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ORIGINAL RESEARCH

# Nano-sawdust–$BF_3$ as a new, cheap, and effective nano catalyst for one-pot synthesis of 2-amino benzo[*h*]chromene derivatives

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**Abstract** An atom-efficient, three-component synthetic methodology has been developed for the preparation of biologically important 2-amino benzo[*h*]chromene using nano-sawdust–$BF_3$ as a new catalyst. The reaction involves the use of 2-naphthol, malononitrile, and various aldehydes. A wide range of aldehydes is compatible in this reaction, producing excellent yields in short time. The morphology of nanocatalyst (nano-sawdust–$BF_3$) was observed using a scanning electron microscopy. Also, the sawdust–$BF_3$ surface was studied by energy dispersive X-ray spectroscopic method to find out the chemical composition.

**Keywords** Benzochromenes · 2-Naphthol · Malononitrile · Green chemistry · Nano-sawdust–$BF_3$

## Introduction

Recently, multi-component, one-pot synthesis have become one of the most attractive reactions due to their vast applications such as high selectivity, mild reaction condition and construction of several bonds in a single operation. These reactions are widely applied in pharmaceutical chemistry for producing different structures and combinatorial libraries for drug discovery [1]. 2-amino benzo[*h*]chromene are some examples of multi-component reactions. 4*H*-chromenes and fused 4*H*-chromene derivatives are attractive, because they generally show biological properties such as anti-microbial, anti-oxidant, anti-tumor, hypotensive and antiproliferation activities [2–6].

In recent years, there has been growing interest in finding inexpensive and effective solid acid nano catalyst such as nanocrystalline $TiO_2$–$HClO_4$ [7], nano-$TiCl_4 \cdot SiO_2$ [8–10] nano-$SnCl_4 \cdot SiO_2$ [11, 12] nano-$BF_3 \cdot SiO_2$ [13–15] $HClO_4$–$SiO_2$ nanoparticles [16] and nano-silica sulfuric acid [17–23]. Sawdust is one of the most common materials that used for various chemical industries such as removing pollutants from water [24], the color removal from textile industry [25], the removing cationic, anionic, and disperse dyes from aqueous solution [26] and the $CuFe_2O_4$/sawdust composite was used for removal of cyanine acid blue from aqueous solution [27].

The sawdust consists of cellulose, lignin, and hemicelluloses. Cellulose is composed of a long chain of glucose molecules, lignin is a complex polymer composed of phenylpropane units, and hemicelluloses are branched polymers composed of xylose, arabinose, galactose, mannose, and glucose [28–31]. The lignocellulosic material of sawdust includes a wide variety of hydroxyl groups that can be used as active sites for the preparation of solid acid catalysts.

In this study, the sawdust has been used as adsorbent for the preparation of nano-sawdust–$BF_3$ whose average size is small and is well distributed. The presence of new functional groups on the surface of sawdust–$BF_3$ resulted in a dramatic increase of surface polarity and acidity, thereby improving the catalytic efficiency of the nano-sawdust–$BF_3$.

Recently some conditions and catalysts have been applied for the 2-amino benzo[*h*]chromene synthesis [32–38]. Although many of the reported methods are effective, but, some of them suffer from disadvantages such as harsh reaction conditions, use of hazardous solvents and toxic

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metals, long reaction times, complex working and purification procedures, long volume of catalyst loading and moderate yields. Therefore, the development of a simple, mild, and efficient method is still needed. In continuation of our previous research on the use of solid nano catalyst in organic synthesis [14–21], the nano-sawdust–$BF_3$ as a new catalyst has been applied for the synthesis of 2-amino benzo[*h*]chromene derivatives.

## Results and discussions

In continuation of our investigation into the application of solid acids in organic synthesis, we studied the application of sawdust as a green, inexpensive and available surface to synthesis of solid acid nano catalyst. In this study, sawdust–$BF_3$ nanoparticles were prepared and characterized. The catalytic activity of nanoparticles was investigated for synthesis of 2-amino benzo[*h*]chromene derivatives, by the condensation of an aldehyde 1a–k, malononitrile 2 and 2-naphthol 3 (Scheme 1).

