

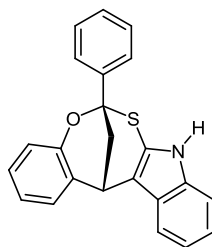
## Efficient and green synthesis of new polycyclic procyanidin derivatives via tandem dinucleophilic addition of indolin-2-thiones to flavylum salts

### Supplementary Information

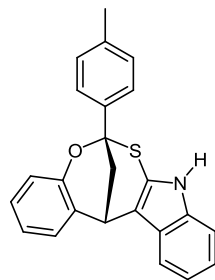
Firouz Matloubi Moghaddam, Behzad Koushki Foroushani, Hamdollah Saeidian, Saghar Nourian, Zohreh Mirjafary, Mostafa Kiamehr

*General procedure for the synthesis of procyanidins 3a-o:* A mixture of indolin-2-thione **1** (0.5 mmol) and flavylum salt **2** (0.5 mmol) in H<sub>2</sub>O/AcOH(glacial) (5 mL, 1/1) was stirred at room temperature for 10 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the solid product was filtered and washed three times with water then air dried. In some cases, column chromatography was performed using Silica gel eluting with petroleum ether/ethyl acetate (2:1) to obtain pure solid product.

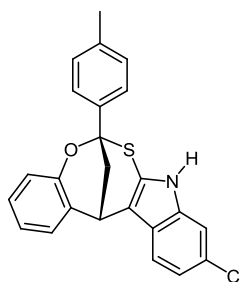
*Analytical data for products:*



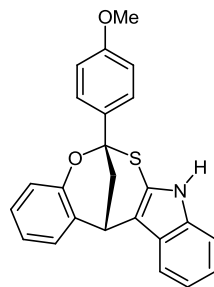
6-Phenyl-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3a**); mp: 132-134 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/DMSO): δ 2.42 (dd, *J* = 13.3, 3.9 Hz, 1H), 2.71 (dd, *J* = 13.3, 2.5 Hz, 1H), 4.27-4.29 (m, 1H), 6.61 (t, *J* = 7.4 Hz, 1H), 6.75-6.78 (m, 2H), 6.81-6.84 (m, 2H), 6.98 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.12-7.16 (m, 1H), 7.21 (t, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 2H), 10.28 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/DMSO): δ 29.6 (CH), 37.2 (CH<sub>2</sub>), 88.3 (C), 111.0 (CH), 111.9 (C), 116.2 (CH), 117.1 (CH), 119.6 (CH), 120.6 (CH), 121.6 (CH), 125.7 (CH), 126.1 (C), 126.2 (C), 126.6 (CH), 126.9 (C), 127.4 (CH), 128.0 (CH), 128.6 (CH), 136.9 (C), 142.8 (C), 152.2 (C). Anal Calcd for C<sub>23</sub>H<sub>17</sub>NOS: C 77.72, H 4.82, N 3.94, Found: C 77.65, H 4.76, N 3.85.



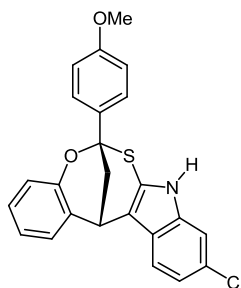
6-(4-Methylphenyl)-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3b**); mp: 164-166 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CCl<sub>4</sub>): δ 2.46 (s, 3H), 2.68 (dd, *J* = 13.3, 3.1 Hz, 1H), 2.92 (dd, *J* = 13.3, 2.5 Hz, 1H), 4.53-4.54 (m, 1H), 6.89 (t, *J* = 7.3 Hz, 1H), 7.06-7.22 (m, 5H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.75 (brs, 1H), 7.76 (d, *J* = 7.8 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CCl<sub>4</sub>): δ 21.6 (CH<sub>3</sub>), 29.9 (CH), 37.5 (CH<sub>2</sub>), 88.9 (C), 110.8 (CH), 113.4 (C), 116.6 (CH), 117.6 (CH), 120.5 (CH), 121.4 (CH), 121.9 (CH), 125.8 (C), 125.9 (CH), 126.7 (C), 127.3 (C), 127.7 (CH), 128.3 (CH), 129.5 (CH), 136.8 (C), 138.6 (C), 140.0 (C), 152.3 (C). Anal Calcd for C<sub>24</sub>H<sub>19</sub>NOS: C 78.02, H 5.18, N 3.79, Found: C 77.17, H 5.22, N 3.64.



