

### [Pyridine-SO<sub>3</sub>H]X: As a multi-versatile ionic liquid

Compiled by Sima Kalhor

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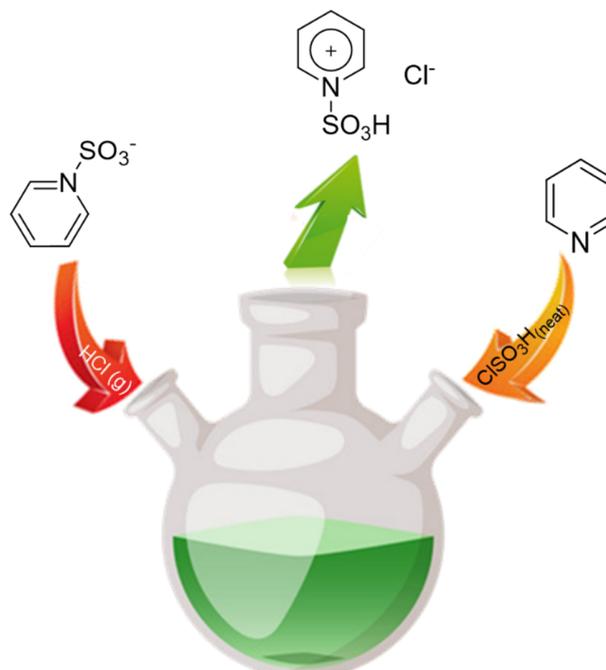


This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

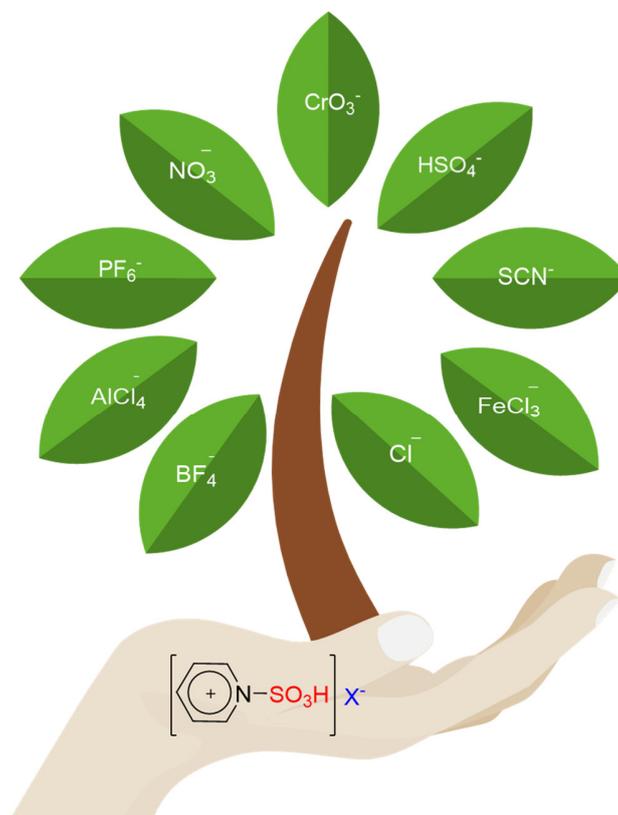
### Introduction

In recent years, ionic liquids (ILs) have been used as solvent, catalyst and reagent [1]. *N*-sulfonic acids ionic liquids such as imidazolium, pyridinium and phosphonium salts have been designed to replace solid acids and traditional mineral liquid acids alike sulfuric acid, hydrochloric acid and so on in the chemical processes [2]. In 2013, Zolfigol and coworkers have introduced novel pyridinium-based *N*-sulfonic acid ionic liquids (ILs) which they have been prepared from reaction of pyridine and chlorosulfonic acid at 0 °C (Scheme 1) [3].

In continued, a wide range of pyridinium-based *N*-sulfonic acid ionic liquids (ILs) have been synthesized via anion exchange method. Over the years, much attention has been paid for changing the properties of ILs via various cations and anions. Physicochemical properties of ILs such as viscosity, melting point, vapor pressure of fluids and fluorescence are dependent to their structures [4]. In this regard, [Pyridine-SO<sub>3</sub>H]Cl has been reacted with FeCl<sub>3</sub>, HNO<sub>3</sub>, NaBF<sub>4</sub>, KSCN, H<sub>2</sub>SO<sub>4</sub>, CrO<sub>3</sub> or KPF<sub>6</sub> for producing [Pyridine-SO<sub>3</sub>H]X. (Scheme 2). A magnetic nanoparticle with [Pyridine-SO<sub>3</sub>H]X tags has been also reported as an efficient catalyst in the synthesis of biological drug candidates [5].



