Supporting information

β-Cyclodextrin catalysed C-C bond formation via C(sp\(^3\))-H Functionalization of 2-Methyl azaarenes with Diones in aqueous medium

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General remarks:

All the reactions were carried out in oven-dried glassware. All the chemicals and reagents were purchased from commercial sources and were used without further purification. HPCL grade Acetonitrile (MERCK) was used for reaction. TLC (Thin Layer Chromatography) was performed on Merck-percoated silica gel 60-F\(_{254}\) and 100-200 mesh silica gel was used for column chromatography. The chromatographic solvents are mentioned as v/v ratios. All the synthesized compounds were fully characterized by \(^1\)H, \(^{13}\)C NMR, IR, and further confirmed through ESI-MS and HRMS analyses. IR spectra were recorded on a Perkin-Elmer FT-IR RXI spectrophotometer and values reported in cm\(^{-1}\). NMR spectra were recorded with 400 MHz spectrometers for \(^1\)H NMR, 100 MHz for \(^{13}\)C NMR respectively. Chemical shifts are reported in δ (ppm) relative to TMS (\(^1\)H) or DMSO-d\(_6\) (\(^{13}\)C) as internal standards. Integrals are in accordance
with assignments; coupling constants are given in Hz. ESI-MS spectra were obtained on a LCQ Advantage Ion trap mass spectrometer (Finnigan thermo fischer scientific).

**Synthesis of β-cyclodextrin derivatives**

O-p-toluenesulfonyl-β-cyclodextrin\(^1\) (**β-CD-Ts**) and Mono-6-deoxy-6-(3-benzylimidazolium)-β-cyclodextrin (**β-CD-BIMOTs**) were synthesized by known method.\(^1\)

**Characterization of β-CD-Ts**

White solid; Yield 58%; mp = 169-171°C; IR (KBr) max 3285, 2932, 1638, 1348, 1156.

**Characterization of β-CD-BIMOTs**

White solid; Yield 89%; mp = 206-208°C; IR (KBr) max 3282, 2936, 1648, 1158.

**Representative experimental procedure for the synthesis of 3-hydroxy-3-(quinolin-2-ylmethyl) indolin-2-one:**

2-Methyl-quinoline (1.2 mmol),isatin (1.0 mmol) and 20 mol % β-cyclodextrin were taken in a 50 mL round bottom flask containing 5 mL water as a solvent. The reaction mixture was stirred at 80°C. The reaction was monitored by TLC. After completion of reaction, the reaction mixture was allowed to cool after attaining room temperature solid precipitate was appeared. The solid product was filtrated on sintered funnel and it was washed 3-4 times by water. The crude product was purified by 100-200 mesh silica gel column chromatography.

**Recyclability of catalyst:**

β-cyclodextrin being soluble in water comes in the filtrate. The β-cyclodextrin was recovered easily from filtrate by evaporating the water under vacuum. The recovered β-cyclodextrin was then successfully used for the next batch without any further purification and slight loss of catalytic activity was observed.

**Characterisation data of all the synthesized compounds:**
3-Hydroxy-3-(pyridin-2-ylmethyl)indolin-2-one (3a):

Light yellow solid; Yield 82%; mp = 167-169°C; IR (KBr) max 3365, 3014, 1748, 1620, 1598, 1374, 1215, 975, 657;\textsuperscript{1}H NMR (400 MHz; CDCl\textsubscript{3}+DMSO-d\textsubscript{6}): δ 10.17 (s, 1H), 8.17 (d, \(J = 8.48\) Hz, 1H), 7.89 (d, \(J = 7.92\) Hz, 1H), 7.79 (d, \(J = 8.32\) Hz, 1H), 7.69 (t, \(J = 7.24\) Hz, 1H), 7.54 (t, \(J = 7.40\) Hz, 1H), 7.37 (d, \(J = 8.44\) Hz, 1H), 7.10 (t, \(J = 7.48\) Hz, 1H), 6.94 (d, \(J = 7.20\) Hz, 1H), 6.81 (t, \(J = 7.40\) Hz, 1H), 6.68 (d, \(J = 7.60\) Hz, 1H), 6.36 (s, 1H), 3.53 (d, \(J = 13.48\) Hz, 1H), 3.38 (d, \(J = 17.32\) Hz, 1H); \textsuperscript{13}C NMR (100 MHz; CDCl\textsubscript{3}+DMSO-d\textsubscript{6}): δ 178.8, 155.3, 147.0, 141.4, 137.8, 130.8, 129.1, 125.5, 122.5, 121.8, 110.0, 75.9, 44.0; ESI-MS (m/z) = 241 [M+H]\textsuperscript{+}; Analysis Calcd. for C\textsubscript{14}H\textsubscript{12}N\textsubscript{2}O\textsubscript{2}: C, 74.47; H, 4.86; N, 9.65; Found: C, 74.41; H, 4.79; N, 9.69; ESI-HRMS Calcd. for C\textsubscript{14}H\textsubscript{12}N\textsubscript{2}O\textsubscript{2}: [M+H]\textsuperscript{+}, 241.0932, Found: m/z 241.0948.

