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Post-synthetic modified MOF for A<sup>3</sup>-coupling reaction of aldehyde, amine, and alkyne

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A new heterogeneous NHC catalyst (Ag-NHC-MOF) was synthesized by the post-synthetic modification of an azoliumcontaining metal-organic framework. The structure of the catalyst was well defined and fully characterized using various techniques such as PXRD, FE-SEM, HR-TEM, XPS, FT-IR, TGA, BET, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, EDS, and ICP. The catalyst showed an excellent activity towards A<sup>3</sup>-coupling reaction with a broad substrates scope. The A<sup>3</sup>-coupling reaction was performed under ambient conditions and full conversion was reached within just 1 hour for the model reaction. The heterogeneous silver NHC MOF (Ag-NHC-MOF) catalyst can be recycled and reused at least four times without significant loss in the activity. In comparison with previously reported heterogeneous catalysts applied for the A<sup>3</sup>-coupling reaction, the Ag-NHC-MOF demonstrates a superior performance for A<sup>3</sup>-coupling reaction.

# Introduction

Metal-Organic Frameworks (MOFs) are one of the new groups of crystalline materials that emerged only two decades ago while due to their various specific properties a rapid grew in their development is observed. Their advantages such as enormous pore size, high surface area, selective adsorption of smaller molecules, and low density make them potential candidates for different applications like gas storage,<sup>1</sup> purification,<sup>2</sup> molecular sensing,<sup>3</sup> drug delivery and catalysis. Metal-organic frameworks (MOFs), particularly at the nanoscale, have been used as effective heterogeneous catalysts because of their tunable nature resulting from their metallic cores and malleable organic linkers.<sup>4</sup> Various competent strategies have been applied for construction of MOFs as catalysts to improve their catalytical activity at the molecular level.<sup>5</sup> These strategies are categorized as follows: unsaturated metal parts at active sites,<sup>6</sup> chemical transformations, and immobilization of other metal nanoparticles inside the pores of the framework,<sup>7,8</sup> employment of designed linkers<sup>9</sup> and postsynthetic modification (PSM).<sup>10</sup> Among them, the postsynthetic modification can be developed on both the metal cores and organic ligands of MOFs.<sup>11</sup> One good example for PSM of MOFs is the employment of N-heterocyclic carbene (NHC) precursor (Fig 1).



Fig 1 1,3-bis(4-carboxyphenlyl)imidazolium chloride

N-Heterocyclic carbenes (NHCs) alone are still powerful catalysts for a valuable series of chemical reactions involving carbon-carbon, carbon-nitrogen, and carbon-oxygen bond formation or deletion.<sup>11</sup> Therefore, integrating NHCs into a MOF would combine various advantageous properties such as generation of the cavities that are appropriate for binding anionic guests, availability of the protons of the azolium which is then accessible for active metals, heterogeneous, and easy separation. This would result in multiple and different catalytical sites close together in one structure that generally cannot be formed simultaneously in catalytical systems.<sup>11</sup> Regarding these advantages, multiple synthetic methods have been developed to create NHC linkers inside MOFs. For example, in one method, the NHC-complexes are presynthesized as organic linkers and utilized for the synthesis of MOFs.<sup>12</sup> While in another method, the N-heterocyclic carbene complexes generated via MOF synthesis.<sup>13-15</sup> However, one of the easiest and practical methods is PSM of frameworks containing azolium based linkers<sup>16,17</sup> which results in the immobilization of homogeneous catalysts and also increases the performance of the final MOF.<sup>18</sup> In this work, crystalline MOF (1) was synthesized according to the previous work of Sen and coworkers.<sup>19</sup> 1 consists of the  $[Zn_8O]$  clusters and angular N-heterocyclic carbene (NHC) containing ligands with

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two aromatic carboxylates (Fig 2). During the post-synthetic modification step, first, the NHC carbon of the **1** linker was deprotonated, forming a stable carbene. The metal is then added to the persistent carbene, to form a novel post-synthetic modified azolium based MOF.



Fig 2 Structure of the 1 consisting of the  $[Zn_8O]$  clusters with six metallomacrocycles and NHC moieties around it<sup>8</sup>

In this regard, the new Ag(I)-NHC MOF was synthesized and fully characterized and utilized as a highly active heterogeneous catalyst for the  $A^3$ -coupling reaction. Notably, this is the first report of using the active site Ag(I)-NHC in MOF catalyst for  $A^3$ -coupling application.

