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# Palladium Nanoparticle-Decorated Porous Metal−Organic-Framework (Zr)@Guanidine: Novel Efficient Catalyst in Cross-Coupling (Suzuki, Heck, and Sonogashira) Reactions and Carbonylative Sonogashira under Mild Conditions

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**ABSTRACT:** A novel heterogeneous Zr-based metal−organic framework containing an amino group functionalized with nitrogen-rich organic ligand (guanidine), through a step-by-step post synthesis modification approach, was successfully modified by the stabilization of palladium metal nanoparticles on the prepared UiO-66-NH$_2$ support in order to synthesize the Suzuki−Murray, Mizoroki−Heck, and copper-free Sonogashira reactions and also the carbonylative Sonogashira reaction incorporating H$_2$O as a green solvent under mild conditions. This newly synthesized highly efficient and reusable UiO-66-NH$_2$@cyanuric chloride@guanidine/Pd-NPs reported catalyst has been utilized to increase anchoring palladium onto the substrate with the aim of altering the construction of the intended synthesis catalyst to form the C−C coupling derivatives. Several strategies, including X-ray diffraction, Fourier transform infrared, scanning electron microscopy, Brunauer−Emmett−Teller, transmission microscopy electron, thermogravimetric analysis, inductively coupled plasma, energy-dispersive X-ray, and elemental mapping analyzes, were used to indicate the successful preparation of the UiO-66-NH$_2$@cyanuric chloride@guanidine/Pd-NPs. In these reactions, the UiO-66-NH$_2$-supported Pd-NPs illustrated superior performances compared to their catalyst, revealing the benefits of providing nanocatalysts. As a result, the proposed catalyst is favorable in a green solvent, and also, the outputs are accomplished with good to excellent outputs. Furthermore, the suggested catalyst represented very good reusability with no remarkable loss in activity up nine sequential runs.
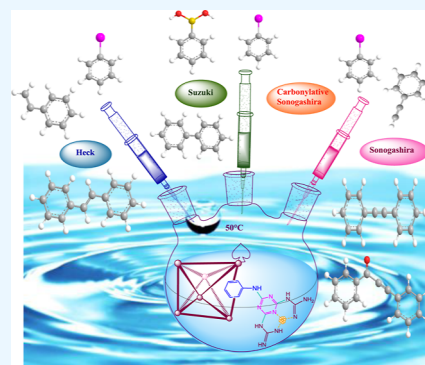
## ■ INTRODUCTION

The palladium-catalyzed cross-coupling reaction is a class of highly successful reactions which has played an essential role to synthesize a variety important chemical structures such as natural products, heterocycles structures, conjugated polymers, and organic complexes, recently.[1−5] Thus, great endeavors have been concentrated on the providing of heterogeneous catalysts upon transition metal palladium. The processes which perform carbon−carbon bond reactions via Pd catalysis have superiorities, namely, moderate circumstances, high resilience to functional groups, the economical profitability, durability of reactants, the accessibility convenience, and segregating outcomes from reaction mixtures conveniently.[6−9]

The cross-coupling process is appraised as one of the main challenges and most efficacious composite proprieties which is devoted to perform carbon−carbon bond reactions.[10−12] The C−C cross-coupling reaction catalysis is often preferred through the way of primary transition metal catalyzed conversions, and the palladium-catalyzed reaction has become the most effective way to prepare the carbon−carbon bond and presently suitable to progression in the construction of functional organic compounds.[13−18] Noteworthy, the synthetic organic chemistry

has been advanced throughout palladium-catalyzed cross-coupling reactions, namely, Suzuki−Miyaura,[19,20] Sonoga-shira−Mizorogi,[21] Heck, Negishi,[22] Silence,[23] Kumada,[24,25] Sonogashira,[26] and carbonylative Sonogashira reactions[27,28] evolved in recent years.[29−32] In this regard, cross-coupling reactions are explicitly devoted to the synthesis of assorted symmetric and asymmetric heteroaryl and biaryl, as critical building blocks to equip natural products, pharmaceuticals along with anti-diabetic, anti-hypertensive, antimycotic agent, disinfectant, tranquillizers, antiseptic agents, and antitumor drugs.[33−35]
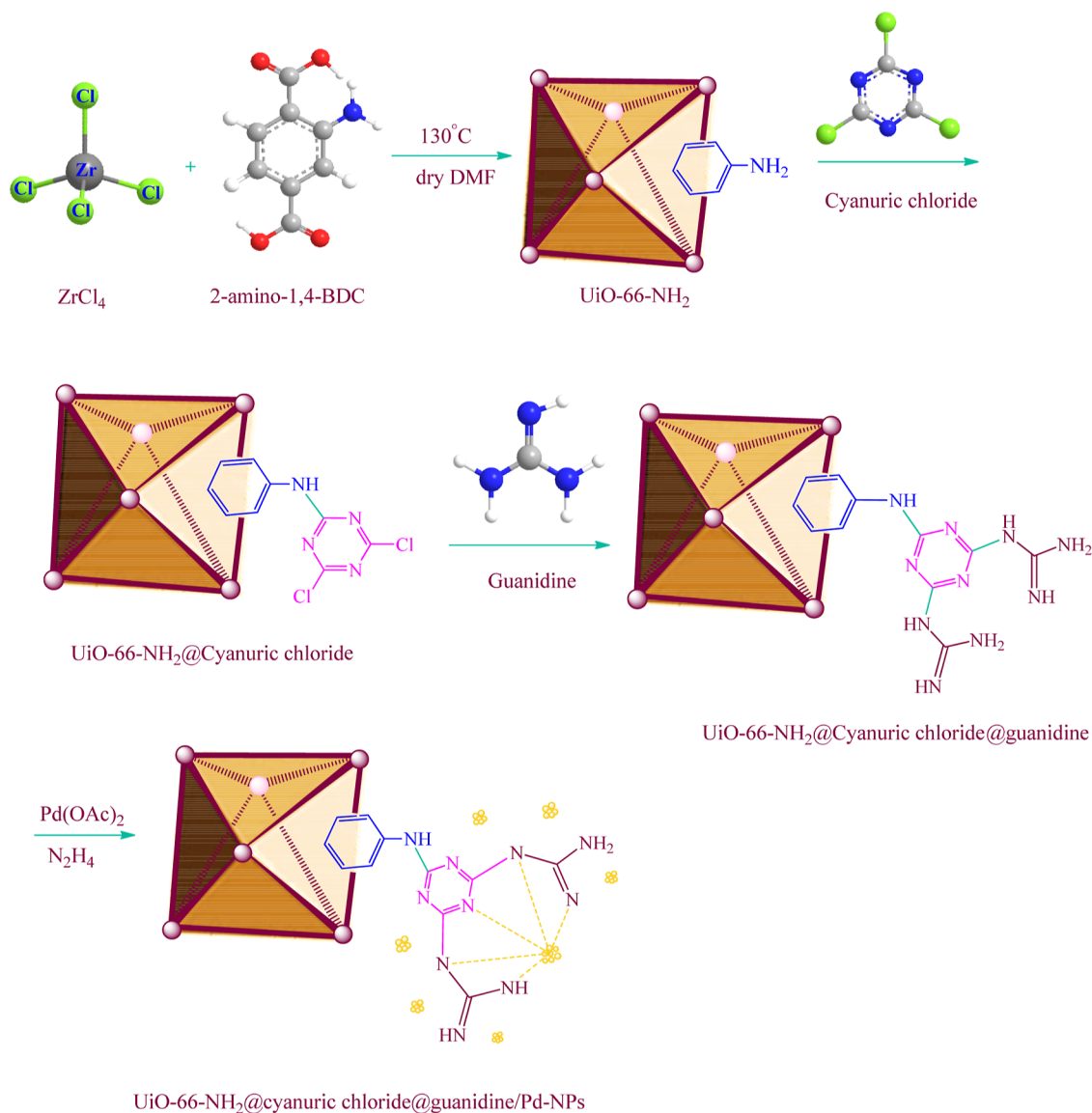
In recent decades, metal−organic frameworks (MOFs) have been noticed as the most distinguished supports in favor of immobilizing Pd nanoparticles (NPs), which is profitable to increase the interlinkage with Pd NPs.[36,37] MOFs have also

**Scheme 1. Graphitic Synthesis of UiO-66-NH$_2$@cyanuric Chloride@guanidine@Pd-NPs**



gained great attention in various fields of application specially in growth catalytic C−C coupling reactions by virtue of their distinctive properties as well as, extent surface area, highly ordered structure, adjustable pore size, uniformly dispensed metal nodes, and good modifiability.[38−40]

