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Nano-SiO_2 as a Reusable Nanocatalyst Promoted Green Synthesis of 2-Amino-4*H*-Chromenes in an Aqueous Solution

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Abstract: A green multi-component tandem strategy for synthesizing 2-amino-4*H*-chromenes *by* Knoevenagel-Michael cyclo condensation is reported using nano-SiO_2 as a reusable nanocatalyst in an aqueous solvent. The prominent benefits of the existing protocol are energy-effectiveness, reusable nanocatalysts, operational simplicity, aqueous solvent as a green medium, great yields, also economical, hence meeting a few elements of manageable and green science. The phenomenal yields and short reaction times were procured by anticipated products, which might solve some expense issues in the industry. However, to make it highly beneficial to address the industrial needs and environmental concerns, the nano-SiO_2 can be recycled a minimum of six times with no crucial decline in catalytic activity.

Keywords: nano-SiO_2; reusable nanocatalyst; aqueous solution; 2-amino-4*H*-chromenes.

1. Introduction

In green chemistry, the most notable objectives of atomic saving include the reduction of by-products, the number of stages of organic synthesis, energy costs, waste generated, and the use of non-hazardous reagents in catalytic protocols. A green catalyst is one of the important factors of green chemistry in recent organic synthetic pathways. Our recent research has focused on developing green catalysts [1,2] in organic synthesis [3-6].

Chromenes and their analogs stand out to them in light of their organic exercises as antiallergenic [7,8], antimicrobial [9], antifungal [10], anti-inflammatory [11], antibacterial [12], antioxidant [13], antileishmanial [14], anti-HIV [15,16], anticancer [17,18], and hypotensive [19]. Some of these compounds could also be used as inhibitors [20,21].

Numerous approaches for synthesizing 2-amino-4*H*-chromenes using multi-component reactions have been reported in the presence of different catalysts such as per-6-NH_2-β-CD [22], mesolite [23], potassium phthalimide [24], $MgFe_2O_4$NPs [25], POM@Dy-PDA [26], P4VPy-CuI [27], nano zeolite clinoptilolite [28], Water Extract of Lemon Fruit Shell Ash (WELFSA) [29], tungstic acid functionalized SBA-15 [30], MIL-101(Cr)-SO_3H [31], $[Et_2NH(CH_2)_2CO_2H][AcO]$ [32], $\{[4,4'\text{-BPyH}][C(CN)_3]_2\}$ [33], DBU [34], Na_2 Eosin Y [35], $[Et_3N\text{-}SO_3H]HSO_4$ [36], Urea immobilized silica-coated Fe_3O_4 MNPs [37], and melamine [38]. A few manufactured strategies likewise contain limitations concerning the metal impetus, cruel response conditions, costly reagents, dull workup process, inadmissible yield, long response time, ecological risk, and utilizing a homogeneous impetus hazardously disengaged from the combination of responses.

In green chemistry, the most notable objectives of atomic saving include the reduction of by-products, the number of stages of organic synthesis, energy costs, waste generated, and the use of non-hazardous reagents in catalytic protocols. One of the important factors of green chemistry in recent organic synthetic pathways is the reusable catalyst. Given the above contemplations and our advantage in creating heterocyclic compound creation [39-45], the study of eco-safe and reusable catalysts under green conditions for appropriately orchestrating these oxygen-containing heterocyclic mixtures has been a significant objective. Here, nano-SiO_2 as a reusable nanocatalyst [46,47] provided green production of 2-amino-4*H*-chromenes in an aqueous solvent as a green medium. The prominent benefits of the existing protocol are energy-effectiveness, reusable nanocatalysts, operational simplicity, aqueous solvent as a green medium, great yields, also economical, hence meeting a few elements of manageable and green science. The phenomenal yields and short reaction times were procured by anticipated products, which might solve some expense issues in the industry. However, to make it highly beneficial to address the industrial needs and environmental concerns, the nano-SiO_2 can be recycled a minimum of six times with no crucial decline in catalytic activity.

