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Ligand-free *N*-arylation of heterocycles using metal-organic framework [Cu(INA)₂] as an efficient heterogeneous catalyst

Thanh Truong*, Chi V. Nguyen, Ngoc T. Truong, Nam T. S. Phan*

Department of Chemical Engineering, HCMC University of Technology, VNU-HCM,

268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam

*Email: <u>ptsnam@hcmut.edu.vn</u>

tvthanh@hcmut.edu.vn

Ph: (+84 8) 38647256 ext. 5681

Fx: (+84 8) 38637504

Abstract

A metal-organic framework $[Cu(INA)_2]$ was synthesized and used as a heterogeneous catalyst for arylation of wide range of *N-H* heterocycles and aryl halides under *ligand-free* conditions. The *N*-arylation reaction involved the use of 5 mol% Cu-MOF catalyst with K₃PO₄ or 'BuOLi as the base in dimethylacetamide (DMA) solvent at 100 °C in 6 h. The $[Cu(INA)_2]$ exhibited higher catalytic activity for the *N*-arylation transformation than that of common homogeneous copper catalysts and other Cu-MOFs with unsaturated open metal sites such as Cu₂(BDC)₂(BPY), Cu₃(BTC)₂, and Cu₂(BDC)₂(DABCO). Interestingly, reaction conditions are compatible with wide range of *N-H* heterocycles, functional groups, and aryl chlorides. Leaching test indicated no contribution of leached active species in reaction filtrate. Furthermore, the [Cu(INA)₂] catalyst could be facilely separated from the reaction mixture and recovered and reused several times without a significant degradation in catalytic activity.

Keywords: Metal-organic framework; *N*-arylation, *N*-*H* heterocycles; C-N coupling; heterogeneous catalyst.

1. Introduction

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N-Arylated heterocycles have emerged as important intermediates commonly used in the synthesis of many biologically active natural products, agrochemicals, and pharmaceutical candidates as well as functional materials [1-3]. They have been conventionally synthesized by the copper-catalyzed Ullmann-type transformation [4]. However, this protocol often required the presence of stoichiometric or even greater quantities of copper salts at high temperatures, leading to the formation of large amounts of hazardous copper-based wastes [4, 5]. Several palladium-catalyzed C-N crosscoupling transformations of aryl halides with azoles in the presence of sterically hindered phosphine ligands have been developed [6, 7]. Although high yields under relatively mild conditions were achieved, using homogeneous phosphine palladium catalysts would suffer a number of drawbacks, such as high cost, relatively rare availability, and tedious work-up. Taillefer and co-workers previously reported the N-arylation of pyrazole using Cu_2O and oxime-type ligands as catalyst systems [8]. Hosseinzadeh and co-workers demonstrated that the N-arylation of diazoles could be accomplished using CuI as catalyst in the presence of 1,10-phenanthroline as ligand [9]. Bolm and Correa developed the Narylation of pyrazole using FeCl₃ in conjunction with N,N'-dimethylethylenediamine as catalyst system [10]. Several publications using copper heterogeneous catalytic systems for this transformation have been disclosed [11-13]. Often, expensive Cs_2CO_3 , long reaction time, soluble ligands, or inert atmosphere was required. Furthermore, difficulty in reusability or loss of activity was also observed [14]. Though our group has disclosed the use of $Cu_2(BDC)_2(DABCO)$ for N-arylation, reaction conditions were only applicable

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to imidazoles [15]. The development of more environmentally benign and robust heterogeneous protocols for the *N*-arylation of heterocycles is still our primary concern in the near future.

