Supporting Information

The Radical Acylarylation of N-Arylacrylamides with Aliphatic Aldehydes using the Photolysis of Hypervalent Iodine(III) Reagents

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General Information

$^1$H NMR spectra were measured on JEOL JNM-ECA500 (500 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in CDCl$_3$, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet-doublet, m = multiplet, app = apparent), coupling constants (Hz), and assignment. $^{13}$C NMR spectra were measured on JEOL JNM-ECA500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. Infrared (IR) spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer. High-resolution mass spectra (HRMS) were performed on Brucker microTOF and Thermo Exactive plus. The products were purified by flash column chromatography (silica gel 60, Merck, 230-400 mesh). Light irradiation was performed with an OptoCode LED lamp (5 μW/cm$^2$, $\lambda$ = 365 nm).

$N$-Arylacrylamides 1 were prepared according to the literature procedure[1]. Commercially available reagents were purchased from Wako, Aldrich, TCI and Alfa-aesar chemicals. Aldehydes were used after the distillation. Dichloromethane (CH$_2$Cl$_2$) was purchased from Wako as “Super Dehydrated”.
Optimization Conditions (Table S1)*

<table>
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<th>Entry</th>
<th>1a</th>
<th>Solvent (M)</th>
<th>Time (h)</th>
<th>3a (%)</th>
<th>3a (%)</th>
<th>3a (%)</th>
<th>4a (%)</th>
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<td>nd</td>
<td>12</td>
<td>31 (R = CH3)</td>
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(a) Unless otherwise specified, reactions were conducted in a solvent in the presence of 1a (0.2 mmol), glycidoxypropionaldehydes (0.8 mmol), and 2 (0.4 mmol) under irradiation with UV light (λ = 365 nm). (b) The yield was determined by °H NMR spectroscopy using nitromethane as the internal standard. (c) Isolated yield. (d) The reaction was conducted on 1 mmol scale.

General Procedure for Acylation / Cyclization of N-Arylacrylamide 1 (Scheme 2)

To a mixture of N-arylacrylamide 1 (0.2 mmol), (diacetoxyiodo)benzene (128.8 mg, 0.4 mmol) in CH2Cl2 (0.2 mL) was added an aldehyde (0.8 mmol) under nitrogen atmosphere at room temperature. The reaction mixture was stirred for 43 h at room temperature under UV light (365 nm). The mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to afford the following product.

3-(2-Cyclohexyl-2-oxoethyl)-1,3-dimethylindolin-2-one (3a) (liquid, 31.0 mg, 54%) °H NMR (500 MHz, CDCl3) δ 7.24 (app t, J = 7.8 Hz, 1H), 7.10 (d, J = 7.1 Hz, 1H), 6.98 (app t, J = 7.4 Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 3.27 (s, 3H), 3.15 (d, J = 17.9 Hz, 1H), 3.08 (d, J = 17.9 Hz, 1H), 2.20-2.15 (m, 1H), 1.71-1.69 (m, 4H), 1.59 (t, J = 12.8 Hz, 1H), 1.32 (s, 3H), 1.25-1.15 (m, 3H), 1.13-1.05 (m, 2H); 13C NMR (125 MHz, CDCl3) δ 210.1, 180.7, 144.0, 133.9, 127.9, 122.2, 121.7, 108.3, 50.6, 48.0, 45.2, 28.4, 28.1, 26.6, 25.9, 25.7, 25.6, 24.7; HRMS calculated for C18H23O2N: m/z 286.1802 ([M + H]+), found: m/z 286.1800 ([M + H]+); IR (neat) 2928, 1708, 1614, 1494, 1378 cm⁻1.
1-Benzyl-3-(2-cyclohexyl-2-oxoethyl)-3-methylindolin-2-one (3b)

