Supporting Information

An Efficient Green Synthesis of Versatile Synthon 3-Chlorooxindoles with NaCl/Oxone
Vanammoole LakshmiReddy, Sai Prathima Parvathaneni* Vaidya Jayathirtha Rao* and Raktani Bikshapathi

FluoroAgro Chemicals, Organic Division II, AcSIR, CSIR-Indian Institute of Chemical Technology (IICT), Tarnaka, Hyderabad –500 007, India,
Fax: +91-040-27193382, Tel: (+) 91 40 27193933.
E-mail: saiprathima.iict@gmail.com, vaidya.opv@gmail.com

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1. General Information

The starting materials and reagents were purchased from various commercial sources and used without further purification. The reactions were performed at room temperature. ACME silica gel (60-120 mesh) was used for column chromatography. Analytical thin-layer chromatography (TLC) was performed on pre-coated TLC plates with silica gel 60-F254 plates and visualized by UV-light. $^1$H NMR and $^{13}$C NMR spectra were recorded, using tetramethylsilane (TMS) in the solvent of CDCl$_3$+DMSO as the internal standard on a 300, 500 MHz spectrometer ($^1$H NMR: TMS at 0.00 ppm, CDCl$_3$ at 7.26 ppm; $^{13}$C NMR: CDCl$_3$ at 77.0 ppm, DMSO at 39.43). Chemical shifts (δ) were recorded in ppm with respect to TMS as an internal standard and coupling constants are quoted in Hertz (Hz). Mass spectra were recorded on a mass spectrometer by the electron spray ionization (ESI) and the data acquired in positive ionization mode. HRMS spectra were determined on TOF type mass analyzer. All the starting materials of aliphatic MBH adducts$^1$, 2-(hydroxy(phenyl)methyl)cyclohex-2-en-1-one$^2$ and 1-phenylprop-2-en-1-ol$^3$ have been synthesized according to the reported literature.

2.1 General Procedure:

In a 25 mL round bottom flask, 1H-indole-3-carbaldehyde substrates1a-1n (1 equiv), Oxone (2 equiv) and NaCl (2 equiv) were dissolved in CH$_3$CN:H$_2$O (1:1). The reaction mixture was stirred at 50 °C temperature for 1-2 h, monitored by TLC. After completion of the reaction, the mixture was diluted with 20 mL of ethyl acetate and then the organic layer was dried over Na$_2$SO$_4$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate to give the desired product.

2.2 Gram-scale synthesis of 2a

In a 250 mL round bottom flask, 1H-indole-3-carbaldehyde substrate 1a (1 equiv, 20mmol, 3g), Oxone (2.0equiv, 41 mmol, 12.7g) and NaCl (2.0equiv, 41mmol, 2.4 g) were dissolved in CH$_3$CN:H$_2$O (1:1) 60 ml of solvent. The reaction mixture was stirred at room temperature for 3h as monitored by TLC. After completion of the reaction the reaction mixture was diluted with ethyl
acetate and then the organic layer was dried over Na₂SO₄ and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate to give the desired product 2a.

3. Characterization Data for the Products:

3-chloroindolin-2-one (2a)

(2a): solid; mp: 134-136°C; Yield: 88%; IR (KBr): 3128, 1760, 1620, 1525, 1471, 1342, 1292, 1073, 959, 843, 744 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.72 (brs, 1H), 7.41 (d,  J = 7.4 Hz, 1H), 7.31 (t,  J = 7.8 Hz, 1H), 7.11 (t,  J = 7.6, 7.4 Hz, 1H), 6.93 (d,  J = 7.7 Hz, 1H), 5.17 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 174.6, 140.9, 130.5, 126.2, 125.8, 123.4, 110.6, 51.9; MS (ESI) m/z (%): 168. [M+H]⁺; HRMS-ESI (m/z) Calcd for C₈H₆ClNO: 168.0270 [M+H]⁺; Found: 169.0273.

