

**Diastereoselective synthesis of benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazoles via  
cycloaddition reaction of benzothiazolium salts with 3-nitrochromenes**

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**Supporting Information**

<b>Figures of the single crystal structures Fig. s1-Fig. s6</b>	<b>2-3</b>
<b><sup>1</sup>HNMR and <sup>13</sup>C NMR spectra of the compounds</b>	<b>4-36</b>

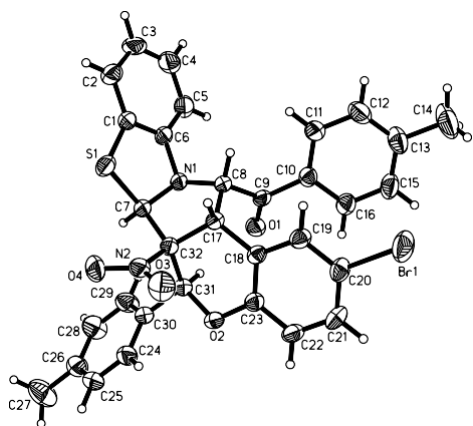


Fig. s1 ORTEP-drawing (50% ellipsoid probability) of the compound **3e**

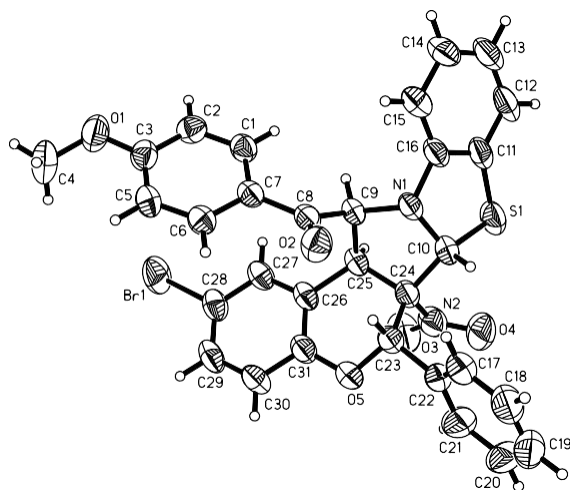


Fig. s2 ORTEP-drawing (50% ellipsoid probability) of the compound **3n**

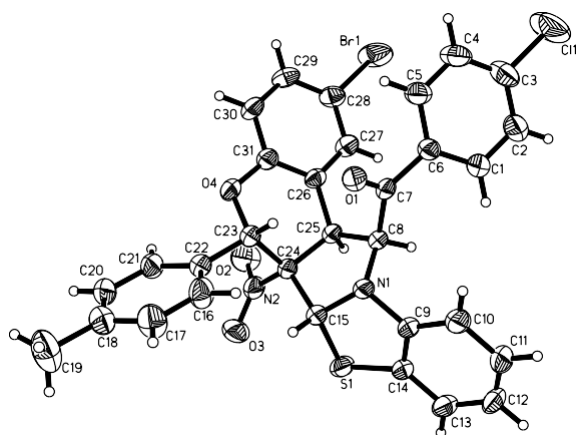


Fig. s3 ORTEP-drawing (50% ellipsoid probability) of the compound **3r**

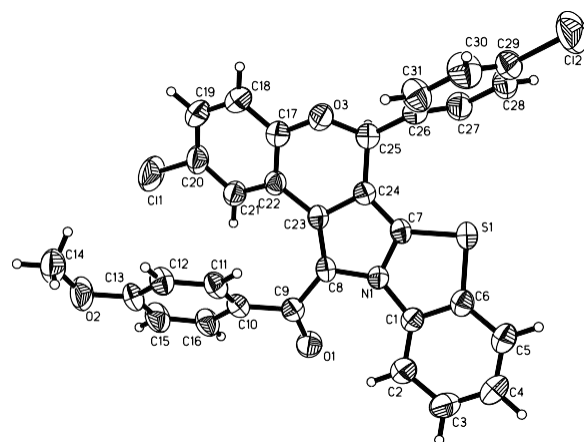


Fig. s4 ORTEP-drawing (50% ellipsoid probability) of the compound **5e**

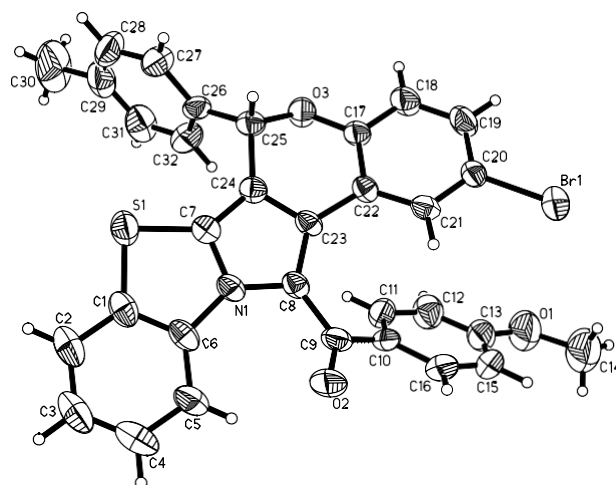


Fig. s5 ORTEP-drawing (50% ellipsoid probability) of the compound **5g**

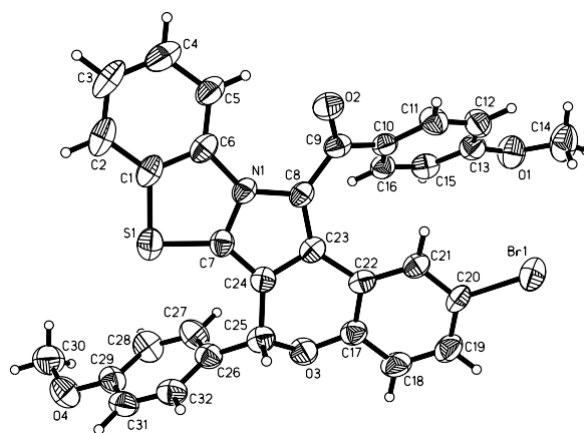
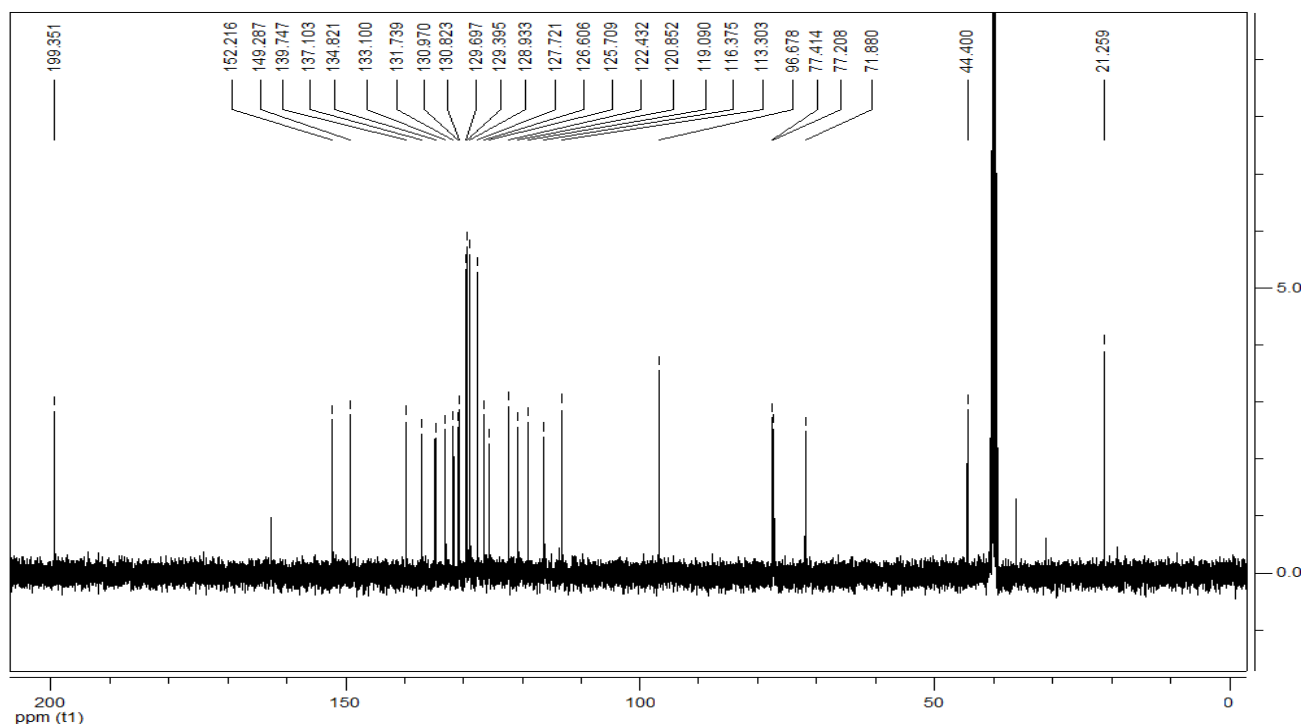
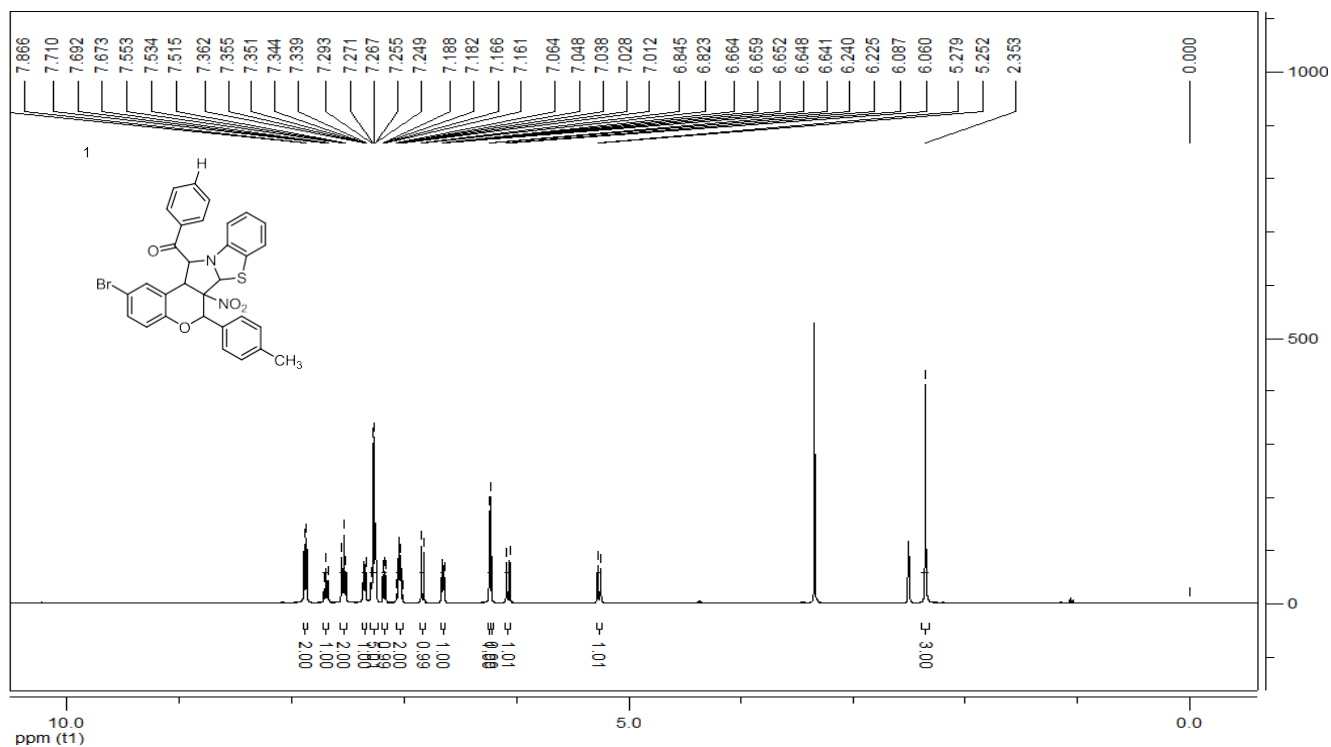
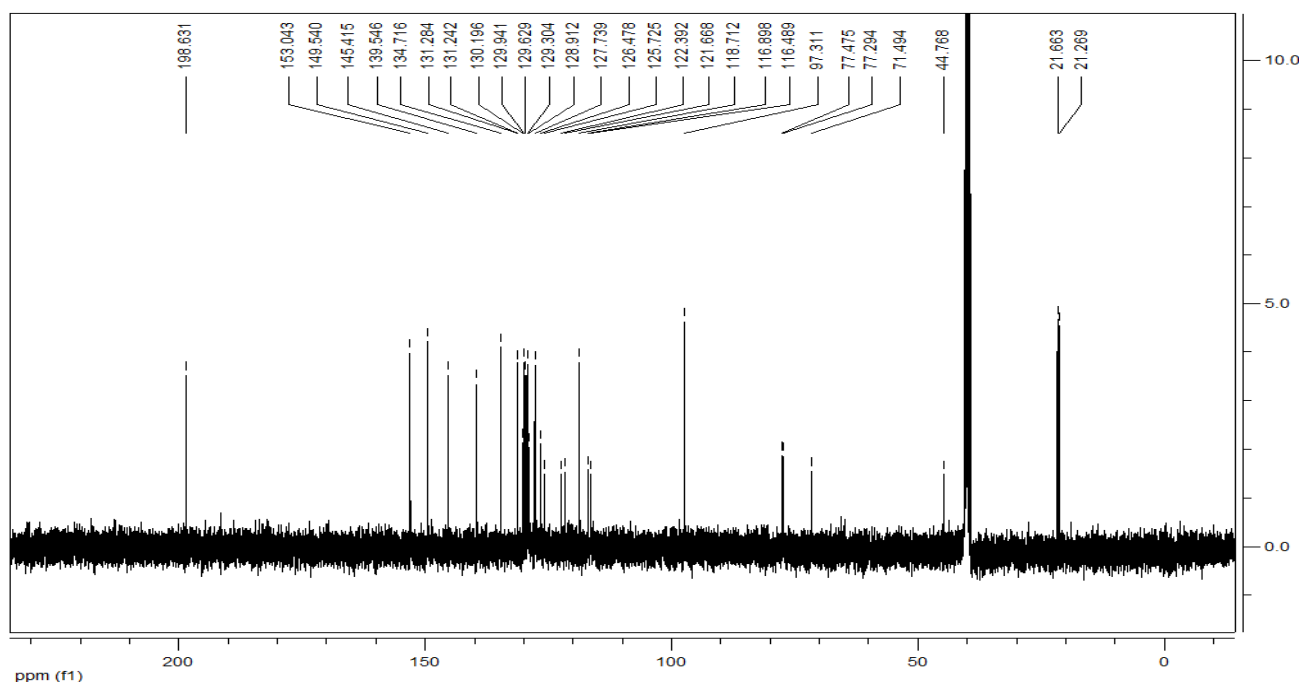
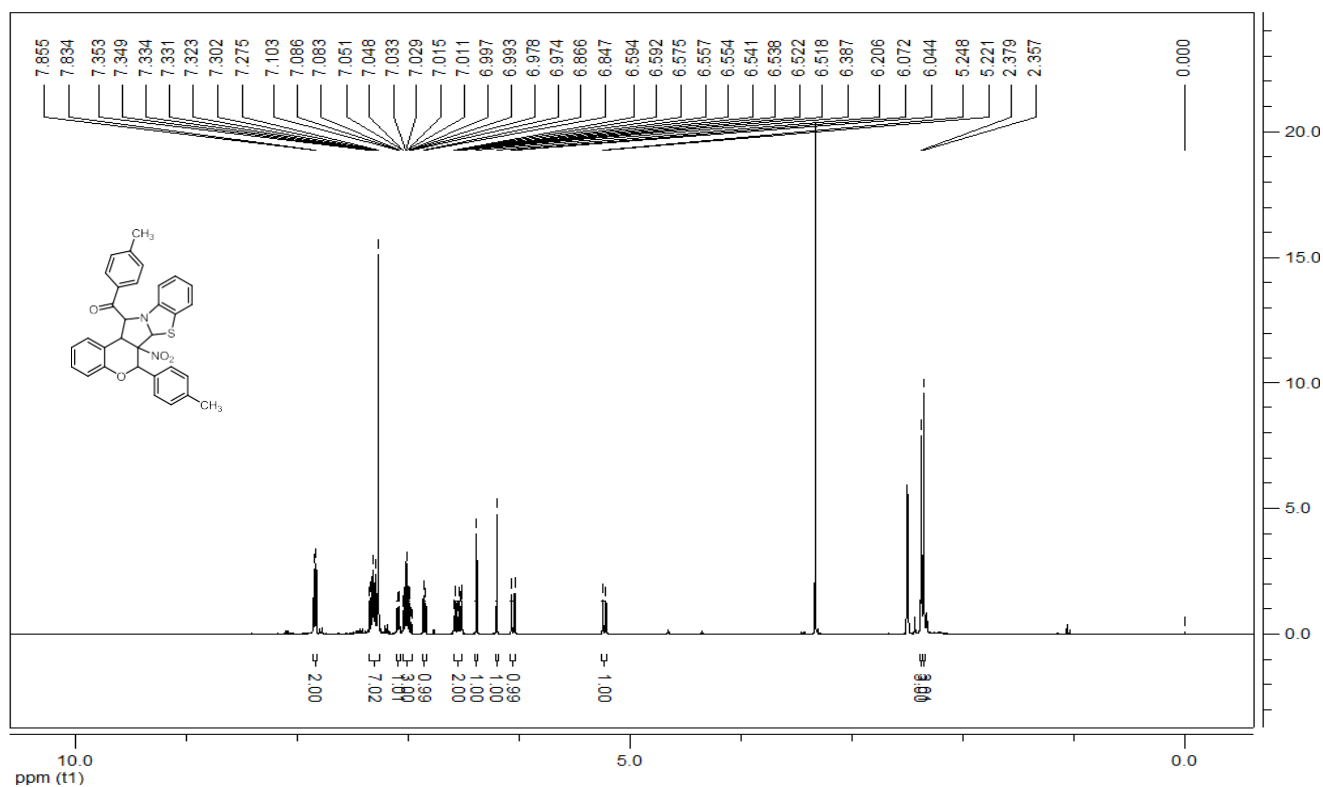


Fig. s6 ORTEP-drawing (50% ellipsoid probability) of the compound **5h**

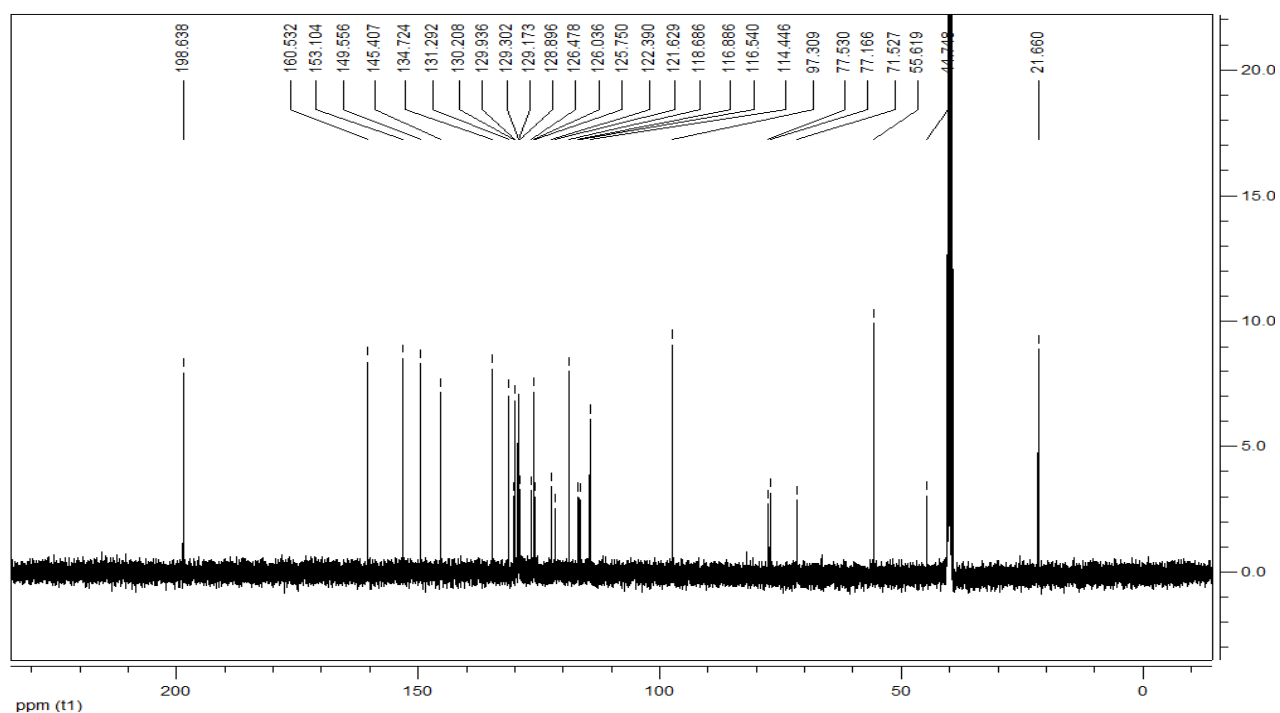
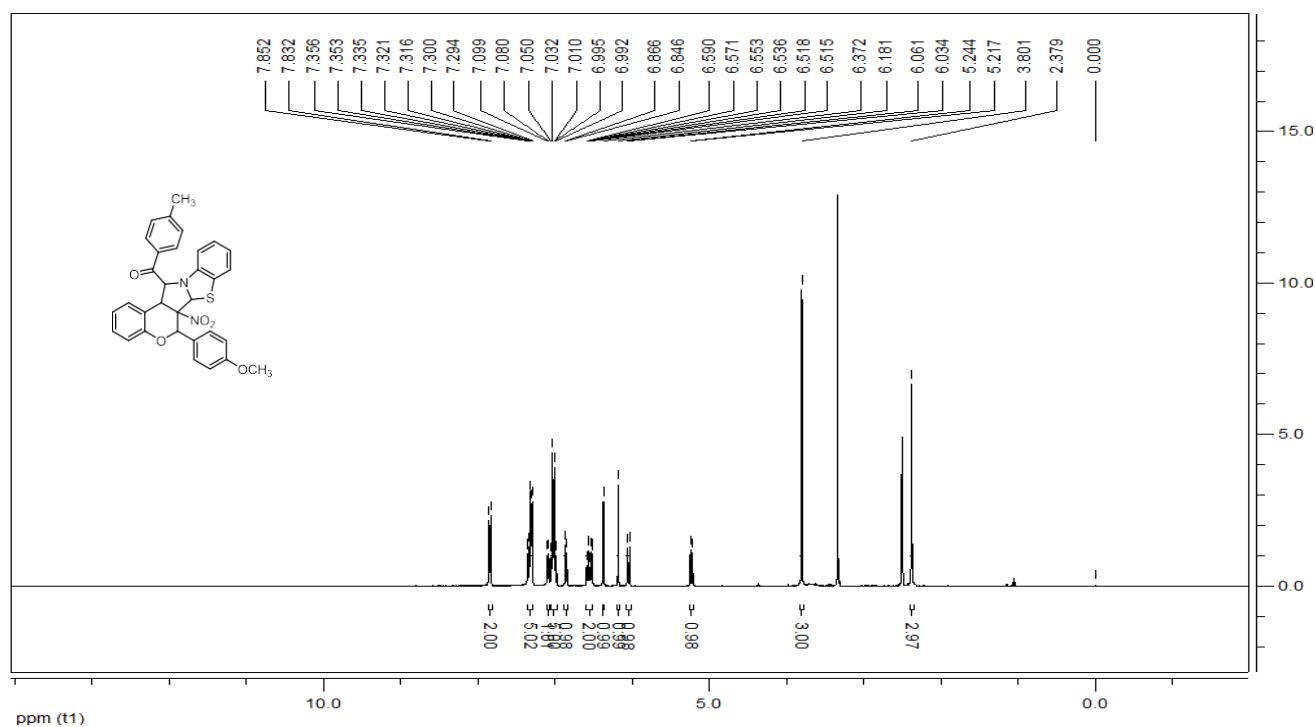
**(2-bromo-6a-nitro-6-(p-tolyl)-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(phenyl)methanone (3a):** yellow solid, 87%, m.p. 197~199°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.88 (d, *J* = 7.6 Hz, 2H, ArH), 7.71~7.67 (m, 1H, ArH), 7.55~7.52 (m, 2H, ArH), 7.36~7.34 (m, 1H, ArH), 7.29~7.25 (m, 5H, ArH), 7.17 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H, ArH), 7.06~7.01 (m, 2H, ArH), 6.83 (d, *J* = 8.8 Hz, 1H, ArH), 6.66~6.64 (m, 1H, ArH), 6.24 (s, 1H, CH), 6.22 (s, 1H, CH), 6.07 (d, *J* = 10.8 Hz, 1H, CH), 5.26 (d, *J* = 10.8 Hz, 1H, CH), 2.35 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 199.3, 152.2, 149.2, 139.7, 137.1, 134.8, 133.1, 131.7, 130.9, 130.8, 129.6, 129.3, 128.9, 127.7, 126.6, 125.7, 122.4, 120.8, 119.0, 116.3, 113.3, 96.6, 77.4, 77.2, 71.8, 44.3, 21.2; MS (*m/z*): HRMS (ESI) Calc. for C<sub>31</sub>H<sub>24</sub>BrN<sub>2</sub>O<sub>4</sub>S ([M+H]<sup>+</sup>): 599.0635. Found: 599.0620; IR (KBr) ν: 3057, 3016, 2914, 1692, 1540, 1472, 1452, 1316, 1227, 1175, 1127, 920, 858, 839, 753, 700 cm<sup>-1</sup>.