(liquid, 40.7 mg, 56%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.38 (d, \(J = 7.4\) Hz, 2H), 7.32 (t, \(J = 7.5\) Hz, 2H), 7.25 (t, \(J = 7.2\) Hz, 1H), 7.12-7.09 (m, 2H), 6.95 (t, \(J = 7.5\) Hz, 1H), 6.69 (d, \(J = 7.7\) Hz, 1H), 5.09 (d, \(J = 15.9\) Hz, 1H), 4.88 (d, \(J = 15.6\) Hz, 1H), 3.21 (d, \(J = 17.9\) Hz, 1H), 3.15 (d, \(J = 17.9\) Hz, 1H), 2.21 (m, 1H), 1.75-1.70 (m, 4H), 1.62 (d, \(J = 12.8\) Hz, 1H), 1.39 (s, 3H), 1.30-1.08 (m, 5H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 209.9, 180.7, 143.0, 136.4, 133.9, 128.8, 127.8, 127.5, 127.4, 122.3, 121.7, 109.4, 50.6, 47.7, 45.3, 44.1, 28.4, 28.2, 25.9, 25.8, 25.6, 25.3; HRMS calculated for C\(_{24}\)H\(_{23}\)O\(_2\)Na: \(m/z\) 384.1934 ([M + Na\(^{\ast}\)], found: \(m/z\) 384.1942 ([M + Na\(^{\ast}\)]); IR (neat) 2930, 1707, 1614, 1489, 907 cm\(^{-1}\).

3-(2-Cyclohexyl-2-oxoethyl)-1-isopropyl-3-methylindolin-2-one (3c)

(liquid, 33.8 mg, 54%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.19 (app t, \(J = 7.8\) Hz, 1H), 7.09 (d, \(J = 7.4\) Hz, 1H), 7.02 (d, \(J = 7.9\) Hz, 1H), 6.95 (t, \(J = 7.4\) Hz, 1H), 4.71-4.62 (m, 1H), 3.12 (d, \(J = 17.9\) Hz, 1H), 3.06 (d, \(J = 17.9\) Hz, 1H), 2.18-2.14 (m, 1H), 1.70 (m, 4H), 1.60 (d, \(J = 11.9\) Hz, 1H), 1.54 (d, \(J = 7.1\) Hz, 3H), 1.51 (d, \(J = 7.1\) Hz, 3H), 1.30 (s, 3H), 1.25-1.06 (m, 5H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 209.8, 180.3, 142.6, 134.4, 127.6, 121.9, 121.6, 110.1, 50.7, 48.0, 45.0, 43.8, 28.4, 28.1, 25.9, 25.8, 25.6, 25.1, 19.6, 19.2; HRMS calculated for C\(_{20}\)H\(_{17}\)O\(_2\)Na: \(m/z\) 336.1934 ([M + Na\(^{\ast}\)], found: \(m/z\) 336.1940 ([M + Na\(^{\ast}\)]); IR (neat) 2928, 1703, 1610, 1355, 753, 737 cm\(^{-1}\).

3-(2-Cyclohexyl-2-oxoethyl)-5-fluoro-1,3-dimethylindolin-2-one (3d)

(liquid, 23.8 mg, 39%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.95-6.91 (m, 1H), 6.86 (dd, \(J = 7.9\), 2.6 Hz, 1H), 6.76 (dd, \(J = 8.5\), 4.0 Hz, 1H), 3.25 (s, 3H), 3.11 (s, 2H), 2.22-2.17 (m, 1H), 1.72 (m, 4H), 1.63-1.60 (m, 1H), 1.31 (s, 3H), 1.25-1.07 (m, 5H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 210.0, 180.3, 159.3 (d, \(J_{C-F} = 240\) Hz), 139.9, 135.6 (d, \(J_{C-F} = 7.5\) Hz), 113.9 (d, \(J_{C-F} = 23.8\) Hz), 110.3 (d, \(J_{C-F} = 23.8\) Hz), 108.6 (d, \(J_{C-F} = 7.5\) Hz), 50.5, 47.9, 45.6, 28.4, 28.2, 26.7, 25.8, 25.7, 25.6, 24.6; HRMS calculated for C\(_{18}\)H\(_{22}\)O\(_2\)NFNa: \(m/z\) 326.1527 ([M + Na\(^{\ast}\)], found: \(m/z\) 326.1530 ([M + Na\(^{\ast}\)]); IR (neat) 2931, 1707, 1495, 907, 730 cm\(^{-1}\).

