Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Molecular diversity of acid promoted domino reaction of 3-hydroxy-3-(indol-3-yl)indolin-2-ones and cyclic mercapto-substituted β-enamino esters

Liu-Na Pan, Qing Wang,* Jing Sun, Quan-Shun Sun, Chao-Guo Yan*

Supporting Information

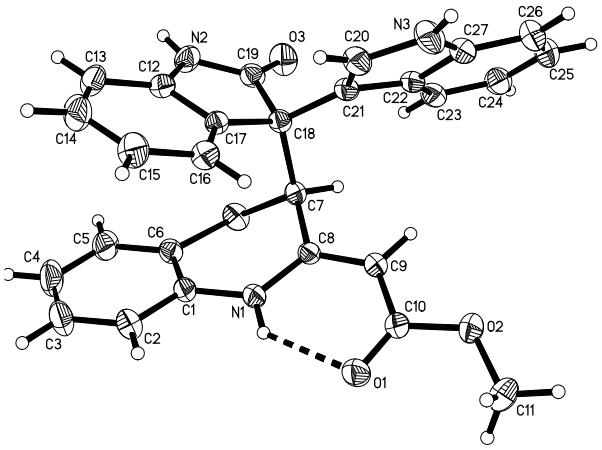


Fig. s1 ORTEP drawing (30%) of the crystal structure of **3a**

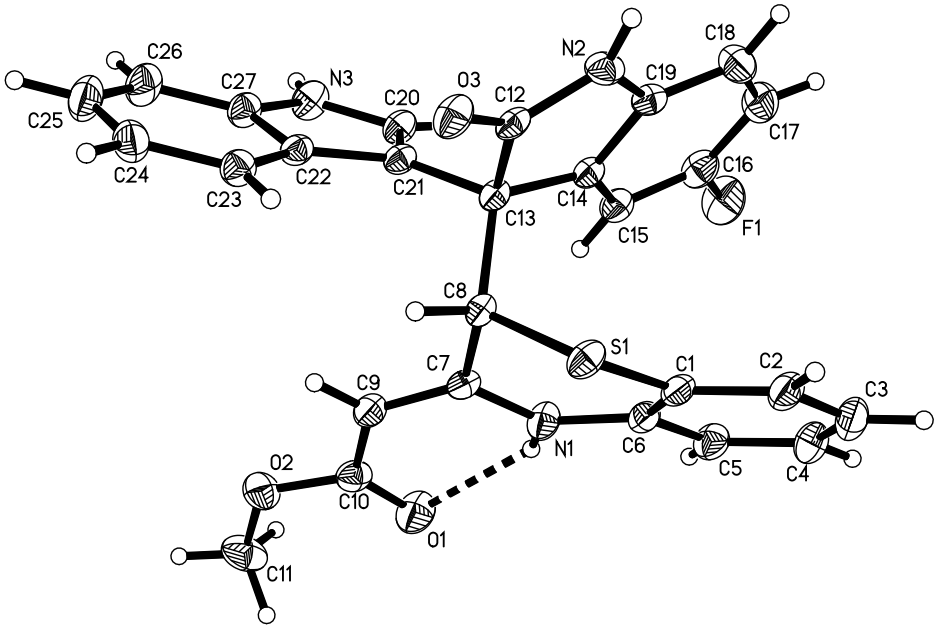


Fig. s2 ORTEP drawing (30%) of the crystal structure of **3d**

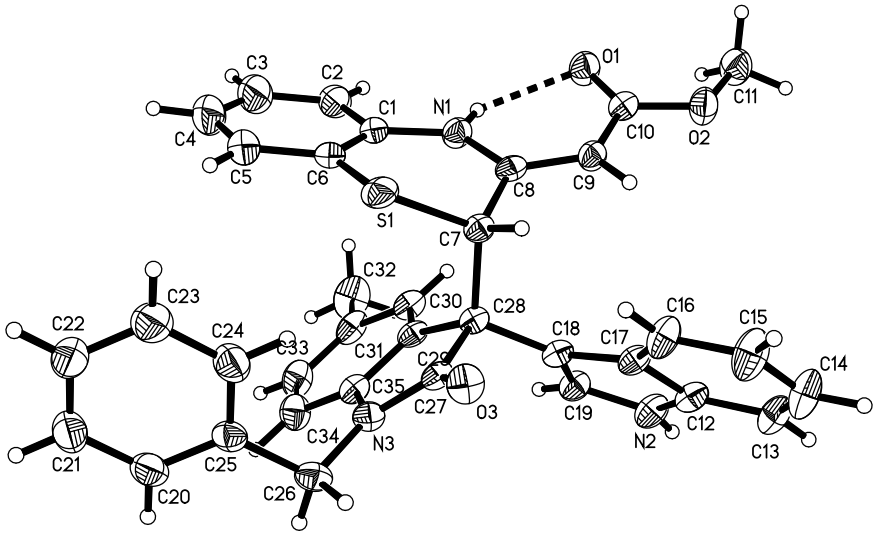


Fig. s3 ORTEP drawing (30%) of the crystal structure of **3f**

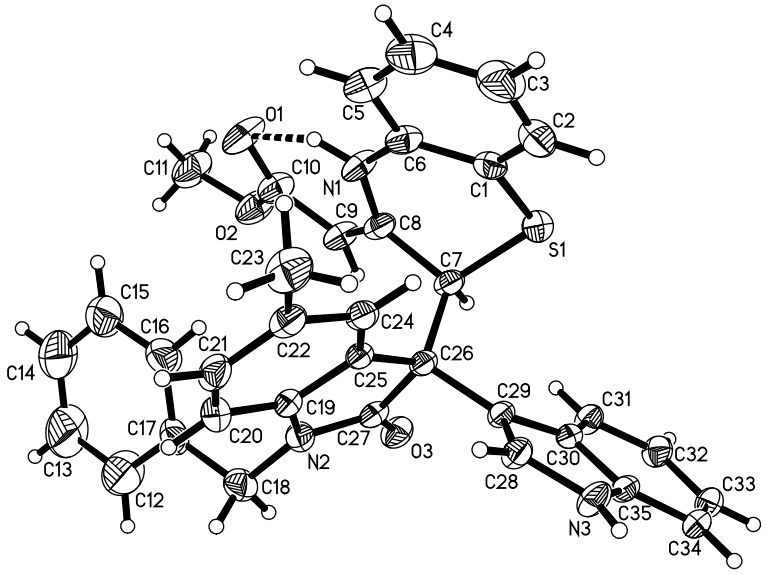


Fig. s4 ORTEP drawing (30%) of the crystal structure of **3f'**

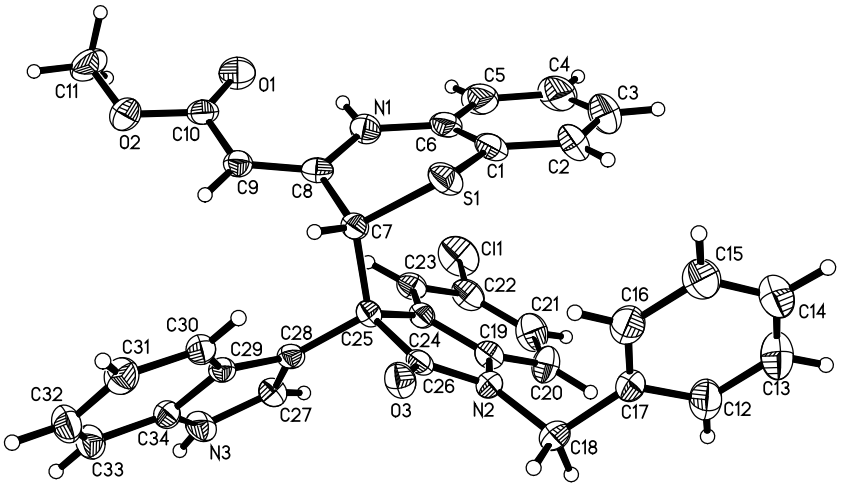


Fig. s5 ORTEP drawing (30%) of the crystal structure of **3g**

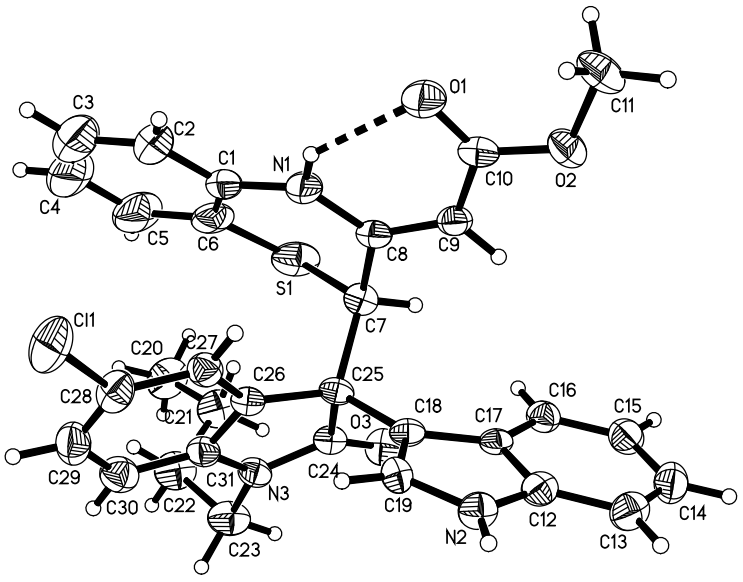


Fig. s6 ORTEP drawing (30%) of the crystal structure of **3h**

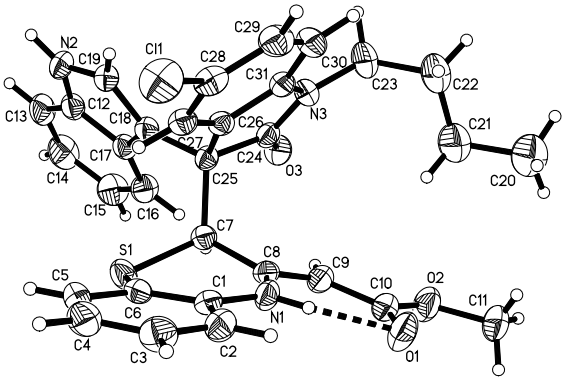


Fig. s7 ORTEP drawing (30%) of the crystal structure of **3h'**

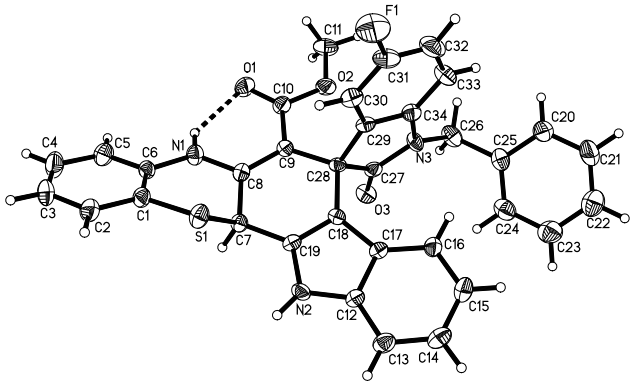


Fig. s8 ORTEP drawing (30%) of the crystal structure of **4d**

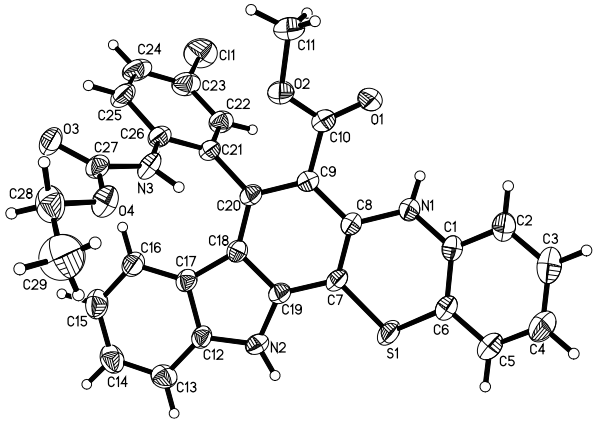


Fig. s9 ORTEP drawing (30%) of the crystal structure of **5c**

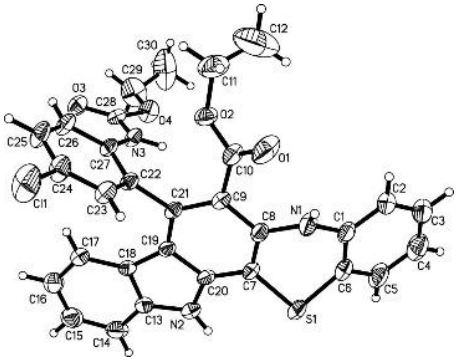


Fig. s10 ORTEP drawing (30%) of the crystal structure of **5f**

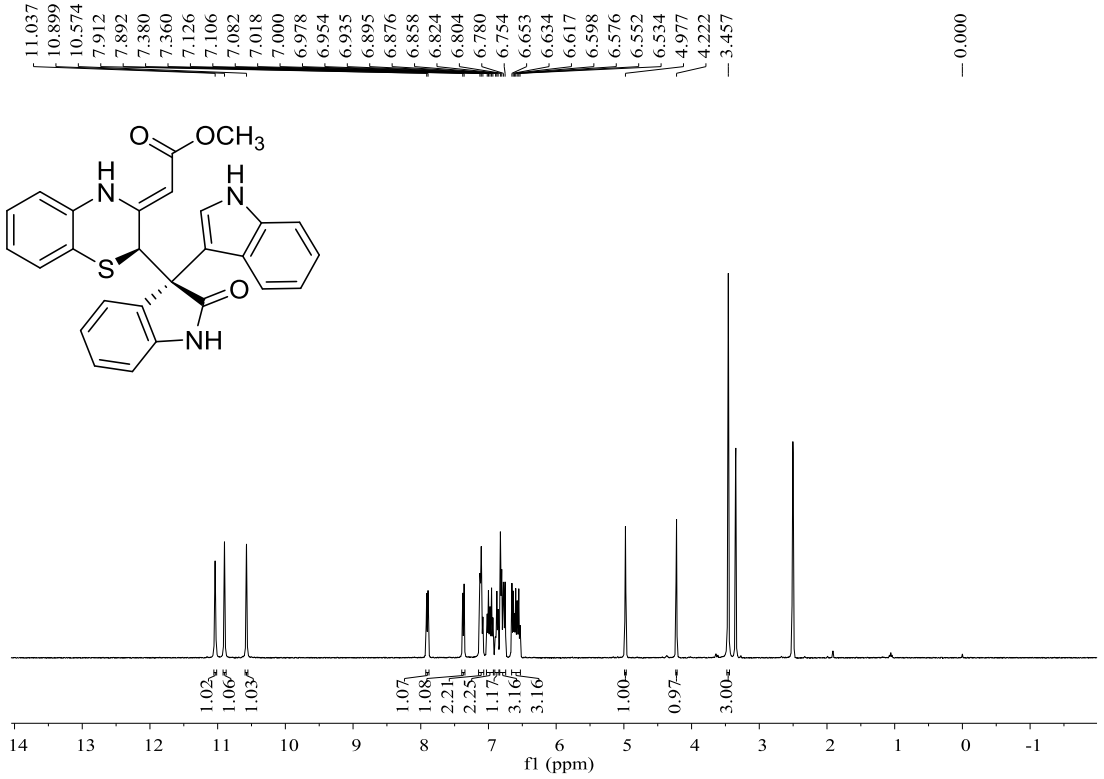
Experimental section

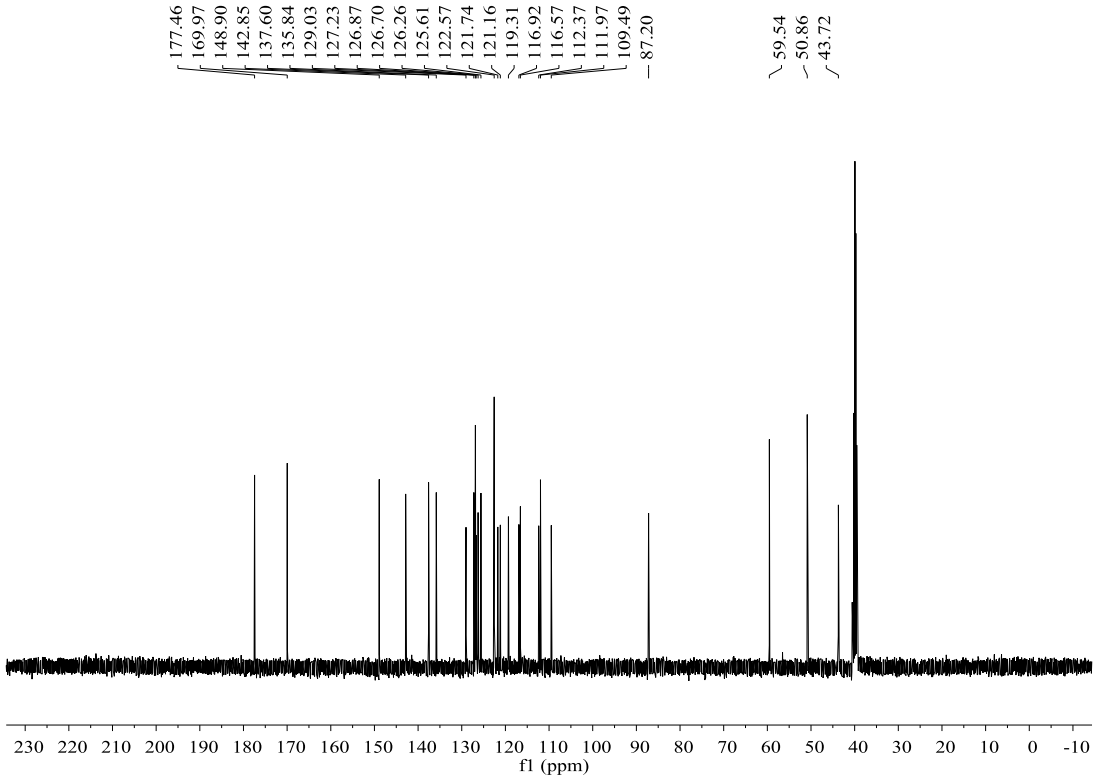
1. General procedure for the preparation of 3,3-disubstituted oxindoles: To a round flask was added cyclic amino ester (1.0 mmol), 3-hydroxy-3-(indol-3-yl)indolin-2-one (1.0 mmol), ethanol (6.0 mL) and acetic acid (2.0 mL). The mixture was stirred at room temperature for twelve hours. After removing the solvent by rotatory evaporation at reduced pressure, the residue was subjected to column chromatography with petroleum ether and methylene dichloride (V/V = 1:3) as eluent to give the pure product **3a-3h** and **3e'-3h'**.

2. General procedure for the preparation of polycyclic spirooxindoles 4a-4n: To a tube was added cyclic amino ester (1.0 mmol), 3-hydroxy-3-(indol-3-yl)indolin-2-one (1.0 mmol), ethanol (6.0 mL) and acetic acid (2.0 mL). The mixture was stirred in sealed tube at 120 ^{o}C for about twelve hours. After cooling to room temperature, the resulting precipitates were collected by filtration and was washed with little alcohol to give the pure product **4a-4n** for analysis.

3. General procedure for the preparation of dihydroindolo[3,2-c]phenothiazines 5a-5i: To a tube was added cyclic amino ester (1.0 mmol), 3-hydroxy-3-(indol-3-yl)indolin-2-one (1.0 mmol), methanol or ethanol (6.0 mL) and acetic acid (2.0 mL). The mixture was stirred in sealed tube at 100 ^{o}C for twenty-four hours. After removing the solvent by rotatory evaporation at reduced pressure, the residue was subjected to column chromatography with petroleum ether and methylene dichloride (V/V = 8:1) as eluent to give the pure product **5a-5i**.

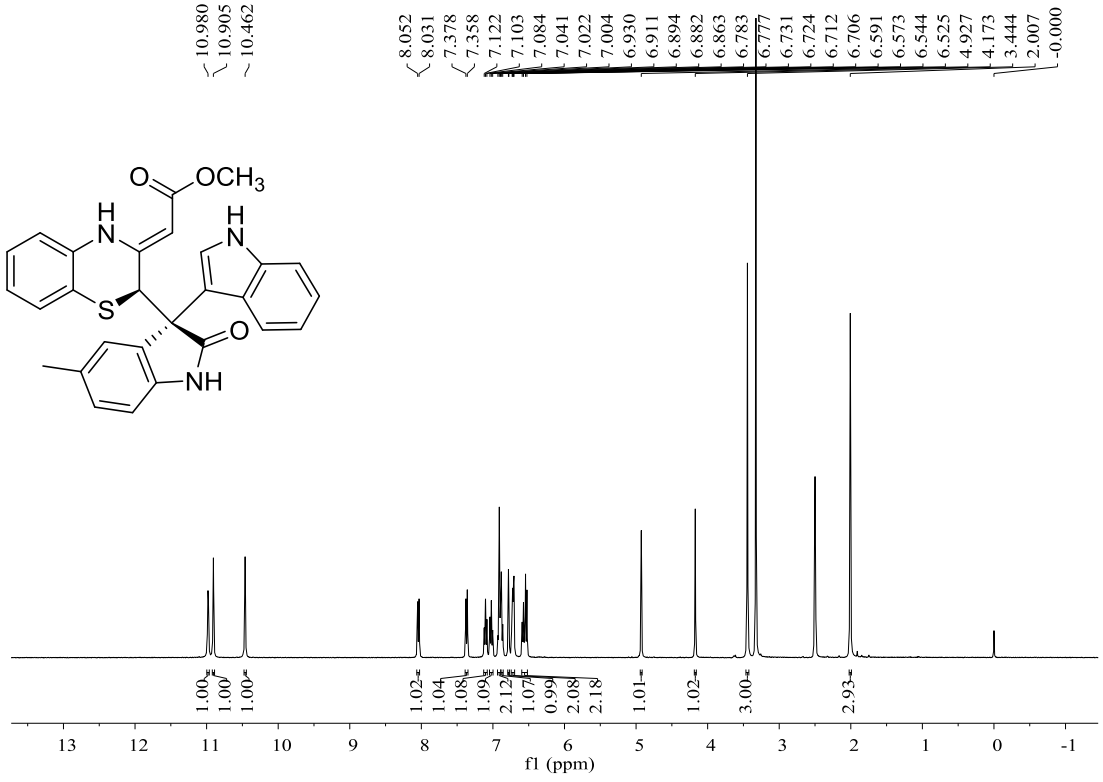
Methyl (*Z*)-2-(2-(3-(1*H*-indol-3-yl)-2-oxoindolin-3-yl)-2*H*-benzo[b][1,4]thiazin-3(4*H*)-ylidene)acetate (**3a**): white solid, 86%, m.p. 220 – 222^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.04 (s, 1H, NH), 10.90 (s, 1H, NH), 10.57 (s, 1H, NH), 7.90 (d, *J* = 7.6 Hz, 1H, ArH), 7.37 (d, *J* = 8.0 Hz, 1H, ArH), 7.13 ~ 7.08 (m, 2H, ArH), 7.02 ~ 6.94 (m, 2H, ArH), 6.90 ~ 6.86 (m, 1H, ArH), 6.82 ~ 6.76 (m, 3H, ArH), 6.65 ~ 6.53 (m, 3H, ArH), 4.98 (s, 1H, CH), 4.22 (s, 1H, CH), 3.46 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 177.5, 170.0, 148.9, 142.9, 137.6, 135.8, 129.0, 127.2, 126.9, 126.7, 126.3, 125.6, 122.6, 121.7, 121.2, 119.3, 116.9, 116.6, 112.4, 112.0 109.5, 87.2, 59.5, 50.9, 43.7; IR (KBr) υ: 3400, 3268, 2971, 2888, 1712, 1609, 1574, 1480, 1441, 1413,1363, 1285, 1220, 1169,1105, 1080, 1044, 927, 905, 869, 793 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{21}N_3O_3S$ ([M+Na]$^{+}$): 490.1196, Found: 490.1193.

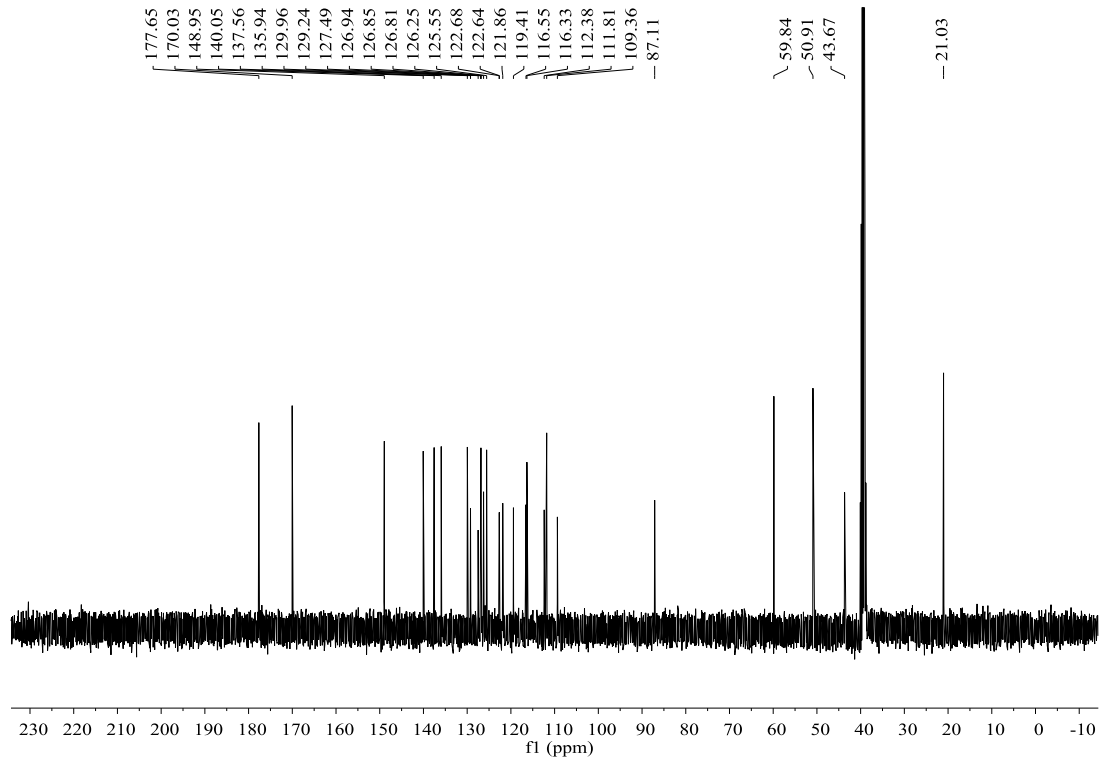



177.46
169.97
148.90
142.85
137.60
135.84
129.03
127.23
126.87
126.70
126.26
125.61
122.57
121.74
121.16
119.31
116.92
116.57
112.37
111.97
109.49
87.20
59.54
50.86
43.72
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


#46 RT: 0.45 AV: 1 NL: 3.01E+005
490.1193
FTMS + p ESI Full ms [100.0000-1500.0000]
m/z

Methyl (*Z*)-2-(2-(3-(1*H*-indol-3-yl)-5-methyl-2-oxoindolin-3-yl)-2*H*-benzo[b][1,4]thiazin-3(4*H*)-ylidene)acetate (**3b**): white solid, 81%, m.p. 224 – 226^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.98 (s, 1H, NH), 10.91 (s, 1H, NH), 10.46 (s, 1H, NH), 8.04 (d, *J* = 8.4 Hz, 1H, ArH), 7.37 (d, *J* = 8.0 Hz, 1H, ArH), 7.11 (t, *J* = 7.6 Hz, 1H, ArH), 7.04 ~ 7.00 (m, 1H, ArH), 6.93 ~ 6.89 (m, 2H, ArH), 6.87 (d, *J* = 7.6 Hz, 1H, ArH), 6.78 (d, *J* = 2.4 Hz, 1H, ArH), 6.73 ~ 6.71 (m, 2H, ArH), 6.59 ~ 6.53 (m, 2H, ArH), 4.93 (s, 1H, CH), 4.17 (s, 1H, CH), 3.44 (s, 3H, OCH_3) , 2.01 (s, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 13C NMR (101 MHz, dmso) δ 177.7, 170.0, 149.0, 140.1, 137.6, 135.9, 130.0, 129.2, 127.5, 126.9, 126.9, 126.8, 126.3, 125.6, 122.7, 122.6, 121.9, 119.4, 116.6, 116.3, 112.4, 111.8, 109.4, 87.1, 59.8, 50.9, 43.7, 21.0; IR (KBr) υ: 3380, 3267, 2943, 2858, 1707, 1609, 1574, 1490, 1438, 1365, 1285, 1219, 1167, 1106, 1080, 1042, 959, 927, 880, 789 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{23}N_3O_3S$ ([M+Na]$^{+}$): 504.1352, Found: 504.1344.

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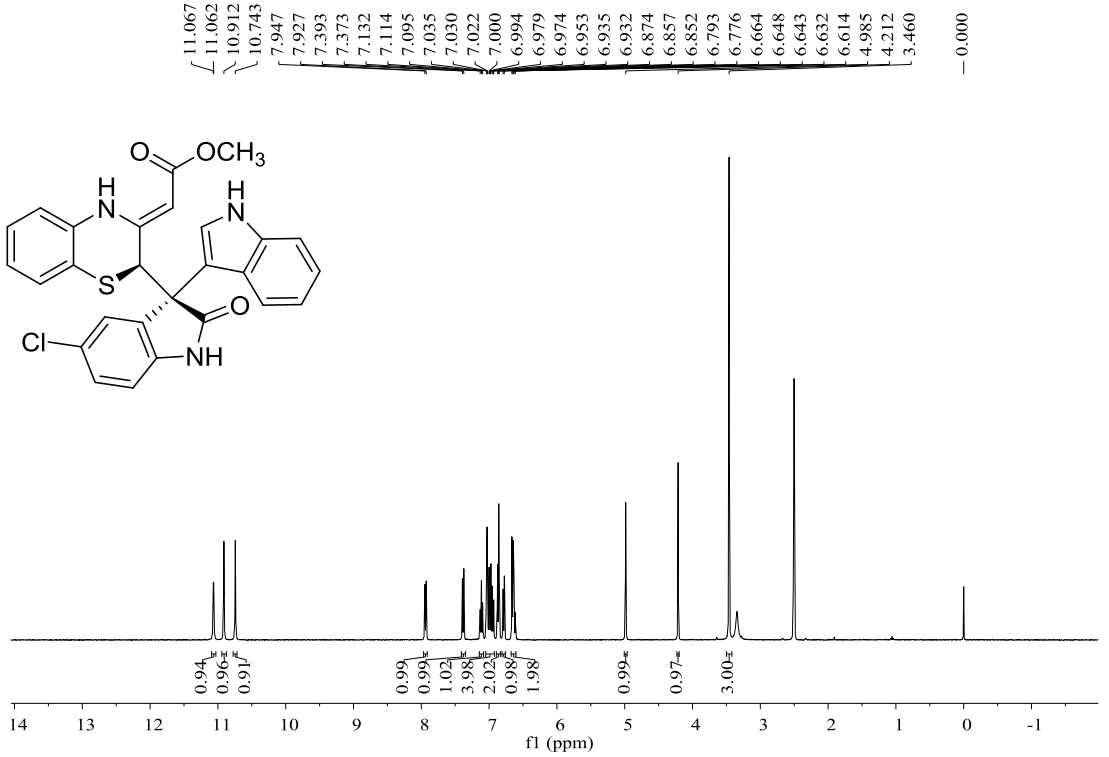
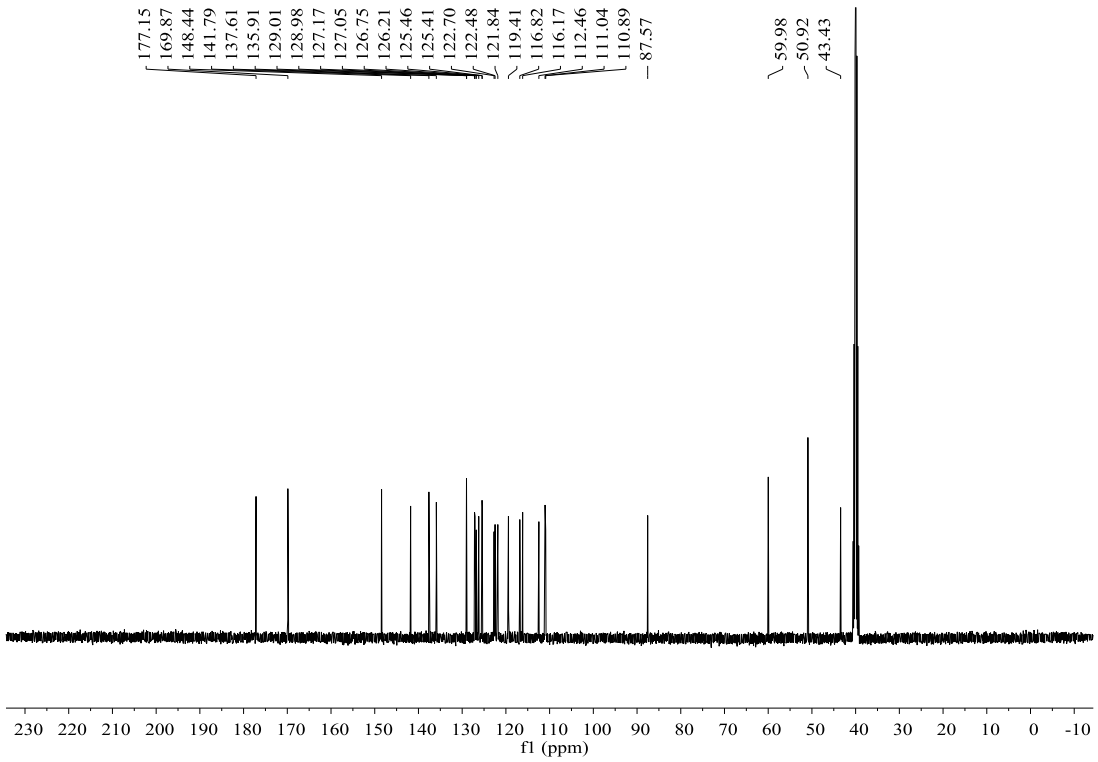
148.95
140.05
137.56
135.94
129.96
129.24
127.49
126.94
126.85
126.81
126.25
125.55
122.68
122.64
121.86
119.41
116.55
116.33
112.38
111.81
109.36
87.11
59.84
50.91
43.67
21.03
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln2 #57 RT: 0.55 AV: 1 NL: 6.58E+005
504.1344
FTMS + p ESI Full ms [100.0000-1500.0000]

Methyl (Z)-2-(2-(5-chloro-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)-2H-benzo[b][1,4]thiazin-3(4H)-ylidene)acetate (**3c**): white solid, 75%, m.p. 211 – 213^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.06 (d, J = 2.0 Hz, 1H, NH), 10.91 (s, 1H, NH), 10.74 (s, 1H, NH), 7.94 (d, J = 8.0 Hz, 1H, ArH), 7.38 (d, J = 8.0 Hz, 1H, ArH), 7.13 ~ 7.10 (m, 1H, ArH), 7.04 ~ 6.93 (m, 4H, ArH), 6.87 ~ 6.85 (m, 2H, ArH), 6.79 ~ 6.78 (m, 1H, ArH), 6.66 ~ 6.61 (m, 2H, ArH), 4.99 (s, 1H, CH), 4.21(s, 1H, CH), 3.46 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 177.2, 169.9, 148.4, 141.8, 137.6, 135.9, 129.0, 129.0, 127.2, 127.1, 126.8, 126.2, 125.5, 125.4, 122.7, 122.5, 121.8, 119.4, 116.8, 116.2, 112.5, 111.0, 110.9, 87.6, 60.0, 50.9, 43.4; IR (KBr) υ: 3343, 3269, 3059,2947, 1707, 1653, 1616, 1579, 1477, 1433, 1282, 1221, 1160, 1077, 1030, 988, 881, 788 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{20}ClN_3O_3S$ ([M+Na]$^{+}$): 524.0806, Found: 524.0799.

