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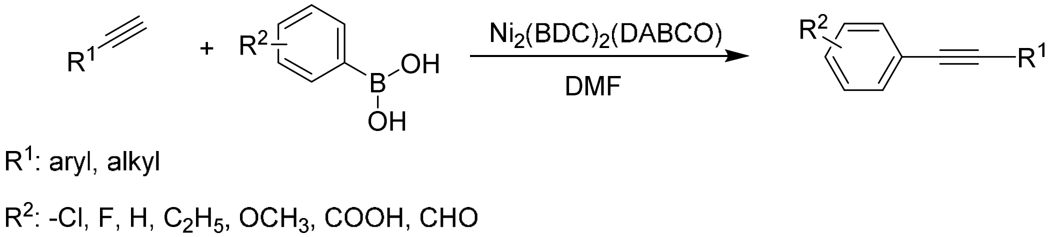
Graphic abstract



The first Ni-catalyzed oxidative coupling of alkynes and aryl boronic acids

Nickel-catalyzed oxidative coupling of alkynes and aryl boronic acids using metal-organic framework $Ni_2(BDC)_2(DABCO)$ as an efficient heterogeneous catalyst

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Abstract

A crystalline porous metal-organic framework $Ni_2(BDC)_2(DABCO)$ was synthesized, and characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR), atomic absorption spectrophotometry (AAS), and nitrogen physisorption measurements. The $Ni_2(BDC)_2(DABCO)$ could be used as an efficient and recyclable heterogeneous catalyst for the cross-coupling reaction between phenylboronic acids with phenylacetylenes in the presence of molecular oxygen in air as the stoichiometric oxidant. High conversions of the cross-coupling products were achieved *with no homo-coupling* products being detected by GC. The $Ni_2(BDC)_2(DABCO)$ exhibited significantly higher catalytic activity in the coupling reaction than that of other Ni-MOFs such as $Ni_3(BTC)_2$ and Ni(HBTC)(BPY). $Zn_2(BDC)_2(DABCO)$ and $Co_2(BDC)_2(DABCO)$ were found to be completely inactive for the transformation, while the reaction using $Cu_2(BDC)_2(DABCO)$ as catalyst led to the formation of 10% homo-coupling product. To the best of our knowledge, a nickel-based

catalyst was not previously used for the oxidative coupling reactions between phenylacetylenes and phenylboronic acids.

Keywords: Metal-organic framework; nickel-catalyzed; alkynylation; heterogeneous catalysts.

1. Introduction

Arylalkyne moieties have emerged as versatile intermediates for the synthesis of several pharmaceutical candidates and agrochemicals, as well as a variety of functional organic materials [1-5]. These structures are conventionally synthesized from the palladium-catalyzed Sonogashira cross-coupling reactions between aryl halides and terminal alkynes in the presence of CuI as co-catalyst and phosphines as ligand [6-9]. Many modifications of the Sonogashira protocol have been developed to improve the efficiency of this transformation. However, homo-coupling by-products of the reactants were normally observed. Zou and co-workers previously reported the oxidative coupling reaction of terminal alkynes with arylboronic acids catalyzed by a Pd(dppf)Cl_2 and Ag_2O system [10]. Yang and Wu extended the scope to the cyclopalladated ferrocenylimine catalyzed cross-coupling reaction of arylboronic acids/esters with terminal alkynes in the presence of Ag_2O as the additive [11]. Subsequently, Li and co-workers developed this protocol to the cross-coupling reactions between a variety of terminal alkynes and numerous boronic acids in the presence of $Pd(OA_C)_2$ and Ag_2O mixture [12]. Bao and co-workers offered an alternative protocol by using porous palladium nanospheres in conjunction with Ag_2O and triphenylphosphine as the catalyst system [13]. To overcome problems associated with palladium-based catalysts, palladium-free cross coupling reactions have been investigated, using CuBr/*rac*-BINOL [14] or Cu_2O [15, 16] as catalysts. Although interesting results have been achieved, the development of a greener protocol for this transformation should be targeted.

Metal-organic frameworks (MOFs) have recently attracted significant attention as a new class of porous materials with potential applications in several fields [17-25]. Although the application of MOFs in catalysis has just emerged as a young research area, MOFs have been used as heterogeneous catalysts for a variety of organic transformations [26, 27], ranging from carbon-carbon [28-33] to carbon-heteroatom [34-37] forming reactions. However, reports on nickel-based MOFs as catalysts for organic transformations have been very limited in the literature [38-41]. Kim and co-workers previously demonstrated that nickel nanoparticles embedded in the pores of a mesoporous MOF exhibited high activity in the hydrogenolysis of nitrobenzene and the hydrogenation of styrene [42]. similarly, Chou and co-workers pointed out that nickel nanoparticles supported on MOF-5 could be a good catalyst for the hydrogenation reaction of crotonaldehyde [43]. Subsequently, Jiang and co-workers synthesized a nickel(salphen)-based MOF and used it as a heterogeneous catalyst for the synthesis of cyclic carbonates [44]. Recently, Canivet and co-workers reported the application of a nickel complex grafted within the MIL-101 framework as a catalyst for the liquid-phase ethylene dimerization to selectively form 1-butene [45]. In this work, we wish to report the application of the Ni-MOF $Ni_2(BDC)_2(DABCO)$ as an efficient and selective heterogeneous catalyst for the oxidative cross-coupling reaction between phenylboronic acid with phenylacetylene. The $Ni_2(BDC)_2(DABCO)$ catalyst could be facilely separated from the reaction mixture, and could be reused without a significant degradation in activity. To the best of our knowledge, a nickel-based catalyst was not previously used for this transformation.

2. Experimental

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 ^oC for 3 h. A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) with a heating rate of 10 $^oC/min$ under a nitrogen atmosphere. X-ray powder diffraction (XRD) patterns were recorded using a Cu Kα 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 $Ni_2(BDC)_2(DABCO)$ 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 = 0.25 μm). The temperature program for GC analysis heated samples from 120 to 130 ^{o}C at 40 ^{o}C/min; heated from 130 to 180 ^{o}C at 40 ^{o}C/min and held them at 180 ^{o}C for 0.5 min; heated them from 180 to 280 ^{o}C at 50 ^{o}C/min and held them at 280 ^{o}C for 2 min. Inlet and detector temperatures were set constant at 280 ^{o}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 μm). The temperature program for GC-MS analysis heated samples from 60 to 280 ^{o}C at 10 ^{o}C/min and held them at 280 ^{o}C for 2 min. Inlet temperature was set constant at 280 ^{o}C. MS spectra were compared with the spectra gathered in the NIST library.

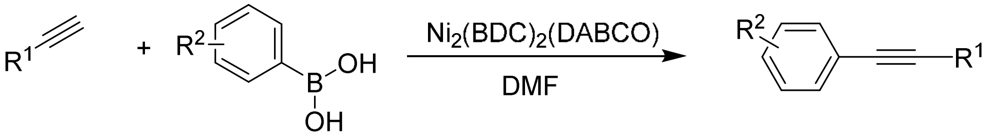
2.2. Synthesis of the metal-organic framework $Ni_2(BDC)_2(DABCO)$

In a typical preparation [46], a solid mixture of H_2BDC (H_2BDC = 1,4-benzenedicarboxylic acid; 0.415 g, 2.5 mmol), DABCO (DABCO = 1,4-diazabicyclo[2.2.2]octane; 0.168 g, 1.5 mmol), and $Ni(NO_3)_2.6H_2O$ (0.58 g, 2 mmol) was dissolved in DMF (DMF = *N,N'*-dimethylformamide; 15 ml). The resulting solution was distributed to two 20 ml vials. The vials were then heated at 100 ^{o}C in an isothermal oven for 48 h. After cooling the vials to room temperature, the solid product was removed by decanting with mother liquor and washed in DMF (3 x 10 ml) for 3 days. Solvent exchange was carried out with methanol (3 x 10 ml) at room temperature for 3 days. The material was then evacuated under vacuum at 140 ^{o}C for 6 h, yielding 0.425 g of $Ni_2(BDC)_2(DABCO)$ in the form of green crystals (76% yield).

2.3. Catalytic studies

The $Ni_2(BDC)_2(DABCO)$ was used as a catalyst for the nickel-catalyzed cross-coupling of phenylacetylene and phenylboronic acids to achieve diphenylacetylenes as the principal product. In a typical experiment, a pre-determined amount of $Ni_2(BDC)_2(DABCO)$ was added to the flask containing a mixture of phenylacetylene (0.110 ml, 1 mmol), phenylboronic acid (0.244 g, 2 mmol), 1,8-diazabicycloundec-7-ene (DBU) (0.299 ml, 2 mmol), 2,2'-bipyridine (0.031 g, 0.2 mmol) as ligand, and *n*-hexadecane (0.1 ml) as internal standard in *N,N*-dimethylformamide (DMF) (5 ml). The catalyst loading as calculated based on the molar ratio of nickel/phenylacetylene. The reaction mixture was stirred at 120 ^{o}C for 180 min. The reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals, quenching with an aqueous KOH solution (5%, 1 ml), drying over anhydrous Na_2SO_4, analyzing by GC with reference to *n*-hexadecane, and further confirming product identity by GC-MS. To investigate the recyclability of $Ni_2(BDC)_2(DABCO)$ in the reaction between phenylacetylene and phenylboronic acid, the catalyst was filtered from the reaction mixture after the experiment, washed with copious amounts of DMF and methanol, dried under air at 85 ^{o}C for 1 h, and reused if necessary. For the leaching test, a catalytic reaction was stopped after 30 min, analyzed by GC, and filtered to remove the solid catalyst. The reaction solution was then stirred for a further 150 min. Reaction progress, if any, was monitored by GC as previously described.

3. Results and discussion



R^1: aryl, alkyl

R^2: -Cl, F, H, C_2H_5, OCH_3, COOH, CHO

Scheme 1. The cross-coupling reaction of phenylacetylene and phenylboronic acids using the $Ni_2(BDC)_2(DABCO)$ as catalyst.

