SUPPORTING INFORMATION FOR

Recyclable Bimetallic CuMoO₄ Nanoparticle for *C-N* Cross-Coupling Reaction Under Mild Condition

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GENERAL INFORMATION

1,4-Dioxane (99.8%), DMSO (99.9%), Toluene (99.8%), DMF (99.8%), t-BuOH (99.5%), Acetonitrile (99.8%) and Deuteriated NMR solvents CDCl₃ (99.8%) CD₃CN (99.8%) is purchased from Sigma-Aldrich. All other solvents is purchased from Merck of high purity grade. DMSO and acetonitrile was sparged with nitrogen (N₂) for 5 min at room temperature and stored under nitrogen atmosphere. All haloarenes such as Iodobenzene (98%), 4-Methoxyiodobenzene (98%), 4-Methyliodobenzene (99%), Bromobenzene (98%), 4-Bromoacetophenone (99%), 4-Chloroacetophenone (99%), 4-nitroiodobenzene (98%), 4-bromoiodobenzene (98%), Chlorobenzene (99.8%) and all amines such as Aniline (99.5%), p-Anisidine(99%), o-Anisidine (99%), o-Toluidine (99%), 2-nitroaniline(98%), 4-nitroaniline(98%), 4-bromoaniline (97%), 4-iodooaniline (98%), N-ethylaniline(98%), Indole(99%), Mopholine (99.5%) Piperidine (99.5%), 3-chloroaniline(99%), 4-chloroaniline (98%), metals such as **CuCl₂** 2H₂O (99.99%), (**NH**₄)₆ **Mo**₇**O**₂₄.**4**H₂**O** (99.98%), and Cs₂CO₃ (*ReagentPlus®*, 99%) and KOH (99%), K₂CO₃ (99%), KO¹Bu(99%) was purchased from Sigma-Aldrich. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath

The ¹H and ¹³C NMR spectra were recorded at 300 MHz, 400 MHz or 500 MHz for ¹H or at ⁷⁵MHz, ¹⁰⁰MHz or ¹²⁵MHz for ¹³C NMR, respectively. Deuterated solvents were purchased from Sigma-aldrich and used as received. All ¹H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvents. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets...etc, br = broad), coupling constant (Hz) and integration. All ¹³C NMR spectra are reported in ppm relative to CDCl₃ (77.0 ppm). 1,4-diiodobenzene was used as an internal standard for NMR yields from proton analysis for the C-S bond formation reaction. Elemental analysis is performed in 2400 Series II CHNS/O analyzer in CHNS mode. Flash column chromatography was performed by using a 90-120 times weight excess of flash silica gel 60-120 μ m from Aldrich. Fractions were analyzed by TLC using TLC silica gel F254 250 μ m precoated-plates from Merck and permanganate stain was used for UV-inactive compounds. Melting point is determined in Digital melting point apparatus, Electronics India (EI)-2935 model; Visualized through LCD Screen and is uncorrected by ±5 °C. Sample purity was determined using 2,4,6-trimehoxybenzene, Internal Standard. XPS is with Al-K α line at IIT Roorke. HRMS is done at University of Hydrabad in ESI mode.

The Synthesis of Bimetallic CuMoO₄ Nanoparticles

1gm of (NH₄)₆Mo₇O₂₄.4H₂O (Purchased from Sigma-aldrich, 99.98%),dissolved in 150 ml distilled water and (1.19 gm) of CuCl₂ 2H₂O(Purchased from Sigma-aldrich 99.99%) dissolved in 150 ml distilled water, respectively. Then CuCl₂ 2H₂O solution was heated at 50 °C for 10 min and finally the ammonium molybdate solution was added drop wise to this solution. After adding all the solution the color becomes green. The solution was heated at 50 °C for 10 minute. Subsequently 10 mL of 2M NaOH solution is added drop wise. Precipitate starts forming after adding 1-2 ml NaOH. Addition of NaOH is continued till the pH of the solution is 8. Now the above precipitate in solution is treated with ultrasonic irradiation with power 100W for 20 minute. The greenish white precipitate was formed and filtered with whatman filter paper 42, washed with distilled water and ethanol several times.

