

Supporting Information for:

A novel and efficient synthesis of azaarene-substituted 3-hydroxy-2-oxindoles via sp^3 C-H functionalization of 2-methyl azaarenes and (2-azaaryl)methanes over heterogeneous, reusable silica-supported dodecatungstophosphoric acid catalyst

Shafeek A. R. Mulla,^{a,*} Mohsinkhan Y. Pathan and Santosh S. Chavan

^a Chemical Engineering & Process Development Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India.

Tel: +91 20 25902316

Fax: +91 20 25902676

E-mail: sa.mulla@ncl.res.in

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1. General experimental details

All reactions were performed under Nitrogen atmosphere. All chemicals and reagents required for the reactions were procured from Sigma-Aldrich with purity >98% and used without further purification. All reactions were monitored by TLC. TLC was performed on 0.25 mm E. Merck pre-coated silica gel plates (60F254). Column chromatography was performed on silica gel, Merck grade 60–120 mesh size. The products were characterized using ^1H NMR, ^{13}C NMR spectra. NMR spectra were recorded on Bruker AC-200 spectrometers. Chemical shifts are reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. All protected isatin are known compounds and prepared according to the literature.^[1]

2. General Procedure for the preparation of DTP/SiO₂

DTP impregnated SiO₂ (20% DTP/SiO₂) catalyst was prepared by a incipient wetness technique^[2] as follows.

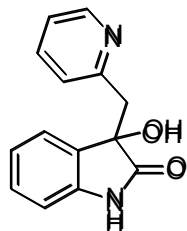
2 g of dry dodecatungstophosphoric acid (DTP) was weighed accurately. This was dissolved in 8 ml of methanol. The solution was added in small aliquots of 1 ml each time to the silica with constant stirring with a glass rod properly. The solution was added at time intervals of 2 min. Initially on addition of the DTP solution, silica was in a powdery form but on complete addition it formed a paste. The paste on further kneading for 10 min resulted in a free flowing powder. The prepared catalyst was dried at 120°C for removal of water and other occluded volatiles and subsequently calcined at 285°C for 3 h.

3. General procedure for the DTP/SiO₂ catalyzed C-H functionalization

A mixture of isatin **1a** (1 mmol), picoline **2a** (2 mmol) in a 5 ml DMF solvent was stirred at 120°C for 8 h in the presence of 50 mg DTP/SiO₂ catalyst. The completion of the reaction was monitored by TLC. After completion of reaction, reaction mixture was diluted with ethyl acetate (10 ml) and catalyst was recovered by filtration. The filtrate was washed with aqueous NaHCO₃ and then with water followed by separation of aqueous layer and organic layer. The organic layer is dried over anhydrous Na₂SO₄ and concentrate in vacuum to gives the crude product. The crude product was purified by silica gel column chromatography using 70:30 ratio of pet ether/ethyl acetate to afford the pure azaarene- substituted 3-hydroxy-2-oxindole.

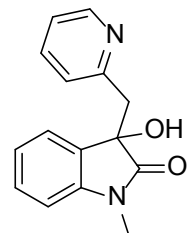
4. Experimental characterization data for products

3-hydroxy-3-(pyridine-2-ylmethyl)indolin-2-one (3a)



White solid, M.P.-152-154 °C; ^1H NMR (200 MHz, DMSO-D_6): δ 10.17 (s, 1H), 8.34 (d, $J=4.55$ Hz, 1H), 7.68 – 7.59 (m, 1H), 7.21 – 7.10 (m, 3H), 6.99-84 (m, 2H), 6.7 (d, $J=7.71$ Hz, 1H), 6.34 (s, 1H), 3.35 (d, $J=13.14$ Hz, 1H), 3.25 (d, $J=13.14$ Hz, 1H); ^{13}C NMR (50 MHz, DMSO-D_6) δ 178.36, 155.88, 148.08, 141.40, 135.59, 130.76, 128.56, 124.36, 124.12, 121.43, 120.87, 109.02, 75.45, 44.89.