It should be noted that the A<sup>3</sup>-coupling reaction is a threecomponent reaction involving aldehyde, alkyne, and amine to produce propargylamine (Fig 3). This reaction attracted many attentions due to the utilization of simple precursors to produce biologically active propargylamines. Propargylamines are an attractive class of compounds with a wide range of applications as enzyme inhibitors,<sup>20,21</sup> antitumor antibiotics,<sup>12</sup> pharmaceutical agent<sup>22</sup> and so on. They can be applied for powerful synthetic methods as a key construction block in various nitrogen-containing heterocycles, like pyrrolidines,<sup>23</sup> pyrrole,<sup>24</sup> pyrrolophanes,<sup>25</sup> aminoindolizines,<sup>26</sup> natural products,<sup>27, 28</sup> as well as in therapeutic drug molecules.<sup>29-33</sup>



Fig 3 A<sup>3</sup>-coupling reaction scheme

Various heterogeneous catalytical systems such as silver nanoparticles<sup>31,34,35</sup> supported by copper (I), nickel complexes,<sup>36</sup> nanocrystalline copper (II) oxide,<sup>37,38</sup> zinc dust,<sup>39</sup> Iron (III) oxide nanoparticles, 40,41, gold nanoparticles supported by zinc oxide,<sup>42</sup> gold nanoparticles supported by magnesium oxide,<sup>43</sup> copper(I) metal-organic frameworks,<sup>44</sup> and so on have been reported previously for the synthesis of different propargylamines. However, the wide use of these catalysts in the industry is inhibited due to the high cost, difficulty in the recovery from the reaction mixture, and high reaction temperature and tedious conditions<sup>45,46</sup>. In this work, we present Ag(I)-NHC-MOF as a simply synthesized MOF, which shows high catalytical activity towards A<sup>3</sup>-coupling reactions. To the best of our knowledge, Ag(I)-NHC-MOF shows superior catalytical performance compared to all previously reported catalysts for A<sup>3</sup>-coupling reaction.

# Experimental

#### Materials and methods

All chemicals were purchased from commercially available sources and were used as received without further purification. The materials were synthesized according to the previous reports with slight modifications.

**Ligand synthesis.** The compounds N,N-bis(4-carboxyphenyl) ethylenediimine (LA) and 1,3-bis(4-carboxyphenyl) imidazolium chloride  $(H_2L^+Cl^-)$  were synthesized according to the previous reports<sup>19,47</sup> with slight modification<sup>+</sup>.

## MOF synthesis.

1: [{(Zn<sub>0.25</sub>)<sub>8</sub>(O)}Zn<sub>6</sub>(L)<sub>12</sub>(H<sub>2</sub>O)<sub>29</sub>(DMF)<sub>69</sub>(NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub><sup>19</sup>

**1** was synthesized following the procedure reported in the literature  $^{8,19}$  +.

**Post-synthetic modification of MOF.** The post-synthetic modification of **1** was performed similarly to a previous report by our group. <sup>8</sup> Ag(OAc) (different amounts) and **1** (60.0 mg, 0.1 mmol) was introduced to a 150 mL two-necked round bottom flask containing 60 mL of  $CH_2Cl_2$  (Table 1). The reaction mixture was stirred at ambient temperature for 12 h and then refluxed for 24 h at 39°C under an inert N<sub>2</sub> atmosphere. The light-brown solid was collected by filtration and washed with  $CH_2Cl_2$  (3 x 5 mL), MeOH, (2 x 5 mL) and  $Et_2O$  (2 x 5 mL) and dried in air.

Table 1. Various amounts of silver acetate used in the synthesis of 1-Ag

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Entry	Silver MOF	Silver Acetate	MOF-1
1	1- Ag (1)	25.0 mg, 0.15 mmol	60.0 mg, 0.1 mmol
2	1-Ag (0.8)	20.0 mg, 0.12 mmol	60.0 mg, 0.1 mmol
3	1-Ag (0.5)	12.5 mg, 0.075 mmol	60.0 mg, 0.1 mmol
4	1-Ag (0.3)	7.5 mg, 0.045 mmol	60.0 mg, 0.1 mmol

**A<sup>3</sup>-Coupling reaction.** In a typical procedure phenylacetylene (110 mg, 1.1 mmol), paraformaldehyde (30 mg, 1.0 mmol), diisopropylamine (111 mg, 1.1 mmol), and **1-Ag** catalyst (5 mg) were added to a 10 mL of Schlenk tube. The mixture was stirred at room temperature for 1 h. After the reaction was completed, the mixture was washed with ethyl ether (3 x 5 mL) and filtered. The compounds were concentrated and the residue was purified by flash chromatography on silica gel (eluant: hexane/ethyl acetate = 3:1, V/V) to give the desired product as a colourless oil (208.87 mg, 97% isolated yield).

**Recycling test.** An important issue to be evaluated in heterogeneous catalysis is the reusability. The **1-Ag** exhibited good reusability in terms of the  $A^3$ -coupling reaction. For this purpose, after carrying out the first reaction, the catalyst was separated by filtration and washed with diethyl ether and dried in the air. Afterward, it was reused directly without further purification. The recovered catalyst was used for further reactions and showed the consistent activity for at least 4 consecutive cycles (Table 6, entries 1–4).

