

One-pot multicomponent reaction for the synthesis of 2-amino-4-chromenes promoted by 1-methyl imidazoliumiodide [mim]Cl ionic-liquid catalyst under solvent-free conditions

Mohammad Reza Poor Heravi*, Mohammad Reza Amirloo

Department of Chemistry, Payame Noor University, P.O. BOX 19395-4697 Tehran, Iran

Received: 17 July 2014, Accepted: 18 August 2014, Published: 18 August 2014

Abstract

A simple, clean, and environmentally benign three-component process for the synthesis of 2-amino-4Hchromenes using [mim]Cl, as an efficient catalyst under solvent-free conditions are described. A wide range of aromatic aldehydes would easily undergo condensations with 1-naphthol and malononitrile under solvent-free conditions in order to afford the desired products of good purity in excellent yields. Taking into account the environmental and economical considerations, the protocol presented here has the merits of environmentally benign, simple operation, convenient work-up and good yields. Furthermore, the catalyst can be easily recovered and reused for at least five cycles without losing its activities.

Keywords: Chromene, multicomponent reactions, 1-methyl imidazoliumiodide [mim]Cl, solvent-free conditions

Introduction

Another window of green chemistry to take into consideration is the development of the one-pot multi-component reactions

(MCRs) which are one of the best tools in the synthesis of organic compounds [1]. Recently, MCRs have emerged as a highly valuable synthesis tool in the context of modern drug dis-

*Corresponding author: Mohammad Reza Poor Heravi

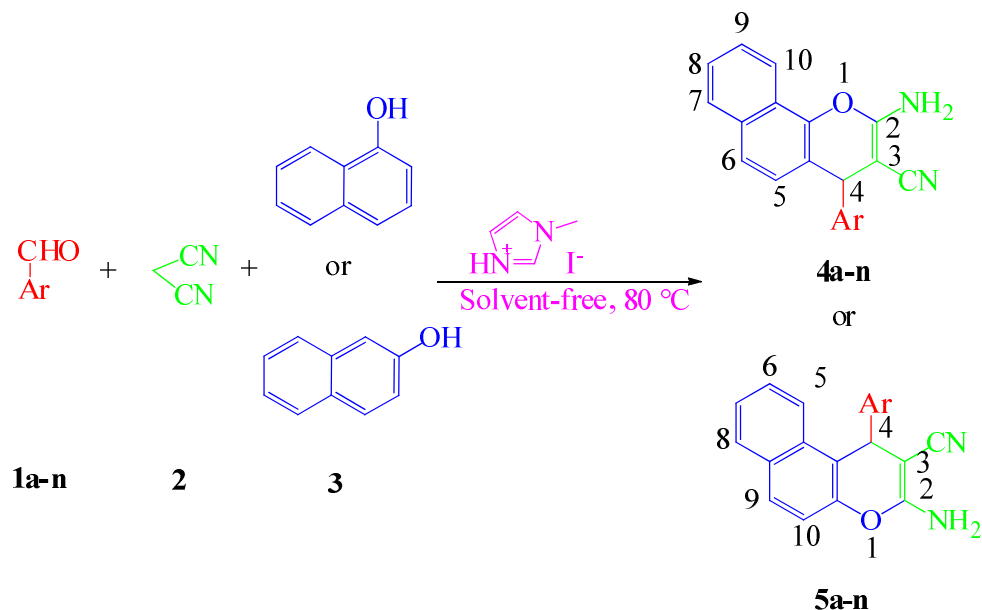
Tel number: +98 (242) 5226932; Fax number: +98 (242) 5224021
E-mail: heravime@yahoo.com

covery. The atom economy and convergent character, the simplicity of a one-pot procedure, the possible structural variations, the accessible complexity of the molecules, and the very large number of accessible compounds are among the described advantages of MCRs. Thus, they are perfectly amenable to automation for combinatorial synthesis.

