

# An efficient, multicomponent approach for solvent-free synthesis of 2-amino-4*H*-chromene scaffold

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Received: 15 August 2009 / Accepted: 14 March 2010 / Published online: 7 April 2010  
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**Abstract** Solvent-free one-pot synthesis of 2-amino-4*H*-chromene scaffold is described in a very simple, efficient, and environmentally benign method using sodium carbonate as a cheap and non-toxic catalyst with up to excellent yields.

**Keywords** 2-Amino-4*H*-chromenes · Solvent-free · Multicomponent reactions · Domino reactions · Knoevenagel–Michael addition

## Introduction

The chromene moiety is an important structural component of many naturally occurring compounds. A particularly interesting group of chromenes are 2-amino-4*H*-chromenes (or 2-amino-4*H*-benzo[*b*]pyrans), since they are used as cosmetics and pigments [1,2], spasmolytic, diuretic, anticoagulant, antianaphylactic [3,4], antibacterial [5], anticancer agents [6], and as potent apoptosis inducers [7].

A multicomponent reaction (MCR) is a one-pot reaction in which three or more reactants are combined together to generate a desired product without the isolation of any intermediate [8,9]. The MCR strategy has gained increasing attention in the past decade because of its capability to prepare com-

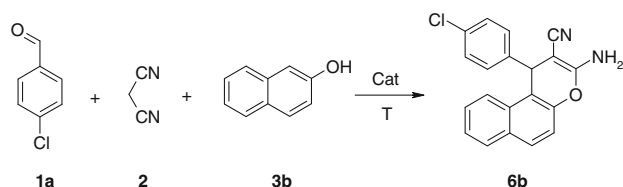
pound libraries in the field of modern medicinal and combinatorial chemistry [10–12]. The combination of solvent-free and MCR reactions represents a very powerful method from both economical and synthetic points of view since the isolation of the intermediates is skipped, the overall reaction time is significantly decreased, higher yields of products are obtained, and due to less use of solvents and reagents the costs are lowered.

2-Amino-4*H*-chromenes are generally prepared by refluxing active methylene compounds (e.g., malononitrile and cyanoacetic acid esters), with an aldehyde and an activated phenol in organic solvents such as ethanol and acetonitrile, and in the presence of organic bases such as piperidine for several hours [13–16]. Recently, several modified catalysts such as cetyltrimethylammonium chloride [17], cetyltrimethylammonium bromide under ultrasound irradiation [18], KSF clay [19], KF/Al<sub>2</sub>O<sub>3</sub> [20], TiCl<sub>4</sub> [21], triethylamine [22], basic  $\gamma$ -alumina [23], MgO [24], heteropolyacids [25], basic ionic liquids [26], iodine/K<sub>2</sub>CO<sub>3</sub> [27], and DABCO [28] have been used in this reaction. However, only a few of these catalysts (e.g., MgO, basic alumina) are suitable to catalyze the reaction of malononitrile with aromatic aldehydes with active  $\alpha$ -naphthol (but not suitable for less active  $\beta$ -naphthols), whereas some others require longer reaction times, difficult workup procedures and afford only moderate yields.

For these reasons and in our continuing interest in the development of environmental friendly protocols for one-pot solvent-free multi-component reactions [29–35], we report herein our results for the synthesis of 2-amino-4*H*-chromene scaffold using Na<sub>2</sub>CO<sub>3</sub> as an efficient catalyst for the three-component solvent-free condensation of an aldehyde, malononitrile and an activated phenol with excellent yields.

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**Scheme 1** The model reaction of *p*-chlorobenzaldehyde (**1a**), malononitrile (**2**) and  $\beta$ -naphthol (**3b**)

## Results and discussion

The model reaction was carried out simply by mixing of *p*-chlorobenzaldehyde (**1a**), malononitrile (**2**) and  $\beta$ -naphthol (**3b**) (1.0 mmol each) and various basic or acidic catalysts (0.1 mmol) in a mortar and pestle (Scheme 1). The resulting mixture was heated in a drying oven at the temperature and for the given time in Table 1.

