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## ARTICLE TYPE

Greener Approach for the Synthesis of Substituted Alkenes by Direct Coupling of Alcohols with Styrenes using Recyclable Bronsted Acidic [NMP]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> Ionic Liquid

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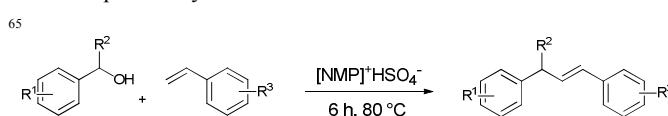
A novel protocol for the synthesis of substituted alkenes from alcohols and styrenes using ionic liquid has been developed. The ionic liquid *N*-methyl-2-pyrrolidone hydrogensulfate [NMP]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> acts as a catalyst as well as solvent. The developed protocol has higher atom efficiency and wider substrate applicability. The catalyst was effectively recycled up to five consecutive cycles.

Carbon-carbon bond formation reactions are the most useful methodology for the synthesis of natural products, bioactive molecules and agrochemicals.<sup>1</sup> Traditionally, various protocols for C-C bond formation were developed by using different coupling reactions like Stille, Negishi, Hiyama and Heck coupling.<sup>2</sup> Although, these protocols were efficient for the C-C bond formation reactions but, they suffer from one or more drawbacks such as use of transition metals, formation of stoichiometric amounts of salts, multistep reactions, requires functionalized starting materials, less atom efficiency and produces toxic waste materials. Hence, environmentally benign, efficient protocol for the C-C bond formation is highly desirable. The alternative protocol for the formation of C-C bond involves the direct coupling of alcohols with alkenes producing only water as green by product.<sup>3</sup> In this regard, significant progress have been made for the coupling of alcohols with alkenes by using various catalytic system such as H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>,<sup>4</sup> Pd,<sup>5</sup> Fe,<sup>6</sup> TfOH,<sup>7</sup> NaHSO<sub>4</sub>/SiO<sub>2</sub>.<sup>8</sup> However, these protocols requires use of transition metals, organic solvents, stoichiometric amount of (CF<sub>3</sub>CO)<sub>2</sub>O, TsOH, lower selectivity and provides less yield of desired products. Thus, the development of highly efficient and environmentally benign solvent free protocol for the direct coupling of alcohols with alkenes is still desired.

Recently, different coupling reactions were performed under more greener and recyclable reaction media such as ionic liquid, glycerol, PEG.<sup>9</sup> Ionic liquids (ILs) have attracted considerable attention as an environmentally benign alternative for various

coupling reactions because of its various attractive physicochemical properties such as low vapor pressure, non-volatility, non-flammability and thermal stability over a wide temperature range.<sup>10</sup> In addition, ionic liquids plays an important role such as catalysts and reagents. Ionic liquids also emerged as a media which have special interactions with the active species and make the possibility of enhancing the reaction activity with selectivity.<sup>11</sup>

Thus, in continuation of our interest in application of ionic liquids for several organic transformations.<sup>12</sup> Here, we have developed a novel, highly efficient, solvent free protocol for the synthesise of prop-2-ene-1,1,3-triyltribenzene derivatives from styrenes and alcohols by using a Bronsted acidic [NMP]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> ionic liquid catalyst.



Scheme 1 Direct coupling of alcohols with styrenes.

## Results and discussion

Initially, we have chosen the cross-coupling reaction of benzhydrol (**1a**) with styrene (**2a**) as a model reaction to optimise the different reaction conditions. The various reaction conditions such as catalyst screening, solvent screening, catalyst loading, substrate mol ratio, reaction time and temperature were studied for the coupling of **1a** with **2a** (Table 1). Initially, various catalysts such as montmorillonite K-10, amberlyst 15@, p-toluene sulfonic acid, -SO<sub>3</sub>H functionalized ionic liquid, Cu(OTf)<sub>2</sub>, In(OTf)<sub>3</sub>, [NMP]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> and [HMIM]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> were screened (Table 1, entries 1–8). It was observed that among screened catalysts, [NMP]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> was effective catalyst providing desired coupling product prop-2-ene-1,1,3-triyltribenzene (**3a**) in 41% yield (Table 1, entry 7). Next, we studied the effect of various solvents for the coupling of **1a** with **2a**. It was found that among the solvent studied, DCE was found to be effective solvent providing **3a** in 50% (Table 1, entries 9–13). However, when reaction was performed in the absence of solvent, it provided **3a** in 61% yield (Table 1, entry 14). Hence, further studies were carried out using [NMP]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> under solvent free condition. Furthermore, we have also examined the

