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# GREEN, EXPEDITIOUS AND RECYCLABLE SPECIFIC ACIDIC IONIC LIQUID [PYRIDINE–$SO_3H$]Cl CATALYZED ONE-POT SYNTHESIS OF 2-AMINO-4-ARYL 4H-CHROMENE-3-CARBONITRILE SCAFFOLDS UNDER MICROWAVE IRRADIATION

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**ABSTRACT:** A facile, eco-conscious and time-effective microwave-assisted green methodology has been developed for the construction of 4*H*-chromene-3-carbonitrile annulated derivatives (**4a-n**) with good yields utilizing [pyridine–$SO_3H$]Cl catalyst via one-pot, multi-component condensation. All the synthesized products were established by IR, $^1$H NMR, $^{13}$C NMR, mass spectral data and elemental analysis. The significant compensation of this method over existing conventional heating, such as high yields in short reaction time, the formation of products is an analytically pure form, straightforward workup procedure, cost-effectiveness, neat reaction profile, recycle and reusability of the catalyst, make this route ‘‘green’’ and environmentally benign.

**KEYWORDS:** Green synthesis, 2-Amino-4-aryl-4H-chromene-3-carbonitrile, One-pot synthesis, Microwave irradiation.

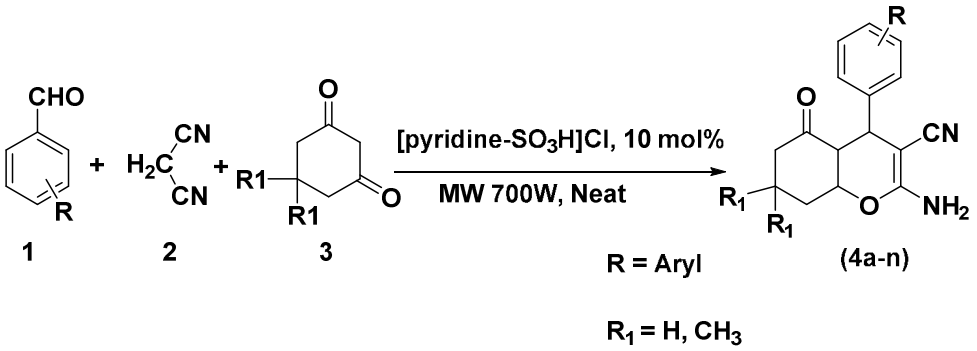
## INTRODUCTION

The multi-component coupling reactions (MCRs) are one of the most persuasive synthetic tool and dexterous bond-forming technique in organic synthesis for the construction of biologically remarkable derivatives in view of the green chemistry. The MCRs have distinctive compensation such as the formation of several new bonds in a one-pot reaction, very flexible, highest selectivity in minimal time, high atom economy, yields are obtained with high purity and operational simplicity [i-vii]. In recent years, Microwave-assisted chemistry has become a constructive technique for a variety of beneficial applications in organic synthesis. Microwave promoted one pot multi-component reactions have been attracting to organic researcher and medicinal chemists because of these reactions show some meticulous or unexpected reactivity’s and their important usefulness in green chemistry [viii-xi]. Currently, ionic liquid catalyzed reactions have fascinated to chemists because of their fascinating properties like eco-friendly nature, non-flammability, elevated thermal stability, an ability to dissolve extensive range of materials and reusability of the catalyst [xii, xiii].