# Characterization

Powder X-ray diffraction spectra (PXRD) were recorded on an Empyrean instrument from PANalytical with a monochromatic Cu K $\alpha$  radiation at ambient conditions. <sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded using a Bruker 500 MHz NMR spectrometer (500 MHz and 100 MHz, respectively) in CDCl<sub>3</sub>. Fourier transform infrared (FT-IR) spectra were collected on a SCIMITAR FTS 2000 spectrometer. A JEOL (JSM-5610LV, 0.5-35 kV) Scanning electron microscope (SEM) was applied to study the texture of the material. TEM analyses were carried out on a Philips CM20 microscope operated at 200 kV. The element distribution map analysis was obtained by an S4800 field emission scanning electron microscope (FE-SEM, Hitachi, Japan) equipped with an X-Max 50 energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments, Britain) with an accelerating voltage of 10 kV. The binding energy was collected using an X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000C ESCA), and C 1s = 297.98 eV was used as a reference. The content of Ag was determined by inductively coupled plasma optical emission spectra (ICP, Varian VISTAMPX). MS spectra were determined using a Trace MS 2000 organic mass spectrometer, and the signals were given in m/z. Thermogravimetric analyses (TGA-DSC) were performed using a Netzsch (STA449c/3G) instrument (heating rate of 10 °C/min, N<sub>2</sub> flow). The micro pore surface measurements were obtained from the Brunauer-Emmett-Teller (BET) analysis.

After the synthesis of **1**, a post-synthetic modification was performed. According to the obtained results, the major diffraction peaks of the PXRD pattern were maintained, hence it can be concluded that **1** can tolerate such modification without collapse of the framework and change in the structure. In addition, a new peak around 8.9-9.0 2 theta/degrees appeared (Fig 5), which corresponds to the silver attached to the metal-organic framework.



## **Results and discussion**

In order to observe the local geometry and phase purity of the crystalline framework of the synthesized compounds, X-ray diffraction (PXRD) was performed and the results are shown in Fig 4 and 5. Fig 4 shows that the structure of the metal organic framework, its homogeneity and phase purity match well with the PXRD patterns previously reported.<sup>8,19</sup> Moreover, the PXRD pattern exhibited a long-range crystalline structure proving that the framework was formed with an unusual secondary building unit (SBU). To be more precise, the SBU coordinated to six azolium linkers creating a three-dimensional structure proving that synthesized MOF **1** is in accordance with the results found in the literature.<sup>8,19</sup>



Fig 4 PXRD pattern of 1 simulated and as synthesized

Fig 5 PXRD pattern of 1 and 1-Ag with various amounts of silver.

The energy dispersive X-ray spectroscopy (EDS) analysis of the post-synthetic modified MOF clearly showed the existence of the silver in the framework (Figure S1 and S2). The elemental mapping of the **1-Ag(1)** indicates the presence of Ag, Zn, C and O as shown in Figure S1. According to Figure S1, the distribution of the silver is not uniform in the framework. The rod-like structures contain definitively more silver, while the stone-like structures are composed of the Zn, C, O, and Ag.

Thereafter, the texture and morphology of the silver modified **1** were investigated using the field emission scanning electron microscope (FE-SEM) (Fig 6). According to Fig 6 (a), it is confirmed that the modified MOF **1** had two different structures: stone-, and rod-like structures that were distributed randomly. The stone-like particles contained mostly the zinc framework (**1**) which was in accord with previous results,<sup>8,19</sup> whereas the rod-like structures were composed of silver agglomerates (Fig 6 (a)). Subsequently, it was decided to reduce the amount of silver added during postsynthetic modification step, in order to avoid agglomerations of silver on **1**.

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Fig 6 FE-SEM images of (a) 1-Ag(1), (b) 1-Ag(0.5) and HR-TEM images of (c) MOF 1, (d) 1-Ag(1), (e) 1-Ag(0.5), (f) 1-Ag(0.3)

After obtaining the results of PXRD, FE-SEM, and HR-TEM analysis, the procedure of the post-synthetic of **1** was modified. Therefore, various amounts of silver acetate were added during the PSM but lower compared to the original **1-Ag(1)**. Three different ratios of the silver acetate to MOF were examined. The new amounts of the silver were decreased to 0.8, 0.5, and 0.3 from the initial amount of **1-Ag(1)**.

Reducing the amount of silver acetate for PSM, affected the distribution of the silver in the metal-organic framework. From the PXRD analysis it is obvious that by stepwise decreasing the silver amount, the corresponding peak of silver declined respectively (Fig 5). Further characterization of the new samples was performed by HR-TEM and FE-SEM and EDS analysis. The high-resolution transmission electron microscopy of the original MOF 1 showed the uniform structure (Fig 6 (c)). After the application of the PSM procedure and decreasing the amount of silver acetate during the synthesis, uniform distribution of areas of silver (black dots) in the metal-organic framework is observed using TEM (Fig 6 (e), (f)). FE-SEM analysis of the newly synthesized 1-Ag(0.5) and 1-Ag(0.3) exhibited the uniform stone-like morphology (Fig 6 (b)). From EDS mapping and analysis of the newly synthesized silver catalyst 1-Ag(0.5) (Fig 7 and 8) a uniform distribution of the silver in the framework is observed. Hence, silver ions are attached to the metal-organic framework.



