

## Green synthesis of 2-amino-7-hydroxy-4-aryl-4*H*-chromene-3-carbonitriles using ZnO nanoparticles prepared with mulberry leaf extract and ZnCl<sub>2</sub>

Akbar MOBINIKHALEDI<sup>1,\*</sup>, Atisa YAZDANIPOUR<sup>1</sup>, Majid GHASHANG<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Arak University, Arak, Iran

<sup>2</sup>Department of Chemistry, Faculty of Science, Najafabad Branch, Islamic Azad University, Najaf Abad, Esfahan, Iran

Received: 25.01.2015

Accepted/Published Online: 14.04.2015

Printed: 30.06.2015

**Abstract:** A highly efficient and environmentally benign protocol for the synthesis of 2-amino-7-hydroxy-4-aryl-4*H*-chromene-3-carbonitrile derivatives in good to high yields (77%–97%) by one-pot three-component coupling reaction of aromatic aldehydes, malononitrile, and resorcinol under reflux condition was developed in aqueous media using ZnO nanoparticles that were prepared in the presence of mulberry leaf extract under mild conditions.

**Key words:** Mulberry leaf extract, ZnO nanoparticles, 2-amino-4*H*-chromene, aqueous media

### 1. Introduction

Heterocyclic compounds containing chromene moieties are of considerable interest as they are a class of natural and synthetic compounds that possess a great variety of biological and pharmaceutical activities.<sup>1,2</sup> These scaffolds are more privileged when they join with rigid hetero ring systems and/or other chemical functional groups. Obviously, functionalization of chromene derivatives has played an ever increasing role in the synthetic approaches to promising compounds in the field of medicinal chemistry. On the other hand, functionalized chromenes appeared as an important structural component in both biologically active and natural compounds.<sup>3–5</sup> For example, some interesting molecules with a chromene framework joined with different functional groups displaying rich medicinal chemistry and numerous applications due to their anti-inflammatory, antioxidant, anti-HIV, antibacterial, and analgesic properties.<sup>6–13</sup> Among them, chromenes with cyano-functionality have potential applications in the treatment of rheumatoid and psoriatic arthritis and cancer.<sup>14</sup> In addition, they are applicable as laser dyes,<sup>15</sup> optical brighteners,<sup>16</sup> and pigments.<sup>17</sup>

Consequently, several methods have been reported for preparation of chromene derivatives involving multicomponent reaction of aldehydes, malononitrile and  $\beta$ -keto esters, diverse enolizable C–H activated acidic compounds, phenols, and  $\alpha$ - and  $\beta$ -naphthols.<sup>18–23</sup> To achieve this aim, several methods using different homogeneous and heterogeneous catalysts were explored. These methods have the advantages of high yields and mild reaction conditions and some disadvantages of using toxic solvents and expensive catalysts. However, the discovery of new synthetic methodologies that facilitate the preparation of organic compounds is of great interest. One approach to address this challenge involves the development of new synthesized environmentally friendly catalysts to catalyze the reaction.

Therefore, as a part of our incessant efforts on the use of heterogeneous catalysts in multicomponent

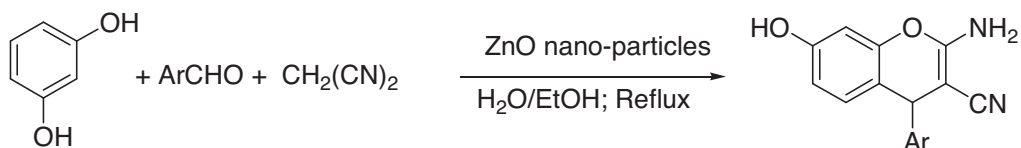
\*Correspondence: akbar\_mobini@yahoo.com

reactions, the scope of the present work was extended to the multicomponent condensation reaction of aldehydes, resorcinol, and malononitrile to afford 2-amino-7-hydroxy-4-aryl-4*H*-chromene-3-carbonitrile derivatives.

Comparatively few methods have been described for the synthesis of 2-amino-7-hydroxy-4-aryl/alkyl-4*H*-chromene-3-carbonitriles applying the use of potassium phthalimide-N-oxy,<sup>18</sup> 2,2,2-trifluoroethanol,<sup>19</sup> Fe<sub>3</sub>O<sub>4</sub>-chitosan nanoparticles,<sup>22</sup> and MgO.<sup>23</sup>