Fused 4H-chromene moiety is the key building block of many oxygen-containing heterocyclic natural products and its derivatives have established useful applications such as used in cosmetics, laser dyes, pigments and potentially biodegradable agrochemicals [xiv-xv]. 4H-chromene substituted derivatives have an assortment of beneficial pharmacological properties such as antibacterial activity [xvi], antitumor [xvii], anti-leukemic [xviii], anti-Alzheimer [xix], as well as photochemical reactivity [xx]. In view of the biological consequence of 2-amino-4H-pyran scaffolds, diverse methods have been previously documented in the literature for the construction of structurally interrelated 4H-chromene derivatives. In recent years efforts have been made to enlarge new methods for the construction of these products. A variety of catalysts reported such as silica-bonded S-sulfonic acid [xxi], $Re(PFO)_3$ [xxii], hexadecyl dimethyl benzyl ammonium bromide [xxiii], $SiO_2$-Pr-$SO_3H$ [xxiv], phenylboronic acid [xxv], diammonium hydrogen phosphate [xxvi], $Fe_3O_4$@$SiO_2$/DABCO [xxvii], $RuBr_2(PPh_3)_4$ [xxviii], $I_2$ [xxix], $N(Et)_4ClO_4$ [xxx], (PPA–$SiO_2$) [xxxi], ([PVP-H]$H_2PO_4$) [xxxii] have been used. However, most of these ways have one or several drawbacks such as large quantities of volatile organic solvents use, inadequate yields, tedious workup procedure, reaction take long times, elevated temperatures and harsh reaction conditions. In addition, the main disadvantage of accessible methods is that the catalysts are ruined cannot be recovered in work-up. As a result, to conquer these limitations and in continuation of our previous research on the development of environmentally friendly procedures and construction of biologically energetic heterocyclic compounds [xxxiii-xxxvii] Here in, we report a facile, well efficient and rapid green method for the construction of 2-amino-3-cyano-4H-chromene scaffolds using [pyridine–$SO_3H$]Cl catalyst. To the best of our knowledge, no method reported in the literature for the construction of these 4*H*-benzo[*b*]pyran products using [pyridine–$SO_3H$]Cl catalyst under solvent-free microwave irradiation.

## RESULTS AND DISCUSSION

2-Amino-3-cyano-4H-chromene derivatives (**4a–n**) were synthesized by involving aryl aldehyde, diketones, and malononitrile under solvent-free microwave irradiation (MW) utilizing acidic ionic liquid 1-sulfopyridinium chloride [pyridine–$SO_3H$]Cl catalyst furnished good yields in petite reaction time. The illustration is shown in **Scheme 1**. The acidic ionic liquid catalyst was prepared according to the literature process [xxxviii].




**Scheme.1** Synthesis of 2-amino-3-cyano-4H-chromene derivatives catalyzed by [pyridine–$SO_3H$]Cl.

In order to optimize the reaction condition primarily, we carried out a model reaction taking benzaldehyde, malononitrile, and dimedone (conventional heating) in the presence of 5mol % ionic liquid catalyst under solvent-free conditions at 80 $^{O}$C for about 3 hours obtained 71 % yield. To get the better yield we escalating the temperature the improvement of the reaction were not satisfactory. Then, we twisted our attention towards MW irradiation as a

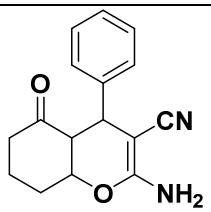
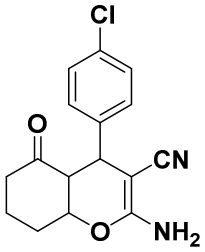
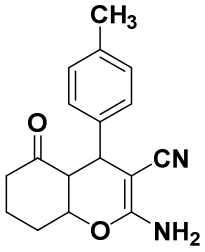
replacement for conventional heating. Amusingly, the desired product was obtained in 82 % in a microwave reactor after 5 m. Later 10 mol % catalyst was loading obtained maximum yield 94 % in solvent-free microwave conditions. Rising the 15 mol% of the catalyst does not change the yield but somewhat slow down the reaction with unnecessary impurities. For more examination of the manipulate of microwave irradiation on the reaction, an assessment was made between microwave irradiation and heating conditions optimization reaction results are shown in **Table 1**.

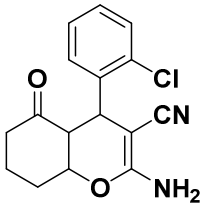
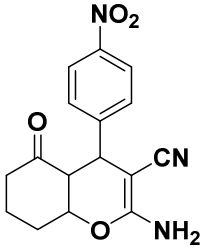
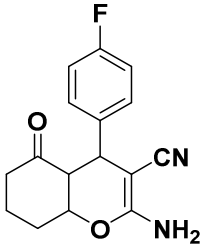
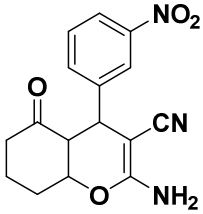
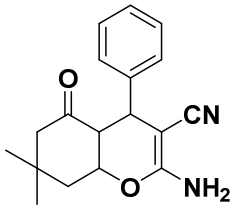
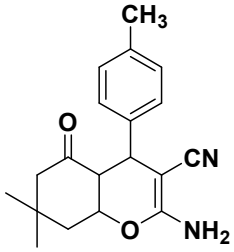
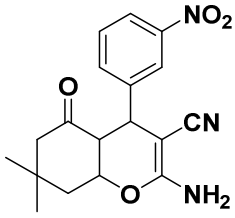
**Table 1** Optimization of the reaction conditions in the presence of [pyridine–$SO_3H$]Cl

