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GREEN METHOD FOR THE SYNTHESIS OF POLYSUBSTITUTED CHROMENE DERIVATIVES IN IONIC LIQUIDS

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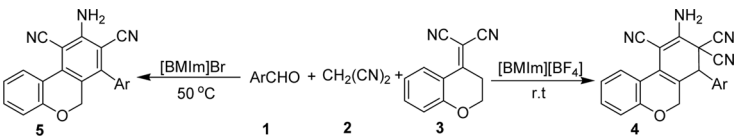
GRAPHICAL ABSTRACT



Abstract *In this article, the same reaction of aromatic aldehyde, malononitrile, and 2-(2,3-dihydrochromen-4-ylidene)malononitrile was performed in ionic liquids of [BMIm]BF_4 and [BMIm]Br, resulting in a green synthesis of 6*H*-benzo[c]chromene-8,8,10(7*H*)-tricarbonitrile and 6*H*-benzo[c]chromene-8,10-dicarbonitrile derivatives in good yields. This procedure has the advantages of good yields, one pot, and environmental friendliness.*

Keywords Chromene; ionic liquids; malononitrile; synthesis

INTRODUCTION

Polysubstituted chromene derivatives are very important heterocyclic compounds that frequently exhibit a variety of biological activities.[1] These activities include anticancer,[2] anticoagulant,[3] and fungicidal activities.[4] They are also find applications as pigments and potential biodegradable agrochemicals. Because of their usefulness, the synthesis of these compounds has attracted a lot of interests.[5]

Ionic liquids have attracted increasing interest in the context of green synthesis in the past few years. They were initially introduced as alternative green reaction media because of their unique chemical and physical properties of nonvolatility, nonflammability, thermal stability, and controlled miscibility.[6] The possibility of recycling them and their low-vapor nature also ensure their utility in environmentally

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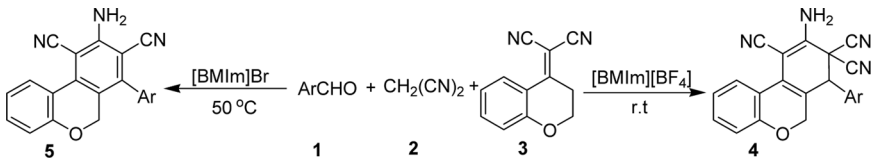


Scheme 1. Reaction of **1**, **2**, and 2-(2,3-dihydrochromen-4-ylidene)malononitrile.

friendly technologies. They have been used as solvents for a large number of organic transformations.[7] Another feature of ionic liquids is their alterable negative ions, such as Cl^-, Br^-, BF_4^-, PF_6^-, $CF_3SO_3^-$, $CF_3CO_2^-$, HSO_4^-, OH^-, and $CH_3CO_2^-$. Some of them are acidic media, such as BF_4^-, PF_6^-, and HSO_4^-, while many ionic liquids are basic, for example, Cl^-, Br^-, and OH^-. Sometimes, they are used not only as a green media but also as easily recyclable catalysts for many organic reactions.[8]

As a continuation of our research devoted to the development of new methods for the preparation of heterocycles in environmentally benign media,[9] we recently performed the same reaction of aromatic aldehyde, malononitrile, and 2-(2,3-dihydrochromen-4-ylidene)malononitrile in $[BMIm]BF_4$ and [BMIm]Br with different products obtained. Herein, we report green syntheses of 6*H*-benzo[*c*]chromene-8,8,10(7*H*)-tricarbonitrile and 6*H*-benzo[*c*] chromene-8,10-dicarbonitrile derivatives using the same reactants by changing the negative anion to control the pH value in ionic liquids.

