Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Efficient synthesis of novel cyclic fused-phenothiazines via domino cyclization of 2-(benzo[*b*][1,4]thiazin-3-ylidene)acetate, aromatic aldehydes and cyclic 1,3-diketones

Jing Sun, Quan-Shun Sun, Chao-Guo Yan*

Supporting Information

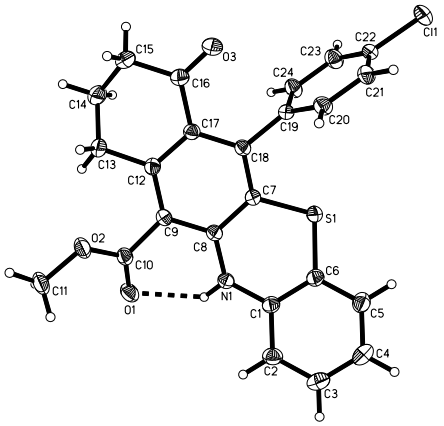


Fig. 4 ORTEP drawing (30%) of the crystal structure of **2n**

Experimental section

1. General procedure for the preparation of 2,3,4,7-tetrahydrobenzo[*c*]phenothiazine-6-carboxylates 1a-1i: A solution of cyclic *β*-enamino ester (1.0 mmol), aromatic aldehyde (1.0 mmol) and dimedone or 1,3-cyclohexanedione (1.0 mmol) in refluxing acetic acid (1.0 mL) and acetonitrile (6.0 mL) for twenty-four hours. The solvent was removed by evaporation at reduced pressure. The residue was subjected to column chromatography with a mixture of light petroleum and ethyl acetate as eluent (V/V = 3:1) to give the pure products **1a-1i** for analysis.

2. General procedure for the preparation of 7,9,10,12-tetrahydrobenzo[*b*]phenothiazine-11-carboxylate 2a-2o: A solution of cyclic *β*-enamino ester (1.0 mmol), aromatic aldehyde (1.0 mmol) and dimedone or 1,3-cyclohexanedione (1.0 mmol) in refluxing acetic acid (8.0 mL) for twenty-four hours. The solvent was removed by evaporation at reduced pressure. The residue was recrystallized in ethanol to give the pure products **2a-2o** for analysis.

3. General procedure for the preparation of cyclopenta[*b*]phenothiazine-11-carboxylates 3a-3b and 4a-4f: The same reaction procedure as above was used by using 1,3-cyclopentanedione

to replacing dimedone. The corresponding cyclopenta[*b*]phenothiazine-11-carboxylates **3a-3b** and **4a-4f** were obtained.

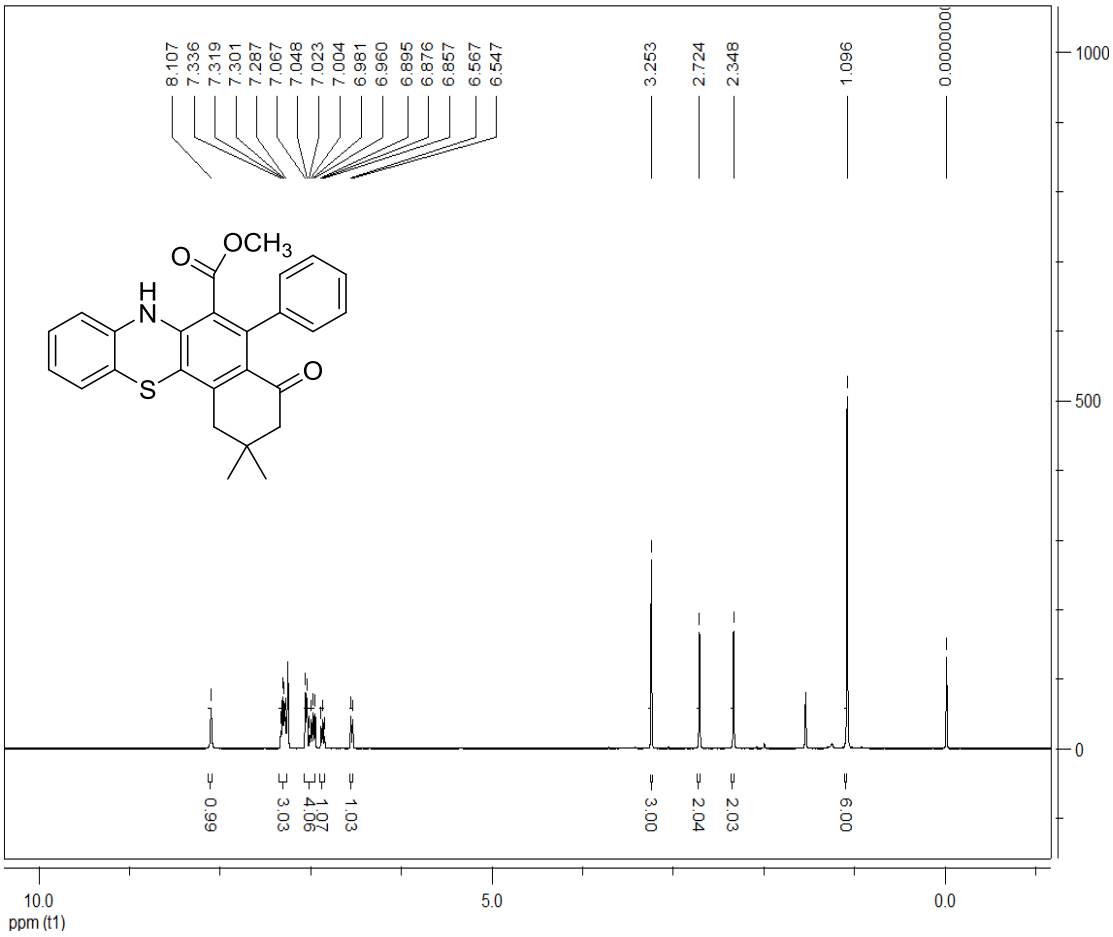
4. General procedure for the preparation of polycyclic compounds 5a-5p and 6a-6e: A solution of cyclic *β*-enamino ester (1.0 mmol), aromatic aldehyde (1.0 mmol) in acetic acid (1.5 mL) and acetonitrile (6.0 mL) was stirred at room temperature for twelve hours. The solvent was removed by evaporation at reduced pressure. The residue was subjected to column chromatography with a mixture of light petroleum and ethyl acetate as eluent (V/V = 3:1) to give the pure products **5a-5p** for analysis. Alternatively, after finishing the first reaction, DDQ (1.5 mmol) was added. The suspension was refluxed for four hours. After removing the solvent, The residue was subjected to column chromatography with a mixture of light petroleum and ethyl acetate as eluent (V/V = 3:1) to give the pure products **6a-6c** for analysis.

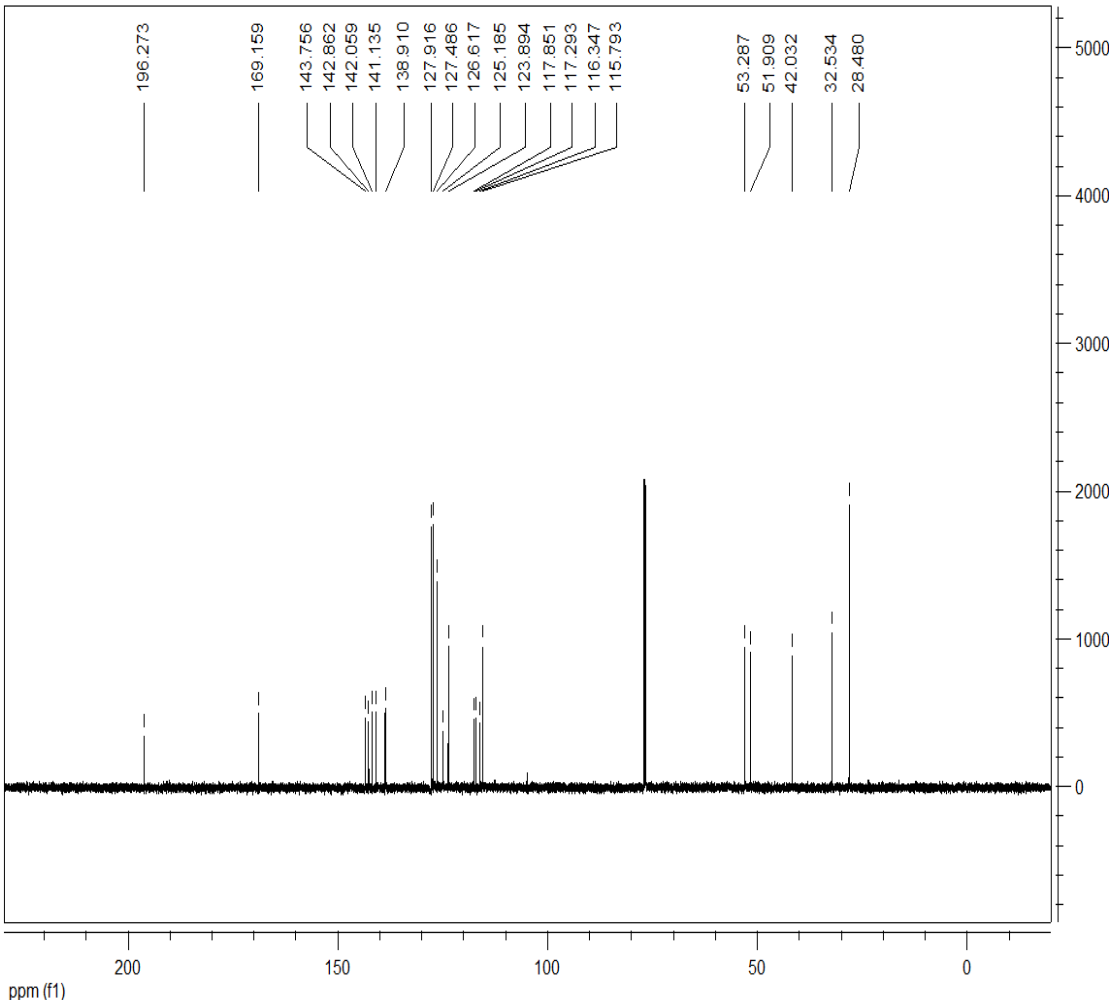
5. General procedure for the preparation of polycyclic compounds 7a-7b and 8a-8b: A solution of cyclic *β*-enamino ester (1.0 mmol), acenaphthequinone or ninhydrin, (1.0 mmol) in acetic acid (1.5 mL) and acetonitrile (6.0 mL) was stirred at room temperature for twelve hours. The solvent was removed by evaporation at reduced pressure. The residue was subjected to column chromatography with a mixture of light petroleum and ethyl acetate as eluent (V/V = 3:1) to give the pure product.

5. General procedure for the preparation of polycyclic compounds 9a-9d: A solution of cyclic *β*-enamino ester (1.0 mmol), phenylglyoxal (0.60 mmol) in acetic acid (1.5 mL) and acetonitrile (6.0 mL) was stirred at room temperature for twelve hours. The solvent was removed by evaporation at reduced pressure. The residue was subjected to column chromatography with a mixture of light petroleum and ethyl acetate as eluent (V/V = 3:1) to give the pure product.

Methyl 2,2-dimethyl-4-oxo-5-phenyl-2,3,4,7-tetrahydro-1H-benzo[c]phenothiazine-6-carboxylate (1a):

yellow solid, 75%, m.p. 161~163℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.11 (s, 1H, NH), 7.34~7.29 (m, 3H, ArH), 7.07~6.96 (m, 4H, ArH), 6.88 (t, *J* = 7.6 Hz, 1H, ArH), 6.56 (d, *J* = 8.0 Hz, 1H, ArH), 3.25 (s, 3H, OCH_3), 2.72 (s, 2H, CH_2), 2.35 (s, 2H, CH_2), 1.10 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.3, 169.2, 143.8, 142.9, 142.1, 141.1, 138.9, 127.9, 127.5, 126.6, 125.2, 123.9, 117.9, 117.3, 116.3, 115.8, 53.3, 51.9, 42.0, 32.5, 28.5; IR (KBr) υ: 3359, 3055, 2950, 1685, 1568,1526, 1472, 1425, 1370, 1311, 1279, 1224, 1130, 978, 938, 851, 807, 747 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{23}NNaO_3S$ ([M+Na]$^+$): 452.1296. Found: 452.1298.

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117.851
117.293
116.347
115.793
53.287
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28.480
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0
200
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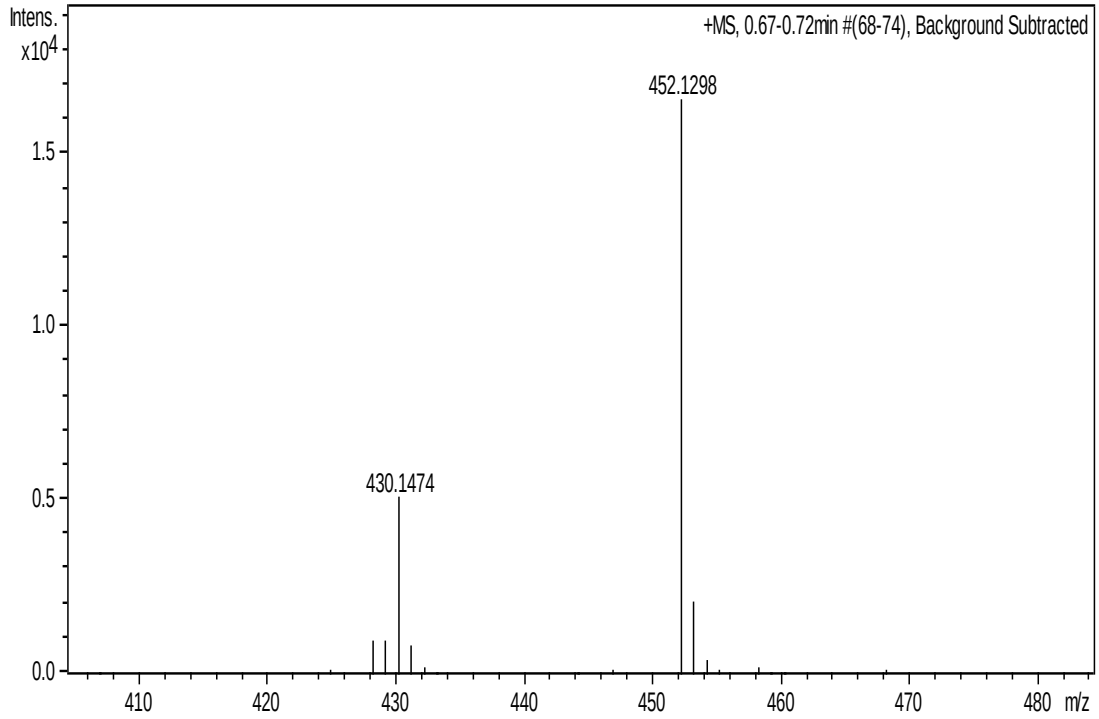
0
ppm (f1)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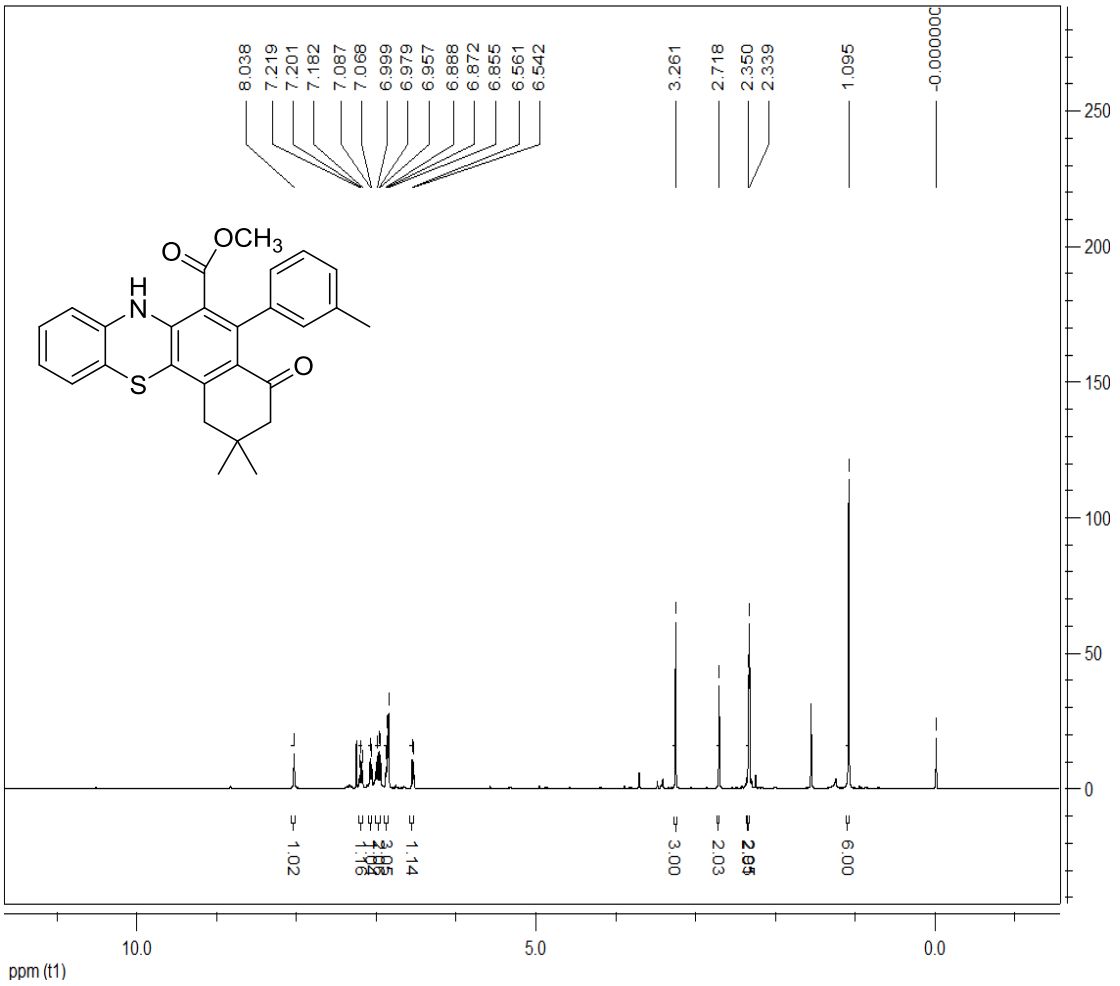
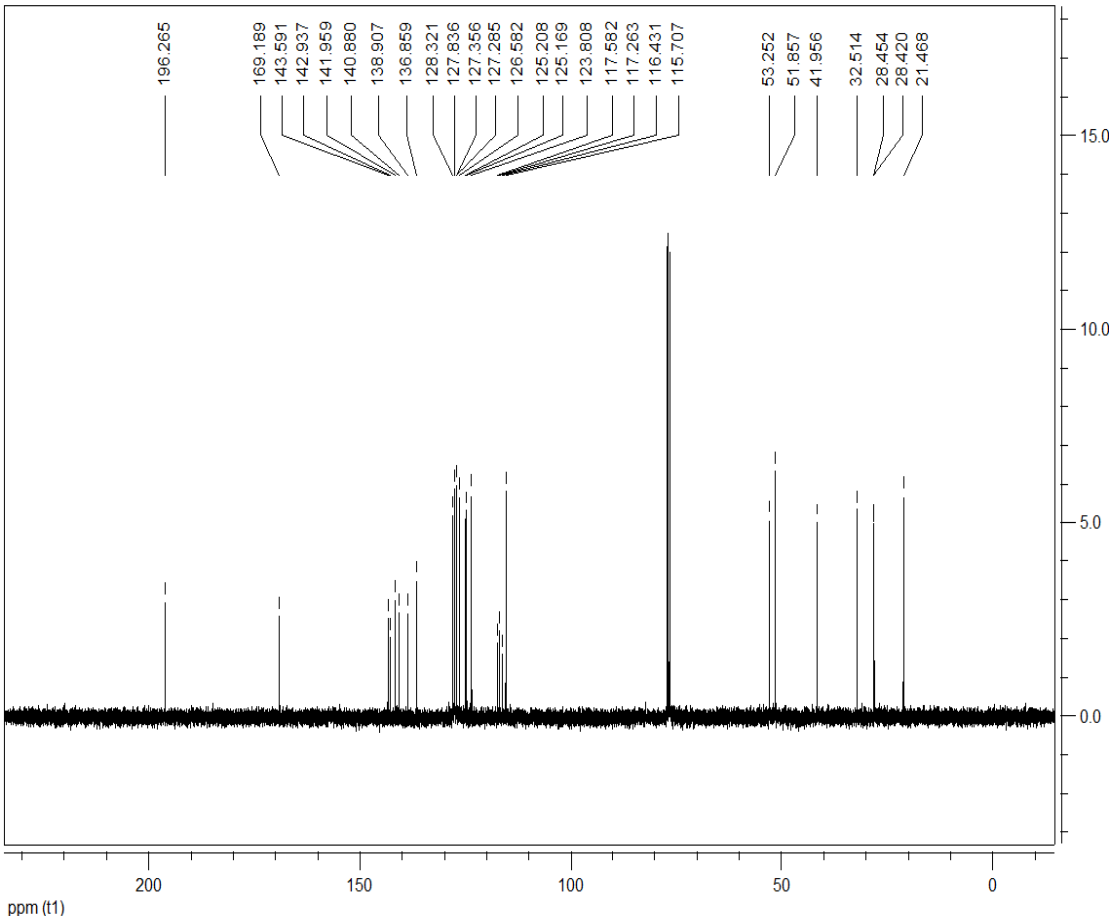
0.5
0.0
410
420
430
440
450
460
470
480
m/z

Methyl 2,2-dimethyl-4-oxo-5-(m-tolyl)-2,3,4,7-tetrahydro-1H-benzo[c]phenothiazine-6-carboxylate (1b):

yellow solid, 71%, m.p. 184~186℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.04 (s, 1H, NH), 7.22~7.18 (m, 1H, ArH), 7.08 (d, *J* = 7.6 Hz, 1H, ArH), 7.00~6.96 (m, 2H, ArH), 6.89~6.86 (m, 3H, ArH), 6.55 (d, *J* = 7.6 Hz, 1H, ArH), 3.26 (s, 3H, OCH_3), 2.72 (s, 2H, CH_2), 2.35 (s, 3H, CH_3), 2.34 (s, 2H, CH_2), 1.10 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.2, 169.1, 143.5, 142.9, 141.9, 140.8, 138.9, 136.8, 128.3, 127.8, 127.3, 127.2, 126.5, 125.2, 125.1, 123.8, 117.5, 117.2, 116.4, 115.7, 53.2, 51.8, 41.9, 32.5, 28.4, 28.4, 21.4; IR (KBr) υ: 3649, 3353, 3020 2951, 2868, 1933, 1686, 1594, 1531, 1475, 1426, 1375, 1277, 1223, 1128, 1090, 1056, 976, 933, 882, 827, 787, 746, 706 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{27}H_{26}NO_3S$ ([M+H]$^{+}$): 444.1633. Found: 444.1637.

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125.208
125.169
123.808
117.582
117.263
116.431
115.707
53.252
51.857
41.956
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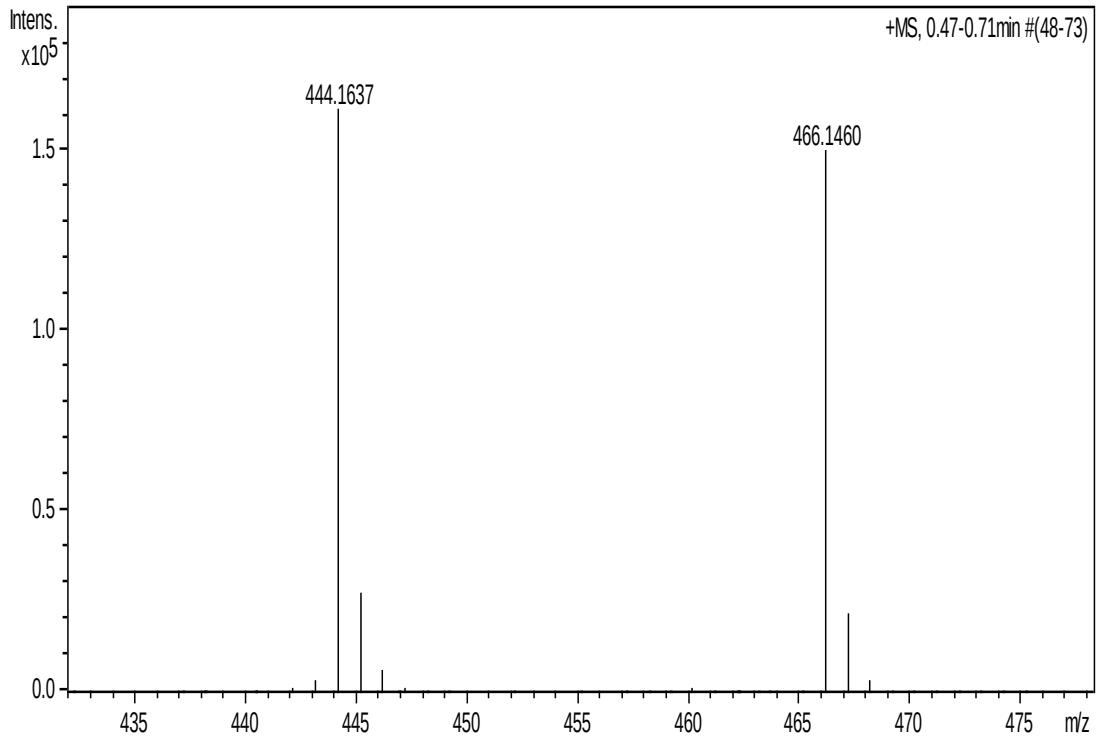
ppm (t1)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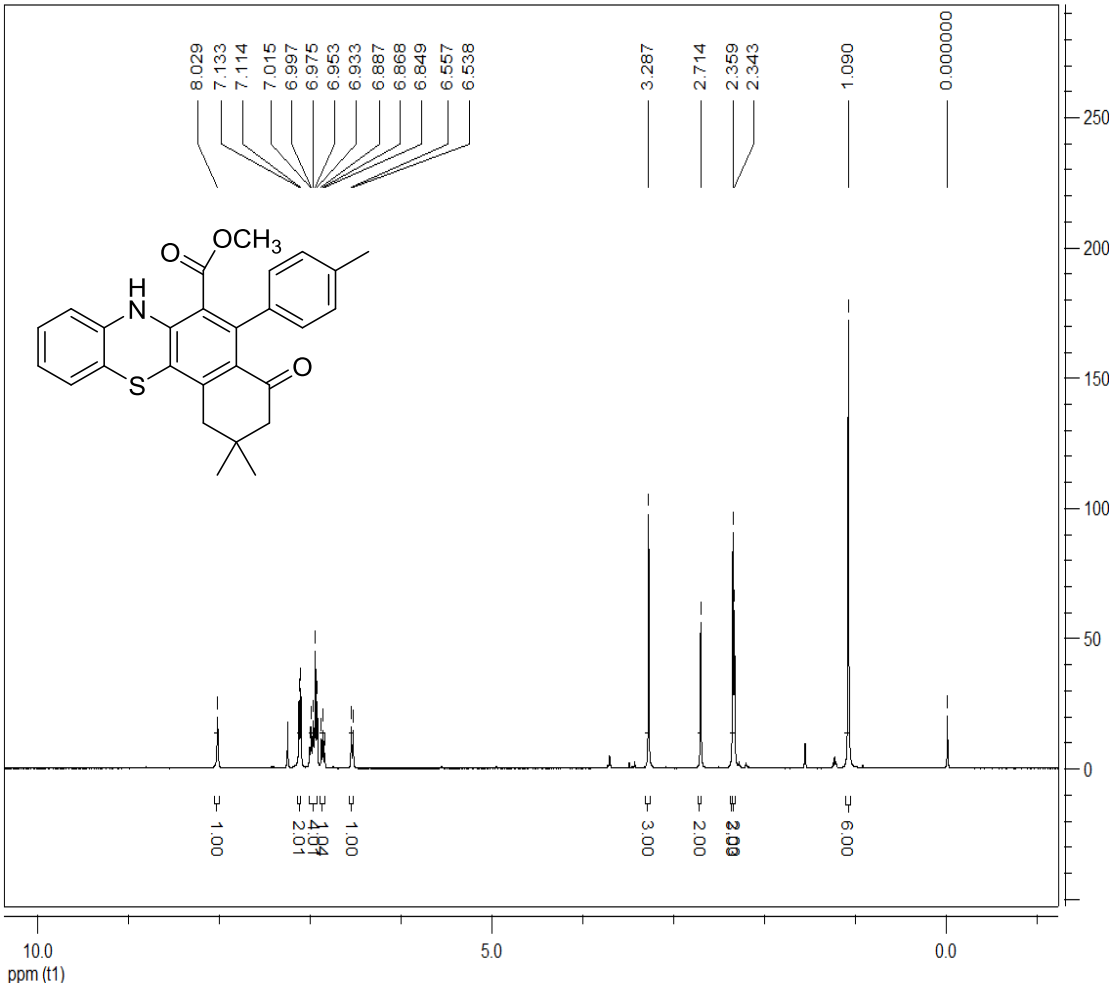
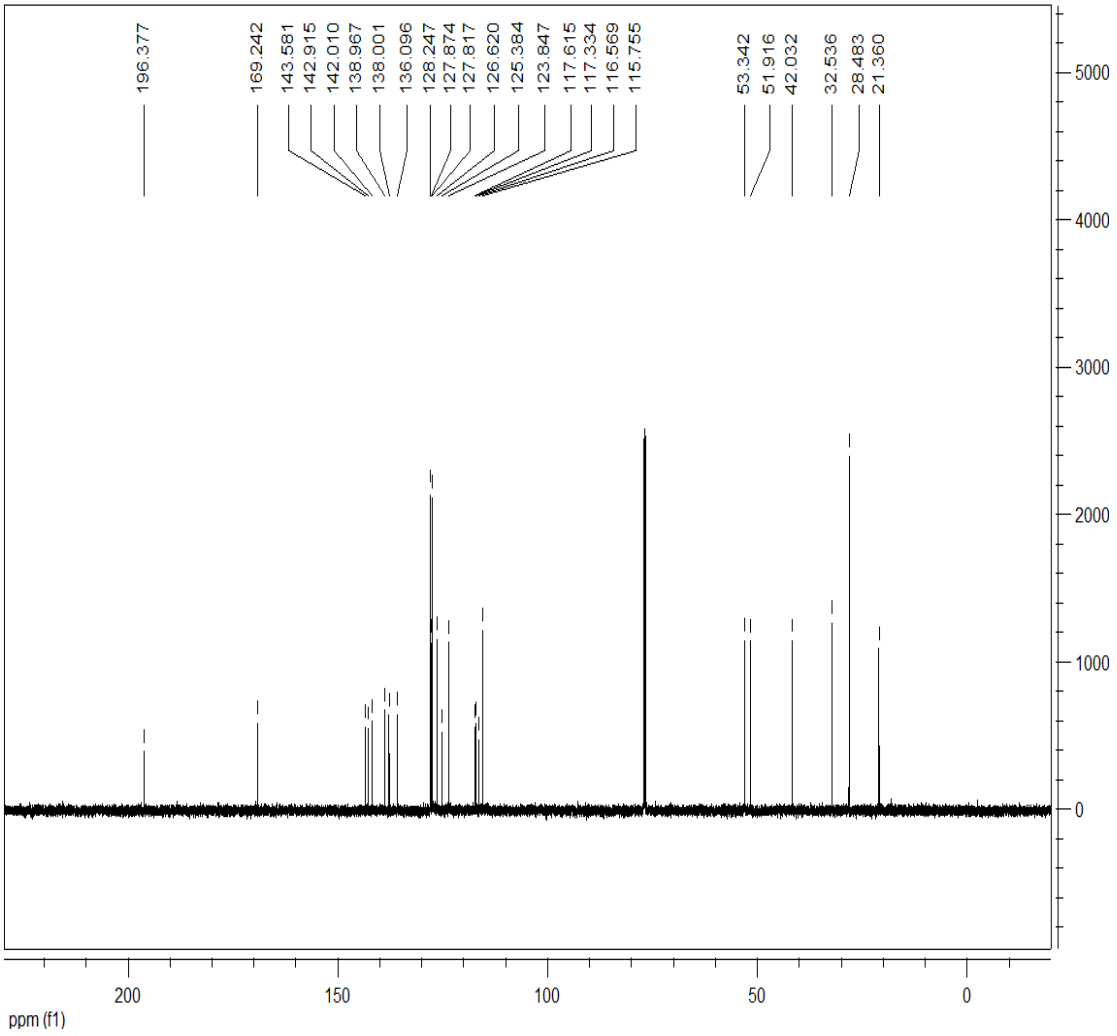
1.0
0.5
0.0
435
440
445
450
455
460
465
470
475
m/z

Methyl 2,2-dimethyl-4-oxo-5-(p-tolyl)-2,3,4,7-tetrahydro-1H-benzo[c]phenothiazine-6-carboxylate (1c):

yellow solid, 93%, m.p. 147~149℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (s, 1H, NH), 7.12 (d, *J* = 7.6 Hz, 2H, ArH), 7.02~6.96 (m, 4H, ArH), 6.87 (t, *J* = 7.6 Hz, 1H, ArH), 5.54 (d, *J* = 7.6 Hz, 1H, ArH), 3.29 (s, 3H, OCH_3), 2.71 (s, 2H, CH_2), 2.36 (s, 3H, CH_3), 2.34 (s, 2H, CH_2), 1.09 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.4, 169.2, 143.6, 142.9, 142.0, 139.0, 138.0, 136.1, 128.2, 127.9, 127.8, 126.6, 125.4, 123.8, 117.6, 117.3, 116.6, 115.8, 53.3, 51.9, 42.0, 32.5, 28.5, 21.4; IR (KBr) υ: 3331, 2953, 1710, 1680, 1593, 1526, 1477, 1430, 1380, 1285, 1224, 1108, 973, 856, 815, 746cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{27}H_{25}NNaO_3S$ ($[M+Na]^+$): 466.1453. Found: 466.1459.

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117.334
116.569
115.755
53.342
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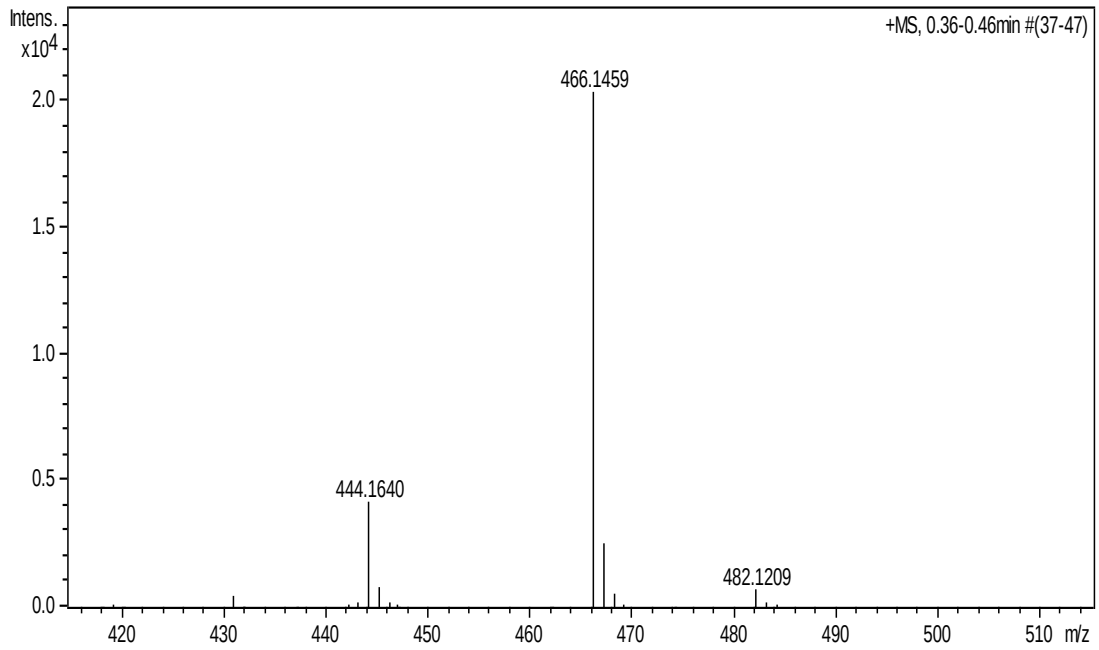
ppm (f1)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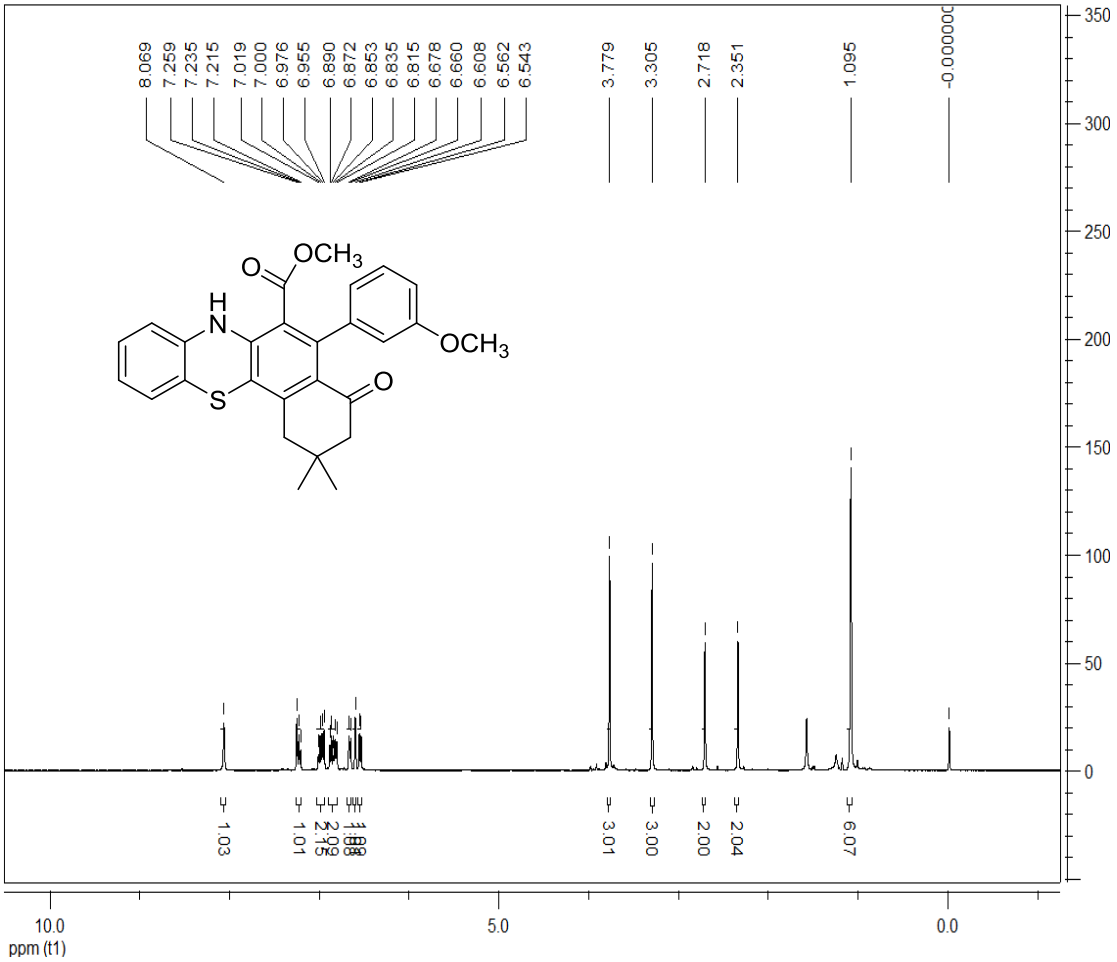
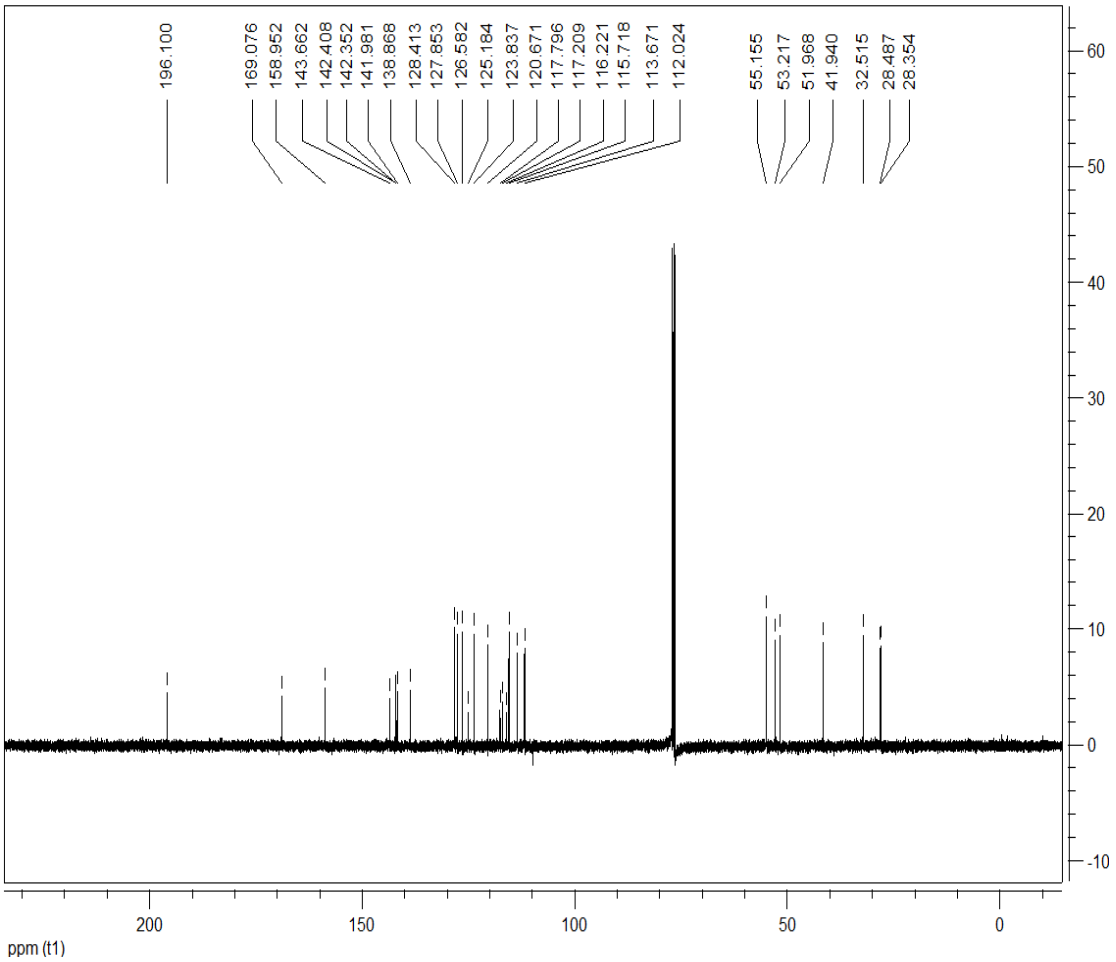
1.0
0.5
0.0
420
430
440
450
460
470
480
490
500
510
m/z

Methyl5-(3-methoxyphenyl)-2,2-dimethyl-4-oxo-2,3,4,7-tetrahydro-1H-benzo[c]phenothiazine-6-carboxylate (1d):

yellow solid, 77%, m.p. 169~171℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07 (s, 1H, NH), 7.26~7.22 (m, 1H, ArH), 7.02~6.96 (m, 2H, ArH), 6.89~6.82 (m, 2H, ArH), 6.66 (d, *J* = 7.2 Hz, 1H, ArH), 6.61 (s, 2H, ArH), 6.05 (d, *J* = 7.6 Hz, 1H, ArH), 3.78 (s, 3H, OCH_3), 3.31 (s, 3H, OCH_3), 2.72 (s, 2H, CH_2), 2.35 (s, 2H, CH_2), 1.10 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.0, 169.0, 158.9, 143.6, 142.4, 142.3, 141.9, 138.8, 128.4, 127.8, 126.5, 125.1, 123.8, 120.6, 117.7, 117.2, 116.2, 115.7, 113.6, 112.0, 55.1, 53.2, 51.9, 41.9, 32.5, 28.4, 28.3; IR (KBr) υ: 3695, 3058, 2949, 1686, 1584, 1530, 1475, 1427, 1377, 1280, 1220, 1132, 1042, 977, 870, 784, 745, 702cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{27}H_{26}NO_4S$ ([M+H]$^+$): 460.1583. Found: 460.1593.

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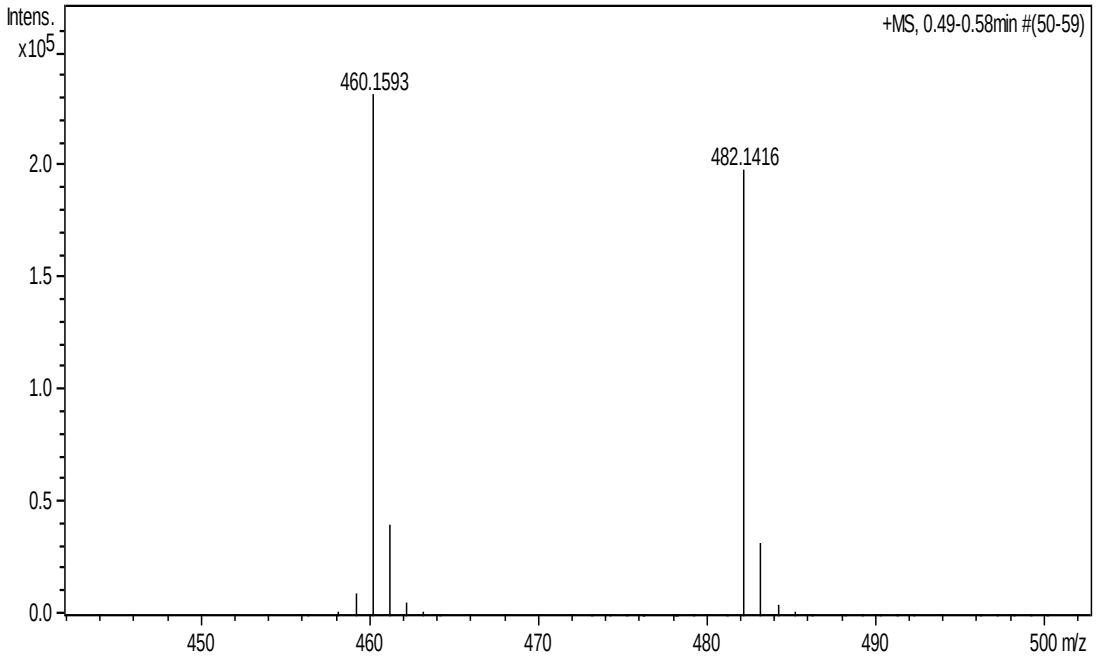
ppm (t1)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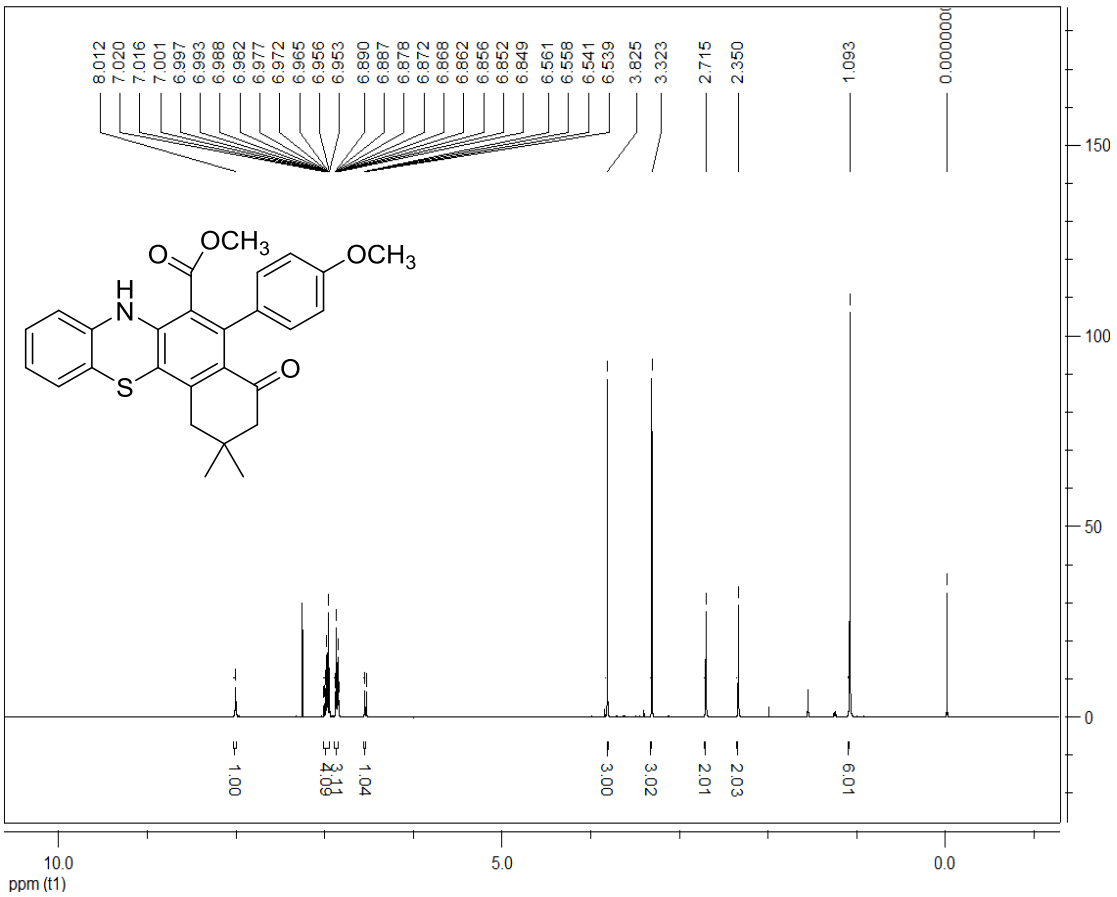
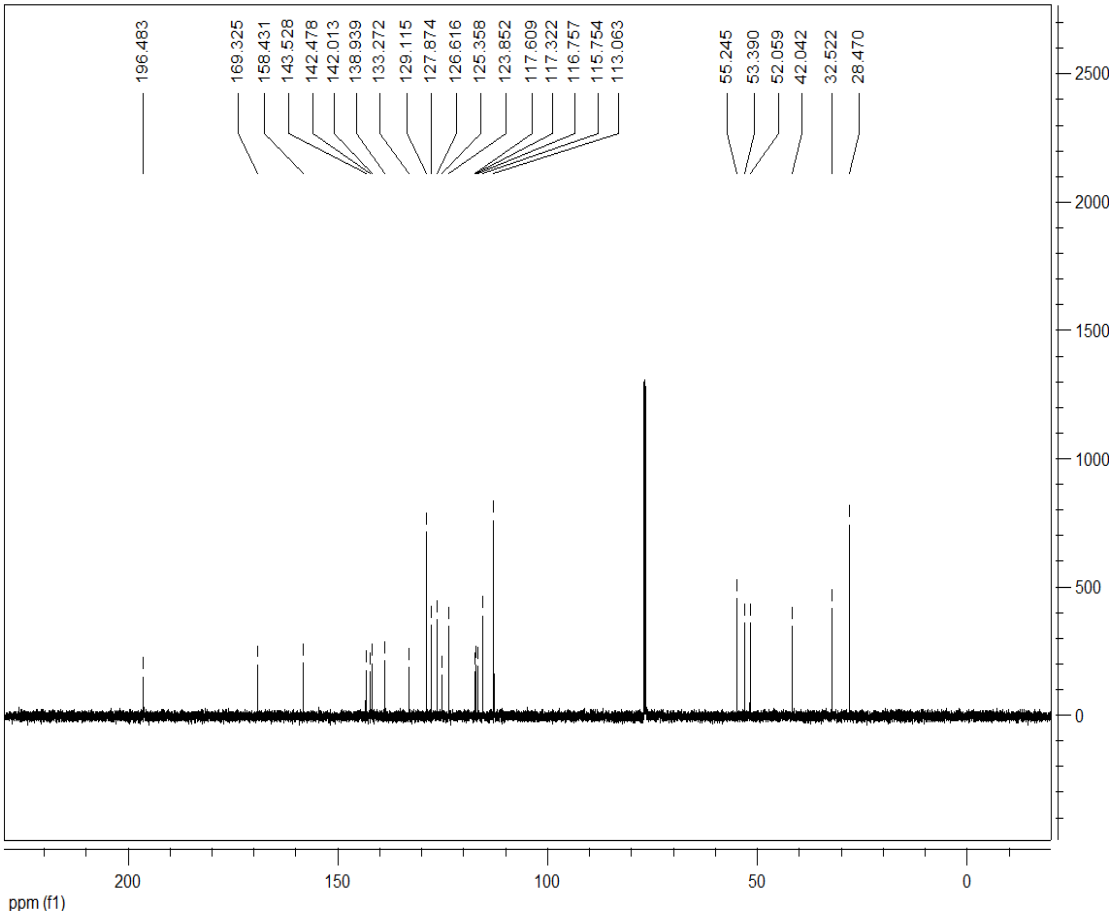
0.0
450
460
470
480
490
500 m/z

Methyl

5-(4-methoxyphenyl)-2,2-dimethyl-4-oxo-2,3,4,7-tetrahydro-1H-benzo[c]phenothiazine-6-carboxylate (1e):

yellow solid, 79%, m.p. 157~159℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (s, 1H, NH), 7.02~6.95 (m, 4H, ArH), 6.89~6.85 (m, 3H, ArH), 6.56~6.54 (m, 1H, ArH), 3.83 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 2.72 (s, 2H, CH_2), 2.35 (s, 2H, CH_2), 1.09 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.5, 169.3, 158.4, 143.5, 142.5, 142.0, 138.9, 133.3, 129.1, 127.9, 126.6, 125.4, 123.9, 117.6, 117.3, 116.8, 115.8, 113.1, 55.2, 53.4, 52.1, 42.0, 32.5, 28.5; IR (KBr) υ: 3329, 3042, 2951, 1697, 1677, 1597, 1524, 1480, 1432, 1375, 1288, 1225, 1183, 1110, 1037, 979, 833, 747cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{23}NNaO_4S$ ([M+Na]$^{+}$): 482.1402. Found: 482.1406.