3-Hydroxy-5-nitro-3-(pyridin-2-ylmethyl)indolin-2-one (3b):

Off white solid; Yield 85%; mp = 160-162°C; IR (KBr) max 3427, 3019, 2399, 1637, 1384, 1150, 929, 669, 627;\textsuperscript{1}H NMR (400 MHz; DMSO-d\textsubscript{6}): δ 10.17 (s, 1H), 8.17 (d, \(J = 8.48\) Hz, 1H), 7.89 (d, \(J = 7.92\) Hz, 1H), 7.79 (d, \(J = 8.32\) Hz, 1H), 7.69 (t, \(J = 7.24\) Hz, 1H), 7.54 (t, \(J = 7.40\) Hz, 1H), 7.37 (d, \(J = 8.44\) Hz, 1H), 7.10 (t, \(J = 7.48\) Hz, 1H), 6.94 (d, \(J = 7.20\) Hz, 1H), 6.81 (t, \(J = 7.40\) Hz, 1H), 6.68 (d, \(J = 7.60\) Hz, 1H), 6.36 (s, 1H), 3.53 (d, \(J = 13.48\) Hz, 1H), 3.38 (d, \(J = 17.32\) Hz, 1H); \textsuperscript{13}C NMR (100 MHz; DMSO-d\textsubscript{6}): δ 179.4, 155.7, 148.9, 148.8, 142.2, 136.6, 132.4, 126.7, 124.9, 122.4, 120.7, 110.0, 75.8, 45.0; ESI-MS (m/z) = 286 [M+H]\textsuperscript{+}; Analysis Calcd. for C\textsubscript{14}H\textsubscript{11}N\textsubscript{3}O\textsubscript{4}: C, 58.95; H, 3.89; N, 14.73; Found: C, 58.84; H, 3.96; N, 14.78; ESI-HRMS Calcd. for C\textsubscript{14}H\textsubscript{11}N\textsubscript{3}O\textsubscript{4}: [M+H]\textsuperscript{+}, 286.0783, Found: m/z 286.0796.

3-Hydroxy-1-methyl-3-(pyridin-2-ylmethyl)indolin-2-one (3c):

Light yellow solid; Yield 86%; mp = 134-136°C; IR (KBr) max 3400, 3019, 2399, 1760, 1720, 1616, 1384, 1093, 929, 669;\textsuperscript{1}H NMR (400 MHz; CDCl\textsubscript{3}+DMSO-d\textsubscript{6}): δ 8.73 (s, 1H), 8.43 (s, 1H), 7.89 (s, 1H), 7.83 (d, \(J = 7.36\) Hz, 1H), 7.34 (d, \(J = 6.48\) Hz, 1H), 7.08-7.00 (m, 3H), 3.52 (d, \(J = 13.68\) Hz, 1H), 3.40 (d, \(J = 13.68\) Hz, 1H), 3.09 (s, 3H); \textsuperscript{13}C NMR (100 MHz; CDCl\textsubscript{3}+DMSO-d\textsubscript{6}): δ 179.1, 157.6, 147.2, 142.3, 135.9, 131.7, 129.7, 129.3, 128.8, 128.1, 126.9, 126.4, 124.9, 123.2, 121.5, 109.8, 76.0, 46.0; ESI-MS (m/z) = 255 [M+H]\textsuperscript{+}; Analysis Calcd.
White solid; Yield 85%; mp = 160-162°C; IR (KBr) max 3413, 3019, 1720, 1612, 1473, 1377, 1215, 1111, 669;1H NMR (400 MHz; CDCl3):δ 8.62 (d, J = 4.08 Hz, 1H), 7.70 (t, J = 7.72 Hz, 1H), 7.51 (s, 1H), 7.36-7.26 (m, 5H), 7.19 (t, J = 7.64 Hz, 1H), 7.10 (d, J = 7.76 Hz, 1H), 6.95 (t, J = 7.44 Hz, 1H), 6.89 (dd, J = 7.36 Hz, 1H), 6.72 (d, J = 7.84 Hz, 1H), 4.99 (d, J = 15.64 Hz, 1H), 4.84 (d, J = 15.64 Hz, 1H), 3.43 (d, J = 14.72 Hz, 1H), 3.21 (d, J = 14.72 Hz, 1H); 13C NMR (100 MHz; CDCl3): δ 177.0, 157.5, 148.3, 142.1, 137.2, 135.7, 131.0, 129.3, 128.8, 127.6, 127.3, 126.7, 124.0, 122.8, 122.3, 109.3, 76.3, 43.7, 43.0; ESI-MS (m/z) = 331 [M+H]+; Analysis Calcd. for C21H18N2O2: C, 76.34; H, 5.49; N, 8.48; Found: C, 76.38; H, 5.28; N, 8.53; ESI-HRMS Calcd. for C21H18N2O2: [M+H]+, 331.1402, Found: m/z 331.1418.

3-Hydroxy-5-methyl-3-(quinolin-2-ylmethyl)indolin-2-one (3f):

