

Aromatic N-arylations catalyzed by heterometallic (Cu^{II}-Ba^{II}) metal–organic framework under heterogeneous base-free conditions in ethanol

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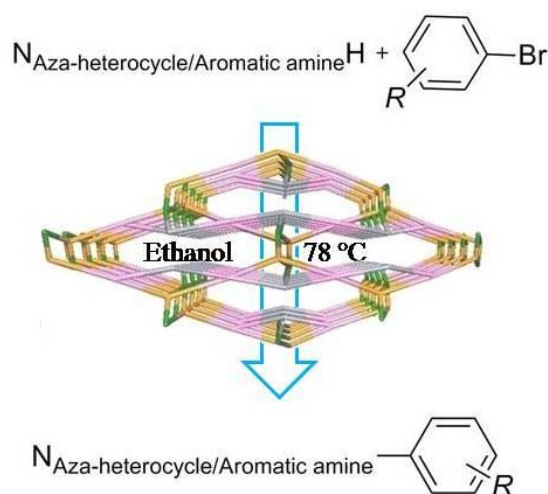
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Abstract

In this study, we report the hydrothermal synthesis of a ready-to-use three-dimensional copper- and barium-containing heterometallic carboxylate framework that features accessible pre-existing coordinatively unsaturated sites (CUS), eliminating the need for activation. It demonstrates excellent heterogeneous catalytic activity in the N-arylation reaction of nitrogen-containing heterocycles with aryl bromides in ethanol at 78 °C, without the need for any external base. In this framework, copper serves as the active center for the catalytic reaction, while barium acts as a Lewis base. This is the first report of a C–N cross-coupling reaction conducted in ethanol without the addition of an external base.



Keywords: N-Arylation, metal-organic framework, heterogeneous Catalysis

Introduction

The synthesis of nitrogen-containing compounds has been a focal point of recent research due to their widespread applications across various fields. Among these compounds, N-arylazoles are particularly noteworthy. They serve crucial roles as enzyme inhibitors and ATP binding inhibitors. Additionally, N-arylazoles are integral to the development of biologically active compounds, pharmaceuticals, agrochemicals and electronic materials.¹⁻⁷ Traditionally, these compounds have been synthesized through nucleophilic aromatic substitution (S_NAr) of N-H-containing π -electron-rich nitrogen heterocycles with aryl halides or by classical Ullmann-type coupling at very high temperatures.⁸⁻⁹ Consequently, transition-metal-catalyzed arylation of nitrogen-containing heterocycles has emerged as a highly efficient and powerful method for synthesizing N-arylazole derivatives.¹⁰⁻¹² However, current methods often rely on costly catalysts, such as palladium and rhodium complexes, for these coupling reactions. Despite its satisfactory performance, the palladium catalyst has several limitations, including high cost, toxicity, and low abundance.

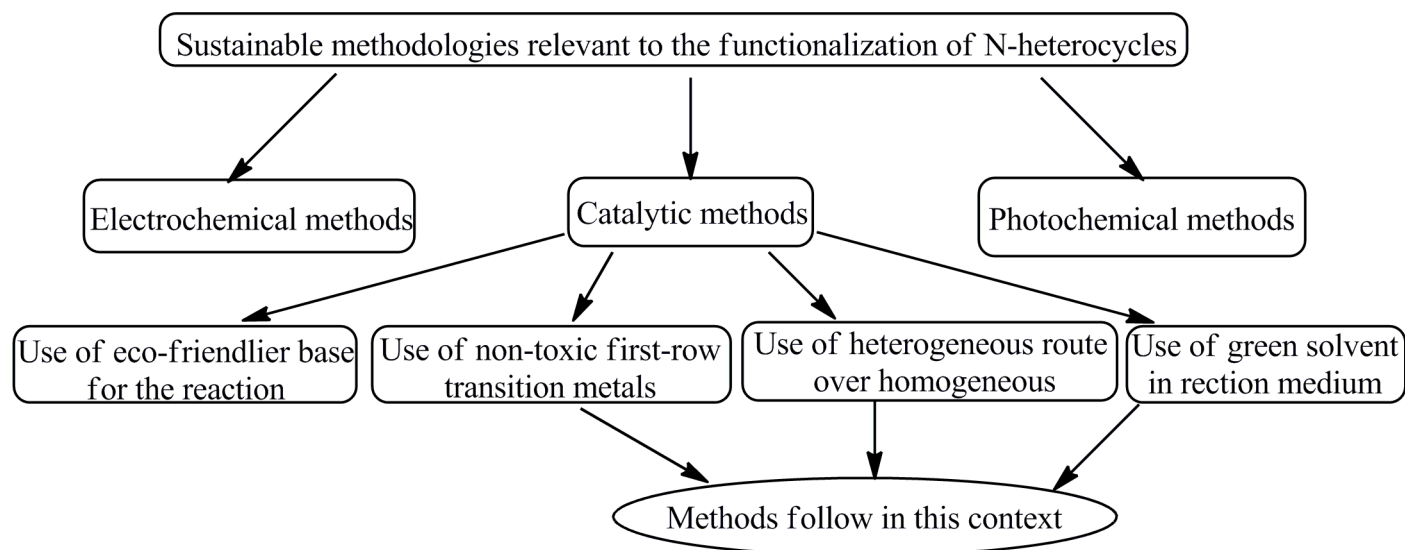


Figure 1. Current state of the art for sustainable methodologies to the functionalization of N-heterocycles.

These drawbacks highlight the need for sustainable and cost-effective alternatives (Figure 1), thereby driving the development of catalysts based on first-row transition metals such as copper, iron, cobalt, and nickel.¹³ Among these, copper-based catalysts have been reported to be versatile and highly productive for $C(sp^2)$ -heteroatom cross-coupling reactions because they can replicate the electronic and coordination properties of N-heterocyclic copper coordination complexes in catalysis.¹⁴⁻¹⁶ On the other hand, most of the catalytic systems reported to date rely on homogeneous processes, which present challenges in catalyst separation and reusability. Consequently, there is a need to develop heterogeneous catalytic systems to address these issues. Xie *et al.* demonstrated that Cu-containing metal-organic framework (MOF) MOF-199 can be employed for Ullmann-type coupling reactions, resulting in target products with yields ranging from moderate to excellent.¹⁷ Phan *et al.* found that the $[Cu(INA)_2]$ MOF showed enhanced catalytic performance for N-arylation reactions, outperforming both standard homogeneous copper catalysts and other Cu-MOFs.¹⁸ Punniyamurthy *et al.* reported that CuO nanoparticles were effective in facilitating a wide range of substrates for C–N cross-coupling reactions involving aryl halides.¹⁹⁻²⁰ Koner *et al.* developed an efficient heterogeneous catalyst for C–N cross-coupling reactions by incorporating a Cu(II) Schiff-base moiety into a porous isorecticular

metal-organic framework (IRMOF-3) using a post-synthetic modification approach.²¹ Pariyar *et al.* reported on the synthesis and characterization of a Cu-1D MOF that features pre-existing CUS, eliminating the need for activation prior to use.²² The presence of these unsaturated sites contributes to the multifunctional catalytic properties of Cu-1D chain, which were showcased through its effectiveness in cross-coupling reactions to form C–X bonds (where X represents N, S, or O) as well as in aziridination reactions. Moreover, an increasing number of reports highlights the direct application of MOFs in coupling reactions.^{23–26} Additionally, MOF-derived porous carbon nanocrystals (NCs) have been noted for their exceptional performance in Ullmann-type C–N cross-coupling reactions.²⁷