Fig 7 EDS mapping of 1-Ag(0.5) indicating the presence of Zn, O, C and Ag



#### Fig 8 EDS spectrum of 1-Ag(0.5)

The quantitative amount of silver in the **1-Ag** samples was obtained by inductively coupled plasma mass spectrometry (ICP-MS). The results illustrated that by decreasing the silver acetate amount, the attached silver to the framework reduced, which is in agreement with PXRD results (Fig 5). According to the ICP-MS analyses, the silver content of **1-Ag(1)**, **1-Ag(0.8)**, **1-Ag(0.5)**, **1-Ag(0.3)** amounts to 15.62 wt%, 14.20 wt%, 11.41 wt%, and 6.23 wt% respectively. On the other hand, (Table S1,†), the percentage of Zn did not change remarkably confirming that the main structure of the framework remained unaffected.



**Fig 9** FT-IR spectra of the ligand  $(H_2L^+Cl^-)$ , **1** and **1-Ag(0.5)**.

Further evidence of silver coordination to the framework is collected by the FT-IR spectra of the ligand, 1, and 1-Ag(0.5) and shown in Fig 9. The strong absorption band at 1701 cm<sup>-1</sup> corresponds to the v(C=O) stretching vibration, of uncoordinated carboxylate acids, the -COOH vibration is not observed in 1 and 1-Ag samples<sup>8</sup> evidencing that all carboxyl groups were totally deprotonated during the synthesis of the 1. Furthermore, in 1, as well as in 1-Ag(0.5) two new peaks, at 1655 cm<sup>-1</sup> and 1317 cm<sup>-1</sup>, corresponding to the stretching vibration of coordinated carboxylate anions, are observed. Those two peaks are not observed in the FT-IR spectrum of the ligand, which confirms the coordination between COO<sup>-</sup> from the ligand and Zn(II) from zinc nitrate.<sup>8</sup> Moreover, the FT-IR spectra of 1 and 1-Ag(0.5) matched well, which implies that the structure of 1 remained unchanged during the postsynthetic modification. In addition, there is a sharp peak in the spectrum of the ligand, around 1173 cm<sup>-1</sup>, which corresponds to the C-H vibration at the C2 position of the imidazolium ring,<sup>8</sup>

which decreases dramatically after the PSM. This proofs that the carbonic carbons of the imidazolium moieties were deprotonated by silver acetate and that silver was coordinated to the respective carbon.

In addition, the TGA analysis of the initial MOF **1** and postsynthetic modified **1-Ag(0.5)** showed no change in the thermal stability of the framework after PSM as the TGA curve pattern remained the same (Figure S4). The BET surface area of the **1** and **1-Ag(0.5)** are 103.01 and 92.35 m<sup>2</sup>/g respectively (Table S2), which is in accordance with previously reported data.<sup>8</sup>

Afterwards, another evidence of silver anchored to framework was obtained from the oxidation state of silver and zinc in the framework analysed by X-ray photoelectron spectra (XPS) analysis. In the general XPS survey (Fig 10 (a)) the existence of Ag, Zn, C, O, and N in the synthesized 1-Ag(0.5) is illustrated and the signal at 400.08 eV corresponds to the binding energy N 1s of the imidazolium moieties.<sup>48-50</sup> According to the highresolution spectra of Ag 3d region (Fig 10 (b)), there is a doublet related to the binding energy of Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$ at 367.38 eV and 373.38 eV respectively. These binding energies are the characteristics of the Ag(I) cation.  $^{\rm 51\text{-}55}$  In case of the presence of silver metal nanoparticles peaks at 368.4 eV and 374.4 eV, corresponding to the binding energy of Ag  $3d_{5/2}$ and Ag  $3d_{3/2}$  respectively should be observed.<sup>47-50,56</sup> The absence of these binding energies confirmed that there were silver metal nanoparticles present in our 1-Ag(0.5).47-50,56 Furthermore, no trace of Ag(OAc) was detected as well, due to the absence of the binding energy peak at 384.4 eV, which is the characteristic for the Ag 3d<sub>5/2</sub> level of binding energy of silver acetate. 47-50,56 Fig 10 (c) demonstrates the highresolution XPS spectrum for Zn. The corresponding peaks of Zn  $2p_{3/2}$  and Zn  $2p_{1/2}$  at 1020.98 eV and 1043.88 eV are characteristic binding energies for Zn(II) cations, which are coordinated with carboxylic groups to form the SBUs.<sup>57-59</sup> Furthermore, the XPS analysis of carbon (Fig 10 (d)) revealed binding energy peaks at 283.68 eV, 287.28 eV, and 290.78 eV, which are assigned to the binding energies of the 1s of C=C of aromatic carbon, imidazolium carbon (C-H) and COO<sup>-</sup> of carboxylate respectively.49,60-62 The XPS analysis data are consistent with the reported values for post-modified 1.<sup>8</sup>





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Binding Energy (eV)

**Fig 10** (a) XPS survey spectra; high-resolution spectra of (b) Ag 3d region, (c) Zn 2p region, (d) C 1s region of **1-Ag(0.5)**.

