

Dalip Kumar,* Gautam Patel, Anil Kumar, and Ram K. Roy

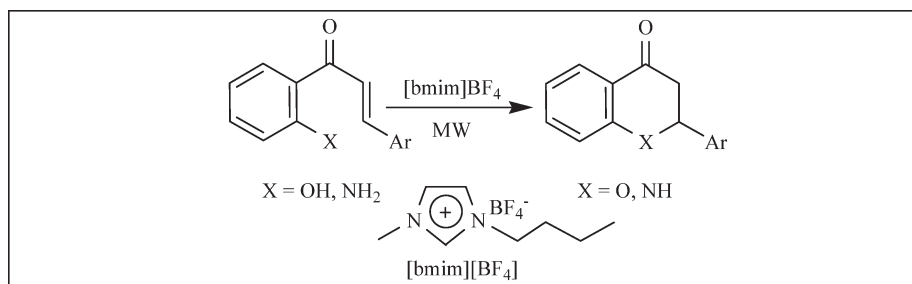
Chemistry Group, Birla Institute of Technology and Science, Pilani, India

*E-mail: dalipk@bits-pilani.ac.in

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A facile and convenient synthesis of 2-aryl-2,3-dihydroquinolin-4(1*H*)-one and 2-aryl-2,3-dihydro-4*H*-chromen-4-one has been described using ionic liquid catalyzed intramolecular cyclization of the corresponding 2'-aminochalcones and 2'-hydroxychalcones, respectively. The rapid and fairly general protocol affords product in good yield. Ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate, was recovered and reused without losing its efficiency.

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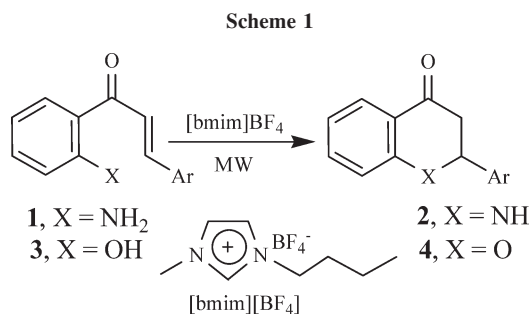
INTRODUCTION

Naturally occurring 2-aryl-2,3-dihydro-quinolin-4(1*H*)-ones and 2-aryl-2,3-dihydro-4*H*-chromen-4-ones are valuable precursors [1] for the synthesis of medicinally important compounds [2]. Because of their diverse biological activities such as hypertensive, antibacterial, antitumor, antifungal, antiinflammatory, etc., synthesis of these compounds has generated significant interest among chemists and biologists. Thus, the synthesis of these compounds has been fuelled due to diverse biological importance and presence of these moieties in various natural products [3]. The common method for the synthesis of 2-aryl-2,3-dihydroquinolin-4(1*H*)-ones and 2-aryl-2,3-dihydro-4*H*-chromen-4-ones is intramolecular cyclization of 2'-hydroxy and 2'-amino chalcones, respectively. Their synthesis following this strategy have been accomplished by using Lewis acid as catalyst, e.g. silica gel supported TaBr₅, K-10 Clay, orthophosphoric acid, sulphuric acid, acetic acid, 30% TFA over silica gel, silica gel [4]. Intramolecular cyclization by basic catalysts such as alumina supported-CeCl₃·7H₂O-NaI, NaOH [5] is well documented in literature. Other methods like thermolysis [6], electrolysis [7], ZnO supported metal oxide [8], light [9], Ni/Zn/K halides [10] were also employed for the cyclization. Many of the reported methods for the synthesis of these biologically important heterocyclic compounds involve the use of toxic fine

chemicals, requires stoichiometric amount of catalysts and afford products in low yields. Therefore, the search continues for an efficient method in terms of operational simplicity and economical viability.

In the last decade, ionic liquids have gained increasing attention of synthetic organic chemists in various organic transformations because of their tunable chemical and physical properties and catalytic behaviour [11–14]. Ionic liquids are salts that contain organic cations and inorganic or organic anions, and are liquid at or close to ambient temperature. In contrast to conventional polar organic solvents such as THF, DMF and DMSO, ionic liquids are nonflammable, nonvolatile and stable to atmospheric conditions. Among all, imidazolium-based ionic liquids with tetrafluoroborate and hexafluorophosphate anions are the most studied ionic liquids for organic synthesis.