Research in coordination chemistry has now reached a high level of sophistication and has considerably matured. Metal-organic frameworks (MOFs) are one such where one can tune their structure by judicious choice of metal salt and ligand in a controlled manner.^{28–37} Several such interesting systems have been reported in the past decade. Koner *et al.* explored the design of a series of heterometallic frameworks by connecting copper-based low-dimensional networks (e.g., 0D or 1D) with alkaline-earth metals, resulting in 2D frameworks that can be further extended to 3D networks using the same carboxylate ligands.³⁸ In their work, Koner *et al.* demonstrated that these frameworks act as multifunctional catalysts. Copper serves as the active center for the epoxidation of olefins, while alkaline-earth metals facilitate the subsequent ring-opening of epoxides, leading to the formation of vicinal diols. They observed that increasing the size of the alkaline-earth metals accelerated the diol formation rate due to the easily accessible metal sites. Further exploration of those compounds in C–N cross-coupling reactions results in the copper-barium carboxylate framework i.e. $[\text{CuBa}(\text{pdc})_2(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}$ (**1**) (where H_2Pdc = pyridine-2,5-dicarboxylic acid) is highly effective for C–N cross-coupling reactions involving various azoles and substituted aryl bromides in ethanol without requiring an external base and that a framework containing accessible pre-existing coordinatively unsaturated copper sites which does not need any prior activation.

Results and Discussion

Compound **1** features a three-dimensional framework built from pentacoordinated Cu(II) centers of a CuO_3N_2 unit. These Cu(II) centers are linked to nonacoordinated pentaqua Ba(II) centers of a BaO_9 unit (Figure 2a). ORTEP diagram of compound **1** is given in Figure S1 of supplementary file. In compound **1**, the carboxylate ligand exhibits two distinct types of connectivity. In one mode, the ligand binds to two Cu centers and two Ba centers via four carboxylate O atoms and one N atom. In the other mode, the ligand connects to one Cu center and two Ba centers through three carboxylate O atoms and one N atom. The network structure in compound **1** is readily visualized: the four corners of the basal plane of an octahedron are occupied by Ba centers, while the two axial positions are occupied by Cu centers. The corners are linked by two pairs of carboxylate ligands with different connectivities (Figure 2a). Topological analysis on compound **1** revealed that this compound is 4-nodal 3D net with the Schläfli symbol $\{4.8^2\}_2\{4^2.8^2.10^2\}\{4^2.8^4\}$ consisting of Cu centers, two types of pdc^{2-} ligands, and Ba centers as three, three, four, and four-coordinated nodes; respectively (Figure 2b).

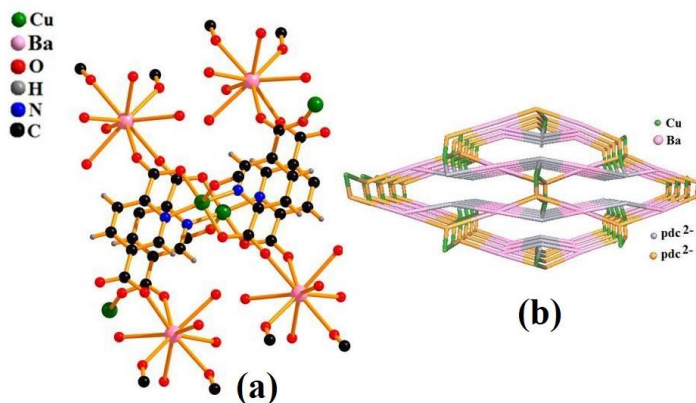
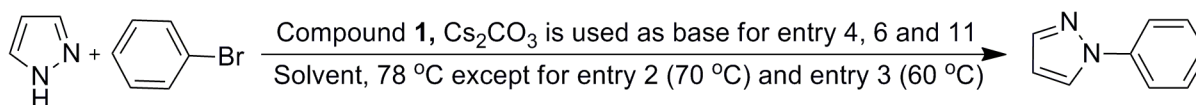


Figure 2. (a) Network connectivity in compound **1**. (b) 3D Topological view of compound **1**.

The optimization of catalytic activity for compound **1** in C–N cross-coupling reactions using pyrazole and phenyl bromide was systematically studied under varying conditions, as summarized in Table 1. The results showed that solvents, bases, and temperature significantly impact the reactivity of the catalyst.

Table 1. Optimization of reaction conditions for N-arylation of pyrazole with bromobenzene



Entry ^a	Catalyst	Base	Solvent	Yield ^b (%)
1	Compound 1	–	Ethanol	78
2	Compound 1	–	Ethanol	72
3	Compound 1	–	Ethanol	60
4	Compound 1	Cs ₂ CO ₃	Ethanol	86
5	Compound 1	–	Acetonitrile	84
6	Compound 1	Cs ₂ CO ₃	Acetonitrile	98
7	Compound 1	–	Toluene	0
8	Compound 1	–	Acetone	66
9	Compound 1	–	DMF	42
10	Compound 1	–	DMSO	48
11	{[Cu(pdc)(im) ₂ ·2H ₂ O]} _n	Cs ₂ CO ₃	Ethanol	52
12	{[Cu(pdc)(im) ₂ ·2H ₂ O]} _n	–	Ethanol	0
13 ^c	Compound 1	–	Ethanol	72
14 ^d	Compound 1	–	Ethanol	0

^aReaction condition: Bromobenzene (1.2 mmol; 0.188 g), pyrazole (1.0 mmol, 0.067 g); Cs₂CO₃ (1 mmol, 0.326 g); catalyst (0.003 mmol, 0.002 g i.e. 0.14 mole percent with respect to reagents); solvent (2 mL) at 78 °C for 10 h in base free conditions and for 6 h in addition of base. In entry 2 and 3 the temperature was 70 °C and 60 °C respectively. ^bIsolated yield. ^cIodobenzene (1.2 mmol, 0.245 g) was used instead of bromobenzene. ^dChlorobenzene (1.2 mmol, 0.135 g) was used instead of bromobenzene.

In the solvent screening phase, ethanol was found to be environmentally favorable and provided yields comparable to that achieved with acetonitrile (Table 1, entries 1 and 5), outperforming other solvents. In

contrast, DMF and DMSO resulted in very low yields (Table 1, entries 9 and 10) due to the leaching of copper from the solid catalyst, a scenario that is undesirable from both environmental and economic perspectives. After screening various bases, Cs_2CO_3 was found to exhibit the best performance in ethanol and acetonitrile mediums. Therefore, only the performance of Cs_2CO_3 as a base is reported here. The use of Cs_2CO_3 as the base in both ethanol and acetonitrile (Table 1, entries 4 and 6) was observed to enhance the reaction rate compared to the base-free conditions. From an environmental perspective, the reactions were conducted in ethanol under base-free conditions. Although this approach is more eco-friendly, it requires a longer reaction time (10 hours) compared to that of in presence of base (6 hours) to achieve satisfactory results. This study represents the first example of a C–N cross-coupling reaction where the reactions were studied in ethanol without the addition of an external base.