Figure-1: Clear aqueous solution of both	Figure-2: Precipitate after adding 2 ml 2M	Figure-3: Precipitate after adding 5 ml 2M
before mixing them	NaOH	NaOH



Catalyst Characterization

The catalyst obtained was dried at 100° C for 60minute. The catalyst was characterized in TEM, SEM, IR and XPS. The particle looks like clay structure with thickness range 13-25 nm and 30-11 nm in length from SEM. The X-ray photoelectron Spectroscopy (XPS) shows that Cu is in +2 (1/2 spin) and Mo is in +6 (5/2 spin) oxidation state, where as most of the molybedenum metal is in +6 state (See Figure 12a-d) ^[1]. The IR value spectra shows there is no direct metal-metal Mo-Cu bond but instead a Cu-O-Mo (IR 817.82 cm⁻¹) bond is there. Along with this (Figure 10) Mo-O (524.6, 420 cm⁻¹); Mo=O bond 960 cm⁻¹ Cu-O (636.5, 584.4, 504.3 cm⁻¹), Cu-O-Mo (817.82, 950.91, 453.36 cm⁻¹)^[2-4]

Reference:

- 1. N. Joseph, J. Varghese, T. Siponkoski, M. Teirikangas, M. T. Sebastian, H. Jantunen, ACS Sustainable Chem. Eng. 2016, 4, 5632
- 2. J. Baek, A. S. Sefat, D. Mandrus, and P. S. Halasyamani, Chem. Mater 2008, 12, 3786.
- 3. K Seevakan, A Manikandan, P Devendran, Y Slimani, A Baykal, T Alagesan Ceramics International 2018, 44, 20075
- 4. P. Santhiyadevi, K. Buvaneswari, J. Nanosci. Tech. 2018, 4, 415





Figure 8: EDXRF of CuMoO₄ nanoparticle in SEM

Element	Арр	Intensity	Weight%	Weight%	Atomic%	
	Conc.	Corrn.		Sigma		
ОК	22.45	0.7942	31.06	0.79	68.49	
Cu L	15.36	0.5144	32.83	0.77	18.23	
Mo L	26.42	0.8041	36.11	0.83	13.28	
Totals			100.00			



Figure 9: IR spectra of original CuMoO₄ nanoparticle



Figure 9a: Expanded version of IR spectra of original CuMoO₄ nanoparticle

X-RAY PHOTOELECTRON Spectra of CuMoO4 catalyst

Al mono 24.6 W 100.0 _ 45.0 _ 55.00 eV





Figure 11: XPS Spectra of MO⁺⁶ of Original Catalyst

General experimental set up and procedure

An oven dried 25 mL of 3-necked round bottom flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with 2.6 mol% CuMoO₄ nanoparticle (3 mg), 1 mL DMSO, amine (0.5 mmol), haloarene (0.55 mmol), base Cs_2CO_3 (194 mg, 1.2 eq.). The reaction mixture was evacuated and purged with inert gas (N₂) three times. The reaction mixture was then placed into an oil bath with stirring maintained at 90°C. The three necked flask is equipped with condenser in One neck, N₂ ballon in second neck and third neck was stopped with Teflon cork. The reaction is monitored after every 2 hr with the help of TLC and KMnO₄ Stain. After the time specified in the reaction schemes, the reaction mixture was worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes). All yields are reported after column chromatography.

Recyclability Test:

After the time specified in the reaction schemes, the reaction mixture was worked up with ethylacetate and water (20×5) ml. The organic layer was separated. The nanoparticles are seen at the Junction of two layer. The water layer is filtered in the Whatmann filter paper-40. The nanoparticles on the filter paper is dried with suction pump followed by 100 °C in Oven for 2h. IR and XPS spectra of catalyst reveals the same peak after the catalyst is recovered (IR and XPS spectra, Fig. 12,13-14). The recovered catalyst is subjected to further reaction of fresh batch of amines and haloarene in presence of 1.2 equiv. of Cs₂CO₃. The reaction proceeded with>80% of yield under similar condition. The catalyst has been tested for another two cycles for catalyzing the reaction.



SI No	Runs	Catalyst	Recovered catalyst	Yield(%) ^{a,b}
1	First	6 mg	5 mg	88
2	Second	5 mg	4 mg	83
3	Third	4 mg	3 mg	80

^aCatalyst 2.6 mol% (6 mg), amine (1 mmol), iodobenzene (1.1 mmol),

Base 1.2 equiv. were stirred for 24 h; ^bisolated yield.



