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Original article

# Novel one-pot synthesis of 4*H*-chromene derivatives using amino functionalized silica gel catalyst



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# 1. Introduction

Base-catalyzed condensation and addition reactions such as the Aldol, Knoevenagel and Michael reactions are well reported in the literature for the production of drugs, fragrances, and chemical intermediates [1–4]. The use of novel environmentally friendly solid catalysts for the synthesis of biologically potent heterocyclic compounds has become one of the most active areas of research. Heterogeneous catalysts, particularly the solid-base catalysts synthesized by the functionalization of several solid-state materials are capable of catalyzing various C–C coupling reactions [5,6].

Recently, mesoporous silica (OMS) and related materials have become popular as catalysts and adsorbents and have found extensive applications as containers for cluster/nanowire growth, *etc.* [7]. These materials have several advantages such as tunable pore diameter and high surface area, for which they have emerged as effective heterogeneous catalysts in organic synthesis [8]. Aminopropyl functionalized mesoporous silica materials are reported to be effective base catalysts for Knoevenagel condensation [9], Aldol condensation [10], Michael addition [9], epoxidation reactions [11], and Claisen–Schmidt condensations [12]. Furthermore, the development of biomimetic catalysts is also well reported in the literature [13]. The use of such heterogeneous

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ABSTRACT

A simple, efficient, and environmentally benign method for the synthesis of 4*H*-chromene derivatives was developed using well ordered and recoverable amino functionalized silica gel as a base catalyst. The 4*H*-chromene derivatives were obtained in short time and excellent yield (87%-96%) by three component reaction of aldehydes, malononitrile and cyclic 1,3-diketones in water at 70 °C.

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catalysts offers several advantages in process development, particularly the separation of products from catalyst, and recycling of catalyst in reactor. Solid acidic and basic catalysts are alternatives for clean technologies and sustainable chemistry for different processes.

Tetrahydrochromene moiety is an important class of benzopyran derivatives found in many natural products [14]. More specifically, 2-amino-4H-chromene-3-carbonitrile derivatives possess many biological activities such as anticancer, anticoagulant, antibacterial, and fungicidal properties [15]. These compounds find extensive applications in different fields, such as cosmetics, pigments, and agrochemicals [16]. Polyfunctionalized 4H-pyrans constitute the essential part of several natural products [17] and are also known as potential calcium channel antagonists [18]. As a result of widespread applications, the synthesis of these compounds has attracted a lot of interest. From the literature survey, numerous methods have been reported for the synthesis of tetrahydrochromene derivatives by one pot three component condensation of aldehyde, malononitrile and 1,3dicarbonyl compounds using acidic or basic catalysts. Mola et al. documented borax catalyzed three component coupling of tetrahydrochromene in refluxing ethanol [19]. Silica-bonded N-propylpiperazine sodium n-propionate was employed as a recyclable catalyst for the synthesis of tetrahydrochromene derivatives [20]. Nano-ZnO catalyzed synthesis of dihydropyrano[2,3-c]chromenes can be accomplished in aqueous medium [21]. The other methods used for the synthesis of these compounds

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Scheme 1. Synthesis of 2-amino-5-oxo-4-phenyl-5,6-dihydro-4H-benzo[H]chromene-3-carbonitrile derivatives.

involve basic catalysts such as piperidine [22], morpholine, pyridine [23], triethylamine [24] and sodium bromide [25]. The reported methods still have drawbacks such as long reaction time, high reaction temperature and use of toxic organic solvents. Therefore, development of a simpler synthesis method for chromene derivatives becomes essential. In the present study we report the synthesis of 2-amino-5-oxo-4-phenyl-5,6-dihydro-4H-benzo[H]chromene-3-carbonitrile derivatives by the reaction of aldehyde (1a) with 5,5-dimethylcyclohexane-1,3-dione (2) and malononitrile (3) at 70 °C using aminopropylated SiO<sub>2</sub> (AP-SiO<sub>2</sub>) as a polyamine heterogeneous base catalyst (Scheme 1).

### 2. Experimental

All solvents were used as commercial grade without further purification. Silica gel coated aluminium sheets (Merck made) were used for thin layer chromatography to monitor progress of reactions. The column chromatography was done over silica gel (80–120 mesh). Melting points were determined in an open capillary tube and are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 300 MHz spectrometer in CDCl<sub>3</sub> solvent. Mass spectra were taken on Polaris-Q Thermoscientific GC–MS. Silica gel supported polyamine catalyst was prepared by a known literature process [27].

