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Sulfonated Core-Shell Magnetic Nanoparticle (Fe_3O_4@SiO_2@$PrSO_3H$) as a Highly Active and Durable Protonic Acid Catalyst; Synthesis of Coumarin Derivatives through Pechmann Reaction

Farhad Kabiri Esfahani,*[a] Daryoush Zareyee,*[b] and Reza Yousefi[c]

Sulfonic acid supported silica coated magnetic nanoparticles (Fe_3O_4@SiO_2@$PrSO_3H$), was prepared by using low cost precursors and a facile immobilization technique. The final catalyst, which was characterized by XRD, FT-IR, vibrating sample magnetometer (VSM), TEM, and TGA techniques, was found to be an efficient and environmentally benign solid acid for the Pechmann condensation of substituted phenols with ethyl acetoacetate leading to the formation of coumarin derivatives. After the reaction, the catalyst could be effortlessly separated by external magnet and reused for 22 consecutive runs, without any significant loss in catalytic efficiency. The catalytic system presented offers a reusable strategy for the efficient synthesis of coumarin, simplicity in operation, and a green reaction profile by avoiding toxic conventional catalysts and solvents.

A large amount of liquid sulfuric acid is used annually as a catalyst in the chemical industry for the production of important chemicals, such as esters, alcohols, ethers, and various starting materials for polymers and resins.[1] Although this catalyst is used in critical chemical processes, it suffers from several drawbacks, such as the large amount of waste produced by neutralization of H_2SO_4, troublesome separation of sulfates (from neutralization processing), and purification of the product, which also involves substantial energy and material use. Consequently, owing to increasingly stringent environmental standards and economic pressures, significant attention has been directed toward the use of solid acid catalysts to achieve effective separation of catalyst, waste reduction, and simplified purification of the products.[2–16] However, a major impediment to such progress is the lack of a solid acid that is as stable, active, and inexpensive as sulfuric acid. A perfect solid acid material for the catalytic applications should have high stability and numerous strong protonic acid sites. Therefore, developing a facile and effective approach to immobilization sulfuric acid on a solid support is would be beneficial. In this regard, many support materials are often used for immobilization of sulfuric acid such as mesoporous silica,[17–23] amorphous silica,[24] mesoporous carbon,[25] amorphous carbon,[26–32] and polymers.[33–38] These supports can be separated by conventional separation techniques such as centrifugation and filtration. Recently, magnetic nanomaterials have emerged as alternatives to conventional materials as readily available, robust, high surface area heterogeneous catalyst supports.[39–42] Notably, one of the interesting features of magnetically supported catalysts is that they can be easily recovered with an external magnet.[43–50]

Herein, we report a simple bench-top synthesis of sulfonated core-shell magnetic nanoparticles (SMNPs) (Fe_3O_4@SiO_2@$PrSO_3H$) and discuss their performance as a very strong solid acid in the Pechmann condensation reaction. Silica coated Fe_3O_4 nanoparticles were prepared by a known procedure, which utilizes cheap starting materials.[51–53] The resulting silica-coated magnetic nanoparticles were then allowed to react under vigorous stirring with an appropriate concentration of (3-mercaptopropyl)trimethoxysilane to give mercaptopropyl-functionalized silica-coated magnetic nanoparticles (Fe_3O_4@SiO_2@PrSH). To this end, the obtained mercaptopropyl-coated Fe_3O_4 were oxidized to the corresponding sulfonic acid derivative using H_2O_2 as the oxidant (Scheme 1).

To confirm the synthesis of the Fe_3O_4 magnetic nanoparticles, XRD analysis was performed (Figure 1). As can be seen in Figure 1, the nanomagnets exhibit six well resolved peaks that are indexable as the (2 0 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0) that exactly match with the standard Fe_3O_4 sample (JCPDS file No. 19-0629). The size of Fe_3O_4 magnetic nanoparticles was estimated to be approximately 40 nm by employing the Debye–Scherrer equation from XRD analysis. Inspection of the catalyst TEM images indicates magnetic nanoparticles with a size distribution of 30–60 nm (average $\approx$40 nm), a value which is in good agreement with the diameter estimated from the XRD spectra (Figure 2).