Figure 12: IR of recovered CuMoO₄ catalyst after reaction

X-RAY PHOTOELECTRON Spectra of Recycled CuMoO4 catalyst

Al mono 24.6 W 100.0 _ 45.0 _ 55.00 eV





Figure 14: XPS Spectra of Mo^{+6} of Recycled Catalyst

MECHANISIM: In nanocluster; copper is believed to play an important role along with molybdenum. Electron rich nanocluster is stabilised by DMSO solvent. The catalyst **a** undergoes oxidative addition of PhI to form precursor complex **b**. Subsequently it is converted to complex **c** with amine and base. Further, reductive elimination of *C-N* cross-coupled product regenerates the catalyst **a** (Scheme 15). The positive charge developed at complex **b** and **c** is anticipated to be stabilized by nanocluster.



Figure 15. Proposed Mechanism by CuMoO₄ Bimetallic nanoparticles

Metal Leaching Test:

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this aniline **2a** (46 mg, 0.5 mmol), Cs₂CO₃ (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After 12h, when 40% conversion is done, the reaction mixture was cooled. The solution after centrifugation was transferred into new test tube, fresh portion of Cs₂CO₃ (194 mg, 1.2 eq.) was added and mixture was heated for 12 h at 90 °C. After filtration of the catalyst, the filtrate was subjected for HRMS-ASI mode. We did not get any leached catalyst such as Ph-Cu-I or Ph-S-Cu , Ph-Mo-I or Ph-Mo-S in HRMS ESI spectra. Which clearly reveals that the leaching of copper or molybedenum was not there in the reaction mixture.

General Procedure C-N Cross Couplings:

A oven dried 25 mL 3-necked round bottom flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. 2.6 mol% CuMoO₄ (3 mg), 1 mL DMSO, amine (0.5 mmol), haloarene (0.55 mmol), base Cs_2CO_3 (194 mg, 1.2 eq.). The reaction mixture was evacuated and purged with inert gas (N₂) three times. The reaction mixture was then placed into an oil bath maintained at 90°C as reported in the scheme. The reaction is monitored after every 2 h up to 12h with the help of TLC in lodine chamber, UV lamp and KMnO₄ Stain. After the time specified in the reaction schemes, After the time specified in the reaction schemes, the reaction mixture was worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes). All yields are reported after column chromatography.

Characterizations of products



N-(Phenyl)aniline (3a) 1

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this aniline **2a** (46 mg, 0.5 mmol), Cs₂CO₃ (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3a** in 86% (72 mg) yield.

Colorless solid; m.p. 51-52 °C;

¹HNMR (400 MHz, CDCl₃) δ 7.34-7.30-7.22 (m, 4H), 7.15-7.11 (m, 4H), 6.99-6.97 (m, 2H), 5.72 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 143.07, 129.29, 120.93, 117.76.

N-(4-Methoxyphenyl)aniline (3b)¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this 4-methoxyaniline **2b** (61 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml.

The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3b** in 88% (87 mg) yield.

Colorless solid; m.p. 103-105 °C;

¹HNMR (400 MHz, CDCl₃) δ 7.18-7.12 (m, 2H), 7.01(d, *J=8Hz*, 2H) 6.84-6.76(m, 5H), 5.41 (s,1H), 3.72(s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 155.27, 145.16, 135.72, 129.28, 122.19, 119.55, 115.63, 114.66, 55.67



N-(2-Methoxyphenyl)aniline (3c).¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this 2-methoxyaniline **2c** (61 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3c** in 76% (75 mg) yield.

Colorless Oil;

¹**H NMR (400 MHz, CDCl₃)** δ 7.23-7.21 (m, 2H), 7.12-7.06 (m, 2H) 6.92-6.88 (m, 1H), 6.86-6.81(m, 2H) 6.80-6.77 (m, 2H), 6.06 (s,1H), 3.79(s, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 148.29, 142.75, 129.23, 128.78, 121.59, 121.11, 120.80, 119.87, 118.57, 114.72, 110.85, 55.58



N-(2-Methylphenyl)aniline (3d).¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this 2-methylaniline **2d** (54 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3d** in 78% (71 mg) yield.