RESULTS AND DISCUSSION

Treatment of aromatic aldehyde **1** with malononitrile **2** and 2-(2,3-dihydrochromen-4-ylidene)malononitrile **3** in $[BMIm]BF_4$ at room temperature produced the corresponding 9-amino-7-aryl-6*H*-benzo[*c*]chromene-8,8,10(7*H*)-tricarbonitrile **4** in good yields (Scheme 1). It is an unaromatized benzo[*c*]chromene moiety; we think the pH value in ionic liquid media plays a key role in the reaction. The CN^- may be lost by eliminating the hydrogen atom in the adjacent carbon atom. As our assumption, to change the negative ions in the ionic liquid from BF_4^- to Br^-, [BMIm]Br was selected to perform the same reaction. To our delight, the design proceeded smoothly and provided excellent yields of aromatized 9-amino-7-aryl-6*H*-benzo[*c*]chromene-8,10-dicarbonitrile derivatives **5** at 50 °C (Scheme 1).

These alterable conditions were applied for the conversion of various kinds of aromatic aldehydes into the corresponding benzo[*c*]chromene analogs (Table 1, entries 1–13). Among these analogs, the yields of **4** or **5** were not sensitive to the electronic properties of the aromatic ring in the presence of electron-withdrawing groups (such as halide and nitro) or electron-donating groups (such as the alkoxyl group). They all gave the desired 6*H*-benzo[*c*]chromene-8,8,10(7*H*)-tricarbonitrile **4** in the acidic ionic liquid of $[BMIm]BF_4$ (Table 1, entries 1–6), while in the basic [BMIm]Br they yielded aromatized 6*H*-benzo[*c*]chromene-8,10-dicarbonitrile derivatives (Table 1, entries 7–13). All the compounds were characterized by ^1H NMR, infrared (IR), and high resolution mass spectrometry (HRMS).

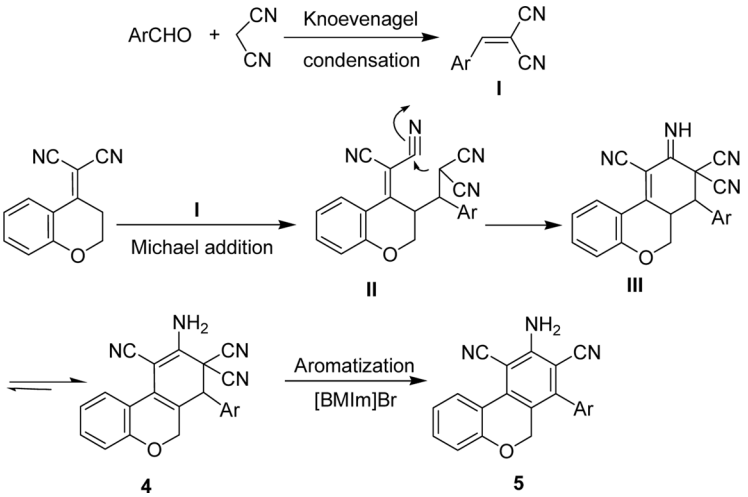
Table 1. Synthetic results of **4** and **5** in ionic liquids[a]

Entry	Ar	Products	Time (h)	Yields (%)[b]
1	4-$NO_2C_6H_4$	**4a**	10	93
2	2-BrC_6H_4	**4b**	8	92
3	3-BrC_6H_4	**4c**	7	90
4	3,4-$(CH_3O)_2C_6H_3$	**4d**	10	93
5	3,5-$(CH_3O)_2C_6H_3$	**4e**	12	85
6	2,4,5-$(CH_3O)_3C_6H_2$	**4f**	11	88
7	3,5-$(CH_3O)_2C_6H_3$	**5a**	8	87
8	3-BrC_6H_4	**5b**	8	88
9	2,3-$(CH_3O)_2C_6H_3$	**5c**	8	88
10	4-ClC_6H_4	**5d**	6	90
11	2-ClC_6H_4	**5e**	7	93
12	2,4-$Cl_2C_6H_3$	**5f**	9	89
13	2,3-$Cl_2C_6H_3$	**5g**	8	90

[a]Reaction conditions: **1** (2 mmol) **2** (0.139 g, 2.1 mmol), 2-(2,3-dihydrochromen-4-ylidene) malononitrile (0.392 g, 2 mmol), and 2 mL [BMIm][BF_4], or [BMIm]Br.
[b]Isolated yields.

