Cu-mediated Nitrogen-Atom Transfer via C≡N Bond Cleavage

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Content

I. General information .............................................................................................................2
II. Typical experimental procedure for the synthesis of aryl nitriles .................................2
III. Optimization of reaction conditions .............................................................................2
IV. Reactions of 4-Bromobenzaldehyde and 4-Iodobenzaldehyde with acetonitrile ..........4
V. Investigation on the reaction mechanism .......................................................................4
VI. ¹H and ¹³C NMR spectra data of the products ..............................................................8
VII. References ......................................................................................................................13
VIII. Copies of ¹H and ¹³C NMR charts of the products ..................................................14
I. General information

Except where otherwise noted, all reactions were carried out in 25 mL sealed Schlenk tubes under anhydrous conditions and O\textsubscript{2} atmosphere, and monitored by GC and/or GC-MS. All solvents were dried and distilled before use according to the standard methods. Column chromatography was performed using Silica Gel 60 (particle size 300–400 μm). The \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on a 400 MHz spectrometer (400 MHz for \textsuperscript{1}H and 100 MHz for \textsuperscript{13}C NMR spectroscopy). CDCl\textsubscript{3} or DMSO-\textit{d}\textsubscript{6} was used as the solvent. Chemical shifts for \textsuperscript{1}H NMR are referred to internal Me\textsubscript{4}Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, integration and coupling constant (Hz). Data for \textsuperscript{13}C NMR are reported in ppm relative to the center line of a triplet at 77.0 ppm for chloroform-\textit{d}. GC-MS results were recorded on GC-MS QP2010, and GC analysis was performed on GC 2010 plus. The electron ionization (EI) method was used as the ionization method for the HRMS measurement, and the mass analyzer type is TOF for EI.

II. Typical experimental procedure for the synthesis of aryl nitriles

An oven-dried 25 mL Schlenk tube, which was equipped with a magnetic stir bar and charged with CuCl (29.7 mg, 0.3 mmol), was evacuated and backfilled with oxygen three times. Then, CH\textsubscript{3}CN (0.67 mL), DMAc (0.33 mL), and 4-methoxybenzaldehyde \textit{1a} (27.2 mg, 0.2 mmol) were added. The reaction mixture was stirred at 130 °C for 24 h and monitored by GC or GC-MS. After completion of the reaction, the resulting solution was cooled to room temperature, and washed with saturated NH\textsubscript{4}Cl solution (10.0 mL). The product was extracted with CHCl\textsubscript{3} (5.0 mL × 3), filtered and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuo. The crude product was purified by column chromatography on silica gel with ethyl acetate / petroleum ether (1 / 10) to afford white solid 4-methoxybenzonitrile \textit{2a} in 83% yield (22.1 mg).

III. Optimization of reaction conditions

\textit{Table S1. Optimization of solvent\textsuperscript{a}}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield %\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH\textsubscript{3}CN</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>DMAc</td>
<td>None</td>
</tr>
<tr>
<td>3</td>
<td>DMAc:CH\textsubscript{3}CN (4:1)</td>
<td>Trace</td>
</tr>
<tr>
<td>4</td>
<td>DMAc:CH\textsubscript{3}CN (2:1)</td>
<td>29</td>
</tr>
<tr>
<td>5</td>
<td>DMAc:CH\textsubscript{3}CN (1:1)</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td>DMAc:CH\textsubscript{3}CN (1:2)</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>DMAc:CH\textsubscript{3}CN (1:3)</td>
<td>80</td>
</tr>
<tr>
<td>8</td>
<td>DMAc:CH\textsubscript{3}CN (1:9)</td>
<td>56</td>
</tr>
<tr>
<td>9</td>
<td>DMSO:CH\textsubscript{3}CN (1:2)</td>
<td>14</td>
</tr>
<tr>
<td>10</td>
<td>NMP:CH\textsubscript{3}CN (1:2)</td>
<td>18</td>
</tr>
<tr>
<td>11\textsuperscript{c}</td>
<td>DMAc:CH\textsubscript{3}CN (1:2)</td>
<td>None</td>
</tr>
<tr>
<td>12\textsuperscript{d}</td>
<td>DMAc:CH\textsubscript{3}CN (1:2)</td>
<td>Trace</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: \textit{1b} (24.0 mg, 0.2 mmol), CuCl (29.7 mg, 0.3 mmol), solvent (1.0 mL), 130 °C, 24 h.
Table S2. Optimization of temperature and time