UiO-66-NH$_2$, a MOF emerged from Zr-terephthalate, which has remarkable chemical, thermal, mechanical stability, intrinsic open metal sites, large surface area, and presence of the amino group, is designated as a superior candidate for postfunctionalization.[41,42] Depending on the application, the organic linker like guanidine can support as a binding center to modify the electronic structure of UiO-66-NH$_2$.[43−46] In order to synthesize UiO-66-NH$_2$, the Zr$_6$ cluster, [Zr$_6$O$_4$(OH)$_4$] octahedral secondary building units (SBUs) have been coordinated to 2-amino-1,4-benzene dicarboxylic acid (BDC) in 1:12 unit ratio 3D and provided significant stability for the composition in aqueous environments.[43,47,48] Various utilizations of UiO-66 derivatives incorporated from post-stabilized metal ions or metal NPs after immobilization have been reported. Eventually, covalent functionalization with guanidine as a superb N-rich organic ligand, to generate amino moieties,

convinces us to appropriate it to immobilize palladium ions onto Zr-UiO-66-NH$_2$.[49,50]

Currently, we improved the structure of remarkable development UiO-66-NH$_2$ MOF functionalized throughout guanidine, a N-rich organic ligand, through a post synthesis modification (PSM) approach and has been accomplished as a support to heterogenize the Pd NPs to perform growing sorts of C−C coupling reactions of Suzuki (C−C), Heck, and copper-free Sonogashira coupling reactions in the presence of H$_2$O as a green solvent, and carbonylative Sonogashira reactions under mild conditions. The demonstrated catalyst illustrates heightened catalytic achievement as the outcome of the PSM, and the findings were recoverable up to nine cycles without a significant decrease. The prospect future of studies attributed to latest advances in the synthesis, catalytic effects, stability, and recovering circumstances of MOF-supported Pd-NPs is considered.

## ■ RESULTS AND DISCUSSION

As a follow-up to our efforts to develop facile and robust methodologies for growing diversified organic reactions, in this
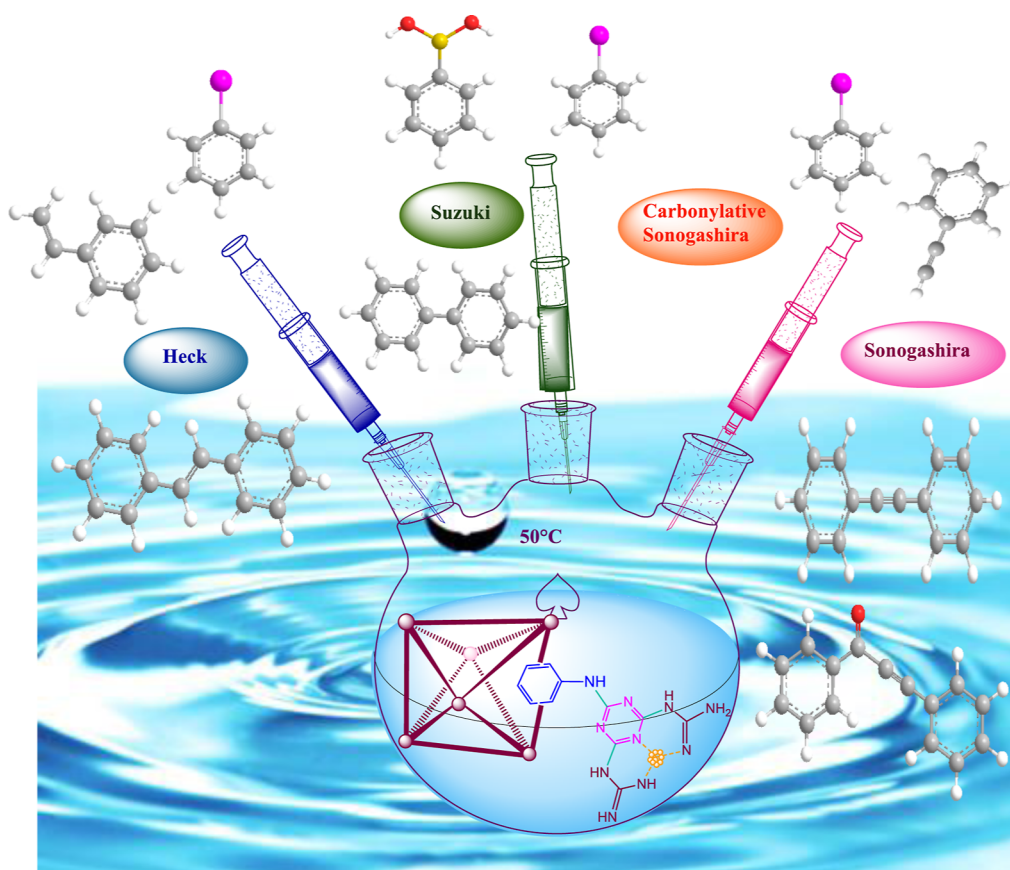
**Figure 1.** UiO-66-NH$_2$@cyanuric chloride@guanidine@Pd-NPs.

research, a highly productive and reusable palladium-based catalyst was introduced for the advancement of C−C coupling reactions. At the beginning, UiO-66-NH$_2$ was altered through N-rich organic ligands. The synthesized framework (UiO-66-NH$_2$) was functionalized by the virtue of the step-by-step PSM method by the cyanuric chloride and guanidine. After that, the synthesized UiO-66-NH$_2$@cyanuric chloride@guanidine was utilized as a support for the stabilization of the Pd-NPs (Scheme 1). Eventually, the produced UiO-66-NH$_2$@cyanuric chloride@ guanidine@Pd-NPs were synthesized as a remarkably efficient catalyst for developing the C−C coupling reaction (Figure 1).

**Fourier Transform Infrared Spectroscopy.** Figure 2 assigns the Fourier transform infrared (FT-IR) spectra of compounds of UiO-66-NH$_2$, UiO-66-NH$_2$@cyanuric chloride,
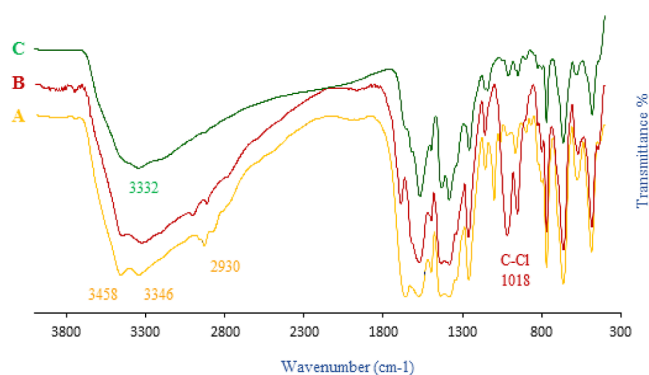
and UiO-66-NH$_2$@cyanuric chloride@guanidine. Therefore, the FT-IR spectra of bare UiO-66-NH$_2$ (Figure 2A) illustrates that the two peaks at 3350−3460 cm$^{-1}$ are relevant to the asymmetric and symmetric vibrational bands, regarding the free NH$_2$ groups. Also, stretching vibrations at 1259 and 1339 cm$^{-1}$ can be relevant to the carbon−nitrogen bonding of the H$_2$BDC-NH$_2$. The peak at 768 cm$^{-1}$ is relevant to the Zr−O stretching vibration. Hence, the modified UiO-66-NH$_2$ through cyanuric chloride represents less intensity for the broad peak of the NH$_2$ group at 3334−3442 cm$^{-1}$, mentioning less free and available uncoordinated NH$_2$. Additionally, another reason proving the presence of cyanuric chloride in the compound is a new sharp peak at 1018 cm$^{-1}$ (Figure 2B). At last, the disappearance of the same peak in the compound UiO-66-NH$_2$@cyanuric chloride@ guanidine would be the result of the bond coordination of guanidine to the cyanuric chloride (Figure 2C). Other characteristic peaks of various parts of the composite overlapped, and other characterization methods were utilized to indicate the performing of the catalyst.

