Cyclometalated Metal-Organic Frameworks as Heterogeneous Catalysts for Allylic N-Alkylation of Amines

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Supporting Information

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MOF Synthesis and Characterization

MOFs Synthesis. DMOF-1-dcppy, BMOF-1-dcppy, DMOF-1-Irdcppy (treated with 2 equiv of [Ir(COD)(OCH$_3$)$_2$]$_2$ based on 5,4′-phenylpyridinedicarboxylate (dcppy), and BMOF-1-Irdcppy (treated with 2 equiv of [Ir(COD)(OCH$_3$)$_2$]$_2$ based on dcppy) were synthesized as reported.$^1$ The MOFs were then rinsed with CHCl$_3$ (3×10 mL) and stored in CHCl$_3$, replacing fresh CHCl$_3$ everyday for 3 d before the catalysis experiments.

Powder X-ray Diffraction (PXRD) Analysis. DMOF-1-Irdcppy was immersed in N,N-dimethylformamide (DMF) for ~4-5 h prior to the PXRD analysis. BMOF-1-Irdcppy was stored in CHCl$_3$ prior to the PXRD analysis. DMOF-1-dcppy and BMOF-1-dcppy were stored in ethyl acetate or THF prior to the PXRD, respectively. Approximately 20-30 mg of MOF was air dried for ~1 min prior to the PXRD analysis. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer using a LynxEye detector at 40 kV, 40 mA for Cu Kα ($\lambda$= 1.5418 Å), with a scan speed of 1 sec/step, a step size of 0.02°, 2θ range of 2-45°.

Energy Dispersive X-ray Fluorescence (EDXRF). MOFs before and after catalysis experiments were washed and stored in CHCl$_3$ (3×10 mL) for 3 d, replacing fresh CHCl$_3$ every day prior to EDXRF analysis. ~30-70 mg of MOFs was dried under vacuum at 120 °C overnight. The dried MOFs were digested with DMSO-$d_6$ (~1-2 mL) and 35% DCl in D$_2$O solution (~100-200 µL). Standard solutions (0.13 wt%, 0.29 wt%, 0.33 wt%, and 0.97 wt% of Ir) were prepared using Zn(NO$_3$)$_2$•6H$_2$O, [Ir(COD)(OCH$_3$)]$_2$, and dcppy in DMSO-$d_6$ (2 mL) and 35% DCl in D$_2$O solution (200 µL). The data was collected on a Panalytical MiniPal4 using a Rh lamp as the X-ray source.

Thermalgravimetric Analysis. Approximately 10-15 mg of MOF was dried under vacuum at 120 °C for at least 12 h prior to the analysis. Samples were analyzed under a stream of N$_2$ (10 mL/min) using a TA Instrument Q600 SDT running from room temperature to 600 °C with a ramping rate of 5 °C/min.
**Mass Spectrometry Analysis.** Electrospray ionization mass spectrometry (ESI-MS) was performed using a ThermoFinnigan LCQ-DECA mass spectrometer and the data was analyzed using the Xcalibur software suite.

**Digestion and Analysis by \(^1\)H NMR and MS.** Approximately 10 mg of MOF materials were dried under a vacuum at room temperature overnight and digested with sonication in 580 µL of DMSO-d<sub>6</sub> and 40 µL of DCl (35% aqueous solution).

**General Methods**
Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). 5-Methyl-2-(p-tolyl)pyridine (model C,N-ligand) was synthesized as described. Proton nuclear magnetic resonance spectra (\(^1\)H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz for \(^1\)H). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, \(J\), were reported in Hertz unit (Hz).

**Allylic N-alkylation of indoline using [Ir(COD)(OCH<sub>3</sub>)\]\_2.** Diallyl carbonate (67 µL, 0.47 mmol) and indoline (53 µL, 0.47 mmol) were added into a CDCl<sub>3</sub> solution (3 mL) in a 20 ml scintillation vial. [Ir(COD)(OCH<sub>3</sub>)\]\_2 (COD = 1,5-cyclooctadiene, 15.5 mg, 0.024 mmol) was added into the vial. The reaction was kept at 55 °C for 24 h. \(^1\)H NMR was used to analyze the reaction after 24 h.

