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Electronic Supplementary Information

Efficient and recyclable copper-based MOFs-catalyzed N-arylation of N-containing heterocycles with aryliodides

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1. General methods

All the reactions were carried out under air using magnetic stirring unless otherwise noted. ¹H NMR spectral and ¹³C NMR were recorded on a Bruker Advance III HD 400 instrument using TMS as internal standard and CDCl₃ as solvent. Mass spectra were recorded on GC-MS (Agilent 7890A/5975C) instrument under EI model. Column chromatography was performed with silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., Ltd. All the other reagents were of analytical grade quality, purchased commercially and used as received.

2. Synthesis and the characterization of MOF-199

Benzene-1,3,5-tricarboxylic acid (4.91 g, 0.0234 mol) was dissolved into ethanol (25 ml), and Cu(NO₃)₂ \cdot 2.5H₂O (10.86 g, 0.0466 mol) was dissolved into water (25 ml). The two solutions were mixed at ambient temperature for 30 min, and the mixture was transferred into an autoclave. The autoclave was heated at temperature 383 K, under hydrothermal conditions for 18 h. The reaction vessel was cooled to ambient temperature, and blue crystals of MOF-199 were isolated by filtration, and washed with water. The product was dried at 383 K overnight. The yield was quantitative (8 g).^[12]





Scheme 1. SEM images of MOF-199



Scheme 2. XRD pattern of MOF-199



Scheme 3. IR spectrogram of the MOF-199.

3. General procedure for MOF-199 catalyzed *N*-arylation of heterocycles with aryl iodides

To a 10 mL of sealed tube was added MOF-199 (0.05 mmol), aryl halides (0.50 mmol), *N*-containing heterocycles (0.75 mmol), NaOH (1.0 mmol) and DMSO (1 mL). The reaction mixture was reacted at 120 °C in a preheated oil bath for 12 h. The reaction mixture was cooled to room temperature, extracted with ethyl acetate (20 mL×3). The combined organic phases was washed with water and brine, dried over anhydrous Na₂SO₄, and concentrated in *vacuo*. The residue was purified by flash column chromatograph on silica gel (ethyl acetate/petroleum ether as the eluent) to

afford the target product **3a-3z**.

4. Recycling of the catalyst MOF-199

After completion of the first run, the reaction mixture was cooled to room temperature, and the MOF-199 catalyst was separated from the reaction mixture by simple centrifugation, washed with copious amounts of H₂O, ethyl acetate and ethyl alcohol, and dried 100 $^{\circ}$ C under vacuum in 6 h. The recovered MOF-199 catalyst was then reused as catalyst in further transformation under identical conditions. The process was then repeated.

5. The NMR spectra data of the products

1-(*p*-Tolyl)-1*H*-pyrrole (3a)^[1]

96% yield for 4-iodotoluene and 10 % for 4-bromotoluene.

¹H NMR (400 MHz, CDCl₃) δ: 7.30-7.34 (m, 2H), 7.25 (dd, J = 8.6, 0.5 Hz, 2H), 7.06-7.12 (m, 2H), 6.32-6.40 (m, 2H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 138.6, 135.5, 130.2, 120.7, 119.5, 110.2, 21.0. GC-MS: m/z = 157 [M]⁺

1-phenyl-1*H*-pyrrole (3b)^[1]

93% yield.

¹H NMR (400 MHz, CDCl₃): δ: 7.39-7.45 (m, 4H), 7.24-7.27 (m, 1H), 7.10 (t, *J* = 2.2 Hz, 2H), 6.36 (t, *J* = 2.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 140.9, 129.7, 125.8, 120.7, 119.5, 110.5.

GC-MS: $m/z = 143 [M]^+$

1-(4-Methoxyphenyl)-1*H*-pyrrole (3c)^[1]

97% yield.

¹H NMR (400 MHz, CDCl₃) δ: 7.32-7.34 (m, 1H), 7.30-7.31 (m, 1H), 7.01 (t, J = 2.2 Hz, 2H), 6.96-6.97 (m, 1H), 6.93-6.95 (m, 1H), 6.33 (t, J = 2.2 Hz, 2H), 3.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 157.8, 134.6, 122.3, 119.8, 114.8, 110.0, 55.7. GC-MS (m/z):173 [M]⁺ 1-([1,1'-Biphenyl]-4-yl)-1*H*-pyrrole (3d)^[3]

95% yield.