The application of ZnO as a catalyst in organic transformations was found to be of increasing interest due to the high effectiveness of ZnO to act as a good Lewis acid in organic synthesis. ZnO has been used as a catalyst in various organic transformations such as 2-aryl-1,3-benzothiazoles and 1,3-benzoxazoles synthesis;<sup>24</sup> synthesis of tetrahydrobenzo[*b*]pyran and dihydropyrimidones;<sup>25</sup> synthesis of naphtha[1,2-*e*]oxazinone and 14-substituted-14*H*-dibenzo[*a, j*]xanthenes;<sup>26</sup> acylation of alcohols, phenols, and amines;<sup>27</sup> Knoevenagel, Wittig, and Wittig–Horner reactions;<sup>28</sup> enamination of 1,3-dicarbonyls;<sup>29</sup> and preparation of 2,4,6-triaryl pyridines.<sup>30</sup>

In view of these reports and in continuation of our work on the synthesis of chromenes,<sup>31,32</sup> we wish to report the synthesis of some 2-amino-7-hydroxy-4-aryl-4*H*-chromene-3-carbonitriles in the presence of ZnO nanoparticles as a green, environmentally friendly catalyst, prepared via a new green biosynthesis method (Scheme 1).



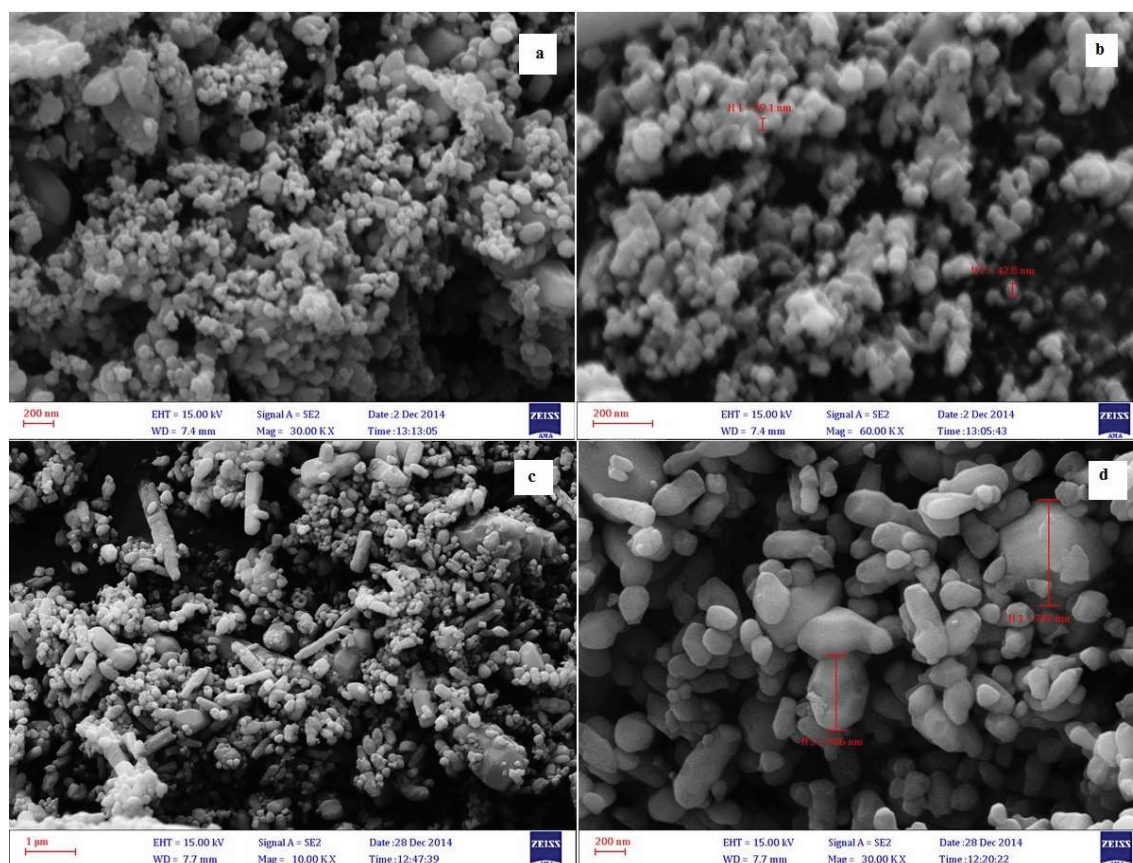
**Scheme 1.** The synthetic pathway of 2-amino-7-hydroxy-4-aryl-4*H*-chromene-3-carbonitriles using ZnO nanoparticles.

