# Introduction of $Fe_3O_4$@MCM-41/Zr@Piperazine as an efficient catalyst for the protection of alcohols and amines

Badruddin Nabizadah [ID], Reyhaneh Pourhasan-Kisomi [ID],
Masoumeh Mazloumi [ID], Farhad Shirini* [ID]

*Department of Organic Chemistry, Faculty of Chemistry, University of Guilan, Rasht, Iran.*

***Corresponding author:** shirini@guilan.ac.ir; fshirini@gmail.com

**Original Research**

**Abstract:**

This article investigates an efficient and eco-friendly protocol for protecting amines and alcohols as important molecules in organic chemistry, using $Fe_3O_4$@MCM-41/Zr@Piperazine as a newly reported magnetic mesoporous nanostructured catalyst. Firstly, the protection of alcohols was developed through their transformation to trimethylsilyl ethers. Then this reagent was applied for the acceleration of the acetylation of amines and alcohols with acetic anhydride and acetyl chloride, respectively. Finally, the influence of this highly active nanocatalyst on the formyl protection of amines was studied. The outgoings of these works illustrated the superiorities of this functionalized mesoporous mixed metal nanocatalyst in terms of accomplishing the reactions in high yields during proper reaction times and its superparamagnetic nature leading to easy separation, and several times, reusability.

## 1. Introduction

Protecting groups are molecular frameworks used in the synthesis to temporarily mask the characteristic chemistry of a functional group aimed to prevent interference with another reaction. Amines and alcohols contain the two most vital functional groups, and their protection, especially in a poly-functional molecule, is of the essence. In this way, their conversion into formamides, acetamides, acetates, and trimethylsilyl ethers is one of the best protecting routes. Formamides, as one of the most important intermediates in the synthesis of organic compounds and the ones with important biological and medicinal properties [1], can be used as precursors in the synthesis of formidines, isocyanides, aryl halides, amino carbonyls [2–4] and fluoroquinoline [5] and as a reagent in the Wilsmeyer formulation reactions [1, 3–5]. Formamide production is also a substantial step in the production of various drugs, such as the antibiotic quinolone [2, 6] and cancer carcinogens [2]. These compounds also have a vital role in the formation of peptides [7–9] and are effective Lewis bases catalyzing several important reactions such as allylation and hydroxylation [1, 7].

Among all the methods available for the generation of formamide derivatives, the reaction of amines with formic acid is the simplest and the most important one [10, 11]. In this way, several catalytic systems have been reported to facilitate reaching this goal. Besides the effective role of these methods in improving the synthesis of formamides, some of their disadvantages, such as high cost, toxicity, harsh reaction conditions, by-product formation, and low and hard recyclability of the catalyst, are still challenging [2, 7]. Acetamides and acetates are important building blocks in polymers, chemicals, agriculture, and the synthesis of various drugs [12–14]. They have antioxidant properties as secondary metabolites [13, 15, 16]. These metabolites have antibacterial and antiviral features in plants, helping to preserve them. Additionally, strong health benefits such as antimicrobial, antifungal, anti-inflammatory, and anti-cancer characteristics are reported for them. In addition, they are efficient markers for kidney and liver function and have anti-aging and cell protection effects [12, 16, 17]. To gain these worthy moieties, which is routinely possible by the reaction with acetic anhydride or acetyl chloride, some re-

ported methods are based on using acids or bases of metal salts, and metal nanoparticles, which face limitations in the refining work process [18], difficult reaction conditions and low efficiency in the production of the desired products [19]. So, a more efficient method is needed to overcome these limitations.

Silyl ethers are the most generally used alcohol-protecting groups which in them, the O-Si bond is stronger relative to the O-H bond in the parent alcohol. Moreover, their remarkable features include easy preparation, oxidation resistance, good thermal stability and low viscosity, and easy recoverability from their parent moiety. Among different silylating methods, trimethylsilylation is the more applicable one which is commonly based on using HMDS as the silylating agent. Hexamethyldisilazane (HMDS) is a cost-effective commercial reagent that is easy to use, does not require special care and caution, and can be easily removed from the reaction medium [20, 21]. However, some negative points like poor silylating ability, the need for forceful reaction conditions, and long reaction times, necessitate the presence of a catalyst to activate this reagent. Although numerous catalytic systems are reported for this purpose [21–23], the effort to achieve an optimized one still remains.

In recent years, mesoporous compounds have been considered by many researchers due to their wide range of applications, especially in the field of catalysis. The mesoporous silica compound with two-dimensional hexagonal pores, named MCM-41, is the most important member of this family [24, 25]. Its unique features, such as having regular and uniform pores, the adjustable pore diameter and pore distribution, which is an efficiently narrow and very high surface area of up to 1500 $m^2$ , which makes it to be an efficient support for catalysis, have made it very prone to become an applicable well-known catalytic system [26, 27]. The use of heterogeneous catalysts has superiorities relative to homogeneous ones. As an important reason, these catalysts can be easily recovered from the mixture of the reaction via filtration or magnetism, while the latter is premier in terms of avoiding manual attempts to filtrate and purify the used catalysts [28–40]. In this line, heterogenization of the MCM-41-based nanocatalysts in the form of magnetic nanoparticles leads to easy catalyst recovery using an external magnetic field and increases the performance of nanocatalysts in the subsequent reuses. Additionally, the stabilization of metal nanoparticles such as Zr on the MCM-41 structure as the support is one of the best selections to obtain impressive and outstanding catalytic capabilities from these magnetic mesoporous moieties. The fine Lewis acidic nature of Zr nanoparticles -resulted from a high coordinating capability due to the higher charge-to-size value of $Zr^{+4}$ compared with most of the metal ions- and high catalytic activity features, along with commercial availability, low price, and low toxicity make this metal as an excellent candidate to be incorporated on the mesoporous support structure [25, 41, 42].

This work prevents the accumulation of them, increases the thermal and hydrothermal stability of the mesostructured framework and makes the metal nanoparticles stable against moisture and corrosiveness and easy to handle. Moreover,

to enhance zirconium catalytic activity in organic reactions, modification of the surface via basic functionality like Piperazine is so impressive [41].

Accordingly, recently, we have introduced $Fe_3O_4$@MCM-41/Zr@Piperazine as a new stable and highly active superparamagnetic nanocatalyst and studied its capability in the acceleration at different organic reactions [27, 41]. The satisfactory outgoings of previous studies about various acidic and basic catalysts, especially zirconium-based and supported reagents, motivated us to extend and evaluate the applicability of $Fe_3O_4$@MCM-41/Zr@Piperazine in other organic transformations. Therefore, in this article, we have discussed some protection reactions we have done with amines and alcohols, leading to the production of formamides, acetamides, acetates, and trimethylsilyl ethers. This reagent can efficiently catalyze the direct coupling of various diamines as well as aromatic and cyclic ones with formic acid and acetic anhydride to afford the corresponding formylated products and acetylated ones, respectively, with high catalytic activity and selectivity. The acetylation and trimethylsilylation of different aromatic and aliphatic alcohols have also been achieved efficiently.

## 2. Experimental

### 2.1 Material and Characterization Techniques

The required raw materials were purchased from Merck, German, Ferroka Swiss Wald rich's trading companies. FT-IR measurements were done as KBr pellets on a Brucker Alpha series in the range of 400-4000 $cm^{-1}$. Magnetic resonance spectra of hydrogen and carbon nuclei ($^1$HNMR) and ($^{13}$CNMR) were prepared using the Bruker AV-400 instrument. The melting points were measured by the IA9100 electro-thermal device [27, 41] and reported without correction. The pureness measurement of the substrate and monitoring of the reaction process were managed by thin-layer chromatography (TLC) on a silica gel Polygram SILG/UV 254 plate.

