

## Supporting information

# Fabrication and characterization of inorganic-organic hybrid copper ferrite anchored on chitosan Schiff base as a reusable green catalyst for synthesis of indeno[1,2-b]indolone derivatives

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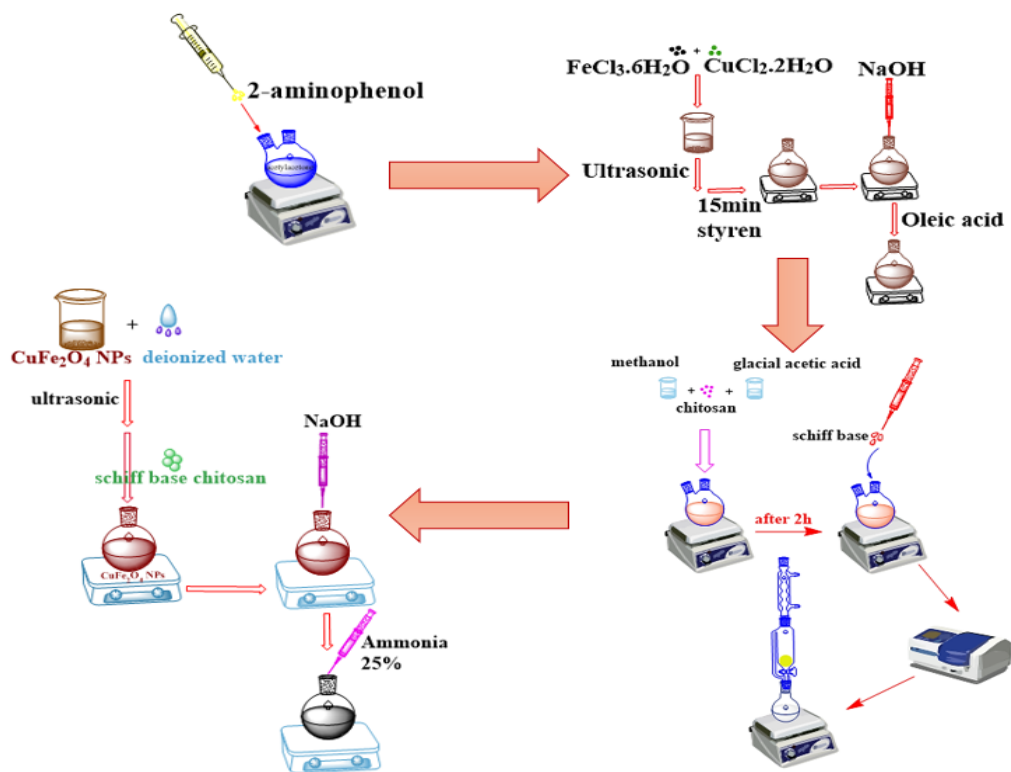
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### **General procedure for the synthesis of indeno indolone**

Exact amounts of aromatic amine(1mmol), 1mmol of dimedone and  $\text{CuFe}_2\text{O}_4@\text{CS-SB}$  catalyst were stirred in distilled water under tidy condition at  $75^\circ\text{C}$ . Subsequently, 1mmol of ninhydrine was added and the reaction mixture was all over again stirred for the suitable time. After the reaction was supplemented (TLC). The reaction mixture was filtered off. In order that with the aim of achieving  $\text{CuFe}_2\text{O}_4@\text{CS-SB}$  catalyst from the products, the  $\text{CuFe}_2\text{O}_4@\text{CS-SB}$  catalyst was separated from the reaction mixture by a strong magnet and washed several times with acetone and ethanol to be used as a catalyst in other reactions. Ultimately, precipitate was washed by petroleum ether and recrystallized from ethanol, if required, to give absolute target products. Every single product was confirmed by

adjusting its melting point and applying spectroscopic methods such as FT-IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.



**Figure S1.** Stepwise of preparation of the  $\text{CuFe}_2\text{O}_4@CS-SB$  catalyst

**4b,9b-dihydroxy-7,7-dimethyl-5-phenyl-4b,5,6,7,8,9b-hexahydroindeno[1,2-b]indole-9,10-dione**  
**(4a):** White solid (93%yield); m.p<sub>rep.</sub>( °C )= 260-265 °C; m.p<sub>lit.</sub>( °C )=210-212 °C[1]; IR (KBr):  $\nu$  3475, 3232, 2931, 2876, 1723, 1606, 1547, 1452, 1277, 1159cm<sup>-1</sup>. <sup>1</sup>H NMR (400MHz, DMSO) (ppm)= 7.72 (d, *J*= 4.0 Hz, 1H, ArH), 7.58-7.45 (m,5H, ArH), 7.30 (s, 2H, ArH), 7.28 (s, 1H,,), 6.60 (d, *J*=8.0 Hz, 1, ArH), 6.01 (s,1H,,), 2.41 (d, *J*=16.0 Hz,1H), 2.15 (d, *J*=16.0 Hz,1H), 1.91 (d, *J*=16.0 Hz,1H), 1.79 (d, *J*=16.0 Hz,1H), 0.96 (s, 3H, Me), 0.89 (s, 3H, Me).

