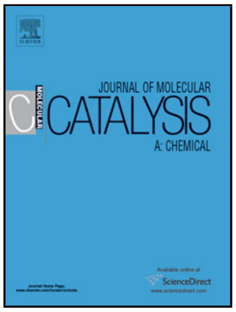

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Design of multifaceted acidic 1, 3-disulfoimidazolium chlorometallate ionic systems as heterogeneous catalysts for the preparation of β-amino carbonyl compounds

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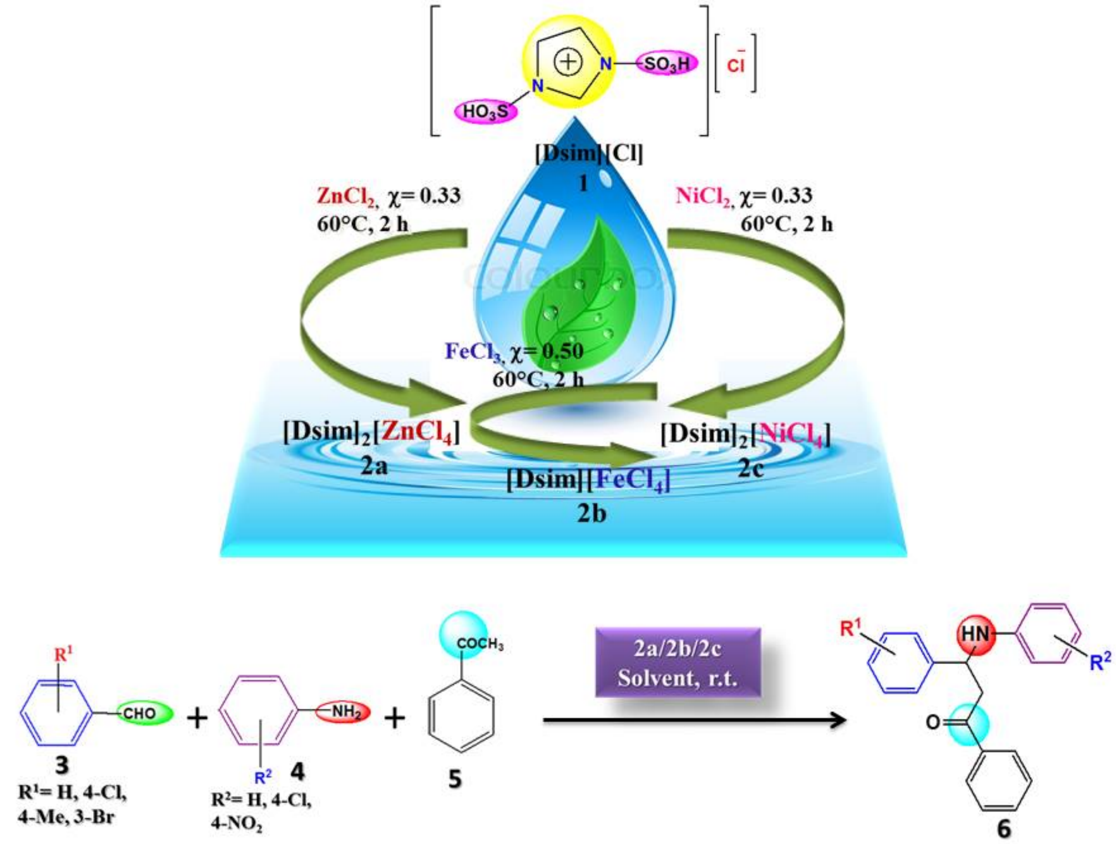
Graphical abstract



Highlights

- A new class of acidic 1,3-disulfoimidazoliumchlorometallate ionic solid system is prepared
- All three materials are characterized by various analytical techniques such as NMR, elemental analysis, UV-vis, FT-IR, Raman, TGA, SEM-EDX etc.
- Metal anion speciation regarding the structure is further confirmed by electronic spectra
- Calculated band gap energies prove these materials as better semiconductors
- Suitable to catalyze as heterogeneous acid catalyst for the synthesis of β–amino carbonyl compounds

Abstract

A new series of 1,3-disulfoimidazolium transition metal chloride systems: $[Dsim]_2[ZnCl_4]$, $[Dsim][FeCl_4]$ and $[Dsim]_2[NiCl_4]$ were synthesized as Brönsted-Lewis acidic solid material and characterized via NMR, FT-IR, Raman, TGA, SEM, EDX, Powder XRD, UV-visible, ICP-OES and elemental analysis. Semiconductor properties of these materials were studied through electronic spectroscopy. The Brönsted acidity of these systems was determined from Hammett plot. All these three materials were successfully tested as reusable catalyst for the one pot three component Mannich-type syntheses of β-amino carbonyl compounds within considerable time frame.

Keywords: Multifaceted acidic solid; 1, 3-disulfoimidazoliumchlorometallates; reusable catalyst; Mannich-type; β-amino carbonyl compound

1. Introduction

Chlorometallate ionic liquids (IL) are considered as functional materials for their distinct and potentially useful properties [1, 2]. The specific characters of such ionic liquid depend on both the nature of metal present and the ratio of metal chloride to organic chloride salt used for this synthesis. The anionic component $[M_xCl_y]^{n-}$ of chlorometallate IL can be varied by considering these two factors and thereby, control its stability and catalytic activity using Lewis acidity or basicity for a given composition. The characteristics and individual properties of these ILs provide wide uses in catalysis, electrochemistry, separation/extraction processes, and synthesis of inorganic semiconductors and conversion of biomass to energy products [3-6]. Chlorometallate systems based on Al were extensively studied for catalysis and electrochemical uses [3, 7-8]. Unfortunately, their extreme sensitivity towards moisture created a major barrier for various applications. Till date several transition metal chlorides have been investigated to design different compositions of chlorometallate anionic ILs [1]. It was seen that most of these ILs were prepared with alkyl group containing imidazolium or pyridinium cations and little work had been done with functionalized cations in halometallate systems [9-12]. Addition of acidic or basic functional groups into the cation may further modify the characteristic properties of each IL. In this context, we tried to develop new bifunctional Brönsted-Lewis acidic chlorometallate ionic salt systems using two $-SO_3H$ group into the cation as an extension of the previous work [13]. Herein, we synthesized and characterized three multifaceted acidic 1, 3-disulfoimidazolium chlorometallate systems: $[Dsim]_2[ZnCl_4]$, $[Dsim][FeCl_4]$ and $[Dsim]_2[NiCl_4]$ in solid state from the reaction of 1,3-disulfoimidazolium chlorides ([Dsim]Cl) with transition metal chlorides ($FeCl_3$, $NiCl_2$, $ZnCl_2$**)** in different molar ratios (1:1 and 2: 1) under neat condition at 60°C for 2 h (**Scheme-1**). The bifunctional acidic sites make them as strong acid catalysts for potential organic reactions with various advantages of heterogeneous catalysis [14, 15].

