

Cite this: *RSC Adv.*, 2017, **7**, 30380Received 29th April 2017
Accepted 31st May 2017DOI: 10.1039/c7ra04834c
rsc.li/rsc-advances

Acid-ionic polymer as recyclable catalyst for one-pot three-component Mannich reaction†

W. Senapak, R. Saeeng and U. Sirion  *

A recyclable solid-catalyst, acid-ionic polymer bearing imidazolium trifluoromethanesulfonate, [PS-Im] [OTf] was presented as an efficient catalyst in a one-pot, three-component Mannich reaction of aldehydes, amines and ketones. The protocol was conducted successfully under mild, convenient and metal-free conditions to afford the corresponding products in moderate to excellent yields. In addition, the catalyst was reused four times with no significant loss in activity.

Introduction

The Mannich reaction is one of the most powerful tools for carbon–carbon bond-forming.¹ It produces β -amino carbonyl compounds, which are crucial building blocks for the synthesis of a wide variety of nitrogen-containing drugs and natural products.² Some of these compounds exhibit biological significance,³ for examples anticancer,⁴ antimicrobial⁵ anti-HIV⁶ and antimalarial⁷ properties (Fig. 1). As a consequence, new synthetic methods to prepare these compounds have been continually developed, especially direct-Mannich reaction in a one-pot three-component process of aldehydes, amines and various nucleophiles.

Generally, one-pot, three-component Mannich reactions have been reported with various catalyst systems. Most catalysts are Lewis acids,⁸ Bronsted acids,⁹ organocatalyst¹⁰ and recently

nanoparticles.^{11,16} However, most of these catalysts have serious disadvantages such as their high cost, toxicity and hazardous nature, in addition to being difficult to separate from the product. Some are unstable, moisture sensitive, environmental contaminants and not reusable. Therefore, high performance non-toxic, inexpensive, reusable and efficient catalysts are desirable. Additionally, practical and metal-free methods with an environmentally benign synthetic process under green context merits more recent attention for one-pot Mannich reactions.

Solid-supported catalysts are currently of great interest as green and reusable catalysts, providing high yields of desirable products for many useful organic reactions.¹² The advantages of these catalysts are moisture resistance, air tolerance, low-toxicity, easily separated post reaction by simple filtration and recyclable. In particular, there are practical advantages in medicinal and pharmacological production because of their non-toxicity and high-throughput synthesis. Mannich reactions that promoted by solid-supported Lewis and Bronsted acid-catalysts have been rare.^{13–16} Kobayashi's group in 2003 used a hydrophobic polymer-supported sulfonic acid as a catalyst for three-component Mannich reaction.¹⁴

Subsequently, in 2007, Wu's group employed $\text{SiO}_2\text{--OSO}_3\text{H}$ as the catalyst for the direct-Mannich reaction.¹⁵ Recently, in 2014, Zareyee's group described the use of a hydrophobic sulfonic acid based nanosilica as the catalyst for one-pot three-component Mannich reaction.¹⁶

Bronsted acidic ionic liquids (BAILS) have received attention in past decades as efficient acidic catalysts under a wide range of reaction conditions.^{17,18} Recently, BAILS has proven to be effective catalysts in the Mannich reactions.¹⁸ Solid-supported acidic ionic liquid catalysts^{19–26} have been reported for acetalization reaction,²⁰ condensation,²¹ Hantzsch reaction,²² multi-component reaction,²³ esterification,²⁴ hydrolysis of cellulose²⁵ and biodiesel synthesis.²⁶ Herein, we would like to present the utilization of polystyrene bearing acidic ionic liquid (acid-IP) as a reusable heterogeneous catalyst for direct-Mannich reaction

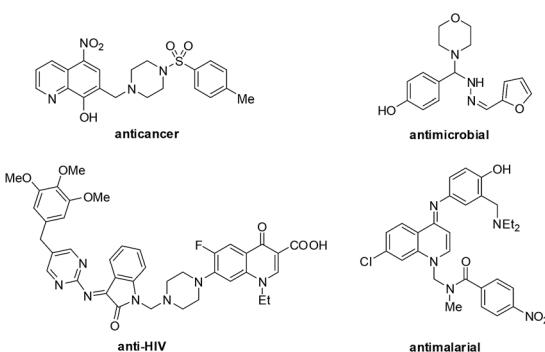
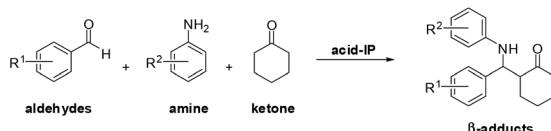


Fig. 1 Examples of bioactive compound of Mannich bases.

Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Burapha University, Sangsook, Chonburi 20131, Thailand. E-mail: uthaiwan@buu.ac.th; Fax: +66-3-839-3494; Tel: +66-98-026-2181

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ra04834c





Scheme 1 Three-component Mannich reaction catalyzed by acid-IP.

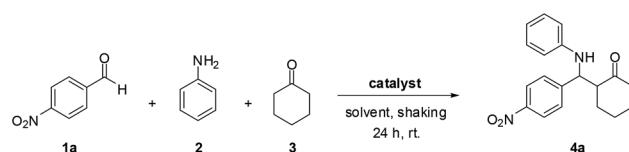
of aldehydes, amines and ketones in one-pot process under mild, convenient and metal-free conditions at ambient temperature (Scheme 1).

Results and discussion

A series of acid-ionic polymers (acid-IP) bearing imidazolium cation with two different acid-anions (*p*TSA and OTf) was investigated as a recyclable heterogeneous catalyst for one-pot, three-component Mannich reaction of aldehydes, amines, and ketones. Preparation of these acid-ionic polymers used commercially available polystyrene beads (PS) with 1.80 mmol g⁻¹ of chloride loading (Scheme 2, see ESI†).

The formation of β -amino carbonyl compound **4a** through one-pot three-component Mannich reaction catalyzed by acid-ionic polymer-based imidazolium salts was investigated using 4-nitrobenzaldehyde **1a**, aniline **2** and cyclohexanone **3** as model substrates (Table 1). Initial experiments, 10 mol% of catalysts were tested using 1.0 mmol of each substrate in acetonitrile (MeCN) at room temperature for 24 h (entries 1–4). The highest yield of the desired product **4a** was obtained with catalyst **III** in 82% (entry 2). Subsequently, with the best catalyst **III**, various solvents were screened in the same reaction condition. Results demonstrated the high yield of desired product **4a** was achieved with polar solvents (MeCN and DMF). This was probably due to the generous swelling of acid-ionic polymer in polar solvents that lead to reaction rate enhancement. However, MeCN was selected as the best solvent for this protocol due to more efficient recyclability.

To improve yield of desired product **4a**, ratio of substrates was adjusted (Table 2). Slight increase of cyclohexanone **3** to 1.2 equivalents, desired product **4a** was produced in higher yield, 89% for 24 h and 93% for 48 h (entry 1). However, reaction time

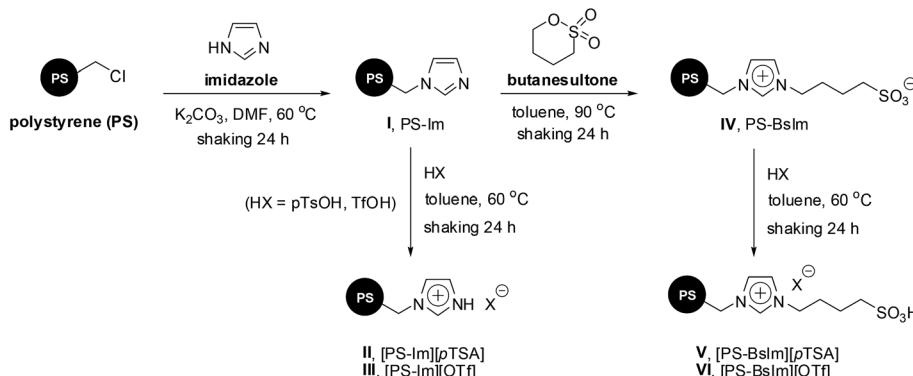
Table 1 Optimization of one-pot three-component Mannich reaction with various catalysts and solvents^a

Entry	Catalyst	Solvent	Yield 4a ^b (%)
1	II , [PS-Im][<i>p</i> TSA]	MeCN	72
2	III , [PS-Im][OTf]	MeCN	82(83) ^c (81) ^d (80) ^e
3	V , [PS-BsIm][<i>p</i> TSA]	MeCN	41
4	VI , [PS-BsIm][OTf]	MeCN	36
5	III , [PS-Im][OTf]	DMF	81(74) ^c (54) ^d (48) ^e
6	III , [PS-Im][OTf]	DCM	38
7	III , [PS-Im][OTf]	DCE	48
8	III , [PS-Im][OTf]	Toluene	27
9	III , [PS-Im][OTf]	THF	60
10	III , [PS-Im][OTf]	1,4-Dioxane	38
11	III , [PS-Im][OTf]	H ₂ O	49
12	III , [PS-Im][OTf]	MeOH	56

^a All reactions were conducted with 1.0 mmol of **1a**, **2** and **3** using 10 mol% of catalyst in 3.0 mL of solvent, shaking 800 rpm at room temperature for 24 h. ^b Isolated yields. ^c Second run. ^d Third run. ^e Fourth run.

was investigated also from 3–48 h and the result indicated that the reaction was almost completed in 48 h.

