Molecular Iodine-Catalyzed Multicomponent Synthesis of α-Cyanopyrrolines with Ambient Air as the Oxidant under Neat Conditions

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1. General Information

All reactions were carried out in anhydrous solvent and commercially available reagents were used as received unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated aluminium-backed silica gel 60 F_{254} plates (EMD Millipore, 200 µm thickness). TLC plates were visualized with ultraviolet light and treatment with KMnO₄ or vanillin stains followed by heating. Flash column chromatography was performed using Tsingtao silica gel (200-300). ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DRX - 400 spectrometers; chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference (CDCl₃: δ_H = 7.26 ppm and δ_C = 77.16 ppm; DMSO-d₆: δ_H = 2.54 ppm and δ_C = 39.60 ppm). Data for ¹H NMR and ¹³C NMR are reported as follows: chemical shift (δ, ppm), multiplicity, integration, and coupling constant (Hz).

2. Experimental Section

General experimental procedures for compounds 4

In a vial was placed alkene (0.5 mmol), TMSCN (0.5 mmol), N,N-disubstituted formamide (0.5 mmol) and molecular iodine (0.05 mmol), then the contents were reacted under 80 °C for 4 h. Upon completion, the reaction mixture was quenched by addition of 10 mL of water. The aqueous layer was extracted three times with EtOAc (10 mL × 3), and the combine organic layers were washed with saturated sodium sulfite solution and dried over anhydrous sodium sulfate, evaporated to dryness, and purified by column chromatography to afford the desired products.

Large-scale synthesis of 4o

In a flask (50 mL) equipped with a stir bar, 4-nitrostyrene (20 mmol, 2.98 g), TMSCN (20 mmol, 1.98 g), N,N-disubstituted formamide (20 mmol, 1.54 g) and molecular iodine (2 mmol, 0.51 g) were added, then the contents were reacted under 80 °C for 4 h. After completion, saturated sodium sulfite solution (25 mL) was added dropwise into the mixture. The precipitates were formed and collected by filtration and wash with ethyl acetate to give the product 4o (3.8 g, 83% yield).
3. Characterization data of products

1-methyl-3-phenyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4a)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta 7.50 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.27 (t, J = 7.6 \text{ Hz}, 2 \text{ H}), 7.17 (t, J = 7.6 \text{ Hz}, 1 \text{ H}), 3.14 (t, J = 9.6 \text{ Hz}, 2 \text{ H}), 2.86 (t, J = 9.6 \text{ Hz}, 2 \text{ H}), 2.68 (s, 3 \text{ H}); \\
\text{^13C NMR (101 MHz, CDCl}_3\text{): } & \delta 133.05, 130.76, 128.76, 127.86, 125.58, 120.14, 114.66, 54.86, 39.09, 32.46.
\end{align*}
\]

3-(1,1'-biphenyl-4-yl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4b)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta 7.69 – 7.67 (m, 2 \text{ H}), 7.63 – 7.60 (m, 4 \text{ H}), 7.46 (t, J = 7.2 \text{ Hz}, 2 \text{ H}), 7.36 (t, J = 7.2 \text{ Hz}, 1 \text{ H}), 3.26 (t, J = 10.0 \text{ Hz}, 2 \text{ H}), 2.99 (t, J = 9.6 \text{ Hz}, 2 \text{ H}), 2.79 (s, 3 \text{ H}); \\
\text{^13C NMR (101 MHz, CDCl}_3\text{): } & \delta 174.94, 141.02, 140.05, 139.10, 128.80, 128.39, 127.55, 127.26, 127.15, 125.96, 108.27, 47.80, 30.20, 27.97; \\
\text{HRMS (ESI) m/z calcd. for } & \text{C}_{18}\text{H}_{17}\text{N}_2 [\text{M+H}]^+: 261.1386, \text{found: 261.1390}.
\end{align*}
\]

