

## Nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> as a highly efficient, green and recyclable catalyst for the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s

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### ABSTRACT

Nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> is used as a highly efficient, mild, green and recyclable nanomagnetite catalyst for the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) derivatives in solvent-free conditions. The condensation of 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one with aromatic aldehydes affords the title compounds in high yields and short reaction times. The nanocatalyst is reusable for seven times without significant loss of its catalytic activity.

**Keywords:** Nanomagnetite-Fe<sub>3</sub>O<sub>4</sub>, Nanomagnetite, 4,4'-(Arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol), 3-Methyl-1-phenyl-1H-pyrazol-5(4H)-one, Aromatic aldehyde.

### 1. Introduction

Green chemistry is the design, development and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment. It is an innovative, non-regulatory and economically driven approach toward sustainability [1]. Solvent-free technique is one of the green chemical protocols, and has different advantages [2]. For reasons of pollution and economy, solvent-free technique is of great importance that modernizes classical reactions making them to perform with higher yields in shorter reaction times, and increases selectivity. Moreover, scale-up is facilitated by application of solvent-free protocol, and products are purified easier in these conditions [2-6].

Nanocatalysts are considered to be a link between heterogeneous and homogeneous catalysis [7]. Nanomaterials prepare high specific surface area of the

active component, thus increase the interaction between catalyst support and reactants [8].

Moreover, higher surface area of nanocatalysts affords more active surface. Nevertheless, they easily agglomerate, and it is hard to separate them from the reaction mixture. Therefore, designing recoverable and well-dispersed catalysts is of importance. Along this line, magnetite nanoparticles (MNPs) could be introduced as recoverable and well-dispersed catalysts or supports because of their magnetic properties and large specific surface area [9-14]. They can be readily separated from the reaction mixture by a magnet for reuse.

Transition-metal catalyzed organic reactions often consume a minimum of reagents or auxiliaries and energy, and minimize waste; thus, they are in good agreement with the green chemistry principles [14].

4,4'-(Arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) derivatives are significant as they have various biological and pharmaceutical activities, such as antipyretic [15], antidepressant [16], antibacterial [17], anti-inflammatory [18] and gastric secretion stimulatory [19] properties. Despite wide application of these compounds, a few methods have been reported

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for their synthesis. These protocols include tandem Knoevenagel-Michael reaction in benzene solutions [20], application of Brønsted acidic catalysts [21-23], the use of piperidine in ethanolic solution [24], the use of poly(ethylene glycol)s media [25], application of sodium dodecyl sulfate [26] and nanosilica supported perchloric acid in aqueous media [27], and electrocatalytic synthesis [28]. It should be mentioned that most of the reported methods for preparation of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s are associated with one or more of the following disadvantages: (i) long reaction times, (ii) moderate yields, (iii) application of hazardous solvents, (iv) tedious workup procedures, and (v) harsh reaction conditions. Thus, introducing an efficient method for synthesis of the title compounds, which don't suffer the above drawbacks, is of importance.

In this paper, we report our results on the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s from 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one with aromatic aldehydes in the presence of catalytic amount of nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> under green and solvent-free conditions (Scheme 1).

## 2. Experimental

### 2.1. General

All chemicals were purchased from Fluka, Merck or Acros chemical companies. Nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> was prepared by the reported procedure [29], and characterized by TEM, FT-IR, XRD and VSM. All known compounds were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. The <sup>1</sup>HNMR (500 and 600 MHz) and <sup>13</sup>CNMR (125 and 150 MHz) were run on a Bruker Avance DPX, FT-NMR spectrometers.

### 2.2. General procedure for synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s

To a mixture of 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (0.35 g, 2 mmol) and aromatic aldehyde (1 mmol) in a test tube, was added nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> (0.0116 g, 0.05 mmol), and the resulting mixture was firstly stirred magnetically, and after solidification of the reaction mixture with a small rod, at 70°C. After

completion of the reaction, as monitored by TLC, warm absolute ethanol (5 mL) was added to the reaction mixture and stirred. The insoluble catalyst was easily collected by a magnet within 20-30 sec, washed by absolute ethanol and dried for reusing. Then, water (1 mL) was added to the residue solution of the reaction mixture, and allowed to stand for few minute. During this time, crystals of the product were formed which collected by filtration. In this work, the nanocatalyst was reused for seven times without significant loss of its catalytic activity.

### Selected spectral data

#### 4,4'-(2-Phenylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol) (1):

<sup>1</sup>HNMR (500 MHz, DMSO-d<sub>6</sub>): δ = 2.33 (s, 6H), 4.88 (s, 1H), 7.07 (m, 1H), 7.18 (m, 6H), 7.44 (t, *J* = 7.5 Hz, 4H), 7.58 (d, *J* = 7.8 Hz, 4H) ppm. <sup>13</sup>CNMR (125 MHz, DMSO-d<sub>6</sub>): δ = 12.0, 33.5, 121.4, 126.2, 126.8, 127.6, 128.2, 129.1, 137.3, 142.9, 146.1 ppm.