The acid catalyzed multicomponent Mannich-type reaction is an important procedure for the preparation of β-amino carbonyl compounds **(Scheme-2**) which act as precursors of various natural products and synthetic bioactive compounds, pharmaceuticals and functional materials [16, 17]. The search of literature provided several modified synthetic methods for its preparation using heterogeneous acid catalyst, ionic liquids, solvent-free condition, microwave energy and aqueous media [18-21]. Various limitations of such procedures also require mitigation of methodology in terms of enhancing the catalytic activities. Therefore, we checked the efficiency of these chlorometallate ionic salts as heterogeneous catalysts for the Mannich-type reaction of acetophenone, aromatic aldehydes and substituted aniline in ethanol at room temperature according to the **Scheme-2.**

2. Experimental

2.1. General techniques

All chemicals were purchased from Merck and used without any further treatment. For catalytic activity comparisons, the known 3-methyl-1-sulfonic acid imidazolium transition metal chlorides [Msim][X] (where X= $[ZnCl_3]^-$, $[FeCl_4]^-$), 1-butyl-3-methylimidazolium chlorometallates $[BMIm]_n[X]$ (**7a-7c**) (m=2 and 1; [X] = $[ZnCl_4]^{2-}$,$[FeCl_4]^-$,$[NiCl_4]^{2-}$) and 1, 3-disulfonic acid imidazolium chloride or carboxylate without metal center [Dsim][X](**8a-8c**) ([X]= Cl^-, CF_3COO^- , CCl_3COO^-) were synthesized using the standard procedure available in literature [13,22-24, 25]. The IR spectra were run on a Nicolet Impact- 410 spectrophotometer. The ^1H NMR and ^{13}C NMR were recorded on a JEOL 400 MHz spectrophotometer (δ in ppm) in DMSO-d_6 and $CDCl_3$ as solvents. The Hammett plots of the solid acids were obtained on a UV 2550 spectrophotometer using 4- nitroaniline as basic indicator. The TGA analysis was done on

Shimadzu TGA-50. Scanning electron microscopy was performed on a JEOL JSM – 6390LV SEM, equipped with energy dispersive X–ray analyzer (EDX). The Raman spectroscopy analyses were done on Horiba LabRAM HR spectrophotometer equipped with a He-Ne laser of excitation wavelength of 514.5 nm. Powder X – Ray diffraction spectra were recorded on Rigaku Multiflex instruments using a nickel filtered CuKα (0.15418 nm) radiation source and scintillation counter detector. Electronic spectra were recorded on a UV 2450, Shimadzu spectrophotometer. ICP-OES analysis was done by ICP-OES Perkin Elmer Optima 2100DV instrument. All the melting points were recorded on Büchi– 560 apparatus.

2.2. Preparation of 1, 3-disulfoimidazolium chlorometallates [Dsim][FeCl$_4$] and [Dsim]$_2$[X] (2a-c), where X$^-$ = [ZnCl$_4$]$^{2-}$, [NiCl$_4$]$^{2-}$:

The three 1, 3-disulfoimidazolium chlorometallates were prepared by two step reactions (**Scheme 1**). The first step involved with the dropwise addition of chlorosulfonic acid (20 mmol) to a stirred solution of imidazole (10 mmol) in dry CH_2Cl_2 (30 mL) at 0°C within a period of 5 min under nitrogen atmosphere in a 100 mL round bottom flask. Then the mixture was stirred for one hour to complete the synthesis of 1, 3-disulfoimidazolium chloride [Dsim][Cl].The viscous ionic liquid layer was washed three times with fresh CH_2Cl_2 (3× 20 mL) by decantation of dichloromethane solution. The residue was dried under vacuum which produced 98% pale yellow viscous oil of [Dsim][Cl]. The 2nd step was performed by mixing of respective metal chlorides with the [Dsim][Cl]. Mole fractions of $ZnCl_2$, $FeCl_3$, and $NiCl_2$ in their respective reaction mixture with [Dsim]Cl were calculated as 0.33 for $ZnCl_2$ (**2a**), 0.5 for $FeCl_3$ (**2b**) and 0.33 for $NiCl_2$ (**2c**) [26]. As an example, synthesis of **2b** with 0.5 mol fraction of $FeCl_3$ (1.62 gm, 10 mmol) was added into [Dsim][Cl] (2.67gm, 10 mmol) and stirred at 60°C in an oil bath for 2 hour. The solid product was washed with dry CH_2Cl_2 (2 x 5 mL) and then dried in vacuum oven at 80 °C to get 96-97 % yields of **2a-c**. Finally they were kept in vacuum desiccator. Melting points of the three ionic salts were observed up to 400°C in Büchi-560 melting point apparatus but their initial colours changed into black or brown without going to liquid state. They may lose their composition at high temperature as shown by TGA analysis (**Fig-5**).

2.3. Characterization of 1, 3-disulfoimidazoliumtransition metal chlorides [Dsim]$_2$[X] and [Dsim][X]

[Dsim]$_2$[ZnCl$_4$] **2a** : Off white solid, 96 % yield; FT-IR (KBr): 3438, 1635, 1588, 1435, 1202, 1054, 884, 761 and 579 cm^{-1}; ^{1}H NMR (DMSO- d$_6$, 400 MHz): 14.3 (s, 4H), 9.03(s, 2H), 7.64(s, 4H); ^{13}C NMR (DMSO-d$_6$, 100 MHz): 134.8, 119.8; CHN analysis (Mol .formula $C_6H_{16}Cl_4N_4O_{12}S_4Zn$): calculated (%) C 10.73, H 2.40, N 8.34; Found C 10.66, H 2.36, N 8.22.

[Dsim][FeCl$_4$] **2b**: Yellow solid; 97 % yield; FT-IR (KBr): 3405, 1635, 1588, 1444, 1194, 1054, 982, 766 and 604 cm^{-1}; CHN analysis (Mol .formula $C_3H_8Cl_4N_2O_6S_2Fe$) calculated (%) C 8.38, H 1.88, N 6.52; Found C 8.31, H 1.80, N 6.48.

[Dsim]$_2$[NiCl$_4$] **2c**: Yellow solid ; 96% yield; FT-IR (KBr): 3386, 1603, 1584,1448, 1177, 1050, 884, 762 and 584 cm^{-1}; ^{1}H NMR (DMSO-d$_6$):14.22 (s, 4H), 9.00 (s, 2H), 7.61 (s, 4H); ^{13}C NMR (DMSO-d$_6$, 100 MHz):134.7, 119.8, 40.02, 39.8, and 39.6 ; CHN analysis (Mol .formula $C_6H_{16}Cl_4N_4O_{12}S_4Ni$) : calculated (%) C 10.84, H 2.43, N 8.43; Found C 10.81, H 2.40, N 8.35.

*2.4. Typical procedure for the synthesis of β-amino carbonyl compounds (**6**)*

A three component reaction of acetophenone (1 mmol), aromatic aldehyde (1 mmol) and aromatic amine (1 mmol) in absolute ethanol (5 mL) was conducted in a 50 mL round bottom flask at ambient temperature with continuous stirring in presence of 5 mol % of 1,3-

disulfoimidazolium chlorometallates $[Dsim]_2[X]$ or $[Dsim][FeCl_4]$ where $X=[ZnCl_4]^{2-}$, $NiCl_4]^{2-}$ respectively. The progress of the reaction was monitored on thin layer chromatographic plate using a mixture of EtOAc and petroleum ether (1: 5) as solvent system. The solvent ethanol was eliminated under reduced pressure in rotary evaporator after completion of the reaction. The solid acidic catalyst was recovered from the dichloromethane solution (5 mL) by filtration which was remaining as insoluble residue. The catalyst was reactivated after washing with CH_2Cl_2 solvent (5 mL) and then dried in vacuum oven at 80 °C for 2 hour for next run. The product was precipitated out from the saturated solution of CH_2Cl_2 by dropwise addition of hexane with continuous stirring at room temperature. The solid product was filtered and again recrystallized from ethanol solution to generate analytically pure product**.**

3. Results and discussions

3.1. Characterization of the catalyst:

3.1.1. IR spectroscopy analyses:

FT-IR spectroscopic analyses of the three solid acids are represented in **Fig. 1**. Strong absorption at 1177-1202, 1050-1054 and 579-604 cm^{-1} were assigned respectively for S-O symmetric and S-O antisymmetric stretching and bending vibration of $–SO_3H$ groups. The presence of –C=N- and -C=C- bonds of basic imidazole unit was confirmed from the stretching frequencies at 1584-1588 cm^{-1} and 1603-1635 cm^{-1} respectively. The peak around 884-982 cm^{-1} expressed both N-S stretching and in plane imidazole ring bending vibrations. The band at 761-766 cm^{-1} appeared because of out of plane ring bending of C-H bond. The broad –OH peak of the three solids at 3386-3438 cm^{-1} expressed the involvement of two $–SO_3H$ groups in H-bonding [27-28]. The IR spectra of **2b** and **2c** in the region 400-200 cm^{-1} were characterized by the distinct metal-chloride vibration of $[FeCl_4]^-$ at 380 cm^{-1} and around 285 cm^{-1} for $[NiCl_4]^{2-}$ according to the reported literature [29-30]. No characteristic absorptions were observed for **2a** in this region.

