# FULL PAPER

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# Metal–organic framework of amine-MIL-53(Al) as active and reusable liquid-phase reaction inductor for multicomponent condensation of Ugi-type reactions

Sadegh Rostamnia<sup>\*</sup> | Maryam Jafari

Organic and Nano Group (ONG), Department of Chemistry, Faculty of Science, University of Maragheh, PO Box 55181-83111, Maragheh, Iran

#### Correspondence

Sadegh Rostamnia, Organic and Nano Group (ONG), Department of Chemistry, Faculty of Science, University of Maragheh, PO Box 55181-83111, Maragheh, Iran. Email: rostamnia@maragheh.ac.ir; srostamnia@gmail.com Metal–organic framework of NH<sub>2</sub>-MIL-53(Al), with coordinative unsaturated aluminium sites, has been shown to be active in the Groebke–Blackburn–Bienaymé multicomponent coupling reaction based on Ugi-type amine and aldehyde condensation over isocyanide and then a cyclization process. Interestingly this reaction occurred under solvent-free conditions with high yield, in which the NH<sub>2</sub>-MIL-53(Al) could be recovered and reused for five reaction cycles, giving a total turnover number of 455.

# KEYWORDS

Groebke–Blackburn–Bienaymé (3-GB2WB), isocyanide, metal–organic framework, multicomponent reaction, NH<sub>2</sub>-MIL-53(Al)

# **1 | INTRODUCTION**

Fused imidazo[1,2-a] annulated nitrogen heterocycles of pyridine constitute a class of biologically active compounds that are potent antibacterial agents and calcium channel blockers and which also exhibit cytoprotective properties (e.g. zolpidem, Figure 1).<sup>[1]</sup> Due to the marked biological activity of N-fused 6,5-membered small molecules, [1,2] a number of different protocols for the Ugi-type Groebke-Blackburn-Bienaymé three-component (3-GBB) reaction have been developed.<sup>[3]</sup> The synthesis of imidazo[1,2-*a*]pyridines has been achieved in the presence of Brønsted acids, as well as with Lewis acids, via isocyanide-based multicomponent condensation.<sup>[3,4]</sup> However, many of these methods have drawbacks such as low yields of products, long reaction times, harsh reaction conditions, tedious work-ups leading to the generation of large amounts of toxic metal-containing waste, the requirement for an inert atmosphere and the use of stoichiometric or relatively expensive reagents.<sup>[4]</sup> As a result, the development of new synthetic methods for this purpose remains an attractive goal.

Porous nanostructures such as MCM-41 and SBA-15 with high surface area, adjustable pore sizes and tunable properties have various advantages related to alternative materials.<sup>[5]</sup> In applications of inorganic porous catalysts, a

major challenge is the mass transfer of organic substrates into the inorganic pores of the material.<sup>[5]</sup> We recently reported successful preparation of hybrid organic–inorganic materials (Org@SBA-15) with lipophilic pore walls, in which organic–inorganic mesochannels in reaction conditions as a catalyst provide a synergistic means of an efficient approach of reactants to catalytic active sites and suitable mesochannels to drive out the products for next cycles, in the presence of ultrasonic irradiation as a mass transfer accelerator.<sup>[6]</sup> We then developed catalytic applications of unfunctionalized SBA-15 in the presence of fluorinated alcohols in one-pot multicomponent reactions in which we revealed that R<sub>F</sub>OH and SBA-15 nanoreactor can be a good pair together in mass transfer and have catalytic properties when they are used in organic reactions.<sup>[6]</sup>

Hybrid metal–organic frameworks (MOFs) which are formed from inorganic building units and organic linkers have attracted much attention in the past decade.<sup>[7]</sup> These new hybrid organic–inorganic compounds have a crystalline three- or two- and one-dimensional open framework and high specific surface area and pore volume and sometimes flexible structures and also elevated level of structural diversity.<sup>[7]</sup> Recently, thermally and chemically stable IRMOF-3 (NH<sub>2</sub>-MOF) has been used as a heterogeneous catalyst by our group and others.<sup>[8]</sup> In these investigations, IRMOF-3 with





