



## Original article

## Sulfonated poly(4-vinylpyridine) heteropolyacid salts: A reusable green solid catalyst for Mannich reaction

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## ABSTRACT

Sulfonated poly(4-vinylpyridine) heteropolyacid salts acted as a heterogeneous catalyst to effectively catalyze the one-pot synthesis of  $\beta$ -amino carbonyl compounds via the Mannich reaction between aromatic aldehydes, aromatic ketone, and aromatic amines. In addition, the catalyst could be easily recovered by the filtration and reused six times without significant loss of catalytic activity.

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## 1. Introduction

Mannich reactions are very important carbon–carbon bond-forming reactions in organic synthesis [1,2]. They provide  $\beta$ -amino carbonyl compounds, which are important synthetic intermediates for various pharmaceuticals and natural products [3,4]. The increasing popularity of the Mannich reaction has been fueled by the ubiquitous use of nitrogen containing compounds in drugs and natural products [5,6]. Therefore, the development of new synthetic methods leading to  $\beta$ -amino carbonyl compounds or their derivatives has attracted much attention. Recently, some modern versions of the Mannich reaction using performed electrophiles, such as imines, and stable nucleophiles, such as enolates, enol ethers, and enamines [7–15], have been developed. However, the preferred route is to use a one-pot, three-component strategy that gives a wide range of structural variations.

Recently, one-pot Mannich reactions of unmodified aldehydes, ketones, and amines have been promoted by a wide array of catalysts, such as ionic liquid [16], SDS–HCl [17,18], proline [19], GuHCl [20], CeCl<sub>3</sub>·7H<sub>2</sub>O [21], polymer-support sulfonic acid (PS–SO<sub>3</sub>H) [22], H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> [23], Lewis acids [24–29], silica–AlCl<sub>3</sub> [30],

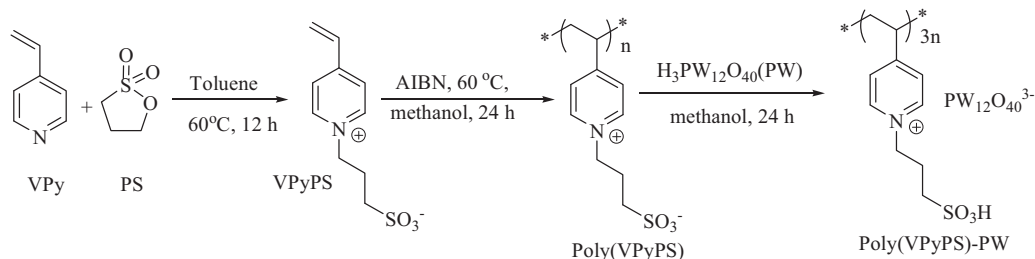
silica sulfuric acid [31], or PEG–SO<sub>3</sub>H [32]. However, most of these procedures have some drawbacks, such as harsh reaction conditions, tedious work-ups, or difficulties recovering, isolating and recycling the expensive, toxic catalysts. Although one-pot Mannich reactions can be carried out in the presence of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> [23] in water, the catalysts cannot be recycled.

Ionic liquids (ILs) have been attracting significant attention as alternative solvents and catalysts for chemical reactions because of their negligible volatility, remarkable solubility, and potential recyclability [33–35]. In recent years, the use of heteropolyacid-based IL (HPA-IL) to catalyze organic reactions is an ongoing research area [36]. Some HPA-IL composites have been reported and employed as catalysts for acid-catalyzed reactions [37–42]. Considering that ionic polymers containing IL units are potentially capable of ILs and polymers, such as high thermal stability, easy modification, corrosion resistance, and a variety of available structures [43,44], the catalytic stabilities of these catalysts need to be improved. Compared with imidazolium ILs, pyridinium ILs are generally more readily biodegradable [45].

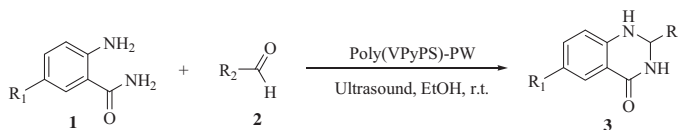
Most recently, we have reported the preparation of sulfonated poly(4-vinylpyridine) heteropolyacid salts (Scheme 1) and used it as a catalyst for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones under ultrasonic irradiation (Scheme 2) [46]. In continuation of our work to develop new catalysts for organic transformations [46–48], here we report the synthesis of  $\beta$ -amino carbonyl compounds in the presence of sulfonated poly(4-vinylpyridine) heteropolyacid salts (Scheme 3).

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**Scheme 1.** Preparation of the poly(VPyPS)-PW catalyst.



**Scheme 2.** The synthesis of 2,3-dihydroquinazolin-4(1H)-ones catalyzed by poly(VPyPS)-PW under sonication.

## 2. Experimental

### 2.1. General

Melting points were determined on a Perkin-Elmer differential scanning calorimeter, and the temperature was uncorrected. The IR spectra were run on a Nicolet spectrometer (KBr). NMR spectra were recorded at 400 ( $^1\text{H}$ ) and 100 ( $^{13}\text{C}$ ) MHz, respectively, on a Varian Mercury plus-400 instrument using  $\text{CDCl}_3$  as solvent and TMS as the internal standard. Thermogravimetric analysis was carried out under nitrogen using a Shimadzu TGA-50 spectrometer. X-ray diffraction (XRD) images were obtained from a Bruker XRD D8 Advance instrument with Cu K $\alpha$  radiation. All the solvents used were strictly dried according to standard operation.

