

Review Article

Ionic Liquids: Synthesis and Applications in Catalysis

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Ionic liquids have emerged as an environmentally friendly alternative to the volatile organic solvents. Being designer solvents, they can be modulated to suit the reaction conditions, therefore earning the name “task specific ionic liquids.” Though primarily used as solvents, they are now finding applications in various fields like catalysis, electrochemistry, spectroscopy, and material science to mention a few. The present review is aimed at exploring the applications of ionic liquids in catalysis as acid, base, and organocatalysts and as soluble supports for catalysts.

1. Introduction

One of the twelve principles of green chemistry is that the use of auxiliary substances such as solvents and separation agents should be made unnecessary and if used should be innocuous [1]. The toxic and hazardous properties of many solvents particularly chlorinated hydrocarbons pose crucial environmental concerns such as atmospheric emissions and contamination of water effluents. It is recognized that employing the use of nonconventional solvents as alternatives for environmentally unfriendly traditional solvents can reduce waste solvent production and hence reduce the negative impact on environment to a great extent [2]. The most prevalent of these new solvent systems includes, but not exclusively, water, supercritical fluids (like supercritical CO₂), ionic liquids, solventless processes, and fluorosolvent techniques [3].

Of all the above mentioned nonconventional solvents of interest, ionic liquids have emerged as a promising alternative [4]. Ionic liquid is defined as a salt with melting point below the boiling point of water [5]. Ionic liquids are known by several different names like neoteric solvents, designer solvents, ionic fluids, and molten salts. Most of the ionic liquids are composed of organic cation and inorganic anions. In order to be liquid at room temperature, the cation should preferably be unsymmetrical; that is, the alkyl groups should be different. Polarity and hydrophilicity/hydrophobicity of

ionic liquids can be tuned by suitable combination of cation and anion. It is this property of ionic liquids which has earned them the accolade “designer solvents.”

As solvents, ionic liquids have found applications in a number of reactions [6–16]. Dupont et al. extensively reviewed the application of ionic liquids as catalytic phase in various organometallic reactions [17]. Catalytic applications of metal nanoparticles have been explored in ionic liquid media by Migowski and Dupont [18, 19].

Besides the use of ionic liquids as alternate solvents, lately further work has led to the progress in designing functional ionic liquids also referred to as “task specific ionic liquids” (TSIL) [20]. The term task specific ionic liquids or functionalized ionic liquids actually indicates an attempt to capitalize on the potential “design” capacity of ionic liquids and make them true working systems rather than just reaction media.

2. Synthesis of Ionic Liquids

The first room temperature ionic liquid [EtNH₃][NO₃] (m.p. 12°C) was discovered in 1914 [21], but interest did not develop until the discovery of binary ionic liquids made from mixtures of aluminum(III) chloride and *N*-alkylpyridinium or 1,3-dialkylimidazolium chloride [22, 23].

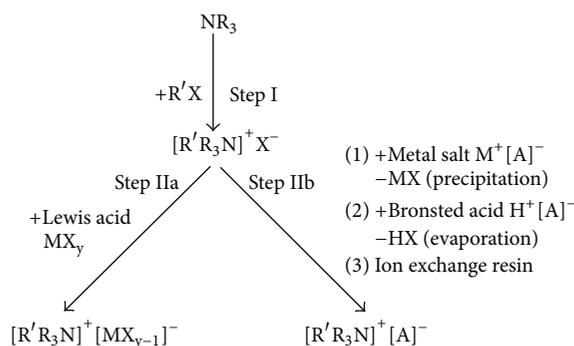
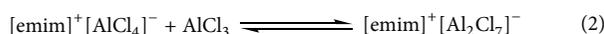


FIGURE 1: Synthesis path for the preparation of ionic liquids [24].



SCHEME 1: Series of equilibria in the reaction between [emim]Cl and AlCl_3 .

Ionic liquids come in two main categories, namely, simple salts (made of a single anion and cation) and binary ionic liquids (salts where equilibrium is involved). For example, $[\text{EtNH}_3][\text{NO}_3]$ is a simple salt whereas mixtures of aluminum(III) chloride and 1,3-dialkylimidazolium chlorides (a binary ionic liquid system) contain several different ionic species, and their melting point and properties depend upon the mole fractions of aluminum(III) chloride and 1,3-dialkylimidazolium chloride present.

The synthesis of ionic liquids can be described in two steps (Figure 1).

(1) *The Formation of the Desired Cation.* The desired cation can be synthesized either by the protonation of the amine by an acid or through quaternization reactions of amine with a haloalkane and heating the mixture.

(2) *Anion Exchange.* Anion exchange reactions can be carried out by treatment of halide salts with Lewis acids to form Lewis acid-based ionic liquids or by anion metathesis.

The most extensively studied and used Lewis acid based ionic liquids are AlCl_3 based salts [25–27]. Such salts involve simple mixing of the Lewis acid and the halide salt which results in the formation of more than one anionic species depending upon the ratio of quaternary halide salt Q^+X^- and Lewis acid MX_n , as illustrated by the reaction between [emim]Cl and AlCl_3 in Scheme 1.

When [emim]Cl is present in molar excess over AlCl_3 the ionic liquid formed is basic (1); however, the molar excess of AlCl_3 leads to the formation of an acidic ionic liquid (3). When both [emim]Cl and AlCl_3 are present in equimolar quantities, it results in the formation of neutral ionic liquids. Apart from AlCl_3 , other Lewis acids used are AlEtCl_2 [28], BCl_3 [29], CuCl [30], and InCl_3 [31] to mention a few.

Anion metathesis is the methodology of choice for the preparation of water and air stable ionic liquids based upon

TABLE 1: Examples of ionic liquids prepared by anion metathesis.

Salt	Anion source	References
[Cation][PF ₆]	HPF ₆	[32–34]
[Cation][BF ₄]	HBf ₄ , NH ₄ Bf ₄ , NaBF ₄	[33–37]
[Cation][(CF ₃ SO ₂) ₂ N]	Li[(CF ₃ SO ₂) ₂ N]	[34, 38]
[Cation][CF ₃ SO ₃]	CF ₃ SO ₃ CH ₃ , NH ₄ [CF ₃ SO ₃]	[38]
[Cation][CH ₃ CO ₂]	Ag[CH ₃ CO ₂]	[35]
[Cation][CF ₃ CO ₂]	Ag[CF ₃ CO ₂]	[35]
[Cation][CF ₃ (CF ₃) ₃ CO ₂]	K[CF ₃ (CF ₃) ₃ CO ₂]	[38]
[Cation][NO ₃]	AgNO ₃ , NaNO ₃	[34, 38]
[Cation][N(CN) ₂]	Ag[N(CN) ₂]	[39]
[Cation][CB ₁₁ H ₁₂]	Ag[CB ₁₁ H ₁₂]	[40]
[Cation][AuCl ₄]	HAuCl ₄	[41]

1,3-dialkylimidazolium cations. This method involves the treatment of the halide salt with the silver/sodium/potassium salts of NO_2^- , NO_3^- , BF_4^- , SO_4^{2-} , and CO_2CH_3^- or with the free acid of the appropriate anion. Table 1 gives examples of the few ionic liquids prepared by anion metathesis.

It is clear from the above discussion that large number of ionic liquids can be envisioned by simple combination of different cations and anions. The estimated number of single ILs is 10^{18} which further increases if we include binary and ternary ionic liquids. Because of their “tailor-made” nature the ionic liquids find applications as storage media for toxic gases, catalysts/solvents in organic syntheses, performance additives in pigments, and matrices [42–44].

Several new and improved methodologies using nonconventional techniques, such as irradiation with microwaves (MW) and power ultrasound (US), whether used alone or in combination, have considerably improved the synthesis of ILs, cutting down reaction times and improving yields [45–47]. The recent introduction of efficient, solventless, one-pot synthetic protocols should make ILs cheaper and thus encourage a wider use of these neoteric solvents [48–50].

3. Task Specific Ionic Liquids (TSILs)

In 1999, Davis Jr. and Forrester demonstrated the concept of designing ionic liquid to interact with a solute in a specific manner by using a thiazolium based IL as a solvent-catalyst for the benzoin condensation and introduced the term “task specific ionic liquid” for such ILs in which functional group

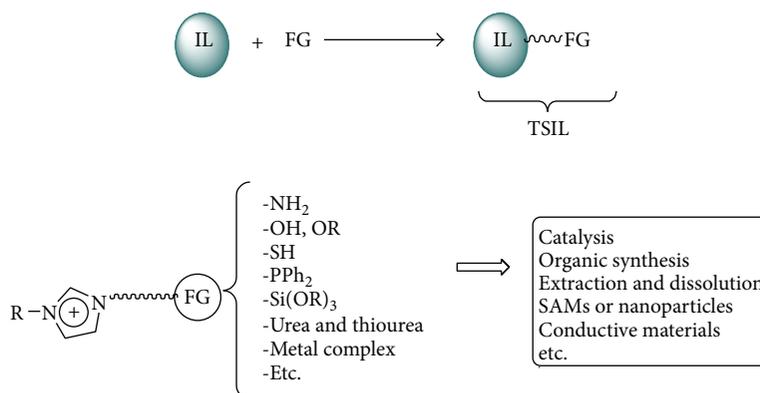


FIGURE 2

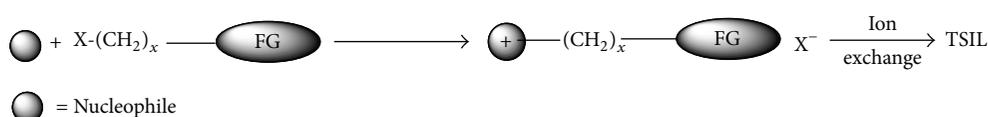


FIGURE 3

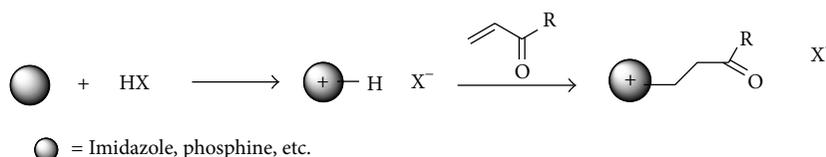


FIGURE 4

is incorporated as a part of the cation and/or anion structure [51, 52]. The covalent attachment of some functional group to cation/anion or both of an ordinary ionic liquid imparts it the capacity to behave not only as solvent but also as reagent and/or catalyst, catalyst in the chemical reactions [53, 54] (see Figures 2 and 3).

- (i) For example, safe to handle Bronsted acidic ionic liquids containing sulphonic acid groups were used as solvent and/or catalyst for esterification and other acid catalyzed reactions [55].
- (ii) Ionic liquids bearing appended amines can separate carbon dioxide from gas streams [56].
- (iii) Ionic liquids with large aromatic head groups show enhanced activity for extraction of aromatics in aqueous biphasic systems [57].
- (iv) Ionic liquids with a tethered hydroxyl group ($-\text{OH}$) have been used as phase transfer catalyst in the synthesis of ethoxybenzene [58].
- (v) Ionic liquids containing metal ligating group find use in the extraction of metal ions from aqueous solution [59].
- (vi) Ionic liquids with appended carboxylate groups have been used as supports for "IL-phase" synthesis which is a versatile extension of the solid phase synthesis concept [60].

