Chapter 6A

Literature on imidazolium/pyridinium based basic ionic liquids and their uses in organic reactions

6A.1. Mulfunctionalized basic ionic liquids

Multifunctionalized ionic liquids especially dicationic and tricationic liquids have been reported to have a wide range of tunable physical properties than most traditional, singly charged ILs such as higher density, melting point, viscosity, surface tension and glass transition temperature [1, 2]. These are possible only by variation of the chemical structures of suitable cation-anion pairs within the ionic liquid composition. More numbers of structural variations of ion-pairs are possible with the dicationic and tricationic ionic liquids. Different types of muiticationic ionic liquids were synthesized based on ammonium [3-5], imidazolium [6], pyridinium [7] and pyrrolidium [1] cations to explore their physical properties.

Armstrong and co-workers [8, 9] studied the effect of various counter ions on the densities of symmetrical tricationic ILs that was in the order of $NTf_2^- > PF_6^- > OTf^- > BF_4^-$ They observed thermal decomposition temperatures of some of the ILs to be greater than 400 °C which was quite encouraging compared to the corresponding monocationic ILs. Their melting points depend on the flexibility of the central core unit. The flexible core structure of tricationic ILs possesses lower melting point when compared to the ILs with rigid core structure unit.

The presence of three charges in very close contact on the flexible tricationic ILs can be described as possible reason for existence of high polarity in such ILs at room temperature [5]. Due to their tunable physicochemical properties, they have been utilized as novel solvent systems in organic synthesis and catalytic studies [10], electrochemistry [11], high temperature lubricants [12], selective gas chromatographic stationary phases [13], molecular pincers for anion recognition [14], ionic liquid crystals [15], host-guest complexes [16], gel phases [17] and so on.

The development of environmentally benign task-specific basic ionic liquids and their uses in some base-catalyzed organic reactions offer a great potential for replacement of toxic, corrosive and water miscible inorganic/ organic bases in catalytic reactions [18]. They exhibit several advantages over inorganic bases such as water and air stability, immiscibility with many organic solvents, noncorrosive and nonvolatile, high catalytic efficiency and easy reusability after simple separation from the reaction mixture.

The acidity or basicity of an ionic liquid is governed by the nature of cation, anion, or by combination of cation and anion. Most of the basic mono cationic ionic liquids are made from combination of basic anions with most common N-alkylimidazolium, alkylammonium or N-alkylpyridinium cations. Other cations include pyrrolidinium, pyrimidinium, pyrazolium, triazolium, pyridazinium, pyrazinium, oxazolium and thiazolium. A wide array of anions including carboxylates, fluorinated carboxylates, hydroxide sulfonates, fluorinated sulfonates, imides, borates, phosphates, antimonates, halides, halometallates etc. can be paired with chosen cation component for achieving Lewis Basic or Brönsted basic ionic liquids [19]. These basic ionic liquids may be classified as Brönsted or Lewis basic depending upon the type of anion used to formulate the ionic liquids. Another method for designing of strong basic ILs relied on attachment of specific basic functionalities to the cation. The ILs derived by this method sometimes exhibit greater thermal stability than those containing only basic anions [20].

The attachment of more number of basic anions in multi-charged ILs may influence the basicity, thermal stability, water sensitivity, viscosity, conductivity and solubility of the ILs in various solvents. The literature review reveals that the basic ionic liquids either work as efficient base catalyst or basic reaction medium for various types of base catalyzed condensation reactions such as Aldol condensation, Knoevenagel reaction, Claisen-Schmidt reaction etc. depending on the strength of basic sites i.e Brönsted basic or Lewis basic [21-23]. As compared to the functionalized acidic ILs, the reports related to the basic ILs are quite few. But, they have the ability to replace conventional basic reagents like NaOH, KOH, K_2CO_3, $NaHCO_3$, NaOAc etc. in organic reactions by acting as reusable basic catalysts. These conventional bases produce excellent results only with stoichiometric amount of bases for any type of base promoted organic reactions. In industrial scale reactions, they release large amount of toxic and corrosive basic waste to the environment. From this point of view, the nature of basic ionic liquids serves its purpose much justifiably and their function to act as both solvent and catalyst make the process much easier to handle. Therefore, it is always an exciting challenge to develop novel Brönsted-type basic catalytic systems that are environment friendly, recyclable and cost effective in nature.

In next section, we include the literature review of pyridinium and imidazolium basic ILs and their applications as basic catalyst/solvents in various organic reactions till 2016.

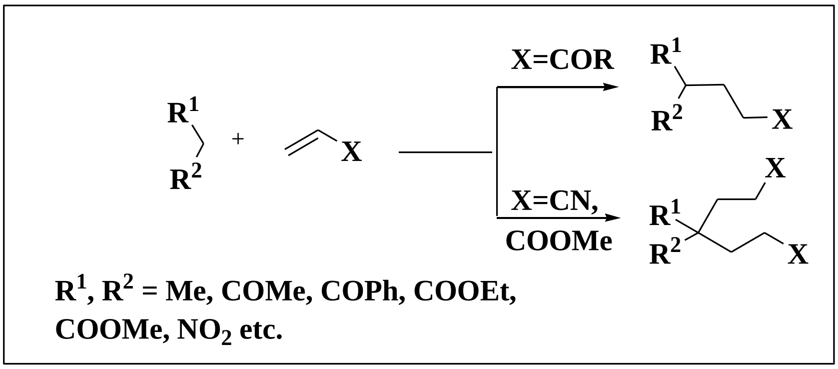
6A.2. Imidazolium and pyridinium based basic ionic liquids and their uses in organic synthesis including Knoevenagel condensation

In literature, a number of basic ionic liquids are found derived from complex halometallate anions and N-alkylpyridinium or N-alkylimidazolium cations [24]. The mole fraction of metal halides utilized to synthesize these ionic salts determines whether the resulting salt will be Lewis acidic or basic or neutral in nature. The most important example is the basic chloroaluminate(III) ionic liquid obtained through reactive dissolution of $AlCl_3$ in excess of chloride-based ionic liquid [cation]Cl with mole fraction of $AlCl_3<0.5$ according to equation (1) [25]. In this situation, the metal ion may be fully saturated with its coordination number and so will not act as Lewis acids.

$$nCl^- + AlCl_3 \rightarrow AlCl_4 + (n-1)Cl^- \ (\chi_{AlCl_3}<0.5) \qquad (1)$$

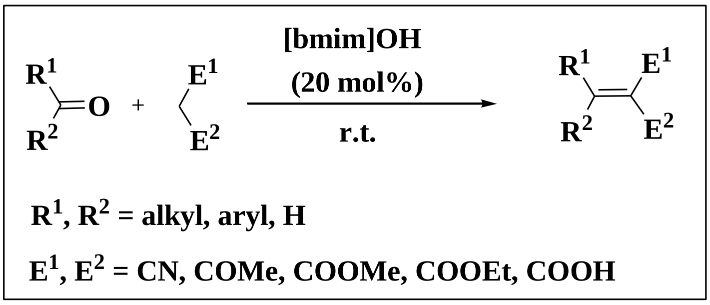
These chlorometallate systems have been found to act as good solvents in electrochemistry, spectroscopy and also in catalysis [26-28].

The imidazolium based Brönsted-basic IL, 1-butyl-3-methylimidazolium hydroxide [bmim][OH] was prepared by Ranu and his co-worker in 2005 using a reaction mixture of [bmim]Br and KOH in dichloromethane under vigorous stirring at room temperature for 10 h [29]. This IL was explored as catalysts/and reaction medium in Michael addition reactions of 1, 3-dicarbonyl compounds, cyano esters, and nitro alkanes to a variety of conjugated ketones, carboxylic esters, and nitriles (**Scheme 6A.1**). The respective mono and bis-addition products were formed in excellent yields within 0.5-4 h time duration. Overall, the method had various advantages over the existing protocols with regard to operational simplicity, reaction time and yield, general applicability, avoid of toxic organic solvent and catalyst etc.



Scheme 6A.1: Michael addition catalyzed by [bmim]OH

Later in 2006, Ranu et al. [22] utilized this IL as catalyst in the Knoevenagel condensation reactions of aliphatic and aromatic aldehydes and ketones with diethyl malonate, malononitrile, ethyl cyanoacetate, malonic acid and ethyl acetoacetate in absence of any organic solvent (**Scheme 6A.2**). The desired products were obtained within short reaction times (10-30 min) at room temperature. With this protocol, the condensation of aliphatic aldehyde with diethyl malonate was easily achieved, which is otherwise a difficult job to achieve.



Scheme 6A.2: Knoevenagel condensation catalyzed by [bmim]OH IL in absence of organic solvent

A large number of studies on uses of [bmim][OH] ionic liquid have been reported in different type of organic reactions as catalyst/solvent/promoter. Some of the base catalyzed reactions include Knoevenagel condensation [22, 30], Markovnikov addition [31], Michael addition [32], aza Michael reactions [33], transesterification [34] and polymerization reaction [35]. It was also utilized for base catalyzed one pot synthesis of oxygen and nitrogen heterocycles. Few examples of such heterocycles are polyfunctionalized-4H-pyrans [36], quinazoline-2,4 (1*H*, 3*H*)-diones [37], quinoline

[38], 2-alkylsubstituted chromanones [39], benzo[g]chromene derivatives [40], pyrazolo [3, 4-b] pyridines [41], 2-aroylbenzofuran-3-ols [42], 2-Amino-4H-chromenes [43], benzo[a]pyrano[2, 3-c]phenazine derivatives [44], substituted benzofurans [45], 1, 4, 5-trisubstituted-1, 2, 3-triazoles [46], polyhydroquinolines [47] etc.

In the same year, Tai et al. [48] developed a Lewis basic 1-ethyl-3-methylimidazolium chloride/tetrafluoroborate ionic liquid The authors studied the electrodeposition of palladium-silver alloy from the ionic liquid solutions containing Pd(II) and Ag(I) within a temperature range of 35-120 °C. Both the electrodeposition involved over potential driven nucleation process and Pd-Ag electrodeposits were obtained in nodular shapes.

At the same time, Cai et al. [49] prepared two amino-functionalized imidazolium based ionic liquid: 1-aminoethyl-3-methylimidazolium hexafluorophosphate ([2-aemim][PF_6]) and 1-aminoethyl-3-methylimidazolium tetrafluoroborate ([2-aemim][BF_4]) (**Fig. 6A.1**) and explored their catalytic activity towards the Knoevenagel condensation of aromatic aldehydes with malononitrile and ethyl cyanoacetate in aqueous media. The combination of room temperature condition, aqueous media and use of recyclable IL as catalyst made this protocol an efficient eco-friendly one. The respective products were obtained in very good to excellent yields.

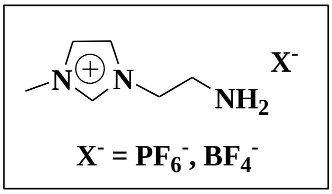
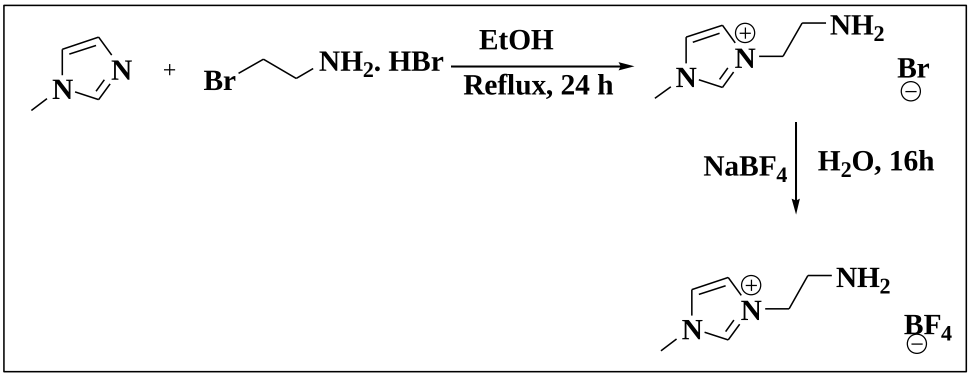


Fig. 6A.1: Structures of [2-aemim][PF_6] and [2-aemim][BF_4]

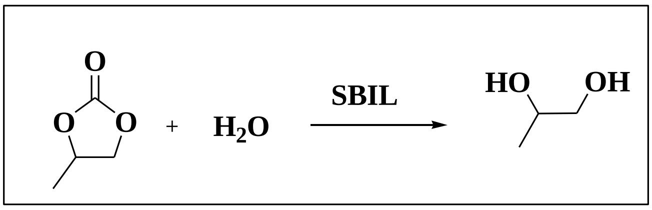
In 2007, Guo-hua et al. [50] prepared 1-(2-amine-ethyl)-3-methyl-imidazolium boron tetrafluoride (**Scheme 6A.3**) as basic IL and used as catalyst for condensation of aldehydes/ketones with activated methylene compounds in aqueous media at 30-50 °C temperature. The IL was quite active and the desired products were formed within considerable time frame in 70-97% yields. It could be easily recycled till six times with little loss in activity.



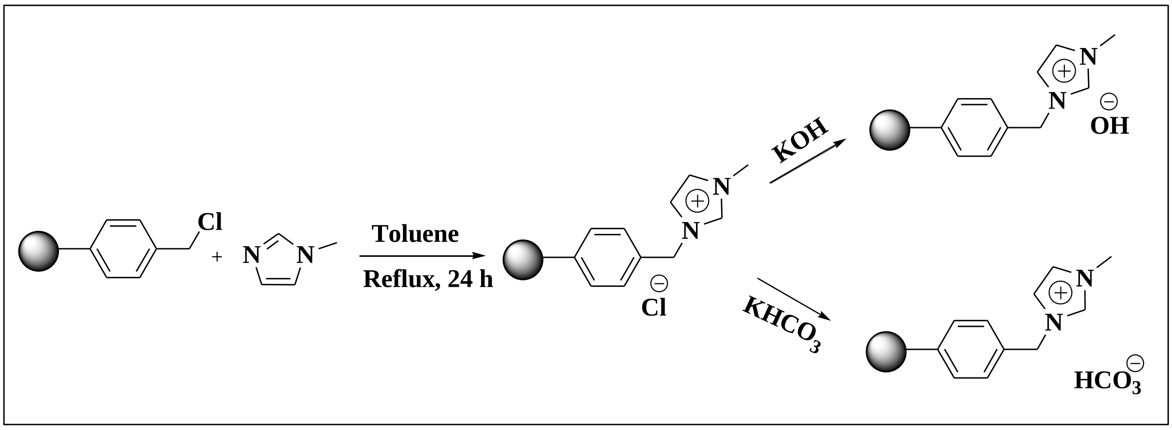
Scheme 6A.3: Preparation of 1-(2-amine-ethyl)-3-methyl-imidazolium boron tetrafluoride IL

In 2008, two basic ionic liquids, 1-butyl-3-methylimidazolium trifluoroacetate ([bmim][CF_3COO]) and 1-butyl-3-methylimidazolium acetate ([bmim][CH_3COO]) were employed for measurement of heat capacities in the temperature range of 5-370 K using adiabatic calorimetry method by Strechan et al.[51]. They observed dependence of thermal behavior of [bmim][CF_3COO] on crystallization procedure.

Xiao et al. [52] explored hydrolysis of propylene carbonate to 1, 2-propylene glycol using a SBIL catalyst (**Scheme 6A.4**). The polystyrene based imidazolium basic catalyst was prepared by following the **Scheme 6A.5**. The effects of temperature, time, molar ratio of water to propylene carbonate, choice of catalyst, and amount of catalyst were investigated. In addition, the catalyst could be reused at least up to five times with slight loss of catalytic activity.



Scheme 6A.4: Hydrolysis of propylene carbonate to 1, 2-propylene glycol



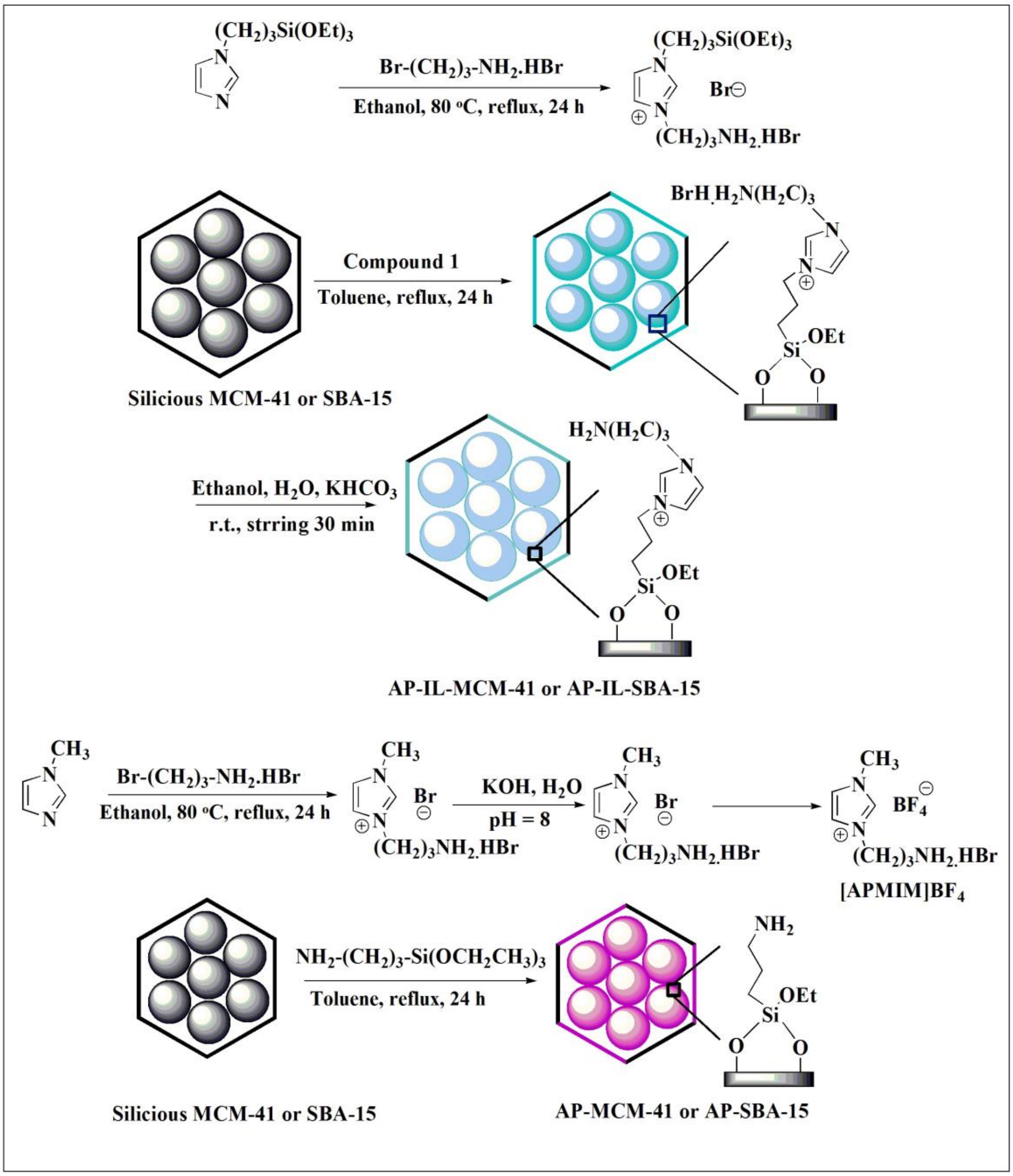
Scheme 6A.5: Preparation of supported ILs (SBIL)

Zhao et al. described the immobilization of basic amino-functionalized task-specific ILs: N-(3-aminopropyl), N(3)-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium bromide hydrobromide on mesoporous silicas of MCM-41 and SBA-11 followed by neutralization of protonated amino group with KOH (**Scheme 6A.6**) [53]. The catalytic activity of this system was tested for the Knoevenagel condensation in aqueous medium (**Scheme 6A.7**).

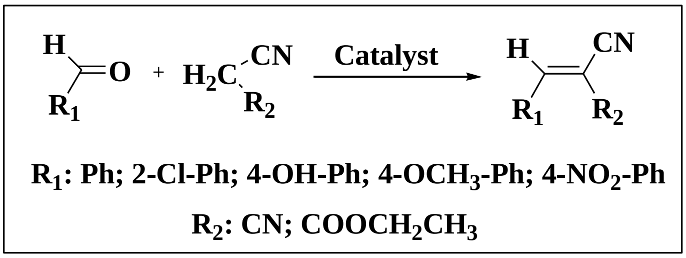
In 2010, an imidazolium based task-specific ionic liquid [**IL-OPPh$_2$]** (**Fig. 6A.2**) was prepared by Valizadeh and Gholipour following a reported procedure [54] that bears a weak Lewis basic phosphinite group in its structure [55]. This IL was examined as reusable catalyst/solvent system for the condensation of arylaldehydes with malononitrile, dimethyl (diethyl) malonate, and ethyl cyanoacetate at 60 °C under solvent-free condition within 8-20 min reaction (**Scheme 6A.8**).

Forsyth et al. [56] in a report described the synthesis of amino-functionalized imidazolium based IL according to **Scheme 6A.9** along with other members of ammonium based ILs. The qualitative basicity of the ILs was evaluated from their interaction with a universal indicator. The catalytic activity of these ILs was evaluated for Heck and Knoevenagel reactions successively.

In 2011, Kowsari and Mallakmohammadi [38] synthesized few basic ionic liquids (BILs) based on imidazolium cation in association with hydroxide anion (**Fig. 6A.3**) and explored their catalytic efficiencies towards the synthesis of quinoline derivatives from the condensation reactions of isatin with ketones by ultrasonic irradiation in aqueous media (**Scheme 6A.10**).