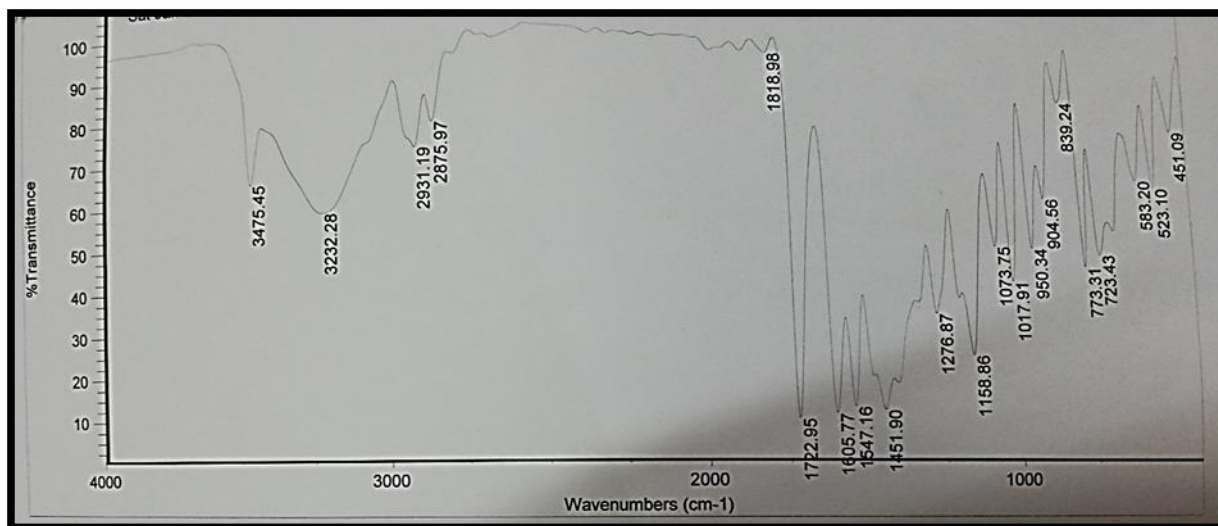


Figure S2. The FT-IR of 4a

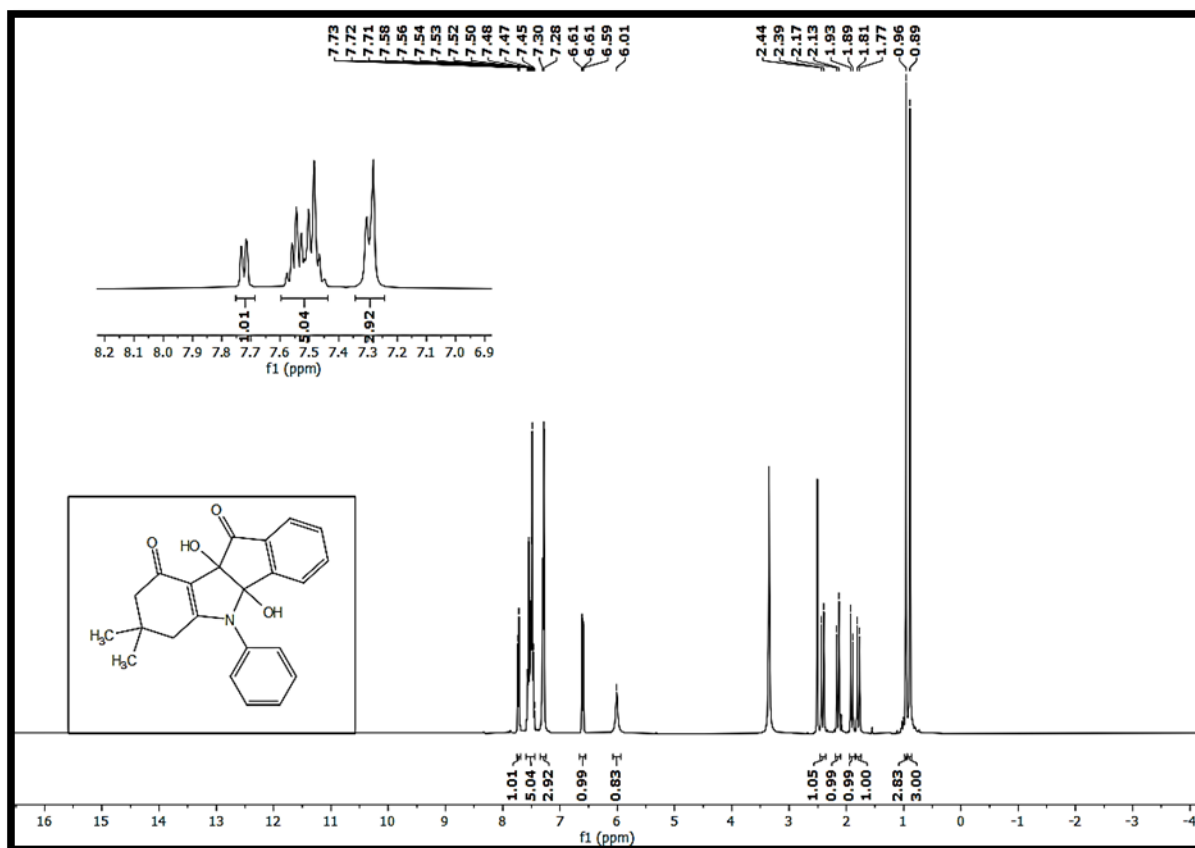


Figure S3. The <sup>1</sup>H NMR of 4a

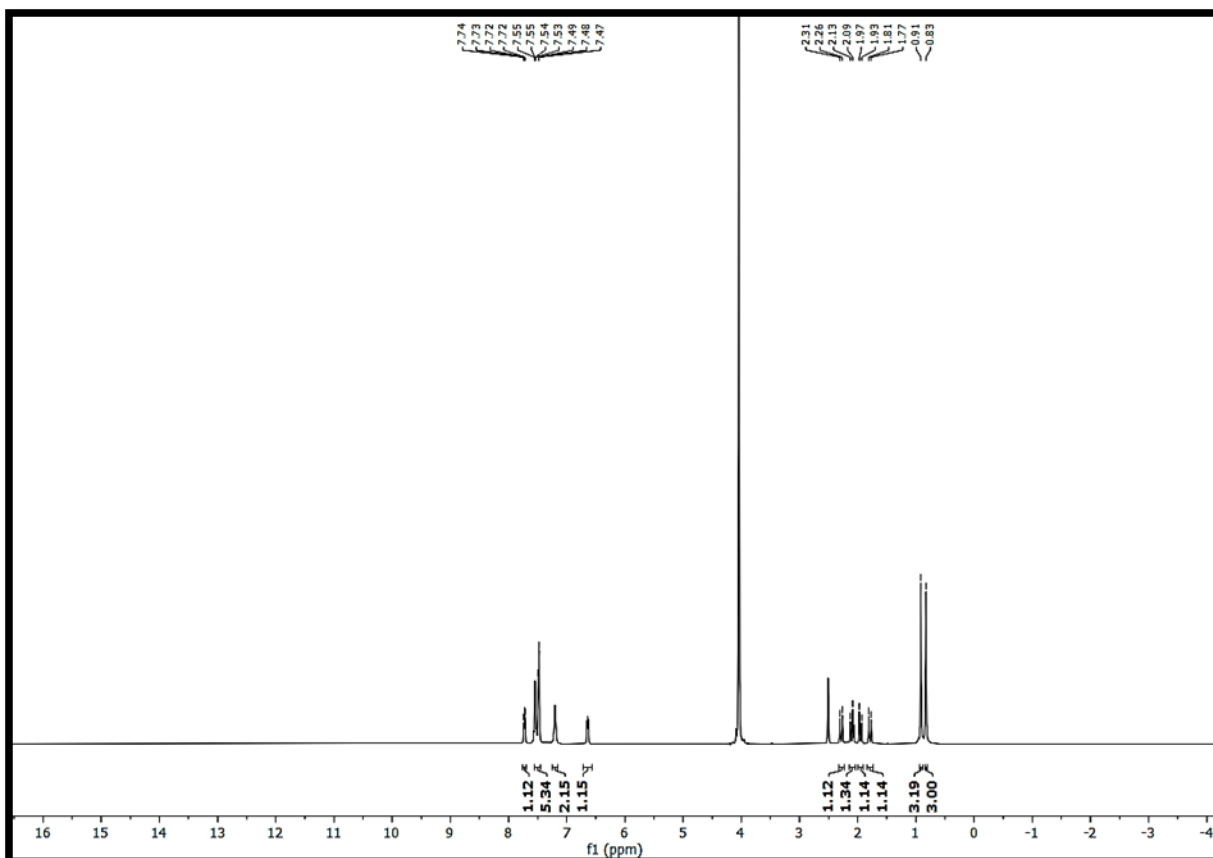


Figure S4. The <sup>1</sup>H NMR of 4a in D<sub>2</sub>O

**5-(4-ethylphenyl)-4b,9b-dihydroxy-7,7-dimethyl-4b,5,6,7,8,9b-hexahydroindeno[1,2-b]indole-9,10-dione (4b):** light brown solid (92%yield); m.p.<sub>rep.</sub>(<sup>o</sup>C)= 145-150 <sup>o</sup>C, IR(KBr):  $\nu$  3398, 2956, 2876, 1724, 1610, 1551, 1156  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (400MHz, DMSO) (ppm)= 7.72 (d,  $J=4.0$  Hz, 1H, ArH ), 7.59-7.51 (m, 2H, ArH), 7.33 (d,  $J=8.0$  Hz, 3H, ArH), 7.21 (s, 2H, ArH), 7.19 (s, 1H), 6.66 (d,  $J=8.0$  Hz, 1H, ArH), 5.97 (s, 1H), 2.7 (d,  $J=8.0$  Hz, 2H, CH<sub>2</sub>), 2.37 (d,  $J=16.0$  Hz, 1H), 2.13 (d,  $J=16.0$  Hz, 1H), 1.90 (d,  $J=16.0$  Hz, 1H), 1.79 (d,  $J=16.0$  Hz, 1H), 1.25 (t,  $J=8.0$  Hz, 3H, Me), 0.88 (s, 3H, Me), 0.86 (s, 3H, Me); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm)= 198.07, 189.57, 147.73, 144.01, 135.30, 135.20, 133.97, 130.62, 129.76, 128.72, 125.41, 123.62, 105.68, 97.10, 83.87, 51.66, 37.47, 33.87, 29.78, 28.27, 27.03, 15.85.

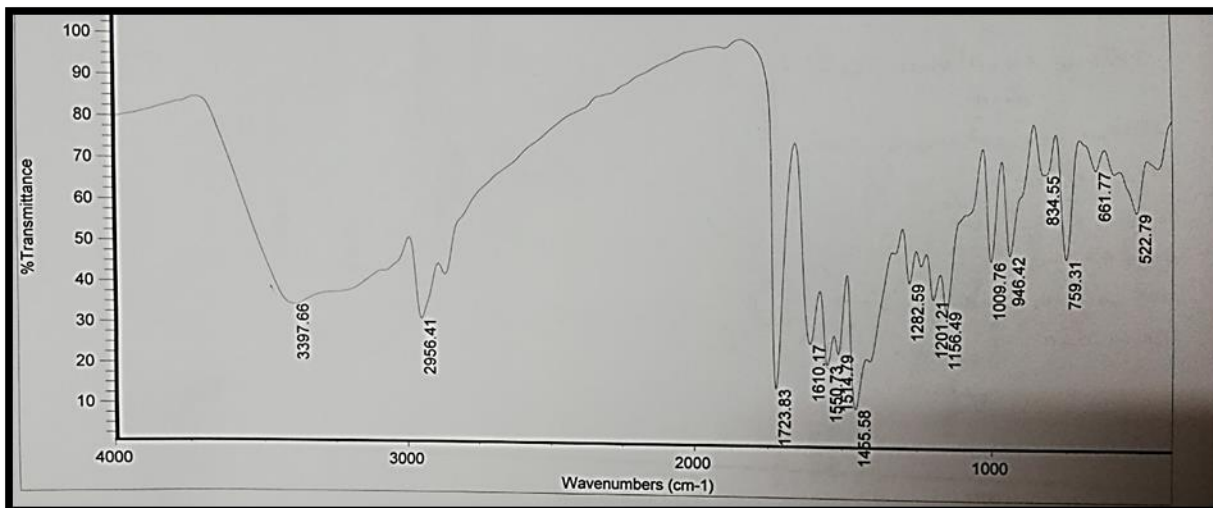


Figure S5. The FT-IR of 4b

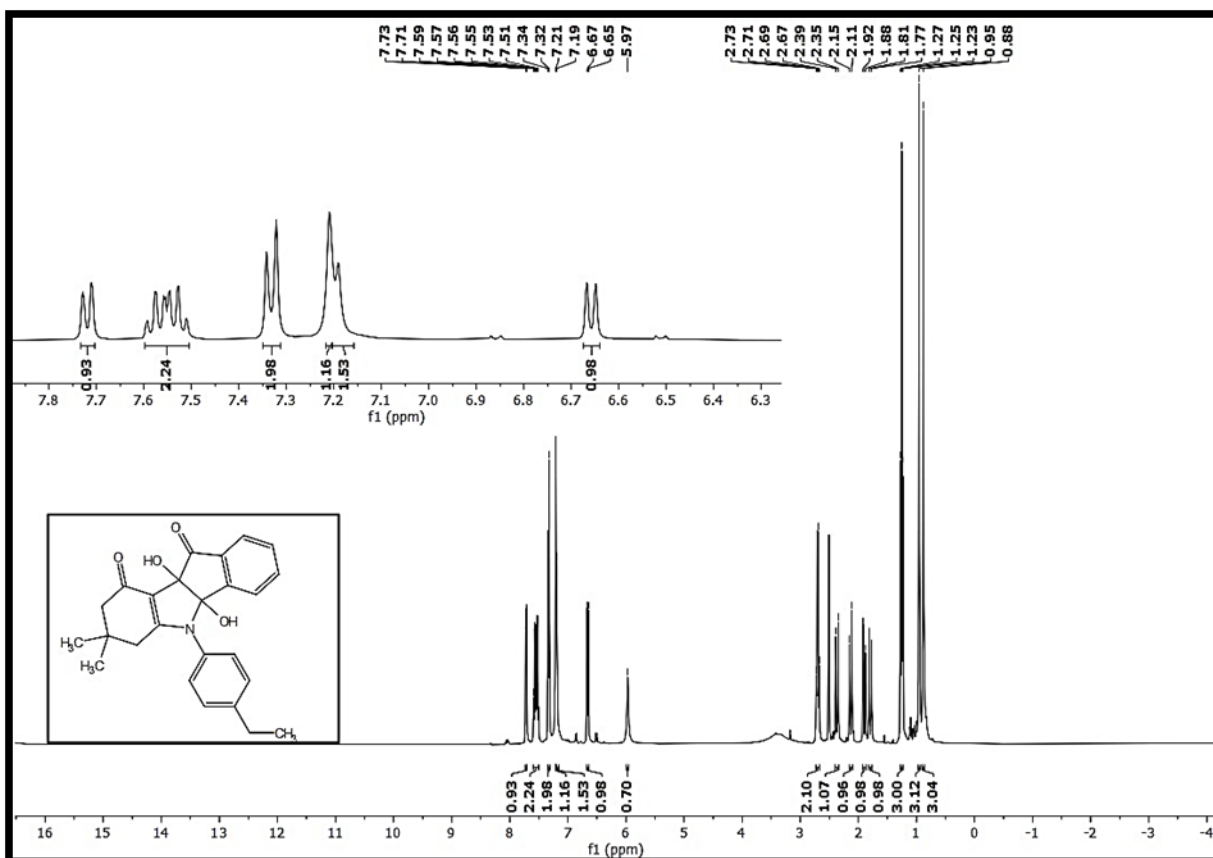


Figure S6. The  $^1\text{H}$  NMR of 4b

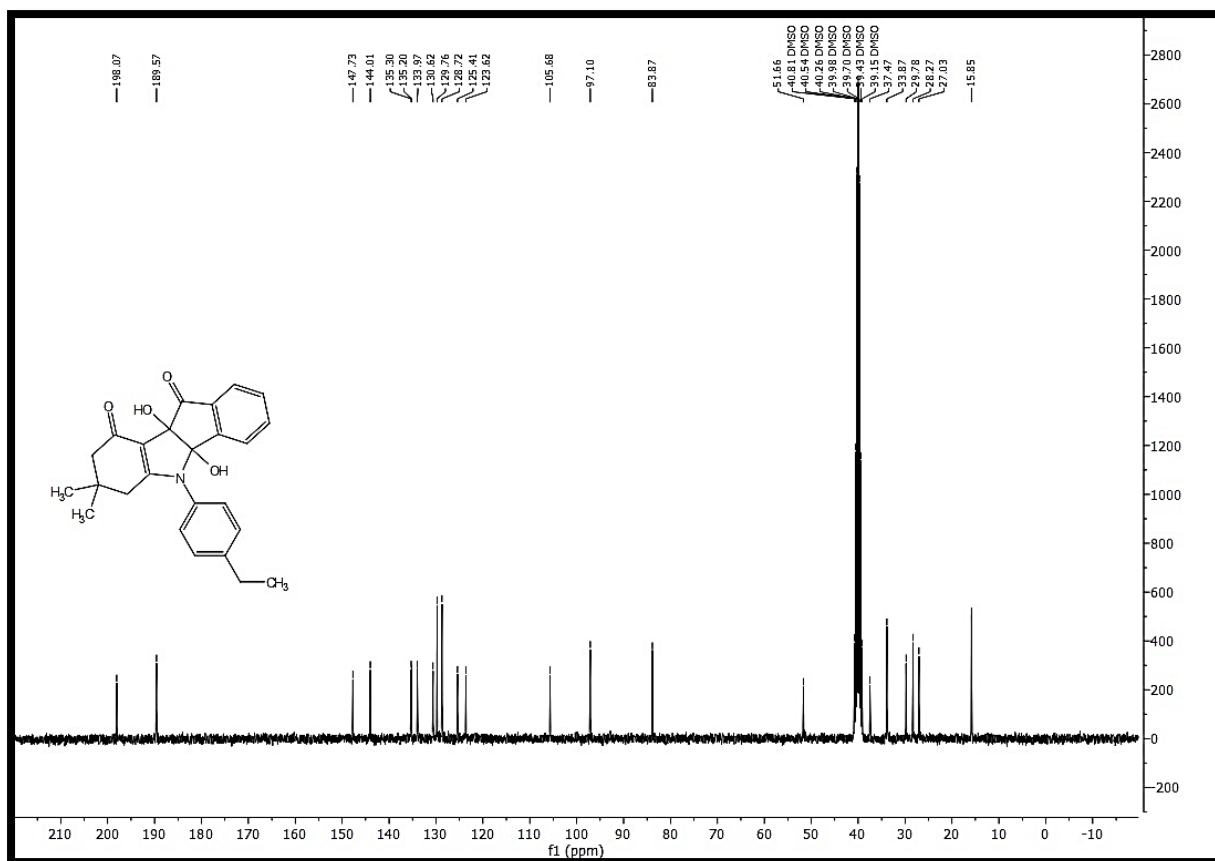


Figure S7. The  $^{13}\text{C}$  NMR of **4b**

**5-(3-chlorophenyl)-4b,9b-dihydroxy-7,7-dimethyl-4b,5,6,7,8,9b-hexahydroindeno [1,2-b] indole-9,10-dione (4c)**: white solid (90% yield);  $m.p_{\text{rep.}}$  ( $^{\circ}\text{C}$ ) = 200-205  $^{\circ}\text{C}$ ;  $m.p_{\text{lit.}}$  ( $^{\circ}\text{C}$ ) = 223-226  $^{\circ}\text{C}$  [19]; IR(KBr):  $\nu$  3564, 3391, 2947, 2873, 1719, 1641, 1480, 1159, 731  $\text{cm}^{-1}$ .  $^1\text{H}$ NMR (400MHz.DMSO) (ppm) = 7.61 (d,  $J=4.0$  Hz, 1H, ArH), 7.51-7.56 (m, 5H, ArH), 7.30 (s, 1H, ArH), 7.18 (d,  $J=8.0$ , 1H, ArH), 2.48 (d,  $J=16.0$  Hz, 1H), 2.15 (d,  $J=16.0$  Hz, 1H), 1.90 (d,  $J=16.0$  Hz, 1H), 1.81 (d,  $J=16.0$  Hz, 1H), 0.96 (s, 3H, Me), 0.91 (s, 3H, Me)