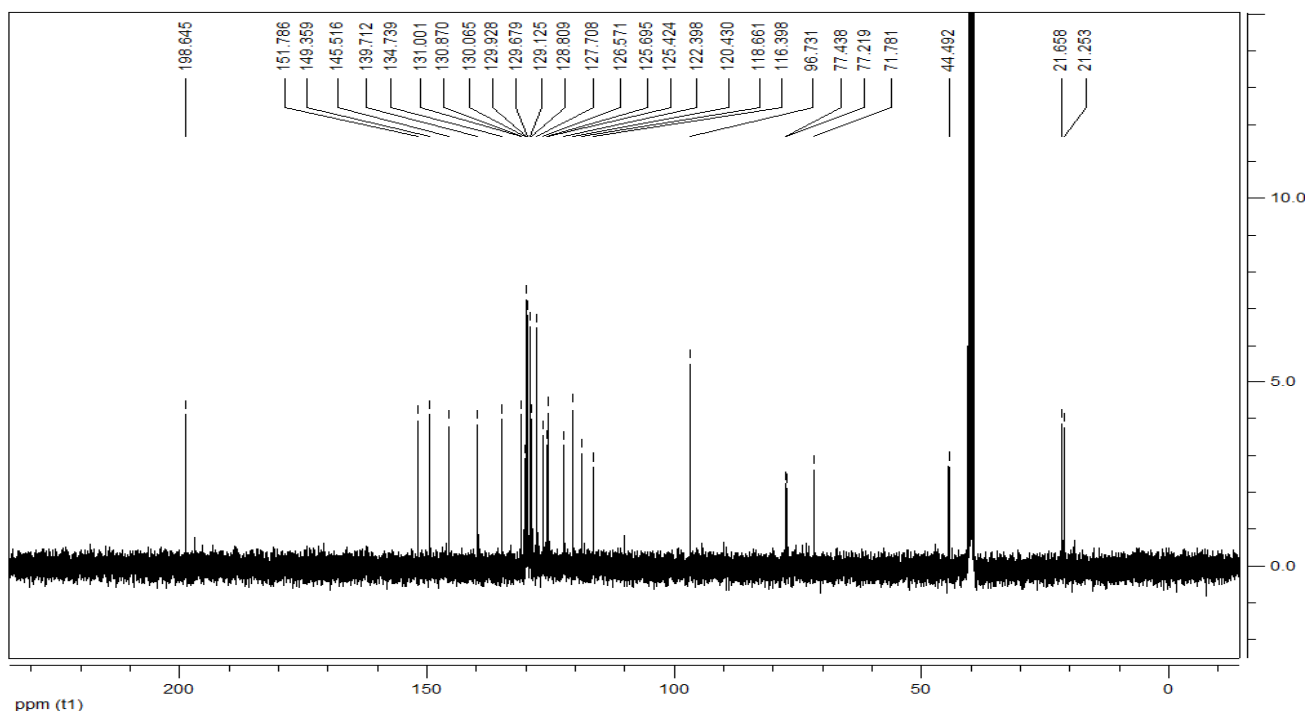
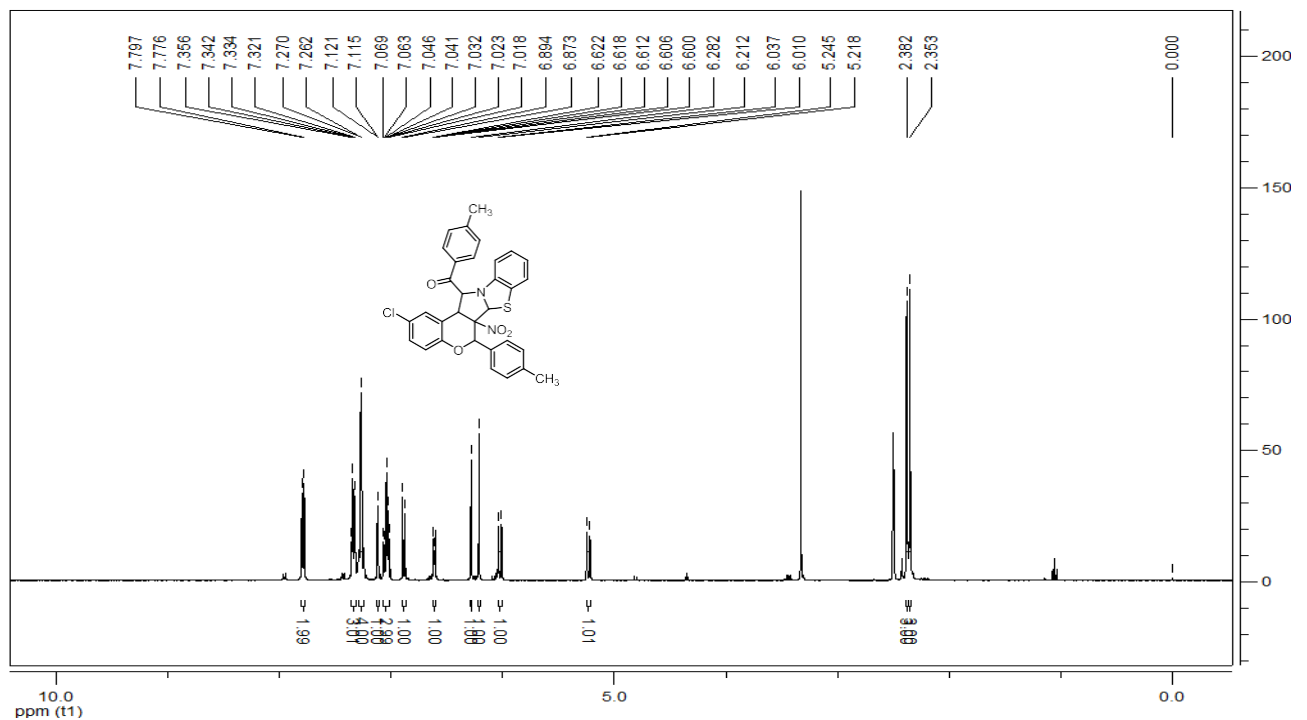
**6a-nitro-6-(p-tolyl)-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(p-tolyl)methanone (3b):** yellow solid, 89%, m.p. 184~185 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.86 (d, *J* = 8.4 Hz, 2H, ArH), 7.35~7.28 (m, 7H, ArH), 7.10~7.08 (m, 1H, ArH), 7.05~6.97 (m, 3H, ArH), 6.85 (d, *J* = 7.6 Hz, 1H, ArH), 6.59~6.52 (m, 2H, ArH), 6.39 (s, 1H, CH), 6.21 (s, 1H, CH), 6.06 (d, *J* = 11.2 Hz, 1H, CH), 5.23 (d, *J* = 10.8 Hz, 1H, CH), 2.38 (s, 3H, CH<sub>3</sub>), 2.36 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 198.6, 153.0, 149.5, 145.4, 139.5, 134.7, 131.2, 131.2, 130.1, 129.9, 129.6, 129.3, 128.9, 127.7, 126.4, 125.7, 122.3, 121.6, 118.7, 116.8, 116.4, 97.3, 77.4, 77.2, 71.4, 44.7, 21.6, 21.2; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub>S ([M+H]<sup>+</sup>): 535.1686. Found: 535.1690; IR (KBr) ν: 3031, 2925, 1688, 1610, 1544, 1457, 1370, 1312, 1177, 1127, 1033, 927, 852, 805, 749 cm<sup>-1</sup>.



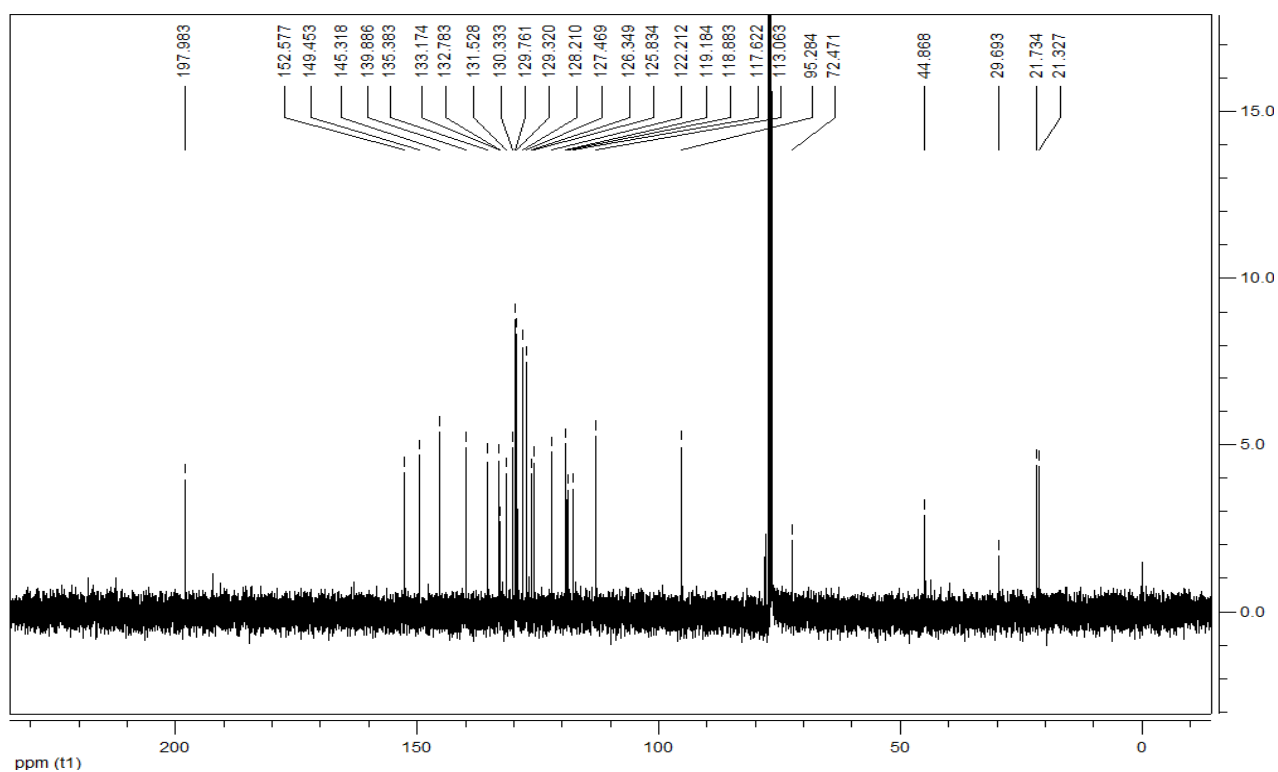
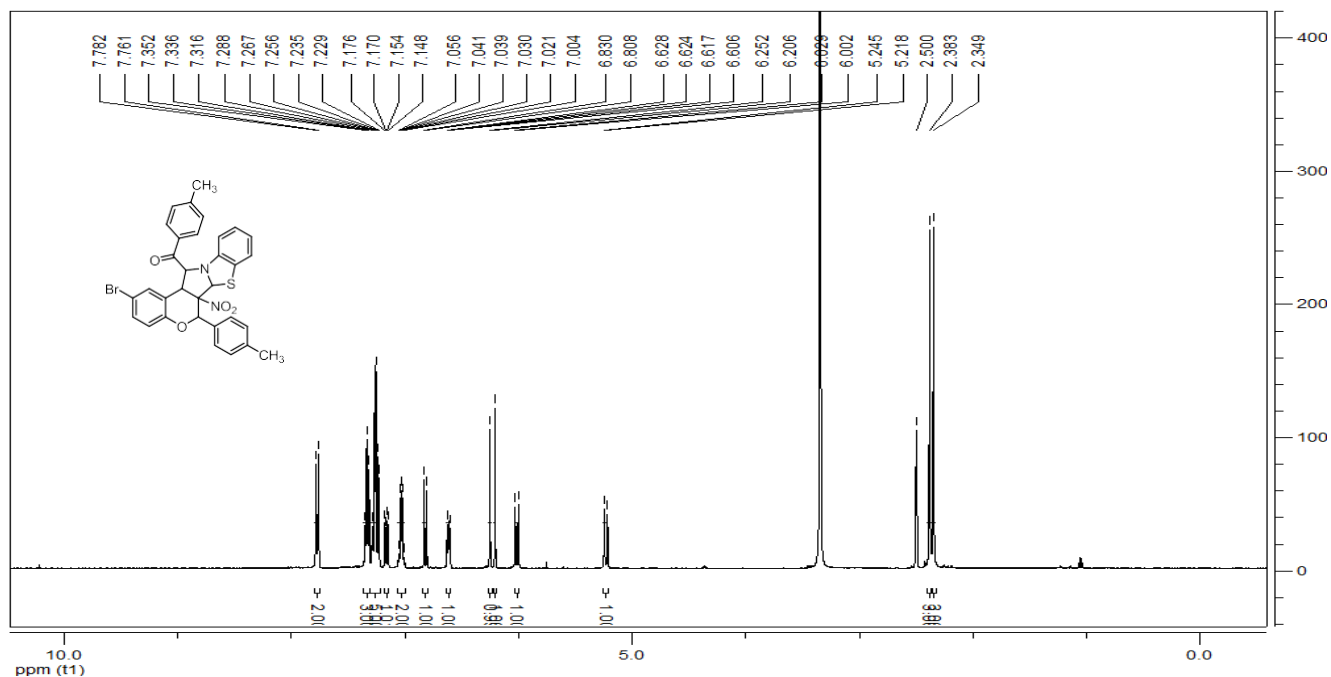
**(6-(4-methoxyphenyl)-6a-nitro-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(p-tolyl)methanone (3c):** yellow solid, 91%, m.p. 179~180°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.84 (d, *J* = 8.8 Hz, 2H, ArH), 7.35~7.29 (m, 5H, ArH), 7.08 (d, *J* = 7.6 Hz, 1H, ArH), 7.04~6.99 (m, 5H, ArH), 6.85 (d, *J* = 7.6 Hz, 1H, ArH), 6.58~6.51 (m, 2H, ArH), 6.37 (s, 1H, CH), 6.18 (s, 1H, CH), 6.04 (d, *J* = 10.8 Hz, 1H, CH), 5.22 (d, *J* = 10.8 Hz, 1H, CH), 3.80 (s, 3H, OCH<sub>3</sub>), 2.35 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 198.6, 160.5, 153.1, 149.5, 145.4, 134.7, 131.2, 130.2, 129.9, 129.3, 129.1, 128.8, 126.4, 126.0, 125.7, 122.3, 121.6, 118.6, 116.8, 116.5, 114.4, 97.3, 77.5, 77.1, 71.5, 55.6, 44.7, 21.6; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>27</sub>N<sub>2</sub>O<sub>5</sub>S ([M+H]<sup>+</sup>): 551.1635. Found: 551.1632; IR (KBr) ν: 2932, 2839, 1688, 1611, 1529, 1456, 1364, 1306, 1250, 1176, 1127, 1033, 927, 822, 747 cm<sup>-1</sup>.



**(2-chloro-6a-nitro-6-(p-tolyl)-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(p-tolyl)methanone (3d)**: yellow solid, 91%, m.p. 210~211 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 7.79 (d,  $J = 8.4$  Hz, 2H, ArH), 7.36~7.33 (m, 3H, ArH), 7.27 (d,  $J = 3.2$  Hz, 4H, ArH), 7.12 (d,  $J = 2.4$  Hz, 1H, ArH), 7.08~7.02 (m, 3H, ArH), 6.89 (d,  $J = 8.4$  Hz, 1H, ArH), 6.63~6.61 (m, 1H, ArH), 6.29 (s, 1H, CH), 6.22 (s, 1H, CH), 6.03 (d,  $J = 10.8$  Hz, 1H, CH), 5.24 (d,  $J = 10.8$  Hz, 1H, CH), 2.39 (s, 3H,  $\text{CH}_3$ ), 2.36 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 198.6, 151.7, 149.3, 145.5, 139.7, 134.7, 131.0, 130.8, 130.0, 129.9, 129.6, 129.1, 128.8, 127.7, 126.5, 125.6, 125.4, 122.3, 120.4, 118.6, 116.3, 96.7, 77.4, 77.2, 71.7, 44.4, 21.6, 21.2; MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{32}\text{H}_{26}\text{ClN}_2\text{O}_4\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 569.1296. Found: 569.1285; IR (KBr)  $\nu$ : 3019, 2922, 1688, 1608, 1540, 1484, 1416, 1359, 1328, 1233, 1034, 929, 853, 816, 754  $\text{cm}^{-1}$ .

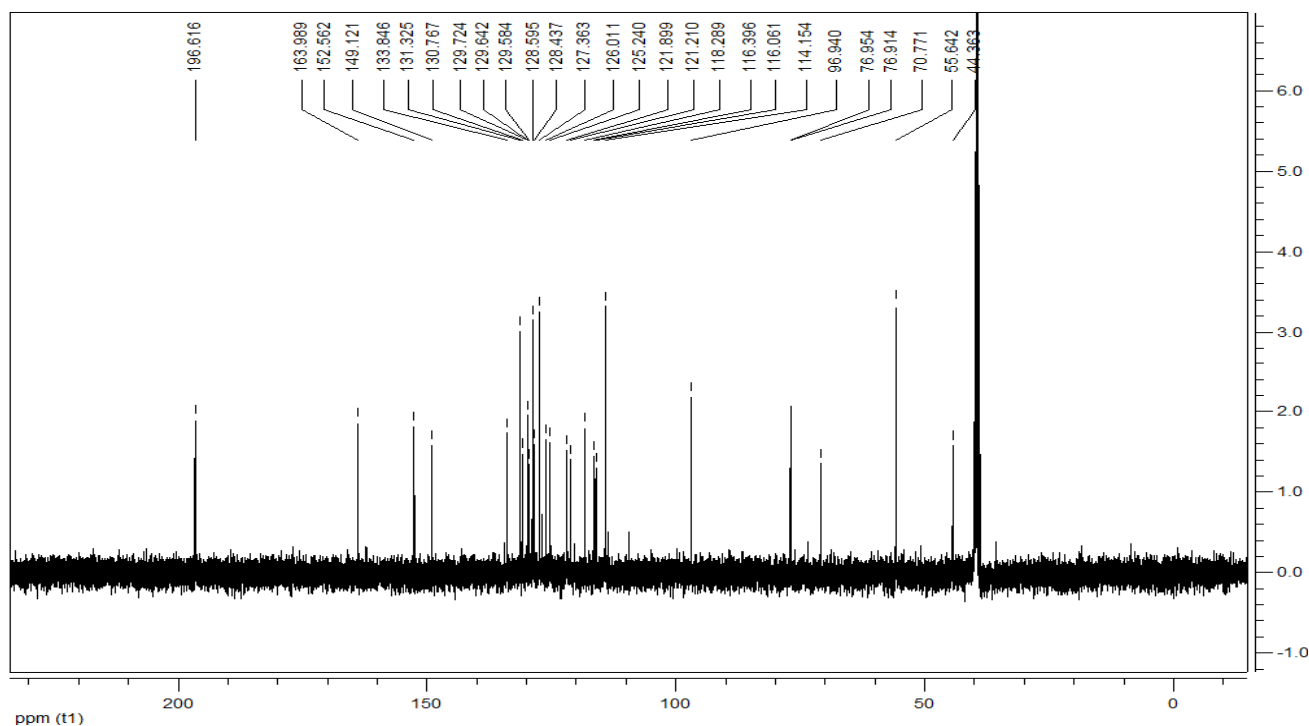
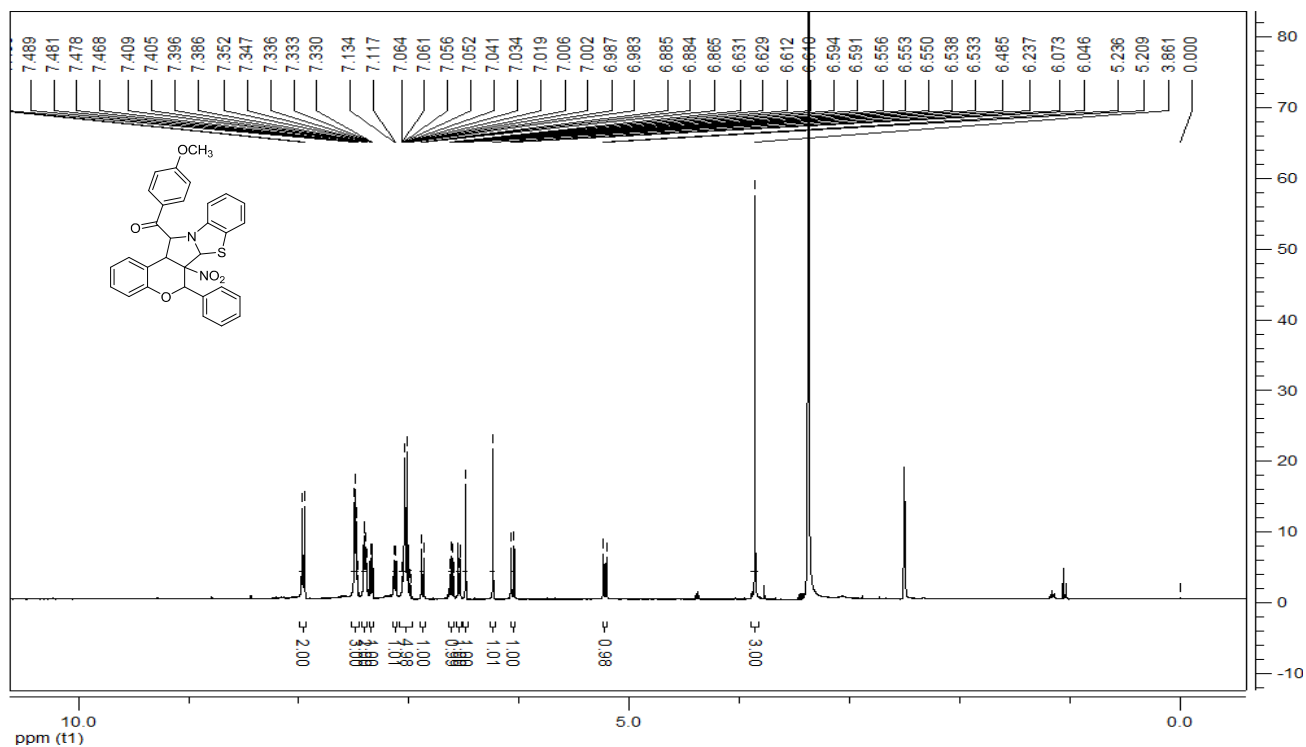


**(2-bromo-6a-nitro-6-(p-tolyl)-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(p-tolyl)methanone (3e):** yellow solid, 89%, m.p. 220~221 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.77 (d, *J* = 8.4 Hz, 2H, ArH), 7.35~7.32 (m, 3H, ArH), 7.29~7.23 (m, 5H, ArH), 7.16 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H, ArH), 7.06~7.00 (m, 2H, ArH), 6.82 (d, *J* = 8.8 Hz, 1H, ArH), 6.63~6.61 (m, 1H, ArH), 6.25 (s, 1H, CH), 6.21 (s, 1H, CH), 6.02 (d, *J* = 10.8 Hz, 1H, CH), 5.23 (d, *J* = 10.8 Hz, 1H, CH), 2.38 (s, 3H, CH<sub>3</sub>), 2.35 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 198.0, 152.6, 149.4, 145.3, 139.9, 135.4, 133.2, 132.8, 131.5, 130.3, 129.8, 129.3, 128.2, 127.5, 126.3, 125.8, 122.2, 119.2, 118.9, 117.6, 113.1, 95.3, 72.5, 44.9, 29.7, 21.7, 21.3; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>26</sub>BrN<sub>2</sub>O<sub>4</sub>S ([M+H]<sup>+</sup>): 613.0791. Found: 613.0783; IR (KBr) ν: 3018, 2919, 1686, 1600, 1538, 1470, 1415, 1368, 1326, 1299, 1240, 1170, 1128, 920, 858, 817, 750 cm<sup>-1</sup>.

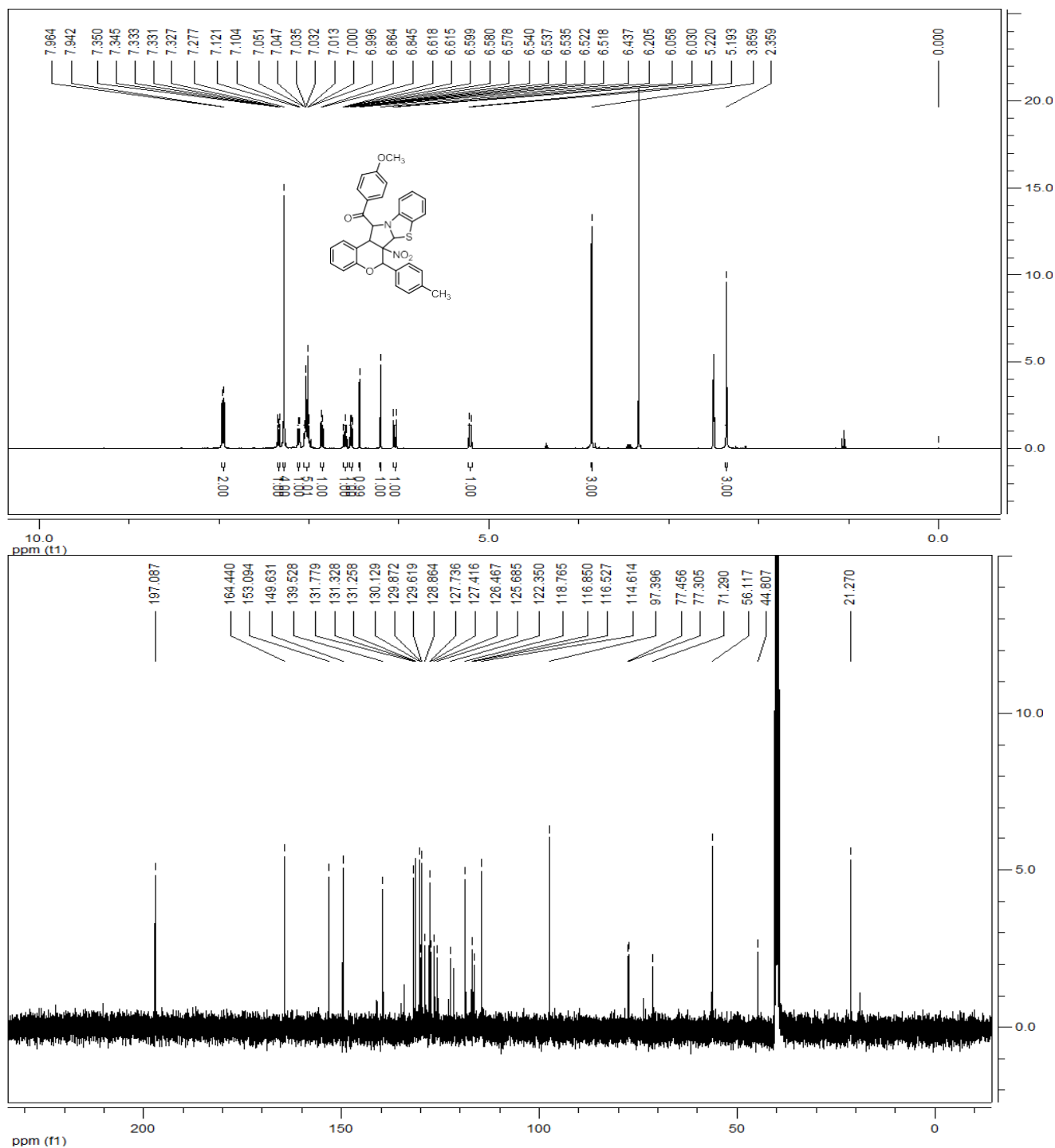




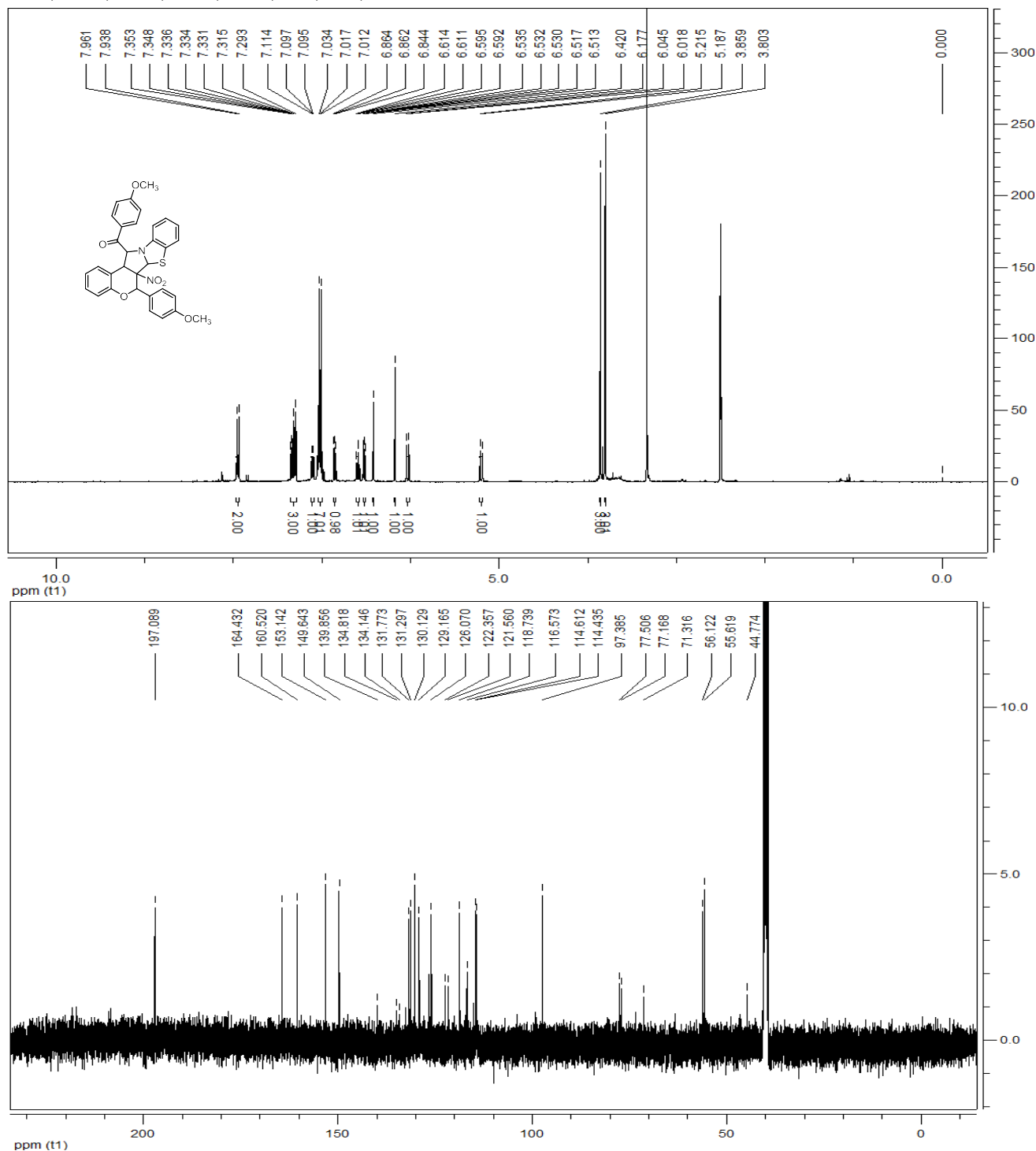
**(4-methoxyphenyl)(6a-nitro-6-phenyl-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)methanone (3f):** yellow solid, 91%, m.p. 189~190°C;  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 7.96 (d,  $J = 8.8$  Hz, 2H, ArH), 7.50~7.47 (m, 3H, ArH), 7.41~7.39 (m, 2H, ArH), 7.35~7.33 (m, 1H, ArH), 7.12 (d,  $J = 6.8$  Hz, 1H, ArH), 7.06~6.98 (m, 5H, ArH), 6.88~6.86 (m, 1H, ArH), 6.63~6.59 (m, 1H, ArH), 6.56~6.53 (m, 1H, ArH), 6.48 (s, 1H, CH), 6.24 (s, 1H, CH), 6.06 (d,  $J = 10.8$  Hz, 1H, CH), 5.22 (d,  $J = 10.8$  Hz, 1H, CH), 3.86 (s, 3H,  $\text{OCH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 196.6, 164.0, 152.6, 149.1, 133.8, 131.3, 130.8, 129.7, 129.6, 129.6, 128.6, 128.4, 127.4, 126.0, 125.2, 121.9, 121.2, 118.3, 116.4, 116.1, 114.2, 96.9, 77.0, 76.9, 70.8, 55.6, 44.4; MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{31}\text{H}_{25}\text{N}_2\text{O}_5\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 537.1479. Found: 537.1475; IR (KBr)  $\nu$ : 3056, 2939, 2840, 1792, 1674, 1596, 1493, 1455, 1370, 1322, 1172, 1121, 925, 839, 746, 702  $\text{cm}^{-1}$ .