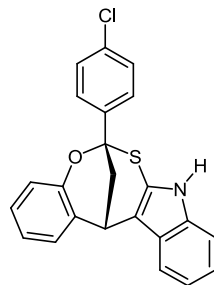
10-Chloro-6-(4-methylphenyl)-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3c**); mp: 129-131 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CCl<sub>4</sub>): δ 2.46 (s, 3H), 2.68 (dd, *J* = 13.3, 4.0 Hz, 1H), 2.91 (dd, *J* = 13.3, 2.5 Hz, 1H), 4.48-4.50 (m, 1H), 6.90 (t, *J* = 7.3 Hz, 1H), 7.05-7.18 (m, 4H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.31 (s, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.71 (brs, 1H), 7.75 (d, *J* = 8.2 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CCl<sub>4</sub>): δ 21.6 (CH<sub>3</sub>), 29.8 (CH), 37.3 (CH<sub>2</sub>), 89.0 (C), 110.8 (CH), 113.4 (C), 117.2 (CH), 117.7 (CH), 121.1 (CH), 122.0 (CH), 125.3 (C), 125.5 (C), 125.8 (CH), 127.2 (C), 127.9 (CH), 128.2 (CH), 128.3 (C), 129.6 (CH), 137.0 (C), 138.7 (C), 139.7 (C), 152.3 (C). Anal Calcd for C<sub>24</sub>H<sub>18</sub>ClNOS: C 71.36, H 4.49, N 3.47, Found: C 71.43, H 4.37, N 3.59.



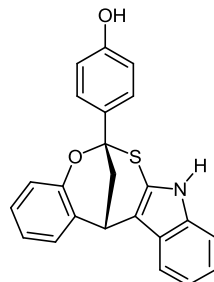
6-(4-Methoxyphenyl)-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3d**); mp: 175-177 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  2.69 (dd,  $J = 13.2, 3.2$  Hz, 1H), 2.93 (dd,  $J = 13.2, 2.5$  Hz, 1H), 3.90 (s, 3H), 4.54-4.55 (m, 1H), 6.89 (t,  $J = 7.1$  Hz, 1H), 6.98 (d,  $J = 8.2$  Hz, 2H), 7.05-7.13 (m, 3H), 7.17 (t,  $J = 7.6$  Hz, 1H), 7.22 (d,  $J = 7.7$  Hz, 1H), 7.34 (d,  $J = 7.4$  Hz, 1H), 7.68 (d,  $J = 7.6$  Hz, 1H), 7.75 (brs, 1H), 7.79 (d,  $J = 8.2$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  29.9 (CH), 37.6 ( $\text{CH}_2$ ), 55.6 ( $\text{CH}_3$ ), 88.9 (C), 110.8 (CH), 113.3 (C), 114.1 (CH), 116.6 (CH), 117.6 (CH), 120.5 (CH), 121.4 (CH), 122.0 (CH), 125.8 (C), 126.7 (C), 126.9 (C), 127.3 (CH), 127.7 (CH), 128.3 (CH), 135.0 (C), 136.8 (C), 152.3 (C), 160.0 (C). Anal Calcd for  $\text{C}_{24}\text{H}_{19}\text{NO}_2\text{S}$ : C 74.78, H 4.97, N, 3.63, Found: C 74.69, H 5.02, N 3.59.