3.1.2. Electronic spectra:

Electronic spectra in **Fig.2** (a) shows different absorbance peaks for different halometallate anions in disulfoimidazolium ionic liquids. Absorbance at 222 nm and 340 nm for **2a** can be assigned as intra-ligand charge transfer in **2a**[31-32]. For **2b**, peaks at 270 nm and 385 nm originate from ligand to metal charge (L→ Fe (+3)) transfer transitions and the other absorption band at 572 nm can be attributed for d-d characteristic transition of $FeCl_4^-$ [33-35]. The absorbance spectrum of **2c** exhibits two bands of almost same intensity at 680 nm and 744 nm for the tetrahedral moiety of $NiCl_4^{2-}$ as supported by the literature data [24]. Band at 261 nm can also be assigned as L→ M charge transfer transition for tetrahedral complexes on the basis of ligand field theory. Also the peak at 405 nm can be reasoned for the equilibrium mixture of a little mono and dichloro nickel species present along with the $NiCl_4^{2-}$ complex [36].

The confirmation of anionic species present in the three materials from the electronic spectra also provided a chance to focus on the semiconducting properties of these materials by calculation of optical band gaps using Tauc equation-1. With the symbols having their usual meaning, the Tauc relation (equation-1) can estimate optical band gap of systems under investigation [37].

$$\alpha h\nu \propto (h\nu - Eg)^n \qquad \text{(equation-1)}$$

Where, α is the absorption coefficient, $h\nu$ is the photon energy and Eg is the optical band gap for indirect transitions (n=2) or direct transitions (n=1/2). Assuming all transitions are direct, and allowed type (n=1/2), the estimated Eg values from the intercepts of plot **Fig.2(b)** $h\nu$ vs $(\alpha h\nu)^2$

are found to be 2.55, 2.41 and 2.30 eV for **2a**, **2b** and **2c** respectively. Thus the three solid compounds with significant band gaps similar to that of semiconductors firmly indicate their importance.

3.1.3 ^{1}H and ^{13}C NMR analyses:

The four proton singlets at 14.0-14.3 ppm in ^{1}H NMR spectra of 1, 3-disulfoimidazolium chlorometallates **2a** and **2c** supported the presence of two –SO_3H groups in imidazole unit. The lower solubility of **2b** in DMSO-d_6 restricted to take the ^{1}H and ^{13}C NMR spectra of [Dsim][$FeCl_4$]. The characteristic signals of imidazole ring carbons were observed in the ^{13}C NMR spectra of **2a** and **2c.** The CHN elemental analyses also confirmed the formation of disulfoimidazolium chlorometallates.

3.1.4 Elemental analyses:

The CHN analyses of these solids showed the percentage of C, H and N in the disulfoimidazolium chlorometallates as included in the experimental section after treatment at 90°C in vacuum oven to remove the physisorbed water for 3 hour. The amount of metal content in each of the solid was estimated from a 30 ppm solution in aqua regia using Inductive Coupled Plasma (ICP) analysis. The measured values were comparable with the original metal content in the respective ionic solid. (Table 1)

3.1.5. Surface morphology:

The SEM images of the three organochlorometallates in **Fig.3** displayed some cracks and deformities on the surfaces of the catalyst particles. Variations of structural arrangement were observed in the solid state of **2a-c** based on the nature of transition metal chlorides. The SEM image (a) portrays a gloomy surface of **2a** where particle visibility is not satisfactory. Image (b) displays the existence of some solid particles even though the surface image is found to be contorted. SEM image (c) demonstrates a surface looked like fused particles. These discontinuities may be accounted to the different moisture sensitivity of the catalysts.

3.1.6. EDX analysis:

Energy dispersion X-ray (EDX) analysis was performed for the three solid acids which confirmed the presence of respective metal chloride along with other constituent's elements of disulfonic imidazolium metal chlorides as shown in **Fig.4**.

3.1.7. TGA analysis:

The thermal stabilities of the three catalysts were investigated by thermo gravimetric analysis (**Fig.5**).The TGA curve for $[Dsim]_2[ZnCl_4]$ showed initial 12 % weight loss below 100°C which can be assigned for physisorbed water followed by another decompositions at 250°C. The TGA analysis of $[Dsim][FeCl_4]$ salt expressed total 25% weight loss up to 310°C including 14% weight loss of absorbed moisture at 90°C along with two other breaks around 125°C and 310°C respectively. For $[Dsim]_2[NiCl_4]$, we observed three steps decomposition around 100 ,220°C and 400 °C with total weight loss of 45% which includes 25 % of moisture from the ionic salt. Thermal decomposition of each material above 100 °C can be attributed for stepwise losing of two –SO_3H groups present in the imidazolium cation by interaction with chlorometallate anion. Analysis of the curves also indicates the presence of certain amount of non-volatile residue which may be accounted for metallic chlorides of the respective metals. Among the three metal salts, this study displayed higher thermal stability of $[Dsim]_2[ZnCl_4]$ up to 250°C.

3.1.8. Powder X-ray diffraction analysis:

Powder XRD pattern of **2a** was displayed in **Fig. 6**. The characteristic XRD diffraction peaks of $ZnCl_2$ in $[Dsim]_2[ZnCl_4]$ were observed at 2Θ = 16.6, 25.5, 29.4 and 34.9° and matched satisfactorily with the XRD database (JCPDS card no. 74-0517) corresponding to (002) ,(101),(102) and (103) reflection planes respectively. The powder XRD analyses of $[Dsim][FeCl_4]$ and $[Dsim]_2[NiCl_4]$ didn't produce the actual pattern which can be attributed for the strong hygroscopic character of these two solids as observed from the TGA graph(**Fig. 5**).

3.1.9. Raman analysis:

In **Fig.7**, Raman spectra of **2a** showed one strong peak at 283 cm^{-1} and one medium peak at 306 cm^{-1}. These Raman shift values can be assigned to the mixture of major amount of $[ZnCl_4]^{2-}$ and minor amount of dimeric $[Zn_3Cl_6]^{2-}$ unit [38-39]. Till date there is no experimental evidence for the support of $[ZnCl_3]^{-}$ in either the solid or liquid state. A strong peak at 336 cm^{-1} referred to the literature value for tetrahedral $[FeCl_4]^{-}$ species in **2b** confirmed the presence of this chlorometallate anion [40]. The Raman spectrum of **2c** satisfactorily produced the characteristic peak at 261 cm^{-1} for $NiCl_4^{2-}$ [41].

3.2. Hammett acidity measurement:

The acidity of the acidic ionic salts was evaluated as Hammett acidity function H^o (Equation-2) obtained on UV-visible spectrophotometer using 4-nitroaniline as basic indicator by Hammett plots (**Fig.8**) [42-43]. The indicator [I] showed maximum absorbance at 378 nm without protonation. As the absorbance of 4-nitroaniline decreases, the acidity of solid acid increases because of higher concentration of low molar absorptivity protonated indicator [HI] in ethanol solution. The ratio of $[I]/[IH^+]$ can be measured from the absorption differences and p*K*(I)aq represents the p*Ka* value of the indicator referred to an aqueous solution.

$$H^o = pK\,(I)\,aq + \log [I]/[IH^+] \qquad \text{(Equation-2)}$$

The procedure involved with the mixing of equal concentration of 4-nitroaniline (5mg/L, p*K*a = 0.99) and the solid acid (5mmol/L) in ethanol solution. The decreasing Brönsted acidity order of the three solid acids against their observed H^o (table-2) values was as: $[Dsim][FeCl_4]$ >$[Dsim]_2[NiCl_4]$ > $[Dsim]_2[ZnCl_4]$ and was further confirmed by the catalytic study for the one-pot Mannich-type synthesis of β-amino carbonyl compounds.