In the absence of any catalyst, no reaction was observed at room temperature and all starting materials remained unchanged, whereas after raising the temperature to 125 °C

*p*-chlorobenzaldehyde (**1a**) and malononitrile (**2**) reacted together to produce **4** (Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>) (Scheme 2). The formation of this intermediate was confirmed by comparison of its mp and NMR spectra as reported in the literature [30]. Below this temperature, only traces of **4** were detected even in the presence of Na<sub>2</sub>CO<sub>3</sub>. As we have previously reported [30], the condensation of malononitrile and an aromatic aldehyde occurs easily under solvent-free conditions even in the absence of a catalyst, but the reaction is incomplete at lower temperatures. However, at 150 °C compound **6b** is formed with an acceptable yield, after *ortho* C-alkylation of  $\beta$ -naphthol (**3b**) by in situ prepared **4** giving the intermediate **5b**, followed by nucleophilic addition of the phenolic OH group to the CN moiety and subsequent tautomerization (Scheme 2). As it is shown in Table 1, quantitative yield of **6b** was obtained using sodium carbonate under solvent-free heating at 125 °C for 1 h.

The scope and the generality of the present method were then further demonstrated by the reaction of various aromatic aldehydes with malononitrile and  $\alpha$ - or  $\beta$ -naphthol. In all cases, up to quantitative yields in reasonable reaction times were obtained. Both  $\alpha$ - and  $\beta$ -naphthol are sufficiently active to give the corresponding products in high yields. Contrary to what has been previously reported [28], no remarkable decrease in the yields was observed for the *ortho*-substituted benzaldehyde derivatives.

The reactions of *p*-hydroxybenzaldehyde with **2** and 4-chloro-1-naphthol, and **1a** and **2** with 4-hydroxycumarine proceed also smoothly to yield **6q** and **6s**, respectively, although with moderate yields.

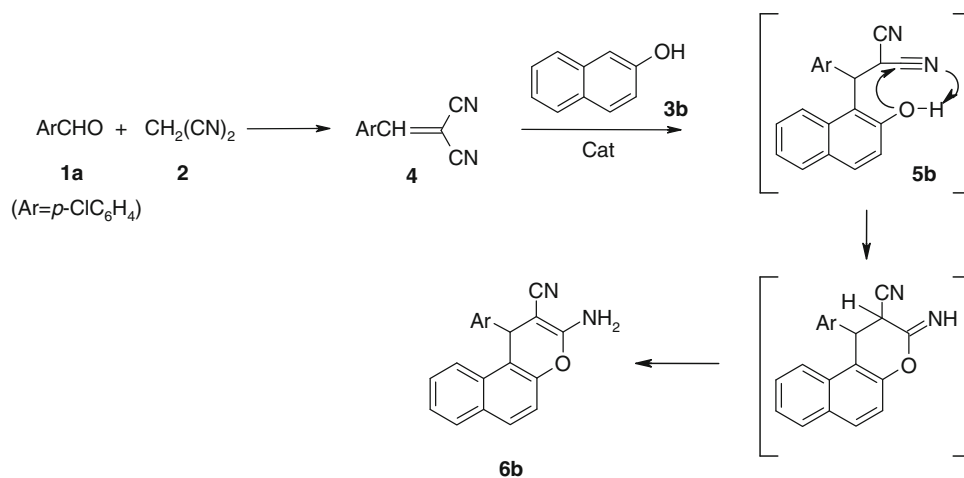
The structures of all products were determined on the basis of their analytical and/or spectral data. The <sup>1</sup>H NMR spectra of the products show a characteristic signal at 4.90–5.90 ppm for H-4 and the <sup>13</sup>C NMR spectra exhibit a specific signal in the region of 54–60 ppm that is related to C-4.

**Table 1** Effect of various catalysts for the preparation of **6b**

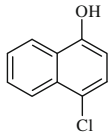
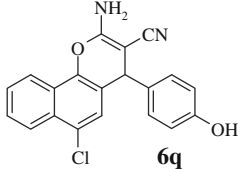
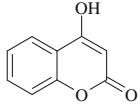
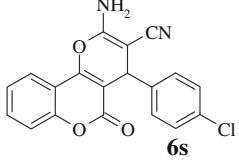
Catalyst <sup>a</sup>	Time (h)	Temperature (°C)	Yield (%) of <b>6b</b>
–	4	rt	–
–	4	125	–
–	4	150	78
Na <sub>2</sub> CO <sub>3</sub>	1	rt	–
Na <sub>2</sub> CO <sub>3</sub>	1	125	100
NaHCO <sub>3</sub>	1	125	89
SiO <sub>2</sub>	4	125	60
Al <sub>2</sub> O <sub>3</sub>	3.5	125	55
Na <sub>2</sub> SO <sub>4</sub>	3.5	125	67