Scheme 6A.6: Synthetic protocol for immobilized basic ILs: [APMIM]BF_4 and amino functionalized mesoporous silicas



R_1: Ph; 2-Cl-Ph; 4-OH-Ph; 4-OCH_3-Ph; 4-NO_2-Ph

R_2: CN; $COOCH_2CH_3$

Scheme 6A.7: Knoevenagel condensation catalyzed by immobilized basic ILs, [APMIM]BF_4 and amino functionalized mesoporous silicas

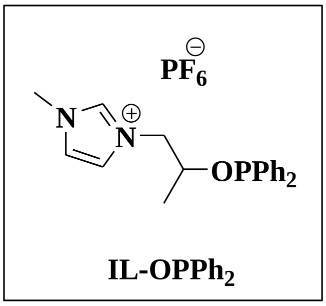
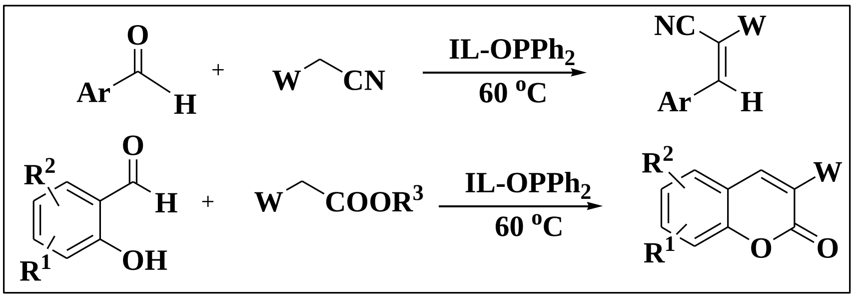
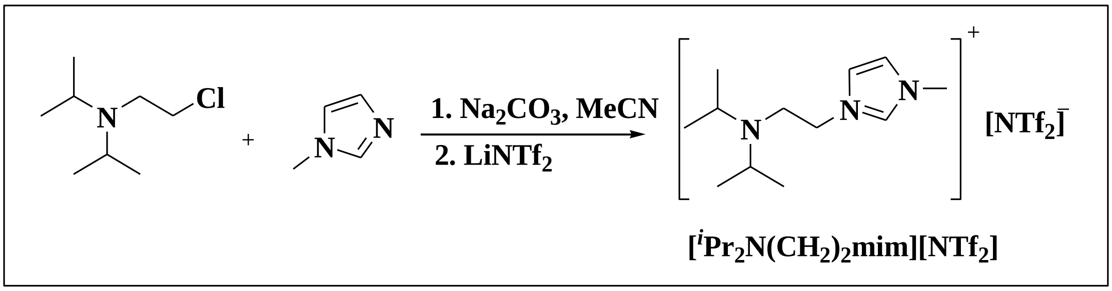


Fig. 6A.2: Structure of IL-OPPh$_2$



Scheme 6A.8: IL-OPPh$_2$ catalyzed Knoevenagel condensation reaction and synthesis of coumarin derivatives



Scheme 6A.9: Preparation of amino-functionalized imidazolium based IL

The use of BILs and ultrasonic irradiation promote the reactions efficiently at room temperature and affect both the reaction time and yield remarkably. Among the BILs used for this study, reusability study for [bmim]OH was carried out and it was found quite promising. The BIL was continuously reused for five times without appreciable loss in catalytic activity.

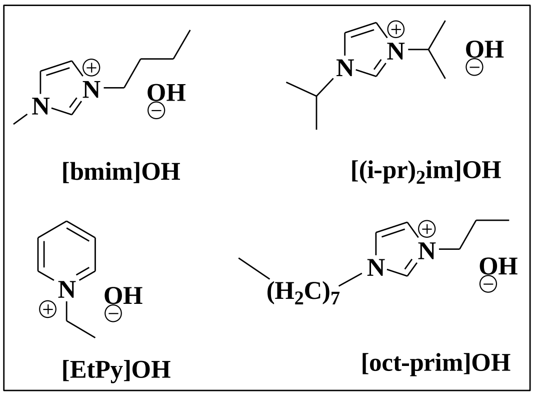
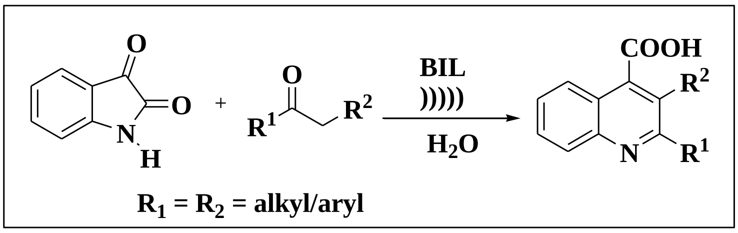
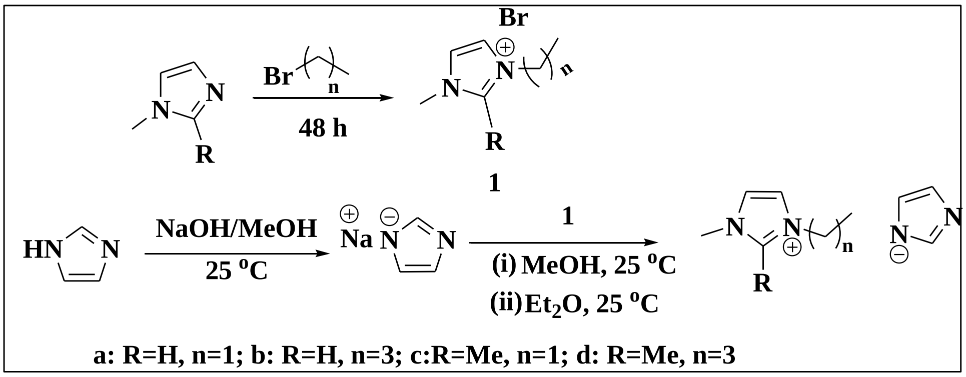


Fig. 6A.3: Imidazolium based BILs containing hydroxide ion

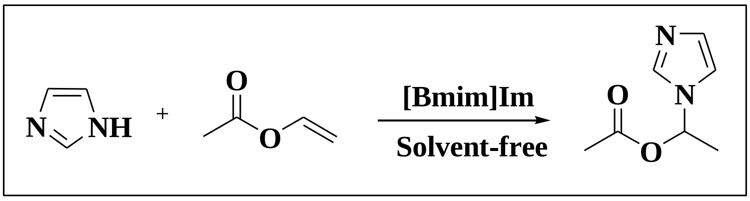


Scheme 6A.10: Synthesis of quinolone derivatives catalyzed by BILs

Chen et al. prepared a series of imidazolium based basic ionic liquids by following the reaction **Scheme 6A.11** [57]. The prepared ILs displayed strong basicity and relatively good thermal stability. Satisfactory catalytic activities were explored for solvent-free aza-Markovnikov addition reactions at room temperature when 2 mol% of [Bmim]Im was used as catalyst in one h (**Scheme 6A.12**). Experimental results revealed that H-bond is not formed between imidazole [Bmim]Im/imidazole and vinyl ester in case of aza-Markovnikov reactions. The use of imidazolide ionic liquids in aza-Michael addition was also studied as well.

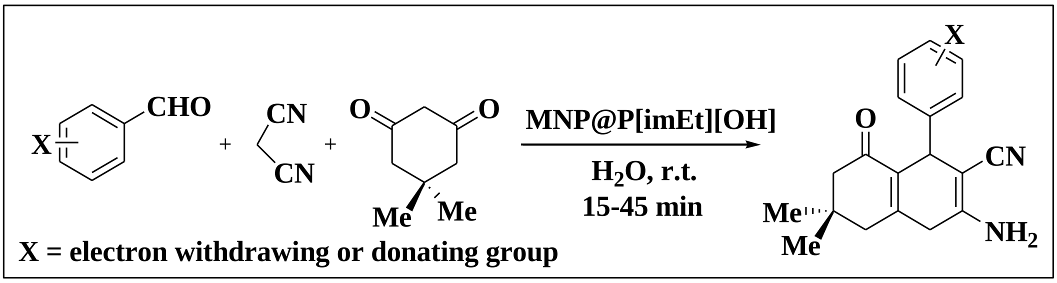


Scheme 6A.11: Synthesis of imidazolide ILs



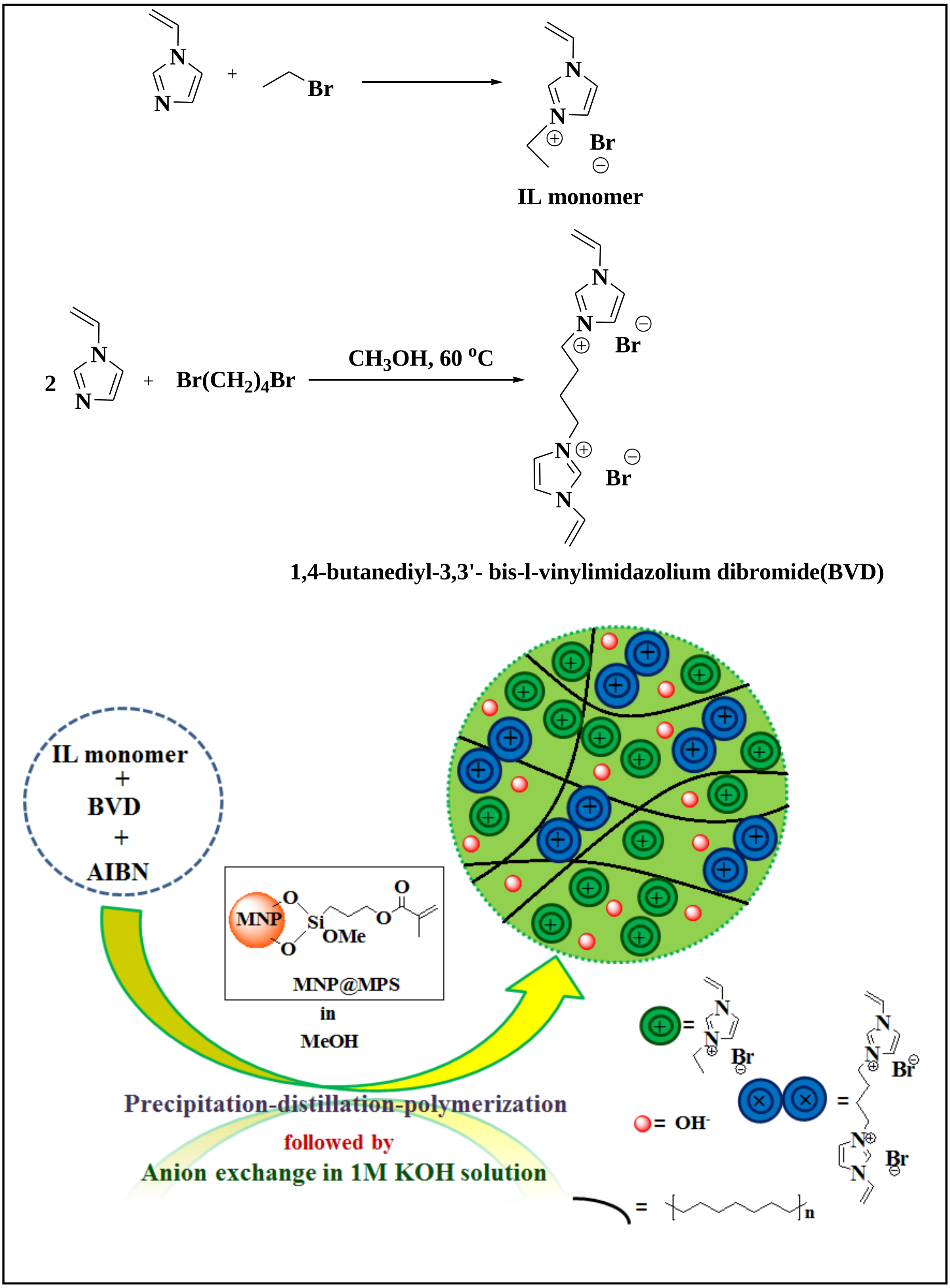
Scheme 6A.12: Markovnikov addition of imidazole to vinyl acetate catalyzed by [Bmim]Im

In 2013, Pourjavadi et al. [58] prepared one heterogeneous Brönsted-type basic catalysts MNP@P[imEt][OH], based on Fe_3O_4 magnetic nanoparticle (MNP) coated with the multilayers of poly(ethylvinylimidazolium) hydroxide, which proved to be highly efficient for the synthesis of 4H-benzo[b]pyrans in water (**Scheme 6A.13**). The separation of the catalyst was readily achieved from the reaction mixture using simple magnetic decantation and the catalyst could be easily recycled with similar catalytic activity. The catalyst was prepared by distillation-precipitation-polymerization of 1-vinyl-3-ethyl imidazolium in the presence of surface modified magnetic nanoparticles (**Scheme 6A.14**).



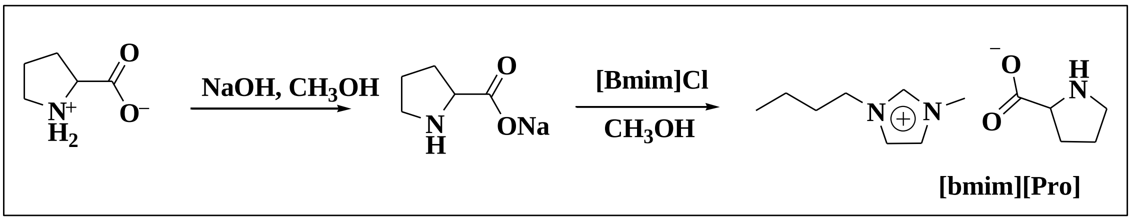
Scheme 6A.13: Synthesis of 4H-benzo[b]pyrans catalyzed by MNP@P[imEt][OH]

Wang et al. used six basic ILs: 1-butyl-3-methylimidazolium acetate([Bmim]OAc), 1-butyl-3-methylimidazolium bicarbonate([Bmim]HCO_3), 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH), 1-ethyl-3-methylimimethylimidazolium hydroxide ([Emim]OH), 1-butyl-3-methylimidazoliumbenzoate ([Bmim]PhCOO), and 1-ethylamine-3-methylimidazolium tetrafluoroborate ([Emim]BF_4) according to the reported procedures [29, 59, 60] and evaluated their catalytic activity in one-pot synthesis of 2-amino-4H-chromenes derivatives [42].



Scheme 6A.14: General procedure for synthesis of MNP@P[imEt][OH]

Hongbing et al. [61] synthesized a pyrrolidine carboxylic functionalized ionic liquid: 1-butyl-3-methylimidazolium-(S)-2-pyrrolidinecarboxylic acid salt ([bmim][Pro]) via an improved procedure (**Scheme 6A.15**). The catalytic activity of this IL was tested for the synthesis of α, β-unsaturated carbonyl compounds via Knoevenagel condensation reaction. Desired products were obtained in good yields from the reaction of active methylene compounds with aldehydes and ketones at room temperature in aqueous media. The IL could be reused efficiently for six cycles.



Scheme 6A.15: Preparation of [bmim][Pro] IL

Shaterian and Azizi [62] utilized two weak basic imidazolium ILs namely 1-butyl-3-methylimidazolium imidazolide and 1-ethyl-3-methylimidazolium acetate (**Fig. 6A.4**) obtained from reported method [63, 64] as reusable catalyst for solvent free synthesis of 7-amino-1, 3-dioxo-1, 2, 3, 5-tetrahydropyrazolo[1, 2-a][1, 2, 4]triazole and 6, 6-dimethyl-2-phenyl-9-aryl-6, 7-dihydro-[1, 2, 4]triazolo[1, 2-a]indazole-1, 3, 8(2H, 5H, 9H)-trione derivatives (**Fig. 6A.5**) separately.

Sun et al. [65] performed a direct synthesis of dimethyl carbonate (DMC) from methanol and carbon dioxide using a series of hydroxyl functionalized basic ionic liquids and compared their task-specific basic nature as catalysts /solvent systems. They utilized various basic ionic liquid namely choline hydroxide, [Etmim][OH] (1-ethoxyl-3-methylimidazolium hydroxide), [Etmim][Br] (1-ethoxyl-3-methylimidazolium bromide), [Emim][OH] (1-ethyl-3-methylimidazolium hydroxide), and [Bmim][OH] (1-butyl-3-methylimidazoliumhydroxide) which were obtained according to the reported literatures [30, 66]. Among the screened ILs, choline hydroxide was found to be an effective catalyst for the conversion of DMC.

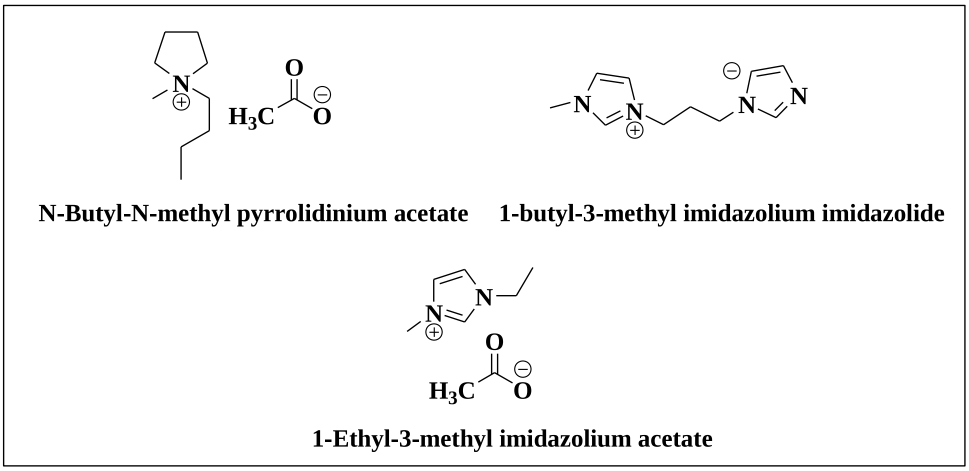


Fig. 6A.4: Structures of basic imidazolium and pyrazolium ILs

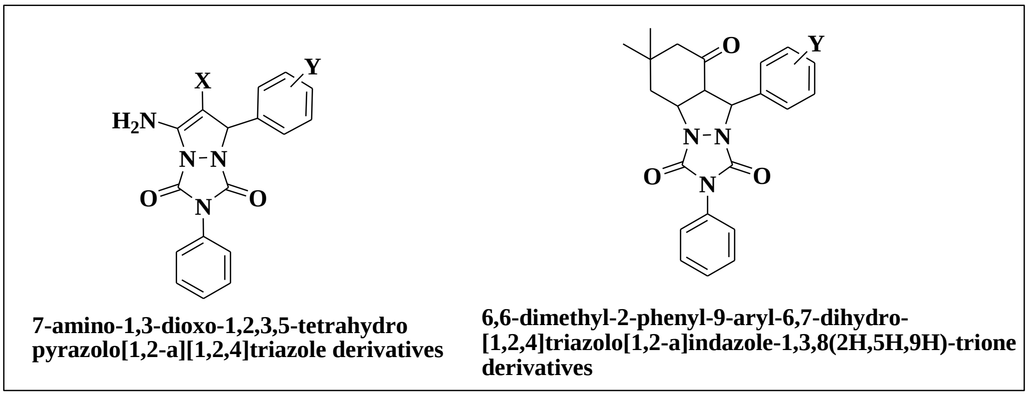
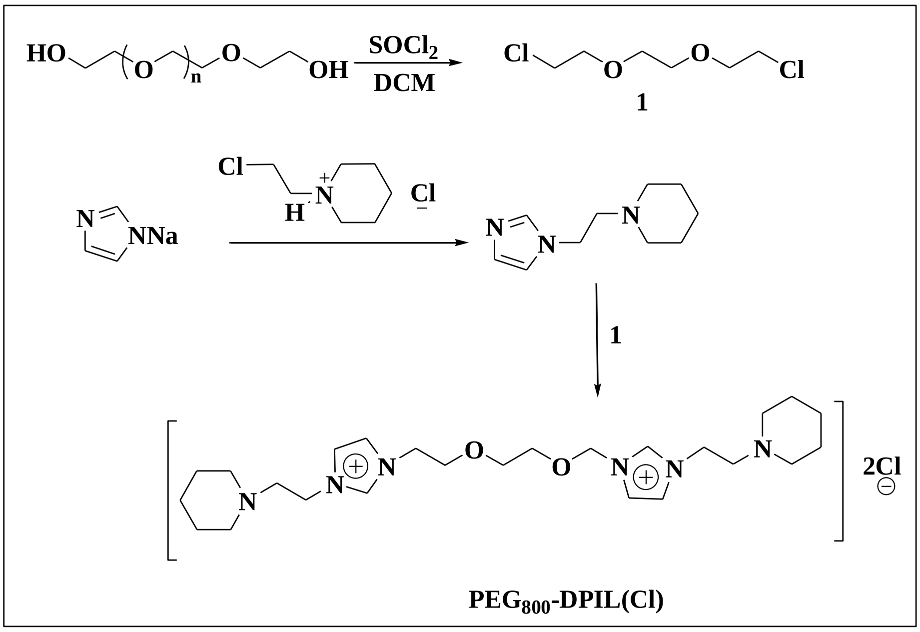


Fig. 6A.5: Structures of synthesized derivatives

Luo et al. [67] prepared a piperidine and imidazole functionalized PEG bridged Lewis basic dicationic IL according to **Scheme 6A.16**. The catalytic activity of the IL was probed in the four component Hantzsch reaction under solvent-free condition. Desired hydroquinolines were obtained with excellent yields within short reaction time. The IL could be recovered easily and recycled successfully for at least eight times.

The dibromination of electron poor and electron-rich alkenes were carried out using catalytic amount of known targeted ILs functionalized with a basic amino-aliphatic chain (**Fig. 6A.6**) [68-70] in aqueous medium by Primerano et al. [71]. The amine functionalized basic ILs effectively catalyzes the direct addition of bromine at ambient temperature. The protocol was both chemo- and regioselective in nature and allowed the recycling of ionic liquids.



Scheme 6A.16: Synthetic route for PEG_{800}-DPIL(Cl)

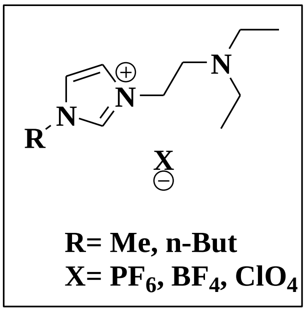


Fig. 6A.6: Structures of amino-alkyl chain functionalized ILs

Guo et al. [72] used three imidazolium based basic ILs with different branched alkyl side chains ([$C_n$mim]OH, n = 2, 3, 4) (**Fig. 6A.7**) and used them as catalysts for green biodiesel production via transesterification reaction under microwave irradiation conditions. Among the screened ILs, [C_2mim]OH exhibited the best catalytic activity affording 96% yield. The method showed quite improvement over the conventional method and it formed clearly biphasic systems immediately after the completion of transesterification of soybean oil.

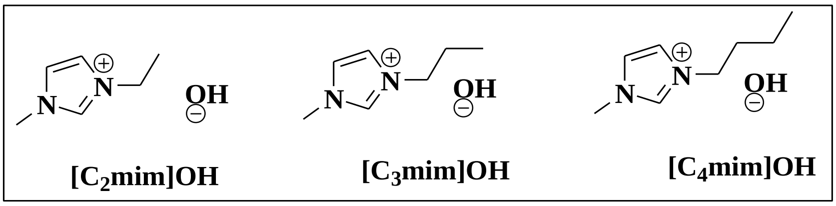
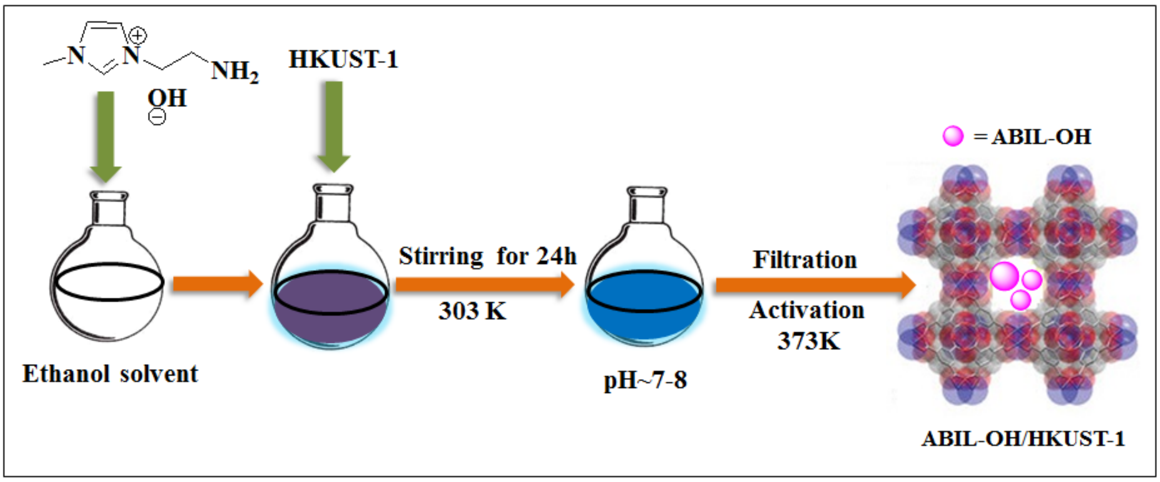


Fig. 6A.7: Structures of imidazolium based basic ILs

In 2014, Al-Sabagh et al. [73] studied the glycolysis of poly(ethylene terephthalate) (PET) catalyzed by Lewis basic ionic liquid [Bmim][OAc] which was synthesized according to a reported procedure [74]. They examined the effect of different factors such as temperature, time, ethylene glycol dosage, PET amount, [Bmim][OAc] dosage over the glycolysis reaction. Under the optimum reaction conditions, using [Bmim][OAc], 100% PET and about 58.2% bis(2-hydroxyethyl)terephthalate (BHET)yield was obtained.

