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FULL PAPER

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Sulfonic acid supported on magnetic nanoparticle as an eco-friendly, durable and robust catalyst for the synthesis of β-amino carbonyl compounds through solvent free Mannich reaction

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A simple, efficient and environmentally benign solid acid catalyst was prepared by anchoring a propyl sulfonic acid on the surface of silica-coated magnetic nanoparticles by low cost precursors. The catalyst has been then engaged in the efficient β-amino carbonyl compounds production via three component Mannich reaction under solvent free reaction condition at room temperature. After the completing the reaction, the catalyst was readily separated by external magnet and reused for 10 successive rounds of reaction, without any significant loss in catalytic efficiency. The solid acidic system presented reusable strategy for the efficient synthesis of β-amino carbonyl compounds, simplicity in operation, and green aspects by avoiding toxic conventional catalysts under solvent-free condition.

KEYWORDS

compounds; Mannich reaction, heterogeneous catalyst, magnetic nanoparticles, solid acid, β-amino carbonyl

1 | INTRODUCTION

β-amino carbonyl compounds are fundamental building blocks for the preparation of peptides, amino alcohols, lactams and as precursors to synthesize amino acids and many nitrogen-containing biologically important compounds.[1–4] In recent years, these materials have been prepared by various significant methods,[5,6] but among them, one-pot three component Mannich reaction of aldehydes, ketones and aryl amines are more desirable route to constructing β-amino carbonyl units. In this context, several approaches based on Lewis acids,[7–15] Lewis base,[16–20] Brønsted acids,[21–28] and transition metal salts[29,30] have been used for three component Mannich reaction. However, despite promising improvements, recycling and reusing of catalysts, toxic reagents and solvents, harsh reaction conditions and difficulty in product separation are still important issues that remain unresolved.

As a matter of fact, one of the best Brønsted acid catalysts, which is highly active in acid-catalyzed reactions, is sulfuric acid. Although liquid sulfuric acid is used annually in critical chemical processes, but it suffers from several disadvantages such as neutralization of H_2SO_4 that produces a large amount of waste, troublesome separation of sulfates (from neutralization processing) and purification of the product which also involves substantial energy and material use. Therefore, due to the stringent environmental standards and economic pressures, much attention has been directed toward to immobilized sulfuric acid on solid support to reducing of waste, effective separation of catalyst and simple purification of the products. Toward this aim, many support materials such as polymers,[31,32] amorphous and mesoporous carbon,[33–36] mesoporous silica[37–41] and amorphous silica[42] are often used for immobilization of sulfuric acid, which can be separated by conventional separation techniques such as centrifugation and filtration.

Over the last few years, magnetic nanomaterials have developed as good alternatives to conventional support materials as readily available heterogeneous catalyst supports with high surface area. It is noteworthy that one of the salient facets of magnetically supports is their separation properties because they can be easily recovered with an external magnet.[43–47] Due to the unique properties of magnetic nanomaterials, it appears that they are good candidates for consolidation of homogeneous catalysts such as sulfuric acid.

On the other hand, in the view of the stringent environmental issues and green chemistry, a growing consensus is directed toward the carrying out organic reactions in solvent free reaction conditions.[48–52] These reactions are becoming more popular because they have many advantages such as cost savings, decreased energy consumption, reduced reaction times, a large reduction in reactor size and capital investment, and make the reactions cleaner, safer, and easier to perform. It is noteworthy that "the best solvent is no solvent and if a solvent (diluent) is needed it should preferably be water" as clearly stated by R. A. Sheldon.[53] Furthermore, the E factor of solvent-free reactions is also reducing that is very suitable for clean technology.[54] Consequently, there