For comparison, the reaction was investigated with 24 h and showed yield was not improved when substrate **3** was increased further to 2.0–5.0 equivalents (entries 2 and 3). Unfortunately, when amount of amine substrate **2** was increased yield of the desired product **4a** declined (entries 4–6). This was attributed to excess amine base quenching the acidity of catalytic system. Highly concentrated reaction volume produced the slight decrease in yield (entry 7). Amount of catalyst **III** with 20 and 5 mol% were examined, and resulted in lower yields of desired product **4a** in 77 and 80% respectively (entries 8 and 9). Due to greater acidity with 20 mol% of catalyst amine substrate was reduced by reacting with acid catalyst, while reaction was incomplete with 5 mol% of catalyst. In addition, confirmation



Scheme 2 Preparation of acid-ionic polymers.



Table 2 Optimization of one-pot three-component Mannich reaction with various amount of substrates^a

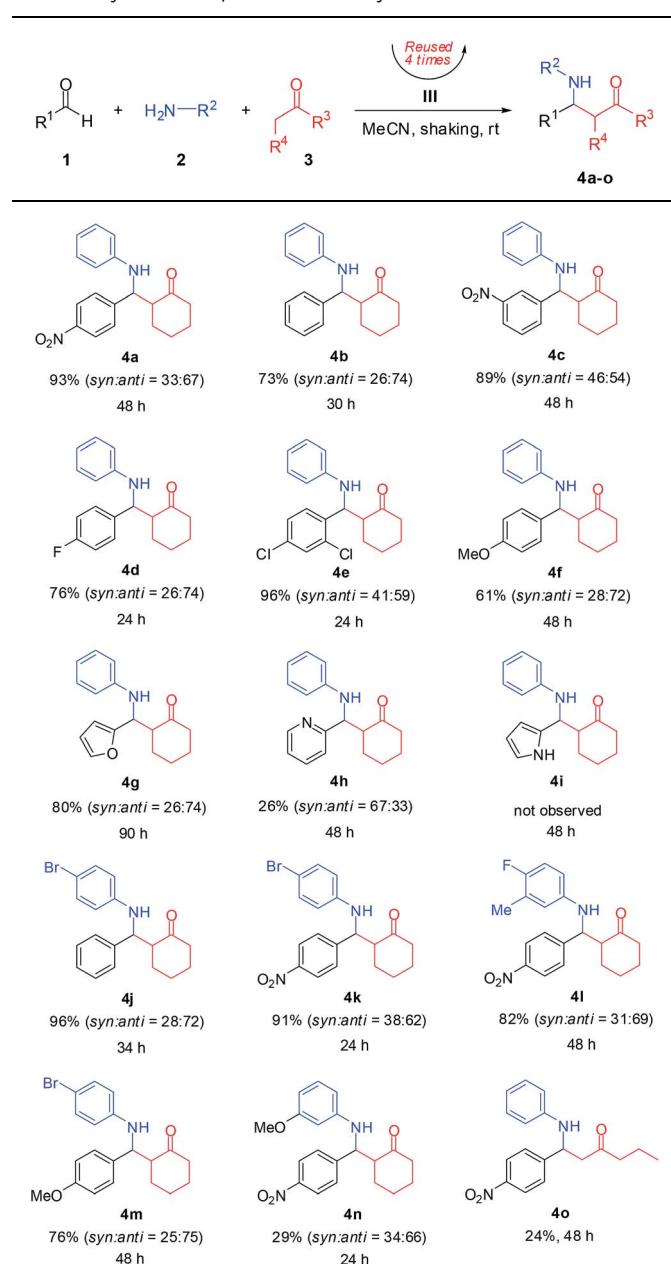
Entry	SM (1a : 2 : 3) (mmol)	Catalyst	Yield 4a ^b (%)	Reaction scheme		
				1a	2	3
1	1 : 1 : 1.2	III, [PS-Im][OTf]	89(93) ^c			
2	1 : 1 : 2.0	III, [PS-Im][OTf]	86			
3	1 : 1 : 5.0	III, [PS-Im][OTf]	86			
4	1 : 1.2 : 1.2	III, [PS-Im][OTf]	75			
5	1 : 2.0 : 1.2	III, [PS-Im][OTf]	71			
6	1 : 5.0 : 1.2	III, [PS-Im][OTf]	50			
7 ^d	1 : 1 : 1.2	III, [PS-Im][OTf]	81			
8 ^e	1 : 1 : 1.2	III, [PS-Im][OTf]	77			
9 ^f	1 : 1 : 1.2	III, [PS-Im][OTf]	80			
10	1 : 1 : 1.2	pTSA	73			
11	1 : 1 : 1.2	TfOH	77			
12	1 : 1 : 1.2	—	0			

