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# Silica-bonded 1,4-diaza-bicyclo[2.2.2]octane-sulfonic acid chloride catalyzed synthesis of spiropyran derivatives

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ABSTRACT

In this research, a novel nanostructured heterogeneous catalyst, namely silica-bonded 1,4-diaza-bicyclo[2.2.2]octane-sulfonic acid chloride (SBDBSAC), as an acidic ionic liquid based on 1,4-diaza-bicyclo[2.2.2]octane ring bonded to silica has been prepared and fully characterized by several techniques such as fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential thermogravimetric (DTG), scanning electron microscope (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDX). The nanostructured catalyst has been suxessfully used as reusable nanostructured catalyst for green, simple and efficient synthesis of spiropyrans by the one-pot tandem Knoevenagel-Michael-cyclization reaction of isatin derivatives or acenaphthenquinone with barbituric acid derivatives, and 1,3-dicarbonyl compounds under aqueous media.



## 1. Introduction

Multi-component reactions (MCRs) achieve significant role in combinatorial chemistry because of the ability to prepare target compounds with more efficiency and atomic economy by the reaction of three or more compounds together in one single step. Additionally, MCRs increase simplicity and synthetic efficiency on the conventional organic transformations [1–5].

Spiropyrans including oxindoles are an important class of attractive heterocyclic compounds with useful biological properties such as spasmolitic, diuretic, anticoagulant, anticancer, and anti-anaphylactic activities [6–9]. Some catalysts have been applied for this transformation, including sodium stearate [9], sulfated choline based heteropolyanion [10], Protic guanidinium ionic liquid [11], 4-dimethylaminopyridine [12], [BMIm]$BF_4$ [13], SBA-Pr-$SO_3H$ [14], (SB-DBU)Cl [15], carbon-sulfonic acid [16], polyethylene glycol (PEG)-stabilized Ni nanoparticles [17], alpha-Amylase [18], ZnS nanoparticles [19], triphenylphosphine [20] and nickel oxide [21]. Therefore, considerable attention has been focused on the development of new methods for the synthesis of these compounds.

Recently, we have prepared a new category of ionic liquids and solid salts (with an organic cation), namely sulfonic acid functionalized imidazolium salts (SAFIS) [22–38]. In this class of salts, S-N bond formation in imidazole ring, as five member's heterocyclic compounds, was reported for the first time. These compounds have been successfully introduced as catalysts or reagent for the preparation of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazoles [22], bis(indolyl)methanes [23], *N*-sulfonyl imines [24], 1-amidoalkyl-2-naphthols [25], various xanthene derivatives [26], 1-carbamatoalkyl-2-naphthols [27], 4,4′-(arylmethylene)-bis(3-methyl-1-phenyl-1H-pyrazol-5-ol)s [28], *N*-boc protected amines [29], hexahydroquinolines [30], nitroaromatic compounds [31,32]. In continuation of our previous projects including the applications of acidic ionic liquids and solid salts in organic transformations, we have prepared, characterized an acidic ionic liquid based on 1,4-diaza-bicyclo[2.2.2]octane ring bonded to silica namely silica-bonded 1,4-diaza-bicyclo[2.2.2]octane-sulfonic acid chloride (SBDBSAC) in nano-size and applied it for the synthesis of spiropyrans by the one-pot tandem Knoevenagel-Michael-cyclization reaction of isatin derivatives or acenaphthenquinone