## 2. Results and discussion

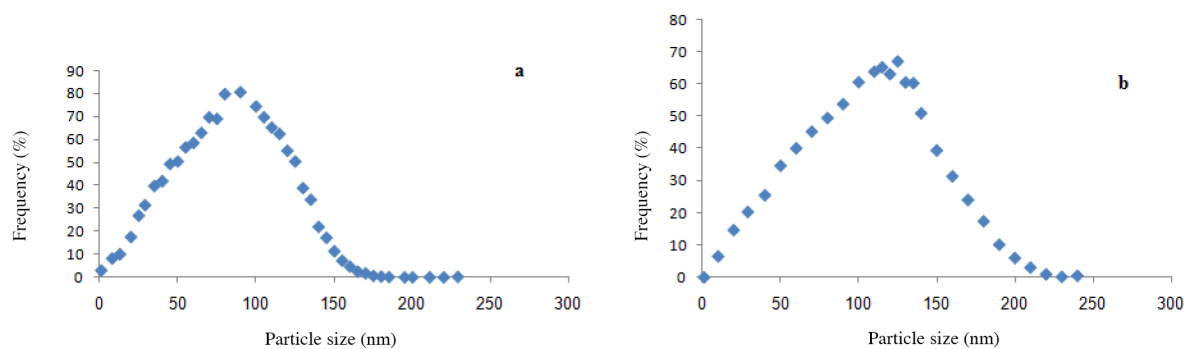
ZnO nanoparticles were synthesized via a simple precipitation method using extract solution of mulberry leaves and ZnCl<sub>2</sub>. The procedure is simple and the method is green and environmentally friendly.

Field emission scanning electronic microscopy (FE-SEM) was used to study the morphology of the surface of the ZnO nanoparticles (Figure 1). The analysis of the picture obtained shows clearly that the surface of the as-prepared ZnO nanoparticles has a relatively homogeneous microstructure made up of spheres or quasospheres of various sizes and forms. The sample forms irregular grains with a minimum size of 40 nm. It is evident that the organic compounds present in the extract might have capped and stabilized the nanoparticles during their formation and thus particles are smaller, well-dispersed, and almost spherical (Figures 1a and 1b). On the other hand, when the ZnO nanoparticles are formed without using the extract, particles are bigger and do not have homogeneous shapes (Figures 1c and 1d). Amino ethanol acts as precipitant agent but it is noteworthy that the influence of the extract and precipitant agent together led to the formation of smaller nanoparticles.

Statistical analysis was performed on the FE-SEM image to obtain information about the particle size distribution of the sample (Figure 2). It was revealed that the diameters of the sample were in the range of 20–160 nm with an average particle size of about 90 nm for the sample prepared via mulberry leaf extract (Figure 2a) and an average particle size of about 120 nm for the sample prepared without extract (Figure 2b). A comparison between the particle size distribution of the ZnO nanoparticles clearly shows that the use of extract led to the formation of particles smaller than without use of extract.



**Figure 1.** FE-SEM micrographs of ZnO nanoparticles prepared using mulberry leaf extract (a, b) and without extract (c, d).

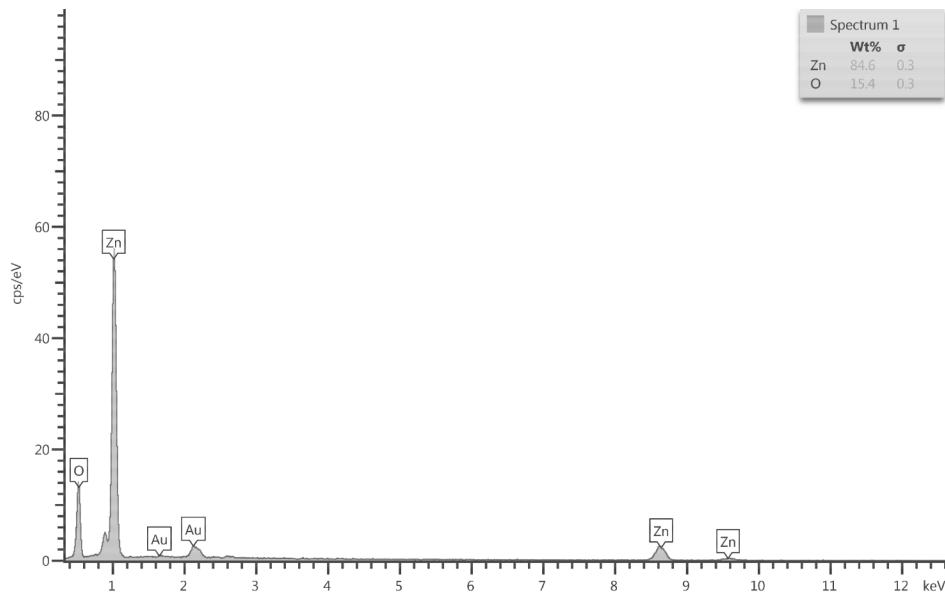


**Figure 2.** The particle size distribution of ZnO nanoparticles prepared using mulberry leaf extract (a) and without extract (b).

