Supporting Information

Fe-promoted radical cyanomethylation/arylation of arylacrylamides to access oxindoles via cleavage of the \( \text{sp}^3 \) C–H of acetonitrile and the \( \text{sp}^2 \) C–H of phenyl group

Changduo Pan, Honglin Zhang and Chengjian Zhu*

E-mail: cjzhu@nju.edu.cn

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Experimental

1. General experimental details
$^1$H NMR and $^{13}$C NMR spectra were measured on 400 MHz spectrometer, using CDCl$_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts ($\delta$) are given in ppm relative to TMS, the coupling constants $J$ are given in Hz. HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode.

**Typical procedure for radical cyanomethylation/arylation of arylacrylamide to access oxindole:** To a sealed tube, the mixture of 1a (0.2 mmol), Fe(acac)$_2$ (5 mol %, 2.5 mg), DTBP (0.6 mmol) and CH$_3$CN (2.0 mL) were added into the flask. The reaction mixture was vigorously stirred at 120 °C for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by preparative TLC on GF254 to afford the products 3aa.

**Intramolecular competition experiment isotopically labeled [D$_1$]-1a**

![Diagram of intramolecular competition experiment isotopically labeled [D$_1$]-1a]

To a sealed tube, the mixture of [D$_1$]-1a (0.2 mmol) Fe(acac)$_2$ (5 mol %, 2.5 mg), DTBP (0.6 mmol) and CH$_3$CN (2.0 mL) were added into the flask. The reaction mixture was vigorously stirred at 120 °C for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by preparative TLC on GF254 to afford the products 3aa and [D$_1$]-3aa.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.34-7.31 (m, 1H), 7.19 (dd, $J = 1.2, 7.4$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 6.89 (d, $J = 7.8$ Hz, 0.54H), 3.23 (s, 3H), 2.38-2.30 (m, 3H), 2.13-1.98 (m, 3H), 1.40 (s, 3H).

**Intermolecular competition experiment with isotopically labeled [D$_5$]-1a**

![Diagram of intermolecular competition experiment with isotopically labeled [D$_5$]-1a]

To a sealed tube, the mixture of [D$_5$]-1a (0.2 mmol) Fe(acac)$_2$ (5 mol %, 2.5 mg), DTBP (0.6 mmol) and CH$_3$CN (2.0 mL) were added into the flask. The reaction mixture was vigorously stirred at 120 °C for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by preparative TLC on GF254 to afford the products 3aa and [D$_5$]-3aa.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.32 (t, $J = 7.7$ Hz, 0.5H), 7.19 (d, $J = 6.6$ Hz, 0.5H),
7.12 (t, J = 7.4 Hz, 0.5H), 6.89 (d, J = 7.8 Hz, 0.5H), 3.23 (s, 3H), 2.35-2.30 (m, 1H), 2.13-1.97 (m, 3H), 1.40 (s, 3H).

The KIE studies on solvent (competition reaction):

\[
\begin{align*}
\text{1a} & \xrightarrow{\text{standard condition}} \text{3aa} \\
\text{CD}_3\text{CN} & \xrightarrow{\text{CH}_3\text{CN}} \text{[D}_2\text{-3aa}}
\end{align*}
\]

To a sealed tube, the mixture of 1a (0.2 mmol), Fe(acac)$_2$ (5 mol %, 2.5 mg), DTBP (0.6 mmol), CH$_3$CN (1.0 mL) and CD$_3$CN (1.0 mL) were added into the flask. The reaction mixture was vigorously stirred at 120 °C for 12 h. After the completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by preparative TLC on GF254 to afford the products 3aa and [D$_2$]-3aa.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.32 (t, $J = 7.7$ Hz, 1H), 7.19 (d, $J = 7.3$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 6.89 (d, $J = 7.8$ Hz, 1H), 3.23 (s, 3H), 2.35-2.30 (m, 1H), 2.14-1.97 (m, 2.78H), 1.40 (s, 3H).