The FT-IR spectrum of SMNPs shows peaks that are characteristic of SO_3H-functionalized magnetic nanoparticles (Fe_3O_4@SiO_2@$PrSO_3H$), which differ from that of the silica-

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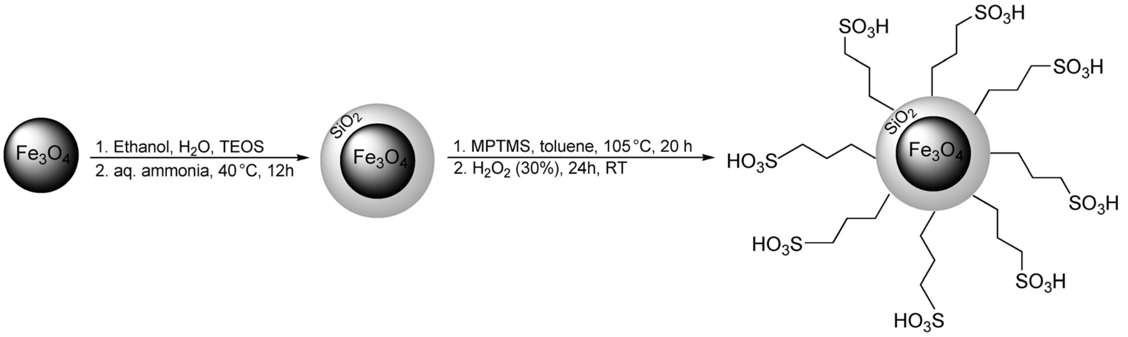


Scheme 1. Synthesis of sulfonated core-shell magnetic nanoparticles (SMNPs, $Fe_3O_4@SiO_2@PrSO_3H$).

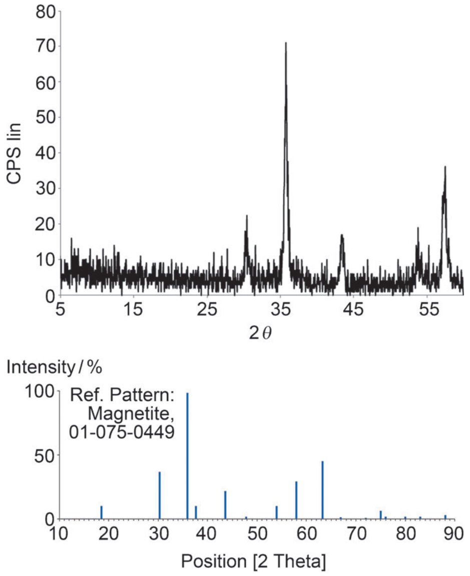


Figure 1. Powder XRD patterns of Fe_3O_4.

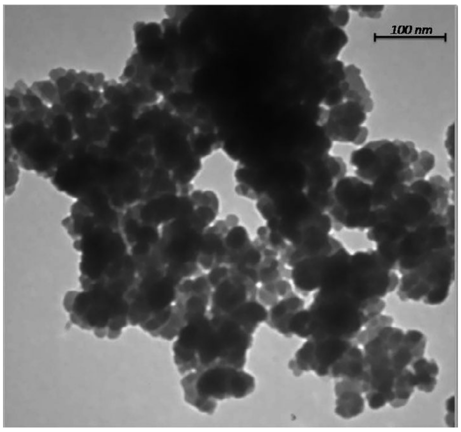


Figure 2. TEM image of the $Fe_3O_4@SiO_2@PrSO_3H$. Scale bar = 100 nm.

coated magnetic nanoparticles ($Fe_3O_4@SiO_2$). The antisymmetric stretching vibrations peaks of Si-O-Si bond in the silica shell are shown around 1084 cm^{-1}. Furthermore, the presence of alkyl groups in the $Fe_3O_4@SiO_2@SO_3H$ is confirmed by the aliphatic weak C–H stretching vibrations at 2923 cm^{-1} (Figure 3 B). Absorbance bands at 3100–3700 cm^{-1} were attributed to the OH groups on the core-shell magnetic nanoparticle surface after the modification and sulfonation (Figure 3 B). The increase in the intensity of this band suggests that there are more OH groups over the surface of final catalyst in comparison with the spectra of the unfunctionalized catalyst (Figure 3 A). This analysis corroborated the successful anchoring of the SO_3H groups on the surface of magnetic nanoparticles (Figure 3).