¹H NMR (400 MHz, CDCl₃) δ: 7.60-7.67 (m, 4H), 7.47 (t, J = 8.0 Hz, 4H), 7.37 (t, J = 8.0 Hz, 1H), 7.15 (td, J = 2.2, 0.7 Hz, 2H), 6.38-6.39 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 140.3, 140.1, 138.6, 129.0, 128.3, 127.5, 127.0, 120.8, 119.4, 110.7.

GC-MS (m/z):219 [M]⁺

1-(3,5-Dimethylphenyl)-1*H*-pyrrole (3e)^[4]



95% yield.

¹H NMR (400 MHz, CDCl₃) δ : 7.13 (t, J = 2.2 Hz, 2H), 7.08 (t, J = 0.5 Hz, 2H), 6.94-6.95 (m, 1H), 6.38-6.40 (m, 2H), 2.42 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ: 140.9, 139.4, 127.4, 119.5, 118.6, 110.2, 21.5.

GC-MS (m/z):171 [M]⁺

1-(4-Chlorophenyl)-1*H*-pyrrole (3f)^[2]

72% yield.

¹H NMR (400 MHz, CDCl₃) δ: 7.37-7.41 (m, 2H), 7.31-7.34 (m, 2H), 7.05 (t, J = 2.2 Hz, 2H), 6.36 (t, J = 2.2 Hz, 2H).

¹³C NMR (100 MHz, CDCl₃) δ: 139.4, 131.2, 129.8, 121.8, 119.4, 111.0.

GC-MS (m/z):177 [M]⁺

1-phenyl-1*H*-indole (3g)^[5]



80% yield.

¹H NMR (400 MHz, CDCl₃) δ: 7.75-7.78 (m, 1H), 7.62-7.66 (m, 1H), 7.57 (dd, J = 4.2, 0.6 Hz, 4H), 7.40-7.43 (m, 2H), 7.22-7.30 (m, 2H), 6.76 (dt, J = 3.2, 1.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 140.0, 136.0, 129.7, 129.4, 128.1, 126.6, 124.5, 122.5, 121.2, 120.5, 110.6, 103.7.

GC-MS (m/z):193 [M]⁺

1-(*p*-Tolyl)-1*H*-indole (3h)^[5]



79% yield for 4-iodotoluene and 15 % for 4-bromotoluene.

¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.34-7.36 (m, 3H), 7.19-7.28 (m, 2H), 6.71-6.72 (m, 1H), 2.47 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ: 137.4, 136.4, 136.1, 130.3, 129.3, 128.2, 124.4, 122.3, 121.2, 120.3, 110.6, 103.3, 21.2.

 $GC-MS(m/z):207[M]^+$

1-(4-Methoxyphenyl)-1*H*-indole (3i)^[5]

87% yield.

¹H NMR (400 MHz, CDCl₃) δ: 7.69 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.16-7.26 (m, 3H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.65-6.66 (m, 1H), 3.83 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ: 158.3, 136.4, 132.9, 129.1, 128.4, 126.0, 122.2, 121.1, 120.2, 114.8, 110.5, 103.0, 55.7. GC-MS (m/z):223 [M]⁺

1-(4-Chlorophenyl)-1*H*-indole (3j)^[6]



84% yield.

¹H NMR (400 MHz, CDCl₃) δ: 7.79 (d, *J* = 8.4 Hz, 1H), 7.60 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.47-7.55 (m, 4H), 7.26-7.36 (m, 3H), 6.78 (dd, *J* = 3.2, 0.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ: 138.4, 135.8, 132.0, 129.9, 129.4, 127.8, 125.6, 122.7, 121.4, 120.7, 110.4, 104.2.

GC-MS (m/z):227 $[M]^+$

1-(4-Nitrophenyl)-1*H*-indole (3k)^[5]



50% yield.

¹H NMR (400 MHz, CDCl₃) δ : 8.41 (d, J = 9.2 Hz, 2H), 7.65-7.72 (m, 4H), 7.39 (d, J

= 3.6 Hz, 1H), 7.22-7.32 (m, 2H), 6.78 (dd, *J* = 3.6, 0.8 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ: 145.3, 145.1, 135.3, 130.2, 127.2, 125.6, 123.5, 123.4, 121.8, 121.7, 110.6, 106.3.

GC-MS (m/z):238 [M]⁺

1-([1,1'-Biphenyl]-4-yl)-1*H*-indole (31)^[5]



82% yield.