2. Materials and Methods

2.1. Experimental.

Utilizing a 9100 electro-termal gadget, the m.p. of all mixtures was found. Also, ^{1}HNMR was performed on Bruker (DRX-300) instruments utilizing DMSO-d_6 as dissolvable. All reagents were bought from compound organizations called Fluka, Merck, and Acros and utilized without extra treatment.

2.2. General procedure.

A mixture of aldehyde derivatives (**1**, 1.0 mmol), malononitrile (**2**, 1.0 mmol) and resorcinol (**3**, 1.0 mmol), and nano-SiO_2 (20 mol%) in H_2O (5 mL) was heated at 70 °C (Scheme 1). The monitoring of reaction progress was conducted by TLC, which employs *n*-hexane/ethyl acetate (7:3). After the finish of the reaction, the accelerated item was sifted and washed with water. The rough item was decontaminated by recrystallization from ethanol to manage the specified item (**4a-r**). Spectra data of selected and known products are represented below:

2-Amino-3-cyano-7-hydroxy-4-(4-methylphenyl)-4H-chromene (4o)

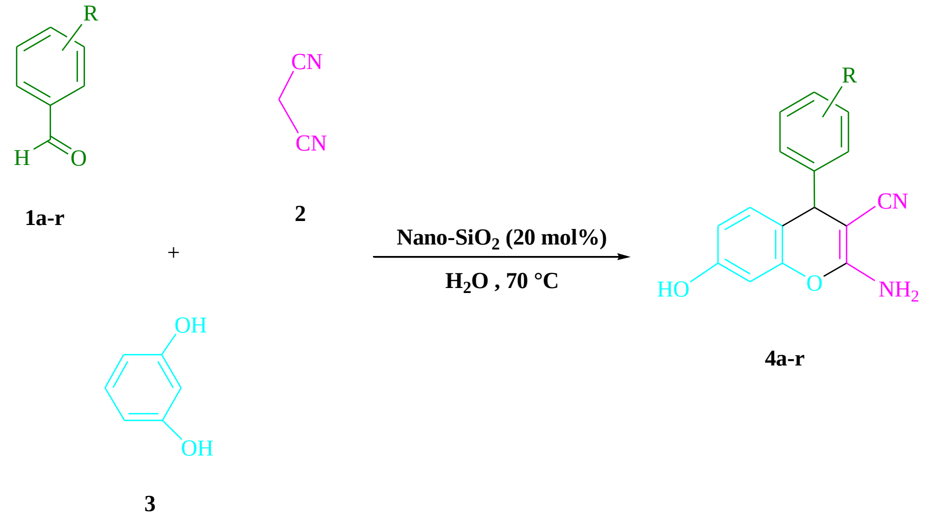
Yield: 93%; M.p. 188-190 °C; ^{1}HNMR (300 MHz, DMSO-d_6): 2.51 (3H, s, CH_3), 4.72 (1H, s, CHAr), 6.21 (1H, d, *J*=9.6 Hz, ArH), 6.70 (1H, d, *J*=9.6 Hz, ArH), 6.84 (1H, d, *J*=10.4 Hz, ArH), 7.03 (2H, s, NH_2), 7.17 (2H, d, *J*=9.6 Hz, ArH), 7.48 (2H, d, *J*=9.6 Hz, ArH), 9.63 (1H, s, OH).

2-Amino-3-cyano-7-hydroxy-4-(4-methoxyphenyl)-4H-chromene (4r)

Yield: 95%; M.p. 211-213 °C; ^{1}HNMR (300 MHz, DMSO-d_6): 3.71 (3H, s, OCH_3), 4.53 (1H, s, CHAr), 6.18 (1H, d, *J*=8.8 Hz, ArH), 6.45 (1H, dd, *J*=7.2, 2.4 Hz, ArH), 6.77 (1H, d, *J*=8.4 Hz, ArH), 6.84 (2H, s, NH_2), 7.25 (2H, d, *J*=8.4 Hz, ArH), 7.83 (2H, d, *J*=9.2 Hz, ArH), 9.78 (1H, s, OH).

