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ONE-POT CATALYTIC MULTICOMPONENT SYNTHESIS OF CHROMENE DERIVATIVES BY 1-ALLYL-3-METHYL-IMIDAZOLIUM HALIDES

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2-amino-3-cyano-4-aryl-4H-benzo[h]chromenes and 2-amino-3-cyano-1-aryl-1H-benzo[f] chromenes were obtained in a one-pot three-component reaction of α or β -naphthol (1a and 1b), aromatic aldehydes (2a-n), malononitrile (3) in the presence of 1-allyl-3-methyl-imidazolium halides as a catalyst under solvent-free conditions. The advantages of this novel protocol include the excellent yield, operational simplicity, short reaction time and environmentally benign method. Furthermore, the catalyst could be reused up to five runs without any significant loss of activity.

INTRODUCTION

Multicomponent coupling reactions (MCRs) are emerging as useful tools for the carbon–carbon and carbon–heteroatom bond-forming reactions and for the synthesis of small drug-like molecules with several degrees of structural diversity. One pot multicomponent reactions provides the possibility of directly synthesizing a complex molecule without needing to isolate the intermediates, which has aroused researchers to design such reactions using different catalysts. ^{2,3}

Ionic liquids are salts which exist in the liquid state at ambient temperatures. Use of ionic liquids as environmentally benign, reusable alternative reaction media in organic synthesis has received special attention because of their other unique properties, for example, high thermal and chemical stability, negligible vapor pressure, nonflammability, high loading capacity, and excellent electrical conductivity. 5-7 Ionic liquids have great promise

not only as alternative green solvents, but also as reagents or catalysts in organic transformations.⁵⁻⁸ 1-allyl-3-methyl-imidazolium halides as a recoverable ionic liquid with weak basic character was synthesized for the first time by Benedict *et al.*⁹

Chromene derivatives are an important class of heterocyclic compounds, widely distributed in natural products. Chromene and its derivatives have also been recognized as one type of 'privileged medicinal scaffolds' due to their unique pharmacological and biological activities. Among various chromene family members, 2-amino-4Hchromenes are especially important for medicinal applications. 10 During the last decade, such compounds had shown interesting pharmacological including antimic robial, mutagenicity, anti proliferative, sexpheromone, antitumor, cancertherapy, and central nervous system activity. 2-Aminochromenes have been prepared by heating a mixture of malononitrile. aldehyde and an activated phenol under reflux in the presence of hazardous organic bases such as

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piperidine and triethylamine. ¹⁴ Several procedures for the preparation of 2-amino-4H-pyrans have been described. Various catalysts such as cetyltrimethylammonium chloride ¹⁵, cetyltrimethylammonium bromide under ultrasound irradiation, ¹⁶ KSF clay, ¹⁷ KF/Al₂O₃, ¹⁸ TiCl₄, ¹⁹ triethylamine, ²⁰ basic γ -alumina, ²¹ MgO, ²² and heteropoly acids ²³ have been used for this reaction. But some of the reported methods have one or the other limitations such as a long duration, reagents in stoichiometric amounts, high temperature, and toxic solvents, and furnish the products in unsatisfactory yields. ¹¹, ¹⁵⁻²³

As part of our program aimed at developing useful new selective and synthesis methods based on the use of functionalized ionic liquids as catalysts of fine chemicals preparation, we report herein a one-pot, efficient, three-component condensation reaction of aromatic aldehydes, malononitrile, and α or β -naphthol to produce the corresponding 2-amino-3-cyano-4-aryl-4H benzo[h]chromenes or 2-amino-3-cyano-1-aryl-1H-benzo[f]chromenes, respectively (Scheme 1).

