

## Efficient one-pot synthesis of 6-amino-4-aryl-5-cyano-2-methyl-4H-pyran-3-carboxylates catalyzed by nano MgO in water

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### Abstract

Water is a versatile solvent in many ways, and in this sense performing organic reactions in this medium is now of great interest. The one-pot reaction of ethyl acetoacetate or benzyl acetoacetate, with benzaldehydes and malononitrile to provide some novel 6-amino-4-aryl-5-cyano-2-methyl-4H-pyran-3-carboxylates has been performed over nano MgO with high performance in water as a green solvent at 80 °C. The nanocrystalline MgO catalyst was characterized *via* X-ray diffraction (XRD), transmission electron microscopy (TEM) and BET analysis. This method offers considerable improvements for the synthesis of 6-amino-4-aryl-5-cyano-2-methyl-4H-pyran-3-carboxylates with concern to the yield of products, facility in operation, and green aspects without using of toxic catalysts and solvents.

**Keywords:** 6-Amino-5-cyano-4H-pyrans; malononitrile; nano MgO; one-pot reaction; water.

### Introduction

The properties of metal oxide nanoparticles are of great interest due to the many potential applications of these materials. Magnesium oxide is one of the most significant materials in the number of the oxides having important technological applications because of its broad bandgap (7.8 eV) and a good chemical and thermal stability [1,2]. Also, magnesium oxide nanoparticles are odorless and non-toxic. They have high hardness, high purity and a high melting point [3]. Applications of nanoparticles in catalytic reactions owe to size decreases, the surface area to volume ratio increases, which enhanced interactions between the reactant and the catalyst, which are needed for high catalytic efficiencies [4]. 4H-Pyrans are

remarkably important as they possess a broad range of biological and pharmacological activities such as anti-alzheimer [5], anti-tumor [6,7], and anti-bacterial [8,9]. Furthermore, 4H-pyrans, are used in cosmetics, pigments, biodegradable agrochemicals and photoactive materials [10, 11]. A number of procedures have been reported for the preparation of 2-amino-4H-pyran derivatives. Some catalysts such as triethylbenzylammonium chloride (TEBAC) [12], TMG/[bmim][BF<sub>4</sub>] [13], Cu(II) oxymetasilicate [14], Mg/La mixed oxide [15], SiO<sub>2</sub> NPs [16], Baker's yeast [17], piperidine/SDS [18], BF<sub>3</sub>:OEt<sub>2</sub> [19] and KF [20], have been applied for these reactions. However, some disadvantages such as the use of

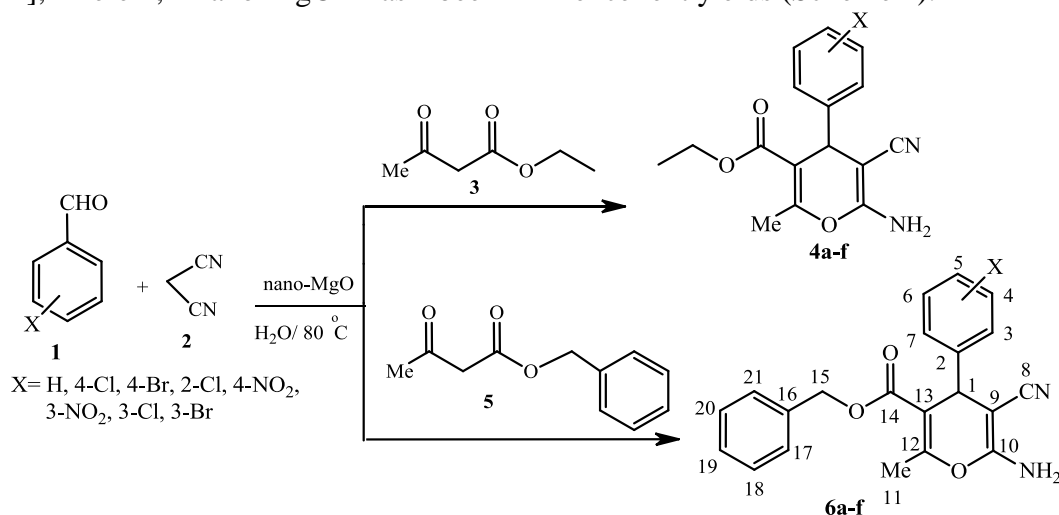
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volatile and flammable organic solvents, longer reaction time, tedious work-up procedures, disagreeable yields, and nonretrievable catalysts still exist. Following our interest in the use of nanocrystalline MgO for the synthesis of pyrido[2,3-*d*]pyrimidines [21], herein, nano-MgO has been

successfully utilized to carry out the three-component reaction of ethyl acetoacetate or benzyl acetoacetate, with arylaldehydes and malononitrile in water at 80 °C to generate 6-amino-4-aryl-5-cyano-2-methyl-4*H*-pyran-3-carboxylate derivatives in good to excellent yields (Scheme 1).



