

## A facile approach for the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones using a microwave promoted Biginelli protocol in ionic liquid

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**Abstract.** Carboxy functionalized ionic liquid [cmmim][BF<sub>4</sub>] has been demonstrated to be an efficient and green catalyst for the one pot synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones heterocycles under microwave irradiation. The ionic liquid-microwave strategy represents an easy access to Biginelli compounds with high yields and purity. The protocol was found to be compatible with different structurally diverse aldehydes. The ionic liquid was recycled and reused in at least six subsequent reactions with consistent activity.

**Keywords.** Ionic liquid; Biginelli reaction; microwave irradiation; recyclability.

### 1. Introduction

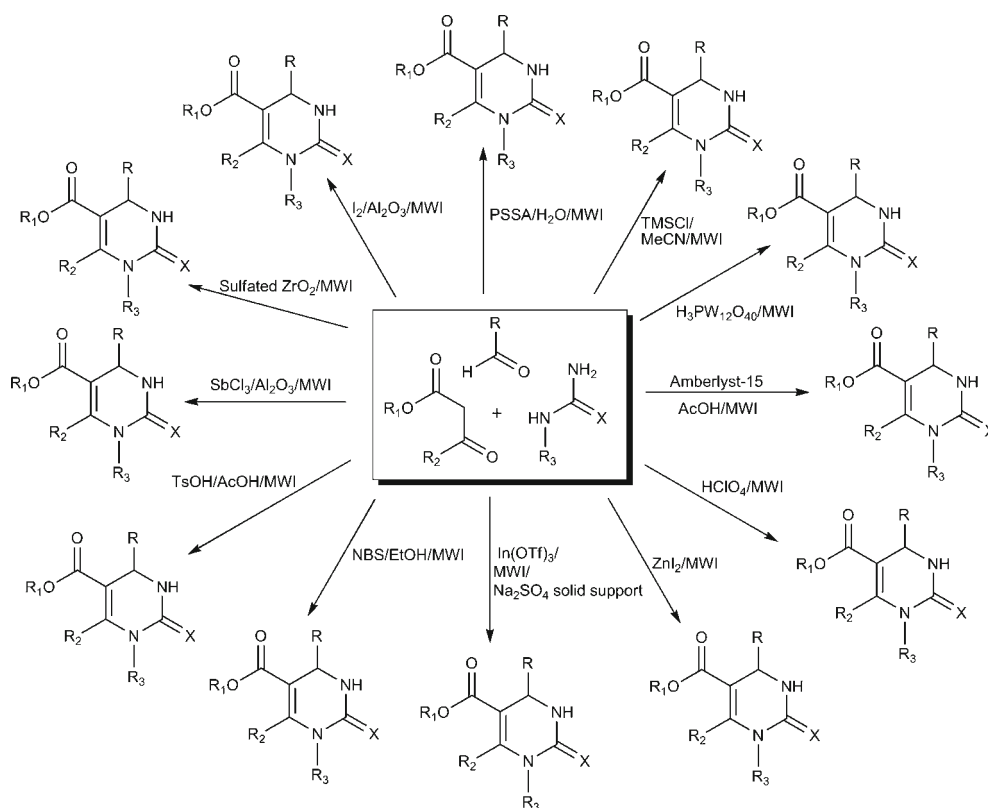
Research interest in 3,4-dihydropyrimidin-2-(1*H*)-ones ('Biginelli compounds', DHPMs), has surged rapidly, owing to the pharmacological properties<sup>1–5</sup> associated with many derivatives of this privileged heterocyclic core. The biological activity<sup>1</sup> of these Biginelli compounds has been found in the form of antiviral, antitumor, antibacterial and antiinflammatory properties. In addition to the medicinal applications, many functionalized DHPMs have emerged as potent calcium channel blockers,<sup>2</sup> antihypertensive agents,<sup>3</sup>  $\alpha_{1a}$ -adrenergic antagonists<sup>4</sup> and neuropeptide Y (NPY) antagonists.<sup>5</sup> Several recently isolated marine alkaloids<sup>6</sup> with interesting biological activities also contain the dihydropyrimidinone-5-carboxylate core. The best-known method for DHPMs is the classical Biginelli synthesis.<sup>7</sup> Although it has been known for more than a century, it is still the most useful method for the preparation of such a class of compounds. Since 1893, the synthesis of the DHPMs nucleus by the Biginelli reaction procedure has been extensively explored.<sup>8</sup> Many catalysts<sup>9</sup> have been reported for the synthesis of DHPMs, either by modification in classical Biginelli reaction or by development of novel multistep strategies. In addition, many catalysts such as amberlyst-15/AcOH,<sup>10</sup> HClO<sub>4</sub>,<sup>11</sup> H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>,<sup>12</sup> TMSCl/MeCN,<sup>13</sup> PSSA/H<sub>2</sub>O,<sup>14</sup> I<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>,<sup>15</sup> sulphated ZrO<sub>2</sub>,<sup>16</sup> SbCl<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>,<sup>17</sup> TsOH/AcOH,<sup>18</sup> NBS/EtOH,<sup>19</sup> In(OTf)<sub>3</sub><sup>20</sup>