### 2.2. General procedure for Mannich reaction

To the mixture of acetophenone (0.30 g, 2.0 mmol), 4-nitrobenzaldehyde (0.21 g, 2.0 mmol) and aniline (0.19 g, 2.0 mmol) in 6 mL of ethanol, poly(VPyPS)-PW (0.03 g) was added. The mixture was stirred at room temperature for the appropriate time indicated in Table 2 until the reaction was completed as monitored by TLC. The resulting mixture was filtered to recover the catalyst, and the filtrate was evaporated off the solvent to give the crude product. The analytical sample was obtained by recrystallization of crude product from ethanol and acetone (2:3). The separated catalyst was washed with cold ethanol, then dried at 60 °C under vacuum for 4 h. The recovered catalyst was directly used for the next run. The product was collected from the filtrate after cooling to room temperature and recrystallization from the ethanol to give compounds **4a–4m**. The  $\beta$ -amino carbonyl compounds were characterized by the use of spectral data and comparison of their physical data with the literature. Spectral data for compound **4c**: White solid; IR (KBr):  $\nu$  3380, 1668;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  7.91 (d, 2H,  $J$  = 8.0 Hz, ArH), 7.57 (t, 1H,  $J$  = 8.8 Hz, ArH), 7.45 (t, 2H,  $J$  = 8.0 Hz, ArH), 7.37 (d, 2H,  $J$  = 8.8 Hz, ArH), 7.12 (t, 2H,  $J$  = 8.0 Hz,

**Table 1**  
Poly(VPyPS)-PW catalyzed Mannich reaction in different solvents.<sup>a</sup>

Entry	Solvents	Catalyst loading (g)	Time (h)	Yield <sup>b</sup>
1	MeCN	0.05	6	16
2	EtOH	0.05	6	75
3	PhMe	0.05	6	0
4	$\text{CH}_2\text{Cl}_2$	0.05	6	0
5	$\text{H}_2\text{O}$	0.05	6	0
6	EtOH	0.04	6	95
7	EtOH	0.03	6	95
8	EtOH	0.02	15	80
9	EtOH	0.01	12	70
10	EtOH	No catalyst	24	0

<sup>a</sup> Reaction condition: benzaldehyde (2.0 mmol), acetophenone (2 mmol) and aniline (2 mmol) were stirred at room temperature for 6 h.

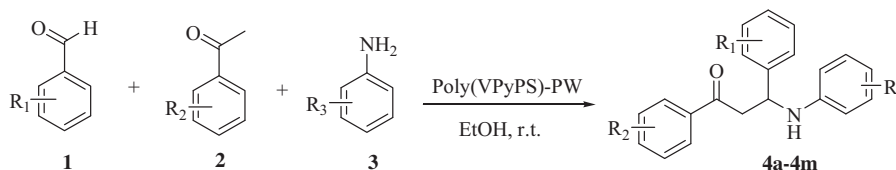
<sup>b</sup> Isolated yields.

ArH), 6.85 (d, 2H,  $J$  = 8.8 Hz, ArH), 6.72 (t, 1H,  $J$  = 7.1 Hz, ArH), 6.63 (d, 2H,  $J$  = 7.6 Hz, ArH), 4.97 (t, 1H,  $J$  = 6.0 Hz, NCH), 3.78 (s, 3H,  $\text{CH}_3\text{O}$ ), 3.53 (d, 2H,  $J$  = 6.0 Hz,  $\text{COCH}_2$ ).

## 3. Results and discussion

In order to establish the optimal experimental conditions for the preparation of  $\beta$ -amino carbonyl compounds, the Mannich reaction between benzaldehyde (2.0 mmol), acetophenone (2.0 mmol) and aniline (2.0 mmol) as model substrates was carried out using poly(VPyPS)-PW as catalyst in various solvents. Several solvents were tested for the reaction, such as EtOH, MeCN,  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}$  and PhMe. The reaction hardly proceeded in  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}$  or PhMe. However, the reaction in EtOH afforded product in high selectivity with nearly complete conversion. It seemed that the solvents also played an important role in the Mannich reaction catalyzed by poly(VPyPS)-PW. Therefore, EtOH was selected as the reaction solvent in the following investigation (Table 1). The results show clearly that poly(VPyPS)-PW is an effective catalyst for this transformation, and in the absence of Poly(VPyPS)-PW the reaction did not take place, even after 24 h. Although a lower catalyst loading (0.01 g of poly(VPyPS)-PW) could be used to accomplish this reaction, 30 mg of poly(VPyPS)-PW was optimum in terms of reaction time and isolated yield.

Encouraged by this result, in order to build the generality of the reaction, a series of aldehydes, aromatic ketones, and aromatic amines were investigated under the optimized reaction conditions (Table 2). As expected, these reactions proceeded smoothly and the



**Scheme 3.** The Mannich reaction catalyzed by Poly(VPyPS)-PW.

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