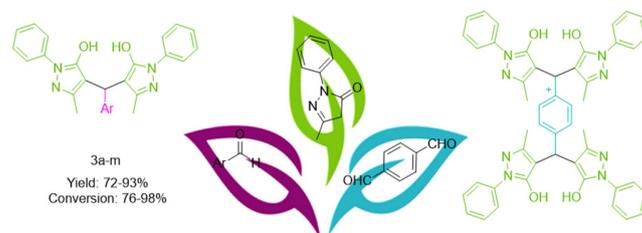
Scheme 1. Synthesis of [Pyridine-SO<sub>3</sub>H]Cl.



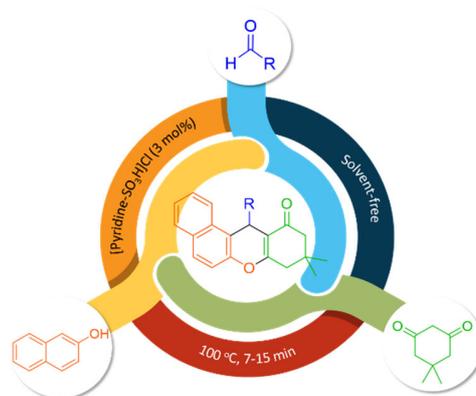
**Scheme 2.** The structure of [Pyridine-SO<sub>3</sub>H]X.

## Abstracts

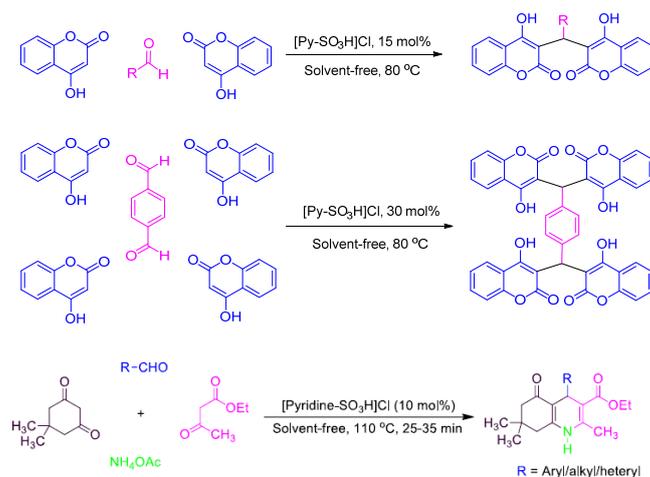
**(A)** In 2013, Zolfigol and coworkers have introduced sulfonic acid functionalized pyridinium salt [Pyridine-SO<sub>3</sub>H]Cl as a novel ionic liquid and efficient catalyst for the synthesis of 4,4'-(arylmethylene)-bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol)s by the reaction of tandem Knoevenagel-Michael reaction of 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one with various aromatic and hetero-aromatic aldehydes at 50 °C [3].



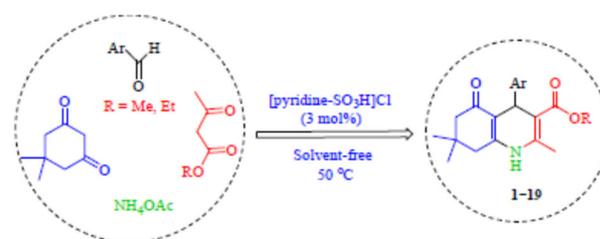
**(B)** The catalytic activity of [Pyridine-SO<sub>3</sub>H]Cl has been developed by its using in the synthesis of various 1-amidoalkyl-2-naphthols *via* one-pot multi-component condensations of  $\beta$ -naphthol, aldehyde and amide derivative at 120 °C with excellent yields and short reaction times [5].



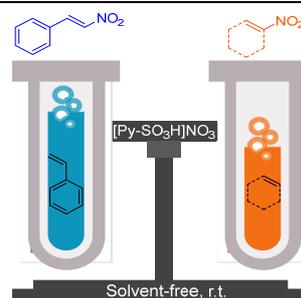
(C) Furthermore, [Pyridine-SO<sub>3</sub>H]Cl has been also applied as a recyclable and eco-benign catalyst for the Friedel-Crafts alkylation of 4-hydroxycoumarin with arylaldehydes under solvent free conditions. The described reaction afforded bis-coumarin derivatives with excellent yields and short reaction times. Also, described catalyst has been tested for the preparation of polyhydroquinolines via four-component Hantzsch condensation of various aldehydes, dimedone, ethyl acetoacetate, and ammonium acetate under solvent-free conditions [6].