3-chloro-1-methylindolin-2-one (2b)

(2b): solid; mp: 97-100°C; Yield: 90%; IR (KBr): 3062, 2965, 1721, 1610, 1466, 1370, 1239, 1089, 751, 685 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.42 (d,  J = 7.4 Hz, 1H), 7.37 (t,  J = 7.8, 7.7 Hz, 1H), 7.12 (t,  J = 7.7, 7.4 Hz, 1H), 6.84 (d,  J = 7.9 Hz, 1H), 5.13 (s, 1H), 3.23 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 171.9, 143.6, 130.4, 125.5, 125.4, 123.2, 108.6, 51.4, 26.5; MS (ESI) m/z (%): 181 [M+H]⁺; HRMS-ESI (m/z) Calcd for C₉H₈ClNO: 182.0373 [M+H]⁺; Found: 182.0373.

3-chloro-1-ethylindolin-2-one (2c)
(2c): solid; mp: 126-128°C; Yield: 92%; IR (KBr): 3062, 2965, 1721, 1610, 1466, 1370, 1239, 1089, 751, 685 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.4 (d, \(J = 7.4\) Hz, 1H), 7.35 (t, \(J = 7.8\) Hz, 1H), 7.11 (t, \(J = 7.8, 7.4\) Hz, 1H), 6.86 (d, \(J = 7.8\) Hz, 1H), 5.11 (s, 1H), 3.77 (m, 2H), 1.29 (t, \(J = 7.3, 7.2\) Hz 3H); \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 171.6, 142.9, 130.3, 125.8, 125.7, 123.1, 108.7, 51.5, 35.1 12.4; MS(ESI) \(m/z\) (%): 196 [M+H]; HRMS-ESI(m/z)Calcd for C\(_{10}\)H\(_9\)ONCl: 196.0524 [M+H]; Found: 196.0523.

1-benzyl-3-chloroindolin-2-one\(^4\) (2d):

(2d): solid; mp: 145-147°C; Yield: 90%; IR (KBr): 3061, 3031, 2955, 1719, 1609, 1486, 1343, 1268, 1157, 1079, 892, 757, 694 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.42 (d, \(J = 7.4\) Hz 1H), 7.35 7.28 (m, 5H), 7.22 (t, \(J = 7.9, 10.2\) Hz, 1H), 7.08 (t, \(J = 8.3\) Hz, 1H), 6.73 (d, \(J = 8.3\) Hz, 1H), 5.22 (s, 1H), 4.91 (d, 2H); \(^1\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 172.0, 141.7, 130.6, 126.0, 125.4, 123.8, 116.9, 108.5, 50.9, 36.3, 16.2; MS (ESI) \(m/z\) (%): 258 [M+H]; HRMS-ESI(m/z)Calcd for C\(_{15}\)H\(_{12}\)ClNO = 258.0683 [M+H]; Found: 258.0680.

1-allyl-3-chloroindolin-2-one (2e):

(2e): solid; mp: 99-101°C; Yield: 91%; IR (KBr): 3055, 3022, 2969, 1719, 1611, 1467, 1356, 1179, 922, 751, 681 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.43 (d, \(J = 7.4\) Hz, 1H), 7.35 (t, \(J = 7.8\) Hz, 1H), 7.11 (t, \(J = 7.8, 7.4\) Hz,
1H), 6.84 (d, J = 7.8 Hz, 1H), 5.84 (m, 1H), 5.26 (m, 2H).5.16 (s, 1H), 4.35 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 171.7, 142.9, 130.5, 130.3, 125.6, 123.2, 118.0, 109.5, 51.3, 42.6; MS (ESI) m/z (%): 208 [M+H]⁺; HRMS-ESI(m/z)Calcd for C₁₁H₁₁ONCl: 208.0525 [M+H]⁺; Found: 208.0523.

Methyl 3-(3-chloro-2-oxoindolin-1-yl)propanoate (2f):

(2f): Colourless Liquid; Yield: 85%; IR (KBr): 3020, 2953, 1729, 1610, 1467, 1365, 1201, 1064, 753, 686 cm⁻¹;¹H NMR (300 MHz, CDCl₃): δ 7.43 (d, J = 7.5 Hz, 1H), 7.36 (t, J = 7.8, 7.7 Hz, 1H), 7.12 (t, J = 7.7, 7.5 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H), 5.13 (s, 1H), 4.02 (t, J= 7.1, 6.9 2H), 3.67 (s, 3H), 2.73 (t, J = 7.1, 6.9 2H); ¹³C NMR (75 MHz, CDCl₃): δ 171.8, 171.1, 142.4, 130.3, 125.6, 125.4, 123.2, 108.8, 51.8, 51.1, 36.1, 31.6; MS (ESI) m/z (%): 350 [M+H]⁺; HRMS-ESI(m/z)Calcd for C₁₂H₁₂O₃NCl: 254.0581 [M+H]⁺; Found: 254.0581.

