



# An environmentally friendly, photocontrollable and highly recyclable catalyst for use in a one-pot three-component Mannich reaction



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## ABSTRACT

An environmentally friendly, photocontrollable and highly recyclable catalyst (ZrOPPAZOSO<sub>3</sub>H) has been synthesized by the immobilization of 4-[4-(6-phosphonic acid-hexanoxyl)phenylazo]benzenesulfonic acid onto zirconium phosphonate. This catalyst was characterized by Fourier transform infrared, scanning electron microscopy, X-ray powder diffraction, nitrogen adsorption-desorption and UV–vis analyses. The catalytic activity of ZrOPPAZOSO<sub>3</sub>H was investigated towards the one-pot three-component Mannich-type reaction of benzaldehyde, aniline and cyclohexanone in water at room temperature, and gave excellent yields. Interestingly, the catalytic activity could be regulated by photoirradiation. Furthermore, upon completion of the reaction, the product could be readily separated by extraction, and the water phase reused in the next run. Lastly, the catalyst could be readily recovered by centrifugation and reused up to six times without any discernible impact on its activity.

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## 1. Introduction

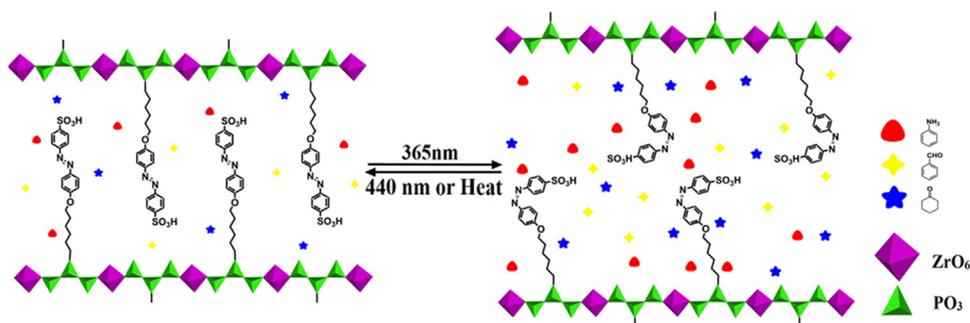
The Mannich reaction involves the reaction of two carbonyl compounds with an amine to give a β-amino-carbonyl compound via a C–C bond-forming reaction in the presence of a proper catalyst [1]. β-Amino-carbonyl compounds are important intermediates in the synthesis of pharmaceutical agents and natural products [2], and the Mannich reaction has therefore attracted considerable interest from numerous research groups. A variety of different catalysts have been developed for the Mannich reaction, including Bronsted acids [3–6], Lewis acids [7–18] and several other organic or inorganic compounds [19–22]. However, most of these methods are conducted in organic solvents [3–7,9–13,15–17,19–22] or organic solvent–water mixtures [14,18]. The development of novel catalysts capable of catalyzing the Mannich reaction of a wide range of substrates in water is therefore highly desired and research in this area has grown considerable, because of the economical and environmental benefits of water. However, the use of water as a solvent has been limited because of the poor solubility of most organic reactants in water. For example, most of the reported Man-

nich reactions conducted in water use silyl enol ethers as precursors [23] or have to be performed in the presence of surfactants (such as sodium dodecyl sulfate) [24,25] or ionic liquids [26,27]. Unfortunately, silyl enol ethers have to be prepared from the corresponding carbonyl compounds and the Mannich reactions of these substrates generally require an organic solvent. The use of surfactants or ionic liquids in these reactions can lead to phase separation issues. Several researchers have reported the use of water-soluble catalysts such as heteropoly acids and its salts [28,29] Bi(OTf)<sub>3</sub>·4H<sub>2</sub>O [30], 5-sulfosalicylic acid [31], calix[*n*]arene quaternary ammonium salts [32] and boron chelate complexes [33]. However, catalysts of this type can be difficult to recover from the reaction mixture because of their good solubility. Catalysts supported on a stable solid substrate are therefore highly desired because they can be readily recycled [34,35].

