Electronic Supplementary Information

A Novel Oxidative Transformation of Alcohols to Nitriles: An Efficient Utility of Azide as a Nitrogen Source

Balaji V. Rokade, Sanjeev K. Malekar and Kandikere Ramaiah Prabhu*

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General experimental

NMR spectra were recorded in CDCl₃, Tetramethylsilane (TMS; δ = 0.00 ppm) served as internal standards for ¹H NMR. The corresponding residual non-deuterated solvent signal (CDCl₃; δ = 77.00 ppm) was used as internal standards for ¹³C NMR. Column chromatography were conducted on silica gel 230-400 mesh or 100-200 mesh (Merck). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Note: Although we have not encountered disastrous results during our experiments, while using azides proper safety precautions should be followed!!!

Starting material preparation:

The starting materials, cinnamyl alcohols were prepared from the corresponding aldehydes using general procedure shown in the following scheme and spectral data are in agreement with the literature.

Benzylic alcohols were prepared from the corresponding aldehydes using sodium borohydride reduction and spectral data are in agreement with the literature.

Typical experimental procedure: synthesis of aryl and alkenyl nitriles from benzyl and allyl alcohols:

Trimethylsilylazide (0.75 mmol) was added dropwise to a well-stirred mixture of alcohol (0.5 mmol), Cu(ClO₄)₂·6H₂O (0.025 mmol), DDQ (1.1 mmol) in 1,2-dichloroethane (2 ml) and stirred at 60 °C till the reaction is completed (monitored by TLC). After removal of the solvent under reduced pressure, the reaction mixture was cooled to room temperature, the residue was dissolved in small amount of CH₂Cl₂ (2 mL), passed through alumina, and purified by column chromatography on silica gel.
Optimization studies: Screening of different solvents

**SI Table 1. Solvent Screening**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>H₂O</td>
<td>nd</td>
</tr>
<tr>
<td>2</td>
<td>MeOH</td>
<td>nd</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>95</td>
</tr>
<tr>
<td>5</td>
<td>CH₃CN</td>
<td>98</td>
</tr>
<tr>
<td>6</td>
<td>DCE</td>
<td>100</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR analyses w.r.t starting material. nd = not detected (<1%).

**SI Table 2. Screening for amount of Cu(ClO₄)₂·6H₂O, TMSN₃ and DDQ**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cu(ClO₄)₂·6H₂O (equiv)</th>
<th>TMSN₃ (equiv)</th>
<th>DDQ (equiv)</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>2.0</td>
<td>3.0</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>2.0</td>
<td>3.0</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>1.5</td>
<td>3.0</td>
<td>98</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>1.1</td>
<td>3.0</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
<td>1.5</td>
<td>2.2</td>
<td>98</td>
</tr>
</tbody>
</table>

<sup>a</sup>Yields were determined by <sup>1</sup>H NMR analyses with respect to starting material.
Control Experiments:

SI Scheme 1. Control experiments

- **Benzyl alcohol**
  - **Reaction**: \( \text{Cu(ClO}_4\text{)}_{2.6\text{H}_2\text{O}} (5 \text{ mol} \%) \), \( \text{TMSN}_3 (1.5 \text{ equiv}) \), \( \text{DCE}, \text{rt}, 10 \text{ min} \)
  - **Yield**: 98%

- **Benzyl alcohol**
  - **Reaction**: \( \text{Cu(ClO}_4\text{)}_{2.6\text{H}_2\text{O}} (5 \text{ mol} \%) \), \( \text{TMSN}_3 (1.5 \text{ equiv}) \), \( \text{DCE}, \text{rt}, 24 \text{h} \)
  - **Result**: no reaction

- **Benzyl formyl**
  - **Reaction**: \( \text{Cu(ClO}_4\text{)}_{2.6\text{H}_2\text{O}} (5 \text{ mol} \%) \), \( \text{TMSN}_3 (1.5 \text{ equiv}) \), \( \text{DDQ} (1.2 \text{ equiv}) \), \( \text{DCE}, \text{rt}, 3 \text{h} \)
  - **Yields**:
    - \( R = \text{-H} \): 99%
    - \( R = \text{-Me} \): 98%
    - \( R = \text{-NO}_2 \): 92%