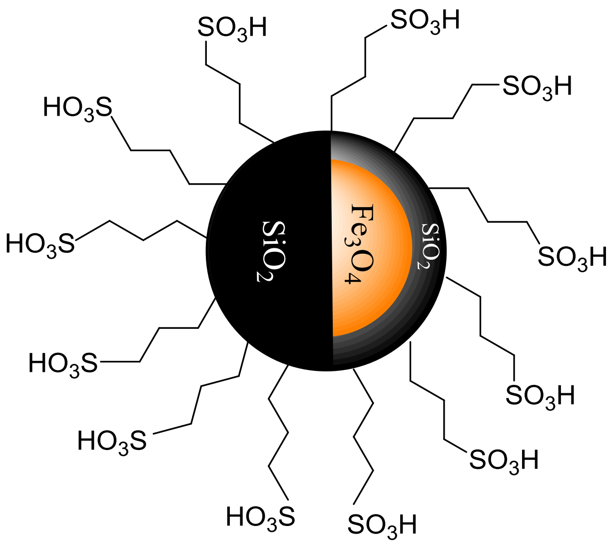
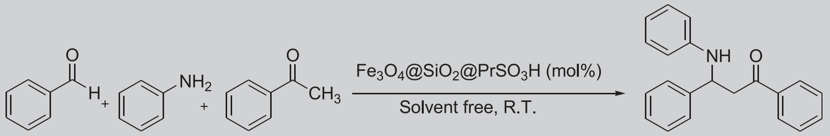


FIGURE 1 Sulfonated core-shell magnetic nanoparticles (SMNPs) ($Fe_3O_4@SiO_2@PrSO_3H$)

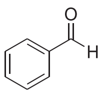
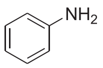
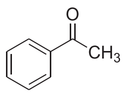
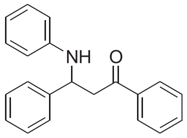
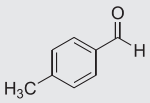
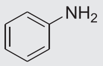
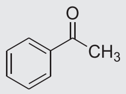
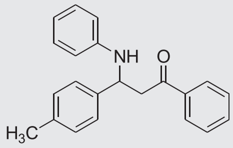
TABLE 1 Screening of catalyst amount on model reaction of benzaldehyde, aniline and acetophenon



Entry	$Fe_3O_4@SiO_2@PrSO_3H$ (mol%)	Time (h)	Yield[a] (%)
1	0	24	NR
2	1	4	55
3	2	4	92
4	3	4	95
5	4	4	96

[a] Isolated yields.

TABLE 2 Synthesis of different β-aminocarbonyl compounds under solvent free condition at room temperature using SMNPs as catalyst[a]

Entry	Aldehyde	Amine	Ketone	Product	Time (h)	Yield [b] (%)
1					4	92
2					3.5	92

(*Continues*)

TABLE 2 (Continued)

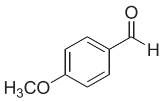
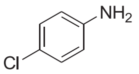
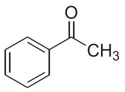
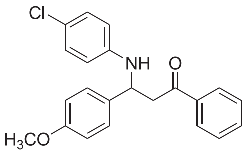
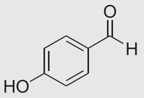
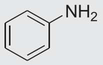
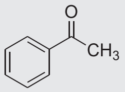
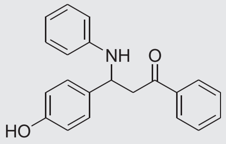
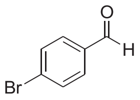
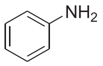
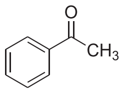
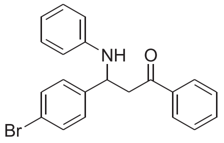
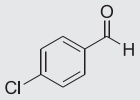
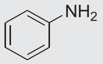
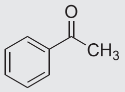
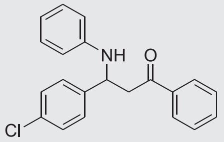
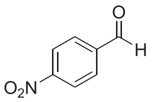
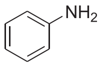
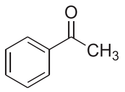
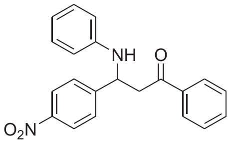
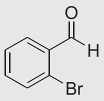
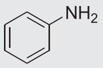
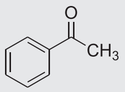
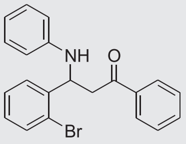
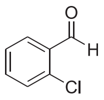
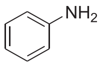
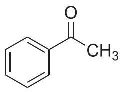
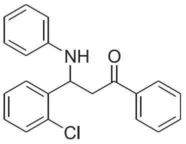
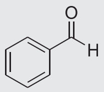
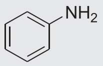
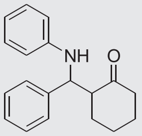
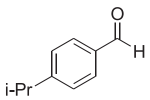
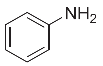
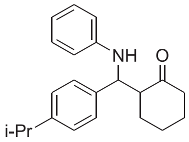
Entry	Aldehyde	Amine	Ketone	Product	Time (h)	Yield [b] (%)
3					7	90
4					4	90
5					4	90
6					4	89
7					6	90
8					6	88
9					6	90
10					4	91
11					4	92