Light Brown solid; Yield 84%; mp = 181-183°C; IR (KBr) max 3402, 3020, 1627, 1387, 1215, 1069, 669;1H NMR (400 MHz; DMSO-d6): δ 10.07 (s, 1H), 8.20 (d, J = 8.40 Hz, 1H), 7.90 (d, J = 7.96 Hz, 1H), 7.81 (d, J = 8.36 Hz, 1H), 7.70 (t, J = 7.24 Hz, 1H), 7.55 (t, J = 7.68 Hz, 1H), 7.37 (d, J = 8.44 Hz, 1H), 6.90 (d, J = 7.04 Hz, 1H), 6.78 (s, 1H), 6.57 (d, J = 7.76 Hz, 1H), 3.50 (d, J = 13.52 Hz, 1H), 3.38 (d, J = 13.40 Hz, 1H), 2.11 (s, 3H); 13C NMR (100 MHz; DMSO-d6): δ 179.0, 157.5, 146.7, 139.8, 136.4, 131.7, 130.3, 130.0, 129.5, 128.3, 128.2, 126.9, 126.6, 125.7, 123.3, 4
3-Hydroxy-5-nitro-3-(quinolin-2-ylmethyl) indolin-2-one (3g):
Off white solid; Yield 84%; mp = 187-189°C; IR (KBr) max 3406, 3019, 1622, 1403, 1215, 1069, 928, 669; $^1$H NMR (400 MHz; DMSO-d$_6$): 9.03 (s, 1H), 8.22 (d, $J$ = 8.44 Hz, 1H), 8.10 (dd, $J$ = 8.60 Hz, 1H), 7.96 (d, $J$ = 2.32 Hz, 1H), 7.88 (d, $J$ = 8.12 Hz, 1H), 7.66 (d, $J$ = 3.72 Hz, 2H), 7.53-7.49 (m, 1H), 7.40 (d, $J$ = 8.48 Hz, 1H), 6.90 (d, $J$ = 8.64 Hz, 1H), 3.74 (d, $J$ = 14.32 Hz, 1H), 3.55 (d, $J$ = 14.32 Hz, 1H); $^{13}$C NMR (100 MHz; DMSO-d$_6$): δ 179.0, 156.5, 149.0, 146.6, 141.8, 135.8, 129.3, 128.0, 127.7, 126.3, 126.2, 126.1, 122.4, 120.0, 109.4, 75.6, 44.7; ESI-MS (m/z) = 336 [M+H]$^+$; Analysis Calcd. for C$_{18}$H$_{13}$N$_3$O$_4$: C, 64.47; H, 3.91; N, 12.53; Found: C, 64.55; H, 3.85; N, 12.63; ESI-HRMS Calcd. for C$_{18}$H$_{13}$N$_3$O$_4$: [M+H]$^+$, 336.0940, Found: m/z 336.0952.

5-Chloro-3-hydroxy-3-(quinolin-2-ylmethyl)indolin-2-one (3h):
Dark brown solid; Yield 85%; mp = 188-190°C; IR (KBr) max 3431, 3019, 1650, 1384, 1216, 1119, 669, 619; $^1$H NMR (400 MHz; DMSO-d$_6$): δ 10.36 (s, 1H), 8.25 (d, $J$ = 8.36 Hz, 1H), 7.94 (d, $J$ = 7.52 Hz, 1H), 7.80 (d, $J$ = 8.44 Hz, 1H), 7.59 (t, $J$ = 8.08 Hz, 1H), 7.42 (d, $J$ = 8.48 Hz, 1H), 7.19 (dd, $J$ = 8.24 Hz, 1H), 7.09 (d, $J$ = 2.20 Hz, 1H), 6.74 (d, $J$ = 8.20 Hz, 1H), 6.48 (s, 1H), 3.63 (d, $J$ = 13.76 Hz, 1H), 3.49 (d, $J$ = 13.72 Hz, 1H); $^{13}$C NMR (100 MHz; DMSO-d$_6$): δ 178.3, 156.7, 146.7, 140.1, 135.6, 133.4, 128.5, 128.2, 127.7, 126.3, 125.0, 124.7, 122.6, 110.6, 75.6, 45.1; ESI-MS (m/z) = 325 [M+H]$^+$; Analysis Calcd. for C$_{18}$H$_{13}$ClN$_3$O$_2$: C, 64.47; H, 3.91; N, 12.53; Found: C, 66.75; H, 4.15; N, 8.86; ESI-HRMS Calcd. ForC$_{18}$H$_{13}$ClN$_3$O$_2$: [M+H]$^+$, 325.0699, Found: m/z 235.0692.

5-Bromo-3-hydroxy-3-(quinolin-2-ylmethyl)indolin-2-one (3i):
Brown solid; Yield 82%; mp = 198-200°C; IR (KBr) max 3432, 3019, 1647, 1384, 1215, 1119, 669, 619; $^1$H NMR (400 MHz; DMSO-d$_6$): δ 10.29 (s, 1H), 8.17 (d, $J$ = 8.48 Hz, 1H), 7.86 (d, $J$ = 8.04 Hz, 1H), 7.72 (d, $J$ = 8.28 Hz, 1H), 7.66-7.62 (m, 1H), 7.50 (t, $J$ = 7.52 Hz, 1H), 7.33 (d, $J$ = 8.44 Hz, 1H), 7.21 (d, $J$ = 8.44 Hz, 1H), 7.24 (d, $J$ = 8.24 Hz, 1H), 7.22 (d, $J$ = 1.72 Hz, 1H), 6.61 (d, $J$ = 8.20 Hz, 1H), 6.39 (s, 1H), 3.55 (d, $J$ = 13.80 Hz, 1H), 3.40 (d, $J$ = 13.80 Hz, 1H); $^{13}$C NMR (100 MHz;}
DMSO-d$_6$): $\delta$ 178.2, 156.7, 146.7, 141.3, 135.6, 133.8, 131.3, 129.3, 128.2, 127.6, 127.4, 126.3, 126.0, 122.6, 112.7, 111.2, 75.5, 45.1; ESI-MS (m/z) = 369 [M+H]$^+$; Analysis Calcd. for C$_{18}$H$_{13}$BrN$_2$O$_2$, C, 58.56; H, 3.55; N, 7.59; Found: C, 58.26; H, 3.37; N, 7.21; ESI-HRMS Calcd. for C$_{18}$H$_{13}$BrN$_2$O$_2$: [M+H]$^+$, 369.0194, Found: m/z 369.0188.