Luo et al. [75] prepared a molecular size and shape-selective catalyst, microporous metal-organic framework HKUST-1 immobilized amino-functionalized basic ionic liquid (ABIL-OH), through facile impregnation and activation (**Scheme 6A.17**). Characterizations of the basic catalysts revealed uniform distribution of active species ABIL-OH in well-defined HKUST-1 nano cavities of copper-based MOFs [$Cu_3(BTC)_2$] (HKUST-1)(BTC = 1, 3, 5-benzenetricarboxylate). The catalytic efficiency was observed for the Knoevenagel condensation and reused for five times with the same efficiency.



Scheme 6A.17: The schematic illustration for synthesizing ABIL-OH/HKUST-1 catalyst

The catalytic uses of nine basic imidazolium functionalized dicationic ILs (1a-l) (**Fig. 6A.8**) were explored by Rizzo et al. [76] for mononuclear rearrangement of (Z)-phenylhydrazone of 3-benzoyl-5-phenyl-1, 2, 4-oxadiazoles to triazoles at 363 K (**Scheme 6A.18**). The authors prepared these ILs according to a reported procedure [77].The basic strength of the ILs were measured by Hammett indicator method. The outcome of the reaction was found to be greatly affected by the nature of interactions operating between cation and anion of the ionic liquid used.

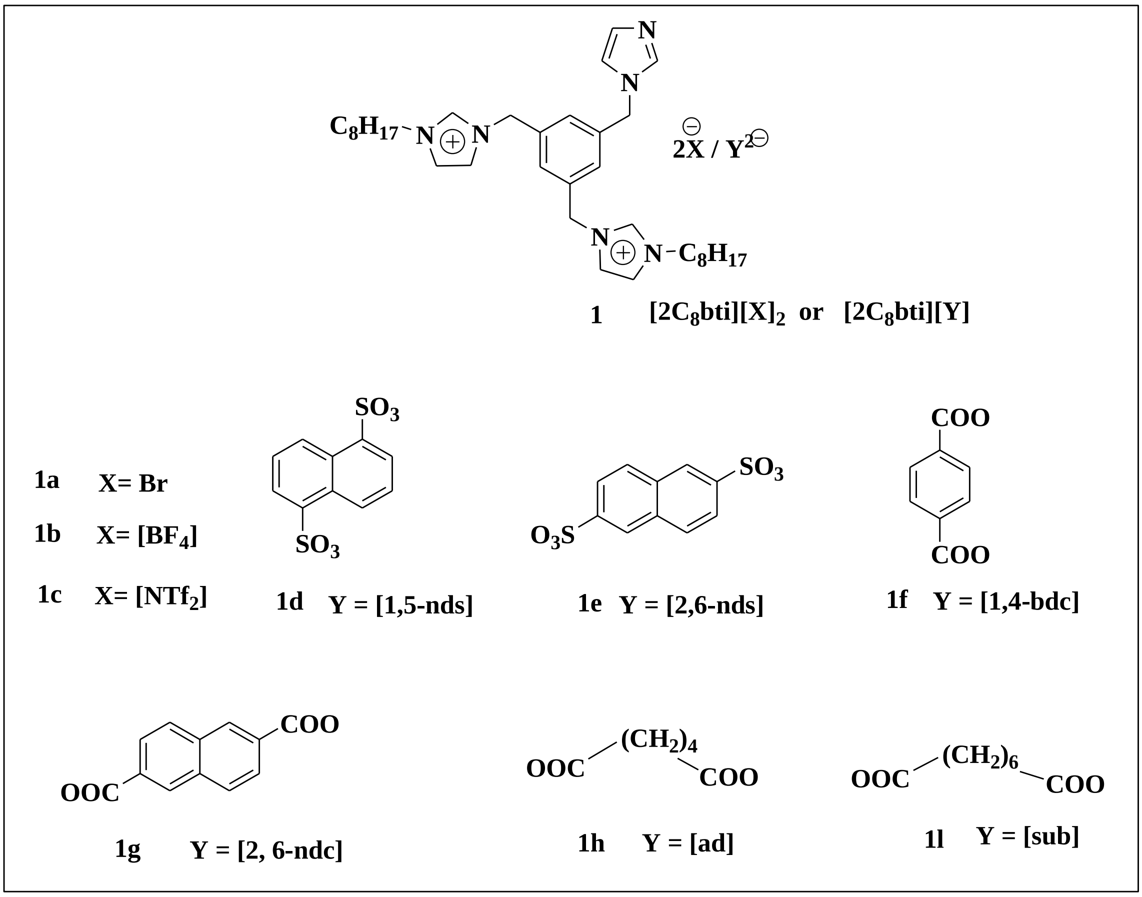
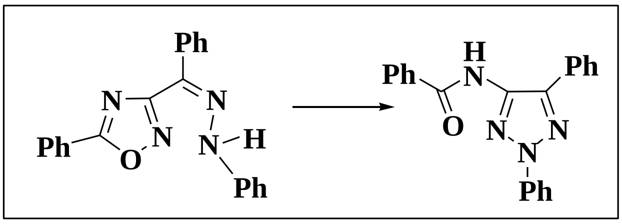


Fig. 6A.8: Structures of basic ILs used by Rizzo et al.



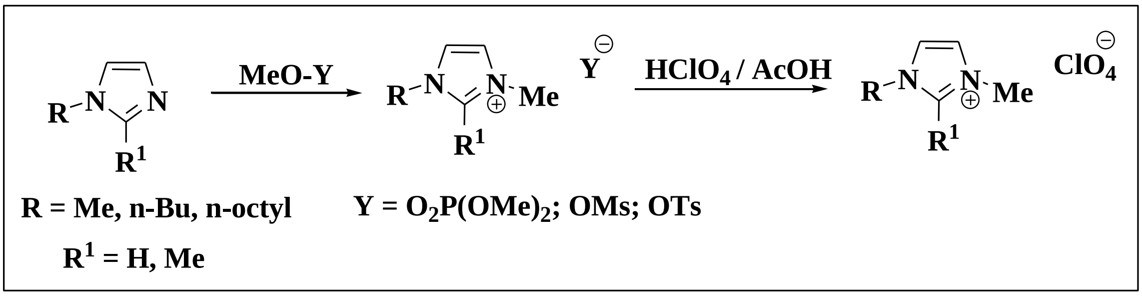
Scheme 6A.18: Rearrangement of (Z)-phenylhydrazone of 3-benzoyl-5-phenyl-1, 2, 4-oxadiazoles to triazoles

Zicmanis and Anteina [78] investigated the influence of main structural elements of 1, 3-dialkylimidazolium salts with different anions methanesulfonate, para-toluenesulfonate, and dimethyl phosphate (DMP)] on their catalytic activities in the Knoevenagel reaction between benzaldehyde and ethyl cyanoacetate. The synthetic strategy for the ILs is presented in **Scheme 6A.19**. The 1, 3-dialkylimidazolium dimethyl phosphate IL could be successfully used both as reaction media and catalysts. Additionally, it was reused for five cycles with significant retention of catalytic activity.

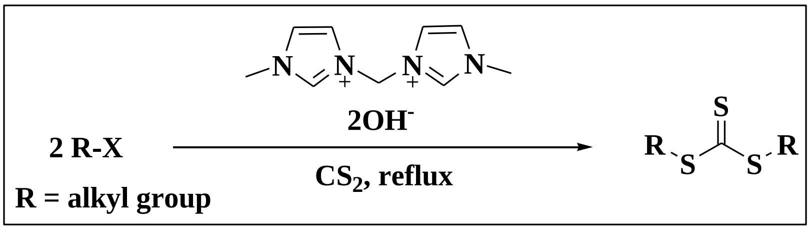
Sayyahi et al. [79] described the synthesis of symmetrical dialkyltrithiocarbonates from alkyl halides using carbon disulphide and a novel basic IL: 1, 1′-bis-methyl-3, 3-methylene-bisimidazolium dihydroxide (**Scheme 6A.20**) as a reagent and phase transfer catalyst. The reaction was simple, rapid and gave high product yields.

In 2015, Luo and co-workers also used [bmim]OH and [bmim]Im alkaline ILs as catalysts in the glycerolysis of soybean oil for monoacyl glycerol synthesis at 200 °C [80]. The [bmim]Im exhibited better catalytic efficiency than the [bmim]OH because of strong basic character. The catalyst could be recycled successfully for six consecutive cycles.

Shiran and co-workers [81] also employed basic ionic liquid 1-methyl-3-*n*-octylimidazolium hydroxide ([omim]OH) (**Fig. 6A.9**) for synthesis of thiazol-2-imine derivatives from the regioselective one pot three-component reaction of aryl amine, alkylisothiocyanate, and various α-haloketones at room temperature(**Scheme 6A.21**). The method had several advantages over the conventional ones in terms of yield, reaction time, facile work up and greater economic benefits.



Scheme 6A.19: Synthesis of 1, 3-dialkylimidazolium salts with different anions



Scheme 6A.20: Synthesis of symmetrical dialkyltrithiocarbonates catalyzed by 1, 1′-bis-methyl-3, 3-methylene-bisimidazolium dihydroxide

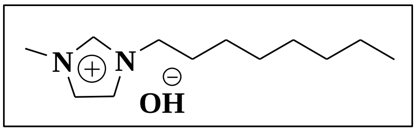
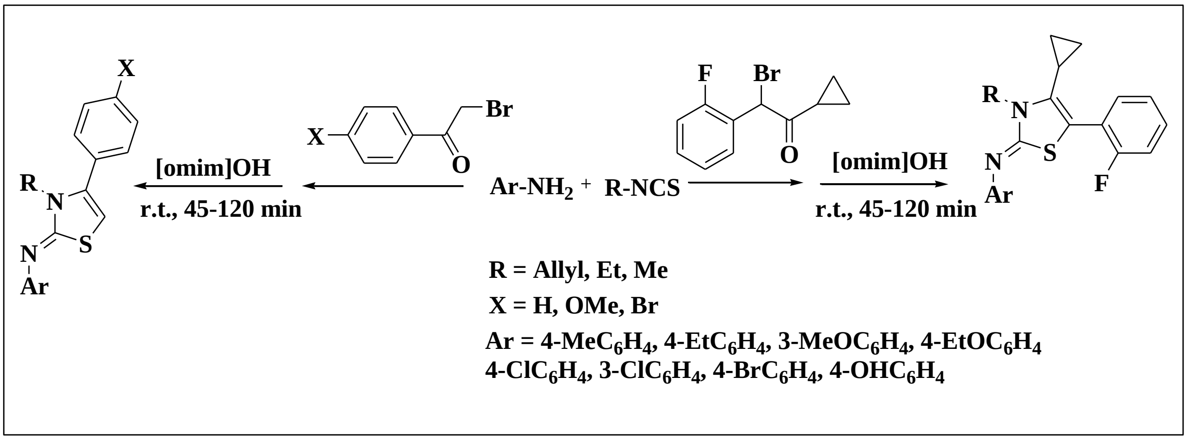


Fig. 6A.9: Chemical structure of 1-methyl-3-*n*-octylimidazolium hydroxide



Scheme 6A.21: Synthesis of thiazol-2-imine derivatives catalyzed by [omim]OH

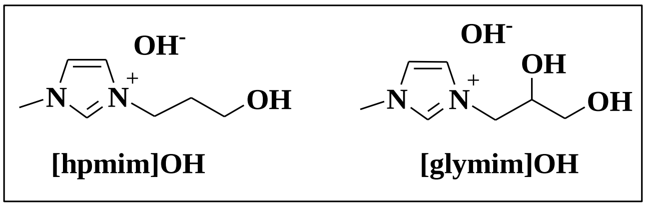
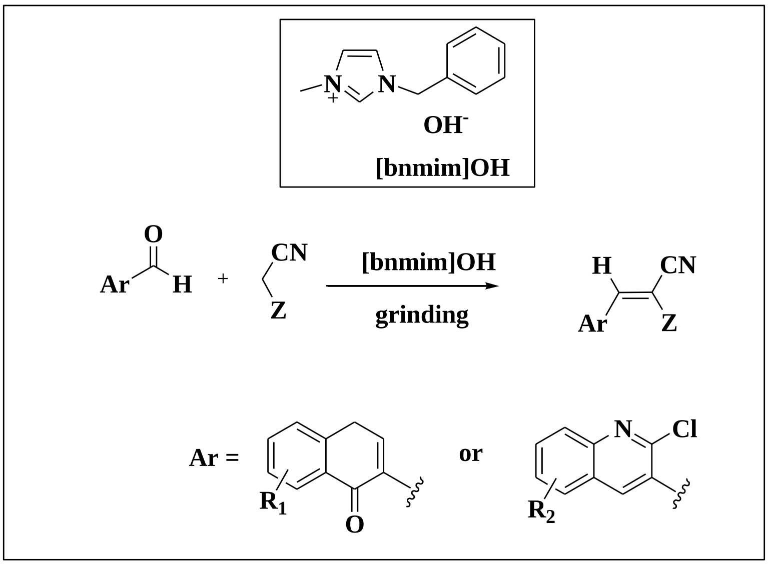


Fig. 6A.10: Structure of [hpmim]OH and [glymim]OH

Nowicki et al. [82] introduced two new imidazolium based basic ILs: 1-methyl-3-alkylimidazolium hydroxide ([hpmim]OH and [glymim]OH (**Fig. 6A.10**). The catalytic activities of the ILs were explored in the transesterification of rapeseed oil with methanol and compared to the well explored [bmim]OH ionic liquid. Nearly 100%

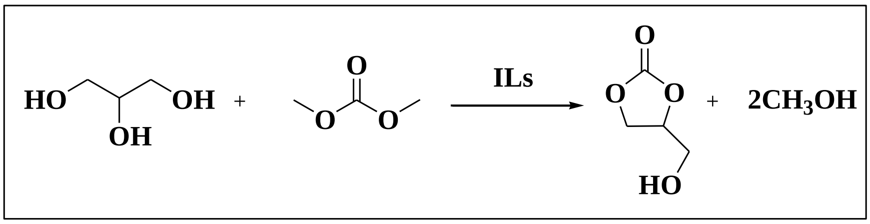
conversion of rapeseed oil was achieved in case of [glymim]OH IL due to its structural similarity to glycerol.

Shelke and Khadse [83] also utilized basic ionic liquid 1-benzyl-3-methylimidazolium hydroxide([bnmim]OH) as catalyst in Knoevenagel condensation of 4-oxo-(4H)-1-benzopyran-3-carbaldehydes and 2-chloroquinoline-3-carbaldehyde with various active methylene compounds viz. malononitrile, ethylcyanoacetate, cyanoacetic acid, cyanoacetamide and Meldrum's acid (**Scheme 6A.22**). Desired products were obtained in short reaction time with excellent yields. Additionally, the IL could be recycled up to fourth consecutive cycle efficiently.

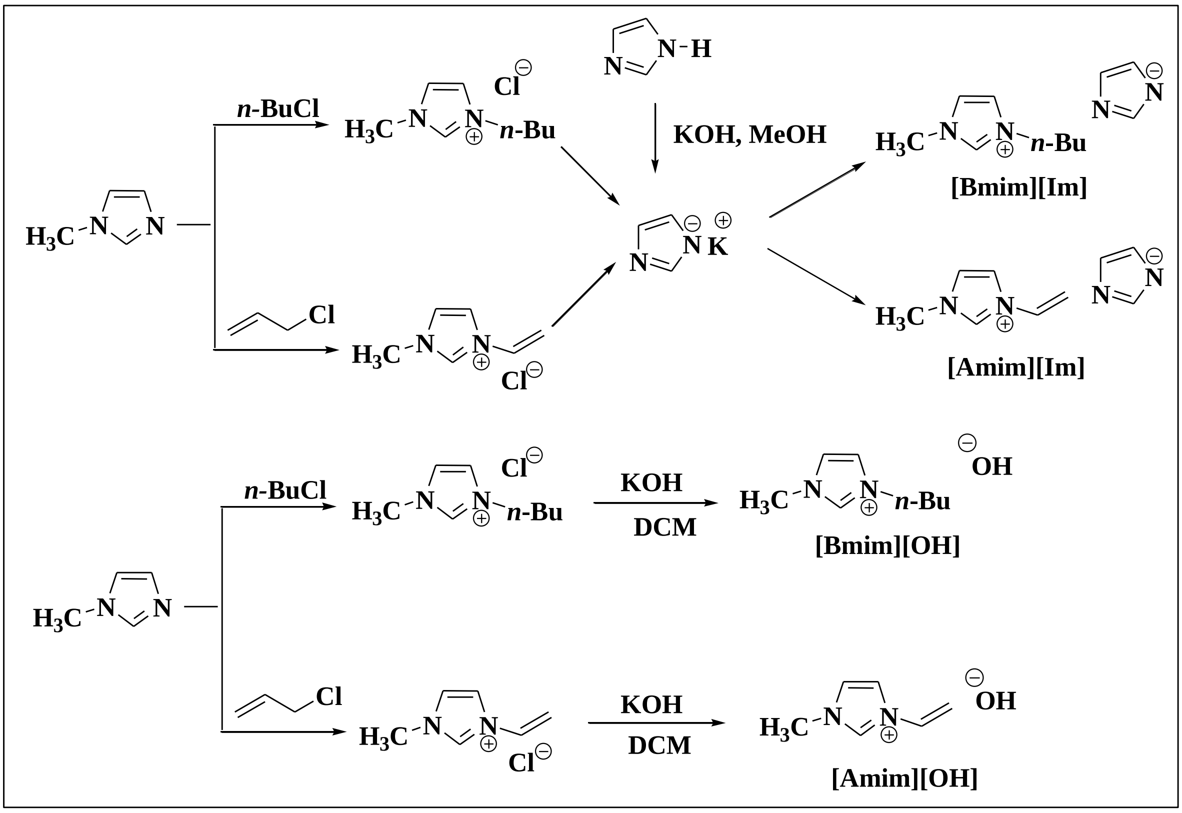


Scheme 6A.22: Knovenagel condensation catalyzed by [bnmim]OH

Again, Yi et al. [84] utilized 1-butyl-3-methylimidazolium imidazolide ([Bmim]Im), 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH), 1-allyl-3-methylimidazolium imidazolide ([Amim]Im), and 1-allyl-3-methylimidazolium hydroxide ([Amim]OH) and used them as catalysts for synthesis of glycerol 1, 2-carbonate from glycerol under solvent-free condition (**Scheme 6A.23**). They prepared these ILs following a reported procedure [85] (**Scheme 6A.24**). Under optimized reaction conditions, using [Bmim]Im as catalyst, 98.4% glycerol conversion and up to 100% GC selectivity at 70 °C under ambient pressure was achieved. The ILs could be recycled and reused for three cycles with the same catalytic activity.

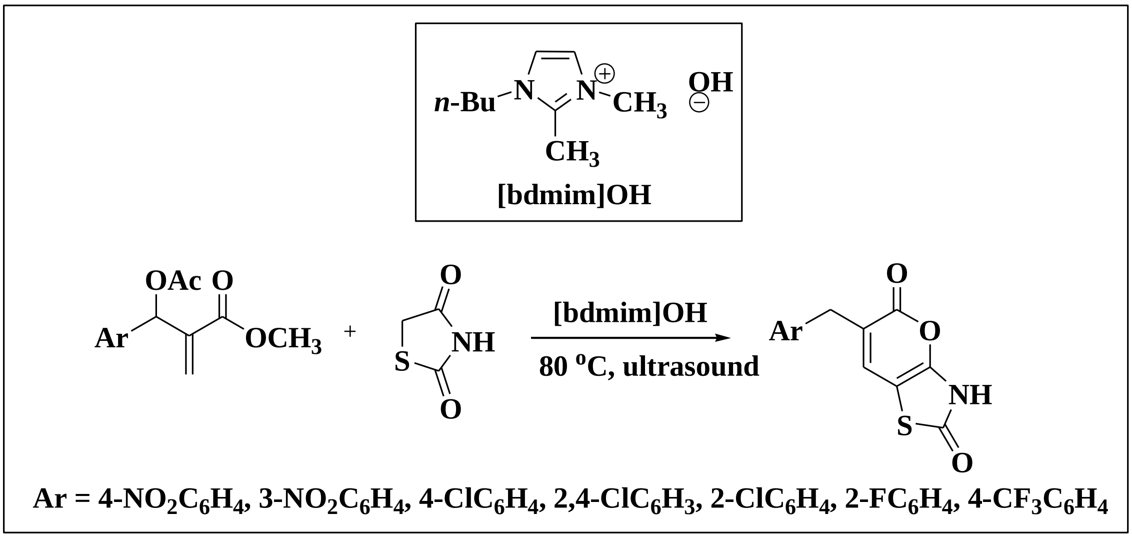


Scheme 6A.23: Synthesis of glycerol 1, 2-carbonate from glycerol in presence of ILs as catalyst



Scheme 6A.24: Synthetic scheme for preparation of ILs used by Yi et al.

In 2015, Mamaghani and Alavi [86] prepared fused α-pyrones from Baylis-Hillman acetates and various cyclic dicarbonyl compounds in the presence of basic ionic liquid 1-butyl-2, 3-dimethylimidazoliumhydroxide ([bdmim]OH) under ultrasonic irradiation (**Scheme 6A.25**). Desired α-pyrones were obtained in good-excellent yields within short reaction times using this IL as catalyst.