Light brown solid; m.p. 35-38 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.25-7.23 (m, 2H), 7.18-7.13(m, 1H) 7.06-7.03(m, 2H), 6.98-6.96(m, 1H), 6.89-6.87(m, 2H), 6.86-6.82(m, 1H), 5.30(s, 1H), 2.18(s, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 143.99, 141.22, 130.94, 129.55, 129.31, 126.76, 122.44, 121.99, 120.47, 118.80, 117.45, 116.49, 17.89

ONTO H

N-(2-Nitrophenyl)aniline (3e)²

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this 2-nitroaniline **2e** (69 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml.

The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3e** in 73% (77 mg) yield.

Red Solid; m.p. 71-73°C;

¹**H NMR (400 MHz, CDCI₃)** δ 9.39(S, 1H), 8.11(d, *J* = 8 Hz, 2H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.24(t, *J* = 8.0 Hz, 1H), 7.18-7.11 (m, 4H), 6.67 (d,t, *J* = 8 Hz, 2H),

¹³C NMR (100 MHz, CDCl₃) δ 143.11, 138.74, 135.68, 133.25, 129.75, 126.68, 125.67, 124.41, 117.51, 116.06.



N-(4-Nitrophenyl)aniline (3f)¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this 4-nitroaniline **2f** (69 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3f** in 82% (87 mg) yield.

Yellow powder; m.p. 132-134 °C;

¹**H NMR (400 MHz, CDCI₃)** δ 8.14 (d, *J* = 8 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.22-7.19 (m, 3H), 6.95 (d, *J* = 8 Hz, 2H), 6.30 (s, 1H);

¹³C NMR (100 MHz, CDCl₃) δ 153.46, 145.63, 140.14, 129.90, 126.49, 125.70, 125.42, 118.10.



N-(2,4-Dinitrophenyl)aniline (3g).

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this 2,4-dinitroaniline **2g** (91 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3g** in 72% (93 mg) yield.

Yellow powder; m.p. 158-159 °C; CAS Number 961-68-2 (Sigma)

¹**H NMR (400 MHz, CDCl₃)** δ 9.99(s, 1H), 9.19 (d, *J* = 4 Hz, 1H), 8.18 (dd, *J* = 8 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.32 (d, J=8 Hz, 2H), 18 (d, *J* = 15 Hz, 1H),

 ^{13}C NMR (100 MHz, CDCl₃) δ 147.12, 136.72, 130.27, 129.93, 127.76, 125.54, 124.10, 116.03



N-Cyclohexylaniline (3h).¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this cyclohexylamine **2h** (50 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N_{2.} After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml.

The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3h** in 83% (72 mg) yield.

Colorless oil;

¹**H NMR (400 MHz, CDCl₃)** δ 7.17-7.13 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.64-6.58 (m, 2H), 3.28-3.23 (m, 1H), 2.09-2.07 (m, 2H), 1.80-1.76 (m, 2H), 1.69-1.65 (m, 3H), 1.38-1.32 (m, 4H);

¹³C NMR (100 MHz, CDCl₃) δ 147.38, 129.25, 116.84, 113.15, 51.70, , 33.48, 25.93, 25.01.



N-Phenylmorpholine (3i).¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this morpholine **2i** (44 mg, 0.5 mmol), Cs₂CO₃ (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3i** in 80% (65 mg) yield.

Colorless solid; m.p. 53-55 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, *J* = 8.0 Hz, 2H), 6.96-6.90 (m, 3H), 3.90 (t, *J* = 4.8 Hz, 4H), 3.19 (t, *J* = 4.8 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 151.30, 129.21, 120.08, 115.74, 66.97, 49.39.



N-(4-Bromophenyl)aniline (3j).¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this 4-bromoaniline **2j** (86 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3j** in 74% (91 mg) yield.

Colorless solid; m.p. 88-90 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.778-7.75 (m,2H), 7.51-4.45 (m, 1H), 7.35(d, *J*=8 Hz, 2H), 7.28 (d, *J*=8 Hz, 1H), 7.06 (d, *J*=8 Hz, 2H), 6.98-6.92 (m, 2H), 5.66(s, 1H);

¹³C NMR (100 MHz, CDCl₃) δ 147.11, 145.16, 136.65, 130.26, 129.93, 127.75, 125.52, 124.11, 116.01.