Figure 1 shows the scanning electron microscopy (SEM) image of sawdust. The morphology and size of sawdust and sawdust–$BF_3$ was observed by SEM images. After adding the $BF_3$ to sawdust, the particles will be smaller and more homogeneous. As shown in Fig. 2, the size of nano-sawdust–$BF_3$ is below 100 nm.

The results of EDX analyses of the sawdust and sawdust–$BF_3$ are given in the following Table 1.

The EDX analysis show how the different elements are distributed. Chemical analysis of sawdust gave carbon and oxygen as the major elements (Fig. 3). The elemental analysis by EDX identified the high peak of fluorine and boron in addition to other elements in the nano-sawdust–$BF_3$ (Fig. 4). Presence of fluorine and boron in the EDX, indicates that the chemical interaction of boron trifluoride etherate with the surface of sawdust.

In order to determine the optimum quantity of nano-sawdust–$BF_3$, the reaction of 2-naphthol, malononitrile, and benzaldehyde was carried out under reflux in ethanol using different quantities of nano-sawdust–$BF_3$. As shown in Table 2, 0.02 g of nano-sawdust–$BF_3$ gives an excellent yield in 20 min. The above reaction was also examined in various solvents (Table 2, entries 1–4). Most of these solvents required a longer time and gave low yields, and the best results were obtained when ethanol was used (Table 2, entry 2). An interesting feature of this method is that the reagent can be regenerated at the end of the reaction and can be used several times without losing its activity. To recover the catalyst, after completion of the reaction, catalyst was separated and washed with ethanol

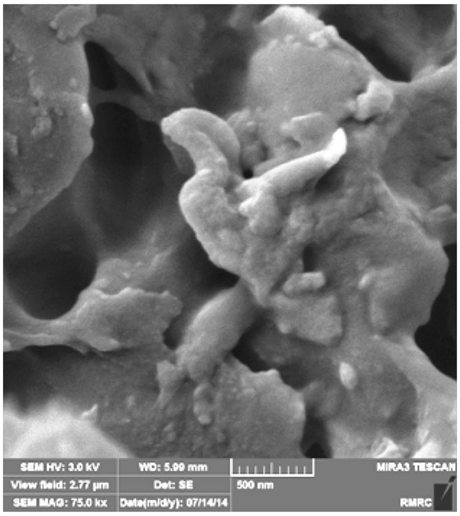


**Fig. 1** SEM micrograph of sawdust

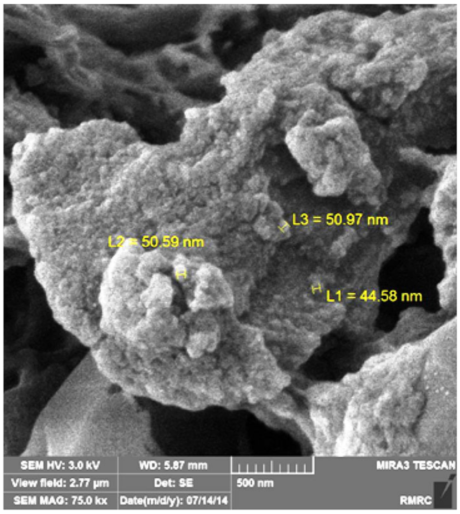
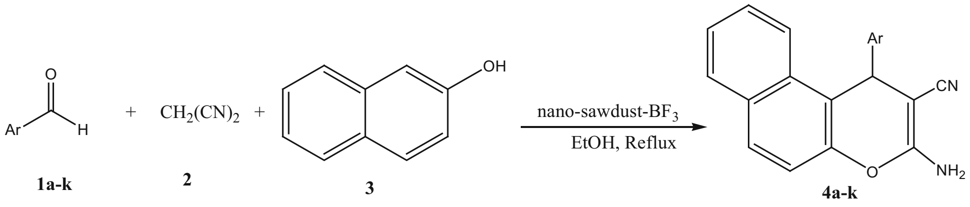


**Fig. 2** SEM micrograph of nano-sawdust–$BF_3$

**Scheme 1** Synthesis of 2-amino benzo[*h*]chromene derivatives in the presence of nano-sawdust–$BF_3$ as catalyst



and then dries the solid residue. This process repeated for two cycles and the yield of product 4a did not change significantly (Table 2, entries 8, 9).