3-Hydroxy-5-iodo-3-(quinolin-2-ylmethyl) indolin-2-one (3j):
Light brown solid; Yield 84%; mp = 199-201°C; IR (KBr) max 3428, 3021, 1648, 1385, 1215, 1119, 669, 619; $^1$H NMR (400 MHz; DMSO-d$_6$): $\delta$ 10.30 (s, 1H), 8.20 (d, $J$ = 8.44 Hz, 1H), 7.77 (d, $J$ = 8.28 Hz, 1H), 7.70 (t, $J$ = 8.44 Hz, 1H), 7.54 (t, $J$ = 8.04 Hz, 1H), 7.43 (dd, $J$ = 8.08 Hz, 1H), 7.37 (d, $J$ = 8.44 Hz, 1H), 7.26 (d, $J$ = 1.64 Hz, 1H), 6.55 (d, $J$ = 8.08 Hz, 1H), 6.39 (s, 1H), 3.56 (d, $J$ = 13.76 Hz, 1H), 3.39 (d, $J$ = 13.84 Hz, 1H); $^{13}$C NMR (100 MHz; DMSO-d$_6$): $\delta$ 178.0, 156.8, 146.7, 141.8, 137.2, 135.5, 134.0, 133.1, 129.3, 128.2, 127.6, 126.4, 126.0, 122.6, 111.7, 83.7, 75.4, 45.1; ESI-MS (m/z) = 417 [M+H]$^+$; Analysis Calcd. for C$_{18}$H$_{13}$IN$_2$O$_2$, C, 51.94; H, 3.15; N, 6.73; Found: C, 51.76; H, 3.37; N, 6.81; ESI-HRMS Calcd. for C$_{18}$H$_{13}$IN$_2$O$_2$: [M+H]$^+$, 417.0055, Found: m/z 417.0048.

7-Fluoro-3-hydroxy-3-(quinolin-2-ylmethyl) indolin-2-one (3k):
Light brown solid; Yield 85%; mp = 179-181°C; IR (KBr) max 3404, 3021, 1633, 1392, 1215, 669; $^1$H NMR (400 MHz; DMSO-d$_6$): $\delta$ 10.69 (s, 1H), 8.18 (d, $J$ = 8.48 Hz, 1H), 7.88 (d, $J$ = 8.08 Hz, 1H), 7.76 (d, $J$ = 8.28 Hz, 1H), 7.69 (t, $J$ = 8.36 Hz, 1H), 7.54 (t, $J$ = 7.96 Hz, 1H), 7.35(d, $J$ = 8.44 Hz, 1H), 7.02 (t, $J$ = 9.60 Hz, 1H), 6.87-6.80 (m, 2H), 6.47 (s, 1H), 3.58(d, $J$ = 13.84 Hz, 1H), 3.46(d, $J$ = 13.88 Hz, 1H); $^{13}$C NMR (100 MHz; DMSO-d$_6$): $\delta$ 179.0, 157.2, 136.1, 134.8, 129.9, 129.3, 128.6, 128.1, 126.8, 126.6, 122.9, 122.5, 120.8, 116.4, 116.2, 76.1, 60.1, 45.8; ESI-MS (m/z) = 309 [M+H]$^+$; Analysis Calcd. for C$_{18}$H$_{13}$FN$_2$O$_2$, C, 70.12; H, 4.25; N, 9.09; Found: C, 70.36; H, 4.38; N, 9.22; ESI-HRMS Calcd. for C$_{18}$H$_{13}$FN$_2$O$_2$: [M+H]$^+$, 309.0995, Found: m/z 309.0998.

3-Hydroxy-1-methyl-3-(quinolin-2-ylmethyl) indolin-2-one (3l):
Brown solid; Yield 91%; mp = 144-146°C; IR (KBr) max 3393, 3185, 3020, 1718, 1615, 1402, 1216, 1091, 760, 669; $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 8.17 (d, $J$ = 8.44 Hz, 1H), 8.13 (d, $J$ = 8.48 Hz, 1H), 7.87 (d, $J$ = 8.04 Hz, 1H), 7.80(t, $J$=8.44 Hz, 1H), 7.61 (t, $J$=8.04 Hz, 1H), 7.30(dd, $J$=15.24 Hz, 1H), 7.21 (d, $J$ = 8.36 Hz, 1H), 6.93 (t, $J$ = 7.48 Hz, 1H), 6.87 (t, $J$ = 7.72 Hz, 1H).
Hz, 2H), 3.60 (d, J = 15.04 Hz, 1H), 3.28 (d, J = 15.08 Hz, 1H), 3.23 (s, 3H). $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ 176.7, 158.6, 146.6, 143.0, 137.1, 131.2, 130.1, 129.4, 128.8, 127.7, 127.1, 126.6, 124.0, 122.8, 122.7, 108.3, 76.3, 43.2, 26.2; ESI-MS (m/z) = 305 [M+H]$^+$; Analysis Calcd. for C$_{19}$H$_{16}$N$_2$O$_2$: C, 74.98; H, 5.30; N, 9.20; Found: C, 74.86; H, 5.27; N, 9.41; ESI-HRMS Calcd. for C$_{19}$H$_{16}$N$_2$O$_2$: [M+H]$^+$, 305.1245, Found: m/z 305.1256.