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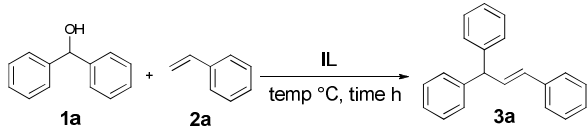
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effect of catalyst loading on the reaction yield. It was observed that yield of **3a** increases with increasing the catalyst loading from 1.5 mmol to 5 mmol (Table 1, entries 15-16). Whereas, on further increase in catalyst loading no significant increase in the yield of **3a** was observed. The substrate ratio of **1a/2a** was also studied and it was found that 1:1.1 was the optimum condition for this transformation (Table 1, entries 17-18). While on increasing the ratio of **2a**, the yield of **3a** was decreases by providing oligomerisation of **2a**. Subsequently, the effect of reaction time and temperature were also studied for the synthesis of **3a**, it was observed that 6 h was the minimum time required for the completion of reaction (Table 1, entries 19-20). During temperature study, it was observed that maximum yield of **3a** obtained at 80 °C (Table 1, entries 20-21). Whereas, on further increase in temperature no profound increase in the yield of **3a** was observed. Subsequently, when reaction was performed in the absence of catalyst under the optimum condition, formation of **3a**

**Table 1** Optimisation for direct coupling of alcohols with styrenes<sup>a</sup>



Entry	Catalyst	Solvent	Time (h)	Temp (°C)	Yield (%) <sup>b</sup>
1 <sup>c</sup>	mont. k-10	toluene	8	80	25
2 <sup>c</sup>	amberlyst-15	toluene	8	80	35
3 <sup>d</sup>	p-TSA	toluene	8	80	10
4 <sup>d</sup>	Cu(OTf) <sub>2</sub>	toluene	8	80	N.D.
5 <sup>d</sup>	In(OTf) <sub>3</sub>	toluene	8	80	N.D.
6	-SO <sub>3</sub> H functionalized IL	toluene	8	80	30
7	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	toluene	8	80	41
8	[HMIM] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	toluene	8	80	34
9	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	dioxane	8	80	38
10	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	cyclohexane	8	80	28
11	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	CH <sub>3</sub> CN	8	80	trace
12	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	CHCl <sub>3</sub>	8	80	43
13	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	DCE	8	80	50
14	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	-	8	80	61
15 <sup>e</sup>	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	-	8	80	76
16 <sup>f</sup>	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	-	8	80	89
17 <sup>g,f</sup>	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	-	8	80	92
18 <sup>h,f</sup>	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	-	8	80	75
19 <sup>g,f</sup>	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	-	4	80	69
20 <sup>g,f</sup>	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	-	6	80	92
21 <sup>g,f</sup>	[NMP] <sup>+</sup> HSO <sub>4</sub> <sup>-</sup>	-	6	70	77
22 <sup>g</sup>	-	-	8	80	N.D.
23 <sup>i</sup>	amberlyst-15	-	6	80	N.D.
24 <sup>f</sup>	-SO <sub>3</sub> H functionalized IL	-	6	80	55

<sup>a</sup> Reaction conditions: **1a** (1 mmol), **2a** (1.0 mmol), catalyst (1.5 mmol). <sup>b</sup> GC Yield. <sup>c</sup> Catalyst (0.75 g). <sup>d</sup> 10 mol%. <sup>e</sup> Catalyst (2.5 mmol). <sup>f</sup> Catalyst (5 mmol). <sup>g</sup> **1a**: **2a** (1 : 1.1). <sup>h</sup> **1a**: **2a** (1 : 1.2). <sup>i</sup> Catalyst (1.5 g). N.D. (not detected).