3-(2-Cyclohexyl-2-oxoethyl)-5-iodo-1,3-dimethylindolin-2-one (3e)

(liquid, 39.6 mg, 48%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.55 (dd, \(J = 8.2\), 1.7 Hz, 1H), 7.36 (d, \(J = 1.7\) Hz, 1H), 6.64 (d, \(J = 8.2\) Hz, 1H), 3.23 (s, 3H), 3.10 (app d, \(J = 1.7\) Hz, 2H), 2.22-2.17 (m, 1H), 1.78-1.71 (m, 4H), 1.62 (d, \(J = 13.0\) Hz, 1H), 1.30 (s, 3H), 1.27-1.08 (m, 5H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 210.0,
179.9, 143.8, 136.7, 136.5, 130.5, 110.4, 84.7, 50.5, 48.0, 45.2, 28.3, 28.3, 26.6, 25.9, 25.7, 25.6, 24.7; HRMS calculated for C_{18}H_{22}O_{2}N_{1}Na: m/z 434.0587 ([M + Na]^+) found: m/z 434.0588 ([M + Na]^+); IR (neat) 2929, 1708, 1604, 1489, 907, 730 cm\(^{-1}\).

3-(2-Cyclohexyl-2-oxoethyl)-5-methoxy-1,3-dimethylindolin-2-one (3f) (liquid, 30.0 mg, 48%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.75-6.73 (m, 3H), 3.77 (s, 3H), 3.24 (s, 3H), 3.10 (app d, \(J = 2.6\) Hz, 2H), 2.21-2.16 (m, 1H), 1.73-1.69 (m, 4H), 1.61 (d, \(J = 11.6\) Hz, 1H), 1.31 (s, 3H), 1.25-1.06 (m, 5H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 210.1, 180.3, 155.9, 137.6, 135.4, 111.5, 109.9, 108.4, 55.9, 50.6, 47.9, 45.6, 28.4, 28.2, 26.6, 25.9, 25.7, 25.6, 24.8; HRMS calculated for C_{19}H_{25}O_{3}N_{1}Na: m/z 338.1727 ([M + Na]^+), found: m/z 338.1735 ([M + Na]^+); IR (neat) 2929, 1708, 1614, 1489, 908 cm\(^{-1}\).

3-(2-Cyclohexyl-2-oxoethyl)-6-methoxy-1,3-dimethylindolin-2-one (3g) (major) (liquid, 19.9 mg, 32%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.19 (app t, \(J = 8.2\) Hz, 1H), 6.53 (app t, \(J = 7.5\) Hz, 2H), 3.81 (s, 3H), 3.58 (d, \(J = 17.6\) Hz, 1H), 3.25 (s, 3H), 2.99 (d, \(J = 17.6\) Hz, 1H), 2.18 (m, 1H), 1.69-1.67 (m, 4H), 1.62-1.58 (m, 1H), 1.35 (s, 3H), 1.27-1.02 (m, 5H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 210.9, 181.1, 155.4, 145.3, 129.0, 119.1, 105.4, 101.9, 55.3, 50.6, 46.7, 45.4, 28.4, 28.0, 26.8, 25.9, 25.9, 25.6, 22.6; HRMS calculated for C_{19}H_{25}O_{3}N_{1}Na: m/z 338.1727 ([M + Na]^+), found: m/z 338.1734 ([M + Na]^+); IR (neat) 2929, 1709, 1608, 1475, 1260, 1070 cm\(^{-1}\).

3-(2-cyclohexyl-2-oxoethyl)-6-methoxy-1,3-dimethylindolin-2-one (3g) (minor) (liquid, 10.2 mg, 16%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.00 (d, \(J = 8.2\) Hz, 1H), 6.48 (dd, \(J = 7.9, 2.3\) Hz, 1H), 6.44 (d, \(J = 2.3\) Hz, 1H), 3.81 (s, 3H), 3.24 (s, 3H), 3.11 (d, \(J = 17.6\) Hz, 1H), 3.03 (d, \(J = 17.9\) Hz, 1H), 2.17-2.19 (m, 1H), 1.70 (app d, \(J = 9.6\) Hz, 4H), 1.61 (app d, \(J = 11.9\) Hz, 1H), 1.30 (s, 3H), 1.08-1.28 (m, 5H).

