Supplementary Materials: A Copper Based Metal-Organic Framework as an Efficient and Reusable Heterogeneous Catalyst for Ullmann and Goldberg Type C–N Coupling Reactions

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1. Additional Figures

Figure S1. SEM images of fresh (a); and used after five catalysis cycles (b) Cu-TDPAT samples.

Figure S2. Nitrogen sorption isotherms of fresh Cu-TDPAT sample at 77 K.
Figure S3. Nitrogen sorption isotherms of used Cu-TDPAT sample after five catalysis cycles at 77 K.

Figure S4. TGA data for the fresh Cu-TDPAT and used Cu-TDPAT samples after five catalysis cycles. The continuous weight loss of 8.3% from room temperature to 250 °C for the fresh Cu-TDPAT sample or the used Cu-TDPAT sample could be attributed to the loss of physisorbed and coordinated water and solvent molecules. Considering the samples were pretreated under the same conditions, the increased weight loss (about 2%) of the used Cu-TDPAT sample was attributed to the adsorption of a few reactant or product molecules in the MOF cavities.

Figure S5. Images of the reaction mixtures after 2 h at 120 °C (a); and at 160 °C (b), respectively. The disappearance of green powder on the bottom indicated the breakage of the MOF framework.
Figure S6. X-ray diffraction patterns for the as-synthesized CuBTC sample.

Figure S7. Nitrogen sorption isotherms of fresh CuBTC sample (The BET surface area of CuBTC was 1295 m²/g).

Figure S8. Continuous wave (CW) EPR spectra of the reaction mixture in toluene at X-band at 90 °C. The decrease of intensity of the EPR signal of the reaction mixture from 0 min to 9 min was about 3.7%, then it became stable.
Figure S9. Continuous wave (CW) EPR spectra of Cu-TDPAT at X-band at room temperature.

Table S1. Characterization results of fresh and used five catalysis cycles Cu-TDPAT samples.

<table>
<thead>
<tr>
<th></th>
<th>( \text{S}_{\text{BET}} ) (m(^2)/g)</th>
<th>( V_{\text{total}} )/cm(^3)-g(^{-1})</th>
<th>( D_{\text{average}} )/nm</th>
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<tbody>
<tr>
<td>Fresh sample</td>
<td>1855</td>
<td>0.889</td>
<td>1.92</td>
</tr>
<tr>
<td>Used sample</td>
<td>1680</td>
<td>0.773</td>
<td>1.84</td>
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2. \(^1\)H-NMR Spectra of All the Products

5-Methyl-1-phenyl-2-(1H)-pyridone

5-Methyl-2-phenoxypyridine
N-Methyldiphenylamine

N-Methyl-N-(4-methoxy)phenylaniline

N-Methyl-N-(2-methoxy)phenylaniline
N-Methyl-N-(4-nitro)phenylaniline

2-(Phenylamino)propanoic acid

Methyl 2-(phenylamino)propanoate
N-Phenyl-2-pyrrolidone

N-Methyl-N-benzoylaniline

N-Phenylindole
3. $^{13}$C-NMR Spectra of All the Products
N-Methyldiphenylamine

N-Methyl-N-(4-methoxy)phenylaniline

N-Methyl-N-(2-methoxy)phenylaniline
N-Methyl-N-(4-nitro)phenylaniline

2-(Phenylamino)propanoic acid

Methyl 2-(phenylamino)propanoate
N-Phenyl-2-pyrrolidone

N-Methyl-N-benzylaniline

N-Phenylindole
N-Phenylimidazole