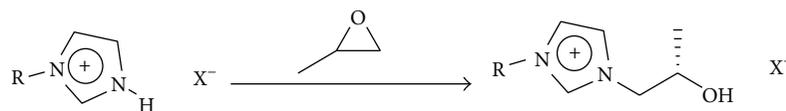
A TSIL can be any of the following two types [61]:

- (i) A room temperature ionic liquid, having covalently attached functional group, behaves not just as reaction media but also as reagent/catalyst.
- (ii) A binary system of some functionalized salt, which may be solid at room temperature, dissolved in conventional ionic liquid.

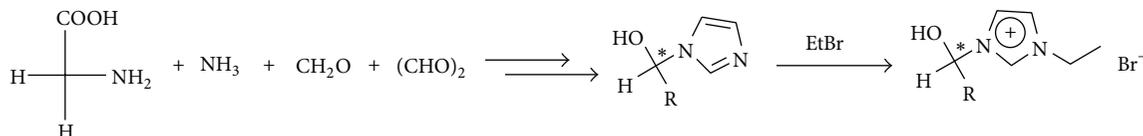
3.1. Synthesis of TSILs. Conventional method used for synthesizing a TSIL involves the displacement of halide from an organic by a parent imidazole, phosphine, and so forth whereby the organic halide already incorporates a desired functional group. The displacement reaction is followed by anion exchange (see Figure 3).

This method is suitable for the synthesis of all ionic liquids which are stable towards bases; however, because of the strong basicity of imidazole, elimination of hydrogen halide or Hoffmann elimination occurs in some cases [62]. Generally the functional groups have been introduced directly to the imidazolium moiety using the direct quaternization route. For example, imidazolium cation with hydroxyl groups [58], carboxyl groups [60], thiol groups [63], alkyne groups [64], allyl groups [65], and fluorinated chains [66] were successfully prepared.

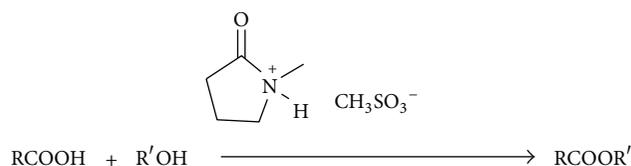
Wasserscheid and coworkers introduced a new methodology to synthesize TSILs by making use of Michael reaction.



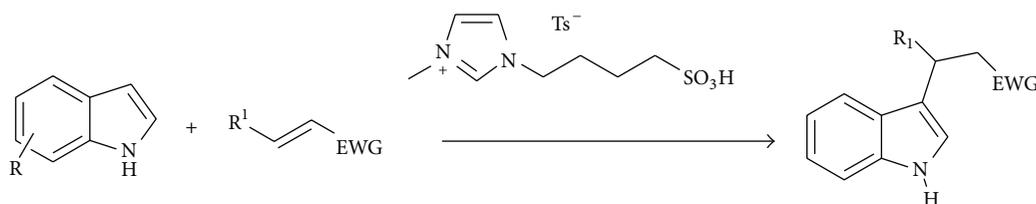
SCHEME 2



SCHEME 3



SCHEME 4



SCHEME 5

In this approach the nucleophile is protonated using the acid form of anion which will eventually be incorporated into the ionic liquid [67] (see Figure 4).

To synthesize -OH group containing TSILs two procedures have been reported as discussed below.

Holbrey et al. have described a simple, high yielding one pot method for the synthesis of alcohol-appended imidazolium TSIL, an ionic liquid type which was previously difficult to prepare cleanly. Preformed imidazolium-H salt of TSIL anion is allowed to react with an epoxide leading to ring opening without further alcohol-epoxide oligomerization [68] (see Scheme 2).

Bao et al. synthesized an imidazolium ring by the four components condensation of amino acids, ammonia, formaldehyde, and glyoxal. The procedure yields an optically active TSIL [69] (see Scheme 3).

4. Ionic Liquids as Catalysts

Although ionic liquids were initially introduced as alternative green reaction media because of their unique physical and chemical properties, today they have marched far beyond this border, showing their significant role in controlling the reaction as catalysts [70–75]. Depending upon the functional

group attached to the cation and/or anion, the ionic liquid may behave as an acidic, basic, or organocatalyst.

4.1. As Acid Catalysts. The application of acidic (Bronsted as well as Lewis) task specific ionic liquids (TSILs) as a catalytic material is growing rapidly in the field of catalysis [76, 77]. Combining the useful characteristics of solid acids and mineral acids, TSILs have been synthesized to replace the traditional mineral liquid acids, such as hydrochloric acid and sulphuric acid, in the chemical reactions. In view of green chemistry, the substitution of harmful liquid acids by reusable TSILs is one of the most promising catalytic systems in chemistry.

The acidic nature of Bronsted acidic ionic liquids as catalysts has been exploited for many organic transformations like Pechmann reaction, Koch carbonylation, asymmetric Aldol condensation, Aza-Michael reaction, Beckmann rearrangement, synthesis of chalcones, oxidation reactions and Prins reaction, synthesis of furfural, biodiesel, Hantzsch reaction, and Mannich reaction to mention a few [78–89].

Esterification of alcohols by carboxylic acids has been carried out in a halogen-free Bronsted acidic ionic liquid, N-methyl-2-pyrrolidinium methyl sulphate under mild conditions, and without additional solvent [90] (see Scheme 4).

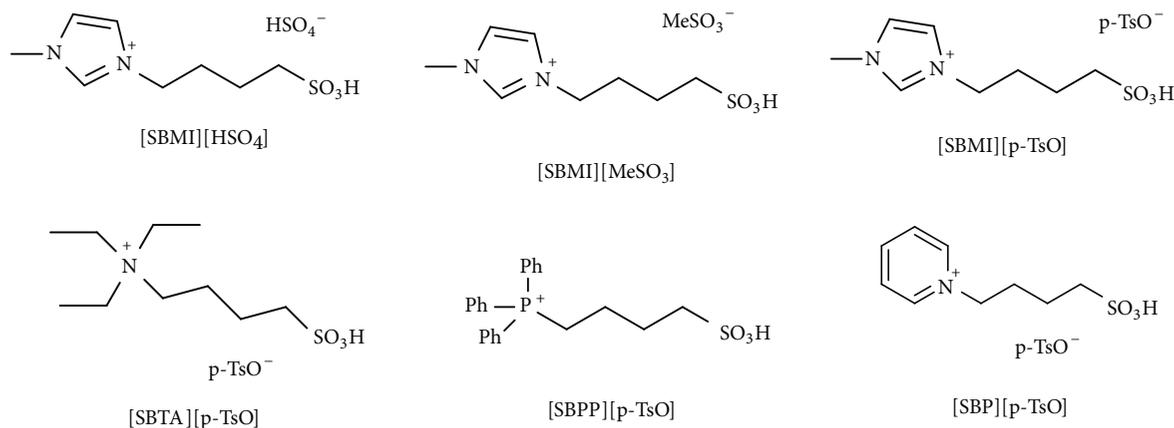


FIGURE 5



SCHEME 6

In a very recent report of TSIL, Das and coworkers have reported a sulfonic acid functionalized IL for efficient synthesis of indole derivatives [91]. The advantage of this IL is that it could be reused up to 10 cycles without any substantial loss of catalytic activity. The catalyst is versatile as it is also applicable to both aliphatic and aromatic amines and in the synthesis of bis(indolyl) methane (see Scheme 5).

Z.-W. Wang and L.-S. Wang reported the Friedel-Crafts reaction of PCl_3 and benzene in $[\text{trEHAm}]\text{Cl-XAlCl}_3$ ionic liquid for the clean synthesis of dichlorophenylphosphine (DCPP) [93] (see Scheme 6).

Compared with the classical methods this protocol allows the simple product isolation and lesser reusable catalyst consumption, which contributes to the greenness of the procedure.

Wang et al. screened various ionic liquids for Saucy-Marbet reaction between unsaturated alcohols and unsaturated ethers leading to corresponding unsaturated ketones [94]. It was observed that, with five ionic liquids bearing $[\text{HSO}_4^-]$ anion, the conversion decreases as the chain length of ionic liquid increases due to its lipophilic character. Among the various acidic ionic liquids $[\text{Et}_3\text{NH}][\text{HSO}_4]$ gave the best results in terms of conversion (88%) and selectivity (97%) for the model reaction involving dehydrolinalool and 2-ethoxypropene.

With neutral ionic liquids like $[\text{bmim}]\text{BF}_4$, the conversion was less than 10%. No reaction was observed when $[\text{bmim}]\text{Cl}$ or $[\text{bmim}]\text{PF}_6$ was used as catalyst. This cost effective, solvent-free protocol has the advantages of easy work-up, recyclability with only slight decrease in activity, low toxicity of ammonium based ionic liquids, high activity, and selectivity (see Scheme 7).

Brandt et al. extensively reviewed the use of ionic liquids as deconstruction solvents for lignocellulosic biomass [95].

Ionic liquid disrupts the lignin and hemicellulosic network while decrystallizing the cellulose portion which further enhances the speed of saccharification.

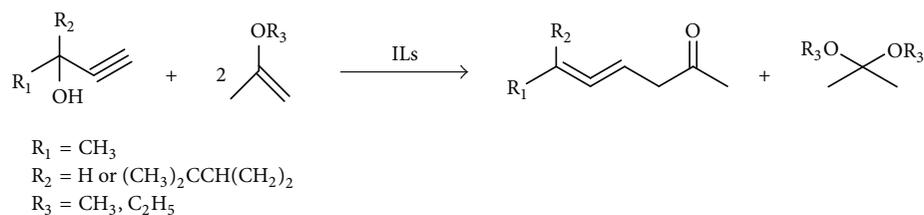
The use of ionic liquids $[\text{C}_4\text{C}_1\text{im}][\text{HSO}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{MeSO}_3]$ for lignocellulosic biomass treatment was successfully investigated even in the presence of significant quantities of water, thus eliminating the need for anhydrous conditions during pretreatment [96].

The use of acidic ionic liquids for the saccharification of cellulose and its subsequent conversion into important platform molecules like hydroxymethylfurfural, furfural, and levulinic acid has been well explored [97–103].

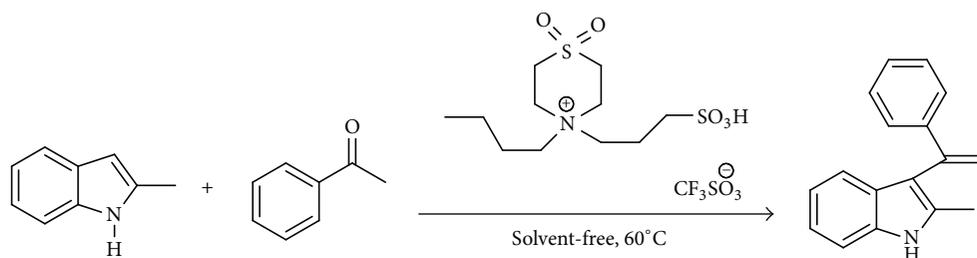
A green solvent-free, metal-free, mild, and efficient protocol for the synthesis of 3-vinyl indoles starting from indoles and ketones has been developed using a sulfonyl containing ionic liquid as a recyclable catalyst [104]. The simultaneous presence of sulfonyl and sulphonic acid groups in the same ionic liquid leads to an augmented catalytic activity. Even the challenging substrates like bulky ketones or ortho-substituted ketones gave satisfactory yields (see Scheme 8).