- **Benzyl azide**
  - **Reaction**: \( \text{DDQ} (1.2 \text{ equiv}) \), \( \text{DCE}, \text{rt}, 1 \text{h} \)
  - **Yields**:
    - \( \text{CN} \): 95%
    - \( \text{CHO} \): 4%

- **Benzyl alcohol**
  - **Reaction**: \( \text{DDQ} (1.2 \text{ equiv}) \), \( \text{DCE}, \text{rt}, 10 \text{ min} \)
  - **Result**: quantitative
Mechanistic studies:

It is known that cinnamyl azide is oxidized in the presence of DDQ to the corresponding nitrile.1 Similarly, benzaldehyde is known to react with TMSN₃ to form corresponding α-silyloxy azido derivatives in the presence of Lewis acids.2 We have also observed that aldehyde and azides were formed as by-products in few control experiments (Table 1 and 2). In light of these observations, we carried out few more control experiments (ESI Scheme 1). The reaction of cinnamyl alcohol with TMSN₃ in the presence of Cu(ClO₄)₂·6H₂O (5 mol %) furnished the corresponding azide in almost quantitative yield. However, under the similar reaction condition, benzyl alcohol failed to furnish the corresponding azide even under forcing conditions. Further, it was observed that the reaction of cinnamaldehyde with Cu(ClO₄)₂·6H₂O (5 mol %), TMSN₃ and DDQ furnished the corresponding cinnamonitrile in almost quantitative yield. These experiments indicate that the benzyl alcohol and cinnamyl alcohol are following different route to furnish their corresponding nitriles.

Characterization data for Nitriles:

(E)-Cinnamitrile (2a):

![Cinnamitrile](image)

Colorless liquid; Yield = 98 %; R_f (15% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. IR (Neat, cm⁻¹): 2218;¹ H NMR (400 MHz, CDCl₃): δ 7.45-7.36 (m, 6H), 5.87 (d, J = 16.8 Hz, 1H);¹³C NMR (100 MHz, CDCl₃): δ 150.5, 133.4, 131.1, 129.0, 127.3, 118.1, 96.2; HRESI-MS (m/z): Calculated for C₉H₇N (M+H): 130.0657, found (M+H): 130.0656.

(E)-4-Methylcinnamitrile (2b):

![4-Methylcinnamitrile](image)

White solid; Yield = 92 %; m_p: 72 - 73 °C (lit.3 72 - 73 °C); R_f (15% EtOAc/Hexane) 0.75; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2215;¹ H NMR (400 MHz, CDCl₃): δ 7.38-7.33 (m, 3H), 7.20 (d, J = 8 Hz, 2H), 5.81 (d, J = 16.8 Hz, 1H), 2.38 (s, 3H);¹³C NMR (100 MHz, CDCl₃): δ 150.5, 141.8, 130.8, 129.8, 127.3, 118.4, 95.0, 21.5; HRESI-MS (m/z): Calculated for C₁₀H₁₀N (M+Na): 166.0633, found (M+Na): 166.0635.
(E)-4-Methoxycinnamionitrile (2c):

White solid; Yield = 86 %; mp: 63 - 65 ºC (lit. 4 62 - 65 ºC); Rf (25% EtOAc/Hexane) 0.65; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2214; ¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, J = 8 Hz, 2H), 7.32 (d, J = 16.8 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 5.71 (d, J = 16.4 Hz, 1H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.0, 150.0, 129.0, 126.3, 118.7, 114.4, 93.3, 55.4; HRESI-MS (m/z): Calculated for C₁₀H₉NO (M+H): 160.0762, found (M+H): 160.0765.

