New Hydrogen-Bond-Enriched 1,3,5-Tris(2-hydroxyethyl) Isocyanurate Covalently Functionalized MCM-41: An Efficient and Recoverable Hybrid Catalyst for Convenient Synthesis of Acridinedione Derivatives

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Supporting Information

ABSTRACT: A new nano-ordered 1,3,5-tris(2-hydroxyethyl) isocyanurate-1,3-propylene covalently functionalized MCM-41 (MCM-41-Pr-THEIC) was designed and prepared at room temperature through a simple procedure. According to various microscopic, spectroscopic, or thermal methods and techniques, the correlation of the catalytic performance of the hybrid mesoporous MCM-41-Pr-THEIC to its structural characteristics was fully confirmed. The new MCM-41-Pr-THEIC organosilica nanomaterials were successfully investigated as a solid mild nanocatalyst through hydrogen-bonding activation provided by its organic moiety, for the pseudo-four-component condensation of dimedone, aldehydes, and ammonium acetate or p-toluidine to afford the corresponding acridinedione derivatives under green conditions. Furthermore, the introduced nanocatalyst could be reused at least four times with negligible loss of its activity, indicating the good stability and high activity of the new hybrid organosilica.

INTRODUCTION

Organocatalysis has been emerged as an environmental and cost-effective alternative pathway to the traditional transition-metal catalysis for fine chemical synthesis especially in pharmaceutical industry over recent decades.1–9 Perfect homogeneous organocatalyst must be available through easy synthetic procedures and are often composed of nontoxic small organic compounds that can be easily degraded in the environment without significant waste generation.5,10–13 However, the usual workup remains a major drawback with tedious and costly procedures for separation of the homogeneous organocatalysts from the reaction mixture. On the other hand, heterogeneously catalyzed procedures have a valuable role in simplification of the processes and decreasing environmental concerns, including less corrosion, simple separation, catalysts recovery, and avoiding the usage of hazardous solvents.14–16 To achieve more sustainable catalytic processes by improving the yield and energy efficiency, recent contributions have also been focused on immobilized organocatalysts onto the surface of solid polymeric supports, in particular silica.17–24 The structure of the obtained organosilica materials is sufficiently attractive and tunable to combine the advantages of a silica matrix, including high surface area, thermal or mechanical stability, as well as chemical inertness with the properties of the grafted organic moieties.22,25–32 Hence, mesoporous silica-based materials (MCM) with very large specific surface areas (up to 2000 m² g⁻¹) and tunable pore radius from approximately 2–50 nm as well as mechanically stable structure have become a new possible candidate for sensors,33 adsorbents,34–36 drug-delivery systems,35,37,38 and CO₂ capture or transformation,39,40 as well as solid supports to immobilize homogeneous catalysts41–46 or directly use them as an ideal heterogeneous catalyst alone.47–53

On the other hand, multicomponent reactions (MCRs) have received great interest from synthetic, environmental, and economical points of view in recent years, especially for the synthesis of heterocycles with high diversity such as acridinedione derivatives.35,54–62 These tricyclic N-containing heterocycles have received a lot of interest as one of the most important classes of heterocyclic scaffolds in the biologically active molecules research. A series of acridinediones containing aromatic substituents are generally known as antibacterial or antiparasitic agents that are capable of intercalating into DNA base pairs.63 Furthermore, there are several pharmacological properties associated with these compounds, including antimalarial,64 antifungal,65 anticancer,66 or GCN5 inhibitor67 properties as well as selective fluoride-ion chemosensor68 and fluorescence enhancement.69 Due to the biological importance