## Activity test

The above-synthesized catalysts were applied for the A<sup>3</sup>coupling reaction between phenylacetylene, paraformaldehyde, and diisopropylamine (as a model reaction) at room temperature in CH<sub>2</sub>Cl<sub>2</sub>. In order to study the catalytical activity, the reaction was studied using several catalysts, such as no catalyst, 1, 1-Ag(0.3), 1-Ag(0.5), and 1-Ag(0.8) (Table 2). According to the obtained results, no conversion was observed when the reaction was performed without any catalyst (Table 2, Entry 1), on the other hand, the reaction can occur with the help of both 1 and 1-Ag catalysts. However, the reaction catalyzed by 1-Ag outperforms 1 with respect to the reaction time of 1 h (Table 2, Entry 4 and 5), whereas reaction catalyzed by 1 reaches >99% conversion only after 24 h (Table 2, Entry The different silver-containing catalysts (1-Ag(0.3), 1-Ag(0.5), and 1-Ag(0.8)) were able to catalyze the reaction showing a good activity within short period of time. However, 1-Ag(0.5) was selected as the catalyst for further investigations

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due to the better distribution of the silver ions inside the framework and better performance.

Table 2 Effect of the catalyst on the A<sup>3</sup>-coupling reaction<sup>a</sup>



<sup>a</sup> Reaction conditions: phenylacetylene (1.1 mmol), paraformaldehyde (1.0 mmol), diisopropylamine (1.1 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL), N<sub>2</sub> atmosphere, **1** or **1-Ag** catalyst, room temperature. <sup>b</sup> Conversions and yields were determined by <sup>1</sup>H NMR spectroscopy

It is evident that **1-Ag(0.5)**, is a much better-performing catalysts for the  $A^3$ -coupling reaction compared to **1** which showed poor activity toward this reaction.

In order to optimize the reaction time, a series of reactions were performed. According to the obtained results, the full conversion of the substrates into the desired product occurred after 24 hours when **1** was used as a catalyst, in the absence of any silver source (Table 3, entry 4). On the other hand, it was found out that the three-component reaction can occur just in 1 hour in the presence of **1-Ag(0.5)** (Table 3, entry 9). Hence, it is clearly demonstrated that silver plays a pivotal role in the catalysis of the  $A^3$ -coupling reaction. This can be assigned to the presence of efficient Ag-NHC active site inside the framework, which is known for its ability to promote three-coupling reaction.<sup>31</sup>

**Table 3** Effect of the time on A<sup>3</sup>-coupling reaction using 1 and1-Ag catalysts<sup>a</sup>

Entry	Catalyst	Time	Conversion (%) <sup>b</sup>	Entry	Catalyst	Time	Conversion (%) <sup>b</sup>	
1	1	2 h	30%	6	1-Ag(0.5)	15 min	22	
2	1	6 h	57%	7	1-Ag(0.5)	30 min	67	
3	1	15 h	86%	8	1-Ag(0.5)	45	83	
4	1	24 h	>99%	9	1-Ag(0.5)	1 h	>99	
5	1	26 h	>00%					

<sup>a</sup> Reaction conditions: phenylacetylene (1.1 mmol), paraformaldehyde (1.0 mmol), diisopropylamine (1.1 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL), N<sub>2</sub> atmosphere, 1 or 1-Ag(0.5) catalyst, room temperature. <sup>b</sup> Conversions were determined by <sup>1</sup>H NMR spectroscopy

Fig 11 summarizes the results of the effect of the catalyst amount on the three-component coupling reaction. In order to do so, the amount of the catalyst was gradually decreased from 35 mg down to 2.5 mg. Experimental results showed that  $A^3$ -coupling reaction can successfully occur using 5 mg of the silver catalyst, whereas 30 mg of **1** is required to convert reactants to products (Fig 11).



**Fig 11** Effect of the amount of the catalyst on A<sup>3</sup>-coupling reaction<sup>a</sup>

<sup>(a</sup> Reaction conditions: phenylacetylene (1.1 mmol), paraformaldehyde (1.0 mmol), diisopropylamine (1.1 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL), N<sub>2</sub> atmosphere, 1 or 1-Ag(0.5) catalyst, room temperature (1 h (for 1-Ag(0.5) and 24 h (for 1)). <sup>b</sup> Conversions were determined by <sup>1</sup>H NMR spectroscopy)

The effect of the solvent on the  $A^3$ -coupling reaction was studied and the results are summarized in Table 4. Among the solvents tested,  $CH_2CI_2$ , acetone, and  $CH_3CN$  were the most suitable solvents for the  $A^3$ -coupling reaction (Table 4, entry 1-3). Reaction in THF and without any solvent generated the desired product, however, residues of substrates were still in the reaction mixture (Table 4, entry 6, and 8). Poor results were obtained when the reaction was carried in toluene (Table 4, entry 7). Furthermore, the reaction did not proceed in the DMSO and DMF (Table 4, entry 4, and 5).