**X-ray Diffraction.** All structures of UiO-66-NH$_2$, UiO-66-NH$_2$@cyanuric chloride, UiO-66-NH$_2$@cyanuric chloride@ guanidine, and UiO-66-NH$_2$@cyanuric chloride@guanidine/ Pd-NPs are attentively examined through the X-ray diffraction (XRD) technique (Figure 3). The XRD figure of raw UiO-66-NH$_2$ discloses the supposed characteristic which proves its crystallinity and successful synthesis (Figure 3A). The XRD figure of UiO-66-NH$_2$@Cyanuric chloride@guanidine demonstrates no distinct exchange compared to the bare MOF, which confirms the accomplishment crystallinity (Figure 3B). Evidently, all the synthesis processes of XRD diffraction patterns, subsequently at $2\theta$ = 7.4, 8.6 and 26.2°, indicate the



**Figure 2.** IR spectra of (A) UiO-66-NH$_2$, (B) UiO-66-NH$_2$@cyanuric chloride, and (C) UiO-66-NH$_2$@cyanuric chloride@guanidine.
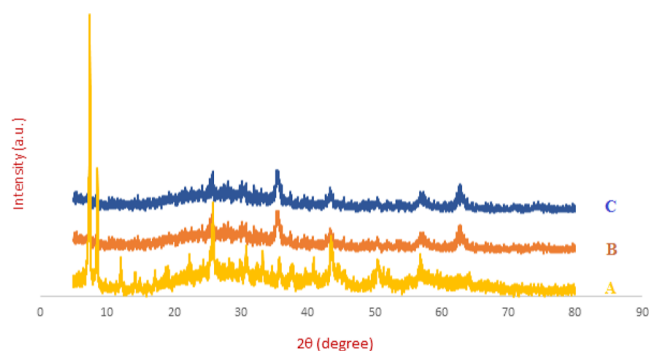
**Figure 3.** XRD spectra patterns of (A) UiO-66-NH₂, (B) UiO-66-NH₂@cyanuric chloride@guanidine, and (C) UiO-66-NH₂@cyanuric chloride@guanidine/Pd-NPs.

maintenance of the internal retention based upon PSM of UiO-66-NH$_2$.[35,51] The diffraction peaks relevant to UiO-66-NH$_2$@cyanuric chloride@guanidine@Pd-NPs correspond to standard Bragg reflections (111), (200), (220), and (311) of Pd-NPs (Figure 3C).[52] This spectrum also exhibits all the characteristics of UiO-66-NH$_2$, with a minor switch to $2\theta$ which is a natural consequence of the catalyst, indicating successful preservation of the MOF crystal structure during all synthesis steps.

**N$_2$ Adsorption−Desorption Experiment.** Figure 4 demonstrates Brunauer−Emmett−Teller (BET) analysis of the surface area of the samples. The N$_2$ adsorption−desorption experiment for raw and altered UiO-66-NH$_2$ at 77 K to ascertain and evaluate the surface area of the porosity of the MOF. The BET isotherm of the pure UiO-66-NH$_2$ indicates a sort of isotherm I (Figure 4C), which proposed the micro-porosity of its structure, with a surface area of 970 cm$^3$ g$^{−1}$. The BJH (Barrett, Joyner, and Halenda) plot of UiO-66-NH$_2$ proves the
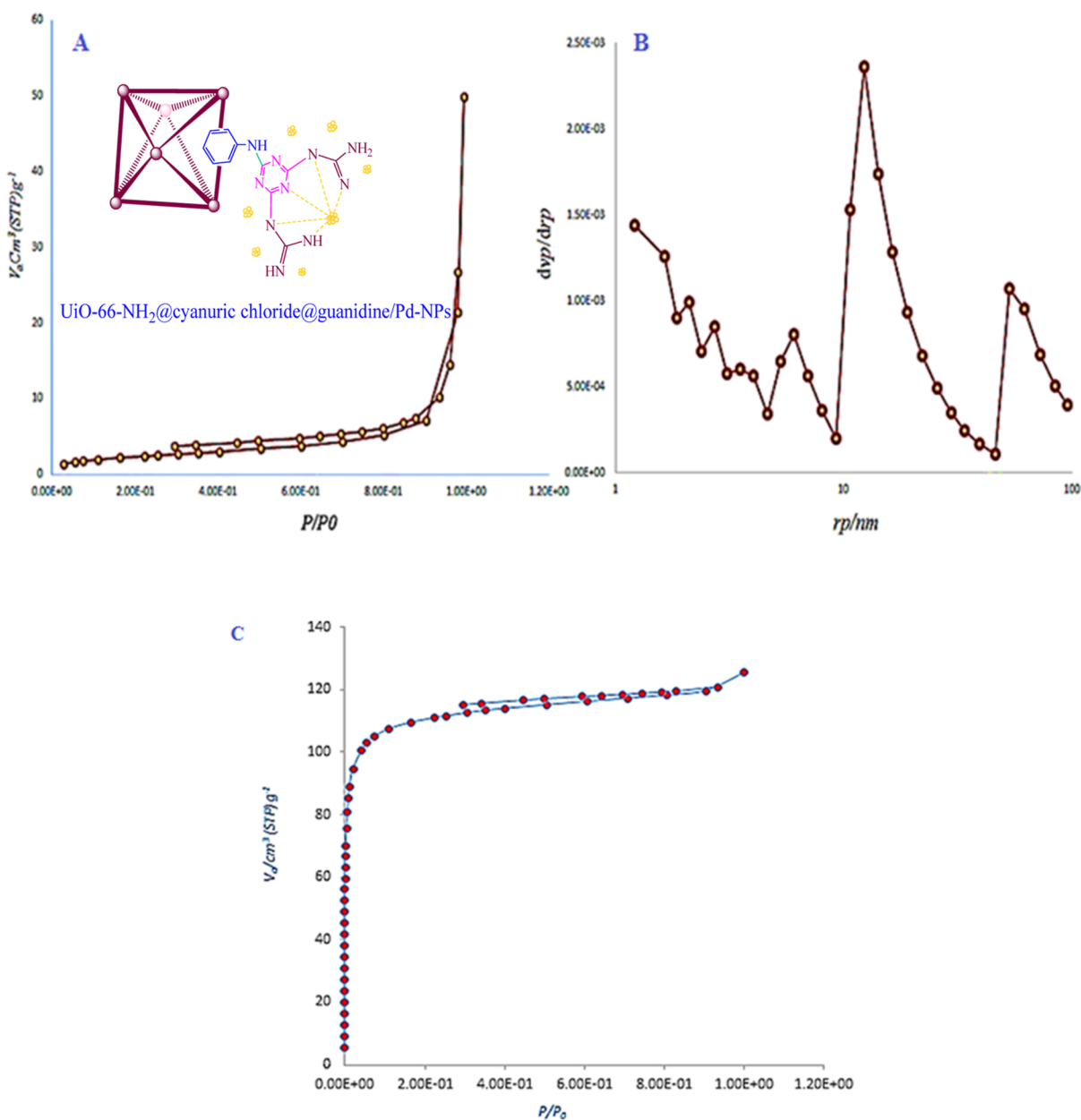


**Figure 4.** (A,B) BET and BJH of UiO-66-NH₂@cyanuric chloride@guanidine and (C) the BET of UiO-66-NH₂.

micro-porosity of the composite. This diagram displays just only one sort of micro-porosity in the raw MOF structure with a pore diameter of 1.49 nm. The modified MOF designates a dramatic decrease in the surface area from bare UiO-66-NH$_2$ 970 cm$^3$ g$^{-1}$ to UiO-66-NH$_2$@cyanuric chloride@guanidine@Pd-NPs 630 cm$^3$ g$^{-1}$ (Figure 4A,B). This is the outcome of the successful PMS of the MOF, in which cyanuric chloride and guanidine filled the pores of UiO-66-NH$_2$ and therefore its surface area was somewhat reduced (Figure 4A−C).

**Field Emission-Scanning Electron Microscopy and Transmission Microscopy Electron.** The construction of UiO-66-NH$_2$@cyanuric chloride@guanidine/Pd-NPs is considered through scanning electron microscopy (SEM) and transmission microscopy electron (TEM) approaches (Figure 5a−d). The figures of SEM illustrate the rough surface of UiO-
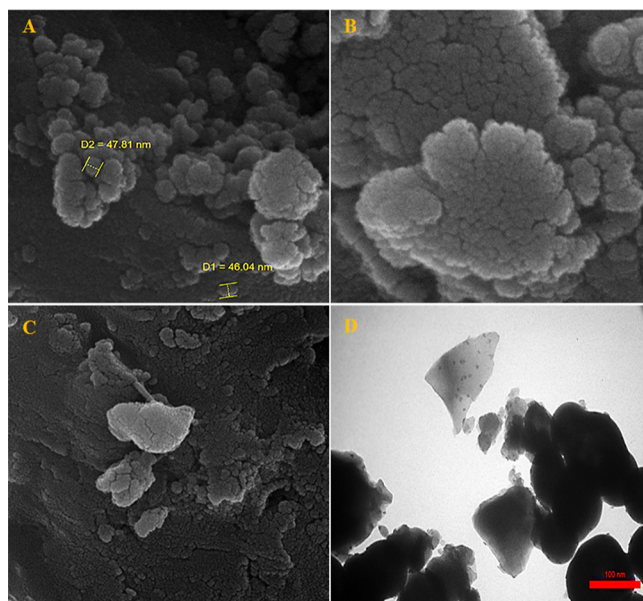


**Figure 5.** (A) SEM and (B−D) TEM images of UiO-66-NH$_2$@cyanuric chloride@guanidine/Pd-NPs.

66-NH$_2$ after the post-synthesis qualification procedure due to a natural consequence of the PSM and composition with the palladium NPs with an average diameter of approximately 46.04−47.81 nm (Figure 5a). The BET results indicate that the pores of the MOF are charged by virtue of the PSM; meanwhile, we tried to utilize the modified MOF surface as a support to load the palladium NPs. In this research, we employed hydrazine hydrate as a reductant, which caused to the bigger nanoparticles compared to other reductants such as NaBH$_4$ in the synthesized catalyst to immobilize Pd-NPs over the surface of modified MOF. TEM image shows the well-dispersed presence of Pd-NPs over the surface of modified UiO-66-NH$_2$ (Figure 5b−d).