The third issue to be addressed in the context of durable development and Green Chemistry is ionic-liquid catalyst. These concepts are at the center of the chemical activity, and the research on high selectivity is the driving force for the conception of all new catalytic processes. At present, it is well known that an ionic-liquid catalyst must have three characteristics: high activity, selectivity and stability (separation, recovery, recycling). The ideas of the new generation of catalysts should include these three aspects.

2-Aminochromenes which represent an important class of compounds can be considered as the main components of many naturally occurring products, and have been of interest in recent years due to their useful biological and pharmacological aspects, such as anticoagulants, spasmolytic, diuretic, insecticide, anticancer, and antianaphylactin activity [2].

Some of them can also be employed as cosmetics and pigments [3], and utilized as potential biodegradable agrochemicals [4]. 2-Aminochromenes are generally prepared by refluxing malononitrile, aldehyde, and activated phenol in the presence of hazardous organic bases like piperidine in organic solvents such as ethanol and acetonitrile for several hours [5]. A literature survey revealed several modified procedures using cetyltrimethylammonium chloride (CTAC), [6] tetrabutylammonium bromide (TBAB), [7] cetyltrimethylammoniumbromide (CTAB) coupled with ultrasound, [8] γ -alumina, [9] K_2CO_3 , [10] nanosize MgO , [11] heteropolyacid, [12] hexadecyltrimethylammonium bromide, (HTMAB), [13] triethylbenzylammonium chloride (TEBA), [14] $[(PhCH_2Me_2N^+CH_2CH_2NMe_2)Cl]$ [15] and $TiCl_4$ [16, 17]. 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 chemical preparation, we have studied using the MCR strategy for the synthesis of substituted 2-aminochromenes using the basic ionic liquid catalyst, 1-methyl imidazoliumidide $[mim]Cl$, under solvent-free conditions.



Scheme 1. Preparation of 2-amino-4-aryl-4H-benzo[h]chromene-3-carbonitrile and 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile using [mim]Cl (IL) as catalyst under solvent-free conditions

Experimental

General

All reagents were purchased from Merck. Aldehydes were distilled before use. Melting points were determined in open capillaries using Melting Electrothermal X6 microscopy, digital melting point apparatus. IR spectra were recorded on a Bruker Equinox 55 spectrometer using KBr pellets. NMR spectra were recorded using a Bruker DRX500 machine at room temperature. ¹H, ¹³C NMR and ¹⁹F NMR spectra were measured using DMSO-*d*₆ as solvent. CHN analyses were performed on Exeter Analytical Inc. 'Model C-400 CHN Analyzer'. Mass spectra were obtained using a Micro Mass LCT machine in EI mode. HRMS ma-

chine on a JMS-700 double focusing Mass spectrometer (JEOL, Tokyo, Japan). The ionic liquid was prepared according to the method reported in the literature.¹⁷ All the reactions were monitored by TLC using 0.25 mm silica gel plates (Merck 60F₂₅₄) UV indicator.

General procedure for the synthesis of 2-amino-4-chromenes

An equimolar (4 mmol) mixture of an aromatic aldehyde (1), malononitrile (2), 1-naphthol (3) and 10 mole% [mim]Cl was vigorously stirred at 80 °C for the specific time indicated in Table 1. The end of the reaction was monitored by TLC. Then, the crude product obtained was added to the distilled water. The resulting precipitated solid was filtered out and

purified by recrystallization from hot methanol to afford the pure products (4). The catalyst remained in the water was reused at another cycle after evaporation of water. All of the products are known and the data are found to be identical with those that reported in the literature (Table 2).

