Supporting Information for

Cu₂O-Catalyzed C(sp³)-H/C(sp³)-H Cross-Coupling Using TEMPO:

Synthesis of 3-(2-Oxoalkyl)-3-hydroxyoxindoles

Baoshuang Wang, Jiayi Zhu, Yang Wei, Guotian Luo,
Hongen Qu,* Liang-Xian Liu*

*Key Laboratory of Jiangxi University for Functional Materials Chemistry, College of Chemistry
and Chemical Engineering, Gannan Normal University, Ganzhou, Jiangxi 341000, P. R. China*

E-mail: lxliu@xmu.edu.cn

CONTENTS

1. General Methods and Materials	2
2. General Procedure and Spectroscopic Data of the Products 6.....	2
3. Copies of ¹ H, ¹³ C Spectra	9

1. General Methods

Infrared spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer using film KBr pellet techniques. ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for ^1H and ^{13}C NMR spectra. CDCl_3 or $\text{DMSO-}d_6$ was used as the NMR solvent. Mass spectra were recorded with Bruker Dalton Esquire 3000 plus LC-MS apparatus. Elemental analysis were carried out on a Perkin-Elmer 240B instrument. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

Materials

Commercially available starting materials and solvents were used as supplied, without further purification.

2. General Procedure for the Preparation of 6.

To a solution of TEMPO (0.04 mmol), Cu_2O (0.05 mmol), and K_3PO_4 (0.02 mmol) in ketone (0.5 mL) was added oxindole (0.2 mmol) under an air atmosphere and the mixture was stirred at room temperature for 4-48 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:4) to yield the corresponding product 6.

Spectroscopic Data of the Products 6.

3-Hydroxy-3-(2-oxopropyl)indolin-2-one (6a)

Amorphous solid. IR (KBr) ν_{max} : 3470, 3413, 1716, 1592, 1129 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 10.23 (s, 1H, NH, D_2O exchangeable), 7.24 (d, $J = 7.4$ Hz, 1H, Ar-H), 7.17 (t, $J = 7.7$ Hz, 1H, Ar-H), 6.91 (t, $J = 7.4$ Hz, 1H, Ar-H), 6.78 (d, $J = 7.7$ Hz, 1H, Ar-H), 5.99 (s, 1H, OH, D_2O exchangeable), 3.28 (d, $J = 16.5$ Hz, 1H, CH), 3.01 (d, $J = 16.5$ Hz, 1H, CH), 2.00 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 205.6, 178.6, 143.0, 132.0, 129.4, 124.1, 121.7, 109.9, 73.1, 50.7, 31.0. MS (ESI): 206 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_3$: C, 64.38; H, 5.40; N, 6.83. Found C, 64.05; H, 5.72; N, 6.61.

3-Hydroxy-3-(2-oxopentyl)indolin-2-one (6b)

Amorphous solid. IR (KBr) ν_{max} : 3436, 1700, 1671, 1623, 1128 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 10.20 (s, 1H, NH), 7.23 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.16 (dt, $J = 1.0, 7.7$ Hz, 1H, Ar-H), 6.89 (dt, $J = 1.0, 7.7$ Hz, 1H, Ar-H), 6.76 (d, $J = 7.5$ Hz, 1H, Ar-H), 5.95 (s, 1H, OH), 3.26 (d, $J = 16.4$ Hz, 1H, CH), 2.97 (d, $J = 16.4$ Hz, 1H, CH), 2.30 (dt, $J = 13.3, 6.9$ Hz, 2H, CH_2), 1.36-1.26 (m, 2H, CH_2), 0.68 (t, $J = 7.4$ Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 207.5, 178.6, 143.0, 131.9, 129.4, 124.1, 121.6, 109.8, 73.2, 49.9, 44.9, 16.8, 13.7. MS (ESI): 234 ($\text{M}+\text{H}^+$,

100). Anal calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found C, 67.26; H, 6.19; N, 5.63.