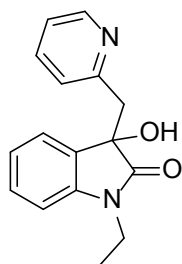
3-hydroxy-1-methyl-3-(pyridine-2-ylmethyl)indolin-2-one (3b)



Yellow solid, mp 135-137 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.49 (s, 1H), 7.60 (t, 1H), 7.25 – 7.15 (m, 2H), 7.0 (d, $J=7.71$ Hz, 1H), 6.82 (t, $J=7.45$ Hz, 1H), 6.78-6.71 (m, 2H), 3.25 (d, $J=14.78$ Hz, 1H), 3.10 (s, 3H), 3.05 (d, $J=14.78$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 176.74, 157.13, 147.72, 142.82, 137.34, 130.76, 129.32, 124.85, 123.85, 122.68,

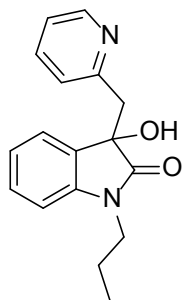
122.34, 108.20, 42.64, 26.09.

1-ethyl-3-hydroxy-3-(pyridine-2-ylmethyl)indolin-2-one (3c)



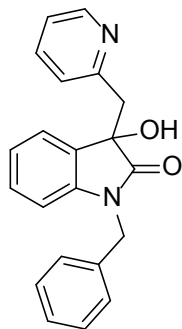
Yellow solid, mp 94-96 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.50 (d, $J=4.3$ Hz, 1H), 7.16-7.57 (m, 1H), 7.26-7.14 (m, 2H), 7.00 (d, $J=7.71$ Hz, 1H), 6.90-6.73 (m, 3H), 3.64 (q, 2H), 3.26 (d, $J=14.53$ Hz, 1H), 3.10 (d, $J=14.53$ Hz, 1H), 1.18 (t, $J=7.20$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 175.60, 156.62, 147.04, 141.34, 138.82, 130.45, 128.67, 124.27, 123.46, 121.88, 121.74, 107.71, 75.40, 42.04, 33.97, 11.85.

3-hydroxy-1-propyl-3-(pyridine-2-ylmethyl)indolin-2-one (3d)



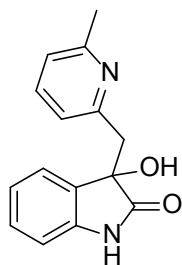
Off white solid, mp 102-104 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.61 (d, $J=4.80$ Hz, 1H), 7.75 (t, $J=7.71$ Hz, 1H), 7.37-7.25 (m, 2H), 7.13 (d, $J=7.71$ Hz, 1H), 7.01-6.94 (m, 2H), 6.85 (d, $J=7.83$ Hz, 1H), 3.68 (sextet, 2H), 3.35 (d, $J=14.65$ Hz, 1H), 3.20 (d, $J=14.65$ Hz, 1H), 1.74 (q, 2H), 0.97 (t, $J=7.45$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 175.95, 156.54, 146.98, 141.68, 136.83, 130.33, 128.61, 124.27, 123.37, 121.83, 107.84, 75.33, 42.13, 40.77, 19.92, 10.65.

1-benzyl-3-hydroxy-3-(pyridine-2-ylmethyl)indolin-2-one(3e)



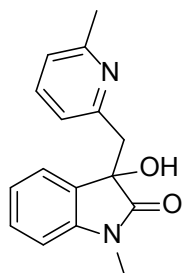
Brown solid, mp 111-113 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.51 (d, $J=4.67$ Hz, 1H), 7.69-6.60 (m, 1H), 7.28-7.03 (m, 8H), 6.87 (t, $J=6.7$ Hz, 2H), 6.60 (d, $J=7.71$ Hz, 1H), 4.85 (d, $J=15.66$, 1H), 4.70 (d, $J=15.66$, 1H), 3.30 (d, $J=14.65$ Hz, 1H), 3.18 (d, $J=14.65$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ = 176.06, 156.20, 146.70, 141.30, 137.19, 134.93, 128.67, 128.08, 126.93, 126.59, 124.53, 123.36, 122.18, 108.62, 75.39, 43.00, 42.03.

3-hydroxy-3-((6-methylpyridin-2-yl)methyl)indolin-2-one (3f)



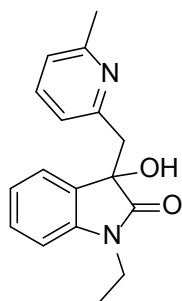
Red solid, mp 178-180 °C; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 10.19 (s, 1H), 7.55 (t, $J=7.71$ Hz, 1H), 7.18 – 6.87 (m, 5H), 6.73 (d, $J=7.58$ Hz, 1H), 6.43 (s, 1H), 3.32 (d, $J=13.39$ Hz, 1H), 3.15 (d, $J=13.26$ Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (50 MHz, $\text{DMSO}-d_6$) δ 178.38, 156.12, 155.27, 141.49, 135.94, 130.95, 128.49, 124.33, 120.93, 120.72, 120.60, 108.96, 75.38, 44.42, 23.54.

