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PAPER
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The role of atropisomers on the photo-reactivity and fatigue of diarylethene-based metal–organic frameworks

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Amine-functionalized MIL-101(Cr) embedded with Co(II) phthalocyanine as a durable catalyst for one-pot tandem oxidative A^3 coupling reactions of alcohols

Ahmad Shaabani,* Reza Mohammadian, Alireza Hashemzadeh, Ronak Afshari, Mostafa M. Amini,*

Faculty of Chemistry, Shahid Beheshti University, G. C., P. O. Box 19396-4716, Tehran, Iran

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*Corresponding authors: Tel: +982129902800, Fax: +982122431663 E-mail address: a-shaabani@sbu.ac.ir; Tel : +982129903109, Fax: +982122431663, E-mail address: m-pouramini@sbu.ac.ir

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Abstract

A newly porous postsynthetic modified metal-organic framework (MIL-101(Cr)-NH_2) was fabricated *via* a covalent immobilization of the cobalt(II) phthalocyanine and characterized by a variety of techniques, including FT-IR, XRD, TGA, SEM, EDS and ICP-OES analysis. This catalyst was successfully used in a one-pot tandem oxidative A^3 coupling reaction of alcohols. The main advantages of this protocol are reusability of catalyst, operational simplicity, mild reaction conditions and high yielding.

Keywords: Metal–organic framework, Postsynthetic modification, Metallophthalocyanines, Heterogeneous catalyst, Tandem oxidation process, A^3 coupling reaction.

1. Introduction

Design of new synthetic methodologies and strategies requires minimization of the reaction steps as much as possible with the more efficient and environmentally benign processes due to environmental concern and time-cost benefits. To this end, tandem reactions in which sequential transformations take place *via* two (or more) mechanistically distinct processes suit these demands well.[1] The tandem oxidation process (TOP) as an innovative and efficient synthetic approach combines the *in-situ* produced aldehyde intermediates from the oxidation of alcohols with nucleophilic trapping agents, meets the chemists demands in modern synthetic strategies designation and total syntheses.[2] Although the vast research efforts have been made in the development of TOP processes,[3] its application in some chemical transformations especially multicomponent reactions (MCRs) is less investigated.[4] The intrinsic complexity of MCRs mechanism and multiple functionalities of these types of reactions prevent the development of such one-pot oxidation/MCR processes; this is while in the majority of influential MCRs aldehydes are ubiquitous substrates. Therefore, improving

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the novel catalytic system to develop such a synthetic protocol would extend the scope of aldehyde-based MCRs.

Propargylamines are important building blocks that have been the object of intense investigations in medicinal chemistry, because of their biological activities and therapeutic properties.[5] They have been identified as one of the most widely prescribed potent drugs for preventing cell death and also as potential and selective irreversible monoamine oxidase type-B (MAO-B) inhibitors.[6] Consequently, various methods have been developed for the synthesis of propargylamine scaffolds.[7] Among these, A^3 coupling reaction (three-component coupling of aldehyde, amine, and alkyne) is more convenient and general approach towards propargylamine. In this type of reaction unlike classical methods in which metal acetylide is produced by applying stoichiometric quantities of the organometallic reagents, only a catalytic amount of transition metal has been used to create metal acetylide intermediate by C–H bond activation of terminal alkynes. In recent years, significant progress has been manifested for expanding the scope of this reaction by applying various homogeneous and heterogeneous catalysts such as Cu(I),[8] Ag(I),[9] Fe(III),[10] Zn(II),[11] Au(I)/Au(III),[12] Ni(II)[6] and In(III)[13] salts, Ir-complexes,[14] Ni–Y–zeolite,[15] copper ferrite nanoparticles,[16] copper-zeolites,[17] Fe_3O_4 nanoparticles,[18] Zn dust[19] and nanocrystalline copper(II) oxide.[20] Although several methods for the synthesis of propargylamine scaffolds have been reported, most of them have limited scope and require high temperature, long reaction times, inert gas and expensive catalysts such as Au, Ag and Ir. Thus, development of more efficient, practical, cheaper, reusable and simple synthetic methods can be beneficial.

Phthalocyanines (Pcs) and metallophthalocyanines (MPcs) have found widespread applications in diverse areas of material science, including catalysis, electrophotography, infrared radiation absorption, optical data storage and liquid crystallography because of their

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excellent optical and electrical properties.[21] Appropriate structural modifications on MPcs by incorporating a variety of catalytically active metals in the phthalocyanine ligand can lead to fundamental changes in the catalytic properties corresponding to the used metals.[22] Up to now, diverse chemical transformations including oxidation, reduction, and various C−C bond formation reactions were efficiently catalyzed by MPcs.[23] However, application of MPcs as catalysts has some drawbacks such as the tendency of these compounds to aggregation and agglomeration which subsequently reduce their catalytic activity; in addition, homogeneous MPc catalysts are separated from the reaction media with difficulty. To overcome these problems, covalently attachment of the MPcs on the insoluble supports can provide recyclable catalysts that prevent aggregation and agglomeration of the MPc complexes, simplify the homogeneous MPcs separation process and increase the heterogeneous MPcs effective surface area.[23-24] Therefore, with these features in mind, designing novel heterogeneous catalysts based on MPcs would develop efficient catalysts that seem to be promising candidates in many reactions.