Figure 3 shows the elemental analysis of ZnO nanoparticles exposed by EDX analysis. The EDX analysis shows that the compound consists of two elements, zinc and oxygen, and there are no other elemental impurities present in the synthesized ZnO nanoparticles.

In order to examine the catalytic activity of ZnO nanoparticles for preparation of chromenes (Scheme 1), a mixture of resorcinol (1 mmol), malononitrile (1 mmol), and benzaldehyde (1 mmol) was stirred in water

under different conditions over ZnO nanoparticles catalyst. No other additive was necessary to promote the reaction. The use of commercial ZnO gave the product (40%), which was lower than that of ZnO nanoparticles (93%).



**Figure 3.** The EDX analysis of ZnO nanoparticles.

Optimization was carried out with variation in the reaction temperature, medium, and catalyst amount. The results are summarized in Table 1. No product was observed at room temperature. As the temperature increased the conversion rate of the product increased as well. This could be due to the providing of the activation energy needed for the reaction conversion, resulting in the formation of 2-amino-7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile. At 80 °C, the reaction proceeded smoothly and almost complete conversion of product was observed. Therefore, we kept the reaction temperature at 80 °C (giving shorter reaction time and higher yield).

**Table 1.** The optimization of reaction conditions for synthesis of 2-amino-7-hydroxy-4-phenyl-4H-chromene-3-carbonitriles.

Entry	Catalyst (mmol)	T (°C)	Solvent (5 mL)	Time (h)	Yield (%) <sup>a</sup>
1	0.4	25 °C	H <sub>2</sub> O/EtOH (5 mL/2 mL)	10	20
2	0.1	80 °C	H <sub>2</sub> O/EtOH (5 mL/2 mL)	6.5	60
3	0.25	80 °C	H <sub>2</sub> O/EtOH (5 mL/2 mL)	3	70
4	0.4	80 °C	H <sub>2</sub> O/EtOH (5 mL/2 mL)	1.5	93
5	0.7	80 °C	H <sub>2</sub> O/EtOH (5 mL/2 mL)	2	90
6	0.4	80 °C	H <sub>2</sub> O	2.5	90
7	0.4	80 °C	EtOH	3	88
8	0.4	80 °C	n-Hexane	24	-
9	0.4	80 °C	CH <sub>2</sub> Cl <sub>2</sub>	24	-
10	0.4	80 °C	CH <sub>3</sub> CN	24	< 10%
11	0.4	80 °C	DMSO	24	< 10%

<sup>a</sup>Isolated yields

The difference in the results indicated the influence of solvent on the reaction mechanism. No yield was obtained in nonpolar solvents or under solvent-free conditions. Polar aprotic solvents like  $\text{CH}_3\text{CN}$  and DMSO afforded low yields. The highest yield of product was achieved in aqueous conditions.

The next reaction was done using various amounts of catalyst loading. The optimal catalyst amount was 0.4 mmol. The use of smaller amounts of ZnO afforded inferior product yield (Table 1). On the other hand, the use of higher quantities of ZnO did not provide any significant advantage in increasing the reaction yield (Table 1).

To study the scope and limitations of this procedure, a series of experiments were carried out using a variety of aromatic aldehydes. The results are presented in Table 2. The reactions worked well with almost all the aldehydes. However, aromatic aldehydes bearing electron withdrawing groups and no steric hindrance showed better reactivity and the reactions were completed in shorter times.

**Table 2.** Preparation of 2-amino-7-hydroxy-4-aryl-4*H*-chromene-3-carbonitriles using ZnO nanoparticles.

Entry	R	Product	Time (h)	Yield (%)
1	$\text{C}_6\text{H}_5$	<b>a</b>	1.5	93
2	$3\text{-NO}_2\text{C}_6\text{H}_6$	<b>b</b>	0.5	95
3	$4\text{-ClC}_6\text{H}_4$	<b>c</b>	3.5	95
4	$4\text{-OHC}_6\text{H}_4$	<b>d</b>	2.5	93
5	$2\text{-MeOC}_6\text{H}_4$	<b>e</b>	3.2	94
6	$3\text{-ClC}_6\text{H}_4$	<b>f</b>	2.5	96
7	$3\text{-OHC}_6\text{H}_4$	<b>g</b>	1.3	90
8	$4\text{-MeOC}_6\text{H}_4$	<b>h</b>	3	88
9	$2,4\text{-Cl}_2\text{C}_6\text{H}_3$	<b>i</b>	4	90
10	$4\text{-NO}_2\text{C}_6\text{H}_4$	<b>j</b>	1	92
11	$4\text{-FC}_6\text{H}_4$	<b>k</b>	1.2	85
12	$4\text{-N, N-Me}_2\text{C}_6\text{H}_4$	<b>l</b>	2	97
13	2-pyridinyl	<b>m</b>	0.7	92
14	$4\text{-MeC}_6\text{H}_4$	<b>n</b>	5	90
15	$2,6\text{-Cl}_2\text{C}_6\text{H}_3$	<b>o</b>	5.5	72
16	$2\text{-ClC}_6\text{H}_4$	<b>p</b>	2	91
17	2-Thienyl	<b>q</b>	0.6	90
18	$4\text{-BrC}_6\text{H}_4$	<b>r</b>	4	88