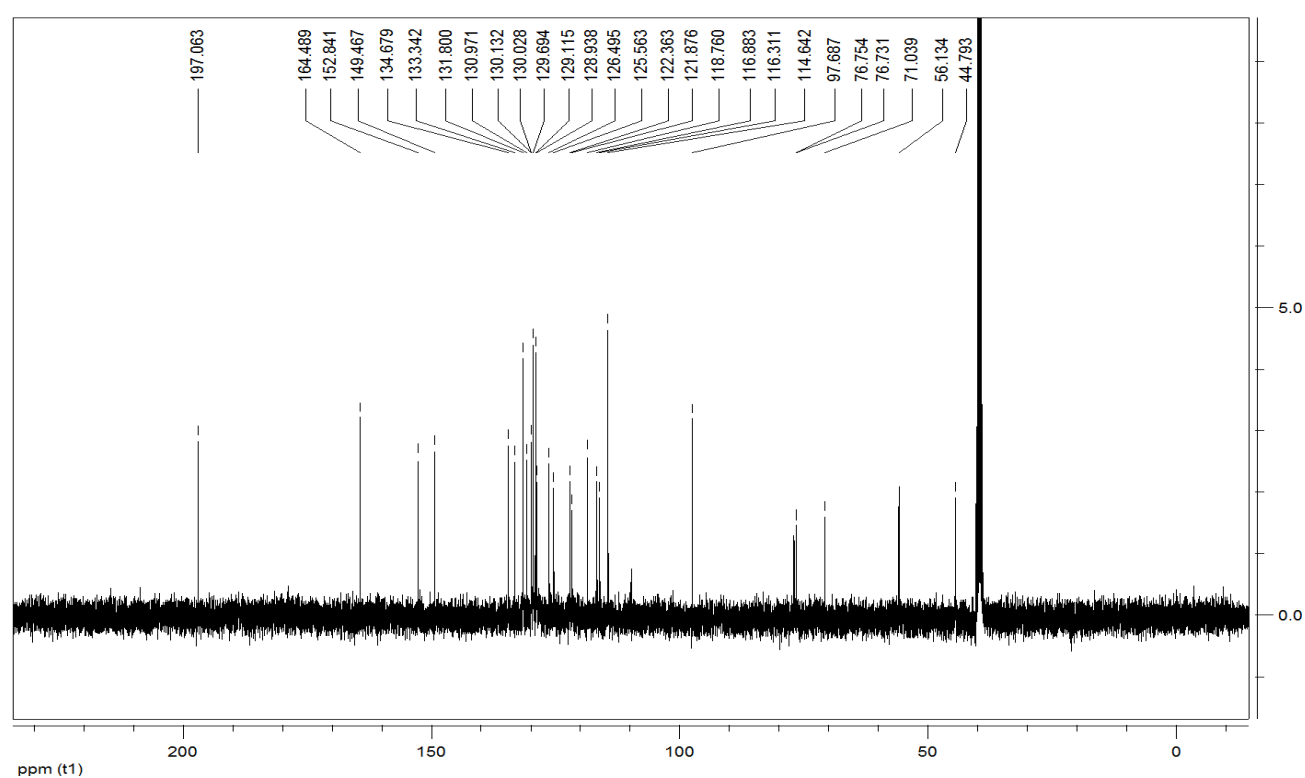
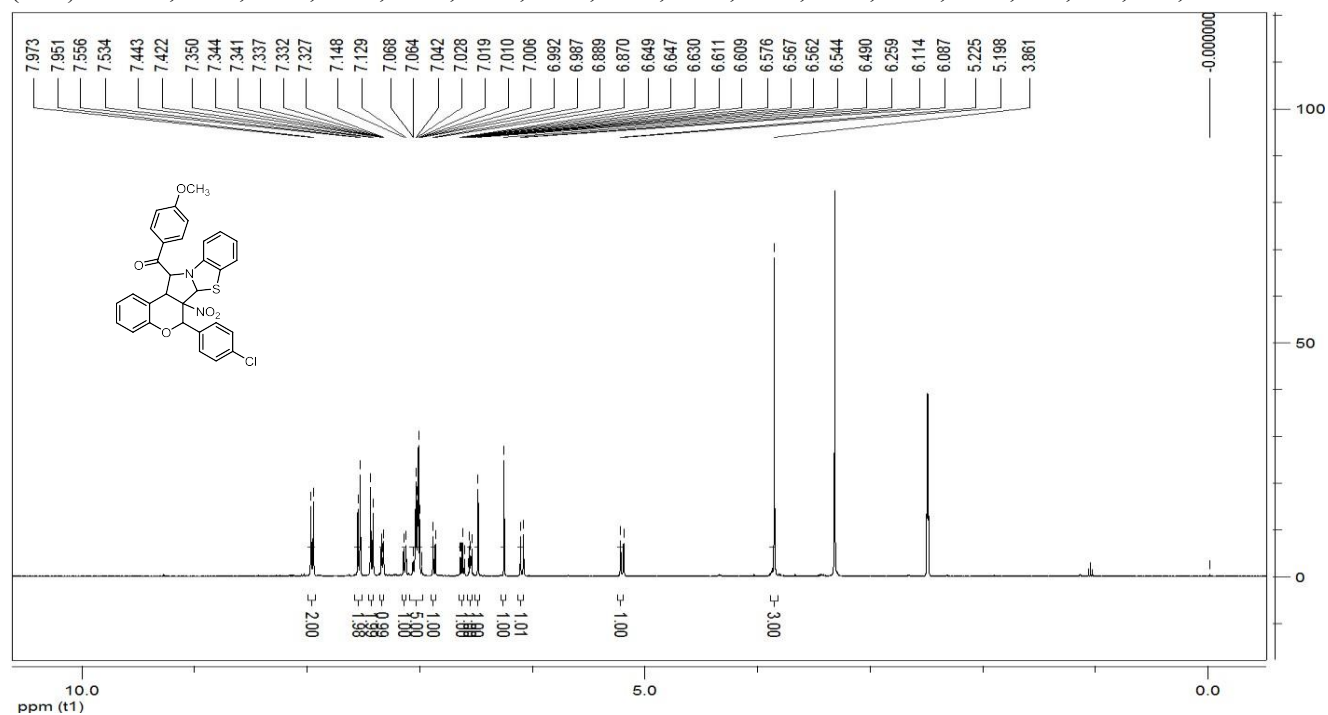
**4-methoxyphenyl)(6a-nitro-6-(p-tolyl)-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)methanone (3g):** yellow solid, 87%, m.p. 192~193°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.95 (d, *J* = 8.8 Hz, 2H, ArH), 7.35~7.33 (m, 1H, ArH), 7.28 (s, 4H, ArH), 7.11 (d, *J* = 6.8 Hz, 1H, ArH), 7.05~7.00 (m, 5H, ArH), 6.85 (d, *J* = 7.6 Hz, 1H, ArH), 6.62~6.58 (m, 1H, ArH), 6.54~6.52 (m, 1H, ArH), 6.44 (s, 1H, CH), 6.20 (s, 1H, CH), 6.04 (d, *J* = 11.2 Hz, 1H, CH), 5.21 (d, *J* = 10.8 Hz, 1H, CH), 3.86 (s, 3H, OCH<sub>3</sub>), 2.36 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 197.0, 164.4, 153.0, 149.6, 139.5, 134.1, 131.7, 131.3, 131.2, 130.1, 129.6, 127.7, 126.4, 125.6, 122.3, 121.5, 118.7, 116.8, 116.5, 114.6, 97.3, 77.4, 77.3, 71.2, 56.1, 44.8, 21.2; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>27</sub>N<sub>2</sub>O<sub>5</sub>S ([M+H]<sup>+</sup>): 551.1635. Found: 551.1627; IR (KBr) ν: 3021, 2934, 1674, 1599, 1541, 1498, 1454, 1322, 1228, 1173, 1119, 1019, 922, 817, 752 cm<sup>-1</sup>.



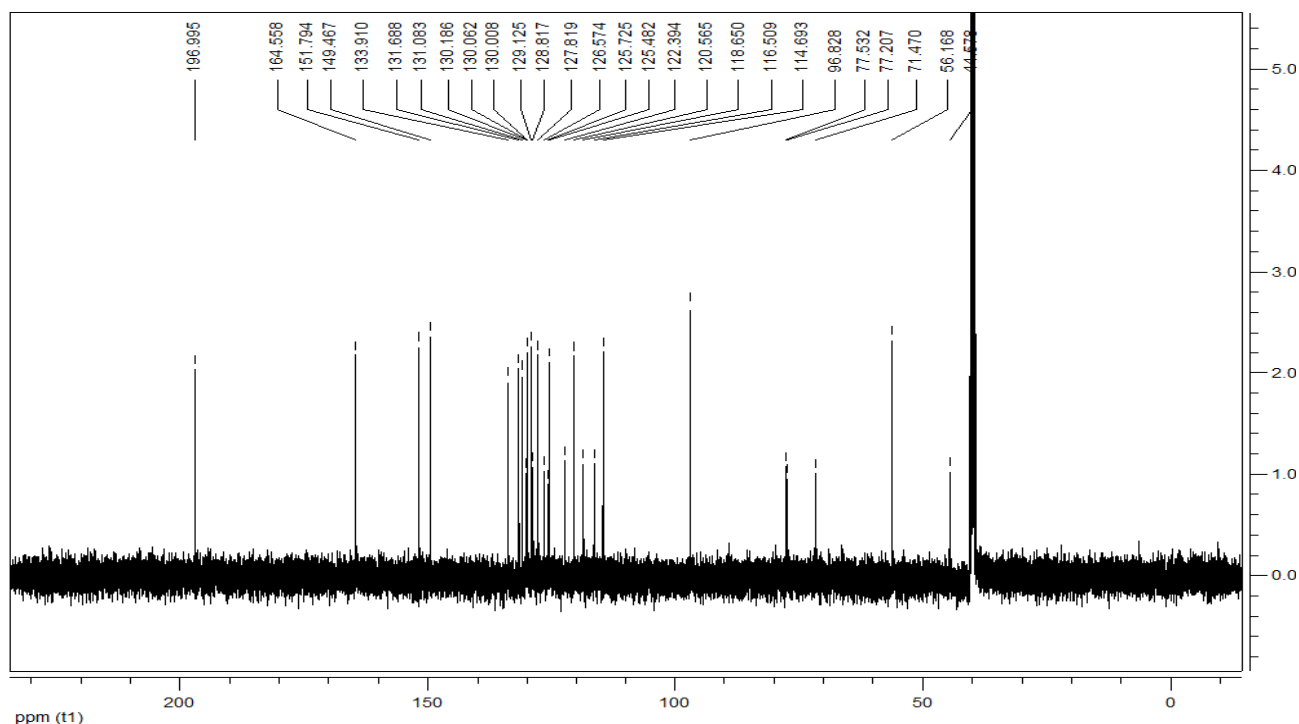
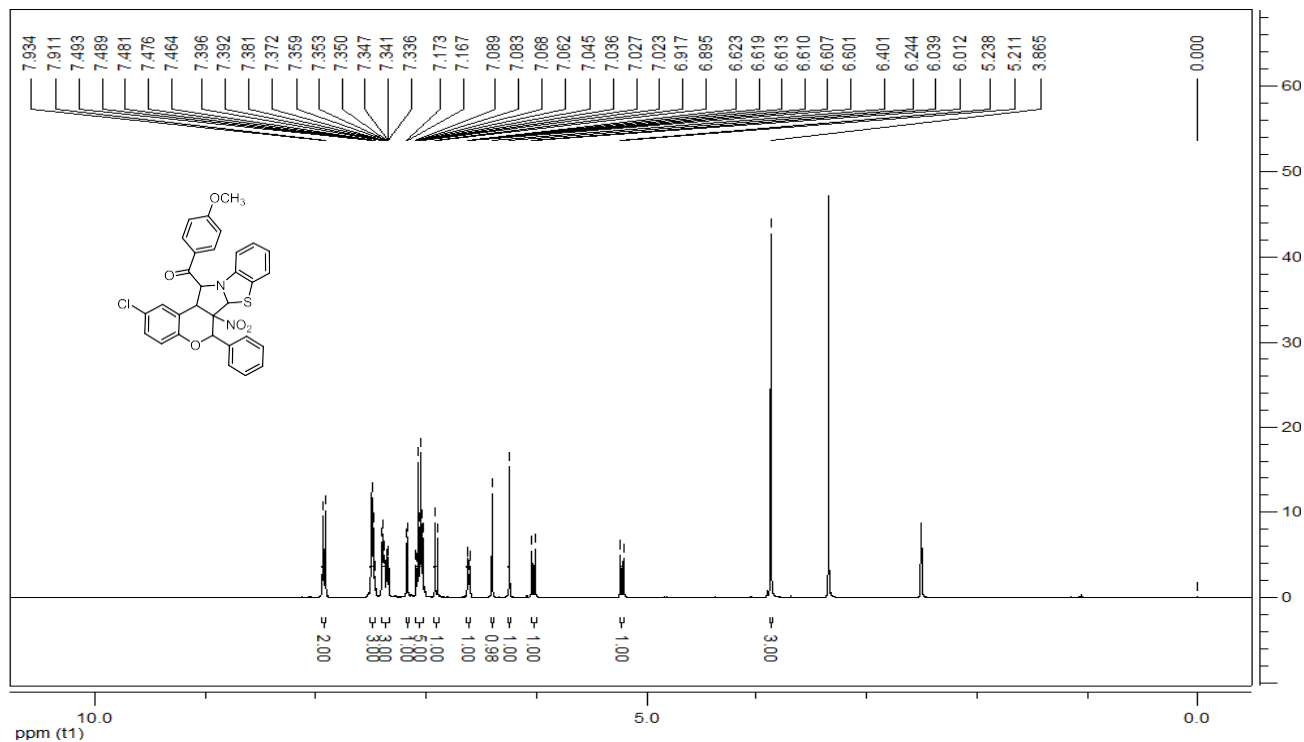
**(4-methoxyphenyl)(6-(4-methoxyphenyl)-6a-nitro-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)methanone (3h)**: yellow solid, 88%, m.p. 190~192 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 7.95 (d,  $J = 9.2$  Hz, 2H, ArH), 7.35~7.29 (m, 3H, ArH), 7.11~7.10 (m, 1H, ArH), 7.03~7.01 (m, 7H, ArH), 6.86~6.84 (m, 1H, ArH), 6.61~6.59 (m, 1H, ArH), 6.54~6.51 (m, 1H, ArH), 6.42 (s, 1H, CH), 6.18 (s, 1H, CH), 6.03 (d,  $J = 10.8$  Hz, 1H, CH), 5.20 (d,  $J = 11.2$  Hz, 1H, CH), 3.86 (s, 3H,  $\text{OCH}_3$ ), 3.80 (s, 3H,  $\text{OCH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 197.0, 164.4, 160.5, 153.1, 149.6, 139.8, 134.8, 134.1, 131.7, 131.2, 130.1, 129.1, 126.0, 122.3, 121.5, 118.7, 116.5, 114.6, 114.4, 97.3, 77.5, 77.1, 71.3, 56.1, 55.6, 44.7; MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{32}\text{H}_{27}\text{N}_2\text{O}_6\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 567.1584. Found: 567.1583; IR (KBr)  $\nu$ : 3056, 3011, 2942, 2838, 1677, 1603, 1548, 1507, 1455, 1364, 1303, 1173, 1030, 926, 825, 751  $\text{cm}^{-1}$ .



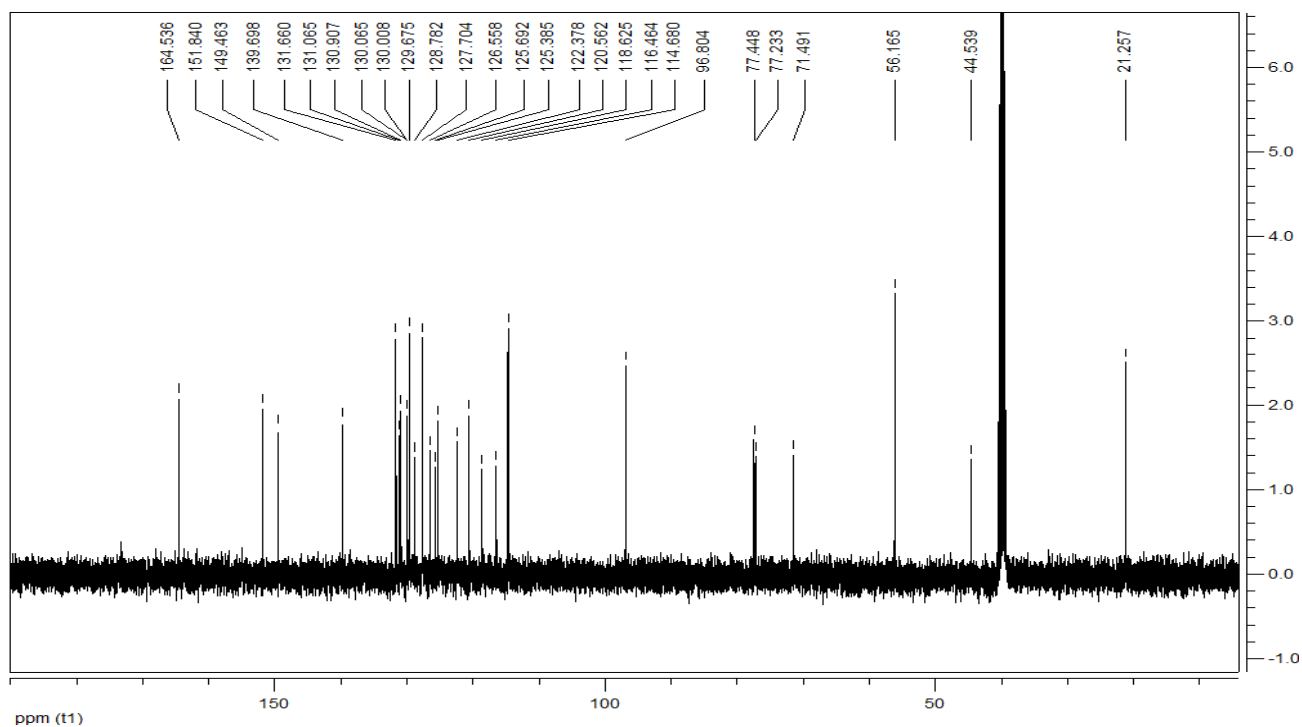
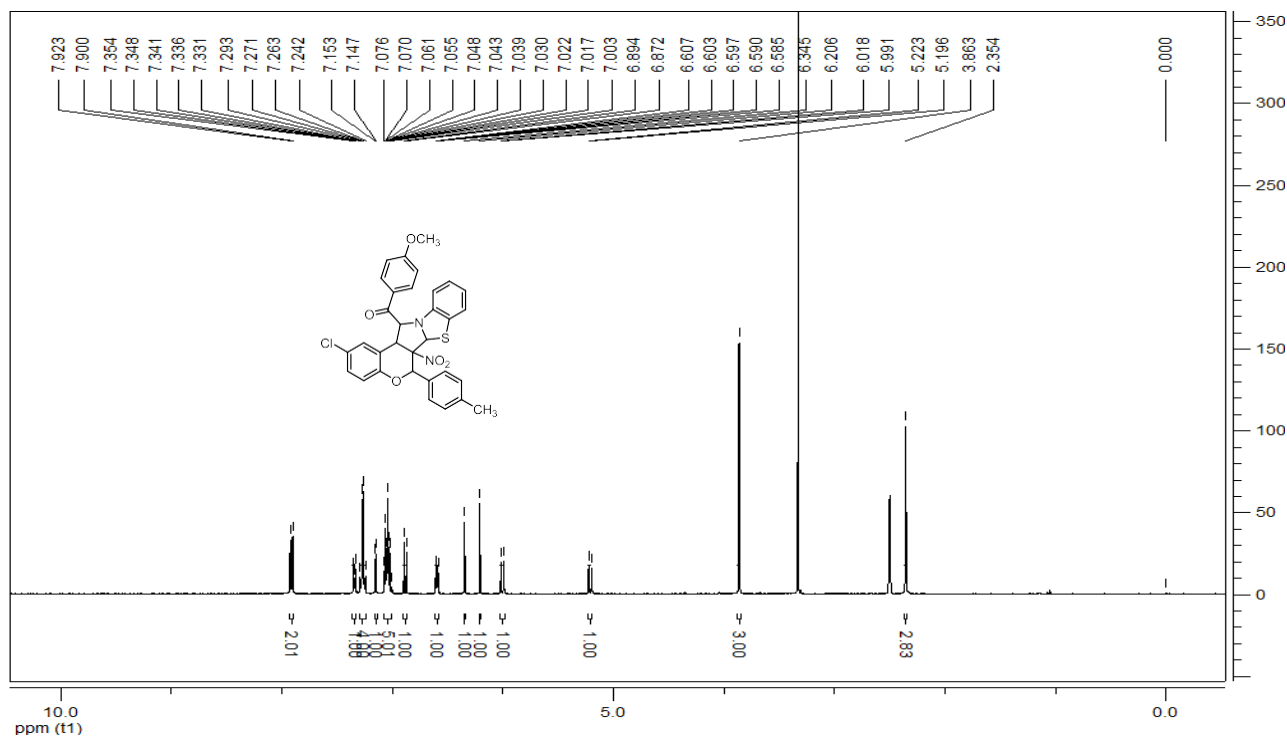
**(6-(4-chlorophenyl)-6a-nitro-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-1-yl)(4-methoxyphenyl)methanone (3i):** yellow solid, 93%, m.p. 178~179°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.96 (d, *J* = 8.8 Hz, 2H, ArH), 7.56 (d, *J* = 7.6 Hz, 2H, ArH), 7.43 (d, *J* = 7.6 Hz, 2H, ArH), 7.35~7.33 (m, 1H, ArH), 7.14 (d, *J* = 8.0 Hz, 1H, ArH), 7.07~6.99 (m, 5H, ArH), 6.88 (d, *J* = 7.6 Hz, 1H, ArH), 6.65~6.61 (m, 1H, ArH), 6.58~6.55 (m, 1H, ArH), 6.49 (s, 1H, CH), 6.26 (s, 1H, CH), 6.10 (d, *J* = 10.8 Hz, 1H, CH), 5.21 (d, *J* = 10.8 Hz, 1H, CH), 3.86 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 197.0, 164.4, 152.8, 149.4, 134.6, 133.3, 131.8, 130.9, 130.1, 130.0, 129.6, 129.1, 128.9, 126.4, 125.5, 122.3, 121.8, 118.7, 116.8, 116.3, 114.6, 97.6, 76.7, 76.7, 71.0, 56.1, 44.7; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>24</sub>ClN<sub>2</sub>O<sub>5</sub>S ([M+H]<sup>+</sup>): 571.1089. Found: 571.1077; IR (KBr) ν: 3071, 3019, 2919, 2841, 1669, 1591, 1546, 1478, 1356, 1310, 1265, 1226, 1106, 946, 889, 837, 743 cm<sup>-1</sup>.



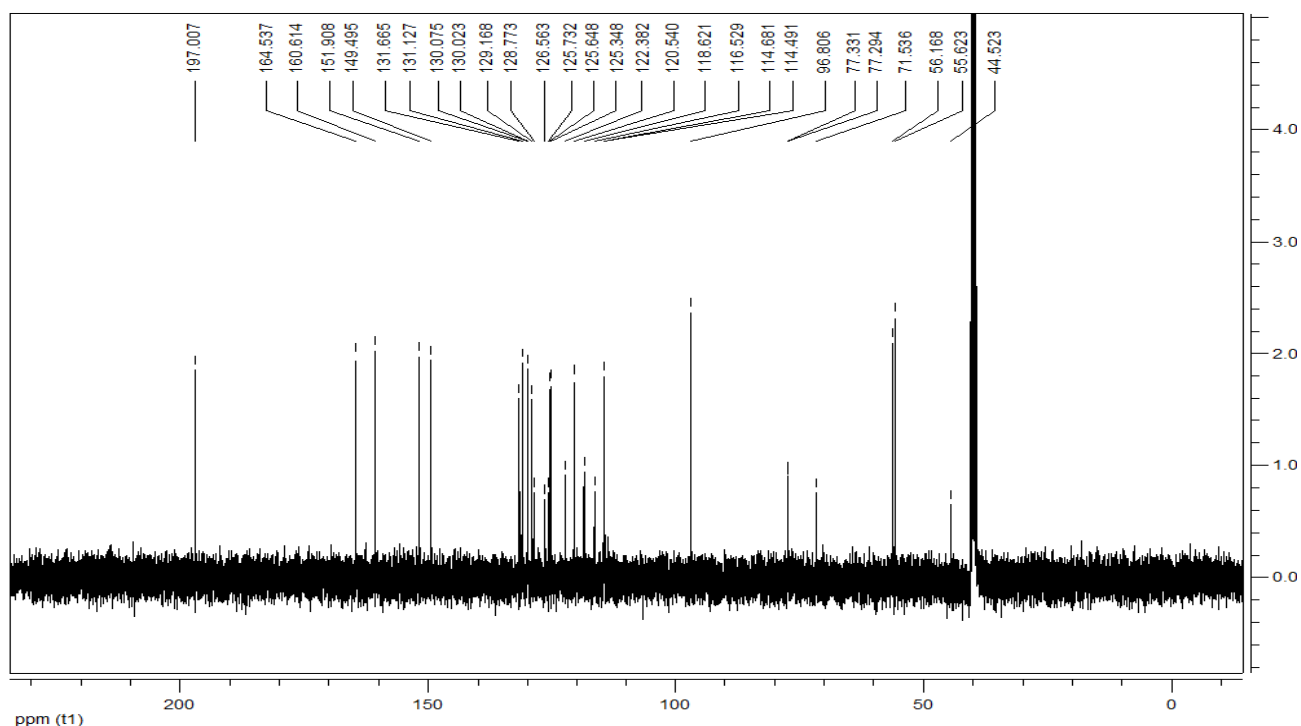
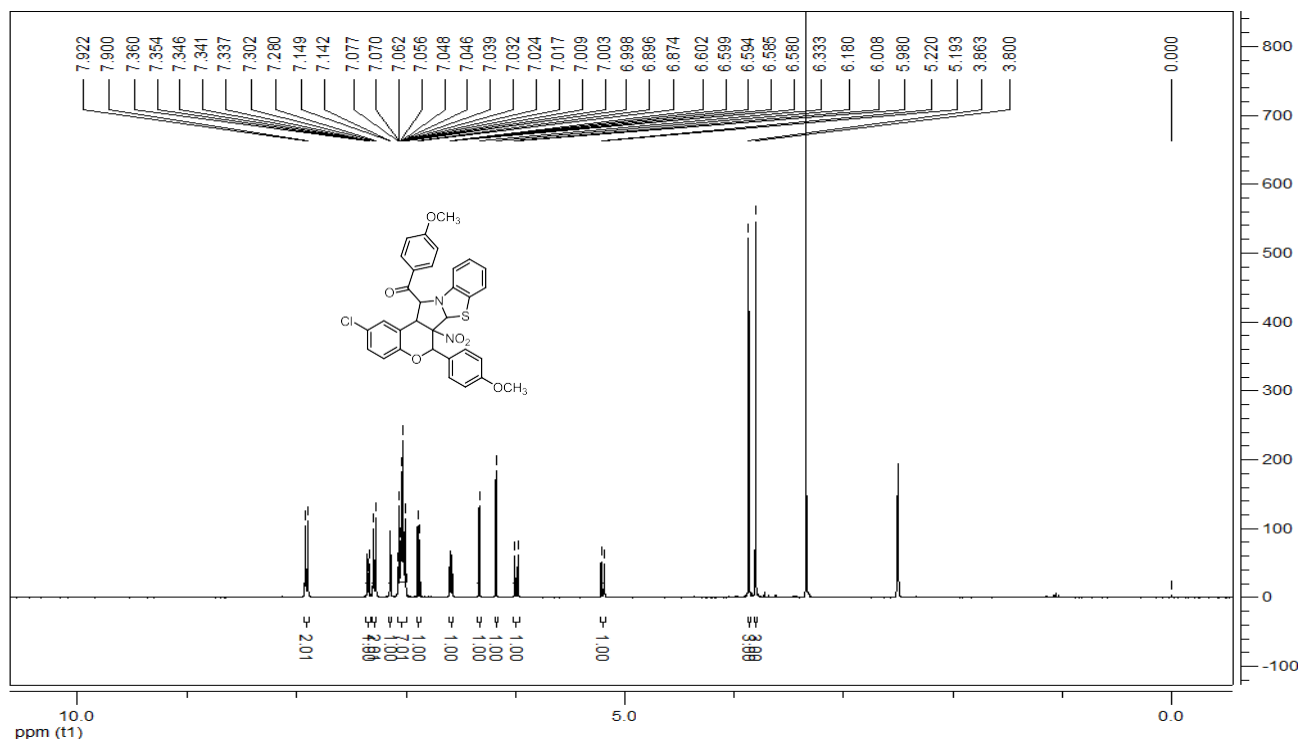
**(2-chloro-6a-nitro-6-phenyl-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-1-yl)(4-methoxyphenyl)methanone (3j):** yellow solid, 86%, m.p. 171~173°C;  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 7.92 (d,  $J = 8.8$  Hz, 2H, ArH), 7.49~7.46 (m, 3H, ArH), 7.39~7.33 (m, 3H, ArH), 7.16 (d,  $J = 2.4$  Hz, 1H, ArH), 7.08~7.02 (m, 5H, ArH), 6.90 (d,  $J = 8.8$  Hz, 1H, ArH), 6.62~6.60 (m, 1H, ArH), 6.40 (s, 1H, CH), 6.24 (s, 1H, CH), 6.21 (d,  $J = 11.2$  Hz, 1H, CH), 5.22 (d,  $J = 10.8$  Hz, 1H, CH), 3.86 (s, 3H,  $\text{OCH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 196.9, 164.5, 151.7, 149.4, 133.9, 131.6, 131.0, 130.1, 130.0, 130.0, 129.1, 128.8, 127.8, 126.5, 125.7, 125.4, 122.3, 120.5, 118.6, 116.5, 114.6, 96.8, 77.5, 77.2, 71.4, 56.1, 44.5; MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{31}\text{H}_{24}\text{ClN}_2\text{O}_5\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 571.1089. Found: 571.1066; IR (KBr)  $\nu$ : 3068, 2925, 2839, 1681, 1594, 1541, 1453, 1363, 1314, 1239, 1168, 1025, 919, 827, 745  $\text{cm}^{-1}$ .