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116.757
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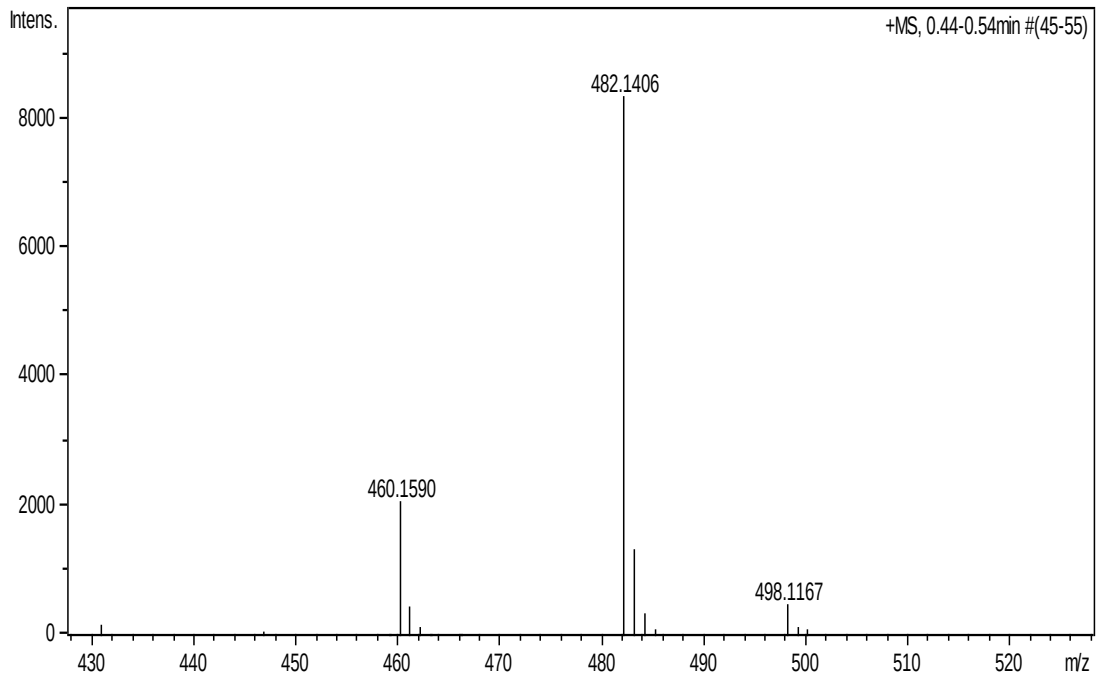
ppm (f1)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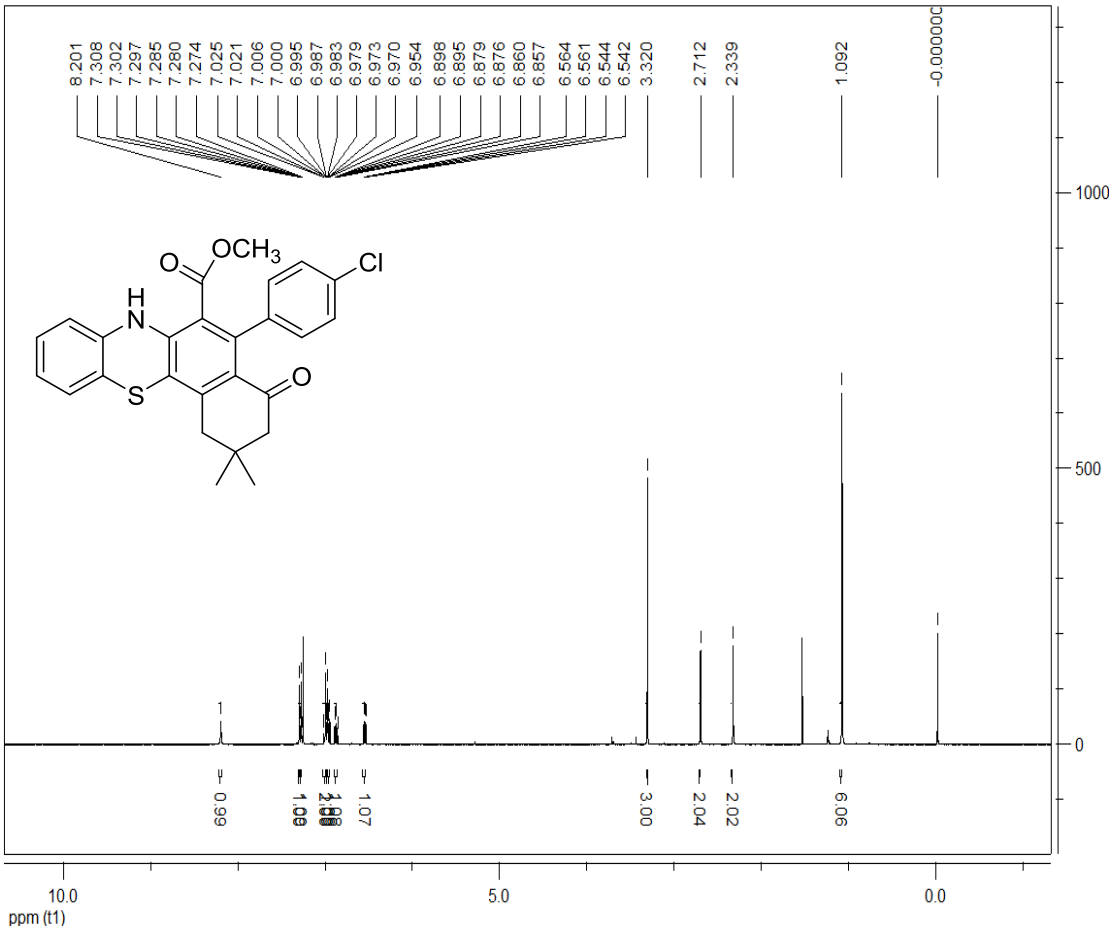
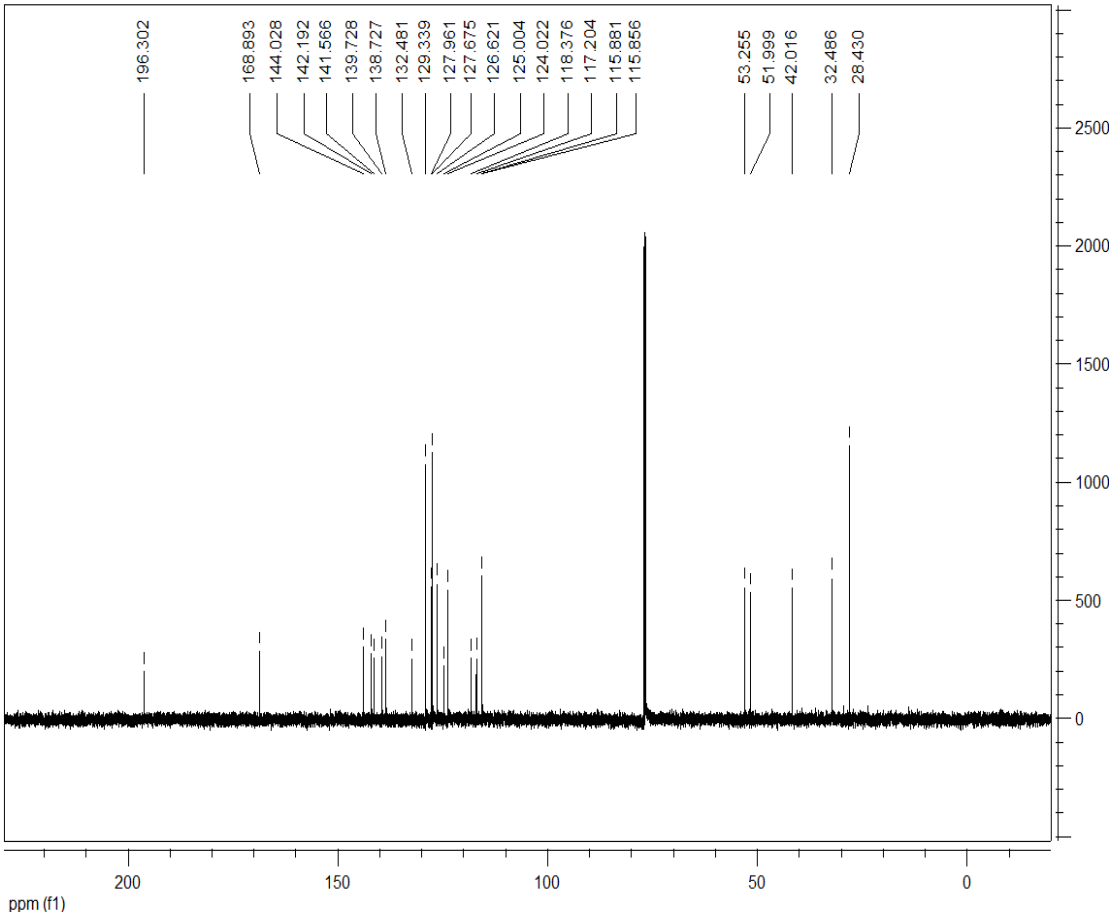
430
440
450
460
470
480
490
500
510
520
m/z

Methyl

5-(4-chlorophenyl)-2,2-dimethyl-4-oxo-2,3,4,7-tetrahydro-1H-benzo[c]phenothiazine-6-carboxylate (1f):

yellow solid, 71%, m.p. 181~182℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20 (s, 1H, NH), 7.31~7.30 (m, 1H, ArH), 7.29~7.27 (m, 1H, ArH), 7.03~7.00 (m, 2H, ArH), 6.99~6.98 (m, 1H, ArH), 6.97~6.95 (m, 1H, ArH), 6.90~6.86 (m, 1H, ArH), 6.56~6.54 (m, 1H, ArH), 3.32 (s, 3H, OCH_3), 2.71 (s, 2H, CH_2), 2.34 (s, 2H, CH_2), 1.09 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.3, 168.9, 144.0, 142.2, 141.6, 139.7, 138.7, 132.5, 129.3, 128.0, 127.7, 126.6, 125.0, 124.0, 118.4, 117.2, 115.9, 115.9, 53.3, 52.0, 42.0, 32.5, 28.4; IR (KBr) υ: 3335, 3056, 2954, 1709, 1677, 1594, 1528, 1476, 1430, 1378, 1284, 1259, 1223, 1106, 1010, 973, 857, 827, 749cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{22}ClNNaO_3S$ ([M+Na]$^{+}$): 486.0907. Found: 486.0911.

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117.204
115.881
115.856
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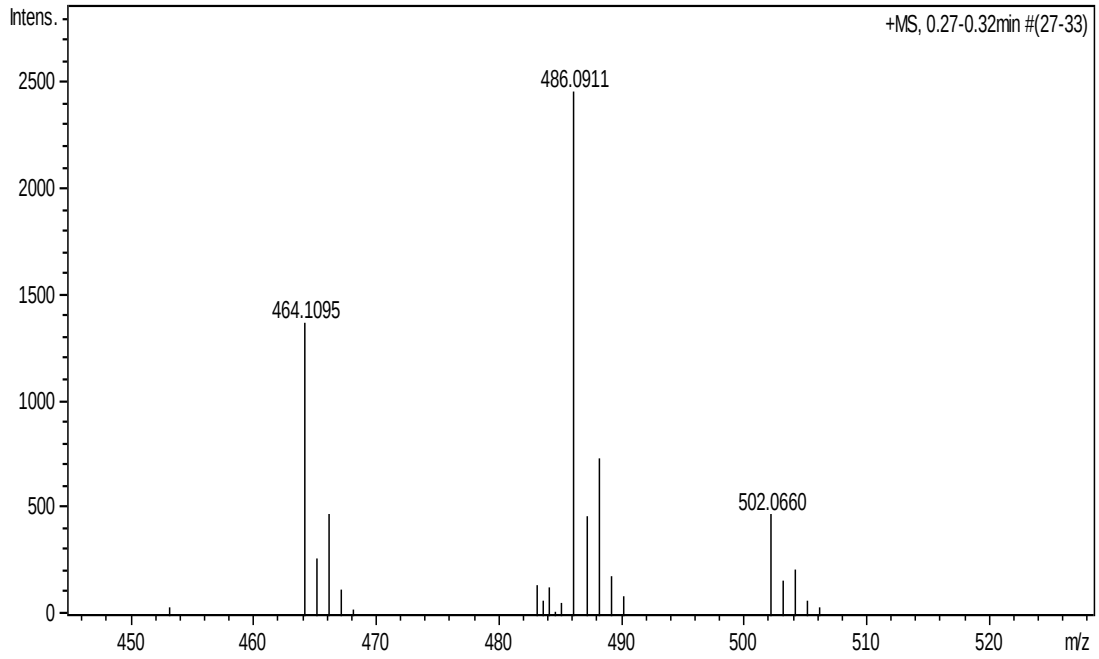
ppm (f1)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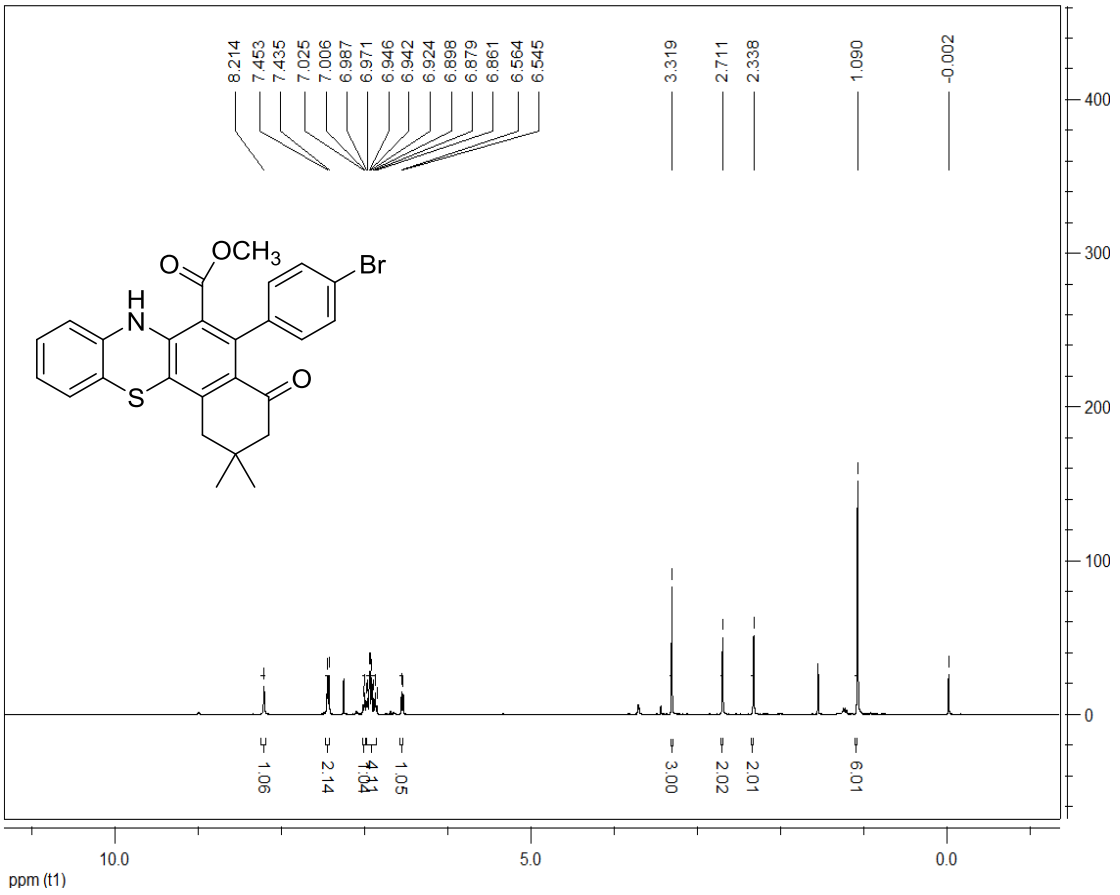
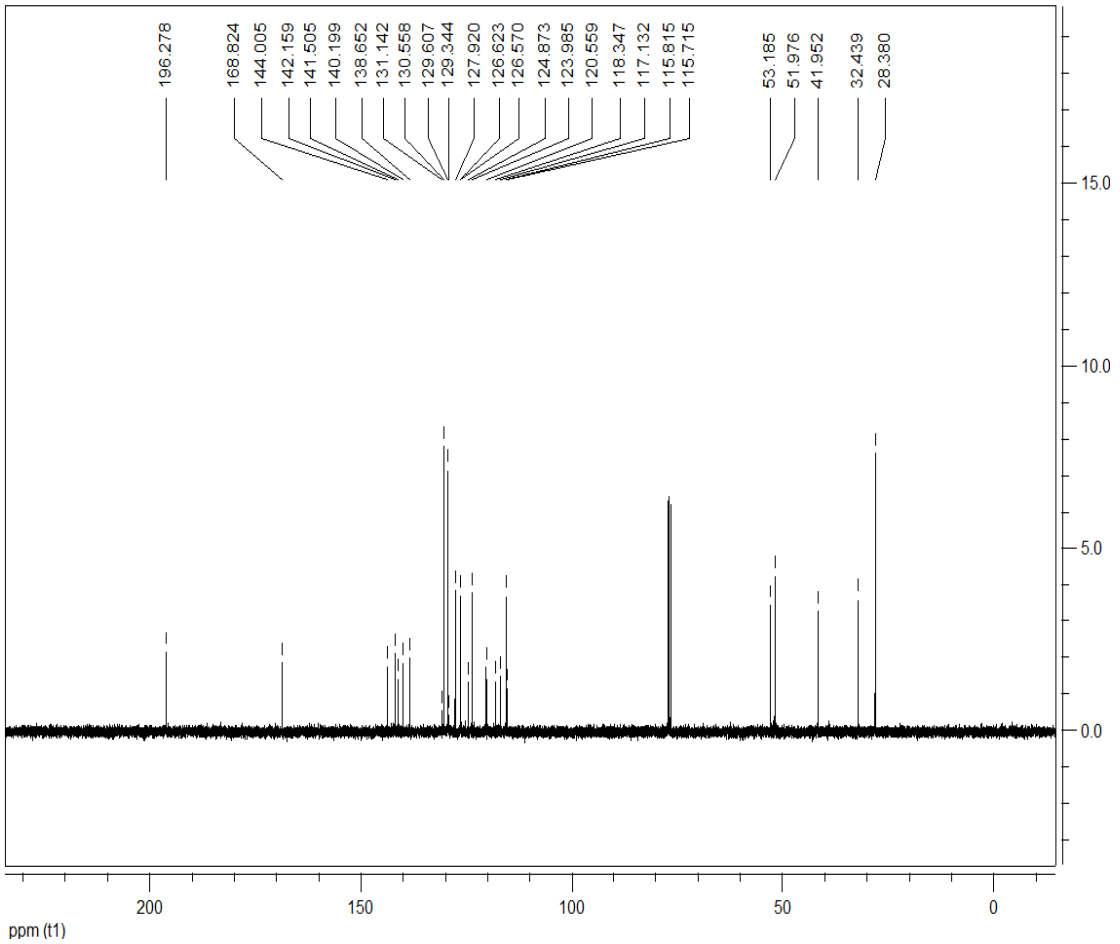
2000
1500
1000
500
0
450
460
470
480
490
500
510
520
m/z

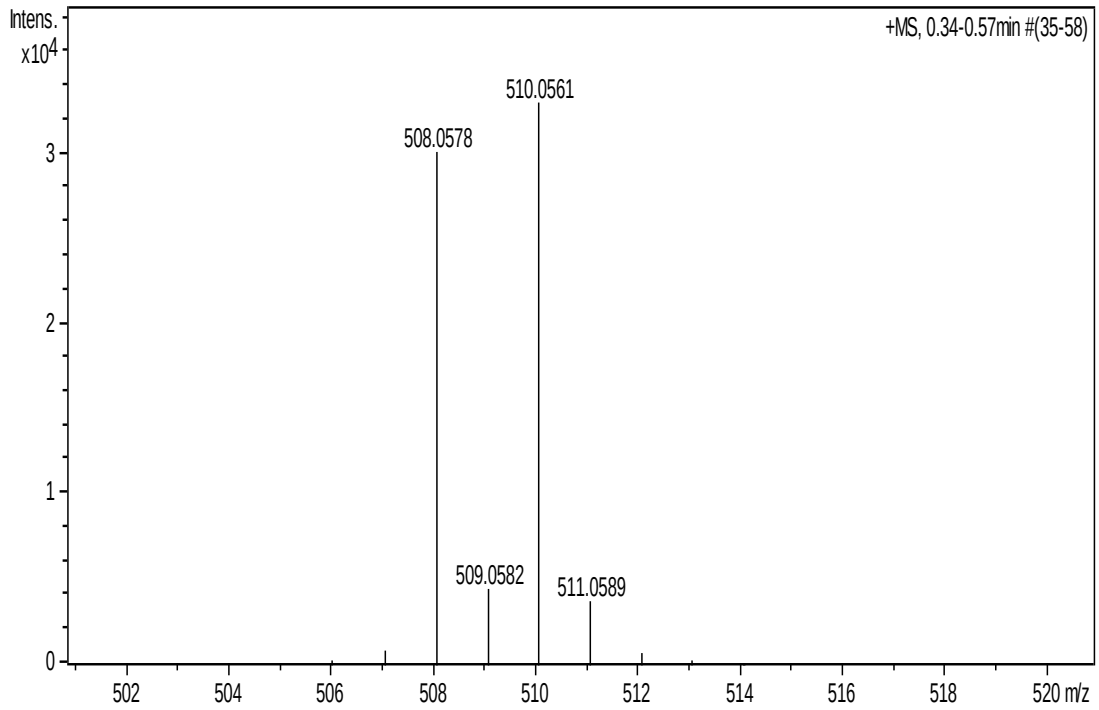
Methyl

5-(4-bromophenyl)-2,2-dimethyl-4-oxo-2,3,4,7-tetrahydro-1H-benzo[c]phenothiazine-6-carb oxylate (1g):

yellow solid, 75%, m.p. 193~195℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (s, 1H, NH), 7.44 (d, *J* = 7.2 Hz, 2H, ArH), 7.03~6.99 (m, 1H, ArH), 6.97~6.86 (m, 4H, ArH), 6.55 (d, *J* = 7.2 Hz, 1H, ArH), 3.32 (s, 3H, OCH_3), 2.71 (s, 2H, CH_2), 2.34 (s, 2H, CH_2), 1.09 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.2, 168.8, 144.0, 142.1, 141.5, 140.1, 138.6, 131.1, 130.5, 129.6, 129.3, 127.9, 126.6, 126.5, 124.8, 123.9, 120.5, 118.3, 117.1, 115.8, 115.7, 53.1, 51.9, 41.9, 32.4, 28.3; IR (KBr) υ: 3694, 3336, 3055, 2953, 2542, 1928, 1709, 1675, 1593, 1526, 1477, 1430, 1377, 1282, 1259, 1221, 1149, 1105, 1067, 1006, 973, 935, 893, 856, 823, 747, 702 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{23}BrNO_3S$ ($[M+H]^+$): 508.0582. Found: 508.0578.

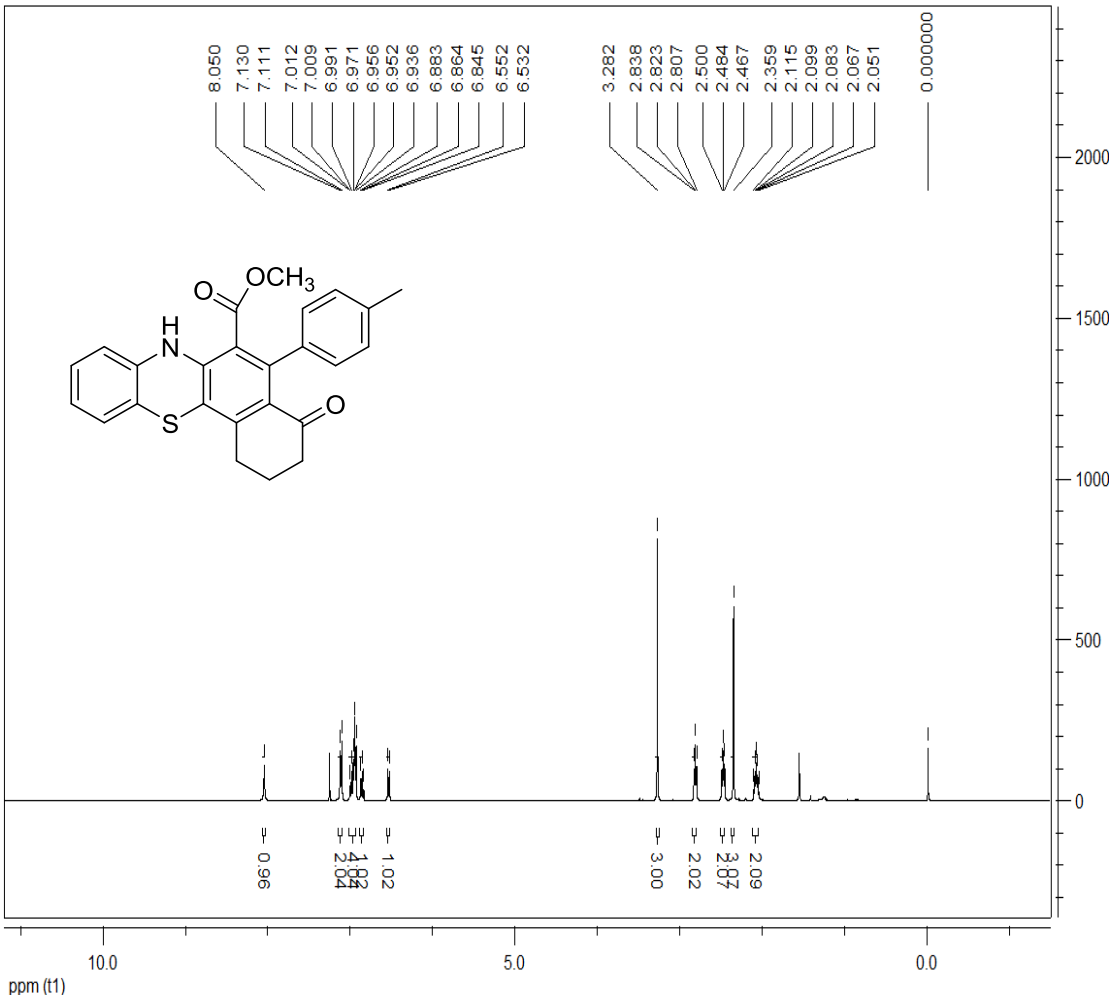


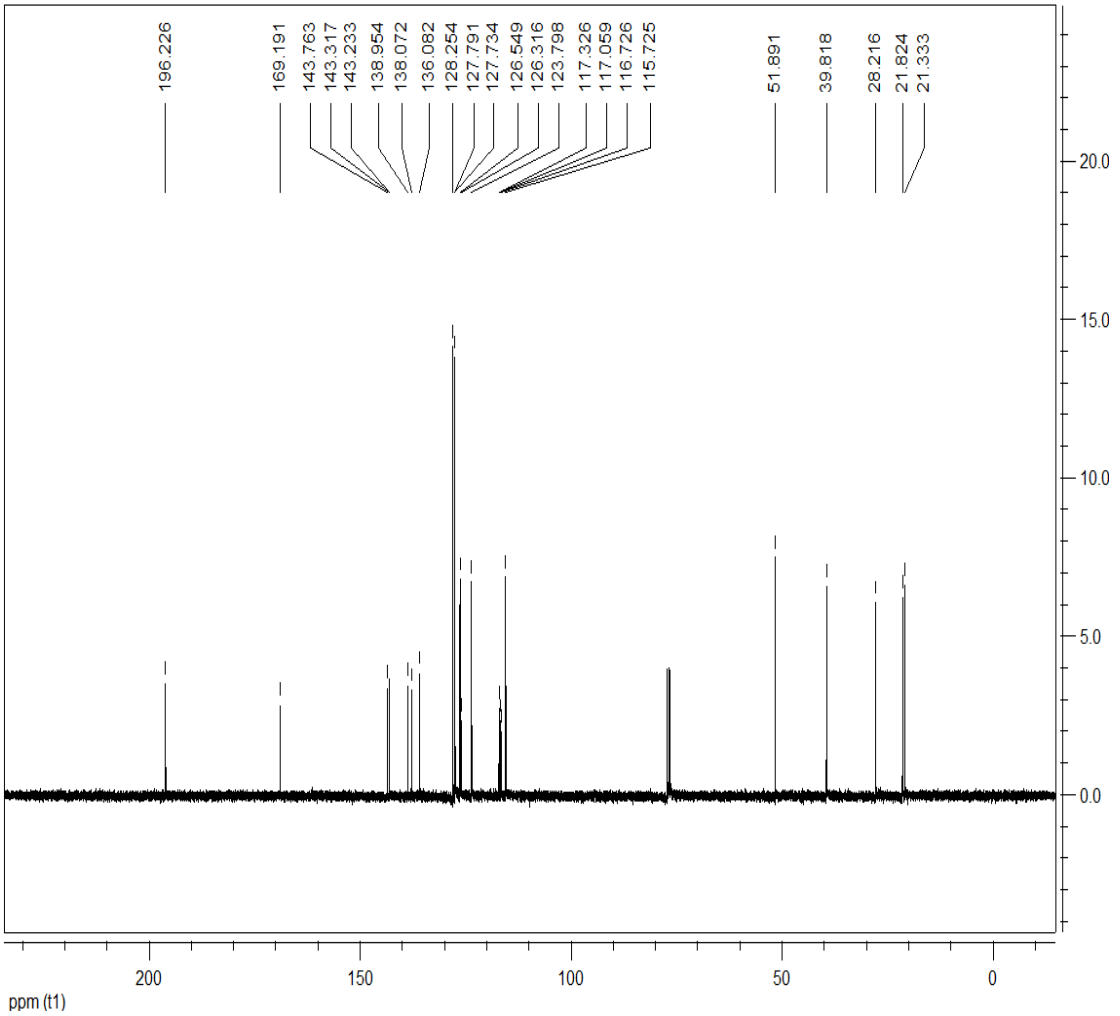

196.278
168.824
144.005
142.159
141.505
140.199
138.652
131.142
130.558
129.607
129.344
127.920
126.623
126.570
124.873
123.985
120.559
118.347
117.132
115.815
115.715
53.185
51.976
41.952
32.439
28.380
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

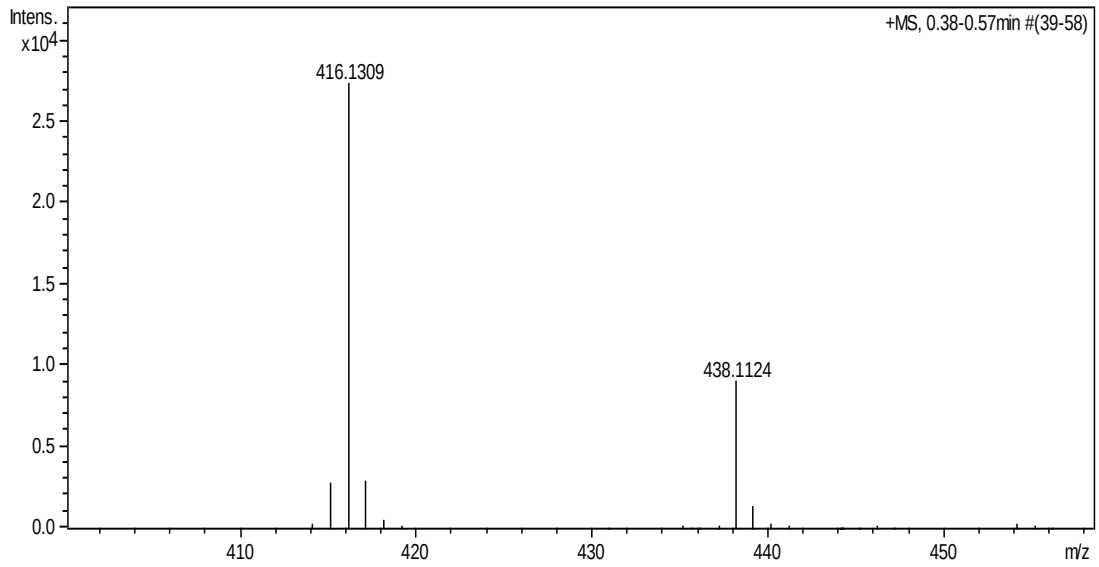

Intens.
x10^4
+MS, 0.34-0.57min #(35-58)
510.0561
508.0578
509.0582
511.0589
3
2
1
0
502
504
506
508
510
512
514
516
518
520 m/z

Methyl 4-oxo-5-(p-tolyl)-2,3,4,7-tetrahydro-1H-benzo[c]phenothiazine-6-carboxylate (1h):

yellow solid, 73%, m.p. 143~145℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (s, 1H, NH), 7.12 (d, *J* = 7.2 Hz, 2H, ArH), 7.01~6.94 (m, 4H, ArH), 6.86 (t, *J* = 7.6 Hz, 1H, ArH), 6.54 (d, *J* = 8.0 Hz, 1H, ArH), 3.28 (s, 3H, OCH_3), 2.82 (t, *J* = 6.0 Hz, 1H, ArH), 2.48 (t, *J* = 6.0 Hz, 1H, ArH), 2.36 (s, 3H, CH_3), 2.11~2.05 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 196.2, 169.1, 143.7, 143.3, 143.2, 138.9, 138.0, 136.0, 128.2, 127.7, 127.7, 126.5, 126.3, 123.7, 117.3, 117.0, 116.7, 115.7, 51.8, 39.8, 28.2, 21.8, 21.3; IR (KBr) υ: 3699, 3354, 3024, 2990, 2916, 1908, 1799, 1710, 1673, 1587, 1526, 1474, 1426, 1382, 1353, 1286, 1255, 1218, 1181, 1106, 1074, 1036, 1005, 976, 932, 886, 821, 749 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{25}H_{22}NO_3S$ ($[M+H]^+$): 416.1320. Found: 416.1309.

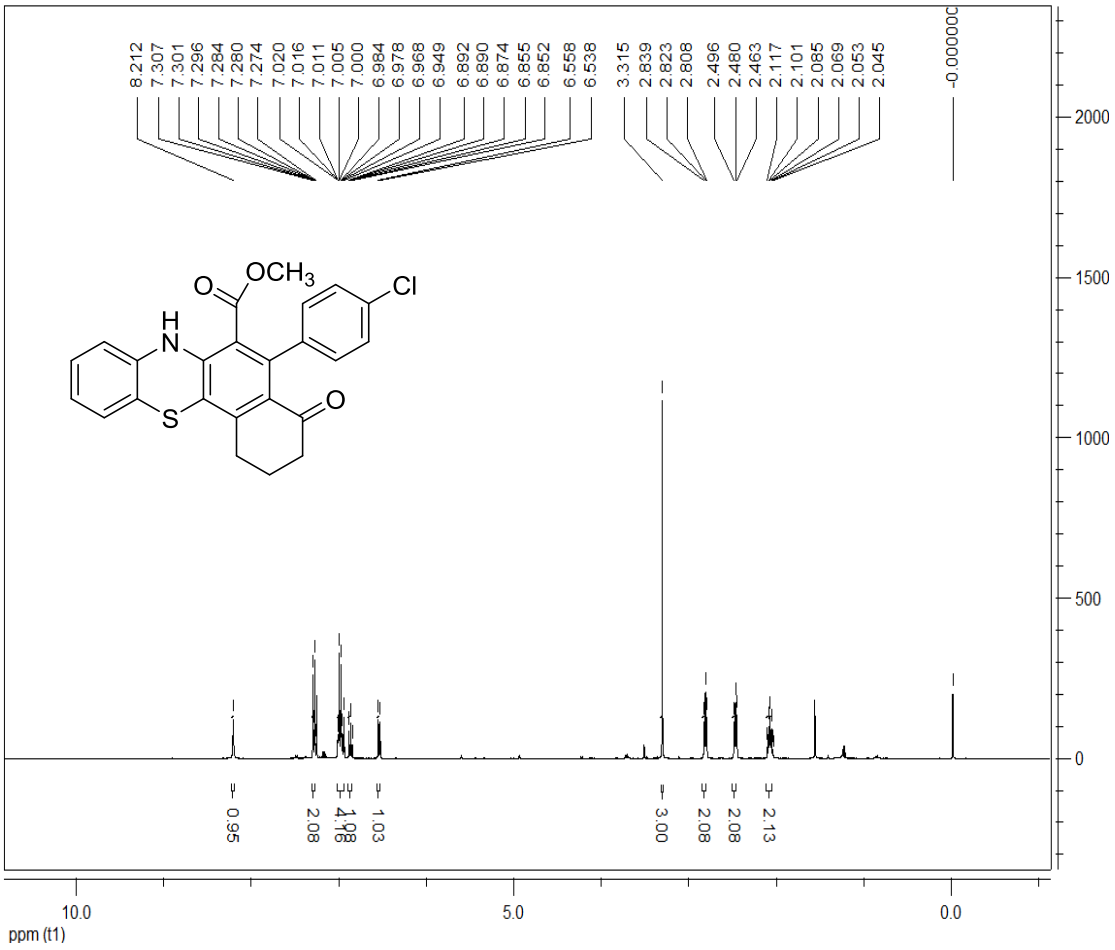


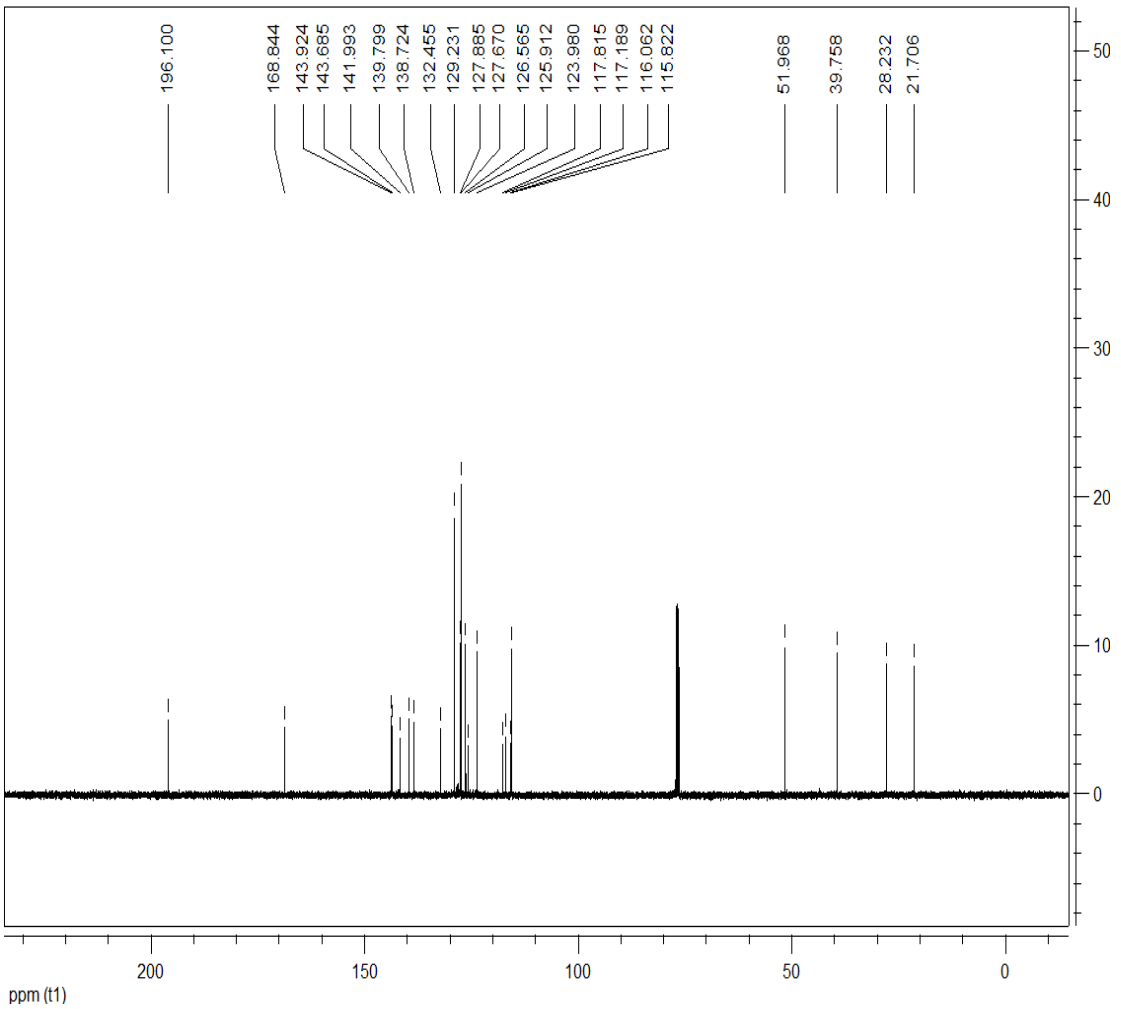

196.226
169.191
143.763
143.317
143.233
138.954
138.072
136.082
128.254
127.791
127.734
126.549
126.316
123.798
117.326
117.059
116.726
115.725
51.891
39.818
28.216
21.824
21.333
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

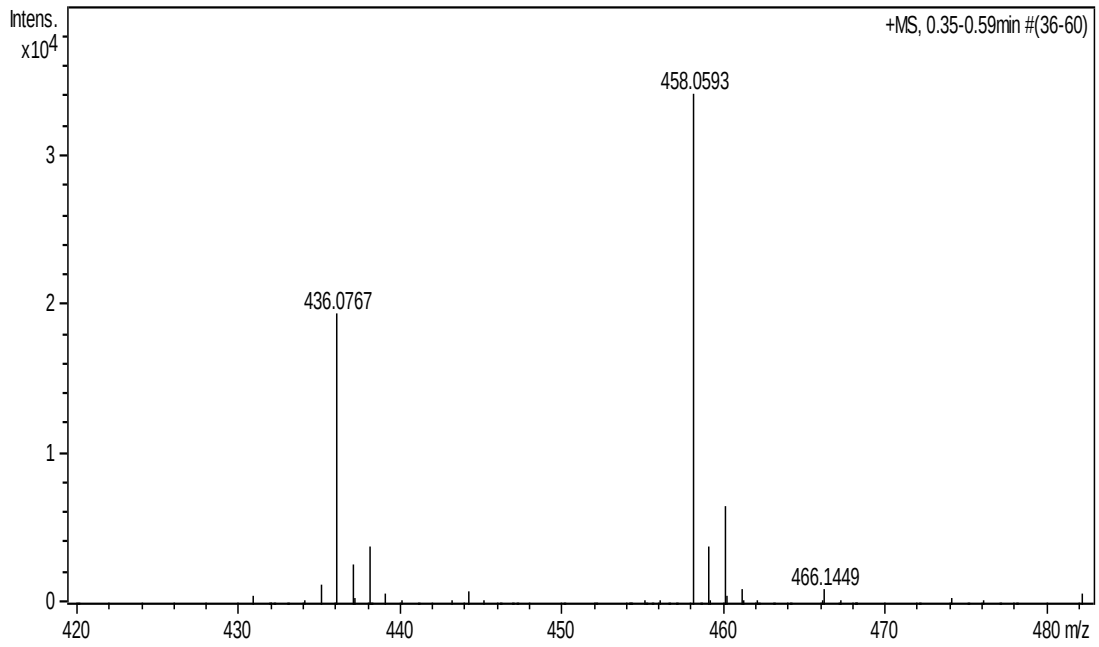

Intens.
x10^4
+MS, 0.38-0.57min #(39-58)
416.1309
438.1124
2.5
2.0
1.5
1.0
0.5
0.0
410
420
430
440
450
m/z

Methyl

5-(4-chlorophenyl)-4-oxo-2,3,4,7-tetrahydro-1H-benzo[c]phenothiazine-6-carboxylate (1i): yellow solid, 71%, m.p. 185~187℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (s, 1H, NH), 7.31~7.29 (m, 2H, ArH), 7.02~6.95 (m, 4H, ArH), 6.89~6.85 (m, 1H, ArH), 6.55 (d, *J* = 8.0 Hz, 1H, ArH), 3.12 (s, 3H, OCH_3), 2.82 (t, *J* = 6.0 Hz, 1H, ArH), 2.48 (t, *J* = 6.0 Hz, 1H, ArH), 2.12~2.05 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 196.0, 168.8, 143.9, 143.6, 141.9, 139.7, 138.7, 132.4, 129.2, 127.8, 127.6, 126.5, 125.9, 123.9, 117.8, 117.1, 116.0, 115.8, 51.9, 39.7, 28.2, 21.7; IR (KBr) υ: 3699, 3340, 3058, 2947, 1891, 1707, 1673, 1592, 1530, 1478, 1431, 1353, 1327, 1284, 1226, 1181, 1085, 1009, 972, 930, 885, 824, 751 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{24}H_{19}ClNO_3S$ ([M+H]$^+$): 436.0774. Found: 436.0767.