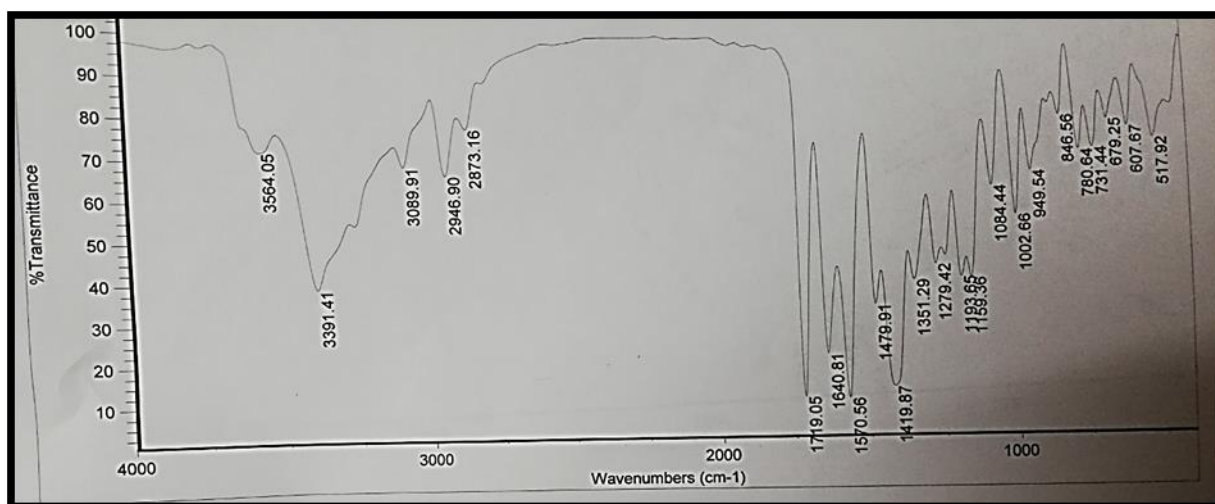


Figure S8. The FT-IR of **4c**

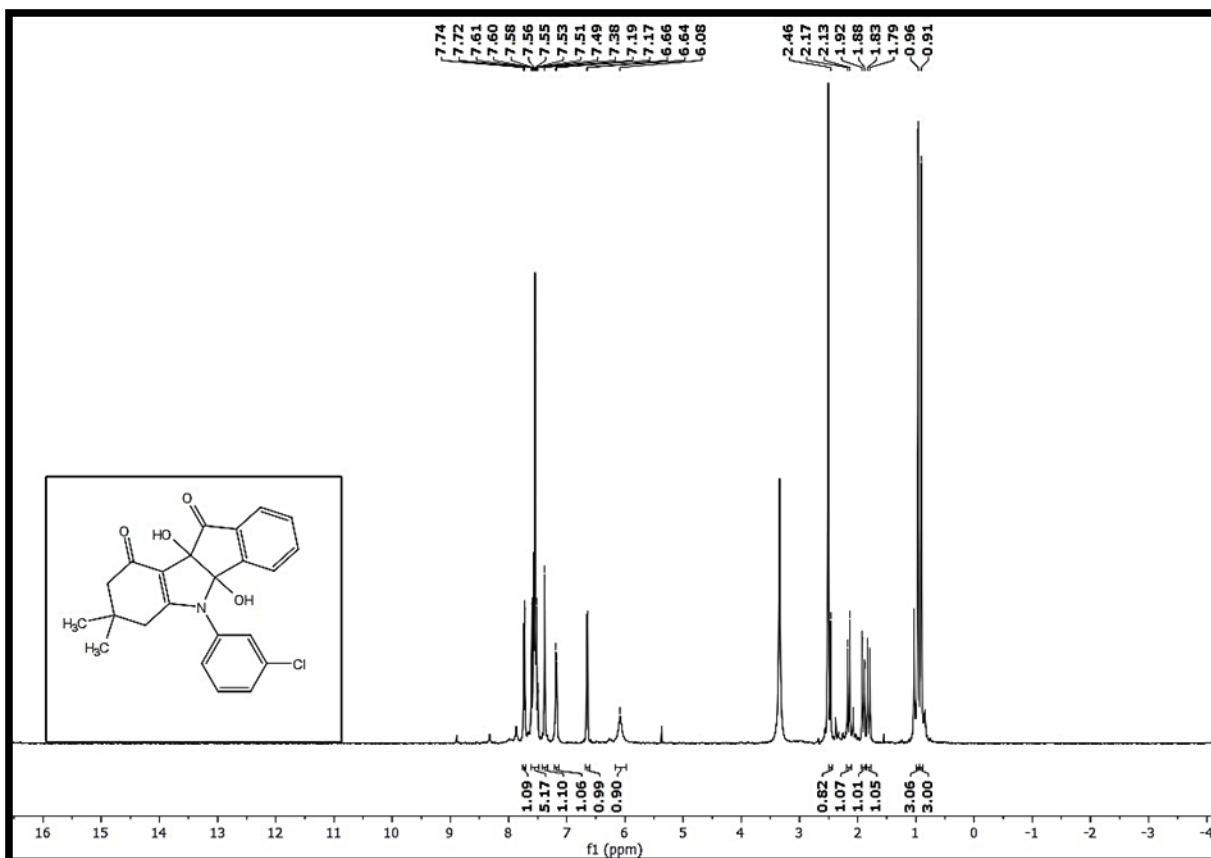


Figure S9. The <sup>1</sup>H NMR of 4c

**5-(4-bromophenyl)-4b,9b-dihydroxy-7,7-dimethyl-4b,5,6,7,8,9b-hexahydroindeno [1,2-b] indole-9,10-dione (4d):** white solid (92% yield); m.p<sub>rep.</sub>(°C) = 195-200 °C; m.p<sub>lit.</sub>(°C) = 160-162 °C [2]; IR (KBr): 9 3465, 2957, 2883, 1722, 1602, 1489, 1148, 518 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) (ppm) = 7.72 (t, *J* = 8.0 Hz, 3H, ArH), 7.61 (t, *J* = 8.0 Hz, 1H, ArH), 7.54 (t, *J* = 8.0 Hz, 1H), 7.35 (s, 1H), 7.26 (d, *J* = 8.0 Hz, 2H, ArH, OH), 6.68 (d, *J* = 8.0 Hz, 1H, ArH), 6.05 (s, 1H, OH), 2.42 (d, *J* = 16.0 Hz, 1H), 2.15 (d, *J* = 16.0 Hz, 1H), 1.90 (d, *J* = 16.0 Hz, 1H), 1.81 (d, *J* = 16.0 Hz, 1H), 0.95 (s, 3H, Me), 0.90 (s, 3H, Me)