The Kinetic Isotopic Effect Studies on Solvent (parallel reaction): In ten parallel sealed tubes, the mixture of 1a (0.2 mmol) was treated by standard condition in acetonitrile or D$_3$-acetonitrile (five experiments for each). Then the reaction was quenched by addition internal standard in Et$_2$OAc in specified time. The mixture was analyzed by GC-MS to give the yield of product. A significant intermolecular kinetic isotope effect ($k_H/k_D = 2.9$) was observed. The results were listed below:

\[
\begin{align*}
\text{1a} & \xrightarrow{\text{standard condition}} \text{3aa} \\
\text{CH}_3\text{CN or CD}_3\text{CN} & \xrightarrow{\text{CH}_3\text{CN or CD}_3\text{CN}} \text{[D}_2\text{-3aa}}
\end{align*}
\]

[D$_2$]-3aa: $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.32 (t, $J = 7.6$ Hz, 1H), 7.19 (d, $J = 7.2$ Hz, 1H), 7.11 (t, $J = 7.5$ Hz, 1H), 6.88 (d, $J = 7.8$ Hz, 1H), 3.22 (s, 3H), 2.32 (d, $J = 13.7$ Hz, 1H), 2.06 (d, $J = 13.7$ Hz, 1H).
2. Experimental characterization data for compounds

3-(1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3aa)

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta 7.32 (t, J = 7.7 Hz, 1H), 7.19 (d, J = 7.3 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 3.23 (s, 3H), 2.35-2.30 (m, 1H), 2.14-1.97 (m, 3H), 1.40 (s, 3H). \]

3- (1,3,5-trimethyl-2-oxoindolin-3-yl)propanenitrile (3ba)

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta 7.11 (d, J = 7.9 Hz, 1H), 7.00 (s, 1H), 6.77 (d, J = 7.9 Hz, 1H), 3.20 (s, 3H), 2.36 (s, 3H), 2.33-2.27 (m, 1H), 2.14-1.96 (m, 3H), 1.39 (s, 3H). \]

3-(5-isopropyl-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3ca)

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta 7.10 (dd, J = 1.5, 8.0 Hz, 1H), 6.97 (d, J = 1.7 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 3.13 (s, 3H), 2.87-2.80 (m, 1H), 2.30-2.20 (m, 1H), 2.06-1.89 (m, 3H), 1.32 (s, 3H), 1.19 (s, 3H), 1.17 (s, 3H). \]

13C NMR (CDCl3, 100 MHz): \( \delta \) 178.9, 144.1, 141.0, 131.7, 126.3, 120.8, 118.9, 108.3, 47.5, 33.9, 33.5, 26.3, 24.3, 24.2, 23.4, 12.8.

HRMS (ESI) \( m/z \) calcd for C_{16}H_{20}N_{2}NaO(M+Na)^+ 279.1468, found 279.1469.

3-(1,3,4,6-tetramethyl-2-oxoindolin-3-yl)propanenitrile (3da)

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta 6.69 (s, 1H), 6.55 (s, 1H), 3.19 (s, 3H), 2.42-2.21 (m, 8H), 2.02-1.82 (m, 2H), 1.45 (s, 3H). \]

13C NMR (CDCl3, 100 MHz): \( \delta \) 179.2, 143.6,

---

138.7, 134.0, 126.1, 125.1, 118.7, 107.2, 48.2, 31.6, 26.4, 22.0, 21.6, 18.1, 13.0.

3-(1,3,5,7-tetramethyl-2-oxoindolin-3-yl)propanenitrile (3ea)

\[
\text{\includegraphics{structure1.png}}
\]

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 6.84-6.81 (m, 2H), 3.47 (s, 3H), 2.53 (s, 3H), 2.34-2.28 (m, 4H), 2.00-1.97 (m, 3H), 1.35 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 179.5, 138.4, 132.7, 132.5, 132.4, 121.1, 119.9, 118.9, 46.7, 33.7, 29.5, 23.9, 20.7, 18.8, 12.8.