(E)-4-Allyloxycinnamionitrile (2d):

White solid; Yield = 73%; mp: 50 - 52 ºC; Rf (25% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2211; ¹H NMR (400 MHz, CDCl₃): δ 7.40-7.30 (m, 3H), 6.92 (d, J = 8.8 Hz, 2H), 6.09-5.99 (m, 1H), 5.71 (d, J = 16.8 Hz, 1H), 5.44-5.30 (dd, 2H), 4.58-4.56 (d, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 160.1, 150.0, 132.5, 129.0, 126.4, 118.7, 118.2, 115.2, 93.4, 68.9; HRESI-MS (m/z): Calculated for C₁₂H₁₁NO (M+Na): 208.0738, found (M+Na): 208.0736.

(E)-4-Chlorocinnamionitrile (2e):

White solid; Yield = 97 %; mp: 78 - 80 ºC (lit. 5 83 - 84 ºC); Rf (25% EtOAc/Hexane) 0.8; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2225; ¹H NMR (400 MHz, CDCl₃): δ 7.39-7.33 (m, 5H), 5.86 (d, J = 16.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 149.1, 137.2, 131.9, 129.4, 128.5, 117.8, 96.9; HRESI-MS (m/z): Calculated for C₉H₆ClN (M+Na): 186.0086, found (M+Na): 186.0087.

(E)-4-Nitrocinnamionitrile (2f):
Yellow Solid; Yield = 83 %; mp: 198 - 200 °C (lit.6 200 - 201 °C); Rf (25% EtOAc/Hexane) 0.56; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2217; ¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 16.8 Hz, 1H), 6.06 (d, J = 16.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 149.0, 147.7, 139.1, 128.1, 124.4, 116.9, 101.0; Anal.Calcd for C₉H₆N₂O₂ C, 62.07; H, 3.47; N, 16.09; Found: C, 62.25; H, 4.06; N, 15.12.

(E)-3-(4-(Trifluoromethyl)phenyl)-2-propenenitrile (2g):

White solid; Yield = 90%; mp: 92 – 94 °C; Rf (15% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2226; ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8Hz, 2H), 7.44 (d, J = 16.8 Hz, 1H), 6.00 (d, J = 16.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 148.7, 136.7, 132.7 (q, J = 32.7 Hz), 127.6, 126.1 (q, J = 3.3 Hz), 123.6 (q, J = 270.7 Hz), 117.3, 99.2; HRESI-MS (m/z): Calculated for C₁₀H₆F₃N (M+H): 198.0531, found (M+H): 198.0530.

(E)-1-Napthylcinnamonitrile (2h):

White solid; Yield = 72 %; mp: 73 - 76 °C (lit.7 72 - 75 °C); Rf (15% EtOAc/Hexane) 0.45; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2217; ¹H NMR (400 MHz, CDCl₃): δ 8.21 (d, J = 16 Hz, 1H), 8.03-7.87 (m, 3H), 7.65-7.46 (m, 4H), 5.95 ( d, J = 16.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 133.6, 131.5, 130.8, 130.6, 128.8, 127.3, 126.5, 125.3, 124.6, 122.7, 118.2, 98.7; HRESI-MS (m/z): Calculated for C₁₃H₉N (M+Na): 202.0633, found (M+Na): 202.0631.

(E)-3-(2-furyl)propenonitrile (2i):

White solid; Yield = 72 %; mp: 35 - 36 °C (lit.8 36 °C); Rf (25% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2226; ¹H NMR (400 MHz, CDCl₃):
ESI - 8

δ 7.49 (s, 1H), 7.11 (d, J = 16.4 Hz, 1H), 6.62 (d, J = 3.6 Hz, 1H), 6.50 (dd, J₁ = 1.6 Hz, J₂ = 3.2 Hz, 1H), 5.76 (d, J = 16.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 149.8, 145.4, 136.1, 118.2, 115.4, 112.6, 93.4; HRESI-MS (m/z): Calculated for C₇H₇NO (M+H): 120.0449, found (M+H): 120.0449.