1-(2-Cyclohexyl-2-oxoethyl)-1-methyl-5,6-dihydro-4H-pyrrolo[3,2-1ij]quinolin-2(1H)-one (3h) (liquid, 33.8 mg, 54%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.98 (d, \(J = 7.4\) Hz, 1H), 6.95 (d, \(J = 7.4\) Hz, 1H), 6.87 (t, \(J = 7.5\) Hz, 1H), 3.78-3.75 (m, 2H), 3.13 (d, \(J = 17.9\) Hz, 1H), 3.04 (d, \(J = 17.9\) Hz, 1H), 2.84-2.74 (m, 2H), 2.20-2.15 (m, 1H), 2.12-1.97 (m, 2H), 1.70 (m, 4H), 1.62-1.59 (m, 1H), 1.34 (s, 3H), 1.28-1.06 (m, 5H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 210.2, 179.5, 139.7, 132.4, 126.7, 121.7, 120.2, 119.8, 50.7, 47.8, 46.5, 39.0, 28.4, 28.1, 25.9, 25.8, 25.6, 24.8, 24.3, 21.3; HRMS calculated for C_{20}H_{25}O_{3}N_{1}Na: m/z 334.1778
([M + Na]+), found: m/z 334.1773 ([M + Na]+); IR (neat) 2928, 1703, 1627, 1355, 907, 728 cm⁻¹.

3-(2-Cyclohexyl-2-oxoethyl)-1-methyl-3-(trifluoromethyl)indolin-2-one (3i)
(solid, m.p.: 89–91 °C, 54.5 mg, 80%) ¹H NMR (500 MHz, CDCl₃) 7.36 (dd, J = 8.1, 7.5 Hz, 1H), 7.19 (d, J = 7.4 Hz, 1H), 7.04 (app t, J = 7.5 Hz, 1H), 6.90 (d, J = 7.9 Hz, 1H), 3.53 (d, J = 17.9 Hz, 1H), 3.45 (d, J = 18.1 Hz, 1H), 3.30 (s, 3H), 2.25 (m, 1H), 1.76-1.70 (m, 4H), 1.62 (d, J = 11.3 Hz, 1H), 1.28-1.17 (m, 3H), 1.14-1.05 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 207.7, 171.8, 145.7, 130.1, 124.6 (q, J_{CF} = 284 Hz), 124.2, 123.5, 122.7, 108.8, 53.3 (q, J_{CF} = 26.4 Hz), 50.5, 41.5, 28.3, 28.1, 27.0, 25.7, 25.6, 25.4; HRMS calculated for C₁₈H₂₀O₂NF₃Na: m/z 362.1338 ([M + Na]+), found: m/z 362.1356 ([M + Na]+); IR (neat) 2932, 1728, 1614, 1262, 1168 cm⁻¹.

3-Benzyl-3-(2-cyclohexyl-2-oxoethyl)-1-methylindolin-2-one (3j)
(liquid, 40.9 mg, 57%) ¹H NMR (500 MHz, CDCl₃) δ 7.15 (app t, J = 7.7 Hz, 1H), 7.10-7.03 (m, 3H), 7.00 (d, J = 7.1 Hz, 1H), 6.95 (app t, J = 7.4 Hz, 1H), 6.79-6.78 (m, 2H), 6.59 (d, J = 7.9 Hz, 1H), 3.23 (app d, J = 3.4 Hz, 2H), 3.02 (d, J = 13.0 Hz, 1H), 3.00 (s, 3H), 2.96 (d, J = 13.0 Hz, 1H), 2.23-2.18 (m, 1H), 1.73-1.68 (m, 4H), 1.61 (d, J = 12.5 Hz, 1H), 1.27-1.04 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 209.9, 179.2, 144.4, 135.1, 131.0, 130.2, 128.0, 127.5, 126.7, 122.6, 121.7, 107.9, 50.9, 50.7, 46.8, 44.3, 28.4, 28.1, 26.1, 25.9, 25.7, 25.6; HRMS calculated for C₂₄H₂₇O₃Na: m/z 384.1934 ([M + Na]+), found: m/z 384.1938 ([M + Na]+); IR (neat) 2932, 1705, 1614, 907, 730 cm⁻¹.