**Table 1** Chemical analysis of sawdust and sawdust–$BF_3$

| | Sawdust | | Sawdust–$BF_3$ | |
|---|---|---|---|---|
| Element | W % | A % | W % | A % |
| C | 56.85 | 65.35 | 57.62 | 64.03 |
| O | 39.89 | 34.42 | 20.60 | 17.19 |
| B | – | – | 8.02 | 9.90 |
| F | – | – | 12.53 | 8.80 |

To study the scope of the reaction, a series of aldehydes with 2-naphthol and malononitrile were examined by nano-sawdust–$BF_3$ as catalyst. The results are shown in Table 3. In all cases, aromatic aldehyde substituted with either electron-donating or electron-withdrawing groups underwent the reaction smoothly and formed products in approving yields.

The proposed mechanism for the formation of nano-sawdust–$BF_3$ catalyzed 2-amino benzo[*h*]chromene is illustrated in Scheme 2. Condensation of aldehyde 1 and malononitrile 2 in the presence of the acidic catalyst of nano-sawdust–$BF_3$ ($A^+$) produce an intermediate 5. Then the Michael addition of 2-naphthol 3 to intermediate 5

**Fig. 3** EDX of sawdust

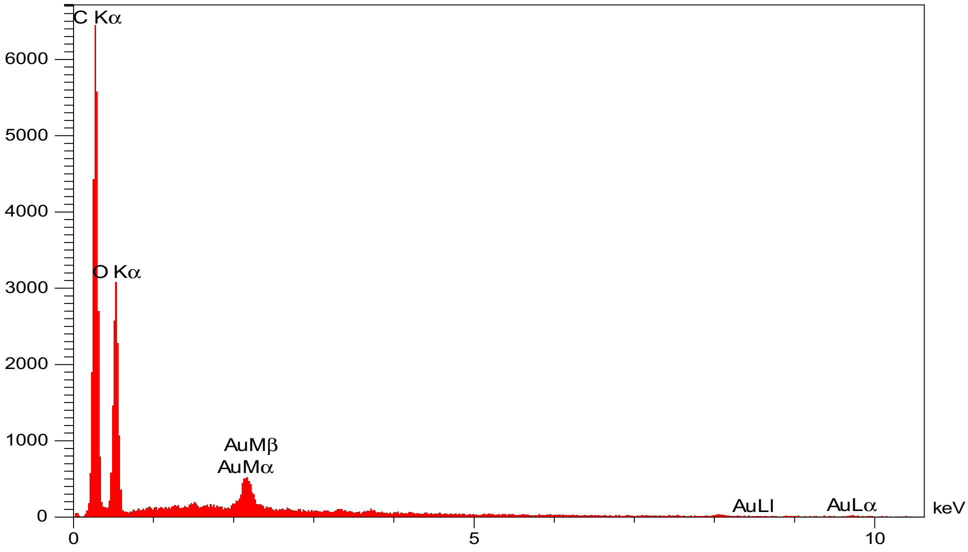


**Fig. 4** EDX of nano-sawdust–$BF_3$

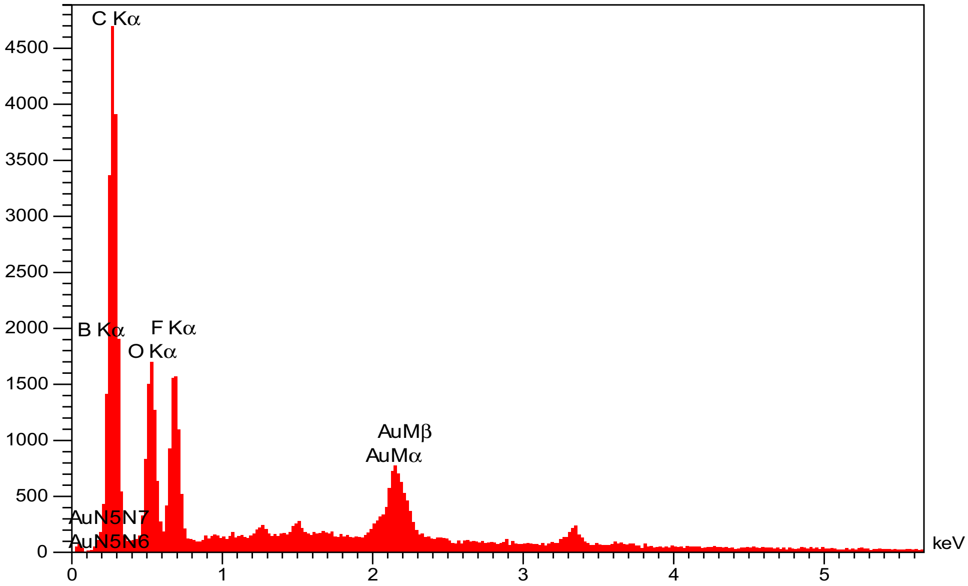


**Table 2** Optimization of the reaction conditions for synthesis of 4a

| Entry | Catalyst (amount) | Solvent/condition | Time (min) | Yield |
|---|---|---|---|---|
| 1 | Nano-sawdust–$BF_3$ (0.02 g) | $CH_2Cl_2$/reflux | 20 | Trace |
| 2 | Nano-sawdust–$BF_3$ (0.02 g) | EtOH/reflux | 20 | 92 |
| 3 | Nano-sawdust–$BF_3$ (0.02 g) | $CH_3CN$/reflux | 20 | Trace |
| 4 | Nano-sawdust–$BF_3$ (0.02 g) | DMF/reflux | 20 | 46 |
| 5 | Nano-sawdust–$BF_3$ (0.02 g) | $H_2O$/reflux | 20 | 82 |
| 6 | Nano-sawdust–$BF_3$ (0.01 g) | EtOH/reflux | 20 | 71 |
| 7 | Nano-sawdust–$BF_3$ (0.03 g) | EtOH/reflux | 20 | 93 |
| 8 | Nano-sawdust–$BF_3$ (0.02 g) 2nd run | EtOH/reflux | 20 | 91 |
| 9 | Nano-sawdust–$BF_3$ (0.02 g) 3rd run | EtOH/reflux | 20 | 87 |

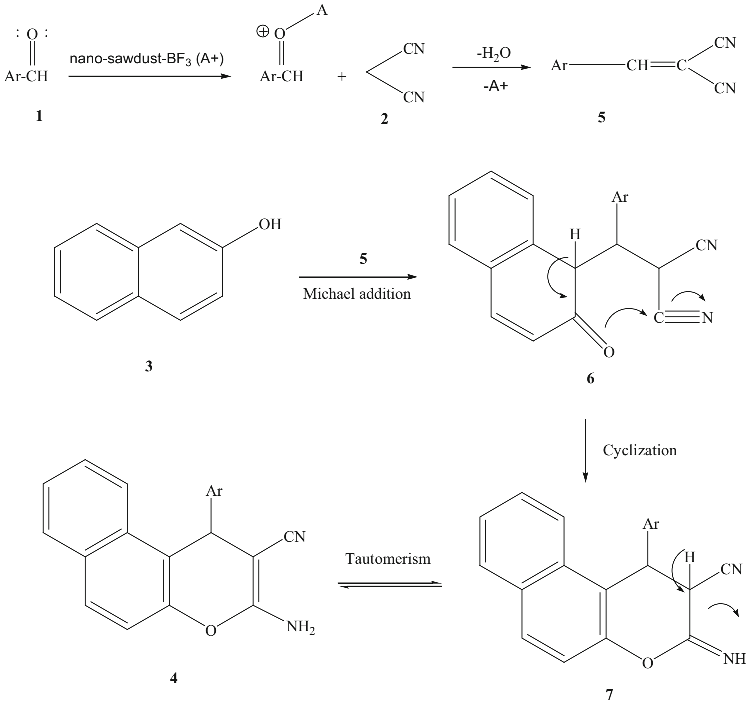
**Table 3** Synthesis of 2-amino benzo[*h*]chromene

