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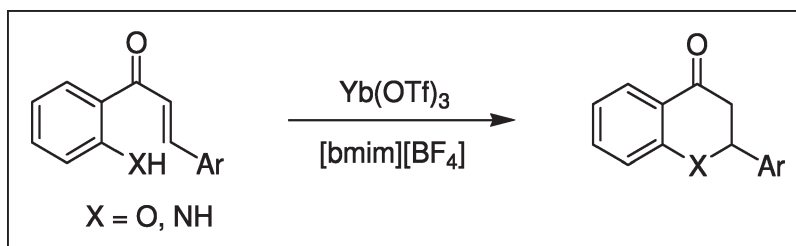
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Isomerization of 2'-hydroxychalcone and 2'-aminochalcone have been investigated using ytterbium(III) trifluoromethanesulfonate {Yb(OTf)<sub>3</sub>} (30 mol %) as Lewis acid catalyst in [bmim][BF<sub>4</sub>] ionic liquid. The effect of different metal triflates as Lewis acid, catalyst loading and reaction media was studied for this isomerization reaction. Advantages of the methodology include short reaction time, excellent yields, catalytic use of Lewis acid, and recovery and reuse of the catalyst.

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## INTRODUCTION

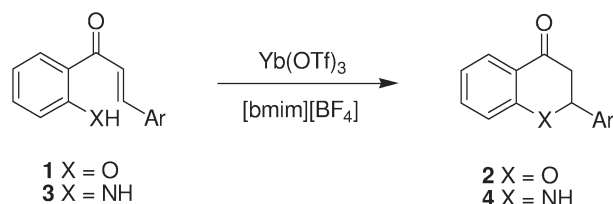
Isomerization of 2'-hydroxychalcones and 2'-aminochalcones affords biologically important heterocyclic compound flavonones and quinolinones, respectively. Because of the presence of these moieties in various natural products of diverse biological importance [1,2], this process has received great attention. This isomerization have been achieved using orthophosphoric acid [3], sulfuric acid [4], zeolites [5], silica gel [6,7], silica-supported reagents [8–10], base catalysts [11–14], PEG-400 [15], microwave irradiation [16,17], and chiral Brønsted acids and bases [18]. Isomerization of 2'-hydroxychalcones into flavonone is never complete; the reaction is very slow and generally proceeds with only moderate yields. In addition to low yield, majority of these methods are associated with certain limitations such as long reaction time or requirement of high energy source, use of halogenated solvents and toxic agents, unwanted side reaction, expensive catalyst, moisture sensitivity of the catalyst, and tedious reaction work up. Thus, mild, simple, nonpolluting, and more efficient methods are still desirable for the isomerization of 2'-hydroxychalcones and 2'-aminochalcones.

Lanthanide triflates are unique Lewis acids, and they have been extensively used to effectively promote several carbon–carbon and carbon–heteroatom bond formation reactions due to their efficacy and their low environmental impact [19–25]. Ytterbium triflate is probably one of the most exploited lanthanide triflate for a variety

of such organic transformations [26–29]. In view of environment friendly methodologies, recovery and recycling of the catalyst is highly desirable. In this regard, neoteric solvents, such as ionic liquids, have played an important role [30–33]. Lanthanide triflates immobilized in ionic liquids have been used as efficient and recyclable catalysts for various organic reactions [34]. In continuation of our efforts toward development of greener and efficient reaction methodologies using Yb(OTf)<sub>3</sub> [35–36], and ionic liquids [37–39], we decided to investigate the use of Yb(OTf)<sub>3</sub> as a catalyst for isomerization of 2'-hydroxychalcones and 2'-aminochalcones in ionic liquid (Scheme 1).

