Supporting information

Cyanomethylation of Alkenes with C-H Bond Activation of Acetonitrile: In-situ Generated Diazonium Salts as Promoter without Transition-metals

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1. Experimental Section

1.1 General information

All reagents were purchased from commercial suppliers and used without further purification. All reactions were conducted in oven-dried schlenk tubes under nitrogen atmosphere. $^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature in CDCl$_3$. Data for $^1$H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for $^{13}$C-NMR are reported in terms of chemical shift (δ ppm). Gas chromatography coupled to electron impact ionization/time-of-flight mass spectrometry (GC/EI-TOF-MS) was performed using a HP6890 gas chromatography with a time of flight mass spectrometry (GCT premier GC-TOFMA, America). Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

1.2 General procedure for the preparation of N-arylacrylamides

\[
\begin{align*}
\text{R = H, CH}_3, \text{OAc} \\
- & \text{Et}_3\text{N} \\
\text{CH}_2\text{Cl}_2, 0^\circ\text{C} \rightarrow \text{r.t.}
\end{align*}
\]

In a dry 100 mL round-bottom flask, a mixture of aniline (10 mmol) and Et$_3$N (30 mmol, 3equiv) in 30 mL of CH$_2$Cl$_2$ were stirred in the ice-water bath. The methacryloyl chloride (15 mmol, 1.5 equiv) was added slowly by a syringe. The reaction was monitored by TLC. After the reaction completed, the mixture was evaporated under reduced pressure and extracted by ethyl acetate. The product was purified by silica gel column chromatography.

\[
\begin{align*}
\text{R} & \text{NH}_2 \\
\text{Cl} & \text{CH}_2\text{Cl}_2, 0^\circ\text{C} \rightarrow \text{r.t.} \\
\text{NaH} & \text{THF, 0^\circ C} \\
\text{MeI} & \text{THF, 0^\circ C}
\end{align*}
\]

In a dry 50 mL round-bottom flask, N-phenylmethacrylamide (5 mmol) was dissolved in 15 mL THF and stirred in the ice-water bath. The NaH (7.5 mmol, 1.5 equiv) was added slowly. After 5 mins, the MeI (7.5 mmol, 1.5equiv) was added to the mixture slowly by a syringe. The reaction was monitored by TLC. When the reaction completed, the mixture was evaporated under reduced pressure and extracted by ethyl acetate. The product was purified by silica gel column chromatography.
2. Experimental Procedures and Spectral Data

2.1 General procedure for the synthesis of oxoindoles

\[
\begin{align*}
\text{N} & \quad \text{O} \\
& + \quad \text{CN} \\
\text{CH}_2\text{CN} & \quad \text{H} \quad \text{CN} \\
\text{p-anisidine} & \quad \text{t-BuONO, KOAc} \\
80^\circ\text{C}, \text{N}_2, 10\text{h} & \quad \text{N} \quad \text{O} \\
\end{align*}
\]

In a dry 25 mL oven-dried Schlenk tubes, N-arylacrylamide (0.5 mmol), aniline (1.5 mmol, 3.0 equiv) and KOAc (1.0 mmol, 2.0 equiv) were dissolved in 4 mL CH$_3$CN under an atmosphere of dry nitrogen at room temperature. Tert-butyl nitrite (1.5 mmol, 3.0 equiv) was then added with a syringe. A fine bubbling was observed and the reaction mixture was heated to 80°C for 10h. Then the solution was cooled to r.t., washed with a saturated aqueous solution of NaCl, extracted by ethyl acetate and dried over by Na$_2$SO$_4$. The product was purified by silica gel column chromatography.

2.2 substrate scope of N-Arylacrylamides

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

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.31 (m, 1H), 7.18 (m, 1H), 7.10 (m, 1H), 6.87 (d, J = 7.6Hz, 1H), 3.22 (s, 3H), 2.32 (m, 1H), 2.05 (m, 3H), 1.39 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 179.1, 143.3, 131.8, 128.9, 123.2, 122.8, 119.0, 108.7, 47.5, 33.6, 26.5, 23.6, 13.0.