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of the acridinedione derivatives, synthesis of these compounds is an interesting research challenge for both organic and medicinal chemists.\textsuperscript{70,71} Literature survey shows that several modified methods for the pseudo-four-component Hantzsch-type condensation of aromatic aldehydes, dimedone, and different nitrogen sources, including urea, methyl amine, aniline, or ammonium acetate, have been reported using different catalytic systems by the traditional heating in organic solvents\textsuperscript{72} or under microwave irradiation.\textsuperscript{73,74} Recently, Zn\textsuperscript{II} doped and immobilized on functionalized magnetic hydrotalcite,\textsuperscript{75} platinum nanoparticles supported on graphene oxide or its reduced form,\textsuperscript{76} carboxylic acid-functionalized multi-walled carbon nanotubes,\textsuperscript{77} TiO\textsubscript{2}-coated magnetite nanoparticle-supported sulfonic acid,\textsuperscript{78,79} sulfuric acid-modified...
poly(vinylpyrrolidone), $^{80}$ SnCl$_4$-functionalized nano-Fe$_3$O$_4$-encapsulated silica,$^{13}$ Eu$_2$O$_3$-modified CeO$_2$ nanoparticles,$^{81}$ Vitamin B$_1$, $^{82}$ morpholinium-based ionic liquids,$^{68}$ and choline chloride:urea $^{83}$ have been described. Although various protocols for the synthesis of acridinedione derivatives have been reported, the use of solid mild materials with simpler experimental setup; lower toxicity, corrosion, or cost; and environmental tolerability is still in demand. At present, it is worth using highly thermally stable, cost-effective, and milder catalytic systems for different organic transformations. In continuation of our ongoing efforts toward expanding efficient and novel heterogeneous catalysts for different MCRs,$^{29,84−89}$ we wish herein to report the preparation and characterization of 1,3,5-tris(2-hydroxyethyl)isocyanurate covalently functionalized MCM-41 (MCM-41-Pr-THEIC, 1) nanocatalyst and examination of its catalytic activity for the pseudo-four-component condensation reaction of dimedone (2), different aldehydes 3, and ammonium acetate (4a) or p-toluidine (4b) to afford the corresponding Hantzsch acridinedione derivatives 5−6 under mild conditions in high to excellent yields and short reaction times (Scheme 1). This nanocatalyst can be considered as a typical example of mild heterogeneous catalysts which activate the substrates and intermediates during the catalytic cycle through hydrogen bonding provided by its organic moiety as well as inorganic silica support whose polarity has been appropriately balanced. To the best of our knowledge, there is no report for the use of 1,3,5-tris(2-hydroxyethyl)isocyanurate grafted on the surface of MCM-41 by 1,3-propylene linker (MCM-41-Pr-THEIC) as a heterogeneous organocatalyst, for different MCRs including Hantzsch acridinedione derivatives 5 or 6.
RESULTS AND DISCUSSION

Characterization of the Covalently Modified Nano-Ordered MCM-41 Using 1,3-Dibromopropane and THEIC (MCM-41-Pr-THEIC, 1). Initially, the MCM-41-Pr-THEIC materials (1) were prepared by grafting of the 1,3,5-tris(2-hydroxyethyl)isocyanurate to the surface of the nano-ordered MCM-41 using 1,3-dibromopropane, as an appropriate and inexpensive linker (Scheme 1). The surface and bulk properties of the new catalyst were studied by several techniques such as Fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), derivative thermogravimetry, energy-dispersive X-ray (EDX) spectroscopy, and CHN elemental analysis.

The preparation of the MCM-41-Pr-THEIC materials (1) and their structure were approved by FTIR spectroscopy. The FTIR spectra of MCM-41 (a), MCM-41-PrBr (b), MCM-41-Pr-THEIC (1, c), MCM-41-Pr-THEIC after four times of recycling (d), and THEIC (e) are compared in Figure 1. It is generally approved that high-intensity bands at 1180−1278 cm\(^{-1}\) are due to the asymmetrical Si−O external stretching vibrations and those at 1000−1100 cm\(^{-1}\) are due to the internal vibrations.90 Moreover, the signals appearing at 1689 and 1471 cm\(^{-1}\) are attributed to the stretching vibrations of the isocyanurate ring. Also, the observed characteristic bands at 3200−3400 cm\(^{-1}\) are attributed to the stretching vibration of the O−H bonds of both MCM-41 and THEIC.