 Table 4 Effect of the solvent on A<sup>3</sup>-coupling reaction using silver-MOF catalyst<sup>a</sup>

		$\mathbb{A}_{\mathbb{H}} \cdot \mathcal{A}_{\mathbb{H}} \cdot \mathcal{A}_{\mathbb{H}}$	Catalyst	
Entry	Catalyst	Solvent	Conversion (%)	Isolated Yield (%)
1	1-Ag(0.5)	CH <sub>2</sub> Cl <sub>2</sub>	>99	97
2	1-Ag(0.5)	Acetone	78	75
3	1-Ag(0.5)	CH <sub>3</sub> CN	92	89
4	1-Ag(0.5)	DMSO		
5	1-Ag(0.5)	DMF		
6	1-Ag(0.5)	THF	62.5	59
7	1-Ag(0.5)	Toluene	29	25
8	1-Ag(0.5)	No solvent	53	50

 $^{\rm a}$  Reaction conditions: phenylacetylene (1.1 mmol), paraformaldehyde (1.0 mmol), diisopropylamine (1.1 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2.0 ml), N<sub>2</sub> atmosphere, **1-Ag(0.5**) catalyst, room temperature.  $^{\rm b}$  Conversions and yields were determined by <sup>1</sup>H NMR spectroscopy

In order to examine the scope of the A<sup>3</sup>-coupling reaction using this **1-Ag** catalyst, the study was extended to different combinations of the substrates. The results are shown in Table 5. Phenylacetylene was used as a model substrate in the beginning. Various cyclic, heterocyclic and acyclic secondary aliphatic amines were reacted with phenylacetylene and paraformaldehyde and afforded excellent conversions to the desired product at room temperature within 1 hour (Table 5, Entry 1,5, 7-10, 17). In addition, aromatic amines in

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combination with alkyne and aldehyde produced the desired propargylamines with high yields (Table 5, Entry 8).

To expand and examine further the scope of the  $A^3$ -coupling reaction, aliphatic and aromatic alkynes were used as one of the substrates. A number of alkynes were combined with aldehydes and amines under A<sup>3</sup>-coupling reaction conditions. Aromatic alkynes containing bromo-, and hydroxy groups demonstrated a good reactivity along with aliphatic ones (Table 5, Entry 17-20). Under the applied reaction conditions, cyclic and acyclic aliphatic aldehydes showed good reactivity (Table 5, Entry 1-4). Good yields were afforded also when combining aromatic aldehydes with electron-donating and electron-withdrawing functional groups (Table 5, Entry 12-16).

Tab	le 5 /	A°-couplii	ng reactio	on catalyz	ed by <b>1-A</b>	g(0.5) <sup>°</sup>
R	=	+ R <sup>1</sup> CHO	+ NHR <sup>2</sup> R <sup>3</sup> -	1-Ag(0.5)	R	
Entry		Alkyne	Aldehyde	Amine	Conversion (%) <sup>b</sup>	NR <sup>2</sup> R <sup>3</sup> Isolated Yield <b>(%)</b>
	1	C <sub>6</sub> H <sub>5</sub> C≡CH	CH <sub>2</sub> O	$\succ^{\natural}\!$	>99	97
	2	C <sub>6</sub> H₅C≡CH	C <sub>6</sub> H <sub>5</sub> CHO	$\succ^{\natural}\!$	94	91
	3	C <sub>6</sub> H <sub>5</sub> C≡CH	\ ↓ s	$\nearrow^{\tt H}\!$	93	90
	4	C <sub>6</sub> H <sub>5</sub> C≡CH	C <sub>6</sub> H <sub>12</sub> CHO	$\nearrow^{\tt H}\!$	90	87
	5	C <sub>6</sub> H <sub>5</sub> C≡CH	CH <sub>2</sub> O		96	93
	6	C <sub>6</sub> H₅C≡CH	C <sub>6</sub> H₅CHO		93	89
	7	C <sub>6</sub> H <sub>5</sub> C≡CH	CH <sub>2</sub> O		90	87
	8	C <sub>6</sub> H₅C≡CH	CH <sub>2</sub> O	$\mathbf{O}^{L}$	90	86
	9	C <sub>6</sub> H₅C≡CH	CH <sub>2</sub> O	()^st	92	89
	10	C <sub>6</sub> H₅C≡CH	CH <sub>2</sub> O		89	87
	11	C <sub>6</sub> H <sub>5</sub> C≡CH	C <sub>6</sub> H <sub>5</sub> CHO		85	83
	12	C <sub>6</sub> H <sub>5</sub> C≡CH	p-NO₂- C <sub>6</sub> H₅CHO		84	82
	13	C <sub>6</sub> H₅C≡CH	<i>p</i> -Br- C <sub>6</sub> H <sub>5</sub> CHO	- Jer	82	79
	14	C <sub>6</sub> H₅C≡CH	p-Cl- C <sub>6</sub> H₅CHO	- And	83	80
	15	C <sub>6</sub> H₅C≡CH	<i>р-</i> ОН- С <sub>6</sub> Н₅СНО	МН	79	77
	16	C <sub>6</sub> H <sub>5</sub> C≡CH	<i>p</i> -CH <sub>3</sub> 0- C <sub>6</sub> H₅CHO	С	78	75
	17	C <sub>6</sub> H <sub>5</sub> C≡CH	CH <sub>2</sub> O	HN Ph	79	76
	18	<i>p</i> -Br- C <sub>6</sub> H₅C≡CH	CH <sub>2</sub> O	HN Ph	86	81
	19	<i>р</i> -ОН- С <sub>6</sub> Н₅С≡СН	CH <sub>2</sub> O	HN Ph	82	79
	20	C₅H <sub>10</sub> C≡C H	CH <sub>2</sub> O	HN Ph	85	82

