Supporting Information

Design and Evolution of Copper Apatite Catalysts for N-Arylation of Heterocycles with Chloro and Fluoroarenes

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General: X-ray photoemission spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg K α anode. The pressure in the spectrometer was about 10⁻⁹ Torr. For energy calibration, we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 284.6 eV. Spectra were deconvoluted using Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species were first determined using the spectrum of a pure sample. The location and FWHM of products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible to within ± 0.1 eV. X-Ray powder Diffraction (XRD) data were collected on a Siemens/ D-5000 diffractometer using Cu-K α radiation ($\lambda=1.5405$ Å). Fourier Transformed Infrared spectra were recorded either as neat liquids or KBr pellets on Nicolet 740 FTIR spectrometer. ICP-MS was performed on a Perkin Elmer Elan DRCII. All reactions were carried out in glassware that was flame-dried or oven-dried and cooled. Flash column chromatography was performed with Sd fine silica gel (60-120 mesh). Thin-layer chromatography was carried out with Merck silica gel 60 F₂₅₄ plates. All products are characterized by ¹H NMR, CHN analysis, IR, GC/MS, EI-MS and HRMS. ¹H NMR spectra were recorded at room temperature on Bruker Avance 300 MHz instrument with respect to TMS. IR spectra were recorded on Nicolet 210 FT-IR (neat or thin film for liquid products, and KBr pellets for solid products). Gas chromatography/mass spectra (GC/MS) were recorded on Shimadzu GC-MS Model No: QP 5050A instrument with mass detector (EI) and a ZB .5 MS 30m x 0.32mm x 0.25 μ m capillary column (stationary phase: 5% diphenyl, 95% dimethyl polysiloxane film, 0.25 μ m). GC/MS method : Initial temperature: 60°C; initial time: 1 min: ramp 8°C min⁻¹; final temp: 240°C: final time: 5 min: EI-MS spectra were analyzed by VG-7070H Micromass (3 KeV, xenon) HRMS

were analyzed VG-Autospec (Micromass,UK). CHN analysis by Vario- EL, Elementen, Germany.

Preparation of Catalysts

Hydroxyapatite¹ [HAP, Ca₁₀(PO₄)₆(OH)₂]

Ca(NO₃)₂ · 4H₂O (15.576 g, 0.066 mol) dissolved in water (60 mL) was brought to pH 11-12 with concentrated NH₄OH and thereafter diluted to 120 mL. A solution of (NH₄)₂HPO₄ (5.28 g, 0.04 mol) in 100 mL water was brought to pH 11-12 with concentrated NH₄OH and thereafter diluted to 160 mL. The calcium solution was vigorously stirred at room temperature, and the phosphate solution was added drop wise over a period of 30 min to produce a milky, some what gelatinous precipitate which was then stirred and boiled for 10 min. The precipitate was filtered, washed, dried at 80 °C overnight and calcined at 500 °C for 3 h. All the synthetic steps were carried out using doubly distilled water.

Fluorapatite² [FAP, Ca₁₀(PO₄)₆(F)₂]

FAP was obtained by co-precipitation method. A mixture of (NH₄)₂HPO₄ (7.92 g, 0.06 mol) and NH₄F (1 g, 0.027 mol) in 250 mL of water, maintained at a pH greater than 12 by addition of NH₄OH (15-20 mL), was introduced into 150 mL of a solution of Ca(NO₃)₂ · 4H₂O (23.6 g, 0.1 mol) under constant stirring. The suspension was refluxed for 4 h. The FAP crystallites were filtered, washed with water, dried overnight at 80 °C and calcined in air at 500 °C for 30 min. All the synthetic steps were carried out using doubly distilled water. (Ca:P:F = 1:0.66:0.16 calculated by XPS)

***Tert*-butoxyapatite [TBAP, Ca₁₀(PO₄)₆(O^tBu)₂]**

A mixture of (NH₄)₂HPO₄ (7.92 g, 0.06 mol) and KO^tBu (2.4 g, 0.02 mol) in 250 mL of water, maintained at a pH greater than 12 by addition of ammonium hydroxide (15-20 mL), was introduced into 150 mL of a solution of Ca(NO₃)₂ · 4H₂O (23.6 g, 0.1 mol) under constant stirring. The suspension was stirred at 50 °C for 4 h. The obtained precipitate was filtered and washed with water and dried in air. All the synthetic steps were carried out using doubly distilled water. (K =6 wt% by XPS and ^tBuO⁻ = 3.48 wt% by TGA).