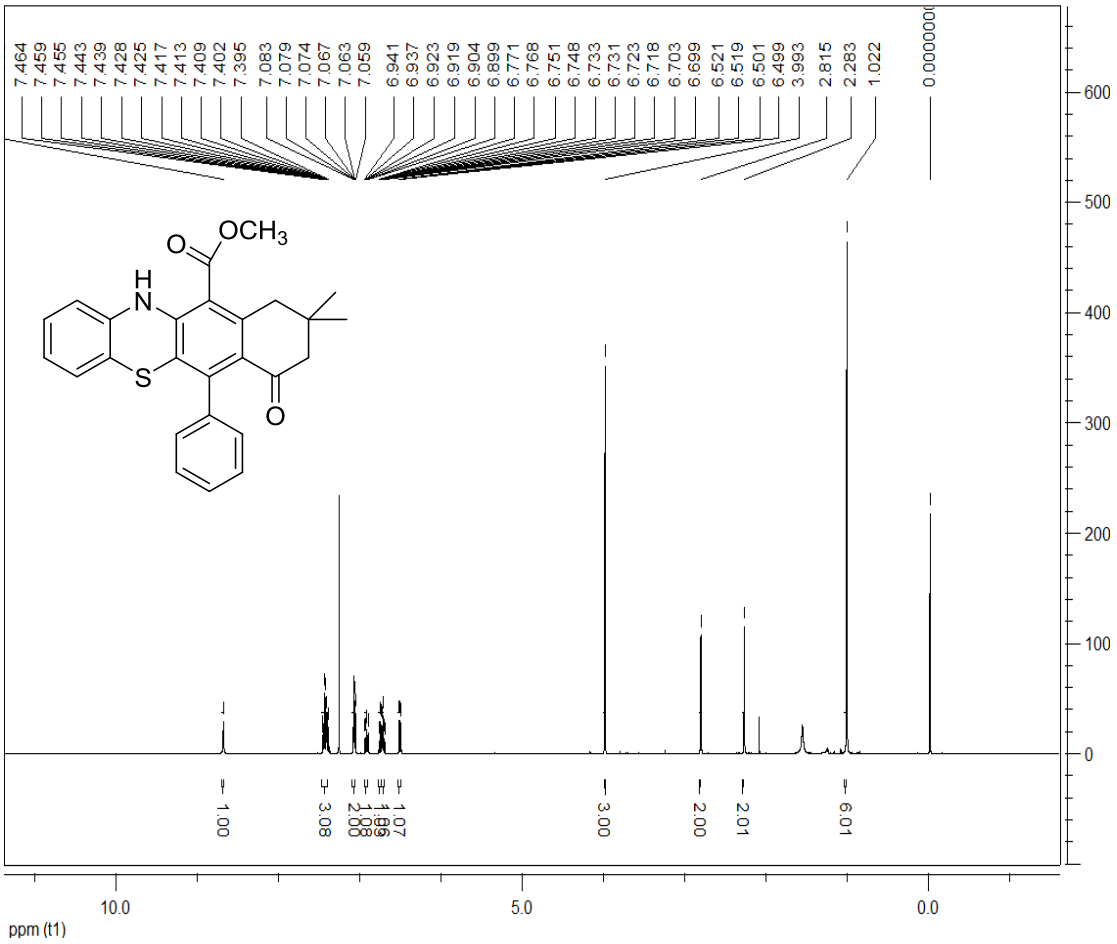

196.100
168.844
143.924
143.685
141.993
139.799
138.724
132.455
129.231
127.885
127.670
126.565
125.912
123.980
117.815
117.189
116.062
115.822
51.968
39.758
28.232
21.706
50
40
30
20
10
0
200
150
100
50
0
ppm (t1)

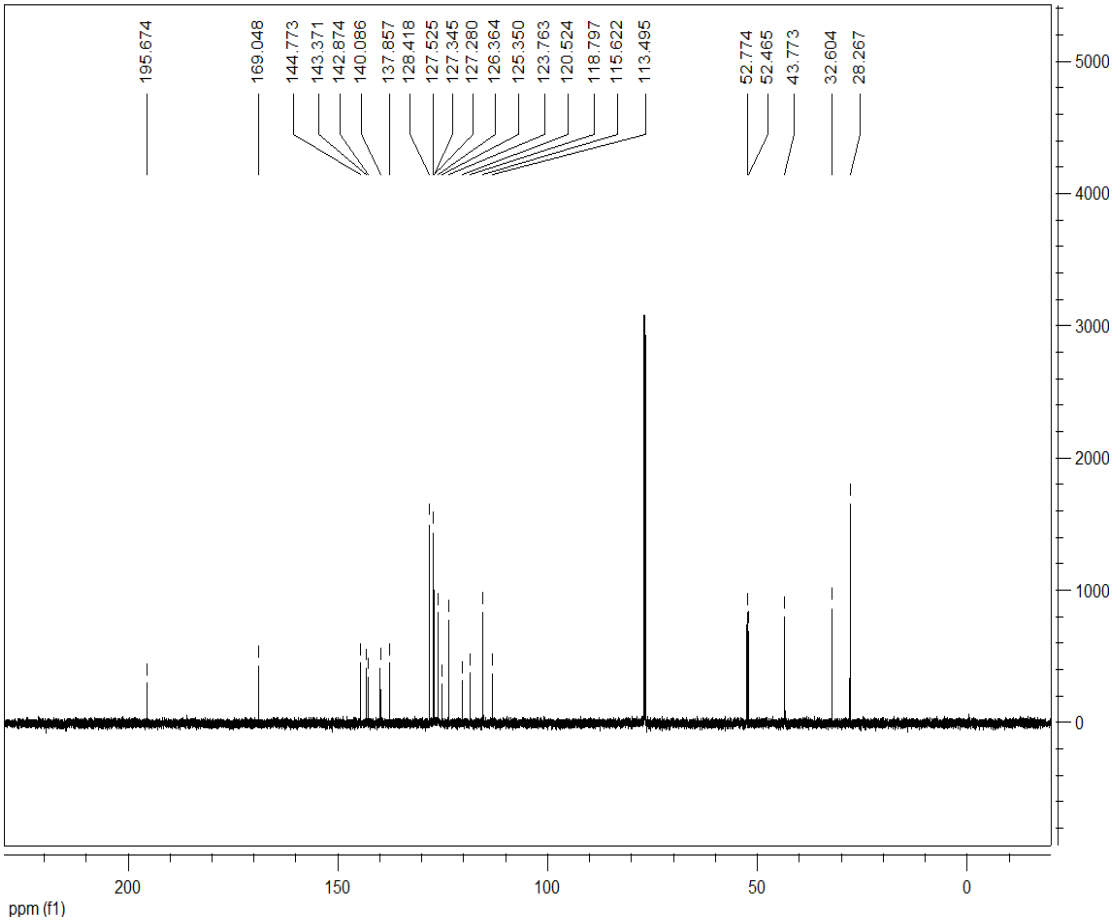

Intens.
x10^4
+MS, 0.35-0.59min #(36-60)
458.0593
436.0767
466.1449
3
2
1
0
420
430
440
450
460
470
480 m/z

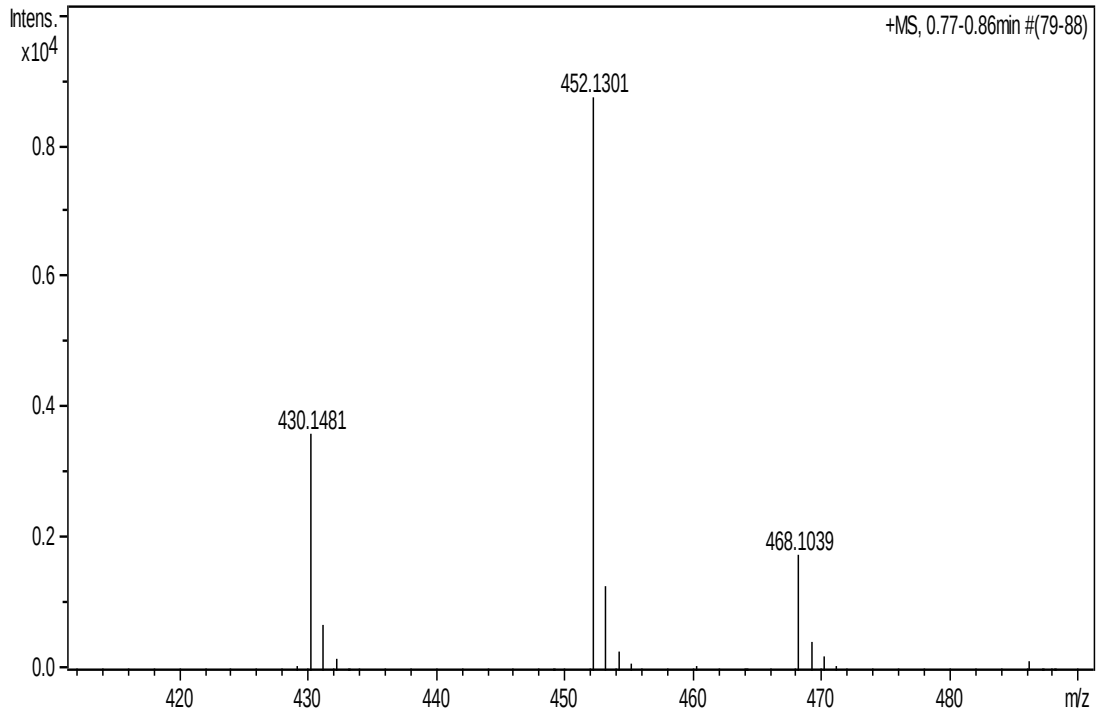
Methyl

9,9-dimethyl-7-oxo-6-phenyl-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate

(2a): yellow solid, 89%, m.p. 207~209℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (s, 1H, NH), 7.46~7.40 (m, 3H, ArH), 7.08~7.06 (m, 2H, ArH), 6.94~6.90 (m, 1H, ArH), 6.77~6.73 (m, 1H, ArH), 6.72~6.70 (m, 1H, ArH), 6.52~6.50 (m, 1H, ArH), 3.99 (s, 3H, OCH_3), 2.82 (s, 2H, CH_2), 2.28 (s, 2H, CH_2), 1.02 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.7, 169.0, 144.8, 143.4, 142.9, 140.1, 137.9, 128.4, 127.5, 127.3, 127.3, 126.4, 125.4, 123.8, 120.5, 118.8, 115.6, 113.5, 52.8, 52.5, 43.8, 32.6, 28.3; IR (KBr) υ: 3397, 3060, 2955, 1727, 1676, 1592, 1530, 1481, 1429, 1272, 1216, 1128, 1078, 977, 845, 738cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{23}NNaO_3S$ ($[M+Na]^+$): 452.1296. Found: 452.1301.

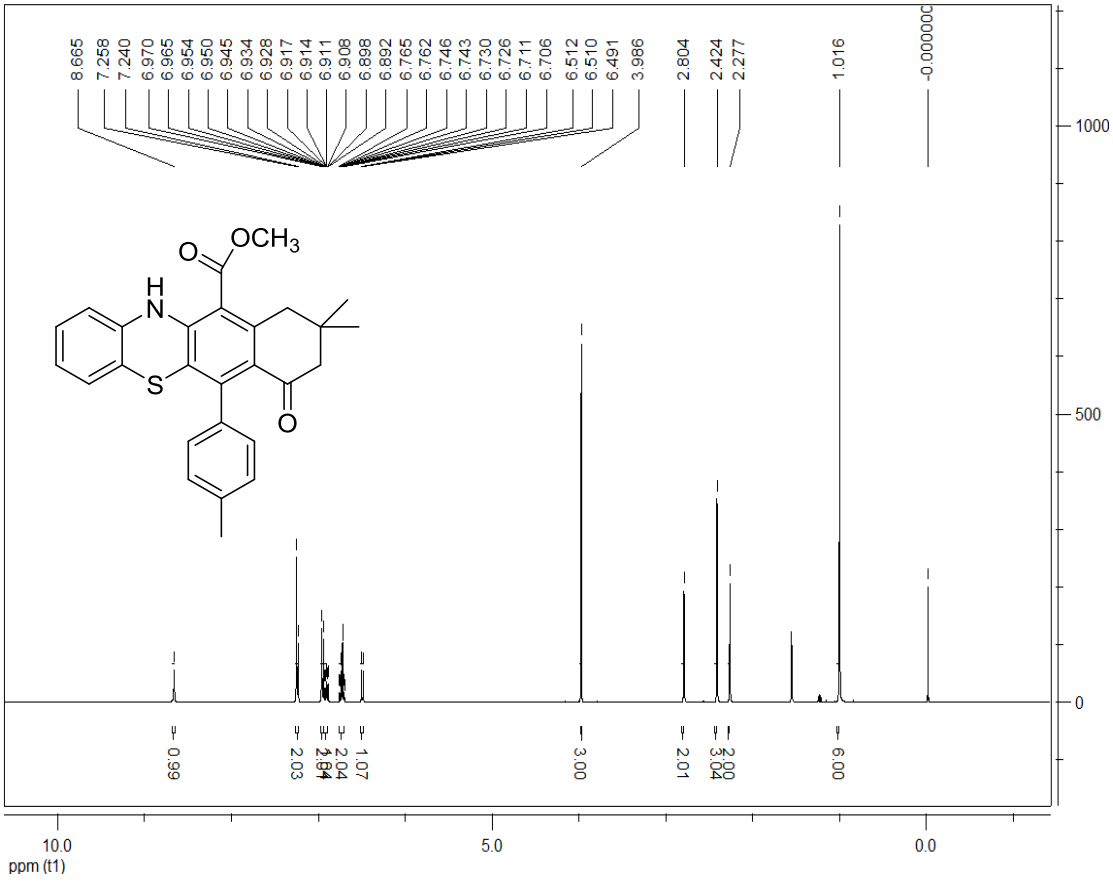


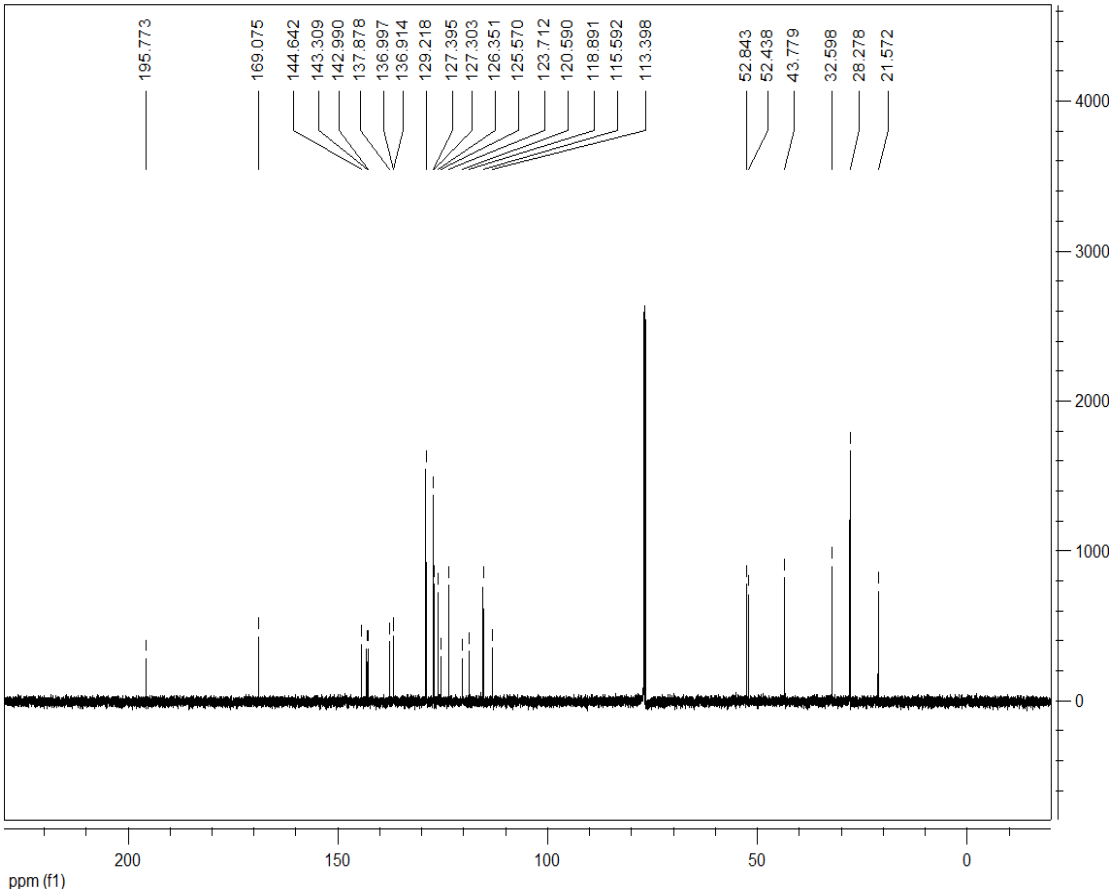

195.674
169.048
144.773
143.371
142.874
140.086
137.857
128.418
127.525
127.345
127.280
126.364
125.350
123.763
120.524
118.797
115.622
113.495
52.774
52.465
43.773
32.604
28.267
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)

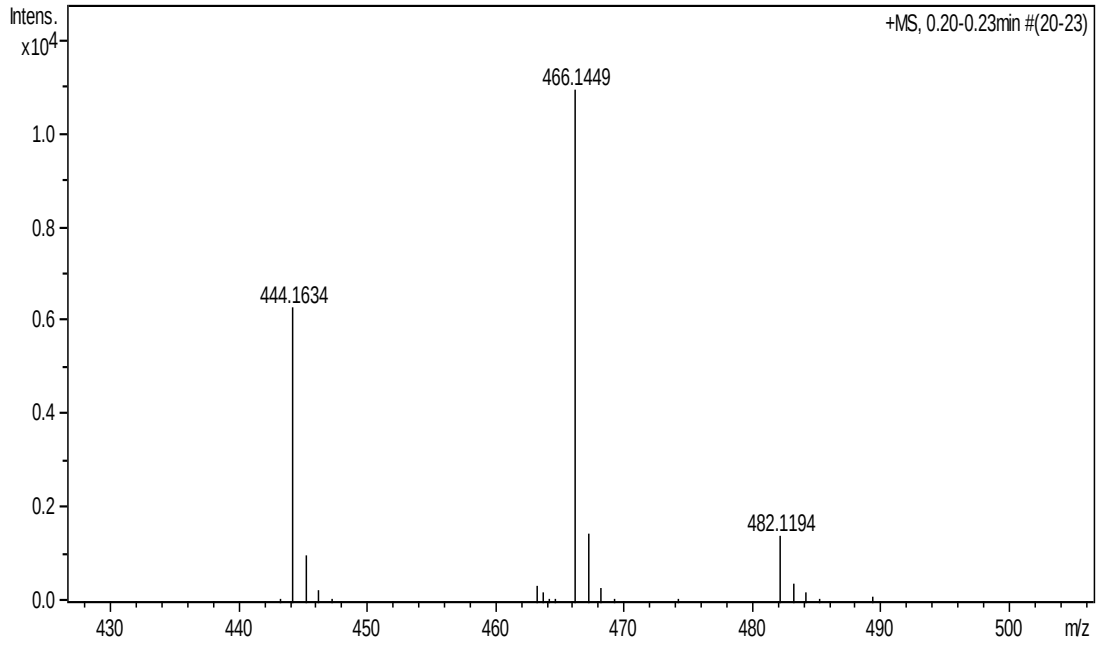

Intens.
x10^4
+MS, 0.77-0.86min #(79-88)
452.1301
430.1481
468.1039
0.8
0.6
0.4
0.2
0.0
420
430
440
450
460
470
480
m/z

Methyl 9,9-dimethyl-7-oxo-6-(p-tolyl)-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate (2b):

yellow solid, 81%, m.p. 160~162℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (s, 1H, NH), 7.25 (d, *J* = 7.6 Hz, 2H, ArH), 6.97~6.95 (m, 2H, ArH), 6.93~6.89 (m, 1H, ArH), 6.77~6.71 (m, 2H, ArH), 6.51~6.49 (m, 1H, ArH), 3.99 (s, 3H, OCH_3), 2.80 (s, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.28 (s, 2H, CH_2), 1.02 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.8, 169.1, 144.6, 143.3, 143.0, 137.9, 137.0, 136.9, 129.2, 127.4, 127.3, 126.4, 125.6, 123.7, 120.6, 118.9, 115.6, 113.4, 52.8, 52.4, 43.8, 32.6, 28.3, 21.6; IR (KBr) υ: 3321, 3052, 2949, 1701, 1672, 1567, 1527, 1474, 1437, 1395, 1289, 1251, 1219, 1139, 196, 1019, 975, 901, 826, 715cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{27}H_{25}NNaO_3S$ ([M+Na]$^{+}$): 466.1453. Found: 466.1449.



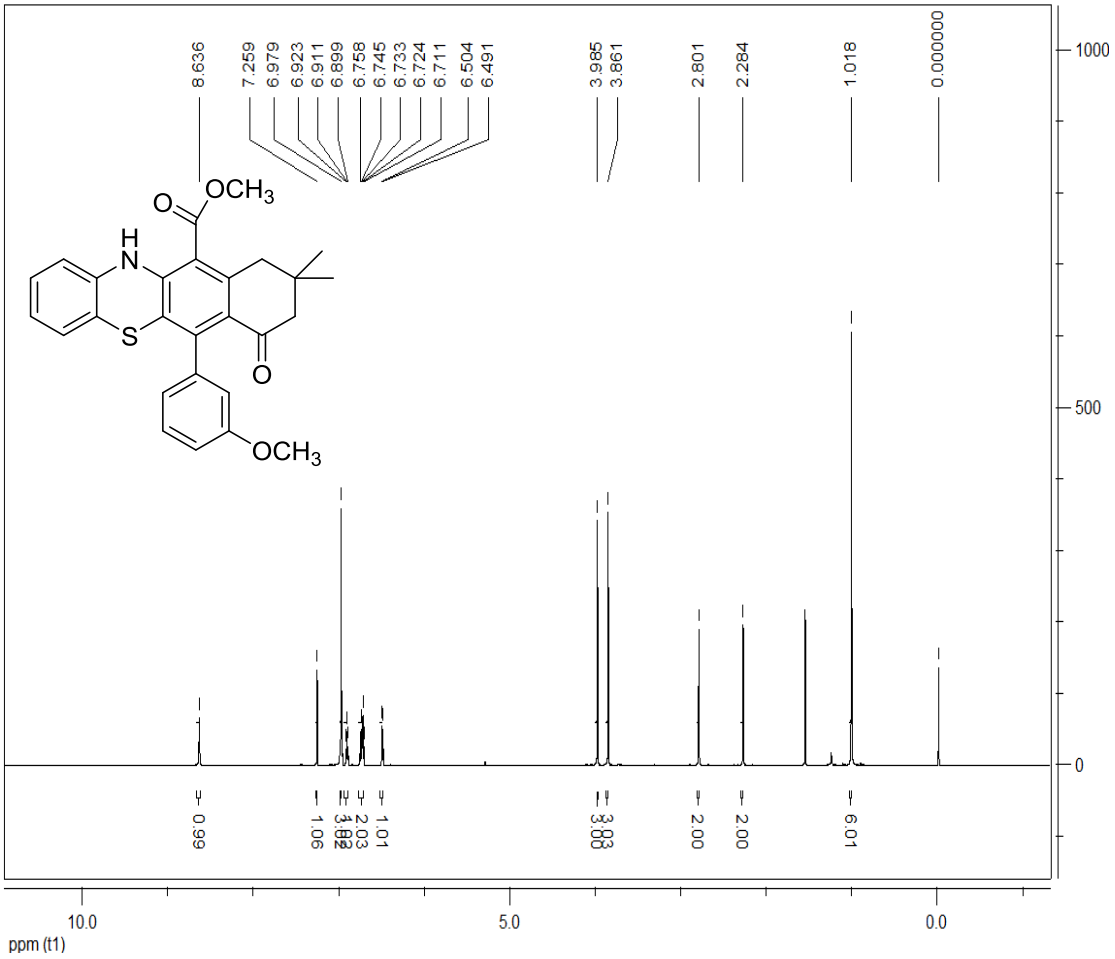

195.773
169.075
144.642
143.309
142.990
137.878
136.997
136.914
129.218
127.395
127.303
126.351
125.570
123.712
120.590
118.891
115.592
113.398
52.843
52.438
43.779
32.598
28.278
21.572
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)

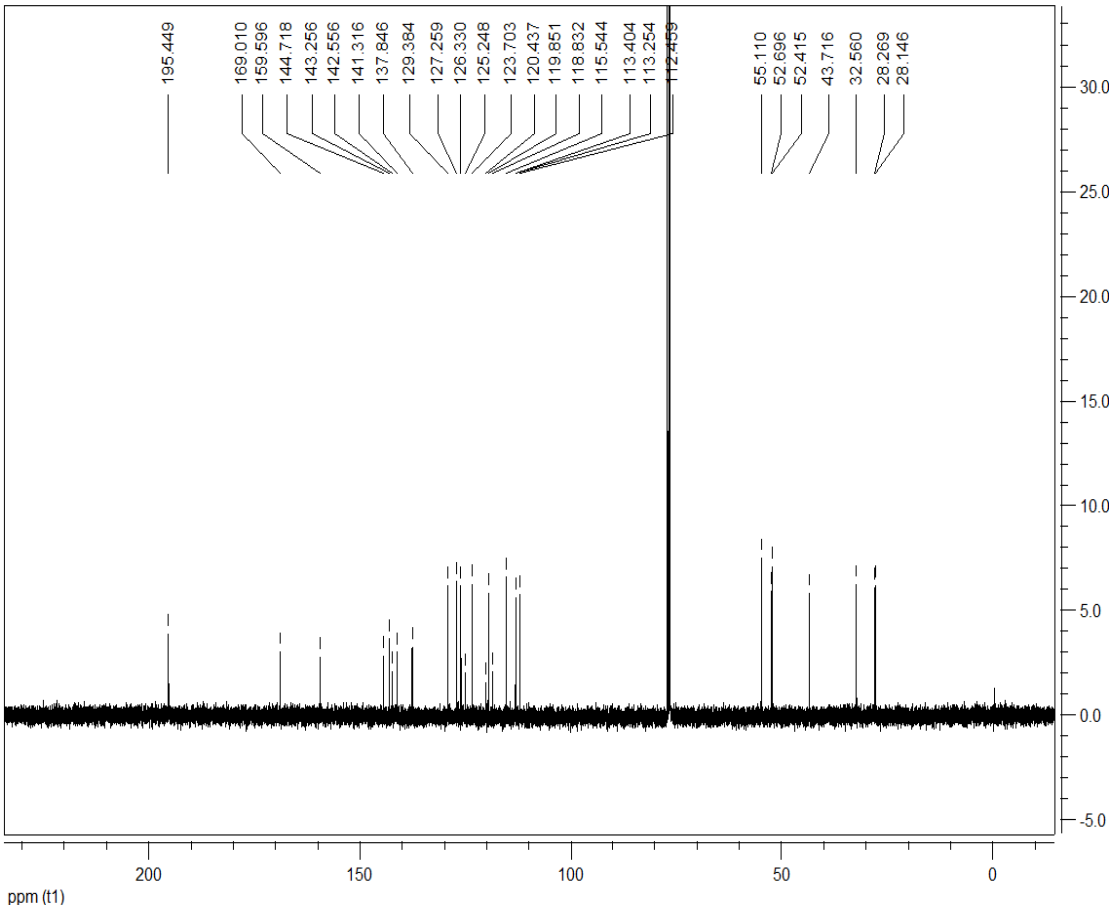

Intens.
x10^4
+MS, 0.20-0.23min #(20-23)
466.1449
444.1634
482.1194
1.0
0.8
0.6
0.4
0.2
0.0
430
440
450
460
470
480
490
500
m/z

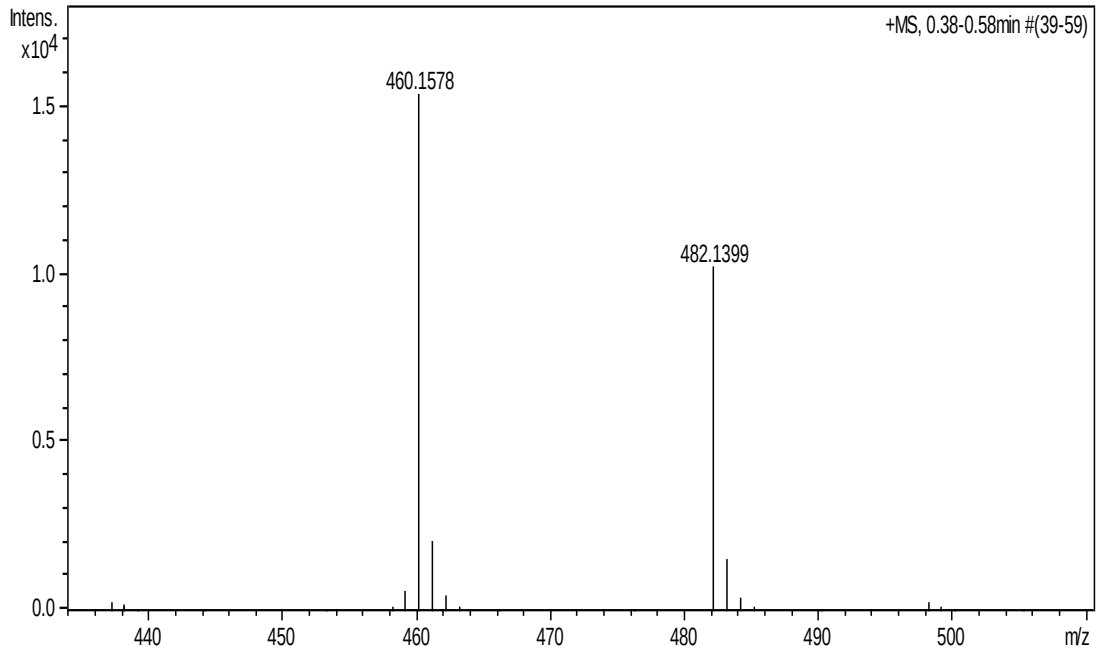
Methyl

6-(3-methoxyphenyl)-9,9-dimethyl-7-oxo-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate (2c):

yellow solid, 82%, m.p. 214~217℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (s, 1H, NH), 7.38~7.34 (m, 1H, ArH), 6.94~6.90 (m, 2H, ArH), 6.77~6.72 (m, 2H, ArH), 6.66 (d, *J* = 7.2 Hz, 1H, ArH), 6.61 (s, 1H, ArH), 6.51 (d, *J* = 8.0 Hz, 1H, ArH), 3.99 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 2.81 (s, 2H, CH_2), 2.29 (s, 2H, CH_2), 1.02 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.4, 169.0, 159.5, 144.7, 143.2, 142.5, 141.3, 137.8, 129.3, 127.2, 126.3, 125.2, 123.7, 120.4, 119.8, 118.8, 115.5, 113.4, 113.2, 112.4, 55.1, 52.6, 52.4, 43.7, 32.5, 28.2, 28.1; IR (KBr) υ: 3729, 3367, 3062, 2956, 1685, 1588, 1528, 1481, 1422, 1291, 1251, 1216, 1129, 1086, 1036, 978, 862, 800, 774, 741 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{27}H_{26}NO_4S$ ($[M+H]^+$): 460.1583. Found: 482.1578.



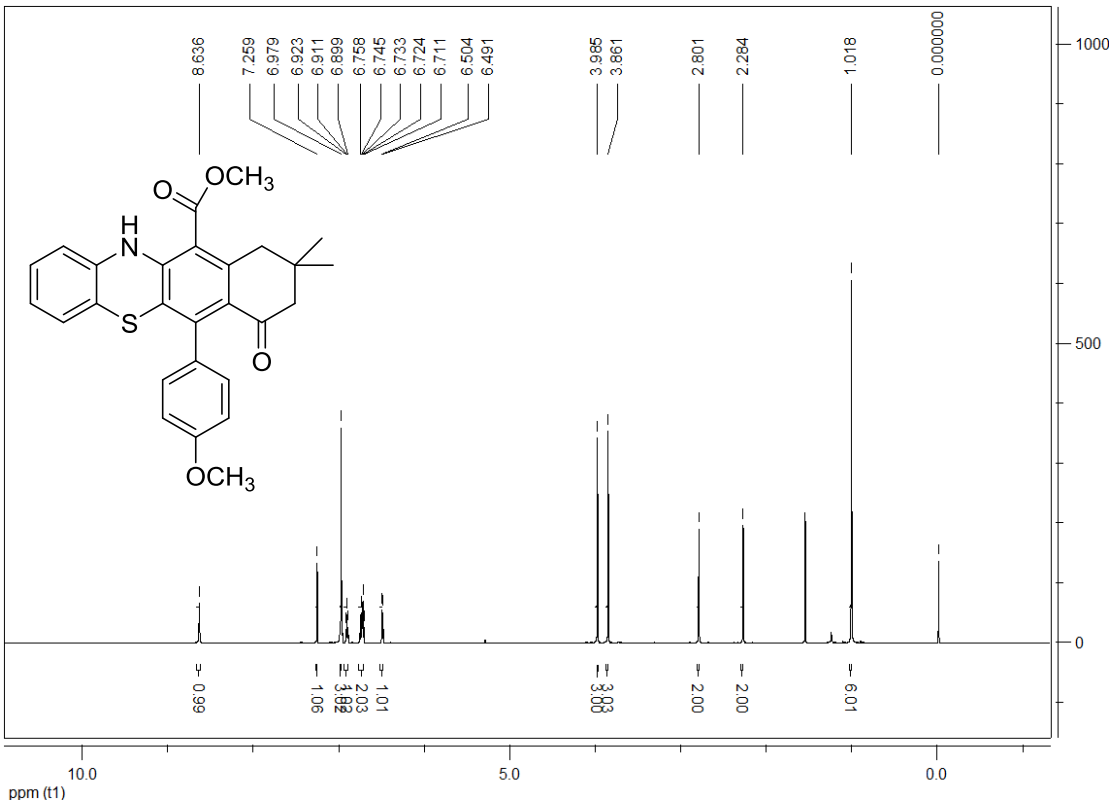

195.449
169.010
159.596
144.718
143.256
142.556
141.316
137.846
129.384
127.259
126.330
125.248
123.703
120.437
119.851
118.832
115.544
113.404
113.254
112.459
55.110
52.696
52.415
43.716
32.560
28.269
28.146
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (t1)

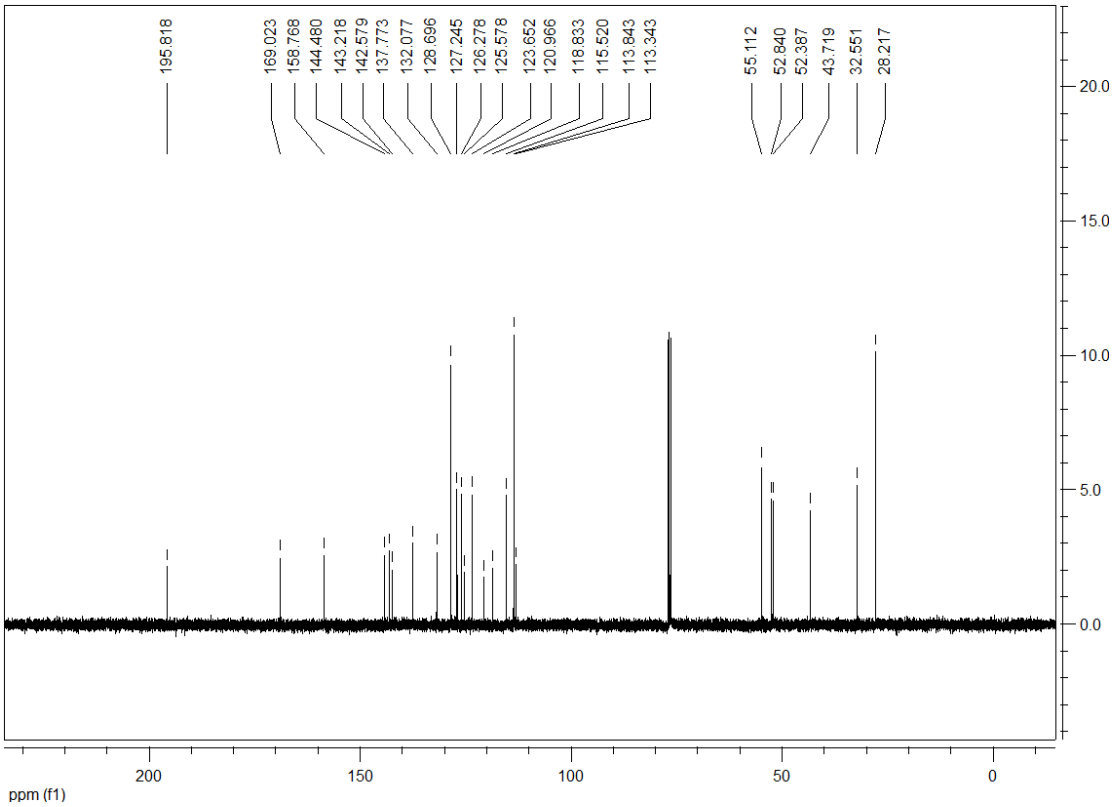

Intens.
x10^4
+MS, 0.38-0.58min #(39-59)
460.1578
482.1399
1.5
1.0
0.5
0.0
440
450
460
470
480
490
500
m/z

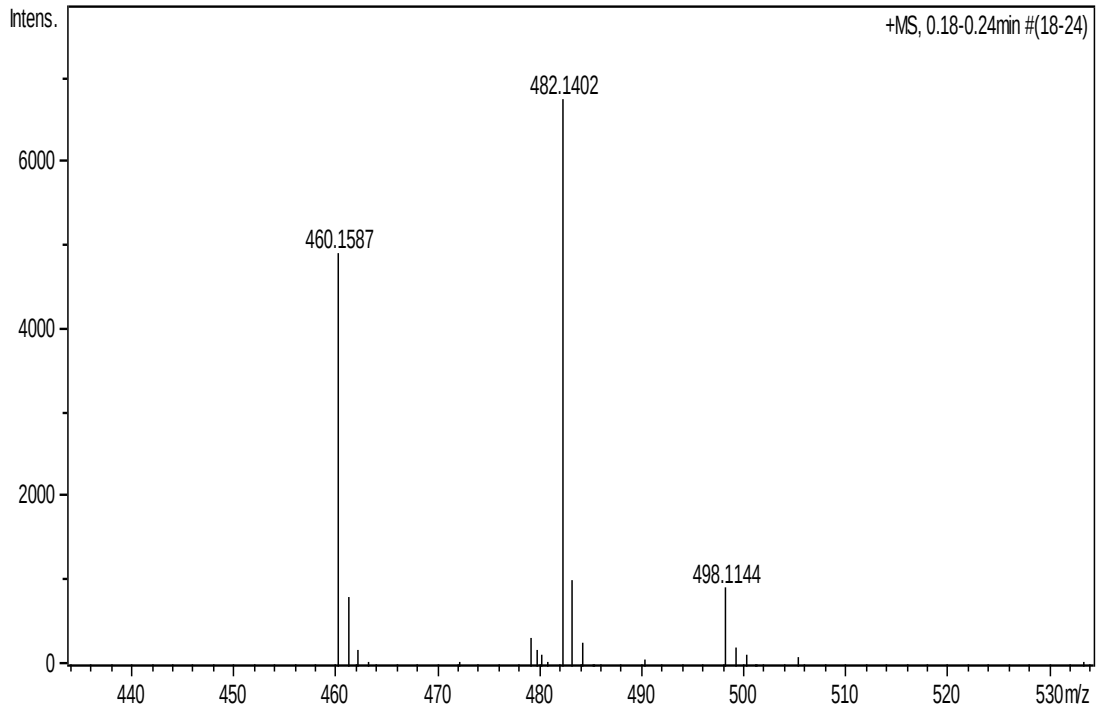
Methyl

6-(4-methoxyphenyl)-9,9-dimethyl-7-oxo-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate (2d):

yellow solid, 93%, m.p. 187~189℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (s, 1H, NH), 7.26 (s, 1H, ArH), 6.98 (s, 3H, ArH), 6.91 (t, *J* = 4.8 Hz, 1H, ArH), 6.76~6.71 (m, 2H, ArH), 6.50 (d, *J* = 5.2 Hz, 1H, ArH), 3.99 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 2.80 (s, 2H, CH_2), 2.28 (s, 2H, CH_2), 1.02 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.8, 169.0, 158.8, 144.5, 143.2, 142.6, 137.8, 132.1, 128.7, 127.2, 126.3, 125.6, 123.7, 121.0, 118.8, 115.5, 113.8, 113.3, 55.1, 52.8, 52.4, 43.7, 32.6, 28.2; IR (KBr) υ: 3394, 3017, 2950, 1729, 1671, 1600, 1524, 1480, 1437, 1252, 1212, 1181, 1121, 1078, 1029, 977, 929, 825, 745cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{23}NNaO_4S$ ($[M+Na]^+$): 482.1402. Found: 482.1402.



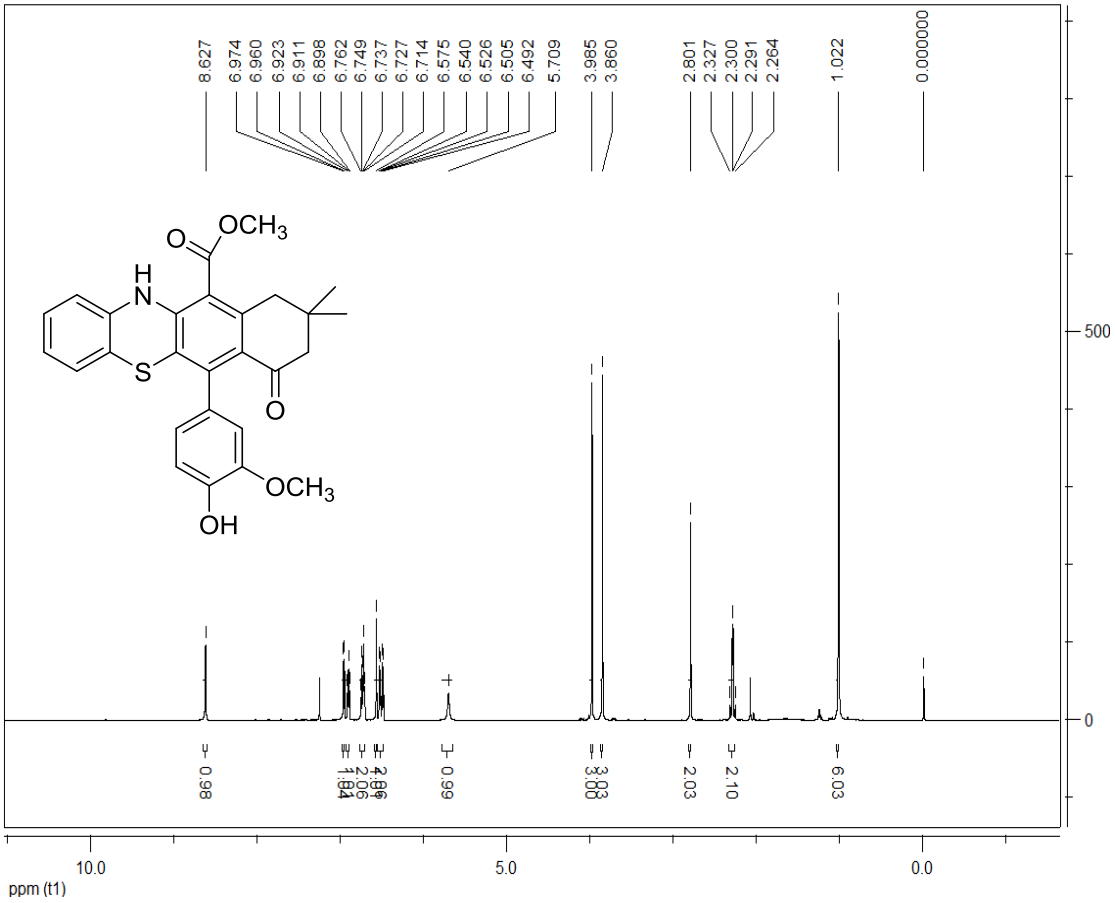

195.818
169.023
158.768
144.480
143.218
142.579
137.773
132.077
128.696
127.245
126.278
125.578
123.652
120.966
118.833
115.520
113.843
113.343
55.112
52.840
52.387
43.719
32.551
28.217
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

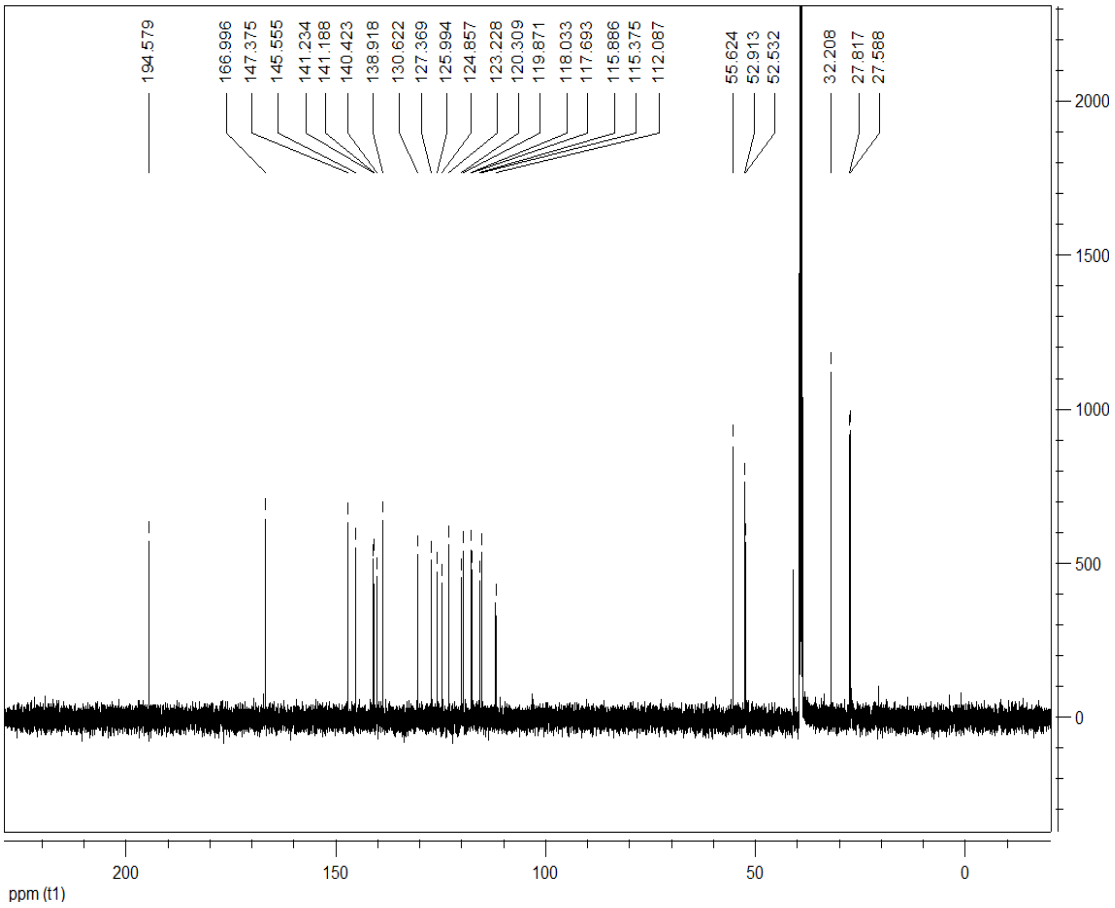

Intens.
+MS, 0.18-0.24min #(18-24)
482.1402
460.1587
498.1144
6000
4000
2000
0
440
450
460
470
480
490
500
510
520
530m/z

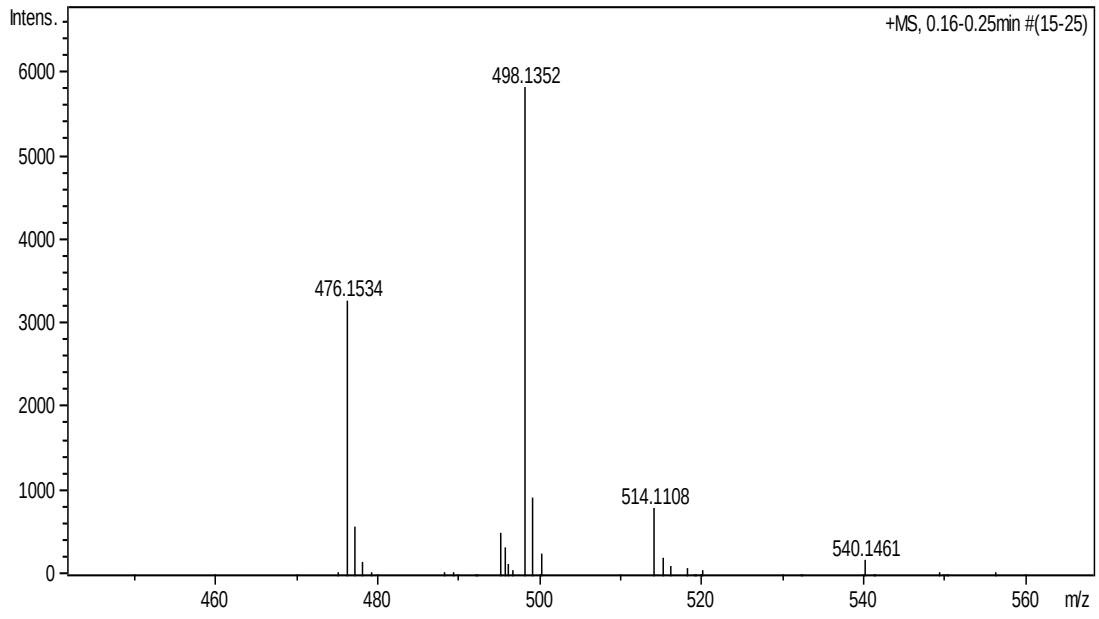
Methyl

6-(4-hydroxy-3-methoxyphenyl)-9,9-dimethyl-7-oxo-7,9,10,12-tetrahydro-8H-benzo[b]pheno thiazine-11-carboxylate (2e):

yellow solid, 84%, m.p. 248~250℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (s, 1H, NH), 6.97 (d, *J* = 5.6 Hz, 1H, ArH), 6.92~6.90 (m, 1H, ArH), 6.76~6.71 (m, 2H, ArH), 6.58 (s, 1H, ArH), 6.54~6.49 (m, 2H, ArH), 5.71 (s, 1H, OH), 3.99 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 2.80 (s, 2H, CH_2), 2.33~2.26 (m, 2H, CH_2), 1.02 (s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.6, 167.0, 147.4, 145.6, 141.2, 141.2, 140.4, 138.9, 130.6, 127.4, 126.0, 124.9, 123.2, 120.3, 119.9, 118.0, 117.7, 115.9, 115.4, 112.1, 55.6, 52.9, 52.5, 32.2, 27.8, 27.6; IR (KBr) υ: 3549, 3388, 2956, 1702, 1678, 1596, 1523, 1482, 1421, 1286, 1259, 1211, 1122, ,1084, 1029, 979, 860, 809, 779, 740cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{27}H_{25}NNaO_5S$ ([M+Na]$^{+}$): 498.1351. Found: 498.1352.