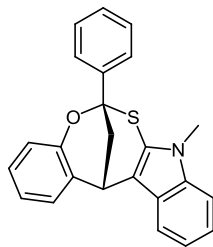
10-Chloro-6-(4-methoxyphenyl)-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3e**); mp: 139-141 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  2.68 (dd,  $J = 13.3, 3.9$  Hz, 1H), 2.92 (dd,  $J = 13.3, 2.1$  Hz, 1H), 3.90 (s, 3H), 4.49-4.50 (m, 1H), 6.85-6.94 (m, 2H), 6.98 (d,  $J = 8.7$  Hz, 2H), 7.05-7.21 (m, 4H), 7.30 (d,  $J = 7.6$  Hz, 1H), 7.57 (d,  $J = 8.4$  Hz, 1H), 7.78 (d,  $J = 8.8$  Hz, 2H), 7.80 (brs, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  30.1 (CH), 30.4 ( $\text{CH}_3$ ), 37.3 ( $\text{CH}_2$ ), 88.9 (C), 108.8 (CH), 111.8 (C), 116.7 (CH), 117.6 (CH), 120.9 (CH), 122.1 (CH), 125.2 (C), 126.0 (CH), 126.2 (C), 127.0 (C), 127.7 (CH), 128.0 (C), 128.4 (CH), 128.9 (CH), 137.8 (C), 143.0 (C), 152.2 (C), 159.7 (C). Anal Calcd for  $\text{C}_{24}\text{H}_{18}\text{ClNO}_2\text{S}$ : C 68.65, H 4.32, N 3.34, Found: C 68.60, H 4.23, N 3.49.



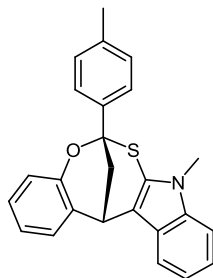
6-(4-Chlorophenyl)-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3f**); mp: 111-113 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  2.67 (dd,  $J = 13.3, 4.0$  Hz, 1H), 2.88 (dd,  $J = 13.3, 2.4$  Hz, 1H), 4.55-4.56 (m, 1H), 6.90 (t,  $J = 7.3$  Hz, 1H), 7.05-7.23 (m, 5H), 7.34 (d,  $J = 6.2$  Hz, 1H), 7.45 (d,  $J = 8.6$  Hz, 2H), 7.67 (d,  $J = 7.8$  Hz, 1H), 7.81 (brs, 1H), 7.82 (d,  $J = 8.6$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  29.8 (CH), 37.5 ( $\text{CH}_2$ ), 88.4 (C), 110.8 (CH), 113.5 (C), 116.7 (CH), 117.6 (CH), 120.6 (CH), 121.6 (CH), 122.2 (CH), 125.5 (C), 126.6 (C), 126.7 (C), 127.5 (CH), 127.8 (CH), 128.4 (CH), 129.0 (CH), 136.8 (C), 138.7 (C), 141.4 (C), 152.0 (C). Anal Calcd for  $\text{C}_{23}\text{H}_{16}\text{ClNOS}$ : C 70.85, H 4.14, N 3.59, Found: C 70.76, H 4.22, N 3.66.



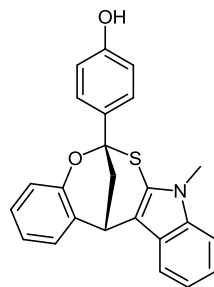
4-(8,13-Dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indol-6-yl)phenol (**3g**); mp: 129-131 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  2.90 (dd,  $J = 13.3, 3.9$  Hz, 1H), 3.15 (dd,  $J = 13.3, 2.1$  Hz, 1H), 4.62-4.63 (m, 1H), 6.94-7.02 (m, 3H), 7.07 (d,  $J = 8.1$  Hz, 1H), 7.11-7.14 (m, 2H), 7.19 (t,  $J = 7.2$  Hz, 1H), 7.26 (d,  $J = 8.0$  Hz, 1H), 7.34 (t,  $J = 7.2$  Hz, 1H), 7.38 (d,  $J = 6.4$  Hz, 1H), 7.52 (d,  $J = 6.9$  Hz, 1H), 7.70 (d,  $J = 7.8$  Hz, 1H), 7.79 (brs, 1H), 7.85 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  29.2 (CH), 35.1 ( $\text{CH}_2$ ), 90.6 (C), 110.9 (CH), 113.4 (C), 116.7 (CH), 117.3 (CH), 119.3 (CH), 120.68 (CH), 120.70 (CH), 121.8 (CH), 123.0 (CH), 125.6 (C), 125.8 (CH), 126.3 (C), 126.5 (C), 127.9 (CH), 128.5 (CH), 131.0 (CH), 131.2 (C), 136.9 (C), 150.9 (C), 155.6 (C). Anal Calcd for  $\text{C}_{23}\text{H}_{17}\text{NO}_2\text{S}$ : C 74.37, H 4.61, N 3.77, Found: C 74.26, H 4.52, N 3.89.