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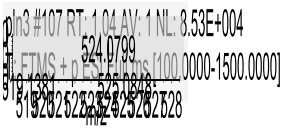
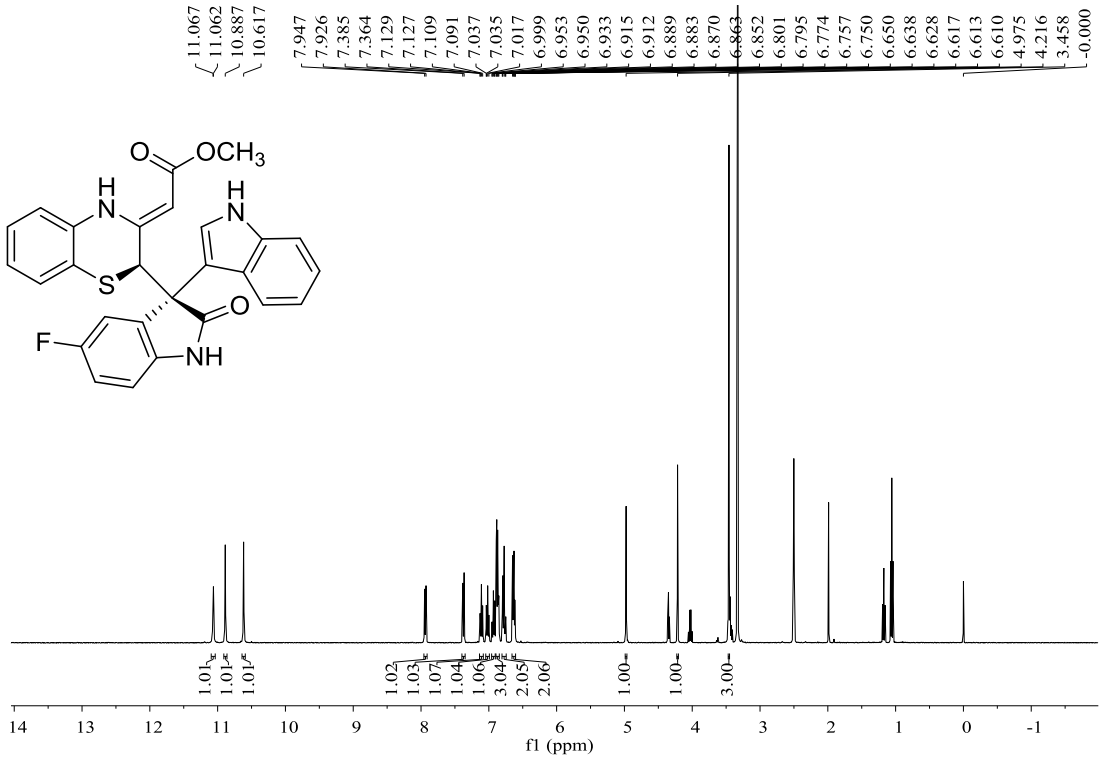
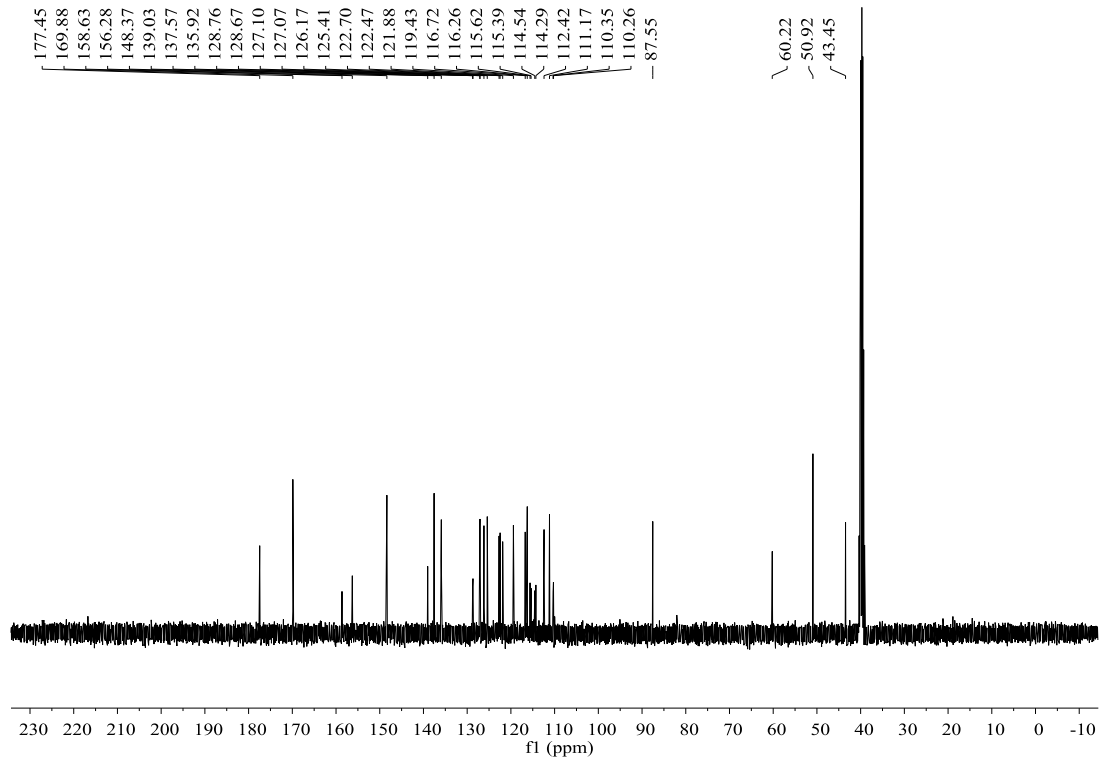
141.79
137.61
135.91
129.01
128.98
127.17
127.05
126.75
126.21
125.46
125.41
122.70
122.48
121.84
119.41
116.82
116.17
112.46
111.04
110.89
87.57
59.98
50.92
43.43
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln3 #107 RT: 1.04 AV: 1 NL: 8.53E+004
524.0799
m/z

Methyl (Z)-2-(2-(5-fluoro-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)-2H-benzo[b][1,4]thiazin-3(4H)-ylidene)acetate (**3d**): white solid, 73%, m.p. 212 – 214^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.06 (d, J = 2.0 Hz, 1H, NH), 10.89 (s, 1H, NH), 10.62 (s, 1H, NH), 7.94 (d, J = 8.4 Hz, 1H, ArH), 7.37 (d, J = 8.4 Hz, 1H, ArH), 7.13 ~ 7.09 (m, 1H, ArH), 7.04 ~ 7.00 (m, 1H, ArH), 6.95 ~ 6.91 (m, 1H, ArH), 6.89 ~ 6.85 (m, 3H, ArH), 6.80 ~ 6.75 (m, 2H, ArH), 6.65 ~ 6.61 (m, 2H, ArH), 4.98 (s, 1H, CH), 4.22 (s, 1H, CH), 3.46 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 177.5, 169.9, 157.5 (d, J = 237.4 Hz), 148.4, 139.0, 137.6, 135.9, 128.7 (d, J = 9.1 Hz), 127.1, 127.1, 126.2, 125.4, 122.7, 122.5, 121.9, 119.4, 116.7, 116.3, 115.5 (d, J = 23.2 Hz), 114.4 (d, J = 25.3 Hz), 112.4, 111.2, 110.3 (d, J = 9.1 Hz), 87.6, 60.2, 50.9, 43.5; IR (KBr) υ: 3344, 3262, 2946, 2873, 1711, 1657, 1617, 1579, 1485, 1445, 1367, 1284, 1221, 1188, 1161, 1081, 1036, 956, 927, 893, 814, 788 cm^{-1}; HRMS (ESI) Calcd. for $C_{27}H_{20}FN_3O_3S$ ([M+Na]$^{+}$): 508.1102, Found: 508.1098.

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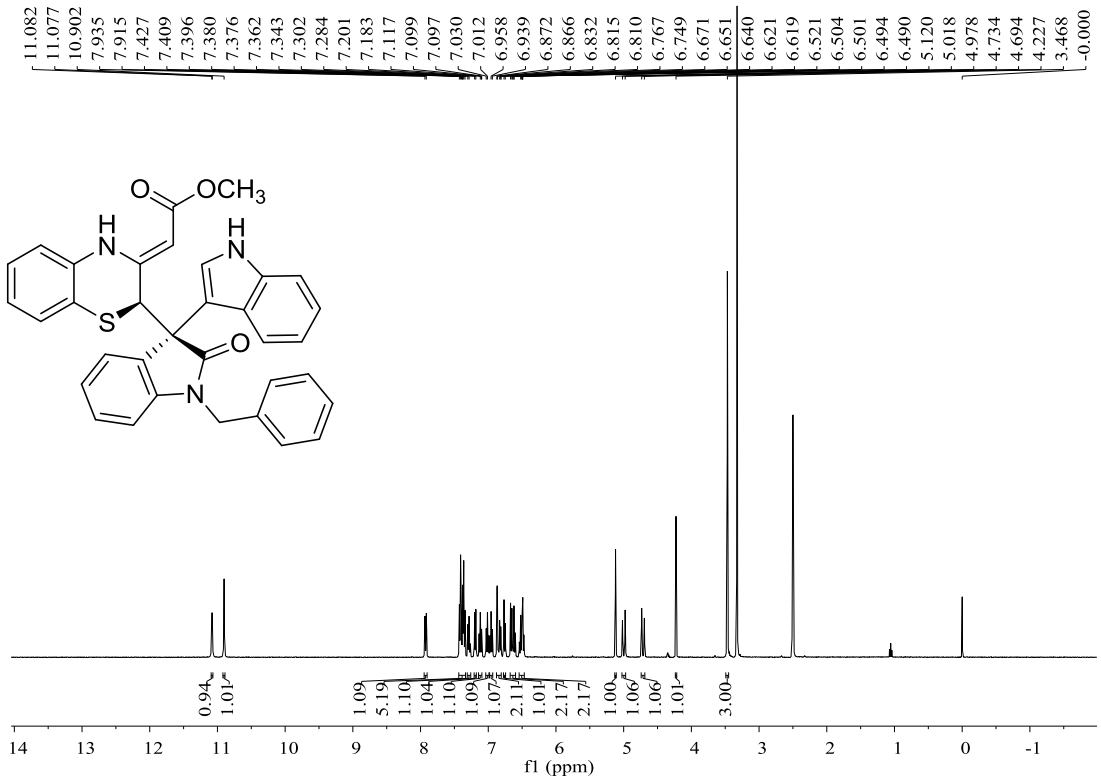
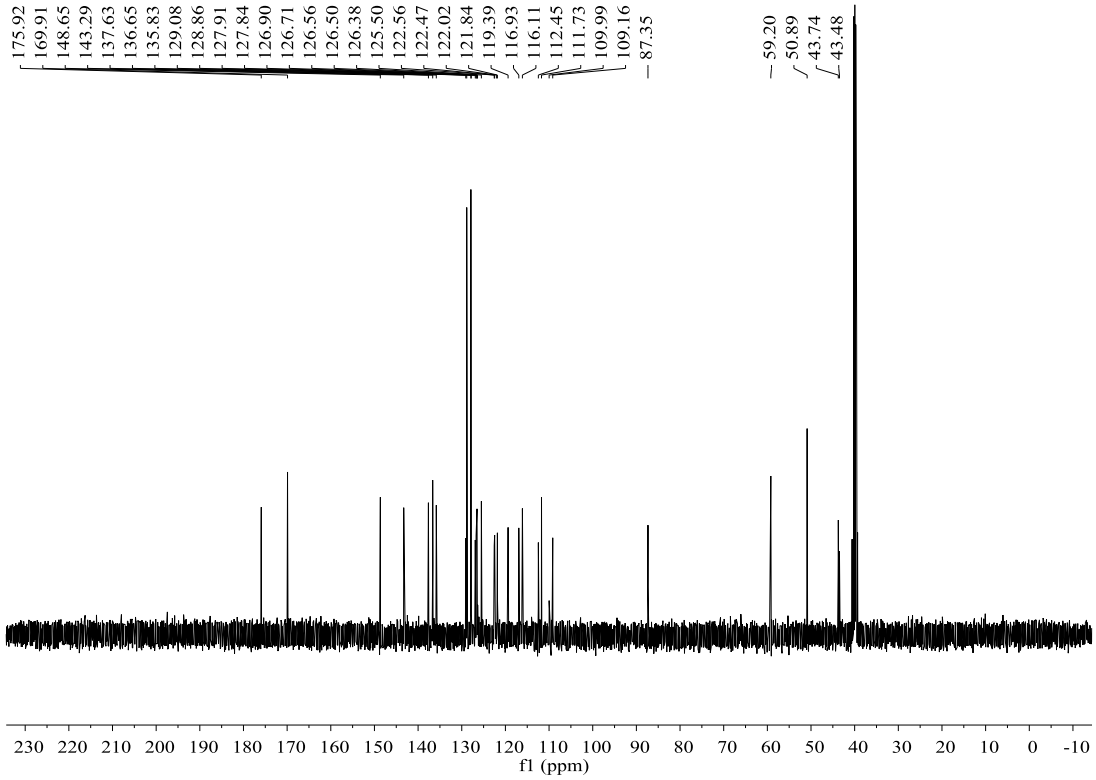
156.28
148.37
139.03
137.57
135.92
128.76
128.67
127.10
127.07
126.17
125.41
122.70
122.47
121.88
119.43
116.72
116.26
115.62
115.39
114.54
114.29
112.42
111.17
110.35
110.26
87.55
60.22
50.92
43.45
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln4 #110 RT: 1.09 AV: 1 NL: 3.63E+004
508.1098
FTMS + p ESI Full ms [100.0000-1500.0000]

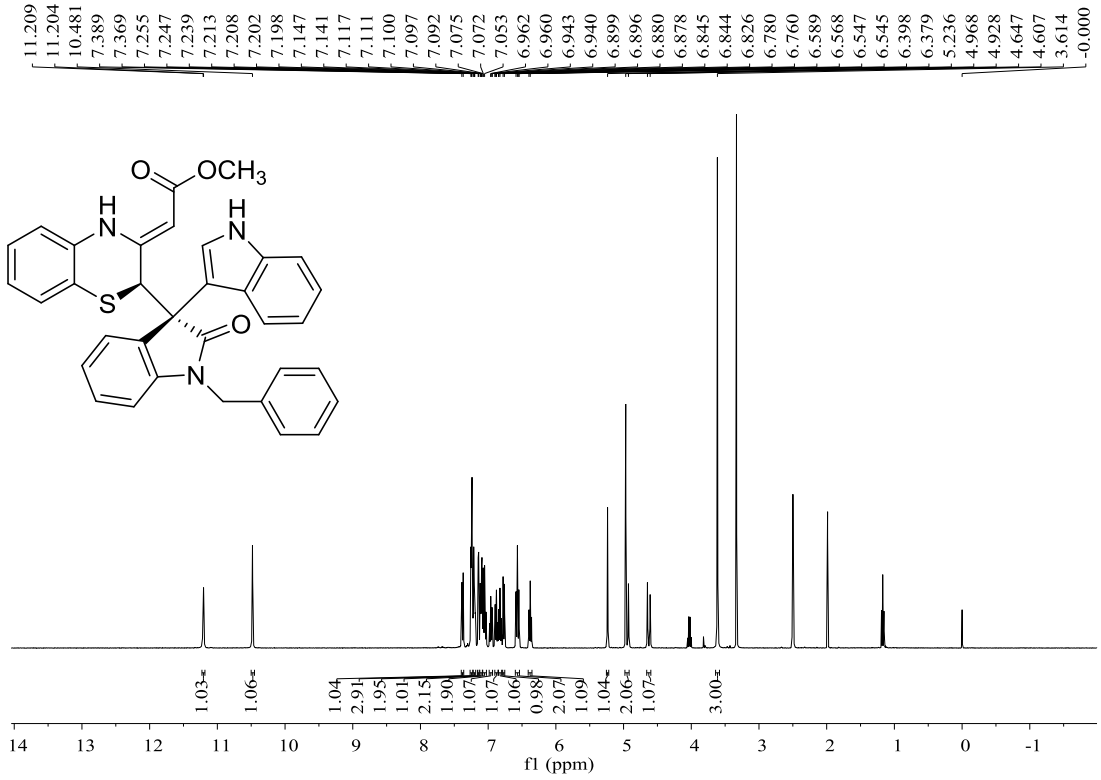
Methyl (Z)-2-(2-(1-benzyl-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)-2H-benzo[b][1,4]thiazin-3(4H)-ylidene)acetate (**3e**): white solid, 48%, m.p. 216 – 218^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.08 (d, *J* = 2.0 Hz, 1H, NH), 10.90 (s, 1H, NH), 7.93 (d, *J* = 8.0 Hz, 1H, ArH), 7.43 ~ 7.34 (m, 5H, ArH), 7.30 ~ 7.27 (m, 1H, ArH), 7.19 (d, *J* = 7.2 Hz, 1H, ArH), 7.14 ~ 7.10 (m, 1H, ArH), 7.03 ~ 6.99 (m, 1H, ArH), 6.98 ~ 6.94 (m, 1H, ArH), 6.87 ~ 6.81 (m, 2H, ArH), 6.76 (d, *J* = 7.2 Hz, 1H, ArH), 6.67 ~ 6.60 (m, 2H, ArH), 6.54 ~ 6.47 (m, 2H, ArH), 5.12 (s, 1H, CH), 5.00 (d, *J* = 16.0 Hz, 1H, CH), 4.71 (d, *J* = 16.0 Hz, 1H, CH), 4.23 (s, 1H, CH), 3.47 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 175.9, 169.9, 148.7, 143.3, 137.6, 136.7, 135.8, 129.1, 128.9, 127.9, 127.8, 126.9, 126.7, 126.6, 126.5, 126.38, 125.5, 122.6, 122.5, 122.0, 121.8, 119.4, 116.9, 116.1, 112.5, 111.7, 110.0, 109.2, 87.4, 59.2, 50.9, 43.7, 43.5; IR (KBr) υ: 3319, 3181, 3046, 2949, 2857, 1694, 1655, 1614, 1579, 1488, 1461, 1434, 1370, 1341, 1287, 1223, 1164, 1112, 1080, 1034, 1010, 927, 896, 850, 789 cm^{-1}; HRMS (ESI) Calcd. for $C_{34}H_{27}N_3O_3S$ ([M+Na]$^{+}$): 580.1665, Found: 580.1662.

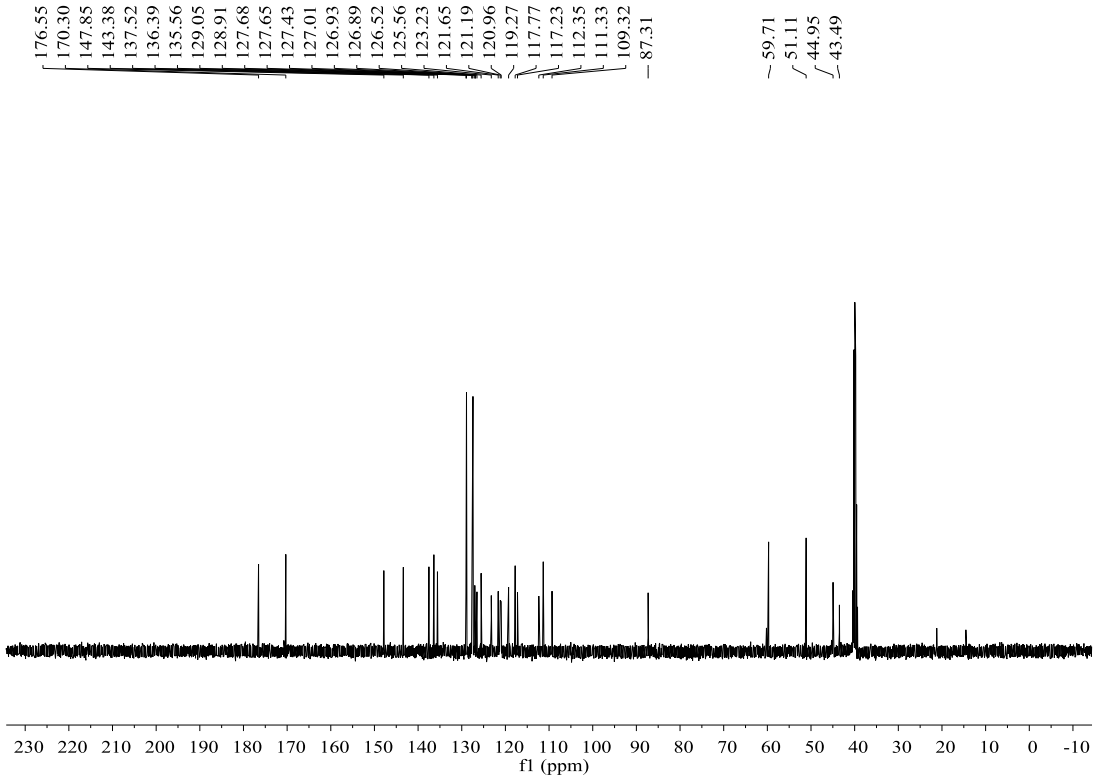



175.92
169.91
148.65
143.29
137.63
136.65
135.83
129.08
128.86
127.91
127.84
126.90
126.71
126.56
126.50
126.38
125.50
122.56
122.47
122.02
121.84
119.39
116.93
116.11
112.45
111.73
109.99
109.16
87.35
59.20
50.89
43.74
43.48
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln5 #101 RT: 1.08 AV: 1 NL: 3.67E+005
580.1662
FTMS

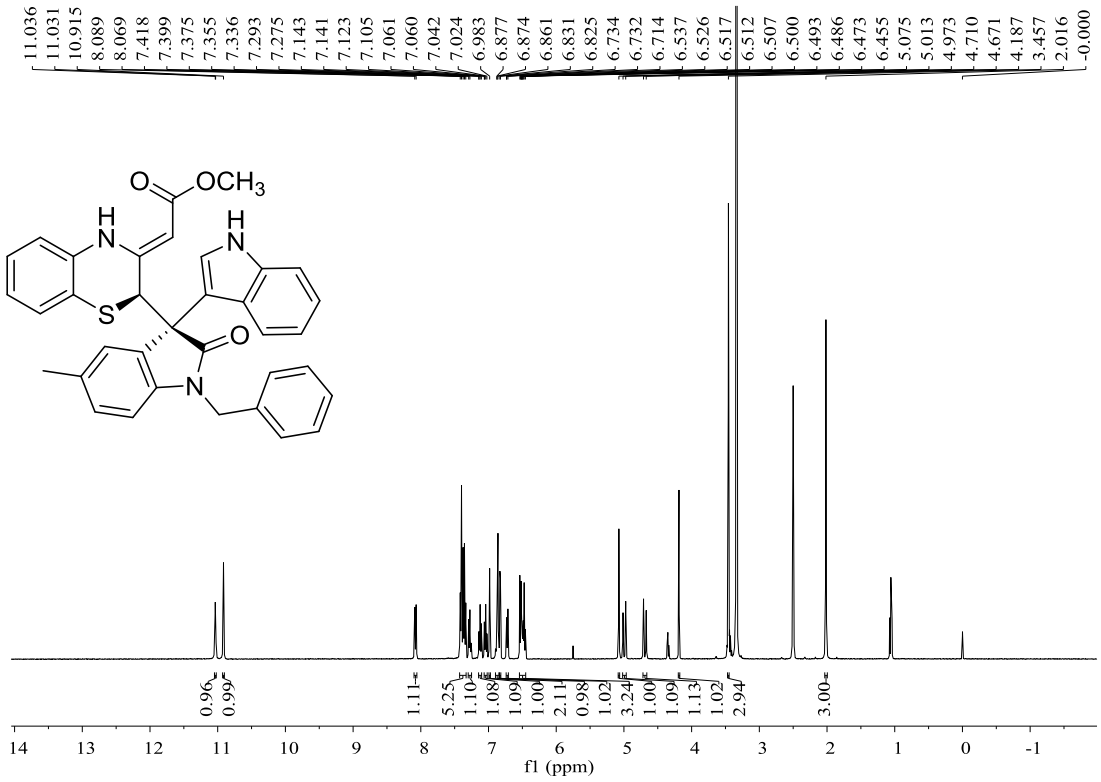
Methyl (Z)-2-(2-(1-benzyl-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)-2H-benzo[b][1,4]thiazin-3(4H)-ylidene)acetate (**3e'**): white solid, 40%, m.p. 200 – 202^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.21 (d, *J* = 2.0 Hz, 1H, NH), 10.48 (s, 1H, NH), 7.38 (d, *J* = 8.0 Hz, 1H, ArH), 7.26 ~ 7.24 (m, 3H, ArH), 7.21 ~ 7.19 (m, 2H, ArH), 7.14 (d, *J* = 2.4 Hz, 1H, ArH), 7.12 ~ 7.09 (m, 2H, ArH), 7.08 ~ 7.03 (m, 2H, ArH), 6.98 ~ 6.94 (m, 1H, ArH), 6.90 ~ 6.86 (m, 1H, ArH), 6.85 ~ 6.81 (m, 1H, ArH), 6.77 (d, *J* = 8.0 Hz, 1H, ArH), 6.59 ~ 6.55 (m, 2H, ArH), 6.40 ~ 6.36 (m, 1H, ArH), 5.24 (s, 1H, CH), 4.97 (s, 1H, CH), 4.95 (d, *J* = 16.0 Hz, 1H, CH), 4.63 (d, *J* = 16.0 Hz, 1H, CH), 3.61 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 176.6, 170.3, 147.9, 143.4, 137.5, 136.4, 135.6, 129.1, 128.9, 127.7, 127.7, 127.4, 127.0, 126.9, 126.9, 126.5, 125.6, 123.2, 121.7, 121.2, 121.0, 119.3, 117.8, 117.2, 112.4, 111.3, 109.3, 87.3, 59.7, 51.1, 45.0, 43.5; IR (KBr) υ: 3362, 3205, 3059, 2944, 2839, 1688, 1662, 1618, 1581, 1488, 1460, 1433, 1366, 1288, 1228, 1163, 1109, 1081, 1040, 935, 898, 844, 794 cm^{-1}; HRMS (ESI) Calcd. for $C_{34}H_{27}N_3O_3S$ ([M+Na]$^{+}$): 580.1665, Found: 580.1659.

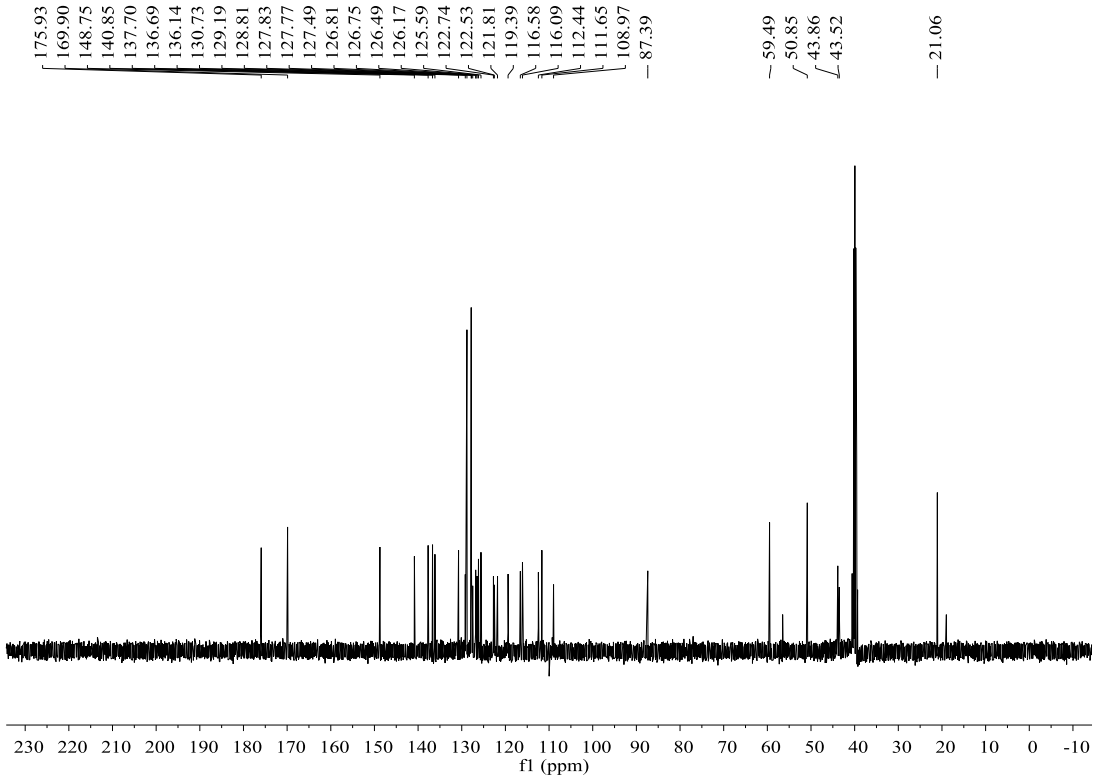



176.55
170.30
147.85
143.38
137.52
136.39
135.56
129.05
128.91
127.68
127.65
127.43
127.01
126.93
126.89
126.52
125.56
123.23
121.65
121.19
120.96
119.27
117.77
117.23
112.35
111.33
109.32
87.31
59.71
51.11
44.95
43.49
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


In6 #53 RT: 0.67 AV: 1 NL: 2.25E+005
580.1659
FTMS
m/z

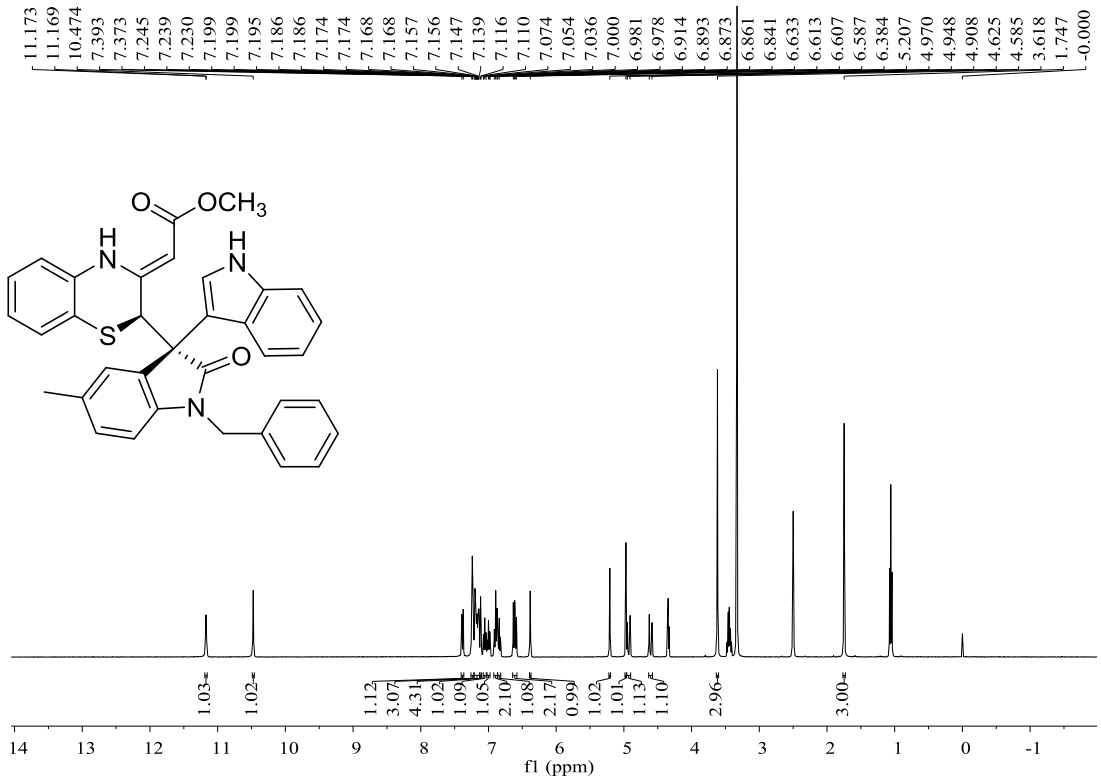
Methyl (Z)-2-(2-(1-benzyl-3-(1H-indol-3-yl)-5-methyl-2-oxoindolin-3-yl)-2H-benzo[b][1,4]thiazin-3(4H)-ylidene)acetate (**3f**): white solid, 45%, m.p. 209 – 211^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.03 (d, J = 2.0 Hz, 1H, NH), 10.92 (s, 1H, NH), 8.08 (d, J = 8.0 Hz, 1H, ArH), 7.42 ~ 7.34 (m, 5H, ArH), 7.29 ~ 7.26 (m, 1H, ArH), 7.14 ~ 7.11 (m, 1H, ArH), 7.06 ~ 7.02 (m, 1H, ArH), 6.98 (s, 1H, ArH), 6.90 ~ 6.85 (m, 2H, ArH), 6.83 (d, J = 2.4 Hz, 1H, ArH), 6.73 ~ 6.71 (m, 1H, ArH), 6.54 ~ 6.46 (m, 3H, ArH), 5.08 (s, 1H, CH), 4.99 (d, J = 16.0 Hz, 1H, CH), 4.69 (d, J = 15.6 Hz, 1H, CH), 4.19 (s, 1H, CH), 3.46 (s, 3H, OCH_3) , 2.02 (s, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 175.9, 169.9, 148.8, 140.9, 137.7, 136.7, 136.1, 130.7, 129.2, 128.8, 127.8, 127.8, 127.5, 126.8, 126.8, 126.5, 126.2, 125.6, 122.7, 122.5, 121.8, 119.4, 116.6, 116.1, 112.4, 111.7, 109.0, 87.4, 59.5, 50.9, 43.9, 43.5, 21.1; IR (KBr) υ: 3318, 3191, 3040, 2944, 2859, 1691, 1655, 1613, 1577, 1492, 1435, 1373, 1340, 1284, 1218, 1160, 1080, 1031, 971, 925, 874, 846, 812, 788 cm^{-1}; HRMS (ESI) Calcd. for $C_{35}H_{29}N_3O_3S$ ([M+Na]$^{+}$): 594.1822, Found: 594.1818.