N-(4-Chlorophenyl)aniline (3k).¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this 4-chloroaniline **2k** (63 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml.

The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3k** in 73% (74 mg) yield.

Colorless solid; m.p. 71-73 °C;

¹**H NMR (400 MHz, CDCl₃)** δ 7.20 (d, *J*=8 Hz, 2H), 7.14 (d, *J*=8 Hz, 2H), 6.98 (d, *J*=8 Hz, 2H), 6.92- 6.86 (m, 3H), 5.59 (s, 1H);

¹³C NMR (100 MHz, CDCl₃) δ 147.44, 146.49, 129.70, 129.32, 129.20, 124.89, 124.27, 123.18, 123.09, 118.86.

N-(4-Iodoophenyl)aniline (3l).³

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this 4-iodoaniline **2I** (108 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3I** in 76% (111 mg) yield.

brown solid; m.p. 100-102°C;

¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J*=8 Hz, 2H), 7.26(d, *J*=8 Hz, 2H), 7.04 (d, *J*=8 Hz, 2H), 7.06.93 (t, *J*=8 Hz, 2H), 6.80 (d, *J*=8 Hz, 2H), 5.64(s, 1H);

¹³C NMR (100 MHz, CDCl₃) δ 143.18, 138.09, 129.45, 121.84, 119.29, 118.58, 82.09.



N-Ethyldiphenylamine (3m).⁴

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this N-ethylaniline **2m** (61 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3m** in 77% (76 mg) yield.

Colorless gummy liquid

¹**H NMR (400 MHz, CDCl₃)** δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.55-7.48 (m, 3H), 7.21(d, *J* = 8.0 Hz, 2H), 6.74(t, *J* = 8.0 Hz, 2H), 3.58-3.52 (m, 2H), 0.88-0.83. (m, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 148.57, 130.97, 129.23, 129.08, 122.84, 117.81, 112.25, 44.97, 12.95



N-Phenylindole (3n).¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this Indole **2m** (59 mg, 0.5 mmol), Cs₂CO₃ (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time

specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3n** in 82% (76 mg) yield.

Colorless oil;

¹**H NMR (400 MHz, CDCl₃)** δ 7.63 (d, *J* = 8 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.44-7.42 (m, 4H), 7.29-7.27 (m, 2H), 7.18-7.09 (m, 2H), 6.62 (d, *J* = 4.0 Hz, 1H);

¹³C NMR (100 MHz, CDCl₃) δ 139.82, 135.83, 129.59, 129.29, 127.93, 126.42, 124.36, 122.32, 121.10, 120.32, 110.48, 103.53



N-Phenylpyrrole (3n1).¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this Indole **2m** (34 mg, 0.5 mmol), Cs₂CO₃ (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3n1** in 83% (59 mg) yield.

Colorless oil;

¹H NMR (400 MHz, CDCl₃) δ 7.46-7.40 3 (m, 4H), 7.28-7.24 (m, 1H), 7.14-7.11 (m, 2H), 6.37 (t, J = 8.0 Hz, 2H), ¹³C NMR (100 MHz, CDCl₃) δ 137.4, 130.2, 129.4, 125.5, 120.4, 119.2, 110.3



1-phenyl-1H-1,2,4-triazole (3n2).¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this Indole **2m** (35 mg, 0.5 mmol), Cs₂CO₃ (194 mg, 1.2 eq.), iodobenzene **1a** (112 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3n1** in 82% (59 mg) yield.

Colorless solid;

¹**H NMR (400 MHz, CDCl₃)** δ 8.56 (s, 1H), 8.10 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), Hz, 1H),

¹³C NMR (100 MHz, CDCl₃) δ 152.6, 136.9, 129.7, 128.2, 120.0,



N-(4-Nitrophenyl)aniline (3o)¹

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this aniline **2o** (47 mg, 0.5 mmol), Cs₂CO₃ (194 mg, 1.2 eq.), 4-nitroiodobenzene **1c** (124 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time

specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3o** in 92% (97 mg) yield.