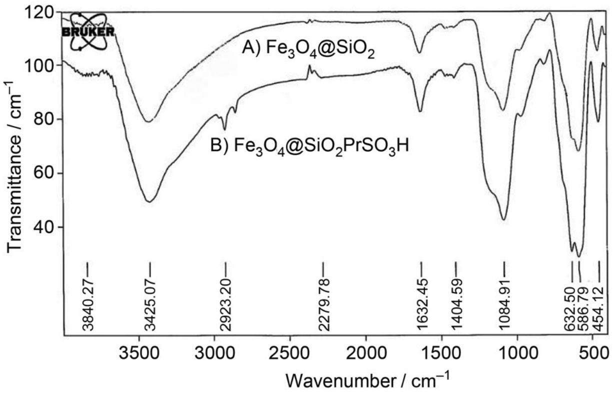


Figure 3. FT-IR spectrum of A) $Fe_3O_4@SiO_2$ B) $Fe_3O_4@SiO_2@PrSO_3H$.

To investigate the magnetic properties of the naked Fe_3O_4 nanoparticles and SMNPs, the vibrating sample magnetometer (VSM) was performed at room temperature and applied magnetic field up to 10 000 Oe. The magnetic hysteresis loop showed ferromagnetic property for both of samples. The magnetic saturation of naked Fe_3O_4 nanoparticles, silica coated magnetic nanoparticles and SMNPs, are 55 emu g^{-1}, 43 emu g^{-1}, and 40 emu g^{-1}, respectively (Figure 4). This reduced magnetic strength is attributed to the silica shells coated on magnetic nanoparticles.

The loading of the SO_3H groups onto the magnetic nanoparticles can be calculated from thermogravimetric analysis (TGA) (Supporting Information), ion exchange pH analysis and elemental analysis, which confirmed a loading of approximately 0.9 mmol g^{-1}.

In continuation of our studies on the catalytic properties of heterogeneous acid catalysts,[20–23,25] the catalytic activity of SMNPs was tested against the Pechmann condensation reaction. We chose this reaction for two reasons: 1) the Pechmann

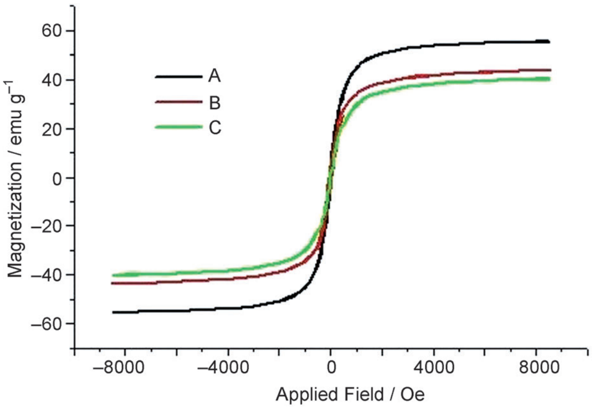
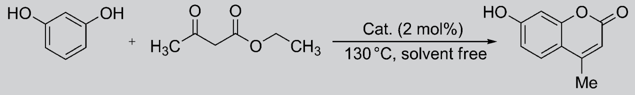


Figure 4. Magnetic hysteresis curves of A) Fe_3O_4, B) Fe_3O_4@SiO_2, C) Fe_3O_4@SiO_2@$PrSO_3H$.

Table 1. Comparison of activity of some homogeneous and heterogeneous sulfonic acid catalysts in Pechmann condensation of resorcinol with ethyl acetoacetate.[a]



Entry	Catalyst	Time [min]	Yield [%][b]
1	Fe_3O_4@SiO_2@$PrSO_3H$	25	96
2	none	25	N.R.
3	H_2SO_4	25	10
4	*p*-TSOH	25	10
5	SBA-15-Ph-$PrSO_3H$[c]	60	90
6	CMK-5-SO_3H[d]	20	95
7	mordenite[e]	420	88
8	zeolite BEA[f]	240	63