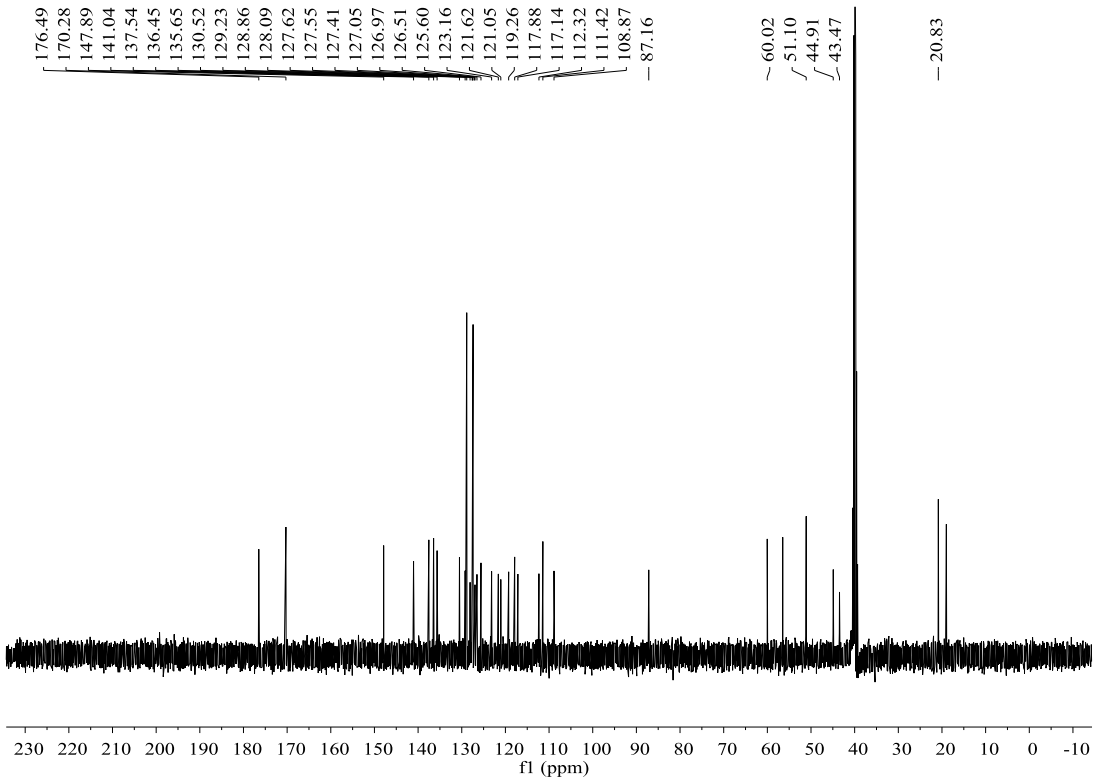



175.93
169.90
148.75
140.85
137.70
136.69
136.14
130.73
129.19
128.81
127.83
127.77
127.49
126.81
126.75
126.49
126.17
125.59
122.74
122.53
121.81
119.39
116.58
116.09
112.44
111.65
108.97
87.39
59.49
50.85
43.86
43.52
21.06
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


#73 RT: 0.93 AV: 1 NL: 8.38E+004
5941818
FTMS + [100.0000-1500.0000]

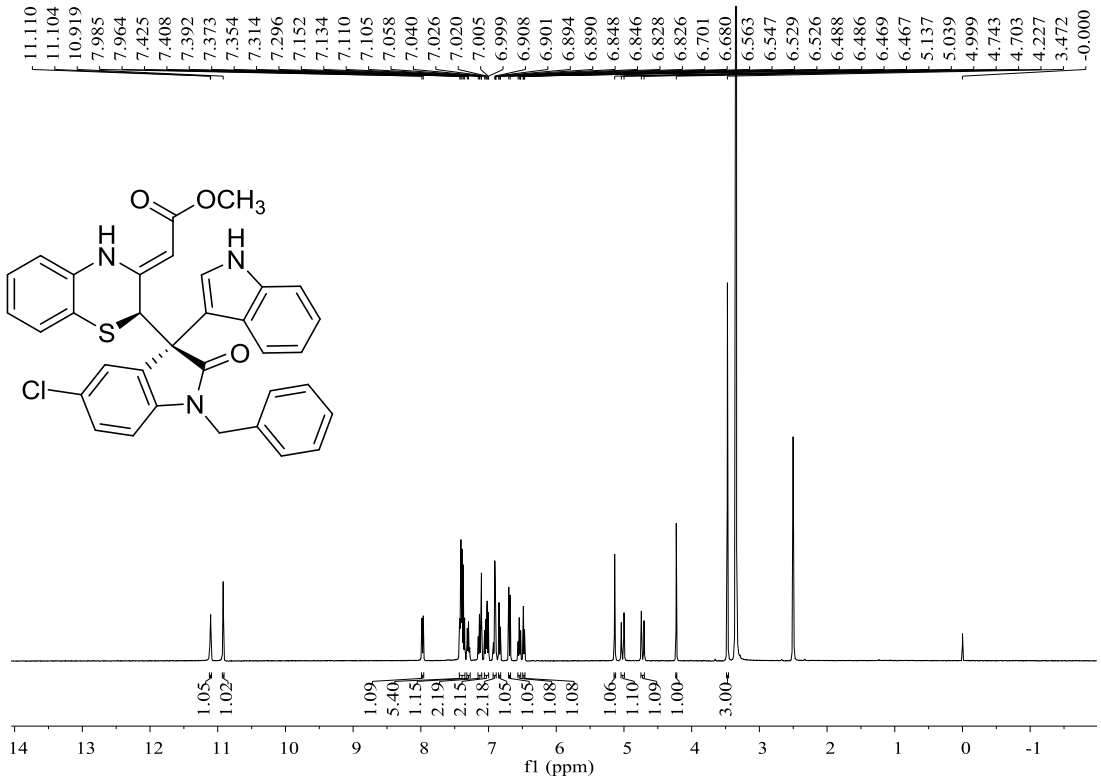
Methyl (Z)-2-(2-(1-benzyl-3-(1H-indol-3-yl)-5-methyl-2-oxoindolin-3-yl)-2H-benzo[b][1,4]thiazin-3(4H)-ylidene)acetate (3f'): white solid, 38%, m.p. 198 – 200^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.17 (d, J = 1.6 Hz, 1H, NH), 10.47 (s, 1H, NH), 7.38 (d, J = 8.0 Hz, 1H, ArH), 7.25 ~ 7.23 (m, 3H, ArH), 7.20 ~ 7.14 (m, 4H, ArH), 7.11 (d, J = 2.4 Hz, 1H, ArH), 7.07 ~ 7.04 (m, 1H, ArH), 7.02 ~ 6.98 (m, 1H, ArH), 6.91 ~ 6.87 (m, 2H, ArH), 6.86 ~ 6.82 (m, 1H, ArH), 6.63 ~ 6.59 (m, 2H, ArH), 6.38 (s, 1H, ArH), 5.21 (s, 1H, CH), 4.97 (s, 1H, CH), 4.93 (d, J = 16.0 Hz, 1H, CH), 4.60 (d, J = 16.0 Hz, 1H, CH), 3.62 (s, 3H, OCH_3) , 1.75 (s, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 176.5, 170.3, 147.9, 141.0, 137.5, 136.5, 135.7, 130.5, 129.2, 128.9, 128.1, 127.6, 127.6, 127.4, 127.1, 127.0, 126.5, 125.6, 123.2, 121.6, 121.1, 119.3, 117.9, 117.1, 112.3, 111.4, 108.9, 87.2, 60.0, 51.1, 44.9, 43.5, 20.8; IR (KBr) υ: 3436, 3249, 3063, 2970, 2883, 1683, 1652, 1616, 1579, 1489, 1434, 1373, 1344, 1288, 1225, 1157, 1108, 1077, 1027, 935, 881, 855, 803 cm^{-1}; HRMS (ESI) Calcd. for $C_{35}H_{29}N_3O_3S$ ([M+Na]$^{+}$): 594.1822, Found: 594.1817.

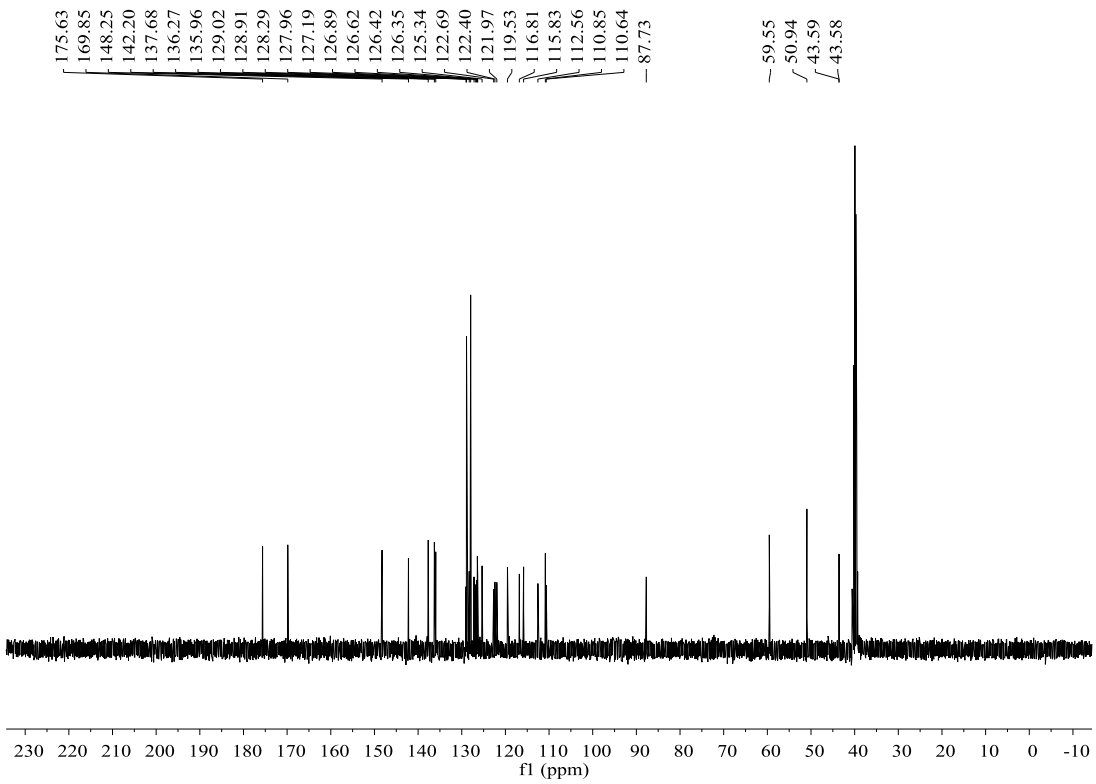



176.49
170.28
147.89
141.04
137.54
136.45
135.65
130.52
129.23
128.86
128.09
127.62
127.55
127.41
127.05
126.97
126.51
125.60
123.16
121.62
121.05
119.26
117.88
117.14
112.32
111.42
108.87
87.16
60.02
51.10
44.91
43.47
20.83
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


In8 #66 RT: 0.84 AV: 1 NL: 1.48E+005
594.1817
FTMS + p ESI Full ms [100.0000-1500.0000]
m/z

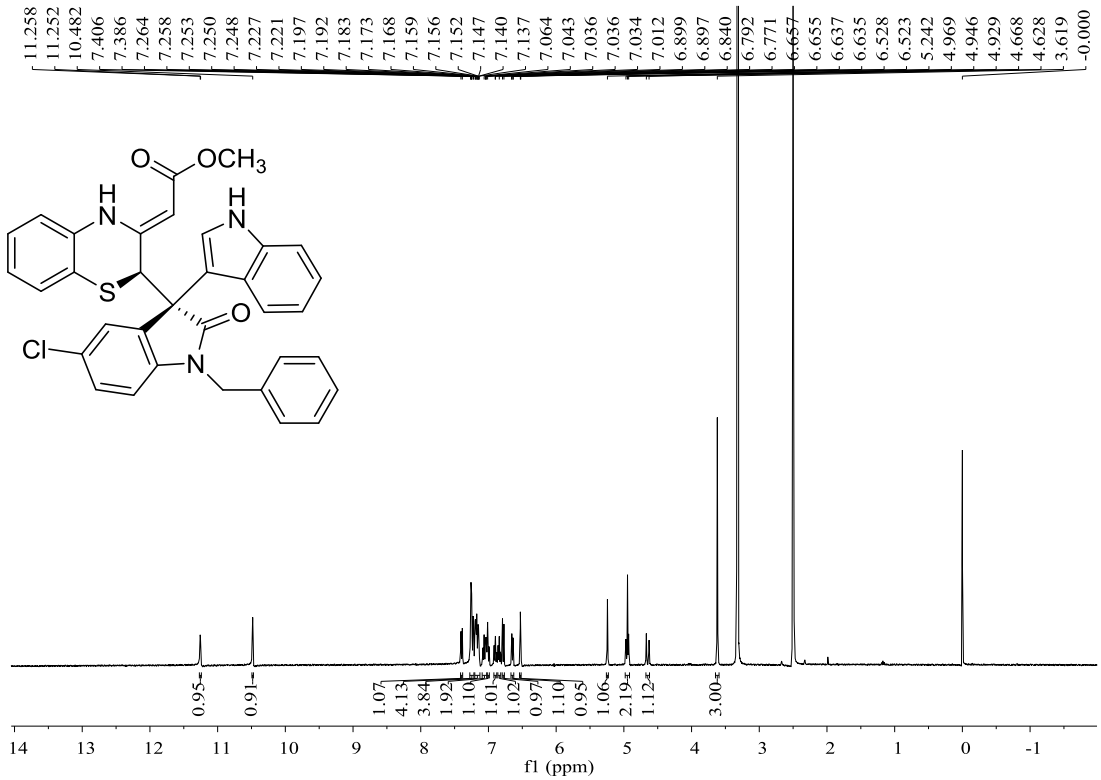
Methyl (Z)-2-(2-(1-benzyl-5-chloro-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)-2H-benzo[b][1,4]thiazin-3(4H)-ylidene)acetate (**3g**): white solid, 46%, m.p. 146 – 148^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.11 (d, J = 2.4 Hz, 1H, NH), 10.92 (s, 1H, NH), 7.97 (d, J = 8.4 Hz, 1H, ArH), 7.43 ~ 7.35 (m, 5H, ArH), 7.31 ~ 7.28 (m, 1H, ArH), 7.15 ~ 7.11 (m, 2H, ArH), 7.06 ~ 7.00 (m, 2H, ArH), 6.93 ~ 6.89 (m, 2H, ArH), 6.85 ~ 6.83 (m, 1H, ArH), 6.69 (d, J = 8.4 Hz, 1H, ArH), 6.57 ~ 6.53 (m, 1H, ArH), 6.49 ~ 6.47 (m, 1H, ArH), 5.14 (s, 1H, CH), 5.02 (d, J = 16.0 Hz, 1H, CH), 4.72 (d, J = 16.0 Hz, 1H, CH), 4.23 (s, 1H, CH), 3.47 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: NMR (101 MHz,) δ 175.6, 169.9, 148.3, 142.2, 137.7, 136.3, 136.0, 129.0, 128.9, 128.3, 128.0, 127.2, 126.9, 126.6, 126.4, 126.4, 125.3, 122.7, 122.4, 122.0, 119.5, 116.8, 115.8, 112.6, 110.9, 110.6, 87.7, 59.6, 50.9, 43.6, 43.6; IR (KBr) υ: 3401, 3182, 3060, 2948, 2841, 1708, 1663, 1615, 1580, 1485, 1432, 1339, 1284, 1219, 1164, 1109, 1080, 1033, 970, 841, 808 cm^{-1}; HRMS (ESI) Calcd. for $C_{34}H_{26}ClN_3O_3S$ ([M+Na]$^{+}$): 614.1276, Found: 614.1269.

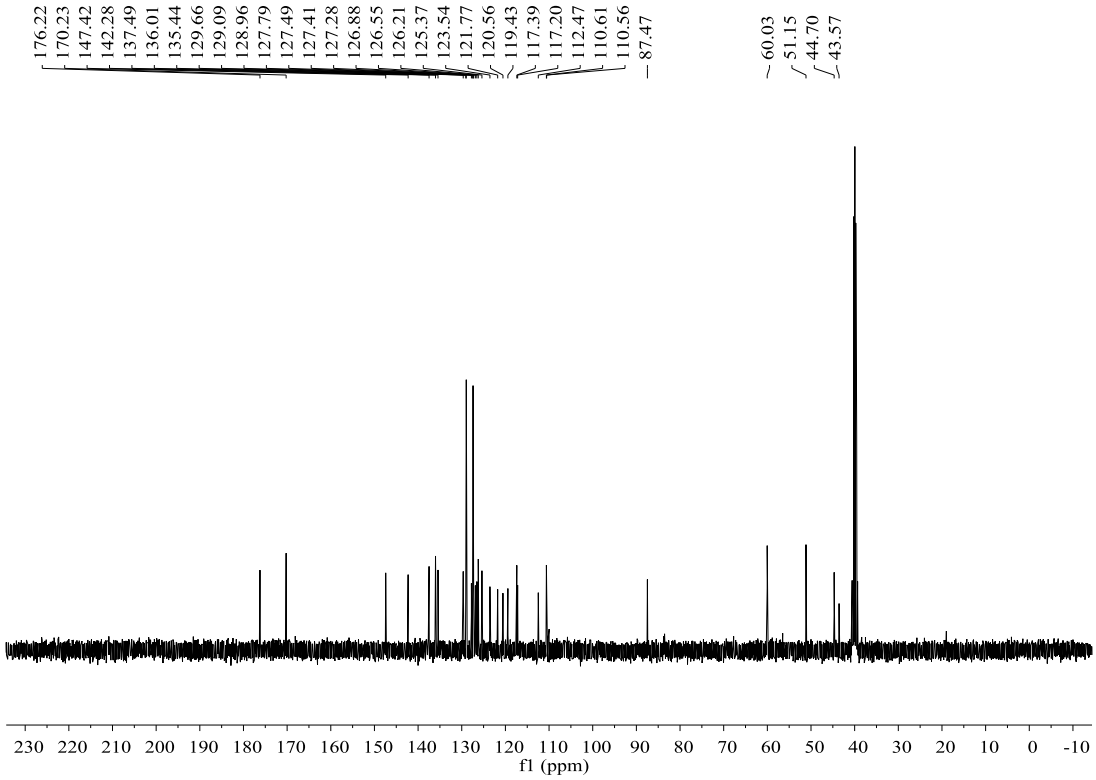


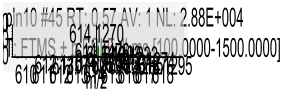

175.63
169.85
148.25
142.20
137.68
136.27
135.96
129.02
128.91
128.29
127.96
127.19
126.89
126.62
126.42
126.35
125.34
122.69
122.40
121.97
119.53
116.81
115.83
112.56
110.85
110.64
87.73
59.55
50.94
43.59
43.58
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


614.1269
m/z

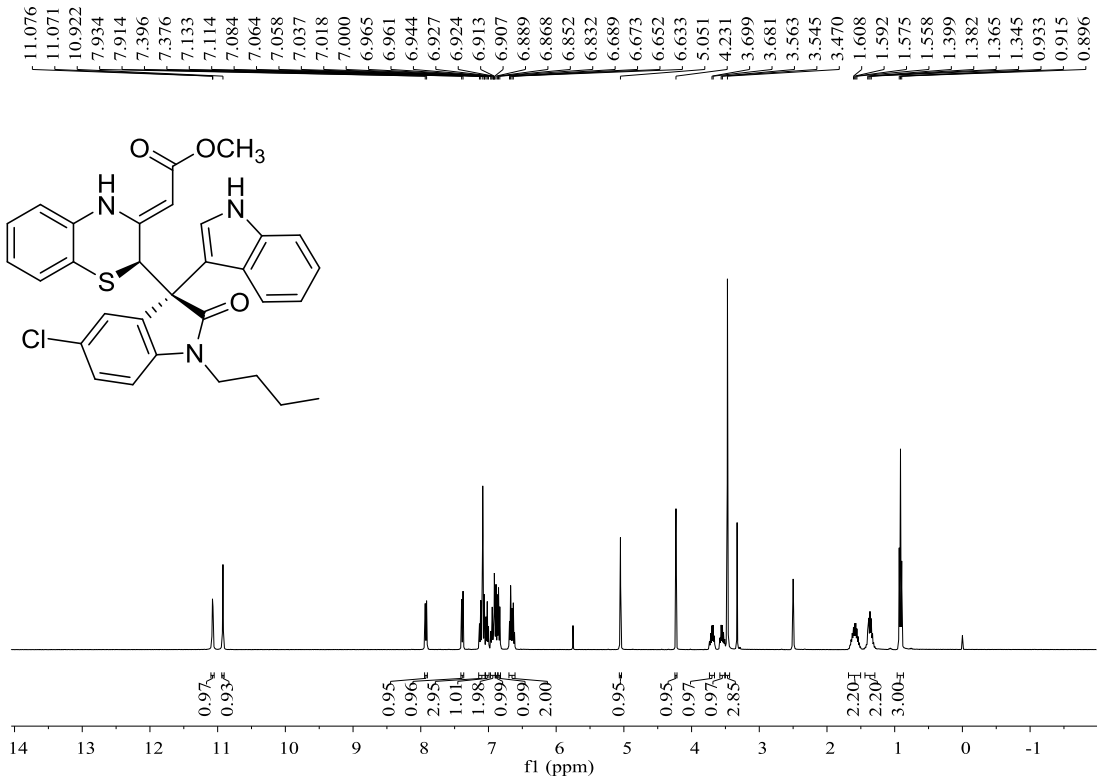
Methyl (Z)-2-(2-(1-benzyl-5-chloro-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)-2H-benzo[b][1,4]thiazin-3(4H)-ylidene)acetate (**3g'**): white solid, 40%, m.p. 205 – 207^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.26 (d, J = 2.4 Hz, 1H, NH), 10.48 (s, 1H, NH), 7.40 (d, J = 8.0 Hz, 1H, ArH), 7.26 ~ 7.22 (m, 4H, ArH), 7.20 ~ 7.14 (m, 4H, ArH), 7.08 ~ 7.03 (m, 2H, ArH), 7.01 ~ 6.99 (m, 1H, ArH), 6.92 ~ 6.88 (m, 1H, ArH), 6.86 ~ 6.82 (m, 1H, ArH), 6.78 (d, J = 8.4 Hz, 1H, ArH), 6.66 ~ 6.64 (m, 1H, ArH), 6.53 (d, J = 2.0 Hz, 1H, ArH), 5.24 (s, 1H, CH), 4.95 (d, J = 16.0 Hz, 1H, CH), 4.95 (s, 1H, CH), 4.65 (d, J = 16.0 Hz, 1H, CH), 3.62 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: NMR (101 MHz,) δ 176.2, 170.2, 147.4, 142.3, 137.5, 136.0, 135.4, 129.7, 129.1, 129.0, 127.8, 127.5, 127.4, 127.3, 126.9, 126.6, 126.2, 125.4, 123.5, 121.8, 120.6, 119.4, 117.4, 117.2, 112.5, 110.6, 110.6, 87.5, 60.0, 51.2, 44.7, 43.6; IR (KBr) υ: 3482, 3272, 3062, 2950, 2855, 1694, 1658, 1615, 1579, 1483, 1433, 1342, 1287, 1225, 1161, 1110, 1080, 1028, 934, 893, 851, 815, 794 cm^{-1}; HRMS (ESI) Calcd. for $C_{34}H_{26}ClN_3O_3S$ ([M+Na]$^{+}$): 614.1276, Found: 614.1270.

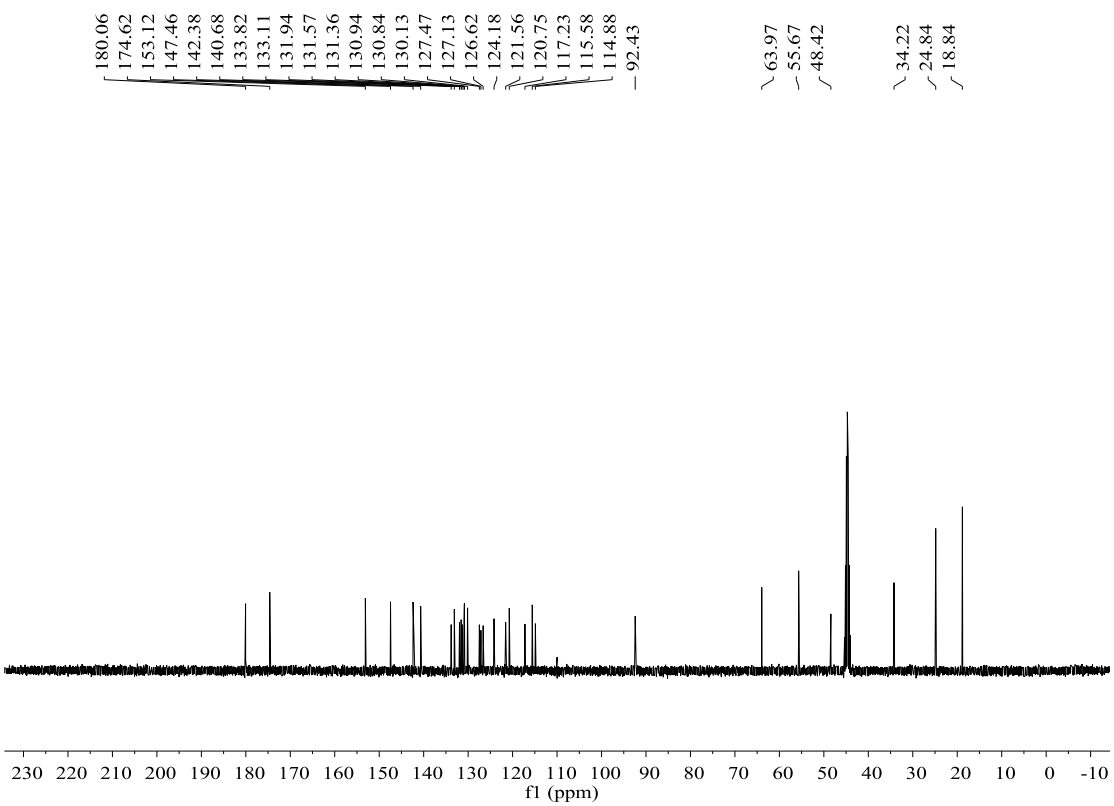



176.22
170.23
147.42
142.28
137.49
136.01
135.44
129.66
129.09
128.96
127.79
127.49
127.41
127.28
126.88
126.55
126.21
125.37
123.54
121.77
120.56
119.43
117.39
117.20
112.47
110.61
110.56
87.47
60.03
51.15
44.70
43.57
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln10 #45 RT: 0.57 AV: 1 NL: 2.88E+004
614.1270
FTMS + 100.0000-1500.0000]
m/z

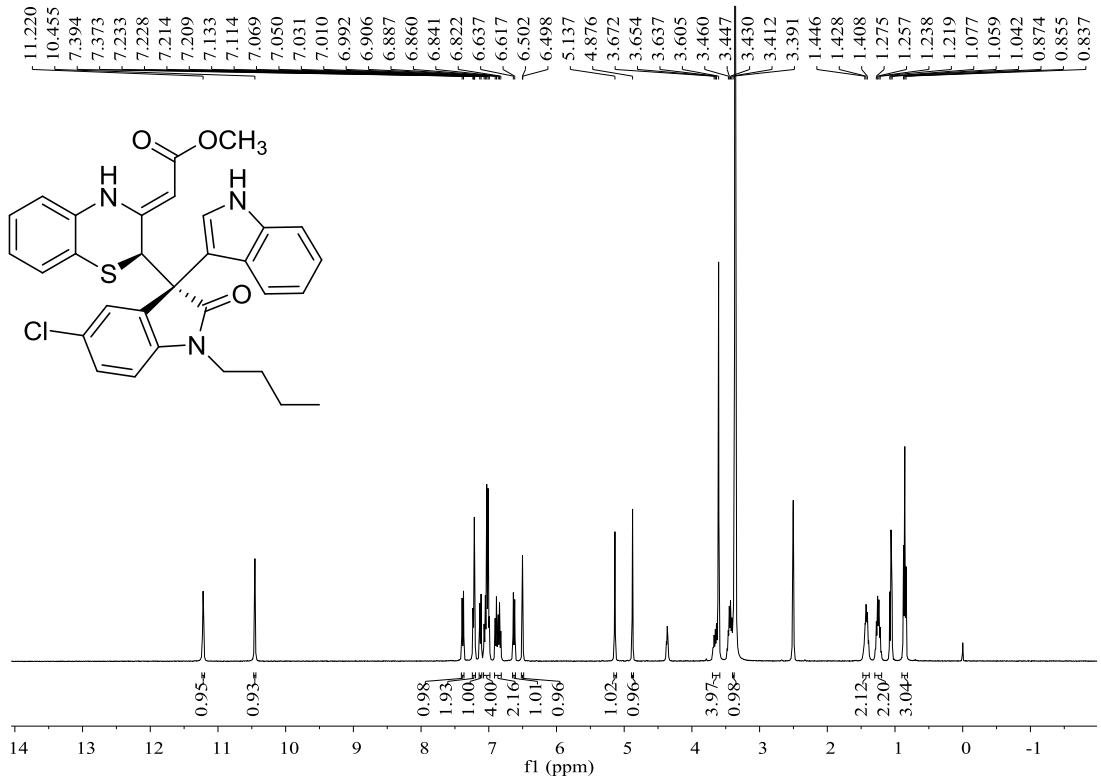
Methyl (Z)-2-(2-(1-butyl-5-chloro-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)-2H-benzo[b][1,4]thiazin-3(4H)-ylidene)acetate (**3h**): white solid, 42%, m.p. 128 – 1301^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.07 (d, J = 2.0 Hz, 1H, NH), 10.92 (s, 1H, NH), 7.92 (d, J = 8.0 Hz, 1H, ArH), 7.39 (d, J = 8.0 Hz, 1H, ArH), 7.13 ~ 7.06 (m, 3H, ArH), 7.04 ~ 7.00 (m, 1H, ArH), 6.97 ~ 6.91 (m, 2H, ArH), 6.88 (d, J = 8.4 Hz, 1H, ArH), 6.84 (d, J = 8.0 Hz, 1H, ArH), 6.69 ~ 6.62 (m, 2H, ArH), 5.05 (s, 1H, CH), 4.23 (s, 1H, CH), 3.74 ~ 3.66 (m, 1H, CH), 3.58 ~ 3.51 (m, 1H, CH), 3.47 (s, 3H, OCH_3), 1.68 ~ 1.51 (m, 2H, CH), 1.43 ~ 1.29 (m, 2H, CH), 0.93 ~ 0.90 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 180.0, 174.6, 153.1, 147.4, 142.3, 140.6, 133.8, 133.1, 131.9, 131.5, 131.3, 130.9, 130.8, 130.1, 127.4, 127.1, 126.6, 124.1, 121.5, 120.7, 117.2, 115.5, 114.8, 92.4, 63.9, 55.6, 48.4, 34.2, 24.8, 18.8; IR (KBr) υ: 3382, 3174, 3067, 2958, 2865, 1700, 1661, 1616, 1581, 1485, 1433, 1348, 1284, 1218, 1163, 1108, 1080, 1032, 939, 878, 845, 805 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{28}ClN_3O_3S$ ([M+Na]$^{+}$): 580.1432, Found: 580.1426.

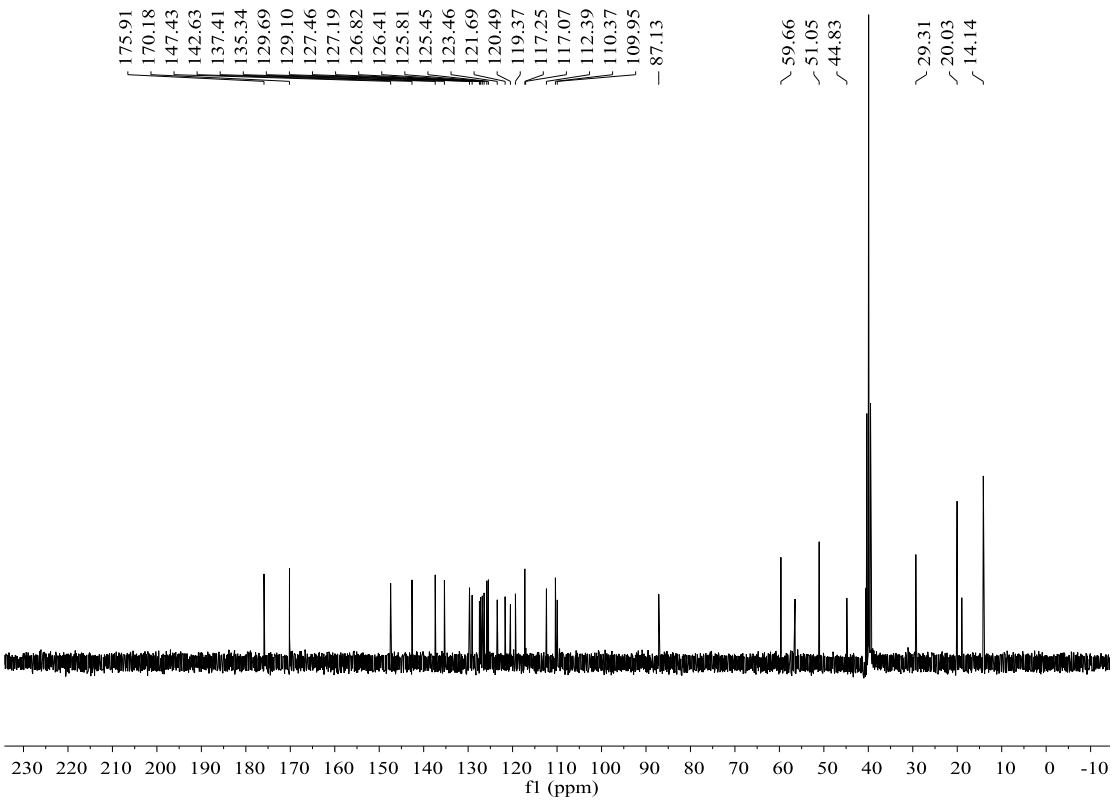



180.06
174.62
153.12
147.46
142.38
140.68
133.82
133.11
131.94
131.57
131.36
130.94
130.84
130.13
127.47
127.13
126.62
124.18
121.56
120.75
117.23
115.58
114.88
92.43
63.97
55.67
48.42
34.22
24.84
18.84
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3.74E+004
580.1426
0000-1500.0000]

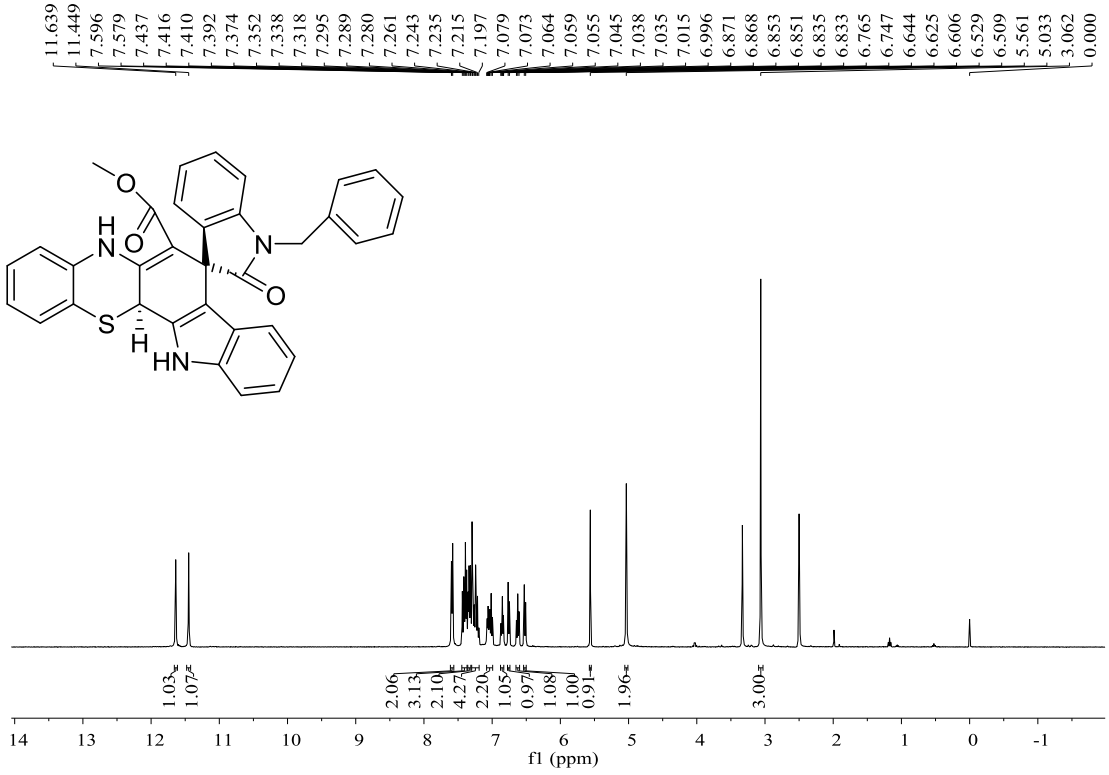
Methyl (Z)-2-(2-(1-butyl-5-chloro-3-(1H-indol-3-yl)-2-oxoindolin-3-yl)-2H-benzo[b][1,4]thiazin-3(4H)-ylidene)acetate (3h'): white solid, 42%, m.p. 122 – 124^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.22 (s, 1H, NH), 10.46 (s, 1H, NH), 7.38 (d, J = 8.4 Hz, 1H, ArH), 7.23 ~ 7.21 (m, 2H, ArH), 7.12 (d, J = 7.6 Hz, 1H, ArH), 7.07 ~ 6.99 (m, 4H, ArH), 6.91 ~ 6.82 (m, 2H, ArH), 6.63 (d, J = 8.0 Hz, 1H, ArH), 6.50 (d, J = 1.6 Hz, 1H, ArH), 5.14 (s, 1H, CH), 4.88 (s, 1H, CH), 3.69 ~ 3.64 (m, 1H, CH), 3.61 (s, 3H, OCH_3), 3.48 ~ 3.39 (m, 1H, CH), 1.47 ~ 1.39 (m, 2H, CH), 1.29 ~ 1.20 (m, 2H, CH), 0.87 ~ 0.84 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 234.3, 175.9, 170.1, 147.4, 142.6, 137.4, 135.3, 129.6, 129.1, 127.4, 127.1, 126.8, 126.4, 125.8, 125.4, 123.4, 121.6, 120.4, 119.3, 117.2, 117.0, 112.3, 110.3, 109.9, 87.1, 59.6, 51.0, 44.8, 29.3, 20.0, 14.1; IR (KBr) υ: 3446, 3248, 3064, 2958, 2869, 1691, 1658, 1616, 1580, 1483, 1435,1353, 1288, 1226, 1163, 1112, 1080, 1039, 932, 888, 796 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{28}ClN_3O_3S$ ([M+Na]$^{+}$): 580.1432, Found: 580.1426.