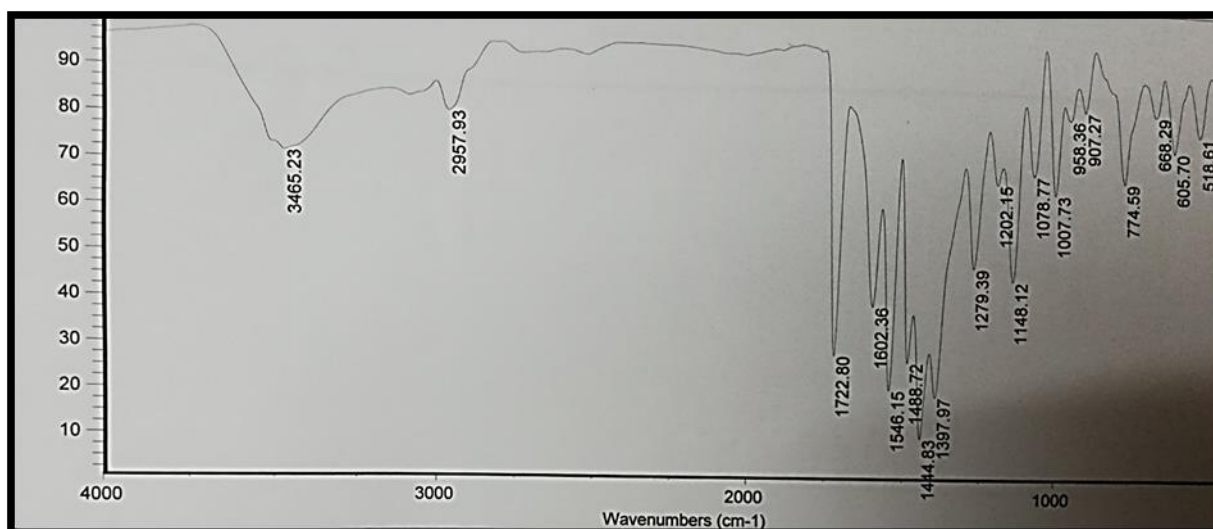


Figure S10. The FT-IR of 4d



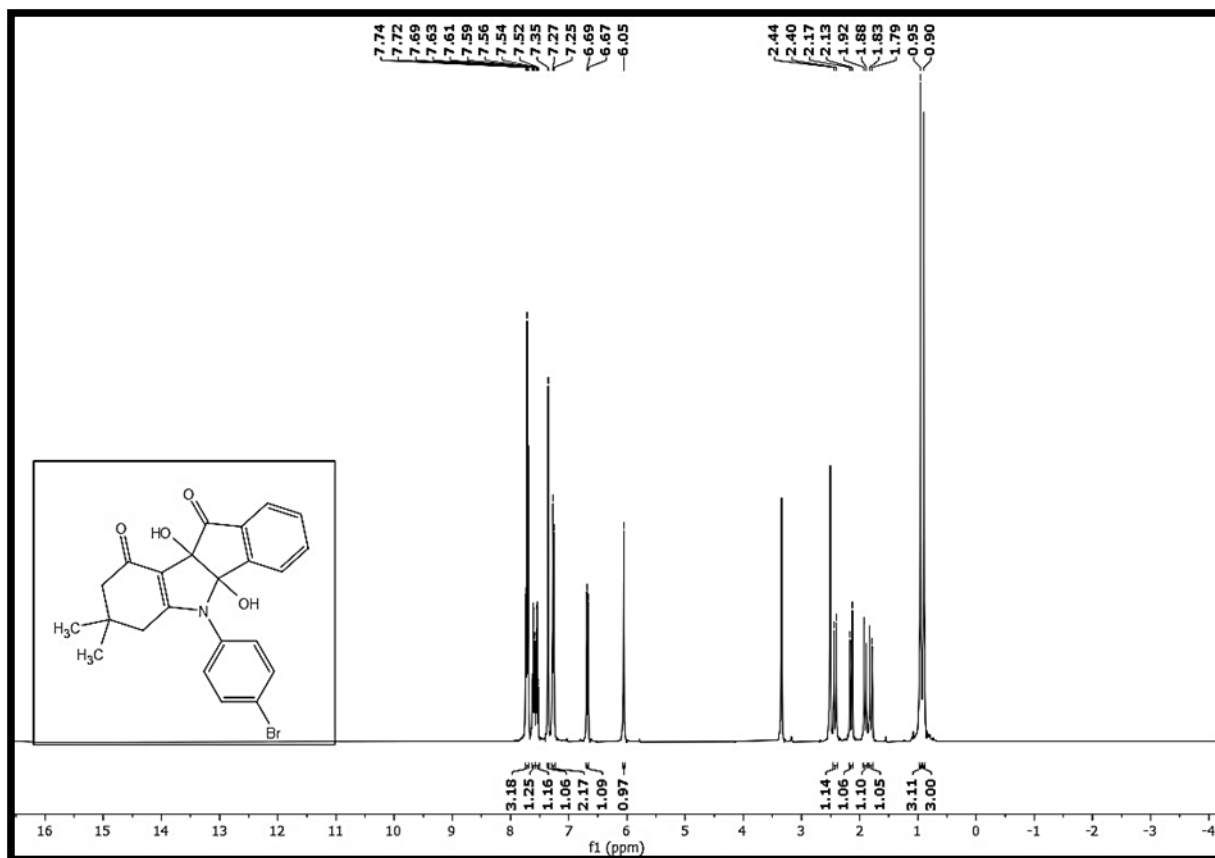


Figure S11. The <sup>1</sup>H NMR of 4d

**4b,9b-dihydroxy-7,7-dimethyl-5-(naphthalene-1-yl)-4b,5,6,7,8,9b-hexahydroindeno [1,2-b] indole-9,10-dione(4e):** light yellow solid; (93% yield); m.p.<sub>rep.</sub>(<sup>o</sup>C)= 205-210 <sup>o</sup>C; m.p.<sub>lit.</sub>(<sup>o</sup>C)=186-188 <sup>o</sup>C [20]; IR(KBr):  $\nu$  3381, 2931, 1712, 1608, 1448, 1157  $\text{cm}^{-1}$ . <sup>1</sup>HNMR (400 MHz, DMSO-d<sub>6</sub>) (ppm)= 8.04-8.13 (m, 1H), 7.99 (d,  $J=8.0\text{Hz}$ , 1H, ArH), 7.93 (d,  $J=8.0\text{Hz}$ , 1H, ArH), 7.70-7.81 (m, 2H, ArH), 7.57-7.63 (m, 1H, ArH), 7.40-7.45 (m, 2H, ArH), 7.05-7.17 (m, 2H, ArH, OH), 6.36 (d,  $J=8.0\text{ Hz}$ , 1H, ArH), 6.29 (d,  $J=4.0\text{ Hz}$ , 1H, ArH), 6.02 (s, 1H, OH), 1.79-2.16 (m, 4H), 0.90 (s, 3H, Me), 0.78 (s, 3H, Me)

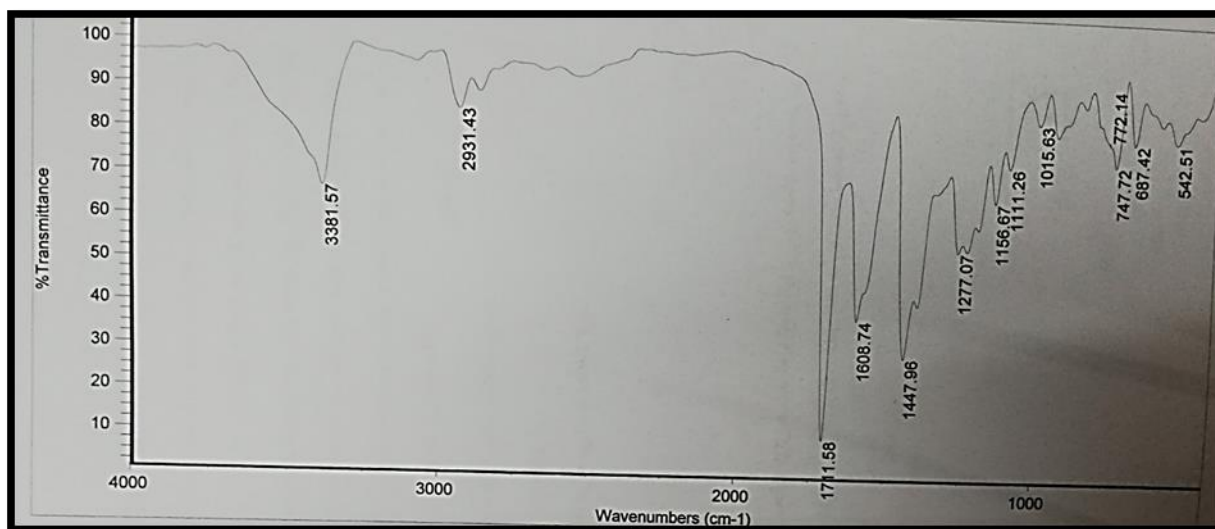


Figure S12. The FT-IR of 4e

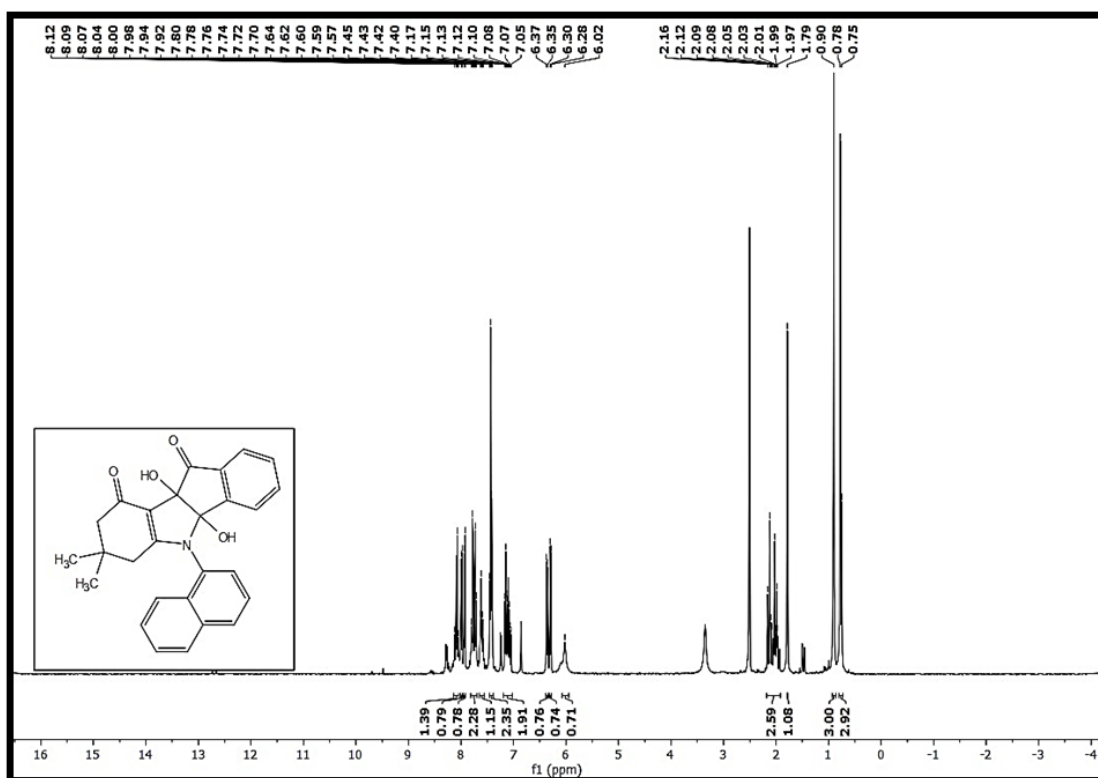


Figure S13. The <sup>1</sup>H NMR of 4e

**5,5'-(1,4-phenylene)bis(4b,9b-dihydroxy-7,7-dimethyl-4b,5,6,7,8,9b-hexahydroindeno [1,2-b] indole-9,10-dione) (4f):** smoky solid (95% yield); m.p.<sub>rep.</sub> (°C) = 305-310°C; IR (KBr): 9 3357, 3176, 2960, 1719, 1567, 1507, 1449, 1380, 1157 cm<sup>-1</sup>. <sup>1</sup>HNMR (400MHz.DMSO) (ppm)= 7.77(d, *J*=8.0Hz, 2H, ArH), 7.68-7.56 (m, 4H, ArH), 7.45-7.39 (m, 6H, ArH, OH), 6.75-6.79 (m, 2H, ArH), 6.09 (s, 2H, OH), 2.56 (d, *J*=16.0 Hz, 2H), 2.18 (d, *J*=16.0 Hz, 2H), 1.95 (d, *J*=4.0 Hz, 2H), 1.92 (d, *J*=16.0 Hz, 2H), 1.02 (s, 6H, Me), 0.95 (s, 6H, Me); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ (ppm)= 198.06, 189.93, 163.66, 147.75, 136.13, 135.31, 130.93, 130.06, 129.81, 123.93, 106.68, 97.40, 83.91, 51.75, 37.56, 34.17, 34.13, 30.05.