Characterization data of some representative 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). ^{13}C 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, $^1J_{\text{CF}}=255.76$ Hz), 147.34, 156.43. ^{19}F NMR (DMSO- d_6 , 470 MHz): -110.8. MS (EI), m/z (%) = 366 (M^+ , 35), 221 (83). HRMS (EI) Found: M^+ , 366.1003. $\text{C}_{21}\text{H}_{13}\text{F}_3\text{N}_2\text{O}$ requires M^+ , 366.1000. Anal Calcd for $\text{C}_{21}\text{H}_{13}\text{F}_3\text{N}_2\text{O}$: 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). ^{13}C 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. $\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}$ requires M^+ , 348.1300. Anal Calcd for $\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}$: 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-benzof[f]chromene-2-carbonitrile (5g)

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). ^{13}C 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, $^1J_{CF}=247.54$ 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. $C_{21}H_{13}F_3N_2O$ requires M^+ , 366.1001. Anal Calcd for $C_{21}H_{13}F_3N_2O$: 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-benzof[f]chromene-2-carbonitrile (5i)

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). ^{13}C 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. $C_{21}H_{16}N_2O_3$ requires M^+ , 344.1209. Anal Calcd for $C_{21}H_{16}N_2O_3$: 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-benzof[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- d_6 , 500 MHz): 3.82 (s, 6H, 2 \times 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). ^{13}C NMR (DMSO- d_6 , 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. $C_{22}H_{19}N_3O$ requires M^+ , 341.1505. Anal Calcd for $C_{22}H_{19}N_3O$: 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-benzof[f]chromene-2-carbonitrile (5n)

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). ^{13}C 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. $C_{24}H_{16}N_2O$ requires M^+ , 348.1301. Anal Calcd for $C_{24}H_{16}N_2O$: C, 82.74; H, 4.63; N, 8.04. Found: C, 82.75; H, 4.64; N, 8.03.

Results and discussion

In order to optimize the reaction conditions, we studied the synthesis of **4e** and **5e** from the condensation of **1** or 2-naphthol, 4-nitrobenzaldehyde and malononitrile in the presence of a variety of solvents (Table 1, Entries 1-7). The successful results of experiments showed that the condensation reaction without [mim]Cl in mixture of water and ethanol (1:1) as polar and protic solvent is substantially better than the corresponding reaction in conventional organic solvents (Table 1, Entry 7). We evaluated the amount of [mim]Cl required for this transformation. It was found that when we increase the amount of IL from 1 to 20 mol%, the yields will increase from 40 to 70% (Table 1, Entries 8-13). Using [mim]Cl (10mol%) in water was sufficient to push the reaction forward (Table 1, Entry 10). The ef-

fect of water in these reactions is attributable in part to its lubricating action, i.e., to its effect in reducing viscosity by decreasing the coulombic interactions between cation and anion geater translation and rotational freedom. Furthermore, the decreased hydrogen bonding with anions [23, 24] should favor the catalytic effect of IL, moreover, it is attributable to hydrogen-bonding between the imidazolium H-2 atom and the carbonyl group of the aryaldehyde [25, 26]. Extra amount of [mim]Cl did not improve the yields (Table 1, Entries 12 and 13). We also investigated the synthesis of our target compounds under solvent-free conditions. The ionic liquid catalyst is in favor of melting the reaction mixture and plays a crucial role in the success of the reaction in terms of the rate and the yields. Reacting 4-nitrobenzaldehyde with (2) and (3) was examined as a reference. In accordance with Table 1 and the general optimization procedure, 10 mol% catalyst and 80 °C were used under solvent-free conditions (Table 1, Entry 18).

Table 1. Optimization of conditions for synthesis of 2-amino-4-aryl-4H-benzo[h]chromene-3-carbonitrile (**4e**) and 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile (**5e**) from 4-nitrobenzaldehydes (**1e**), malononitrile (2), and 1 or 2-naphthol (3) using [mim]Cl as catalyst under solvent-free conditions

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time (h)	Yield (%) ^a	
					4e	5e
1	Non	H ₂ O	25	24	25	25
2	Non	Ether	25	48	Nul	Nul
3	Non	CH ₂ Cl ₂	25	24	5	5