#### 4,4'-((4-Nitrophenyl)methylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol) (2):

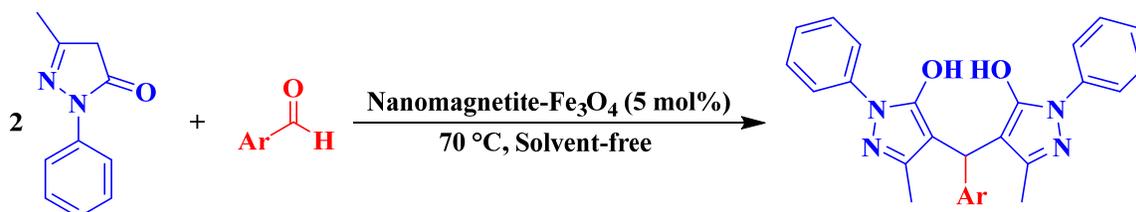
<sup>1</sup>HNMR (500 MHz, DMSO-d<sub>6</sub>): δ = 2.35 (s, 6H), 5.13 (s, 1H), 7.25-7.27 (m, 2H), 7.43-7.46 (t, *J* = 7.0 Hz, 4H), 7.51-7.53 (d, *J* = 8.0 Hz, 2H), 7.70-7.72 (d, *J* = 8.0 Hz, 4H), 8.16-8.18 (d, *J* = 8.0 Hz, 2H), 12.64 (s, 1H, OH), 13.86 (s, 1H, OH) ppm. <sup>13</sup>CNMR (125 MHz, DMSO-d<sub>6</sub>): δ = 12.4, 19.4, 34.0, 56.9, 121.5, 124.2, 126.6, 129.5, 129.8, 146.8, 147.1, 151.2 ppm.

#### 4-(Bis(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methyl)benzotrile (5):

<sup>1</sup>HNMR (600 MHz, DMSO-d<sub>6</sub>): δ = 2.32 (s, 6H), 5.05 (s, 1H), 7.25 (d, *J* = 7.16 Hz, 2H), 7.42-7.45 (m, 6H), 7.68 (d, *J* = 7.88 Hz, 4H), 7.75 (d, *J* = 8.32 Hz, 2H), 12.46 (s, 1H, OH), 13.86 (s, 1H, OH) ppm. <sup>13</sup>CNMR (150 MHz, DMSO-d<sub>6</sub>): δ = 12.1, 33.2, 108.7, 118.9, 120.5, 128.3, 128.9, 132.0, 139.3, 142.4, 148.1 ppm.

#### 4,4'-(*p*-Tolylmethylene)bis-(3-methyl-1-phenyl-1*H*-pyrazol-5-ol) (6):

<sup>1</sup>HNMR (500 MHz, DMSO-d<sub>6</sub>): δ = 2.24 (s, 3H), 2.31 (s, 6H), 4.91 (s, 1H), 7.08-7.71 (m, 14H), 12.40 (s, 1H, OH), 13.92 (s, 1H, OH) ppm. <sup>13</sup>CNMR (125 MHz, DMSO-d<sub>6</sub>): δ 12.5, 21.4, 33.6, 40.9, 121.4, 126.4, 127.9, 129.5, 129.8, 135.7, 140.0, 147.1 ppm.



**Scheme 1.** Preparation of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s catalyzed by nanomagnetite-Fe<sub>3</sub>O<sub>4</sub>.

**4,4'-((3-Bromophenyl)methylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (8):**

<sup>1</sup>HNMR (500 MHz, DMSO-d<sub>6</sub>): δ = 2.30 (s, 6H), 4.89 (s, 1H), 6.82-7.71 (m, 14H), 12.40 (s, 1H, OH), 13.92 (s, 1H, OH) ppm. <sup>13</sup>CNMR (125 MHz, DMSO-d<sub>6</sub>): δ = 9.9, 14.3, 117.9, 123.6, 125.4, 127.2, 127.7, 128.3, 128.7, 129.7, 132.4, 133.6, 140.4, 145.9, 154.4 ppm.