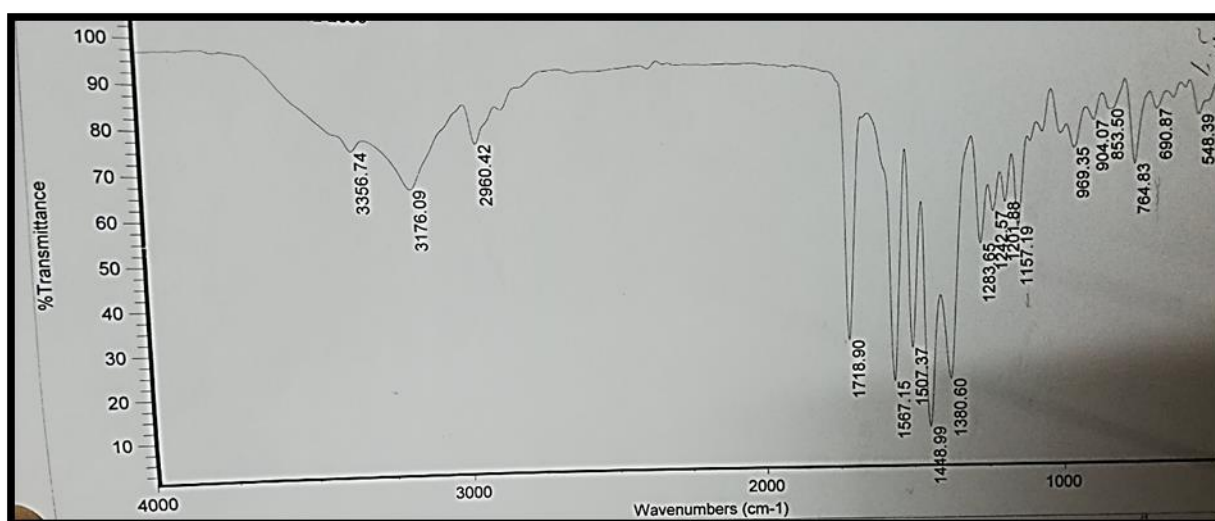


Figure S14. The FT-IR of 4f

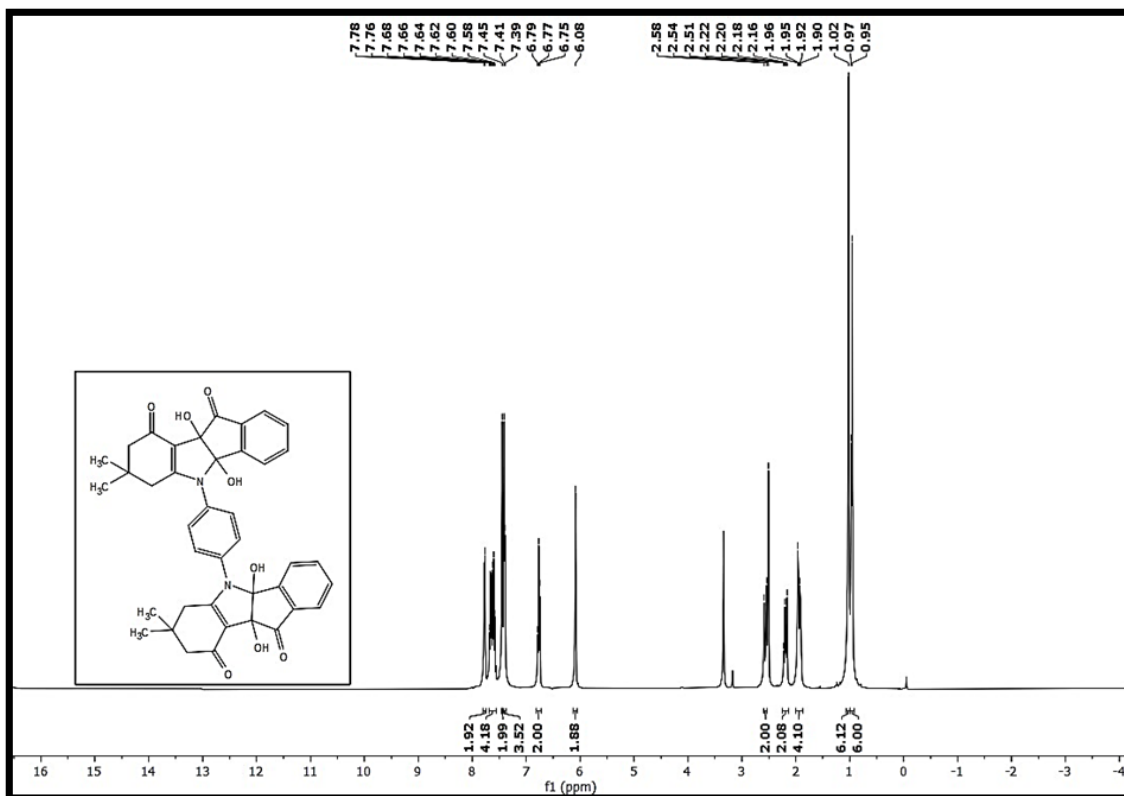


Figure S15. The  $^1\text{H NMR}$  of 4f

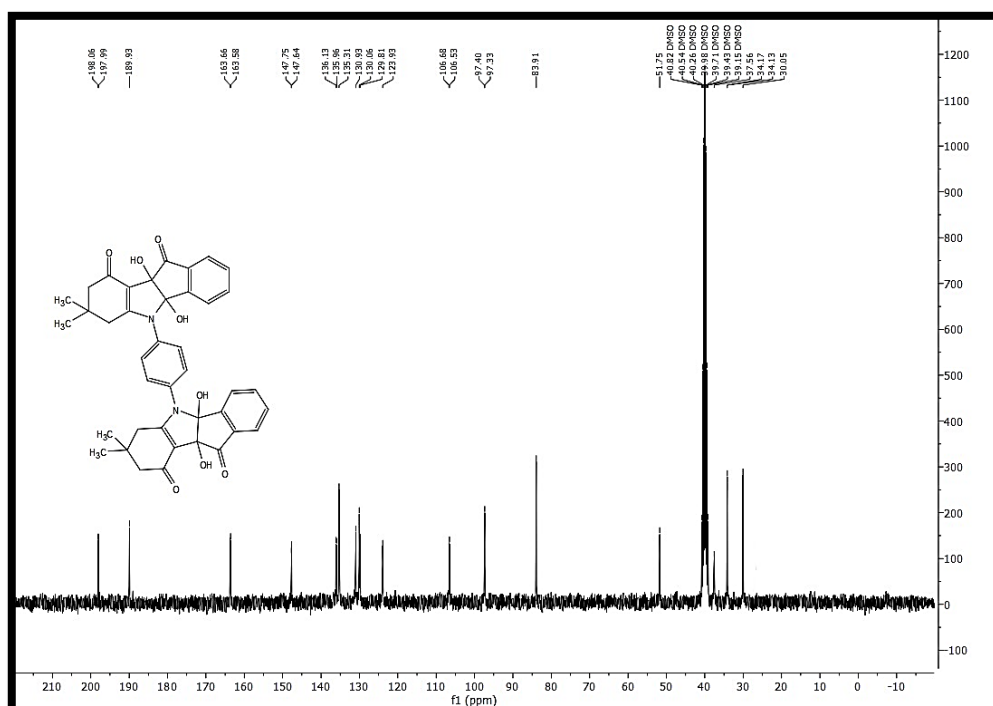


Figure S16. The  $^{13}\text{C NMR}$  of 4f

**5-(2-chlorophenyl)-4b,9b-dihydroxy-7,7-dimethyl-4b,5,6,7,8,9b-hexahydroindeno [1,2-b] indole-9,10-dione (4g):** white solid (92% yield); m.p<sub>rep.</sub>(°C) = 240-245 °C; m.p<sub>lit.</sub>(°C) = 230-231 °C [1]; IR (KBr): 9 3417, 2955, 2874, 1714, 1571, 1446, 1155, 772 cm<sup>-1</sup>. <sup>1</sup>HNMR (400MHz.DMSO) (ppm) = 2.83 (d, *J*=4.0Hz, 1H, ArH), 7.74 (d, *J*=8.0Hz, 1H, ArH), 7.53-7.55 (m, 5H, ArH), 7.38 (s, 1H, OH), 6.66(d, *J*=4.0 Hz, ArH), 5.96 (s, 1H, OH), 2.08-1.95 (m, 4H), 0.97 (s, 3H, Me), 0.87 (s, 3H, Me)

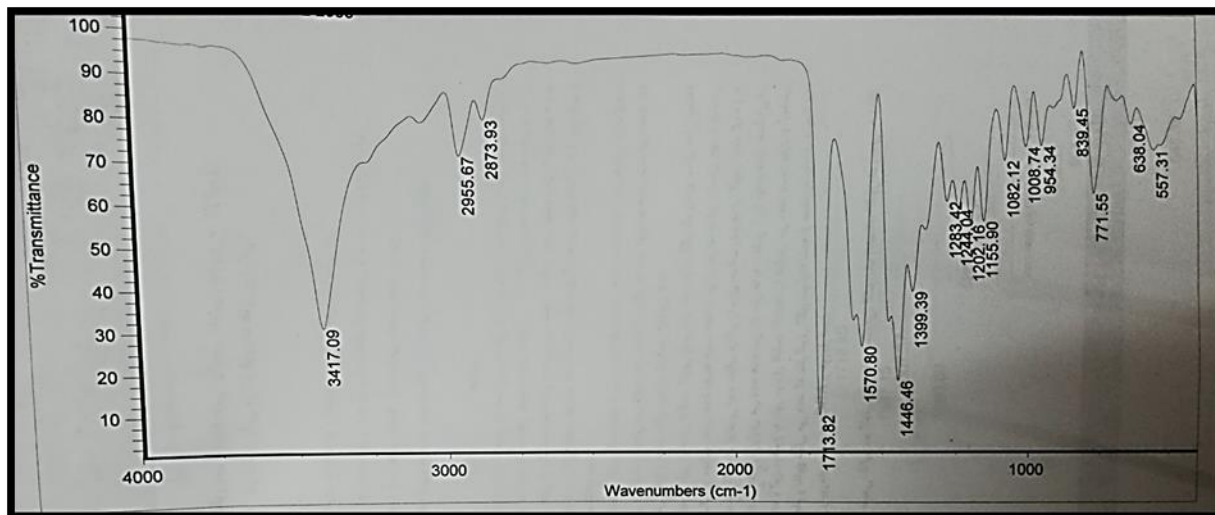


Figure S17. The FT-IR of **4g**

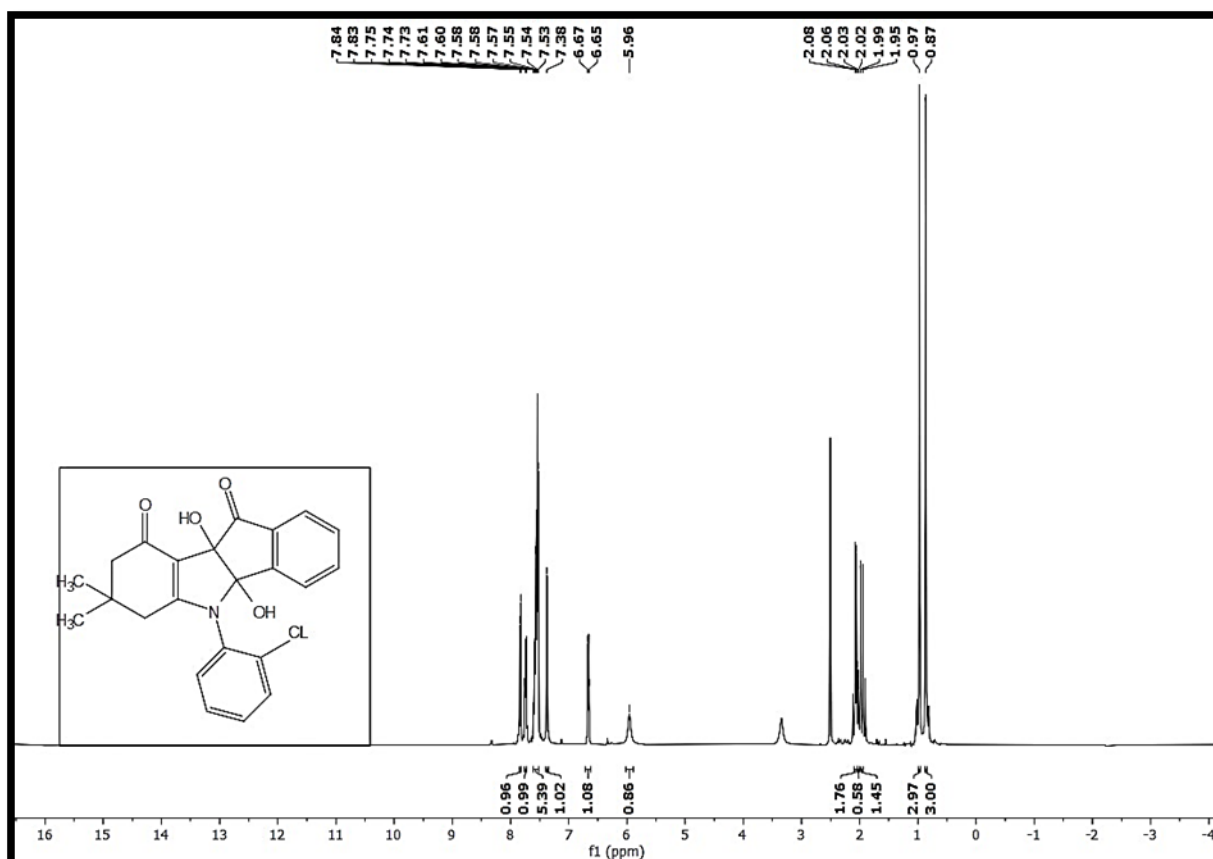


Figure S18. The <sup>1</sup>H NMR of **4g**

**4b,9b-dihydroxy-5-(4-methoxyphenyl)-7,7-dimethyl-4b,5,6,7,8,9b-hexahydroindeno [1,2-b] indole-9,10-dione (4h):** gray solid (91% yield); m.p<sub>rep.</sub>(°C) = 210-215 °C; m.p<sub>lit.</sub>(°C) = 224-226 °C [1];

IR (KBr):  $\nu$  3410, 3037, 2951, 2715, 1728, 1607, 1512, 1441, 1149  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400MHz.DMSO) (ppm)= 7.72(d,  $J=8.0\text{Hz}$ , 1H, ArH), 7.60-7.51 (m, 2H, ArH), 7.31-7.16 (m, 5H, ArH, OH), 6.66 (d,  $J=8.0\text{Hz}$ , 1H, ArH), 5.98 (s, 1H, OH), 2.39 (s, 3H, OMe), 2.35 (s, 1H), 2.13 (d,  $J=16.0\text{ Hz}$ , 1H), 1.89 (d,  $J=16.0\text{ Hz}$ , 1H), 1.77 (d,  $J=16.0\text{ Hz}$ , 1H), 0.91 (s, 3H, Me), 0.88 (s, 3H, Me)