HRMS (EI, $m/z$): calcd for C$_{13}$H$_{14}$N$_2$O: 214.1106; found: 214.1100.

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

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.10 (m, 1H), 7.09 (s, 1H), 6.75 (d, J = 6.3Hz, 1H), 3.18 (s, 3H), 2.35 (s, 3H), 2.30 (m, 1H), 2.03 (m, 3H), 1.37 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 178.7, 140.6, 132.5, 131.5, 128.7, 123.3, 118.8, 108.1, 47.2, 33.3, 26.2, 23.3, 21.0, 12.7.

HRMS (EI, $m/z$): calcd for C$_{14}$H$_{16}$N$_2$O: 228.1263; found: 228.1268.
3-(5-chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.22 (m, 1H), 7.1 (m, 1H), 6.74 (d, $J = 6.6$Hz, 1H), 3.13 (s, 3H), 2.25 (m, 1H), 1.98 (m, 3H), 1.32 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 178.2, 141.6, 133.3, 128.5, 128.2, 123.1, 118.4, 109.4, 47.4, 33.0, 26.3, 23.2, 12.6.

HRMS (EI, $m/z$): calcd for C$_{13}$H$_{13}$ClN$_2$O: 248.0716; found: 248.0711.

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

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.01 (m, 1H), 6.94 (m, 1H), 6.80 (m, 1H), 3.19 (s, 3H), 2.29 (m, 1H), 2.02 (m, 3H), 1.38 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 178.4, 160.5, 158.1, 138.9, 138.9, 133.3, 133.2, 118.4, 114.9, 114.7, 110.9, 110.7, 109.0, 109.0, 47.6, 47.6, 33.1, 26.3, 23.2, 12.6.

HRMS (EI, $m/z$): calcd for C$_{13}$H$_{13}$FN$_2$O: 232.1012; found: 232.1010.

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

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.44 (m, 1H), 7.30 (m, 1H), 6.76 (d, $J = 8.3$Hz, 1H), 3.20 (s, 3H), 2.33 (m, 1H), 2.06 (m, 3H), 1.40 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 178.2, 142.1, 133.7, 131.5, 125.9, 118.7, 115.7, 109.9, 47.4, 33.2, 26.4, 23.4, 12.8.

HRMS (EI, $m/z$): calcd for C$_{13}$H$_{13}$BrN$_2$O: 292.0211; found: 292.0207.

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

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 6.79 (m, 3H), 3.99 (q, $J = 5.6$Hz, 2H), 3.17 (s, 3H), 2.29 (m, 1H), 2.01 (m, 3H), 1.39 (t, $J = 5.6$Hz, 3H), 1.36 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 178.4, 155.6, 136.3, 132.8, 118.7, 113.1, 110.7, 108.7, 64.0, 47.6, 33.3, 26.2, 23.4, 14.7, 12.7.

HRMS (EI, $m/z$): calcd for C$_{13}$H$_{18}$N$_2$O$_2$: 258.1368; found: 258.1364.
3-(4-chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile  3-(6-chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.26 (m, 1.3H), 7.10 (m, 1H), 7.04 (m, 1.1H), 6.89 (m, 0.4H), 6.81 (m, 1.1H), 3.23 (s, 3H), 3.21 (s, 1.1H), 2.53 (m, 1.2H), 2.38 (m, 1.7H), 2.03 (m, 3.7H), 1.53 (s, 3H), 1.39 (s, 1.3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 178.7, 178.2, 144.9, 144.2, 134.3, 130.6, 129.9, 129.9, 123.7, 123.5, 122.7, 118.5, 118.3, 109.2, 107.0, 48.9, 46.9, 33.0, 30.2, 26.5, 26.3, 23.3, 21.1, 13.0, 12.7.

HRMS (EI, m/z): calcd for C$_{13}$H$_{13}$ClN$_2$O: 248.0716; found: 248.0720.