[a] Reaction condition: resorcinol (1 mmol), ethyl acetoacetate (1 mmol), catalyst (≈1.6 mol%) at 130 °C. [b] Isolated yields. [c] ≈7 mol% of SBA-15-Ph-$PrSO_3H$ was used. [d] 3 mol% of CMK-5-SO_3H was used. [e] Reaction condition: resorcinol (10 mmol), ethyl acetoacetate (10 mmol), 60 °C, catalysts (0.3 g), ultrasound.[62] [f] Reaction condition: resorcinol (8.5 mmol), ethyl acetoacetate (10 mmol), catalyst (0.2 g), solvent $PhNO_2$, 130 °C.[63]

reaction is usually performed in high temperature, and hence the stability and reusability of the catalyst can be investigated under this harsh reaction conditions; 2) Coumarins as the products of this reaction are extremely valuable in the range from additive in foods, perfumes, cosmetics, pharmaceuticals, and in the preparation of insecticides,[54] optical brighteners,[55] and dispersed fluorescent and tunable laser dyes.[56] Additionally, some coumarins have varied bioactivities, such as, inhibitory of platelet aggregation,[57] antibacterial,[58] anticancer,[59] and inhibitory of HIV-1 protease.[60] Coumarins also act as intermediate for the synthesis of furocoumarins, chromones, coumarones, and 2-acylresorcinols.[61] These wide-ranging properties mean that coumarins are very interesting to chemists.

In this sense, the feasibility of the reaction was initially examined with resorcinol and ethyl acetoacetate. At the outset, we found that, when a mixture of resorcinol (1 mmol), ethyl acetoacetate (1 mmol), and a small amount of SMNPs (1.6 mol% of SO_3H groups), at 130 °C was stirred for 25 min, the corresponding coumarin was obtained in a 96% yield (Table 1, entry 1). As expected, reaction did not proceed without catalyst (Table 1, entry 2). 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, SBA-15-Ph-$PrSO_3H$, and CMK-5-SO_3H under the same reaction condition and compared with zeolites under different conditions (Table 1, entries 3–8). It can be clearly seen that Fe_3O_4@SiO_2@$PrSO_3H$ with lower catalyst loading exhibits higher activity in Pechmann coupling reaction of resorcinol and ethyl acetoacetate under the same reaction condition. The most important issue that should be considered for practical applications of heterogeneous systems is the easy recovery of catalyst from the reaction. In compared with other heterogeneous catalysts (Table 1), SMNPs can recover more easily from reaction mixture with an external magnet and reused for several times without decrease in catalytic activity.

Encouraged by these results and having established that Fe_3O_4@SiO_2@$PrSO_3H$ constitutes an active catalyst system for von Pechmann condensation, we then investigated substrate generality of substituted phenols and ethyl acetoacetate under optimized conditions (Table 2). Resorcinol, hydroquinone, and substrates with electron-donating groups *para* to the site of electrophilic substitution afforded good yields of corresponding coumarin derivatives (Table 2, entries 1–5). Interestingly, 3-methoxyphenol showed no detectable demethylation under the given conditions (Table 2, entry 3) and 3-aminophenol reacted to provide the amino coumarin in good yield with high chemoselectivity (Table 2, entry 5). Pyrogallol, phloroglucinol, orcinol, 3,5-dimethyl phenol, and 2,6-dihydroxy toluene (Table 2, entries 6–10) also gave excellent yields in shorter reaction times. However, 1-naphthol and 2-naphthol required longer reaction times, owing to the presence of another phenyl rings (Table 2, entries 11–12).

Our attention next turned to the recycling performance of the catalyst in the condensation of resorcinol with ethyl acetoacetate. After the completion of the first run, the catalyst was effortlessly separated from the reaction medium by an external magnet. As shown in Figure 5, the recovered catalyst could be directly reused in twenty two successive runs without significant loss of activity.