2E,4E/ 2Z,4E - Phenylpenta-2,4-dienenitrile (2j): 2E,4E : 2Z,4E = 8.9 : 1.1

Yellow oil; Yield = 60%; Rf (15% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure. IR (Neat, cm⁻¹): 2217; ²E,4E(major isomer): ¹H NMR (400 MHz, CDCl₃): δ 7.52-7.35 (m, 5H), 7.18-7.12 (m, 1H), 6.91-6.78 (m, 2H), 5.44 (d, J = 16 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 150.3, 141.4, 135.2, 129.6, 128.9, 127.6, 125.4, 118.3, 98.2; HRESI-MS (m/z): Calculated for C₁₁H₉N (M+Na): 178.0633, found (M+Na): 178.0632.

Benzonitrile¹ (6a):

Colorless liquid; Yield = 80%; Rf (10% EtOAc/Hexane) 0.80; Prepared as shown in general experimental procedure. IR (Neat, cm⁻¹): 2225; ¹H NMR (400 MHz, CDCl₃): δ 7.66-7.59 (m, 3H), 7.49-7.45 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 132.7, 132.0, 129.0, 118.8, 112.3.

1-Naphthonitrile (6b):

White solid; Yield = 72%; mp: 55 - 57 °C (lit. ⁹ 56 - 58 °C); Rf (10 % EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2222; ¹H NMR (400 MHz, CDCl₃): δ 8.23 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.93 - 7.90 (m, 2H), 7.69 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 133.2, 132.9, 132.6, 132.3, 128.6, 128.5, 127.5, 125.1, 124.9, 117.8, 110.1; HRESI-MS (m/z): Calculated for C₁₁H₇N (M+): 153.0578, found (M+): 153.0578.
4-Methylbenzonitrile (6c):

White solid; Yield = 78 %; *mp*: 27 – 29 °C (lit.10 26 – 28 °C); *Rf* (15 % EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. **IR** (KBr, cm–1): 2228; **1H NMR** (400 MHz, CDCl3): δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8 Hz, 2H), 2.42 (s, 3H); **13C NMR** (100 MHz, CDCl3): δ 143.6, 132.0, 129.8, 119.1, 109.2, 21.8; **HRESI-MS (m/z)**: Calculated for C₈H₇N (M+H): 118.0657, found (M+H): 118.0649

4-Methoxybenzonitrile (6d):

White solid; Yield = 82 %, *mp*: 55 – 57 °C (lit.1 56 - 57 °C); *Rf* (10 % EtOAc/Hexane) 0.40; Prepared as shown in general experimental procedure. **IR** (KBr, cm-1): 2222; **1H NMR** (400 MHz, CDCl3): δ 7.58 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); **13C NMR** (100 MHz, CDCl3): δ 162.8, 133.9, 119.2, 114.7, 103.9, 55.5; **HRESI-MS (m/z)**: Calculated for C₈H₇NO (M+Na): 156.0425, found (M+Na): 156.0422.

4-(allyloxy)benzonitrile (6e):

Brown solid; Yield = 82 %; *mp*: 41 - 43 °C (lit.11 43 - 44 °C); *Rf* (10% EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure. **IR** (KBr, cm–1): 2218 ; **1H NMR** (400 MHz, CDCl3): δ 7.58 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.08 – 5.98 (m, 1H), 5.42 (d, *J* = 17.2 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 4.59 (d, *J* = 5.2 Hz, 2H); **13C NMR** (100 MHz, CDCl3): δ 161.8, 133.9, 132.0, 119.1, 118.4, 115.4, 104.0, 68.9; **HRESI-MS (m/z)**: Calculated for C₁₀H₉NO (M+Na): 182.0582, found (M+Na): 182.0583.