Copper exchanged HAP, FAP and TBAP

HAP, FAP and TBAP (1 g) were stirred with aqueous Cu(OAc)₂ (0.400 g, 2 mmol) each independently in 25 mL water at 60 °C for a period of 10 h. The obtained slurries were filtered, washed with water and dried over night at 80 °C yielding copper exchanged hydroxyapatite (CuHAP), copper exchanged fluorapatite (CuFAP) and copper exchanged *tert*-butoxyapatite (CuTBAP), respectively as a light blue powder (Cu content by means of ICP-MS: CuHAP-0.66 mmolg⁻¹, CuFAP-0.73 mmolg⁻¹, CuTBAP-0.78 mmolg⁻¹).

Characterization of catalysts

The surface and bulk compositions (Ca, P and Cu) of the standard support materials and copper catalysts were investigated using XPS and ICP-MS, respectively and

reported in Table 1S. The Cu/(Cu+Ca) elemental ratios obtained *via* XPS are about 4 times higher than those measured for the bulk samples *via* ICP-MS, which indicates that Cu does not deeply enter in to the nonporous apatite crystallites (similar trends were observed in Ru exchanged hydroxyapatite catalyst).³

Calcium apatites (HAP, FAP, and TBAP) of Ca/P 1.51-1.52 synthesized are slightly calcium deficient compared to stoichiometric CaHAP ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) in which the Ca/P ratio is 1.67. Calcium fluoroapatite of Ca/P =1.51 (FAP) synthesized in the present case was used as the starting material for copper exchange. The XPS shows the occurrence of 0.45 moles of Cu^{2+} in CuFAP and a loss of 0.57 moles of Ca^{2+} originally present in FAP during exchange process, which amounts to 0.77 moles of Cu^{2+} substitution per mole of Ca^{2+} in CuFAP, which is less than equimolar. Similarly, in CuHAP and CuTBAP, XPS results show the occurrence of 0.41 and 0.26 moles of Cu^{2+} and loss of 0.52 and 0.33 moles of Ca^{2+} originally present in HAP and TBAP, respectively, which amounts to 0.79 moles of Cu^{2+} substitution per mole of Ca^{2+} in both the samples. Thus, the XPS data provided enough information for the exchange of Ca^{2+} by Cu^{2+} .

Table 1S: Elemental Analysis of Catalysts by XPS and ICP-MS

catalyst	XPS		ICP-MS	
	Ca/P	Cu/Cu+Ca	Ca/P	Cu/Cu+Ca
HAP	1.51	—	1.54	—
FAP	1.51	—	1.52	—
TBAP	1.52	—	1.55	—
CuHAP	0.99	0.28	—	0.077
CuFAP	0.94	0.31	—	0.085
CuTBAP	1.19	0.42	—	0.089

X-ray Powder Diffraction (XRD) of the catalysts (calcined HAP, FAP, TBAP, CuHAP, CuFAP, CuTBAP) shows apatite structure [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (CaHAP, JCPDS 9-432)] with small differences in lattice parameters. All these catalysts crystallize in the hexagonal system with the space group $\text{P6}_3/\text{m}$ as hydroxyapatite (Figure 1S).⁴ The crystallographic parameters of the unit cells deduced from X-ray measurements are reported in **Table 2S**.

Table 2S: Lattice Parameters of Various Catalysts

catalyst	a (Å)	c (Å)
HAP	9.395	6.878
FAP	9.354	6.870
TBAP	9.456	6.867
CuHAP	9.457	6.873
CuFAP	9.413	6.879
CuTBAP	9.388	6.877

Figure 1S. XRD spectrum of (a) calcined HAP (b) FAP (c) TBAP (d) CuHAP (e) CuFAP (f) CuTBAP