Microwave-assisted organic synthesis offers many advantages including faster and cleaner reaction, high product yield, and operational simplicity [15]. Several methods have been developed for performing reactions with microwave irradiation in solution and under solvent free conditions [16], but a homogeneous mixture is preferred to obtain uniform heating. The excellent dielectric properties of ionic liquids offer added advantages when used as solvent in microwave-assisted organic reactions [17]. Ionic liquids couple very efficiently with



microwave through an ionic conduction mechanism [18]. Nucleophilic aromatic substitution reactions have been reported with and without solvent under microwave irradiations [19]. In continuation of our study on the development of new cost effective methodologies utilizing this unconventional energy source, we herein report an ionic liquid catalyzed intramolecular cyclization of 2'-aminochalcones and 2'-hydroxychalcones with enhanced yields and efficiency under microwave irradiation to obtain 2-aryl-2,3-dihydro-quinolin-4(1*H*)-ones and 2-aryl-2,3-dihydro-4*H*-chromen-4-ones, respectively (Scheme 1).

RESULTS AND DISCUSSION

Our initial attempts under conventional conditions to cyclize 2'-aminochalcones and 2'-hydroxychalcones using 1-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF₄ failed at room temperature. On heating the reaction mixture for 48 h at 135°C, very little product was produced. Further heating at this temperature generated more impurities. Encouraged by reported efficient coupling of ionic liquids with microwave [18], we next investigated this intramolecular cyclization under microwave irradiation. After several attempts, it was realized that intermittent microwave exposure for 20 s (total microwave exposure time 120 s) followed by cooling

(20 s) is optimum in terms of efficient intramolecular cyclization and product yield. Among ionic liquids, [bmim]BF₄ is found to be best choice for the efficient intramolecular cyclization with shorter reaction time and good yield. After standardizing the reaction conditions for this reaction, cyclization of substituted 2'-aminochalcones **1a–g** to the corresponding 2-aryl-2,3-dihydroquinolin-4(1*H*)-ones **2a–g** were achieved satisfactorily (Table 1).

Encouraged by the successful cyclization of 2'-aminochalcones, we next explored the intramolecular cyclization of analogues 2'-hydroxychalcones **3a–g** to prepare 2-aryl-2,3-dihydro-4*H*-chromen-4-ones **4a–g**. Microwave exposure (1.0–1.5 min) of a thick paste of 2'-hydroxychalcones **3a–g** in [bmim]BF₄ led to the formation of 2-aryl-2,3-dihydro-4*H*-chromen-4-ones **4a–g** in moderate yields (Table 2). In all the cases, some unreacted 2'-hydroxychalcones was recovered along with the product. Further increasing the amount of [bmim]BF₄ and prolonging microwave irradiation does not improve the product yield.

To determine if the ionic liquid, [bmim]BF₄ was an essential factor to promote this intramolecular cyclization, the cyclization of **2a** as a model reaction was carried out in polar organic solvents such as DMF and DMSO under microwave irradiation. This resulted in poor yield of product along with unchanged starting material. Ionic liquids are known to couple efficiently with microwave energy to accelerate the reaction. Further, ionic liquids are reported to stabilize the charged species formed as intermediate in different reactions and enhance the nucleophilicity of various nucleophiles [20]. It is expected that enhanced stability of the polar activated complex formed during intramolecular cyclization (Figure 1) and enhanced nucleophilicity of amino or hydroxyl group by ionic liquid along with the effect of microwave radiations are probable reasons for the increased reaction rate. It is also worth to mention that in absence of ionic liquid reaction did not proceed under

Table 1

Synthesis of 2-aryl-2,3-dihydroquinolin-4(1*H*)-ones.

Substrate (1)	Ar	Product ^a (2)	Time (min)	Yield ^b (%)
1a	C ₆ H ₅	2a	2.0	89 ^c
1b	4-ClC ₆ H ₄	2b	2.0	85
1c	4-MeC ₆ H ₄	2c	2.0	87
1d	4-(C ₆ H ₅ CH ₂ O)C ₆ H ₄	2d	2.0	84
1e	2,6-Cl ₂ C ₆ H ₃	2e	2.0	82
1f	2-Furyl	2f	2.0	88

^a All the products gave satisfactory NMR (¹H and ¹³C) and Mass data.