1-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4c)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta 7.49 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.17 (d, J = 8.0 \text{ Hz}, 2 \text{ H}), 3.21 (t, J = 10.0 \text{ Hz}, 2 \text{ H}), 2.93 (t, J = 9.2 \text{ Hz}, 2 \text{ H}), 2.75 (s, 3 \text{ H}), 2.35 (s, 3 \text{ H}); \\
\text{^13C NMR (101 MHz, CDCl}_3\text{): } & \delta 138.01, 131.35, 129.50, 126.58, 125.59, 119.42, 114.89, 54.97, 39.31, 32.58, 21.39; \\
\text{HRMS (ESI) m/z calcd. for } & \text{C}_{13}\text{H}_{15}\text{N}_2 [\text{M+H}]^+: 199.1230, \text{found: 199.1235}.
\end{align*}
\]

3-(4-(tert-butyl)phenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4d)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta 7.55 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.22 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 3.21 (t, J = 9.2 \text{ Hz}, 2 \text{ H}), 2.94 (t, J = 9.6 \text{ Hz}, 2 \text{ H}), 2.76 (s, 3 \text{ H}), 1.36 – 1.32 (m, 9 \text{ H}); \\
\text{^13C NMR (101 MHz, CDCl}_3\text{): } & \delta 151.17, 131.15, 127.59, 125.69, 125.39, 119.47, 114.86, 54.93, 39.24, 34.77, 32.48, 31.30; \\
\text{HRMS (ESI) m/z calcd. for } & \text{C}_{16}\text{H}_{21}\text{N}_2 [\text{M+H}]^+: 241.1699, \text{found: 241.1704}.
\end{align*}
\]

3-(4-methoxyphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4e)

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta 7.55 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 7.22 (d, J = 8.4 \text{ Hz}, 2 \text{ H}), 3.21 (t, J = 9.2 \text{ Hz}, 2 \text{ H}), 2.94 (t, J = 9.6 \text{ Hz}, 2 \text{ H}), 2.76 (s, 3 \text{ H}), 1.36 – 1.32 (m, 9 \text{ H}); \\
\text{^13C NMR (101 MHz, CDCl}_3\text{): } & \delta 151.17, 131.15, 127.59, 125.69, 125.39, 119.47, 114.86, 54.93, 39.24, 34.77, 32.48, 31.30; \\
\text{HRMS (ESI) m/z calcd. for } & \text{C}_{16}\text{H}_{21}\text{N}_2 [\text{M+H}]^+: 241.1699, \text{found: 241.1704}.
\end{align*}
\]
$^1$H NMR (400 MHz, CDCl$_3$): δ 7.54 (d, $J = 8.8$ Hz, 2 H), 7.44 (d, $J = 8.4$ Hz, 2 H), 3.82 (s, 3 H), 3.19 (t, $J = 9.6$ Hz, 2 H), 2.91 (t, $J = 9.2$ Hz, 2 H), 2.73 (s, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 159.32, 131.33, 126.95, 125.57, 118.33, 114.99, 114.13, 55.31, 54.85, 39.35, 32.57; HRMS (ESI) m/z calcd. for C$_{13}$H$_{15}$N$_2$O [M+H]$^+$: 215.1179, found: 215.1184.

3-(4-fluorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4f)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.57 – 7.54 (m, 2 H), 7.05 (t, $J = 8.8$ Hz, 2 H), 3.22 (t, $J = 8.8$ Hz, 2 H), 2.92 (q, $J = 9.6$ Hz, 2 H), 2.75 (s, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 163.45 (d, $J = 249.3$ Hz), 129.80, 129.33 (d, $J = 3.5$ Hz), 127.38 (d, $J = 8.1$ Hz), 119.95, 115.92 (d, $J = 21.8$ Hz), 114.62, 54.84, 39.15, 32.66; HRMS (ESI) m/z calcd. for C$_{12}$H$_{12}$FN$_2$ [M+H]$^+$: 203.0979, found: 203.0981.

3-(4-chlorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4g)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.52 – 7.48 (m, 2 H), 7.33 – 7.28 (m, 2 H), 3.24 (t, $J = 10.0$ Hz, 2 H), 2.92 (t, $J = 9.6$ Hz, 2 H), 2.76 (s, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 133.32, 131.57, 129.08, 128.94, 126.70, 120.57, 114.43, 54.72, 38.92, 32.35; HRMS (ESI) m/z calcd. for C$_{13}$H$_{12}$ClN$_2$ [M+H]$^+$: 218.0684, found: 218.0690.