and ZnI<sub>2</sub><sup>21</sup> were employed for reaction along with microwave irradiation (scheme 1). However, limitations such as use of toxic solvents, expensive catalyst, requirement of excess reagents/catalysts, laborious work up procedures, etc. restrict the practical synthetic utility of this chemistry.

The concept of speeding up synthetic transformations by microwave irradiation has been the focus of considerable attention in recent years and is becoming an increasingly popular technology.<sup>22</sup> Recently, popular trend in this area is to use ionic liquids or mixture of ionic liquids as reaction media in microwave animated transformation.<sup>23</sup> Likewise, the use of room-temperature ionic liquids (ILs) as green reaction media in organic transformation has gained considerable importance due to their solvating ability, negligible vapour pressure and easy recyclability.<sup>24</sup> Moreover, due to their high polarity and ionic nature, ionic liquids couple very effectively with microwaves through a dipolar polarization and ionic conduction mechanism<sup>25</sup> to push the reaction in forward direction very quickly.

The literature survey reveals that the potentiality of microwave/ionic liquid (MW/ILs) synergetic couple uniquely for the synthesis of Biginelli compounds has not been explored much. Therefore, it appeared to us that a MW/ILs strategy would be ideally suited for the synthesis of this privileged heterocycle. Proceeding in the same direction, we opted to evolve an efficient and eco-friendly process for the preparation of ionic liquid 1-carboxymethyl-3-methylimidazolium tetrafluoroborate [cmmim][BF<sub>4</sub>] via microwave irradiation.

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**Scheme 1.** Various catalysts employed for the synthesis of DHPMs under microwave irradiation.

We report here a microwave sponsored modified preparation of [cmmim][BF<sub>4</sub>] and disclose the successful outcome of MW/ILs strategy to synthesize 3,4-dihydropyrimidin-2-(1*H*)-ones heterocycle in excellent isolated yields. The IL could be recycled and successfully reused in at least six consequent runs. The process holds well without the need of additional catalyst.

## 2. Experimental

All chemicals were of research grade and were used as obtained from Sigma-Aldrich, Alfa-Aesar and SDFCL. The melting points were determined in capillary tubes using heavy paraffin liquid in Thiele tube. Melting points were uncorrected and were compared with the reported literature values. The reaction progress and purity of products were determined by TLC silica gel plates (Merck 60 F<sub>254</sub>). The reactions were performed in scientific microwave system (Catalyst system 'CATA-R', 700 W) using 25 mL round-bottomed flask. IR Spectra were recorded on a Shimadzu FT-IR 8400 spectrometer. Mass spectra were recorded on AB APPLIED BIOSYSTEMS IMDS SCIEX, API-2000 LC/MS/MS

instrument. <sup>1</sup>H NMR, <sup>13</sup>C NMR and DEPT-135 spectra were recorded on Bruker Avance 400 MHz spectrometer in CDCl<sub>3</sub>/DMSO-d<sub>6</sub> with TMS as the internal standard.