^b Isolated yield.

^c **2a** was obtained in 81% when ionic liquid was recycled and reused.

Table 2

Synthesis of 2-aryl-2,3-dihydro-4*H*-chromen-4-one.

Substrate (3)	Ar	Product ^a (4)	Time (min)	Yield ^b (%)
3a	C ₆ H ₅	4a	1.0	58
3b	4-MeC ₆ H ₄	4b	1.0	57
3c	4-MeOC ₆ H ₄	4c	1.0	52
3d	4-FC ₆ H ₄	4d	1.5	51
3e	4-ClC ₆ H ₄	4e	1.5	49
3f	2,6-Cl ₂ C ₆ H ₃	4f	1.5	55
3g	2-Furyl	4g	1.5	51

^a All the products gave satisfactory NMR (¹H and ¹³C) and mass data.

^b Isolated yield.

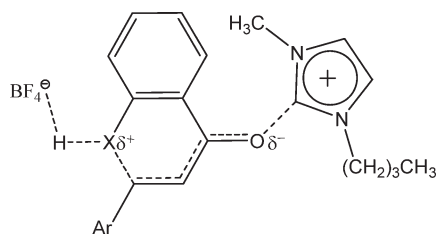


Figure 1. Proposed activated complex of [Bmim] BF₄ catalyzed intramolecular cyclization of 2'-amino/2'-hydroxychalcones.

microwave irradiation. Results of this intramolecular cyclization in other ionic liquids were also poor. Thus [bmim]BF₄ and microwave irradiation plays very important role in this rapid intramolecular cyclization.

The slow reactivity of 2'-hydroxychalcones relative to 2'-aminochalcones can be rationalized from the corresponding activation energy (E_{act}) values. For example, the transition states corresponding to the cyclization process of **1a** and **3a** are optimized using *ab initio* quantum chemical method (HF/6-31G**). The E_{act} value for the cyclization of **1a** is found to be 57 kcal/mol, whereas for cyclization of **3a** the value is 117.886 kcal/mol. To find out the exact reason of this difference in E_{act} between the two types of chalcone derivatives we used conceptual density functional theory (DFT) based local reactivity descriptors. As both types of chalcones have same number of electrons (if *R* remains same) local nucleophilicity of the N_{NH_2} (*N*-atom of the NH₂ group) and O_{OH} (*O*-atom of OH group) should be an ideal descriptor to reveal the relative electron donating ability of the two atoms during cyclization process [21]. One such descriptor is condensed local softness (S_k^-) [22]. The S_k^- values generated using the same HF/6-31G** method were 0.37 and 0.29 for N_{NH_2} and O_{OH} , respectively. These values clearly demonstrate that *N*-atom of the NH₂ group is more nucleophilic than *O*-atom of the OH group, favouring cyclization by lowering the activation energy values.

In conclusion, this article describes a practical and facile way to make 2-aryl-2,3-dihydroquinolin-4(1H)-ones and 2-aryl-2,3-dihydro-4H-chromen-4-ones in moderate to good yields. Relatively faster cyclization of 2'-aminochalcone in comparison with 2'-hydroxychalcone has been explained using theoretical calculations. A plausible explanation for the ionic liquid-mediated expeditious cyclizations of 2'-aminochalcones and 2'-hydroxychalcones under the influence of microwave irradiation has also been provided. When compared with literature procedures, this method has the advantages of simple reaction procedure, shorter reaction time, and reuse of [bmim]BF₄ as a catalyst.

EXPERIMENTAL

Melting points were determined in open capillary tubes on a MPA120-Automated Melting Point apparatus and are uncor-

rected. IR spectra were recorded with a JASCO IR-Report-100. ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on Bruker-400 instrument in CDCl₃ solution with TMS as an internal standard. Column chromatography was performed on silica gel (100–200 mesh, S. D. Fine, Pilani, India). Amino- and hydroxychalcones were prepared using the appropriate aldehyde and the corresponding *o*-substituted acetophenones [23]. The 2-aminoacetophenone and 2-hydroxyacetophenone (Sigma-Aldrich) were used as purchased. Aromatic aldehydes were obtained from E-Merck (India) Ltd. [bmim]BF₄ was prepared according to literature procedure [24]. Theoretical calculations were performed using Gaussian 03 Rev E.0.1 software. Reactions were performed in a domestic LG microwave MG607APR model (900 W).

