were recorded in DMSO-d6 solvent on Ascend 500 MHz Bruker NMR spectrometer with tetramethylsilane (TMS) as internal reference. The HRMS data was taken in methanol solvent using High Resolution Mass Spectrometer (HRMS, Bruker Germany, Model Impact HD, UHR Impact II ESI-Q-TOF).

## 3. RESULTS AND DISCUSSION

The phase purity and morphology of prepared nanocrystalline Cu–ZnO catalyst was determined using following techniques.

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# 3.1. FTIR Patterns of As-Synthesized ZnO and Cu–ZnO

Figure 1 shows the FT-IR pattern of as-synthesized nanocrystalline ZnO and Cu–ZnO. The metal oxygen stretching frequency of ZnO is confirmed by peak at 607.55 cm<sup>-1</sup> (Fig. 1(a)). The Cu(II)–O bonds formation peak appears at 601 and 508 cm<sup>-1</sup> indicates the doping of Cu in ZnO nanomaterials.<sup>36</sup> The occurrence of sharp peaks at 516.18 and 599.47 cm<sup>-1</sup> in the spectrum of Cu–ZnO nanoparticles (Fig. 1(b)) is the characteristic of Cu–ZnO bond formation. The overall FTIR analysis is well matched with the reported data which implies the presence of Cu in ZnO matrix.

#### 3.2. X-ray Diffraction Analysis

The XRD patterns of as-synthesized ZnO and Cu–ZnO by solvent based precipitation technique are depicted in Figure 2. The XRD pattern displayed in Figure 2(a) is well matched with hexagonal phase of ZnO while, the XRD pattern displayed in Figure 2(b) is well matched with the monoclinic phase of CuO (tenorite) nano particles along with hexagonal phase of ZnO. (In well concurrence with the JCPDS Card no: 89-2531).

The crystallite size of pure ZnO and Cu–ZnO was calculated using Scherrer's equation.

The average particle size was found to be in the range 20–40 nm for ZnO and 15–35 nm for Cu–ZnO.



Figure 1. FTIR of as-synthesized (a) ZnO and (b) Cu–ZnO nanostructures.

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Figure 2. XRD pattern of as-synthesized (a) ZnO and (b) Cu-ZnO.

#### 3.3. Morphological Study by FE-SEM

Figure 3 shows the field emission scanning electron microscope photographs of typical ZnO (3a and 3b) as well as Cu–ZnO samples (3c and 3d).

The pure ZnO indicates the presence of thin sheets like morphology having irregular shape composed of spongy ZnO particles (Figs. 3(a and b)). With Cu-doping, the appearance of irregular shaped flakes made up of evenly distributed spherical ZnO particles is noticed (Figs. 3(c and d)). Morphological study reveals the particle size of this material is in the range 30–50 nm for both the samples.

# 3.4. Energy-Dispersive X-ray Spectroscopy (EDS) Analysis

Figure 4, exhibits the Energy-dispersive X-ray spectroscopy (EDS) analysis of as-synthesized Cu–ZnO. The EDS analysis showed presence of Cu, Zn and O elements in the material. The EDS analysis illustrates nearby 35.11 wt.% Zinc, 26.50 wt.% Copper and 38.39 wt.% Oxygen, elements present in the material. The percent doping (pre-chosen values) for the precipitation technique is in close agreement with EDS report.

# 3.5. Synthesis of 4,4'-((phenyl)methylene)bis(3methyl-1-phenyl-1H-pyrazol-5-ol) Derivatives

The different bispyrazolone derivatives were obtained as per the procedure given in the experimental section. It has Nanocrystalline Cu-ZnO as an Green Catalyst for bis-pyrazolyl and Allied Derivatives



Figure 3. Field emission microscopes (FE-SEM) of ZnO (a and b) and Cu-ZnO (c and d).