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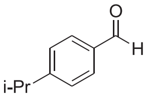
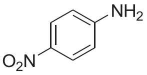
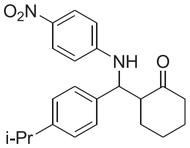
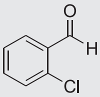
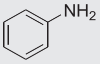
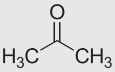
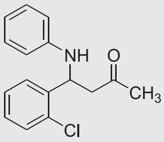
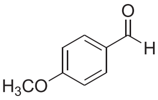
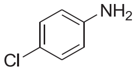
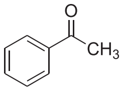
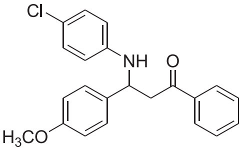
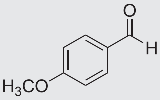
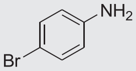
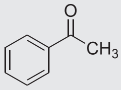
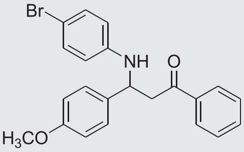
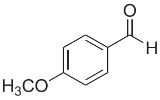
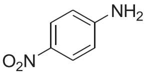
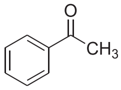
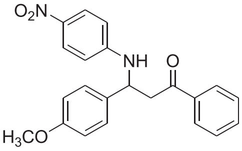
TABLE 2 (Continued)

Entry	Aldehyde	Amine	Ketone	Product	Time (h)	Yield [b] (%)
12					5	90
13					6	83
14					7	90
15					7	89
16					7	85

[a] Reaction condition: aldehyde (1 mmol), amine (1 mmol), ketone (1 mmol), $Fe_3O_4@SiO_2@PrSO_3H$ (2 mol%), solvent free, room temperature. [b] Isolated yields after recrystallization.

are great demands for development of environmentally benign reaction systems that operate in a safe media and with efficient and easily recoverable heterogeneous catalysts.

Toward these aims, herein we wish to report a simple, efficient and green procedure for the synthesis of β-amino carbonyl compounds under solvent free condition by using sulfonated core-shell magnetic nanoparticles (SMNPs) ($Fe_3O_4@SiO_2@PrSO_3H$) as a renewable and reusable strong solid acid catalyst (Figure 1).

2 | EXPERIMENTAL

2.1 | General procedure for the preparation of β–amino carbonyl compounds:

To the mixture of aldehyde (1 mmol), ketone (1 mmol) and amine (1 mmol) under solvent free reaction condition (Table 1), $Fe_3O_4@SiO_2@PrSO_3H$ (0.03 g, 2 mol%) was added. The mixture was stirred at room temperature for

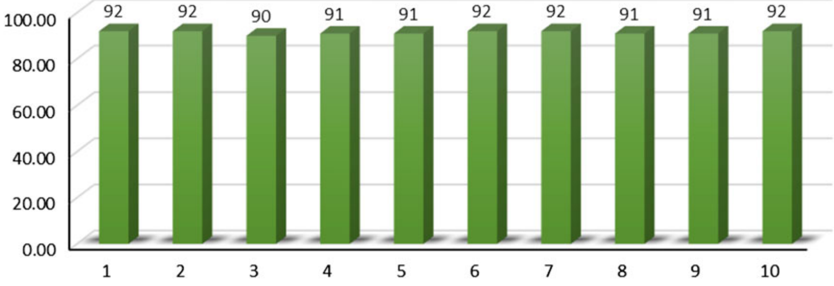


FIGURE 2 Recyclability of the SMNPs catalyst for the Mannich reaction of benzaldehyde, aniline and acetophenone after 4 h

appropriate time indicated in Table 2 until the reaction was completed as monitored by thin-layer chromatography. The analytical sample was obtained by recrystallization of crude product from ethanol. Spectroscopic data for selected examples listed below.

