

# Application of Sulfonic Acid Functionalized Nanoporous Silica (SBA-Pr-SO<sub>3</sub>H) in the Green One-pot Synthesis of Polyhydroacridine Libraries

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**ABSTRACT:** 1,8-Dioxo-decahydroacridines have been synthesized by the three-component reaction of aromatic aldehydes, aromatic amines (or ammonium acetate), and dimedone in the presence of sulfonic acid functionalized nanoporous silica (SBA-Pr-SO<sub>3</sub>H) under solvent-free conditions. Excellent yields, short reaction times, mild reaction conditions, and easy work-up procedures are advantages of this green method.

**KEY WORDS:** Acridine derivatives, Nano-reactor, Functionalized mesoporous materials, Dimedone.

## INTRODUCTION

Multi-Component Reactions (MCRs) have recently appeared as powerful alternatives to more traditional strategies, mainly by means of their operational simplicity and high atom economy [1-4]. The current literature reveals that 1,4-dihydropyridine derivatives exhibit interesting biological activities such as anti-microbial [5], anti-viral [6], anti-HIV [7], and anti-cancer [8, 9] activities. Acridines and their derivatives as polyfunctionalized 1,4-dihydropyridines, have been found to possess a wide spectrum of biological activities [10, 11], but recent research has mainly focused on their utility as anticancer [12], antitumor [13], and anti-Alzheimer's disease drugs [14]. In the literature some methods

are available for the synthesis of acridine compounds containing 1,4-dihydropyridines, from the reaction of dimedone, aldehydes and ammonium acetate or different substituted anilines via traditional heating in organic solvents [15], using ionic liquids [16], or microwave/ H<sub>2</sub>O [17], and in the presence of different catalysts such as TEBAC/H<sub>2</sub>O [18], silica-bonded s-sulfonic acid [19], *p*-dodecyl benzenesulfonic acid [20], amberlyst-15 [21], CeCl<sub>3</sub>·7H<sub>2</sub>O [22], tris(pentafluorophenyl) borane [23], HY zeolite [24], and PEG-400/ CAN [25].

Mesoporous materials have been receiving considerable attention in recent years because of their

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potential application as catalysts [26], supports [27], adsorbents [28] as well as nano-reactors [29]. The SBA-15 is new nanoporous silica with hexagonal structure, high surface area, large pore size, great pore wall thickness, and high thermal stability. It has been functionalized with different groups to produce highly active and selective catalysts [30, 31]. Integration of acidic functional groups (e.g.,  $\text{SO}_3\text{H}$ ) into SBA-15 has also been explored to produce promising solid acids [32]. Recently, there has been an increasing number of reports about the applications of these materials as catalysts in chemical transformations [33-36].

In continuation of our work on the application of heterogeneous solid catalysts in multi-component synthesis of heterocyclic compounds [37-40], herein we want to report the synthesis of acridinedione derivatives in the presence of sulfonic acid functionalized SBA-15 (SBA-Pr- $\text{SO}_3\text{H}$ ).

## EXPERIMENTAL SECTION

All chemicals were obtained commercially and used without further purification. IR spectra were recorded from KBr disk using a FT-IR Bruker Tensor 27 instrument. Melting points were measured by using the capillary tube method with an electro thermal 9200 apparatus. The  $^1\text{H}$  NMR (500 MHz) was run on a Bruker DPX, 500 MHz. GC-Mass analysis was performed on a GC-Mass model: 5973 network mass selective detector, GC 6890 Agilent. SEM analysis was performed on a Philips XL-30 field-emission scanning electron microscope operated at 16 kV while TEM was carried out on a Tecnai G<sup>2</sup> F30 at 300 kV.

### Synthesis and functionalization of SBA-15

The nanoporous compound SBA-15 was synthesized and functionalized according to our previous report [38] and the modified SBA-Pr- $\text{SO}_3\text{H}$  was used as nanoporous solid acid catalyst in the following reaction.

### General procedure for the synthesis of 1,8-dioxo-decahydroacridine derivatives 4a-h

The SBA-Pr- $\text{SO}_3\text{H}$  (0.02 g) was activated in vacuum at 100 °C and then after cooling to room temperature, dimedone **1** (2 mmol, 0.28 g), aromatic aldehyde **2** (1 mmol), and aryl amine or ammonium acetate **3** (1.2 mmol) were added to it. The mixture was heated under solvent-free condition for an appropriate time while the reaction was monitored by TLC. After completion of the reaction,

the crude product was dissolved in hot ethanol and then the catalyst was removed by filtration. The pure product was obtained by cooling of filtrate. The catalyst was washed subsequently with diluted acid solution, distilled water and then acetone, dried under vacuum and re-used for several times without loss of significant activity.