<sup>a</sup> 0.1 mmol each for 1.0 mmol of **1a**

**Scheme 2** Possible mechanism for the reaction of *p*-chlorobenzaldehyde (**1a**), malononitrile (**2**) and  $\beta$ -naphthol (**3b**) to yield (**6b**)



**Table 2** Synthesis of 2-amino-4*H*-chromenes under solvent-free condition catalyzed by sodium carbonate <sup>a</sup>

Entry	Ar	Naphthol	Product	Time (min)	Yield (%) <sup>b</sup>	M P (°C)
1	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	$\alpha$ -naphthol	<b>6a</b>	30	99	232(231–232) [26]
2	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	$\beta$ -naphthol	<b>6b</b>	60	100	203–205(206–208) [26]
3	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	$\alpha$ -naphthol	<b>6c</b>	60	91	210–212(188–189) [24]
4	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	$\beta$ -naphthol	<b>6d</b>	120	90	185–186(188) [26]
5	<i>p</i> -OMeC <sub>6</sub> H <sub>4</sub>	$\alpha$ -naphthol	<b>6e</b>	40	91	179–181(176–179) [25]
6	<i>p</i> -OMeC <sub>6</sub> H <sub>4</sub>	$\beta$ -naphthol	<b>6f</b>	120	88	188–189(182–183) [26]
7	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	$\alpha$ -naphthol	<b>6g</b>	30	96	235–237(236–237) [17]
8	<i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	$\beta$ -naphthol	<b>6h</b>	40	94	259–261(259–261) [17]
10	<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	$\alpha$ -naphthol	<b>6i</b>	15	98	210–213(208–211) [25]
11	<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	$\beta$ -naphthol	<b>6j</b>	30	92	232–235(239–241) [23]
12	<i>p</i> -OHC <sub>6</sub> H <sub>4</sub>	$\alpha$ -naphthol	<b>6k</b>	45	100	227–228(187–188) [17]
13	<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	$\beta$ -naphthol	<b>6l</b>	30	98	258–261(258–260) [23]
14	<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	$\alpha$ -naphthol	<b>6m</b>	50	95	275–277(285–287) [23]
15	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	$\beta$ -naphthol	<b>6n</b>	30	99	241–243(241–243) [23]
16	<i>o</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	$\alpha$ -naphthol	<b>6o</b>	15	100	237–239(241–242) [23]
17	C <sub>6</sub> H <sub>5</sub>	$\beta$ -naphthol	<b>6p</b>	40	100	273–275(280) [26]
18	<i>p</i> -OHC <sub>6</sub> H <sub>4</sub>			60	76	242–243(241–242) [36]
19	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>			150	67	263–266(263–265) [37]

<sup>a</sup> mmol ratio of aldehyde/malononitrile/naphthol/Na<sub>2</sub>CO<sub>3</sub> is 1.0/1.0/1.0/0.1<sup>b</sup> The yields refer to isolated yields

## Conclusions

In summary, we have reported a new and effective methodology for the eco-compatible preparation of 2-amino-4*H*-chromenes via one-pot three component reaction of aromatic aldehydes, malononitrile, and active naphthols using a catalytic amount of Na<sub>2</sub>CO<sub>3</sub> under solvent-free conditions. This is of special interest, because Na<sub>2</sub>CO<sub>3</sub> is a very cheap, environmental friendly and commercially available catalyst. The use of an inexpensive catalyst, avoiding use of hazardous organic bases and organic solvents, easy workup, short reaction times, and mild reaction conditions make this method very attractive and practical.

## Material and methods

All chemicals used in this study were purchased from Merck or Fluka and used without further purification. Melting points

were determined with an Electrothermal melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded with a Shimadzu 8400s FT-IR spectrometer using potassium bromide pellets. <sup>1</sup>HNMR spectra (500MHz) were recorded on a DRX-500 Advance Bruker spectrometer. The chemical shifts are reported in ppm ( $\delta$ -scale) relative to internal TMS and coupling constants are reported in DMSO-*d*<sub>6</sub>. All products are known compounds and were identified by comparing of their physical and spectra data with those reported in the literature.

## General procedure for preparation of 2-Amino-4*H*-Chromenes

In a typical experiment, a stoichiometric mixture of an aldehyde, malononitrile, naphthol (1.0 mmol each), and sodium carbonate (0.1 mmol) mixed together using a mortar and pestle. The result mixture was heated in a drying oven at 125 °C.