Metal-organic frameworks (MOFs), also known as coordination polymers, have emerged as a relatively new class of porous, crystalline materials constructed from metalcontaining nodes and multidirectional organic linkers [16-18]. Due to their special physical properties, MOFs have been considered as promising materials for potential applications in gas storage media, separations, chemical sensors, thin film devices, optics, drug carriers, biomedical imaging, and catalysis [19-27]. The application of MOFs in catalysis has currently attracted significant attention from both academics and industry, and relevant publications have increased significantly in the last few years [28-30]. Indeed, both carbon-carbon [31-38] and carbon-heteroatom forming transformations using MOFs as catalysts or catalyst supports have recently been explored [39-49]. There should be no doubts that the catalysis application of MOFs will be expanded in the near future. Among several kinds of MOFs as heterogeneous catalysts, copper-based MOFs could offer promising activity and selectivity for a variety of organic reactions due to their unsaturated open copper metal sites [41, 50-57]. In this work, we present a heterogeneous protocol for N-arylation of wide range of heterocycles using the metalorganic framework $[Cu(INA)_2]$ as an efficient heterogeneous catalyst and inexpensive K_3PO_4 base under ligand-free conditions. Under reported conditions, the [Cu(INA)₂] offered higher catalytic activity for the transformation than that of other Cu-MOFs such as $Cu_2(BDC)_2(BPY)$, $Cu_3(BTC)_2$ and $Cu_2(BDC)_2(DABCO)$, and that of homogeneous copper catalysts such as CuI, CuCl₂, Cu(NO₃)₂, Cu(OAc)₂, and CuSO₄. Interestingly, the optimized conditions are applicable for aryl chlorides, which previously required palladium catalysts or complicated ligands under copper catalysis.

2. Experimental

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2.1. Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich and Merck, and were used as received without any further purification unless otherwise noted. Nitrogen physisorption measurements were conducted using a Micromeritics 2020 volumetric adsorption analyzer system. Samples were pretreated by heating under vacuum at 150 °C for 3 h. A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 10 °C/min under a nitrogen atmosphere. X-ray powder diffraction (XRD) patterns were recorded using a Cu Ka radiation source on a D8 Advance Bruker powder diffractometer. Scanning electron microscopy studies were conducted on a S4800 Scanning Electron Microscope (SEM). Transmission electron microscopy studies were performed using a JEOL JEM 1400 Transmission Electron Microscope (TEM) at 100 kV. The [Cu (INA)₂] sample was dispersed on holey carbon grids for TEM observation. Elemental analysis with atomic absorption spectrophotometry (AAS) was performed on an AA-6800 Shimadzu. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 6700 instrument, with samples being dispersed on potassium bromide pallets.

Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25μ m). The temperature program for

GC analysis held samples at 80 °C for 1 min; heated them from 80 to 280 °C at 35 °C/min; held them at 280 °C for 10 min. Inlet and detector temperatures were set constant at 290 °C. *n*-Hexadecane was used as an internal standard to calculate reaction conversions. GC-MS analyses were performed using a Hewlett Packard GC-MS 5972 with a RTX-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.5 μ m). The temperature program for GC-MS analysis heated samples from 60 to 280 °C at 10 °C/min and held them at 280 °C for 10 min. Inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library. The ¹H and ¹³C NMR were recorded in CDCl₃ using residual solvent peak as a reference on a Bruker spectrophotometer at 500 MHz and 125 MHz, respectively.

2.2. Synthesis of the metal-organic framework [Cu(INA)₂]

In a typical preparation, a mixture of $Cu(NO_3)_2.3H_2O(0.193 \text{ g}; 0.8 \text{ mmol})$ in DMF (17.5 mL) and isonicotinic acid (INAH) (0.049 g; 0.4 mmol) in NMP (7 mL) was mixed, and stirred for 5 min. Pyridine (1.5 mL) was then added, and the resulting solution was distributed to ten 5 mL vials. The vials were then heated at 100 °C in an isothermal oven for 72 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 20 mL) for 3 days. Solvent exchange was carried out with DCM (3 x 20 mL) at room temperature. The material was then evacuated under vacuum at 140 °C for 3 h, yielding 0.032 g of $[Cu(INA)_2]$ in the form of blue crystals (65 % based on isonicotinic acid).