Figure 6 represents the energy-dispersive X-ray (EDS)-mapping analysis, which consider the elemental composition and spatial distribution of elements in the final composite of the investigation (Figure 6 and inset images). SEM−EDS analysis corroborated the existence of Zr, O, N, C, and Pd in the composite of UiO-66-NH$_2$@cyanuric chloride@guanidine/Pd-NPs with 7.28 wt % loading of palladium NPs, and STEM-elemental mapping reveals uniform elemental dispersion in the proposed catalyst, verifying its successful formation (Figure 6a−f).
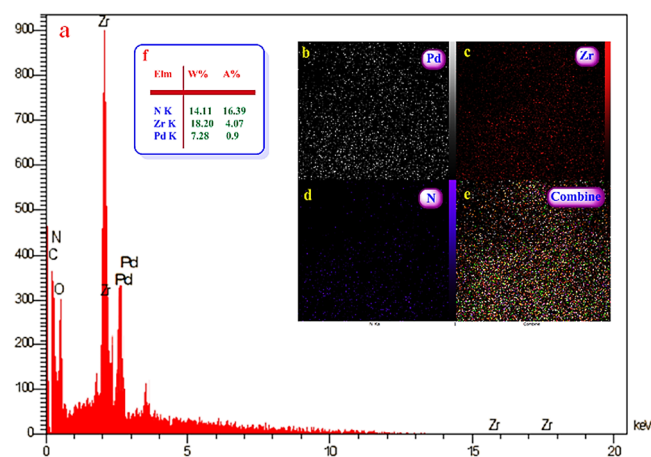


**Figure 6.** (a) EDS spectra of UiO-66-NH$_2$@cyanuric chloride@guanidine/Pd-NPs. EDS mapping of (b) zirconium, (c) nitrogen, and (d) palladium, and (e) combined (f) element percentage table from EDS.

**Thermogravimetric Analysis.** The thermogravimetric analysis (TGA) of UiO-66-NH$_2$ is illustrated in Figure 7. The
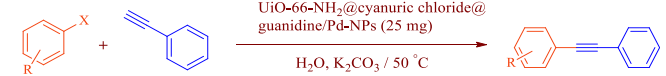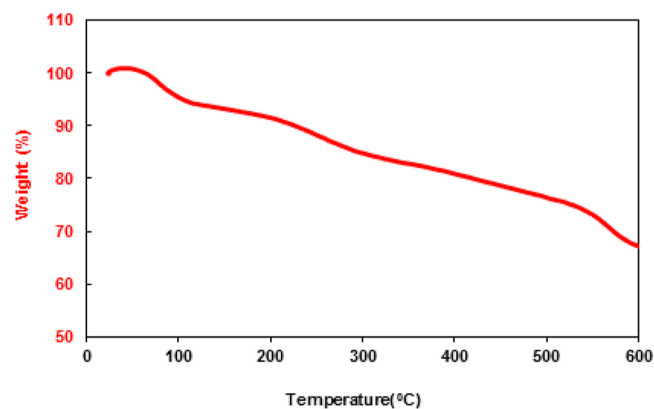


**Figure 7.** TGA of UiO-66-NH$_2$@cyanuric chloride@guanidine.

two-step weight loss was represented at the TGA. The first weight loss appears at 90 °C, which is related to the loss of adsorbed gas and coordinated hydroxyl groups to the zirconium cluster. The another step takes place at 550 °C, which is attributed to the devastation of the frameworks. The TGA curves of the UiO-66-NH$_2$@cyanuric chloride@guanidine show weight loss with the final residue of 92.15 and 74.02% correspondingly, emphasizing the higher thermal resistance of modified UiO-66-NH$_2$ (Figure 7).

**Catalytic Performance.** After successful identification of the suggested catalyst, the catalytic activities of UiO-66-NH$_2$@cyanuric chloride/guanidine/Pd-NPs were evaluated to perform various coupling reactions, including Suzuki, Heck, and copper-free Sonogashira in the presence of H$_2$O as a green solvent and carbonylative Sonogashira reaction under mild conditions. Subsequently, evaluation of the catalytic efficiency of the proposed catalyst was started to develop the Sonogashira reaction. The reaction among iodobenzene and phenylacetylene incorporated with UiO-66-NH$_2$@cyanuric chloride/guanidine/Pd-NPs is considered as the template reaction. In Table S1, the analysis's amount, temperature, time, and sort of solvents and base have been studied on reaction parameters. To determine the optimal solvent of the process, the Sonogashira-coupling

## Table 1. Fabrication of Diverse Desired Organic Compounds through Sonogashira Reaction under Optimum Circumstances[a]



| Entry | Arylhalide | Arylbronic acid | Product | Time (min) | Yield (%) | Entry | Arylhalide | Arylbronic acid | Product | Time (min) | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | 20 | 99 | 21 | | | | 20 | 79 |
| 2 | | | | 20 | 97 | 22 | | | | 20 | 87 |
| 3 | | | | 20 | 99 | 23 | | | | 20 | 93 |
| 4 | | | | 20 | 95 | 24 | | | | 20 | 93 |
| 5 | | | | 20 | 93 | 25 | | | | 20 | 63 |
| 6 | | | | 20 | 91 | 26 | | | | 20 | 92 |
| 7 | | | | 20 | 85 | 27 | | | | 20 | 61 |
| 8 | | | | 20 | 88 | 28 | | | | 20 | 72 |
| 9 | | | | 20 | 87 | 29 | | | | 20 | 96 |
| 10 | | | | 20 | 84 | 30 | | | | 20 | 98 |
| 11 | | | | 20 | 83 | 31 | | | | 20 | 99 |
| 12 | | | | 20 | 86 | 32 | | | | 20 | 88 |
| 13 | | | | 20 | 95 | 33 | | | | 20 | 82 |
| 14 | | | | 20 | 99 | 34 | | | | 20 | 82 |
| 15 | | | | 20 | 92 | | | | | | |
| 16 | | | | 20 | 90 | | | | | | |
| 17 | | | | 20 | 97 | | | | | | |
| 18 | | | | 20 | 88 | | | | | | |
| 19 | | | | 20 | 99 | | | | | | |
| 20 | | | | 20 | 85 | | | | | | |

[a]Reaction conditions: 1 mmol aryl halide, 1.2 mmol terminal alkynes, 2 mmol base, and 3 mL of solvent.

reaction as the template reaction in association with the recommended synthesized catalyst in diverse solvents, inclusive of dimethyl sulfoxide (DMSO), $CH_2Cl_2$, water, dimethylformamide (DMF), toluene, MeCN, 50% ethanol and water, ethanol, tetrahydrofuran, and NMP, was observed. The investigations

indicate that $H_2O$ gives the best satisfying outcome. The temperature was heightened to 80 °C, and the best outcome was observed at 50 °C. A further increase in the temperature did not boost the yield of the reaction. The reaction was achieved at 50 °C in $H_2O$ as a green solvent after 20 min employing the TLC

technique to detect the progress of the reaction. The optimal catalyst's amount was ascertained via discerning the development of the reaction in association with diverse amounts of the catalyst. The outcomes of the research demonstrated that 25 mg of the prepared catalyst is sufficient to progress the Sonogashira reaction. Consequently, as a pursuant to experiments, the best favorable outcome has been accomplished with 25 mg of UiO-66-NH$_2$@cyanuric chloride/guanidine/Pd-NPs catalyst at 50 °C with H$_2$O as solvent and K$_2$CO$_3$ as the base after 20 min. Also, the carbonylative Sonogashira reaction of iodobenzene, phenylacetylene, formic acid, acetic anhydride, base, ligand (10 mol %), and solvent was performed in the presence of the suggested catalyst. According to this study, using toluene as the solvent and the Et$_3$N as the base in the presence of 30 mg of UiO-66-NH$_2$@cyanuric chloride/guanidine/Pd-NPs as the proposed catalyst at 50 °C after 8 h is summarized in Table S2, which resulted in the best yield for the carbonylative Sonogashira reaction.

