A Green, Organometallic Catalyzed Synthesis of a Series of Novel Functionalized 4-Aroyl-4*H*-benzo[*g*]chromenes through One-pot, Three Component Reaction

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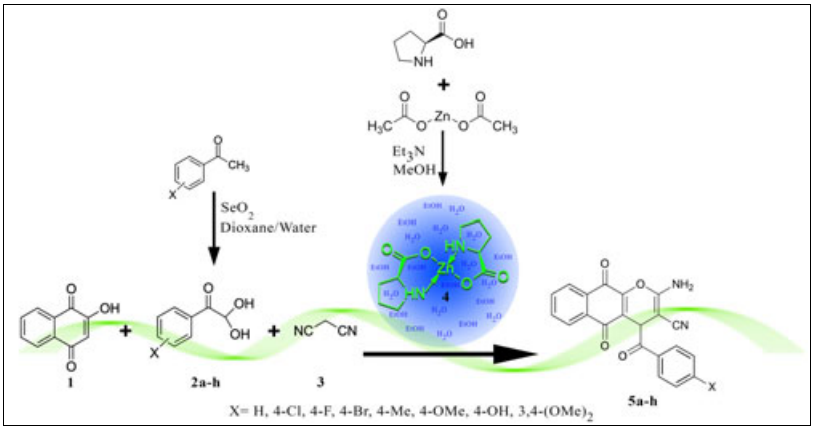

A new series of 4-aroyl-4*H*-benzo[*g*]chromene derivatives have been synthesized through an efficient, straightforward, and environmentally acceptable one-pot, three component reaction of malononitrile, different arylglyoxals, and 2-hydroxy-1,4-naphtoquinone (lawsone) in short reaction times and high to excellent yields. The zinc complex of amino acid L-proline, that is, Zn[L-proline]$_2$ has been prepared and used as highly active, recyclable, noncorrosive, and water soluble Lewis acid catalyst for this transformation.

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INTRODUCTION

Chemical compounds with benzo[*g*]chromene heterocyclic scaffold have a variety of biological activities including anti-inflammatory [1], antimalarial [2], and pesticidal [3] activities. There are also several biologically active natural products that incorporate benzo[*g*]chromene core [4–6]. Recent investigations show that natural product β-lapachone is a potential anticancer [7,8] agent and has synergic effect with Taxol against tumor growth.

Designing or redesigning chemical processes in order to increase their efficiency and safety has been a subject of immense attention among chemists in the last decade [9,10]. Catalysts are the master key toward green chemistry goals [11], and by decreasing the activation energy, catalysts can make a chemical reaction happen in shorter time, more benign, and energy-efficient conditions. Properly catalyzed reactions can be performed at lower temperatures and pressures, needing less toxic reagents and organic solvents [11]. The L-proline (bis[(L) prolinato-N,O]Zn complex, Zn[L-proline]$_2$ (**4**) as an organometallic Lewis acid has recently been used to catalyze many organic transformations such as direct aldol reaction [12], Knovenagel condensation [13], synthesis of dicoumarols [14], pyrano[2,3-*d*]pyrimidine derivatives [15], xanthenediones [16], and pyrazoles [17]. This catalyst is dissolved but not dissociated in water [12]; it is easily preparable, inexpensive, and very stable under reaction conditions, and because of its water solubility, it can be easily separated from the reaction mixture after completion of the reaction and be recycled for the next reaction runs without significant loss of activity.

