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# Advances in Functionalized Ionic Liquids as Reagents and Scavengers in Organic Synthesis

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**Abstract:** Functionalized ionic liquids (FILs) synthesized with specific desired chemical properties have shown promising results in various areas of organic synthesis. In supported organic synthesis, FILs have become known as a new alternative to commonly used PEG and fluorous soluble supports. This review summarizes the progress of recent development in the synthesis of functionalized ionic liquids with emphasis on their applications as reagents and scavengers in organic synthesis.

**Keywords:** Supported reagents, ionic liquid, functionalized ionic liquid, reagents, scavenger and soluble support

## 1. Introduction

Supported materials have facilitated the organic synthetic process by virtue of their inimitable advantages, such as facile separation and purification of products and making the process environmentally friendly by increasing reusability and recyclability. This branch of chemistry has become a boon to pharmaceutical companies by assisting them to find the new drugs rapidly for high-throughput screening technologies, thus saving a significant amount of money and ultimately changing their fundamental approach towards drug discovery.

Solid-phase organic synthesis (SPOS) is a widely used technique in organic synthesis for the preparation of libraries of molecules for various purposes.<sup>1-11</sup> The advantages of this strategy have been thoroughly described in the literature. Merrifield pioneered the concept of solid phase synthesis to attain an efficient method for the synthesis of polypeptides.<sup>12</sup> This method was successfully applied for the synthesis of biopolymers such as DNA, RNA and peptides, as the chemistry required for chain extension is consistent for each step. Later, SPOS proved to be an efficient technique in combinatorial synthesis that facilitated the synthesis of many pharmacologically important compounds and made the purification process more facile.<sup>8, 13-16</sup> A broad range of polymer-supported materials<sup>1-11, 17</sup> and silica-supported materials<sup>18-20</sup> have been developed for SPOS. Despite its great success, SPOS suffers from some serious drawbacks, such as inability to purify and characterize the compounds prior to the final cleavage from the solid support, heterogeneous reaction conditions and non-linear kinetics.

To overcome these drawbacks soluble supports such as PEG<sup>21-26</sup> and fluorous phase<sup>27-31</sup> were utilized as an alternative to the solid phase. The reactions using these soluble supports are performed under conventional solution phase conditions. Another interesting feature of PEG supports is that a change in the polarity of the solvent leads to precipitation of the support, thus resulting in facile separation by filtration after the completion of the reaction. PEG-supported synthesis often combines the advantage of both product isolation and purification of solid-phase

chemistry with the solubility benefits of solution phase chemistry. However, maximum loading capacity of a PEG support is <1 mmol that is even lower than that of polystyrene-supported reagents.<sup>15, 32-35</sup> Moreover, due to its high oxygenating ability, PEG may interfere in certain types of reactions that may lead to degeneration of the support. In case of fluorous-supported synthesis, special solvents requirement and cost are some serious concerns.<sup>36, 37</sup> Thus, search of new soluble support led to the development of ionic liquid as alternative soluble support to PEG and fluorous supports in the last decade.<sup>38, 39</sup> In view of their unique characteristics, ionic liquid-supported reagents and catalyst have attracted great interest both from academia and industry.<sup>40</sup>

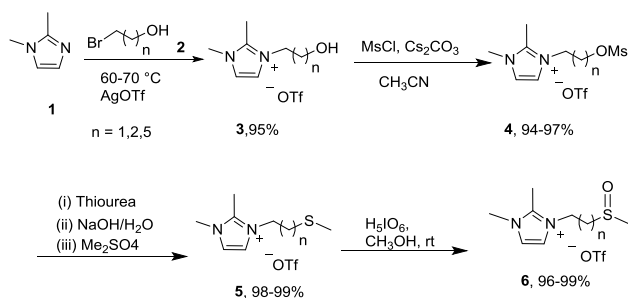
Ionic liquids are salts with melting points below the boiling point of water and they are solely composed of ions in their molten state. These materials have been termed as 'designer solvents' as their properties such as thermal stability, vapor pressure, and solvating ability can be tuned by appropriately varying combination of ions. The initial focus of organic chemists has been to use ionic liquids as an alternative to volatile organic compound solvents (VOCs) in various organic transformations.<sup>41-45</sup>

In last decade new class of functionalized ionic liquids (FILs) also known as task-specific ionic liquids (TSILs) have been synthesized with specific desired chemical properties.<sup>46-48</sup> The functional groups in FILs are covalently tethered to the anion, cation or both to get the desired properties for specific chemical tasks.<sup>49-54</sup> A plethora of FILs has been synthesized and used as reagents,<sup>50, 51</sup> catalysts,<sup>52, 53</sup> and scavengers<sup>55-58</sup> in organic synthesis. A number of excellent reviews have appeared on FILs dealing with ionic liquid-supported catalysis.<sup>45, 59-61</sup> However, review articles on developments of ionic liquid-supported reagents as scavengers are limited.<sup>62</sup> In this article, we have reviewed the synthesis of ionic liquid-supported reagents and their application as reagents and scavengers in organic synthesis. Synthesis of chiral ionic liquids and ionic liquid-supported catalysts are beyond the scope of this manuscript, and interested readers are directed to some excellent review articles published focusing on this area.<sup>63-67</sup>

## 2. Ionic liquid-supported reagents

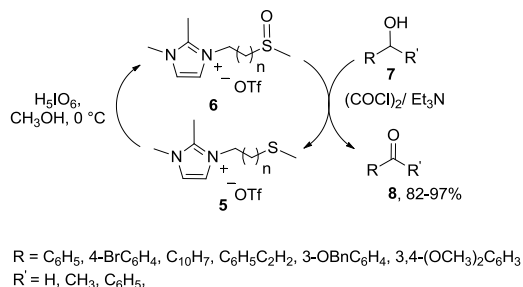
### 2.1. Ionic liquid-supported Swern oxidation reagent

Swern oxidation is a well known and widely used process for the oxidation of alcohols to the corresponding carbonyl compounds.<sup>68, 69</sup> Dimethyl sulfide, co-product of Swern oxidation process is volatile, noxious, foul-smelling and difficult to recover. To overcome the drawbacks associated with this protocol, Chan and co-workers prepared non-volatile and odourless ionic liquid-supported sulfoxides **6**.<sup>70</sup> Compound **6** was synthesized by simple reaction sequences as shown in Scheme 1. Alkylation of 1,2-dimethylimidazole **1** with bromo alcohols **2** followed by treatment with AgOTf gave ionic liquid-supported alcohols **3**, which were subjected to mesylation under basic conditions to give mesylated ionic liquid **4**. Sequential reactions involving, treatment of **4** with thiourea, followed by base hydrolysis and quenching the reaction mixture with dimethyl sulphate resulted in ionic liquid-supported sulphide **5**. Controlled oxidation of **5** with periodic acid gave desired ionic liquid-supported sulfoxide **6**. Due to the negligible vapor pressure, these newly synthesized ionic liquid-sulfur compounds **5** and **6** do not possess odor.



**Scheme 1:** Synthesis of IL-supported Swern reagent **6**.

Alcohols **7** were successfully oxidized to corresponding carbonyl compounds **8** in excellent yields (82-97%) under the Swern oxidation conditions using **6** (Scheme 2). In addition to the odorless conditions, simple ether extraction, excellent yields, and high purity without the need of chromatographic purification are silent features of the method. Moreover, the recovered **5** was regenerated and reused up to four cycles with comparable activity.

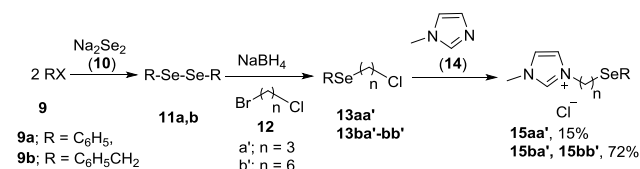


**Scheme 2:** Oxidation of alcohols using IL-supported Swern reagent **6**.

### 2.2. Ionic liquid-supported selenium reagent

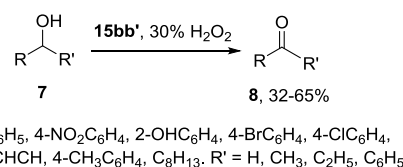
Ying group reported novel ionic liquid-supported selenium

reagents **15** to overcome the purification and handling problems encountered with selenium dioxide and organic selenides in the oxidation reactions.<sup>71</sup> Selenium reagent **15** was synthesized by treating Na<sub>2</sub>Se<sub>2</sub> with phenyl halide **9a** or benzyl halide **9b** to give dialkylselenane **11**. Reduction of **11** with NaBH<sub>4</sub> followed by reaction with bromochloroalkane **12** gave alkyl hypochloroselenite **13**, which upon reaction with 1-methylimidazole gave ionic liquid-supported selenium reagent **15** (Scheme 3).



**Scheme 3:** Synthesis of IL-supported selenium **15**.

Reagent **15b** in the presence of two fold excess of H<sub>2</sub>O<sub>2</sub> oxidized alcohols **7** to corresponding carbonyl compounds **8** in good to moderate yields (Scheme 4). The conventional solubility difference in reagent **15** and carbonyl compounds allowed easy isolation of the product from the reaction mixture. In addition to simplifying purification process, **15** was also recycled and reused effectively up to four times.



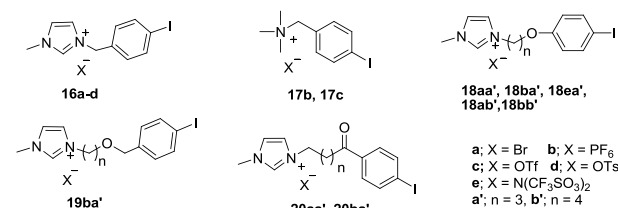
**Scheme 4:** Oxidation of alcohols using IL-supported selenium **15** in the presence of H<sub>2</sub>O<sub>2</sub>.

### 2.3. Ionic liquid-supported iodobenzene and hypervalent iodine reagents

Hypervalent iodine reagents have received great interest in organic synthesis in recent years as they are used to carry out several organic transformations under metal free conditions as well as in the presence of transition metals and their reactivity can be tuned accordingly.<sup>72-75</sup> With their increasing use in organic transformations, isolation of co-product and reuse of these reagents is a great challenge for synthetic chemists.

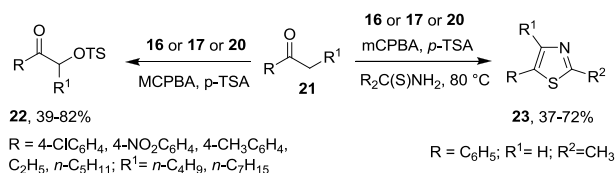
#### 2.3.1. Ionic liquid-supported iodobenzene

To improve synthetic utility of hypervalent iodine reagents, Togo and co-workers have designed and synthesized several ionic liquid-supported iodobenzenes (Figure 1).<sup>76-78</sup>



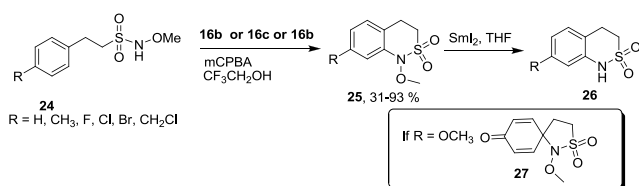
**Figure 1:** Structures of various IL-supported iodobenzenes.

