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Green and efficient synthesis of novel bispyrazoles through a tandem Knoevenagel and Michael type reaction using nanowire zinc oxide as a powerful and recyclable catalyst

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Abstract: Zinc oxide nanowires (ZnO NWs) were prepared and characterized by scanning electron microscopy, powder X-ray diffraction, and transmission electron microscopy analyses. ZnO NWs were then employed as heterogeneous and recyclable catalyst for green synthesis of some new and known bispyrazole derivatives through a tandem Knoevenagel and Michael type addition reaction of aromatic aldehyde and pyrazolone. The synthetic method is operationally simple and affords product with high yields in short reaction times.

Key words: Zinc oxide nanowire, bispyrazole, aldehyde, green synthesis, nanocatalyst

1. Introduction

The discovery of new synthetic strategies to facilitate the efficient and green preparation of organic compounds is a vital issue of research in modern organic chemistry.[1−3] During the past decade, many attempts have been made to approach this aim,[4−7] which frequently focused on the preparation of organic compounds via one-pot multicomponent reactions.[8,9] Among the categories of nanoscience, nanocatalysis has an important part that has recently gained much attention from chemists. Nanocatalysts have distinguishing features compared to the bulk ones. For example, nanosized systems dramatically increase the contact between reactants and catalysts.[10] Among safe and environmentally friendly nanomaterials, ZnO nanomaterials have emerged as safe and efficient catalysts in organic reactions.[11−13] Replacement of toxic organic solvents by safe and clean ones is another effective way to prevent waste production in chemical reactions.[14−16]

Pharmaceutically, pyrazoles are small di-aza heterocyclic compounds that have a wide domain of approved biological activity, such as antianxiety, antipyretic, analgesic, and anti-inflammatory properties.[17−20] In regard to this background, synthesis of pyrazole derivatives has attracted considerable interest among some organic and pharmaceutical chemists. So far, several synthetic routes to bispyrazoles have been presented in the literature. In recent studies, some research groups focused on catalyzed synthesis of bispyrazoles in which aromatic aldehydes condense with pyrazolones in various conditions.[21−30] Despite the significant synthetic potential and ecological advantages, some of the present methods suffer from drawbacks including long reaction times, low product yield, and use of extra tools and unrecyclable catalysts. Above all, herein, we wish to report a convenient, green, and efficient approach to 4,4′-(arylmethylene)bis(1*H*-pyrazol-5-ol)s syntheses using recyclable ZnO nanowires in aqueous media.

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2. Results and discussion

ZnO nanowire was synthesized and characterized by X-ray diffraction (XRD) pattern and scanning electron microscopy (SEM). The morphology of the ZnO nanowires was studied by scanning electron microscopy (SEM). Figure 1 shows the typical SEM image of ZnO nanowires synthesized by the solvothermal method. The ZnO nanowires have a diameter of about 20 nm and a length of a few micrometers.

The XRD spectrum of the ZnO nanowires is shown in Figure 2. ZnO nanowires exhibited prominent (100), (002), and (101) peaks corresponding to a ZnO wurtzite structure.[31]

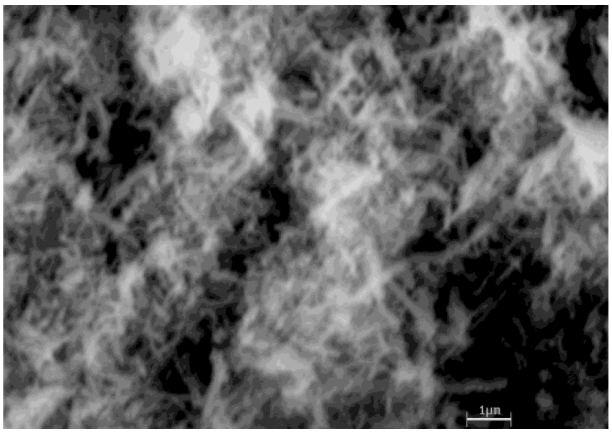


Figure 1. Scanning electron microscopy of ZnO nanowires.