3-(3-Ethyl-2-oxoheptyl)-1,3-dimethylindolin-2-one (3k)
The title compound was obtained as a diastereomeric mixture.
(liquid, 30.5 mg, 51%) ¹H NMR (500 MHz, CDCl₃) δ 7.24 (app t, J = 7.7 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 6.98 (app t, J = 7.4 Hz, 1H), 6.85 (d, J = 7.7 Hz, 1H), 3.28 (s, 3H), 3.13 (d, J = 18.1 Hz, 1H), 3.06 (dd, J = 18.0, 3.0 Hz, 1H), 2.23 (m, 1H), 1.51-1.16 (m, 9H), 1.10-0.94 (m, 2H), 0.84-0.79 (m, 3H), 0.74 (t, J = 7.5 Hz, 1.5H), 0.66 (t, J = 7.5 Hz, 1.5H); ¹³C NMR (125 MHz, CDCl₃) δ 211.0, 210.9, 180.6, 144.1, 133.7, 127.9, 122.1, 121.8, 108.2, 53.6, 53.5, 50.0, 49.6, 45.2, 31.1, 30.8, 29.6, 29.4, 26.6, 24.7, 24.6, 22.9, 14.0, 11.9, 11.6 (diastereomeric mixture); HRMS calculated for C₁₉H₂₄O₂Na: m/z 324.1934 ([M + Na]+), found: m/z 324.1939 ([M + Na]+); IR (neat) 2928, 1707, 1614, 1469, 1348, 752 cm⁻¹.
3-(3-Ethyl-2-oxopentyl)-1,3-dimethylindolin-2-one (3l)

(liquid, 19.3 mg, 35%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.23 (app t, \(J = 7.7\) Hz, 1H), 7.10 (d, \(J = 7.4\) Hz, 1H), 6.98 (app t, \(J = 7.5\) Hz, 1H), 6.85 (d, \(J = 7.9\) Hz, 1H), 3.27 (s, 3H), 3.13 (d, \(J = 18.1\) Hz, 1H), 3.07 (d, \(J = 18.1\) Hz, 1H), 2.20-2.15 (m, 1H), 1.53-1.41 (m, 2H), 1.32 (s, 3H), 1.38-1.28 (m, 2H), 0.74 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 210.9, 180.6, 144.0, 133.8, 127.9, 122.1, 121.7, 108.3, 55.0, 49.9, 45.2, 26.6, 24.7, 24.3, 24.2, 11.9, 11.6; HRMS calculated for C\(_{17}\)H\(_{23}\)O\(_2\)NNa: m/z 296.1621 ([M + Na\(^+\)], found: m/z 296.1624 ([M + Na\(^+\)]) ; IR (neat) 2963, 1708, 1614, 752 cm\(^{-1}\).

1,3-Dimethyl-3-(4-methyl-2-oxopentyl)indolin-2-one (3m)

(liquid, 24.8 mg, 48%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.24 (t, \(J = 8.1\) Hz, 1H), 7.12 (d, \(J = 7.4\) Hz, 1H), 6.99 (t, \(J = 7.5\) Hz, 1H), 6.86 (d, \(J = 7.7\) Hz, 1H), 3.26 (s, 3H), 3.05 (s, 2H), 2.12 (d, \(J = 2.6\) Hz, 1H), 2.11 (d, \(J = 1.7\) Hz, 1H), 2.01-1.93 (m, 1H), 1.32 (s, 3H), 0.77 (d, \(J = 1.7\) Hz, 3H), 0.76 (d, \(J = 1.7\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 206.9, 180.5, 143.9, 133.7, 128.0, 122.3, 121.9, 108.3, 51.9, 50.4, 45.3, 26.5, 24.7, 24.6, 22.6, 22.5; Other spectral data of the title compound were consistent with previously reported data.\(^{[2]}\)

1,3-Dimethyl-3-(2-oxo-4-phenylbutyl)indolin-2-one (3n)

(liquid, 41.2 mg, 67%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.29-7.15 (m, 4H), 7.09 (d, \(J = 7.4\) Hz, 1H), 7.02 (m, 3H), 6.87 (d, \(J = 7.7\) Hz, 1H), 3.27 (s, 3H), 3.09 (d, \(J = 17.9\) Hz, 1H), 3.03 (d, \(J = 17.6\) Hz, 1H), 2.71 (t, \(J = 7.7\) Hz, 2H), 2.64-2.51 (m, 2H), 1.33 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 206.1, 180.2, 143.8, 140.9, 133.5, 128.6, 128.3, 128.1, 126.2, 122.4, 121.9, 108.3, 50.0, 45.3, 44.5, 29.5, 26.5, 24.6; HRMS calculated for C\(_{20}\)H\(_{21}\)O\(_2\)NNa: m/z 330.1465 ([M + Na\(^+\)], found: m/z 330.1471 ([M + Na\(^+\)]) ; IR (neat) 2927, 1708, 1614, 1495, 908, 704 cm\(^{-1}\).

