Supporting Information

Synthesis of 3-(Diarylmethylene)oxindoles via a Palladium-Catalyzed One-pot Reaction; Sonogashira/Heck/Suzuki–Miyaura Combined Reaction

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General Remarks

All reactions were performed under an argon atmosphere with dry solvents, unless otherwise stated. Dry diethyl ether (Et₂O), tetrahydrofuran (THF), acetonitrile (MeCN), toluene, and methylene chloride (CH₂Cl₂) were obtained from Ultimate Solvent Purification System (JC Meyer Solvent System). Other dry solvents were purchased as anhydrous grade. All commercially available reagents were purchased and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on silica gel plates (Merck TLC Silica Gel 60 F₂₅₄) using UV light, PMA (an ethanolic solution of phosphomolybdic acid) or ANIS (an ethanolic solution of para-anisaldehyde) as visualizing agent. Purification of products was conducted by column chromatography through silica gel 60 (0.060–0.200 mm). Melting points of all solid compounds were determined by Buchi M-565. NMR spectra were obtained on Bruker AVANCE III 500 MHz using residual undeuterated solvent or TMS (tetramethylsilane) as an internal reference. IR spectra were recorded on a Jasco P-2000 FT-IR spectrometer. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6530 Q-TOF mass spectrometer using ESI (electrospray ionization) or a JEOL JMS-700 using EI (electron impact).

General procedures for the synthesis of substrates 4 and 6a-e

\[ \text{R}^+ \text{Br} \text{NH}_2 \xrightarrow{\text{DCC, CH}_2\text{Cl}_2, \text{rt, 12 h}} \text{R}^+ \text{Br} \text{NH} \xrightarrow{\text{NaH, MeI, THF, rt, 6 h}} \text{R}^+ \text{NH} \]

Step 1: Amide formation

To a stirred solution of commercially available or known bromoaniline compound (1.0 mmol) in CH₂Cl₂ (5 mL) and the corresponding propiolic acid (1.3 mmol, 1.3 equiv) was added dicyclohexyl carbodimide (DCC, 1.3 mmol, 1.3 equiv) at 0 °C. Then, the temperature was gradually raised to 25 °C over 30 min. The mixture was stirred at the same temperature for 12 h, and diluted with EtOAc (50 mL) and sat. aq. NH₄Cl (30 mL). The organic layer was separated,
dried (Na₂SO₄), filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography (silica gel, hexanes:EtOAc 8:1 or CH₂Cl₂ only) to afford propiolamides 4-s, 6a-s–6e-s.

**Step 2: N-Methylation**

To a stirred suspension of NaH (60% in mineral oil, 1.0 mmol, 1.0 equiv) in THF (5.0 mL) was added a solution of the corresponding propiolamide (1.0 mmol) in THF (5 mL) at 0 °C. After 30 min stirring, MeI (1.3 mmol, 1.3 equiv) was added dropwise at the same temperature. Then, the temperature was gradually raised to 25 °C. The mixture was stirred for 6 h at 25 °C, and diluted with sat. aq. NH₄Cl (50 mL). The mixture was extracted with EtOAc (50 mL X 2). The combined organic layer was dried (Na₂SO₄), filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography (silica gel, hexanes:EtOAc 5:1 or 3:1) to yield N-methyl propiolamides 4, 6a-e.

**General procedures for palladium catalyzed one-pot reaction**

To a stirred solution of N-methylpropiolamide (6a-e) (0.5 mmol, 1.0 equiv) in DMF (5 mL) were added the corresponding aryl iodide (0.55 mmol, 1.1 equiv), CuI (0.025 mmol, 5 mol%), NaOAc (1.5 mmol, 3.0 equiv) and Pd(PPh₃)₄ (0.05 mmol, 10 mol%) at 25 °C. The reaction mixture was stirred at 60 °C for 1 h. Then, the corresponding aryl boronic acid (0.6 mmol, 1.2 equiv) was quickly added to the mixture. Reaction temperature was raised to 90 °C or 110 °C. After 24 h stirring at the indicated temperature, the mixture was cooled to 25 °C and diluted with EtOAc (200 mL). Organic layer was washed with H₂O (30 mL X 3) and brine (30 mL), then dried (Na₂SO₄), filtered and concentrated under reduced pressure. The crude residue was purified by column chromatography (silica gel, hexane:EtOAc) to yield 3-(diarylmethylene)oxindoles (5, 7a-g, 8a-d). In the case of using silver additives, it was added with aryl boronic acid at the second step.
**N-(2-bromophenyl)-3-phenylpropionamide (4-s):**