The optimization tests were also performed on the Heck and Suzuki reactions incorporated with the suggested catalyst. The results of these studies for the Heck and Suzuki interactions have been summarized in the Tables S3 and T4, subsequently. The reaction of iodobenzene and styrene was performed as the template reaction for the Heck reaction, and the reaction of iodobenzene and phenylboronic acid was selected as the template reaction for the Suzuki reaction. As specified by this research, utilizing H$_2$O as the solvent and the K$_2$CO$_3$ as the base in the presence of 30 mg of UiO-66-NH$_2$@cyanuric chloride/ guanidine/Pd-NPs as the catalyst at 50 °C after 120 min (2 h) was obtained with the highest output for the Heck reaction (Tables S3). The similarity experiments illustrate that the optimum condition for the advancement of the Suzuki reaction is 20 mg of catalyst in H$_2$O in the presence of K$_2$CO$_3$ at 50 °C and 40 min of reaction time (Table S4).

Having determined the optimal conditions, we carry out the generalizability of our suggested procedure throughout synthesizing various biphenyl derivatives from a variety of precursors. In this regard, diverse aryl halides and terminal alkyne reacted in the presence of the prepared catalyst under optimal circumstances (Table 1).

Therefore, the outputs in this table represents that in the presence of aryl halides, the reaction proceeds with high yields. This applies regardless of whether the aryl halides are ortho-substituted, meta-substituted, and para-substituted. As shown in the table below, the usage of diverse aliphatic halides has always resulted in higher quality products. The synthesized catalyst is highly efficient and widely applicable, which is demonstrated through its competence to catalyze the Sonogashira coupling process in the presence of iodine, bromine, and chlorine derivatives of aromatic compounds.

Also, the Sonogashira carbonylative reaction was performed in the presence of the proposed catalyst, and the outputs are shown in Table 2. We also performed a generalization analysis of the methods proposed by the virtue of Heck and Suzuki's responses, and the results are demonstrated in Tables 3 and 4, appropriately. This research demonstrated that UiO-66-NH$_2$@ cyanuric chloride/guanidine/Pd-NPs are really efficient catalysts to proceed this sort of reactions in good to excellent outputs; otherwise, the results of some products of the Sonogashira reaction were relatively lower.

**Proposed Mechanism.** The suggested mechanism for the Sonogashira cross-coupling reaction utilizing UiO-66-NH$_2$@ Cyanuric chloride@Guanidine@Pd-NPs catalysts, which corre-
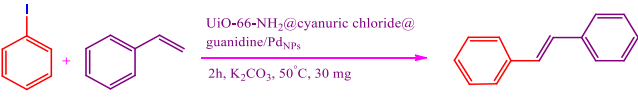
**Table 2. Fabrication of Diverse Desired Organic Compounds through Carbonylative Sonogashira Reaction under Optimum Circumstances[a]**
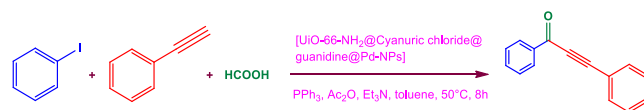


| Entry | Arylhalide | Arylbronic acid | Product | Time (h) | Yield (%) |
|---|---|---|---|---|---|
| 1 | | | | 8 | 96 |
| 2 | | | | 8 | 97 |
| 3 | | | | 8 | 94 |
| 4 | | | | 8 | 59 |
| 5 | | | | 8 | 61 |
| 6 | | | | 8 | 56 |
| 7 | | | | 8 | 79 |
| 8 | | | | 8 | 96 |
| 9 | | | | 8 | 98 |
| 10 | | | | 8 | 85 |
| 11 | | | | 8 | 91 |
| 12 | | | | 8 | 75 |
| 13 | | | | 8 | 84 |
| 14 | | | | 8 | 89 |

[a]Reaction Condition: aryl iodides (0.2 mmol), aryl acetylenes (0.4 mmol), proposed catalyst UiO-66-NH$_2$@Cyanuric chloride@Guanidine@Pd-NPs (30 mg), PPh$_3$ (10 mol %), Et$_3$N (3 mmol), HCOOH (2.0 mmol), acetic anhydride (Ac$_2$O) (2 mmol), toluene (2.0 mL), 50 °C, 8 h.

sponds to the mechanism of copper-free Sonogashira coupling reactions, is illustrated in Figure 8.[18] To begin with, the oxidative

## Table 3. Fabrication of Diverse Desired Organic Compounds through Heck Reaction under Optimum Circumstances[a]



| Entry | Aryl halide | Aryl boronic acid | Product | Time (h) | Yield (%) |
|---|---|---|---|---|---|
| 1 | | | | 2 | 98 |
| 2 | | | | 2 | 83 |
| 3 | | | | 2 | 70 |
| 4 | | | | 2 | 99 |
| 5 | | | | 2 | 93 |
| 6 | | | | 2 | 82 |
| 7 | | | | 2 | 98 |
| 8 | | | | 2 | 97 |
| 9 | | | | 2 | 92 |
| 10 | | | | 2 | 96 |
| 11 | | | | 2 | 93 |
| 12 | | | | 2 | 89 |
| 13 | | | | 2 | 96 |
| 14 | | | | 2 | 82 |
| 15 | | | | 2 | 84 |
| 16 | | | | 2 | 90 |
| 17 | | | | 2 | 87 |

[a]Reaction conditions: 1 mmol aryl halide, 1.1 mmol styrene, 2 mmol base, and 3 mL of solvent.

addition from aryl halide to the palladium catalyst was carried out. Subsequently, complex palladium acetylide III was produced from the coordination of terminal alkyne to the intermediate. Finally, the coupled production was provided by the reductive elimination of complex III along with the production of the Pd(0) to enter the next catalytic cycle (Figure 8).

The Sonogashira, Heck, Suzuki, and catalytic achievement of prepared catalyst, UiO-66-NH$_2$@cyanuric chloride/guanidine/Pd-NPs, are compared to other published catalysts in the literature in Tables 5−8. Based on these findings, our new synthesized catalyst has the most successful recorded findings, which can be a reason from meticulous post-synthesis alteration using the N-rich organic ligand to modify composite of the UiO-66-NH$_2$. The modified structure of the UiO-66-NH$_2$ has been altered throughout the incorporation of guanidine, which increases the catalytic capacity of the palladium NPs in the completed composite.

**Result of Experiment for the Heterogeneous Catalyst.** The reaction among 1 mmol iodobenzene and 1 mmol phenylboronic acid in the presence of UiO-66-NH$_2$@cyanuric chloride/guanidine/Pd-NPs is chosen as the template reaction in order to perform 99% production. Therefore, according to these considerations, the highest yields are attained in corporate with 20 mg of UiO-66-NH$_2$@cyanuric chloride/guanidine/Pd-NPs prepared catalyst in H$_2$O at 50 °C after 40 min. Also, the same test is recommended to confirm the heterogeneous nature of the catalyst. The reaction conditions were similar for the two reaction vessels. Halfway through the reaction time, the catalyst was removed from one of the reaction vessels and the reaction continued without a catalyst for 90 min. The rate of reaction and the rate of production of products were measured. The result of the reaction for container 1, until half of the reaction of both containers 1 and 2, and the product percentage was 50% of the product after 20 min. However, after 40 min, the container containing the catalyst had 99% product and the container from which the catalyst was separated, the product percentage was the same as 50% of the product and no more product was added.
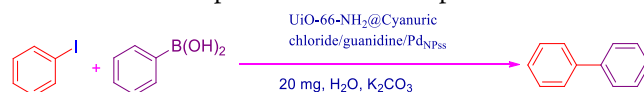


**Recyclability.** The renewability of the catalyst is one of the essential aspects of its usage, which caused the synthesized catalyst to allow multiple illustrated runs of the same reaction. Also, to evaluate the recovered quality of proposed catalyst, we filtered it from the reaction liquid and washed it several times with ethyl acetate. Therefore, our research team considered the validity and strength of the recovered catalyst for the copper-free Sonogashira, Heck, Suzuki, and carbonylative Sonogashira reactions over nine total cycles. As illustrated in Figure 9, there was no deterioration in the catalyst's achievement after three cycles; after nine cycles, it was still running 80−85% above its original usage level. The extraordinary renewable of the prepared catalyst can be attributed to the structural tolerance of UiO-66-NH$_2$ in aqueous environments. Additionally, the PSM of the UiO-66-NH$_2$ prohibits the availability of H$_2$O to the zirconium SBU through filling the pores of MOF and caused to proceed its durability.

As indicated in Figure 10, the SEM (A, B) and TEM (C, D) images of recycled catalyst compared with that of the fresh one confirmed that the catalyst will well-preserve the catalytic performance after nine runs of usage (Figure 10).