3-Hydroxy-3-(2-oxohexyl)indolin-2-one (6c)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3360, 1715, 1622, 1472, 1125 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 8.70 (s, 1H, NH), 7.32 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.24 (t, $J = 7.8$ Hz, 1H, Ar-H), 7.03 (t, $J = 7.5$ Hz, 1H, Ar-H), 6.88 (d, $J = 7.8$ Hz, 1H, Ar-H), 4.83 (s, 1H, OH), 3.19 (d, $J = 16.9$ Hz, 1H, CH), 2.98 (d, $J = 16.9$ Hz, 1H, CH), 2.41 (t, $J = 7.2$ Hz, 2H, CH_2), 1.55-1.46 (m, 2H, CH_2), 1.30-1.20 (m, 2H, CH_2), 0.86 (t, $J = 7.3$ Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 210.0, 178.6, 140.7, 130.3, 129.9, 124.1, 123.0, 110.6, 74.7, 48.0, 43.8, 25.3, 22.1, 13.7. MS (ESI): 248 ($\text{M}+\text{H}^+$, 100). Anal calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found C, 67.72; H, 7.29; N, 5.47.

3-Hydroxy-3-(2-oxoheptyl)indolin-2-one (6d)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3364, 1715, 1622, 1472, 1123 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 8.70 (s, 1H, NH), 7.33 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.25 (dt, $J = 1.0, 7.8$ Hz, 1H, Ar-H), 7.04 (dt, $J = 1.0, 7.5$ Hz, 1H, Ar-H), 6.89 (d, $J = 7.8$ Hz, 1H, Ar-H), 4.48 (s, 1H, OH), 3.18 (d, $J = 16.9$ Hz, 1H, CH), 2.98 (d, $J = 16.9$ Hz, 1H, CH), 2.41 (t, $J = 7.1$ Hz, 2H, CH_2), 1.92 (s, 1H), 1.57-1.49 (m, 2H, CH_2), 1.31-1.16 (m, 3H, CH_2), 0.86 (t, $J = 7.0$ Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ 210.2, 178.5, 140.6, 130.2, 130.0, 124.1, 123.1, 110.5, 74.6, 47.9, 44.1, 31.1, 22.9, 22.4, 13.8. MS (ESI): 262 ($\text{M}+\text{H}^+$, 100). Anal calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found C, 68.57; H, 7.41; N, 5.05.

3-Hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (6e)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3475, 3410, 1715, 1619, 1126 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 10.30 (s, 1H, NH), 7.89 (dd, $J = 7.4, 1.0$ Hz, 2H, Ar-H), 7.62 (t, $J = 7.4$ Hz, 1H, Ar-H), 7.49 (t, $J = 7.7$ Hz, 2H, Ar-H), 7.28 (d, $J = 7.4$ Hz, 1H, Ar-H), 7.16 (dt, $J = 1.0, 7.4$ Hz, 1H, Ar-H), 6.86 (t, $J = 7.4$ Hz, 1H, Ar-H), 6.82 (d, $J = 7.7$ Hz, 1H, Ar-H), 6.08 (s, 1H, OH), 4.08 (d, $J = 17.6$ Hz, 1H, CH), 3.59 (d, $J = 17.6$ Hz, 1H, CH). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 196.9, 178.8, 143.4, 136.7, 133.8, 132.2, 129.4, 129.2, 128.3, 124.1, 121.6, 109.9, 73.5, 46.2. MS (ESI): 268 ($\text{M}+\text{H}^+$, 100). Anal calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found C, 71.75; H, 5.14; N, 4.97.

3-Hydroxy-3-(2-oxo-2-*p*-tolylethyl)indolin-2-one (6f)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3437, 1650, 1622, 1508, 1446, 1130 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 10.22 (s, 1H, NH), 7.77 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.28 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.25 (d, $J = 7.6$ Hz, 1H, Ar-H), 7.15 (dt, $J = 1.2, 7.6$ Hz, 1H, Ar-H), 6.84 (dt, $J = 1.2, 7.6$ Hz, 1H, Ar-H), 6.79 (d, $J = 7.6$ Hz, 1H, Ar-H), 6.01 (s, 1H, OH), 4.01 (d, $J = 17.5$ Hz, 1H, CH), 3.53 (d, $J = 17.5$ Hz, 1H, CH), 2.34 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 196.4, 178.8, 144.2, 143.4, 134.3, 132.2, 129.7, 129.3, 128.5, 124.0, 121.5, 109.8, 73.5, 46.1, 21.6. MS (ESI): 282 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_3$: C, 72.58; H, 5.37; N, 4.98. Found C, 72.83; H, 5.11; N, 5.17.