4	Non	CH ₃ Cl ₃	25	24	5	5
5	Non	CH ₃ CN	25	24	10	5
6	Non	EtOH	25	20	30	25
7	Non	H ₂ O+ EtOH	25	20	35	35
8	1	H ₂ O	25	20	40	40
9	5	H ₂ O	25	20	55	50
10	10	H ₂ O	25	20	75	70
11	15	H ₂ O	25	20	75	70
12	20	H ₂ O	25	20	75	70
13	25	H ₂ O	25	20	70	70
14	Non	Sovent-free	25	24	20	15
15	1	Sovent-free	50	0.8	76	65
16	5	Sovent-free	50	0.6	80	70
17	5	Sovent-free	80	0.5	83	75
18	10	Sovent-free	80	0.5	95	95
19	15	Sovent-free	80	0.5	95	95
20	20	Sovent-free	80	0.5	92	92

^aIsolated yields

The three-component, one-pot condensation of aldehydes, malononitrile and 1-naphthol or 2-naphthol proceeded in the presence of 10 mole% of [mim]Cl basic ionic liquids smoothly to give the corresponding products in high yields and the results are summarized in Table 2.

The scope and the generality of the present method were then demonstrated by the reaction of (1) with (2) and (3) (Scheme 1). In all cases, good yields with good selectivity were obtained. All of the results are shown in Table 2. As can be seen from Table 2, electronic effects and the nature of substitute on the aromatic ring did show strong effects in

terms of reaction time under the reaction conditions mentioned above. When aromatic aldehydes containing electron-donating groups (such as hydroxyl, alkoxy, or methyl group) were employed (Table 2, Entries 8, 22, 12, 26, 11 and 25), a longer reaction time was required than those of electron-withdrawing groups (such as nitro group, halide) on aromatic rings (Table 2, Entries 2–7 and 16–21). It is worthy of note that the reaction proceeded without the protection of acidic hydroxyl substituent (Table 2, Entries 9, 23, 13 and 27).

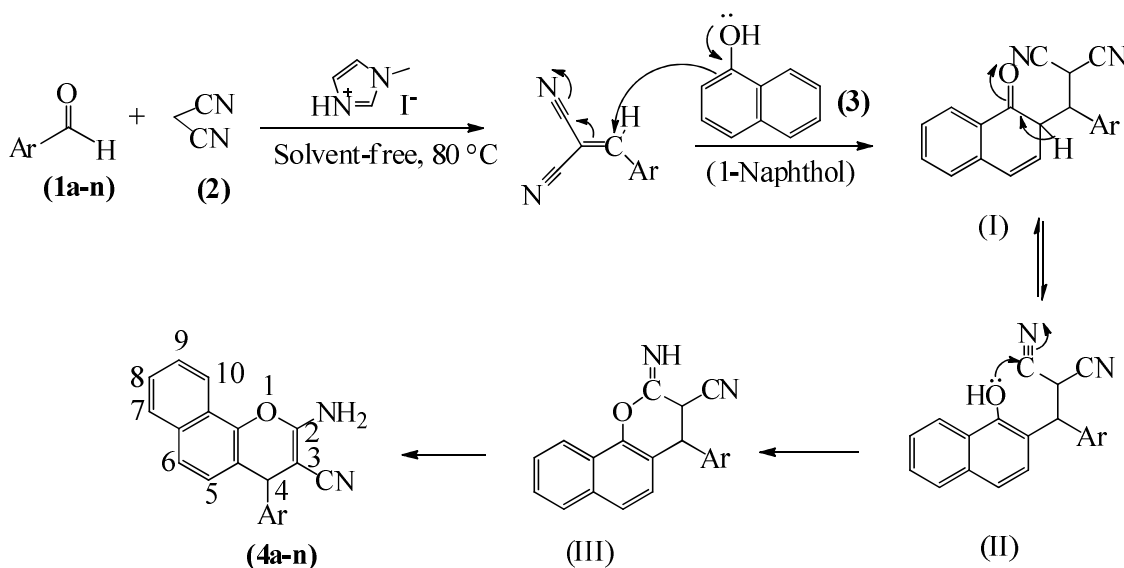
Table 2. Synthesis of 2-amino-4-aryl-4H-benzo[h]chromene-3-carbonitrile and 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile using [mim]Cl as catalyst under solvent-free conditions

