Supporting Information for

Copper-Catalyzed, Ceric Ammonium Nitrate Mediated N-Arylation of Amines

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**General method:** Air and/or moisture sensitive reactions were carried out in anhydrous solvents under an atmosphere of argon in an oven or flame-dried glassware. All anhydrous solvents were distilled prior to use: THF, benzene, toluene, diethyl ether from Na and benzophenone; CH$_2$Cl$_2$, DMSO, DMF, hexane from CaH$_2$; MeOH, EtOH from Mg cake. Commercial reagents were used without purification. Column chromatography was carried out by using silica gel (100–200 mesh). $^1$H and $^{13}$C NMR chemical shifts are reported in ppm downfield from tetramethylsilane and coupling constants ($J$) are reported in hertz (Hz). The following abbreviations are used to designate signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

**Experimental Section**

**General Procedure:** To a 5 mL scintillation vial equipped with a Teflon-coated magnetic stir bar were loaded with aryl/alkyl amine (1 equiv, 1 mmol), aryl boronic acid (1.2 equiv, 1.2 mmol), CAN (1.5 equiv, 1.5 mmol) and Cu(OAc)$_2$ (0.1 equiv, 0.1 mmol) in toluene at room temperature and stirred for 12-24 h. Monitored by TLC until the starting materials were consumed. The solvent was removed by rotavapor to give a residue, from which the product was isolated by column chromatography on silica gel with MeOH/CH$_2$Cl$_2$ or EtOAc/petroleum ether (1% Et$_3$N as modifier) as eluents. Appropriate fractions were evaporated to afford the desired product.
Table 1:

3a: 4-Methoxy-N-phenylaniline
The compound data were in accordance with the literature.¹

\[
\begin{align*}
&\text{Ph} & \text{N} & \text{OMe} \\
&\text{H} & & \\
\end{align*}
\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.25 (dd, \(J = 10.2, 5.3\) Hz, 2H), 7.10 (s, 2H), 7.01 – 6.72 (m, 5H), 5.30 (s, 1H), 3.84 (s, 3H).
\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 155.3, 145.1, 135.7, 129.2, 122.1, 119.6, 115.6, 114.6, 55.5.

4a: 4-Chloro-N-phenylaniline
The compound data were in accordance with the literature.¹

\[
\begin{align*}
&\text{Ph} & \text{N} & \text{Cl} \\
&\text{H} & & \\
\end{align*}
\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.16 (m, 4H), 7.12 – 6.92 (m, 5H), 5.68 (s, 1H).
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 142.6, 141.8, 129.4, 129.4, 129.3, 125.5, 121.5, 118.8, 118.1.

4b: N-phenyl-4-(trifluoromethyl)aniline
The compound data were in accordance with the literature.²

\[
\begin{align*}
&\text{Ph} & \text{N} & \text{CF}_3 \\
&\text{H} & & \\
\end{align*}
\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.49 (d, \(J = 8.6\) Hz, 2H), 7.44 – 7.31 (m, 2H), 7.17 (dd, \(J = 7.5, 1.1\) Hz, 2H), 7.12 – 6.99 (m, 3H), 5.92 (s, 1H).
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 146.8, 141.2, 129.6, 126.7 (q, \(J = 3.8\) Hz), 124.6, 122.9, 121.7 (q, \(J = 32.4\)), 120.0, 115.3.

4c: 4-(phenylamino)benzonitrile
The compound data were in accordance with the literature.  

\[ \text{Ph} \text{CN} \text{H} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.53 – 7.43 (m, 2H), 7.36 (t, \(J = 7.6\) Hz, 2H), 7.26 (d, \(J = 1.3\) Hz, 2H), 7.14 (ddd, \(J = 14.7, 8.5, 1.0\) Hz, 1H), 7.03 – 6.92 (m, 2H), 6.05 (s, 1H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 148.0, 140.0, 133.8, 129.6, 124.0, 121.3, 119.7, 114.9, 101.7.