RESULTS AND DISCUSSION

In the present paper, we wish to report a new, efficient, convenient and green protocol for the synthesis of chromene derivatives via a one-pot three-component reaction of α or β -naphthol, aromatic aldehydes and malononitrile catalyzed by 1-allyl-3-methyl-imidazolium halides under solvent-free conditions. In order to optimize the reaction conditions, a series of experiments were performed by variation of reaction parameter under solvent-free condition. Our first goal was finding an appropriate kind of 1-isobutylimidazolium halides as a catalyst, so several available

1-isobutylimidazolium halides catalysts were used such as: 1-allyl-3-methyl-imidazolium chloride, 1-allyl-3-methyl-imidazolium bromide, and 1-allyl-3-methyl-imidazolium iodide. After investigation of the results, 1-allyl-3-methyl-imidazolium iodide was selected as the best catalyst (Table 1).

After selecting an appropriate catalyst, it was trying to find the best ratio of the catalysts for this reaction (Table 2). Therefore, solvent-free reaction of 4-nitrobenzaldehyde, malononitrile, and α or β -naphthol in the presence of different amounts of the 1-isobutylimidazolium iodide (non, 20, 1, 5, 10 or 15 mol%) as catalyst was studied at different temperatures (25, 50, or 80 °C).

As shown in Table 2, 1-allyl-3-methylimidazolium iodide (10 mol%) as catalyst at 80 °C afforded 2-amino-4-aryl-4H-benzo[h]chromene-3-carbonitrile and 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile in 30 min with 95% of yield.

In order to assess the efficiency and the scope of the catalyst for the preparation of chromene derivatives, the reaction of α - or β -naphthol with various aldehydes and malononitrile was examined in the presence of 10 mol% of the catalyst. As shown in Table 3, the effect of electron deficiency and the nature of substituent on the aromatic ring of aldehyde showed some effect on this conversion. When aromatic aldehydes containing electron-donating groups (such as hydroxyl, alkoxyl, or methyl group) were employed (Table 3, entries 9-13 and 23-26), a longer reaction time was required than those of electron-withdrawing groups (such as nitro group, halide) on aromatic rings (Table 3, entries 2–8 and 16-22). It is worthy of note that the reaction proceeded without the protection of acidic hydroxyl substituent (Table 3, entries 10 and 13). The results are displayed in Table 3.

OH

OH

OH

Ar

$$Ar$$
 Ar
 CN
 X^{-}
 $Solvent free- 80 °C$
 $X = Cl, Br and l$

Sa-m

Scheme 1 – Synthesis of chromene derivatives using 1-allyl-3-methyl-imidazolium halides as a catalyst under solvent-free conditions.

Table 1

Comparison of different catalysts in the synthesis of 2-amino-4-phenyl-4H-benzo[h]chromene-3-carbonitrile and 3-amino-1- phenyl-1H-benzo[f]chromene-2-carbonitrile from benzaldehydes, malononitrile, and α or β -naphthol to get the best catalyst among the catalysts used in the present study

| Entry | Catalyst | Amount (mol%) | Yield (%) ^a | | |
|-------|---------------------------------------|-----------------|------------------------|----|--|
| | Catalyst | Amount (moi 78) | 4a | 5a | |
| 1 | 1-allyl-3-methyl-imidazolium Chloride | 5 | 67 | 63 | |
| 2 | 1-allyl-3-methyl-imidazolium Bromide | 5 | 73 | 69 | |
| 3 | 1-allyl-3-methyl-imidazolium Iodide | 5 | 83 | 75 | |
| 4 | 1-allyl-3-methyl-imidazolium Chloride | 10 | 76 | 73 | |
| 5 | 1-allyl-3-methyl-imidazolium Bromide | 10 | 83 | 79 | |
| 6 | 1-allyl-3-methyl-imidazolium Iodide | 10 | 92 | 92 | |
| 7 | 1-allyl-3-methyl-imidazolium Chloride | 15 | 84 | 79 | |
| 8 | 1-allyl-3-methyl-imidazolium Bromide | 15 | 88 | 86 | |
| 9 | 1-allyl-3-methyl-imidazolium Iodide | 15 | 92 | 92 | |