### 2.2 General procedure for the protection reactions

### 2.2.1 Formylation of amines

In a round-bottom flask, 1 mmol of the aromatic amine was added to a mixture of formic acid (0.040 mL) and $Fe_3O_4$@MCM-41/Zr@Piperazine as the catalyst (16 mg). The mixture was stirred magnetically at 50 °C while the reaction process was monitored by TLC (*n*-hexane: ethylacetate; 7:3). After fulfilling the reaction, to separate and reuse the catalyst, 10 mL of ethyl acetate was added to the mixture. The catalyst was then isolated by an external magnet. After washing with ethanol and drying at 50 °C, it was ready to use again [we were able to repeat this routine at least 5 times for the catalyst as its stability and catalytic strength were maintained (Figure 1). The main product was isolated and purified from the additional reaction moieties by adding the amount of water with ethyl acetate using a decanter. For this purpose, after removing the aqueous phase, the organic phase was washed with brine and dried over $Na_2SO_4$. Eventually,the solvent was removed using a rotary evaporator, and the product was obtained. The spectral data of representative compounds are as follows:
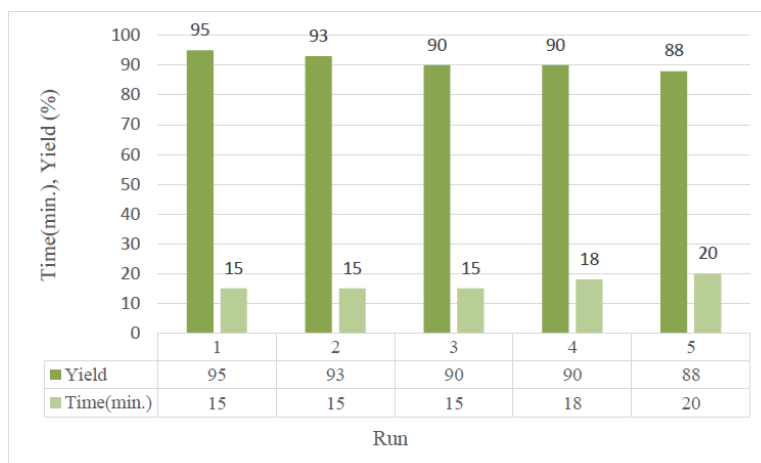
**Figure 1.** Recoverability of the $Fe_3O_4$@MCM-41/Zr@Piperazine catalyst in the synthesis of formamides.

*N − (Phenyl) formamide (Table 2, entry 1)*: mp 45-47 °C; ^{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 9.30 (0.48H, s), 8.73 (1H, d, *J* = 11.3 Hz), 8.35 (0.52H, s), 7.63 – 7.56 (1H, m), 7.41 – 7.27 (2H, m), 7.25 – 7.09 (2H, m); ^{13}C NMR (101 MHz, *CDCl$_3$*) $\delta$ 163.3, 159.9, 137.1, 136.9, 129.8, 129.1, 125.3, 124.8, 120.2, 118.8 [43].

*N-(4-Chlorophenyl) formamide (Table 2, entry 2)*: mp 98-100 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) $\delta$(ppm): $\delta$ 8.77 (0.43H, d, *J* = 11.6 Hz), 8.58 (0.5H, d, *J* = 11.3 Hz), 8.28 (0.66H, d, *J* = 1.8 Hz), 7.81 (0.61H, s), 7.43 (1H, d, *J* = 8.8 Hz), 7.23 (2H, dd, *J* = 17.2, 8.8 Hz), 6.97 (1H, d, *J* = 8.7 Hz); ^{13}C NMR (101 MHz, CDCl$_3$) $\delta$ 162.8, 159.3, 135.5, 135.4, 130.7, 129.9, 129.1, 121.3, 120.0 [43].

### 2.2.2 Acetylation of amines and alcohols with acetic anhydride and acetyl chloride, respectively

In a round-bottom flask, a specific amount of acetic anhydride (0.1 mL) or acetyl chloride (0.05 mL) was added to a mixture of aromatic amine (0.032 g) or alcohol (0.054 g) and the nanocatalyst (10 mg). While the mixture was stirred magnetically at room temperature, the reaction progress was managed by TLC (*n*-hexane: ethyl acetate: 10:3). To separate the catalyst and merit reusable, after the end of the

reaction, the amount of ethyl acetate 10 ml was added to the mixture to dissolve any moieties except the solid magnetic catalyst. So, the catalyst was isolated from the product by an external magnet, washed with ethanol, and dried at 50 °C to be reusable. With this procedure in hand, this catalyst could be recycled up to 5 times in the synthesis of acetates and acetamides individually. The related diagrams are shown in Figures 2 and 3.

To obtain the isolated and pure product from the remaining ethyl acetate solution using a decanter, an amount of water was added to this solution. Finally, the aqueous phase was removed, and the organic phase was washed with brine and dried over $Na_2SO_4$. At last, evaporation of the solvent with a rotary evaporator gave us a pure product. The spectral data of representative compounds are as follows:

*N, N-(1,4-Phenylene) diacetamide (Table 5, entry 9)*: ^{1}H NMR (700 MHz, DMSO-d$_6$) $\delta$= 9.79 (s, 1H), 7.47 (s, 2H), 2.01 (s, 3H); ^{13}C NMR (175 MHz, DMSO-d6) $\delta$=169.3, 135.0, 119.8, 24.2 [44].

*4-Bromobenzyl acetate (Table 5, entry 15)*: mp: 77-79 °C, ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta$ = 7.46 (d, *J* = 8.3 Hz, 2 H), 7.21 (d, *J* = 8.2 Hz, 2 H), 5.03 (s, 2 H), 2.08 (s, 3 H). ^{13}C NMR (125 MHz, CDCl$_3$): $\delta$= 170.69, 135.00, 131.68,
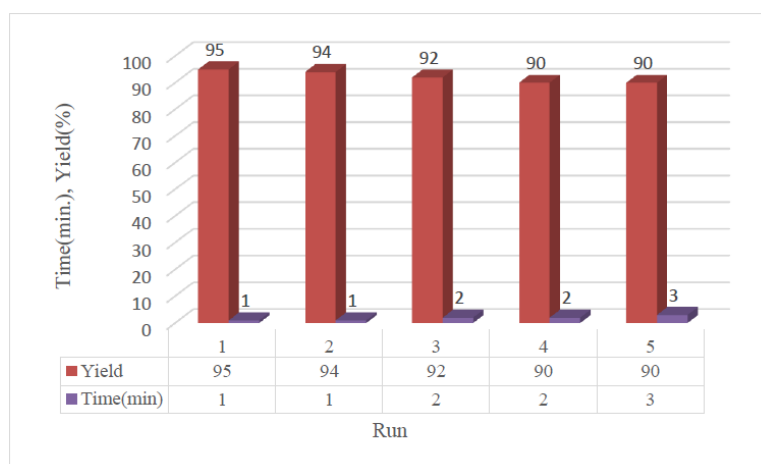