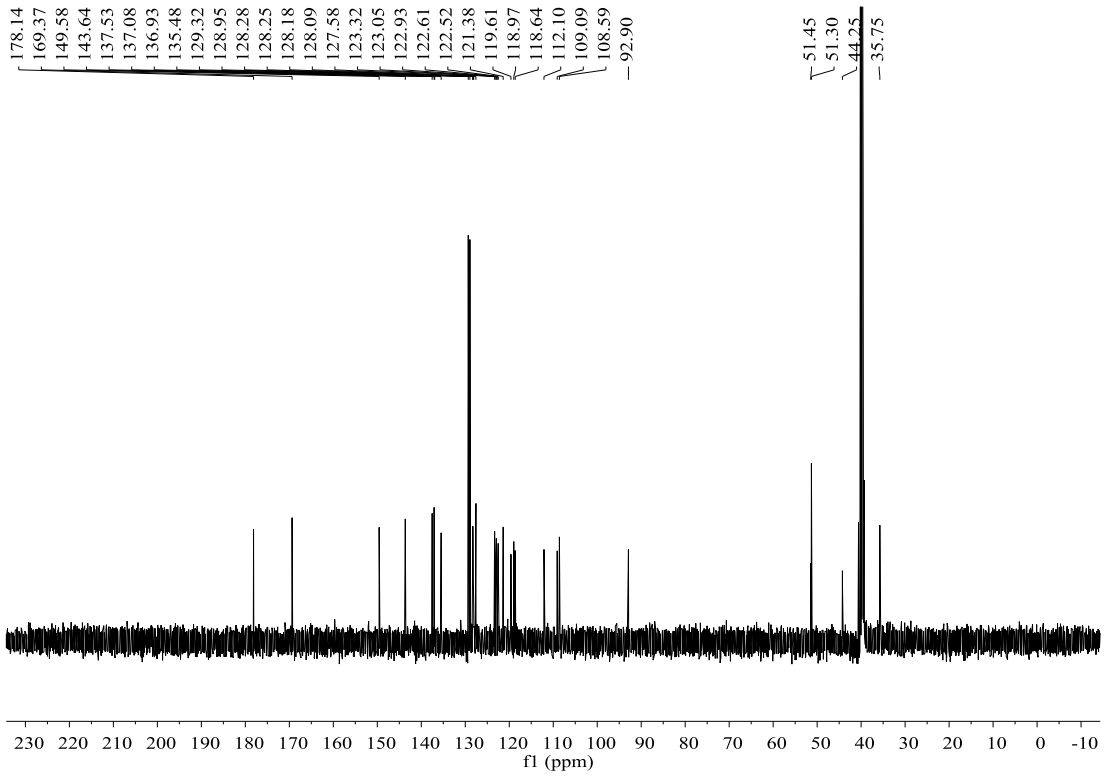


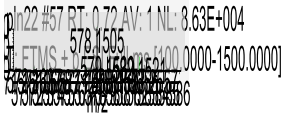

175.91
170.18
147.43
142.63
137.41
135.34
129.69
129.10
127.46
127.19
126.82
126.41
125.81
125.45
123.46
121.69
120.49
119.37
117.25
117.07
112.39
110.37
109.95
87.13
59.66
51.05
44.83
29.31
20.03
14.14
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


4.87E+004
580.1426

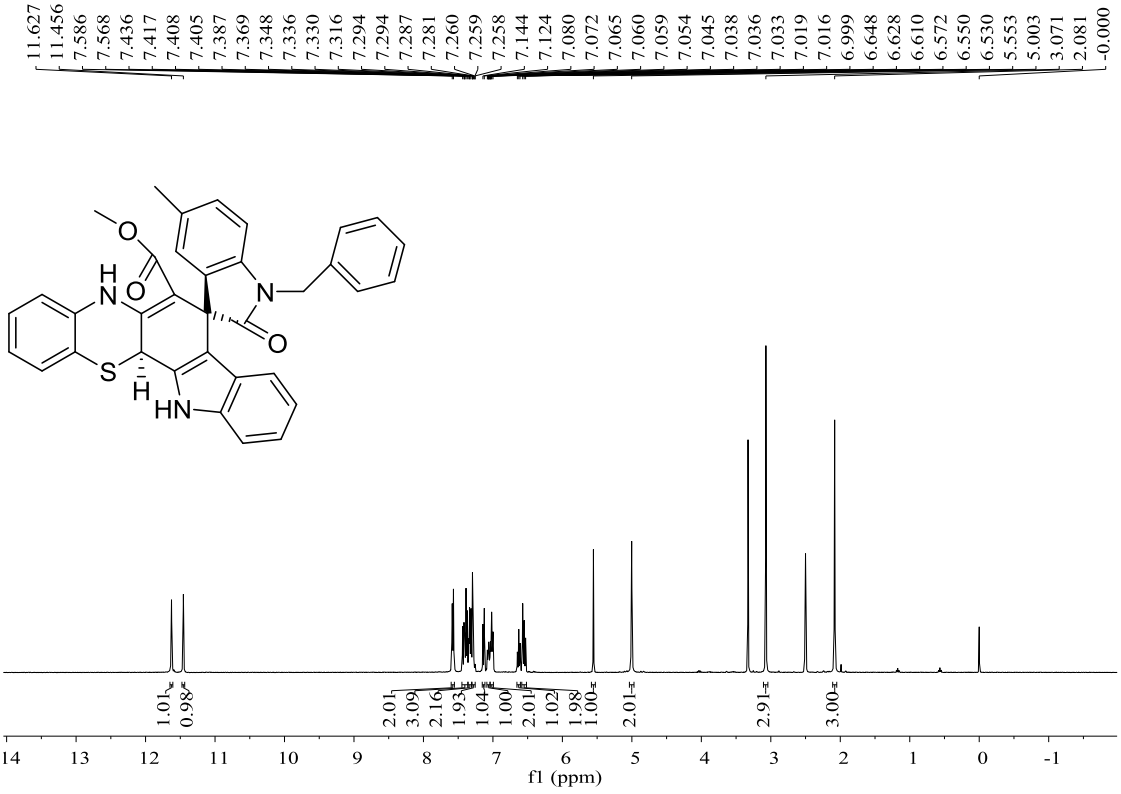
Methyl 1-benzyl-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4a**): white solid, 50%, m.p. 273 – 276^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.64 (s, 1H, NH), 11.45 (s, 1H, NH), 7.59 (d, J = 6.8 Hz, 2H, ArH), 7.44 ~ 7.37 (m, 3H, ArH), 7.35 ~ 7.32 (m, 2H, ArH), 7.29 ~ 7.20 (m, 4H, ArH), 7.08 ~ 7.00 (m, 2H, ArH), 6.87 ~ 6.83 (m, 1H, ArH), 6.76 (d, J = 7.2 Hz, 1H, ArH), 6.63 (t, J = 7.6 Hz, 1H, ArH), 6.52 (d, J = 8.0 Hz, 1H, ArH), 5.56 (s, 1H, CH), 5.03 (s, 2H, CH), 3.06 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 178.1, 169.4, 149.6, 143.6, 137.5, 137.1, 136.9, 135.5, 129.3, 129.0, 128.3, 128.3, 128.2, 128.1, 127.6, 123.3, 123.1, 122.9, 122.6, 122.5, 121.4, 119.6, 119.0, 118.6, 112.1, 109.1, 108.6, 92.9, 51.5, 51.3, 44.3, 35.8; IR (KBr) υ: 3240, 3064, 2949, 1695, 1662, 1609, 1565, 1484, 1459, 1371, 1347, 1245, 1179, 1072, 1043, 1001, 952, 924, 843, 787 cm^{-1}; HRMS (ESI) Calcd. for $C_{34}H_{25}N_3O_3S$ ([M+Na]$^{+}$): 578.1509, Found: 578.1505.

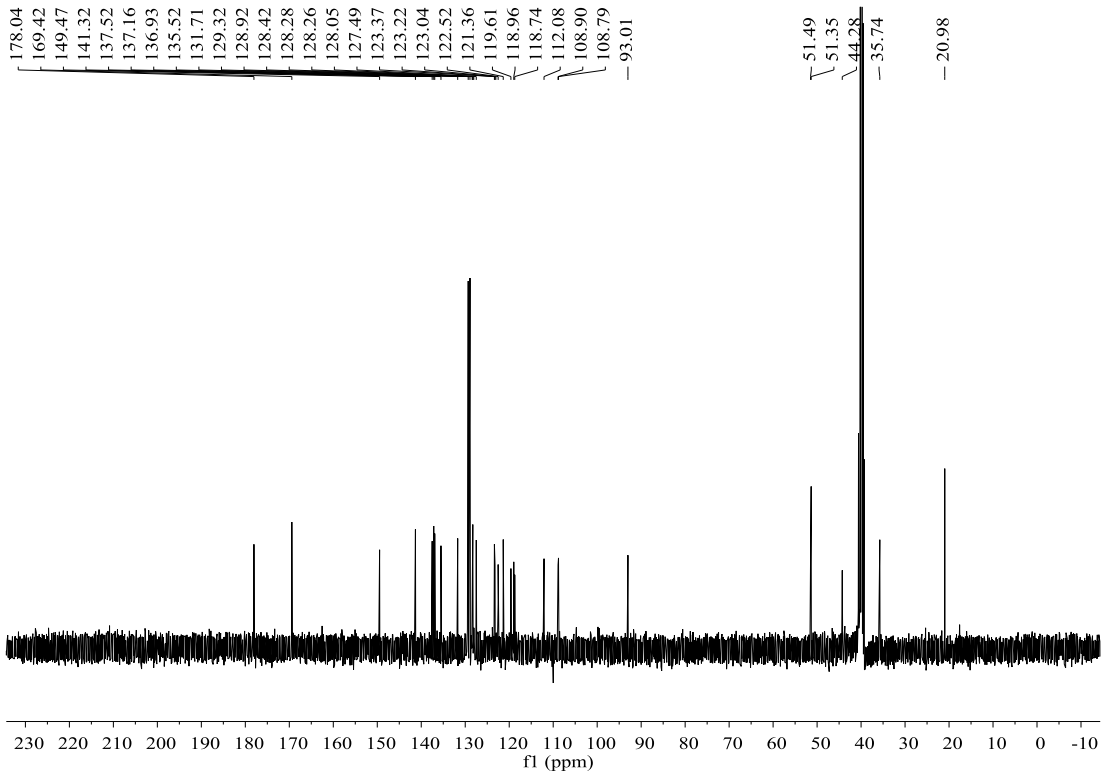


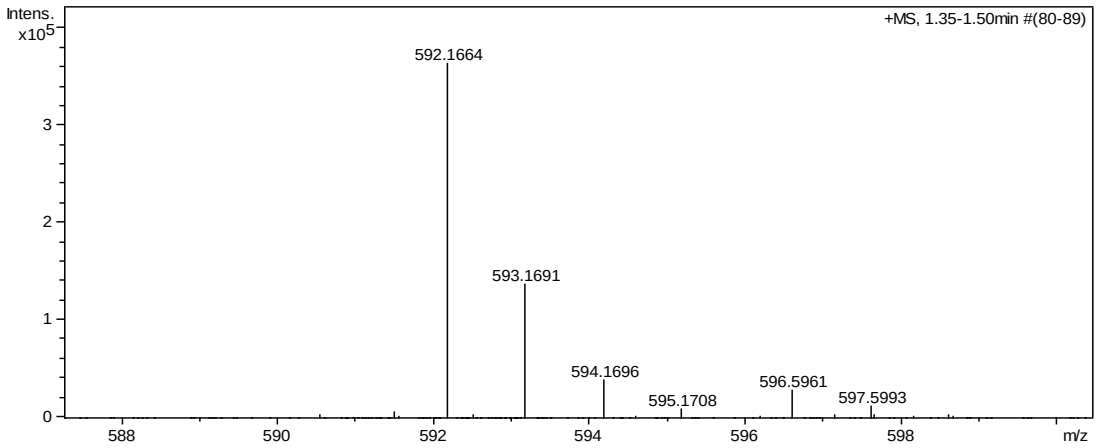

178.14
169.37
149.58
143.64
137.53
137.08
136.93
135.48
129.32
128.95
128.28
128.25
128.18
128.09
127.58
123.32
123.05
122.93
122.61
122.52
121.38
119.61
118.97
118.64
112.10
109.09
108.59
92.90
51.45
51.30
44.25
35.75
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


578.1505
m/z

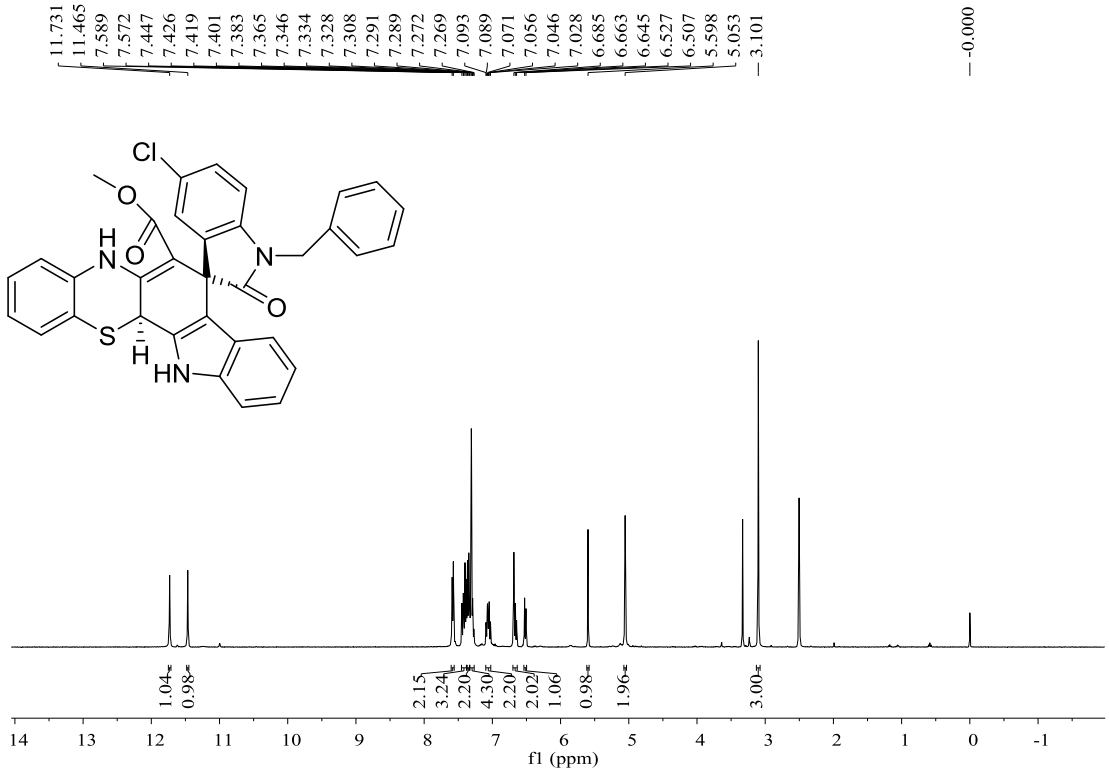
Methyl 1-benzyl-5-methyl-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4b**): white solid, 48%, m.p. 302 – 304^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.63 (s, 1H, NH), 11.46 (s, 1H, NH), 7.58 (d, *J* = 7.2 Hz, 2H, ArH), 7.44 ~ 7.37 (m, 3H, ArH), 7.35 ~ 7.32 (m, 2H, ArH), 7.29 ~ 7.26 (m, 2H, ArH), 7.13 (d, *J* = 8.0 Hz, 1H, ArH), 7.08 ~ 7.05 (m, 1H, ArH), 7.04 ~ 7.00 (m, 2H, ArH), 6.65 ~ 6.61 (m, 1H, ArH), 6.57 ~ 6.53 (m, 2H, ArH), 5.55 (s, 1H, CH), 5.00 (s, 2H, CH), 3.07 (s, 3H, OCH_3) , 2.08 (s, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d$_6$) δ: 178.0, 169.4, 149.5, 141.3, 137.5, 137.2, 136.9, 135.5, 131.7, 129.3, 128.9, 128.4, 128.3, 128.3, 128.1, 127.5, 123.4, 123.2, 123.0, 122.5, 121.4, 119.6, 119.0, 118.7, 112.1, 108.9, 108.8, 93.0, 51.5, 51.4, 44.3, 35.7, 21.0; IR (KBr) υ: 3184, 3065, 2950, 1691, 1661, 1609, 1591, 1566, 1489, 1459, 1435, 1373, 1330, 1248, 1183, 1073, 1028, 925, 800, 780 cm^{-1}; HRMS (ESI) Calcd. for $C_{35}H_{27}N_3O_3S$ ([M+Na]$^{+}$): 592.1665, Found: 592.1664.

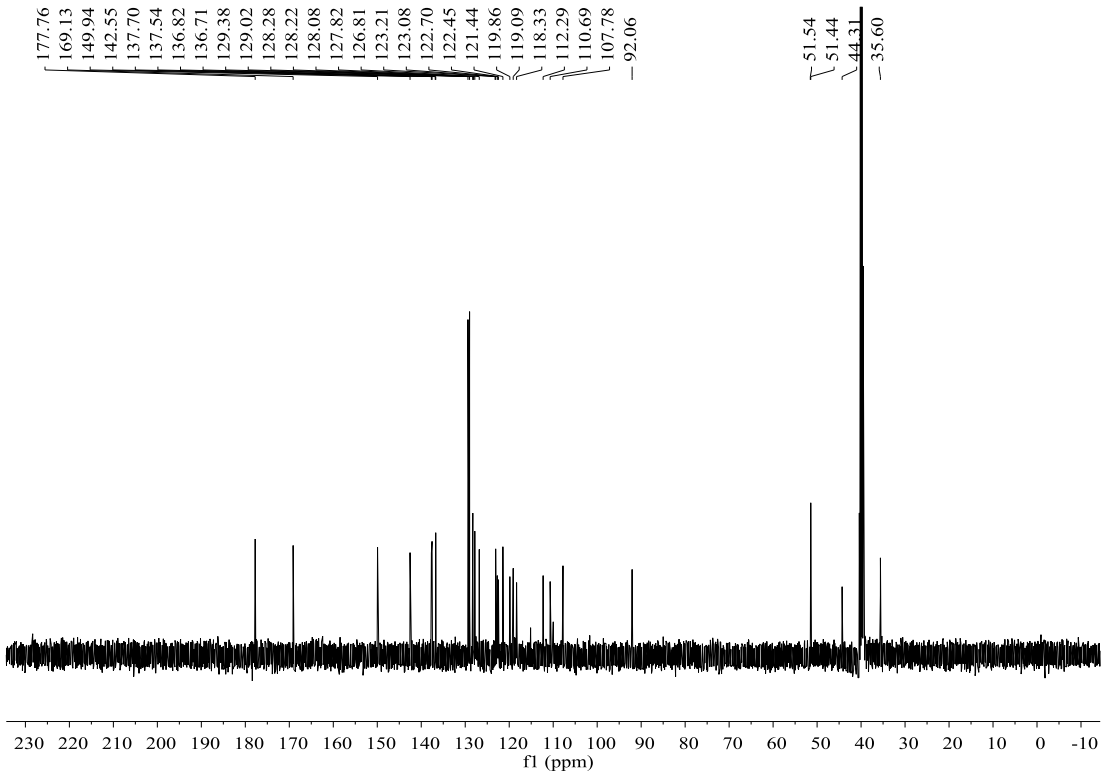



178.04
169.42
149.47
141.32
137.52
137.16
136.93
135.52
131.71
129.32
128.92
128.42
128.28
128.26
128.05
127.49
123.37
123.22
123.04
122.52
121.36
119.61
118.96
118.74
112.08
108.90
108.79
93.01
51.49
51.35
44.28
35.74
20.98
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 1.35-1.50min #(80-89)
592.1664
593.1691
594.1696
595.1708
596.5961
597.5993
0
1
2
3
588
590
592
594
596
598
m/z

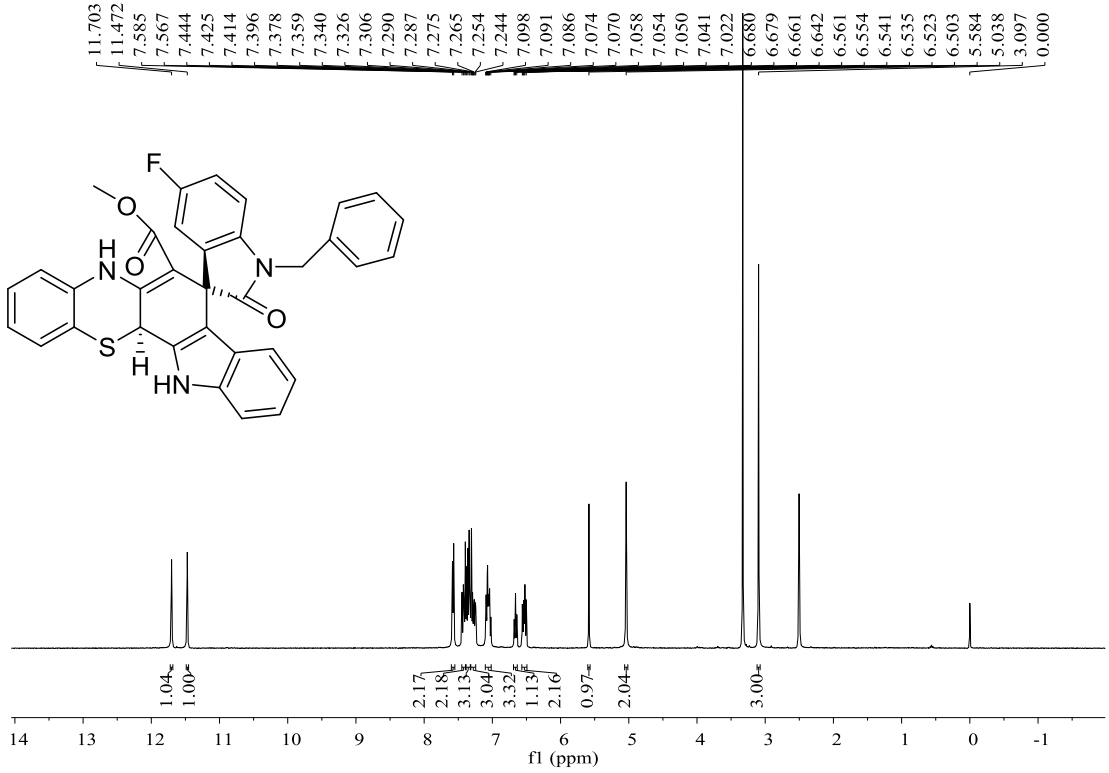
Methyl 1-benzyl-5-chloro-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4c**): white solid, 49%, m.p. 268 – 270^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.73 (s, 1H, NH), 11.47 (s, 1H, NH), 7.58 (d, *J* = 6.8 Hz, 2H, ArH), 7.45 ~ 7.38 (m, 2H, ArH), 7.37 ~ 7.33 (m, 2H, ArH), 7.33 ~ 7.27 (m, 4H, ArH), 7.09 ~ 7.03 (m, 2H, ArH), 6.69 ~ 6.65 (m, 2H, ArH), 6.52 (d, *J* = 8.0 Hz, 1H, ArH), 5.60 (s, 1H, CH), 5.05 (s, 2H, CH), 3.10 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 177.8, 169.1, 149.9, 142.6, 137.7, 137.5, 136.8, 136.7, 129.4, 129.0, 128.3, 128.2, 128.1, 127.8, 126.8, 123.2, 123.1, 122.7, 122.5, 121.4, 119.9, 119.1, 118.3, 112.3, 110.7, 107.8, 92.1, 51.5, 51.4, 44.3, 35.6; IR (KBr) υ: 3290, 3066, 2953, 1697, 1659, 1610, 1588, 1565, 1480, 1430, 1327, 1246, 1168, 1111, 1073, 1031, 936, 890, 802 cm^{-1}; HRMS (ESI) Calcd. for $C_{34}H_{24}ClN_3O_3S$ ([M+Na]$^{+}$): 612.1119, Found: 612.1110.

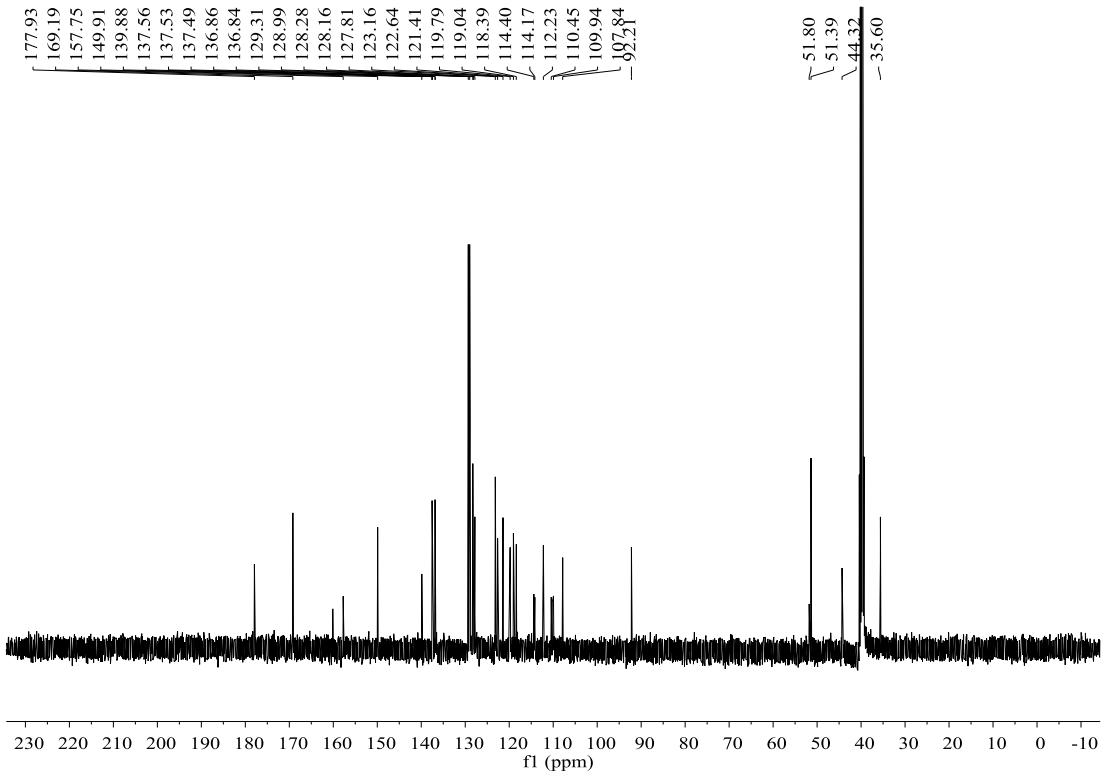


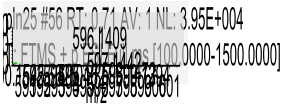

177.76
169.13
149.94
142.55
137.70
137.54
136.82
136.71
129.38
129.02
128.28
128.22
128.08
127.82
126.81
123.21
123.08
122.70
122.45
121.44
119.86
119.09
118.33
112.29
110.69
107.78
92.06
51.54
51.44
44.31
35.60
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


n24 #64 RT: 0.81 AV: 1 NL: 2.32E+004
612.1110
FTMS + [100.0000-1500.0000]

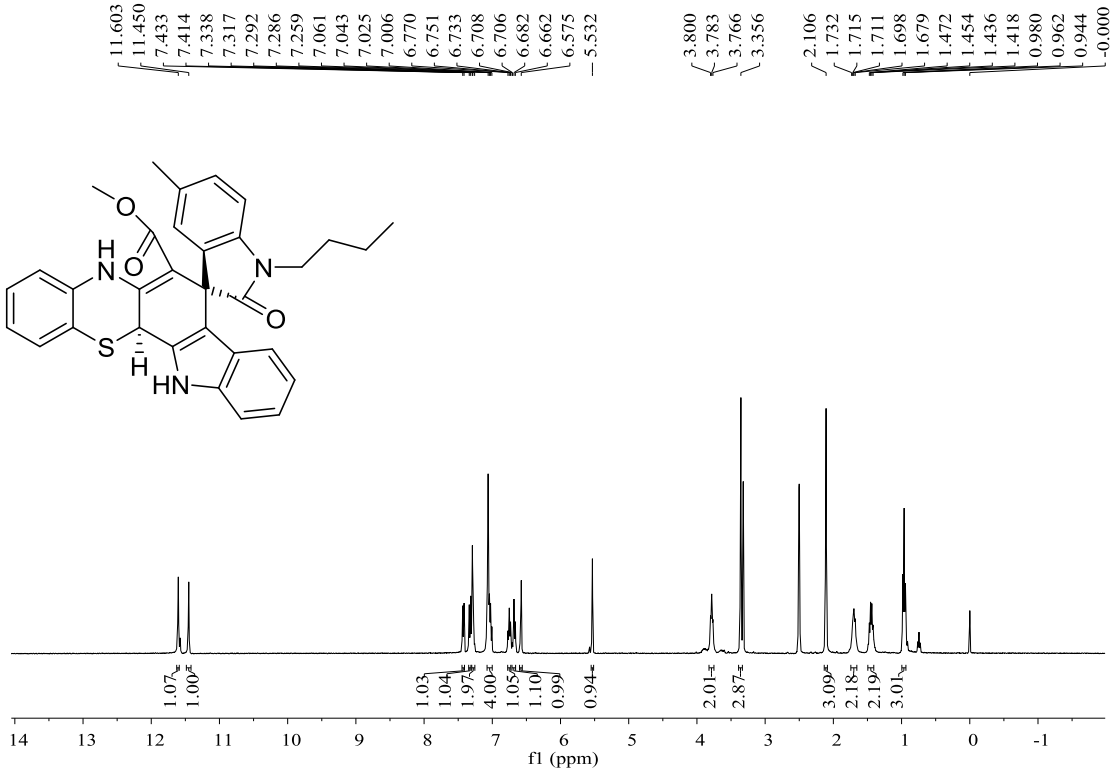
Methyl 1-benzyl-5-fluoro-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4d**): white solid, 57%, m.p. 269 – 271^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.70 (s, 1H, NH), 11.47 (s, 1H, NH), 7.58 (d, *J* = 7.2 Hz, 2H, ArH), 7.44 ~ 7.40 (m, 2H, ArH), 7.38 ~ 7.33 (m, 3H, ArH), 7.31 ~ 7.24 (m, 3H, ArH), 7.10 ~ 7.02 (m, 3H, ArH), 6.68 ~ 6.64 (m, 1H, ArH), 6.56 ~ 6.50 (m, 2H, ArH), 5.58 (s, 1H, CH), 5.04 (s, 2H, CH), 3.10 (s, 3H, OCH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 177.9, 169.2, 158.9 (d, *J* = 239.4 Hz), 149.9, 139.9, 137.6, 137.5, 137.5, 136.9 (d, *J* = 2.0 Hz), 129.3, 129.0, 128.3, 128.2, 127.8, 123.2, 122.6, 121.4, 119.8, 119.0, 118.4, 114.3 (d, *J* = 23.2 Hz), 112.2, 110.3 (d, *J* = 25.3 Hz), 110.0 (d, *J* = 8.1 Hz), 107.8, 92.2, 51.8, 51.4, 44.3, 35.6; IR (KBr) υ: 3184, 3065, 2949, 1699, 1663, 1612, 1586, 1564, 1486, 1454, 1336, 1250, 1172, 1075, 1048, 1025, 943, 861, 806, 777 cm^{-1}; HRMS (ESI) Calcd. for $C_{34}H_{24}FN_3O_3S$ ([M+Na]$^{+}$): 596.1415, Found: 596.1409.