Six different Bronsted acidic ionic liquids (BAILs) have been synthesized and used as recyclable reaction media as well as acid promoters for Pd-phosphine catalyzed methoxy carbonylation of ethylene to produce methyl propionate in excellent yields [105] (see Figure 5). The use of BAILs not only hampered the formation of undesirable palladium black but also leads to the formation of a biphasic reaction media with the product thereby facilitating the product as well as catalyst recovery. The catalytic system has been found to be recyclable up to fifteen cycles without any appreciable loss in activity (see Scheme 9).

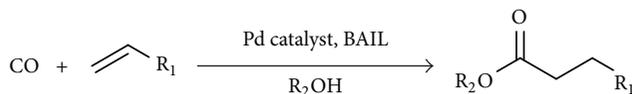
Titze-Frech and coworkers developed an efficient and selective methodology for the alkylation of phenol and anisole using Bronsted acidic triflate ionic liquid $[\text{MIMBS}][\text{OTf}]$ as catalyst in a biphasic reaction medium [106]. This protocol is advantageous over the existing ones as it negates the need for the neutralization of excess acid formed as a by-product. Also, ionic liquid catalyst being less oxophilic as compared to mineral acids leads to greater selectivities (see Scheme 10).



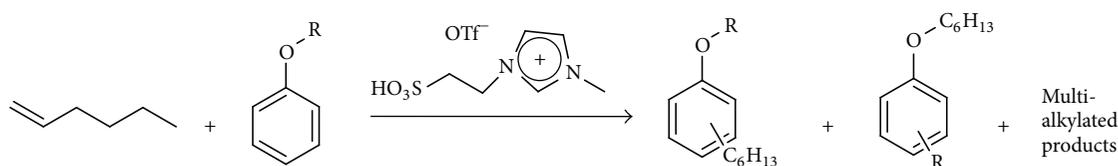
SCHEME 7



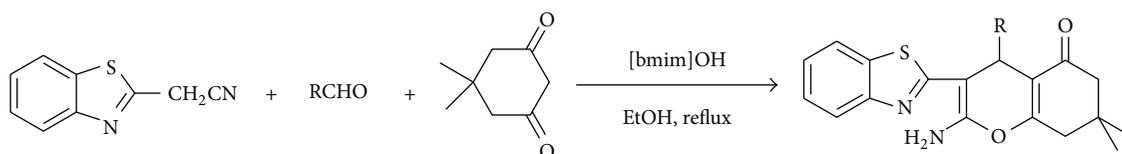
SCHEME 8



SCHEME 9



SCHEME 10



SCHEME 11

4.2. As Base Catalysts. Basic functionalized ionic liquids have aroused unprecedented interest because they showed more advantages, such as convenient recycling and higher catalytic efficiency than the mixture of inorganic base and ionic liquid for some base-catalyzed processes [107].

Basic ionic liquids have been used to catalyze a number of reactions like aza-Michael addition reaction, Michael addition of active methylene compounds, condensation reaction of aldehydes and ketones with hydroxylamine, synthesis of quinolines, pyrroles, and AGET ATRP of methyl methacrylate to mention a few [108–113].

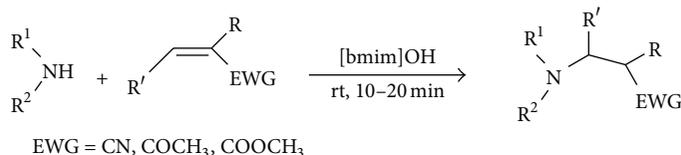
A facile, mild, and quantitative procedure for the preparation of tetrahydrobenzo[b]pyran derivatives in the presence of an easily accessible basic ionic liquid [bmim]OH as catalyst

has been developed by Wen et al. [114]. The ionic liquid was used for at least nine times with consistent activity (see Scheme 11).

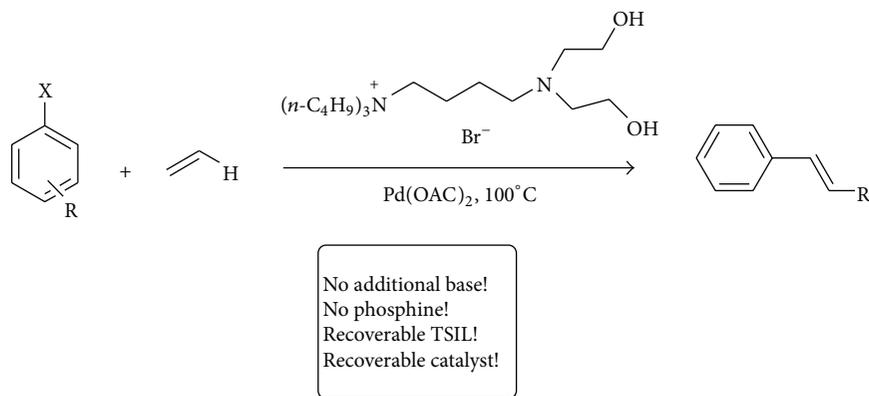
Xu et al. developed a green protocol for the Michael addition of N-heterocycles to α,β -unsaturated compounds at room temperature using a basic ionic liquid [bmim]OH as a catalyst and reaction medium [115] (see Scheme 12).

Wang and coworkers described synthesis and application of ethanolamine functionalized TSIL for the palladium-catalyzed Heck reaction [116] (see Scheme 13).

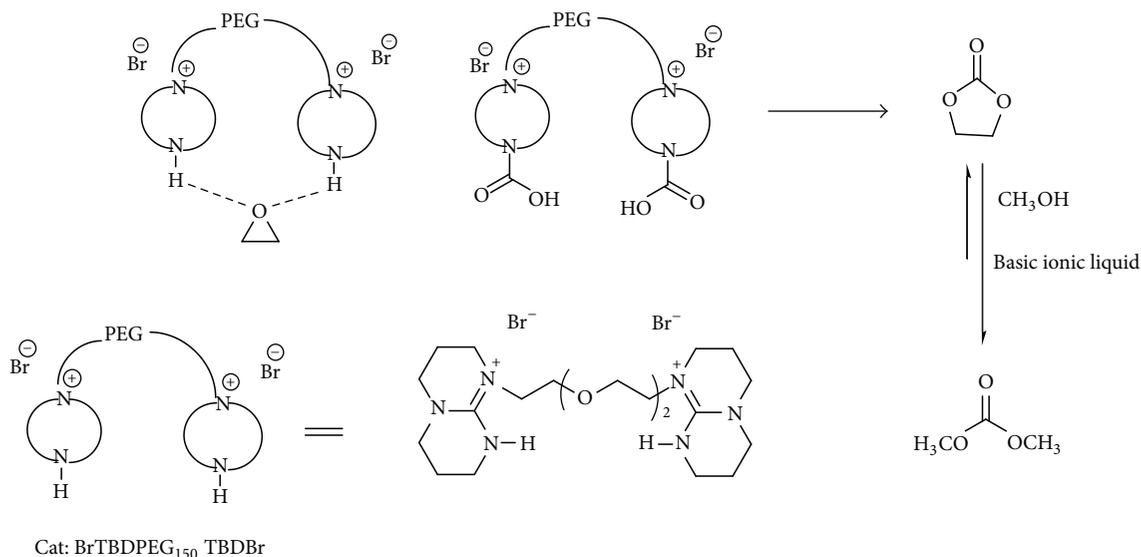
Here this IL performs a multifunctional role of base, ligand, and reaction media with added advantage of recyclability of the system. The catalyst system is very effective for a wide spectrum of substrates giving excellent yields.



SCHEME 12



SCHEME 13



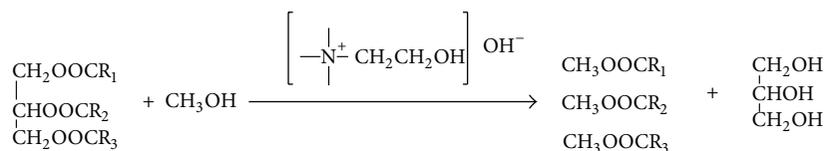
SCHEME 14

Yang et al. designed a series of PEG functionalized basic ionic liquids based on 1,2-dimethyl imidazole (DMIm); 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU); 1,5-diazabicyclo [4.3.0] non-5-ene (DBN); 1-methyl imidazole (MIm) and 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD); and tested them as catalysts, under identical conditions, for the conversion of carbon dioxide into useful organic carbonates [117]. Of all these catalysts BrTBDPEG₁₅₀ TBDBr has been found to be excellent recyclable catalyst under solvent-free conditions at low pressure (see Scheme 14).

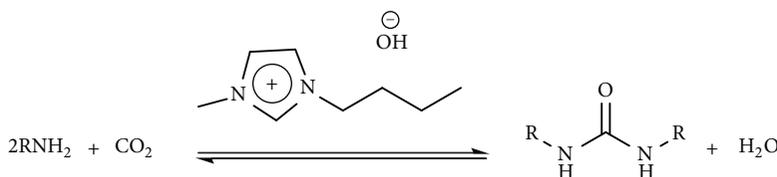
The presence of both secondary and tertiary nitrogens in the cation of BrTBDPEG₁₅₀ TBDBr endows it with the ability

to activate methanol leading to high activity for transesterification of ethylene carbonate with methanol. Therefore the use of basic ionic liquid BrTBDPEG₁₅₀ TBDBr as catalyst allows the integration of cycloaddition as well as transesterification as a single process.

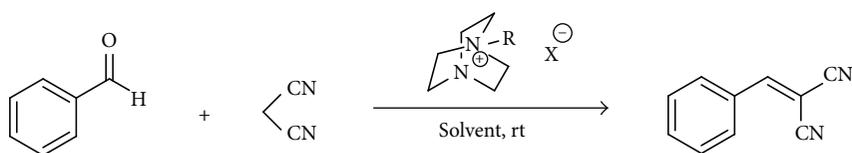
Basic ionic liquids choline hydroxide [ChOH], choline methoxide (ChOMe), and choline imidazolium (ChIm) have been synthesized and checked for their catalytic activity for the production of biodiesel from soybean oil [118]. Of all the three ionic liquids, choline hydroxide was found to give the best results in terms of yield, efficiency, and recyclability. After studying various reaction parameters, 4 wt% catalyst



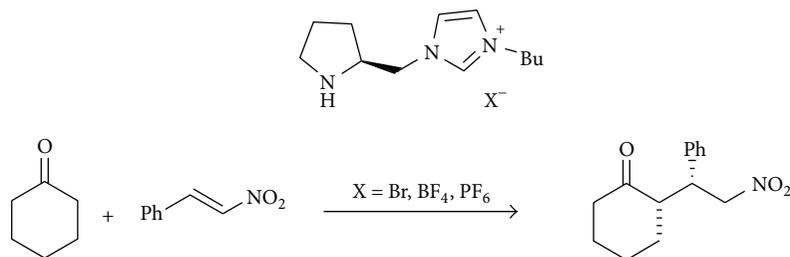
SCHEME 15



SCHEME 16



SCHEME 17



SCHEME 18

dosage at a temperature of 60°C was optimized to give the best results when the ratio of methanol to soybean oil was 9 : 1 (see Scheme 15).