At completion, monitored by thin-layer chromatography (TLC), the reaction mixture was allowed to reach room temperature. A little amount of water (5 mL) was added to the mixture, and the crude product was isolated by filtration. The water in the filtrate was removed by distillation under reduced pressure, and the ionic liquid in the residue was then recovered for reuse by evaporating it at 80 °C for several hours in a vacuum. Investigations using 4-nitrobenzaldehyde, **2**, and **3** as model substrates showed the successfull reuse of the recycled ionic liquid. Even in the fourth round, the yield of the product **4a** is fairly good (91%).

Although the detailed mechanism of the reaction has not been clarified, the formation of benzo[*c*]chromene derivatives **4** and **5** can be tentatively explained by the



Scheme 2. Possible mechanism for the formation of products **4** and **5**.

pathway presented in Scheme 2. The product **I** may be formed first from a Knoevenagel condensation of aromatic aldehyde and malononitrile. In the following step, the Michael addition reaction between **3** and **I** takes place to produce intermediate **II**, followed by intramolecular cyclization to form **III**. Then **III** isomerizes to give the unaromatized benzo[*c*]chromenes **4**. The deprotonation in basic ionic liquid followed by the elimination of CN^- may take place in the last step to afford the final aromatized 6*H*-benzo[*c*]chromene derivatives **5**.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a Tensor 27 spectrometer in KBr pellets. ^{1}H NMR spectra was obtained from a solution in dimethylsulfoxide (DMSO-d_6) with Me_4Si as internal standard using a Bruker-400 spectrometer. HRMS analyses were carried out using a Bruker micro-TOF-Q-MS analyzer.

General Procedure for the Synthesis of 9-Amino-7-aryl-6*H*-benzo[*c*]-chromene-8,8,10(7*H*)-tricarbonitrile 4

A dry 50-mL flask was charged with aromatic aldehyde (2.0 mmol), malononitrile (0.139 g, 2.1 mmol), 2-(2,3-dihydrochromen-4-ylidene)malononitrile (0.392 g, 2.0 mmol), and ionic liquid of [BMIm][BF_4] (2 mL). The reaction mixture was stirred at room temperature for 7–12 h, and then a small amount of water (5 mL) was added to the mixture. The generated yellow solid was filtered off. The water in the filtrate was removed by distillation under reduced pressure, and the ionic liquid in the residue could be reused by evaporation at 80 °C for 4 h in a vacuum. The crude yellow products were washed with water and purified by recrystallization from EtOH and water, then dried at 80 °C for 2 h under a vacuum to give **4**.

9-Amino-7-(4-nitrophenyl)-6*H*-benzo[*c*]chromene-8,8,10(7*H*)-tricarbonitrile (4a). Mp 180–181 °C; IR (KBr, ν, cm^{-1}): 3530, 3423, 3322, 3197, 3080, 2921, 2828, 2210, 1646, 1606, 1576, 1518, 1489, 1457, 1350, 1246, 1224, 1109, 1014, 829, 784, 773, 713; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.43 (d, $J = 15.2$ Hz, 1H, CH_2), 4.58 (d, $J = 15.2$ Hz, 1H, CH_2), 5.14 (s, 1H, CH), 6.96 (d, $J = 8.0$ Hz, 1H, ArH), 7.09 (t, $J = 7.6$ Hz, 1H, ArH), 7.30 (t, $J = 7.2$ Hz, 1H, ArH), 7.69 (t, $J = 8.8$ Hz, 3H, ArH), 8.00 (s, 2H, NH_2), 8.34 (d, $J = 8.8$ Hz, 2H, ArH). HRMS (ESI, m/z) calcd for $C_{22}H_{13}N_5NaO_3$ ($M + Na^+$) 418.0916, found 418.0903.