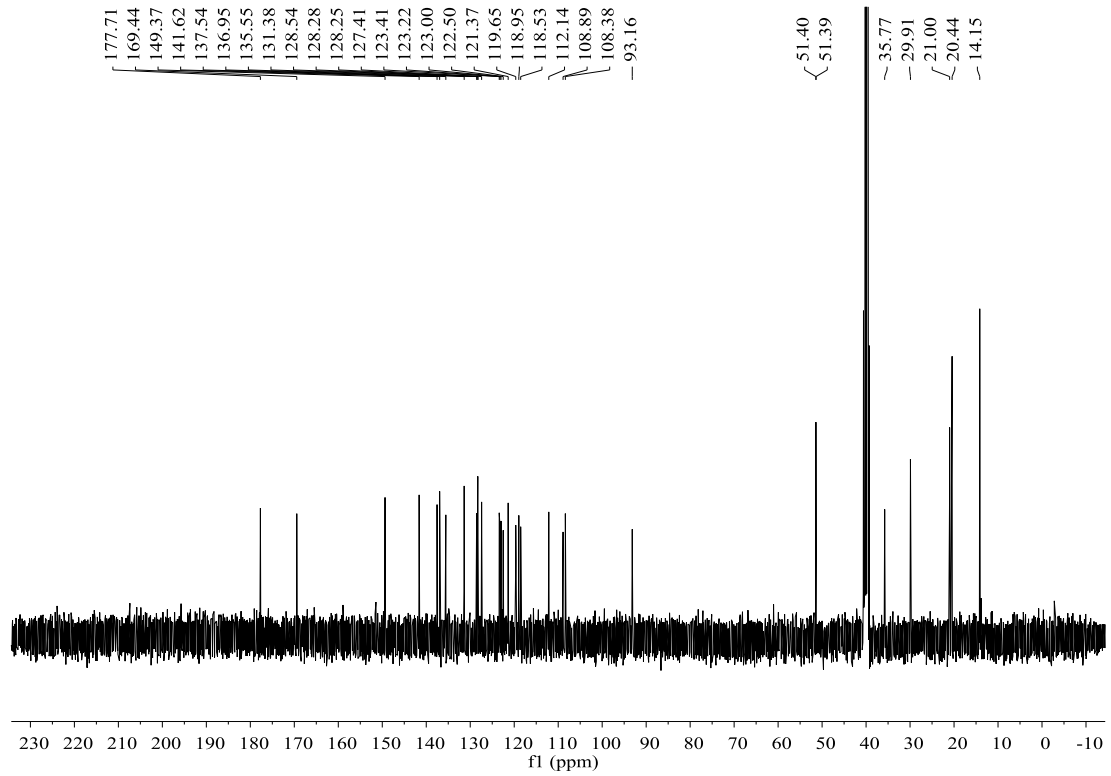



177.93
169.19
157.75
149.91
139.88
137.56
137.53
137.49
136.86
136.84
129.31
128.99
128.28
128.16
127.81
123.16
122.64
121.41
119.79
119.04
118.39
114.40
114.17
112.23
110.45
109.94
107.84
92.21
51.80
51.39
44.32
35.60
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln25 #56 RT: 0.71 AV: 1 NL: 3.95E+004
596.1409
m/z

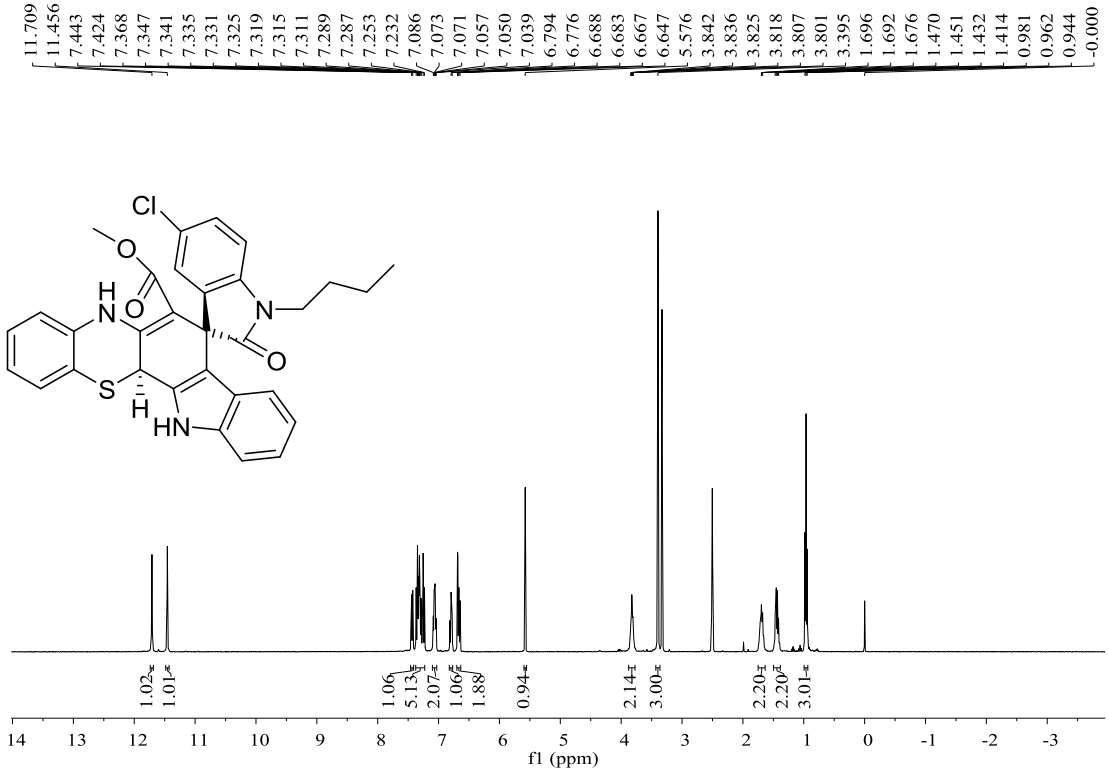
Methyl 1-butyl-5-methyl-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4e**): white solid, 38%, m.p. 245 – 247^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.60 (s, 1H, NH), 11.45 (s, 1H, NH), 7.42 (d, J = 7.6 Hz, 1H, ArH), 7.33 (d, J = 8.4 Hz, 1H, ArH), 7.29 ~ 7.26 (m, 2H, ArH), 7.06 ~ 7.01 (m, 4H, ArH), 6.77 ~ 6.73 (m, 1H, ArH), 6.71 ~ 6.66 (m, 1H, ArH), 6.58 (m, 1H, ArH), 5.53 (s, 1H, CH), 3.80 ~ 3.77 (m, 2H, CH), 3.36 (s, 3H, OCH_3), 2.11 (s, 3H, CH_3), 1.73 ~ 1.66 (m, 2H, CH), 1.49 ~ 1.41 (m, 2H, CH), 0.98 ~ 0.94 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d$_6$) δ: 177.7, 169.4, 149.4, 141.6, 137.5, 137.0, 135.6, 131.4, 128.5, 128.3, 128.3, 127.4, 123.4, 123.2, 123.0, 122.5, 121.4, 119.7, 119.0, 118.5, 112.1, 108.9, 108.4, 93.2, 51.4, 51.4, 35.8, 29.9, 21.0, 20.4, 14.2; IR (KBr) υ: 3175, 2954, 2870, 1693, 1659, 1598, 1565, 1488, 1437, 1378, 1349, 1250, 1193, 1136, 1053, 888, 807 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{29}N_3O_3S$ ([M+Na]$^{+}$): 558.1822, Found: 558.1816.

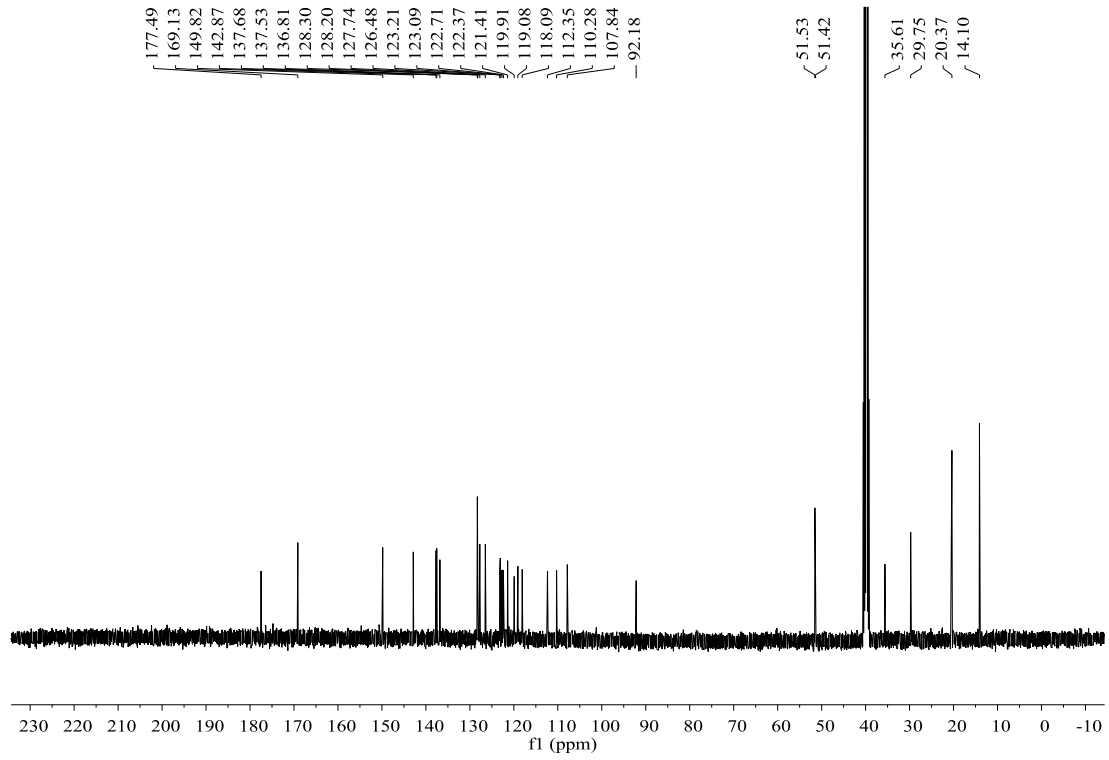


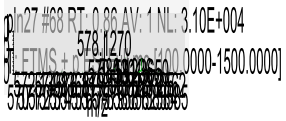

177.71
169.44
149.37
141.62
137.54
136.95
135.55
131.38
128.54
128.28
128.25
127.41
123.41
123.22
123.00
122.50
121.37
119.65
118.95
118.53
112.14
108.89
108.38
93.16
51.40
51.39
35.77
29.91
21.00
20.44
14.15
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln26 #46 RT: 0.58 AV: 1 NL: 1.17E+005
558.1815

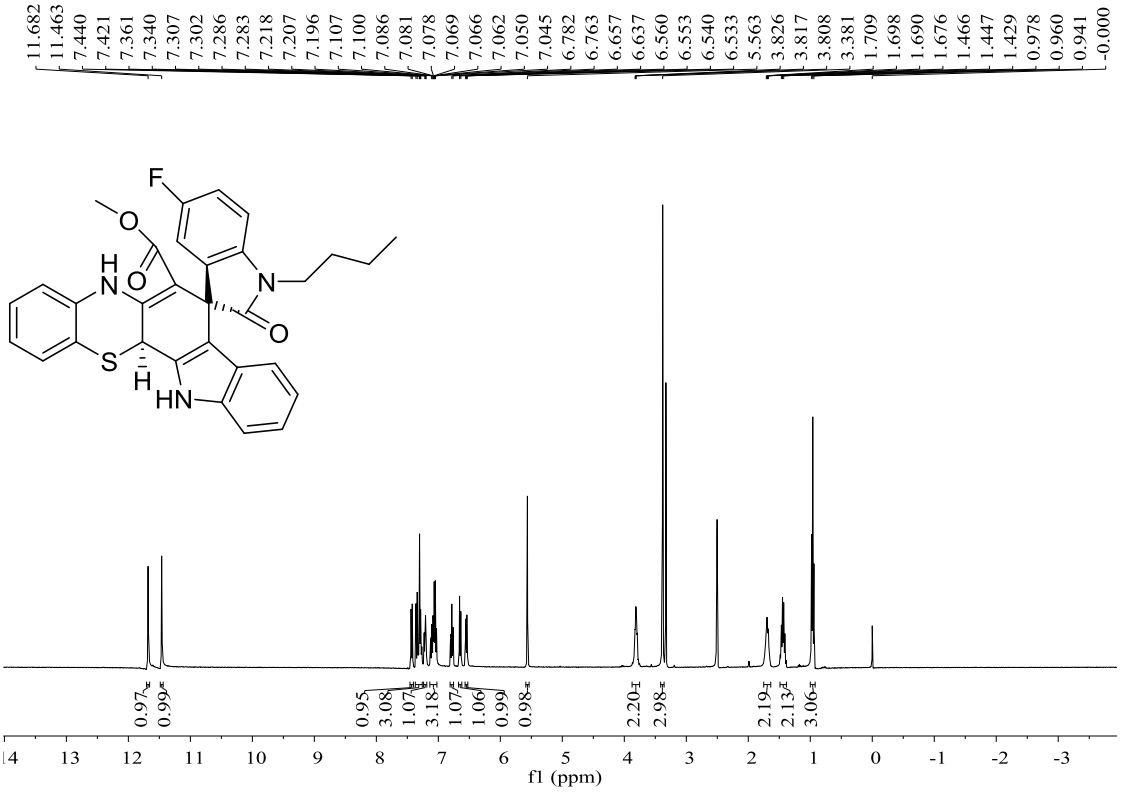
Methyl 1-butyl-5-chloro-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4f**): white solid, 43%, m.p. 267 – 269^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.71 (s, 1H, NH), 11.46 (s, 1H, NH), 7.43 (d, J = 7.6 Hz, 1H, ArH), 7.37 ~ 7.23 (m, 5H, ArH), 7.09 ~ 7.04 (m, 2H, ArH), 6.81 ~ 6.78 (m, 1H, ArH), 6.69 ~ 6.65 (m, 2H, ArH), 5.58 (s, 1H, CH), 3.88 ~ 3.77 (m, 2H, CH), 3.40 (s, 3H, OCH_3), 1.75 ~ 1.64 (m, 2H, CH), 1.49 ~ 1.40 (m, 2H, CH), 0.98 ~ 0.94 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d$_6$) δ: 177.5, 169.1, 149.8, 142.9, 137.7, 137.5, 136.8, 128.3, 128.2, 127.7, 126.5, 123.2, 123.1, 122.7, 122.4, 121.4, 119.9, 119.1, 118.1, 112.4, 110.3, 107.8, 92.2, 51.5, 51.4, 35.6, 29.8, 20.4, 14.1; IR (KBr) υ: 3170, 2955, 2869, 1696, 1663, 1591, 1565, 1479, 1431, 1347, 1246, 1189, 1139, 1106, 1071, 1025, 930, 888, 803 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{26}ClN_3O_3S$ ([M+Na]$^{+}$): 578.1276, Found: 578.1270.

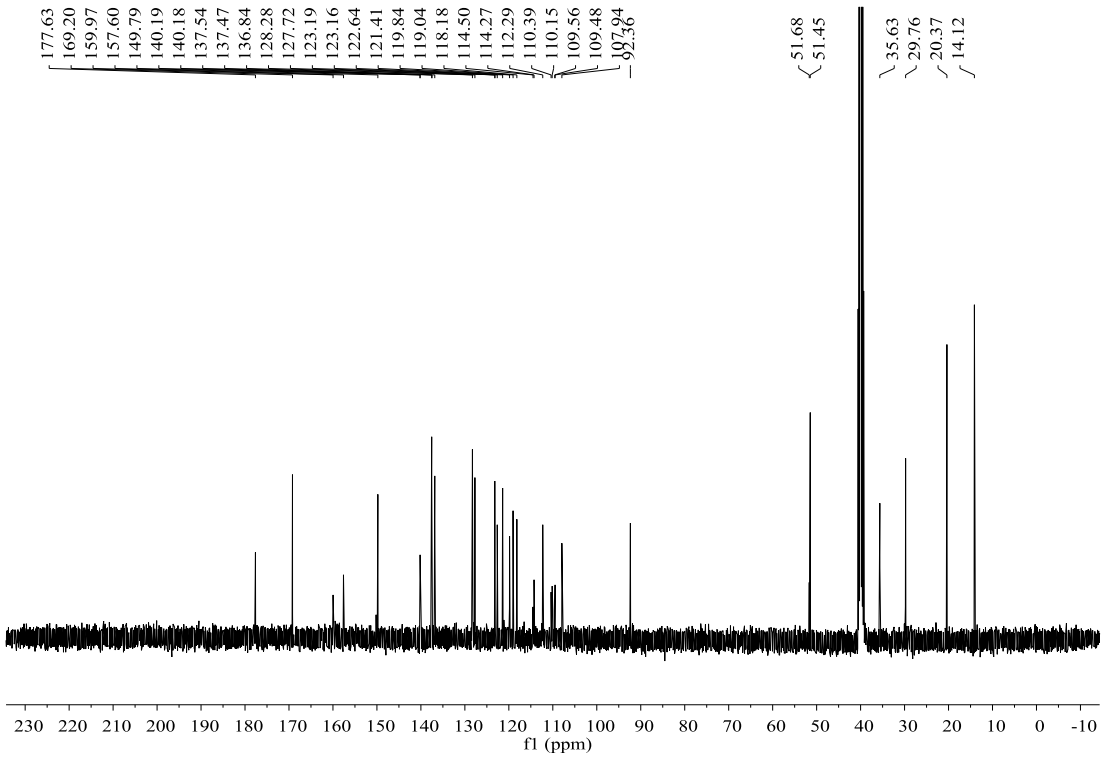



177.49
169.13
149.82
142.87
137.68
137.53
136.81
128.30
128.20
127.74
126.48
123.21
123.09
122.71
122.37
121.41
119.91
119.08
118.09
112.35
110.28
107.84
92.18
51.53
51.42
35.61
29.75
20.37
14.10
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln27 #68 RT: 0.86 AV: 1 NL: 3.10E+004
578.1270
FTMS + p ESI Full ms [400.0000-1500.0000]
m/z

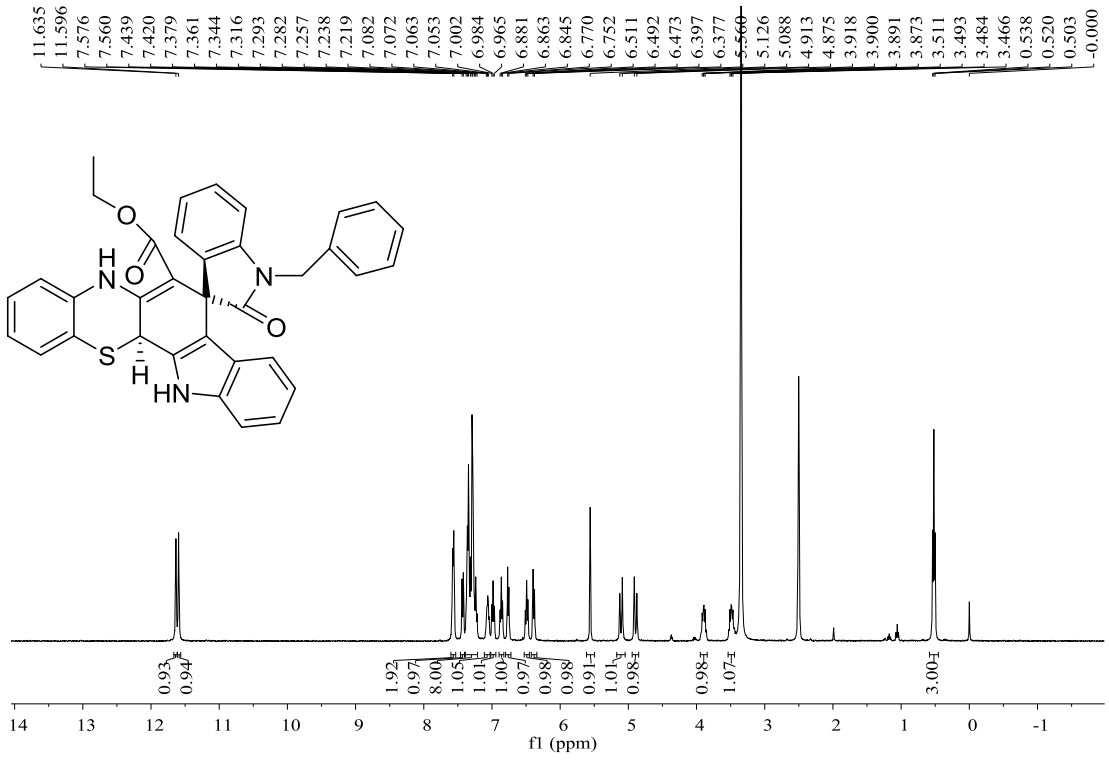
Methyl 1-butyl-5-fluoro-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4g**): white solid, 56%, m.p. 274 – 276^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.68 (s, 1H, NH), 11.46 (s, 1H, NH), 7.43 (d, *J* = 7.6 Hz, 1H, ArH), 7.36 ~ 7.26 (m, 3H, ArH), 7.23 ~ 7.20 (m, 1H, ArH), 7.13 ~ 7.03 (m, 3H, ArH), 6.80 ~ 6.76 (m, 1H, ArH), 6.65 (d, *J* = 8.0 Hz, 1H, ArH), 6.56 ~ 6.53 (m, 1H, ArH), 5.56 (s, 1H, CH), 3.87 ~ 3.76 (m, 2H, CH), 3.38 (s, 3H, OCH_3), 1.73 ~ 1.65 (m, 2H, CH), 1.48 ~ 1.39 (m, 2H, CH), 0.98 ~ 0.94 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 177.6, 169.2, 160.0, 157.6, 150.2, 149.8, 140.2 (d, *J* = 1.0 Hz), 137.5, 137.5, 136.8, 128.3, 127.7, 123.2, 123.2, 122.6, 121.4, 119.8, 119.0, 118.2, 114.4 (d, *J* = 23.2 Hz), 112.3, 110.3 (d, *J* = 24.2 Hz), 109.5 (d, *J* = 8.1 Hz), 107.9, 92.4, 51.7, 51.5, 35.6, 29.8, 20.4, 14.1; IR (KBr) υ: 3180, 2956, 2872, 1687, 1662, 1614, 1586, 1565, 1485, 1456, 1380, 1350, 1250, 1189, 1133, 1054, 1026, 999, 943, 881, 862, 818 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{26}FN_3O_3S$ ([M+H]$^{+}$): 562.1571, Found: 562.1566.

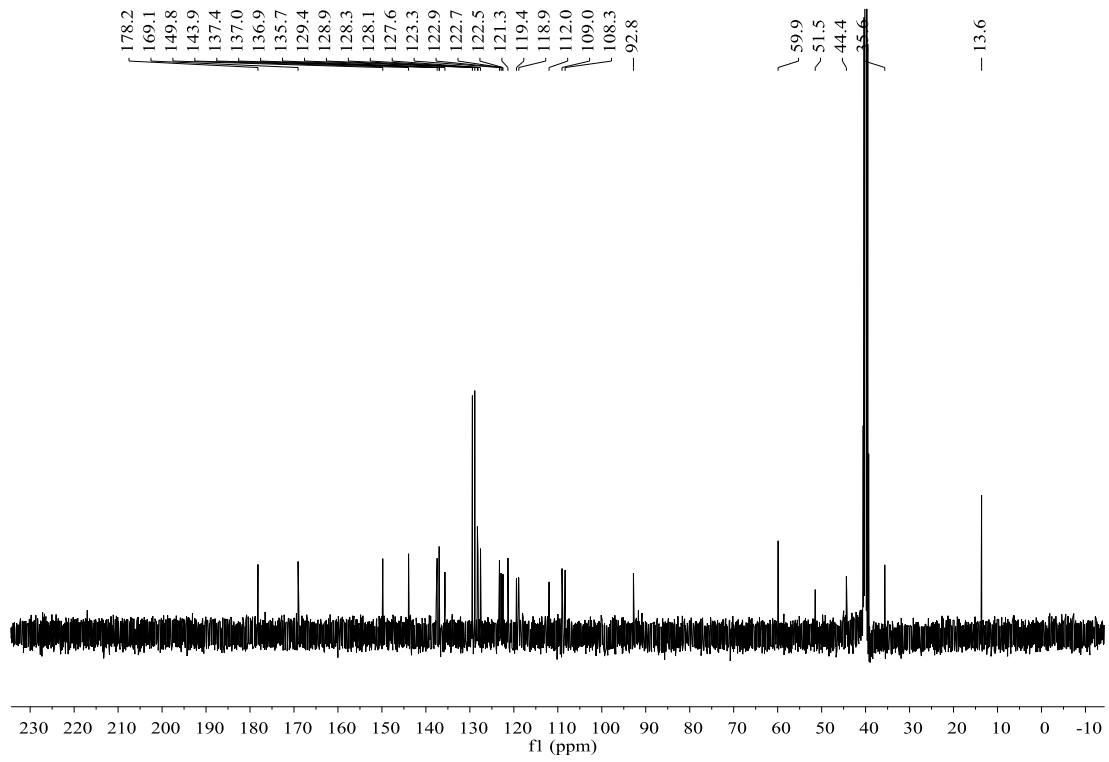


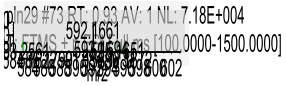

177.63
169.20
159.97
157.60
149.79
140.19
140.18
137.54
137.47
136.84
128.28
127.72
123.19
123.16
122.64
121.41
119.84
119.04
118.18
114.50
114.27
112.29
110.39
110.15
109.56
109.48
107.94
92.36
51.68
51.45
35.63
29.76
20.37
14.12
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln28 #72 RT: 0.92 AV: 1 NL: 5.29E+004
562.1566

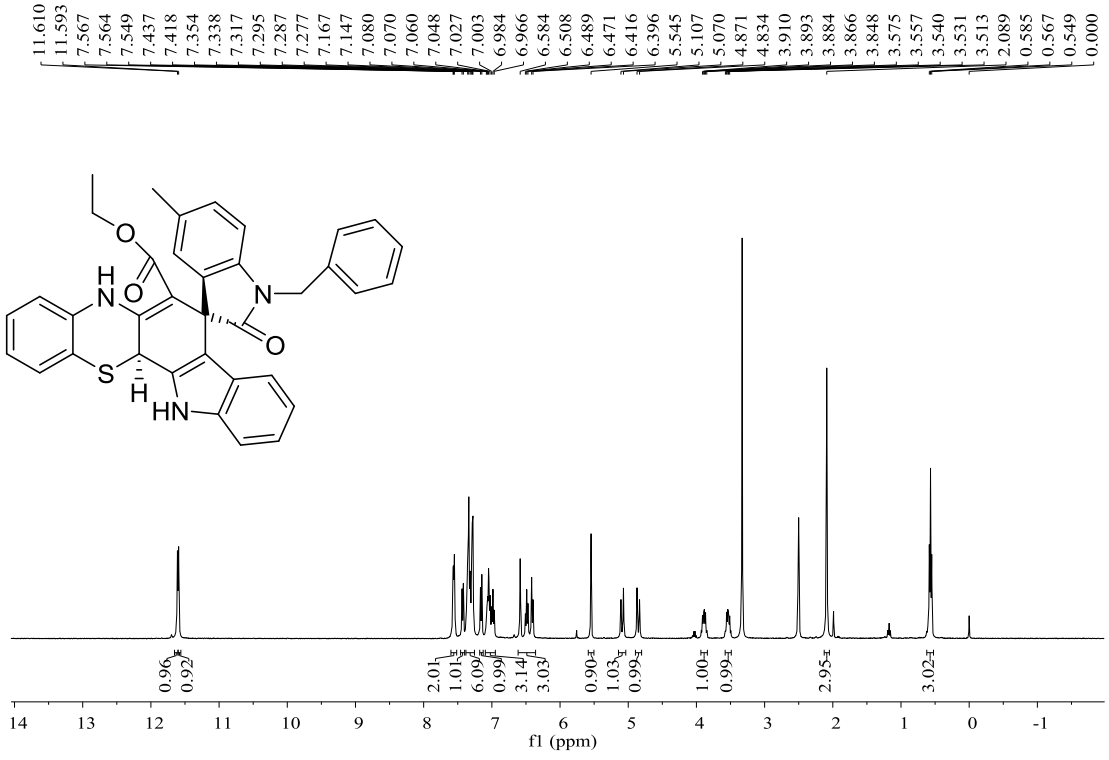
Ethyl 1-benzyl-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4h**): white solid, 41%, m.p. 256 – 258^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.64 (s, 1H, NH), 11.60 (s, 1H, NH), 7.57 (d, *J* = 6.4 Hz, 2H, ArH), 7.43 (d, *J* = 7.6 Hz, 1H, ArH), 7.38 ~ 7.22 (m, 8H, ArH), 7.08 ~ 7.04 (m, 1H, ArH), 7.00 ~ 6.97 (m, 1H, ArH), 6.88 ~ 6.85 (m, 1H, ArH), 6.76 (d, *J* = 7.2 Hz, 1H, ArH), 6.51 ~ 6.47 (m, 1H, ArH), 6.39 (d, *J* = 8.0 Hz, 1H, ArH), 5.56 (s, 1H, CH), 5.11 (d, *J* = 15.2 Hz, 1H, CH), 4.89 (d, *J* = 15.2 Hz, 1H, CH), 3.94 ~ 3.86 (m, 1H, CH), 3.53 ~ 3.45 (m, 1H, CH), 0.54 ~ 0.50 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d$_6$) δ: 178.2, 169.1, 149.8, 143.9, 137.4, 137.0, 136.9, 135.7, 129.4, 128.9, 128.3, 128.1, 127.6, 123.3, 122.9, 122.7, 122.5, 121.4, 119.4, 118.9, 112.0, 109.0, 108.3, 92.8, 59.9, 51.5, 44.4, 35.6, 13.6; IR (KBr) υ: 3216, 2982, 2905, 1695, 1654, 1610, 1565, 1481, 1459, 1347, 1243, 1178, 1077, 1048, 1003, 928, 786 cm^{-1}; HRMS (ESI) Calcd. for $C_{35}H_{27}N_3O_3S$ ([M+Na]$^{+}$): 592.1665, Found: 592.1661.

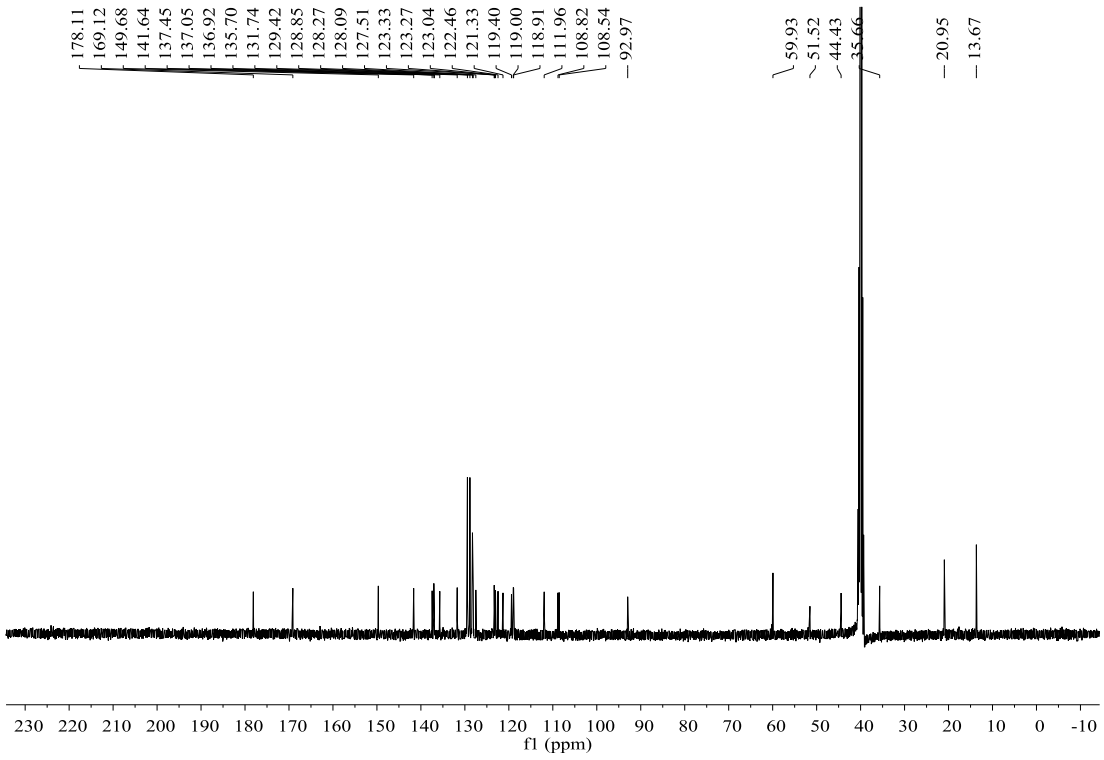



178.2
169.1
149.8
143.9
137.4
137.0
136.9
135.7
129.4
128.9
128.3
128.1
127.6
123.3
122.9
122.7
122.5
121.3
119.4
118.9
112.0
109.0
108.3
92.8
59.9
51.5
44.4
25.6
13.6
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


592.1661

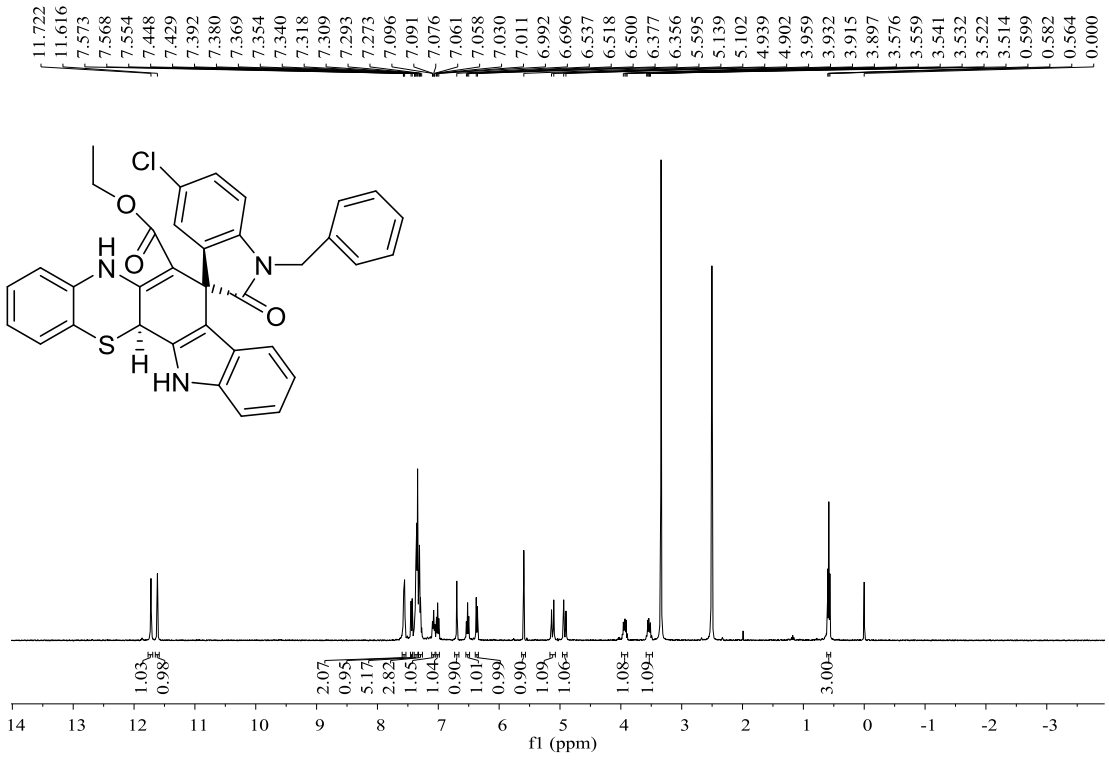
Ethyl 1-benzyl-5-methyl-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4i**): white solid, 35%, m.p. 268 – 270^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.61 (s, 1H, NH), 11.59 (s, 1H, NH), 7.57 ~ 7.55 (m, 2H, ArH), 7.43 (d, J = 7.6 Hz, 1H, ArH), 7.35 ~ 7.28 (m, 6H, ArH), 7.16 (d, J = 8.0 Hz, 1H, ArH), 7.08 ~ 6.97 (m, 3H, ArH), 6.58 ~ 6.40 (m, 3H, ArH), 5.55 (s, 1H, CH), 5.09 (d, J = 10.8 Hz, 1H, CH), 4.85 (d, J = 10.8 Hz, 1H, CH), 3.93 ~ 3.85 (m, 1H, CH), 3.58 ~ 3.50 (m, 1H, CH), 2.09 (s, 3H, CH_3) , 0.59 ~ 0.55 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d$_6$) δ: 178.1, 169.1, 149.7, 141.6, 137.5, 137.1, 136.9, 135.7, 131.7, 129.4, 128.9, 128.3, 128.1, 127.5, 123.3, 123.3, 123.0, 122.5, 121.3, 119.4, 119.0, 118.9, 112.0, 108.8, 108.5, 93.0, 59.9, 51.52, 44.4, 35.7, 21.0, 13.7; IR (KBr) υ: 3174, 2978, 2889, 1692, 1654, 1608, 1566, 1490, 1460, 1375, 1339, 1250, 1179, 1087, 1044, 928, 840, 805, 781 cm^{-1}; HRMS (ESI) Calcd. for $C_{36}H_{29}N_3O_3S$ ([M+Na]$^{+}$): 606.1822, Found: 606.1819.