1. 86% Yield; white solid; mp = 121–122 °C; 
   \( R_f = 0.43 \) (silica gel, hexanes:EtOAc 8:1); IR (film) 3061, 1658, 1517, 1434, 1300, 751, 688 cm\(^{-1}\); 
2. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.37 \) (d, \( J = 8.0 \) Hz, 1H), 7.99 (brs, 1H), 7.62 (d, \( J = 7.5 \) Hz, 2H), 7.57 (d, \( J = 7.5 \) Hz, 1H), 7.46 (t, \( J = 7.5 \) Hz, 1H), 7.40 (t, \( J = 7.5 \) Hz, 2H), 7.35 (t, \( J = 8.0 \) Hz, 1H), 7.02 (t, \( J = 7.5 \) Hz, 1H) ppm; 
3. \(^13\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 151.0, 144.2, 135.4, 132.9, 132.7, 132.5, 130.6, 128.8, 128.7, 128.5, 125.9, 122.4, 119.9, 119.5, 115.9, 113.2, 109.5, 86.5, 83.4 \) ppm; HRMS (ESI-TOF): calcd for C\(_{15}\)H\(_{10}\)\(^{79}\)BrNO [M + H\(^+\)]: 300.0024, found 300.0031.

**N-(2-bromophenyl)-N-methyl-3-phenylpropionamide (4):**

1. 92% Yield; white solid; mp = 93.9 °C; 
   \( R_f = 0.24 \) (silica gel, hexanes:EtOAc 4:1); IR (film) 2217, 1644, 1583, 1477, 1442, 1361, 1312, 1131, 1027, 933, 759 cm\(^{-1}\); 
2. \(^1\)H NMR (500 MHz, CDCl\(_3\), 10:1 atropisomeric mixture, major peaks): \( \delta = 7.72 \) (dd, \( J = 8.0, 1.5 \) Hz, 1H), 7.43–7.41 (m, 2H), 7.33–7.29 (m, 2H), 7.22 (t, \( J = 7.5 \) Hz, 2H), 7.08 (dd, \( J = 8.3, 1.3 \) Hz, 1H), 3.32 (s, 3H) ppm; 
3. \(^13\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 154.6, 142.3, 133.9, 133.7, 132.7, 132.6, 130.8, 130.2, 130.1, 128.9, 128.7, 128.4, 124.1, 120.4, 90.6, 82.3, 39.8, 35.3 \) ppm; HRMS (ESI-TOF): calcd for C\(_{16}\)H\(_{12}\)\(^{79}\)BrNO [M + H\(^+\)]: 314.0181, found 314.0186.

**N-(2-bromophenyl)propionamide (6a-s):**

1. 75% Yield; off white solid; mp = 94.3 °C (lit. 96-98 °C); 
   \( R_f = 0.37 \) (silica gel, hexanes:EtOAc 4:1); IR (film) 3283, 2107, 1668, 1590 cm\(^{-1}\); 
   \(^1\)H
NMR (500 MHz, CDCl₃): δ = 8.30 (dd, J = 8.5, 1.0 Hz, 1H), 7.95 (brs, 1H), 7.56 (dd, J = 8.0, 1.5 Hz, 1H), 7.35–7.31 (m, 1H), 7.04–7.01 (m, 1H), 3.00 (s, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 149.6, 135.0, 132.5, 128.7, 126.2, 122.4, 113.2, 82.1, 74.8 ppm; HRMS (ESI-TOF): calcd for C₉H₇BrNO [M + H⁺]: 223.9711, found 223.9714.

\[
\begin{align*}
\text{N-(2-bromophenyl)-N-methylpropiolamide (6a),} & \text{ 3 89% Yield; off white solid; mp = 72.8 °C (lit.}^3 \text{ 88-89 °C); } R_f = 0.32 \text{ (silica gel, hexanes:EtoAc 4:1); IR (film) 3221, 2107, 1646, 1372, 763 cm}^{-1}; \text{H NMR (500 MHz, CDCl₃, 7:1 atropisomeric mixture, major peaks): } \delta = 7.68 \text{ (dd, } J = 8.0, 1.0 \text{ Hz, 1H), 7.41–7.21 (m, 3H), 3.25 (s, 3H), 2.73 (s, 1H) ppm; } \text{¹³C NMR (125 MHz, CDCl₃): } \delta = 153.3, 141.7, 133.9, 133.8, 130.5, 130.4, 129.9, 129.3, 128.9, 128.8, 123.8, 80.0, 78.9, 76.1, 39.0, 35.4 \text{ ppm; HRMS (ESI-TOF): calcd for C}_{10}H_{8}^{79}\text{BrNO [M + H⁺]: 237.9868, found 237.9872.}
\end{align*}
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\begin{align*}
\text{N-(2-bromo-5-chlorophenyl)-propiolamide (6b-s):} & \text{ 73% Yield; off white solid; mp = 136.6 °C; } R_f = 0.22 \text{ (silica gel, hexanes:EtoAc 8:1); IR (film) 3371, 3228, 3117, 2360, 2109, 1669, 1583, 1519 cm}^{-1}; \text{H NMR (500 MHz, CDCl₃): } \delta = 8.39 \text{ (d, } J = 2.0 \text{ Hz, 1H), 7.93 \text{ (brs, 1H), 7.47 \text{ (d, } J = 8.5 \text{ Hz, 1H), 7.02 \text{ (dd, } J = 8.5, 2.0 \text{ Hz, 1H), 3.04 \text{ (s, 1H) ppm; } \text{¹³C NMR (125 MHz, CDCl₃): } \delta = 149.5, 135.8, 134.6, 133.1, 126.1, 122.1, 110.7 \text{ ppm; HRMS (ESI-TOF): calcd for C}_{9}H_{8}^{79}\text{BrClNO [M + H⁺]: 257.9321, found 257.9325.}}
\end{align*}
\]