Temperature also played a crucial role in the yield of the products. The isolated yield was found to be optimal at 78 °C in ethanol. Lower temperatures resulted in incomplete conversion (Table 1, entries 2 and 3). Therefore, the most favourable conditions for achieving the highest yield of the desired product in an environmentally friendly manner were identified as ethanol as the solvent and maintaining the reaction temperature at 78 °C. This catalytic system also has the advantage of being tolerant to air and moisture, eliminating the need for an inert atmosphere.

To investigate the roles of copper(II) and barium(II) centers in compound **1**, we conducted several control experiments. It is well-documented that copper(II) is an effective catalyst in N-arylation reactions.¹⁷⁻²⁶ Accordingly, we tested a 1D five coordinated copper(II) complex, $\{[\text{Cu}(\text{pdc})(\text{im})_2] \cdot 2\text{H}_2\text{O}\}_n$ (where im = imidazole), known to catalyze N-arylation reactions under heterogeneous conditions (Table 1, entry 11).³⁹ However, under identical conditions specifically, without the addition of an external base, the reaction did not proceed with $\{[\text{Cu}(\text{pdc})(\text{im})_2] \cdot 2\text{H}_2\text{O}\}_n$ (Table 1, entry 12). Based on the results, it can be concluded that in compound **1**, the barium center functions as a Lewis base.

Under the optimized conditions, the catalytic activities of compound **1** were evaluated across a wide range of substrates in this cross-coupling reaction, resulting in the isolation of the desired products with moderate to excellent yields (Table 2). Among the non-substituted aryl halides, both iodobenzene and bromobenzene yielded comparable results (Table 1, entries 1 and 13). Typically, iodobenzene is more reactive than bromobenzene in cross-coupling reactions. However, recent studies suggest that iodine species, such as I^- or I_2 , produced from iodobenzene, might act as inhibitors during the catalytic process.^{21, 40} Additionally, the catalyst was found to be ineffective with chlorobenzene, likely due to its relative inertness (Table 1, entry 14).

Table 2. N-Arylation reaction of different N-containing heterocycles with substituted aryl bromide^a

$$\text{N}_{\text{Aza-heterocycle/Aromatic amine}}\text{H} + \text{R-C}_6\text{H}_4\text{-Br} \xrightarrow[\text{Ethanol, 78 } ^\circ\text{C}]{\text{Compound 1}} \text{N}_{\text{Aza-heterocycle/Aromatic amine}}\text{-C}_6\text{H}_4\text{-R}$$

<i>R1</i>		<i>R2</i>	
Entry	<i>R1</i>	<i>R</i>	Yield ^b (wt%) of the product <i>R2</i>
1a	Pyrazole	H	78, 78 ^c
1b	Pyrazole	<i>p</i> -NO ₂	88
1c	Pyrazole	<i>m</i> -NO ₂	80
1d	Pyrazole	<i>o</i> -NO ₂	75
1e	Pyrazole	<i>p</i> -CN	84
1f	Pyrazole	<i>p</i> -COMe	82
1g	Pyrazole	<i>p</i> -OMe	70
1h	Pyrazole	<i>p</i> -Me	58
2a	3-phenylpyrazole	<i>p</i> -NO ₂	66
3a	3-methylpyrazole	<i>p</i> -NO ₂	76
4a	5-methylpyrazole	<i>p</i> -NO ₂	40
5a	Indazole	<i>p</i> -NO ₂	56
6a	3,5-dimethylpyrazole	<i>p</i> -NO ₂	26
7a	Imidazole	H	78, 78 ^c
7b	Imidazole	<i>p</i> -NO ₂	86
7c	Imidazole	<i>m</i> -NO ₂	81
7d	Imidazole	<i>o</i> -NO ₂	74
7f	Imidazole	<i>p</i> -CN	80
7g	Imdazole	<i>p</i> -OMe	70
8a	Benzimidazole	H	48
8b	Benzimidazole	<i>p</i> -NO ₂	60
8c	Benzimidazole	<i>o</i> -NO ₂	35
8d	Benzimidazole	<i>p</i> -CN	55
8f	Benzimidazole	<i>p</i> -OMe	43
9a	1,2,4-triazole	<i>o</i> -NO ₂	71
10a	1,2,3-triazole	<i>o</i> -NO ₂	70
11a	Aniline	H	73
12a	<i>p</i> -toluidine	<i>p</i> -NO ₂	79

^aReaction condition: Aryl halide (1.2 mmol), N-containing aza-heterocycles/Aromatic amine (1.0 mmol), catalyst (0.003 mmol, 0.002 g i.e. 0.14 mole percent with respect to reagents); ethanol (2 mL) at 78 °C for 10 h.

^bIsolated yield. ^cfifth cycle.

The N-arylation reaction of pyrazole with differently substituted bromobenzenes was investigated. It appears that substitution at the 3-position of the pyrazole ring did not hinder the cross-coupling reaction (Table 2, entries 2a, and 3a). Notably, this reaction exhibited high sensitivity to the 5-substituent of the pyrazole ring, resulting in lower yields for 5-methylpyrazole (Table 2; entry 4a), indazole (Table 2; entry 5a) and 3,5-dimethylpyrazole (Table 2; entry 6a). This decrease in yield may be attributed to the steric crowding and electron-donating effects of the methyl groups during the cross-coupling reaction. However, reactions

involving all of these asymmetric pyrazoles (3-phenyl-1*H*-pyrazole, 3-methyl-1*H*-pyrazole, and 5-methyl-1*H*-pyrazole) with aryl bromides consistently produced only one regioisomeric product. Reactions with *p*-NO₂ and *m*-NO₂ substituted aryl bromides with pyrazole and imidazole yielded excellent results, whereas *o*-nitrobromobenzene gave a lower yield due to steric hindrance (Table 2, entries 1b, 1c, 1d and 7b, 7c, 7d).

The presence of other electron-withdrawing groups such as acetyl, nitrile at the *p*-position of bromobenzene also gave satisfactory results (Table 2; entries 1e and 1f). Notably, the reaction with *p*-methoxybromobenzene produced a moderately good yield (Table 2, entry 1g and 7g), which was better than anticipated. Although the methoxy group has a strong positive resonance effect, it may lose some effectiveness due to interaction with the metal center. In contrast, reaction of pyrazole with *p*-methylbromobenzene yielded comparatively low amount of product due to electron-donating ability of methyl group (Table 2; entry 1h). Additional experiments with other electron-donating groups on the aryl bromides such as amino, phenoxy are not feasible due to the homocoupling reaction. We also explored the reactivity of other N-containing heterocycles such as benzimidazole, 1,2,4-triazole, and 1,2,3-triazole in the coupling reaction with substituted aryl bromides (Table 2, entries 8a-10a). Imidazole exhibited similar reactivity to pyrazole, while benzimidazole, 1,2,4-triazole, and 1,2,3-triazole gave moderate yields. Here also only one regioisomeric product is formed. Additionally, aromatic amines (aniline and *p*-toluidine) were successfully coupled with bromobenzene to yield the desired product (Table 2, entry 11a and 12a).