Metal-organic frameworks (MOFs) as a kind of crystalline porous materials constructed from metal-ion containing nodes and multitopic organic linkers have gathered considerable attention due to their promising applications in gas and chemical storage, separation, drug delivery, conductivity, and catalysis.[25] Although novel applications are added to an already above impressive list as the chemistry of MOFs progresses, one of the challenges in the area of material sciences is the emergence of new applications which emphasizes the requirement of new types of materials.[26] In this regard, postsynthetic modification (PSM) of MOFs are known convert MOFs to a series of new materials which bears different chemical functionalities with the same basic structure of MOF. It has been shown this approach is general and practical for incorporating a wide range of functional groups into MOFs.[27] The resulted new MOF materials are entirely different from those of the parent MOF in catalytic

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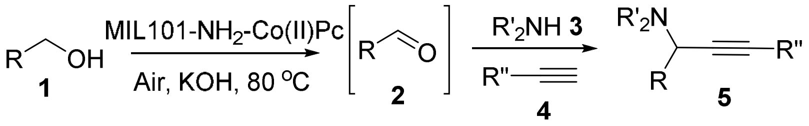
behavior and can be used as a novel heterogeneous catalyst in chemical reactions. In this aspect and in continuation of our interest in developing catalytic systems based on MPcs for synthetic methodologies[28] and multicomponent reactions,[29] herein, we report the synthesis of MIL-101-NH_2 MOF covalently anchored to cobalt(II) phthalocyanine by postsynthetic modification process and investigation of its catalytic activity in the tandem oxidative A^3 coupling-three component reaction in one-pot (Scheme 1). To the best of our knowledge, covalent binding of cobalt(II) phthalocyanine to MOF which is presented here has not yet been described in the literature.



Scheme 1. MIL-101-NH_2-Co(II)Pc-catalyzed tandem oxidative A^3 coupling reaction.

2. Results and Discussion

MIL-101 MOF based on chromium and containing amine functional groups previously synthesized by Kong and co-workers.[30] Since the amine moieties are present in the linker (2-aminoterephthalic acid) of the MOFs, functionalization of the material is available using chemical transformations. Therefore, postsynthetic modified MOFs can be prepared by covalent modification via nucleophilic attack of NH_2 groups on the fairly positive carbon atom of acyl chloride moieties present in tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II), producing an amide group between MOF and MPc (Scheme 2).

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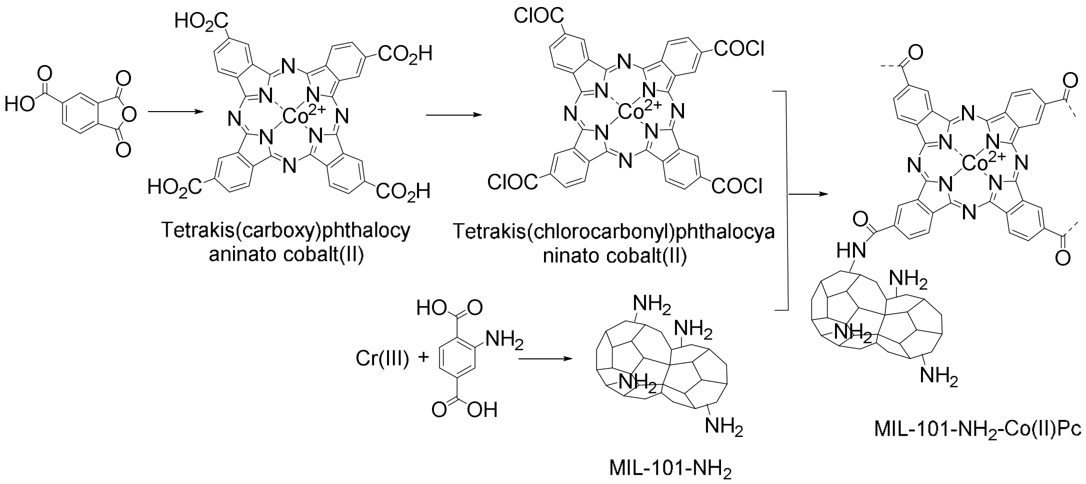

Scheme 2. Preparation of MIL-101-NH$_2$-Co(II)Pc.

The synthesized catalyst was characterized by FT-IR, XRD, TGA, SEM, EDS and ICP-OES analysis. Covalent immobilization of the cobalt(II) phthalocyanine on MIL-101-NH$_2$ was supported by FT-IR spectroscopy based on diminution of stretching band at 1708 cm^{-1} related to C=O bond of acyl chloride moieties present in tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) and enhancement of stretching band at 1627 cm^{-1} in agreement with the formation of amide group. Also, in confirming the desired catalyst formation, two stretching bands related to tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) exhibited at 1029 and 1078 cm^{-1} distinctly appeared in IR spectrum of MIL-101-NH$_2$-Co(II)Pc (Figure 1).

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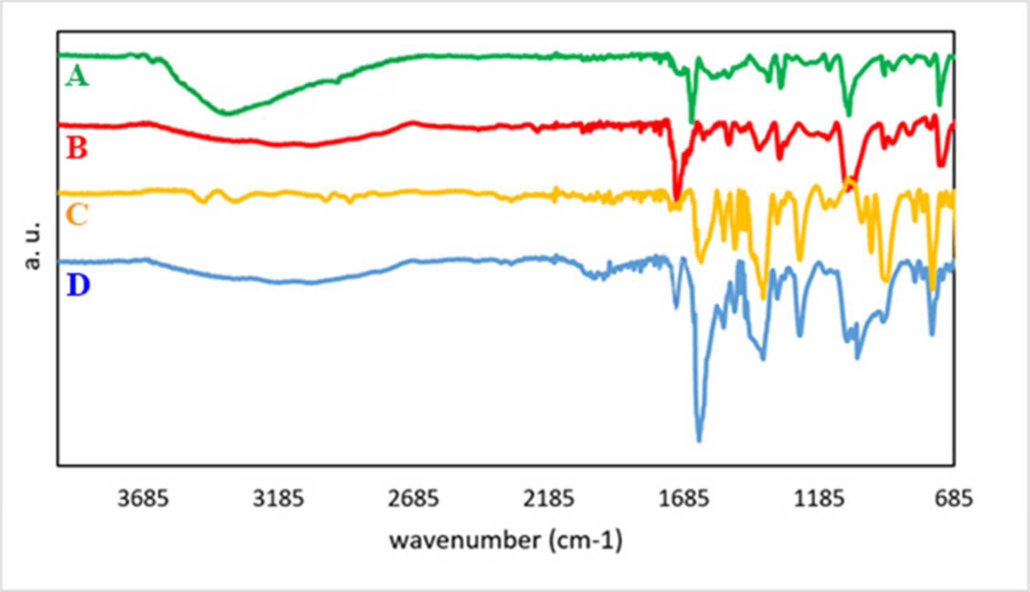

Figure 1. FT-IR spectra of tetrakis(carboxy)phthalocyaninato cobalt(II) (A), tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) (B), MIL-101-NH$_2$ (C), and MIL-101-NH$_2$-Co(II)Pc (D).