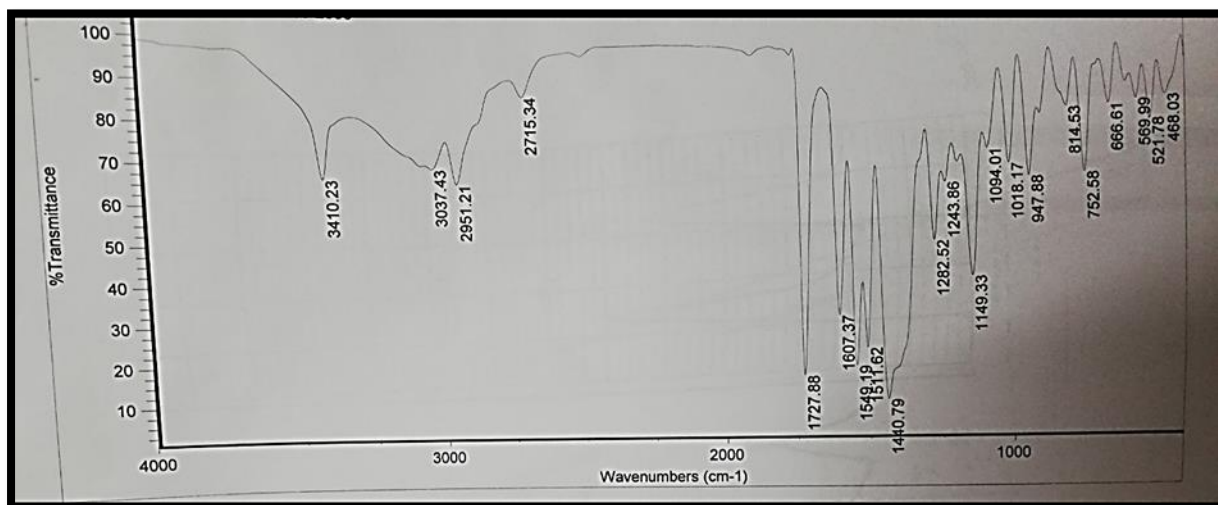


Figure S19. The FT-IR of **4h**

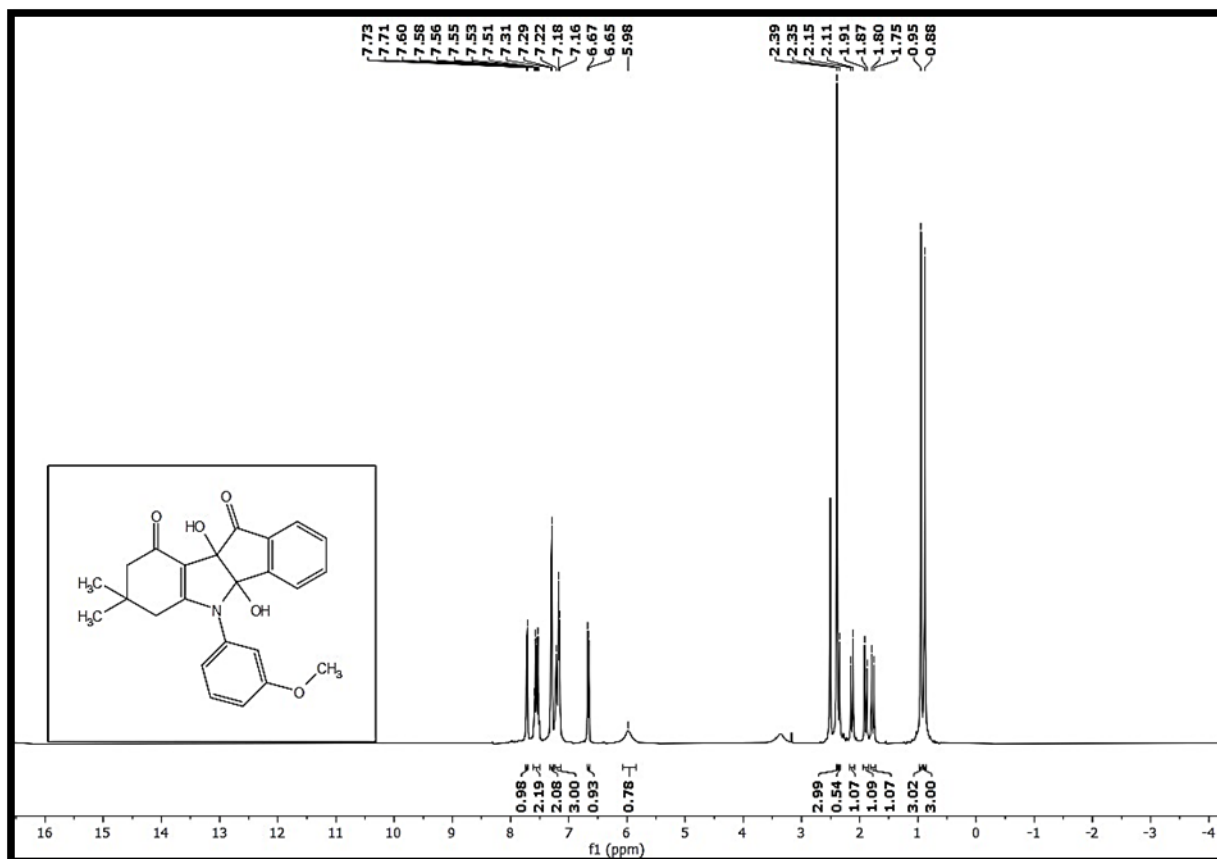


Figure S20. The  $^1\text{H NMR}$  of **4h**

**5-(4-chlorophenyl)-4b,9b-dihydroxy-7,7-dimethyl-4b,5,6,7,8,9b-hexahydroindeno [1,2-b] indole-9,10-dione (4i)**: white solid (93% yield);  $m.p_{\text{rep.}}$  ( $^{\circ}\text{C}$ ) = 223-228  $^{\circ}\text{C}$ ;  $m.p_{\text{lit.}}$  ( $^{\circ}\text{C}$ ) = 235-236  $^{\circ}\text{C}$  [1]; IR (KBr):  $\nu$  3423, 2952, 1713, 1621, 1553, 1449, 1183, 771  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (400MHz.DMSO) (ppm)= 7.73

(d,  $J=8.0\text{Hz}$ , 1H, ArH), 7.62-7.52 (m, 4H, ArH), 7.36 (s, 1H, OH), 7.33 (d,  $J=8.0\text{Hz}$ , 2H, ArH), 6.67 (d,  $J=8.0\text{Hz}$ , 1H, ArH), 6.06 (s, 1H, OH), 2.42 (d,  $J=20.0\text{ Hz}$ , 1H), 2.15 (d,  $J=16.0\text{ Hz}$ , 1H), 1.90 (d,  $J=16.0\text{ Hz}$ , 1H), 1.80 (d,  $J=20.0\text{ Hz}$ , 1H), 0.96 (s, 3H, Me), 0.90 (s, 3H, Me)

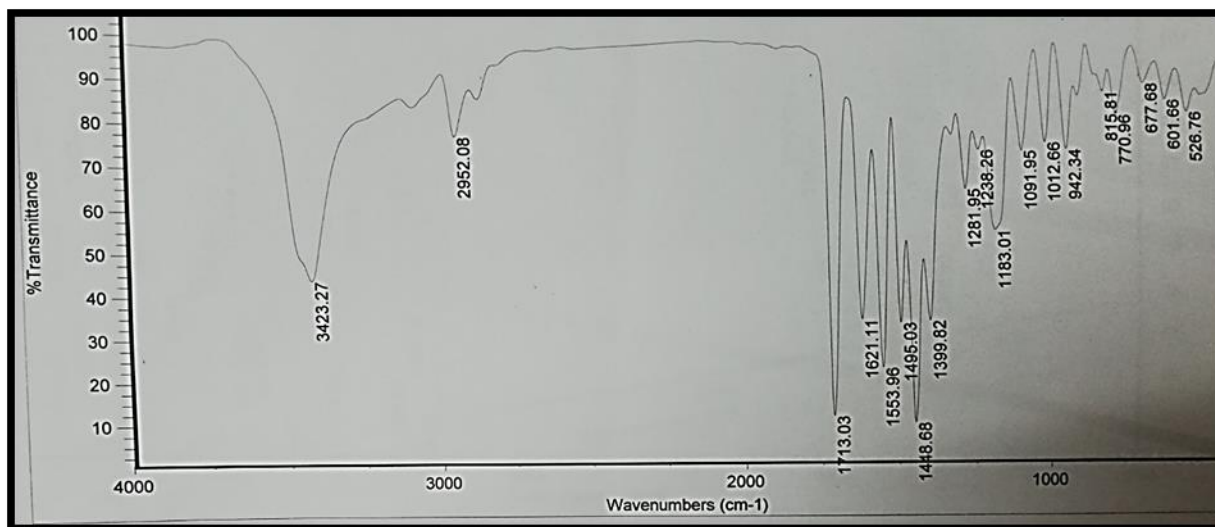


Figure S21. The FT-IR of **4i**

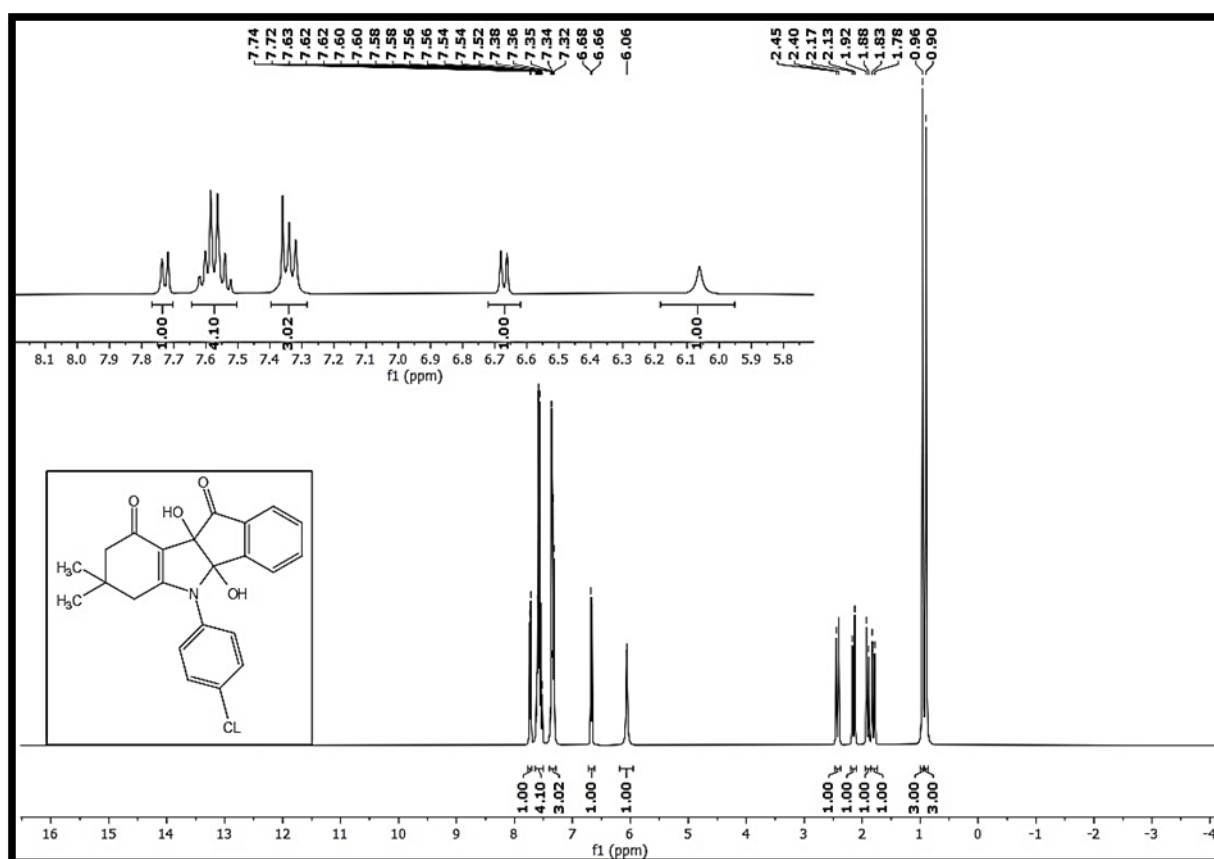


Figure S22. The  $^1\text{H}$  NMR of **4i**

**5,5'-(pyridine-2,6-diyl)bis(4b,9b-dihydroxy-7,7-dimethyl-4b,5,6,7,8,9b-hexahydroindeno [1,2-b] indole-9,10-dione) (4j)**: pale yellow (94% yield);  $m.p_{\text{rep.}}(^{\circ}\text{C}) = 215-220$ ; IR (KBr):  $\nu$  3389, 3254, 2943, 2879, 1713, 1660, 1607, 1464, 1255, 1164  $\text{cm}^{-1}$ .  $^1\text{H}$ NMR (400MHz,DMSO) (ppm)= 8.34-8.21 (m, 2H, ArH), 8.87-7.43 (m, 11H, ArH, OH), 6.28 (s, 2H, OH), 2.37-1.99 (m, 8H), 1.03 (s, 6H, Me),

0.85 (s, 6H, Me);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm)= 197.55, 193.18, 175.94, 152.58, 147.25, 136.62, 134.70, 131.88, 125.30, 123.47, 112.94, 111.67, 91.09, 90.91, 82.60, 51.58, 37.63, 33.45, 27.81.