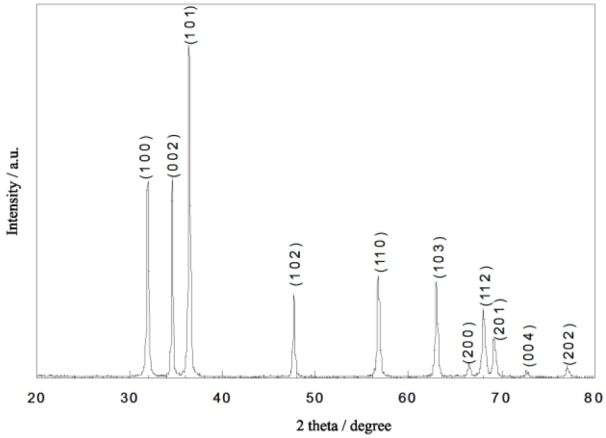


Figure 2. X-ray diffraction spectra of ZnO nanowires.

Furthermore, transmission electron microscopy (TEM) analysis was performed for detailed characterization of the ZnO NWs' structure (Figure 3). The TEM image reveals that the ZnO nanowire has a homogeneous diameter size of about 20 nm that does not vary significantly along the wire length.

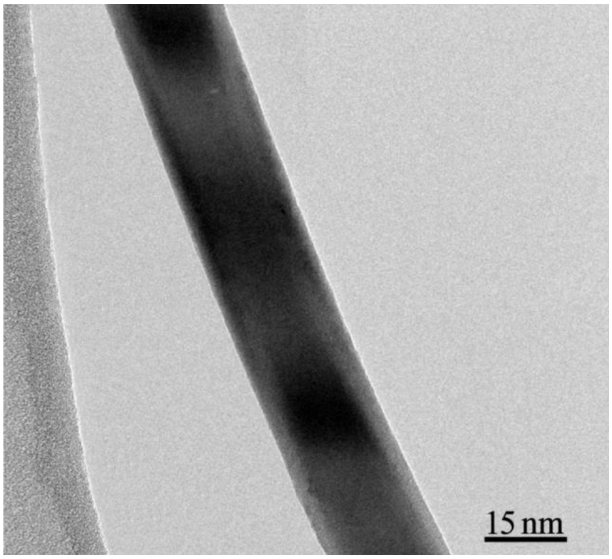
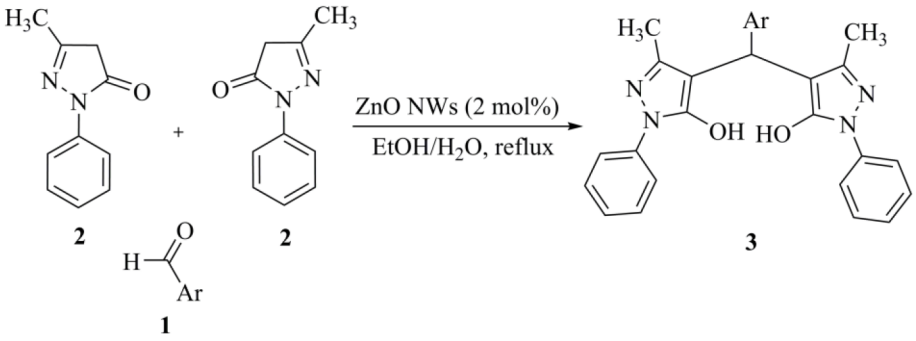