### 2.1 Synthesis of 1-carboxymethyl-3-methylimidazolium tetrafluoroborate [cmmim][BF<sub>4</sub>] under microwave irradiation

Synthesis of [cmmim][BF<sub>4</sub>] was reported by Gonghua Song *et al.* via conventional method.<sup>26</sup> We have successfully attempted the same under microwave irradiation in comparatively short duration. Aliquots of chloroacetic acid (1 equiv.) was added over a period of 60 min to 1-methyl-imidazole (1 equiv.) at room temperature under stirring, and then this set-up was irradiated in the MW oven 4 times at the 20% power level (140 W) and 4 times at the 30% power level (210 W) for 60 s with 2 min intermittent cooling period after each irradiation cycle. The solid thus obtained was washed with acetonitrile, and dried under vacuum. The intermediate, 1-carboxymethyl-3-methylimidazolium chloride was obtained as a white solid (mp, 172–174°C). The [cmmim][Cl] (1 equiv.) and NaBF<sub>4</sub> (1 equiv.) were dissolved in H<sub>2</sub>O and irradiated in the MW oven at

60% power level (420 W) for 10 min with intermittent cooling of 2 min after 5 min of irradiation. Water was removed from the reaction mixture by subjecting it to distillation for 4 h at 80°C under reduced pressure (10 mmHg) to give the product [cmmim][BF<sub>4</sub>] as a slight yellowish oil. Ionic liquid was characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. All the data were in good agreement with the reported one.

## 2.2 General procedure for the preparation of DHPMs

A mixture of aldehyde **1** (10 mmol), ethyl acetoacetate **2** (EAA, 10 mmol), urea (or thiourea) **3** (11 mmol) and [cmmim][BF<sub>4</sub>] (200 mg) was charged into a 25 mL round bottom flask. The mixture was stirred gently with a spatula for a few seconds and was subjected to microwave irradiation at 40% power level (CATA-R, 700 W) for appropriate time as shown in table 1. After completion of the reaction (as indicated by TLC) the

reaction mixture was poured onto crushed ice (~20 gm) and stirred well. The solid separated was washed with ice cold water and then recrystallized from hot ethanol or ethyl acetate to afford pure DHPMs, **4a–x**. The combined aqueous filtrate was subjected to vacuum at 80°C under reduced pressure (10 mmHg) for 4 h to leave behind the IL in near complete recovery, pure enough to recycle. The recovered ionic liquid was found to be equally effective for at least six cycles in the synthesis of **4a**.

## 2.3 Spectral data of some selected compounds

2.3a 5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (**4a**): IR (KBr) 3233, 2954, 1730, 1690, 1206, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 9.21 (s, 1H), 7.74 (s, 1H), 7.25 (m, 5H), 5.14 (s, 1H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR δ 13.9, 17.7, 53.9, 59.1, 99.2, 126.1, 127.1, 128.3, 144.7, 148.2, 152.0, 165.2. Calc. for

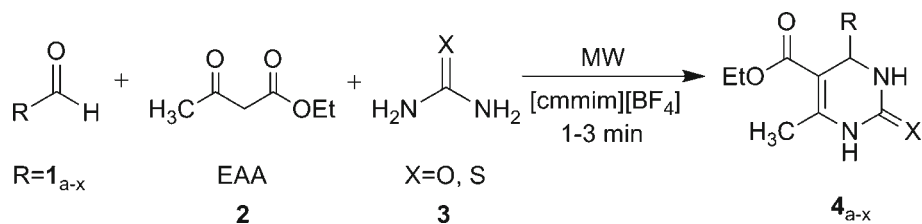
**Table 1.** Synthesis of DHPMs using various aldehydes with ethyl acetoacetate and urea/thiourea in [cmmim][BF<sub>4</sub>].

