Supporting Information for:

Copper-catalyzed cyanopropylation of activated alkenes

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General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Flush column chromatography was performed using silica gel (200-300 mesh) and a petroleum ether/ethyl acetate combination was used as the eluent. Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F₂₅₄ (0.25 mm) plates. Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline KMnO₄ solution followed by heating.

Apparatus. Proton and carbon nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Varian Mercury 400 (¹H NMR, 400 MHz; ¹³C NMR, 101 MHz) spectrometer with solvent resonance (¹H NMR, CHCl₃ at 7.26 ppm, and SiMe₄ at 0 ppm; ¹³C NMR, CDCl₃ at 77.0 ppm and SiMe₄ at 0 ppm) as the internal standard. ¹H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, br = broad), coupling constants (Hz), and integration.

Chemicals. Unless otherwise noted, reagents were commercially available and were used without further purification. Anhydrous THF was distilled from sodium/benzophenone prior to use. Preparation of *N*-arylacrylamides **1** were prepared according to literature

procedures.¹

2. Mechanistic Studies

a) Intramolecular kinetic isotope effect (KIE) experiment using AIBN: To a mixture of [D₁]-**1a** (0.5 mmol), AIBN (2.0 equiv), CuI (5 mol%) in CH₃CN (2.0 mL) was added *t*BuOO*t*Bu (2.0 equiv) dropwise, and then the resulting solution was stirred at 80 °C for 12 h. The solvent was evaporated under reduced pressure and the resulted mixture was filtered through a Florisil pad, diluted with Et₂O, and washed with water and then brine. The organic layer was dried over anhydrous MgSO₄ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the mixture of **3a** and [D₁]-**3a**. A small kinetic isotope effect ($K_{H/D} = 1.3$) was observed, which suggested that either the *SEAr* mechanism or the free radical mechanism was involved in the reactions.²

Figure S1 ^1H NMR for Intramolecular kinetic isotope effect experiment

b) Interomolecular KIE experiment using AIBN: To a mixture of $[\text{D}_5]\text{-1a}$ (0.3mmol), **1a** (0.3 mmol), AIBN (2.0 equiv), CuI (5 mol%) in CH_3CN (2.0 mL) was added $t\text{BuOO}^t\text{Bu}$ (2.0 equiv) dropwise, and then the resulting solution was stirred at 80°C for 2 h. The solvent was evaporated under reduced pressure and the resulted mixture was filtered through a Florisil pad, diluted with Et_2O , and washed with water and then brine. The organic layer was dried over anhydrous MgSO_4 and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to afford the mixture of **3a** and $[\text{D}_4]\text{-3a}$. No kinetic isotope effect ($K_{\text{H/D}} = 1$) was observed indicated that the C-H bond cleavage of aromatic ring was not a rate-limiting step.¹

Figure S2 ^1H NMR for Interomolecular kinetic isotope effect experiment

3. General Procedures

General Procedure for the synthesis of oxindoles with 3^o alkyl nitrile moiety. To a mixture of *N*-arylacrylamide **1** (0.5 mmol), AIBN or its analogues (2.0 equiv.), CuI (5 mol%) in CH_3CN (2.0 mL) was added $t\text{BuOO}t\text{Bu}$ (2.0 equiv.) dropwise, and then the resulting solution was stirred at indicated temperature for 12-15 h. The solvent was evaporated under reduced pressure and the resulted mixture was filtered through a Florisil pad, diluted with Et_2O , and washed with water and then brine. The organic layer was dried over anhydrous MgSO_4 and concentrated in *vacuo*. The residue was purified by

flash chromatography on silica gel to afford the the corresponding oxindoles with 3° alkyl nitrile moiety in a yield listed in Scheme 1.

4. New compounds characterization

3-(1,3-Dimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3a). Colorless solid, m.p. 100-101 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.25 (m, 2H), 7.09 (t, $J = 6.0$ Hz, 1H), 6.90 (d, $J = 6.4$ Hz, 1H), 3.23 (s, 3H), 2.32 (d, $J = 11.6$ Hz, 1H), 2.16 (d, $J = 11.6$, 1H), 1.34 (s, 3H), 1.13 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.5, 143.1, 130.9, 128.6, 124.6, 123.9, 122.4, 108.5, 47.0, 46.5, 30.7, 29.6, 27.4, 26.8, 26.4; IR (KBr): 2234, 1716, 1610, 1432, 1378, 1335 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 242 [M^+] (32), 160 (100); HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}$ [$\text{M}+\text{H}]^+$: 243.1492, found: 243.1495.