**4d: \(N\)-phenyl-3-(trifluoromethyl)aniline**

The compound data were in accordance with the literature.  

\[ \text{Ph} \text{CF}_3 \text{H} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.30 (m, 3H), 7.28 (dd, \(J = 4.9, 4.3\) Hz, 1H), 7.23 – 7.17 (m, 1H), 7.17 – 7.08 (m, 3H), 7.08 – 6.96 (m, 1H), 5.65 (s, 1H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 144.0, 141.8, 131.6 (q, \(J = 33\) Hz), 129.8, 129.5, 124.1 (q, \(j = 180\) Hz), 122.3, 119.7, 119.1, 116.9 (q, \(j = 4\) Hz), 113.2.

**4e: 3-bromo-N-phenylaniline**

The compound data were in accordance with the literature.  

\[ \text{Ph} \text{Br} \text{H} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.42 – 7.28 (m, 2H), 7.23 (dt, \(J = 4.1, 2.3\) Hz, 1H), 7.18 – 7.09 (m, 3H), 7.08 – 7.00 (m, 2H), 7.00 – 6.91 (m, 1H), 5.71 (s, 1H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 144.9, 141.9, 130.7, 129.5, 123.4, 123.2, 122.2, 119.6, 119.0, 115.6.

**4f: 2-fluoro-N-phenylaniline**

The compound data were in accordance with the literature.  

\[ \text{Ph} \text{F} \text{H} \]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.42 – 7.28 (m, 2H), 7.23 (dt, \(J = 4.1, 2.3\) Hz, 1H), 7.18 – 7.09 (m, 3H), 7.08 – 7.00 (m, 2H), 7.00 – 6.91 (m, 1H), 5.71 (s, 1H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 144.9, 141.9, 130.7, 129.5, 123.4, 123.2, 122.2, 119.6, 119.0, 115.6.
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.51 – 7.19 (m, 2H), 7.17 – 6.86 (m, 6H), 6.88 – 6.69 (m, 1H), 5.76 (s, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 152.9 (d, $J = 241.0$ Hz), 141.9, 129.3, 124.2, 124.2, 121.7, 120.4 (d, $J = 7.3$ Hz), 118.6, 117.1, 115.4 (d, $J = 19.2$ Hz).

4g: 2-chloro-$N$-phenylaniline
The compound data were in accordance with the literature.$^6$

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.51 – 7.25 (m, 4H), 7.25 – 6.96 (m, 4H), 6.85 (t, $J = 7.6$ Hz, 1H), 6.15 (s, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 141.5, 140.3, 129.8, 129.5, 127.5, 122.7, 121.5, 120.4, 120.2, 115.6.

4h: 2-methoxy-$N$-phenylaniline
The compound data were in accordance with the literature.$^6$

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.45 – 7.28 (m, 3H), 7.25 (d, $J = 8.1$ Hz, 2H), 7.08 – 6.93 (m, 4H), 6.26 (s, 1H), 3.98 – 3.94 (m, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 148.3, 142.8, 133.0, 129.3, 121.2, 120.9, 119.9, 118.6, 114.8, 110.6, 55.6.

4i: 3,5-dimethoxy-$N$-phenylaniline
The compound data were in accordance with the literature.$^1$
\[ \text{Ph} \]

\[ \text{H NMR (300 MHz, CDCl}_3 \text{)} \delta 7.44 - 7.21 (m, 2H), 7.18 - 7.05 (m, 2H), 7.04 - 6.83 (m, 1H), 6.32 - 6.17 (m, 2H), 6.13 - 5.97 (m, 1H), 5.72 (s, 1H), 3.82 - 3.69 (m, 6H). \]

\[ \text{C NMR (75 MHz, CDCl}_3 \text{)} \delta 161.6, 145.2, 142.5, 129.3, 121.4, 118.8, 95.7, 92.9, 55.3. \]