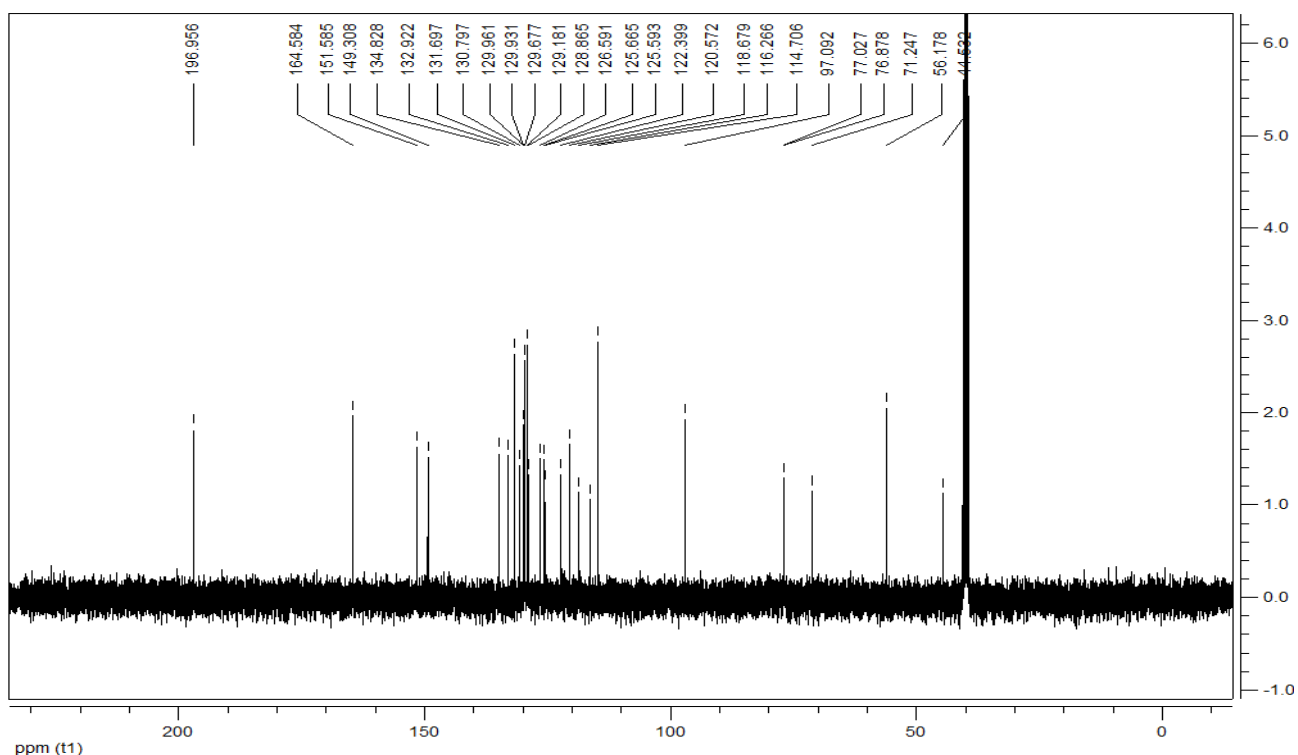
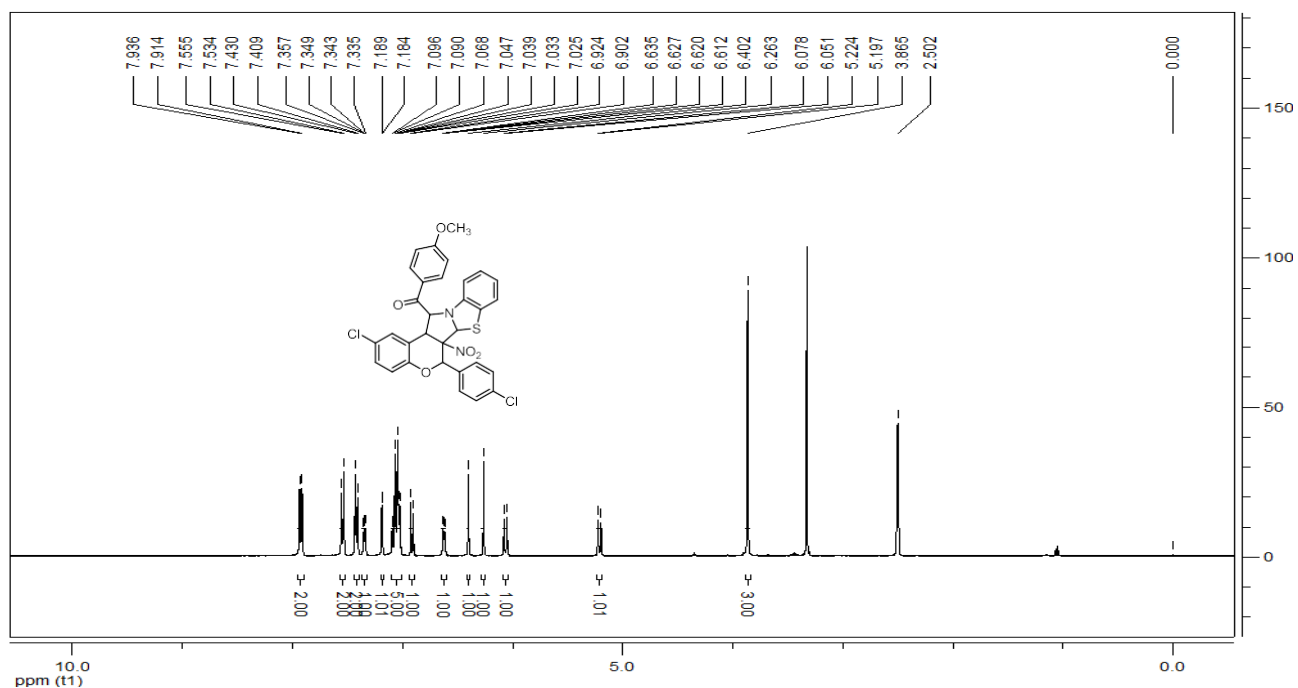
**2-chloro-6a-nitro-6-(p-tolyl)-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-1 3-yl)(4-methoxyphenyl)methanone (3k):** yellow solid, 89%, m.p. 193~194 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.91 (d, *J* = 9.2 Hz, 2H, ArH), 7.35~7.33 (m, 1H, ArH), 7.29~7.24 (m, 4H, ArH), 7.15 (d, *J* = 2.4 Hz, 1H, ArH), 7.07~7.00 (m, 5H, ArH), 6.88 (d, *J* = 8.8 Hz, 1H, ArH), 6.61~6.58 (m, 1H, ArH), 6.34 (s, 1H, CH), 6.21 (s, 1H, CH), 6.00 (d, *J* = 10.8 Hz, 1H, CH), 5.21 (d, *J* = 10.8 Hz, 1H, CH), 3.86 (s, 3H, OCH<sub>3</sub>), 2.35 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 164.5, 151.8, 149.4, 139.6, 131.6, 131.0, 130.9, 130.0, 130.0, 129.6, 128.7, 127.7, 126.5, 125.6, 125.3, 122.3, 120.5, 118.6, 116.4, 114.6, 96.8, 77.4, 77.2, 71.4, 56.1, 44.5, 21.2; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>26</sub>ClN<sub>2</sub>O<sub>5</sub>S ([M+H]<sup>+</sup>): 585.1245. Found: 585.1236; IR (KBr) ν: 3020, 2925, 1681, 1598, 1542, 1454, 1367, 1314, 1238, 1170, 1126, 1028, 919, 861, 821, 751 cm<sup>-1</sup>.



**(2-chloro-6-(4-methoxyphenyl)-6a-nitro-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl)methanone (31):** yellow solid, 86%, m.p. 191~192°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.91 (d, *J* = 9.2 Hz, 2H, ArH), 7.36~7.33 (m, 1H, ArH), 7.30~7.28 (m, 2H, ArH), 7.14 (d, *J* = 2.4 Hz, 1H, ArH), 7.07~6.99 (m, 7H, ArH), 6.88 (d, *J* = 8.8 Hz, 1H, ArH), 6.59~6.58 (m, 1H, ArH), 6.33 (s, 1H, CH), 6.18 (s, 1H, CH), 5.99 (d, *J* = 10.8 Hz, 1H, CH), 5.20 (d, *J* = 10.8 Hz, 1H, CH), 3.86 (s, 3H, OCH<sub>3</sub>), 3.80 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 197.0, 164.5, 160.6, 151.9, 149.4, 131.6, 131.1, 130.0, 130.0, 129.1, 128.7, 126.5, 125.7, 125.6, 125.3, 122.3, 120.5, 118.6, 116.5, 114.6, 114.4, 96.8, 77.3, 77.2, 71.5, 56.1, 55.6, 44.5; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>26</sub>ClN<sub>2</sub>O<sub>6</sub>S ([M+H]<sup>+</sup>): 601.1195. Found: 601.1195; IR (KBr) ν: 2930, 2839, 1683, 1601, 1541, 1455, 1364, 1303, 1240, 1170, 1125, 1028, 922, 859, 822, 752 cm<sup>-1</sup>.

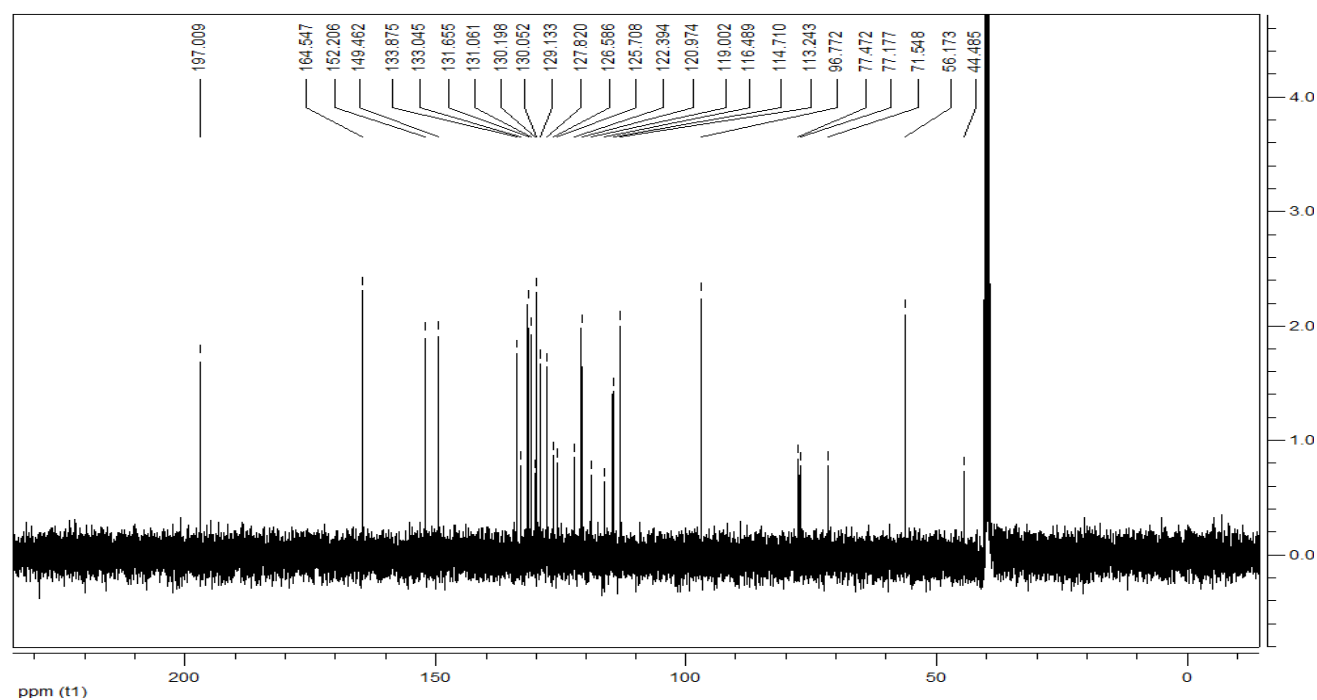
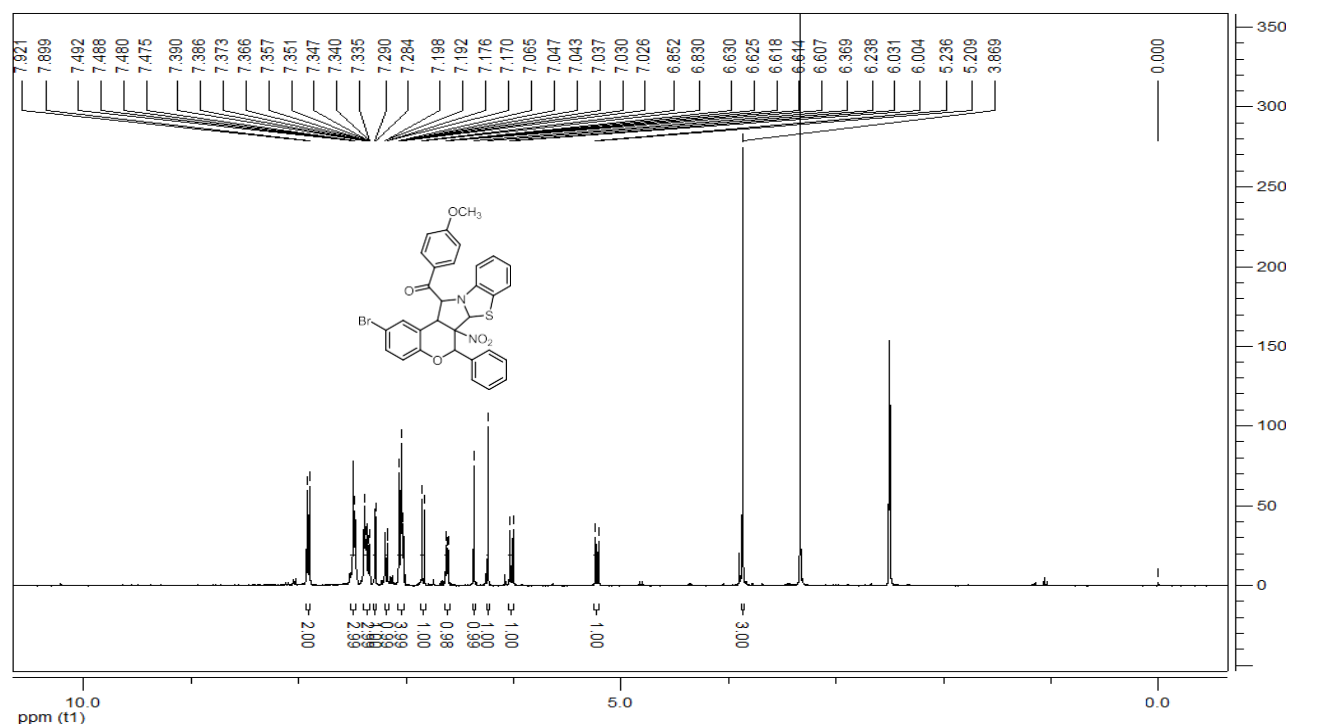


**(2-chloro-6-(4-chlorophenyl)-6a-nitro-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl)methanone (3m):** yellow solid, 89%, m.p. 177~179°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.93 (d, *J* = 8.8 Hz, 2H, ArH), 7.55 (d, *J* = 8.4 Hz, 2H, ArH), 7.42 (d, *J* = 8.4 Hz, 2H, ArH), 7.36~7.34 (m, 1H, ArH), 7.19 (d, *J* = 2.0 Hz, 1H, ArH), 7.10~7.03 (m, 5H, ArH), 6.92 (d, *J* = 8.8 Hz, 1H, ArH), 6.64~6.62 (m, 1H, ArH), 6.40 (s, 1H, CH), 6.26 (s, 1H, CH), 6.06 (d, *J* = 10.8 Hz, 1H, CH), 5.21 (d, *J* = 10.4 Hz, 1H, CH), 3.87 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 196.9, 164.5, 151.5, 149.3, 134.8, 132.9, 131.6, 130.7, 129.9, 129.9, 129.6, 129.1, 128.8, 126.5, 125.6, 125.5, 122.3, 120.5, 118.6, 116.2, 114.7, 97.0, 77.0, 76.8, 71.2, 56.1, 44.5; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>23</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S ([M+H]<sup>+</sup>): 605.0699. Found: 605.0684; IR (KBr) ν: 3064, 2925, 2841, 1794, 1681, 1594, 1541, 1417, 1336, 1315, 1237, 1167, 918, 861, 827, 749 cm<sup>-1</sup>.

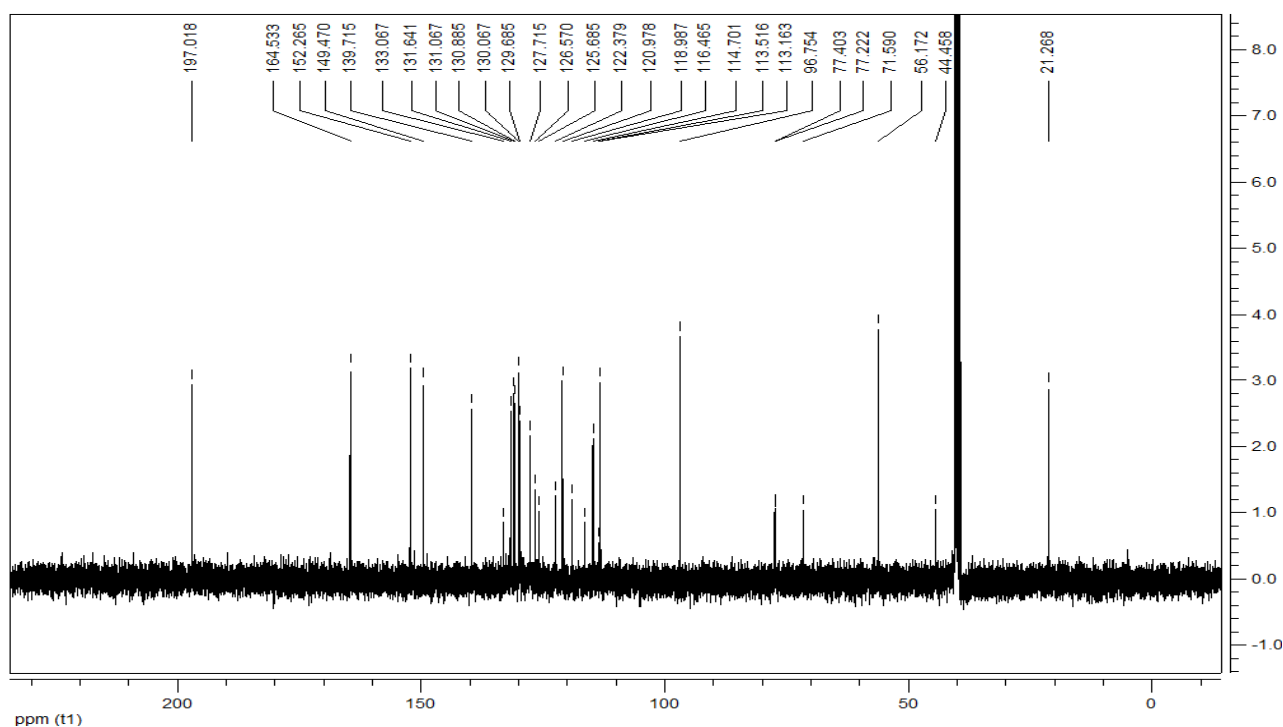
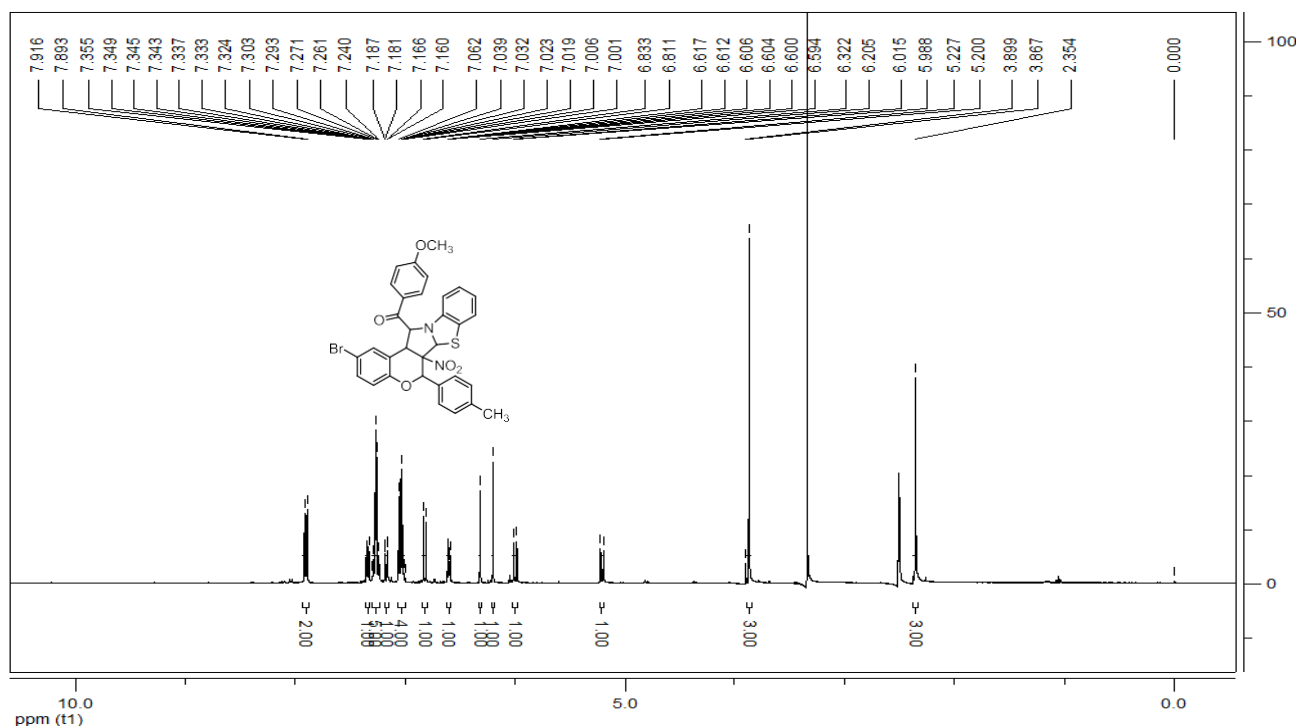




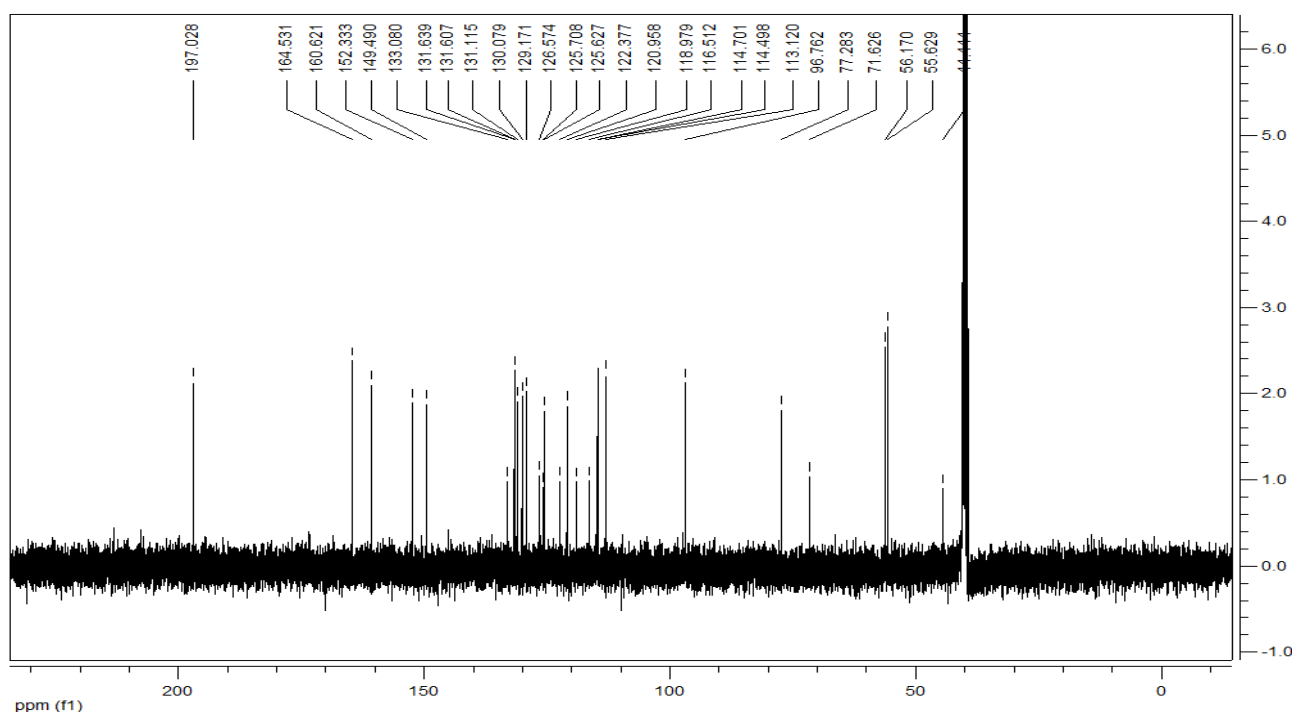
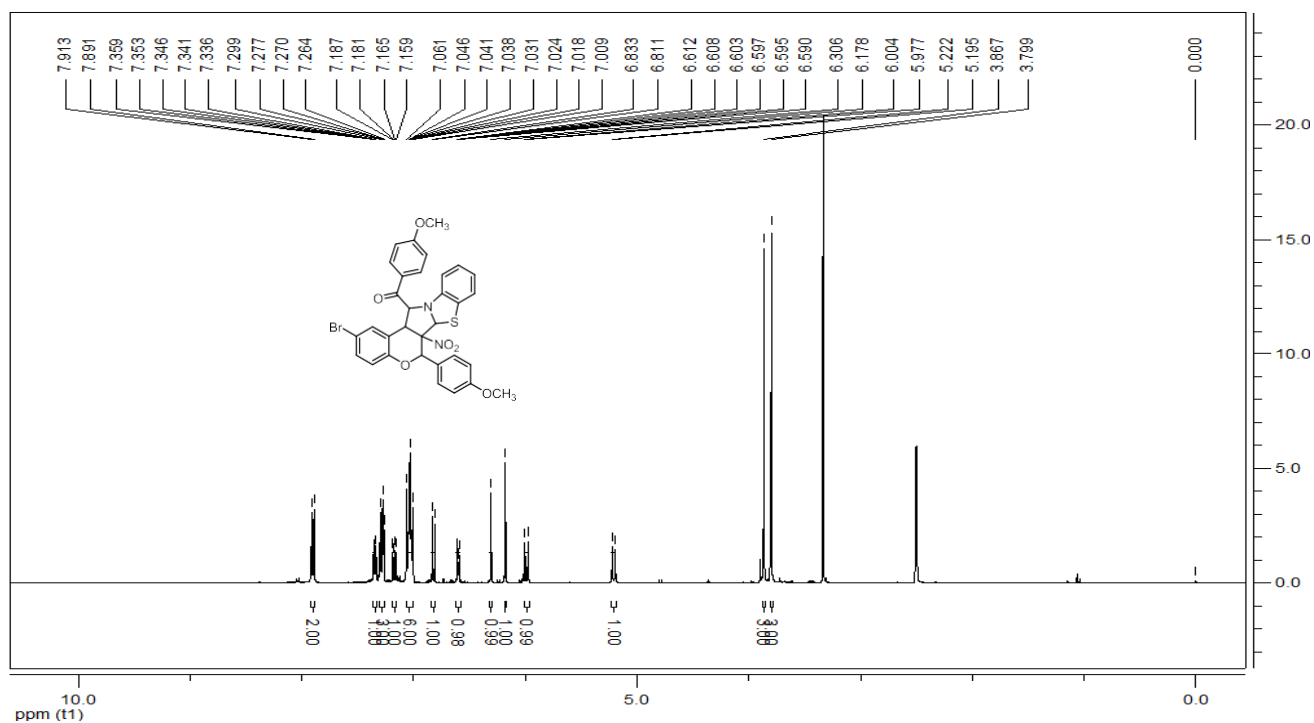
**(2-bromo-6a-nitro-6-phenyl-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-1-yl)(4-methoxyphenyl)methanone (3n):** yellow solid, 83%, m.p. 192~193 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.91 (d, *J* = 9.2 Hz, 2H, ArH), 7.49~7.48 (m, 3H, ArH), 7.39~7.34 (m, 3H, ArH), 7.29 (d, *J* = 2.4 Hz, 1H, ArH), 7.18 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H, ArH), 7.06~7.02 (m, 4H, ArH), 6.84 (d, *J* = 8.8 Hz, 1H, ArH), 6.63~6.61 (m, 1H, ArH), 6.37 (s, 1H, CH), 6.24 (s, 1H, CH), 6.02 (d, *J* = 10.8 Hz, 1H, CH), 5.22 (d, *J* = 10.8 Hz, 1H, CH), 3.87 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 197.0, 164.5, 152.2, 149.4, 133.8, 133.0, 131.6, 131.0, 130.1, 130.0, 129.1, 127.8, 126.5, 125.7, 122.3, 120.9, 119.0, 116.4, 114.7, 113.2, 96.7, 77.4, 77.1, 71.5, 56.1, 44.4; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>24</sub>BrN<sub>2</sub>O<sub>5</sub>S ([M+H]<sup>+</sup>): 615.0584. Found: 615.0576; IR (KBr) ν: 3055, 2928, 1678, 1595, 1541, 1464, 1366, 1243, 1168, 1134, 1028, 909, 823, 749, 702 cm<sup>-1</sup>.