**FIGURE 1** Zolpidem, a pharmacologically important imidazo[1,2-*a*] pyridine

non-coordinated amino groups demonstrates that the basicity of the aniline-like amino group is enhanced when incorporated inside the pores of MOF channels.<sup>[8]</sup> Various authors have prepared a NH<sub>2</sub>-MIL-53(Al) material, in which the organic ligand is coordinated to unsaturated aluminium ions (Al<sup>3+</sup>).<sup>[8b,8h,8i]</sup> These catalysts have been used for basic catalysed Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate, and their activity was compared to that of IRMOF-3. In one report, the basic NH<sub>2</sub>-MIL-53(Al) was less active for the condensation product (ethyl (E)- $\alpha$ cyanocinnamate) in the pores of the framework.<sup>[8a]</sup> On the other hand, well-dispersed Pd nanoparticles supported on NH<sub>2</sub>-MIL-53(Al) were prepared and used as highly active catalysts for the Suzuki reaction by Cao and co-workers.<sup>[9]</sup> In the work reported here, we synthesized and investigated the action of NH<sub>2</sub>-MIL-53(Al) in a 3-GBB reaction.

## 2 | EXPERIMENTAL

# 2.1 | Chemicals and characterization

All reagents were obtained from Sigma Aldrich (Germany) and Fluka (Switzerland) and were used without further purification. Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vector 22 FT-IR instrument. Melting points were measured with an Electrothermal 9100 apparatus. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured (CDCl<sub>3</sub>) with a Bruker DRX-300 AVANCE spectrometer at 300 and 75 MHz, respectively.

#### 2.2 | Synthesis of NH<sub>2</sub>-MIL-53(Al)

NH<sub>2</sub>-MIL-53(Al) was synthesized based on a previously published method with slight modifications.<sup>[8b,8h]</sup> In a typical method, aluminium chloride hexahydrate (2.55 g) and 2aminoterephthalic acid (2.8 g) were dissolved in 25 ml of dimethylformamide (DMF). The produced mixture was then moved to a Teflon-lined autoclave and heated for 70 h at 423 K, then cooled slowly at a rate of  $0.4^{\circ}$ C min<sup>-1</sup> to room temperature. The resulting product was washed once with methanol. Then, for removing organic species trapped within the pores, the sample was washed with excess hot methanol (70°C) for 5 h and then filtered and dried at 80°C overnight. The MOF was then characterized using a variety of techniques.

In the FT-IR spectrum (Figure 2), a broad band centred at around 3620 cm<sup>-1</sup> could be assigned to the bridging hydroxyl group of the MIL-53.<sup>[8i]</sup> Two sharp bands at 3496 and 3386 cm<sup>-1</sup> are due to symmetric and asymmetric



FIGURE 2 FT-IR spectrum of NH<sub>2</sub>-MIL-53(Al) at 25°C

vibrations of NH<sub>2</sub> groups, respectively. Carboxylate C-O asymmetric stretching gives rise to a band at 1624  $\text{cm}^{-1}$ , and the band at 1389  $\text{cm}^{-1}$  is assigned to carboxylate C–O symmetric stretching. The two bands at 1495 and 1439  $\text{cm}^{-1}$ correspond to aromatic C–C stretching. The 1334  $\text{cm}^{-1}$  band can be assigned to C-N stretching vibrations. Bands at 1255 and 776  $\text{cm}^{-1}$  are assigned to aromatic C-H in-plane bending and out-of-plane bending, respectively. The peak centred at 661 cm<sup>-1</sup> was ascribed to H–N–H wagging.<sup>[8i]</sup> An additional absorption peak is observed at around 1670 cm<sup>-1</sup>, which can be attributed to molecules of free DMF trapped in MOF pores.<sup>[8h]</sup> Based on investigations of Gascon and coworkers,<sup>[8h]</sup> the amino groups of NH<sub>2</sub>-MIL-53(Al) are free of hydrogen bonding interactions with basic properties. According to the FT-IR wavelength analysis of the hydroxyl groups (appearing at  $3620 \text{ cm}^{-1}$ ) the OH groups show a stronger basicity in the NH2-MIL-53(Al), with carbon dioxide adsorptions, hydrogen carbonates may be formed due to the interaction of CO<sub>2</sub> with the hydroxyl groups of the MOF.<sup>[8b,8g]</sup>