9-Amino-7-(2-bromophenyl)-6*H*-benzo[*c*]chromene-8,8,10(7*H*)-tricarbonitrile (4b). Mp 221–224 °C; IR (KBr, ν, cm^{-1}): 3385, 3321, 3207, 3065, 2923, 2847, 2216, 1657, 1607, 1588, 1489, 1470, 1458, 1376, 1282, 1246, 1218, 1112, 1025, 784, 766, 732; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.31 (d, $J = 15.2$ Hz, 1H, CH_2), 4.61 (d, $J = 15.6$ Hz, 1H, CH_2), 5.00 (s, 1H, CH), 6.95 (d, $J = 7.6$ Hz, 1H, ArH), 7.11 (t, $J = 7.6$ Hz, 1H, ArH), 7.30 (t, $J = 7.6$ Hz, 1H, ArH), 7.41 (dd, $J = 19.2$ Hz, $J' = 8.0$ Hz, 2H, ArH), 7.49 (t, $J = 7.6$ Hz, 1H, ArH), 7.68 (d, $J = 8.0$ Hz, 1H, ArH), 7.83 (d, $J = 8.0$ Hz, 1H, ArH), 8.05 (s, 2H, NH_2). HRMS (ESI, m/z) calcd. for $C_{24}H_{13}BrN_4NaO$ ($M + Na^+$) 451.0170; found 451.0192.

9-Amino-7-(3-bromophenyl)-6*H*-benzo[*c*]chromene-8,8,10(7*H*)-tricarbonitrile (4c). Mp 201–203 °C; IR (KBr, ν, cm^{-1}): 3442, 3311, 3201, 3057, 2212, 1648, 1621, 1573, 1488, 1429, 1373, 1275, 1238, 1215, 1179, 1156, 1111, 1075, 1041, 1018, 796, 763, 732; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.44 (d, $J = 11.6$ Hz, 1H, CH_2), 4.57 (d, $J = 11.6$ Hz, 1H, CH_2), 4.90 (s, 1H, CH), 6.95 (d, $J = 8.0$ Hz, 1H, ArH), 7.10 (t, $J = 7.6$ Hz, 1H, ArH), 7.30 (t, $J = 7.6$ Hz, 1H, ArH), 7.37–7.46 (m, 2H, ArH), 7.61–7.69 (m, 3H, ArH), 7.94 (s, 2H, NH_2). HRMS (ESI, m/z) calcd. for $C_{24}H_{13}BrN_4NaO$ ($M + Na^+$) 451.0170; found 451.0149.

9-Amino-7-(3,4-dimethoxyphenyl)-6*H*-benzo[*c*]chromene-8,8,10(7*H*)-tricarbonitrile (4d). Mp 216–218 °C; IR (KBr, ν, cm^{-1}): 3437, 3344, 3243, 2955, 2937, 2912, 2837, 2203, 1644, 1633, 1605, 1593, 1574, 1519, 1489, 1469, 1447, 1420, 1384, 1347, 1277, 1259, 1238, 1141, 1110, 1027, 781, 764; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.72 (s, 3H, CH_3O), 3.77 (s, 3H, CH_3O), 4.45 (d, $J = 15.2$ Hz, 1H, CH_2), 4.54 (d, $J = 15.2$ Hz, 1H, CH_2), 4.78 (s, 1H, CH), 6.91–6.96 (m, 2H, ArH), 7.02 (d, $J = 8.4$ Hz, 2H, ArH), 7.09 (t, $J = 7.6$ Hz, 1H, ArH), 7.28 (t, $J = 8.0$ Hz, 1H, ArH), 7.62 (d, $J = 7.6$ Hz, 1H, ArH), 7.90 (s, 2H, NH_2). HRMS (ESI, m/z) calcd. for $C_{24}H_{18}N_4NaO_3$ ($M + Na^+$) 433.1477; found 433.1287.