**Scheme 1.** Synthesis of 6-amino-4-aryl-5-cyano-2-methyl-4*H*-pyran-3-carboxylates

### Experimental

High-purity chemical reagents were purchased from the Merck Chemical Company. Melting points were determined using an Electrothermal Mk3 apparatus and are uncorrected. The crystalline structure of the nano MgO was investigated by X-ray diffraction with Cu-K $\alpha$ ,  $l = 0.1541874$  Å radiation. The surface area of nano MgO was observed using N<sub>2</sub> adsorption-desorption isotherms with surface analyzer equipment at 77 K. The size and morphology of the nano MgO were determined by transmitting electron microscope (TEM, Philips EM208). The NMR spectra were recorded in CDCl<sub>3</sub> with TMS as an internal standard on a Bruker Avance DRX 400 MHz spectrometer. FT-IR spectra were determined on an SP-1100, P-UV-Com instrument. Elemental analyses were done on a Carlo-Erba EA1110CNNO-S analyzer and agreed with the calculated values.

The products were characterized by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, elemental analyses and by comparison with authentic samples reported in the literature.

### Preparation of Nano MgO

The nano MgO was prepared according to the procedure reported elsewhere [24].

### General Procedure for the Synthesis of 6-Amino-5-cyano-4*H*-pyrans

A mixture of arylaldehydes (1 mmol: 0.106 g of benzaldehyde, 0.140 g of 4-Cl-benzaldehyde, 0.185 g of 4-Br-benzaldehyde, 0.140 g of 2-Cl-benzaldehyde, 0.151 g of 4-NO<sub>2</sub>-benzaldehyde, 0.151 g of 3-NO<sub>2</sub>-benzaldehyde, 0.140 g of 3-Cl-benzaldehyde, 0.185 g of 3-Br-benzaldehyde), ethyl acetoacetate (1 mmol: 0.130 g) or benzyl acetoacetate (1 mmol: 0.192 g), malononitrile (1 mmol: 0.66 g) and nano-MgO (25 mol

%, 0.01 g) were dissolved in H<sub>2</sub>O (5 ml) and were heated at 80 °C for 45-80 minute. The progress of the reaction is monitored by TLC. After completion of the reaction, the corresponding product was obtained through simple filtering, and the crude solid residue recrystallized from ethanol to generate the highly pure 6-amino-5-cyano-4H-pyran derivatives.

**Benzyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate (6a)**

Yellow solid; mp 136-138 °C. FT-IR (KBr) ( $\nu_{\max}$ , cm<sup>-1</sup>): 3323 and 3450 (NH<sub>2</sub> stretching), 2192 (CN stretching), 1718 (C=O stretching), 1596 and 1448 (C=C Aromatic stretching), 1222 (C-N stretching), 1058 (C-O stretching), 734, 692 (oop C-H); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.26-7.28 (m, 6H, H-17, H-18, H-19, H-20, H-21 and H-7), 7.15-7.24 (m, 2H, H-4 and H-6), 7.03-7.14 (m, 2H, H-3 and H-5), 5.04 (d, 1H, *J* = 12.4 Hz, CH<sub>2</sub>), 4.98 (d, 1H, *J* = 12.4 Hz, CH<sub>2</sub>), 4.48 (s, 2H, NH<sub>2</sub>), 4.45 (s, 1H, H-1), 2.38 (s, 3H, H-11); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 164.0 (C-14), 156.5 (C-10), 156.2 (C-12), 142.9 (C-2), 134.3 (C-16), 127.6 (2C, C-18 and C-20), 127.5 (2C, C-4 and C-6), 127.0 (2C, C-3 and C-7), 126.9 (2C, C-17 and C-21), 126.4 (C-19), 126.1 (C-5), 117.8 (C-8), 106.5 (C-13), 65.4 (C-15), 61.3 (C-9), 37.6 (C-1); 17.5 (C-11); Anal Calc. for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>: C, 72.81; H, 5.23; N, 8.08. Found: C, 72.85; H, 5.16; N, 8.13.