3-Hydroxy-3-(2-(4-isobutylphenyl)-2-oxoethyl)indolin-2-one (6g)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3450, 3414, 1731, 1620, 1128 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 8.91 (s, 1H, NH), 7.82 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.38 (d, $J = 7.4$ Hz, 1H, Ar-H), 7.25-7.17 (m, 3H, Ar-H), 6.98 (t, $J = 7.4$ Hz, 1H, Ar-H), 6.90 (d, $J = 7.8$ Hz, 1H, Ar-H), 5.04 (s, 1H, OH), 3.85 (d, $J = 17.4$ Hz, 1H, CH), 3.59 (d, $J = 17.4$ Hz, 1H, CH), 2.52 (d, $J = 7.2$ Hz, 2H, CH_2), 1.94-1.83 (m, 1H, CH), 0.93 (d, $J = 6.6$ Hz, 6H, $2\times\text{CH}_3$). ^{13}C NMR (100 MHz, CDCl_3): δ 198.0, 179.0, 148.6, 141.0, 134.1, 130.6, 129.8, 129.4, 128.2, 124.2, 122.9, 110.7, 75.0, 45.4, 44.4, 30.1, 22.3. MS (ESI): 324 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_3$: C, 74.28; H, 6.55; N, 4.33. Found C, 73.93; H, 6.62; N, 4.07.

3-Hydroxy-3-(1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)indolin-2-one (6h)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3430, 1725, 1676, 1616, 1467, 1124 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 10.28 (s, 1H, NH), 7.63 (dd, $J = 7.8, 1.0$ Hz, 1H, Ar-H), 7.52 (dt, $J = 1.2, 7.5$ Hz, 1H, Ar-H), 7.36 (d, $J = 7.6$ Hz, 1H, Ar-H), 7.26 (t, $J = 7.8$ Hz, 1H, Ar-H), 7.23 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.16 (dt, $J = 1.2, 7.8$ Hz, 1H, Ar-H), 6.82 (d, $J = 7.6$ Hz, 1H, Ar-H), 6.80 (dt, $J = 1.0, 7.6$ Hz, 1H, Ar-H), 6.07 (s, 1H, OH), 3.30 (d, $J = 4.1$ Hz, 1H, CH), 3.09 (s, 1H), 3.07 (d, $J = 4.1$ Hz, 1H, CH), 2.76-2.69 (m, 1H), 2.28-1.16 (m, 1H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 196.8, 179.2, 144.9, 144.1, 134.1, 132.3, 130.8, 129.4, 129.3, 127.0, 126.7, 124.9, 121.3, 109.9, 74.8, 55.3, 29.6, 23.8. MS (ESI): 294 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_3$: C, 73.71; H, 5.15; N, 4.78. Found C, 73.85; H, 4.91; N, 4.72.

3-Hydroxy-3-(2-(2-methoxyphenyl)-2-oxoethyl)indolin-2-one (6i)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3436, 1701, 1624, 1466, 1127 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 10.23 (s, 1H, NH), 7.50 (dt, $J = 1.7, 8.5$ Hz, 1H, Ar-H), 7.28 (dd, $J = 7.7, 1.7$ Hz, 1H, Ar-H), 7.19 (d, $J = 7.2$ Hz, 1H, Ar-H), 7.15 (t, $J = 7.7$ Hz, 1H, Ar-H), 7.14 (d, $J = 8.5$ Hz, 1H, Ar-H), 6.93 (t, $J = 7.7$ Hz, 1H, Ar-H), 6.84 (t, $J = 7.2$ Hz, 1H, Ar-H), 6.78 (d, $J = 7.7$ Hz, 1H, Ar-H), 5.97 (s, 1H, OH), 3.91 (s, 3H, OCH_3), 3.90 (d, $J = 17.9$ Hz, 1H, CH), 3.58 (d, $J = 17.9$ Hz, 1H, CH). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 198.0, 178.8, 158.9, 143.4, 134.5, 132.2, 129.7, 129.2, 127.6, 123.9, 121.5, 120.8, 113.0, 109.8, 73.4, 56.3, 51.4. MS (ESI): 298 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_4$: C, 68.68; H, 5.09; N, 4.71. Found C, 69.03; H, 4.87; N, 4.59.