The field emission scanning electron microscopy (FESEM) images illustrated in Figure 2a–f reveal the general morphology of MCM-41 and MCM-41-Pr-THEIC (1). As it can be found from the FESEM images of MCM-41-Pr-THEIC (1, Figure 2d–f), the morphological structure of the MCM-41-Pr-THEIC (1) materials is different from that of the pure MCM-41; moreover, the particles size of MCM-41-Pr-THEIC (1) is slightly higher than that of pure MCM-41 (12.1–16.5 nm). On the other hand, the transmission electron microscopy (TEM) images shown in Figure 3 confirms the presence of 1,3,5-tris(2-hydroxyethyl)isocyanurate grafted to the 1,3-propylene linker in the channels of the nanosized MCM-41-Pr-THEIC (1) sample compared to pure MCM-41.91,92

The thermal stability of the MCM-41-Pr-THEIC nanomaterials (1) was also investigated using the thermogravimetric analysis (TGA) technique (Figure 4). The TGA curve of the MCM-41-Pr-THEIC (1) shows three steps of weight loss. The 7% weight loss in the first step corresponds to desorption of physisorbed water or solvent molecules held in the pores of MCM-41-Pr-THEIC (1). Furthermore, the sharp 46% weight loss in the second step (between 200 and 400 °C) can be mainly attributed to the decomposition of 2-hydroxyethyl moiety existing in the structure of THEIC or 1,3-propylene linker in the nanomaterial 1 framework. On the other hand, the slight 13% weight loss at >400 °C was related to the decomposition of thermally stable isocyanurate ring located on the surface of MCM-41 channels.29,86,93,94 These results also indicate that 1,3,5-tris(2-hydroxyethyl)isocyanurate has been successfully grafted onto the surface of MCM-41.95

The CHN analysis of functionalized MCM-41 with THEIC 1 was also used to quantify the organic molecules anchored to its surface. The percentage of nitrogen was observed to be 2.46%. This means that loading of the 1,3,5-tris(2-hydroxyethyl)isocyanurate per gram of the MCM-41-Pr-THEIC (1) is about 0.59 mmol. Furthermore, EDX analysis of MCM-41-Pr-THEIC (1) clearly confirmed the presence of C, N, O, and Si (Figure 5). These findings, especially the presence of nitrogen and absence of halogen impurity in the composition of the nanomaterials 1, demonstrate grafting of the 1,3,5-tris(2-hydroxyethyl) isocyanurate onto the surface of the MCM-41 matrices. Indeed, EDX and CHN analyses show a good agreement with those data obtained in TGA as well as

Figure 3. TEM images of the MCM-41-Pr-THEIC (1) nanomaterials.

Figure 4. TGA of the MCM-41-Pr-THEIC (1) nanomaterials.
FESEM and TEM images, which strongly confirm the successful functionalization of inorganic MCM-41 by the 1,3,5-tris(2-hydroxyethyl)isocyanurate organic moiety.

On the other hand, Figure 6 shows the X-ray diffraction (XRD) patterns of MCM-41-Pr-THEIC (1). It is obvious that the characteristic highly ordered uniform hexagonal mesopores of MCM-41 still exist in the MCM-41-Pr-THEIC (1) nanomaterials (Figure 6, top). Furthermore, other peaks in the high-angle region of the XRD pattern can be attributed to the presence of 1,3,5-tris(2-hydroxyethyl)isocyanurate covalently grafted through the 1,3-propylene linker onto the surface of MCM-41 (Figure 6, down).

As shown in Figure 7, the adsorption–desorption isotherm of the MCM-41-Pr-THEIC (1) sample corresponds to a type V isotherm with H2 hysteresis loop according to the classification of Brunauer, Deming, Deming, and Teller. It is generally accepted that there is a correlation between the shape of the hysteresis loop and the texture (e.g., pore size distribution, pore geometry, and connectivity) of a mesoporous material. Indeed, grafting of THEIC groups through 1,3-propylene linker onto the surface of pore walls of MCM-41 can block them, leading to the decrease of surface area and broad pore distribution.

