Iranian Journal of Catalysis Spotlight 9(3), 2019, 269-272

IRANIAN JOURNAL OF CATALYSIS

[Dsim]X: As multi-purpose compounds

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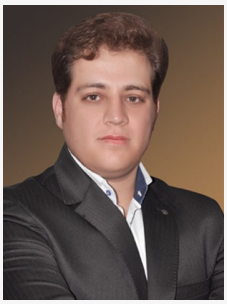
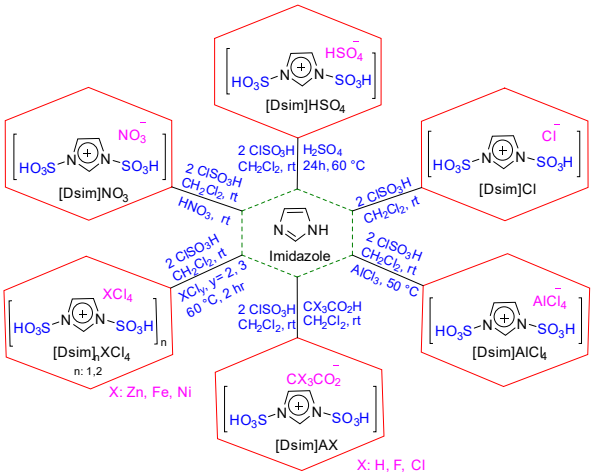


This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

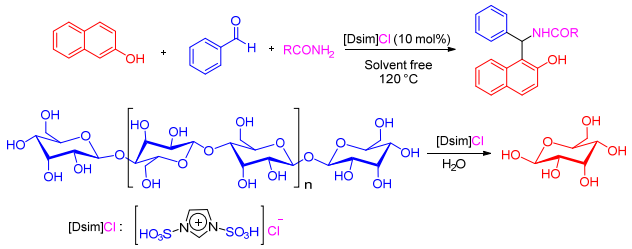
Ionic liquids (ILs), due to useful properties such as low volatility, non-flammability, high thermal stability, negligible vapor pressure, and ability to dissolve a wide range of materials, have been used as solvents, catalysts and reagents in organic functional groups transformations [1-5]. Advantages of using of ionic liquids in organic functional groups transformations are high reaction yields, short reaction times, low catalyst loading, inexpensive catalysts, regioselectivity and safety of reaction conditions. Zolfigol group have introduced SAFIS (sulfonic acid functionalized imidazolium salts) which reacted with imidazole and chlorosulfonic acid at room temperature [6]. [Dsim]X with anion such as chloride, nitrate, aluminate, hydrogen sulfate, carboxylate and chlorometallate (Scheme 1) as an efficient catalyst and reagent were used in the synthesis of 1-amidoalkyl-2-naphthols, cellulose hydrolysis to glucose [6] benzimidazoles [7], 4,4-(arylmethylene)- *bis*(3-methyl-1-phenyl- 1*H*pyrazol-5-ol)s [8], hexahydroquinolines, 1-amidoalkyl-2-naphthols, pyrimido[4,5-b]-quinoline, coumarins, various xanthene, quinolone derivatives, 1,2,4,5-tetrasubstituted imidazoles, α,α'-bis(arylidene)cyclo alkanones [9], *N*-boc derivatives, chemoselective trimethylsilylation of hydroxyl groups [10], 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*] pyrazoles [11], *N*-sulfonyl imines [12], nitroarenes, nitroolefins [13], regioselective sulfonation of aromatic compounds [14], 1-amidoalkyl-2-naphthols, 14*H*-dibenzo[*a*,*j*]xanthene, 1,8-dioxo-decahydroacridine derivatives [15] and *β*-amino carbonyl compounds [16] respectively.



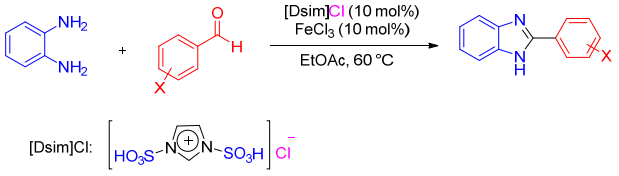
Scheme 1. The preparation of various form of [Dsim]X.