The $Ni_2(BDC)_2(DABCO)$ was synthesized by a solvothermal method, using the reaction of nickel nitrate hexahydrate and 1,4-benzenedicarboxylic acid in DMF, according to a literature procedure [46]. The material was then characterized by several techniques, including XRD, SEM, TEM, TGA, FT-IR, AAS, and nitrogen physisorption measurements (Fig. S1 – Fig. S7). The Ni-MOF was used as a solid catalyst for the nickel-catalyzed cross-coupling of phenylacetylene and phenylboronic acid to achieve diphenylacetylene as the principal product (Scheme 1). Initial studies addressed the effect of temperature on the reaction conversion. The cross-coupling reaction was carried out in DMF using 10 mol% $Ni_2(BDC)_2(DABCO)$ as catalyst, in the presence of two equivalents of DBU as a base and 20 mol% 2,2'-bipyridine as a ligand, with the phenylacetylene:phenylboronic acid molar ratio of 1:2, at 80 ^oC, 100 ^oC, and 120 ^oC, respectively. Aliquots were withdrawn from the reaction mixture at different time intervals and analyzed by GC, giving kinetic data during the course of the reaction. It was found that the reaction carried out at 120 ^oC could afford 86% conversion after 180 min. As expected, decreasing the reaction temperature to 100 ^oC resulted in a significant drop in the reaction rate, with 76% conversion being observed after 180 min. The reaction proceeded with dificulty at 80 ^{o}C, though 51% conversion was still obtained after 180 min (Fig. 1). Moreover, it was observed that a phenylacetylene/phenylboronic acid molar ratio of 1/2 should be used. Using more than two equivalents of phenylboronic acid was unnecessary as the reaction rate was not enhanced significantly (Fig. 2).

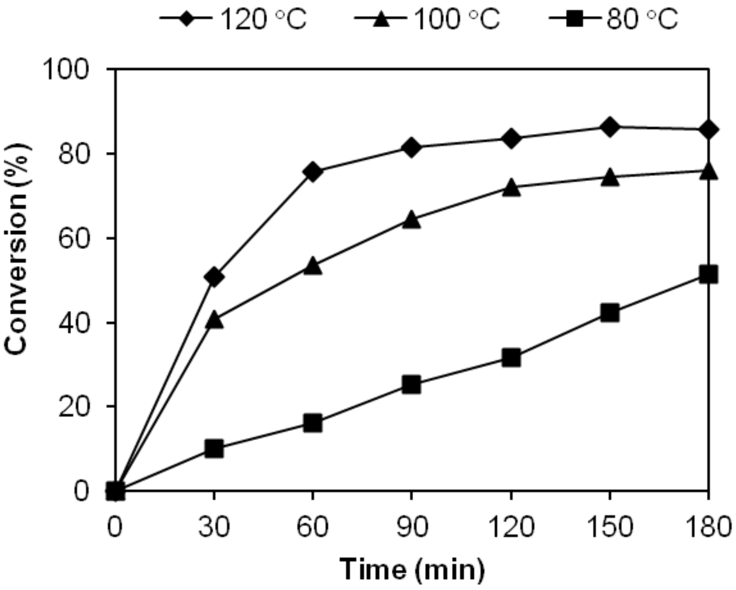


Fig. 1. Effect of temperature on reaction conversions.

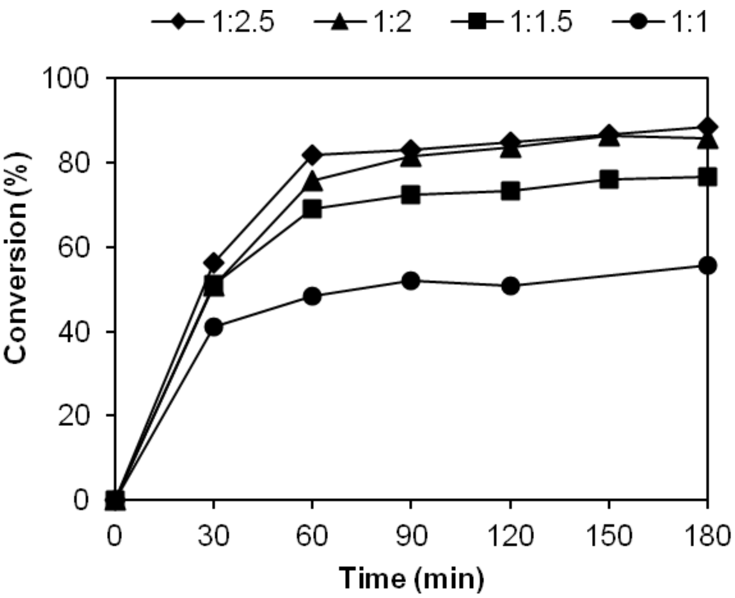


Fig. 2. Effect of phenylacetylene:phenylboronic acid molar ratio on reaction conversion.

The effect of percent of catalyst was then investigated. It was found that the percent of catalyst exhibited a significant effect on the reaction conversion. The reaction using 10 mol% $Ni_2(BDC)_2(DABCO)$ as catalyst could proceed to 86% conversion after 180 min. Decreasing the catalyst loading to 7.5 mol% resulted in 78% conversion, while the reaction using 5 mol% catalyst afforded 69% conversion after 180 min (Fig. 3). Previously, the oxidative cross-coupling reaction between terminal alkynes with arylboronic acids could occur in the presence of different amounts of catalyst, depending on the nature of catalyst as well as the nature of the substrates. These catalyst systems included 0.01 mol% $Pd(OAc)_2$ and 150 mol% Ag_2O [12], 0.5 mol% cyclopalladated ferrocenylpyridine and 100 mol% Ag_2O [47], 1 mol% cyclopalladated ferrocenylimine and 100 mol% Ag_2O [11], 1 mol% palladium nanoparticles in conjunction with 10 mol%

triphenylphosphine and 100 mol% Ag_2O [13], 5 mol% $Pd(OAc)_2$ and 15 mol% TEMPO under electrooxidation condition with Ag anode [48], and 10 mol% Cu_2O [15, 16].

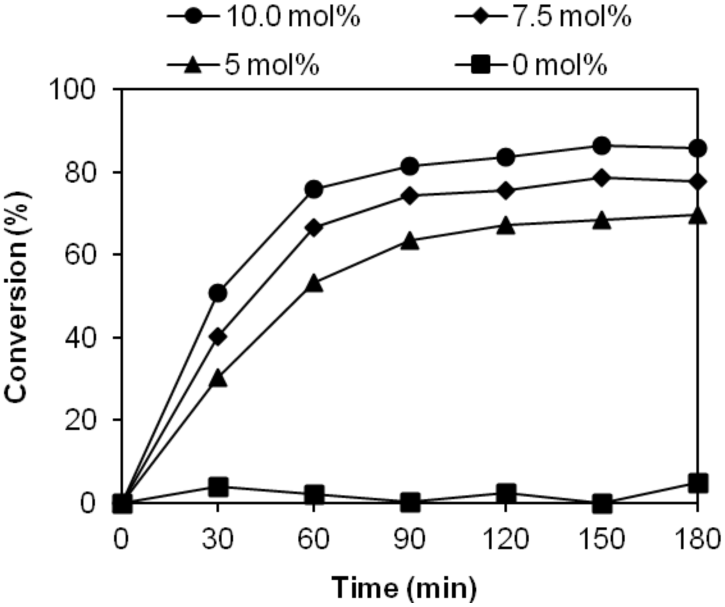


Fig. 3. Effect of catalyst loading on reaction conversions.

The oxidative cross-coupling reaction between terminal alkynes with arylboronic acids were previously carried out in different solvents [49, 50]. Yang and Wu carried out the reaction with cyclopalladated ferrocenylimine and Ag_2O as catalyst in dichloromethane [11], while Li and co-workers reported that acetonitrile was the solvent of choice for the reaction using $Pd(OAC)_2$ and Ag_2O mixture as catalyst [12]. For Cu_2O-catalyzed coupling reactions, Rao and co-workers demonstrated that the transformation should be carried out in chloroform [16], whereas Li and co-workers pointed out that the reaction proceeded readily in a mixture of dioxane and isopropanol [15]. The cross-coupling reactions were carried out in DMF, DEF, DMAc, DMSO, and NMP as solvent. It was found that DEF was not suitable for the reaction, affording only 33% conversion after 180 min. This value could be improved to 67% and 72% for the reaction carried out in DMAc and NMP, respectively. Both DMF and DMSO could be used as solvent for the reaction, with 86% conversion being achieved after 180 min (Fig. 4).

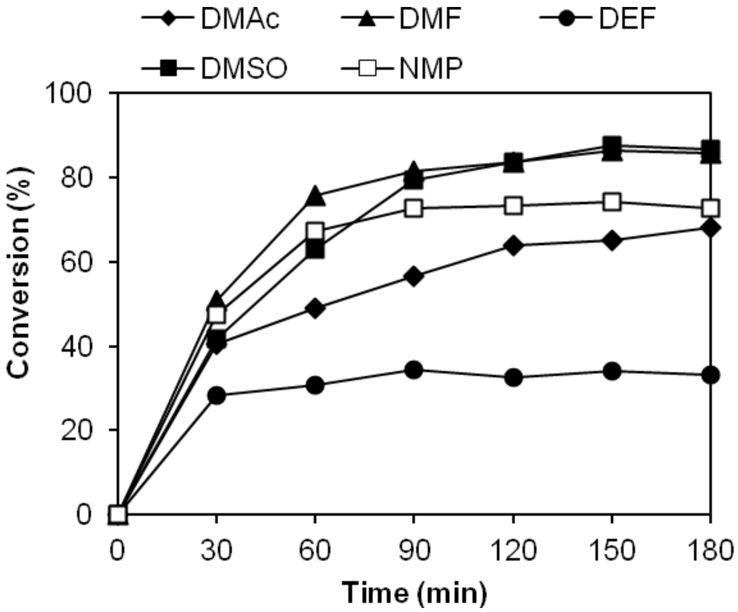


Fig. 4. Effect of different solvents on reaction conversion.

Li and co-workers previously employed a series of bases for the reaction between terminal alkynes and boronic acids in the presence of Pd(OAC)$_2$ and Ag$_2$O mixture, and reported that best results were achieved with K$_2$CO$_3$ as the base [12]. However, Yang and Wu tested various bases for the palladium-catalyzed oxidative coupling, and pointed out that the transformation should be carried out in the presence of KOAc [11]. Using Cu$_2$O as catalyst, Li and co-workers also screened several bases for the arylation transformation, and achieved best results with *t*-BuOK [15]. Rao and co-workers did not employed a base for the Cu$_2$O-catalyzed reaction between terminal alkynes with arylboronic acids, though the presence of pyridine as an additive was required [16]. In this work, a series of bases were employed for the $Ni_2(BDC)_2(DABCO)$-catalyzed oxidative coupling reaction, including DBU, triethylamine, piperidine, K_3PO_4, K_2CO_3, Na_2CO_3, NaOAc, and *t*-BuOK, respectively. Experimental results indicated that among these bases, only DBU should be used for the transformation, with 86% conversion being achieved after 180 min. The transformation proceeded with difficulty in the presence of other bases (Fig. 5). Moreover, it was also found that using less than two equivalents of the base resulted in a significant drop in the reaction rate, with 38% conversion being detected after 180 min for the reaction using one equivalent of DBU. Employing more than two equivalents of DBU for the reaction did not accelerate the cross-coupling significantly. It should be noted that no product was detected for the reaction in the absence of the base (Fig. 6).