**4,4'-((2-Bromophenyl)methylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (9):**

<sup>1</sup>HNMR (600 MHz, DMSO-d<sub>6</sub>): δ = 2.28 (s, 6H), 5.10 (s, 1H), 7.14 (t, *J* = 7.64 Hz, 1H), 7.24 (t, *J* = 7.24 Hz, 2H), 7.33 (t, *J* = 7.88 Hz, 1H), 7.43 (t, *J* = 7.96 Hz, 4H), 7.56-7.57 (d, *J* = 7.16 Hz, 1H), 7.68 (d, *J* = 7.92 Hz, 4H), 7.81 (d, *J* = 7.08 Hz, 1H), 12.43 (s, 1H, OH), 13.72 (s, 1H, OH) ppm. <sup>13</sup>CNMR (150 MHz, DMSO-d<sub>6</sub>): δ = 12.0, 34.2, 120.5, 127.4, 128.3, 128.8, 130.4, 132.7, 141.0 ppm.

**4,4'-((4-Fluorophenyl)methylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (13):**

<sup>1</sup>HNMR (600 MHz, DMSO-d<sub>6</sub>): δ = 2.31 (s, 6H), 5.34 (s, 1H), 7.19-7.38 (m, 4H), 7.40-7.45 (m, 5H), 7.68-7.70 (m, 5H), 11.44 (s, 1H, OH), 13.93 (s, 1H, OH) ppm. <sup>13</sup>CNMR (150 MHz, DMSO-d<sub>6</sub>): δ = 12.3, 32.4, 114.5, 114.7, 117.9, 120.5, 124.8, 125.5, 128.7, 128.8, 129.0, 138.1, 146.1, 159.4, 161.8 ppm.

**4,4'-((4-Chloro-3-nitrophenyl)methylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (14):**

<sup>1</sup>HNMR (600 MHz, DMSO-d<sub>6</sub>): δ = 2.02 (s, 6H), 5.09 (s, 1H), 7.25 (t, *J* = 7.30 Hz, 2H), 7.44 (t, *J* = 7.76 Hz, 4H), 7.57 (d, *J* = 8.36 Hz, 1H), 7.68 (m, 5H), 7.85 (s, 1H), 12.47 (s, 1H, OH), 13.87 (s, 1H, OH) ppm. <sup>13</sup>CNMR (150 MHz, DMSO-d<sub>6</sub>): δ = 12.4, 32.5, 118.9, 120.5, 125.5, 128.8, 129.5, 130.8, 132.7, 141.6, 146.1 ppm.

**4,4'-(2-Furylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (15):**

<sup>1</sup>HNMR (500 MHz, DMSO-d<sub>6</sub>): δ = 2.21 (s, 6H), 4.87 (s, 1H), 6.14 (s, 1H), 6.48 (s, 1H), 7.37 (t, 2H), 7.44 (t, 4H), 7.53 (s, 1H), 7.78 (d, 4H) ppm. <sup>13</sup>CNMR (125 MHz, DMSO-d<sub>6</sub>): δ = 12.2, 28.6, 106.4, 110.2, 121.6, 126.4, 129.9, 142.4, 146.9, 154.4 ppm.

**4,4',4'',4'''-(1,4-phenylenebis(methanetriyl))-tetrakis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (17):**

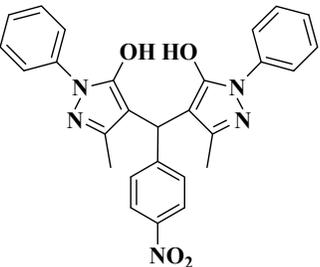
<sup>1</sup>HNMR (500 MHz, DMSO-d<sub>6</sub>): δ = 2.16 (s, 12H), 4.71 (s, 2H), 7.00-7.03 (t, *J* = 7.5 Hz, 4H), 7.06 (s, 4H), 7.17-7.21 (t, *J* = 8.0 Hz, 8H), 7.55-7.57 (d, *J* = 8.0 Hz, 8H), 13.40 (s, 4H, OH) ppm. <sup>13</sup>CNMR (125 MHz, DMSO-d<sub>6</sub>): δ = 12.2, 33.8, 120.6, 121.5, 125.9, 127.5, 129.0, 131.1, 137.0, 139.2, 146.7 ppm.

**3. Results and Discussion****3.1. Characterization of the catalyst**

After the full characterization of nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffractometer (XRD) and vibrating sample magnetometer (VSM) (see Supplementary Information, Figures S1-S4), we examined its catalytic activity to promote the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s. For this purpose, as a model reaction, a mixture of 3-methyl-1-phenyl-1H-pyrazol-5(4H)-one (2 mmol) and 4-nitrobenzaldehyde (1 mmol) was stirred in the presence of different amounts of nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> at range of 50 to 80°C in the absence of solvent; the respective results are summarized in Table 1.

As it can be seen in Table 1, 5 mol% of the catalyst was sufficient to promote the reaction efficiently at 70°C; in these conditions, the corresponding 4,4'-

**Table 1.** Effect of the catalyst amount and temperature on the reaction between 1-phenyl-3-methylpyrazol-5-one (2 mmol) with 4-nitrobenzaldehyde (1 mmol).