^aIsolated yields

Table 2

Optimization of conditions for synthesis of 2-amino-4-aryl-4H-benzo[h]chromene-3-carbonitrile and 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile from 4-nitrobenzaldehydes, malononitrile, and α or β -naphthol using 1-allyl-3-methyl-imidazolium iodide as catalyst under solvent-free conditions

OH

1a

or

OH

$$CHO$$
 $Solvent free-80 °C$

Oz

 CN
 OzN
 O

| | | | 5e | e | | | |
|--------|-----------------|------------------|----------|---------|------------------|--|--|
| Enter- | Catalyst (mol%) | Temperature (°C) | Time (h) | Yield (| √o) ^a | | |
| Entry | | | | 4e | 5e | | |
| 1 | Non | 25 | 24 | 25 | 20 | | |
| 2 | 20 | 25 | 1 | 70 | 60 | | |
| 3 | 1 | 50 | 0.8 | 76 | 65 | | |
| 4 | 5 | 50 | 0.6 | 80 | 70 | | |
| 5 | 5 | 80 | 0.5 | 83 | 75 | | |
| 6 | 10 | 80 | 0.5 | 95 | 95 | | |
| 7 | 15 | 80 | 0.5 | 95 | 95 | | |

^aIsolated yields

Table 3

Synthesis of 2-amino-4-aryl-4H-benzo[h]chromene-3-carbonitrile and 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile using 1-allyl-3-methyl-imidazolium Iodide as catalyst under solvent-free conditions

| Entry | Ar | Phenol | Product | Time/min | Yields(/%) ^a | Mp/°C | Lit. Mp/°C |
|-------|---|-------------|---------|----------|-------------------------|---------|--------------|
| 1 | C_6H_5 | α- naphthol | 4a | 40 | 92 | 209–211 | 210-211 [17] |
| 2 | 4-ClC ₆ H ₄ | α- naphthol | 4b | 30 | 93 | 231–232 | 231-232 [19] |
| 3 | $2-C1C_6H_4$ | α- naphthol | 4c | 40 | 70 | 237–238 | 236-237 [17] |
| 4 | $2,4$ - $Cl_2C_6H_3$ | α- naphthol | 4d | 35 | 82 | 220–222 | 222-224 [21] |
| 5 | $4-NO_2C_6H_4$ | α- naphthol | 4e | 30 | 95 | 230–232 | 231-234 [19] |
| 6 | $3-NO_2C_6H_4$ | α- naphthol | 4f | 35 | 94 | 208-210 | 208-211 [14] |
| 7 | $4-FC_6H_4$ | α- naphthol | 4g | 30 | 98 | 228-230 | 229-231 [24] |
| 8 | $4-CF_3C_6H_4$ | α- naphthol | 4h | 35 | 98 | 213-214 | 212-214 [30] |
| 9 | $4\text{-CH}_3\text{OC}_6\text{H}_4$ | α- naphthol | 4i | 70 | 92 | 194–195 | 195-196 [19] |
| 10 | 3-CH ₃ O-4-OHC ₆ H ₃ | α- naphthol | 4j | 75 | 90 | 136–138 | 137-139 [17] |
| 11 | $4-(CH_3)_2NC_6H_4$ | α- naphthol | 4k | 60 | 85 | 201–203 | 203-205 [17] |
| 12 | $4-CH_3C_6H_4$ | α- naphthol | 41 | 50 | 90 | 205–206 | 205-206 [22] |
| 13 | $4\text{-HOC}_6\text{H}_4$ | α- naphthol | 4m | 50 | 88 | 244–246 | 245-247 [25] |
| 14 | 2-Naphthyl | α- naphthol | 4n | 45 | 92 | 255-257 | 256-257 [30] |
| 15 | C_6H_5 | β- naphthol | 5a | 60 | 92 | 279–280 | 278-280 [27] |
| 16 | $4-C1C_6H_4$ | β- naphthol | 5b | 75 | 93 | 209–210 | 208-210 [27] |
| 17 | $2-C1C_6H_4$ | β- naphthol | 5c | 80 | 70 | 237–238 | 274-276 [28] |
| 18 | $2,4-Cl_2C_6H_3$ | β- naphthol | 5d | 60 | 82 | 220–222 | 219-222 [29] |
| 19 | $4-NO_2C_6H_4$ | β- naphthol | 5e | 50 | 95 | 230–232 | 188-189 [28] |
| 20 | $3-NO_2C_6H_4$ | β- naphthol | 5f | 50 | 94 | 211–213 | 210-212 [24] |
| 21 | $4-FC_6H_4$ | β- naphthol | 5g | 55 | 98 | 231-232 | 232-233 [15] |
| 22 | $4-CF_3C_6H_4$ | β- naphthol | 5h | 55 | 98 | 236-238 | 235-237 [30] |
| 23 | $4\text{-CH}_3\text{OC}_6\text{H}_4$ | β- naphthol | 5i | 85 | 92 | 190–192 | 191-193 [15] |
| 24 | 3-CH ₃ O-4-OHC ₆ H ₃ | β- naphthol | 5j | 90 | 90 | 157–158 | 156-158 [30] |
| 25 | $4-(CH_3)_2NC_6H_4$ | β- naphthol | 5k | 95 | 85 | 251–253 | 251-253 [30] |
| 26 | $4-CH_3C_6H_4$ | β- naphthol | 51 | 75 | 90 | 205-206 | 270-272 [29] |
| 27 | 2-Naphthyl | β- naphthol | 5m | 60 | 92 | 263-265 | 262-264 [30] |