Figure 4. EDS image of Cu-ZnO nanocomposite.

been observed, the catalytic reactivity of desired nanosized ZnO and Cu doped ZnO as a heterogeneous catalyst for the model reaction (Reaction scheme) was determined in various solvents, different temperatures and by changing mol percent of Cu–ZnO catalyst.

Reaction Scheme

The nanocrystalline Cu-ZnO makes carbonyl group of ethyl acetoacetate [A] more electron deficient and at the same time attack of lone pair of nitrogen form phenyl hydrazine [B] which creates more chances to remove ethoxide group and to creates the co-ordinations with catalysts. Further, it may be more possible to form the intermediate in situ complex [C] which subsequently helps to forms pyrazolone [D]. Then the intermediate pyrazolone [D] undergoes knoevenagel type condensation with aromatic aldehyde [E] in presence of the catalyst to form intermediate [F]. Simultaneously, the intermediate [D], may react as second molecule pyrazolone with intermediate [F] in presence of the catalyst to convert into intermediate [G]. Then intermediate [G] may get hydrolyzed to yield 4,4'-((phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) [H]. The proposed mechanism for the synthesis of 4,4'-((phenyl)methylene)bis(3-methyl-1phenyl-1H-pyrazol-5-ol) by Tandem Knoevenagel/Michael reaction by using Cu-ZnO nanosized catalyst is as shown below.



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Proposed mechanism for synthesis of 4,4'-((phenyl)methylene)bis(3-methyl-1-phenyl-1H- pyrazol-5ol)s by using Cu–ZnO Nanocatalyst.

One pot synthesis of Pyrazolone and its Tandem Knoevenagel/Michael reaction with aromatic aldehyde has been performed successively with different catalyst such as ZnO and Cu-ZnO in various solvents at different temperature (Table I, Entry 1 to 10). Generally, the synthesis of homogenous pyrazolone derivative is more favored by acid catalysis. Hence, in the present protocol, we have doped Cu in ZnO to be used as heterogeneous catalyst. The doping of Cu in inorganic metal oxide is useful to increase the surface acidity.<sup>38</sup> Reported reaction is also favored to acid catalyst which causes the enhancement in the yield as compared to undoped ZnO (Table I, Entry 7 to 10). We observed 94% yield (Table I, Entry 7) of compound 5a (as per the reaction scheme) in the ethanol solvent with reflux condition as compared to the other solvents. The increase of yield in ethanol solvent may be due to

its polar protic behavior and also low dielectric constant. Same reaction has been conceded out at different mmol of catalyst (Table II, Entry 1 to 7). The increased mmol of catalyst directly effects the yield of reaction. At the optimized reaction conditions, recyclability study of catalyst has been done for the synthesis stated in 5a (Fig. 5). The catalyst was recycled up to 5 times and it was found that recycled catalyst also confers the almost equal yield for the same transformation.

Besides, the effect of electron donating or electron withdrawing substitution on aromatic aldehyde at o/p position has been studied for the synthesis of 5a–j at optimized reaction conditions, using 0.25 mmol of Cu–ZnO catalyst at refluxing condition in ethanol solvent (Table III, Entry 1 to 10). Presence of electron donating OH (o/p) group on aromatic aldehyde reduces the yield of reaction (Table III, Entry 10). The halogenated aromatic aldehyde compound (Table III, Entry 2, 3, 4 and 5) yielded better than nitro aromatic aldehyde (Table III, Entry 7). The

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 Table I. Optimization of reaction conditions for synthesis of 4,4'-((phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s (5a).

*Notes*: <sup>*a*</sup>Reaction condition: Phenyl hydrazine (1 mmol) 1, Ethyl Acetoacetate (1 mmol) 2, Benzaldehyde (0.5 mmol) 4a, Catalyst (1 mmol). <sup>*b*</sup>Isolated yield.

benzaldehyde, 4 methyl benzaldehyde and 4 methoxy benzaldehyde yielded the best value (Table III, Entry 1, 6 and 7) at optimized reaction condition.

