

**One-pot synthesis of 6,11-dihydro-5H-indolizino[8,7-b]indoles via formation of  $\beta$ -enamino ester and sequential Michael addition and Pictet-Spengler reactions**

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**Supporting Information**

**Figure s1 and s2**

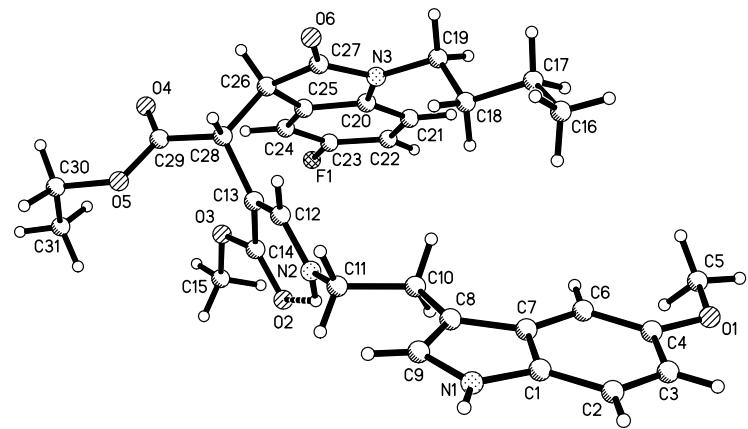
**of compounds**

**$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra**

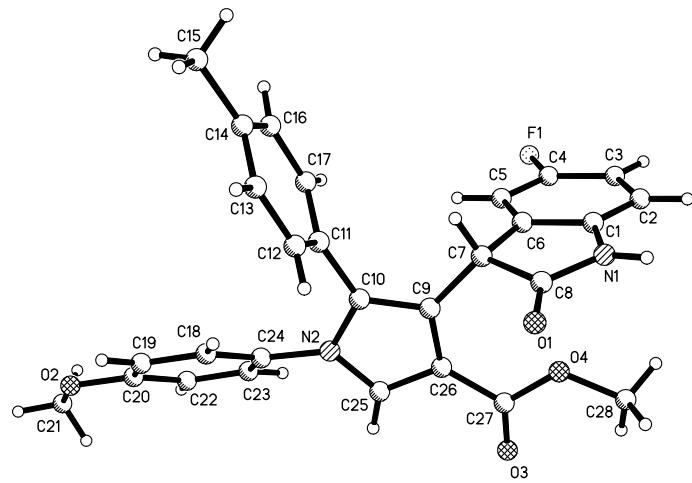
**2 Characterization**

**3-12**

**13-34**



**Fig. s1** Crystal structure of intermediate 3b



**Fig. s2** Crystal structure of intermediate 4e

**Methyl 1-(2-(1H-indol-3-yl)ethyl)-4-(5-chloro-2-oxoindolin-3-yl)-5-phenyl-1H-pyrrole-3-carboxylate (1a):** white solid, 87%, m.p. 190-192°C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: keto-form: 10.82 (s, 1H, NH), 10.43 (s, 1H, NH), 7.67 (s, 1H, ArH), 7.52-7.51 (m, 3H, ArH), 7.45-7.44 (m, 2H, ArH), 7.31 (d, *J* = 8.4Hz, 1H, ArH), 7.08-7.00 (m, 2H, ArH), 6.98 (brs, 1H, ArH), 6.90-6.86 (m, 1H, ArH), 6.83-6.79 (m, 1H, ArH), 4.20 (s, 1H, CH), 4.14-4.07 (m, 2H, CH), 3.38 (s, 3H, OCH<sub>3</sub>), 3.01-2.96 (m, 1H, CH), 2.94-2.89 (m, 1H, CH); enol-form: 10.77 (s, 1H, NH), 10.09 (s, 1H, NH), 7.26 (d, *J* = 7.2Hz, 2H, ArH), 7.16-7.15 (m, 3H, ArH), 6.90-6.86 (m, 2H, ArH), 6.52 (d, *J* = 8.4Hz, 1H, ArH), 5.51 (s, 1H, CH), 3.90 (t, *J* = 7.2Hz, 2H, CH), 3.78 (s, 3H, OCH<sub>3</sub>), 2.85 (t, *J* = 7.2Hz, 2H, CH); keto/enol = 4:1; <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ: 177.7, 163.4, 142.0, 136.3, 136.0, 133.1, 130.8, 130.0, 128.8, 128.6, 128.1, 127.0, 126.8, 124.8, 123.0, 122.5, 121.0, 118.3, 117.9, 115.3, 111.3, 111.2, 110.2, 109.9, 56.0, 50.0, 48.2, 44.7, 26.8, 18.5; IR (KBr) ν: 3548, 3010, 2355, 1694, 1622, 1585, 1537, 1476, 1453, 1406, 1373, 1333, 1244, 1173, 1097, 1066, 1017, 884, 825 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>30</sub>H<sub>24</sub>ClN<sub>3</sub>NaO<sub>3</sub> ([M+Na]<sup>+</sup>): 532.1397. Found: 532.1398.

**Methyl 1-(2-(1H-indol-3-yl)ethyl)-4-(1-benzyl-5-chloro-2-oxoindolin-3-yl)-5-p-tolyl-1H-pyrrole-3-carboxylate (1b):** white solid, 92%, m.p. 149-151°C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: keto-form: 10.83 (brs, 1H, NH), 7.67 (s, 1H, ArH), 7.41-7.40 (m, 2H, ArH), 7.37-7.36 (m, 2H, ArH), 7.34-7.30 (m, 4H, ArH), 7.28-7.24 (m, 2H, ArH), 7.06-6.99 (m, 3H, ArH), 6.95-6.93 (m, 1H, ArH), 6.88 (t, *J* = 7.2Hz, 2H, ArH), 6.81 (d, *J* = 8.4Hz, 1H, ArH), 5.05-5.03 (m, 1H, CH), 4.79-4.76 (m, 1H, CH), 4.43 (s, 1H, CH), 4.12-4.11 (m, 2H, CH), 3.31 (s, 3H, OCH<sub>3</sub>), 3.00-2.92 (m, 2H, CH), 2.39 (s, 3H, CH<sub>3</sub>); enol-form: 10.77 (s, 1H, NH), 7.18 (d, *J* = 7.8Hz, 6H, ArH), 7.12 (d, *J* = 7.2Hz, 1H, ArH), 6.95-6.92 (m, 4H, ArH), 6.59 (d, *J* = 7.8Hz, 1H, ArH), 6.55 (brs, 1H, ArH), 4.57-4.54 (m, 1H, CH), 4.15 (brs, 1H, CH), 3.89 (brs, 2H, CH), 3.79 (s, 3H, OCH<sub>3</sub>), 2.86-2.84 (m, 2H, CH), 2.29 (s, 3H, CH<sub>3</sub>). keto/enol = 4:1; <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ: 176.0, 163.4, 142.5, 138.2, 136.5, 136.0, 136.0, 132.3, 130.8, 129.5, 128.5, 128.4, 128.0, 127.4, 127.2, 127.2, 127.0, 126.9, 126.8, 125.7, 123.0, 122.4, 120.9, 118.2, 118.0, 114.9, 113.0, 111.0, 110.2, 109.5, 50.1, 48.2, 44.2, 43.2, 26.8, 20.9; IR (KBr) ν: 3561, 2946, 2355, 1692, 1618, 1560, 1527, 1476, 1454, 1396, 1336, 1099, 1014, 930, 877, 815, 769 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>38</sub>H<sub>32</sub>ClN<sub>3</sub>NaO<sub>3</sub> ([M+Na]<sup>+</sup>): 636.2020. Found: 636.2024.

**Methyl 1-(2-(1H-indol-3-yl)ethyl)-5-(4-chlorophenyl)-4-(5-methyl-2-oxoindolin-3-yl)-1H-pyrrole-3-carboxylate (1c):** white solid, 85%, m.p. 190-192°C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: keto-form: 10.84 (s, 1H, NH), 10.19 (s, 1H, NH), 7.67 (s, 1H, ArH), 7.54 (d, *J* = 7.8Hz, 2H, ArH), 7.41 (d, *J* = 7.8Hz, 2H, ArH), 7.32 (d, *J* = 8.4Hz, 1H, ArH), 7.06-7.01 (m, 2H, ArH), 6.97 (brs, 1H, ArH), 6.91-6.86 (m, 1H, ArH), 6.67 (d, *J* = 7.8Hz, 1H, ArH), 6.59 (s, 1H, ArH), 4.13-4.11 (m, 3H, CH), 3.34 (s, 3H, OCH<sub>3</sub>), 2.99-2.96 (m, 1H, CH), 2.94-2.90 (m, 1H, CH), 2.19 (s, 3H, CH<sub>3</sub>); enol-form: 10.78 (s, 1H, NH), 9.88 (s, 1H, NH), 7.69 (brs, 1H, ArH), 7.28 (d, *J* = 8.4Hz, 1H, ArH), 7.13 (brs, 2H, ArH), 6.71 (brs, 1H, ArH), 6.46 (d, *J* = 7.8Hz, 1H, ArH), 5.43 (s, 1H, CH), 3.88 (t, *J* = 7.2Hz, 2H, CH), 3.78 (s, 3H, OCH<sub>3</sub>), 2.85 (t, *J* = 7.2Hz, 2H, CH); keto/enol = 7:3; <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ: 177.9, 177.1, 164.9, 163.4, 140.6, 136.1, 136.0, 134.7, 133.5, 132.5, 132.4, 130.9, 129.5, 129.2, 129.0, 128.8, 128.3, 127.6, 127.5, 127.3, 126.8, 126.7, 123.3, 123.0, 122.9, 121.0, 118.2, 118.1, 116.6, 111.6, 111.4, 111.3, 110.1, 108.4, 50.7, 49.8, 48.1, 47.7, 44.6, 42.9, 42.9, 26.8, 26.7, 20.7; IR (KBr) ν: 3548, 3231, 3005, 2930, 2895, 2335, 1689, 1626, 1556, 1458, 1428, 1397, 1335, 1243, 1120, 1091, 1011, 978, 876, 812 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>26</sub>ClN<sub>3</sub>NaO<sub>3</sub> ([M+Na]<sup>+</sup>): 546.1555. Found: 546.1555.

**Ethyl 4-(5-chloro-2-oxoindolin-3-yl)-1-(2-(5-methoxy-1H-indol-3-yl)ethyl)-5-phenyl-1H-pyrrole-3-carboxylate (1d):** white solid, 90%, m.p. 190-192°C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: keto-form: 10.67 (s, 1H, NH), 10.42 (s, 1H, NH), 7.72 (s, 1H, ArH), 7.50-7.51 (m, 1H, ArH), 7.49-7.45 (m, 2H, ArH), 7.42-7.40 (m, 1H, ArH), 7.23-7.20 (m, 1H, ArH), 7.18-7.15 (m, 1H, ArH), 6.94 (brs, 1H, ArH), 6.78 (d, *J* = 8.4Hz, 1H, ArH), 6.76 (brs, 1H, ArH), 6.63 (brs, 1H, ArH), 4.37 (s, 1H, CH), 3.86 (t, *J* = 6.6Hz, 2H, CH), 3.66 (s, 3H, OCH<sub>3</sub>), 3.00-2.85 (m, 2H, CH), 0.97 (t, *J* = 7.2Hz, 3H, CH<sub>3</sub>); enol-form: 10.62 (s, 1H, NH), 10.06 (s, 1H, NH), 7.12 (brs, 1H, ArH), 7.06-7.05 (m, 1H, ArH), 6.87 (brs, 1H, ArH), 6.83 (brs, 1H, ArH), 6.66-6.65 (m, 1H, ArH), 6.51-6.49 (m, 2H, ArH), 5.51 (s, 1H, CH), 4.27 (t, *J* = 7.2Hz, 2H, CH), 3.64 (s, 3H, OCH<sub>3</sub>), 1.31 (t, *J* = 6.6Hz, 3H, CH<sub>3</sub>); keto/enol = 4:1; <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ: 178.1, 163.5, 153.5, 142.4, 136.9, 133.6, 131.6, 131.2, 130.5, 129.2, 129.1, 128.4, 127.6, 127.4, 125.3, 124.1, 123.0, 115.4, 112.2, 111.9, 110.5, 110.4, 100.0, 58.9, 55.8, 48.6, 45.3, 27.3, 14.5; IR (KBr) ν: 3320, 3180, 3057, 2996, 2740, 1964, 1698, 1618, 1559, 1527, 1477, 1443, 1380, 1328, 1296, 1239, 1173, 1091, 1068, 1032, 927, 891, 765 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>28</sub>ClN<sub>3</sub>NaO<sub>4</sub> ([M+Na]<sup>+</sup>): 576.1665. Found: 576.1661.

**Methyl 2-(5-chloro-2-oxoindolin-3-yl)-3-phenyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2a):** brown solid, 68%, m.p. 282-284°C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 10.94 (s, 1H, NH), 10.52 (s, 1H, NH), 7.65-7.51 (m, 7H, ArH), 7.19 (d, *J* = 8.4Hz, 1H, ArH), 7.14 (d, *J* = 7.8Hz, 1H, ArH), 7.05 (t, *J* = 7.2Hz, 1H, ArH), 6.94 (s, 1H, ArH), 6.87 (d, *J* = 8.4Hz, 1H, ArH), 4.38 (s, 1H, CH), 4.11-4.06 (m, 2H, CH), 3.34 (s, 3H, OCH<sub>3</sub>), 3.18-3.10 (m, 2H, CH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ: 177.9, 165.1, 141.6, 137.1, 136.0, 133.4, 130.7, 129.5, 128.9, 127.1, 126.0, 125.3, 125.1, 122.5, 122.3, 119.5, 118.5, 118.3, 114.9, 112.4, 110.1, 108.8, 106.4, 50.1, 45.1, 43.7, 19.9s; IR (KBr) ν: 3926, 3746, 2947, 2371, 2343, 1871, 1847, 1831, 1796, 1773, 1703, 1686, 1656, 1637, 1621, 1576, 1560, 1543, 1522, 1475, 1455, 1365, 1334, 1269, 1216, 1169, 1133, 1033, 895, 819, 788 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>30</sub>H<sub>21</sub>ClN<sub>3</sub>NaO<sub>3</sub> ([M+Na]<sup>+</sup>): 530.1232. Found: 530.1242.

**Methyl 2-(5-fluoro-2-oxoindolin-3-yl)-3-p-tolyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2b) :** brown solid, 65%, m.p. 190-194°C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 10.95 (s, 1H, NH), 10.45 (s, 1H, NH), 7.62 (d, *J* = 8.4Hz, 1H, ArH), 7.55-7.54 (m, 2H, ArH), 7.49-7.48 (m, 1H, ArH), 7.38 (d, *J* = 7.8Hz, 2H, ArH), 7.13 (t, *J* = 7.8Hz, 1H, ArH), 7.05 (d, *J* = 7.8Hz, 2H, ArH), 6.99-6.96 (m, 1H, ArH), 6.85-6.81 (m, 2H, ArH), 4.36 (s, 1H, CH), 4.09 (d, *J* = 7.2Hz, 2H, CH), 3.32 (s, 3H, OCH<sub>3</sub>), 3.16-3.09 (m, 2H, CH), 2.39 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ: 178.1, 165.2, 138.8, 138.4, 137.0, 136.0, 133.1, 130.6, 129.8, 129.4, 126.6, 126.0, 125.3, 122.3, 119.5, 118.3, 115.0, 113.3, 113.1, 112.4, 108.7, 106.5, 50.0, 45.4, 43.6, 28.9, 20.9, 19.9; IR (KBr) ν: 3615, 2922, 2852, 2367, 1712, 1618, 1483, 1454, 1366, 1332, 1267, 1180, 1138, 1114, 943, 814, 780 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>24</sub>FN<sub>3</sub>NaO<sub>3</sub> ([M+Na]<sup>+</sup>): 528.1682. Found: 528.1694.

**Methyl 2-(5-chloro-2-oxoindolin-3-yl)-3-(4-methoxyphenyl)-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2c):** brown solid, 68%, m.p. 190-191°C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 10.93 (s, 1H, NH), 10.51 (s, 1H, NH), 7.62-7.51 (m, 4H, ArH), 7.19 (d, *J* = 8.4Hz, 1H, ArH), 7.13-7.12 (m, 3H, ArH), 7.05 (t, *J* = 7.8Hz, 1H, ArH), 6.93 (brs, 1H, ArH), 6.87 (d, *J* = 8.4Hz, 1H, ArH), 4.37 (s, 1H, CH), 4.08 (d, *J* = 6.6Hz, 2H, CH), 3.82 (s, 3H, OCH<sub>3</sub>), 3.34 (s, 3H, OCH<sub>3</sub>), 3.17-3.08 (m, 2H, CH), 2.39 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ: 178.0, 165.2, 159.7, 141.6, 137.0, 136.0, 133.5, 132.0, 129.8, 127.0, 126.1, 125.3, 125.1, 122.5, 122.3, 121.5, 119.5, 118.3, 114.8, 114.3, 112.4, 110.0, 108.7, 106.3, 55.2, 50.0, 45.2, 43.6, 19.9; IR (KBr) ν: 3055,

2949, 2838, 2374, 1712, 1687, 1615, 1592, 1500, 1476, 1452, 1365, 1332, 1268, 1249, 1214, 1174, 1136, 1115, 1087, 1032, 945, 886, 838, 814, 790 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>24</sub>ClN<sub>3</sub>NaO<sub>4</sub> ([M+Na]<sup>+</sup>): 560.1341; Found: 560.1361.

**Methyl 8-methoxy-2-(2-oxoindolin-3-yl)-3-p-tolyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2d):** brown solid, 67%, m.p. 198-200 °C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 10.82 (s, 1H, NH), 10.45 (s, 1H, NH), 7.52-7.51 (m, 3H, ArH), 7.39-7.37 (m, 2H, ArH), 7.14 (t, *J* = 7.2 Hz, 1H, ArH), 7.03 (brs, 1H, ArH), 6.91-6.90 (m, 1H, ArH), 6.86 (d, *J* = 8.4 Hz, 2H, ArH), 6.77-6.76 (m, 1H, ArH), 4.34 (s, 1H, CH), 4.08-4.07 (m, 2H, CH), 3.78 (s, 3H, OCH<sub>3</sub>), 3.28 (s, 3H, OCH<sub>3</sub>), 3.15-3.06 (m, 2H, CH), 2.39 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ: 183.6, 170.5, 159.0, 147.9, 143.6, 142.0, 136.4, 135.2, 134.7, 132.4, 131.9, 131.9, 130.9, 127.7, 126.3, 120.9, 118.4, 118.1, 113.9, 113.6, 111.7, 104.9, 60.5, 55.2, 50.3, 48.9, 26.1, 25.3; IR (KBr) ν: 3748, 2941, 2832, 2365, 1710, 1685, 1620, 1574, 1520, 1471, 1454, 1364, 1330, 1296, 1267, 1218, 1170, 1130, 1032, 964, 928, 822, 786, 751 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>27</sub>N<sub>3</sub>NaO<sub>4</sub> ([M+Na]<sup>+</sup>): 540.1884. Found: 540.1894.

**Methyl 3-(4-chlorophenyl)-8-methoxy-2-(5-methyl-2-oxoindolin-3-yl)-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2e):** brown solid, 70%, m.p. 196-198 °C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 10.82 (s, 1H, NH), 10.34 (s, 1H, NH), 7.65 (s, 4H, ArH), 7.52 (d, *J* = 8.4 Hz, 1H, ArH), 7.04 (s, 1H, ArH), 6.95-6.94 (m, 1H, ArH), 6.78-6.73 (m, 3H, ArH), 4.30 (s, 1H, CH), 4.09 (brs, 2H, CH), 3.78 (s, 3H, OCH<sub>3</sub>), 3.29 (s, 3H, OCH<sub>3</sub>), 3.15-3.08 (m, 2H, CH), 2.18 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ: 178.2, 165.2, 153.8, 140.2, 135.4, 133.7, 132.5, 131.2, 131.2, 130.3, 130.0, 129.0, 128.5, 127.4, 126.4, 125.6, 123.1, 116.2, 113.2, 113.0, 108.6, 108.5, 106.4, 99.6, 55.3, 50.0, 44.9, 43.7, 20.6, 20.0; IR (KBr) ν: 3687, 2947, 2392, 2355, 2330, 1841, 1711, 1649, 1624, 1573, 1555, 1537, 1518, 1488, 1472, 1453, 1365, 1331, 1296, 1269, 1220, 1171, 1135, 1032, 1013, 964, 818 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>26</sub>ClN<sub>3</sub>NaO<sub>4</sub> ([M+Na]<sup>+</sup>): 574.1497. Found: 574.1504.