3-(4-bromophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4h)

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.48 – 7.42 (m, 4 H), 7.24 (t, $J = 9.6$ Hz, 2 H), 2.92 (t, $J = 9.6$ Hz, 2 H), 2.76 (s, 3 H); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 131.93, 131.33, 129.18, 126.98, 121.49, 120.71, 114.42, 54.74, 38.91, 32.31; HRMS (ESI) m/z calcd. for C$_{13}$H$_{12}$BrN$_2$ [M+H]$^+$: 263.0178, found: 263.0182.

3-(4-iodophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4i)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.66 (d, $J = 8.4$ Hz, 2 H), 7.30 (d, $J = 8.4$ Hz, 2 H), 3.24 (t, $J = 10.0$ Hz, 2 H), 2.90 (t, $J = 9.6$ Hz, 2 H), 2.76 (s, 3 H); $^1$C NMR (101 MHz, CDCl$_3$): $\delta$ 137.82, 132.54, 128.98, 127.07, 120.75, 114.36, 92.84, 54.67, 38.83, 32.14; HRMS (ESI) m/z calcd. for C$_{12}$H$_{12}$IN$_2$ [M+H]$^+$: 311.0046, found: 311.0046.

1-methyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4j)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.65 (d, $J = 8.4$ Hz, 2 H), 7.58 (d, $J = 8.4$ Hz, 2 H), 3.29 (t, $J = 9.6$ Hz, 2 H), 4.07 (t, $J = 9.6$ Hz, 2 H), 2.80 (s, 3 H); $^1$C NMR (101 MHz, CDCl$_3$): $\delta$ 136.61, 129.27, 128.94, 127.72 (d, $J = 3.8$ Hz), 125.45, 122.86, 122.02, 114.11, 54.57, 38.57, 32.15; HRMS (ESI) m/z calcd. for C$_{13}$H$_{12}$F$_3$N$_2$ [M+H]$^+$: 253.0947, found: 253.0950.

3-(4-formylphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4k)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.96 (s, 1 H), 7.84 (d, $J = 8.4$ Hz, 2 H), 7.70 (d, $J = 8.4$ Hz, 2 H), 3.33 (t, $J = 10.0$ Hz, 2 H), 3.00 (t, $J = 9.6$ Hz, 2 H), 2.83 (s, 3 H); $^1$C NMR (101 MHz, CDCl$_3$): $\delta$ 191.40, 139.10, 134.86, 130.21, 127.39, 125.50, 122.68, 114.04, 54.41, 38.31, 31.97; HRMS (ESI) m/z calcd. for C$_{13}$H$_{13}$N$_2$O [M+H]$^+$: 213.1022, found: 213.1026.

4-(2-cyano-1-methyl-4,5-dihydro-1H-pyrrol-3-yl)benzoic acid (4l)

$^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 12.96 (s, 1 H), 7.97 (d, $J = 8.4$ Hz, 2 H), 7.66 (d, $J = 8.4$ Hz, 2 H), 3.11 (t, $J = 10.0$ Hz, 2 H), 3.01 (t, $J = 9.6$ Hz, 2 H), 2.76 (s, 3 H); $^1$C NMR (101 MHz, DMSO-d$_6$): $\delta$ 166.87, 136.93, 129.77, 129.18, 128.35, 124.92, 121.08, 114.16, 53.96, 37.98, 31.52; HRMS (ESI) m/z calcd. for C$_{16}$H$_{19}$N$_2$O$_2$ [M+H]$^+$: 229.0972, found: 229.0976.

4-(2-cyano-1-methyl-4,5-dihydro-1H-pyrrol-3-yl)phenyl acetate (4m)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.58 (d, $J = 8.8$ Hz, 2 H), 7.08 (d, $J = 8.8$ Hz, 2 H), 3.22 (t, $J = 7.3$ Hz, 2 H), 2.92 (t, $J = 9.2$ Hz, 2 H), 2.75 (s, 3 H), 2.29 (s, 3 H); $^1$C NMR (101 MHz, CDCl$_3$): $\delta$ 169.37, 150.05, 130.77, 129.72, 126.59, 121.93, 120.17, 114.55, 54.78, 39.02, 32.50, 21.18; HRMS (ESI) m/z calcd. for C$_{14}$H$_{15}$N$_2$O$_2$ [M+H]$^+$: 243.1128, found: 243.1134.