#### 2.1. General procedure for the synthesis of 4H-chromene derivatives

The mixture of aromatic aldehyde (1 mmol), 5,5-dimethylcyclohexane-1,3-dione **2** (1 mmol), and malononitrile **3** (1 mmol) was taken in water. To this mixture 10 mol% of solid aminopropylated SiO<sub>2</sub> catalyst was added. The reaction mixture was stirred at 70 °C for the appropriate time (as shown in Table 1) and the progress of reaction was monitored by thin layer chromatography. After completion of reaction as indicated by TLC, the reaction mixture was cooled at room temperature. The solvent was removed under vacuum to obtain the crude product. To the crude product, ethyl acetate was added and the solid catalyst was filtered off. The organic layer was evaporated to obtain the solid product. The obtained product was purified by recrystallization using ethyl acetate to get the desired compound **4a–n**. All compounds were characterized by comparing their spectral data with those reported in literature [15,26–27]. Spectral data for representative and newly synthesized compounds is listed below.

2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (**4a**): White solid, mp 235–237 °C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.79–7.89 (m, 2H), 7.41–7.50 (m, 1H), 6.88–7.04 (m, 2H), 6.57 (brs, 2H, NH), 4.29 (s, 1H), 2.58 (s, 2H), 2.26 (m, 1H), 2.01 (m, 1H), 1.23 (s, 3H), 0.84 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  201.2, 162.3, 155.8, 145.6, 128.7, 127.5, 119.2, 112.1, 57.6, 49.9, 40.3, 39.9, 36.1, 27.4; GC–MS: *m/z* 294 (M+); Elem. Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>: C, 73.45; H, 6.16; N, 9.52; O, 10.87; found: C, 73.43; H, 6.18; N, 9.54; O, 10.90.

2-Amino-7,7-dimethyl-5-oxo-4-(3,4,5-trimethoxyphenyl)-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**4f**): Yellow solid, mp 247–249 °C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.29–7.41 (m, 2H), 6.71 (brs, 2H, NH), 4.22 (s, 1H), 3.73 (s, 9H), 2.51 (s, 2H), 2.23 (m, 1H), 2.17 (m, 1H), 1.10 (s, 3H), 0.92 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  201.1, 160.0, 157.8, 132.0, 129.6, 129.0, 119.1, 107.2, 106.4, 60.3, 59.3, 57.1, 50.0, 38.0, 32.3, 28.9; GC–MS *m*/*z* 384 (M+); Elem. Anal. Calcd. for C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>5</sub>: C, 65.61; H, 6.29; N, 7.29; O, 20.81; found: C, 65.63; H, 6.26; N, 7.31; O, 20.83.

2-Amino-7,7-dimethyl-5-oxo-4-(2,3-dichlorophenyl)-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**4i**): White solid, mp 225–227 °C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.17–7.21 (m, 1H), 7.40–7.47 (m, 1H), 7.82–7.90 (m, 1H), 6.72 (brs, 2H, NH), 4.24 (s, 1H), 2.61 (s, 2H), 2.28 (m, 1H), 2.06 (m, 1H), 0.94 (s, 3H), 0.74 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  200.7, 159.8, 154.0, 140.1, 131.3, 130.2, 130.0, 119.2, 113.2, 67.6, 60.0, 44.3, 41.2, 32.1, 28.6; GC–MS: *m*/*z* 363 (M+); Elem. Anal. Calcd. for C<sub>18</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 59.52; H, 4.44; Cl, 19.52; N, 7.71; O, 8.81; found: C, 59.53; H, 4.43; Cl, 19.55; N, 7.69; O, 8.83.