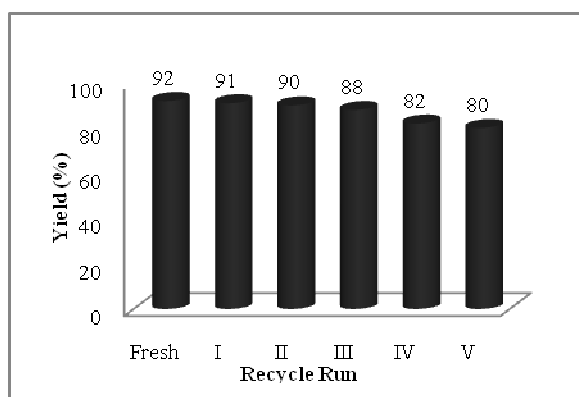
**Table 2** Direct coupling of alcohols with styrenes<sup>a</sup>

Entry	Alcohol	Styrene	Product	Yield (%) <sup>b</sup>
1	<b>1a</b>	<b>2a</b>	<b>3a</b>	90
2	<b>1a</b>	<b>2b</b>	<b>3b</b>	90
3 <sup>c</sup>	<b>1a</b>	<b>2c</b>	<b>3c</b>	89
4	<b>1a</b>	<b>2d</b>	<b>3d</b>	93
5	<b>1a</b>	<b>2e</b>	<b>3e</b>	91
6	<b>1a</b>	<b>2f</b>	<b>3f</b>	83
7	<b>1a</b>	<b>2g</b>	<b>3g</b>	85
8	<b>1a</b>	<b>2h</b>	<b>3h</b>	88
9 <sup>c</sup>	<b>1a</b>	<b>2i</b>	<b>3i</b>	89
10	<b>1b</b>	<b>2a</b>	<b>3j</b>	90
11	<b>1c</b>	<b>2a</b>	<b>3k</b>	89
12 <sup>c</sup>	<b>1d</b>	<b>2a</b>	<b>3l</b>	86
13	<b>1e</b>	<b>2a</b>	<b>3m</b>	90
14	<b>1f</b>	<b>2a</b>	<b>3n</b>	N.D.
15	<b>1g</b>	<b>2a</b>	<b>3o</b>	N.D.

<sup>a</sup> Reaction conditions: Alcohols (1 mmol), styrenes (1.1 mmol), catalyst (5 mmol), 80°C, 6 h. <sup>b</sup> Isolated yield. <sup>c</sup> 8 h. N.D. (not detected).

was not observed (Table 1, entry 22). To compare the catalytic activity of  $[\text{NMP}]^+\text{HSO}_4^-$  IL (Table 1, entry 20) with amberlyst 15@ and  $-\text{SO}_3\text{H}$  functionalized ionic liquid (Table 1, entries 23-24) at higher loading under solvent free condition, we observed that amberlyst 15@ catalyst doesn't give any conversion while  $-\text{SO}_3\text{H}$  functionalized IL gives lower yield (55%) of the desired product. Hence, the optimized reaction condition for the synthesis of **3a**: **1a** (1 mmol), **2a** (1.1 mmol),  $[\text{NMP}]^+\text{HSO}_4^-$  IL (5 mmol), 80 °C, 6 h. While, studying the catalyst amberlyst 15@ and  $-\text{SO}_3\text{H}$  functionalized ionic liquid at optimized reaction condition the yield of desired product **3a** was not observed.