**Methyl 8-methoxy-2-(5-methyl-2-oxoindolin-3-yl)-3-p-tolyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2f):** brown solid, 66%, m.p. 244-246 °C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 10.81 (s, 1H, NH), 10.27 (s, 1H, NH), 7.50 (brs, 3H, ArH), 7.38 (brs, 2H, ArH), 7.03 (brs, 1H, ArH), 6.94 (brs, 1H, ArH), 6.78-6.72 (m, 3H, ArH), 4.31 (brs, 1H, CH), 4.08 (brs, 2H, CH), 3.78 (s, 3H, OCH<sub>3</sub>), 3.10 (brs, 2H, CH); <sup>13</sup>C NMR (150 MHz,

DMSO-*d*<sub>6</sub>) δ: 178.3, 165.3, 153.8, 140.2, 138.3, 136.7, 131.3, 131.2, 130.0, 130.0, 129.4, 127.4, 126.7, 126.6, 125.7, 123.1, 115.8, 113.2, 112.8, 108.4, 106.5, 99.6, 56.0, 55.3, 49.9, 45.0, 43.7, 20.8, 20.6, 20.0, 18.5; IR (KBr) ν: 3818, 3747, 3029, 2919, 1710, 1687, 1623, 1591, 1543, 1491, 1474, 1455, 1366, 1332, 1296, 1265, 1277, 1134, 1110, 1031, 963, 817 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>33</sub>H<sub>29</sub>N<sub>3</sub>NaO<sub>4</sub> ([M+Na]<sup>+</sup>): 554.2041. Found: 554.2050.

**Methyl 8-methoxy-2-(5-methyl-2-oxoindolin-3-yl)-3-phenyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2g):** brown solid, 63%, m.p. 208-210°C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 10.84 (s, 1H, NH), 10.33 (s, 1H, NH), 7.65-7.57 (m, 4H, ArH), 7.53-7.51 (m, 2H, ArH), 7.04 (brs, 1H, ArH), 6.94 (d, *J* = 7.8Hz, 1H, ArH), 6.78-6.74 (m, 3H, ArH), 4.31 (s, 1H, CH), 4.12-4.09 (m, 2H, CH), 3.78 (s, 3H, OCH<sub>3</sub>), 3.30 (s, 3H, OCH<sub>3</sub>), 3.15-3.08 (m, 2H, CH), 2.18 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ: 178.3, 165.3, 153.7, 140.2, 136.7, 131.2, 131.1, 130.1, 129.9, 129.6, 128.9, 128.8, 127.4, 126.5, 123.1, 115.9, 113.3, 112.9, 108.5, 108.4, 106.5, 99.5, 55.2, 50.0, 45.0, 43.7, 20.6, 20.0; IR (KBr) ν: 3346, 2947, 1716, 1624, 1575, 1489, 1455, 1365, 1268, 1136, 964, 810 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>27</sub>ClN<sub>3</sub>NaO<sub>4</sub> ([M+Na]<sup>+</sup>): 540.1891. Found: 540.1894.

**Methyl 2-(5-fluoro-2-oxoindolin-3-yl)-8-methoxy-3-p-tolyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2h):** brown solid, 71%, m.p. 189-191°C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 10.84 (s, 1H, NH), 10.44 (s, 1H, NH), 7.53-7.48 (m, 3H, ArH), 7.38-7.37 (m, 2H, ArH), 7.03 (brs, 1H, ArH), 6.97 (t, *J* = 7.8Hz, 1H, ArH), 6.84-6.76 (m, 3H, ArH), 4.35 (s, 1H, CH), 4.07 (brs, 2H, CH), 3.78 (s, 3H, OCH<sub>3</sub>), 3.35 (s, 3H, OCH<sub>3</sub>), 3.11-3.08 (m, 2H, CH), 2.39 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ: 178.2, 165.2, 153.8, 138.8, 138.4, 136.9, 133.2, 133.1, 131.2, 130.6, 130.1, 129.4, 126.6, 126.6, 125.6, 114.9, 113.3, 113.2, 113.2, 112.9, 110.4, 109.3, 109.2, 108.5, 106.3, 99.6, 55.3, 50.0, 45.5, 43.7, 20.9, 20.0; IR (KBr) ν: 3747, 2949, 2833, 2372, 2309, 1869, 1845, 1714, 1685, 1653, 1623, 1575, 1541, 1521, 1484, 1456, 1383, 1365, 1331, 1396, 1268, 1219, 1186, 1135, 1032, 962, 819, 777, 750 cm<sup>-1</sup>; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>26</sub>FN<sub>3</sub>NaO<sub>4</sub> ([M+Na]<sup>+</sup>): 558.1792. Found: 558.1800.

**Methyl 2-(5-chloro-2-oxoindolin-3-yl)-8-methoxy-3-(4-methoxyphenyl)-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2i):** brown solid, 65%, m.p. 270-272°C; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ: 10.83 (s, 1H, NH), 10.55 (s, 1H, NH), 7.59-7.49 (m, 3H, ArH), 7.20 (d, *J* = 7.8Hz, 1H, ArH), 7.13 (brs, 2H, ArH), 7.03 (brs, 1H, ArH), 6.94 (s, 1H, ArH), 6.87 (d, *J* = 7.8Hz,

1H, ArH), 6.77 (dd,  $J_1$  = 1.8Hz,  $J_2$  = 1.2Hz, 1H, ArH), 4.37 (s, 1H, CH), 4.06 (t,  $J$  = 7.2Hz, 2H, CH), 3.82 (s, 3H, OCH<sub>3</sub>), 3.78 (s, 3H, OCH<sub>3</sub>), 3.32 (s, 3H, OCH<sub>3</sub>), 3.15-3.05 (m, 2H, CH); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ: 178.0, 165.1, 159.7, 153.8, 141.6, 136.9, 133.5, 132.0, 131.2, 123.0, 127.0, 126.6, 125.7, 125.1, 122.4, 121.5, 114.8, 114.3, 113.2, 112.9, 110.0, 108.4, 106.1, 99.6, 55.3, 55.2, 50.0, 45.2, 43.6, 20.0; IR (KBr) ν: 3616, 3167, 2950, 2833, 2369, 1709, 1682, 1619, 1592, 1574, 1500, 1475, 1454, 1364, 1333, 1290, 1268, 1249, 1222, 1174, 1132, 1032, 966, 882, 838, 816, 780 cm<sup>-1</sup>; MS (m/z): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>26</sub>ClN<sub>3</sub>NaO<sub>5</sub> ([M+Na]<sup>+</sup>): 590.1445. Found: 590.1457.

**Ethyl 2-(5-chloro-2-oxoindolin-3-yl)-8-methoxy-3-phenyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2j):** brown solid, 65%, m.p. 197-199°C; <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>) δ: 10.94 (s, 1H, NH), 10.57 (s, 1H, NH), 7.65 (brs, 1H, ArH), 7.57-7.52 (m, 5H, ArH), 7.21 (d,  $J$  = 7.2Hz, 1H, ArH), 7.04-6.98 (m, 2H, ArH), 6.86-6.77 (m, 2H, ArH), 4.38 (s, 1H, CH), 4.08 (brs, 2H, CH), 3.90-3.86 (m, 2H, CH), 3.78 (s, 3H, OCH<sub>3</sub>), 3.12 (brs, 2H, CH), 0.84 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ: 177.9, 164.7, 153.8, 141.5, 137.1, 133.5, 131.1, 130.7, 130.4, 129.6, 128.9, 127.0, 126.6, 125.6, 125.1, 122.5, 114.6, 113.2, 113.0, 110.2, 108.6, 106.7, 99.6, 59.1, 55.3, 45.3, 43.8, 20.0, 13.7; IR (KBr) ν: 3448, 3187, 2982, 2827, 2366, 1711, 1620, 1574, 1475, 1450, 1371, 1332, 1299, 1264, 1221, 1172, 1130, 1073, 1029, 921, 884, 843, 820, 790, 770 cm<sup>-1</sup>; MS (m/z): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>26</sub>ClN<sub>3</sub>NaO<sub>4</sub> ([M+Na]<sup>+</sup>): 574.1499. Found: 574.1504.

**4-Ethyl 1-methyl 2-((2-(1H-indol-3-yl)ethylamino)methylene)-3-(5-fluoro-2-oxoindolin-3-yl)succinate (3a):** white solid, 60%, m.p. 70-71°C; <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>) δ: 10.83 (s, 1H, NH), 10.39 (s, 1H, NH), 8.02 (brs, 1H, NH), 7.53 (d,  $J$  = 7.2Hz, 1H, ArH), 7.32 (d,  $J$  = 8.4Hz, 1H, ArH), 7.11 (s, 1H, ArH), 7.06 (d,  $J$  = 8.4Hz, 1H, ArH), 7.00-6.96 (m, 1H, ArH), 6.89 (d,  $J$  = 13.2Hz, 1H, ArH), 6.74-6.73 (m, 1H, ArH), 4.11 (t,  $J$  = 6.6Hz, 2H, CH), 3.91-3.80 (m, 2H, CH), 3.40-3.36 (m, 2H, CH), 3.31 (s, 3H, OCH<sub>3</sub>), 2.83 (t,  $J$  = 6.0Hz, 2H, CH), 1.60 (t,  $J$  = 6.6Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ: 177.2, 172.7, 168.0, 158.1, 156.5, 153.8, 139.2, 136.2, 129.2, 129.1, 127.0, 122.8, 120.9, 118.3, 118.2, 114.0, 113.8, 113.7, 113.6, 111.3, 110.9, 109.5, 109.4, 87.2, 60.3, 56.0, 49.6, 48.7, 48.6, 46.0, 27.1, 18.5, 14.0; IR (KBr) ν: 3307, 2917, 2849, 1715, 1668, 1607, 1484, 1445, 1381, 1308, 1227, 1193, 1183, 1040, 932 cm<sup>-1</sup>; MS (m/z): HRMS

(ESI) Calcd. for  $C_{26}H_{26}FN_3NaO_5$  ( $[M+Na]^+$ ): 502.1760. Found: 502.1749.

**4-Ethyl 1-methyl 2-((2-(1H-indol-3-yl)ethylamino)methylene)-3-(1-butyl-5-fluoro-2-oxoindolin-3-yl)succinate (3b):** white solid, 65%, m.p. 102-103°C;  $^1H$  NMR (600 MHz, DMSO- $d_6$ )  $\delta$ : 10.84 (s, 1H, NH), 8.01-7.99 (m, 1H, NH), 7.52 (d,  $J$  = 7.8Hz, 1H, ArH), 7.32 (d,  $J$  = 7.8Hz, 1H, ArH), 7.11-7.05 (m, 4H, ArH), 6.97-6.93 (m, 2H, ArH), 6.83 (d,  $J$  = 13.2Hz, 1H, ArH), 4.15-4.10 (m, 2H, CH), 3.97 (d,  $J$  = 4.8Hz, 1H, CH), 3.85 (d,  $J$  = 5.4Hz, 1H, CH), 3.68-3.63 (m, 1H, CH), 3.59-3.51 (m, 1H, CH), 3.39-3.34 (m, 2H, CH), 3.29 (s, 3H, OCH<sub>3</sub>), 2.82 (t,  $J$  = 7.2Hz, 2H, CH), 1.47 (t,  $J$  = 7.8Hz, 3H, CH), 1.25-1.21 (m, 2H, CH), 1.16 (t,  $J$  = 7.2Hz, 3H, CH<sub>3</sub>), 0.85 (t,  $J$  = 7.8Hz, 3H, CH);  $^{13}C$  NMR (150 MHz, DMSO- $d_6$ )  $\delta$ : 175.1, 172.6, 168.0, 158.4, 156.9, 153.8, 140.2, 136.3, 128.5, 128.4, 127.0, 122.7, 121.0, 118.2, 114.0, 113.9, 113.8, 113.7, 111.3, 110.8, 108.7, 108.6, 86.9, 60.4, 48.5, 48.7, 48.1, 46.4, 29.0, 27.1, 19.3, 14.0, 13.4; IR (KBr)  $\nu$ : 3315, 2917, 2850, 1730, 1684, 1665, 1616, 1486, 1465, 1382, 1207, 1227, 1198, 1152, 1102, 1039, 1001, 889 cm<sup>-1</sup>; MS (m/z): HRMS (ESI) Calcd. for  $C_{30}H_{34}FN_3NaO_5$  ( $[M+Na]^+$ ): 558.2386. Found: 558.2375.

**Methyl 5-(4-chlorophenyl)-4-(2-oxoindolin-3-yl)-1-p-tolyl-1H-pyrrole-3-carboxylate (4a):** white solid, 76%, m.p. 250-252°C;  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : keto-form: 10.39 (s, 1H, NH), 7.70 (s, 1H, CH), 7.43 (d,  $J$  = 8.4Hz, 2H, ArH), 7.28 (d,  $J$  = 8.4Hz, 2H, ArH), 7.19 (d,  $J$  = 8.4Hz, 2H, ArH), 7.13 (d,  $J$  = 8.0Hz, 2H, ArH), 7.03-7.00 (m, 1H, ArH), 6.94 (d,  $J$  = 7.2Hz, 1H, ArH), 6.85 (t,  $J$  = 8.4Hz, 2H, ArH), 4.35 (s, 1H, CH), 3.37 (s, 3H, OCH<sub>3</sub>), 2.30 (s, 3H, CH<sub>3</sub>); enol-form: 10.13 (s, 1H, NH), 7.73 (s, 1H, CH), 7.43 (d,  $J$  = 8.4Hz, 2H, ArH), 7.28 (d,  $J$  = 8.4Hz, 2H, ArH), 7.19 (d,  $J$  = 8.4Hz, 2H, ArH), 7.13 (d,  $J$  = 8.0Hz, 2H, ArH), 7.03-7.00 (m, 1H, ArH), 6.94 (d,  $J$  = 7.2Hz, 1H, ArH), 6.85 (t,  $J$  = 8.4Hz, 2H, ArH), 5.55 (s, 1H, CH), 3.79 (s, 3H, OCH<sub>3</sub>), 2.21 (s, 3H, CH<sub>3</sub>). keto/enol = 3:1.  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$ : 128.3, 163.7, 143.5, 137.6, 136.5, 135.1, 133.5, 132.7, 131.0, 130.2, 130.0, 129.4, 129.3, 129.1, 127.7, 125.8, 123.1, 121.3, 118.1, 113.0, 109.2, 50.6, 45.0, 20.9; IR (KBr)  $\nu$ : 3135, 3080, 3033, 2944, 2891, 2843, 1701, 1653, 1618, 1519, 1457, 1253, 1232, 1197, 1105, 1085, 879, 831, 752 cm<sup>-1</sup>; MS (m/z): HRMS (ESI) Calcd. for  $C_{27}H_{21}ClN_2O_3$  ( $[M+Na]^+$ ): 479.1140. Found: 479.1133.

**Methyl 4-(5-chloro-2-oxoindolin-3-yl)-5-(4-methoxyphenyl)-1-p-tolyl-1H-pyrrole-3-carboxylate (4b):** white solid, 74%, m.p. 250-253°C;  $^1H$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : keto-

form: 10.50 (s, 1H, NH), 7.66 (s, 1H, CH), 7.21-7.15 (m, 7H, ArH), 6.97 (brs, 2H, ArH), 6.92 (d, *J* = 8.4Hz, 2H, ArH), 6.83 (d, *J* = 8.4Hz, 1H, ArH), 4.36 (s, 1H, CH), 3.73 (s, 3H, OCH<sub>3</sub>), 3.41 (s, 3H, OCH<sub>3</sub>), 2.29 (s, 3H, CH<sub>3</sub>); enol-form: 10.18 (s, 1H, NH), 7.13 (brs, 1H, ArH), 7.80 (d, *J* = 7.6Hz, 2H, ArH), 7.01 (brs, 1H, ArH), 6.63 (d, *J* = 8.4Hz, 2H, ArH), 6.45 (d, *J* = 8.0Hz, 2H, ArH), 5.56 (s, 1H, CH), 3.81 (s, 3H, OCH<sub>3</sub>), 3.64 (s, 3H, OCH<sub>3</sub>), 2.24 (s, 3H, CH<sub>3</sub>). Keto/enol = 5:1. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 178.1, 163.8, 159.5, 142.5, 137.4, 136.8, 136.6, 133.4, 132.4, 130.0, 128.7, 127.5, 125.8, 125.3, 123.1, 122.5, 116.6, 114.4, 113.3, 110.5, 55.5, 50.6, 45.2, 20.9; IR (KBr) ν: 3178, 3123, 3034, 2946, 2918, 2860, 1698, 1625, 1518, 1490, 1248, 1204, 1123, 1096, 1024, 836, 810 cm<sup>-1</sup>; MS (m/z): HRMS (ESI) Calcd. for C<sub>28</sub>H<sub>23</sub>ClN<sub>2</sub>O<sub>4</sub> ([M+Na]<sup>+</sup>): 509.1235. Found: 509.1239

**Methyl 4-(5-chloro-2-oxoindolin-3-yl)-1,5-bis(4-methoxyphenyl)-1H-pyrrole-3-carboxylate (4c):** white solid, 80%, m.p. 245-248°C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: keto-form: 10.49 (s, 1H, NH), 7.63 (s, 1H, CH), 7.21-7.18 (m, 5H, ArH), 6.97 (brs, 1H, ArH), 6.93-6.91 (m, 4H, ArH), 6.88 (d, *J* = 8.0Hz, 1H, ArH), 4.34 (s, 1H, CH), 3.75 (s, 3H, OCH<sub>3</sub>), 3.72 (s, 3H, OCH<sub>3</sub>), 3.41 (s, 3H, OCH<sub>3</sub>); enol-form: 10.17 (s, 1H, NH), 7.05 (d, *J* = 8.4Hz, 2H, ArH), 6.64 (d, *J* = 8.4Hz, 2H, ArH), 6.50 (m, 5H, ArH), 5.56 (s, 1H, CH), 3.81 (s, 3H, OCH<sub>3</sub>), 3.70 (s, 3H, OCH<sub>3</sub>), 3.63 (s, 3H, OCH<sub>3</sub>). keto/enol = 5:1. <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 178.1, 163.8, 159.5, 158.7, 142.5, 136.8, 133.5, 132.5, 132.2, 128.8, 127.5, 127.5, 127.4, 125.3, 123.1, 122.5, 116.4, 114.6, 114.4, 113.1, 110.5, 55.8, 55.5, 50.6, 45.3; IR (KBr) ν: 3309, 3123, 3002, 2932, 2836, 1733, 1699, 1653, 1616, 1558, 1540, 1508, 1251, 1199, 1177, 1094, 1027, 813 cm<sup>-1</sup>; MS (m/z): HRMS (ESI) Calcd. for C<sub>28</sub>H<sub>23</sub>ClN<sub>2</sub>O<sub>5</sub> ([M+Na]<sup>+</sup>): 525.1184. Found: 525.1188.