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S	vnthesis of 4H-benzo[b]pv	ran derivatives	using aminopre	opylated sili	ca gel catalyst.
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Entry	R	Product	Time (min)	Yield (%) <sup>a</sup>	Mp (°C)	
					Obs	Lit
1	Ph	4a	90	93	235-237	234-236 [20]
2	$4-Me-C_6H_4$	4b	60	94	208-210	209-210 [15]
3	$4-OH-C_6H_4$	4c	120	96	223-225	224-226 [21]
4	$4-Br-C_6H_4$	4d	90	89	199-200	197-199 [25]
5	4-OMe-C <sub>6</sub> H <sub>4</sub>	4e	120	95	200-202	201-203 [26]
6	3,4,5-OMe-C <sub>6</sub> H <sub>2</sub>	<b>4</b> f	150	96	247-249	-
7	$4-Cl-C_6H_4$	4g	90	92	213-214	215-216 [25]
8	$2-Cl-C_6H_4$	4h	90	89	201-203	200-202 [25]
9	2,3-Cl-C <sub>6</sub> H <sub>3</sub>	4i	90	88	225-227	
10	$4-NO_2-C_6H_4$	4j	45	90	152-154	151-153 [20]
11	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	4k	60	92	209-211	210-212 [20]
12	$4-F-C_6H_4$	41	60	89	210-212	208-210 [25]
13	3-Pyridine carbaldehyde	4m	90	87	187-189	-
14	Furfuraldehyde	4n	90	90	201-203	198–200 [26]

<sup>a</sup> Isolated yield.

2-Amino-7,7-dimethyl-5-oxo-4-(pyridin-3-yl)-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**4m**): Brownish solid; mp 187– 189 °C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.17–7.21 (m, 1H), 7.40–7.47 (m, 1H), 7.82–7.90 (m, 1H), 6.72 (brs, 2H, NH), 4.24 (s, 1H), 2.61 (s, 2H), 2.28 (m, 1H), 2.06 (m, 1H), 0.94 (s, 3H), 0.74 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  200.0, 161.3, 154.0, 153.6, 142.8, 135.1, 129.9, 122.8, 119.1, 114.1, 59.9, 53.5, 38.1, 37.5, 31.3, 30.7; GC–MS: *m/z* 295 (M+); Elem. Anal. Calcd. for C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>: C, 69.14; H, 5.80; N, 14.23; O, 10.83; found: C, 69.15; H, 5.77; N, 14.25; O, 10.81.

# 2.2. Synthesis of solid aminopropylated SiO<sub>2</sub>

Silica gel was synthesized under acidic conditions. A known weight of sodium silicate solution (23.31 SiO<sub>2</sub>%; 7.48 Na<sub>2</sub>O%) was diluted with deionized water. 12% (w/v) SiO<sub>2</sub> was added to 5.1 mol/L H<sub>2</sub>SO<sub>4</sub> solution under stirring with a peristaltic pump over 12.5 min at room temperature to adjust the SiO<sub>2</sub> concentration to 8% (w/v), aged for 2 h, and then kept at 100  $^{\circ}$ C for 12 h in a closed Simax glass bottle. The gel obtained was washed until it was sulfate free (BaCl<sub>2</sub> test), dried at 100 °C in an oven, and further calcined at 600 °C for 6 h. Samples were cooled under vacuum and stored in a capped bottle over P<sub>2</sub>O<sub>5</sub> in a desiccator. Surface functionalization of the silica gel was carried out by suspending the gel in a solution of 3-aminopropyltrimethoxysilane in dry toluene (solid:liquid, 10:100, w/v) and refluxed at boiling temperature for 24 h. Samples were filtered, washed with isopropanol thoroughly, and dried at 100 °C for overnight. Two different functionalized silica samples were prepared with APTMS using different APTMS: silica ratios (w/w), viz. 0.1 (0.56 mmol/g), which were designated as GN1. The synthesized material was characterized by powder X-ray diffraction and <sup>29</sup>Si solid state NMR analysis.

Powder X-ray diffraction: Powder X-ray diffraction (PXRD) patterns of functionalized silica showed the hexagonal structure of GN1; a typical mesoporous structure with three sharp peaks corresponding to the (1 0 0), (1 1 0), and (2 0 0) planes (Fig. 1). It has been seen that the value of  $d_{1 0 0}$  and  $a_0$  remained almost constant with the standard deviation of 0.35, indicating that the surface modification did not result in structural properties of GN1.

<sup>29</sup>Si NMR spectra: The <sup>29</sup>Si NMR spectra of silica gel samples treated at different temperatures and functionalized silica gels are shown in Fig. 2. The three peaks at  $\delta$  –112, –102 and –92 can be



Fig. 1. PXRD patterns of silica gel G and aminopropylated silica gel.