With these optimized reaction condition in hand, the scope of developed protocol was applied for the coupling of various substituted alcohols with styrene derivatives to furnish corresponding prop-2-ene-1,1,3-triyltribenzene derivatives (Table 2). The coupling of **1a** with **2a** provided the desired product prop-2-ene-1,1,3-triyltribenzene **3a** in 90% yield (Table 2, entry 1). It was found that direct coupling of benzhydrol with electron donating ( $-\text{Me}$ ,  $-\text{OMe}$ ,  $-\text{C}(\text{CH}_3)_3$ ) styrene derivatives furnished the corresponding compounds **3b**, **3c**, **3d**, **3e** in excellent yield (Table 2, entries 2-5). Furthermore, styrene derivative bearing halo substituents ( $-\text{Cl}$ ,  $-\text{Br}$ ) were also furnished good to excellent yields of their corresponding products **3f**, **3g** (Table 2, entries 6,7). It was observed that the reaction also worked well with the styrene bearing electron-withdrawing group (*p*-acetoxy) providing corresponding 4-(3,3-diphenylprop-1-en-1-yl)phenyl acetate (**3h**) in 88% yield (Table 2, entry 8). Hence, electronic effect was not observed on the present catalytic system. It was observed that alpha-methyl styrene also provided respective product but-2-ene-1,1,3-triyltribenzene (**3i**) in 89% yield (Table 2, entry 9). Next, we have also studied the cross coupling of benzhydrol derivatives with styrene. It was found that benzhydrol bearing electron-donating groups ( $-\text{Me}$ ,  $-\text{OMe}$ ) also gave excellent yield of desired products **3j**, **3k** (Table 2, entries 10-11). Furthermore, benzhydrol bearing halo group also furnished the corresponding **3l** in excellent yield (Table 2, entry 12). Subsequently, 1-Phenylethanol also provided but-1-ene-1,3-diyltribenzene **3m** in 90% yield (Table 2, entry 13). However, benzylic and allylic alcohols did not produce the desired products under the optimized reaction conditions (Table 2, entries 14-15).

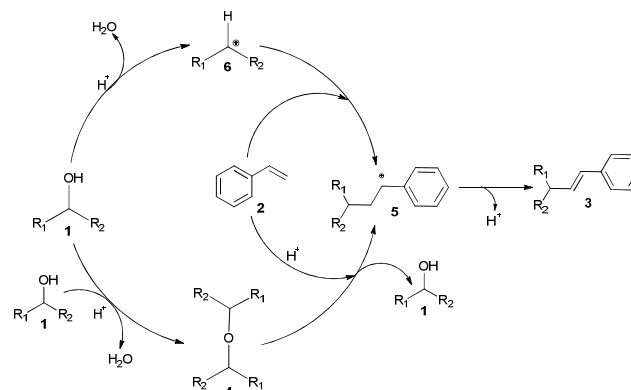


**Fig 1** Catalyst recyclability study. Reaction conditions: **1a** (1mmol), **2a** (1.1 mmol), catalyst (5 mmol), 80 °C, 6 h. GC yield.

In order to craft the greener and economical aspect of the

developed protocol, recyclability of present catalytic system was examined for the direct coupling of **1a** with **2a** (Fig 1). We have studied the respective transformation up to five times and observed that catalyst was effective for the recyclability study without much loss in its activity and the decrease in yield is might be due to handling loss as well as deactivation of  $[\text{NMP}]^+\text{HSO}_4^-$  ionic liquid in diethyl ether during work up procedure of recyclability study.

Based on our experimental observation and literature study.<sup>7,14</sup> Here, we proposed tentative mechanism for present protocol (Scheme 2). One pathway could be the formation of self coupling dimeric ether **4** from alcohol **1** in the presence of ionic liquid  $[\text{NMP}]^+\text{HSO}_4^-$ . We have isolated the intermediate **4** and characterized by GCMS. Subsequently, the dimeric ether **4** gets activated in the presence of ionic liquid  $[\text{NMP}]^+\text{HSO}_4^-$  and then couples with styrene **2**, leading to the formation of the corresponding alkyl cation **5** with regeneration the alcohol **1**. Finally, the alkyl cation **5** undergoes deprotonation to provide desired product **3**. Next, we have performed the reaction of intermediate **4** with styrene **2** without ionic liquid, no product formation was observed. This confirms that ionic liquid plays an important role during reaction pathway by protonating intermediate **4** and facilitates its coupling with **2** providing the corresponding product **3**. However, another possible pathway can not be ruled out at the present stage, which involves generation of carbocation **6** from the alcohol **1** in the presence of ionic liquid  $[\text{NMP}]^+\text{HSO}_4^-$ . Next, electrophilic addition of styrene with **6** provides corresponding methylarylcarbenium ion **5**, which undergoes deprotonation to provide the desired product **3**.