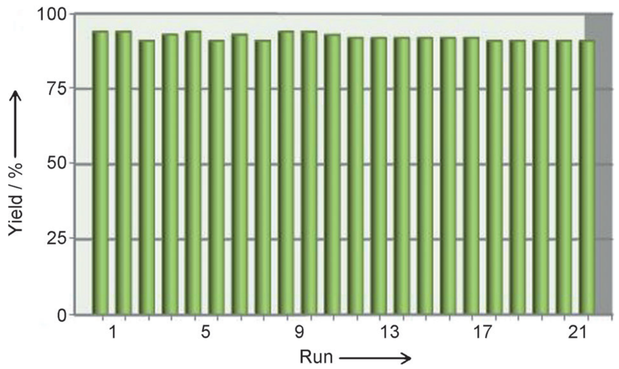
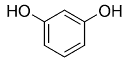
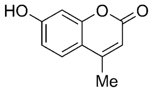
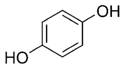
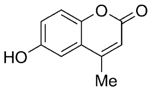
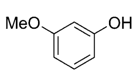
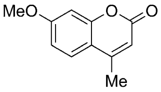
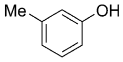
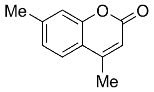
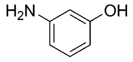
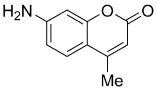
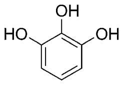
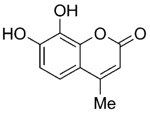
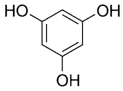
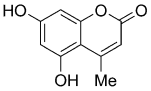
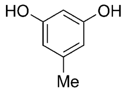
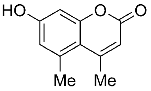
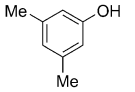
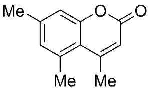
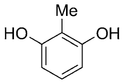
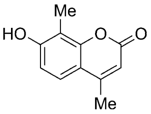
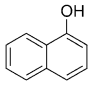
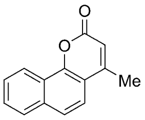
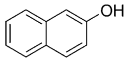
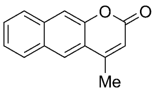


Figure 5. Recyclability of the catalyst for the Pechmann condensation of resorcinol.

Table 2. Synthesis of coumarins by Fe_3O_4@SiO_2@$PrSO_3H$.

Entry	Substrate	Product[a]	Time [min]	Yield [%][b,c]
1			25	96
2			30	90
3			35	88
4			35	87
5			30	93
6			25	97
7			20	98
8			25	94
9			30	90
10			3	89
11			50	91
12			45	88

[a] Reaction condition: substrates (1 mmol), ethyl acetoacetate (1 mmol), Fe_3O_4@SiO_2@$PrSO_3H$ (1.6 mol%),130 °C. [b] All products were characterized by comparison of their ^1H and ^{13}C NMR spectra with those of authentic samples. [c] Isolated yields after recrystallization.

In conclusion, sulfonated core-shell magnetic nanoparticles (Fe_3O_4@SiO_2@$PrSO_3H$) was established as a simple and highly recyclable solid acid, which can be prepared by low cost precursors and facile immobilization technique. Fe_3O_4@SiO_2@$PrSO_3H$ was an effective catalyst for the Pechmann condensation reaction of a neat mixture of phenols with ethyl acetoacetate leading to the formation of excellent yields of coumarin derivatives at 130 °C. The excellent catalytic capacity and outstanding recyclability of catalyst, the simple separation and solvent-free reaction conditions add to the versatility of this method. Further study to catalytic applications of this system especially for bio-diesel formation is under way in our group.

Experimental Section

Chemicals were either prepared in our laboratories or were purchased from Alderich or Fluka chemical companies. Reaction monitoring was achieved by TLC on silica-gel polygram SILG/UV 254 plates. The products were characterized by ^1H and ^{13}C NMR spectroscopy by using Bruker 250 or 400 MHz apparatus. X-ray diffraction (XRD) patterns were recorded by an Xpert-Pro, X-ray diffractometer using CuKα radiation. A transmission electron microscope, TEM (Philips CM-10), was also used to obtain TEM images.

Synthesis of magnetic nanoparticles (Fe_3O_4): In a typical preparation procedure, $FeCl_2$ (5.4 g) and $FeCl_3$ (2 g) was dissolved in aqueous hydrochloride acid (2 M, 25 mL) at room temperature and sonicated until the salts dissolved completely. Subsequently, aqueous ammonia (25%, 40 mL) was added slowly over 20 min to the mixture. The resultant solution was stirred for 30 min under argon atmosphere at room temperature. The Fe_3O_4 nanoparticles were then separated by external magnet and thoroughly washed with distilled water and ethanol and dried under vacuum to obtain the final product. Also, the Fe_3O_4 nanoparticles could be re-suspended in ethanol and stored in the refrigerator to use.