Ar = 4-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 4-ClC_6H_4, 2,4-ClC_6H_3, 2-ClC_6H_4, 2-FC_6H_4, 4-$CF_3C_6H_4$

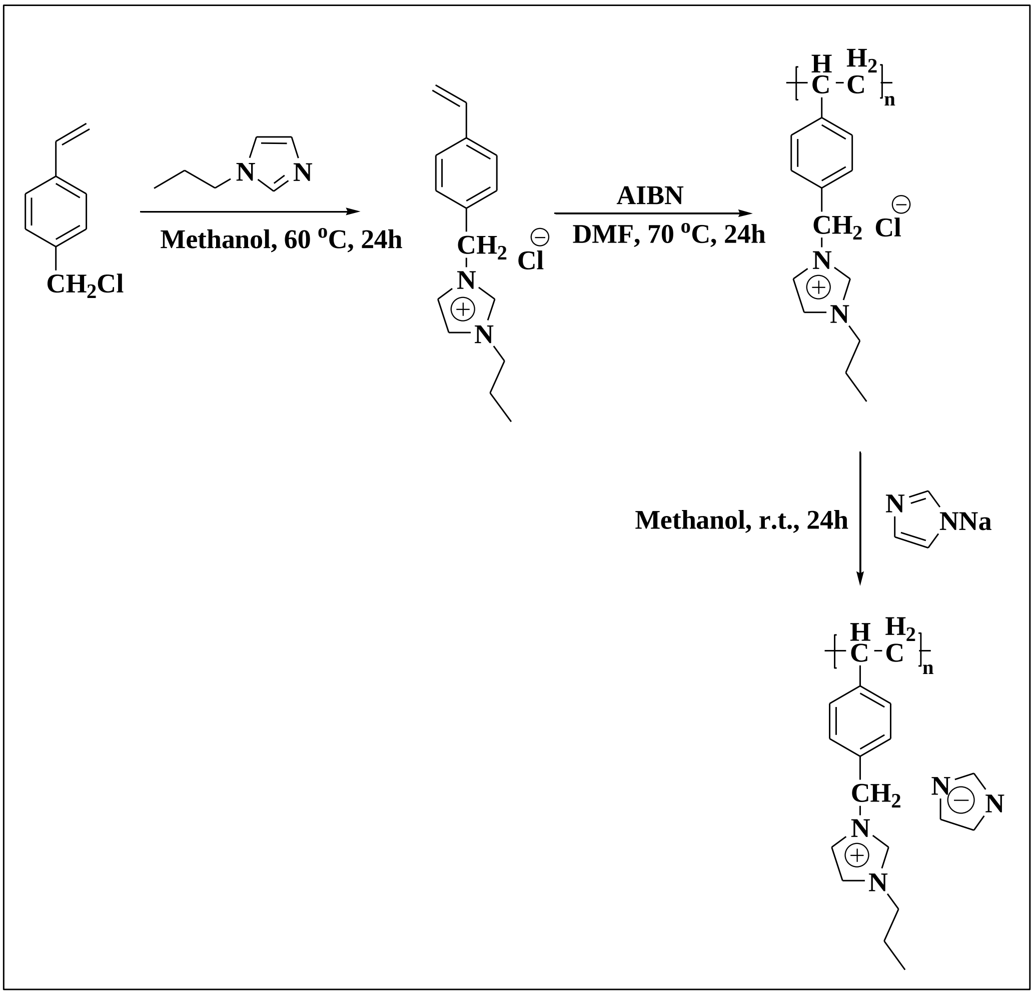
Scheme 6A.25: Synthesis of fused α-pyrones in presence of [bdmim]OH as catalyst

Ding et al. [87] reported the synthesis of a novel basic polymerized ionic liquid (BPIL): polymeric 1-[(4-ethenylphenyl)methyl]-3-propylimidazolium imidazolide and explored its catalytic efficiency in aqueous Knoevenagel reaction of a wide range of aldehydes and ketones with active methylene compounds at room temperature. The route for synthesis of the IL is presented in **Scheme 6A.26**. In comparison to the conventional inorganic bases, the basic IL effectively catalyzes the reactions due to intensive base sites and high surface activity. The catalytic system showed high catalytic activity up to fifth consecutive cycle.

Chaugule et al. [88] demonstrated the synthesis and uses of a binary catalyst systems of tricationic imidazolium room temperature ILs such as $[GLY(mim)_3][NTf_2]_3$IL/DBU, $[GLY(mim)_3][NTf_2]_3$/MTBD and $[GLY(mim)_3][NTf_2]_3$/TBD for direct preparation of dimethyl carbonate from CO_2 and methanol without the need of a dehydration system (**Scheme 6A.27**). The $[GLY(mim)_3][NTf_2]_3$ IL/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) system was found to have 37% MeOH conversion and 93% DMC selectivity under mild reaction conditions. Moreover, the $[GLY(mim)_3][NTf_2]_3$ IL/DBU catalytic system could be easily recovered and reused three times with similar catalytic activity.

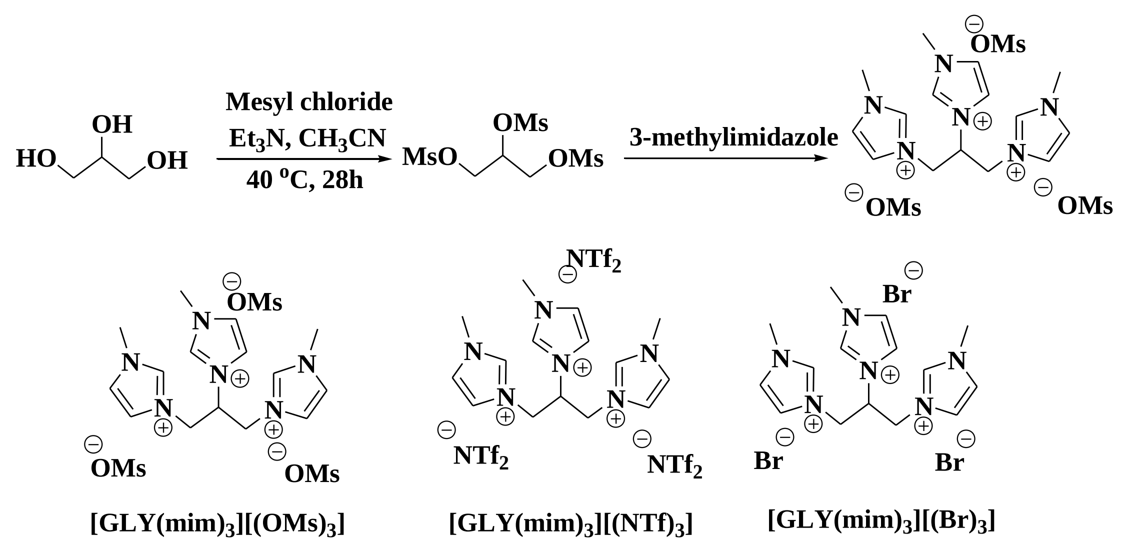
Haidarizadeh and Taheri [89] developed polystyrene-supported 1, 4-bis(3-methylimidazolium-1-yl)butane dihydroxide basic dicationic ionic liquid as heterogeneous catalyst for one-pot synthesis of chromene derivatives (**Fig. 6A.11**)

(**Scheme 6A.28**). The unique features of the catalyst were high thermal stability, recyclability, excellent catalytic activity in terms of yield and reaction time, high turnover number and turnover frequency, and also using water as a solvent.



Scheme 6A.26: Preparation of BPIL

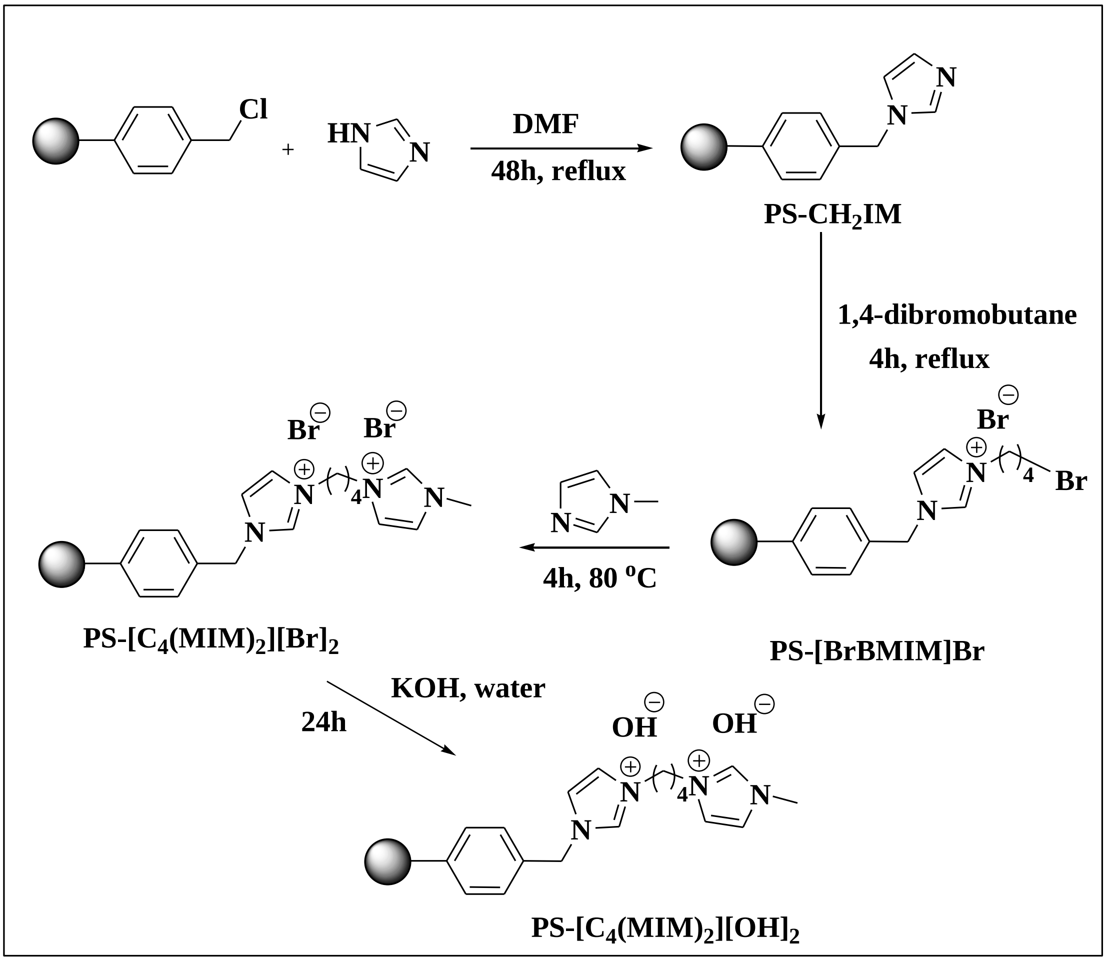
Chen et al. developed [90] an interesting observation for tuning of basicity of ILs with the change of substituted imidazolium or triazolium anions in combination with phosphonium cation (**Fig. 6A.12**) for efficient synthesis of alkylidene carbonates according to **Scheme 6A.29** using atmosphere CO_2. Excellent yields were obtained due to basic ionic liquids' dual roles both as absorbents and as activators.



Scheme 6A.27: Preparation of tricationic imidazolium room temperature ILs

Wang et al. [91] prepared basic morpholinium ionic liquid [Nbmm][OH] (**Fig. 6A.13**) from a mixture of N-butyl morpholine, N-butyl bromide, and KOH by two-step method and was used to catalyze transesterification of soybean oil with methanol to biodiesel. The effects of molar ratio of methanol to oil, reaction temperature, and amount of catalyst on the biodiesel yield were investigated. The optimized condition yielded of 94.5% yield with catalyst amount of 3.0 wt%, and methanol to soybean oil molar ratio of 14:1 at reaction temperature of 60 °C for 6 h. The catalyst retained activity up to six consecutive cycles.

Jiao et al. [92] prepared magnetic $CoFe_2O_4$ nanoparticles supported basic poly(ionic liquid)s catalysts (g-p[VRIm][OH]/MCFs) (**Scheme 6A.30**) through surface grafting method. The catalyst showed higher loading of ionic liquids, better stability and excellent paramagnetic property which could not be observed by conventional co-polymerization method. The catalytic activities were evaluated for the transesterification and Knoevenagel condensation. Additionally, the catalysts could be easily separated with the assistance of an external magnetic field. The catalyst was reused for four times with slight loss of catalytic efficiencies.



Scheme 6A.28: Immobilization of basic IL PS-[C$_4$(MIM)$_2$][OH]$_2$ on to the polystyrene

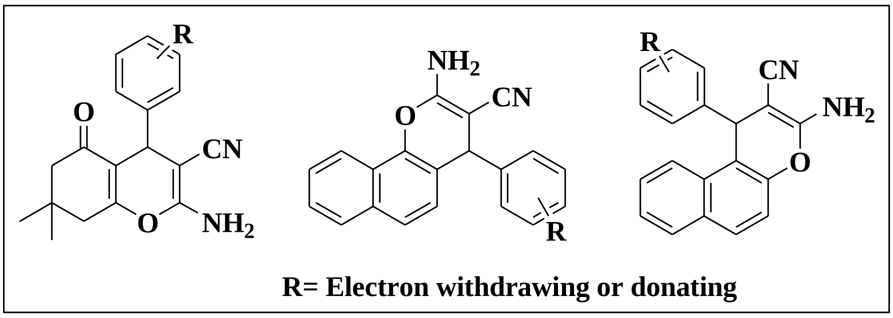


Fig. 6A.11: General structures of substituted 2-amino-4H-benzo[h]chromenes, 2-amino-4H-benzo[f]chromenes, and 2-amino-4H-tetrahydrochromene derivatives synthesized

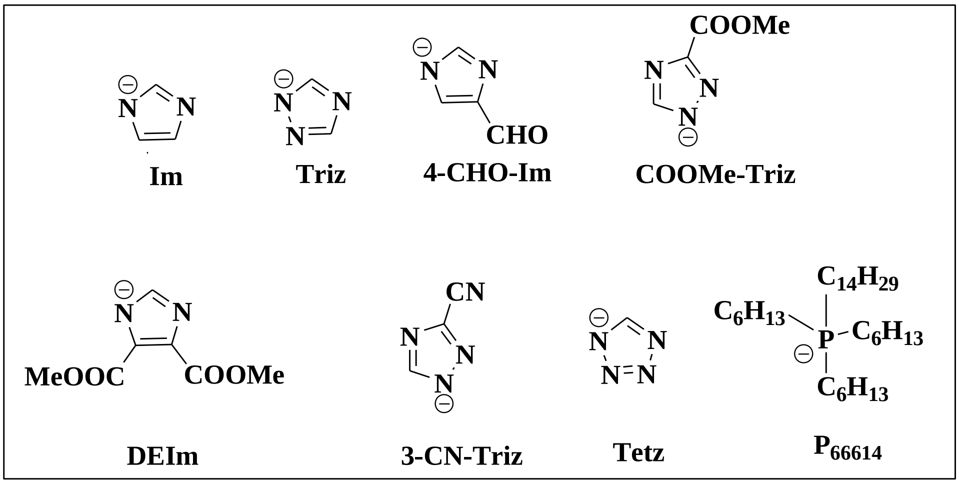
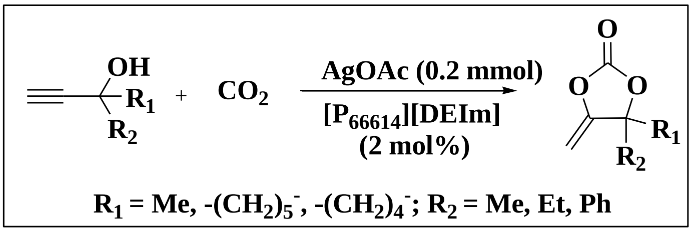


Fig. 6A.12: Structures of the anions and the cations in basic ILs



Scheme 6A.29: Synthesis of alkylidene carbonates catalyzed by basic ILs

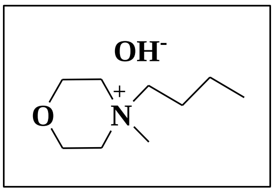
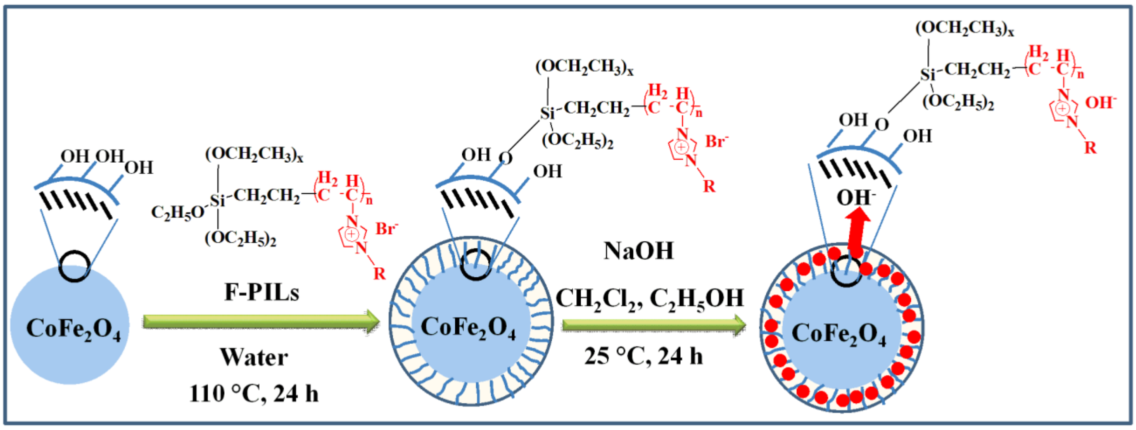


Fig. 6A.13: Structure of morpholinium ionic liquid [Nbmm][OH]

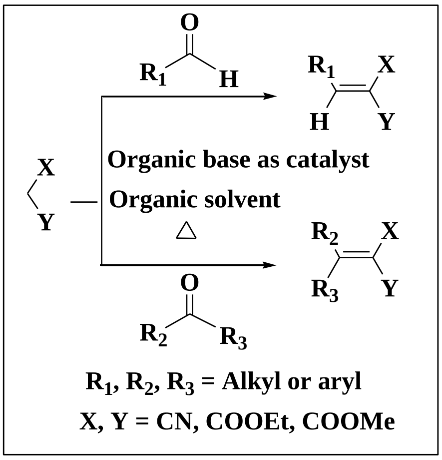


Scheme 6A.30: Synthetic procedure for preparation of g-p[VRIm][OH]/MCFs

6A.3. Base catalyzed Knoevenagel condensation reaction

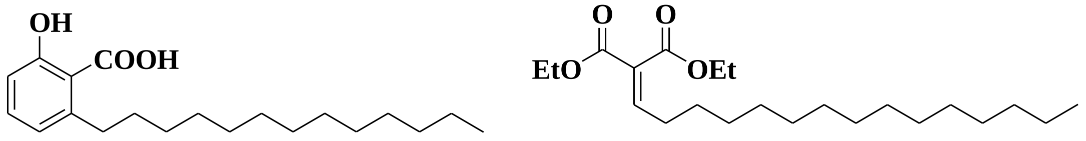
The Knoevenagel condensation is an important, general and versatile C-C bond formation reaction in organic synthesis [93-95] which is usually catalyzed by a base, an acid, or a heterogeneous neutral support. The reaction is also considered as one of the modified version of Aldol condensation.

Classically, the Knoevanagel condensation occurs in between carbonyl or heterocarbonyl compound and any compound having an active methylene compound to produce α, β-unsaturated compounds using organic base such as piperidine, pyridine, amines or their salts [96, 97] in organic solvents such as benzene, toluene, THF, DCM etc. at different temperature (**Scheme 6A.31**). The use of excess amount of aliphatic aldehydes (4-6 times) is necessary for some reactions to produce sufficient yield of the products in less reaction time when the reaction rate is slow in presence of organic base catalyst [98]. The α, β-unsaturated product obtained in this path have been widely used in organic synthesis, in biological science, natural product chemistry, polymer chemistry, fine chemicals, medicine, agriculture and light emitting materials [1,13-15]. For example, the structural variation of benzylidenes or alkylidenes intermediates through the Knoevenagel reaction is possible by changing the structure of nucleophilic reagents such as β-keto ester [99, 100], diketones [99], ketothioesters [99], malonates, malononitriles [101], keto amides, and cyclic esters, along with different aromatic [102] or aliphatic aldehydes [103].



Scheme 6A.31: General scheme for Knoevenagel condensation

The biological activity of alkylidene malonate was observed in case of long-chain alkylidene malonates (LoCAM) namely pentadecylidene malonate, a simplified analogue of anacardic acid, exhibits a good modulation of the activity of histone acetyltransferases (**Fig. 6A.14**) [103].



Anacardic acid (KAT inhibitor)

Pentadecylidenemalonate
KAT3A inhibitor/KAT2B activator

Fig. 6A.14: KAT inhibitors and activator: anacardic acid and pentadecylidene malonate

Jung et al. [104] utilized the Knoevanagel condensation as key synthetic step for the total synthesis of anticoagulant flocoumafen. In addition to the above mentioned amino bases, a large number of modified basic catalytic systems have been developed for the Knœvenagel condensation in recent years which include Al_2O_3[105], fly ash supported CaO [106], NH_4OAC [107], CdI_2 [108], K_2O-Al_2O_3 [109], zeolites [110], organic resins [111], mixed magnesium-aluminium oxides derived from hydrotalcites [112], sepiolites [113], aluminophosphonatesoxynitrides (AIPON) [114], synthetic phosphate $Na_2CaP_2O_7$ [115], ion-exchange resins [116], potassium fluoride (KF) [117], layered silicate PLS-1 [118], silica gel [119], niobium chloride [120], MgO/ZrO_2 [121], $Yb(OTf)_3$ [122], chitosan [123], fluorapatite [121] and ionic liquids [27, 48, 52] etc.

The use of task specific basic ILs as dual solvent-catalyst system is an attractive alternative of the above mentioned some non-reusable basic catalyst for the synthesis of benzylidene or alkylidene derivatives in absence of organic solvent at mild condition. Although, some of the ILs such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) or 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) [124] and Lewis acidic chloroaluminate ILs were employed as medium/catalyst with or without any added catalyst for performing the condensation with many limitations [125].

The presence of one or more Brönsted/Lewis base sites within the basic ILs make them suitable for studying the catalytic efficiencies of basic ILs through the Knoevenagel condensation reactions using variety of aliphatic or aromatic carbonyl compounds and different active methylene compounds. The review of literature reveals several applications of basic ILs based on TMG (tetramethyl guanidine) [126], cyclic guanidine [127], alkanolamine [128-133], methoxylpropylamine [134], DABCO [135, 136], DBU [137], N, N, N′, N′-tetramethyl-N′-hexyl-ethylenediamine (TMHEDA) [138], pyrrolidine [139-141], piperidine [142], N,N-dimethylethanolamnium (DMEA) [143], tetrabutylphosphonium [144], hexamethylenetetramine [145], tetrabutylammonium [146] for the Knoevenagel condensation under solvent free medium or in presence of other solvent at different temperatures and reaction time to produce low to high yields of products. Most of the tested ILs are monocationic possessing only one basic site which may cause reducing basicity of the IL to abstract the more acidic methylene proton for nucleophiic attack on the carbonyl group [137]. Only few reports are found for dicationic basic ILs catalyst [147] and no examples are found for the tricationic basic ILs.

By considering the review of literature, we planned to synthesize new series of triethylamine bridged tricationic basic ILs containing imidazolium, pyridinium moiety as cations with variation of three anions such as hydroxide, acetate and imidazolide by following the reaction **Scheme 6B.1** (**6B.1. Results and discussion**). As basic ionic liquids, they were tested as recyclable homogeneous catalysts for Knovenagel condensation of aromatic or aliphatic aldehydes/aliphatic ketone with active methylene compounds in absence of solvent and also in solution at room temperature.