3-hydroxy-1-methyl-3-((6-methylpyridin-yl)methyl)indolin-2-one (3g)



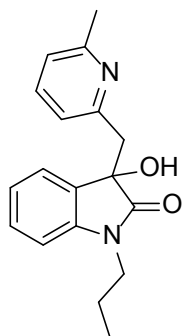
Yellow solid, mp 126-127 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.01 (s, 1H), 7.62 (t, $J=7.45$ Hz, 1H), 7.34 (m, 1H), 7.12 (d, $J=7.71$ Hz, 1H), 6.90 (m, 1H), 6.73 (m, 3H), 3.30 (d, $J=14.53$ Hz, 1H), 3.22 (s, 3H), 2.99 (d, $J=14.53$ Hz, 1H), 2.67 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 175.99, 157.06, 156.71, 142.21, 137.76, 130.52, 128.59, 123.16, 121.99, 121.39, 107.50, 41.48, 25.44, 24.06.

1-ethyl-3-hydroxy-3-((6-methylpyridin-2-yl)methyl)indolin-2-one (3h)



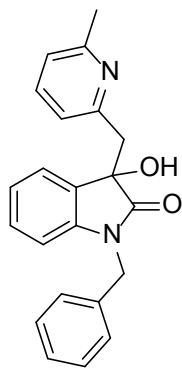
Yellow solid, mp 126-127 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.13-7.53 (m, 2H), 7.23 (t, $J=7.45$ Hz, 2H), 6.90-6.74 (m, 3H), 3.65 (q, 2H), 3.20 (d, $J=14.53$ Hz, 1H), 3.16 (d, $J=14.53$ Hz, 1H), 2.57 (s, 3H), 1.19 (t, $J=7.07$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 176.81, 157.46, 142.56, 138.45, 132.02, 129.86, 124.74, 123.13, 112.17, 108.96, 75.30, 42.56, 35.25, 24.74, 13.18.

3-hydroxy-3-((6-methylpyridin-2-yl)methyl)-1-propylindolin-2-one (3i)



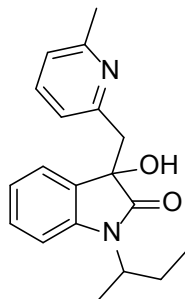
Yellow solid, mp 101-103 °C; ^1H NMR (200 MHz, CDCl_3) δ 7.90 (s, 1H), 7.59 (t, $J=7.71$ Hz, 1H), 7.31 (t, $J=7.71$ Hz, 1H), 7.19 (d, $J=7.71$ Hz, 1H), 6.98-6.83 (m, 4H), 3.68 (sextet, 2H), 3.32 (d, $J=14.65$ Hz, 1H), 3.08 (d, $J=14.65$ Hz, 1H), 2.64 (s, 3H), 1.75 (q, 2H), 0.98 (t, $J=7.45$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ = 176.71, 157.11, 156.78, 142.38, 137.68, 131.39, 129.23, 124.06, 122.49, 122.07, 121.79, 108.54, 76.06, 42.50, 41.47, 24.14, 20.68, 11.37.

1-benzyl-3-hydroxy-3-((6-methylpyridin-2-yl)methyl)indolin-2-one (3j)



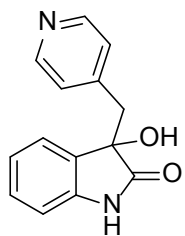
Yellow solid, mp 176-178 °C; ^1H NMR (200 MHz, CDCl_3) δ 7.55 (t, $J=7.58$ Hz, 1H), 7.24-7.04 (m, 8H), 6.85 (s, 3H), 6.62 (d, $J=7.71$ Hz, 1H), 4.86 (d, $J=15.66$ Hz, 1H), 4.74 (d, $J=15.66$ Hz, 1H), 3.30 (m, 2H), 2.58 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 176.63, 156.83, 141.88, 135.63, 131.14, 129.22, 128.74, 127.57, 127.22, 124.00, 122.79, 109.24, 75.97, 43.61, 42.18, 15.22.