1,3-Dimethyl-3-(2-oxopentyl)indolin-2-one (3o)

(liquid, 22.8 mg, 46%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.25 (app t, \(J = 8.0\) Hz, 1H), 7.13 (d, \(J = 7.4\) Hz, 1H), 7.00 (app t, \(J = 7.5\) Hz, 1H), 6.86 (d, \(J = 7.7\) Hz, 1H), 3.26 (s, 3H), 3.06 (s, 2H), 2.29-2.16 (m, 2H), 1.43 (m, 2H), 1.33 (s, 3H), 0.77 (t, \(J = 7.5\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 207.1, 180.5, 143.9, 133.7, 128.0, 122.3, 121.9, 108.3, 49.8, 45.3, 44.8, 26.5, 24.6, 17.0, 13.7; Other spectral data of the title compound were consistent with previously reported data.\(^{[2]}\)
1,3-Dimethyl-3-(2-oxo-2-phenylethyl)indolin-2-one (3p)

(liquid, 22.2 mg, 40%) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.83 (d, \(J = 7.9\) Hz, 2H), 7.51 (t, \(J = 7.4\) Hz, 1H), 7.39 (t, \(J = 7.8\) Hz, 2H), 7.25 (t, \(J = 7.7\) Hz, 1H), 7.14 (d, \(J = 7.4\) Hz, 1H), 6.98 (t, \(J = 7.5\) Hz, 1H), 6.90 (d, \(J = 7.9\) Hz, 1H), 3.72 (d, \(J = 17.9\) Hz, 1H), 3.65 (d, \(J = 18.1\) Hz, 1H), 3.31 (s, 3H), 1.44 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 196.2, 180.7, 144.0, 136.5, 133.9, 133.3, 128.6, 128.1, 128.0, 122.3, 121.9, 108.3, 46.2, 45.4, 26.6, 25.1; Other spectral data of the title compound were consistent with previously reported data.\(^2\)

2-Cyclohexyl-3a,8-dimethyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (5)

To a stirred solution of 3a (66.3 mg, 0.23 mmol) in THF (1.7 mL) was added LiAlH\(_4\) (17.5 mg, 0.46 mmol) at 0 °C under argon atmosphere in one portion. After stirring for 1.2 h at the same temperature, the reaction was quenched with H\(_2\)O, and the resulting mixture was stirred at room temperature until the generation of gas ceased. The reaction mixture was filtered through a plug of Celite with ethyl acetate. The filtrate was extracted with ethyl acetate, the combined organic layer was dried over Na\(_2\)SO\(_4\), and concentrated. The residue was purified by flash column chromatography on silica gel (eluting with ethyl acetate/hexane = 1/100) to afford the title compound as a diastereomeric mixture (liquid, 36.5 mg, 58%, dr = 12/1). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.10 (t, \(J = 7.7\) Hz, 1H), 7.02 (d, \(J = 7.4\) Hz, 1H), 6.68 (t, \(J = 7.4\) Hz, 1H), 6.39 (d, \(J = 7.9\) Hz, 1H), 4.95 (s, 1H), 3.73 (m, 1H), 2.93 (s, 3H), 2.07 (dd, \(J = 12.5, 6.5\) Hz, 1H), 1.94-1.91 (m, 1H), 1.88 (dd, \(J = 12.5, 8.0\) Hz, 1H), 1.68-1.58 (m, 3H), 1.48-1.45 (m, 1H), 1.37 (s, 3H), 1.18-1.03 (m, 4H), 0.93-0.78 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 149.1, 136.4, 128.0, 122.3, 117.6, 106.6, 106.1, 83.3, 52.0, 44.2, 42.8, 31.9, 30.3, 29.3, 26.6, 26.0, 25.9, 24.1; HRMS calculated for C\(_{18}\)H\(_{25}\)ONa: \(m/z\) 294.1828 ([M + Na\(^+\)], found: \(m/z\) 294.1830 ([M + Na\(^+\)]); IR (neat) 2925, 1608, 1491, 1019, 906, 729 cm\(^{-1}\).
To a stirred solution of 3a (84.0 mg, 0.29 mmol) in MeOH/CHCl₃ (0.29 mL/0.29 mL) was added NaBH₄ (32.9 mg, 0.87 mmol) at -10 °C under argon atmosphere in portionwise. The reaction mixture was then stirred at room temperature for 2.5 h. The residue was quenched with H₂O and extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by flash column chromatography on silica gel (eluting with ethyl acetate/hexane = 1/1) to afford the title compound (liquid, 72.3 mg, 87%). ¹H NMR (500 MHz, CDCl₃) δ 7.27 (t, J = 7.7 Hz, 1H), 7.19 (d, J = 6.8 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.86 (d, J = 7.7 Hz, 1H), 3.64 (q, J = 4.8 Hz, 1H), 3.34 (s, 1H), 3.22 (s, 3H), 1.98 (d, J = 14.7 Hz, 1H), 1.76-1.62 (m, 7H), 1.42 (s, 1H), 1.32-0.98 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 182.1, 142.6, 135.4, 128.1, 123.1, 122.6, 108.5, 72.5, 47.4, 44.5, 42.0, 29.2, 27.8, 26.7, 26.5 (two peaks overlapped), 26.4, 23.0; HRMS calculated for C₁₈H₂₅O₂NNa: m/z 310.1778 ([M + Na]⁺), found: m/z 310.1784 ([M + Na]⁺); IR (neat) 3399, 2925, 1684, 1613, 1380, 907, 730 cm⁻¹.