Abstracts

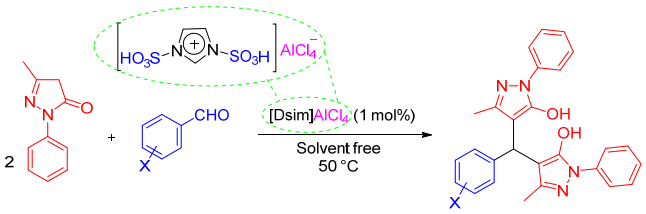
(A) In 2011, Zolfigol *et al.* have prepared [Dsim]Cl, *via* the reaction of imidazole and chlorosulfonic acid in CH_2Cl_2 as solvent under nitrogen atmosphere, as a novel and efficient catalyst. [Dsim]Cl (10 mol%) was used as catalyst for the convenient synthesis of 1-amidoalkyl-2-naphthols by the reaction of β-naphthol, aldehyde and amide derivatives at 120 °C under solvent-free condition. [Dsim]Cl has been also used as catalyst for hydrolysis of cellulose to glucose in water as solvent [6].



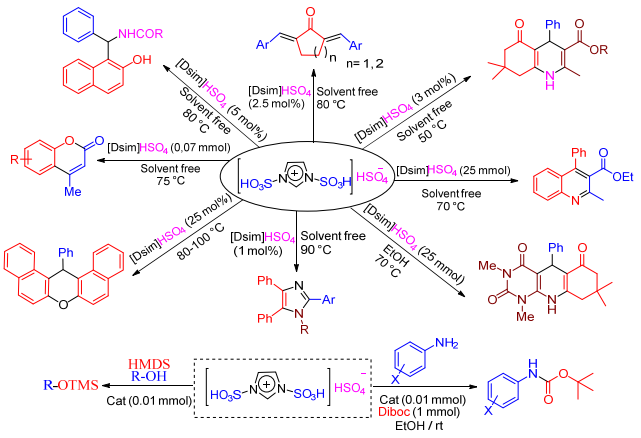
(B) The catalytic activity of [Dsim]Cl/$FeCl_3$ has been used as a source of anomeric based oxidation (ABO) for the synthesis of various benzimidazoles in EtOAc as solvent at 60 °C. The products were prepared in excellent yields [7].



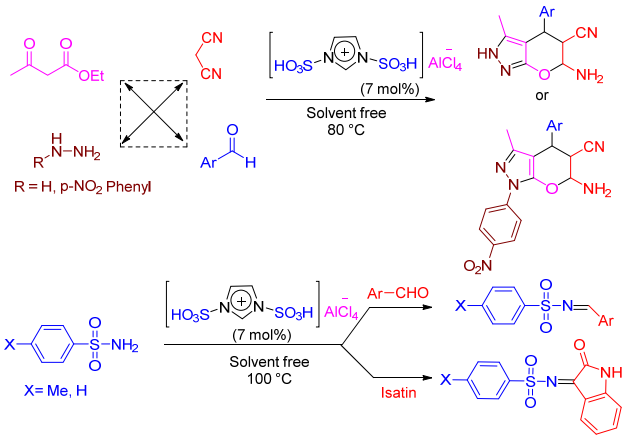
(C) 1,3-Disulfonic acid imidazolium tetrachloro aluminate [Dsim]$AlCl_4$, was prepared by a simple reaction of [Dsim]Cl and $AlCl_3$, as a new, heterogeneous and reusable catalyst for the synthesis of 4,4-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s by the condensation of 1-phenyl-3-methylpyrazol-5-one with a good range of aromatic aldehydes under solvent-free condition [8].



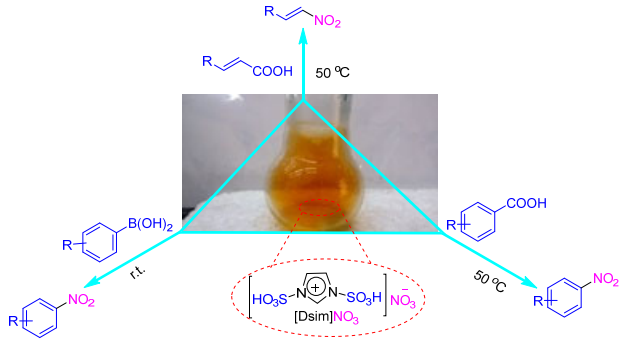
(D) Novel Brønsted acidic ionic liquid 1,3-disulfonic acid imidazolium hydrogen sulfate [Dsim]HSO_4 was prepared with anion exchange of [Dsim]Cl with H_2SO_4. [Dsim]HSO_4 as a highly efficient, homogeneous and reusable catalyst was applied for the preparation of hexahydroquinolines, 1-amidoalkyl-2-naphthols, pyrimido[4,5-b]-quinoline, coumarins, xanthenes, 1,2,4,5-tetrasubstituted imidazoles, α,α'-bis(arylidene)cyclo alkanones and quinolone derivatives [9]. Furthermore, [Dsim]HSO_4 was also used as a catalyst for the protection of amines and chemoselective trimethylsilylation of hydroxyl groups. A simple, highly efficient method, clean reaction, very short reaction times, high yields, easy preparation and high TOF (turn over frequency) values of the catalyst in comparison with other those reported catalysts are the major advantages of described works [10].



