SUPPORTING INFORMATION

Cu(0)@Al$_2$O$_3$/SiO$_2$ NPs: An Efficient Reusable Catalyst for the Cross Coupling Reactions of Aryl Chlorides with Amines and Anilines

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General Remarks:

All chemicals were purchased from Aldrich and were used as received. All solvents used were analytical grade and were used as received from Merck India Pvt. Ltd. Alumina/silica (Al₂O₃/SiO₂) was purchased from Sasol, Germany. X-ray powder diffraction (XRD) data were collected on a Simens/D-5000 diffractometer using Cu Kα radiation. The Cu weight percentage was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and SEM-EDAX (Philips XL30 electron micrograph). The particle size and external morphology of the samples were observed on a JEOL JEM-2010 high resolution transmission electron microscope (HRTEM). Brunauer, Emmett and Teller (BET) surface area of supported catalyst and specific surface area of metallic copper was performed using Quantachrome ASiQ instrument. Temperature programmed reduction (TPR) measurements were carried out on Automated chemisorption analyzer (ChemBET pulsar TPR/TPD, Quantachrome). XPS spectra were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα 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 285.0 eV. Spectra were deconvoluted using the 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 the products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. The Cu weight percentage was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). ¹H and ¹³C spectra were recorded on a Jeol Spectrospin spectrometer at 400 MHz and 100 MHz respectively. Chemical shifts were reported in ppm relative to the residual CDCl₃ (δ 7.28 ppm ¹H; δ 75 ppm ¹³C) Coupling constants (J) were reported in Hertz. Mass spectral data were recorded on a Jeol-AccuTOF JMS-T100LC and micromass LCT Mass Spectrometer/Data system. Copper nanoparticles on alumina/silica were prepared by wet impregnation method. ¹HNMR and ¹³C NMR of the compounds were proved
either by comparison to the known compounds or the synthesized compounds according to the literature. ACME SILICA GEL (100-200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck precoated silica gel 60-F<sub>254</sub> plates.

**Preparation of catalysts:**

(i) Typical procedure for synthesis of Cu(II)@Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> NPs:

Cu(II)@Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> was prepared as follows: Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O (33.35 g, 0.138 moles) was suspended in doubly deionised water (500 ml) in 1 L four neck round bottom flask and stirred at 25 °C with overhead mechanical stirrer. To this 100 g of Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> was added and aged at 65 °C for twelve hours. The solid product was isolated by filtration, washed thoroughly with doubly deionised water dried at 65 °C for 12 h to obtain 130 g of pale blue powder of Cu(II)@Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> NPs.

(ii) Typical procedure for synthesis of CuO@Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> NPs:

Cu(II)@Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> (100 g) was taken in a crucible and calcined in the presence of air at a ramping temperature of 150 °C/1 h and 800 °C/3 h. The calcined catalyst was then cooled to room temperature to obtain 65 g of grey coloured CuO@Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> NPs.

(iii) Typical procedure for synthesis of Cu(0)@Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> NPs:

Cu(0)@Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> (5 g) was taken in a SS reactor and reduced at 250 °C temperature and 10 bar hydrogen pressure with a flow rate of 1 L/h to obtain 4.8 g black colored Cu(0)@Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>.
**Figure S1.** Stainless steel (SS) units used for reduction of copper oxide on alumina/silica support.

The Cu loading on Cu(0)@Al₂O₃/SiO₂ was found to be 2.06 wt% from SEM-EDAX elemental analysis and particle size of Cu(0) on Al₂O₃/SiO₂ was estimated to be 4-6 nm which is well matched with high resolution transmission electron microscopy (HR-TEM).

**H₂-Temperature Programmed Reduction (H₂-TPR)**

Temperature programmed reduction (TPR) measurements were carried out on Automated chemisorption analyzer (Chem BET pulsar TPR/TPD, Quantachrome). Upon loading of 0.10 g of CuO@Al₂O₃/SiO₂ into a quartz U-tube, the sample was degassed at 200 °C for 30 min under helium. When the temperature dropped to 20 °C, the gas was changed to 9.9% H₂/Ar. Finally, the sample was heated from 20 °C to 800 °C with 10 °C min⁻¹ in 9.9% H₂/Ar with a gas flow of 30 mL min⁻¹. The amount of H₂ uptake during the reduction was measured by a thermal conductivity detector (TCD). For H₂ consumption quantification, CuO (99.99%) was used as the calibration standard sample.