Powder X-ray diffraction (PXRD) patterns of MIL-101-NH$_2$, tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) and MIL-101-NH$_2$-Co(II)Pc were recorded and employed to investigate the structure of the synthetic catalysts. As shown in Figure 2, the characteristic diffractions of tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) appeared at 2θ values of 28^o, 40.5^o, 50.1^o and 66.3^o as four sharp diffractions and the PXRD pattern of MIL-101-NH$_2$ show characteristic diffractions at $2\theta = 3.3^o$, 5.1^o, 8.9^o and 16.6^o. The X-ray diffraction patterns of synthetic catalyst reveal that almost all the diffractions are maintained even after the post-synthetic reaction indicating that the structure of the materials is not changed during the functionalization process.

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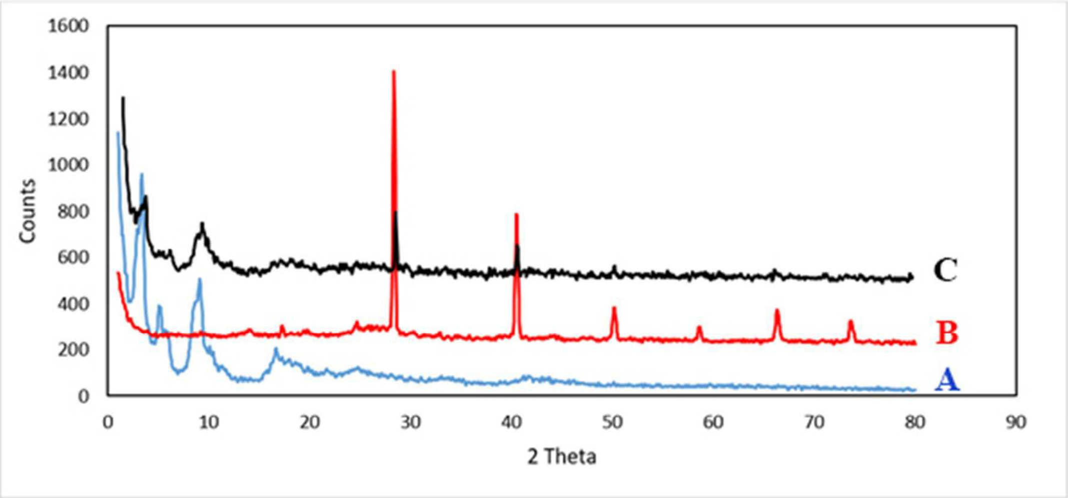

Figure 2. XRD patterns of MIL-101-NH_2 (A), tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) (B) and MIL-101-NH_2-Co(II)Pc (C).

Thermal gravimetric analysis (TGA) was performed on MIL-101-NH_2, and MIL-101-NH_2-Co(II)Pc in the air to investigate the thermal stability of catalysts and the results are illustrated in Figure 3. Thermogravimetric curves of MIL-101-NH_2 and MIL-101-NH_2-Co(II)Pc revealed initial loss of adsorbed water and volatile materials in the temperature range of 76-129 and 86-138 ^{o}C, respectively. The thermogram of MIL-101-NH_2 and MIL-101-NH_2-Co(II)Pc also show a weight loss of about 78% and 67% at the temperature higher than 600 ^{o}C, respectively. Thus, 11% difference between residual weight losses is attributed to the simultaneous presence of the chromium and cobalt metals which are stable at this temperature. Also, the results proved that the functionalization of MIL-101-NH_2 with Co(II)Pc caused the thermal stability of final composite to be enhanced to around of 200 ^{o}C.

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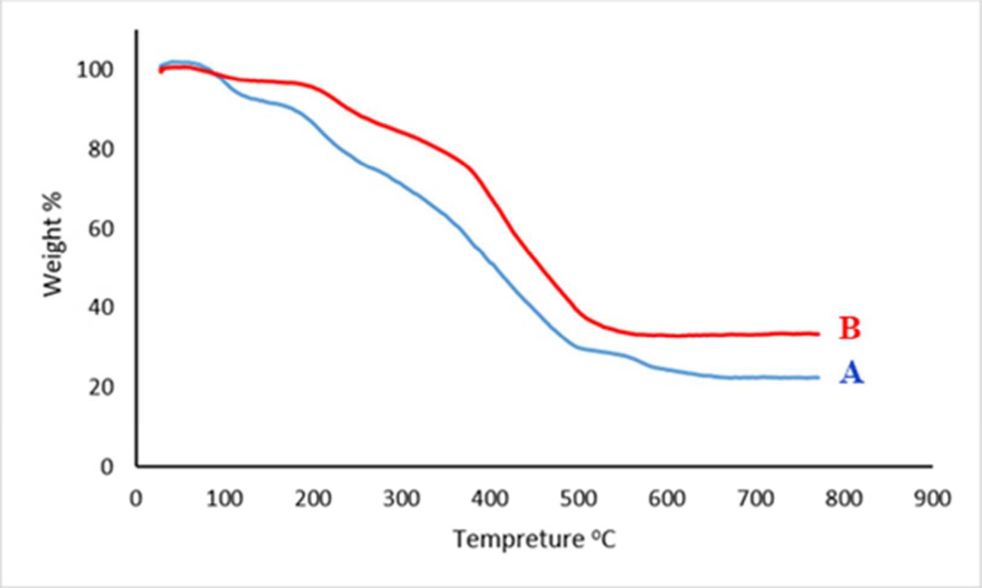

Figure 3. TGA curves of MIL-101-NH$_2$ (A) and MIL-101-NH$_2$-Co(II)Pc (B).