\[
\begin{align*}
\text{N-(2-bromo-5-chlorophenyl)-N-methylpropiolamide (6b):} & \text{ 83% Yield; yellow solid; mp = 95.6 °C; } R_f = 0.26 \text{ (silica gel, hexanes:EtoAc 8:1); IR (film) 3224, 3062, 2107, 1647, 1465, 1360}
\end{align*}
\]
cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$, 7:1 atropisomeric mixture): $\delta = 7.62$ (d, $J =$ 8.5 Hz, 1H, major), 7.59 (d, $J =$ 8.5 Hz, 1H, minor), 7.36 (d, $J =$ 2.5 Hz, 1H, major), 7.28 (dd, $J =$ 8.5, 2.5 Hz, 1H, major), 7.26 (d, $J =$ 2.5 Hz, 1H, minor), 7.22 (dd, $J =$ 8.5, 2.5 Hz, 1H, minor), 3.50 (s, 3H, minor), 3.27 (s, 1H, minor), 3.24 (s, 3H, major), 2.80 (s, 1H, major) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 153.0, 142.6, 141.3, 134.6, 134.5, 134.3, 134.2, 130.7, 130.6, 130.1, 129.7, 122.0, 120.4, 80.4, 79.3, 75.8, 38.9, 35.3 ppm; HRMS (ESI-TOF): calcd for C$_{10}$H$_7$BrClNO [M$^+$/H$^+$]: 271.9478, found 271.9483.

**N-(2-bromo-5-(trifluoromethyl)phenyl)propiolamide (6c-s):** 92% Yield; off white solid; mp = 140.7 °C; $R_f = 0.23$ (silica gel, hexanes:EtOAc 8:1); IR (film) 3232, 2362, 2113, 1633, 1327, 1119 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.64$ (s, 1H), 8.05 (brs, 1H), 7.69 (d, $J =$ 8.5 Hz, 1H), 7.28 (d, $J =$ 8.5 Hz, 1H), 3.06 (s, 1H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 149.7, 135.7, 133.1, 131.3, 124.6, 122.5, 119.0, 116.6, 75.6$ ppm; HRMS (ESI-TOF): calcd for C$_{10}$H$_5$BrF$_3$NO [M$^+$/H$^+$]: 291.9585, found 291.9591.

**N-(2-bromo-5-(trifluoromethyl)phenyl)-N-methylpropiolamide (6c):** 90% Yield: yellow oil; $R_f = 0.26$ (silica gel, hexanes:EtOAc 4:1); IR (film) 3228, 3069, 2109, 1651, 1333, 1130, 1079 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$, 4:1 atropisomeric mixture): $\delta = 7.84$ (d, $J =$ 8.5 Hz, 1H, major), 7.81 (d, $J =$ 8.5 Hz, 1H, minor), 7.62 (d, $J =$ 2.0 Hz, 1H, major), 7.55 (dd, $J =$ 8.0, 2.0 Hz, 1H, minor), 7.52 (d, $J =$ 2.0 Hz, 1H, minor), 7.49 (dd, $J =$ 8.0, 2.0 Hz, 1H, minor), 3.53 (s, 3H, minor), 3.28 (s, 3H, major, 1H, minor), 2.78 (s, 1H, major) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 152.9, 142.4, 134.7, 134.6, 131.7, 131.1, 128.2, 127.7, 127.6, 127.1, 126.6, 124.3, 122.1, 80.5, 79.5, 75.7, 38.9, 35.3 ppm; HRMS (EI): calcd for C$_{11}$H$_7$BrF$_3$NO [M$^+$]: 304.9663, found 304.9665.
**N-(2-bromo-5-nitrophenyl)propiolamide (6d-s):** 87% Yield; yellow solid; mp = 144.5 °C; $R_f = 0.20$ (silica gel, hexanes:EtOAc 4:1); IR (film) 3220, 2109, 1670, 1531, 1350 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 9.22 (s, 1H), 8.04 (brs, 1H), 7.90 (dd, $J =$ 9.0, 2.5 Hz, 1H), 7.76 (d, $J =$ 9 Hz, 1H), 3.09 (s, 1H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta =$ 149.6, 147.9, 136.0, 133.2, 120.3, 119.5, 116.9, 76.0 ppm; HRMS (ESI-TOF): calcd for C$_9$H$_5$BrN$_2$O$_3$ [M + H$^+$]: 268.9562, found 268.9565.