3.3. Leaching test:

The leaching test of the three salts was performed in absolute EtOH, H_2O, CH_2Cl_2 and EtOAc etc. 20 mg of each **2a, 2b** and **2c** was stirred separately in 5 mL solvent for 2.5 hour at room temperature and then filtered to measure the pH of the filtrate. This study expressed neutral character of EtOH, CH_2Cl_2 and EtOAc solution except in case of H_2O (pH= 1-2).

3.4. Catalytic test:

3.4.1. Reaction condition optimization:

The catalytic efficiency of these three multi-functionalized acidic salts were investigated for the three component Mannich-type synthesis of β-amino ketones utilizing acetophenone (1 mmol), benzaldehyde (1 mmol) and aniline (1 mmol) in ethanol using 5, 10 and 20 mol % of each catalyst at room temperature (table-3, entries 1-3). It was perceived that 5 mol % of the each solid catalyst could be preferable to produce 85-94% yield of **6a** within 45-80 min in EtOH under mild condition. Thus, the acidity order of three catalysts as observed from the Hammett study strictly followed the same catalytic activity order for the preparation of **6a** in terms of reaction time (table-3, entries 1-3).

The three catalysts expressed similar type of catalytic activity in dichloromethane and ethyl acetate with 5 mol% at room temperature stirring (table-3, entries 4-5). From the solvent study results, we selected ethanol as the suitable safer solvent to extend the synthesis of β -

amino carbonyl compound with variety of substituted aromatic aldehydes and substituted anilines.

It was specially mentioned in literature that this one-pot reaction is sensitive to temperature for further decomposition of β-amino ketones to side products in presence of acidic catalyst [44-46]. To avoid these problems, low temperature reactions are highly desirable for this reaction and therefore we optimized the reaction condition at ambient temperature.

3.4.2. Substrate scope study and plausible mechanism of the Mannich-type reaction:

From the optimization study we found that the hygroscopic nature of **2b** and **2c** didn't affect the overall efficacy of the catalysts. As results, the three catalysts worked successfully under the optimized conditions to generate library of β-amino carbonyl derivatives from the three component reaction of acetophenone with substituted aromatic aldehyde and different group bearing aniline in ethanol (table-4). Most of the reactions were completed within the specific reaction time for each catalyst irrespective of the nature of substituent present in both aromatic aldehyde and aniline derivatives (table-4).

The possible mechanism of [Dsim][$FeCl_4$] catalyzed three component synthesis of β-amino ketone derivative can be proposed through interaction of aldehyde functionality by –SO_3H group of IL catalyst for nucleophilic attack with $FeCl_4^-$ activated amino group of aniline according to **Scheme-3**.

3.4.3. Comparison of catalytic efficiency with other ionic liquid systems:

The model reaction was extended for 3-methyl-1-sulfonic acid imidazolium transition metal chlorides [Msim][X] (where X= $[ZnCl_3]^-$, $[FeCl_4]^-$) using 5 mol % of the solid acid in ethanol at ambient condition (table-5, entry-1)[13]. Disulfonic analogues **2a** and **2b** expressed better catalytic efficiency than monosulfonic analogues (table-5, entry 4). The role of two –SO_3H groups attached to imidazolium cation in enhancement of the activity of three catalytic systems (**2a**, **2b** and **2c**) was also clearly understood by performing the above synthesis with 5 mol % of 1-butyl-3-methylimidazolium chlorometallates $[BMIm]_n[X]$ (**7a-7c**) (m=2 and 1; [X] = $[ZnCl_4]^{2-}$,$[FeCl_4]^-$,$[NiCl_4]^{2-}$) at room temperature stirring to afford 65-75 % yields of **6a** (table-5, entry 2)

[22-24]. Also the activity of 1, 3-disulfoimidazolium chloride and carboxylate ILs without metal center [Dsim][X](**8a-8c**) ([X]= Cl^-, CF_3COO^-, CCl_3COO^-) were observed for comparison with the disulfonic chlorometallates **2a**, **2b** and **2c** (table-5, entry 3) [25]. This table clearly demonstrated the higher catalytic activity of the three chlorometallates under the optimized condition for the preparation of model compound **6a (**table-5, entry 4**).**

3.5. Reusability test of catalysts:

To determine the reusability of the three catalysts we performed the model reaction of optimization study in 5 mmol scale in ethanol. The catalysts can be recovered as solid residue after filtration of the product solution in CH_2Cl_2 which was suitable for further use. **Fig. 9** depicts the clear picture of reusability of each catalyst for the preparation of **6a** in absolute ethanol for three runs. An appreciable catalytic activity is noted for all the three catalysts. The spent catalysts were again characterized by ICP-OES analysis (table-1) which presented the similar amount of metal content to describe the catalytic activity up to three runs.

4. Conclusion

In our work, we have developed a new series of $–SO_3H$ functionalized imidazolium chlorometallate ionic salt systems: [Dsim][$FeCl_4$] and $[Dsim]_2[X]$, where X= $ZnCl_4^{2-}$ and $NiCl_4^{2-}$. The systems were fully characterized by various analytical techniques such as NMR, FT-IR, Raman, UV-visible, PXRD, SEM-EDX, ICP-OES, TGA, CHN etc. Anions speciations of the solid ionic systems were established via electronic spectroscopy and Raman analysis. All the three systems were demonstrated as semiconducting material with required band gap energies. Considering the enhanced acidity and the thermal stability of these systems, they were satisfactorily employed as catalysts for the synthesis of β- amino carbonyl compounds. It was also relevant that we have recovered the catalysts and utilized them up to three consecutive cycles. In these imidazolium chlorometallate systems, the presence of functionalized imidazolium cation played a major role in determining the behavior of these solids in conjunction to the chlorometallate anions. Both the cation and the anionic part of the systems open the possibility of an easy and considerable tunability of these materials for future prospects.

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Figure Captions

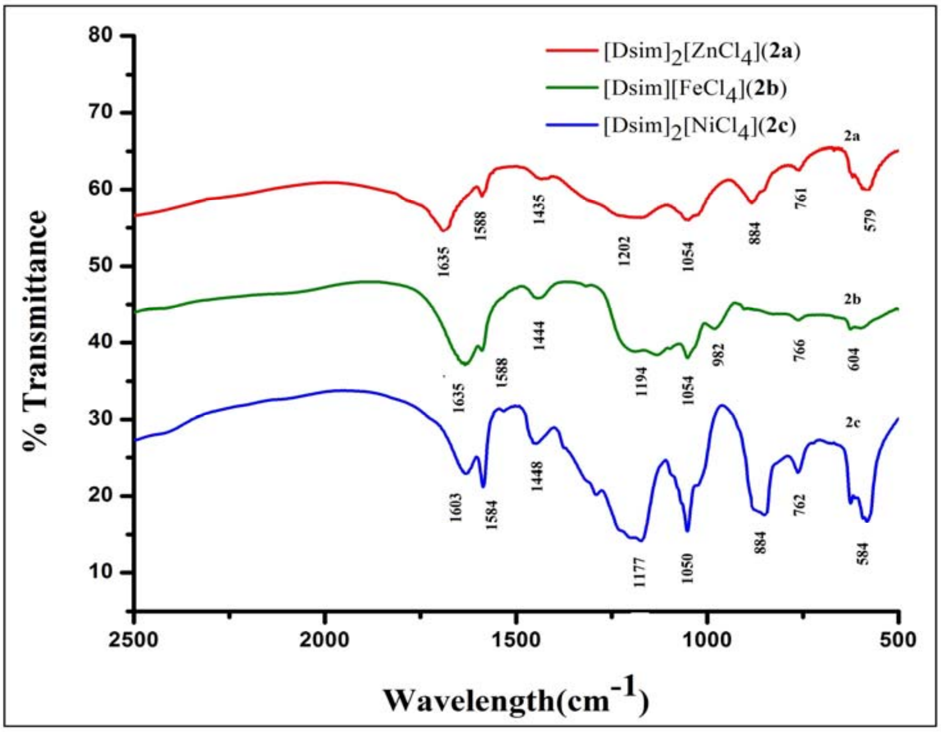
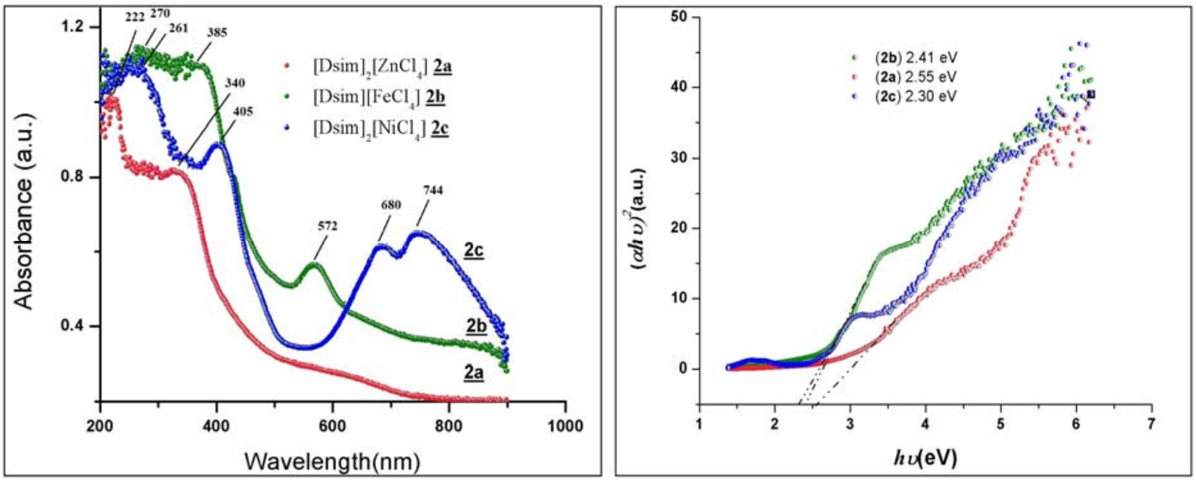