Yellow powder; m.p. 132-134 °C;

¹**H NMR (400 MHz, CDCl₃)** δ 8.14 (d, *J* = 8 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.22-7.19 (m, 3H), 6.95 (d, *J* = 8 Hz, 2H), 6.30 (s, 1H);

¹³C NMR (100 MHz, CDCl₃) δ 153.46, 145.63, 140.14, 129.90, 126.49, 125.70, 125.42, 118.10.



1-(4-nitrophenyl)piperidine (3p)

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this piperidine **2p** (43 mg, 0.5 mmol), Cs₂CO₃ (194 mg, 1.2 eq.), 4-nitroiodobenzene **1c** (124 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3p** in 90% (92 mg) yield.

Yellow powder; m.p. 103-105 °C; CAS Number 6574-15-8

¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 3.42 (t, *J* = 8 Hz, 4H), 1.65-1.67 (m, 6H);



4-(4-nitrophenyl)morpholine (3q)²

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this morpholine **2q** (44 mg, 0.5 mmol), Cs_2CO_3 (194 mg, 1.2 eq.), 4-nitroiodobenzene **1c** (124 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3q** in 92% (95 mg) yield.

Yellow powder; m.p. 153-156 °C; CAS 10389-51-2

¹**H NMR (400 MHz, CDCl₃)** δ 8.16 (d, J = 8 Hz, 2H), 6.85 (d, J = 8.0 Hz, 2H), 3.86 (t, J = 8 Hz, 4H), 3.37 (t, J = 8 Hz, 4H),

4-chloro-N-(4-nitrophenyl)aniline (3r).5

The flask was charged with 2.6 mol% CuMoO₄ (3 mg) and 1 mL DMSO. To this 4-chloroaniline **2r** (64 mg, 0.5 mmol), Cs₂CO₃ (194 mg, 1.2 eq.), 4-nitroiodobenzene **1c** (124 mg, 0.55 mmol) were added and stirred at 90°C under N₂. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water

(20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (EtOAc and hexanes as eluent) to afford **3r** in 88% (109 mg) yield.

Pale Yellow powder; m.p. 53-56 °C;

¹H NMR (400 MHz, CDCl₃) δ 7.19 (t, J = 8 Hz, 3H), 6.99 (t, J = 8.0 Hz, 4H), 6.85 (t, J = 8 Hz, 2H), 65.62 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 143.15, 129.35, 121.02, 117.84.

N-(Phenyl)aniline (3a) ¹	N-(4-Bromophenyl)aniline (3j) ¹
N-(4-Methoxyphenyl)aniline (3b) ¹	N-(4-Chlorophenyl)aniline (3k) ¹
N-(2-Methoxyphenyl)aniline (3c) ¹	N-(4-Iodophenyl)aniline (31). ³
N-(2-Methylphenyl)aniline (3d) ¹	<i>N</i> -Ethyldiphenylamine (3m). ⁴
N-(2-Nitrophenyl)aniline (3e) ²	<i>N</i> -Phenylindole $(3n)^1$
<i>N</i> -(4-Nitrophenyl)aniline (3f)	1-(4-nitrophenyl)piperidine (3p) ¹ CAS Number 6574-15-8
<i>N</i> -(2,4-Dinitrophenyl)aniline (3g) CAS-961-68-2	$4-(4-nitrophenyl)$ morpholine $(3q)^2$
<i>N</i> -Cyclohexylaniline (3h). ¹	4-chloro-N-(4-nitrophenyl)aniline (3r) ⁵
<i>N</i> -Phenylmorpholine (3i). ¹	

Reference:

- 1. L. Rout, S. Jammi, T. Punniyamurthy, 2007, Org. Lett, 9, 3397
- 2. X. Zhang, G.-P. Lu; C. Cai, *Green Chem.* 2016, 18, 5580.
- 3. S. Roscales and A. G. Csaky, Org. Lett., 2018, 20, 1667
- 4. F. M. Moghaddam, R. Pourkaveh, M. Gholamtajari Applied Organomettalics, 2018, 32, e4568
- 5. J. Yu, Y. Wang, P. Zhang, J. Wu, Synlett 2013, 24, 1448

¹H NMR and 13C Spectra of Compounds













































































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