3-(1-Ethyl-3-methyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3b). colorless solid, m.p. 71-72 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.31 (m, 2H), 7.09 (t, $J = 7.2$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 2H), 3.90-3.70 (m, 2H), 2.32 (d, $J = 14.4$ Hz, 1H), 2.16 (d, $J = 14.4$, 1H), 1.32 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.20 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.2, 142.1, 131.0, 128.5, 125.0, 124.2, 122.2, 108.6, 46.0, 46.1, 30.8, 29.8, 27.9, 26.1, 25.8, 12.2; IR (KBr): 2247, 1713, 1611, 1431, 1376, 1337 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 256 [M^+] (27), 174 (100). HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}$ [$\text{M}+\text{H}]^+$: 257.1649, found: 257.1653.

3-(1-Benzyl-3-methyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3c). Yellow solid. 80-81°C. ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.20 (m, 7H), 7.05 (t, $J = 7.2$ Hz, 1H), 6.83 (d, $J = 8.0$ Hz, 2H), 5.12 (d, $J = 15.6$ Hz, 1H), 4.72 (d, $J = 15.6$ Hz, 1H), 2.36 (d,

$J = 14.8$ Hz, 1H), 2.22 (d, $J = 14.4$ Hz, 1H), 1.40 (s, 3H), 1.19 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.7, 142.3, 130.8, 128.7, 128.5, 127.7, 127.6, 124.8, 124.1, 122.4, 119.9, 109.5, 47.0, 46.2, 44.1, 30.8, 29.7, 28.1, 26.3; MS IR (KBr): 2233, 1701, 1610, 1432, 1376, 1332 cm^{-1} ; (EI, 70 eV): m/z (%) = 318 [M^+] (22), 236 (100). HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}$ [$\text{M}+\text{H}$] $^+$: 319.1805, found: 319.1801.

3-(1-Ethyl-5-methoxy-3-methyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3e). yellow solid. m.p. 111-112 °C. ^1H NMR (400 MHz, CDCl_3) δ 6.95 (s, 1H), 6.86-6.79 (m, 2H), 3.84-3.67 (m, 2H), 3.80 (s, 3H), 2.30 (d, $J = 14.8$ Hz, 1H),

2.17 (s, $J = 14.8$ Hz, 1H), 1.31 (s, 3H), 1.29-1.20 (m, 6H), 1.04 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.9, 166.7, 135.5, 132.3, 124.3, 113.2, 112.4, 108.9, 55.9, 47.3, 46.0, 30.8, 29.8, 29.7, 28.0, 25.8, 12.2; IR (KBr): 2237, 1702, 1596, 1431, 1384, 1337 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 286 [M^+] (17), 204 (100); HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}_2$ [$\text{M}+\text{H}$] $^+$: 287.1755, found: 287.1752.

3-(5-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3f). pale yellow solid. m.p. 107-108 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.10-7.00 (m, 2H), 6.60-6.71 (m, 1H), 3.21 (s, 3H), 2.32 (d, $J = 14.8$ Hz, 1H), 2.11 (d, $J = 14.8$ Hz,

1H), 1.34 (s, 3H), 1.16 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.2, 159.2 (d, $J = 204.4$ Hz), 139.1, 132.6, 123.7, 114.8 (d, $J = 23.4$ Hz), 112.7 (d, $J = 24.5$ Hz), 109.0, 47.4, 46.5, 30.6, 29.1, 23.3, 26.9, 26.5; IR (KBr): 2234, 1718, 1617, 1435, 1383, 1335 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 260 [M^+] (17), 178 (100); HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{FN}_2\text{O}$ [$\text{M}+\text{H}$] $^+$: 261.1397, found: 261.1399.

3-(5-Chloro-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3g). pale yellow solid. m.p. 128-129 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.25 (m, 2H), 6.81 (d, $J = 8.0$ Hz, 1H), 3.21 (s, 3H), 2.32 (d, $J = 14.4$ Hz, 1H), 2.10 (d, $J = 14.4$ Hz, 1H), 1.34 (s,

3H), 1.15 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.0, 141.7, 132.7, 127.9, 125.0, 123.9, 123.6, 109.4, 47.2, 46.6, 30.5, 29.6, 27.3, 27.1, 26.5; IR (KBr): 2233, 1715, 1610, 1432, 1383, 1345 cm^{-1} . MS (EI, 70 eV): m/z (%) = 276 [M^+] (12), 194 (100); HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{18}\text{ClN}_2\text{O}$ [$\text{M}+\text{H}$] $^+$ 277.1103, found: 277.1106.