Basic ionic liquid [bmim]OH has been successfully used as an efficient catalyst for the synthesis of substituted ureas starting from carbon dioxide and amines [119]. The main advantages of this methodology are solvent-free reaction conditions, no need of dehydrating agents to remove the water formed as a by-product, recyclability of catalyst, and operational simplicity. The developed protocol is quite general as aliphatic amines, cyclohexylamine, and benzylamine were converted to corresponding ureas efficiently and selectively (see Scheme 16).

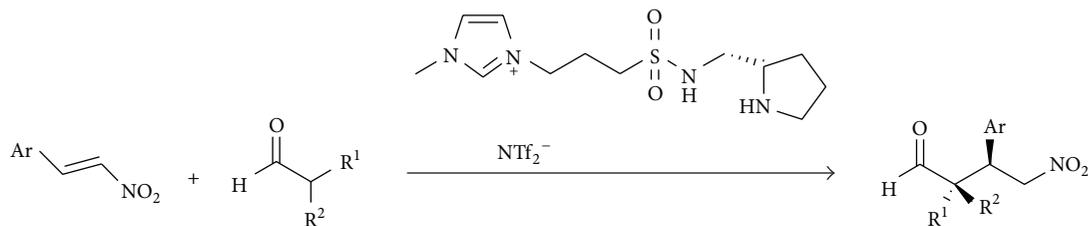
Various [DABCO] based ionic liquids have been screened for executing Knoevenagel condensation reaction [120]. Of all these ionic liquids [C₄dabco] [BF₄] was found to give the best results. Using [C₄dabco] [BF₄] as catalyst in aqueous media various aromatic/aliphatic/heterocyclic/ α,β unsaturated aldehydes and cyclic/acyclic ketones have been found to undergo efficient Knoevenagel condensation with active

methylene compounds. No product purification was required and the catalyst was found to be recyclable up to seven cycles without any decrease in activity. The reaction is highly stereoselective giving alkenes with E-geometry only (see Scheme 17).

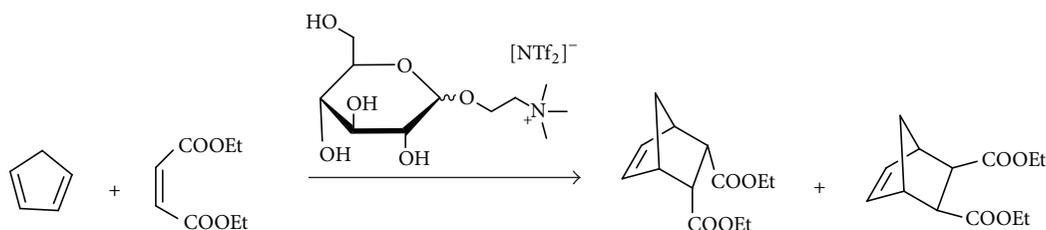
4.3. As Organocatalysts. In the last few years a renewed interest in the use of organic compounds as catalysts has begun to emerge. Ionic liquids have the potential to have a huge impact in this area [121–124]. One of the promising approaches to organocatalysis is through hydrogen bonding interactions, and the reactions to which this has been most often applied are Diels-Alder cycloadditions and their derivatives.

Luo and coworkers used a functionalized chiral ionic liquid as an efficient reusable organocatalyst for asymmetric Michael addition of ketones/aldehydes with nitroalkenes [125] (see Scheme 18).

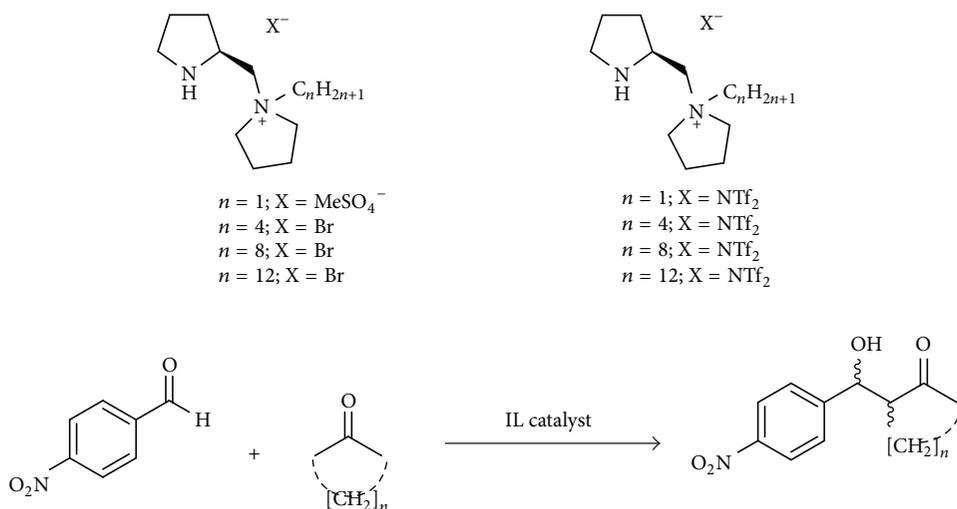
Pyrrolidine-based chiral ionic liquid has been developed by Ni and coworkers [126]. This chiral ionic liquid was found to catalyze the Michael addition reaction of aldehydes



SCHEME 19



SCHEME 20



SCHEME 21

and nitrostyrenes to give moderate yields, good enantioselectivities, high diastereoselectivities, and recyclability (see Scheme 19).

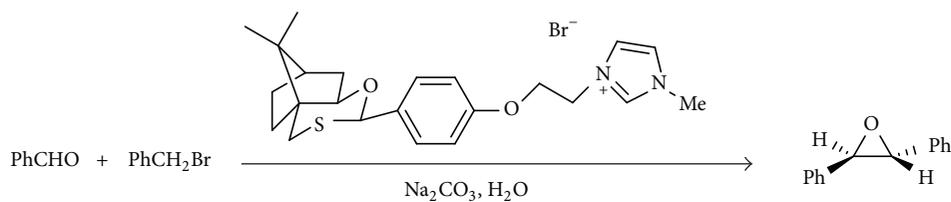
Though ionic liquids are green solvents, they are synthesized from the materials which use fossil fuels as their resource. Synthesizing ionic liquids from renewable raw materials will add to the green attributes of ionic liquids. Sugars are suitable, abundantly available raw material for the synthesis of ionic liquids. Also the presence of hydroxyl groups in the ionic liquids derived from sugars makes them highly coordinating solvents thus enabling them to be used in stereoselective and metal catalyzed reactions.

Erfut et al. synthesized novel hydrogen bond rich ionic liquids based on D-glucosopyranoside derivatives as cation precursor and low coordinating bistriflimide as anion [127]. Chloroalcohols have been utilized as source of hydroxyl

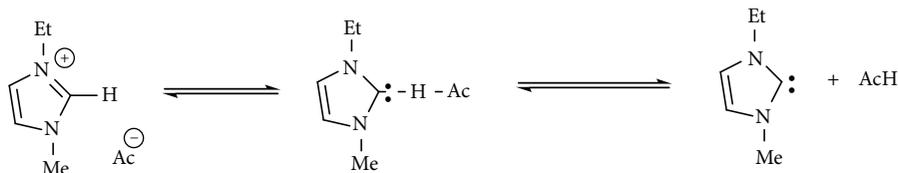
groups for the construction of ionic liquid cation. The synthesized ionic liquids were successfully used as organocatalysts (4 mol% with respect to dienophile) for Diels-Alder reaction of various dienes and dienophiles. Influence of number of hydroxyl groups on the reaction course has been thoroughly investigated. With all the ionic liquids the endo selectivity was found to be prevalent (see Scheme 20).

Starting from (S)-proline, several chiral ionic liquids have been synthesized by Vasileiu and coworkers [128]. These ionic liquids were successfully used as organocatalysts to execute asymmetric aldol condensation giving good yields and selectivity up to 80% ee.

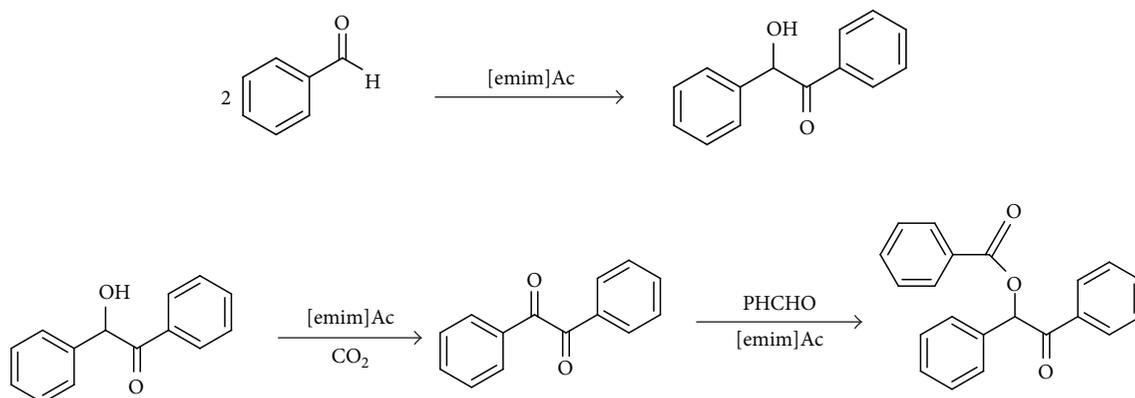
It has been observed that hydrophilic triflimide based chiral ionic liquids lead to greater yields and higher selectivities as compared to ionic liquids bearing methyl sulphate or bromide anions. This methodology not only negates



SCHEME 22



SCHEME 23



SCHEME 24

the requirement of corrosive trifluoroacetic acid but also widens the substrate scope for organocatalysis towards acid sensitive compounds (see Scheme 21).

Li et al. synthesized a sulphur functionalized chiral ionic liquid which has been used as an organocatalyst for epoxidation reaction of various aromatic aldehydes with benzyl bromide in water giving trans-epoxides with high diastereoselectivity and enantioselectivity up to 72% ee [129]. Sodium carbonate has been found to be the best base for this process. Work-up of this reaction is quite simple as the organocatalyst is insoluble in ether and soluble in water. The catalytic system is recyclable up to five cycles without any appreciable reduction in yields and enantioselectivities (see Scheme 22).