Entry	Ar	Naphthol	Product	Time/min	Yields(%) ^a	Mp/°C	Lit. Mp/°C
1	C ₆ H ₅	1	4a	40	92	209–211	210–211 [8]
2	4-ClC ₆ H ₄	1	4b	30	93	231–232	231–232 [11]
3	2-ClC ₆ H ₄	1	4c	40	70	237–238	236–237 [8]
4	2,4-Cl ₂ C ₆ H ₃	1	4d	35	82	220–222	222–224 [13]
5	4-NO ₂ C ₆ H ₄	1	4e	30	95	230–232	231–234 [11]
6	4-FC ₆ H ₄	1	4f	30	98	228-230	229-231 [18]
7	4-CF ₃ C ₆ H ₄	1	4g	35	98	212-214	New Comp.
8	4-CH ₃ OC ₆ H ₄	1	4h	70	92	194–195	195-196 [11]
9	3-CH ₃ O-4-OHC ₆ H ₃	1	4i	75	90	136–138	137–139 [8]
10	3-NO ₂ C ₆ H ₄	1	4j	35	94	208–210	208–211 [11]
11	4-(CH ₃) ₂ NC ₆ H ₄	1	4k	60	85	201–203	203–205 [7]
12	4-CH ₃ C ₆ H ₄	1	4l	50	90	205–206	205–206 [14]
13	4-HOC ₆ H ₄	1	4m	50	88	244–246	245-247 [15]
14	2-Naphthyl	1	4n	45	92	256-257	New Comp.
15	C ₆ H ₅	2	5a	60	92	279–280	278–280 [19]
16	4-ClC ₆ H ₄	2	5b	75	93	209–210	208–210 [19]
17	2-ClC ₆ H ₄	2	5c	80	70	237–238	274–276 [20]
18	2,4-Cl ₂ C ₆ H ₃	2	5d	60	82	220–222	219–222 [22]
19	4-NO ₂ C ₆ H ₄	2	5e	50	95	230–232	188–189 [21]
20	4-FC ₆ H ₄	2	5f	55	98	231-232	232-233 [6]
21	4-CF ₃ C ₆ H ₄	2	5g	55	98	235-237	New Comp.
22	4-CH ₃ OC ₆ H ₄	2	5h	85	92	190–192	191-193 [6]
23	3-CH ₃ O-4-OHC ₆ H ₃	2	5i	90	90	156–158	New Comp.
24	3-NO ₂ C ₆ H ₄	2	5j	50	94	211–213	210–212 [18]

25	4-(CH ₃) ₂ NC ₆ H ₄	2	5k	95	85	251–253	New Comp.
26	4-CH ₃ C ₆ H ₄	2	5l	75	90	205–206	270–272 [22]
27	4-HOC ₆ H ₄	1	5m	50	85	234–236	235–237 [15]
28	2-Naphthyl	2	5n	60	92	262–264	New Comp.

^aIsolated yield

The mechanism proposed for preparation of 2-amino-4-aryl-4H-benzo[h]chromene-3-carbonitrile and 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile from arylaldehydes, malononitrile, and 1 or 2-naphthol using [mim]Cl as catalyst under solvent-free conditions is depicted in Scheme 2. According to the literature [6], arylidene malononitrile, containing an electron-poor C=C double bond, is formed quantitatively by the Knoevenagel addition of malononitrile to the aromatic aldehyde in the presence of ionic liquids as cata-



Scheme 2. Proposed mechanisms for preparation of 2-amino-4-chromenes promoted by [mim]Cl ionic-liquid catalyst under solvent-free conditions

In view of the green chemistry, the catalyst was further explored for the reusability by a model reaction of 4-nitrobenzaldehyde and reactants **2** and **3** (1 or 2-naphthol) under similar conditions in the presence of 10 mole% catalyst. The catalyst was easily recovered by washing the reaction mixture with distilled water and then was directly reused for the next

turn after evaporation of water under reduced pressure. The recycled catalyst has been reused five times to catalyze the model reaction affording the corresponding chromene in 92, 91, 90, 89, and 87% yields, and without appreciable decreases of yield.