3-(3-chloro-2-oxoindolin-1-yl)propanoic acid (2g):

(2g): solid; mp: 130-132°C; Yield: 82%; IR (KBr): 3414, 3062, 2954, 1761, 1731, 1681, 1596, 1447, 1264, 1215, 1187, 1018, 990, 798, 688, 638, 616 cm⁻¹;¹H NMR (300 MHz, CDCl₃): δ 7.43 (d, J = 7.58 Hz, 1H), 7.36 (t, J = 7.82, 7.70 Hz, 1H), 7.12 (t, J = 8.43, 7.58 Hz, 1H), 6.95 (d, J = 7.82 Hz, 1H), 5.13 (s, 1H), 4.02 (t, J= 7.20, 7.09 2H), 2.73 (t, J = 7.09, 6.96 2H); ¹³C NMR (75 MHz, CDCl₃): δ 187.8, 166.3, 133.8, 132.9, 129.5, 128.5, 64.0, 57.4, 37.2; MS (ESI) m/z (%): 242 [M+H]⁺; HRMS-ESI(m/z)Calcd for C₁₁H₁₀O₃NCl = 242.2845 [M+H]⁺; Found: 242.2845.
3-(3-chloro-2-oxoindolin-1-yl)propanenitrile (2h):

(2h): solid; mp: 142-144 °C; Yield: 84%; IR (KBr): 3062, 2926, 2854, 2252, 1728, 1612, 1467, 1361, 1174, 1061, 754, 685 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.46 (d, J = 7.4 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.16 (t, J = 7.9, 7.4 Hz, 1H), 6.95 (d, J = 7.9 Hz, 1H), 5.18 (s, 1H), 4.03 (t, 2H), 2.79 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 172.0, 141.7, 130.6, 126.0, 125.4, 123.8, 116.9, 108.5, 50.9, 36.3, 16.2; MS (ESI) m/z (%): 221 [M+H]⁺; HRMS-ESI(m/z) Calcd for C₁₁H₁₀O N₂Cl = 221.0478 [M+H]⁺; Found: 221.0476.

5-bromo-3-chloroindolin-2-one (2i):

(2i): solid; mp: 251-253 °C; Yield: 90%; IR (KBr): 3407, 2926, 1741, 1604, 1482, 1343, 1209, 1104, 816, 794 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.92 (brs, 1H), 7.54 (s, 1H), 7.44 (d, J = 8.3 Hz, 1H), 6.79 (t, J = 8.3 Hz, 1H), 5.31 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 172.2, 140.7, 132.1, 127.6, 127.4, 113.7, 111.2, 50.7; MS (ESI) m/z (%): 247 [M+H]⁺; HRMS-ESI(m/z) Calcd for C₈H₅ONBrCl: 247.0887 [M+H]⁺; Found: 247.0881.

5-bromo-3-chloro-1-ethylindolin-2-one (2j):
(2j): solid; mp: 138-140°C; Yield: 92%; IR (KBr): 3144, 2931, 1741, 1683, 1616, 1471, 1386, 1205, 1171, 886, 820, 798, 690 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.55 (s, 1H), 7.48 (d, J = 8.3 Hz, 1H), 6.75 (t, J = 8.3 Hz, 1H), 5.09 (s, 1H), 4.05 (m, 2H), 1.27 (t, J = 7.3, 7.2 Hz 3H); ¹³C NMR (75 MHz, CDCl₃): δ 170.0, 144.5, 143.1, 130.4, 128.3, 121.3, 111.3, 29.6; MS (ESI) m/z (%): 275 [M+H]⁺; HRMS-ESI(m/z) Calcd for C₁₀H₁₀ONBrCl: 275.9612 [M+H]⁺; Found: 275.9612.