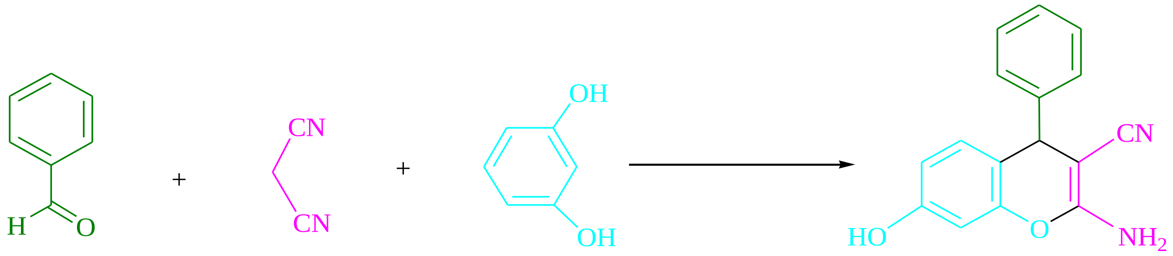
3. Results and Discussion

Initially, the reaction between benzaldehyde (1 mmol), malononitrile (1 mmol), and resorcinol (1 mmol) for the preparation of **4a** were studied in various solvents and temperatures in the presence of different molars of nano-SiO_2. In the absence of nano-SiO_2, a small amount of **4a** was observed at 70 °C and rt for 45 min in water solvent (Table 1, entries 6, 7). As Table 1 shows, products were produced in DMF and THF at higher reaction times and lower yields. The reaction rate and yield improve in solvent-free, H_2O/EtOH (1:1), MeOH, and EtOH. With an exceptional yield and rate, the response occurred in H_2O. Also, different molars of nano-SiO_2 (5, 10, 15, 20, and 25 mol%) have been determined—also, the best outcomes with nano-SiO_2 (20 mol%) (Table 1, entry 4). The cyclo condensation was investigated at a range of rt-80 °C in H_2O (5 mL) (Table 1). As Table 1 indicates, reasonable results were observed at 70 °C. The Increment of the temperature up to 80 °C didn't significantly improve the reaction results (Table 1, entry 12). With increasing the amount of catalyst to 25 mol %, no significant change in yield and reaction time was observed (Table 1, entry 5). The best outcomes were found in the presence of nano-SiO_2 (20 mol %) at 70 °C in H_2O (5 mL). Finally, the nano-SiO_2 catalyzed synthesis of 2-amino-4*H*-chromenes was further expanded with various aldehydes with malononitrile and resorcinol. The aldehydes bearing either electron-pulling out or electron-giving gatherings responded acceptably to the comparing 2-amino-4*H*-chromenes. Table 2 and Scheme 1 show that this technique can function in multifarious substrates with good to high yields and relatively short reaction times.



Scheme 1. 2-amino-4*H*-chromenes synthesize.