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Chapter 6B

Synthesis of triethylamine bridged basic tricationic ionic liquids (TILs) and evaluation of their catalytic efficiencies towards synthesis of functionalized alkenes

6A.1. Mulfunctionalized basic ionic liquids

Multifunctionalized ionic liquids especially dicationic and tricationic liquids have been reported to have a wide range of tunable physical properties than most traditional, singly charged ILs such as higher density, melting point, viscosity, surface tension and glass transition temperature [1, 2]. These are possible only by variation of the chemical structures of suitable cation-anion pairs within the ionic liquid composition. More numbers of structural variations of ion-pairs are possible with the dicationic and tricationic ionic liquids. Different types of muiticationic ionic liquids were synthesized based on ammonium [3-5], imidazolium [6], pyridinium [7] and pyrrolidium [1] cations to explore their physical properties.

Armstrong and co-workers [8, 9] studied the effect of various counter ions on the densities of symmetrical tricationic ILs that was in the order of $NTf_2^- > PF_6^- > OTf^- > BF_4^-$ They observed thermal decomposition temperatures of some of the ILs to be greater than 400 °C which was quite encouraging compared to the corresponding monocationic ILs. Their melting points depend on the flexibility of the central core unit. The flexible core structure of tricationic ILs possesses lower melting point when compared to the ILs with rigid core structure unit.

The presence of three charges in very close contact on the flexible tricationic ILs can be described as possible reason for existence of high polarity in such ILs at room temperature [5]. Due to their tunable physicochemical properties, they have been utilized as novel solvent systems in organic synthesis and catalytic studies [10], electrochemistry [11], high temperature lubricants [12], selective gas chromatographic stationary phases [13], molecular pincers for anion recognition [14], ionic liquid crystals [15], host-guest complexes [16], gel phases [17] and so on.

The development of environmentally benign task-specific basic ionic liquids and their uses in some base-catalyzed organic reactions offer a great potential for replacement of toxic, corrosive and water miscible inorganic/ organic bases in catalytic reactions [18]. They exhibit several advantages over inorganic bases such as water and air stability, immiscibility with many organic solvents, noncorrosive and nonvolatile, high catalytic efficiency and easy reusability after simple separation from the reaction mixture.

The acidity or basicity of an ionic liquid is governed by the nature of cation, anion, or by combination of cation and anion. Most of the basic mono cationic ionic liquids are made from combination of basic anions with most common N-alkylimidazolium, alkylammonium or N-alkylpyridinium cations. Other cations include pyrrolidinium, pyrimidinium, pyrazolium, triazolium, pyridazinium, pyrazinium, oxazolium and thiazolium. A wide array of anions including carboxylates, fluorinated carboxylates, hydroxide sulfonates, fluorinated sulfonates, imides, borates, phosphates, antimonates, halides, halometallates etc. can be paired with chosen cation component for achieving Lewis Basic or Brönsted basic ionic liquids [19]. These basic ionic liquids may be classified as Brönsted or Lewis basic depending upon the type of anion used to formulate the ionic liquids. Another method for designing of strong basic ILs relied on attachment of specific basic functionalities to the cation. The ILs derived by this method sometimes exhibit greater thermal stability than those containing only basic anions [20].

The attachment of more number of basic anions in multi-charged ILs may influence the basicity, thermal stability, water sensitivity, viscosity, conductivity and solubility of the ILs in various solvents. The literature review reveals that the basic ionic liquids either work as efficient base catalyst or basic reaction medium for various types of base catalyzed condensation reactions such as Aldol condensation, Knoevenagel reaction, Claisen-Schmidt reaction etc. depending on the strength of basic sites i.e Brönsted basic or Lewis basic [21-23]. As compared to the functionalized acidic ILs, the reports related to the basic ILs are quite few. But, they have the ability to replace conventional basic reagents like NaOH, KOH, K_2CO_3, $NaHCO_3$, NaOAc etc. in organic reactions by acting as reusable basic catalysts. These conventional bases produce excellent results only with stoichiometric amount of bases for any type of base promoted organic reactions. In industrial scale reactions, they release large amount of toxic and corrosive basic waste to the environment. From this point of view, the nature of basic ionic liquids serves its purpose much justifiably and their function to act as both solvent and catalyst make the process much easier to handle. Therefore, it is always an exciting challenge to develop novel Brönsted-type basic catalytic systems that are environment friendly, recyclable and cost effective in nature.

In next section, we include the literature review of pyridinium and imidazolium basic ILs and their applications as basic catalyst/solvents in various organic reactions till 2016.

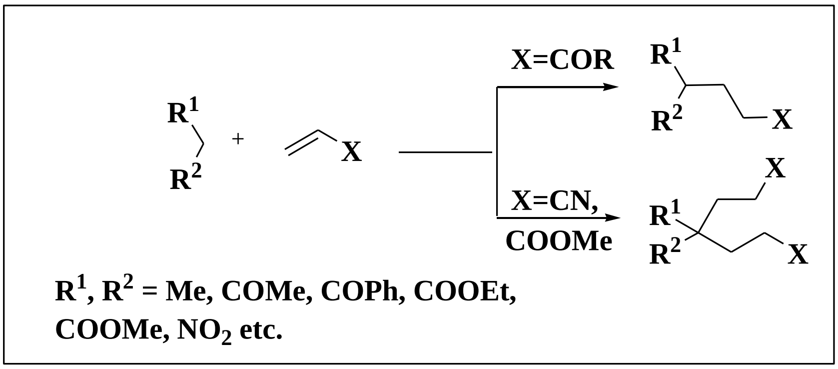
6A.2. Imidazolium and pyridinium based basic ionic liquids and their uses in organic synthesis including Knoevenagel condensation

In literature, a number of basic ionic liquids are found derived from complex halometallate anions and N-alkylpyridinium or N-alkylimidazolium cations [24]. The mole fraction of metal halides utilized to synthesize these ionic salts determines whether the resulting salt will be Lewis acidic or basic or neutral in nature. The most important example is the basic chloroaluminate(III) ionic liquid obtained through reactive dissolution of $AlCl_3$ in excess of chloride-based ionic liquid [cation]Cl with mole fraction of $AlCl_3<0.5$ according to equation (1) [25]. In this situation, the metal ion may be fully saturated with its coordination number and so will not act as Lewis acids.

$$nCl^- + AlCl_3 \rightarrow AlCl_4 + (n-1)Cl^- \ (\chi_{AlCl_3}<0.5) \qquad (1)$$

These chlorometallate systems have been found to act as good solvents in electrochemistry, spectroscopy and also in catalysis [26-28].

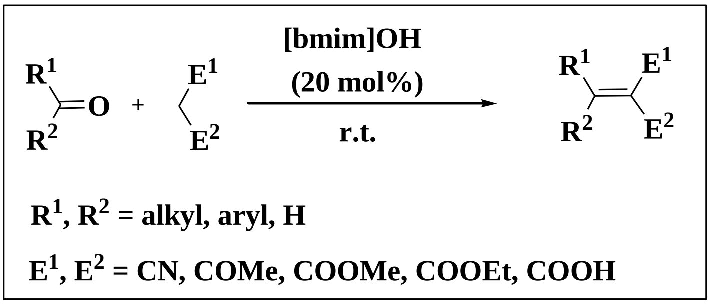
The imidazolium based Brönsted-basic IL, 1-butyl-3-methylimidazolium hydroxide [bmim][OH] was prepared by Ranu and his co-worker in 2005 using a reaction mixture of [bmim]Br and KOH in dichloromethane under vigorous stirring at room temperature for 10 h [29]. This IL was explored as catalysts/and reaction medium in Michael addition reactions of 1, 3-dicarbonyl compounds, cyano esters, and nitro alkanes to a variety of conjugated ketones, carboxylic esters, and nitriles (**Scheme 6A.1**). The respective mono and bis-addition products were formed in excellent yields within 0.5-4 h time duration. Overall, the method had various advantages over the existing protocols with regard to operational simplicity, reaction time and yield, general applicability, avoid of toxic organic solvent and catalyst etc.



R^1, R^2 = Me, COMe, COPh, COOEt, COOMe, NO_2 etc.

Scheme 6A.1: Michael addition catalyzed by [bmim]OH

Later in 2006, Ranu et al. [22] utilized this IL as catalyst in the Knoevenagel condensation reactions of aliphatic and aromatic aldehydes and ketones with diethyl malonate, malononitrile, ethyl cyanoacetate, malonic acid and ethyl acetoacetate in absence of any organic solvent (**Scheme 6A.2**). The desired products were obtained within short reaction times (10-30 min) at room temperature. With this protocol, the condensation of aliphatic aldehyde with diethyl malonate was easily achieved, which is otherwise a difficult job to achieve.



R^1, R^2 = alkyl, aryl, H

E^1, E^2 = CN, COMe, COOMe, COOEt, COOH

Scheme 6A.2: Knoevenagel condensation catalyzed by [bmim]OH IL in absence of organic solvent

A large number of studies on uses of [bmim][OH] ionic liquid have been reported in different type of organic reactions as catalyst/solvent/promoter. Some of the base catalyzed reactions include Knoevenagel condensation [22, 30], Markovnikov addition [31], Michael addition [32], aza Michael reactions [33], transesterification [34] and polymerization reaction [35]. It was also utilized for base catalyzed one pot synthesis of oxygen and nitrogen heterocycles. Few examples of such heterocycles are polyfunctionalized-4H-pyrans [36], quinazoline-2,4 (1*H*, 3*H*)-diones [37], quinoline

[38], 2-alkylsubstituted chromanones [39], benzo[g]chromene derivatives [40], pyrazolo [3, 4-b] pyridines [41], 2-aroylbenzofuran-3-ols [42], 2-Amino-4H-chromenes [43], benzo[a]pyrano[2, 3-c]phenazine derivatives [44], substituted benzofurans [45], 1, 4, 5-trisubstituted-1, 2, 3-triazoles [46], polyhydroquinolines [47] etc.

In the same year, Tai et al. [48] developed a Lewis basic 1-ethyl-3-methylimidazolium chloride/tetrafluoroborate ionic liquid The authors studied the electrodeposition of palladium-silver alloy from the ionic liquid solutions containing Pd(II) and Ag(I) within a temperature range of 35-120 °C. Both the electrodeposition involved over potential driven nucleation process and Pd-Ag electrodeposits were obtained in nodular shapes.

At the same time, Cai et al. [49] prepared two amino-functionalized imidazolium based ionic liquid: 1-aminoethyl-3-methylimidazolium hexafluorophosphate ([2-aemim][PF_6]) and 1-aminoethyl-3-methylimidazolium tetrafluoroborate ([2-aemim][BF_4]) (**Fig. 6A.1**) and explored their catalytic activity towards the Knoevenagel condensation of aromatic aldehydes with malononitrile and ethyl cyanoacetate in aqueous media. The combination of room temperature condition, aqueous media and use of recyclable IL as catalyst made this protocol an efficient eco-friendly one. The respective products were obtained in very good to excellent yields.

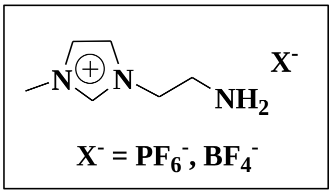
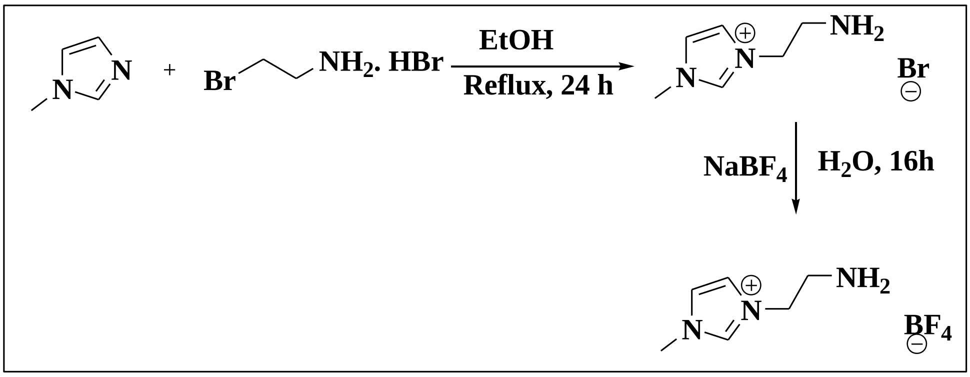


Fig. 6A.1: Structures of [2-aemim][PF_6] and [2-aemim][BF_4]

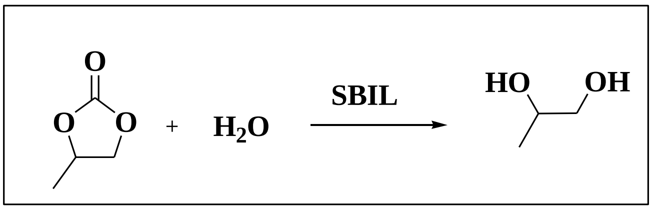
In 2007, Guo-hua et al. [50] prepared 1-(2-amine-ethyl)-3-methyl-imidazolium boron tetrafluoride (**Scheme 6A.3**) as basic IL and used as catalyst for condensation of aldehydes/ketones with activated methylene compounds in aqueous media at 30-50 °C temperature. The IL was quite active and the desired products were formed within considerable time frame in 70-97% yields. It could be easily recycled till six times with little loss in activity.



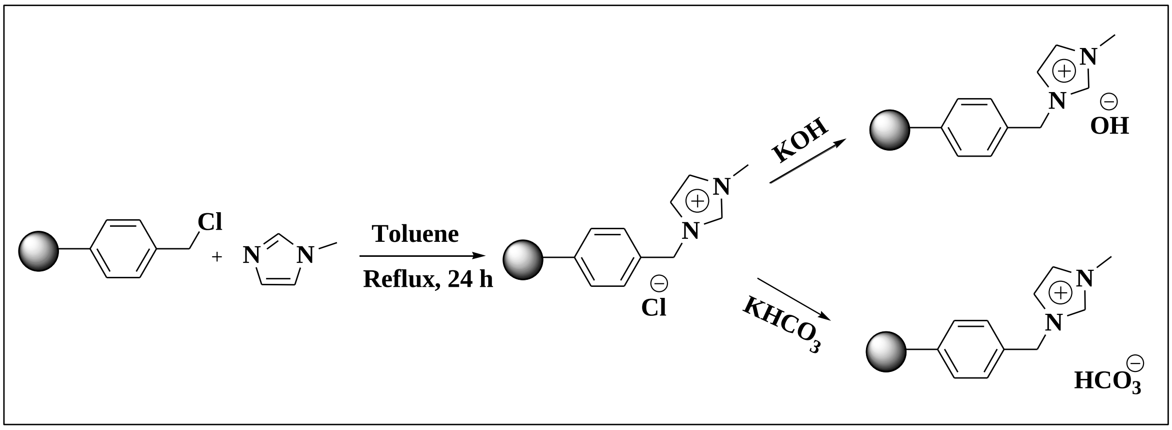
Scheme 6A.3: Preparation of 1-(2-amine-ethyl)-3-methyl-imidazolium boron tetrafluoride IL

In 2008, two basic ionic liquids, 1-butyl-3-methylimidazolium trifluoroacetate ([bmim][CF_3COO]) and 1-butyl-3-methylimidazolium acetate ([bmim][CH_3COO]) were employed for measurement of heat capacities in the temperature range of 5-370 K using adiabatic calorimetry method by Strechan et al.[51]. They observed dependence of thermal behavior of [bmim][CF_3COO] on crystallization procedure.

Xiao et al. [52] explored hydrolysis of propylene carbonate to 1, 2-propylene glycol using a SBIL catalyst (**Scheme 6A.4**). The polystyrene based imidazolium basic catalyst was prepared by following the **Scheme 6A.5**. The effects of temperature, time, molar ratio of water to propylene carbonate, choice of catalyst, and amount of catalyst were investigated. In addition, the catalyst could be reused at least up to five times with slight loss of catalytic activity.



Scheme 6A.4: Hydrolysis of propylene carbonate to 1, 2-propylene glycol



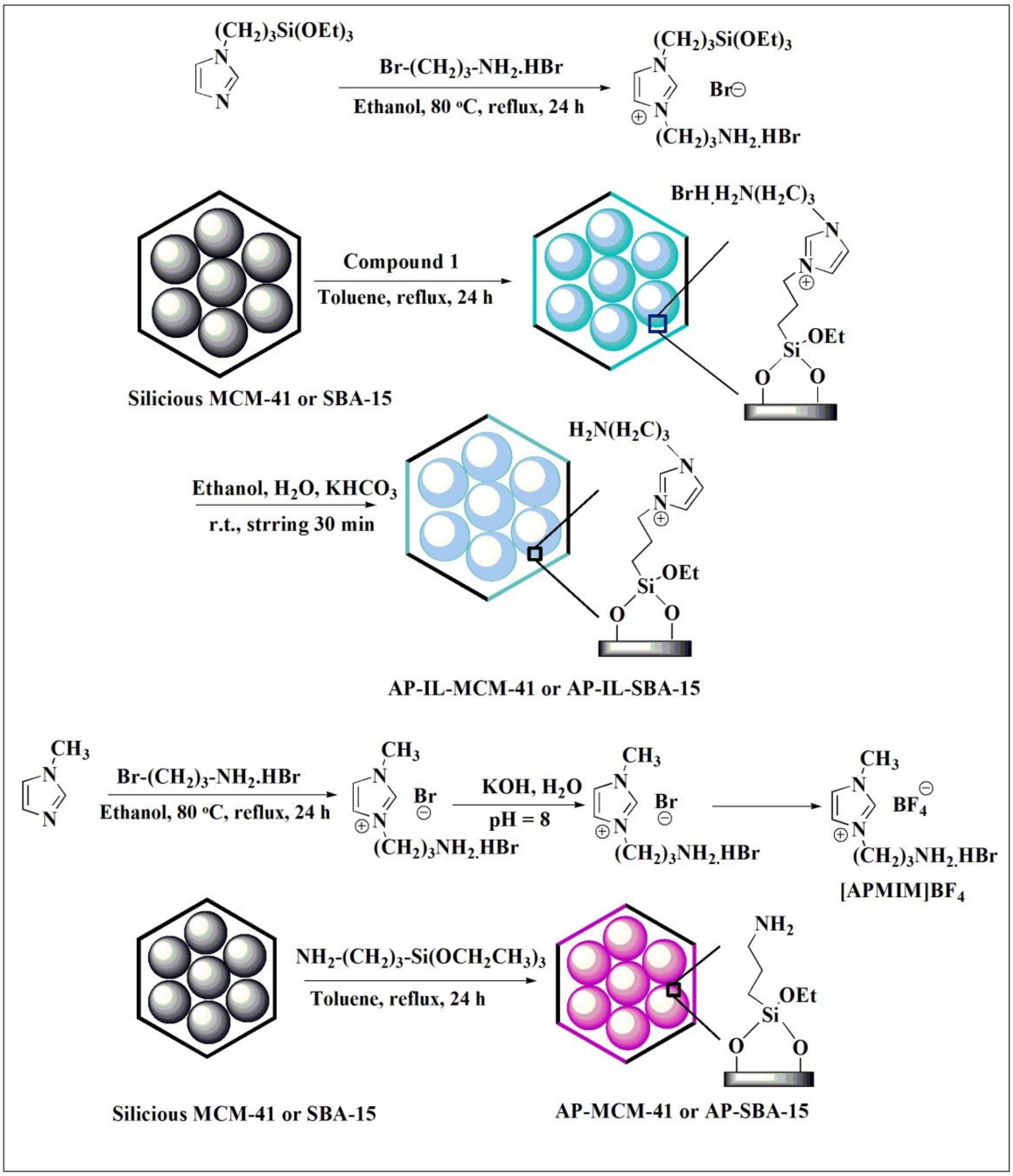
Scheme 6A.5: Preparation of supported ILs (SBIL)

Zhao et al. described the immobilization of basic amino-functionalized task-specific ILs: N-(3-aminopropyl), N(3)-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium bromide hydrobromide on mesoporous silicas of MCM-41 and SBA-11 followed by neutralization of protonated amino group with KOH (**Scheme 6A.6**) [53]. The catalytic activity of this system was tested for the Knoevenagel condensation in aqueous medium (**Scheme 6A.7**).

In 2010, an imidazolium based task-specific ionic liquid [**IL-OPPh$_2$]** (**Fig. 6A.2**) was prepared by Valizadeh and Gholipour following a reported procedure [54] that bears a weak Lewis basic phosphinite group in its structure [55]. This IL was examined as reusable catalyst/solvent system for the condensation of arylaldehydes with malononitrile, dimethyl (diethyl) malonate, and ethyl cyanoacetate at 60 °C under solvent-free condition within 8-20 min reaction (**Scheme 6A.8**).

Forsyth et al. [56] in a report described the synthesis of amino-functionalized imidazolium based IL according to **Scheme 6A.9** along with other members of ammonium based ILs. The qualitative basicity of the ILs was evaluated from their interaction with a universal indicator. The catalytic activity of these ILs was evaluated for Heck and Knoevenagel reactions successively.

In 2011, Kowsari and Mallakmohammadi [38] synthesized few basic ionic liquids (BILs) based on imidazolium cation in association with hydroxide anion (**Fig. 6A.3**) and explored their catalytic efficiencies towards the synthesis of quinoline derivatives from the condensation reactions of isatin with ketones by ultrasonic irradiation in aqueous media (**Scheme 6A.10**).



Scheme 6A.6: Synthetic protocol for immobilized basic ILs: [APMIM]BF_4 and amino functionalized mesoporous silicas

R_1: Ph; 2-Cl-Ph; 4-OH-Ph; 4-OCH_3-Ph; 4-NO_2-Ph

R_2: CN; $COOCH_2CH_3$

Scheme 6A.7: Knoevenagel condensation catalyzed by immobilized basic ILs, [APMIM]BF_4 and amino functionalized mesoporous silicas

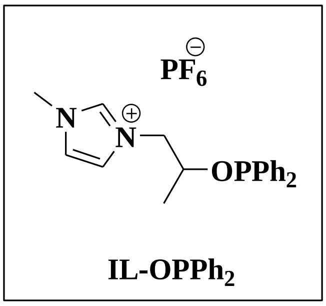
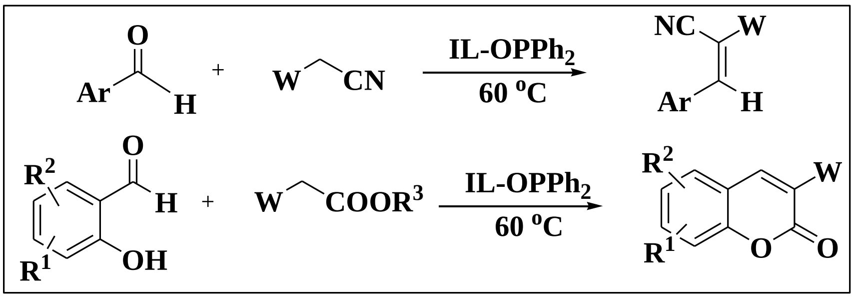
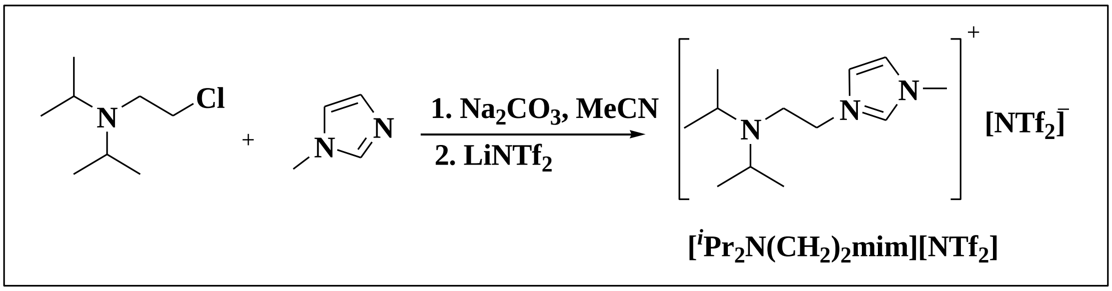


Fig. 6A.2: Structure of IL-OPPh$_2$



Scheme 6A.8: IL-OPPh$_2$ catalyzed Knoevenagel condensation reaction and synthesis of coumarin derivatives



Scheme 6A.9: Preparation of amino-functionalized imidazolium based IL

The use of BILs and ultrasonic irradiation promote the reactions efficiently at room temperature and affect both the reaction time and yield remarkably. Among the BILs used for this study, reusability study for [bmim]OH was carried out and it was found quite promising. The BIL was continuously reused for five times without appreciable loss in catalytic activity.