The catalyst, compound **1**, was successfully recovered and reused multiple times through centrifugation without a significant decrease in catalytic activity. The catalytic performance of the reused catalyst was comparable to that of the fresh catalyst in each cycle (Table 2). A hot filtration test suggests that the coupling reaction do not proceed further after separation of the catalyst from the reaction mixture. Atomic absorption spectroscopy (AAS) analysis (sensitivity up to 0.001 ppm) of the supernatant solution collected by filtration also confirmed the absence of copper or barium ions in the liquid phase.

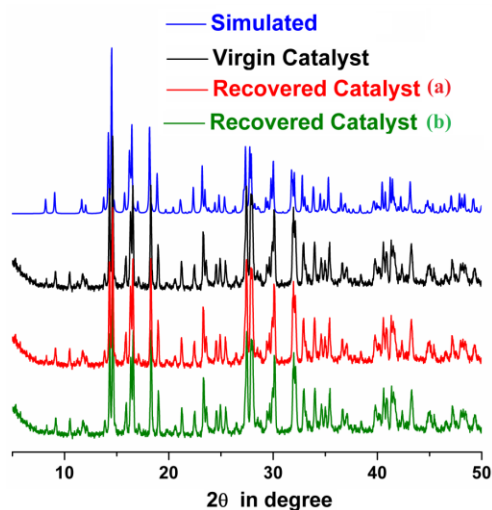


Figure 3. X-ray powder pattern of virgin catalyst and recovered catalyst ('a' for N-arylation of pyrazole with bromobenzene and 'b' for N-arylation of imidazole with bromobenzene).

To assess the stability of the recovered catalyst, it was further characterized using powder X-ray diffraction (XRD). A comparison of the XRD patterns (Figure 3) of the fresh and recovered catalysts indicated that the structural integrity of compound **1** was preserved after multiple reaction cycles.

Conclusions

In summary, the copper- and barium-containing carboxylate framework serves as an active catalyst for the C–N cross-coupling reaction between various azoles and differently substituted aryl bromides under environmentally friendly heterogeneous conditions, without the need for any external base and in ethanol medium. In this framework, copper(II) acts as the active site for the catalytic reaction, while barium(II) functions as a Lewis base. The compound features accessible pre-existing coordinatively unsaturated copper sites that do not require prior activation. Additionally, the compound is recyclable and stable under reaction conditions, offering practical advantages over homogeneous catalysis. Furthermore, this catalytic system is tolerant to air and moisture, thereby eliminating the need for an inert atmosphere.

Experimental Section

General. Barium nitrate, copper nitrate trihydrate, and solvents were obtained from Merck (India). The solvents were distilled and dried prior to use. Pyridine-2,5-dicarboxylic acid and other chemicals were sourced from either Sigma–Aldrich or Merck (India) and were used as received. Elemental analysis was conducted using a Perkin-Elmer 240C elemental analyzer. Fourier-transformed infrared (FT-IR) spectra were recorded on a Perkin-Elmer RX I FT-IR spectrometer, with samples prepared as KBr pellets. ^1H NMR ^{13}C NMR spectra were acquired on a Bruker Avance DPX 300 NMR spectrometer (300 MHz). The metal content of the sample was determined on a Varian Techtron AA-ABQ atomic absorption spectrometer. Mass spectra were recorded using a Waters XEVO–G2QTOF#YCA351 high resolution mass spectrometer. Powder X-ray diffraction (PXRD) patterns were obtained using a Bruker D8 Advance X-ray powder diffractometer equipped with Cu-K α radiation. X-ray diffraction data for compound **1** were collected using a Bruker SMART APEX CCD X-ray diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Integrated intensities and cell refinement were conducted using the SAINT software package, which employs a narrow-frame integration algorithm.⁴¹ An empirical absorption correction was applied using the SADABS program.⁴² Structures were determined by direct methods and refined with the full-matrix least-squares technique against F^2 , employing anisotropic displacement parameters for non-hydrogen atoms. This refinement was carried out using the SHELXS97 and SHELXL97 programs.⁴³ Hydrogen atoms were refined with isotropic thermal parameters. In the final difference Fourier maps, no significant peaks were observed, apart from ghost peaks near the metal centers.

General method for the preparation of compound 1. The compound $\{[\text{CuBa}(\text{pdc})_2(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}\}_n$ (**1**) was synthesized using a hydrothermal method. The initial reaction mixture was prepared as follows: 0.167 g (1 mmol) of pyridine-2,5-dicarboxylic acid and 0.136 g (2 mmol) of imidazole were dissolved in 10 ml of Milli-Q water and stirred for 0.5 hours. Barium nitrate (0.130 g, 0.5 mmol) and copper nitrate trihydrate (0.120 g, 0.5 mmol) were then added, and the mixture was stirred for an additional 0.25 hours. The resulting solution was transferred to a 20 ml Teflon-lined acid digestion bomb and heated at 175 °C for 3 days. After the reaction, the system was allowed to cool slowly to room temperature at a rate of 5 °C per hour. Crystals suitable for X-ray analysis were obtained.

$\{[\text{CuBa}(\text{pdc})_2(\text{H}_2\text{O})_5] \cdot \text{H}_2\text{O}\}_n$ (1**).** Blue rods; 84% based on copper, IR (KBr, ν , cm^{-1}): 1642, 1568 (asymmetric CO_2^-), 1386 (symmetric CO_2^-), 1345, 1278 (symmetric C–O), 3442 (O–H). Anal. Calcd. for $\text{C}_{14}\text{H}_{18}\text{BaCuN}_2\text{O}_{14}$ (639); C, 26.31; H, 2.84; N, 4.38. Found; C, 26.36; H, 2.88; N, 4.35. Crystal data and refinement parameters for the

compound were compared with previously reported values. A summary of crystal data and relevant refinement parameters of compound **1** is given in Table S1 of supplementary file.