**Benzyl 6-amino-4-(3-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (6b)**

Yellow solid; mp 168-170 °C, FT-IR (KBr) ( $\nu_{\max}$ , cm<sup>-1</sup>): 3326 and 3396 (NH<sub>2</sub> stretching), 2190 (CN stretching), 1681 (C=O stretching), 1604 and 1460 (C=C Aromatic stretching), 1265 (C-N stretching), 1060 (C-O stretching), 790,

698 (oop C-H); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.28-7.30 (m, 3H, H-21, H-17 and H-5), 7.19-7.26 (m, 2H, H-6 and H-7), 7.10-7.17 (m, 3H, H-29, H-19 and H-18), 7.01-7.07 (m, 1H, H-3), 5.04 (d, 1H, *J* = 12.2 Hz, CH<sub>2</sub>), 4.98 (d, 1H, *J* = 12.2 Hz, CH<sub>2</sub>), 4.51 (s, 2H, NH<sub>2</sub>), 4.41 (s, 1H, H-1), 2.40 (s, 3H, H-11); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 164.3 (C-14), 156.9 (C-10), 156.4 (C-12), 144.7 (C-2), 134.1 (C-16), 133.4 (C-4), 128.8 (C-6), 127.4 (2C, C-18 and C-20), 127.2 (C-19), 127.1 (C-3), 126.5 (2C, C-17 and C-21), 126.4 (C-5), 124.8 (C-7), 117.5 (C-8), 105.9 (C-13), 65.7 (C-15), 60.6 (C-9), 37.4 (C-1), 17.5 (C-11); Anal Calc. for C<sub>21</sub>H<sub>17</sub>ClN<sub>2</sub>O<sub>3</sub>: C, 66.23; H, 4.49; N, 7.35. Found: C, 66.43; H, 4.56; N, 7.28.

**Benzyl 6-amino-4-(3-bromophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (6c)**

Yellow solid; mp 174-176 °C, FT-IR (KBr) ( $\nu_{\max}$ , cm<sup>-1</sup>): 3328 and 3390 (NH<sub>2</sub> stretching), 2190 (CN stretching), 1685 (C=O stretching), 1606 and 1460 (C=C Aromatic stretching), 1265 (C-N stretching), 1060 (C-O stretching), 790, 694 (oop C-H); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 7.36-7.34 (m, 1H, H-3), 7.31-7.26 (m, 4H, H-5, H-17, H-18 and H-21), 7.14-7.06 (m, 4H, H-19, H-20, H-6, H-7), 4.98 (d, 1H, *J* = 12.2 Hz, CH<sub>2</sub>), 5.04 (d, 1H, *J* = 12.2 Hz, CH<sub>2</sub>), 4.56 (s, 2H, NH<sub>2</sub>), 4.40 (s, 1H, H-1), 2.39 (s, 3H, H-11); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 164.3 (C-14), 157.0 (C-10), 156.4 (C-12), 144.9 (C-2), 134.1 (C-16), 129.4 (C-3), 129.3 (C-6), 129.1 (C-5), 127.5 (2C, C-18 and C-20), 127.2 (C-19), 127.1 (2C, C-17 and C-21), 125.3 (C-7), 121.7 (C-4), 117.5 (C-8), 105.9 (C-13), 65.7 (C-15), 60.6 (C-9), 37.4 (C-1), 17.6 (C-11); Anal Calc. for C<sub>21</sub>H<sub>17</sub>BrN<sub>2</sub>O<sub>3</sub>: C, 59.30; H, 4.02; N, 6.58. Found: C, 59.38; H, 4.06; N, 6.64.