4-(2-propynyloxy)benzonitrile (6f):
White solid; Yield = 74 %; \textit{mp}: 109 - 111 °C (lit.\textsuperscript{12} 113 - 114 °C); \( R_f \) (15% EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure. IR (KBr, cm\textsuperscript{-1}): 2223; \( ^1\text{H NMR} \) (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.61 (d, \( J = 8.8 \) Hz, 2H), 7.04 (d, \( J = 8.8 \) Hz, 2H), 4.75 (d, \( J = 2.4 \) Hz, 2H), 2.57 (t, \( J = 2.4 \) Hz, 1H); \( ^{13}\text{C NMR} \) (100 MHz, CDCl\textsubscript{3}): \( \delta \) 160.6, 133.9, 118.9, 115.6, 104.9, 76.7, 76.5, 55.9; \textit{HRESI-MS} (\textit{m}/\textit{z}): Calculated for C\textsubscript{10}H\textsubscript{7}NO (M+Na): 180.0425, found (M+Na): 180.0422.

4-(Benzyloxy)benzonitrile (6g):

![4-(Benzyloxy)benzonitrile (6g)](image)

White solid; Yield = 96 %; \textit{mp}: 92 - 94 °C (lit.\textsuperscript{13a} 91 - 94 °C); \( R_f \) (10% EtOAc/Hexane) 0.45; Prepared as shown in general experimental procedure. IR (KBr, cm\textsuperscript{-1}): 2217; \( ^1\text{H NMR} \) (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.58 (d, \( J = 8.8 \) Hz, 2H), 7.41 - 7.35 (m, 5H), 7.02 (d, \( J = 8.8 \) Hz, 2H), 5.11 (s, 2H); \( ^{13}\text{C NMR} \) (100 MHz, CDCl\textsubscript{3}): \( \delta \) 161.9, 135.6, 134.0, 128.7, 128.4, 127.4, 119.1, 115.5, 104.2, 70.2; \textit{HRESI-MS} (\textit{m}/\textit{z}): Calculated for C\textsubscript{14}H\textsubscript{11}NO (M+Na): 232.0738, found (M+Na): 232.0735.

Piperonylnitrile (6h):

![Piperonylnitrile (6h)](image)

White solid; Yield = 82 %; \textit{mp}: 83 - 85 °C (lit.\textsuperscript{11} 90 - 93 °C); \( R_f \) (15 % EtOAc/Hexane) 0.8; Prepared as shown in general experimental procedure. IR (KBr, cm\textsuperscript{-1}): 2223; \( ^1\text{H NMR} \) (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.21 (d, \( J = 8 \) Hz, 1H), 7.03 (s, 1H), 6.86 (d, \( J = 8 \) Hz, 1H), 6.07 (s, 2H); \( ^{13}\text{C NMR} \) (100 MHz, CDCl\textsubscript{3}): \( \delta \) 151.5, 148.0, 128.2, 118.8, 111.3, 109.1, 104.9, 102.2; \textit{HRESI-MS} (\textit{m}/\textit{z}): Calculated for C\textsubscript{8}H\textsubscript{5}NO\textsubscript{2} (M+Na): 170.0218, found (M+Na): 170.0218.

4-(Phenyl)benzonitrile (6i):

![4-(Phenyl)benzonitrile (6i)](image)

White solid; Yield = 79 %; \textit{mp}: 82 - 83 °C (lit.\textsuperscript{14} 83 - 84 °C); \( R_f \) (15% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. IR (KBr, cm\textsuperscript{-1}): 2225; \( ^1\text{H NMR} \) (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.73-7.67 (m, 4H), 7.58 (d, \( J = 7.6 \) Hz, 2H), 7.50-7.42 (m, 3H); \( ^{13}\text{C NMR} \) (100 MHz, CDCl\textsubscript{3}): \( \delta \) 145.6, 139.1, 132.5, 129.0, 128.6, 127.7, 127.2, 118.9, 110.8; \textit{HRESI-MS} (\textit{m}/\textit{z}): Calculated for C\textsubscript{13}H\textsubscript{9}N (M+Na): 202.0633, found (M+Na): 202.0630.
4-chlorobenzonitrile (6j):

![4-chlorobenzonitrile](image)