Preparation of 2-aryl-2,3-dihydro-4(1H)-quinolinones (2a-g). A neat mixture of 2'-aminochalcone (1 mmol) and [bmim]BF₄ (50 mg) was subjected to microwave irradiation at 50% power for 2 min with intermittent heating (20 s) and cooling (20 s). After completion of reaction, as indicated by TLC, the product was extracted into diethyl ether (3 × 5 mL). Combined diethyl ether layer was distilled off under reduced pressure. The residue so obtained was percolated through a bed of silica gel using hexane:ethyl acetate (8:2) as eluent to afford pure product.

2-Phenyl-2,3-dihydro-4(1H)-quinolinone (2a). mp 149–152°C, lit. [25] 149–150°C; IR (KBr): 3325 (NH), 1690 cm⁻¹(C=O) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.87 (d, *J* = 7.6 Hz, 1H), 7.47–7.32 (m, 6H), 6.80 (dd, *J* = 7.2, 7.6 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 4.76 (dd, *J* = 4.0, 13.6 Hz, 1H), 4.52 (br s, 1H, NH), 2.88 (dd, *J* = 13.6, 16.4 Hz, 1H), 2.77 (dd, *J* = 3.6, 16.0 Hz, 1H); ¹³C NMR (CDCl₃): δ = 193.41, 151.70, 141.17, 135.55, 129.15, 128.63, 127.78, 126.77, 119.21, 118.62, 116.05, 58.66, 46.59.

2-(4'-Chlorophenyl)-2,3-dihydro-4(1H)-quinolinone (2b). mp 168–170°C, lit. [25] 167–168°C; IR (KBr): 3300 (NH), 1640 (C=O) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.85 (d, *J* = 7.6 Hz, 1H), 7.41–7.32 (m, 5H), 6.79 (dd, *J* = 7.20, 7.24 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 4.73 (dd, *J* = 4.16, 13.20 Hz, 1H), 4.52 (br s, 1H, NH), 2.83 (dd, *J* = 16.20, 18.00 Hz, 1H), 2.74 (dd, *J* = 2.40, 16.20 Hz, 1H); ¹³C NMR (CDCl₃): δ = 192.98, 151.50, 139.72, 135.64, 134.33, 129.32, 128.13, 127.74, 123.66, 122.08, 119.23, 118.84, 116.13, 58.00, 46.55.

2-(*p*-Tolyl)-2,3-dihydro-4(1H)-quinolinone (2c). mp 148–149°C, lit. [25] 149°C; IR (KBr): 3300 (NH), 1640 (C=O) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.85 (d, *J* = 8.0 Hz, 1H), 7.34–7.19 (m, 5H), 6.79–6.75 (m, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 4.69 (dd, *J* = 3.40, 13.60 Hz, 1H), 4.57 (br s, 1H, NH), 2.85 (dd, *J* = 13.80, 16.20 Hz, 1H), 2.72 (dd, *J* = 2.40, 16.4 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (CDCl₃): δ = 193.52, 151.66, 138.25, 136.49, 135.38, 129.60, 127.56, 126.52, 118.95, 118.31, 115.94, 58.16, 46.44, 21.13.

2-(4'-Benzyloxyphenyl)-2,3-dihydro-4(1H)-quinolinone (2d). [25e] mp 130–133°C; IR (KBr): 3325 (NH), 1648 (C=O) cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.85 (d, *J* = 5.6 Hz, 1H), 7.44–7.32 (m, 8H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.78 (dd, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 5.01 (s, 2H), 4.68 (dd, *J* = 3.60, 14.0 Hz, 1H), 4.46 (br s, 1H, NH), 2.85 (ddd, *J* = 3.73, 13.84, 17.90 Hz, 1H), 2.73 (dd, *J* = 3.13, 16.15 Hz, 1H); ¹³C NMR (CDCl₃): δ = 193.59, 158.99, 151.73, 136.94, 135.48, 133.50, 128.77, 128.19, 128.00, 127.76, 127.57, 119.18, 118.52, 116.01, 115.40, 70.25, 58.06, 46.66.