**N-(2-bromo-5-nitrophenyl)-N-methylpropiolamide (6d):** 74% Yield; yellow solid; mp = 123.3 °C; $R_f = 0.27$ (silica gel, hexanes:EtOAc 4:1); IR (film) 3226, 2109, 1650, 1527, 1348 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$, 4:1 atropisomeric mixture): $\delta =$ 8.23 (d, $J =$ 2.5 Hz, 1H, major), 8.16 (dd, $J =$ 9.0, 3.0 Hz, 1H, major), 8.14 (d, $J =$ 2.5 Hz, 1H, minor), 8.10 (dd, $J =$ 9.0, 3.0 Hz, 1H, minor), 7.90 (d, $J =$ 9.0 Hz, 1H, major), 7.87 (d, $J =$ 9.0 Hz, 1H, minor), 3.56 (s, 3H, minor), 3.32 (s, 1H, minor), 3.30 (s, 3H, major), 2.79 (s, 1H, major) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta =$ 152.7, 147.9, 142.8, 134.8, 131.9, 125.7, 124.9, 124.4, 80.9, 79.9, 75.6, 38.7, 35.3 ppm; HRMS (EI): calcd for C$_{10}$H$_7$BrN$_2$O$_3$ [M$^+$]: 281.9640, found 281.9645.

**N-(2-bromo-5-methoxyphenyl)propiolamide (6e-s):** 40% Yield; off white solid; mp = 79.0 °C; $R_f = 0.33$ (silica gel, hexanes:EtOAc 4:1); IR (film) 3380, 3274, 2107, 1673, 1587, 1520, 1225 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 8.00 (d, $J =$ 3.0 Hz, 1H), 7.93 (brs, 1H), 7.41 (d, $J =$ 9.0 Hz, 1H), 6.61 (dd, $J =$ 9.0, 3.0 Hz, 1H), 3.80 (s, 3H), 2.99 (s, 1H) ppm; $^{13}$C NMR (125 MHz,
CDCl₃): δ = 159.7, 149.6, 135.7, 132.6, 112.7, 107.5, 103.3, 77.5, 74.7, 55.8 ppm; HRMS (ESI-TOF): calcd for C₁₀H₇BrNO₂ [M + H⁺]: 253.9817, found 253.9824.

N-(2-bromo-5-methoxyphenyl)-N-methylpropiolamide (6e): 73% Yield; off white solid; mp = 84.0 °C; Rᵥ = 0.26 (silica gel, hexanes:EtOAc 4:1); IR (film) 3222, 2939, 2360, 2107, 1646, 1478 cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 7:1 atropisomeric mixture, major peaks): δ = 7.54 (t, J = 8.5 Hz, 1H), 6.89 (d, J = 3.0 Hz, 1H), 6.85 (dd, J = 8.5, 3.0 Hz, 1H), 3.82 (s, 3H), 3.24 (s, 3H), 2.76 (s, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 159.8, 153.2, 142.2, 134.1, 133.9, 116.3, 116.1, 116.0, 114.7, 113.9, 80.0, 78.8, 76.1, 55.9, 55.8, 39.0, 35.3 ppm; HRMS (ESI-TOF): calcd for C₁₁H₁₀⁷⁹BrNO₂ [M + H⁺]: 267.9973, found 267.9980.

3-(diphenylmethylene)-1-methylindolin-2-one (5): Yellow solid, mp = 165.9 °C (lit ¹ 153.2-154.9 °C); Rᵥ = 0.33 (silica gel, hexanes:EtOAc 4:1); IR (film) 3054, 2923, 1700, 1606, 1469 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.45–7.41 (m, 3H), 7.37–7.32 (m, 7H), 7.17 (t, J = 7.5, 1.0 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.68 (td, J = 7.5, 1.0 Hz, 1H), 6.42 (dd, J = 7.5, 1.0 Hz, 1H), 3.21 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 167.0, 154.7, 143.5, 141.5, 140.1, 130.1, 129.5, 129.3, 129.2, 129.1, 128.9, 128.0, 124.4, 123.4, 123.3, 121.5, 107.8, 26.0 ppm; HRMS (ESI-TOF): calcd for C₂₂H₁₇NO [M + H⁺]: 312.1388, found 312.1394.
3-(bis(4-methoxyphenyl)methylene)-1-methylindolin-2-one (7a): Brown solid; mp = 192.2 °C; $R_f = 0.2$ (silica gel, hexanes:EtOAc 4:1); IR (film) 3017, 1691, 1603, 1251 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 7.29-7.24 (m, 4H), 7.14 (td, $J = 8.0$, 1.5 Hz, 1H), 6.93 (d, $J = 9.0$ Hz, 2H), 6.88 (d, $J = 9.0$ Hz, 2H), 6.77 (d, $J = 8.0$ Hz, 1H), 6.70 (td, $J = 8.0$, 1.5 Hz, 1H), 6.57 (dd, $J = 7.5$, 0.5 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.22 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta =$ 167.3, 161.0, 160.8, 155.1, 142.8, 133.9, 132.9, 132.4, 132.1, 128.0, 124.3, 122.7, 122.5, 121.3, 114.2, 113.2, 107.7, 55.5, 55.4, 26.0 ppm; HRMS (ESI-TOF): calcd for C$_{24}$H$_{21}$NO$_3$ [M + H$^+$]: 372.1600, found 372.1611.