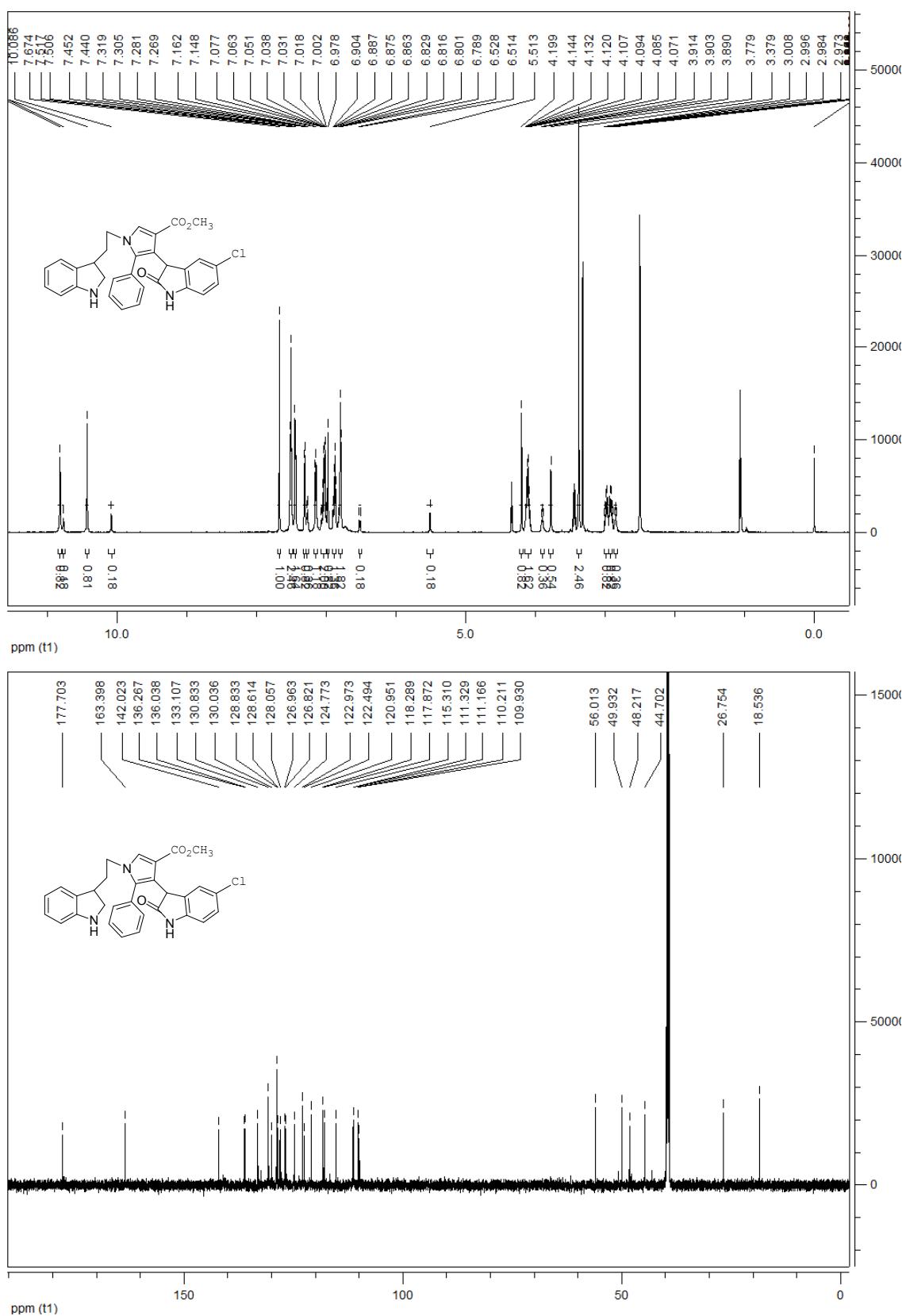
**Methyl 4-(5-chloro-2-oxoindolin-3-yl)-1,5-dip-tolyl-1H-pyrrole-3-carboxylate (4d):** white solid, 70%, m.p. 240-242°C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ: keto-form: 10.50 (s, 1H, NH), 7.67 (s, 1H, CH), 7.19-7.12 (m, 8H, ArH), 6.96 (brs, 1H, ArH), 6.83 (d, *J* = 8.4Hz, 1H, ArH), 4.37(s, 1H, CH), 3.41 (s, 3H, OCH<sub>3</sub>), 2.29 (s, 3H, CH<sub>3</sub>), 2.27 (s, 3H, CH<sub>3</sub>); enol-form: 10.21 (s, 1H, NH), 7.12 (brs, 1H, ArH), 7.08 (d, *J* = 8.0Hz, 2H, ArH), 6.70 (brs, 2H, ArH), 6.79 (d, *J* = 7.2Hz, 2H, ArH), 6.64 (d, *J* = 8.0Hz, 1H, ArH), 6.42 (d, *J* = 6.8Hz, 2H, ArH), 5.59 (s, 1H, CH), 3.81 (s, 3H, OCH<sub>3</sub>), 2.24 (s, 3H, CH<sub>3</sub>), 2.15 (s, 3H, CH<sub>3</sub>). Keto/enol = 5:1. <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 178.0, 163.8, 142.5, 138.0, 137.4, 136.7, 136.7, 133.4, 131.0, 130.0, 129.6, 128.9, 127.5, 127.4, 125.9, 125.3, 123.1, 116.7, 113.4, 110.5, 56.5, 50.7, 45.2, 21.2, 20.9, 19.0; IR (KBr)

$\nu$ : 3341, 3184, 3130, 3034, 2948, 2921, 2857, 1695, 1653, 1618, 1558, 1518, 1476, 1257, 1231, 1199, 1113, 1091, 823  $\text{cm}^{-1}$ ; MS (m/z): HRMS (ESI) Calcd. for  $\text{C}_{28}\text{H}_{23}\text{ClN}_2\text{O}_3$  ( $[\text{M}+\text{Na}]^+$ ): 493.1258. Found: 493.1397.

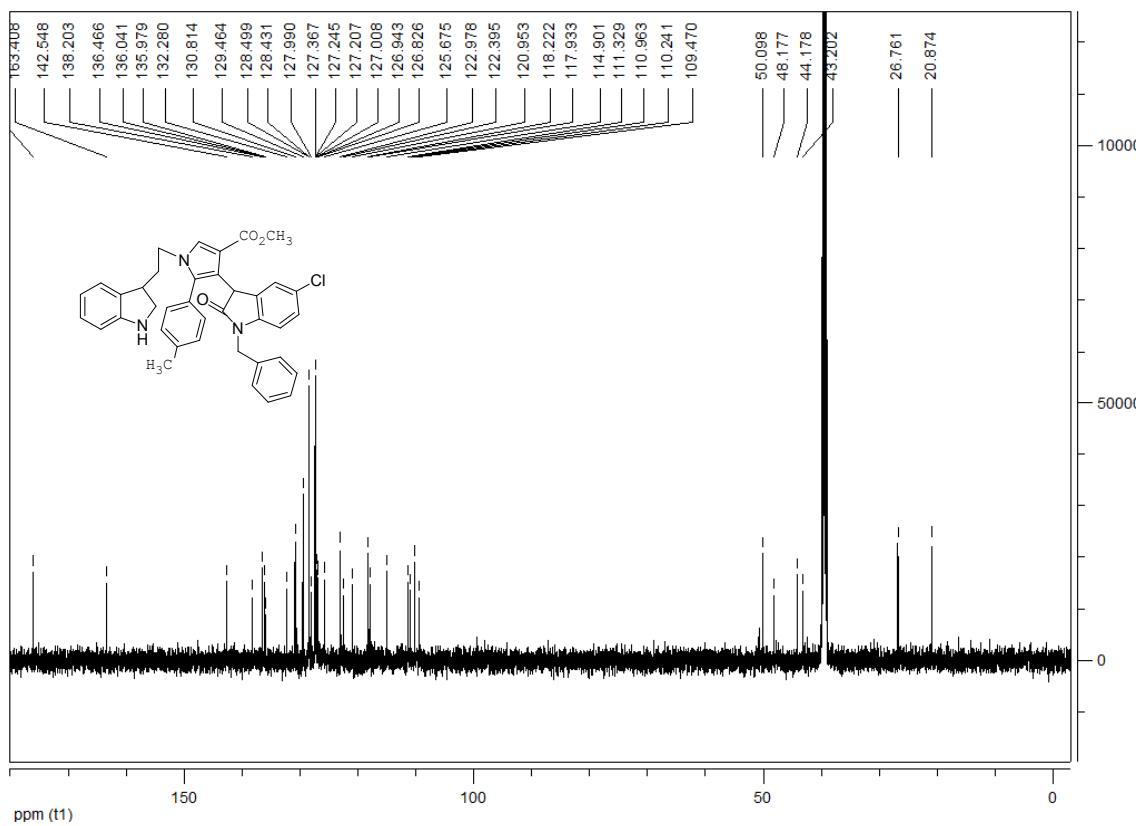
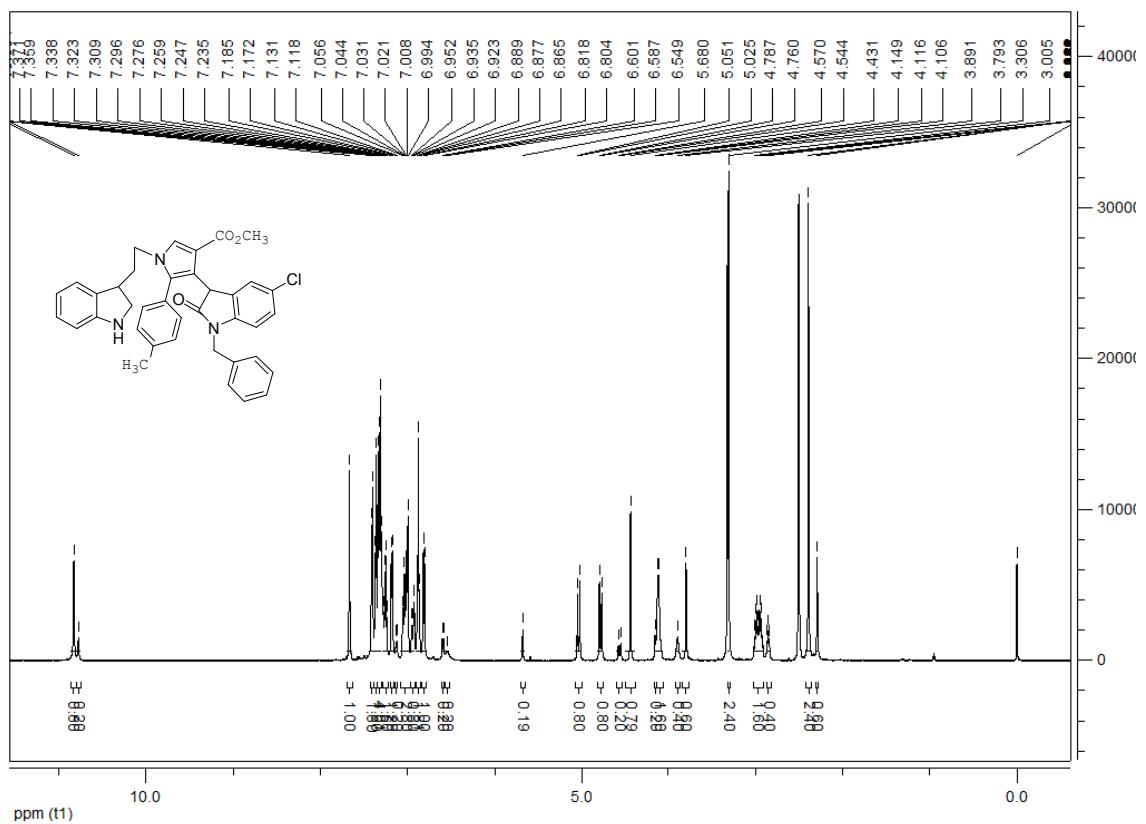
**Methyl 4-(5-fluoro-2-oxoindolin-3-yl)-1-(4-methoxyphenyl)-5-p-tolyl-1H-pyrrole-3-carboxylate (4e):** white solid, 76%, m.p. 245-248°C;  $^1\text{H}$  NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$ : keto-form: 10.38 (s, 1H, NH), 7.64 (s, 1H, CH), 7.19-7.16 (m, 6H, ArH), 6.97-6.90 (m, 3H, ArH), 6.82-6.78 (m, 2H, ArH), 4.34 (s, 1H, CH), 3.75 (s, 3H, OCH<sub>3</sub>), 3.40 (s, 3H, OCH<sub>3</sub>), 2.27 (s, 3H, CH<sub>3</sub>); enol-form: 10.10 (s, 1H, NH), 7.04 (d,  $J = 8.4\text{Hz}$ , 2H, ArH), 6.83 (brs, 2H, ArH), 6.61 (brs, 1H, ArH), 6.44 (d,  $J = 7.2\text{Hz}$ , 1H, ArH), 5.60 (s, 1H, CH), 3.81 (s, 3H, OCH<sub>3</sub>), 3.70 (s, 3H, OCH<sub>3</sub>), 2.14 (s, 3H, CH<sub>3</sub>). Keto/enol = 5:1.  $^{13}\text{C}$  NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 178.3, 163.8, 158.8, 157.1, 139.7, 138.0, 136.9, 132.2, 131.0, 129.5, 129.0, 127.5, 127.4, 116.6, 114.6, 114.5, 113.8, 113.6, 113.3, 111.1, 110.9, 109.7, 109.6, 55.7, 50.6, 45.6, 21.2; IR (KBr)  $\nu$ : 3178, 3139, 2948, 2920, 2867, 2838, 1703, 1653, 1627, 1611, 1559, 1515, 1483, 1459, 1296, 1249, 1235, 1197, 1124, 1105, 1082, 1033, 928, 828  $\text{cm}^{-1}$ ; MS (m/z): HRMS (ESI) Calcd. for  $\text{C}_{28}\text{H}_{23}\text{FN}_2\text{O}_4$  ( $[\text{M}+\text{Na}]^+$ ): 493.1529. Found: 493.1534.

**methyl 5-(4-chlorophenyl)-1-(4-methoxyphenyl)-4-(5-methyl-2-oxoindolin-3-yl)-1H-pyrrole-3-carboxylate (4f):** white solid, 77%, m.p. 230-232°C;  $^1\text{H}$  NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : keto-form: 8.58 (s, 1H, NH), 7.56 (s, 1H, CH), 7.28-7.27 (m, 3H, ArH), 7.05 (d,  $J = 8.4\text{Hz}$ , 2H, ArH), 6.96 (d,  $J = 7.8\text{Hz}$ , 1H, ArH), 6.83 (d,  $J = 8.4\text{Hz}$ , 2H, ArH), 6.79 (d,  $J = 7.8\text{Hz}$ , 1H, ArH), 6.73-6.72 (m, 2H, ArH), 4.61 (s, 1H, CH), 3.80 (s, 3H, OCH<sub>3</sub>), 3.46 (s, 3H, OCH<sub>3</sub>), 2.25 (s, 3H, CH<sub>3</sub>); enol-form: 8.41 (s, 1H, NH), 7.25 (brs, 2H, ArH), 6.99 (brs, 1H, ArH), 6.20 (d,  $J = 9.0\text{Hz}$ , 1H, ArH), 6.87 (d,  $J = 8.4\text{Hz}$ , 2H, ArH), 6.62 (d,  $J = 7.8\text{Hz}$ , 1H, ArH), 6.52 (d,  $J = 7.8\text{Hz}$ , 2H, ArH), 5.80 (s, 1H, CH), 3.89 (s, 3H, OCH<sub>3</sub>), 3.74 (s, 3H, OCH<sub>3</sub>), 2.27 (s, 3H, CH<sub>3</sub>). Keto/enol = 3:1;  $^{13}\text{C}$  NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 178.3, 163.7, 158.8, 141.0, 135.2, 133.5, 132.7, 132.5, 131.9, 131.1, 130.1, 129.5, 129.4, 129.0, 127.9, 127.8, 127.4, 123.8, 117.9, 114.8, 114.6, 113.7, 109.0, 55.8, 50.6, 45.1, 21.1; IR (KBr)  $\nu$ : 3197, 3077, 3038, 2945, 2918, 2864, 1703, 1652, 1624, 1558, 1520, 1490, 1252, 1201, 1117, 1093, 818, 773  $\text{cm}^{-1}$ ; MS (m/z): HRMS (ESI) Calcd. for  $\text{C}_{28}\text{H}_{23}\text{ClN}_2\text{O}_4$  ( $[\text{M}+\text{Na}]^+$ ): 509.1238. Found: 509.1239.

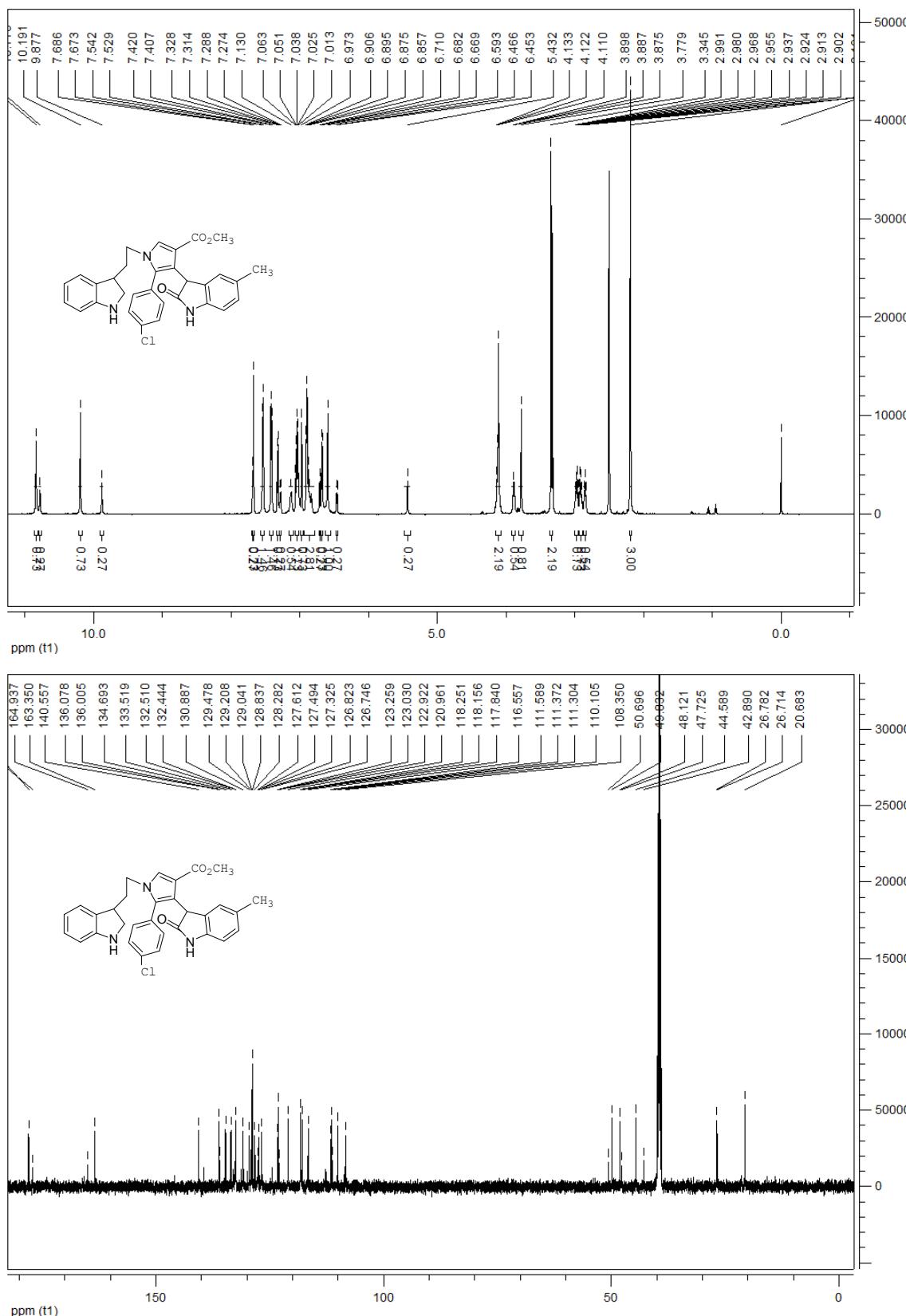
**Methyl 1-(2-(1H-indol-3-yl)ethyl)-4-(5-chloro-2-oxoindolin-3-yl)-5-phenyl-1H-pyrrole-3-carboxylate (1a):**