### 3,3,6,6-Tetramethyl -9-(2-methoxyphenyl) -1,8-dioxo-decahydroacridine (4a)

IR (KBr): 3314, 3285, 2953, 1638, 1589, 1485, 1366, 1225, 1143  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.86 (s, 6H, 2 $\text{CH}_3$ ), 1.01 (s, 6H, 2 $\text{CH}_3$ ), 2.07 (d,  $J$  = 16.5 Hz, 2H,  $\text{CH}_2$ ), 2.17 (d,  $J$  = 16.6 Hz, 2H,  $\text{CH}_2$ ), 2.29 (d,  $J$  = 16.5 Hz, 2H,  $\text{CH}_2$ ), 2.36 (d,  $J$  = 16.6 Hz, 2H,  $\text{CH}_2$ ), 3.77 (s, 3H,  $\text{OCH}_3$ ), 5.20 (s, 1H, CH), 6.20 (s, 1H, NH), 6.74-6.81 (m, 1H, ArH), 7.04-7.22 (m, 1H, ArH), 7.23 (d,  $J$  = 8.7 Hz, 1H, ArH), 7.39 (d,  $J$  = 8.7 Hz, 1H, ArH) ppm. MS:  $m/z$  (%) 380 [ $\text{M}^+$ ], 363, 349, 296, 273, 217.

### 3,3,6,6-Tetramethyl -9-(2,3-dimethoxyphenyl) -1,8-dioxo-decahydroacridine (4c)

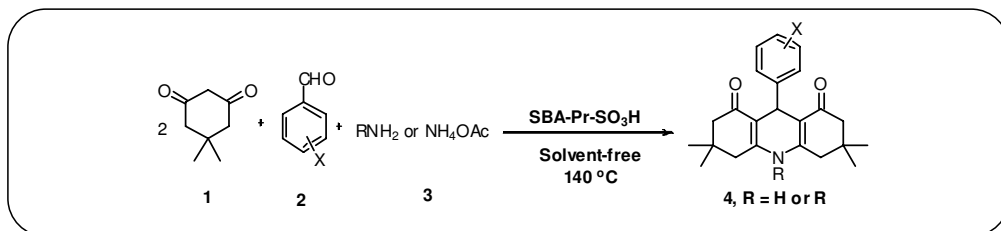
IR (KBr): 3283, 2959, 1640, 1614, 1487, 1364, 1225, 1143  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.99 (s, 6H, 2 $\text{CH}_3$ ), 1.09 (s, 6H, 2 $\text{CH}_3$ ), 2.18 (d,  $J$  = 16.5 Hz, 2H,  $\text{CH}_2$ ), 2.20 (d,  $J$  = 16.6 Hz, 2H,  $\text{CH}_2$ ), 2.30 (d,  $J$  = 16.5 Hz, 2H,  $\text{CH}_2$ ), 2.36 (d,  $J$  = 16.6 Hz, 2H,  $\text{CH}_2$ ), 3.73 (s, 3H,  $\text{OCH}_3$ ), 3.75 (s, 3H,  $\text{OCH}_3$ ), 5.32 (s, 1H, CH), 6.35 (s, 1H, NH), 6.74-6.76 (m, 1H, ArH), 7.20 (d,  $J$  = 8.7 Hz, 1H, ArH), 7.26 (d,  $J$  = 8.7 Hz, 1H, ArH) ppm. MS:  $m/z$  (%) 410 [ $\text{M}^+$ ], 379, 323, 295, 273, 217.

### 3,3,6,6-Tetramethyl -9-(4-nitrophenyl) -1,8-dioxo-octahydroxanthene (5a)

IR (KBr): 3448, 2958, 1637, 1578, 1488, 1363, 1341, 1221, 1145  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.00 (s, 6H, 2 $\text{CH}_3$ ), 1.11 (s, 6H, 2 $\text{CH}_3$ ), 2.18 (d,  $J$  = 17.6 Hz, 2H, 2  $\times$  CH), 2.35 (d,  $J$  = 16 Hz, 2H, 2  $\times$  CH), 2.47 (d,  $J$  = 16 Hz, 2H, 2  $\times$  CH), 2.63 (d,  $J$  = 17.6 Hz, 2H, 2  $\times$  CH), 4.07 (s, 1H, CH), 7.49 (d,  $J$  = 8.8 Hz, 2H, ArH), 7.54 (d,  $J$  = 8.8 Hz, 2H, ArH) ppm. MS:  $m/z$  (%) 395 [ $\text{M}^+$ ].

### 3,3,6,6-Tetramethyl -9-(2-methoxyphenyl) -1,8-dioxo-octahydroxanthene (5b)

IR (KBr): 2954, 1661, 1623, 1421, 1426, 1360, 1250  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.97 (s, 6H, 2 $\text{CH}_3$ ), 1.1 (s, 6H, 2 $\text{CH}_3$ ), 2.12 (d,  $J$  = 17.6 Hz, 2H, 2  $\times$  CH),



Scheme 1

2.15 (d,  $J = 16$  Hz, 2H, 2  $\times$  CH), 2.20 (d,  $J = 16$  Hz, 2H, 2  $\times$  CH), 2.36 (d,  $J = 17.6$  Hz, 2H, 2  $\times$  CH), 3.78 (s, 3H, CH<sub>3</sub>O), 4.86 (s, 1H, CH), 6.78-7.10 (m, 2H, ArH), 7.42 (d,  $J = 8.8$  Hz, 2H, ArH) ppm. MS:  $m/z$  (%) 380 [M<sup>+</sup>].