Product	Entry	Catalyst amount (mol%)	Temp. (°C)	Time (min)	Yield (%) <sup>a</sup>
	1	-	70	25	85
	2	2.5	70	7	92
	3	5	70	4	95
	4	7.5	70	5	85
	5	5	50	15	87
	6	5	60	9	89
	7	5	80	4	92

<sup>a</sup>Isolated yield.

(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol) was obtained in 95% in 4 min (Table 1, entry 2). The reaction was also examined under catalyst-free conditions in which the product was obtained in 85% after 25 min (Table 1, entry 1); increasing the reaction time didn't improve the yield. In order to assess the efficacy and the generality of the nanomagnetite catalyst, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one was reacted with electronically and structurally diverse arylaldehydes (benzaldehyde, arylaldehyde possessing electron-withdrawing substituents, electron-donating

substituents and halogens on their aromatic rings, bis-aldehydes and heteroaromatic aldehydes), under the optimized reaction conditions; the results are displayed in Table 2. As it is shown in Table 2, all reactions proceeded efficiently to afford the corresponding 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s in high yields and in short reaction times. Thus, nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> was highly efficient and general catalyst to promote a useful organic reaction, i.e. the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s.

**Table 2.** The solvent-free synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s from 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one and arylaldehydes using nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> at 70 °C.

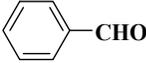
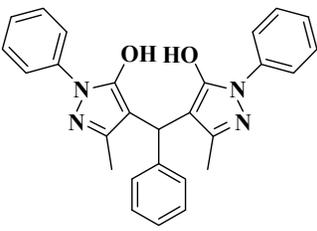
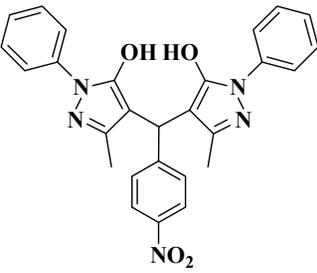
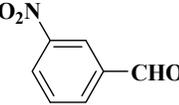
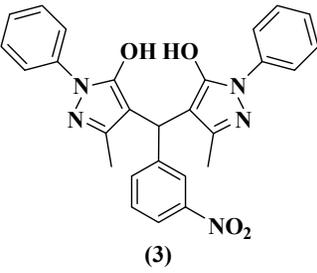
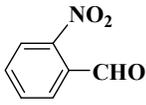
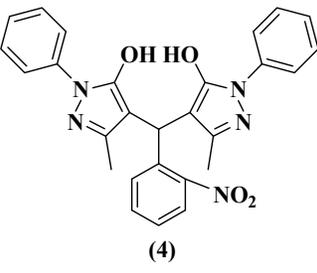
Aldehyde	Product	Time (min)	Yield (%) <sup>a</sup>	m.p. (°C)		Ref.
				Found	Reported	
	 (1)	7	90	168-170	171-172	[26]
	 (2)	4	95	228-230	230-232	[26]
	 (3)	5	92	146-148	149-150	[26]
	 (4)	7	87	221-223	221-223	[21]

Table 2. (Continued).

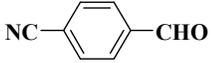
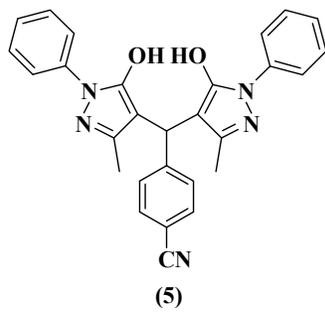
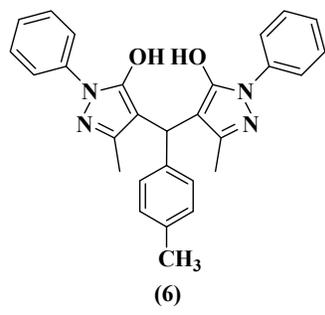
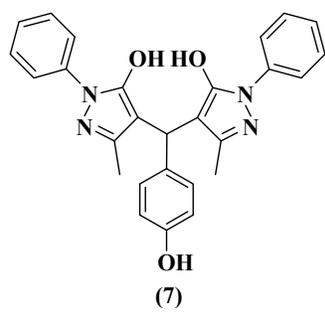
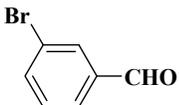
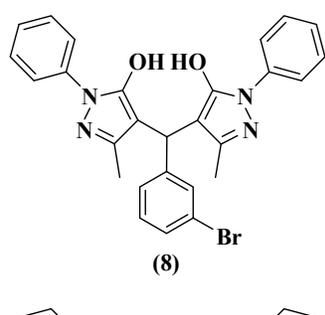
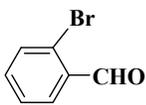
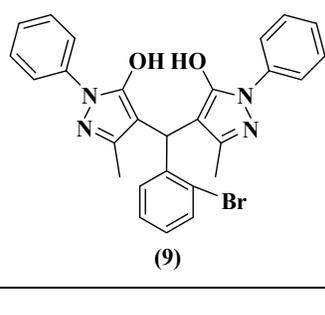
	 <p>(5)</p>	6	88	215-217	214-219	[23]
	 <p>(6)</p>	4	93	202-204	203-205	[21]
	 <p>(7)</p>	9	85	150-151	152-153	[26]
	 <p>(8)</p>	6	88	172-174	173-175	[22]
	 <p>(9)</p>	7	85	248-250	248-250	[23]