3-(1,3-Dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)-2,2-dimethylpropanenitrile (3h). yellow solid. m.p. 114-115 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (d, J = 8.4 Hz, 1H), 7.52 (s, 1H), 6.96 (d, J = 8.4 Hz, 1H), 3.26 (s, 3H), 2.33 (d, J = 14.8 Hz, 1H), 2.15 (d, J = 14.8 Hz, 1H), 1.37 (s, 3H), 1.11 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.4, 146.1, 131.6, 126.3 (q, J = 3.9 Hz), 124.0 (q, J = 32.8 Hz), 123.4, 121.6 (q, J = 3.5 Hz), 120.2, 108.3, 47.0, 46.5, 30.5, 29.5, 27.2, 27.1, 26.6; IR (KBr): 2235, 1715, 1624, 1432, 1385, 1327 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 310 [M^+] (32), 228 (100); HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{18}\text{F}_3\text{N}_2\text{O}$ [$\text{M}+\text{H}$] $^+$: 311.1366, found: 311.1367.

A mixture of 2,2-dimethyl-3-(1,3,6-trimethyl-2-oxoindolin-3-yl)propanenitrile (3j) and 2,2-dimethyl-3-(1,3,4-trimethyl-2-oxoindolin-3-yl)propanenitrile (3j'). 3j:3j' = 2:1

^1H NMR (400 MHz, CDCl_3) δ 7.26-7.15 (m, 3H), 6.90-6.83 (m, 3H), 6.74-6.70 (m, 3H), 2.20 (s, 9H), 2.42 (s, 6H), 2.36 (s, 3H), 2.36-2.22 (m, 5 H), 2.12 (d, J = 14.8 Hz, 1H), 2.39 (s, 6H), 2.30 (s, 3H), 1.15 (s, 6H), 1.13 (s, 3H), 1.07 (s, 6H), 1.05 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 180.0, 179.6, 143.3, 143.1, 138.7, 135.8, 128.5, 128.1, 125.3, 124.4, 123.4, 122.9, 109.4, 106.2, 46.8, 46.4, 45.1, 44.2, 30.8, 30.7, 30.5, 30.3, 29.6, 29.1, 27.5, 26.6, 26.4, 24.7; IR (KBr): 2233, 1702, 1610, 1434, 1372, 1327 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 256 [M^+] (26), 174 (100); HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}$ [$\text{M}+\text{H}$] $^+$: 257.1649, found: 257.1654.

2,2-Dimethyl-3-(1,3,7-trimethyl-2-oxoindolin-3-yl)propanenitrile (3k). Yellow solid, m.p. 84-85 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.12

(d, $J = 7.6$ Hz, 1H), 7.04 (d, $J = 7.6$ Hz, 1H), 6.99 (t, $J = 7.6$ Hz, 1H), 3.51 (s, 3H), 2.59 (s, 3H), 2.21 (d, $J = 14.4$ Hz, 1H), 2.11 (d, $J = 14.4$ Hz, 1H), 1.31 (s, 3H), 1.14 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 180.3, 140.9, 132.3, 131.6, 123.9, 122.5, 122.3, 120.1, 46.7, 46.3, 30.7, 29.7, 29.6, 27.8, 26.8, 19.1; IR (KBr): 2232, 1702, 1600, 1432, 1363, 1327 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 256 [M^+] (22), 174 (100); HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}$ [$\text{M}+\text{H}]^+$: 257.1649, found: 257.1652.

3-(7-Methoxy-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3l). Yellow solid. m.p. 93-94 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.01 (t, $J = 8.4$ Hz, 2H), 6.90-6.71 (m, 2H), 3.85 (s, 3H), 3.49 (s, 3H), 2.28 (d, $J = 14.8$ Hz, 1H), 2.12 (d, $J = 14.8$ Hz, 1H), 1.30 (s, 3H), 1.17 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.8, 146.6, 132.6, 130.9, 123.9, 122.9, 117.3, 112.2, 55.8, 46.9, 46.5, 30.7, 29.7, 27.7, 26.4, 25.8; IR (KBr): 2233, 1700, 1612, 1439, 1365, 1333 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 272 [M^+] (35), 190 (100); HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}_2$ [$\text{M}+\text{H}]^+$: 273.1598, found: 273.1603.