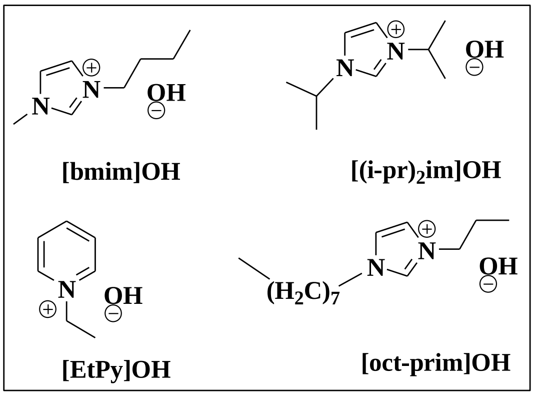
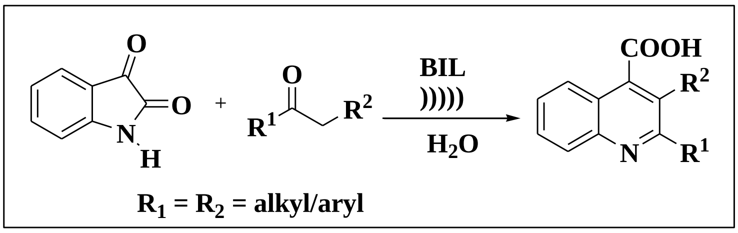
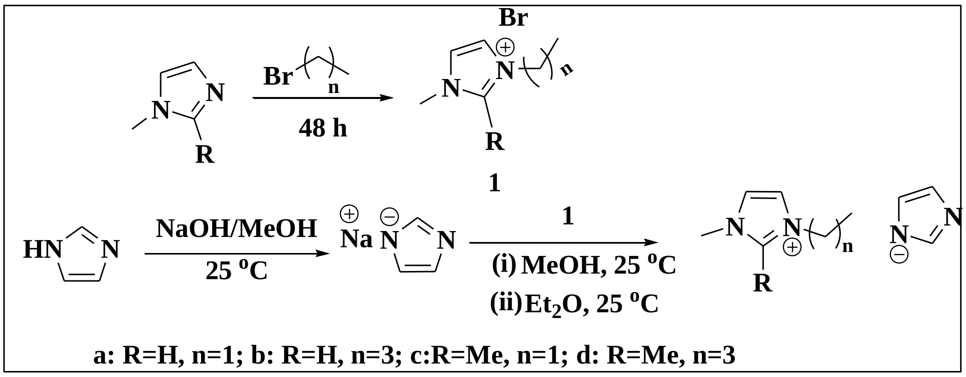


Fig. 6A.3: Imidazolium based BILs containing hydroxide ion

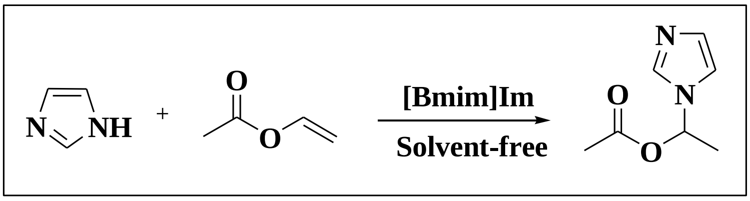


Scheme 6A.10: Synthesis of quinolone derivatives catalyzed by BILs

Chen et al. prepared a series of imidazolium based basic ionic liquids by following the reaction **Scheme 6A.11** [57]. The prepared ILs displayed strong basicity and relatively good thermal stability. Satisfactory catalytic activities were explored for solvent-free aza-Markovnikov addition reactions at room temperature when 2 mol% of [Bmim]Im was used as catalyst in one h (**Scheme 6A.12**). Experimental results revealed that H-bond is not formed between imidazole [Bmim]Im/imidazole and vinyl ester in case of aza-Markovnikov reactions. The use of imidazolide ionic liquids in aza-Michael addition was also studied as well.

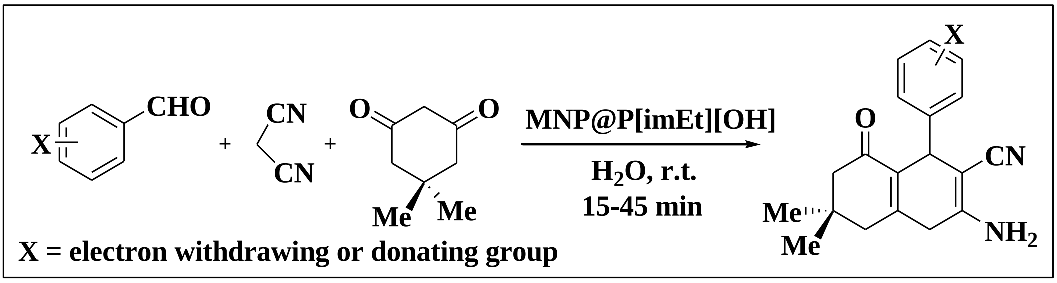


Scheme 6A.11: Synthesis of imidazolide ILs



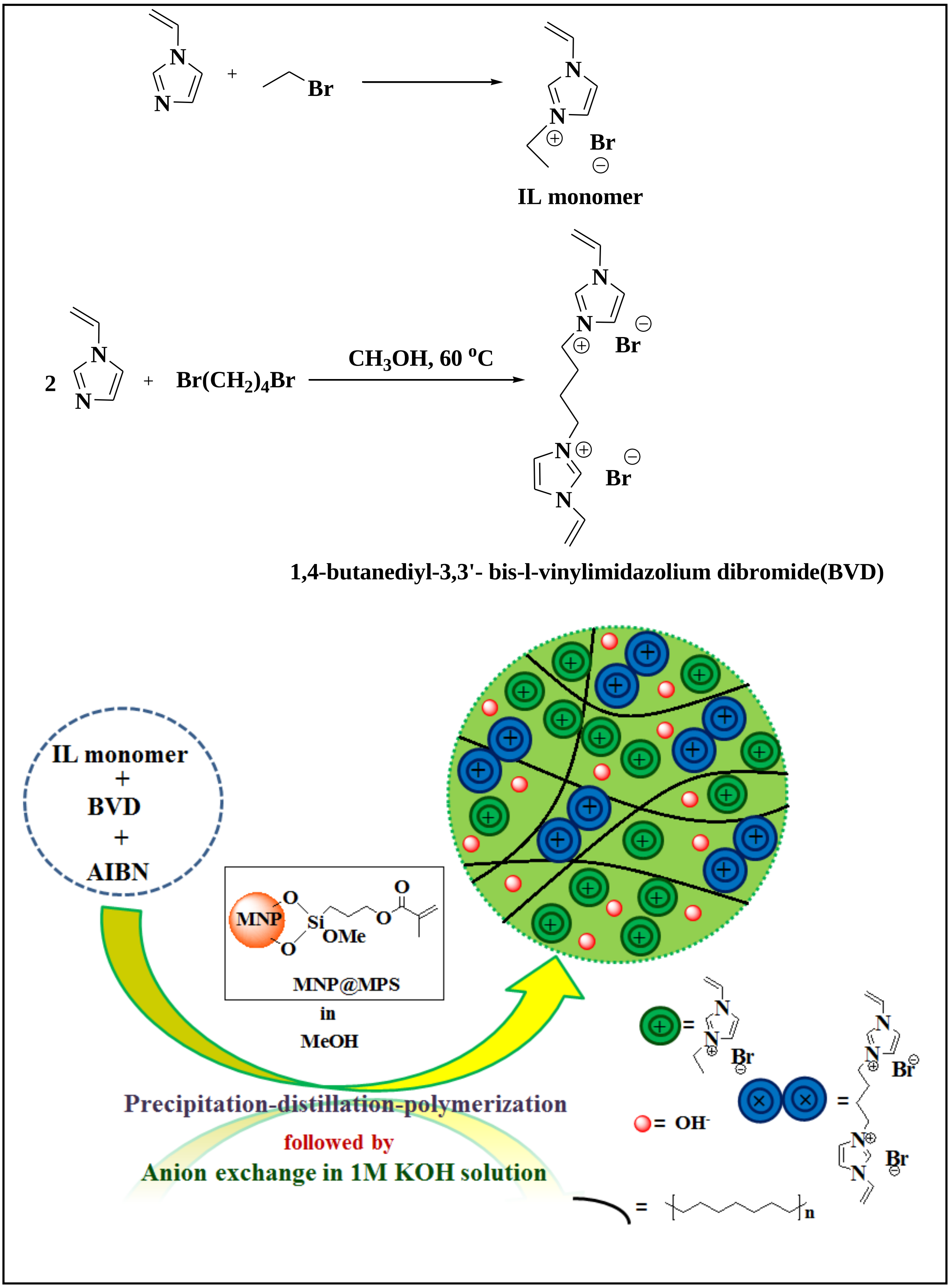
Scheme 6A.12: Markovnikov addition of imidazole to vinyl acetate catalyzed by [Bmim]Im

In 2013, Pourjavadi et al. [58] prepared one heterogeneous Brönsted-type basic catalysts MNP@P[imEt][OH], based on Fe_3O_4 magnetic nanoparticle (MNP) coated with the multilayers of poly(ethylvinylimidazolium) hydroxide, which proved to be highly efficient for the synthesis of 4H-benzo[b]pyrans in water (**Scheme 6A.13**). The separation of the catalyst was readily achieved from the reaction mixture using simple magnetic decantation and the catalyst could be easily recycled with similar catalytic activity. The catalyst was prepared by distillation-precipitation-polymerization of 1-vinyl-3-ethyl imidazolium in the presence of surface modified magnetic nanoparticles (**Scheme 6A.14**).



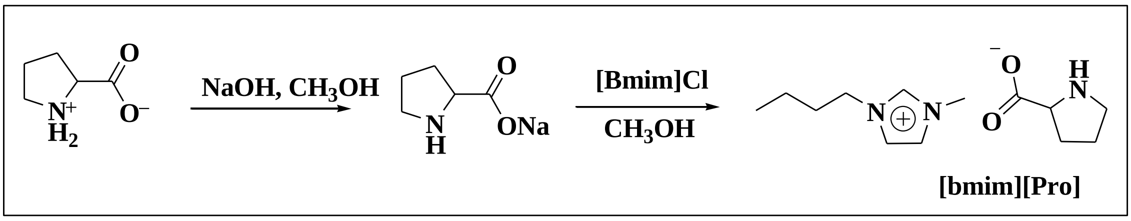
Scheme 6A.13: Synthesis of 4H-benzo[b]pyrans catalyzed by MNP@P[imEt][OH]

Wang et al. used six basic ILs: 1-butyl-3-methylimidazolium acetate([Bmim]OAc), 1-butyl-3-methylimidazolium bicarbonate([Bmim]HCO_3), 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH), 1-ethyl-3-methylimimethylimidazolium hydroxide ([Emim]OH), 1-butyl-3-methylimidazoliumbenzoate ([Bmim]PhCOO), and 1-ethylamine-3-methylimidazolium tetrafluoroborate ([Emim]BF_4) according to the reported procedures [29, 59, 60] and evaluated their catalytic activity in one-pot synthesis of 2-amino-4H-chromenes derivatives [42].



Scheme 6A.14: General procedure for synthesis of MNP@P[imEt][OH]

Hongbing et al. [61] synthesized a pyrrolidine carboxylic functionalized ionic liquid: 1-butyl-3-methylimidazolium-(S)-2-pyrrolidinecarboxylic acid salt ([bmim][Pro]) via an improved procedure (**Scheme 6A.15**). The catalytic activity of this IL was tested for the synthesis of α, β-unsaturated carbonyl compounds via Knoevenagel condensation reaction. Desired products were obtained in good yields from the reaction of active methylene compounds with aldehydes and ketones at room temperature in aqueous media. The IL could be reused efficiently for six cycles.



Scheme 6A.15: Preparation of [bmim][Pro] IL

Shaterian and Azizi [62] utilized two weak basic imidazolium ILs namely 1-butyl-3-methylimidazolium imidazolide and 1-ethyl-3-methylimidazolium acetate (**Fig. 6A.4**) obtained from reported method [63, 64] as reusable catalyst for solvent free synthesis of 7-amino-1, 3-dioxo-1, 2, 3, 5-tetrahydropyrazolo[1, 2-a][1, 2, 4]triazole and 6, 6-dimethyl-2-phenyl-9-aryl-6, 7-dihydro-[1, 2, 4]triazolo[1, 2-a]indazole-1, 3, 8(2H, 5H, 9H)-trione derivatives (**Fig. 6A.5**) separately.

Sun et al. [65] performed a direct synthesis of dimethyl carbonate (DMC) from methanol and carbon dioxide using a series of hydroxyl functionalized basic ionic liquids and compared their task-specific basic nature as catalysts /solvent systems. They utilized various basic ionic liquid namely choline hydroxide, [Etmim][OH] (1-ethoxyl-3-methylimidazolium hydroxide), [Etmim][Br] (1-ethoxyl-3-methylimidazolium bromide), [Emim][OH] (1-ethyl-3-methylimidazolium hydroxide), and [Bmim][OH] (1-butyl-3-methylimidazoliumhydroxide) which were obtained according to the reported literatures [30, 66]. Among the screened ILs, choline hydroxide was found to be an effective catalyst for the conversion of DMC.

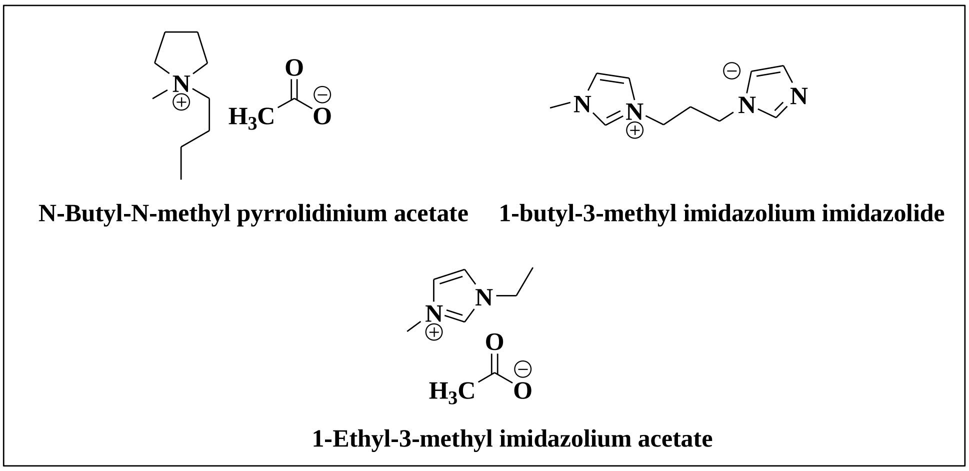


Fig. 6A.4: Structures of basic imidazolium and pyrazolium ILs

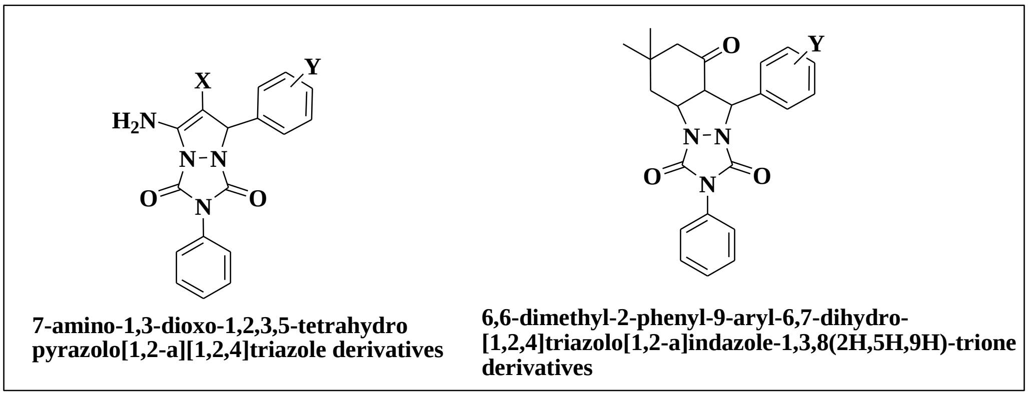
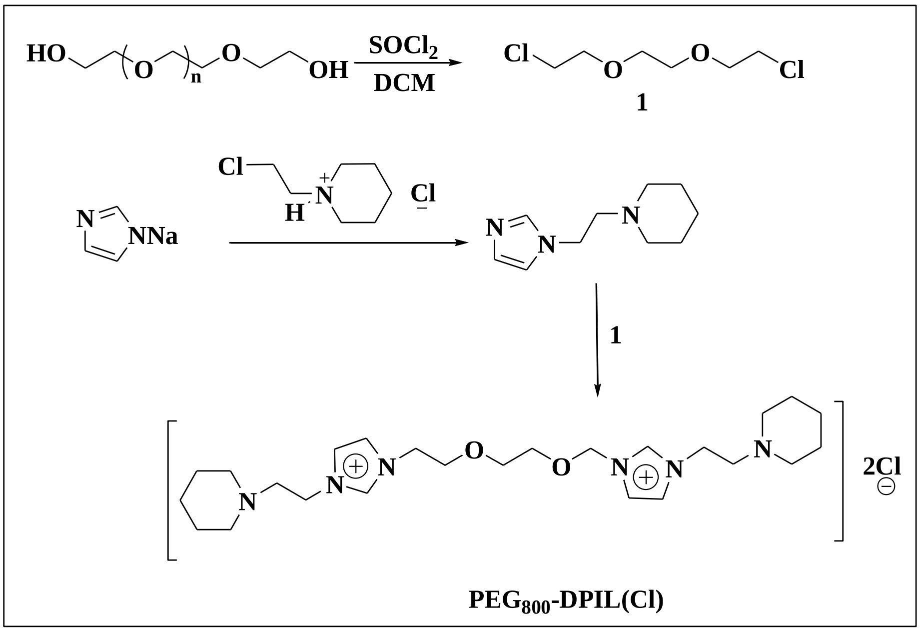


Fig. 6A.5: Structures of synthesized derivatives

Luo et al. [67] prepared a piperidine and imidazole functionalized PEG bridged Lewis basic dicationic IL according to **Scheme 6A.16**. The catalytic activity of the IL was probed in the four component Hantzsch reaction under solvent-free condition. Desired hydroquinolines were obtained with excellent yields within short reaction time. The IL could be recovered easily and recycled successfully for at least eight times.

The dibromination of electron poor and electron-rich alkenes were carried out using catalytic amount of known targeted ILs functionalized with a basic amino-aliphatic chain (**Fig. 6A.6**) [68-70] in aqueous medium by Primerano et al. [71]. The amine functionalized basic ILs effectively catalyzes the direct addition of bromine at ambient temperature. The protocol was both chemo- and regioselective in nature and allowed the recycling of ionic liquids.



Scheme 6A.16: Synthetic route for PEG$_{800}$-DPIL(Cl)

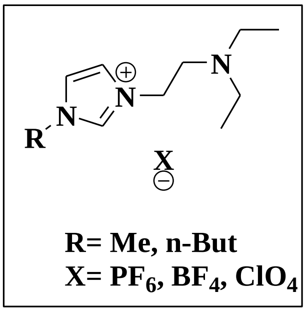


Fig. 6A.6: Structures of amino-alkyl chain functionalized ILs

Guo et al. [72] used three imidazolium based basic ILs with different branched alkyl side chains ([C$_n$mim]OH, n = 2, 3, 4) (**Fig. 6A.7**) and used them as catalysts for green biodiesel production via transesterification reaction under microwave irradiation conditions. Among the screened ILs, [C$_2$mim]OH exhibited the best catalytic activity affording 96% yield. The method showed quite improvement over the conventional method and it formed clearly biphasic systems immediately after the completion of transesterification of soybean oil.

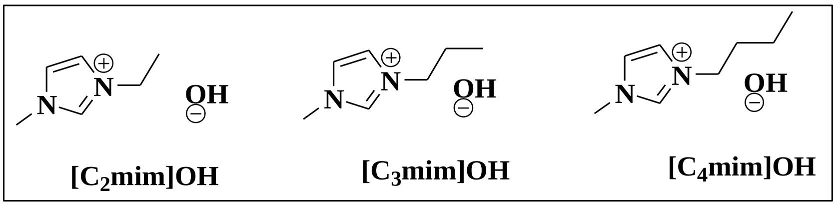
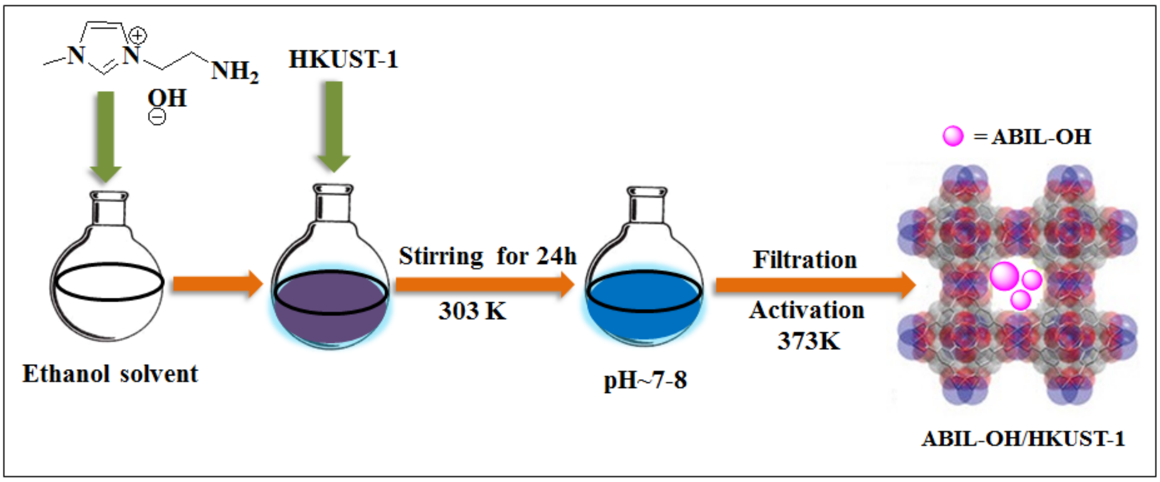


Fig. 6A.7: Structures of imidazolium based basic ILs

In 2014, Al-Sabagh et al. [73] studied the glycolysis of poly(ethylene terephthalate) (PET) catalyzed by Lewis basic ionic liquid [Bmim][OAc] which was synthesized according to a reported procedure [74]. They examined the effect of different factors such as temperature, time, ethylene glycol dosage, PET amount, [Bmim][OAc] dosage over the glycolysis reaction. Under the optimum reaction conditions, using [Bmim][OAc], 100% PET and about 58.2% bis(2-hydroxyethyl)terephthalate (BHET)yield was obtained.