The recyclability study of the catalyst showed that the catalyst could be reused without any significant loss in its activity. The condensation reaction of resorcinol, malononitrile, and 3-nitrobenzaldehyde was chosen as a model of the reaction for the recovery investigations. The catalyst was recovered four times by simple filtration and washed with acetone and dried in an oven each time. The results are given in Table 3. The recovery samples showed similar activity to fresh samples, albeit with a loss of ZnO during recovery. In order to investigate the role of ZnO as catalyst in the reaction, IR spectra of fresh and recovered catalyst were obtained. The absorption bands located at around  $430$  and  $493\text{ cm}^{-1}$  are characteristic of Zn–O bond absorption.<sup>33</sup> The IR spectra showed that the catalyst can be efficiently recovered from the reaction mixture and no change in the structure of ZnO occurred.

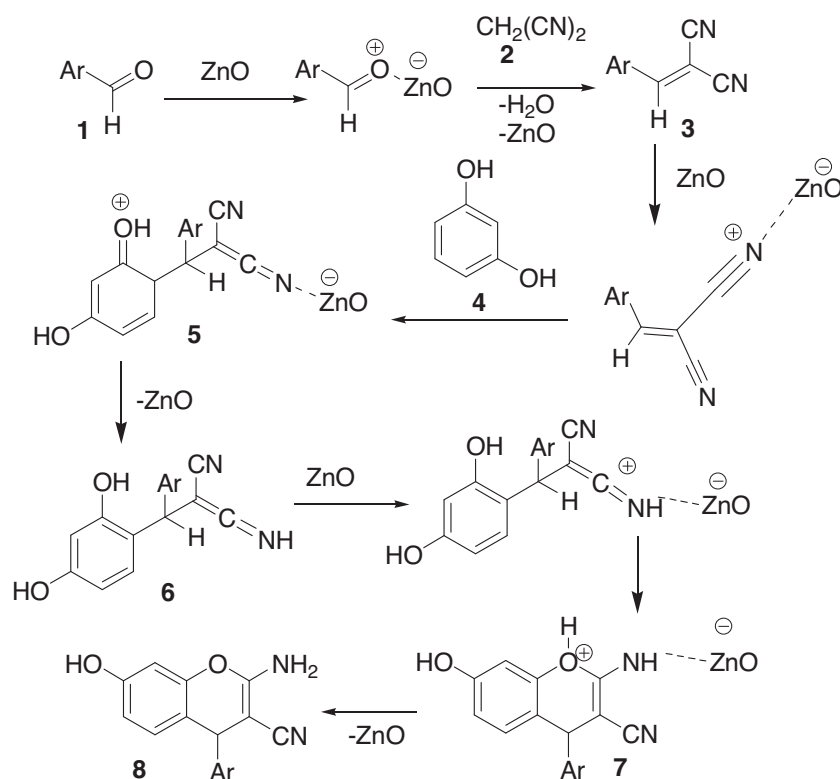
Taking into consideration the reported literature, a plausible reaction mechanism is outlined in Scheme 2. At first, aldehyde (**1**) was activated by ZnO to generate 2-arylidene malononitrile (**3**), which formed by condensation reaction of activated aldehyde with malononitrile (**2**). 2-Arylidene malononitrile after activation with ZnO underwent nucleophilic attack by resorcinol (**4**) to generate active intermediates (**5**), which simultaneously

aromatized (**6**), activated, and underwent cyclization (**7**) to form the final product (**7**), and ZnO was recovered from the reaction mixture.

**Table 3.** Reusability of ZnO nanoparticles.

Run	Time (min)	Yield (%) <sup>a</sup>
1	30	95
2	30	94
3	30	92
4	30	90

<sup>a</sup> Isolated yields. Reaction conditions: malononitrile (1 mmol), 3-nitrobenzaldehyde (1 mmol), and resorcinol (1 mmol)



**Scheme 2.** Plausible mechanism for the formation of 2-amino-7-hydroxy-4-aryl-4H-chromene-3-carbonitrile derivatives.

A relative study was executed for the use of ZnO nanoparticles with some of the reported literature for the synthesis of 2-amino-7-hydroxy-4-aryl-4H-chromene-3-carbonitrile derivatives (Table 4). The results showed that ZnO is comparable with other catalysts in terms of time and yield of the reaction product and could be considered an environmentally friendly catalyst.