**Benzyl 6-amino-4-(4-bromophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (6d)**

Yellow solid; mp 162-164 °C, FT-IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3319 and 3436 (NH<sub>2</sub> stretching), 2196 (CN stretching), 1712 (C=O stretching), 1595 and 1407 (C=C Aromatic stretching), 1251 (C-N stretching), 1058 (C-O stretching), 835 (oop C-H); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.36 (d,  $J$  = 8.32 Hz, 2H, H-4 and H-6), 7.29-7.01 (m, 5H, H-17, H-18, H-19, H-20, H-21), 7.36 (d,  $J$  = 8.32 Hz, 2H, H-3 and H-7), 5.06 (d, 1H,  $J$  = 12.2 Hz, CH<sub>2</sub>), 4.98 (d, 1H,  $J$  = 12.2 Hz, CH<sub>2</sub>), 4.47 (s, 2H, NH<sub>2</sub>), 4.41 (s, 1H, H-1), 2.38 (s, 3H, H-11); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 164.4 (C-14), 156.7 (C-10), 156.2 (C-12), 141.6 (C-2), 134.1 (C-16), 130.7 (2C, C-4 and C-6), 128.2 (2C, C-3 and C-7), 127.4 (2C, C-18 and C-20), 127.2 (C-19), 127.1 (2C, C-17 and C-21), 120.0 (C-5), 117.5 (C-8), 106.0 (C-13), 65.6 (C-15), 60.9 (C-9), 37.2 (C-1), 17.5 (C-11); Anal Calc. for C<sub>21</sub>H<sub>17</sub>BrN<sub>2</sub>O<sub>3</sub>: C, 59.30; H, 4.02; N, 6.58. Found: C, 59.41; H, 4.08; N, 6.54.

**Benzyl 6-amino-5-cyano-2-methyl-4-(3-nitrophenyl)-4H-pyran-3-carboxylate (6e)**

Yellow solid; m.p. 169-171 °C, FT-IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3325 and 3419 (NH<sub>2</sub> stretching), 2198 (CN stretching), 1720 (C=O stretching), 1604 and 1400 (C=C Aromatic stretching), 1521 and 1344 (NO<sub>2</sub> stretching), 1222 (C-N stretching), 1056 (C-O stretching), 811 and 688 (oop C-H); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.04-8.07 (m, 1H, H-5), 7.94 (t, 1H,  $J$  = 1.8 Hz, H-3), 7.45 (d, 1H,  $J$  = 7.7 Hz, H-7), 7.38 (t, 1H,  $J$  = 7.8 Hz, H-6), 7.23-7.26 (m, 3H, H-18, H-19 and H-20), 7.05-7.07 (m, 2H, H-17 and H-21), 5.06 (d, 1H,  $J$  = 12.1 Hz, CH<sub>2</sub>), 4.93 (d, 1H,  $J$  = 12.1 Hz, CH<sub>2</sub>), 4.57 (s, 2H, NH<sub>2</sub>), 4.55 (s, 1H, H-1),

2.43 (s, 3H, H-11); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 164.0 (C-14), 157.5 (C-10), 156.4 (C-12), 147.4 (C-4), 144.8 (C-2), 132.9 (C-16), 128.4 (2C, C-18 and C-20), 127.5 (C-19), 127.4 (C-7), 127.3 (2C, C-17 and C-21), 121.4 (C-6), 121.3 (C-5), 117.1 (C-8), 105.5 (C-13), 65.8 (C-15), 59.8 (C-9), 37.6 (C-1), 17.7 (C-11); Anal Calc. for C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>O<sub>5</sub>: C, 64.44; H, 4.37; N, 10.73. Found: C, 64.51; H, 4.42; N, 10.79.