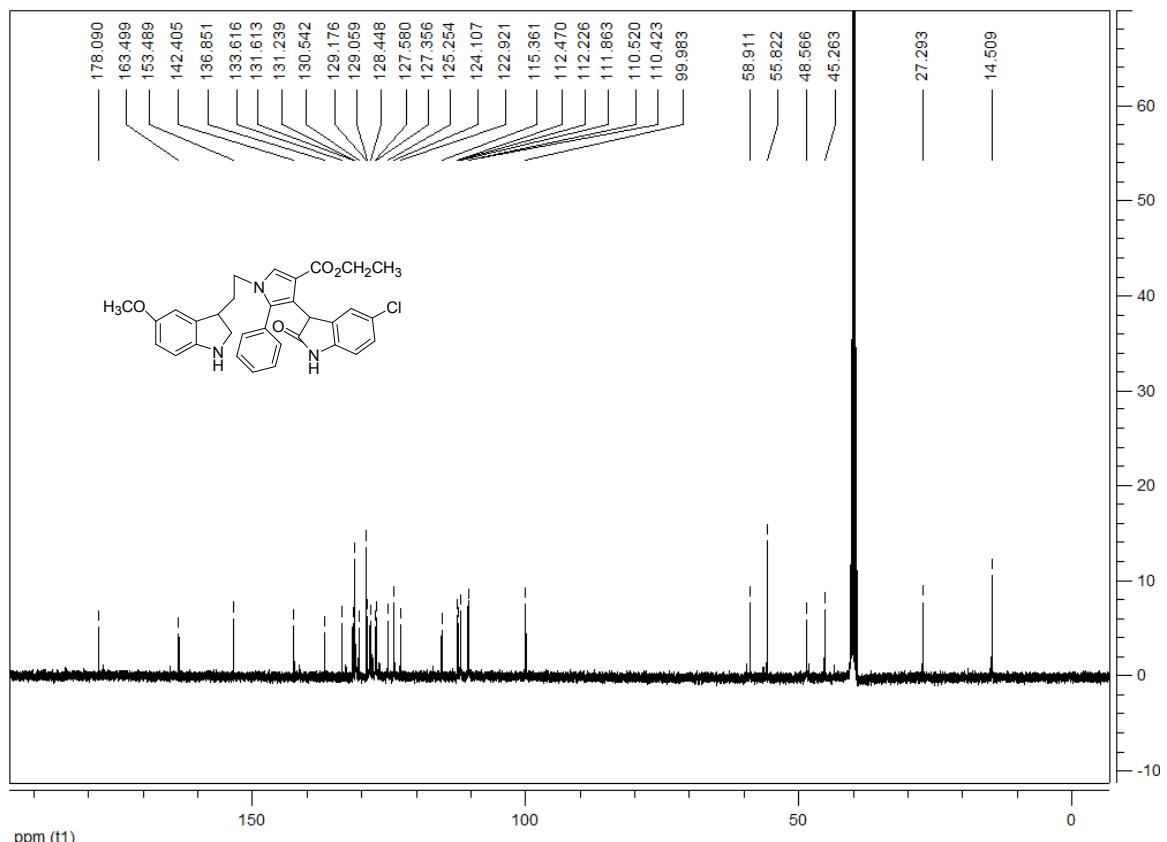
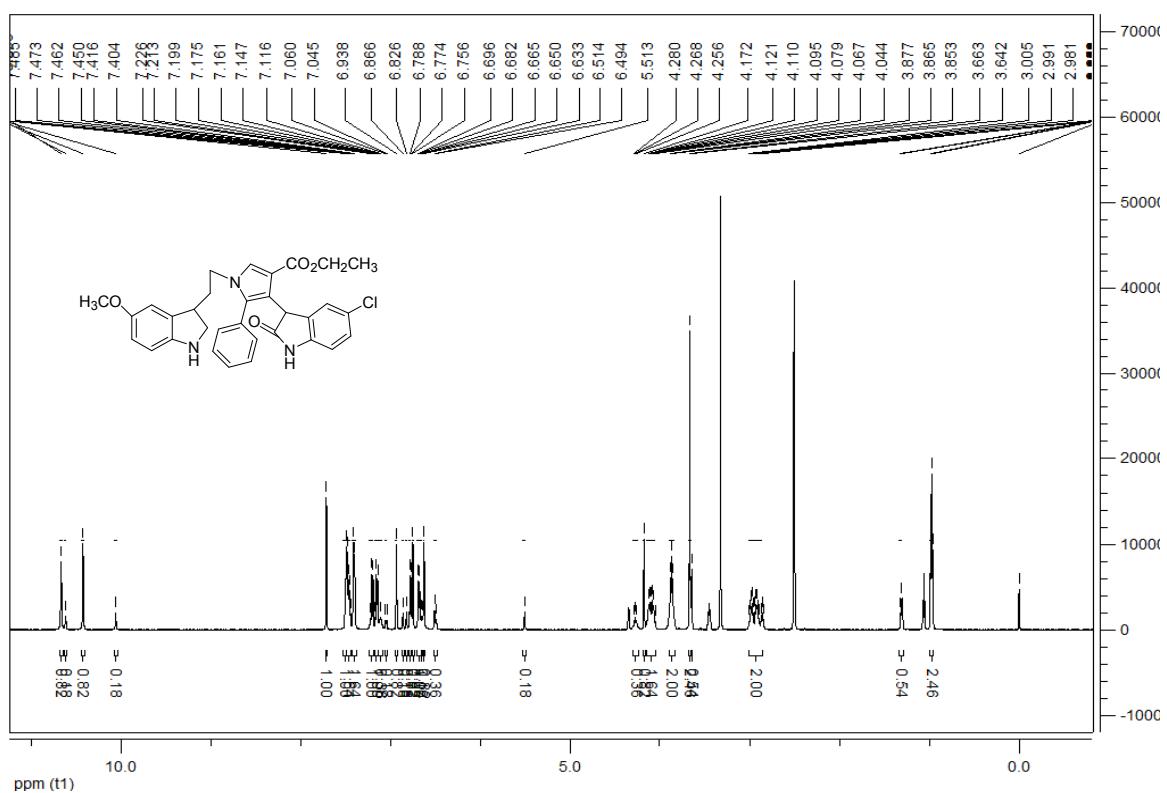
**Methyl 1-(2-(1H-indol-3-yl)ethyl)-4-(1-benzyl-5-chloro-2-oxoindolin-3-yl)-5-p-tolyl-1H-pyrrole-3-carboxylate (1b):**



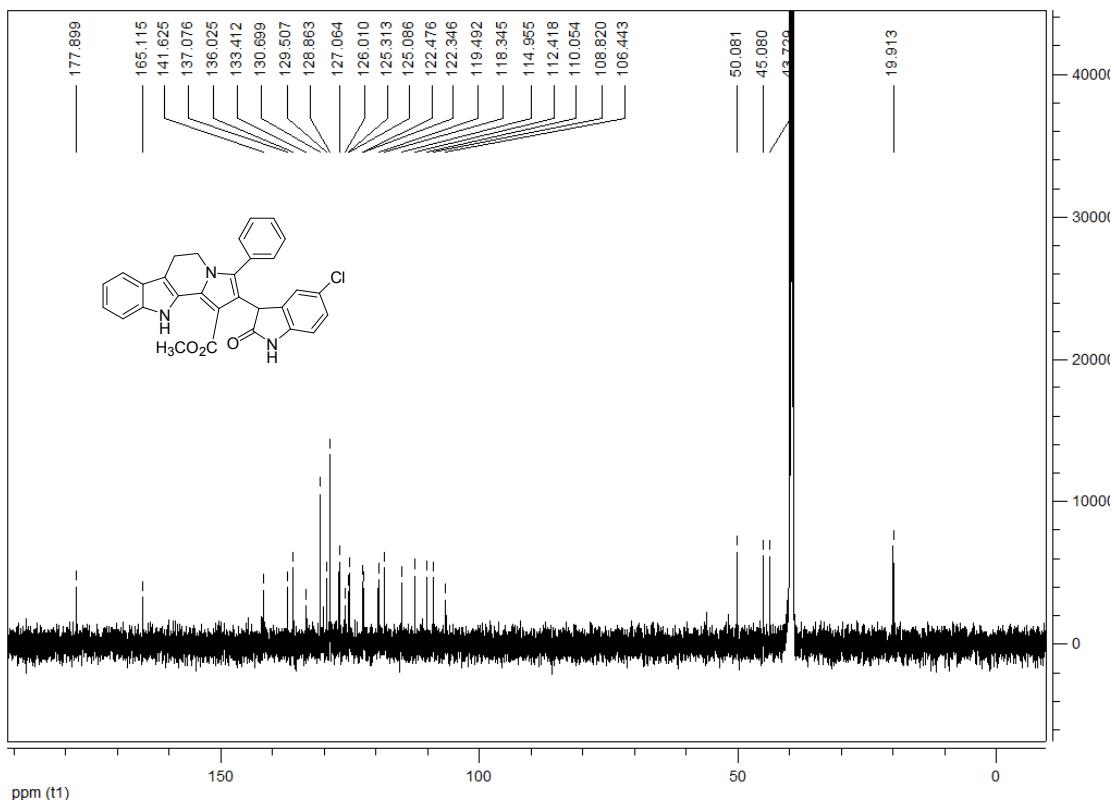
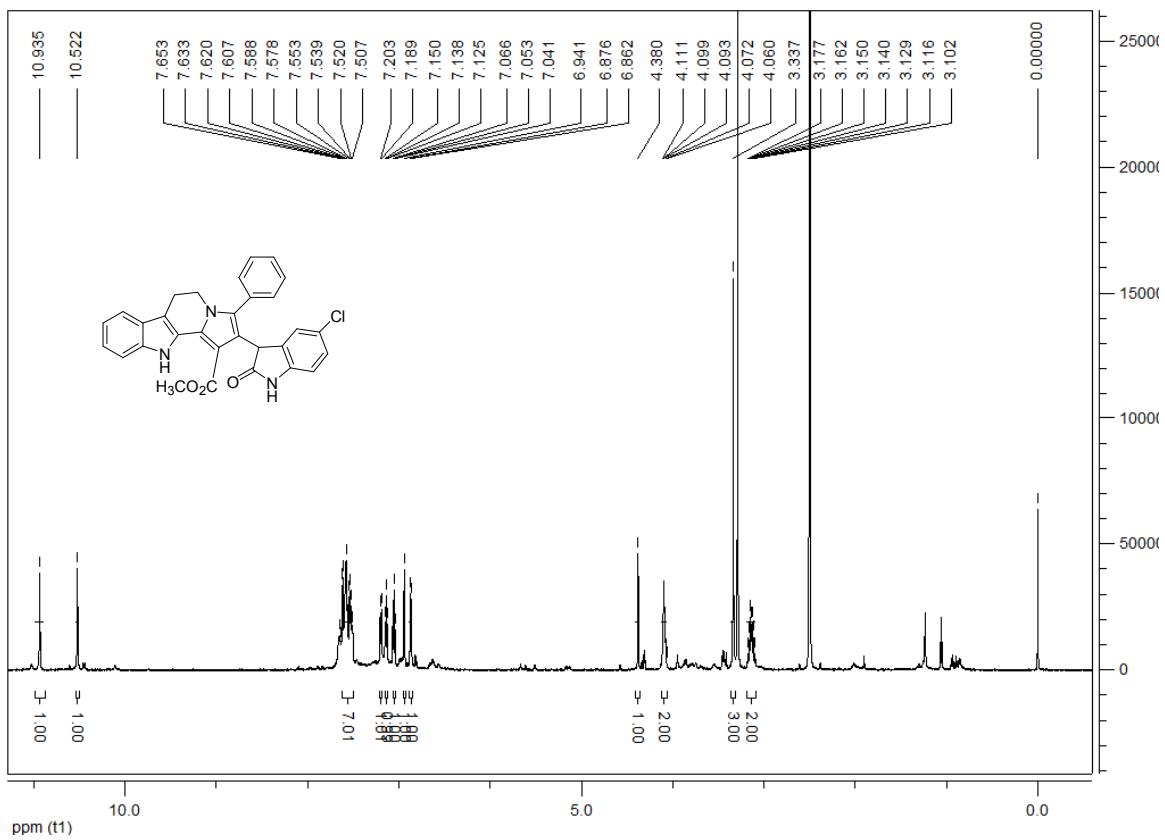
**Methyl 1-(2-(1H-indol-3-yl)ethyl)-5-(4-chlorophenyl)-4-(5-methyl-2-oxoindolin-3-yl)-1H-pyrrole-3-carboxylate (1c):**



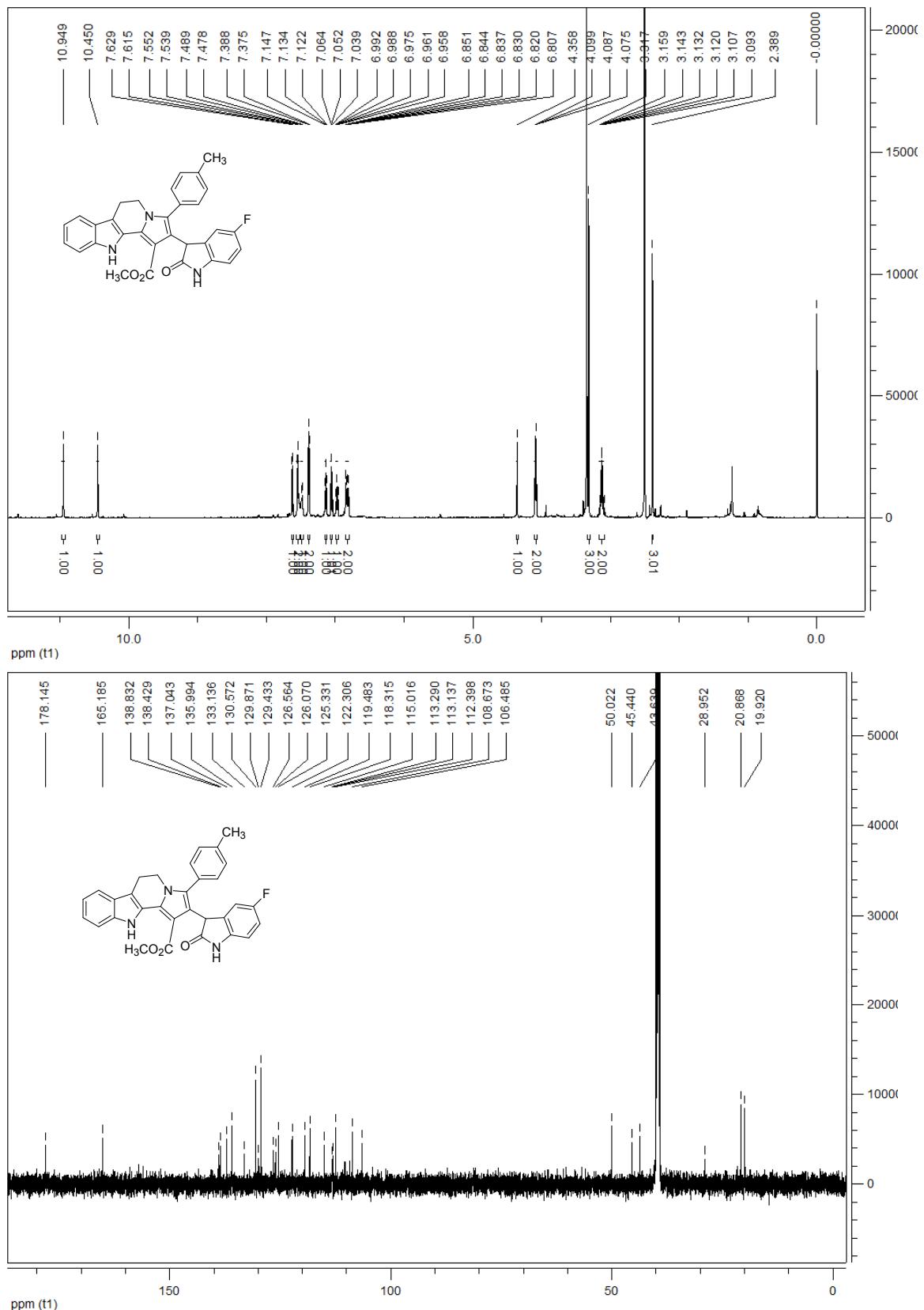
**Ethyl 4-(5-chloro-2-oxoindolin-3-yl)-1-(2-(5-methoxy-1H-indol-3-yl)ethyl)-5-phenyl-1H-pyrrole-3-carboxylate (1d):**



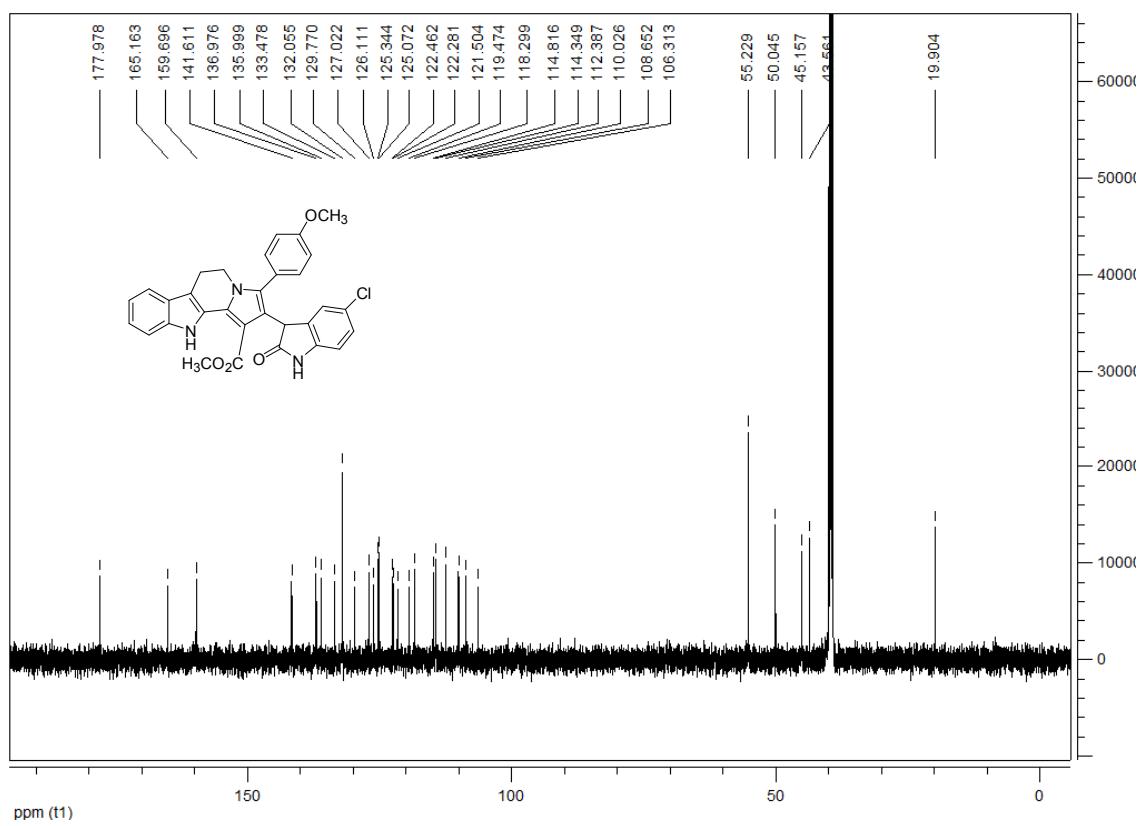
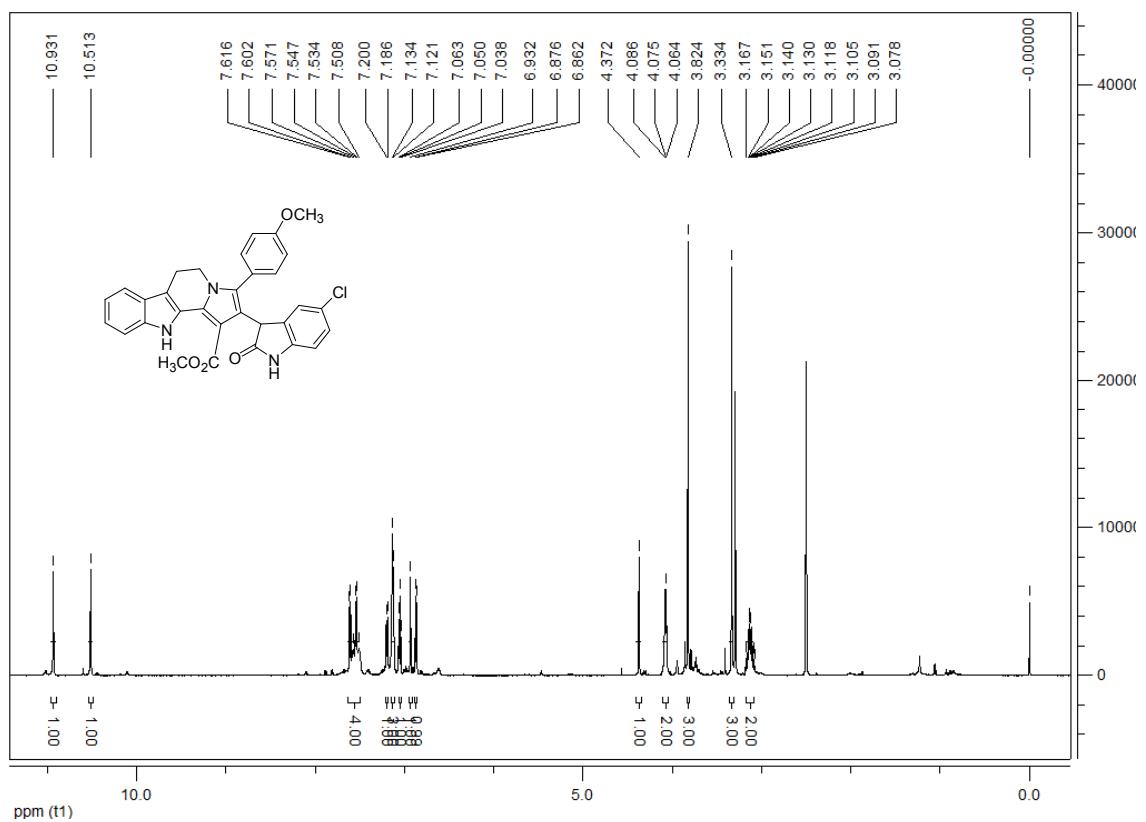
### Methyl 2-(5-chloro-2-oxoindolin-3-yl)-3-phenyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2a)