General method of catalytic reaction. For the catalytic reaction, 1.2 mmol aryl halide (Bromobenzene 0.188 g, 2/3/4-nitrobromobenzene 0.242 g, 4-bromobenzonitrile 0.218 g, 4-acetylbromobenzene 0.239 g, 4-methoxybromobenzene 0.224 g, 4-methylbromobenzene 0.205 g) was combined with 0.002 g (0.003 mmol) of compound **1** in a glass batch reactor. To this solid mixture, 1.0 mmol of a nitrogen-containing heterocycle (Pyrazole/Imidazole 0.067 g, 3-phenylpyrazole 0.143 g, Indazole/Benzimidazole 0.117 g, 3/5-methylpyrazole 0.081 g, 3,5-dimethylpyrazole 0.095 g, 1,2,4-triazole/1,2,3-triazole 0.068 g)/Aniline 0.093 g/*p*-toluidine 0.107 g and 2 mL of ethanol were added (with the solid heterocycles introduced directly with the catalyst). The reaction was then stirred in a two-neck, 50 mL round-bottom flask equipped with a water condenser and maintained at 78 °C in an oil bath. After cooling the mixture to room temperature, compound **1** was separated by centrifugation. The remaining solution was extracted with water and diethyl ether (2 × 15 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under vacuum. The resulting residue was purified by column chromatography on silica gel (mesh 60–120) using an *n*-hexane/ethyl acetate mixture as the eluent to yield the desired product. Due to the small quantity of 0.002 g of the solid catalyst, it was challenging to recover, reuse, and characterize it individually. Therefore, catalyst samples were collected from different batches within the same catalytic cycle, and the average data from these samples are reported here. For each cycle, cross-coupling reactions were conducted with bromobenzene and pyrazole/imidazole, adhering to the optimized reaction conditions. After the initial reaction cycle, the catalyst was recovered by centrifugation, thoroughly washed with diethyl ether, and then dried under vacuum at 80 °C overnight. To confirm the heterogeneous nature of the catalyst, a hot filtration test was conducted. The reaction mixture, consisting of 1 mmol (0.067 g) of pyrazole and 0.002 g (0.003 mmol) of compound **1** in 2 mL of ethanol, was combined with 1.2 mmol (0.188 g) of bromobenzene and stirred in a two-neck, 50 mL round-bottom flask equipped with a water condenser. The reaction was maintained at 78 °C in an oil bath, and the progress was monitored by TLC. After 2 hours, compound **1** was separated from the reaction mixture by filtration at the reaction temperature using Whatman 1 filter paper (pore size 11 μm). The mixture was then stirred at the same temperature for an additional 16 hours. The reaction progress was assessed by TLC analysis. The product of the catalytic reaction was analyzed using ¹H and ¹³C NMR spectroscopy, HRMS and the results were compared with literature values (see the supplementary file for the NMR and HRMS of the products). The spectroscopic data for the products were found to be consistent with those reported in the literature.^{22, 26, 44-50}

1-Phenyl-1H-pyrazole (1a). Cross-coupling product of pyrazole (1 mmol, 0.067 g) and bromobenzene (1.2 mmol, 0.188 g); Purified by column chromatography (silica gel, 10% EtOAc in *n*-hexane) to give white solid (0.112 g, 78%); mp 35–38 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.86–7.84 (m, 1H), 7.70–7.61 (m, 3H), 7.41–7.30 (m, 3H), 6.48–6.40 (m, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 140.7, 138.2, 136.0, 130.5, 126.8, 120.2, 107.1. HRMS (ESI, +ve) C₉H₉N₂⁺ [M+H]⁺ requires *m/z* 145.0687, found 145.0591. Anal. Calcd. for C₉H₈N₂ (144); C, 74.98%; H, 5.59%; N, 19.43%. Found; C, 74.92%; H, 5.63%; N, 19.44%.

1-(4-nitrophenyl)-1H-pyrazole (1b). Cross-coupling product of pyrazole (1 mmol, 0.067 g) and 4-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.166 g, 88%); mp 105–108 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.34 (d, *J* 9 Hz, 2H), 8.04 (d, *J* 2.3 Hz, 1H), 7.89 (d, *J* 9 Hz, 2H), 7.80 (s, 1H), 6.56 (s, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 145.5, 144.4, 142.8, 127.1, 125.4, 118.6, 109.3. HRMS (ESI, +ve) C₉H₇N₃O₂⁺ [M+H]⁺ requires *m/z* 190.0617, found 190.0613. Anal. Calcd. for C₉H₇N₃O₂ (189); C, 57.14%; H, 3.73%; N, 22.21%. Found; C, 57.18%; H, 3.71%; N, 22.19%.

1-(3-Nitrophenyl)-1H-pyrazole (1c). Cross-coupling product of pyrazole (1 mmol, 0.067 g) and 3-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.151 g, 80%); mp 94-95 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.57-8.56 (m, 1H), 8.15-8.04 (m, 3H), 7.78 (s, 1H), 7.67-7.61 (m, 1H); 6.55-6.55 (m, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 141.1, 140.7, 138.1, 130.2, 126.9, 126.0, 121.4, 109.3, 98.0. HRMS (ESI, +ve) C₉H₈N₃O₂⁺ [M+H]⁺ requires *m/z* 190.0617, found 190.0616. Anal. Calcd. for C₉H₇N₃O₂ (189); C, 57.14%; H, 3.73%; N, 22.21%. Found; C, 57.19%; H, 3.76%; N, 22.16%.

1-(2-Nitrophenyl)-1H-pyrazole (1d). Cross-coupling product of pyrazole (1 mmol, 0.067 g) and 2-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.141 g, 75%); mp 87-88 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.87-7.84 (m, 1H), 7.73-7.65 (m, 3H), 7.59-7.48 (m, 2H), 6.50-6.48 (m, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 144.6, 142.3, 133.4, 133.1, 129.8, 128.4, 126.2, 125.0, 108.2. HRMS (ESI, +ve) C₉H₈N₃O₂⁺ [M+H]⁺ requires *m/z* 190.0617, found 190.0618. Anal. Calcd. for C₉H₇N₃O₂ (189); C, 57.14%; H, 3.73%; N, 22.21%. Found; C, 57.21%; H, 3.81%; N, 22.28%.

4-(1H-Pyrazol-1-yl)benzonitrile (1e). Cross-coupling product of pyrazole (1 mmol, 0.067 g) and 4-bromobenzonitrile (1.2 mmol, 0.218 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.142 g, 84%); mp 140-142 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.97 (d, *J* 2.52 Hz, 1H), 7.8 (d, *J* 8.82 Hz, 2H), 7.73-7.67 (m, 3H), 6.5 (t, *J* 1.8 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 142.9, 142.4, 133.6, 126.9, 118.9, 118.4, 109.5, 109.0. HRMS (ESI, +ve) C₉H₈N₃O₂⁺ [M+H]⁺ requires *m/z* 170.0718, found 170.0717. Anal. Calcd. for C₁₀H₇N₃ (169); C, 70.99%; H, 4.17%; N, 24.84%. Found; C, 80.08%; H, 4.15%; N, 24.88%.

1-(4-Acetylphenyl)-1H-pyrazole (1f). Cross-coupling product of pyrazole (1 mmol, 0.067 g) and 4-acetylbromobenzene (1.2 mmol, 0.239 g); Purified by column chromatography (silica gel, 15% EtOAc in *n*-hexane) to give white solid (0.152 g, 82%); mp 92-95 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.03-7.98 (m, 3H), 7.78-7.73 (m, 3H), 6.48 (d, *J* 1.83 Hz, 1H), 2.58 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 196.7, 143.3, 142.0, 134.8, 130.0, 126.9, 118.3, 108.5, 26.5. HRMS (ESI, +ve) C₁₁H₁₁N₂O⁺ [M+H]⁺ requires *m/z* 187.0793, found 187.0777. Anal. Calcd. for C₁₁H₁₀N₂O (186); C, 70.95%; H, 5.41%; N, 15.04%. Found; C, 70.99%; H, 5.35%; N, 15.09%.