3-(bis(4-chlorophenyl)methylene)-1-methylindolin-2-one (7b): Yellow solid; mp = 134.4 °C; $R_f = 0.33$ (silica gel, hexanes:EtOAc 4:1); IR (film) 3054, 2927, 1699, 1604, 1486, 1089 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 7.41 (dd, $J = 7.0$, 2.0 Hz, 2H), 7.33 (dd, $J = 7.0$, 2.0 Hz, 2H), 7.26-7.20 (m, 5H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.73 (td, $J = 7.5$, 1.0 Hz, 1H), 6.52 (d, $J = 7.5$ Hz, 1H), 3.20 (s, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta =$ 166.7, 151.4, 143.5, 139.3, 138.0, 135.7, 135.6, 131.7, 131.1, 129.5, 129.4, 128.3, 125.1, 123.2, 122.8, 121.7, 108.1, 26.0 ppm; HRMS (ESI-TOF): calcd for C$_{22}$H$_{15}$Cl$_2$NO [M + H$^+$]: 380.0609, found 380.0612.
3-(bis(4-nitrophenyl)methylene)-1-methylindolin-2-one (7c): Brown solid; mp = 244.5 °C; \( R_f = 0.21 \) (silica gel, hexanes:EtOAc 3:1); IR (film) 3073, 1703, 1617, 1486, 1344, 1098 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 8.34 \) (dd, \( J = 7.0, 2.0 \) Hz, 2H), 8.24 (dd, \( J = 7.0, 2.0 \) Hz, 2H), 7.56 (dd, \( J = 7.0, 2.0 \) Hz, 2H), 7.48 (dd, \( J = 7.0, 2.0 \) Hz, 2H), 7.29 (dd, \( J = 7.5, 1.0 \) Hz, 1H), 6.83 (d, \( J = 8.0 \) Hz, 1H), 6.76 (td, \( J = 8.0, 1.0 \) Hz, 1H), 6.45 (d, \( J = 7.5, 1.0 \) H), 3.20 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 166.0, 148.4, 148.1, 147.1, 146.3, 145.6, 144.3, 130.9, 130.6, 130.4, 127.5, 124.8, 123.6, 123.6, 122.2, 121.4, 108.7, 26.1 \) ppm; HRMS (ESI-TOF): calcd for C\(_{22}\)H\(_{15}\)N\(_3\)O\(_5\) [M + H\(^+\)]: 402.1092, found 402.1097.

![Image of compound 7c]

6-chloro-3-(diphenylmethylene)-1-methylindolin-2-one (7d): Yellow solid; mp = 140.8 °C; \( R_f = 0.24 \) (silica gel, hexanes:EtOAc 8:1); IR (film) 3057, 2930, 1703, 1601, 1367, 1290 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.45–7.28 \) (m, 10H), 6.76 (d, \( J = 1.5 \) Hz, 1H), 6.65 (dd, \( J = 8.5, 2.0 \) Hz, 1H), 6.31 (d, \( J = 8.0 \) Hz, 1H), 3.19 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 166.9, 155.4, 144.4, 141.2, 139.7, 134.5, 130.2, 129.5, 129.5, 129.5, 129.1, 128.0, 124.1, 123.4, 121.9, 121.4, 108.4, 26.1 \) ppm; HRMS (ESI-TOF): calcd for C\(_{22}\)H\(_{16}\)ClNO [M + H\(^+\)]: 346.0999, found 346.1008.

![Image of compound 7d]

3-(diphenylmethylene)-1-methyl-6-(trifluoromethyl)indolin-2-one (7e): Yellow solid; mp = 141.2 °C; \( R_f = 0.35 \) (silica gel, hexanes:EtOAc 4:1); IR (film) 3059, 1706, 1467, 1322, 1121 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.48–7.29 \) (m, 10H), 6.97 (s, 1H), 6.96 (d, \( J = 10.5 \) Hz, 1H), 6.47 (d, \( J = 8.0 \) Hz, 1H), 3.25 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 166.6, 157.9, 144.4, 141.2, 139.7, 134.5, 130.2, 129.6, 129.5, 129.5, 129.5, 129.1, 128.0, 124.1, 123.4, 121.9, 121.4, 108.4, 26.1 \) ppm; HRMS (ESI-TOF): calcd for C\(_{22}\)H\(_{16}\)ClNO [M + H\(^+\)]: 346.0999, found 346.1008.
143.5, 140.9, 139.4, 130.3, 129.5, 129.2, 128.0, 123.2, 118.5, 118.5, 104.4, 104.4, 104.4, 26.1 ppm; HRMS (ESI-TOF): calcd for C_{23}H_{16}F_{3}NO [M + H^+] 380.1262, found 380.1269.