**Inductively Coupled Plasma−Optical Emission Spectroscopy Analysis Results.** As reported by the results of inductively coupled plasma−optical emission spectroscopy (ICP−OES) analysis, the Pd loading of the new catalyst was 0.91. It was mentioned that the ICP analysis of the recovered catalyst's activities to evaluate reused demonstrated a very slight decrease in palladium (Pd) leaching, less than 0.03%, after nine

**Table 4. Fabrication of Diverse Desired Organic Compounds through Suzuki Coupling Reaction under Optimum Circumstances[a]**



| Entry | Aryl halide | Aryl boronic acid | Product | Time (min) | Yield (%) | Entry | Aryl halide | Aryl boronic acid | Product | Time (min) | Yield (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | | 40 | 97 | 12 | | | | 40 | 99 |
| 2 | | | | 40 | 97 | 13 | | | | 40 | 76 |
| 3 | | | | 40 | 99 | 14 | | | | 40 | 95 |
| 4 | | | | 40 | 99 | 15 | | | | 40 | 90 |
| 5 | | | | 40 | 77 | 16 | | | | 40 | 98 |
| 6 | | | | 40 | 92 | 17 | | | | 40 | 96 |
| 7 | | | | 40 | 95 | 18 | | | | 40 | 98 |
| 8 | | | | 40 | 99 | 19 | | | | 40 | 97 |
| 9 | | | | 40 | 98 | 20 | | | | 40 | 95 |
| 10 | | | | 40 | 99 | 21 | | | | 40 | 94 |
| 11 | | | | 40 | 92 | | | | | | |

[a]Conditions for the chemical reaction: 1 mmol aryl halide, 1.1 mmol aryl boronic acid, 50 °C, $H_2O$, $K_2CO_3$.

runs of synthesized catalyst. In Table 9, the palladium load of the catalyst was determined by using ICP analysis.

## CONCLUSIONS

In this research, the UiO-66-NH$_2$ was settled as a support for the preparation of the heterogenization of the Pd NPs because of high activity for PSM, surface area, and inherent structural rebellious. PSM of the MOF was implemented using a gradient strategy, in which a series of N-rich organic compounds were coordinated to the NH$_2$ groups of the organic MOF bonds. The UiO-66-NH$_2$@cyanuric chloride/guanidine/Pd-N$_{Ps}$ was determined via FT-IR, XRD, BET, SEM, TGA, TEM, EDS, ICP, and elemental mapping analyzes, exhibiting its worthwhile construction. The proposed composite was employed to progress the sort of C−C coupling reactions, like the Suzuki, Heck, and copper-free Sonogashira, and carbonylative Sonogashira reaction under mild condition, which illustrated superior performance. Hence, due to the intrinsic resistance of the UiO-66-NH$_2$
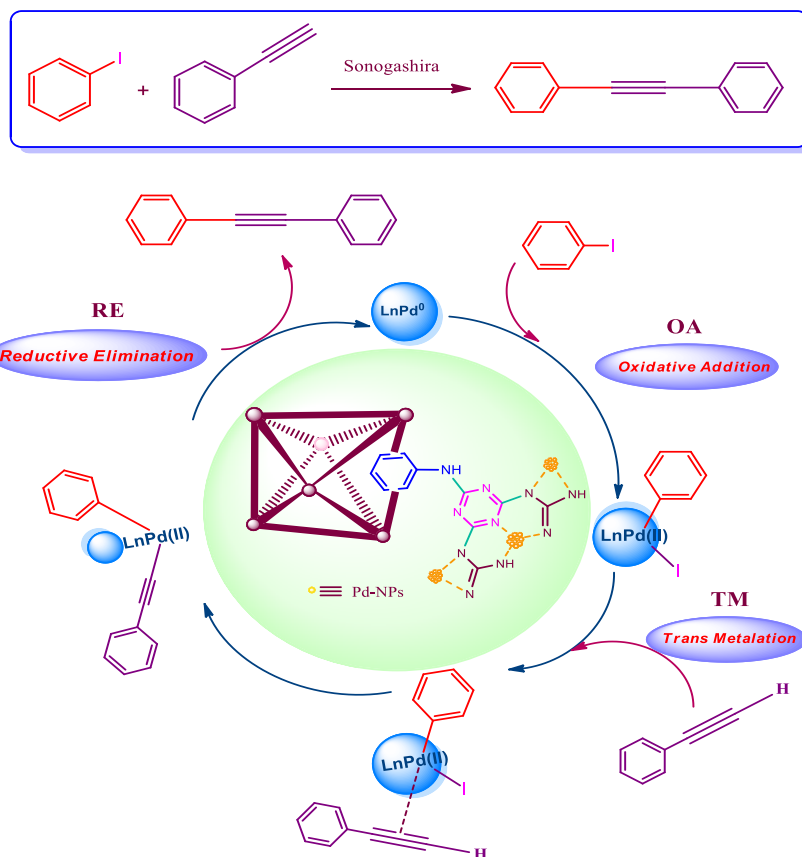
**Figure 8.** Plausible mechanism for the copper-free Sonogashira coupling reaction using UiO-66-NH$_2$@cyanuric chloride@guanidine@Pd-NPs.

**Table 5. Catalytic Activity of the Synthesized Catalyst in Order to Perform the Sonogashira Reaction in Comparison with Other Catalysts[a]**

| entrance | catalyst | yield (%) | time (min) | Pd (mmol g$^{-1}$) | leaching Pd (mmol g$^{-1}$) |
|---|---|---|---|---|---|
| 1 | UiO-66-NH$_2$@ cyanuric chloride@ guanidine@Pd-NPs | 99 | 20 | 0.085 | 0.009 |
| 2 | UiO-66-NH$_2$@ cyanuric chloride@ Pd-NPs | 85 | 20 | 0.079 | 0.02 |
| 3 | UiO-66-NH$_2$@Pd-NPs | 80 | 20 | 0.067 | 0.03 |

[a]Reaction conditions: 1 mmol of aryl halide, 1.1 mmol of terminal alkyne, 2 mmol of base, 3 mL of solvent.

MOF and the induced resistance generated by the virtue of the PSM, the proposed catalyst demonstrated excellent recycling performance. Additionally, the proposed catalyst can be reused up to nine runs. It should be noted that, in any case, the required catalyst was used under aqueous solvent conditions, and the Suzuki, Sonogashira, and Heck reactions were performed under very mild conditions.

## ■ EXPERIMENTAL SECTION

All the applied materials and reagents used in this study were purchased from Merck and Sigma-Aldrich companies and used without further purification.

**Synthesis of UiO-66-NH$_2$.** To synthesize UiO-66-NH$_2$, 65 mL of DMF was poured to a three-neck balloon, and then, 2.05 g of 2-amino-1,4-benzene terephthalic acid (H$_2$BDC-NH$_2$) was

added and stirred for 10 min at room temperature. After that, 2.65 g of ZrCl$_4$ and 55 mL of DMF were added to this solution. This mixture was charged with 2.5 mL of concentrated HCl as a modulator, and the obtained solution was stirred under reflux conditions at an argon atmosphere at 130 °C for 24 h. Ultimately, the yellow powder was separated from the reaction and washed with DMF and methanol three times. The obtained powder of MOF was activated by soaking the as-synthesized UiO-66-NH$_2$ in methanol for 3 days and drying under a vacuum at 60 °C.

**Synthesis of UiO-66-NH$_2$@cyanuric Chloride.** Alteration of the post-synthesis UiO-66-NH$_2$ was accomplished through the subsequent process. Initially, after dissolving 0.6 g of cyanuric chloride in 55 mL of dry DMSO at 32 °C, 1 g of pure UiO-66-NH$_2$ was added to the mixture and stirred for 29 h at 55 °C. For purification, the obtained solid was filtered and washed with DMSO two times.

**Synthesis of UiO-66-NH$_2$@cyanuric Chloride@guanidine.** In the following, the modification post synthesis of UiO-66-NH$_2$@cyanuric chloride has been furthermore performed by the virtue of guanidine. Next, 1 g synthesized UiO-66-NH$_2$@ cyanuric chloride was added to a balloon involving absolute ethanol (20 mL) and stirred about 12 min. To another beaker containing 20 mL of absolute ethanol, 1 g of guanidine was added and stirred until it was completely dissolved. Subsequently, the guanidine dissolved in ethanol, it was added to UiO-66-NH$_2$@cyanuric chloride and stirred for 24 h at 65 °C. Finally, after filtering and washing the precipitate with absolute ethanol, it was dried at 50 °C.