![Chemical structure of reaction 1b to 2b]

<table>
<thead>
<tr>
<th>Entry</th>
<th>T/°C</th>
<th>t/h</th>
<th>Yield %&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>24</td>
<td>Trace</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>24</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>130</td>
<td>24</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>140</td>
<td>24</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>130</td>
<td>12</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>130</td>
<td>16</td>
<td>54</td>
</tr>
<tr>
<td>7</td>
<td>130</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>8</td>
<td>130</td>
<td>28</td>
<td>92</td>
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</tbody>
</table>

<sup>a</sup>Reaction conditions: 1b (24.0 mg, 0.2 mmol), CuCl (29.7 mg, 0.3 mmol), solvent (1.0 mL), 130 °C, 24 h.
<sup>b</sup>GC yield.

Table S3. Optimization of copper loading

![Chemical structure of reaction 1b to 2b]

<table>
<thead>
<tr>
<th>Entry</th>
<th>CuCl (eq.)</th>
<th>Yield %&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>Trace</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>1.1</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>79</td>
</tr>
<tr>
<td>5</td>
<td>1.3</td>
<td>82</td>
</tr>
<tr>
<td>6</td>
<td>1.4</td>
<td>87</td>
</tr>
<tr>
<td>7</td>
<td>1.5</td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
<td>91</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 1b (24.0 mg, 0.2 mmol), solvent (1.0 mL), 130 °C, 24 h. <sup>b</sup>GC yield.

Table S4. Optimization of Cu salts

![Chemical structure of reaction 1b to 2b]

<table>
<thead>
<tr>
<th>Entry</th>
<th>[Cu]</th>
<th>Yield %&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>CuCl</td>
<td>90</td>
</tr>
</tbody>
</table>
IV. Reactions of 4-Bromobenzaldehyde and 4-Iodobenzaldehyde with acetonitrile

<table>
<thead>
<tr>
<th>Entry</th>
<th>X</th>
<th>Yield %</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-Br</td>
<td>2s, 64a (85)b</td>
<td>2i, 17a (4)b</td>
</tr>
<tr>
<td>2</td>
<td>-I</td>
<td>2t, 52a (80)b</td>
<td>2i, 23a (8)b</td>
</tr>
</tbody>
</table>

aReaction conditions: 1b (24.0 mg, 0.2 mmol), [Cu] (0.3 mmol), 130 °C, 24 h. bGC yield.

V. Investigation on the reaction mechanism

1. 13C Labeled CH3CN and 4-methoxybenzaldehyde Test

Acetonitrile-1-13C (99 atom%, 13C, cat. No. 485160) were purchased from Aldrich, Anisaldehyde-[7-13C] (98% atom%, 13C, cat. No. A673202) were purchased from TRG, the isotope reagents were used without further purification.

An oven-dried 25 mL Schlenk tube, which was equipped with a magnetic stir bar and charged with CuCl (29.7 mg, 0.3 mmol), was evacuated and backfilled with oxygen three times. Then, CH313CN (1.0 mL) and 4-methoxybenzaldehyde 1a (27.2 mg, 0.2 mmol) were added. The reaction mixture was stirred at 130 °C
for 24 h and monitored by GC or GC-MS. After completion of the reaction, the resulting solution was cooled to room temperature, and washed with saturated NH₄Cl solution (10.0 mL). The product was extracted with CHCl₃ (5.0 mL × 3), filtered and dried over anhydrous Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1/10) to afford white solid 4-methoxybenzonitrile 2a in 37% yield (9.8 mg).