1-Sec-butyl-3-hydroxy-3-((6-methylpyridin-2-yl)methyl)indolin-2-one (3k)



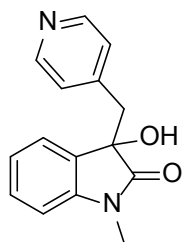
Red Gum; ^1H NMR (200 MHz, CDCl_3) δ 7.34 (t, $J=7.71$ Hz, 1H), 7.15-7.08 (m, 2H), 6.88-6.82 (m, 4H), 4.22 (m, 1H), 2.59 (s, 3H), 1.98-1.62 (m, 2H), 1.37 (d, 3H), 1.13 (t, 1H), 0.86-0.78 (m, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 176.65, 158.84, 156.51, 141.82, 137.85, 131.67, 129.03, 124.28, 122.17, 109.90, 109.74, 75.60, 49.85, 49.62, 42.89, 42.60, 26.41, 26.25, 23.85, 22.57, 17.79, 17.52, 11.30.

3-hydroxy-3-(pyridine-4-ylmethyl)indolin-2-one (3l)



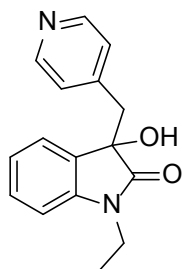
Red solid, mp 183-1185 °C; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 10.19 (s, 1H), 8.36 (d, $J=4.29$ Hz, 2H), 7.24 – 7.14 (m, 2H), 7.01 – 6.94 (m, 3H), 6.7 (d, $J=7.71$ Hz, 1H), 6.32 (s, 1H), 3.25 (d, $J=12.38$ Hz, 1H), 3.04 (d, $J=12.51$ Hz, 1H); ^{13}C NMR (50 MHz, $\text{DMSO}-d_6$) δ 178.15, 148.54, 143.93, 141.29, 130.26, 128.94, 124.32, 121.18, 109.25, 75.80, 42.38.

3-hydroxy-1-methyl-3-(pyridin-4-ylmethyl)indolin-2-one (3m)



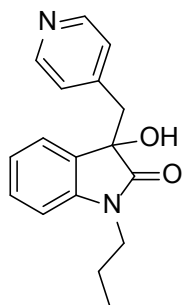
Yellow solid, mp 201-203 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.22 (s, 1H), 7.20 (t, $J=7.58$ Hz, 1H), 7.1 (d, $J=6.32$ Hz, 1H), 7.00 (d, $J=7.33$ Hz, 1H), 6.90 (d, $J=5.05$ Hz, 1H), 6.58 (d, $J=7.71$ Hz, 1H), 4.88 (s, 1H), 3.24 (d, $J=12.63$ Hz, 1H), 3.08 (d, $J=12.51$ Hz, 1H), 2.92 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ = 177.95, 148.34, 143.74, 143.51, 130.58, 129.52, 124.83, 123.66, 109.06, 44.55, 26.58.

1-ethyl-3-(4-pyridylmethyl)-3-hydroxyindolin-2-one (3n)



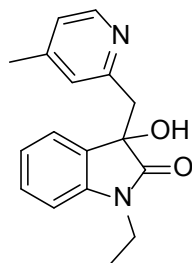
Brown solid, mp 171-173 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.21 (d, $J=6.06$ Hz, 2H), 7.25-7.17 (m, 2H), 7.01 (t, $J=7.96$ Hz, 1H), 6.86 (d, $J=6.06$ Hz, 2H), 6.60 (d, $J=7.45$ Hz, 1H), 4.60 (s, 1H), 3.48 (q, 2H), 3.26 (d, $J=12.51$ Hz, 1H), 3.12 (d, $J=12.51$ Hz, 1H), 0.92 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 176.07, 147.00, 144.52, 141.44, 129.38, 128.36, 125.28, 123.71, 122.30, 107.96, 62.54, 43.57, 33.90, 11.46.