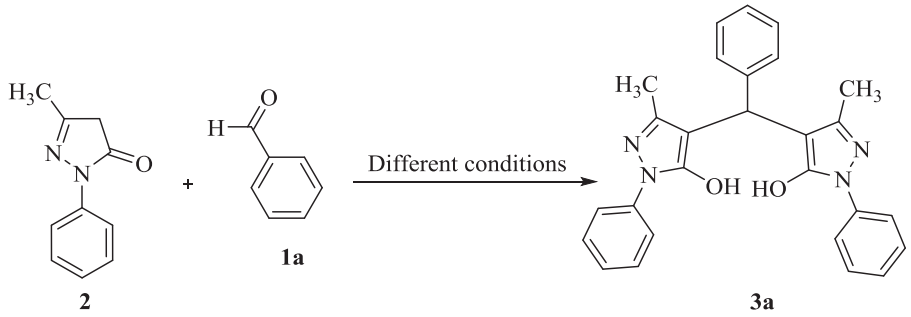
Figure 3. TEM image of the ZnO nanowires grown by solvothermal synthesis method.

In continuation of our previous studies on development of green synthetic methodologies for the preparation of organic compounds,[32–35] herein we report a new green condition for the synthesis of some novel and known 4,4′-(arylmethylene)bis(1*H*-pyrazol-5-ol) **3** from the condensation reaction of aromatic aldehydes **1** with pyrazolone **2** in the presence of catalytic amounts of ZnO NWs (Scheme 1).

To optimize the reaction conditions, the treatment of benzaldehyde **1a** with **2** was selected as a model (Scheme 2).



Scheme 1. Synthesis of bispyrazoles by employing ZnO NWs.



Scheme 2. The model reaction to optimize the conditions.

From the perspective of green chemistry, an equal mixture of H_2O/EtOH (1:1) was used as the reaction medium. It should be noted that reaction progress in absolute water and/or absolute ethanol was not better than that of the mixture of these solvents. From the different ratios of H_2O/EtOH mixtures, H_2O/EtOH (1:1) mixture was considered the most effective ratio. Initially, the model reaction was established under reflux in an equal mixture of H_2O/EtOH (1:1) in the presence of various amounts of ZnO NWs. This reaction was firstly examined in the absence of catalyst that did not show any appreciable progress even after 120 min. Upon screening, the results clearly showed that the reaction proceeded efficiently when 2 mol% of ZnO NWs were added. Moreover, increasing the catalyst amount did not improve the results (Figure 4).

The reaction was also established at room temperature in an equal mixture of H_2O/EtOH (1:1) in the presence of ZnO NWs (2 mol%); however, the results showed that at room temperature no reaction took place even after 120 min. Afterwards, the feasibility of the reaction was further studied with various aromatic aldehydes under optimized conditions, which successfully led to products with high yields in short reaction times. The results are listed in Table 1.

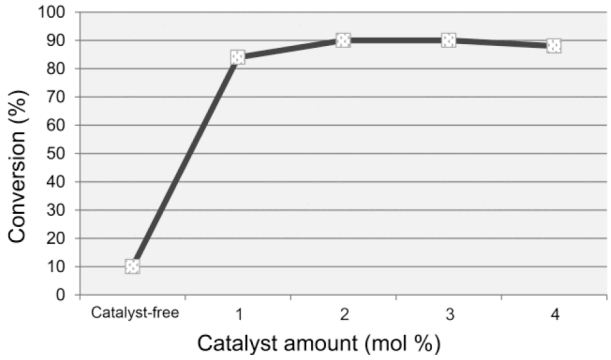
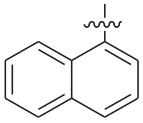
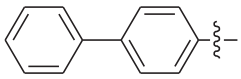
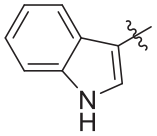


Figure 4. The effect of catalyst amount on synthesis of compound **3a**. Reaction time: 20 min.

Table 1. Synthesis of bispyrazoles **3** using ZnO NWs (2 mol%).