3-Hydroxy-3-(2-(naphthalen-1-yl)-2-oxoethyl)indolin-2-one (6j)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3436, 1700, 1671, 1623, 1128 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 10.33 (s, 1H, NH), 8.10 (t, $J = 7.7$ Hz, 2H, Ar-H), 8.02 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.97 (d, $J = 8.4$ Hz, 1H, Ar-H), 7.59 (t, $J = 7.7$ Hz, 1H, Ar-H), 7.53 (dt, $J = 1.3, 8.4$ Hz, 1H, Ar-H), 7.47 (dt, $J = 1.3, 8.4$ Hz, 1H, Ar-H), 7.33 (d, $J = 7.7$ Hz, 1H, Ar-H), 7.17 (dt, $J = 1.3, 7.7$ Hz, 1H, Ar-H), 6.86 (t, $J = 7.7$ Hz, 1H, Ar-H), 6.80 (d, $J = 7.7$ Hz, 1H, Ar-H), 6.12 (s, 1H, OH), 4.06 (d, $J = 16.8$ Hz, 1H, CH), 3.71 (d, $J = 16.8$ Hz, 1H, CH). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 201.2, 178.7, 143.3, 135.6, 133.8, 133.0, 132.0, 129.6, 129.4, 128.8, 128.6, 128.0, 126.8, 125.4, 125.2, 124.3, 121.6, 109.9, 73.8, 49.6. MS (ESI): 318 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{20}\text{H}_{15}\text{NO}_3$: C, 75.70; H, 4.76; N, 4.41. Found C, 76.03; H, 4.43; N, 4.48.

3-(2-(furan-2-yl)-2-oxoethyl)-3-hydroxyindolin-2-one (6k)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3430, 1720, 1615, 1373, 1245, 1163, 750 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 10.26 (s, 1H, NH), 7.93 (d, $J = 1.1$ Hz, 1H, Ar-H), 7.47 (d, $J = 3.5$ Hz, 1H, Ar-H), 7.26 (d, $J = 7.2$ Hz, 1H, Ar-H), 7.14 (dt, $J = 1.1, 7.7$ Hz, 1H, Ar-H), 6.84 (dt, $J = 1.1, 7.2$ Hz, 1H, Ar-H), 6.77 (d, $J = 7.7$ Hz, 1H, Ar-H), 6.66 (dd, $J = 3.5, 1.1$ Hz, 1H, Ar-H), 6.11 (s, 1H, OH), 3.79 (d, $J = 16.3$ Hz, 1H, CH), 3.30 (d, $J = 16.3$ Hz, 1H, CH). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 184.8, 178.5, 152.0, 148.5, 143.1, 131.6, 129.5, 124.3, 121.6, 119.6, 113.0, 109.9, 73.4, 45.6. MS (ESI): 258 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{14}\text{H}_{11}\text{NO}_4$: C, 65.37; H, 4.31; N, 5.44. Found C, 65.12; H, 4.60; N, 5.19.

3-Hydroxy-3-(2-oxocycloheptyl)indolin-2-one (6l)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3434, 1697, 1618, 1506, 1446, 1129 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 8.61 (s, 1H, NH), 8.32 (s, 1H, NH), 7.42 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.31 (d, $J = 7.5$ Hz, 1H, Ar-H), 7.26 (dt, $J = 2.0, 7.7$ Hz, 1H, Ar-H), 7.25 (dt, $J = 2.0, 7.7$ Hz, 1H, Ar-H), 7.06 (dt, $J = 0.9, 7.6$ Hz, 1H, Ar-H), 7.04 (dt, $J = 0.9, 7.6$ Hz, 1H, Ar-H), 6.88 (t, $J = 7.7$ Hz, 2H, Ar-H), 5.10 (s, 1H, OH), 4.91 (s, 1H, OH), 3.29 (dd, $J = 11.0, 2.9$ Hz, 1H, Ar-H), 2.95 (dd, $J = 11.0, 2.9$ Hz, 1H, Ar-H), 2.71-2.46 (m, 4H), 1.70-1.50 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 217.1, 178.8, 177.7, 141.2, 141.0, 129.9, 129.8, 129.5, 129.4, 125.7, 124.3, 123.2, 123.1, 110.4, 110.3, 78.5, 78.3, 57.5, 56.4, 44.7, 44.6, 30.1, 29.2, 24.8, 24.6. MS (ESI): 407 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_5$: C, 67.97; H, 5.46; N, 6.89. Found C, 70.26; H, 5.81; N, 6.57.