The SEM analyses carried out to study the structure and morphology of the obtained catalyst, and the result is illustrated in Figure 4. Since tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) has the bulky structure and covalently supported on the surface of the MIL-101-NH$_2$, loading of the Co(II)Pc functionality should affect the nanomorphology of MOF. As shown in Figure 4 (right), the synthesized catalyst almost affected the morphology of parent MOF; however, in some areas initial morphology has been retained. Finally, the energy dispersive spectroscopy (EDS) analysis determined the chemical composition of MIL-101-NH$_2$-Co(II)Pc and revealed that the chromium and cobalt metals are present in the catalyst (Figure 5). Furthermore, to determine the loading of cobalt in the catalyst, the inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis of MIL-101-NH$_2$-Co(II)Pc was carried out. The results showed 0.15 mmol/gr cobalt loading in the final catalyst.

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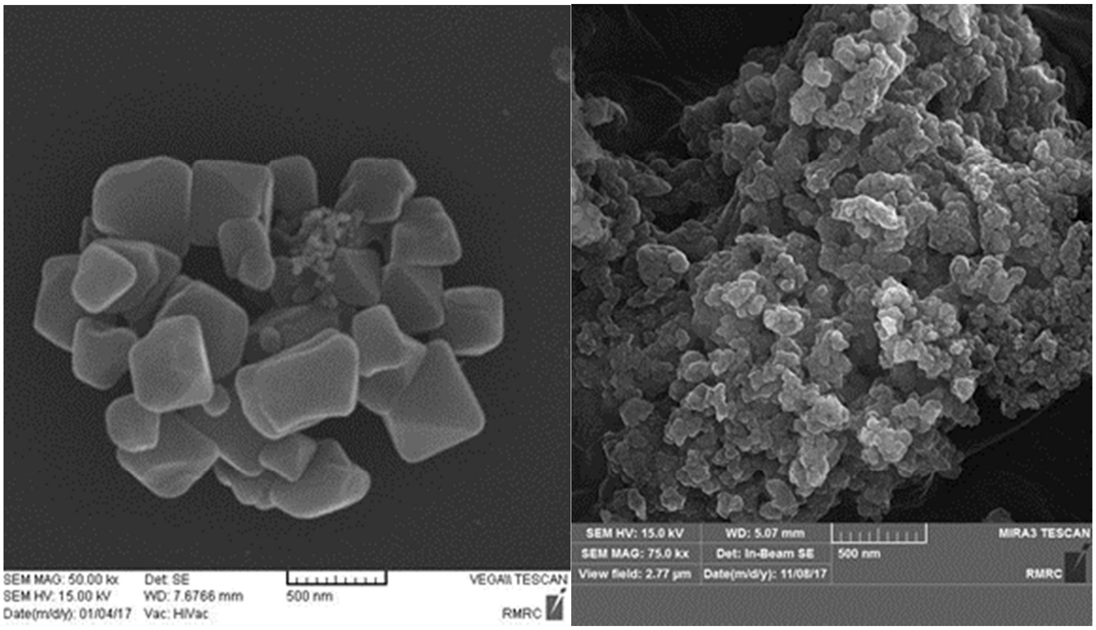

Figure 4. SEM images of MIL-101-NH_2 (left) and MIL-101-NH_2-Co(II)Pc (right).

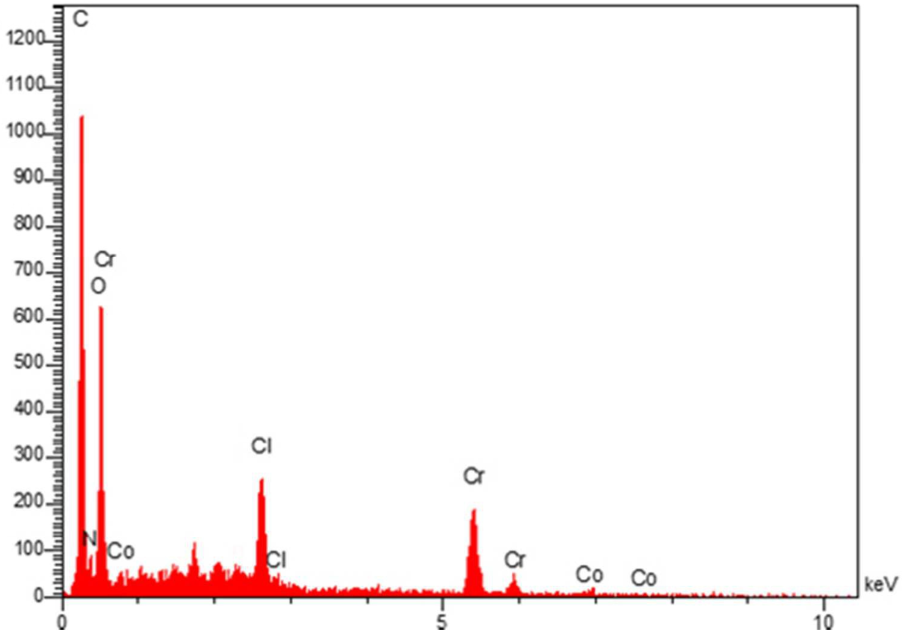

Figure 5. EDS result for MIL-101-NH_2-Co(II)Pc.