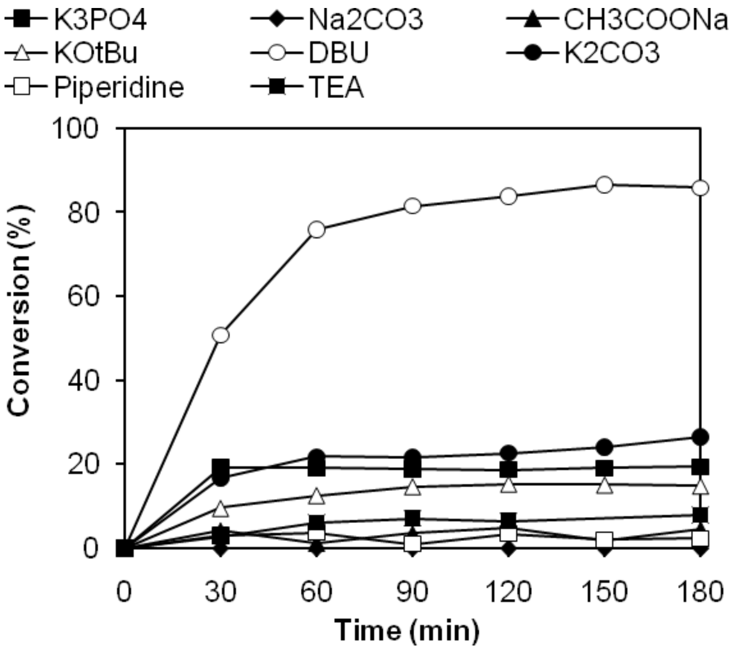


Fig. 5. Effect of different bases on reaction conversion.

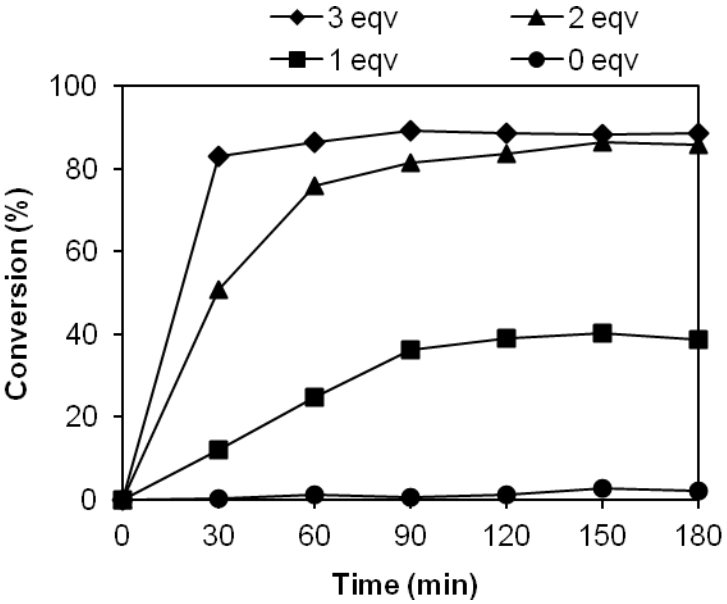


Fig. 6. Effect of base concentration on reaction conversion.

It was decided to investigate the effect of ligand nature on the reaction conversion, having used 1,10-phenanthroline, 2,2'-bipyridine, ethylenediamine, and acetylacetone as ligand, respectively. The reaction was carried out in DMF at 120 ^{o}C using 10 mol% $Ni_2(BDC)_2(DABCO)$ as catalyst, in the presence of two equivalents of the base and 20 mol% ligand, with the phenylacetylene:phenylboronic acid molar ratio of 1:2. It was observed that ethylenediamine and acetylacetone were ineffective for the reaction, with less than 5% conversion being detected after 180 min. The reaction conversion could be improved to 60% after 180 min in the presence of 1,10-phenanthroline as ligand, while the reaction using 2,2'-bipyridine as ligand could proceed to 86% conversion after 180 min (Fig. 7). Moreover, in the absence of the ligand, only 26% conversion was afforded. Decreasing the amount of ligand to one equivalent resulted in a drop in the reaction rate, though 77% conversion was still obtained after 180 min. However, it was found that using three equivalents of the ligand also slowed down the reaction, with 78% conversion being detected after 180 min (Fig. 8).

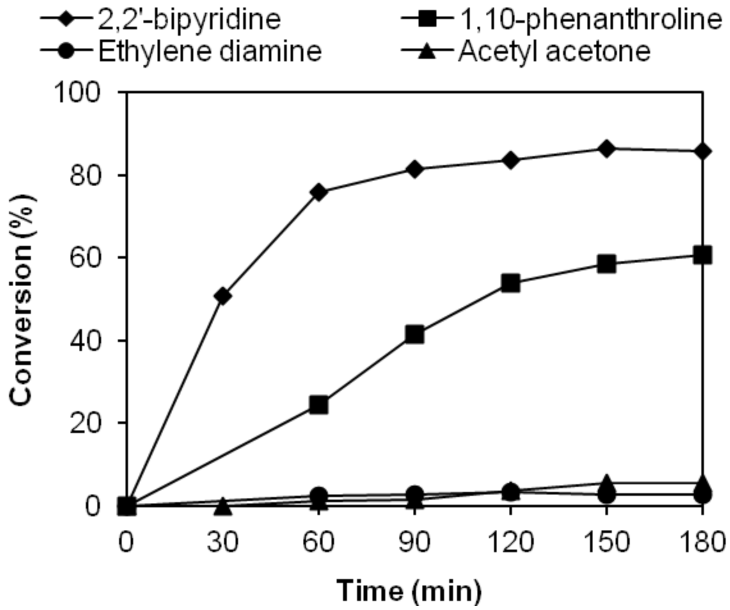


Fig. 7. Effect of different ligands on reaction conversion.

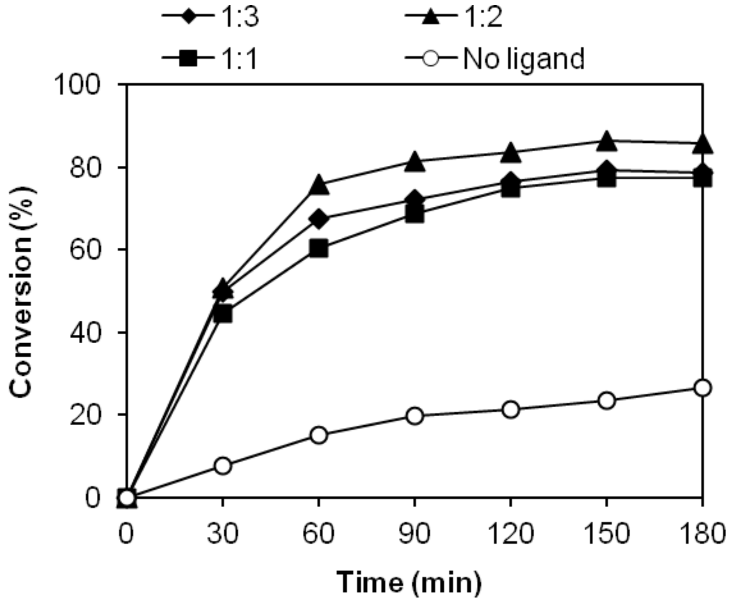
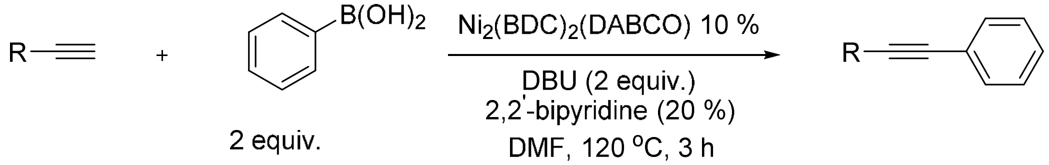
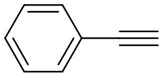
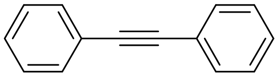
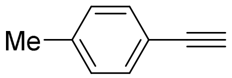
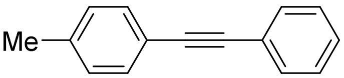
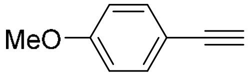
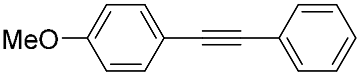
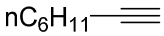
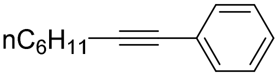


Fig. 8. Effect of ligand concentration on reaction conversions.

Table 1. Reaction scope with respect to alkynes



Entry	Alkynes	Product	Convesion (%)
1			86
2			67
3			81
4			47

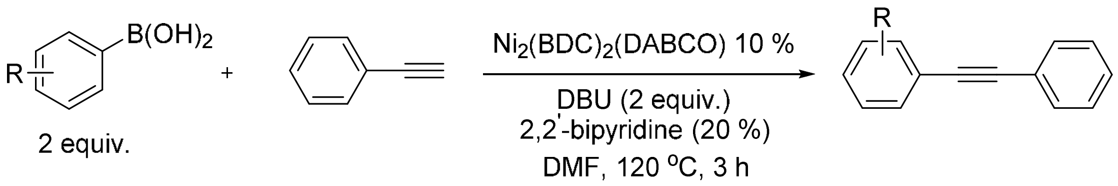
Conditions: DMF (5 mL), alkynes (1 mmol), arylboronic acids (2 mmol).