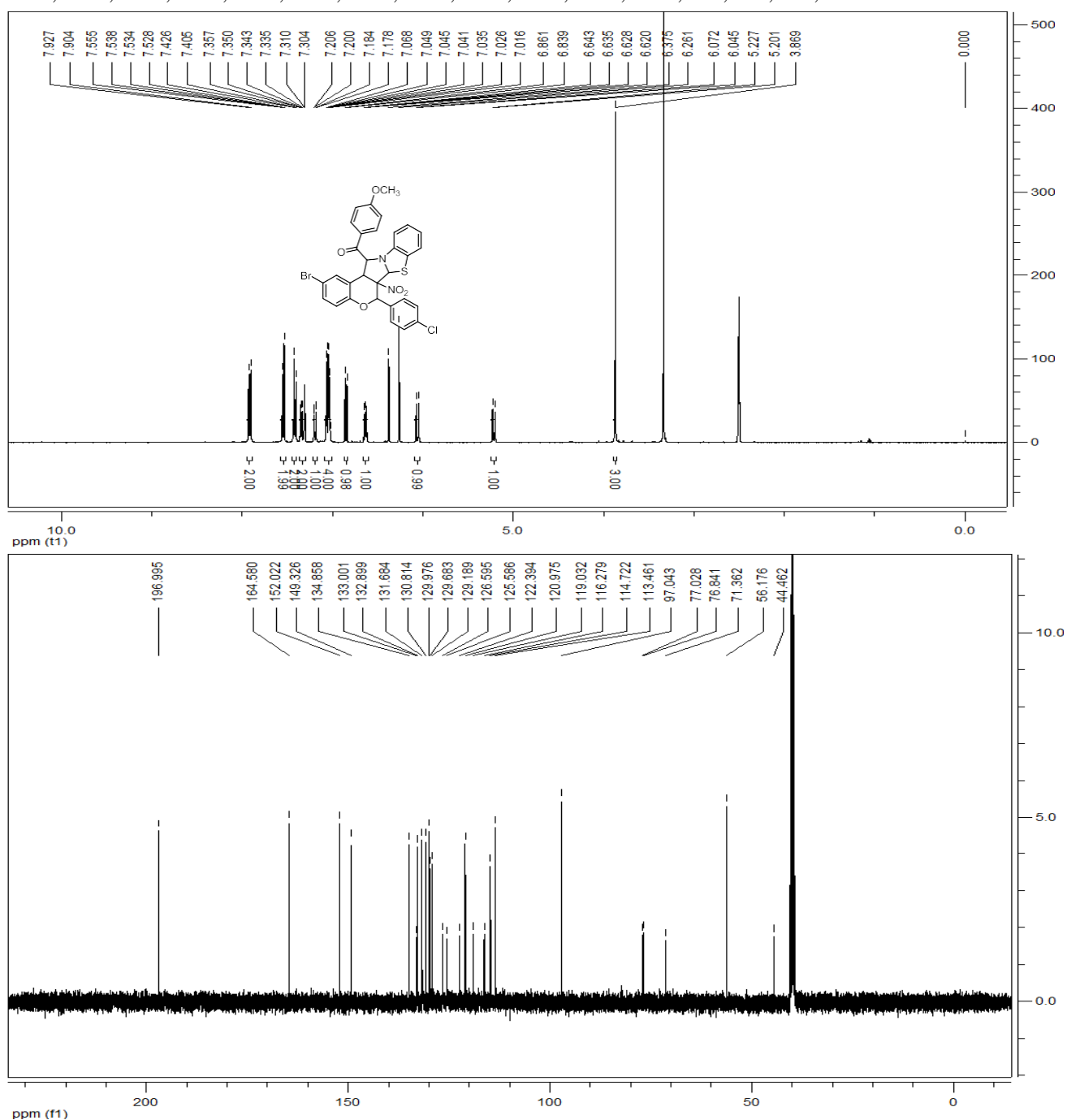
**(2-bromo-6a-nitro-6-(p-tolyl)-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl)methanone (3o):** yellow solid, 88%, m.p. 198~200°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.91 (d, *J* = 9.2 Hz, 2H, ArH), 7.36~7.33 (m, 1H, ArH), 7.31~7.24 (m, 5H, ArH), 7.18 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H, ArH), 7.07~7.00 (m, 4H, ArH), 6.83 (d, *J* = 4.4 Hz, 1H, ArH), 6.62~6.60 (m, 1H, ArH), 6.33 (s, 1H, CH), 6.21 (s, 1H, CH), 6.00 (d, *J* = 11.2 Hz, 1H, CH), 5.22 (d, *J* = 10.8 Hz, 1H, CH), 3.87 (s, 3H, OCH<sub>3</sub>), 2.36 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 197.0, 164.5, 152.3, 149.5, 139.7, 133.1, 131.6, 131.1, 130.9, 130.1, 129.7, 127.7, 126.6, 125.7, 122.4, 121.0, 119.0, 116.5, 114.7, 113.5, 113.2, 96.8, 77.4, 77.2, 71.6, 56.1, 44.4, 21.3; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>26</sub>BrN<sub>2</sub>O<sub>5</sub>S ([M+H]<sup>+</sup>): 629.0740. Found: 629.0741; IR (KBr) ν: 3019, 2923, 2845, 1681, 1594, 1541, 1453, 1415, 1365, 1314, 1238, 1125, 1027 919, 860, 821, 751 cm<sup>-1</sup>.



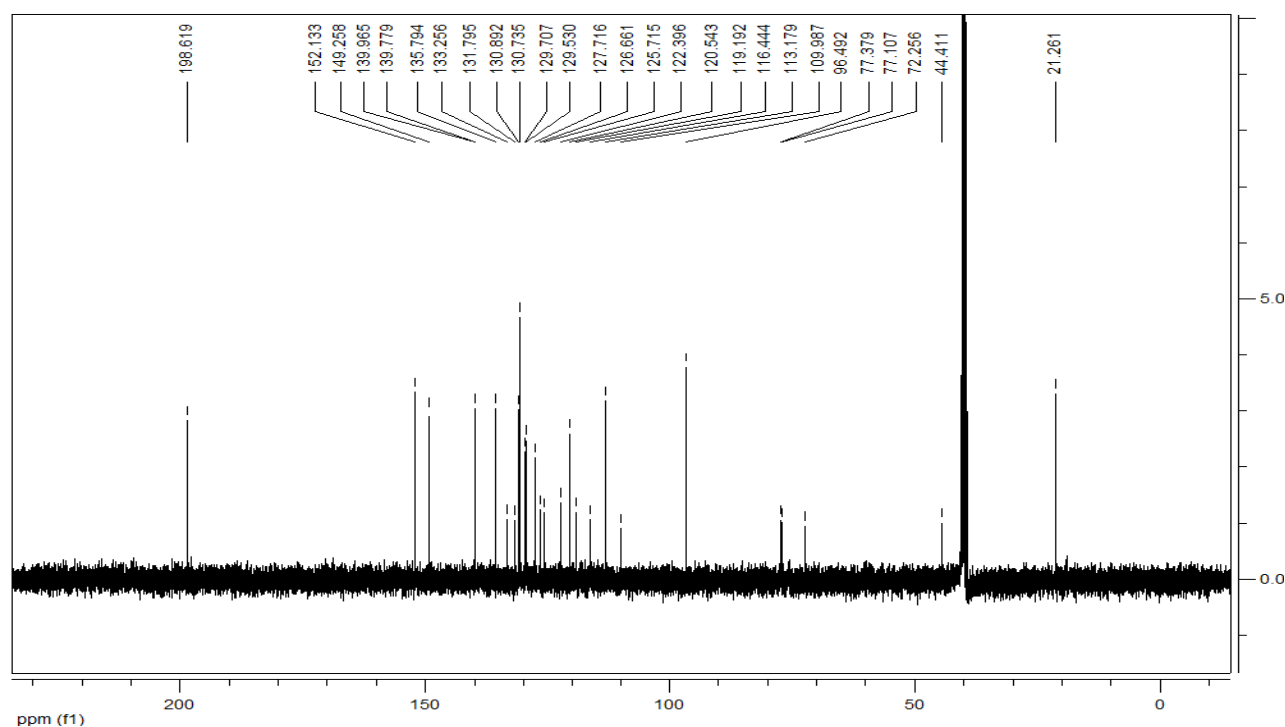
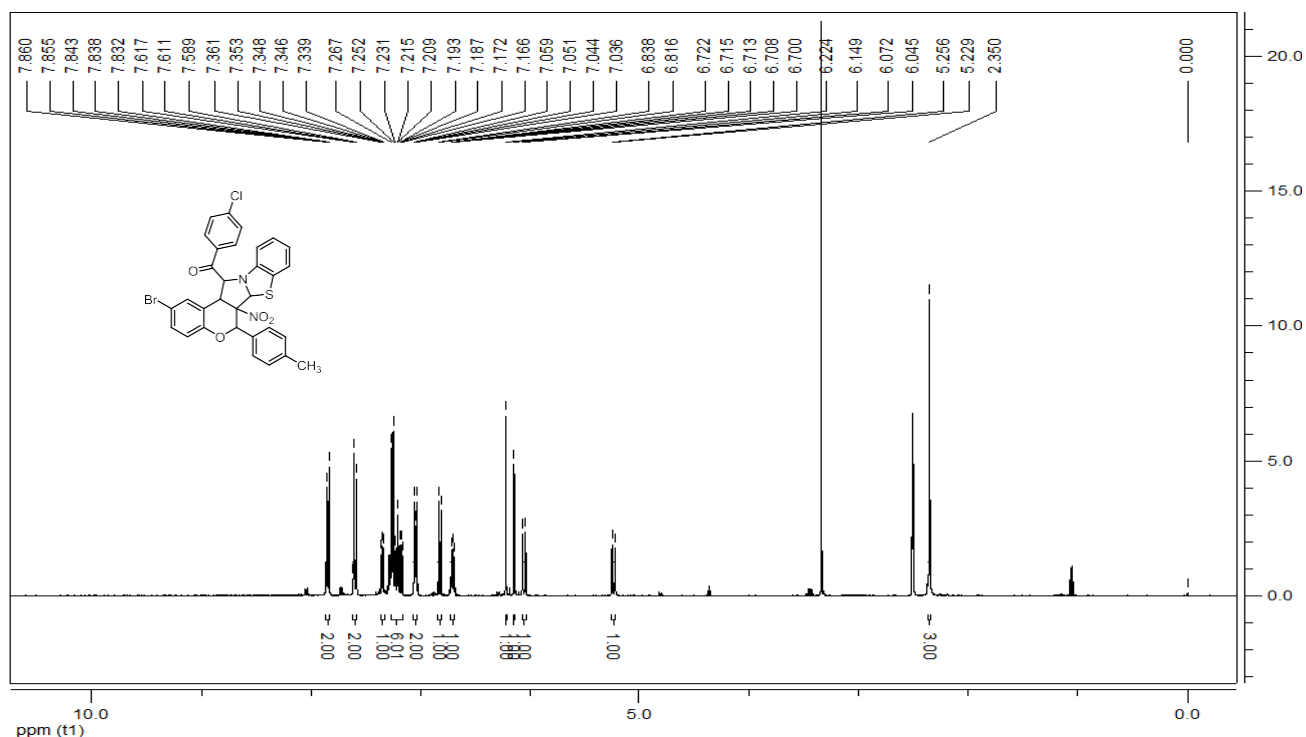
**(2-bromo-6-(4-methoxyphenyl)-6a-nitro-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl)methanone (3p):** yellow solid, 92%, m.p. 194~195°C;  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 7.90 (d,  $J = 8.8$  Hz, 2H, ArH), 7.35~7.33 (m, 1H, ArH), 7.29~7.26 (m, 3H, ArH), 7.17 (dd,  $J_1 = 8.8$  Hz,  $J_2 = 2.4$  Hz, 1H, ArH), 7.06~7.00 (m, 6H, ArH), 6.82 (d,  $J = 8.4$  Hz, 1H, ArH), 6.61~6.58 (m, 1H, ArH), 6.30 (s, 1H, CH), 6.17 (s, 1H, CH), 5.98 (d,  $J = 10.8$  Hz, 1H, CH), 5.20 (d,  $J = 10.8$  Hz, 1H, CH), 3.86 (s, 3H,  $\text{OCH}_3$ ), 3.79 (s, 3H,  $\text{OCH}_3$ );  $^{13}\text{C NMR}$  (150 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 197.0, 164.5, 160.6, 152.3, 149.4, 133.0, 131.6, 131.6, 131.1, 130.0, 129.1, 126.5, 125.7, 125.6, 122.3, 120.9, 118.9, 116.5, 114.7, 114.4, 113.1, 96.7, 77.2, 71.6, 56.1, 55.6, 44.4; MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{32}\text{H}_{26}\text{BrN}_2\text{O}_6\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 645.0689. Found: 645.0682; IR (KBr)  $\nu$ : 2928, 2838, 1681, 1600, 1540, 1466, 1364, 1303, 1239, 1170, 1124, 1028, 921, 821, 750  $\text{cm}^{-1}$ .



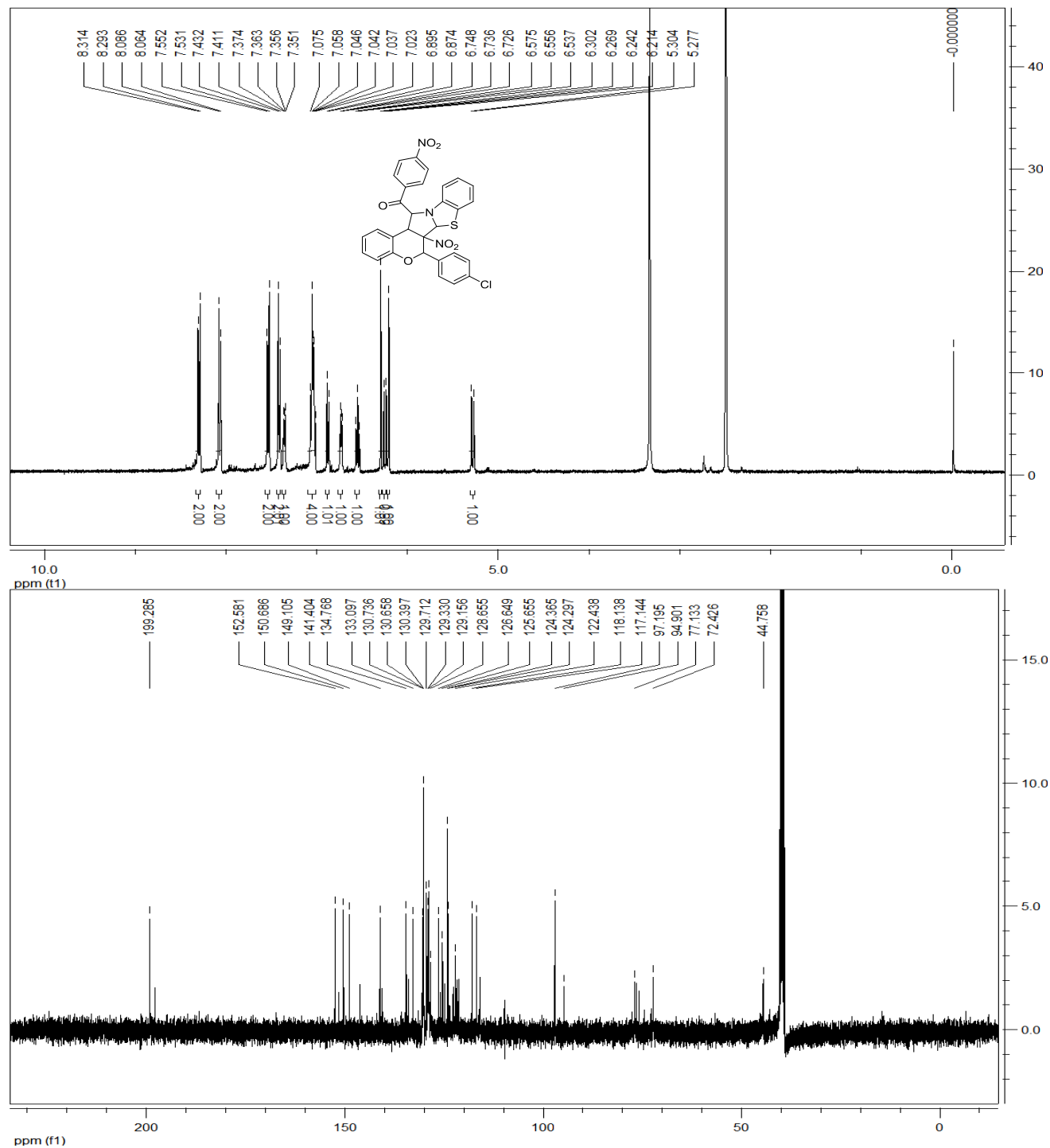
**(2-bromo-6-(4-chlorophenyl)-6a-nitro-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl)methanone (3q):** yellow solid, 86%, m.p. 189~191 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.92 (d, *J* = 9.2 Hz, 2H, ArH), 7.56~7.53 (m, 2H, ArH), 7.43~7.40 (m, 2H, ArH), 7.36~7.30 (m, 2H, ArH), 7.19 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H, ArH), 7.07~7.02 (m, 4H, ArH), 6.84 (d, *J* = 8.8 Hz, 1H, ArH), 6.64~6.62 (m, 1H, ArH), 6.38 (s, 1H, CH), 6.26 (s, 1H, CH), 6.05 (d, *J* = 10.8 Hz, 1H, CH), 5.21 (d, *J* = 10.8 Hz, 1H, CH), 3.86 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 196.9, 164.5, 152.0, 149.3, 134.8, 133.0, 132.8, 131.6, 130.8, 129.9, 129.6, 129.1, 126.5, 125.5, 122.3, 120.9, 119.0, 116.2, 114.7, 113.4, 97.0, 77.0, 76.8, 71.3, 56.1, 44.4; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>23</sub>BrClN<sub>2</sub>O<sub>5</sub>S ([M+H]<sup>+</sup>): 649.0194. Found: 649.0208; IR (KBr) ν: 3063, 2921, 2841, 1680, 1593, 1541, 1467, 1414, 1366, 1314, 1167, 1125, 918, 860, 821, 749 cm<sup>-1</sup>.



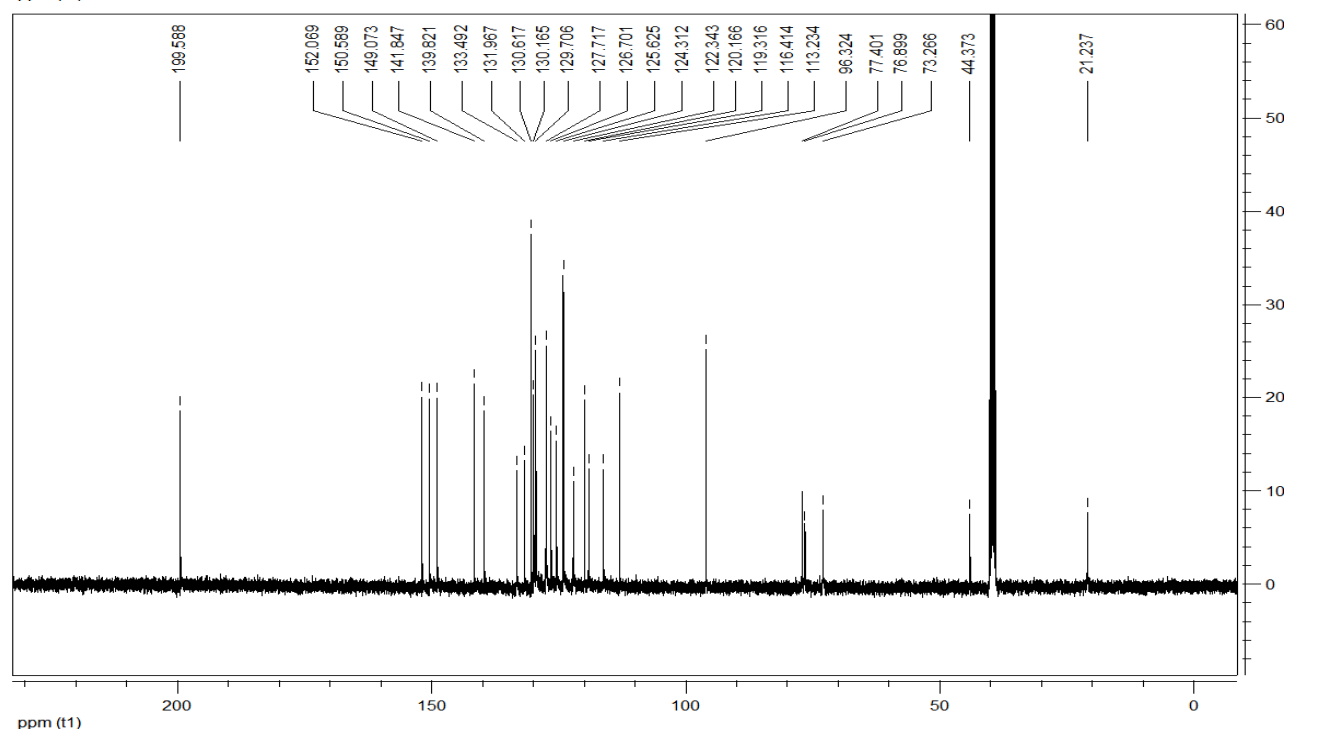
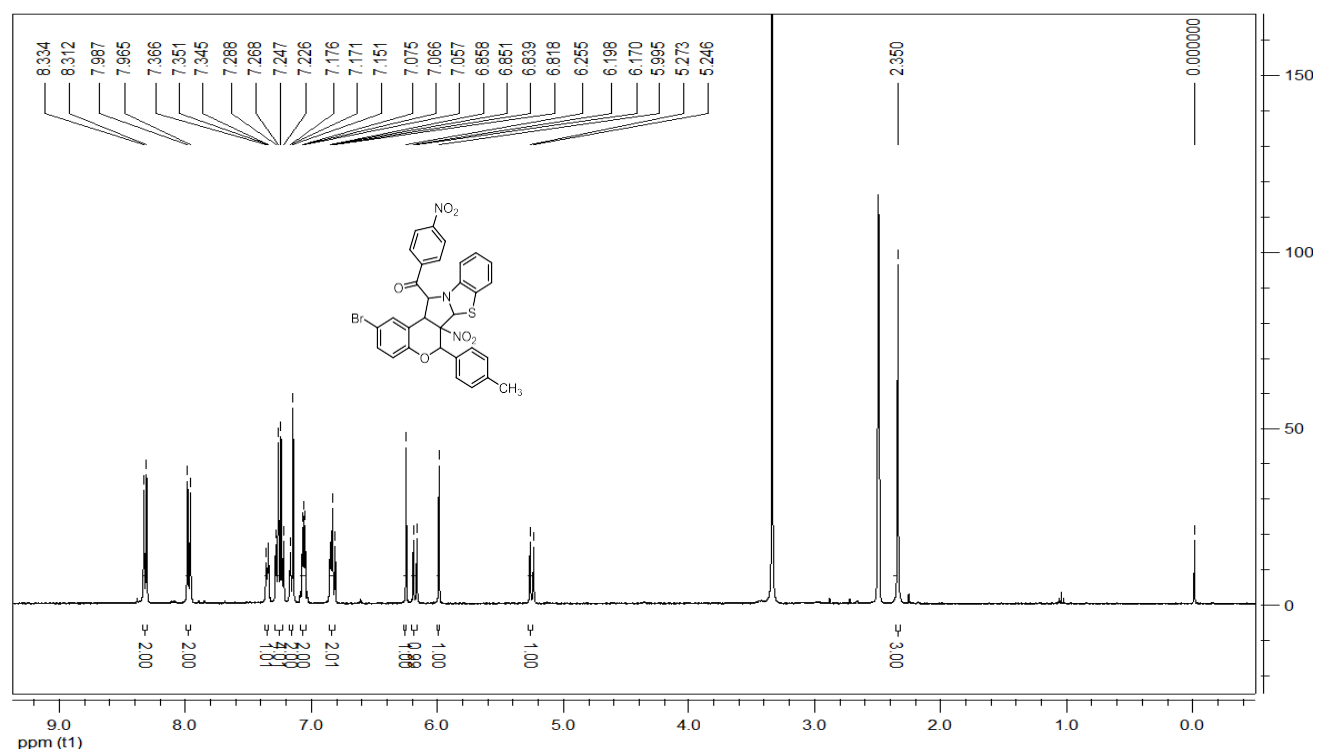
**(2-bromo-6a-nitro-6-(p-tolyl)-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-chlorophenyl)methanone (3r):** yellow solid, 95%, m.p. 208~210°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 7.86~7.83 (m, 2H, ArH), 7.61~7.58 (m, 2H, ArH), 7.35~7.33 (m, 1H, ArH), 7.28~7.16 (m, 6H, ArH), 7.05~7.03 (m, 2H, ArH), 6.82 (d,  $J$  = 8.8 Hz, 1H, ArH), 6.72~6.70 (m, 1H, ArH), 6.22 (s, 1H, CH), 6.14 (s, 1H, CH), 6.05 (d,  $J$  = 11.2 Hz, 1H, CH), 5.24 (d,  $J$  = 10.8 Hz, 1H, CH), 2.35 (s, 3H, CH<sub>3</sub>);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$ : 198.6, 152.1, 149.2, 139.9, 139.7, 135.7, 133.2, 131.7, 130.8, 130.7, 129.7, 129.5, 127.7, 126.6, 125.7, 122.3, 120.5, 119.1, 116.4, 113.1, 109.9, 96.4, 77.3, 77.1, 72.2, 44.4, 21.2; MS ( $m/z$ ): HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>23</sub>BrClN<sub>2</sub>O<sub>4</sub>S ([M+H]<sup>+</sup>): 633.0245. Found: 633.0184; IR (KBr)  $\nu$ : 3060, 2923, 1783, 1690, 1582, 1542, 1541, 1473, 1407, 1364, 1321, 1177, 1087, 1029, 919, 858, 815, 747 cm<sup>-1</sup>.