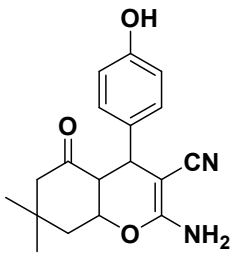
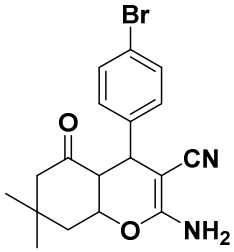
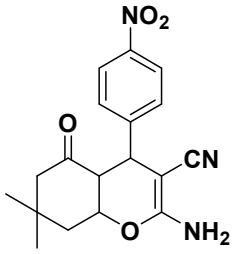
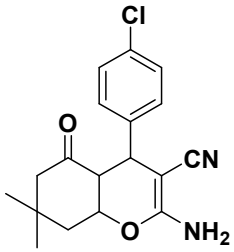
| Entry | Solvent | Conventional method | | Microwave method | |
|---|---|---|---|---|---|
| | | Time (h) | Yield,(%)[b] | Time(m) | Yield,(%) |
| 1 | $CH_3CN$ | 3 | 69 | 7 | 81 |
| 2 | Methanol | 2.5 | 74 | 9 | 85 |
| 3 | THF | 3 | 77 | 8 | 84 |
| 4 | $C_2H_5OH$ | 2 | 81 | 6 | 87 |
| 5 | Neat | 2 | 87 | 3 | 94 |

In the path of study we pragmatic that [pyridine–$SO_3H$]Cl 10 mol % was the mainly effective catalyst for obtaining the yields (94%) under solvent-free condition. Under these reaction condition ([pyridine–$SO_3H$]Cl 10 mol %, solvent-free) We have synthesized 2-amino-3-cyano-4H-chromene scaffolds under microwave irradiation exposed in **Table 2.**

**Table 2** Synthesis of 2-amino-3-cyano-4H-chromene scaffolds under MWI.

| **Analog** | **R** | **$R_1$** | **Products** | **Time (m)** | **Yield[a] (%)** | **M.P. $^{O}$C (Found)** | **M.P. $^{O}$C (Report)** |
|---|---|---|---|---|---|---|---|
| 4a | $C_6H_5$ | H |  | 3 | 94 | 241-243 | 240–242 [xxi] |
| 4b | 4-Cl-$C_6H_4$ | H |  | 3.5 | 91 | 235-237 | 234-236 [xxxii] |
| 4c | 4-$CH_3C_6H_4$ | H |  | 3 | 90 | 223-225 | 224–226 [xxiii] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 4d | 2-Cl- $C_6H_4$ | H |  | 2 | 94 | 211-213 | 212–214 [xxi] |
| 4e | 4-$NO_2C_6H_4$ | H |  | 3.5 | 93 | 236-238 | 235-237 [xxxii] |
| 4f | 4-F- $C_6H_4$ | H |  | 4 | 91 | 216-218 | 213–215 [xxi] |
| 4g | 3-$NO_2$-$C_6H_4$ | H |  | 2 | 93 | 191-193 | 190-192 [xxi] |
| 4h | $C_6H_5$ | $CH_3$ |  | 2.5 | 92 | 229-231 | 231-233 [xxxii] |
| 4i | 4-$CH_3C_6H_4$ | $CH_3$ |  | 4 | 94 | 214-216 | 216–218 [xxi] |
| 4j | 3-$NO_2C_6H_4$ | $CH_3$ |  | 3.5 | 90 | 210-213 | 212-214 [xxii] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 4k | 4-OH-$C_6H_4$ | $CH_3$ |  | 4 | 92 | 217-218 | 216–218 [xxv] |
| 4l | 4-Br- $C_6H_4$ | $CH_3$ |  | 3 | 93 | 199-201 | 200-203 [xxxii] |
| 4m | 4-$NO_2$ $C_6H_4$ | $CH_3$ |  | 2.5 | 94 | 179-181 | 182–184 [xxiii] |
| 4n | 4-Cl- $C_6H_4$ | $CH_3$ |  | 3 | 91 | 238-240 | 237–239 [xxiii] |

[a]isolated yields.