mixture of 3-(5,6-dichloro-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3n) and 3-(4,5-dichloro-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3n')
3n: 3n' = 1:3, ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 8.4$ Hz, 1H), 7.36 (s, 0.3H), 6.98 (s, 0.3H), 6.77 (d, $J = 14.4$ Hz, 1H), 3.21 (s, 3H), 3.20 (s, 1 H), 2.68 (d, $J = 14.4$ Hz, 1H), 2.31 (d, $J = 14.4$ Hz, 0.3 H), 2.21 (d, $J = 14.4$ Hz, 1H), 2.10 (d, $J = 14.4$ Hz, 0.3 H), 1.48 (s, 3H), 1.33 (s, 1H), 1.18 (s, 4H), 1.12 (s, 3H), 1.09 (s, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 178.9, 178.4, 143.3, 142.7, 130.9, 130.4, 130.3, 129.7, 126.5, 123.9, 123.6, 121.5, 123.1, 110.9, 107.8, 47.0, 46.4, 44.2, 43.4, 30.6, 30.5, 30.4, 30.3, 29.7, 28.2, 28.0, 27.3, 26.9, 26.6, 25.8; IR (KBr): 2235, 1723, 1602, 1473, 1376, 1325 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 310 [M^+] (35), 227 (100); HRMS m/z (ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{Cl}_2\text{N}_2\text{O}$ [$\text{M}+\text{H}]^+$: 311.0713, found: 311.0717.

3-(4-Chloro-1,3,7-trimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3o). Yellow solid. m.p. 78-79 °C. ^1H NMR (400 MHz, CDCl_3) δ 6.98 (d, J = 8.4 Hz, 1H), 6.88 (d, J = 8.4 Hz, 1H), 3.5 (s, 3H), 2.60 (d, J = 14.4 Hz, 1H), 2.57 (s, 3H), 2.19 (d, J = 14.4 Hz, 1H), 1.47 (s, 3H), 1.18 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.6, 142.7, 123.5, 129.8, 129.1, 128.5, 128.1, 118.8, 47.6, 44.1, 30.7, 29.7, 28.2, 28.0, 23.8, 19.0; IR (KBr): 2231, 1717, 1636, 1457, 1384 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 290 [M^+] (23), 208 (100); HRMS m/z (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{ClN}_2\text{O}$ [$\text{M}+\text{H}$] $^+$: 291.1259, found: 291.1256.

2,2-Dimethyl-3-(1-methyl-2-oxo-2,4,5,6-tetrahydro-1H-pyrrolo[3,2,1-ij]quinolin-1-yl)propanenitrile (3p). Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.20 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 3.85-3.74 (m, 2H), 2.93-2.79 (m, 2H), 2.38 (d, J = 14.4 Hz, 1H), 2.19 (d, J = 14.4 Hz, 1H), 2.11-2.09 (m, 2H), 1.41 (s, 3H), 1.22 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.3, 139.8, 130.3, 128.1, 124.8, 123.3, 122.6, 121.4, 49.1, 47.2, 31.6, 30.4, 27.9, 27.7, 25.4, 21.9; IR (KBr): 2232, 1710, 1608, 1473, 1372, 1341 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 268 [M^+] (29), 186 (100); HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{21}\text{N}_2\text{O}$ [$\text{M}+\text{H}$] $^+$: 269.1649, found: 269.1653.

2,2-Dimethyl-3-(1-methyl-2-oxo-3-phenylindolin-3-yl)propanenitrile (3q). Yellow solid. m.p. 121-122 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.50-7.48 (m, 7H), 7.18 (t, J = 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 3.22 (s, 3H), 2.82 (d, J = 14.4 Hz, 1H), 2.49 (d, J = 14.4 Hz, 1H), 1.23 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 177.4, 144.1, 140.7, 140.4, 129.4, 128.0, 127.5, 125.4, 124.2, 123.8, 122.5, 108.9, 54.6, 46.6, 30.7, 30.2, 29.0, 28.7; IR (KBr): 2234, 1713, 1611, 1470, 1372, 1341 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 304 [M^+] (35), 222 (100); HRMS m/z (ESI) calcd for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}$ [$\text{M}+\text{H}$] $^+$: 305.1649,

found: 305.1647.