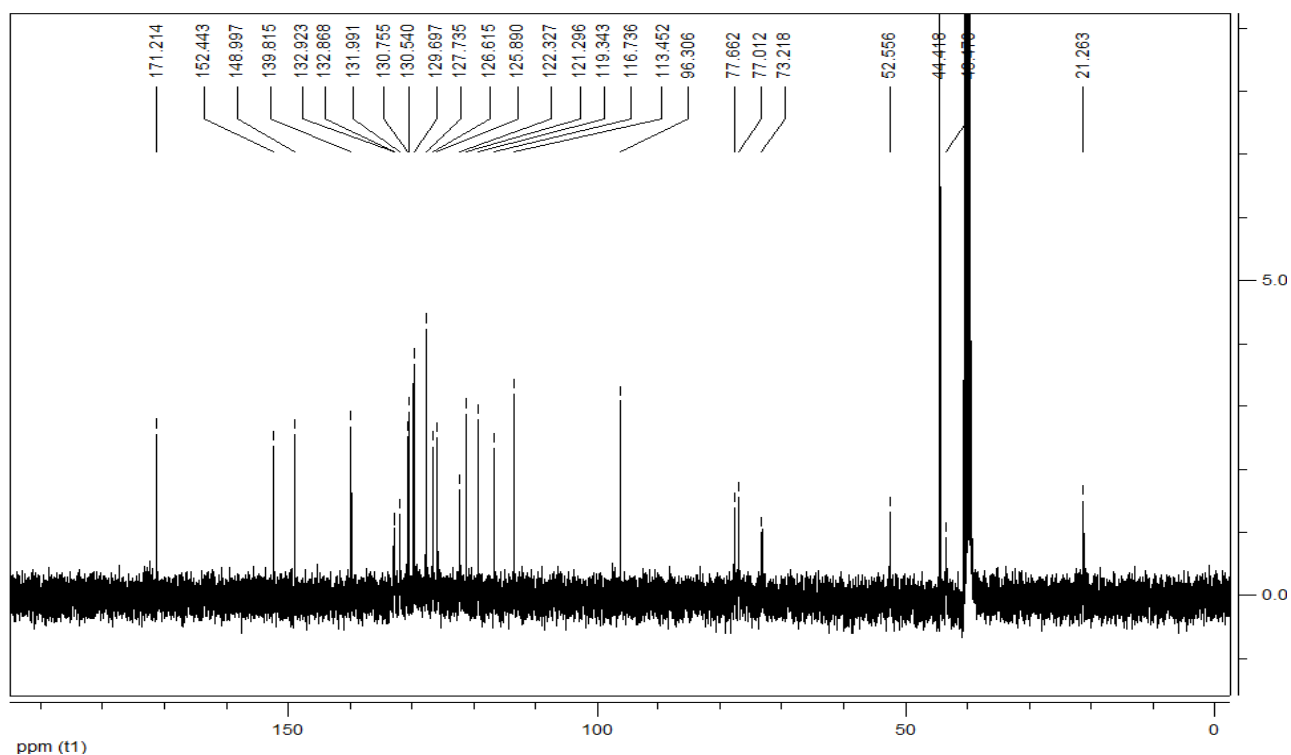
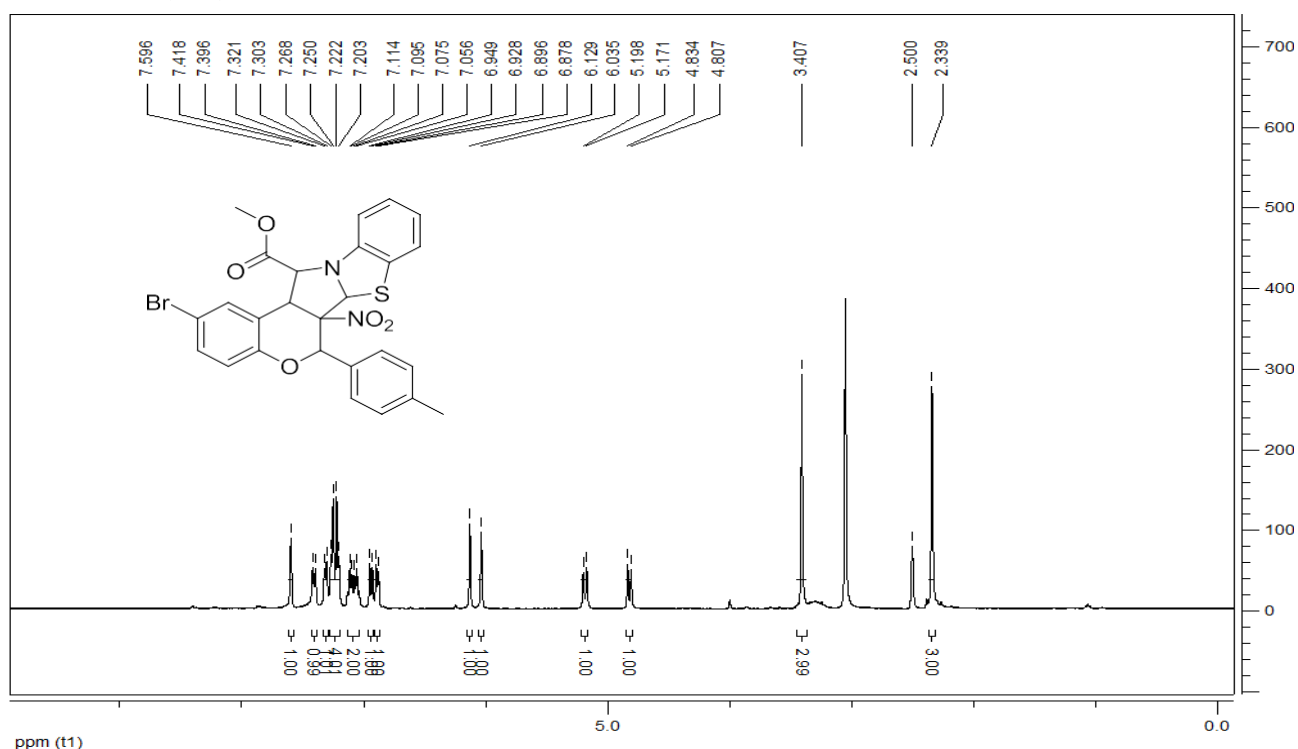
**(6-(4-chlorophenyl)-6a-nitro-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-1-3-yl)(4-nitrophenyl)methanone (3s):** Orange solid, 87%, m.p. 200~201 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.31~8.29 (m, 2H, ArH), 8.09~8.06 (m, 2H, ArH), 7.55~7.53 (m, 2H, ArH), 7.43~7.41 (m, 2H, ArH), 7.37~7.35 (m, 1H, ArH), 7.08~7.02 (m, 4H, ArH), 6.90~6.87 (m, 1H, ArH), 6.75~6.73 (m, 1H, ArH), 6.58~6.54 (m, 1H, ArH), 6.30 (s, 1H, CH), 6.26 (d, *J* = 11.2 Hz, 1H, CH), 6.21 (s, 1H, CH), 5.30 (d, *J* = 11.2 Hz, 1H, CH); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 199.2, 152.5, 150.6, 149.1, 141.4, 134.7, 133.0, 130.7, 130.6, 130.3, 129.7, 129.3, 129.1, 128.6, 126.6, 125.6, 124.3, 124.2, 122.4, 118.1, 117.1, 97.1, 94.9, 77.1, 72.4, 44.7; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>30</sub>H<sub>20</sub>ClN<sub>3</sub>O<sub>6</sub>S ([M+H]<sup>+</sup>): 586.0834. Found: 586.0845; IR (KBr) ν: 3066, 2972, 1703, 1602, 1544, 1458, 1252, 1227, 1013, 943, 911, 850, 762 cm<sup>-1</sup>.



**(2-bromo-6a-nitro-6-(p-tolyl)-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-nitrophenyl)methanone (3t):** orange solid, 83%, m.p. 210~211 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.33~8.31 (m, 2H, ArH), 7.99~7.96 (m, 2H, ArH), 7.37~7.34 (m, 1H, ArH), 7.29~7.23 (m, 4H, ArH), 7.18~7.15 (m, 2H, ArH), 7.08~7.06 (m, 2H, ArH), 6.86~6.82 (m, 2H, ArH), 6.26 (s, 1H, CH), 6.18 (d, *J* = 11.2 Hz, 1H, CH), 6.00 (s, 1H, CH), 5.26 (d, *J* = 11.2 Hz, 1H, CH), 2.35 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 199.5, 152.0, 150.5, 149.0, 141.8, 139.8, 133.4, 131.9, 130.6, 130.1, 129.7, 127.7, 126.7, 125.6, 124.3, 122.3, 120.1, 119.3, 116.4, 113.2, 96.3, 77.4, 76.8, 73.2, 44.3, 21.2; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>22</sub>BrN<sub>3</sub>O<sub>6</sub>S ([M+H]<sup>+</sup>): 644.0485. Found: 543.0489; IR (KBr) ν: 3046, 2970, 1701, 1600, 1542, 1521, 1479, 1279, 1044, 951, 910, 752 cm<sup>-1</sup>.

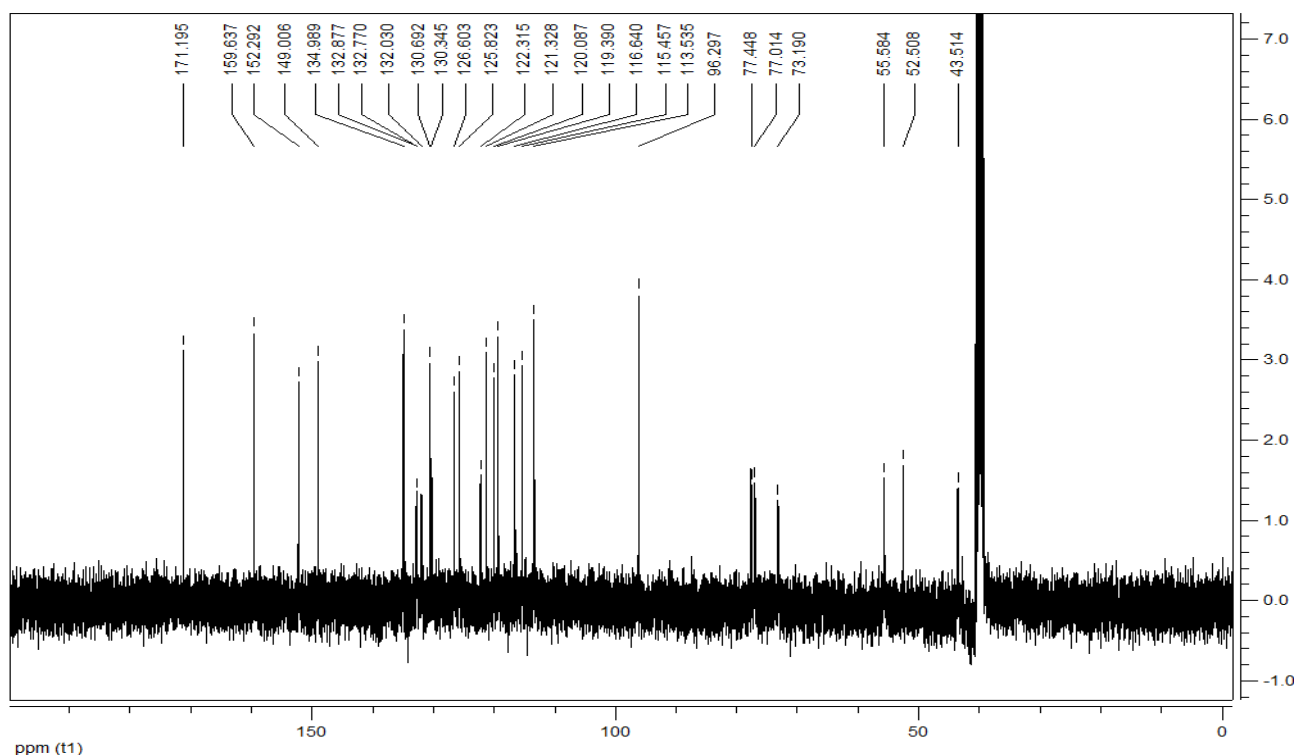
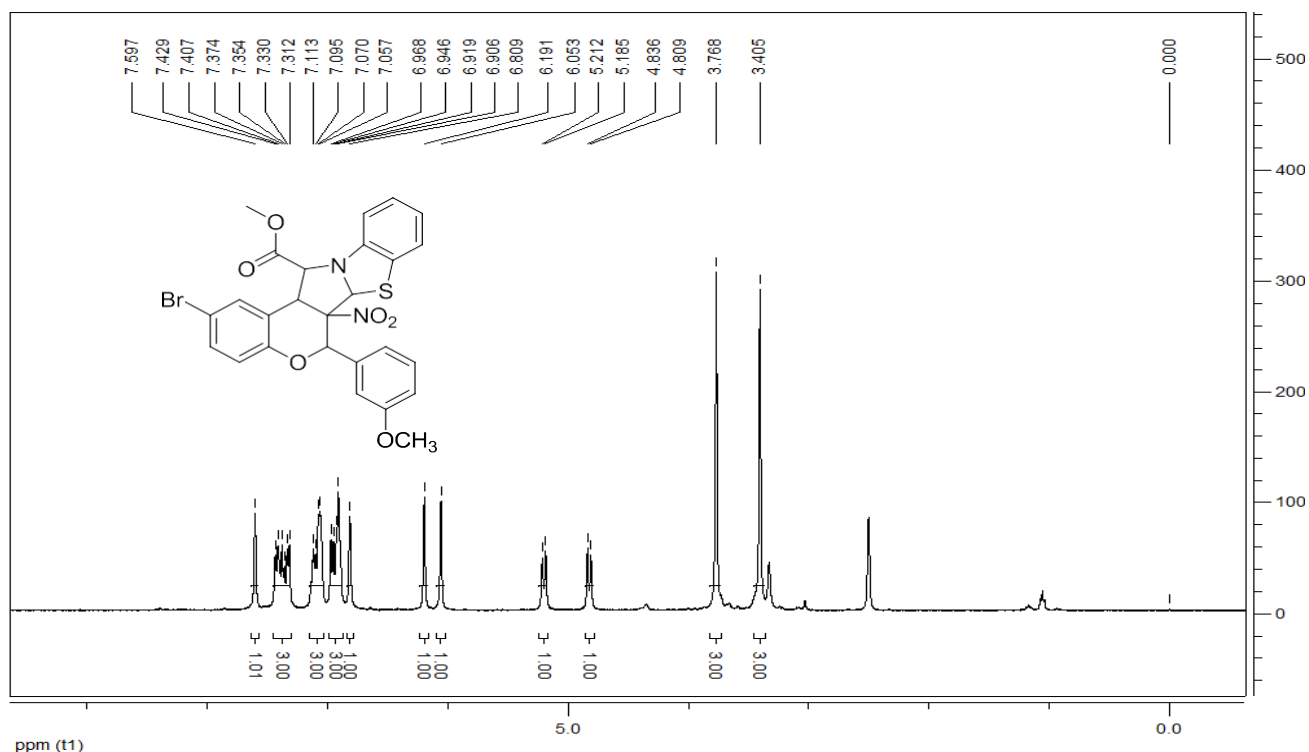


**methyl 2-bromo-6a-nitro-6-(p-tolyl)-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazole-13-carboxylate (4a):** Light yellow solid, 72%, m.p. 159~160°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.60 (s, 1H, ArH), 7.41 (d, 1H, ArH), 7.31 (d, 1H, ArH), 7.27~7.20 (m, 4H, ArH), 7.11~7.06 (m, 2H, ArH), 6.94 (d, 1H, ArH), 6.89 (d, 1H, ArH), 6.13 (s, 1H, CH), 6.04 (s, 1H, CH), 5.18 (d, *J* = 10.8 Hz, 1H, CH), 4.82 (d, *J* = 10.8 Hz, 1H, CH), 3.41 (s, 3H, OCH<sub>3</sub>), 2.34 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 171.2, 152.4, 149.0, 139.8, 132.9, 132.9, 132.0, 130.7, 130.5, 129.7, 127.7, 126.6, 125.9, 122.3, 121.3, 119.3, 116.7, 113.4, 96.3, 77.7, 77.0, 73.2, 52.6, 44.4, 43.5, 21.3; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>26</sub>H<sub>21</sub>BrN<sub>2</sub>O<sub>5</sub>S ([M+H]<sup>+</sup>): 553.0433. Found: 553.0418; IR (KBr) ν: 3079, 30038, 2964, 1785, 1668, 1570, 1478, 1448, 1270, 1028, 927, 908, 752 cm<sup>-1</sup>.

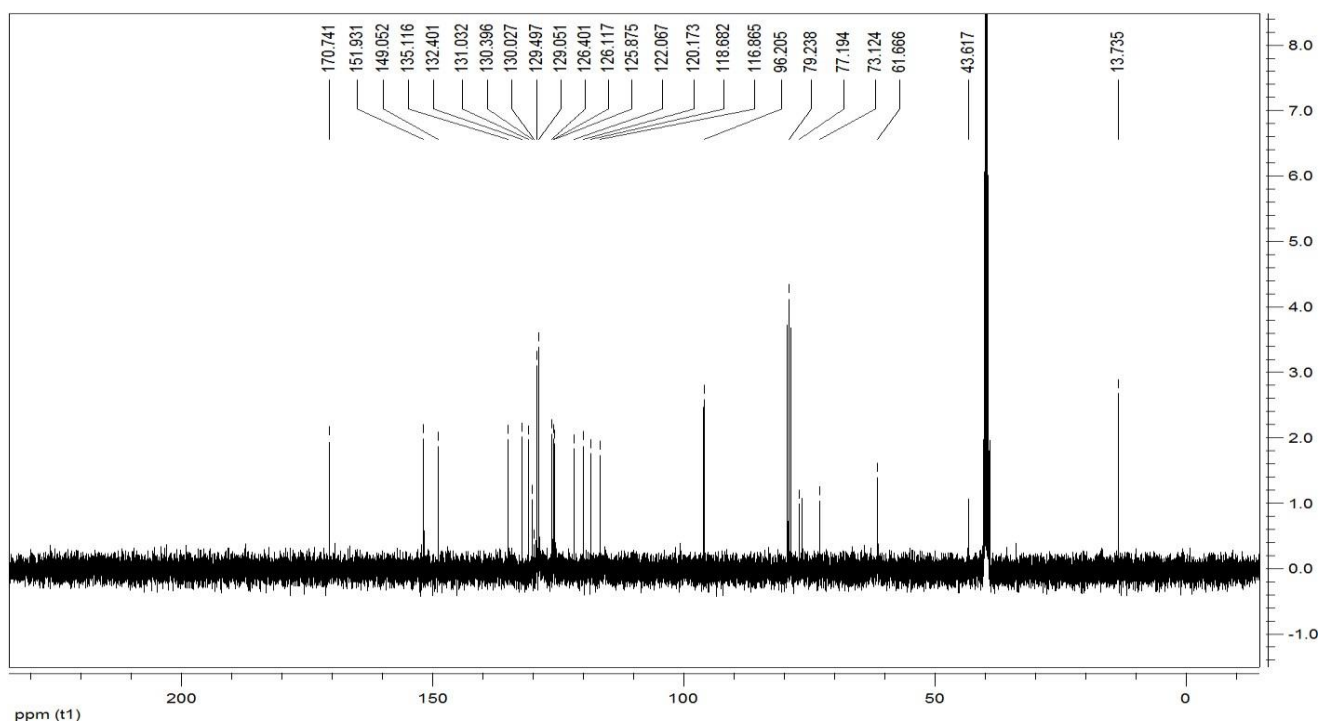
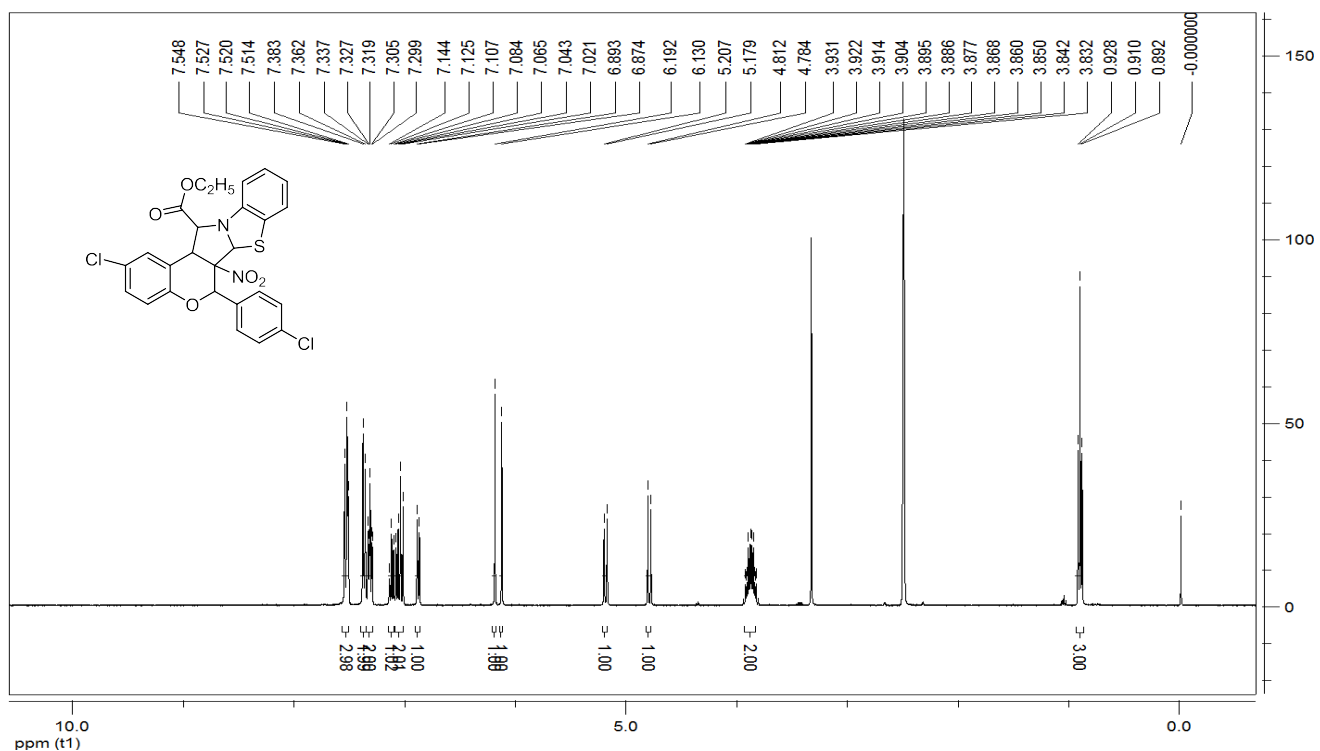




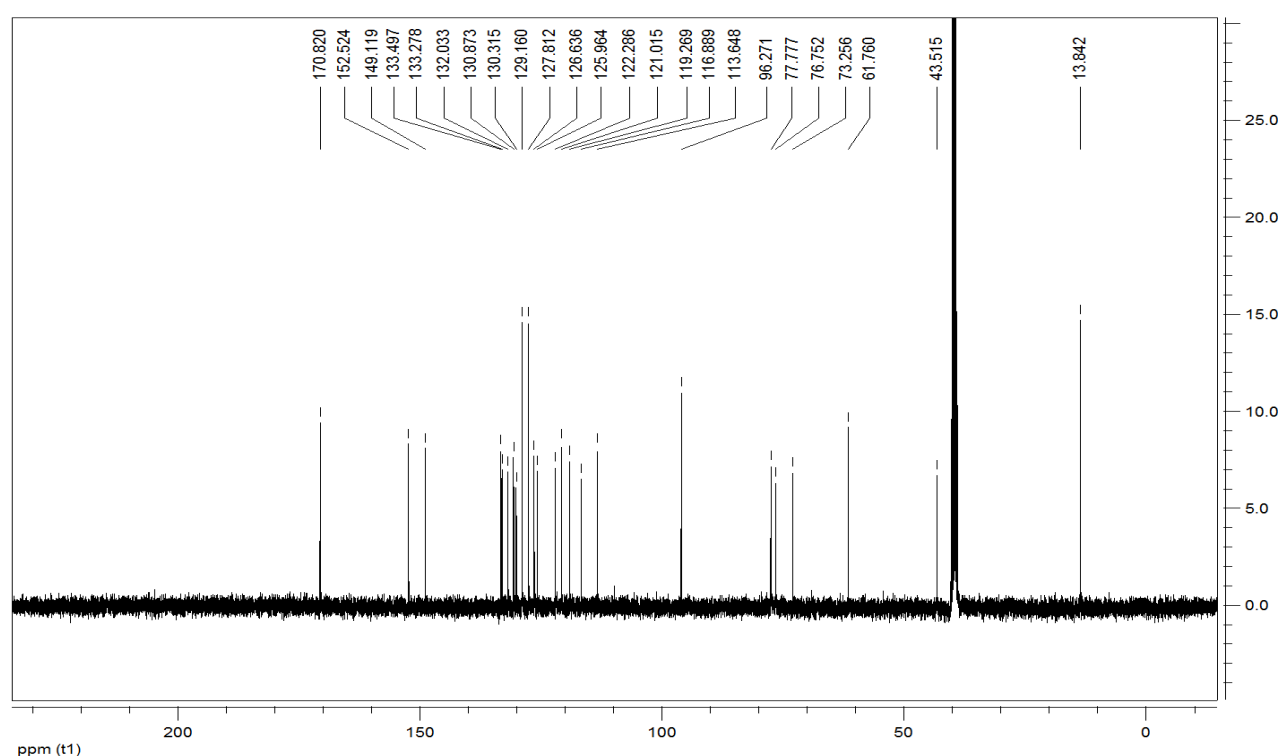
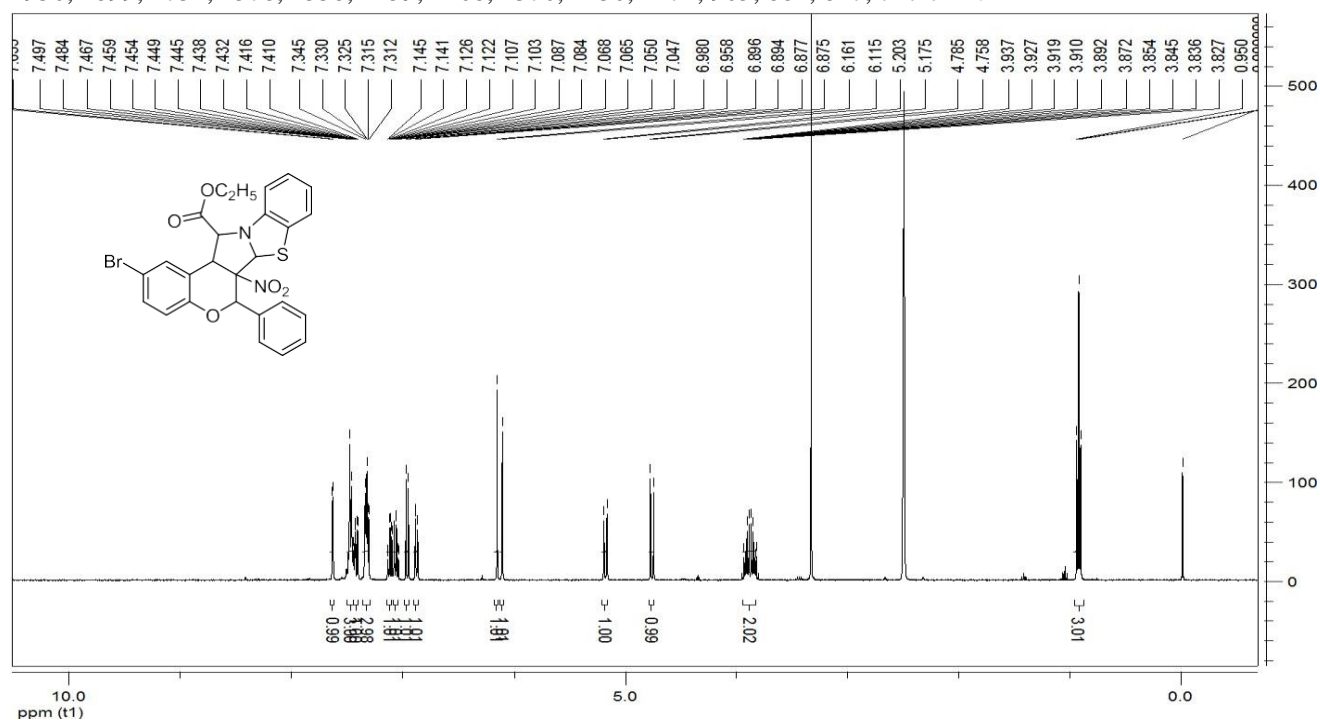
**methyl 2-bromo-6-(3-methoxyphenyl)-6a-nitro-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]-pyrrolo[2,1-b]thiazole-13-carboxylate (4b):** Light yellow solid, 69%, m.p. 162~163°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.60 (s, 1H, ArH), 7.43~7.31 (m, 3H, ArH), 7.11~7.06 (m, 3H, ArH), 6.97~6.91 (m, 3H, ArH), 6.81 (s, 1H, ArH), 6.19 (s, 1H, CH), 6.05 (s, 1H, CH), 5.20 (d, *J* = 10.8 Hz, 1H, CH), 4.82 (d, *J* = 10.8 Hz, 1H, CH), 3.77 (s, 3H, OCH<sub>3</sub>), 3.40 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 171.2, 159.6, 152.3, 149.0, 135.0, 132.9, 132.7, 132.0, 130.7, 130.3, 126.6, 125.8, 122.3, 121.3, 120.1, 119.4, 116.6, 115.4, 113.5, 96.2, 77.4, 77.0, 73.2, 55.5, 52.5, 43.5 ; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>26</sub>H<sub>21</sub>BrN<sub>2</sub>O<sub>6</sub>S ([M+H]<sup>+</sup>): 569.0382. Found: 569.0370; IR (KBr) ν: 3061, 2987, 2914, 2932, 2875, 1744, 1577, 1444, 1402, 1386, 1336, 1230, 1098, 785, 765 cm<sup>-1</sup>.