At low copper loading, copper was present as highly dispersed clusters or isolated Cu ions, which interact strongly with the alumina-silica-type oxide, thus requiring higher reduction temperature. Support effects on the dispersion and reducibility of copper oxide have been documented in the literature. [2,3] The H₂-TPR curves of the three samples, for the as synthesised Cu(II)@Al₂O₃/SiO₂ catalyst sample, the H₂ consumption peak was located between 150–300 °C and for calcined CuO@Al₂O₃/SiO₂ sample, it was in between 200–300 °C, while for the commercial CuO, it was in between 400–600 °C. These results indicates that the as synthesised Cu(II)@Al₂O₃/SiO₂ and calcined CuO@Al₂O₃/SiO₂ are much easier to reduce than the commercial CuO. But in our reaction conditions for the reduction of calcined CuO@Al₂O₃/SiO₂ catalyst we used higher reduction temperatures because of high dispersion of copper ions.
Figure S2. Hydrogen- Temperature Programmed Reduction [A] Cu(II)@Al₂O₃/SiO₂ [B] calcined CuO@Al₂O₃/SiO₂ and [C] Commercial CuO (Aldrich)

Characterization of the recycled catalyst:

X-ray photoelectron spectroscopy (XPS) of recycled Cu(0)@Al₂O₃/SiO₂ catalyst

The X-ray photoelectron spectroscopic analysis of 5th reused Cu(0)@Al₂O₃/SiO₂ catalyst revealed that there was no deviation in the binding energy values of copper Cu(0) 2p₃/₂ such as 932.48 and 952.11 eV, which conforms the presence of exclusively Cu(0) oxidation state as shown in Figure S2. The TEM analysis of recycled catalyst revealed the no change in the internal morphology of catalyst (Figure S3).

Figure S2. XPS spectra of recycled Cu(0)@Al₂O₃/SiO₂ (5th run, A).
Figure S3. TEM pictures of reused Cu(0)@Al₂O₃/SiO₂ [A, B and C]

Figure S4: SEM-EDAX analysis of Cu(0)@Al₂O₃/SiO₂ (Cu(0): 2.06 wt%)

Spectroscopic data of representative compounds:

\[ \text{1a} \]

1-(4-nitrophenyl)-1H-imidazole (Table 2, Entry 1a)\(^4\): Pale yellow solid, mp 197-200; \(^1\)H NMR (400 MHz, CDCl₃) : δ = 8.38 (d, J = 9.16 Hz, 2H), 7.99 (s, 1H), 7.58 (d, J = 9.16 Hz, 2H), 7.38 (s, 1H), 7.28 (s, 1H); \(^13\)C NMR (100 MHz, CDCl₃): δ = 146.2, 141.9, 135.3, 131.7, 125.7, 121.0, 117.6.
1-(2-nitrophenyl)-1H-imidazole (Table 2, Entry 1b): Pale yellow solid, mp 95-97; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.01$ (dd, $J = 8.39$ Hz, 1.53 Hz, 1H), 7.74 (dt, $J = 7.63$ Hz, 1.53 Hz, 1H), 7.68-7.60 (m, 2H), 7.51-7.46 (m, 1H), 7.22 (s, 1H), 7.08 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 145.3, 137.2, 133.7, 130.5, 130.3, 129.6, 128.6, 125.3, 120.4.$

1-(3-nitrophenyl)-1H-imidazole (Table 2, Entry 1c): White solid, mp: 107-109; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.30-8.28$ (m, 1H), 8.26-8.27 (m, 1H), 7.96 (s, 1H), 7.39-7.37 (m, 1H), 7.20 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 149.03, 138.17, 135.38, 131.40, 131.02, 126.76, 121.98, 117.89, 116.16.$

4-(1H-imidazol-1-yl)benzonitrile (Table 2, Entry 1d): White solid, mp 151-154; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.97$ (s, 1H), 7.81 (d, $J = 8.39$ Hz, 2H), 7.54 (d, $J = 8.39$ Hz, 2H), 7.34 (s, 1H), 7.27 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 140.3, 135.2, 134.1, 131.2, 121.3, 117.7, 117.5, 111.1.$