3-((6-Fluoroquinolin-2-yl) methyl)-3-hydroxy-1-methylindolin-2-one (3m):

Dark brown solid; Yield 89%; mp = 148-150°C; IR (KBr) max 3432, 3019, 1720, 1615, 1508, 1472, 1384, 1216, 1121, 770, 669, 619; $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 8.11 (dd, J = 9.08 Hz, 2H), 7.55 (t, J = 8.92 Hz, 1H), 7.47 (dd, J = 8.76 Hz, 1H), 7.30 (dd, J = 15.08 Hz, 1H), 7.23 (d, J = 8.48 Hz, 1H), 6.95-6.89 (m, 2H), 6.84 (d, J = 7.76 Hz, 1H), 3.55 (d, J = 14.92 Hz, 1H), 3.32 (d, J = 14.96 Hz, 1H), 3.20 (s, 3H); $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ 176.7, 158.6, 157.8, 143.8, 143.1, 136.4, 131.3, 131.2, 130.9, 129.5, 127.7, 127.6, 124.0, 123.5, 122.8, 120.4, 120.2, 110.8, 110.6, 108.4, 76.3, 43.3, 26.2; ESI-MS (m/z) = 323 [M+H]$^+$; Analysis Calcd. for C$_{19}$H$_{15}$FN$_2$O$_2$: C, 70.80; H, 4.69; N, 8.69; Found: C, 70.54; H, 4.84; N, 8.59; ESI-HRMS Calcd. for C$_{19}$H$_{15}$FN$_2$O$_2$: [M+H]$^+$, 323.1151, Found: m/z 323.1164.

3-((6-Chloroquinolin-2-yl) methyl)-3-hydroxy-1-methylindolin-2-one (3n):

White solid; Yield 86%; mp = 152-154°C; IR (KBr) max 3381, 3016, 1718, 1614, 1470, 1384, 1217, 1092, 765; $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 8.06 (t, J = 8.72 Hz, 2H), 7.83 (d, J = 2.24 Hz, 1H), 7.70 (d, J = 9.04 Hz, 1H), 7.35 (s, 1H), 7.30 (t, J = 9.00 Hz, 1H), 7.23 (d, J = 8.40 Hz, 1H), 6.95-6.88 (m, 2H), 6.83 (d, J = 7.80 Hz, 1H), 3.55 (d, J = 14.96 Hz, 1H), 3.32 (d, J = 14.96 Hz, 1H), 3.20 (s, 3H); $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ 176.7, 158.8, 145.1, 143.1, 136.1, 132.3, 131.0, 130.9, 130.4, 129.5, 127.6, 126.4, 124.0, 123.6, 122.5, 108.4, 76.2, 43.4, 26.2; ESI-MS (m/z) = 339 [M+H]$^+$; Analysis Calcd. for C$_{19}$H$_{15}$ClN$_2$O$_2$: C, 70.80; H, 4.46; N, 8.69; Found: C, 70.54; H, 4.84; N, 8.59; ESI-HRMS Calcd. for C$_{19}$H$_{15}$ClN$_2$O$_2$: [M+H]$^+$, 323.1151, Found: m/z 323.1164.

3-((6-Chloroquinolin-2-yl) methyl)-3-hydroxy-1-methylindolin-2-one (3o):

Light brown solid; Yield 84%; mp = 154-156°C; IR (KBr) max 3432, 3019, 2400, 1721, 1615, 1500, 1472, 1384, 1119, 928, 669, 619; (400 MHz; CDCl$_3$): $\delta$ 8.20 (d, J = 8.36 Hz, 1H), 7.91
(d, J = 7.36 Hz, 1H), 7.80 (d, J = 8.04 Hz, 1H), 7.54 (t, J = 7.88 Hz, 1H), 7.31 (s, 1H), 7.28 (d, J = 5.32 Hz, 1H), 7.02 (d, J = 7.04 Hz, 1H), 6.95 (t, J = 7.44 Hz, 1H), 6.86 (d, J = 7.80 Hz, 1H), 3.62 (d, J = 15.48 Hz, 1H), 3.38 (d, J = 15.48 Hz, 1H), 3.22 (s, 3H); 13C NMR (100 MHz; CDCl3): δ 176.6, 159.6, 143.1, 142.8, 137.6, 132.9, 131.3, 130.1, 129.4, 128.3, 126.8, 126.6, 124.1, 123.4, 122.8, 108.3, 76.2, 42.8, 26.2; ESI-MS (m/z) = 339 [M+H]+; Analysis Calcd. for C19H15ClN2O2: C, 67.36; H, 4.46; N, 8.27; Found: C, 67.18; H, 4.54; N, 8.36; ESI-HRMS Calcd. for C19H15ClN2O2: [M+H]+, 339.0856, Found: m/z 339.0862.

3-((6-Bromoquinolin-2-yl) methyl)-3-hydroxy-1-methylindolin-2-one(3p):
White solid; Yield 84%; mp = 151-153°C; IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619; 1H NMR (400 MHz; CDCl3): δ 8.07 (d, J = 8.44 Hz, 1H), 8.02 (s, 1H), 8.00 (d, J = 8.96 Hz, 1H), 7.85 (dd, J = 8.96 Hz, 1H), 7.35 (s, 1H), 7.24 (d, J = 8.40 Hz, 1H), 6.95 (t, J = 7.36 Hz, 1H), 6.90 (d, J = 7.28 Hz, 1H), 6.85 (d, J = 7.80 Hz, 1H), 3.55 (d, J = 15.00 Hz, 1H), 3.32 (d, J = 14.96 Hz, 1H), 3.22 (s, 3H); 13C NMR (100 MHz; CDCl3): δ 176.6, 159.0, 145.3, 143.1, 136.0, 133.6, 130.9, 130.5, 129.7, 129.5, 128.1, 124.0, 123.6, 122.8, 108.4, 76.2, 43.4, 26.2; ESI-MS (m/z) = 383 [M+H]+; Analysis Calcd. for C19H15BrN2O2: C, 59.55; H, 3.95; N, 7.31; Found: C, 59.68; H, 3.86; N, 7.16; ESI-HRMS Calcd. for C19H15BrN2O2: [M+H]+, 383.0350, Found: m/z 383.0363.