^aIsolated yield

The mechanism proposed for preparation of 2amino-4-aryl-4H-benzo[h]chromene-3-carbonitrile 3-amino-1-aryl-1H-benzo[f]chromene-2carbonitrile from arylaldehydes, malononitrile, and α or β-naphthol using 1-isobutylimidazolium iodide as catalyst under solvent-free conditions is depicted in Scheme 2. According to the literature, ¹² arylidene malononitrile, containing an electron-poor C=C quantitatively double bond, formed is Knoevenagel addition of malononitrile to the aromatic aldehyde in the presence of ionic liquid as catalyst, ortho C-alkylation of the electrophilic C=C double bond by α or β -naphthol then gives intermediates (I) or (IV). Tautomerization converts intermediate (I) or (IV) to intermediate (II), (V), which is then cyclized by nucleophilic attack of an OH group on the cyano (CN) moiety to give intermediate (III) or (VI). Subsequently tautomerization produced the 2-amino-4-aryl-4H-benzo[h]chromene-3-carbonitrile (4a-n) and 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile (5a-m).

In order to check the reusability of the catalyst, the reaction of 4-chlorobenzaldehyde, malononitrile and reactants 1 (α or β -naphthol) was studied under similar conditions in the presence of 10 mol% of catalyst (Table 3, entries 2 and 16). After the completion of the reaction, the catalyst was easily recovered by washing the reaction mixture with distilled water and directly reused for the next turn after evaporation of water under reduced pressure. It was found that the catalyst could be reused for the next cycle (five runs) without any appreciable loss of its activity (Table 4).

Scheme 2 – Proposed mechanism for preparation of 2-amino-4-chromenes promoted by 1-allyl-3-methyl-imidazolium Iodide ionic-liquid catalysis under solvent-free conditions.