## RESULT AND DISCUSSION

In a first set of experiment, isomerization was carried out with different Lewis acids as catalyst in ionic liquid [bmim][BF<sub>4</sub>] using 2'-hydroxychalcone (**1a**) as a model substrate (Table 1). The ionic liquid [bmim][BF<sub>4</sub>] was chosen as solvent for this reaction, as it has been found that [bmim][BF<sub>4</sub>] itself acts as a catalyst for isomerization of 2'-hydroxychalcones and 2'-aminochalcones under microwave irradiation [17]. Among the catalysts screened, Ce(OTf)<sub>3</sub>, Yb(OTf)<sub>3</sub>, In(OTf)<sub>3</sub>, Zn(OTf)<sub>2</sub>, and *p*TSA were found to give good to excellent yield of **2a** (Table 1, entry 4, 8–10, and 14), and Yb(OTf)<sub>3</sub> gave the highest yield of **2a** under these conditions and, thus, was selected as choice of catalyst. The structure of **2a**

**Scheme 1.** Isomerization of 2'-hydroxychalcones and 2'-aminochalcones.

was confirmed by spectroscopic data. In IR spectra, a broad peak for hydroxyl group at  $2995 \text{ cm}^{-1}$  disappeared along with a shift of carbonyl peak from  $1660$  to  $1697 \text{ cm}^{-1}$ , double doublets at  $\delta$  5.43, 3.11, and 2.86 each for a single proton appeared along with other protons in  $^1\text{H}$  NMR spectra, and two peaks for  $m/z$  258.9804  $[\text{M} + \text{H}]^+$ , 280.9562  $[\text{M} + \text{Na}]^+$  were observed in HRMS spectra.

Next, we optimized the catalysts quantity using different amount of catalyst and found that increasing the catalyst loading beyond 30 mol % did not lead to an improved results (Table 1, entry 1–6). It is worthy to mention that use of  $\text{Yb}(\text{OTf})_3$  as Lewis acid in  $[\text{bmim}][\text{BF}_4]$  has dramatically increased the yield of **2a** when compared with that in only  $[\text{bmim}][\text{BF}_4]$  (Table 1, entry 1 and 4).

To demonstrate the advantage of the reaction in ionic liquid  $[\text{bmim}][\text{BF}_4]$ , isomerization of **1a** catalyzed by  $\text{Yb}(\text{OTf})_3$  was investigated in different organic solvents, ionic liquids, and water. Interestingly, the best yield was observed in ionic liquid  $[\text{bmim}][\text{BF}_4]$  at  $130^\circ\text{C}$ . When shifting the solvent to acetonitrile, water, THF, DCM, or toluene, only small amount or a trace of desired product

**Table 1**  
Yields of **2a** by different catalysts in  $[\text{bmim}][\text{BF}_4]$ .

Sr. No.	Catalysts	Catalyst (mol %)	Time (h)	Yield (%) <sup>a</sup>
1	–	–	12	38 <sup>b</sup>
2	$\text{Yb}(\text{OTf})_3$	10	4	61
3	$\text{Yb}(\text{OTf})_3$	20	4	73
4	$\text{Yb}(\text{OTf})_3$	30	4	86
5	$\text{Yb}(\text{OTf})_3$	40	4	79
6	$\text{Yb}(\text{OTf})_3$	50	4	63
7	$\text{Sc}(\text{OTf})_3$	30	4	53
8	$\text{Zn}(\text{OTf})_2$	30	4	58
9	$\text{Ce}(\text{OTf})_3$	30	4	76
10	$\text{Y}(\text{OTf})_3$	30	4	55
11	$\text{Ba}(\text{OTf})_2$	30	4	52
12	$\text{In}(\text{OTf})_3$	30	4	66
13	$\text{Er}(\text{OTf})_3$	30	4	54
14	PTSA	30	4	64
15	$\text{MgO}$	30	4	57

<sup>a</sup> Isolated yields.<sup>b</sup> 1-Phenyl-3-(4'-chlorophenyl)propenone (**1a**) gave **2a** in 49% yield in  $[\text{bmim}][\text{BF}_4]$  under MW irradiation after 1.5 min.[17]**Table 2**Comparison yield of **2a** in different solvents catalyzed by  $\text{Yb}(\text{OTf})_3$  (30 mol %).