1-allyl-5-bromo-3-chloroindolin-2-one (2k):

(2k): solid; mp: 110-112°C; Yield: 92%; IR (KBr): 3055, 3022, 2969, 1719, 1611, 1467, 1356, 1179, 751, 681 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.55 (s, 1H), 7.48 (d, J = 8.3 Hz, 1H), 6.75 (t, J = 8.3 Hz, 1H), 5.81 (m, 1H), 5.26 (m, 2H), 5.16 (s, 1H), 4.33 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 171.1, 141.9, 133.1, 130.2, 128.8, 127.4, 118.3, 115.8, 111.0, 50.7, 42.7; MS (ESI) m/z (%): 284 [M+H]⁺; HRMS-ESI(m/z) Calcd for C₁₁H₁₀ONBrCl: 284.1747 [M+H]⁺; Found: 284.1747.

3-(5-bromo-3-chloro-2-oxoindolin-1-yl)propanenitrile (2l):

(2l): solid; mp: 145-147°C; Yield: 86%; IR (KBr): 3062, 2926, 2854, 2252, 1738, 1622, 1487, 1361, 1174, 1061, 980, 820, 754, 685 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.59 (s, 1H), 7.53 (d, J = 8.3 Hz, 1H), 6.86 (t, J = 8.3 Hz, 1H), 5.16 (s, 1H), 4.02 (m, 2H), 2.78 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 171.8, 171.1, 142.4, 130.3, 125.6, 125.4, 123.2, 108.8, 51.8, 51.1, 36.1, 31.6; MS (ESI) m/z (%): 300 [M+H]⁺; HRMS-ESI(m/z) Calcd for C₁₁H₈BrClN₂O: 300.1657 [M+H]⁺; Found: 300.1686.
Methyl 3-(3-chloro-2-oxoindolin-1-yl)propanoate (2m):

\[
\begin{align*}
\text{(2m): Solid; mp: 120-122^\circ C; Yield: 86%; IR (KBr): 3049, 2949, 1723, 1608, 1482, 1363, 1206, 1169, 1118, 1070, 986, 816, 639 cm}^{-1}; \quad &
{^1H NMR (300 MHz, CDCl}_3): \delta 7.54 (s, 1H), 7.49 (d, J = 8.3 Hz, 1H), 6.86 (t, J = 8.3 Hz, 1H), 5.10 (s, 1H), 3.99 (t, J= 7.0, 6.8 Hz, 2H), 3.67 (s, 3H), 2.77 (t, J= 7.0 , 6.8 Hz, 2H); \\
{^{13}C NMR (75 MHz, CDCl}_3): \delta 171.8, 171.1,142.4, 130.3, 125.6, 125.4, 123.2, 108.8, 51.8, 51.1, 36.1, 31.6; \\
MS (ESI) m/z (%): 333 [M+H]^+; \\
HRMS-ESI(m/z)Calcd for C_{12}H_{11}O_3NBrCl: 333.9679 [M+H]^+; Found: 333.9679.
\end{align*}
\]

methyl 3-(3-chloro-5-methoxy-2-oxoindolin-1-yl)propanoate (2n):

\[
\begin{align*}
\text{(2n): Colourless Liquid; Yield: 79%; IR (KBr): 3042, 2952, 2838, 1729, 1601, 1492, 1438, 1283, 1206, 1174, 1027, 816, 743, 688 cm}^{-1}; \quad &
{^1H NMR (300 MHz, CDCl}_3): \delta 7.03 (d, J = 2.3 Hz, 1H), 6.88 (d, J = 2.3 Hz, 1H), 6.86 (s, 1H), 5.09 (s, 1H), 3.99 (t, J = 7.1 Hz, 2H), 3.89 (t, 3H), 3.67 (t, 3H), 2.72 (t, J = 7.1 Hz, 2H); \\
{^{13}C NMR (75 MHz, CDCl}_3): \delta 171.8, 171.4, 156.3, 135.7, 126.7, 115.2, 112.5, 109.5, 55.7, 51.9, 51.5, 36.4, 31.7; \\
MS (ESI) m/z (%): 284 [M+H]^+; \\
HRMS-ESI(m/z)Calcd for C_{13}H_{14}O_4NCl: 284.0689 [M+H]^+; Found: 284.0689.
\end{align*}
\]