3-(diphenylmethylene)-1-methyl-6-nitroindolin-2-one (7f): Brown solid; mp = 92.2 °C; R_f = 0.24 (silica gel, hexanes:EtOAc 4:1); IR (film) 3059, 2929, 1707, 1652, 1341, 1129 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ = 7.61–7.59 (m, 2H), 7.53–7.44 (m, 5H), 7.39 (t, J = 7.5 Hz, 2H), 7.35 (d, J = 7.0 Hz, 2H), 7.30 (d, J = 7.0 Hz, 2H), 6.49 (d, J = 9.0 Hz, 1H), 3.30 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): δ = 166.5, 160.5, 147.7, 143.7, 140.6, 139.1, 130.6, 130.5, 130.4, 129.8, 129.7, 129.3, 128.0, 123.1, 122.7, 117.2, 102.7, 26.4 ppm; HRMS (ESI-TOF): calcd for C_{22}H_{16}N_{2}O_{3} [M + H^+] 357.1239, found 357.1244.

3-(diphenylmethylene)-6-methoxy-1-methylindolin-2-one (7g): Yellow solid; mp = 141.7 °C; R_f = 0.23 (silica gel, hexanes:EtOAc 4:1); IR (film) 2934, 1701, 1621, 1373, 1096 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ = 7.41 (t, J = 3.0 Hz, 3H), 7.36–7.30 (m, 7H), 6.33 (dd, J = 5.5, 3.0 Hz, 2H), 6.20 (dd, J = 8.5, 2.5 Hz, 1H), 3.78 (s, 3H), 3.17 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): δ = 167.5, 160.9, 151.6, 145.0, 141.7, 140.2, 130.0, 129.4, 129.0, 128.8, 127.9, 124.3, 124.0, 116.3, 105.7, 95.3, 55.6, 26.0 ppm; HRMS (ESI-TOF): calcd for C_{23}H_{19}NO_{2} [M + H^+] 342.1494, found 342.1500.

\[n\]

S11
7-bromo-3-(diphenylmethylene)-4-methoxy-1-methylindolin-2-one (7g-1): Yellow solid; mp = 133.9 °C; \( R_f = 0.52 \) (silica gel, hexanes:EtOAc 4:1); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.44 \) (tt, \( J = 7.5, 2.0 \) Hz, 1H), 7.39–7.32 (m, 3H), 7.30–7.25 (m, 4H), 7.08 (d, \( J = 7.0 \) Hz, 2H), 6.25 (d, \( J = 9.0 \) Hz, 1H), 3.60 (s, 3H), 3.06 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 167.8, 156.2, 153.2, 144.8, 141.3, 141.2, 134.8, 131.9, 130.5, 129.7, 127.7, 127.4, 122.1, 114.2, 106.5, 93.8, 54.9, 29.7 \) ppm; HRMS (ESI-TOF): calcd for C\(_{23}\)H\(_{19}\)\(^{79}\)BrNO\(_2\) [M + H\(^+\)]: 420.0599, found 420.0599.

\( (E)-3-((4\text{-methoxyphenyl})(\text{phenyl})\text{methylene})-1\text{-methylindolin-2-one} \) \((E\text{-}8a)\): Yellow solid; mp = 118.1 °C (lit.\(^4\) 163.8-164.3 °C); \( R_f = 0.26 \) (silica gel, hexanes:EtOAc 4:1); IR (film) 3053, 2927, 1696, 1603, 1508, 1469, 1250 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.39–7.25 \) (m, 7H), 7.17 (td, \( J = 7.5, 1.5 \) Hz, 1H), 6.93 (dd, \( J = 7.0, 2.0 \) Hz, 2H), 6.78-6.67 (m, 3H), 3.87 (s, 3H), 3.20 (s, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta = 167.1, 160.8, 154.9, 143.3, 140.6, 133.6, 132.7, 131.7, 130.5, 129.3, 129.0, 128.6, 127.9, 122.9, 121.4, 114.3, 107.8, 55.5, 26.0 \) ppm; HRMS (ESI-TOF): calcd for C\(_{23}\)H\(_{19}\)NO\(_2\) [M + H\(^+\)]: 342.1494, found 342.1498.
**(Z)-3-((4-methoxyphenyl)(phenyl)methylene)-1-methylindolin-2-one (Z-8a):** Yellow solid; mp = 153.0 °C (lit. 5 163.8-164.3 °C); Rf = 0.24 (silica gel, hexanes:EtOAc 4:1); IR (film) 2931, 1696, 1604, 1250 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.46-7.40 (m, 3H), 7.32-7.29 (m, 4H), 7.15 (t, J = 13.0 Hz, 1H), 6.88 (dd, J = 7.0, 2.0 Hz, 2H), 6.76 (d, J = 8.0 Hz, 1H), 6.66 (t, J = 7.5 Hz, 1H), 6.32 (d, J = 7.5 Hz, 1H), 3.84 (s, 3H), 3.23 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ = 167.1, 161.0, 154.9, 143.0, 141.7, 132.7, 131.9, 129.9, 129.3, 129.0, 128.4, 123.9, 123.0, 121.4, 113.2, 107.7, 55.4, 26.0 ppm; HRMS (ESI-TOF): calcd for C₂₃H₁₉NO₂ [M + H⁺]: 342.1494, found 342.1503.