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Catalytic activity of MIL-101-NH_2-Co(II)Pc

At the outset, the catalytic activity of the newly synthesized MIL-101-NH_2-Co(II)Pc was evaluated in the tandem oxidative A^3 coupling reaction. Initially, the model tandem reaction between benzyl alcohol, phenylacetylene and piperidine were investigated under various conditions (Table 1). In the absence of the catalyst at 100 ^{o}C for 24 h in toluene, no desired product was obtained, and most of starting material was recovered (Table 1, Entry 1). When the reaction was run in the presence of MIL-101-NH_2-Co(II)Pc (20 mg) at room temperature, the desired product was not obtained, but by raising the temperature to 80 ^{o}C, 62% yields were obtained within 12 h (Table 1, Entry 3). The optimal amount of the MIL-101-NH_2-Co(II)Pc was found to be 40 mg due to higher yield and shorter reaction time than the other amount of catalyst loading (Table 1, Entry 4). In order to confirm the catalytic efficiency of MIL-101-NH_2-Co(II)Pc in the model tandem reaction, the catalytic activity of the aforementioned catalyst was compared with a number of other catalysts such as MIL-101-NH_2 and tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) individually and the results reveal that MIL-101-NH_2-Co(II)Pc has superior catalytic efficiency than the two other catalysts in the model reaction (Table 1, Entry 6-7). The reaction of benzyl alcohol, piperidine and phenylacetylene was also tested in the absence and presence of various bases. Considering the obtained results, the most appropriate and optimal amount of base in this reaction is 10 mol% KOH. The model reaction was also examined in various solvents (Table 1, Entry 11-13). Results showed that the toluene was the most appropriate reaction medium due to the highest yield (91%) of the product. Finally, the turnover number (TON) and turnover frequency (TOF) of the catalyst for the model reaction were determined to be 151 and 19 h^{-1}, respectively.

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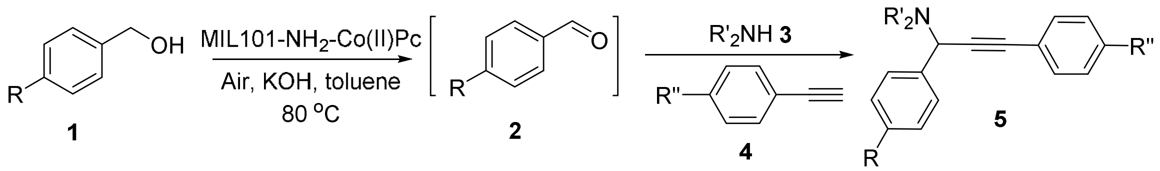
Table 1. Optimization of reaction conditions for the synthesis of propargylamine[a] *via* a tandem oxidative A^3 coupling reaction of benzyl alcohol[a]

Entry	Catalyst (mg)	Base (mol%)	Solvent	Temperature (°C)	Time (h)	Yield[b] (%)
1	-	KOH (10)	toluene	100	24	-
2	MIL-101-NH$_2$-Co(II)Pc (20)	KOH (10)	toluene	r.t.	24	-
3	MIL-101-NH$_2$-Co(II)Pc (20)	KOH (10)	toluene	80	12	62
4	**MIL-101-NH$_2$-Co(II)Pc (40)**	**KOH (10)**	**toluene**	**80**	**8**	**91**
5	MIL-101-NH$_2$-Co(II)Pc (50)	KOH (10)	toluene	80	8	94
6	MIL-101-NH2 (40)	KOH (10)	toluene	80	8	Trace
7	Co(II)Pc (40)	KOH (10)	toluene	80	8	43
8	MIL-101-NH$_2$-Co(II)Pc (40)	-	toluene	80	8	37
9	MIL-101-NH$_2$-Co(II)Pc (40)	KOH (5)	toluene	80	8	81
10	MIL-101-NH$_2$-Co(II)Pc (40)	K_2CO_3 (10)	toluene	80	8	54
11	MIL-101-NH$_2$-Co(II)Pc (40)	KOH (10)	water	80	8	Trace
12	MIL-101-NH$_2$-Co(II)Pc (40)	KOH (10)	acetonitrile	80	8	12
13	MIL-101-NH$_2$-Co(II)Pc (40)	KOH (10)	xylene	80	8	85

[a] Reaction conditions: benzylalcohol (1.3 mmol), piperidine (1.00 mmol), phenylacetylene (1.00 mmol), base, air and catalyst
[b] Isolated yield

Following the aforementioned promising results, the optimized conditions were used for the synthesis of different propargylamines by using a series of benzyl alcohols bearing various substituents such as H, OMe, Me, Cl and NO_2, various amines and phenylacetylene derivatives. It can be seen that all the reactions gave products in moderate to good yields.

Table 2. Synthesis of propargylamines *via* tandem oxidative A^3 coupling reaction of benzyl alcohols using MIL-101-NH$_2$-Co(II)Pc[a]



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Entry	Alcohol	Amine	Alkyne	Time (h)	Yield[b] (%)	Product
1	$PhCH_2OH$	Piperidine	PhCCH	8	91	**5a**
2	$PhCH_2OH$	Pyrrolidine	PhCCH	8	93	**5b**
3	$4\text{-}ClC_6H_4CH_2OH$	Piperidine	PhCCH	7.5	90	**5c**
4	$4\text{-}MeC_6H_4CH_2OH$	Pyrrolidine	PhCCH	9	86	**5d**
5	$4\text{-}MeC_6H_4CH_2OH$	Morpholine	PhCCH	9	83	**5e**
6	$4\text{-}MeOC_6H_4CH_2OH$	Piperidine	PhCCH	9	84	**5f**
7	$4\text{-}MeOC_6H_4CH_2OH$	Pyrrolidine	PhCCH	9	87	**5g**
8	$4\text{-}NO_2C_6H_4CH_2OH$	Piperidine	PhCCH	8	89	**5h**
9	$PhCH_2OH$	Piperidine	$4\text{-}MeC_6H_4CCH$	8	92	**5i**
10	$4\text{-}MeC_6H_4CH_2OH$	Piperidine	$4\text{-}MeC_6H_4CCH$	9	85	**5j**