Investigation of the Catalytic Activity of MCM-41-Pr-THEIC (1) for the Synthesis of Acridinediones 5–6. To evaluate the catalytic activity of MCM-41-Pr-THEIC (1) for the synthesis of acridinediones 5–6, the pseudo-four-component condensation of 4-chlorobenzaldehyde (3a, 1.0 mmol), dimedone (2, 2.0 mmol), and ammonium acetate (4a, 1.2 mmol) or p-toluidine (4b, 1.0 mmol) was investigated as the model reaction. In a systematic study, the effects of several crucial variables such as solvent and temperature, catalyst loading, and reaction time were studied. The results are summarized in Table 1. In the first step, to optimize the reaction conditions, a variety of solvents and temperatures were screened in the model reaction. In the absence of any solvent, the model reaction was slow and the yield of the desired product 9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (5a) was low to moderate, even at 120 °C and after 1.5 h (Table 1, entry 1). The model reaction was then studied in solvents such as H2O, EtOH, MeOH, THF, EtOAc, CH3CN, EtOH/H2O (1:1), EtOH/H2O (2:1), and EtOH/H2O (1:2) using MCM-41-Pr-THEIC (1) 20 mg loading (entries 2–14). The results clearly indicated that the model reaction did not proceed substantially at room temperature (Table 1, entries 2, 8, and 10). Interestingly, higher yield of the desired product 5a was obtained in EtOH/H2O (1:2) under reflux conditions (Table 1, entry 15). Encouraged by this result, the model reaction was examined in EtOH/H2O (1:2) under reflux conditions using different amounts of catalyst loading (entries 15–19). To our delight, it was found that 15 mg of catalyst 1 was sufficient to promote the model reaction efficiently (entry 15). On the other hand, to demonstrate the synergic impact of hydroxyl functional groups of MCM-41 and 1,3,5-tris(2-hydroxyethyl) isocyanurate on the catalytic activity of nanomaterial 1, the
catalytic performances of MCM-41, MCM-41-PrBr, or 1,3,5-tris(2-hydroxyethyl) isocyanurate were also examined under the same reaction conditions (Table 1, entries 20–22). Indeed, the results strongly confirmed the role of all MCM-41-Pr-THEIC (1) components to promote the synthesis of acridinedione 5a. Therefore, MCM-41-Pr-THEIC (1, 15 mg) in EtOH/H2O (1:2, 2 mL) under reflux conditions as the optimized reaction conditions were developed to other aromatic aldehydes (3b−j) for the synthesis of a wide range of the desired products 5–6. The results are summarized in Table 2.

The obtained results showed that aldehydes 3 having an electron-donating group on their aromatic ring generally reacted faster or afforded higher yields compared to those with an electron-donating group. It is also significant that even ortho-substituted benzaldehydes, considering their intrinsic steric hindrance, afforded the desired products in high yields under optimized conditions. These observations strongly approve the appropriate catalytic activity of MCM-41-Pr-THEIC (1) to promote the Hantzsch pseudo-four-component reaction of different aldehydes 3, dimedone (2), and nitrogen sources 4a–b.

According to the obtained results, the above mechanism can be proposed for the synthesis of acridinediones 5–6 catalyzed by MCM-41-Pr-THEIC (1) through the MCR strategy (Scheme 2). In the first step, MCM-41-Pr-THEIC (1) activates the carbonyl functional group of both dimedone (2) and aldehydes 3, through hydrogen bonding made by hydroxyl groups of THEIC or silanol groups on the surface of MCM-41, to form the corresponding Knoevenagel intermediate (II). This intermediate is further activated by MCM-41-Pr-THEIC (1) to be involved for the next Michael addition of the enol form of dimedone 2. The next step comprises the formation of intermediate IV from the second equivalent of dimedone. Then, one of the keto functional groups in the intermediate IV is activated by MCM-41-Pr-THEIC (1) to react with the ammonia source 4 affording imine intermediate V. The cyclization between enamine and keto functional group, followed by proton transfer, and finally elimination of third H2O molecules affords the desired acridinediones 5–6.53,107−112 Indeed, the THEIC moiety attached by 1,3-propylene linker appropriately modifies the surface of MCM-41 for a prompt catalytic activity of MCM-41-Pr-THEIC nanomaterials (1). Moreover, the byproduct water molecules can be simply adsorbed on the surface of MCM-41-Pr-THEIC nanomaterials (1).

On the other hand, reusability of a heterogeneous catalyst is a significant feature for its industrial applications. Therefore, the recycled MCM-41-Pr-THEIC (1) was washed with acetone to remove any organic impurities and then heated in an oven to be reused in the model reactions for the next run. This procedure was repeated for three more consecutive runs.