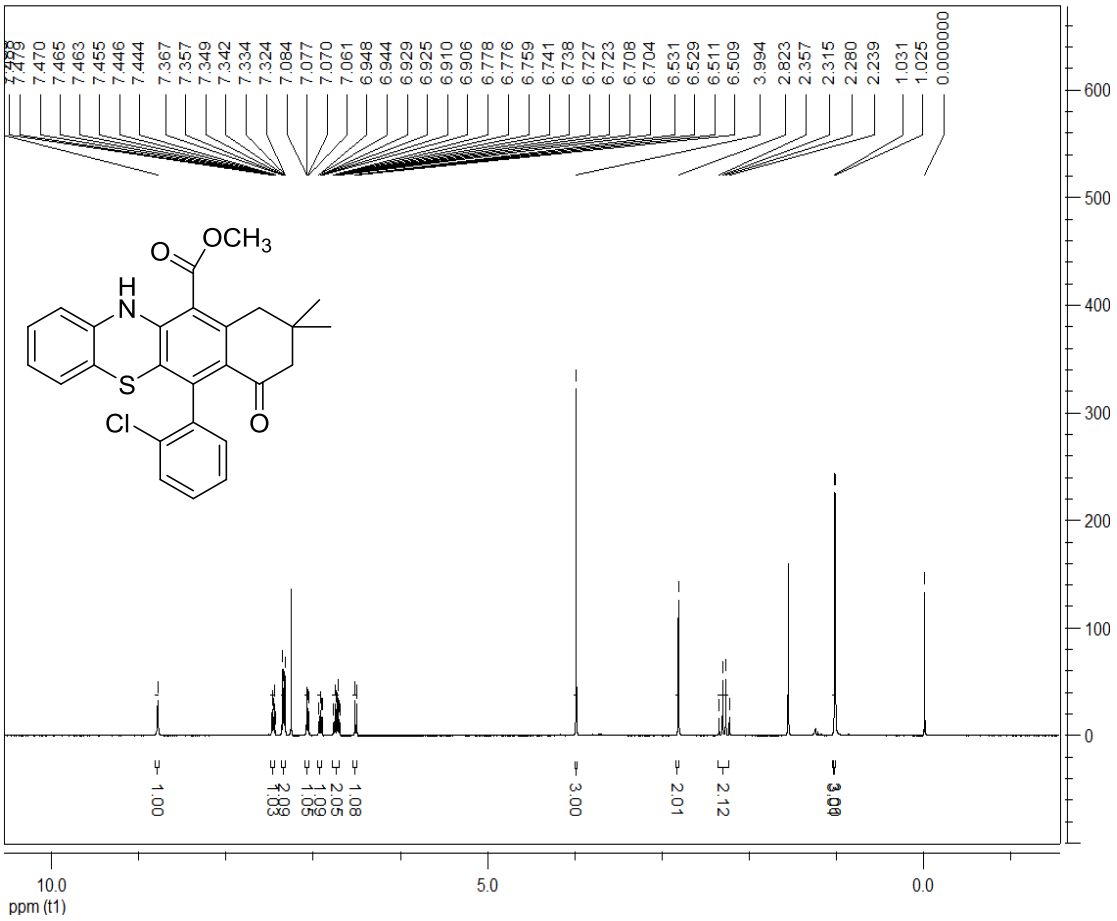

194.579
166.996
147.375
145.555
141.234
141.188
140.423
138.918
130.622
127.369
125.994
124.857
123.228
120.309
119.871
118.033
117.693
115.886
115.375
112.087
55.624
52.913
52.532
32.208
27.817
27.588
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)

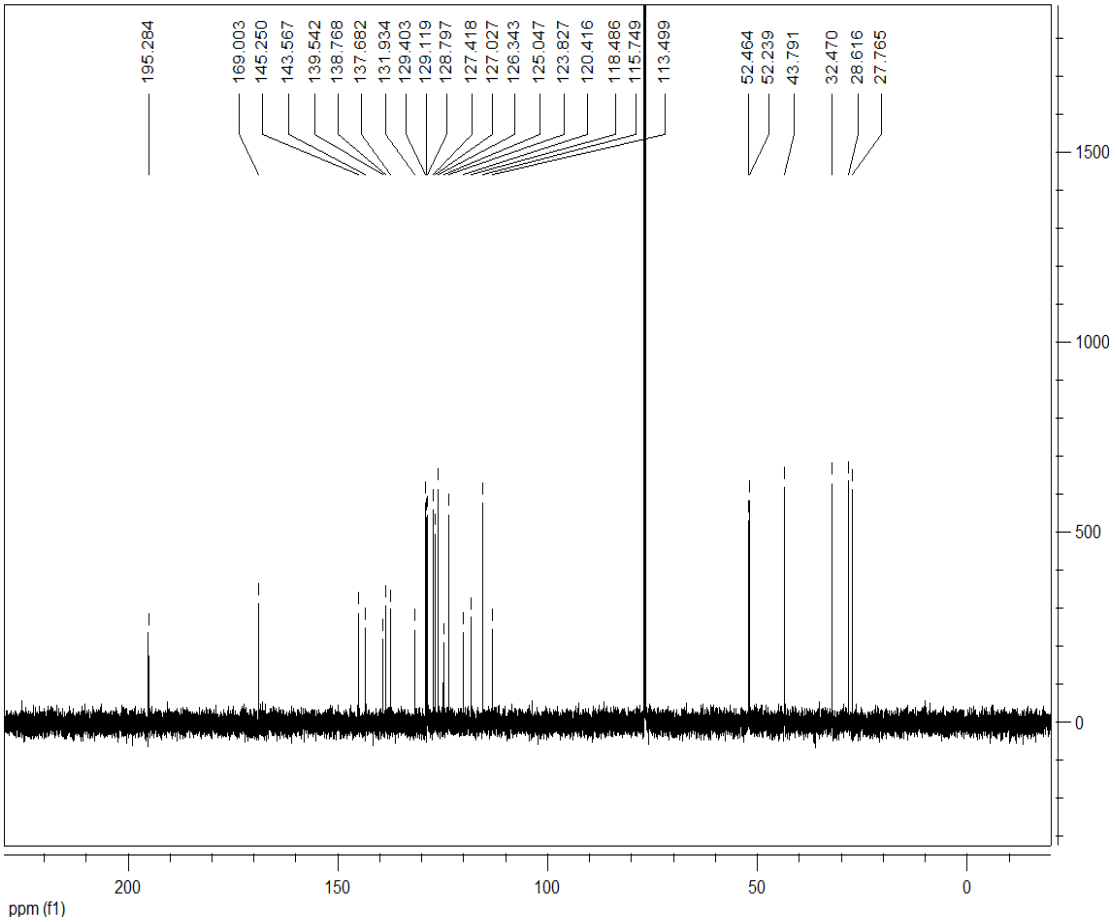

Intens.
+MS, 0.16-0.25min #(15-25)
6000
5000
4000
3000
2000
1000
0
498.1352
476.1534
514.1108
540.1461
460
480
500
520
540
560
m/z

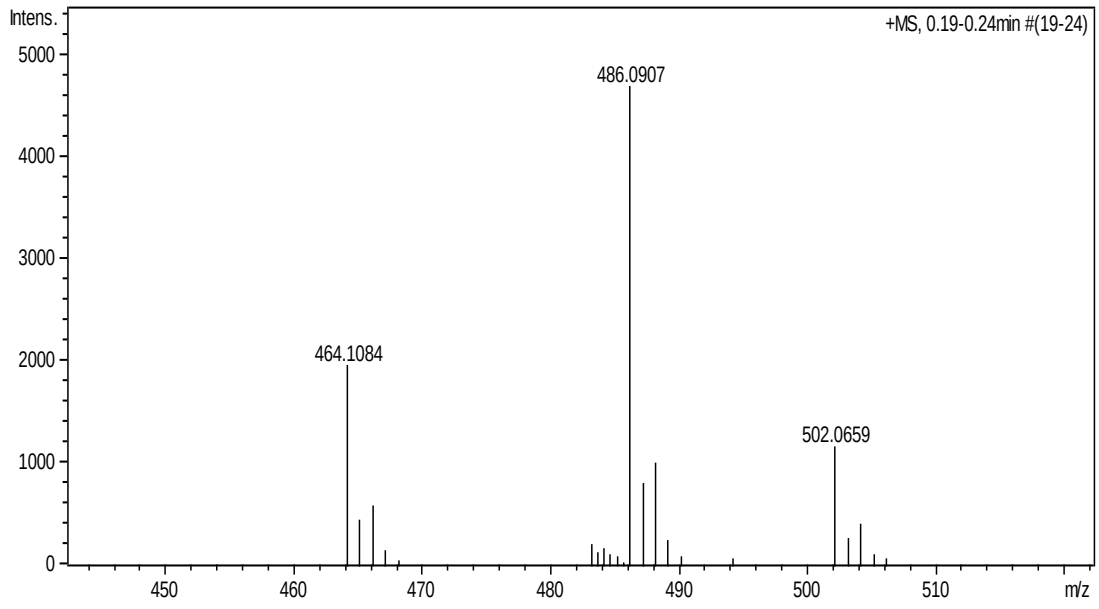
Methyl

6-(2-chlorophenyl)-9,9-dimethyl-7-oxo-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate (2f):

yellow solid, 90%, m.p. 142~144℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (s, 1H, NH), 7.49~7.44 (m, 1H, ArH), 7.37~7.32 (m, 2H, ArH), 7.08~7.06 (m, 1H, ArH), 6.78~6.70 (m, 2H, ArH), 6.53~6.51 (m, 1H, ArH), 3.99 (s, 3H, OCH_3), 2.82 (s, 2H, CH_2), 2.36~2.24 (m, 2H, CH_2), 1.03 (s, 3H, CH_3), 1.03 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.3, 169.0, 145.3, 143.6, 139.5, 138.8, 137.7, 131.9, 129.4, 129.1, 128.8, 127.4, 127.0, 126.3, 125.0, 123.8, 120.4, 118.5, 115.7, 113.5, 52.5, 52.2, 43.8, 32.5, 28.6, 27.8; IR (KBr) υ: 3320, 3058, 2950, 1697, 1670, 1572, 1529, 1477, 1431, 1280, 1215, 1141, 1092, 978, 799, 743cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{22}ClNNaO_3S$ ([M+Na]$^{+}$): 486.0907. Found: 486.0907.



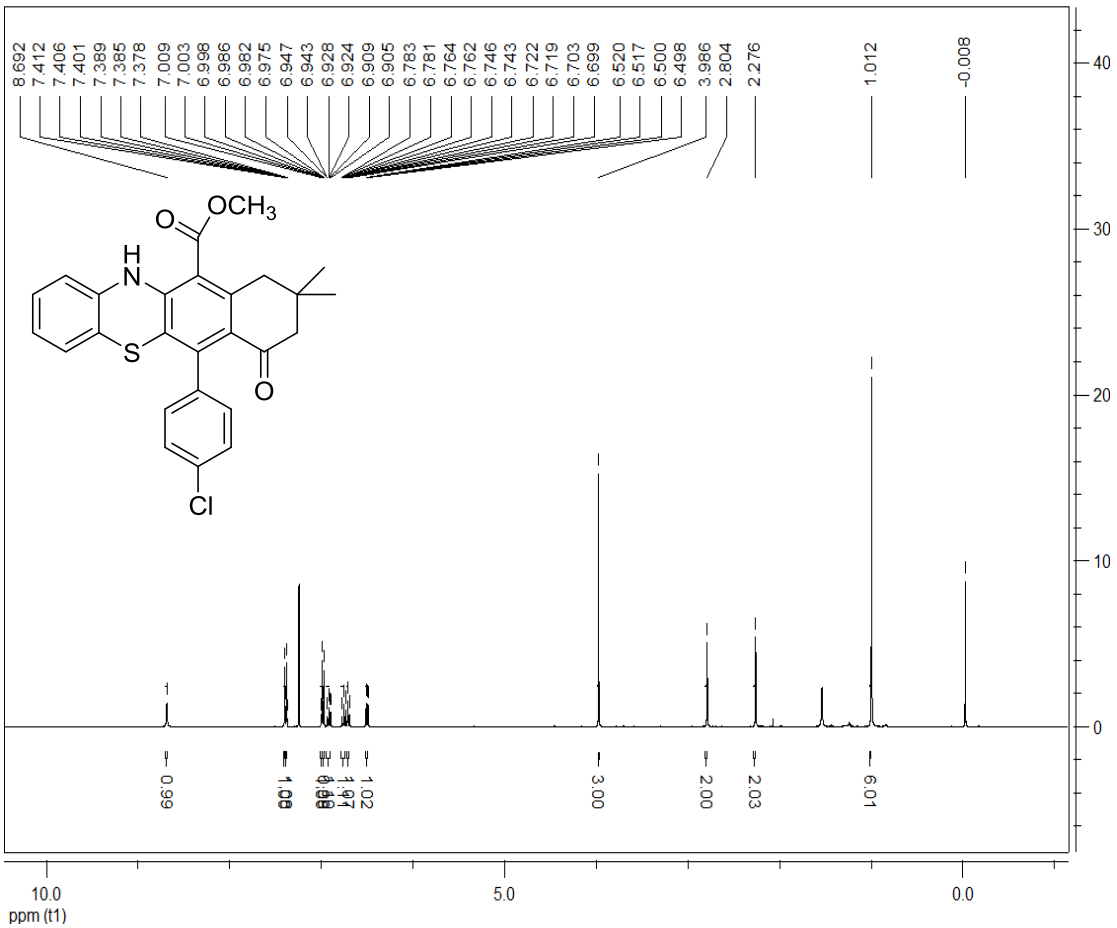

195.284
169.003
145.250
143.567
139.542
138.768
137.682
131.934
129.403
129.119
128.797
127.418
127.027
126.343
125.047
123.827
120.416
118.486
115.749
113.499
52.464
52.239
43.791
32.470
28.616
27.765
1500
1000
500
0
200
150
100
50
0
ppm (f1)

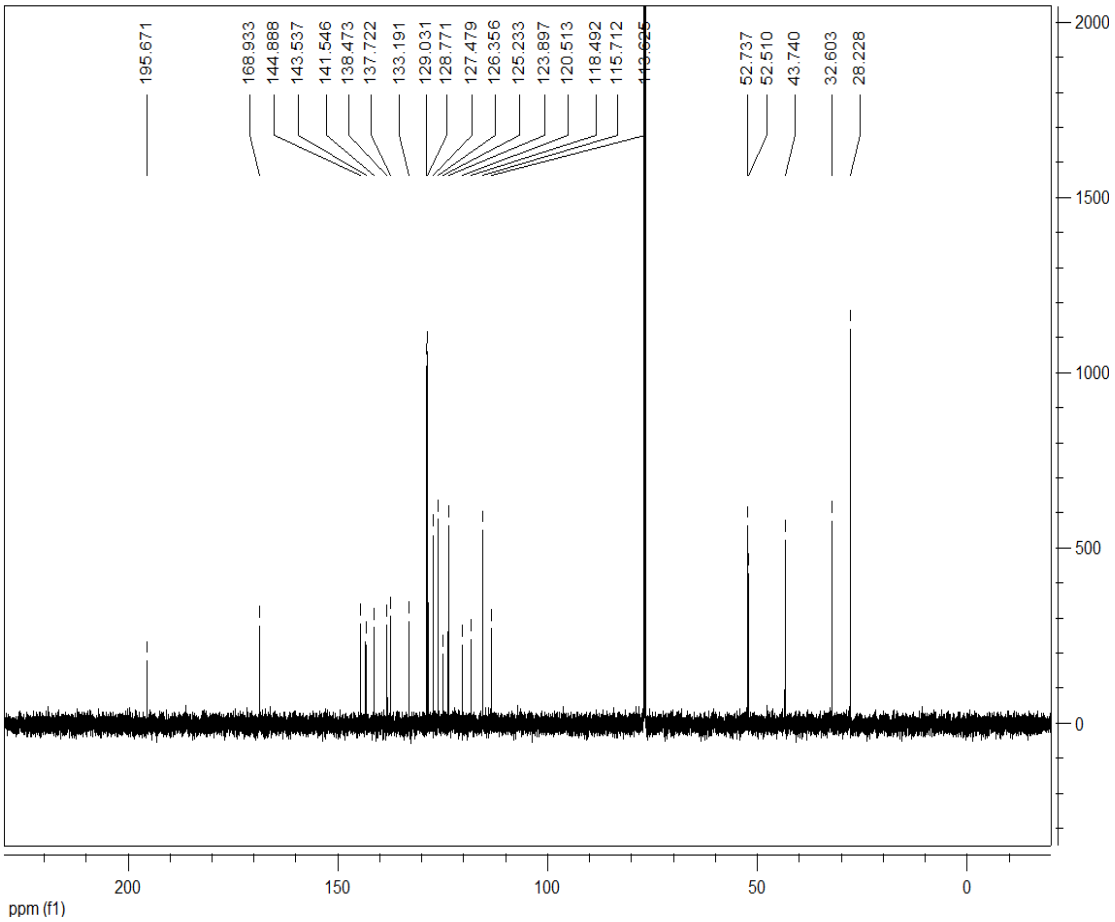

Intens.
+MS, 0.19-0.24min #(19-24)
5000
4000
3000
2000
1000
0
486.0907
464.1084
502.0659
450
460
470
480
490
500
510
m/z

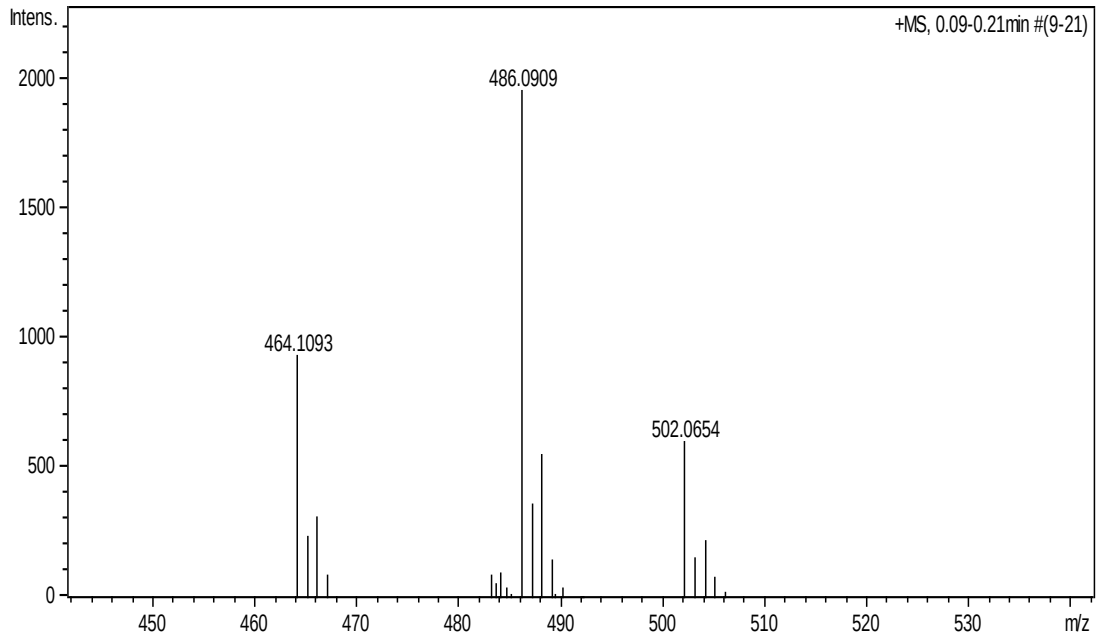
Methyl

6-(4-chlorophenyl)-9,9-dimethyl-7-oxo-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate (2g):

yellow solid, 79%, m.p. 214~216℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (s, 1H, NH), 7.41~7.38 (m, 1H, ArH), 7.39~7.38 (m, 2H, ArH), 7.01~7.00 (m, 1H, ArH), 6.99~6.98 (m, 1H, ArH), 6.97~6.91 (m, 1H, ArH), 6.78~6.74 (m, 1H, ArH), 6.72~6.70 (m, 1H, ArH), 6.52~6.50 (m, 1H, ArH), 3.99 (s, 3H, OCH_3), 2.80 (s, 2H, CH_2), 2.28 (s, 2H, CH_2), 1.02 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.7, 168.9, 144.9, 143.5, 141.5, 138.5, 137.7, 133.2, 129.0, 128.8, 127.5, 126.4, 125.2, 123.9, 120.5, 118.5, 115.7, 113.6, 52.7, 52.5, 43.7, 32.6, 28.2; IR (KBr) υ: 3375, 3058, 2960, 1685, 1578, 1530, 1485, 1413, 1286, 1222, 1137, 1084, 1012, 980, 896, 836, 810, 741cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{22}ClNNaO_3S$ ([M+Na]$^{+}$): 486.0907. Found: 486.0909.

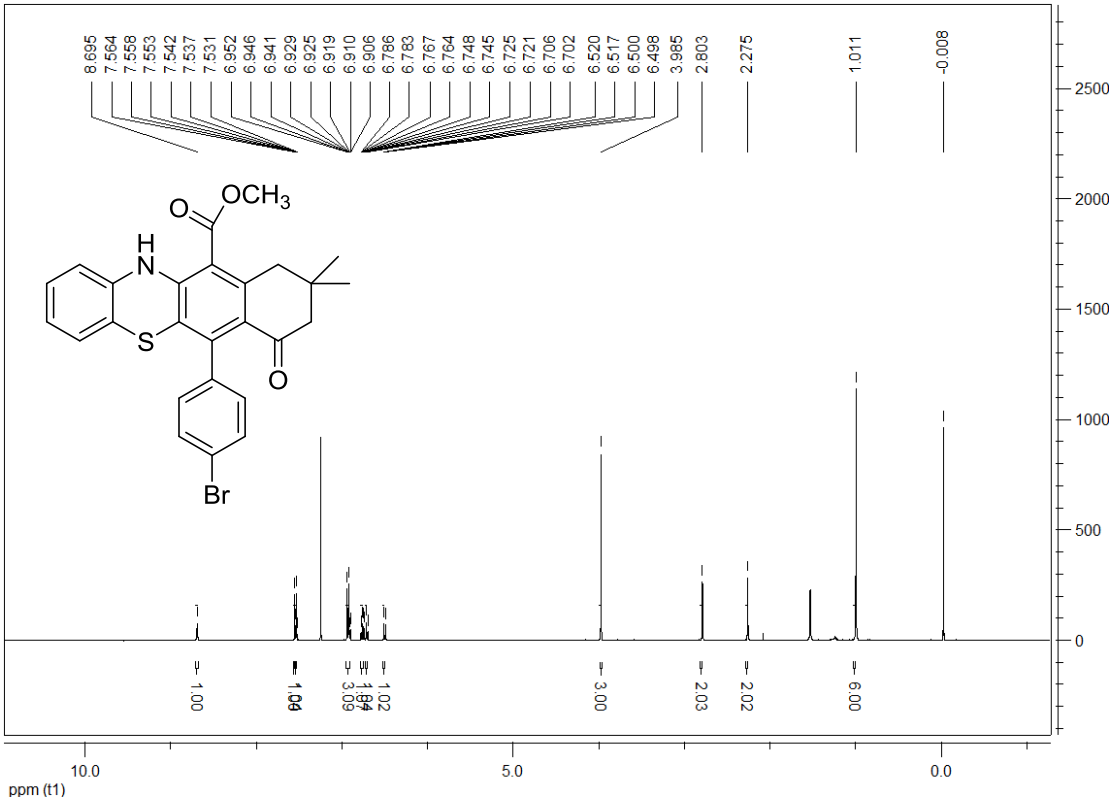


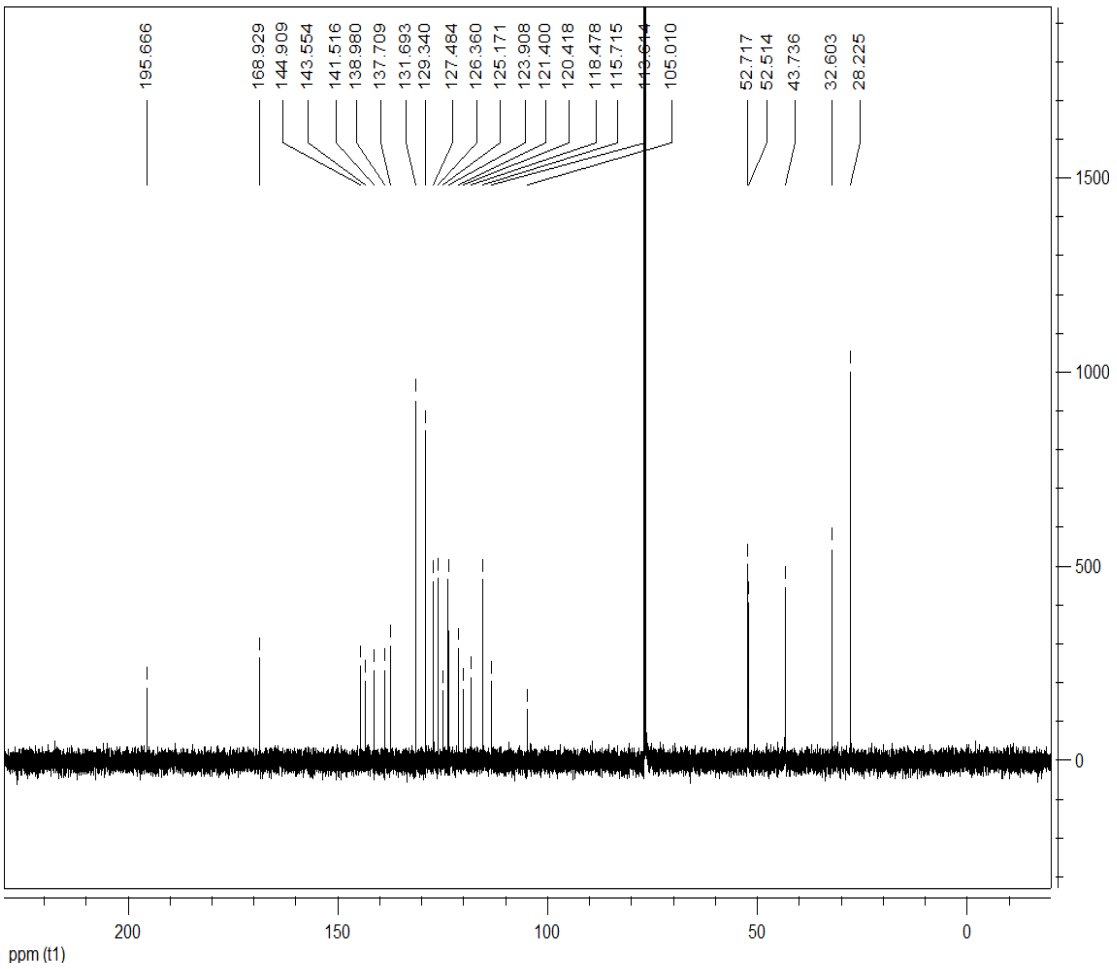

195.671
168.933
144.888
143.537
141.546
138.473
137.722
133.191
129.031
128.771
127.479
126.356
125.233
123.897
120.513
118.492
115.712
113.625
52.737
52.510
43.740
32.603
28.228
2000
1500
1000
500
0
200
150
100
50
0
ppm (f1)

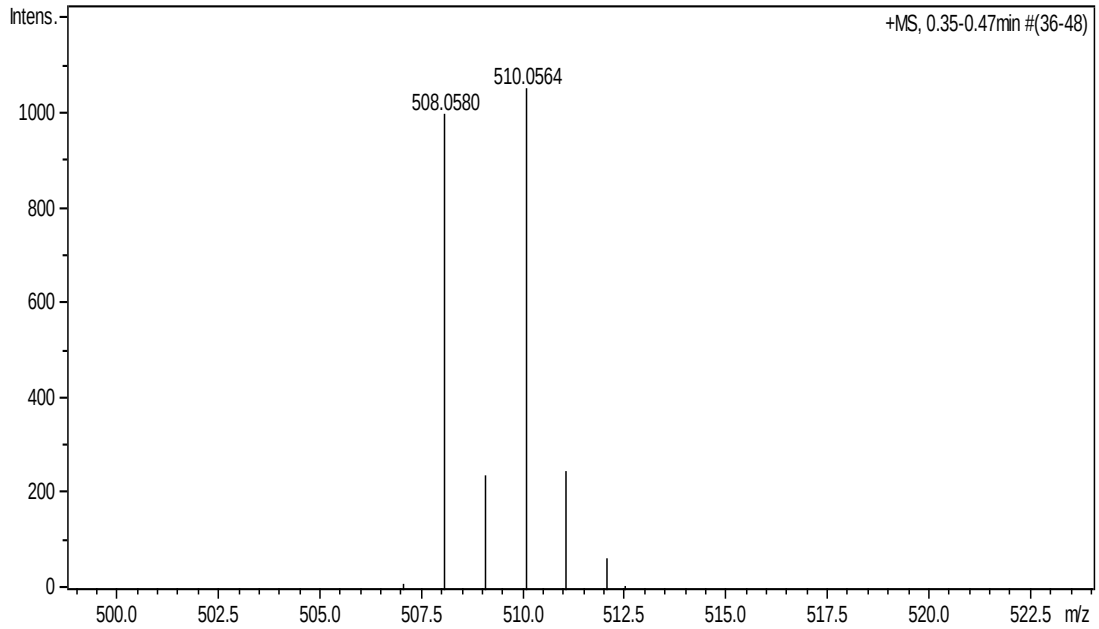

Intens.
+MS, 0.09-0.21min #(9-21)
2000
1500
1000
500
0
486.0909
464.1093
502.0654
450
460
470
480
490
500
510
520
530
m/z

Methyl6-(4-bromophenyl)-9,9-dimethyl-7-oxo-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate (2h):

yellow solid, 85%, m.p. 202~204℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.70 (s, 1H, NH), 7.56~7.55 (m, 1H, ArH), 7.54~7.53 (m, 1H, ArH), 6.95~6.91 (m, 3H, ArH), 6.79~6.75 (m, 1H, ArH), 6.73~6.70 (m, 1H, ArH), 6.52~6.50 (m, 1H, ArH), 3.99 (s, 3H, OCH_3), 2.80 (s, 2H, CH_2), 2.28 (s, 2H, CH_2), 1.02 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.7, 168.9, 144.9, 143.6, 141.5, 139.0, 137.7, 131.7, 129.3, 127.5, 126.4, 125.2, 123.9, 121.4, 120.4, 118.5, 115.7, 113.6, 105.0, 52.7, 52.5, 43.7, 32.6, 28.2; IR (KBr) υ: 3374, 2960, 1684, 1579, 1529, 1485, 1412, 1285, 1222, 1137, 1088, 1009, 980, 896, 809, 740, 705 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{23}BrNO_3S$ ($[M+H]^+$): 508.0582. Found: 508.0580.



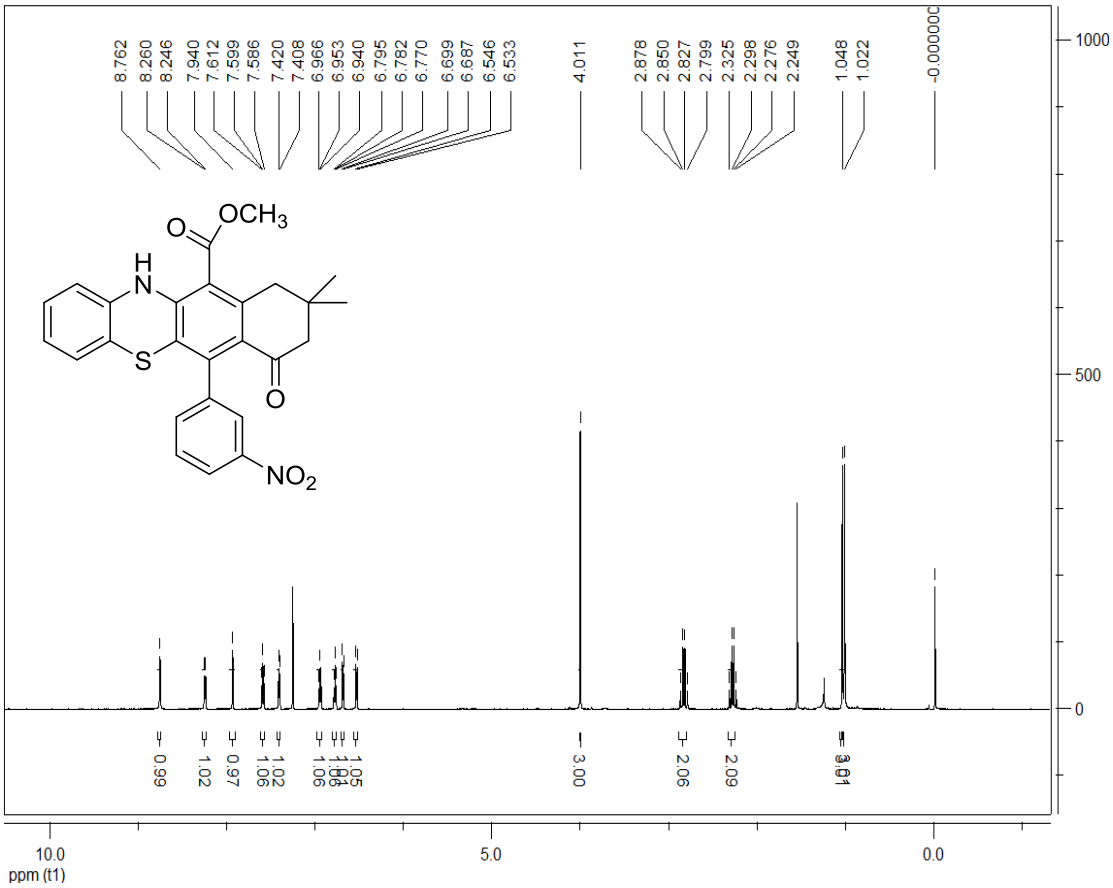

195.666
168.929
144.909
143.554
141.516
138.980
137.709
131.693
129.340
127.484
126.360
125.171
123.908
121.400
120.418
118.478
115.715
113.614
105.010
52.717
52.514
43.736
32.603
28.225
1500
1000
500
0
200
150
100
50
0
ppm (t1)

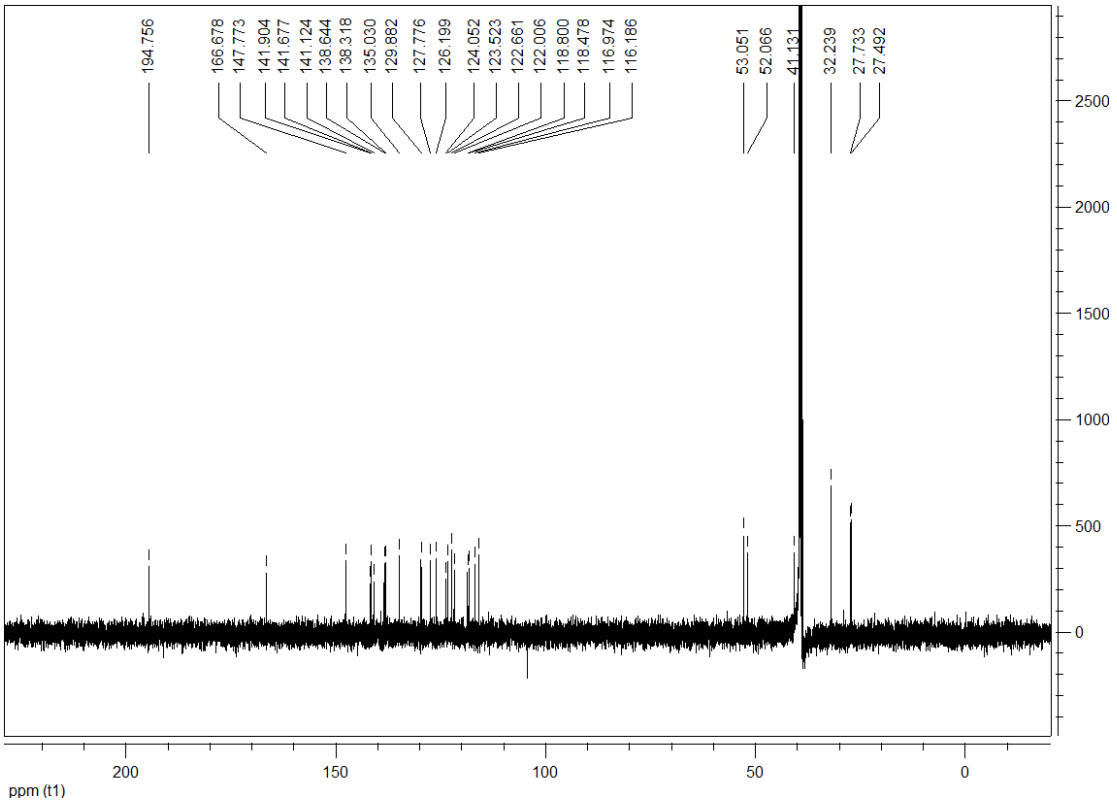

Intens.
+MS, 0.35-0.47min #(36-48)
510.0564
508.0580
1000
800
600
400
200
0
500.0
502.5
505.0
507.5
510.0
512.5
515.0
517.5
520.0
522.5
m/z

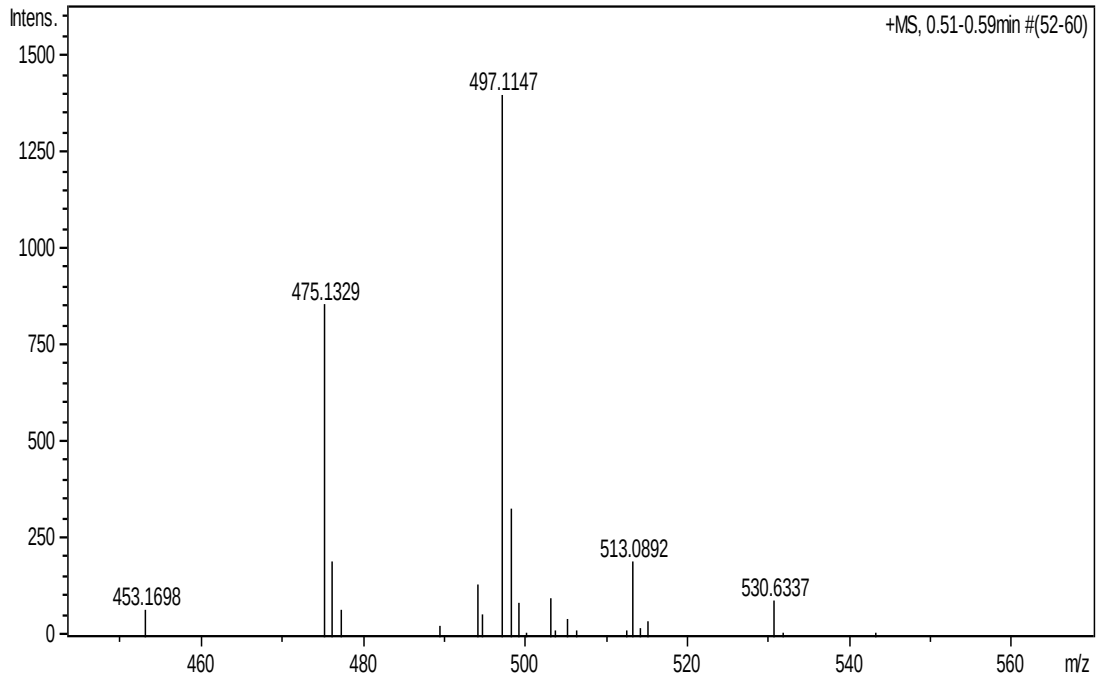
Methyl

9,9-dimethyl-6-(3-nitrophenyl)-7-oxo-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate (2i):

yellow solid, 83%, m.p. 225~227℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 (s, 1H, NH), 8.25 (d, *J* = 5.6 Hz, 1H, ArH), 7.94 (s, 1H, ArH), 7.41 (d, *J* = 4.8 Hz, 1H, ArH), 6.95 (t, *J* = 5.2 Hz, 1H, ArH), 6.80~6.77 (m, 1H, ArH), 6.69 (d, *J* = 4.8 Hz, 1H, ArH), 6.54 (d, *J* = 5.2 Hz, 1H, ArH), 4.01 (s, 3H, OCH_3), 2.88~2.80 (m, 2H, CH_2), 2.33~2.25 (m, 2H, CH_2), 1.05 (s, 3H, CH_3), 1.02 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.8, 166.7, 147.8, 141.9, 141.7, 141.1, 138.6, 138.3, 135.0, 129.9, 127.8, 126.2, 124.1, 123.5, 122.7, 122.0, 118.8, 118.5, 117.0, 116.2, 53.1, 52.1, 41.1, 32.2, 27.7, 27.5; IR (KBr) υ: 2956, 1679, 1575, 1529, 1482, 141, 1348, 1286, 1223, 1145, 193, 980, 805, 744, cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{22}N_2NaO_5S$ ($[M+Na]^+$): 497.1147. Found: 497.1147.



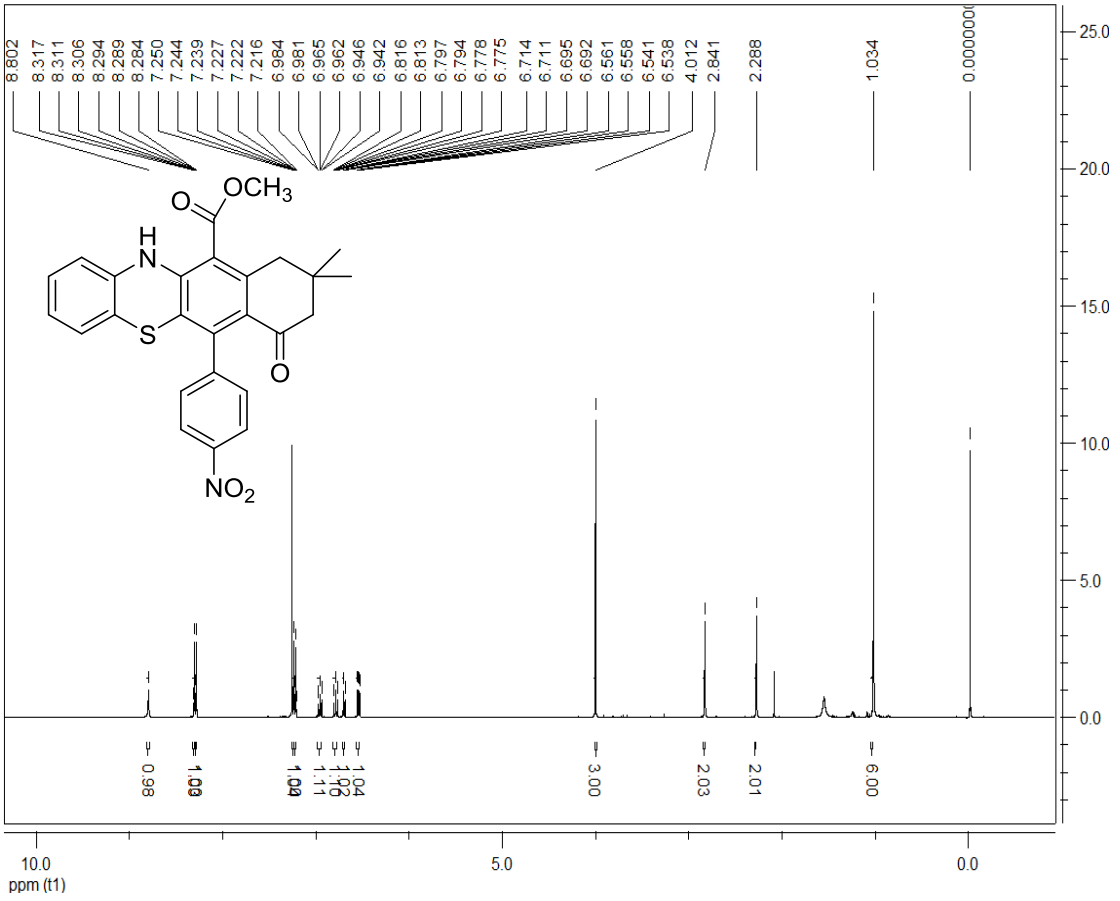

194.756
166.678
147.773
141.904
141.677
141.124
138.644
138.318
135.030
129.882
127.776
126.199
124.052
123.523
122.661
122.006
118.800
118.478
116.974
116.186
53.051
52.066
41.131
32.239
27.733
27.492
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)

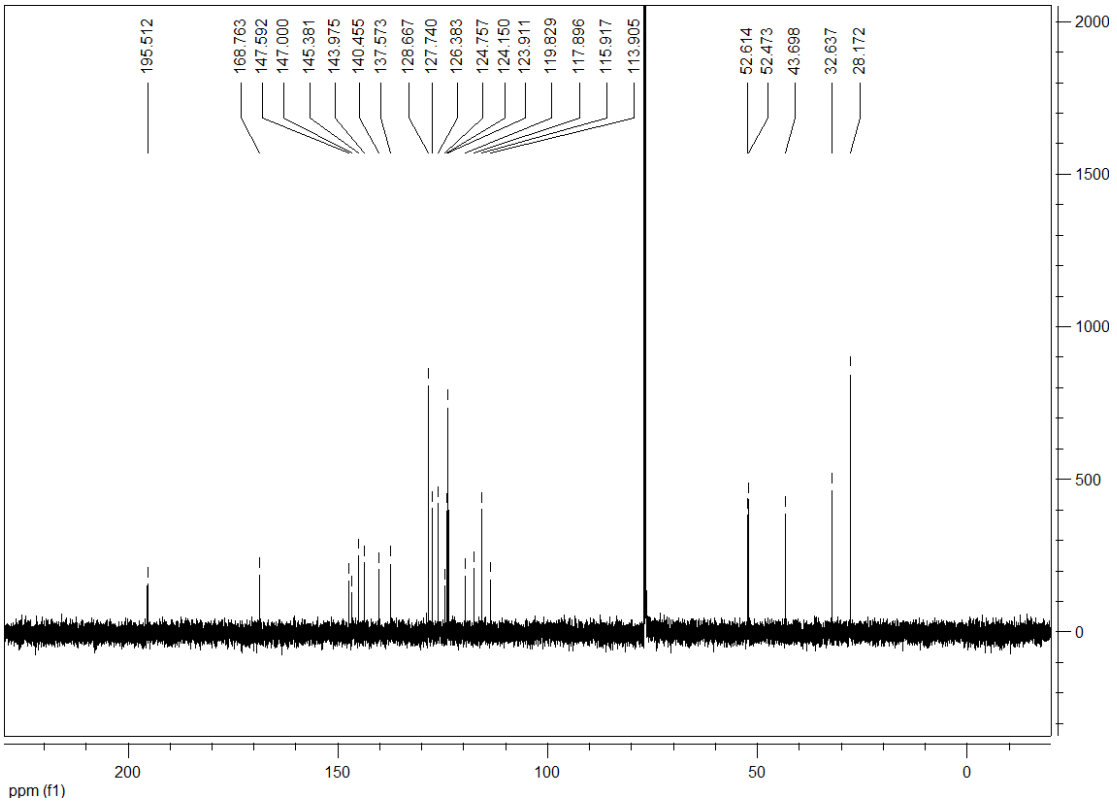

Intens.
+MS, 0.51-0.59min #(52-60)
1500
1250
1000
750
500
250
0
497.1147
475.1329
513.0892
530.6337
453.1698
460
480
500
520
540
560
m/z

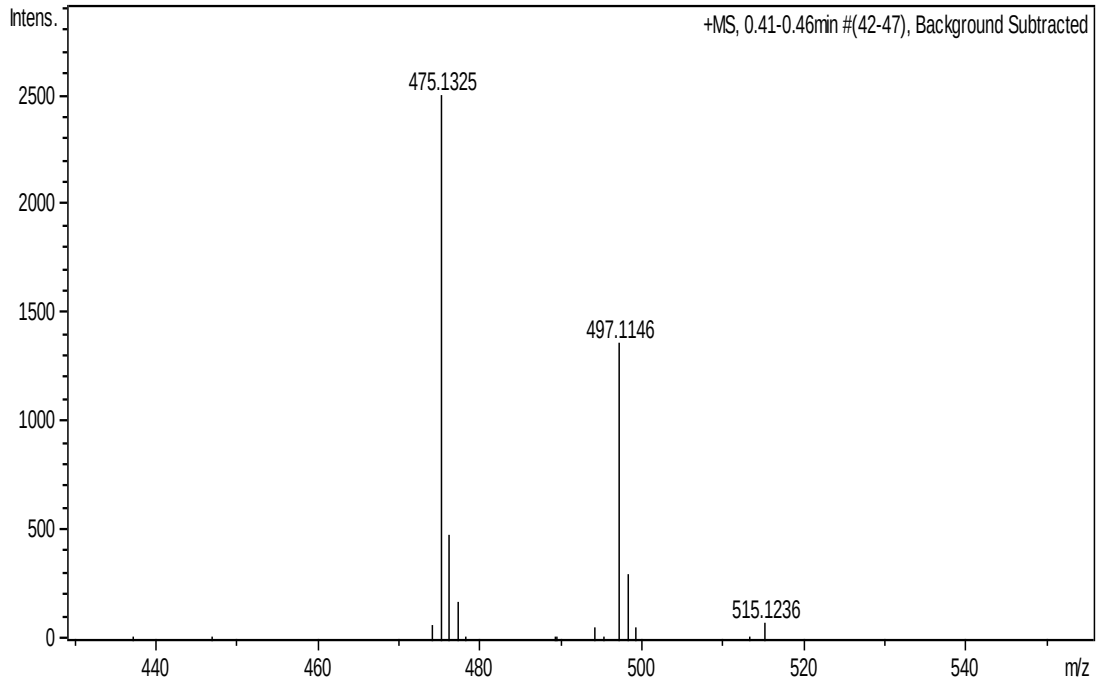
Methyl

9,9-dimethyl-6-(4-nitrophenyl)-7-oxo-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate (2j):

yellow solid, 87%, m.p. 258~260℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (s, 1H, NH), 8.32~8.31 (m, 1H, ArH), 8.29~8.28 (m, 1H, ArH), 7.25~7.24 (m, 1H, ArH), 7.23~7.22 (m, 1H, ArH), 6.98~6.94 (m, 1H, ArH), 6.82~6.78 (m, 1H, ArH), 6.71~6.69 (m, 1H, ArH), 6.56~6.54 (m, 1H, ArH), 4.01 (s, 3H, OCH_3), 2.84 (s, 2H, CH_2), 2.29 (s, 2H, CH_2), 1.03 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.5, 168.8, 147.6, 147.0, 145.4, 144.0, 140.5, 137.6, 128.7, 127.7, 126.4, 124.8, 124.1, 123.9, 119.8, 117.9, 115.9, 113.9, 52.6, 52.5, 43.7, 32.6, 28.2; IR (KBr) υ: 3379, 2957, 171, 1675, 1596, 1529, 1481, 1427, 1343, 1285, 1223, 1137, 982, 852, 749, 703cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{22}N_2NaO_5S$ ([M+Na]$^+$): 497.1147. Found: 497.1146.