**Allylic N-alkylation of indoline using [Ir(COD)(OCH<sub>3</sub>)\]\_2 and 5-methyl-2-(p-tolyl)pyridine.** [Ir(COD)(OCH<sub>3</sub>)\]\_2 (15.5 mg, 0.024 mmol) and 5-methyl-2-(p-tolyl)pyridine (model C,N-ligand, ~4.3 mg, 0.024 mmol) were dissolved in CDCl<sub>3</sub> (3 mL) in a 20 mL scintillation vial. The vial was kept at 55 °C for 24 h. Diallyl carbonate (67 µL, 0.47 mmol) and indoline (53 µL, 0.47
mmol) were added into a CDCl$_3$ solution. The reaction was kept at 55 °C for 24 h. $^1$H NMR was used to analyze the reaction after 24 h.

Control Experiments for allylic N-alkylation of Amines (indoline, 4-phenylpiperidine, and dihexylamine). For each catalysis experiment, the MOF was dried under vacuum at room temperature for ~1 min. DMOF-1-dcppy (~30 mg, ~0.08 mmol of dcppy), amine (1.6 mmol, ~20 equiv), and diallyl carbonate (1.6 mmol, ~20 equiv) were placed in 3 mL of CDCl$_3$ in a 20 mL scintillation vial. Similarly, for BMOF-1-dcppy (~65 mg, ~0.17 mmol of dcppy), amine (3.4 mmol, ~20 equiv), and diallyl carbonate (3.4 mmol, ~20 equiv) were placed in 3 mL of CDCl$_3$ in a 20 mL scintillation vial. In addition, blank reactions containing no MOF, but with identical quantities of amines and diallyl carbonate, were run in parallel. The reactions were then incubated in an isothermal oven at 55 °C for 24 h. In all of these cases, no conversion of the substrate was observed by $^1$H NMR.

Allylic N-alkylation of Indoline (1:1 mol ratio). DMOF-1-Irdcppy (~35 mg, ~0.022 mmol of Ir), indoline (49 µL, 0.44 mmol, ~20 equiv), and diallyl carbonate (63 µL, 0.44 mmol, ~20 equiv) were placed in 3 mL of CDCl$_3$ in a 20 mL scintillation vial. Similarly, BMOF-1-Irdcppy (~70 mg, ~0.023 mmol of Ir), indoline (52 µL, 0.46 mmol, ~20 equiv), and diallyl carbonate (66 µL, 0.46 mmol, ~20 equiv) were placed in 3 mL of CDCl$_3$ in a 20 mL scintillation vial. The reactions were then incubated in an isothermal oven at 55 °C. The reactions were monitored every day for 5 days using $^1$H NMR. The yields of the reactions are summarized in Figure S2.

Allylic N-alkylation of Indoline (1:10 mol ratio). DMOF-1-Irdcppy (~35 mg, ~0.022 mmol of Ir), indoline (49 µL, 0.44 mmol, ~20 equiv), and diallyl carbonate (631 µL, 4.4 mmol, ~200 equiv) were placed in 3 mL of CDCl$_3$ in a 20 mL scintillation vial. Similarly, BMOF-1-Irdcppy (~70 mg, ~0.023 mmol of Ir), indoline (52 µL, 0.46 mmol, ~20 equiv), and diallyl carbonate (660 µL, 4.6 mmol, ~200 equiv) were placed in 3 mL of CDCl$_3$ in a 20 mL scintillation vial. The reactions were then incubated in an isothermal oven at 55 °C and monitored every 2 h using $^1$H NMR. The yields of the reactions are summarized in Figure 1. The reaction was also carried out on a preparatory scale under the conditions described above using BMOF-1-Irdcppy as the catalyst and twice the amount of all reagents (including the catalyst). The desired product, 1-
allylindoline, was isolated as a colorless liquid using column chromatography (5% EtOAc in hexane). Isolated Yield: 56 mg (0.35 mmol, 80%).

*Testing Catalyst Heterogenity.* Catalysis experiments (1:10 mol ratio between indoline and diallyl carbonate) were performed as above. The MOF catalysts were removed from the reactions after 2 h by filtration. The reactions were then incubated at 55 °C and \(^{1}\)H NMR was used to characterize the reaction before and after the removal of MOF catalysts to show the heterogeneity of the catalyst (Figure 3).