In summary, a high yielding one-pot condensation reaction of resorcinol, aromatic aldehydes, and malononitrile for the synthesis of 2-amino-7-hydroxy-4-aryl-4H-chromene-3-carbonitriles was developed. ZnO nanoparticles prepared via a green method were used in catalytic quantities. Various aromatic aldehydes afforded the corresponding products in high yields. The main advantage of the present work is the use of a new method for the preparation of ZnO nanoparticles via green biosynthesis.

**Table 4.** Comparison results of ZnO nanoparticles with other catalysts reported in the literature.

Entry	Catalyst	Condition	Yield (%) <sup>a</sup>	Reference
1	KOH	H <sub>2</sub> O; r.t.; 2 h	50	23
2	MgO	H <sub>2</sub> O; r.t.; 1.5 h	62	23
3	POPINO	H <sub>2</sub> O; reflux; 20 min	90	18
4	2,2,2-trifluoroethanol	2,2,2-trifluoroethanol, reflux; 5 h	90	19
5	Fe <sub>3</sub> O <sub>4</sub> -chitosan nanoparticles	ultrasound irradiation, 50 °C, 20 min	99	22
6	ZnO nanoparticles	H <sub>2</sub> O/EtOH; 80 °C, 1.5 h	93	present work

<sup>a</sup>Isolated yields; based on the preparation of 2-amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitriles

### 3. Experimental

All reagents were purchased from Merck and Aldrich and used without further purification. FE-SEM images were obtained on a HITACHI S-4160. The NMR spectra were recorded on a Bruker Avance DPX 400 MHz instrument. The spectra were measured in DMSO-d<sub>6</sub> relative to TMS (0.00 ppm). Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on silica gel Polygram SIL G/UV 254 plates. IR spectra were recorded on a Galaxy 5000 FT-IR spectrophotometer. All of the compounds were solid and solid state IR spectra were recorded using the KBr disk technique.

#### 3.1. Preparation of ZnO nanoparticles

At first, 20 g of mulberry leaves were ground and inserted in a 250 mL balloon flask containing 150 mL of deionized water and 50 mL of ethanol. The mixture was refluxed for 4 h and the extract was filtered to remove unnecessary substances. Next two different solutions were prepared: Solution A: To a solution of ZnCl<sub>2</sub> (50 mmol) in 100 mL of water, mulberry leaf extract (50 mL) and *n*-hexane (100 mL) were added; Solution B: a solution of 2-amino ethanol (150 mmol) in 50 mL of mulberry leaf extract. Solution B was poured into solution A slowly and dropwise under vigorous magnetic stirring and the resulting precipitate was filtered, washed with water several times, dried, and calcinated at 500 °C for 2 h.

#### 3.2. General procedure for synthesis of 2-amino-7-hydroxy-4-aryl-4*H*-chromene-3-carbonitriles

A mixture of aldehyde (1 mmol), resorcinol (1 mmol), malononitrile (1 mmol), and ZnO (0.4 mmol) in H<sub>2</sub>O/EtOH (5 mL/2 mL) was refluxed for the appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was dissolved in the least amount of hot ethanol needed. The catalyst was removed by simple filtration. The filtrate was concentrated and the obtained crude product was separated and purified by recrystallization from ethanol.

##### Selected data:

**2-Amino-7-hydroxy-4-phenyl-4*H*-chromene-3-carbonitrile (Table 2, Product a):** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 4.63 (s, 1H, CH), 6.40–6.51 (m, 2H), 6.80 (d, *J* = 8.5 Hz, 1H), 6.96 (s, 2H, NH<sub>2</sub>), 7.18–7.30 (m, 5H), 9.73 (s, 1H, OH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 54.1, 102.3, 112.6, 113.8, 120.1, 126.9, 127.5, 128.9, 129.8, 146.2, 148.8, 157.5, 160.1 ppm. Anal. Calcd. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.72; H, 4.58; N, 10.60%. Found: C, 72.87; H, 4.69; N, 10.84%;

**2-Amino-4-(4-chlorophenyl)-7-hydroxy-4*H*-chromene-3-carbonitrile (Table 2, Product c):** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 4.67 (s, 1H, CH), 6.41–6.51 (m, 2H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.94 (s, 2H, NH<sub>2</sub>), 7.19 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 9.75 (s, 1H, OH) ppm; <sup>13</sup>C NMR (100 MHz,

DMSO-d<sub>6</sub>):  $\delta = 55.7, 102.2, 112.4, 119.7, 120.5, 128.3, 128.4, 129.8, 131.1, 145.3, 148.7, 157.2, 160.2, 192.1$  ppm. Anal. Calcd. for C<sub>16</sub>H<sub>11</sub>ClN<sub>2</sub>O<sub>2</sub>: C, 64.33; H, 3.71; N, 9.38%. Found: C, 64.53; H, 3.56; N, 9.49%.