The basic site distribution are measured by pulse chemisorption of CO₂ using 10% CO₂ in He through a six-port valve followed by TPD of CO₂. Pretreatment has been performed by passing He at 250 °C for 2 h and then cooling to 100 °C. In a typical experiment, 100 mg of the catalyst sample is placed in a micro-reactor of 3 mm i.d., and 250 mm long quartz reactor. The outlet of the reactor is connected to a micro-thermal conductivity detector (TCD) equipped GC (GC 17A, M/S. Shimadzu Instruments, Japan) through a bulk column. After the pretreatment of the catalyst, pulses of 10% CO₂ in He are injected at 100 °C through a 500 µl loop connected to the six-port valve until no further change in the intensity of the outlet CO₂ is observed. After the completion of the pulse chemisorption, the reactor temperature is maintained at 100 °C for 2 h to remove the physisorbed CO₂. The temperature is then increased linearly with programmed rate of 5 °C/min from 100 °C to 700 °C where 30 min isothermal conditions are maintained.

The basicity of the catalysts (CuFAP, CuTBAP and CuHAP) was determined by TPD of carbon dioxide, which shows the order of basicity: CuFAP>CuTBAP>CuHAP (**Figure 2S**).

Figure 2S. CO₂ TPD patterns of a) CuHAP b) CuTBAP c) CuFAP

DTA of calcined HAP, TBAP, KO^tBu and DTA-MS of TBAP are shown in **Figure 3S**. The first endotherm of TBAP sample below 120 °C corresponds to the release of surface adsorbed water. The second endotherm at 290 °C which corresponds to

the *tert*-butoxy group. The DTA-MS of the TBAP indicates a loss of pyrolysis product ($m/z = 73$ amu) corresponding to the 'BuO^- .

Figure 3S. DTA of calcined HAP and TBAP, DTA-MS of TBAP

Fourier transform infrared spectroscopy (FTIR) spectra of all the catalysts (calcined HAP, FAP, TBAP) were recorded. In agreement with literature,³ bands are observed in all the spectra at 964 cm^{-1} for the symmetric P-O stretching ν_1 , at 1053 and 1077 cm^{-1} for the asymmetric P-O stretching ν_3 , and at 432 , 451 , 592 and 611 cm^{-1} for the O-P-O bending modes ν_2 and ν_4 . In the case of TBAP, it shows an additional band at 1380 cm^{-1} which corresponds to the stretching vibration of *tert*-butoxy group (**Figure 4S**).⁵

Figure 4S. FTIR spectrum of TBAP

Mechanistic Studies

Synthesis of CuFAP-imidazole complex intermediate

CuFAP (100 mg, Cu content: 0.73 mmol g^{-1}), imidazole (68 mg, 1 mmol) were added to DMF (4 mL) in a 100 mL of Schlenk flask and heated to 120°C and stirred for 6 h, the solution was filtered and washed with water and acetone to obtain CuFAP-imidazole complex.

The FTIR spectrum of Cu-imidazole complex, which shows an extra band at 867 cm^{-1} corresponding to the P-OH vibration,⁷ disappeared in the used catalyst obtained under normal conditons. (**Figure 5S, a,b**).

Figure 5S. FTIR spectrum of (a) CuFAP-imidazole complex (b) CuFAP used catalyst

X-ray photoelectron spectroscopic (XPS) investigation of CuFAP and CuFAP-imidazole complex and CuFAP used catalyst (normal reaction conditions) at the Cu 2p level shows 2p_{3/2} line at 935.1, 935.2 and 935.5 eV, which corresponds to +2 oxidation state (**Figure 6S, a-c**). While, XPS of the used catalyst (reaction carried out under inert atmosphere) Cu 2p level shows 2p_{3/2} line at 933.4 eV, which indicates that the copper is in the reduced form (**Figure 6S, d**). The XPS of N 1s of CuFAP-imidazole complex shows two lines at 399.6 eV for C=N and 401.8 eV for Cu-N (**Figure 6S, e**).⁶

Figure 6S: XPS of Cu 2p_{3/2} for (a) Copper fresh catalyst (b) Cu-imidazole complex (c) Used copper catalyst (d) Used copper catalyst under inert conditions (e) XPS of N 1s for Cu-imidazole complex (f) XPS of C 1s in Cu-imidazole complex.