**4j: 4-methyl-N-phenylaniline**

The compound data were in accordance with the literature.¹

\[ \text{Ph} \]

\[ \text{H NMR (300 MHz, CDCl}_3 \text{)} \delta 7.32 - 7.19 (m, 2H), 7.16 - 6.96 (m, 6H), 6.90 (t, J = 7.1 Hz, 1H), 5.61 (s, 1H), 2.33 (s, 3H). \]

\[ \text{C NMR (75 MHz, CDCl}_3 \text{)} \delta 143.9, 140.3, 131.0, 129.9, 129.3, 129.1, 120.3, 118.9, 116.9, 20.7. \]

**4k: 4-(methylthio)-N-phenylaniline**

The compound data were in accordance with the literature.⁷

\[ \text{Ph} \]

\[ \text{H NMR (300 MHz, CDCl}_3 \text{)} \delta 7.30 - 7.22 (m, 4H), 7.11 - 6.98 (m, 4H), 6.93 (dt, J = 18.7, 6.1 Hz, 1H), 5.68 (s, 1H), 2.46 (d, J = 4.3 Hz, 3H). \]

\[ \text{C NMR (75 MHz, CDCl}_3 \text{)} \delta 143.0, 141.3, 129.9, 129.4, 129.0, 121.1, 118.5, 117.7, 17.9. \]

**4l: N-phenylpyridin-2-amine**

The compound data were in accordance with the literature.⁵
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.20 (s, 1H), 7.50 (t, $J$ = 7.8 Hz, 1H), 7.40 – 7.15 (m, 4H), 7.13 – 6.97 (m, 1H), 6.96 – 6.79 (m, 2H), 6.77 – 6.61 (m, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 155.9, 147.7, 140.1, 138.0, 129.3, 123.1, 120.6, 114.9, 108.3.

Table 2:

6a: Diphenylamine

The compound data were in accordance with the literature.$^1$

6b: N-Phenynaphthalen-1-amine

The compound data were in accordance with the literature.$^1$

6c: 4-Phenoxyphenyl)phenylamine
The compound data were in accordance with the literature.\(^8\)

\[
\begin{align*}
\text{PhO} & - \text{N} - \text{Ph} \\
\end{align*}
\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.30 \ (\text{dddd}, J = 8.4, 7.4, 4.8, 2.1 \text{ Hz}, 4 \text{H}), 7.15 - 6.87 \ (\text{m}, 10 \text{H}), 5.62 \ (\text{s}, 1 \text{H}).\)

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 158.5, 151.6, 144.2, 130.0, 129.9, 129.7, 123.0, 120.9, 120.9, 120.7, 118.3, 118.2, 117.2.\)

\textbf{6d: 4-Ethyl-N-phenylaniline}

The compound data were in accordance with the literature.\(^1\)

\[
\begin{align*}
\text{N} & - \text{Ph} \\
\end{align*}
\]

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 7.36 - 7.19 \ (\text{m}, 2 \text{H}), 7.42 - 6.83 \ (\text{m}, 2 \text{H}), 7.07 \ (\text{dd}, J = 5.2, 3.2 \text{ Hz}, 4 \text{H}), 6.95 \ (\text{dd}, J = 10.5, 4.2 \text{ Hz}, 1 \text{H}), 5.65 \ (\text{s}, 1 \text{H}), 2.67 \ (\text{q}, J = 7.6 \text{ Hz}, 2 \text{H}), 1.30 \ (\text{t}, J = 7.6 \text{ Hz}, 3 \text{H}).\)

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 143.9, 140.6, 137.4, 129.4, 128.7, 120.4, 118.9, 118.8, 117.0, 28.2, 15.8.\)

\textbf{6e: 3-Methoxy-N-phenylaniline}

The compound data were in accordance with the literature.\(^1\)
$^1$H NMR (600 MHz, CDCl$_3$) δ 7.24 (t, $J = 7.7$ Hz, 2H), 7.13 (t, $J = 7.9$ Hz, 1H), 7.05 (d, $J = 7.9$ Hz, 2H), 6.91 (t, $J = 7.3$ Hz, 1H), 6.62 (d, $J = 8.5$ Hz, 2H), 6.46 (d, $J = 8.2$ Hz, 1H), 5.68 (s, 1H), 3.73 (s, 3H).
$^{13}$C NMR (151 MHz, CDCl$_3$) δ 160.8, 144.7, 142.9, 130.2, 129.4, 121.3, 118.4, 110.3, 106.3, 103.4, 55.3.