(2)

\[
\text{MeO-}^{13}\text{CHO} \xrightarrow{\text{CuCl (1.5 eq.), CH₃CN (1.0 mL), O₂, 130 °C, 24 h}} \text{MeO-}^{13}\text{CN}
\]

39% isolated yield (98.5% ¹³C)

An oven-dried 25 mL Schlenk tube, which was equipped with a magnetic stir bar and charged with CuCl (29.7 mg, 0.3 mmol), was evacuated and backfilled with oxygen three times. Then, CH₃CN (1.0 mL) and Anisaldehyde-[7-¹³C] (27.4 mg, 0.2 mmol) were added. The reaction mixture was stirred at 130 °C for 24 h and monitored by GC or GC-MS. After completion of the reaction, the resulting solution was cooled to room temperature, and washed with saturated NH₄Cl solution (10.0 mL). The product was extracted with CHCl₃ (5.0 mL × 3), filtered and dried over anhydrous Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel with ethyl acetate/petroleum ether (1/10) to afford white solid 4-methoxybenzonitrile 2a-¹³C in 39% yield (10.5 mg).

4-Methoxybenzonitrile-¹³C (¹³C-2a): 98.5% of ¹³C incorporation; HRMS (ESI+) exact mass calc’d for (C₁₇H₁₃NO)⁺ (M+H)⁺ requires m/z: 134.0571, found m/z: 134.0559.

4-Methoxybenzonitrile (2a): Inverse gated decoupling ¹³C NMR (100 MHz, CDCl₃): δ 55.5 (int. = 1.00), 119.1 (-C≡N, int. = 0.29)

4-Methoxybenzonitrile-¹³C (2a-¹³C): Inverse gated decoupling ¹³C NMR (100 MHz, CDCl₃): δ 55.5 (int. = 1.00), 119.2 (-C≡N, int. = 28.57). (¹³C incorporation: 28.57 / 0.29 = 98.5%).
Copies of $^{13}$C NMR charts of 2a

Copies of $^{13}$C NMR charts of $^{13}$C-2a
2. Control experiments

(1) The free-radical experiments

A) \[
\text{CuCl (1.5 eq.)} \quad \overset{\text{CH$_3$CN-DMAC (2:1) (1.0 mL)}}{\text{O$_2$, 130 °C, 24 h}} \quad \text{CuCN (10%)} \quad \text{Trace}
\]

B) \[
\text{CuCl (1.5 eq.)} \quad \overset{\text{CH$_3$CN-DMAC (2:1) (1.0 mL)}}{\text{O$_2$, 130 °C, 2 h}} \quad \text{[M+H]$^+$ (m/z = 197.1)}
\]

(2) Reactivities of nitriles
(3) Reactivities of other substrates

A) 

\[
\text{Ph-CN} \quad \text{CuCl (1.5 eq.)}
\quad \text{DMAC (1.0 mL), O}_2 \quad 130^\circ C, 24 \text{ h}
\rightarrow \text{Me-CN}
\]

0.2 mmol \hspace{1cm} 0.3 mmol

60%

3%

2%

trace

B) 

\[
\text{O-H} \quad \text{CuCl (1.5 eq.)}
\quad \text{CH}_3\text{CN:DMAC (2:1) (1.0 mL), O}_2 \quad 130^\circ C, 24 \text{ h}
\rightarrow \text{Me-CN}
\]

0.2 mmol

3.0 mmol

0.2 mmol

0.2 mmol

47%

trace

none

5%

trace

3. The capture of CO$_2$

The reactions were carried out under standard conditions with a large scale. After completion of the reactions, the reaction systems were contacted with lime-water, they became muddy immediately.