9-Amino-7-(3,5-dimethoxyphenyl)-6*H*-benzo[*c*]chromene-8,8,10(7*H*)-tricarbonitrile (4e). Mp 216–218 °C; IR (KBr, ν, cm^{-1}): 3274, 3029, 3015, 2975, 2930, 2887, 2837, 2218, 1609, 1590, 1574, 1561, 1481, 1468, 1453, 1431, 1365, 1336, 1309, 1220, 1205, 1158, 1130, 1075, 1062, 1024, 887, 828, 762; ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.05 (d, $J = 11.2$ Hz, 1H, CH_2), 3.84–3.87 (m, 1H, CH_2), 3.33 (s, 6H, $2CH_3O$), 4.27–4.31 (m, 1H, CH), 6.57–6.66 (m, 3H, ArH), 6.97 (d, $J = 8.4$ Hz, 1H, ArH), 7.11–7.13 (m, 1H, ArH), 7.51–7.55 (m, 1H, ArH), 8.39 (d, $J = 8.4$ Hz, 1H, NH_2), 10.82 (s, 1H, NH_2). HRMS (ESI, m/z) calcd. for $C_{24}H_{18}N_4NaO_3$ ($M + Na^+$) 433.1477; found 433.1294.

9-Amino-7-(2,4,5-trimethoxyphenyl)-6*H*-benzo[*c*]chromene-8,8,10(7*H*)-tricarbonitrile (4f). Mp 216–218 °C; IR (KBr, ν, cm^{-1}): 3443, 3422, 2998, 2949, 2927, 2224, 1656, 1608, 1581, 1528, 1512, 1471, 1453, 1438, 1299, 1276, 1230, 1210, 1048, 1026, 826, 764; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.15–3.26 (m, 1H, CH_2), 3.44–3.62 (m, 1H, CH_2), 3.74 (s, 3H, CH_3O), 3.79 (s, 3H, CH_3O), 3.82 (s, 3H, CH_3O), 3.94–3.98 (m, 1H, CH), 6.75 (s, 1H, ArH), 6.95 (d, $J = 8.4$ Hz, 1H, ArH), 7.07–7.11 (m, 2H, ArH), 7.25 (s, 1H, ArH), 7.42–7.47 (m, 1H, ArH), 7.92–7.94 (m, 1H, NH_2). HRMS (ESI, m/z) calcd. for $C_{25}H_{20}N_4NaO_4$ ($M + Na^+$) 463.1382; found 463.1367.

General Procedure for the Synthesis of 9-Amino-7-aryl-6*H*-benzo[*c*]-chromene-8,10-dicarbonitrile derivatives 5

A dry 50-mL flask was charged with aromatic aldehyde (2.0 mmol), malononitrile (0.139 g, 2.1 mmol), 2-(2,3-dihydrochromen-4-ylidene)malononitrile (0.392 g, 2.0 mmol), and ionic liquid of [BMIm]Br (2 mL). The reaction mixture was stirred at 50 °C for 6–9 h and then cooled down to room temperature. A small amount of water (5 mL) was added to the mixture, and the generated yellow solid was filtered off. The water in the filtrate was removed by distillation under reduced pressure,

and the ionic liquid in the residue could be reused by being evaporated at 80 °C for 4 h in a vacuum. The crude yellow products were washed with water, purified by recrystallization from DMF and water, and then dried at 80 °C for 2 h under vacuum to give **5**.