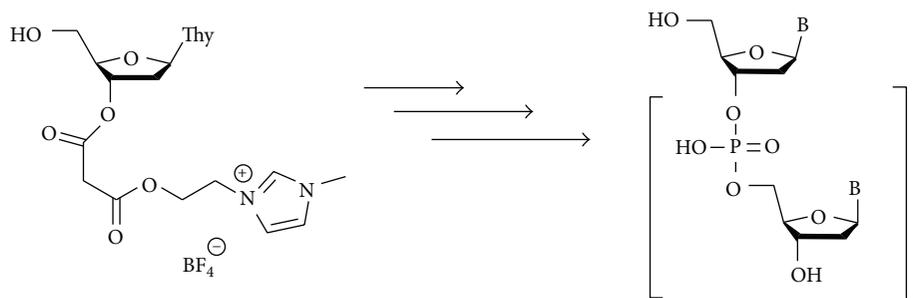
Imidazolium based ionic liquids can be used as pre-catalysts for N-heterocyclic carbene catalyzed reactions whereby the catalyst can be obtained by deprotonation (see Scheme 23).

Kelemen and coworkers successfully used imidazolium acetate as organocatalysts for benzoin condensation, hydroacylation and oxidation of alcohols using carbon-dioxide and air [130] (see Scheme 24).

5. Ionic Liquids as Soluble Supports

Due to their tunable solubility and practically nonvolatile nature, ionic liquids have been used as soluble supports for catalyst/reagent immobilization [92] (see Figure 6). Ionic liquid supported synthesis (ILSS) has been successfully applied for a number of organic reactions like 1,3-cycloadditions [131], Knoevenagel reaction [60], Suzuki coupling [132], synthesis of thiazolidinones [133], oligosaccharide synthesis [134], and Grieco's multicomponent synthesis of tetrahydroquinolines [135].

Donga and coworkers described the synthesis of oligonucleotides in solution using a soluble ionic liquid support.



SCHEME 25

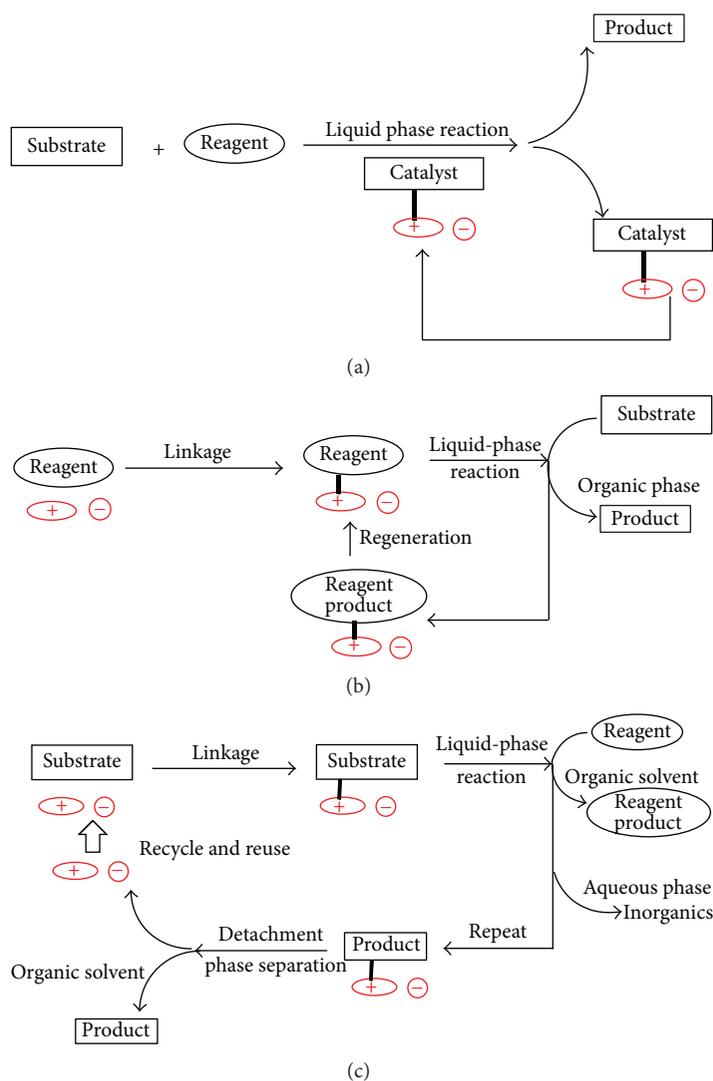
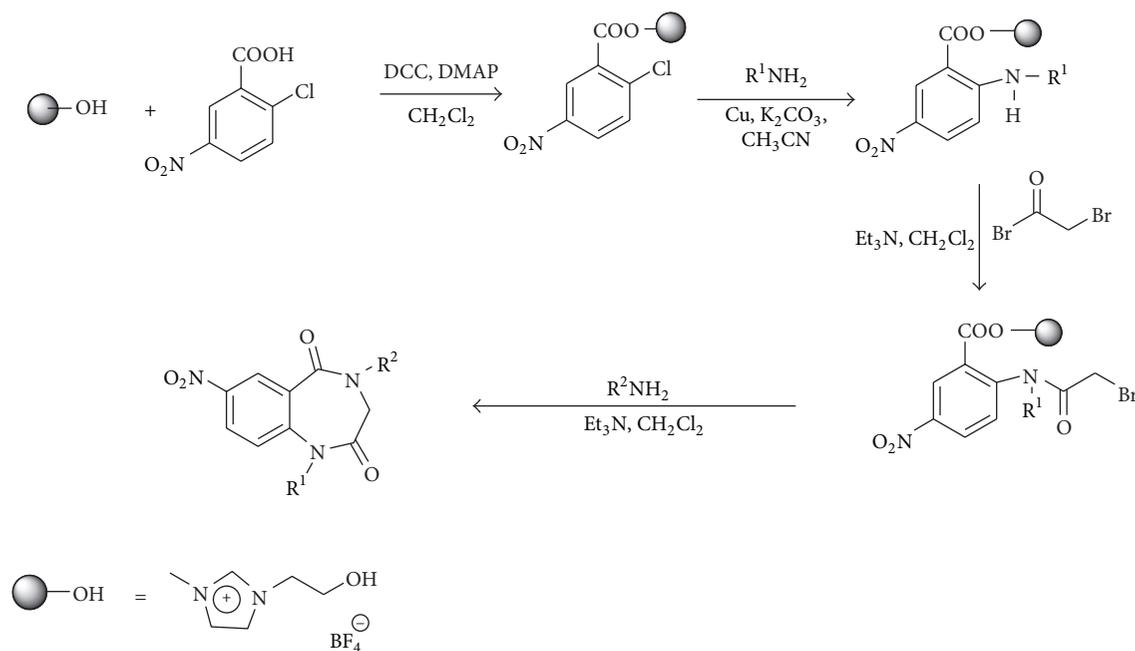


FIGURE 6: Ionic liquid supported synthesis (ILSS) (a) catalyst, (b) reagent, and (c) substrate [92].

Oligonucleotides up to tetrameric species have been synthesized and shown to be comparable to the products generated using standard automated DNA synthesis techniques [136] (see Scheme 25).

A novel and efficient route using ionic liquids as soluble supports has been reported for the synthesis of 1,4-benzodiazepine-2,5-dione by Xie et al. [137] (see Scheme 26).



SCHEME 26

6. Conclusion

This review is focused on the synthesis, importance, and applications of ionic liquids. Not particularly as solvents, they are nowadays finding use as catalysts and catalytic supports in organic chemistry. Their scope has marched beyond academic research laboratories to industries where their practical applications have been leading to various sustainable technologies. Flexibility to modulate properties by changing design endows freedom to a chemist to design an ionic liquid according to one's own requirement. To conclude it can be said that the field of ionic liquid catalysis holds enormous possibilities to be explored.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

References

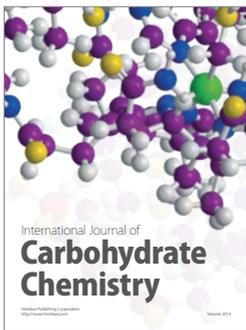
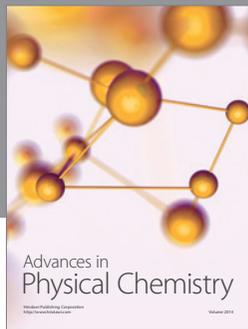
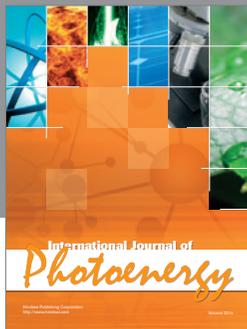
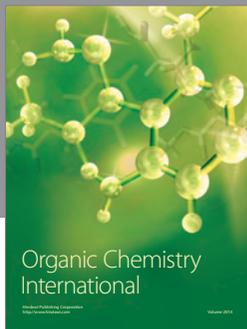
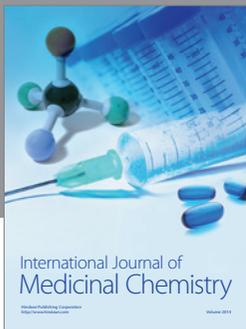
- [1] P. T. Anastas and T. C. Williamson, *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes*, Oxford University Press, 1998.
- [2] D. J. Adams, P. J. Dyson, and S. J. Tavener, *Chemistry in Alternative Reaction Media*, John Wiley & Sons, Chichester, UK, 2004.
- [3] P. Pollet, E. A. Davey, E. E. Ureña-Benavides, C. A. Eckert, and C. L. Liotta, "Solvents for sustainable chemical processes," *Green Chemistry*, vol. 16, no. 3, pp. 1034–1055, 2014.
- [4] P. Wassercheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, New York, NY, USA, 2nd edition, 2008.
- [5] T. Welton, "Room-temperature ionic liquids: solvents for synthesis and catalysis," *Chemical Reviews*, vol. 99, no. 8, pp. 2071–2083, 1999.
- [6] C. E. Song, "Enantioselective chemo- and bio-catalysis in ionic liquids," *Chemical Communications*, no. 9, pp. 1033–1043, 2004.
- [7] Y. Xiao and S. V. Malhotra, "Diels-Alder reactions in pyridinium based ionic liquids," *Tetrahedron Letters*, vol. 45, no. 45, pp. 8339–8342, 2004.
- [8] S. T. Handy, "Grignard reactions in imidazolium ionic liquids," *Journal of Organic Chemistry*, vol. 71, no. 12, pp. 4659–4662, 2006.
- [9] S. Anjaiah, S. Chandrasekhar, and R. Gree, "Carbon-Ferrier rearrangements in ionic liquids using $\text{Yb}(\text{OTf})_3$ as catalyst," *Journal of Molecular Catalysis A: Chemical*, vol. 214, pp. 133–136, 2004.
- [10] P. Mastrorilli, C. F. Nobile, R. Paolillo, and G. P. Suranna, "Catalytic Pauson-Khand reaction in ionic liquids," *Journal of Molecular Catalysis A: Chemical*, vol. 214, no. 1, pp. 103–106, 2004.
- [11] M. Lombardo, M. Chiarucci, and C. Trombini, "A recyclable triethylammonium ion-tagged diphenylphosphine palladium complex for the Suzuki-Miyaura reaction in ionic liquids," *Green Chemistry*, vol. 11, no. 4, pp. 574–579, 2009.
- [12] Z. L. Shen, W. J. Zhou, Y. T. Liu, S. J. Ji, and T. P. Loh, "One-pot chemoenzymatic syntheses of enantiomerically-enriched *O*-acetyl cyanohydrins from aldehydes in ionic liquid," *Green Chemistry*, vol. 10, no. 3, pp. 283–286, 2008.
- [13] L.-C. Feng, Y.-W. Sun, W.-J. Tang et al., "Highly efficient chemoselective construction of 2,2-dimethyl-6-substituted 4-piperidones via multi-component tandem Mannich reaction in ionic liquids," *Green Chemistry*, vol. 12, no. 6, pp. 949–952, 2010.
- [14] D. Singh, S. Narayanaperumal, K. Gul, M. Godoi, O. E. D. Rodrigues, and A. L. Braga, "Efficient synthesis of selenoesters