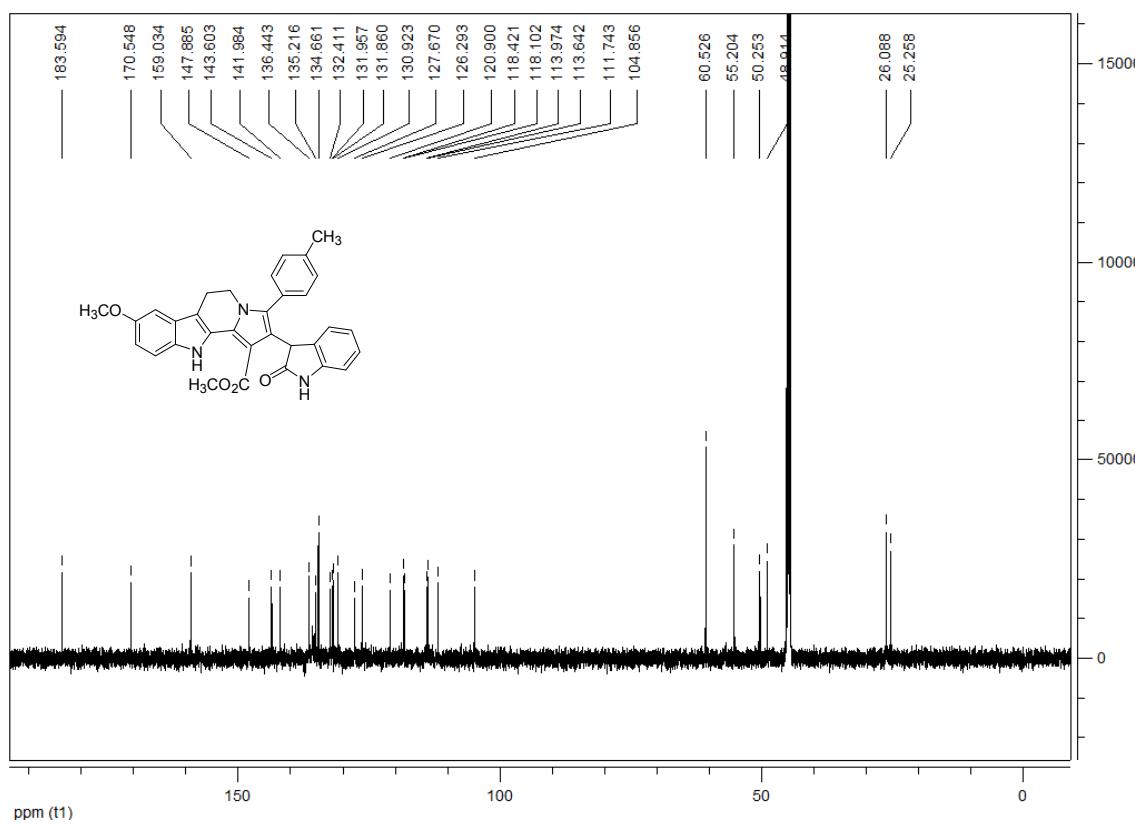
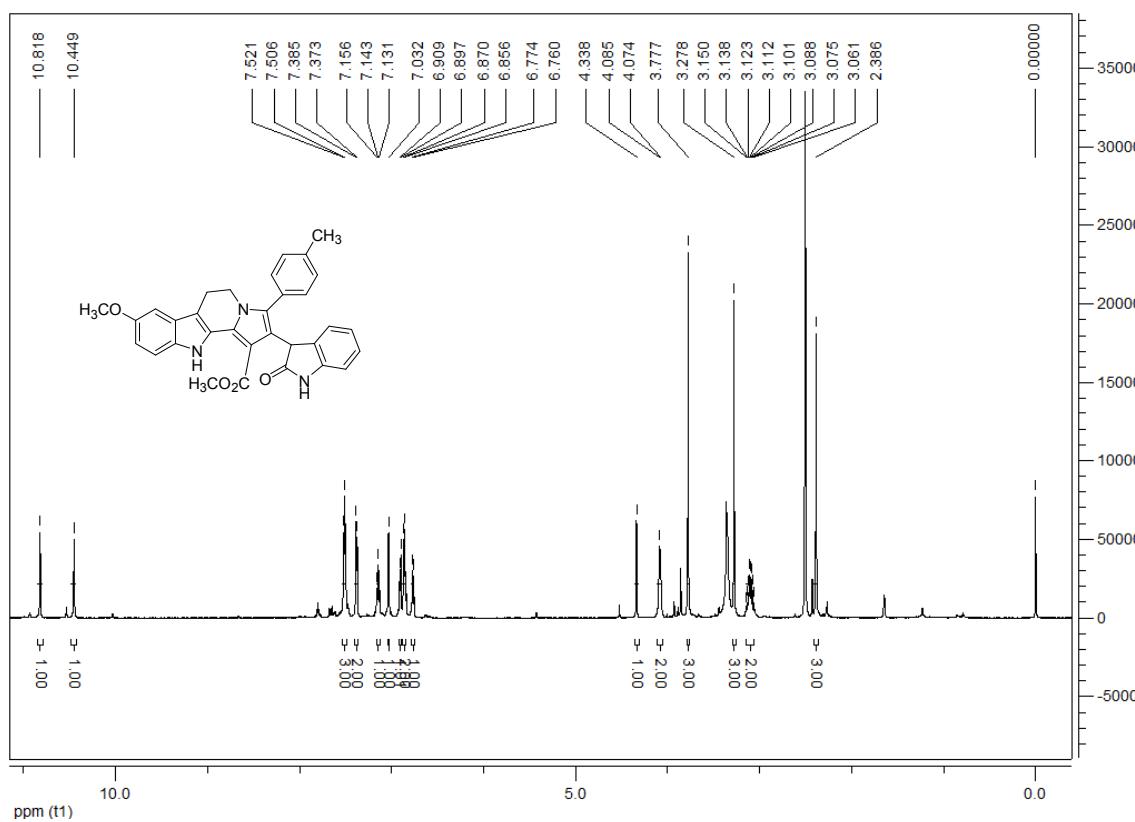
**Methyl 2-(5-fluoro-2-oxoindolin-3-yl)-3-p-tolyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2b) :**



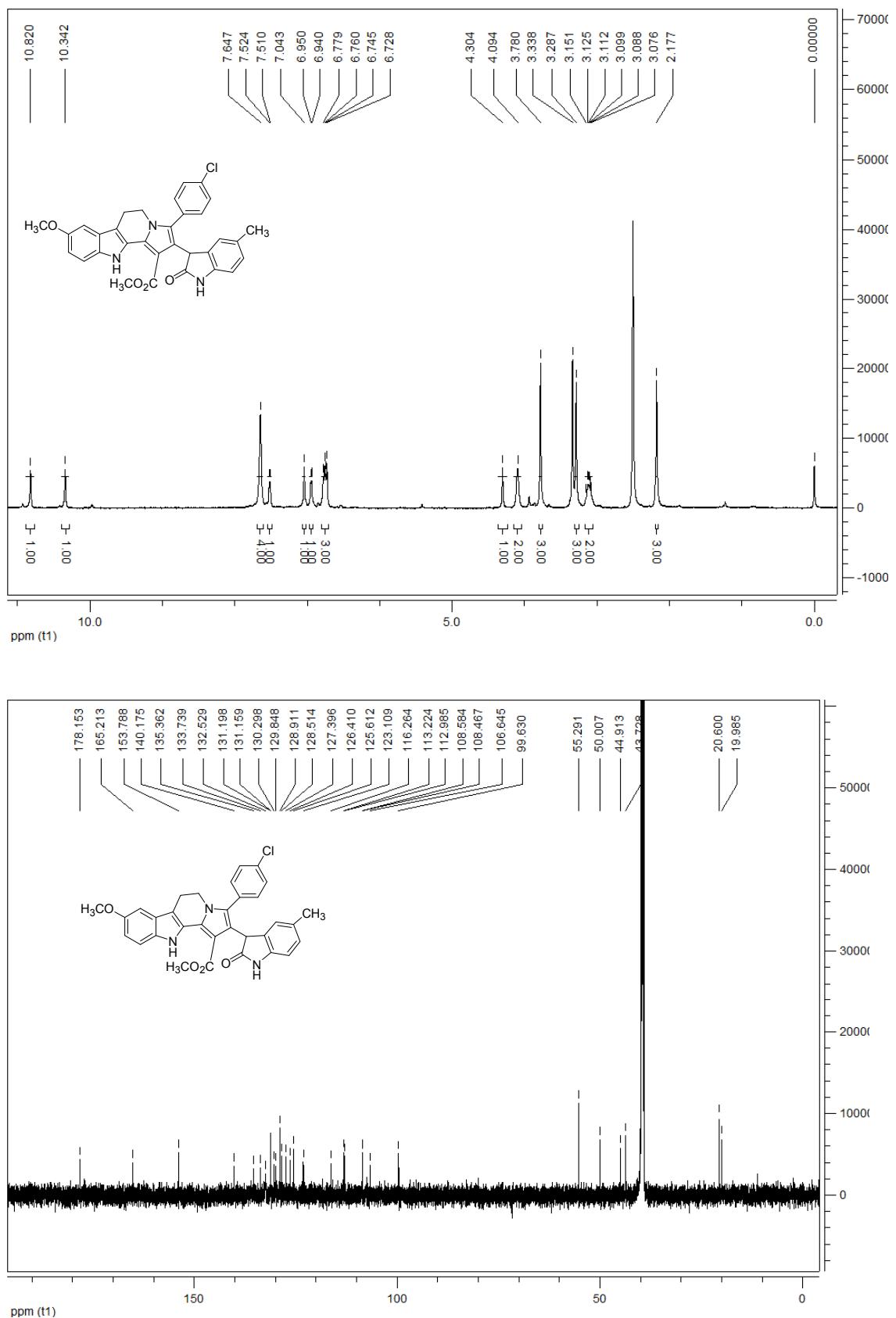
**Methyl 2-(5-chloro-2-oxoindolin-3-yl)-3-(4-methoxyphenyl)-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2c):**



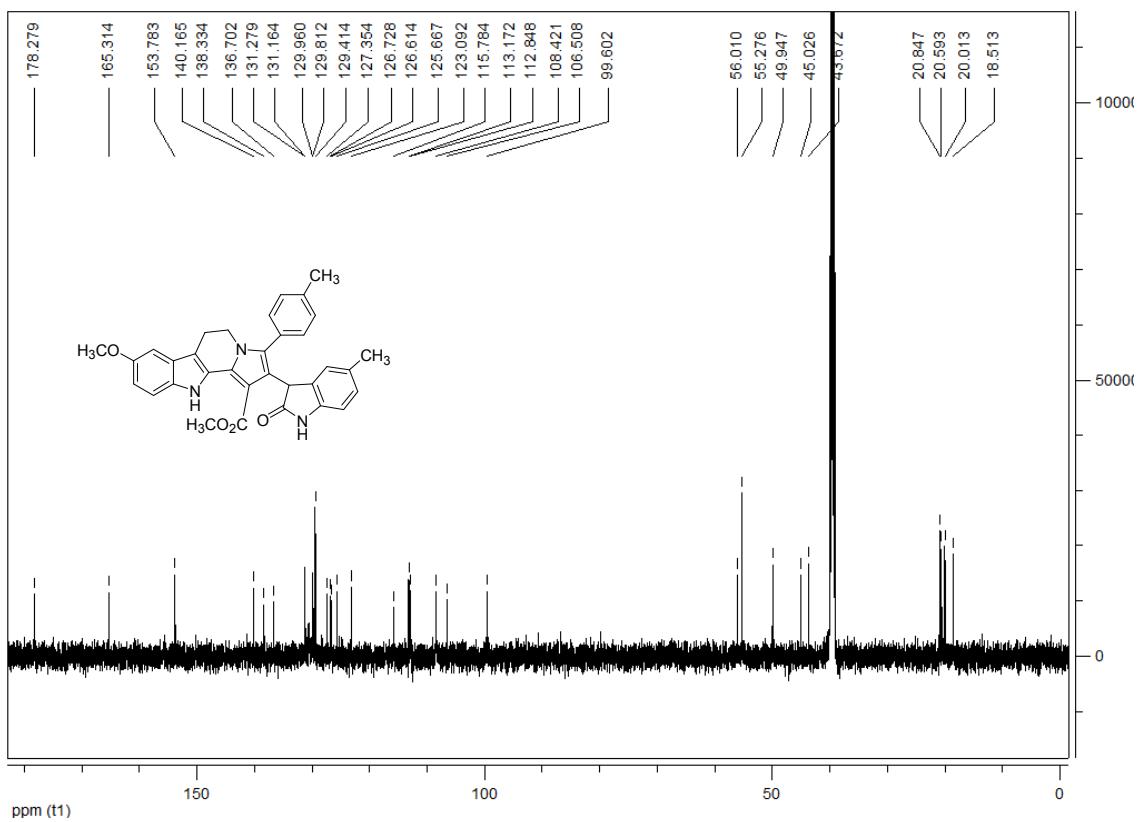
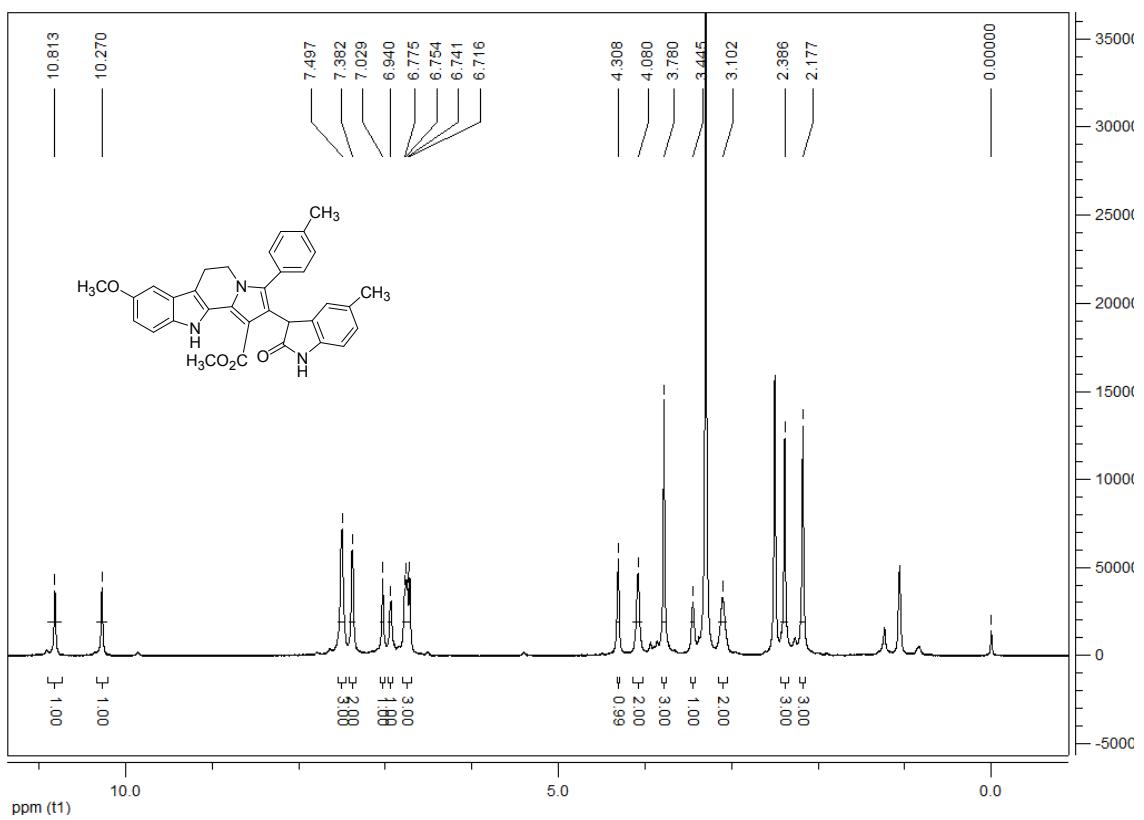
**Methyl 8-methoxy-2-(2-oxoindolin-3-yl)-3-p-tolyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2d):**



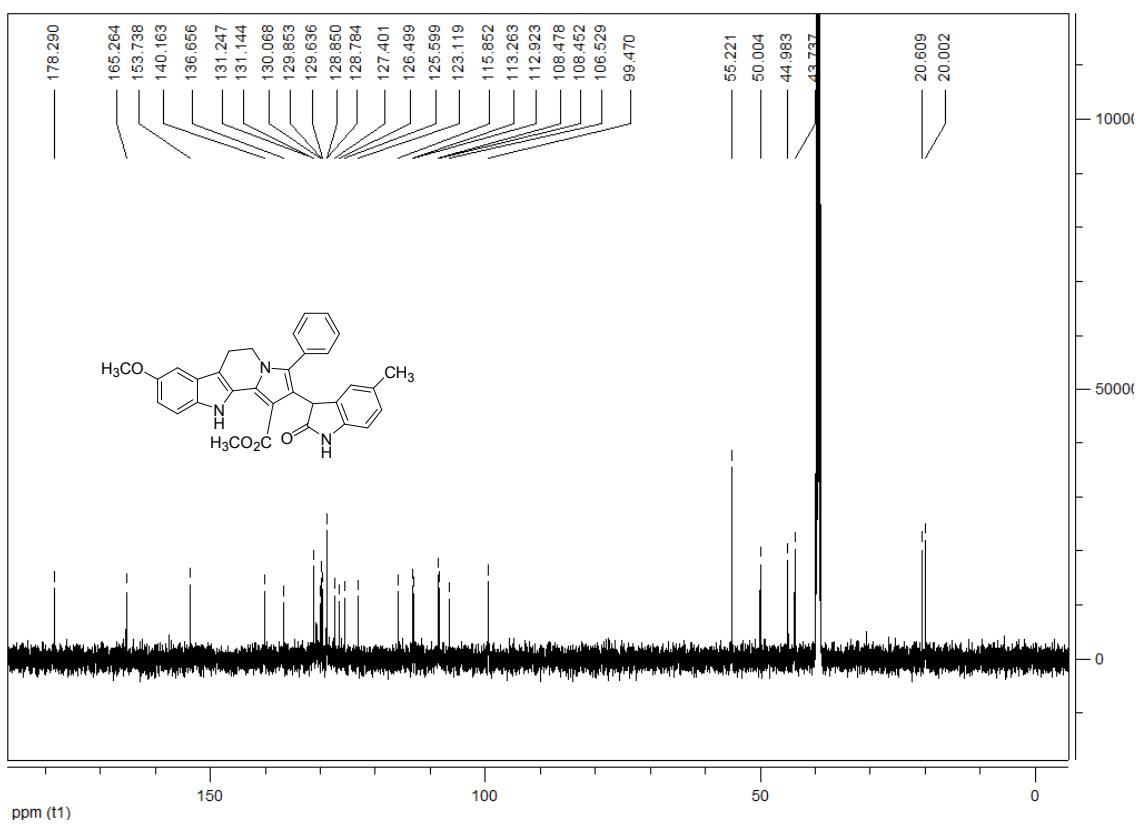
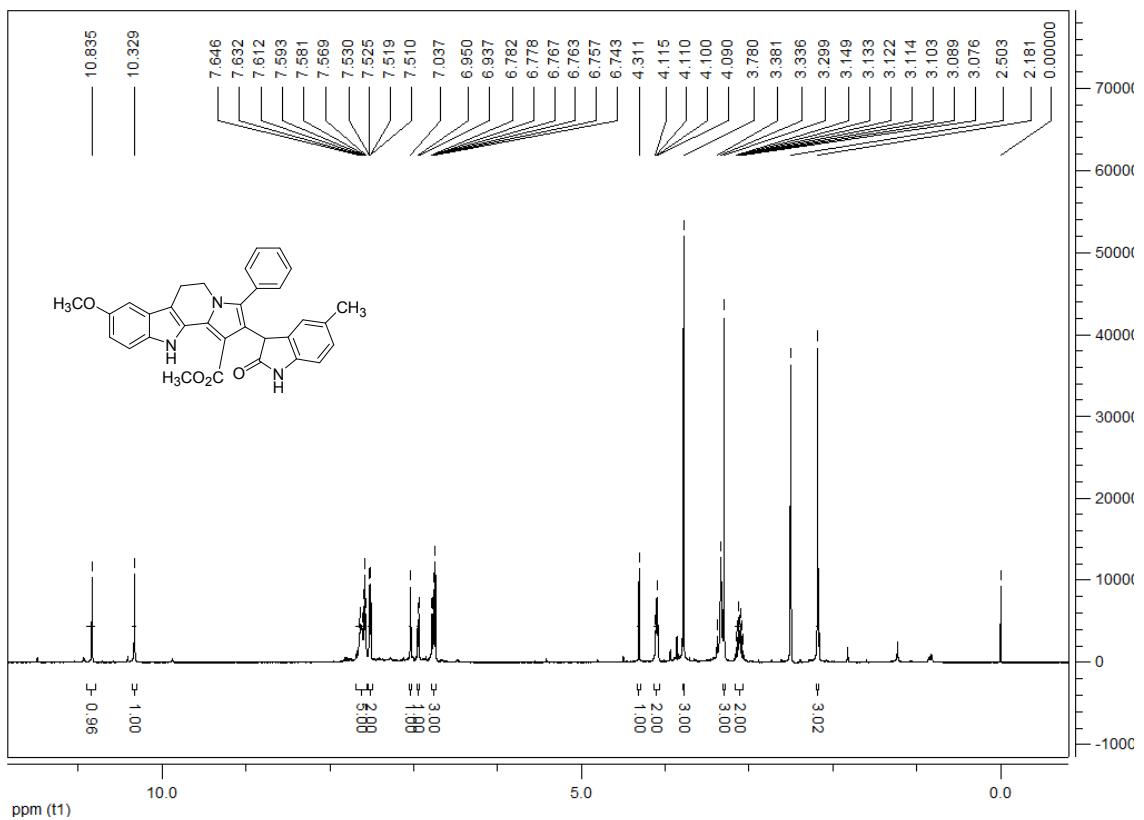
**Methyl 3-(4-chlorophenyl)-8-methoxy-2-(5-methyl-2-oxoindolin-3-yl)-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2e):**