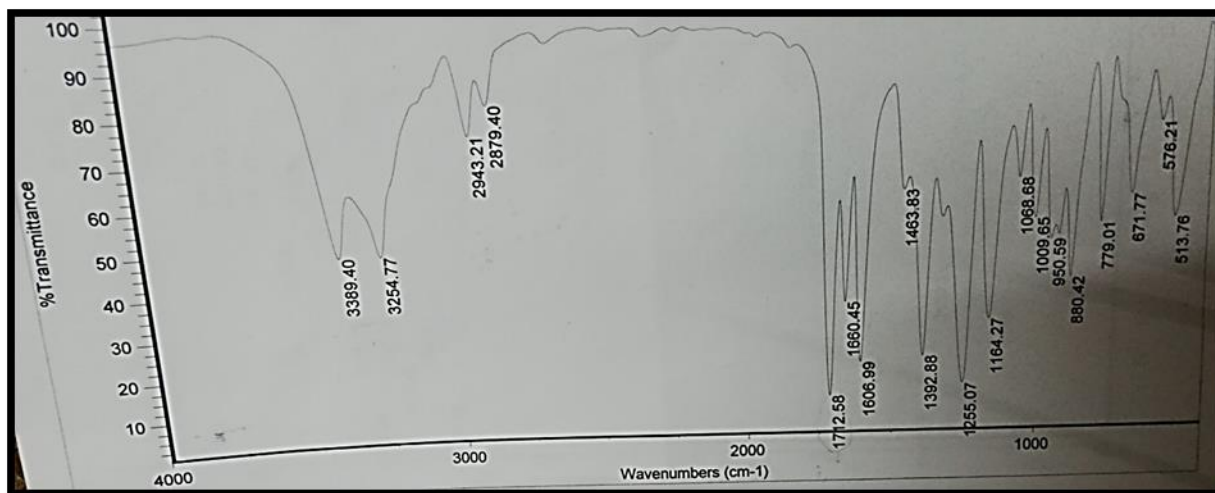


Figure S23. The FT-IR of **4j**

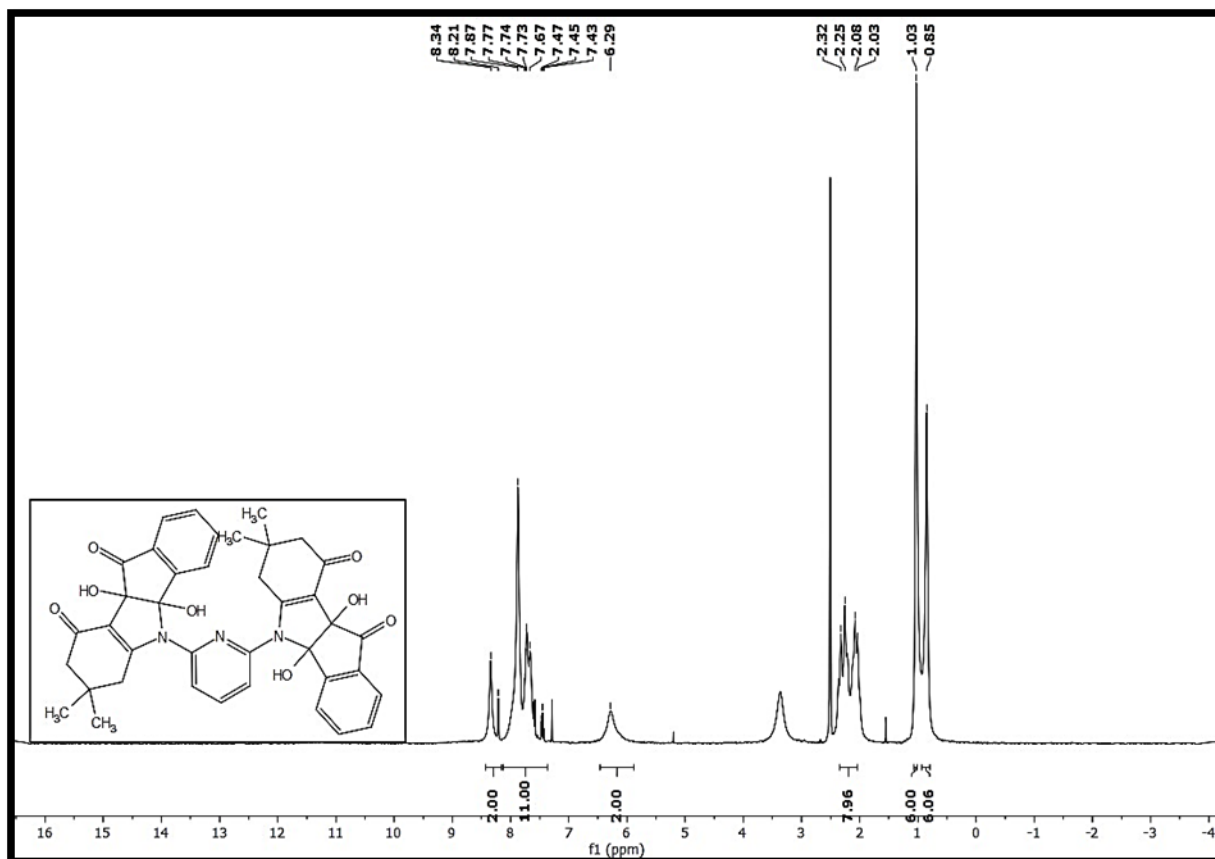


Figure S24. The  $^1\text{H}$  NMR of **4j**

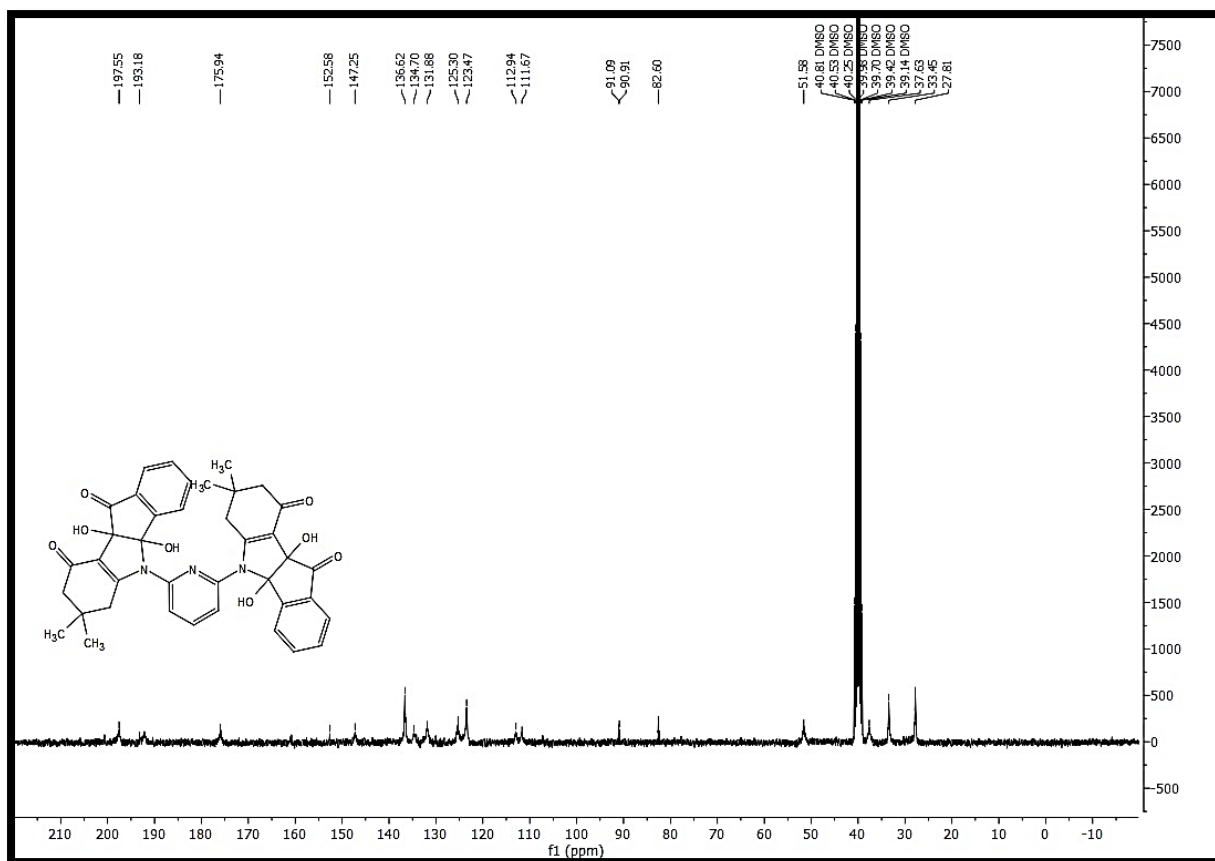


Figure S25. The <sup>13</sup>C NMR of 4j

**5,5'-(sulfonylbis(4,1-phenylene))bis(4b,9b-dihydroxy-7,7-dimethyl-4b,5,6,7,8,9b-hexahydroindeno [1,2-b] indole-9,10-dione) (4k):** white solid (95% yield); m.p.<sub>rep.</sub>(<sup>o</sup>C)= 290-295 <sup>o</sup>C; FT-IR (KBr): 9 3393, 2959, 2879, 1724, 1624, 1560, 1493, 1432, 1289 cm<sup>-1</sup>. <sup>1</sup>H NMR (400MHz.DMSO) (ppm)= 8.16-8.19 (m, 3H), 7.72 (d, *J*=4Hz, 2H), 7.65 (d, *J*=8Hz, 4H), 7.58 (s, 2H), 7.49-7.55 (m, 5H), 6.54-6.58 (m, 2H), 6.19 (s, 2H), 2.53-2.57 (m, 2H), 2.12-2.19 (m, 2H), 1.86-1.94 (m, 4H), 0.94 (s,6H,Me), 0.88 (s, 6H, Me); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ (ppm)= 197.75, 190.35, 147.37, 142.04, 139.80, 135.51, 135.13, 130.89, 130.04, 129.03, 124.91, 123.85, 113.61, 108.00, 97.82, 83.98, 51.68, 37.55, 34.25, 29.86.