![Molecule Image](image)

**(E)-3-((4-chlorophenyl)(phenyl)methylene)-1-methylindolin-2-one (E-8b):** Yellow solid; mp = 54.8 °C; Rf = 0.35 (silica gel, hexanes:EtOAc 4:1); ¹H NMR (500 MHz, CDCl₃): δ = 7.41-7.18 (m, 9H), 7.19 (td, J = 7.5, 1.0 Hz, 1H), 6.78 (d, J = 7.5 Hz, 1H), 6.73 (td, J = 7.5, 1.0 Hz, 1H), 6.53 (dd, J = 7.5, 0.5 Hz, 1H), 3.20 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 166.8, 153.0, 143.6, 139.8, 139.7, 135.5, 131.1, 130.2, 129.4, 129.4, 129.2, 128.1, 124.7, 123.2, 123.0, 121.6, 108.0, 26.0 ppm; HRMS (EI): calcd for C₂₂H₁₆ClNO [M⁺]: 345.0920, found 345.0919.

![Molecule Image](image)

**(Z)-3-((4-chlorophenyl)(phenyl)methylene)-1-methylindolin-2-one (Z-8b):** Yellow solid; mp = 59.0 °C; Rf = 0.37 (silica gel, hexanes:EtOAc 4:1); IR (film) 3054, 1698, 1606, 1486, 1335, 1090 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.48–7.43 (m, 3H), 7.48–7.43 (m, 3H), 3.20 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 166.9, 153.0, 143.5, 141.0, 138.4,
135.3, 131.6, 129.5, 129.5, 129.2, 129.1, 128.2, 124.7, 123.4, 123.2, 121.6, 107.9, 26.0 ppm; HRMS (EI): calcd for C<sub>22</sub>H<sub>16</sub>ClNO [M⁺]: 345.0920, found 345.0916.

(\(E\))-1-methyl-3-((4-nitrophenyl)(phenyl)methylene)indolin-2-one (\(E\)-8c):\(^4\) Yellow solid; mp = 201.2 °C (lit.\(^4\) 198.8–200.8 °C); \(R_f = 0.25\) (silica gel, hexanes:EtOAc 4:1); IR (film) 3056, 1701, 1604, 1519, 1469, 1345 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl<sub>3</sub>): \(\delta = 8.30\) (t, \(J = 4.25\) Hz, 2H), 7.54 (d, \(J = 9.0\) Hz, 2H), 7.41-7.21 (m, 6H), 6.80 (d, \(J = 8.0\) Hz, 1H), 6.71 (t, \(J = 7.75\) Hz, 1H), 6.36 (d, \(J = 7.5\) Hz, 1H), 3.21 (s, 3H) ppm; \(^13\)C NMR (125 MHz, CDCl<sub>3</sub>): \(\delta = 166.4, 150.9, 148.2, 147.9, 143.9, 138.8, 130.6, 130.0, 129.9, 129.7, 128.3, 125.7, 124.4, 123.3, 122.4, 121.8, 108.3, 26.1 ppm; HRMS (EI): calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub> [M⁺]: 356.1161, found 356.1161.

(\(Z\))-1-methyl-3-((4-nitrophenyl)(phenyl)methylene)indolin-2-one (\(Z\)-8c): Yellow solid; mp = 186.6 °C; \(R_f = 0.28\) (silica gel, hexanes:EtOAc 4:1); IR (film) 3057, 1699, 1603, 1510, 1342 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl<sub>3</sub>): \(\delta = 8.22\) (dd, \(J = 7.0, 1.5\) Hz, 2H), 7.50–7.44 (m, 5H), 7.32 (dd, \(J = 8.0, 2.0\) Hz, 2H), 7.22 (t, \(J = 7.5\) Hz, 1H), 6.80 (d, \(J = 8.0\) Hz, 1H), 6.73 (t, \(J = 7.75\) Hz, 1H), 6.52 (d, \(J = 8.0\) Hz, 1H), 3.20 (s, 3H) ppm; \(^13\)C NMR (125 MHz, CDCl<sub>3</sub>): \(\delta = 166.6, 150.8, 147.8, 147.0, 143.9, 140.0, 130.7, 129.9, 129.8, 129.4, 129.2, 126.1, 123.7, 123.4, 122.4, 121.9, 108.2, 26.0 ppm; HRMS (ESI-TOF): calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub> [M + H⁺]: 357.1239, found 357.1249.
(E)-3-((4-acetylphenyl)(phenyl)methylene)-1-methylindolin-2-one (E-8d): Yellow solid; mp = 144.7 °C; R<sub>f</sub> = 0.33 (silica gel, hexanes:EtOAc 2:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 8.02 (dd, <i>J</i> = 6.75, 1.75 Hz, 2H), 7.45 (dd, <i>J</i> = 6.75, 1.75 Hz, 2H), 7.33–7.30 (m, 3H), 7.26–7.23 (m, 2H), 7.13 (td, <i>J</i> = 7.5, 1.0 Hz, 1H), 6.79 (d, <i>J</i> = 8.0 Hz, 1H), 6.69 (td, <i>J</i> = 7.8, 1.0 Hz, 1H), 6.40 (d, <i>J</i> = 7.5 Hz, 1H), 3.21 (s, 3H), 2.66 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 197.7, 166.6, 152.8, 146.1, 143.7, 139.4, 137.4, 130.0, 129.8, 129.4, 129.4, 129.1, 128.1, 125.0, 123.3, 122.8, 121.7, 108.0, 26.9, 26.0 ppm; HRMS (EI): calcd for C<sub>24</sub>H<sub>19</sub>NO<sub>2</sub> [M<sup>+</sup>]: 353.1416, found 353.1415.