*Long-term stability of DMOF-1-Irdcppy and BMOF-1-Irdcppy.* DMOF-1-Irdcppy or BMOF-1-Irdcppy was stored in CHCl\(_3\) for 2 months. The MOFs were then used for allylic N-alkylation of indoline (1:10 mol ratio between indoline and diallyl carbonate) as above. The catalysis reactions reached completion after ~30 h for DMOF-1-Irdcppy and ~8 h for BMOF-1-Irdcppy.

*Comparison the catalytic activity between homogeneous and BMOF-1-Irdcppy for the allylic N-alkylation of indoline.* BMOF-1-Irdcppy (~70 mg, ~0.023 mmol of Ir), indoline (129 µL, 1.15 mmol, ~50 equiv), and diallyl carbonate (131 µL, 1.15 mmol, ~50 equiv) were placed in 3 mL of dry tetrahydrofuran (THF) in a 100 mL schlenk tube under Ar atmosphere. The reactions were then incubated at 55 °C. The catalysis reaction reached completion after ~25 h. Under identical condition, homogeneous Ir catalysts can convert indoline quantitatively ranging in 2 h to 36 h depending on the co-ligands.

*Allylic N-alkylation of 4-Phenylpiperidine (1:10 mol ratio).* BMOF-1-Irdcppy (~70 mg, ~0.023 mmol of Ir), 4-phenylpiperidine (74 mg, 0.46 mmol, ~20 equiv), and diallyl carbonate (660 µL, 4.6 mmol, ~200 equiv) were placed in 3 mL of CDCl\(_3\) in a 20 mL scintillation vial. The reaction was incubated in an isothermal oven at 55 °C. After 24 h, the reaction was characterized via \(^{1}\)H NMR and GC-MS and the yield was determined to be >95% by GC-MS.

*Allylic N-alkylation of Dihexylamine (1:10 mol ratio).* BMOF-1-Irdcppy (~70 mg, ~0.023 mmol of Ir), dihexylamine (107 µL, 0.46 mmol, ~20 equiv), and diallyl carbonate (660 µL, 4.6 mmol, ~200 equiv) were placed in 3 mL of CDCl\(_3\) in a 20 mL scintillation vial. The reactions were then
incubated in an isothermal oven at 55 °C. After 24 h, the reaction was characterized via $^1$H NMR and ESI-MS and the yield was determined to be >95% by $^1$H NMR.

**Reusability of MOF Catalysts toward Allylic N-alkylation of Indoline with re-isolation of the catalyst under ambient condition.** After the completion of the first catalytic cycle (1:10 mol ratio between indoline and diallyl carbonate) using BMOF-1-Irdcppy, the catalyst was rinsed with CHCl$_3$ (3 × 10 mL) everyday for 3 days prior to the next cycle. The second catalytic cycle was performed under the same conditions as the first cycle. However, the yield of the catalysis reaction only reached ~30% even after 3 days of incubation.

**Thermal Stability.** DMOF-1-Irdcppy (~35 mg, ~0.022 mmol of Ir) in CDCl$_3$ (3 mL) and diallyl carbonate (631 µL, 4.44 mmol, ~200 equiv) were incubated separately at 55 °C for 24 h. The diallyl carbonate and indoline (49 µL, 0.44 mmol, 20 equiv) were then added into the vial containing DMOF-1-Irdcppy. The reaction was incubated at 55 °C and reached completion after ~30 h. Similar catalysis experiment was performed using BMOF-1-Irdcppy and the reaction reached completion after ~8 h.

**Product and Substrate Inhibition Experiments.** Pristine DMOF-1-Irdcppy (~35 mg, ~0.022 mmol of Ir) or BMOF-1-Irdcppy (~70 mg, ~0.023 mmol of Ir) was immersed in a CDCl$_3$ (3 mL) containing ~200 equiv of diallyl carbonate and 20 equiv of 1-allylindoline. To this solution was added indoline (20 equiv) and the reaction was incubated at 55 °C. The reaction reached completion after ~30 h (DMOF-1-Irdcppy) or ~8 h (BMOF-1-Irdcppy).