A typical procedure for N-arylation of imidazole with chloroarenes

In a typical experimental procedure, chlorobenzene (0.1 mL, 1 mmol), imidazole (81 mg, 1.2 mmol), potassium carbonate (276 mg, 2 mmol), potassium *tert*-butoxide (11 mg, 10 mol% in case of electron rich chloroarenes only) and the catalyst (CuFAP, 100 mg) were stirred in DMF (4 mL) at 120°C for 36 h. After 36 h, the catalyst was filtered and the filtrate was quenched with aqueous sodium hydrogen carbonate and the product was extracted with ethyl acetate. The combined organic extracts were dried over anhydrous sodium sulfate and filtered. Solvent was evaporated under reduced pressure and concentrated in vacuo to give the crude product. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate, 70/30) to afford the N-phenylimidazole (115 mg, 80%, Table1, entry 9.).

The known coupling products are well compared with the reported spectral data and melting points. For the new compounds HRMS data are included.

1) 1-(4-Nitrophenyl)-1*H*-imidazole (Table 1, entry 1). M.p. 203 °C; ¹H NMR (300 MHz, CDCl₃): δ= 8.37 (d, *J* = 9.0 Hz, 2H), 7.93 (br s, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.32 (br s, 1H), 7.24 (br s, 1H); EI-MS: 189 (100%), 159, 141, 116, 89, 50; GC/MS: *t_R* = 23.843 min; *m/z*: 189.25; HRMS: calcd. for C₉H₇N₃O₂ .189.053, found 189.053; IR: (KBr) cm⁻¹; 3130.96, 1599.57, 1528.72, 1340.33, 1052.66, 854.85.

2) 1-(2-nitrophenyl)-1*H*-imidazole (Table 1, entry 2). ¹H NMR (300 MHz, CDCl₃): δ= 7.98 (dd, *H J* = 1.5, 8.3 Hz), 7.7 (dt 1H *J* = 1.5, 7.5 Hz), 7.64-7.57 (m, 2H) 7.47 (dd, 1H *J* = 1.5, 7.5 Hz) 7.18 (br s, 1H), 7.03 (br s 1H); EI-MS: 189 (100%), 159, 141, 116, 89, 50; GC/MS: *t_R* = 21.77 min; *m/z*: 189.25; HRMS: calcd. for C₉H₇N₃O₂. 189.053, found 189.053; IR: (KBr) cm⁻¹ 3103.38, 1606.83, 1523.15, 1356.61, 1058.66, 739.53, 657.61.

3) 1-(4-Cyanophenyl)-1*H*-imidazole (Table 1, entry 3). ¹H NMR (300MHz, CDCl₃): δ= 7.90 (br s, 1H), 7.79 (d, 2H, *J* = 8.3 Hz), 7.53 (d, 2H, *J* = 8.3 Hz), 7.29 (br s, 1H), 7.22 (br s, 1H); EI MS: 169 (100%), 142, 115, 102, 75, 50; GC/MS: *t_R* = 22.11 min; *m/z*: 169.20 IR: (KBr) cm⁻¹ 2923.75, 2226.63, 1609.35, 1521.97, 1304.78, 1057.90, 835.57.

4) 1-(4-Trifluoromethyl-2-cyanophenyl)-1*H*-imidazole (Table 1, entry 4). M.p. 68 °C; ¹H NMR (300 MHz, CDCl₃): δ=8.1(d, 1H, *J* = 2.26Hz), 8.01 (dd, 1H, *J* = 2.26, 8.30Hz), 7.95(br s, 1H), 7.64 (d, 1H, *J* = 8.30 Hz), 7.42(br s, 1H), 7.32 (br s, 1H), 7.23 (br s, 1H); EI-MS: 237 (100%), 210, 183, 170; GC/MS: *t_R* = 19.25 min; *m/z*: 237.20; HRMS:

calcd.for $C_{11}H_6N_3F_3$.237.051, found 237.050.; IR (KBr) cm^{-1} 3083.11, 2233.47, 1616.81, 1519.06, 1338.65, 1176.64, 1049.21, 734.84.