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3-(4-cyanophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4n)

\[
\begin{align*}
\text{Me} & \quad \text{NC} \\
\text{NC} & \quad \text{N} \\
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.64 – 7.59 (m, 4 H), 3.33 (t, $J = 9.6$ Hz, 2 H), 2.96 (t, $J = 9.6$ Hz, 2 H), 2.83 (s, 3 H); $^1$C NMR (101 MHz, CDCl$_3$): $\delta$ 168.87, 137.61, 132.53, 128.97, 125.49, 122.89, 113.84, 110.22, 54.37, 38.27, 31.84; HRMS (ESI) m/z calcd. for C$_{13}$H$_{12}$N$_3$ [M+H]$^+$: 210.1026, found: 210.1030.

1-methyl-3-(4-nitrophenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4o)

\[
\begin{align*}
\text{Me} & \quad \text{NC} \\
\text{O} & \quad \text{N} \\
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.14 (d, $J = 9.2$ Hz, 2 H), 7.63 (d, $J = 9.2$ Hz, 2 H), 3.36 (t, $J = 10.0$ Hz, 2 H), 2.98 (t, $J = 10.0$ Hz, 2 H), 2.84 (s, 3 H); $^1$C NMR (101 MHz, CDCl$_3$): $\delta$ 145.78, 139.61, 125.49, 125.19, 124.09, 123.39, 113.68, 54.11, 37.92, 31.72; HRMS (ESI) m/z calcd. for C$_{12}$H$_{12}$N$_3$O$_2$ [M+H]$^+$: 230.0924, found: 230.0928.

1-methyl-3-(m-tolyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4p)

\[
\begin{align*}
\text{Me} & \quad \text{NC} \\
\text{Me} & \quad \text{N} \\
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.41 (t, $J = 8.0$ Hz, 1 H), 7.38 (s, 1 H), 7.25 (t, $J = 7.6$ Hz, 1 H), 7.09 (d, $J = 7.6$ Hz, 1 H), 3.22 (t, $J = 9.2$ Hz, 2 H), 2.94 (t, $J = 9.2$ Hz, 2 H), 2.76 (s, 3 H) 2.36 (s, 3 H); $^1$C NMR (101 MHz, CDCl$_3$): $\delta$ 138.36, 133.00, 131.11, 128.76, 126.26, 122.81, 120.01, 114.73, 108.40, 54.92, 39.19, 32.56, 21.57; HRMS (ESI) m/z calcd. for C$_{13}$H$_{15}$N$_2$ [M+H]$^+$: 199.1230, found: 199.1235.

1-methyl-3-(o-tolyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4q)

\[
\begin{align*}
\text{Me} & \quad \text{NC} \\
\text{Me} & \quad \text{N} \\
\end{align*}
\]

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.28 – 7.19 (m, 4 H), 3.26 (t, $J = 9.6$ Hz, 2 H), 2.90 (t, $J = 9.6$ Hz, 2 H), 2.76 (s, 3 H) 2.38 (s, 3 H); $^1$C NMR (101 MHz, CDCl$_3$): $\delta$ 136.18, 134.11, 133.24, 130.80, 128.92, 128.39, 126.08, 123.68, 113.61, 55.94, 39.57, 35.38, 20.44; HRMS (ESI) m/z calcd. for C$_{13}$H$_{15}$N$_2$ [M+H]$^+$: 199.1230, found: 199.1236.

3-(2-chlorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4r)
1H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.43 – 7.41 (m, 1 H), 7.40 – 7.38 (m, 1 H), 7.31 – 7.28 (m, 1 H), 7.27 – 7.25 (m, 1 H), 3.29 (t, J = 10.0 Hz, 2 H), 3.04 (t, J = 8.8 Hz, 2 H), 2.78 (s, 3 H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 133.10, 132.69, 131.21, 130.59, 130.28, 129.51, 127.09, 124.56, 113.24, 55.91, 39.14, 34.31; HRMS (ESI) m/z calcd. for C\textsubscript{12}H\textsubscript{12}ClN\textsubscript{2} [M+H]\textsuperscript{+}: 219.0684, found: 219.0688.