1-(4-Methoxyphenyl)-1H-pyrazole (1g). Cross-coupling product of pyrazole (1 mmol, 0.067 g) and 4-methoxybromobenzene (1.2 mmol, 0.224 g); Purified by column chromatography (silica gel, 15% EtOAc in *n*-hexane) to give white solid (0.121 g, 70%); mp 92-94 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.83 (s, 1H), 7.70 (s, 1H), 7.60-7.57 (m, 2H), 6.99-6.96 (m, 2H), 6.44 (s, 1H), 3.85 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 158.2, 140.6, 134.0, 126.8, 120.9, 114.5, 107.1, 55.5. HRMS (ESI, +ve) C₁₀H₁₁N₂O⁺ [M+H]⁺ requires *m/z* 175.0793, found 175.0781. Anal. Calcd. for C₁₀H₁₀N₂O (174); C, 68.95%; H, 5.79%; N, 16.08%. Found; C, 68.99%; H, 5.86%; N, 16.14%.

1-(*p*-Tolyl)-1H-pyrazole (1h). Cross-coupling product of pyrazole (1 mmol, 0.067 g) and 4-methylbromobenzene 0.205 g (1.2 mmol, 0.205 g); Purified by column chromatography (silica gel, 5% EtOAc in *n*-hexane) to give white solid (0.091 g, 58%); mp 82-84 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.89-7.58 (m, 6H), 6.48 (d, *J* 1.83 Hz, 1H), 2.38 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 140.70, 138.2, 136.0, 130.5, 126.8, 120.2, 107.1, 20.0. HRMS (ESI, +ve) C₁₀H₁₁N₂⁺ [M+H]⁺ requires *m/z* 159.0922, found 159.0966. Anal. Calcd. for C₁₀H₁₀N₂ (158); C, 75.92%; H, 6.37%; N, 17.71%. Found; C, 75.88%; H, 6.33%; N, 17.77%.

1-(4-Nitrophenyl)-3-phenyl-1H-pyrazole (2a). Cross-coupling product of 3-phenylpyrazole (1 mmol, 0.143 g) and 4-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.175 g, 66%); mp 194-195 °C. (300 MHz, CDCl₃, δ, ppm): δ (ppm): 8.37-8.34

(m, 2H), 8.07 (d, *J* 2.6 Hz, 1H), 7.97-7.91 (m, 4H), 7.49-7.38 (m, 3H), 6.86 (d, *J* 2.6 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 154.6, 144.4, 144.4, 132.2, 128.8, 128.8, 128.2, 126.0, 125.4, 118.3, 106.9. HRMS (ESI, +ve) C₁₅H₁₂N₃O₂⁺ [M+H]⁺ requires *m/z* 266.0930, found 266.0932. Anal. Calcd. for C₁₅H₁₁N₃O₂ (265); C, 67.92%; H, 4.18%; N, 15.84%. Found; C, 67.99%; H, 4.24%; N, 15.87%.

1-(4-Nitrophenyl)-3-methyl-1H-pyrazole (3a). Cross-coupling product of 3-methylpyrazole (1 mmol, 0.081 g) and 4-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 15% EtOAc in *n*-hexane) to give pale yellow solid (0.154 g, 76%); mp 92-95 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.29 (d, *J* 9.2 Hz, 2H), 7.91 (d, *J* 2.4 Hz, 1H), 7.81 (d, *J* 9.2 Hz, 2H), 6.33 (d, *J* 2.4 Hz, 1H), 2.38 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 152.6, 144.9, 144.4, 127.6, 125.3, 117.9, 109.6, 13.7. HRMS (ESI, +ve) C₁₀H₁₀N₃O₂⁺ [M+H]⁺ requires *m/z* 204.0773, found 204.0772. Anal. Calcd. for C₁₀H₉N₃O₂ (203); C, 59.11%; H, 4.46%; N, 20.68%. Found; C, 59.1%; H, 4.5%; N, 20.7%.

1-(4-Nitrophenyl)-5-methyl-1H-pyrazole (4a). Cross-coupling product of 5-methylpyrazole (1 mmol, 0.081 g) and 4-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 15% EtOAc in *n*-hexane) to give pale yellow solid (0.081 g, 40%); mp 92-95 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.31 (d, *J* 9 Hz, 2H), 7.68-7.62 (m, 3H), 6.35 (s, 1H), 2.33 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 145.8, 145.4, 139.4, 138.5, 124.9, 123.5, 108.3, 12.0. HRMS (ESI, +ve) C₁₀H₁₀N₃O₂⁺ [M+H]⁺ requires *m/z* 204.0773, found 204.0771. Anal. Calcd. for C₁₀H₉N₃O₂: C, 59.11%; H, 4.46%; N, 20.68%. Found; C, 59.17%; H, 4.52%; N, 20.75%.

1-(4-Nitrophenyl)-1H-indazole (5a). Cross-coupling product of Indazole (1 mmol, 0.117 g) and 4-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.134 g, 56%); mp 259-261 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.35-8.24 (m, 3H), 7.93-7.90 (m, 2H), 7.81 (d, *J* 8.2 Hz, 2H), 7.53-7.48 (m, 1H), 7.30 (d, *J* 7.2 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 147.3, 143.5, 134.1, 133.7, 125.0, 123.1, 118.8, 118.8, 116.8, 116.7, 103.4. HRMS (ESI, +ve) C₃H₁₀N₃O₂⁺ [M+H]⁺ requires *m/z* 240.0773, found 240.0773. Anal. Calcd. for C₁₃H₉N₃O₂ (239); C, 65.27%; H, 3.79%; N, 17.56%. Found; C, 65.36%; H, 3.85%; N, 17.61%.

1-(4-Nitrophenyl)-3,5-dimethyl-1H-pyrazole (6a). Cross-coupling product of 3,5-dimethylpyrazole (1 mmol, 0.095 g) and 4-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 15% EtOAc in *n*-hexane) to give pale yellow solid (0.056 g, 26%); mp 100-102 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.31 (d, *J* 9.1 Hz, 2H), 7.67 (d, *J* 9.0 Hz, 2H), 6.07 (s, 1H), 2.42 (s, 3H), 2.29 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 150.8, 145.6, 145.0, 139.8, 124.7, 123.5, 109.3, 13.5, 13.1. HRMS (ESI, +ve) C₁₁H₁₂N₃O₂⁺ [M+H]⁺ requires *m/z* 218.0930, found 218.0928. Anal. Calcd. for C₁₁H₁₁N₃O₂ (217); C, 60.82%; H, 5.10%; N, 19.34%. Found; C, 60.89%; H, 5.07%; N, 19.38%.