# 3.6. Spectral Data of As-Synthesized Compounds 3.6.1. 4,4'-((phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table III, Entry 1, 5a)

<sup>1</sup>H NMR (500 MHz, DMSO-d6) *d* ppm: 2.31 (*s*, 6H, CH<sub>3</sub>), 4.92 (*s*, 1H, CH), 7.16 (*m*, 1H), 7.22 (*m*, 2H), 7.28 (*m*, 4H), 7.43 (*t*, J = 8.0 Hz, 4H), 7.73 (*d*, J = 8.0 Hz, 4H), 14.42, (*bs*, 2H); <sup>13</sup>C-NMR (75 MHz, DMSO-d6) *d* ppm: 12.27, 33.77, 120.86, 125.76, 126.25, 127.66, 128.55, 129.32, 129.53, 138.20, 143.23, 146.70; HRMS *m*/*z* Calcd. for C<sub>27</sub>H<sub>24</sub>O<sub>2</sub>N<sub>4</sub> [M + H]: 437.19 Found: 437.1985.

# 3.6.2. 4,4'-((4-chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table III, Entry 2, 5b)

2.174 (s, 6H, CH<sub>3</sub>), 4.660 (s, 1H, CH), 7.07 (t, J = 7.8 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 7.32 (m, 6H), 7.88 (d, 7.8 Hz, 4H), 13.92 (bs, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-d6) d ppm: 13.10, 34.19, 102.92, 119.96, 124.17,

Table II.Synthesis of 4,4'-((phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)(5a) under different mol% of Cu–ZnO catalytic condition.

Entry	Catalyst <sup>a</sup> (mmol)	Time (h)	Yield $(5A)^b$
1	Nil	4.0	Trace
2	0.10	2.0	60
3	0.15	1.5	82
4	0.20	1.5	90
5	0.25	1.5	94
6	0.50	1.5	94
7	1.0	1.5	94

*Notes:* <sup>a</sup>Reaction condition: Phenyl hydrazine (1 mmol) 1, Ethyl Acetoacetate (1 mmol) 2, Benzaldehyde (0.5 mmol) 4, Catalyst. <sup>b</sup>Isolated yield.



**Figure 5.** Reusability study of Cu–ZnO for synthesis of 4,4'-((phenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) in ethanol solvent at 1.5 hr.

128.13, 128.91, 129.65, 130.22, 140.21, 146.34; HRMS m/z Calcd. For  $C_{27}H_{24}O_2N_4Cl$  [M + H]: 471.15, Found:  $C_{27}H_{24}O_2N_4Cl$  [M + H]: 471.15.

### 3.6.3. 4,4'-((2-chlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table III, Entry 3, 5c)

2.30 (*s*, 6H, CH<sub>3</sub>), 5.14 (*s*, 1H, CH), 7.25 (*m*, J = 7.8 Hz, 3H), 7.30 (*dt*, J = 7.6 and 1.1 Hz, 1H), 7.40 (*dd*, J = 7.9 and 1.1, 1H), 7.44 (*d*, 7.8 Hz, 4H), 7.70 (*d*, 7.85 Hz, 4H), 7.82 (*d*, 7.0 Hz, 1H), 14.03 (*bs*, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-d6) *d* ppm: 12.38, 32.07, 121.16, 126.12, 127.39, 128.51, 129.39, 129.92, 130.71, 132.29, 140.05, 146.37; HRMS *m*/*z* Calcd. for C<sub>27</sub>H<sub>24</sub>O<sub>2</sub>N<sub>4</sub>Cl [M + H]: 471.15, Found: C<sub>27</sub>H<sub>24</sub>O<sub>2</sub>N<sub>4</sub>Cl [M + H]: 471.1592.