5-Fluoro-3-hydroxy-3-(2-oxopropyl)indolin-2-one (6m)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3438, 1715, 1608, 1511, 1128 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 10.24 (s, 1H, NH), 7.15 (dd, $J = 8.3, 2.7$ Hz, 1H, Ar-H), 7.00 (dq, $J = 8.5, 2.7$ Hz, 1H, Ar-H), 6.76 (dd, $J = 8.5, 4.4$ Hz, 1H, Ar-H), 6.09 (s, 1H, OH), 3.34 (d, $J = 17.0$ Hz, 1H, CH), 3.05 (d, $J = 17.0$ Hz, 1H, CH), 2.01 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 205.6, 178.6, 156.8 (d, $J = 236.5$ Hz), 139.2 (d, $J = 1.4$ Hz), 133.8 (d, $J = 7.8$ Hz), 115.4 (d, $J = 23.1$ Hz), 112.1 (d, $J = 24.5$ Hz), 110.5 (d, $J = 7.9$ Hz), 73.3, 50.5, 30.9. MS (ESI): 224 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{11}\text{H}_{10}\text{FNO}_3$: C, 59.19; H, 4.52; N, 8.51. Found C, 58.87; H, 4.65; N, 8.79.

5-Fluoro-3-hydroxy-3-(2-oxo-2-phenylethyl)indolin-2-one (6n)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3443, 1710, 1611, 1506, 1128 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 10.29 (s, 1H, NH), 7.88 (d, $J = 7.5$ Hz, 2H, Ar-H), 7.62 (t, $J = 7.5$ Hz, 1H, Ar-H), 7.49 (t, $J = 7.5$ Hz, 2H, Ar-H), 7.20 (dd, $J = 8.4, 2.6$ Hz, 1H, Ar-H), 6.98 (dd, $J = 8.4, 2.6$ Hz, 1H, Ar-H), 6.78 (q, $J = 8.4$ Hz, 1H, Ar-H), 6.19 (s, 1H, OH), 4.10 (d, $J = 17.7$ Hz, 1H, CH), 3.61 (d, $J = 17.7$ Hz, 1H, CH). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 201.7, 183.5, 163.0 (d, $J = 236.2$ Hz), 144.3, 141.3, 138.8 (d, $J = 7.6$ Hz), 138.7, 133.9, 133.1, 120.1 (d, $J = 23.2$ Hz), 116.8 (d, $J = 24.4$ Hz), 115.2 (d, $J = 7.7$ Hz), 78.5, 50.9. MS (ESI): 286 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{16}\text{H}_{12}\text{FNO}_3$: C, 67.36; H, 4.24; N, 4.91. Found C, 67.05; H, 4.47; N, 5.06.

5-Fluoro-3-hydroxy-3-(2-(naphthalen-1-yl)-2-oxoethyl)indolin-2-one (6o)

Amorphous solid. IR (KBr) $\nu_{\max}$: 1728, 1375, 1246, 1161, 757 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 10.35 (s, 1H, NH), 8.12 (d, J = 7.4 Hz, 2H, Ar-H), 8.07 (d, J = 8.2 Hz, 1H, Ar-H), 7.96 (d, J = 7.4 Hz, 1H, Ar-H), 7.59 (t, J = 8.2 Hz, 1H, Ar-H), 7.55 (t, J = 6.6 Hz, 1H, Ar-H), 7.49 (t, J = 6.6 Hz, 1H, Ar-H), 7.26 (dd, J = 7.4, 2.5 Hz, 1H, Ar-H), 6.99 (dt, J = 2.5, 9.6 Hz, 1H, Ar-H), 6.78 (dd, J = 8.2, 4.3 Hz, 1H, Ar-H), 6.24 (s, 1H, OH), 4.12 (d, J = 17.1 Hz, 1H, CH), 3.72 (d, J = 17.1 Hz, 1H, CH). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 205.9, 183.5, 163.1 (d, J = 236.5 Hz), 144.2, 140.1, 138.6, 138.5 (d, J = 7.8 Hz), 137.9, 134.3, 133.7, 133.6, 132.9, 131.6, 130.1, 130.0, 120.2 (d, J = 23.2 Hz), 117.0 (d, J = 24.5 Hz), 115.3 (d, J = 7.8 Hz), 78.8, 54.2. MS (ESI): 336 ($\text{M}+\text{H}^+$, 100). Anal calcd for $\text{C}_{20}\text{H}_{14}\text{FNO}_3$: C, 71.64; H, 4.21; N, 4.18. Found C, 71.27; H, 4.50; N, 4.14.