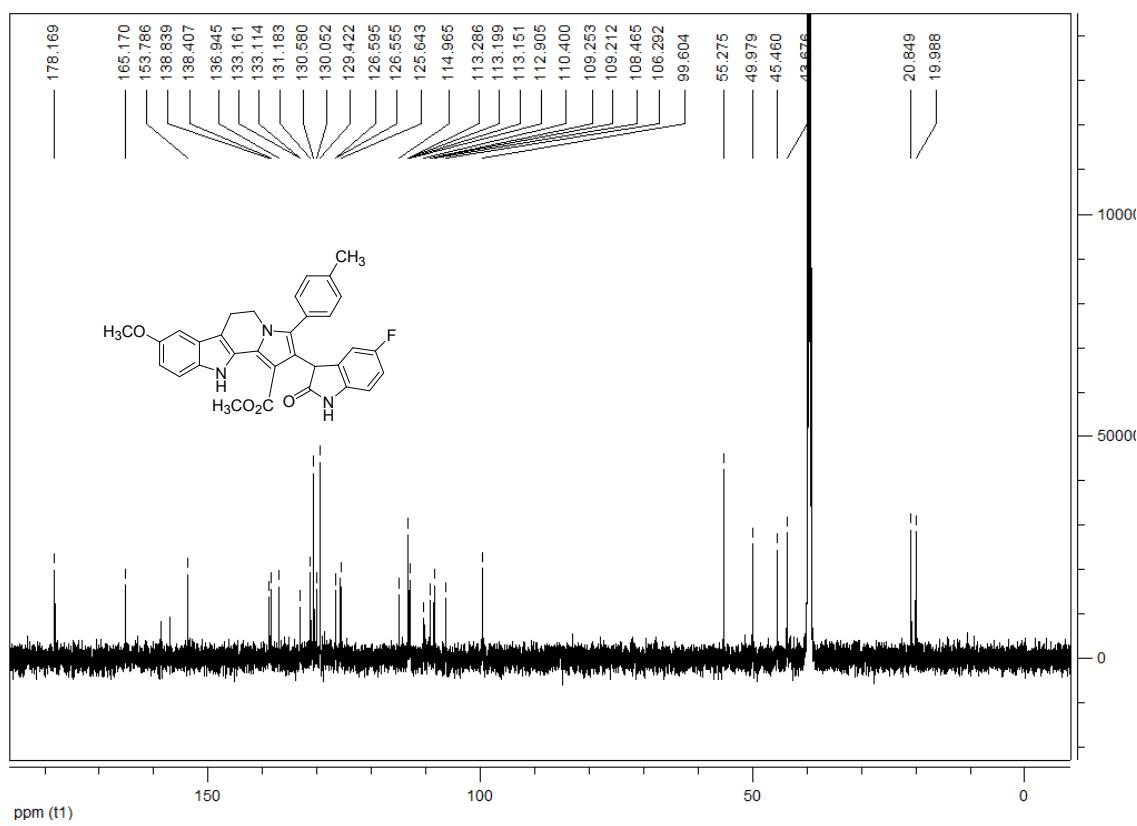
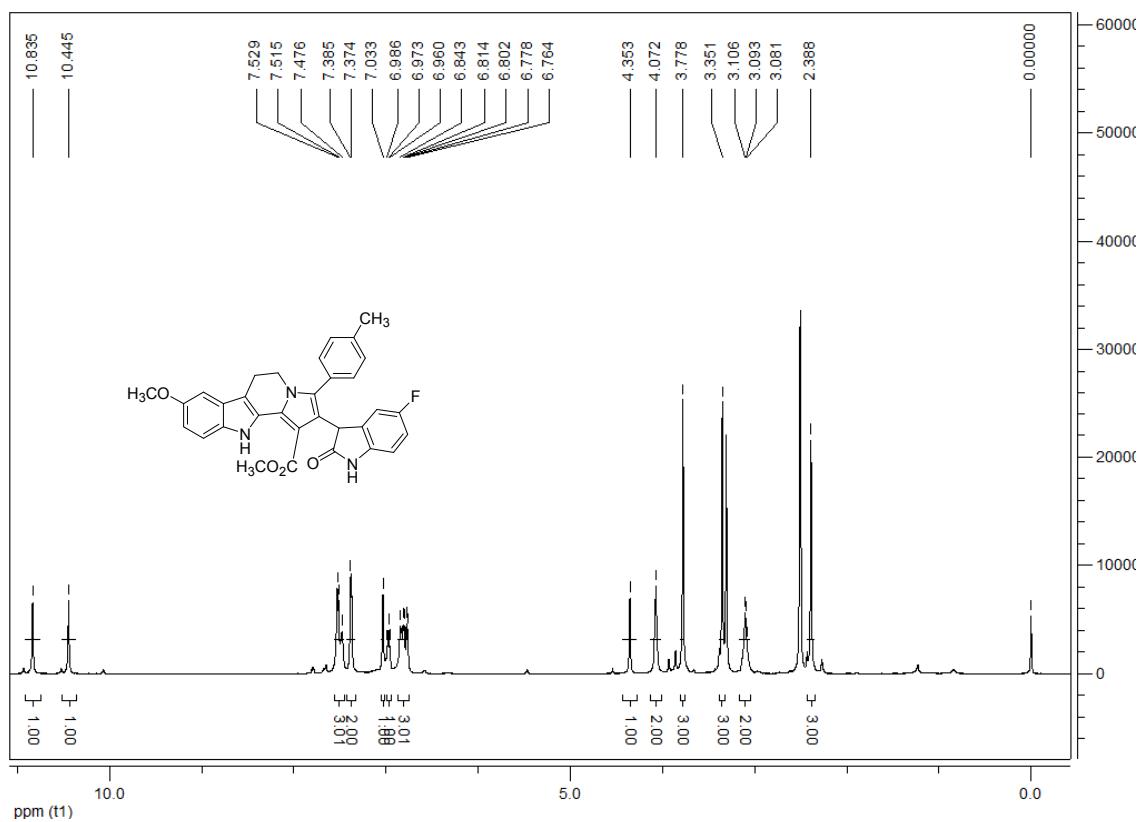
**Methyl 8-methoxy-2-(5-methyl-2-oxoindolin-3-yl)-3-p-tolyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2f):**



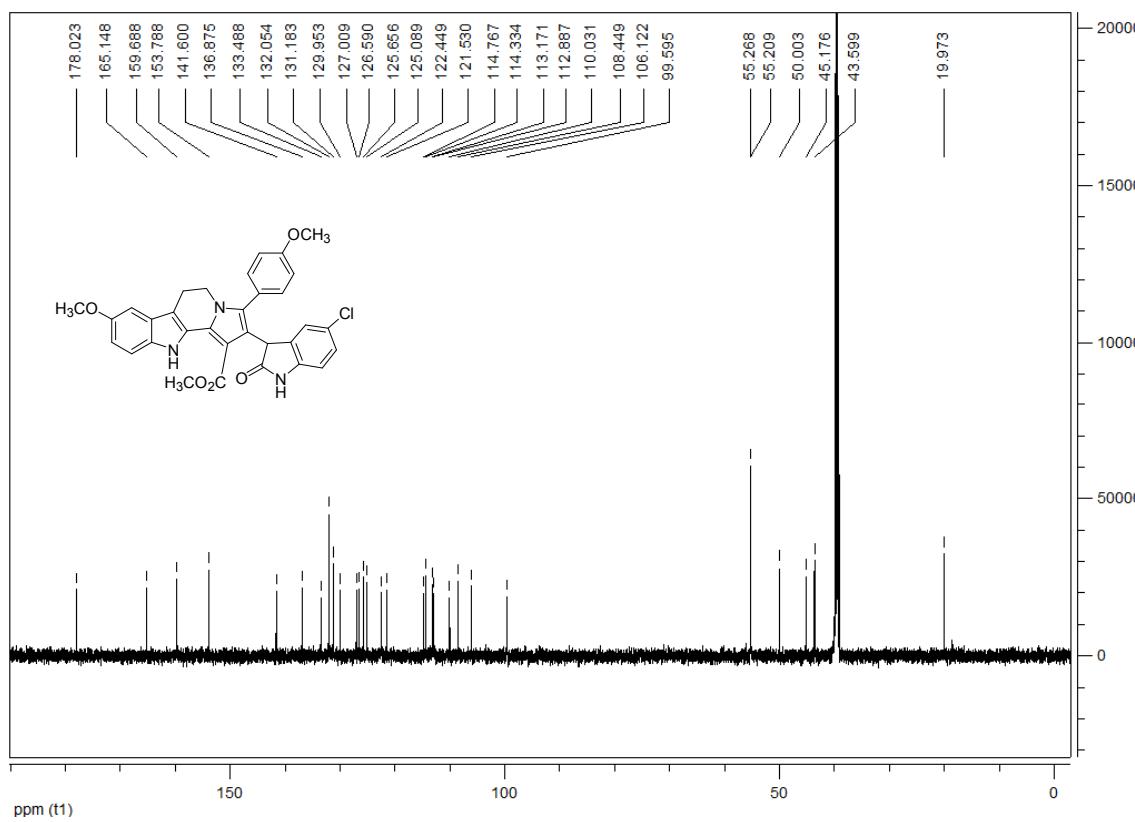
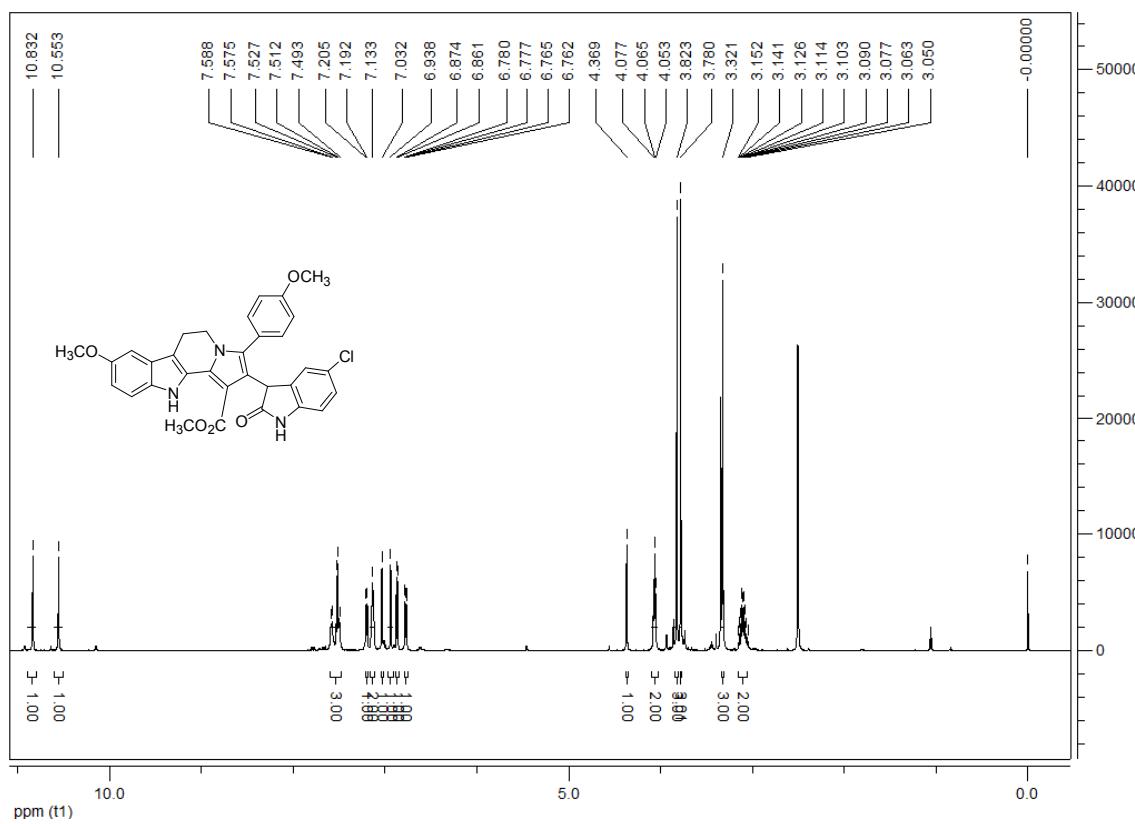
**Methyl 8-methoxy-2-(5-methyl-2-oxoindolin-3-yl)-3-phenyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2g):**



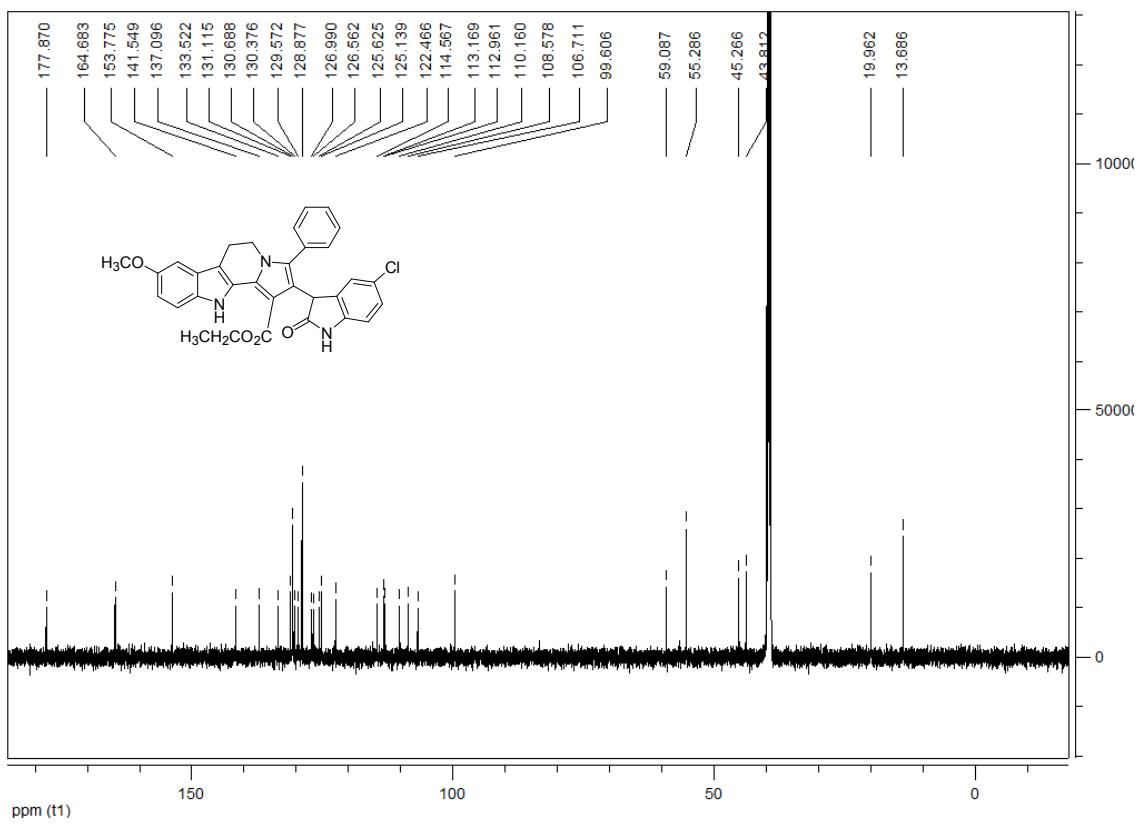
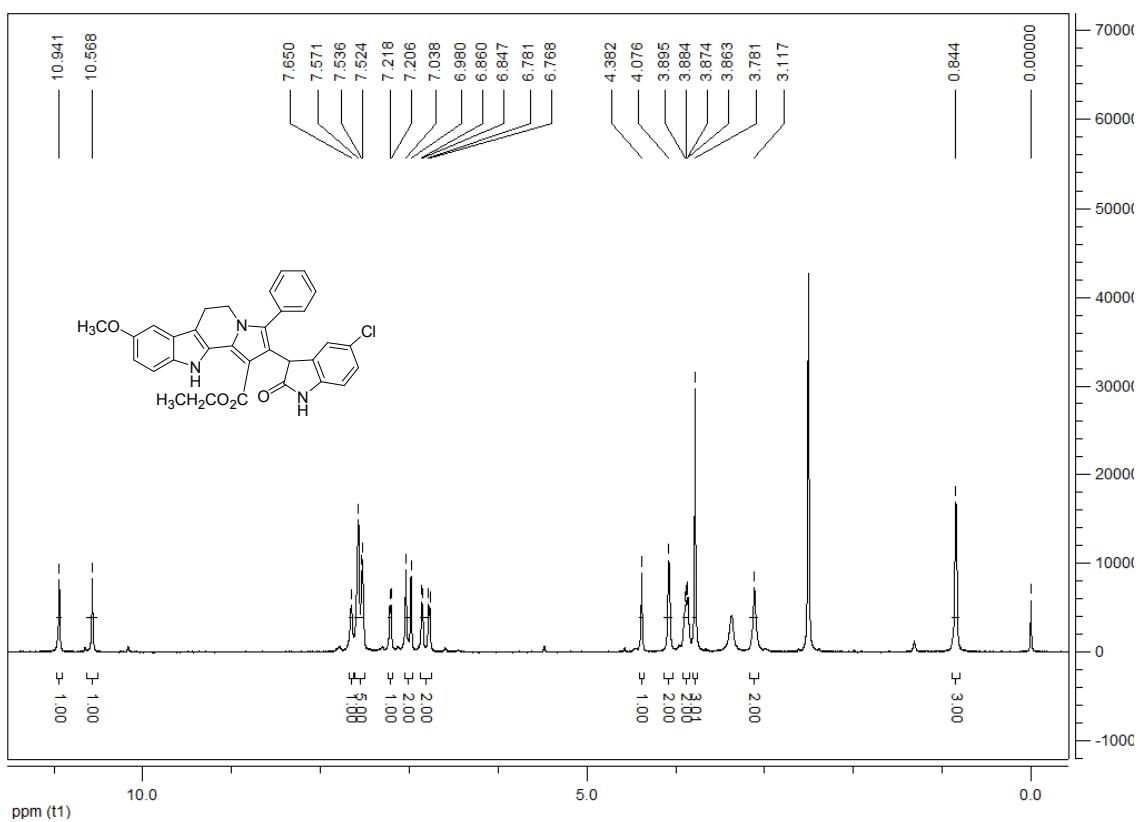
**Methyl 2-(5-fluoro-2-oxoindolin-3-yl)-8-methoxy-3-p-tolyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2h):**