### Table 1. Optimization of Conditions in the Reaction of Dime done (2), 4-Chlorobenzaldehyde (3a), Ammonium Acetate (4a) or p-toluidine (4b) under Different Conditions

| entry | catalyst | catalyst loading (mg) | solvent | temperature (°C) | time (min) | yield (%) | 5a | yield (%) | 6a |
|-------|----------|-----------------------|---------|------------------|------------|-----------|----|-----------|----|
| 1     | MCM-41-Pr-THEIC | 20 | EtOH | rt | 120 | 90 | 76 | 80 |
| 2     | MCM-41-Pr-THEIC | 20 | MeOH | reflux | 90 | 60 | 69 |
| 3     | MCM-41-Pr-THEIC | 20 | THF | reflux | 180 | 50 | 58 |
| 4     | MCM-41-Pr-THEIC | 20 | EtOH | reflux | 180 | 42 | 49 |
| 5     | MCM-41-Pr-THEIC | 20 | H2O | rt | 120 | 56 | 62 |
| 6     | MCM-41-Pr-THEIC | 20 | H2O | reflux | 180 | 38 | 45 |
| 7     | MCM-41-Pr-THEIC | 20 | H2O | reflux | 90 | 70 | 78 |
| 8     | MCM-41-Pr-THEIC | 20 | EtOH/H2O (1:1) | rt | 150 | 40 | 48 |
| 9     | MCM-41-Pr-THEIC | 20 | EtOH/H2O (1:1) | reflux | 100 | 78 | 83 |
| 10    | MCM-41-Pr-THEIC | 20 | EtOH/H2O (2:1) | reflux | 40 | 85 | 91 |
| 11    | MCM-41-Pr-THEIC | 20 | EtOH/H2O (2:1) | reflux | 60 | 80 | 85 |
| 12    | MCM-41-Pr-THEIC | 20 | EtOH/H2O (1:2) | reflux | 35 | 89 | 92 |
| 13    | MCM-41-Pr-THEIC | 20 | EtOH/H2O (1:2) | reflux | 45 | 90 | 92 |
| 14    | MCM-41-Pr-THEIC | 20 | EtOH/H2O (1:2) | reflux | 60 | 82 | 86 |
| 15    | MCM-41-Pr-THEIC | 20 | EtOH/H2O (1:2) | reflux | 90 | 76 | 77 |
| 16    | MCM-41-Pr-THEIC | 20 | EtOH/H2O (1:2) | reflux | 120 | 57 | 65 |
| 17    | MCM-41-Pr-THEIC | 20 | EtOH/H2O (1:2) | reflux | 180 | 36 | 40 |
| 18    | MCM-41-Pr-THEIC | 20 | EtOH/H2O (1:2) | reflux | 60 | 76 | 84 |
| 19    | MCM-41-Pr-THEIC | 20 | EtOH/H2O (1:2) | reflux | 60 | 70 | 79 |
| 20    | MCM-41-Pr | 20 | EtOH/H2O (1:2) | reflux | 90 | 68 | 79 |

*Reaction conditions: Dime done (2, 2 mmol), 4-chlorobenzaldehyde (3a, 1 mmol), ammonium acetate (4a, 1.2 mmol), or p-toluidine (4b, 1 mmol), MCM-41-Pr-THEIC (1), and solvent (2 mL). *Isolated yields.
Table 2. Scope of the Synthesis of 9-(aryl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione Derivatives 5a–j and 6a–j Catalyzed by MCM-41-Pr-THEIC (1) via the Pseudo-Four-Component Reaction Strategy

| Entry | Aldehyde 3 | Product 5-6 | Time (min) | Yield (%) | Mp °C (Obs.) | Mp °C [Lit.] |
|-------|------------|-------------|------------|-----------|--------------|-------------|
| 1     | 4-ClC₆H₄  | ![image](5a.png) | 45         | 91        | 243-245      | 243-245 97  |
| 2     | C₆H₅      | ![image](5b.png) | 55         | 87        | 275-276      | 272 98      |
| 3     | 4-NO₂C₆H₄ | ![image](5c.png) | 50         | 80        | 300          | 302-304 99  |
| 4     | 3-NO₂C₆H₄ | ![image](5d.png) | 60         | 82        | 293-295      | 294-296 100 |
| 5     | 4-CH₃OC₆H₄ | ![image](5e.png) | 55         | 89        | 275          | 278-280 101 |
| Entry | Aldehyde | Product 5-6 | Time (min) | Yield (%) | Mp °C (Obs.) | Mp °C [Lit.] |
|-------|----------|-------------|------------|-----------|--------------|--------------|
| 6     | 4-OHC₆H₄ | ![Image](5f)  | 70         | 78        | >300         | >300 ¹⁰²     |
| 7     | 4-CH₃C₆H₄| ![Image](5g)  | 60         | 86        | >300         | >300 ⁹⁸     |
| 8     | 2-ClC₆H₄| ![Image](5h)  | 60         | 90        | 261-263      | 263-264 ¹⁰³  |
| 9     | 4-OH-3-CH₃OC₆H₃| ![Image](5i) | 55         | 82        | 297          | 295-298 ¹⁰⁴  |
| 10    | ![Image](5j)| ![Image](5j) | 45         | 84        | 245          | 248-250 ⁹⁸  |
| 11    | 4-ClC₆H₄| ![Image](6a)  | 45         | 92        | 271          | 273-275 ⁹⁷  |
### Table 2. continued

| Entry | Aldehyde 3 | Product 5-6 | Time (min) | Yield (%)<sup>c</sup> | Mp °C (Obs.) | Mp °C [Lit.] |
|-------|------------|-------------|------------|------------------------|--------------|--------------|
| 12    | C₆H₅       |             | 60         | 85                     | 267-268      | 265-267<sup>105</sup> |
| 13    | 4-NO₂C₆H₄  |             | 60         | 87                     | >300         | >300<sup>106</sup>  |
| 14    | 3-NO₂C₆H₄  |             | 60         | 81                     | 285-287      | 285-287<sup>105</sup> |
| 15    | 4-CH₃OC₆H₄ |             | 50         | 86                     | 237-239      | 241-243<sup>106</sup> |
| 16    | 4-OHC₆H₄   |             | 65         | 68                     | 348          | 350-352<sup>105</sup> |
It was found that the reactivity of catalyst 1 for the Hantzsch pseudo-four-component synthesis of acridinedione derivatives 5a and 6a decreases slightly (approximately 8%) after five runs. The latest isolated yields of 5a or 6a after four times of catalyst recycling were 82 and 84%, respectively. To demonstrate the appropriate catalytic activity of the new hybrid heterogeneous nano-ordered catalyst MCM-41-Pr-THEIC (1), its performance has been compared to that of some recently reported catalytic systems for the synthesis of acridinedione derivatives 5a and 6a. The summarized results in Table 3 obviously show that some of the reported catalysts are homogeneous and cannot be reused. Furthermore, the present protocol provides better performance in terms of product yield, catalyst loading, reaction time, operational simplicity, and frequency of recycling compared to most of previously published catalytic systems.

**CONCLUSIONS**

In summary, we have developed a novel and powerful 1,3,5-tris(2-hydroxyethyl)isocyanurate covalently functionalized nano-ordered MCM-41 (MCM-41-Pr-THEIC) as a robust and recoverable catalyst for the pseudo-four-component condensation of dimeredone, aldehydes, and ammonium acetate.

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(Figure 8) It was found that the reactivity of catalyst 1 for the Hantzsch pseudo-four-component synthesis of acridinedione derivatives 5a and 6a decreases slightly (approximately 8%) after five runs. The latest isolated yields of 5a or 6a after four times of catalyst recycling were 82 and 84%, respectively.

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or p-toluidine to afford the acridinedione derivatives under extremely green conditions. The notable advantages of this method are clean reaction profiles, short reaction time, and high to quantitative yields without using precious or toxic metals and hazardous organic solvents, which makes it an improved and more practical alternative to the existing methods. Additionally, the catalyst could be simply separated and reused without apparent loss of its activity at least after four cycles. Due to the notable advantages of the MCM-41-Pr-THEIC nanocatalyst, its applications in other organic reactions are currently underway in our lab and would be reported in due course.

### EXPERIMENTAL SECTION

**Reagents and Apparatus.** All chemicals were purchased from Merck or Aldrich with the highest purity available, and benzaldehyde was used as a freshly distilled sample. The morphological, structural, and compositional characterizations of the nanocatalyst 1 were properly carried out using FESEM TESCAN-MIRA3, EDX Numerix DXP-X10P, Philips CM30,
Shimadzu FTIR-8400S, TGA Bahr company STA 504, and CHN Elemental instruments. Characterization of introduced nanocatalyst 1 was performed by transmission electron microscopy (TEM, Philips CM30). A Shimadzu FTIR-8400S spectrometer and a Bruker DRX-500 Avance spectrometer (ambient temperature in DMSO-d$_6$) were used for recording FTIR, $^1$H NMR (500 MHz), and $^{13}$C NMR (125 MHz) spectra of products. The analytical thin-layer chromatography (TLC) experiments were performed using Merck 0.2 mm silica gel 60 F-254 Al-plates for observation progress of reactions. All melting points were determined using a digital Electrothermal 9100 capillary melting point apparatus. The isolated yields of products have been reported. All of the products, except 6a, were filtered and washed with toluene and EtOH several times to remove any excess of the linker. Next, dried white solids (1.0 g) were dispersed in dry toluene (30 mL). Then, the mixture was stirred continuously at room temperature for 18 h. After this time, the obtained solids were filtered and washed with toluene and EtOH several times. Finally, the residues were dried in a vacuum drying oven at 60 °C for 8 h. The schematic route for the preparation of MCM-41-Pr-THEIC (1) nanomaterials is shown in Scheme 1.

**General Procedure for Preparation of the MCM-41-Pr-THEIC (1) Nanomaterials.** In a 200 mL round-bottom flask, 1,3-dibromopropane (49 mmol, $d$ = 1.98 g cm$^{-3}$, 5 mL) was added to a suspension containing MCM-41 (1.0 g) in dry toluene (30 mL). Then, the mixture was stirred continuously at room temperature for 18 h. After this time, the obtained solids were filtered and washed. The remaining solids were dried at 45 °C, and calcined at 550 °C for 45 h to remove the residual CTAB template.

**Typical Procedure for Preparation of MCM-41.** MCM-41 materials were prepared by direct hydrothermal synthesis according to a known procedure as follows: In a general procedure, dimethylamine (60 mmol, 2.70 g) was added to deionized water (42 mL) in a 200 mL beaker while the mixture was stirred at room temperature. Then, CTAB (4 mmol, 1.47 g) was added to the above solution to obtain a clear solution after stirring for 30 min. Tetraethyl orthosilicate (10 mmol, 2.10 g) was then added into the mixture with stirring. By dropwise addition of HCl solution (1 M), the pH of the mixture was adjusted to 8.5, to obtain a final precipitate. After 2 h stirring, white precipitates were obtained, which were filtered, washed with deionized water, dried at 45 °C, and calcined at 550 °C for 45 h to remove the residual CTAB template.

| entry | catalyst | product | catalyst loading | conditions | time (min) | yield (%) | catalyst reuse times | reference |
|-------|----------|---------|-----------------|------------|------------|-----------|----------------------|-----------|
| 1     | β-cyclodextrin monosulfonic acid | 5a | 30 mg | H$_2$O/60°C | 120 | 91 | 5 | 113 |
| 2     | ascorbic acid | 5a | 8.8 mg | solvent-free/80 °C | 180 | 89 | 114 |
| 3     | SnCl$_4$-functionalized nano-Fe$_3$O$_4$-encapsulated silica | 5a | 25 mg | EtOH/reflux | 15 | 93 | 4 | 13 |
| 4     | TiO$_2$-coated magnetite nanoparticle-supported sulfonic acid | 5a | 10 mg | solvent-free/110 °C | 40 | 95 | 78 |
| 5     | Fe$_3$O$_4$@TiO$_2$@O$_2$P$_2$([CH$_3$)$_2$NHSO$_3$] | 5a | 7 mg | solvent-free/90 °C | 25 | 92 | 4 | 79 |
| 6     | 1-n-butyl-3-methylimidazolium bromide ([bmim][Br]) | 5a | 10 mL (Excess) | 90 °C | 40 | 93 | 115 |
| 7     | Zn$^{n}$-doped and immobilized on functionalized magnetic hydroxocarbonate | 5a | 8 mg | solvent-free/70 °C | 5 | 90 | 6 | 75 |
| 8     | MCM-41-Pr-THEIC | 5a | 15 mg | EtOH/H$_2$O (1:2)/reflux | 45 | 91 | 5 | this work |
| 9     | 1-n-butyl-3-methylimidazolium bromide ([bmim][Br]) | 6a | 10 mL | 90 °C | 120 | 96 | 115 |
| 10    | carbon-based solid acid | 6a | 30 mg | 100 °C solvent-free | 30 | 88 | 3 | 116 |
| 11    | fluorous silica gel-supported hafnium(IV) bis(perfluorocarbonsulfonyl) imide complex | 6a | 1 mol % | EtOH/H$_2$O (1:1)/reflux | 390 | 66 | 3 | 117 |
| 12    | polyvinylpolypyrrolidone-supported boron trifluoride | 6a | 100 mg | CH$_2$CN reflux | 210 | 97 | 4 | 118 |
| 13    | MCM-41-Pr-THEIC | 6a | 15 mg | EtOH/H$_2$O (1:2)/reflux | 45 | 92 | 5 | this work |
(eluents: EtOAc:n-hexane, 1:3). After completion of the reaction, 96% EtOH (2 mL) was added and the mixture was heated to dissolve any solid products 5–6 and the solid catalyst I remained insoluble. The catalyst was then separated by filtration and n-hexane (one to three drops) was added to the filtrate and then allowed to cool over time to give pure crystals of the desired acridinedione derivatives 5–6. The separated catalyst was suspended in acetone (1 mL), stirred for 30 min, and then filtered off. The residue white powder was then heated in an oven at 60 °C for 1.5 h and reused for successive runs.