Entry	Ar	Time (min)	Yield[a] (%)	Mp (°C)/(Reported)
3a	C_6H_5	20	90	162–164 (171–172) [21]
3b	2,4-$(OMe)_2$-C_6H_3	20	88	190–192 (-)
3c	3-OEt-4-OH-C_6H_3	30	86	212–213 (-)
3d		30	90	228–230 (-)
3e		15	90	218–220 (-)
3f		30	85	242–244 (-)
3g	2,4-$(Cl)_2$-C_6H_3	20	86	228–230 (227–229) [21]
3h	3-NO_2-C_6H_5	15	90	161–163 (151–153) [21]
3i	4-NO_2-C_6H_5	15	90	226–228 (225–227) [21]
3j	4-Me-C_6H_5	30	88	203–205 (202–204) [21]
3k	2-Cl-C_6H_5	15	90	238–240 (235–237) [21]
3l	4-MeO-C_6H_5	20	84	165–167 (176–177) [21]
3m	3-Br-C_6H_5	30	90	174–176 (173–175) [21]

[a]Isolated yields.

As can be seen from Table 1, the nature of the substituents on the aromatic ring showed no important effects in terms of reaction time or product yields under the optimized conditions mentioned above. In fact, the aromatic aldehyde bearing both electron donating/withdrawing groups reacted well with compound **2**. When the aliphatic aldehydes were replaced, however, the reactions were unsuccessful. It seems that the problem in the case of aliphatic ones is likely to be enolyzed.

In the final study, the recyclability of the ZnO NWs was investigated upon the synthesis of model compound **3a**. In this case, after being recovered, the catalyst was reused for the next reaction and it was

observed that the system did not show an apparent loss in catalytic activity of the ZnO NWs during 4 cycles (Figure 5).

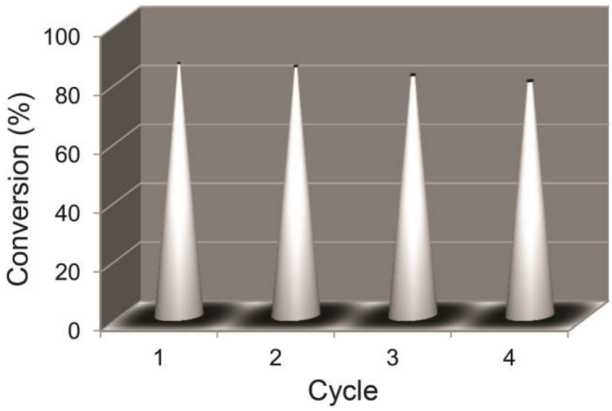


Figure 5. Recyclability of the catalyst. Reaction time: 20 min.

To compare the present method with ones previously reported in the literature, Table 2 provides brief data. According to the results summarized in Table 2, the merits of the presented method are confirmable due to its efficiency in the generation of desired compounds in higher yield and shorter reaction time than the other ones.