Luo et al. [75] prepared a molecular size and shape-selective catalyst, microporous metal-organic framework HKUST-1 immobilized amino-functionalized basic ionic liquid (ABIL-OH), through facile impregnation and activation (**Scheme 6A.17**). Characterizations of the basic catalysts revealed uniform distribution of active species ABIL-OH in well-defined HKUST-1 nano cavities of copper-based MOFs [$Cu_3(BTC)_2$] (HKUST-1)(BTC = 1, 3, 5-benzenetricarboxylate). The catalytic efficiency was observed for the Knoevenagel condensation and reused for five times with the same efficiency.



Scheme 6A.17: The schematic illustration for synthesizing ABIL-OH/HKUST-1 catalyst

The catalytic uses of nine basic imidazolium functionalized dicationic ILs (1a-l) (**Fig. 6A.8**) were explored by Rizzo et al. [76] for mononuclear rearrangement of (Z)-phenylhydrazone of 3-benzoyl-5-phenyl-1, 2, 4-oxadiazoles to triazoles at 363 K (**Scheme 6A.18**). The authors prepared these ILs according to a reported procedure [77].The basic strength of the ILs were measured by Hammett indicator method. The outcome of the reaction was found to be greatly affected by the nature of interactions operating between cation and anion of the ionic liquid used.

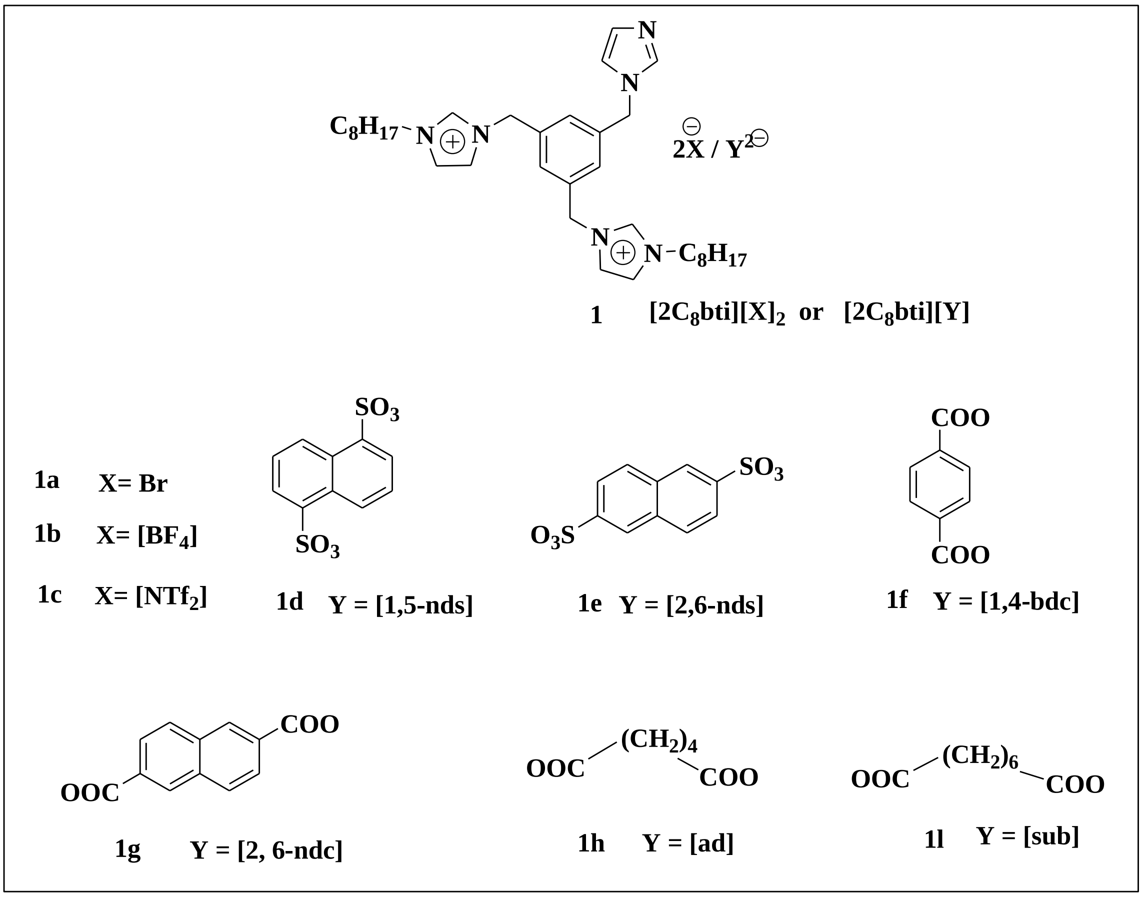
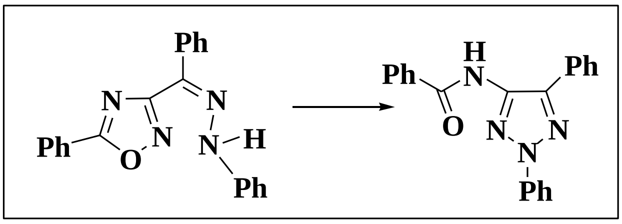


Fig. 6A.8: Structures of basic ILs used by Rizzo et al.



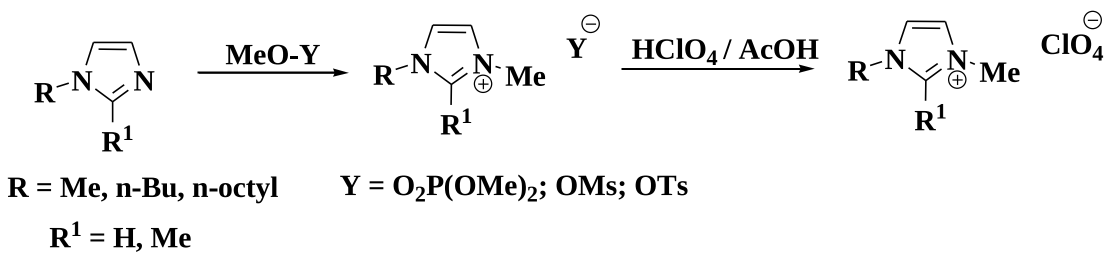
Scheme 6A.18: Rearrangement of (Z)-phenylhydrazone of 3-benzoyl-5-phenyl-1, 2, 4-oxadiazoles to triazoles

Zicmanis and Anteina [78] investigated the influence of main structural elements of 1, 3-dialkylimidazolium salts with different anions methanesulfonate, para-toluenesulfonate, and dimethyl phosphate (DMP)] on their catalytic activities in the Knoevenagel reaction between benzaldehyde and ethyl cyanoacetate. The synthetic strategy for the ILs is presented in **Scheme 6A.19**. The 1, 3-dialkylimidazolium dimethyl phosphate IL could be successfully used both as reaction media and catalysts. Additionally, it was reused for five cycles with significant retention of catalytic activity.

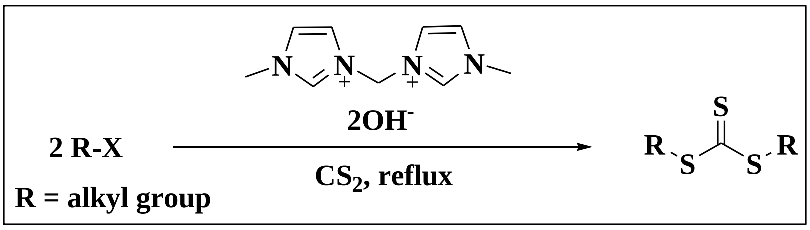
Sayyahi et al. [79] described the synthesis of symmetrical dialkyltrithiocarbonates from alkyl halides using carbon disulphide and a novel basic IL: 1, 1′-bis-methyl-3, 3-methylene-bisimidazolium dihydroxide (**Scheme 6A.20**) as a reagent and phase transfer catalyst. The reaction was simple, rapid and gave high product yields.

In 2015, Luo and co-workers also used [bmim]OH and [bmim]Im alkaline ILs as catalysts in the glycerolysis of soybean oil for monoacyl glycerol synthesis at 200 °C [80]. The [bmim]Im exhibited better catalytic efficiency than the [bmim]OH because of strong basic character. The catalyst could be recycled successfully for six consecutive cycles.

Shiran and co-workers [81] also employed basic ionic liquid 1-methyl-3-*n*-octylimidazolium hydroxide ([omim]OH) (**Fig. 6A.9**) for synthesis of thiazol-2-imine derivatives from the regioselective one pot three-component reaction of aryl amine, alkylisothiocyanate, and various α-haloketones at room temperature(**Scheme 6A.21**). The method had several advantages over the conventional ones in terms of yield, reaction time, facile work up and greater economic benefits.



Scheme 6A.19: Synthesis of 1, 3-dialkylimidazolium salts with different anions



Scheme 6A.20: Synthesis of symmetrical dialkyltrithiocarbonates catalyzed by 1, 1′-bis-methyl-3, 3-methylene-bisimidazolium dihydroxide

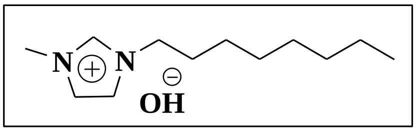
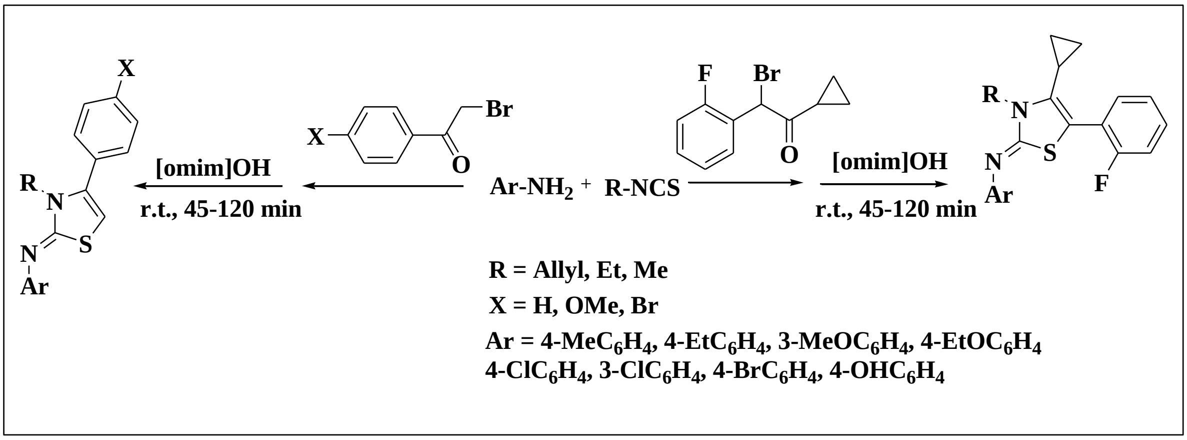


Fig. 6A.9: Chemical structure of 1-methyl-3-*n*-octylimidazolium hydroxide



Scheme 6A.21: Synthesis of thiazol-2-imine derivatives catalyzed by [omim]OH

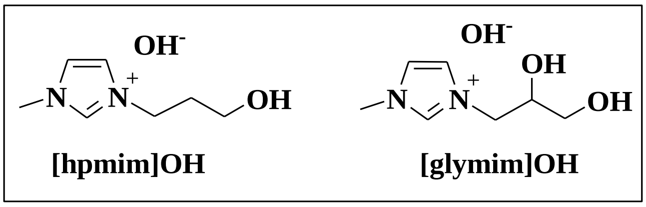
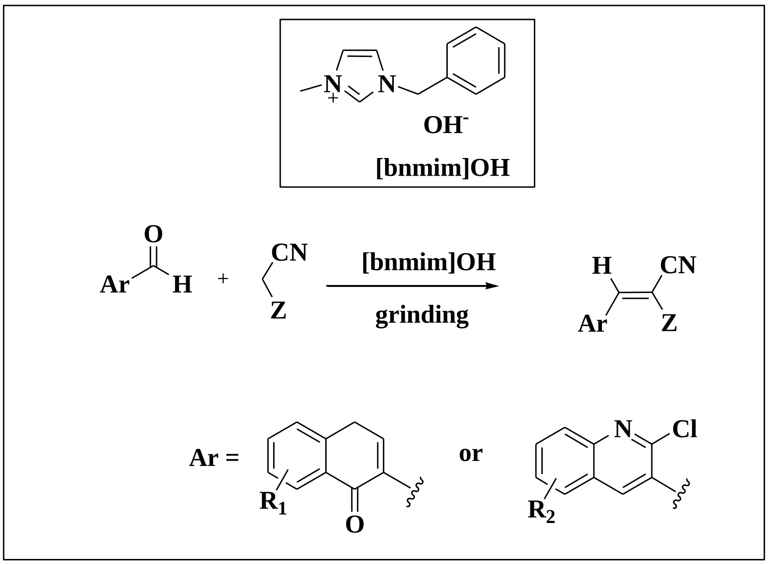


Fig. 6A.10: Structure of [hpmim]OH and [glymim]OH

Nowicki et al. [82] introduced two new imidazolium based basic ILs: 1-methyl-3-alkylimidazolium hydroxide ([hpmim]OH and [glymim]OH (**Fig. 6A.10**). The catalytic activities of the ILs were explored in the transesterification of rapeseed oil with methanol and compared to the well explored [bmim]OH ionic liquid. Nearly 100%

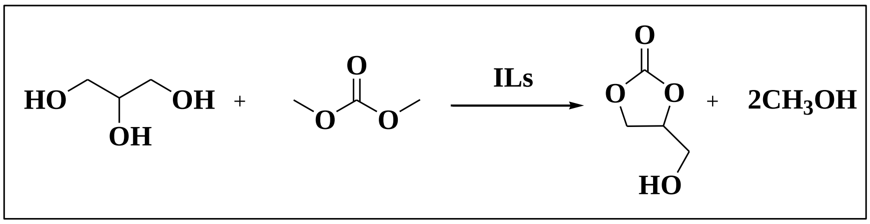
conversion of rapeseed oil was achieved in case of [glymim]OH IL due to its structural similarity to glycerol.

Shelke and Khadse [83] also utilized basic ionic liquid 1-benzyl-3-methylimidazolium hydroxide([bnmim]OH) as catalyst in Knoevenagel condensation of 4-oxo-(4H)-1-benzopyran-3-carbaldehydes and 2-chloroquinoline-3-carbaldehyde with various active methylene compounds viz. malononitrile, ethylcyanoacetate, cyanoacetic acid, cyanoacetamide and Meldrum's acid (**Scheme 6A.22**). Desired products were obtained in short reaction time with excellent yields. Additionally, the IL could be recycled up to fourth consecutive cycle efficiently.

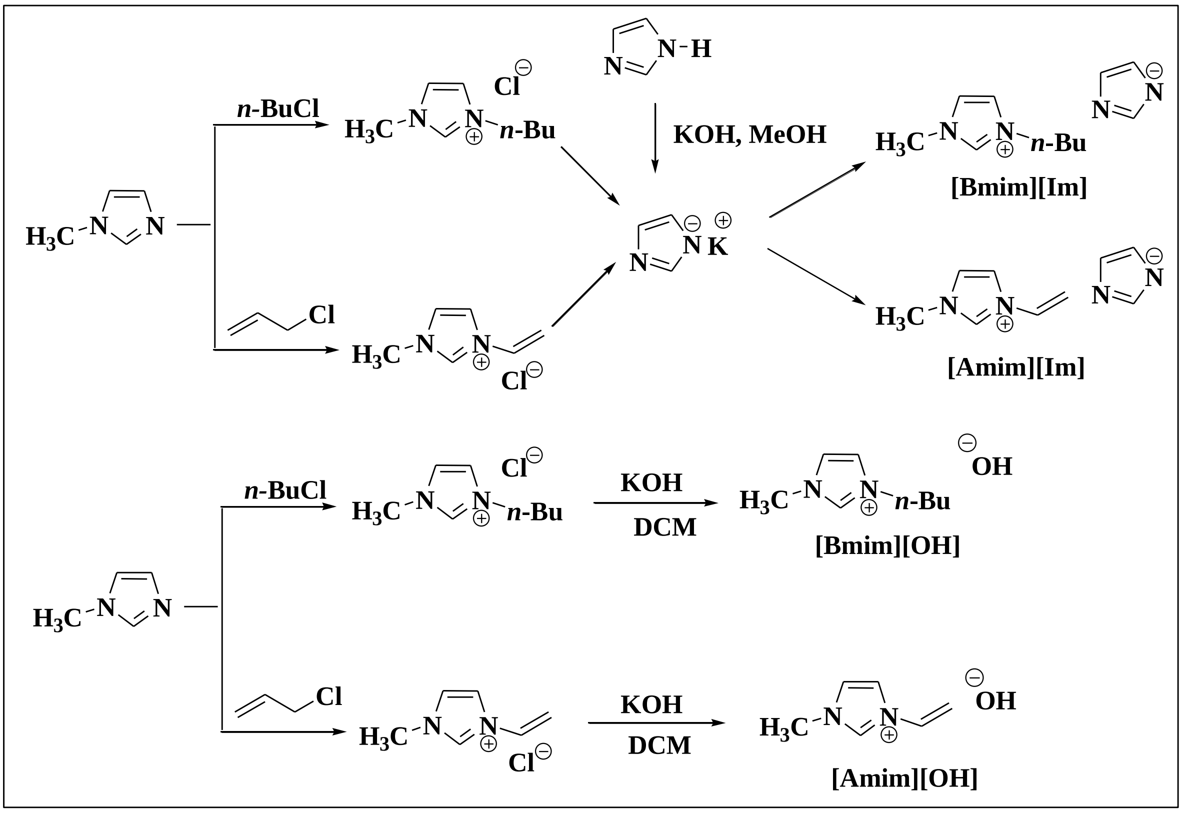


Scheme 6A.22: Knovenagel condensation catalyzed by [bnmim]OH

Again, Yi et al. [84] utilized 1-butyl-3-methylimidazolium imidazolide ([Bmim]Im), 1-butyl-3-methylimidazolium hydroxide ([Bmim]OH), 1-allyl-3-methylimidazolium imidazolide ([Amim]Im), and 1-allyl-3-methylimidazolium hydroxide ([Amim]OH) and used them as catalysts for synthesis of glycerol 1, 2-carbonate from glycerol under solvent-free condition (**Scheme 6A.23**). They prepared these ILs following a reported procedure [85] (**Scheme 6A.24**). Under optimized reaction conditions, using [Bmim]Im as catalyst, 98.4% glycerol conversion and up to 100% GC selectivity at 70 °C under ambient pressure was achieved. The ILs could be recycled and reused for three cycles with the same catalytic activity.

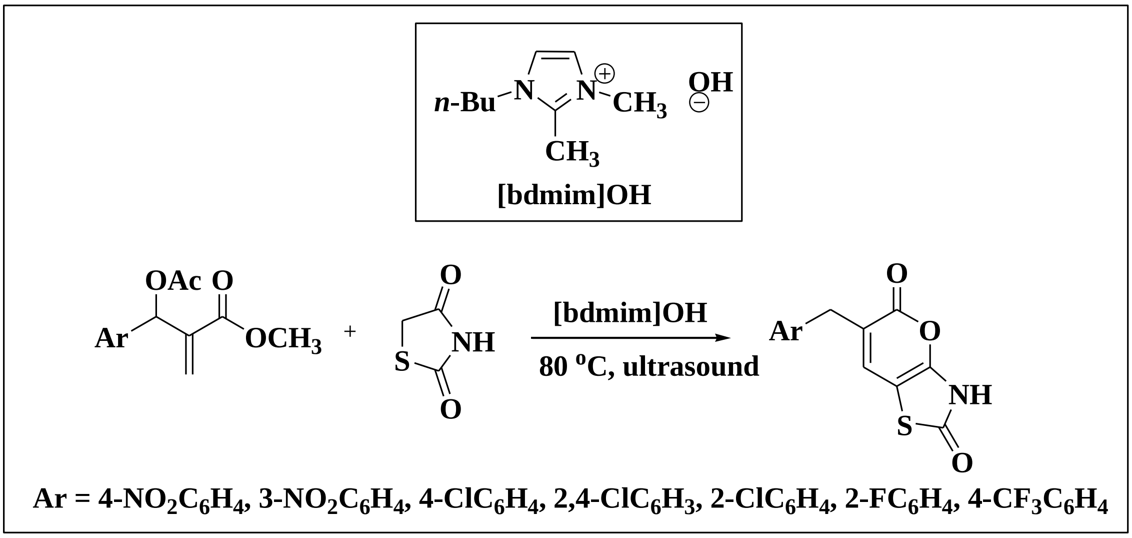


Scheme 6A.23: Synthesis of glycerol 1, 2-carbonate from glycerol in presence of ILs as catalyst



Scheme 6A.24: Synthetic scheme for preparation of ILs used by Yi et al.

In 2015, Mamaghani and Alavi [86] prepared fused α-pyrones from Baylis-Hillman acetates and various cyclic dicarbonyl compounds in the presence of basic ionic liquid 1-butyl-2, 3-dimethylimidazoliumhydroxide ([bdmim]OH) under ultrasonic irradiation (**Scheme 6A.25**). Desired α-pyrones were obtained in good-excellent yields within short reaction times using this IL as catalyst.