HRMS (ESI) \(m/z\) calcd for \(\text{C}_{15}\text{H}_{18}\text{N}_2\text{O}\) (M+Na\(^+\)) 265.1311, found 265.1314.

3-(1,3,7-trimethyl-2-oxoindolin-3-yl)propanenitrile (3fa)\(^1\)

\[
\text{\includegraphics{structure2.png}}
\]

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.05-6.97 (m, 3H), 3.50 (s, 3H), 2.59 (s, 3H), 2.34-2.27 (m, 1H), 2.07-1.95 (m, 3H), 1.37 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 179.6, 140.9, 132.3, 122.9, 120.4, 120.2, 118.8, 46.6, 33.7, 29.6, 23.9, 19.0, 12.8.

3-(4-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile and 3-(6-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3ga)

\[
\text{\includegraphics{structure3.png}}
\]

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.28 (t, \(J = 8.3\) Hz, 0.7H), 7.08 (d, \(J = 8.1\) Hz, 0.31H), 6.65 (d, \(J = 8.4\) Hz, 0.63H), 6.61 (d, \(J = 8.1\) Hz, 0.31H), 6.54 (d, \(J = 7.7\) Hz, 0.63H), 6.46 (d, \(J = 2.2\) Hz, 0.31H), 3.87 (s, 2H), 3.83 (s, 1H), 3.20 (s, 3H), 2.42-2.21 (m, 2H), 2.08-1.94 (m, 2H), 1.44 (s, 2H), 1.37 (s, 1H).

3-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3ha)\(^1\)

\[
\text{\includegraphics{structure4.png}}
\]

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 6.85-6.77 (m, 3H), 3.81 (s, 3H), 3.20 (s, 3H), 2.38-2.28 (m, 1H), 2.14-1.97 (m, 3H), 1.39 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 178.5, 156.4, 136.5, 133.0, 118.8, 112.6, 110.3, 108.9, 55.8, 47.8, 33.5, 26.4, 23.5, 12.8.
3-(1,3-dimethyl-2-oxo-5-(trifluoromethoxy)indolin-3-yl)propanenitrile (3ia)

\[
\begin{align*}
\text{F}_3\text{CO} & \quad \text{N} \\
\text{O} & \quad \text{CN}
\end{align*}
\]

\[^{1}\text{H NMR (CDCl}_3, 400 \text{ MHz):} \delta 7.21 (d, J = 8.4 \text{ Hz, 1H}), 7.09 (s, 1H), 6.89 (d, J = 8.4 \text{ Hz, 1H}), 3.23 (s, 3H), 2.37-2.31 (m, 1H), 2.14-2.03 (m, 3H), 1.42 (s, 3H). \]^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz):} \delta 178.6, 145.0, 141.8, 133.3, 121.8, 119.2, 118.4, 116.7, 109.0, 47.6, 33.2, 26.5, 23.3, 12.8.

3-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)propanenitrile (3ja)

\[
\begin{align*}
\text{F}_3\text{CO} & \quad \text{N} \\
\text{O} & \quad \text{CN}
\end{align*}
\]

\[^{1}\text{H NMR (CDCl}_3, 400 \text{ MHz):} \delta 7.62 (d, J = 0.9, 8.2 \text{ Hz, 1H}), 7.43 (d, J = 1.1 \text{ Hz, 1H}), 6.97 (d, J = 8.2 \text{ Hz, 1H}), 3.26 (s, 3H), 2.41-2.32 (m, 1H), 2.16-2.05 (m, 3H), 1.44 (s, 3H). \]^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz):} \delta 178.8, 146.2, 141.8, 132.4, 126.5 (q, J_{C-F} = 3.9 \text{ Hz}), 125.3 (q, J_{C-F} = 32.6 \text{ Hz}), 124.2 (q, J_{C-F} = 270.0 \text{ Hz}), 119.7 (q, J_{C-F} = 3.6 \text{ Hz}), 118.3, 108.3, 47.2, 33.1, 26.5, 23.3, 12.8.