1-methyl-3-(4-vinylphenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4s)

1H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.55 (d, J = 8.4 Hz, 2 H), 7.39 (d, J = 8.4 Hz, 2 H), 6.73 – 6.66 (m, 1 H), 5.76 (s, 1 H), 5.26 (d, J = 10.8 Hz, 1 H), 3.23 (t, J = 9.6 Hz, 2 H), 2.92 (t, J = 9.6 Hz, 2 H), 2.77 (s, 3 H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 137.05, 136.36, 132.43, 130.40, 126.58, 125.68, 120.00, 114.76, 114.30, 54.82, 39.08, 32.36; HRMS (ESI) m/z calcd. for C\textsubscript{14}H\textsubscript{15}N\textsubscript{2} [M+H]\textsuperscript{+}: 211.1230, found: 211.1234.

3-(4-hydroxy-3-methoxyphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4t)

1H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.35 (d, J = 2.0 Hz, 1 H), 6.96 – 6.93 (m, 1 H), 6.89 (d, J = 8.4 Hz, 1 H), 5.76 (s, 1 H), 3.92 (s, 3 H), 3.19 (t, J = 9.6 Hz, 2 H), 2.92 (t, J = 9.2 Hz, 2 H), 2.74 (s, 3 H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 146.69, 145.92, 131.92, 125.47, 119.61, 118.43, 115.30, 114.58, 107.93, 56.13, 55.01, 39.51, 32.72; HRMS (ESI) m/z calcd. for C\textsubscript{13}H\textsubscript{15}N\textsubscript{2}O\textsubscript{2} [M+H]\textsuperscript{+}: 231.1128, found: 231.1132.

1-methyl-3-(naphthalen-2-yl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4u)

1H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.94 – 7.92 (m, 1 H), 7.82 – 7.80 (m, 4 H), 7.50 – 7.44(m, 2 H), 3.27 (t, J = 10.4 Hz, 2 H), 3.06 (q, J = 9.2 Hz, 2 H), 2.80 (s, 3 H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 174.99, 137.44, 133.56, 132.58, 128.60, 127.83, 127.67, 126.74, 126.15, 126.06, 125.77, 108.54, 48.24, 47.86, 30.24, 28.04; HRMS (ESI) m/z calcd. for C\textsubscript{16}H\textsubscript{15}N\textsubscript{2} [M+H]\textsuperscript{+}: 235.1230, found: 235.1235.

1-methyl-3-(pyridin-2-yl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4v)
1H NMR (400 MHz, CDCl3): δ 8.57 (d, J = 4.4 Hz, 1 H), 7.65 – 7.61 (m, 1 H), 7.54 (t, J = 8.0 Hz, 1 H), 7.11 – 7.08 (m, 1 H), 3.30 (t, J = 10.0 Hz, 2 H), 3.04 (t, J = 9.6 Hz, 2 H), 2.81 (s, 3 H); 13C NMR (101 MHz, CDCl3): δ 151.89, 149.53, 136.30, 129.53, 123.04, 121.66, 119.89, 114.04, 54.86, 38.37, 31.16; HRMS (ESI) m/z calcd. for C11H12N3 [M+H]+: 186.1026, found: 186.1030.

1,4-dimethyl-3-phenyl-1H-pyrrole-2-carbonitrile (4w)

1H NMR (400 MHz, CDCl3): δ 7.48 – 7.46 (m, 2 H), 7.29 (t, J = 8.0 Hz, 2 H), 7.19 (t, J = 7.6 Hz, 1 H), 3.40 – 3.31 (m, 1 H), 3.20 (t, J = 9.6 Hz, 1 H), 2.92 – 2.86 (m, 1 H), 2.67 (s, 3 H), 1.09 (d, J = 6.8 Hz, 3 H); 13C NMR (101 MHz, CDCl3): δ 136.16, 132.35, 128.88, 127.83, 126.31, 119.88, 114.66, 62.73, 38.92, 29.84, 18.14; HRMS (ESI) m/z calcd. for C13H15N2 [M+H]+: 199.1230, found: 199.1234.