5) 1-(4-Formylphenyl)-1*H*-imidazole (Table 1, entry 5). 1H NMR (300MHz, $CDCl_3$): δ = 10.02 (s, 1H), 8.00 (d, 2H, J = 8.3 Hz), 7.93 (br s, 1H), 7.57 (d, 2H, J = 8.3 Hz), 7.33 (br s, 1H), 7.21 (br s, 1H); EI-MS: 172, 143, 116, 89, 77, 51, 43.; GC/MS: t_R = 21.6 min; m/z: 172.25.; IR: (KBr) cm^{-1} : 3110.95, 1687.04, 1526.81, 1312.79, 1222.12, 1062.90, 834.15, 649.93

6) 2-(1*H*-1-imidazolyl)pyridine (Table 1, entry 6). 1H NMR (300 MHz ($CDCl_3$)): δ =8.48 (dd, 1H, J = 1.5 Hz, J = 4.6 Hz), 8.33 (br s, 1H), 7.81 (d, 1H, J = 2.3, 8.6 Hz), 7.63 (br s, 1H), 7.37 (d, 1H, J = 8.8 Hz), 7.28 – 7.15 (m, 2H); EI-MS: 145 (100%), 118, 91, 78, 51, 43; GC/MS: t_R = 17.5 min; m/z: 145.15; IR: (thin film /neat): cm^{-1} :3388, 2925, 2853, 1686, 1594, 1485, 1443, 1305, 1259, 1104, 1056, 970, 780, 657, 621,520.

7) 2-(1*H*-1-imidazolyl)pyrimidine (Table 1, entry 7). M.p. 124 °C; 1H NMR (300MHz, $CDCl_3$): δ =8.68 (d, 2H, J = 4.5 Hz), 8.58 (br s, 1H), 7.84 (br s, 1H), 7.18 (t, 1H, J = 4.5 Hz), 7.03 (br s, 1H); EI-MS: 146 (100%), 119, 92, 79, 53; GC/MS: t_R = 17.19min; m/z: 146.15.; HRMS: calcd.for $C_7H_6N_4$.146.059, found 146.059; IR: (KBr) cm^{-1} : 3142.13, 1610.12, 1570.06, 1446.03, 1313.58, 1053.72, 751.76, 650.89.

8) 1-(3-Benzoylphenyl)-1*H*-imidazole (Table 1, entry 8). 1H NMR (300 MHz ($CDCl_3$)): δ 7.97 (br s, 1H), 7.93 (d, 2H, J = 9.0 Hz), 7.79 (d, 2H, J = 6.7 Hz), 7.64 – 7.45 (m, 5H), 7.33 (br s, 1H), 7.23 (br s, 1H), Hz); EI-MS: 248 (100%), 171, 141, 116, 105, 89, 77; GC/MS: t_R = 23.5 min; m/z:248.05; IR: (KBr) cm^{-1} ;

9) 1-Phenyl-1*H*-imidazole (Table 1, entry 9). 1H NMR (300MHz, $CDCl_3$): δ 7.83 (br s, 1H), 7.50-7.30 (m, 5H), 7.25 (br s, 1H), 7.18 (br s, 1 H); EI-MS: 144 (100%), 117, 77, 51 GC/MS: t_R = 16.20 min; m/z: 144.20; IR: (thin film/neat): cm^{-1} : 3424, 3117, 1600, 1509, 1304, 1253, 1110, 1058, 908, 760, 690, 659, 520.

10) 1-(4-Methylphenyl)-1*H*-imidazole (Table 1, entry 10). ¹H NMR (300MHz, CDCl₃): δ= 7.76 (br s, 1H), 7.24 (br s, 4H), 7.19 (br s, 1H), 7.13 (br s, 1H), 2.39 (s, 3H); EI-MS: 158, 131, 104, 91 (100%) 50; GC/MS: t_R = 23.61min; m/z: IR:(thin film /neat):cm⁻¹; 3391, 3115, 2924, 1612, 1522, 1488, 1304, 1249, 1112, 1058, 964, 908, 816, 735, 661, 616, 523.

11) 1-(4-Methoxyphenyl)-1*H*-imidazole (Table 1, entry 11). ¹H NMR (300MHz, CDCl₃): δ 7.71 (br s, 1H), 7.28 (d, 2H, *J*= 9.0Hz), 7.15 (br s, 1H), 7.11 (br s, 1H), 6.94 (d, 2H, *J* = 9.0 Hz), 3.83 (s, 3H); EI-MS: 174 (100%), 159, 147, 132, 120, 77; GC/MS: t_R = 20.65 min; m/z: 174.07; IR: (thin film /neat): cm⁻¹; 3415, 2928, 1675, 1520, 1464, 1302, 1250, 1181, 1113, 1059, 1029, 833, 764, 661, 614, 536