2-(1H-imidazol-1-yl)benzonitrile (Table 2, Entry 1e): White solid, mp 145-147; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.82-7.74$ (m, 2H), 7.72-7.65 (m, 1H), 7.47 (t, $J = 7.63$ Hz, 1H), 7.40 (d, $J = 7.63$ Hz, 1H), 7.29 (s, 1H), 7.20 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 139.3, 136.6, 134.5, 134.2, 130.7, 128.4, 125.6, 119.5, 115.7, 108.0.$
1-(4-(1H-imidazol-1-yl)phenyl)ethanone (Table 2, Entry 1f): White solid, mp 112-114; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.06$ (d, $J = 8.39$ Hz, 2H), 7.95 (s, 1H), 7.47 (d, $J = 8.39$ Hz, 2H), 7.33 (s, 1H), 7.22 (s, 1H), 2.61 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 196.5, 140.6, 135.7, 135.3, 131.0, 130.3, 120.6, 117.6, 26.6$.

1-(4-methoxyphenyl)-1H-imidazole (Table 2, Entry 1g): Colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.72$ (s, 1H), 7.23 (d, $J = 9.16$ Hz, 2H), 7.14 (s, 2H), 6.91 (d, $J = 9.16$ Hz, 2H), 3.78 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 158.8, 135.7, 130.5, 123.1, 118.7, 114.8, 55.5$.

1-(3-methoxyphenyl)-1H-imidazole (Table 2, Entry 1h): Colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.83$ (s, 1H), 7.35-7.19 (m, 3H), 6.91 (d, $J = 7.63$ Hz, 1H), 6.84-6.81 (m, 2H), 3.86 (s, 3H); 160.64, 130.71, 113.66, 112.62, 107.72, 55.51.

1-phenyl-1H-imidazole (Table 2, Entry 1i): Colorless liquid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.83$ (s, 1H), 7.47-7.40 (m, 2H), 7.37-7.29 (m, 3H), 7.24 (s, 1H), 7.16 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 137.1, 135.4, 130.3, 129.7, 127.4, 121.3, 118.1$. 
1-(p-tolyl)-1H-imidazole (Table 2, Entry 1j): Off white mp 46-48; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.80\) (s, 1H), 7.26 (s, 4H), 7.23 (s, 1H), 7.18 (s, 1H), 2.39 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 137.4, 135.5, 134.9, 130.2, 130.1, 121.3, 118.3, 20.9\).

4-(1H-imidazol-1-yl)phenol (Table 2, Entry 1k): Off white solid, mp 192-196; \(^1\)H NMR (400 MHz, DMSO): \(\delta = 9.70\) (s, 1H, OH), 8.13 (s, 1H), 7.63 (s, 1H), 7.39 (d, \(J = 8.39\) Hz, 2H), 7.13 (s, 1H), 6.85 (d, \(J = 8.39\) Hz, 2H); \(^{13}\)C NMR (100 MHz, DMSO): \(\delta = 156.3, 128.9, 122.2, 116.0\).

1-(4-chlorophenyl)-1H-imidazole (Table 2, Entry 1l): Off white solid, mp 64-66; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.80\) (s, 1H), 7.41 (d, \(J = 8.39\) Hz, 2H), 7.30 (d, \(J = 8.39\) Hz, 2H), 7.21 (s, 1H), 7.17 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 135.7, 135.4, 133.1, 130.5, 129.9, 122.6, 118.1\).

2-(1H-imidazol-1-yl)nicotinonitrile (Table 2, Entry 1m): Off white solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.75-8.71\) (m, 1H), 8.52 (s, 1H), 8.18-8.14 (m, 1H), 7.92 (s, 1H), 7.45-7.39 (m, 1H), 7.25 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 152.84, 149.27, 143.98, 136.41, 130.95, 121.72, 117.53, 115.48, 99.67\).
2-chloro-6-(1H-imidazol-1-yl)pyridine (Table 2, Entry 1n)\textsuperscript{11}: colorless liquid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 8.33\) (s, 1H), 7.82-7.76 (m, 1H), 7.62 (s, 1H), 7.28 (t, \(J = 6.87\), 2H), 7.19 (s, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 150.66, 148.63, 141.25, 134.95, 130.87, 122.16, 116.09, 110.21\).