(Z)-3-((4-acetylphenyl)(phenyl)methylene)-1-methylindolin-2-one (Z-8d): Yellow solid, mp = 151.4 °C (lit.<sup>4</sup> 185.2–187.1 °C); R<sub>f</sub> = 0.30 (silica gel, hexanes:EtOAc 2:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.96 (d, <i>J</i> = 8.5 Hz, 2H), 7.46–7.42 (m, 5H), 7.33–7.31 (m, 2H), 7.20 (t, <i>J</i> = 7.5 Hz, 1H), 6.78 (d, <i>J</i> = 7.5 Hz, 1H), 6.71 (t, <i>J</i> = 7.8 Hz, 1H), 6.50 (d, <i>J</i> = 7.5 Hz, 1H), 3.20 (s, 3H), 2.61 (s, 3H) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 197.7, 166.7, 152.6, 145.1, 143.7, 140.5, 137.0, 130.1, 129.5, 129.4, 129.2, 128.1, 125.3, 123.4, 122.8, 121.7, 108.0, 26.8, 26.0 ppm; HRMS (EI): calcd for C<sub>24</sub>H<sub>19</sub>NO<sub>2</sub> [M<sup>+</sup>]: 353.1416, found 353.1420.
E/Z Isomerization test under reaction conditions

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<tr>
<th>SM</th>
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<td>E-8a</td>
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<tr>
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<td>NO₂</td>
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<td>1:4</td>
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</table>
N-(2-bromophenyl)-3-phenylpropionamide (4-s)
N-(2-bromophenyl)-N-methyl-3-phenylpropiolamide (4)
N-(2-bromophenyl)propiolamide (6a-s)
N-(2-bromophenyl)-N-methylpropiolamide (6a)
$N$-(2-bromo-5-chlorophenyl)propiolamide (6b-s)
N-(2-bromo-5-chlorophenyl)-N-methylpropiolamide (6b)
N-(2-bromo-5-(trifluoromethyl)phenyl)propiolamide (6c-s)
N-(2-bromo-5-(trifluoromethyl)phenyl)-N-methylpropiolamide (6c)
N-(2-bromo-5-nitrophenyl)propiolamide (6d-s)
N-(2-bromo-5-nitrophenyl)-N-methylpropiolamide (6d)
$N$-(2-bromo-5-methoxyphenyl)propiolamide (6e-s)
N-(2-bromo-5-methoxyphenyl)-N-methylpropiolamide (6e)
3-(diphenylmethylene)-1-methylindolin-2-one (5)
3-(bis(4-methoxyphenyl)methylene)-1-methylnindolin-2-one (7a)
S31
3-(bis(4-nitrophenyl)methylene)-1-methylindolin-2-one (7c)
6-chloro-3-(diphenylmethylene)-1-methylindolin-2-one (7d)
3-(diphenylmethylene)-1-methyl-6-(trifluoromethyl)indolin-2-one (7c)
3-(diphenylmethylene)-1-methyl-6-nitroindolin-2-one (7f)
3-(diphenylmethylene)-6-methoxy-1-methylindolin-2-one (7g)
7-bromo-3-(diphenylmethylene)-4-methoxy-1-methylindolin-2-one (7g-1)
(E)-3-((4-methoxyphenyl)(phenyl)methylene)-1-methylindolin-2-one (E-8a)
(Z)-3-((4-methoxyphenyl)(phenyl)methylene)-1-methylindolin-2-one (Z-8a)
(E)-3-((4-chlorophenyl)(phenyl)methylene)-1-methylindolin-2-one (E-8b)
ROESY spectrum of E-8b
(Z)-3-((4-chlorophenyl)(phenyl)methylene)-1-methylindolin-2-one (Z-8b)
ROESY spectrum of Z-8b
(\textit{E})-1-methyl-3-((4-nitrophenyl)(phenyl)methylene)indolin-2-one (\textit{E}-8c)
(Z)-1-methyl-3-((4-nitrophenyl)(phenyl)methylene)indolin-2-one (Z-8c)
ROESY spectrum of Z-8c
(E)-3-((4-acetylphenyl)(phenyl)methylene)-1-methylindolin-2-one (E-8d)
ROESY spectrum of E-8d
(Z)-3-((4-acetylphenyl)(phenyl)methylene)-1-methylindolin-2-one (Z-8d)
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(1) Likhar, P.R.; Racharlawar, S.S.; Karkhelikar, M.V.; Subhas, M.S.; Sridharb, B. Synthesis. 2011, 2407.