Table 2, Entry 2: ^{1}H NMR (400 MHz; CDCl$_3$): δ_H = 2.34 (s, 3H), 3.48–3.60 (m, 2H), 5.01 (t, ^{3}J = 8 Hz, 1H), 6.65 (d, ^{3}J = 8 Hz, 2H), 6.73 (t, ^{3}J = 8 Hz, 1H), 7.11–7.20 (m, 3H), 7.35–7.37 (d, ^{3}J = 8.4 Hz, 2H), 7.47 (t, ^{3}J = 8 Hz, 2H), 7.57–7.61 (m, 1H), 7.96 (d, ^{3}J = 8.4 Hz, 2H).

Table 2, Entry 3: ^{1}H NMR (400 MHz; CDCl$_3$): δ_H = 3.50–3.58 (m, 2H), 3.80 (s, 3H), 5.00 (t, ^{3}J = 6.4 Hz, 1H), 6.63 (d, ^{3}J = 8 Hz, 2H), 6.72 (t, ^{3}J = 7.6 Hz, 1H), 6.88 (d, ^{3}J = 8.4 Hz, 2H), 7.11–7.15 (m, 2H), 7.39 (d, ^{3}J = 8.4 Hz, 2H), 7.47 (t, ^{3}J = 7.2 Hz, 2H), 7.59 (t, ^{3}J = 7.2 Hz, 1H), 7.93 (t, ^{3}J = 7.2 Hz, 2H), ^{13}C NMR (100 MHz, CDCl$_3$): δ_C = 46.1, 54.8, 55.3, 114.2, 114.4, 118.4, 127.7, 128.2, 128.5, 128.7, 129.2, 133.5, 134.4, 136.7, 158.9, 198.4.

Table 2, Entry 5: ^{1}H NMR (400 MHz; CDCl$_3$): δ_H = 3.46–3.57 (m, 2H), 5.00 (t, ^{3}J = 6.4 Hz, 1H), 6.61 (d, ^{3}J = 8 Hz, 2H), 6.75 (t, ^{3}J = 8 Hz, 1H), 7.14 (t, ^{3}J = 8 Hz, 2H), 7.37 (d, ^{3}J = 8.4 Hz, 2H), 7.46–7.53 (m, 4H), 7.61 (t, ^{3}J = 7.2 Hz,1H), 7.93 (t, ^{3}J = 7.2 Hz, 2H), ^{13}C NMR (100 MHz, CDCl$_3$): δ_C = 45.8, 54.8, 114.4, 118.7, 121.2, 128.2, 128.4, 128.8, 129.2, 131.9, 133.6, 136.5, 141.6, 197.8.

Table 2, Entry 6: ^{1}H NMR (400 MHz; CDCl$_3$): δ_H = 3.44–3.56 (m, 2H), 5.02 (t, ^{3}J = 6.8 Hz, 1H), 6.59 (d of d, ^{3}J = 10 Hz, ^{3} J = 0.8 Hz, 2H), 6.71 (t, ^{3}J = 10 Hz, 1H), 7.11–7.16 (m, 2H), 7.30–7.33 (m, 2H), 7.41–7.44 (m, 2H), 7.47–7.51 (m, 2H), 7.59–7.63 (m, 1H), 7.92–7.95 (m, 2H), ^{13}C NMR (100 MHz, CDCl$_3$): δ_C = 46.0, 54.4, 114.1, 118.4, 127.9, 128.2, 128.8, 129.0, 129.2, 133.1, 133.6, 136.6, 141.3, 146.4, 197.9.

3 | RESULTS AND DISCUSSION

Very recently, we prepared magnetic catalyst $Fe_3O_4@SiO_2@PrSO_3H$.[55,56] Now, the catalytic performance of catalyst studied in the three component Mannich reaction, because this reaction is usually carried out in high catalyst loading and hence the reactivity and reusability of the catalyst can be studied under this reaction conditions.