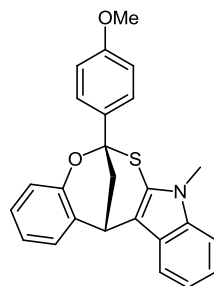
8-Methyl-6-phenyl-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3h**); mp: 191-193 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  2.74 (dd,  $J = 13.3, 3.9$  Hz, 1H), 2.94 (dd,  $J = 13.3, 2.1$  Hz, 1H), 3.60 (s, 3H), 4.59-4.60 (m, 1H), 6.90 (t,  $J = 7.5$  Hz, 1H), 7.07-7.24 (m, 5H), 7.35 (d,  $J = 7.1$  Hz, 1H), 7.42 (d,  $J = 7.1$  Hz, 1H), 7.49-7.52 (m, 2H), 7.70 (d,  $J = 7.7$  Hz, 1H), 7.91 (d,  $J = 7.6$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  29.9 (CH), 37.5 ( $\text{CH}_2$ ), 55.6 ( $\text{CH}_3$ ), 88.9 (C), 110.6 (C), 110.8 (CH), 113.3 (C), 113.4 (CH), 114.2 (CH), 117.2 (CH), 117.6 (CH), 121.1 (CH), 122.0 (CH), 125.3 (C), 125.5 (C), 126.5 (CH), 127.2 (CH), 127.9 (CH), 128.2 (CH), 137.0 (C), 152.3 (C), 160.1 (C). Anal Calcd for  $\text{C}_{24}\text{H}_{19}\text{NOS}$ : C 78.02, H 5.18, N 3.79, Found: C 78.11, H 5.26, N 3.83.



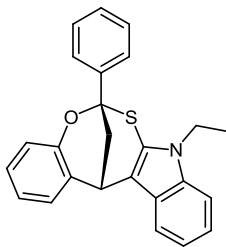
8-Methyl-6-(4-methylphenyl)-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3i**); mp: 173-175 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  2.42 (s, 3H), 2.68 (dd,  $J = 13.3, 4.0$  Hz, 1H), 2.87 (dd,  $J = 13.3, 2.3$  Hz, 1H), 3.55 (s, 3H), 4.53-4.54 (m, 1H), 6.85 (t,  $J = 7.2$  Hz, 1H), 7.01-7.17 (m, 5H), 7.25 (d,  $J = 8.1$  Hz, 2H), 7.30 (d,  $J = 7.4$  Hz, 1H), 7.65 (d,  $J = 7.6$  Hz, 1H), 7.73 (d,  $J = 8.1$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  21.7 ( $\text{CH}_3$ ), 30.1 (CH), 30.4 ( $\text{CH}_3$ ), 37.3 ( $\text{CH}_2$ ), 88.7 (C), 108.8 (CH), 111.8 (C), 116.7 (CH), 117.6 (CH), 120.0 (CH), 120.8 (CH), 122.0 (CH), 125.87 (C), 125.94 (CH), 126.2 (C), 127.7 (CH), 128.4 (CH), 129.6 (CH), 129.9 (C), 137.8 (C), 138.6 (C), 140.2 (C), 152.3 (C). Anal Calcd for  $\text{C}_{25}\text{H}_{21}\text{NOS}$ : C 78.30, H 5.52, N 3.65, Found: C 78.36, H 5.43, N 3.59.