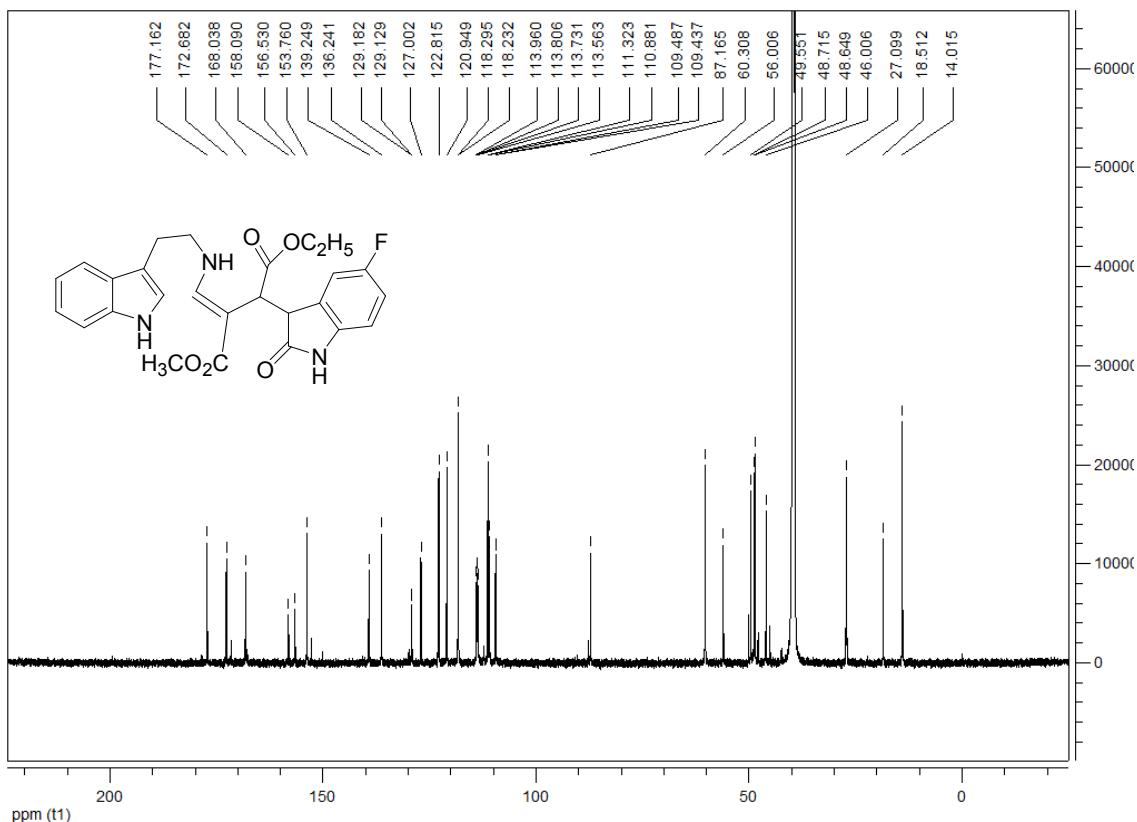
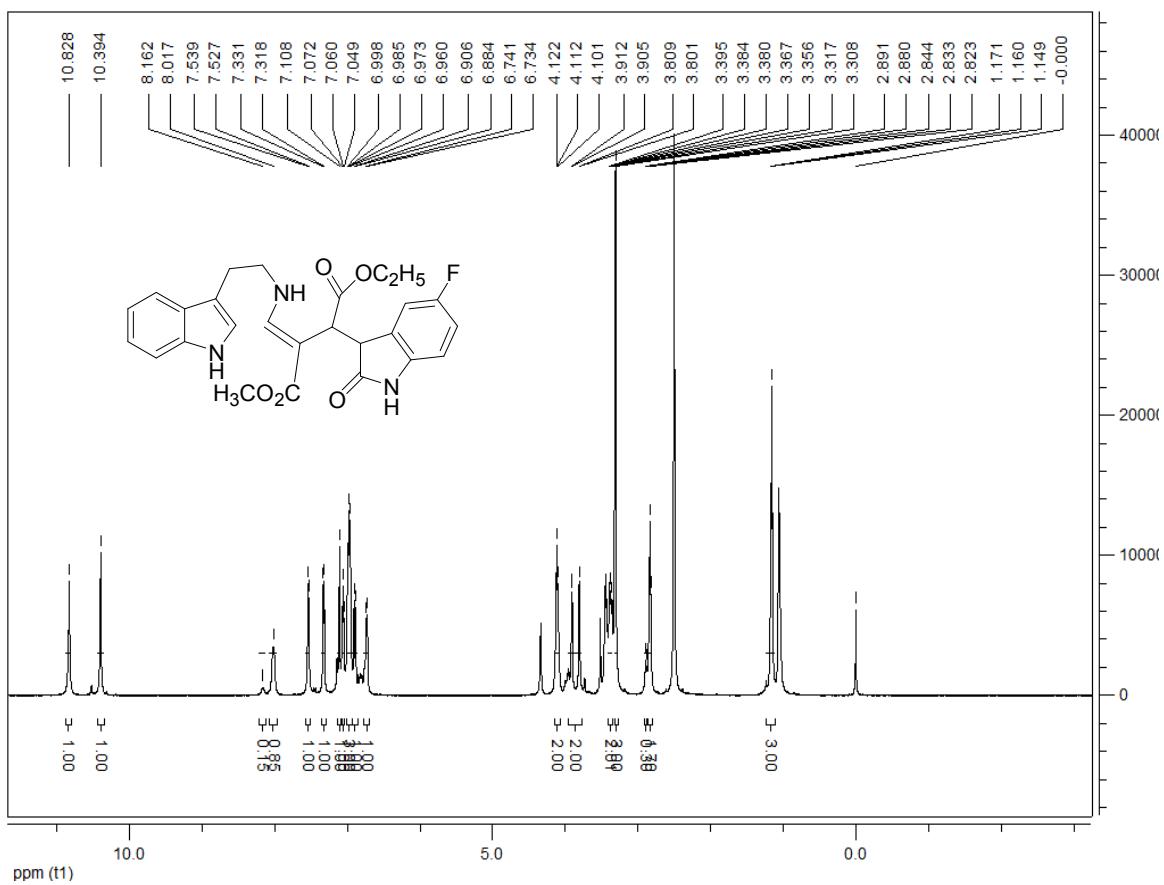
**Methyl 2-(5-chloro-2-oxoindolin-3-yl)-8-methoxy-3-(4-methoxyphenyl)-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2i):**



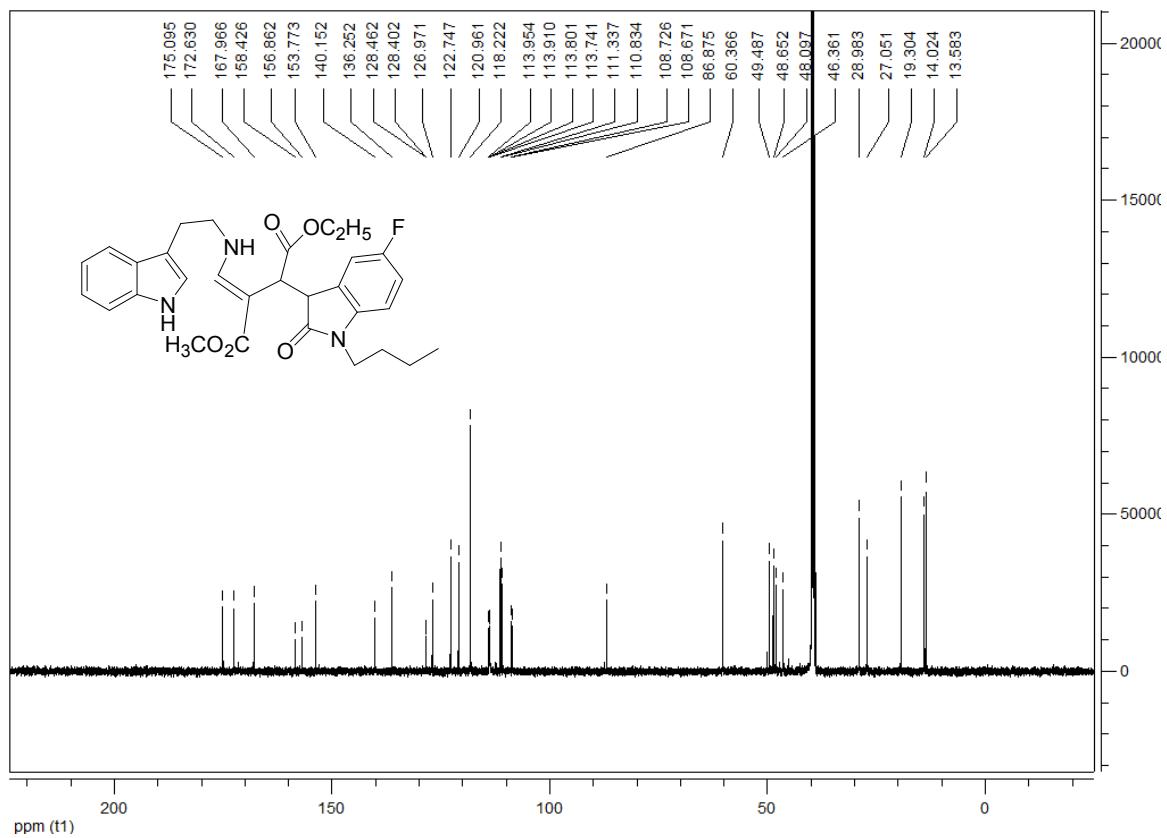
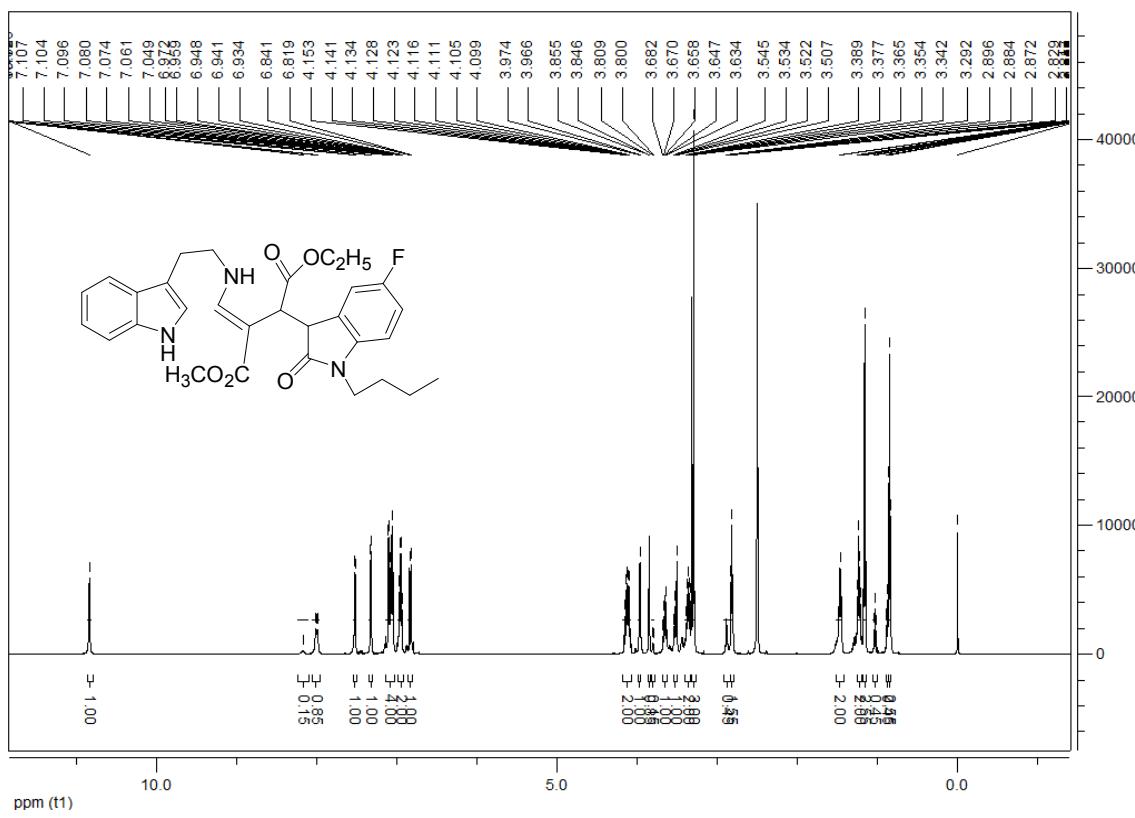
**Ethyl 2-(5-chloro-2-oxoindolin-3-yl)-8-methoxy-3-phenyl-6,11-dihydro-5H-indolizino[8,7-b]indole-1-carboxylate (2j):**



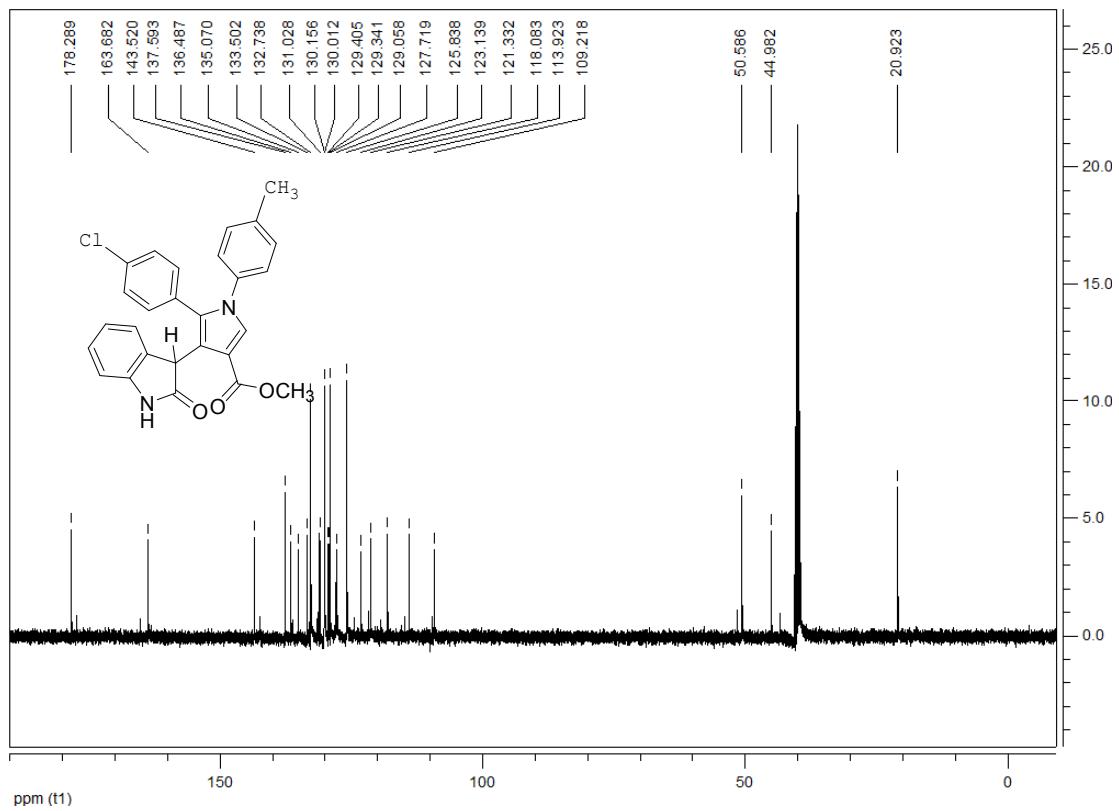
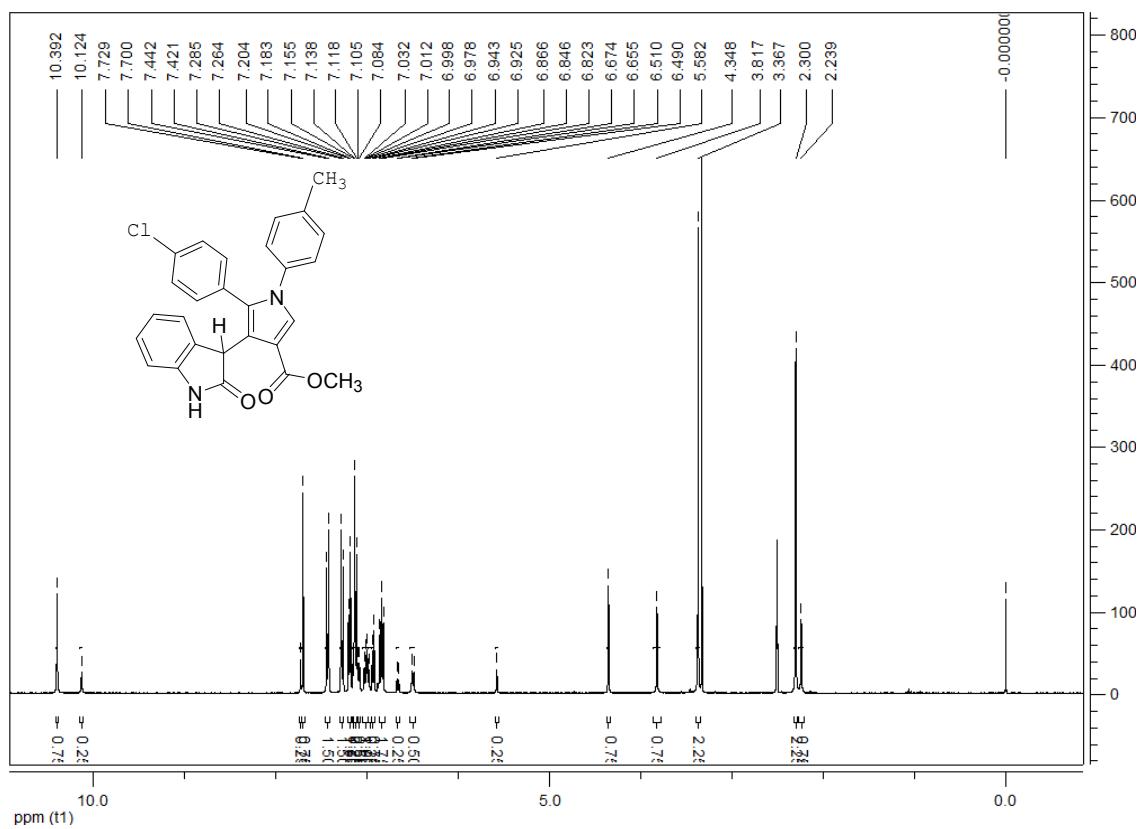
**4-Ethyl 1-methyl 2-((2-(1H-indol-3-yl)ethylamino)methylene)-3-(5-fluoro-2-oxoindolin-3-yl)succinate (3a):**



**4-Ethyl 1-methyl 2-((2-(1H-indol-3-yl)ethylamino)methylene)-3-(1-butyl-5-fluoro-2-oxoindolin-3-yl)succinate (3b):**

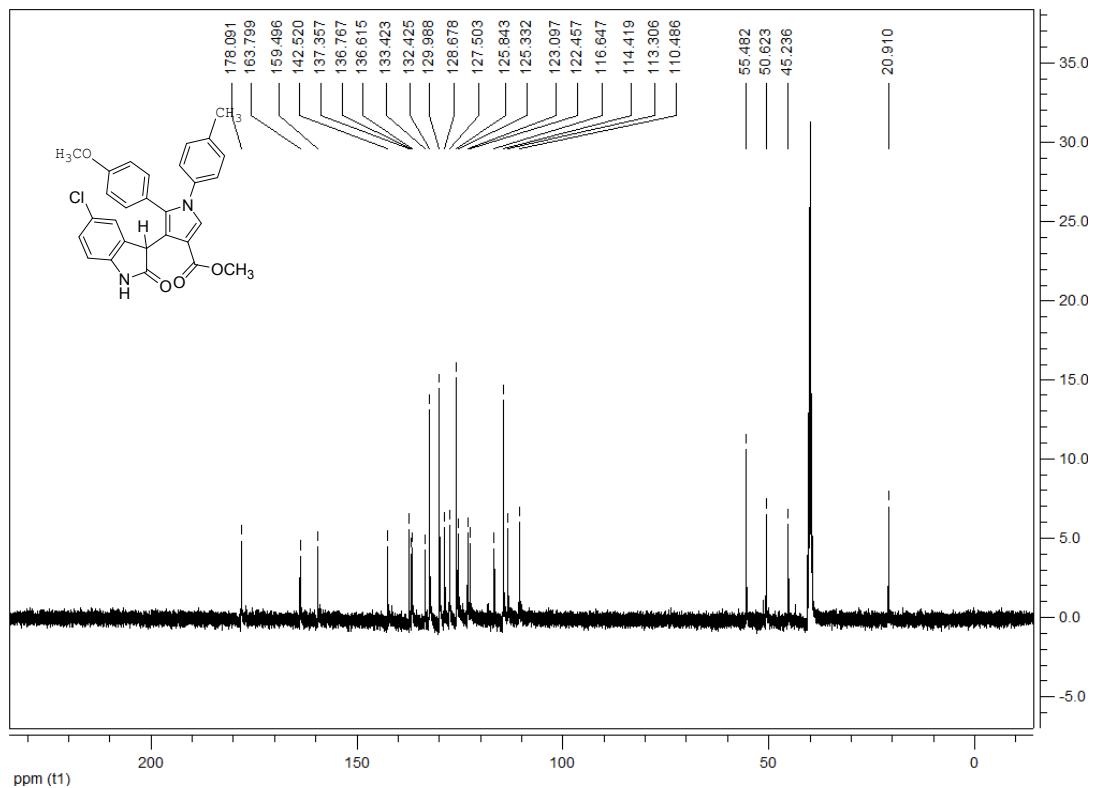
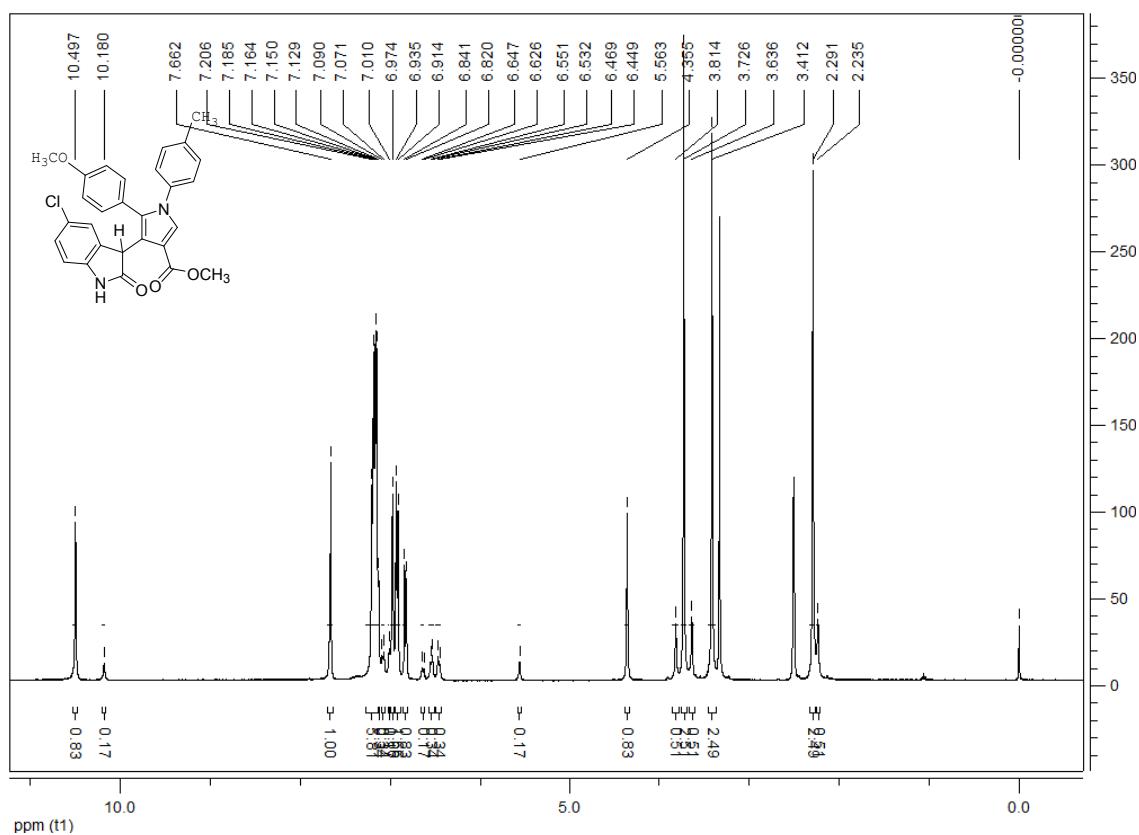