3-Bromoindolin-2-one (3a):
(3a): colourless solid; mp: 138-140°C; Yield: 80%; IR (KBr): 3246, 3032, 2849, 1717, 1619, 1471, 1329, 1192, 1168, 1099, 905, 727, 649 cm⁻¹; ¹H NMR (300 MHz, CDCl₃):  δ 9.18 (brs, 1H), 7.39 (d, J = 7.4 Hz, 1H), 7.28 (t, J = 7.7, 7.4 Hz, 1H), 7.09 (t, J = 7.6, 7.4 Hz, 1H), 6.94 (d, J = 7.7 Hz, 1H), 5.17 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 174.7, 140.9, 133.3, 130.4, 126.2, 123.4, 110.6, 38.9; MS (ESI) m/z (%): 211.99[M+H]+; HRMS-ESI(m/z)Calcd for C₈H₆BrN: 212.0089 [M+H]+; Found: 212.0093.

3-Bromo-1-ethylindolin-2-one (3b): Colourless solid; mp: 144-146°C; Yield: 75 %; IR (KBr): 2978, 2935, 1715, 1615, 1477, 1430, 1338, 1266, 1194, 1106, 809, 745, 683 cm⁻¹; ¹H NMR (300 MHz, CDCl₃):  δ 7.41 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.8, Hz, 1H), 7.10 (t, J = 7.8, 7.5 Hz, 1H), 6.84 (d, J = 7.5 Hz, 1H), 5.25 (s, 1H), 3.78 (m, 2H),  1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 174.7, 140.9, 133.3, 130.4, 126.2, 123.4, 110.6, 38.7, 35.2, 12.4; MS (ESI) m/z (%): 240 [M+H]+; HRMS-ESI(m/z)Calcd for C₁₀H₁₀BrNO: 241.0689 [M+H]+; Found: 241.0695.

3,5-Bibromo-1-ethylindolin-2-one (3c):
(3c): solid; mp: 160-162°C; Yield: 60 %; IR (KBr): 2978, 2935, 1715, 1615, 1477, 1430, 1338, 1266, 1194, 1106, 809, 745, 683 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.53 (s, 1H), 7.46 (dd, J = 8.3 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 5.22 (s, 1H), 3.76 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 171.3, 141.8, 133.1, 129.2, 115.5, 110.2, 128.1, 37.6, 35.4, 12.2; MS (ESI) m/z (%): 317 [M+H⁺]; HRMS-ESI (m/z) Calcd for C₁₀H₆Br₂NO: 317.3521 [M+H⁺]; Found: 317.3525.

3-(3,5-dibromo-2-oxoindolin-1-yl)propanenitrile (3d):

(3d): solid; mp: 154-156°C; Yield: 62 %; IR (KBr): 3035, 2931, 2227, 1747, 1623, 1495, 1454, 1371, 1214, 1142, 1025, 957, 739, 697 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.57 (s, 1H), 7.50 (dd, J = 8.3, 8.4 Hz, 1H), 6.84 (d, J = 8.4 Hz, 1H), 5.27 (s, 1H), 4.01 (m, 2H), 2.78 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 169.3, 136.9, 134.5, 132.5, 129.5, 117.1, 116.5, 110.5, 42.4, 37.0, 16.1; MS (ESI) m/z (%): 343[M+H⁺]; HRMS-ESI (m/z) Calcd for C₁₁H₈Br₂N₂O: 344.5632 [M+H⁺]; Found: 344.5638.

Indoline-2, 3-dione (4a):

(4a) orange solid; Yield: 84 %; mp 198-200 °C; IR (KBr): 3189, 1728, 1615, 1460, 1328, 1269, 1196, 1091, 769, 658 cm⁻¹; ¹H NMR (300 MHz, CDCl₃+d₆-DMSO): δ 10.7 (s, 1H), 7.53-7.47 (m, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 8.1 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃+d₆-
DMSO): $\delta$ 184.0, 159.2, 150.8, 138.0, 124.5, 122.8, 117.5, 112.2; MS (ESI): (m/z) = 170 (M+Na)$^+$. HRMS (ESI) (M+Na)$^+$ m/z calcd for C$_8$H$_5$NO$_2$Na = 170.0212, found = 170.0212.