3-(5-fluoro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3ka)

\[
\begin{align*}
\text{F} & \quad \text{N} \\
\text{O} & \quad \text{CN}
\end{align*}
\]

\[^{1}\text{H NMR (CDCl}_3, 400 \text{ MHz):} \delta 7.05-7.01 (m, 1H), 6.97-6.95 (m, 1H), 6.83-6.80 (m, 1H), 3.22 (s, 3H), 2.36-2.28 (m, 1H), 2.14-2.01 (m, 3H), 1.40 (s, 3H). \]^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz):} \delta 178.5, 159.5 (d, J_{C-F} = 240.4 \text{ Hz}), 139.0 (d, J_{C-F} = 1.9 \text{ Hz}), 133.4 (d, J_{C-F} = 7.7 \text{ Hz}), 118.5, 115.0 (d, J_{C-F} = 23.3 \text{ Hz}), 110.0 (d, J_{C-F} = 24.6 \text{ Hz}), 109.1 (d, J_{C-F} = 8.1 \text{ Hz}), 47.8 (d, J_{C-F} = 1.7 \text{ Hz}), 33.3, 23.4, 12.8.

3-(5-chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3la)

\[
\begin{align*}
\text{Cl} & \quad \text{N} \\
\text{O} & \quad \text{CN}
\end{align*}
\]

\[^{1}\text{H NMR (CDCl}_3, 400 \text{ MHz):} \delta 7.30 (dd, J = 2.1, 8.4 \text{ Hz, 1H}), 7.18 (d, J = 2.0 \text{ Hz, 1H}), 6.81 (d, J = 8.3 \text{ Hz, 1H}), 3.21 (s, 1H), 2.34-2.30 (m, 1H), 2.12-2.01 (m, 3H), 1.40 (s, 3H). \]^{13}\text{C NMR (CDCl}_3, 100 \text{ MHz):} \delta 178.4, 141.7, 133.4, 128.6, 128.5, 123.2, 118.5, 109.5, 47.5, 33.2, 26.5, 23.4, 12.8.
3-(5-bromo-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3ma)\(^1\)

\[
\begin{align*}
\end{align*}
\]

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta 7.45\) (dd, \(J=1.8, 8.2\) Hz, 1H), 7.31 (d, \(J=1.8\) Hz, 1H), 6.77 (d, \(J=8.2\) Hz, 1H), 3.21 (s, 3H), 2.35-2.30 (m, 1H), 2.12-2.01 (m, 3H), 1.40 (s, 3H).

\(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 178.2, 142.2, 133.8, 131.5, 125.9, 118.5, 115.7, 110.0, 47.5, 33.2, 26.4, 23.4, 12.8\).


3-(5-iodo-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3na)\(^1\)

\[
\begin{align*}
\end{align*}
\]

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta 7.64\) (d, \(J=1.6, 8.2\) Hz, 1H), 7.47 (d, \(J=1.6\) Hz, 1H), 6.67 (d, \(J=8.2\)Hz, 1H), 3.20 (s, 3H), 2.35-2.28 (m, 1H), 2.11-2.00 (m, 3H), 1.39 (s, 3H).

\(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 178.1, 142.9, 137.5, 134.2, 131.5, 118.5, 110.6, 85.6, 47.3, 33.2, 26.4, 23.4, 12.8\).


3-(7-iodo-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3oa)

\[
\begin{align*}
\end{align*}
\]

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta 7.72\) (d, \(J=1.0, 8.1\) Hz, 1H), 7.13 (d, \(J=1.0, 8.3\) Hz, 1H), 6.82 (d, \(J=7.6\) Hz, 1H), 3.60 (s, 3H), 2.35-2.28 (m, 1H), 2.13-1.99 (m, 3H), 1.38 (s, 3H).