Table 4

Use of the catalysts was further explored for the reusability by a model reaction of 4-chlorobenzaldehyde and reactants 1 $(\alpha \text{ or } \beta\text{-naphthol})$ and 3 under similar conditions in the presence of 10 mol% catalysts

OH

1a

or

OH

CHO

$$CN$$

Solvent free- 80 °C

 CN
 CN
 CN
 CN
 CN
 CN
 CN
 NH_2
 CN
 NH_2
 NH_2

| | | | | | | 5b | | | | | | |
|-------|---------------------------------------|------|----------------------|----|---------|----|---------|----|---------|----|---------|--|
| Entur | Catalyst | Cycl | Cycle 1 ^a | | Cycle 2 | | Cycle 3 | | Cycle 4 | | Cycle 5 | |
| Entry | | 4b | 5b | 4b | 5b | 4b | 5b | 4b | 5b | 4b | 5b | |
| 1 | 1-allyl-3-methyl-imidazolium Chloride | 75 | 74 | 74 | 74 | 73 | 71 | 72 | 70 | 70 | 69 | |
| 2 | 1-allyl-3-methyl-imidazolium Bromide | 82 | 82 | 81 | 81 | 80 | 80 | 79 | 78 | 77 | 77 | |
| 3 | 1-allyl-3-methyl-imidazolium Iodide | 93 | 92 | 92 | 91 | 91 | 90 | 89 | 89 | 87 | 87 | |

^a Isolated yield

EXPERIMENTAL

All chemicals were purchased from Merck (Darmstadt, Germany) and Fluka (Switzerland), and used without further purification. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were measured on a Jasco 6300 FT-IR spectrometer (KBr disks). ¹H and ¹³C NMR spectra (DMSO-*d*₆) were recorded on a Bruker DRX- 500 Avance spectrometer at 500 and 125 MHz, respectively. Elemental analyses were performed using a Exeter Analytical Inc. 'Model C-400 CHN Analyzer'. Mass spectra were obtained using a Micro Mass LCT machine in ES or EI mode. The ionic liquid was prepared according to the method reported in literature.⁹ All the reactions were monitored by TLC using 0.25 mm silica gel plates (Merck 60F₂₅₄ UV indicator).

General procedure for the synthesis of chromene derivatives

A mixture of aldehyde (1 mmol), malononitrile (1 mmol), α or β -naphthol (1 mmol) and 1-allyl-3-methyl-imidazolium halides (10 mol%) was vigorously stirred at 80 °C for the appropriate time (Table 3). Upon completion (monitored by TLC), the reaction mixture was cooled to room temperature, and then water (10 mL) was added to the reaction mixture, and the resulting solid was separated by filtration. The crude product was recrystallized from ethanol to afford the pure product. The desired pure products were characterized by comparison of their physical data with those of known compounds.

2-amino-4-(4-(trifluoromethyl)phenyl)-4H-benzo[h]chromene-3-carbonitrile (4g). 0.359g (98%); white solid; mp 212-214 °C. IR (KBr): 3387, 3121, 2971, 2219, 1651, 1522, 1474, 1109, 802 cm⁻¹. ¹H NMR (DMSO- d_6 , 500 MHz): 4.86 (s, 1H, H-4), 6.79 (s, 2H, NH₂), 7.11 (d, 1H, H-5, J=8.0 Hz), 7.51-7.79 (m, 4H, Ar-H), 7.80-7.88 (m, 3H, Ar-H), 7.91 (d, 1H, H-7, J=8.0 Hz), 8.10 (d, 1H, H-7, J=8.0 Hz). ¹³C NMR (DMSO- d_6 , 125 MHz): δ 48.87, 59.42, 121.43, 122.54, 123.21, 123.98, 124.54, 125.65, 126.32, 127.08, 128.21, 129.76, 130.54, 131.32, 133.83, 134.12, 135.65, 136.09, 137.96 (q, ${}^{J}J_{\rm CF}$ =255.76 Hz), 147.34, 156.43. ¹⁹F NMR (DMSO- d_6 , 470 MHz): -110.8. MS (EI), m/z (%) =366 (M⁺, 35), 221 (83). HRMS (EI) Found: M⁺, 366.1003. C₂₁H₁₃F₃N₂O requires M⁺, 366.1000. Anal Calcd for C₂₁H₁₃F₃N₂O: C, 68.85; H, 3.58; N, 7.65. Found: C, 68.89, H, 3.56; N, 7.67.