Fig. 1: FT-IR spectra of 1, 3- disulfoimidazolium chlorometallates



(a) **(b)**

Fig. 2: (a) UV-visible absorbance spectra of **2a**, **2b** and **2c** and **(b)** TAUC plot for the determination of band gap of prepared chlorometallates

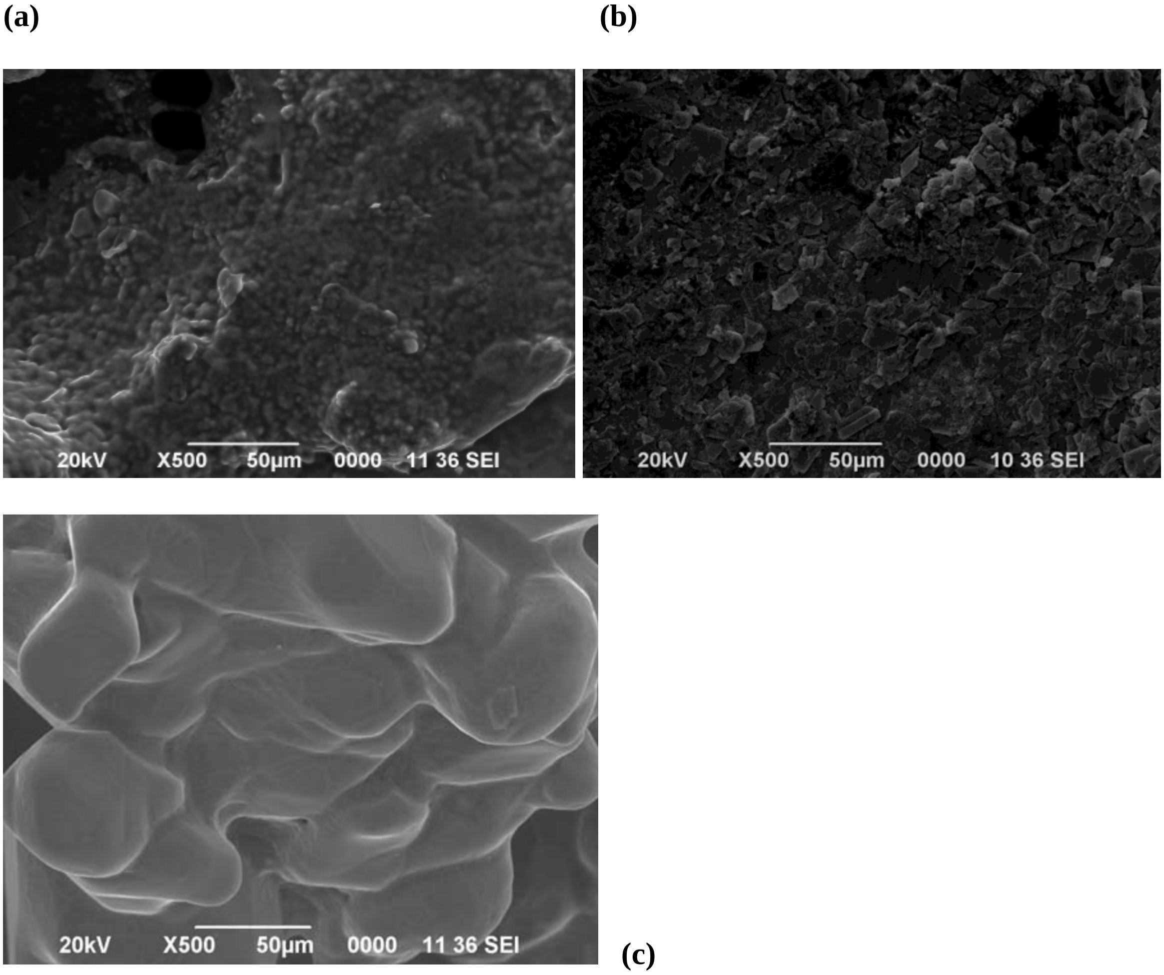
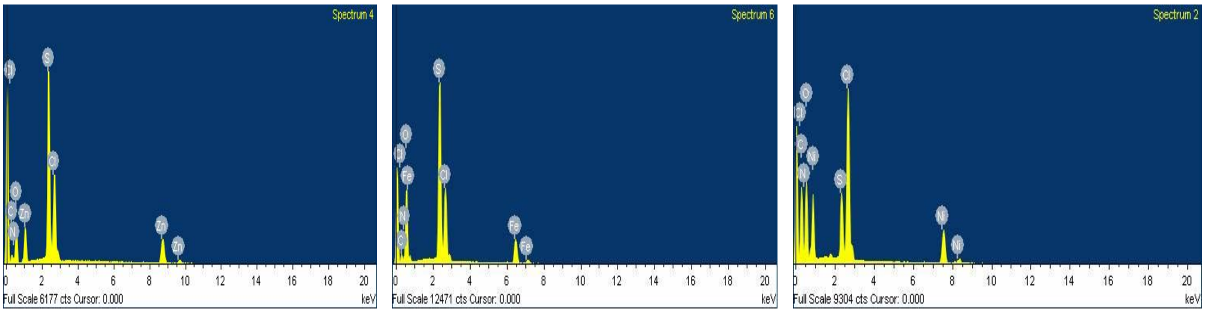


Fig. 3: SEM images of **(a)** $[Dsim]_2[ZnCl_4]$, **(b)** $[Dsim][FeCl_4]$ and **(c)** $[Dsim]_2[NiCl_4]$



(a) **(b)** **(c)**

Fig. 4 EDX images of **(a)** $[Dsim]_2[ZnCl_4]$, **(b)** $[Dsim][FeCl_4]$ and **(c)** $[Dsim]_2[NiCl_4]$