2.3. Catalytic studies

In a typical experiment, a mixture of 4-iodoacetophenone (0.492 g, 2.0 mmol), pyrazole (0.272 g, 4.0 mmol), K_3PO_4 as a base (0.848 g, 4.0 mmol), and *n*-hexandecane (0.15

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mL) as an internal standard in DMA (4 mL) was added into a 25 mL flask containing the pre-determining amount of $[Cu(INA)_2]$ catalyst. The catalyst amount was calculated based on the molar ratio of copper/4-iodoacetophenone. The reaction mixture was magnetically stirred at 100 °C for 6 h.

Reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals, quenching with aqueous KOH solution (1 %, 0.2 mL). The organic components were then extracted into diethyl ether (2 mL), dried over anhydrous Na₂SO₄, analyzed by GC with reference to *n*-hexadecane. The product identity was further confirmed by GC-MS and NMR. To investigate the recyclability of the [Cu(INA)₂], the catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of DMF and DCM, dried 140 °C under vacuum in 2 h, and reused if necessary. For the leaching test, a catalytic reaction was stopped after 1 h, analyzed by GC, and centrifuged to remove the solid catalyst. The reaction solution was then stirred for a further 5 h at 120 °C. Reaction progress, if any, was monitored by GC as previously described.

3. Results and discussion

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The metal-organic framework $[Cu(INA)_2]$ was synthesized according to a modified literature procedure, and was characterized by several techniques, including XRD, SEM, TEM, TGA, FT-IR, AAS, and nitrogen physisorption measurements (Fig. 1 and Fig. S7 – Fig. S13). The analysis results were in good agreement with previous reports [58, 59]. Structurally, the building block unit of the framework is composed of Cu(II) squarepyramidal geometry linked by five isonicotinate ligands while the carboxylate oxygen atoms from the other two isonicotinate ligands occupy the rest of the two vertices [58-

59]. We hypothesized that this structure would result in weak interaction between copper centers within the network structure. Therefore, it is suitable for association/dissociation in catalytic cycle. Furthermore, weak interaction also indicated the metal-metal interaction behavior [59]. It was recently reported that bimetallic copper center possessed exceptionally strong activity toward cross coupling reactions [60]



Fig. 1. PXRD and TGA of synthesized [Cu(INA)₂]

In optimization studies, the $[Cu(INA)_2]$ was used as catalyst for the *N*-arylation of heterocycles by 4-iodoacetophenone (Scheme 1). Pyrazole was chosen due to its poor activity toward arylation in reported procedures. Condition screening was initially conducted with 5 mol% $[Cu(INA)_2]$ catalyst, 4-iodoacetophenone: pyrazole molar ratio of 1: 2, and inexpensive K₃PO₄ base in DMF solvent.

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Scheme 1. The *N*-arylation of pyrazole with 4-iodoacetophenone using [Cu(INA)₂]

catalyst.

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Fig. 2. Effect of temperature on reaction conversions.

Effect of temperature on reaction conversion was kinetically investigated (Fig. 2). It was found that the $[Cu(INA)_2]$ -catalyzed *N*-arylation reaction could proceed to 88% conversion after 6 h at 100 °C. Decreasing the temperature resulted in a significant drop in the reaction rate, with 66% and 61% conversions being observed for the reaction carried out at 90 °C and 80 °C, respectively. It should be noted that the *N*-arylation reaction could not occur at room temperature in the presence of $[Cu(INA)_2]$ catalyst, with no trace amount of product being detected. Indeed, the *N*-arylation of pyrazole was previously carried out in the temperature range of 110 - 140 °C under different catalysis conditions [8-10, 61, 62].



Fig. 3. Effect of reagent molar ratio on reaction conversion.



Fig. 4. Effect of catalyst amount on reaction conversion.