Entries	Solvents	Temperature ( $^\circ\text{C}$ )	Yield (%) <sup>a</sup>
1	Acetonitrile	Reflux	10
2	$\text{H}_2\text{O}$	100	– <sup>b</sup>
3	THF	Reflux	– <sup>b</sup>
4	DCM	Reflux	– <sup>b</sup>
5	Toluene	Reflux	– <sup>b</sup>
6	DMSO	130	79
7	$[\text{bmim}][\text{BF}_4]$	130	86
8	$[\text{bmim}][\text{PF}_6]$	130	61
9	$[\text{bmim}][\text{Br}]$	130	45

<sup>a</sup> Isolated yield.<sup>b</sup> Trace of product formation was observed.

was detected (Table 2, entries 1–5), and reactions remained incomplete even after heating at higher temperature for long time. Moderate to good yield were observed in DMSO and ionic liquid  $[\text{bmim}][\text{Br}]$  and  $[\text{bmim}][\text{PF}_6]$  (Table 2, entries 6–8). Significant solvent effect was observed in our investigation with solvent screen, and, thus, ionic liquid  $[\text{bmim}][\text{BF}_4]$  was selected as the solvent of choice for continuing this isomerization study.

To examine the scope and generality of isomerization, different 2'-hydroxychalcones substituted with electron-donating or electron-withdrawing groups were used as the reaction substrates (Table 3). The substrates with electron-donating substituent in the aldehydic aromatic group afforded the corresponding cyclic products (flavonones) in excellent yields, whereas substrates with electron-withdrawing substituent in the aldehydic aromatic group resulted in poor yield of cyclized product. For instance, **1d** required only 4 h to give **2d** in 81% yield, whereas **1h** did not give desired product (**2h**) even after heating at  $160^\circ\text{C}$  for 12 h. This perhaps is due to reversal of polarity of  $\beta$ -carbon in case of **1h** by electron-withdrawing substituent in the aromatic ring of aldehydic aryl group.

Having ascertained the efficacy of  $\text{Yb}(\text{OTf})_3$  catalyzed isomerization of 2'-hydroxychalcones in  $[\text{bmim}][\text{BF}_4]$ , this methodology was extended to isomerization of 2'-aminochalcones (**3a**) to give cyclized product (**4a**) in 92% yield. The structure of **4a** was characterized by mass,  $^1\text{H}$  NMR, and IR spectroscopic data. Peaks at  $m/z$  257.9977 and 279.9736 in HRMS for  $[\text{M} + \text{H}]^+$  and  $[\text{M} + \text{Na}]^+$  ions, double doublets at  $\delta$  4.73, 2.83, and 2.74 ppm in  $^1\text{H}$  NMR along with other protons, and a shift in IR from 1643 and 3333 and  $3456 \text{ cm}^{-1}$  to 1651 and  $3302 \text{ cm}^{-1}$ , respectively, confirmed the structure of **4a**. Encouraged with the excellent result for isomerization of **3a**, we performed reaction of different 2'-aminochalcones (**3b–g**) under similar conditions, and the results are summarized in Table 4. The influence of field effect of substituent in the aromatic ring of aldehydic aryl

**Table 3**  
Isomerization of 2'-hydroxychalcones.

Sr. No.	Substrate (1)	Ar	Product (2) <sup>a</sup>	Time (h)	Yield (%) <sup>b</sup>
1	<b>1a</b>	4-ClPh	<b>2a</b>	4	86
2	<b>1b</b>	Ph	<b>2b</b>	4	79 <sup>c</sup>
3	<b>1c</b>	3-ClPh	<b>2c</b>	4	80
4	<b>1d</b>	4-CH <sub>3</sub> OPh	<b>2d</b>	4	81
5	<b>1e</b>	4-CH <sub>3</sub> Ph	<b>2e</b>	4	78
6	<b>1f</b>	3-NO <sub>2</sub> Ph	<b>2f</b>	6	20 <sup>d</sup>
7	<b>1g</b>	2-Furyl	<b>2g</b>	4	74
8	<b>1h</b>	4-NO <sub>2</sub> Ph	<b>2h</b>	12	— <sup>e</sup>

<sup>a</sup> All the products gave satisfactory <sup>1</sup>H NMR and mass data.