7-chloro-4-(1H-imidazol-1-yl)quinolone (Table 2, Entry 1o)\textsuperscript{12}: Off white solid, ; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 9.02\) (d, \(J = 5.34\) Hz, 1H), 8.23 (d, \(J = 1.53\) Hz, 1H), 7.85 (s, 1H), 7.79 (d, \(J = 8.39\) Hz, 1H), 7.59 (dd, \(J = 9.16\) Hz, \(J = 2.29\) Hz, 1H), 7.39-7.31 (m, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 151.61, 150.03, 141.85, 137.55, 130.74, 129.18, 129.07, 123.81, 121.93, 120.71, 116.90\).

1-(4-methoxyphenyl)-1H-benzo[d]imidazole (Table 2, Entry 1p)\textsuperscript{13}: Pale yellow solid, mp 99-101; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 7.98\) (s, 1H), 7.83-7.77 (m, 1H), 7.41-7.36 (m, 1H), 7.33 (d, \(J = 9.16\) Hz, 2H), 7.28-7.23 (m, 2H), 7.0 (d, \(J = 9.16\) Hz, 2H), 3.81 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 159.2, 143.6, 142.4, 134.1, 129.0, 125.6, 123.4, 122.5, 120.3, 115.0, 110.2, 55.5\).
1-(4-(1H-benzo[d]imidazol-1-yl)phenyl)ethanone (Table 2, Entry 1q)\textsuperscript{13}: Pale yellow solid, mp 132-134; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.21-8.16$ (m, 3H), 7.93-7.87 (m, 1H), 7.65 (d, $J = 8.70$ Hz, 2H), 7.62-7.58 (m, 1H), 7.41-7.35 (m, 2H), 2.68 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 196.6$, 144.2, 141.7, 140.2, 136.1, 133.0, 124.1, 123.3, 120.8, 110.4, 26.6

1-(4-nitrophenyl)-1H-benzo[d]imidazole (Table 2, Entry 1r)$^4$: Yellow solid, mp 185-187; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.47$ (d, $J = 9.16$ Hz, 2H), 8.20 (s, 1H), 7.93-7.88 (m, 1H), 7.75 (d, $J = 9.16$ Hz, 2H), 7.64-7.59 (m, 1H), 7.44-7.38 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 146.4$, 144.3, 141.6, 141.5, 132.7, 125.8, 124.5, 123.7, 123.6, 121.1, 110.2.

1-(4-nitrophenyl)-1H-1,2,4-triazole (Table 2, Entry 1s)$^{14}$: White solid, mp 186-189; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.72$ (s, 1H), 8.41 (d, $J = 9.16$ Hz, 2H), 8.17 (s, 1H), 7.93 (d, $J = 9.16$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 153.4$, 146.7, 141.2, 125.5, 119.8.

4-nitro-N-octylaniline (Table 3, Entry 2a)$^{15}$: White solid, mp 66-68; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.07$ (d, $J = 9.16$ Hz, 2H), 6.51 (d, $J = 9.16$ Hz, 2H), 4.54 (brs, 1H, NH), 3.2 (q, $J = 6.87$ Hz, 2H), 1.65 (m, 2H), 1.45-1.21 (m, 10H), 0.92-0.81 (m, 3H); $^{13}$C
NMR (100 MHz, CDCl₃): δ = 153.4, 137.6, 126.4, 110.8, 43.3, 31.7, 29.2, 29.1, 29.0, 26.9, 22.5, 14.0.

2b

4-(octylamino)benzonitrile (Table 1, Entry 2b)¹⁶: Colorless liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.41 (d, J = 9.16 Hz, 2H), 6.53 (d, J = 9.16 Hz, 2H), 4.16 (brs, 1H, NH), 3.13 (q, J = 7.63, 2H), 1.67-1.59 (m, 2H), 1.43-1.23 (m, 10H), 0.92-0.85 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 151.4, 133.6, 120.5, 112.0, 98.3, 43.2, 31.7, 29.2, 29.1, 27.0, 22.6, 14.0.