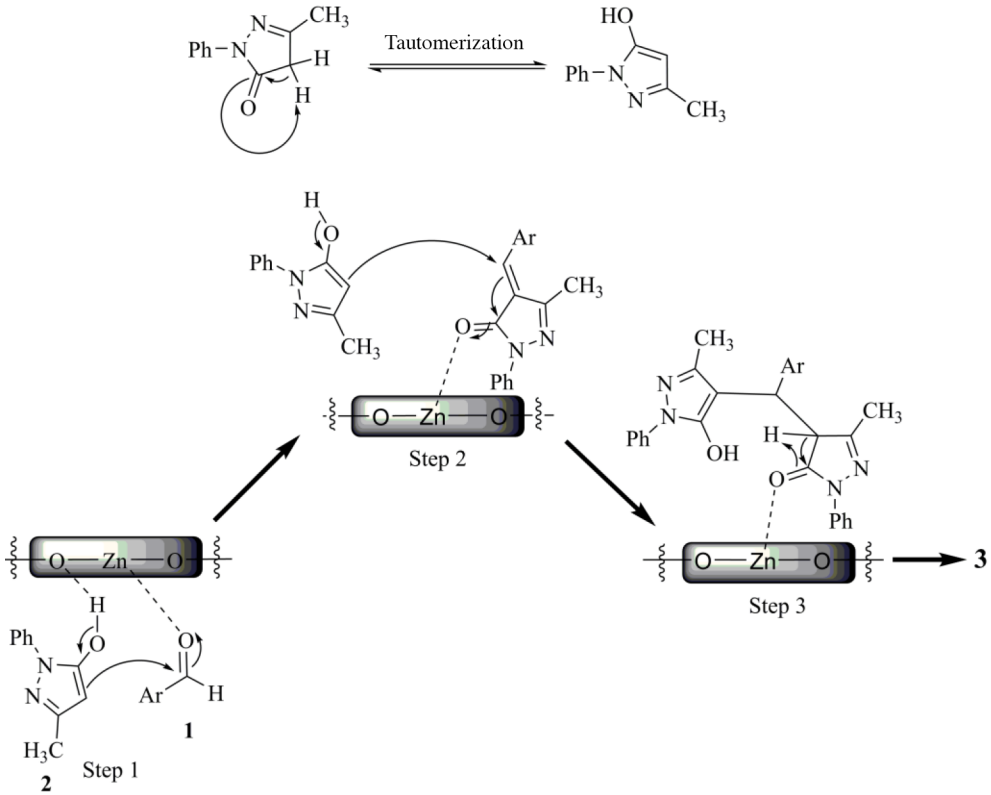
Table 2. Comparison of present work with other methods reported in the literature for synthesis of **3a**.

Entry	Conditions	Time (min)	Yield (%) [Lit.]
1	SBSSA[a] (0.1 g), EtOH, Reflux	120	80 [21]
2	SASPSPE[b] (0.1 g), EtOH, Reflux	180	90 [22]
3	Cellulose sulfuric acid (0.2 g), H_2O/EtOH, Reflux	120	74 [23]
5	Electrolysis, EtOH, NaBr (0.1 g), 20 °C	33	82 [24]
4	[Dsim]$AlCl_4^c$ (1 mol%), 50 °C	60	86 [25]
6	Sodium dodecyl sulfate (5 mol%), H_2O, Reflux	60	86.8 [26]
7	ZnO NWs (2 mol%), H_2O/EtOH, Reflux	20	90[d]

[a] Silica-bonded S-sulfonic acid. [b] Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester. [c] 1,3-disulfonic acid imidazolium tetrachloroaluminate. [d] Present work.

A sequence of reactions such as Knoevenagel condensation followed by Michael type addition takes place during the formation of the product **3**. The proposed mechanism for the ZnO catalyzed synthesis of bispyrazols **3** is depicted in Scheme 3. In the first step, the reaction undergoes the Knoevenagel condensation between aldehyde **1** and pyrazolone **2** to generate α,β-unsaturated adduct. Subsequent 1,4-addition of **2** on α,β-unsaturated adduct followed by [1,3]-sigmatropic proton shift led to the formation of the target molecule **3**.

In conclusion, we have demonstrated the efficiency of ZnO NWs as heterogeneous catalyst for the condensation reaction between aromatic aldehyde and 3-methyl-1-phenyl-5-pyrazolone in a molar ratio of 1:2, respectively. The major advantages of the present method are its excellent yields, short reaction times, simple experimental procedure, and low catalyst loading, and the recyclability of the ZnO NWs, which make this method more attractive and in accordance with sustainable chemistry.



Scheme 3. A plausible reaction mechanism for ZnO catalyzed synthesis of **3**.