6f: N-(3-Biphenyl)aniline
The compound data were in accordance with the literature.$^9$

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.65 (ddd, $J = 4.3$, 3.5, 1.9 Hz, 2H), 7.50 (ddd, $J = 7.6$, 4.5, 1.3 Hz, 2H), 7.46 – 7.33 (m, 5H), 7.30 – 7.16 (m, 3H), 7.16 – 7.09 (m, 1H), 7.03 (ddd, $J = 8.4$, 2.2, 1.1 Hz, 1H), 5.82 (s, 1H).
$^{13}$C NMR (75 MHz, CDCl$_3$) δ 143.5, 142.9, 142.4, 141.1, 129.6, 129.3, 128.7, 127.3, 127.1, 121.1, 119.8, 117.9, 116.5, 116.4.

6g: N-(3-Fluorophenyl)-N-phenylamine
The compound data were in accordance with the literature.$^{10}$

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.46 – 7.28 (m, 2H), 7.27 – 7.10 (m, 3H), 7.04 (dt, $J = 14.6$, 4.1 Hz, 1H), 6.88 – 6.73 (m, 2H), 6.72 – 6.65 (m, 1H), 5.78 (s, 1H).
$^{13}$C NMR (151 MHz, CDCl$_3$) δ 163.8 (d, $J = 243.9$ Hz), 145.4 (d, $J = 10.5$ Hz), 141.9, 130.4 (d, $J = 10.0$ Hz), 129.4, 122.0, 119.0, 112.4, 106.9 (d, $J = 21.5$ Hz), 103.5 (d, $J = 25.1$ Hz).
6h: 3-Chloro-N-phenylaniline
The compound data were in accordance with the literature.\textsuperscript{11}

![3-Chloro-N-phenylaniline](image)

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 7.42 – 7.23 (m, 2H), 7.3-6.9 (m, J = 15.9, 7.7 Hz, 5H), 6.91 (dd, J = 9.2, 4.0 Hz, 2H), 5.70 (s, 1H).
\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) δ 144.8, 141.9, 135.0, 130.3, 129.5, 122.1, 120.5, 119.0, 116.6, 115.1.

Table 3:

8a: \textit{N}-benzylaniline
The compound data were in accordance with the literature.\textsuperscript{11}

![\textit{N}-benzylaniline](image)

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 7.41 – 7.26 (m, 5H), 7.24 – 7.15 (m, 2H), 6.79 – 6.69 (m, 1H), 6.69 – 6.60 (m, 2H), 4.34 (s, 2H), 4.08 (bs, 1H).
\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) δ 148.1, 139.4, 129.3, 128.6, 127.5, 127.2, 117.5, 112.8, 48.3.

8b: 1,4-Diphenylpiperazine
The compound data were in accordance with the literature.\textsuperscript{12}

![1,4-Diphenylpiperazine](image)

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 7.32 – 7.25 (m, 4H), 6.99 (dd, J = 7.9, 0.7 Hz, 4H), 6.90 (td, J = 7.3, 0.7 Hz, 2H), 3.34 (d, J = 4.9 Hz, 8H).
\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) δ 151.3, 129.3, 129.2, 120.1, 116.4, 49.5.