### 3,3,6,6-Tetramethyl -9-(4-hydroxyphenyl) -1,8-dioxo-octahydroxanthene (5c)

IR (KBr): 3399, 2960, 1653, 1615, 1421, 1365, 1225, 1197 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.00 (s, 6H, 2CH<sub>3</sub>), 1.1 (s, 6H, 2CH<sub>3</sub>), 2.17 (d,  $J = 17.6$  Hz, 2H, 2  $\times$  CH), 2.23 (d,  $J = 16$  Hz, 2H, 2  $\times$  CH), 2.26 (d,  $J = 16$  Hz, 2H, 2  $\times$  CH), 2.46 (d,  $J = 17.6$  Hz, 2H, 2  $\times$  CH), 4.68 (s, 1H, CH), 7.12 (d,  $J = 8.8$  Hz, 4H, ArH) ppm. MS:  $m/z$  (%) 366 [M<sup>+</sup>].

## RESULTS AND DISCUSSION

In this paper, the synthesis of 1,8-dioxo-decahydroacridine derivatives **4** through the three-component condensation of dimedone **1**, aromatic aldehydes **2**, and nitrogen source like ammonium acetate or aromatic amines **3** in the presence of SBA-Pr-SO<sub>3</sub>H as an efficient nanoparticle with acidic properties has been studied (Scheme 1). For finding the best reaction conditions, at first, we investigated the effects of solvents on this synthesis. The reaction of dimedone **1**, 4-methoxybenzaldehyde **2b** and ammonium acetate **3** was selected as the reaction model. Among the different conditions such as H<sub>2</sub>O, EtOH, MeCN, H<sub>2</sub>O/EtOH, and solvent-free condition, it was found that solvent-free condition results in the highest yield in a reasonable time (Table 1). Therefore, the evaluation of this reaction was made under solvent-free condition at 140 °C for the synthesis of 1,8-dioxo-decahydroacridines **4a-h** and the results are summarized in Table 2. Surprisingly, contrary to our expectation, in the case of aromatic amines

such as 4-nitroaniline, 2-nitroaniline, and 4-bromoaniline, 1,8-dioxo-octahydroxanthenes **5a-c** were obtained as the major products. A wide range of aromatic aldehydes containing both electron-donating and electron-withdrawing groups have been used in this reaction and in all cases, high yields of products were obtained. It was reported that in the absence of the catalyst the product was obtained in low yield (30%) [41].

A proposed mechanism for the synthesis of decahydroacridines **4a-h** is outlined in Scheme 2. At first, the acid catalyst changes aldehyde **2** into the convenient electrophile via protonation of carbonyl group which then, condenses with one molecule of dimedone **1** in a fast Knoevenagel condensation to produce intermediate **6**. Simultaneously, the condensation of another molecule of dimedone **1** with amine **3** gives the enamine intermediate **7** which reacts to intermediate **6** via Michael addition reaction to produce the adduct product **8**. Finally, after an intramolecular cyclization followed by dehydration, the compound **8** is converted to the expected product **4**.

In this procedure, SBA-Pr-SO<sub>3</sub>H plays a crucial role in accelerating the reaction. The reaction takes place in the pores of SBA-Pr-SO<sub>3</sub>H which acts as a nano-reactor (Fig. 1). After completion of reaction, the crude product was dissolved in hot EtOH and SBA-Pr-SO<sub>3</sub>H was easily filtrated from the reaction mixture. The catalyst washed subsequently with diluted acid solution, distilled water and then acetone, dried under vacuum and re-used for several times without significant loss of activity. The reusability of the catalyst was investigated under optimized conditions for the synthesis of the model compound **4b**. As it is shown in Fig. 2, the process of recycling was completed four times and no significant decrease in activity was observed. The yields for the four runs were found to be 92%, 86%, 79%, and 71%, respectively.

**Table 1: The effects of different conditions on the synthesis of 4b.**

| Entry | Solvent                      | Time (h) | Yield (%) |
|-------|------------------------------|----------|-----------|
| 1     | H <sub>2</sub> O             | 5        | 43        |
| 2     | EtOH                         | 5        | 34        |
| 3     | EtOH/ H <sub>2</sub> O (1:1) | 5        | 48        |
| 4     | CH <sub>3</sub> CN           | 3        | 57        |
| 5     | Neat                         | 25 min   | 92        |

**Table 2: The synthesis of 1,8-dioxo-decahydroacridines 4 in the presence of SBA-Pr-SO<sub>3</sub>H.**

| Entry | Product | Time (min) | Yield (%) | Mp (°C) | Mp (L)       |
|-------|---------|------------|-----------|---------|--------------|
| 1     | 4a      | 25         | 70        | 287-290 | 294-296 [42] |
| 2     | 4b      | 25         | 92        | 304-307 | 298-300 [43] |
| 3     | 4c      | 25         | 59        | 316-318 | 324-326 [42] |
| 4     | 4d      | 25         | 59        | 292-294 | 296-297 [43] |
| 5     | 4e      | 25         | 62        | 298-301 | 296-298 [44] |
| 6     | 4f      | 25         | 77        | 316-320 | 318-320 [22] |
| 7     | 4g      | 25         | 66        | 290     | 290-291 [45] |
| 8     | 4h      | 25         | 58        | 249-251 | 260-262 [46] |
| 9     | 5a      | 40         | 59        | 227-231 | 225-227 [47] |
| 10    | 5b      | 45         | 90        | 192-195 | 190-191 [48] |
| 11    | 5c      | 40         | 63        | 245-248 | 245-250 [47] |