- from acyl chlorides mediated by CuO nanopowder in ionic liquid," *Green Chemistry*, vol. 12, no. 6, pp. 957–960, 2010.
- [15] T. Fukuyama, T. Inouye, and I. Ryu, "Atom transfer carbonylation using ionic liquids as reaction media," *Journal of Organometallic Chemistry*, vol. 692, no. 1–3, pp. 685–690, 2007.
- [16] A. Schenzel, A. Hufendiek, C. Barner-Kowollik, and M. A. R. Meier, "Catalytic transesterification of cellulose in ionic liquids: sustainable access to cellulose esters," *Green Chemistry*, vol. 16, no. 6, pp. 3266–3271, 2014.
- [17] J. Dupont, R. F. de Souza, and P. A. Z. Suarez, "Ionic liquid (molten salt) phase organometallic catalysis," *Chemical Reviews*, vol. 102, no. 10, pp. 3667–3692, 2002.
- [18] P. Migowski and J. Dupont, "Catalytic applications of metal nanoparticles in imidazolium ionic liquids," *Chemistry*, vol. 13, no. 1, pp. 32–39, 2007.
- [19] J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, and S. R. Teixeira, "Transition-metal nanoparticles in imidazolium ionic liquids: recyclable catalysts for biphasic hydrogenation reactions," *Journal of the American Chemical Society*, vol. 124, no. 16, pp. 4228–4229, 2002.
- [20] L. Zhen, Z. Yingwei, H. Feng et al., "Catalysis and applications of task-specific ionic liquids," *Scientia Sinica Chimica*, vol. 4, pp. 502–524, 2012.
- [21] P. Walden, "Ueber die Molekulargrösse und elektrische Leitfähigkeit einiger geschmolzenen Salze," *Bulletin de l'Académie Impériale des Sciences de St.-Petersbourg*, vol. 8, no. 6, pp. 405–422, 1914.
- [22] H. L. Chum, V. R. Koch, L. L. Miller, and R. A. Osteryoung, "An electrochemical scrutiny of organometallic iron complexes and hexamethylbenzene in a room temperature molten salt," *Journal of the American Chemical Society*, vol. 97, no. 11, pp. 3264–3265, 1975.
- [23] J. S. Wilkes, "A short history of ionic liquids - From molten salts to neoteric solvents," *Green Chemistry*, vol. 4, no. 2, pp. 73–80, 2002.
- [24] P. Wasserscheid and W. Keim, "Ionic liquids—new "solutions" for transition metal catalysis," *Angewandte Chemie International Edition*, vol. 39, no. 21, pp. 3773–3789, 2000.
- [25] F. H. Hurley and T. P. Wier, "Electrodeposition of metals from fused quaternary ammonium salts," *Journal of The Electrochemical Society*, vol. 98, no. 5, pp. 203–206, 1951.
- [26] J. Robinson and R. A. Osteryoung, "An electrochemical and spectroscopic study of some aromatic hydrocarbons in the room temperature molten salt system aluminum chloride-*n*-butylpyridinium chloride," *Journal of the American Chemical Society*, vol. 101, no. 2, pp. 323–327, 1979.
- [27] J. S. Wilkes, J. A. Levinsky, R. A. Wilson, and C. L. Hussey, "Dialkylimidazolium chloroaluminate melts: a new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis," *Inorganic Chemistry*, vol. 21, pp. 1263–1264, 1982.
- [28] Y. Chauvin, S. Einloft, and H. Olivier, "Catalytic dimerization of propene by nickel-phosphine complexes in 1-butyl-3-methylimidazolium chloride/AlEt_xCl_{3-x} (x = 0, 1) ionic liquids," *Industrial and Engineering Chemistry Research*, vol. 34, no. 4, pp. 1149–1155, 1995.
- [29] S. D. Williams, J. P. Schoebrechts, J. C. Selkirk, and G. Maman-tov, "A new room temperature molten salt solvent system: organic cation tetrachloroborates," *Journal of the American Chemical Society*, vol. 109, no. 7, pp. 2218–2219, 1987.
- [30] Y. Chauvin and H. O. Bourbigou, "Nonaqueous ionic liquids as reaction solvents," *Chemtech*, vol. 25, no. 9, pp. 26–30, 1995.
- [31] K. R. Seddon, C. Hardacre, and B. J. McAuley, "Catalyst comprising indium salt and organic ionic liquid and process for friedel-crafts reactions," WO 2003028883, 2003.
- [32] J. G. Huddleston and R. D. Rogers, "Room temperature ionic liquids as novel media for "clean" liquid–liquid extraction," *Chemical Communications*, no. 16, pp. 1765–1766, 1998.
- [33] J. Fuller, R. T. Carlin, H. C. de Long, and D. Haworth, "Structure of 1-ethyl-3-methylimidazolium hexafluorophosphate: model for room temperature molten salts," *Journal of the Chemical Society, Chemical Communications*, no. 3, pp. 299–300, 1994.
- [34] L. Cammarata, S. G. Kazarian, P. A. Salter, and T. Welton, "Molecular states of water in room temperature ionic liquids," *Physical Chemistry Chemical Physics*, vol. 3, no. 23, pp. 5192–5200, 2001.
- [35] J. S. Wilkes and M. J. Zaworotko, "Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids," *Journal of the Chemical Society, Chemical Communications*, no. 13, pp. 965–967, 1992.
- [36] J. D. Holbrey and K. R. Seddon, "The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates; ionic liquids and ionic liquid crystals," *Journal of the Chemical Society, Dalton Transactions*, no. 13, pp. 2133–2140, 1999.
- [37] N. L. Lancaster, T. Welton, and G. B. Young, "A study of halide nucleophilicity in ionic liquids," *Journal of the Chemical Society, Perkin Transactions 2*, no. 12, pp. 2267–2270, 2001.
- [38] P. Bonhote, A.-P. Dias, N. Papageorgiou, K. Kalyansundaram, and M. Gratzel, "Hydrophobic, highly conductive ambient-temperature molten salts," *Inorganic Chemistry*, vol. 35, no. 5, pp. 1168–1178, 1996.
- [39] D. R. MacFarlane, S. A. Forsyth, J. Golding, and G. B. Deacon, "Ionic liquids based on imidazolium, ammonium and pyrrolidinium salts of the dicyanamide anion," *Green Chemistry*, vol. 4, no. 5, pp. 444–448, 2002.
- [40] A. S. Larsen, J. D. Holbrey, F. S. Tham, and C. A. Reed, "Designing ionic liquids: Imidazolium melts with inert carborane anions," *Journal of the American Chemical Society*, vol. 122, no. 30, pp. 7264–7272, 2000.
- [41] M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, A. Steiner, and N. Winterton, "Gold compounds as ionic liquids. Synthesis, structures, and thermal properties of N,N'-dialkylimidazolium tetrachloroaurate salts," *Inorganic Chemistry*, vol. 38, no. 25, pp. 5637–5641, 1999.
- [42] N. D. Khupse and A. Kumar, "Ionic liquids: new materials with wide applications," *Indian Journal of Chemistry Section A: Inorganic, Physical, Theoretical and Analytical Chemistry*, vol. 49, no. 5–6, pp. 635–648, 2010.
- [43] P. Domínguez de María, "Nonsolvent" applications of ionic liquids in biotransformations and organocatalysis," *Angewandte Chemie International Edition*, vol. 47, no. 37, pp. 6960–6968, 2008.
- [44] V. Blasucci, R. Hart, V. L. Mestre et al., "Single component, reversible ionic liquids for energy applications," *Fuel*, vol. 89, no. 6, pp. 1315–1319, 2010.
- [45] M. Deetlefs and K. R. Seddon, "Improved preparations of ionic liquids using microwave irradiation," *Green Chemistry*, vol. 5, no. 2, pp. 181–186, 2003.
- [46] J.-M. Lévêque, J.-L. Luche, C. Pétrier, R. Roux, and W. Bonrath, "An improved preparation of ionic liquids by ultrasound," *Green Chemistry*, vol. 4, no. 4, pp. 357–360, 2002.
- [47] J.-M. Lévêque, S. Desset, J. Suptil et al., "A general ultrasound-assisted access to room-temperature ionic liquids," *Ultrasonics Sonochemistry*, vol. 13, no. 2, pp. 189–193, 2006.