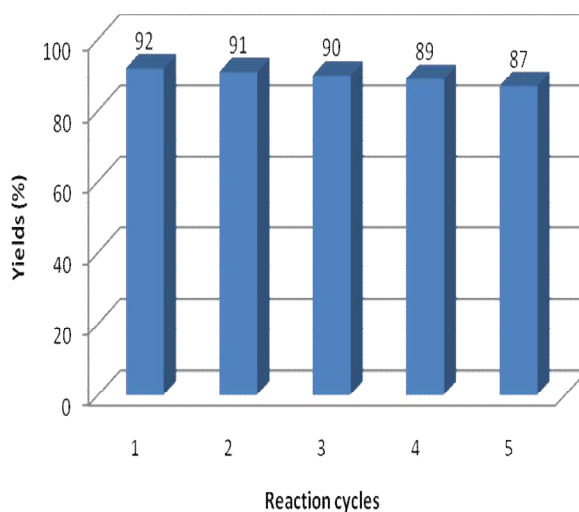


Figure 1. Reusability of [mim]Cl ionic-liquid catalyst. Reaction of 4-nitrobenzaldehyde, malononitrile, and 1-naphthol or 2-naphthol was used as model reaction

In conclusion, we describe a practical and efficient procedure for the preparation of 2-amino-4-criminals through the three-component reaction of aromatic aldehydes (**1a-n**), malononitrile (**2**), and 1-naphthol (**3**) using a catalytic amount of [mim]Cl catalyst under solvent-free conditions. This procedure offers several advantages, including mild reaction conditions, cleaner reaction, and satisfactory yields of products, as well as a simple ex-

periment and isolated procedure made it a useful and attractive protocol for the synthesis of these compounds. The catalyst was reused by another cycle after evaporation of water. All of the products are known and the data are found to be identical with those that reported in the literature (Table 2).

Conclusion

In this research, mild ionic liquid [mim]Cl was used as catalysts, for the first time, for

preparation of 2-amino-4-aryl-4H-benzo[h]chromene-3-carbonitrile and 3-amino-1-aryl-1H-benzo[f]chromene-2-carbonitrile under solvent-free conditions at 80 °C. The attractive features of this method are the simple procedure, cleaner reaction, and use of inexpensive and reusable ionic liquid as a catalyst under solvent-free conditions. Satisfactory yields and simple isolation and purification of the products make it a useful procedure for synthesis of these compounds.

Acknowledgments

We are grateful to the Payame Noor University of Tehran for the support of this study.