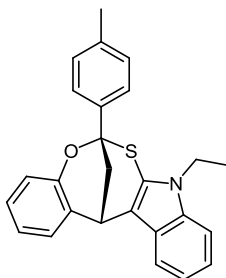
4-(8-Methyl-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indol-6-yl)phenol (**3j**); mp: 155-157 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/DMSO): δ 2.44 (dd, *J* = 13.3, 3.9 Hz, 1H), 2.67 (dd, *J* = 13.3, 2.5 Hz, 1H), 3.35 (s, 3H), 4.31-4.32 (m, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.82-6.90 (m, 3H), 6.96 (d, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.87 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/DMSO): δ 29.9 (CH), 30.3 (CH<sub>3</sub>), 37.1 (CH<sub>2</sub>), 88.8 (C), 108.7 (CH), 111.4 (C), 115.7 (CH), 116.5 (CH), 117.3 (CH), 119.8 (CH), 120.6 (CH), 121.7 (CH), 126.00 (C), 126.04 (C), 127.0 (CH), 127.4 (CH), 128.2 (CH), 129.9 (C), 133.2 (C), 137.5 (C), 152.3 (C), 158.0 (C). Anal Calcd for C<sub>24</sub>H<sub>19</sub>NO<sub>2</sub>S: C 74.78, H 4.97, N 3.63, Found: C 74.69, H 5.02, N 3.71.



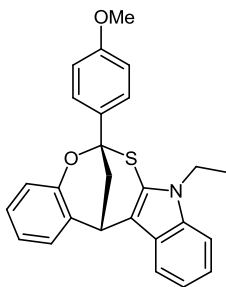
6-(4-Methoxyphenyl)-8-methyl-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3k**); mp: 178-180 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CCl<sub>4</sub>): δ 2.71 (dd, *J* = 13.3, 3.9 Hz, 1H), 2.91 (dd, *J* = 13.3, 2.1 Hz, 1H), 3.60 (s, 3H), 3.91 (s, 3H), 4.57-4.58 (m, 1H), 6.89 (t, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 7.05-7.21 (m, 5H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CCl<sub>4</sub>): δ 30.1 (CH), 30.4 (CH<sub>3</sub>), 37.4 (CH<sub>2</sub>), 55.6 (CH<sub>3</sub>), 88.6 (C), 108.8 (CH), 111.7 (C), 114.1 (CH), 116.6 (CH), 117.6 (CH), 120.0 (CH), 120.8 (CH), 122.0 (CH), 125.9 (C), 126.2 (C), 127.2 (CH), 127.6 (CH), 128.4 (CH), 129.9 (C), 135.1 (C), 137.8 (C), 152.3 (C), 160.1 (C). Anal Calcd for C<sub>25</sub>H<sub>21</sub>NO<sub>2</sub>S: C 75.16, H 5.30, N 3.51, Found: C 75.22, H 5.26, N 3.59.



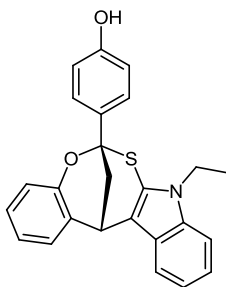
8-Ethyl-6-phenyl-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3l**); mp: 174-176 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  1.37 (t,  $J = 7.2$  Hz, 3H), 2.74 (dd,  $J = 13.3, 3.9$  Hz, 1H), 2.97 (dd,  $J = 13.3, 2.3$  Hz, 1H), 3.98-4.10 (m, 2H), 4.58-4.59 (m, 1H), 6.91 (t,  $J = 7.2$  Hz, 1H), 7.07-7.24 (m, 5H), 7.36 (d,  $J = 7.5$  Hz, 1H), 7.41-7.51 (m, 3H), 7.71 (d,  $J = 7.7$  Hz, 1H), 7.91 (d,  $J = 7.4$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  15.5 (CH<sub>3</sub>), 30.1 (CH), 37.2 (CH<sub>2</sub>), 39.3 (CH<sub>2</sub>), 88.6 (C), 108.8 (CH), 111.7 (C), 116.8 (CH), 117.5 (CH), 119.9 (CH), 120.8 (CH), 122.0 (CH), 125.9 (CH), 126.4 (C), 127.7 (CH), 128.2 (C), 128.3 (CH), 128.7 (C), 128.87 (CH), 128.92 (CH), 136.7 (C), 143.0 (C), 152.3 (C). Anal Calcd for C<sub>25</sub>H<sub>21</sub>NOS: C 78.30, H 5.52, N 3.65, Found: C 78.34, H 5.49, N 3.68.