Fig. 2. <sup>29</sup>Si MAS NMR spectra of silica gel and aminopropyl functionalized silica gels.

attributed to silicon in the siloxane binding environment without hydroxyl groups  $Q^4[(SiO)_4Si]$ , isolated silanol groups  $Q^3[(SiO)_3Si-OH]$ , and geminal silanol groups  $Q^2[(SiO)_2-Si-(OH)_2]$  of the silica gel.

#### 3. Results and discussion

The presence of several free NH<sub>2</sub> groups in the catalyst (such as GN3) [28] may lead to the formation of excess hydrogen bonding with acidic hydrogens of substrates such as phenols and hence may require prolonged time for completion of reaction. In the case of the GN 1 catalyst the probability of such interactions is less due to the presence of a single NH<sub>2</sub> group. Hence, it catalyzes the reaction more efficiently in a short time to afford the corresponding products in high yields.

Preliminary efforts were mainly focused on the evaluation of different molar ratios of the catalyst AP-SiO<sub>2</sub>. Initially, the reaction was carried out using 5 mol% of the catalyst in ethanol; the product **4a** was obtained in lower than 52% yield within 12 h. When the reaction was carried out using 10 mol% of catalyst, the reaction was completed in 5.5 h and the yield obtained of product **4a** was 64%. Further increase in catalyst concentration did not show any significant effect on reaction time and yield of 4a. The reaction proceeds well in the presence of 10 mol% of the catalyst in ethanol at room temperature but require longer time for completion. As the temperature of reaction was raised slowly (Table 2); it was found that the reaction proceeds giving excellent yield at 70 °C temperature within 1.5 h. Further increase in reaction temperature to 80 °C showed similar results without change in yield or reaction time, and thus the optimized reaction conditions involve the use of 10 mol% of the catalyst at 70 °C with a 1.5 h reaction time.

Under the optimized reaction conditions, the ability of catalyst was explored in multicomponent reaction. Both electron-rich and electron deficient aryl aldehydes afforded 4*H*-chromene derivatives in 73%–98% yield in relatively short reaction times. Comparatively, the rate of reaction of electron-deficient aryl aldehyde was faster than the electron-rich aryl aldehyde. 4*H*-Chromene derivatives formed were obtained in pure form by

Table 2Effect of temperature on synthesis of 4a.

Entry	Temperature (°C)	Time (h)	Yield (%) <sup>a</sup>
1	r.t.	4.5	69
2	50	3.0	78
3	60	2.0	86
4	70	1.5	93
5	80	1.5	92

<sup>a</sup> Isolated yield.



Fig. 3. Reusability of solid aminopropylated SiO<sub>2</sub> as a catalyst for the synthesis of 4a.

recrystallization process. In order to extend the scope of amino propylated silica gel catalyzed multicomponent reactions, it was also successfully applied to aromatic heterocyclic aldehydes (Table 1).

After performing the condensation of C–H activated ketones with aromatic aldehydes and alkylmalonates for the synthesis of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile derivatives under present conditions, ethyl acetate was added to the reaction mixture. The catalyst was separated by a simple filtration from the resulting heterogeneous mixture, washed with water 3–4 times, dried, and reused for consecutive runs under the same reaction conditions. The average isolated yield of **4a** for five consecutive runs was 89%, which clearly demonstrates the practical reusability of this catalyst (Fig. 3). Structure of the recovered catalyst was also studied with XRD analysis. The powder XRD pattern of the recovered catalyst was similar to that of the fresh catalyst indicating that the recovered catalyst remains unaffected in its structure.

#### 4. Conclusion

In summary, we synthesized silica gel supported amino functionalized heterogeneous solid aminopropylated SiO<sub>2</sub> as a base catalyst. After structural characterization, its capability in organic transformations was investigated to synthesize 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile **4a**. The catalyst was found to catalyze the reaction under mild reaction conditions. The solid catalyst aminopropylated SiO<sub>2</sub> was efficient for the synthesis of **4a** and showed excellent stability and activity. The scope of the catalyst was further explored to catalyze the synthesis of 4*H*-chromene derivatives using different aromatic and heterocyclic aldehydes. The reactions proceeded well on all kind of aldehydes giving excellent yield of products in shorter reaction time. Finally, silica supported amine catalyst can be recovered by simple filtration procedure and reused without much loss in its activity.

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