| Product   | R-  | X | Reaction time (min) <sup>a</sup> |     | % Yield <sup>b</sup> |    | Mp/°C observed (lit.)           |
|-----------|---|---|----------------------------------|-----|----------------------|----|---------------------------------|
|           |   |   | MW                               | Δ   | MW                   | Δ  |                                 |
| <b>4a</b> | Ph-   | O | 1.5                              | 90  | 97                   | 92 | 201–202 (202–204) <sup>28</sup> |
| <b>4b</b> | 4-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -        | O | 3.0                              | 240 | 96                   | 88 | 206–208 (207–209) <sup>29</sup> |
| <b>4c</b> | 4-F-C <sub>6</sub> H <sub>4</sub> -                       | O | 2.5                              | 180 | 93                   | 83 | 174–176 (175–176) <sup>31</sup> |
| <b>4d</b> | 3-Cl-C <sub>6</sub> H <sub>4</sub> -                      | O | 2.5                              | 150 | 96                   | 90 | 192–194 (193–195) <sup>28</sup> |
| <b>4e</b> | 4-H <sub>3</sub> C-C <sub>6</sub> H <sub>4</sub> -        | O | 1.5                              | 120 | 95                   | 89 | 214–215 (215–216) <sup>29</sup> |
| <b>4f</b> | 4-MeO-C <sub>6</sub> H <sub>4</sub> -                     | O | 1.5                              | 150 | 97                   | 86 | 200–202 (202–204) <sup>28</sup> |
| <b>4g</b> | 2-Furyl-  | O | 2.0                              | 90  | 92                   | 81 | 208–210 (209–211) <sup>28</sup> |
| <b>4h</b> | 2-Cl-C <sub>6</sub> H <sub>4</sub> -                      | O | 2.5                              | 90  | 97                   | 84 | 221–222 (222–224) <sup>28</sup> |
| <b>4i</b> | 4-HO-C <sub>6</sub> H <sub>4</sub> -                      | O | 1.5                              | 150 | 96                   | 88 | 228–230 (230–232) <sup>28</sup> |
| <b>4j</b> | 3,4,5-(MeO) <sub>3</sub> -C <sub>6</sub> H <sub>2</sub> - | O | 2.0                              | 180 | 94                   | 83 | 178–180 (180–182) <sup>30</sup> |
| <b>4k</b> | 4-HO,3-MeO-C <sub>6</sub> H <sub>3</sub> -                | O | 2.0                              | 150 | 95                   | 87 | 202–203 (204–205) <sup>30</sup> |
| <b>4l</b> | 2-Thienyl   | O | 2.0                              | 120 | 93                   | 81 | 214–216 (215–217) <sup>28</sup> |
| <b>4m</b> | 2-HO-C <sub>6</sub> H <sub>4</sub> -                      | O | 1.5                              | 90  | 91                   | 82 | 198–200 (200–202) <sup>30</sup> |
| <b>4n</b> | 2-Br-C <sub>6</sub> H <sub>4</sub> -                      | O | 2.0                              | 120 | 92                   | 86 | 206–208 (205–207) <sup>33</sup> |
| <b>4o</b> | 3-Br-C <sub>6</sub> H <sub>4</sub> -                      | O | 2.0                              | 150 | 94                   | 92 | 196–198 (196–197) <sup>33</sup> |
| <b>4p</b> | 2,5-(MeO) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> -   | O | 2.5                              | 150 | 96                   | 94 | 212–214 (212) <sup>35</sup>     |
| <b>4q</b> | 3,4-(MeO) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> -   | O | 3.0                              | 180 | 92                   | 89 | 174–176 (175–177) <sup>30</sup> |
| <b>4r</b> | 2-Pyridyl   | O | 1.5                              | 150 | 89                   | 81 | 212–214 (212–214) <sup>36</sup> |
| <b>4s</b> | 3-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -        | O | 2.0                              | 180 | 92                   | 82 | 228–230 (230–232) <sup>34</sup> |
| <b>4t</b> | 2-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -        | O | 2.5                              | 210 | 94                   | 80 | 208–210 (210) <sup>35</sup>     |
| <b>4u</b> | 4-Cl-C <sub>6</sub> H <sub>4</sub> -                      | O | 2.0                              | 180 | 95                   | 88 | 210–212 (212–213) <sup>30</sup> |
| <b>4v</b> | Ph-   | S | 2.5                              | 120 | 92                   | 86 | 207–208 (208–210) <sup>28</sup> |
| <b>4w</b> | 4-MeO-C <sub>6</sub> H <sub>4</sub> -                     | S | 3.0                              | 150 | 95                   | 84 | 150–151 (150–152) <sup>28</sup> |
| <b>4x</b> | 3,4,5-(MeO) <sub>3</sub> -C <sub>6</sub> H <sub>2</sub> - | S | 3.0                              | 270 | 91                   | 79 | 201–203 (202–204) <sup>32</sup> |

MW = Microwave irradiation (280 W); Δ = Conventional method (80°C)

<sup>a</sup>All the reactions were run till the completion as indicated by TLC

<sup>b</sup>yield after crystallization



**Scheme 2.** General reaction scheme for the synthesis of DHPMs.

$\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3$ : C, 64.60; H, 6.20; N, 10.76. Found: C, 64.61; H, 6.18; N, 10.74. MS: 261 (M+1).