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

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.19 (t, J = 6.3Hz, 1H), 7.04 (d, J = 6Hz, 0.6H), 6.89 (d, J = 6Hz, 0.7H), 6.84 (d, J = 6.2Hz, 1H), 6.70 (m, 1.5H), 3.17 (m, 4.4H), 2.36 (m, 5.3H), 2.26 (m, 1.9H), 2.00 (m, 4.7H), 1.45 (s, 3H), 1.35 (s, 1.8H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 179.0, 178.7, 143.3, 143.0, 138.6, 134.2, 128.4, 128.3, 127.9, 125.3, 123.3, 122.1, 118.7, 118.5, 109.3, 106.1, 48.7, 46.9, 33.2, 31.2, 26.2, 26.0, 23.3, 21.6, 21.6, 18.0, 12.8, 12.6.

HRMS (EI, m/z): calcd for C$_{14}$H$_{16}$N$_2$O: 228.1263; found: 228.1260.

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

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 6.99 (m, 3H), 3.49 (s, 3H), 2.57 (s, 3H), 2.30 (m, 1H), 2.00 (m, 3H), 1.36 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 179.5, 140.7, 132.2, 132.1, 122.8, 120.3, 120.1, 118.8, 46.5, 33.5, 29.5, 23.7, 18.9, 12.7.

HRMS (EI, m/z): calcd for C$_{14}$H$_{16}$N$_2$O: 228.1263; found: 228.1259.
3-(7-chloro-1,3-dimethyl-2-oxoindolin-3-yl)propanenitrile

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.25 (m, 1H), 7.07 (m, 1H), 7.01 (m, 1H), 3.59 (s, 3H), 2.33 (m, 1H), 2.06 (m, 3H), 1.40 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 179.0, 139.0, 134.5, 131.0, 123.8, 121.1, 118.5, 116.0, 47.1, 33.5, 29.6, 23.8, 12.8.

HRMS (EI, $m/z$): calcd for C$_{13}$H$_{13}$ClN$_2$O: 248.0716; found: 248.0722.

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

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.29 (m, 1H), 7.17 (m, 1H), 7.09 (m, 1H), 6.89 (d, J = 6.2Hz, 1H), 3.75 (m, 2H), 2.30 (m, 1H), 2.05 (m, 3H), 1.37 (s, 3H), 1.25 (t, J = 5.8Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 178.3, 142.0, 131.7, 128.5, 122.7, 122.6, 118.7, 108.5, 47.1, 34.6, 33.3, 23.3, 12.6, 12.5.

HRMS (EI, $m/z$): calcd for C$_{14}$H$_{16}$N$_2$O: 228.1263; found: 228.1269.

3-(1-butyl-3-methyl-2-oxoindolin-3-yl)propanenitrile

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.30 (m, 1H), 7.18 (m, 1H), 7.08 (m, 1H), 6.88 (d, J = 6.2Hz, 1H), 3.7 (t, J = 6.0Hz, 2H), 2.31 (m, 1H), 2.05 (m, 3H), 1.64 (t, J = 6.9Hz, 2H), 1.37 (m, 4H), 0.96 (t, J = 5.9Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 178.7, 142.5, 131.8, 128.6, 122.8, 122.7, 118.9, 108.8, 47.2, 39.8, 33.4, 29.5, 23.6, 20.1, 13.7, 12.8.

HRMS (EI, $m/z$): calcd for C$_{16}$H$_{20}$N$_2$O: 256.1576; found: 256.1570.

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

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.27 (m, 1H), 7.18 (m, 1H), 7.09 (m, 1H), 7.05 (m, 1H), 4.62 (m, 1H), 2.33 (m, 1H), 2.30 (m, 3H), 1.47 (m, 6H), 1.37 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 178.4, 141.7, 132.0, 128.3, 122.8, 122.4, 118.8, 110.1, 46.9, 43.8, 33.5, 23.6, 19.4, 19.3, 12.6.

HRMS (EI, $m/z$): calcd for C$_{15}$H$_{18}$N$_2$O: 242.1419; found: 242.1415.
3-(3-(methoxymethyl)-1-methyl-2-oxoindolin-3-yl)propanenitrile

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.24 (m, 2H), 7.04 (t, $J = 6.0$ Hz, 1H), 6.80 (d, $J = 6.2$ Hz, 1H), 3.59 (d, $J = 7.1$ Hz, 1H), 3.42 (d, $J = 7.1$ Hz, 1H), 3.19 (s, 3H), 3.14 (s, 3H), 2.26 (m, 1H), 2.02 (m, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 176.4, 143.7, 128.9, 128.8, 123.7, 122.9, 118.7, 108.3, 75.7, 59.4, 52.4, 28.9, 26.2, 12.3.