3-Hydroxy-3-(pyridin-2-ylmethyl)benzo[b]thiophen-2(3H)-one (4a):
Yellow solid; Yield 81%; mp = 161-163°C; IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619; 1H NMR (400 MHz; DMSO-d6): δ 8.24 (d, J = 5.68 Hz, 1H), 8.09 (dd, J = 8.64 Hz, 1H), 7.83 (d, J = 2.36 Hz, 1H), 7.61 (t, J = 7.68 Hz, 1H), 7.18 (d, J = 7.80 Hz, 1H), 7.13-7.10 (m, 1H), 6.87 (d, J = 8.64 Hz, 1H), 6.64 (s, 1H), 3.45 (d, J = 13.36 Hz, 1H), 3.29 (d, J = 13.36 Hz, 1H); 13C NMR (100 MHz; DMSO-d6): δ 179.2, 155.5, 148.6, 148.6, 142.0, 136.4, 132.2, 126.5, 124.7, 122.1, 120.4, 109.8, 75.5, 44.8; ESI-MS (m/z) = 258 [M+H]+; Analysis Calcd. for C14H11NO2S: C, 65.35; H, 4.31; N, 5.44; Found: C, 65.28; H, 4.39; N, 5.56; ESI-HRMS Calcd. for C14H11NO2S: [M+H]+, 258.0544, Found: m/z 258.0544.

3-Hydroxy-3-(quinolin-2-ylmethyl)benzo[b]thiophen-2(3H)-one (4b):
Yellow solid; Yield 87%; mp = 166-168°C; IR (KBr) max 3401, 3020, 2400, 1717, 1598, 1509, 1422, 1215, 1070, 927, 898, 670; 1H NMR (400 MHz; CDCl3): δ 8.17 (d, J = 8.36 Hz, 1H), 8.13
(d, J = 8.52 Hz, 1H), 7.87 (d, J = 8.12 Hz, 1H), 7.81 (t, J = 8.40 Hz, 1H), 7.61 (t, J = 8.04 Hz, 1H), 7.37-7.32 (m, 2H), 7.23 (dd, J = 3.72 Hz, 2H), 7.18 (d, J = 8.36 Hz, 1H), 3.45 (d, J = 14.80 Hz, 1H), 3.40 (d, J = 14.84 Hz, 1H); ^13^C NMR (100 MHz; CDCl$_3$): δ 205.1, 157.1, 146.6, 138.4, 137.5, 132.7, 130.3, 129.7, 128.7, 127.7, 127.2, 126.8, 126.7, 125.3, 123.4, 122.5, 85.0, 45.0; ESI-MS (m/z) = 308[M+H]$^+$; Analysis Calcd. for C$_{18}$H$_{13}$NO$_2$S: C, 70.34; H, 4.26; N, 4.56; Found: C, 70.42; H, 4.26; N, 4.45; ESI-HRMS Calcd. For C$_{18}$H$_{13}$NO$_2$S: [M+H]$^+$, 308.0701, Found: m/z 308.0714.

3-((6-Fluoroquinolin-2-yl)methyl)-3-hydroxybenzo[b]thiophen-2(3H)-one (4c):

Light yellow solid; Yield 88%; mp = 162-164°C; IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619; ^1^H NMR (400 MHz; DMSO-d$_6$): δ 8.19 (d, J = 8.44 Hz, 1H), 7.89 (d, J = 7.80 Hz, 1H), 7.77 (d, J = 8.36 Hz, 1H), 7.69 (t, J = 8.32 Hz, 1H), 7.54 (t, J = 7.96 Hz, 1H), 7.37 (d, J = 8.44 Hz, 1H), 6.93 (t, J = 9.60 Hz, 1H), 6.86 (dd, J = 8.28 Hz, 1H), 6.65 (dd, J = 8.40 Hz, 1H), 6.45 (s, 1H), 3.56 (d, J = 13.56 Hz, 1H), 3.42 (d, J = 13.60 Hz, 1H); ^13^C NMR (100 MHz; CDCl$_3$): δ 178.9, 157.3, 147.9, 147.2, 145.5, 136.0, 134.9, 129.8, 129.5, 129.3, 128.7, 128.1, 126.8, 126.5, 125.3, 124.5, 123.8, 123.2, 121.6, 109.9, 75.9, 45.8; ESI-MS (m/z) = 326[M+H]$^+$; Analysis Calcd. for C$_{18}$H$_{12}$FNO$_2$S: C, 66.45; H, 3.72; N, 4.31; Found: C, 66.38; H, 3.94; N, 4.29; ESI-HRMS Calcd. for C$_{18}$H$_{12}$FNO$_2$S: [M+H]$^+$, 326.0606, Found: m/z 326.0626.

3-((4-Chloroquinolin-2-yl)methyl)-3-hydroxybenzo[b]thiophen-2(3H)-one (4d):

Light yellow solid; Yield 86%; mp = 162-164°C; IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619; ^1^H NMR (400 MHz; DMSO-d$_6$): δ 8.19 (d, J = 8.44 Hz, 1H), 7.89 (d, J = 7.80 Hz, 1H), 7.77 (d, J = 8.36 Hz, 1H), 7.69 (t, J = 8.32 Hz, 1H), 7.54 (t, J = 7.96 Hz, 1H), 7.37 (d, J = 8.44 Hz, 1H), 6.93-6.88 (m, 1H), 6.86 (dd, J = 8.28 Hz, 1H), 6.65 (dd, J = 8.40 Hz, 1H), 6.45 (s, 1H), 3.56 (d, J = 13.56 Hz, 1H), 3.43 (d, J = 13.60 Hz, 1H); ^13^C NMR (100 MHz; DMSO-d$_6$): δ 178.9, 158.0, 148.0, 142.2, 140.7, 131.5, 131.0, 129.4, 128.0, 124.9, 124.5, 123.8, 123.2, 121.6, 109.9, 75.9, 45.8; ESI-MS (m/z) = 342 [M+H]$^+$; Analysis Calcd. For C$_{18}$H$_{12}$ClNO$_2$S: C, 63.25; H, 3.54; N, 4.10; Found: C, 63.52; H, 3.59; N, 4.08; ESI-HRMS Calcd. For C$_{18}$H$_{12}$ClNO$_2$S: [M+H]$^+$, 342.0311, Found: m/z 342.0324.