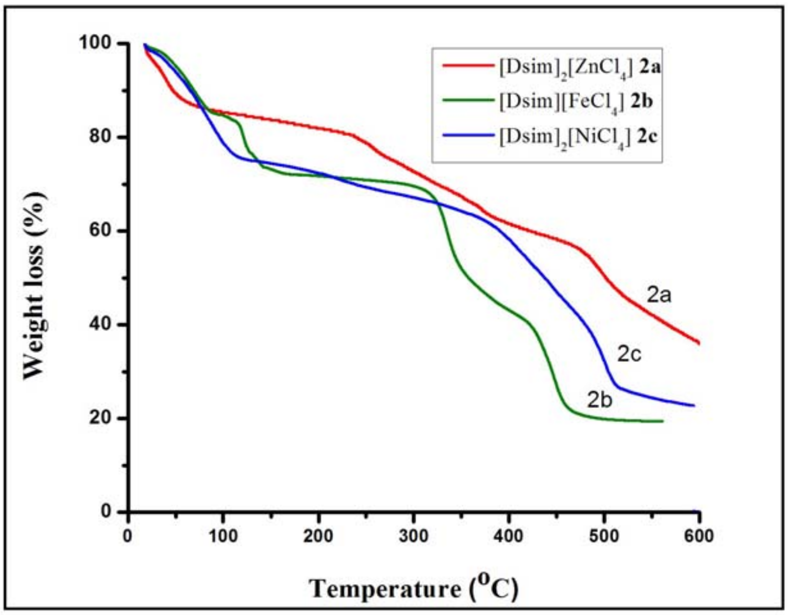


Fig. 5: TGA curves of the three ionic solid acids

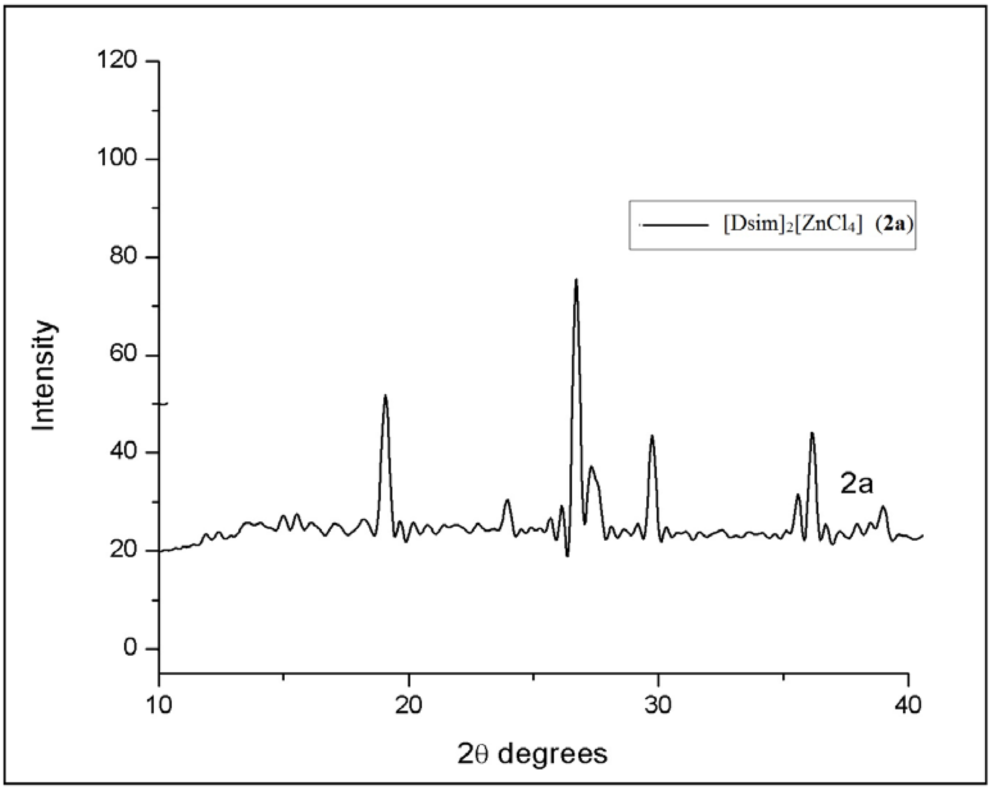


Fig. 6: Powder XRD pattern of **2a**

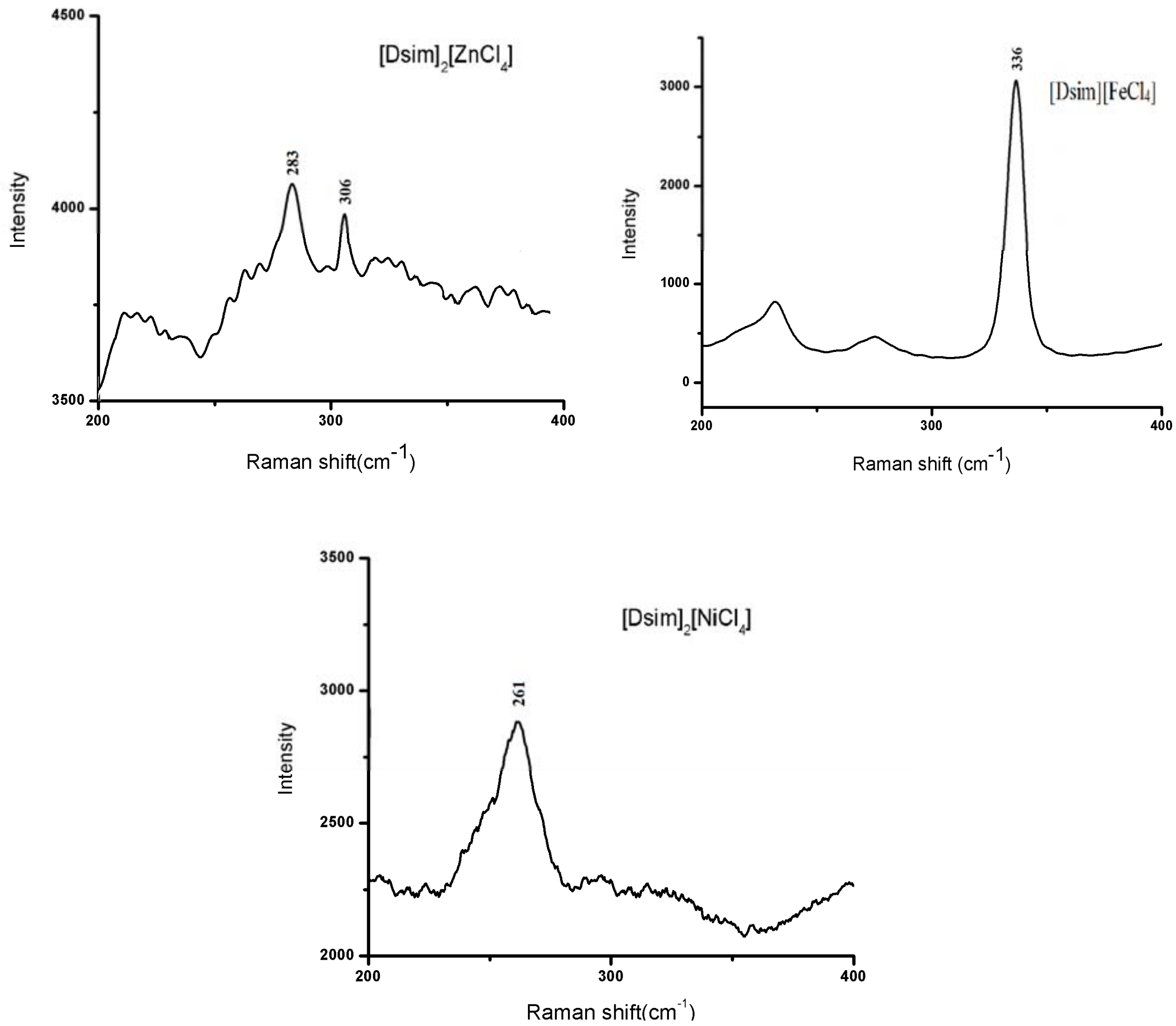


Fig. 7 : Raman spectra of **2a** , **2b** and **2c**