**Scheme 2** Plausible mechanism for direct coupling of alcohol with styrene.

## Conclusions

In conclusion, we have developed a simple, novel, efficient methodology for the direct coupling of alcohols with styrenes by using  $[\text{NMP}]^+\text{HSO}_4^-$  ionic liquid. This is the first metal free, solvent free, base free, additive free protocol for the synthesis of substituted alkenes from alcohols and styrenes. The present catalytic system has greater substrate compatibility and effectively recycled upto five consecutive cycles without any significant loss in its catalytic activity. Hence, the developed protocol is highly efficient, greener, economically and environmentally more compatible for the direct coupling of alcohols with styrenes.

## Experimental Section

All chemicals and reagents were purchased from firms of repute with their highest purity available and were used without further purification. For this study, ionic liquids were synthesized according to the procedures reported in the literature.<sup>13</sup>

### Procedure for synthesis of *N*-methyl-2-pyrrolidone hydrogen sulfate [NMP]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> ionic liquid:

In a 100 mL round bottom flask containing magnetic stirrer placed a 1-methyl-2-pyrrolidone (0.4 mol). Next, equimolar amount of concentrated sulphuric acid (98 wt%) was added drop wise slowly into the flask at 80 °C for 12 h. The mixture was then extensively washed with ether (3 × 10 ml) to remove unreacted non-ionic residue and dried under vacuum by a rotary evaporator to obtain the viscous clear ionic liquid.

### A typical experimental procedure for the direct coupling of alcohols with styrenes:

A mixture of benzhydrol **1a** (1 mmol), styrene **2a** (1.1 mmol), and [NMP]<sup>+</sup>HSO<sub>4</sub><sup>-</sup> (5 mmol) was stirred at 80 °C in a sealed 10 mL tube for 6 h. The progress of the reaction was monitored by gas chromatography. After the completion of reaction, it was cooled to room temperature. In order to separate the ionic liquid, a 10 mL of water was added to the reaction mixture and the product was extracted with ethyl acetate (3 × 8 mL). Thus, the residue obtained was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and purified by column chromatography (silica gel, 60–120 mesh; petroleum ether) to give the corresponding product prop-2-ene-1,1,3-triyltribenzene **3a** in 90% yield. The structure of the product was confirmed by GC-MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopic techniques. The purity of the compound was determined by GC-MS analysis.

### Recyclability study

The reaction was carried out as mentioned above in typical experimental procedure. However, after completion of reaction, the reaction mixture was extracted with diethyl ether (3 × 10 mL). Thus, the ionic liquid layer obtained was dried under reduced pressure for 2 h and directly used for next run.

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## References

- (a) *Metal-Catalyzed Cross-Coupling Reactions*, ed. A. de Meijere and F. Diederich, Wiley-VCH, Weinheim, 2nd edn, 2004, vol. 1 and 2; (b) K. C. Nicolaou, P. G. Bulger and D. Sarlah, *Angew. Chem., Int. Ed.*, 2005, **44**, 4442; (c) A. Suzuki, *Angew. Chem., Int. Ed.*, 2011, **50**, 6723; (d) V. P. Mehta and E. V. Van der Eycken, *Chem. Soc. Rev.*, 2011, **40**, 4925; (e) J. Moran, A. Preetz, R. A. Mesch and M. J. Krische, *Nat. Chem.*, 2011, **3**, 287; (f) D. H. Lee, K.-H. Kwon and C. S. Yi, *Science*, 2011, **333**, 1613; (g) Z. Shao and H. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 560; (h) F. A. Kang, Z. Sui and W. V. Murray, *J. Am. Chem. Soc.*, 2008, **130**, 11300.
- (a) H. Tang, K. Menzel and G. C. Fu, *Angew. Chem.*, 2003, **115**, 5233; *Angew. Chem. Int. Ed.*, 2003, **42**, 5079; (b) J. Zhou and G. C. Fu, *J. Am. Chem. Soc.*, 2003, **125**, 12527; (c) S. R. Dubbaka and P. Vogel, *J. Am. Chem. Soc.*, 2003, **125**, 15292; (d) S. L. Wiskur, A.