The effect of reagent molar ratio (pyrazole/4-iodoacetophenone) on the reaction conversion was investigated (Fig. 3). It was observed that using the molar ratio less than 1.5 resulted in a drop in the reaction conversion, though 66% conversion was still achieved for the reaction using 1.0 equivalents of pyrazole. With respect to catalyst

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loading, as expected, decreasing the catalyst concentration led to a dramatic drop in the reaction rate, though 72% and 54% conversions were still achieved with 3 mol% and 1 mol% Cu-MOF catalyst, respectively. It should be noted that almost no reaction occurred in the absence of the $[Cu(INA)_2]$ catalyst, indicating the necessity of using the Cu-MOF as catalyst for the *N*-arylation reaction (Fig. 4). In the first example of the ligand-free *N*-arylation reaction of pyrazole, Rao and co-workers used 10 mol% graphite-supported iron catalyst [61]. Other groups also employed 10 mol% catalyst for the same transformation, though different ligands were required in the systems [8, 10, 62].



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Fig. 5. Effect of solvent on reaction conversion.

In several cases, the solvent could dramatically accelerate or slow down the transformation, depending on the nature of the catalyst material [63, 64]. Taillefer and co-workers previously carried out the *N*-arylation of pyrazole with aryl or heteroaryl bromides or iodides in toluene, DMF or acetonitrile using Cu₂O and oxime-type ligands as catalyst systems [8]. Bolm and Correa reported the FeCl₃-catalyzed *N*-arylation of

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pyrazole carried out in toluene using *N*,*N*'-dimethylethylenediamine as ligand [10]. Hosseinzadeh and co-workers employed xylene as solvent for the CuI-catalyzed *N*arylation of diazoles in the presence of 1,10-phenanthroline as ligand [9]. Teo and coworkers performed the same reaction using MnCl₂ catalyst with *trans*-1,2diaminocyclohexane as the assisting ligand in water [62]. In the first example of the ligand-free *N*-arylation reaction of pyrazole using graphite-supported iron catalyst, Rao and co-workers carried out the reaction in DMSO [61]. Therefore, different solvents including DMF, DMA, NMP, 1,4-dioxane, *o*-xylene, and toluene were then examined (Fig. 5). It was found that the transformation proceeded with difficulty in *o*-xylene and toluene, with only 28% and 19% conversions respectively. The reaction carried out in 1,4-dioxane afforded 46% conversion. Cyclic amide solvent NMP was also found to be not effective. Noticeably, DMA was found to be optimal solvent with up to 92% conversion was obtained.



Fig. 6. Effect of base on reaction conversion.



Fig. 7. Effect of various amount of K₃PO₄ on reaction conversion.

Next, various common inorganic and organic bases were employed (Fig. 6). Particularly, almost no reaction occurred in the absence of base indicating the .importance of the base in the transformation. Both K_2CO_3 and CH_3COONa were found to be unsuitable with only 24% conversion. The *N*-arylation reaction using CH_3ONa base afforded 41% conversion while approximate 50 % conversion was obtained with NaOH. It was found that both K_3PO_4 and 'BuOLi could be used for the [Cu(INA)₂]-catalyzed *N*-arylation reaction, with 92% and 94% conversions. From the industrial point of view, K_3PO_4 would be more commercially available and therefore should be used for the transformation. Furthermore, investigation of using different amount of K_3PO_4 confirmed that 1.5 equivalent was optimal. In particular, reaction using more than 1.5 equivalent did not significantly increase the reaction conversion while only 32 % was obtained when 0.5 equivalent of K_3PO_4 was employed.



Fig. 8. Different Cu-MOFs as catalyst for the N-arylation reaction.

To highlight the significant aspect of using the $[Cu(INA)_2]$ as catalyst for *N*-arylation, the catalytic activity of the $[Cu(INA)_2]$ was compared with that of other Cu-MOFs which previously reported to possess open metal sites and high catalytic activity toward cross coupling reactions [65-74] (Fig. 8). Although MOF-199 were commonly used as efficient catalyst for several copper-catalyzed organic transformations [64-71], this Cu-MOF offered significantly lower catalytic activity than the $[Cu(INA)_2]$. The *N*-arylation reaction using $Cu_2(BDC)_2(DABCO)$ catalyst also proceeded slowly, though 63% conversion was still observed after 6 h. The reaction conversion could be improved to 75% when $Cu_2(BDC)_2(BPY)$ catalyst was employed.