**Figure 2.** Recycling diagram of $Fe_3O_4$@MCM-41/Zr@Piperazine catalyst in the synthesis of acetamide.

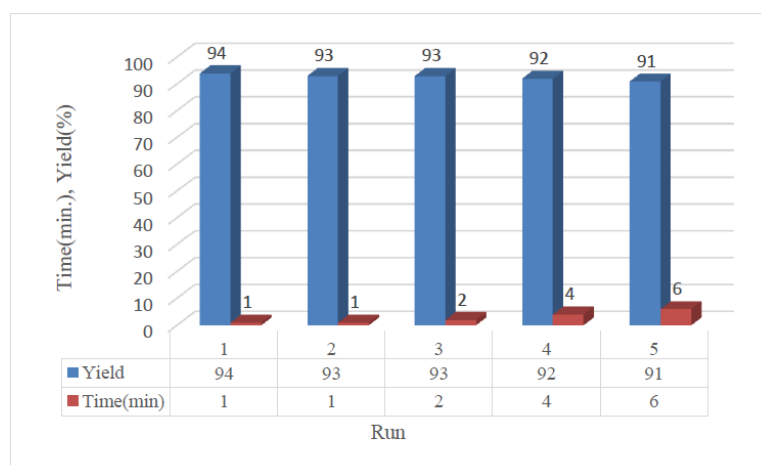**Figure 3.** Recycling diagram of $Fe_3O_4$@MCM-41/Zr@Piperazine catalyst in the synthesis of acetates.

129.91, 122.23, 65.44, 20.93 [45].

**2.3  Trimethylsilylation of alcohols**

In a round-bottom flask, benzylic alcohol was mixed with HMDS (0.08 g) and the catalyst (20 mg) was added to the mixture while it was stirred magnetically at 70-80 °C in the absence of solvent. The reaction progress was monitored by TLC (*n*-hexane: ethyl acetate; 20:3). To separate the catalyst and merit reusable, after the end of the reaction, the amount of ethyl acetate 10 ml was added to the mixture to dissolve any moieties except the solid magnetic catalyst. So, the catalyst was isolated from the product by an external magnet, washed with ethanol, and dried at 50 °C to be reusable.

With this procedure in hand, this catalyst could be recycled up to 5 times in the synthesis of acetates and acetamides individually. The related diagrams are shown in Figure 5.

To obtain the isolated and pure product from the remained ethyl acetate solution using a decanter, an amount of water was added to this solution. Finally, the aqueous phase was removed, and the organic phase was washed with brine and dried over $Na_2SO_4$. At last, evaporation of the solvent with a rotary evaporator gave us a pure product. The spectral data of representative compounds are as follows:

*(Benzyloxy)trimethylsilane (Table 9, entry 1)*: ^{1}H-NMR (DMSO, 500 MHz): $\delta$(ppm): 0.22 (s, 9H) , 4.76 (s, 2H), 7.30-7.42 (m, 5H) ppm. ^{13}C NMR (101 MHz, CDCl3) $\delta$ (ppm) = 146.5, 128.2, 126.9, 125.4, 70.6, 26.9, 0.1.  IR (KBr, $\nu$, cm$^{-1}$): 3030 (m), 957 (s), 2864 (m), 1607 (w), 1496 (m), 1251 (s), 1095 (s), 1069 (s), 874 (s), 750 (s), 728 (s), 695 (s) [46].

# 3. Results and discussion

As the first protection reaction, we tried to transform a range of aromatic amines into their corresponding N-formylated derivatives. We used formic acid as the most efficient formulating reagent and aniline as the substrate. In this way, initially, we aimed to optimize the reaction conditions to reach the best results, which means surveying the effect of some important factors on the proceeding of the reaction. So, the received outcomes of changing the amounts of formic acid, catalyst, and temperature under the solvent-free condition were indicated in Table 1, and the selected conditions were illustrated in Scheme 1.
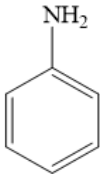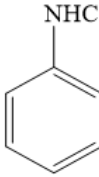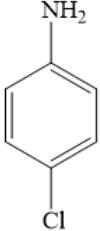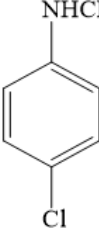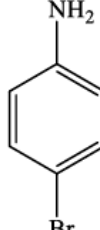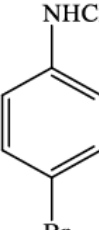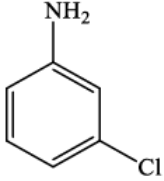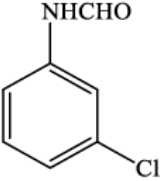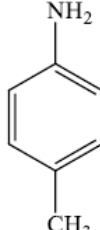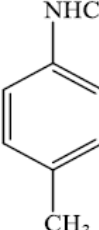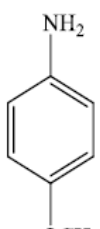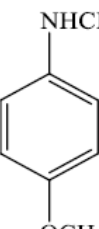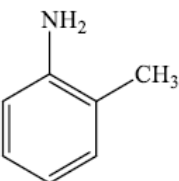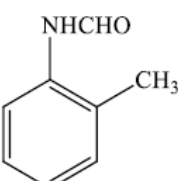
In the next step, to achieve the desired samples, we studied the results of the model reaction performed with a variety of available simple amines under the selected conditions. The obtained results are shown in Table 2. As can be seen, the related formamides were achieved in high yields at proper reaction times.

Based on the proposed mechanism, the initial step includes the activation of the carbonyl group of formic acid and also

**Table 1.** Optimization of the reaction conditions for formylation of amines in the presence of $Fe_3O_4$@MCM-41/Zr@Piperazine.

| Entry | Amount of formic acid (mL) | Amounts of the Catalyst (mg) | Temperature (°C) | Time (min.) | Conversion (%) |
|---|---|---|---|---|---|
| 1 | 0.024 | 20 | 50-60 | 80 | No reaction |
| 2 | 0.032 | 20 | 50-60 | 80 | No reaction |
| 3 | 0.040 | 20 | 50-60 | 80 | No reaction |
| 4 | 0.040 | 16 | 20-30 | 80 | No reaction |
| 5 | 0.040 | 20 | 50-60 | 25 | 96 |
| 6 | 0.040 | 20 | 50-60 | 15 | 100 |
| **7** | **0.040** | **16** | **50-60** | **15** | **100** |

**Table 2.** Formylation of amines catalyzed by $Fe_3O_4$@MCM-41/Zr@Piperazine.

| Entry | Amine | Product | Time (min.) | Yield (%)[a] | m.p (°C) [Refs.] |
|-------|-------|---------|-------------|--------------|------------------|
| 1 | | | 15 | 95 | 45-47 [43] |
| 2 | | | 15 | 95 | 98-100 [43] |
| 3 | | | 18 | 93 | 110-112 [43] |
| 4 | | | 60 | 94 | 79-80 [47] |
| 5 | | | 30 | 94 | 48-50 [43] |
| 6 | | | 30 | 95 | 75-77 [43] |
| 7 | | | 85 | 89 | Oil [47] |

Continue of Table 2.

| Entry | Amine | Product | Time (min.) | Yield (%)[a] | m.p (°C) [Refs.] |
|---|---|---|---|---|---|
| 8 | NH₂ ... OH | NHCHO ... OH | 15 | 94 | 136-137 [48] |
| 9 | © | CH₂NHCHO | 15 | 94 | Oil [43] |
| 10 | NH₂ | NHCHO | 50 | 95 | 140-142 [10] |
| 11 | N   NH | N   NHCHO | 30 | 92 | Oil [2] |
| 12 | NH₂ ... NH₂ | NHCHO ... NHCHO | 20 | 92[b] | 210-212 [49] |
| 13 | NH₂ ... Cl | NHCHO ... Cl | 35 | 94 | 80-81 [10] |
| 14 | NH₂ ... NH₂ | H N ... N | 15 | 95[b] | 167-169 [50] |

[a] Isolated yields.
[b] 0.01 g of formic acid was used.

the amine group of the substrate by the acidic and basic parts of the catalyst, respectively. The result of the activation step is the nucleophilic attack of the nonbonding electron pair of the nitrogen to the electrophilic carbonyl moiety, which generates the intermediate a. Absorbing hydrogen from the ammonium part of the catalyst provides the intermediate b.