Incorporation of several starting materials in one-pot and single step through multicomponent reaction strategy allows the production of highly functionalized molecules with high atom efficiency and minimized use of hazardous organic solvents in separation and work-up steps [18]. These results are clearly compatible with green chemistry goals. On the other hand, using arylglyoxlas in synthetic heterocyclic chemistry has been increased in recent years [19]. In continuation of our interest in synthesis of new heterocyclic compounds using one-pot, multicomponent strategy [20–24], herein, we wish to report the synthesis of a series of 4-aroyl-4*H*-benzo[*g*]chromene derivatives by one-pot, three component reaction of arylglyoxals, 2-hydroxy-1,4-naphtoquinone, and malononitrile in the presence of Zn[L-proline]$_2$ as an organometallic catalyst in high to

excellent yields. To the best of our knowledge, there is only one report on the synthesis of functionalized 4-aroyl-4*H*-benzo[*g*]chromenes under microwave condition at 110°C [25]. However, there are some reports on synthesis of similar benzo[*g*]chromene derivatives from the reaction of aldehydes, malononitrile, and 2-hydroxy-1,4-naphtoquinone (lawsone), and several catalytic systems such as DBU [26], *o*-benzenedisulfonimide [27], basic ionic liquid [28], triethylbenzylammonium chloride [29], and TEA [30] have been used for that purpose. So we were interested to study the possibility of synthezing a new series of benzo[*g*]chromenes from the reaction of malononitrile, arylglyoxlas, and lawsone using Zn[L-proline]$_2$ as a water soluble Lewis acid catalyst.

RESULTS AND DISCUSSION

As the first effort to synthesize our desired products, the reaction of phenylglyoxal (**2a**), malononitirle (**3**), and lawsone (**1**) (mole ratio 1:1:1) was chosen as model reaction (Fig. 1) and was investigated in the presence of different catalytic systems including acid catalysts sulfanilic acid, sulfamic acid, and *p*-toluenesulfonic acid, neutral phase transfer catalyst tetrabutylammonium bromide, aminoacids L-proline and L-cysteine, and the zinc complex of L-proline.

Different reaction conditions from room temperature to reflux were examined, and the reaction was performed in water, ethanol, and aqueous ethanol media. According to the outcome of the investigations, poor results were obtained when sulfamic acid and *p*-toluenesulfonic acid were used as the catalyst (Table 1, entries 2 and 3), and changing the reaction temperature and solvent and increasing the catalyst loading had no significant effect when these catalysts were used; however, in the presence of sulfanilic acid, no desired product was formed in any conditions (Table 1, entry 1). The other catalyst that was examined was tetrabutylammonium bromide that gave no desired product even under reflux conditions (Table 1, entry 4). The thin layer chromatography (TLC) of the reaction medium after 2 h showed a mixture of undesirable products. At the next stage, the effect of amino acids L-proline and L-cysteine was examined to catalyze the reaction. Interestingly, by performing the reaction in the presence of catalytic amount of L-proline (20 mol%), moderately good result was obtained at 50°C in ethanol:water (1:1) (Table 1, entry 5). It was found that under the same reaction conditions, L-cysteine can also catalyze the reaction but affording lower yield compared

Table 1

Screening of the catalyst for synthesis of the desired novel benzo[*g*] chromene derivatives[a].

Entry	Catalyst	Time (min)	Yield (%)
1	Sulfanilic acid	90	-
2	Sulfamic acid	90	20
3	*p*-TSA	120	56
4	TBAB	120	-
5	L-Proline	50	80
6	L-Cysteine	70	78
7	Zn[L-Proline]$_2$	30	91
8	No catalyst	120	-

-, no products have been formed; p-TSA, *p*-toluenesulfonic acid; TBAB, tetrabutylammonium bromide.
[a]Reagents and conditions: Lawsone **1** (1 mmol), arylglyoxals **2a–h** (1 mmol), malononitrile **3** (1 mmol), and appropriate catalyst (20 mol%) EtOH:H_2O (1:1), at 50°C.

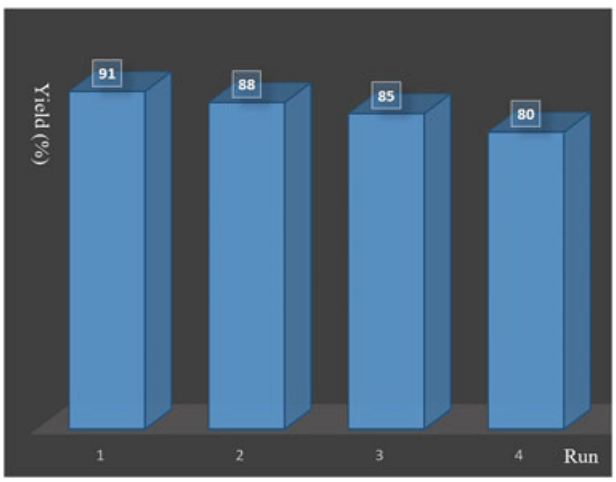

Figure 2. Reusability of Zn[L-proline]$_2$ for the synthesis of 4-aroyl-4*H*-benzo[*g*]chromene derivatives. [Color figure can be viewed at wileyonlinelibrary.com]

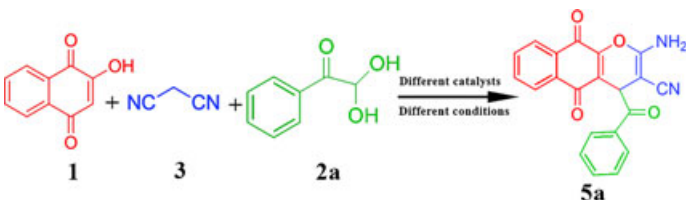

Figure 1. Model reaction for synthesis of 4-aroyl-4*H*-benzo[*g*]chromene derivatives. [Color figure can be viewed at wileyonlinelibrary.com]

with L-proline (Table 1, entry 6). Finally, we were interested to prepare the zinc complex of L-proline and study its efficacy as catalyst for this reaction, as illustrated in Table 1, and 20 mol% of Zn[L-proline]$_2$ can catalyze the reaction of phenylglyoxal, malononitirle, and lawsone to afford the desired benzo[*g*]chromenes in shorter reaction time and significantly higher yield at 50°C in aqueous ethanol media (1:1) that we can call the optimal reaction conditions now (Table 1, entry 7). Increasing the catalyst loading did not improve the reaction rate or shorten the reaction time. On the other hand, performing the model reaction in water using the same catalyst afforded lower yield of the desired product. Increasing the reaction temperature to reflux condition seemed to cause degradation of the product as proved by TLC analysis and the formation of a dark, sticky substance that cannot be separated. Another reaction was also performed under the optimized conditions but in the absence of catalyst that led to no product formation (Table 1, entry 8). In order to develop the scope of the reaction and the optimal reaction conditions, more investigations were performed by repeating the reaction in the presence of different arylglyoxals with electron-donating and electron-withdrawing substituents at different positions. Interestingly, all the corresponding benzo[*g*]chromene derivatives were synthesized in high yields. A new set of pharmaceutically important chemical compounds known as 4-aroyl-4*H*-benzo[*g*]chromenes can be synthesized through one-pot, three component reaction of malononitrile, different arylglyoxlas, and lawsone

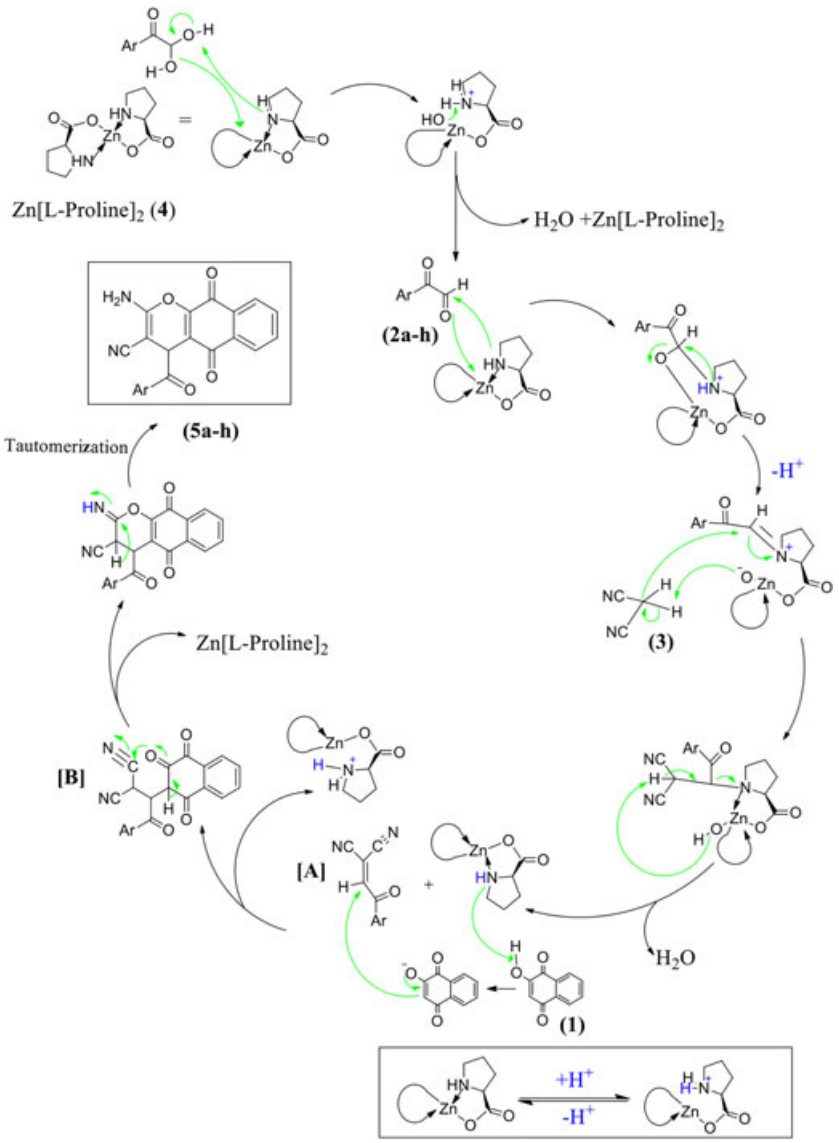

Figure 3. A proposed mechanism for the synthesis of 4-aroyl-4*H*-benzo[*g*]chromenes **5a–h**. [Color figure can be viewed at wileyonlinelibrary.com]

(mole ratio 1:1:1) in the presence of 20 mol% of Zn[L-proline]$_2$ in H_2O:EtOH (1:1) media at 50°C in very short time and high yields.

The recyclability of Zn[L-proline]$_2$ was also examined in the synthesis of **5a**. For that purpose, phenylglyoxal, malononitrile, and lawsone (3 mmol of each) were added to a 25-mL round bottom flask containing 12-mL aqueous ethanol (1:1) and Zn[L-proline]$_2$ (20 mol%), and the mixture was stirred at 50°C to completion. The solid precipitate was filtered and washed several times with distilled water in order to completely wash off the catalyst. The aqueous ethanol mixture was removed under reduced pressure. To the obtained solid mixture, diethyl ether was added, and catalyst being insoluble in organic solvents was separated from the mixture by filtration and washed with diethyl ether and dried at 70°C for 2 h to get recycled Zn[L-proline]$_2$ ready for another catalytic cycle. It was observed that the catalyst can be reused at least three times without significant loss of activity (Fig. 2).

A proposed mechanism of the reaction is presented in Figure 3. It is believed that Zn[L-proline]$_2$ facilitates cyanoolefine intermediate [**A**] formation and synthesis of 4-aroyl-4*H*-benzo[*g*]chromenes **5a–h**. After dehydration of the arylglyoxal by the catalyst, a *Knoevenagel* condensation occurs between malononitrile (**3**) and arylglyoxal **2** that is facilitated by Zn[L-proline]$_2$ via C–H activation on malononitrile. The formed cyanoolefine [**A**] intermediate reacts with 2-hydroxy-1,4-naphtoquinone by Michael addition to give the intermediate [**B**] that undergoes heterocyclization and tautomerization to afford the desired products **5a–h.**

CONCLUSIONS

We have developed a one-pot, three component reaction toward the synthesis of a new series of 4-aroyl-4*H*-benzo[*g*]chromenes **5a–h** using readily available precursors as starting materials in the presence of Zn[L-proline]$_2$ as organometallic water soluble catalyst.

Some important advantages of this method include the use of a recoverable catalyst, shorter reaction times, ease of separation, very high yields, and using green solvent and mild reaction conditions.

The new benzo[*g*]chromenes may have useful biological and pharmaceutical applications.

EXPERIMENTAL

Chemicals were purchased from Merck and Sigma-Aldrich companies and used as received. TLC was used to monitor reaction progress and was carried out using Merck 0.2-mm silica gel 60 F-254 Al-plates (Kenilworth, NJ). Melting points were determined on a digital melting point apparatus (Electrothermal, Cole-Parmer, Staffordshire, UK) and reported uncorrected. Infrared spectra were recorded on a Thermo Nicolet (Nexus 670) FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA), using KBr disks. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded with a Bruker spectrometer at 300 and 75 MHz, respectively (Bruker, Billerica, MA). The spectra were measured in DMSO-d_6 using TMS as the internal standard. Elemental analyses were performed using a Leco Analyzer 932 (Leco Corp., St. Joseph, MI).

The arylglyoxals were prepared as their hydrates by oxidation of the corresponding acetophenones with SeO_2 [31].

The zinc–amino acid complex was prepared according to the method defined by Darbre and Machuqueiro [12]. To a solution of L-proline (2 mmol) in MeOH (10 mL), 0.3 mL of Et_3N was added, and the reaction mixture was stirred for 10 min. The zinc acetate (1 mmol) was added, and the mixture was stirred for further 45 min until a white precipitate was formed and collected by filtration. The complex was characterized by FTIR.

General procedure for the synthesis of products (5a–h). The arylglyoxal (1 mmol), malononitrile (1 mmol), catalytic amount of Zn[L-Proline]$_2$ (0.2 mmol), and 2-hydroxy-1,4-naphtoquinone (1 mmol) were added stepwise to a 10-mL round bottom flask containing 4-mL aqueous ethanol (1:1) as the solvent, and the mixture was stirred at 50°C for appropriate time as mentioned in Table 1. After completion of the reaction (determined by TLC using ethyl acetate: n-hexane, 2:1 as eluent), the mixture was left to settle. The upper solvent was sucked by Pasteur pipette (Sinaglass, Tehran, Iran), and another fresh 4 mL of aqueous ethanol (1:1) was added again, and the mixture was stirred for 2 min, then the mixture was added to crush ice and left for 1 h. The solid was filtered and washed with distilled water and aqueous ethanol (1:1) several times to obtain pure colored powders, and the products may be recrystallized with DMSO if necessary.

The structures of substituted 4-aroyl-4*H*-benzo[*g*]chromenes **5a–h** were characterized by their FTIR and ^{1}H-NMR and ^{13}C-NMR spectra. The singlets in the ^{1}H-NMR spectra of the novel derivatives at δ = 5.38–5.51 ppm and at δ = 7.50–7.65 ppm were ascribed to the CH and NH_2 groups, respectively, and were present in all products. In the ^{13}C-NMR spectra of the products, signals located at δ = 164.41–177.10, 182.94–183.02, and 196.00–198.28 ppm were attributed to three different carbonyl groups. In the FTIR spectra, the characteristic bands at 3185–3468 and 2199–2200 cm^{-1} could be assigned to the vibrations of the NH_2 and CN groups, respectively.

2-Amino-4-benzoyl-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-3-carbonitrile (5a). Yield: 91% (81 mg); light brown solid, mp: 238–240°C (Lit. [30], 233–245); IR: (KBr) υ: 3461, 3340, 3211, 3165, 3073, 2928, 2193, 1991, 1660, 1588, 1402, 1354, 1206, 1047, 947, 853, 763, 724, 681, 602, 511 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ: 5.50 (s, 1H, CH), 7.59 (s, 2H, NH_2), 7.62 (t, *J* = 7.5 Hz, 2H, ArH), 7.75 (t, *J* = 7.5 Hz, 1H, ArH), 7.88 (d, *J* = 3.0, 3H, ArH), 8.07–8.16 (m, 3H, ArH) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 37.66, 51.94, 119.10, 121.55, 126.39, 126.85, 129.38, 129.66, 130.90, 131.00, 134.58, 135.04, 135.13, 135.63, 150.45, 160.36, 177.02, 183.00, 198.28 ppm.

2-Amino-4-(4-chlorobenzoyl)-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-3-carbonitrile (5b). Yield: 93% (90 mg); light brown solid, mp: 212–213°C; IR (KBr) υ: 3439, 3338, 3215, 3073, 2925, 2192, 1665, 1588, 1478, 1406, 1366, 1292, 1207, 1087, 1047, 987, 848, 790, 716 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ: 5.50 (s, 1H, CH), 7.62 (s, 2H, NH_2), 7.69 (d, *J* = 8.4, 2H, ArH), 7.84–7.91 (m, 3H, ArH), 8.07–8.09 (m, 1H, ArH), 8.17 (d, *J* = 8.4, 2H, ArH) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 37.73, 51.68, 119.07, 121.24, 126.41, 126.86, 129.58, 130.92, 130.96, 131.54, 134.41, 135.06, 135.34, 139.69, 150.45, 160.32, 176.96, 183.02, 197.47 ppm. *Anal.* Calcd for $C_{21}H_{11}ClN_2O_4$: C, 64.55; H, 2.84; N, 7.17. Found: C, 64.74; H, 2.70; N, 7.02.

2-Amino-4-(4-methylbenzoyl)-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-3-carbonitrile (5c). Yield: 90% (83 mg); light brown solid, mp: 215–217°C; IR (KBr) υ: 3468, 3343, 3204, 3168, 3039, 2921, 2363, 2194, 1662, 1593, 1402, 1357, 1299, 1241, 1202, 1044, 949, 842, 787, 723, 595, 507 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ: 2.43 (s, 3H, CH_3), 5.45 (s, 1H, CH), 7.41 (d, *J* = 7.8 Hz, 2H, ArH), 7.56 (s, 2H, NH_2) 7.88–7.90 (m, 3H, ArH), 8.03–8.06 (m, 3H, ArH) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 21.72, 37.49, 52.09, 121.65, 126.38, 129.95, 130.89, 131.02, 135.02, 135.25, 145.20, 170.55, 171.10, 183.00, 197.64 ppm. *Anal.* Calcd for $C_{22}H_{14}N_2O_4$: C, 71.35; H, 3.81; N, 7.56. Found: C, 71.64; H, 3.68; N, 7.67.

2-Amino-4-(4-methoxybenzoyl)-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-3-carbonitrile (5d). Yield: 85% (82 mg); light brown solid, mp: 236–239°C (Lit. [30], 234–236); IR: (KBr) υ: 3328, 3185, 2979, 2944, 2845, 2623, 2200, 1667, 1590, 1514, 1415, 1320, 1237, 1176, 1025, 958, 842, 785, 719, 588, 528 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ: 3.89 (s, 3H, CH_3), 5.44 (s, 1H, CH), 7.12 (d, *J* = 8.7 Hz, 2H, ArH), 7.54 (s, 2H, NH_2), 7.87–7.90 (m, 3H, ArH), 8.07–8.14 (m, 3H, ArH) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 37.28, 52.29, 56.15, 114.64, 121.75, 126.37, 126.83, 128.32, 130.87, 131.03, 132.18, 135.01, 135.34, 162.33, 164.41, 177.12, 182.99, 196.47 ppm.

2-Amino-4-(3,4-dimethoxybenzoyl)-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-3-carbonitrile (5e). Yield: 84% (87 mg); light brown solid, mp: 219–220°C; IR (KBr) υ: 3849, 3742, 3379, 3320, 3203, 3081, 2936, 2843, 2694, 2611, 2550, 248, 2357, 2331, 2268, 2195, 2031, 1915, 1669, 1591, 1514, 1418, 1356, 1254, 1197, 1162, 1022, 954, 882, 776, 719, 619, 532 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ: 3.84 (s, 3H, OMe), 3.90 (s, 3H, OMe), 5.47 (s, 1H, CH), 7.16 (d, *J* = 8.4 Hz, 1H, ArH), 7.55 (s, 2H, NH_2), 7.56 (s, 1H, ArH), 7.88–7.91 (m, 4H, ArH), 8.07–8.10 (m, 1H, ArH) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 37.25, 52.36, 55.99, 56.33, 111.44, 111.66, 119.31, 121.84, 126.81, 128.13, 130.88, 131.06, 135.33, 149.13, 150.45, 154.38, 160.39, 177.10, 182.94, 196.22 ppm. *Anal.* Calcd for $C_{23}H_{16}N_2O_6$: C, 66.34; H, 3.87; N, 6.73. Found: C, 66.11; H, 3.69; N, 6.89.

2-Amino-4-(4-bromobenzoyl)-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-3-carbonitrile (5f). Yield: 82% (89 mg); dark brown solid, mp: 246–248°C; IR (KBr) υ: 3435, 3336, 3211, 3085, 2920, 2642, 2251, 2197, 1664, 1583, 1486, 1366, 1239, 1063, 1001, 840, 792, 727, 601, 481 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ: 5.40 (s, 1H, CH), 7.56 (bs, 2H, ArH), 7.65 (s, 2H, NH_2), 7.78–7.80 (m, 2H, ArH), 7.87 (bs, 5H, ArH), 8.04 (bs, 1H, ArH); ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 51.66, 114.10, 114.36, 119.08, 121.23, 127.71, 130.15, 130.71, 130.95, 132.05, 132.86, 134.43, 134.72, 160. 31, 176.96, 194.27, 197.69 ppm. *Anal.* Calcd for $C_{21}H_{11}BrN_2O_4$: C, 57.95; H, 2.55; N, 6.44. Found: C, 58.08; H, 2.47; N, 6.32.

2-Amino-4-(4-hydroxybenzoyl)-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-3-carbonitrile (5g). Yield: 84% (78 mg); dark brown solid, mp 260–261°C; IR (KBr) υ: 3462, 3332, 3276, 2193, 1661, 1588, 1360, 1298, 1216, 1042, 952, 849, 798, 723, 601, 523 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ: 5.38 (s, 1H, CH), 6.92 (d, *J* = 6.9 Hz, 2H, ArH), 7.51 (s, 2H, NH_2), 7.89 (s, 3H, ArH), 8.01–8.06 (t, *J* = 8.0, 3H, ArH), 10.57 (s, 1H, OH) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 37.11, 52.42, 115.95, 119.20,121.86, 126.88, 130.86, 131.05, 132.47, 150.42, 160.31, 163.44, 177.08, 182.96, 196.00 ppm. *Anal.* Calcd for $C_{21}H_{12}N_2O_5$: C, 67.74; H, 3.25; N, 7.52. Found: C, 67.91; H, 3.08; N, 7.41.

2-Amino-4-(4-fluorobenzoyl)-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromene-3-carbonitrile (5h). Yield: 95% (88 mg); red solid, mp: 236–237°C (Lit. [30], 254–256); IR (KBr) υ: 3463, 3333, 3206, 3168, 3079, 2193, 1664, 1589, 1509, 1403, 1358, 1302, 1208, 1043, 951, 851, 796, 721, 589, 510 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ: 5.51 (s, 1H, CH), 7.45 (t, *J* = 7.4 Hz, 2H, ArH), 7.60 (s, 2H, NH_2), 7.87–7.94 (m, 3H, ArH), 8.09 (t, *J* = 7.5 Hz, 1H, ArH), 8.26 (t, *J* = 8.7 Hz, 2H, ArH) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 37.67, 51.81, 116.36, 116.65, 119.09, 121.34, 126.39, 126.86, 130.91, 130.98, 132.43, 132.76, 132.87, 135.05, 135.33, 150.44, 160.33, 162.33, 176.99, 183.01, 196.97 ppm.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.