5-chloroindoline-2, 3-dione $^6$ (4b):

(4b) Orange solid; Yield: 81%; mp 256-258 °C; IR(KBr): 3099, 2986, 1747, 1705, 1616, 1450, 1308, 1217, 1119, 845, 746. $^1$H NMR (500 MHz, CDCl$_3$+d$_6$-DMSO): $\delta$ 10.94 (s, 1H), 7.46 (m, 2H), 6.90 (d, 1H, $J$ = 8.8 Hz). $^{13}$C NMR (75 MHz, d$_6$-DMSO): $\delta$ 112.9, 117.5, 123.4, 127.0, 136.5, 148.3, 158.0, 182.5. MS (ESI): (m/z) = 204 (M+Na)$^+$. HRMS (ESI) (M+H)$^+$ m/z calcd for C$_8$H$_5$ClNO$_2$ = 182.0003, found = 182.0003.

5-bromoindoline-2, 3-dione$^6$ (4c):

(4c) pale yellow solid; Yield: 85 %; mp 248-250 °C; IR (KBr): 3204, 1750, 1709, 1613, 1446, 1269, 1208, 1121, 843, 680 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$+d$_6$-DMSO): $\delta$ 10.94 (s, 1H), 7.46 (m, 2H), 6.90 (d, $J$ = 8.8 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$+d$_6$-DMSO):$\delta$ 182.4, 158.0, 148.7, 139.8, 126.4, 117.9, 114.5, 113.8; MS (ESI): (m/z) = 248 (M+Na)$^+$. HRMS (ESI) (M+1)$^+$ m/z calcd for C$_8$H$_5$BrNO$_2$ = 225.9498, found = 225.9498.

5-methylindoline-2, 3-dione $^6$ (4d):
(4d) **Orange solid**: Yield: 80 %; mp 183-184 °C. **IR (KBr)**: 3286, 1744, 1490, 1302, 1191, 1126, 830, 656 cm⁻¹. **¹H NMR (300 MHz, CDCl₃+d₆-DMSO)**: δ 10.5 (s, 1H), 7.3 (s, 2H), 6.80 (d, 1H, J = 8.1 Hz), 2.3 (s, 3H). **¹³C NMR (75 MHz, d₆-DMSO)**: δ 184.2, 159.3, 148.1, 138.5, 132.2, 124.7, 117.2, 111.8, 20.0. **MS (ESI)**: (m/z) = 184(M+Na)⁺. **HRMS (ESI) (M+Na)⁺ m/z calcd for C₉H₇NO₂Na = 184.0369, found = 184.0369.

5-methoxyindoline-2, 3-dione(4e):

(4e) **Yellow solid**: Yield: 81 %; mp 196-198 °C; **IR (KBr)**: 2854, 2925, 1733, 1606, 1491, 1241, 1032, 981, 824, 739 cm⁻¹; **¹H NMR (300 MHz, CDCl₃+d₆-DMSO)**: δ 10.6 (s, 1H), 7.53 (s, 1H), 7.1 (m, 1H), 6.84 (d, 1H, J = 8.4 Hz), 3.79 (s, 3H); **¹³C NMR (75 MHz, CDCl₃+d₆-DMSO)**: δ 183.6, 158.4, 154.4, 143.6, 123.8, 116.6, 112.1, 107.4, 54.3; **MS (ESI)**: (m/z) = 200 (M+Na)⁺. **HRMS (ESI) (M+Na)⁺ m/z calcd for C₈H₄N₂O₄ = 200.0318, found = 200.0319.