After cooling, the mixture was washed with hot water and purified by recrystallization from hot ethanol, if necessary. The results are summarized in Table 2.

#### Selected characterization data

**Compound 6a:** 4*H*-Naphtho[1,2-*b*]pyran-3-carbonitrile, 2-amino-4-(4-chlorophenyl)

White solid, IR (KBr),  $\nu(\text{cm}^{-1})$ : 3408, 3326, 2190, 1649, 1590;  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz),  $\delta$  (ppm): 5.36 (s, 1H, CH), 7.0 (s, 2H,  $\text{NH}_2$ ), 7.20 (d, 2H,  $J=8.2$  Hz, ArH), 7.33–7.38 (m, 3H, ArH), 7.41–7.47 (m, 2H, ArH), 7.81 (d, 1H,  $J=8.02$  Hz, ArH), 7.91–7.96 (m, 2H, ArH).

**Compound 6b:** 1*H*-Naphtho[2,1-*b*]pyran-2-carbonitrile, 3-amino-1-(4-chlorophenyl)

White solid, IR (KBr),  $\nu(\text{cm}^{-1})$ : 3452, 3334, 2190, 1666, 1590, 1409;  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz),  $\delta$  (ppm): 4.95 (s, 1H, CH), 7.09 (d, 1H,  $J=8.53$  Hz, ArH), 7.19 (s, 2H,  $\text{NH}_2$ ), 7.27 (d, 2H,  $J=8.37$  Hz, ArH), 7.36 (d, 2H,  $J=8.35$  Hz, ArH), 7.57–7.66 (m, 3H, ArH), 7.89 (d, 1H,  $J=8.02$  Hz, ArH), 8.24 (d, 1H,  $J=8.31$  Hz, ArH).

**Compound 6j:** 1*H*-Naphtho[2,1-*b*]pyran-2-carbonitrile, 3-amino-1-(3-nitrophenyl)

Pale yellow solid, IR (KBr),  $\nu(\text{cm}^{-1})$ : 3462, 3356, 2190, 1654, 1589;  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz),  $\delta$  (ppm): 5.63 (s, 1H, CH), 7.17 (s, 2H,  $\text{NH}_2$ ), 7.38 (d, 1H,  $J=8.9$  Hz, ArH), 7.42–7.48 (m, 2H, ArH), 7.57 (t, 1H,  $J=7.8$  Hz, ArH), 7.67 (d, 1H,  $J=7.7$  Hz, ArH), 7.86 (d, 1H,  $J=8.2$  Hz, ArH), 7.93 (d, 1H,  $J=7.6$  Hz, ArH), 7.98 (d, 1H,  $J=8.9$  Hz, ArH), 8.03 (d, 1H,  $J=8.07$  Hz, ArH), 8.08 (s, 1H, ArH),  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz), 57.82, 115.47, 117.74, 121.04, 122.18, 122.72, 124.36, 126.03, 128.28, 129.48, 130.78, 130.95, 131.33, 131.73, 134.59, 147.84, 148.75, 148.86, 160.84.

**Compound 6o:** 4*H*-Naphtho[1,2-*b*]pyran-3-carbonitrile, 2-amino-4-(2-nitrophenyl)

Pale yellow solid, IR (KBr),  $\nu(\text{cm}^{-1})$ : 3419, 3326, 2192, 1651, 1590;  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz),  $\delta$  (ppm): 4.94 (s, 1H, CH), 7.09 (d, 1H,  $J=7.9$  Hz, ArH), 7.19 (s, 2H,  $\text{NH}_2$ ), 7.21–7.23 (d, 2H,  $J=7.6$  Hz, ArH), 7.51 (d, 2H,  $J=7.33$  Hz, ArH), 7.59–7.65 (m, 3H, ArH), 7.89 (d, 1H,  $J=7.7$  Hz, ArH), 8.23 (d, 1H,  $J=7.9$  Hz, ArH).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz), 56.62, 118.19, 120.95, 121.24, 121.58, 123.59,

124.89, 126.94, 127.62, 127.75, 128.57, 130.82, 132.48, 133.62, 143.61, 145.95, 161.02.

**Acknowledgment** We acknowledge Iran University of Science and Technology (IUST) for partial financial support of this study.

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