8c: 1-Phenyl-4-(pyridin-2-yl)piperazine
The compound data were in accordance with the literature.\textsuperscript{12}

![1-Phenyl-4-(pyridin-2-yl)piperazine](image)

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) δ 7.32 – 7.25 (m, 4H), 6.99 (dd, J = 7.9, 0.7 Hz, 4H), 6.90 (td, J = 7.3, 0.7 Hz, 2H), 3.34 (d, J = 4.9 Hz, 8H).
\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) δ 151.3, 129.3, 129.2, 120.1, 116.4, 49.5.
$^1$H NMR (300 MHz, CDCl$_3$) δ 8.22 (dd, $J = 5.0$, 1.3 Hz, 1H), 7.52 (ddd, $J = 8.9$, 7.2, 2.0 Hz, 1H), 7.34 – 7.26 (m, 2H), 6.98 (dd, $J = 13.0$, 5.1 Hz, 2H), 6.89 (t, $J = 7.3$ Hz, 1H), 6.75 – 6.62 (m, 2H), 3.71 (dd, $J = 6.1$, 4.3 Hz, 4H), 3.31 (dd, $J = 6.1$, 4.3 Hz, 4H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 159.2, 151.2, 147.6, 137.9, 129.2, 120.1, 116.4, 113.6, 107.5, 49.2, 45.4.

8d: 2-(4-Phenylpiperazin-1-yl)pyrimidine

The compound data were in accordance with the literature.$^{13}$

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.55 – 8.18 (m, 2H), 7.44 – 7.17 (m, 3H), 7.03 – 6.94 (m, 1H), 6.94 – 6.84 (m, 1H), 6.52 (dd, $J = 6.2$, 3.2 Hz, 1H), 4.10 – 3.88 (m, 4H), 3.23 (dd, $J = 23.1$, 18.0 Hz, 4H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 161.7, 157.8, 151.3, 129.2, 120.2, 116.5, 110.1, 49.4, 43.7.

References:


1H and 13C NMR of 4-Methoxy-N-phenylaniline (3a)
$^{1}\text{H}$ and $^{13}\text{C}$ NMR of 4-Chloro-N-phenylaniline (4a)
$^1$H and $^{13}$C NMR of N-phenyl-4-(trifluoromethyl)aniline (4b)
$^1$H and $^{13}$C NMR of 4-(phenylamino)benzonitrile (4c)
$^1$H and $^{13}$C NMR of N-phenyl-3-(trifluoromethyl)aniline (4d)
$^1$H and $^{13}$C NMR of 3-bromo-N-phenylaniline (4e)
$^{1}$H and $^{13}$C NMR of 2-fluoro-N-phenylaniline (4f)
$^1$H and $^{13}$C NMR of 2-chloro-N-phenylaniline (4g)
$^1$H and $^{13}$C NMR of 2-methoxy-N-phenylaniline (4h)
$^1$H and $^{13}$C NMR of 3,5-dimethoxy-N-phenylaniline (4i)
$^1$H and $^{13}$C NMR of 4-Methyl-N-phenylaniline (4j)
$^1$H and $^{13}$C NMR of 4-(methylthio)-N-phenylaniline (4k)
$^{1}H$ and $^{13}C$ NMR of $N$-phenylpyridin-2-amine (4I)
$^1$H and $^{13}$C NMR of Diphenylamine (6a)
$^1$H and $^{13}$C NMR of N-Phenynaphthalen-1-amine (6b)
$^1$H and $^{13}$C NMR of 4-Phenoxyphenyl)phenylamine (6c)
$^1$H and $^{13}$C NMR of 4-Ethyl-N-phenylaniline (6d)
$^1$H and $^{13}$C NMR of 3-Methoxy-N-phenylaniline (6e)
$^1$H and $^{13}$C NMR of N-(3-Biphenyl)aniline (6f)
$^1$H and $^{13}$C NMR of N-(3-Fluorophenyl)-N-phenylamine (6g)
$^1$H and $^{13}$C NMR of 3-Chloro-N-phenylaniline (6h)
$^1$H and $^{13}$C NMR of $N$-benzylaniline (8a)
1H and 13C NMR of 1,4-Diphenylpiperazine (8b)
$^1$H and $^{13}$C NMR of 1-Phenyl-4-(pyridin-2-yl)piperazine (8c)
$^1$H and $^{13}$C NMR of 2-(4-Phenylpiperazin-1-yl)pyrimidine (8d)