9-Amino-7-(3,5-dimethoxyphenyl)-6*H*-benzo[*c*]chromene-8,10-dicarbonitrile (5a). Mp 281–282 °C; IR (KBr, ν, cm^{-1}): 3363, 3341, 3241, 2942, 2844, 2216, 1641, 1608, 1562, 1488, 1452, 1434, 1372, 1300, 1261, 1206, 1166, 1068, 1000, 944, 835, 760; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.79 (s, 6H, $2CH_3O$), 4.65 (s, 2H, CH_2), 6.55 (d, $J = 2.0$ Hz, 2H, NH_2), 6.65 (t, $J = 2.0$ Hz, 1H, ArH), 6.80 (s, 2H, ArH), 7.09 (d, $J = 7.6$ Hz, 1H, ArH), 7.23 (t, $J = 7.2$ Hz, 1H, ArH), 7.48 (t, $J = 8.4$ Hz, 1H, ArH), 8.31 (d, $J = 8.0$ Hz, 1H, ArH). HRMS (ESI, m/z) calcd. for $C_{23}H_{18}N_3O_3$ ($M + H^+$) 384.1384; found 384.1327.

9-Amino-7-(3-bromophenyl)-6*H*-benzo[*c*]chromene-8,10-dicarbonitrile (5b). Mp 254–255 °C; IR (KBr, ν, cm^{-1}): 3461, 3360, 3243, 2850, 2218, 1666, 1643, 1607, 1586, 1570, 1553, 1494, 1468, 1436, 1386, 1295, 1265, 1228, 1155, 1077, 1013, 985, 833, 809, 757, 741; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.62 (s, 2H, CH_2), 6.86 (s, 2H, NH_2), 7.10 (d, $J = 8.0$ Hz, 1H, ArH), 7.24 (t, $J = 7.6$ Hz, 1H, ArH), 7.39 (d, $J = 8.4$ Hz, 2H, ArH), 7.49 (t, $J = 7.2$ Hz, 1H, ArH), 7.77 (d, $J = 8.0$ Hz, 2H, ArH), 8.31 (d, $J = 7.6$ Hz, 1H, ArH). HRMS (ESI, m/z) calcd. for $C_{21}H_{12}BrN_3ONa$ ($M + Na^+$) 424.0061; found 424.0059.

9-Amino-7-(2,3-dimethoxyphenyl)-6*H*-benzo[*c*]chromene-8,10-dicarbonitrile (5c). Mp 286–288 °C; IR (KBr, ν, cm^{-1}): 3465, 3329, 3227, 2983, 2930, 2842, 2207, 1631, 1607, 1583, 1562, 1474, 1432, 1369, 1297, 1266, 1211, 1159, 1118, 1083, 1003, 942, 862, 802, 758; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 3.60 (s, 3H, CH_3O), 3.89 (s, 3H, CH_3O), 4.50 (dd, $J = 18.8$ Hz, $J' = 13.2$ Hz, 2H, CH_2), 6.80 (s, 2H, NH_2), 6.82–6.84 (m, 1H, ArH), 7.09 (d, $J = 8.0$ Hz, 1H, ArH), 7.22–7.25 (m, 3H, ArH), 7.48 (t, $J = 7.2$ Hz, 1H, ArH), 8.35 (d, $J = 7.6$ Hz, 1H, ArH). HRMS (ESI, m/z) calcd. for $C_{23}H_{18}N_3O_3$ ($M + H^+$) 384.1384; found 384.1340.

9-Amino-7-(4-chlorophenyl)-6*H*-benzo[*c*]chromene-8,10-dicarbonitrile (5d). Mp 245–246 °C; IR (KBr, ν, cm^{-1}): 3467, 3356, 3246, 2852, 2219, 1645, 1608, 1586, 1555, 1498, 1437, 1362, 1295, 1265, 1228, 1094, 1017, 986, 838, 810, 754; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.61 (s, 2H, CH_2), 6.85 (s, 2H, NH_2), 7.10 (d, $J = 8.0$ Hz, 1H, ArH), 7.24 (t, $J = 7.6$ Hz, 1H, ArH), 7.44–7.50 (m, 3H, ArH), 7.63 (d, $J = 8.4$ Hz, 2H, ArH), 8.31 (d, $J = 8.0$ Hz, 1H, ArH). HRMS (ESI, m/z) calcd. for $C_{21}H_{12}ClN_3ONa$ ($M + Na^+$) 380.0567; found 380.0569.