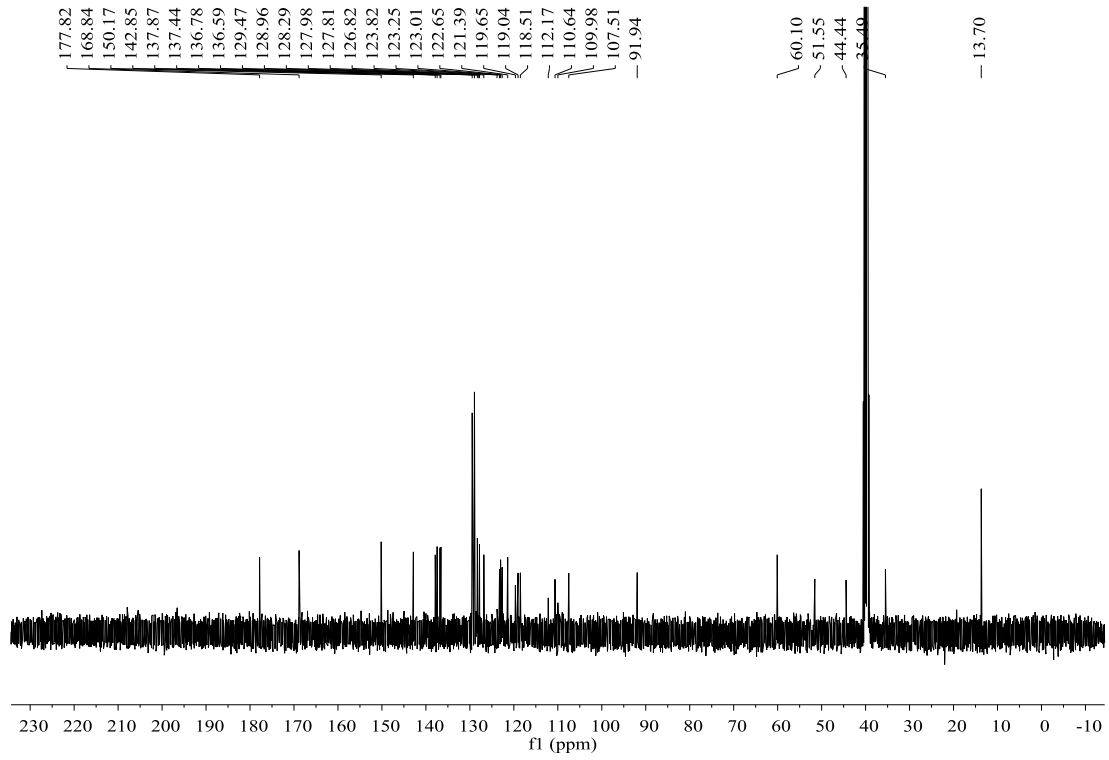


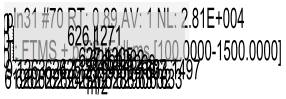

178.11
169.12
149.68
141.64
137.45
137.05
136.92
135.70
131.74
129.42
128.85
128.27
128.09
127.51
123.33
123.27
123.04
122.46
121.33
119.40
119.00
118.91
111.96
108.82
108.54
92.97
59.93
51.52
44.43
35.66
20.95
13.67
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


606.1819

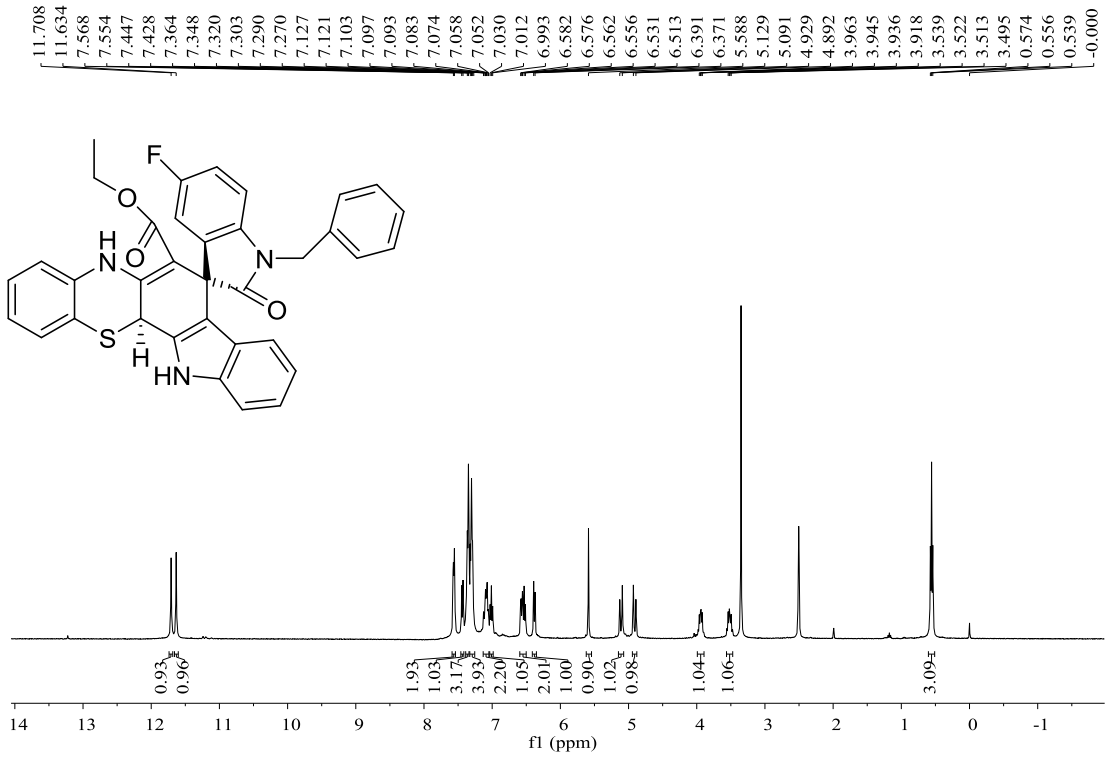
Ethyl 1-benzyl-5-chloro-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4j**): white solid, 42%, m.p. 320 – 322^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.72 (s, 1H, NH), 11.62 (s, 1H, NH), 7.57 ~ 7.55 (m, 2H, ArH), 7.44 (d, *J* = 7.2 Hz, 1H, ArH), 7.39 ~ 7.34 (m, 5H, ArH), 7.32 ~ 7.27 (m, 3H, ArH), 7.10 ~ 7.06 (m,1H, ArH), 7.03 ~ 6.99 (m,1H, ArH), 6.70 (s,1H, ArH), 6.54 ~ 6.50 (m,1H, ArH), 6.37 (d, *J* = 8.4 Hz, 1H, ArH), 5.60 (s, 1H, CH), 5.12 (d, *J* = 14.8 Hz, 1H, CH), 4.92 (d, *J* = 14.8 Hz, 1H, CH), 3.98 ~ 3.90 (m, 1H, CH), 3.58 ~ 3.50 (m, 1H, CH), 0.60 ~ 0.56 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d$_6$) δ: 177.8, 168.8, 150.2, 142.9, 137.9, 137.4, 136.8, 136.6, 129.5, 129.0, 128.3, 128.0, 127.8, 126.8, 123.8, 123.3, 123.0, 122.7, 121.4, 119.7, 119.0, 118.5, 112.2, 110.6, 110.0, 107.5, 91.9, 60.1, 51.6, 44.4, 35.5, 13.7; IR (KBr) υ: 3186, 2986, 2876, 1698, 1654, 1610, 1566, 1525, 1482, 1426, 1336, 1175, 1044, 893 cm^{-1}; HRMS (ESI) Calcd. for $C_{35}H_{26}ClN_3O_3S$ ([M+Na]$^{+}$): 626.1276, Found: 626.1271.

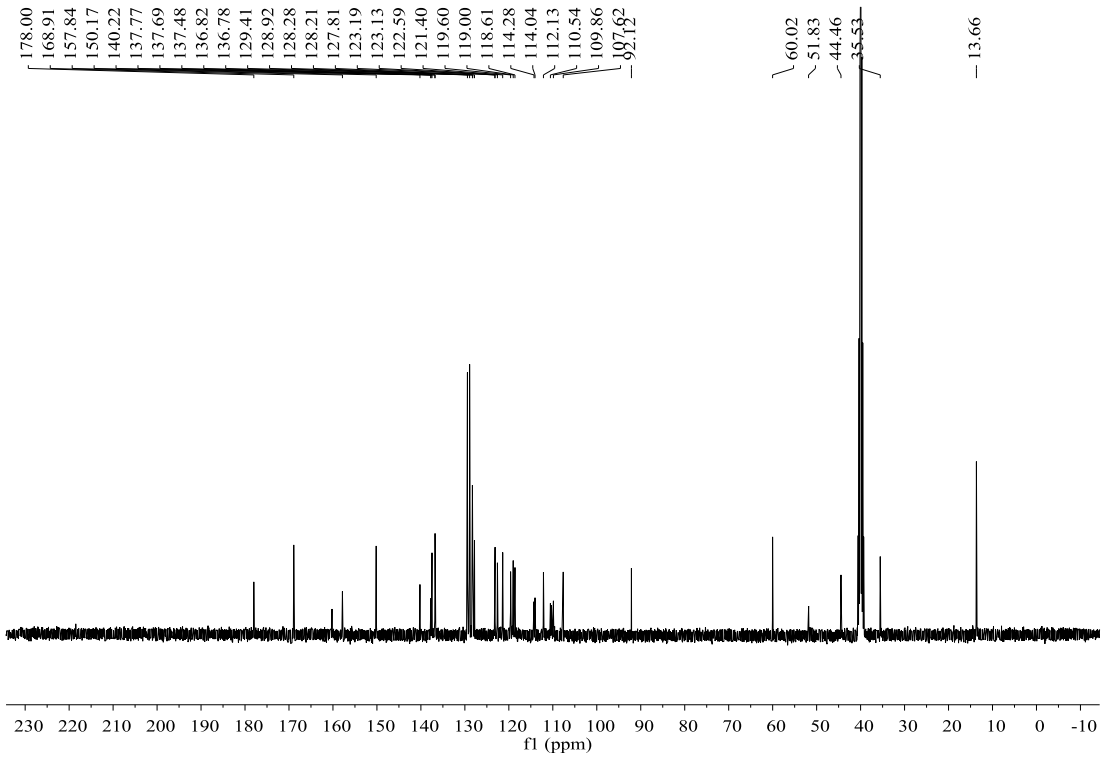



177.82
168.84
150.17
142.85
137.87
137.44
136.78
136.59
129.47
128.96
128.29
127.98
127.81
126.82
123.82
123.25
123.01
122.65
121.39
119.65
119.04
118.51
112.17
110.64
109.98
107.51
91.94
60.10
51.55
44.44
35.49
13.70
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln31 #70 RT: 0.89 AV: 1 NL: 2.81E+004
626.1271
FTMS

Ethyl 1-benzyl-5-fluoro-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4k**): white solid, 48%, m.p. 254 – 257^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.71 (s, 1H, NH), 11.63 (s, 1H, NH), 7.57 ~ 7.55 (m, 2H, ArH), 7.44 (d, *J* = 7.6 Hz, 1H, ArH), 7.36 ~ 7.35 (m, 3H, ArH), 7.32 ~ 7.27 (m, 2H, ArH), 7.13 ~ 7.05 (m, 2H, ArH), 7.03 ~ 6.99 (m, 1H, ArH), 6.58 ~ 6.51 (m, 2H, ArH), 6.38 (d, *J* = 8.0 Hz, 1H, ArH), 5.59 (s, 1H, CH), 5.11 (d, *J* = 15.2 Hz, 1H, CH), 4.91 (d, *J* = 15.2 Hz, 1H, CH), 3.98 ~ 3.90 (m, 1H, CH), 3.56 ~ 3.48 (m, 1H, CH), 0.57 ~ 0.54 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 178.0, 168.9, 129.0 (d, *J* = 240.4 Hz), 150.2, 140.2, 137.7 (d, *J* = 8.1 Hz), 137.5, 136.8, 136.8, 129.4, 128.9, 128.3, 128.2, 127.8, 123.2, 123.1, 122.6, 121.4, 119.6, 119.0, 118.6, 114.2 (d, *J* = 24.2 Hz), 112.1, 110.4 (d, *J* = 24.2 Hz), 109.9 (d, *J* = 8.1 Hz), 107.6, 92.1, 60.0, 51.8, 44.5, 35.5, 13.7; IR (KBr) υ: 3225, 3062, 2985, 1697, 1654, 1612, 1587, 1566, 1484, 1451, 1330, 1242, 1167, 1043, 928, 865, 810, 778 cm^{-1}; HRMS (ESI) Calcd. for $C_{35}H_{26}FN_3O_3S$ ([M+Na]$^{+}$): 610.1571, Found: 610.1566.




178.00
168.91
157.84
150.17
140.22
137.77
137.69
137.48
136.82
136.78
129.41
128.92
128.28
128.21
127.81
123.19
123.13
122.59
121.40
119.60
119.00
118.61
114.28
114.04
112.13
110.54
109.86
107.62
92.12
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35.53
13.66
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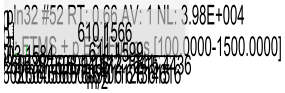
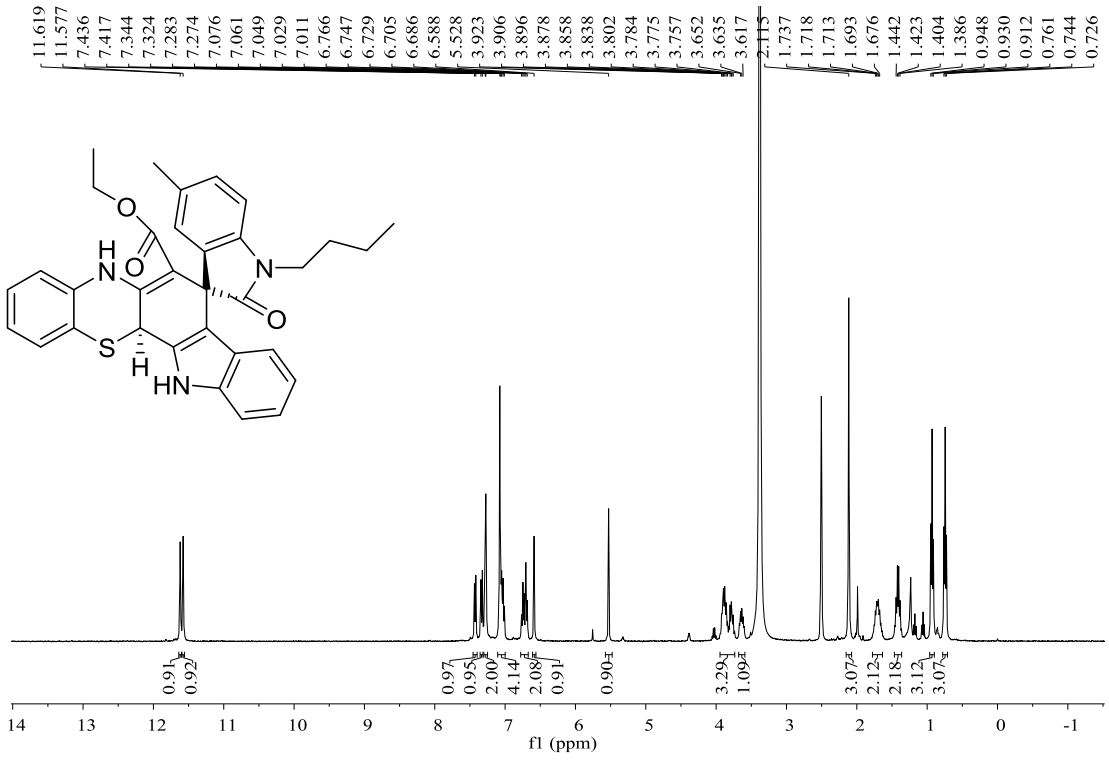
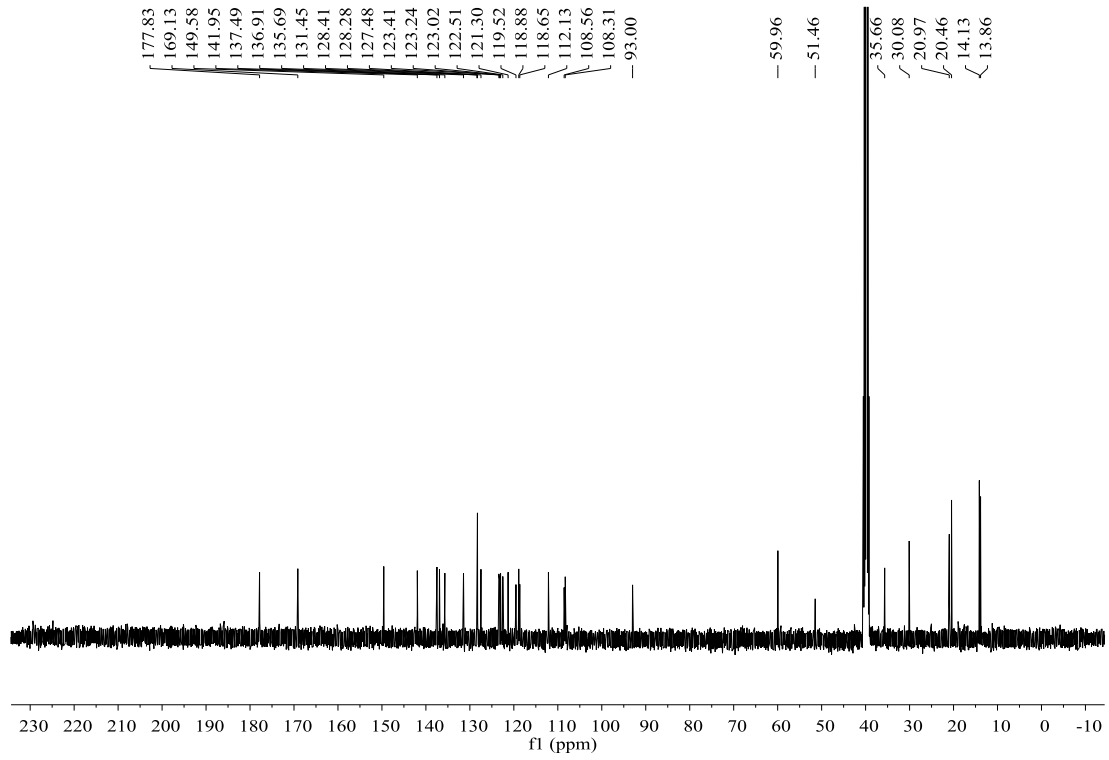
f1 (ppm)


pln32 #52 RT: 0.66 AV: 1 NL: 3.98E+004
610.1566
m/z

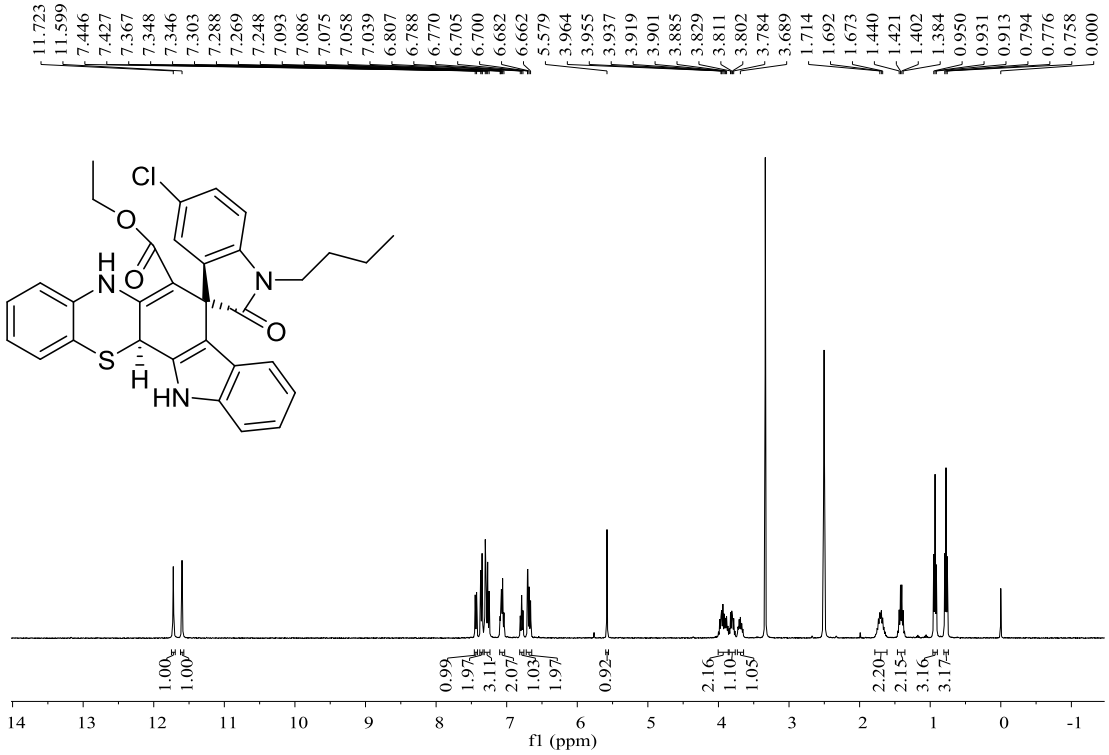
Ethyl 1-butyl-5-methyl-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4l**): white solid, 33%, m.p. 250 – 252^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.62 (s, 1H, NH), 11.58 (s, 1H, NH), 7.43 (d, *J* = 7.6 Hz, 1H, ArH), 7.33 (d, *J* = 8.0 Hz, 1H, ArH), 7.28 (d, *J* = 3.6 Hz, 1H, ArH), 7.08 ~ 7.01 (m, 4H, ArH), 6.77 ~ 6.69 (m, 2H, ArH), 6.59 (s, 1H, ArH), 5.53 (s, 1H, CH), 3.94 ~ 3.74 (m, 3H, CH), 3.67 ~ 3.60 (m, 1H, CH), 2.12 (s, 3H, CH_3), 1.77 ~ 1.64 (m, 2H, CH), 1.46 ~ 1.37 (m, 2H, CH), 0.95 ~ 0.91 (m, 3H, CH_3) , 0.76 ~ 0.73 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 177.8, 169.1, 149.6, 142.0, 137.5, 136.9, 135.7, 131.5, 128.4, 128.3, 127.5, 123.4, 123.2, 123.0, 122.5, 121.3, 119.5, 118.9, 118.7, 112.1, 108.6, 108.3, 93.0, 60.0, 51.5, 35.7, 30.1, 21.0, 20.5, 14.1, 13.9; IR (KBr) υ: 3207, 2959, 2934, 2868, 1694, 1655, 1609, 1589,1564, 1487, 1348, 1236, 1199, 1134, 1053, 1009, 928, 888, 810 cm^{-1}; HRMS (ESI) Calcd. for $C_{33}H_{31}N_3O_3S$ ([M+Na]$^{+}$): 572.1978, Found: 572.1974.

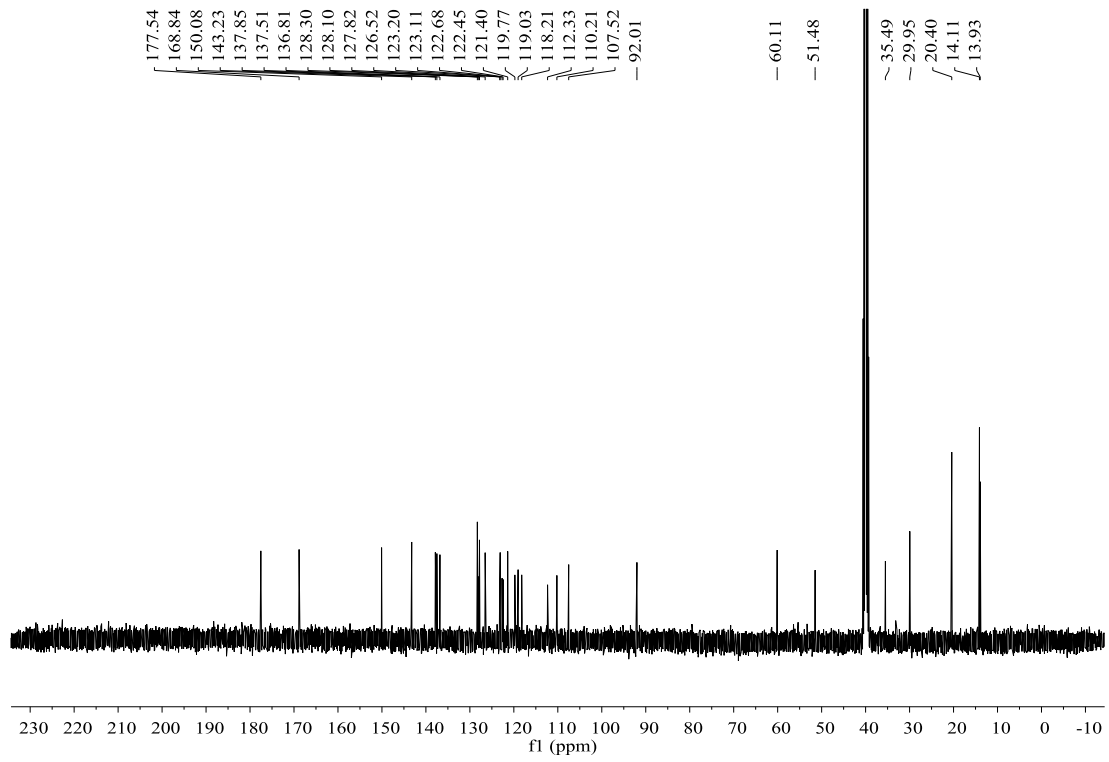



177.83
169.13
149.58
141.95
137.49
136.91
135.69
131.45
128.41
128.28
127.48
123.41
123.24
123.02
122.51
121.30
119.52
118.88
118.65
112.13
108.56
108.31
93.00
59.96
51.46
35.66
30.08
20.97
20.46
14.13
13.86
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln33 #81 RT: 1.03 AV: 1 NL: 5.49E+004
572.1974
m/z

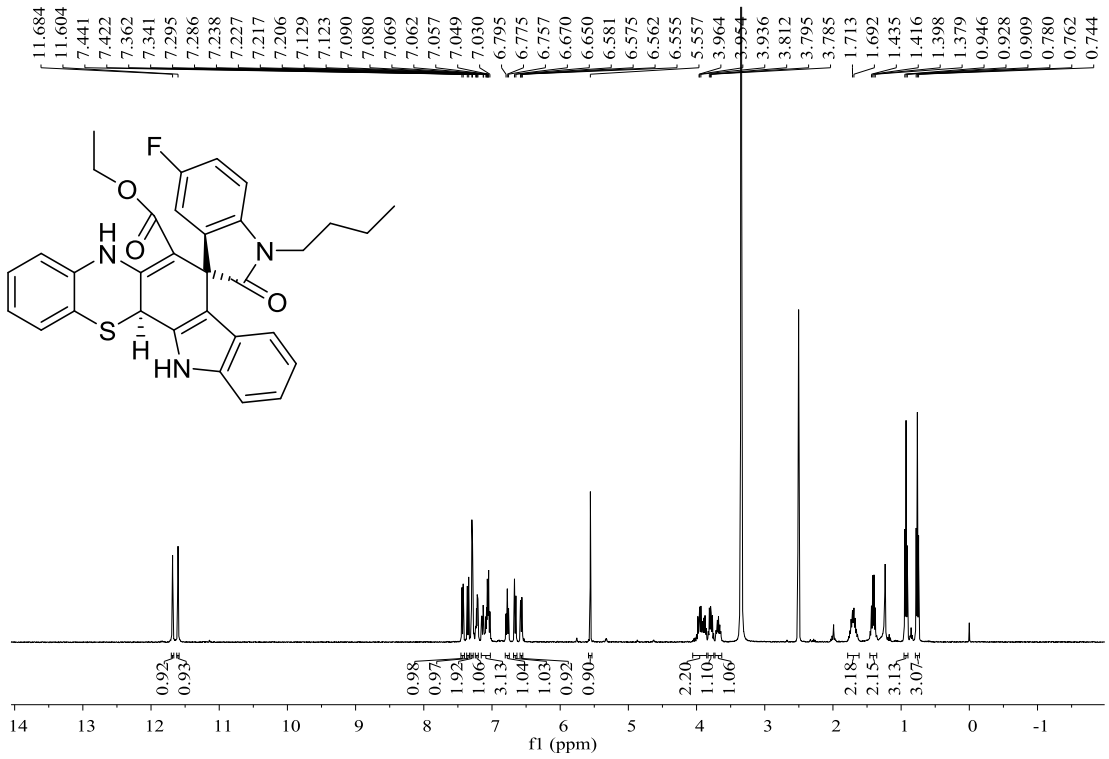
Ethyl 1-butyl-5-chloro-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4m**): white solid, 40%, m.p. 267 – 269^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.72 (s, 1H, NH), 11.60 (s, 1H, NH), 7.44 (d, J = 7.6 Hz, 1H, ArH), 7.37 ~ 7.35 (m, 2H, ArH), 7.32 ~ 7.25 (m, 3H, ArH), 7.09 ~ 7.04 (m, 2H, ArH), 6.81 ~ 6.77 (m, 1H, ArH), 6.71 ~ 6.66 (m, 2H, ArH), 5.58 (s, 1H, CH), 4.00 ~ 3.87 (m, 2H, CH), 3.85 ~ 3.77 (m, 1H, CH), 3.72 ~ 3.65 (m, 1H, CH), 1.77 ~ 1.62 (m, 2H, CH), 1.46 ~ 1.37 (m, 2H, CH), 0.95 ~ 0.91 (m, 3H, CH_3) , 0.79 ~ 0.76 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 177.5, 168.8, 150.1, 143.2, 137.9, 137.5, 136.8, 128.3, 128.1, 127.8, 126.5, 123.2, 123.1, 122.7, 122.5, 121.4, 119.8, 119.0, 118.2, 112.3, 110.2, 107.5, 92.0, 60.1, 51.5, 35.5, 30.0, 20.4, 14.1, 13.9; IR (KBr) υ: 3181, 2961, 2933, 2870,1698, 1658, 1590, 1566, 1479, 1425, 1345, 1242, 1183, 1139, 1105, 1053, 928, 880, 804 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{28}ClN_3O_3S$ ([M+Na]$^{+}$): 592.1432, Found: 592.1426.