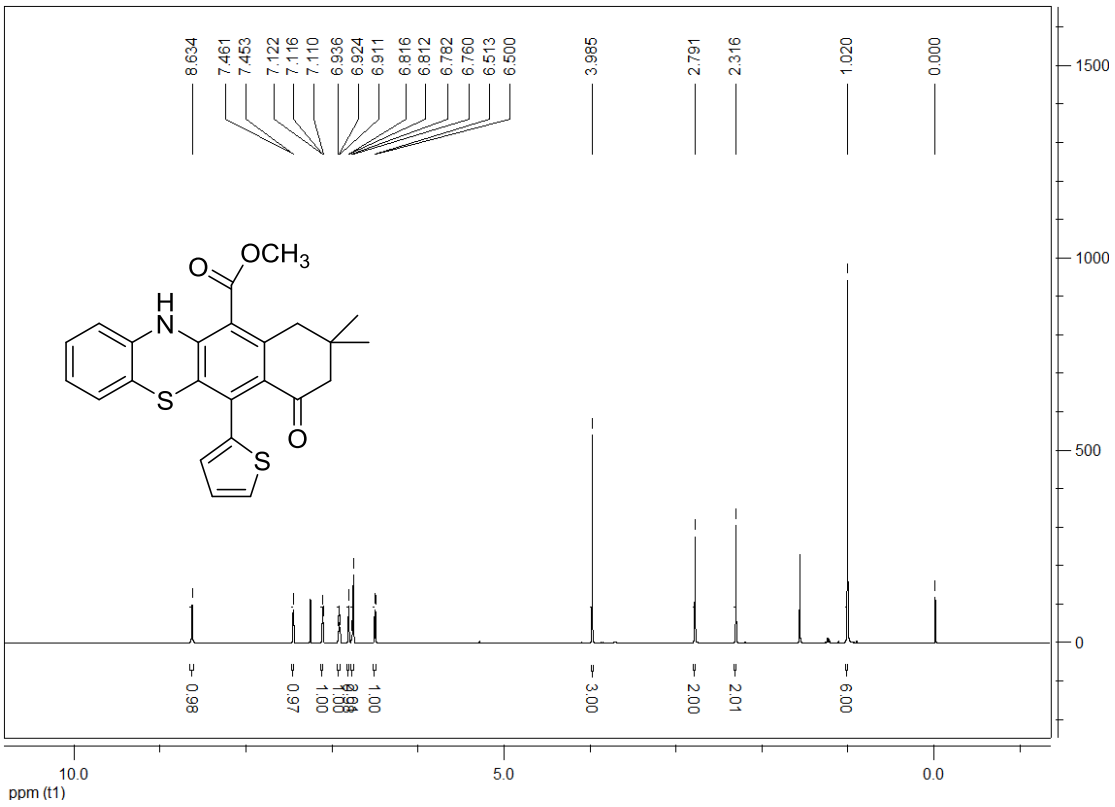


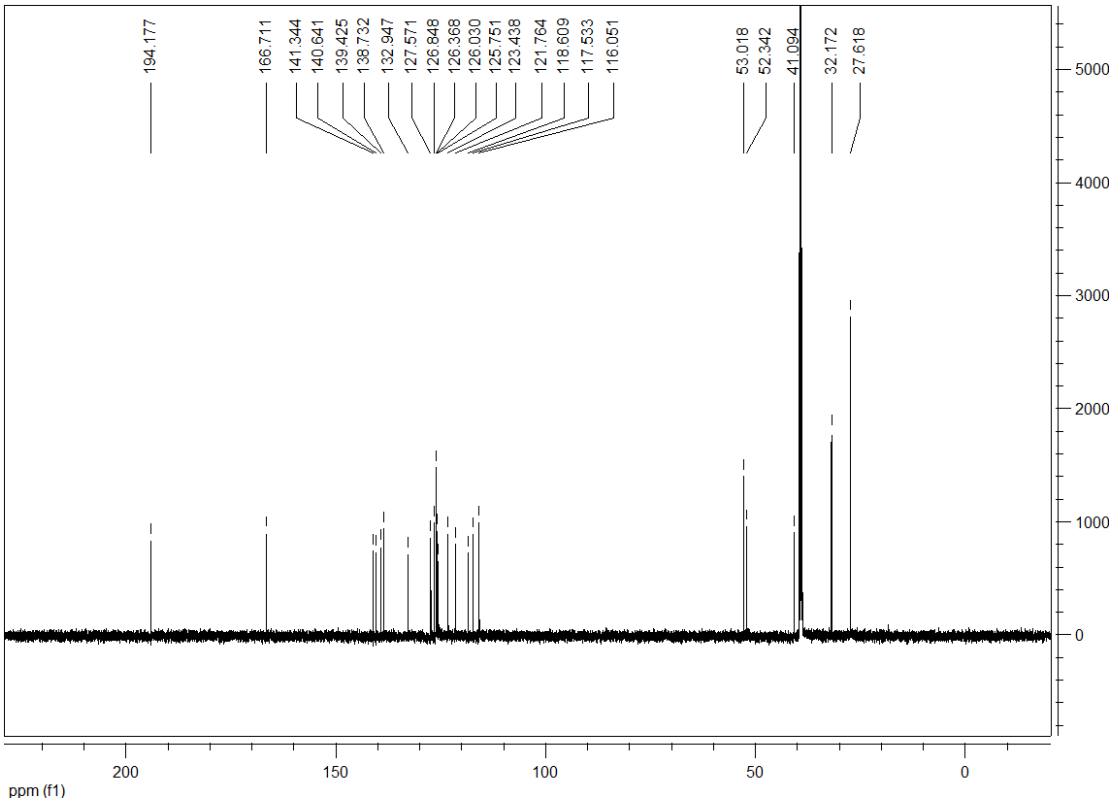

195.512
168.763
147.592
147.000
145.381
143.975
140.455
137.573
128.667
127.740
126.383
124.757
124.150
123.911
119.829
117.896
115.917
113.905
52.614
52.473
43.698
32.637
28.172
2000
1500
1000
500
0
200
150
100
50
0
ppm (f1)

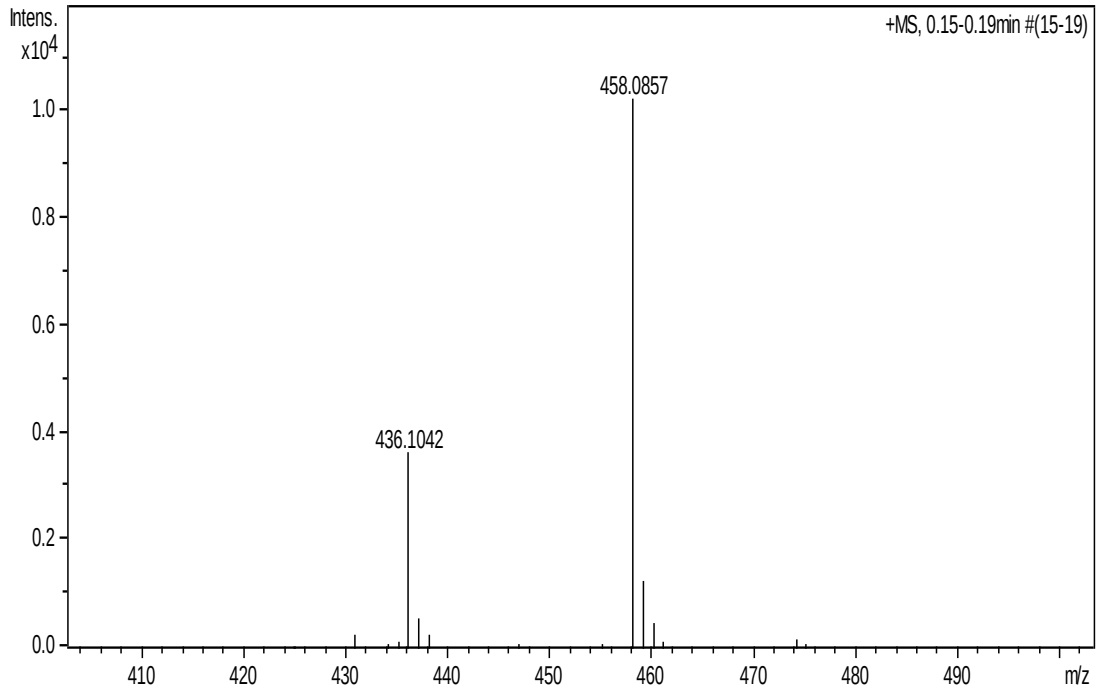

Intens.
+MS, 0.41-0.46min #(42-47), Background Subtracted
475.1325
497.1146
515.1236
2500
2000
1500
1000
500
0
440
460
480
500
520
540
m/z

Methyl
9,9-dimethyl-7-oxo-6-(thiophen-2-yl)-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate (2k):

yellow solid, 79%, m.p. 163~165℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.63 (s, 1H, NH), 7.46 (t, *J* = .2.4 Hz, 1H, ArH), 7.16 (d, *J* = 1.6 Hz, 1H, ArH), 6.94~6.91 (m, 1H, ArH), 6.81 (d, *J* = 1.6 Hz, 1H, ArH), 6.78~6.76 (m, 2H, ArH), 6.51 (d, *J* = 5.2 Hz, 1H, ArH), 3.99 (s, 3H, OCH_3), 2.79 (s, 2H, CH_2), 2.32 (s, 2H, CH_2), 1.02 (s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.2, 166.7, 141.3, 140.6, 139.4, 138.7, 132.9, 127.6, 126.8, 126.4, 126.0, 125.8, 123.4, 121.8, 118.6, 117.5, 116.1, 53.0, 52.3, 41.1, 32.2, 27.6; IR (KBr) υ: 3289, 2946, 2867, 1670, 1578, 1532, 1483, 1438, 1407, 1300, 1227, 1122, 976, 888, 797, 748cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{24}H_{21}NNaO_3S_2$ ([M+Na]$^{+}$): 458.0861. Found: 458.0857.

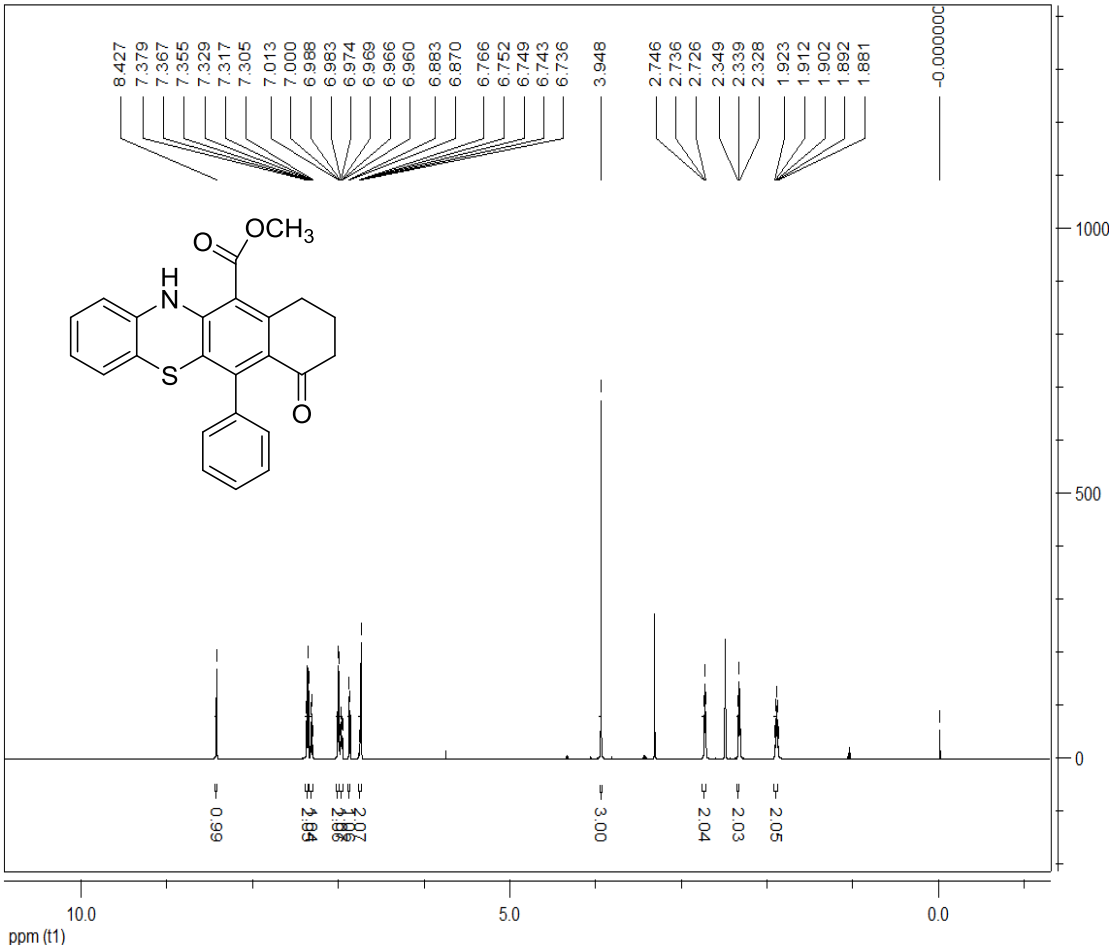


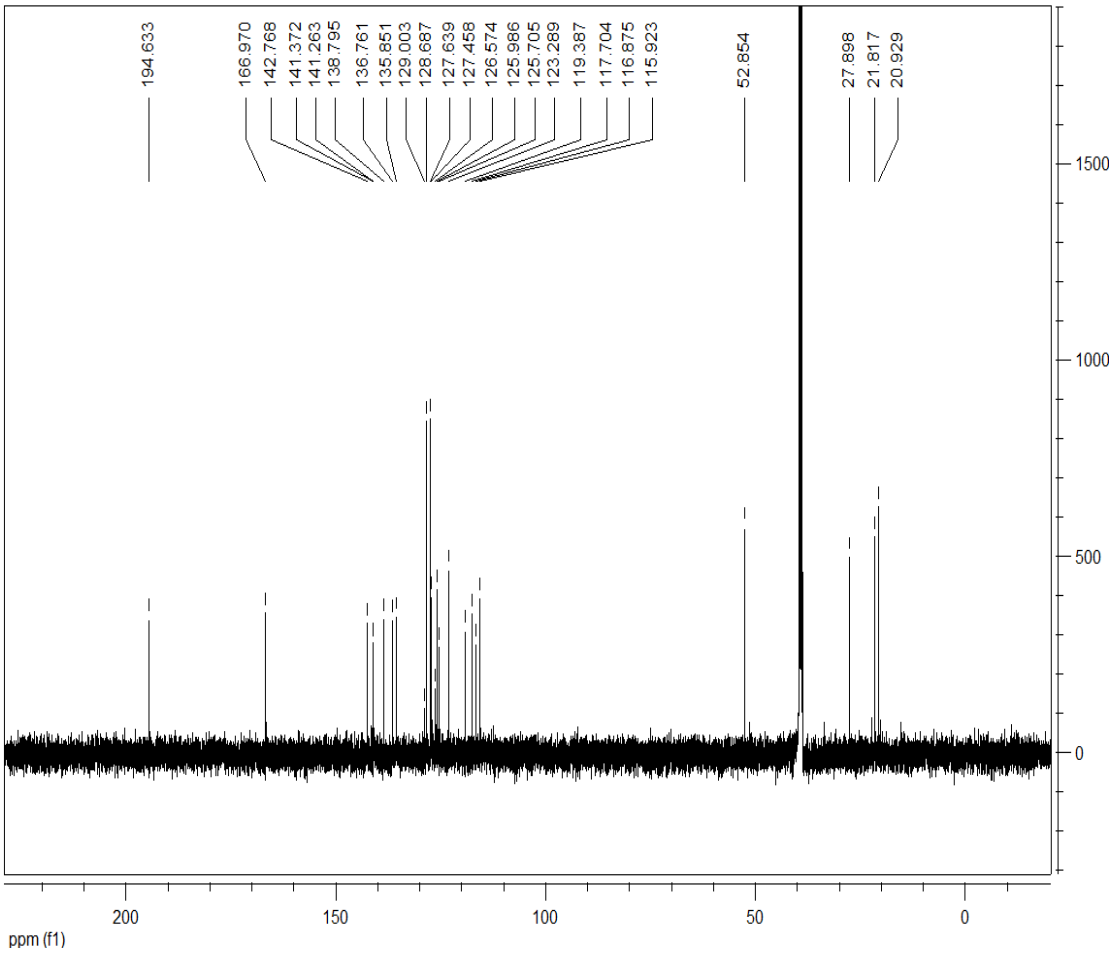

194.177
166.711
141.344
140.641
139.425
138.732
132.947
127.571
126.848
126.368
126.030
125.751
123.438
121.764
118.609
117.533
116.051
53.018
52.342
41.094
32.172
27.618
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)

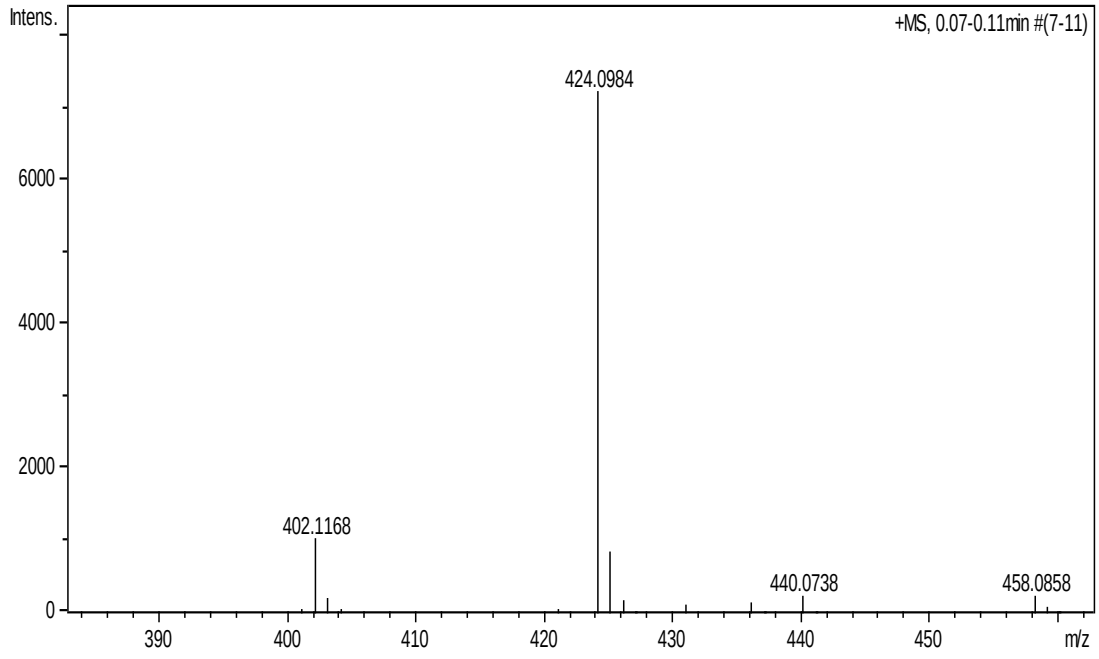

Intens.
x10^4
+MS, 0.15-0.19min #(15-19)
458.0857
436.1042
1.0
0.8
0.6
0.4
0.2
0.0
410
420
430
440
450
460
470
480
490
m/z

Methyl 7-oxo-6-phenyl-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate (2l)

yellow solid, 91%, m.p. 196~198℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43 (s, 1H, NH), 7.38~7.36 (m, 2H, ArH), 7.33~7.31 (m, 1H, ArH), 7.01 (d, *J* = 5.2 Hz, 2H, ArH), 6.99~6.96 (m, 1H, ArH), 6.88 (d, *J* = 5.2 Hz, 1H, ArH), 6.77~6.74 (m, 1H, ArH), 3.95 (s, 3H, OCH_3), 2.74 (t, *J* = 4.0 Hz, 2H, CH_2), 2.34 (t, *J* = 4.0 Hz, 2H, CH_2), 1.92~1.88 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.6, 167.0, 142.8, 141.4, 141.3, 138.8, 136.8, 135.9, 129.0, 128.7, 127.6, 127.5, 126.6, 126.0, 125.7, 123.3, 119.4, 117.7, 116.9, 115.9, 52.9, 27.9, 21.8, 20.9; IR (KBr) υ: 3313, 2953, 1681, 1571, 1527, 1478, 1436, 1400, 1357, 1300, 1267, 1233, 1187, 1134, 970, 928, 804, 750, 701cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{24}H_{19}NNaO_3S$ ([M+Na]$^{+}$): 424.0983. Found: 424.0984.

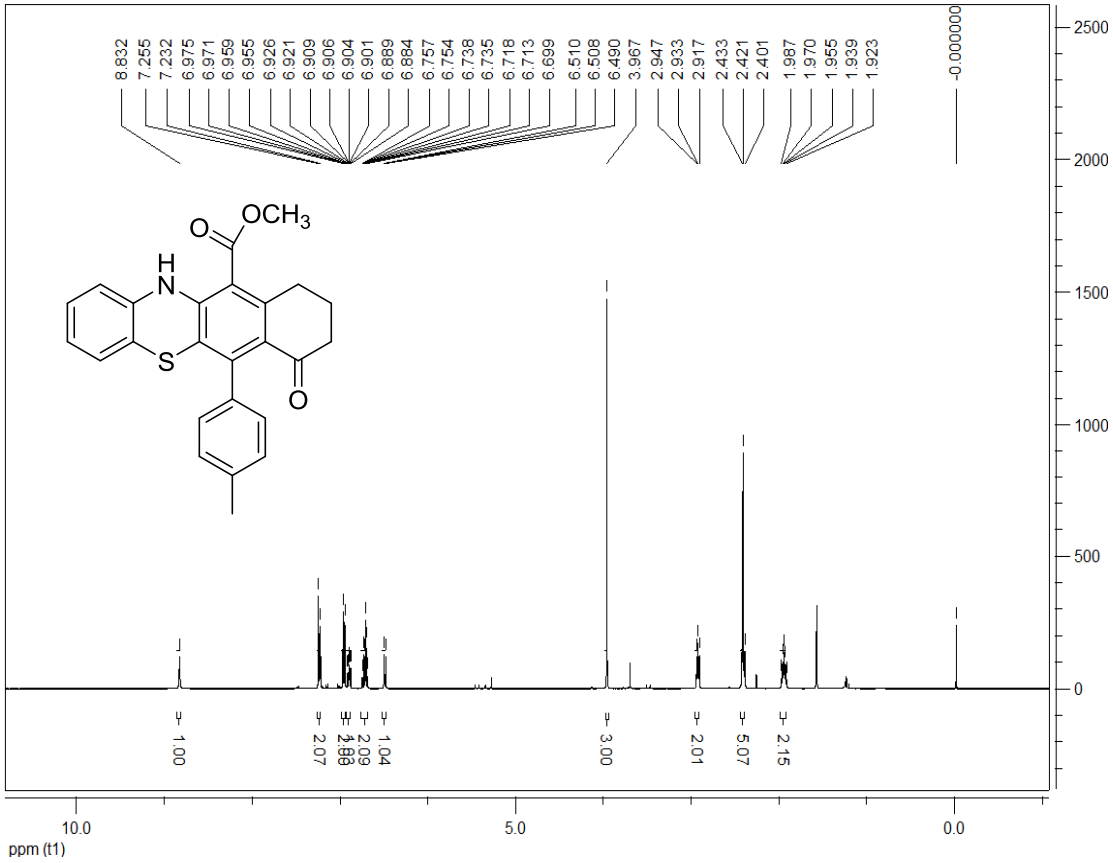


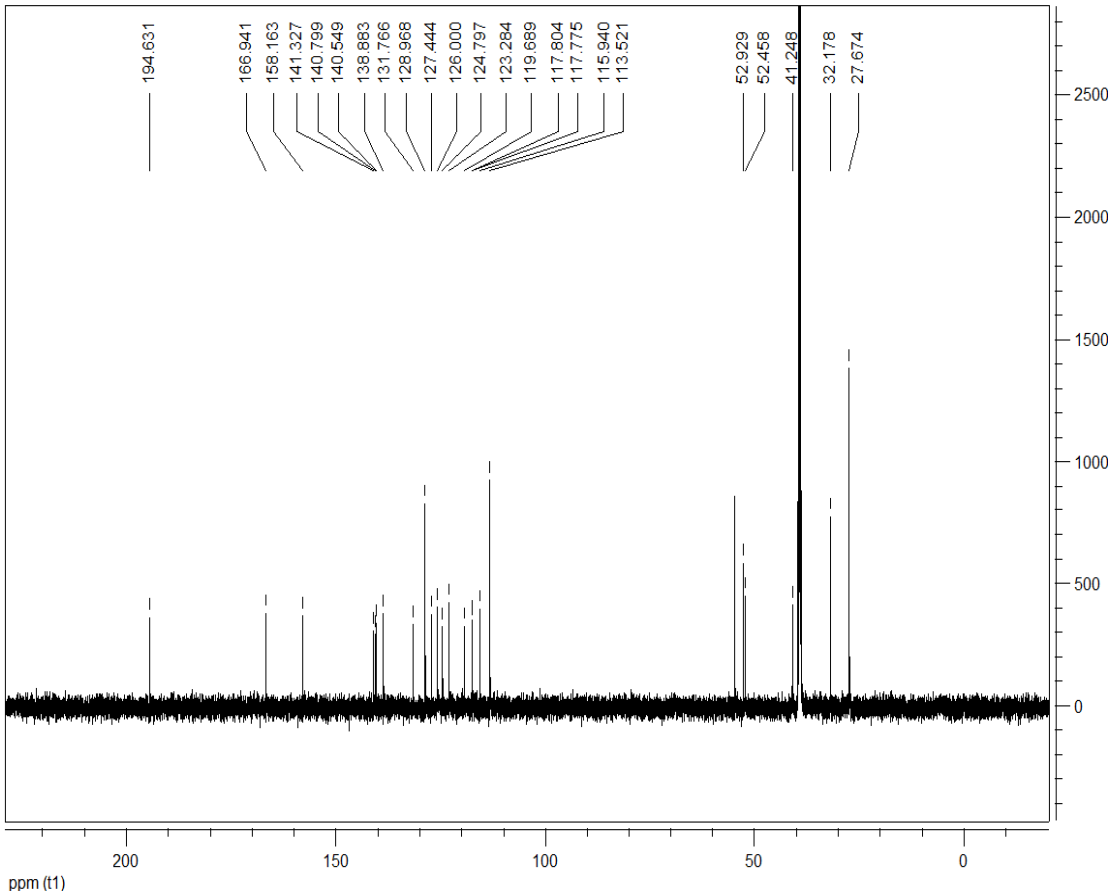

194.633
166.970
142.768
141.372
141.263
138.795
136.761
135.851
129.003
128.687
127.639
127.458
126.574
125.986
125.705
123.289
119.387
117.704
116.875
115.923
52.854
27.898
21.817
20.929
1500
1000
500
0
200
150
100
50
0
ppm (f1)

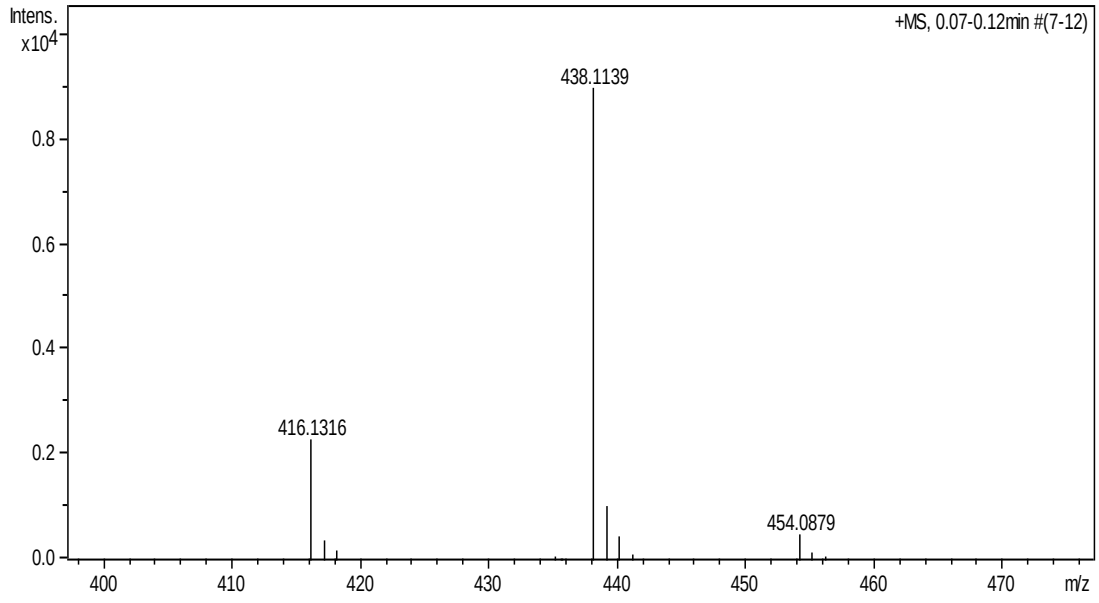

Intens.
+MS, 0.07-0.11min #(7-11)
424.0984
6000
4000
2000
0
402.1168
440.0738
458.0858
390
400
410
420
430
440
450
m/z

Methyl 7-oxo-6-(p-tolyl)-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate (2m):

yellow solid, 79%, m.p. 167~169℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.83 (s, 1H, NH), 7.24 (d, *J* = 5.2 Hz, 2H, ArH), 6.93~6.88 (m, 2H, ArH), 6.76~6.70 (m, 1H, ArH), 3.97 (s, 3H, OCH_3), 2.95~2.92 (m, 2H, CH_2), 2.43~2.40 (m, 2H, CH_2), 1.99~1.92 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.6, 166.9, 158.2, 141.3, 140.8, 140.5, 138.9, 131.8, 129.0, 127.4, 126.0, 124.8, 123.3, 119.7, 117.8, 117.8, 115.9, 113.5, 52.9, 52.5, 41.2, 32.2; IR (KBr) υ: 3290, 3020, 2940, 1672, 1573, 1527, 1476, 1436, 1403, 1263, 1224, 1184, 1143, 1099, 978, 925, 809, 751cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{25}H_{21}NNaO_3S$ ([M+Na]$^{+}$): 438.1140. Found: 438.1139.




194.631
166.941
158.163
141.327
140.799
140.549
138.883
131.766
128.968
127.444
126.000
124.797
123.284
119.689
117.804
117.775
115.940
113.521
52.929
52.458
41.248
32.178
27.674
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)

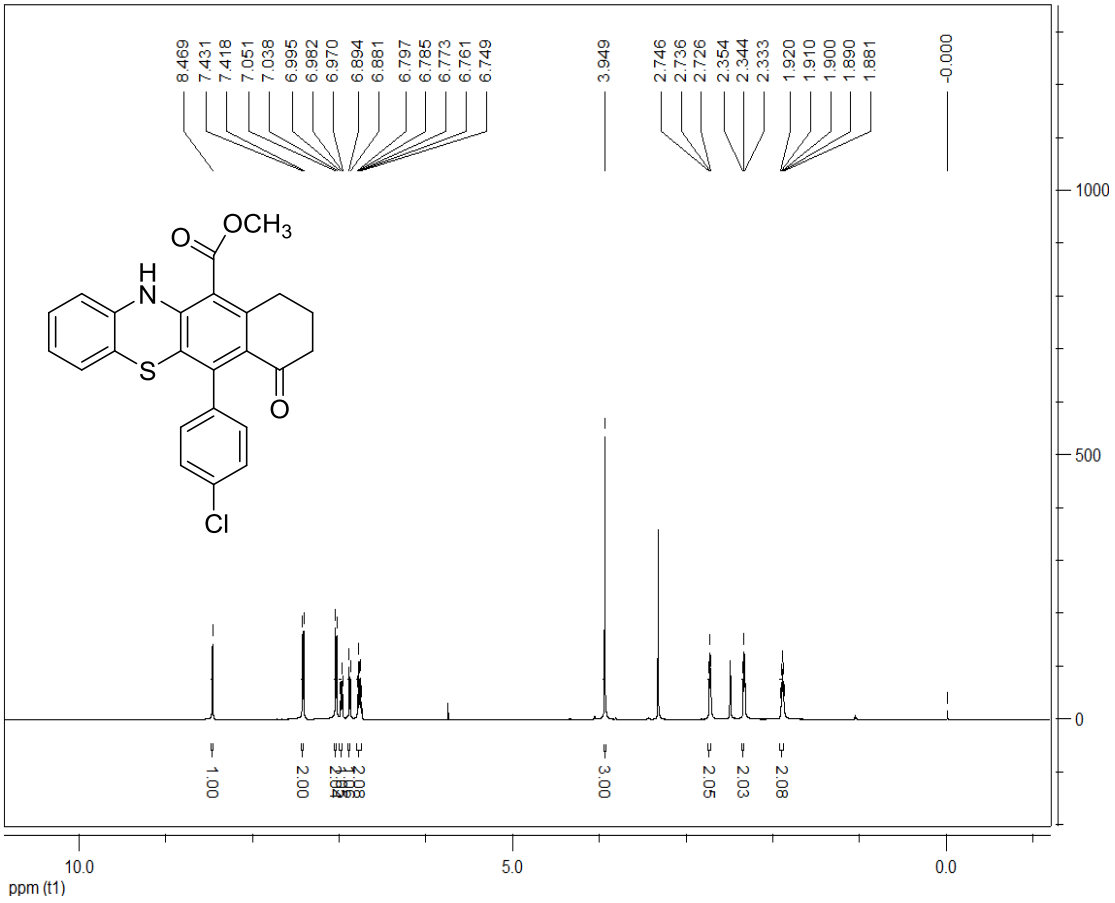

Intens.
x10^4
+MS, 0.07-0.12min #(7-12)
438.1139
416.1316
454.0879
0.8
0.6
0.4
0.2
0.0
400
410
420
430
440
450
460
470
m/z

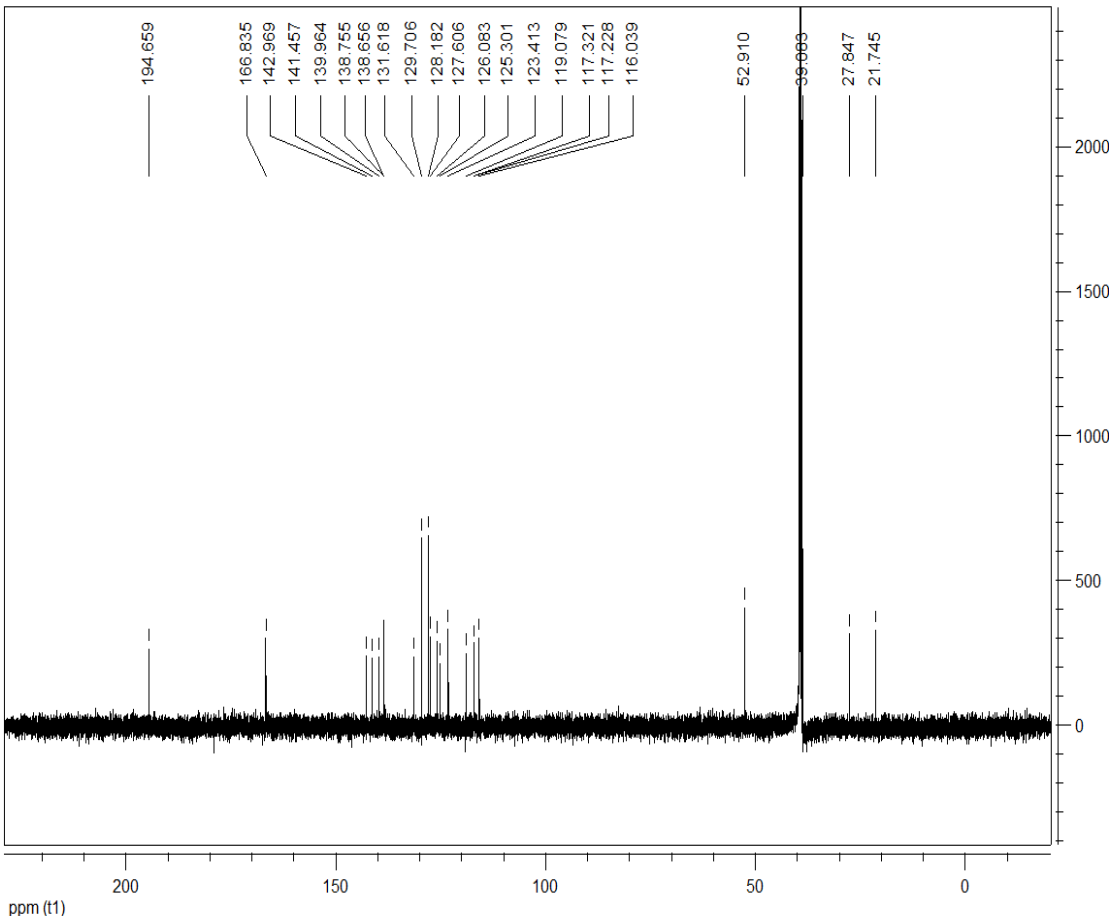
Methyl

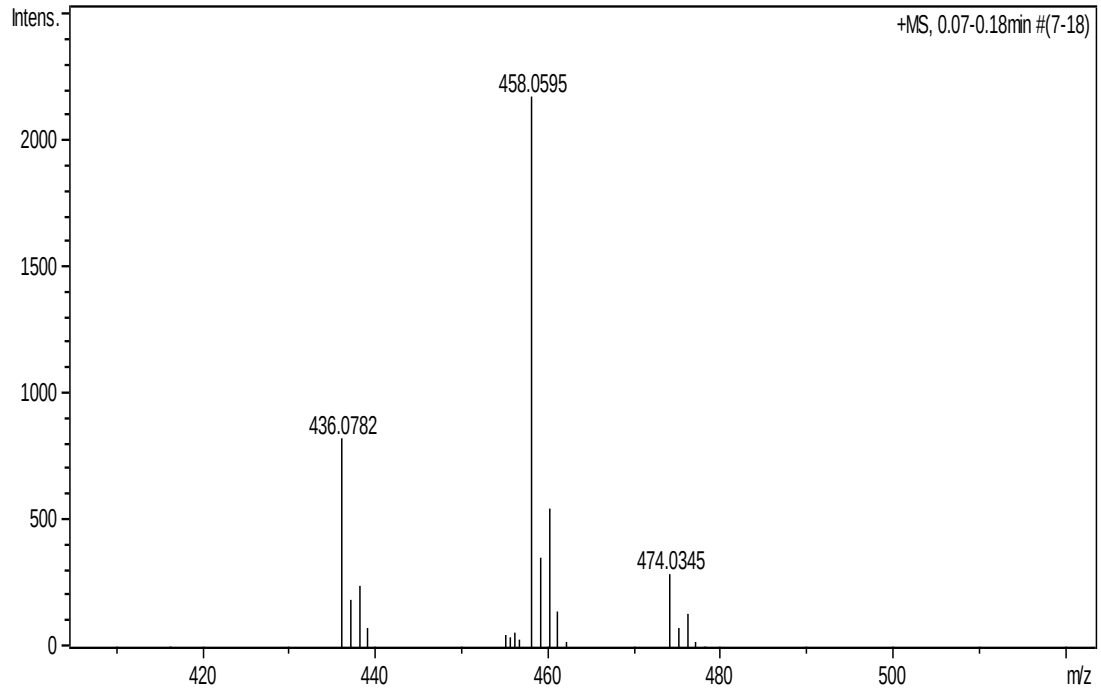
6-(4-chlorophenyl)-7-oxo-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate

(2n):

yellow solid, 81%, m.p. 213~215℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.47 (s, 1H, NH), 7.42 (d, J = 5.2 Hz, 2H, ArH), 7.04 (d, J = 5.2 Hz, 2H, ArH), 7.00~6.97 (m, 1H, ArH), 6.89 (d, J = 5.2 Hz, 1H, ArH), 6.80~6.75 (m, 2H, ArH), 3.97 (s, 3H, OCH_3), 2.74 (t, J = 4.0 Hz, 2H, CH_2), 2.35~2.33 (m, 2H, CH_2), 1.92~1.88 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.7, 166.8, 143.0, 141.5, 140.0, 138.8, 138.7, 131.6, 129.7, 128.2, 127.6, 126.1, 125.3, 123.4, 119.1, 117.3, 117.2, 116.0, 52.9, 39.1, 27.8, 21.7; IR (KBr) υ: 3294, 2939, 1667, 1570, 1528, 1478, 1436, 1405, 1360, 1325, 1297, 1267, 1224, 1185, 1145, 188, 1011, 977, 923, 819, 752cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{24}H_{18}ClNNaO_3S$ ([M+Na]$^+$): 458.0594. Found: 458.0595.




194.659
166.835
142.969
141.457
139.964
138.755
138.656
131.618
129.706
128.182
127.606
126.083
125.301
123.413
119.079
117.321
117.228
116.039
52.910
39.693
27.847
21.745
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)

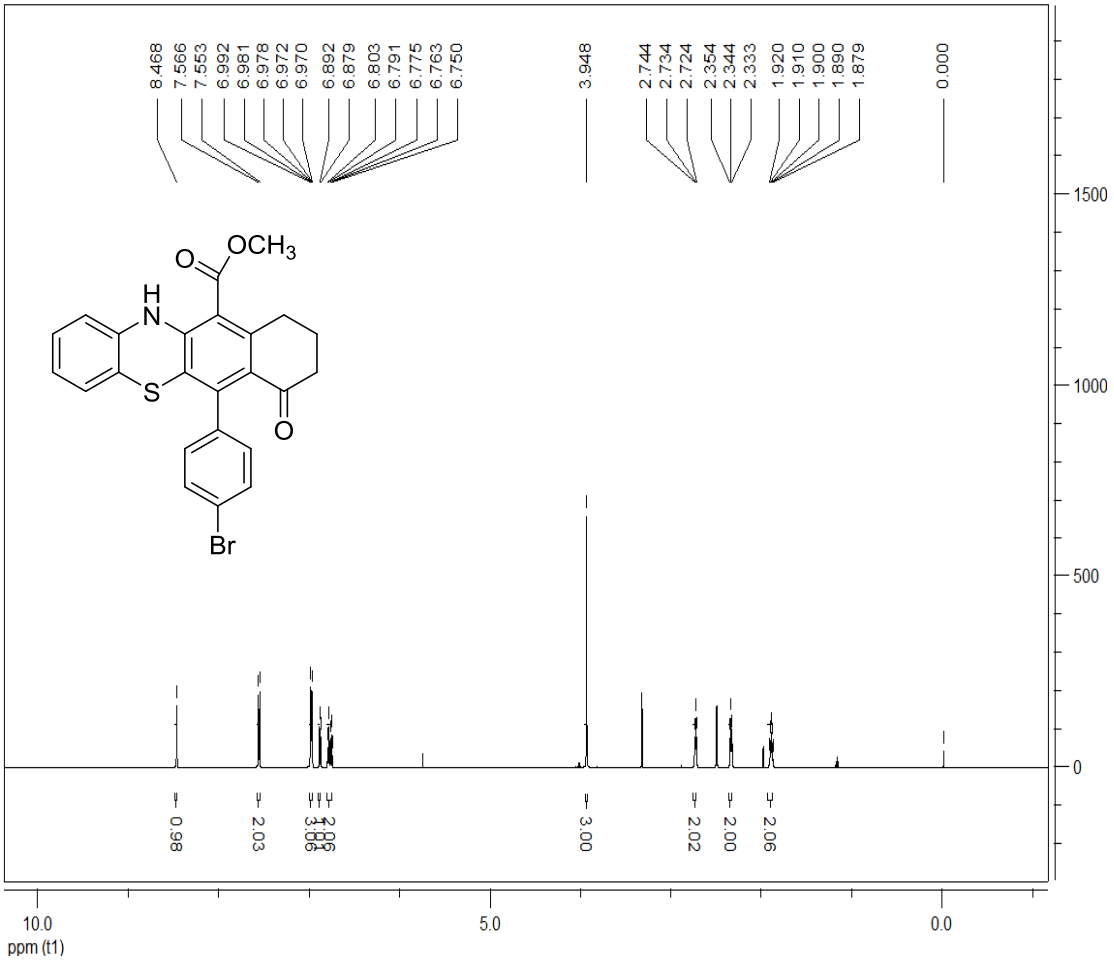

Intens.
+MS, 0.07-0.18min #(7-18)
458.0595
436.0782
474.0345
2000
1500
1000
500
0
420
440
460
480
500
m/z

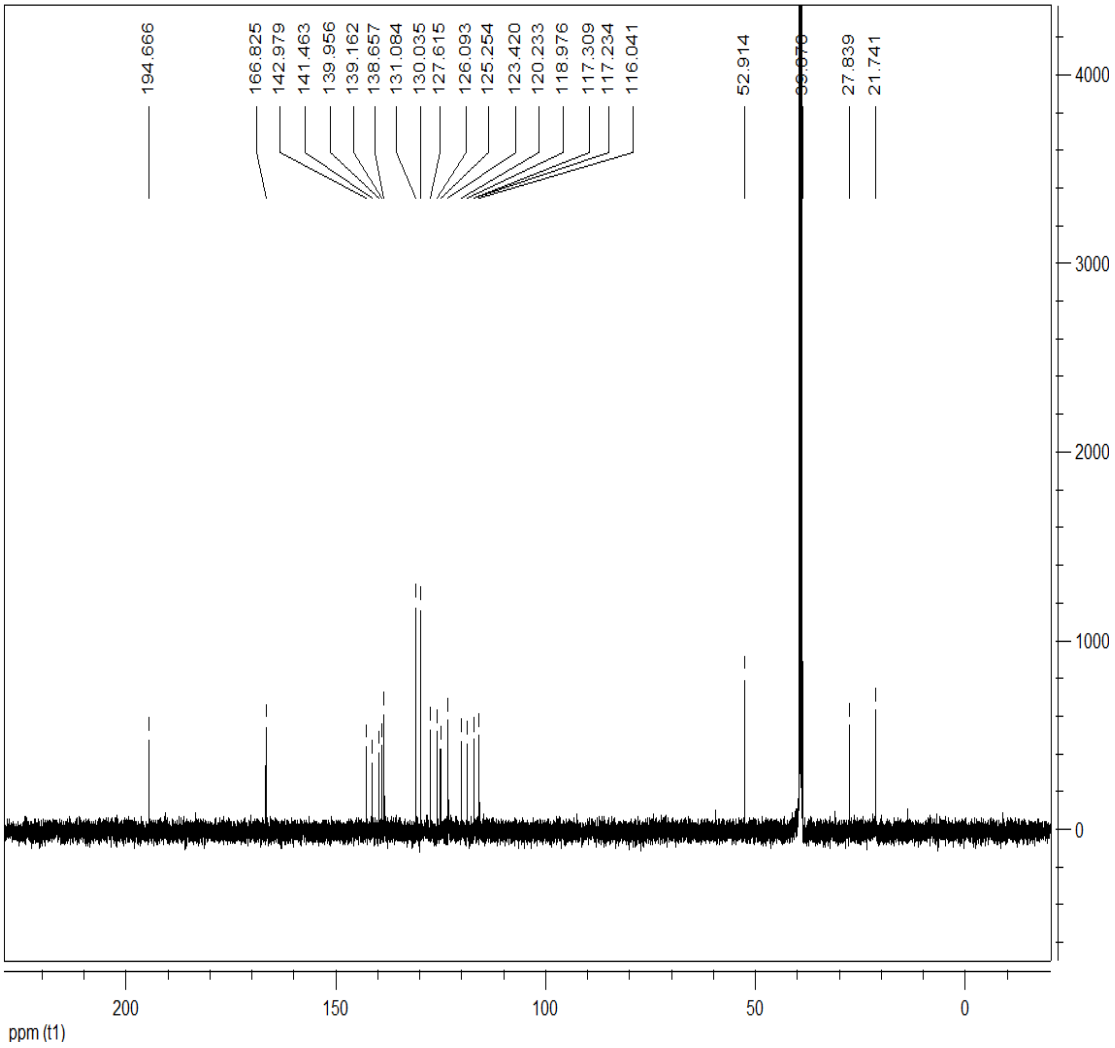
Methyl

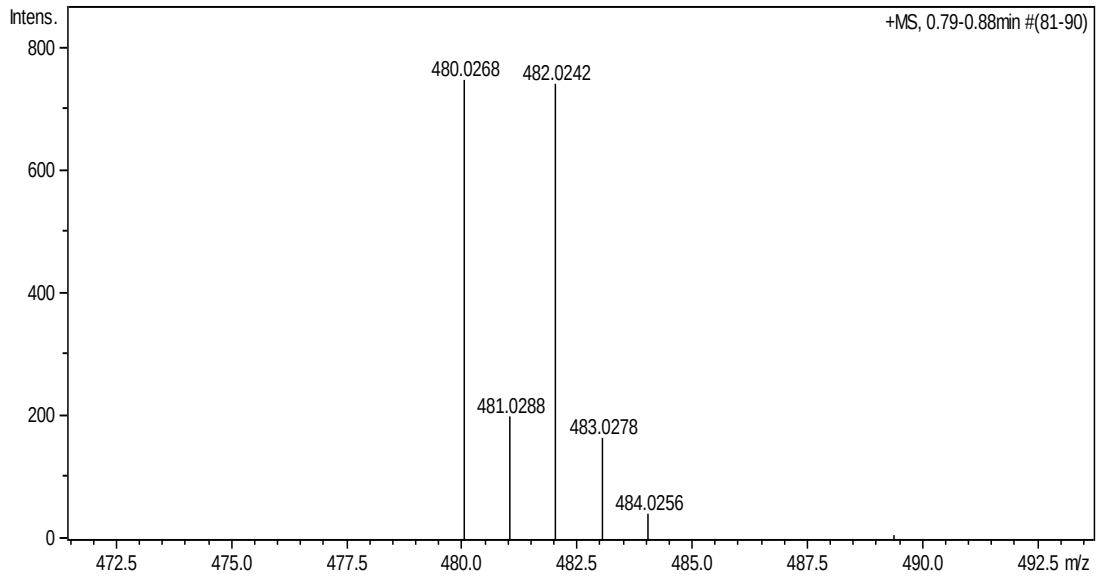
6-(4-bromophenyl)-7-oxo-7,9,10,12-tetrahydro-8H-benzo[b]phenothiazine-11-carboxylate

(2o):

yellow solid, 80%, m.p. 234~236℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.47 (s, 1H, NH), 7.56 (d, J = 5.2 Hz, 2H, ArH), 7.00~6.97 (m, 1H, ArH), 6.89 (d, J = 5.2 Hz, 3H, ArH), 6.80~6.75 (m, 2H, ArH), 3.95 (s, 3H, OCH_3), 2.73 (t, J = 4.0 Hz, 2H, CH_2), 2.35~2.33 (m, 2H, CH_2), 1.92~1.88 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.7, 166.8, 143.0, 141.5, 140.0, 139.2, 138.7, 131.1, 130.0, 127.6, 126.1, 125.3, 123.4, 120.2, 119.0, 117.3, 117.2, 116.0, 52.9, 39.1, 27.8, 21.7; IR (KBr) υ: 3296, 2940, 1667, 1569, 1528, 1477, 1435, 1406, 1360, 1325, 1267, 1223, 1185, 1145, 1097, 1007, 977, 923, 817, 751, 702cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{24}H_{19}BrNO_3S$ ([M+H]$^{+}$): 480.0269. Found: 480.0268.