9-Amino-7-(2-chlorophenyl)-6*H*-benzo[*c*]chromene-8,10-dicarbonitrile (5e). Mp 280–282 °C; IR (KBr, ν, cm^{-1}): 3466, 3353, 3242, 2848, 2214, 1641, 1608, 1586, 1557, 1491, 1451, 1368, 1300, 1275, 1226, 1160, 1121, 1047, 985, 948, 878, 812, 762, 744; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.45 (d, $J = 13.2$ Hz, 1H, CH_2), 4.51 (d, $J = 13.2$ Hz, 1H, CH_2), 6.91 (s, 2H, NH_2), 7.10 (d, $J = 8.0$ Hz, 1H, ArH), 7.24 (t, $J = 16.0$ Hz, 1H, ArH), 7.46–7.61 (m, 4H, ArH), 7.71 (d, $J = 8.0$ Hz, 1H, ArH), 8.36 (d, $J = 8.0$ Hz, 1H, ArH). HRMS (ESI, m/z) calcd. for $C_{21}H_{12}ClN_3ONa$ ($M + Na^+$) 380.0567; found 380.0571.

9-Amino-7-(2,4-dichlorophenyl)-6*H*-benzo[*c*]chromene-8,10-dicarbonitrile (5f). Mp 245–246 °C; IR (KBr, ν, cm^{-1}): 3456, 3351, 3243, 3185, 2221, 1671, 1640, 1607, 1588, 1563, 1491, 1434, 1385, 1301, 1262, 1225, 1104, 1061, 1031, 986, 820, 763, 733; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.47 (d, $J = 13.2$ Hz, 1H, CH_2), 4.53 (d, $J = 13.2$ Hz, 1H, CH_2), 6.97 (s, 2H, NH_2), 7.10 (d, $J = 8.0$ Hz, 1H, ArH), 7.24 (t, $J = 7.6$ Hz, 1H, ArH), 7.48–7.54 (m, 2H, ArH), 7.65 (d, $J = 8.4$ Hz, 1H, ArH), 7.93 (d, $J = 8.0$ Hz, 1H, ArH), 8.35 (d, $J = 8.0$ Hz, 1H, ArH). HRMS (ESI, m/z) calcd. for $C_{21}H_{11}Cl_2N_3ONa$ ($M + Na^+$) 414.0177; found 414.0178.

9-Amino-7-(2,3-dichlorophenyl)-6*H*-benzo[*c*]chromene-8,10-dicarbonitrile (5g). Mp > 295 °C; IR (KBr, ν, cm^{-1}): 3386, 2850, 2211, 1626, 1606, 1584, 1557, 1489, 1432, 1406, 1364, 1302, 1278, 1231, 1186, 1156, 1105, 1047, 925, 819, 806, 768, 742; ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 4.47 (d, $J = 13.2$ Hz, 1H, CH_2), 4.53 (d, $J = 13.2$ Hz, 1H, CH_2), 6.98 (s, 2H, NH_2), 7.10 (d, $J = 8.0$ Hz, 1H, ArH), 7.25 (t, $J = 7.6$ Hz, 1H, ArH), 7.47–7.52 (m, 2H, ArH), 7.57 (t, $J = 8.0$ Hz, 1H, ArH), 7.85 (d, $J = 8.0$ Hz, 1H, ArH), 8.36 (d, $J = 7.2$ Hz, 1H, ArH). HRMS (ESI, m/z) calcd. for $C_{21}H_{12}Cl_2N_3O$ ($M + H^+$) 392.0357; found 392.0365.

CONCLUSION

In summary, this article describes an efficient and green method for the synthesis of polysubstituted chromene derivatives in ionic liquids. The structure of all the obtained substances has been characterized by spectral methods including IR, ^{1}H NMR and HRMS. This procedure has the advantages of good yields, one pot, and environmental friendliness.

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