3-hydroxy-1-propyl-3-(4-pyridylmethyl)indolin-2-one (3o)



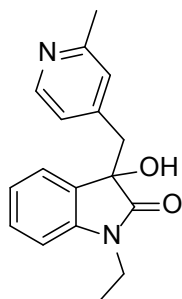
White solid, mp 164-166 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.15 (d, $J=5.94$ Hz, 2H), 7.23-7.15 (m, 2H), 7.02 (t, $J=6.7$ Hz, 1H), 6.85-6.82 (m, 2H), 6.60-6.56 (m, 1H), 5.07 (s, 1H), 3.54-3.08 (m, 4H), 1.29 (q, 2H), 0.69 (t, $J=7.58$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 177.28, 148.18, 144.34, 142.57, 129.78, 129.14, 125.68, 124.27, 122.76, 108.76, 108.64, 75.63, 43.96, 41.43, 20.35, 11.14.

1-ethyl-3-hydroxy-3-((4-methylpyridin-2-yl)methyl)indolin-2-one (3p)



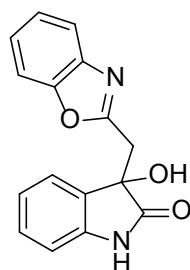
Brown solid, mp 98-100 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.35 (d, $J=5.05$ Hz, 1H), 7.22-7.14 (m, 1H), 7.02 (d, $J=4.17$ Hz, 1H), 6.89-6.73 (m, 4H), 3.66 (q, 2H), 3.24 (d, $J=14.64$ Hz, 1H), 2.95 (d, $J=14.64$ Hz, 1H), 2.25 (s, 3H), 1.18 (t, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 175.74, 156.67, 147.89, 146.99, 141.35, 137.04, 130.74, 128.55, 124.84, 123.45, 122.61, 121.81, 107.65, 75.50, 41.79, 33.95, 20.44, 11.88.

1-ethyl-3-hydroxy-3-((2-methylpyridin-4-yl)methyl)indolin-2-one (3q)



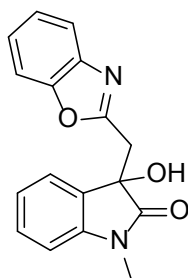
White solid, mp 109-111 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.14 (d, $J=5.56$ Hz, 1H), 7.20 (t, $J=7.20$ Hz, 3H), 7.02 (t, $J=7.33$ Hz, 3H), 6.87 (s, 1H), 6.78 (d, $J=4.93$ Hz, 1H), 6.64 (d, $J=7.83$ Hz, 1H), 3.43 (q, 2H), 3.26 (d, $J=12.51$ Hz, 1H), 3.12 (d, $J=12.51$ Hz, 1H), 2.46 (s, 3H), 0.94 (t, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ = 176.59, 156.46, 146.03, 142.06, 130.06, 128.87, 126.00, 124.37, 122.92, 108.61, 76.36, 44.21, 34.57, 22.81, 12.15.

3-(benzo[d]oxazol-2-ylmethyl)-3-hydroxyindolin-2-one (3r)



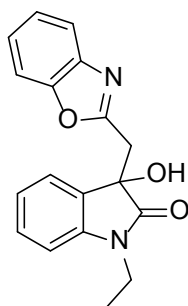
Faint Yellow solid, mp 157-159 °C; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 10.39 (s, 1H), 8.07-8.03 (m, 1H), 7.94 – 7.89 (m, 1H), 7.54 – 7.38 (m, 2H), 7.27-7.19 (m, 1H), 7.13 (d, $J=6.69$ Hz, 1H), 6.98-6.90 (m, 1H), 6.80 (d, $J=7.71$ Hz, 1H), 6.61 (s, 1H), 3.72 (d, $J=14.15$ Hz, 1H), 3.58 (d, $J=14.15$ Hz, 1H); ^{13}C NMR (50 MHz, $\text{DMSO}-d_6$) δ 177.16, 164.59, 151.23, 141.25, 134.78, 129.69, 128.89, 125.20, 124.28, 123.86, 121.62, 121.20, 120.95, 109.08, 73.85, 40.11.