(3-(2-Cyano-2-methylpropyl)-1-methyl-2-oxoindolin-3-yl)methyl acetate (3s). Yellow oil, ^1H NMR (400 MHz, CDCl_3) δ 7.37 (m, 2H), 7.07 (t, $J = 7.6$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 4.34 (d, $J = 10.4$ Hz, 1H), 4.00 (d, $J = 10.8$ Hz, 1H), 3.24 (s, 3H), 2.28 (s, 2H), 1.90 (s, 3H), 1.17 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.3, 170.2, 143.9, 129.4, 125.9, 123.7, 122.5, 108.5, 68.5, 50.9, 41.6, 30.3, 27.8, 26.8, 26.5, 20.5; IR (KBr): 2234, 1732, 1710, 1614, 1491, 1378, 1340 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 300 [M^+] (14), 242 (30), 174 (100); HRMS m/z (ESI) calcd for $\text{C}_{17}\text{H}_{21}\text{N}_2\text{O}_3$ [$\text{M}+\text{H}$] $^+$:

1-((1,3-Dimethyl-2-oxoindolin-3-yl)methyl)cyclohexanecarbonitrile (3u). yellow solid. m.p. 158-159 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3). δ 7.32-7.28 (m, 2H), 7.06 (t, $J = 7.6$ Hz, 1H), 6.87 (d, $J = 8.0$ Hz, 1H), 3.21 (s, 3H), 2.39 (d, $J = 14.4$ Hz, 1H), 2.14 (d, $J = 14.4$ Hz, 1H), 1.64-1.03 (m, 10H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.8, 143.0, 131.3, 128.5, 124.6, 122.4, 122.1, 108.5, 46.7, 46.6, 38.1, 37.0, 35.0, 27.7, 26.4, 24.8, 22.8, 22.5; IR (KBr): 2231, 1701, 1614, 1471 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 282 [M^+] (15), 160 (100); HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}$ [$\text{M}+\text{H}$] $^+$: 283.1805, found: 283.1808.

1-((1,3,5-Trimethyl-2-oxoindolin-3-yl)methyl)cyclohexanecarbonitrile (3v). Yellow solid, m.p. 145-146 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3). δ 7.11 (s, 1H), 7.07 (d, $J = 7.6$ Hz, 1H), 6.74 (d, $J = 8.0$ Hz, 1H), 3.17 (s, 3H), 2.31 (s, 3H), 2.25 (d, $J = 14.8$ Hz, 1H), 2.11 (d, $J = 14.8$ Hz, 1H), 1.28-1.09 (m, 10H), 1.28 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.8, 140.6, 131.8, 131.2, 128.6, 125.5, 122.2, 108.1, 46.7, 46.5, 38.1, 37.0, 34.8, 27.8, 26.4, 24.8, 22.7, 22.5, 21.2; IR (KBr): 2233, 1706, 1617, 1496 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 296 [M^+] (15), 174 (100); HRMS m/z (ESI) calcd for $\text{C}_{19}\text{H}_{25}\text{N}_2\text{O}$

$[M+H]^+$: 297.1962 found: 297.1965.

1-((5-Fluoro-1,3-dimethyl-2-oxoindolin-3-yl)methyl)cyclohexanecarbonitrile (3w). yellow solid, m.p. 150-151°C. ^1H NMR (400 MHz, CDCl_3). δ 7.05- 6.97 (m, 2H), 6.81-6.77 (m, 1H), 3.20 (s, 3H), 2.39 (d, 14.8 Hz, 1H), 2.19 (d, J = 14.8 Hz, 1H), 1.52-0.99 (m, 10H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.4, 159.1 (d, J = 241Hz), 139.0, 133.0 (d, J = 7.8Hz), 121.9, 114.6, 112.6 (d, J = 24.5Hz), 108.9 (d, J = 7.1 Hz), 47.1, 46.6, 38.1, 36.9, 35.3, 27.6, 26.5, 24.5, 22.7, 22.5; IR (KBr): 2234, 1713, 1621, 1451 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 300 [M^+] (19), 178 (100); HRMS m/z (ESI) calcd for $\text{C}_{18}\text{H}_{22}\text{FN}_2\text{O}$ [$M+H$] $^+$: 301.1711, found: 301.1714.

ethyl

3-((1-Cyanocyclohexyl)methyl)-1,3-dimethyl-2-oxoindoline-5-carboxylate (3s). yellow solid, m.p. 140-141°C. ^1H NMR (400 MHz, CDCl_3). δ 8.05 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.90 (s, 1H), 6.90 (d, J = 8.4 Hz, 1H), 4.34 (q, J = 6.8 Hz, 2H), 3.25 (s, 3H), 2.32 (d, J = 14.4 Hz, 1H), 2.25 (d, J = 14.4 Hz, 1H), 1.61-0.98 (m, 10H), 1.37 (t, J = 7.2 Hz, 3H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 179.9, 166.3, 147.2, 131.5, 131.1, 125.4, 124.6, 121.6, 108.0, 60.9, 46.7, 46.6, 37.9, 36.9, 36.1, 27.5, 26.6, 24.8, 22.7, 22.5, 14.3; IR (KBr): 2235, 1726, 1701, 1612, 1475 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 354 [M^+] (13), 232 (100); HRMS m/z (ESI) calcd for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_3$ [$M+H$] $^+$: 355.2017, found: 355.2019.