\(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 179.5, 143.5, 141.3, 134.8, 124.7, 122.4, 118.6, 72.1, 46.8, 33.6, 30.2, 23.8, 12.8\).

HRMS (ESI) \(m/z\) calc'd for \(\text{C}_{13}\text{H}_{13}\text{IN}_2\text{NaO}(\text{M}+\text{Na})^+\) 362.9965, found 362.9967.


3-(4,6-dichloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile (3pa)

\[
\begin{align*}
\end{align*}
\]

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta 7.06\) (d, \(J=1.6\) Hz, 1H), 6.81 (d, \(J=1.6\) Hz, 1H), 3.21 (s, 3H), 2.52-2.34 (m, 2H), 2.07-2.02 (m, 2H), 1.52 (s, 3H).

\(^1\)C NMR (CDCl\(_3\), 100 MHz): \(\delta 178.3, 145.9, 135.4, 131.2, 125.9, 123.4, 118.2, 108.0, 48.8, 30.2, 26.7, 21.3, 13.2\).

HRMS (ESI) \(m/z\) calc'd for \(\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{N}_2\text{NaO}(\text{M}+\text{Na})^+\) 305.0219, found 305.0221.
3-(1,3-dimethyl-2-oxo-7-phenylindolin-3-yl)propanenitrile (3qa)¹

\[
\begin{align*}
\text{H NMR (CDCl}_3, 400 \text{ MHz):} & \quad \delta 7.42-7.33 (m, 5H), 7.20-7.17 (m, 1H), 7.15-7.09 (m, 2H), 2.73 (s, 3H), 2.42-2.31 (m, 1H), 2.15-2.06 (m, 3H), 1.44 (s, 3H). \\
\text{¹C NMR (CDCl}_3, 100 \text{ MHz):} & \quad \delta 179.9, 140.0, 138.5, 132.7, 131.6, 129.8, 127.9, 127.8, 125.9, 122.3, 121.6, 118.8, 46.6, 33.7, 30.2, 23.8, 12.8.
\end{align*}
\]

Ethyl 3-(2-cyanoethyl)-1,3-dimethyl-2-oxindoline-5-carboxylate (3ra)

\[
\begin{align*}
\text{H NMR (CDCl}_3, 400 \text{ MHz):} & \quad \delta 8.08 (dd, J = 1.6, 8.2 \text{ Hz}, 1H), 7.87 (s, 1H), 6.93 (d, J = 8.2 \text{ Hz}, 1H), 4.41-4.36 (m, 2H), 3.26 (s, 3H), 2.39-2.32 (m, 1H), 2.14-2.05 (m, 3H), 1.44-1.40 (m, 6H). \\
\text{¹C NMR (CDCl}_3, 100 \text{ MHz):} & \quad \delta 179.2, 166.1, 147.1, 131.7, 131.3, 125.3, 123.8, 118.5, 108.0, 61.1, 47.1, 33.1, 26.5, 23.4, 14.3, 12.8. \\
\text{HRMS (ESI) m/z} & \quad \text{calcd for } C_{16}H_{18}N_{2}NaO_{3} (M+Na)^+ 309.1210, \text{ found } 309.1211.
\end{align*}
\]

3-(1,3-dimethyl-5-nitro-2-oxindolin-3-yl)propanenitrile (3sa)¹

\[
\begin{align*}
\text{H NMR (CDCl}_3, 400 \text{ MHz):} & \quad \delta 8.32 (dd, J = 2.2, 8.6 \text{ Hz}, 1H), 8.12 (d, J = 2.2 \text{ Hz}, 1H), 7.00 (d, J = 8.4 \text{ Hz}, 1H), 3.31 (s, 3H), 2.41-2.34 (m, 1H), 2.19-2.12 (m, 3H), 1.48 (m, 3H). \\
\text{¹C NMR (CDCl}_3, 100 \text{ MHz):} & \quad \delta 179.0, 148.8, 143.7, 132.7, 126.0, 118.7, 118.1, 108.2, 47.3, 32.9, 26.8, 23.4, 12.8.
\end{align*}
\]