A) 

\[
\text{MeO-CHO} + \text{CH}_3\text{CN} \quad \text{CuCl (1.5 eq.)}
\quad \text{O}_2 \text{ (balloon), 130}^\circ \text{ C, 36 h}
\rightarrow \text{MeO-} + \text{CO}_2
\]

10 mmol \hspace{1cm} 15 mL

B) 

\[
\text{MeO-CHO} + \text{pentanenitrile} \quad \text{CuCl (1.5 eq.)}
\quad \text{O}_2 \text{ (balloon), 130}^\circ \text{ C, 36 h}
\rightarrow \text{MeO-} + \text{CO}_2
\]

10 mmol \hspace{1cm} 15 mL

C) 

\[
\text{MeO-CHO} + \text{CH}_3\text{CN} + \text{DMAC} \quad \text{CuCl (1.5 eq.)}
\quad \text{O}_2 \text{ (balloon), 130}^\circ \text{ C, 36 h}
\rightarrow \text{MeO-} + \text{CO}_2
\]

10 mmol \hspace{1cm} 10 mL \hspace{1cm} 5 mL

VI. $^1$H and $^{13}$C NMR spectra data of the products
4-Methoxybenzonitrile (2a)\(^2\)

![Structure of 4-Methoxybenzonitrile](image)

White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.58 \ (d, \ J = 9.0 \ Hz, \ 2H)\), 6.95 (d, \(J = 8.9 \ Hz, \ 2H\)), 3.86 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 162.8, \ 133.9, \ 119.1, \ 114.7, \ 103.9, \ 55.5\).

4-Methylbenzonitrile (2b)\(^2\)

![Structure of 4-Methylbenzonitrile](image)

Yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.54 \ (d, \ J = 8.1 \ Hz, \ 2H)\), 7.27 (d, \(J = 6.8 \ Hz, \ 2H\)), 2.42 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 143.6, \ 132.0, \ 129.7, \ 119.1, \ 109.2, \ 21.8\).

2-Methylbenzonitrile (2c)\(^2\)

![Structure of 2-Methylbenzonitrile](image)

White liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.61 \ (d, \ J = 7.8 \ Hz, \ 1H)\), 7.49 (t, \(J = 7.6 \ Hz, \ 1H\)), 7.33–7.27 (m, \(2H\)), 2.56 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 141.9, \ 132.6, \ 132.4, \ 130.1, \ 126.1, \ 118.1, \ 112.7, \ 20.4\).

2,4,6-Trimethylbenzonitrile (2d)\(^3\)

![Structure of 2,4,6-Trimethylbenzonitrile](image)

White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 6.93 \ (s, \ 2H)\), 2.48 (s, \(6H\)), 2.32 (s, \(3H\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 142.7, \ 141.9, \ 128.1, \ 117.6, \ 110.2, \ 21.5, \ 20.6\).

4-(t-Butyl)benzonitrile (2e)\(^3\)

![Structure of 4-(t-Butyl)benzonitrile](image)

Yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.59 \ (d, \ J = 8.4 \ Hz, \ 2H)\), 7.48 (d, \(J = 8.4 \ Hz, \ 2H\)), 1.32 (s, \(9H\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 156.5, \ 131.9, \ 126.1, \ 119.1, \ 109.2, \ 35.2, \ 30.9\).

4-Phenylbenzonitrile (2f)\(^3\)

![Structure of 4-Phenylbenzonitrile](image)

White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.72 \ (d, \ J = 8.4 \ Hz, \ 2H)\), 7.68 (d, \(J = 8.4 \ Hz, \ 2H\)), 7.59 (d, \(J = 7.2 \ Hz, \ 2H\)), 7.50–7.41 (m, \(3H\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 145.5, \ 139.0, \ 132.5, \ 129.0, \ 128.5, \ 127.6, \ 127.1, \ 118.8, \ 110.8\).

2,3-Dihydro-1,4-benzodioxine-6-carbonitrile (2g)\(^4\)

![Structure of 2,3-Dihydro-1,4-benzodioxine-6-carbonitrile](image)
White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.15–7.12 (m, 2H), 6.91 (d, $J = 8.4$ Hz, 1H), 4.32–4.27 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.6, 143.7, 125.9, 121.2, 118.8, 118.2, 104.4, 64.5, 64.0.