Table 2. (Continued).

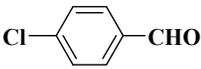
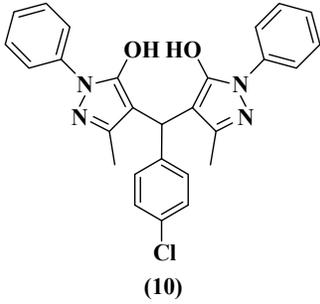
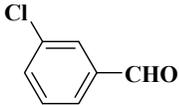
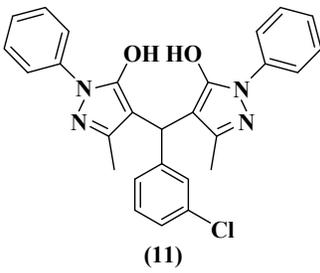
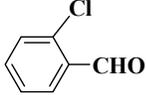
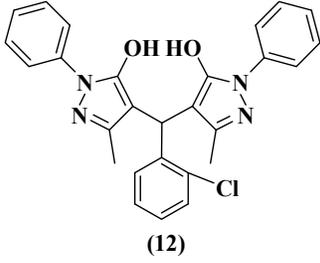
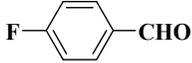
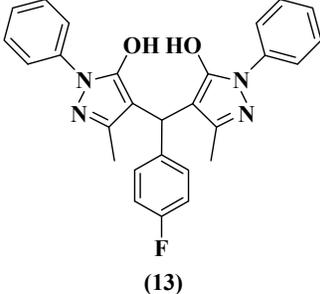
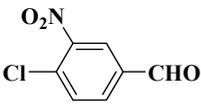
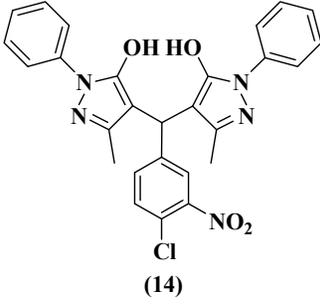
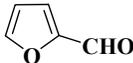
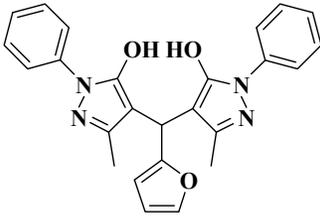
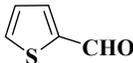
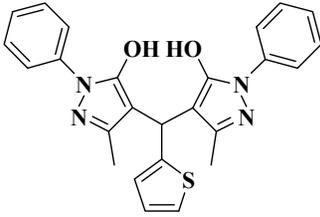
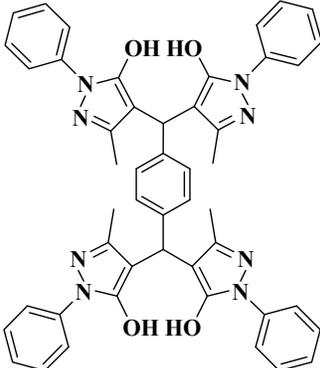
	 <p>(10)</p>	3	87	213-215	213-215	[22]
	 <p>(11)</p>	6	89	151-153	150-152	[25]
	 <p>(12)</p>	3	93	234-236	235-236	[25]
	 <p>(13)</p>	5	91	146-149	143-150	[23]
	 <p>(14)</p>	5	93	234-237	232-238	[23]

Table 2. (Continued).

  (15)	6	74	189-191	189-191	[25]
  (16)	9	78	192-194	190-192	[25]
  (17)	8	79 <sup>b</sup>	194-196	193-196	[25]

<sup>a</sup>Isolated yield.

<sup>b</sup>In this case, 4.2 mmol of 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one was reacted with 1 mmol of terephthalaldehyde.