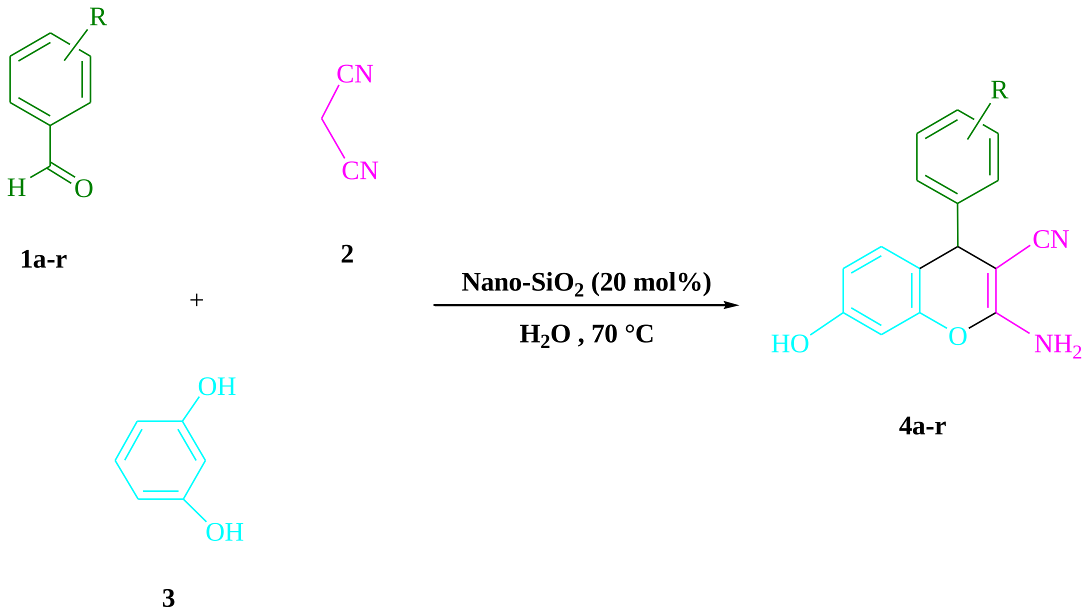
Table 1. Improvement of the response conditions on the production of **4a**

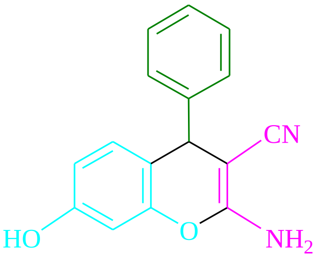
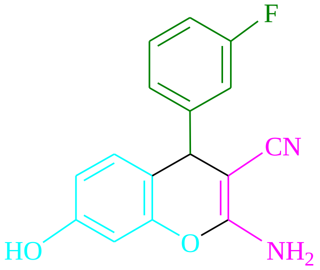
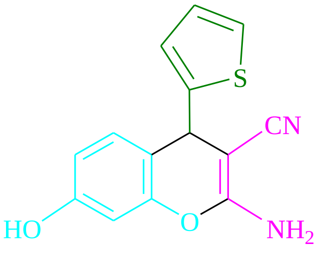