[a]Reaction conditions: benzylalcohol (1.3 mmol), secondary amine (1.00 mmol), phenylacetylene (1.00 mmol), KOH (10 mol%), air and 40 mg MIL-101-NH_2-Co(II)Pc

[b]Isolated yield

Based on literature reports of catalytic applications of Co(II)Pc in the oxidation of alcohols,[31] a proposed mechanism for the first stage of the reaction (oxidation process) proceeds through the adsorption of oxygen atom in benzyl alcohol on Co(II) which increases the rate of hydrogen elimination by KOH. Then, the transition complex formed between cobalt and benzyl alcohol underwent removal of a hydrogen atom from the carbon attached to the hydroxyl group of alcohols by KOH and aldehyde products were obtained (Scheme 3). There are two plausible mechanisms for the second stage of the reaction (A^3 coupling process). One mechanism is based on Co(I)-Co(III)-Co(I) cycle[32] in which Co(II) species were reduced by alkyne and Co(I) can be generated. Next, nucleophilic attack of acetylide ion from alkynyl–Co(III) complex to the immonium ion which generated from aldehydes and secondary amines produces the corresponding propargylamine, and the Co(I) species can be regenerated by a reductive elimination. The second possible mechanism proceeds through Co(II) species without any change in oxidative state of the catalyst.[32a] In this mechanism, Co(II) species can activate the terminal alkyne and increase its acidity. Subsequently, the

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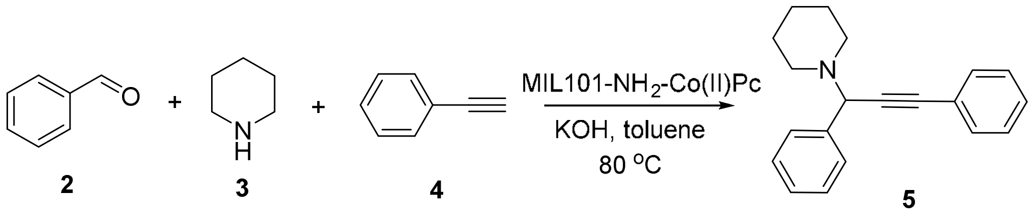
coupling of Co(II) acetylide intermediate which is generated in the presence of a base to the iminium ion leads to desired products and regenerates the Co(II) catalyst for further cycles.

To investigate these two tentative mechanisms, three component reactions of benzaldehyde, piperidine and phenylacetylene were tested in the absence and presence of the base, and results are represented in Table 3. Screening different conditions revealed that by increasing the amount of the base, the reaction time could be decreased to 3 h and the yield can be increased to 95%. These results show that the second mechanism could be more probable due to the greater role of the base in the second proposed mechanism.

Table 3. Screening of the base amount in the synthesis of propargylamines via A^3 coupling reaction of benzaldehyde, piperidine and phenylacetylene using MIL-101-NH_2-Co(II)Pc[a]



Entry	Base (mol%)	Time (h)	Yield[b] (%)
1	KOH (0)	6	40
2	KOH (5)	5	82
3	KOH (10)	4.5	93
4	KOH (15)	3	95

[a] Reaction conditions: benzyladehyde (1.00 mmol), piperidine (1.00 mmol), phenylacetylene (1.00 mmol), base and 40 mg MIL-101-NH_2-Co(II)Pc

[b] Isolated yield

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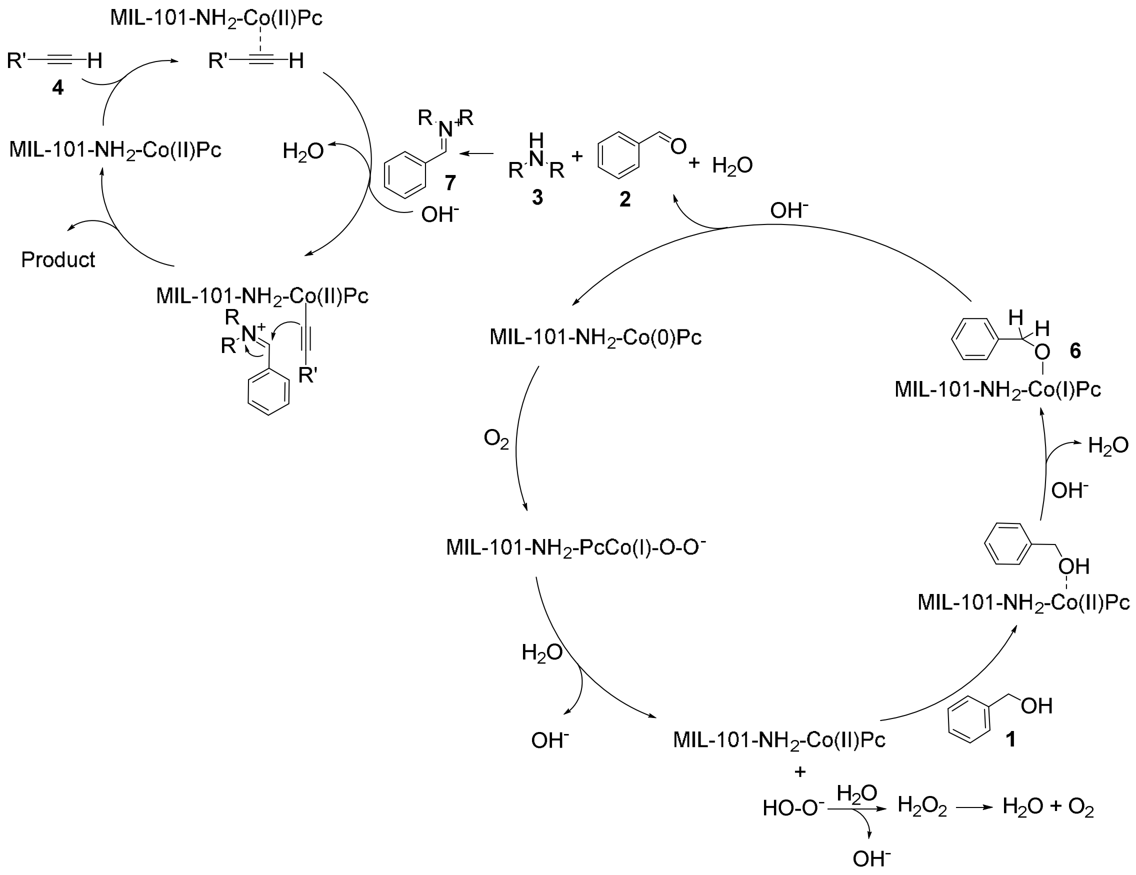