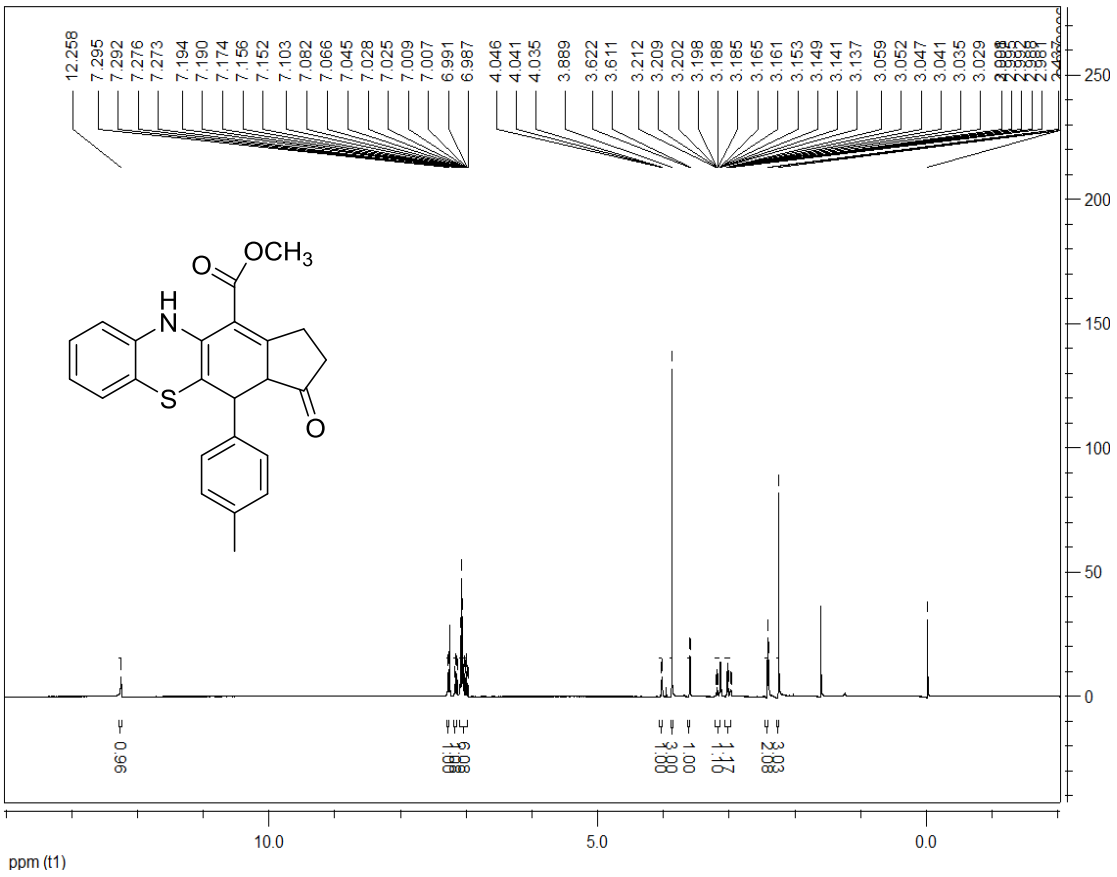


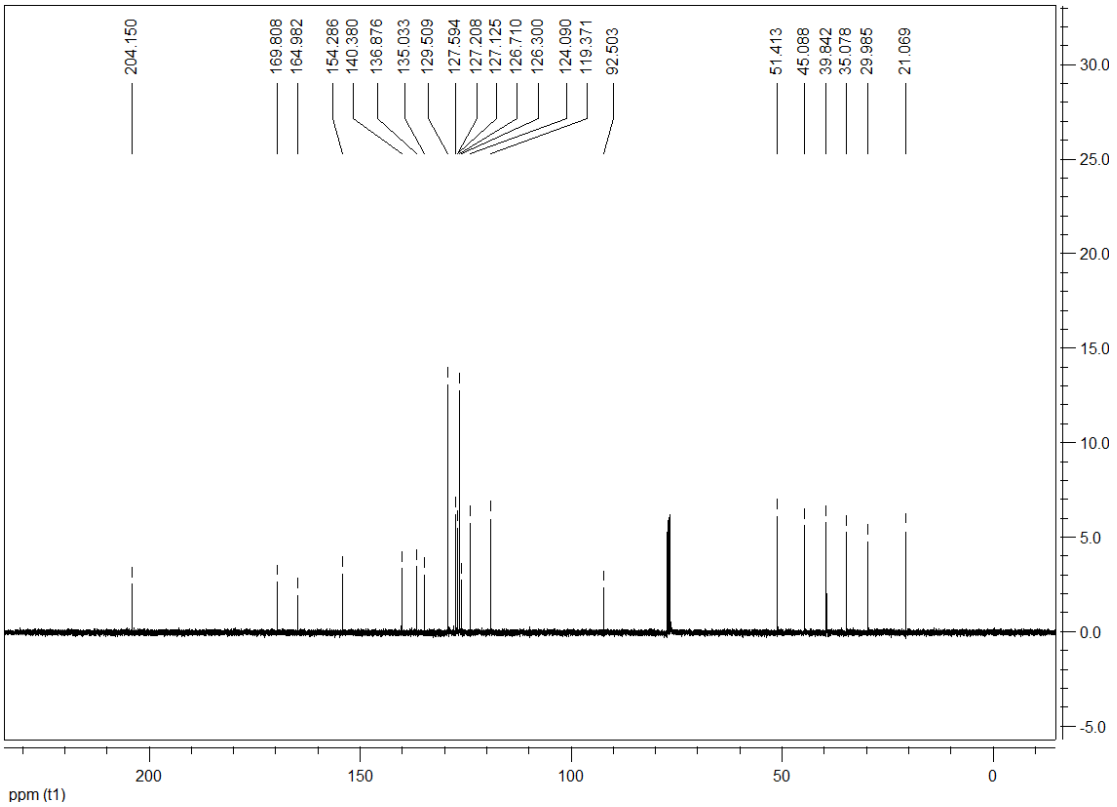

194.666
166.825
142.979
141.463
139.956
139.162
138.657
131.084
130.035
127.615
126.093
125.254
123.420
120.233
118.976
117.309
117.234
116.041
52.914
27.839
21.741
4000
3000
2000
1000
0
200
150
100
50
0
ppm (t1)

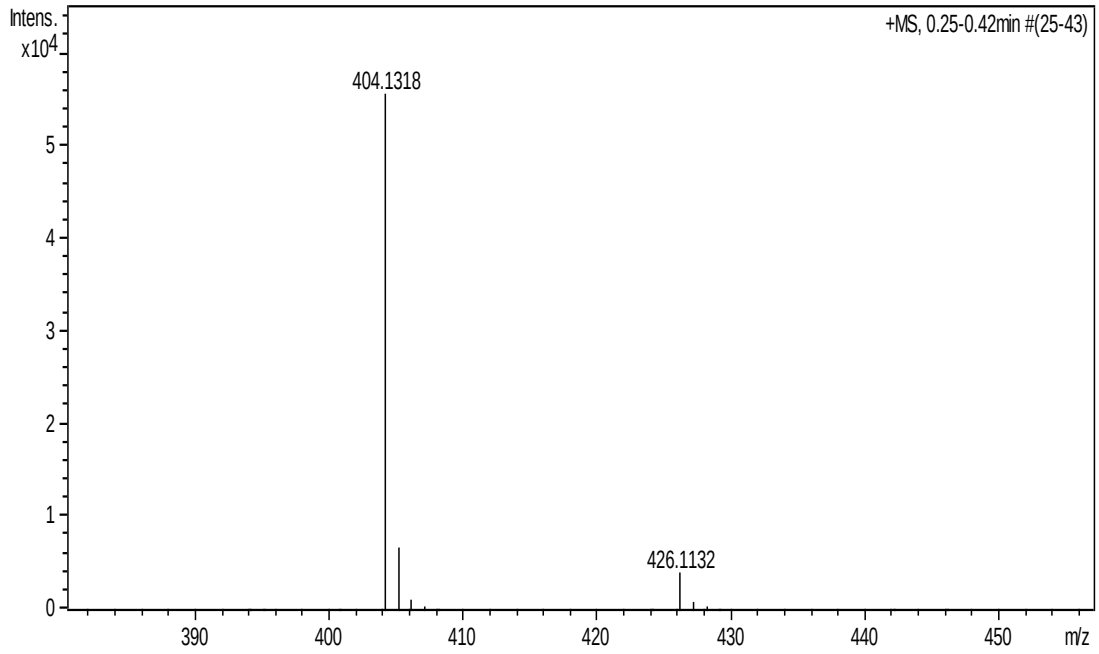

Intens.
+MS, 0.79-0.88min #(81-90)
800
600
400
200
0
480.0268
482.0242
481.0288
483.0278
484.0256
472.5
475.0
477.5
480.0
482.5
485.0
487.5
490.0
492.5 m/z

Methyl 3-oxo-4-(p-tolyl)-1,2,3,3a,4,10-hexahydrocyclopenta[b]phenothiazine-11-carboxylate (3a):

yellow solid, 91%, m.p. 153~155℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.26 (s, 1H, NH), 7.30~7.27 (m, 1H, ArH), 7.19~7.15 (m, 1H, ArH), 7.10~6.99 (m, 6H, ArH), 3.89 (s, 3H, OCH_3), 3.62 (d, *J* = 4.4 Hz, 1H, CH), 3.21~3.14 (m, 2H, CH_2), 3.06~2.98 (m, 1H, CH), 2.43 (t, *J* = 4.4 Hz, 2H, CH_2), 2.27 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.1, 169.8, 164.9, 154.2, 140.3, 136.8, 135.0, 129.5, 127.5, 127.2, 127.1, 126.7, 126.2, 124.0, 119.3, 92.5, 51.4, 45.0, 39.8, 35.0, 29.9, 21.0; IR (KBr) υ: 3157, 2938, 1695, 1591, 1539, 1483, 1415, 1295, 1266, 1233, 1142, 985, 830, 788, 759cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{24}H_{22}NO_3S$ ($[M+H]^+$): 404.1320. Found: 404.1318.

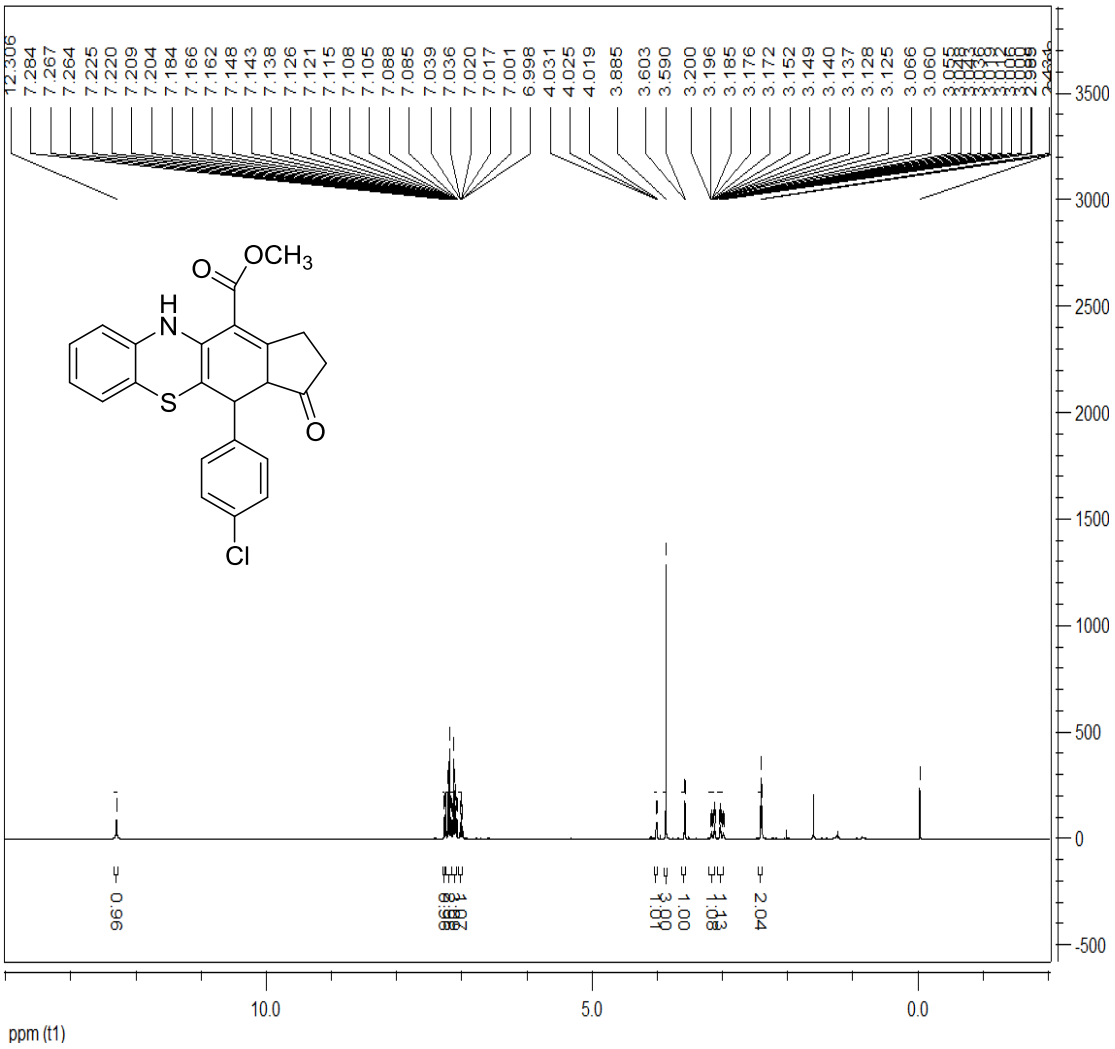


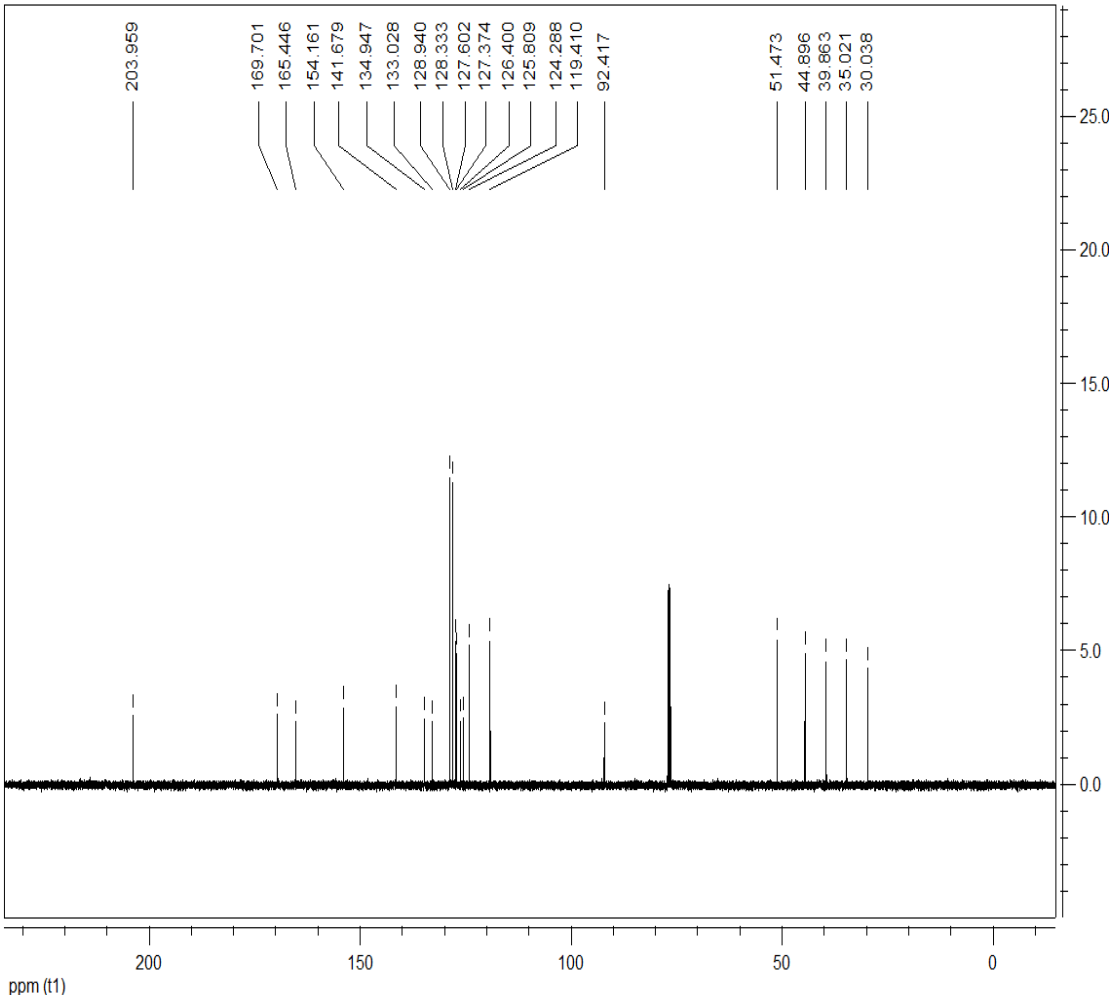

204.150
169.808
164.982
154.286
140.380
136.876
135.033
129.509
127.594
127.208
127.125
126.710
126.300
124.090
119.371
92.503
51.413
45.088
39.842
35.078
29.985
21.069
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (t1)

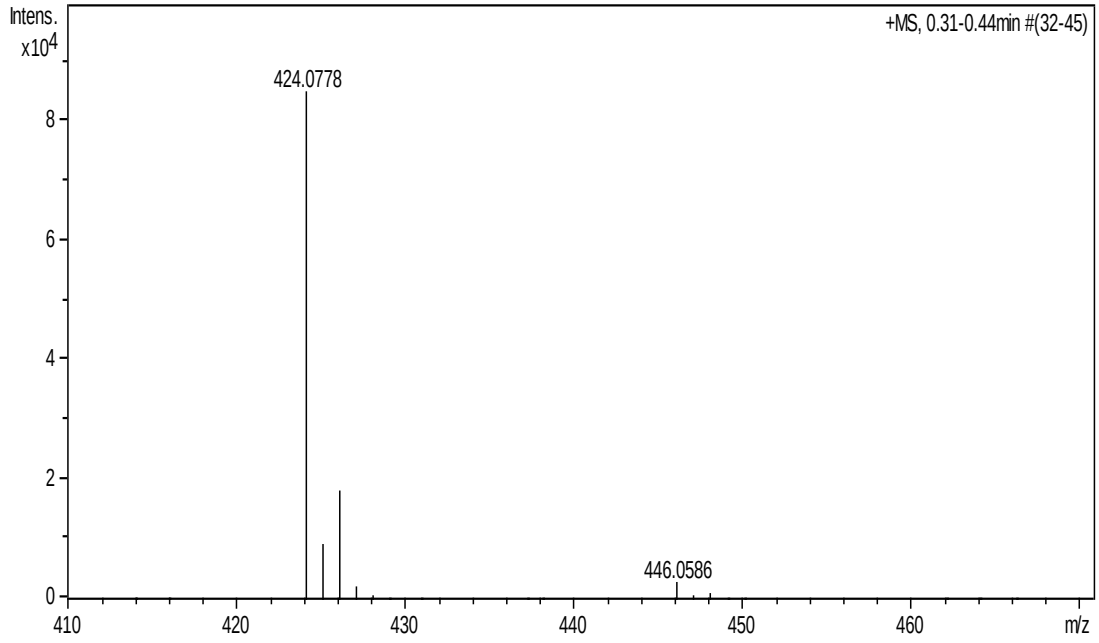

Intens.
x10^4
+MS, 0.25-0.42min #(25-43)
404.1318
426.1132
5
4
3
2
1
0
390
400
410
420
430
440
450
m/z

Methyl4-(4-chlorophenyl)-3-oxo-1,2,3,3a,4,10-hexahydrocyclopenta[b]phenothiazine-11-carboxylate (3b):

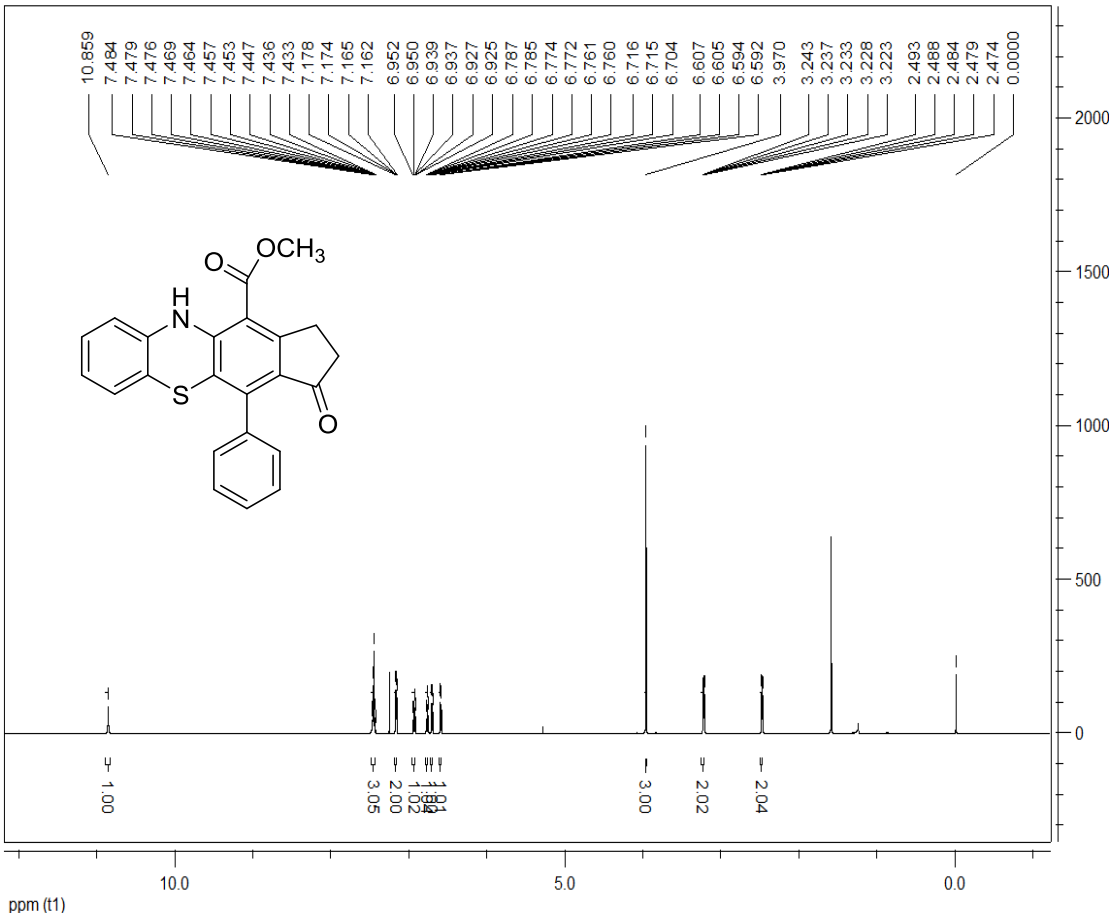
yellow solid, 81%, m.p. 201~203℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.31 (s, 1H, NH), 7.28~7.26 (m, 1H, ArH), 7.23~7.16 (m, 3H, ArH), 7.15~7.09 (m, 3H, ArH), 7.04~7.00 (m, 1H, ArH), 4.03~4.02 (m, 1H, CH), 3.89 (s, 3H, OCH_3), 3.60 (d, *J* = 5.2 Hz, 1H, CH), 3.20~3.13 (m, 1H, CH), 3.07~2.99 (m, 1H, CH), 2.42 (t, *J* = 4.4 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 203.9, 169.7, 165.4, 154.1, 141.6, 134.9, 133.0, 128.9, 128.3, 127.6, 127.3, 126.3, 125.8, 124.2, 119.4, 92.4, 51.4, 44.8, 39.8, 35.0, 30.0; IR (KBr) υ: 3157, 2938, 1695, 1591, 1539, 1483, 1415, 1295, 1266, 1233, 1142, 985, 830, 788, 759cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{24}H_{19}NNaO_3S$ ([M+Na]$^{+}$): 424.0774. Found: 424.0778.

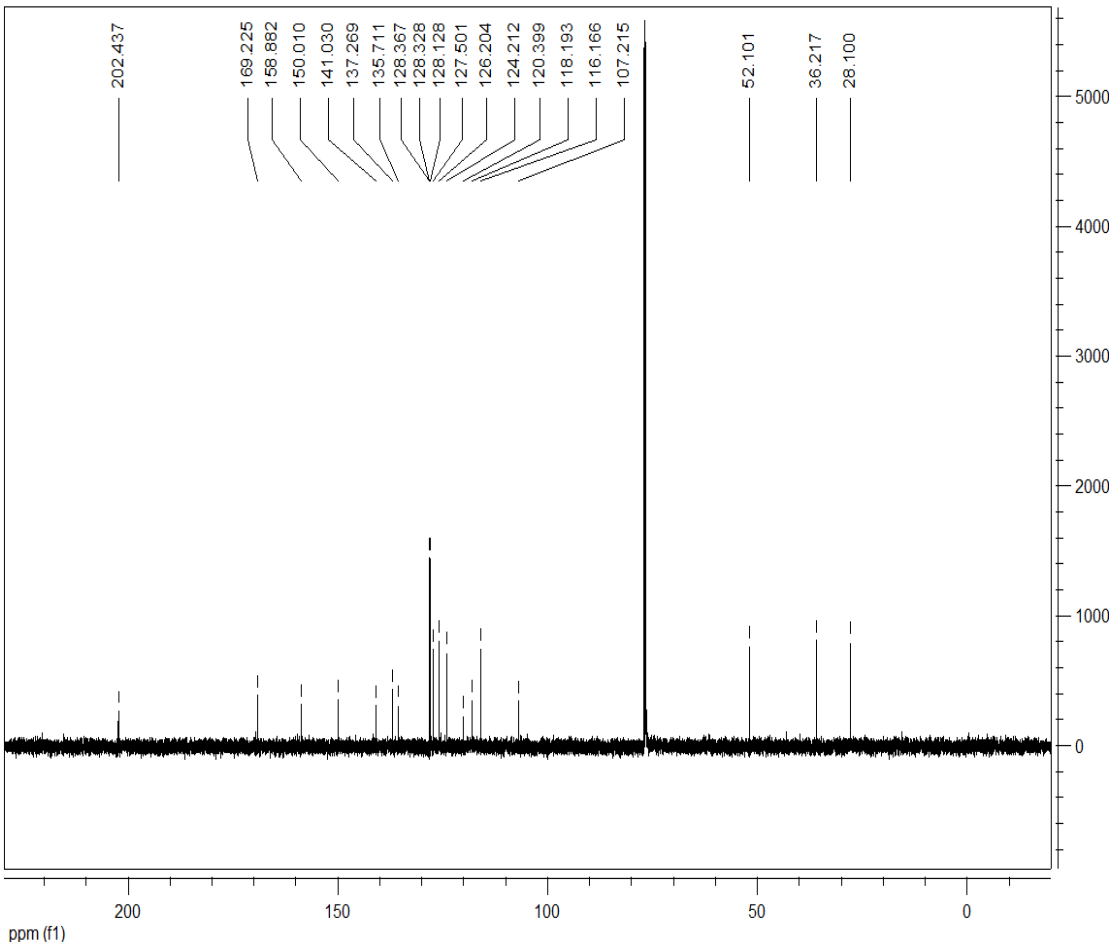


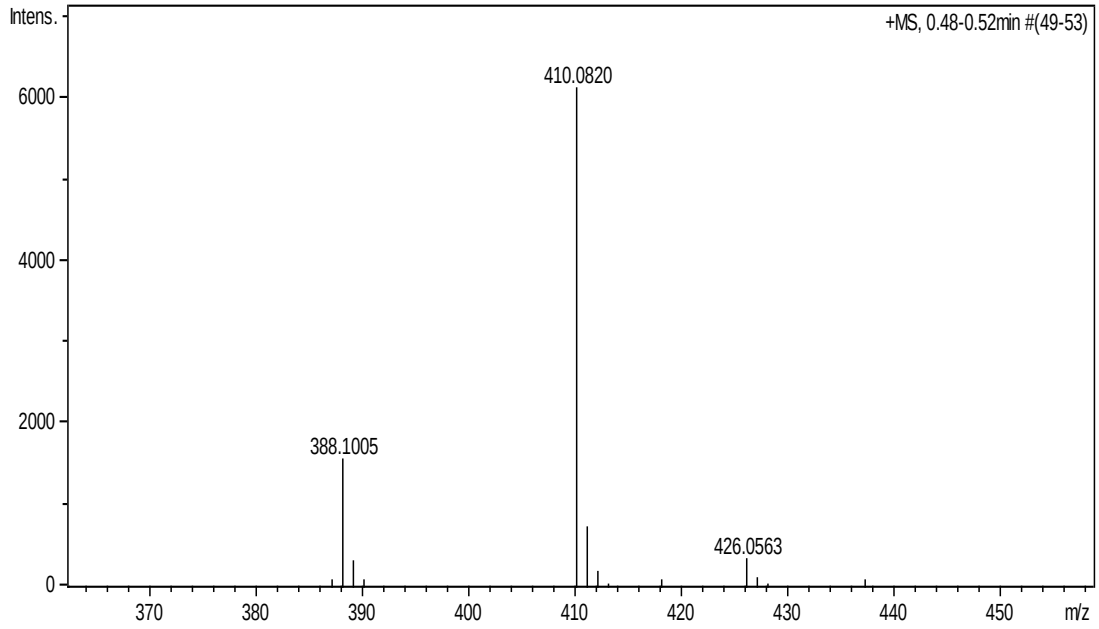

203.959
169.701
165.446
154.161
141.679
134.947
133.028
128.940
128.333
127.602
127.374
126.400
125.809
124.288
119.410
92.417
51.473
44.896
39.863
35.021
30.038
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)


Intens.
x10^4
+MS, 0.31-0.44min #(32-45)
424.0778
446.0586
8
6
4
2
0
410
420
430
440
450
460
m/z

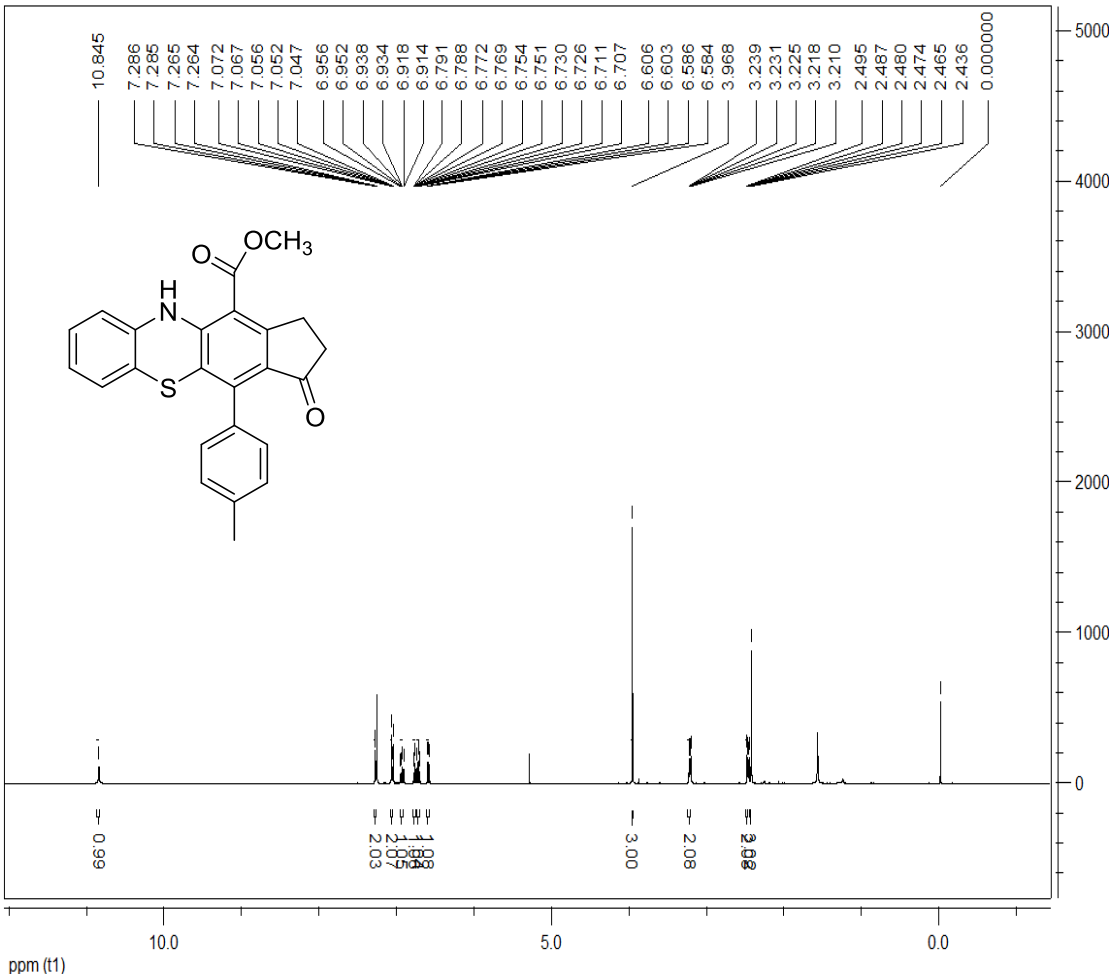
Methyl 3-oxo-4-phenyl-1,2,3,10-tetrahydrocyclopenta[b]phenothiazine-11-carboxylate (4a): yellow solid, 89%, m.p. 286~289℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.86 (s, 1H, NH), 7.48~7.43 (m, 3H, ArH), 7.18~7.16 (m, 2H, ArH), 6.95~6.93 (m, 1H, ArH), 6.79~6.76 (m, 1H, ArH), 6.72~6.70 (m, 1H, ArH), 6.61~6.59 (m, 1H, ArH), 3.97 (s, 3H, OCH_3), 3.24~3.22 (m, 2H, CH_2), 2.49~2.47 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.4, 169.2, 158.9, 150.0, 141.0, 137.3, 135.7, 128.4, 128.3, 128.1, 127.5, 126.2, 124.2, 120.4, 118.2, 116.2, 107.2, 52.1, 36.2, 28.1; IR (KBr) υ: 3291, 2977, 1675, 1569, 1514, 1435, 1410, 1325, 1299, 1249, 1220, 1146, 965, 933, 846, 749cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{23}H_{17}NNaO_3S$ ([M+Na]$^{+}$): 410.0827. Found: 410.0820.

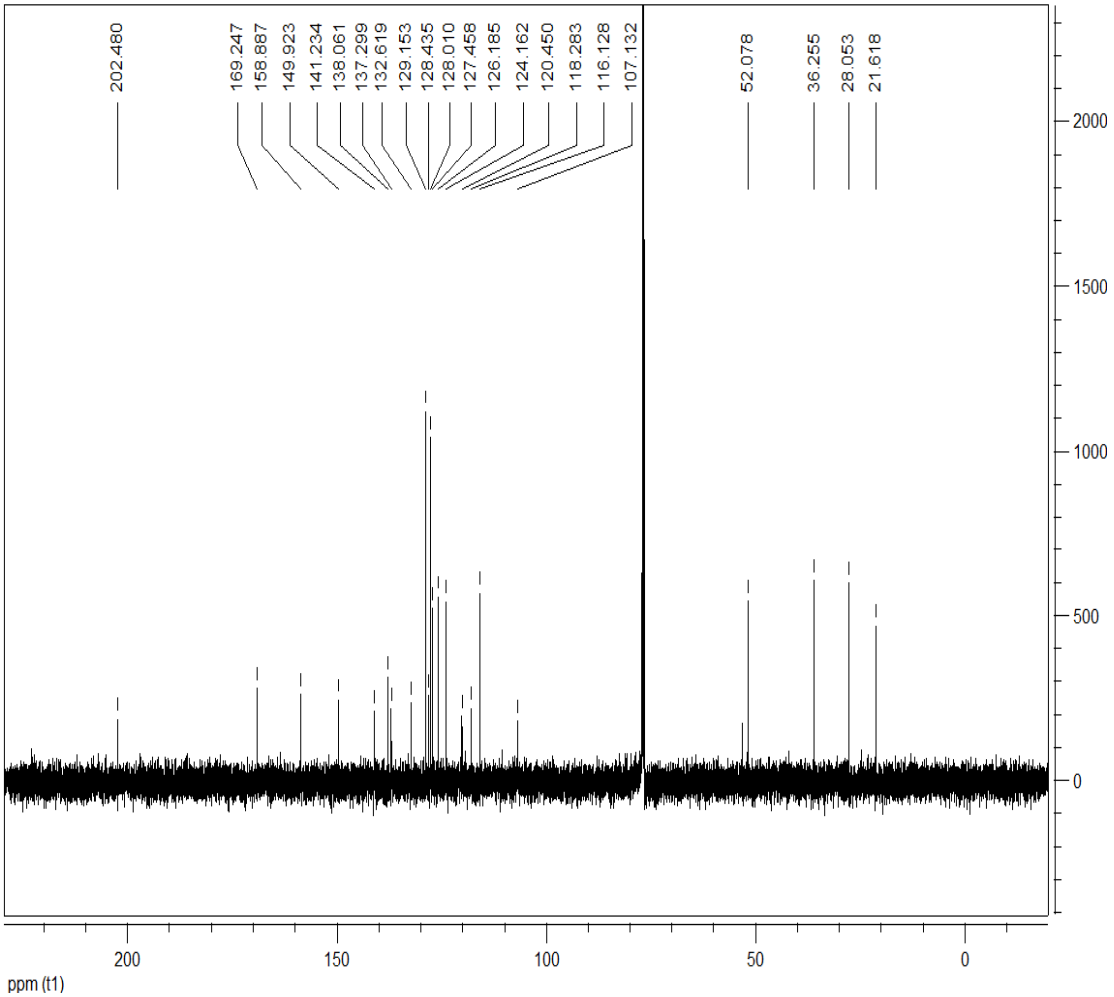


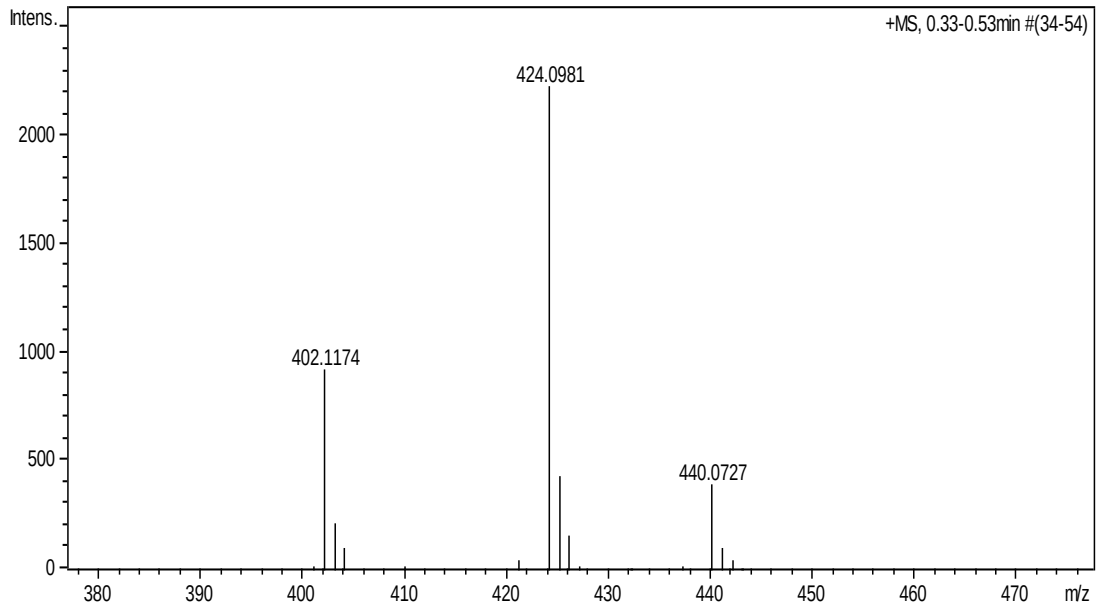

202.437
169.225
158.882
150.010
141.030
137.269
135.711
128.367
128.328
128.128
127.501
126.204
124.212
120.399
118.193
116.166
107.215
52.101
36.217
28.100
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.48-0.52min #(49-53)
410.0820
6000
4000
2000
388.1005
426.0563
0
370
380
390
400
410
420
430
440
450
m/z

Methyl 3-oxo-4-phenyl-1,2,3,10-tetrahydrocyclopenta[b]phenothiazine-11-carboxylate (4b): yellow solid, 95%, m.p. 240~242℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.85 (s, 1H, NH), 7.29~7.26 (m, 2H, ArH), 7.07~7.05 (m, 2H, ArH), 6.97~6.91 (m, 1H, ArH), 6.79~6.75 (m, 1H, ArH), 6.73~6.71 (m, 1H, ArH), 6.61~6.58 (m, 1H, ArH), 3.97 (s, 3H, OCH_3), 3.24~3.21 (m, 2H, CH_2), 2.35~2.33 (m, 2H, CH_2), 2.24 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.5, 169.2, 158.9, 149.9, 141.2, 138.1, 137.3, 132.6, 129.2, 128.4, 128.0, 127.5, 126.2, 124.2, 120.5, 118.3, 116.1, 107.1, 52.1, 36.3, 28.1, 21.6; IR (KBr) υ: 3157, 2938, 1695, 1591, 1539, 1483, 1415, 1295, 1266, 1233, 1142, 985, 830, 788, 759cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{24}H_{19}NNaO_3S$ ($[M+Na]^+$): 424.0983. Found: 424.0981.




202.480
169.247
158.887
149.923
141.234
138.061
137.299
132.619
129.153
128.435
128.010
127.458
126.185
124.162
120.450
118.283
116.128
107.132
52.078
36.255
28.053
21.618
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)

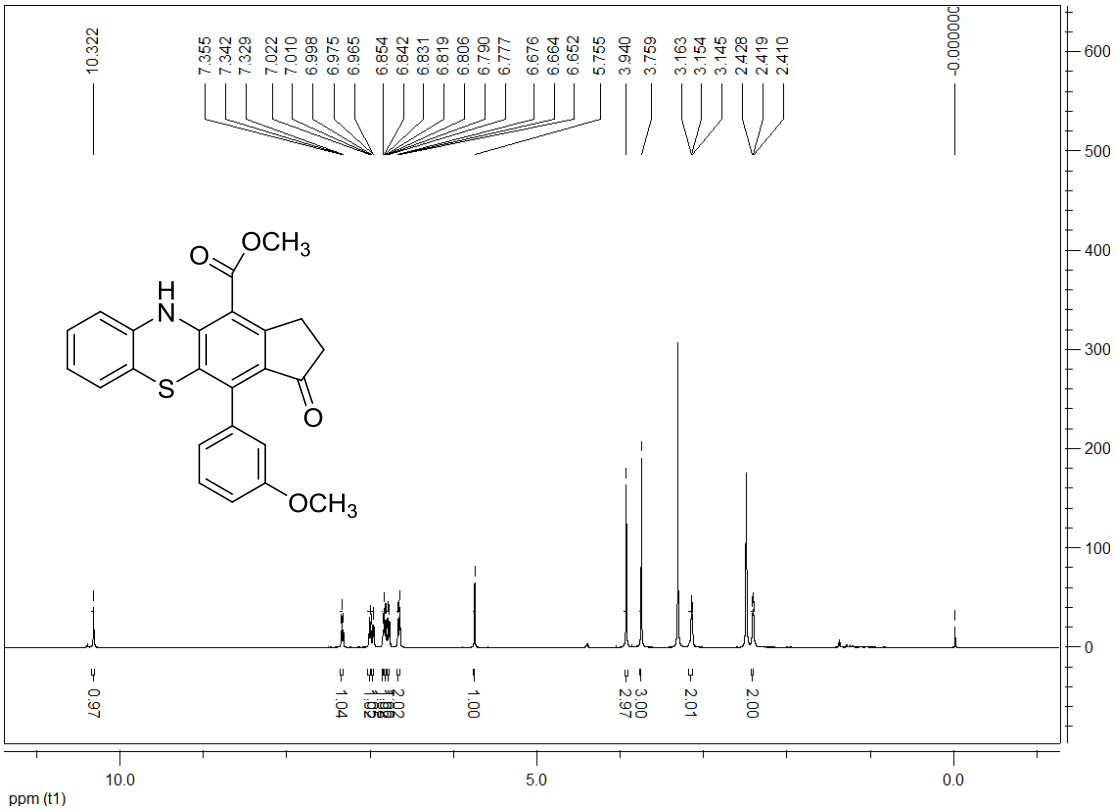

Intens.
+MS, 0.33-0.53min #(34-54)
424.0981
402.1174
440.0727
2000
1500
1000
500
0
380
390
400
410
420
430
440
450
460
470
m/z

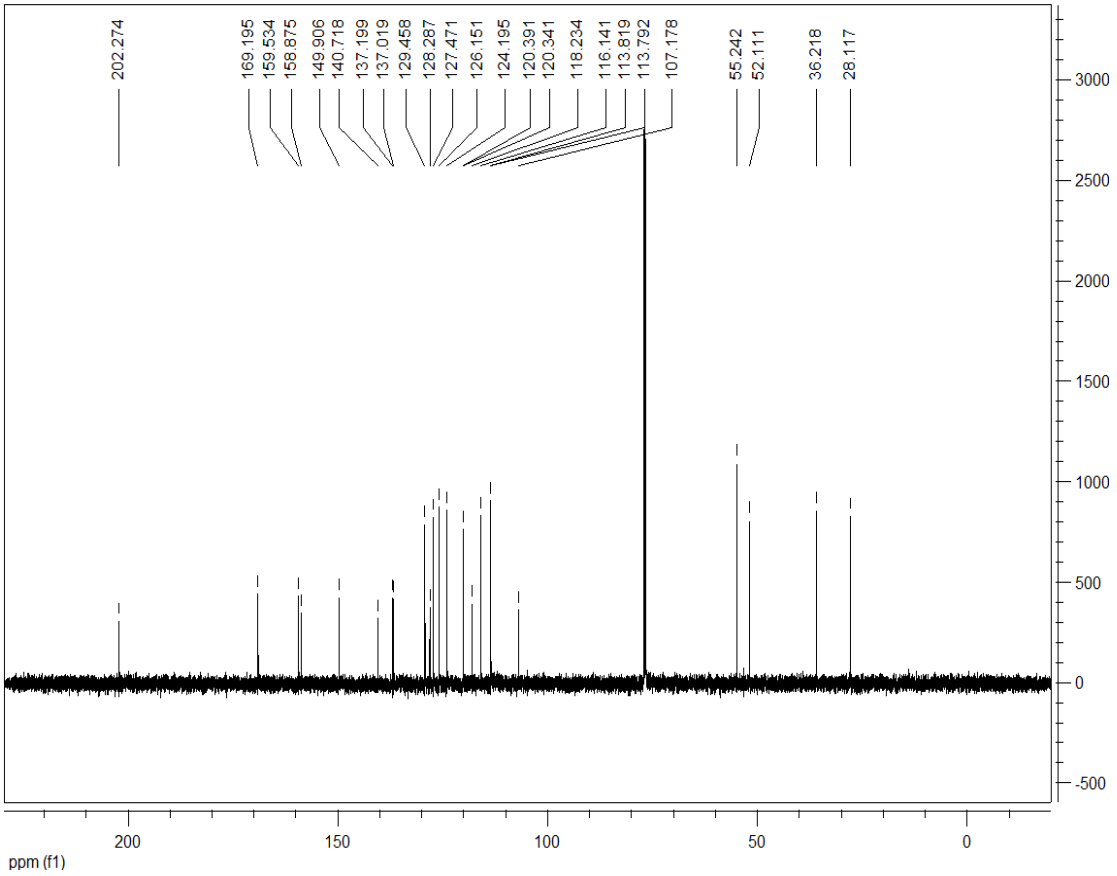
Methyl

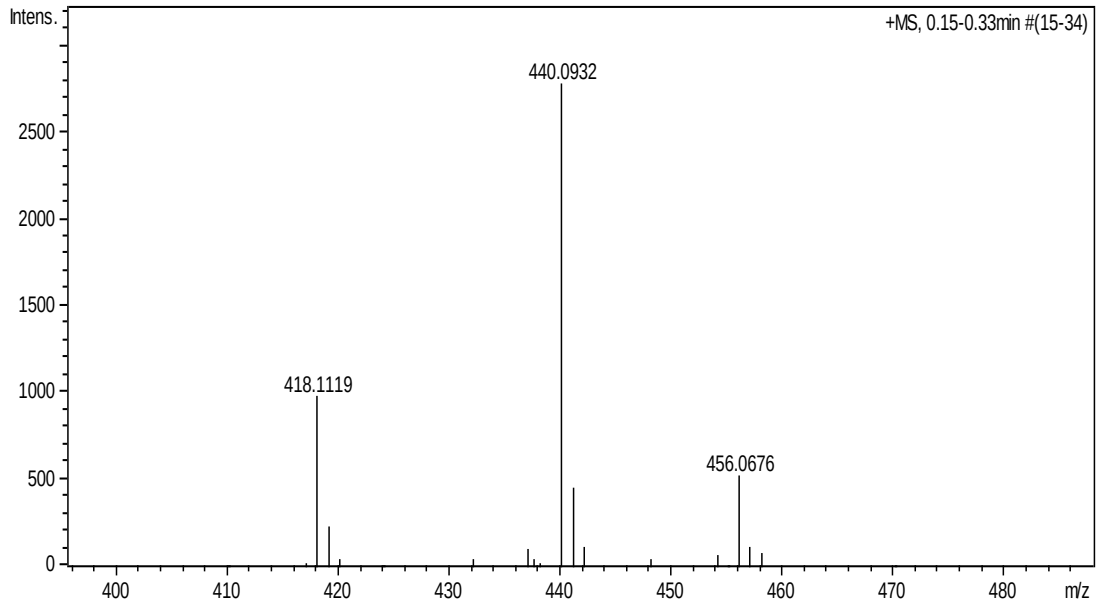
4-(3-methoxyphenyl)-3-oxo-1,2,3,10-tetrahydrocyclopenta[b]phenothiazine-11-carboxylate

(4c):

yellow solid, 91%, m.p. 233~235℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.32 (s, 1H, NH), 7.34 (t, *J* = 5.2 Hz, 1H, ArH), 7.01 (t, *J* = 4.8 Hz, 1H, ArH), 6.97 (d, *J* = 4.0 Hz, 1H, ArH), 6.85 (d, *J* = 4.8 Hz, 1H, ArH), 6.83~6.81 (m, 2H, ArH), 6.78 (d, *J* = 5.2 Hz, 1H, ArH), 6.68~6.65 (m, 2H, ArH), 5.76 (s, 1H, ArH), 3.94 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.24~3.21 (m, 2H, CH_2), 3.15 (t, *J* = 3.6 Hz, 2H, CH_2), 2.42 (t, *J* = 3.6 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.3, 169.2, 159.5, 158.9, 149.9, 140.7, 137.2, 137.0, 129.5, 128.3, 127.5, 126.2, 124.2, 120.4, 120.3, 118.2, 116.1, 113.8, 113.8, 107.2, 55.2, 52.1, 36.2, 28.1; IR (KBr) υ: 3733, 3318, 3112, 3071, 3015, 2947, 1927, 1736, 1662, 1609, 1580, 1545, 1472, 1437, 1375, 1322, 1271, 1233, 1198, 1088, 1006, 933, 861, 841, 791, 757 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{24}H_{19}NNaO_4S$ ([M+Na]$^{+}$): 440.0932. Found: 440.0932.