Synthesis of silica-coated magnetic nanoparticles: The resulting Fe_3O_4 was then dispersed in deionized water (6 mL) and ethanol (35 mL) and gently sonicated for 15 min to obtain a homogeneous dispersion of magnetic nanoparticles. Subsequently tetraethyl orthosilicate (TEOS, 1.5 mL) was added slowly to the mixture and sonicated for 10 min. and then aqueous ammonia (10%, 1.4 mL) was added slowly over 10 min under mechanical stirrer. The mixture was heated at 40 °C for 12 h. To this end, the silica coated magnetic nanoparticles (Fe_3O_4@SiO_2) were separated by an external magnet and washed three times with ethanol and dried under vacuum.

Synthesis of the mercaptopropyl silica-coated magnetic nanoparticles: The resulting Fe_3O_4@SiO_2 (10 g) was then dispersed in toluene (200 mL) and gently sonicated for 30 min to produce a homogeneously mixed solution. After that, (3-mercaptopropyl)trimethoxysilane (2.5 mL) was added under mechanical stirring and the mixture was slowly heated to 105 °C and kept at this temperature for 20 h. The final material was separated by an external magnet and washed three times with distilled water and ethanol and dried under vacuum. The concentrated product stored in a refrigerator to use.

Synthesis of sulfonic acid supported on the silica coated magnetic nanoparticles (SMNPs): The resulting MMNPs were then dispersed in hydrogen peroxide (30%, 100 mL) and the mixture was stirred vigorously for 24 h under room temperature. After 12 h, sulfuric acid (6 M, 200 mL) was added slowly to the mixture. The final catalyst was separated by an external magnet and washed several times with distilled water and ethanol and dried under vacuum. The concentrated product could be stored in a refrigerator to use.

General procedure for the Pechmann condensation: In a round bottom flask, SMNPs (0.018 g, 1.6 mol%) was added to the mixture of phenolic compounds (1 mmol) and ethylacetoacetate (1 mmol) at 130 °C and the reaction mixture stirred for the appropriate time. The progress of reaction was monitored by TLC (eluent, *n*-hexane/

ethyl acetate, 4:1). After the completion of the reaction, the reaction mixture was diluted with ethanol and the catalyst separated with an external magnet to obtain the crude product. Compounds with purity below 95 % were further purified using column chromatography on silica gel and then recrystallized from hot ethanol to afford pure coumarin derivatives. All compounds were identified by comparison of ^{1}H NMR, and ^{13}C NMR with those reported. The ^{1}H and ^{13}C spectra of the products are reported in the Supporting Information.

General procedure for recycling magnetized species: After the completion of first condensation of resorcinol with ethyl acetoacetate in quantitative yield, the catalyst was separated by an external magnet and washed with EtOH (5 mL), and finally used directly for a subsequent round of reaction without further purification. A new reaction was then performed with fresh reactants, under the same conditions. Moreover, the catalyst could be recycled and reused in more than twenty two subsequent reaction cycles without significant loss of catalytic activity.

Keywords: condensation · coumarin · heterogeneous catalysis · nanoparticles · solid acid

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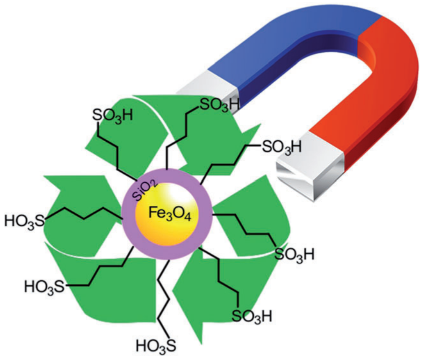
Sulfonated Core-Shell Magnetic Nanoparticle (Fe_3O_4@SiO_2@$PrSO_3H$) as a Highly Active and Durable Protonic Acid Catalyst; Synthesis of Coumarin Derivatives through Pechmann Reaction



Green earth and blue sky: Herein, we wish to disclose a simple bench top procedure for the synthesis of sulfonated core-shell magnetic nanoparticles (SMNPs) (Fe_3O_4@SiO_2@$PrSO_3H$) and discuss its performance as a very strong solid acid in the Pechmann condensation reaction.