8-Ethyl-6-(4-methylphenyl)-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3m**); mp: 169-171 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  1.36 (t,  $J = 7.2$  Hz, 3H), 2.47 (s, 3H), 2.72 (dd,  $J = 13.2, 3.8$  Hz, 1H), 2.94 (dd,  $J = 13.2, 2.2$  Hz, 1H), 3.97-4.10 (m, 2H), 4.57-4.58 (m, 1H), 6.90 (t,  $J = 6.6$  Hz, 1H), 7.06-7.23 (m, 5H), 7.29 (d,  $J = 8.0$  Hz, 2H), 7.35 (d,  $J = 7.6$  Hz, 1H), 7.71 (d,  $J = 7.5$  Hz, 1H), 7.78 (d,  $J = 8.1$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CCl}_4$ ):  $\delta$  15.5 (CH), 21.6 (CH<sub>3</sub>), 30.1 (CH<sub>3</sub>), 37.3 (CH<sub>2</sub>), 39.2 (CH<sub>2</sub>), 88.6 (C), 108.8 (CH), 111.7 (C), 116.8 (CH), 117.5 (CH), 119.9 (CH), 120.7 (CH), 121.9 (CH), 125.8 (CH), 126.0 (C), 126.5 (C), 127.6 (CH), 128.4 (CH), 128.8 (C), 129.5 (CH), 136.7 (C), 138.6 (C), 140.2 (C), 152.3 (C). Anal Calcd for C<sub>26</sub>H<sub>23</sub>NOS: C 78.55, H 5.83, N 3.52, Found: C 78.61, H 5.86, N 3.59.



8-Ethyl-6-(4-methoxyphenyl)-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indole (**3n**); mp: 130-132 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CCl<sub>4</sub>): δ 1.36 (t, *J* = 7.1 Hz, 3H), 2.71 (dd, *J* = 13.3, 3.9 Hz, 1H), 2.94 (dd, *J* = 13.3, 2.2 Hz, 1H), 3.90 (s, 3H), 3.94-4.10 (m, 2H), 4.56-4.57 (m, 1H), 6.89 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.04-7.23 (m, 5H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CCl<sub>4</sub>): δ 15.5 (CH<sub>3</sub>), 30.1 (CH), 37.4 (CH<sub>2</sub>), 39.2 (CH<sub>2</sub>), 55.6 (CH<sub>3</sub>), 88.6 (C), 108.8 (CH), 111.6 (C), 114.1 (CH), 116.8 (CH), 117.5 (CH), 119.9 (CH), 120.7 (CH), 121.9 (CH), 126.0 (C), 126.5 (C), 127.2 (CH), 127.6 (CH), 128.3 (CH), 128.9 (C), 135.2 (C), 136.7 (C), 152.3 (C), 160.1 (C). Anal Calcd for C<sub>26</sub>H<sub>23</sub>NO<sub>2</sub>S: C 75.52, H 5.61, N 3.39, Found: C 75.60, H 5.54, N 3.46.



2-(8-Ethyl-8,13-dihydro-6,13-methano[1,3]benzoxathiocino[4,5-*b*]indol-6-yl)phenol (**3o**); mp: 165-167 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CCl<sub>4</sub>): δ 1.36 (t, *J* = 7.1 Hz, 3H), 2.93 (dd, *J* = 13.2, 3.9 Hz, 1H), 3.16 (dd, *J* = 13.2, 2.8 Hz, 1H), 3.95-4.08 (m, 2H), 4.66-4.67 (m, 1H), 6.97-7.03 (m, 3H), 7.11-7.26 (m, 5H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 8.00 (brs, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CCl<sub>4</sub>): δ 15.5 (CH<sub>3</sub>), 30.1 (CH), 34.8 (CH<sub>2</sub>), 39.4 (CH<sub>2</sub>), 90.4 (C), 109.1 (CH), 111.6 (C), 116.9 (CH), 117.2 (CH), 119.2 (CH), 120.0 (CH), 120.8 (CH), 121.1 (CH), 123.0 (CH), 125.6 (CH), 126.0 (C), 126.3 (C), 126.6 (C), 127.4 (CH), 127.9 (CH), 128.6 (C), 131.1 (CH), 136.8 (C), 150.8 (C), 155.6 (C). Anal Calcd for C<sub>25</sub>H<sub>21</sub>NO<sub>2</sub>S: C 75.16, H 5.30, N 3.51, Found: C 75.22, H 5.28, N 3.63.