1-methylindoline-2, 3-dione(4f):

(4f) **Orange solid**: Yield: 78 %; mp 134-136 °C; **IR (KBr)**: 2940, 1726, 1606, 1469, 1326, 1159, 1089, 756, 474 cm⁻¹; **¹H NMR (300 MHz, CDCl₃+d₆-DMSO)**: δ 7.66-7.58 (m, 2H), 7.15 (t, 1H, J = 7.5 Hz), 6.94 (d, 1H, J = 7.9 Hz), 3.26 (s, 3H); **¹³C NMR (75 MHz, CDCl₃+d₆-DMSO)**: δ 182.8, 157.6, 150.8, 137.9, 124.4, 123.2, 116.8, 109.5, 25.6; **MS (ESI)**: (m/z) = 184 (M+Na)⁺. **HRMS (ESI) (M+H)⁺ m/z calcd for C₉H₈NO₂ = 162.0549, found = 162.0549.

1-ethylindoline-2, 3-dione(4g):
(4g) orange solid, Yield: 80 %, mp 94-96 °C; IR(KBr): 2987, 1727, 1609, 1469, 1352, 1288, 1091, 1051, 868, 759, 472 cm⁻¹; ¹H NMR (500 MHz, CDCl₃+d₆-DMSO): δ 7.65-7.57 (m, 2H), 7.13 (t, 1H, J = 7.5 Hz), 6.96 (d, 1H, J = 7.9 Hz), 3.79 (q, 2H), 1.32 (t, 3H, J = 7.3 Hz). ¹³C NMR (100 MHz, d₆-DMSO): δ 11.8, 34.2, 109.6, 116.8, 123.0, 124.6, 137.9, 149.9, 157.1, 183.1. MS (ESI): (m/z) = 198 (M+Na)⁺. HRMS (ESI) (M+H)⁺ m/z calcd for C₁₀H₁₀NO₂ = 176.0706, found = 176.0703.

1-benzylindoline-2, 3-dione (4h):

(4h) yellow solid; Yield: 75 %; mp 136-138 °C; IR (KBr): 3028, 1732, 1611, 1468, 1346, 1174, 1075, 750, 692,469 cm⁻¹; ¹H NMR (300 MHz, CDCl₃+d₆-DMSO): δ 7.62 (d, 1H, J = 6.7 Hz), 7.48 (t, 1H, J = 7.7 Hz), 7.34 (s, 5H), 7.09 (t, 1H, J = 7.5 Hz), 6.78 (d, 1H, J = 8.1 Hz), 4.93 (s, 2H); ¹³C NMR (75 MHz, CDCl₃+d₆-DMSO): δ 182.5, 157.5, 149.9, 137.7, 133.9, 128.2, 127.3, 126.6, 124.4, 123.1, 116.7, 110.4, 43.1; MS (ESI): (m/z) = 260 (M+Na)⁺. HRMS (ESI) (M+1)⁺ m/z calcd for C₁₅H₁₂NO₂ = 238.0868, found = 238.0881.

(Z)-methyl 2-((3-chloro-2-oxoindolin-3-yl)methyl)-3-(o-tolyl)acrylate (5a):
(5a) solid; mp: 120-122°C; Yield: 85%; IR (KBr): 3128, 2923, 2812, 1850, 1760, 1620, 1525, 1471, 1342, 1292, 1143, 1073, 959, 843, 744 cm⁻¹; \(^1\)H NMR (300 MHz, CDCl₃): \(\delta\) 9.0 (d, \(J =\) 7.4 Hz, 1H), 7.99 (s, 1H), 7.19 (t, \(J =\) 7.7 Hz, 1H), 7.15-7.09 (m, 4H), 6.79 (t, \(J =\) 7.9, 7.4 Hz, 1H), 6.42 (d, \(J =\) 7.7 Hz, 1H), 4.82 (s, 2H), 3.78 (s, 3H), 2.18 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl₃): \(\delta\) 167.2, 166.8, 143.9, 137.7, 133.4, 130.2, 130.0, 128.8, 128.4, 125.9, 125.5, 124.9, 121.9, 110.8, 108.2, 52.2, 36.9, 29.6, 19.6; MS (ESI) \(m/z\) (%): 353 [M+H]+; HRMS-ESI(\(m/z\)) Calcd for C₂₀H₁₈O₃NCl: 353.1515 [M+H]+; Found: 353.1515.