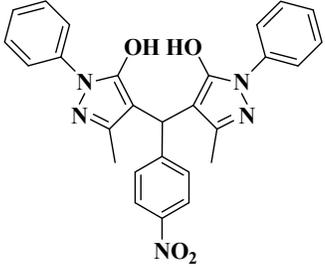
One of the attractive and important advantages of nanocatalysts is their recyclability; thus, we studied recyclability of nanomagnetite-Fe<sub>3</sub>O<sub>4</sub>. For this purpose, the condensation of 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one with 4-nitrobenzaldehyde was achieved, and the catalyst was separated according to the general procedure. Catalytic activity of nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> was restored within the limits of the experimental errors for eight successive runs (see Table 3).

To compare the efficiency of nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> with the reported catalysts for the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s, we have tabulated the results of the condensation of 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one with 4-nitrobenzaldehyde catalyzed by nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> and the reported catalysts, in Table 4. As Table 4 indicates, nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> is superior with respect to the reported catalysts in terms of reaction time, yield

and conditions. In addition, our catalyst was recyclable for seven times.

A plausible mechanism for the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s catalyzed by nanomagnetite-Fe<sub>3</sub>O<sub>4</sub>, is shown in Scheme 2. At first, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one **I** converts to the other tautomer (**II**); nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> could accelerate the tautomerization. Then, **II** attacks to the carbonyl group of aldehyde, which has activated *via* coordination of the lone pair electron of the aldehydic carbonyl with empty orbitals of the catalyst, to give intermediate **III** after removing one molecule of H<sub>2</sub>O. Another molecule of tautomer **II** is added to intermediate **III**, which has activated by nanomagnetite-Fe<sub>3</sub>O<sub>4</sub>, to afford intermediate **IV**. Finally, **IV** converts to the product after tautomerization and aromatization. The proposed mechanism is confirmed based on the literature [22].

**Table 3.** Recyclability of nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> in the preparation of compound 2.

Product	Run	Time (min)	Yield (%) <sup>a</sup>
	1 <sup>b</sup>	4	95
	2	4	93
	3	4	92
	4	4	91
	5	4	89
	6	5	87
	7	6	84
	8	6	82

<sup>a</sup>Isolated yield.<sup>b</sup>First use of the catalyst.

#### 4. Conclusions

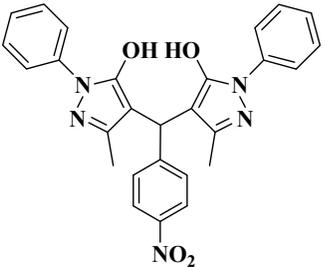
In summary, we have developed a new attractive protocol for the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol) derivatives from 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one and aromatic aldehydes using nanomagnetite-Fe<sub>3</sub>O<sub>4</sub>. Short reaction times, high yields, generality, efficiency, recyclability of the catalyst for seven times, simple

purification, clean reaction, and agreement with the green chemistry protocols are some advantages of in this method.