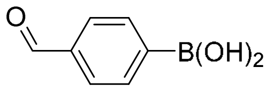
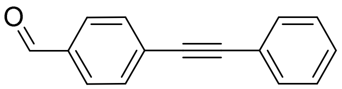
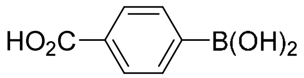
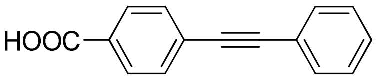
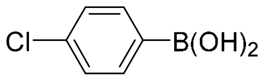
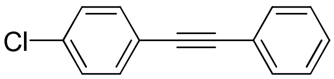
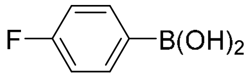
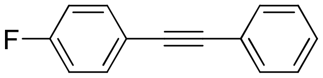
Reaction scope with respect to various alkynes was shown in Table 1. Alkynylations by phenyl boronic acids were conducted under optimal conditions. Phenylacetylenes with methyl or methoxy group substituents were active and arylated products were obtained in 67 % and 81 %, respectively (entries 2 and 3). Interestingly, alkynylation by aliphatic terminal alkyne was also possible and arylation of 1-octyne afforded moderate yield (entry 4). It is worth to mention that arylation of aliphatic alkynes, in many cases, require strict conditions due to their facile isomerization [51].

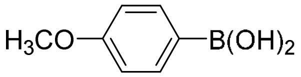
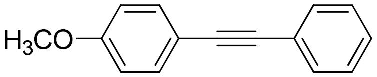
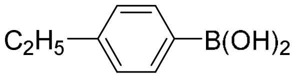
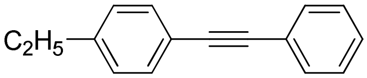
We then expanded the research to the $Ni_2(BDC)_2(DABCO)$-catalyzed oxidative coupling reaction using different phenylboronic acids. It was observed that 4-

carboxyphenylboronic acid was not suitable for the system due to the interaction with the base in the reaction mixture. 4-Formylphenylboronic acid was found to be more reactive than phenylboronic acid, affording 91% conversion after 180 min. The presence of a halogen atom in the phenylboronic acid slowed down the reaction, with 69% and 51% conversions being observed after 180 min of 4-chlorophenylboronic acid and 4-florophenylboronic acid, respectively. 4-Methoxyphenylboronic acid and 4-ethylphenylboronic acid were also found to be less reactive than phenylboronic (Table 2). Bao and co-workers previously used porous palladium nanospheres in conjuction with Ag_2O and triphenylphosphine as the catalyst system for the oxidative cross coupling reactions and demonstrated that no obvious differences were detected between the case of arylboronic acids with electron-withdrawing and with electron-donating groups [13].

Table 2. Arylation of phenylacetylene by various aryl boronic acids



Entry	Boronic acids	Product	Convesion (%)
1			92
2			< 2
3			70
4			51

5			65
6			30

Conditions: DMF (5 mL), alkynes (1 mmol), arylboronic acids (2 mmol).

To highlight the advantages of using the $Ni_2(BDC)_2(DABCO)$ catalyst, the catalytic activity of the $Ni_2(BDC)_2(DABCO)$ was compared with that of other Ni-MOFs including $Ni_3(BTC)_2$ and Ni(HBTC)(BPY), and that of other $M_2(BDC)_2(DABCO)$ including $Zn_2(BDC)_2(DABCO)$, $Cu_2(BDC)_2(DABCO)$, and $Co_2(BDC)_2(DABCO)$. Interestingly, it was observed that $Ni_3(BTC)_2$ and Ni(HBTC)(BPY) were significantly less active than the $Ni_2(BDC)_2(DABCO)$, affording 51% and 59% conversions after 180 min. Under the same condition, the reaction using $Ni_2(BDC)_2(DABCO)$ could proceed to 86% conversion after 180 min. These results would confirm the necessary of the DABCO linker of the Ni-MOF structure in the cross-coupling reaction. Moreover, $Zn_2(BDC)_2(DABCO)$ and $Co_2(BDC)_2(DABCO)$ were found to be inactive, with no trace amount of the product being detected by GC. In contrast, the reaction using $Cu_2(BDC)_2(DABCO)$ as catalyst could proceed 72% conversion after 180 min (Fig. 9). However, this copper-catalyzed transformation led to the formation of 10% homo-coupling product in the product mixture. It should be noted that no homo-coupling product was detected by GC in the $Ni_2(BDC)_2(DABCO)$-catalyzed oxidative reaction. These observations would emphasize the advantages of using the $Ni_2(BDC)_2(DABCO)$ catalyst.

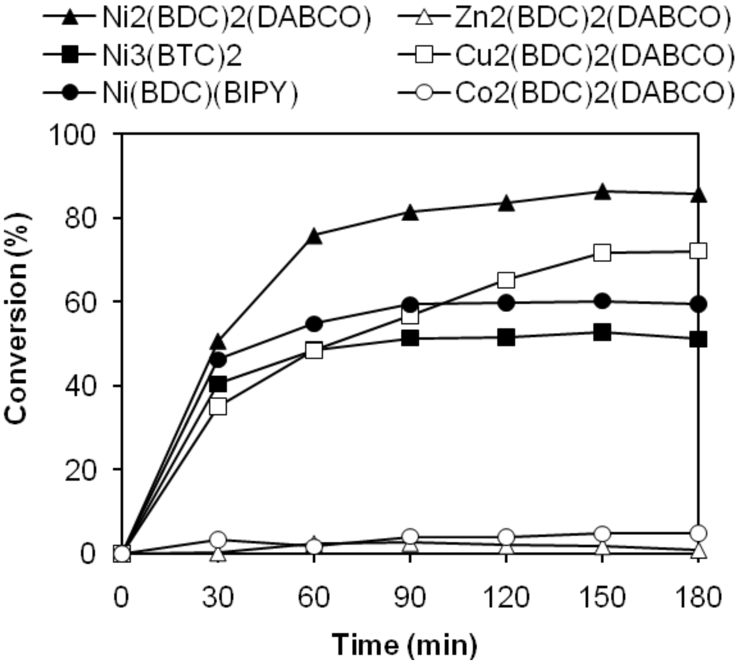


Fig. 9. Effect of different MOFs catalysts on reaction conversions.

To gain insights into the reaction pathway of the $Ni_2(BDC)_2(DABCO)$-catalyzed oxidative transformation, the role of the air was clarified. The reaction was carried out in DMF at 120 °C using 10 mol% Ni-MOF as catalyst, in the presence of two equivalents of the base and 20 mol% ligand, with the phenylacetylene:phenylboronic acid molar ratio of 1:2. After 30 min under air with 50% conversion, argon was introduced to the system to replace the air, and the reaction mixture was heated at 120 °C with magnetic stirring for another 60 min. Interestingly, no further reaction was observed in the absence of air, with 50% conversion was obtained after 90 min. It should be noted that the reaction could proceed to 81% conversion after 90 min under air. After 90 min, air was introduced back to the system, and the reaction mixture was heated at 120 °C with magnetic stirring for additional 90 min. It was found that the reaction rate was significantly enhanced in the presence of air, as compared to the case of argon (Fig. 10). We also investigated whether contaminated water in air could play an important role on reaction. Specifically, only trace amount of product was detected by GC when the reaction was carried out under argon atmosphere with added H_2O (0.5 mmol). These results would confirm the role of the oxygen as an oxidant. Furthermore, we applied pure oxygen, *tert*-butyl hydroperoxide, *tert*-butyl perbenzoate, and cumyl peroxide, respectively, as the oxidants for the reaction. However, it was observed that most of phenylacetylene was converted to benzoic acid in the presence of these oxidants, while the cross-coupling product was detected only in trace amounts. Apparently, employing atmospheric oxygen as the stoichiometric oxidant should be the best choice for economical and environmentally benign processes.

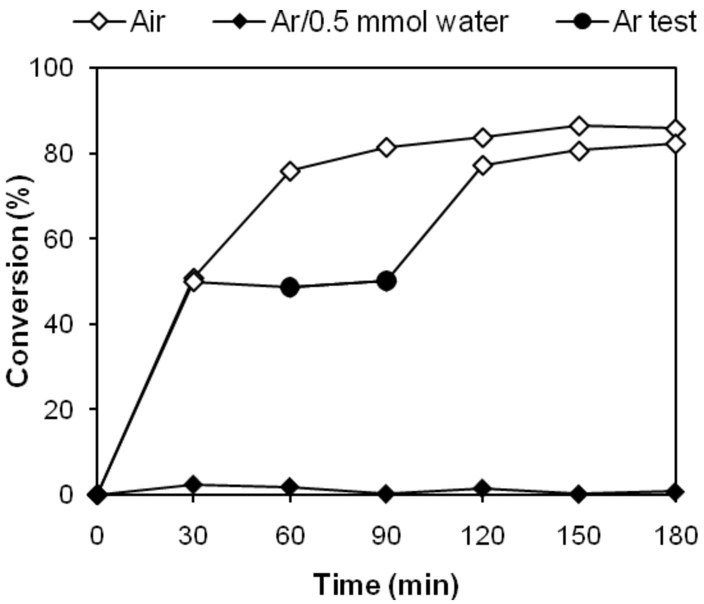


Fig. 10. Effect of argon and water on reaction conversions.

In further mechanistic studies, a radical trapping reagent, (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO), was added to the reaction mixture. If the reactions proceed through a radical pathway, it is likely that the catalytic cycle would be terminated in the presence of TEMPO. The reaction was carried out with added TEMPO (1 equiv.). It was observed that similar conversions were obtained for reactions with and without TEMPO (Fig. 11). With all of these results, the reaction mechanism was proposed (Scheme 2).

