

[Msim]X: As a versatile catalyst and reagent

Compiled by Mahmoud Zarei

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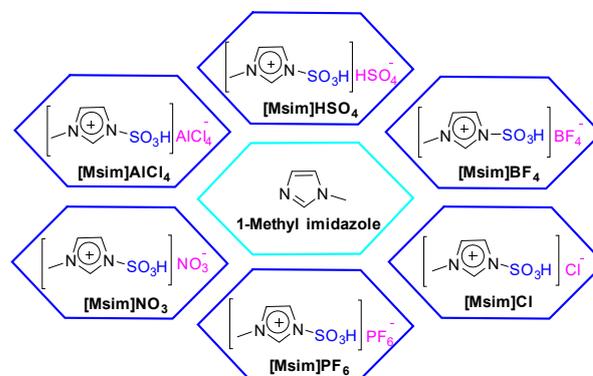


This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

Nowadays, Ionic Liquids (ILs) have been used as solvent, catalyst and reagent for various purposes [1]. Brønsted acidic ionic liquids have been designed for replacing of solid acids and traditional mineral liquid acids like sulfuric acid and hydrochloric acid in chemical procedures. Anion exchange is a subjective way to design and build ionic liquids with other anions that cannot be directly prepared. Over the years, much attention has been paid to the study of changes in the properties of ionic liquids by the exchange of their counter ions, which change physical and chemical properties such as viscosity, melting point, vapor pressure of fluids, viscosity, solubility, polarity, fluorescence properties and so on [2,3]. Zolfigol and coworkers have introduced 3-methyl-1-sulfonic acid imidazolium chloride ([Msim]Cl) by the reaction of 1-methyl imidazole with chlorosulfonic acid at room temperature [4]. Anion exchange of [Msim]Cl have done *via* the reaction of [Msim]Cl with AlCl_3 , HNO_3 , FeCl_3 ,

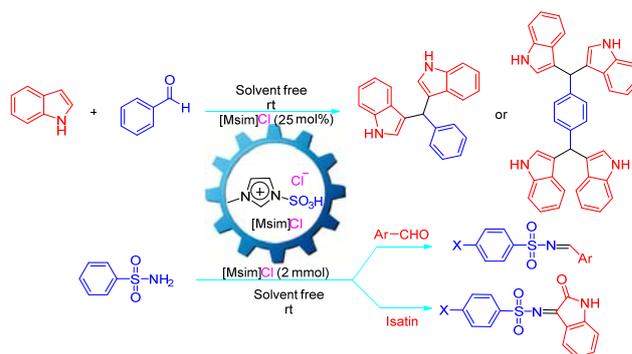
NaBF_4 or KPF_6 to produce [Msim]X (Scheme 1). The category of [Msim]X is considered to be as efficient catalysts and/or reagent in the synthesis of *bis*(Indolyl)methanes, 1-amidoalkyl-2-naphthols, β -acetamido ketones, xanthene derivatives, benzylation of aromatic compounds, TEX, protection of hydroxyl groups and nitration aromatic compounds etc.



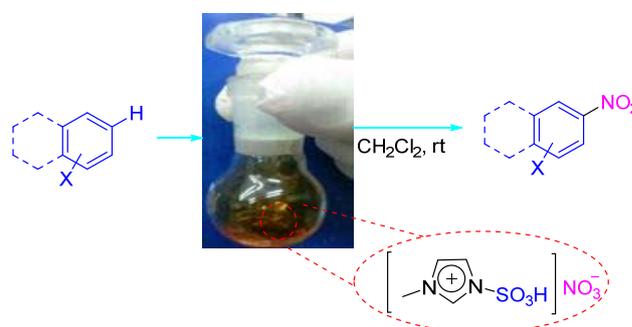
Scheme 1. The structures of [Msim]X.

Abstracts

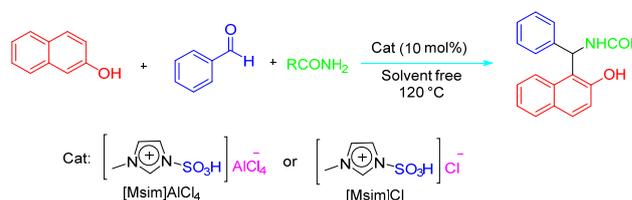
(A) In 2010, Zolfigol *et al.* introduced [Msim]Cl as a novel and efficient ionic liquid by the condensation of 1-methyl imidazole and chlorosulfonic acid in CH_2Cl_2 as solvent at room temperature. The catalyst was used in a convenient method for the synthesis of *bis(indolyl)methanes* by the reaction of indole and aldehyde in the presence of described ionic liquid [Msim]Cl (25 mol%) at room temperature. The mentioned ionic liquid was also applied for the preparation of *N*-sulfonyl imines via the condensation of sulfonamides with aldehydes as well as isatin under solvent-free conditions [4].