5-Chloro-3-hydroxy-3-(2-oxopropyl)indolin-2-one (6p)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3435, 3238, 1702, 1622, 1185, 1130 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 10.35 (s, 1H, NH), 7.31 (d, J = 2.0 Hz, 1H, Ar-H), 7.21 (dd, J = 8.2, 2.0 Hz, 1H, Ar-H), 6.78 (d, J = 8.2 Hz, 1H, Ar-H), 6.09 (s, 1H, OH), 3.38 (d, J = 17.4 Hz, 1H, CH), 3.06 (d, J = 17.4 Hz, 1H, CH), 2.00 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 205.7, 178.3, 142.0, 134.2, 129.1, 125.7, 124.4, 111.3, 73.1, 50.4, 30.8. MS (ESI): 240 ($\text{M}+\text{H}^+$, 100), 242 ($\text{M}+\text{H}^+$, 30). Anal calcd for $\text{C}_{11}\text{H}_{10}\text{ClNO}_3$: C, 55.13; H, 4.21; N, 5.84. Found C, 55.22; H, 4.38; N, 5.52.

5-Chloro-3-hydroxy-3-(2-oxo-2-*p*-tolylethyl)indolin-2-one (6q)

Amorphous solid. IR (KBr) $\nu_{\max}$: 3446, 1672, 1615, 1443, 1131 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 10.40 (s, 1H, NH), 7.78 (d, J = 8.2 Hz, 2H, Ar-H), 7.37 (d, J = 2.2 Hz, 1H, Ar-H), 7.29 (d, J = 8.2 Hz, 2H, Ar-H), 7.20 (dd, J = 8.3, 2.2 Hz, 1H, Ar-H), 6.81 (d, J = 8.3 Hz, 1H, Ar-H), 6.18 (s, 1H, OH), 4.10 (d, J = 17.9 Hz, 1H, CH), 3.58 (d, J = 17.9 Hz, 1H, CH), 2.35 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 196.5, 178.5, 144.4, 142.4, 134.5, 134.0, 129.7, 129.0, 128.5, 125.6, 124.4, 111.2, 73.5, 46.0, 21.6. MS (ESI): 316 ($\text{M}+\text{H}^+$, 100), 318 ($\text{M}+\text{H}^+$, 30). Anal calcd for $\text{C}_{17}\text{H}_{14}\text{ClNO}_3$: C, 64.67; H, 4.47; N, 4.44. Found C, 64.51; H, 4.83; N, 4.16.

5-Chloro-3-hydroxy-3-(2-(naphthalen-1-yl)-2-oxoethyl)indolin-2-one (6r)

Amorphous solid. IR (KBr) ν_{max} : 3428, 3189, 1703, 1616, 1450, 1125 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 10.45 (s, 1H, NH), 8.13 (t, $J = 7.4$ Hz, 2H, Ar-H), 8.10 (dd, $J = 7.4, 1.2$ Hz, 1H, Ar-H), 7.97 (dd, $J = 7.4, 1.2$ Hz, 1H, Ar-H), 7.59 (t, $J = 7.4$ Hz, 1H, Ar-H), 7.54 (dt, $J = 1.4, 7.6$ Hz, 1H, Ar-H), 7.50 (dt, $J = 1.4, 7.6$ Hz, 1H, Ar-H), 7.43 (d, $J = 2.2$ Hz, 1H, Ar-H), 7.22 (dd, $J = 8.3, 2.2$ Hz, 1H, Ar-H), 6.82 (d, $J = 8.3$ Hz, 1H, Ar-H), 6.25 (s, 1H, OH), 4.16 (d, $J = 17.3$ Hz, 1H, CH), 3.72 (d, $J = 17.3$ Hz, 1H, CH). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ 201.2, 178.5, 142.2, 135.1, 134.2, 133.8, 133.2, 129.6, 129.2, 129.0, 128.9, 128.2, 126.8, 125.7, 125.3, 125.2, 124.6, 111.3, 73.8, 49.4. MS (ESI): 352 ($\text{M}+\text{H}^+$, 100), 354 ($\text{M}+\text{H}^+$, 30). Anal calcd for $\text{C}_{20}\text{H}_{14}\text{ClNO}_3$: C, 68.28; H, 4.01; N, 3.98. Found C, 67.93; H, 4.29; N, 4.05.

3. Copies of ^1H , ^{13}C NMR Spectra

Compound 6a

Compound 6b

Compound 6c

Compound **6d**

Compound 6e

Compound 6f

Compound 6g

KYB-62AC
KYB-62AC-H

Compound 6h

Compound 6i

Compound 6j

Compound 6k

Compound 6l

Compound 6m

Compound 6n

Compound 60

Compound 6p

KYD-68A
KYD-68A-H

Compound **6q**

KYB-76B
KYB-76B-II