**Synthesis and Stabilization of Pd-NPs.** Initially, after dissolving 0.04 g of palladium acetate (Pd(OAc)$_2$) in 45 mL of

**Table 6. Catalytic Activity of the Synthesized Catalyst in Order to Perform the Sonogashira Reaction in Comparison with Some Related Reports in the Literature**

| entry | catalyst | reaction condition | time (min) | yield (%) | refs |
|---|---|---|---|---|---|
| 1 | Pd−B$_3$-Azo$_4$ (0.08 mol %) | PL-XQ 350 W, Xe lamp with 420 nm UV cut-off, $h\nu$ | 3 | 94 | 53 |
| 2 | (Pd$^{II}$−NHCs)$_n$@nSiO$_2$ (0.54 mol %) | Et$_3$N, H$_2$O, 90 °C | 0.15 | 92 | 54 |
| 3 | Pd(II)−acylthiourea complex | KO$^t$Bu, DMAc, 80 °C | 3 | 99 | 55 |
| 4 | Pd@PTC-POP (0.3 mol %) | Et$_3$N, H$_2$O, 100 °C | 2 | 99 | 56 |
| 5 | Pd-catalyst CuI/trimethylamine (5 mol %) | microwave, H$_2$O, 100 °C | 2 | 60 | 57 |
| 6 | Pd@CS/PEO (7.0 mol %) | DMF, glycol, K$_2$CO$_3$, 110 °C | 5 | 93 | 58 |
| 7 | Pd@ONO-IL (0.15 mol %) | piperidine, DMF, 70 °C | 2 | 94 | 59 |
| 8 | Pd-NPs/CENFs (0.06 mol %) | Na$_3$PO$_4$·12H$_2$O, i-PrOH, reflux | 3 | 88 | 60 |
| 9 | Pd-LHMS-3 (0.03 g) | DMF, hexamine, N2 atm, 120 °C | 14 | 80 | 61 |
| 10 | Pd(0)/MCoS-1 (0.02 g) | H$_2$O, Et$_3$N, 80 °C | 6 | 94 | 62 |
| 11 | Ru/Al$_2$O$_3$ (5 mol %) | CH$_3$CN, Et$_3$N, 90 °C | 24 | 85 | 63 |
| 12 | UiO-66-NH$_2$@cyanuric chloride@guanidine@Pd-NPs | K$_2$CO$_3$, H$_2$O, 50 °C | 20 | 99 | this research |

**Table 7. Catalytic Activity of the Synthesized Catalyst in Order to Perform the Heck Reaction in Comparison with Some Related Reports in the Literature**
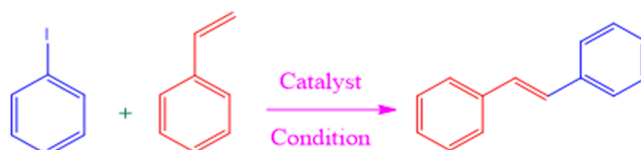
| entry | catalyst | reaction condition | time (h) | yield (%) | refs |
|---|---|---|---|---|---|
| 1 | GA-FSNP@Pd (0.47) | DMF/H$_2$O (2:1), Cs$_2$CO$_3$, 110 °C | 0.5 | 95 | 64 |
| 2 | Pd-biomagnetic (5) | DMF, TEA, 120 °C | 3 | 100 | 65 |
| 3 | Pd/N-MCNPs | DMAN, TEA, 120 °C | 3 | 97.6 | 66 |
| 4 | SBA-TMG-Pd (0.05) | solvent-free, Net$_3$, 140 °C | 4 | 90 | 67 |
| 5 | Fe$_3$O$_4$@PUNP−Pd (0.1) | H$_2$O, K$_2$CO$_3$, reflux | 12 | trace | 68 |
| 6 | Pd/graphene oxide (0.54) | toluene, NEt$_3$, reflux | 5 | 62 | 69 |
| 7 | Pd/MCPPY | DMA, TBA, 120 °C | 3 | 97 | 70 |
| 8 | Pd/HCN (0.255) | DMF, K$_2$CO$_3$, 120 °C | 1 | 100 | 71 |
| 9 | Pd/Fe$_3$O$_4$@C (0.308) | DMF, K$_2$CO$_3$, 120 °C | 2 | 66 | 72 |
| 10 | PdNs-PAMAM-g-MWCNTs (0.3) | NMP, K$_2$CO$_3$, 100 °C | 2.5 | 95 | 73 |
| 11 | Pd-MNPSS (0.36) | K$_2$CO$_3$, H$_2$O, 100 °C | 4 | 90 | 74 |
| 12 | PdCl$_2$ (1.5), TDTAT (3 wt %) | K$_2$CO$_3$, H$_2$O, 80 °C | 6 | 96 | 75 |
| 13 | hydrogel@Pd NPs | K$_2$CO$_3$, H$_2$O,85 °C | 0/5 | 98 | 76 |
| 14 | h-BN@Sal@Pd(OAc)$_2$ (0.05 mol) | H$_2$O, 90 °C | 3.5 | 92 | 77 |
| 15 | PdL$_n$@β-CD (3) | K$_2$CO$_3$, H$_2$O, reflux | 4 | 94 | 78 |
| 16 | Pd-MPTA-1 (10 mg) | K$_2$CO$_3$, H$_2$O, 100 °C | 6 | 92 | 79 |
| 17 | Pd@CSP (0.5), TBAB | NEt$_3$, H$_2$O, reflux | 7 | 90 | 80 |
| 18 | UiO-66-NH$_2$@cyanuric chloride@guanidine@Pd-NPs | K$_2$CO$_3$, H$_2$O, 60 °C, 2 h | 2 | 98 | this research |

acetonitrile at r.t., the next step, 0.2 g of the synthesized UiO-66-NH$_2$@cyanuric chloride@guanidine was added to the balloon involving a clear, amber-colored solution of palladium acetate in acetonitrile and continued stirring at 40−45 °C for 8 h. After that, the temperature was reduced to room temperature and 0.3 mL of the freshly prepared hydrazine hydrate solution (three drops of hydrazine hydrate dissolved in 3 mL of deionized water) was added to the reaction mixture and stirring was maintained at room temperature for 24 more hours. Ultimately, the reaction mixture was separated through a centrifuge at 9000 rpm, washed once with acetonitrile, and dried in the oven.

**General Procedure for the Sonogashira Reaction.** Occasionally, acetylene (1.2 mmol) and halo benzene (1 mmol) were mixed in distilled water (3 mL) in a balloon. After that, synthesized UiO-66-NH$_2$@cyanuric chloride/guanidine/

Pd-NPs catalyst (25 mg) and in addition K$_2$CO$_3$ (2 mmol) were poured to the balloon, and the temperature was raised to 50 °C and continued stirring for suitable time (Table 1). The progress of the reaction was monitored by the virtue of TLC usage an n-Hex/EtOAc 8:1 solvent ratio. After each reaction was completed, the filtration, washing with ethanol and drying of catalyst at 60 °C were performed. The filtered solution was cooled to ambient temperature, so to obtain its desired organic content, it was extracted with pure diethyl ether (Et$_2$O). Additionally, having purified the outcomes using column chromatography, the solvent ratio was n-hexane/ethyl acetate = 9:1. In order to identify the products, we utilized FT-IR, NMR, and physical data (melting point) (Supporting Information).

**General Procedure for the Carbonylative Sonogashira Reaction.** General procedure was carried out in the presence of

**Table 8. Catalytic Activity of the Synthesized Catalyst in Order to Perform the Suzuki Reaction in Comparison with Some Related Reports in the Literature**