<sup>b</sup> Isolated yield.

<sup>c</sup> Yield of **2b** was 86, 82, 79, 74, 76 and 73% in six successive runs, respectively.

<sup>d</sup> Yield at 160°C, almost quantitatively reactant was recovered at 80°C.

<sup>e</sup> No product was observed even at 160°C.

group was similar to that in case of 2'-hydroxychalcones (Table 4, entries 3–6). It was also observed that the isomerization for 2'-aminochalcone was faster when compared with 2'-hydroxychalcones. The higher reactivity of 2'-aminochalcones relative to 2'-hydroxychalcones could be rationalized based on differential nucleophilicity of amino group versus hydroxyl group and differences in the activation energy ( $E_{act}$ ) for the cyclization, which is 57 Kcal/mole for 2'-aminochalcones when compared with 117.886 Kcal/mole for 2'-hydroxychalcones [17].

Finally, recycling of the catalysts was studied using **1b** as model substrate and found that recycled Yb(OTf)<sub>3</sub> in [bmim][BF<sub>4</sub>] showed good catalytic activity yielding **2b** in 86, 82, 79, 74, 76, and 73% yield in six successive runs, respectively.

The mechanism of the isomerization reaction seems to be similar to the Lewis acid-catalyzed nucleophilic addition to  $\alpha,\beta$ -unsaturated ketones. A plausible mechanism is shown in Scheme 2. The higher rate of reaction is probably due to the higher acidity of Yb(OTf)<sub>3</sub> compared to other lanthanide triflates and ability of ionic liquid to stabilize the formation of charged species by coordination of Yb(OTf)<sub>3</sub> with carbonyl oxygen. It is expected that this coordination of Yb(OTf)<sub>3</sub> activates the nucleophilic attack at  $\beta$ -carbon by inducing electro-

philic character at this carbon, and it also allows rotation through the O=C—C $\alpha$  bond to give *trans-s-trans* conformations required for cyclization from its original *trans-s-cis* conformations [40] by disrupting intramolecular hydrogen bonding.

## CONCLUSIONS

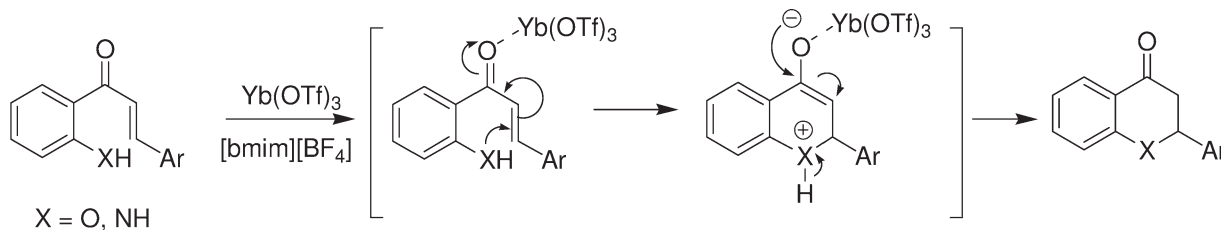
In summary, we have developed a simple, economical, and more efficient method for isomerization of 2'-hydroxychalcones and 2'-aminochalcones using Yb(OTf)<sub>3</sub> (30 mol %) as catalyst in ionic liquid. Apart from the efficient and environmentally benign reaction conditions, excellent yield, and short reaction time, possibility to recycle Yb(OTf)<sub>3</sub>/[bmim][BF<sub>4</sub>] system offers significant advantage for this process. Synthetic applications of the reaction and insight into its detailed mechanism are currently in progress.