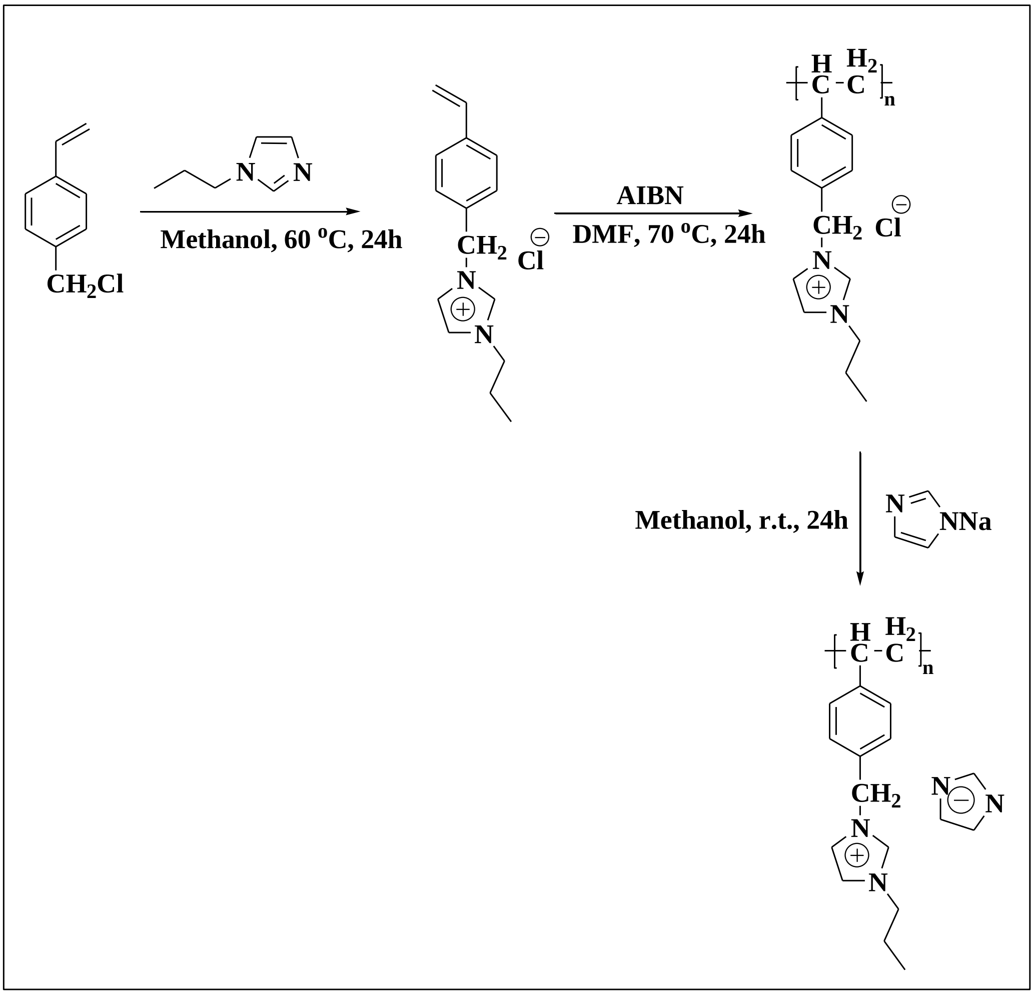
Scheme 6A.25: Synthesis of fused α-pyrones in presence of [bdmim]OH as catalyst

Ding et al. [87] reported the synthesis of a novel basic polymerized ionic liquid (BPIL): polymeric 1-[(4-ethenylphenyl)methyl]-3-propylimidazolium imidazolide and explored its catalytic efficiency in aqueous Knoevenagel reaction of a wide range of aldehydes and ketones with active methylene compounds at room temperature. The route for synthesis of the IL is presented in **Scheme 6A.26**. In comparison to the conventional inorganic bases, the basic IL effectively catalyzes the reactions due to intensive base sites and high surface activity. The catalytic system showed high catalytic activity up to fifth consecutive cycle.

Chaugule et al. [88] demonstrated the synthesis and uses of a binary catalyst systems of tricationic imidazolium room temperature ILs such as [GLY(mim)$_3$][NTf$_2$]$_3$IL/DBU, [GLY(mim)$_3$][NTf$_2$]$_3$/MTBD and [GLY(mim)$_3$][NTf$_2$]$_3$/TBD for direct preparation of dimethyl carbonate from CO_2 and methanol without the need of a dehydration system (**Scheme 6A.27**). The [GLY(mim)$_3$][NTf$_2$]$_3$ IL/1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) system was found to have 37% MeOH conversion and 93% DMC selectivity under mild reaction conditions. Moreover, the [GLY(mim)$_3$][NTf$_2$]$_3$ IL/DBU catalytic system could be easily recovered and reused three times with similar catalytic activity.

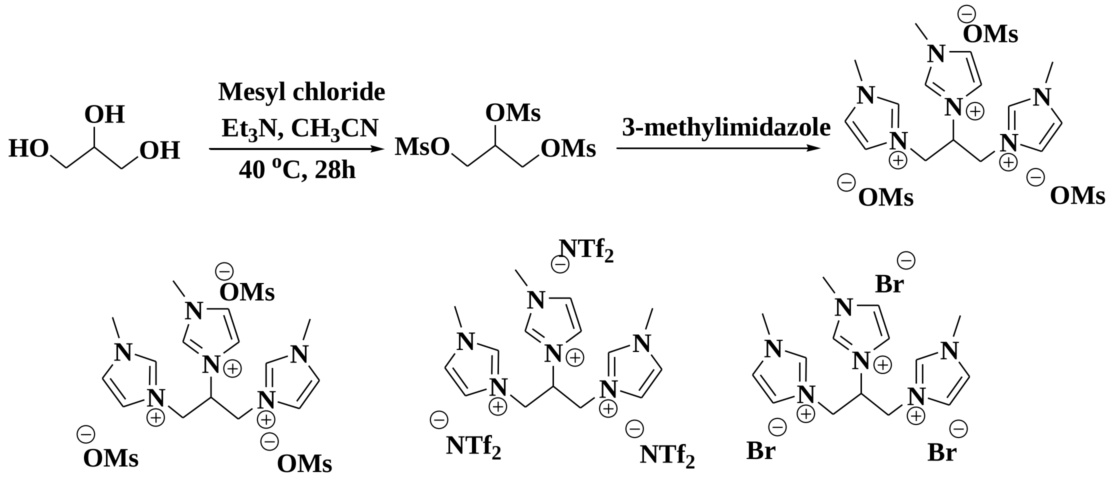
Haidarizadeh and Taheri [89] developed polystyrene-supported 1, 4-bis(3-methylimidazolium-1-yl)butane dihydroxide basic dicationic ionic liquid as heterogeneous catalyst for one-pot synthesis of chromene derivatives (**Fig. 6A.11**)

(**Scheme 6A.28**). The unique features of the catalyst were high thermal stability, recyclability, excellent catalytic activity in terms of yield and reaction time, high turnover number and turnover frequency, and also using water as a solvent.



Scheme 6A.26: Preparation of BPIL

Chen et al. developed [90] an interesting observation for tuning of basicity of ILs with the change of substituted imidazolium or triazolium anions in combination with phosphonium cation (**Fig. 6A.12**) for efficient synthesis of alkylidene carbonates according to **Scheme 6A.29** using atmosphere CO_2. Excellent yields were obtained due to basic ionic liquids' dual roles both as absorbents and as activators.

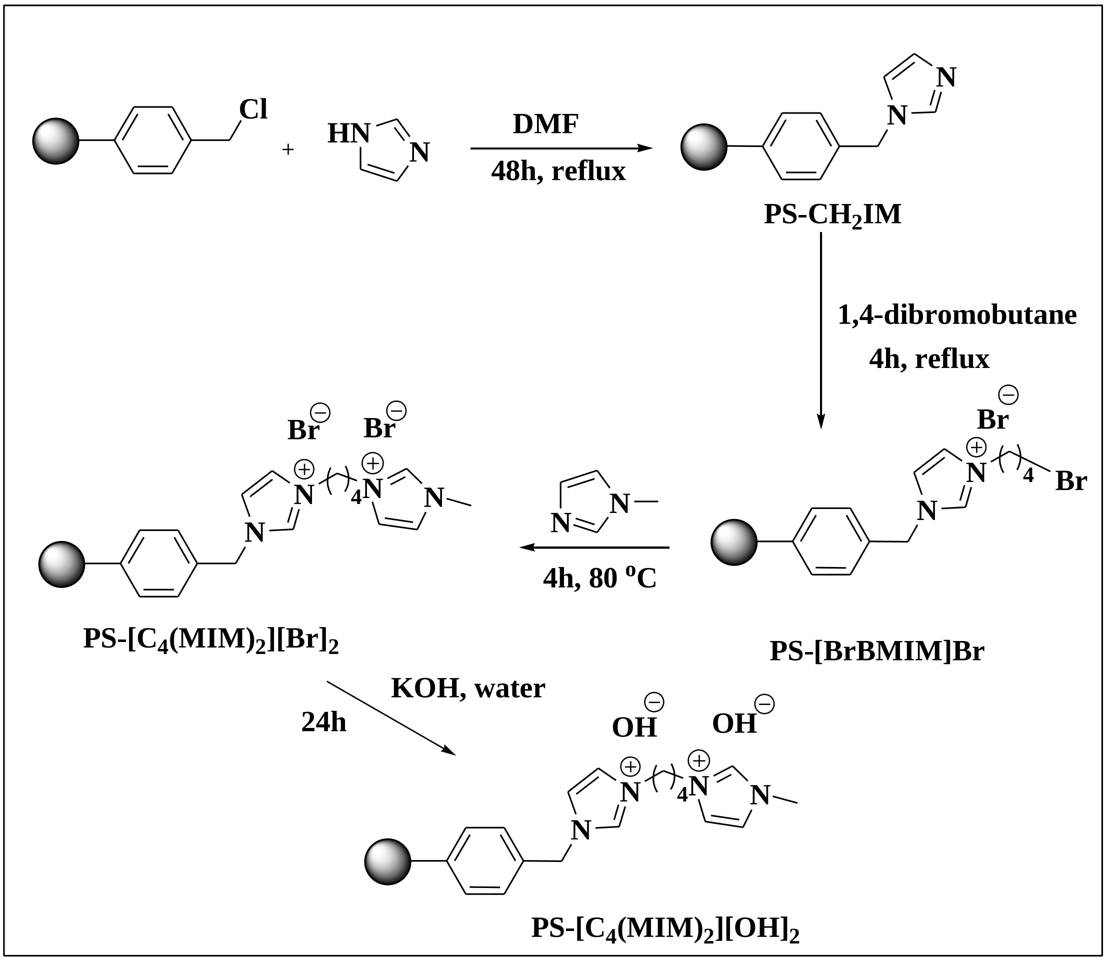


[GLY(mim)$_3$][(OMs)$_3$] [GLY(mim)$_3$][(NTf)$_3$] [GLY(mim)$_3$][(Br)$_3$]

Scheme 6A.27: Preparation of tricationic imidazolium room temperature ILs

Wang et al. [91] prepared basic morpholinium ionic liquid [Nbmm][OH] (**Fig. 6A.13**) from a mixture of N-butyl morpholine, N-butyl bromide, and KOH by two-step method and was used to catalyze transesterification of soybean oil with methanol to biodiesel. The effects of molar ratio of methanol to oil, reaction temperature, and amount of catalyst on the biodiesel yield were investigated. The optimized condition yielded of 94.5% yield with catalyst amount of 3.0 wt%, and methanol to soybean oil molar ratio of 14:1 at reaction temperature of 60 °C for 6 h. The catalyst retained activity up to six consecutive cycles.

Jiao et al. [92] prepared magnetic $CoFe_2O_4$ nanoparticles supported basic poly(ionic liquid)s catalysts (g-p[VRIm][OH]/MCFs) (**Scheme 6A.30**) through surface grafting method. The catalyst showed higher loading of ionic liquids, better stability and excellent paramagnetic property which could not be observed by conventional co-polymerization method. The catalytic activities were evaluated for the transesterification and Knoevenagel condensation. Additionally, the catalysts could be easily separated with the assistance of an external magnetic field. The catalyst was reused for four times with slight loss of catalytic efficiencies.



Scheme 6A.28: Immobilization of basic IL PS-[C$_4$(MIM)$_2$][OH]$_2$ on to the polystyrene

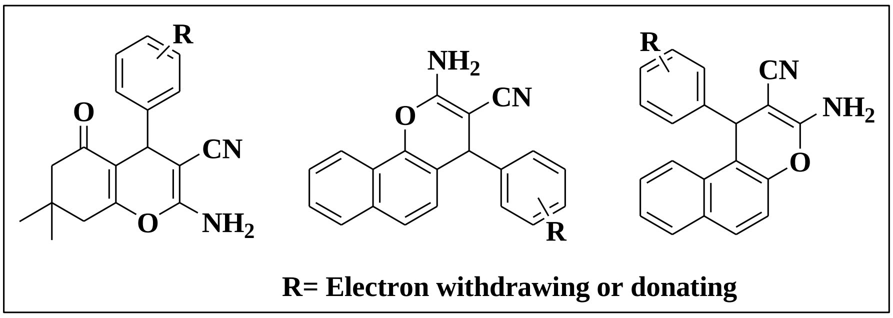


Fig. 6A.11: General structures of substituted 2-amino-4H-benzo[h]chromenes, 2-amino-4H-benzo[f]chromenes, and 2-amino-4H-tetrahydrochromene derivatives synthesized

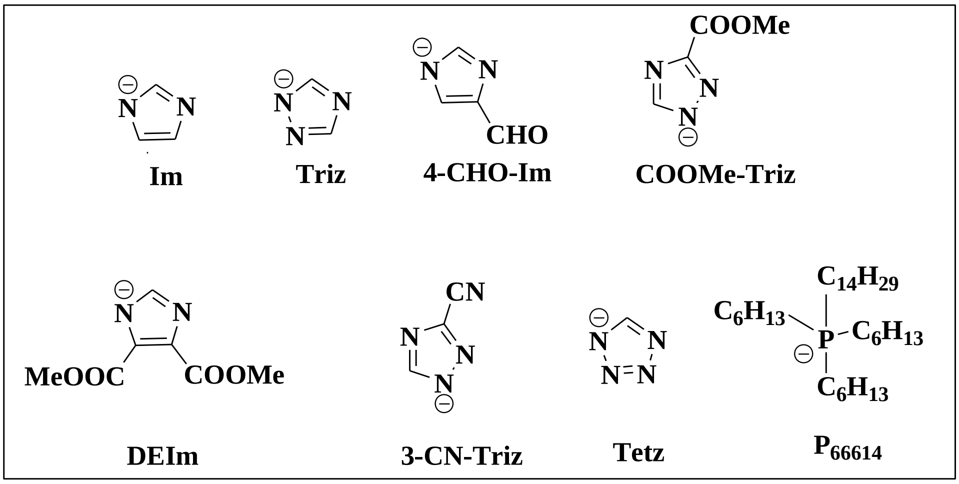
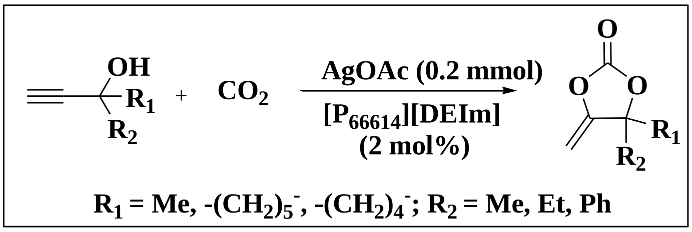


Fig. 6A.12: Structures of the anions and the cations in basic ILs



Scheme 6A.29: Synthesis of alkylidene carbonates catalyzed by basic ILs

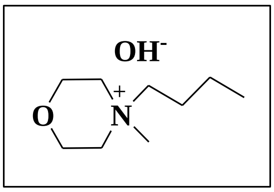
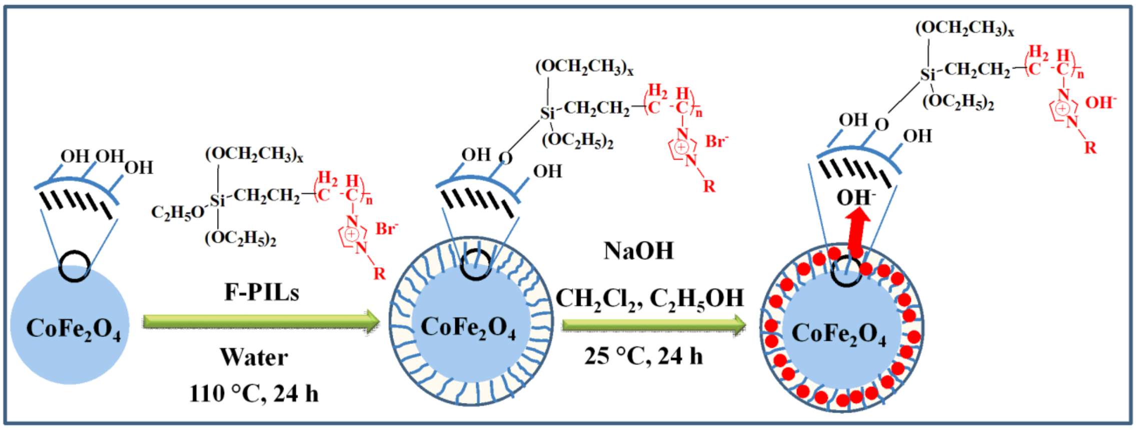


Fig. 6A.13: Structure of morpholinium ionic liquid [Nbmm][OH]

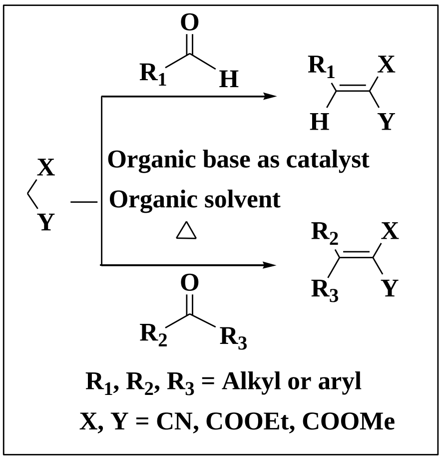


Scheme 6A.30: Synthetic procedure for preparation of g-p[VRIm][OH]/MCFs

6A.3. Base catalyzed Knoevenagel condensation reaction

The Knoevenagel condensation is an important, general and versatile C-C bond formation reaction in organic synthesis [93-95] which is usually catalyzed by a base, an acid, or a heterogeneous neutral support. The reaction is also considered as one of the modified version of Aldol condensation.

Classically, the Knoevanagel condensation occurs in between carbonyl or heterocarbonyl compound and any compound having an active methylene compound to produce α, β-unsaturated compounds using organic base such as piperidine, pyridine, amines or their salts [96, 97] in organic solvents such as benzene, toluene, THF, DCM etc. at different temperature (**Scheme 6A.31**). The use of excess amount of aliphatic aldehydes (4-6 times) is necessary for some reactions to produce sufficient yield of the products in less reaction time when the reaction rate is slow in presence of organic base catalyst [98]. The α, β-unsaturated product obtained in this path have been widely used in organic synthesis, in biological science, natural product chemistry, polymer chemistry, fine chemicals, medicine, agriculture and light emitting materials [1,13-15]. For example, the structural variation of benzylidenes or alkylidenes intermediates through the Knoevenagel reaction is possible by changing the structure of nucleophilic reagents such as β-keto ester [99, 100], diketones [99], ketothioesters [99], malonates, malononitriles [101], keto amides, and cyclic esters, along with different aromatic [102] or aliphatic aldehydes [103].



Scheme 6A.31: General scheme for Knoevenagel condensation

The biological activity of alkylidene malonate was observed in case of long-chain alkylidene malonates (LoCAM) namely pentadecylidene malonate, a simplified analogue of anacardic acid, exhibits a good modulation of the activity of histone acetyltransferases (**Fig. 6A.14**) [103].

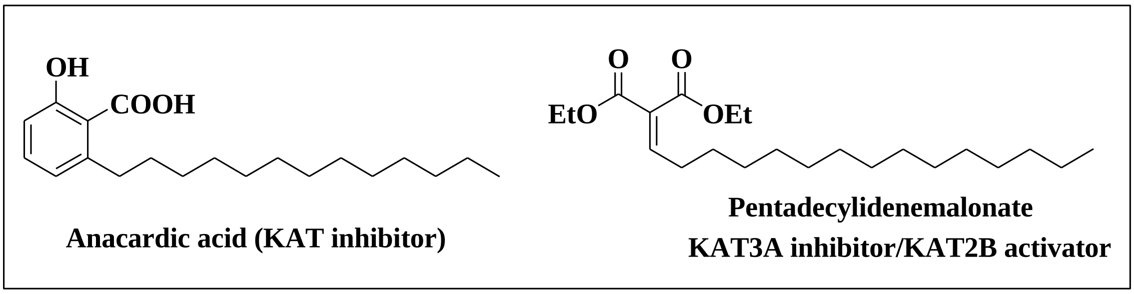


Fig. 6A.14: KAT inhibitors and activator: anacardic acid and pentadecylidene malonate

Jung et al. [104] utilized the Knoevanagel condensation as key synthetic step for the total synthesis of anticoagulant flocoumafen. In addition to the above mentioned amino bases, a large number of modified basic catalytic systems have been developed for the Knœvenagel condensation in recent years which include Al_2O_3[105], fly ash supported CaO [106], NH_4OAC [107], CdI_2 [108], K_2O-Al_2O_3 [109], zeolites [110], organic resins [111], mixed magnesium-aluminium oxides derived from hydrotalcites [112], sepiolites [113], aluminophosphonatesoxynitrides (AIPON) [114], synthetic phosphate $Na_2CaP_2O_7$ [115], ion-exchange resins [116], potassium fluoride (KF) [117], layered silicate PLS-1 [118], silica gel [119], niobium chloride [120], MgO/ZrO_2 [121], $Yb(OTf)_3$ [122], chitosan [123], fluorapatite [121] and ionic liquids [27, 48, 52] etc.

The use of task specific basic ILs as dual solvent-catalyst system is an attractive alternative of the above mentioned some non-reusable basic catalyst for the synthesis of benzylidene or alkylidene derivatives in absence of organic solvent at mild condition. Although, some of the ILs such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) or 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) [124] and Lewis acidic chloroaluminate ILs were employed as medium/catalyst with or without any added catalyst for performing the condensation with many limitations [125].

The presence of one or more Brönsted/Lewis base sites within the basic ILs make them suitable for studying the catalytic efficiencies of basic ILs through the Knoevenagel condensation reactions using variety of aliphatic or aromatic carbonyl compounds and different active methylene compounds. The review of literature reveals several applications of basic ILs based on TMG (tetramethyl guanidine) [126], cyclic guanidine [127], alkanolamine [128-133], methoxylpropylamine [134], DABCO [135, 136], DBU [137], N, N, N′, N′-tetramethyl-N′-hexyl-ethylenediamine (TMHEDA) [138], pyrrolidine [139-141], piperidine [142], N,N-dimethylethanolamnium (DMEA) [143], tetrabutylphosphonium [144], hexamethylenetetramine [145], tetrabutylammonium [146] for the Knoevenagel condensation under solvent free medium or in presence of other solvent at different temperatures and reaction time to produce low to high yields of products. Most of the tested ILs are monocationic possessing only one basic site which may cause reducing basicity of the IL to abstract the more acidic methylene proton for nucleophiic attack on the carbonyl group [137]. Only few reports are found for dicationic basic ILs catalyst [147] and no examples are found for the tricationic basic ILs.

By considering the review of literature, we planned to synthesize new series of triethylamine bridged tricationic basic ILs containing imidazolium, pyridinium moiety as cations with variation of three anions such as hydroxide, acetate and imidazolide by following the reaction **Scheme 6B.1** (**6B.1. Results and discussion**). As basic ionic liquids, they were tested as recyclable homogeneous catalysts for Knovenagel condensation of aromatic or aliphatic aldehydes/aliphatic ketone with active methylene compounds in absence of solvent and also in solution at room temperature.

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