Hydroxyl(tosyloxy)iodobenzene (HTIB) also known as Koser's reagent is an excellent reagent for the synthesis of  $\alpha$ -tosyloxy ketones from ketones.<sup>79</sup> Togo *et al.* developed an alternative procedure, in which various ketones **21** were converted into corresponding  $\alpha$ -tosyloxy ketones **22** using *m*-chloroperbenzoic acid (*m*CPBA) and *p*-toluenesulfonic acid (*p*-TsOH) in the presence of a catalytic amount of ionic liquid-supported iodobenzenes **16a**, **17**, or **20** (Scheme 5).<sup>78</sup> The scope of this procedure was further extended by synthesizing 2-methyl-5-phenylthiazole **23** directly from **21** without isolating **22** (Scheme 5). The ionic liquid-supported iodobenzenes were recovered and reused for up to three cycles.



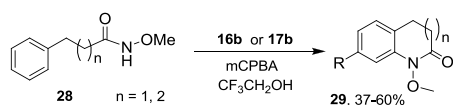
**Scheme 5:** Synthesis of  $\alpha$ -tosyloxy ketones and thiazoles using IL-supported iodobenzenes.

Inspired by the *in-situ* formation of Koser's reagent, Togo and his group developed an efficient cyclization protocol for the synthesis of *N*-methoxy-3,4-dihydro-2,1-benzothiazine-2,2-dioxide derivatives **25** (Scheme 6).<sup>76</sup> The ionic liquid-supported iodobenzenes (**16b**, **16c** and **17b**) in the presence of *m*CPBA and *p*-TsOH catalyzed the cyclization of *N*-methoxy-2-arylethanesulfonamide derivatives **24** to give **25**. Among various ion supported-iodobenzenes studied in the synthesis of **25**, **16b** and **16c** were found to be the more efficient than **16a** and **16d**. Replacing *p*-TsOH with trifluoroethanol (TFE) gave better yields of **25** in a shorter period of time. Compound **25** was further reduced to **26** using samarium iodide (Scheme 6), however, *p*-methoxy substituted **24** resulted in spiro-sultam derivatives **27**. Recycling of ionic liquid-supported iodobenzenes showed that the reagents could be recycled and reused for at least five cycles without much loss in its catalytic activity.



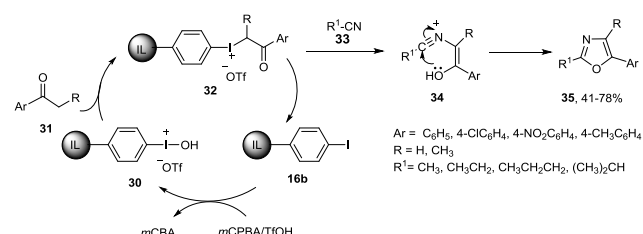
**Scheme 6:** Cyclization of sulfonamide **24** using **16**.

Same group further explored application of **16b** or **17b** for the cyclization of *N*-methoxy-3-phenylalkanamides **28** to **29** (Scheme 7). Excellent yields of **29** were obtained, and the work-up procedure was quite simple.



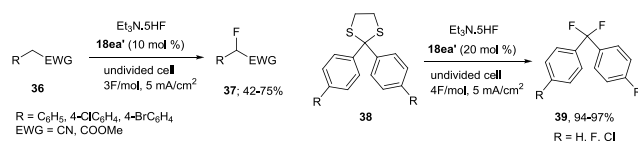
**Scheme 7:** Cyclization of *N*-methoxy-3-phenylalkanamides using **16** or **17**.

Togo group also compared ionic liquid-supported iodobenzene **16b** with polymer-supported iodobenzene for the synthesis of 2,4,5-trisubstituted oxazoles **35** from corresponding ketones **31** and found that the catalytic activity of ionic liquid-supported iodobenzene is superior over polymer-supported iodobenzene.<sup>77</sup> The reaction proceeded *via in situ* generation of trivalent arylodonium species **30**, which in turn reacted with aryl ketones **31** to form  $\beta$ -keto-aryliodonium salt **32**. Addition of nitrile **33** to **32** followed by an intermolecular cyclization gave desired oxazoles **35** (Scheme 8).



**Scheme 8:** Proposed mechanism for the synthesis of oxazoles using IL-supported iodobenzene **16b**

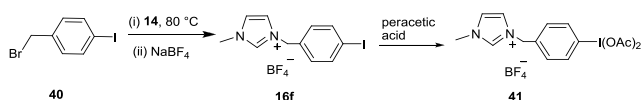
Fuchigami group has reported indirect electrochemical fluorination of active methylene group containing compounds, employing ionic liquid-supported iodobenzene **18ea'** as a mediator and  $\text{Et}_3\text{N} \cdot \text{HF}$  as fluoride source.<sup>80</sup> Fluorination of **36**, in the absence of **18ea'** (direct electrochemical fluorination) engendered anode passivation and resulted in poorer yields. Whereas employing **18ea'** as mediator (indirect electrochemical fluorination) significantly enhanced the product yield and overcame the anode passivation (Scheme 9). The reason for enhanced activity was attributed to the lesser mobility of ionic liquid-supported iodobenzene **18ea'** in  $\text{Et}_3\text{N} \cdot \text{HF}$ , which enabled the fluorination effectively. The procedure was further extended to cyclic dithioacetals **38** to get corresponding fluorinated product **39** (Scheme 9). Simple ether extraction gave the products in pure form. It was found that **18ea'** remains intact with  $\text{Et}_3\text{N} \cdot \text{HF}$  and can be reused several times without apparent loss in its activity.



**Scheme 9:** Electrochemical fluorination using IL-supported iodobenzene **18ea'**.

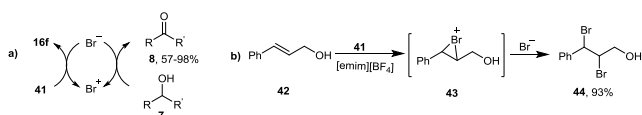
### 2.3.2. Ionic liquid-supported iodobenzene diacetate

Zhang group synthesized ionic liquid-supported iodobenzene diacetate **41** by reacting 4-iodobenzylbromide **40** with 1-methylimidazole **14** at 80 °C followed by anion exchange with  $\text{BF}_4^-$  and oxidation with peracetic acid (Scheme 10).<sup>81</sup> They further explored the application of **41** for the oxidation of alcohols **7** to ketones **8** in ionic liquid  $[\text{emim}][\text{BF}_4]$ . The oxidation of alcohols **7** is believed to be catalyzed by some excess bromide ions present in the  $[\text{emim}][\text{BF}_4]$  ionic liquid (Scheme 11).



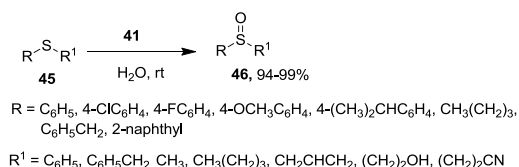
**Scheme 10:** Synthesis of IL-supported iodobenzene diacetate **41**.

The investigators believed that bromide ions were oxidized by the ionic liquid-supported reagent **41** to form an extremely reactive bromonium ion ( $\text{Br}^+$ ) intermediate which then oxidized the alcohol to its corresponding carbonyl compound. Formation of 2,3-dibromo-3-phenyl propanol **44** from cinnamyl alcohol instead of cinnamaldehyde supported formation of  $\text{Br}^+$  ions in the reaction mixture (Scheme 11). The method provides a high degree of selectivity along with easy workup and the reusability of the reagent. By comparing the reactivities of **41** with  $\text{PhI}(\text{OAc})_2$ , it was found that **41** gives better yields in shorter reaction time. The improved activity is attributed due to the electron withdrawing nature of imidazolium ions. Additionally, the presence of the  $[\text{emim}][\text{BF}_4]$  solvent is believed to have prevented the over oxidation of primary alcohols to carboxylic acids.



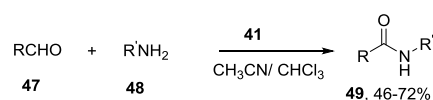
**Scheme 11:** a) Oxidation of alcohols to carbonyl compounds using **41** b) Reaction of cinnamyl alcohol with **41**.

Qian *et al.* reported oxidation of sulphides **45** to sulfoxides **46** using ionic liquid-supported iodobenzene diacetate **41** (Scheme 12).<sup>82</sup> Reagent **41** selectively oxidized sulfides **45** to the corresponding sulfoxides **46** in excellent yields at room temperature with high tolerance of various functional groups such as ester, nitrile, methoxy, hydroxyl and alkenes. Of the various solvents screened for the reaction, water was found to be the best choice in terms of the yield and reaction time. It is believed that the phase transfer property of reagent **41** facilitated the solubility of substrates in water and thus accelerated the reaction.



**Scheme 12:** Oxidation of sulphides to sulfoxides using IL-supported iodobenzene diacetate **41**.

Bao group demonstrated oxidative amidation of aldehydes using **41** (Scheme 13).<sup>83</sup> Although, the yield of amides **49** were found to be lower than those obtained by the conventional reagent  $\text{PhI}(\text{OAc})_2$  but easy separation of products and recyclability were inherent advantages of this protocol.

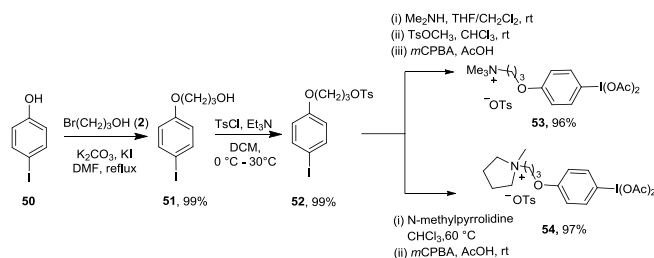


$\text{R} = \text{C}_6\text{H}_5$ , 4- $\text{ClC}_6\text{H}_4$ , 2- $\text{ClC}_6\text{H}_4$ , 4- $\text{BrC}_6\text{H}_4$ , 4- $\text{IC}_6\text{H}_4$ , 4- $\text{OCH}_3\text{C}_6\text{H}_4$ , 4- $\text{CH}_3\text{C}_6\text{H}_4$ , 3,4,5- $(\text{OCH}_3)_3\text{C}_6\text{H}_2$ , 4- $\text{NO}_2\text{C}_6\text{H}_4$ , 3- $\text{NO}_2\text{C}_6\text{H}_4$ , 1-naphthyl

$\text{R}' = \text{CH}_3(\text{CH}_2)_2$ ,  $\text{CH}_3(\text{CH}_2)_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2$

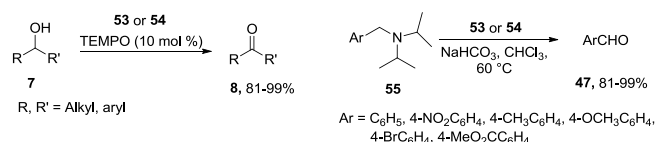
**Scheme 13** Synthesis of amides from aldehydes and amines using IL-supported iodobenzene diacetate **41**.

Togo and co-workers synthesized new class of ionic liquid-supported iodobenzene diacetates **53** and **54** from 4-iodophenol as shown in scheme 14.<sup>84</sup> The reaction of 4-iodophenol **50** with 1-bromo-3-propanol **2** in the presence of  $\text{K}_2\text{CO}_3$  and KI afforded **51**, which upon tosylation gave **52**. Reaction of **52** with *N*-methylpyrrolidine followed by oxidation with *m*CPBA gave **54** in excellent yields. In an approach, reaction of **52** with dimethylamine followed by methylation with  $\text{TsOCH}_3$  and controlled oxidation with *m*CPBA gave **53** in excellent yields (Scheme 14).