### 3.6.4. 4,4'-((4-fluorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table III, Entry 4, 5d)

2.16 (s, 6H, CH<sub>3</sub>), 4.63 (s, 1H, CH), 7.03 (m, 4H), 7.31 (t, J = 7.6 Hz, 4H), 7.36 (q, J = 8.5 Hz, 2H), 7.90 (d, J = 8.0 Hz, 4H), <sup>13</sup>C NMR (75 MHz, DMSO-d6) d ppm: 13.42, 34.43, 102.68, 114.58, 114.75, 119.65, 123.58, 128.75, 129.39, 129.45, 146.23; HRMS m/z Calcd. for C<sub>27</sub>H<sub>24</sub>O<sub>2</sub>N<sub>4</sub>F [M + H]: 455.15, Found: C<sub>27</sub>H<sub>24</sub>O<sub>2</sub>N<sub>4</sub>F [M + H]: 455.1888.

#### 3.6.5. 4,4'-((4-bromophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table III, Entry 5, 5e)

2.16 (s, 6H, CH<sub>3</sub>), 4.61 (s, 1H, CH), 7.05 (t, J = 8.0 Hz, 4H), 7.30 (q, J = 8.5 Hz, 4H), 7.38 (d, J = 8.5 Hz, 2H), 7.88 (d, J = 8.0 Hz, 4H), <sup>13</sup>C NMR (75 MHz, DMSOd6) d ppm: 13.40, 34.59, 102.31, 118.48, 119.78, 123.68, 128.62, 128.76, 130.13, 130.95, 140.87, 146.34, 157.76; HRMS m/z Calcd. for C<sub>27</sub>H<sub>24</sub>O<sub>2</sub>N<sub>4</sub>Br [M + H]: 517.10, Found: C<sub>27</sub>H<sub>24</sub>O<sub>2</sub>N<sub>4</sub>Br [M + H]: 517.1067.

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Compound (5a-j)

Time (min.)

90

90

Yield

95

96

Table III. Contiuned.

Entry

6

7

### 3.6.6. 4,4'-((4-methylphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table III, Entry 6, 5f)

2.25 (s, 3H, CH<sub>3</sub>), 3.31 (s, 6H, CH<sub>3</sub>), 4.90 (s, 1H, CH), 7.07 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 7.5 Hz, 2H), 7.44 (t, 8.2 Hz, 4H), 7.71 (d, 8.0 Hz, 4H), 13.97 (bs, 2H); <sup>13</sup>C NMR (75 MHz, DMSOd6) d ppm: 12.13, 21.00, 33.24, 120.95, 125.97, 127.54, 129.15, 129.38, 129.59, 135.26, 137.91, 139.72, 146.68; HRMS m/z Calcd. for  $C_{28}H_{27}O_2N_4$  [M + H]): 451.21, Found:  $C_{28}H_{27}O_3N_4$  [M + H]): 451.2139.

Table III. Synthesis of (5a-j) using Cu-ZnO catalyst in ethanol solvent



2.261 (s, 6H, CH<sub>3</sub>), 3.907 (s, 3H, OCH<sub>3</sub>), 4.789 (s, 1H, CH), 6.81 (d, J = 8.5 Hz 2H), 7.18 (m, 4H), 7.39 (t, J = 8.5 Hz, 4H), 7.77 (d, 7.6 Hz, 4H), 13.41 (bs,2H); <sup>13</sup>C NMR (75 MHz, DMSO-d6) *d* ppm: 12.37, 33.62, 55.44, 104.48, 113.82, 114.85, 118.80, 120.53, 125.09,

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Melting

point (°C)

204

 $(203 - 204)^6$ 

180

128.64, 129.14, 136.20, 139.02, 146.56, 157.74; HRMS m/z Calcd. for  $C_{28}H_{26}O_3N_4$  [M + H]: 467.53 Found:  $C_{28}H_{27}O_3N_4$  [M + H]: 467.2093.