Scheme 3. Proposed mechanism for the one-pot tandem oxidation/A^3 coupling reaction using MIL-101-NH_2-Co(II)Pc.

The reusability and activity potential of MIL-101-NH_2-Co(II)Pc were investigated to three consecutive cycles for the model reaction using benzyl alcohol, phenylacetylene, and piperidine. After completion of the reaction, the catalyst was separated from the reaction mixture by filtration, washed with chloroform, ethanol, and acetone, dried and reused in the next run. The recycled catalyst was efficiently used in the next five consecutive cycles without significant loss of catalytic activity as shown in Figure 6.

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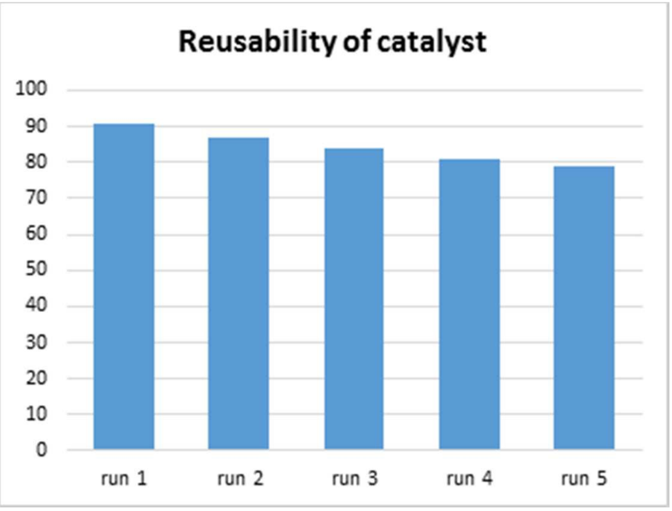

Figure 6. Recycle of the MIL-101-NH_2-Co(II)pc nanocatalyst for the synthesis of the propargylamine.

In order to confirm the reusability and stability of MIL-101-NH_2-Co(II)Pc during the reaction, the recovered catalyst was analyzed by powder X-ray diffraction (PXRD) and ICP-OES and results compared to that of the fresh one. No significant changes were observed in PXRD (Figure 7). The trivial differences between some of the reflection intensities of recovered and the fresh catalyst patterns could be due to the variation in the orientation of powder samples during PXRD patterns recording. The PXRD patterns of the MIL-101-NH_2-Co(II)Pc are same before and after several consecutive use; this revealed that the structure of catalyst remained intact during the reaction. Furthermore, less than 5% leaching of cobalt in the recovered catalyst after several runs, according to the ICP-OES analysis, clearly indicates stability of the catalyst.

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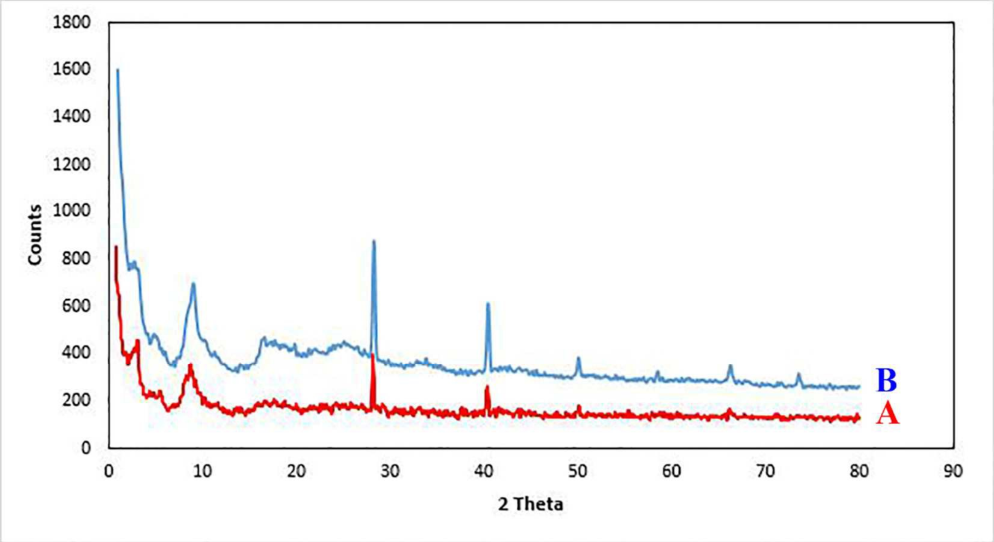

Figure 7. PXRD patterns of MIL-101-NH_2-Co(II)Pc before (A), after using (B)

3. Conclusions

In summary, postsynthetic modified MIL-101-NH_2 was prepared *via* covalent immobilization of the tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) and used in a one-pot tandem oxidative A^3 coupling reaction to afford propargylamines with fairly good yields. Notably, ease of synthetic procedure and the simple preparation of the catalyst will present novel material for the development of new types of organic reactions. In addition, short reaction time, high product yield, reusability of the catalyst which can be efficiently recycled with no significant loss of catalytic activity are the other advantages of this newly catalytic system.