**4-Fluorobenzonitrile (2h)**

Yellow solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.70–7.65 (m, 2H), 7.20–7.14 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.0 (d, $J_{C-F} = 256.7$ Hz), 134.6 (d, $J_{C-F} = 9.3$ Hz), 118.0, 116.8 (d, $J_{C-F} = 22.7$ Hz), 108.5 (d, $J_{C-F} = 3.7$ Hz).

**4-Chlorobenzonitrile (2i)**

White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (d, $J = 8.5$ Hz, 2H), 7.46 (d, $J = 8.5$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 139.5, 133.3, 129.6, 117.9, 110.7.

**2-Chlorobenzonitrile (2j)**

White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.68 (dd, $J = 7.8$, 1.3 Hz, 1H), 7.57–7.50 (m, 2H), 7.39–7.35 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 136.8, 133.9, 133.8, 130.0, 127.1, 115.9, 113.3.

**Benzonitrile (2k)**

Colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.65–7.58 (m, 3H), 7.47 (t, $J = 7.7$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 132.7, 132.0, 129.0, 118.7, 112.3.

**N-(4-cyanophenyl)acetamide (2l)**

White solid. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 10.38 (s, 1H), 7.74 (s, 4H), 2.08 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 169.1, 143.4, 133.2, 119.1, 118.9, 104.6, 24.2.
4-(Phenylethynyl)benzonitrile (2m)\(^6\)

White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.64 (d, J = 8.3 \text{ Hz}, 2H), 7.60 (d, J = 8.4 \text{ Hz}, 2H), 7.55-7.53 (m, 2H), 7.39-7.36 (m, 3H). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 132.0, 132.0, 131.7, 129.1, 128.4, 128.2, 122.1, 118.5, 111.4, 93.7, 87.6.\)

*(E)-4-styrylbenzonitrile (2n)\(^7\)*

White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.64 (d, J = 8.4 \text{ Hz}, 2H), 7.59 (d, J = 8.4 \text{ Hz}, 2H), 7.54 (d, J = 7.4 \text{ Hz}, 2H), 7.39 (t, J = 7.5 \text{ Hz}, 2H), 7.32 (t, J = 7.3 \text{ Hz}, 1H), 7.22 (d, J = 16.3 \text{ Hz}, 1H), 7.09 (d, J = 16.3 \text{ Hz}, 1H). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 141.8, 136.2, 132.4, 132.3, 128.8, 128.6, 126.8, 126.6, 119.0, 110.5.\)

4-(Trifluoromethyl)benzonitrile (2o)\(^2\)

White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.81 (d, J = 8.3 \text{ Hz}, 2H), 7.76 (d, J = 8.4 \text{ Hz}, 2H), 7.54 (d, J = 7.4 \text{ Hz}, 2H), 7.39 (t, J = 7.5 \text{ Hz}, 2H), 7.32 (t, J = 7.3 \text{ Hz}, 1H), 7.22 (d, J = 16.3 \text{ Hz}, 1H), 7.09 (d, J = 16.3 \text{ Hz}, 1H). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 134.5 (d, J_{C-F} = 33.3 \text{ Hz}), 132.6, 126.1 (q, J_{C-F} = 3.7 \text{ Hz}), 123.0 (d, J_{C-F} = 272.9 \text{ Hz}), 117.4, 116.0.\)

4-Nitrobenzonitrile (2p)\(^2\)

White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.36 (d, J = 8.8 \text{ Hz}, 2H), 7.89 (d, J = 8.8 \text{ Hz}, 2H). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 133.4, 130.4, 124.2, 118.3, 116.7.\)

Terephthalonitrile (2q)\(^2\)

White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.80 (s, 4H). \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 132.7, 116.9, 116.7.\)

Methyl 4-cyanobenzoate (2r)\(^3\)

White solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 8.13 (d, J = 8.1 \text{ Hz}, 2H), 7.74 (d, J = 8.2 \text{ Hz}, 2H), 3.95 (s, 3H).\)
**13C NMR (100 MHz, CDCl3): δ 165.3, 133.8, 132.1, 129.9, 117.8, 116.2, 52.6.**

**4-bromobenzonitrile (2s)**

![4-bromobenzonitrile](https://example.com/4-bromobenzonitrile.png)

White solid. 1H NMR (400 MHz, CDCl3): δ 7.64 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H). 13C NMR (100 MHz, CDCl3): δ 133.3, 132.6, 128.0, 118.0, 111.2.