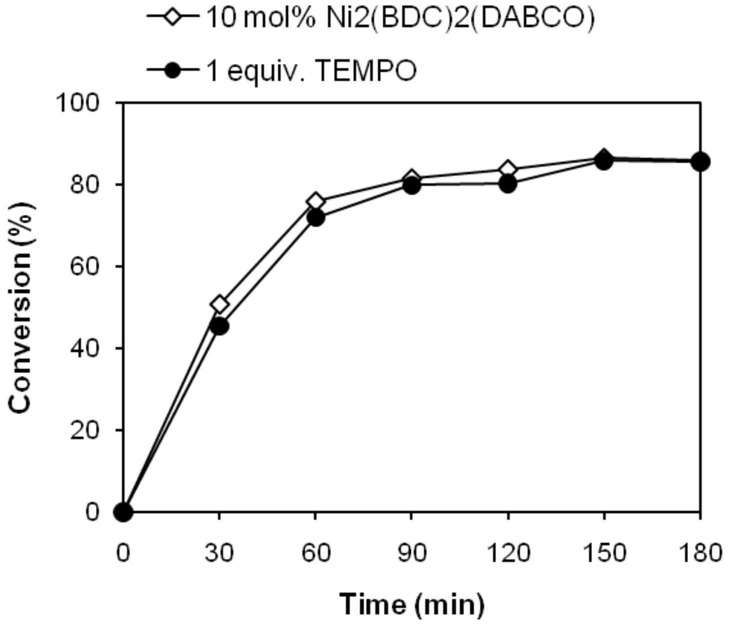
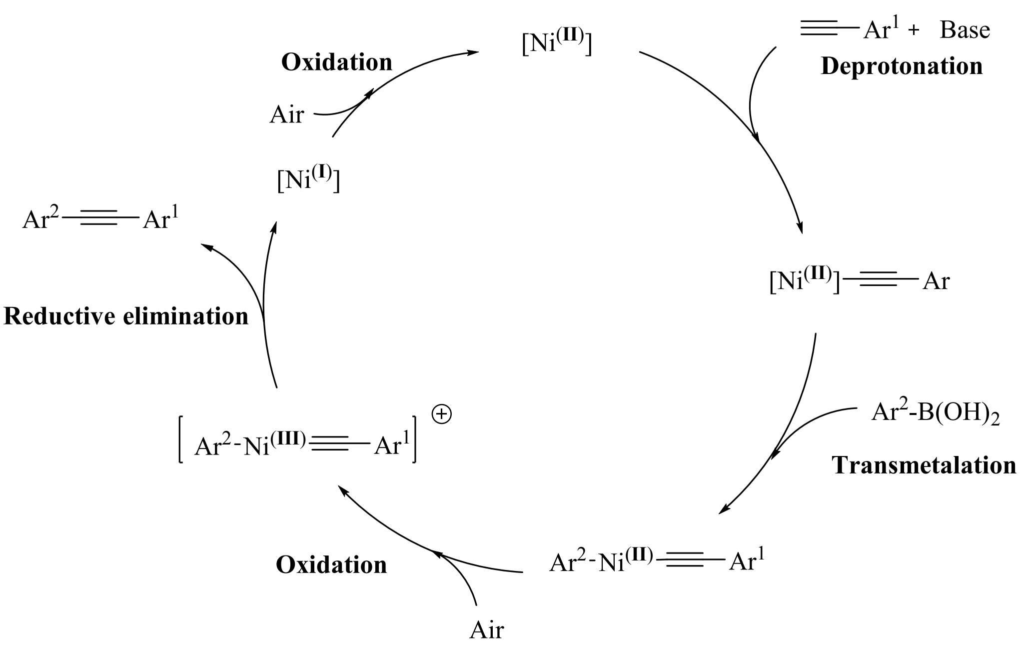


Fig. 11. Effect of TEMPO on reaction routes

Our proposed mechanism is consistent with experimental data and similar to Chan-Lam reaction mechanism [52]. Deprotonation of phenylacetylenes followed by nucleophilic attack to form phenylacetylide Ni(II) species. Transmetalation with aryl boronic acid affords diaryl Ni(II) intermediates. This step was previously reported to be facile in the presence of base [53]. Atmospheric oxygen is required to oxidize diaryl Ni(II) to diaryl Ni(III) complexes before reductive elimination. It is well-known that reductive elimination is much faster from high oxidation state metal species [54]. Nickel (I) intermediates formed by reductive elimination reacts with oxygen oxidant to regenerate Ni(II) complexes and finish the catalytic cycle. The intermediacy of Ni(II)/Ni(III) catalytic cycles was recently proposed in the literature [55].



Scheme 2. Proposed reaction mechanism through Ni(II)/Ni(III) catalytic cycle

In order to confirm if active nickel species dissolved from the solid $Ni_2(BDC)_2(DABCO)$ catalyst could contribute to the total conversion of the oxidative coupling reaction between phenylacetylene and phenylboronic acid, a control experiment was carried out using a simple filtration during the course of the reaction. The coupling reaction was carried out in DMF at 120 °C using 10 mol% $Ni_2(BDC)_2(DABCO)$ as catalyst, in the presence of two equivalents of the base and 20 mol% ligand, with the phenylacetylene:phenylboronic acid molar ratio of 1:2. The $Ni_2(BDC)_2(DABCO)$ catalyst was separated from the reaction mixture after 30 min reaction time by simple filtration. The reaction solution was then transferred to a new reactor vessel, and stirred for an additional 150 min at 120 °C with aliquots being sampled at different time intervals, and analyzed by GC. It was found that almost no further conversion was detected after the $Ni_2(BDC)_2(DABCO)$ catalyst was removed from the reaction mixture (Fig. 12). This result could confirm that the reaction between phenylacetylene and phenylboronic acid could only occur in the presence of the solid $Ni_2(BDC)_2(DABCO)$ catalyst, and the contribution of catalytically active species soluble in the solution, if any, was negligible.

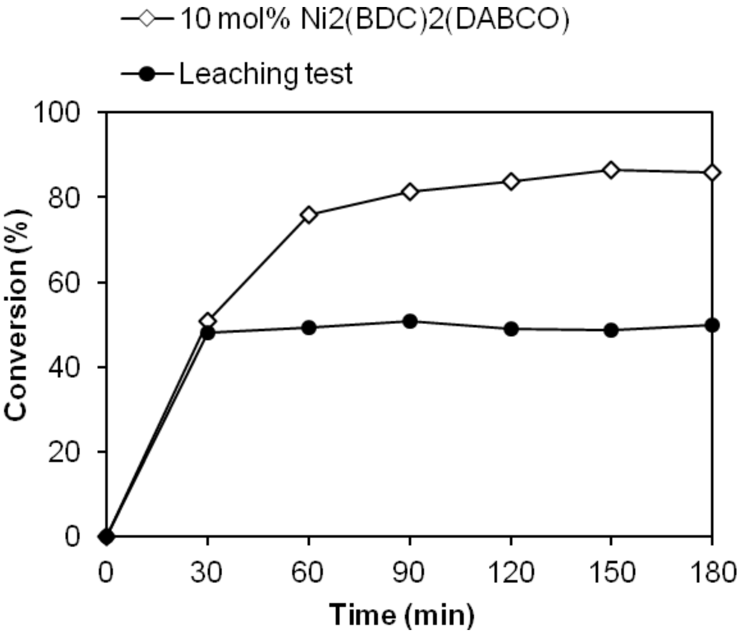


Fig. 12. Leaching test indicated no contribution from homogeneous catalysis of active species leaching into reaction solution.

The $Ni_2(BDC)_2(DABCO)$ catalyst was also investigated for recoverability and reusability over six successive runs, by repeatedly separating the Ni-MOF catalyst from the reaction mixture, washing it and then reusing it. The coupling reaction was carried out in DMF at 120 °C using 10 mol% $Ni_2(BDC)_2(DABCO)$ as catalyst, in the presence of two equivalents of the base and 20 mol% ligand, with the phenylacetylene:phenylboronic acid molar ratio of 1:2. After the cross-coupling reaction was completed, the $Ni_2(BDC)_2(DABCO)$ catalyst was separated by simple filtration, washed with copious amounts of DMF and methanol to remove any physisorbed reagents, and dried under air at 120 °C for 1 h. The recovered Ni-MOF was then reused in further reactions under identical conditions to those of the first run. It was observed that the $Ni_2(BDC)_2(DABCO)$ catalyst could be recovered and reused several times without a significant degradation in catalytic activity. Indeed, a conversion of 86% was still achieved in the 4th run. However, lower conversion was observed from the 5th run (Fig. 13). The recovered Ni-MOF was also characterized by FT-IR and XRD. The FT-IR spectra of the reused $Ni_2(BDC)_2(DABCO)$ exhibited a similar absorption as compared to that of the fresh Ni-MOF (Fig. 14). It was observed that the crystallinity of the reused Ni-MOF was slightly different to that of the fresh catalyst. However, XRD result indicated that the reused $Ni_2(BDC)_2(DABCO)$ was still highly crystalline (Fig. 15).

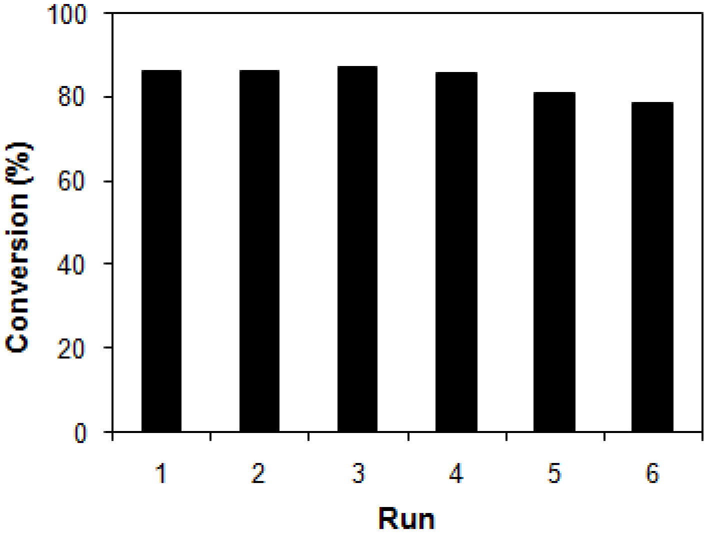


Fig. 13. Catalyst recycling studies

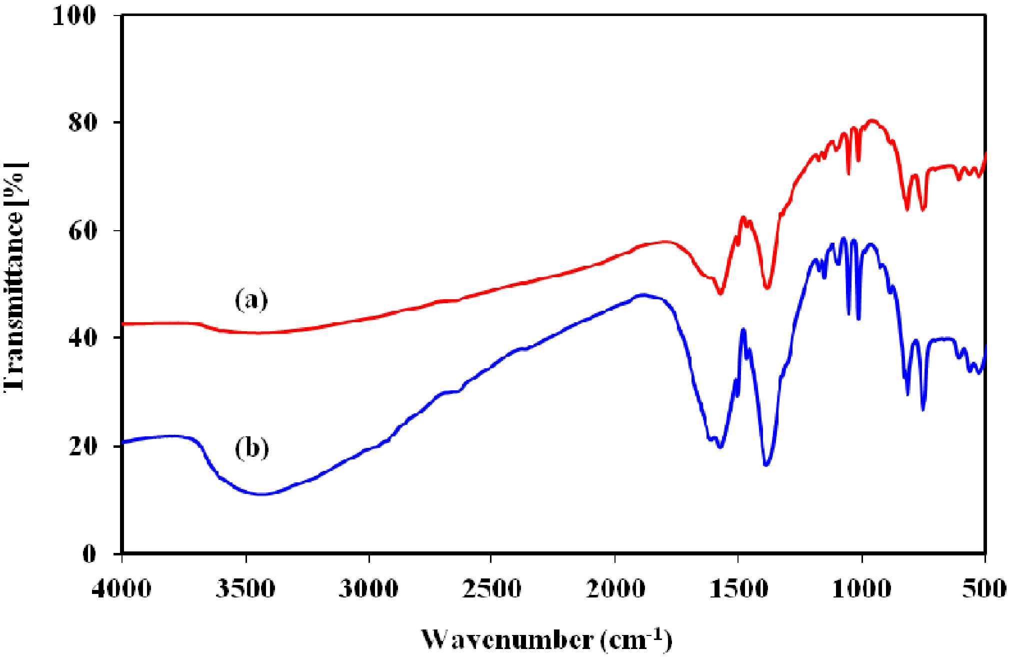


Fig. 14. FT-IR spectra of the fresh (a) and reused (b) $Ni_2(BDC)_2(DABCO)$ catalyst.