^a All reactions were conducted with 1.0 mmol of 1, 1–5 mmol of 2 and 1–5 mmol of 3 using 10 mol% of catalyst in 3.0 mL of MeCN, shaking at 800 rpm at room temperature for 24 h. ^b Isolated yields. ^c 48 h. ^d 1.0 mL MeCN. ^e 20 mol% of III. ^f 5 mol% of III.

of catalytic activity of catalyst **III**, the control reactions were tested with general acids such as *p*TSA and TfOH and found to give lower yields of the desired product **4a** (entries 10 and 11) and no product in the absence of catalyst (entry 12).

Recycle performance of catalyst **III** was also examined with the optimum reaction over 48 h (Table 2, entry 1). After the first run, the resin catalyst **III** was recovered by simple filtration and washed with ethyl acetate and dried under vacuum pump. Recovered resin catalyst **III** was reused, giving similar yields even after four cycles with 93, 91, 92 and 90% of the desired product **4a**, respectively.

Under optimum reaction condition (Table 2, entry 1), a variety of both aldehydes and anilines were investigated for their performance (Table 3). Corresponding product yields depended on steric hindrance and electronic effect of substrates. Reaction of aromatic aldehyde substrates with electron-withdrawing group (–NO₂, –F, –Cl, including –H) produced good to excellent yields (73–96% for products **4a–e** and **4j–l**). Notably, electron-withdrawing group at *para*-position gave a superior yield than at *meta*-position (**4a** compared to **4c**; –NO₂). While aromatic aldehyde substrates with an electron-donating group (–OMe) provided products in moderate and good yields (61 and 76% of **4f** and **4m**, respectively). Moreover, heteroaromatic aldehydes gave good yields with furan-2-carbaldehyde (80%; **4g**), low yield with 2-pyridinecarboxaldehyde (26%; **4h**), and no desirable product (**4i**) with pyrrole-2-carbaldehyde. This result is likely due to basicity of nitrogen atom on substrates that could easily attach to an acid-catalyst and reduce catalytic activity. Aniline substrates with an electron-withdrawing group (–Br, –F) could improve product yields (**4j–m**), by providing a higher electrophilicity of an iminium ion intermediate. Unfortunately, yields

Table 3 Synthesis of β -amino carbonyl derivatives^a

^a All reactions were conducted with aldehyde (1, 1.0 mmol), amine (2, 1.0 mmol) and ketone (3, 1.2 mmol) using 10 mol% of catalyst **III** in MeCN (3.0 mL), shaking 800 rpm at room temperature; % yields were reported as isolated yields; the ratio of *syn* : *anti* was determined by NMR.

were lower in the case of an electron-donating group (–OMe) on aniline substrate (29%; **4n**) because the instability of an iminium ion intermediate and product led to generating undesirable products. Moreover, 2-pentanone was investigated as a nucleophile, resulting in low yields of desired products with 24% (**4o**).

Conclusions

In summary, we have demonstrated a metal-free and convenient method for the preparation of β -amino carbonyl compounds *via*



one-pot three-component Mannich reaction of aldehydes, amines and cyclohexanone at ambient temperature catalyzed by recyclable heterogeneous acid-ionic polymer. The acid-ionic polymer-based imidazolium cation with OTf anion, [PS-Im]⁺[OTf]⁻ (III) exhibited the most efficient catalyst to produce desirable products in moderate to excellent yields with a wide range of aldehyde and amine substrates. In addition, the catalysts are easily separated from the reaction mixture by simple filtration and reusability of catalyst was possible for subsequent reactions.

Acknowledgements

This work was financially supported by Thailand Research Fund (Grant no. TRG5780298), the Center of Excellence for Innovation in Chemistry (PERCH-CIC) and the Research Grant of Burapha University through National Research Council of Thailand (Grant no. 28/2555 and 16/2556). Special thanks to Prof. Dr Frederick W. H. Beamish, Faculty of Science, Burapha University, for his comments and English correction and Dr Byoung Se Lee (FutureChem Co. Ltd., Korea) for helpful discussion.

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