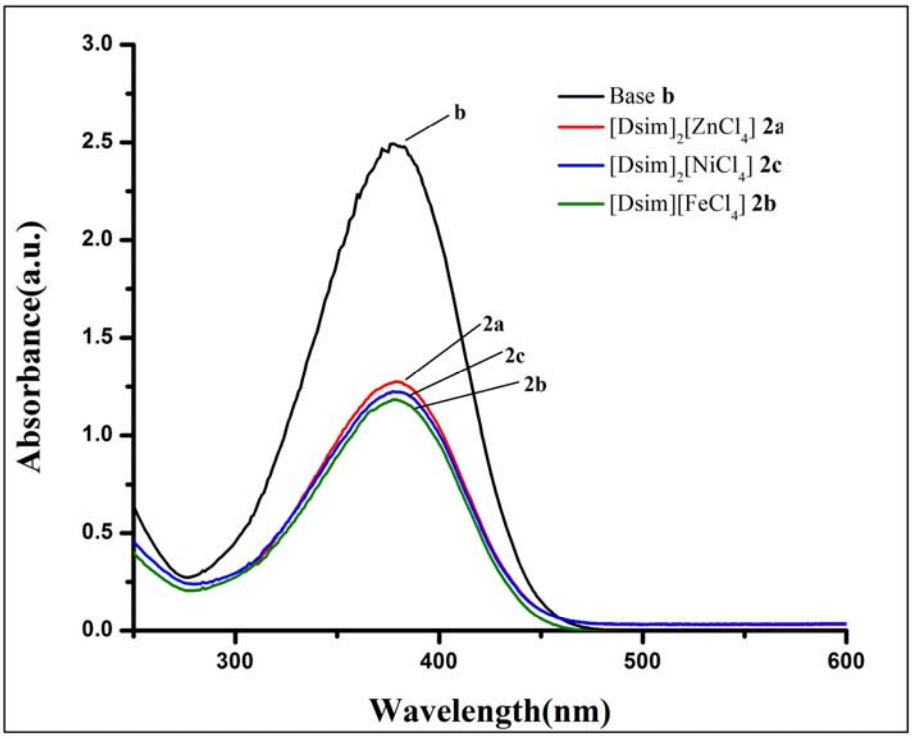


Fig. 8: Absorption spectra of *p*-nitroaniline in the presence of ionic salts in ethanol

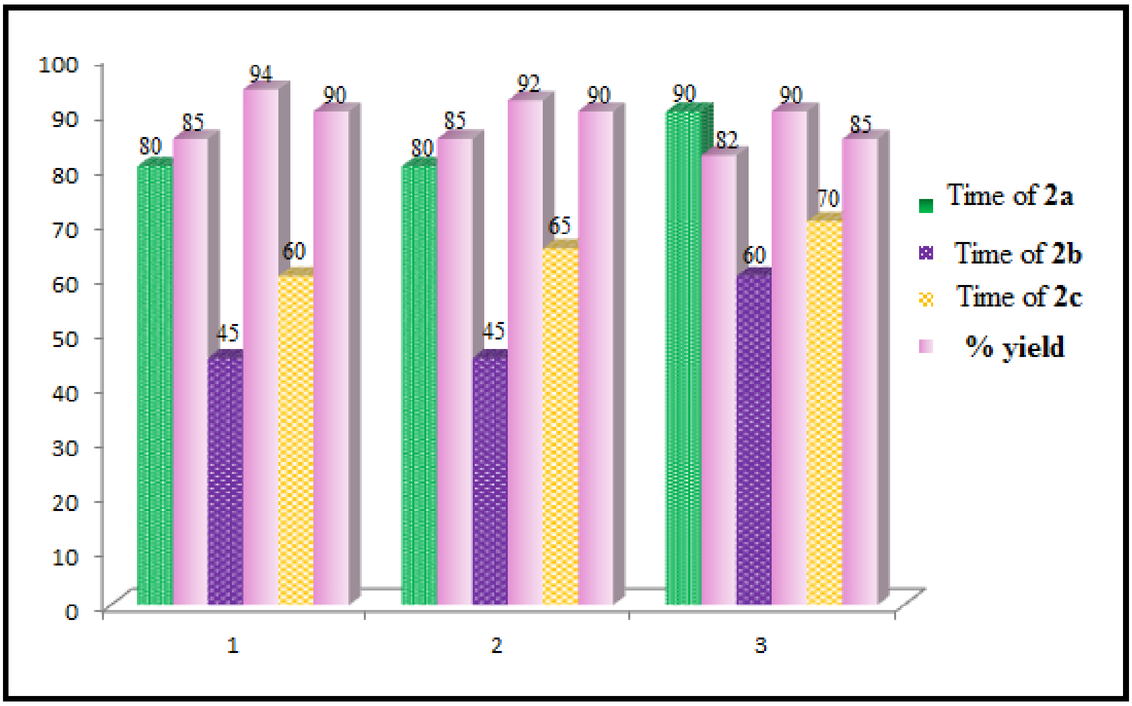
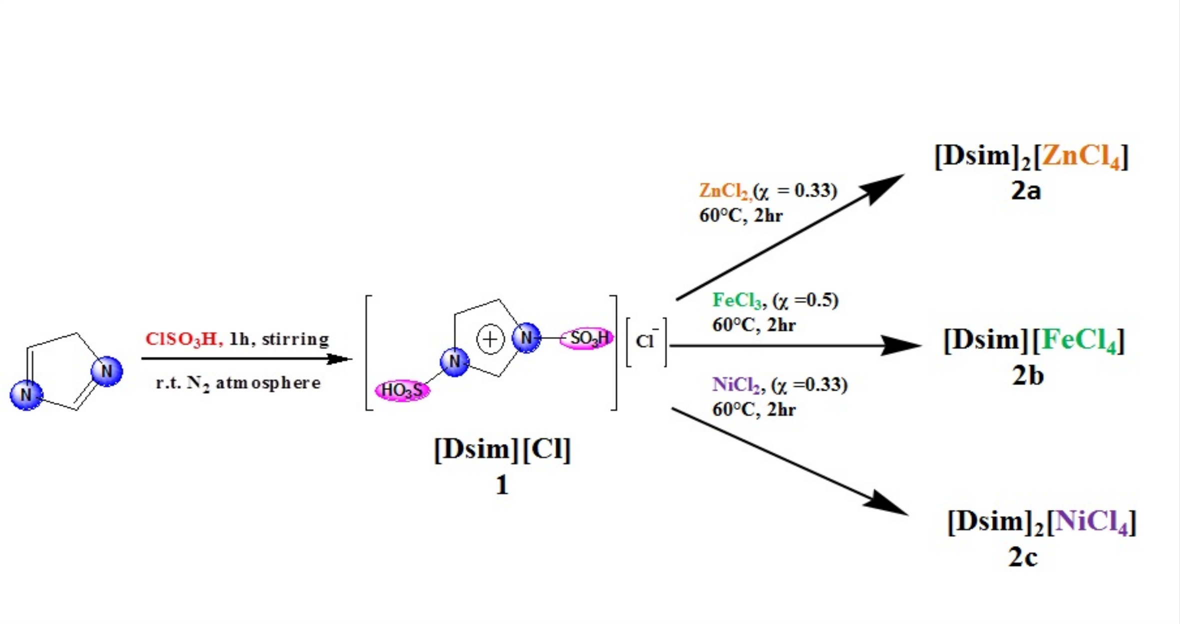
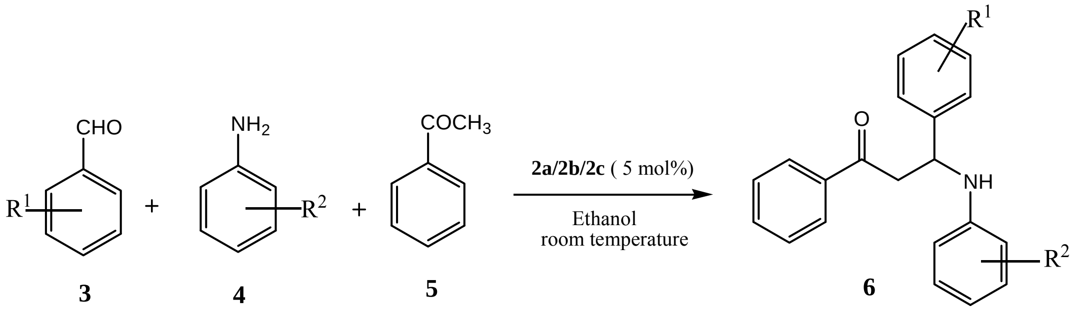