3-(1,3,6-trimethyl-2-oxo-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)propanenitrile (3ta)

\[
\begin{align*}
\text{H NMR (CDCl}_3, 400 \text{ MHz):} & \quad \delta 7.33 (d, J = 7.4 \text{ Hz}, 1H), 6.86 (d, J = 7.4 \text{ Hz}, 1H), 3.29 (s, 3H), 2.52 (s, 3H), 2.33-2.28 (m, 1H), 2.21-2.01 (m, 3H), 1.40 (s, 3H). \\
\text{¹C NMR (CDCl}_3, 100 \text{ MHz):} & \quad \delta 178.2, 157.3, 156.1, 130.4, 122.6, 118.6, 117.5, 46.8, 32.9, 25.4, 24.2, 23.0, 12.8.
\end{align*}
\]
HRMS (ESI) m/z calcd for C_{13}H_{15}N_{3}NaO (M+Na)^+ 252.1107, found 252.1107.

3-(1-isopropyl-3-methyl-2-oxoindolin-3-yl)propanenitrile (4aa)

\[ \text{\includegraphics[width=0.2\textwidth]{4aa}} \]

$^{1}$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.30-7.26 (m, 1H), 7.19 (d, $J$ = 7.4 Hz, 1H), 7.08 (t, $J$ = 7.4 Hz, 1H), 7.04 (d, $J$ = 8.0 Hz, 1H), 4.67-4.60 (m, 1H), 2.10-1.91 (m, 3H), 1.48 (dd, $J$ = 1.7, 7.0 Hz, 6H), 1.37 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 178.5, 142.8, 132.1, 128.4, 122.9, 122.5, 118.8, 110.2, 47.0, 43.9, 33.6, 23.7, 19.5, 19.4, 12.7.

HRMS (ESI) m/z calcd for C_{13}H_{15}N_{3}NaO (M+Na)^+ 252.1107, found 252.1107.

3-(1-ethyl-3-methyl-2-oxoindolin-3-yl)propanenitrile (4ba)

\[ \text{\includegraphics[width=0.2\textwidth]{4ba}} \]

$^{1}$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.33-7.29 (m, 1H), 7.20 (d, $J$ = 6.8 Hz, 1H), 7.12-7.08 (m, 1H), 6.90 (d, $J$ = 7.8 Hz, 1H), 3.82-3.71 (m, 2H), 2.38-2.27 (m, 1H), 2.12-2.94 (m, 3H), 1.39 (s, 3H), 1.27 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 178.5, 142.2, 131.9, 128.6, 122.9, 122.8, 118.8, 108.6, 47.2, 34.7, 33.5, 23.5, 12.8, 12.7.

HRMS (ESI) m/z calcd for C_{14}H_{16}N_{2}O (M+Na)^+ 265.1311, found 265.1312.

3-(3-methyl-2-oxo-1-phenylindolin-3-yl)propanenitrile (4ca)

\[ \text{\includegraphics[width=0.2\textwidth]{4ca}} \]

$^{1}$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.55-7.51 (m, 2H), 7.44-7.39 (m, 3H), 7.25-7.22 (m, 2H), 7.16-7.12 (m, 1H), 6.87 (d, $J$ = 7.7 Hz, 1H), 2.46-2.38 (m, 1H), 2.27-2.11 (m, 3H), 1.52 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 178.4, 143.1, 134.1, 131.5, 129.7, 128.6, 128.3, 126.4, 123.5, 122.9, 118.8, 109.9, 47.5, 33.7, 23.9, 12.9.