4. Experimental

4.1. Materials and Methods

All reagents were purchased from Sigma-Aldrich and used without further purification. The X-ray powder diffraction (XRD) patterns were recorded on a STOE diffractometer with Cu-Kα radiation (λ=1.5418 Å). The FT-IR spectra were recorded on a Bomem MB-Series

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FT-IR spectrometer. The ^1H NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 MHz using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. Thermogravimetric analysis (TGA) was carried out using STA 1500 instrument at a heating rate of 10 °C min^{-1} in the air. The loading of cobalt was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES; Varian Vista PRO Radial). Scanning electron microscopy (SEM) observations were carried out on an electron microscopy Philips XL-30 ESEM. All samples were sputtered with gold before observation.

4.2. Preparation of the MIL-101-NH_2

The MIL-101-NH_2 was synthesized according to the previously reported method.[30] Chromic nitrate hydrate (2.40 g, 6.00 mmol), 2-aminoterephthalic acid (1.08 mg, 6.00 mmol) and sodium hydroxide (0.59 g, 15.00 mmol) were sonicated in deionized water (45 ml) and thoroughly stirred. The suspension was transferred in an autoclave and kept at 150 °C for 12 h. After the autoclave was cooled, the green precipitate was filtered off and washed with DMF to remove unreacted ligands. Finally, the solid was further purified by alcohol at 100 °C for 24 h in an autoclave, filtered off, and dried at 80 °C in air.

4.3. Preparation of the tetrakis(carboxy)phthalocyaninato cobalt(II)

The tetrakis(carboxy)phthalocyaninato cobalt(II) was prepared according to the procedure reported in the literature.[33] Trimellitic anhydride 3.18 g (16.60 mmol), urea 8 g (130 mmol), ammonium molybdate tetrahydrate 0.0618 g (5.00 mmol), ammonium chloride 0.4029 g (7.50 mmol), and 5 mmol of $CoCl_2$ were mixed together until homogeneous powder resulted. The obtained powder was placed in a beaker and heated for 5 h at 220 °C. The produced mixture was cooled to room temperature, washed with aqueous HCl (1 N, 20 mL), H_2O (50 mL) filtrated and dried. The product was mixed and heated at 90 °C for 2 days in

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100 mL of 5 N NaOH and supersaturated NaCl solution. After cooling, the mixture was diluted with distilled water until no residual could be detected. The solution was filtered, and the dark blue filtrate was acidified by 6 N HCl until tetrakis(carboxy)phthalocyaninato cobalt(II) complexes were precipitated. The product was separated by centrifugation. The residue was redissolved in 0.1 N NaOH solution and filtered to separate the insoluble materials. The compound was reprecipitated with 1.0 N HCl and centrifuged to obtain the solid material. Dissolution and precipitation steps were repeated twice. The product was washed with distilled water until the filtrate became neutral. The product was dried at 70 °C.

4.4. Preparation of the tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II)

The tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) was prepared according to the previously reported method[34] by converting the carboxylic acid groups of tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) to formyl chloride via a reaction with thionyl chloride ($SOCl_2$). In a round-bottomed flask, an excess amount of $SOCl_2$ (30 mL) was added to tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) (0.100 g). The mixture was refluxed at 75 ^{o}C for 48 h. Subsequently, the sample was evaporated under reduced pressure, followed by the complete removal of unreacted $SOCl_2$ on a rotary evaporator with a vacuum pump. The remaining solid was washed three times with anhydrous tetrahydrofuran and dried in an oven for 5 h at 60 ^{o}C.

4.5. Preparation of the MIL-101-NH_2-Co(II) phthalocyanine

In a round-bottomed flask, the prepared MIL-101-NH_2 0.764 gr (1.00 mmol), tetrakis(chlorocarbonyl)phthalocyaninato cobalt(II) 0.821 gr (1.00 mmol) and anhydrous DMF (5 mL) were added and stirred for 3 days at 50 ^{o}C. The resulted dark green solution was cooled to room temperature, and then the obtained solid was isolated by centrifugation,

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washed with anhydrous DMF and ethanol three times. Finally, the collected solid was dried in vacuum at 80 °C for 24 h.

4.6. General catalytic procedure for the synthesis of propargylamines

In a typical procedure, a mixture of benzyl alcohol (1.30 mmol,), KOH (10 mol%) and MIL-101-NH_2-Co(II)Pc (40 mg) in dry toluene (5 mL) were added to a 25 mL round-bottomed flask. Then, the resulting solution was heated under air with the 400 mL.min^{-1} flow rate at 80 ^{o}C for 3 h. Afterwards, secondary amine (1.00 mmol) and phenylacetylene (1.00 mmol) were added to above mixture and reaction was stirred at 80 ^{o}C for an appropriate time (Tables 2). After completion of the reaction (monitored by TLC), the reaction mixture was cooled to the room temperature, and the catalyst was separated by filtration and washed with chloroform, ethanol, and acetone followed by drying at 60 °C for 3 h. The crude product was purified by column chromatography on silica gel using n-hexane/EtOAc as elution solution to afford the corresponding pure product.

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Table of contents

In this study, we have reported the postsynthetic modified metal-organic framework (MIL-101(Cr)-NH_2) *via* a covalent immobilization of the cobalt(II) phthalocyanine as an efficient and mild catalytic system.