## EXPERIMENTAL

Ytterbium triflate was purchased from Sigma–Aldrich. All commercial reagents and solvents were used without further purification unless otherwise specified. NMR spectra were recorded on a Bruker Heaven Avance 11 400 spectrophotometer using TMS as internal standard and CDCl<sub>3</sub> as solvent, and the chemical shifts were expressed in ppm. The IR spectra were recorded using KBr pellets on Shimadzu Prestige-21 FTIR spectrophotometer, and  $\nu_{max}$  was expressed in cm<sup>-1</sup>. Mass spectra were recorded on a QSTAR<sup>®</sup> ELITE LX/MS/MS mass spectrometer from applied biosystem. The purity of the products was determined on silica-coated aluminum plates (Merck). 2'-Hydroxychalcone and 2'-aminochalcones were prepared using the appropriate aldehyde and the corresponding *ortho*-substituted acetophenones [41]. The ionic liquid, [bmim][BF<sub>4</sub>], was prepared from 1-methylimidazole by minor modification of literature procedure [42].

**General procedure for the isomerization.** To a mixture of 2'-hydroxychalcone/2'-aminochalcone (0.712 mmol) and ionic liquid [bmim][BF<sub>4</sub>] (2 mL) was added Yb(OTf)<sub>3</sub> (81 mg, 30 mol %). The whole reaction mass was stirred at 130°C. The reaction progress was followed by TLC (hexanes/AcOEt 8:2). After stirring the reaction mixture for appropriate time as mentioned in Tables 3 and 4, diethyl ether (10 mL) was added, and the organic layer was separated. The solvent was dried with anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was percolated through a band of

**Scheme 2.** A plausible mechanism for isomerization of 2'-hydroxychalcones and 2'-aminochalcones.



**Table 4**  
Isomerization of 2'-aminochalcones.

Sr. No.	Substrate (I)	Ar	Product (2) <sup>a</sup>	Time (Min)	Yield (%) <sup>a</sup>
1	<b>1a</b>	4-CIPh	<b>4a</b>	5	92
2	<b>1b</b>	Ph	<b>4b</b>	5	85
3	<b>1c</b>	4-CH <sub>3</sub> Ph	<b>4c</b>	5	93
4	<b>1d</b>	2,4-(CH <sub>3</sub> O) <sub>2</sub> Ph	<b>4d</b>	5	94
5	<b>1e</b>	3-NO <sub>2</sub> Ph	<b>4e</b>	30	70
6	<b>1f</b>	4-NO <sub>2</sub> Ph	<b>4f</b>	360	60 <sup>c</sup>
7	<b>1g</b>	2-Furyl	<b>4g</b>	10	89

<sup>a</sup> All the products gave satisfactory <sup>1</sup>H NMR and mass data.

<sup>b</sup> Isolated yield.

<sup>c</sup> Yield at 160°C.

silica gel (60–120) using hexane/AcOEt (9:1 v/v) as an eluent to afford corresponding compounds in 20–94% yield.

**2-(4'-Chlorophenyl)-2,3-dihydro-4H-chromen-4-one (2a).** Colorless solid, mp 95–97°C. IR (KBr) cm<sup>-1</sup>: 1697 (C=O), 1300, 1221. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.92 (dd, *J* = 7.60, 1.60 Hz, 1H), 7.51 (dt, *J* = 7.60, 1.60 Hz, 1H), 7.41–7.39 (m, 4H), 7.08–7.04 (m, 2H), 5.46 (dd, *J* = 2.80, 13.20 Hz, 1H), 3.04 (dd, *J* = 13.20, 16.80 Hz, 1H), 2.88 (dd, *J* = 2.80, 16.80 Hz, 1H). HRMS: *m/z* Calcd. for C<sub>15</sub>H<sub>11</sub>ClO<sub>2</sub>: 258.0448 [M<sup>+</sup>], found: 258.9804 [M + H]<sup>+</sup>, 280.9562 [M + Na]<sup>+</sup>.