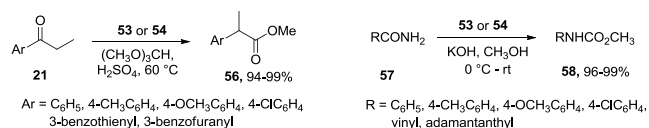
**Scheme 14:** Synthesis of IL-supported iodobenzene diacetates **53** & **54**.

Reagents **53** and **54** were used for the oxidation of alcohols **7** to carbonyl compounds **8** in the presence of catalytic amounts of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and oxidation of *N,N*-diisopropylbenzylamines to aromatic aldehydes (Scheme 15).



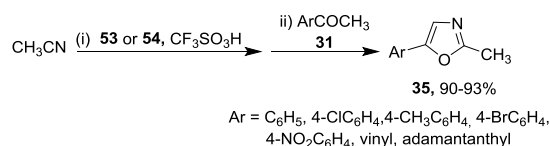
**Scheme 15:** Oxidation of alcohols and benzylamines using IL-supported-iodobenzene diacetates **53** and **54**.

The reaction of aryl propiophenones **21** with **53** or **54** under acidic conditions underwent 1,2-rearrangement to give methyl-2-arylpropanoates **56** (Scheme 16). On the other hand, Hofmann rearrangement of primary amides **57** in the presence of **53** or **54** under basic conditions gave carbamates **58** in excellent yields and high purities (Scheme 16).



**Scheme 16:** 1,2-Rearrangement of propiophenones and Hofmann rearrangement of amides using **53** and **54**.

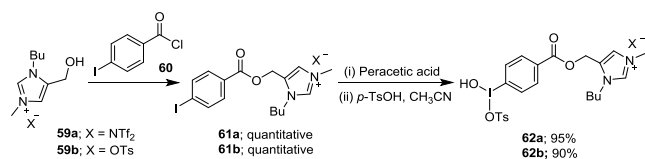
Togo group also developed a new procedure for the synthesis of oxazoles **35** from acetophenones **31** and acetonitrile using **53** or **54** (Scheme 17). The procedure was quite similar to ionic liquid-supported iodobenzene and *m*CPBA.<sup>77</sup> Use of  $\text{PhI}(\text{OAc})_2$  in place of **53** or **54** resulted in comparative yields but the purity of the products were poor due to the release of iodobenzene (co-product), and chromatographic separation was required to get pure compounds. On the other hand, when **53** or **54** were used, the products were isolated in high purity by simple ether extraction.



**Scheme 17:** Synthesis of oxazoles from nitriles and ketones using IL-supported iodobenzene diacetates **53** and **54**.

### 2.3.3. Ionic liquid-supported HTIB or Koser's salt

Handy and Okello prepared a novel ionic liquid-supported hydroxyl(tosyloxy)iodobenzene (HTIB) or Koser's salt **62** as shown in Scheme 18.<sup>85</sup> Initially, 4-iodobenzoyl chloride **60** was anchored onto the fructose derived ionic liquid alcohol **59**<sup>86, 87</sup> by an ester linkage. Oxidation of **61** with peracetic acid followed by treatment with *p*-TsOH, gave corresponding reagent **62** in good yields.



**Scheme 18:** Synthesis of IL-supported Koser's salt **62**.

The synthesized IL-supported Koser's salt was used for the tosyloxylation of ketones (Scheme 19). The reaction of ketones **21** with **62a** gave tosyloxyketone **63** in good yields. However, chromatographic purification was required to separate the product from the by-product **61a** due to its high solubility in organic solvents such as acetone, ether, ethyl acetate, and dichloromethane. When **62b** in which triflamide ion of **62a** was replaced with harder tosylate ( $^-\text{OTs}$ ) ion, tosyloxyketones **63** were isolated by simple ether extraction as the by-product **61b** was less soluble in ether. It is important to note that  $\alpha$ -tosylation was faster with **63** compared to Koser's salt due to the electron withdrawing ester linkage.

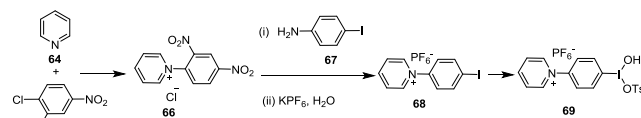


$\text{R} = \text{CH}_3$ ,  $\text{CH}_3\text{CH}_2$ ,  $\text{C}_6\text{H}_5$ ,  $\text{R}' = \text{H}$ ,  $\text{CH}_3$ ,  $\text{R-R}' = -(\text{CH}_2)_4-$ ,  $-(\text{CH}_2)_2-$

**Scheme 19:** Synthesis of  $\alpha$ -tosyloxy ketones using IL-supported Koser's salt **62**.

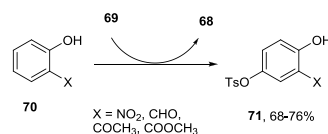
Taking into the account that alteration in the anion or cation

may lead to the stability of ionic liquid, Zhang group developed a novel pyridinium salt-supported HTIB **69** (Scheme 20).<sup>88</sup> Reagent **69** was prepared by using modified Zincke's reaction in three steps. *N*-alkylation of pyridine with 1-chloro-2,4-dinitrobenzene **65** gave **66**, which upon reaction with 4-iodoaniline **67** followed by anion exchange gave **68**. Oxidation of **68** with *m*CPBA followed by the tosylation yielded pyridinium salt-supported HTIB **69** (Scheme 20). Reagent **69** was found to be relatively more stable than previously reported ionic liquid-supported HTIBs.<sup>85</sup>



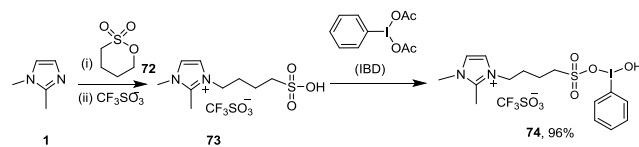
**Scheme 20:** Synthesis of pyridinium salt-supported HTIB **69**.

Tosyloxylation of various *ortho*-substituted phenolic compounds **70** was explored using **69** (Scheme 21). The reaction of **69** with phenols bearing electron withdrawing groups at *ortho* positions resulted in desired products **71** but failed to give desired products from simple phenol and electron rich phenols. Reagent **69** can be regenerated from by-product **68** and reused up to 3 cycles without loss in reactivity.



**Scheme 21:** Tosyloxylation of phenols using **69**.

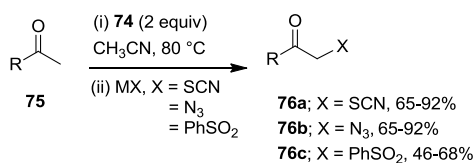
Recently, we have successfully developed a novel imidazolium based ionic liquid-supported hypervalent iodine reagent **74** and employed it in a 'catch and release' strategy.<sup>89</sup> Synthesis of **74** was achieved by mixing a homogeneous solution of ionic liquid-supported sulfonic acid **73** in  $\text{CH}_3\text{CN}$  with a hot solution of iodobenzene diacetate (IBD) and keeping it at room temperature for one week (Scheme 22).



**Scheme 22:** Synthesis of IL-supported hypervalent iodine reagent **74**.

After successfully synthesizing **74**, it was used to develop a chromatographic free protocol for the synthesis of  $\alpha$ -substituted acetophenones **76** by first capturing acetophenones **75** on ionic liquid followed by nucleophilic release with  $\text{KSCN}$ ,  $\text{NaN}_3$  and  $\text{PhSO}_2\text{Na}$  (Scheme 23).<sup>89</sup> Small library of  $\alpha$ -thiocynato- $\beta$ -ketones **76a**,  $\alpha$ -azido- $\beta$ -ketones **76b** and  $\beta$ -ketosulfones **76c** have been

synthesized in good to excellent yields (46-92%) using this strategy. Superior loading capacity and chromatography-free synthesis are inherent advantages of this process.

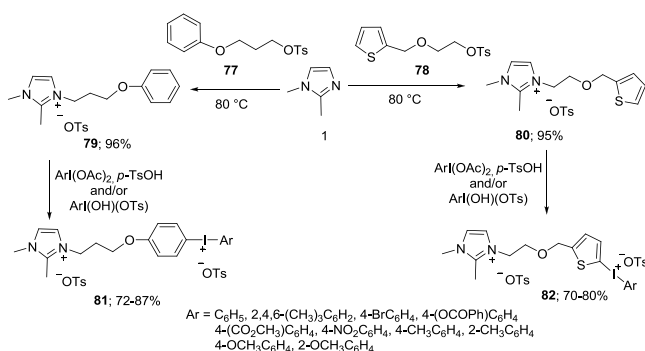


R = 4-ClC<sub>6</sub>H<sub>4</sub>, 3-ClC<sub>6</sub>H<sub>4</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>,  
4-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>9</sub>S, 2-naphthyl

**Scheme 23:** Synthesis of  $\alpha$ -substituted ketones using IL-supported hypervalent iodine reagent **74**.

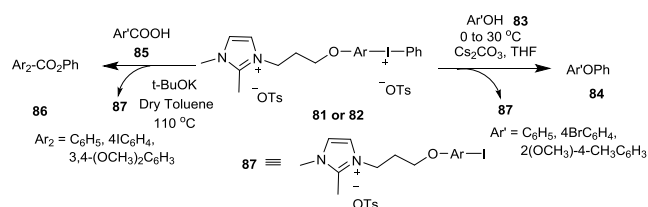
### 2.3.4. Ionic liquid-supported diaryliodonium salts

Diaryliodonium salts serves as proficient and potent electrophilic arylating source for the carbon-carbon and carbon-heteroatom bond formation reactions.<sup>90</sup> To deal with the purification, isolation, and loading problems of diaryliodonium salts, recently we have developed new ionic liquid-supported diaryliodonium salts.<sup>91</sup> Electron-rich aryl groups, like alkoxyphenyl and thiophene, have been grafted on ionic liquids for the facile synthesis of ionic liquid-supported diaryliodonium salts as shown in the Scheme 24. These imidazolium-supported aryls **79** and **80** further reacted with hydroxyl(tosyloxy)iiodoarene (HTIA) or (diacetoxyiodo)arenes to give corresponding ionic liquid-supported diaryliodonium salts **81** and **82**. They were isolated in pure form by simple washing with organic solvents like chloroform and tetrahydrofuran, without requiring chromatographic purification; moreover, these salts are quite stable and have not shown any sign of decomposition or loss of reactivity even after one month of storing at 5 °C.



**Scheme 24:** Synthesis of IL-supported diaryliodonium salts.

Metal-free electrophilic phenylation of phenols **83** and carboxylic acids **85** was performed using **81** or **82** to give phenyl ether **84** and carboxylic esters **86**, respectively, in good yields (Scheme 25). Products **84** and **86** were isolated simply by evaporating the reaction solvent followed by extraction with a hexane/ethyl acetate mixture. This left behind the by-product supported on the ionic liquid, which can potentially be reused as a supported reagent in many other organic transformations. Better yields for phenylation were obtained using **81** as compared with **82**.



**Scheme 25:** Electrophilic phenylation of phenols and carboxylic acids using **81** or **82**.

### 2.4. Ionic liquid-supported TEMPO

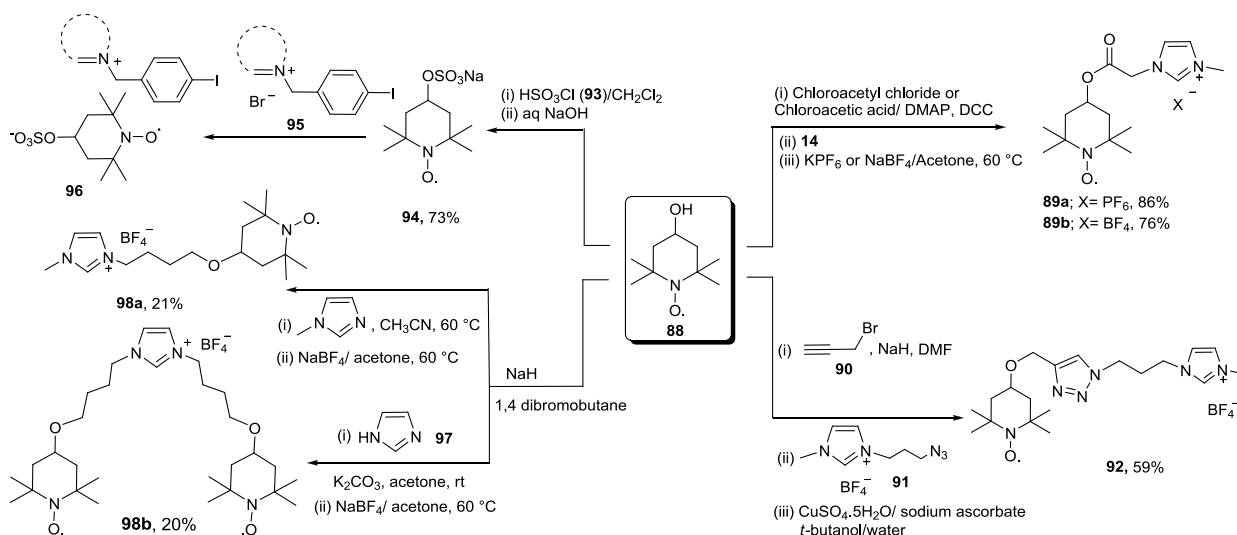
Chemoselective oxidation of alcohols to corresponding carbonyl compounds is an important process in synthetic organic chemistry.<sup>92</sup> TEMPO is widely used co-catalyst along with terminal oxidant for this process due to its non-metallic nature.<sup>93</sup> Although the amount of TEMPO required for the oxidation process is quite less (1-5 mol %), in order to make the whole process cost effective, there is a need to recycle and reuse the co-catalyst. To address the problems associated with recyclability and reusability, TEMPO has been grafted onto various supports.<sup>94</sup>

Wu *et al.* synthesized ionic liquid-supported TEMPO **89** from 4-hydroxy-TEMPO **88** in a two-step process.<sup>95</sup> Coupling of **88** with chloroacetyl chloride or chloroacetic acid followed by quaternization with 1-methylimidazole **14** and anion exchange with KPF<sub>6</sub> or NaBF<sub>4</sub> gave **89** in good yields (Scheme 26). Qian *et al.* also reported the synthesis of various ionic liquid-supported TEMPO **89b**, **98a** and **98b** by grafting **88** onto an imidazolium ion as shown in Scheme 26.<sup>81</sup> Oxidation of alcohols **7** using **89** along with terminal oxidant sodium hypochlorite (NaClO<sub>4</sub>) in a biphasic mixture of [bmim][PF<sub>6</sub>]-water gave excellent yield (86-96%) of carbonyl compounds **8** (Scheme 27, method A).<sup>95</sup> Comparable catalytic activity was observed for **89a** to that of TEMPO and efficient recyclability and reusability of **89** were inherent advantages of this process.

Tong group developed a heterogeneous method for the oxidation of alcohols **7** to carbonyl compounds **8**, by impregnating **89b** and CuCl on to various silica supports including SiO<sub>2</sub>, MCM-41 and SBA-15.<sup>96</sup> The heterogeneous catalyst has shown superior catalytic activity compared to ionic liquid-TEMPO/CuCl system (Scheme 27, method B). Fall *et al.* reported a new ionic liquid-supported TEMPO **92** via a click reaction as shown in Scheme 26.<sup>97</sup> Reaction of **88** with propargyl bromide **90** in DMF followed by click reaction with azido functionalized ionic liquid **91** in the presence of CuSO<sub>4</sub>/sodium ascorbate gave **92** in moderate yield (59%). The catalytic activity of **92** for the oxidation of alcohols **7** was evaluated in various ionic liquids such as [hmim][BF<sub>4</sub>], [hmim][Cl], [bmim][BF<sub>4</sub>] & [omim][Cl]. Among all these ionic liquids, [hmim][BF<sub>4</sub>] proved to be the solvent of choice for this reaction (Scheme 27, method C).

Zhdankin and group have synthesized a bifunctional hybrid-type ionic liquid-supported TEMPO **96** (Scheme

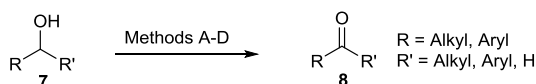




**Scheme 26:** Synthesis of various IL-supported TEMPO.

26).<sup>98</sup> For the synthesis of **96**, iodobenzene was integrated to the cationic part of ionic liquid by quaternization of 1-methylimidazole or pyridine with 1-(bromomethyl)-4-iodobenzene to generate ionic liquid **95**. TEMPO was introduced as the anion part of ionic liquid by anion metathesis of **95** with Na[TEMPO-OSO<sub>3</sub>] **94**.

Qian *et al.* also studied catalytic activity of **89b** and **98** in the oxidation of alcohols **7** using a stoichiometric amount of terminal oxidants like peracetic acid, IBD, [dibmim][BF<sub>4</sub>], sodium hypochlorite, and iodine (Scheme 27, method D). Superior catalytic activity was observed for **98b** due to its higher loading capacity, whereas **89b** and **98a** showed similar catalytic activity to TEMPO. Of the various terminal oxidants that were screened, [dibmim][BF<sub>4</sub>] gave the best result and this may be attributed to its complete solubility in water.



**Method A:** **89a** (1 mol %), NaOCl (1.2 equiv), KBr (10 mol %), pH = 8.6, [bmim][PF<sub>6</sub>], H<sub>2</sub>O, 0 °C, 86-96%

**Method B:** **89a**/CuCl<sub>2</sub>/SiO<sub>2</sub>, O<sub>2</sub>, *n*-Octane, 70 °C

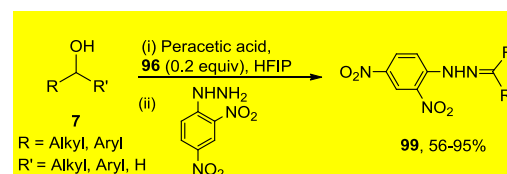
**Method C:** **92** (10 mol %), IBD (1.1 equiv), [hmim][BF<sub>4</sub>], H<sub>2</sub>O, 30 °C, 86-99%

**Method D:** **89b**, **98a**, or **98b** (5 mol %), [dibmim][BF<sub>4</sub>], H<sub>2</sub>O, 30 °C, 78-99%

**Scheme 27:** Oxidation of alcohols using IL-supported TEMPO.

Zhdankin *et al.* has further studied oxidation of alcohols **7** to hydrazone derivatives **99** using catalytic amount of **96** along with stoichiometric amount of peracetic acid (Scheme 28).<sup>98</sup> Remarkable rate-enhancing effect has been noticed when 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) was used as co-solvent in this oxidation process. Due to the presence of both functionalities (iodobenzene and TEMPO) on the same moiety (**96**), oxidation process is believed to be intramolecular rather than intermolecular. Superior catalytic activities, no apparent loss in catalytic activity even after five cycles, and easy separation of products from the

reaction mixture are advantages of this process.



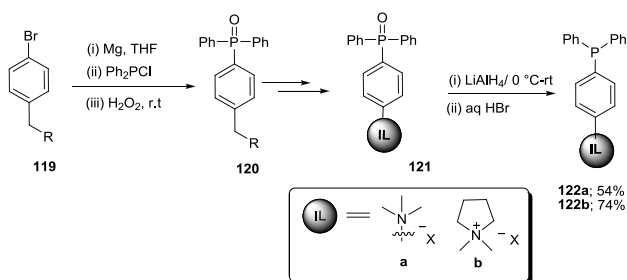
**Scheme 28:** Conversion of alcohols **7** to hydrazones **99** using IL-supported TEMPO **96**.

In all these cases, the biphasic system offered easy isolation of products from the reaction mixture, and ionic liquid-supported TEMPO could be reused several times without much loss of catalytic activity. These systems offer clean, convenient and environmentally benign method for the selective oxidation of alcohols.

## 2.5. Ionic liquid-supported nitrating reagent

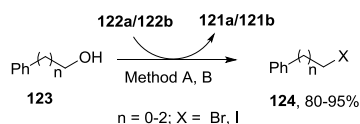
In an interesting study, Zolfigol *et al.* reported a novel bifunctional ionic liquid **101** having sulfonic acid and nitrate ion.<sup>50</sup> Synthesis of **101**, was achieved by the reaction of 1-methylimidazole **14** with chlorosulfonic acid to give **100** followed by addition of nitric acid to **100** under solvent free conditions (Scheme 29). Nitration of aromatic compounds **105** were nitrated under mild conditions in good to excellent yields. Successful nitration of aniline and a significant decrease in the yield on employing free radicals scavengers (iodine, butylated hydroxytoluene) are clear evidence that nitration occurs due to the generation of NO<sub>2</sub> radical rather than NO<sub>2</sub><sup>+</sup> ion. Moreover, 21% weight loss on heating the reagent **101** from 60 to 160 °C and formation of Cu(NO<sub>3</sub>)<sub>2</sub> by the reaction of copper metal during the heating process are some other evidences that support that this nitration process proceeds *via* NO<sub>2</sub> radical rather than NO<sub>2</sub><sup>+</sup>. The reagent **101** can be regenerated and reused efficiently (Scheme 29).

Triphenylphosphine (Ph<sub>3</sub>P) is widely used as a ligand in transition metal catalyzed coupling reactions. Removal of Ph<sub>3</sub>P and Ph<sub>3</sub>PO (co-product in some reactions) from the reaction mixture is very troublesome and requires repetitive column chromatography. Keeping this in view, Togo *et al.* synthesized ionic liquid-supported triphenylphosphines **122**.<sup>103</sup> The reagents **122a** and **122b** were prepared from substituted aryl bromides **119** as shown in Scheme 33. *In situ* generation of Grignard reagent from **119**, followed by reaction with Ph<sub>2</sub>PCl and oxidation yielded phosphine oxide **120**, which was anchored onto an ionic liquid by quaternization of tertiary amines to give **121**. Reduction of **121** using LiAlH<sub>4</sub> followed by acidification with HBr gave reagents **122a** and **122b** in good yields (Scheme 33).



**Scheme 33:** Synthesis of IL-supported triphenylphosphine.

Reagent **122a**, **122b** and  $\text{Ph}_3\text{P}$  were screened independently for the halogenation of alcohols **123** to corresponding halides **124** (Scheme 34).<sup>103, 104</sup> When **122** was employed as a reagent, products were isolated in good yields with high purity (>70%) by simple filtration and by-products **121a** and **121b** were recovered in over 90% yield. The recovered **121** were again reduced to **122** and reused. On the other hand, when  $\text{Ph}_3\text{P}$  was employed, the purity of the products **124** was quite less (<45%) and they were purified by column chromatography.

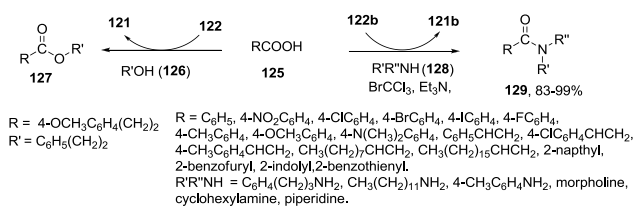


**Method A:**  $\text{CBr}_4$  (1.1 equiv) **122a** (1.2 equiv) or **122b** (1.5 equiv), solvent, 40 °C - 60 °C.

**Method B:**  $\text{I}_2$  (1.5 equiv), **122a** (1.2 equiv) or **122b** (1.5 equiv), imidazole (1.5 equiv), KI (1.5 equiv), 40 °C - 60 °C

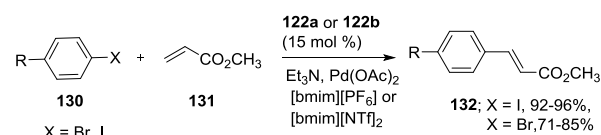
**Scheme 34:** Halogenation of alcohols using **122**.

Togo group further explored application of **122** in Mitsunobu and amide bond formation reactions (Scheme 35). Carboxylic acids **125** were converted to corresponding esters **126** by reaction with alcohols **126** in the presence of **122** in excellent yields, and the ionic liquid-supported phosphine oxide **121** was recovered. Similarly, amides **129** were obtained in excellent yields (83-99%) and high purity by the reaction of **125** with amines **128** in the presence of **122b**.

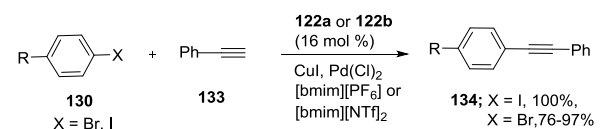


**Scheme 35:** Ester and amide bond formation using **122**.

The success of these reactions encouraged Togo group to examine **122** as ligands in the Mizoroki-Heck and Sonogashira coupling reaction.<sup>103</sup> A comparative study performed for the reuse of the catalyst for these coupling reactions in the absence and presence of **122** showed that when **122** was employed not only the rate of the reactions were dramatically accelerated but  $\text{Pd}(\text{OAc})_2$  and  $\text{CuI}$  could be recovered and reused several times (Scheme 36). The coupling products **132** and **134** were isolated in pure form by simple extraction with appropriate organic solvents.



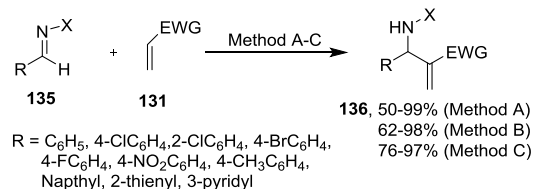
		Reuse					Reuse		
Solvent	Catalyst	0	1	2	Solvent	Catalyst	0	1	2
[bmim][PF <sub>6</sub> ]	-	88	50	14	[bmim][NTf <sub>2</sub> ]	-	92	50	27
<b>122a</b>		90	91	76	<b>122a</b>		95	96	90
<b>122b</b>		95	83	81	<b>122b</b>		96	96	95



		Reuse					Reuse		
Solvent	Catalyst	0	1	2	Solvent	Catalyst	0	1	2
[bmim][PF <sub>6</sub> ]	-	75	68	40	[bmim][NTf <sub>2</sub> ]	-	75	73	52
<b>122a</b>		100	100	97	<b>122a</b>		100	100	100
<b>122b</b>		100	100	100	<b>122b</b>		100	100	100

**Scheme 36:** Mizoroki-Heck and Sonogashira coupling reactions in the absence and presence of **122**.

Togo group also developed an efficient procedure for Aza-Morita-Baylis-Hillman reaction using **122** as a reusable catalyst.<sup>104</sup> Various *N*-benzylidene carbamate imines and *N*-tosylarylimines **135** were reacted with alkenes **131** in the presence of **122a** and **122b** to give corresponding Baylis-Hillman adducts **136** in good to excellent (50-99%) yields and high purity (Scheme 37). Among various solvents that were screened, best yield of **136** was obtained in  $\text{CH}_2\text{Cl}_2$ . Further increase in the yield and purity was observed when molecular sieves (MS 4Å) were added to the reaction mixture. The increase in the yield of products is attributed to the removal of moisture from **122** by MS 4Å.



X = Ts, Cbz,

EWG = CN, COOCH<sub>3</sub>,

COCH<sub>3</sub>, COC<sub>2</sub>H<sub>5</sub>

**Method A:** **122a** or **122b** (0.5 equiv), DCM, MS 4Å, rt

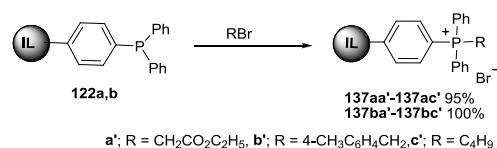
**Method B:** **180ab'** (0.3 equiv), MeOH (2 equiv),

**Method C:** **180ca'** (0.2 equiv),

**Scheme 37:** Aza-Morita-Baylis-Hillman reaction using **122**.

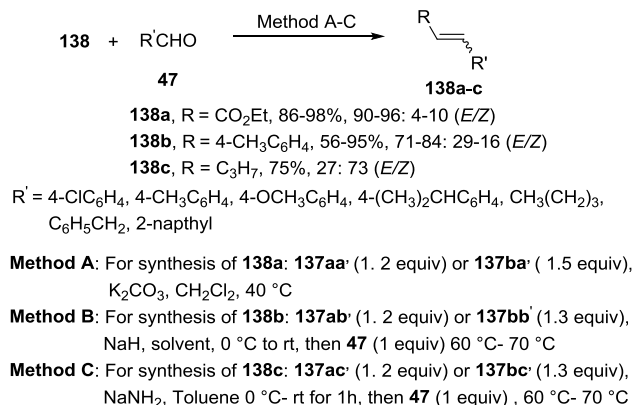
## 2.7.2. Ionic liquid-supported phosphonium salts

liquid-supported phosphonium salts **137aa'-ac'** and **137ba'-bc'** were synthesized by the alkylation of **122a** and **122b** with *p*-methylbenzyl bromide, ethyl bromoacetate and *n*-butyl bromide as shown in Scheme 38.<sup>105</sup>



**Scheme 38:** Synthesis of IL-supported phosphonium salts.

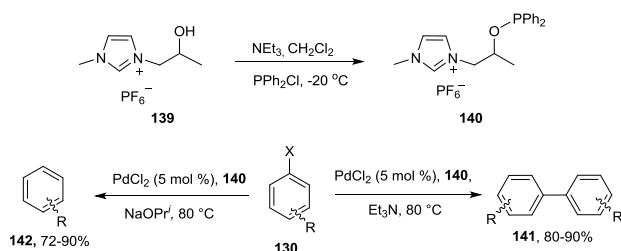
Ionic liquid-supported phosphonium salts **137** were used in Wittig reaction as alkyl source. Aldehydes **47** were converted to corresponding alkenes **138** in high yields and excellent purities by reacting with **137** (Scheme 39).<sup>105</sup> *Trans*-isomer was obtained as a major product in case of **138a** and **138b** whereas *cis*-isomer was a major product in case of **138c**.



**Scheme 39:** Wittig reaction using **137**.

### 2.7.3. Diphenylphosphinite-functionalized ionic liquids

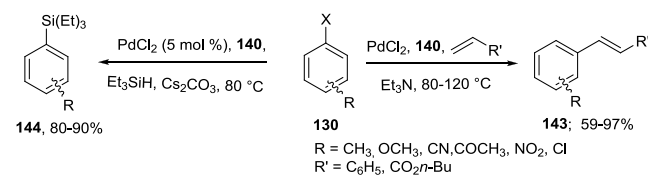
Iranpoor and co-workers have described the synthesis of diphenylphosphinite-functionalized ionic liquids (IL-OPPh<sub>2</sub>) **140** by the reaction of chlorodiphenylphosphine ( $\text{PPh}_2\text{Cl}$ ) with ionic liquid alcohol **139** in the presence of  $\text{Et}_3\text{N}$  (Scheme 40).<sup>106</sup> Dehalogenation and homocoupling reactions of aryl halides **130** were carried out using **140** both as a reagent and reaction medium (Scheme 40).<sup>107, 108</sup> The outcome of the reaction relied on the reactants and the bases employed in the reaction. For example, aryl halide **130**, in the presence of reagent **140**,  $\text{PdCl}_2$  and  $\text{Et}_3\text{N}$  resulted in homocoupled product **141**. On the contrary, replacement of  $\text{Et}_3\text{N}$  with sodium isopropoxide ( $\text{NaOPr}$ ) resulted in the dehalogenation of aryl halides to give **142**. The method proved to be tolerant to various functional groups, such as nitro, keto, and nitrile.



**Scheme 40:** Synthesis of IL-OPPh<sub>2</sub> and its application in homocoupling and dehalogenation reaction of aryl halides.

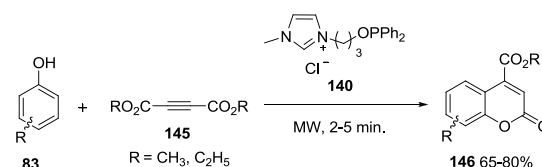
Later, **140** was also used as reusable and recyclable ligand in Heck reactions and silylation of aryl halides (Scheme 41).<sup>109</sup> Aryl halides **130** in the presence of **140**,  $\text{PdCl}_2$ , and  $\text{Et}_3\text{N}$  reacted with styrene or *n*-butyl acrylate to give corresponding Heck coupled products **143** in good to excellent yields (59-97%). Interestingly, less reactive aryl chlorides also underwent Heck coupling reaction under

given reaction conditions. On the other hand, the reaction of aryl halides with triethylsilanes in the presence of  $\text{Cs}_2\text{CO}_3$  gave arylsilanes **144**. Surprisingly, in the absence of the base same system resulted dehalogenated products **142**.



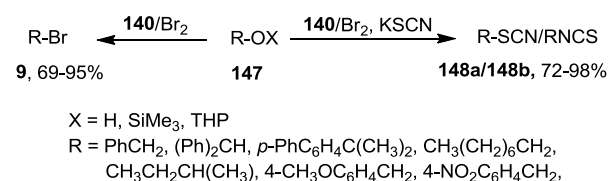
**Scheme 41:** Heck reaction and silylation of aryl halides using IL-OPPh<sub>2</sub>.

Valizadeh *et al.* has reported an elegant microwave-assisted synthesis of coumarins **146** from phenols and dialkyl but-2-ynedioate using diphenylphosphinite-functionalized ionic liquid **140** (Scheme 42).<sup>110</sup> Coumarins were obtained in good yields (65-80%), and the reagent **140** could be reused at least three times without apparent loss in its activity.



**Scheme 42:** Microwave-assisted synthesis of coumarins using IL-OPPh<sub>2</sub>.

Iranpoor and co-workers reported bromination of alcohols, trimethylsilyl and THP-ethers **147** by bromine in the presence of **140** (Scheme 43).<sup>106</sup> Although the procedure was applicable to all alcohols, trimethylsilyl and THP-ethers, the reagent is highly selective for primary alcohols in the presence secondary alcohols and similarly for primary and secondary alcohols over trimethylsilyl and THP-ethers. The study was further extended to the synthesis of thiocyanates and isothiocyanates by reacting alcohols and their derivatives using IL-OPPh<sub>2</sub>(SCN) which is prepared by the reaction of **140** with bromine followed by the reaction of  $\text{KSCN}$ . It is worth to emphasize that primary alcohol selectively gave thiocyanates (**148a**) while tertiary alcohols yielded isothiocyanates (**148b**). A mixture of thiocyanates and isothiocyanates was obtained from secondary alcohols.<sup>106</sup> The products were isolated by simple extraction with diethyl ether.