- [48] R. S. Varma and V. V. Namboodiri, "Solvent-free preparation of ionic liquids using a household microwave oven," *Pure and Applied Chemistry*, vol. 73, no. 8, pp. 1309–1313, 2001.
- [49] R. S. Varma and V. V. Namboodiri, "An expeditious solvent-free route to ionic liquids using microwaves," *Chemical Communications*, no. 7, pp. 643–644, 2001.
- [50] P. D. Vu, A. J. Boydston, and C. W. Bielawski, "Ionic liquids via efficient, solvent-free anion metathesis," *Green Chemistry*, vol. 9, no. 11, pp. 1158–1159, 2007.
- [51] J. H. Davis Jr., K. J. Forrester, and T. Merrigan, "Novel organic ionic liquids (OILs) incorporating cations derived from the antifungal drug miconazole," *Tetrahedron Letters*, vol. 39, no. 49, pp. 8955–8958, 1998.
- [52] J. H. Davis Jr. and K. J. Forrester, "Thiazolium-ion based organic ionic liquids (OILs). Novel oils which promote the benzoin condensation," *Tetrahedron Letters*, vol. 40, no. 9, pp. 1621–1622, 1999.
- [53] J. H. Davis Jr., "Task-specific ionic liquids," *Chemistry Letters*, vol. 33, no. 9, pp. 1072–1077, 2004.
- [54] A. D. Sawant, D. G. Raut, N. B. Darvatkar, and M. M. Salunkhe, "Recent developments of task-specific ionic liquids in organic synthesis," *Green Chemistry Letters and Reviews*, vol. 4, no. 1, pp. 41–54, 2011.
- [55] H. Xing, T. Wang, Z. Zhou, and Y. Dai, "Novel Brønsted-acidic ionic liquids for esterifications," *Industrial and Engineering Chemistry Research*, vol. 44, no. 11, pp. 4147–4150, 2005.
- [56] E. D. Bates, R. D. Mayton, I. Ntai, and J. H. Davis Jr., "CO₂ capture by a task-specific ionic liquid," *Journal of the American Chemical Society*, vol. 124, no. 6, pp. 926–927, 2002.
- [57] A. E. Visser, J. D. Holbrey, and R. D. Rogers, "Hydrophobic ionic liquids incorporating N-alkylisoquinolinium cations and their utilization in liquid-liquid separations," *Chemical Communications*, no. 23, pp. 2484–2485, 2001.
- [58] G. R. Feng, J. J. Peng, H. Y. Qiu, J. X. Jiang, L. Tao, and G. Q. Lai, "Synthesis of novel greener functionalized ionic liquids containing appended hydroxyl," *Synthetic Communications*, vol. 37, no. 16, pp. 2671–2675, 2007.
- [59] A. E. Visser, R. P. Swatloski, W. M. Reichert et al., "Task-specific ionic liquids for the extraction of metal ions from aqueous solutions," *Chemical Communications*, no. 1, pp. 135–136, 2001.
- [60] J. Fraga-Dubreuil and J. P. Bazureau, "Grafted ionic liquid-phase-supported synthesis of small organic molecules," *Tetrahedron Letters*, vol. 42, no. 35, pp. 6097–6100, 2001.
- [61] S.-G. Li, "Functionalized imidazolium salts for task-specific ionic liquids and their applications," *Chemical Communications*, no. 10, pp. 1049–1063, 2006.
- [62] A. Horvath, "Michael adducts in regioselective synthesis of N-substituted azoles," *Synthesis*, no. 9, pp. 1183–1189, 1995.
- [63] H. Itoh, K. Naka, and Y. Chujo, "Synthesis of gold nanoparticles modified with ionic liquid based on the imidazolium cation," *Journal of the American Chemical Society*, vol. 126, no. 10, pp. 3026–3027, 2004.
- [64] Z. Fei, D. Zhao, R. Scopelliti, and P. J. Dyson, "Organometallic complexes derived from alkyne-functionalized imidazolium salts," *Organometallics*, vol. 23, no. 7, pp. 1622–1628, 2004.
- [65] D. Zhao, Z. Fei, T. J. Geldbach, R. Scopelliti, G. Laurenczy, and P. J. Dyson, "Allyl-functionalised ionic liquids: synthesis, characterisation, and reactivity," *Helvetica Chimica Acta*, vol. 88, no. 3, pp. 665–675, 2005.
- [66] T. L. Merrigan, E. D. Bates, S. C. Dorman, and J. H. Davis Jr., "New fluorinated ionic liquids function as surfactants in conventional room-temperature ionic liquids," *Chemical Communications*, no. 20, pp. 2051–2052, 2000.
- [67] P. Wassercheid, B. Drieffen-Hölscher, R. van Hal, H. C. Steffers, and J. Zimmermann, "New, functionalised ionic liquids from Michael-type reactions—a chance for combinatorial ionic liquid development," *Chemical Communications*, no. 16, pp. 2038–2039, 2003.
- [68] J. D. Holbrey, M. B. Turner, W. M. Reichert, and R. D. Rogers, "New ionic liquids containing an appended hydroxyl functionality from the atom-efficient, one-pot reaction of 1-methylimidazole and acid with propylene oxide," *Green Chemistry*, vol. 5, no. 6, pp. 731–736, 2003.
- [69] W. Bao, Z. Wang, and Y. Li, "Synthesis of chiral ionic liquids from natural amino acids," *The Journal of Organic Chemistry*, vol. 68, pp. 591–593, 2003.
- [70] T. Welton, "Ionic liquids in catalysis," *Coordination Chemistry Reviews*, vol. 248, no. 21–24, pp. 2459–2477, 2004.
- [71] A. K. Chakraborti and S. R. Roy, "On catalysis by ionic liquids," *Journal of the American Chemical Society*, vol. 131, no. 20, pp. 6902–6903, 2009.
- [72] X. Li, D. Zhao, Z. Fei, and L. Wang, "Applications of functionalized ionic liquids," *Science in China, Series B: Chemistry*, vol. 49, no. 5, pp. 385–401, 2006.
- [73] D. Zhao, M. Wu, Y. Kou, and E. Min, "Ionic liquids: applications in catalysis," *Catalysis Today*, vol. 74, no. 1–2, pp. 157–189, 2002.
- [74] V. I. Pârvulescu and C. Hardacre, "Catalysis in ionic liquids," *Chemical Reviews*, vol. 107, no. 6, pp. 2615–2665, 2007.
- [75] Z. Fei, T. J. Geldbach, D. Zhao, and P. J. Dyson, "From dysfunction to bis-function: on the design and applications of functionalised ionic liquids," *Chemistry A: European Journal*, vol. 12, no. 8, pp. 2122–2130, 2006.
- [76] T. L. Greaves and C. J. Drummond, "Protic ionic liquids: properties and applications," *Chemical Reviews*, vol. 108, no. 1, pp. 206–237, 2008.
- [77] L. He, G. H. Tao, W. S. Liu, W. Xiong, T. Wang, and Y. Kou, "One-pot synthesis of Lewis acidic ionic liquids for Friedel-Crafts alkylation," *Chinese Chemical Letters*, vol. 17, pp. 321–324, 2006.
- [78] F. Dong, C. Jian, G. Kai, S. Qunrong, and L. Zuliang, "Synthesis of coumarins via pechmann reaction in water catalyzed by acyclic acidic ionic liquids," *Catalysis Letters*, vol. 121, no. 3–4, pp. 255–259, 2008.
- [79] K. Qiao and C. Yokoyama, "Koch carbonylation of tertiary alcohols in the presence of acidic ionic liquids," *Catalysis Communications*, vol. 7, no. 7, pp. 450–453, 2006.
- [80] G. Pousse, F. L. Cavelier, L. Humphreys, J. Rouden, and J. Blanchet, "Brønsted acid catalyzed asymmetric aldol reaction: a complementary approach to enamine catalysis," *Organic Letters*, vol. 12, no. 16, pp. 3582–3585, 2010.
- [81] X. B. Liu, M. Lu, T. T. Lu, and G. L. Gu, "Functionalized ionic liquid promoted aza-michael addition of aromatic amines," *Journal of the Chinese Chemical Society*, vol. 57, no. 6, pp. 1221–1226, 2010.
- [82] R. Turgis, J. Estager, M. Draye, V. Ragaini, W. Bonrath, and J.-M. Lévêque, "Reusable task-specific ionic liquids for a clean ϵ -Caprolactam synthesis under mild conditions," *ChemSusChem*, vol. 3, no. 12, pp. 1403–1408, 2010.
- [83] J. Shen, H. Wang, H. Liu, Y. Sun, and Z. Liu, "Bronsted acidic ionic liquid as dual catalyst and solvent for environmentally friendly synthesis of Chalcone," *Journal of Molecular Catalysis A: Chemical*, vol. 280, no. 1–2, pp. 24–28, 2008.

- [84] A. C. Chaskar, S. R. Bhandari, A. B. Patil, O. P. Sharma, and S. Mayeker, "Solvent-free oxidation of alcohols with potassium persulphate in the presence of bronsted acidic ionic liquids," *Synthetic Communications*, vol. 39, no. 2, pp. 366–370, 2009.
- [85] W. Wang, L. Shao, W. Cheng, J. Yang, and M. He, "Koch carbonylation of tertiary alcohols in the presence of acidic ionic liquids," *Catalysis Communications*, vol. 7, no. 7, pp. 450–453, 2006.
- [86] J. C. S. Ruiz, J. M. Campelo, M. Francavilla et al., "Efficient microwave-assisted production of furfural from C₅ sugars in aqueous media catalysed by Brønsted acidic ionic liquids," *Catalysis Science & Technology*, vol. 2, no. 9, pp. 1828–1832, 2012.
- [87] L. Zhang, M. Xian, Y. He et al., "A Brønsted acidic ionic liquid as an efficient and environmentally benign catalyst for biodiesel synthesis from free fatty acids and alcohols," *Bioresource Technology*, vol. 100, no. 19, pp. 4368–4373, 2009.
- [88] D. Patil, D. Chandam, A. Mulik et al., "Novel Brønsted acidic ionic liquid ([CMIM][CF₃COO]) prompted multicomponent hantzsch reaction for the eco-friendly synthesis of acridine-diones: an efficient and recyclable catalyst," *Catalysis Letters*, vol. 144, no. 5, pp. 949–958, 2014.
- [89] L. He, S. Qin, T. Chang, Y. Sun, and J. Zhao, "Geminal brønsted acid ionic liquids as catalysts for the mannich reaction in water," *International Journal of Molecular Sciences*, vol. 15, no. 5, pp. 8656–8666, 2014.
- [90] H. Zhang, F. Xu, X. Zhou, G. Zhang, and C. Wang, "A Brønsted acidic ionic liquid as an efficient and reusable catalyst system for esterification," *Green Chemistry*, vol. 9, no. 11, pp. 1208–1211, 2007.
- [91] S. Das, M. Rahman, D. Kundu, A. Majee, and A. Hajra, "Task-specific ionic-liquid-catalyzed efficient synthesis of indole derivatives under solvent-free conditions," *Canadian Journal of Chemistry*, vol. 88, no. 2, pp. 150–154, 2010.
- [92] W. Miao and T. H. Chan, "Ionic-liquid-supported synthesis: a novel liquid-phase strategy for organic synthesis," *Accounts of Chemical Research*, vol. 39, no. 12, pp. 897–908, 2006.
- [93] Z.-W. Wang and L.-S. Wang, "Friedel–Crafts phosphorylation of benzene catalyzed by [trEHAm]Cl-XAlCl₃ ionic liquids," *Applied Catalysis A: General*, vol. 262, no. 1, pp. 101–104, 2004.
- [94] C. Wang, W. Zhao, H. Li, and L. Guo, "Solvent-free synthesis of unsaturated ketones by the Saucy-Marbet reaction using simple ammonium ionic liquid as a catalyst," *Green Chemistry*, vol. 11, no. 6, pp. 843–847, 2009.
- [95] A. Brandt, J. Gräsvik, J. P. Hallett, and T. Welton, "Deconstruction of lignocellulosic biomass with ionic liquids," *Green Chemistry*, vol. 15, no. 3, pp. 550–583, 2013.
- [96] A. Brandt, M. J. Ray, T. Q. To, D. J. Leak, R. J. Murphy, and T. Welton, "Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid-water mixtures," *Green Chemistry*, vol. 13, no. 9, pp. 2489–2499, 2011.
- [97] A. S. Amarasekara and O. S. Owereh, "Hydrolysis and decomposition of cellulose in bronsted acidic ionic liquids under mild conditions," *Industrial & Engineering Chemistry Research*, vol. 48, no. 22, pp. 10152–10155, 2009.
- [98] C. Li and Z. K. Zhao, "Efficient acid-catalyzed hydrolysis of cellulose in ionic liquid," *Advanced Synthesis and Catalysis*, vol. 349, no. 11–12, pp. 1847–1850, 2007.
- [99] M. E. Zakrzewska, E. B. Lukasik, and R. B. Lukasik, "Ionic liquid-mediated formation of 5-hydroxymethylfurfural—a promising biomass-derived building block," *Chemical Reviews*, vol. 111, pp. 397–417, 2011.
- [100] T. Ståhlberg, W. Fu, J. M. Woodley, and A. Riisager, "Synthesis of 5-(hydroxymethyl)furfural in ionic liquids: paving the way to renewable chemicals," *ChemSusChem*, vol. 4, no. 4, pp. 451–458, 2011.
- [101] J. C. S. Ruiz, J. M. Campelo, M. Francavilla et al., "Efficient microwave-assisted production of furfural from C₅ sugars in aqueous media catalysed by Brønsted acidic ionic liquids," *Catalysis Science and Technology*, vol. 2, pp. 1828–1832, 2012.
- [102] Z. Sun, M. Cheng, H. Li et al., "One-pot depolymerization of cellulose into glucose and levulinic acid by heteropolyacid ionic liquid catalysis," *RSC Advances*, vol. 2, no. 24, pp. 9058–9065, 2012.
- [103] H. Ren, Y. Zhou, and L. Liu, "Selective conversion of cellulose to levulinic acid via microwave-assisted synthesis in ionic liquids," *Bioresource Technology*, vol. 129, pp. 616–619, 2013.
- [104] A. Taheri, C. Liu, B. Lai, C. Cheng, X. Pan, and Y. Gu, "Brønsted acid ionic liquid catalyzed facile synthesis of 3-vinylindoles through direct C3 alkenylation of indoles with simple ketones," *Green Chemistry*, vol. 16, no. 8, pp. 3715–3719, 2014.
- [105] E. J. García-Suárez, S. G. Khokarale, O. N. van Buu, R. Fehrmann, and A. Riisager, "Pd-catalyzed ethylene methoxy-carbonylation with Brønsted acid ionic liquids as promoter and phase-separable reaction media," *Green Chemistry*, vol. 16, no. 1, pp. 161–166, 2014.
- [106] K. Titze-Frech, N. Ignatiev, M. Uerdingen, P. S. Schulz, and P. Wasserscheid, "Highly selective aromatic alkylation of phenol and anisole by using recyclable brønsted acidic ionic liquid systems," *European Journal of Organic Chemistry*, no. 30, pp. 6961–6966, 2013.
- [107] A. R. Hajipour and F. Rafiee, "Basic ionic liquids: a short review," *Journal of the Iranian Chemical Society*, vol. 6, no. 4, pp. 647–678, 2009.
- [108] B. C. Ranu and S. Banerjee, "Ionic liquid as catalyst and reaction medium. The dramatic influence of a task-specific ionic liquid, [bmIm]OH, in Michael addition of active methylene compounds to conjugated ketones, carboxylic esters, and nitriles," *Organic Letters*, vol. 7, no. 14, pp. 3049–3052, 2005.
- [109] L. Yang, L.-W. Xu, W. Zhou, L. Li, and C.-G. Xia, "Highly efficient aza-Michael reactions of aromatic amines and N-heterocycles catalyzed by a basic ionic liquid under solvent-free conditions," *Tetrahedron Letters*, vol. 47, no. 44, pp. 7723–7726, 2006.
- [110] H. Zang, M. Wang, B. W. Cheng, and J. Song, "Ultrasound-promoted synthesis of oximes catalyzed by a basic ionic liquid [bmIm]OH," *Ultrasonics Sonochemistry*, vol. 16, no. 3, pp. 301–303, 2009.
- [111] E. Kowsari and M. Mallakmohammadi, "Ultrasound promoted synthesis of quinolines using basic ionic liquids in aqueous media as a green procedure," *Ultrasonics Sonochemistry*, vol. 18, pp. 447–454, 2011.
- [112] I. Yavari and E. Kowsari, "Efficient and green synthesis of tetrasubstituted pyrroles promoted by task-specific basic ionic liquids as catalyst in aqueous media," *Molecular Diversity*, vol. 13, no. 4, pp. 519–528, 2009.
- [113] Z. Deng, J. Guo, L. Qiu, Y. Zhou, L. Xia, and F. Yan, "Basic ionic liquids: a new type of ligand and catalyst for the AGET ATRP of methyl methacrylate," *Polymer Chemistry*, vol. 3, no. 9, pp. 2436–2443, 2012.