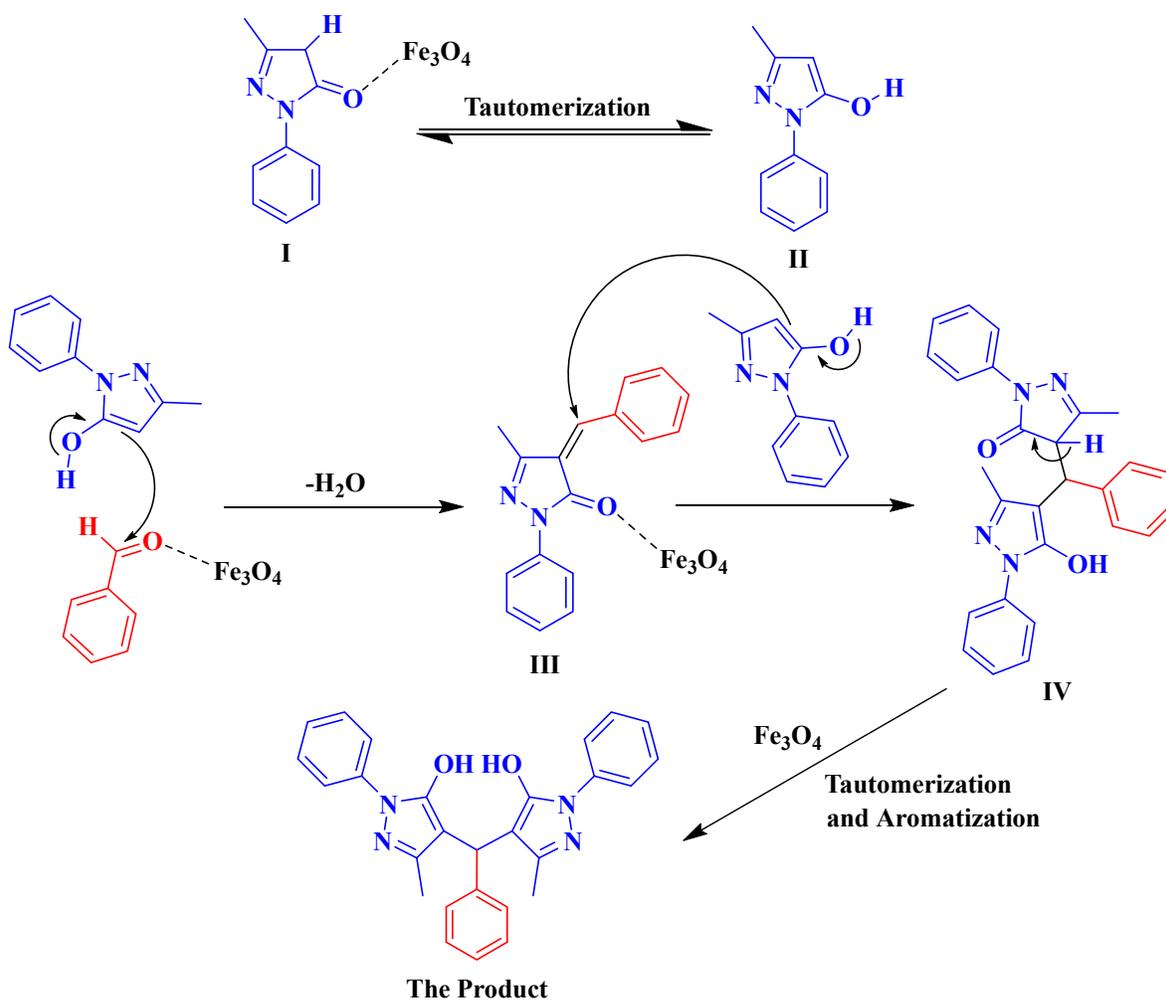
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**Table 4.** Comparison of the efficiency of nanomagnetite-Fe<sub>3</sub>O<sub>4</sub> with the reported catalysts for the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s.

Product	Catalyst	Conditions	Time (min)	Yield (%) <sup>a</sup>	Ref.
	Nanomagnetite-Fe <sub>3</sub> O <sub>4</sub>	Solvent-free, 70°C	4	95	-
	PEG-SO <sub>3</sub> H <sup>a</sup>	H <sub>2</sub> O, Reflux	15	93	[21]
	[Dsim]AlCl <sub>4</sub> <sup>b</sup>	Solvent-free, 50°C	40	91	[22]
	[Pyridine-SO <sub>3</sub> H]Cl	Solvent-free, 50°C	8	94	[23]
	Catalyst-free	PEG-400 <sup>c</sup> , 110°C	60	94	[25]
	Nano-SiO <sub>2</sub> /HClO <sub>4</sub>	H <sub>2</sub> O, Reflux	20	96	[27]
	SBPPSA <sup>d</sup>	Solvent-free, 80°C	35	91	[30]
	Cellulose sulfuric acid	H <sub>2</sub> O/EtOH, Reflux	10	83	[31]
	THSB <sup>e</sup>	EtOH, 75°C	3	96	[32]
	SASPSPE <sup>f</sup>	EtOH, Reflux	120	88	[33]
	Ph <sub>3</sub> CCl	Solvent-free, 60°C	6	93	[34]

<sup>a</sup>Poly(ethylene glycol)-bound sulfonic acid.<sup>b</sup>1,3-Disulfonic acid imidazolium chloroaluminate.<sup>c</sup>Poly(ethylene glycol)-400.<sup>d</sup>Silica -bonded *N*-propylpiperazine sulfamic acid.<sup>e</sup>1,3,5-Tris(hydrogensulfato)benzene.<sup>f</sup>Sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester.



**Scheme 2.** The proposed mechanism for the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s promoted by nanomagnetite-Fe<sub>3</sub>O<sub>4</sub>.