White solid; Yield = 98%; \textit{mp}: 91 – 92 °C (lit.\textsuperscript{15a} 90 - 92 °C); \textit{Rf} (15% EtOAc/Hexane) 0.7; Prepared as shown in general experimental procedure. \textbf{IR} (KBr, cm\textsuperscript{-1}): 2226; \textbf{\textit{H NMR}} (400 MHz, CDCl\textsubscript{3}): \delta 7.60 (d, \textit{J} = 8.4 Hz, 2H), 7.47 (d, \textit{J} = 8.4 Hz, 2H); \textbf{\textit{13C NMR}} (100 MHz, CDCl\textsubscript{3}): \delta 139.5, 133.3, 129.6, 117.9, 110.7; Anal. Calcd for C\textsubscript{7}H\textsubscript{4}ClN: C, 61.12; H, 2.93; N, 10.18; Found: C, 61.26; H, 3.28; N, 10.22.

Terephthalonitrile1 (6k):

![Terephthalonitrile1](image)

White solid; Yield = 77%; \textit{mp}: 225 – 227 °C (lit.\textsuperscript{9} 226 - 228 °C); \textit{Rf} (15% EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure. \textbf{IR} (KBr, cm\textsuperscript{-1}): 2233; \textbf{\textit{H NMR}} (400 MHz, CDCl\textsubscript{3}): \delta 7.81 (s, 4H); \textbf{\textit{13C NMR}} (100 MHz, CDCl\textsubscript{3}): \delta 132.7, 116.9, 116.6; \textbf{MS} (m/z): 128 (M\textsuperscript{+}).

4-carbomethoxybenzonitrile (6l):

![4-carbomethoxybenzonitrile](image)

White solid; Yield = 82%; \textit{mp}: 67 - 68 °C (lit.\textsuperscript{15c} 67 - 69 °C); \textit{Rf} (15% EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure. \textbf{IR} (KBr, cm\textsuperscript{-1}): 2233; \textbf{\textit{H NMR}} (400 MHz, CDCl\textsubscript{3}): \delta 8.14 (d, \textit{J} = 8.4 Hz, 2H), 7.75 (d, \textit{J} = 8.4 Hz, 2H), 3.96 (s, 3H); \textbf{\textit{13C NMR}} (100 MHz, CDCl\textsubscript{3}): \delta 166.4, 133.8, 132.2, 130.0, 117.9, 116.3, 52.7; \textbf{HRESI-MS} (m/z): Calculated for C\textsubscript{9}H\textsubscript{7}NO\textsubscript{2} (M+H): 162.0555, found (M+H): 162.0552.

(E)-methyl 3-(4-cyanophenyl)acrylate (6m):

![E-methyl 3-(4-cyanophenyl)acrylate](image)
White solid; Yield = 99 %; mp: 111 - 114 °C (lit.16 118 - 121 °C); Rf (25% EtOAc/Hexane) 0.6; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2225;¹H NMR (400 MHz, CDCl₃): δ 7.69 – 7.60 (m, 5H), 6.52 (d, J = 16 Hz, 1H), 3.83 (s, 3H);¹³C NMR (100 MHz, CDCl₃): δ 166.6, 142.4, 138.6, 132.6, 128.4, 121.3, 118.3, 113.4, 52.0; Anal. Calcd for C₁₁H₉NO₂: C, 70.58; H, 4.85; N, 7.48; Found: C, 71.80; H, 5.58; N, 6.84.

4-cyano-N,N-diethylbenzamide (6n):

White solid; Yield = 73 %; mp: 77 - 78 °C (lit.15b 79 - 80 °C); Rf (50% EtOAc/Hexane) 0.35; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2231;¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, J = 8 Hz, 2H), 7.48 (d, J = 8Hz, 2H), 3.55 (br, 2H), 3.20 (br, 2H), 1.26 (br, 3H), 1.11 (br, 3H);¹³C NMR (100 MHz, CDCl₃): δ 169.2, 141.4, 132.4, 127.0, 118.1, 113.0, 43.2, 39.4, 14.2, 12.8; HRESI-MS (m/z): Calculated for C₁₂H₁₄N₂O (M+Na): 225.1004 found (M+Na): 225.1003.