**Methyl 5-(4-chlorophenyl)-4-(2-oxoindolin-3-yl)-1-p-tolyl-1H-pyrrole-3-carboxylate (4a):**

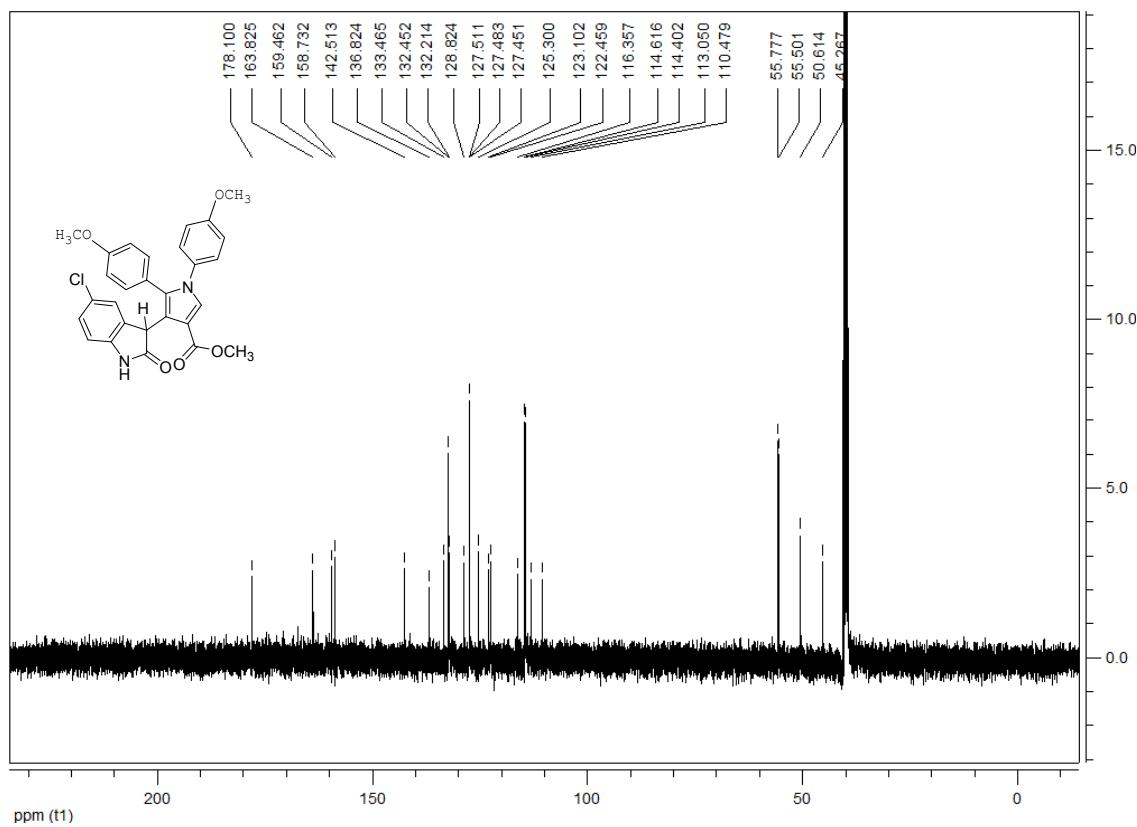
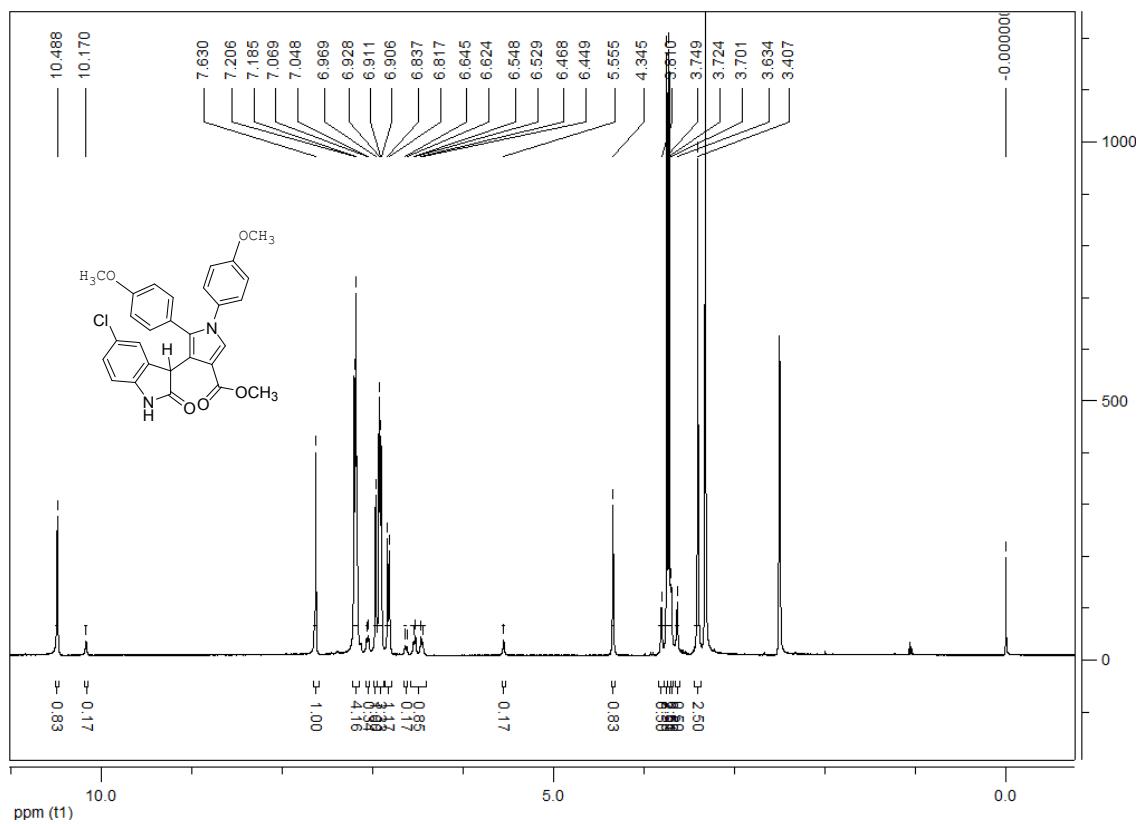


Methyl 4-(5-chloro-2-oxoindolin-3-yl)-5-(4-methoxyphenyl)-1-p-tolyl-1H-pyrrole-3-

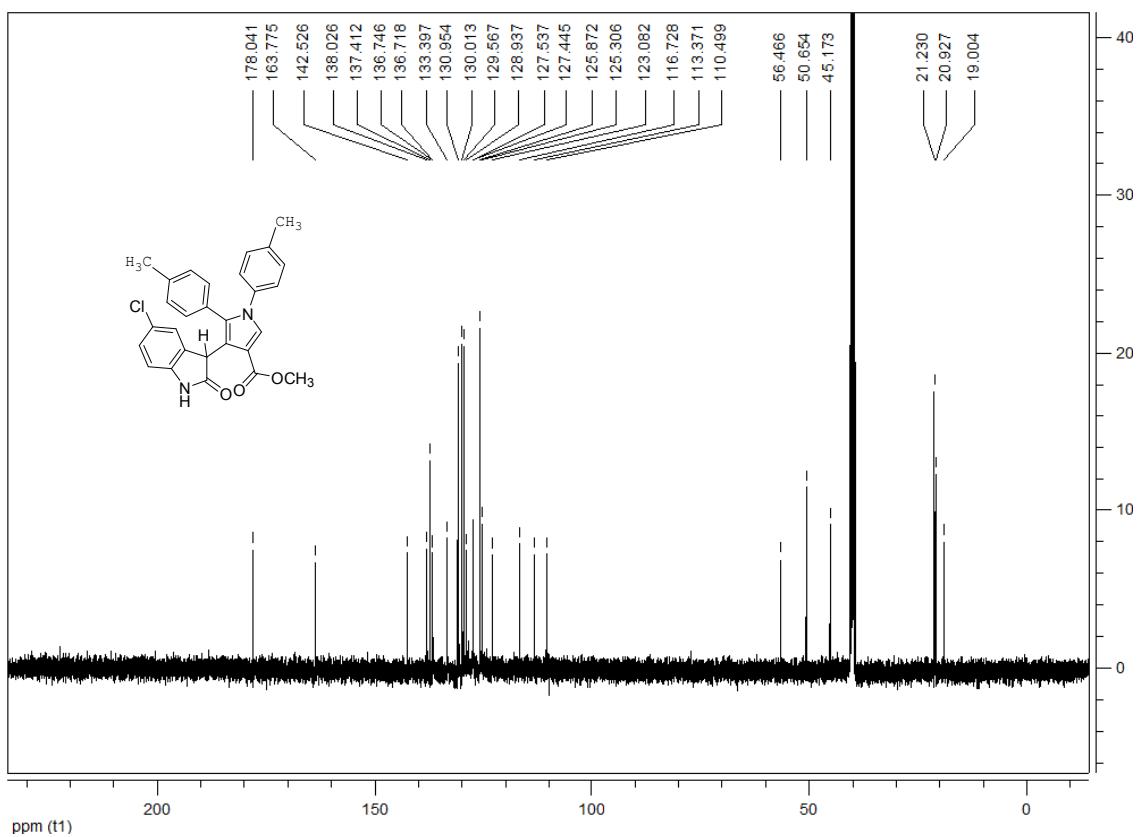
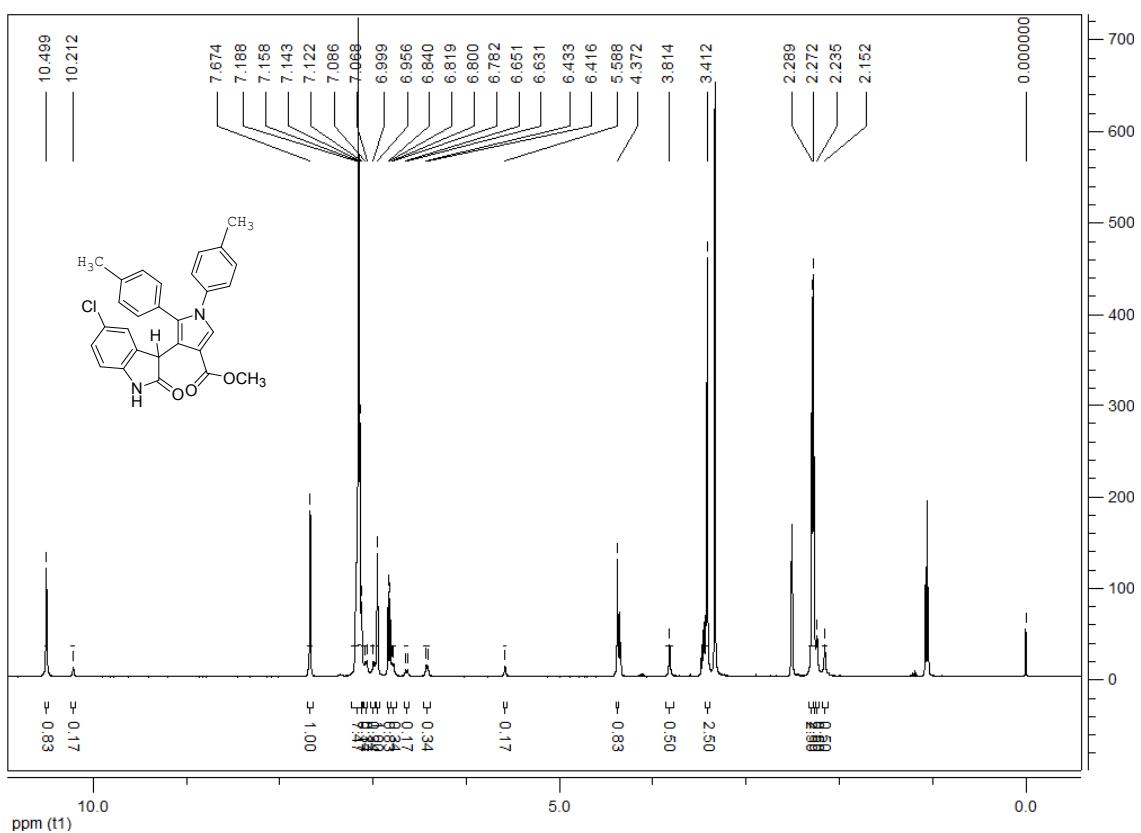
**carboxylate (4b):**



**Methyl 4-(5-chloro-2-oxoindolin-3-yl)-1,5-bis(4-methoxyphenyl)-1H-pyrrole-3-carboxylate (4c):**



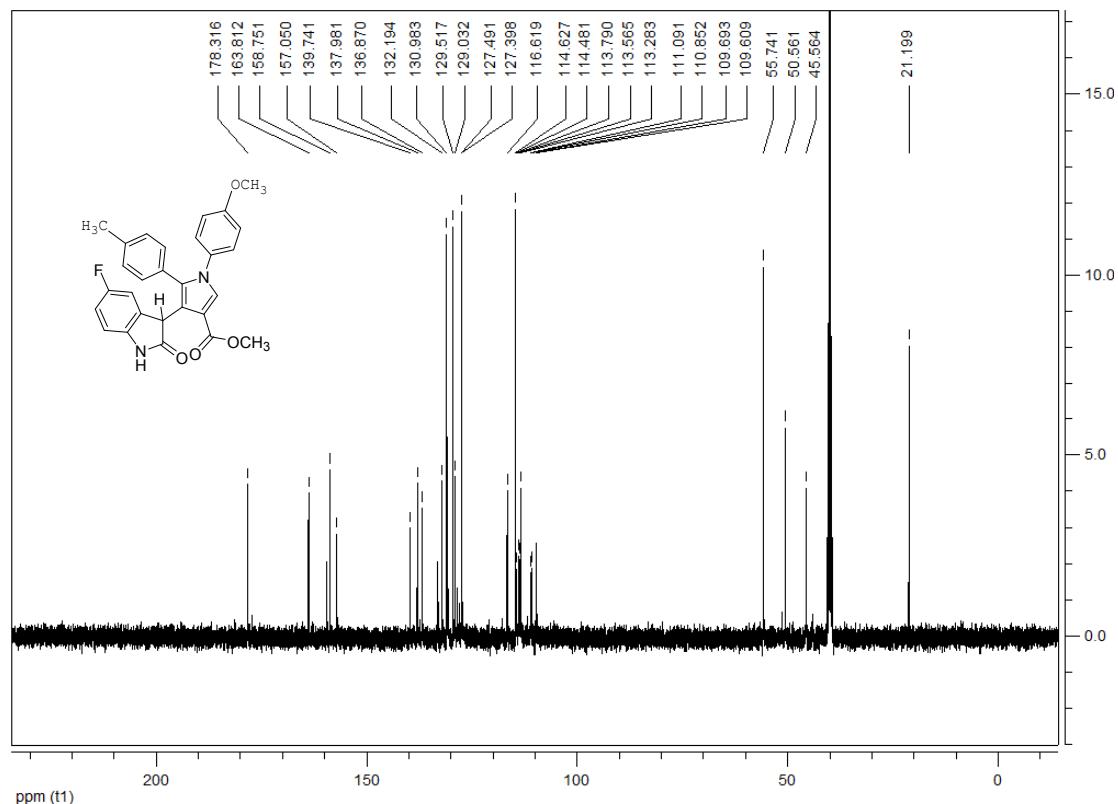
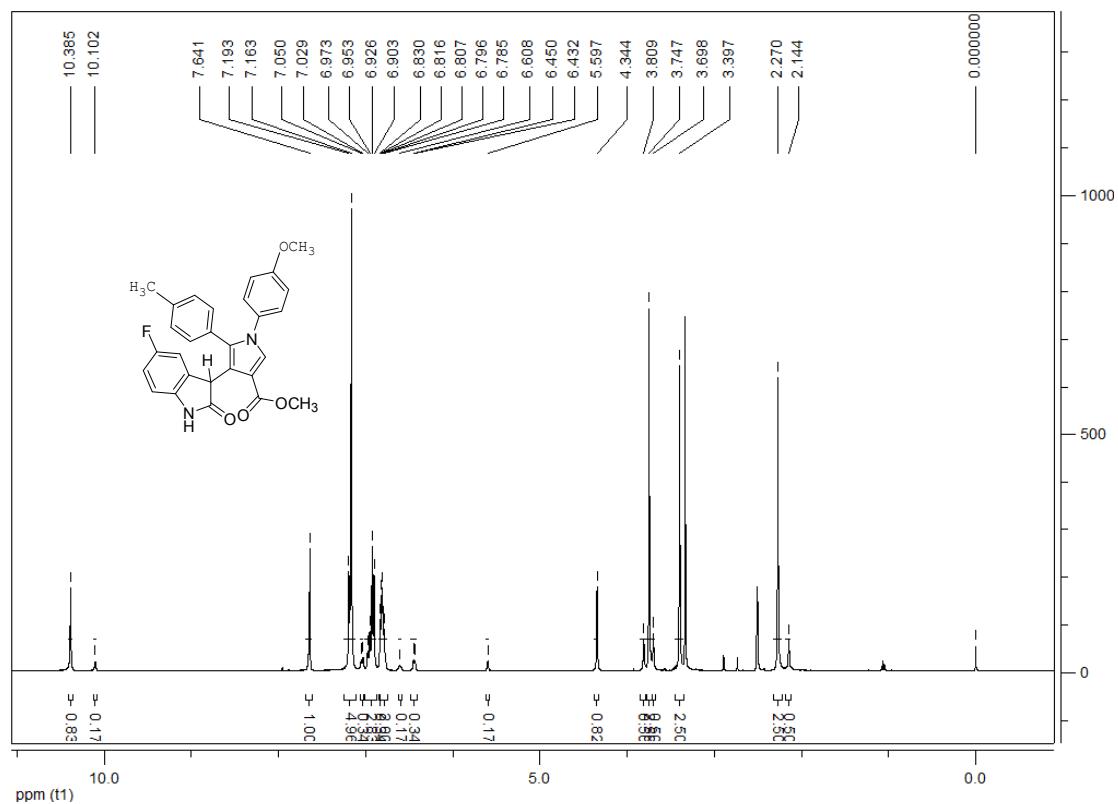
**Methyl 4-(5-chloro-2-oxoindolin-3-yl)-1,5-diphenyl-1H-pyrrole-3-carboxylate (4d):**



methyl

4-(5-fluoro-2-oxoindolin-3-yl)-1-(4-methoxyphenyl)-5-p-tolyl-1H-pyrrole-3-

**carboxylate (4e):**



Methyl 5-(4-chlorophenyl)-1-(4-methoxyphenyl)-4-(5-methyl-2-oxoindolin-3-yl)-1H-pyrrole-

**3-carboxylate (4f):**