- (e) D. A. Powell, T. Maki and G. C. Fu, *J. Am. Chem. Soc.*, 2005, **127**, 510; (f) X. Dai, N. A. Strotman and G. C. Fu, *J. Am. Chem. Soc.*, 2008, **130**, 3302; (g) N. Tsukada, T. Sato and Y. Inoue, *Chem. Commun.*, 2001, 237; (h) L. Firmansjah and G. C. Fu, *J. Am. Chem. Soc.*, 2007, **129**, 11340.
- R. Kumar and E. V. Van der Eycken, *Chem. Soc. Rev.*, 2013, **42**, 1121.
- A. Tarlani, A. Riahi, M. Abedini, M. M. Amini and J. Muzart, *J. Mol. Catal. A: Chem.*, 2006, **260**, 187.
- H. Narahashi, T. Shimizu and A. Yamamoto, *J. Organomet. Chem.*, 2008, **693**, 283.
- Z.-Q. Liu, Y. Zhang, L. Zhao, Z. Li, J. Wang, H. Li and L.-M. Wu, *Org. Lett.*, 2011, **13**, 2208.
- H. L. Yue, W. Wei, M. M. Li, Y.R. Yang and J.X. Jia, *Adv. Synth. Catal.*, 2011, **353**, 3139.
- T. Aoyama, S. Koda, Y. Takeyoshi, T. Ito, T. Takido and M. Kodomari, *Chem. Commun.*, 2013, **49**, 6605.
- (a) D. K. T. Yadav, S. S. Rajak and B. M. Bhanage, *Tetrahedron Lett.*, 2014, **55**, 931; (b) K. M. Deshmukh, Z. S. Qureshi, K. P. Dhake and B. M. Bhanage, *Catal. Commun.*, 2010, **12**, 207; (c) R. A. Watile, D. B. Bagal, Y. P. Patil and B. M. Bhanage, *Tetrahedron Lett.*, 2011, **52**, 6383.
- (a) P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, 2nd ed., Wiley-VCH, 2002; (b) R. D. Rogers and K. R. Seddon, *Ionic Liquids as Green Solvents: Progress and Prospects*, ACS Symposium Series 856, American Chemical Society, Oxford University Press, Oxford, 2003; (c) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (d) P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.*, 2000, **39**, 3772; (e) R. Sheldon, *Chem. Commun.*, 2001, 2399; (f) Z. S. Qureshi, K. M. Deshmukh and B. M. Bhanage, *Clean Techn Environ Policy.*, 2013, DOI: 10.1007/s10098-013-0660-0.
- (a) M. J. Earle, S. P. Katdare and K. R. Seddon, *Org. Lett.*, 2004, **6**, 707; (b) P. Dominguez de Maria, *Angew. Chem., Int. Ed.* 2008, **47**, 6960.
- (a) Z. S. Qureshi, K. M. Deshmukh, M. D. Bhor and B. M. Bhanage, *Catal. Commun.*, 2009, **10**, 833; (b) K. M. Deshmukh, Z. S. Qureshi, N. S. Nandurkar and B. M. Bhanage, *Can. J. Chem.*, 2009, **87**, 401; (c) Z. S. Qureshi, K. M. Deshmukh, P. J. Tambade, K. P. Dhake and B. M. Bhanage, *Eur. J. Org. Chem.*, 2010, 6233; (d) Z. S. Qureshi, K. M. Deshmukh, K. P. Dhake and B. M. Bhanage, *RSC Adv.*, 2011, **1**, 1106.
- (a) W. Wang, L. Shao, W. Cheng, J. Yang and M. He, *Catal. Commun.*, 2008, **9**, 337; (b) A. R. Hajipour, L. Khazdooz and A. E. Ruoho, *Catal. Commun.*, 2008, **9**, 89; (c) Y. Gu, F. Shi and Y. Deng, *J. Mol. Catal. A: Chem.*, 2004, **212**, 71.
- (a) M. Yasuda, T. Somyo and A. Baba, *Angew. Chem.*, 2006, **118**, 807; *Angew. Chem. Int. Ed.*, 2006, **45**, 793; (b) R. Sanz, D. Miguel, A. Martnez, J. M. lvarez-Gutierrez and F. Rodriguez, *Org. Lett.*, 2007, **9**, 2027; (c) H. A. Kalviri and F. M. Kerton, *Adv. Synth. Catal.*, 2011, **353**, 3178.