2-Hydroxy-2-(pyridin-2-ylmethyl)acenaphthylen-1(2H)-one (5a):
White solid; Yield 82%; mp = 161-163°C; IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619; $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 8.65 (d, $J = 4.20$ Hz, 1H), 8.14 (d, $J = 8.12$ Hz, 1H), 8.00 (d, $J = 7.00$ Hz, 1H), 7.87 (d, $J = 8.36$ Hz, 1H), 7.77 (t, $J = 8.00$ Hz, 1H), 7.70 (t, $J = 7.68$ Hz, 2H), 7.55 (t, $J = 8.32$ Hz, 1H), 7.33 (t, $J = 6.92$ Hz, 1H), 7.07 (dd, $J = 15.40$ Hz, 2H), 3.48 (d, $J = 14.80$ Hz, 1H), 3.19 (d, $J = 14.80$ Hz, 1H); $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ 203.6, 158.3, 148.3, 140.8, 140.7, 137.2, 131.9, 130.7, 130.6, 128.6, 128.3, 125.1, 124.6, 122.3, 122.2, 120.4, 80.0, 42.6; ESI-MS (m/z) = 276[M+H]$^+$; Analysis Calcd. for C$_{18}$H$_{13}$NO$_2$: C, 78.53; H, 4.76; N, 5.09; Found: C, 78.76; H, 4.38; N, 5.13; ESI-HRMS Calcd. For C$_{18}$H$_{13}$NO$_2$: [M+H]$^+$, 276.0980, Found: m/z 276.0992.

2-Hydroxy-2-(quinolin-2-ylmethyl)acenaphthylen-1(2H)-one (5b):

White solid; Yield 88%; mp = 165-167°C; IR (KBr) max 3413, 1725, 1603, 1503, 1422, 1215, 1080, 831, 757; $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 8.17 (t, $J = 8.20$ Hz, 3H), 8.04 (d, $J = 7.00$ Hz, 1H), 7.96 (s, 1H), 7.89-7.76 (m, 4H), 7.63 (t, $J = 7.16$ Hz, 1H), 7.50 (t, $J = 8.32$ Hz, 1H), 7.18 (d, $J = 8.32$ Hz, 1H), 7.09 (d, $J = 6.92$ Hz, 1H), 3.71 (d, $J = 15.08$ Hz, 1H), 3.35 (d, $J = 15.08$ Hz, 1H); $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ 203.3, 159.1, 146.7, 140.9, 140.8, 137.2, 131.9, 130.7, 130.2, 128.8, 128.6, 128.3, 127.7, 127.1, 126.6, 125.1, 122.8, 122.2, 120.6, 80.1, 43.0; ESI-MS (m/z) = 326[M+H]$^+$; Analysis Calcd. for C$_{22}$H$_{15}$NO$_2$: C, 81.21; H, 4.65; N, 4.30; Found: C, 81.46; H, 4.71; N, 4.38; ESI-HRMS Calcd. For C$_{22}$H$_{15}$NO$_2$: [M+H]$^+$, 326.1136, Found: m/z 326.1128.

2-Hydroxy-2-(pyridin-2-ylmethyl)aceanthrylen-1(2H)-one (6a):

White solid; Yield 88%; mp = 184-186°C; IR (KBr) max 3399, 3010, 1708, 1627, 1384, 1215, 1067, 669; $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 9.17 (dd, $J = 8.56$ Hz, 1H), 8.71 (s, 1H), 8.67 (dd, $J = 4.92$ Hz, 1H), 8.18 (d, $J = 8.52$ Hz, 1H), 7.96 (d, $J = 8.64$ Hz, 1H), 7.78 (t, $J = 8.44$ Hz, 1H), 7.71 (t, $J = 7.68$ Hz, 1H), 7.67 (t, $J = 8.24$ Hz, 1H), 7.51 (t, $J = 8.64$ Hz, 1H), 7.35 (t, $J = 6.76$ Hz, 1H), 7.08 (d, $J = 7.76$ Hz, 1H), 7.05 (d, $J = 6.52$ Hz, 1H), 3.57 (d, $J = 14.80$ Hz, 1H), 3.25 (d, $J = 14.80$ Hz, 1H); $^{13}$C NMR (100 MHz; CDCl$_3$): $\delta$ 203.5, 158.5, 148.2, 143.0, 140.9, 137.2, 133.5, 132.8, 129.3, 129.2, 128.5, 128.3, 127.7, 126.5, 125.2, 124.8, 124.7, 123.6, 122.3, 119.9, 80.0, 42.5; ESI-MS (m/z) = 326[M+H]$^+$; Analysis Calcd. for C$_{22}$H$_{15}$NO$_2$: C, 81.21; H, 4.65; N, 4.30;
Found: C, 81.46; H, 4.71; N, 4.38; ESI-HRMS Calcd. for C\textsubscript{22}H\textsubscript{15}NO\textsubscript{2}: [M+H]\textsuperscript{+}, 326.1136, Found: m/z 326.1142.