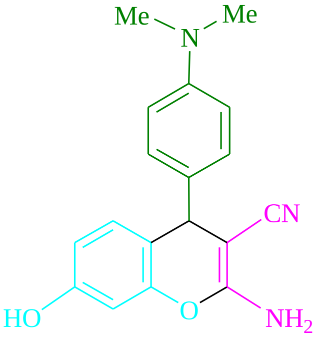
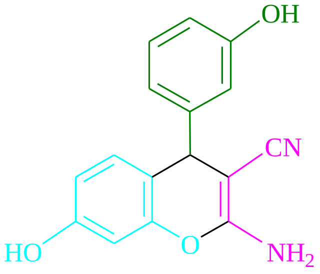
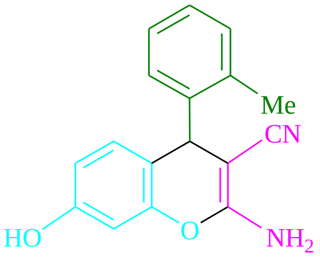
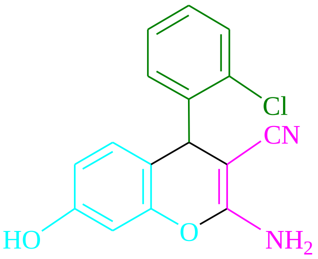
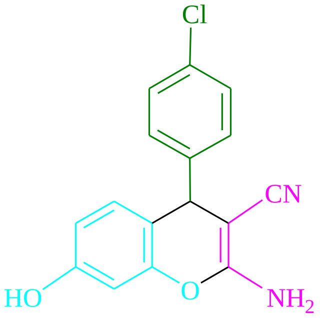
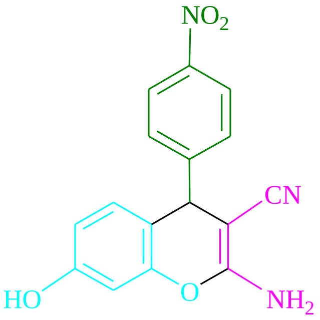
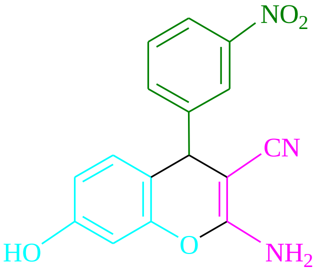
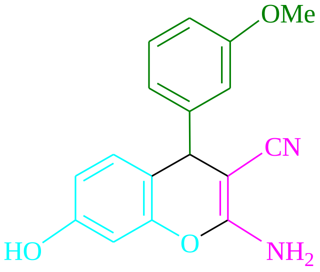
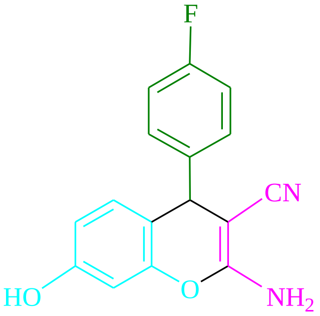
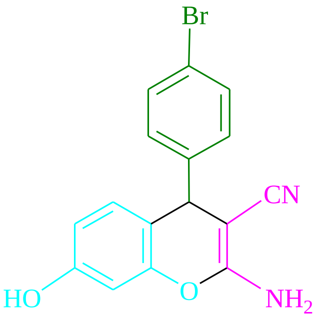
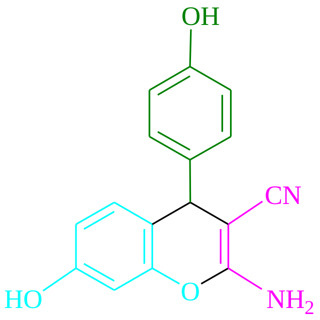
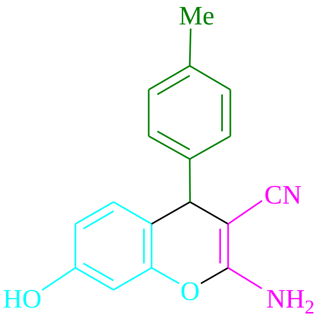
Entry	Nano-SiO_2 (mol%)	Solvent/Conditions	Time (min)	Isolated Yields (%)
1	5	H_2O, 70 °C	20	38

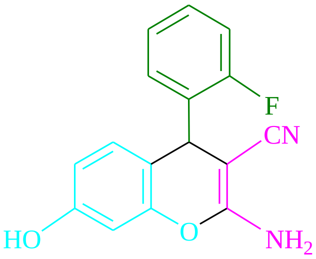
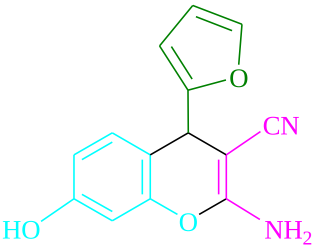
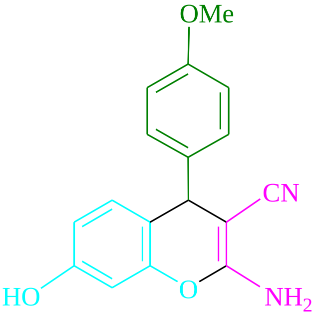
Entry	Nano-SiO$_2$ (mol%)	Solvent/Conditions	Time (min)	Isolated Yields (%)
2	10	H_2O, 70 °C	15	64
3	15	H_2O, 70 °C	10	82
4	**20**	**H_2O, 70 °C**	**10**	**95**
5	25	H_2O, 70 °C	10	95
6	Catalyst-free	H_2O, 70 °C	45	trace
7	Catalyst-free	H_2O, rt	45	trace
8	20	Solvent-free, 70 °C	20	52
9	20	H_2O, rt	45	43
10	20	H_2O, 40 °C	25	60
11	20	H_2O, 60 °C	10	81
12	20	H_2O, 80 °C	10	95
13	20	DMF, 70 °C	60	38
14	20	H_2O/EtOH (1:1), 70°C	10	79
15	20	MeOH, reflux	20	55
16	20	EtOH, 70°C	15	70
17	20	THF, reflux	60	43

Table 2. Nano-SiO$_2$ promoted green synthesis of 2-amino-4*H*-chromenes.