1-Cyclohexyl-2-(1,3-dimethyl-2-oxoindolin-3-yl)ethyl Methanesulfonate (7)

To a stirred solution of 6 (70.4 mg, 0.24 mmol) in CH₂Cl₂ (1.5 mL) was added triethylamine (0.13 mL, 0.96 mmol) and MsCl (74.3 μL, 0.96 mmol) at 0 °C under argon atmosphere in dropwise. After stirring for 30 min at the same temperature, the reaction was quenched with H₂O and extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by flash column chromatography on silica gel (eluting with ethyl acetate/hexane = 1/2) to afford the title compound (liquid, 59.4 mg, 68%). ¹H NMR (500 MHz, CDCl₃) δ 7.28-
7.23 (m, 2H), 7.08 (t, \( J = 7.5 \) Hz, 1H), 6.87 (d, \( J = 7.9 \) Hz, 1H), 4.38-4.35 (m, 1H), 3.23 (s, 3H), 2.35 (s, 3H), 2.29 (dd, \( J = 15.0 \) Hz, 1H), 2.20 (dd, \( J = 15.5 \), 8.0 Hz, 1H), 1.76-1.50 (m, 6H), 1.37 (s, 3H), 1.27-0.96 (m, 5H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 179.6, 143.4, 133.4, 128.1, 123.3, 122.7, 108.6, 84.0, 46.9, 42.5, 38.1, 37.6, 27.8, 27.3, 26.44, 26.41, 26.2 (three peaks overlapped); HRMS calculated for C\(_{19}\)H\(_{27}\)O\(_4\)NNa: \( m/z \) 388.1553 ([M + Na]\(^+\)), found: \( m/z \) 388.1560 ([M + Na]\(^+\)); IR (neat) 2929, 1708, 1612, 1330, 1172, 905, 731 cm\(^{-1}\).

3-(2-Azido-2-cyclohexylethyl)-1,3-dimethylindolin-2-one (8)