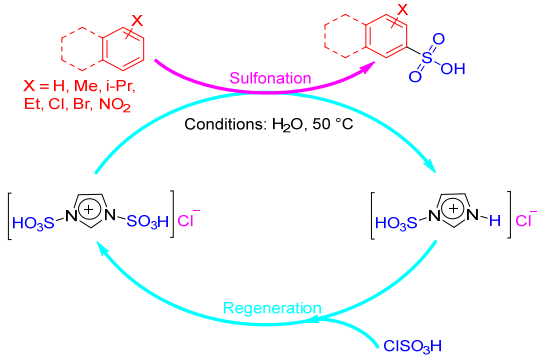
(E) Moosavi-Zare *et al*. have reported 1,3-disulfonic acid imidazolium chloroaluminate [Dsim]$AlCl_4$ as a green, simple and efficient catalyst for the synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazoles by the one-pot multi-component condensation of aryl aldehydes with ethyl acetoacetate, malononitrile and hydrazine hydrate at 80 °C under solvent-free conditions [11]. Also, [Dsim]$AlCl_4$ was applied as catalyst for the preparation of *N*-sulfonyl imines *via* the condensation of sulfonamides with various aldehydes as well as isatin under solvent-free conditions [12].



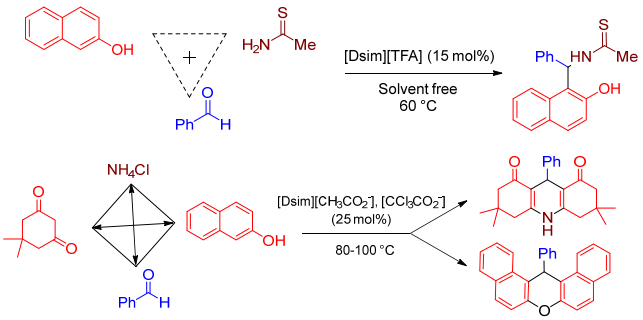
(F) In 2018, we have synthesized 1,3-disulfonic acid imidazolium nitrate [Dsim]NO_3, by a simple reaction of [Dsim]Cl and pure nitric acid as a new ionic liquid. It has been used as an efficient nitrating agent for the *ipso*-nitration of various arylboronic acids, *α,β*-unsaturated acids and benzoic acids, *via in-situ* generation of NO_2 to give their corresponding nitroarenes and nitroolefins without using any co-catalysts and solvents under mild conditions [13].



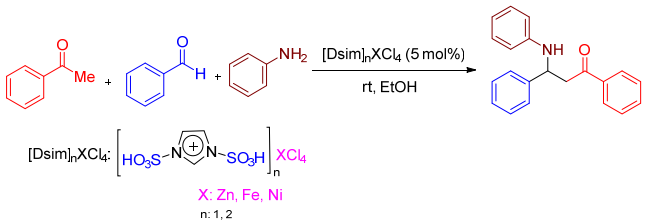
(G) In another investigation, regioselective sulfonation of aromatic compounds over 1,3-disulfonic acid imidazolium chloride was introduced. [Dsim]Cl, has been also used as a novel sulfonating agent for the sulfonation of various aromatic compounds by *in-situ* generation of sulfuric acid at 50 °C under aqueous and mild conditions. Sulfonation of aromatic compounds was successfully carried out with excellent yields and very short reaction times [14].



(H) In another exploration, 1,3-disulfonic acid imidazolium carboxylate ionic liquids [DSIM][X] (where X = $[CH_3CO_2^-]$, $[CCl_3CO_2^-]$, $[CF_3CO_2^-]$) have been introduced as a dual-functional catalyst, for the synthesis of 1-amidoalkyl-2-naphthols, 14*H*-dibenzo[*a,j*]xanthenes and 1,8-dioxo-decahydro acridines under solvent-free conditions with high yields and very short reaction times [15].



(I) In another exploration, 1,3-disulfoimidazolium transition metal chloride systems: $[Dsim]_2[ZnCl_4]$, $[Dsim][FeCl_4]$ and $[Dsim]_2[NiCl_4]$ were prepared with anion exchange of [Dsim]Cl with $ZnCl_2$, $FeCl_3$, and $NiCl_2$. $[Dsim]_nXCl_4$ as Brönsted-Lewis acidic catalyst, for the one pot three component Mannich-type syntheses of β-amino carbonyl compounds at room temperature in EtOH as solvent with high yields and very short reaction times [16].



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