2-Hydroxy-2-(quinolin-2-ylmethyl) aceanthrylen-1(2H)-one (6b)

White solid; Yield 91%; mp = 198-200\textdegree{}C; IR (KBr) max 3433, 3019, 1617, 1384, 1215, 1120, 669, 619; \textsuperscript{1}H NMR (400 MHz; CDCl\textsubscript{3}): \textit{δ} 9.20 (d, \textit{J} = 8.52 Hz, 1H), 8.72 (s, 1H), 8.19 (dd, \textit{J} = 8.28 Hz, 3H), 8.03 (s, 1H), 7.95 (d, \textit{J} = 8.68 Hz, 1H), 7.90 (d, \textit{J} = 8.08 Hz, 1H), 7.83-7.75 (m, 2H), 7.68-7.60 (m, 2H), 7.46 (t, \textit{J}=8.56 Hz, 1H), 7.21 (d, \textit{J} = 8.32 Hz, 1H), 7.06 (d, \textit{J} = 6.60 Hz, 1H), 3.79 (d, \textit{J} = 15.08 Hz, 1H), 3.39 (d, \textit{J} = 15.12 Hz, 1H); \textsuperscript{13}C NMR (100 MHz; CDCl\textsubscript{3}): \textit{δ} 203.3, 159.5, 146.7, 143.1, 141.1, 137.1, 133.5, 132.8, 130.2, 129.3, 129.2, 128.4, 128.5, 128.4, 127.7, 127.1, 126.6, 126.5, 125.2, 124.9, 123.7, 122.8, 120.0, 80.1, 42.9; ESI-MS (m/z) = 376[M+H]\textsuperscript{+}; Analysis Calcd. for C\textsubscript{26}H\textsubscript{17}NO\textsubscript{2}: C, 83.18; H, 4.56; N, 3.73; Found: C, 83.46; H, 4.68; N, 3.52; ESI-HRMS Calcd. for C\textsubscript{26}H\textsubscript{17}NO\textsubscript{2}: [M+H]\textsuperscript{+}, 376.1293, Found: m/z 376.1288.
Figure 1: $^1$H NMR of compound 3a

Figure 2: $^{13}$C NMR of compound 3a
Figure 3: $^1$H NMR of compound 3b

Figure 4: $^{13}$C NMR of compound 3b
Figure 5: $^1$H NMR of compound 3c

Figure 6: $^{13}$C NMR of compound 3c
Figure 7: $^1$H NMR of compound 3d

Figure 8: $^{13}$C NMR of compound 3d
Figure 9: $^1$H NMR of compound 3e

Figure 10: $^{13}$C NMR of compound 3e
Figure 11: $^1$H NMR of compound of 3f

Figure 12: $^{13}$C NMR of compound 3f
Figure 13: $^1$H NMR of compound 3g

Figure 14: $^{13}$C NMR of compound 3g
Figure 15: $^1$H NMR of compound 3h

Figure 16: $^{13}$C NMR of compound 3h
Figure 17: $^1$H NMR of compound 3i

Figure 18: $^{13}$C NMR of compound 3i
Figure 19: $^1$H NMR of compound 3j

Figure 20: $^{13}$C NMR of compound 3j
Figure 21: $^1$H NMR of compound 3k

Figure 22: $^{13}$C NMR of compound 3k
Figure 23: $^1$H NMR of compound 3l

Figure 24: $^{13}$C NMR of compound 3l
Figure 25: $^1$H NMR of compound 3m

Figure 26: $^{13}$C NMR of compound 3m
Figure 27: $^1$H NMR of compound 3n

Figure 28: $^{13}$C NMR of compound 3n
Figure 29: $^1$H NMR of compound 3o

Figure 30: $^{13}$C NMR of compound 3o
Figure 31: $^1$H NMR of compound 3p

Figure 32: $^{13}$C NMR of compound 3p
Figure 33: $^1$H NMR of compound 4a

Figure 34: $^{13}$C NMR of compound 4a
Figure 35: $^1$H NMR of compound 4b

Figure 36: $^{13}$C NMR of compound 4b
Figure 37: $^1$H NMR of compound 4c

Figure 38: $^{13}$C NMR of compound 4c
Figure 39: $^1$H NMR of compound 4d

Figure 40: $^{13}$C NMR of compound 4d
Figure 41: $^1$H NMR of compound 5a

Figure 42: $^{13}$C NMR of compound 5a
Figure 43: $^1$H NMR of compound 5b

Figure 44: $^{13}$C NMR of compound 5b
Figure 45: $^1$H NMR of compound 6a

Figure 46: $^{13}$C NMR of compound 6a
Figure 47: $^{13}$C NMR of compound 6b

Figure 48: $^{13}$C NMR of compound 6b
$^1$H NMR spectral evidence for association of $\beta$-CD with 2-methylazaarene and Diones

**Fig. 49:** $^1$H NMR spectra of (a) $\beta$-CD and (b) $\beta$-CD complex with 2-methylquinoline and isatin after 2 h

**Fig. 50:** $^1$H NMR spectra of (a) $\beta$-CD and (b) $\beta$-CD complex with 2-methylquinoline and 1-methylisatin after 2 h
**Fig. 51:** $^1$H NMR spectra of (a) $\beta$-CD and (b) $\beta$-CD complex with 2-methylquinoline and benzo[b]thiophene-2, 3-dione after 2 h.

**Fig. 52:** $^1$H NMR spectra of (a) $\beta$-CD and (b) $\beta$-CD complex with 2-methylquinoline and acenaphthylene-1, 2-dione after 2 h.
Fig. 53: $^1$H NMR spectra of (a) β-CD and (b) β-CD complex with 2-methylquinoline and aceanthrylene-1, 2-dione after 2 h

References