**ethyl 2-chloro-6-(4-chlorophenyl)-6a-nitro-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]-pyrrolo[2,1-b]thiazole-13-carboxylate (4c):** yellow solid, 72%, m.p. 164~165°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.55~7.51 (m, 3H, ArH), 7.37 (d, *J* = 8.4 Hz, 2H, ArH), 7.34~7.30 (m, 2H, ArH), 7.14~7.11 (m, 1H, ArH), 7.08~7.02 (m, 2H, ArH), 6.88 (d, *J* = 7.6 Hz, 1H, ArH), 6.19 (s, 1H, CH), 6.13 (s, 1H, CH), 5.19 (d, *J* = 11.2 Hz, 1H, CH), 4.80 (d, *J* = 10.8 Hz, 1H, CH), 3.93~3.83 (m, 2H, CH<sub>2</sub>), 0.91 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 170.7, 151.9, 149.0, 135.1, 132.4, 131.0, 130.3, 130.0, 129.4, 129.0, 126.4, 126.1, 125.8, 122.0, 120.1, 118.6, 116.8, 96.2, 79.2, 77.1, 73.1, 61.6, 43.6, 13.7; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>26</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S ([M+H]<sup>+</sup>): 543.0470. Found: 543.0478; IR (KBr) ν: 3052, 2980, 2924, 1733, 1590, 1545, 1485, 1459, 1309, 1245, 1203, 1087, 1021, 941, 910, 857, 762 cm<sup>-1</sup>.

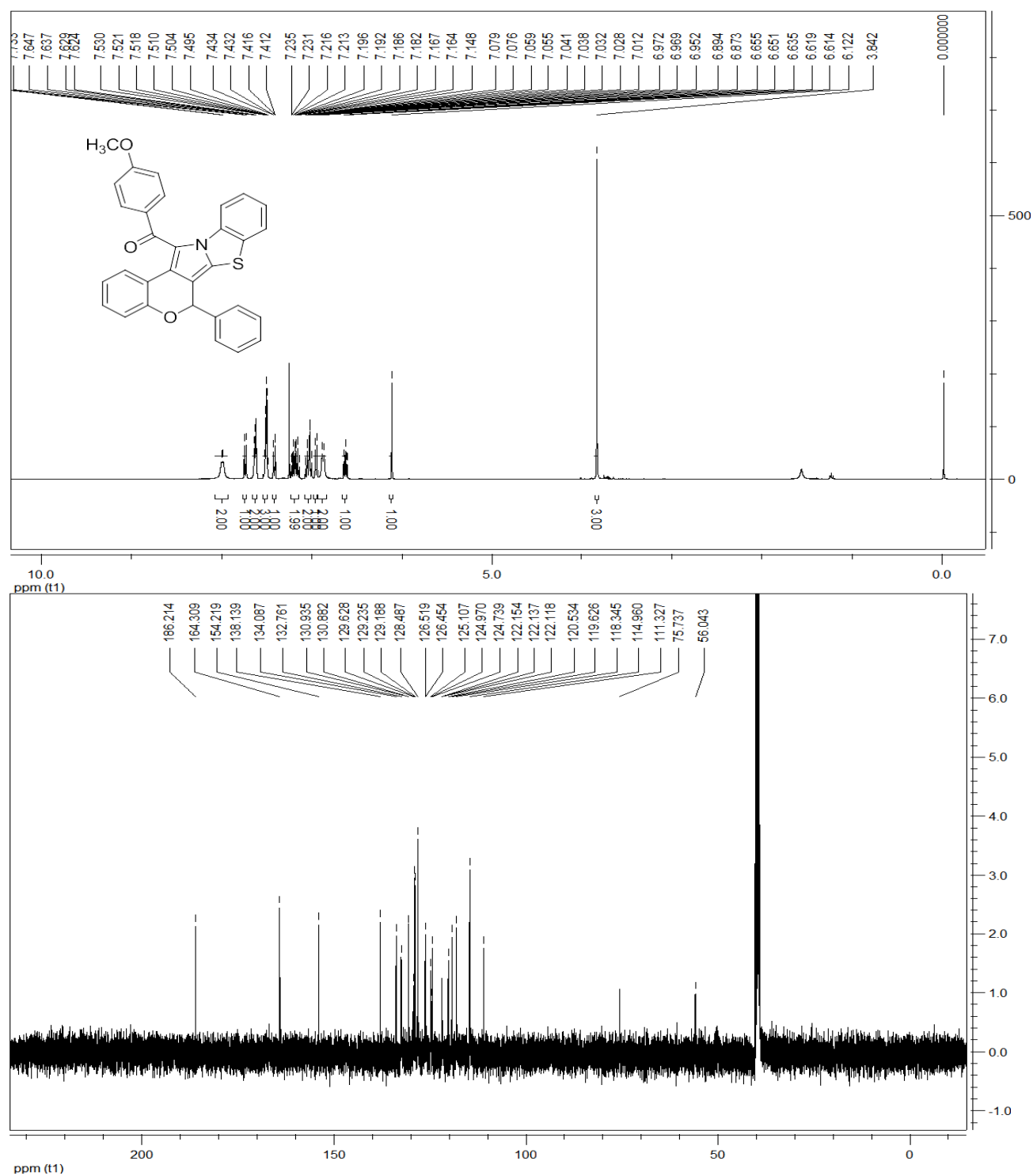


**ethyl 2-bromo-6a-nitro-6-phenyl-6a,6b,13,13a-tetrahydro-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazole-13-carboxylate (4d):** yellow solid, 70%, m.p. 167~168 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.64 (d, *J* = 2.4 Hz, 1H, ArH), 7.50~7.44 (m, 3H, ArH), 7.42 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H, ArH), 7.34~7.31 (m, 3H, ArH), 7.14~7.10 (m, 1H, ArH), 7.09~7.05 (m, 1H, ArH), 6.97 (d, *J* = 8.8 Hz, 1H, ArH), 6.90~6.88 (m, 1H, ArH), 6.16 (s, 1H, CH), 6.12 (s, 1H, CH), 5.19 (d, *J* = 11.2 Hz, 1H, CH), 4.77 (d, *J* = 10.8 Hz, 1H, CH), 3.94~3.83 (m, 2H, CH<sub>2</sub>), 0.93 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 170.8, 152.5, 149.1, 133.4, 133.2, 132.0, 130.8, 130.3, 129.1, 127.8, 126.6, 125.9, 122.2, 121.0, 119.2, 116.8, 113.6, 96.2, 77.7, 76.7, 73.2, 61.7, 43.5, 13.8; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>26</sub>H<sub>21</sub>BrN<sub>2</sub>O<sub>5</sub>S ([M+H]<sup>+</sup>): 553.0427. Found: 553.0411; IR (KBr) ν: 3068, 2982, 2930, 2899, 1732, 1578, 1538, 1459, 1408, 1376, 1230, 1171, 905, 882, 817, 747 cm<sup>-1</sup>.

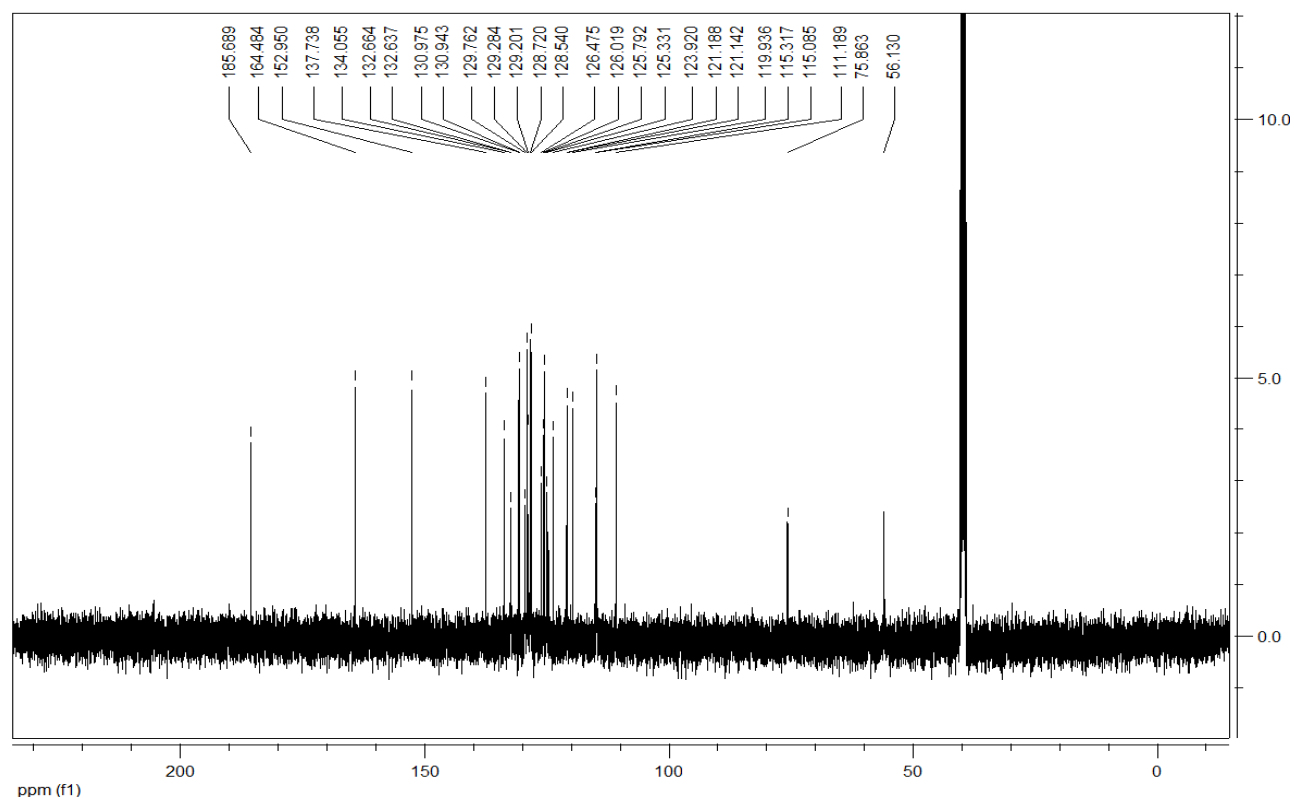
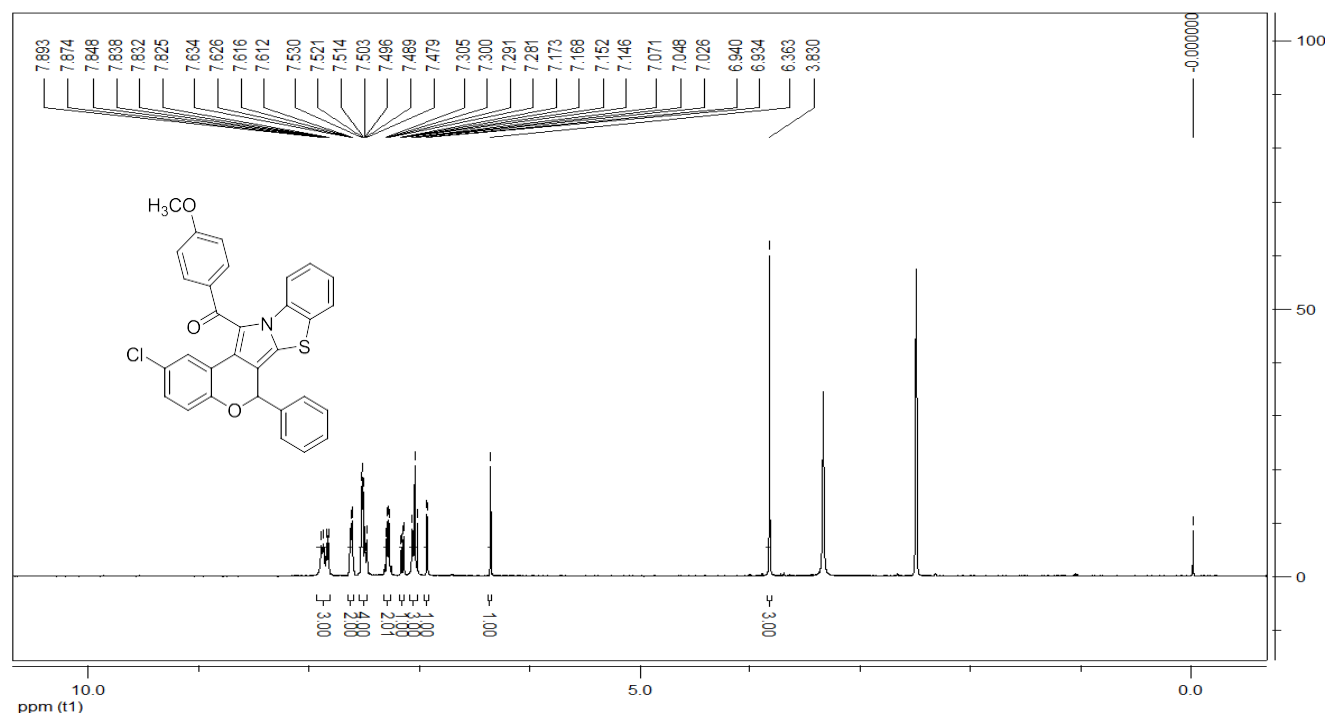


**(4-methoxyphenyl)(6-phenyl-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)methanone (5a):**

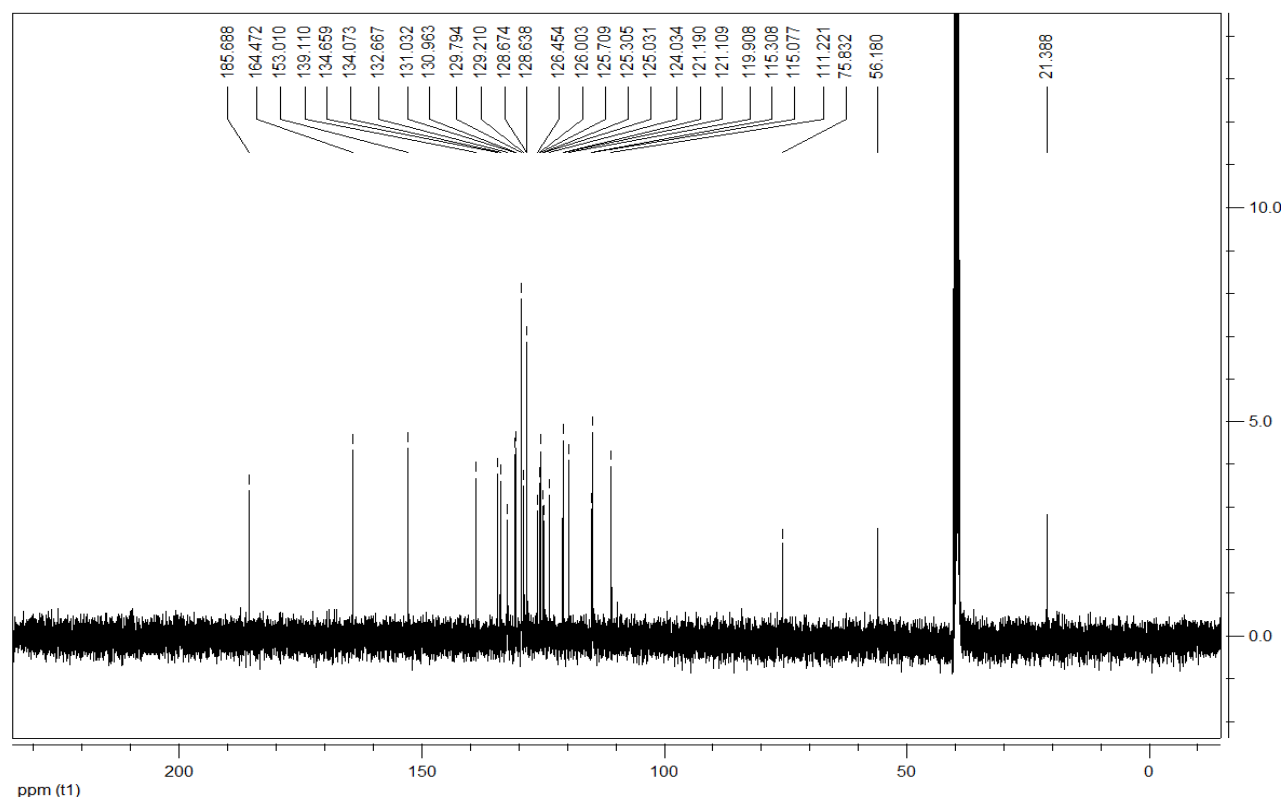
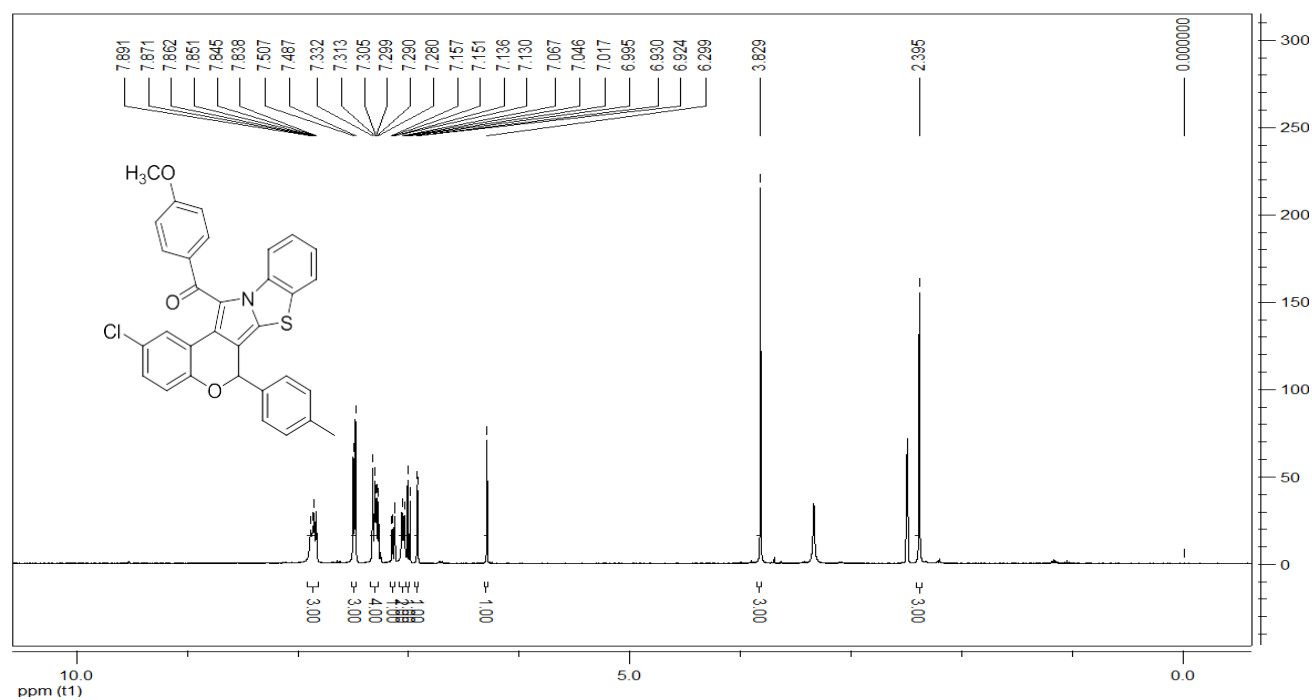
Yellow solid, 67%, m.p. 235~236°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.01~7.99 (m, 2H, ArH), 7.74 (d, *J* = 8.0 Hz, 1H, ArH), 7.65~7.62 (m, 2H, ArH), 7.53~7.50 (m, 3H, ArH), 7.43~7.41 (m, 1H, ArH), 7.24~7.15 (m, 2H, ArH), 7.08~7.01 (m, 2H, ArH), 6.97~6.95 (m, 1H, ArH), 6.88 (d, *J* = 7.6 Hz, 2H, ArH), 6.66~6.61 (m, 1H, ArH), 6.12 (s, 1H, CH), 3.84 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 186.2, 164.3, 154.2, 138.1, 134.0, 132.7, 130.9, 130.8, 129.6, 129.2, 129.1, 128.4, 126.5, 126.4, 125.1, 124.9, 124.7, 122.1, 122.1, 122.1, 120.5, 119.6, 118.3, 114.9, 111.3, 75.7, 56.0; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>21</sub>NO<sub>3</sub>S ([M+H]<sup>+</sup>): 488.1320. Found: 488.0436; IR (KBr) ν: 3064, 2962, 2876, 1622, 1561, 1501, 1455, 1383, 1293, 1251, 1212, 1025, 915, 827, 746 cm<sup>-1</sup>.



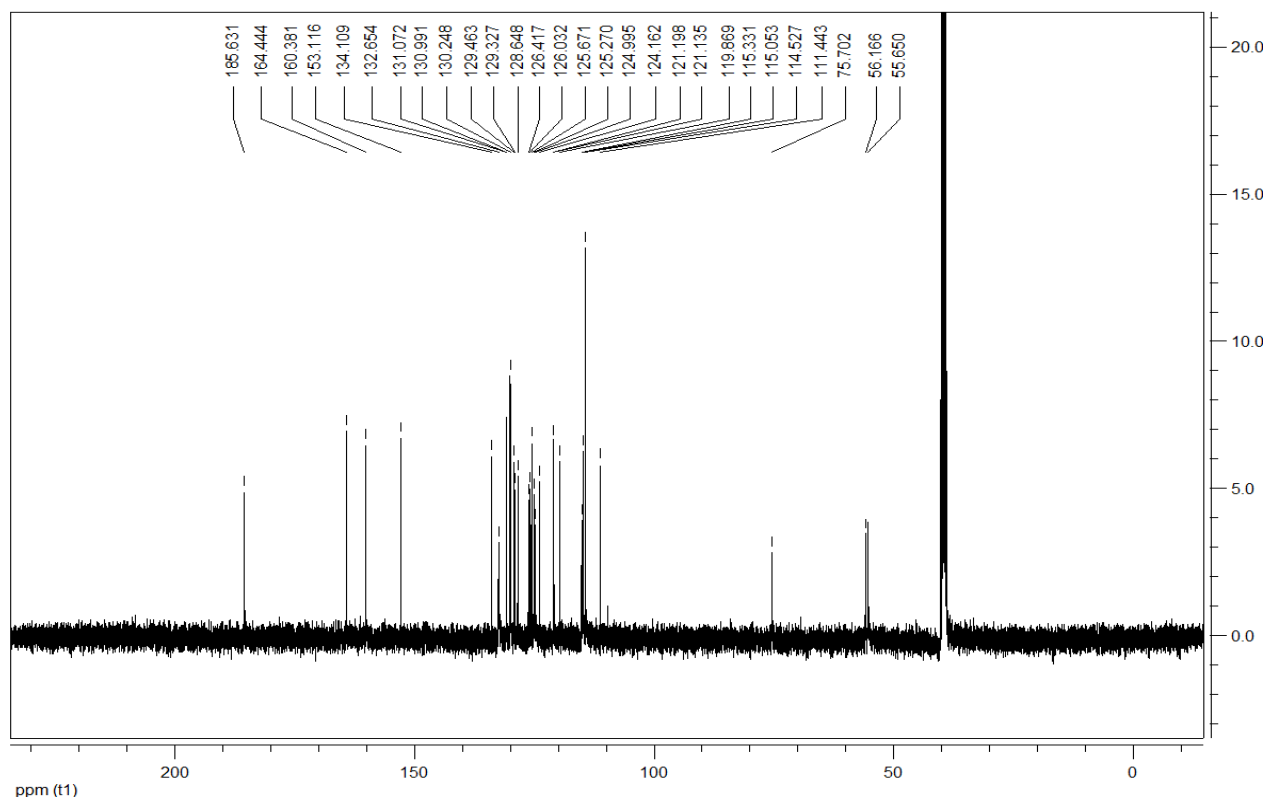
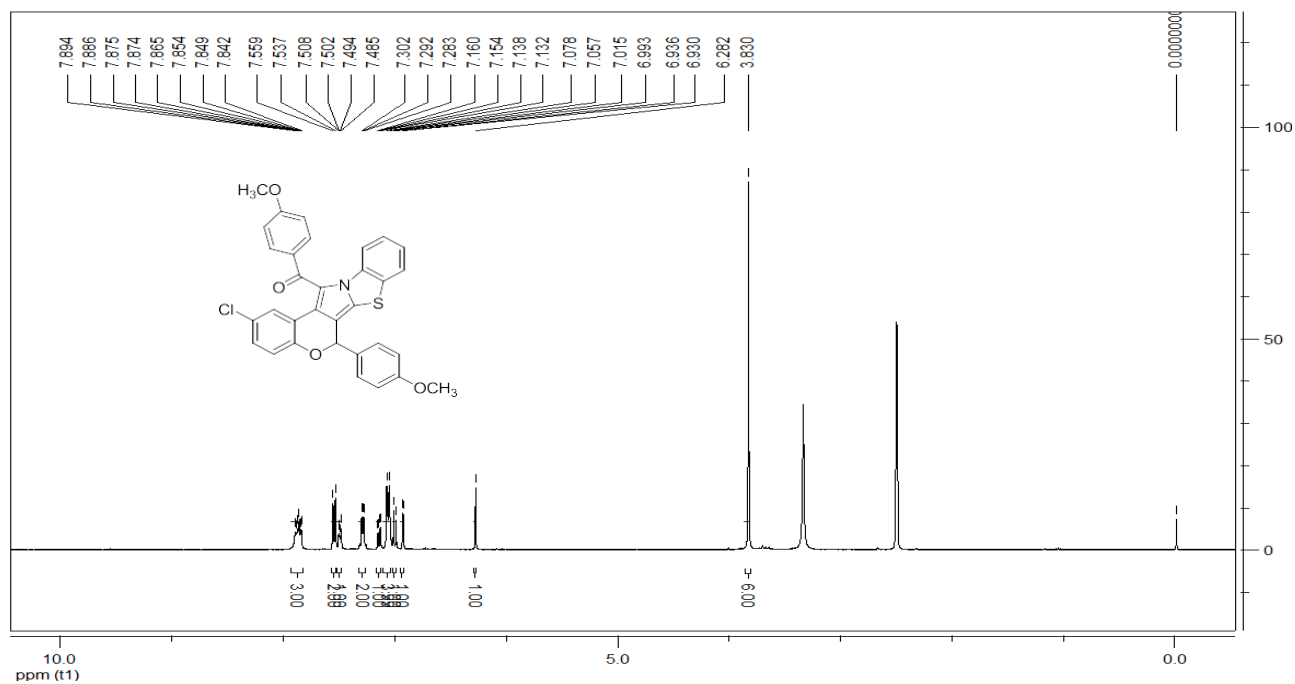
**(2-chloro-6-phenyl-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl)methanone** (**5b**): Yellow solid, 77%, m.p. 242~243°C;  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 7.89~7.82 (m, 3H, ArH), 7.63~7.61 (m, 2H, ArH), 7.53~7.48 (m, 4H, ArH), 7.30~7.28 (m, 2H, ArH), 7.17~7.15 (m, 1H, ArH), 7.07~7.03 (m, 3H, ArH), 6.94 (d,  $J = 2.4$  Hz, 1H, ArH), 6.38 (s, 1H, CH), 3.83 (s, 3H,  $\text{OCH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$ : 185.6, 164.4, 152.9, 137.7, 134.0, 132.6, 132.6, 130.9, 130.9, 129.7, 129.2, 129.2, 128.7, 128.5, 126.4, 126.0, 125.7, 125.3, 123.9, 121.1, 121.1, 119.9, 115.3, 115.0, 111.1, 75.8, 56.1; MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{31}\text{H}_{20}\text{ClNO}_3\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 522.0931. Found: 521.9903; IR (KBr)  $\nu$ : 3064, 3007, 2962, 2836, 1603, 1568, 1501, 1455, 1371, 1337, 1291, 1031, 941, 908, 725  $\text{cm}^{-1}$ .