| Entry | Ar | Product | Time (min) | Yield[a] | M.P. (°C) Ref.[b] |
|---|---|---|---|---|---|
| 1 | $C_6H_5$ | 4a | 20 | 92 | 278–280 (278–279) [32] |
| 2 | 4-$ClC_6H_4$ | 4b | 15 | 88 | 205–207 (208) [32] |
| 3 | 2-$ClC_6H_4$ | 4c | 15 | 86 | 264–265 (265–267) [32] |
| 4 | 4-$FC_6H_4$ | 4d | 10 | 90 | 234–236 (237–238) [32] |
| 5 | 3-$NO_2C_6H_4$ | 4e | 10 | 93 | 235–237 (235–236) [37] |
| 6 | 4-$NO_2C_6H_4$ | 4f | 10 | 90 | 182–184 (185) [33] |
| 7 | 4-$CH_3OC_6H_4$ | 4g | 25 | 82 | 191–193 (193) [33] |
| 8 | 4-OH–3-$OCH_3C_6H_3$ | 4h | 25 | 84 | 249–250 (252–253) [37] |
| 9 | 4-Cl–3-$NO_2C_6H_3$ | 4i | 10 | 90 | 184–186 (181–183) [37] |
| 10 | 4-$OHC_6H_4$ | 4j | 30 | 87 | 288–290 (289–291) [37] |
| 11 | $C_5H_4N$ | 4k | 20 | 89 | 172–174 |

Ratio of aldehyde (mmol): 2-naphtol (mmol): malononitrile (mmol): catalyst (g) is 1:1:1.2:0.02 in 5 mL EtOH

[a] Isolated yield

[b] All products were identified by their melting points, IR, and $^1$H NMR spectra



**Scheme 2** Plausible mechanism for the formation of 2-amino benzo[*h*]chromene derivatives

would furnish intermediate 6. Finally, the product 4 was obtained by an intramolecular cyclization and tautomerism.

## Conclusions

The present investigation shows that nano-sawdust–BF$_3$ a capable nanocatalyst to be used for 2-amino benzo[*h*]-chromene synthesis via one-pot reaction of aldehydes, malononitrile, and 2-naphthol. Nano-sawdust–BF$_3$ was successfully prepared and characterized using EDX and SEM. Prominent among the advantages of this method are such as shorter reaction times, simple work-up, affords excellent yield, and re-usable for a number of times without appreciable loss of activity. The present method does not involve any hazardous organic solvent. Therefore, this procedure could be classified as green chemistry.

## Methods

### Instrumentation

Melting points were determined with an Electrothermal 9100 apparatus. IR spectra were recorded on a Shimadzu IR-470 spectrometer. $^1$H NMR spectra were obtained using Bruker Avance 400. The morphologies of the nanoparticles were observed using FESEM of a MIRA3 TESCAN microscope with an accelerating voltage of 15 kV. The EDX analysis was done using a SAMx-analyser. The chemicals for this work were purchased from Merck or Fluka chemical companies.

### Synthesis of nano-sawdust–BF$_3$

The sawdust was collected from sawmill in Farrokhi city, Iran. Sawdust was washed several times to remove adhering dirt and then dried at 60 °C for 24 h. The dried sawdust was ground to pass through a 1 mm sieve and labeled as sawdust [27]. The nano-sawdust–BF$_3$ was prepared by combination of BF$_3$·OEt$_2$ (0.6 g, 4.2 mmol) drop by drop over 10 min via a syringe to sawdust powder (0.4 g) in a 50 ml flask include 5 ml diethyl ether at room temperature. The reaction mixture was stirred and then after 30 min, the ashy powder was separated and dried in an oven at 60 °C for 4 h and pulverized at the mortar. The size of particles was obtained below 100 nm using SEM.