**Reusability of MOF Catalysts toward Allylic N-alkylation of Indoline without re-isolation of the catalyst.** After the completion of the first catalytic cycle (1:10 mol ratio between indoline and diallyl carbonate) using BMOF-1-Irdcppy, indoline (~20 equiv) was added into the reaction mixture. The reaction was then kept at 55 °C and monitored every day for 3 days by $^1$H NMR. The yield of the reaction after 3 days is ~65%.

**Catalyst Pre-saturatation Experiment.** BMOF-1-Irdcppy (~70 mg, ~0.023 mmol of Ir) was incubated for 24 h with either 100 (330 µL, 2.3 mmol) or 200 equiv of diallyl carbonate (660 µL,
4.6 mmol, 200 equiv) in CDCl₃ (3 mL) at 55 °C. After 24 h, indoline (52 µL, 0.46 mmol, 20 equiv) was added into each reaction. The reaction mixtures were incubated at 55 °C and monitored every day for 3 d using ^1^H NMR. The yields of these reactions are summarized in Table S3.

Reusability of MOF Catalysts toward Allylic N-alkylation under Ar atmosphere. The first catalytic cycle (1:10 mol ratio between indoline and diallyl carbonate) using BMOF-1-Irdeppy was performed under Ar atmosphere and in dry CHCl₃. After the completion of the first cycle, the catalyst was rinsed with dry CHCl₃ (3×10 mL) everyday for 3 days under an Ar atmosphere prior to the next cycle. The second and third catalytic cycles were performed under identical conditions as the first cycle. The yields of the second and the third cycle are >90% after ~16 h.
Figure S1. $^1$H NMR of a 1:1 mole solution of indoline and diallyl carbonate (red), after incubation at 55 °C for 24 h (blue), with BMOF-1-dcppy (green), with BMOF-1-Irdcppy (black), and the corresponding functionalized indoline separated from the reaction (magenta).
Figure S2. ESI-MS(+) analysis of the reaction solution of the allylic N-alkylation of indoline using DMOF-1-Irdcppy at 55 ºC after 24 h (top), and ESI-MS(+) analysis (bottom) of the reaction solution catalyzed by homogeneous [Ir(COD)(OCH₃)]₂ and 5-methyl-2-(p-tolyl)pyridine under the similar conditions and the proposed structures of the observed by-products.
**Figure S3.** Picture of crystals of DMOF-1-Irdcppy (~1.8×0.4×0.4 mm, $V_{\text{crystal}} \approx 0.3 \text{ mm}^3$) and BMOF-1-Irdcppy (~1.8×0.4×0.2 mm, $V_{\text{crystal}} \approx 0.2 \text{ mm}^3$) after 2 months of storage showing the similar crystal sizes and the homogeneous crystallites.
Figure S4. $^1$H NMR analysis of the allylic $N$-alkylation of indoline using DMOF-1-Irdcppy (black), [Ir(COD)(OCH$_3$)$_2$] (red), and [Ir(COD)(OCH$_3$)$_2$] with 5-methyl-2-(p-tolyl)pyridine (blue).
Figure S5. PXRD of DMOF-1-Irdecppy as synthesized (black) and after 2 months stored in CHCl₃ at ambient conditions (red). BMOF-1-Irdecppy as synthesized (blue) and after 2 months stored in CHCl₃ at ambient conditions (green).
Figure S6. PXRD of DMOF-1-dcppy (black), DMOF-1-dcppy after catalysis (no reaction observed, red), BMOF-1-dcppy (blue), and BMOF-1-dcppy after allylic N-alkylation of indoline reaction (green).
Figure S7. Thermalgravimetric analysis of DMOF-1-Irdcppy (solid blue line) after the first catalytic cycle (solid green line), and after the second cycle (solid red line). BMOF-1-Irdcppy (dotted black line) after the first catalytic cycle (dotted grey line), and after the second catalytic cycle (dotted cyan line).
Figure S8. $^1$H NMR of a 1:1 mol ratio solution of 4-phenylpiperidine and diallyl carbonate (black), after incubation at 55 °C for 24 h (red), with BMOF-1-dcppy (blue), and with BMOF-1-Irdcppy (green), showing new protons’ environments correspond to the product. Yield of this reaction was determined using GC-MS.
Figure S9. ESI-MS of the allylic N-alkylation of 4-phenylpiperidine using BMOF-1-Irdeppy after 24 h at 55 °C.
Figure S10. $^1$H NMR of a 1:1 mol ratio solution of dihexylamine and diallyl carbonate (black), after incubation at 55 °C for 24 h (red), with BMOF-1-dcppy (blue), and with BMOF-1-Ir_dcppy (green). The reaction yield was determined based on the annotated protons.
**Figure S11.** ESI-MS of the allylic N-alkylation of dihexylamine using BMOF-1-Irdcppy after 24 h at 55 °C.
Figure 12. PXRD of BMOF-1-dcppy (black), BMOF-1-dcppy after catalysis (no reaction observed, red), BMOF-1-Irdcppy (blue), BMOF-1-Irdcppy after the allylic N-alkylation of 4-phenylpyridine (green), and BMOF-1-Irdcppy after the allylic N-alkylation of dihexylamine (magenta).
Figure S13. $^1$H NMR analysis of diallyl carbonate, showing the thermal stability of the substrate.
**Figure S14.** FT-IR spectra of BMOF-1-dcppy (black), BMOF-1-Irdcppy after the completion of the first cycle without the re-isolation process (magenta) and with the re-isolation process (blue, showing the weak vibrational signal at ~2000 cm$^{-1}$, red star), and the reaction solution (green).
Figure S15. $^1$H NMR of a mixture of substrates and products (red). Digested BMOF-1-Irdecppy after one catalytic cycle (blue, no rinsing) and after re-isolation with extensive CHCl$_3$ washing (black). Black arrows highlight trace amounts of products remaining in the MOF catalysts.
Table S1. Yields of the catalysis reactions using DMOF-1-dcppy, DMOF-1-Irdeppy, BMOF-1-dcppy, and BMOF-1-Irdeppy.