(Z)-methyl 2-((3-bromo-2-oxoindolin-3-yl)methyl)-3-(o-tolyl)acrylate (7a):

(7a) solid; mp: 120-122°C; Yield: 81%; IR (KBr): 3128, 2923, 2812, 1850, 1760, 1620, 1525, 1471, 1342, 1292, 1143, 1073, 959, 843, 744 cm⁻¹; \(^1\)H NMR (300 MHz, CDCl₃): \(\delta\) 9.0 (d, \(J =\) 7.9, 8.8 Hz, 1H), 7.99 (s, 1H), 7.19 (t, \(J =\) 7.7, 8.8 Hz, 1H), 7.15-7.09 (m, 4H), 6.79 (t, \(J =\) 7.9, 8.6 Hz, 1H), 6.42 (d, \(J =\) 7.7 Hz, 1H), 4.82 (s, 2H), 3.78 (s, 3H), 2.18 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl₃): \(\delta\) 167.2, 166.8, 143.9, 137.7, 133.4, 130.2, 130.0, 128.8, 128.4, 125.9, 125.5, 124.9, 121.9, 110.8, 108.2, 52.2, 36.9, 29.6, 19.6; MS (ESI) \(m/z\) (%): 353 [M+H]+; HRMS-ESI(\(m/z\)) Calcd for C₂₀H₁₈O₃NCl: 353.1515 [M+H]+; Found: 353.1515.
124.9, 121.9, 110.8, 108.2, 52.2, 36.9, 29.6, 19.6; **MS (ESI) m/z (%)**: 400 [M+H]⁺; **HRMS-ESI(m/z)**: Calcd for C₂₀H₁₈O₃BrN : 401.1535 [M+H]⁺; Found: 401.1540.

(6a)2-Nitro-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-one⁷:

(6a) Solid; Yield: 58%; **¹H NMR (500 MHz, CDCl₃)**: δ 4.35 (d, J = 6.3 Hz, 1H), 5.46 (d, J = 6.3 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 7.10 (t, J = 7.9 Hz, 1H), 7.29-7.34 (m, 6H), 7.38 (d, J = 7.6 Hz, 1H), 8.34 (br s, 1H); **¹³C NMR (125 MHz, CDCl₃)**: δ 40.4, 41.8, 72.0, 110.3, 122.5, 122.9, 123.4, 128.4, 128.5, 128.8, 129.0, 129.8, 141.4, 171.4; **MS (ESI) m/z (%)**: 279.

4. **¹H NMR and ¹³C NMR Spectra of the Products**

¹H & ¹³CNMR of compound 2a:
$^1$H & $^{13}$C NMR of compound 2b:
$^{1}H$ & $^{13}C$ NMR of compound 2c:
$^1$H & $^{13}$C NMR of compound 2d:
$^1$H & $^{13}$C NMR of compound 2e:
$^1$H & $^{13}$C NMR of compound 2f:
$^1$H & $^{13}$C NMR of compound 2g:
$^{1}H$ & $^{13}C$ NMR of compound 2h:
$^1$H & $^{13}$C NMR of compound 2i:
$^1$H & $^{13}$C NMR of compound 2j:
$^{1}$H & $^{13}$C NMR of compound 2k:
$^1$H & $^{13}$C NMR of compound 2l:
$^1$H & $^{13}$C NMR of compound 2m:
$^{1}H$ & $^{13}C$ NMR of compound 2n:
$^1$H & $^{13}$C NMR of compound 3a:
$^{1}$H & $^{13}$C NMR of compound 3b:
$^1$H & $^{13}$C NMR of compound 3c:
$^1$H & $^{13}$C NMR of compound 3d:
$^1\text{H} \& ^{13}\text{C}$ NMR of compound 4a:
$^1$H & $^{13}$C NMR of compound 4b:
$^1$H & $^{13}$C NMR of compound 4c:
$^{1}H \& ^{13}C$ NMR of compound 4d:
$^{1}H$ & $^{13}C$ NMR of compound 4e:
$^1$H & $^{13}$C NMR of compound 4f:
$^1$H & $^{13}$C NMR of compound 4g:
$^1$H & $^{13}$C NMR of compound 4h:
$^1$H & $^{13}$C NMR of compound 5a:
$^1$H & $^{13}$C NMR of compound 6a:
$^1$H & $^{13}$C NMR of compound 7a:
References:


