Recent Developments on Task Specific Ionic Liquids

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Abstract: Task specific ionic liquids (TSILs) have received increased attention over the last few years as it is possible to form any specific ionic liquid composition depending upon user's need of the desired physical, chemical and biological properties. The present review gives an update of recent developments in the field of TSILs with emphasis on their applications in organic synthesis.

Key Words: Ionic liquids, task specific ionic liquids, green reaction media, chiral ionic liquids.

INTRODUCTION

From simple detergents to life saving drugs to the plastics, many of life's essential commodities would be impossible without the chemical industry. Few people choose to live without the benefits of modern chemistry, but often the benefits are associated with other fields, such as medicine, materials, or engineering. Over recent decades, the chemical industry has been increasingly regulated by stringent and compelling demands for greener processes, and the development of cost-effective and environmentally benign catalytic systems in order to reduce harmful emissions and effluents and ensure worker safety. However, many chemical industry processes have been or still are highly polluting. The past 15 years, ionic liquids have provided solution to problems accompanying increased production with sustainable green approaches. It is mainly attributed to their unique physical properties that are mainly in accordance to a green chemistry point of view and a chemical point of view. Such properties include polar, non-coordinating nature, generally low flammability due primarily to low volatility, and their ability to dissolve a range of organic and inorganic compounds. Exploitation of these properties has resulted in an increased use of ionic liquids in both separations and in catalysis.

Even though the term ionic liquid was introduced only recently, the history of ionic liquids dates back to 1914 when Walden [1] reported the physical properties of ionic liquid [EtNH$_3$][NO$_3$]. Earlier developments in the field of ionic liquids were critically reviewed by Gorden [2] in 1969. It was the pioneering study of Wilkes and co- workers [3,4] that resulted in increasing popularity of ionic liquids as reaction and extraction media in research and development, and then it has widely been promoted as "green - solvents." The first successful use of an ionic liquid, dialkylimidazolium chloroaluminate, as a catalyst in Friedel-Crafts acylations was reported in 1986 [5]. However, moisture sensitivity and decomposition of this chloroaluminate salt under normal atmospheric conditions were two major drawbacks that precluded their practical use. After this report, a resurgence of the rich chemistry of ionic liquids began. The pioneering work of Seddon and his associates then engraved the ionic liquids to its well- known versatility [6].
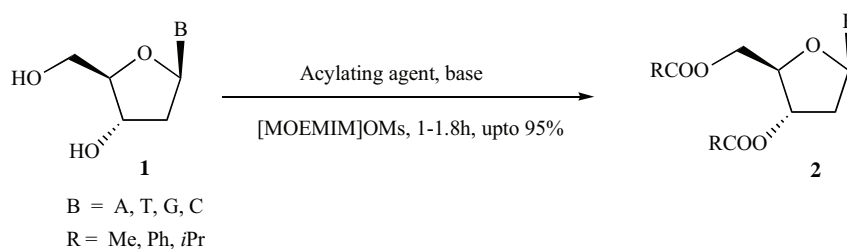
Davis and co-workers [7] first demonstrated the concept of designing ionic liquid (IL) to interact with a solute in a specific fashion, showing that a thiazolium IL could function as solvent-catalyst for the benzoin condensation. He then outlined the concept in a

brief review [8] by introducing the term ''task-specific ionic liquids'' (TSILs) to describe IL which incorporate functional groups designed to impart to them particular properties or reactivities [9]. The task specific ionic liquids (TSILs) may be defined as ionic liquids in which functional group is covalently tethered to the cation or anion (or both) of the IL. These can be considered as liquid version of solid supported catalyst with added advantage of kinetic mobility and large operational surface area. Today, TSILs form an important class of ionic liquids that has received increasing attention over the last few years because it is possible to form any specific IL composition depending upon user's needs of desired physical, chemical and biological properties. Apart from this, there are several rationales for the incorporation of a functional group into an IL. First, the inclusion of the functional group will doubtless alter the solvent parameters of an IL. The parameters like polarity, H-bond acidity and basicity, polarizability, *etc.* are the attributes that make any chemical a good or poor solvent for a given solute. A second rationale for the inclusion of a functional group in an IL is to imbue the salt with a capacity to covalently bind to or catalytically activate a dissolved substrate. For example, a primary amine functionalized imidazolium salt can separate CO$_2$ from gas streams [10], while ionic liquids bearing appended sulfonic acid groups were used as solvent-catalyst for esterification [11]. In last five years various types of TSILs have been designed to accomplish the specific tasks like catalysis, organic synthesis, chiral induction, synthesis and stabilization of nano-materials, electrochemical applications, catalyst surface modifiers *etc.*, and they have been comprehensively reviewed by various authors. The first in depth review in the field of TSIL appeared in the year 2004 by Davis [8] which dealt with synthesis of TSIL and their applications in organic synthesis, catalysis, separation, and electrochemistry. Later on, developments in the field of functionalized imidazolium TSILs has been reviewed by Sang-gi Lee [12]. Winkel *et al*. [13] gave an account of applications of task specific chiral ionic liquids in asymmetric synthesis. The present review attempts to give an update of recent developments in the field of TSILs with particular emphasis on their applications in organic synthesis, catalysis and nanoparticle synthesis.
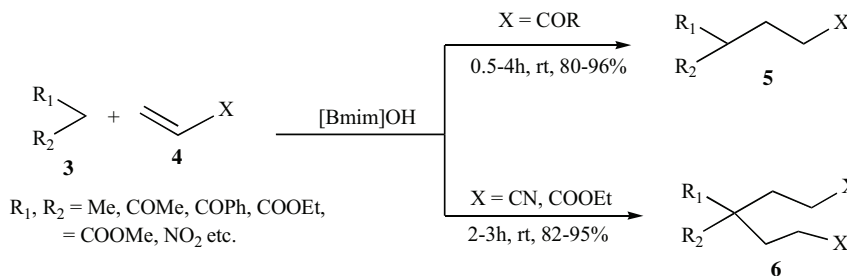
1. TSILS AS REACTION MEDIA AND CATALYST

The chemical property that imparts a variety of physical characteristics to the ionic liquids which has been little investigated is the relative acidity or basicity of the component ions. The common place starting point that many of the ions are innert is not always correct as one looks further a field for task specific ions. Here, we describe recent work with a range of anions and cations having
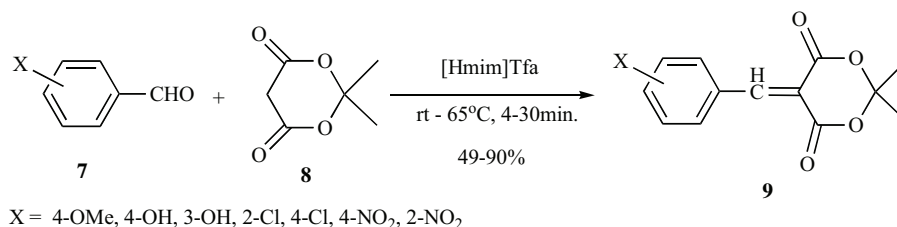
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Scheme 1.

B = A, T, G, C

R = Me, Ph, *i*Pr

Scheme 2.

R₁, R₂ = Me, COMe, COPh, COOEt,
= COOMe, NO₂ etc.

Scheme 3.

X = 4-OMe, 4-OH, 3-OH, 2-Cl, 4-Cl, 4-NO₂, 2-NO₂

distinct Lewis acidity or --basicity and functionalization of anion or cation depending upon the task. The ionic liquids containing Lewis base anions can exhibit a base catalysis phenomenon, which can be utilized, for example, in a variety of acetylation reactions. The majority of ions used in the formulation of ionic liquids can be considered in terms of the Lewis definition of acids and bases *i.e.* whether they are capable of accepting or donating an electron pair. However, there are also a number of ions that must be considered according to the Brønsted definition; those that are able to donate or accept a proton. For example, a number of ionic liquids containing protonated cations and anions like dihydrogen phosphate and hydrogen sulfate fall into this category.

Nucleoside chemistry is an important area of research, but one in which solvent choice is severely compromised by poor solubility. Most organic solvents are not suitable, the exceptions are undesirable from an environmental point of view. Salunkhe and their coworkers have investigated [14] that the ionic liquids were suitable, since the solubility of nucleosides was very good, especially in a series of methanesulfonate salts. The acylation of 2'-deoxyribonuclosides **1** was studied in various ionic liquids wherein the best yields of the acylated products **2** were achieved using 1-methoxyethyl-3-methylimidazolium methane sulfonate [MOEMIM]OMs as a TSIL. This investigation illustrated the benefits of solubility and recoverability, as well as efficient reaction conditions, which ionic liquids can provide for nucleosides (Scheme **1**).

The chemoselectivity of task specific ionic liquid, 1-butyl-3-methylimidazolium hydroxide [Bmim]OH through the Michael addition of active methylene compounds **3** with conjugated ketones,
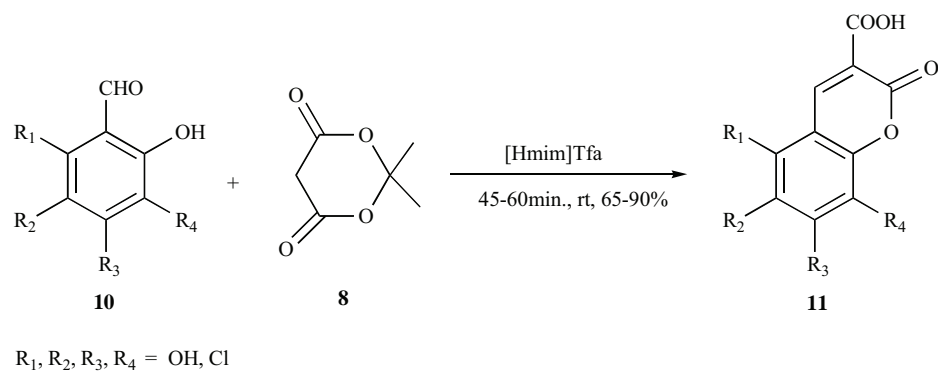
esters, and nitriles **4** was demonstrated by Ranu and Banerjee [15]. They realized that vinyl ketones and chalcones gave mono-adducts **5** while the unsaturated esters and nitriles gave *bis*-adducts **6** in quantitative yields (80-96%) at room temperature (Scheme **2**).

Later on, Salunkhe and coworkers have investigated the Knoevenagel condensation of Meldrum's acid **8** with variety of aldehydes **7** using various kinds of ionic liquids such as 1-butyl-3-methylimidazolium hexafluoroborate [Bmim]PF₆, 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim]BF₄, 1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim]BF₄, and 1-methylimidazolium-trifluoroacetate, [Hmim]Tfa afforded corresponding ylidene derivatives **9**. They have studied the effect of these ionic liquids on the yields of the products and found that best yields were achieved using ionic liquid [Hmim]Tfa [16] (**Scheme 3**) at room temperature. Furthermore, ionic liquid is easily reused without any appreciable loss in activity.
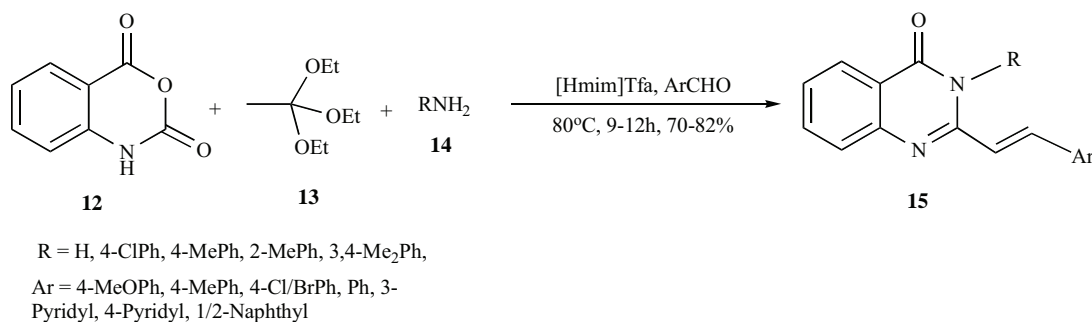
Recently, Salunkhe and their coworkers have further investigated [17] the utility of task specific ionic liquid [Hmim]Tfa for the synthesis of variety of coumarin-3-carboxylic acids **11** through the reaction of various substituted *ortho*-hydroxy aryl aldehydes **10** with Meldrum's acid **8** at room temperature (Scheme **4**).

The utility of task specific ionic liquid [Hmim]Tfa was further extended in the synthesis of variety of 2-styryl-4(*3H*)-quinozolines **15** through the reaction of isatoic anhydride **12**, triethylorthoformate **13**, using various amines **14** and variety of substituted aromatic aldehydes by Dabiri and coworkers [18] (Scheme **5**).
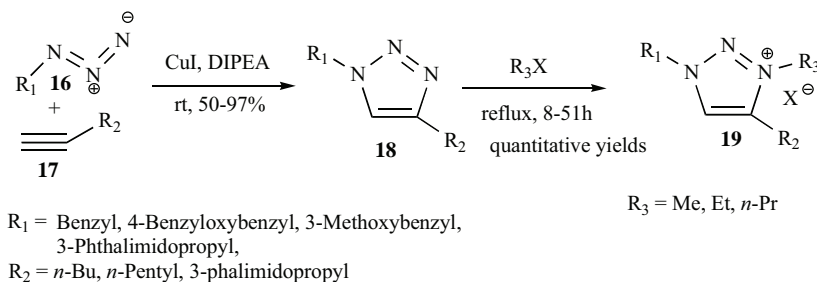
Recently, TSILs based on 1,2,3 triazolium salts **19** have been prepared by well known Cu catalyzed click reaction between various azides **16** with variety of alkynes **17** followed by alkylation of
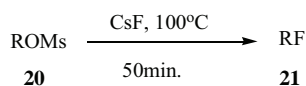
Scheme 4.

R = H, 4-ClPh, 4-MePh, 2-MePh, 3,4-Me₂Ph,

Ar = 4-MeOPh, 4-MePh, 4-Cl/BrPh, Ph, 3-
Pyridyl, 4-Pyridyl, 1/2-Naphthyl

Scheme 5.

R₁ = Benzyl, 4-Benzyloxybenzyl, 3-Methoxybenzyl,
        3-Phthalimidopropyl,
R₂ = *n*-Bu, *n*-Pentyl, 3-phalimidopropyl

Scheme 6.

triazoles **18** with various alkyl halides, with the intention of simul-taneous multifunctionalization of the cation (Scheme **6**) [19]. This has an added advantage of controlling both chemical (introduction of functional moiety) and physical (introduction of alkyl chain) properties at a time. This has brought forward the new concept of "Multi Task Specific Ionic Liquids".

Chi and coworkers studied [20] the synergistic effect of *tert.* al-cohol functionalized ionic liquid in nucleophilic fluorination through the reaction of various mesylates **20** with cesium fluoride afforded corresponding fluoro-compound **21** (Scheme **7**). The dual advantage of combination of ionic liquid and tertiary alcohol was acceleration of reaction with minimization of side reactions (see Table **1**). The weak H-F hydrogen bonding maintained the inherent nucleophilicity and reduced the basicity of fluoride anion which in turn reduced the side reactions.

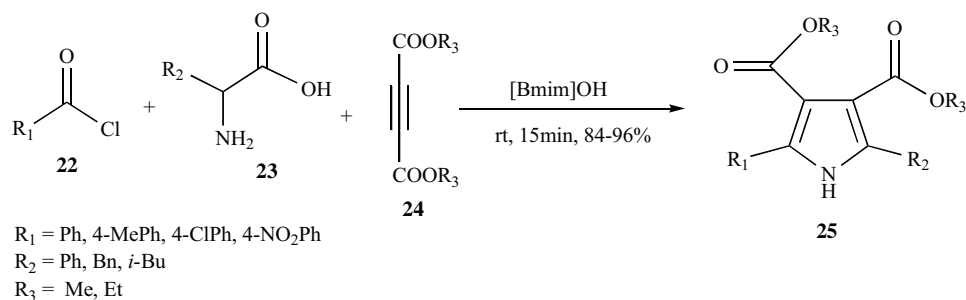R = 2-Naphthyloxypropane, Protected glycosides, protected steroids

Scheme 7.

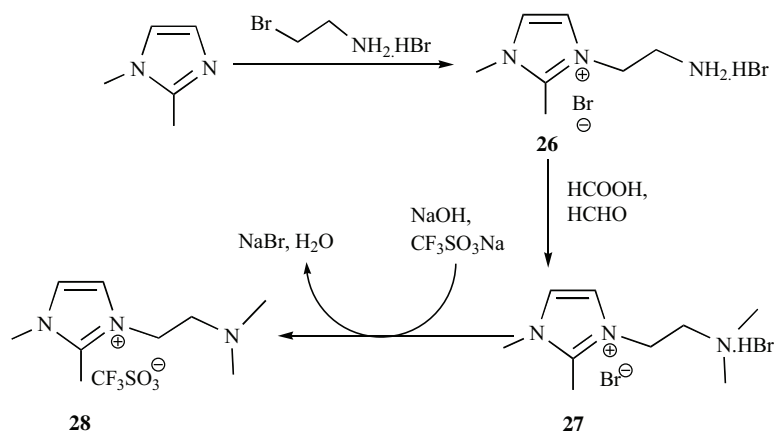**Table 1. Effect of IL on Nucleophilic Fluorination**

Solvent/Ionic Liquid	Equivalent	Isolated Yields (%)
*tert.*Butanol	0.5	22
[Bmim]OMs	0.5	30
[Bmim]OMs/*tert.*Butanol	0.5/0.5	37
	0.5	97

A basic functionalized ionic liquid, 1-butyl-3-methylimidazolium hydroxide [Bmim]OH, catalyzed the three-component condensation reaction of acid chlorides **22**, amino acids **23**, and dialkyl acetylenedicarboxylates **24** in water to afford func-tionalized pyrroles **25** in high yields [21]. Yavari and co-workers studied the reaction in ten different ionic liquids out of which [Bmim]OH was found to be effective at 80ºC. The reaction was found to be faster for benzoyl chlorides containing electron-withdrawing substituents (Scheme **8**).
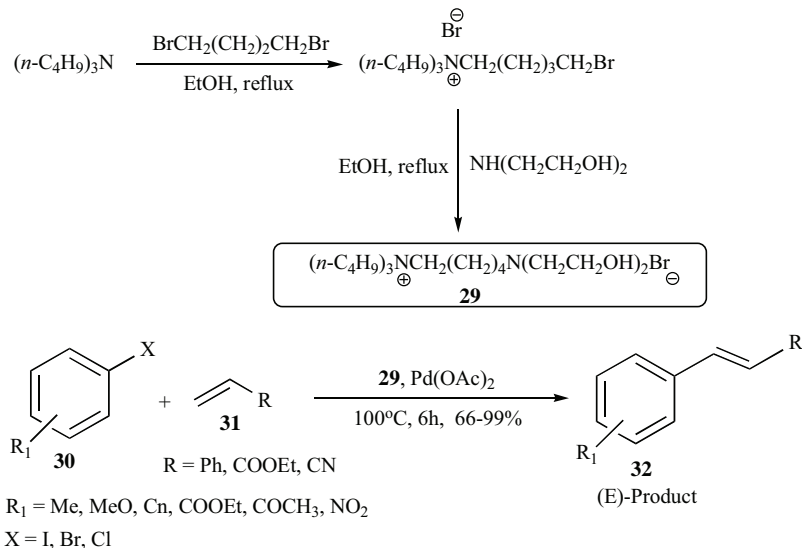
Zhang *et al.* [22] synthesized and used the basic TSIL, 1-(*N,N*-dimethylaminoethyl)-2,3-dimethylimidazolium   trifluoromethane-

R$_1$ = Ph, 4-MePh, 4-ClPh, 4-NO$_2$Ph
R$_2$ = Ph, Bn, *i*-Bu
R$_3$ = Me, Et

Scheme 8.

Scheme 9.

R = Ph, COOEt, CN

R$_1$ = Me, MeO, Cn, COOEt, COCH$_3$, NO$_2$
X = I, Br, Cl

Scheme 10.

sulfonate **28**, [Mammim]TfO for promotion of hydrogenation of CO$_2$ to formic acid with ruthenium supported on silica as heterogeneous catalyst (Scheme **9**). The advantage of this method is that it has satisfactory activity and high selectivity. The unique features of recovery of formic acid and reuse of catalyst makes this approach compatible to industrial application.

Pavlinac and their coworkers recently published review [23] has taken an account of halogenation of organic compounds in ionic liquids with special focus on fluorofunctionalization and chlorofunctionalization. Wang and coworkers have designed [24], synthesized and used an ethanolamine functionalized task specific ionic

liquid, 4-di(hydroxyethyl) aminobutyl tributylammonium bromide, **29** for the Heck coupling reaction where IL performs the role of base, ligand and reaction medium with added advantage of recyclability of the system (Scheme **10**).

Bellina *et al.* [25] synthesized a series of glycerylimidazolium based task specific ionic liquids **33, 34** aiming that their applications to palladium catalyzed coupling reactions (Fig. **1**). They extensively studied the physical and physico-chemical parameters such as thermal stability, hydrogen bonding, conductivity and application of these series of TSIL for Heck reaction.
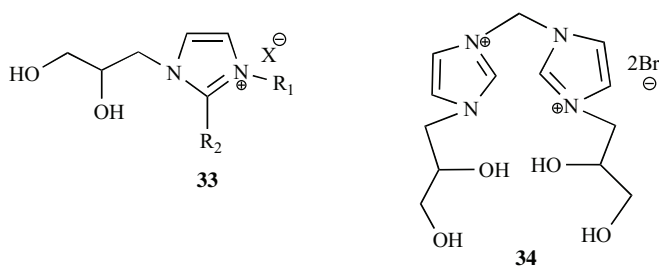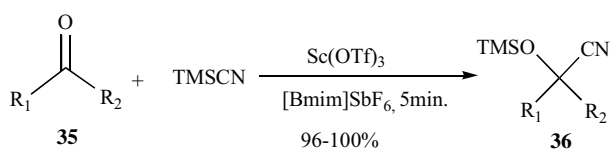
Fig. (1).

Fig. (2).

Park and co-workers [26] studied the cynosilylation of carbonyl compounds **35** afforded compound **36** using scandium triflate as catalyst and found a dramatic increase of catalytic activity using ionic liquid 1-butyl-3-methylimidazolium antimony hexafluoride, [Bmim]SbF$_6$. It is attributed to enhancement of the Lewis acidity of the catalyst by anion exchange between ionic liquid and scandium triflate (Scheme **11**).
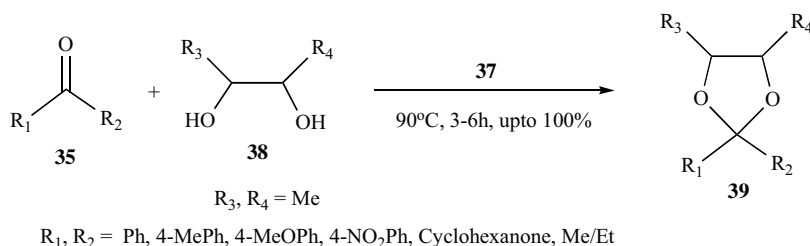
heteropolyanion. Their melting points above 100ºC make them non-conventional ionic liquids. These ionic liquids being soluble in starting materials *i.e.* carboxylic acids and alcohols works as homogeneous catalyst and being insoluble in product *i.e.* esters at the end of reaction IL comes out of reaction mixture as if it is a heterogeneous catalyst.

Fig. (3).

R$_1$ = 2/3/4-MeOPh, 4-ClPh, 2-Naph., 2-Furaldehyde, *n*-Propyl, Isopropyl
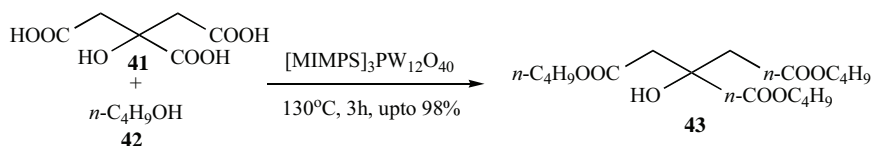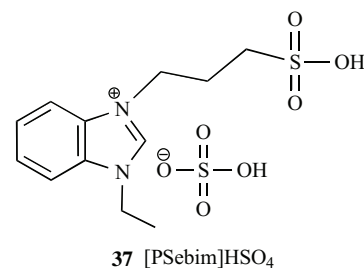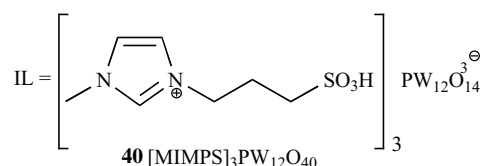R$_2$ = CH$_3$, Et, Ph,

Scheme 11.

Wang and their coworkers developed [27] variety of structurally diverse Brønsted acidic benzimidazolium based ionic liquids and explored their use as environmentally benign catalysts for acetalization of various aldehydes **35** using substituted 1,2-ethanediols **38** afforded protected acetals **39** in high yields (Scheme **12**). Out of various catalysts tested, they found that ionic liquid 1-ethyl-3-(3-sulfopropyl)benzimidazolium hydrogen sulfate, [PSebim]HSO$_4$ **37** (Fig. **2**) was efficient for acetalization reaction.

Both the homogeneous and heterogeneous catalysts have counter (interlocking) advantages and disadvantages. So the catalyst having properties of both can be a "dream catalyst". Leng and coworkers developed [28] a non-conventional propane sulphonate functionalized heteropoly-acid based ionic liquid **40** (Fig. **3**) for esterification of citric acid **41** with *n*-butanol **42** (Scheme **13**). These ionic liquids contain three-organic cations and an inorganic

2. TASK SPECIFIC IONIC LIQUIDS-SOLID CATALYSTS

Green and cost-effective catalysts with high efficiency and selectivity are the cornerstones of contemporary synthetic chemistry. Even though easily separable heterogeneous catalysts are preferred in industry, these have some shortcomings like heat or mass transfer and lower chemo and steroselectivities. This can be circumvented by surface modification of solid catalysts. Recently the concepts of Solid catalysts with ionic liquids (SCILs) and Supported ionic liquid phase catalysts (SILPCs) have drawn much attention because, their combination is looked upon as a future option to integrate heterogeneous and homogeneous catalysts. In their first of its kind report Menhert [29,30] and Riisger [31,32] demonstrated the use of ionic liquids in supported liquid phase catalysts (SLPC). Gu [33] and others used hydrophobic ionic liquid for coating the solid- surface of silica supported sulphonic acid catalyst to enhance the selectivity. They successfully demonstrated (Scheme **14**) the significant impact on activity of silica-supported sodium catalyst (Fig. **4**) by
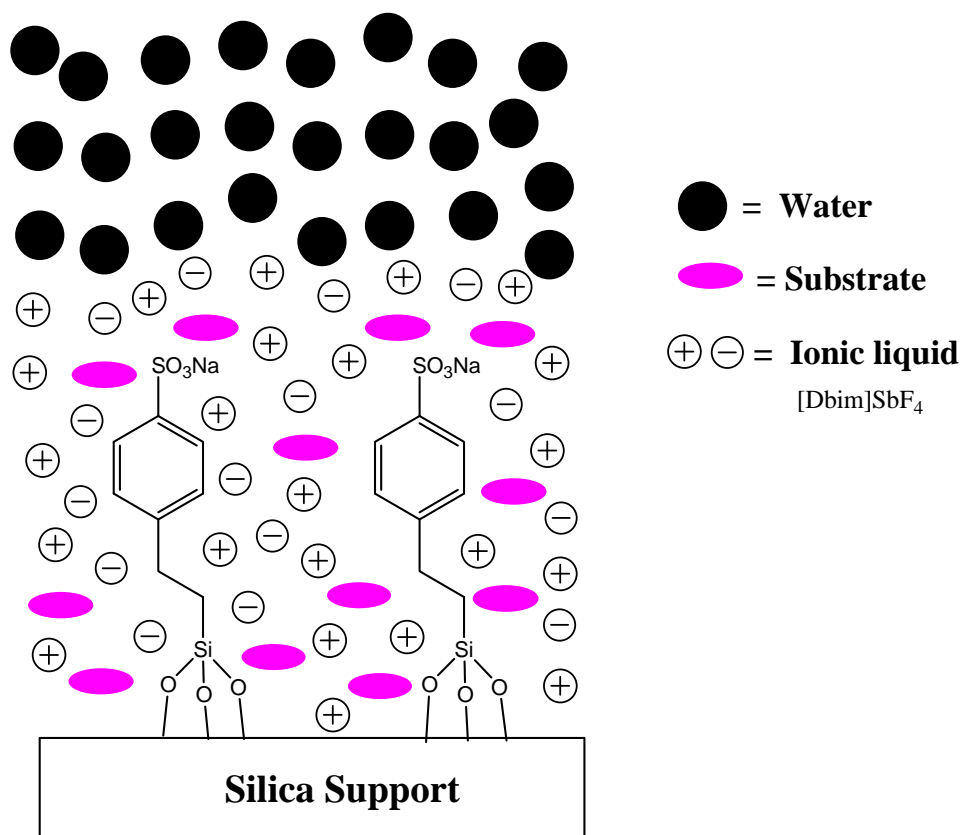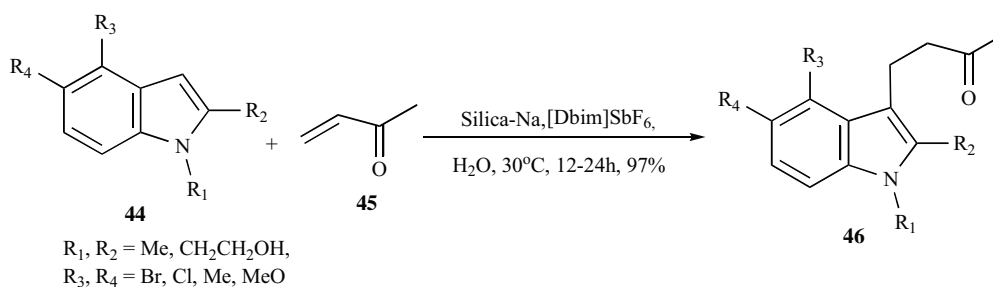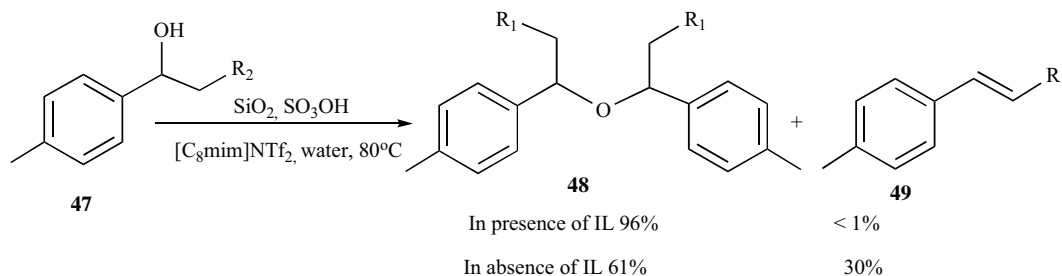

R$_3$, R$_4$ = Me
R$_1$, R$_2$ = Ph, 4-MePh, 4-MeOPh, 4-NO$_2$Ph, Cyclohexanone, Me/Et

Scheme 12.

Scheme 13.

Fig. (4).

R₁, R₂ = Me, CH₂CH₂OH,
R₃, R₄ = Br, Cl, Me, MeO

Scheme 14.

In presence of IL 96%   < 1%

In absence of IL 61%   30%

Scheme 15.

coating it with the IL [Dbim]SbF$_6$ (1-butyl-3- decylimidazolium) leading to enhanced activity towards the Michael reaction of substituted indoles **44** and α,β-unsaturated ketones **45** in water (Scheme **14**). The enhanced activity provides scope to perform the reaction under neutral conditions making it possible to carry out the reaction with acid labile substrates. Interestingly this reaction did not proceed without IL highlighting the significance of IL.
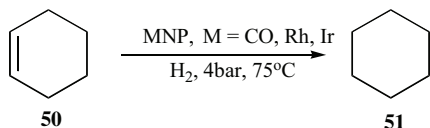
Apart from enhanced activity, catalytic selectivity is another significance of coating the supported catalysts with ILs. The IL showed catalytic selectivities when a set of organic reactions in water were catalyzed by catalyst coated with IL. Etherification of 1-tolyl-1-ethanol **47** catalyzed by SiO$_2$-SO$_3$H leds to 30% of 4-methylstyrene **49** as side product reducing the yield of the desired ether **48** to 61%. However coating of SiO$_2$-SO$_3$H with 25 wt % of [C$_8$mim]NTf$_2$, (1-methyl-3-octylimidazolium) led to a significant selectivity improvement [34] and the ether was obtained in 96% (Scheme **15**).
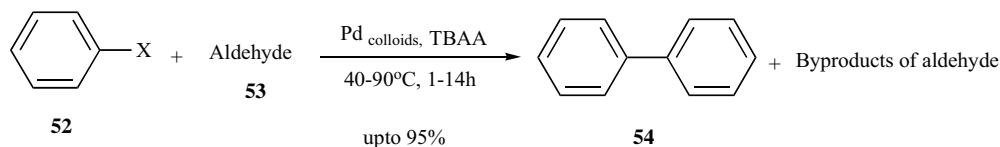
3. NANOMATERIALS IN IONIC LIQUIDS

The search for more efficient catalytic systems that might combine the advantages of both homogeneous (catalyst modulation) and heterogeneous (catalyst recycling) catalysis is an essential requirement of modern chemistry. With the advances of nanochemistry, it has been possible to prepare "soluble" analogues of heterogeneous catalysts. However one of the difficulty of using nanoparticles as catalyst is providing stability of small nanoparticles while retaining the activity. Ionic liquids have been shown to provide "electrostatic" stabilization for metal nanoparticles and more surface area for the reaction to take place [35]. So ionic liquids inturn controls the stability and activity of nanoparticles. Multiphase systems of Ionic liquid-nanoparticles facilitate easy recovery of nanoparticles. There have been several reviews [35,36] about the preparation and application of nanoparticles in ionic liquids, with the most recent having been published in the 2009 [37]. The present review is intended to update the reader about the recent work in the field of combination of two cutting edge topics- nanoparticles and ionic liquids.

Recently, Redel and coworkers [38] have synthesized stable cobalt, rhodium and iridium nanoparticles by thermal decomposition under argon from $Co_2(CO)_8$, $Rh_6(CO)_{16}$ and $Ir_4(CO)_{12}$ dissolved in the ionic liquids [Bmim]BF$_4$, [Bmim]OTf and [Btma]NTf$_2$ [Bmim = *n*-butyl-methyl-imidazolium, Btma = *n*-butyl-tri-methyl-ammonium, OTf = O_3SCF_3, NTf$_2$ = $N[O_2SCF_3]_2$. They achieved very small and uniform nanoparticle size of about 1–3nm in [Bmim]BF$_4$. Increase in size was observed with increase in molecular volume of the ionic liquid anion from [Bmim]OTf to [Btma]NTf$_2$. Importantly, among these nanoparticles the rhodium or iridium nanoparticle/IL systems function as highly effective and recyclable catalysts in the biphasic liquid–liquid hydrogenation of cyclohexene **50** to cyclohexane **51** (Scheme **16**) with activities of up to 1900 mol$_{product}$/(mol$_{metal}$h) and quantitative conversion.

R-N₃ + R₁ ——alkyne——

or expensive phosphane ligands and allows catalyst recycling. The role of tetrabutylammonium acetate (TBAA) is crucial for this process, as this ionic liquid behaves simultaneously as a base, ligand and reaction medium and has effect on the chemoselectivity of the catalysis which cannot be obtained by replacing this ionic liquid with a generic source of acetate anions.

Taher and coworkers [40] reported Pd-NHC–ionic liquid matrix immobilized into ionic liquid layers coated on the surface of Fe$_3$O$_4$ by a simple process (Scheme **18**). These immobilized Pd-NHC exhibited both high catalytic activity and stability for the Suzuki coupling reaction between aryl bromide **52** and arylboronic acid **55** in water. Importantly, this catalyst was simply recovered by an external permanent magnet and recycled without a significant loss in the catalytic activity.

Salunkhe and their coworkers have recently demonstrated [41] the dramatic effect of ionic liquids on shape of copper nanoparticles and their application in 1,3-dipolar cycloaddition reactions of azides **56** and aryl and sugar based terminal alkynes **57** afforded corresponding cycloaddition products **58** (Scheme **19**). Change in anion has led to change in shape of the nanoparticle. Spherical nanoparticles were obtained in [Bmim]BF$_4$ while cubical nanoparticles were obtained in [Bmim]PF$_6$. Both types of nanoparticles have shown profound effect on the cycloaddition reaction between azides and terminal alkynes (Fig. **5**).

$$R\text{-}N_3 + R_1 \xrightarrow[\text{rt, 15-50min., 89-95\%}]{\text{Cu NPs ionic liquid}} \text{product } 58$$

56   **57**

R = Ph, Bz,3-NO$_2$Ph, 2-ClPh, 2-MePh
R$_1$ = Ph, (CH$_2$)$_3$OH, (CH$_2$)$_2$OH, CH$_2$OPh

Scheme 19.

4. CHIRAL IONIC LIQUIDS

Chiral Ionic liquids (CILs) are receiving increasing attention due to their ease of synthesis and properties. These new chiral solvents could play a central role in enantioselective organic chemistry and hopefully expand the scope of chiral solvents. A significant transfer of chirality in these solvents can be expected due to their high degree of organization. It has been reported that most of the ILs possess a polymeric behavior and are highly ordered H-bonded liquids (three-dimensional networks of anions and cations linked together by hydrogen bonds). These specific properties suggest that

$$\text{50} \xrightarrow[\text{H}_2, \text{4bar, 75}^\circ\text{C}]{\text{MNP, M = CO, Rh, Ir}} \text{51}$$
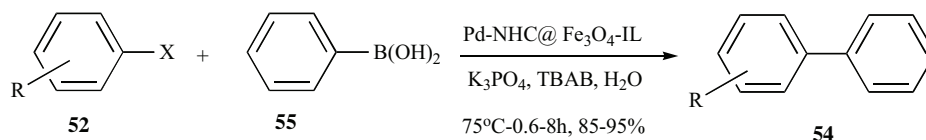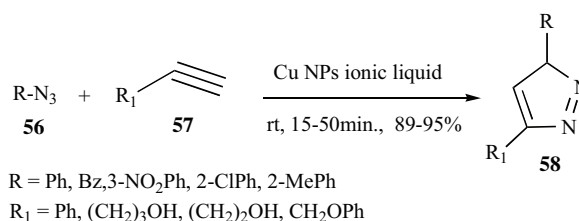
Scheme 16.

Nacci and their coworkers have reported [39] the use of palladium nanoparticles for Ullmann reactions in tetra-*n*-butyl ammonium salt ionic liquids as a reservoir of catalyst with aldehydes **53** as the reductant (Scheme **17**). This type of "ligand-free" catalysis is gaining considerable importance because it avoids the use of toxic

$$\text{52} + \text{Aldehyde } \textbf{53} \xrightarrow[\text{40-90}^\circ\text{C, 1-14h}]{\text{Pd }_{colloids}, \text{TBAA}} \text{54} + \text{Byproducts of aldehyde}$$

upto 95%

Scheme 17.

$$\text{52} + \text{55} \xrightarrow[\text{K}_3\text{PO}_4, \text{TBAB}, \text{H}_2\text{O} \quad 75^\circ\text{C-0.6-8h, 85-95\%}]{\text{Pd-NHC@ Fe}_3\text{O}_4\text{-IL}} \text{54}$$

Scheme 18.

(A) [Bmim]BF₄/water with PVP   **(B) [Bmim]PF₆/DCM with PVP**

Fig. (5).

62
62a, X = Br
62b, X = BF₄,
62c, X = PF₆,
62d, X = NTf₂

63
63a, X = Br,
63b, X = BF₄,
63c, X = PF₆,
63d, X = NTf₂

64
64a, X = Br,
64b, X = BF₄,
64c, X = PF₆,
64d, X = NTf₂

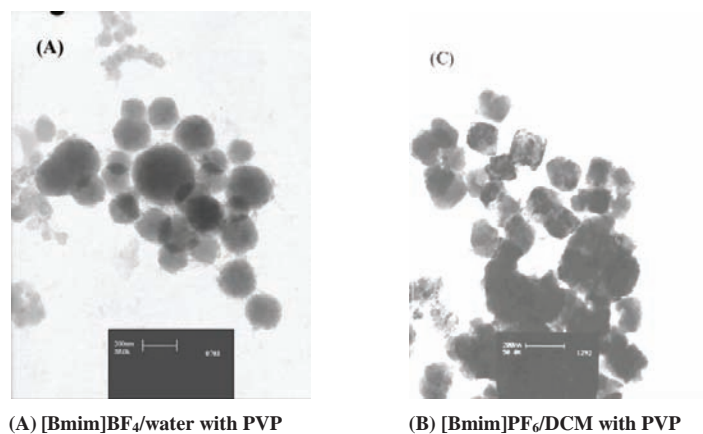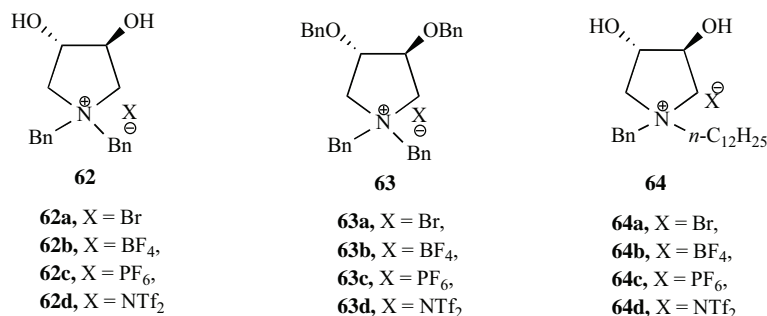**Fig. (6).**

CILs could outperform the classical chiral solvents for asymmetric induction [42-44].

Many chiral ionic liquids have been synthesized which incorporate one or more functional groups, and thus they belong to the class of functionalized chiral ionic liquids. Since the functional group is intended to perform a desired task, these functionalized ionic liquids are also referred to as task specific ionic liquids. Chiral ionic liquids and functionalized chiral ionic liquids are discussed in this section [45]. There have been several reviews about the preparation and application of chiral ionic liquids, with the most recent two having been published in the middle of 2005 [46,47]. The present review is intended to update the reader about the recent work in the field of chiral ionic liquids and functionalized chiral ionic liquids since then.

The more efficient, economic, and simple way to prepare enantiomerically pure ILs is to use precursors derived from the chiral pool either for the generation of the CILs anion or cation or for both. Therefore, chiral ionic liquids are mainly compounds having a central chirality. However, some new CILs having an axial or a planar chirality have also been developed. The first example dealing with the preparation of such a chiral ionic liquid was reported by Earle and their coworkers (Scheme **20**) [48]. The chirality was brought by the lactate anion. The [Bmim]lactate ionic liquid **61** was simply prepared by anion exchange between [Bmim]Cl **59** and commercially available sodium (*S*)-2-hydroxypropionate **60** in acetone.

Later on, many novel chiral ionic liquids have been synthesized. Recently, Bonanni and coworkers have reported [49] a straightforward strategy for the synthesis of series of novel pyrrolidinium salt based on L-(+)-tartaric acid ionic liquids **62, 63, 64** (Fig. **6**).
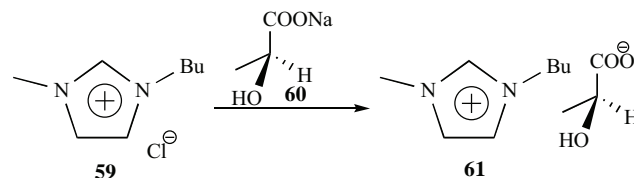
Scheme 20.

Siyutkin *et. al.* designed [50] and synthesized (*S*)-proline modified task specific ionic liquid **65** for the direct asymmetric aldol reaction between various cycloalkanones **66** and aromatic aldehydes **67** in the presence of water afforded aldol products **68** in high yields (upto 95%) with excellent enatiomeric excess (upto 99% ee) of the desired products. (Fig. **7** & Scheme **21**).
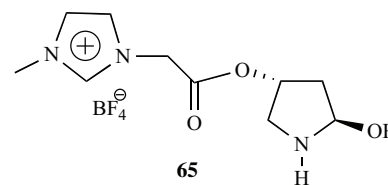

Fig. (7).

Li and co-workers have synthesized [51] novel sulfur-functionalized ionic liquids **69**. Epoxidation reaction was achieved using aromatic aldehydes **70** with benzyl bromides **71** using this organocatalyst CIL. *Trans*-epoxides were obtained with excellent diastereoselectivity and enantioselectivity up to 72% ee. The organocatalyst could be easily reused for five times without remarkable decrease in yields and enantioselectivities (Scheme **22**).
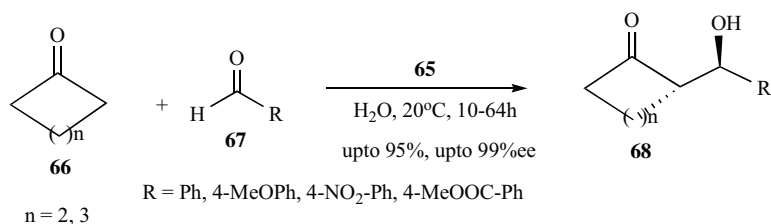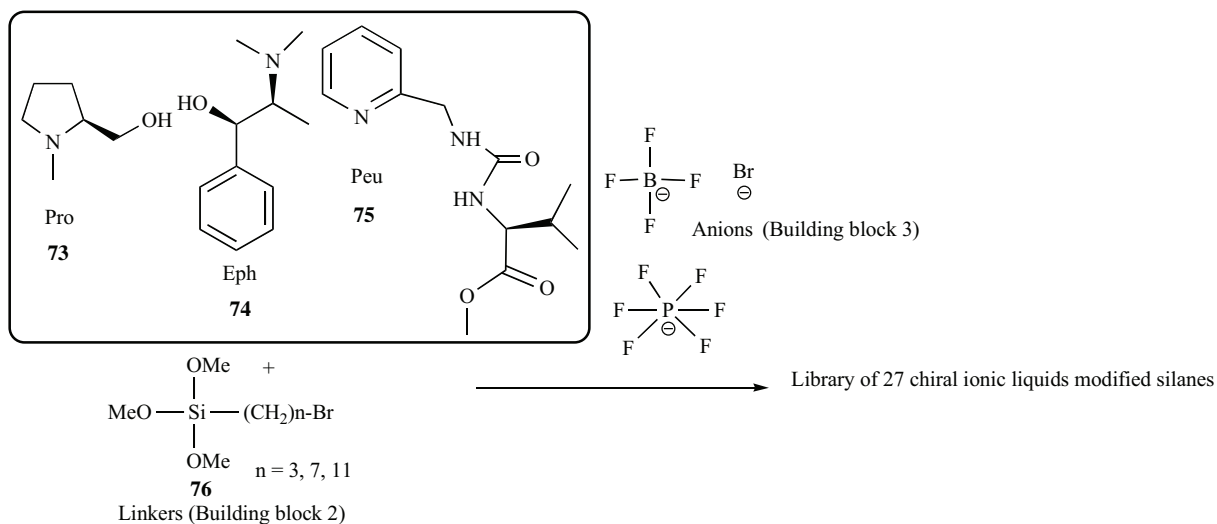
Scheme 21.
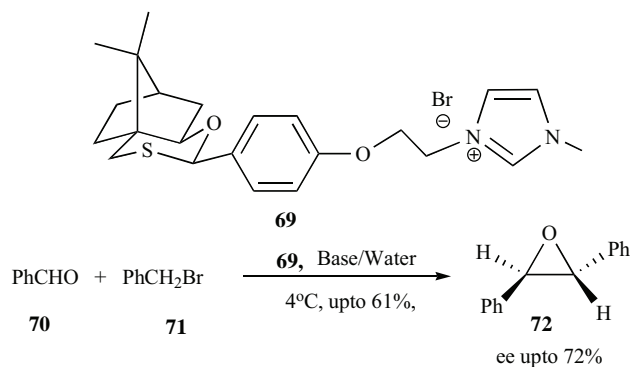
Scheme 22.

A library of novel CIL-modified silanes was synthesized using combinatorial approach by M. Li and co-workers [52]. The chiral
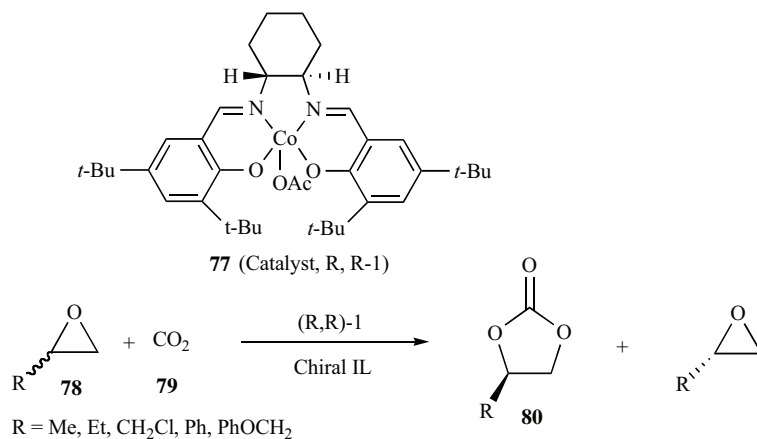
discrimination abilities of these chiral ionic liquids were screened using ^{19}F-NMR spectroscopy (Scheme **23**).

The chiral ionic liquids prepared from TBAB and natural amino acids were used as cocatalysts in the asymmetric cycloaddition of carbon dioxide **79** to propylene oxide **78** (PO) at room temperature in presence of chiral salen-Co(OAc) catalyst **77**. The synergistic effect between catalyst and IL was studied. The system was found to exhibit good activity for the asymmetric cycloaddition of carbon dioxide to epoxide under very mild conditions (Scheme **24**) [53].

A polymeric ionic liquid (IL)-functionalized chiral salen ligand (PICL) was synthesized by covalent polymerization between amino (–NH$_2$) group of 1,3- dipropylamineimidazolium bromide with chloromethyl (–CH$_2$Cl) group at two sides of 5,5' positions in the typical chiral salen ligand (Fig. **8**). Treatment of the synthesized PICL with Mn(OAc)$_2$·4H$_2$O and LiCl under aerobic oxidation yielded the corresponding polymeric IL-functionalized chiral salen
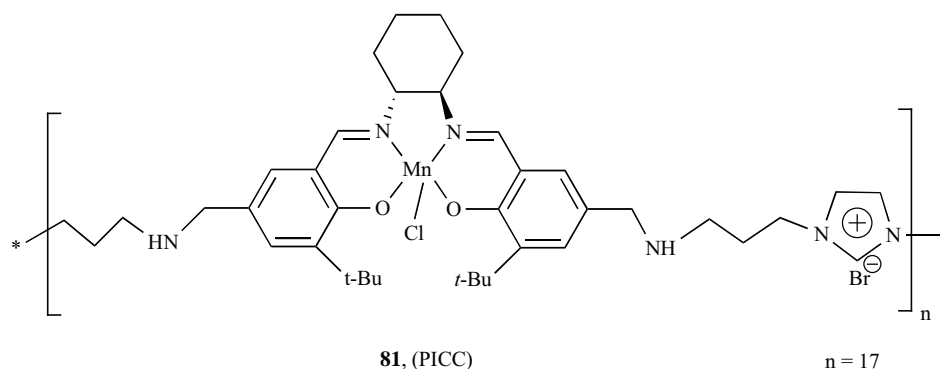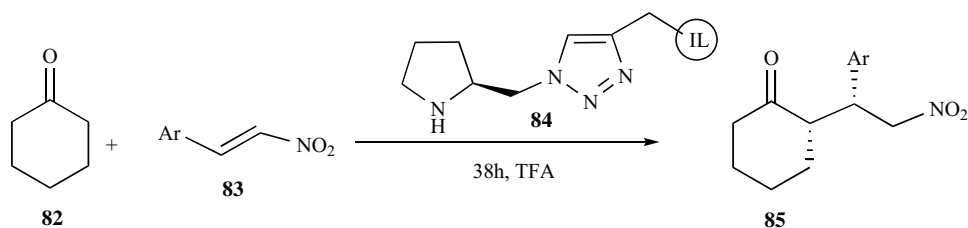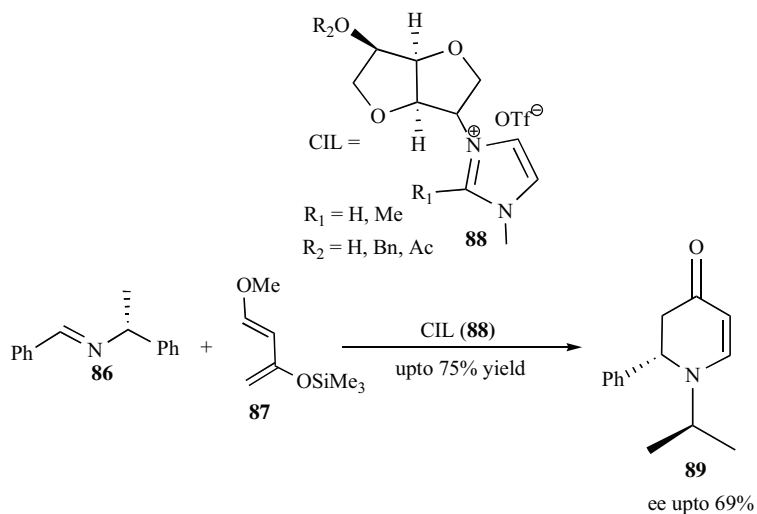

Scheme 23.

Scheme 24.

81, (PICC)   n = 17

Fig. (8).

Scheme 25.

CIL =

R_1 = H, Me

R_2 = H, Bn, Ac   **88**

CIL (**88**)

upto 75% yield

89

ee upto 69%

Scheme 26.