To determine the optimal experimental conditions, the impact of various loading of SMNPs were examined and it was found that 2 mol% of catalyst was better suited for this purpose under solvent free condition at room temperature (Table 1). It should be noted that decreasing of the catalyst loading resulted in significantly lower yield. Notably, increasing the amount of SMNPs to more than 2 mol% resulted in slightly higher yields. Thus, because of small

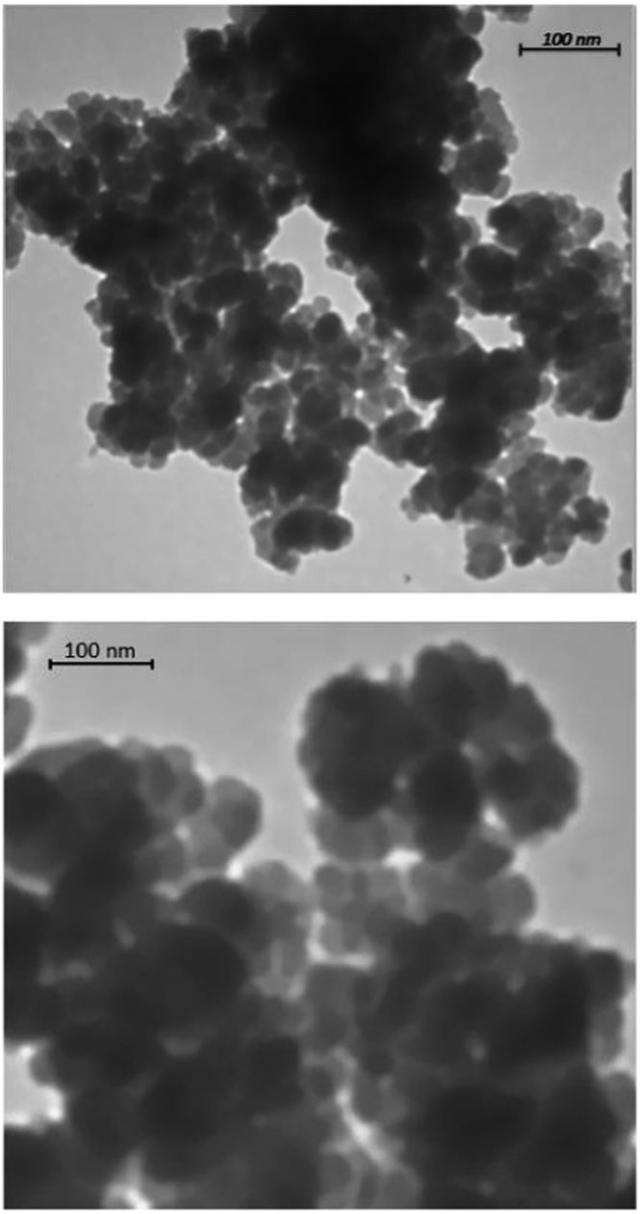


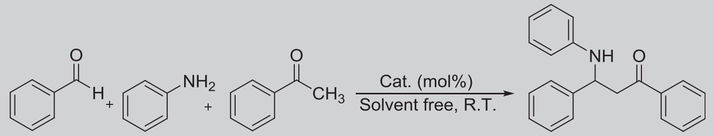
FIGURE 3 TEM images of catalyst before (left) and after (right) the 10th reaction cycle

difference in the yield of product, 2 mol% of catalyst selected as optimum amount.

With the optimal reaction conditions to hand, the activity of the catalyst was then investigated in the three component Mannich reaction of numerous electron-rich and electron-poor benzaldehydes with different ketones and amines (Table 2). The aromatic aldehydes bearing electron-donating groups, namely, 4-methylbenzaldehyde (Table 2, entry 2), 4-methoxybenzaldehyde (Table 2, entry 3), and 4-hydroxybenzaldehyde (Table 2, entry 4), also afforded high yields of the corresponding coupling adducts. Furthermore, the other aromatic aldehydes bearing electron-withdrawing groups, such as 4-boromobenzaldehyde (Table 2, entry 5), 4-chlorobenzaldehyde (Table 2, entry 6), and 4-nitrobenzaldehyde (Table 2, entry 7), also gave excellent yields of Mannich products under the same reaction conditions. It is also noteworthy that in Mannich reaction of more sterically demanding ortho-substituted substrates, which are usually less reactive compounds in organic transformations, the corresponding β-amino carbonyl compounds were obtained in good yields (Table 2, entries 8 and 9). Notably, this method was equally applicable to the reaction of both linear and cyclic aliphatic enolizable ketones, giving the respective carbonyl compounds in good to excellent yields (Table 2, entries 10–13). Additionally, SMNPs also shows excellent tolerance for a broad range of substituted aromatic amine and converted these substrates to their corresponding products (Table 2, entries 14–16). These results demonstrate the high performance and activity of the designed catalyst for the preparation of a wide range of Mannich products bearing different functional groups, which are important in the syntheses of amino acids and many nitrogen-containing biologically important compounds.