## References

- [1] J.B. Manley, P.T. Anastas, B.W. Cue Jr, *J. Clean Prod.* 16 (2008) 743-750.
- [2] P.T. Anastas, J.C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York (1998).
- [3] K. Tanaka, *Solvent-Free Organic Synthesis*, Wiley-VCH, GmbH and KGaA, Weinheim (2004).
- [4] A. Zare, M. Merajoddin, M.A. Zolfigol, *Iran. J. Catal.* 3 (2013) 83-90.
- [5] A. Hasaninejad, A. Zare, M. Shekouhy, J. Ameri-Rad, *Green Chem.* 13 (2011) 958-964.
- [6] A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, F. Abi, A. Zare, H. Kaveh, V. Khakyzadeh, M. Kazem-Rostami, A. Parhami, H. Torabi-Monfared, *Tetrahedron* 69 (2013) 212-218.
- [7] S. Shylesh, V. Schunemann, W.R. Thiel, *Angew. Chem. Int. Ed.* 49 (2010) 3428-3459.
- [8] V. Polshettiwar, R.S. Varma, *Green Chem.* 12 (2010) 743-754.
- [9] V. Polshettiwar, R.S. Varma, *Org. Biomol. Chem.* 7 (2009) 37-40.
- [10] J. Safari, Z. Zarnegar, *Iran. J. Catal.* 2 (2012) 121-128.
- [11] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J.-M. Basset, *Chem. Rev.* 111 (2011) 3036-3075.
- [12] M. Ma, Q. Zhang, D. Yin, J. Dou, H. Zhang, H. Xu, *Catal. Commun.* 17 (2012) 168-172.
- [13] V. Polshettiwar, Á. Molnár, *Tetrahedron* 63 (2007) 6949-6976.
- [14] M.A. Zolfigol, V. Khakyzadeh, A.R. Moosavi-Zare, A. Zare, P. Arghavani-Hadi, Z. Mohammadi, M.H. Beyzavi, *S. Afr. J. Chem.* 65 (2012) 280-285.
- [15] L.C. Behr, R. Fusco, C.H. Jarboe, *The Chemistry of Heterocyclic Compounds, Pyrazoles, Pyrazolines, Pyrazolidines, Indazoles and Condensed Rings*, Weissberger, A. (Ed.), Interscience Publishers, New York (1967).
- [16] D.M. Bailey, P.E. Hansen, A.G. Hlavac, E.R. Baizman, J. Pearl, A.F. Defelice, M.E. Feigenson, *J. Med. Chem.* 28 (1985) 256-260.
- [17] R.N. Mahajan, F.H. Havaladar, P.S. Fernandes, *J. Ind. Chem. Soc.* 68 (1991) 245-246.

- [18] S. Sugiura, S. Ohno, O. Ohtani, K. Izumi, T. Kitamikado, H. Asai, K. Kato, *J. Med. Chem.* 20 (1977) 80-85.
- [19] C.E. Rosiere, M.I. Grossman, *Science* 113 (1951) 651-651.
- [20] B.I. Buzykin, T.I. Lonschakova, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* (1971) 2224-2226.
- [21] A. Hasaninejad, M. Shekouhy, A. Zare, S.M.S. Hoseini Ghattalia, N. Golzar, *J. Iran. Chem. Soc.* 8 (2011) 411-423.
- [22] A. Khazaei, M.A. Zolfigol, A.R. Moosavi-Zare, Z. Asgari, M. Shekouhy, A. Zare, A. Hasaninejad, *RSC Adv.* 2 (2012) 8010-8013.
- [23] A.R. Moosavi-Zare, M.A. Zolfigol, M. Zarei, A. Zare, V. Khakyzadeh, A. Hasaninejad, *Appl. Catal. A* 467 (2013) 61-68.
- [24] D. Singh, D. Singh, *J. Chem. Eng. Data* 29 (1984) 355-356.
- [25] A. Hasaninejad, A. Zare, M. Shekouhy, N. Golzar, *Org. Prep. Proced. Int.* 43 (2011) 131-137.
- [26] W. Wang, S.-X. Wang, X.-Y. Qin, J.-T. Li, *Synth. Commun.* 35 (2005) 1263-1269.
- [27] B. Sadeghi, M. Ghorbani Rad, *Iran. J. Catal.* 4 (2014) 67-70.
- [28] M.N. Elinson, A.S. Dorofeev, R.F. Nasybullin, G.I. Nikishin, *Synthesis* (2008) 1933-1937.
- [29] S. Qu, H. Yang, D. Ren, S. Kan, G. Zou, D. Li, M. Li, *J. Colloid Interface Sci.* 215 (1999) 190-192.
- [30] S. Tayebi, K. Niknam, *Iran. J. Catal.* 2 (2012), 69-74.
- [31] E. Mosaddeghi, A. Hassankhani, A. Baghizadeh, *J. Chil. Chem. Soc.* 55, (2010) 419-420.
- [32] Z. Karimi-Jaberi, B. Pooladian, M. Moradi, E. Ghasemi, *Chin. J. Catal.* 33 (2012)1945-1949.
- [33] S. Tayebi, M. Baghernejad, D. Saberi, K. Niknam, *Chin. J. Catal.* 32 (2011)1477-1483.
- [34] A. Zare, M. Merajoddin, A. R. Moosavi-Zare, M. Zarei, *Chin. J. Catal.* 35 (2014) 85-89.