- [114] L.-R. Wen, H.-Y. Xie, and M. Li, "A basic ionic liquid catalyzed reaction of benzothiazole, aldehydes, and 5,5-dimethyl-1,3-cyclohexanedione: efficient synthesis of tetrahydrobenzo[b]pyrans," *Journal of Heterocyclic Chemistry*, vol. 46, no. 5, pp. 954–959, 2009.
- [115] J.-M. Xu, Q. Wu, Q.-Y. Zhang, F. Zhang, and X.-F. Lin, "Basic ionic liquid as catalyst and reaction medium: a rapid and facile protocol for Aza-Michael addition reactions," *European Journal of Organic Chemistry*, pp. 1798–1802, 2007.
- [116] L. Wang, H. Li, and P. Li, "Task-specific ionic liquid as base, ligand and reaction medium for the palladium-catalyzed Heck reaction," *Tetrahedron*, vol. 65, no. 1, pp. 364–368, 2009.
- [117] Z. Z. Yang, Y. N. Zhao, L. N. He, J. Gao, and Z. S. Yin, "Highly efficient conversion of carbon dioxide catalyzed by polyethylene glycol-functionalized basic ionic liquids," *Green Chemistry*, vol. 14, no. 2, pp. 519–527, 2012.
- [118] M. Fan, J. Huang, J. Yang, and P. Zhang, "Biodiesel production by transesterification catalyzed by an efficient choline ionic liquid catalyst," *Applied Energy*, vol. 108, pp. 333–339, 2013.
- [119] T. Jiang, X. Ma, Y. Zhou, S. Liang, J. Zhang, and B. Han, "Solvent-free synthesis of substituted ureas from CO₂ and amines with a functional ionic liquid as the catalyst," *Green Chemistry*, vol. 10, no. 4, pp. 465–469, 2008.
- [120] D.-Z. Xu, Y. Liu, S. Shi, and Y. Wang, "A simple, efficient and green procedure for Knoevenagel condensation catalyzed by [C₄dabco][BF₄] ionic liquid in water," *Green Chemistry*, vol. 12, no. 3, pp. 514–517, 2010.
- [121] F.-L. Yu, R.-L. Zhang, C.-X. Xie, and S.-T. Yu, "Synthesis of thermoregulated phase-separable triazolium ionic liquids catalysts and application for Stetter reaction," *Tetrahedron*, vol. 66, no. 47, pp. 9145–9150, 2010.
- [122] D. Z. Xu, Y. Liu, S. Shi, and Y. Wang, "Chiral quaternary alkylammonium ionic liquid [Pro-dabco][BF₄]: as a recyclable and highly efficient organocatalyst for asymmetric Michael addition reactions," *Tetrahedron Asymmetry*, vol. 21, no. 20, pp. 2530–2534, 2010.
- [123] O. V. Maltsev, A. S. Kucherenko, A. L. Chimishkyan, and S. G. Zlotin, " α,α -Diarylprolinol-derived chiral ionic liquids: recoverable organocatalysts for the domino reaction between α,β -enals and N-protected hydroxylamines," *Tetrahedron Asymmetry*, vol. 21, no. 21–22, pp. 2659–2670, 2010.
- [124] S. S. Khan, J. Shah, and J. Liebscher, "Ionic-liquid tagged prolines as recyclable organocatalysts for enantioselective α -aminooxylations of carbonyl compounds," *Tetrahedron*, vol. 67, no. 10, pp. 1812–1820, 2011.
- [125] S. Luo, X. Mi, L. Zhang, S. Liu, H. Xu, and J.-P. Cheng, "Functionalized chiral ionic liquids as highly efficient asymmetric organocatalysts for Michael addition to nitroolefins," *Angewandte Chemie International Edition*, vol. 45, pp. 3093–3097, 2006.
- [126] B. Ni, Q. Zhang, and A. D. Headley, "Functionalized chiral ionic liquid as recyclable organocatalyst for asymmetric Michael addition to nitrostyrenes," *Green Chemistry*, vol. 9, no. 7, pp. 737–739, 2007.
- [127] K. Erfut, I. Wandzik, K. Walczak, K. Matuszek, and A. Chrobok, "Hydrogen-bond-rich ionic liquids as effective organocatalysts for Diels–Alder reactions," *Green Chemistry*, vol. 16, no. 7, pp. 3508–3514, 2014.
- [128] M. Vasiloiu, D. Rainer, P. Gaertner, C. Reichel, C. Schröder, and K. Bica, "Basic chiral ionic liquids: a novel strategy for acid-free organocatalysis," *Catalysis Today*, vol. 200, no. 1, pp. 80–86, 2013.
- [129] J. Li, X.-K. Xie, F. Liu, and Z.-Z. Huang, "Synthesis of new functionalized chiral ionic liquid and its organocatalytic asymmetric epoxidation in water," *Catalysis Communications*, vol. 11, pp. 276–279, 2009.
- [130] Z. Kelemen, O. Holloczki, J. Nagy, and L. Nyulaszi, "An organocatalytic ionic liquid," *Organic & Biomolecular Chemistry*, vol. 9, pp. 5362–5364, 2011.
- [131] J. F. Dubreuil and J. P. Bazureau, "Rate accelerations of 1,3-dipolar cycloaddition reactions in ionic liquids," *Tetrahedron Letters*, vol. 41, no. 38, pp. 7351–7355, 2000.
- [132] W. Miao and T. H. Chan, "Exploration of ionic liquids as soluble supports for organic synthesis. demonstration with a Suzuki coupling reaction," *Organic Letters*, vol. 5, no. 26, pp. 5003–5005, 2003.
- [133] J. Fraga-Dubreuil and J. P. Bazureau, "Efficient combination of task-specific ionic liquid and microwave dielectric heating applied to one-pot three component synthesis of a small library of 4-thiazolidinones," *Tetrahedron*, vol. 59, no. 32, pp. 6121–6130, 2003.
- [134] J.-Y. Huang, M. Lei, and Y.-G. Wang, "A novel and efficient ionic liquid supported synthesis of oligosaccharides," *Tetrahedron Letters*, vol. 47, no. 18, pp. 3047–3050, 2006.
- [135] F. Hassine, S. Gmouh, M. Pucheault, and M. Vaultier, "Task specific onium salts and ionic liquids as soluble supports in Grieco's multicomponent synthesis of tetrahydroquinolines," *Monatshefte für Chemie*, vol. 138, no. 11, pp. 1167–1174, 2007.
- [136] R. A. Donga, S. M. Khaliq-Uz-Zaman, T.-H. Chan, and M. J. Damha, "A novel approach to oligonucleotide synthesis using an imidazolium ion tag as a soluble support," *Journal of Organic Chemistry*, vol. 71, no. 20, pp. 7907–7910, 2006.
- [137] H. Xie, C. Lu, G. Yang, and Z. Chen, "Synthesis of 1,4-Benzodiazepine-2,5-diones using an ionic liquid as a Soluble Support," *Synthesis*, vol. 2009, no. 2, pp. 205–210, 2009.



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