From academic and industrial point of view, the most important issue that should be considered for practical applications of heterogeneous catalyst systems is the lifetime of the catalyst and the easy separation of catalyst from the reaction media. In this regard, we investigated the recycling performance of the catalyst in the Mannich reaction of benzaldehyde, aniline, and acetophenone. After the completion of the first run, the SMNPs were effortlessly separated from the reaction mixture with an external magnet. The recovered catalyst was then directly reused under the same conditions for at least ten reaction cycles without significant loss of activity (Figure 2), indicating the high stability and reusability of the catalyst during the reaction process. This can be attributed to the efficient immobilizing of the SO_3H groups on silica coated magnetic nanoparticles. Comparison

TABLE 3 Comparison of activity of some homogeneous and heterogeneous sulfonic acid catalysts in Mannich reaction of benzaldehyde, aniline and acetophenon



Entry	Catalyst	Mol %	Time (h)	Yield[a] (%)	Ref.
1	$Fe_3O_4@SiO_2@PrSO_3H$ [b]	2	4	92	-
2	None	-	24	NR	-
3	H_2SO_4	2	4	5	-
4	*p*-TSOH	2	4	30	-
5	$KHSO_4$	2	4	Trace	-
6	CH_3SO_3H	2	4	10	-
7	SBA-15-Ph-$PrSO_3H$	5	4	92	[23]
8	5/1-butyl-1-aza-[18-C-6KSO_3H][TFA]$_2$	10	5	83	[57]
9	PS-SO_3H[c]	1	24	75	[58]
10	PS-PTSA [d]	0.65 g	45 min	96.7	[24]
11	$[Hmim]^+Tfa^-$[e]	16	12	85	[59]
12	H_3BO_3 [f], [i]	10	44	80	[27]
13	[DOPA][Tos][j],[i]	10	6	89	[26]
14	Alginic acid aerogel (AG 1)[h],[i]	20	18–20	90	[21]

[a] Isolated yields. [b] catalyst (2 mol%, 0.03 g). [c] ethanol, room temperature [d] 30°C, H_2O. [e] benzaldehyde: aniline: acetophenone, 1:1:1 (mole ratio), ionic liquid = PS-PTSA (0.65 g). Two drops of water (0.06 g) was added to the ionic liquid. [f] $[Hmim]^+TFA^- = 3.11$ g. [g] benzaldehyde, aniline and cyclohexanone, glycerol (1–2 drops), 45°C, H_2O. [h] benzaldehyde, aniline and cyclohexanone, H_2O. [i] benzaldehyde, aniline and cyclohexanone, $CH_3CN–H_2O$ 8:2, R.T. [j] Compare with entry 10, Table 2.

of the TEM images of catalyst before and after ten times recovery showed that the size distribution of 30–60 nm (average ~ 40 nm) unchanged after recovery (Figure 3). Additionally, the loading of the SO_3H function in recovered SMNPs calculated again from elemental analysis and ion exchange pH analysis, showed intact loading of approximately 0.9 mmol g^{-1}.

For a better comparison of the catalytic performance of $Fe_3O_4@SiO_2@PrSO_3H$, a set of individual catalytic experiments were conducted by employing H_2SO_4, p-TSOH, $KHSO_4$ and CH_3SO_3H under the same reaction condition (Table 3, entries 3–6). These results compared with some homogeneous and heterogeneous Brønsted acid catalysts under different conditions (Table 3, entries 7–14). It should be noted that $Fe_3O_4@SiO_2@PrSO_3H$ with lower catalyst loading and under solvent free condition exhibits higher activity in Mannich reaction. In comparison with other heterogeneous catalysts (Table 3). SMNPs can recycle more easily from the reaction mixture with an external magnet and reuse for several times without decrease in catalytic activity.

4 | CONCLUSIONS

In summary, covalent functionalization of propylsulfonic acid on core-shell magnetic nanoparticle gives a heterogeneous, green and reusable catalyst for the solvent-free synthesis of β-amino carbonyl compounds through Mannich reaction at room temperature. The advantages of this method include low catalyst loading, easy separation of catalyst by external magnet, recyclability of catalyst, simple procedure, excellent yields and short reaction times. This results reveals suitable environment for production of β-amino carbonyl compounds and this system represents a recyclable solid acid catalyst.

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