12) 1-(2-cyanophenyl)-1*H*-imidazole (Table 1, entry 12). ¹H NMR (300MHz, DMSO-d₆): δ 7.57 –7.32 (m, 3H), 7.27 – 7.12 (m, 2H), 7.02 (br s, 1H), 6.80 (br s, 1H); EIMS: 169(100 %), 142, 129, 115, 102, 75, 51; GC/MS: t_R = 21.10 min; m/z: 169.10
IR: (KBr) cm⁻¹; 2924.64, 2224.08, 1600.0, 1507.69, 1384.38, 1309, 1258.74, 1062.93, 825.17, 774.82.

13) 1-(4-Formylphenyl)-1*H*-imidazole (Table 1, entry 13). ¹H NMR (300MHz, CDCl₃): δ=10.02 (s, 1H), 8.00 (d, 2H, *J* = 8.3 Hz), 7.93 (br s, 1H), 7.57 (d, 2H, *J* = 8.3 Hz), 7.33 (br s, 1 H), 7.21 (br s, 1H); EI-MS: 172, 143, 116, 89, 77, 51, 43; GC/MS: t_R = 21.6 min; m/z: 172.25; IR: (KBr) cm⁻¹: 3110.95, 1687.04, 1526.81, 1312.79, 1222.12, 1062.90, 834.15, 649.93.

14) 1-(4-Nitrophenyl)-1*H*-imidazole (Table 1, entry 14). ¹H NMR (300 MHz (CDCl₃): δ 8.37 (d, *J*= 9.0 Hz, 2H), 7.93 (br s, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.32 (br s, 1H), 7.24 (br s, 1H).; EI-MS: 189 (100%), 159, 141, 116, 89, 50; GC/MS: t_R = 23.843 min; m/z: 189.25.; HRMS: calcd.for C₉H₇N₃O₂ .189.053, found 189.053.; IR: (KBr) cm⁻¹ ; 3130.96, 1599.57, 1528.72, 1340.33, 1052.66, 854.85.

15) 1-(2-Chloro-4-nitrophenyl)-1*H*-imidazole (Table 1, entry 15). M.p. 181 °C; ¹H NMR (300 MHz, CDCl₃): δ=8.46 (d, 1H, ⁴*J*=2.2 Hz), 8.26 (dd, 1H, ⁴*J*= 2.2, ³*J* = 8.3 Hz), 7.7 (br s, 1H), 7.56 (d, 1H, ³*J* = 8.3 Hz), 7.22 (br s, 1H), 7.20 (br s, 1H).; EI-MS: 223 (100%), 150, 123, 114, 75, 63.; GC/MS: *t_R* = 24.4 min; *m/z*: 223.10.; HRMS: calcd. for C₉H₆N₃O₂Cl .223.014, found 223.014.; IR:(KBr)cm⁻¹; 3011.59, 1588.74, 1519.34, 1346.38, 1242.54, 1043.18, 744.91, 657.96.

16) 1-(4-Nitrophenyl)-1*H*-pyrrole (Table 2, entry 1). ¹H NMR (300MHz, CDCl₃): δ=8.3-8.4 (m, 2H), 7.5-7.6 (m, 2H), 7.1 (m, 2H), 6.4 (m, 2H); EI MS: 188 (100%), 142, 115 GC/MS: *t_R*=21.77 min; *m/z*: 188.10; IR: (KBr) cm⁻¹; 2924.15, 1594.27, 1507.34, 1316.98, 1061.34, 850.21, 743.74.

17) 1-(4-Nitrophenyl)-1*H*-pyrazole (Table 2, entry 2). ¹H NMR (300MHz, DMSO-*d*₆) 8.71 (dd, 1H), 8.36 (m, 2H), 8.11 (m, 2H), 7.88 (dd, 1H), 6.65 (dd, 1H).; EI-MS: 189. GC/MS: *t_R* = 22 min; *m/z*: 189.10.; IR: (KBr) cm⁻¹ 3119.69, 1596.47, 1516.20, 1334.04, 1206.71, 926.72, 852.13, 765.45.