**2-Amino-4-(4-bromophenyl)-7-hydroxy-4H-chromene-3-carbonitrile (Table 2, Product r):** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta = 4.65$  (s, 1H, CH), 6.40–6.51 (m, 2H), 6.79 (d,  $J = 8.8$  Hz, 1H), 6.94 (s, 2H, NH<sub>2</sub>), 7.13 (d,  $J = 8.4$  Hz, 2H), 7.51 (d,  $J = 8.4$  Hz, 2H), 9.75 (s, 1H, OH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta = 55.7, 102.2, 112.4, 113.1, 119.7, 120.5, 128.9, 131.2, 132.3, 145.7, 148.8, 157.2, 160.2, 192.3$  ppm. Anal. Calcd. for C<sub>16</sub>H<sub>11</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 56.00; H, 3.23; N, 8.16%. Found: C, 56.24; H, 3.01; N, 8.37%.

**2-Amino-7-hydroxy-4-(4-nitrophenyl)-4H-chromene-3-carbonitrile (Table 2, Product j):** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta = 4.87$  (s, 1H, CH), 6.44–6.52 (m, 2H), 6.81 (d,  $J = 8.4$  Hz, 1H), 7.06 (s, 2H, NH<sub>2</sub>), 7.45 (d,  $J = 8.8$  Hz, 2H), 8.20 (d,  $J = 8.8$  Hz, 2H), 9.82 (s, 1H, OH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta = 55.3, 102.6, 112.5, 112.8, 120.6, 124.2, 128.9, 130.2, 146.5, 149.1, 154.0, 157.7, 160.6$  ppm. Anal. Calcd. for C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>O<sub>4</sub>: C, 62.14; H, 3.58; N, 13.59%. Found: C, 62.02; H, 3.41; N, 13.71%.

**2-Amino-7-hydroxy-4-p-tolyl-4H-chromene-3-carbonitrile (Table 2, Product n):** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta = 2.27$  (s, 3H), 4.69 (s, 1H, CH), 6.41–6.52 (m, 2H), 6.79 (d,  $J = 8.4$  Hz, 1H), 6.95 (s, 2H, NH<sub>2</sub>), 7.09 (d,  $J = 8.3$  Hz, 2H), 7.27 (d,  $J = 8.3$  Hz, 2H), 9.71 (s, 1H, OH) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>):  $\delta = 21.2, 49.6, 57.3, 113.1, 113.6, 114.8, 119.2, 126.7, 129.3, 132.1, 139.7, 141.4, 155.7, 158.7, 163.3$  ppm. Anal. Calcd. for C<sub>17</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 73.37; H, 5.07; N, 10.07%. Found: C, 73.51; H, 5.25; N, 10.30%

## Acknowledgments

We are grateful to the Arak University research council for partial support of this research. Also the authors wish to thank Ms Somayeh Veyseh for her valuable help in this study for characterization of FE-SEM and EDX.

## References

1. Curini, M.; Cravotto, G.; Epofano, F.; Giannone, G. *Curr. Med. Chem.* **2006**, *13*, 199–222.
2. Litvinov, Y. M.; Shestopalov, A. M. *Adv. Heterocycl. Chem.* **2011**, *103*, 175–260.
3. Desimone, R. W.; Currie, K. S.; Mitchell, S. A.; Darrow, J. W.; Pippin, D. A. *Comb. Chem. High T. Scr.* **2004**, *7*, 473–494.
4. Patchett, A. A.; Nargund, R. P. *Ann. Rep. Med. Chem.* **2000**, *35*, 289–298.
5. Kemnitzer, W.; Kasibhatla, S.; Jiang, S.; Zhang, H.; Zhao, J.; Jia, S.; Xu, L.; Crogan-Grundy, C.; Denis, R.; Barriault, N.; et al. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 4745–4751.
6. McKee, T. C.; Fuller, R. W.; Covington, C. D.; Cardellina, J. H. II.; Gulakowski, R. J.; Krepps, B. L.; McMahon, J. B.; Boyd, M. R. *J. Nat. Prod.* **1996**, *59*, 754–758.
7. Galinis, D. L.; Fuller, R. W.; McKee, T. C.; Cardellina, J. H. II.; Gulakowski, R. J.; McMahon, J. B.; Boyd, M. R. *J. Med. Chem.* **1996**, *39*, 4507–4510.
8. Cardellina, J. H. II.; Bokesch, H. R.; McKee, T. C.; Boyd, M. R. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 1011–1014.
9. Garino, C.; Bihel, F.; Pietrancosta, N.; Laras, Y.; Quéléver, G.; Woo, I.; Klein, P.; Bain, J.; Boucher, J.-L.; Kraus, J. L. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 135–138.
10. Shanthi, G.; Perumal, P. T.; Rao, U.; Sehgal, P. K. *Indian J. Chem.* **2009**, *48B*, 1319–1323.
11. Johnson, A. J.; Kumar, R. A.; Rasheed, S. A.; Chandrika, S. P.; Chandrasekhar, A.; Baby, S.; Subramoniam, A. *J. Ethnopharmacol.* **2010**, *130*, 267–271.