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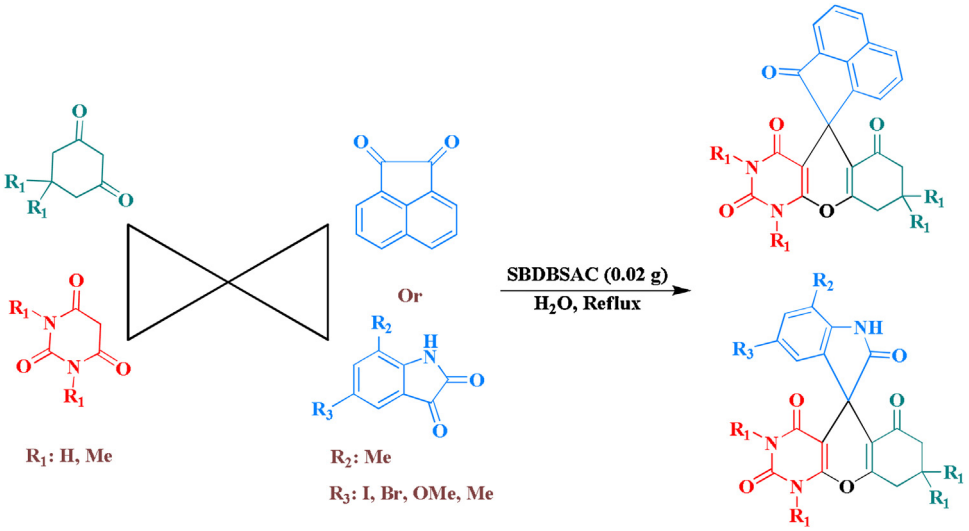
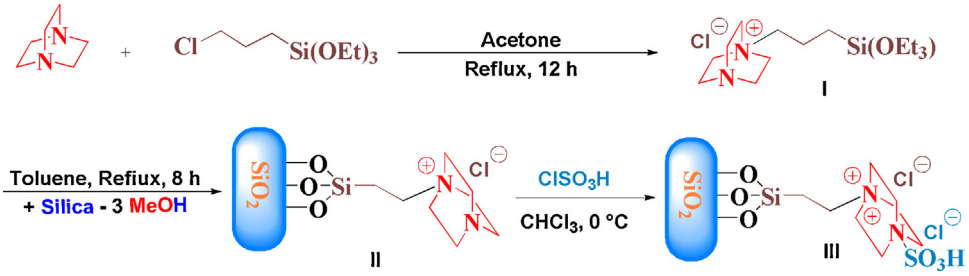



**Scheme 1.** The preparation of spiropyrans by the reaction of isatin derivatives or acenaphthenquinone with barbituric acid and 1, 3-dicarbonyl compounds using SBDBSAC.




**Scheme 2.** The preparation of silica-bonded 1,4-diaza-bicyclo[2.2.2]octane-sulfonic acid chloride (SBDBSAC).

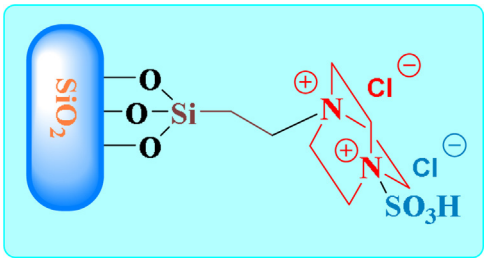



**Fig. 1.** The structure of silica-bonded 1,4-diaza-bicyclo[2.2.2]octane-sulfonic acid chloride (SBDBSAC).

with barbituric acid derivatives, and 1,3-dicarbonyl compounds under aqueous media (Fig. 1) (Scheme 1).

## 2. Experimental

### 2.1. General

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates.

The $^{1}$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) were recorded on a Bruker Avance DPX FT-NMR spectrometer (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Thermogravimetric (TG) and differential thermal gravimetric (DTG) were analyzed by a Perkin Elmer (Model: Pyris 1). TG/DTG analysis (0–600 °C, temperature increase rate of 10 °C min$^{-1}$, nitrogen atmosphere). The crystal structure of synthesized materials was determined by an X-ray diffractometer (Italstructure ADP2000 XRD diffractometer) at an ambient temperature.

### 2.2. Catalyst preparation

A mixture of 1,4-diaza-bicyclo[2.2.2]octane (0.56 g, 5 mmol), (3-chloropropyl)triethoxysilane (1.125 g, 5 mmol) and acetone (15 mL) in a 50 mL round-bottomed flask connected to a reflux condenser, was stirred for 12 h under reflux conditions. In the next step, the obtained white precipitate, was filtered to separate from acetone, and reacted with silica (0.3 g, 5 mmol) in refluxed toluene (15 mL) for 8 h. After removing of the solvent, the resulted product was added to a 50 mL round-bottomed flask in an ice water bath (0 °C), and a solution of chlorosulfonic acid (5 mmol) in chloroform (10 mL) was added dropwise to it, and stirred for 2 h. Afterward, the residue was triturated with chloroform (3 × 10 mL), and dried under powerful vacuum at 90 °C to give silica-bonded 1,4-diaza-bicyclo[2.2.2]octane acid chloride (SBDBSAC) as a white precipitate in 95% yield.

### 2.3. General procedure for the preparation of spiropyrans

A mixture of isatin derivatives or acenaphthenquinone (1 mmol), barbituric acid (1 mmol), 1, 3-dicarbonyl compounds (1 mmol), SBDBSAC (0.02 g) and $H_2O$ (5 mL) was added to a in a 25 mL round-bottomed flask connected to a reflux condenser, and stirred under reflux conditions. After completion of the reaction, as monitored by TLC, the reaction mixture was cooled to room temperature. Methanol (20 mL) was added, stirred and refluxed for 3 min. Then, the resulting mixture was centrifuged for the separation of