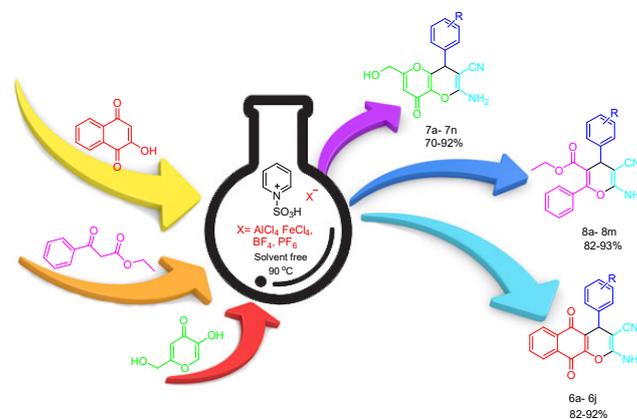
(D) In 2013, Khazaei *et al.* have been introduced [pyridine-SO<sub>3</sub>H]Cl as highly efficient and reusable Brønsted acidic catalyst for the synthesis of hexahydroquinolines according to the one-pot multi-component condensation of aldehydes, dimedone, (5,5-dimethylcyclohexane-1,3-dione), ammonium acetate and  $\beta$ -ketoesters under solvent-free conditions in excellent yields and very short reaction times [7].



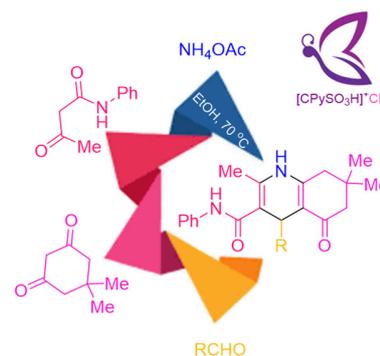
(E) 1-Sulfonypyridinium nitrate [pyridine-SO<sub>3</sub>H]NO<sub>3</sub> has been prepared via ion exchange method from reaction of [pyridine-SO<sub>3</sub>H]Cl and nitric acid. Described reagent *in situ* generates NO<sub>2</sub> radical without any co-catalysts to produce a wide range of nitroarenes in high yields and very short reaction times. Direct nitration of aniline and styrene at room temperature is another point in this method [8].



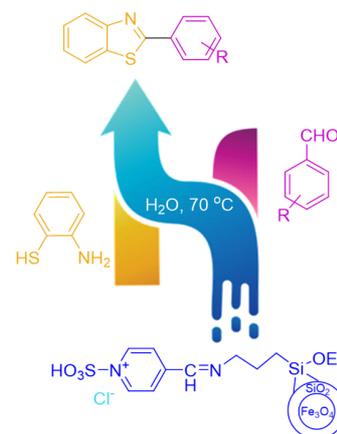
(F) The catalytic activity of nano ionic liquid (NIL) and nano molten salts (NMSs) are utilized as a highly efficient, inexpensive, mild and green catalysts for the synthesis of six membered *O*-heterocycles by the one-pot multi-component reaction between *O*-derivatives (2-hydroxynaphtalen-1,4-dione, 5-hydroxy-2-(hydroxymethyl)-4*H*-pyran-4-one or ethyl benzoylacetate), malononitrile and aldehydes. *O*-Heterocycles have been synthesized easily in the presence of nano molten salts [PySO<sub>3</sub>H]PF<sub>6</sub>, [PySO<sub>3</sub>H]AlCl<sub>4</sub>, [PySO<sub>3</sub>H]FeCl<sub>4</sub> or ionic liquid [PySO<sub>3</sub>H]BF<sub>4</sub> at 90 °C under solvent-free condition. Under presented conditions, the title compounds are produced in high to excellent yields and relatively short reaction times [9].



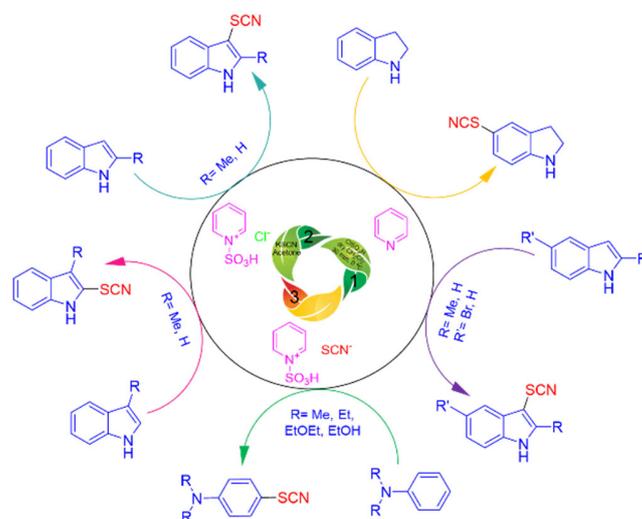
**(G)** Mokhtary *et al.* have been introduced 3-carboxy-1-sulfonylpyridin-1-ium chloride [CPySO<sub>3</sub>H]Cl as a reusable catalyst. Then, described catalyst has been used for one-pot synthesis of hexahydroquinoline-3-carboxamide derivatives by a four-component reaction of an arylaldehyde, dimedone, acetoacetanilide and ammonium acetate under solvent free condition in excellent yields and very short reaction times [10].