12. Alizadeh, B. H.; Foroumadi, A.; Ardestani, S. K.; Poorrajab, F.; Shafiee, A. *Turk. J. Chem.* **2009**, *33*, 47–58.
13. El-Sayed Ali, T.; Abdel-Aghfaar Abdel-Aziz, S.; Metwali-Shafer, H.; Hanafy, F. I.; El-Fauomy, A. Z. *Turk. J. Chem.* **2008**, *32*, 365–374.
14. Gao, Y.; Yang, W.; Du, D. M. *Tetrahedron: Asymmetr.* **2012**, *23*, 339–344.
15. Reynolds, G. A.; Drexhage, K. H. *Opt. Commun.* **1975**, *13*, 222–225.
16. Zollinger, H. *Color Chemistry*; 3rd ed.; Verlag Helvetica Chimica Acta: Zurich and Wiley-VCH: Weinheim, Germany 2003.
17. Ellis, G. P. In *The Chemistry of Heterocyclic of Compounds. Chromenes, Harmones and Chromones*; Weissberger, A., Taylor, E. C., Eds.; John Wiley: New York, NY, USA, 1977; Chapter II.
18. Dekamin, M. G.; Eslami, M.; Maleki, A. *Tetrahedron* **2013**, *69*, 1074–1085.
19. Khaksar, S.; Rouhollahpour, A.; Mohammadzadeh Talesh, S. *J. Fluorine Chem.* **2012**, *141*, 11–15.
20. Shi, D. Q.; Zhang, S. I.; Zhuang, Q. Y.; Wang, X. S. *Chin. J. Org. Chem.* **2003**, *23*, 1419–1421.
21. Lu, C.; Huang, X. J.; Li, Y. Q.; Zhou, M. Y.; Zheng, W. *Monatsh. Chem.* **2009**, *140*, 45–47.
22. Safari, J.; Javadian, L. *Ultrason. Sonochem.* **2015**, *22*, 331–338.
23. Safari, J.; Zarnegar, Z.; Heydarian, M. *J. Taibah Univ. Sci.* **2013**, *7*, 17–25.
24. Banerjee, S.; Payra, S.; Saha, A.; Sereda, G. *Tetrahedron Lett.* **2014**, *55*, 5515–5520.
25. Banerjee, S.; Saha A. *New J. Chem.* **2013**, *37*, 4170–4175.
26. Dharma Rao, G. B.; Kaushik, M. P.; Halve, A. K. *Tetrahedron Lett.* **2012**, 2741–2744.
27. Hosseini Sarvari, M.; Sharghi, H. *Tetrahedron* **2005**, *61*, 10903–10907.
28. Moison, H.; Texier-Boullet, F.; Foucaud, A. *Tetrahedron* **1987**, *43*, 537–542.
29. Indulkar, U. U.; Kale, S. R.; Gawande, M. B.; Jayaram, R. V. *Tetrahedron Lett.* **2012**, *53*, 3857–3860.
30. Mohammad Shafiee, M. R.; Moloudi, R.; Ghashang, M. *APCBEE Procedia* **2012**, *1*, 221–225.
31. Mobinikhaledi, A.; Foroughifar, N.; Mosleh, T.; Hamta A. *Iran. J. Pharm. Res.* **2014**, *13*, 873–879.
32. Mobinikhaledi, A.; Moghanian, H.; Sasani, F. *Syn. React. Inorg. Met-Org. Chem.* **2011**, *41*, 262–265.
33. Ambrožič, G.; Djerdj, I.; Škapin, S. D.; igon, M.; Crnjak Orel, Z. *Cryst. Eng. Comm.* **2010**, *12*, 1862–1868.