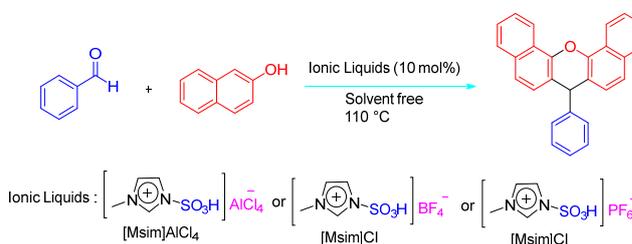
(B) Zolfigol *et al.* reported 3-methyl-1-sulfonic acid imidazolium nitrate [Msim] NO_3 by the reaction of the 3-methyl-1-sulfonic acid imidazolium chloride and nitric acid. The described ionic liquid was tested for the nitration of aromatic compounds *via in situ* generation of NO_2 as a radical without any co-catalysts to produce a wide range of nitro aromatic compounds in high yields and very short reaction times. Direct nitration of aniline at room temperature is another major advantage of abovementioned reported method [5].



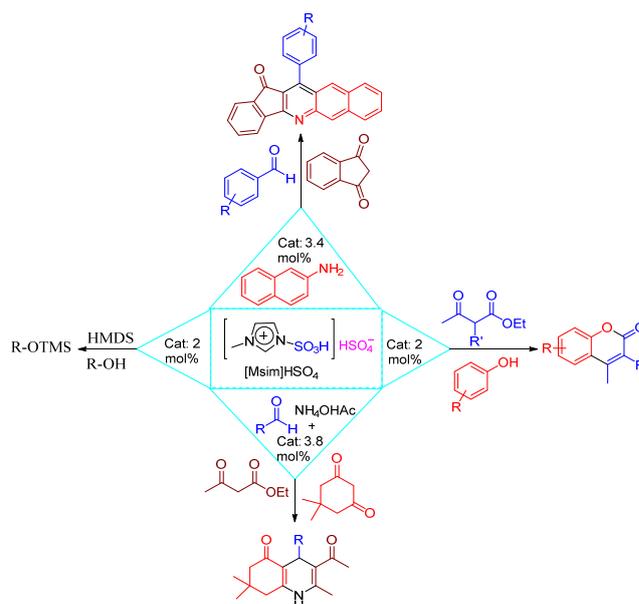
(C) The catalytic activities of the sulfonic acid functionalized imidazolium salts such as [Msim]Cl and [Msim] AlCl_4 have studied as novel catalysts for the synthesis of 1-amidoalkyl-2-naphthols by the one-pot multi-component condensation of β -naphthol, aldehyde and amide derivatives at 120 °C. The products were prepared with excellent yields and in very short reaction times [6].



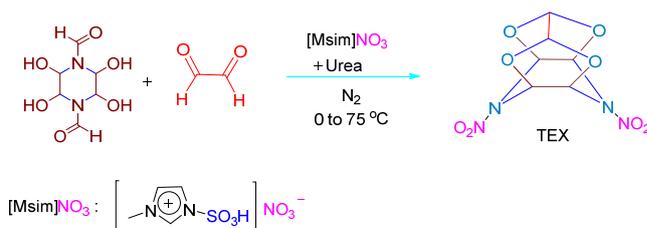
(D) In 2012, Zolfigol *et al.* introduced a novel category of ionic liquids namely sulfonic acid functionalized imidazolium salts (SAFIS) such as [Msim] AlCl_4 , [Msim] BF_4 and [Msim] PF_6 as highly efficient and reusable catalysts for the synthesis of (i) 14-aryl-14*H*-dibenzo[*a,j*]xanthenes by the reaction of β -naphthol and arylaldehydes, (ii) the preparation of tetrahydrobenzo[*a*]xanthene-11-ones by the reaction of β -naphthol, arylaldehydes and dimedone, and (iii) the synthesis of 1,8-dioxo-octahydroxanthenes by the condensation of dimedone and aromatic aldehydes under solvent-free conditions in excellent yields and in very short reaction times [7].