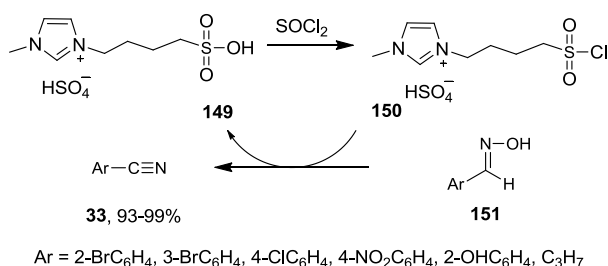


**Scheme 43:** Bromination and thiocyanation using **140**.

### 2.8. Ionic liquid-supported sulfonyl chloride

Qiao group synthesized an acidic ionic liquid, 1-4[(chlorosulfonyl)butyl]-3-methylimidazolium

chlorosulfate [cbmim][SO<sub>3</sub>Cl] **150** from [sbmim][HSO<sub>4</sub>] **149** by reacting with SOCl<sub>2</sub> (Scheme 44).<sup>111</sup> Compound **150** features acidic sites on both the anion and cation part of ionic liquid. Dehydration of aldoximes **151** was performed to give nitriles **33** using both **149** and **150** as a catalyst. The reagent **150** was found to be more efficient than **149**, and nitriles were obtained in 93-95% yield using **150** (Scheme 44). Moreover, self-induced phase separation of the reaction mixture after completion of the reaction provided simple and effortless isolation of the products from the reaction mixture.<sup>111</sup> Recovered **149** was converted to **150** on reacting with SOCl<sub>2</sub>.

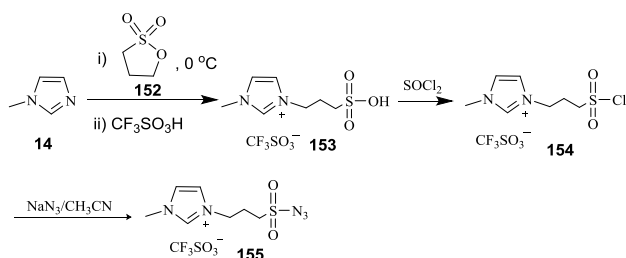


Ar = 2-BrC<sub>6</sub>H<sub>4</sub>, 3-BrC<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, 2-OHC<sub>6</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>7</sub>

**Scheme 44:** Synthesis of IL-supported sulfonyl chloride **150** and its application in dehydration of aldoximes.

## 2.9. Ionic liquid-supported sulfonyl azide

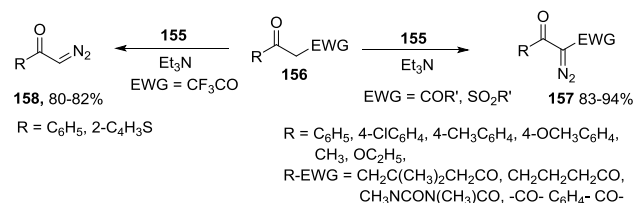
Wider utility of sulfonyl azides in organic synthesis and problems associated with their safety and purification of the product, encouraged us to synthesize a new ionic liquid-supported sulfonyl azide **155**.<sup>112</sup> Synthesis of **155** was achieved as shown in Scheme 45. Initially, the reaction of 1-methylimidazole **14** with 1,3-propanesultone **152** at 0 °C followed by acidification with trifluoromethanesulfonic acid (TfOH) at room temperature gave **153**. Reaction of **153** with thionyl chloride under reflux conditions, followed by reaction with sodium azide afforded **155**. The differential scanning calorimetry (DSC) analysis of **155** revealed that the exothermic decomposition temperature of pure **155** is above 150 °C and it is much higher compared to most of the traditional diazo transfer reagents.



**Scheme 45:** Synthesis of IL-supported sulfonyl azide **155**.

The scope of reagent **155** as a diazotransfer reagent was evaluated by treating it with various active methylene compounds like 1,3-diketones, β-ketoester, and 1,3-diester **156** (Scheme 46).<sup>112</sup> Reagent **155** afforded diazo compounds **157** in excellent yields with high purity under solvent free conditions in a short period. β-Ketosulfones that have been previously reported as poor substrates for the diazotransfer

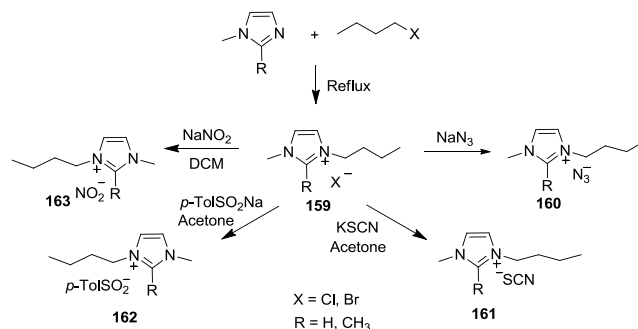
reaction gave corresponding diazo compounds in excellent yields with reagent **155**. Moreover, **155** was also used as a detrifluoroacetylative diazotransfer reagent to synthesize **158** from **155**. The products were isolated in the pure form by simple extraction with hexane-ethyl acetate mixture where as in the case of traditional sulfonyl azide product isolation proved to be tricky as it required repetitive column chromatography to remove tosylamide from the products.



**Scheme 46:** Diazotransfer and detrifluoroacetylative diazotransfer reaction using **155**.

## 2.10. Nucleophilic Ionic liquids

Nucleophilic ionic liquids (NILs)<sup>113</sup> are a unique class of ionic liquid based reagents in which the anion of the ionic liquid acts as nucleophile. One common characteristic amongst these NILs are that the nucleophilicity of these anions is generally higher than that of their inorganic salts. The increase in nucleophilicity may be attributed to the presence of an ionic liquid. Similar effect of ionic liquid has been reported for fluorination by nucleophilic substitution,<sup>114</sup> nucleophilic substitution of activated aryl halides with secondary amines,<sup>115</sup> and reactivity of anionic nucleophiles in ionic liquids.<sup>116, 117</sup> Synthesis of NILs **160-163** has been achieved by the anion metathesis of halide ion of ionic liquid **159** using corresponding sodium or potassium salts (Scheme 47).

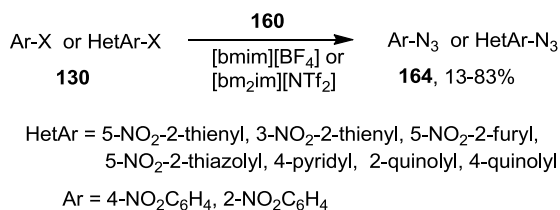


**Scheme 47:** Synthesis of nucleophilic ionic liquids.

Anna *et al.* were the first to report the use of [bmim][N<sub>3</sub>] **160** in aromatic nucleophilic substitution reaction (S<sub>N</sub>Ar) (Scheme 48).<sup>51</sup> A comprehensive discussion of solvent effect and substrate scope revealed interesting aspects of the reaction. Hydrogen bond donor ability (α) of the solvent played a key role in the outcome of the reaction. It was found that high α disfavors the reaction by stabilizing the nucleophile through coordination. Better yield of aryl azides **164** were obtained by using **160** in [bmim][BF<sub>4</sub>] compared to NaN<sub>3</sub> in MeOH. Also the acidic C2-proton of [bmim] ion in [bmim][BF<sub>4</sub>] coordinates with the N<sub>3</sub><sup>-</sup> ion and decrease its

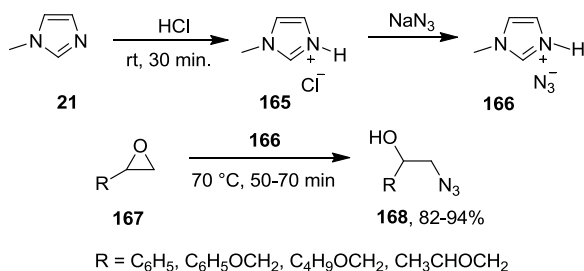


nucleophilicity. Replacing C2-proton with the methyl group in [bm<sub>2</sub>m][N<sub>3</sub>] and using [bm<sub>2</sub>m][NTf<sub>2</sub>] as solvent improved the yield of aryl azides.



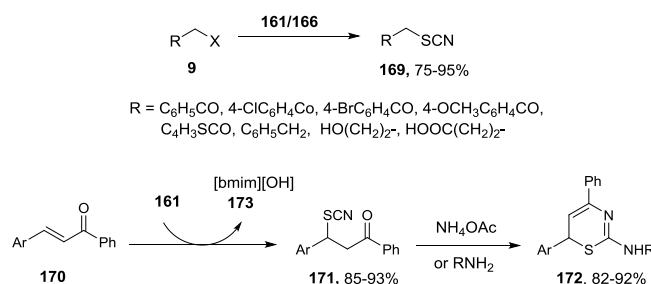
**Scheme 48:** Aromatic nucleophilic substitution reaction using [bmim][N<sub>3</sub>] & [bm<sub>2</sub>m][N<sub>3</sub>].

Heidarizadeh and co-workers described the synthesis of a novel protic azido functionalized nucleophilic ionic liquid **166** from 1-methylimidazole **21** (Scheme 49).<sup>118</sup> The reaction of **21** with hydrochloric acid at room temperature gave 1-methyl-1H-imidazol-3-ium chloride **165** which on anion exchange with NaN<sub>3</sub> in dry CH<sub>3</sub>CN resulted in **166**. The nucleophilic ability of reagent **166** was evaluated for the ring opening of epoxides **167** to 1,2-azidoalcohols **168**.<sup>118</sup> In this reaction multiple-functions such as solvent, reagent and an activator were accomplished by **166**. The acidic hydrogen of **166** activated the reaction, and azide anion acted as the nucleophilic source.



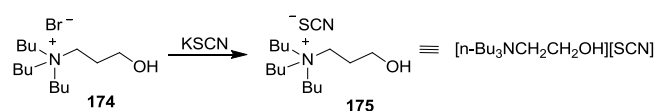
**Scheme 49:** Synthesis of NIL **166** and application in ring opening of epoxides.

Thiocyanate functionality is generally introduced *via* nucleophilic substitution reaction of alkyl halides with metal thiocyanates.<sup>119</sup> Prolonged heating at 50 °C and the chromatographic purification with silica gel leads to the formation of thermodynamically favoured isothiocyanates. To overcome these difficulties, Kamal and Chouhan reported novel NILs [bmim][SCN] **161**.<sup>120</sup> Reagent **161** was prepared by the anion exchange of **159** with KSCN in acetone. A variety of alkyl halides and substituted phenacyl bromides **9** were converted to corresponding alkyl thiocyanates **169** in high yields at room temperature using **161** under solvent free conditions (Scheme 50). In this reaction [bmim][SCN] plays dual roles as reagent and solvent that obviates the necessity of additional solvent in the reaction mixture. Comparative study of a nucleophilic displacement reaction of alkyl halides was carried out using reagent **161** and KSCN. Complete conversion of **9** to **169** was observed when **161** was employed as the nucleophilic source whereas only 20-30% of **169** were formed in the case of KSCN.