### General procedure for the synthesis 2-amino benzo[*h*]chromenes

Nano-sawdust–BF$_3$ (0.02 g) was added to a stirred mixture of the aromatic aldehyde (1 mmol), malononitrile (1.2 mmol), and 2-naphthol (1 mmol) in EtOH (5 mL). The materials were mixed and refluxed for the appropriate time. The progress of the reaction was followed by TLC (*n*-hexane:ethyl acetate 5:1). After completion of the reaction, the mixture was filtered to remove the catalyst. After evaporation of the solvent, the crude product was re-crystallized from hot ethanol to obtain the pure compound.

### 3-Amino-1-phenyl-1*H*-benzo[*f*]chromene-2-carbonitrile (4a)

Mp: 278–280 °C; IR (KBr, cm$^{-1}$): 3427, 3342, 2188, 1642, 1590, 1421; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 4.57$ (s, 2H), 5.24 (s,1H), 7.20 (t, $J = 7.36$ Hz, 3H), 7.25 (d, $J = 8.88$ Hz, 2H), 7.38 (q, $J = 3.36$ Hz, 2H), 7.68 (q, $J = 3.44$ Hz, 2H), 7.77–7.81 (m, 2H) ppm.

### 3-Amino-1-(4-chlorophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (4b)

Mp: 205–207 °C; IR (KBr,cm$^{-1}$): 3424, 3325, 2192, 1653, 1590, 1405; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 4.61$ (s, 2H), 5.23 (s, 1H), 7.11 (d, $J = 8.44$ Hz, 1H), 7.25(d, $J = 8.88$ Hz, 2H), 7.24 (q, $J = 8.52$ Hz, 2H),7.40 (q, $J = 3.36$ Hz, 2H), 7.61 (q, $J = 5.8$ Hz, 1H), 7.78–7.82 (m, 2H) ppm.

### 3-Amino-1-(2-chlorophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (4c)

Mp: 264–265 °C;IR (KBr, cm$^{-1}$): 3462, 3367, 2180, 1658, 1571, 1410; $^1$H MR (CDCl$_3$, 400 MHz) $\delta = 4.62$ (s, 2H), 5.88 (s, 1H), 6.90 (q, $J = 1.76$ Hz,1H), 7.02-7.11 (m, 2H), 7.23(s, 1H), 7.38-7.45 (m, 3H), 7.65 (d, $J = 8.12$ Hz, 1H), 7.77–7.80 (m, 2H) ppm.

### 3-Amino-1-(4-fluorophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (4d)

Mp: 234–236 °C; IR (KBr, cm$^{-1}$): 3458, 3358, 2187, 1665, 1594, 1411; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 4.66$ (s, 2H), 5.26 (s, 1H), 6.96 (t, $J = 8.4$ Hz, 2H), 7.18 (q, $J = 5.2$ Hz, 2H), 7.28 (s, 1H), 7.42 (q, $J = 3.2$ Hz, 2H), 7.64 (t, $J = 4.2$ Hz, 1H), 7.83 (t, $J = 6.0$ Hz, 2H) ppm.

### 3-Amino-1-(3-nitrophenyl)-1*H*-benzo[*f*]chromene-2-carbonitile (4e)

Mp: 235–237 °C; IR (KBr,cm-$^1$): 3465, 3349, 2190, 1658, 1593, 1529, 1411; $^1$H NMR (DMSO,400 MHz) $\delta = 5.60$ (s, 1H), 7.13 (s, 2H), 7.36–7.47 (m, 3H), 7.56 (t, $J = 8.48$ Hz,1H), 7.64 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 7.84$ Hz, 1H), 7.91–8.06 (m, 4H) ppm.