202.274
169.195
159.534
158.875
149.906
140.718
137.199
137.019
129.458
128.287
127.471
126.151
124.195
120.391
120.341
118.234
116.141
113.819
113.792
107.178
55.242
52.111
36.218
28.117
3000
2500
2000
1500
1000
500
0
-500
200
150
100
50
0
ppm (f1)

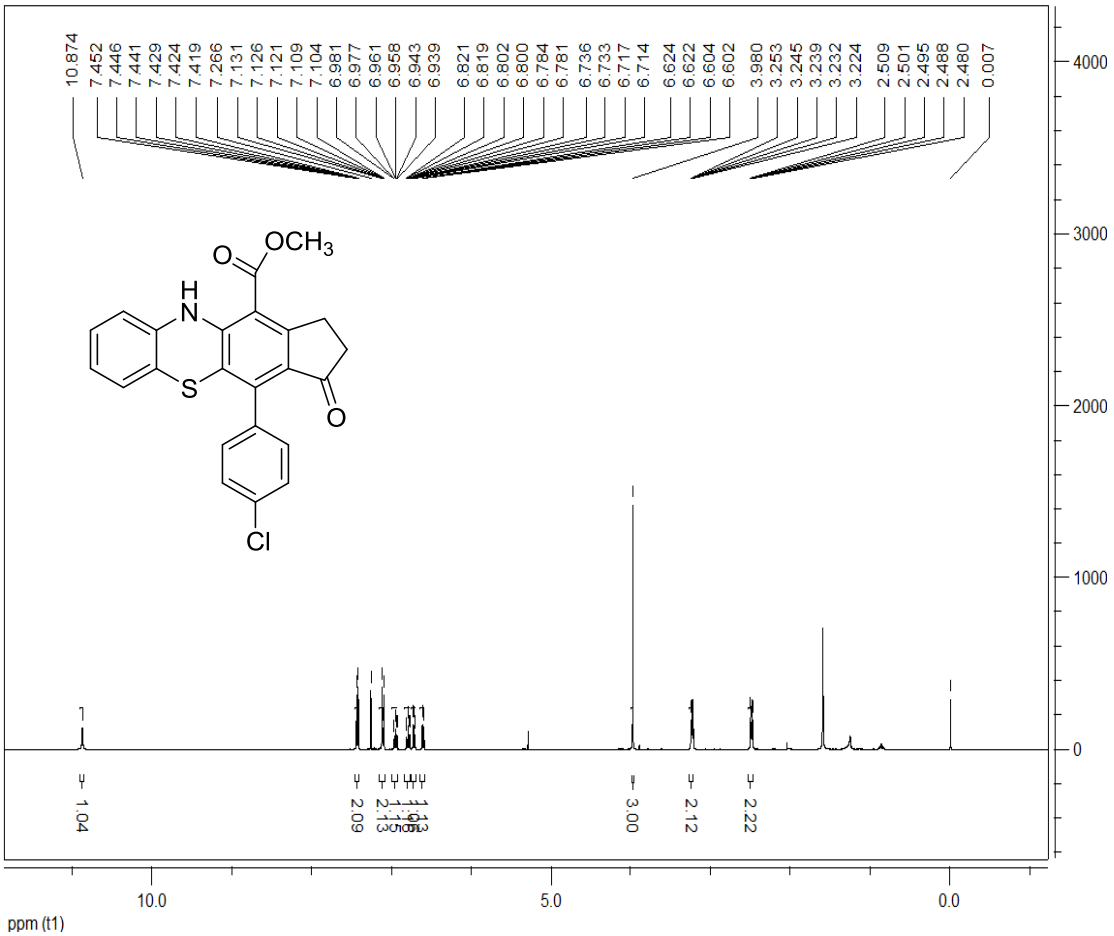

Intens.
+MS, 0.15-0.33min #(15-34)
440.0932
418.1119
456.0676
2500
2000
1500
1000
500
0
400
410
420
430
440
450
460
470
480
m/z

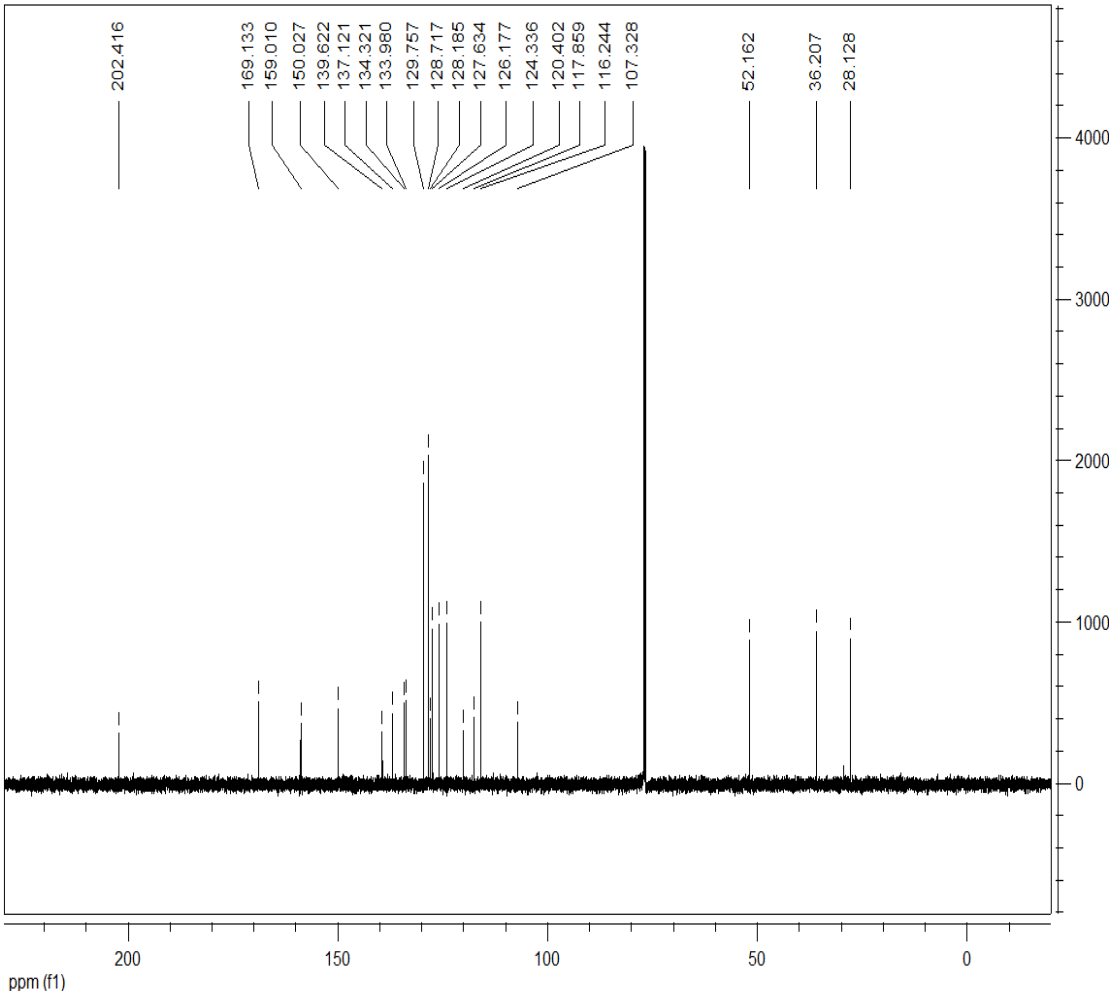
Methyl

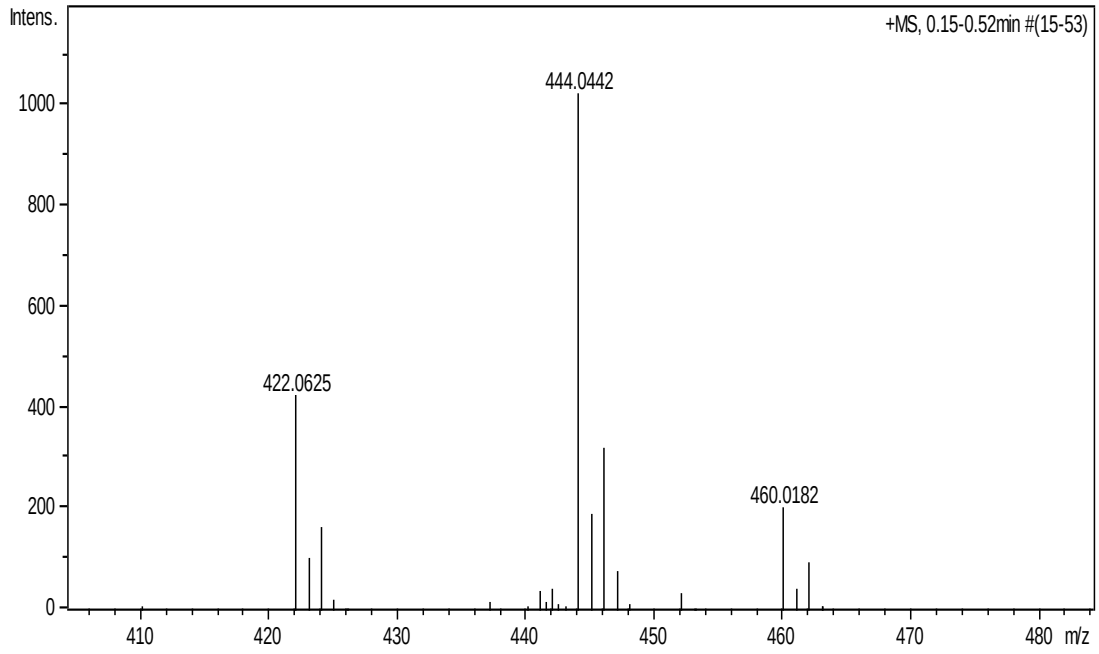
4-(4-chlorophenyl)-3-oxo-1,2,3,10-tetrahydrocyclopenta[b]phenothiazine-11-carboxylate

(4d):

yellow solid, 88%, m.p. 248~250℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.87 (s, 1H, NH), 7.45~7.42 (m, 2H, ArH), 7.13~7.10 (m, 2H, ArH), 6.98~6.94 (m, 1H, ArH), 6.82~6.78 (m, 1H, ArH), 6.74~6.71 (m, 1H, ArH), 6.62~6.60 (m, 1H, ArH), 3.98 (s, 3H, OCH_3), 3.25~3.22 (m, 2H, CH_2), 2.51~2.48 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.4, 169.1, 159.0, 150.0, 139.6, 137.1, 134.3, 134.0, 129.8, 128.7, 128.2, 127.6, 126.2, 124.3, 120.4, 117.9, 116.2, 107.3, 52.2, 36.2, 28.1; IR (KBr) υ: 3733, 3318, 3112, 3071, 3015, 2947, 1927, 1736, 1662, 1609, 1580, 1545, 1472, 1437, 1375, 1322, 1271, 1233,1198, 1088, 1006, 933, 861, 841, 791, 757 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{23}H_{16}ClNNaO_3S$ ([M+Na]$^+$): 444.0437. Found: 444.0442.

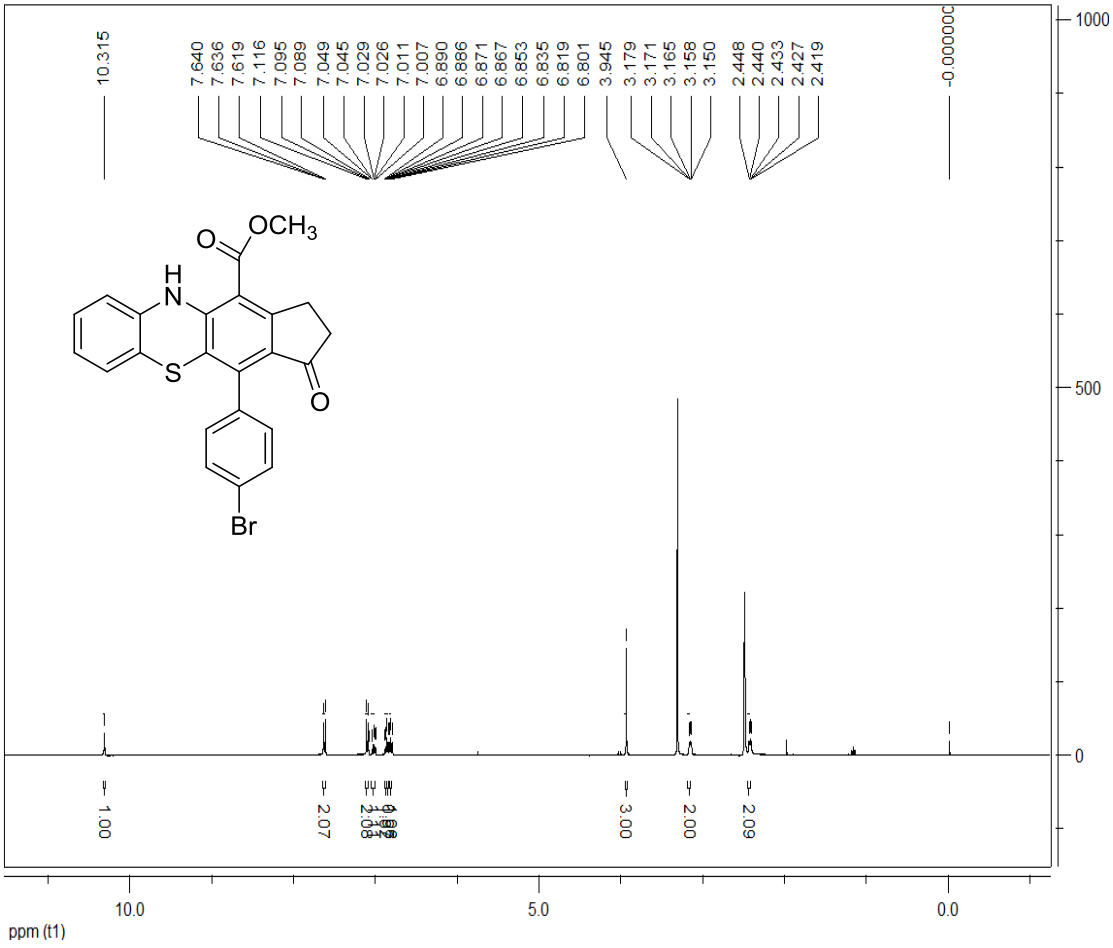


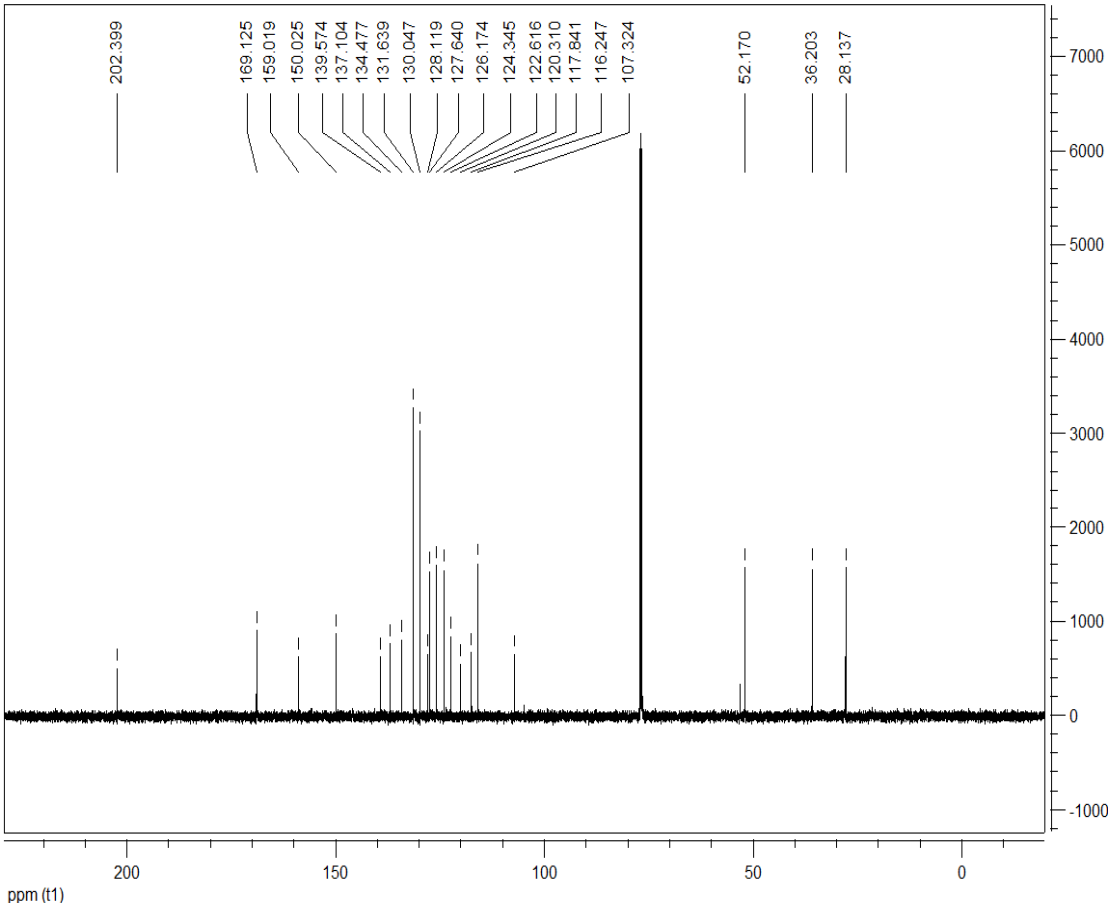

202.416
169.133
159.010
150.027
139.622
137.121
134.321
133.980
129.757
128.717
128.185
127.634
126.177
124.336
120.402
117.859
116.244
107.328
52.162
36.207
28.128
4000
3000
2000
1000
0
200
150
100
50
0
ppm (f1)

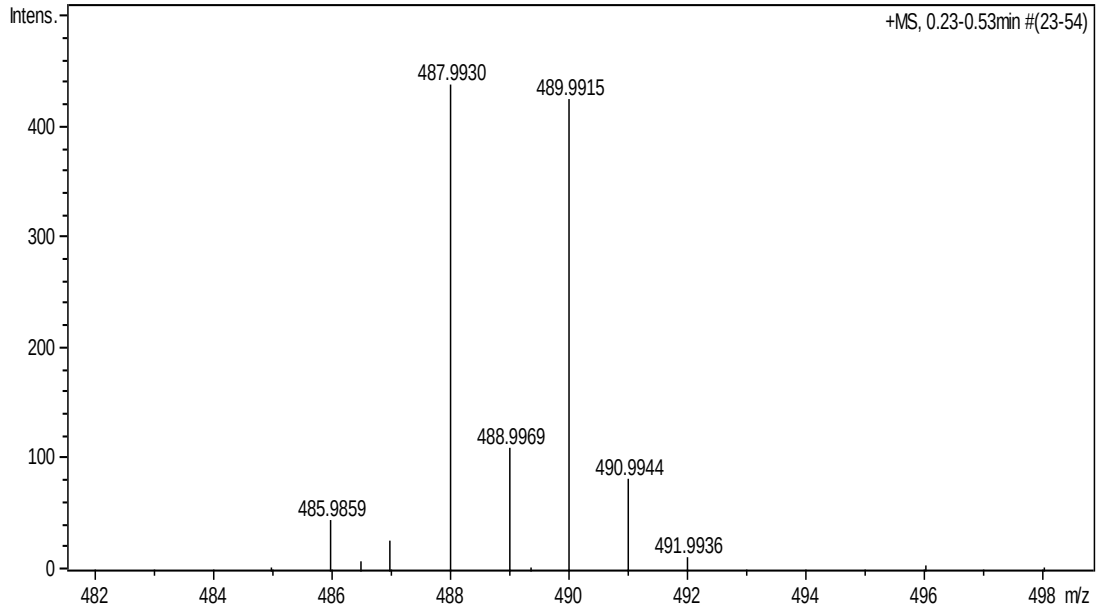

Intens.
+MS, 0.15-0.52min #(15-53)
444.0442
422.0625
460.0182
1000
800
600
400
200
0
410
420
430
440
450
460
470
480
m/z

Methyl4-(4-bromophenyl)-3-oxo-1,2,3,10-tetrahydrocyclopenta[b]phenothiazine-11-carboxylate (4e):

yellow solid, 87%, m.p. 234~236℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.32 (s, 1H, NH), 7.64~7.62 (m, 2H, ArH), 7.12~7.09 (m, 2H, ArH), 6.98~6.87 (m, 1H, ArH), 6.84 (d, J = 4.0 Hz, 1H, ArH), 6.81 (d, J = 4.8 Hz, 1H, ArH), 3.95 (s, 3H, OCH_3), 3.18~3.15 (m, 2H, CH_2), 2.45~2.42 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.4, 169.1, 159.0, 150.0, 139.6, 137.1, 134.5, 131.6, 130.0, 128.1, 127.6, 126.2, 124.3, 122.6, 120.3, 117.8, 116.2, 107.3, 52.2, 36.2, 28.1; IR (KBr) υ: 3515, 2936, 1701, 1673, 1592, 1538, 1483, 1414, 1294, 1263, 1229, 1141, 1072, 1012, 835, 788, 763 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{23}H_{16}BrNNaO_3S$ ([M+Na]$^{+}$): 487.9932. Found: 487.9930.



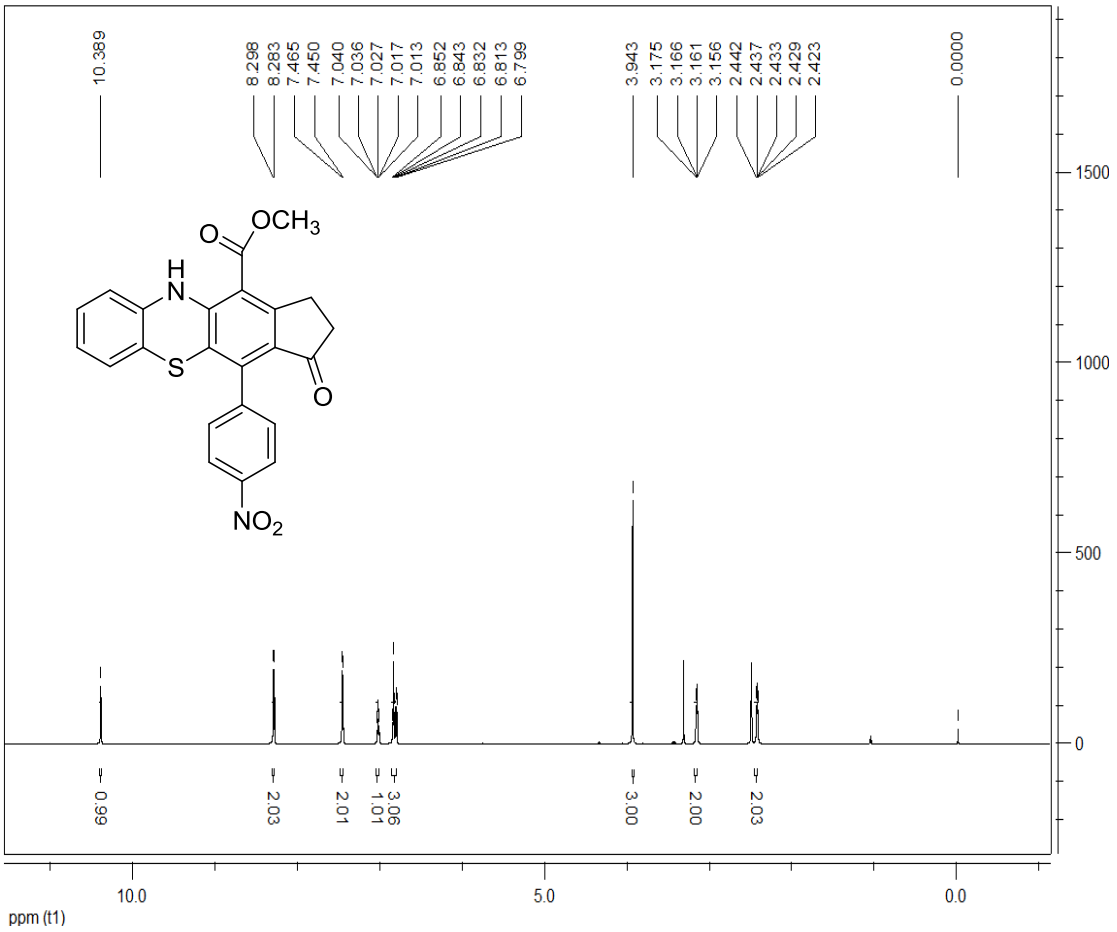

202.399
169.125
159.019
150.025
139.574
137.104
134.477
131.639
130.047
128.119
127.640
126.174
124.345
122.616
120.310
117.841
116.247
107.324
52.170
36.203
28.137
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
150
100
50
0
ppm (t1)

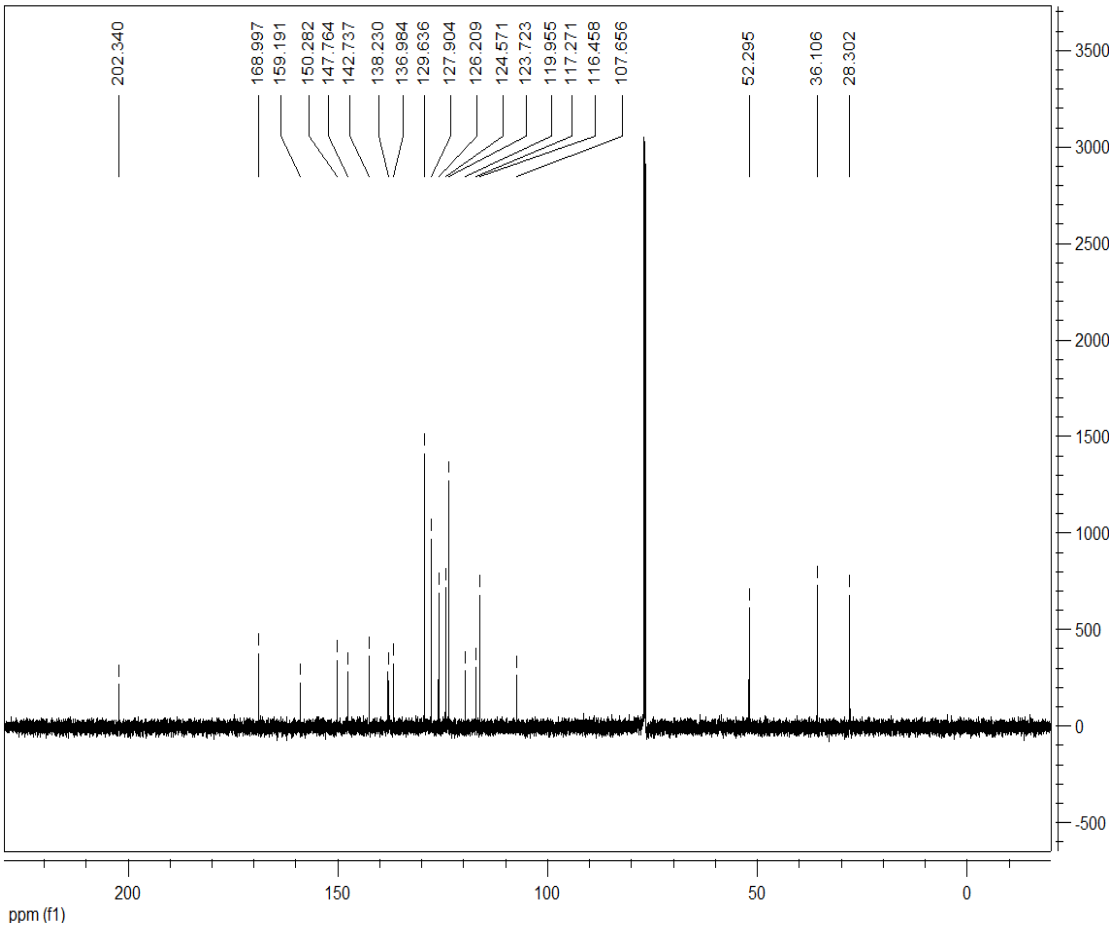

Intens.
+MS, 0.23-0.53min #(23-54)
487.9930
489.9915
488.9969
490.9944
485.9859
491.9936
400
300
200
100
0
482
484
486
488
490
492
494
496
498
m/z

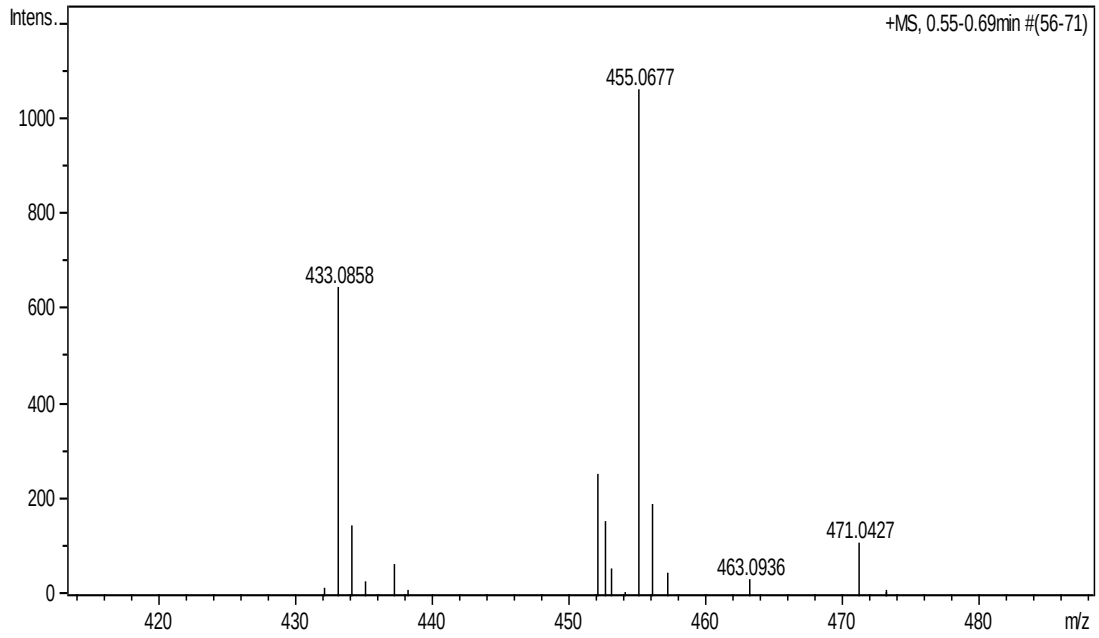
Methyl

4-(4-nitrophenyl)-3-oxo-1,2,3,10-tetrahydrocyclopenta[b]phenothiazine-11-carboxylate (4f):

yellow solid, 92%, m.p. 248~250℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.39 (s, 1H, NH), 8.29 (d, J = 6.0 Hz, 2H, ArH), 7.46 (d, J = 6.0 Hz, 2H, ArH), 7.04~7.01 (m, 1H, ArH), 6.85~6.80 (m, 3H, ArH), 3.94 (s, 3H, OCH_3), 3.18~3.16 (m, 2H, CH_2), 2.44~2.42 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.3, 169.0, 159.2, 150.3, 147.8, 142.7, 138.2, 137.0, 129.6, 127.9, 126.2, 124.6, 123.7, 120.0, 117.3, 116.5, 107.7, 52.3, 36.1, 28.3; IR (KBr) υ: 3169, 2955, 1681, 1588, 1483, 1437, 1412, 1340, 1293, 1261, 1215, 1137, 1104, 973, 860, 795, 749, 722cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{23}H_{16}N_2NaO_5S$ ([M+Na]$^+$): 455.0678. Found: 455.0677.



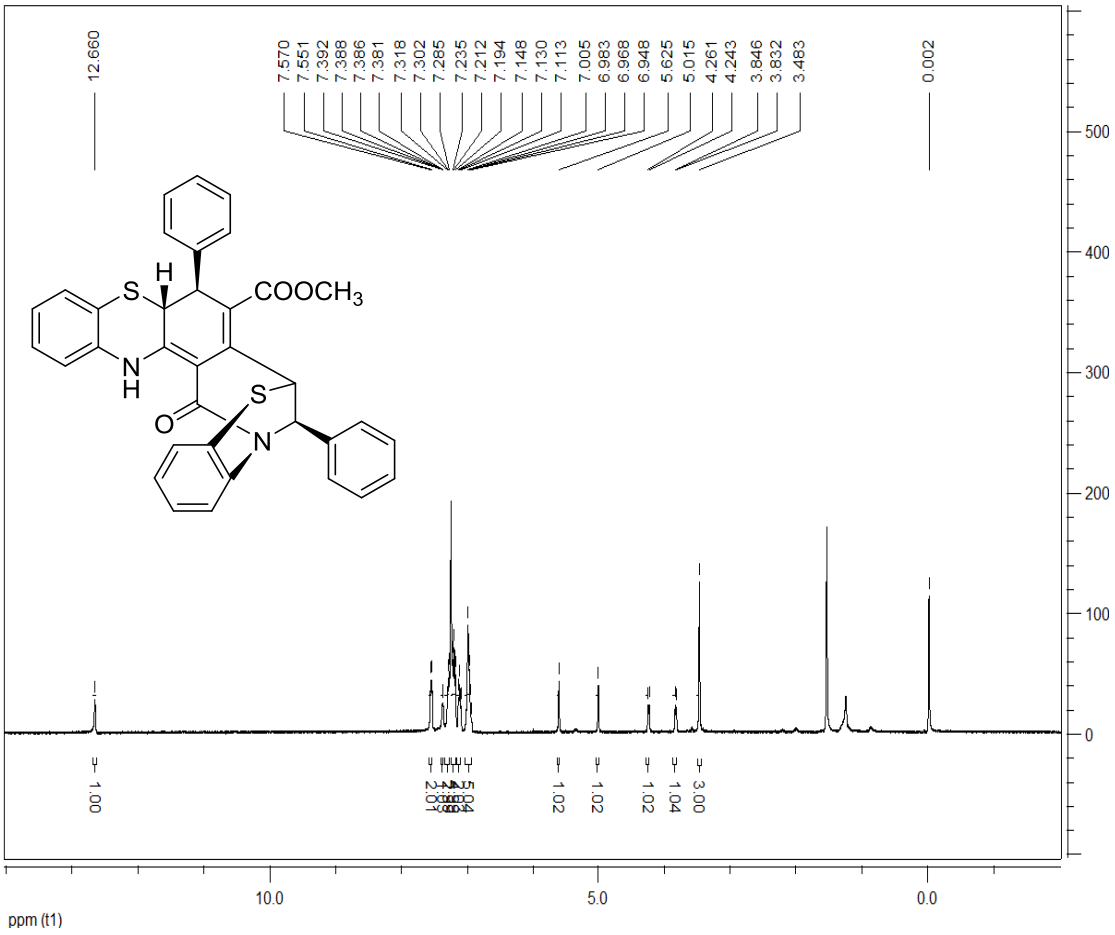

202.340
168.997
159.191
150.282
147.764
142.737
138.230
136.984
129.636
127.904
126.209
124.571
123.723
119.955
117.271
116.458
107.656
52.295
36.106
28.302
3500
3000
2500
2000
1500
1000
500
0
-500
200
150
100
50
0
ppm (f1)

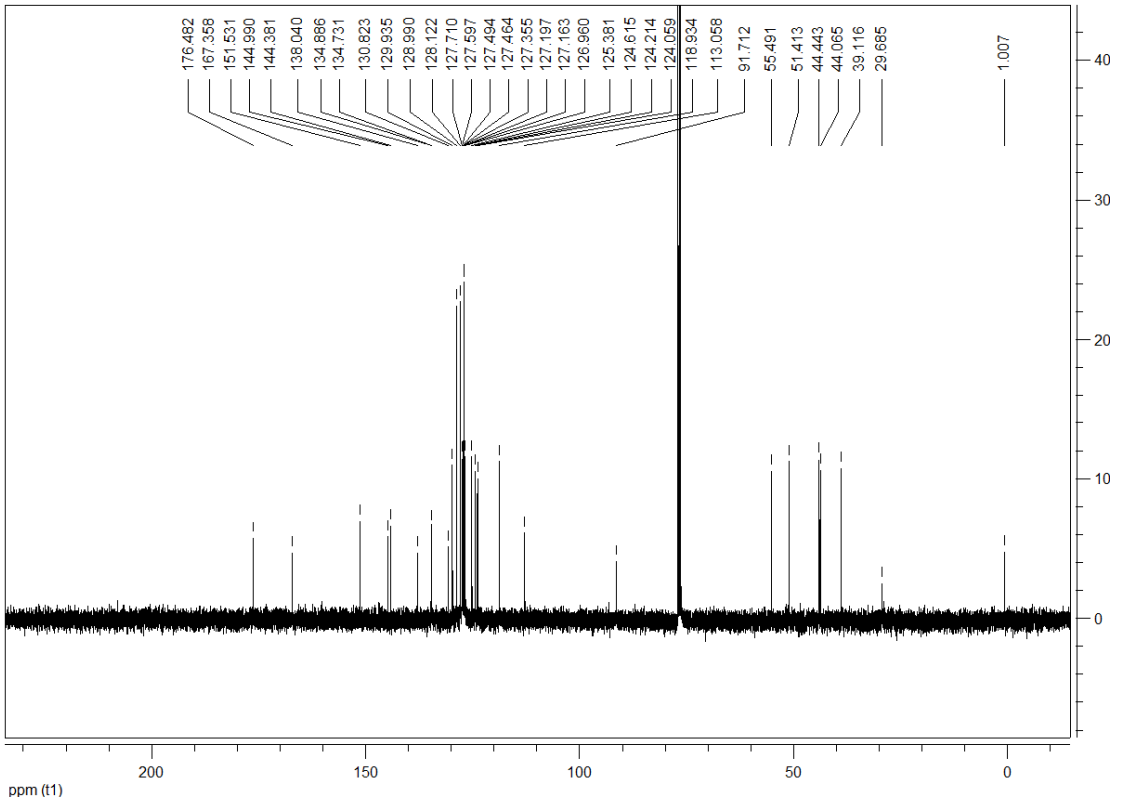

Intens.
+MS, 0.55-0.69min #(56-71)
455.0677
433.0858
471.0427
463.0936
1000
800
600
400
200
0
420
430
440
450
460
470
480
m/z

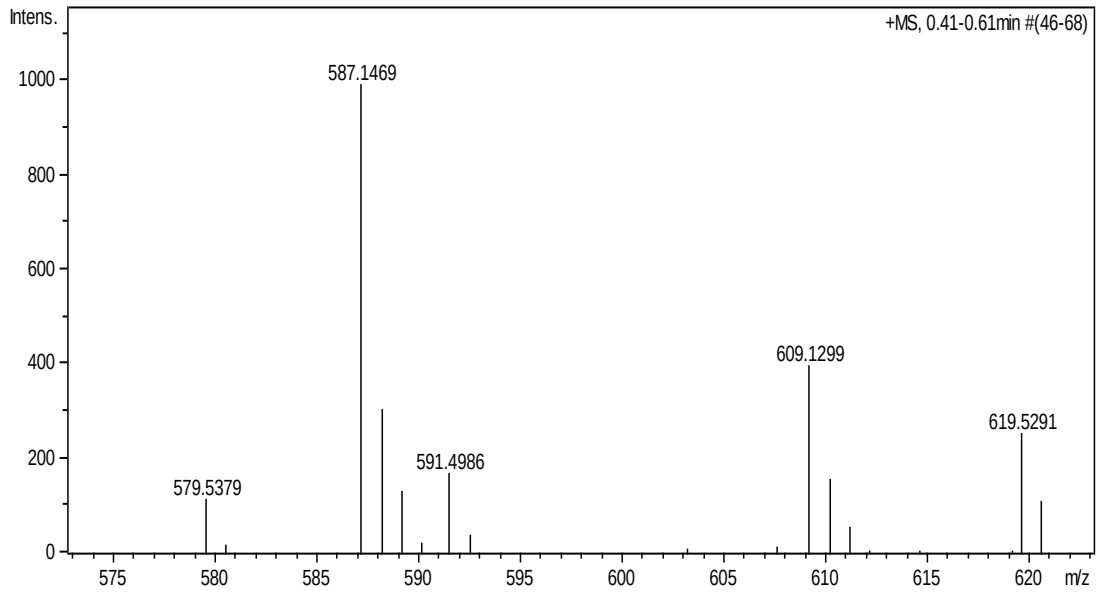
Methyl

15-oxo-6,17-diphenyl-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5a):

yellow solid, 78%, m.p. 213~215℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.66 (s, 1H, NH), 7.61 (d, *J* = 7.6 Hz, 2H, ArH), 7.39~7.38 (m, 1H, ArH), 7.32~7.29 (m, 3H, ArH), 7.24~7.19 (m, 5H, ArH), 7.15~7.11 (m, 2H, ArH), 7.01~6.95 (m, H, ArH), 5.63 (s, 1H, CH), 5.02 (s, 1H, CH), 4.25 (d, *J* = 7.2 Hz, 1H, CH), 3.84 (d, *J* =5.6 Hz, 1H, CH), 3.48 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.1, 149.9, 139.0, 135.7, 134.2, 133.7, 129.9, 129.7, 129.6, 129.1, 128.8, 128.8, 128.3, 126.9, 126.6, 126.2, 124.7, 123.3, 120.9, 119.3, 115.8, 114.4, 107.1, 73.2, 51.4, 24.9, 21.2, ; IR (KBr) υ: 3454, 2943, 1713, 1609, 1594,1579, 1554, 1480, 1464, 1431, 1346, 1303, 1274, 1228, 1150, 1126, 1029, 887, 840, 812, 752 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{27}N_2O_3S_2$ ($[M+H]^+$): 587.1463. Found: 587.1469.



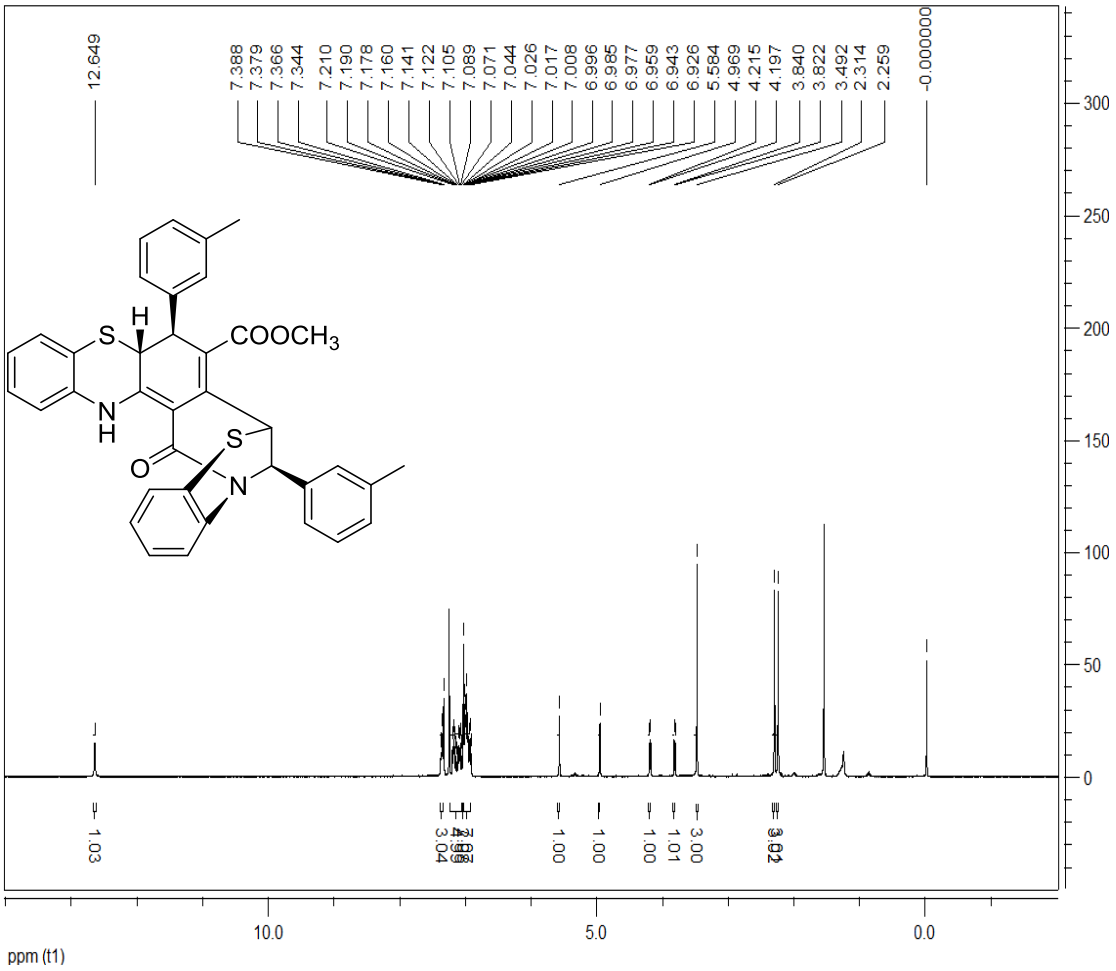

176.482
167.358
151.531
144.990
144.381
138.040
134.886
134.731
130.823
129.935
128.990
128.122
127.710
127.597
127.494
127.464
127.355
127.197
127.163
126.960
125.381
124.615
124.214
124.059
118.934
113.058
91.712
55.491
51.413
44.443
44.065
39.116
29.685
1.007
40
30
20
10
0
200
150
100
50
0
ppm (t1)

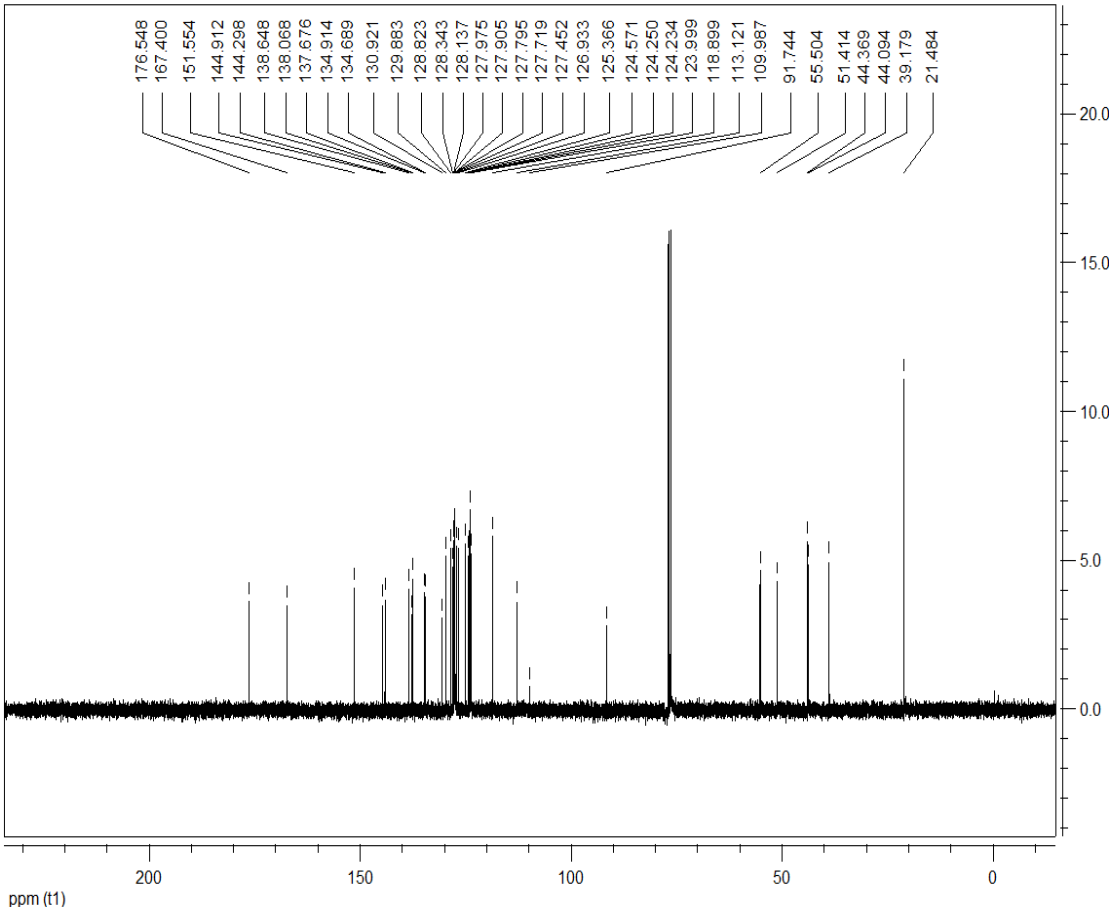

Intens.
+MS, 0.41-0.61min #(46-68)
587.1469
609.1299
619.5291
591.4986
579.5379
1000
800
600
400
200
0
575
580
585
590
595
600
605
610
615
620
m/z

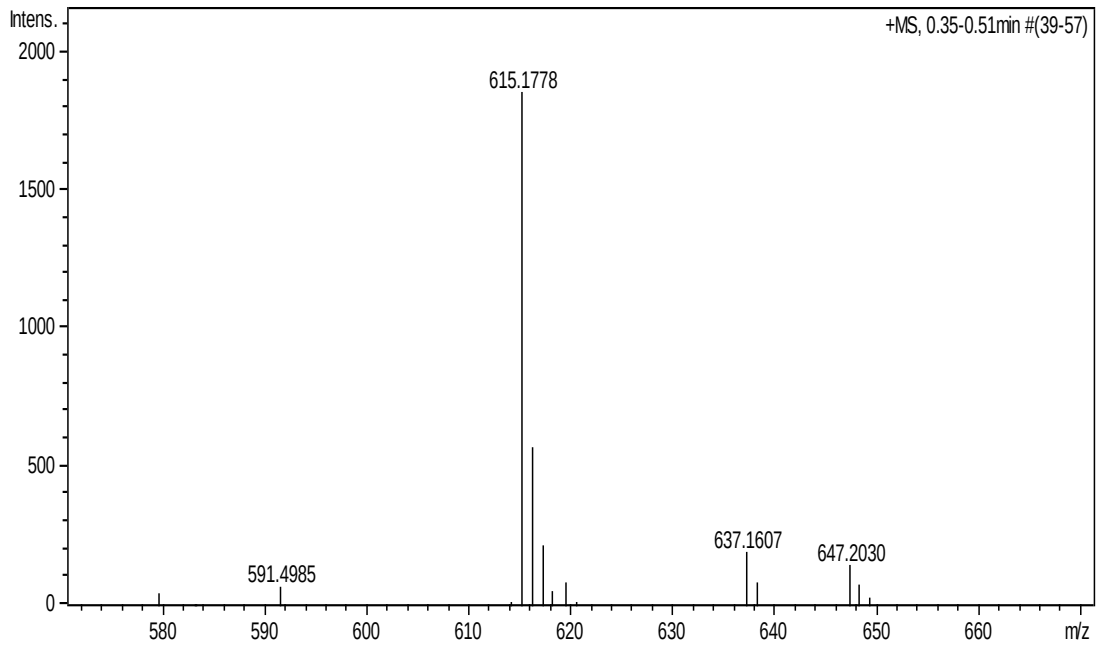
Methyl

15-oxo-6,17-di-m-tolyl-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5b):

yellow solid, 79%, m.p. 265~267℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.65 (s, 1H, NH), 7.39~7.34 (m, 3H, ArH), 7.21~7.07 (m, 5H, ArH), 7.04 (s, 2H, ArH), 7.03~6.93 (m, 7H, ArH), 5.58 (s, 1H, CH), 4.97 (s, 1H, CH), 4.21 (d, *J* = 7.2 Hz, CH), 3.83 (d, *J* = 7.2Hz, CH), 3.49 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3), 2.26 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.0, 149.3, 137.1, 135.7, 133.7, 129.7, 129.1, 128.9, 128.8, 128.4, 127.1, 126.9, 126.4, 126.3, 126.2, 122.8, 120.8, 118.8, 116.1, 107.1, 73.3, 51.5, 24.9; IR (KBr) υ: 3861, 3019, 2946, 1702, 1579, 1552, 1515, 1466, 1433, 1347, 1274, 1230, 1129, 1059, 1023, 981, 900, 813, 781, 754, 743, 709 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{31}N_2O_3S_2$ ([M+H]$^+$): 615.1776. Found: 615.1779.