3. Experimental

Chemicals were purchased from Merck and Aldrich chemical companies. SEM studies of the nanostructures were carried out with a JEOL JEM 3010 instrument operating at an accelerating voltage of 300 kV. XRD (D_8, Advance, Bruker, AXS) patterns were obtained for characterization of the heterogeneous catalyst. TEM study of the nanostructures was carried out with a JEOL JEM 3010 instrument operating at an accelerating voltage of 300 kV. Melting points were measured on an electro thermal KSB1N apparatus. IR spectra were recorded in the matrix of KBr with a JASCO FT-IR-680 plus spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a FT-NMR Bruker AVANCE UltraShield Spectrometer at 300.13 (400.13 and 250.13 MHz for a few products) and 76.46 MHz (100.62 and 62.6 MHz for a few products), respectively, in DMSO-d_6 as the solvent in the presence of tetra methyl silane as the internal standard. TLC was performed on TLC-grade silica gel-G/UV 254 nm plates. All of the products were isolated, purified, and deduced from their elemental analyses (C, H, N), IR, ^{1}H NMR, and ^{13}C NMR spectral data.

3.1. Preparation of ZnO NWs

ZnO nanowires were obtained by a slight modification of the method reported in the literature.[36,37] First 0.315 g (1.43 mmol) of zinc acetate dihydrate [$Zn(OAc)_2.2H_2O$] was dissolved in 66 mL of ethanol and then 1.67 g (41 mmol) of NaOH was added followed by stirring for 1.5 h to make it dissolve at room temperature. The resulting cloudy solution was sealed in a 70 mL Teflon-lined stainless-steel autoclave and heated at 120 °C for 24 h. The autoclave was then allowed to cool down to room temperature. White precipitate was collected by

centrifugation and washed with water and ethanol several times until the washing solution was free of NaOH. The average diameter of the ZnO nanowires is ∼20 nm with lengths going up to a few micrometers.

3.2. Synthesis of 4,4′-(arylmethylene)bis(1H-pyrazol-5-ol) using ZnO NWs

A solution of the aromatic aldehyde **1** (1 mmol), the pyrazolone **2** (2 mmol), and ZnO NWs (2 mol%) in $EtOH/H_2O$ (1:1, 10 mL) was stirred under reflux for a stipulated time. The progress of the reaction was checked by TLC. After completion, the reaction mixture was cooled to room temperature and solvent was evaporated under reduced pressure. The precipitate was dried and dissolved in hot EtOH to separate the catalyst. The product **3** was obtained after recrystallization from EtOH and no further purification was needed.

3.3. Representative spectral data

4,4′-(Phenylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (**3a**): Light yellow crystals; FT-IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3424 (OH), 3062 (sp^2 C–H), 2917 (sp^3 C–H), 1598 (C=N), 1498 (C=C), 1284 (Ar–O), 755, 692 (monosub. Ph); ^{1}H NMR (400.13 MHz, DMSO-d_6) δ (ppm): 13.96 (s, 1H, OH), 12.39 (s, 1H, OH), 7.71 (d, J = 8.4 Hz, 4H, aromatic CH), 7.45 (t, J = 8.4 Hz, 4H, aromatic CH), 7.31–7.24 (m, 6H, aromatic CH), 7.20–7.17 (m, 1H, aromatic CH), 5.00 (s, 1H, CH), 2.33 (s, 6H, $2CH_3$); ^{13}C NMR (100.62 MHz, DMSO-d_6) δ (ppm): 157.6, 146.4, 140.7, 136.9, 128.8, 128.3, 127.1, 126.4, 126.2, 121.3, 105.7, 33.6, 11.5; Anal. calcd. for $C_{27}H_{24}N_4O_2$: C, 74.29; H, 5.54; N, 12.84; found: C, 74.31; H, 5.50; N, 12.82%.