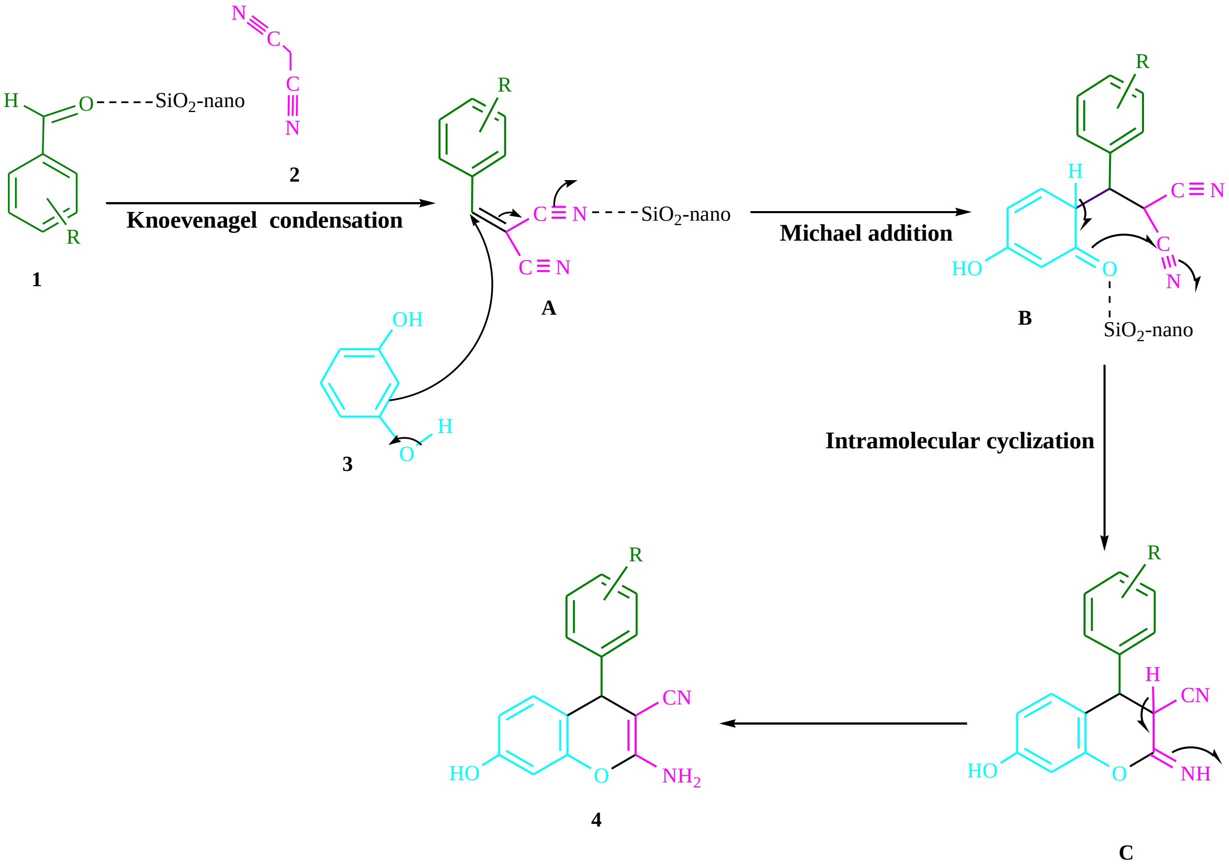


 **4a** (10 min, 95%) Mp. 231-233 °C Lit. 232-234 °C [27]	 **4b** (8 min, 96%) Mp. 150-152 °C Lit. 148-150 °C [29]	 **4c** (10 min, 93%) Mp. 211-213 °C Lit. 210-212 °C [24]