Eventually, by removing a hydroxyl group, the N-fomylated product can be obtained (Scheme 2).

From the catalytic capability point of view to improve such a reaction, a comparison between the effect of this nanocatalyst with the results of the influence of some other reported catalytic systems on the acceleration of this type of reaction along with their specific reaction conditions is presented in Table 3, confirming the superiorities of $Fe_3O_4$@MCM-41/Zr@Piperazine.

Further development of the catalytic capability of $Fe_3O_4$@MCM-41/Zr@Piperazine was afforded via the preparation of various acetamides and acetate derivatives in the presence of this reagent. To gain these products via the acetylation of amines and alcohols efficiently, the reaction conditions were optimized, at first. Accordingly,

doing the reaction at room temperature with 0.05 mol of the acetylating agent and 10 mg of the catalyst with no need for solvent gave the best results (Table 4, Schemes 3 and 4). Subsequently, different types of amines and alcohols were applied to generate the related products under the selected condition. The results of this study can be seen in Table 5, which indicates the substantial impact of the applied catalyst on the promotion of the synthesis of the mentioned compounds. However, the fast formation of acetamides in comparison with acetates is notable.

Additionally, this catalyst has a good performance in such reactions among other reported ones as represented in Tables 6 and 7. As can be seen, lesser amounts of $Fe_3O_4$@MCM-41/Zr@Piperazine are capable to accelerate the compared reactions during shorter reaction times with relatively higher
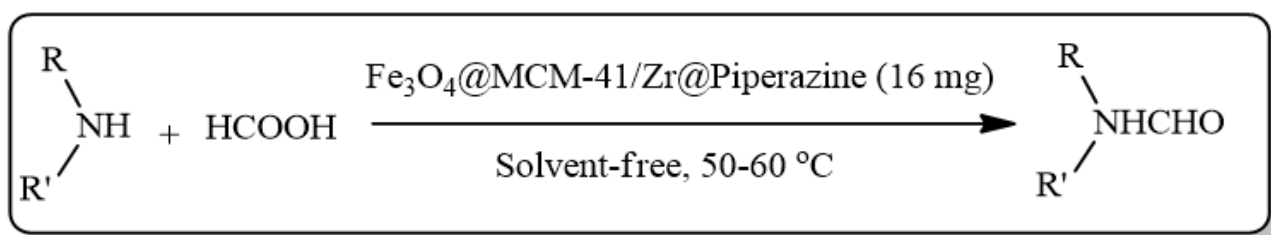


**Scheme 1.** Formylation of amines catalyzed by $Fe_3O_4$@MCM-41/Zr@Piperazine.
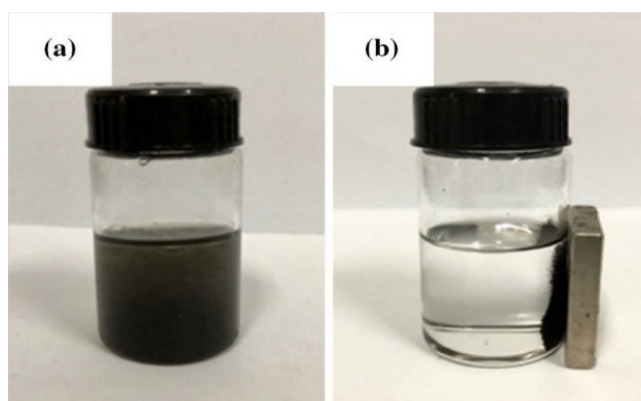


**Figure 4.** Photographs of an aqueous suspension of $Fe_3O_4$@MCM-41/Zr@Piperazine magnetic nanocomposite before (a) and after (b) magnetic capture.



| Run | Yield | Time (min) |
|---|---|---|
| 1 | 94 | 5 |
| 2 | 92 | 5 |
| 3 | 92 | 6 |
| 4 | 90 | 8 |
| 5 | 89 | 8 |
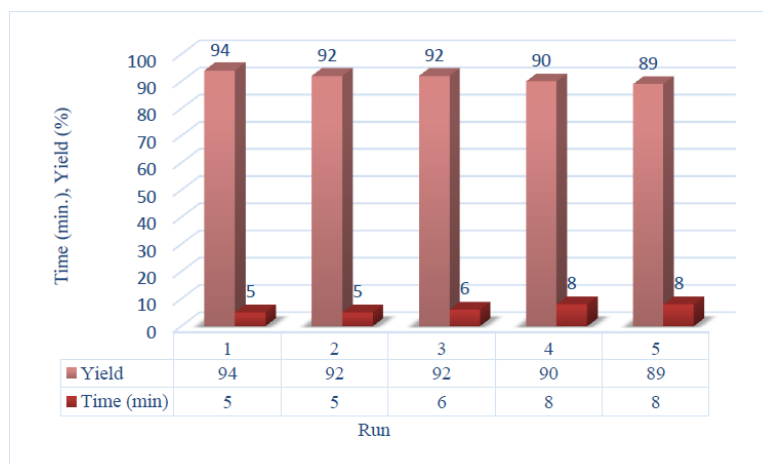
**Figure 5.** Recovery diagram of $Fe_3O_4$@MCM-41/Zr@Piperazine catalyst in the synthesis of trimethylsilyl ethers.

**Table 3.** Comparison of the results obtained from the formyl protection of amines in the presence of Fe$_3$O$_4$@MCM-41/Zr@Piperazine with some other reported catalytic systems.

| Entry | Catalyst | Amount | Conditions | Time (min.) | Yield(%) | [Ref.] |
|-------|----------|--------|------------|-------------|----------|--------|
| 1 | FSG-Hf(NPf$_2$)$_4$ | 1 mol (%) | Solvent-free/70 °C | 60 | 86 | [51] |
| 2 | (NH$_2$)$_3$[FeMO$_6$O$_{18}$(OH)$_6$] | 0.05 mol | Solvent-free / 80 °C | 120 | 99 | [52] |
| 3 | MLS-TA@Cu | 30 mg | Solvent-free / r.t. | 45 | 90 | [53] |
| 4 | Co (nano-catalyst) | 20 mg | Solvent-free / r.t. | 16 | 94 | [14] |
| 6 | NaY/SA/Cu(II) | 5 mol | Solvent-free / r.t. | 25 | 82 | [54] |
| 7 | NaY/SA/Cu(II) | 10 mg | CHCl$_3$/ r.t. | 20 | 65 | [54] |
| 8 | HCO$_2$H-ZnO | 40 mg | Solvent-free 80 °C | 20 | 92 | [55] |
| 9 | γ-Fe$_2$O$_3$@HAp-SO$_3$H | 0.09 mol | HCOOH / r.t. | 40 | 92 | [56] |
| 10 | HEU zeolite | 50 mg | Solvent-free /C$_2$H$_3$N | 55 | 82 | [57] |
| **11** | **Fe$_3$O$_4$@MCM-41/Zr@piperazine** | **16 mg** | **Solvent-free / 50 °C** | **15** | **95** | **[This work]** |

**Table 4.** Optimization of the reaction conditions for the acetylation of amines by Fe$_3$O$_4$@MCM-41/Zr@Piperazine.

| Entry | Acetylating agent | Amounts of the Catalyst (mg) | Temperature (°C) | Solvent | Time (min.) | Conversion (%) |
|-------|-------------------|------------------------------|------------------|---------|-------------|----------------|
| 1 | 0.1 | 16 | r.t. | Solvent-free | 1 | 100 |
| **2** | **0.1** | **10** | **r.t.** | **Solvent-free** | **1** | 100 |
| 3 | 0.1 | 8 | r.t. | Solvent-free | 5 | **100** |
| 4 | 0.05 | 12 | r.t. | Solvent-free | 10 | **90** |
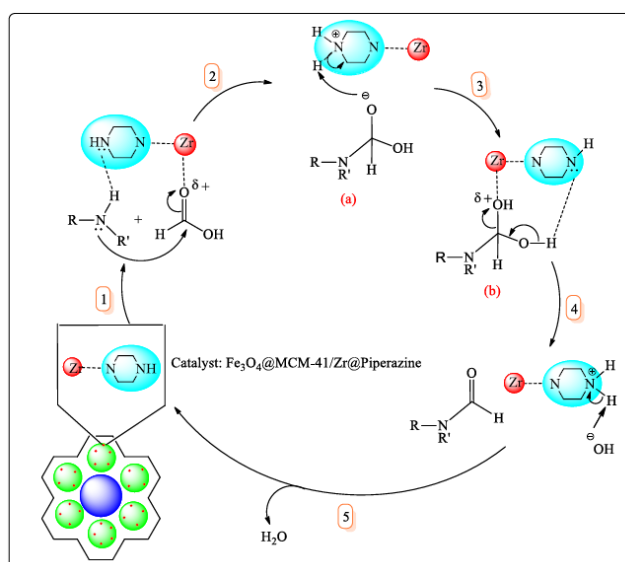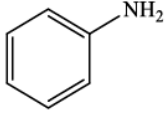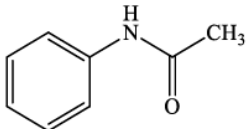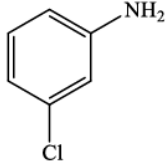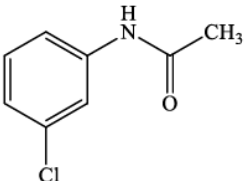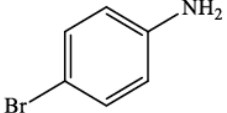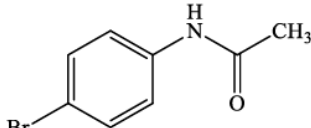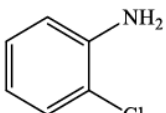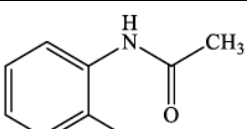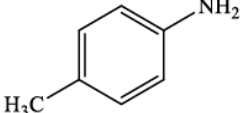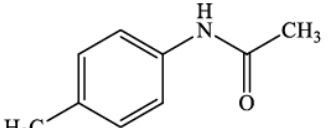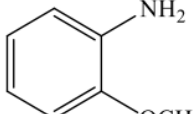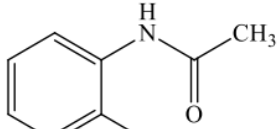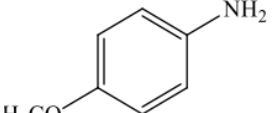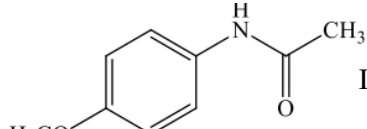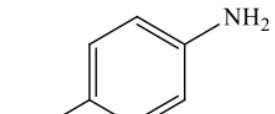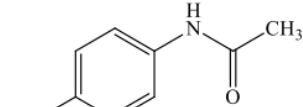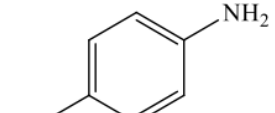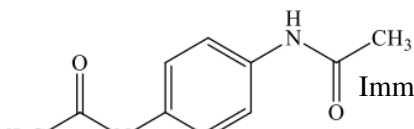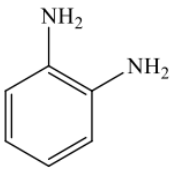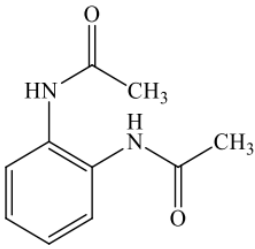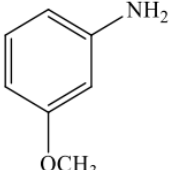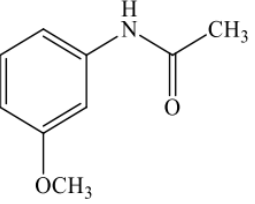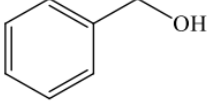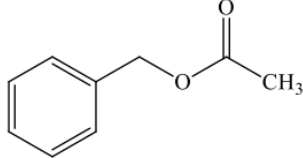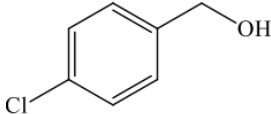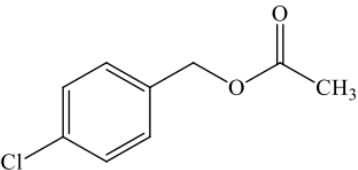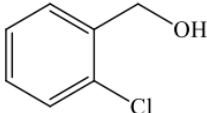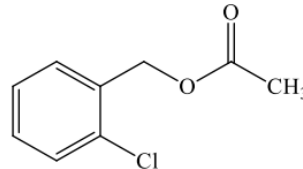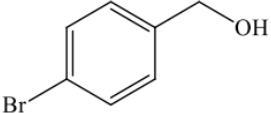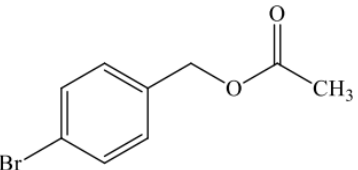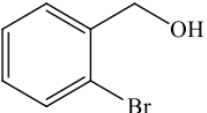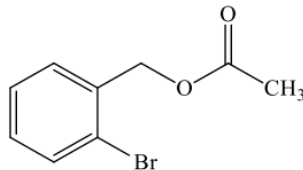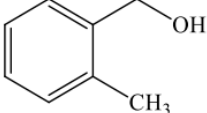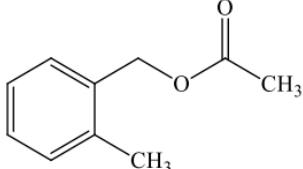


**Scheme 2.** The Proposed mechanism for the synthesis of N-formylation reactions in the presence of Fe$_3$O$_4$@MCM-41/Zr@Piperazine.
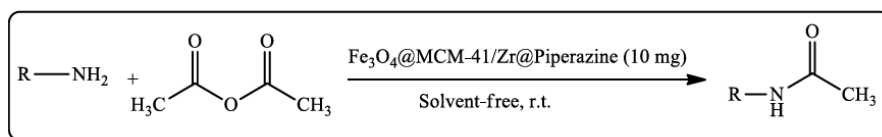


**Scheme 3.** Acetylation of amines catalyzed by Fe$_3$O$_4$@MCM-41/Zr@Piperazine.
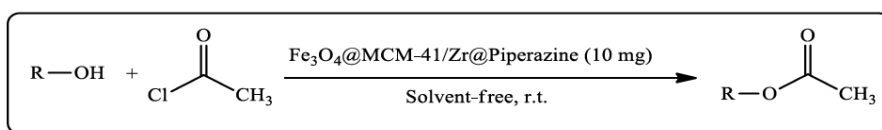


**Scheme 4.** Acetylation of alcohols catalyzed by Fe$_3$O$_4$@MCM-41/Zr@Piperazine.
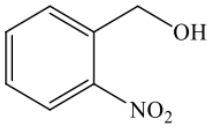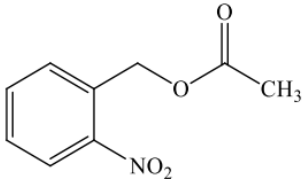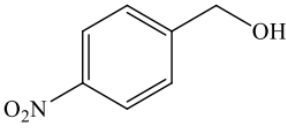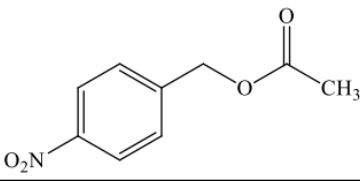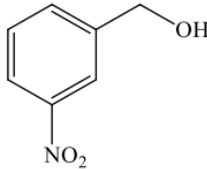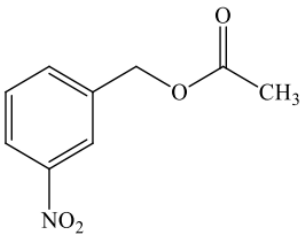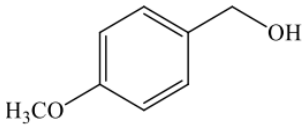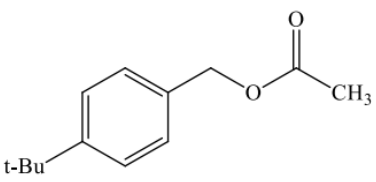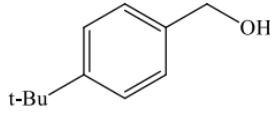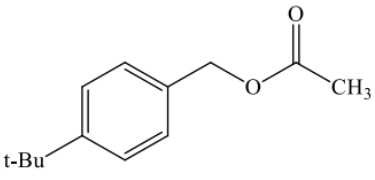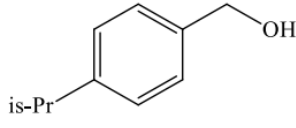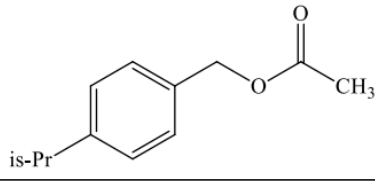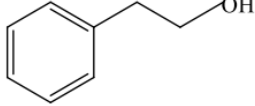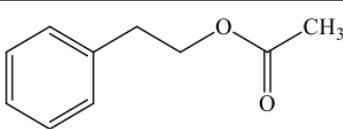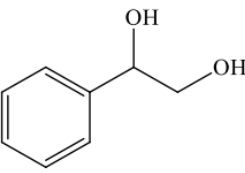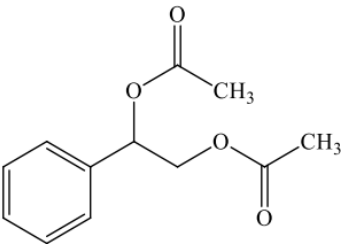
**Table 5.** Acetylation of amines and alcohols with acetic anhydride and acetyl chloride catalyzed by Fe$_3$O$_4$@MCM-41/Zr@Piperazine in Solvent-free condition at room temperature.

| Entry | Amines | Product | Time (min.) | Yield (%) [Refs.][a] |
|---|---|---|---|---|
| 1 | | | Immediately[b] | 95 [58] |
| 2 | | | Immediately[b] | 94 [59] |
| 3 | | | Immediately[b] | 95 [60] |
| 4 | | | Immediately[b] | 93 [59] |
| 5 | | | Immediately[b] | 93 [61] |
| 6 | | | Immediately[b] | 94 [58] |
| 7 | | | Immediately[b] | 95 [62] |
| 8 | | | Immediately[b] | 95 [29] |
| 9 | | | Immediately[b] | 94[c] [44] |

Continue of Table 5.

| Entry | Amines | Product | Time (min.) | Yield (%) [Refs.][a] |
|-------|--------|---------|-------------|----------------------|
| 10 |  |  | Immediately[b] | 93[c] [44] |
| 11 |  |  | Immediately[b] | 94 [58] |
| 12 |  |  | Immediately[b] | 90 [63] |
| 13 |  |  | Immediately[b] | 94 [45] |
| 14 |  |  | 4 | 94 [45] |
| 15 |  |  | Immediately[b] | 95 [45] |
| 16 |  |  | 4 | 91 [45] |
| 17 |  |  | Immediately[b] | 95 [45] |

Continue of Table 5.

| Entry | Amines | Product | Time (min.) | Yield (%) [Refs.][a] |
|---|---|---|---|---|
| 18 | | | 9 | 91 [61] |
| 19 | | | 4 | 92 [64] |
| 20 | | | 18 | 93 [12] |
| 21 | | | Immediately[b] | 94 [45] |
| 22 | | | Immediately[b] | 90 [45] |
| 23 | | | 22 | 90 [45] |
| 24 | | | 14 | 92 [63] |
| 25 | | | 46 | 85[c] [61] |

[a] Isolated yields.
[b] Immediately ≤ 3 min.
[c] 2 mmol of the acetylating agent was used.

yields than other previously reported catalysts. Based on the suggested mechanism, the dual activating feature of Fe$_3$O$_4$@MCM-41/Zr@Piperazine on the starting materials facilitates the first nucleophilic attack of the substrate to the acetylating agent which directly gives the acetylated amines or alcohols, as the desired protected moieties. In
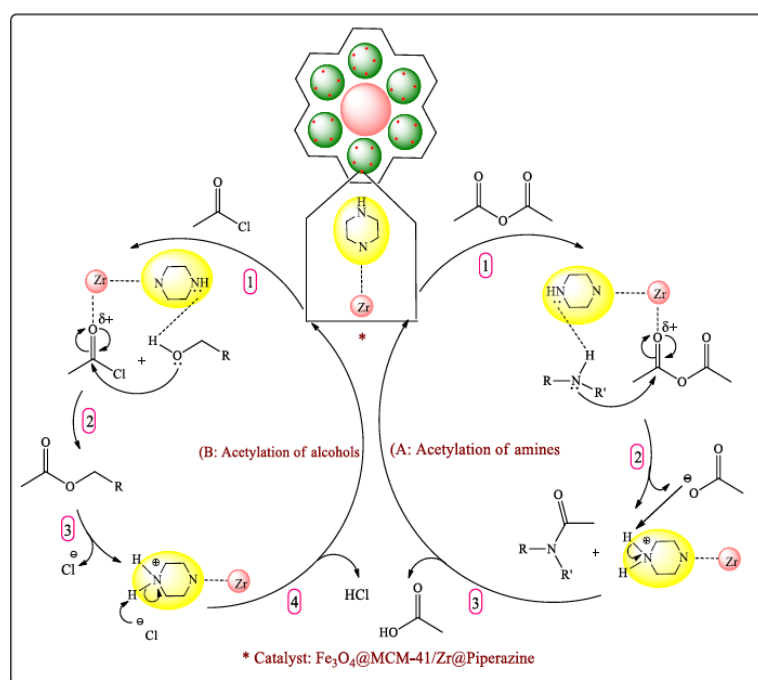


**Scheme 5.** The Proposed mechanism for the acetylation of amines and alcohols in the presence of Fe$_3$O$_4$@MCM-41/Zr@Piperazine.

**Table 6.** Comparison of the performance of different catalysts with Fe$_3$O$_4$@MCM-41/Zr@Piperazine in the synthesis of acetamide derivatives.

| Entry | Catalyst | Amount | Conditions | Time (min.) | Yield(%) | [Ref.] |
|-------|----------|--------|------------|-------------|----------|--------|
| 1 | DMAc and CDI | (0.1:1) mol | Solvent-free / 120 °C | 2-6 h | 80 | [13] |
| 2 | TMSCl-KI | 1 mol | Solvent-free / 110 °C | 24 h | 80 | [65] |
| 3 | TMSCl-KI | 0.2 mol | Reflux / CH$_3$CN | 15 | 80 | [65] |
| 4 | Ni-nanoparticles | 10 mol | Solvent-free / CH$_3$CN | 35 | 90 | [66] |
| 5 | ZnAl$_2$O$_4$@SiO$_2$ nanocomposite | 100 mg | Solvent-free / r.t. | 3 | 96 | [61] |
| 6 | ZnAl$_2$O$_4$ nanoparticles | 100 mg | Solvent-free / r.t. | 8 | 92 | [67] |
| **7** | **Fe$_3$O$_4$@MCM-41/Zr@Piperazine** | **10 mg** | **Solvent-free / r.t.** | **Immediately** | **95** | **[This work]** |

**Table 7.** Comparison of the performance of different catalysts with Fe$_3$O$_4$@MCM-41/Zr@Piperazine in the synthesis of acetate derivatives.

| Entry | Catalyst | Amount | Conditions | Time (min.) | Yield(%) | [Ref.] |
|-------|----------|--------|------------|-------------|----------|--------|
| 1 | nano-ZnAl$_2$O$_4$ | 100 mg | Solvent-free / r.t. | 18 | 90 | [67] |
| 2 | bulk-ZnAl$_2$O$_4$ | 100 mg | Solvent-free / r.t. | 65 | 78 | [67] |
| 3 | CaO | 2000 mg | 2-MeTHF / r.t. | 6 | 97 | [68] |
| 4 | K$_2$CO$_3$ | 2000 mg | 2-MeTHF / r.t. | 8 | 57 | [68] |
| 5 | Fe/Al-SBA-15 | 0.005 mol | Solvent-free / 40 °C | 25 | 94 | [69] |
| **6** | **Fe$_3$O$_4$@MCM-41/Zr@Piperazine** | **10 mg** | **Solvent-free / r.t.** | **Immediately** | **98** | **[This work]** |
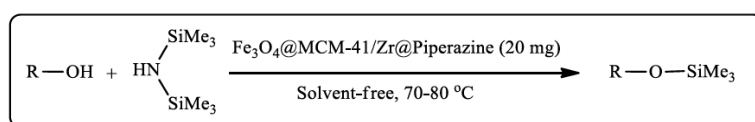


**Scheme 6.** Trimethylsilylation(HMDS) of alcohols catalyzed by Fe$_3$O$_4$@MCM-41/Zr@Piperazine.

the last step, the absorption of a hydrogen atom from the formated ammonium part of the catalyst can regenerate its basic form.

Given the high power of $Fe_3O_4$@MCM-41/Zr@Piperazine as the applied nanocatalyst, which was demonstrated in the successful synthesis of previously protected compounds, we further decided to evaluate its capability to produce catalytic products resulting from other important protection reactions. For this purpose, we tried to trimethylsilylate a wide range of alcohols using $1,1,1,3,3,3-$ *hexamethyldisilazane* (HMDS) as the most common silylating agent. In the first step, the appropriate conditions for this reaction were determined by investigating the effect of different amounts of the catalyst, temperature, and solvents, including $CH_3CN$, EtOH, $H_2O$, and solvent-free conditions in the model reaction. Based on our observations, 20 mg of the catalyst at 70-80 °C under solvent-free conditions can accelerate the model reaction efficiently (Table 8, Scheme 6). Subsequently, various alcohols were reacted

with HMDS under the optimized reaction condition. All the reactions proceeded efficiently with good yields showing the generality of this reaction system (Table 9).

In order to demonstrate the recyclability of the catalyst, 4-chlorobenzyl trimethylsilyl ether was re-examined. After completion of the reaction, ethyl acetate was added to the reaction mixture and the catalyst was separated by a magnetic magnet, as shown in Figure 4. It was then washed with ethanol, and dried at 50 °C, and used in the next reaction without any additional process. This recycled catalyst can accelerate the target reaction several times efficiently at the proper time (Figure 5).

The considerable ability of $Fe_3O_4$@MCM-41/Zr @Piperazine in the trimethylsilyl protection of alcohols can be presented by comparison of the results obtained from the trimethylsilylation of benzyl alcohol in the presence of this and other catalysts.

The proposed mechanism of trimethylsilylation reaction begins with the nucleophilic attack of the alcoholic oxygen
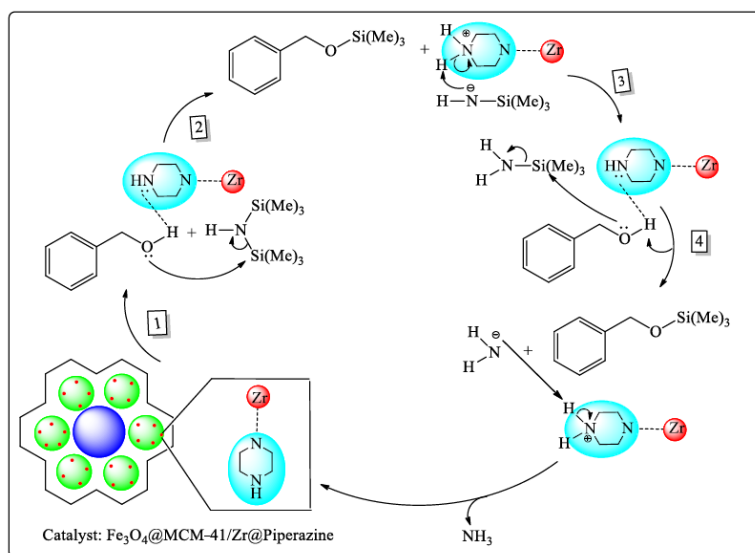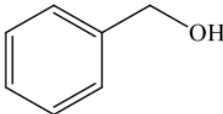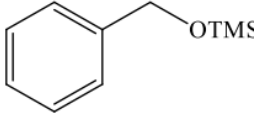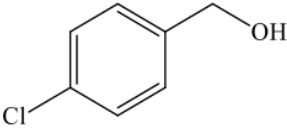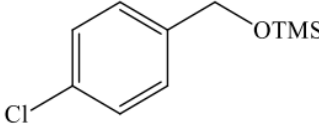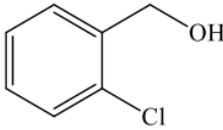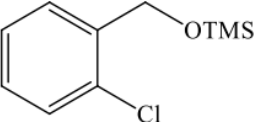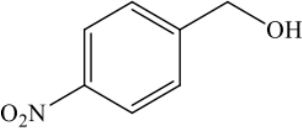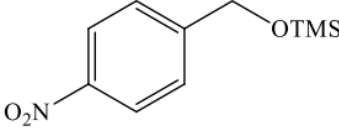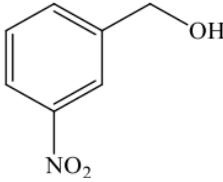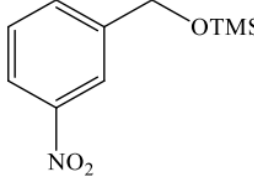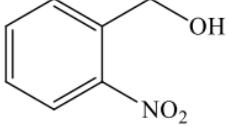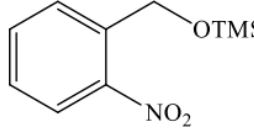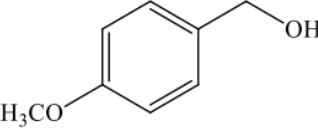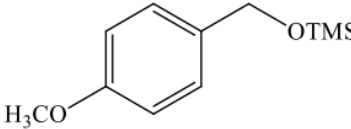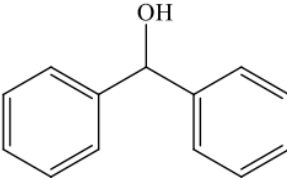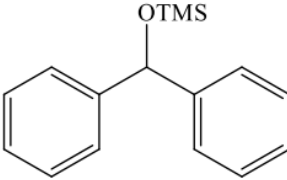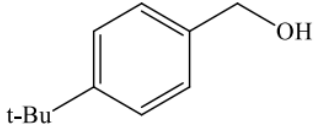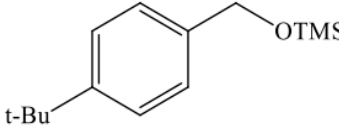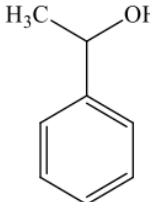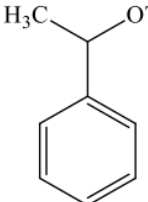


**Scheme 7.** The Proposed mechanism for the synthesis of trimethylsilyl ether in the presence of $Fe_3O_4$@MCM-41/Zr@Piperazine.

**Table 8.** Optimization of the reaction conditions for the silylation of alcohols catalyzed by $Fe_3O_4$@MCM-41/Zr@Piperazine.

| Entry | Amounts of the Catalyst (mg) | Temperature (°C) | Solvent | Time (min.) | Conversion (%) |
|---|---|---|---|---|---|
| 1 | 20 | r.t. | $CH_3CN$ | 35 | No reaction |
| 2 | 20 | r.t. | - | 67 | No reaction |
| 3 | 20 | r.t. | EtOH | 80 | No reaction |
| 4 | 20 | r.t. | $H_2O$ | 60 | No reaction |
| 5 | 20 | 70-80 | EtOH | 71 | No reaction |
| 6 | 20 | 70-80 | $CH_3CN$ | 40 | 95 |
| 7 | 20 | 70-80 | $H_2O$ | 25 | No reaction |
| **8** | **20** | **70-80** | **-** | **5** | **100** |
| 9 | 16 | 70-80 | - | 10 | 100 |
| 10 | 12 | 70-80 | - | 10 | 100 |
| 11 | 20 | 70-80 | - | 8 | 98 |
| 12 | 20 | r.t. | - | 20 | 98 |

**Table 9.** Trimethylsilylation of alcohols catalyzed by Fe$_3$O$_4$@MCM-41/Zr@Piperazine.

| Entry | Alcohol | Product | Time (min.) | Yield (%) [Refs.][a] |
|:---:|:---:|:---:|:---:|:---:|
| 1 | | | 5 | 96 [46] |
| 2 | | | 13 | 90 [46] |
| 3 | | | 15 | 92 [21] |
| 4 | | | 5 | 94 [70] |
| 5 | | | 10 | 93 [71] |
| 6 | | | 24 | 89 [21] |
| 7 | | | 15 | 90 [72] |
| 8 | | | 55 | 88 [72] |
| 9 | | | 26 | 89[46] |
| 10 | | | 15 | 87 [72] |

Continue of Table 9.

| Entry | Alcohol | Product | Time (min.) | Yield (%) [Refs.][a] |
|---|---|---|---|---|
| 11 | is-pr—C6H4—CH2OH | is-pr—C6H4—CH2OTMS | 7 | 93 [21] |
| 12 | Br—C6H4—CH2OH | Br—C6H4—CH2OTMS | 7 | 89 [70] |
| 13 | o-Br-C6H4—CH2OH | o-Br-C6H4—CH2OTMS | 8 | 90 [21] |
| 14 | o-CH3-C6H4—CH2OH | o-CH3-C6H4—CH2OTMS | 6 | 95 [21] |
| 15 | C6H5—CH2CH2OH | C6H5—CH2CH2OTMS | 57 | 87 [23] |
| 16 | cyclohexanol (OH) | cyclohexyl OTMS | 49 | 85 [70] |

[a] Isolated yields.

**Table 10.** Comparison of the results obtained from the synthesis of trimethylsilyl ether derivative of benzyl alcohols in the presence of $Fe_3O_4$@MCM-41/Zr@Piperazine with the other reported catalysts.

| Entry | Catalyst | Amount | Conditions | Time (min.) | textbfYield (%) | [Ref.] |
|---|---|---|---|---|---|---|
| 1 | $InBr_3$ | 5 mol (%) | Solvent-free / r.t. | 5.0 h | 84 | [20] |
| 2 | $Bi(OTf)_3$ | 0.5 mol | Solvent-free / 60 °C | 10 | 88 | [70] |
| 3 | $Fe(HSO_4)_3$ | 87 mg | Solvent-free / 100 °C | 13 | 90 | [73] |
| 4 | $H_3PW_{12}O_{40}$ | 28 mg | Solvent-free /60 °C | 23 | 90 | [72] |
| 5 | Nanocrystalline $TiO_2$ | 30 mg | $CH_3CN$ / r.t. | 10 | 95 | [6] |
| 6 | Sulfonic acid-function alized ordered nanoporous silica/$CH_2Cl_2$ | 19 mg | Solvent-free /$CH_2Cl_2$ | 80 | 98 | [74, 75] |
| 7 | $Fe(HSO_4)_3$ | 87 mg | Reflux /$CH_3CN$ | 120 | 70 | [73, 75] |
| **8** | **$Fe_3O_4$@MCM-41/Zr@Piperazine** | **20 mg** | **Solvent-free / 70-80 °C** | **5** | **96** | **[This work]** |

on the silicon atom of HMDS. Again, the nucleophilic attack of the other alcoholic substrate to the silicium bonded amine group gives the second mole of the silylated alcoholic product. The basic form of the catalyst is regenerated as the remaining part of HMDS absorbs hydrogen from the formatted ammonium part of the catalyst, in each step.

## 4. Conclusion

Based on the results of using $Fe_3O_4$@MCM41/Zr @Piperazine as the catalyst in the protection reactions of amines and alcohols, it is deduced that this functionalized mixed-metal magnetic mesoporous compound plays an impressive catalytic role and facilitates the protection reactions of amines and alcohols efficiently. Using this recoverable catalyst, the obtained products involved acetates, acetamides, formamides, and trimethylsilyl ethers were achieved with high yields during acceptable reaction times.

**Authors Contributions**
Authors have equal contribution role in preparing the paper.

**Availability of Data and Materials**
The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Conflict of Interests**
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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