4,4′-((2,4-Dimethoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (**3b**): Yellow crystals; FT-IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3428 (OH), 2996 (sp^2 C–H), 2958 (sp^3 C–H), 1613 (C=N), 1503, 1460 (C=C), 1294, 1209 (Ar–O), 1122, 1041 (C–O); ^{1}H NMR (300.13 MHz, DMSO-d_6) δ (ppm): 14.35 (s, 1H, OH), 12.38 (s, 1H, OH), 7.69 (d, J = 7.8 Hz, 4H, aromatic CH), 7.50–7.39 (m, 5H, aromatic CH), 7.22 (t, J = 7.2 Hz, 2H, aromatic CH), 6.46 (t, J = 8.4 Hz, 2H, aromatic CH), 5.09 (s, 1H, CH), 3.79 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 2.26 (s, 6H, $2CH_3$); ^{13}C NMR (76.46 MHz, DMSO-d_6) δ (ppm): 158.8, 156.7, 146.1, 137.6, 137.4, 137.3, 137.1, 136.7, 133.6, 131.9, 128.8, 125.4, 122.9, 120.5, 104.1, 98.2, 55.4, 55.0, 26.9, 11.6; Anal. calcd. for $C_{29}H_{28}N_4O_4$: C, 70.15; H, 5.68; N, 11.28; found: C, 70.22; H, 5.62; N, 11.25%.

4,4′-((3-Ethoxy-4-hydroxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (**3c**): Chocolate crystals; FT-IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3420, 3219 (OH), 2985 (sp^2 C–H), 2927 (sp^3 C–H), 1596 (C=N), 1498 (C=C), 1275, 1214 (Ar–O), 1126, 1043 (C–O); ^{1}H NMR (300.13 MHz, DMSO-d_6) δ (ppm): 13.97 (s, 1H, OH), 12.36 (s, 1H, OH), 8.67 (s, 1H, OH), 7.69 (d, J = 8.1 Hz, 4H, aromatic CH), 7.42 (t, J = 7.8 Hz, 4H, aromatic CH), 7.22 (t, J = 7.2 Hz, 2H, aromatic CH), 6.82 (s, 1H, aromatic CH), 6.66 (s, 2H, aromatic CH) 4.82 (s, 1H, CH), 3.90 (q, J = 6.9 Hz, 2H, CH_2), 2.29 (s, 6H, $2CH_3$), 1.25 (t, J = 6.9 Hz, 3H, CH_3). ^{13}C NMR (76.46 MHz, DMSO-d_6) δ (ppm): 146.1, 145.1, 142.6, 137.3, 137.0, 133.1, 131.6, 128.9, 125.5, 120.5, 119.7, 115.2, 113.4, 63.9, 32.7, 14.7, 11.6; Anal. calcd. for $C_{29}H_{28}N_4O_4$: C, 70.15; H, 5.68; N, 11.28; found: C, 70.19; H, 5.57; N, 11.26%.

4,4′-(Naphthalen-1-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (**3d**): Navajo white crystals; FT-IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3419 (OH), 3062 (sp^2 C–H), 2922 (sp^3 C–H), 1608 (C=N), 1542, 1497 (C=C), 1132 (Ar–O); ^{1}H NMR (300.13 MHz, DMSO-d_6) δ (ppm): 13.15 (s, 1H, OH), 12.19 (s, 1H, OH), 8.00–7.90 (m, 2H, aromatic CH), 7.81–7.70 (m, 6H, aromatic CH), 7.53–7.41 (m, 7H, aromatic CH), 7.15–7.25 (m, 2H, aromatic CH), 5.61 (s, 1H, CH), 2.25 (s, 6H, $2CH_3$); ^{13}C NMR (76.46 MHz, DMSO-d_6) δ (ppm): 146.0, 144.1, 140.6,

137.3, 136.7, 133.6, 130.7, 128.8, 128.7, 127.0, 125.9, 125.7, 125.3, 125.2, 123.5, 119.9, 105.6, 30.9, 11.9, 11.8; Anal. calcd. for $C_{31}H_{26}N_4O_2$: C, 76.52; H, 5.39; N, 11.51; found: C, 76.57; H, 5.33; N, 11.48%.