¹H NMR (400 MHz, CDCl₃) δ : 7.58-7.76 (M, 8H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.38-7.42 (m, 2H), 7.18-7.28 (m, 2H), 6.72 (dd, *J* = 3.2, 0.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ : 140.3, 139.4, 139.1, 135.9, 129.5, 129.0, 128.3, 128.0, 127.6, 127.2, 124.6, 122.6, 121.3, 120.6, 110.7, 103.9. GC-MS (m/z):269 [M]⁺

5-methoxy-1-(*p*-Tolyl)-1*H*-indole (3m)^[5]



92% yield.

¹H NMR (400 MHz, CDCl₃) δ: 7.53-7.58 (m, 1H), 7.44-7.46 (m, 2H), 7.36-7.39 (m, 3H), 7.25-7.28 (m, 1H), 6.99-7.03 (m, 1H), 6.69-6.72 (m, 1H), 3.97 (s, 3H), 2.51 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ: 154.6, 137.5, 136.1, 131.3, 130.2, 129.8, 128.5, 124.0, 112.4, 111.4, 103.0, 102.7, 55.9, 21.1.

GC-MS (m/z): 237 $[M]^+$

5-bromo-1-(*p*-Tolyl)-1*H*-indole (3n)^[7]



66% yield.

¹H NMR (400 MHz, CDCl₃) δ : 7.84 (d, J = 2.0 Hz, 1H), 7.41 (d, J = 8.8 Hz, 1H),

7.30-7.38 (m, 6H), 6.63 (dd, *J* = 3.2, 0.4 Hz, 1H), 2.47 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ: 136.9, 134.8, 130.9, 130.4, 129.3, 125.1, 124.4, 123.6,

113.5, 112.1, 102.8, 100.0, 21.2.

GC-MS (m/z): 286 [M]⁺

1-phenyl-1*H*-1,2,4-triazole (30)^[8]



92% yield.

¹H NMR (400 MHz, CDCl₃) δ: 8.55 (s, 1H), 8.09 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 152.6, 140.9, 137.0, 129.8, 128.3, 120.1.

GC-MS (m/z):145 [M]⁺

1-(*p*-Tolyl)-1*H*-1,2,4-triazole (3*p*)^[8]



67% yield for 4-iodotoluene and 13 % for 4-bromotoluene.

¹H NMR (400 MHz, CDCl₃) δ: 8.50 (s, 1H), 8.08 (s, 1H), 7.52-7.56 (m, 2H), 7.29 (d,

J = 8.4 Hz, 2H), 2.40 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ: 152.5, 140.9, 138.4, 134.8, 130.4, 120.2, 21.2.

GC-MS (m/z):159 [M]⁺

1-(4-Methoxyphenyl)-1*H*-1,2,4-triazole (3q)^[9]



83% yield.

¹H NMR (400 MHz, CDCl₃) δ : 8.63 (s, 1H), 8.11 (s, 1H), 7.59 (d, J = 8.8 Hz, 2H),

7.01 (d, *J* = 9.2 Hz, 2H), 3.86 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ: 159.7, 151.9, 140.8, 130.4, 122.0, 115.0, 55.8.

GC-MS (m/z): 175 [M]⁺

1-(3,5-Dimethylphenyl)-1*H*-1,2,4-triazole (3r)



73% yield.

¹H NMR (400 MHz, CDCl₃) δ : 8.49 (s, 1H), 8.04 (t, J = 2.2 Hz, 1H), 7.24-7.25 (m, 2H), 6.98 (s, 1H), 2.34 (s, 6H). ¹³C NMR (100 MHz, CDCl) δ : 152.2, 140.8, 130.6, 136.8, 120.7, 117.7, 21.2

¹³C NMR (100 MHz, CDCl₃) δ: 152.2, 140.8, 139.6, 136.8, 129.7, 117.7, 21.2.

GC-MS (m/z):173 $[M]^+$

1-(4-Chlorophenyl)-1*H*-1,2,4-triazole (3s)^[9]



90% yield.

¹H NMR (400 MHz, CDCl₃) δ: 8.54 (s, 1H), 8.10 (s, 1H), 7.61-7.65 (m, 2H), 7.46-7.50 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ: 152.9 , 140.9, 135.6, 134.0, 130.0, 121.3.

GC-MS (m/z):179 [M]⁺

1-(4-Nitrophenyl)-1*H*-1,2,4-triazole (3t)^[8]



56% yield.