2-amino-4-(naphthalen-2-yl)-4H-benzo[h]chromene-3-carbonitrile (4n). 0.274g (92%); white solid; mp 256-257 °C. IR (KBr): 3234, 3054, 2980, 2211, 1650, 1512, 1465, 1119, 810 cm⁻¹. ¹H NMR (DMSO- d_6 , 500 MHz): 4.75 (s, 1H, H-4), 6.85 (s, 2H, NH₂), 7.23 (d, 1H, H-5, J=8.0 Hz), 7.43-7.56 (m, 4H, Ar-H), 7.62-7.98 (m, 6H, Ar-H), 8.04 (d, 1H, H-7, J=8.0 Hz), 8.21 (d, 1H, H-7, J=8.0 Hz). ¹³C NMR (DMSO- d_6 , 125 MHz): δ 31.43, 60.42, 120.83, 121.54, 122.43, 122.58, 123.54, 126.02, 126.28, 127.01, 129.06, 130.35, 132.93, 133.76, 136.98, 137.96, 141.65, 143.54, 147.34, 151.54, 156.43. MS (EI), m/z (%) =348 (M⁺, 15), 221 (75). HRMS (EI) Found: M⁺, 348.1301. C₂₄H₁₆N₂O requires M⁺, 348.1300. Anal Calcd for C₂₄H₁₆N₂O: C, 82.74; H, 4.63; N, 8.04; Found: C, 82.73, H, 4.65; N, 8.06.

3-amino-1-(4-(trifluoromethyl)phenyl)-1H-benzo[f]chromene-2-carbonitrile (**5h**). 0.358g (98%); white solid; mp 235-237 °C. IR (KBr): 3124, 3054, 2975, 2233, 1643, 1523, 1455, 1143, 809 cm⁻¹. ¹H NMR (DMSO-*d*₆, 500 MHz): 5.34 (s, 1H,

H-4), 6.79 (s, 2H, NH₂), 7.23-7.43 (m, 2H, Ar-H), 7.45-7.52 (d, 2H, J=8.0 Hz, H-3,5), 7.60 (d, 1H, J=8.0 Hz, H-9), 7.63-7.75 (m, 2H, Ar-H), 7.78 (d, 1H, J=8.0 Hz, H-10), 7.81-7.96 (d, 2H, J=8.0 Hz, H-2,6). ¹³C NMR (DMSO- d_6 , 125 MHz): δ 29.93, 58.92, 121.63, 122.74, 122.96, 123.88, 123.96, 125.12, 125.98, 126.11, 129.11, 131.65, 132.03, 132.86, 135.08, 137.06(q, ${}^{J}C_{\rm F}$ =247.54 Hz), 140.55, 143.04, 148.34, 153.50, 159.03. MS (EI), m/z (%) =366 (M $^{+}$, 25), 221 (65). HRMS (EI) Found: M $^{+}$, 366.1008. C₂₁H₁₃F₃N₂O: c, 68.85; H, 3.58; N, 7.65. Found: C, 68.73, H, .61; N, 7.66.

3-amino-1-(4-hydroxy-3-methoxyphenyl)-1H-

benzo[f]chromene-2-carbonitrile (5j). 0.309g (90%); white solid; mp 156-158 °C. IR (KBr): 3156, 3078, 2956, 2198, 1676, 1534, 1412, 1123, 805 cm⁻¹. ¹H NMR (DMSO- d_6 , 500 MHz): 3.67 (s, 3H, OCH₃), 5.32 (s, 1H, H-4), 5.53 (s, 1H, OH), 6.67 (s, 2H, NH₂), 7.16-7.31 (m, 4H, Ar-H), 7.32-7.45 (m, 2H, Ar-H), 7.32-7.45 (m, 3H, Ar-H),. ¹³C NMR (DMSO- d_6 , 125 MHz): δ 39.53, 58.02, 59.43, 120.93, 121.04, 122.54, 122.88, 124.43, 125.32, 125.92, 128.11, 129.98, 130.76, 131.73, 133.76, 134.08, 135.16, 142.05, 144.94, 147.74, 151.80, 157.43. MS (EI), m/z (%) =344 (M⁺, 15), 221 (55). HRMS (EI) Found: M⁺, 344.1202. C₂₁H₁₆N₂O₃ requires M⁺, 344.1209. Anal Calcd for C₂₁H₁₆N₂O₃: C, 73.25; H, 4.67; N, 8.12. Found: C, 73.24; H, 4.68; N, 8.13.