**Scheme 50:** Thiocyanation of alkyl halides and chalcones using [bmim][SCN].

To tune the solubility of nucleophilic ionic liquid with thiocyanate anion, Mohanazadeh and Aghvami synthesized a new ionic liquid 2-hydroxy-*N,N,N*-tributylethanaminium thiocyanate [n-Bu<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>OH][SCN], **175** by an anion metathesis from its corresponding bromide salt **174** (Scheme 51).<sup>121</sup> Reagent **166** is soluble in acetone, chloroform, dichloromethane, and ethanol but insoluble in water, ether, and hexane. This differential solubility is very useful for the separation of product from the reaction mixture. Compound **175** has been used as a reagent and solvent in the synthesis of **169** from **9**.

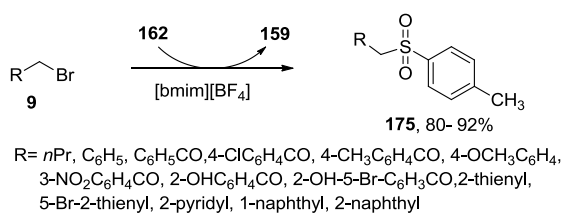


**Scheme 51:** Synthesis of [n-Bu<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>OH][SCN].

Later, Yadav *et al.* developed an efficient method for conjugative hydro thiocyanation of chalcones **170** using **161** (Scheme 50).<sup>122</sup> The superior nucleophilicity of **161** led to the formation of β-thiocyanato α,β-unsaturated ketones **171** in very good yields (85-93%). Compound **171** was further transformed to the pharmaceutically interesting molecule 2-amino-1,3-thiazines **172** by reacting with ammonium acetate or alkyl amines. The advantage of the method is easy purification and it does not require chromatographic separation and thus the possibility of rearrangement of thiocyanate to isothiocyanates was minimized. The reagent **161** could be recycled by treating co-product [bmim][OH] **170** with conc. HCl followed by reaction with KSCN at room temperature.

We also reported the synthesis of a novel nucleophilic ionic liquid reagent [bmim][*p*-TolSO<sub>2</sub>] **162**.<sup>123</sup> Synthesis of **162** was achieved by the reaction of [bmim][Br] with sodium *p*-toluenesulfonate (*p*-TolSO<sub>2</sub>Na) in acetone (Scheme 47). Furthermore, **162** was utilized for the synthesis of sulfones and β-ketosulfones **176** from alkyl and phenacyl bromides (Scheme 52). Detailed solvent study was carried out to find the best suitable solvent for the synthesis of **176**.<sup>122</sup> Of the solvents screened, [bmim][BF<sub>4</sub>] was found to be most efficient due to its non-coordinating nature, while solvents like [bmim][Br] and CH<sub>3</sub>CN did not result in the product formation. By comparing the yield of **176** using *p*TolSO<sub>2</sub>Na and reagent **162** in [bmim][BF<sub>4</sub>], it was found that higher yields were obtained in case of **162**. Thus, it is proposed that

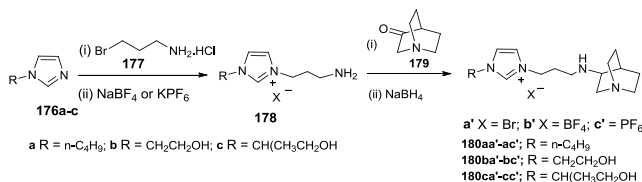
the nucleophilicity of *p*-TolSO<sub>2</sub><sup>-</sup> ion is higher for **162** than that of *p*-TolSO<sub>2</sub>Na.



**Scheme 52:** Synthesis of sulfones and  $\beta$ -ketosulfones from using [bmim][*p*-TolSO<sub>2</sub>].

## 2.11. Ionic liquid-supported quinuclidine

Cheng *et al.* have synthesized quinuclidine-functionalized ionic liquids **181**.<sup>124, 125</sup> The target ionic liquids **181** were obtained as shown in **Scheme 53**. Initially, quaternization of imidazoles **176** with 4-bromobutyl amine **177** gave amino-functionalized ionic liquid **178**. Reductive amination of **178** with quinuclidin-3-one **179** gave **180aa'-ac'** that on further anion exchange with NaBF<sub>4</sub> or KPF<sub>6</sub> led to **180ba'-bc'** and **180ca'-cc'**, respectively.

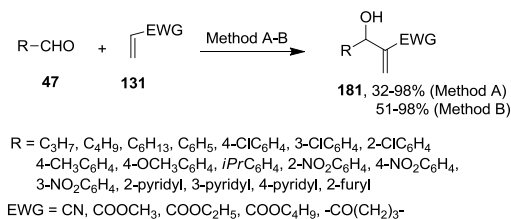


**Scheme 53:** Synthesis of quinuclidine-functionalized ionic liquids **181**.

Morita-Baylis-Hillman (MBH) reaction is an efficient and simple carbon-carbon bond forming reactions in organic synthesis. Stoichiometric amount of Lewis bases such as DABCO, DBU, DMAP, PPh<sub>3</sub> and imidazole are required to facilitate the MBH reaction.<sup>126, 127</sup> To solve the problems associated with the recovery and reuse of Lewis base **180** was used as homogeneous catalysts in the MBH reaction of aldehydes **47** with alkenes **131** (**Scheme 54**). Of all the solvents screened for the MBH reaction, polar protic solvents like methanol proved to be the most efficient. Further examination revealed that the amount of methanol also had a pronounced effect on the yield of **181** and optimal yield was achieved when **180ab'** was employed with two equiv of methanol in the reaction mixture (**Scheme 54**, Method A). When ionic liquids [bmim][BF<sub>4</sub>], [bmim][PF<sub>6</sub>], [bupy][BF<sub>4</sub>] and [bmmim][BF<sub>4</sub>] were used as solvents the yields of **181** were found to be substantially lower than those in methanol. Remarkably, the catalyst **180ab'** was equally efficient for poor substrates like cyclicenones and *p*-methoxybenzaldehyde. Moreover, **181b** exhibited much better catalytic activity than some well known Lewis bases such as 3-quinuclidinone and DABCO under the given reaction conditions.

Quinuclidine functionalized ionic liquid with a hydroxyl group in alkyl side chain **180ba'-bc'** and **180ca'-cc'** showed higher catalytic activity as compared to the non hydroxyl

counterpart **180aa'-ac'** even at lower catalyst loading (20 mol %) under solvent free conditions (**Scheme 54**, method A vs method B). This is attributed to hydrogen bond activation and/or the promotion of intramolecular proton transfer by the hydroxyl group of **180ba'-bc'** and **180ca'-cc'**. As the catalyst offered a homogenous reaction and heterogeneous separation **180** can be easily separated from the products and reused at least six times without significant loss of activity. Moreover, MBH reactions of *N*-sulfonated imines **135** with various substrates such as methyl acrylate and acrylonitrile were promoted to give exclusively the desired adducts **136** (**Scheme 37**, method B & C).



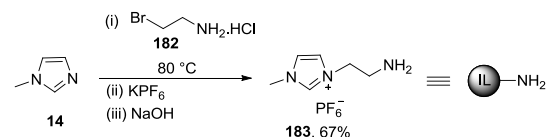
Method A: **180ab'** (0.3 equiv), MeOH (2 equiv), 62–98%  
 Method B: **180ca'** (0.2 equiv)

**Scheme 54:** Morita-Baylis-Hillman reaction catalysed by **180**.

## 3. Functionalized ionic liquid as scavengers

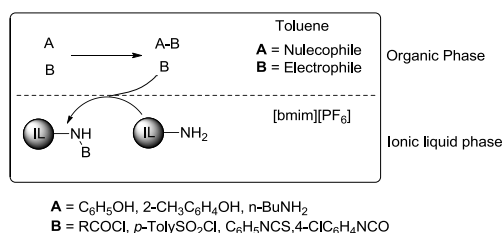
### 3.1 Amino functionalized ionic liquids

Song and group synthesized amino functionalized ionic liquid **183** by *n*-alkylation of 1-methylimidazole **14** with 2-bromoethylamine hydrobromide **182**, followed by anion exchange with KPF<sub>6</sub> and neutralization with NaOH (**Scheme 55**).<sup>56</sup> They further demonstrated the application of **183** as scavengers to remove excess of electrophiles like *p*-toluenesulfonyl chloride, acid chlorides, isothiocyanate, and isocyanates from the reaction mixture (Figure 2).



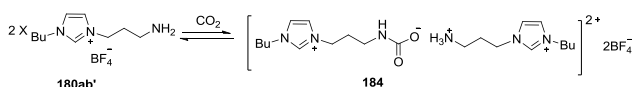
**Scheme 55:** Synthesis of amino functionalized ionic liquid.

Due to the viscous nature of **183**, a longer time (over 9 h) was required to scavenge *p*-toluenesulfonyl chloride from a toluene solution (Figure 2). Addition of conventional ionic liquid [bmim][PF<sub>6</sub>] into the reaction mixture dramatically enhanced the scavenging process (35 min). The large difference in special gravity and high interfacial tension between ionic liquid phase ([bmim][PF<sub>6</sub>], **183**, and organic solvents (toluene) caused the phase separation. The electrophile-free organic phase was separated by decantation, and the pure compound was extracted using CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O from ionic liquid phase. A small library of aromatic esters has been synthesized from various benzoyl chlorides with different phenols using **183** as scavenger. The products were obtained in high yields (>97%) and purity (>97%). Moreover, the reagent **183** was regenerated and reused for three cycles with comparable activity.



**Figure 2:** Scavenging of electrophiles using **183**.

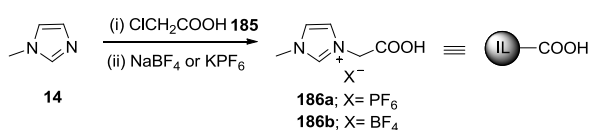
Davis and co-workers have used amino functionalized ionic liquid **180ab'** as a recyclable scavenger for carbon dioxide.<sup>128</sup> In general, aqueous amines are used for the removal of carbon dioxide from natural gas. Conversely, in these systems, the uptake of the volatile amine sequestering agent and water into the gas stream is problematic. To deal with these problems Davis group used **180ab'** to capture CO<sub>2</sub> as carbamate **184** (Scheme 56). The molar uptake of CO<sub>2</sub> per mole of **180ab'** was close to 0.5, which is the theoretical maximum for CO<sub>2</sub> as an ammonium carbamate. Moreover, the uptake of **180ab'** is comparable to the regular sequestering amines, such as diisopropanolamine (DIPA), β,β'-hydroxyaminoethyl ether (DGA), and monoethanolamine (MEA). The process is reversible and CO<sub>2</sub> could be expelled from the **184** by heating in vacuum. The recovered ionic liquid **180ab'** can be reused for five cycles effectively. FT-IR and NMR spectroscopic techniques were used to analyze the gas-treated ionic liquid.