| entry | catalyst | reaction condition | yield (%) | time (h) | refs |
|---|---|---|---|---|---|
| 1 | Pd@Mag-MSN (1) | $K_2CO_3$, $CH_2Cl_2$, 80 °C | 85 | 6 | 81 |
| 2 | xerogel g1-MNPs (1) | $Na_2CO_3$, $CH_3OH$, 60 °C | 99 | 2 | 82 |
| 3 | Pd/$NiFe_2O_4$ (0.1) | $Na_2CO_3$, DMF, 90 °C | 50 | 2 | 83 |
| 4 | Pd–$Fe_3O_4$ (1) | $K_2CO_3$, DME/$H_2O$ 3:1, reflux | 71 | 24 | 84 |
| 5 | C/Co@PNIPAM-$PPh_2$-Pd (3) | $K_2CO_3$, toluene/$H_2O$ 2:1, 85 °C | 99 | 16 | 85 |
| 6 | Co@C@Pd (1.1) | $Na_2CO_3$, THF/$H_2O$ 1:2, 65 °C | 96 | 2 | 86 |
| 7 | Pd/$Fe_3O_4$@C (0.3) | $K_2CO_3$, EtOH, reflux | 100 | 1 | 87 |
| 8 | Pd@$Fe_3O_4$ (0.816) | $K_3PO_4$, $CH_3OH$, 40–65 °C | 90 | 18 | 88 |
| 9 | $Fe_3O_4$@PUNP[a]-Pd(0.1) | $K_2CO_3$, $H_2O$, 90 °C | 98 | 1 | 68 |
| 10 | GA-FSNP@Pd (0.28) | $K_2CO_3$, solvent free, 90 °C | 92 | 0.25 | 64 |
| 11 | Pd-IPG (0.1) | NaOH, EtOH/$H_2O$, 60 °C | 99 | 1 | 89 |
| 12 | GO/NHC–Pd (1) | $Na_3PO_4\cdot12H_2O$, $H_2O$, 100 °C | 91.6 | 6 | 90 |
| 13 | Pd NPs on polymer (0.08) | $K_2CO_3$, $H_2O$, 25–100 °C | 83 | 5 | 91 |
| 14 | Pd-HoMOF(0.4) | KOH, DMF, 100 °C | 99 | 1 | 92 |
| 15 | $(Pd(II)–NHCs)_n@nSiO_2$ (0.27) | $K_2CO_3$, DMF/$H_2O$ (2:1), 60 °C | 97 | 6 min | 93 |
| 16 | Pd(II)–$NiFe_2O_4$ (0.5) | $K_2CO_3$, EtOH/$H_2O$, 80 °C | 96 | 3 | 83 |
| 17 | GO-CPTMS@Pd-TKHPP (10) | $K_2CO_3$, EtOH/$H_2O$, 80 °C | 99 | 15 min | 94 |
| 18 | UiO-66-$NH_2$@cyanuric chloride@guanidine@Pd-NPs | $H_2O$, $K_2CO_3$, 60 °C | 99 | 60 min | this study |
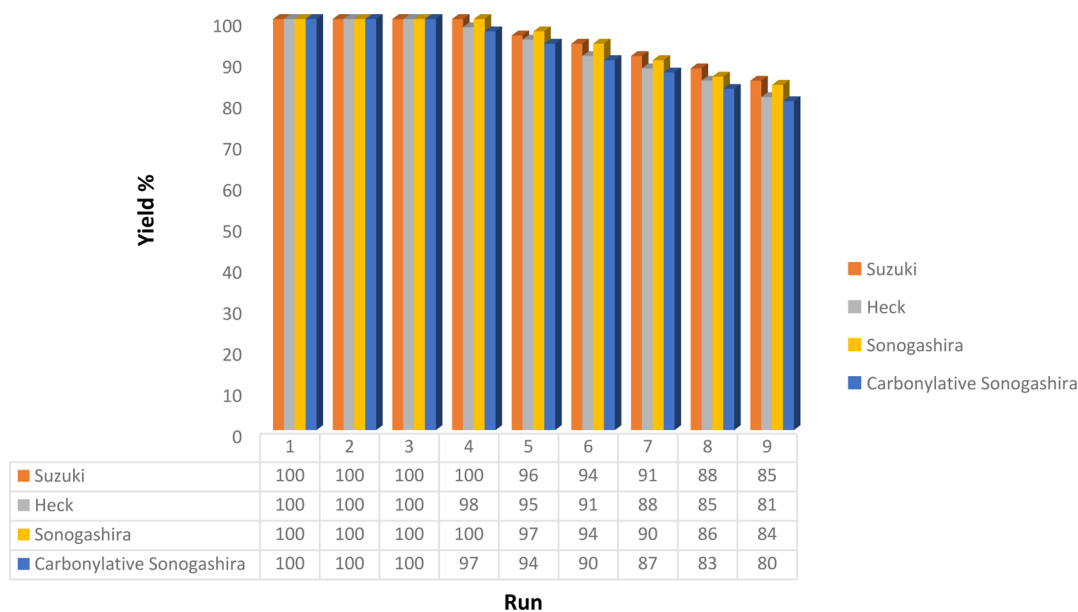


**Figure 9.** Recyclability of the UiO-66-$NH_2$@cyanuric chloride@guanidine@Pd-NPs catalyst.

UiO-66-$NH_2$@cyanuric chloride@guanidine@Pd-NPs (30 mg) and $PPh_3$ (10 mol %), were charged to a desiccant tube (15 mL), which was placed under vacuum and refilled several times with nitrogen. Toluene (2.0 mL), $Et_3N$ (1.0 mmol), alkyne (0.4 mmol), and aryl iodide (0.2 mmol) were added to the dried tube via a syringe, and acetic anhydride format (2.0 mmol) with $Et_3N$ (2.0 mmol) were charged to the 1.5 mL vial. After that, the tube was closed under stirring circumstances at 50 °C about 8 h (Table 2). After completion of the reaction, the reaction mixture was filtered and concentrated under vacuum at 55 °C. Ultimately, to achieve the alkynone product, the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 95/5, volume ratio).

**General Procedure for the Heck Reaction.** In a convenient balloon (10 mL), aryl halide (1 mmol), olefin (1.1 mmol), $K_2CO_3$ (2 mmol), distilled water (3 mL), and novel synthesized UiO-66-$NH_2$@cyanuric chloride/guanidine/Pd-

NPs catalyst (30 mg) were poured at 50 °C (Table 3). At the end of the reaction process, the mixture was centrifuged to separate the catalyst. After cooling the resulting mixture, the products were extracted using ethyl acetate. Having evaporated the organic solvent, it was dried using $MgSO_4$. Eventually, to obtain the products, the crude products were purified through column chromatography on silica gel (n-hexane/ethyl acetate = 9/1). In order to recognize the products, the FT-IR, NMR, and physical data (melting point) was utilized for identification (Supporting Information).

**General Procedure for the Suzuki Reaction.** Occasionally, aryl halide (1 mmol) and aryl boronic acid (1.1 mmol) were mixed in distilled $H_2O$ (3 mL) in a balloon (10 mL). To this mixture, synthesized UiO-66-$NH_2$@cyanuric chloride/guanidine/Pd-NPs catalyst (20 mg) and $K_2CO_3$ (2 mmol) were added and agitated. Also, the appropriate temperature was at 50 °C and for an appropriate time (Table 4). Also, having
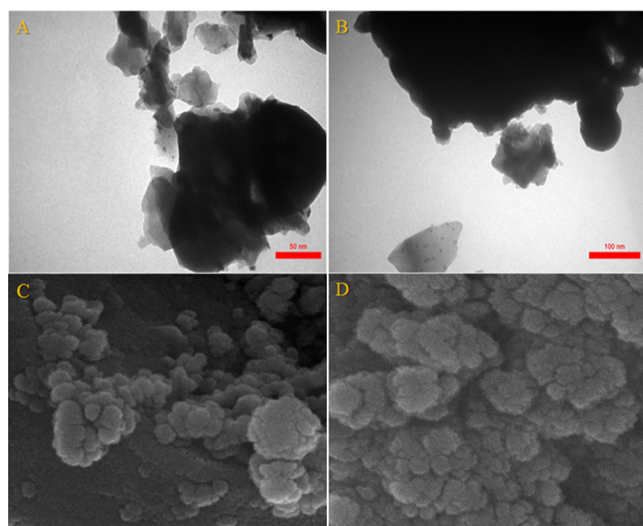
**Figure 10.** (A,B) SEM image of the recycled catalyst and (C,D) TEM image of recycled catalyst UiO-66-NH$_2$@cyanuric chloride@guanidine/Pd-NPs.

**Table 9. Loading of Palladium**

| entrance | catalyst | (mol %) Pd |
|---|---|---|
| 1 | order 1 | 0.91 |
| 2 | order 2 | 0.9 |
| 3 | order 3 | 0.87 |
| 4 | order 4 | 0.82 |
| 5 | order 5 | 0.79 |
| 6 | order 6 | 0.77 |
| 7 | order 7 | 0.72 |
| 8 | order 8 | 0.7 |
| 9 | order 9 | 0.68 |

monitored the progress of the reaction through TLC was performed with the solvent ratio (*n*-Hex/EtOAc 7:3). After completion of each reaction, at the end of each reaction, the catalyst was filtered, and the mixture was cooled to 25 °C, and the organic phase was extracted with diethyl acetate. Then, it was dried over magnesium sulfate (MgSO$_4$). Afterward, the organic solvent was attained through separation and filtration MgSO$_4$. Eventually, to obtain the products, the crude products were purified through column chromatography on silica gel (*n*-hexane/ethyl acetate = 9/1). In order to recognize the products, the FT-IR, NMR, and physical data (melting point) were utilized for identification (Supporting Information).

## ASSOCIATED CONTENT

### ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c01179.

Tables and spectrums related to Suzuki derivatives, Heck derivatives, and Sonogashira derivatives (PDF)

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### Author Contributions

L.M. synthesized the novel synthesized catalyst UiO-66-NH$_2$@Cyanuric chloride@guanidine/Pd-NPs and synthesized and identified the C−C coupling reaction and carbonylative Sonogashira desired. L.M. wrote and collected the manuscript, and M.R.V. edited the manuscript.

### Notes

The authors declare no competing financial interest.
All data generated or analyzed during this study are included in this published article (and its Supporting Information files).

## ■ ACKNOWLEDGMENTS

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