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Synthesis of α-aminonitriles using silica-bonded *N*-propylpiperazine sulfamic acid as a recyclable catalyst

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Abstract

α-Aminonitriles were synthesized *via* a one-pot three-component condensation of aldehydes, amines, and trimethylsilyl cyanide using silica-bonded *N*-propylpiperazine sulfamic acid (SBPPSA) as a recyclable solid acid at room temperature. SBPPSA showed much the same efficiency when used in consecutive reaction runs.

Keywords: Silica-bonded *N*-propylpiperazine sulfamic acid; α-Aminonitriles; Aldehydes; Amines; Catalyst; Solid acid

The addition of cyanide anion to imines (the Strecker reaction) [1] provides one of the most important and straightforward method for the synthesis of α-aminonitriles, which are useful intermediates for the synthesis of amino acids [2] and nitrogen containing heterocycles such as thiadiazoles and imidazoles. [3,4]. The classical Strecker reaction usually is carried out in aqueous solution and the work-up procedure is also tedious. Thus several modifications of Strecker reaction have been reported using a variety of cyanide reagents [5], such as diethyl phosphorocyanidate and α-trimethylsiloxy nitriles, as well as catalysts such as $InCl_3$ [6], [bmim]BF_4 [7], montmorillonite KSF clay [8], silica sulfuric acid [9], I_2 [10], $Fe(Cp)_2PF_6$ [11], xanthan sulfuric acid [12], hydrophobic sulfonic acid based nanoreactors [13], silica-bonded *S*-sulfonic acid [14], and sulfamic acid-functionalized magnetic Fe_3O_4 nanoparticles [15] under various reaction conditions. The use of trimethylsilyl cyanide is a safer and more effective cyanide anion source for the nucleophillic addition reactions of imines under mild conditions [16,17]. However, many of these methods involve the use of expensive reagents, harsh conditions, extended reaction times, and also require tedious workup leading to the generation of a large amount of toxic waste. Furthermore many of these catalysts are deactivated or sometimes decomposed by amines and water that exist during imine formation. In order to overcome these problems, recently one-pot procedures have been developed for this transformation [18].

Recently we prepared silica-bonded *N*-propylpiperazine sulfamic acid (SBPPSA) and used as a catalyst for the synthesis of 1,2,4,5-tetrasubstituted imidazoles [19] (Scheme 1).

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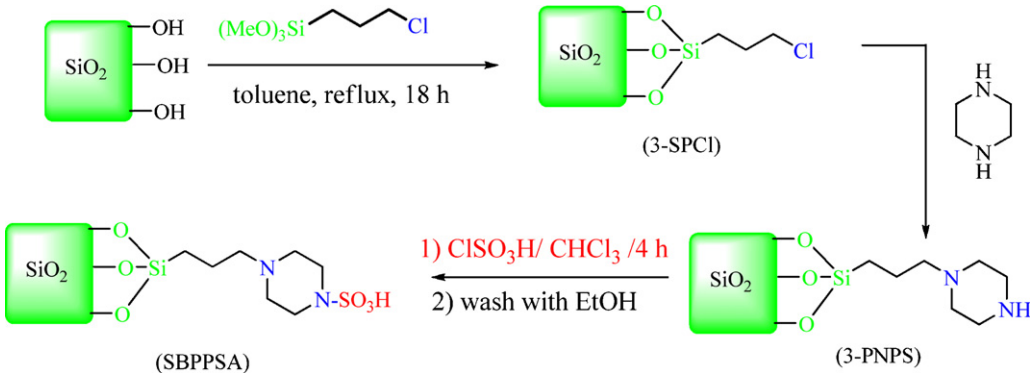
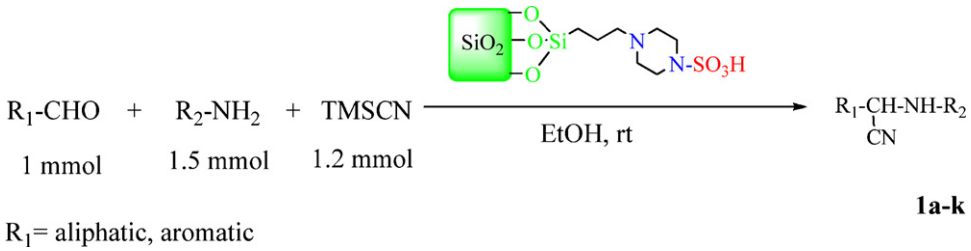


Scheme 1. Preparation of silica-bonded *N*-propylpiperazine sulfamic acid (SBPPSA).



Scheme 2. Condensation of aldehydes, amines and trimethylsilyl cyanide catalyzed by SBPPSA.

In continuation of our studies toward the preparation and applications of heterogeneous solid acid catalysts [19–25], herein we wish to report a valid and an efficient procedure for the synthesis of α-aminonitriles *via* one-pot three-component condensation of aldehydes, amines and trimethylsilyl cyanide in the presence of SBPPSA as an inexpensive solid acid catalyst (Scheme 2).

Initial studies were carried out on the condensation reaction between benzaldehyde and aniline with TMSCN in the presence of catalytic amounts of SBPPSA as a model reaction (Table 1). A blank experiment without catalyst the reaction did not proceed even after 24 h. The optimal amount of SBPPSA was 0.2 g (equal to 0.24 mmol of H^+) per 1 mmol of aldehyde in ethanol at room temperature.

Next, we prepared a range of α-aminonitriles under the optimized conditions (Table 2). Both aromatic and aliphatic aldehydes reacted with amines and TMSCN in the presence of SBPPSA in this one-pot three-component condensation to afford excellent yields of corresponding α-aminonitriles. Moreover, aldehydes with electron-withdrawing or electron-donating groups, *i.e.* 3-nitrobenzaldehyde or 4-methoxybenzaldehyde, and 3,4,5-trimethoxybenzaldehyde were converted into the corresponding α-aminonitriles **1d–1f** in high yields (Table 2, entries 4–6).

The acid sensitive substrate thiophene-2-carbaldehyde gave the expected α-aminonitrile **1g** in very good yield (Table 2, entry 7). Aliphatic aldehydes such as 2-methylpropanal gave the corresponding product **1h** in 76% yield

Table 1
The reaction of benzaldehyde, aniline and TMSCN in the presence of different amounts of SBPPSA.[a]

Entry	The amounts of catalyst (g)	Time (min)	Yield (%)[b]
1	–	24 h	<10
2	0.08	140	58
3	0.10	110	69
4	0.20	5	90
5	0.30	5	90

[a] Reaction conditions: benzaldehyde (1 mmol), aniline (1.5 mmol), TMSCN (1.5 mmol), EtOH (2 mL), and room temperature.
[b] Isolated yield.