HRMS (EI, $m/z$): calcd for C$_{14}$H$_{16}$N$_2$O$_2$: 244.1212; found: 244.1211.

2-(1-methyl-2-oxo-1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinolin-1-yl)acetonitrile

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.02 (m, 3H), 3.72 (m, 2H), 2.79 (t, $J = 6.0$ Hz, 2H), 2.28 (m, 1H), 2.06 (m, 5H), 1.40 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 177.6, 138.8, 130.0, 127.3, 122.3, 120.5, 120.3, 118.8, 48.5, 38.7, 33.1, 24.4, 23.1, 21.0, 12.8.

HRMS (EI, $m/z$): calcd for C$_{14}$H$_{14}$N$_2$O: 226.1106; found: 226.1100.

3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$: 7.46 (m, 1H), 7.32 (m, 1H), 7.09 (m, 1H), 7.03 (m, 1H), 5.58 (q, $J = 5.2$ Hz, 1H), 3.11 (s, 3H), 2.94 (m, 1H), 2.78 (m, 1H), 1.27 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$: 178.9, 143.6, 131.0, 128.8, 123.9, 122.7, 109.1, 71.5, 49.4, 47.1, 26.7, 26.7.

HRMS (EI, $m/z$): calcd for C$_{12}$H$_{13}$Cl$_2$NO: 257.0374; found: 257.0370.
1,3-dimethyl-3-(2,2,2-trichloroethyl)indolin-2-one

**H NMR (CDCl$_3$, 400 MHz)**: $\delta$: 7.54 (m, 1H), 7.28 (m, 1H), 7.03 (m, 2H), 3.71 (m, 1H), 3.43 (m, 1H), 3.14 (s, 3H), 1.29 (s, 3H).

**C NMR (CDCl$_3$, 100 MHz)**: $\delta$: 178.4, 143.5, 129.8, 128.8, 125.3, 122.0, 109.1, 97.3, 59.1, 47.9, 26.8, 26.7.

**HRMS (EI, m/z)**: calcd for C$_{12}$H$_{12}$Cl$_3$NO: 290.9984; found: 290.9988.

### 3. Control Experiments.

![Chemical structure](image)

In a dry 25 mL oven-dried schlenk tubes, N-arylacrylamide (0.5 mmol), aniline (1.5 mmol, 3.0 equiv), KOAc (1.0 mmol, 2.0 equiv) and TEMPO (or BHT) (1.5 mmol, 3.0 equiv) were dissolved in 4 mL CH$_3$CN under an atmosphere of dry nitrogen at room temperature. Tert-butyl nitrite (1.5 mmol, 3.0 equiv) was then added with a syringe. The reaction mixture was heated to 80°C for 10h. Then the solution was cooled to r.t., washed with a saturated aqueous solution of NaCl, extracted by ethyl acetate and dried over by Na$_2$SO$_4$. The mixture was detected by GC-MS and the exact molecular weight of compound 3 was confirmed by HRMS.
Chemical Formula: C₉H₁₈NO⁺
Exact Mass: 156.14

Chemical Formula: C₇H₉NO
Exact Mass: 123.07

HRMS (ESI, m/z): calcd for C₁₁H₂₁N₂O⁺: 197.1648; found: 197.1653.
Chemical Formula: C_{11}H_{13}NO
Exact Mass: 175.10
4. NMR Spectra

\[ \text{NMR Spectra of 2a} \]

[Diagram of NMR Spectra]

\[ \text{NMR Spectra of 2a} \]

[Diagram of NMR Spectra]
2h

\[
\text{C}_2\text{H}_3\text{O} \quad \text{CH}_2\text{CN}
\]

2h

\[
\text{C}_2\text{H}_3\text{O} \quad \text{CH}_2\text{CN}
\]