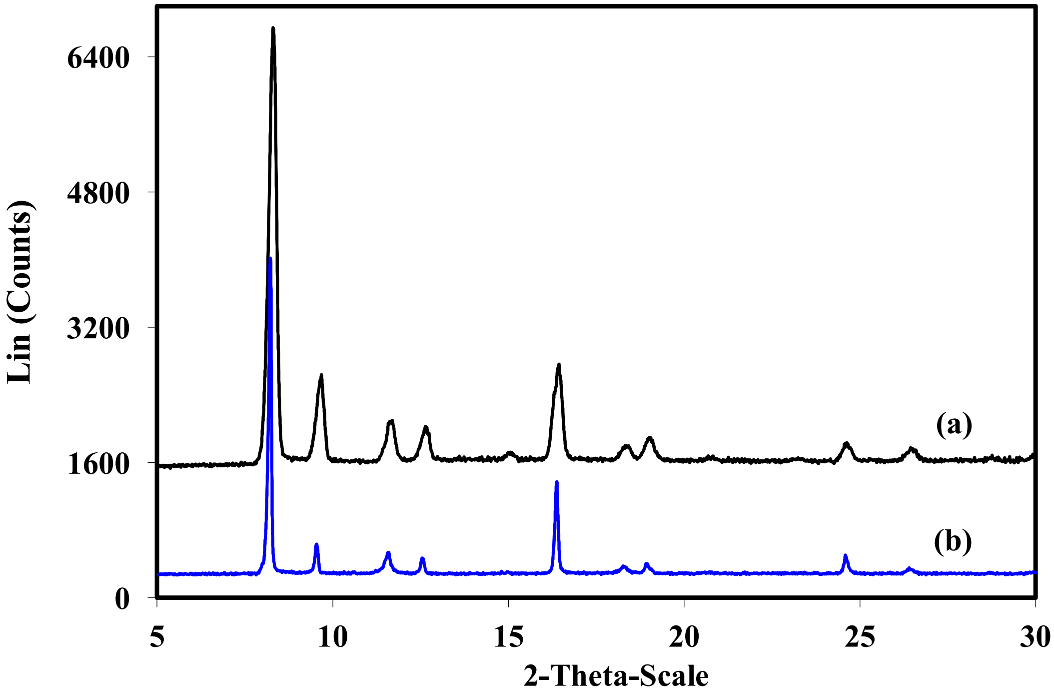


Fig. 15. X-ray powder diffractograms of the fresh (a) and reused (b) $Ni_2(BDC)_2(DABCO)$ catalyst.

The concern about the actual catalyst in the reaction was also addressed. AAS analysis indicated that 29.6 ppm of copper and less than 5 ppm of palladium were presented in the catalyst. To test the possibility that contaminated palladium and copper can promote the formation of desired product, several control experiments were conducted using identical conditions (Fig.16). In particular, reactions with 10 % of CuI or $Cu(OAc)_2$ afforded less than 60 % conversion under optimal conditions. Noticeably, only trace amount of product was detected in similar reaction using 0.1 % $Pd(OAc)_2$. These results revealed that the copper and palladium catalysis is unlikely and Ni-MOF is actual catalyst for the transformation.

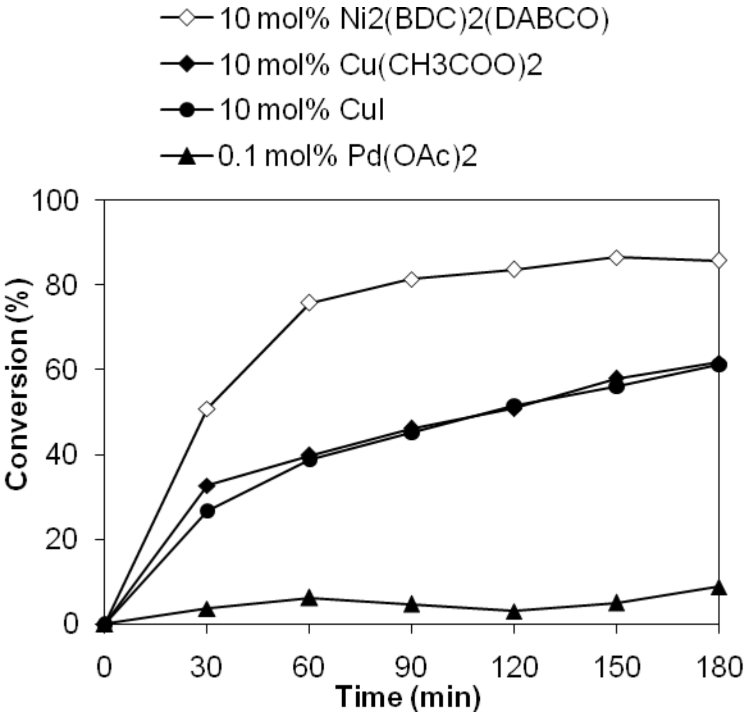


Fig. 16. Control experiments using homogeneous copper and palladium catalysts

4. Conclusions

In summary, the metal-organic framework $Ni_2(BDC)_2(DABCO)$ was synthesized, and characterized by several techniques including XRD, SEM, TEM, FT-IR, TGA, AAS, and nitrogen physisorption measurements. The Ni-MOF could be used as an efficient heterogeneous catalyst for the oxidative cross-coupling reaction between phenylboronic acid with phenylacetylene in the presence of molecular oxygen in air as the stoichiometric oxidant. High conversion to the cross-coupling product was achieved with no homo-coupling product being detected by GC. The $Ni_2(BDC)_2(DABCO)$ exhibited significantly higher catalytic activity in the oxidative cross coupling reactions than that of $Ni_3(BTC)_2$, Ni(HBTC)(BPY), $Zn_2(BDC)_2(DABCO)$, $Cu_2(BDC)_2(DABCO)$, and $Co_2(BDC)_2(DABCO)$. Moreover, although $Cu_2(BDC)_2(DABCO)$ could proceed to reasonable conversion, approximately 10% homo-coupling product was observed. The $Ni_2(BDC)_2(DABCO)$ could be recovered and reused several times without a significant degradation in catalytic activity. The fact that no homo-coupling product was detected for the $Ni_2(BDC)_2(DABCO)$-catalyzed coupling reaction was therefore advantageous. To the best of our knowledge, a nickel-based catalyst was not previously used for the oxidative reaction between phenylacetylene and phenylboronic acid.

Acknowledgements

The Viet Nam National Foundation for Science and Technology Development - NAFOSTED is acknowledged for financial support through project code 104.99-2012.25.

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Nickel-catalyzed oxidative coupling of alkynes and aryl boronic acids using metal-organic framework $Ni_2(BDC)_2(DABCO)$ as an efficient heterogeneous catalyst

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Supporting information

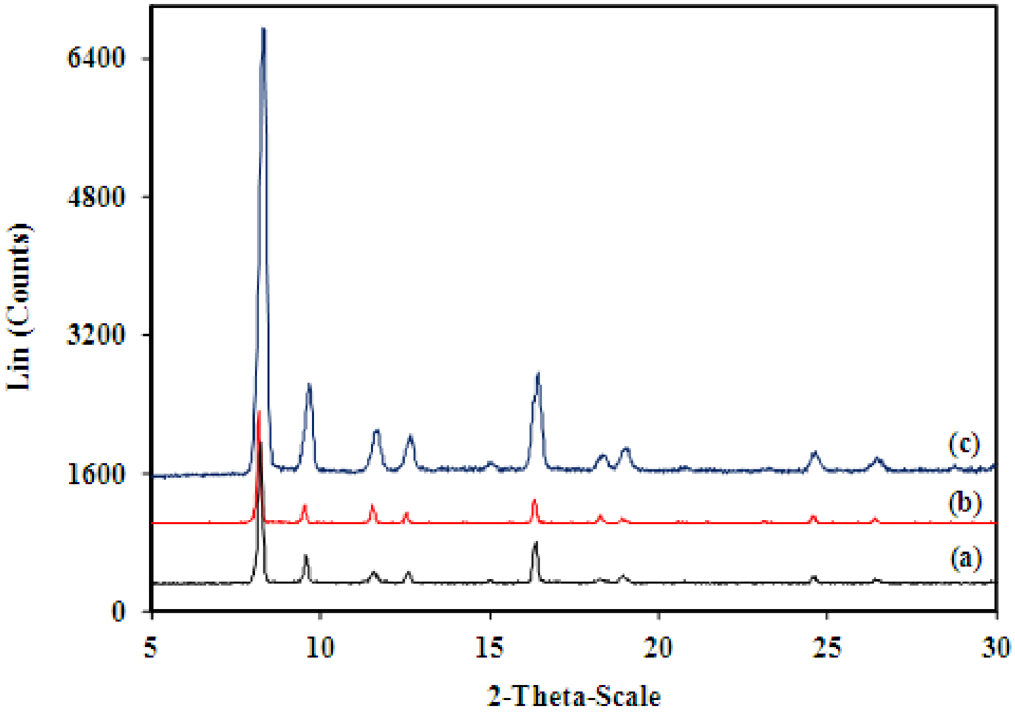

Fig. S1. X-ray powder diffractograms of the as-synthesized (a), CH_3OH-exchanged (b), and activated (c) $Ni_2(BDC)_2(DABCO)$.

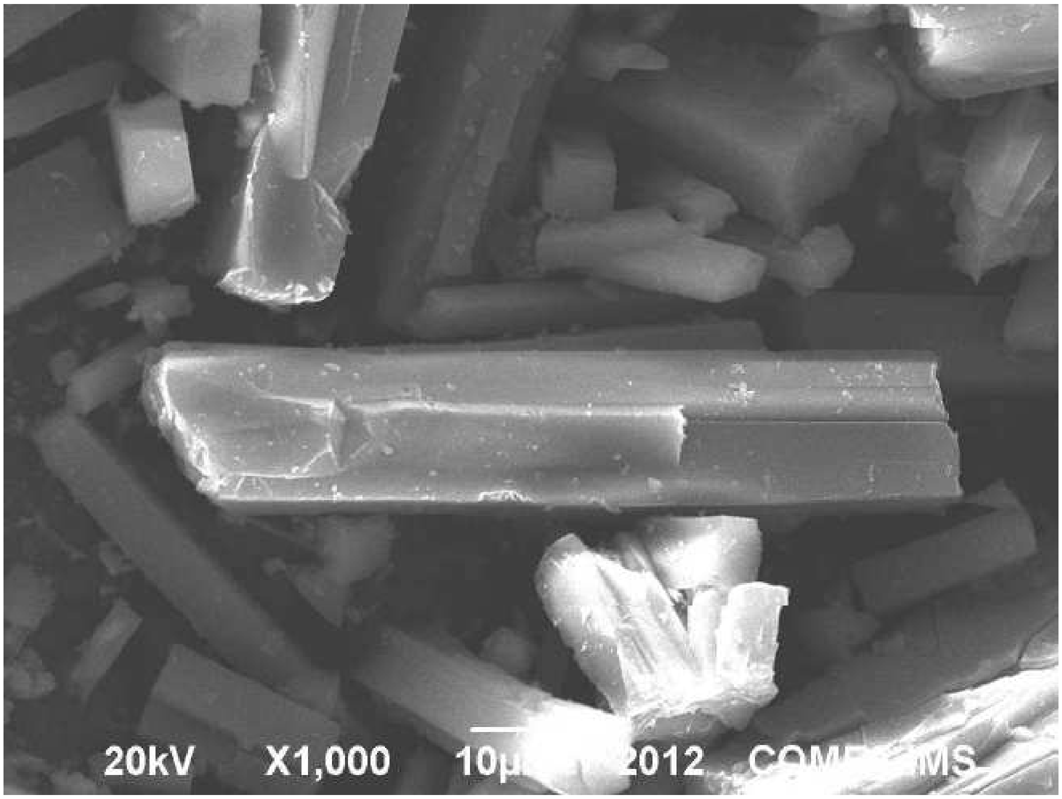

Fig. S2. SEM micrograph of the $Ni_2(BDC)_2(DABCO)$.

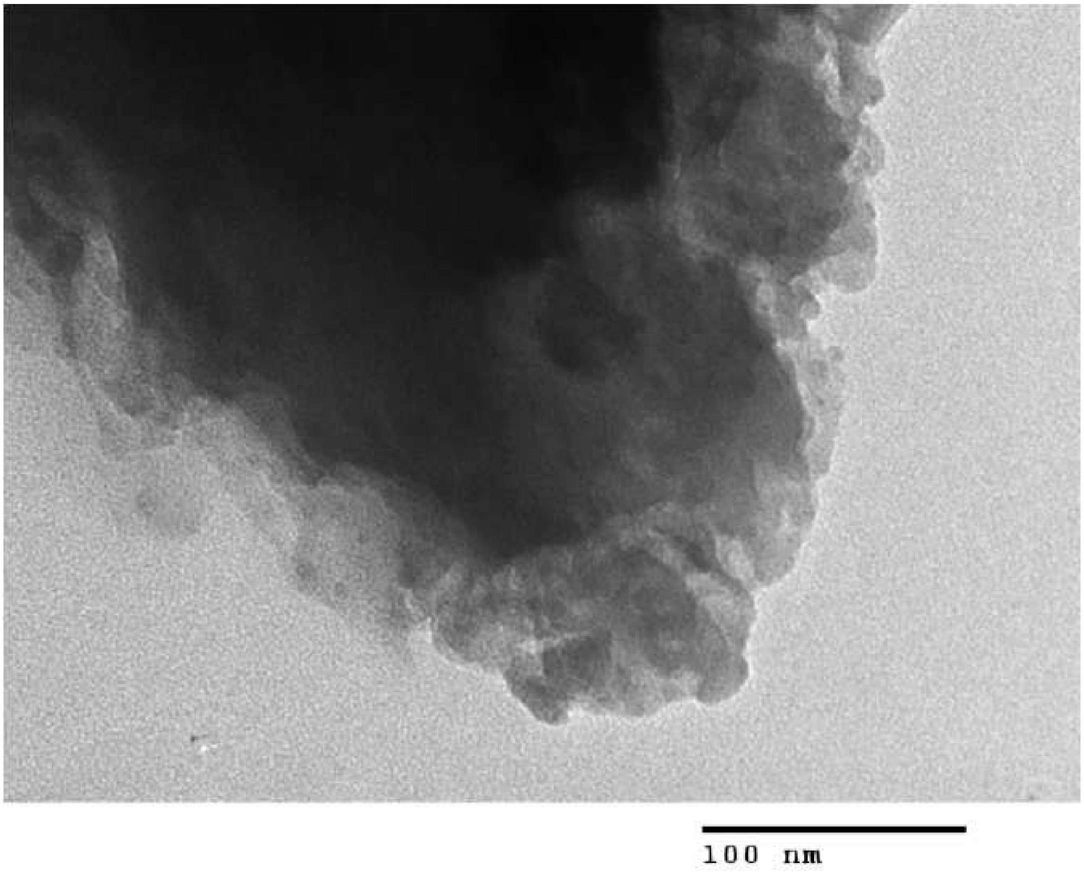

Fig. S3. TEM micrograph of the $Ni_2(BDC)_2(DABCO)$.

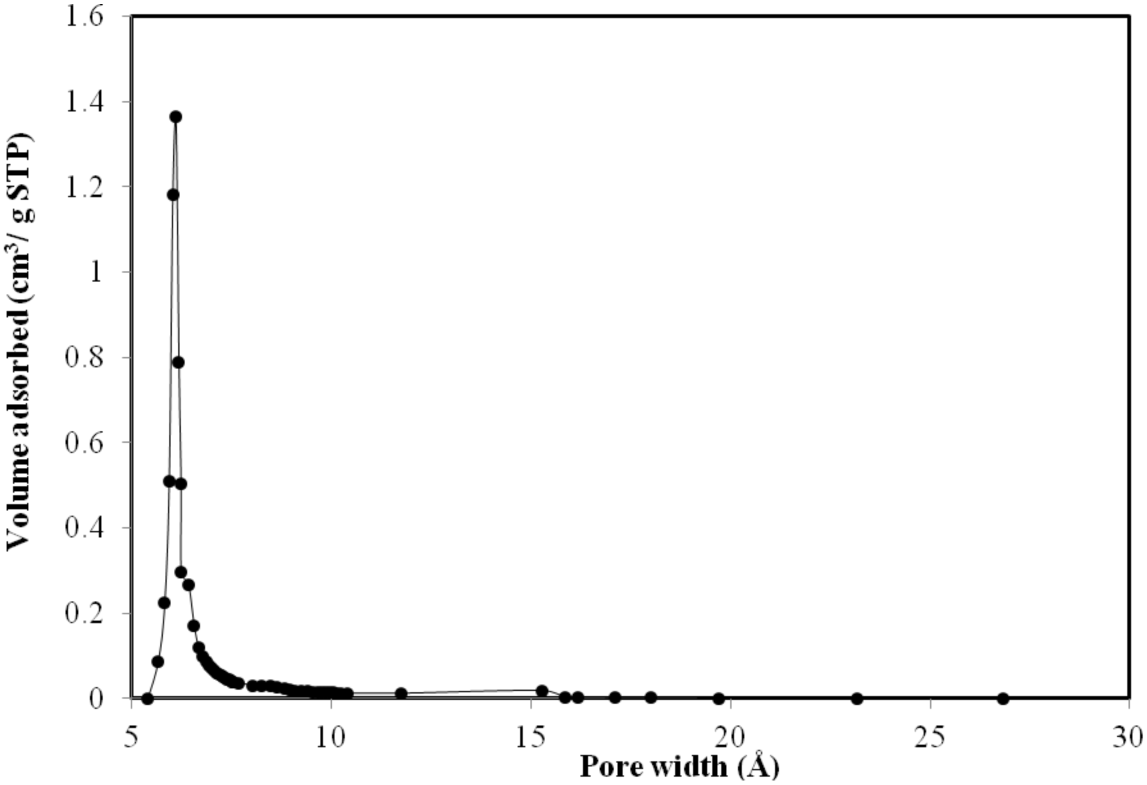

Fig. S4. Pore size distribution of the $Ni_2(BDC)_2(DABCO)$.

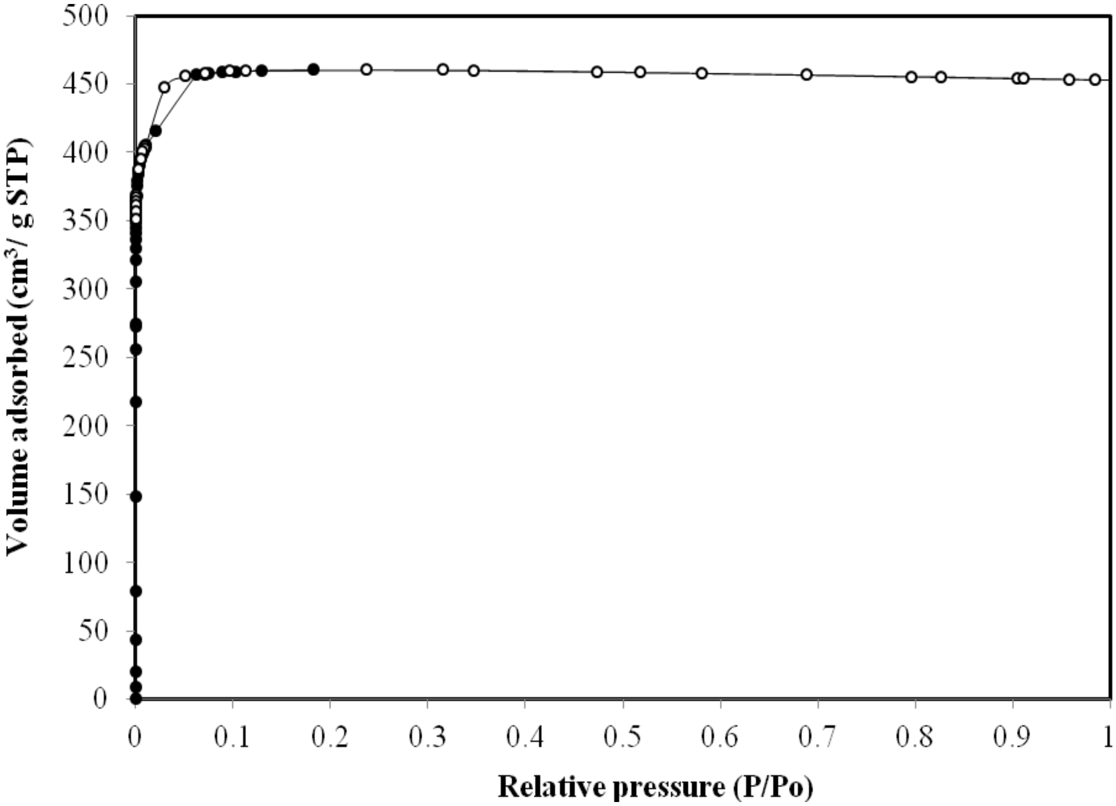

Fig. S5. Nitrogen adsorption/desorption isotherm of the $Ni_2(BDC)_2(DABCO)$.