3-(1-benzyl-3-methyl-2-oxoindolin-3-yl)propanenitrile (4da)

\[ \text{\includegraphics[width=0.2\textwidth]{4da}} \]

$^{1}$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.34-7.26 (m, 5H), 7.23-7.19 (m, 1H), 7.08 (t, $J$ = 7.5 Hz, 1H).
Hz, 1H), 6.79 (d, J = 7.7 Hz, 1H), 4.91 (q, 2H), 2.42-2.34 (m, 1H), 2.16-1.95 (m, 3H), 1.45 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 179.0, 142.2, 135.7, 131.7, 128.9, 128.6, 127.8, 127.3, 123.1, 122.7, 118.8, 109.5, 47.3, 43.8, 33.5, 23.8, 12.8.

HRMS (ESI) m/z calc'd for C$_{19}$H$_{18}$N$_2$O (M+Na)$^+$ 313.131, found 313.1313.

3-(3-benzyl-1-methyl-2-oxoindolin-3-yl)propanenitrile (4ea) $^1$

![Image of 3-(3-benzyl-1-methyl-2-oxoindolin-3-yl)propanenitrile (4ea)]

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.25-7.21 (m, 1H), 7.14-7.02 (m, 5H), 6.80-6.78 (m, 2H), 6.62 (d, J = 7.8 Hz, 1H), 3.12 (d, J = 12.8 Hz, 1H), 3.01 (d, J = 12.8 Hz, 1H), 2.96 (s, 3H), 2.54-2.46 (m, 1H), 2.25-2.18 (m, 1H), 2.11-2.03 (m, 1H), 1.97-1.88 (m, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 177.5, 143.8, 134.7, 129.8, 128.8, 126.8, 123.6, 122.6, 118.8, 108.3, 53.7, 44.4, 31.9, 25.9, 12.9.

3-(1-methyl-2-oxo-3-phenylindolin-3-yl)propanenitrile (4fa) $^1$

![Image of 3-(1-methyl-2-oxo-3-phenylindolin-3-yl)propanenitrile (4fa)]

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.40-7.25 (m, 7H), 7.19-7.14 (m, 1H), 6.94 (d, J = 7.8 Hz, 1H), 3.24 (s, 3H), 2.86-2.78 (m, 1H), 2.52-2.45 (m, 1H), 2.21-2.07 (m, 2H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 177.0, 143.7, 138.4, 130.0, 129.2, 128.9, 127.9, 126.6, 124.7, 123.2, 118.7, 108.9, 55.4, 33.2, 26.6, 13.1.

3-(3-(methoxymethyl)-1-methyl-2-oxoindolin-3-yl)propanenitrile (4ga) $^1$

![Image of 3-(3-(methoxymethyl)-1-methyl-2-oxoindolin-3-yl)propanenitrile (4ga)]

$^1$H NMR (CDCl$_3$, 400 MHz): δ 7.36-7.30 (m, 2H), 7.11 (d, J = 7.5 Hz, 1H), 6.88 (d, J = 7.8 Hz, 1H), 3.66 (d, J = 8.8 Hz, 1H), 3.50 (d, J = 8.8 Hz, 1H), 3.26 (s, 3H), 3.22 (s, 3H), 2.37-2.30 (m, 1H), 2.22-2.02 (m, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 176.5, 143.8, 129.0, 128.9, 123.8, 123.0, 118.8, 108.4, 75.8, 59.5, 52.5, 29.0, 26.3, 12.4.

(3-(2-cyanoethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (4ha) $^1$

![Image of (3-(2-cyanoethyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (4ha)]

S10
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.37 (t, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 7.4$ Hz, 1H), 7.13 (t, $J = 7.5$ Hz, 1H), 6.91 (d, $J = 7.8$ Hz, 1H), 4.47 (d, $J = 10.9$ Hz, 1H), 4.14 (d, $J = 10.9$ Hz, 1H), 3.25 (s, 3H), 2.43-2.34 (m, 1H), 2.24-2.02 (m, 3H), 1.95 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 175.7, 170.1, 143.9, 129.4, 127.4, 127.3, 123.7, 123.2, 118.4, 108.6, 66.5, 51.3, 28.9, 26.4, 20.5, 12.4.