**Benzyl 6-amino-5-cyano-2-methyl-4-(4-nitrophenyl)-4H-pyran-3-carboxylate (6f)**

Orange solid; mp 151-153 °C, FT-IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3321 and 3423 (NH<sub>2</sub> stretching), 2196 (CN stretching), 1716 (C=O stretching), 1598 and 1407 (C=C Aromatic stretching), 1517 and 1344 (NO<sub>2</sub> stretching), 1220 (C-N stretching), 1058 (C-O stretching), 869 (oop C-H); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), 8.06 (d, 2H,  $J$  = 8.14 Hz, H-4 and H-6), 7.23-7.29 (m, 5H, H-17, H-18, H-19, H-20 and H-21), 7.03 (d, 2H,  $J$  = 8.14 Hz, H-3 and H-7), 5.07 (d, 1H,  $J$  = 12.1 Hz, CH<sub>2</sub>), 4.92 (d, 1H,  $J$  = 12.1 Hz, CH<sub>2</sub>), 4.60 (s, 2H, NH<sub>2</sub>), 4.53 (s, 1H, H-1), 2.42 (s, 3H, H-11); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 164.0 (C-14), 157.5 (C-10), 156.4 (C-12), 149.7 (C-2), 145.9 (C-5), 133.8 (C-16), 128.2 (2C, C-18 and C-20), 127.5 (C-19), 127.4 (2C, C-17 and C-21), 127.3 (2C, C-3 and C-7), 122.9 (2C, C-4 and C-6), 117.1 (C-8), 105.4 (C-13), 65.8 (C-15), 59.8 (C-9), 37.6 (C-1), 17.6 (C-11); Anal Calc. for C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>O<sub>5</sub>: C, 64.44; H, 4.37; N, 10.73. Found: C, 64.49; H, 4.43; N, 10.81.

**Results and discussion**

The X-ray diffraction pattern of nano MgO is illustrated in Figure 1. All the diffraction peaks matched well with the face centered cubic structure of

periclose MgO (JCPDS No. 87-0653). The main peaks at  $2\theta$  values of  $37.1^\circ$ ,  $43.0^\circ$ ,  $62.4^\circ$ ,  $74.8^\circ$  and  $78.6^\circ$  can be

indexed to the lattice planes of (111), (200), (220), (311) and (222) respectively.

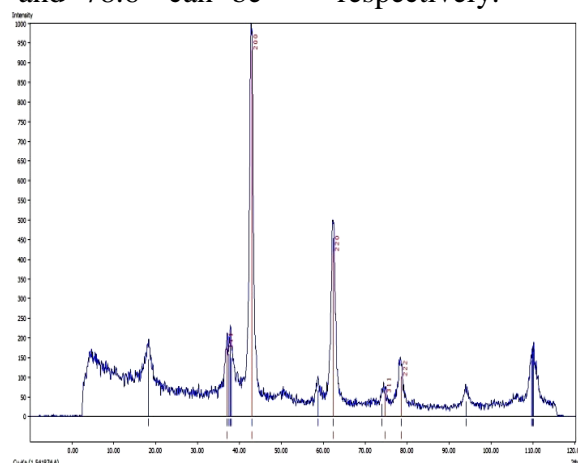


Figure 1. X-ray powder diffraction pattern of nano MgO

The particle size was also examined by TEM. Figure 2 shows TEM micrographs of nanocrystalline

MgO, revealing that the particle size is about 50 nm.

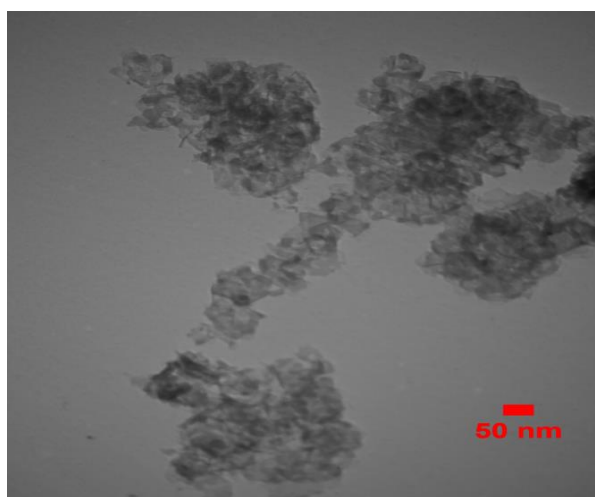


Figure 2. TEM micrograph of nanocrystalline MgO

By BET analysis, the specific surface area of nano MgO sample was found to be  $63.32 \text{ m}^2/\text{g}$ . To optimize the reaction conditions and achieve the best catalytic activity, the reaction of ethyl acetoacetate (1 mmol), benzaldehyde (1 mmol), and malononitrile (1 mmol) was used as a model, and was directed under various reaction parameters such as solvent and catalyst. At first, the

model reaction was performed in various solvents such as EtOH, MeOH,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{CN}$ , THF, and EtOAc to explore the effect of solvent. In this study, it was found that  $\text{H}_2\text{O}$  at  $80^\circ\text{C}$  is a better solvent, with regard to reaction time and yield of the desired product. In order to study the effect of nano MgO as catalyst, the model reaction was performed in the presence of different

amounts of nano-MgO. It was observed that the variation for nano MgO had an effective influence. The best amount of nano-MgO which is 25 mol% generated the desired product in 93% yields. After optimization the reaction conditions, a series of 6-amino-4-aryl-5-cyano-2-methyl-4*H*-pyran-3-carboxylates was prepared from ethyl acetoacetate, with benzaldehydes and malononitrile in the presence of nano-MgO in water at 80 °C in good to excellent yields (Table 1, entries 1-6). Also, this reaction was carried out with benzyl acetoacetate and the corresponding novel products were achieved in very good yields under similar conditions (Table 1, Entries 7-12). It is noteworthy that the

corresponding 6-amino-4-aryl-5-cyano-2-methyl-4*H*-pyran-3-carboxylates were separated by crystallization from the crude filtrate. This one-pot condensation reaction proceeds through dual activation of substrates by nano MgO which have a number of Lewis acid Mg<sup>2+</sup> and O<sup>2-</sup> as anionic oxidic Lewis basic moiety [22]. The Lewis base site of the catalyst activates the methylene group of malononitrile. The carbonyl group of aldehyde coordinates with the Lewis acid site enhancing the electrophilicity of the carbonyl group and as a result makes it probable to perform the reaction in shorter time.

**Table 1.** Synthesis of 6-amino-5-cyano-4*H*-pyran derivatives catalyzed using nano-MgO<sup>a</sup>

Entry	R	Ar	Product	Time (min)	Yields (%) <sup>b</sup>	Mp °C	
						Found	Reported
1	Et	C <sub>6</sub> H <sub>5</sub>	<b>4a</b>	75	93	191-192	192-194 [17]
2	Et	4-Cl-C <sub>6</sub> H <sub>4</sub>	<b>4b</b>	70	95	176-178	175-177 [22]
3	Et	4-Br-C <sub>6</sub> H <sub>4</sub>	<b>4c</b>	70	96	174-176	172-174 [17]
4	Et	2-Cl-C <sub>6</sub> H <sub>4</sub>	<b>4d</b>	75	92	189-191	190-192 [11]
5	Et	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	<b>4e</b>	65	95	175-177	176-178 [15]
6	Et	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	<b>4f</b>	70	93	181-183	182-183 [11]
7	PhCH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	<b>6a</b>	80	94	136-138	-
8	PhCH <sub>2</sub>	3-Cl-C <sub>6</sub> H <sub>4</sub>	<b>6b</b>	60	95	168-170	-
9	PhCH <sub>2</sub>	3-Br-C <sub>6</sub> H <sub>4</sub>	<b>6c</b>	65	93	174-176	-
10	PhCH <sub>2</sub>	4-Br-C <sub>6</sub> H <sub>4</sub>	<b>6d</b>	75	94	162-164	-
11	PhCH <sub>2</sub>	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	<b>6e</b>	50	94	151-153	-
12	PhCH <sub>2</sub>	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	<b>6f</b>	45	95	169-171	-

<sup>a</sup>Reaction and conditions: ethyl acetoacetate or benzyl acetoacetate (1 mmol), aldehyde (1 mmol), malononitrile (1 mmol) and MgO (25 mol %) in H<sub>2</sub>O (5 mL) at 80 °C.

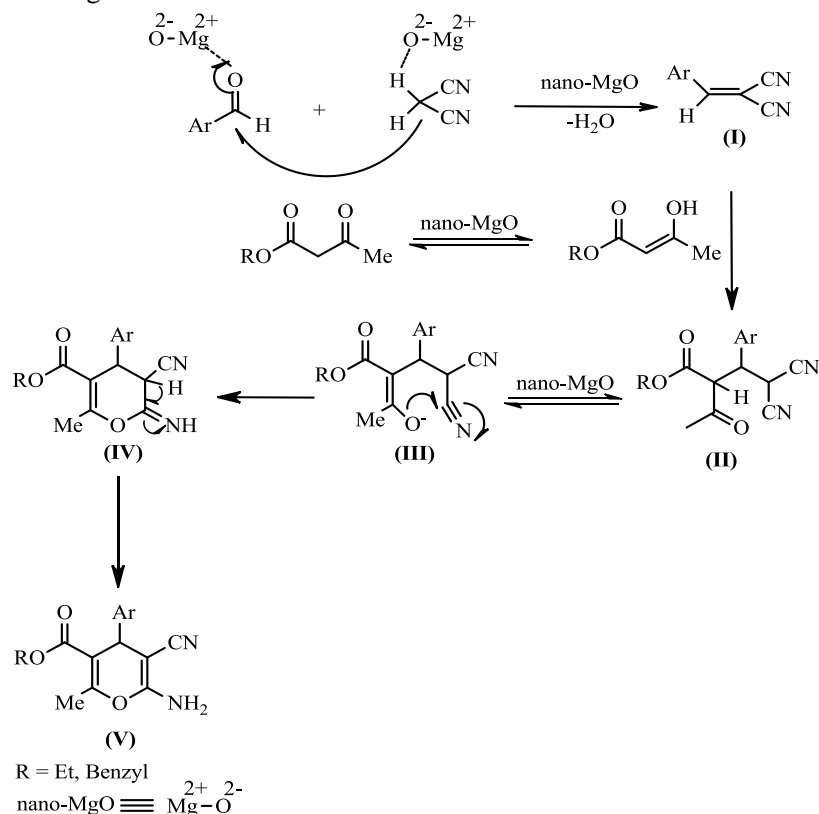
<sup>b</sup>All yields refer to isolated products.

In a possible mechanism, it is assumed that the reaction may begin at first via the Knoevenagel condensation between aromatic aldehyde and malononitrile to form intermediate **I**. Subsequent, addition of the enolat form of ethyl acetoacetate or benzyl acetoacetate to intermediate **I** give **II**. Intermediate **II**

converts to **III** through deprotonation an acidic proton of intermediate **II** (nano MgO can act as a mild base for the deprotonation of an acidic proton of intermediate **II**). Next, intermediate **III** converts to **IV** through intramolecular cyclization. Then, product **V** is formed after tautomerisation of intermediate **IV**

(Scheme 2). It is remarkable that the bulk MgO exhibits lower catalytic activity than nanocrystalline MgO in this reaction and

the products were obtained with lower yields and longer time.



**Scheme 2.** A possible mechanism for the 6-amino-4-aryl-5-cyano-2-methyl-4H-pyran-3-carboxylates

The high efficiency of the nano MgO oxides is from their high surface area and high concentration of low-coordinated sites and structural defects on their surface [23]. It is notable to highlight that the nano MgO could be regenerated and reused without a considerable loss of its activity as showed in Table 2. Upon completion of the reaction, the nano MgO catalyst was isolated by centrifugation and the recovered catalyst was washed with ethanol followed by drying in an oven

at 100 °C and reused as such for the next reactions.

To investigate the efficiency of this procedure for the synthesis of 6-amino-4-aryl-5-cyano-2-methyl-4H-pyran-3-carboxylates, compound **4a** was compared with some of those reported in the literature (Tables 3). As can be seen, our results represent good yields compared to the previously reported data with regard to all conditions such as yields, reaction times, and reaction solvents.

**Table 2.** Recycling of nano MgO for the preparation of **4a**

Run	1	2	3	4	5
Yield (%)	93	92	90	87	86

## Conclusion

In summary, an effective method for the synthesis of some novel 6-amino-4-aryl-5-cyano-2-methyl-4*H*-pyran-3-carboxylates by one-pot reaction of

ethyl acetoacetate or benzyl acetoacetate, benzaldehydes and malononitrile using nano MgO as an efficient catalyst in water as a green solvent has developed.

**Table 3.** Comparison of this work with other reported data for the preparation of **4a**

Entry	Catalyst	Reaction conditions	Time/min	Yield (%)	Ref.
1	TMG/[bmim][BF <sub>4</sub> ]	80 °C	50	83	[14]
2	Cu(II) oxymetasilicate	CH <sub>3</sub> CN/ reflux	60	88	[15]
3	Mg/La mixed oxide	CH <sub>3</sub> OH/ 65 °C	60	83	[16]
4	SiO <sub>2</sub> NPs	EtOH/ r.t.	120	85	[17]
5	Baker's yeast	DMAc/ r.t.	1800	65	[18]
6	Piperidine/SDS	H <sub>2</sub> O/ reflux	10	85	[19]
7	nano-MgO	H <sub>2</sub> O/ 80 °C	75	93	This work

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