<table>
<thead>
<tr>
<th>MOFs/ Duration</th>
<th>1 day\textsuperscript{b}</th>
<th>3 days\textsuperscript{b}</th>
<th>5 days\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMOF-1-dcppy</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>DMOF-1-Irdeppy\textsuperscript{a}</td>
<td>32%</td>
<td>53%</td>
<td>69%</td>
</tr>
<tr>
<td>BMOF-1-dcppy</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>BMOF-1-Irdeppy\textsuperscript{a}</td>
<td>37%</td>
<td>57%</td>
<td>62%</td>
</tr>
</tbody>
</table>

\textsuperscript{a} \textasciitilde 5 mol\% of Ir, 1:1 mol ratio between indoline and diallyl carbonate, 55 °C.

\textsuperscript{b} The yields were determined using \textsuperscript{1}H NMR.

Table S2. Ir content of MOFs before and after allylic \textit{N}-alkylation of indoline determined using EDXRF spectroscopy.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>Before Catalysis Experiment\textsuperscript{a}</th>
<th>After Catalysis Experiment\textsuperscript{b}</th>
<th>Reaction solution\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMOF-1-Irdeppy</td>
<td>11.6\pm0.3 wt%</td>
<td>11.5\pm0.5 wt%</td>
<td>Not detected</td>
</tr>
<tr>
<td>BMOF-1-Irdeppy</td>
<td>6.4\pm0.2 wt%</td>
<td>6.4\pm0.1 wt%</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The results were calculated from three independent measurements.

\textsuperscript{b} The results were calculated from two independent measurements.

Table S3. Ir content of BMOF-1-Irdeppy before and after allylic \textit{N}-alkylation of 4-phenylpiperidine and dihexylamine using EDXRF spectroscopy.

<table>
<thead>
<tr>
<th>Before catalysis\textsuperscript{a}</th>
<th>After allylic \textit{N}-alkylation of 4-phenylpiperidine</th>
<th>After allylic \textit{N}-alkylation of dihexylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4\pm0.2 wt%</td>
<td>6.3 wt%</td>
<td>6.4 wt%</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The results were calculated from two independent measurements.
Table S4. Yields of the pre-saturated MOF catalysts with diallyl carbonate catalysis experiments.

<table>
<thead>
<tr>
<th>Equiv of diallyl carbonate</th>
<th>Yield after 24 h</th>
<th>Yield after 72 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 equivalents</td>
<td>~36%</td>
<td>~67%</td>
</tr>
<tr>
<td>200 equivalents</td>
<td>~56%</td>
<td>~90%</td>
</tr>
</tbody>
</table>

Reference