3-methyl-3-(1-methyl-2-oxoindolin-3-yl)butanenitrile (4ia)

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.33-7.29 (m, 2H), 7.12 (t, $J = 7.5$ Hz, 1H), 7.04 (t, $J = 7.7$ Hz, 1H), 3.43 (s, 3H), 2.88-2.82 (m, 1H), 2.79-2.76 (m, 1H), 2.56-2.50 (m, 1H), 1.45 (s, 3H), 1.18 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 168.4, 138.4, 133.4, 128.1, 124.3, 123.9, 119.0, 115.5, 48.8, 36.2, 30.2, 25.9, 22.4, 14.2.

HRMS (ESI) m/z calcd for C$_{14}$H$_{18}$N$_2$O (M+Na)$^+$ 251.1155, found 251.1157.

3-(1,3-dimethyl-2-oxoindolin-3-yl)butanenitrile (4ja: 4ja′ = 1.4:1 d.r.)

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.31 (t, $J = 7.6$ Hz, 1H), 7.21-7.15 (m, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.87 (d, $J = 7.7$ Hz, 1H), 3.21 (d, $J = 2.4$ Hz, 3H), 2.54-2.11 (m, 3H), 1.40 (d, $J = 0.9$ Hz, 3H), 1.15 (d, $J = 6.8$ Hz, 1.76Hz), 1.05 (d, $J = 6.8$ Hz, 1.24Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 178.9, 178.6, 143.2, 143.1, 131.8, 128.5, 128.4, 123.0, 123.0, 122.9, 122.8, 118.7, 108.4, 50.2, 50.0, 37.9, 37.5, 26.1, 21.7, 20.9, 20.2, 19.8, 14.7, 14.4.

HRMS (ESI) m/z calcd for C$_{14}$H$_{16}$N$_2$O (M+Na)$^+$ 251.1155, found 251.1158.

3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3ab)

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.36-7.31 (m, 2H), 7.12 (t, $J = 7.5$ Hz, 1H), 6.91 (d, $J = 7.7$ Hz, 1H), 3.25 (s, 3H), 2.33 (d, $J = 14.6$ Hz, 1H), 2.17 (d, $J = 14.6$ Hz, 1H), 1.35 (s, 3H), 1.16 (s, 3H), 1.09 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 179.6, 143.1, 130.9, 128.6, 124.7, 123.9, 122.5, 108.5, 46.9, 46.5, 30.7, 29.6, 27.4, 26.6, 26.4.

S11
HRMS (ESI) \( m/z \) calcd for C\(_{15}\)H\(_{18}\)N\(_2\)O(M+Na\(^+\)) 265.1311, found 265.1310.

3-ethyl-1,3-dimethylindolin-2-one (5aa)\(^2\)

\[ \text{1H NMR (CDCl}_3, 400 MHz): \delta \ 7.27 \ (t, J = 7.6 \text{ Hz, 1H}), 7.16 \ (d, J = 7.8 \text{ Hz, 1H}), 6.91 \ (t, J = 7.5 \text{ Hz, 1H}), 6.84 \ (d, J = 7.7 \text{ Hz, 1H}), 3.21 \ (s, 3H), 1.97-1.88 \ (m, 1H), 1.82-1.82 \ (m, 1H), 1.35 (s, 3H), 0.58 (t, J = 7.4 \text{ Hz, 3H}). \]

$^1$H NMR of 3ga and 3ga'

$^1$H NMR of 3ha
$^1$H NMR of 3sa

$^13$C NMR of 3ra
$^{13}$C NMR of 4da

$^1$H NMR of 4ea
$^{13}$C NMR of 4a

$^1$H NMR of 4ga
$^{13}C$ NMR of 4ga

$^1H$ NMR of 4ha
$^{13}$C NMR of 4ja

$^{13}$C NMR of 3ab