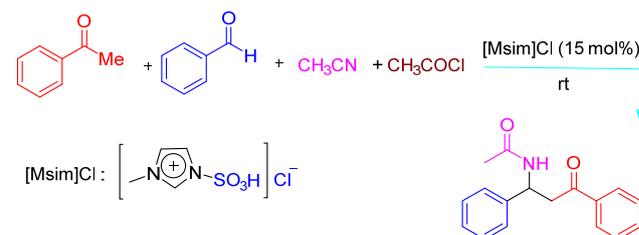
(E) 3-Methyl-1-sulfonic acid imidazolium hydrogen sulfate {[Msim]HSO₄} was produced as a new, recyclable and eco-benign catalyst for the chemoselective trimethylsilylation of hydroxyl groups under solvent-free conditions to afford the corresponding protected alcohols with trimethylsilanes in excellent yields and in very short reaction times. Furthermore, [Msim]HSO₄ was also used for the synthesis of polyhydroquinolines, coumarins and 13-aryl-12*H*-benzo[*f*]indeno[1,2-*b*]quinoline-12-ones. A simple, efficient, clean reaction, short reaction times, high yields, easy preparation and high TOF (turn over frequency) values of the catalyst in comparison with other reported catalysts are some advantages of this work [8].



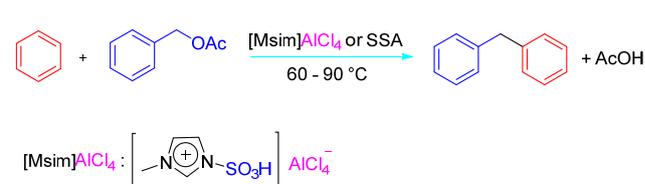
(F) ([Msim]NO₃) as an efficient nitrating agent was also introduced for the synthesis of TEX *via* nitration of DFTHP (1,4-diformyl-2,3,5,6-tetrahydropiperazine) with the highest efficiency, short reaction time and under mild conditions. TEX (4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane or 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo [5. 5. 0. 0^{5,9}. 0^{3,11}] dodecane) is more demanding because they are used as energetic materials in commercial or military affairs [9].



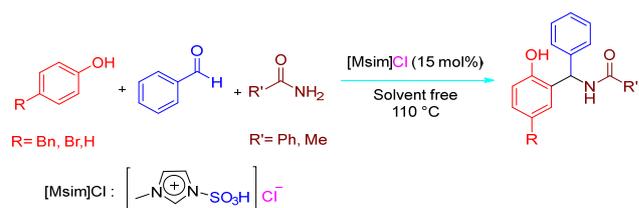
(G) The catalytic activity of the [Msim]Cl is utilized as a highly efficient, inexpensive, mild and green catalyst for the synthesis of β -acetamido ketones by the one-pot multi-component coupling between acetophenones, arylaldehydes, acetonitrile and acetyl chloride at room temperature. Under these conditions, the compounds are produced in high to excellent yields and in relatively short reaction times. In addition, this method is superior to the previously reported methods, for the synthesis of β -acetamido ketones and is applicable for the synthesis of tris(β -acetamido ketone) [10].



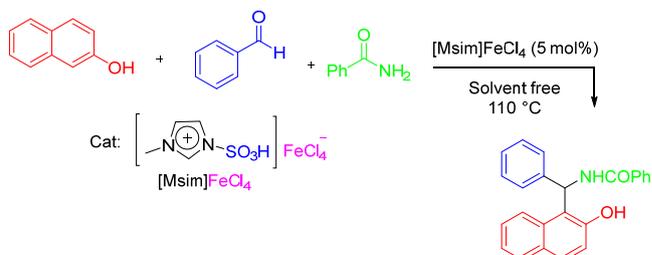
(H) [Msim]AlCl₄ as a highly efficient and green catalyst was successfully used for the benzylation of aromatic compounds by the reaction of benzene derivatives with benzyl acetate under solvent-free condition. The resulted products are an interesting group of bioactive compounds, which they were prepared in excellent yields and very short reaction times [11].



(I) In another exploration, 1-amidoalkyl phenols is introduced as a category compounds by three-compound condensation of various phenols, aromatic aldehyde and amide in the presence of sulfonic acid functionalized by imidazolium salt [Msim]Cl (15 mol%) under solvent free conditions [12]



(J) Moosavi-Zare *et al.* have introduced 3-methyl-1-sulfonic acid imidazolium tetrachloroferrate {[Msim]FeCl₄} as an efficient catalyst, for the tandem reaction of β -naphthol with aromatic aldehydes and benzamide at 110 °C under solvent free conditions for preparation of 1-amidoalkyl-2-naphthols in high yields and very short reaction times [13].