Selected Spectral Data. 9-(4-Chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (5a). Mp: 243–245 °C; IR (KBr): υ 3277, 3205, 2929, 2870, 1663, 1508, 1397, 1223, 1171 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): δ 0.85 (s, 6H), 1.96–1.99 (d, J = 12.8 Hz, 2H), 2.15–2.18 (d, J = 12.8 Hz, 2H), 2.30–2.33 (d, J = 14.9 Hz, 2H), 2.49–2.46 (d, J = 14.9 Hz, 2H), 4.77 (s, 1H, C–H₈benzyl), 7.15–7.20 (m, 4H, H aromatic), 9.33 (br s, 1H, N–H) ppm.

3,3,6,6-Tetramethyl-9-(p-tolyl)-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (5f). Mp: 275 °C; IR (KBr): υ 3277, 3205, 3082, 2929, 2870, 1663, 1508, 1397, 1223, 1171 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆): δ 0.86 (s, 6H), 1.96–1.98 (d, J = 16.1 Hz, 2H), 2.14–2.17 (d, J = 16.1 Hz, 2H), 2.29–2.32 (d, J = 17.1 Hz, 2H), 2.44–2.41 (d, J = 17.1 Hz, 2H), 2.35 (s, 3H methyl), 4.37 (t, 1H, C–H₈benzyl), 6.71–6.69 (d, J = 8.4 Hz, 2H), 7.03–7.05 (d, J = 8.4 Hz, 2H), 9.24 (br s, 1H, N–H) ppm.

1H NMR (500 MHz, DMSO-d₆): δ 0.85 (s, 6H), 1.96–1.99 (d, J = 12.8 Hz, 2H), 2.15–2.18 (d, J = 12.8 Hz, 2H), 2.30–2.33 (d, J = 14.9 Hz, 2H), 2.49–2.46 (d, J = 14.9 Hz, 2H), 4.77 (s, 1H, C–H₈benzyl), 7.15–7.20 (m, 4H, H aromatic), 9.33 (br s, 1H, N–H) ppm.

FTIR spectra of MCM-41, MCM-41-Pr-THEIC, and THEIC; FESEM images of MCM-41 and MCM-41-Pr-THEIC; TEM images of MCM-41-Pr-THEIC; TGA of MCM-41-Pr-THEIC; XRD patterns of MCM-41 and MCM-41-Pr-THEIC; BET analysis of MCM-41-Pr-THEIC; CHN elemental analysis of MCM-41-Pr-THEIC; and FTIR, 1H NMR, and 13C NMR spectra of the selected products (PDF).

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Notes
The authors declare no competing financial interest.

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**NOTE ADDED AFTER ASAP PUBLICATION**

This paper was published ASAP on November 12, 2019 with the image for Scheme 2 duplicated as Scheme 1. The corrected version was reposted on November 15, 2019.