### 3-Amino-1-(4-nitrophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (4f)

Mp: 182–184 °C; IR (KBr, cm$^{-1}$): 3435, 3348, 2191, 1654, 1590, 1518, 1412; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 5.20$ (s, 1H), 7.13 (s, 2H), 7.37 (d, $J = 8.96$ Hz, 1H), 7.44–7.49 (m, 4H), 7.79 (t, $J = 7.16$ Hz, 1H), 7.92–7.98 (m, 2H), 8.15 (d, $J = 8.67$ Hz, 2H) ppm.

### 3-Amino-1-(4-methoxyphenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (4g)

Mp: 191–193 °C; IR (KBr,cm$^{-1}$): 3437, 3354, 2186, 1648, 1590, 1421; $^1$H NMR (CDCl$_3$, 400 MHz) $\delta = 3.72$ (s, 3H), 4.59 (s, 2H), 5.19 (s, 1H), 6.79 (d, $J = 8.6$ Hz, 2H), 7.10 (d, $J = 6.08$ Hz, 2H), 7.23 (d, $J = 8.97$ Hz, 1H), 7.37–7.39 (m, 2H), 7.69 (t, $J = 5.96$ Hz, 1H), 7.79 (d, $J = 8.48$ Hz, 2H) ppm.

### 3-Amino-1-(4-hydroxy-3-methoxyphenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (4 h)

Mp: 249–250 °C; IR (KBr, cm$^{-1}$): 3438, 3335, 2188, 1659, 1587, 1410; $^1$H NMR(CDCl$_3$, 400 MHz) $\delta = 3.85$ (s, 3H), 4.57 (s, 2H), 5.21(s, 1H), 5.49 (s, 1H), 6.60 (d, $J = 8.4$ Hz, 1H), 6.78 (t, $J = 5.6$ Hz, 2H), 7.29–7.31 (m, 1H), 7.42–7.44 (m, 2H), 7.72–7.74 (m, 1H),7.83 (d, $J = 8.8$ Hz, 2H) ppm.

### 3-Amino-1-(4-chloro-3-nitrophenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (4i)

Mp: 184–186 °C; IR (KBr, cm$^{-1}$): 3454, 3369, 2196, 1678, 1589, 1415, 1357; $^1$H NMR (DMSO,400 MHz) $\delta = 5.55$ (s, 1H), 7.15 (s, 2H), 7.37 (d, $J = 8.96$ Hz, 1H), 7.42–7.49 (m, 3H), 7.66 (d, $J = 8.36$ Hz, 1H), 7.82 (d, $J = 8.16$ Hz, 1H), 7.92–7.99 (m, 3H) ppm.

### 3-Amino-1-(4-hydroxyphenyl)-1*H*-benzo[*f*]chromene-2-carbonitrile (4j)

Mp: 288–290 °C; IR (KBr, cm$^{-1}$): 3454, 3346, 3182, 2196, 1653, 1589, 1415; $^1$H NMR (DMSO, 400 MHz) $\delta = 5.15$ (s, 1H), 6.62 (d, $J = 8.4$ Hz, 2H), 6.87–6.99 (m, 3H), 7.16 (s, 1H), 7.29–7.45 (m, 3H), 7.82–7.91 (m, 3H), 9.27 (s, 1H) ppm.

### 3-Amino-1-(pyridine-2-yl)-1*H*-benzo[*f*]chromene-2-carbonitrile (4 k)

Mp: 172–174 °C; IR (KBr, cm$^{-1}$): 3458, 3349, 2186, 1662, 1593, 1406; $^1$H NMR (DMSO, 400 MHz) $\delta = 5.04$ (s, 1H), 7.09 (d, $J = 8.5$ Hz, 1H), 7.19 (s, 2H), 7.47–7.56 (m, 3H), 7.64 (t, $J = 7.9$ Hz, 1H), 7.74 (d, $J = 6.6$ Hz, 1H), 7.89 (d, $J = 8.1$ Hz, 1H), 8.07 (s, 1H), 8.13 (d, $J = 11.2$ Hz, 1H), 8.24 (d, J = 8.5 Hz, 1H) ppm.

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