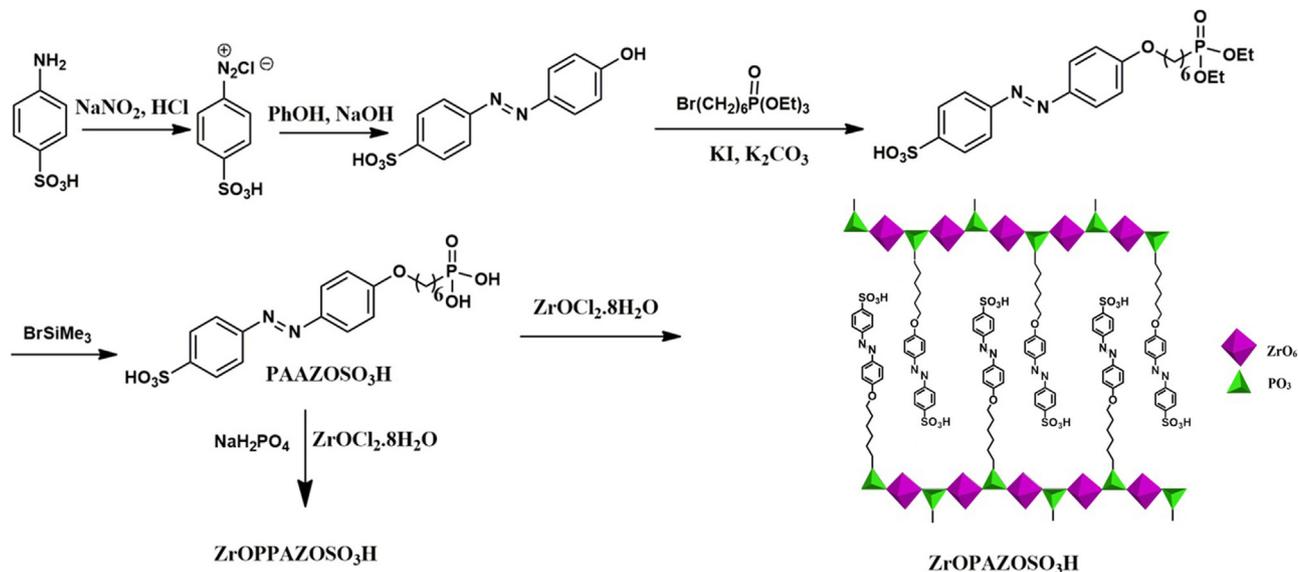
To address these challenges, we developed a novel environmentally friendly, recyclable and photocontrollable catalyst (ZrOPPAZOSO<sub>3</sub>H, Scheme 1) for a one-pot three-component Mannich reaction in water by tethering a sulfonated azobenzene to zirconium phosphate. It was envisaged that the sulfonic acid group in this catalyst would serve as a catalytic moiety, as well as enhancing the aqueous solubility of the catalyst. The recyclability of the catalyst could be realized by tethering the azobenzene moiety to zirconium phosphate, which is a versatile material

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**Scheme 1.** Chemical structure of ZrOPPAZOSO<sub>3</sub>H and its photoisomerization.



**Scheme 2.** Synthetic route for ZrOPPAZOSO<sub>3</sub>H.

with a layered structure. Azobenzene chromophores [36–40] are well-known photoresponsive moieties, and the photoirradiation of these systems can induce *trans/cis* isomerization processes, resulting in pronounced changes in their geometry, which can promote or slow down specific reactions. The catalyst developed in this study demonstrated photo-controllability, as well as being environmentally friendly and highly recyclable for the one-pot three-component Mannich reaction of unmodified aldehydes, ketones and amines in water. Indeed, photo-activated or photo-controllable catalysts for Mannich reactions are rarely found in literature and the current system is interesting for further exploring its potential applications in inhibition reactions.

## 2. Experimental details

### 2.1. Materials and methods

All of the chemicals used in the current study were purchased from Aladdin Co. (Shanghai, China) and used without further purification.

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer Model GX Spectrometer (Perkin-Elmer, Waltham, USA) as KBr pellets using polystyrene as a standard. X-ray diffraction (XRD) patterns were recorded on a LabX XRD-6100X-ray Diffractometer (SHIMADZU, City, Japan) with Cu-K $\alpha$  monochromated radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 36 kV and 20 mA. The morphological characteristics of the ZrOPPAZOSO<sub>3</sub>H catalyst

were determined by scanning electron microscopy (SEM; S-4800, Hitachi, Tokyo, Japan). <sup>1</sup>H NMR and <sup>13</sup>C NMR (300 MHz) spectra were recorded on a Bruker AV-300NMR instrument (Bruker, USA) at ambient temperature using TMS as an internal reference standard. Nitrogen adsorption-desorption analysis was conducted at 77 K on an Autosorb-1 apparatus (Quantachrome, USA). The specific surface areas and pore diameters were calculated using the BET and BJH models, respectively. UV–vis spectra were recorded with an UV-4802 spectrophotometer (UNICO Shanghai Instruments Co., Ltd., Shanghai, China) using a CEL-S500 Xe lamp (Beijing Zhongjiao Jinyuan Keji Co., Ltd., Beijing, China) as a light source. Wavelengths of 365 and 440 nm were selected using 365 and 440 nm filters, respectively.

### 2.2. Synthesis of ZrOPPAZOSO<sub>3</sub>H

The synthesis of ZrOPPAZOSO<sub>3</sub>H was completed over five steps (Scheme 2).

#### 2.2.1. Synthesis of 4-[(4-Hydroxy)phenylazo]benzenesulfonic acid

4-[(4-Hydroxy)phenylazo]benzenesulfonic acid was synthesized according to a modified version of previous methods reported by Ma and co-workers [41–43]. Briefly, sulfanilic acid (3.48 g, 20.0 mmol), sodium nitrite (1.52 g, 22.0 mmol) and water (8.0 mL) were added to a 250 mL round-bottomed flask, and the resulting mixture was cooled in an ice bath under stirring. An ice-cold mixture of water (8.0 mL) and conc. HCl (36%, 8.0 mL) was then

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