Reaction conditions: phenylacetylene (1.1 mmol), paraformaldehyde (1.0 mmol), diisopropylamine (1.1 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL), N<sub>2</sub> atmosphere, **1** or **1-Ag(0.5**) catalyst, room temperature. <sup>b</sup> Conversions and yields were determined by <sup>1</sup>H NMR spectroscopy

The hot filtration test was performed under the optimized reaction conditions, in order to investigate the heterogeneous nature of the silver catalyst. Phenylacetylene (1.1 mmol), paraformaldehyde (1.0 mmol) and diisopropylamine (1.1 mmol) were added together with 1-Ag(0.5) (5 mg) and 2 mL of DCM under room temperature. After 20 min 60% conversion of reactants was observed and the catalyst was filtered out from the mixture, leaving the reaction to proceed for 1h. During that time, no further formation of the product was observed, which clearly shows that no leaching of silver(I) occurred during reaction.

In order to examine the decomposition of the catalyst and its recyclability, several reactions were performed. Thereafter, the catalyst was filtered and washed with diethyl ether (2 mL x 3), air-dried and reused again without further purifications. The recovered catalyst was used again in the next cycle and an almost consistent activity was noticed for 4 consecutive cycles (Table 6). A slight loss of the activity of catalyst was observed and can be attributed to the filtration process, by which catalyst was collected after each reaction cycle. There is a possibility that during filtration some of the particles of the catalyst were lost, which lead to the slight reduction in the vield.



	$H \stackrel{O}{\longrightarrow}_{H} H \stackrel{V}{\longrightarrow} \stackrel{V}{\longrightarrow} \stackrel{Catalyst}{\longrightarrow}$	()-=-H <sub>2</sub> C-N
Cycle	Conversion (%)	Isolated Yield (%)
1	>99	97
2	>99	96.5
3	96	94
4	94	91

<sup>a</sup> Reaction conditions: phenylacetylene (1.1 mmol), paraformaldehyde (1.0 mmol), diisopropylamine (1.1 mmol), CH2Cl2 (2.0 mL), N2 atmosphere, 1 or 1-Ag(0.5) catalyst, room temperature <sup>b</sup> Conversion by <sup>1</sup>H-NMR

Fig 12 represents the PXRD pattern for 1-Ag(0.5) before and after the catalytical activity. It can be seen that the structural integrity of the metal organic framework of catalysts was not affected significantly as the main peaks characterizing the material remained unchanged. However, the minor differences were observed on the PXRD pattern. The possible reason is that during the catalytical synthesis some residues of the substrates were being trapped in the pores of the catalyst, which lead to the decrease of the surface area of reused catalyst, as confirmed by BET analysis (Table S2, Entry 3) and caused the appearance of additional signals on the PXRD pattern. FE-SEM images confirm that the morphology is not affected by the reaction (Figure S5). The silver catalyst can be reused without the loss of the activity as well as without any significant collapse of the structure. Additionally, silver leaching of the catalyst was examined as well. Inductively coupled plasma (ICP) analysis indicated that silver content

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slightly changed from 11.41 % before the reaction to 11.33 %  $II.^{46}$  after the catalytical reaction (Table S1).



Fig 12 PXRD pattern of the 1-Ag(0.5) catalyst before and after the reaction

To stress out the good catalytical performance and efficiency of the silver-MOF catalyst a comparison to various catalysts in the literature was made. The recently reported efficient catalysts are summarized in Table 7 below. Among reported catalysts, the high yields were obtained using the following catalysts: PS-supported NHC-Ag(I) (Table 7, entry 1), ZnII/HAP/Fe3O4 (Table 7, entry 4), Ag nanoparticles (Table 7, entry 7), Cu2(BPDC)2(BPY) (Table 7, entry 11) and Cu[(2pymo)2] (1%) (Table 7, entry 12). Obviously, the mentioned catalysts are very active, however, some of them require long reaction time (Table 7, entry 1-3. 7-10), and others perform only at high temperatures (Table 7, entry 2-4, 7-11). Besides those, MOF-Cu2I2(BTTP4) catalyst demonstrated good reaction conditions, but the yield of the product was slightly lower than for the synthesized silver catalyst. From the Table 7. it is obvious that most of the methods reported in the literature are suffering from various drawbacks related to reaction conditions. In comparison to that, the synthesized 1-Ag(0.5) is superior to the other catalyst because it can overcome mentioned weaknesses. The advantages of the heterogeneous 1-Ag(0.5) catalyst are a minimum time of reaction to achieve the desired yield of the product, easy to be separated from the mixture, easy to be recycled and re-used without further purification.