Main diffraction peaks at around  $2\theta = 9.1^{\circ}$ ,  $11.6^{\circ}$  and 18.3° are readily recognized in the X-ray diffraction (XRD) pattern (Figure 3b).<sup>[8h]</sup> The analysis of the XRD pattern reveals that the peaks at  $2\theta = 9.1^{\circ}$  and  $11.6^{\circ}$  correspond to the (110) and (200) reflections, respectively. The peak at  $2\theta = 18.3^{\circ}$  corresponds to the (211) and (220) reflections which are merged into a single peak.<sup>[8h]</sup> The observed diffraction peaks agree with the structure of NH<sub>2</sub>-MIL-53(Al).<sup>[8b,8g,8h,9]</sup> Results from elemental analysis (dried MOF) are as follows for the dried material (wt%): C, 44.6; H, 4.5; N, 9.1. The BET surface area for the synthesized MOF is 712 m<sup>2</sup> g<sup>-1</sup> and its total pore volume is  $0.96 \text{ cm}^3 \text{ g}^{-1}$ . The crystal structure of NH<sub>2</sub>-MIL-53(Al) seems to change to amorphous after being reused five times. Figure 3(a) shows a scanning electron microscopy (SEM) image of the as-synthesized NH<sub>2</sub>-MIL-53(Al) sample. SEM images of NH2-MIL-53(Al) were obtained to investigate the morphology of the particles of this organic-inorganic hybrid material. Figure 3(a) shows that the NH<sub>2</sub>-MIL-53(Al) material is composed of small nanosheets.





**FIGURE 3** (a) SEM micrograph of NH<sub>2</sub>-MIL-53(Al) and (b) XRD patterns of the synthesized (black) and recycled (blue) NH<sub>2</sub>-MIL-53(Al)

#### 2.3 | Synthesis of aminoimidazo[1,2-*a*]pyridine

A mixture of aldehyde (1 mmol), 2-aminopyridine (1 mmol) and isocyanide (1.2 mmol) with a catalytic amount of NH<sub>2</sub>-MIL-53(Al) (2 mol%, 0.0042 g) under solvent-free conditions was stirred at 50°C for 3 h. NH<sub>2</sub>-MIL-53(Al) (0.02 g) was heated at 60°C in solvent-free conditions. After completion of the reaction the solvent was removed under vacuum. After complete disappearance of starting material as indicated by TLC, the resulting mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>. The catalyst was completely recovered from the residue. The CH<sub>2</sub>Cl<sub>2</sub> was evaporated under reduced pressure and the reaction mixture was then subjected to column chromatography on silica gel using ethyl acetate and n-hexane (2:1) to afford the aminoimidazopyridine product in high purity and all isolated products gave satisfactory spectral and physical data (see supporting information).<sup>[2b,2c]</sup> The isolated catalyst could be reused on addition of new portions of substrate.

# 2.4 | Recovery and turnover number (TON) study

The recycling possibility and activity of the magnetic catalyst were studied using model reactions in the presence of  $NH_2$ -MIL-53(Al). During this study (scale of the reaction selected was 5 mmol), when the reaction was completed (TLC), the catalyst was easily separated from the product (after adding  $CH_2Cl_2$ ), following decantation of the reaction solution.

The catalyst was washed with  $CH_2Cl_2$  and diethyl ether to remove residual product and dried under vacuum and reused in a subsequent reaction. TON represents the average number of substrate molecules converted into product per molecule of catalyst.

## **3** | **RESULTS AND DISCUSSION**

A few air- and moisture-stable MOFs for catalytic proposes have been reported.<sup>[10]</sup> Among the new MOF catalytic systems, IRMOF-3 and NH<sub>2</sub>-MIL-53 family as amine-reach catalysts have been employed.<sup>[7–10]</sup> The NH<sub>2</sub>-MIL-53(Al) material was prepared with 2-aminoterephthalic acid and aluminium chloride hexahydrate in DMF using a solvothermal method in a Teflon-lined autoclave. This MOF is a crystalline material with one-dimensional diamond-shaped pores (Figure 4).

the Duo to pharmaceutical prominence of imidazopyridines, several catalysts and precursors have been reported for the synthesis of these components.<sup>[1]</sup> On order to determine the conditions for Ugi-like multicomponent synthesis of imidazopyridines and the catalytic activity of NH2-MIL-53(Al) we investigated the MOF-catalysed 3-GBB condensation by a systematic study both for reactivity and efficiency, and also for heterogeneity and reusability features based on green chemistry principles. To our surprise, NH2-MIL-53(Al) acts as a heterogeneous green catalyst for the 3-GBB condensation reaction. For our study, cyclohexyl isocyanide, benzaldehyde and 2-aminopyridine were chosen as the benchmark substrates in the model reaction (Scheme 1).

Due to the fact that the nature of the amine-decorated NH<sub>2</sub>-MIL-53 (Al(OH)[O<sub>2</sub>C-C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>-CO<sub>2</sub>) or its synthetic component may play an important role in the synthesis of **4a**, in comparison with the same structure of non-amine



FIGURE 4 Preparation process of NH<sub>2</sub>-MIL-53(Al)



SCHEME 1 Expected products of 3-GBB condensation



FIGURE 5 Reaction scale (2.2 mmol)

 TABLE 1
 Study of model reaction under various conditions<sup>a</sup>

| Entry | Solvent <sup>b</sup> | MOF (mol%) | Time<br>(min) | Temp. (°C) | Yield<br>(%) |
|-------|----------------------|------------|---------------|------------|--------------|
| 1     | $H_2O$               | 4          | 90            | r.t.       | 15           |
| 2     | $H_2O$               | 4          | 180           | r.t.       | 25           |
| 3     | MeOH                 | 4          | 90            | 65         | 65           |
| 4     | EtOH                 | 4          | 240           | 50         | 87           |
| 5     | EtOH                 | 4          | 90            | 65         | 70           |
| 6     | $CH_2Cl_2$           | 4          | 90            | r.t.       | 10           |
| 7     | PhMe                 | 4          | 90            | 65         | 80           |
| 8     | $S-F^{c}$            | 4          | 90            | 65         | 84           |
| 9     | S-F                  | 2          | 90            | 65         | 80           |
| 10    | S-F                  | 3          | 180           | 65         | 95           |
| 11    | S-F                  | 2          | 180           | r.t.       | 35           |
| 12    | S-F                  | 2          | 200           | 65         | 95           |
| 13    | S-F                  | 1          | 180           | 65         | 76           |

<sup>a</sup>Reaction conditions: 2-aminopyridine (1 mmol), benzaldehyde (1 mmol), isocyanide (1.2 mmol), MOF (0.02 g).

<sup>b</sup>4 ml of solvent.

<sup>c</sup>S-F, solvent-free.

TABLE 2 NH<sub>2</sub>-MIL-53(Al)-catalysed 3-GBB condensation

MOF (MIL-53(Al)), the initial reaction was carried out using 4 mol% neutral aluminium triacetate (Al(CH<sub>3</sub>CO<sub>2</sub>)<sub>3</sub>) as noncoordination polymeric and non-porous carboxylic acid aluminium complex, 2-aminoterephthalic ester (NH<sub>2</sub>-TE), NH<sub>2</sub>-MIL-53 and MIL-53 catalyst at 50°C in 4 ml of ethanol. The NH<sub>2</sub>-MIL-53 was assessed for its catalytic activity in the 3-GBB condensation by studying the model reaction to produce **4a** as the principal product. When the model reaction was run using NH<sub>2</sub>-MIL-53, the product **4a** was obtained 87% yield during 4 h (Figure 5).

The model reaction was examined in polar and non-polar solvents such as toluene, dichloromethane, methanol, ethanol and water using 2 mol% MOF (Table 1). When the reaction was run under solvent-free conditions, the product was obtained in 46% yield at 25°C in 3 h. Under solvent-free conditions the yield increased sharply when the temperature was raised from room temperature to 65°C. Experimental results show that in various solvents the yield of reaction at 65°C is better that that at room temperature. However, solvent-free conditions and 3 h at 65°C are the best conditions for this reaction (Table 1, entry 12).

We examined several reactions to obtain the optimum amount of catalyst in solvent-free conditions (Table 1, entries 8–13). Results show that 2 mol% catalyst is the optimum amount for the model reaction giving a yield of 95%. Of course by increasing the temperature and amount of catalyst the yield can be increased to 98%, but based on an energy point of view this is not economic.

We then used NH<sub>2</sub>-MIL-53(Al) with the optimized conditions for the synthesis of imidazo[1,2-*a*]pyridine derivatives **4** from substrates **1**, **2** and **3** (Table 2). It can be seen that all the isocyanides and aminopyridines with aldehyde derivatives gave good to excellent yields. There was no significant difference in the yield of product between electron-rich and

|       |     | $ \begin{array}{c}                                     $ | + NH <sub>2</sub> Cat. (2 mo<br>S-F, 65 ° | R' 4a NHR                  |            |                        |
|-------|-----|--|---|----------------------------|------------|------------------------|
| Entry | 4   | R′   | Ar  | R                          | Time (min) | Yield (%) <sup>a</sup> |
| 1     | 4a  | Н  | $C_6H_5$                                  | <i>c</i> -Hex <sup>b</sup> | 180        | 95                     |
| 2     | 4b  | Н  | $4-NO_2C_6H_4$                            | c-Hex                      | 180        | 88                     |
| 3     | 4c  | Н  | $4-ClC_6H_4$                              | c-Hex                      | 180        | 94                     |
| 4     | 4d  | Н  | $3-NO_2C_6H_4$                            | c-Hex                      | 180        | 90                     |
| 5     | 4e  | Н  | C <sub>6</sub> H <sub>5</sub>             | <i>t</i> -Bu               | 160        | 95                     |
| 6     | 4f  | 6-Me   | C <sub>6</sub> H <sub>5</sub>             | c-Hex                      | 180        | 87                     |
| 7     | 4 g | 6-Me   | 4-ClC <sub>6</sub> H <sub>4</sub>         | c-Hex                      | 180        | 91                     |
| 8     | 4i  | 6-Me   | $3-NO_2C_6H_4$                            | c-Hex                      | 180        | 82                     |
| 9     | 4j  | 6-Me   | $4-NO_2C_6H_4$                            | c-Hex                      | 200        | 85                     |
| 10    | 4 k | 6-Me   | $4-NO_2C_6H_4$                            | <i>t</i> -Bu               | 160        | 85                     |
| 11    | 41  | 5-Me   | C <sub>6</sub> H <sub>5</sub>             | c-Hex                      | 200        | 80                     |
| 12    | 4 m | 5-Me   | 4-ClC <sub>6</sub> H <sub>4</sub>         | c-Hex                      | 180        | 92                     |

<sup>a</sup>Isolated yield.

<sup>b</sup>*c*-Hex, cyclohexyl.

unsubstituted aminopyridines. On the basis of these results, to extend the scope and generality of this method, the 3-GBB reaction of substituted aldehydes was also investigated. The results obtained indicated that NH<sub>2</sub>-MIL-53(Al) is a suitable reaction inductor for 3-GBB condensation in solvent-free conditions.

When reactions involve the use of solid catalysts, the reusability and recovery of the catalysts are important factors. So, in the next step we investigated the recyclability of NH<sub>2</sub>-MIL-53(Al). After completion of reaction, by increasing dichloromethane and centrifugation the catalyst can be separated from the reaction mixture. For the model reaction, it was found that NH<sub>2</sub>-MIL-53(Al) could be recovered and reused in five reaction cycles (Figure 3b), giving a total TON of 455 (Table 3).

A proposed mechanism (pathways A and B) for this reaction is shown in Scheme 2. Although this mechanism has not been exactly demonstrated by experiment, but based on *literature* reports of catalytic applications of  $NH_2$ -MIL-53(Al),<sup>[1–3,8–10]</sup> the most probable mechanisms for the synthesis of 3-aminoimidazo[1,2-*a*]pyridines **4** are outlined in Scheme 2 incorporating the roles of the Lewis acidic and amine-based organocatalytic pathways in activating the aldehydes and intermediate imines.

To investigate the chemoselectivity and size selectivity of the our MOF, the 3-GBB reaction was performed using an equimolecular mixture of benzaldehyde (1 mmol) and pnitrobenzaldehyde (1 mmol) under the same reaction conditions as described in Section 2. After 70 min of reaction, the yield of **4a** was 44%, whereas **4b** was 11% (Scheme 3).

TABLE 3 Recyclability and TON study for the synthesis of 4a

| Run <sup>a</sup>                  | 1           | 2  | 3  | 4        | 5               |
|-----------------------------------|-------------|----|----|----------|-----------------|
| Yield 4a (%)                      | 95          | 93 | 92 | 89       | 86 <sup>b</sup> |
| TON =455                          |             |    |    |          |                 |
| <sup>a</sup> Time of the reaction | on was 3 h. |    |    |          |                 |
| <sup>b</sup> After 5 h.           |             |    |    |          |                 |
|                                   |             |    |    |          |                 |
|                                   |             |    |    |          |                 |
|                                   | $\frown$    |    |    | $\frown$ |                 |
|                                   | ( MIL)      |    | (  | MIL)     |                 |



SCHEME 2 Plausible mechanisms (pathways A and B) for the 3-GBB reaction using MOF



SCHEME 3 Test for chemoselectivity and size selectivity of the MOF

This indicates that there is some amount of reactivity occurring outside of the framework or via defects present in the crystal domains which facilitate guest diffusion.<sup>[8a,8c]</sup>

# 4 | CONCLUSIONS

We successfully synthesized NH<sub>2</sub>-MIL-53(Al) and utilized it for the synthesis of 3-aminoimidazo[1,2-*a*]pyridines. The advantage of this MOF-catalysed reaction is that it can be carried out under solvent-free conditions and in a short reaction time. Additionally, using this method, a small amount of catalyst was used and facilely recycled, and especially the use of toxic organic solvents in the reaction was avoided, which provides a green and effective method for 3-GBB condensation.

# REFERENCES

- a) A. Gueiffier, S. Mavel, M. Lhassani, A. Elhakmaoui, R. Snoeck, G. Andrei, O. Chavignon, J. C. Teulade, M. Witvrouw, J. Balzarini, E. De-Clercq, J. P. Chapat, *J. Med. Chem.* **1998**, *41*, 5108. b) L. Almirante, L. Polo, A. Mugnaini, E. Provinciali, P. Rugarli, A. Biancotti, A. Gamba, W. Murmann, *J. Med. Chem.* **1965**, *8*, 305. c) K. S. Gudmundsson, J. D. Williams, J. C. Drach, L. B. Townsend, *J. Med. Chem.* **2003**, *46*, 1449.
- [2] a) M. Adib, M. Mahdavi, M. Alizadeh, P. Mirzaei, *Tetrahedron Lett.* 2007, 48, 7263. b) S. Rostamnia, K. Lamei, M. Mohammadquli, M. Sheykhan, A. Heydari, *Tetrahedron Lett.* 2012, 53, 5257 and references therein c) S. Rostamnia, A. Hassankhani, *RSC Adv.* 2013, 3, 18626.
- [3] a) K. Groebke, L. Weber, F. Mehlin, *Synlett* 1998, 661. b) H. Bienayme,
   K. Bouzid., *Angew. Chem. Int. Ed.* 1998, 37, 2234. c) S. Rostamnia, *RSC Adv.* 2015, 5, 97044.
- [4] a) J. J. Chen, A. Golebiowski, J. Clenaghan, S. R. Klopfenstein, L. West, *Tetrahedron Lett.* 2001, 42, 2269. b) A. Shaabani, E. Soleimani, A. Maleki, J. Moghimi-Rad, *Synth. Commun.* 2008, 38, 1090. c) S. K. Guchhait, C. Maadan, *Synlett* 2009, 628. d) A. L. Rousseau, P. Matlaba, C. J. Parkinson, *Tetrahedron Lett.* 2007, 48, 4079.
- [5] a) C. M. Crudden, M. Sateesh, R. Lewis, J. Am. Chem. Soc. 2005, 127, 10045. b) B. W. Glasspoole, J. D. Webb, C. M. Crudden, J. Catal. 2009, 265, 148. c) C. M. Crudden, K. McEleney, S. L. MacQuarrie, A. Blanc, M. Sateesh, J. D. Webb, Pure Appl. Chem. 2007, 79, 247. d) S. Rostannia, E. Doustkhah, RSC Adv. 2014, 4, 28238. e) S. Rostannia, F. Pourhassan, Chin. Chem. Lett. 2013, 24, 401.
- [6] a) S. Rostamnia, H. Xin, X. Liu, K. Lamei, J. Mol. Catal. A 2013, 374–375, 85. b) S. Rostamnia, H. Xin. J. Mol. Liq. 2014, 195, 30. c) S. Rostamnia, X. Liu, D. Zheng. J. Colloid Interface Sci. 2014, 432, 86. d) S. Rostamnia, E. Doustkhah, Tetrahedron Lett. 2014, 55, 2508. e) S. Rostamnia, E. Doustkhah, A. Nuri, J. Fluorine, Chem. 2014, 153, 1. f) S. Rostamnia, H. Xin, Appl. Organometal. Chem. 2013, 27, 348. g) S. Rostamnia, A. Zabardasti, J. Fluorine, Chem. 2013, 144, 69.

- [7] a) Z. Q. Wang, S. M. Cohen, J. Am. Chem. Soc. 2007, 129, 12368. b) H. Li,
   M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, Nature 1999, 402, 276. c) J. L. C.
   Rowsell, O. M. Yaghi, Micropor. Mesopor. Mater. 2004, 73, 3.
- [8] a) F. X. L. Xamena, F. G. Cirujano, A. Corma, *Micropor. Mesopor. Mater.* **2012**, *157*, 112. b) J. Gascon, U. Aktay, M. D. Hernandez-Alonso, G. P. M. van Klink, F. Kapteijn, J. Catal. **2009**, *261*, 75. c) S. Rostamnia, H. Xin, N. Nouruzi, *Micropor. Mesopor. Mater.* **2013**, *179*, 99. d) S. Rostamnia, A. Morsali, *RSC Adv.* **2014**, *4*, 10514. e) S. Rostamnia, A. Morsali, *Inorg. Chim. Acta* **2014**, *411*, 113. f) S. Rostamnia, H. Xin, *Appl. Organometal. Chem.* **2014**, *28*, 359. g) S. Couck, J. F. M. Denayer, G. V. Baron, T. Remy, J. Gascon, F. Kapteijn, J. Am. Chem. Soc. **2009**, *131*, 6326. h) X. Cheng, A. Zhang, K. Hou, M. Liu, Y. Wang, C. Song, G. Zhang, X. Guo, Dalton Trans. **2013**, *42*, 13698. i) C. M. Doherty, G. Grenci, R. Riccò, J. I. Mardel, J. Reboul, S. Furukawa, S. Kitagawa, A. J. Hill, P. Falcaro, *Adv. Mater.* **2013**, *25*, 4701.
- [9] Y. Huang, Z. Zheng, T. Liu, J. Lü, Z. Lin, H. Li, R. Cao, Catal. Commun. 2011, 14, 27.
- [10] a) M. D-Lange, J. Gutierrez-Sevillano, S. Hamad, T. Vlugt, S. Calero, J. Gascon, F. Kapteijn, J. Phys. Chem. C 2013, 117, 7613. b) P. Serra-Crespo,

E. Gobechiya, E. V. Ramos-Fernandez, J. Juan-Alcañiz, A. Martinez-Joaristi,
 E. Stavitski, C. Kirschhock, J. Martens, F. Kapteijn, J. Gascon, *Langmuir* 2012, 285, 12916.

#### SUPPORTING INFORMATION

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