2-methyl-1,2,8,8a-tetrahydroindenof[1,2-c]pyrrole-3-carbonitrile (4x)

1H NMR (400 MHz, CDCl3): δ 7.57 (t, J = 3.2 Hz, 1 H), 7.22 (d, J = 7.2 Hz, 3 H), 3.97 (t, J = 8.4 Hz, 1 H), 3.67 (t, J = 9.2 Hz, 1 H), 7.34 – 7.21 (m, 2 H), 3.09 – 3.06 (m, 1 H), 2.77 (s, 3 H); 13C NMR (101 MHz, CDCl3): δ 173.88, 141.94, 139.50, 127.86, 127.27, 125.14, 124.80, 113.20, 55.76, 53.61, 38.90, 34.62, 29.76; HRMS (ESI) m/z calcd. for C13H13N2 [M+H]+: 197.1073, found: 197.1076.

2-methyl-3,3a,4,5-tetrahydro-2H-benzo[e]isoindole-1-carbonitrile (4y)

1H NMR (400 MHz, CDCl3): δ 8.08 (d, J = 7.2 Hz, 1 H), 7.21 – 7.14 (m, 3 H), 3.65 (t, J = 8.8 Hz, 1 H), 3.23 – 3.13 (m, 1 H), 2.90 – 2.88 (m, 1 H), 2.73 (s, 3 H), 2.51 (q, J = 8.8 Hz, 1 H), 2.16 – 2.10 (m, 1 H), 1.71 – 1.60 (m, 2 H); 13C NMR (101 MHz, CDCl3): δ 136.62, 132.14, 129.44, 128.64, 128.03, 126.75, 124.24, 116.81, 114.97, 61.78, 43.42, 39.15, 29.99, 27.86; HRMS (ESI) m/z calcd. for C14H15N2 [M+H]+: 211.1230, found: 211.1234.

(E)-1-methyl-3-styryl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4z)
1H NMR (400 MHz, CDCl3): δ 7.43 (d, J = 7.6 Hz, 2 H), 7.33 (t, J = 7.2 Hz, 2 H), 7.23 (t, J = 7.2 Hz, 1 H), 7.06 (d, J = 16.0 Hz, 1 H), 6.39 (d, J = 15.6 Hz, 1 H), 3.26 (t, J = 9.6 Hz, 2 H), 2.82 (t, J = 9.2 Hz, 2 H), 2.75 (s, 3 H); 13C NMR (101 MHz, CDCl3): δ 137.17, 132.13, 129.29, 128.87, 127.82, 126.53, 123.37, 120.72, 113.21, 55.00, 38.60, 29.85; HRMS (ESI) m/z calcd. for C14H15N2 [M+H]+: 211.1230, found: 211.1236.

1-ethyl-5-methyl-3-phenyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4aa)

![Structure of 1-ethyl-5-methyl-3-phenyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4aa)](image)

1H NMR (400 MHz, CDCl3): δ 7.57 (d, J = 7.6 Hz, 2 H), 7.35 (t, J = 7.6 Hz, 2 H), 7.23 (t, J = 7.6 Hz, 1 H), 3.65 – 3.55 (m, 1 H), 3.31 – 3.22 (m, 1 H), 3.19 – 3.09 (m, 2 H), 2.62 – 2.55 (m, 1 H), 1.31 (d, J = 6.0 Hz, 3 H), 1.16 (t, J = 7.2 Hz, 3 H); 13C NMR (101 MHz, CDCl3): δ 133.34, 128.74, 127.49, 125.39, 118.32, 114.99, 57.17, 42.53, 40.53, 19.68, 12.15; HRMS (ESI) m/z calcd. for C14H17N2+[M+H]+: 213.1386, found: 213.1390.