 **4d** (12 min, 91%) Mp. 192-194 °C Lit. 194-196 °C [24]	 **4e** (20 min, 82%) Mp. 218-220 °C Lit. 219-221 °C [33]	 **4f** (8 min, 96%) Mp. 228-230 °C Lit. 228-231 °C [25]
 **4g** (15 min, 84%) Mp. 191-193 °C Lit. 189-191 °C [27]	 **4h** (20 min, 86%) Mp. 162-164 °C Lit. 162-163 °C [27]	 **4i** (10 min, 94%) Mp. 167-169 °C Lit. 166-168 °C [23]
 **4j** (10 min, 91%) Mp. 166-168 °C Lit. 168-170 °C [32]	 **4k** (10 min, 93%) Mp. 179-181 °C Lit. 180-182 °C [33]	 **4l** (8 min, 94%) Mp. 186-188 °C Lit. 188-190 °C [27]
 **4m** (20 min, 81%) Mp. 220-222 °C Lit. 222-224 °C [24]	 **4n** (20 min, 85%) Mp. 249-251 °C Lit. 250-252 °C [23]	 **4o** (8 min, 93%) Mp. 188-190 °C Lit. 186-188 °C [28]

 **4p** (8 min, 95%) Mp. 201-203 °C Lit. 200-202 °C [34]	 **4q** (10 min, 96%) Mp. 189-191 °C Lit. 190-192 °C [32]	 **4r** (12 min, 95%) Mp. 211-213 °C Lit. 210-212 °C [29]

Scheme 2 shows the suggested mechanism for synthesizing 2-amino-4*H*-chromenes. The reaction was encouraged by creating an inclusion of the intermediate **A** was readily created in situ from Knoevenagel condensation between arylaldehyde **1** and methylene compound **2** in the presence of nano-SiO_2. This can be demonstrated by the arylaldehydes' steric influences on the reaction effectiveness (Table 2). Nano-SiO_2 also catalyzed the resorcinol **3** attack on intermediate **A** as Michael acceptor, giving **B** that, after cyclizing and tautomerizing, affords the target products **4**. Also, a comparison of the catalytic capacity of a number of catalysts referred to in the present paper for the production of 2-amino-4*H*-chromenes has been shown in Table 3. TON and TOF are calculated in Table 3. The higher the TON and TOF numerical value, the higher the value, and the more efficient the catalyst.



Scheme 2. The suggested way for producing 2-amino-4*H*-chromenes.

Table 3. Comparison of the catalytic ability of some of the catalysts in the manuscript for producing 2-amino-4H-chromene scaffolds [a].

Entry	Catalyst	Conditions	Time/Yield (%)	TON	TOF	References
1	potassium phthalimide	ball milling, rt	17 min/97	19.4	1.14	[24]
2	POM@Dy-PDA	EtOH/H_2O, reflux	15 min/95	9.5	0.6	[26]
3	MIL-101(Cr)-SO_3H	H_2O, 100 °C	180 min/82	221.6	1.2	[31]
4	$[Et_2NH(CH_2)_2CO_2H][AcO]$	solvent-free, 60 °C	12 min/92	4.6	0.3	[32]
5	DBU	MW, EtOH, 50 °C	3 min/94	18.8	6.2	[34]
6	nano-SiO_2	H_2O, 70 °C	10 min/95	4.7	0.47	This work

[a] 3-component reaction: benzaldehyde, resorcinol, and malononitrile.