Mn(III) complex **81** (PICC). Comparable catalytic activity and enantioselectivity relative to the monomeric chiral salen Mn(III) complex were observed. Furthermore, recovery of the polymeric catalyst was readily accomplished by simple precipitation in *n*-hexane, and subsequently reused (10 times) without significant loss of reactivity and enantioselectivity [54].

Highly enantioselective Michael addition of cyclohexanone **82** to aryl nitro-olefins **83** in the presence of an ionic liquid anchored pyrrolidine **84**(10 mol%) and TFA (5 mol%) generated the corresponding adducts **85** in high yields (up to 95%) with excellent diastereoselectivities (up to > 99:1 dr) and enantioselectivities (up to > 99% ee) (Scheme **25**). Furthermore, the catalyst could be recycled and reused at least eight times without loss of its catalytic activity [55].

A novel family of chiral imidazolium-based ionic liquids **88** containing a chiral moiety and a free hydroxyl function were designed and synthesized using isosorbide as a biorenewable substrate

(Scheme **26**). These chiral ionic liquids were found to- -catalyze the aza-Diels–Alder reaction between Danishefsky's diene **87** with a chiral imine **86** to give good yields and moderate diastereoselectivities of the products **89**. Chiral ionic liquids were recycled without much loss in efficiency [56].

Various chiral ionic liquids based on simple chiral natural products such as carbohydrates [57] (Fig. (**9**), terpenes [58] (Fig. **10**), abietane [59] (Fig. (**11**) have been synthesized recently. These ionic liquids could find applications as new chiral solvents or catalyst for a range of asymmetric reactions in future.

CONCLUSION

Even though, ionic liquids have been explored for last 15 years, the domain of task specific ionic liquids is still in infant stage. The ionic liquids in conglomeration of their basic properties with desired properties for the reaction under study could become the next
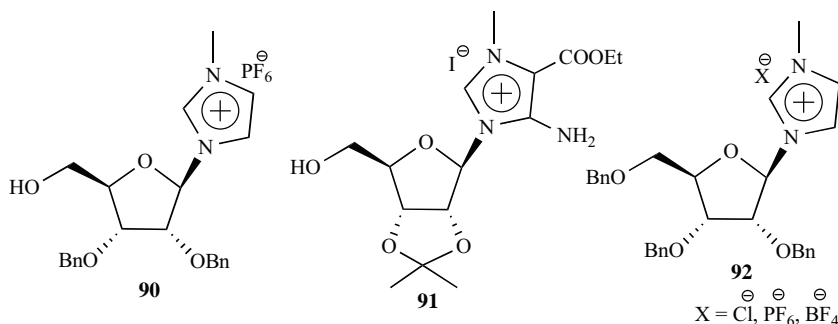
Fig. (9).

arsenals available in the armory of green chemistry. There are some limitations with the use of ILs. The exact role of ionic liquids in carrying out reactions is still under explored. Apart from this, the other issues such as toxicity, purification and development of improved product isolations are needed to be addressed in future research. However taking into account the wide window of properties and applications of ILs the research in the field of task specific ionic liquids have great potential to grow in near future.
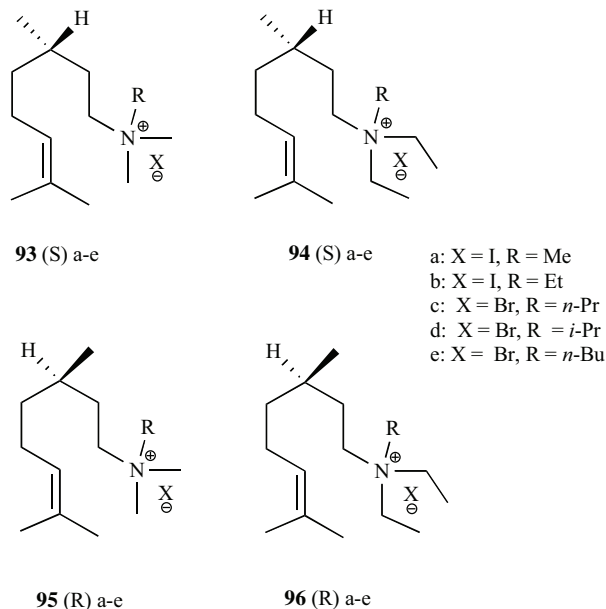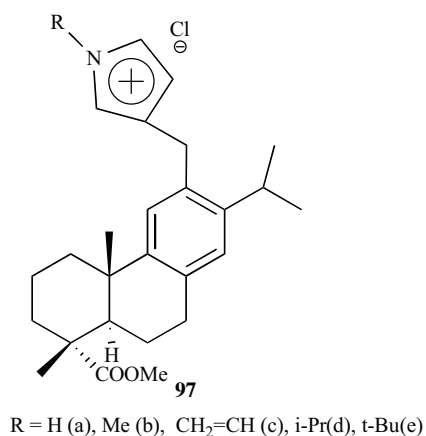

93 (S) a-e   **94** (S) a-e

a: X = I, R = Me
b: X = I, R = Et
c: X = Br, R = *n*-Pr
d: X = Br, R = *i*-Pr
e: X = Br, R = *n*-Bu

95 (R) a-e   **96** (R) a-e

Fig. (10).

R = H (a), Me (b), CH₂=CH (c), i-Pr(d), t-Bu(e)

Fig. (11).

LIST OF ABBREVIATIONS

[Bmim]BF$_4$	=	1-*n*-Butyl-3-methylimidazolium tetra-fluoroborate
[Bmim]PF$_6$	=	1-*n*-Butyl-3-methylimidazolium hex-aflourophosphate
[Bmim]F	=	1-*n*-Butyl-3-methylimidazolium fluoride
[Bmim]Cl	=	1-*n*-Butyl-3-methylimidazolium chloride
[Bmim]Br	=	1-*n*-Butyl-3-methylimidazolium bromide
[Bmim]I	=	1-*n*-Butyl-3-methylimidazolium iodide
[Bmim]OH	=	1-*n*-Butyl-3-methylimidazolium hydroxide
[Bmim]HSO$_4$	=	1-*n*-Butyl-3-methylimidazolium hydrogen sulfate
[Bmim]TFA	=	1-*n*-Butyl-3-methylimidazolium trifluoroacetate
[Bmim]OTf	=	1-*n*-Butyl-3-methylimidazolium triflate
[Bmim]NTf$_2$	=	1-*n*-Butyl-3-methylimidazolium *bis*(trifluoromethyl sulfonyl) iodide
[MOEMIM]OMs	=	1-Methoxyethyl-3-methylimidazolium methane sulfonate
[Tmba]NF$_2$	=	*N*-Trimethyl-*n*-butylammonium *bis*-(trifluoromethyl sulfonyl)-imide
[C$_8$mim]HSO$_4$	=	1-*n*-Butyl-3-octylimidazolium hydrogensul-fate
[Hmim]TFA	=	1-Methyl imidazoilum trifluoroacetate
[Hmim]BF$_4$	=	1-Methyl imidazoilum tetrafluoroborate
[Hmim]PF$_6$	=	1-Methyl imidazolium hexafluorophaophate
[Hmim]OTf	=	1-Methyl imidazoilum triflate
[C$_8$mim]NTf$_2$	=	1-Methyl-imidazolium *bis*(trifluoromethyl sulfonyl) iodide
[Btma]NTf$_2$	=	1-Butyltrimethyl ammonium *bis*(trifluoromethyl sulfonyl) iodide
[Bmim]	=	1-Butyl-3-methylimidazolium hexafluoro antimonate
[PSebim]HSO$_4$	=	1-Ethyl-3-(3-sulfopropyl)-benzimidazolium hydrogen sulfate

[PSebim]BF$_4$　　=　1-Ethyl-3-(3-sulfopropyl)-benzimidazolium tetrafluoroborate.

[Dbim]BF$_4$　　=　1-Butyl-3-decylimidazolium hexafluoroborate.

[TBAA]　　　=　Tetrabutyl ammonium acetate

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