¹H NMR (400 MHz, CDCl₃) δ: 8.72 (s, 1H), 8.37-8.41 (m, 2H), 8.15 (s, 1H), 7.90-7.94 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ: 153.6, 146.9, 141.4, 135.3, 125.7, 120.0.

GC-MS (m/z): 190 $[M]^+$

1-([1,1'-Biphenyl]-4-yl)-1*H*-1,2,4-triazole (3u)^[10]



94% yield.

¹H NMR (400 MHz, CDCl₃) δ: 8.60 (s, 1H), 8.13 (s, 1H), 7.72-7.77 (m, 4H), 7.60-7.63 (m, 2H), 7.46-7.50 (m, 2H), 7.37-7.42 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ: 152.8, 141.4, 141.0, 139.8, 136.2, 129.1, 128.5, 128.0, 127.2, 120.5.

GC-MS (m/z):221 [M]⁺

1-(4-(1*H*-1,2,4-Triazol-1-yl)phenyl)ethanone (3v)^[11]



50% yield.

¹H NMR (400 MHz, CDCl₃) δ: 8.66 (s, 1H), 8.14 (s, 1H), 8.09-8.13 (m, 2H), 7.80-7.83 (m, 2H), 2.64 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ: 196.6, 153.2, 141.2, 140.2, 136.5, 130.3, 119.6, 26.8. GC-MS (m/z):187 [M]⁺

1-phenyl-1*H*-imidazole (3w)^[2]

85% yield.

¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.27 (s, 1H), 7.74 (s, 1H), 7.65 (dd, *J* = 8.6, 0.6 Hz, 2H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.13 (s, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ: 136.9, 135.5, 130.0, 129.8, 126.8, 120.3, 118.0.

 $GC-MS(m/z):144[M]^+$

1-(*p*-Tolyl)-1*H*-imidazole (3x)^[2]



88% yield for 4-iodotoluene and 38 % for 4-bromotoluene.

¹H NMR (400 MHz, DMSO- d_6) δ : 8.21 (s, 1H), 7.69 (s, 1H), 7.52 (d, J = 8.4 Hz, 2H),

7.30 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 1H), 2.33 (s, 3H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ: 136.2, 135.4, 134.6, 130.2, 129.7, 120.2, 118.0, 20.4.

GC-MS (m/z):158 [M]⁺

1-(4-Methoxyphenyl)-1*H*-imidazole (3y)^[2]



73% yield.

¹H NMR (400 MHz, CDCl₃) δ: 7.76 (s, 1H), 7.27-7.31 (m, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 6.95-6.99 (m, 2H), 3.84 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ: 159.0, 136.0, 130.8, 130.1, 123.3, 118.9, 115.0, 55.7. GC-MS (m/z):174 [M]⁺

1-(4-Chlorophenyl)-1*H*-imidazole (3z)^[2]



85% yield.

¹H NMR (400 MHz, CDCl₃) δ : 7.85 (s, 1H), 7.43 (dd, J = 8.8, 2.4 Hz, 2H), 7.26-7.33 (m, 4H).

¹³C NMR (100 MHz, DMSO-*d*₆) δ: 135.8, 134.9, 131.0, 130.1, 129.7, 122.0, 118.2. GC-MS (m/z):178 [M]⁺

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6. Copies of ¹H NMR and ¹³C NMR spectra

1-(*p*-Tolyl)-1*H*-pyrrole (3a)





1-(4-Methoxyphenyl)-1*H*-pyrrole (3c)





1-(3,5-Dimethylphenyl)-1*H*-pyrrole (3e)







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

1-phenyl-1*H*-indole (3g)









210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



1-(4-Nitrophenyl)-1*H*-indole (3k)







5-bromo-1-(p-Tolyl)-1H-indole (3n)



1-phenyl-1*H*-1,2,4-triazole (30)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

1-(*p*-Tolyl)-1*H*-1,2,4-triazole (3p)



1-(4-Methoxyphenyl)-1*H*-1,2,4-triazole (3q)





1-(3,5-Dimethylphenyl)-1*H*-1,2,4-triazole (3r)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

1-(4-Chlorophenyl)-1*H*-1,2,4-triazole (3s)



1-(4-Nitrophenyl)-1*H*-1,2,4-triazole (3t)







1-phenyl-1*H*-imidazole (3w)



1-(*p*-Tolyl)-1*H*-imidazole (3x)



1-(4-Methoxyphenyl)-1*H*-imidazole (3y)



1-(4-Chlorophenyl)-1*H*-imidazole (3z)