3.1. Reusability of the catalyst.

Since the reusability of the catalyst is economically and environmentally important, the reusability of the nano-SiO_2 catalyst has been investigated over the next few periods. Recovery and reuse of the catalyst for the preparation of 2-amino-3-cyano-7-hydroxy-4-(4-phenyl)-4*H*-chromene (**4a**) was examined. After the culmination of the response (checked by TLC), the response combination was cooled to room temperature; the dissolvable was taken out under diminished pressure. Then, at that point, the blend was weakened with dichloromethane, and the impetus was isolated by centrifugation and washed with CH_2Cl_2 (2×5 mL) to really look at the reusability. The emptied arrangement containing the item was dissipated to give the strong unrefined. The nano-SiO_2 was reused for six rounds of recycling, while the detached product had sufficient potential to be cost-effective, as shown in Figure 1. In the first, second, third, fourth, fifth, and sixth reactions, there were very low reductions in yield (93%, 92%, 92%, 91%, 88%, and 86%, respectively).

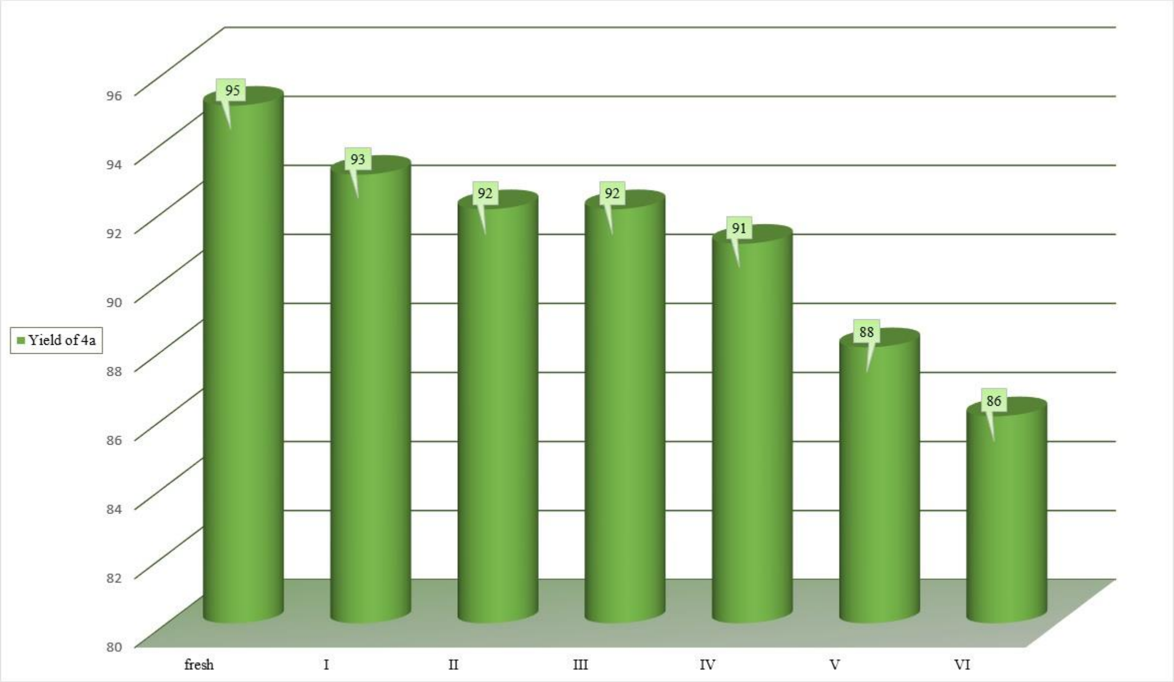


Figure 1. The recyclability of the nano-SiO_2 in the preparation of **4a**.

4. Conclusions

The current survey revealed that nano-SiO_2 is able to be employed as an eco-safe and reusable nanocatalyst for one-pot simple synthesizing 2-amino-4*H*-chromenes in H_2O as a green solvent. Utilizing great yields, efficient sides of the reaction, reusable nanocatalyst, direct workup without column chromatographic separation, secure reaction circumstances, green media, appropriate and expedient procedure, and cheap substances are the most conspicuous pros of this green protocol. These characteristics have caused this procedure to be highly beneficial in facing environmental worries and industrial needs. Also, the nanocatalyst was stable and could be reused in six consecutive periods without significant structural change and loss of activity.

Funding

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Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

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