**2-Phenyl-2,3-dihydro-4H-chromen-4-one (2b).** White solid, mp 75–77°C. IR (KBr) cm<sup>-1</sup>: 1692, 1310, 1218 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.91 (dd, *J* = 8.00, 2.80 Hz, 1H), 7.47–7.36 (m, 6H), 7.05–7.04 (m, 2H), 5.48 (d, *J* = 13.60 Hz, 1H), 3.11–3.03 (m, 1H), 2.88 (dd, *J* = 4.40, 16.80 Hz, 1H). HRMS: *m/z* Calcd. for C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>: 224.0837, found 225.0308 [M + H]<sup>+</sup>, 247.0061 [M + Na]<sup>+</sup>.

**2-(3'-Chlorophenyl)-2,3-dihydro-4H-chromen-4-one (2c).** Pale white solid, mp 97–99°C. IR (KBr) cm<sup>-1</sup>: 1694 (C=O) 1302, 1220 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.93 (d, *J* = 6.80 Hz, 1H), 7.51 (m, 2H), 7.35 (m, 3H), 7.06 (d, *J* = 7.60 Hz, 2H), 5.45 (dd, *J* = 2.80, 13.20 Hz, 1H), 3.03 (dd, *J* = 13.60 Hz, *J* = 16.80 Hz, 1H), 2.88 (dd, *J* = 2.80, 16.80 Hz, 1H). HRMS: *m/z* Calcd. for C<sub>15</sub>H<sub>11</sub>ClO<sub>2</sub>: 258.0448, found 258.9804, 280.9552 [M + Na]<sup>+</sup>.

**2-(4'-Methoxyphenyl)-2,3-dihydro-4H-chromen-4-one (2d).** White solid, mp 88–89°C. IR (KBr) cm<sup>-1</sup>: 1689 (C=O), 1311, 1222 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.93 (d, *J* = 6.4 Hz, 1H), 7.48 (d, *J* = 6.8 Hz, 1H), 7.41 (d, *J* = 6.40 Hz, 2H), 7.04–7.02 (m, 2H), 6.96 (d, *J* = 6.40 Hz, 2H), 5.41 (d, *J* = 11.20 Hz, 1H), 3.82 (s, 3H), 3.13–3.10 (m, 1H), 2.87–2.83 (m, 1H). HRMS: *m/z* Calcd. for C<sub>16</sub>H<sub>14</sub>O<sub>3</sub>: 254.0942, found 255.0326 [M + H]<sup>+</sup>, 277.0081 [M + Na]<sup>+</sup>.

**2-(*p*-Tolyl)-2,3-dihydro-4H-chromen-4-one (2e).** Pale white solid, mp 82–84°C. IR (KBr) cm<sup>-1</sup>: 1683, 1325, 1220 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.92 (d, *J* = 6.40 Hz, 1H), 7.49 (m, 1H), 7.37 (d, *J* = 5.60 Hz, 2H), 7.24 (d, *J* = 5.60 Hz, 2H), 7.04 (m, 2H), 5.44 (d, *J* = 9.2 Hz, 1H), 3.12–3.08 (m, 1H), 2.88–2.84 (m, 1H), 2.37 (s, 3H). HRMS: *m/z* Calcd. for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>: 238.0993, found 239.0426 [M + H]<sup>+</sup>, 261.0186 [M + Na]<sup>+</sup>.