18) 1-(4-Nitrophenyl)-1*H*-benzimidazole (Table 2, entry 3). ¹H NMR (300 MHz (CDCl₃): δ=8.47(d, 2H, *J* = 9.0 Hz), 8.12 (br s, 1H), 7.88 (m, 1H), 7.74 (d, 2H, *J* = 9.0Hz), 7.56 (m, 1H), 7.41-7.33 (m, 2H); EI MS: 239 (100%), 209, 192, 167, 141, GC/MS: *t_R*=23.5 min; *m/z*: 239.05. IR: (KBr) cm⁻¹; 2924.88, 1652.78, 1602.76, 1520.89, 1442.35, 1270.07, 1151.13, 1055.61, 937.36, 858.97, 726.86, 696.64, 655.90 498.65.

19) 1-(4-Nitrophenyl)-1*H*-piperidine (Table 2, entry 4). ¹H NMR (300MHz, CDCl₃): δ= 8.15 (d, 2H), 6.76 (d, 2H), 3.36 (m, 4H), 1.64 (m, 6H).; EI MS: 206 (100%), 159, 119, 55 GC/MS: *t_R* = 27.6 min; *m/z*: 205.5.; IR: (KBr)cm⁻¹; 2942.35, 1600.24, 1476.65, 1313.64, 1247.72, 1110.34, 819.59, 753.86, 689.17.

Recycling of the CuFAP catalyst :

The catalyst is recycled four times with a slight decrease in activity as can be seen from the results given below (**Table 3S**). The deactivation is due to leaching of copper, which was determined by AAS in the used catalysts and by ICP-MS in the

filtrate. There is no reaction with the filtrate, when a fresh amount of the reactant was added. This result indicates that the copper bound to CuFAP is only active.

Table 3S.

Recyclability	Time(h)	GC-Yields
1 st cycle	1	100%
2 nd cycle	1	100%
3 rd cycle	1	92%
4 th cycle	1	90%
5 th cycle	1	90%

Elemental analysis

CuFAP (Fresh)	0.73 mmol g ⁻¹
Used cat -recycle 1	0.72 mmol g ⁻¹
Used cat-recycle 2	0.693 mmol g ⁻¹
Used cat-recycle 3	0.682 mmol g ⁻¹
Used cat-recycle 4	0.66 mmol g ⁻¹

ICP analysis of the filtrate

1 st cycle	0.01 mmol g ⁻¹
2 nd cycle	0.01 mmol g ⁻¹
3 rd cycle	0.04 mmol g ⁻¹
4 th cycle	0.02 mmol g ⁻¹
5 th cycle	0.02 mmol g ⁻¹

Reaction of 1-Chloro-4-nitrobenzene vs 1-Fluoro-4-nitrobenzene :

The rate of the arylation of imidazole with 1-fluoro-4-nitrobenzene is faster than with 1-chloro-4-nitrobenzene(**Figure 7S**) .

Figure 7S: Conversion as a function of time between fluoro and chloro nitrobenzenes.

Table 3S. Screening of Copper Sources for N-Arylation of Imidazole with Chlorobenzene^a

entry	catalyst	yield (%) ^b
1	Cu(OAc) ₂	0
2	CuI	0
3	Cu Powder	0
4	CuHAP	0
5	CuTBAP	55
6	CuFAP	72 (60) ^c
7	CuTBAP/10 mol% K-O ^t Bu	75
8	CuFAP/10 mol% K-O ^t Bu	85 (80) ^c

^a Chlorobenzene (1 mmol), imidazole (1.2 mmol), K₂CO₃ (2 mmol), DMF, 120 °C.

^b GC yields

^c Isolated yields.

These N-arylation results of deactivated chloroarenes using K_2CO_3 as a base are quite impressive over the unreactive system using nanocopper and Cs_2CO_3 base. Our results are compared with the results of Hyeon et al and are tabulated in **Table 4S**.

Table 4S.

Entry	Ar-X	Isolated yield (%)	
		a	b
1	Chlorobenzene	60	0
2	Chloroanisole	52	0

^a Our process: ArX (1 mmol), imidazole (1.2 mmol), catalyst (100 mg), K_2CO_3 (2 mmol), DMF (4 ml), 120°C, 36 h; ^b Hyeon process : 5 mol% Cu_2O coated Cu nanoparticles and 2 eq. imidazole used, Cs_2CO_3 , DMSO, 150°C, 18 h.

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