Adsorption data are shown as closed circles and desorption data as open circles.

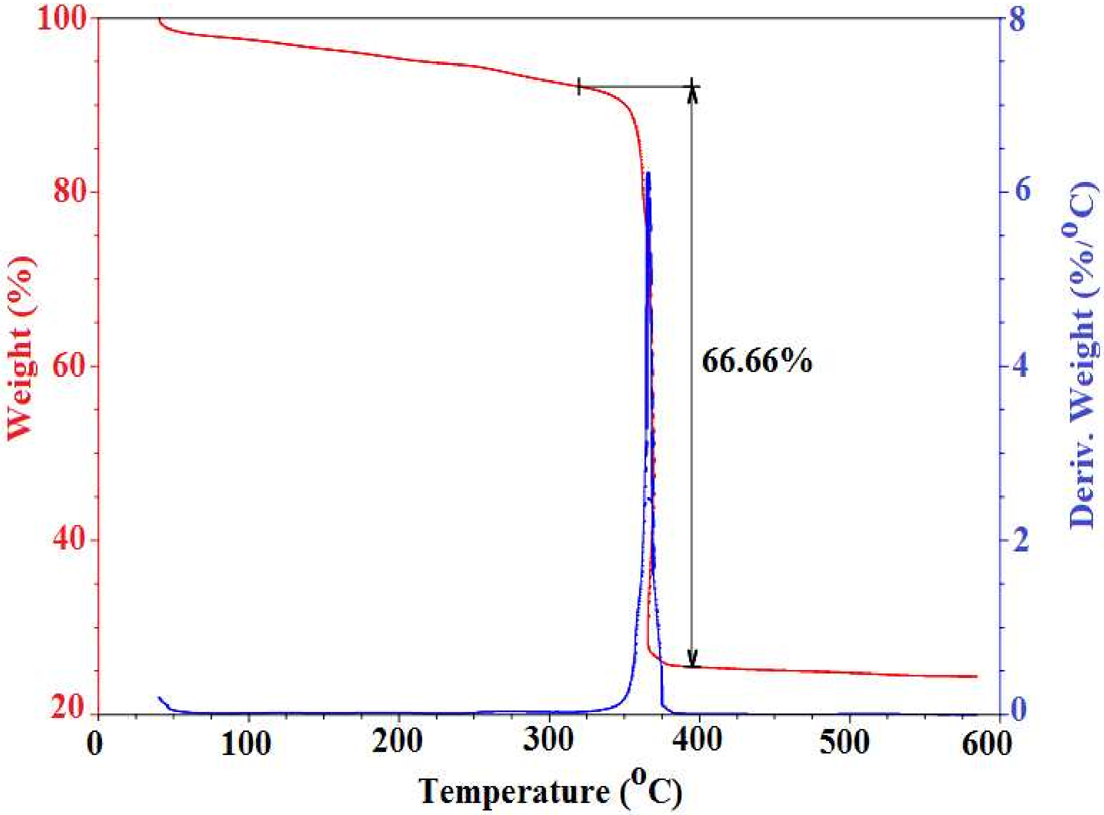

Fig. S6. TGA analysis of the $Ni_2(BDC)_2(DABCO)$.

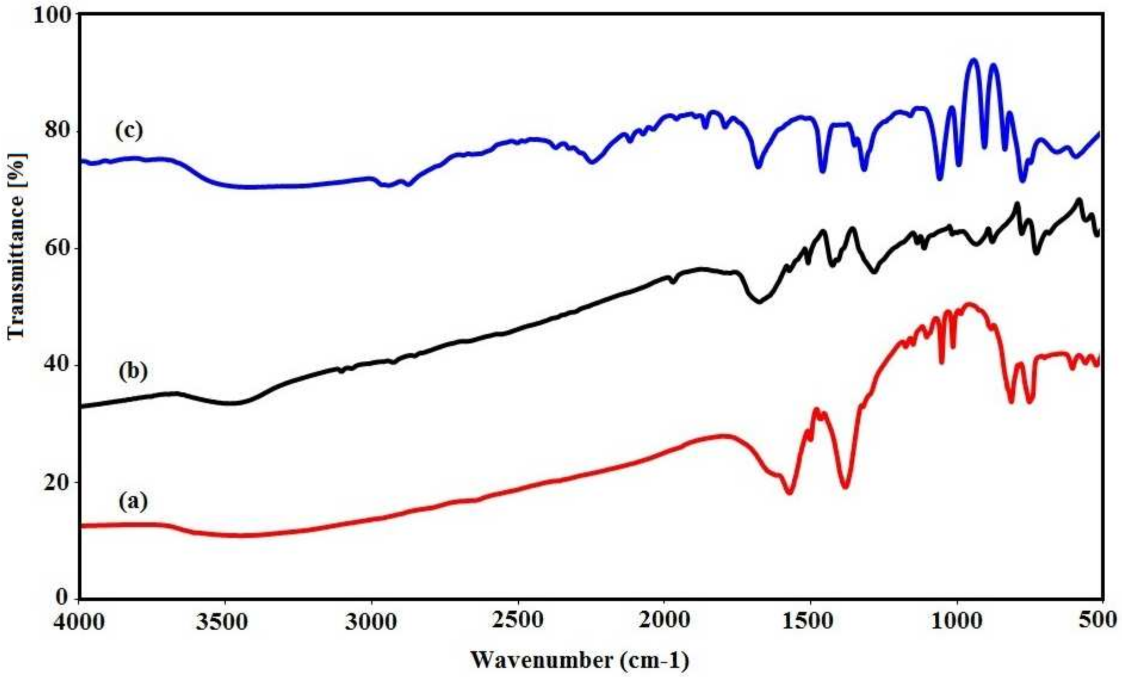

Fig. S7. FT-IR spectra of the $Ni_2(BDC)_2(DABCO)$ (a), 1,4-benzenedicarboxylic acid (b), and 1,4-diazabicyclo[2.2.2]octane (c).

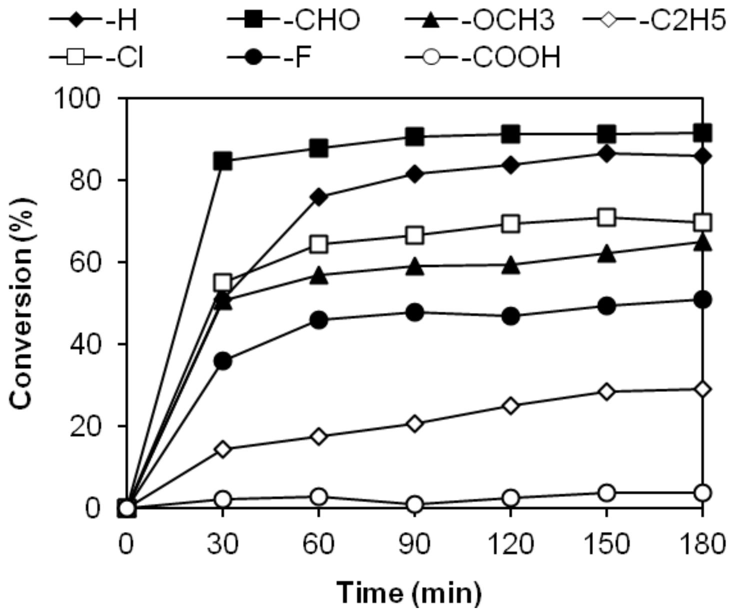

Fig. S8. Effect of different phenylboronic acids on reaction conversions.

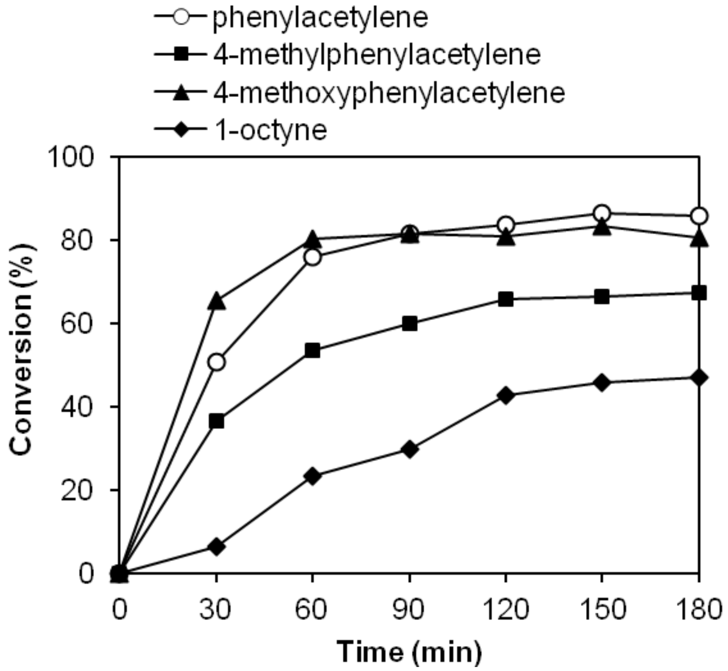

Fig. S9. Effect of different alkynes on reaction conversions.