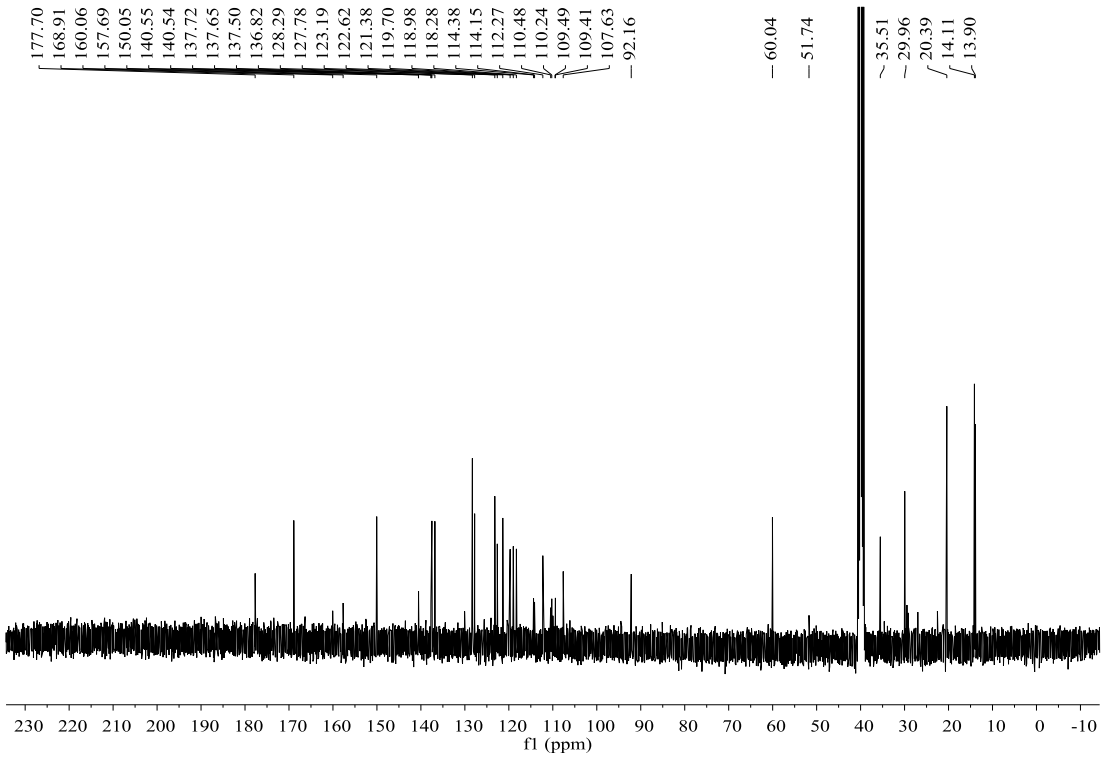



177.54
168.84
150.08
143.23
137.85
137.51
136.81
128.30
128.10
127.82
126.52
123.20
123.11
122.68
122.45
121.40
119.77
119.03
118.21
112.33
110.21
107.52
92.01
60.11
51.48
35.49
29.95
20.40
14.11
13.93
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


4.39E+004
592.1426

Ethyl 1-butyl-5-fluoro-2-oxo-12',12b'-dihydro-5'H-spiro[indoline-3,7'-indolo[3,2-c]phenothiazine]-6'-carboxylate (**4n**): white solid, 50%, m.p. 272 – 274^{O}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.68 (s, 1H, NH), 11.60 (s, 1H, NH), 7.43 (d, *J* = 7.6 Hz, 1H, ArH), 7.35 (d, *J* = 8.4 Hz, 1H, ArH), 7.29 (d, *J* = 3.6 Hz, 2H, ArH), 7.24 ~ 7.21 (m, 1H, ArH), 7.15 ~ 7.03 (m, 3H, ArH), 6.80 ~ 6.76 (m, 1H, ArH), 6.66 (d, *J* = 8.0 Hz, 1H, ArH), 6.58 ~ 6.56 (m, 1H, ArH), 5.56 (s, 1H, CH), 4.06 ~ 3.86 (m, 2H, CH), 3.83 ~ 3.75 (m, 1H, CH), 3.71 ~ 3.64 (m, 1H, CH), 1.79 ~ 1.62 (m, 2H, CH), 1.45 ~ 1.36 (m, 2H, CH), 0.95 ~ 0.91 (m, 3H, CH_3) , 0.78 ~ 0.74 (m, 3H, CH_3); ^{13}C NMR (101 MHz, DMSO-d$_6$) δ: 177.7, 168.9, 158.9 (d, *J* = 239.4 Hz), 150.1, 140.5 (d, *J* = 1.0 Hz), 137.7 (d, *J* = 7.1 Hz), 137.5, 136.8, 128.3, 127.8, 123.2, 122.6, 121.4, 119.7, 119.0, 118.3, 114.3 (d, *J* = 23.2 Hz), 112.3, 110.4 (d, *J* = 24.2 Hz), 109.5 (d, *J* = 8.1 Hz), 107.6, 92.2, 60.0, 51.8, 35.5, 30.0, 20.4, 14.1, 13.9.; IR (KBr) υ: 3172, 2958, 2926, 2871, 1691, 1654, 1612, 1586, 1565, 1485, 1454, 1348, 1251, 1185, 1132, 1052, 933, 865, 817, 763 cm^{-1}; HRMS (ESI) Calcd. for $C_{32}H_{28}FN_3O_3S$ ([M+Na]$^{+}$): 576.1728, Found: 576.1721.




177.70
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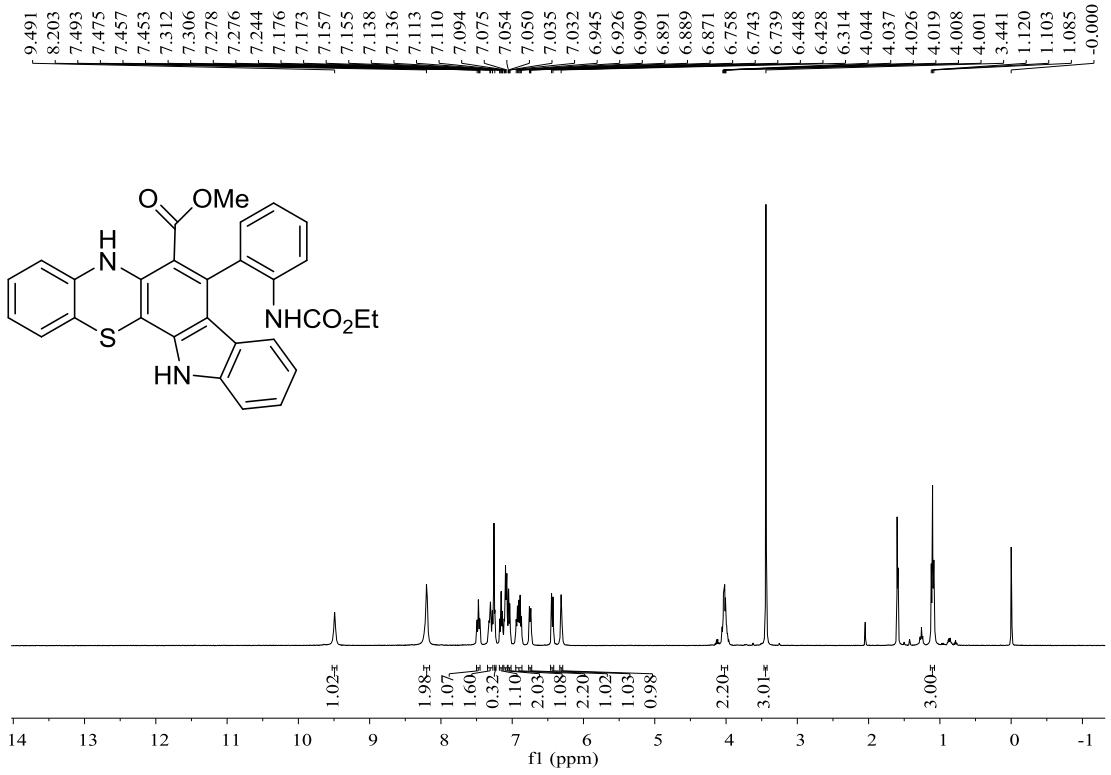
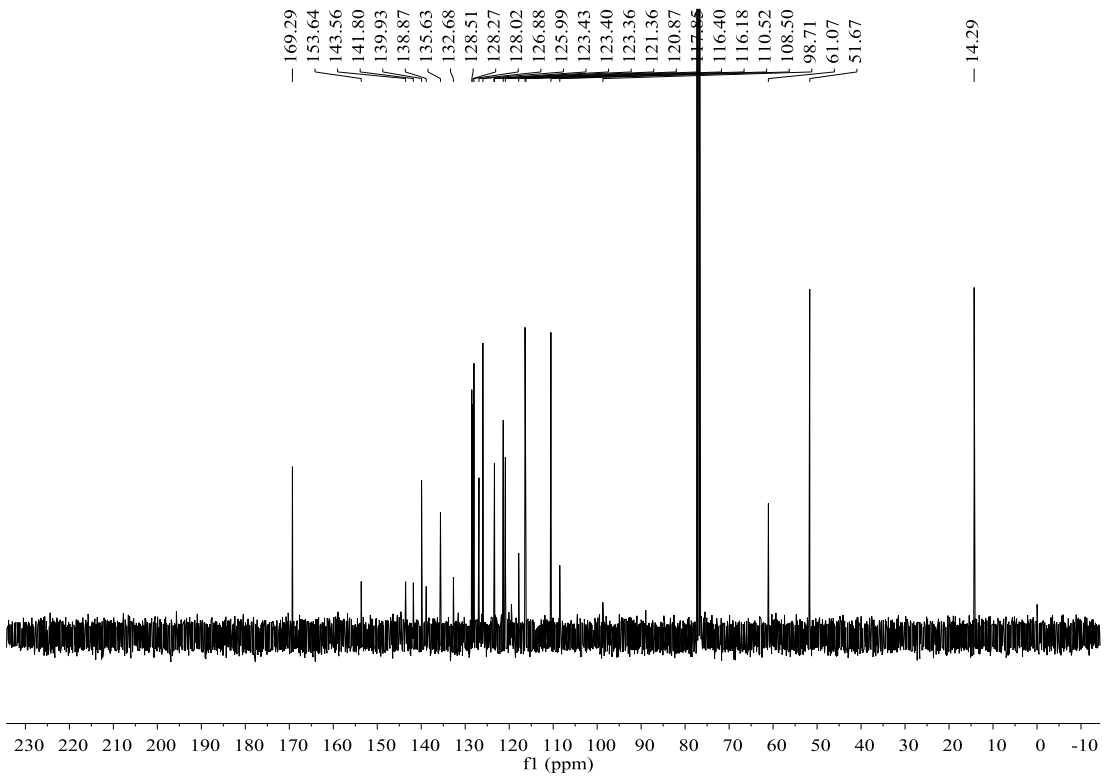
160.06
157.69
150.05
140.55
140.54
137.72
137.65
137.50
136.82
128.29
127.78
123.19
122.62
121.38
119.70
118.98
118.28
114.38
114.15
112.27
110.48
110.24
109.49
109.41
107.63
92.16
60.04
51.74
35.51
29.96
20.39
14.11
13.90
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln35 #82 RT: 1.04 AV: 1 NL: 3.25E+004
576.1721
m/z

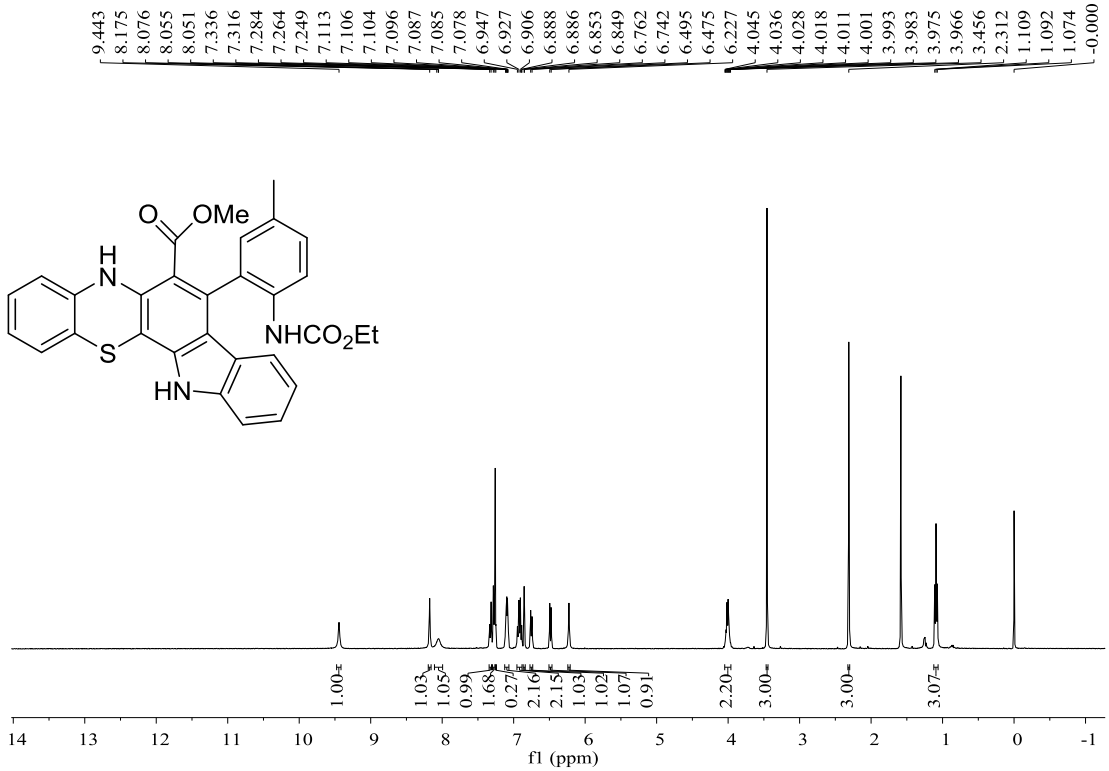
Methyl 7-(2-((ethoxycarbonyl)amino)phenyl)-5,12-dihydroindolo[3,2-c]phenothiazine-6-carboxylate (**5a**): yellow solid, 59%, m.p. 215 – 217^{O}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 9.49 (s, 1H, NH), 8.20 (s, 2H, [NH]2), 7.50 ~ 7.45 (m, 1H, ArH), 7.33 ~ 7.24 (m, 2H, ArH), 7.18 ~ 7.14 (m, 1H, ArH), 7.11 ~ 7.08 (m, 2H, ArH), 7.05 ~ 7.03 (m, 1H, ArH), 6.95 ~ 6.87 (m, 2H, ArH), 6.76 ~ 6.74 (m, 1H, ArH), 6.44 (d, *J* = 8.0 Hz, 1H, ArH), 6.31 (s, 1H, ArH), 4.06 ~ 3.98 (m, 2H, CH), 3.44 (s, 3H, OCH_3), 1.12 ~ 1.09 (m, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.3, 153.6, 143.6, 141.8, 139.9, 138.9, 135.6, 132.7, 128.5, 128.3, 128.0, 126.9, 126.0, 123.4, 123.4, 123.4, 121.4, 120.9, 117.9, 116.4, 116.2, 110.5, 108.5, 98.8, 61.1, 51.7, 14.3; IR (KBr) υ: 3412, 3315, 3059, 2978, 2947, 1718, 1678, 1582, 1528, 1489, 1458, 1383, 1341, 1316, 1287, 1227, 1161, 1112, 1064, 978, 880, 801 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{23}N_3O_4S$ ([M+Na]$^{+}$): 532.1301, Found: 532.1292.

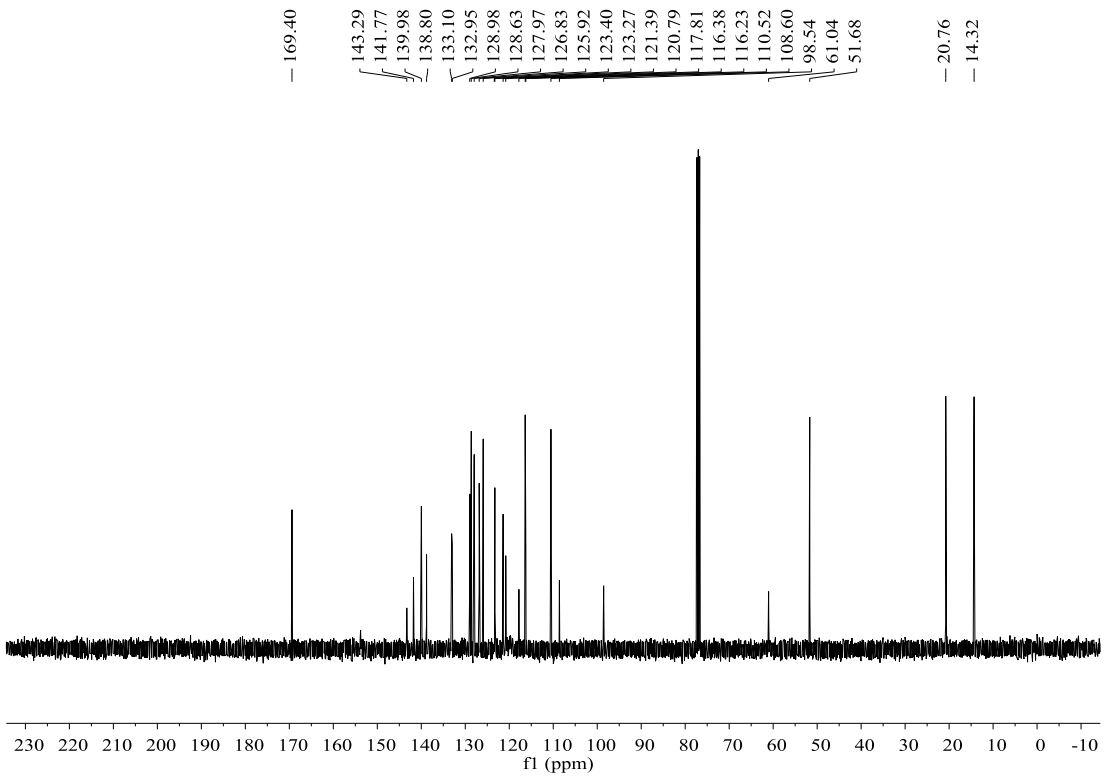



169.29
153.64
143.56
141.80
139.93
138.87
135.63
132.68
128.51
128.27
128.02
126.88
125.99
123.43
123.40
123.36
121.36
120.87
116.40
116.18
110.52
108.50
98.71
61.07
51.67
14.29
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3.56E+005
532.1292

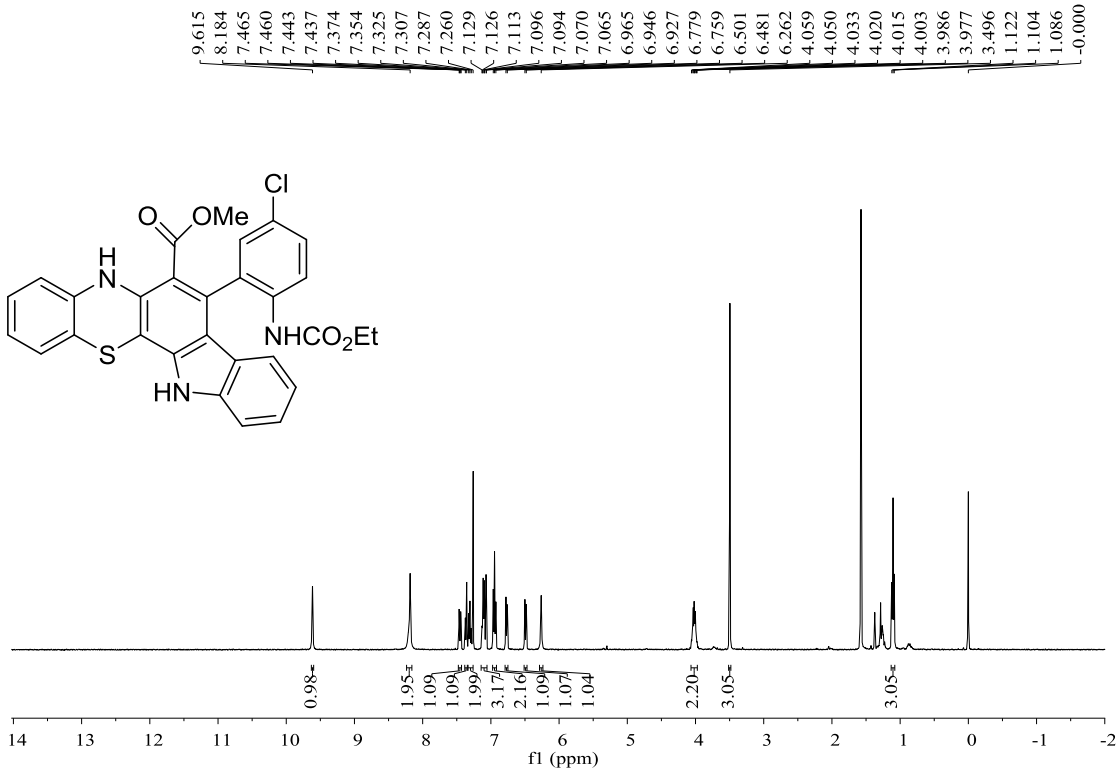
Methyl 7-(2-((ethoxycarbonyl)amino)-5-methylphenyl)-5,12-dihydroindolo[3,2-c]phenothiazine-6-carboxylate (**5b**): yellow solid, 46%, m.p. 221 – 223^{O}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 9.44 (s, 1H, NH), 8.18 (s, 1H, NH), 8.08 ~ 8.05 (m, 1H, NH), 7.33 (d, *J* = 8.0 Hz, 1H, ArH), 7.28 ~ 7.25 (m, 2H, ArH), 7.11 ~ 7.08 (m, 2H, ArH), 6.95 ~ 6.89 (m, 2H, ArH), 6.85 (d, *J* = 1.6 Hz, 1H, ArH), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 6.49 (d, *J* = 8.0 Hz, 1H, ArH), 6.23 (s, 1H, ArH), 4.05 ~ 3.97 (m, 2H, CH), 3.46 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3), 1.11 ~ 1.07 (m, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.4, 143.3, 141.8, 140.0, 138.8, 133.1, 133.0, 129.0, 128.6, 128.0, 126.8, 125.9, 123.4, 123.3, 121.4, 120.8, 117.8, 116.4, 116.2, 110.5, 108.6, 98.5, 61.0, 51.7, 20.8, 14.3; IR (KBr) υ: 3414, 3290, 3060, 2973, 2947, 1712, 1680, 1603, 1574.87 1525.58 1490.68 1384, 1338.89 1289.68 1228, 1116, 1058, 977, 880, 842, 814 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{25}N_3O_4S$ ([M+Na]$^{+}$): 546.1458, Found: 546.1453.

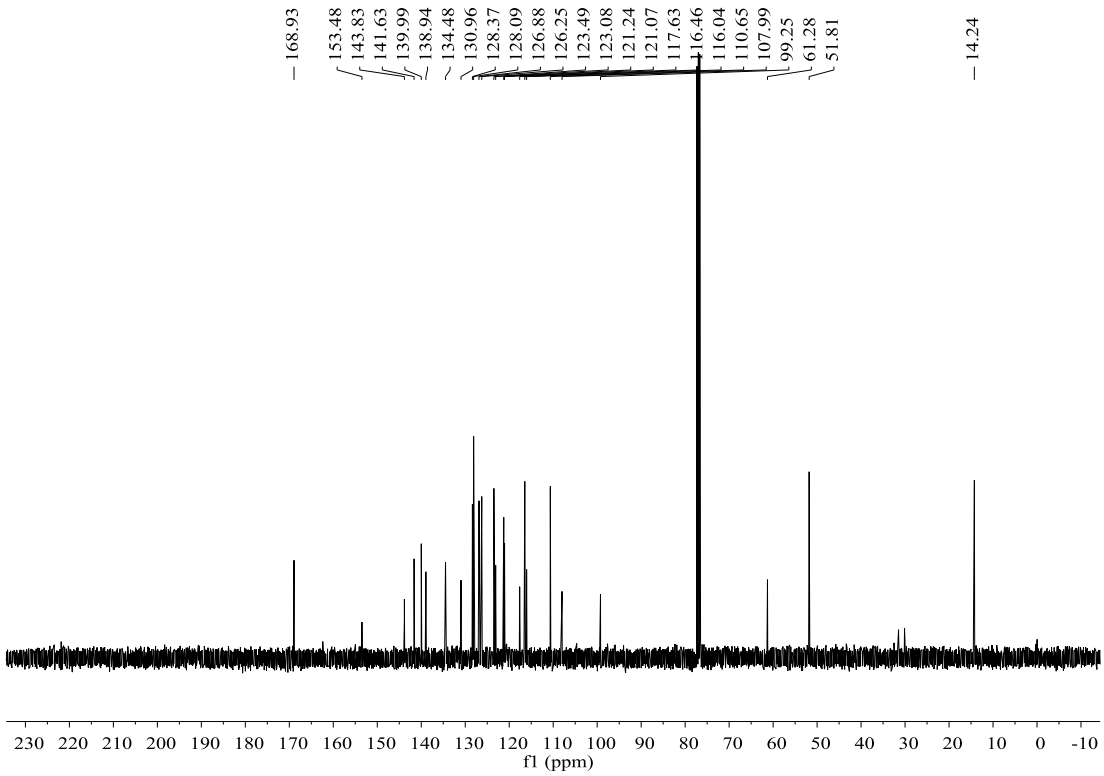



169.40
143.29
141.77
139.98
138.80
133.10
132.95
128.98
128.63
127.97
126.83
125.92
123.40
123.27
121.39
120.79
117.81
116.38
116.23
110.52
108.60
98.54
61.04
51.68
20.76
14.32
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln14 #54 RT: 0.69 AV: 1 NL: 3.71E+005
546.1453
FTMS + [100.0000-1500.0000]

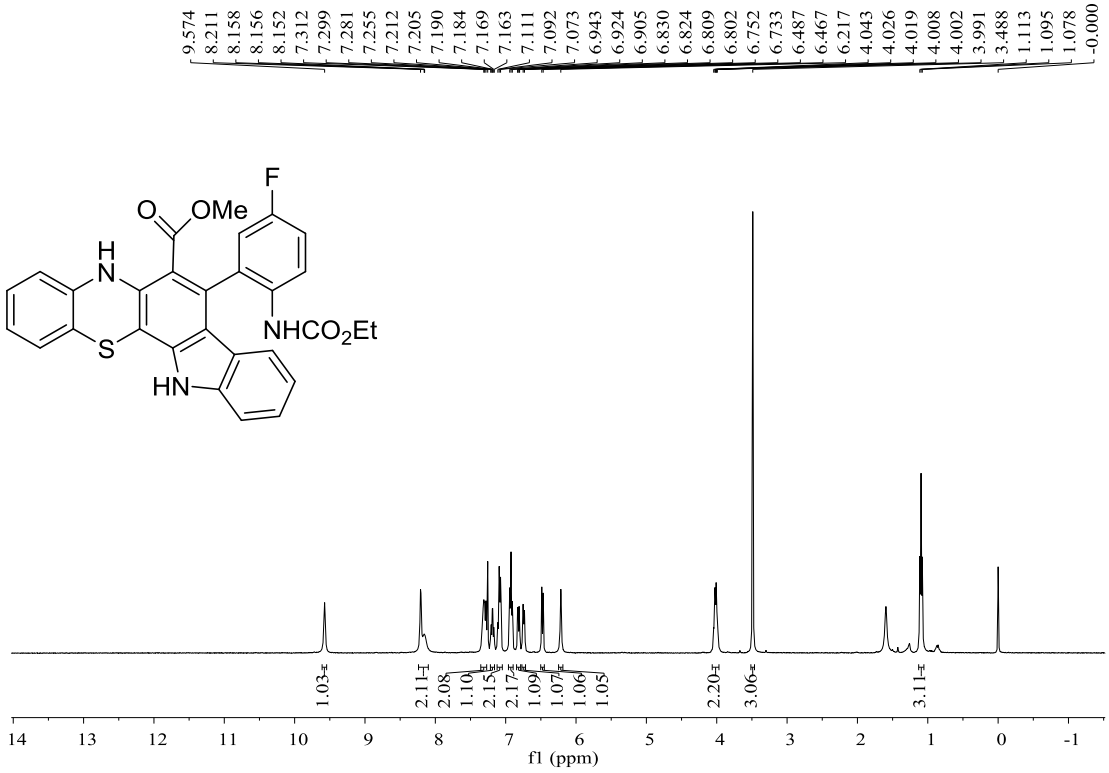
Methyl 7-(5-chloro-2-((ethoxycarbonyl)amino)phenyl)-5,12-dihydroindolo[3,2-c]phenothiazine-6-carboxylate (**5c**): yellow solid, 56%, m.p. 182 – 184^{O}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 9.62 (s, 1H, NH), 8.18 (s, 2H, [NH]2), 7.47 ~ 7.44 (m, 1H, ArH), 7.36 (d, *J* = 8.0 Hz, 1H, ArH), 7.33 ~ 7.26 (m, 2H, ArH), 7.13 ~ 7.07 (m, 3H, ArH), 6.96 (t, *J* = 7.6 Hz, 1H, ArH), 6.77 (d, *J* = 8.0 Hz, 1H, ArH), 6.49 (d, *J* = 8.0 Hz, 1H, ArH), 6.26 (s, 1H, ArH), 4.06 ~ 3.98 (m, 2H, CH), 3.50 (s, 3H, OCH_3), 1.12 ~ 1.09 (m, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.9, 153.5, 143.8, 141.6, 140.0, 139.0, 134.5, 131.0, 128.4, 128.1, 126.9, 126.3, 123.5, 123.1, 121.2, 121.1, 117.6, 116.5, 116.0, 110.7, 108.0, 99.3, 61.3, 51.8, 14.2; IR (KBr) υ: 3409, 3381, 3061, 2979, 2953, 1723, 1680, 1603, 1578, 1509,1452, 1435, 1373, 1339, 1322, 1288, 1218, 1099, 1056, 975, 943, 884, 856, 825 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{22}ClN_3O_4S$ ([M+Na]$^{+}$): 566.0912, Found: 566.0906.

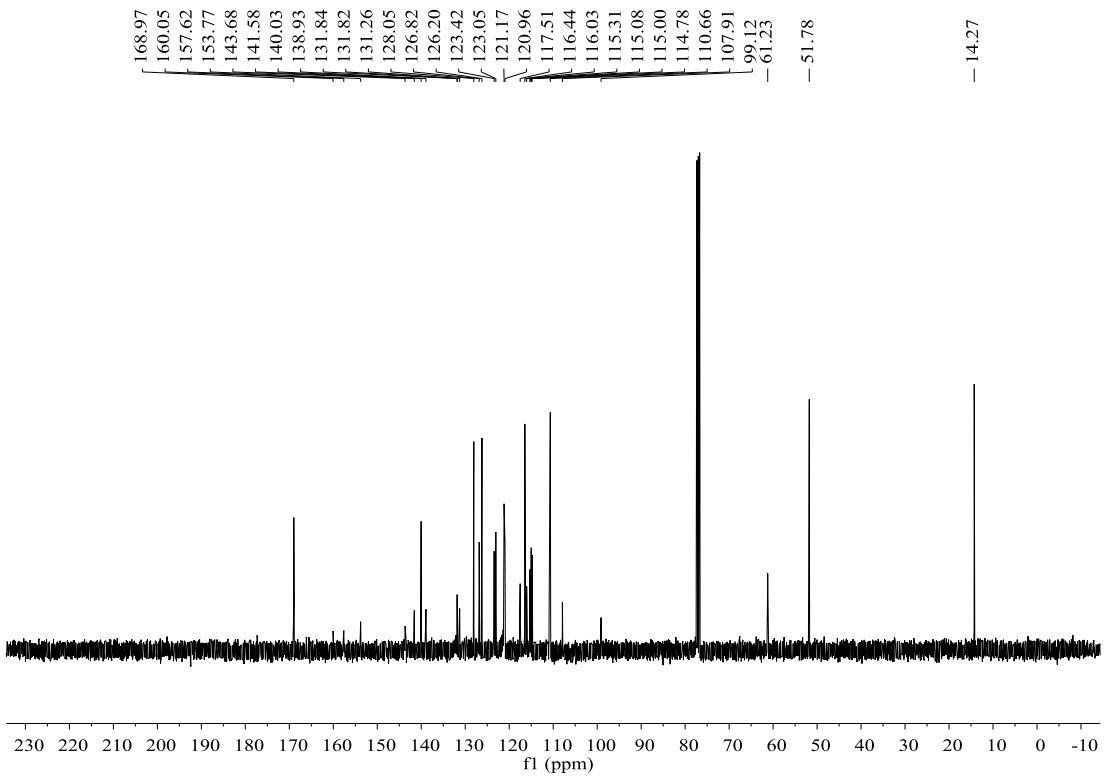



168.93
153.48
143.83
141.63
139.99
138.94
134.48
130.96
128.37
128.09
126.88
126.25
123.49
123.08
121.24
121.07
117.63
116.46
116.04
110.65
107.99
99.25
61.28
51.81
14.24
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln15 #84 RT: 1.07 AV: 1 NL: 5.89E+004
566.0906
FTMS + 0000-1500.0000]

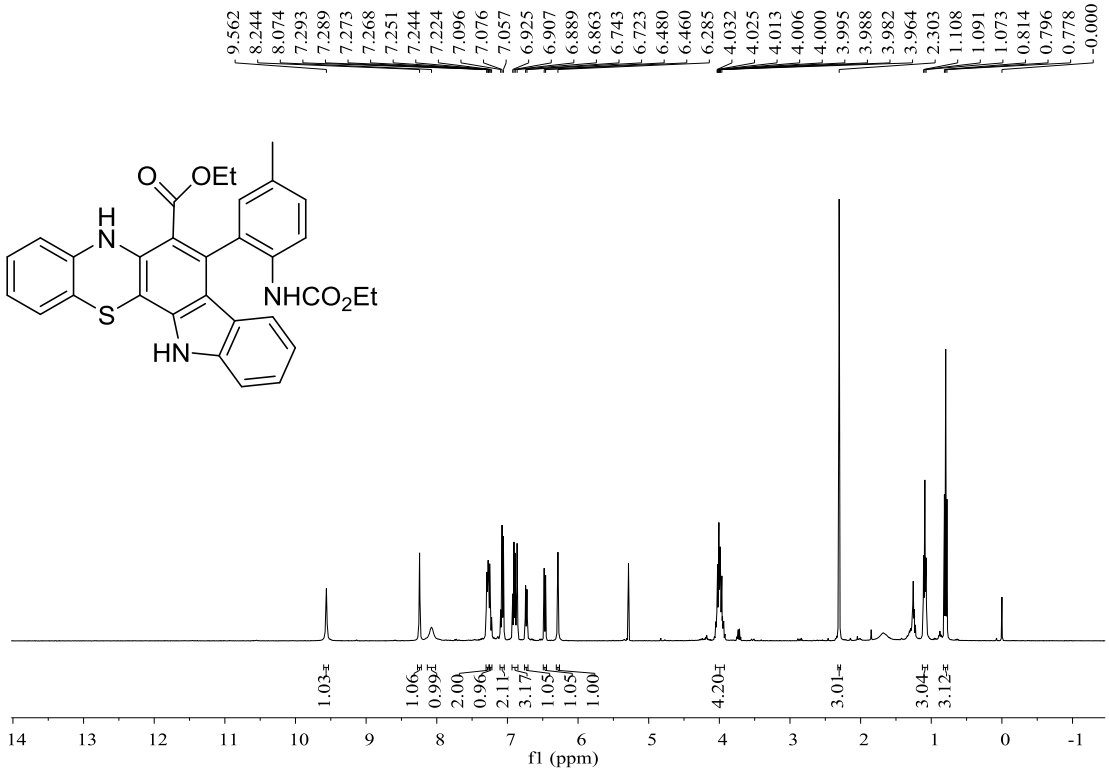
Methyl 7-(2-((ethoxycarbonyl)amino)-5-fluorophenyl)-5,12-dihydroindolo[3,2-c]phenothiazine-6-carboxylate (**5d**): yellow solid, 52%, m.p. 190 – 192^{O}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 9.57 (s, 1H, NH), 8.21 (s, 1H, NH), 8.16 ~ 8.15 (m, 1H, NH), 7.31 ~ 7.26 (m, 2H, ArH), 7.21 ~ 7.16 (m, 1H, ArH), 7.11 ~ 7.07 (m, 2H, ArH), 6.93 (t, *J* = 7.6 Hz, 1H, ArH), 6.83 ~ 6.80 (m, 1H, ArH), 6.74 (d, *J* = 7.6 Hz, 1H, ArH), 6.48 (d, *J* = 8.0 Hz, 1H, ArH), 6.22 (s, 1H, ArH), 4.04 ~ 3.99 (m, 2H, CH), 3.49 (s, 3H, OCH_3), 1.11 ~ 1.08 (m, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.0, 158.8 (d, *J* = 245.4 Hz), 153.8, 143.7, 141.6, 140.0, 138.9, 131.8 (d, *J* = 2.0 Hz), 131.3, 128.1, 126.8, 126.2, 123.4, 123.1, 121.2, 121.0, 117.5, 116.4, 116.0, 115.2 (d, *J* = 23.2 Hz), 114.9 (d, *J* = 22.2 Hz), 110.7, 107.9, 99.1, 61.2, 51.8, 14.3; IR (KBr) υ: 3413, 3319, 3059, 2979, 2951, 1719, 1680,1607, 1578, 1529, 1487, 1454, 1383, 1340, 1287, 1227, 1105, 1062, 978, 879, 852, 821, 798 cm^{-1}; HRMS (ESI) Calcd. for $C_{29}H_{22}FN_3O_4S$ ([M+Na]$^{+}$): 550.1207, Found: 550.1201.