2-(2',6'-Dichlorophenyl)-2,3-dihydro-4(1H)-quinolinone (2e). Viscous liquid lit. [25]; IR (KBr): 3315 (NH), 1640 (C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.89 (d, J = 8.0 Hz, 1H), 7.38–7.20 (m, 4H), 6.76 (t, J = 7.8 Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H), 5.74 (dd, J = 4.04, 15.24 Hz, 1H), 4.40 (br s, 1H, NH), 3.65 (dd, J = 15.42, 16.40 Hz, 1H), 2.59 (dd, J = 4.00, 16.40 Hz, 1H); ^{13}C NMR (CDCl_3): δ = 193.03, 151.28, 135.87, 135.52, 133.87, 130.09, 129.98, 127.94, 118.62, 118.21, 115.99, 54.17, 40.06.

2-(Furan-2-yl)-2,3-dihydro-4(1H)-quinolinone (2f). [25d,e] Viscous liquid; IR (KBr): 3325 (NH), 1690 (C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.85 (d, J = 8.0 Hz, 1H), 7.38–7.26 (m, 2H), 6.79–6.69 (m, 2H), 6.32 (d, J = 1.39 Hz, 1H), 6.25 (d, J = 1.53 Hz, 1H), 4.84–4.78 (m, 2H), 3.07–2.92 (m, 2H); ^{13}C NMR (CDCl_3): δ = 192.72, 153.48, 150.61, 142.59, 135.54, 127.56, 119.34, 118.69, 116.14, 113.25, 110.49, 50.72, 42.07.

Preparation of 2-aryl-2,3-dihydro-4H-chromen-4-one (4a-g). A neat mixture of 2'-hydroxychalcone (1 mmol) and [bmim]BF₄ (50 mg) was subjected to microwave irradiation at 50% power for 2 min with intermittent heating (20 s) and cooling (20 s). After completion of reaction, as indicated by TLC, the product was extracted into diethyl ether (3 \times 5 mL). The combined organic phase was distilled off under reduced pressure. The residue so obtained was percolated through a bed of silica gel using hexane:ethyl acetate (8:2) as eluent to afford pure product.

2-Phenyl-2,3-dihydro-4H-chromen-4-one (4a). mp 75–76°C, lit. [25] 77–78°C; IR (KBr): 1685 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.94 (dd, J = 1.28, 7.8 Hz, 1H), 7.53–7.38 (m, 6H), 7.07–7.04 (m, 2H), 5.48 (dd, J = 2.8, 13.36 Hz, 1H), 3.09 (dd, J = 13.6, 16.8 Hz, 1H), 2.89 (dd, J = 2.8, 16.8 Hz, 1H); ^{13}C NMR (CDCl_3): δ = 191.92, 161.53, 138.72, 136.16, 128.82, 128.74, 127.03, 126.12, 121.59, 120.92, 118.10, 79.57, 43.64.

2-(p-Tolyl)-2,3-dihydro-4H-chromen-4-one (4b). mp 82–83°C, lit. [25] 83–84°C; IR (KBr): 1680 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.9 (dd, J = 2.0, 6.0 Hz, 1H), 7.5 (dd, J = 7.6, 11.2 Hz, 1H), 7.3 (dd, J = 1.6, 8.0 Hz, 2H), 7.24 (d, J = 7.2 Hz, 2H), 7.0 (d, J = 7.2 Hz, 2H), 5.45 (d, J = 13.6 Hz, 1H), 3.09 (dd, J = 2.4, 15.2 Hz, 1H), 2.8 (dt, J = 2.4, 16.8 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (CDCl_3): δ = 192.12, 161.64, 138.69, 136.12, 135.77, 129.48, 127.03, 126.18, 121.52, 120.95, 118.14, 79.53, 44.56, 21.17.