5-ethyl-3-phenyl-1-propyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4ab)

![Structure of 5-ethyl-3-phenyl-1-propyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4ab)](image)

1H NMR (400 MHz, CDCl3): δ 7.58 (d, J = 7.6 Hz, 2 H), 7.34 (t, J = 7.6 Hz, 2 H), 7.23 (t, J = 7.6 Hz, 1 H), 3.48 – 3.40 (m, 1 H), 3.11 – 3.05 (m, 2 H), 2.66 – 2.59 (m, 1 H), 1.85 – 1.75 (m, 1 H), 1.70 – 1.49 (m, 4 H), 0.96 (t, J = 7.2 Hz, 6 H); 13C NMR (101 MHz, CDCl3): δ 133.45, 128.72, 127.33, 127.22, 125.32, 118.98, 115.08, 63.80, 50.89, 37.70, 26.83, 21.03, 11.59, 9.65; HRMS (ESI) m/z calcd. for C16H21N2+[M+H]+: 241.1699, found: 241.1704.

2-phenyl-1,5,6,7,8,8a-hexahydroindolizine-3-carbonitrile (4ac)

![Structure of 2-phenyl-1,5,6,7,8,8a-hexahydroindolizine-3-carbonitrile (4ac)](image)

1H NMR (400 MHz, CDCl3): δ 7.57 (d, J = 7.2 Hz, 2 H), 7.35 (t, J = 7.6 Hz, 2 H), 7.23 (t, J = 7.6 Hz, 1 H), 3.69 – 3.65 (m, 1 H), 3.25 – 3.17 (m, 1 H), 2.98 – 2.92 (m, 1 H), 2.76 – 2.70 (m, 1 H), 2.60 – 2.53 (m, 1 H), 1.87 (d, J = 12.8 Hz, 1 H), 1.76 – 1.68 (m, 2 H), 1.62 – 1.51 (m, 2 H), 1.46 – 1.35 (m, 1 H); 13C NMR (101 MHz, CDCl3): δ 133.63, 128.74, 128.36, 127.39, 125.27, 118.20, 114.39, 63.81, 47.57, 38.44, 29.68, 25.25, 24.13; HRMS (ESI) m/z calcd. for C15H17N2+[M+H]+: 225.1386, found: 225.1388.
4. References

5. $^1$H and $^{13}$C NMR spectra of products

1-methyl-3-phenyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4a)
3-((1,1'-biphenyl)-4-yl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4b)
1-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrrrole-2-carbonitrile (4c)
3-(4-(tert-butyl)phenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4d)
3-(4-methoxyphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4e)
3-(4-fluorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4f)
3-(4-chlorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4g)
3-(4-bromophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4h)
3-(4-iodophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4i)
1-methyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4j)
3-(4-formylphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4k)
4-(2-cyano-1-methyl-4,5-dihydro-1H-pyrrol-3-yl)benzoic acid (4l)
4-(2-cyano-1-methyl-4,5-dihydro-1H-pyrrol-3-yl)phenyl acetate (4m)
3-(4-cyanophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4n)
1-methyl-3-(4-nitrophenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4o)
1-methyl-3-(m-tolyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4p)
1-methyl-3-(o-tolyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4q)
3-(2-chlorophenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4r)
1-methyl-3-(4-vinylphenyl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4s)
3-(4-hydroxy-3-methoxyphenyl)-1-methyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4t)
1-methyl-3-(naphthalen-2-yl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4u)
1-methyl-3-(pyridin-2-yl)-4,5-dihydro-1H-pyrrole-2-carbonitrile (4v)
1,4-dimethyl-3-phenyl-1H-pyrrole-2-carbonitrile (4w)
2-methyl-1,2,8,8a-tetrahydroindeno[1,2-c]pyrrole-3-carbonitrile (4x)
2-methyl-3,3a,4,5-tetrahydro-2H-benzo[e]isoindole-1-carbonitrile (4y)
(E)-1-methyl-3-styryl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4z)
1-ethyl-5-methyl-3-phenyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4aa)
5-ethyl-3-phenyl-1-propyl-4,5-dihydro-1H-pyrrole-2-carbonitrile (4ab)
2-phenyl-1,5,6,7,8,8a-hexahydroindolizine-3-carbonitrile (4ac)