3-(benzo[d]oxazol-2-ylmethyl)-3-hydroxy-1-methylindolin-2-one (3s)



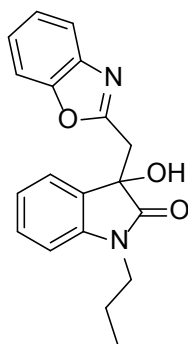
White solid, mp 102-104 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.05 (d, $J=7.83$ Hz, 1H), 7.87 (d, $J=6.69$ Hz, 1H), 7.54-7.27 (m, 3H), 7.13-6.99 (m, 2H), 6.83 (d, $J=7.83$ Hz, 1H), 5.43 (s, 1H), 3.75 (d, $J=15.16$ Hz, 1H), 3.55 (d, $J=15.28$ Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 175.92, 166.09, 151.74, 143.09, 134.53, 129.86, 129.49, 126.30, 125.32, 124.20, 123.02, 122.67, 121.42, 108.36, 75.14, 40.83, 26.21.

3-(benzo[d]oxazol-2-ylmethyl)-1-ethyl-3-hydroxyindolin-2-one (3t)



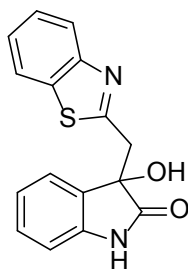
Red solid, mp 112-114 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.04 (d, $J=7.45$ Hz, 1H), 7.89-7.83 (m, 1H), 7.56-7.26 (m, 3H), 7.13 (d, $J=7.45$ Hz, 1H), 7.00 (d, $J=7.45$ Hz, 1H), 6.84 (d, $J=7.83$ Hz, 1H), 4.49 (s, 1H), 3.78 (q, 2H), 3.72 (d, $J=15.03$ Hz, 1H), 3.56 (d, $J=15.03$ Hz, 1H), 1.27 (t, $J=7.20$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 175.59, 165.67, 152.22, 142.22, 134.69, 129.78, 126.15, 125.18, 124.41, 122.80, 121.35, 108.45, 75.19, 41.06, 34.72, 12.42.

3-(benzo[d]oxazol-2-ylmethyl)-3-hydroxy-1-propylindolin-2-one (3u)



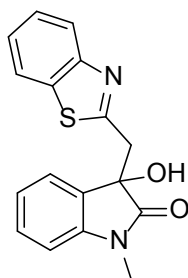
Red Thick Gum; ^1H NMR (200 MHz, CDCl_3) δ 8.05-7.82 (m, 2H), 7.55-7.25 (m, 4H), 7.13-6.80 (m, 2H), 3.77-3.49 (m, 4H), 1.72 (q, 2H), 0.99 (t, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 176.08, 165.58, 152.59, 142.68, 134.85, 129.81, 126.14, 125.17, 124.67, 124.40, 122.96, 122.81, 121.41, 108.68, 75.25, 41.63, 41.27, 20.65, 11.39.

3-(benzo[d]thiazol-2-ylmethyl)-3-hydroxyindolin-2-one (3v)



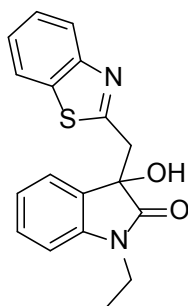
Brown solid, mp 117-119 °C; ^1H NMR (200 MHz, $\text{DMSO}-d_6$) δ 10.33 (s, 1H), 8.01-7.83 (m, 2H), 7.48-7.36 (m, 2H), 7.21-7.06 (m, 2H), 6.88 (t, $J=7.45$ Hz, 1H), 6.74 (d, $J=7.71$ Hz, 1H), 6.55 (s, 1H), 3.67 (d, $J=14.15$ Hz, 1H), 3.52 (d, $J=14.15$ Hz, 1H); ^{13}C NMR (50 MHz, CDCl_3) δ 177.7, 166.58, 165.09, 152.90, 151.81, 141.82, 135.39, 130.24, 129.33, 125.78, 125.78, 125.63, 124.73, 124.55, 124.37, 122.16, 121.83, 121.72, 121.62, 121.41, 109.63, 74.39, 41.92.

3-(benzo[d]thiazol-2-ylmethyl)-3-hydroxy-1-methylindolin-2-one (3w)



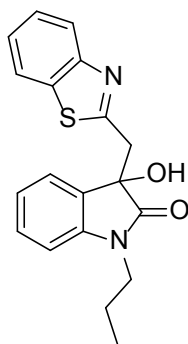
Reddish solid, mp 113-115 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.05-7.93 (m, 1H), 7.87-7.80 (m, 1H), 7.53-7.24 (m, 4H), 7.08-6.92 (m, 2H), 6.80 (d, $J=7.71$ Hz, 1H), 3.70 (d, $J=15.16$ Hz, 1H), 3.50 (d, $J=15.16$ Hz, 1H), 3.20 (s, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 176.04, 165.87, 143.21, 129.94, 129.62, 126.29, 126.02, 125.31, 124.82, 124.29, 123.09, 122.94, 122.40, 121.48, 108.43, 75.31, 40.99, 26.32.