1-Phenyl-1H-imidazole (7a). Cross-coupling product of Imidazole (1 mmol, 0.067 g) and bromobenzene (1.2 mmol, 0.188 g); Purified by column chromatography (silica gel, 10% EtOAc in *n*-hexane) to give colourless liquid (0.112 g, 78%). ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.85 (s, 1H), 7.50-7.32 (m, 5H), 7.27 (m, 1H), 7.18 (s, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 136.9, 135.5, 130.3, 129.7, 128.2, 122.2, 118.2. HRMS (ESI, +ve) C₉H₉N₂⁺ [M+H]⁺ requires *m/z* 145.0687, found 145.0681. Anal. Calcd. for C₉H₈N₂ (144); C, 74.98%; H, 5.59%; N, 19.43%. Found; C, 75.05%; H, 5.64%; N, 19.47%.

1-(4-Nitrophenyl)-1H-imidazole (7b). Cross-coupling product of Imidazole (1 mmol, 0.067 g) and 4-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.162 g, 86%); mp 198-205 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.38 (d, *J* 8.9 Hz, 2H), 7.98 (s, 1H), 7.58 (d, *J* 8.9 Hz, 2H), 7.38 (s, 1H), 7.27 (d, *J* 6.1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 146.3, 142.0, 135.5, 131.8, 125.8, 121.1, 117.7. HRMS (ESI, +ve) C₉H₈N₃O₂⁺ [M+H]⁺ requires *m/z* 190.0617, found 190.0619. Anal. Calcd. for C₉H₇N₃O₂ (189); C, 57.14%; H, 3.73%; N, 22.21%. Found; C, 57.19%; H, 3.78%; N, 22.29%.

1-(3-Nitrophenyl)-1H-imidazole (7c). Cross-coupling product of Imidazole (1 mmol, 0.067 g) and 3-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.153 g, 81%); mp 92-94 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.36 (s, 1H), 8.22 (d, *J* 8.9 Hz, 2H), 7.93-7.91 (m, 1H), 7.70 (d, *J* 8.9 Hz, 1H), 7.45 (s, 1H), 7.25 (s, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 138.8, 138.2, 135.4, 130.2, 130.0, 128.0, 123.4, 118.3, 100.1. HRMS (ESI, +ve) C₉H₇N₃O₂⁺ [M+H]⁺ requires *m/z* 190.0617, found 190.0515. Anal. Calcd. for C₉H₇N₃O₂ (189); C, 57.14%; H, 3.73%; N, 22.21%. Found; C, 57.17%; H, 3.75%; N, 22.18%.

1-(2-Nitrophenyl)-1H-imidazole (7d). Cross-coupling product of Imidazole (1 mmol, 0.067 g) and 2-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.139 g, 74%); mp 96-98 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.96 (d, *J* 8.1 Hz, 1H), 7.73-7.68 (m, 1H), 7.61-7.56 (m, 2H), 7.44-7.36 (m, 1H), 7.15 (s, 1H), 7.03 (s, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 145.2, 137.2, 133.9, 130.4, 130.0, 129.8, 128.7, 125.5, 120.4. HRMS (ESI, +ve) C₉H₇N₃O₂⁺ [M+H]⁺ requires *m/z* 190.0617, found 190.0618. Anal. Calcd. for C₉H₇N₃O₂ (189); C, 57.14%; H, 3.73%; N, 22.21%. Found; C, 57.19%; H, 3.77%; N, 22.28%.

4-(1H-Imidazol-1-yl)benzonitrile (7e). Cross-coupling product of Imidazole (1 mmol, 0.067 g) and 4-bromobenzonitrile (1.2 mmol, 0.218 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.135 g, 80%); mp 151-154 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.03-7.97 (m, 1H), 7.84-7.81 (m, 2H), 7.57-7.54 (m, 2H), 7.37 (s, 1H), 7.28 (s, 1H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 140.5, 134.4, 134.1, 131.5, 121.3, 119.7, 117.8, 111.0. HRMS (ESI, +ve) C₁₀H₈N₃⁺ [M+H]⁺ requires *m/z* 170.0718, found 170.0716. Anal. Calcd. for C₁₀H₇N₃ (169); C, 70.99%; H, 4.17%; N, 24.84%. Found; C, 80.08%; H, 4.22%; N, 24.89%.

1-(4-Methoxyphenyl)-1H-imidazole (7f). Cross-coupling product of Imidazole (1 mmol, 0.067 g) and 4-methoxybromobenzene (1.2 mmol, 0.224 g); Purified by column chromatography (silica gel, 15% EtOAc in *n*-hexane) to give white solid (0.121 g, 70%); mp 60-68 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.75 (s, 1H), 7.28 (d, *J* 8.9 Hz, 2H), 7.18 (d, *J* 6.3 Hz, 2H), 6.97 (d, *J* 8.8, 2H), 3.83 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 159.0, 135.9, 130.7, 130.0, 123.2, 118.8, 114.9, 55.6. HRMS (ESI, +ve) C₁₀H₁₁N₂O⁺ [M+H]⁺ requires *m/z* 175.0793, found 175.0781. Anal. Calcd. for C₁₀H₁₀N₂O (174); C, 68.95%; H, 5.79%; N, 16.08%. Found; C, 68.99%; H, 5.85%; N, 16.13%.

1-Phenyl-1H-benzimidazole (8a). Cross-coupling product of Benzimidazole (1 mmol, 0.117 g) and bromobenzene (1.2 mmol, 0.188 g); Purified by column chromatography (silica gel, 10% EtOAc in *n*-hexane) to give white solid (0.094 g, 48%); mp 95-98 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.11 (s, 1H), 7.90-7.87 (m, 1H), 7.59-7.43 (m, 6H), 7.37-7.32 (m, 2H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 144.0, 142.3, 136.4, 133.7, 130.1, 128.0, 124.1, 123.7, 122.8, 120.6, 110.5. HRMS (ESI, +ve) C₁₃H₁₁N₂⁺ [M+H]⁺ requires *m/z* 195.0922, found 195.0916. Anal. Calcd. for C₁₃H₁₀N₂ (164); C, 80.39%; H, 5.19%; N, 14.42%. Found; C, 80.47%; H, 5.25%; N, 14.47%.

1-(4-Nitrophenyl)-1H-benzimidazole (8b). Cross-coupling product of Benzimidazole (1 mmol, 0.117 g) and 4-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.143 g, 60%); mp 175-178 °C. ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.46 (d, *J* 8.8 Hz, 2H), 8.19 (s, 1H), 7.91-7.88 (m, 1H), 7.74 (d, *J* 8.8 Hz, 2H), 7.62-7.60 (m, 1H), 7.41-7.38 (m, 2H). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 146.6, 144.4, 141.7, 141.6, 132.8, 125.8, 124.6, 123.7, 123.7, 121.2, 110.3. HRMS (ESI, +ve) C₁₃H₁₀N₃O₂⁺ [M+H]⁺ requires *m/z* 240.0773, found 240.0774. Anal. Calcd. for C₁₃H₉N₃O₂ (239); C, 65.27%; H, 3.79%; N, 17.56%. Found; C, 65.3%; H, 3.8%; N, 17.5%.