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5 Copies of ^1H NRM and ^{13}C NRM spectra

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

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

3-(1-ethyl-3-methyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3b)

3-(1-ethyl-3-methyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (3b)

3-(1-benzyl-3-methyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3c)

3-(1-benzyl-3-methyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3c)

3-(1-ethyl-5-methoxy-3-methyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile(3e)

3-(1-ethyl-5-methoxy-3-methyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile(3e)

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

3-(5-fluoro-1,3-dimethyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3g)

3-(5-chloro-1,3-dimethyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3h)

3-(5-chloro-1,3-dimethyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3h)

3-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)-2,2-dimethylpropanenitrile (3i).

3-(1,3-dimethyl-2-oxo-5-(trifluoromethyl)indolin-3-yl)-2,2-dimethylpropanenitrile (3i)

The mixture of 2,2-dimethyl-3-(1,3,6-trimethyl-2-oxoindolin-3-yl)propanenitrile (3j) and 2,2-dimethyl-3-(1,3,4-trimethyl-2-oxoindolin-3-yl)propanenitrile (3j')

The mixture of 2,2-dimethyl-3-(1,3,6-trimethyl-2-oxoindolin-3-yl)propanenitrile (3j) and 2,2-dimethyl-3-(1,3,4-trimethyl-2-oxoindolin-3-yl)propanenitrile (3j')

2,2-dimethyl-3-(1,3,7-trimethyl-2-oxindolin-3-yl)propanenitrile(3k)

2,2-dimethyl-3-(1,3,7-trimethyl-2-oxindolin-3-yl)propanenitrile(3k)

3-(7-methoxy-1,3-dimethyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3I)

3-(7-methoxy-1,3-dimethyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3l)

Mixture of 3-(5,6-dichloro-1,3-dimethyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3n) and
 -(4,5-dichloro-1,3-dimethyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3n')

Mixture of 3-(5,6-dichloro-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile(3n) and -(4,5-dichloro-1,3-dimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile(3n')

3-(4-chloro-1,3,7-trimethyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3o)

3-(4-chloro-1,3,7-trimethyl-2-oxindolin-3-yl)-2,2-dimethylpropanenitrile (3o)

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

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

2,2-dimethyl-3-(1-methyl-2-oxo-3-phenylindolin-3-yl)propanenitrile (3q)

2,2-dimethyl-3-(1-methyl-2-oxo-3-phenylindolin-3-yl)propanenitrile (3q)

(3-(2-cyano-2-methylpropyl)-1-methyl-2-oxindolin-3-yl)methyl acetate (3s)

(3-(2-cyano-2-methylpropyl)-1-methyl-2-oxindolin-3-yl)methyl acetate (3s)

1-((1,3-dimethyl-2-oxindolin-3-yl)methyl)cyclohexanecarbonitrile (3u)

1-((1,3-dimethyl-2-oxindolin-3-yl)methyl)cyclohexanecarbonitrile (3u)

1-((1,3,5-trimethyl-2-oxindolin-3-yl)methyl)cyclohexanecarbonitrile (3v)

1-((1,3,5-trimethyl-2-oxindolin-3-yl)methyl)cyclohexanecarbonitrile (3v)

1-((5-fluoro-1,3-dimethyl-2-oxindolin-3-yl)methyl)cyclohexanecarbonitrile (3w),

1-((5-fluoro-1,3-dimethyl-2-oxindolin-3-yl)methyl)cyclohexanecarbonitrile (3w),

ethyl 3-((1-cyanocyclohexyl)methyl)-1,3-dimethyl-2-oxindoline-5-carboxylate (3s)

ethyl 3-((1-cyanocyclohexyl)methyl)-1,3-dimethyl-2-oxindoline-5-carboxylate (3s)

Figure S3 ORTEP drawing for 3-(1,3-dimethyl-2-oxoindolin-3-yl)-2,2-dimethylpropanenitrile (**3a**)