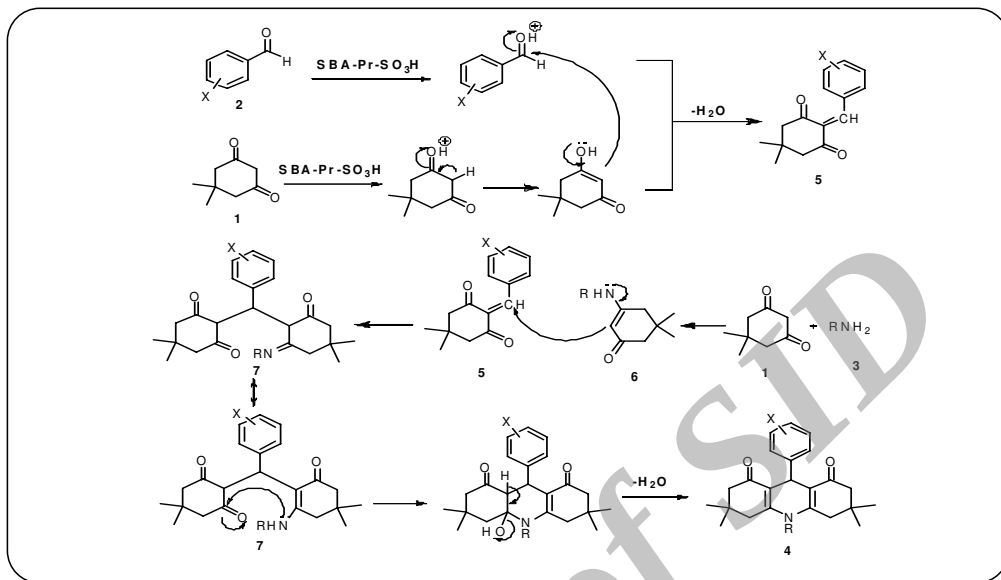
The efficiency of various catalysts in the synthesis of 1,8-dioxo-decahydroacridines **4** has been compared in Table 3. Short reaction times and high yield of products and, in contrast with other existing methods, demonstrated that SBA-Pr-SO<sub>3</sub>H acts as an efficient nano-reactor in this reaction.

The SBA-15 as a new nanoporous silica can be prepared by using commercially available triblock copolymer pluronic P126 as a structure directing agent [51]. The sulfonic acid functionalized SBA-15 was usually synthesized through direct synthesis or post-grafting [52, 53]. A schematic illustration for the preparation of SBA-Pr-

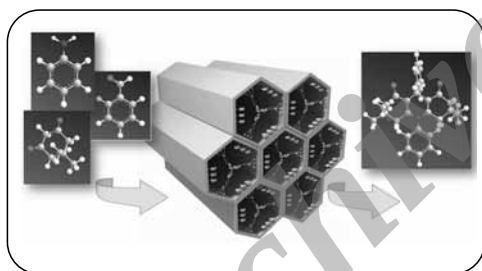
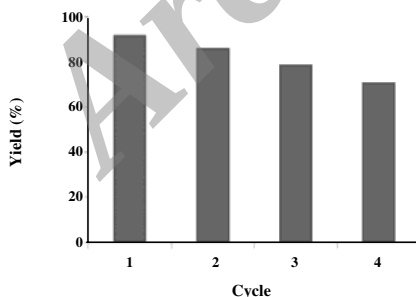
SO<sub>3</sub>H was shown in Fig. 3. At First, the calcined SBA-15 silica was functionalized with (3-mercaptopropyl) trimethoxysilane (MPTS) and then, the thiol groups were oxidized to sulfonic acid by hydrogen peroxide.

The surface of the catalyst was analyzed by different methods such as TGA, BET and other methods which were demonstrated that the organic groups (propyl sulfonic acid) were immobilized into the pores [38].

Fig. 4 illustrates the SEM and TEM images of SBA-Pr-SO<sub>3</sub>H. SEM image (Fig. 4, a) shows uniform particles about 1μm which the same morphology was observed for SBA-15. It can be concluded that morphology of the solid



Scheme 2

Fig. 1: SBA-Pr-SO<sub>3</sub>H acts as a nano-reactor.Fig. 2: Reusability of SBA-Pr-SO<sub>3</sub>H in the synthesis of compound 4b.

was saved without change during the surface modifications. On the other hand, the TEM image (Fig. 4, b) reveals the parallel channels, which resemble the pores configuration of SBA-15. This indicates that the pore of SBA-Pr-SO<sub>3</sub>H was not collapsed during two steps reactions.

## CONCLUSIONS

In conclusion, an efficient methodology for Hantzsch reaction using SBA-Pr-SO<sub>3</sub>H as a nano-reactor was introduced. SBA-15 functionalized with Brønsted sulfonic sites shows the favorable acidity to activate the substrate molecules to obtain 1,8-dioxo-decahydroacridines in excellent yield. The catalyst could be recovered and reused for several reaction cycles without noticeable loss of reactivity. Mild reaction condition, simplicity of the procedure, and short reaction times are the significant advantages of this methodology.

## Acknowledgements

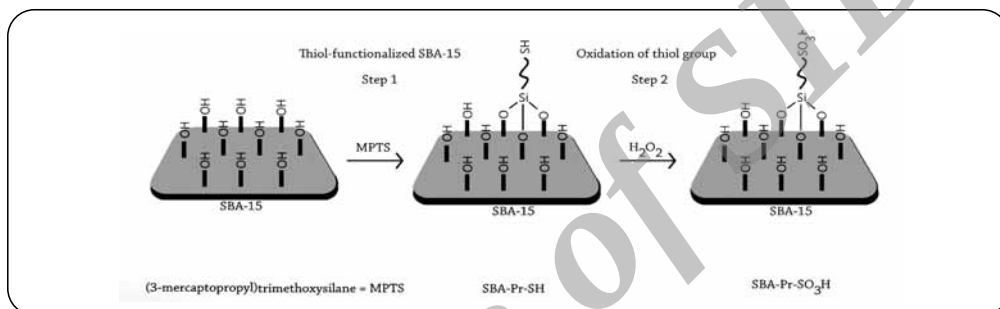
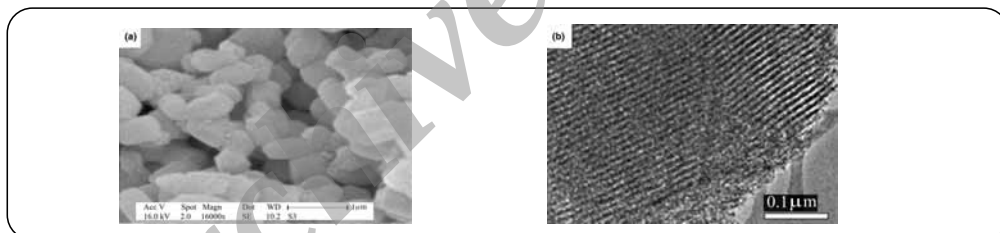
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Table 3: Comparison of different conditions in the synthesis of 1,8-dioxo-decahydroacridines.

| Entry | Catalyst                 | Solvent          | Condition | Time (h) | Yield | Year      | Ref  |
|-------|--------------------------|------------------|-----------|----------|-------|-----------|------|
| 1     | TEBAC <sup>a</sup>       | H <sub>2</sub> O | Reflux    | 4-8      | 90-98 | 2006      | [18] |
| 2     | [Hmim]TFA <sup>b</sup>   | —                | Heating   | 4-7      | 78-89 | 2008      | [16] |
| 3     | HY-Zeolite               | EtOH             | Reflux    | 2.5-3.5  | 70-90 | 2009      | [24] |
| 4     | SDS <sup>c</sup>         | H <sub>2</sub> O | Reflux    | 6-20     | 56-72 | 2009      | [49] |
| 5     | SBSSA <sup>d</sup>       | EtOH             | Reflux    | 1-4.5    | 84-96 | 2010      | [19] |
| 6     | SBNPSA <sup>e</sup>      | EtOH             | Reflux    | 2-5      | 86-93 | 2010      | [50] |
| 7     | CAN <sup>f</sup>         | PEG-400          | Heating   | 3.5-4    | 93-98 | 2010      | [25] |
| 8     | SBA-Pr-SO <sub>3</sub> H | —                | Heating   | 25min    | 58-92 | This work |      |

a) Triethylbenzylammonium chloride. b) 1-Methylimidazolium trifluoroacetate. c) Sodium 1-dodecanesulfonic.

d) Silica-bonded S-sulfonic acid. e) Silica bonded N-propyl sulfamic acid. f) Ceric ammonium nitrate.

Fig. 3: Schematic illustration for the preparation of SBA-Pr-SO<sub>3</sub>H.Fig. 4: SEM image (a) and TEM image (b) of SBA-Pr-SO<sub>3</sub>H.

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## REFERENCES

- [1] Bienaymé H., Hulme C., Odon G., Schmitt P., Maximizing Synthetic Efficiency: Multi-component Transformations Lead the Way, *Chem. Eur. J.*, **6**, p. 3321 (2000).
- [2] Ramón D.J., Yus M., Asymmetric Multicomponent Reactions (AMCRs): The New Frontier, *Chem. Int. Ed.*, **44**, p. 1602 (2005).
- [3] Hulme C., Gore V., Multi-Component Reactions: Emerging Chemistry in Drug Discovery from Xylocain to Crixivan, *Curr. Med. Chem.*, **10**, p. 51 (2003).
- [4] Tietze L.F., Modi A., Multicomponent Domino Reactions for the Synthesis of Biologically Active Natural Products and Drugs, *Med. Res. Rev.*, **20**, p. 304 (2000).
- [5] Vijesh A.M., Isloor A.M., Peethambar S.K., Shivananda K.N., Arulmoli T., Isloor N.A., Hantzsch Reaction: Synthesis and Characterization of Some New 1,4-Dihydropyridine Derivatives as Potent Antimicrobial and Antioxidant Agents, *Eur. J. Med. Chem.*, **46**, p. 5591 (2011).
- [6] Saeed B.A., Saour K.Y., Elias R.S., Al-Masoudi N.A., Antiviral and Quantitative Structure Activity Relationship Study for Dihydropyridones Derived from Curcumin, *Am. J. Immunol.*, **6**, p. 25 (2010).

- [7] Li A.M., Liu X.Y., Wang X.W., Liu J.Y., Design, Synthesis and Anti-HIV-1 Activity of 4,6-Dibenzyl-2-oxo-1,2-dihydropyridine-3-carbonitrile, *J. Chin. Pharm. Sci.*, **20**, p. 447 (2011).
- [8] Surendra Kumar R., Idhayadulla A., Jamal Abdul Nasser A., Murali K., Synthesis and Anticancer Activity of Some New Series of 1, 4-Dihydropyridine Derivatives, *Indian J. Chem. Sect. B*, **50**, p. 1140 (2011).
- [9] Al-Said M.S., Bashandy M.S., Al-Qasoumi S.I., Ghorab M.M., Anti-Breast Cancer Activity of Some Novel 1,2-Dihydropyridine, Thiophene and Thiazole Derivatives, *Eur. J. Med. Chem.*, **46**, p. 137 (2011).
- [10] Nagarajan G., Anush K.V.S., Mahesh A., Spandana B.L.V.M., Saminathan K., Balasubramaniam V., Manjunath K.S., Synthesis and Anti-inflammatory Activity of 6-(Substituted acridin-9-yl amino)-2,3-dihydro-3-thioxo-[1,2,4] triazolo [4,3-f][1,2,4] triazin-8 (5h)-one, *Orient. J. Chem.*, **24**, p. 1053 (2008).
- [11] Nadaraj V., Thamarai Selvi S., Mohan S., Microwave-induced Synthesis and Anti-microbial Activities of 7,10,11,12-Tetrahydrobenzo[c]acridin-8(9H)-one Derivatives, *Eur. J. Med. Chem.*, **44**, p. 976 (2009).
- [12] Belmont P., Bosson J., Godet T., Tiano M., Acridine and Acridone Derivatives, Anticancer Properties and Synthetic Methods: Where Are We Now?, *Anti-Cancer Agents Med. Chem.*, **7**, p. 139 (2007).
- [13] Bacherikov V.A., Chou T.C., Dong H.J., Chen C.H., Lin Y.W., Tsai T.J., Su T.L., Potent Antitumor N-mustard Derivatives of 9-Anilinoacridine, Synthesis and Antitumor Evaluation, *Bioorg. Med. Chem. Lett.*, **14**, p. 4719 (2004).
- [14] Zhou J., Hu X., Zhang H., Qian H., Huang W., Qi F., Zhang Y., Synthesis and Biological Evaluation of 5,6-Dihydro-benzo[c]acridin-7-ol Derivatives as Anti-Alzheimer's Disease Drugs, *Lett. Drug Des. Discovery*, **6**, p. 623 (2009).
- [15] Martin N., Quinteiro M., Seoane C., Soto J.L., Mora A., Suarez M., Ochoa E., Morales A., Del Bosque J.R., Synthesis of Conformational Study of Acridine Derivatives Related to 1,4-Dihydropyridines, *J. Heterocycl. Chem.*, **32**, p. 235 (1995).
- [16] Dabiri M., Baghbanzadeh M., Arzroomchilar E., 1-Methylimidazolium trifluoroacetate ([Hmim]TFA): An Efficient Reusable Acidic Ionic Liquid for the Synthesis of 1,8-Dioxo-octahydroxanthenes and 1,8-Dioxo-decahydroacridines, *Catal. Commun.*, **9**, p. 939 (2008).
- [17] Singh S.K., Singh K.N., Eco-friendly and Facile One-pot Multicomponent Synthesis of Acridinediones in Water under Microwave, *J. Heterocycl. Chem.*, **48**, p. 69 (2011).
- [18] Wang X.S., Zhang M.M., Shi D.Q., Tu S.J., Wei X.Y., Zong Z.M., An Improved Synthesis of Reduced 9-Arylacridine-1,8-diones from 3-Amino-5,5-dimethylcyclohex-2-enone, Arylaldehydes and 1,3-Dicarbonyl Compounds in Aqueous Medium, *J. Chem. Res.*, p. 719 (2006).
- [19] Niknam K., Panahi F., Saberi D., Mohagheghnejad M., Silica-bonded S-sulfonic Acid as Recyclable Catalyst for the Synthesis of 1,8-Dioxo-decahydroacridines and 1,8-Dioxo-octahydroxanthenes, *J. Heterocycl. Chem.*, **47**, p. 292 (2010).
- [20] Jin T.S., Zhang J.S., Guo T.T., Wang A.Q., Li T.S., One-Pot Clean Synthesis of 1,8-Dioxo-decahydroacridines Catalyzed by p-Dodecylbenzenesulfonic Acid in Aqueous Media, *Synthesis*, p. 2001 (2004).
- [21] Das B., Thirupathi P., Mahender I., Reddy V.S., Rao Y.K., Amberlyst-15: An Efficient Reusable Heterogeneous Catalyst for the Synthesis of 1,8-Dioxo-octahydroxanthenes and 1,8-Dioxo-decahydroacridines, *J. Mol. Catal. A: Chem.*, **247**, p. 233 (2006).
- [22] Fan X., Li Y., Zhang X., Qu G., Wang J., An Efficient and Green Preparation of 9-Arylacridine-1,8-dione Derivatives, *Heteroat. Chem.*, **18**, p. 786 (2007).
- [23] Chandrasekhar S., Rao Y.S., Sreelakshmi L., Mahipal B., Reddy C.R., Tris(pentafluorophenyl)borane-catalyzed Three-component Reaction for the Synthesis of 1,8-Dioxodecahydroacridines under Solvent-free Conditions, *Synthesis*, p. 1737 (2008).
- [24] Nikpassand M., Mamaghani M., Tabatabaeian K., An Efficient One-pot Three-component Synthesis of Fused 1,4-Dihydropyridines using HY-Zeolite, *Molecules*, **14**, p. 1468 (2009).
- [25] Kidwai M., Bhatnagar D., Ceric Ammonium Nitrate (CAN) Catalyzed Synthesis of N-substituted Decahydroacridine-1,8-diones in PEG, *Tetrahedron Lett.*, **51**, p. 2700 (2010).
- [26] Taguchi A., Schüth F., Ordered Mesoporous Materials in Catalysis, *Microporous Mesoporous Mater.*, **77**, p. 1 (2005).
- [27] Muylaert I., Verberckmoes A., De Decker J., Van Der Voort P., Ordered Mesoporous Phenolic Resins: Highly Versatile and Ultra Stable Support Materials, *Adv. Colloid Interface Sci.*, **175**, p. 39 (2012).
- [28] Wu Z., Zhao D., Ordered Mesoporous Materials as Adsorbents, *Chem. Commun.*, **47**, p. 3332 (2011).
- [29] Karimi B., Zareyee D., Design of a Highly Efficient and Water-tolerant Sulfonic Acid Nanoreactor Based on Tunable Ordered Porous Silica for the Von Pechmann Reaction, *Org. Lett.*, **10**, p. 3989 (2008).
- [30] Badiei A., Goldoos H., Ziarani G.M., Abbasi A., One pot Synthesis of Functionalized SBA-15 by Using an 8-Hydroxyquinoline-5-sulfonamide-modified Organosilane as Precursor, *J. Colloid Interface Sci.*, **357**, p. 63 (2011).

- [31] Saikia L., Srinivas D., Redox and Selective Oxidation Properties of Mn Complexes Grafted on SBA-15, *Catal. Today*, **141**, p. 66 (2009).
- [32] Margolese D., Melero J.A., Christiansen S.C., Chmelka B.F., Stucky G.D., Direct Syntheses of Ordered SBA-15 Mesoporous Silica Containing Sulfonic Acid Groups, *Chem. Mater.*, **12**, p. 2448 (2000).
- [33] Kureshy R.I., Ahmad I., Pathak K., Khan N.H., Abdi S.H.R., Jasra R.V., Sulfonic Acid Functionalized Mesoporous SBA-15 as an Efficient and Recyclable Catalyst for the Synthesis of Chromenes from Chromanols, *Catal. Commun.*, **10**, p. 572 (2009).
- [34] Naik M.A., Sachdev D., Dubey A., Sulfonic Acid Functionalized Mesoporous SBA-15 for One-Pot Synthesis of Substituted Aryl-14H-dibenzo Xanthenes and Bis(indolyl)methanes, *Catal. Commun.*, **11**, p. 1148 (2010).
- [35] Reddy S.S., Raju B.D., Kumar V.S., Padmasri A.H., Narayanan S., Rama Rao K.S., Sulfonic Acid Functionalized Mesoporous SBA-15 for Selective Synthesis of 4-Phenyl-1,3-dioxane, *Catal. Commun.*, **8**, p. 261 (2007).
- [36] Srinivas D., Saikia L., Functionalized SBA-15 and Its Catalytic Applications in Selective Organic Transformations, *Catal. Surv. Asia*, **12**, p. 114 (2008).
- [37] Mohammadi Ziarani G., Badiei A., Haddadpour M., Application of Sulfonic Acid Functionalized Nanoporous Silica (SBA-Pr-SO<sub>3</sub>H) for One-Pot Synthesis of Quinoxaline Derivatives, *Int. J. Chem.*, **3**, p. 87 (2011).
- [38] Mohammadi Ziarani G., Badiei A.R., Khaniania Y., Haddadpour M., One Pot Synthesis of Polyhydroquinolines Catalyzed by Sulfonic Acid Functionalized SBA-15 as a New Nanoporous Acid Catalyst under Solvent Free Conditions, *Iran. J. Chem. Chem. Eng.*, **29**(2), p. 1 (2010).
- [39] Mohammadi Ziarani G., Badiei A., Shahjafari F., Pourjafar T., A Highly Efficient Solvent-Free Acetalization of Aldehydes to 1,1-Diacetates Catalyzed by SiO<sub>2</sub>-Pr-SO<sub>3</sub>H, *S. Afr. J. Chem.*, **65**, p. 10 (2012).
- [40] Mohammadi Ziarani G., Badiei A., Azizi, M., Zaradadi, P., Synthesis of 3,4-Dihydropyrano[c]Chromene Derivatives Using Sulfonic Acid Functionalized Silica (SiO<sub>2</sub>PrSO<sub>3</sub>H), *Iran. J. Chem. Chem. Eng.*, **30**(2), p. 59 (2011).
- [41] Balalaie S., Chadehgan F., Darviche F., Bijanzadeh H.R., One-pot Synthesis of 1,8-Dioxo-decahydroacridine Derivatives in Aqueous Media, *Chin. J. Chem.*, **27**, p. 1953 (2009).
- [42] Mohammadi Ziarani G., Badiei A., Hassanzadeh M., Mousavi S., Synthesis of 1,8-Dioxo-Decahydroacridine Derivatives Using Sulfonic Acid Functionalized Silica (SiO<sub>2</sub>-Pr-SO<sub>3</sub>H) under Solvent Free Conditions, *Arabian J. Chem.*, In Press, Doi: 10.1016/j.arabjc.2011.01.037.
- [43] Wang G.W., Xia J.J., Miao C.B., Wu X.L., Environmentally Friendly and Efficient Synthesis of Various 1,4-Dihydropyridines in Pure Water, *Bull. Chem. Soc. Jpn.*, **79**, p. 454 (2006).
- [44] Tu S., Gao Y., Miao C., Li T., Zhang X., Zhu S., Fang F., Shi D., A Novel Reaction of Aldeoxime with Dimedone under Microwave Irradiation, *Synth. Commun.*, **34**, p. 1289 (2004).
- [45] Shchekotikhin Y.M., Getmanenko Y.A., Nikolaeva T.G., Kriven'ko A.P., Synthesis of 9-R1-10-R-1,8-Dioxo-decahydroacridines and Dioximes Based on Them, *Chem. Heterocycl. Compd.*, **37**, p. 1228 (2001).
- [46] Shen W., Wang L.M., Tian H., Tang J., Yu J.J., Brønsted Acidic Imidazolium Salts Containing Perfluoroalkyl Tails Catalyzed One-pot Synthesis of 1,8-Dioxo-Decahydroacridines in Water, *J. Fluorine Chem.*, **130**, p. 522 (2009).
- [47] Kantevari S., Bantu R., Nagarapu L., HClO<sub>4</sub>-SiO<sub>2</sub> and PPA-SiO<sub>2</sub> Catalyzed Efficient One-pot Knoevenagel Condensation, Michael Addition and Cyclo-Dehydration of Dimedone and Aldehydes in Acetonitrile, Aqueous and Solvent Free Conditions: Scope and Limitations, *J. Mol. Catal. A*, **269**, p. 53 (2007).
- [48] Mahdavinia G.H., Bigdeli M.A., Saeidi Hayeniaz Y., Covalently Anchored Sulfonic Acid on Silica Gel (SiO<sub>2</sub>-R-SO<sub>3</sub>H) as an Efficient and Reusable Heterogeneous Catalyst for the One-pot Synthesis of 1,8-Dioxo-octahydroxanthenes under Solvent-Free Conditions, *Chin. Chem. Lett.*, **20**, p. 539 (2009).
- [49] Shi D.Q., Shi J.W., Yao H., Three-component One-pot Synthesis of Polyhydroacrodine Derivatives in Aqueous Media, *Synth. Commun.*, **39**, p. 664 (2009).
- [50] Rashedian F., Saberi D., Niknam K., Silica-bonded N-propyl Sulfamic Acid: A Recyclable Catalyst for the Synthesis of 1,8-Dioxo-decahydroacridines, 1,8-Dioxo-octahydroxanthenes and Quinoxalines, *J. Chin. Chem. Soc.*, **57**, p. 998 (2010).
- [51] Zhao D., Feng J., Huo Q., Melosh N., Fredrickson G.H., Chmelka B.F., Stucky G.D., Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores, *Science*, **279**, p. 548 (1998).
- [52] Lim M.H., Blanford C.F., Stein A., Synthesis of Ordered Microporous Silicates with Organosulfur Surface Groups and Their Applications as Solid Acid Catalysts, *Chem. Mater.*, **10**, p. 467 (1998).
- [53] Wight A.P., Davis M.E., Design and Preparation of Organic-Inorganic Hybrid Catalysts, *Chem. Rev.*, **102**, p. 3589 (2002).