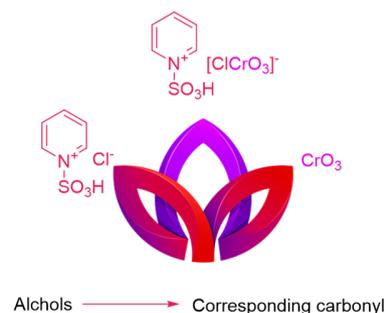
**(H)** In another exploration, magnetic nanoparticles [Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@(CH<sub>2</sub>)<sub>3</sub>NPC-SO<sub>3</sub>H]Cl has been prepared as a highly efficient and reusable catalyst. Then, the presented catalyst has been applied for the synthesis of benzothiazole derivatives by the reaction of various aldehydes and orto-aminothiophenol in the presence of [Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@(CH<sub>2</sub>)<sub>3</sub>NPC-SO<sub>3</sub>H]Cl (30 mg) in water (5 mL) at 70 °C [11].



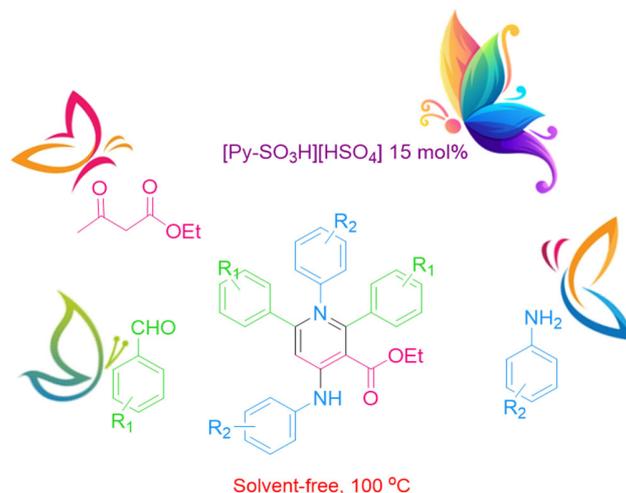
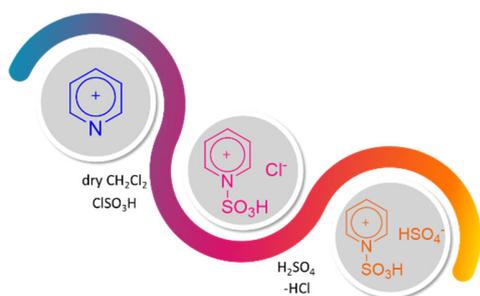
**(I)** In continuation of other studies, pyridinium sulfonic acid thiocyanate [pyridine-SO<sub>3</sub>H]SCN has been prepared by ion exchange reaction of [pyridine-SO<sub>3</sub>H]Cl and KSCN at room temperature. [Pyridine-SO<sub>3</sub>H]SCN as a highly efficient reagent for the synthesis of aryl and heteroaryl thiocyanates *via* the condensation of anilines, indoles, pyrroles, and their derivatives in the presence of H<sub>2</sub>O<sub>2</sub> as a green oxidant in mixed solvents EtOH:H<sub>2</sub>O (1:1) at room temperature [12].



**(J)** In 2010, pyridinium sulfonate chlorochromate (VI), [pyridine-SO<sub>3</sub>H][CrO<sub>3</sub>Cl] had been synthesized by a condensation reaction between CrO<sub>3</sub> and [pyridine-SO<sub>3</sub>H]Cl. The [pyridine-SO<sub>3</sub>H][CrO<sub>3</sub>Cl] has been used as new reagent for the oxidation primary, secondary, benzylic, and allylic alcohols under very mild conditions to give the corresponding carbonyl compounds [13].



(K) In 2015, pyridinium hydrogen sulfate [pyridine-SO<sub>3</sub>H]HSO<sub>4</sub> has been synthesized and fully characterized via an anion exchange method from reaction between [Pyridine-SO<sub>3</sub>H]Cl and sulfuric acid. Described [pyridine-SO<sub>3</sub>H]HSO<sub>4</sub> has been used as an efficient catalyst for the one-pot synthesis of highly functionalized tetrahydropyridines by reaction of aldehydes, ethyl acetoacetate, and substituted anilines under solvent-free conditions [14].



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