**Scheme 56:** Scavenging of CO<sub>2</sub> as carbamate using **180ab'**.

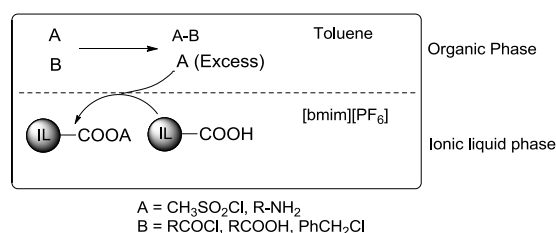
### 3.2. Carboxyl functionalized ionic liquids

Song and group have also synthesized a carboxyl functionalized ionic liquid **186** from 1-methylimidazole **14** as shown in Scheme 57. The reaction of **14** with chloroacetic acid **185** followed by anion exchange with KPF<sub>6</sub> or NaBF<sub>4</sub> resulted in corresponding carboxyl functionalized ionic liquid **186**.<sup>55</sup>



**Scheme 57:** Synthesis of carboxyl functionalized ionic liquid.

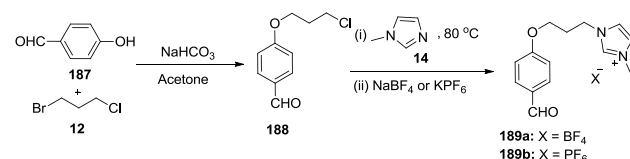
Reagent **186** was used as a scavenger for the removal of excess of materials present in the reaction mixture of the synthesis of sulfonyl esters, amides and acid anhydrides (Figure 3).<sup>55</sup> The products were isolated in pure form by simple decantation of toluene, followed by extraction with CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. The generality of the method was further extended by employing **186** in the synthesis of *N*-acyl-*N*-alkylpiperazines. Also **186** was regenerated by the hydrolysis of the ionic phase and recycled thrice without any marked decrease in activity.



**Figure 3:** Scavenging of excess benzyl chlorides, sulfonyl chlorides, and amines using **186**.

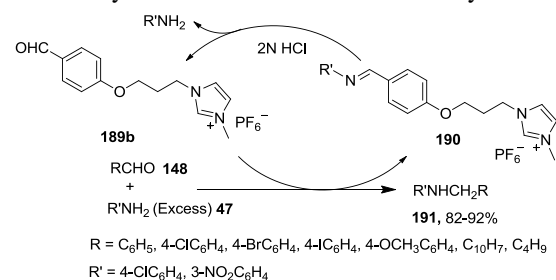
### 3.3. Aldehyde functionalized ionic liquid

Reductive amination is a powerful tool for synthesis of structurally diverse secondary amines that are used in high throughput synthesis. Over alkylation is the main concern in reductive amination process, which leads to the formation of tertiary amines. Excess of primary amine has been employed to prevail over alkylation.<sup>129, 130</sup> The excess amine has to be removed by tedious column chromatography or traditional distillations in order to get pure compounds. These techniques are often time consuming, labor-intensive, expensive process, and may not result always in a pure compound. To overcome these problems, recently our group designed and synthesized an aldehyde functionalized ionic liquid **189**.<sup>131</sup> Synthesis of **189** was achieved in three steps as shown in Scheme 58. Initially, *O*-alkylation of 4-hydroxybenzaldehyde with 1-bromo-3-chloropropane **12** gave 4-(3-chloropropoxy)benzaldehyde **188**. Reaction of **188** with **14** followed by anion exchange with NaBF<sub>4</sub> or KPF<sub>6</sub> afforded desired ionic liquids **189**.



**Scheme 58:** Synthesis of aldehyde functionalized ionic liquid.

Scavenging of excess amines in the synthesis of secondary amines was studied using **189** (Scheme 59). A self induced phase separation of the reaction mixture was observed when **189b** was used as scavenger, which led to simple and effortless isolation of the products from reaction mixture by simple filtration. A small library of secondary amines **191** was synthesized in high yields (82-90%) with excellent purity. Reagent **189b** can be regenerated and reused effectively without much loss in the activity.



**Scheme 59:** Scavenging of amines using **189**.



Huang group has synthesized three aldehyde functionalized ionic liquids and these aldehyde functionalized ionic liquids were easily transformed to corresponding carboxyl functionalized ionic liquids, benzylic alcohol functionalized

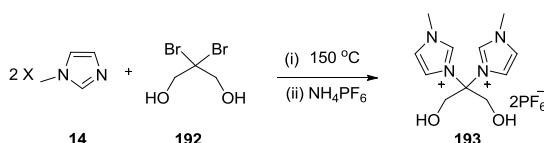
ionic liquids, hydrazone functionalized ionic liquids, and secondary amine functionalized ionic liquids.<sup>132</sup>

**Table 1:** Capture and release of aldehydes in the presence of ketones using diol-functionalized ionic liquid **193**.

Entry	Mixture	% Capture	% Release	Entry	Mixture	% Capture	% Release
1	C <sub>6</sub> H <sub>5</sub> CHO	100	92	5	C <sub>6</sub> H <sub>5</sub> CHO	100	93
	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	0	0		4-BrC <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	0	0
2	2,6-(Cl) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	100	91	6	2-ClC <sub>6</sub> H <sub>4</sub> CHO	100	92
	C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>	0	0		4-BrC <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	0	0
3	2,6-(Cl) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	100	90	7	2,6-(Cl) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	100	90
	C <sub>2</sub> H <sub>5</sub> COC <sub>4</sub> H <sub>9</sub>	0	0		4-BrC <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	0	0
4	2,6-(Cl) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	100	91	8	2,6-(Cl) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	63	92
	Cyclohexanone	0	0		C <sub>6</sub> H <sub>5</sub> CHO	37	0

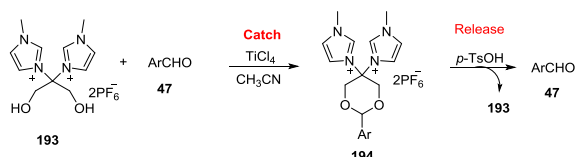
### 3.4. Diol-functionalized ionic liquid

Cai and Liu reported synthesis of a novel diol-functionalized ionic liquid, 2,2-bis(1-(1-methylimidazolium)methylpropane-1,3-diol hexafluorophosphate **193**.<sup>57</sup> Synthesis of **193** has been achieved as shown in Scheme 60. Reaction of **14** with 2,2-bis(bromomethyl)-1,3-propanediol **192** at 150 °C, followed by anion exchange with NH<sub>4</sub>PF<sub>6</sub> yielded diol functionalized ionic liquid **193**.



**Scheme 60:** Synthesis of diol functionalized ionic liquid.

The capture and release studies of different aldehydes were studied using **193** (Scheme 61). The aldehydes were selectively captured as 1,3-dioxane **194** when a mixture of aldehydes and ketones was treated with **193** in the presence of TiCl<sub>4</sub> (Table 1, entry 1-4). The captured aldehydes were further released by the hydrolysis of **194** in the presence of TsOH and recovered **193** was reused four times without significant loss of activity.<sup>57</sup>

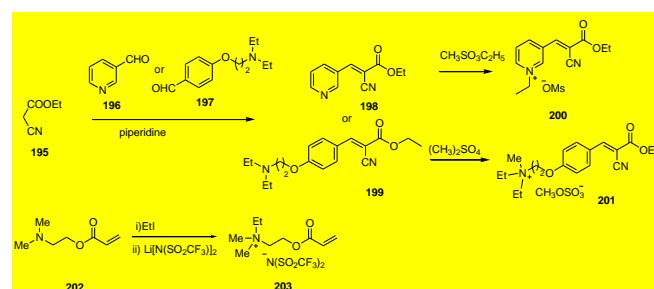


**Scheme 61:** Capture and release of aldehydes using **193**.

### 3.5 Ionic liquid functionalized with Michael acceptors

The removal of malodorous and toxic volatile sulfur compounds is a major concern in oil refineries, food processing and in paper mills. Gunaratne *et al.* have synthesized trialkylammonium and alkylpyridinium based

three ionic liquids functionalized with Michael acceptors **200**, **201** and **203** for scavenging thiols and hydrogen sulfide.<sup>133</sup> Synthesis of ionic liquids **200** and **201** was achieved from ethyl cyanoacetate **195** as shown in scheme 62. Reaction of **195** with pyridine carboxaldehyde **196** and functionalized benzaldehyde **197** followed by quaternization with dimethyl sulfate or ethylmethyl sulfate resulted in formation of ionic liquids **200** and **201**, respectively. On the other hand ionic liquid **203** was synthesized from 2-(dimethylamino)ethyl acrylate **202** by quaternization with ethyl iodide followed by anion exchange with Li[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]. The ionic liquids **200**, **201** and **203** have been used as Michael acceptors for the scavenging of thiols and hydrogen sulfide. Among these three ionic liquids **203** has shown superior reactivity as scavenger for thiols and H<sub>2</sub>S. The non-volatile nature, easy phase separation and masking the malodors property of volatile sulfur compounds are the main advantageous of these ionic liquids.



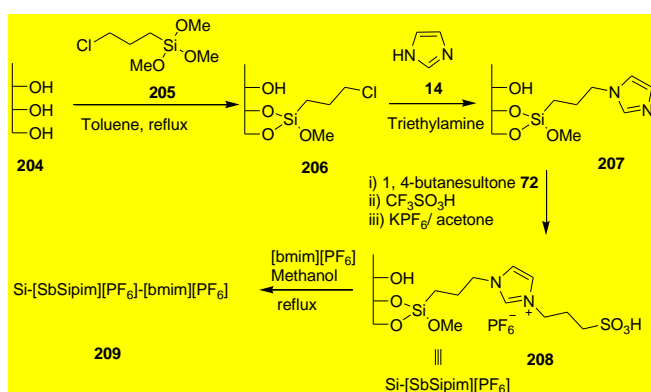
**Scheme 62:** Synthesis of ionic liquids **200**, **201** & **203**.

### 3.6 Silica-supported sulfonic acid functionalized ionic liquid

To overcome the separation issues due to solubility of some of the ionic liquid-supported scavengers, Song and his group synthesized a heterogeneous silica-supported sulfonic acid functionalized ionic liquid Si-[SbSipim][PF<sub>6</sub>] **208**.<sup>134</sup> Synthesis of **208**, was achieved by sequential reaction of

silica with (3-chloropropyl)trimethoxysilane **205**, imidazole **14** and 1,4-butanedithione **72** followed by neutralization with trifluoromethanesulfonic acid and anion exchange with PF<sub>6</sub><sup>-</sup> (Scheme 63).

Reagent **208** was utilized for the scavenging of excess amines during synthesis of amides and sulfonamides. It was found that scavenging of anilines in toluene using reagent **208** was sluggish and took longer time (>10h). This longer scavenging time may be due to the heterogeneous nature of reagent **208**. However, use of **209** with a coating of conventional ionic liquid [bmim][PF<sub>6</sub>] on to the reagent **208** has dramatically shortened the scavenging process time (100 min). Using this strategy small library of amides and sulfonamides has been synthesized in excellent yields (96-98%) with high purity (>97.6%). The reagent can be regenerated and reused effectively several times without much significant difference in activity.



**Scheme 63:** Synthesis of silica-supported sulfonic acid functionalized ionic liquids **208** & **209**.

## Conclusion

The excellent articles published on the use of FILs as reagents in various organic transformations in the last decade are underpinning their importance and great potential in organic synthesis. FILs have provided efficient ways of addressing some of the disadvantages of solid-phase synthesis. They have offered advantages of increased loading of the reagent, fast reaction times in homogeneous environments, easy intermediate analysis using modern techniques, and ready adaptability to literature conditions. Enormous range of combinations with tailor-made properties could be synthesized by varying the anions and cations. These materials have apparent advantages over other soluble supports such as PEG and perfluorinated compounds.

The application of functionalized ionic liquids (FILs) as reagents and scavengers in organic synthesis are still in the early stage of development. The linker strategy developed for solid-phase synthesis and fluorous phase synthesis can be applied to ionic liquids to generate new functionalized ionic liquids. With increased availability of functionalized ionic liquids, they should find applications in the synthesis of complex molecules and biomolecules.

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