4,4′-([1,1'-biphenyl]-4-ylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (**3e**): Navajo white crystals; FT-IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3444 (OH), 3026 (sp^2 C–H), 2922 (sp^3 C–H), 1599 (C=N), 1580, 1499 (C=C), 1294 (Ar–O), 818 (para-disub. Ph); ^{1}H NMR (300.13 MHz, DMSO-d_6) δ (ppm): 14.05 (s, 1H, OH), 12.48 (s, 1H, OH), 7.74 (d, J = 7.8 Hz, 4H, aromatic CH), 7.62–7.55 (m, 4H, aromatic CH), 7.46–7.34 (m, 9H, aromatic CH), 7.23 (t, J = 7.2 Hz, 2H, aromatic CH), 5.01 (s, 1H, CH), 2.35 (s, 6H, $2CH_3$); ^{13}C NMR (76.46 MHz, DMSO-d_6) δ (ppm): 146.3, 141.5, 140.0, 137.9, 137.4, 137.3, 128.9, 128.8, 127.8, 127.1, 126.5, 125.5, 120.5, 104.9, 104.6, 32.8, 11.6; Anal. calcd. for $C_{33}H_{28}N_4O_2$: C, 77.32; H, 5.51; N, 10.93; found: C, 77.38; H, 5.43; N, 10.84%.

4,4′-((1H-indol-3-yl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (**3f**): Yellow crystals; mp: 242–244 °C; FT-IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3470 (OH, NH), 3042 (sp^2 C–H), 2920 (sp^3 C–H), 1618 (C=N), 1540, 1488 (C=C), 1136 (Ar–O); ^{1}H NMR (400.13 MHz, DMSO-d_6) δ (ppm): 12.65 (s, 2H, 2OH), 9.85 (s, 1H, NH), 8.13–8.11 (m, 2H, aromatic CH), 8.06 (s, 1H, aromatic CH), 8.05–8.01 (m, 3H, aromatic CH), 7.60–7.58 (m, 1H, aromatic CH), 7.42 (t, J = 7.6 Hz, 4H, aromatic CH), 7.32–7.29 (m, 3H, aromatic CH), 7.15 (t, J = 7.6 Hz, 1H, aromatic CH), 3.49 (s, 1H, CH), 2.39 (s, 6H, $2CH_3$); ^{13}C NMR (100.62 MHz, DMSO-d_6) δ (ppm): 162.7, 150.8, 138.9, 138.2, 136.9, 136.4, 128.6, 128.1, 123.8, 123.4, 122.0, 118.5, 118.0, 112.8, 112.2, 18.5, 12.9; Anal. calcd. for $C_{29}H_{25}N_5O_2$: C, 73.25; H, 5.30; N, 14.73; found: C, 73.31; H, 5.23; N, 14.66%.

4,4′-((2,4-Dichlorophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (**3g**): Bisque crystals, mp: 228–229 °C; FT-IR (KBr) ($\bar{\upsilon}_{max}$, cm^{-1}): 3420 (OH), 3057 (sp^2 C–H), 2920 (sp^3 C–H), 1597 (C=N), 1572, 1500, 1470 (C=C), 1189 (Ar–O); ^{1}H NMR (250.13 MHz, DMSO-d_6) δ (ppm): 13.95 (s, 1H, OH), 12.67 (s, 1H, OH), 7.72–7.65 (m, 5H, aromatic CH), 7.53 (d, J = 2.0 Hz, 1H, aromatic CH), 7.44–7.36 (m, 5H, aromatic CH), 7.22 (t, J = 7.2 Hz, 2H, aromatic CH), 5.05 (s, 1H, CH), 2.26 (s, 6H, $2CH_3$); ^{13}C NMR (62.89 MHz, DMSO-d_6) δ (ppm): 148.3, 147.1, 146.0, 137.3, 134.9, 128.8, 125.4, 120.5, 119.2, 111.6, 111.5, 104.9, 104.6, 31.7, 11.6; Anal. calcd. for $C_{27}H_{22}Cl_2N_4O_2$: C, 64.17; H, 4.39; N, 11.09; found: C, 64.20; H, 4.30; N, 10.98%.

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