3-(benzo[d]thiazol-2-ylmethyl)-1-ethyl-3-hydroxyindolin-2-one (3x)



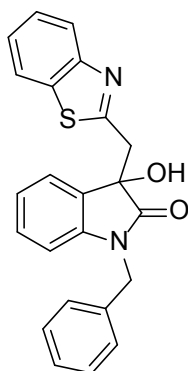
Red solid, mp 109-111 °C; ^1H NMR (200 MHz, CDCl_3) δ 7.92 (d, $J=8.46$ Hz, 1H), 7.76 (d, $J=6.82$ Hz, 1H), 7.44-7.15 (m, 4H), 7.01 (d, $J=7.33$ Hz, 1H), 6.87 (t, $J=6.69$ Hz, 1H), 6.72 (d, $J=7.83$ Hz, 1H), 3.73-3.58 (m, 3H), 3.41 (d, $J=15.03$ Hz, 1H), 1.16 (t, $J=6.95$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 175.72, 165.63, 152.47, 142.24, 129.85, 129.70, 126.18, 125.21, 124.45, 122.93, 122.87, 121.42, 108.54, 75.29, 41.14, 34.78, 12.49.

3-(benzo[d]thiazol-2-ylmethyl)-3-hydroxy-1-propylindolin-2-one (3y)



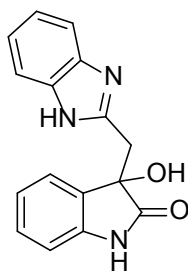
Red solid, mp 102-104 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.05-7.82 (m, 2H), 7.54-7.25 (m, 4H), 7.13-6.97 (m, 2H), 6.82 (d, $J=7.83$ Hz, 2H), 3.77-3.49 (m, 4H), 1.70 (q, 2H), 0.96 (t, $J=7.45$ Hz, 3H); ^{13}C NMR (50 MHz, CDCl_3) δ 176.20, 142.66, 125.88, 129.60, 126.23, 125.47, 125.26, 124.43, 122.96, 122.92, 121.46, 108.76, 75.33, 60.33, 41.69, 29.75, 20.69, 11.42.

3-(benzo[d]thiazol-2-ylmethyl)-1-benzyl-3-hydroxyindolin-2-one (3z)



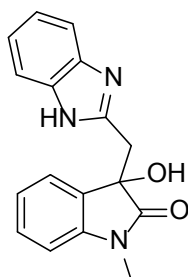
Red solid, mp 122-124 °C; ^1H NMR (200 MHz, CDCl_3) δ 8.03 (d, $J=7.71$ Hz, 1H), 7.84 (d, $J=8.08$ Hz, 1H), 7.54-7.37 (m, 4H), 7.18-7.13 (m, 6H), 6.96 (t, $J=7.58$ Hz, 1H), 6.66 (d, $J=7.58$ Hz, 1H), 5.02 (d, $J=15.54$ Hz, 1H), 4.72 (d, $J=15.66$ Hz, 1H), 3.81-3.58 (m, 2H); ^{13}C NMR (50 MHz, CDCl_3) δ 176.21, 152.52, 135.34, 129.96, 128.81, 127.69, 127.20, 126.29, 125.32, 124.37, 123.08, 121.52, 109.60, 75.47, 43.97, 41.37, 29.75.

3-((1*H*-benzo[d]imidazol-2-yl)methyl)-3-hydroxyindolin-2-one (3aa)



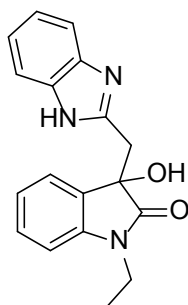
Off white solid, mp 192-194 °C; ^1H NMR (200 MHz, DMSO- D_6) δ 12.08 (s, 1H), 10.36 (s, 1H), 7.48-7.43 (m, 2H), 7.18-7.08 (m, 3H), 6.92-6.79 (m, 2H), 6.76 (d, $J=7.71$ Hz, 1H), 6.50 (s, 1H), 3.38 (d, $J=14.27$ Hz, 1H), 3.19 (d, $J=14.40$ Hz, 1H); ^{13}C NMR (50 MHz, DMSO- D_6) δ 178.33, 151.44, 150.16, 141.91, 131.22, 129.30, 124.49, 121.41, 109.73, 74.60, 36.77,.