**2.3b** *5-Ethoxycarbonyl-6-methyl-4-(4-fluorophenyl)-3,4-dihydropyrimidin-2(1H)-one (4c)*: IR (KBr) 3240, 2980, 1730, 1640, 1230, 1150, 790  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  9.25 (s, 1H), 7.77 (s, 1H), 7.21 (m, 4H), 5.15 (s, 1H), 3.99 (q,  $J = 7.1$  Hz, 2H), 2.26 (s, 3H), 1.09 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR  $\delta$  13.9, 17.8, 53.6, 59.5, 123.4, 127.5, 145.2, 149.3, 151.6, 152.1, 164.8. Calc. for  $\text{C}_{14}\text{H}_{15}\text{FN}_2\text{O}_3$ : C, 60.42; H, 5.43; N, 10.07. Found: C, 60.44; H, 5.42; N, 10.10.

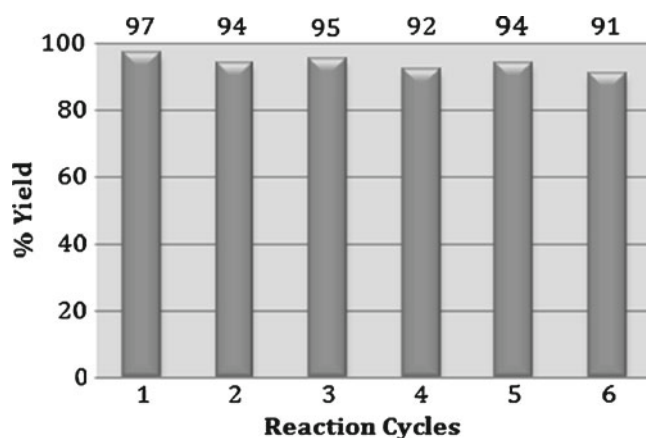
**2.3c** *5-Ethoxycarbonyl-6-methyl-4-(4-methoxyphenyl)-3,4-dihydropyrimidin-2(1H)-one (4f)*: IR (KBr) 3206, 2956, 1740, 1679, 1245, 1180, 1040, 875  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  9.14 (s, 1H), 7.66 (s, 1H), 6.99 (m, 4H), 5.07 (s, 1H), 3.96 (q,  $J = 6.8$  Hz, 2H), 3.70 (s, 3H), 2.23 (s, 3H), 1.09 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR  $\delta$  14.5, 18.2, 53.78, 55.47, 59.60, 99.9, 114.1, 127.8, 136.4, 148.3, 158.8, 165.8. Calc. for  $\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}_4$ : C, 62.06; H, 6.25; N, 9.65. Found: C, 62.04; H, 6.28; N, 9.67. MS: 291 (M+1).

**2.3d** *5-Ethoxycarbonyl-6-methyl-4-(3,4,5-trimethoxyphenyl)-3,4-dihydropyrimidin-2(1H)-thione (4x)*: IR (KBr) 3284, 2967, 1720, 1632, 1234, 1140, 780  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  10.21 (s, 1H), 9.49 (s, 1H), 7.29 (m, 2H), 5.02 (s, 1H), 6.40 (s, 2H), 3.94 (q,  $J = 6.6$  Hz, 2H), 3.57 (s, 9H), 2.13 (s, 3H), 1.04 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR  $\delta$  14.9, 17.7, 54.2, 56.1, 60.1, 60.4, 101.2, 103.5, 137.1, 139.4, 145.7, 153.3, 165.4, 174.5. Calc. for  $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_5\text{S}$ : C, 55.72; H, 6.05; N, 7.64. Found: C, 55.69; H, 6.03; N, 7.62.

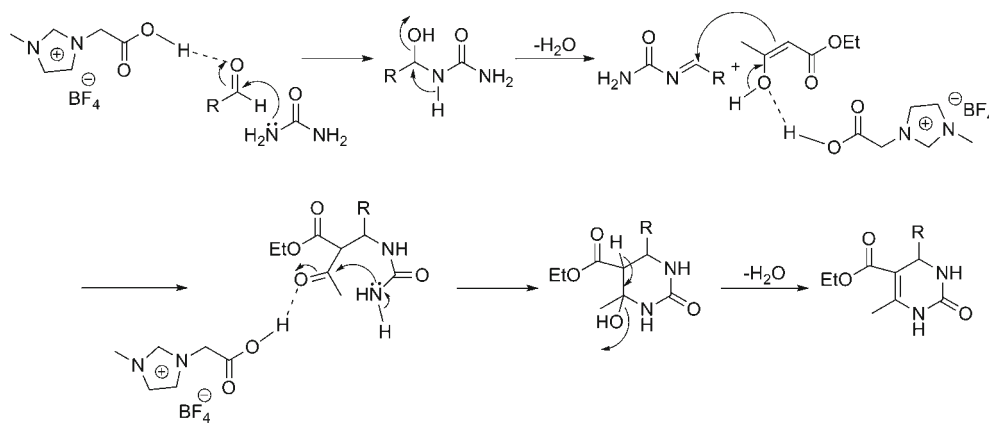
### 3. Results and discussion

A variety of aldehydes (1a-x) were chosen to be condensed with ethyl acetoacetate (2) and urea/thiourea (3) as shown in the scheme 2.

In order to carry out such transformation by eliminating the use of molecular solvent, we examined the influence of MW irradiation on a neat mixture of ethyl acetoacetate, benzaldehyde, urea and carboxy functionalized ionic liquid 1-carboxymethyl-3-methylimidazolium tetrafluoroborate [cmmim][BF<sub>4</sub>]. In order to investigate the proportion of IL, irradiation time and power level of MW set-up, we carried out series of experiments. From these experiments, we found an optimum set of conditions that afford DHPMs in excellent isolated yields. Evidently, this optimum condition employed aldehyde 1, ethyl acetoacetate 2 and urea (or thiourea) 3 in the ratio of 1.0:1.0:1.1 by using 200 mg [cmmim][BF<sub>4</sub>] as reaction promoter at power level 4 (280 W). Time taken for the completion of each conversion, aldehyde employed, isolated yields and melting points of products are summarized in table 1. The amount of IL does not appear to be critical as we have run successful experiments with 50–200 mg of IL per mmol of aldehyde. However, the presence of about 200 mg of IL ensures the homogeneity of the reaction mixture in particular when solid aldehydes were employed. All the reactions were monitored by TLC and taken to completion. All the compounds were well-characterized by melting points,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and DEPT-135 spectral data. Additional confor-



**Figure 1.** Recyclability of ionic liquid.



**Scheme 3.** Plausible mechanistic pathway.

mation of compounds was also achieved by IR and mass spectral studies. All the data were in agreement with the reported literature. All the aldehydes have reacted in short reaction times under MW irradiations to afford DHPMs in excellent isolated yields. MW/ILs induced protocol showed the ability to tolerate variations in aromatic aldehydes containing both electron donating and electron withdrawing substituents.

In a typical experiment, three reaction components along with IL were simply mixed in a 25 mL round bottom flask and irradiated under MW. After cooling, the products were easily isolated by dilution with water followed by filtration of precipitated DHPMs. The DHPMs, thus isolated were pure enough for all practical purposes. However, all the DHPMs were subjected to crystallization and the yields reported after purification step. The aqueous filtrate was subjected to vacuum at 80°C/10 mm Hg for 4 h to remove water and leave behind [cmmim][BF<sub>4</sub>] pure enough for the next run. The ionic liquid thus recycled was used at least six times for the microwave-induced reaction of **4a** with prominent retention in its activity. The obtained results are plotted in figure 1.

From the series of experiments, it was observed that the reaction did not proceed even after several minutes of irradiation in molecular solvents such as ethanol, ethyl acetate and acetonitrile instead of IL under similar MW set-up conditions. No formation of the desired heterocycle was observed when reaction was carried out under simple stirring at 30°C. For the comparison purpose, the reactions were also carried out in the presence of the same amount of the [cmmim][BF<sub>4</sub>] in an oil bath at 80°C. The results are summarized in table 1. It is clear that the reactions under microwave irradiation led to relatively high yields in shorter reaction time. From this experimental evidence, it can be stated that it is the synergetic effect of MW/ILs couple that has promoted this transformation in absence of any added catalyst.

IL promotes the reactions due to its inherent Brønsted acidity. Hydrogen bonding is formed between carboxylic proton of IL and carbonyl oxygen of aldehyde as well as ethyl acetoacetate during the reaction. The formation of hydrogen bond between IL and substrate leads them to the activation.<sup>27</sup> Based on this, the plausible mechanistic pathway for this reaction is suggested (scheme 3).

#### 4. Conclusion

The combined effect of microwave-ionic liquid couple provides an easy and green route to synthesize DHPMs via Biginelli reaction. The milder reaction conditions, absence of additional catalyst, high reaction rates, excellent yields, easy work up procedures and MW-IL strategy make this procedure an attractive alternative to the conventional acid/base catalysed thermal processes and is environment friendly with minimal or no waste.

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