**2,3-Dihydro-2-(3-nitrophenyl)chromen-4-one (2f).** Pale yellow solid, mp 101–103°C. IR (KBr) cm<sup>-1</sup>: 1681 (C=O), 1547, 1327, 1223 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ =

8.21 (s, 1H), 8.16 (m, 1H), 7.97–7.70 (m, 2H), 7.06–7.00 (m, 2H), 6.45 (s, 1H), 6.39 (s, 1H), 5.53 (dd, *J* = 3.63, 11.45 Hz, 1H), 3.25 (m, 1H), 2.97 (m, 1H). *m/z* (ESI-MS) Calcd. for C<sub>15</sub>H<sub>11</sub>NO<sub>4</sub>: 269.0688, found 270.0017 [M + H]<sup>+</sup>.

**2-(Furan-2'-yl)-2,3-dihydro-4H-chromen-4-one (2g).** White solid, mp 78–79°C. IR (KBr) cm<sup>-1</sup>: 1680 (C=O), 1315, 1223 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.91 (dd, *J* = 7.60, 2.40 Hz, 1H), 7.50–7.46 (m, 2H), 7.06–7.00 (m, 2H), 6.45 (s, 1H), 6.39 (s, 1H), 5.53 (dd, *J* = 3.60, 11.60 Hz, 1H), 3.26 (m, 1H), 2.98 (m, 1H). HRMS: *m/z* Calcd. for C<sub>13</sub>H<sub>10</sub>O<sub>3</sub>: 214.0629, found 215.0155 [M + H]<sup>+</sup>.

**2-(4'-Chlorophenyl)-2,3-dihydro-4(1H)-quinolinone (4a).** Pale yellow solid, mp 168–170°C. IR (KBr) cm<sup>-1</sup>: 3302 (NH), 1651 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.85 (d, *J* = 7.60 Hz, 1H), 7.41–7.32 (m, 5H), 6.79 (dd, *J* = 7.20, 7.24 Hz, 1H), 6.72 (d, *J* = 8.40 Hz, 1H), 4.73 (dd, *J* = 4.16, 13.20 Hz, 1H), 4.52 (brs, 1H), 2.83 (dd, *J* = 13.20, 16.20 Hz, 1H), 2.74 (dd, *J* = 4.16, 16.20 Hz, 1H). HRMS: *m/z* Calcd. for C<sub>15</sub>H<sub>12</sub>ClNO: 257.0607, found 257.9585 [M + H]<sup>+</sup>.

**2-Phenyl-2,3-dihydro-4(1H)-quinolinone (4b).** Pale yellow solid, mp 150–151°C. IR (KBr) cm<sup>-1</sup>: 3325 (NH), 1648 cm<sup>-1</sup>(C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.87 (d, *J* = 7.66 Hz, 1H), 7.47–7.32 (m, 6H), 6.80 (dd, *J* = 7.64, 7.23 Hz, 1H), 6.71 (d, *J* = 8.41 Hz, 1H), 4.76 (dd, *J* = 4.00, 13.62 Hz, 1H), 4.52 (brs, 1H), 2.88 (dd, *J* = 13.62, 16.41 Hz, 1H), 2.77 (dd, *J* = 3.98, 16.42 Hz, 1H). HRMS: *m/z* Calcd. for C<sub>15</sub>H<sub>13</sub>NO: 223.0997, found 224.0154 [M + H]<sup>+</sup>.

**2-(*p*-Tolyl)-2,3-dihydro-4(1H)-quinolinone (4c).** Pale yellow solid, mp 149–150°C. IR (KBr) cm<sup>-1</sup>: 3350 (NH), 1649 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.85 (d, *J* = 8.00 Hz, 1H), 7.34–7.19 (m, 5H), 6.79–6.75 (m, 1H), 6.70 (d, *J* = 8.00 Hz, 1H), 4.69 (dd, *J* = 3.40, 13.60 Hz, 1H), 4.57 (brs, 1H), 2.85 (dd, *J* = 13.80, 16.20 Hz, 1H), 2.72 (dd, *J* = 2.40, 16.4 Hz, 1H), 2.36 (s, 3H). HRMS: *m/z* Calcd. For C<sub>16</sub>H<sub>15</sub>NO: 237.1153, found 238.0259 [M + H]<sup>+</sup>.