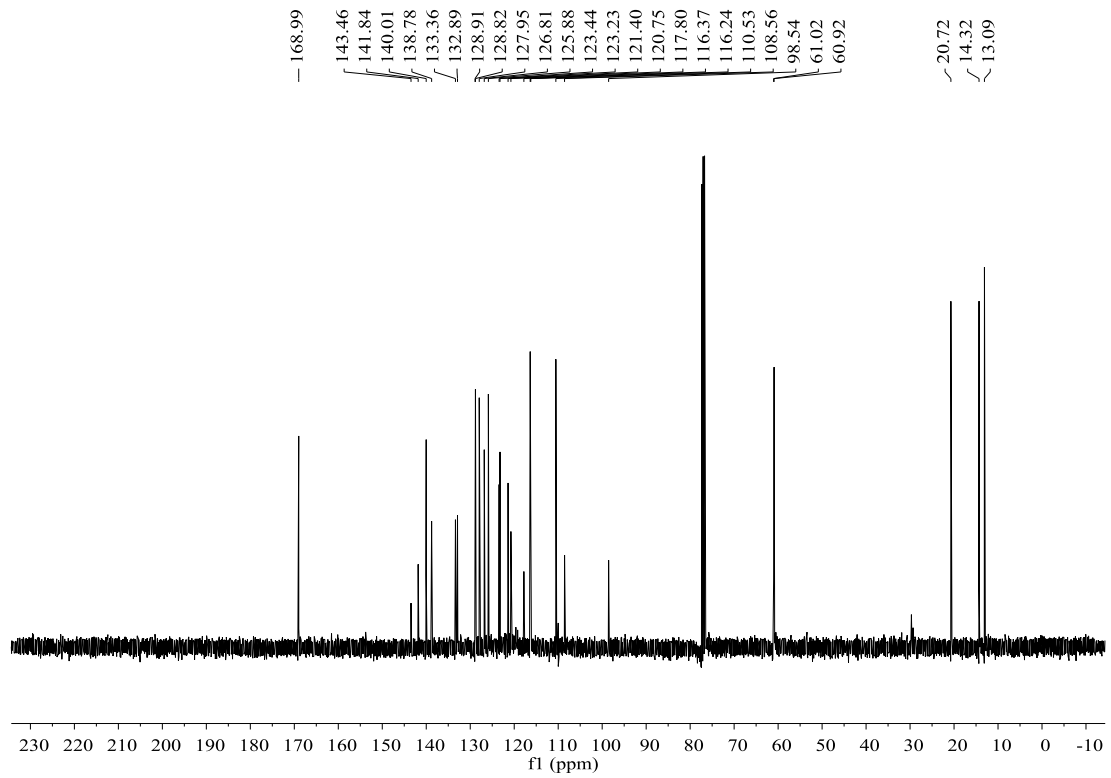



168.97
160.05
157.62
153.77
143.68
141.58
140.03
138.93
131.84
131.82
131.26
128.05
126.82
126.20
123.42
123.05
121.17
120.96
117.51
116.44
116.03
115.31
115.08
115.00
114.78
110.66
107.91
99.12
61.23
51.78
14.27
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3.04E+005
550.1204

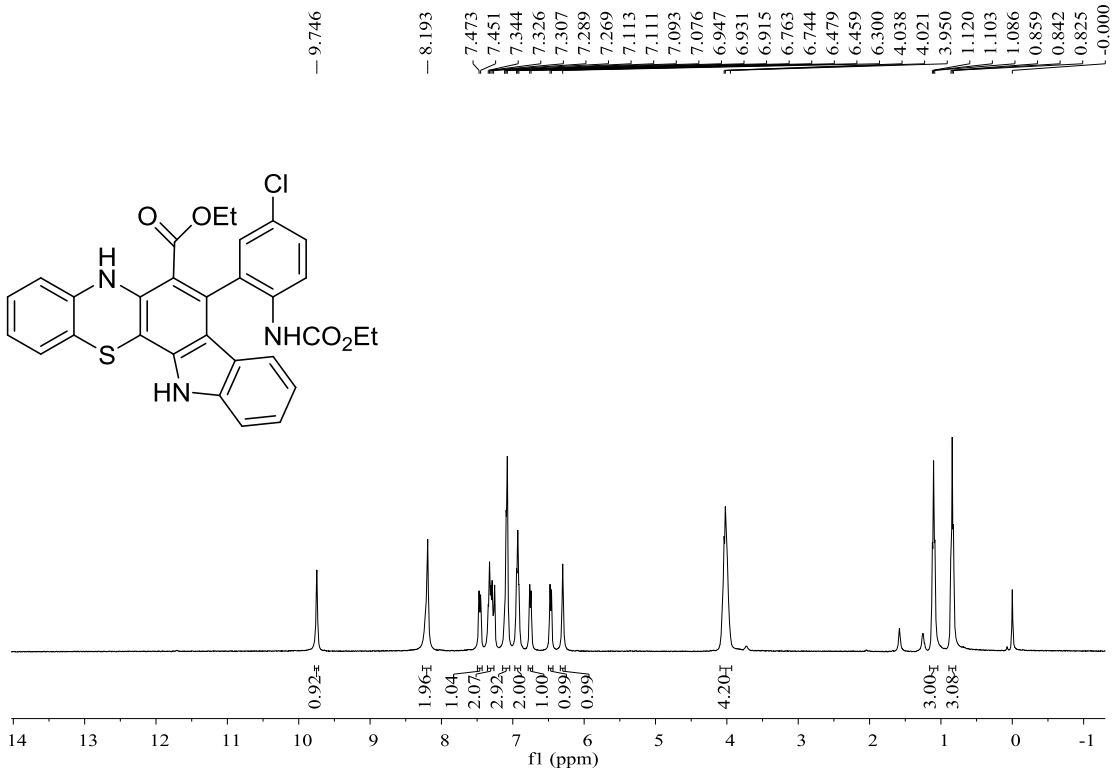
Ethyl 7-(2-((ethoxycarbonyl)amino)-5-methylphenyl)-5,12-dihydroindolo[3,2-c]phenothiazine-6-carboxylate (**5e**): yellow oil, 40%, m.p.; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 9.56 (s, 1H, NH), 8.24 (s, 1H, NH), 8.07 (s, 1H, NH), 7.29 ~ 7.27 (m, 2H, ArH), 7.25 ~ 7.22 (m, 1H, ArH), 7.10 ~ 7.06 (m, 2H, ArH), 6.93 ~ 6.86 (m, 3H, ArH), 6.73 (d, *J* = 8.4 Hz, 1H, ArH), 6.47 (d, *J* = 8.4 Hz, 1H, ArH), 6.29 (s, 1H, ArH), 4.03 ~ 3.96 (m, 4H, CH), 2.30 (s, 3H, CH_3), 1.11 ~ 1.07 (m, 3H, CH_3), 0.81 ~ 0.78 (m, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.0, 143.5, 141.8, 140.0, 138. 8, 133.4, 132. 9, 128.9, 128.8, 128.0, 126.8, 125.9, 123.4, 123.2, 121.4, 120.8, 117.8, 116.4, 116.2, 110.5, 108. 6, 98.5, 61.0, 60.9, 20.7, 14.3, 13.1; IR (KBr) υ: 3415, 3331, 2981, 2926, 1726, 1677, 1592, 1519, 1459, 1378, 1328, 1291, 1222, 1118, 1060, 831 cm^{-1}; HRMS (ESI) Calcd. for $C_{31}H_{27}N_3O_4S$ ([M+H]$^+$): 560.1614, Found: 560.1609.

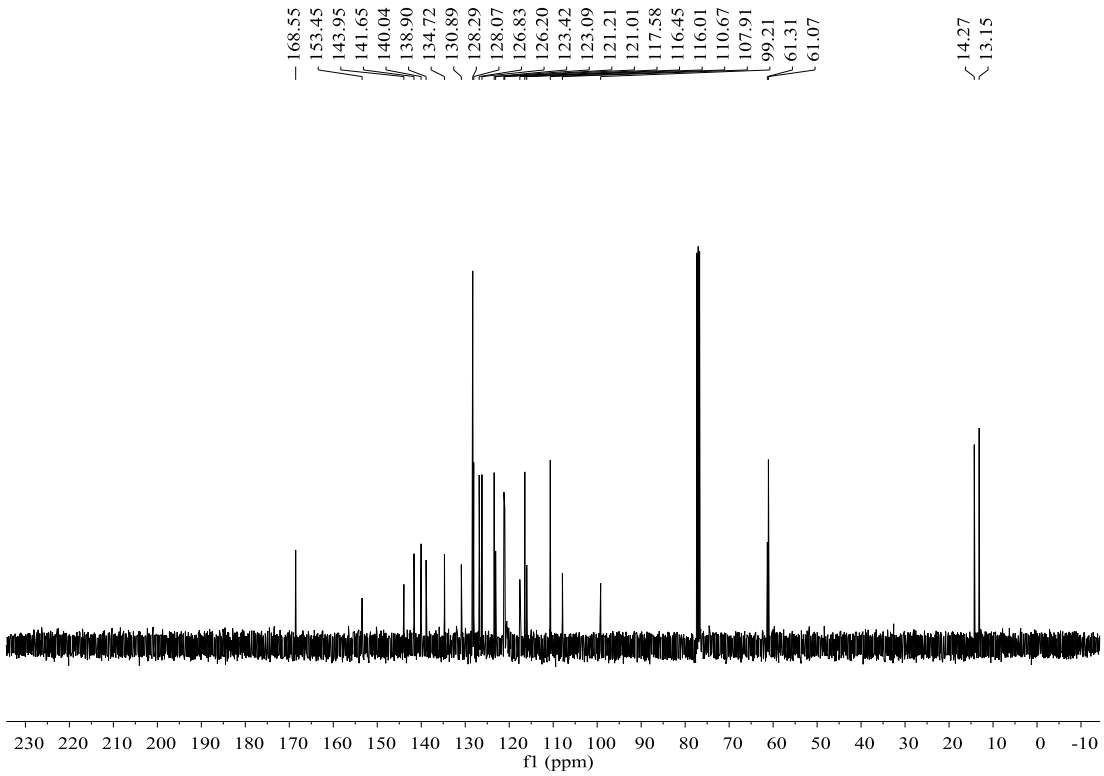


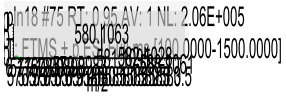

168.99
143.46
141.84
140.01
138.78
133.36
132.89
128.91
128.82
127.95
126.81
125.88
123.44
123.23
121.40
120.75
117.80
116.37
116.24
110.53
108.56
98.54
61.02
60.92
20.72
14.32
13.09
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln17 #80 RT: 1.02 AV: 1 NL: 2.57E+005
560.1609

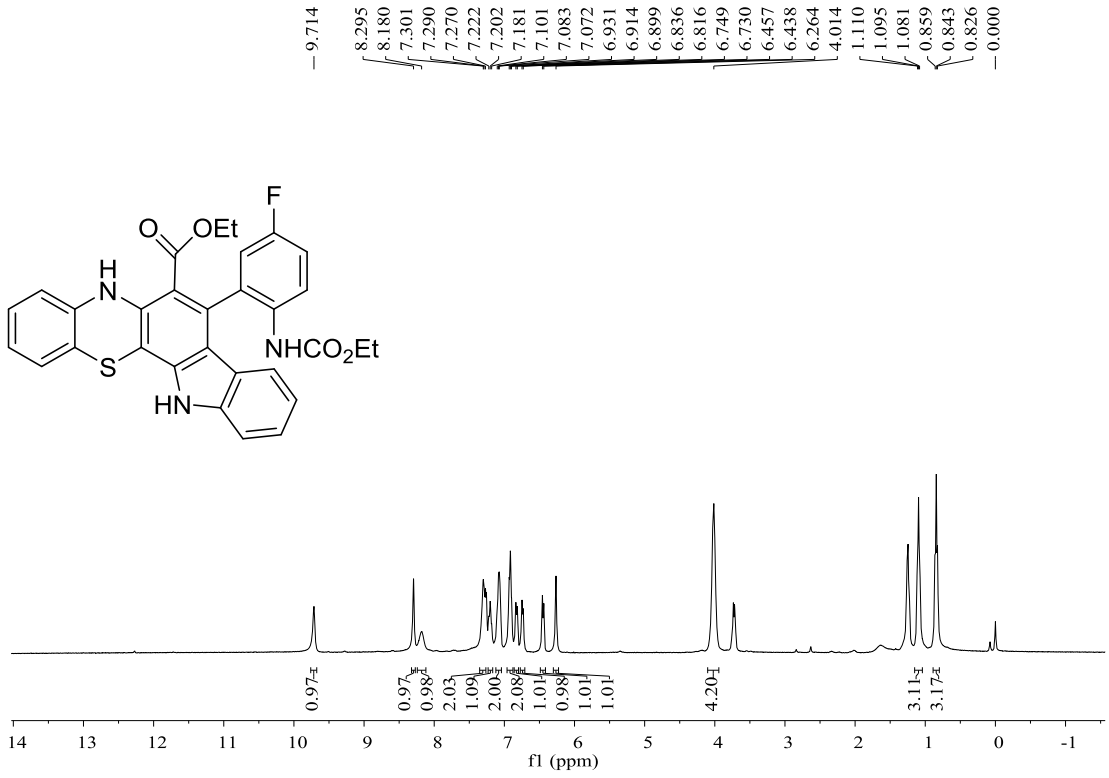
Ethyl 7-(5-chloro-2-((ethoxycarbonyl)amino)phenyl)-5,12-dihydroindolo[3,2-c]phenothiazine-6-carboxylate (**5f**): yellow solid, 45%, m.p. 209 – 211^{O}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 9.75 (s, 1H, NH), 8.19 (s, 2H, [NH]2), 7.46 (d, *J* = 8.8 Hz, 1H, ArH), 7.34 ~ 7.27 (m, 2H, ArH), 7.11 ~ 7.08 (m, 3H, ArH), 6.95 ~ 6.92 (m, 2H, ArH), 6.75 (d, *J* = 7.6 Hz, 1H, ArH), 6.47 (d, *J* = 8.0 Hz, 1H, ArH), 6.30 (s, 1H, ArH), 4.08 ~ 3.95 (m, 4H, CH), 1.12 ~ 1.09 (m, 3H, CH_3), 0.86 ~ 0.83 (m, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.6, 153.5, 144.0, 141.7, 140.0, 138.9, 134.7, 130.9, 128.3, 128.1, 126.8, 126.2, 123.4, 123.1, 121.2, 121.0, 117.6, 116.5, 116.0, 110.7, 107.9, 99.2, 61.3, 61.1, 14.3, 13.2; IR (KBr) υ: 3409, 3300, 3061, 2978, 1716, 1676, 1605, 1577, 1515, 1452, 1378, 1330, 1288, 1219, 1096, 1055, 1013, 946, 859, 812 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{24}ClN_3O_4S$ ([M+Na]$^{+}$): 580.1068, Found: 580.1063.

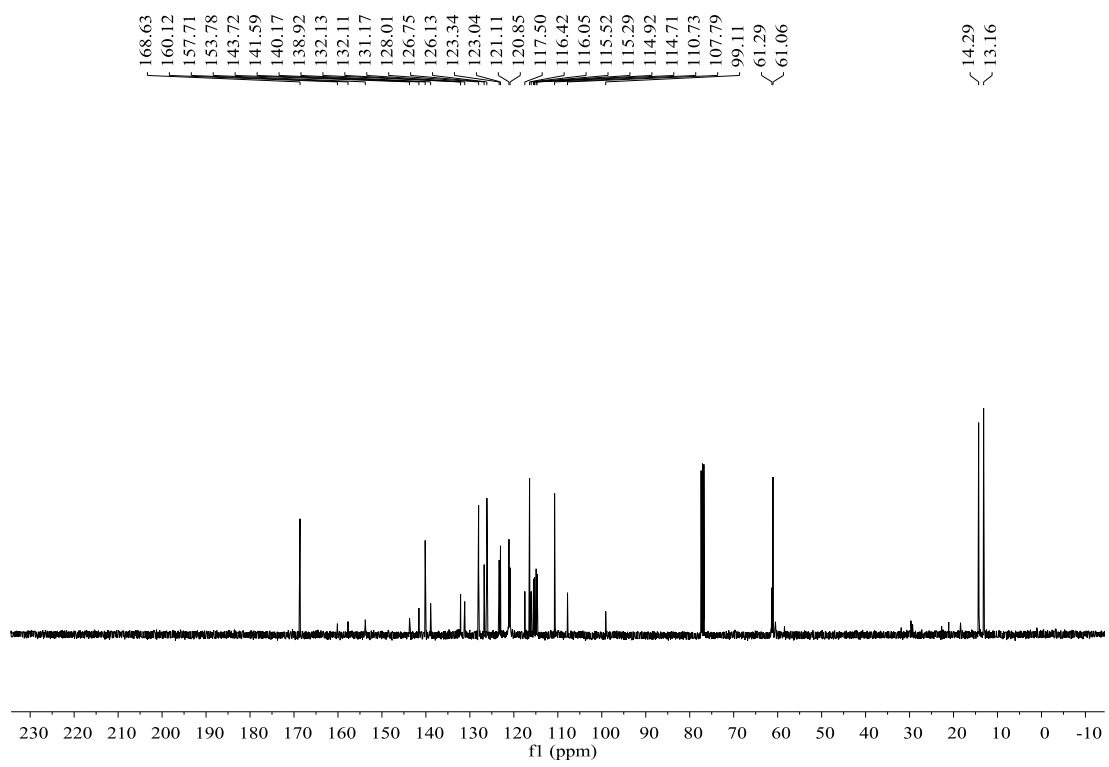


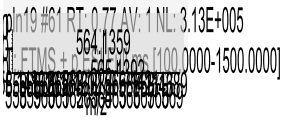

168.55
153.45
143.95
141.65
140.04
138.90
134.72
130.89
128.29
128.07
126.83
126.20
123.42
123.09
121.21
121.01
117.58
116.45
116.01
110.67
107.91
99.21
61.31
61.07
14.27
13.15
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln18 #75 RT: 0.95 AV: 1 NL: 2.06E+005
580.1063

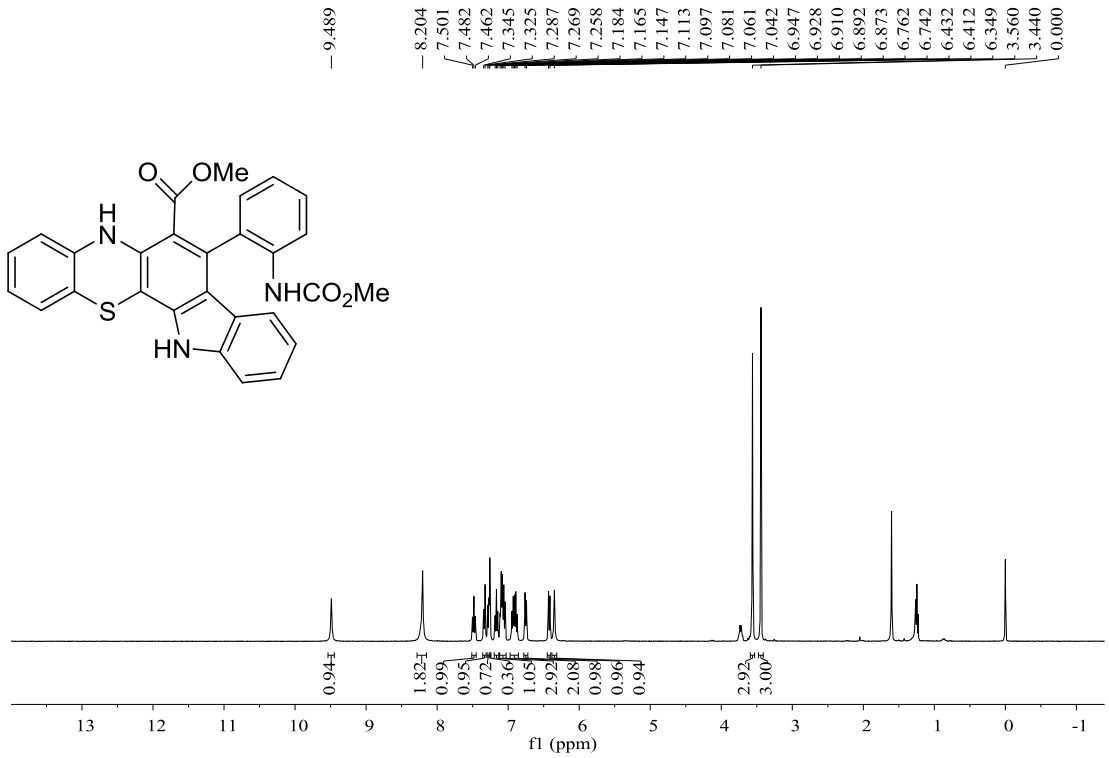
Ethyl 7-(2-((ethoxycarbonyl)amino)-5-fluorophenyl)-5,12-dihydroindolo[3,2-c]phenothiazine-6-carboxylate (**5g**): yellow oil, 38%, m.p.; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 9.71 (s, 1H, NH), 8.30 (s, 1H, NH), 8.18 (s, 1H, NH), 7.30 ~ 7.27 (m, 2H, ArH), 7.22 ~ 7.18 (m, 1H, ArH), 7.10 ~ 7.07 (m, 2H, ArH), 6.93 ~ 6.90 (m, 2H, ArH), 6.83 (d, *J* = 8.0 Hz, 1H, ArH), 6.74 (d, *J* = 7.6 Hz, 1H, ArH), 6.45 (d, *J* = 7.6 Hz, 1H, ArH), 6.26 (s, 1H, ArH), 4.01 (m, 4H, CH), 1.11 ~ 1.08 (m, 3H, CH_3), 0.86 ~ 0.83 (m, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.6, 158.9(d, *J* = 243.4 Hz), 153.78, 143.7, 141.59, 140.17, 138.9, 132.1 (d, *J* = 2.0 Hz), 131.17, 128.0, 126.75, 126.1, 123.3, 123.0, 121.1, 120.85, 117.5, 116.4, 116.1, 115.4 (d, *J* = 23.2 Hz), 114.8 (d, *J* = 21.1 Hz), 110.7, 107.8, 99.1, 61.3, 61.1, 14.3, 13.2; IR (KBr) υ: 3446, 3334, 3076, 2989, 1702, 1684, 1601, 1569, 1513, 1459, 1373, 1336, 1292, 1231, 1107, 1053, 1015, 949, 862, 808 cm^{-1}; HRMS (ESI) Calcd. for $C_{30}H_{24}FN_3O_4S$ ([M+Na]$^+$): 564.1364, Found: 564.1359.

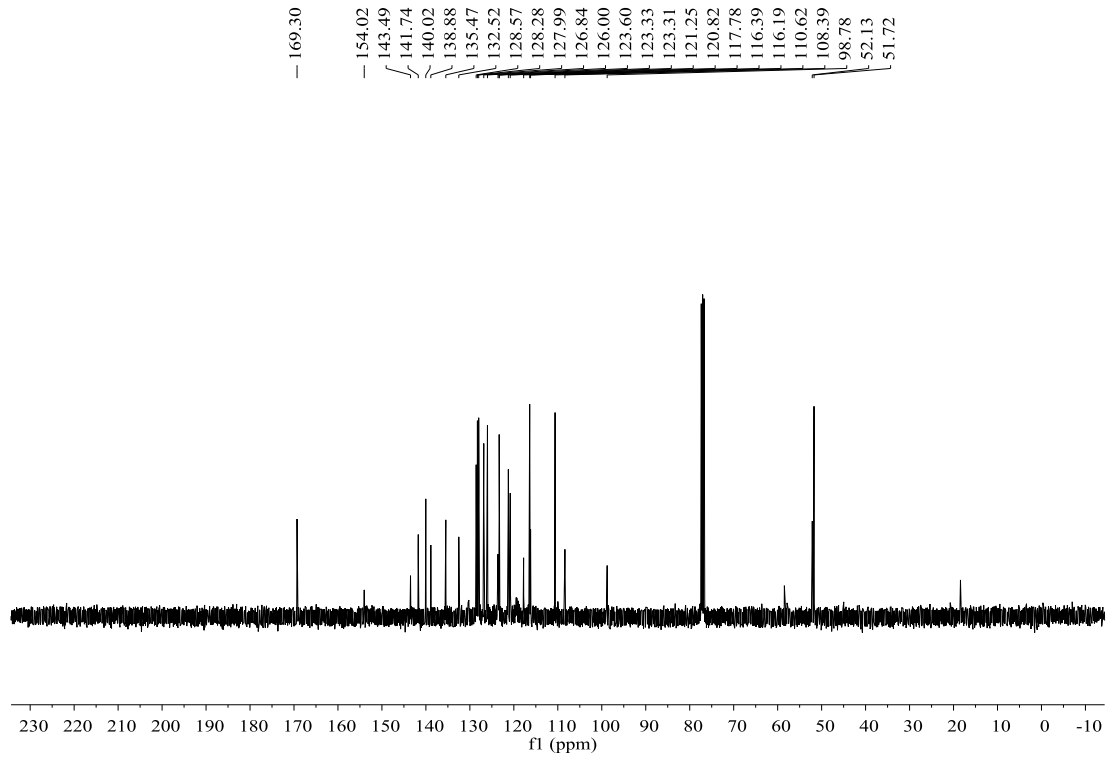



168.63
160.12
157.71
153.78
143.72
141.59
140.17
138.92
132.13
132.11
131.17
128.01
126.75
126.13
123.34
123.04
121.11
120.85
117.50
116.42
116.05
115.52
115.29
114.92
114.71
110.73
107.79
99.11
61.29
61.06
14.29
13.16
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln19 #61 RT: 0.77 AV: 1 NL: 3.13E+005
564.1359
m/z

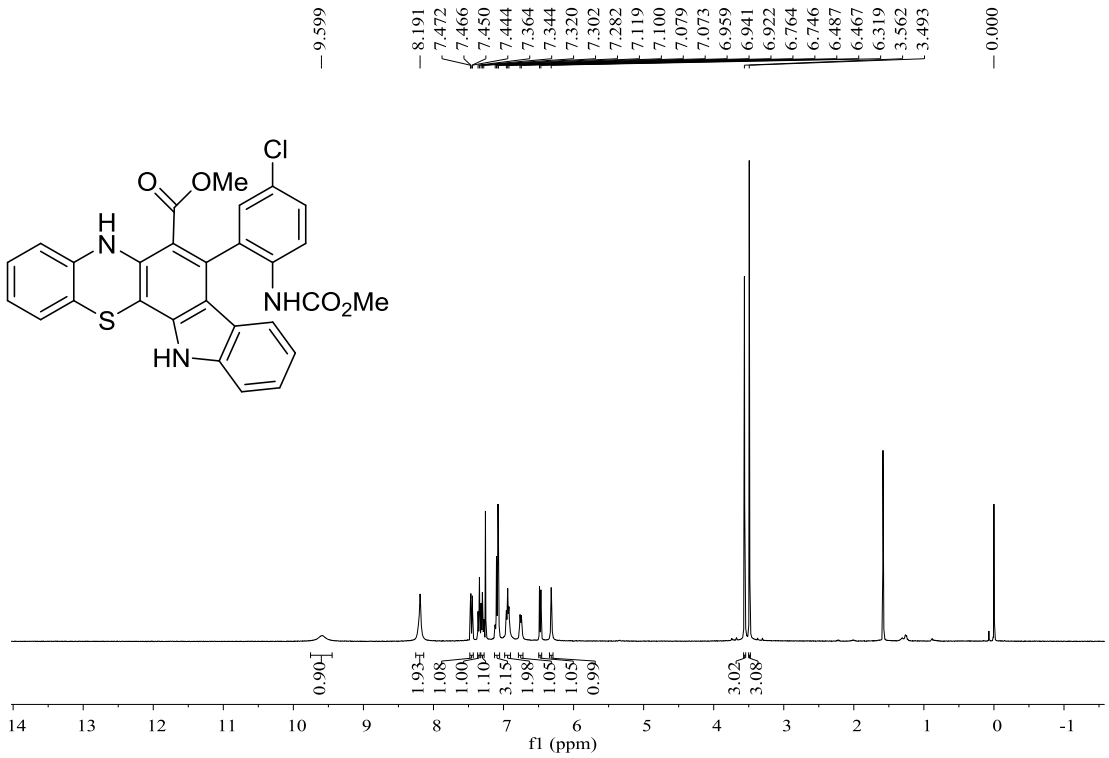
Methyl 7-(2-((methoxycarbonyl)amino)phenyl)-5,12-dihydroindolo[3,2-c]phenothiazine-6-carboxylate (**5h**): yellow solid, 49%, m.p. 121 – 123^{O}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 9.49 (s, 1H, NH), 8.20 (s, 2H, [NH]2), 7.50 ~ 7.46 (m, 1H, ArH), 7.34 (d, *J* = 8.0 Hz, 1H, ArH), 7.29 ~ 7.26 (m, 1H, ArH), 7.18 ~ 7.15 (m, 1H, ArH), 7.11 ~ 7.04 (m, 3H, ArH), 6.95~ 6.87 (m, 2H, ArH), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 6.42 (d, *J* = 8.0 Hz, 1H, ArH), 6.35 (s, 1H, ArH), 3.56 (m, 3H, OCH_3), 3.44 (m, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 169.3, 154.0, 143.5, 141.7, 140.0, 138.9, 135.5, 132.5, 128.6, 128.3, 128.0, 126.8, 126.0, 123.6, 123.3, 123.3, 121.3, 120.8, 117.8, 116.4, 116.2, 110.6, 108.4, 98.8, 52.1, 51.7; IR (KBr) υ: 3372, 3274, 3057, 2950, 1732, 1666, 1603, 1579, 1520, 1491, 1452, 1382, 1341, 1287, 1222, 1111, 1062, 974, 879, 849, 802 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{21}N_3O_4S$ ([M+Na]$^{+}$): 518.1145, Found: 518.1136.

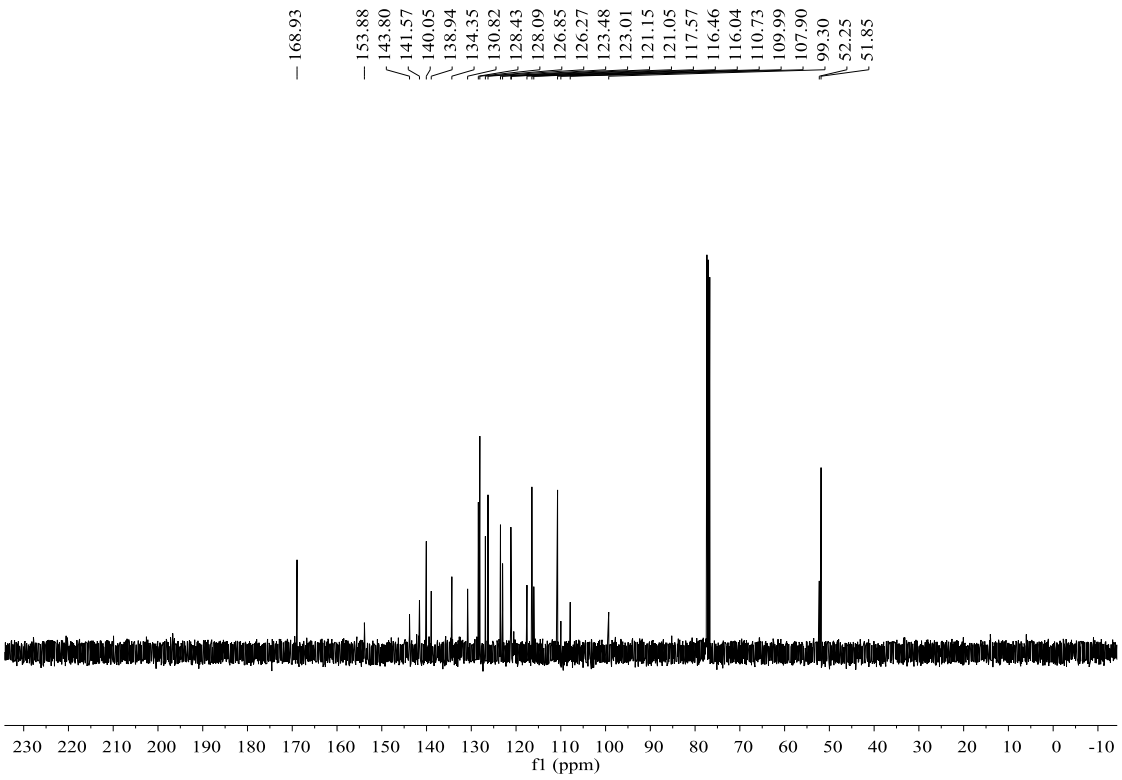



169.30
154.02
143.49
141.74
140.02
138.88
135.47
132.52
128.57
128.28
127.99
126.84
126.00
123.60
123.33
123.31
121.25
120.82
117.78
116.39
116.19
110.62
108.39
98.78
52.13
51.72
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


518.4136
3.02E+005

Methyl 7-(5-chloro-2-((methoxycarbonyl)amino)phenyl)-5,12-dihydroindolo[3,2-c]phenothiazine-6-carboxylate (**5i**): yellow solid, 53%, m.p. 171 – 173^{O}C; ^{1}H NMR (400 MHz,$CDCl_3$) δ: 9.60 (s, 1H, NH), 8.19 (s, 2H, [NH]2), 7.47 ~ 7.44 (m, 1H, ArH), 7.35 (d, *J* = 8.0 Hz, 1H, ArH), 7.32 ~ 7.28 (m, 1H, ArH), 7.12 ~ 7.07 (m, 3H, ArH), 6.96 ~ 6.92 (m, 2H, ArH), 6.76 (d, *J* = 7.2 Hz, 1H, ArH), 6.48 (d, *J* = 8.0 Hz, 1H, ArH), 6.32 (s, 1H, ArH), 3.56 (m, 3H, OCH_3), 3.49 (m, 3H, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 168.9, 153.9, 143.8, 141.6, 140.1, 138.9, 134.4, 130.8, 128.4, 128.1, 126.9, 126.3, 123.5, 123.0, 121.2, 121.1, 117.6, 116.5, 116.0, 110.7, 110.0, 107.9, 99.3, 52.3, 51.9; IR (KBr) υ: 3403, 3291, 3060, 2950, 1717, 1675, 1605, 1576, 1515, 1449, 1379, 1342, 1288, 1218, 1098, 1059, 976, 883, 855, 818 cm^{-1}; HRMS (ESI) Calcd. for $C_{28}H_{20}ClN_3O_4S$ ([M+H]$^{+}$): 552.0755, Found: 552.0750.




168.93
153.88
143.80
141.57
140.05
138.94
134.35
130.82
128.43
128.09
126.85
126.27
123.48
123.01
121.15
121.05
117.57
116.46
116.04
110.73
109.99
107.90
99.30
52.25
51.85
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ln21 #64 RT: 0.81 AV: 1 NL: 2.45E+005
552.0750
m/z