1-(2-Nitrophenyl)-1H-benzimidazole (8c). Cross-coupling product of Benzimidazole (1 mmol, 0.117 g) and 2-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-

hexane) to give pale yellow solid (0.084 g, 35%); mp 190-195 °C. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 8.07 (d, J 1.4 Hz, 1H), 7.98 (s, 1H), 7.84-7.81 (m, 1H), 7.75 (m, 1H), 7.62 (m, 1H), 7.52-7.49 (m, 1H), 7.29-7.24 (m, 2H), 7.11-7.09 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm): 145.8, 143.3, 142.5, 134.4, 134.4, 130.1, 129.8, 129.3, 125.9, 124.2, 123.2, 120.7, 109.5. HRMS (ESI, +ve) $\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$ requires m/z 240.0773, found 240.0772. Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_2$ (239); C, 65.27%; H, 3.79%; N, 17.56%. Found; C, 65.36%; H, 3.85%; N, 17.59%.

4-(1H-Benzimidazol-1-yl)benzonitrile (8d). Cross-coupling product of Benzimidazole (1 mmol, 0.117 g) and 4-bromobenzonitrile (1.2 mmol, 0.218 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give pale yellow solid (0.120 g, 55%); mp 131-136 °C. ^1H NMR (300 MHz, $\text{DMSO}-d_6$, δ , ppm): 8.67 (s, 1H), 8.09 (d, J 8.62 Hz, 2H), 7.93 (d, J 8.61 Hz, 2H), 7.80-7.78 (m, 1H), 7.72-7.69 (m, 1H), 7.38-7.32 (m, 2H). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$, δ , ppm): 144.5, 143.7, 140.3, 134.8, 132.8, 124.4, 124.3, 123.5, 120.6, 118.8, 111.4, 110.3. HRMS (ESI, +ve) $\text{C}_{14}\text{H}_{10}\text{N}_3^+$ $[\text{M}+\text{H}]^+$ requires m/z 220.0875, found 220.0874. Anal. Calcd. for $\text{C}_{14}\text{H}_9\text{N}_3$ (219); C, 76.70%; H, 4.14%; N, 19.17. Found; C, 76.77%; H, 4.18%; N, 19.15.

1-(4-Methoxyphenyl)-1H-benzimidazole (8e). Cross-coupling product of Benzimidazole (1 mmol, 0.117 g) and 4-methoxybromobenzene (1.2 mmol, 0.224 g); Purified by column chromatography (silica gel, 15% EtOAc in *n*-hexane) to give white solid (0.096 g, 43%); mp 98-102 °C. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 8.04 (s, 1H), 7.88-7.85 (m, 1H), 7.46-7.37 (m, 3H), 7.33-7.29 (m, 2H), 7.06 (d, J 8.9 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm): 159.4, 143.6, 142.5, 134.2, 129.1, 125.7, 123.6, 122.7, 120.4, 115.1, 110.4, 55.6. HRMS (ESI, +ve) $\text{C}_{14}\text{H}_{13}\text{N}_2\text{O}^+$ $[\text{M}+\text{H}]^+$ requires m/z 225.1028, found 225.1027. Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}$ (224); C, 74.98%; H, 5.39%; N, 12.49%. Found; C, 75.06%; H, 5.46%; N, 12.55%.

1-(2-Nitrophenyl)-1H-1,2,4-triazole (9a). Cross-coupling product of 1,2,4-triazole (1 mmol, 0.068 g) and 2-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 25% EtOAc in *n*-hexane) to give pale yellow solid (0.135 g, 71%); mp 186-189 °C. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 8.40 (s, 1H), 8.09 (s, 1H), 8.02-7.99 (m, 1H), 7.76-7.73 (m, 1H), 7.68-7.56 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm): 153.0, 144.5, 143.8, 133.8, 130.4, 130.1, 127.4, 125.5. HRMS (ESI, +ve) $\text{C}_8\text{H}_7\text{N}_4\text{O}_2^+$ $[\text{M}+\text{H}]^+$ requires m/z 191.0569, found 191.0566. Anal. Calcd. for $\text{C}_8\text{H}_6\text{N}_4\text{O}_2$ (190); C, 50.53%; H, 3.18%; N, 29.46%. Found; C, 50.58%; H, 3.25%; N, 29.49%.

1-(2-Nitrophenyl)-1H-1,2,3-triazole (10a). Cross-coupling product of 1,2,3-triazole (1 mmol, 0.068 g) and 2-nitrobromobenzene (1.2 mmol, 0.242 g); Purified by column chromatography (silica gel, 25% EtOAc in *n*-hexane) to give pale yellow solid (0.133 g, 70%); mp 202-205 °C. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.93-7.81 (m, 4H), 7.70-7.67 (m, 1H), 7.57-7.54 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm): 143.7, 136.8, 132.8, 132.2, 129.0, 129.0, 125.37, 124.7. HRMS (ESI, +ve) $\text{C}_8\text{H}_7\text{N}_4\text{O}_2^+$ $[\text{M}+\text{H}]^+$ requires m/z 191.0569, found 191.0568. Anal. Calcd. for $\text{C}_8\text{H}_6\text{N}_4\text{O}_2$ (190); C, 50.53%; H, 3.18%; N, 29.46%. Found; C, 50.59%; H, 3.23%; N, 29.51%.

N-(Phenyl)-aniline (11a). Cross-coupling product of Aniline (1 mmol, 0.093 g) and bromobenzene (1.2 mmol, 0.188 g); Purified by column chromatography (silica gel, 10% EtOAc in *n*-hexane) to give white solid (0.123 g, 73%); mp 50-54 °C. ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.29-7.24 (m, 4H), 7.12-7.03 (m, 4H), 6.95-6.90 (m, 2H), 5.73 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3 , δ , ppm): 142.4, 129.6, 121.9, 120.6. HRMS (ESI, +ve) $\text{C}_{12}\text{H}_{12}\text{N}^+$ $[\text{M}+\text{H}]^+$ requires m/z 170.0970, found 170.0971. Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{N}$ (169); C, 85.17%; H, 6.55%; N, 8.28%. Found; C, 85.26%; H, 6.59%; N, 8.34%.

N-(4-Nitrophenyl)-4-methylaniline (12a). Cross-coupling product of *p*-toluidine (1 mmol, 0.107 g) and bromobenzene (1.2 mmol, 0.188 g); Purified by column chromatography (silica gel, 20% EtOAc in *n*-hexane) to give white solid (0.180 g, 79%); mp 115-118 °C. ^1H -NMR (300 MHz, CDCl_3 , δ , ppm): 8.12-8.07 (m, 2H), 7.20-7.09 (m, 3H), 6.88-6.85 (m, 1H), 6.61-6.58 (m, 2H), 6.31 (s, 1H), 2.35 (s, 3H). ^{13}C -NMR (75 MHz, CDCl_3 , δ , ppm): 150.9, 139.4, 134.8, 130.3, 126.2, 126.1, 122.7, 113.2, 20.9. HRMS (ESI, +ve) $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$ requires m/z

229.0977, found 229.0977. Anal. Calcd. for $C_{13}H_{12}N_2O_2$ (228); C, 68.41%; H, 5.30%; N, 12.27%. Found; C, 68.48%; H, 5.37%; N, 12.32%.

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Supplementary Material

Supplementary data associated with this article is available in the Supplementary Material.

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