# 3.6.8. 4,4'-((2-nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table III, Entry 8, 5h)

2.16 (s, 6H, CH<sub>3</sub>), 5.32 (s, 1H, CH), 7.13 (t, J = 7.5 Hz 2H), 7.36 (t, J = 8.0 Hz, 4H), 7.39 (d, J = 8.2 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.64 (d, J = 7.5 Hz, 1H), 7.80 (d, J = 8.0 Hz, 4H), 7.87 (d, J = 8.0 Hz, 1H), 14.40 (s, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-d6) d ppm: 12.71, 29.98, 102.44, 120.24, 123.99, 124.64, 127.43, 129.00, 130.95, 131.99, 137.23, 139.64, 145.99, 149.84, 157.99; HRMS m/z Calcd. for C<sub>27</sub>H<sub>24</sub>O<sub>4</sub>N<sub>5</sub> [M + H]: 481.18, Found: C<sub>27</sub>H<sub>24</sub>O<sub>4</sub>N<sub>5</sub> [M + H]: 482.1836.

#### 3.6.9. 4,4'-((4-nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table III, Entry 9, 5i)

2.15 (s, 6H, CH<sub>3</sub>), 5.31 (s, 1H, CH), 7.12 (t, J = 7.5 Hz 2H), 7.35 (t, J = 8.0 Hz, 4H), 7.39 (d, J = 8.0 Hz, 1H), 7.57 (t, J = 8.0 Hz, 1H), 7.63 (d, J = 7.0 Hz, 1H), 7.80 (d, J = 8.0 Hz, 4H), 7.87 (d, J = 8.0 Hz, 1H), 14.40 (s, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-d6) d ppm: 12.73, 29.97, 102.39, 120.17, 123.97, 124.58, 127.40, 128.99, 130.95, 131.98, 137.30, 139.71, 145.94, 149.82, 157.99; HRMS m/z Calcd. for  $C_{27}H_{24}O_4N_5$  [M + H]: 482.18, Found:  $C_{27}H_{24}O_4N_5$  [M + H]: 482.1836.

# 3.6.10. 4,4'-((2-hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (Table III, Entry 10, 5j)

<sup>1</sup>H NMR (500 MHz, DMSO-d6) *d* ppm: 2.208 (*s*, 6H, CH<sub>3</sub>), 5.09 (*s*, 1H, CH), 6.66 (*t*, J = 7.5 Hz 1H), 6.70 (*d*, J = 7.5 Hz, 1H), 6.91 (*dt*, J = 2 and 8.0 Hz, 1H), 7.11 (*t*, J = 7.5 Hz, 2H), 7.35 (*t*, J = 7.8 Hz, 4H), 7.69 (*d*, J = 2 and 7.5 Hz, 1H), 7.81 (*d*, J = 7.8 Hz, 4H), 12.96 (*s*, 1H), 13.62 (*bs*, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-d6) *d* ppm: 12.68, 29.31, 102.42, 120.44, 123.70, 123.64, 125.43, 129.50, 130.25, 131.19, 136.23, 139.24, 145.19, 151.84, 157.99; HRMS *m*/*z* Calcd. for C<sub>27</sub>H<sub>24</sub>N<sub>4</sub>O<sub>3</sub> [M + H]: 452.18, Found: C<sub>27</sub>H<sub>24</sub>N<sub>4</sub>O<sub>3</sub> [M + H]: 452.1836.

The spectral data of as-synthesized bispyrozolone derivatives is well matched with reported compounds.

## 4. CONCLUSION

One pot synthesis of bispyrozolone derivatives has been performed using Cu–ZnO nanomaterial. It is found that, our nanocrystalline Cu–ZnO sample worked as a green and recyclable catalyst with enhanced yield of product within short time. We speculate that nanocrystalline Cu–ZnO will become an alternative and efficient catalyst for heterogeneous organic Tandem Knoevenagel/Michael reaction. The as-synthesized catalyst is environment friendly. **Acknowledgment:** Santosh Shinde is indebted to Council of Scientific and Industrial Research (CSIR), Delhi for financial support to this work. He is also thankful to the Principal of Radhabai Kale Mahila Mahavidyalaya, Ahmednagar for providing necessary facilities. Dr. Kaluram Kanade is very much thankful to the management of Rayat Shikshan Sanstha, Satara for supporting this research work.

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