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Fig 9. Comparison in catalytic activity of [Cu(INA)₂] with several copper salts.

Despite the high thermal stability, low reactivity of heterogeneous catalysts was often observed mainly due to their structural rigidity or loss of activation by the aggregation of active species [75]. With exceptionally high surface area, semi-rigid properties, and no metal aggregation, MOFs containing transition metals are expected to overcome these major problems of solid catalysts while still maintain their beneficial properties in handling and separation as compared to homogeneous counterparts. To further verify the excellent catalytic activity of $[Cu(INA)_2]$, the catalytic performance of several homogeneous copper salts was then investigated under optimal conditions (Fig. 9). Interestingly, all of these tested copper salts were less active than the $[Cu(INA)_2]$ for the *N*-arylation reaction, though up to 75% conversion was still obtained after 6 h for the case of CuI. It should be noted that isonicotinic acid exhibited no activity for the *N*-arylation reaction, with no trace amount of product being detected while Cu(NO₃)₂ cluster afforded

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only 65% conversion. These observation would imply that synergetic impact of linkers on metal cluster would be of significant importance for the transformation, though further studies would be necessary to elucidate the reaction mechanism of the $[Cu(INA)_2]$ catalyzed *N*-arylation reaction.



Fig. 10. Leaching test indicated no contribution from homogeneous catalysis of active species leaching into reaction solution.

In order to clarify if active copper species dissolved from the solid $[Cu(INA)_2]$ catalyst, if any, could be active for the *N*-arylation reaction, a control experiment was carried out using a simple filtration during the course of the reaction. After 1 h with a conversion of 55% being observed, the $[Cu(INA)_2]$ catalyst was separated from the reaction mixture by simple filtration. The liquid phase was then transferred to a new reactor vessel, and magnetically stirred for an additional 5 h at 100 °C with aliquots being sampled at different time intervals. It was found that almost no further conversion was observed for the *N*-arylation reaction after the $[Cu(INA)_2]$ catalyst was removed (Fig. 10). Furthermore, ICP-MS of reaction filtrate indicated the presence of <10 ppm of Cu²⁺.

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These observations would indicate that contribution from catalytically active species soluble in the liquid phase is unlikely.



Fig. 11. Catalyst recycling studies.

The recoverability and reusability of the $[Cu(INA)_2]$ catalyst in the *N*-arylation of pyrazole with 4-iodoacetophenone over five successive runs was studied by repeatedly separating the Cu-MOF catalyst from the reaction mixture. After each catalysis run, the Cu-MOF catalyst was filtered from the reaction mixture, washed with copious amounts of DMA and DCM to remove any physisorbed reagents, dried at 140 °C under vacuum in 2 h, then reused in further catalysis runs under identical conditions to those of the previous experiment. It was found that the $[Cu(INA)_2]$ catalyst could be recovered and reused several times in the *N*-arylation reaction without a significant degradation in catalytic activity. Indeed, a conversion of 84% was still achieved in the 5th run (Fig. 11). The XRD result of the recovered $[Cu(INA)_2]$ revealed that the crystallinity of the Cu-MOF catalyst could be maintained, though slight difference in the diffractogram was detected (Fig. 12). FT-IR spectra of the reused $[Cu(INA)_2]$ showed a similar absorption

as compared to that of the fresh catalyst (Fig. 13) except the peak at about 1700 cm-1. In particular, within the Cu(INA)₂, the carboxylates tailing inside of the cavities are able to interact with guest molecules. The absence of peak at about 1700 cm-1 in reused Cu(INA)₂ could be rationalized by the interaction of carboxylate with solvent molecules. Furthermore, N₂ absorption/desorption examination of the used catalyst indicated that only slight decrease in BET surface area was observed (Fig. S10).



Fig. 12. X-ray powder diffractograms of the fresh (a) and reused (b) [Cu(INA)₂] catalyst.



Fig. 13. FT-IR spectra of the fresh (a) and reused (b) [Cu(INA)₂] catalyst.

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Table 1. Reaction scope with respect to coupling partners.^a



^a2.0 mmol scale, DMA (4 mL), numbers in parenthesis indicated the isolated yields.^b ^tBuOLi was used.

The generality of optimized conditions was examined by using various aryl halides and N-H heterocycles coupling counterparts (Table 1). With respect to aryl halides, excellent reactions conversions were obtained with aryl iodides containing electron-withdrawing groups (entries 1, 2). Similar numbers between conversion and isolated yields indicated the good selectivity under optimized conditions. In addition, good conversions were still obtained with iodobenzene, 4-iodoanisole, and 4-iodotoluene (entries 3-5). Interestingly, reaction is highly selective toward heterocyclic N-H and only trace amount of homocoupling of 4-iodoaniline was observed (entry 6). Mono-arylion using using 1,4diiodobenzene is possible and product was obtained in good yield (entry 7). Interestingly, optimized conditions are also applicable for aryl bromides and aryl chlorides (entries 3, 4, 8) It is worth mentioning that complex ligands were required for arylation using aryl halides under homogeneous catalysis while all reported heterogeneous catalytic systems were not effective when any chloride coupling partners were employed [11-15]. Furthermore, the optimized conditions are not limited to pyrazole. Specifically, arylation of pyrrole, 3-methylindole, 6-bromoindole, imidazole afforded products with excellent conversions (entries 9-12). Amination by aliphatic cyclic N-Hs such as morpholine and pyrrolidine were also performed with high yields (entries 13, 14).

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Reaction mechanism was proposed in Scheme 2. In the presence of base, oxidative addition of Cu complex with aryl halides was occurred. Interaction of *N*-*H* bonds with copper halide intermediate (I) afforded copper complex (II) after elimination of HX. Reductive elimination generated desired product and recovered copper complex back to catalytic cycle. The exceptional catalytic activities of Cu(INA)₂ toward *N*-arylation could be rationalized by: (1) synergetic effect of rigid linkers as coordinating ligands; (2) bimetallic copper complexes; (3) strong coordination of *N*-*H* amines with copper complex intermediates within the framework.

4. Conclusions

In summary, the metal-organic framework $[Cu(INA)_2]$ was solvothermaly synthesized from the reaction of copper nitrate trihydrate and isonicotinic acid and characterized by several techniques including XRD, SEM, TEM, FT-IR, TGA, AAS, and nitrogen physisorption measurements. The $[Cu(INA)_2]$ was used as an efficient heterogeneous catalyst for the *N*-arylation of heterocycles under *ligand-free* conditions. Optimal conditions involved the use of $[Cu(INA)_2]$ (5% mol), K₃PO₄ base (2 equiv.) in DMA

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solvent at 100°C in 6h. Reaction conditions are compatible with wide range of *N-H* heterocycles, functional groups, and aryl chlorides. Interestingly, the $[Cu(INA)_2]$ was more catalytically active than common homogeneous copper catalysts such as CuI, CuCl₂, Cu(NO₃)₂, Cu(OAc)₂, and CuSO₄. The $[Cu(INA)_2]$ also exhibited higher catalytic activity for the transformation than that of other Cu-MOFs such as Cu₂(BDC)₂(BPY), Cu₃(BTC)₂, and Cu₂(BDC)₂(DABCO). The reactions could only proceed in the presence of the solid $[Cu(INA)_2]$ catalyst with no contribution from leached active copper species. The $[Cu(INA)_2]$ catalyst could be facilely separated from the reaction mixture and recovered and reused several times without a significant loss in catalytic activity.

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