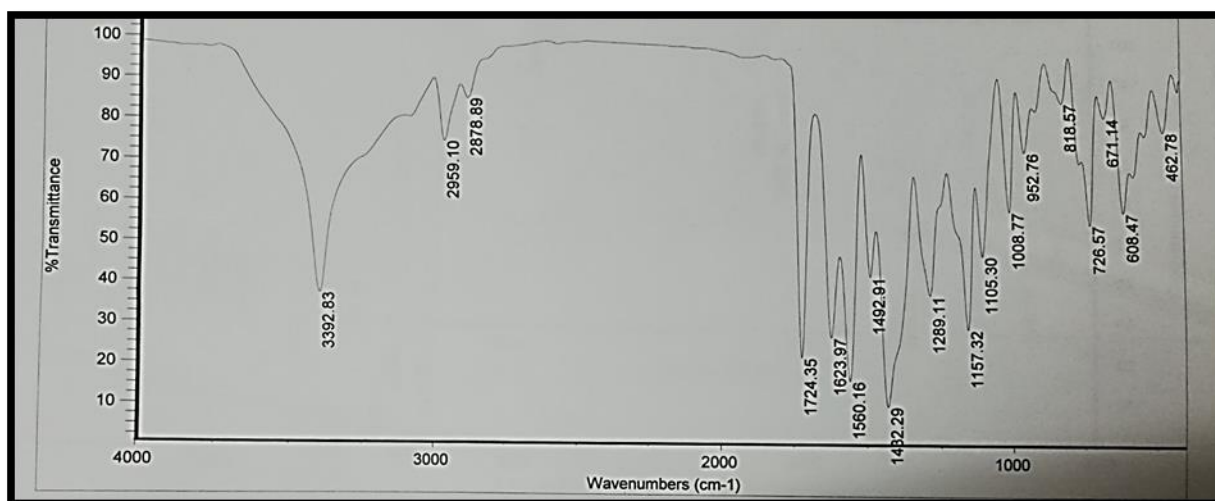


Figure S26. The FT-IR of 4k



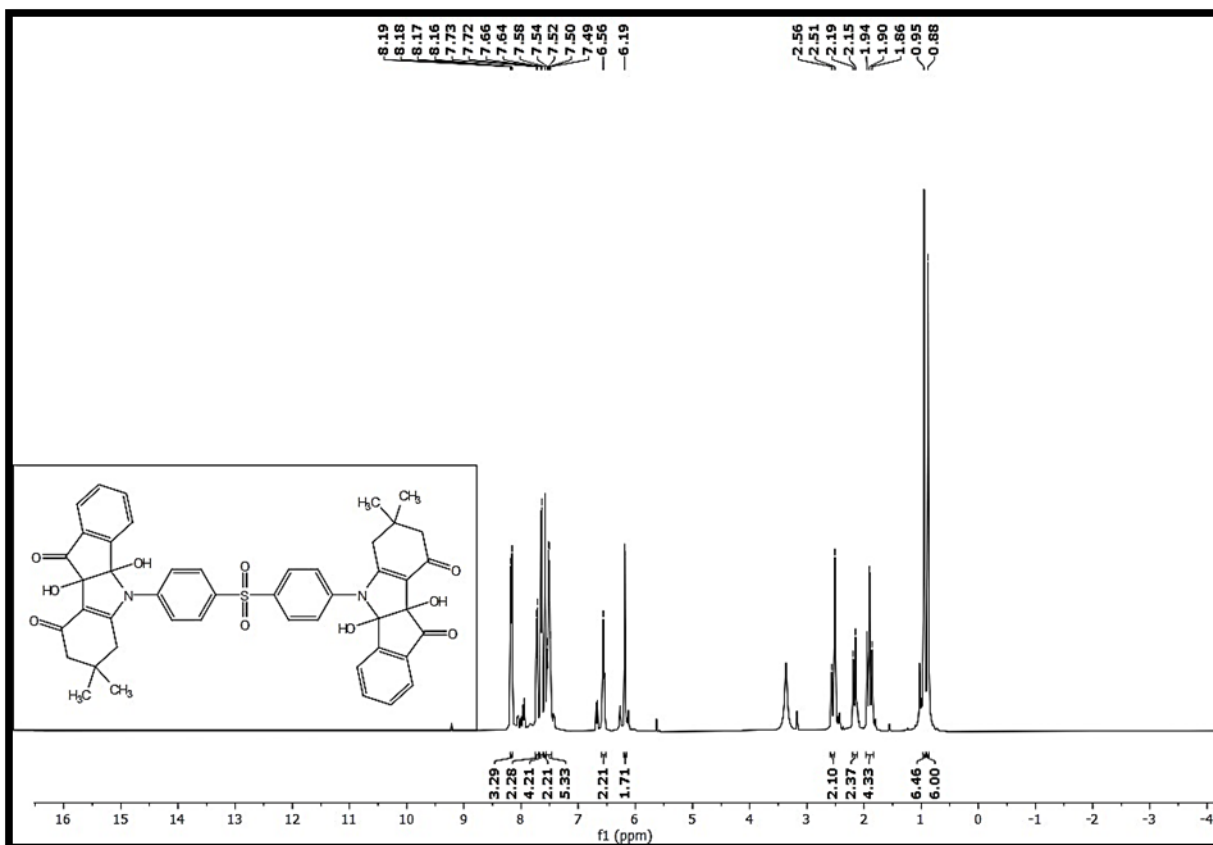
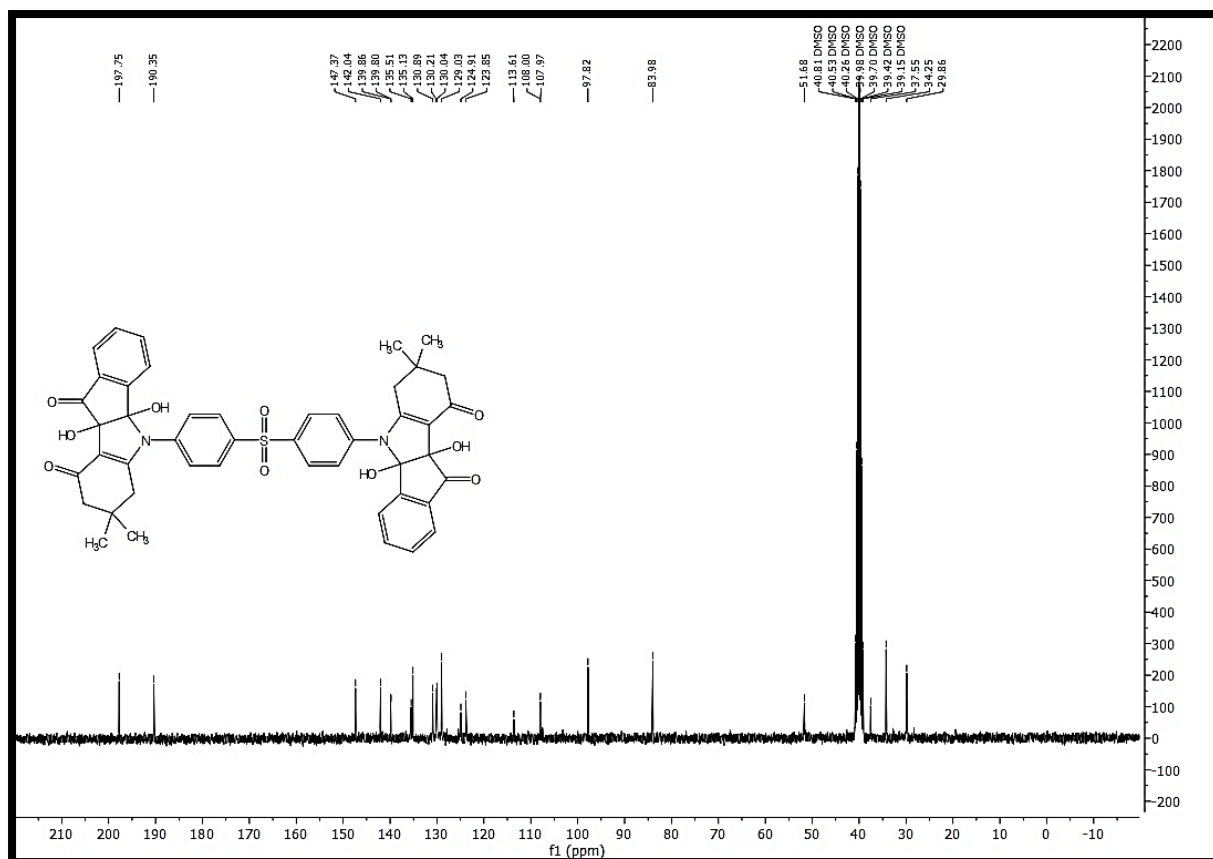
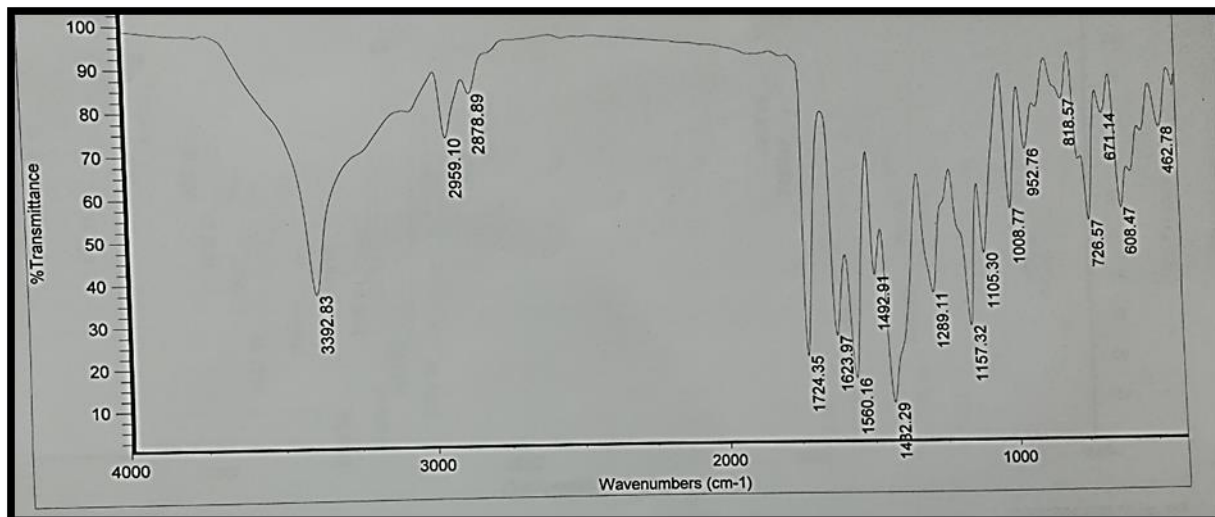


Figure S27. The  $^1\text{H}$  NMR of 4k

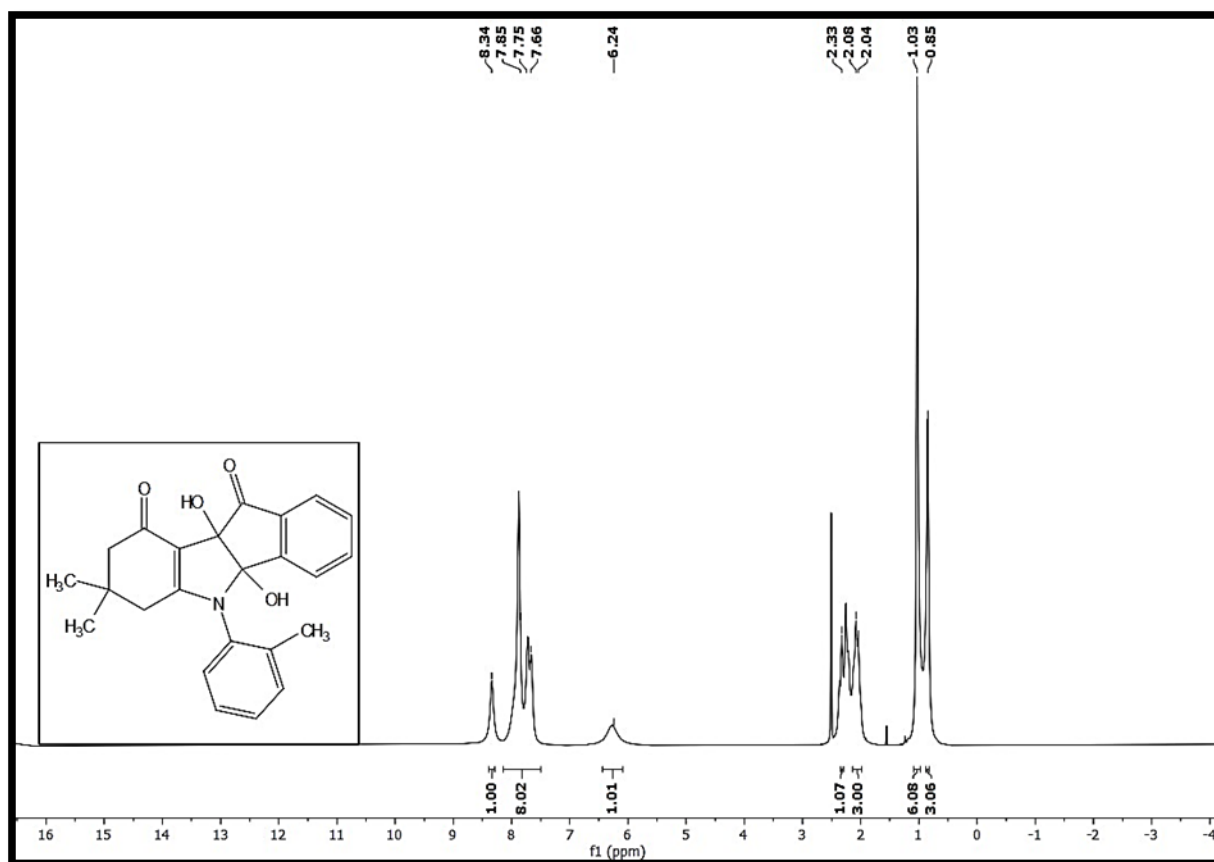


**Figure S28.** The  $^{13}\text{C}$  NMR of **4k**

**4b,9b-dihydroxy-7,7-dimethyl-5-(o-tolyl) -4b,5,6,7,8,9b- hexahydroindeno [1,2-b] indole-9,10-dione (4l):** white solid (92% yield);  $m.p_{\text{rep.}}(^{\circ}\text{C})=215-220^{\circ}\text{C}$ ;  $m.p_{\text{lit.}}(^{\circ}\text{C})=217-216^{\circ}\text{C}$ [1]; FT-IR (KBr): 9 3392, 2959, 1724, 1624, 1493, 1289, 1157  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400MHz.DMSO) (ppm)= 8.34 (s, 1H), 7.66-7.88 (m, 8H), 6.29 (s, 1H), 2.33 (s, 1H), 2.00-2.12 (m, 3H), 1.03 (s, 6H, Me), 0.85 (s, 3H, Me).



**Figure S29.** The FT-IR of **4l**



**Figure S30.** The  $^1\text{H}$  NMR of **4l**