All the synthesized products were established by spectral data, as well as elemental analyses and their melting points of the known products were also compared with the reported literature values where both were excellent conformity. later than completion of the reaction, the catalyst was recovered by evaporating the aqueous layer, washed with warm ethyl acetate, after that dried under vacuum at 100 $^{O}$C for about 2.5 h and reused for further five cycles. In this way, we establish a small decrease in catalyst activity in terms of products yield. For example, the reaction of benzaldehyde (1), malononitrile (2) and dimedone (3) gave the desired compounds (4a) in 94, 92, 91, 89, and 88 % yields obtained over an additional five cycles shown in Fig 1.

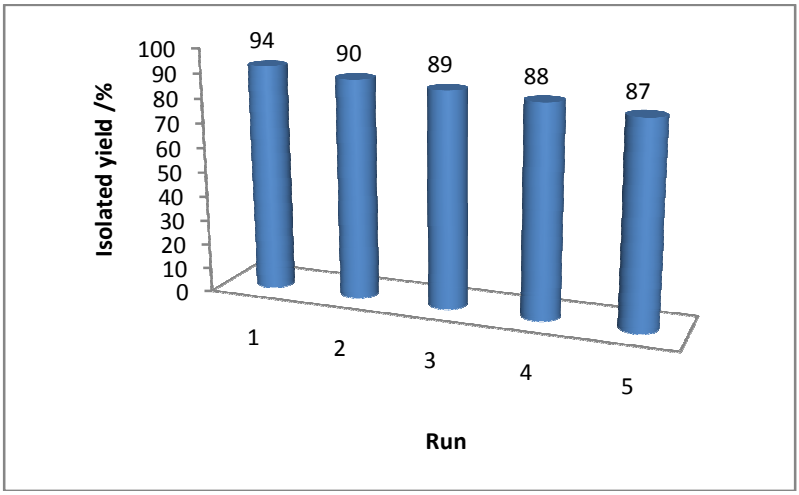



**Fig 1** Effect of recycling the [pyridine-$SO_3H$]Cl on 2-amino-3-cyano-4H-chromene derivative (4a) yields.

## EXPERIMENTAL

All the chemicals and solvents were purchased from Aldrich/Merck and used without additional purification. The melting points were resolute on a Buchi melting point apparatus and are uncorrected. The improvement of the reaction was checkered by with F254 silica-gel pre-coated TLC plates. $^1$H NMR spectra were recorded on a Bruker 400 MHz spectrometer and mass spectra were obtained using a Jeol JMSD-400 spectrometer. IR spectra were recorded on a Perkin Elmer FT-IR spectrophotometer using KBr pellets. Elemental analyses were performed on a Carlo-Erba model EA1108 analytical unit.

**Procedure for the synthesis of 2-amino-3-cyano-4H-chromene derivatives under conventional method (4a-n)**

Ionic liquid catalyst, [pyridine–$SO_3H$]Cl (10 mol%, 19.56 mg) was added to a mixture of aldehyde (1 mmol), malononitrile, (3 mmoL), dimedone (1 mmol, 140.18 mg) and heated at 100 $^O$C under neat conditions for an appropriate time, as described in Table 2. After completion of the reaction monitored by TLC, the mixture was diluted with water and the product was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure, and then purified by recrystallization from methanol to obtain the pure 2-amino-3-cyano-4H-chromene derivatives. The recovered catalyst was washed with ethyl acetate, dried under vacuum at 90 $^O$C for about 3 hours and reused for subsequent reactions.

**General procedure for the synthesis of 2-amino-3-cyano-4H-chromene derivatives under microwave irradiation (4a-n)**

Ionic liquid catalyst, [pyridine–$SO_3H$]Cl (10 mol%, 19.56 mg) was added to a mixture of aldehyde (1 mmoL), malononitrile, (3 mmoL), dimedone (1 mmoL, 140.18 mg) put in the hole of the microwave reactor. The mixture was irradiated at (mono-mode, CEM Discover microwave synthesis system at 700 W) for 4-6 m. After completion of the reaction monitored by TLC, the mixture was diluted with water and the product was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over $Na_2SO_4$ and concentrated under reduced pressure and then purified by recrystallization from ethanol to obtain the pure 2-amino-3-cyano-4H-chromene derivatives. The recovered catalyst was washed with ethyl acetate, dried under vacuum at 90 $^O$C for about 3.5 hours recycle and reused for successive five reactions.

***2-Amino-4-aryl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4a)***
IR: 3323, 3171, 3002, 2192, 1652, 1610, 1369, 1210 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.29-7.26 (d, $J$ = 7.2 Hz, 2H arom), 7.19-7.14 (m, 3H arom), 6.99 (s, 2H), 4.18 (s, 1H), 2.62–2.58 (m, 2H), 2.30–2.24 (m, 2H), 1.87–1.95 (m, 2H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 195.8, 164.4, 158.4, 144.7, 128.3, 127.0, 126.5, 119.7, 113.7, 58.1, 36.3, 35.4, 26.4. ESI-MS: *m/z* 267 $[M+H]^+$ Anal. Calc. For $C_{16}H_{14}N_2O_2$: C, 72.18; H, 5.26; N, 10.52; Found: C, 72.29; H, 5.27; N, 10.63 %.

***2-Amino-4-(4-chloro aryl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4b)***
IR: 3284, 3179, 2952, 2831, 1639, 1476, 1354, 1235 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.38-7.27 (d, $J$ = 7.4 Hz, 2H arom), 7.20-7.15 (d, $J$ = 7.2 Hz, 2H arom), 6.88 (s, 2H), 4.21 (s, 1H), 2.64–2.56 (m, 2H), 2.39 (m, 2H), 1.95–1.82 (m, 2H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 194.9, 163.7, 158.2, 143.8, 128.5, 127.7, 126.3, 120.5, 113.3, 57.9, 37.4, 35.6, 27.2. ESI-MS: *m/z* 301 $[M+H]^+$ Anal. Calc. For $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.32; N, 9.32; Found: C, 63.64; H, 4.37; N, 9.36 %.

***2-Amino-4-(4-methyl aryl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4c)***
IR: 3344, 3212, 3216, 2209, 1653, 1612, 1368, 1224 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.08-7.06 (d, $J$ = 7.4 Hz, 2H arom), 7.03 (d, $J$ = 7.2 Hz, 2H arom), 6.95 (s, 2H), 4.13 (s, 1H), 2.61–2.57 (m, 2H), 2.29-2.20 (m, 5H), 1.97–1.85 (m, 2H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 195.7, 164.1, 158.3, 141.8, 135.5, 128.8, 126.9, 119.7, 113.9, 58.3, 36.2, 34.9, 26.4. ESI-MS: *m/z* 281 $[M+H]^+$ Anal. Calc. For $C_{17}H_{16}N_2O_2$: C, 72.85; H, 5.71; N, 10.00; Found: C, 72.89; H, 5.83; N, 10.15 %.

***2-Amino-4-(2-chloro aryl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4d)***
IR: 3319, 3085, 2965, 2874, 1640, 1521, 1353 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.57-7.32 (d, $J$ = 7.4 Hz, 2H arom), 7.25-7.16 (m, 2H arom), 6.83 (s, 2H), 4.25 (s, 1H), 2.67–2.55 (m, 2H), 2.37 (m, 2H), 1.96–1.85 (m, 2H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 194.3, 164.7, 158.4, 143.6, 128.3, 127.4, 126.7, 120.1, 114.3, 58.5, 37.8, 35.4, 27.6. ESI-MS: *m/z* 301 $[M+H]^+$ Anal. Calc. For $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.32; N, 9.32; Found: C, 63.78; H, 4.25; N, 9.34 %.

***2-Amino-4-(4-nitro aryl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile* (4e)**
IR: 3355, 3114, 2167, 1685, 1614, 1542, 1357 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.54-7.37 (d, $J$ = 7.5 Hz, 2H arom), 7.28-7.16 (d, $J$ = 7.2 Hz, 2H arom), 6.64 (s, 2H), 4.32 (s, 1H), 2.63–2.52 (m, 2H), 2.41 (m, 2H), 1.98–1.79 (m, 2H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 165.7, 158.9, 144.5, 128.3, 127.6, 126.7, 121.5, 113.6, 58.7, 37.6, 35.2, 28.4. ESI-MS: *m/z* 312 $[M+H]^+$ Anal. Calc. For $C_{16}H_{13}N_3O_4$: C, 61.73; H, 4.18; N, 13.50; Found: C, 61.73; H, 4.21; N, 13.42 %.

***2-amino-4-(4-fluoro aryl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3 carbonitrile (4f)***
IR: 3158, 3117, 2242, 1653, 1614, 1521, 1364 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.39 (d, $J$ = 7.4 Hz, 2H arom), 7.37 (d, $J$ = 7.2 Hz, 2H arom), 6.79 (s, 2H), 4.40 (s, 1H), 2.58–2.53 (m, 2H), 2.27-2.25 (m, 2H), 1.96–1.89 (m, 2H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 195.6, 164.7, 158.4, 144.3, 128.7, 127.3, 126.6, 120.2, 113.8, 58.9, 37.4, 35.6, 28.3. ESI-MS: *m/z* 301 $[M+H]^+$ Anal. Calc. For $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.32; N, 9.32; Found: C, 63.84; H, 4.37; N, 9.36 %.

***2-Amino-4-(3-nitro aryl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4g)***
IR: 3267, 3202, 2242, 1698, 1624, 1516, 1342 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.56-7.34 (d, $J$ = 7.5 Hz, 2H arom), 7.29-7.16 (m, 2H arom), 6.84 (s, 2H), 4.27 (s, 1H), 2.74 (m, 2H), 2.39 (m, 2H), 1.97–1.75 (m, 2H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 194.0, 163.1, 154.0, 137.0, 132.3, 129.4, 128.6, 115.6, 112.9, 40.7, 36.8, 36.1, 26.2, 20.7. ESI-MS: *m/z* 312 $[M+H]^+$ Anal. Calc. For $C_{16}H_{13}N_3O_4$: C, 61.73; H, 4.18; N, 13.50; Found: C, 61.65; H, 4.23; N, 13.51 %.

***2-amino-7,7-dimethyl-5-oxo-4-aryl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4h)***

IR: 3397, 3326, 3257, 2961, 1682, 1663, 1604, 1371, 1218 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.35-7.27 (m, 2H arom), 7.16 (t, $J$ = 7.12 Hz, 3H), 6.85 (s, 2H), 4.13 (s, 1H), 2.68-2.56 (m, 2H), 2.27-2.08 (m, 2H), 1.06 (s, 3H), 0.97 (s, 3H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$):$\delta$ 195.5, 162.43, 158.4, 144.6, 127.9, 127.11, 119.6, 112.4, 58.3, 49.9, 35.3, 31.6, 28.3, 26.4. ESI-MS: *m/z* $[M+H]^+$ Anal. Calc. For $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52; Found: C, 73.53; H, 6.27; N, 9.58%.

***2-Amino-4-(4-methylaryl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3 carbonitrile (4i)***

IR: 3327, 3253, 3186, 2961, 1671, 1564 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.43-7.29 (d, $J$ = 7.4 Hz, 2H arom), 7.16 (d, $J$ = 7.2 Hz, 2H arom), 6.63 (s, 2H), 4.21 (s, 1H), 2.67-2.56 (m, 2H), 2.29-2.17 (m, 2H), 2.09 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 194.0, 163.4, 153.6, 136.9, 134.9, 129.3, 129.1, 127.4, 126.7, 115.8, 113.5, 41.0, 37.0, 36.2, 26.2, 20.8. ESI-MS: *m/z* 309 $[M+H]^+$ Anal. Calc. For $C_{19}H_{20}N_2O_2$: C, 74.02; H, 6.49; N, 9.09. Found: C, 74.08; H, 6.41; N, 9.14 %.

***2-amino-7,7-dimethyl-4-(3-nitroaryl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4j)***

IR: 3286, 2957, 2192, 1678, 1663, 1617, 1352, 1218 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.43-7.29 (d, $J$ = 7.4 Hz, 2H arom), 7.16 (d, $J$ = 7.6 Hz, 2H arom), 6.63 (s, 2H), 4.21 (s, 1H), 2.67-2.56 (m, 2H), 2.29-2.17 (m, 2H), 1.07 (s, 3H), 0.96 (s, 3H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 195.6, 163.1, 158.6, 147.7, 146.9, 134.1, 129.9, 121.7, 121.1, 119..2, 111.7, 57.1, 49.8, 35.3, 31.7, 28.2, 26.7. ESI-MS: *m/z* 340.12 $[M+H]^+$ Anal. Calc. For $C_{18}H_{17}N_3O_4$: C, 63.71; H, 5.05; N, 12.38; Found: C, 63.79; H, 5.16; N, 12.28 %.

***2-Amino-4-(4-hydroxy aryl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro- 4H-chromene-3-carbonitrile (4k)***

IR: 3423, 3336, 3204, 2970, 2208, 1666, 1553 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 9.57(s, 1H), 7.52-7.35 (d, $J$ = 7.5 Hz, 2H arom), 7.24 (d, $J$ = 7.2 Hz, 2H arom), 6.67 (s, 2H), 4.17 (s, 1H), 2.68-2.54 (m, 2H), 2.17 (m, 2H), 1.05 (s, 3H), 0.97 (s, 3H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 195.7, 164.2, 157.5, 147.7, 146.9, 134.1, 129.3, 123.6, 121.1, 112.5, 58.4, 49.4, 36.5, 31.6, 28.7, 26.4. ESI-MS: *m/z* 311 $[M+H]^+$ Anal. Calc. For $C_{18}H_{18}N_2O_3$: C, 69.67; H, 5.80; N, 9.03; Found: C, 69.74; H, 5.83; N, 9.15 %.

***2-Amino-4-(4-bromoaryl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4l)***

IR: 3389, 3255, 3198, 2964, 2216, 1661, 1573 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.43-7.31 (d, $J$ = 7.4 Hz, 2H arom), 7.29 (d, $J$ = 7.2 Hz, 2H arom), 6.76 (s, 2H), 4.19 (s, 1H), 2.62 (m, 2H), 2.16 (m, 2H), 1.07 (s, 3H), 0.94 (s, 3H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 196.3, 164.7, 156.6, 148.3, 146.9, 133.5, 129.3, 128.7, 121.3, 112.7, 58.4, 49.4, 37.5, 31.6, 28.4, 26.5. ESI-MS: *m/z* 373.9 $[M+H]^+$ Anal. Calc. For $C_{18}H_{17}BrN_2O_2$: C, 57.92; H, 4.56; N, 7.50; Found: C, 57.84; H, 4.63; N, 7.48 %.

***2-Amino-7,7-dimethyl-4-(4-nitroaryl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile (4m)***

IR: 3411, 3343, 3202, 2977, 2203, 1652, 1552 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.39-7.25 (d, $J$ = 7.4 Hz, 2H arom), 7.25 (d, $J$ = 7.8 Hz, 2H arom), 6.58 (s, 2H), 4.14 (s, 1H), 2.65 (m, 2H), 2.19 (s, 2H), 1.06 (s, 3H), 0.92 (s, 3H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 195.7, 164.5, 155.3, 148.3, 147.6, 134.5, 129.8, 128.3, 121.4, 112.7, 57.4, 49.6, 37.2, 31.7, 28.5, 26.4. ESI-MS: *m/z* 340 $[M+H]^+$ Anal. Calc. For $C_{18}H_{17}N_3O_4$: C, 63.71; H, 5.01; N, 12.39; Found: C, 63.79; H, 5.17; N, 12.52 %.

***2-amino-4-(4-chloroaryl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4Hchromene-3-carbonitrile (4n)***

IR: 3394, 3325, 2964, 2193, 1685, 1658, 1370, 1214 $cm^{-1}$. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.64-7.48 (d, $J$ = 7.6 Hz, 2H arom), 7.28-7.19 (d, $J$ = 7.2 Hz, 2H arom), 6.73 (s, 2H), 4.17 (s, 1H), 2.58 (s, 2H), 2.14 (m, 2H), 1.02 (s, 3H), 0.96 (s, 3H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 195.6, 162.0, 158.3, 157.8, 136.8, 128.1, 119.7, 113.6, 112.9, 58.5, 54.9, 49.9, 34.7, 31.7, 28.3, 26.7. ESI-MS: *m/z* 329.24 $[M+H]^+$ Anal. Calc. For $C_{18}H_{17}ClN_2O_2$: C, 65.75; H, 10.78; N, 8.52; Found: C, 65.83; H, 10.64; N, 8.43%.

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