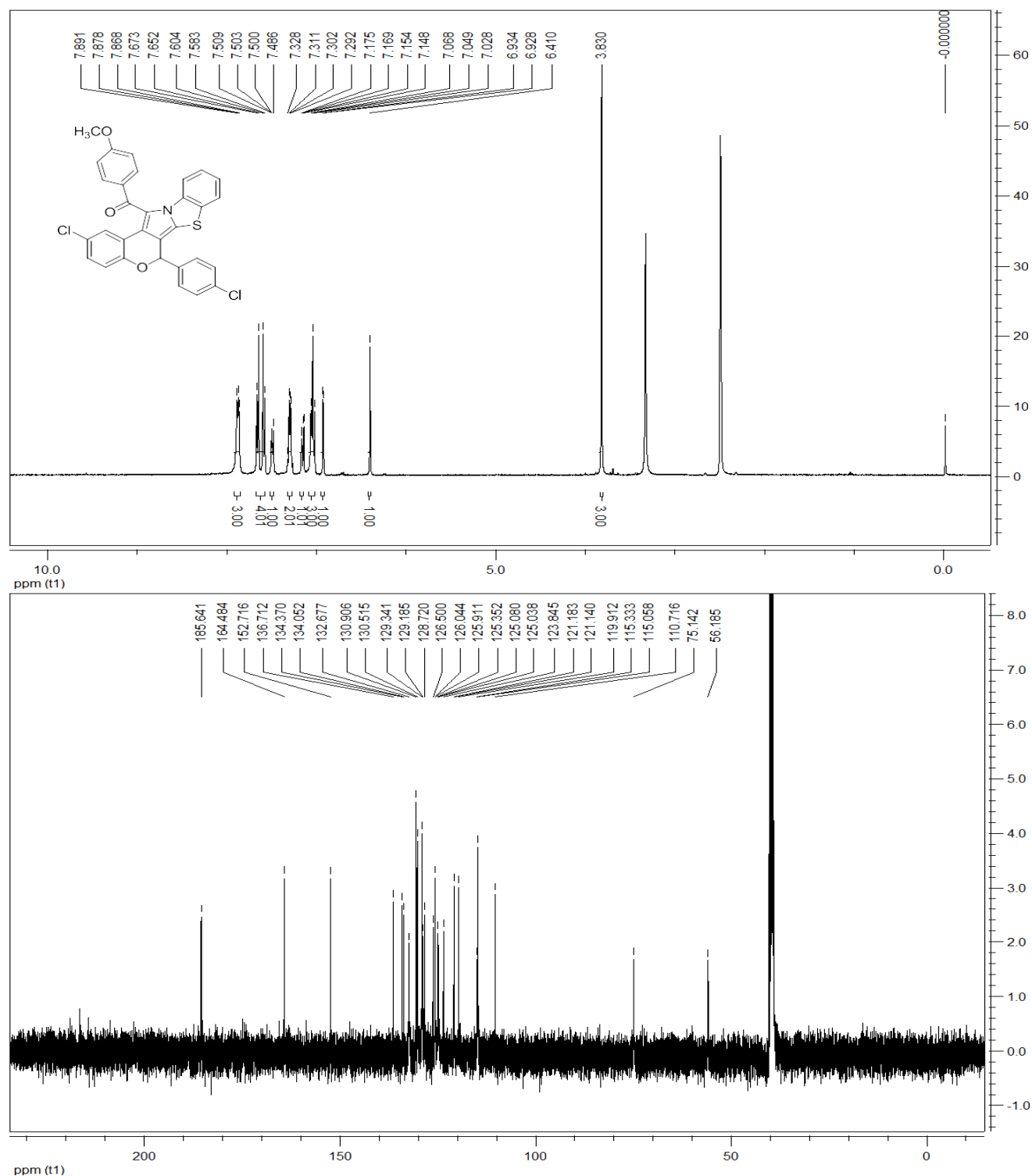
**(2-chloro-6-(p-tolyl)-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl)methanone (5c):** Yellow solid, 79%, m.p. 267~268°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.89~7.84 (m, 3H, ArH), 7.51~7.48 (m, 3H, ArH), 7.33~7.28 (m, 4H, ArH), 7.16~7.13 (m, 1H, ArH), 7.07~7.05 (m, 2H, ArH), 7.02~7.00 (m, 1H, ArH), 6.93 (d, *J* = 2.4 Hz, 1H, ArH), 6.30 (s, 1H, CH), 3.83 (s, 3H, OCH<sub>3</sub>), 2.40 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 185.6, 164.4, 153.0, 139.1, 134.6, 134.0, 132.6, 131.0, 130.9, 129.7, 129.2, 128.6, 128.6, 126.4, 126.0, 125.7, 125.3, 125.0, 124.0, 121.1, 121.1, 119.9, 115.3, 115.0, 111.2, 75.8, 56.1, 21.3; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>22</sub>ClNO<sub>3</sub>S ([M+H]<sup>+</sup>): 536.1087. Found: 536.0043; IR (KBr) ν: 3008, 2962, 2851, 1620, 1598, 1565, 1462, 1415, 1371, 1336, 1255, 1026, 972, 854 cm<sup>-1</sup>.



**(2-chloro-6-(4-methoxyphenyl)-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl)methanone (5d):** Yellow solid, 83%, m.p. 259~260 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.89~7.84 (m, 3H, ArH), 7.54 (d, *J* = 8.8 Hz, 2H, ArH), 7.51~7.48 (m, 1H, ArH), 7.30~7.28 (m, 2H, ArH), 7.16~7.13 (m, 1H, ArH), 7.08~7.06 (m, 4H, ArH), 7.02~6.99 (m, 1H, ArH), 6.93 (d, *J* = 2.4 Hz, 1H, ArH), 6.28 (s, 1H, CH), 3.83 (s, 6H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 185.6, 164.4, 160.3, 153.1, 134.1, 132.6, 131.0, 130.9, 130.2, 129.4, 129.3, 128.6, 126.4, 126.0, 125.6, 125.2, 124.9, 124.1, 121.1, 121.1, 119.8, 115.3, 115.0, 114.5, 111.4, 75.7, 56.1, 55.6; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>22</sub>ClNO<sub>4</sub>S ([M+H]<sup>+</sup>): 552.1036. Found: 551.9908; IR (KBr) ν: 3003, 2933, 2839, 1608, 1557, 1513, 1493, 1457, 1418, 1290, 1031, 946, 907, 722 cm<sup>-1</sup>.

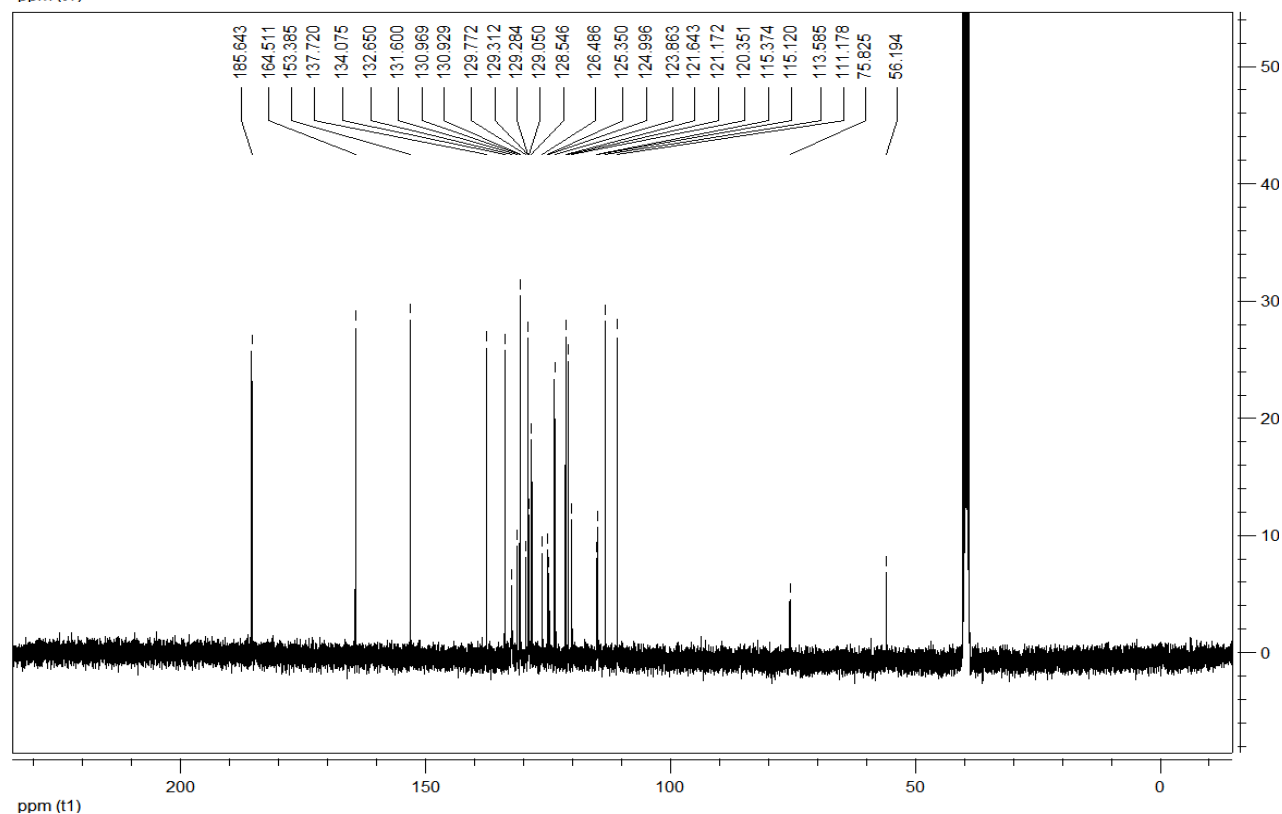
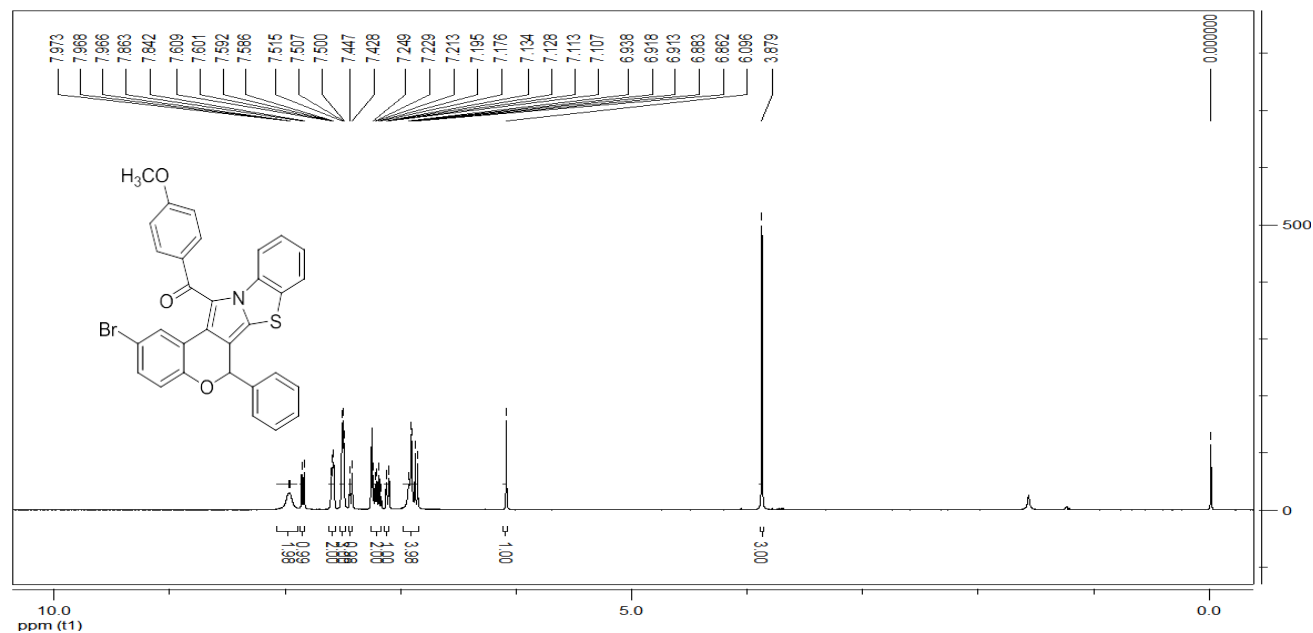


**(2-chloro-6-(4-chlorophenyl)-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl) methanone (5e):** Yellow solid, 81%, m.p. 259~260°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.89~7.87 (m, 3H, ArH), 7.67~7.58 (m, 4H, ArH), 7.51~7.49 (m, 1H, ArH), 7.33~7.29 (m, 2H, ArH), 7.18~7.14 (m, 1H, ArH), 7.07~7.03 (m, 3H, ArH), 6.93 (d, *J* = 2.4 Hz, 1H, ArH), 6.41 (s, 1H, CH), 3.83 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ: 185.6, 164.4, 152.7, 136.7, 134.3, 134.0, 132.6, 130.9, 130.5, 129.3, 129.1, 128.7, 126.5, 126.0, 125.9, 125.3, 125.0, 123.8, 121.1, 121.1, 119.9, 115.3, 115.0, 110.7, 75.1, 56.1; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>31</sub>H<sub>19</sub>Cl<sub>2</sub>NO<sub>3</sub>S ([M+H]<sup>+</sup>): 556.0541. Found: 555.9433; IR (KBr) ν: 3002, 2936, 2840, 1606, 1590, 1492, 1455, 1413, 1359, 1289, 1254, 1030, 948, 895, 726 cm<sup>-1</sup>.

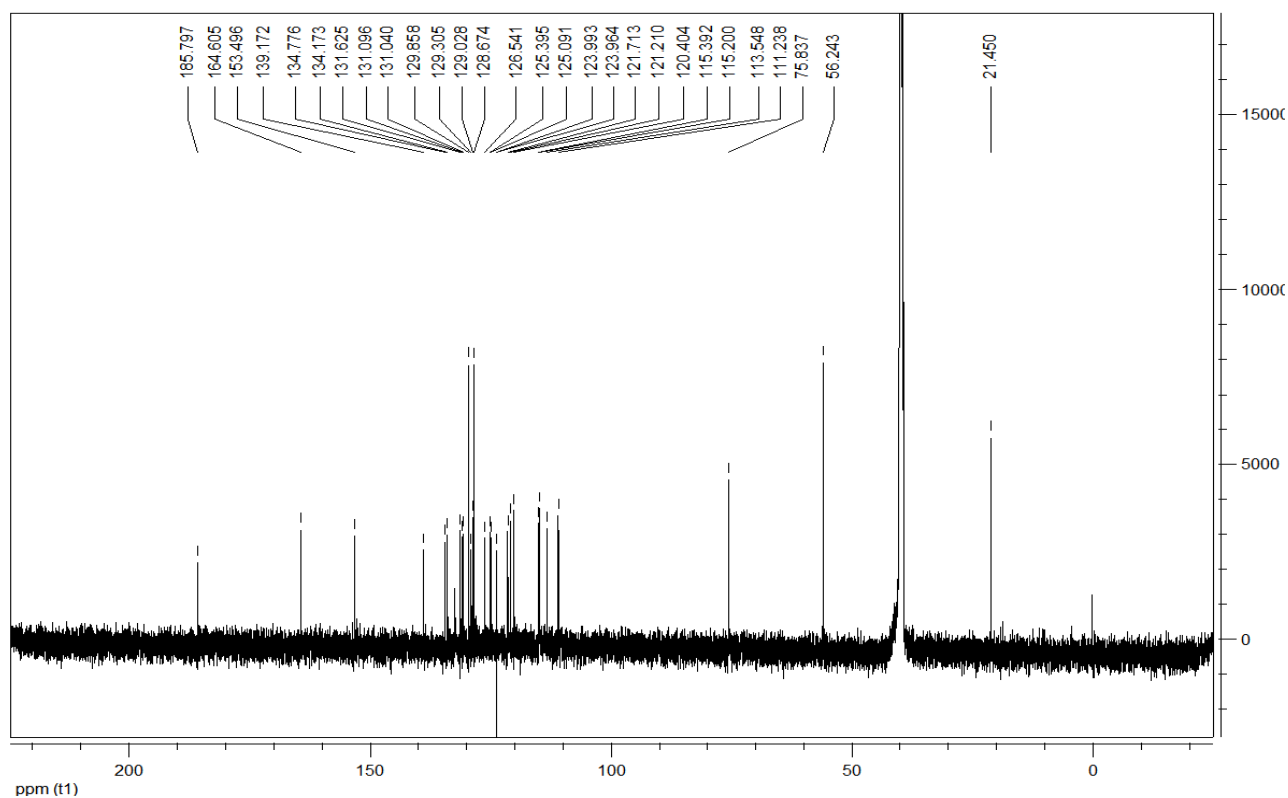
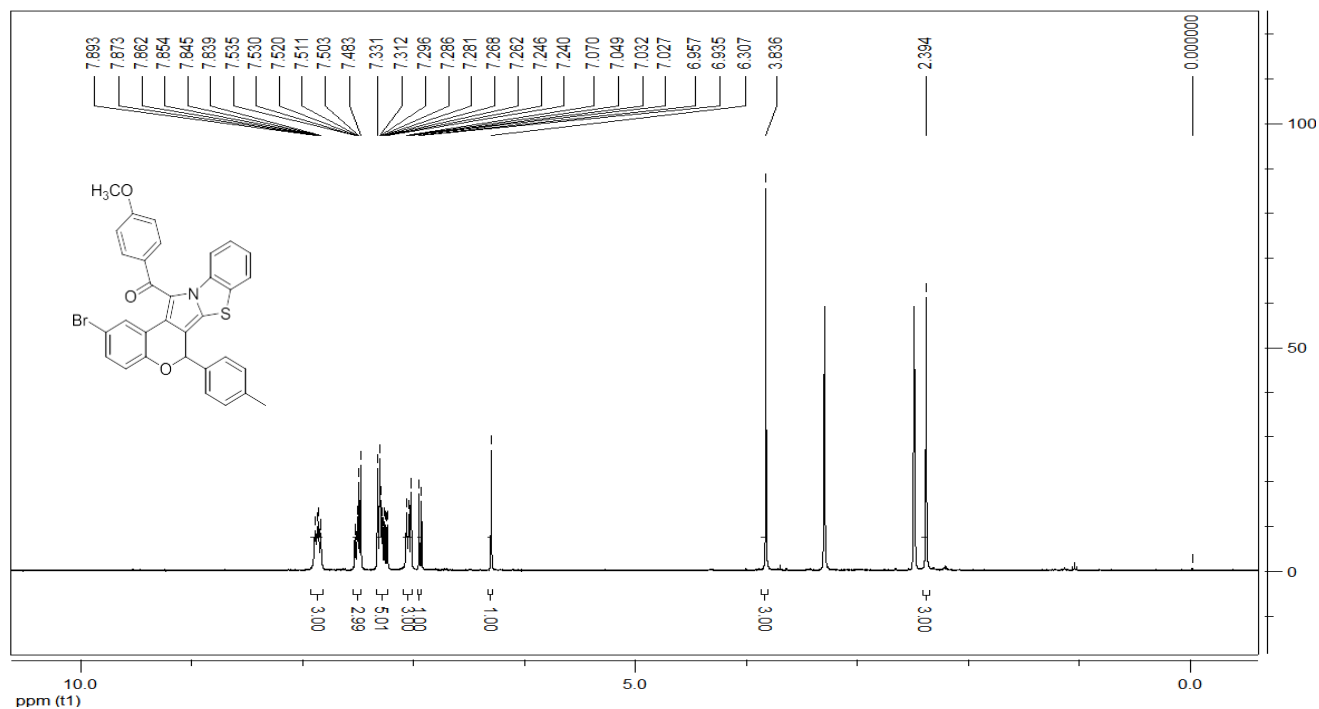




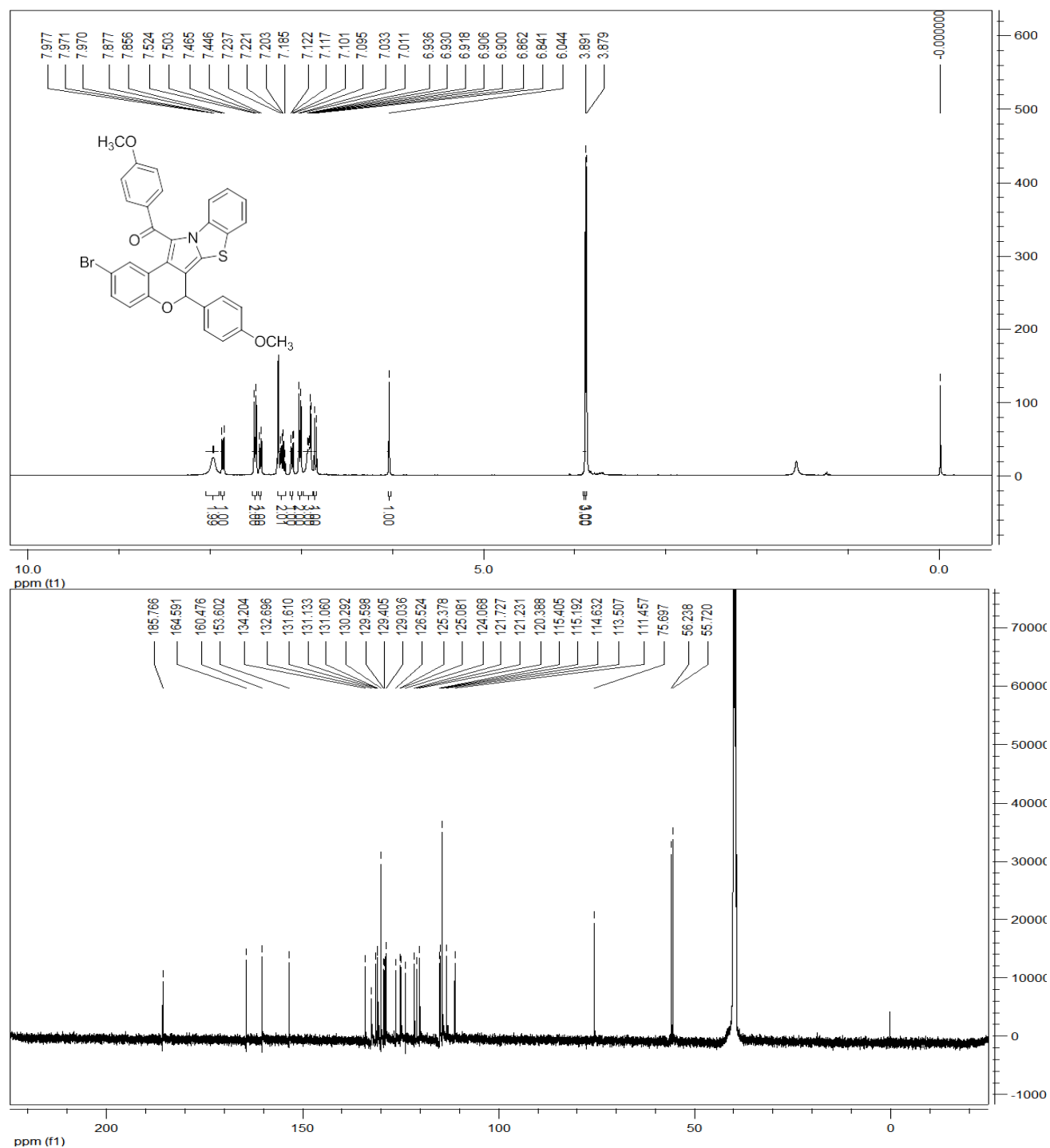
**(2-bromo-6-phenyl-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl)methanone (5f):** Yellow solid, 74%, m.p. 237~238 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.97~7.96 (m, 2H, ArH), 7.85 (d,  $J = 8.4$  Hz, 1H, ArH), 7.61~7.59 (m, 2H, ArH), 7.52~7.50 (m, 3H, ArH), 7.45~7.43 (m, 1H, ArH), 7.25~7.18 (m, 2H, ArH), 7.13~7.11 (m, 1H, ArH), 6.94~6.86 (m, 4H, ArH), 6.10 (s, 1H, CH), 3.88 (s, 3H,  $\text{OCH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : 185.6, 164.5, 153.3, 137.7, 134.0, 132.6, 131.6, 130.9, 130.9, 129.7, 129.3, 129.2, 129.0, 128.5, 126.4, 125.3, 124.9, 123.8, 121.6, 121.1, 120.3, 115.3, 115.1, 113.5, 111.1, 75.8, 56.2; MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{31}\text{H}_{20}\text{BrNO}_3\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 566.0426. Found: 566.0175; IR (KBr)  $\nu$ : 3063, 3006, 2980, 2835, 1600, 1568, 1499, 1459, 1389, 1289, 1255, 1031, 973, 926, 762  $\text{cm}^{-1}$ .



**(2-bromo-6-(p-tolyl)-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl)methanone (5g):** Yellow solid, 75%, m.p. 271~272°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 7.89~7.84 (m, 3H, ArH), 7.54~7.48 (m, 3H, ArH), 7.33~7.24 (m, 5H, ArH), 7.07~7.03 (m, 3H, ArH), 6.95 (d, *J* = 8.8 Hz, 1H, ArH), 6.31 (s, 1H, CH), 3.84 (s, 3H, OCH<sub>3</sub>), 2.39 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ: 185.7, 164.6, 153.4, 139.1, 134.7, 134.1, 131.6, 131.0, 131.0, 129.8, 129.3, 129.0, 128.6, 126.5, 125.3, 125.0, 123.9, 123.9, 121.7, 121.2, 120.4, 115.3, 115.1, 113.5, 111.2, 75.8, 56.2, 21.4; MS (*m/z*): HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>22</sub>BrNO<sub>3</sub>S ([M+H]<sup>+</sup>): 580.0582. Found: 579.9494; IR (KBr) ν: 3006, 2950, 2837, 1619, 1596, 1460, 1411, 1369, 1298, 1026, 949, 752 cm<sup>-1</sup>.



**(2-bromo-6-(4-methoxyphenyl)-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl)methanone (5h):** Yellow solid, 81%, m.p. 256~257°C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.98~7.97 (m, 2H, ArH), 7.86 (d,  $J = 8.4$  Hz, 1H, ArH), 7.52~7.50 (m, 2H, ArH), 7.46~7.45 (m, 1H, ArH), 7.24~7.18 (m, 2H, ArH), 7.12~7.10 (m, 1H, ArH), 7.02 (d,  $J = 8.8$  Hz, 2H, ArH), 6.94~6.90 (m, 3H, ArH), 6.85 (d,  $J = 8.8$  Hz, 1H, ArH), 6.04 (s, 1H, CH), 3.89 (s, 3H,  $\text{OCH}_3$ ), 3.88 (s, 3H,  $\text{OCH}_3$ );  $^{13}\text{C NMR}$  (150 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : 185.7, 164.5, 160.4, 153.6, 134.2, 132.6, 131.6, 131.1, 131.0, 130.2, 129.5, 129.4, 129.0, 126.5, 125.3, 125.0, 124.0, 121.7, 121.2, 120.3, 115.4, 115.1, 114.6, 113.5, 111.4, 75.6, 56.2, 55.7; MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{32}\text{H}_{22}\text{BrNO}_4\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 596.0531. Found: 595.9366; IR (KBr)  $\nu$ : 3059, 3011, 29752, 2836, 1602, 151, 1489, 1461, 1335, 1214, 1025, 957, 911, 711  $\text{cm}^{-1}$ .



**(2-bromo-6-(4-chlorophenyl)-6H-benzo[d]chromeno[3',4':3,4]pyrrolo[2,1-b]thiazol-13-yl)(4-methoxyphenyl) methanone (5i):** Yellow solid, 79%, m.p. 259~260°C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.96~7.95 (m, 2H, ArH), 7.84 (d,  $J = 7.6$  Hz, 1H, ArH), 7.53~7.46 (m, 5H, ArH), 7.27~7.19 (m, 2H, ArH), 7.13~7.10 (m, 1H, ArH), 6.93~6.90 (m, 3H, ArH), 6.84 (d,  $J = 8.4$  Hz, 1H, ArH), 6.07 (s, 1H, CH), 3.87 (s, 3H,  $\text{OCH}_3$ );  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO}-d_6$ )  $\delta$ : 185.6, 164.5, 153.1, 136.7, 134.3, 134.0, 132.6, 131.6, 130.9, 130.8, 130.5, 129.3, 129.2, 129.0, 126.5, 125.4, 125.1, 123.7, 121.5, 121.2, 120.3, 115.3, 115.1, 113.7, 110.7, 75.0, 56.2; MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{31}\text{H}_{19}\text{BrClNO}_3\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 600.0036. Found: 599.8865; IR (KBr)  $\nu$ : 3005, 2954, 2836, 1619, 1596, 1567, 1480, 1410, 1334, 1216, 1023, 971, 891, 762  $\text{cm}^{-1}$ .