4-Nitrobenzonitrile (6o):

White solid; Yield = 76 %; mp: 148 - 149 °C (lit.11 148 - 149 °C); Rf (25% EtOAc/Hexane) 0.5; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2222;¹H NMR (400 MHz, CDCl₃): δ 8.37 (d, J = 8.96 Hz, 2H), 7.90 (d, J = 8.92 Hz, 2H);¹³C NMR (100 MHz, CDCl₃): δ 150.0, 133.4, 124.2, 118.3, 116.8; Anal. Calcd for C₇H₄N₂O₂: C, 56.76; H, 2.72; N, 18.91; Found: C, 56.67; H, 3.26; N, 19.14.

4-((tert-butyldiphenylsilyl)oxy)benzonitrile (6p):

White solid; Yield = 98 %; mp: 100 – 103 °C (lit.13b 106 -108 °C); Rf (15% EtOAc/Hexane) 0.55; Prepared as shown in general experimental procedure. IR (KBr, cm⁻¹): 2226;¹H NMR (400 MHz, CDCl₃): δ 7.68 – 7.66 (m, 4H), 7.47 - 7.37 (m, 8H), 6.80 – 6.78 (m, 2H), 1.10 (s, 9H);¹³C NMR (100 MHz, CDCl₃): δ 159.4, 135.3, 133.8, 131.6, 130.3, 128.0, 120.6, 119.1, 104.4, 26.3, 19.4; HRESI-MS (m/z): Calculated for C₂₃H₂₃NOSi (M+Na): 380.1447, found (M+Na): 380.1446.
4-((tert-butyldimethylsilyl)oxy)benzonitrile (6q):

White solid; Yield = 90 %; mp: 56 - 58 °C; Rf (10% EtOAc/Hexane) 0.8; Prepared as shown in general experimental procedure. IR (KBr, cm\(^{-1}\)): 2227; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.54 (d, \(J = 8.8\) Hz, 2H), 6.88 (d, \(J = 8.8\) Hz, 2H), 0.98 (s, 9H), 0.23 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 159.6, 133.9, 120.8, 119.2, 104.5, 25.4, 18.1, -04.5; HRESI-MS (m/z): Calculated for C\(_{13}\)H\(_{19}\)NOSi (M+Na): 256.1134, found (M+Na): 256.1130.

3-Cyanophenyl(phenyl) ether (6r):

Light yellow oil; Yield = 95 %; Rf (15 % EtOAc/Hexane) 0.75; Prepared as shown in general experimental procedure. IR (Neat, cm\(^{-1}\)): 2233; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.43 - 7.34 (m, 4H), 7.25 – 7.18 (m, 3H), 7.03 (d, \(J = 8\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 158.1, 155.4, 130.6, 130.1, 126.3, 124.7, 122.7, 121.0, 119.7, 118.2, 113.5; HRESI-MS (m/z): Calculated for C\(_{13}\)H\(_{9}\)NO (M+Na): 218.0582, found (M+Na): 218.0586.

3-Cyanoindole (6s):

White solid; Yield = 72 %; mp: 174 - 176 °C (lit.\(^{17}\) 175 - 177 °C); Rf (20 % EtOAc/Hexane) 0.4; Prepared as shown in general experimental procedure. IR (KBr, cm\(^{-1}\)): 2222; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.8 (br, 1H), 7.79 - 7.74 (m, 2H), 7.48 (d, \(J = 7.6\) Hz, 1H), 7.36 - 7.28 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 134.8, 131.8, 126.9, 124.3, 122.4, 119.7, 115.8, 112.0, 87.5; HRESI-MS (m/z): Calculated for C\(_9\)H\(_6\)N\(_2\) (M+Na): 165.0429, found (M+Na): 165.0428.
References:

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CDCl₃ ¹³H NMR 400 MHz
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$^{13}$C NMR in CDCl$_3$ 100 MHz
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