2c

2-(octylamino)benzonitrile (Table 3, Entry 2c)¹⁵: Colorless liquid; ¹H NMR (400 MHz, CDCl₃): δ = 7.41-7.34 (m, 2H), 6.68-6.61 (m, 2H), 4.52 (brs, 1H, NH), 3.18 (q, J = 6.10 Hz, 2H), 1.72-1.62 (m, 2H), 1.45-1.32 (m, 10H), 0.98-0.88 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 151.5, 134.0, 133.8, 130.0, 127.1, 115.8, 113.4, 42.2, 33.8, 31.8, 29.4, 29.2, 26.8, 26.6, 14.0.

2d

2-(octylamino)benzoic acid (Table 3, Entry 2d)¹⁷: White solid, mp 82-84; ¹H NMR (400 MHz, CDCl₃): δ = 7.97 (d, J = 7.63 Hz, 1H), 7.38 (t, J = 7.63 Hz, 1H), 6.67 (d, J = 8.39 Hz, 1H), 6.58 (t, J = 7.63 Hz, 1H), 3.19 (t, J = 7.63, 2H), 1.68 (m, 2H), 1.46-1.39 (m, 2H), 1.37-1.19 (m, 10H), 0.92-0.82 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 173.9, 151.8, 135.4, 132.6, 114.2, 111.2, 108.4, 42.8, 31.7, 29.3, 29.2, 29.0, 27.1, 22.6, 14.0.
N-cyclopentyl-4-nitroaniline (Table 3, Entry 2e)\textsuperscript{18}: Thick yellow liquid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 8.03\) (d, \(J = 9.16\) Hz, 2H), 6.48 (d, \(J = 9.16\) Hz, 2H), 4.59 (brs, 1H, NH), 3.88-3.78 (m, 1H), 2.10- 1.99 (m, 2H), 1.78- 1.59 (m, 4H), 1.54-1.43 (m, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 153.0, 137.4, 126.3, 111.2, 54.3, 33.3, 23.9\).

N-cyclopentyl-2-nitroaniline (Table 3, Entry 2f)\textsuperscript{19}: Thick yellow liquid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 8.16\) (dd, \(J = 8.39\) Hz, 1.53 Hz, 1H), 8.11 (brs, 1H, NH), 7.45-7.38 (m, 1H), 6.88 (d, \(J = 9.16\) Hz, 1H), 6.61 (t, \(J = 9.16\) Hz, 1H), 4.02-3.92 (m, 1H), 2.16-2.05 (m, 2H), 1.88-1.77 (m, 2H), 1.75-1.60 (m, 4H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 145.1, 135.9, 131.8, 126.8, 114.8, 114.6, 53.9, 33.5, 24.0\).

N-(4-nitrophenyl)cycloheptanamine (Table 3, Entry 2g)\textsuperscript{20}: Thick yellow liquid; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 8.07\) (d, \(J = 9.16\) Hz, 2H), 6.45 (d, \(J = 9.16\) Hz, 2H), 4.48 (brs, 1H, NH), 3.59- 3.49 (m, 1H), 2.08-1.96 (m, 2H), 1.79-1.47 (m, 10H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 152.2, 137.3, 126.5, 112.2, 53.6, 34.5, 28.0, 24.1\).
4-morpholinobenzonitrile (Table 3, Entry 2h)\textsuperscript{21}: Colorless solid, mp 74-76; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta = 7.48$ (d, $J = 9.16$ Hz, 2H), 6.83 (d, $J = 9.16$ Hz, 2H), 3.82 (t, $J = 4.58$ Hz, 4H), 3.24 (t, $J = 4.58$ Hz, 4H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): $\delta = 153.4$, 133.6, 119.9, 114.1, 101.0, 66.4, 47.5.

2-morpholinobenzonitrile (Table 3, Entry 2h)\textsuperscript{22}: Colorless solid, mp 82-84; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta = 7.61-7.56$ (m, 1H), 7.54-7.48 (m, 1H), 7.07-7.0 (m, 2H), 3.91 (t, $J = 4.58$ Hz, 4H), 3.21 (t, $J = 4.58$ Hz, 4H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): $\delta = 155.4$, 134.3, 133.8, 122.1, 118.4, 118.2, 106.0, 66.8, 51.7.

4-(4-methoxyphenyl)morpholine (Table 3, Entry 2j)\textsuperscript{23}: Colorless solid, mp 66-68; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta = 6.91-6.83$ (m, 4H), 3.85 (t, $J = 5.34$ Hz, 4H), 3.77 (s, 3H), 3.05 (t, $J = 5.34$ Hz, 4H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): $\delta = 153.9$, 145.6, 117.8, 114.4, 67.0, 55.5, 50.8.

7-chloro-4-(4-(2-nitrophenyl)piperazin-1-yl)quinoline (Table 3, Entry 2k): Pale yellow solid, mp 177-179; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): $\delta = 8.76$ (d, $J = 5.04$ Hz, 1H),
8.07 (d, \( J = 2.29 \) Hz, 1H), 7.99 (d, \( J = 8.70 \) Hz, 1H), 7.82 (dd, \( J = 8.24 \) Hz, \( J = 1.83 \) Hz, 1H), 7.59-7.53 (m, 1H), 7.45 (dd, \( J = 8.70 \) Hz, \( J = 1.83 \) Hz, 1H), 7.30-7.27 (m, 1H), 7.18-7.11 (m, 1H), 6.91 (d, \( J = 5.04 \) Hz, 1H), 3.42-3.33 (m, 8H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \( \delta = 156.6, 152.0, 150.1, 145.6, 144.0, 134.9, 133.5, 128.9, 126.3, 125.8, 124.9, 122.7, 121.8, 121.4, 109.3, 52.2, 51.8\); ESI-HRMS (m/z) Anal. Calcd. for C\(_{19}\)H\(_{18}\)ClN\(_4\)O\(_2\): 369.1113 (MH\(^+\)); Found: 369.1119 (MH\(^+\)).

7-chloro-4-(4-(4-nitrophenyl)cyclohexyl)quinolone (Table 3, Entry 2l): Pale yellow solid, mp 235-237; \(^1\)H NMR (400 MHz, CDCl\(_3\)) : \( \delta = 8.77 \) (d, \( J = 5.34 \) Hz, 1H), 8.18 (d, \( J = 9.16 \) Hz, 2H), 8.08 (d, \( J = 2.29 \) Hz, 1H), 8.0 (d, \( J = 9.16 \) Hz, 1H), 7.48 (dd, \( J = 9.16 \) Hz, \( J = 2.29 \) Hz, 1H), 6.97-6.89 (m, 4H), 3.70 (t, \( J = 5.34 \) Hz, 4H), 3.39 (t, \( J = 5.34 \) Hz, 4H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) : \( \delta = 156.2, 154.7, 151.9, 150.1, 139.1, 135.2, 129.0, 126.6, 125.9, 124.7, 121.7, 113.1, 109.1, 51.6, 47.2\).

7-chloro-N-(2-(4-(2-nitrophenyl)piperazin-1-yl)ethyl)quinolin-4-amine (Table 3, Entry 2m): Pale yellow solid, mp 103-105; \(^1\)H NMR (400 MHz, CDCl\(_3\)) : \( \delta = 8.41 \) (s, 1H), 8.05 (s, 1H), 7.92 (d, \( J = 8.70 \) Hz, 1H), 7.79-7.75 (m, 1H), 7.53-7.47 (m, 1H), 7.38 (d, \( J = 8.70 \) Hz, 1H), 7.17 (d, \( J = 8.24 \) Hz, 1H), 7.07 (t, \( J = 7.79 \) Hz, 1H), 6.43 (d, \( J = 4.58 \) Hz, 1H), 3.73 (brs, 1H, NH), 3.51-3.44 (m, 2H), 3.18-3.10 (m, 4H), 2.90 (t, \( J = 5.50 \) Hz, 2H), 1.97 (m, 4H), 1.38 (m, 4H), 0.98 (t, \( J = 7.00 \) Hz, 3H).
HZ, 2H), 2.78-2.71 (m, 4H); $^{13}$C NMR (100 MHz, DMSO): $\delta = 151.9, 149.9, 149.0, 134.1, 133.3, 131.5, 128.7, 127.5, 125.6, 124.8, 124.1, 123.9, 117.3, 98.7, 56.5, 54.3, 45.6; ESI-HRMS (m/z) Anal. Calcd. for C$_{21}$H$_{23}$ClN$_{5}$O$_{2}$: 412.1535 (MH)$^+$; Found: 412.1549 (MH)$^+$.

N-(4-methoxyphenyl)-2-nitroaniline (Table 4, Entry 3a)$^{25}$: Brown solid, mp 87-89; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.33$ (brs, 1H, NH), 8.11 (d, $J = 8.39$ Hz, 1H), 7.28-7.22 (m, 1H), 7.12 (d, $J = 8.39$ Hz, 2H), 6.95-6.86 (m, 3H), 6.67-6.60 (m, 1H), 3.76 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 157.9, 144.4, 135.7, 132.2, 131.1, 127.1, 126.5, 116.7, 115.7, 114.9, 55.5.

2-nitro-N-(p-tolyl)aniline (Table 4, Entry 3b)$^{25}$: Brown solid, mp 68-70; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.45$ (brs, 1H, NH), 8.22-8.17 (m, 1H), 7.37-7.29 (m, 1H), 7.22 (d, $J = 8.39$ Hz, 2H), 7.19-7.12 (m, 3H), 6.76-6.70 (m, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 143.7, 135.8, 135.7, 135.6, 132.7, 130.2, 126.6, 124.8, 117.0, 115.9, 20.9

N-(4-isopropylphenyl)-2-nitroaniline (Table 4, Entry 3c): Brown liquid; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.48$ (brs, 1H, NH), 8.19 (dd, $J = 8.70$ Hz, $J = 1.83$ Hz, 1H), 7.37-7.32 (m, 1H), 7.30-7.25 (m, 2H), 7.22-7.16 (m, 3H), 6.77-6.71 (m, 1H), 3.00-2.88 (m, 1H), 1.32-1.24 (d, $J = 6.87$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 146.6, 143.6, 136.1,
3,5-dimethoxy-N-(2-nitrophenyl)aniline (Table 4, Entry 3d): Brown solid, mp 85-87; $^1$H NMR (400 MHz, CDCl$_3$) : $\delta = 9.41$ (brs, 1H, NH), 8.19 (d, $J = 8.39$ Hz, 1H), 7.42-7.30 (m, 2H), 6.78 (t, $J = 7.63$ Hz, 1H), 6.43 (d, $J = 2.29$ Hz, 2H), 6.33 (t, $J = 2.29$ Hz, 1H), 3.79 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 161.6, 142.5, 140.4, 135.6, 133.6, 126.5, 117.6, 116.6, 102.1, 97.5, 54.4$; ESI-HRMS (m/z) Anal. Calcd. For C$_{14}$H$_{15}$N$_2$O$_4$: 275.1026 (MH$^+$); Found: 275.1056 (MH$^+$).
2H), 6.71-6.65 (m, 1H), 3.74 (brs, 2H, NH₂); ¹³C NMR (100 MHz, CDCl₃): δ = 144.9, 135.6, 132.1, 129.0, 127.3, 126.5, 116.3, 115.9, 115.8, 102.3; ESI-HRMS (m/z) Anal. Calcd. For C₁₂H₁₂N₃O₂: 230.0924 (MH)+; Found: 230.0924 (MH)+.

References:


S-24
S-25
Cpd 2: C15 H23 N O2: +ESI MFE Spectrum (0.131-0.748 min) Frag=135.0V PLRL-52.d

* 250/1805
((C15 H23 N O2)+H)+

516.3805
(2(C15 H23 N O2)+NH4)+

Counts vs. Mass-to-Charge (m/z)
Cpd 1: C19 H17 Cl N4 O2; +ESI MFE Spectrum (0.130-0.764 min) Frag=135.0V ATH-19.d

369.1119
([C19 H17 Cl N4 O2]+H)+
MFE MS Spectrum

Cpd 3: C21 H22 Cl N5 O2; +ESI MFE Spectrum (0.123-0.707 min) Frag=135.0V PRLC-308.d

412.1549
([C21 H22 Cl N5 O2]+H)+

Counts vs. Mass-to-Charge (m/z)

S-54
Cpd 24: C14 H14 N2 O4: +ESI MFE Spectrum (0.144-0.428 min) Frag=135.0V PLRC-59A.d

275.1056
([C14 H14 N2 O4]+H)+

MFE MS Spectrum

Counts vs. Mass-to-Charge (m/z)