3-((1*H*-benzo[*d*]imidazol-2-yl)methyl)-3-hydroxy-1-methylindolin-2-one (3ab)



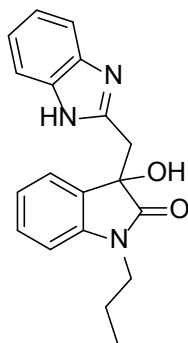
Off white solid, mp 162-164 °C; ^1H NMR (200 MHz, DMSO- D_6) δ 12.19 (s, 1H), 7.47-6.86 (m, 8H), 3.43-2.86 (m, 5H); ^{13}C NMR (50 MHz, DMSO- D_6) δ 176.44, 151.24, 149.83, 143.26, 130.39, 129.22, 123.82, 122.02, 121.21, 121.03, 108.40, 74.11, 26.84, 14.62.

3-((1*H*-benzo[*d*]imidazol-2-yl)methyl)-1-ethyl-3-hydroxyindolin-2-one (3ac)



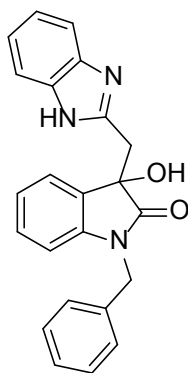
Red solid, mp 147-149 °C; ^1H NMR (200 MHz, $\text{DMSO}-\text{D}_6$) δ 12.03 (s, 1H), 7.43-7.39 (m, 2H), 7.21 (t, $J=7.45$ Hz, 1H), 7.10-6.87 (m, 5H), 6.49 (s, 1H), 3.77-3.58 (m, 2H), 3.44-3.20 (m, 2H), 1.12 (t, $J=7.07$ Hz, 3H); ^{13}C NMR (50 MHz, $\text{DMSO}-\text{D}_6$) δ 176.24, 162.53, 149.83, 142.50, 130.78, 129.40, 124.20, 122.00, 108.60, 74.39, 36.98, 34.06, 12.28.

3-((1*H*-benzo[*d*]imidazol-2-yl)methyl)-3-hydroxy-1-propylindolin-2-one (3ad)



Yellow solid, mp 105-107 °C; ^1H NMR (200 MHz, $\text{DMSO}-\text{D}_6$) δ 12.03 (s, 1H), 7.44-7.40 (m, 2H), 7.25-7.17 (m, 1H), 7.11-6.87 (m, 5H), 6.51 (s, 1H), 3.67-3.20 (m, 4H), 1.57 (q, 2H), 0.8 (t, $J=7.45$ Hz, 3H); ^{13}C NMR (50 MHz, $\text{DMSO}-\text{D}_6$) δ 176.66, 162.53, 149.84, 143.04, 130.65, 129.39, 124.17, 121.99, 108.77, 74.35, 36.99, 27.06, 20.39, 11.48.

3-((1*H*-benzo[*d*]imidazol-2-yl)methyl)-1-benzyl-3-hydroxyindolin-2-one (3ae)



Red solid, mp 132-134 °C; ^1H NMR (200 MHz, DMSO- D_6) δ 12.10 (s, 1H), 7.47-7.42 (m, 2H), 7.32-7.20 (m, 6H), 7.15-7.07 (m, 4H), 6.93 (t, $J=8.08$ Hz, 1H), 6.62 (s, 1H), 5.04 (d, $J=16.04$ Hz, 1H), 4.72 (d, $J=16.17$ Hz, 1H), 3.56-3.42 (m, 2H); ^{13}C NMR (50 MHz, DMSO- D_6) δ 176.96, 149.88, 142.84, 136.51, 130.81, 129.53, 128.85, 127.42, 124.44, 122.59, 109.46, 74.79, 43.10, 36.97.

Reference

- [1] B. M. Trost, J. Xie, J. D. Sieber, *J. Am. Chem. Soc.*, **2011**, 133, 20611-20622.
- [2] G. D. Yadav, H. G. Manyar, *Microporous and Mesoporous Materials*, **2003**, 63, 85.