According to our obtained results, the three-coupling reaction can be catalyzed by both unmodified and PSM metal-organic frameworks (Table 3). Fig 13 demonstrates the plausible mechanism of the **1** and **1-Ag(0.5)** to catalyze the A<sup>3</sup>-coupling reaction. The mechanism suggests that reaction can occur by two different pathways. First, the reaction can undergo the mechanism that is activated by zinc metal in the framework.<sup>46,71</sup> Here, at first the alkyne is coordinated to Zn(II) to produce the alkyne complex I. After, the catalyst is inserted into the C-H bond of the terminal alkyne, the acetylide complex is deprotonated and gives zinc acetylide intermediate II.<sup>46,71</sup> On the other hand, the iminium ions are formed from aldehyde and amine, through the coordination of the carbonyl group of aldehyde to Zn (II). This iminium ion reacts with zinc acetylide intermediate II to give intermediate III. Finally, the nucleophilic attack of the acetylide ion on the iminium carbon generates the desired product and regenerates the initial catalyst.<sup>46,71</sup>

The second path involves the silver side of the metal-organic framework. The synthesized silver metal-organic framework (**1-Ag(0.5)**) contains the NHC moiety that is attached to the silver. Therefore, it can be assumed that reaction follows the following mechanism , which is slightly modified from the originally proposed mechanism by Li.<sup>63</sup> In the beginning, the Ag(I) inserts into the C-H of the alkyne, followed by an elimination of the H which will generate the silver alkynide and the amine hydrogen halide salt.<sup>32,45,72</sup> Thereafter, the amine hydrogen halide salt reacts with the aldehyde to give the iminium halide, which then reacts with the silver alkynide to produce the desired product and regenerate the initial catalyst.<sup>32,45,72</sup> Further studies to shed light on the mechanism of A<sup>3</sup>-coupling reaction are currently ongoing in our laboratory.

## Conclusions

To sum up, a novel, efficient and environmentally friendly heterogeneous silver catalyst was synthesized and successfully applied for the three-component coupling reaction between alkyne, aldehyde, and amine. The reaction proceeds at room temperature within 1 hour using a low 1-Ag(0.5) catalyst loading. The reaction gives the desired propargylamine product in high yields without using high temperatures and long reaction times. It was demonstrated that the 1-Ag(0.5) is superior to the other reported catalyst due to the mild reaction conditions, easy separation, and high recyclable features. The catalyst can be used for several consecutive cycles without significant loss in the activity and without collapse of the metal-organic framework structure. The provided mechanism demonstrates that both 1 and 1-Ag(0.5) can be applied for the catalysis of the A<sup>3</sup>-coupling reaction to synthesize propargylamines from a variety of alkynes, amines, and aldehydes, which have a great potential to be applied in biochemistry, in medicine as pharmaceuticals agents and in chemistry as a basis for the synthesis of variety of nitrogenous compounds.

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Entry	Catalyst	Time	Temp	Solvent	Recyclability	Yield (%)	Ref.
1	PS-supported NHC-Ag(I)	24 h	r.t.	Solvent-free	12 cycles	97	19
2	Agl	14 h	100°C	Water or organic solvents	No data	75	20
3	Pd@MOF1	12-30 h	90°C	toluene	4 cycles	91	21
4	ZnII/HAP/Fe <sub>3</sub> O <sub>4</sub>	4-7 h	110°C	Solvent-free	7 cycles	95	22
5	MOF-Cu <sub>2</sub> I <sub>2</sub> (BTTP <sub>4</sub> )	2 h	r.t.	CH <sub>3</sub> CN	4 cycles	90	23
6	IRMOF-3-GI-Cu	6 h	40°C	CHCl <sub>3</sub>	4 cycles	91	24
7	Ag nanoparticles	10-20 h	100°C	PEG	3 cycles	95	25
8	MCM-TS Cul solid catalyst	4-10 h	80°C	Toluene	7 cycles	92	26
9	Au-nanoparticles	3-13 h	75–80°C	CH <sub>3</sub> CN	4 cycles	92	27
10	Tetra-nuclear macrocyclic Cu(II) complex	12 h	80-120°C	Dioxane	4 cycles	93.5	28
11	Cu <sub>2</sub> (BPDC) <sub>2</sub> (BPY)	3 h	80°C	Toluene	7 cycles	94	29
12	Cu[(2-pymo) <sub>2</sub> ] (1%)	21 h	40°C	Dioxane	5 cycles	99	30
13	Silver-MOF	1 h	r.t.	DCM	4 cycles	97	This work

Table 7 Comparison between efficiency of Silver-MOF catalyst and other catalysts for A<sup>3</sup>-coupling reaction

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Fig 13 Proposed mechanism for A<sup>3</sup>-coupling reaction catalyzed by 1 and 1-Ag(0.5)

# **Conflicts of interest**

There are no conflicts to declare

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