References

- [1] (a) G. H. Posner, *Chem. Rev.*, **1986**, *86*, 831-844; (b) K. Kumaravel, G. Vasuki, *Curr. Org. Chem.*, **2009**, *13*, 1820-1841; (c) L. A. Wessjohann, D. G. Rivera, O. E. Vercillo, *Chem. Rev.*, **2009**, *109*, 796-814; E. Vessally, A. Ramazani, E. Yaghoubi, *Monatsch. Chem.*, **2011**, *142*, 1143-1147.
- [2] L. Bonsignore, G. Loy, D. Secci, A. Calignano, *Eur. J. Med. Chem.*, **1993**, *28*, 517-520.
- [3] G. P. Ellis, *The Chemistry of heterocyclic compounds chromenes, chromanes and chromones*, Chap. II. In: Weissberger A, Taylor EC (eds). Wiley, New York, **1997**, p11-43.
- [4] E. A. A. Hafez, M. H. Elnagdi, A. G. A. Elagamey, F. M. A. El-Taweel, *Heterocycles* **1987**, *26*, 903-907.
- [5] A. G. A. Elagamey, F. M. A. El-Taweel, *Indian J. Chem. B* **29B**, **1990**, 885-886.
- [6] R. Ballini, G. Bosica, M. L. Conforti, R. Maggi, A. Mazzacanni, P. Righi, G. Sartori, *Tetrahedron*, **2001**, *57*, 1395-1402.
- [7] T. S. Jin, J. C. Xiao, S. J. Wang, T. S. Li, X. R. Song, *Syn lett*, **2003**, 2001-2004.
- [8] T. S. Jin, J.C. Xiao, S. J. Wang, T. S. Li, *Ultrason. Sonochem.*, **2004**, *11*, 393-397.
- [9] R. Maggi, R. Ballini, G. Sartori, R. Sartorio, *Tetrahedron Lett.*, **2004**, *45*, 2297-2299.
- [10] M. Kidwai, S. Saxena, M. K. Rahman Khan, S. S. Thukral, *Bioorg. Med. Chem. Lett.*, **2005**, *15*, 4295-4298.
- [11] D. Kumar, V. B. Reddy, G. B. Mishra, R. K. Rana, M. N. Nadagouda, R. S. Varma, *Tetrahedron*, **2007**, *63*, 3093-3097.
- [12] M. M. Heravi, K. Bakhtiari, V. Zadsirjan, F. F. Bamoharram, O. M. Heravi, *Bioorg. Med. Chem. Lett.*, **2007**, *17*, 4262-4265.

- [13] T. S. Jin, J. S. Zhang, L. B. Liu, A. Q. Wang, T. S. Li, *Synth. Commun.*, **2006**, *36*, 2009-2015.
- [14] D. Q. Shi, S. Zhang, Q. Y. Zhuang, X. S. Wang, *Chin. J. Org. Chem.*, **2003**, *23*, 1419-1421.
- [15] L. Chen, X. J. Huang, Y. Q. Li, M. Y. Zhou, W. J. Zheng, *Monatsh. Chem.*, **2009**, *140*, 45-47.
- [16] B. S. Kumar, N. Srinivasulu, R. H. Udupi, B. Rajitha, Y. T. Reddy, P. N. Reddy, P. S. Kumar, *J. Heterocycl. Chem.*, **2006**, *43*, 1691-1693.
- [17] K. M. Chan Benedict, N. H. Chang, M. Ross Grimmett, *Aust. J. Chem.*, **1977**, *30*, 2005-13.
- [18] H. Mehrabi, N. Kamali, *J. Iran. Chem. Soc.*, **2012**, *9*, 599-605.
- [19] M. M. Heravi, B. Baghernejad, H. A. Oskooie, *J. Chin. Chem. Soc.*, **2008**, *55*, 3-7.
- [20] A. Zhang, H. Zhang, H. Chen, *Synth. Commun.*, **2007**, *37*, 231-235.
- [21] D. Q. Shi, S. Zhang, Q. Y. Zhuang, S. J. Tu, H. W. Hu, *J. Org. Chem.*, **2003**, *23*, 809-812.
- [22] Q. Y. Zhuang, L. C. Rong, D. Q. Shi, *Chin. J. Org. Chem.*, **2003**, *23*, 671-673.
- [23] H. V. R. Annapureddy, Z. H. Hu, J. C. Xia, C. J. Margulis, *J. Phys. Chem. B*, **2008**, *112*, 1770-1776.
- [24] M. Klän, C. Stüber, A. Seduraman, P. Wu, *J. Phys. Chem. B*, **2010**, *114*, 2856-2868.
- [25] A. Aggarwal, N. L. Lancaster, A. R. Sethi, T. Welton, *Green Chem.*, **2002**, *4*, 517-520.
- [26] S. R. Roy, A. K. Chakraborti, *Org. Lett.*, **2010**, *12*, 3866-3869.