Fig. 9: Bar diagram showing the reusability of three catalysts

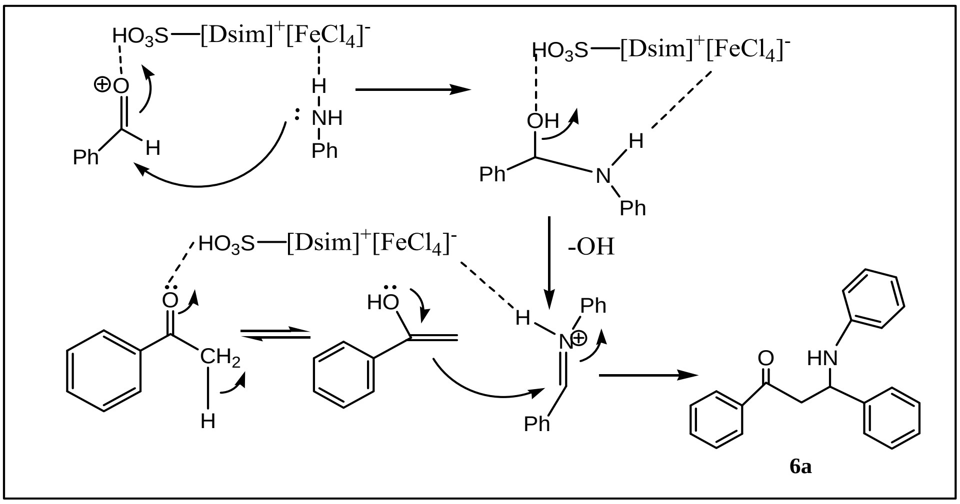


Scheme 1: Synthesis of 1, 3-disulfoimidazolium chlorometallate ionic liquids [Dsim]$_2$[ZnCl$_4$] **2a**, [Dsim][FeCl$_4$] **2b** and [Dsim]$_2$[NiCl$_4$] **2c**



Where, R^1 = H, 4-Cl, 4-Me, 3-Br and R^2 = H, 4-Cl, 4-NO_2

Scheme 2: Synthesis of β-amino carbonyl compounds



Scheme-3: Plausible mechanism of -SO_3H bearing IL catalyzed Mannich-type reaction

Tables

Table 1: ICP analyses of the three disulfoimidazolium chlrometallates

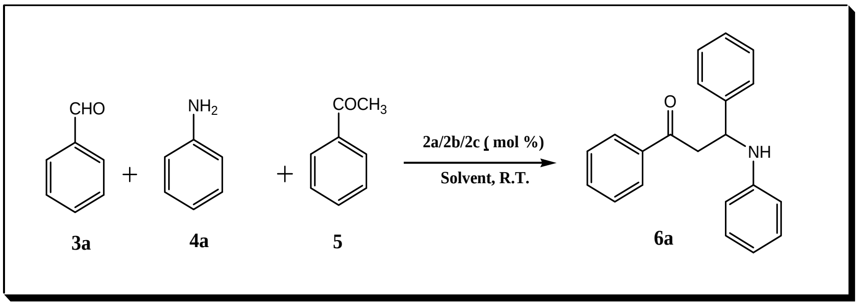
Entry	Catalysts	Metal analyzed	Metal amount (mg/L)		
			calculated	Experimental	
				Fresh	Used [a]
1	$[Dsim]_2[ZnCl_4]$	Zn	2.92	2.88	2.86
2	$[Dsim][FeCl_4]$	Fe	3.92	3.95	3.88
3	$[Dsim]_2[NiCl_4]$	Ni	2.65	2. 55	2.52

[a] Estimated after 3rd cycles of the catalytic Mannich-type reaction

Table 2: Hammett functions of ionic salts (**2a-c)**

Entry	IL	Amax	[I]%	$[IH^+]\%$	H^o
1	-	2.493	100	0	-
2	$[Dsim]_2[ZnCl_4]$	1.276	51.2	48.8	1.0107
3	$[Dsim][FeCl_4]$	1.183	47.4	52.6	0.9447
4	$[Dsim]_2[NiCl_4]$	1.225	49.1	50.9	0.9741

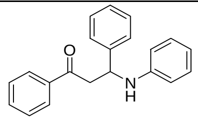
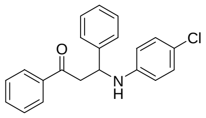
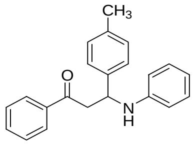
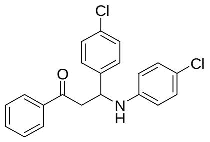
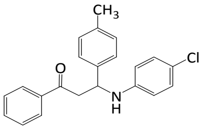
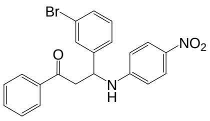
Table 3: Optimization of reaction condition for the preparation of β-amino ketone derivative at room temperature



Entry	Catalyst	Amount (mol %)	Time (min)	Yield %[a] **6a**
1	$[Dsim]_2[ZnCl_4]$**2a**	5/10/20[a]	80/60/45	85/91/90
2	$[Dsim][FeCl_4]$ **2b**	5/10/20[a]	45/30/15	94/95/97
3	$[Dsim]_2[NiCl_4]$**2c**	5/10/20[a]	60/45/30	90/91/95
4	**2a/2b/2c**	5[b]	1.5 h / 50 /60	83/92/87
5	**2a/2b/2c**	5[c]	1.5h /50 / 60	84/90/85

[a] Using 1 mmol of acetophenone, 1 mmol of benzaldehyde and 1mmol of aniline in ethanol ; [b] Reaction was performed in CH_2Cl_2 ; [c] Reaction was conducted in EtOAc

Table 4: Synthesis of β- amino ketone derivatives using **2a**, **2b** and **2c** catalysts

Entry	R^1	R^2	Product	Time ^{a} min **2a/2b/2c**	Yield^b % **6(a-f)**	Mp.(°C) found	Mp. (°C) reported
1	H	H	 **6a**	80/45/60	85/94/90	159-161.8	165-167 [47]
2	H	4-Cl	 **6b**	70/45/55	88/95/92	161.1-165.7	170-171 [48]
3	4-CH_3	H	 **6c**	1.5 h / 1 h /1.5	82/85/85	127.2-132.5	134-135 [48]
4	4-Cl	4-Cl	 **6d**	70/30/50	90/96/91	121.4-122.8	114-119 [48]
5	4-CH_3	4-Cl	 **6e**	80/50/60	84/95/90	159.2-160.9	163-165 [47]
6	3-Br	4-NO_2	 **6f**	1.5 h /50 /1 h	82/88/85	130.5-134.3	130-132 [47]

^{a} Method using 5 mol% of **2a** /**2b/2c** as catalyst in ethanol (5 mL) ; ^{b} Isolated yields

Table 5: Comparison of catalytic efficiency of **2a-2c** with other ionic liquid systems

Entry	Catalyst	Amount (mol %)	Time (min)	Yield % [a] **6a**
1	[Msim][$ZnCl_3$]/ [Msim][$FeCl_4$]	5	2 h/80	80/86
2	**7a**/**7b**/**7c**	5[b]	4h/3h/3.5h	65/75/73
3	**8a**/**8b**/**8c**	5 [c]	2.5 h/80/2h	82/87/85
4	**2a**/**2b**/**2c**	5	80/45/60	85/94/90

[a] Using 1 mmol of acetophenone, 1 mmol of benzaldehyde and 1mmol of aniline in ethanol ; [b] The three catalysts (**7a**-**7c**) were prepared using the standard literature procedure [22-24]; [c] Other three 1,3-disulfoimidazolium catalysts (**8a-8c)** were synthesized by the reported procedure [25].