**2-(2',4'-Dimethoxyphenyl)-2,3-dihydro-4(1H)-quinolinone (4d).** Pale yellow solid, mp 117–118°C. IR (KBr) cm<sup>-1</sup>: 3326 (NH), 1649 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.85 (d, *J* = 7.78 Hz, 1H), 7.11 (d, *J* = 7.64, 1H), 6.79–6.75 (m, 1H), 6.73 (d, *J* = 7.64, 1H), 6.70 (d, *J* = 7.76 Hz, 1H), 6.63 (s, 1H), 4.69 (dd, *J* = 3.46, 13.60 Hz, 1H), 4.54 (brs, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 2.88 (dd, *J* = 13.80, 16.44 Hz, 1H), 2.72 (dd, *J* = 3.46, 16.44 Hz, 1H). HRMS: *m/z* Calcd. for C<sub>17</sub>H<sub>17</sub>NO<sub>3</sub>: 283.1208, found 284.0089 [M + H]<sup>+</sup>, 305.9772 [M + Na]<sup>+</sup>.

**2-(3'-Nitrophenyl)-2,3-dihydro-4(1H)-quinolinone (4e).** Pale yellow solid, mp 159–160°C. IR (KBr) cm<sup>-1</sup>: 3351 (NH), 1653 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.37 (s, 1H), 8.20 (td, *J* = 8.20, 1.32, 1H), 7.97 (d, *J* = 7.64 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.36 (td, *J* = 8.32, 1.56 Hz, 1H), 7.27 (s, 1H), 6.91 (d, *J* = 8.32 Hz, 1H), 6.68 (t, *J* = 7.80 Hz, 1H), 4.97 (dd, *J* = 4.24, 11.52 Hz, 1H), 2.90 (dd, *J* = 11.80, 16.08 Hz, 1H), 2.77 (dd, *J* = 4.32, 16.08 Hz, 1H). HRMS: *m/z* Calcd. for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>: 268.0847, found 269.0281 [M + H]<sup>+</sup>, 290.0031 [M + Na]<sup>+</sup>.

**2-(4'-Nitrophenyl)-2,3-dihydro-4(1H)-quinolinone (4f).** Orange solid, mp 199–200°C. IR (KBr) cm<sup>-1</sup>: 3338 (NH), 1649 (C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.26 (d, *J* = 8.64 Hz, 1H), 7.77 (d, *J* = 8.64 Hz, 1H), 7.60 (d, *J* = 7.88 Hz, 1H), 7.35 (td, *J* = 7.62, 1.24 Hz, 1H), 7.28 (s, 1H), 6.90 (d, *J* = 8.32 Hz, 1H), 6.67 (t, *J* = 7.64 Hz, 1H), 4.96 (dd, *J* =



4.72, 10.88 Hz, 1H), 2.87–2.74 (m, 2H). HRMS:  $m/z$  Calcd. for  $C_{15}H_{12}N_2O_3$  268.0847, found 269.0282  $[M + H]^+$ , 290.0029  $[M + Na]^+$ .

**2-(Furan-2'-yl)-2,3-dihydro-4(1H)-quinolinone (4g).** Viscous liquid. IR (KBr)  $cm^{-1}$ : 3331 (NH), 1658 (C=O)  $cm^{-1}$ .  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  = 7.85 (d,  $J$  = 8.00 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). HRMS:  $m/z$  calcd. for  $C_{13}H_{11}NO_2$  213.0789, found 214.0136  $[M + H]^+$ , 235.0146  $[M + Na]^+$ .

**General procedure for recovery and reuse of catalyst.** After extracting the product using diethyl ether, the ionic liquid layer containing  $Yb(OTf)_3$  was dried under vacuum. The flask containing recovered  $Yb(OTf)_3$  in ionic liquid was again charged with **2b** (185 mg, 0.712 mmol), and the same procedure was repeated as given in general procedure for isomerization.

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