To a stirred solution of 7 (77.4 mg, 0.21 mmol) in DMSO (0.53 mL) was added NaN\(_3\) (245.7 mg, 3.78 mmol) at room temperature under argon atmosphere. The reaction mixture was stirred at 70 °C for 12 h and then cooled to room temperature. The reaction was quenched with H\(_2\)O and extracted with ethyl acetate/hexane (1/3). The combined organic layer was washed with brine, dried over Na\(_2\)SO\(_4\), and concentrated. The residue was purified by flash column chromatography on silica gel (eluting with ethyl acetate/hexane = 1/5) to afford the title compound (liquid, 31.1 mg, 47%). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.31 (t, \( J = 7.7 \) Hz, 1H), 7.13 (d, \( J = 7.4 \) Hz, 1H), 7.08 (t, \( J = 7.4 \) Hz, 1H), 6.90 (d, \( J = 7.7 \) Hz, 1H), 3.27 (s, 3H), 2.62 (m, 1H), 2.17 (dd, \( J = 14.0 \), 11.5 Hz, 1H), 1.93 (dd, \( J = 14.5 \), 2.6 Hz, 1H), 1.72-1.62 (m, 5H), 1.37 (s, 3H), 1.35-0.91 (m, 6H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 180.5, 143.7, 132.8, 128.4, 122.7, 122.5, 108.6, 66.0, 46.9, 43.3, 40.2, 29.8, 28.8, 26.6, 26.3, 26.2, 26.1, 25.3; HRMS calculated for C\(_{18}\)H\(_{24}\)ON\(_4\)Na: \( m/z \) 335.1842 ([M + Na]\(^+\)), found: \( m/z \) 335.1851 ([M + Na]\(^+\)); IR (neat) 2927, 2097, 1714, 1613, 1471, 753, 731 cm\(^{-1}\).
To a stirred solution of 8 (51.0 mg, 0.16 mmol) in toluene (2.8 mL) was added sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al®) (0.72 mL, 65 wt% in toluene; 2.4 mmol) at 0 °C under argon atmosphere. The reaction mixture was allowed to warm to room temperature. After stirring for 1.5 h, the reaction mixture was heated to 100 °C for 14 h. After cooling to room temperature, the mixture was quenched with saturated aqueous sodium potassium tartrate, diluted with ethyl acetate, and stirred vigorously for 1 h. The mixture was then diluted with water and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by flash column chromatography on silica gel (eluting with ethyl acetate/hexane = 1/2) to afford the title compound (liquid, 32.0 mg, 74%).

**References**

[1] For N-arylacrylamide synthesis,

$^1$H NMR spectrum of 3a

$^{13}$C NMR spectrum of 3a
$^{1}$H NMR spectrum of 3b

$^{13}$C NMR spectrum of 3b
$^1$H NMR spectrum of 3c

$^{13}$C NMR of spectrum of 3c
$^{1}$H NMR of spectrum of 3d

$^{13}$C NMR of spectrum of 3d
$^{1}$H NMR of spectrum of 3e

$^{13}$C NMR of spectrum of 3e
$^1$H NMR of spectrum of 3f

$^{13}$C NMR of spectrum of 3f
$^1$H NMR of spectrum of 3g (major)

$^{13}$C NMR of spectrum of 3g
$^1$H NMR of spectrum of 3g (minor)

$^1$H NMR of spectrum of 3g (crude)
$^{1}$H NMR of spectrum of 3h

$^{13}$C NMR of spectrum of 3h
$^1$H NMR of spectrum of 3i

$^{13}$C NMR of spectrum of 3i
$^1$H NMR of spectrum of 3j

$^{13}$C NMR of spectrum of 3j
$^1$H NMR of spectrum of 3k

![H NMR spectrum of 3k](image)

$^{13}$C NMR of spectrum of 3k

![C NMR spectrum of 3k](image)
$^1$H NMR of spectrum of 3m

$^{13}$C NMR of spectrum of 3m
$^{1}$H NMR of spectrum of 3n

$^{13}$C NMR of spectrum of 3n
$^1$H NMR of spectrum of 3o

![1H NMR spectrum](image)

$^{13}$C NMR of spectrum of 3o

![13C NMR spectrum](image)
$^1$H NMR of spectrum of 3p

$^{13}$C NMR of spectrum of 3p
$^1$H NMR of spectrum of 5

$^{13}$C NMR of spectrum of 5
$^1$H NMR of spectrum of 6

$^{13}$C NMR of spectrum of 6
$^1$H NMR of spectrum of 7

$^{13}$C NMR of spectrum of 7
$^1$H NMR of spectrum of 8

$^{13}$C NMR of spectrum of 8
$^1$H NMR of spectrum of 9

$^{13}$C NMR of spectrum of 9
$^1$H-NMR spectrum of the reaction crude (Table 1, entry 1). (Ref: J. Q. Chen, Y. L. Wei, G. Q. Xu, Y. M. Liang and P. F. Xu *Chem. Commun.*, 2016, 52, 6455.)
$^1$H-NMR spectrum of the reaction crude (Table 1, entry 6). (Ref: J. Y. Wang, Y. M. Su, F. Yin, Y. Bao, X. Zhang, Y. M. Xu and X. S. Wang Chem. Commun., 2014, 50, 4108.)