References

- [1] (a) P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2008. (b) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* 39 (2000) 3772-3789. (c) G. Cheng, X. Duan, X. Qi, C. Lu, *Catal. Commun.* 10 (2008) 201-204. (d) J.P. Hallett, T. Welton, *Chem. Rev.* 111 (2011) 3508-3576. (e) J. Pavlinac, M. Zupan, K.K. Laali, S. Stavber, *Tetrahedron* 65 (2009) 5625-5662. (f) A.R. Moosavi-Zare, M.A. Zolfigol, M. Zarei, A. Zare, V. Khakyzadeh, A. Hasaninejad, *Appl. Catal. A* 467 (2013) 61-68. (g) A.R. Moosavi-Zare, M.A. Zolfigol, M. Zarei, A. Zare, V. Khakyzadeh, *J. Mol. Liq.* 186 (2013) 63-69. (h) M.A. Zolfigol, A.R. Moosavi-Zare, M. Zarei, C. R. Chim. 17 (2014) 1264-1267. (i) A.R. Moosavi-Zare, M.A. Zolfigol, M. Zarei, E. Noroozizadeh, M.H. Beyzavi, *RSC Adv.* 6 (2016) 89572-89577.
- [2] M. Marszalek, Z. Fei, D.R. Zhu, R. Scopelliti, P.J. Dyson, S.M. Zakeeruddin, M. Gratzel, *Inorg. Chem.* 50 (2011) 11561-11567.
- [3] A.R. Moosavi-Zare, M.A. Zolfigol, M. Zarei, A. Zare, V. Khakyzadeh, A. Hasaninejad, *Appl. Catal. A* 467 (2013) 61-68.
- [4] (a) M.A. Zolfigol, A. Khazaei, A.R. Moosavi-Zare, A. Zare, *Org. Prep. Proced. Int.* 42 (2010) 95-102. (b) M.A. Zolfigol, A. Khazaei, A.R. Moosavi-Zare, A. Zare, *J. Iran. Chem. Soc.* 7 (2010) 646-651.
- [5] (a) M.A. Zolfigol, A. Khazaei, A.R. Moosavi-Zare, A. Zare, H. G. Kruger, Z. Asgari, V. Khakyzadeh, M. Kazem-Rostami., *J. Org. Chem.* 77 (2012) 3640-3645. (b) A. Khazaei, M.A. Zol_gol, A.R. Moosavi-Zare, A. Zare, *Sci. Iran.* 17 (2010) 31-36.
- [6] M.A. Zolfigol, A. Khazaei, A.R. Moosavi-Zare, A. Zare, V. Khakyzadeh, *Appl. Catal. A* 400 (2011) 70-81.
- [7] M.A. Zolfigol, V. Khakyzadeh, A.R. Moosavi-Zare, A. Zare, S.B. Azimi, Z. Asgari, A. Hasaninejad, *C.R. Chim.* 15 (2012) 719-736.
- [8] (a) A. Zare, F. Abi, A.R. Moosavi-Zare, M.H. Beyzavi, M.A. Zolfigol., *J. Mol. Liq.* 178 (2013) 113-121. (b) N. Ghaffari Khaligh, *Chin. J. Catal.* 35 (2014) 1036-1042. (c) N. Ghaffari Khaligh, *J. Mol. Catal. A: Chem.* 349 (2011) 63-70. (d) N. Ghaffari Khaligh, *Catal. Sci. Technol.*, 2012, 2, 1633-1636. (e) N. Ghaffari Khaligh, *Res Chem Intermed.* 41 (2015) 5411-5421.
- [9] H. Ghaderi, M.A. Zolfigol, Y. Bayat, M. Zarei, E. Noroozizadeh, *Synlett* 27 (2016) 2246-2250.
- [10] A. Zare, T. Hekmat-Zadeh, S. Mirzaei-Monfared, M. Merajoddin, H. Torabi-Monfared, M.A. Zolfigol, A.R. Moosavi-Zare, E. Rostami, M. Mokhlesi, F. Derakhshan-Panah, S. Porbahi, S. Balandeh, *S. Afr. J. Chem.* 65 (2012) 63-68.
- [11] M.A. Zolfigol, H. Vahedi, S. Azimi, A.R. Moosavi-Zare, *Synlett* 24 (2013) 1113-1116
- [12] A.R. Moosavi-Zare, M.A. Zolfigol, M. Daraei, *Synlett* 25 (2014) 1173-1177.
- [13] A. Khazaei, A.R. Moosavi-Zare, S. Firoozmand, M.R. Khodadadian, *Appl Organometal Chem.* (2017) 4058-4065.