**4-Iodobenzonitrile (2t)**

![4-Iodobenzonitrile](https://example.com/4-Iodobenzonitrile.png)

White solid. 1H NMR (400 MHz, CDCl3): δ 7.85 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H). 13C NMR (100 MHz, CDCl3): δ 138.4, 133.1, 118.2, 111.7, 100.3.

**1-Naphthonitrile (2u)**

![1-Naphthonitrile](https://example.com/1-Naphthonitrile.png)

Colorless liquid. 1H NMR (400 MHz, CDCl3): δ 8.24 (d, J = 8.3 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H), 7.92 (dd, J = 7.4, 5.2 Hz, 2H), 7.70 (t, J = 7.2 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H). 13C NMR (100 MHz, CDCl3): δ 133.2, 132.8, 132.6, 132.3, 128.6, 128.5, 127.5, 125.1, 124.8, 117.8, 110.1.

**2-Naphthonitrile (2v)**

![2-Naphthonitrile](https://example.com/2-Naphthonitrile.png)

White solid. 1H NMR (400 MHz, CDCl3): δ 8.21 (s, 1H), 7.89 (t, J = 8.4 Hz, 3H), 7.66-7.58 (m, 3H). 13C NMR (100 MHz, CDCl3): δ 134.5, 134.0, 132.1, 129.1, 128.9, 128.3, 127.9, 127.5, 126.2, 119.1, 109.2.

**Anthracene-9-carbonitrile (2w)**

![Anthracene-9-carbonitrile](https://example.com/Anthracene-9-carbonitrile.png)

Yellow-green solid. 1H NMR (400 MHz, CDCl3): δ 8.67 (s, 1H), 8.42 (d, J = 8.7 Hz, 2H), 8.07 (d, J = 8.5 Hz, 2H), 7.73–7.69 (m, 2H), 7.60–7.56 (m, 2H). 13C NMR (100 MHz, CDCl3): δ 133.3, 132.7, 130.6, 128.9, 126.3, 125.2, 117.2, 105.4.

**1-Methyl-1H-indole-3-carbonitrile (2x)**
Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.74 (d, $J$ = 7.9 Hz, 1H), 7.53 (s, 1H), 7.39–7.27 (m, 3H), 3.83 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 135.9, 135.5, 127.6, 123.7, 122.0, 119.7, 115.9, 110.2, 85.2, 33.5.

1-Phenyl-1H-indole-3-carbonitrile (2y)$^9$

White solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.84–7.82 (m, 1H), 7.81 (s, 1H), 7.60–7.56 (m, 2H), 7.53–7.47 (m, 4H), 7.37–7.32 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.7, 135.5, 134.6, 130.0, 128.3, 127.9, 124.8, 124.5, 122.7, 120.0, 115.5, 111.5, 88.0.

Thiophene-3-carbonitrile (2z)$^9$

Pale yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.94 (dd, $J$ = 3.0, 1.0 Hz, 1H), 7.43 (dd, $J$ = 5.1, 3.0 Hz, 1H), 7.30 (dd, $J$ = 5.1, 1.0 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 135.3, 128.6, 127.2, 115.0, 110.6.

Cinnamonitrile (2za)$^2$

Yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46–7.38 (m, 6H), 5.89 (d, $J$ = 16.7 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.5, 133.4, 131.1, 129.0, 127.2, 118.1, 96.2.

VII. References

VIII. Copies of $^1$H and $^{13}$C NMR charts of the products