2-(4'-Methoxyphenyl)-2,3-dihydro-4H-chromen-4-one (4c). mp 87–88°C, lit. [25] 88–89°C; IR (KBr): 1690 (C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.93 (d, J = 7.8 Hz, 1H), 7.50 (dd, J = 1.4, 7.52 Hz, 1H), 7.41 (d, J = 8.6 Hz, 2H), 7.06–7.02 (m, 2H), 6.96 (d, J = 8.6 Hz, 2H), 5.43 (dd, J = 2.72, 13.36 Hz, 1H), 3.83 (s, 3H), 3.11 (dd, J = 13.44, 16.88 Hz, 1H), 2.86 (dd, J = 2.76, 16.84 Hz, 1H); ^{13}C NMR (CDCl_3): δ = 192.23, 161.64, 159.99, 136.15, 130.78, 127.73, 127.03, 121.52, 120.92, 118.13, 114.21, 79.35, 55.36, 44.46.

2-(4'-Fluorophenyl)-2,3-dihydro-4H-chromen-4-one (4d). mp 96–98°C, lit. [26] 79–80°C; IR (KBr): 1690 (C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.94 (d, J = 7.62 Hz, 1H), 7.53–7.40 (m, 3H), 7.15–7.02 (m, 3H), 6.97–6.95 (m, 1H), 5.44 (dd, J = 14.8, 17.2 Hz, 1H), 3.09 (dd, J = 3.6, 13.2 Hz, 1H), 2.92–2.85 (m, 1H); ^{13}C NMR (CDCl_3): δ = 192.31, 161.68, 159.38, 136.29, 130.60, 128.08, 128.03, 127.05, 121.78, 120.94, 118.15, 79.41, 44.47.

2-(4'-Chlorophenyl)-2,3-dihydro-4H-chromen-4-one (4e). mp 95–96°C, lit. [25] 94–95°C; IR (KBr): 1690 (C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.93 (dd, J = 1.76, 7.72 Hz, 1H), 7.54–7.49 (m, 1H), 7.42–7.41 (m, 4H), 7.09–7.04 (m, 2H), 5.47 (dd, J = 3.0, 12.08 Hz, 1H), 3.04 (dd, J = 3.48, 13.24 Hz, 1H), 2.88 (dd, J = 3.12, 16.84 Hz, 1H); ^{13}C NMR (CDCl_3): δ = 191.51, 161.30, 137.27, 136.29, 134.59, 129.04, 127.50, 127.09, 121.81, 120.89, 118.08, 78.81, 44.58.

2-(2',6'-Dichlorophenyl)-2,3-dihydro-4H-chromen-4-one (4f). [25c,e] mp 148–149°C; IR (KBr): 1680 (C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.97 (d, J = 7.85 Hz, 1H), 7.54–7.50 (m, 1H), 7.41–7.38 (m, 2H), 7.29–7.24 (m, 1H), 7.10–7.03 (m, 2H), 6.30 (dd, J = 2.8, 14.8 Hz, 1H), 3.79 (dd, J = 3.33, 17.11 Hz, 1H), 2.70 (dd, J = 3.02, 17.02 Hz, 1H); ^{13}C NMR (CDCl_3): δ = 189.22, 159.12, 134.07, 133.01, 130.29, 128.10, 127.53, 125.03, 119.40, 118.43, 115.91, 73.71, 37.37.

2-(Furan-2'-yl)-2,3-dihydro-4H-chromen-4-one (4g). mp 74–75°C, lit. [27] 80°C; IR (KBr): 1680 (C=O) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ = 7.92 (d, J = 8.0 Hz, 1H), 7.51–7.48 (m, 2H), 7.06–7.01 (m, 2H), 6.46 (d, J = 3.24 Hz, 1H), 6.40 (d, J = 3.05 Hz, 1H), 5.55 (dd, J = 3.28, 11.53 Hz, 1H), 3.27 (dd, J = 11.56, 17.05 Hz, 1H), 2.98 (dd, J = 3.50, 16.92 Hz, 1H); ^{13}C NMR (CDCl_3): δ = 191.24, 160.74, 150.89, 143.43, 136.24, 126.95, 121.73, 120.93, 118.12, 110.51, 109.34, 72.27, 40.80.

General procedure for recovery and reuse of ionic liquid. After extracting the product using diethyl ether, the recovered ionic liquid was dried under reduced pressure. The flask containing recovered ionic liquid (50 mg) was again charged with 2'-aminochalcone (1 mmol) and following the aforementioned general procedure, 2-phenyl-2,3-dihydro-4(1H)-quinolinone **2a** was isolated in 81% yield.

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