3-amino-1-(4-(dimethylamino)phenyl)-1H-benzo[f]chromene-2-carbonitrile (**5k**). 0.289g (85%); white solid; mp 251-253 °C. IR (KBr): 3124, 3065, 2981, 2198, 1666, 1544, 1451, 1107, 802 cm⁻¹. ¹H NMR (DMSO-d₆, 500 MHz): 3.82 (s, 6H, 2×CH₃), 5.43 (s, 1H, H-4), 6.67 (s, 2H, NH₂), 7.17-7.34 (m, 4H, Ar-H), 7.47-7.54 (m, 3H, Ar-H), 7.56-7.67 (m, 3H, Ar-H),. ¹³C NMR (DMSO-d₆, 125 MHz): δ 44.83, 56.93, 67.54, 119.03, 121.94, 122.43, 122.43, 123.03, 124.42, 127.02, 128.54, 129.68, 130.54, 132.33, 133.46, 134.78, 138.16, 143.95, 146.34, 148.04, 153.40, 158.52. MS (EI), m/z (%) =341 (M⁺, 17), 221 (43). HRMS (EI) Found: M⁺, 341.1502. C₂₂H₁₉N₃O requires M⁺, 341.1505. Anal Calcd for C₂₂H₁₉N₃O: C, 77.40; H, 5.61; N, 12.31. Found: C, 77.44; H, 5.64; N, 12.33.

3-amino-1-(naphthalen-2-yl)-1H-benzo[f]chromene-2-carbonitrile (5m). 0.320g (92%); white solid; mp 262-264 °C. IR (KBr): 3146, 3079, 2978, 2236, 1624, 1545, 1434, 1121, 803 cm⁻¹. ¹H NMR (DMSO- d_6 , 500 MHz): 5.28 (s, 1H, H-4), 6.57 (s, 2H, NH₂), 7.11-7.31 (m, 4H, Ar-H), 7.40-7.51 (m, 3H, Ar-H), 7.53-7.72 (m, 3H, Ar-H), 7.81-8.06 (m, 3H, Ar-H). ¹³C NMR (DMSO- d_6 , 125 MHz): δ 31.09, 65.54, 118.63, 120.87, 120.93, 122.09, 122.93, 125.02, 126.92, 128.54, 130.08, 131.98, 132.98, 133.76, 136.98, 141.16, 145.05, 147.38, 149.94, 152.80, 157.92, 161.98. MS (EI), m/z (%) =348 (M⁺, 23), 221 (56). HRMS (EI) Found: M⁺, 348.1302. C₂₄H₁₆N₂O: C, 82.74; H, 4.63; N, 8.04. Found: C, 82.75; H, 4.64; N, 8.03.

CONCLUSION

In conclusion, an efficient, clean, and simple method for the synthesis of 2-amino-3-cyano-4-aryl-4H-benzo[h]chromenes and 2-amino-3-cyano-1-aryl-1H-benzo[f]chromenes in the presence of 1-allyl-3-methyl-imidazolium iodide as a catalyst under solvent-free conditions is reported. The attractive features of the presented method are the

simple experimental procedure, simple work-up, short reaction time, high yield of product and use of inexpensive and reusable ionic liquids as catalysts under solvent-free conditions.

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