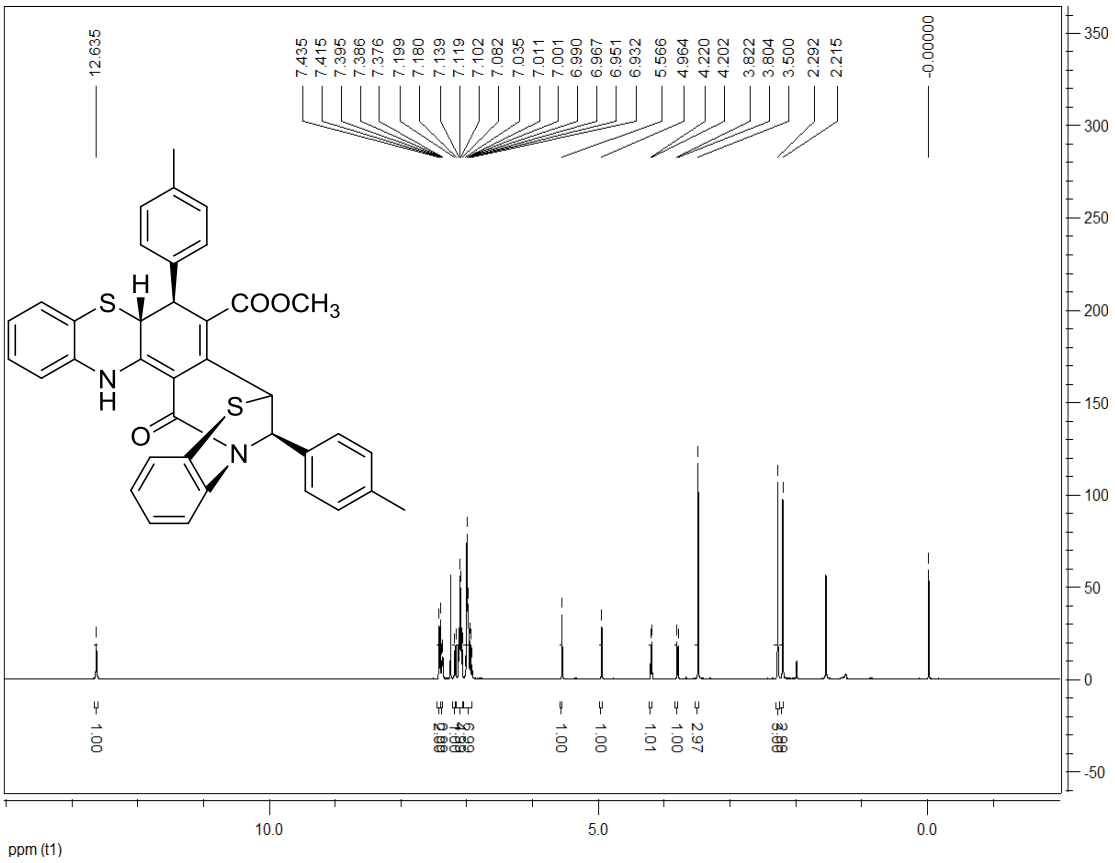

176.548
167.400
151.554
144.912
144.298
138.648
138.068
137.676
134.914
134.689
130.921
129.883
128.823
128.343
128.137
127.975
127.905
127.795
127.719
127.452
126.933
125.366
124.571
124.250
124.234
123.999
118.899
113.121
109.987
91.744
55.504
51.414
44.369
44.094
39.179
21.484
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

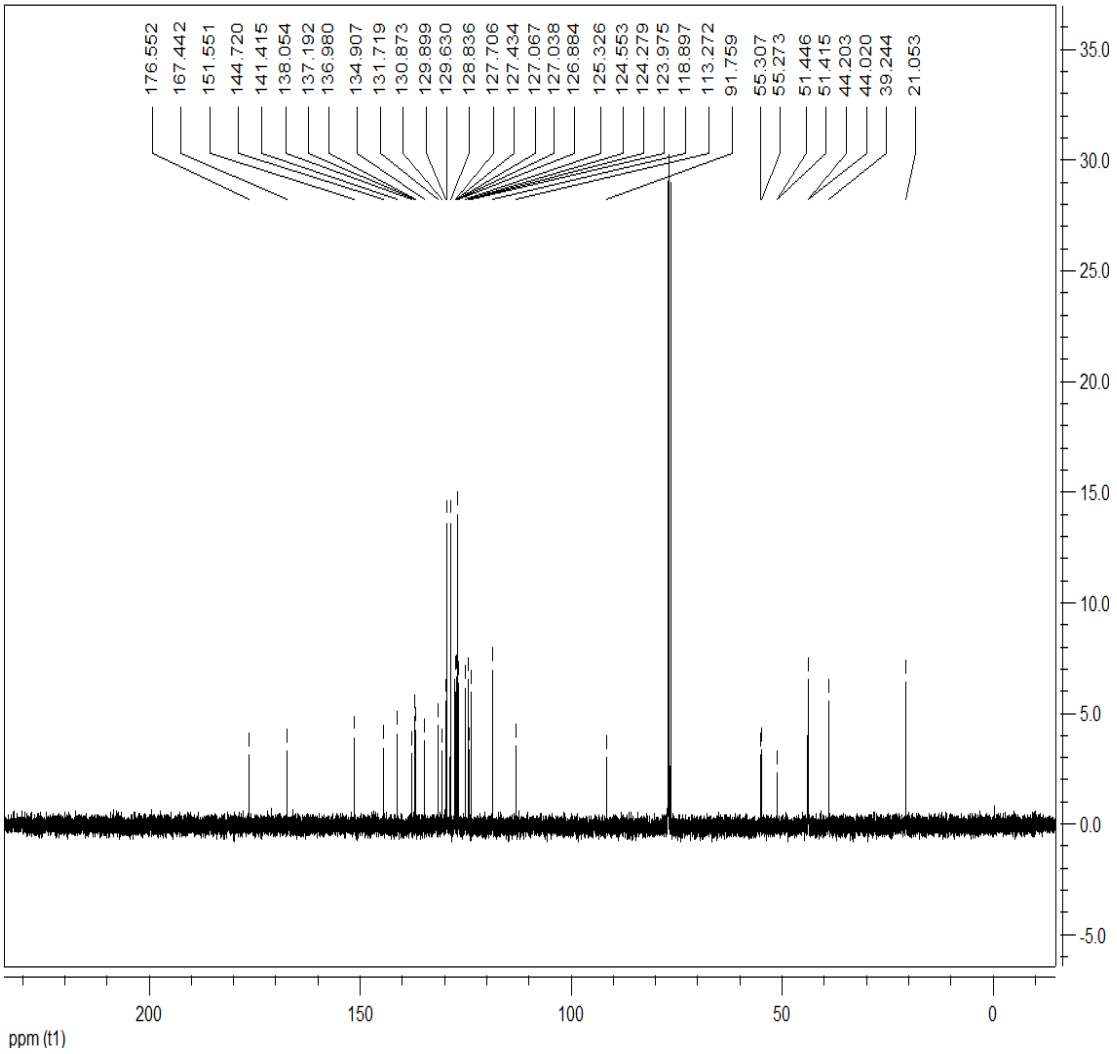

Intens.
+MS, 0.35-0.51min #(39-57)
2000
1500
1000
500
0
615.1778
637.1607
647.2030
591.4985
580
590
600
610
620
630
640
650
660
m/z

Methyl

15-oxo-6,17-di-p-tolyl-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5c):

yellow solid, 82%, m.p. 201~204℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.64 (s, 1H, NH), 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 7.40~7.38(m, 1H, ArH), 7.19 (d, *J* = 7.8 Hz, 1H, ArH), 7.14~7.08 (m, 5H, ArH), 7.04~6.93 (m, 7H, ArH), 5.57 (s, 1H, CH), 4.96 (s, 1H, CH), 4.21 (d, *J* = 7.2 Hz, 1H, CH), 3.21 (d, *J* = 7.2 Hz, 1H, CH), 3.50 (s, 3H, OCH_3), 2.29 (s, 3H, CH_3), 2.22 (s, 3H, CH_3),; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.9, 149.0, 135.9, 135.7, 135.1, 133.6, 129.9, 129.7, 129.2, 128.9, 127.2, 127.1, 126.9, 126.4, 126.3, 125.9, 122.6, 120.6, 118.7, 116.2, 107.2, 72.5, 51.5, 29.7, 25.0; IR (KBr) υ: 3861, 2948, 1700, 1609, 1580, 1551, 1467, 1431, 1349, 1272, 1228, 1202, 1126, 1031, 998, 891, 828, 777, 755, 740, 703cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{31}N_2O_3S_2$ ($[M+H]^+$): 615.1776. Found: 615.1778.

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144.720
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138.054
137.192
136.980
134.907
131.719
130.873
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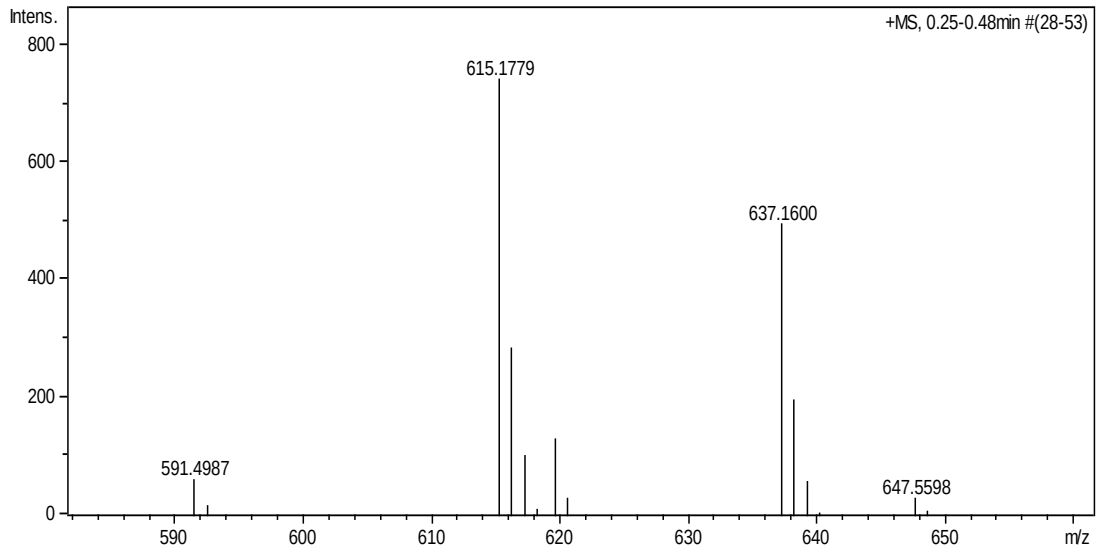
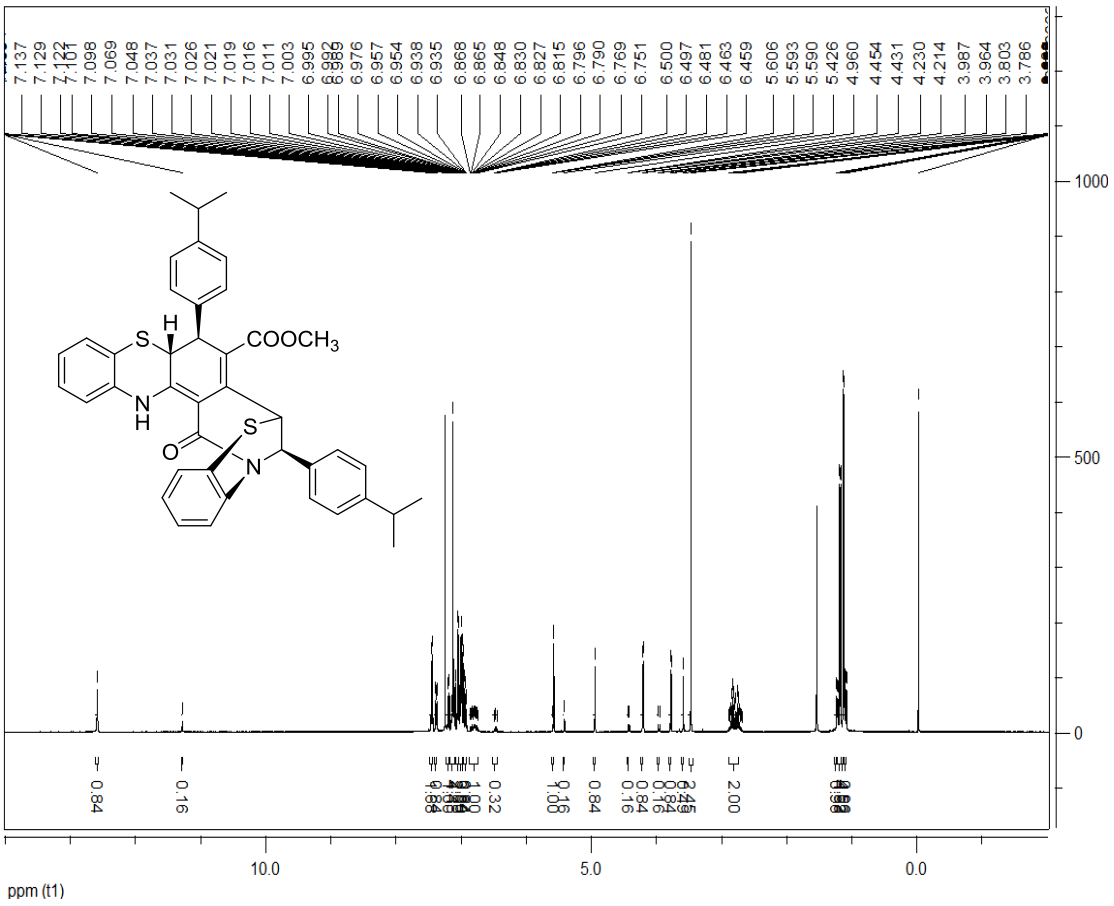
128.836
127.706
127.434
127.067
127.038
126.884
125.326
124.553
124.279
123.975
118.897
113.272
91.759
55.307
55.273
51.446
51.415
44.203
44.020
39.244
21.053
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (t1)

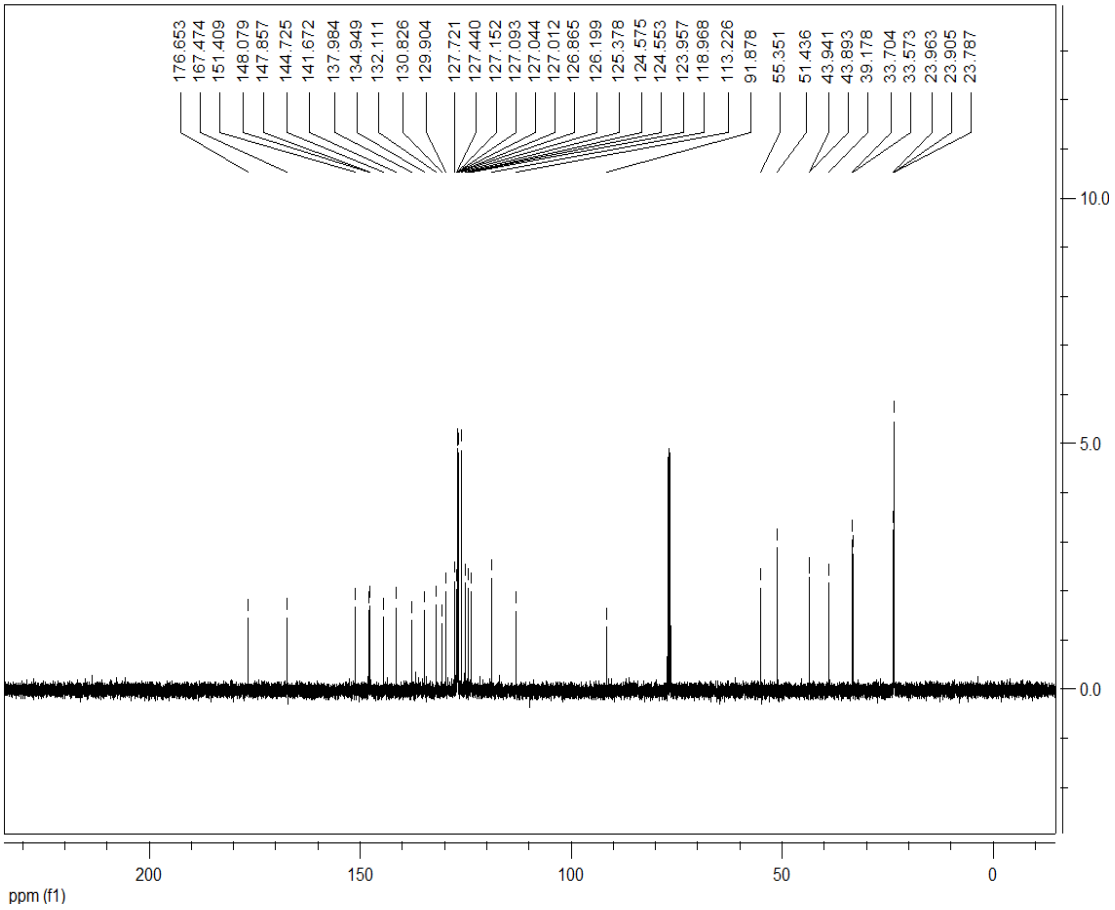

Intens.
+MS, 0.25-0.48min #(28-53)
800
600
400
200
0
615.1779
637.1600
591.4987
647.5598
590
600
610
620
630
640
650
m/z

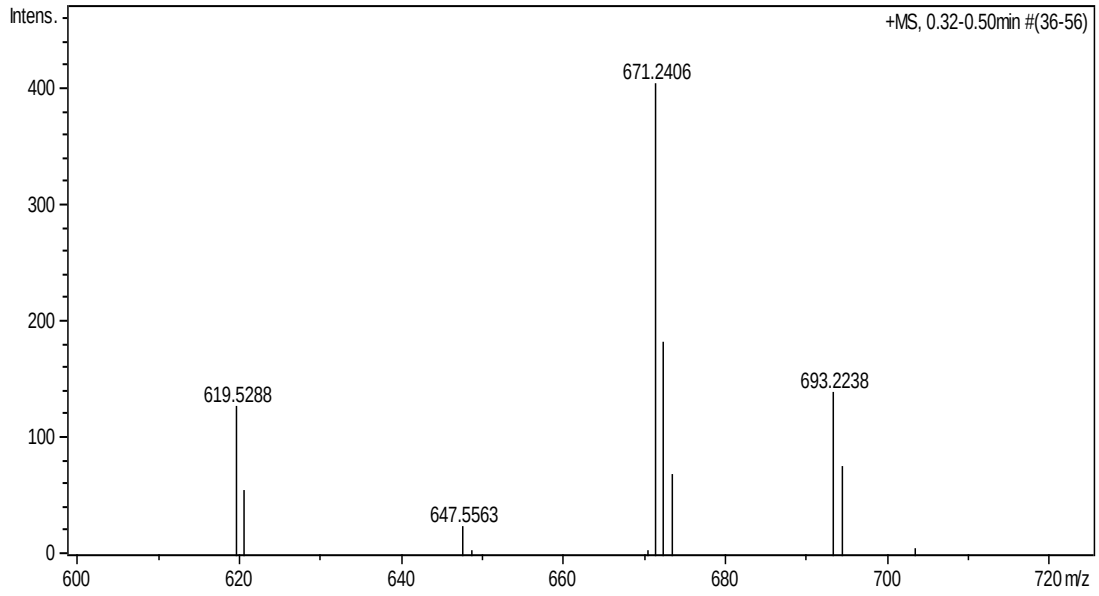
Methyl

6,17-bis(4-isopropylphenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5d):

yellow solid, 65%, m.p. 249~252℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.59 (s, 1H, NH), 7.46 (d, *J* = 8.0 Hz, 2H, ArH), 7.40~7.38 (m, 1H, ArH), 7.22~7.19 (m, 1H, ArH), 7.16~7.10 (m, 4H, ArH), 7.09~6.94 (m, 6H, ArH), 6.87~6.75 (m, 6H, ArH), 5.59 (d, *J* = 1.2 Hz, 1H, CH), 4.96 (s, 1H, CH), 4.22 (d, *J* = 6.4 Hz, 1H, CH), 3.79 (d, *J* = 7.2 Hz, 1H, CH), 3.49 (s, 3H, OCH_3), 2.90~2.70 (m, 2H, CH), 1.21~1.19 (m, 6H, CH_3), 1.14 (d, *J* = 7.2 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 167.5, 151.4148.1, 147.9, 144.7, 141.7, 138.0, 134.9, 132.1, 130.8, 129.9, 127.7, 127.4, 127.2, 127.1, 127.0, 127.0, 126.9, 126.2, 125.4, 124.6, 124.6, 124.0, 119.0, 113.2, 91.9, 55.4, 51.4, 43.9, 43.9, 39.2, 33.7, 33.6, 24.0, 23.9, 23.8; IR (KBr) υ: 3849, 2958, 1700, 1642, 1611, 1576, 1551, 1513, 1468, 1433, 1351, 1265, 1233, 1126, 1056, 1020, 981, 895, 832, 817, 794, 776, 755cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{39}N_2O_3S_2$ ([M+H]$^+$): 671.2402. Found: 671.2406.



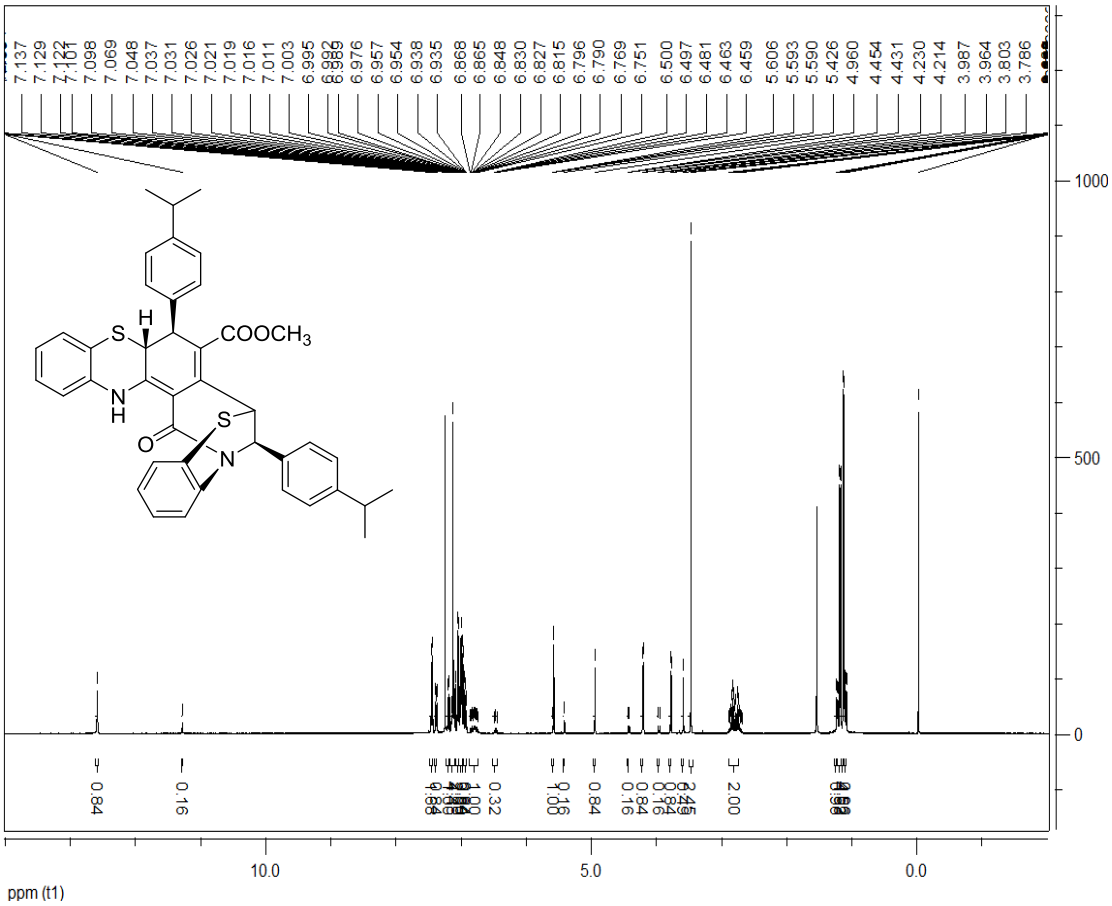

176.653
167.474
151.409
148.079
147.857
144.725
141.672
137.984
134.949
132.111
130.826
129.904
127.721
127.440
127.152
127.093
127.044
127.012
126.865
126.199
125.378
124.575
124.553
123.957
118.968
113.226
91.878
55.351
51.436
43.941
43.893
39.178
33.704
33.573
23.963
23.905
23.787
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

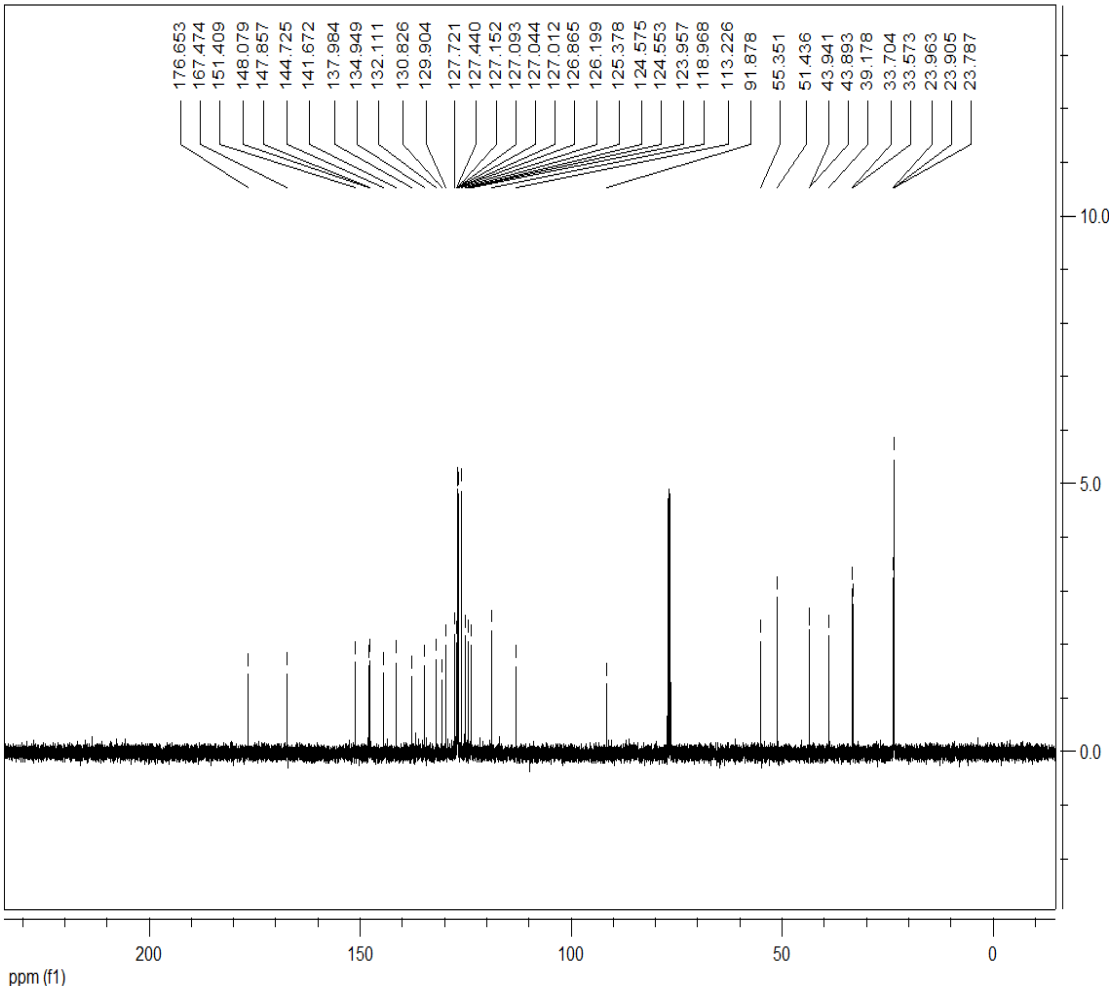

Intens.
+MS, 0.32-0.50min #(36-56)
671.2406
693.2238
619.5288
647.5563
400
300
200
100
0
600
620
640
660
680
700
720 m/z

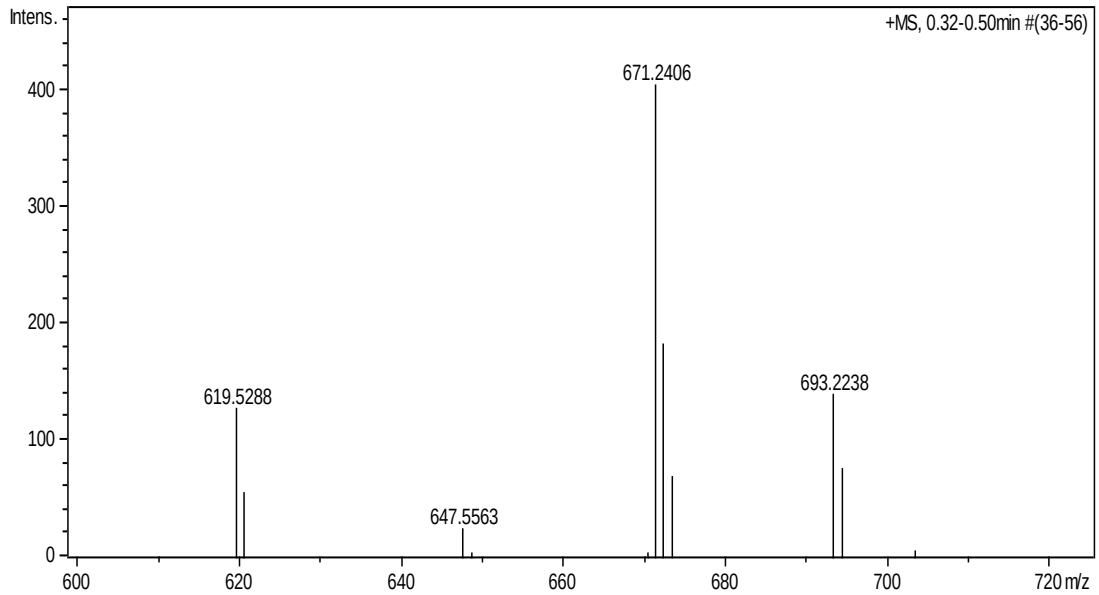
Methyl

6,17-bis(4-isopropylphenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5d'):

yellow solid, 16%, m.p. 242~252℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.29 (s, 1H, NH), 6.50~6.46 (m, 2H, ArH), 5.61 (d, *J* = 1.2 Hz, 1H, CH), 5.43 (s, 1H, CH), 4.44 (d, *J* = 6.4 Hz, 1H, CH), 3.98 (d, *J* = 7.2 Hz, 1H, CH), 3.60 (s, 3H, OCH_3), 2.90~2.70 (m, 2H, CH), 1.26~1.23 (m, 6H, CH_3), 1.12~1.10 (m, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 167.5, 151.4148.1, 147.9, 144.7, 141.7, 138.0, 134.9, 132.1, 130.8, 129.9, 127.7, 127.4, 127.2, 127.1, 127.0, 127.0, 126.9, 126.2, 125.4, 124.6, 124.6, 124.0, 119.0, 113.2, 91.9, 55.4, 51.4, 43.9, 43.9, 39.2, 33.7, 33.6, 24.0, 23.9, 23.8; IR (KBr) υ: 3849, 2958, 1700, 1642, 1611, 1576, 1551, 1513, 1468, 1433, 1351, 1265, 1233, 1126, 1056, 1020, 981, 895, 832, 817, 794, 776, 755cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{39}N_2O_3S_2$ ([M+H]$^+$): 671.2402. Found: 671.2406.



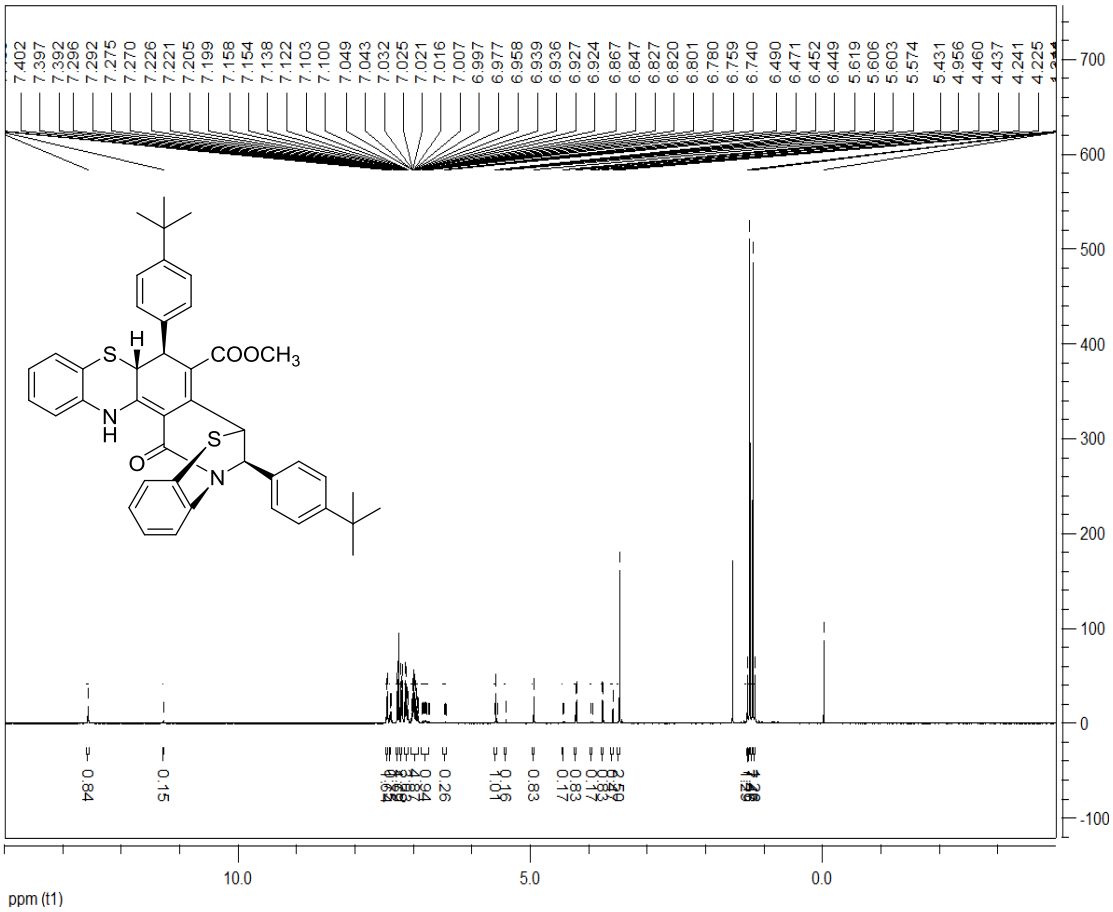

176.653
167.474
151.409
148.079
147.857
144.725
141.672
137.984
134.949
132.111
130.826
129.904
127.721
127.440
127.152
127.093
127.044
127.012
126.865
126.199
125.378
124.575
124.553
123.957
118.968
113.226
91.878
55.351
51.436
43.941
43.893
39.178
33.704
33.573
23.963
23.905
23.787
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

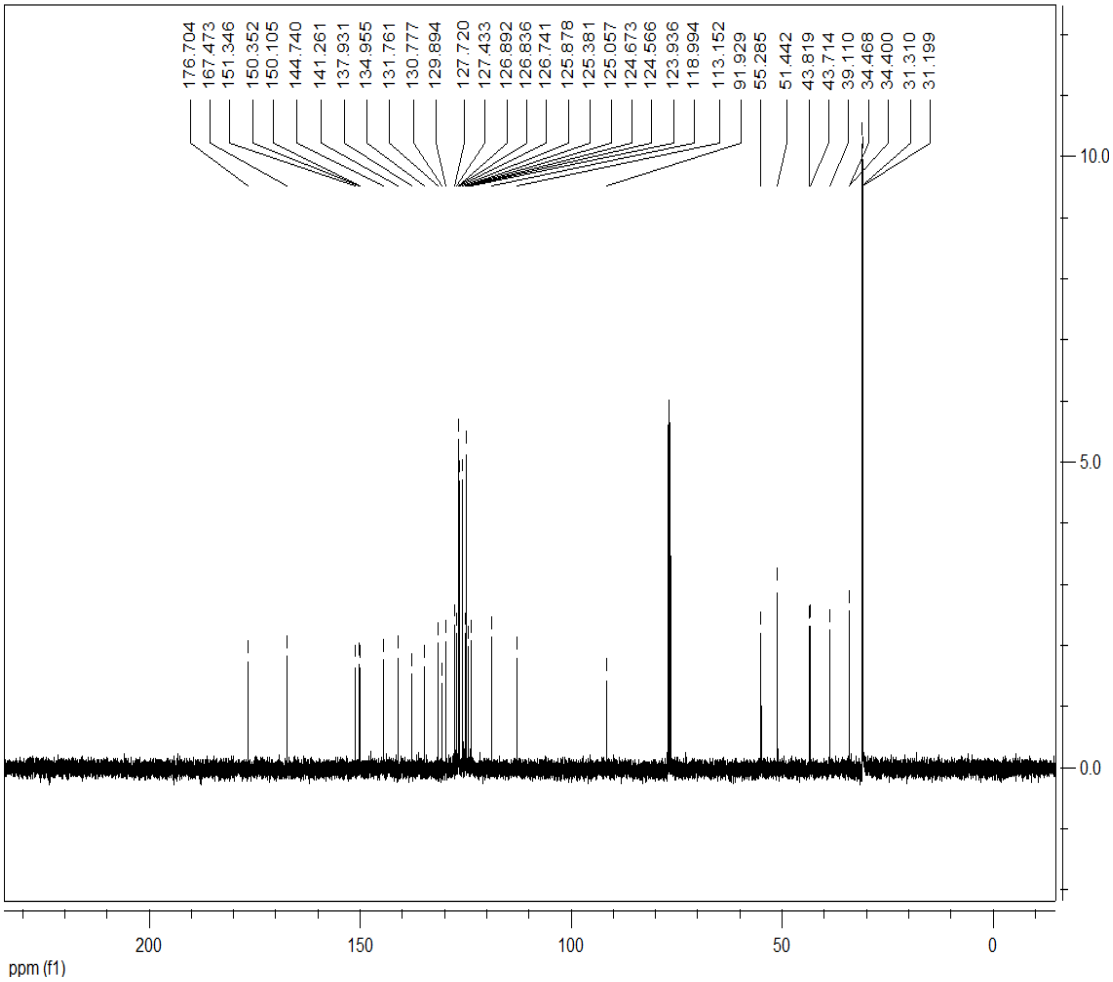

Intens.
+MS, 0.32-0.50min #(36-56)
671.2406
693.2238
619.5288
647.5563
400
300
200
100
0
600
620
640
660
680
700
720 m/z

Methyl

6,17-bis(4-(tert-butyl)phenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5e):

yellow solid, 63%, m.p. 270~274℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.58 (s, 1H, NH), 7.47 (d, *J* = 8.0 Hz, 2H, ArH), 7.42~7.39 (m, 1H, ArH), 7.29 (d, *J* = 8.4 Hz, 2H, ArH), 7.22 (d, *J* = 8.4 Hz, 2H, ArH), 7.16~7.10 (m, 3H, ArH), 7.05~6.92 (m, 4H, ArH), 6.87~6.74 (m, 1H, ArH), 5.60 (d, *J* = 1.2 Hz, 1H, CH), 4.96 (s, 1H, CH), 4.23 (d, *J* = 6.4 Hz, 1H, CH), 3.78 (d, *J* = 7.2 Hz, 1H, CH), 3.49 (s, 3H, OCH_3), 1.26 (s, 9H, CH_3), 1.21 (s, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 167.5, 151.3, 150.4, 150.1, 144.7, 141.3, 137.9, 135.0, 131.8, 130.8, 129.9, 127.7, 127.4, 126.9, 126.8, 126.7, 125.9, 125.4, 125.1, 124.7, 124.6, 123.9, 119.0, 113.2, 91.9, 55.3, 51.4, 43.8, 43.7, 39.1, 34.5, 34.4, 31.3, 31.2; IR (KBr) υ: 3060, 2962, 2902, 2867, 1700, 1643, 1611, 1576, 1550, 1470, 1433, 1352, 1292, 1265, 1234, 1215, 1128, 1116, 1058, 1019, 894, 833, 794, 755, 745, 712cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{43}N_2O_3S_2$ ([M+H]$^+$): 699.2715. Found: 699.2721.




176.704
167.473
151.346
150.352
150.105
144.740
141.261
137.931
134.955
131.761
130.777
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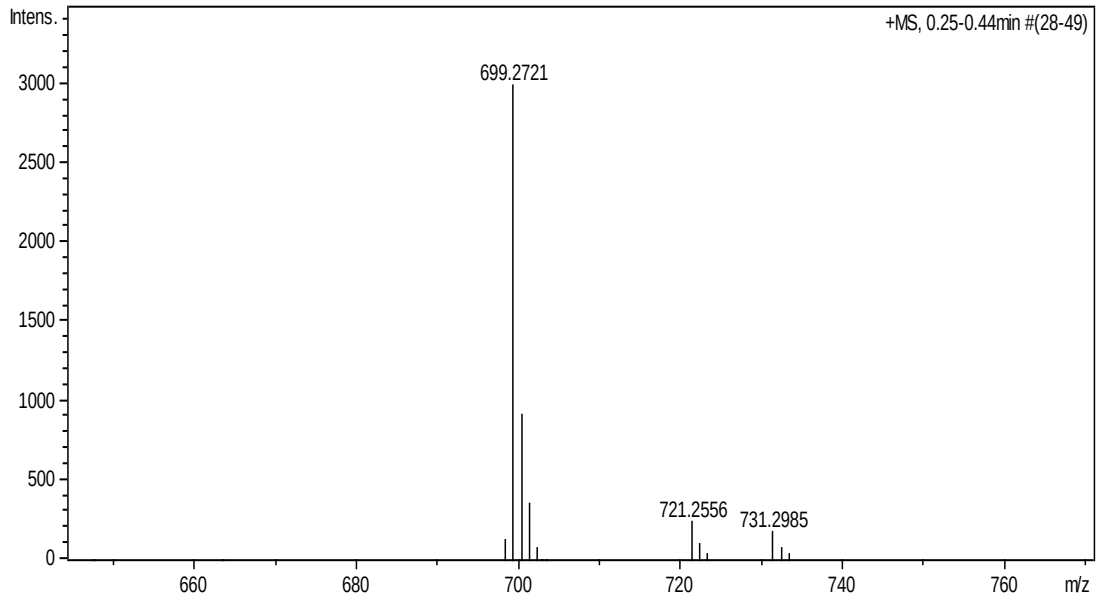
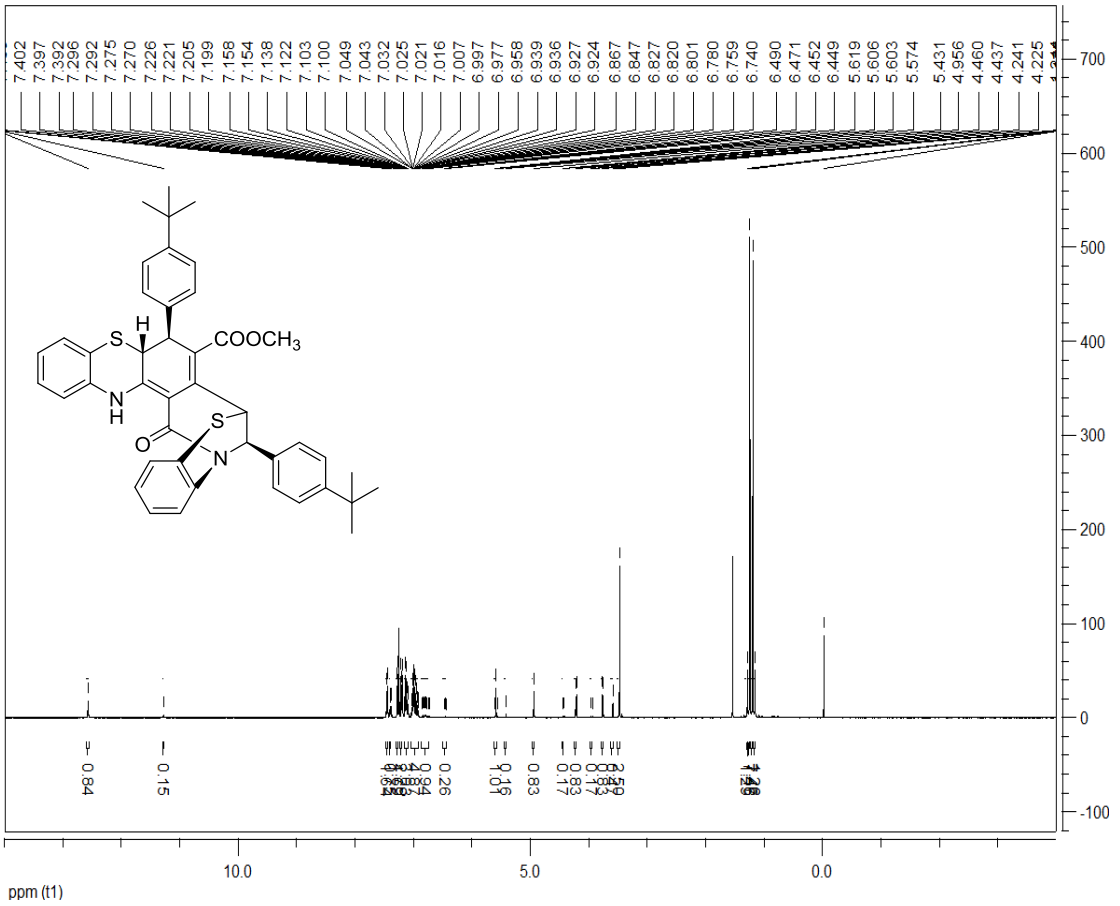
127.720
127.433
126.892
126.836
126.741
125.878
125.381
125.057
124.673
124.566
123.936
118.994
113.152
91.929
55.285
51.442
43.819
43.714
39.110
34.468
34.400
31.310
31.199
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

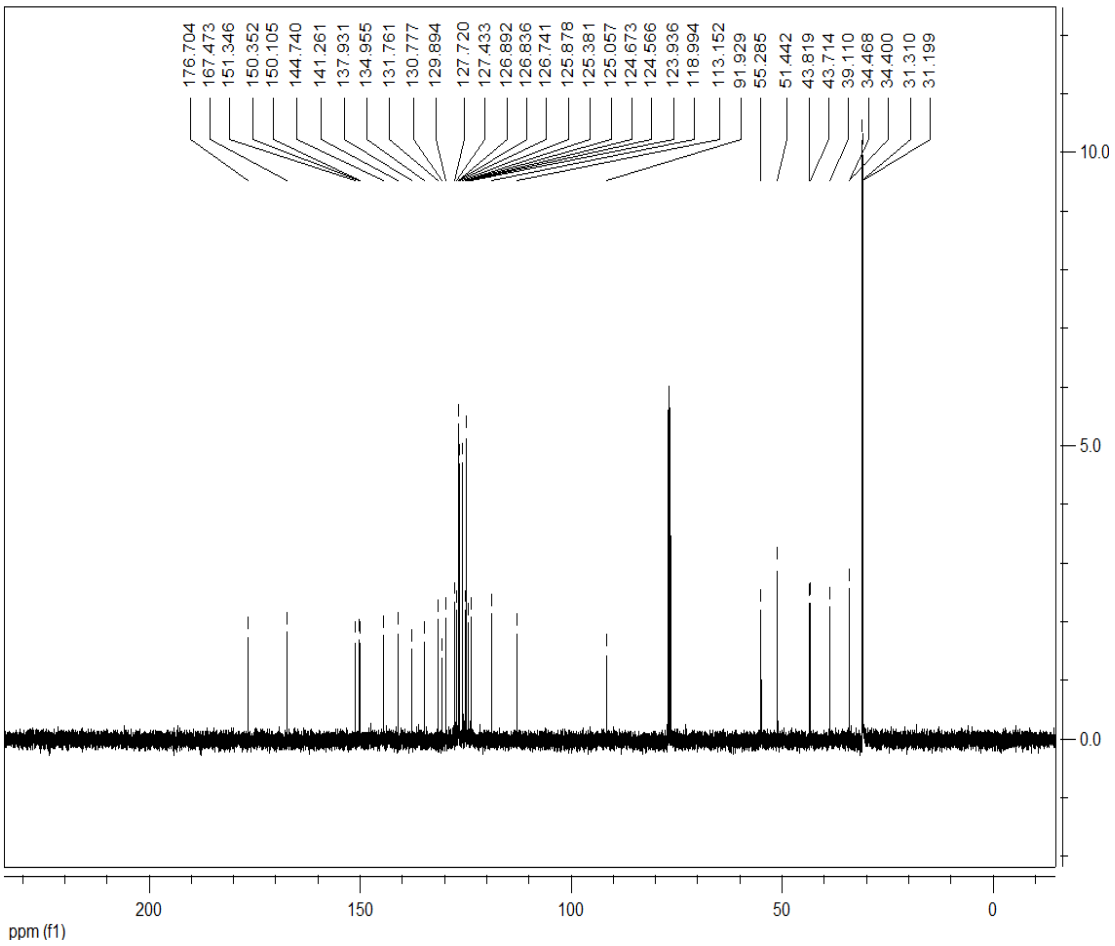

Intens.
+MS, 0.25-0.44min #(28-49)
699.2721
721.2556
731.2985
3000
2500
2000
1500
1000
500
0
660
680
700
720
740
760
m/z

Methyl

6,17-bis(4-(tert-butyl)phenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4] thiazocino[6,7-a]phenothiazine-7-carboxylate (5e'):

yellow solid, 15%, m.p. 270~274℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.29 (s, 1H, NH), 6.49~6.45 (m, 2H, ArH), 5.62~5.57 (m, 1H, CH), 5.43 (s, 1H, CH), 4.45 (d, *J* = 9.2 Hz, 1H, CH), 3.97 (d, *J* = 9.2 Hz, 1H, CH), 3.61 (s, 3H, OCH_3), 1.31 (s, 9H, CH_3), 1.18 (s, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 167.5, 151.3, 150.4, 150.1, 144.7, 141.3, 137.9, 135.0, 131.8, 130.8, 129.9, 127.7, 127.4, 126.9, 126.8, 126.7, 125.9, 125.4, 125.1, 124.7, 124.6, 123.9, 119.0, 113.2, 91.9, 55.3, 51.4, 43.8, 43.7, 39.1, 34.5, 34.4, 31.3, 31.2; IR (KBr) υ: E. 3060, 2962, 2902, 2867, 1700, 1643, 1611, 1576, 1550, 1470, 1433, 1352, 1292, 1265, 1234, 1215, 1128, 1116, 1058, 1019, 894, 833, 794, 755, 745, 712cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{43}N_2O_3S_2$ ([M+H]$^+$): 699.2715. Found: 699.2721.

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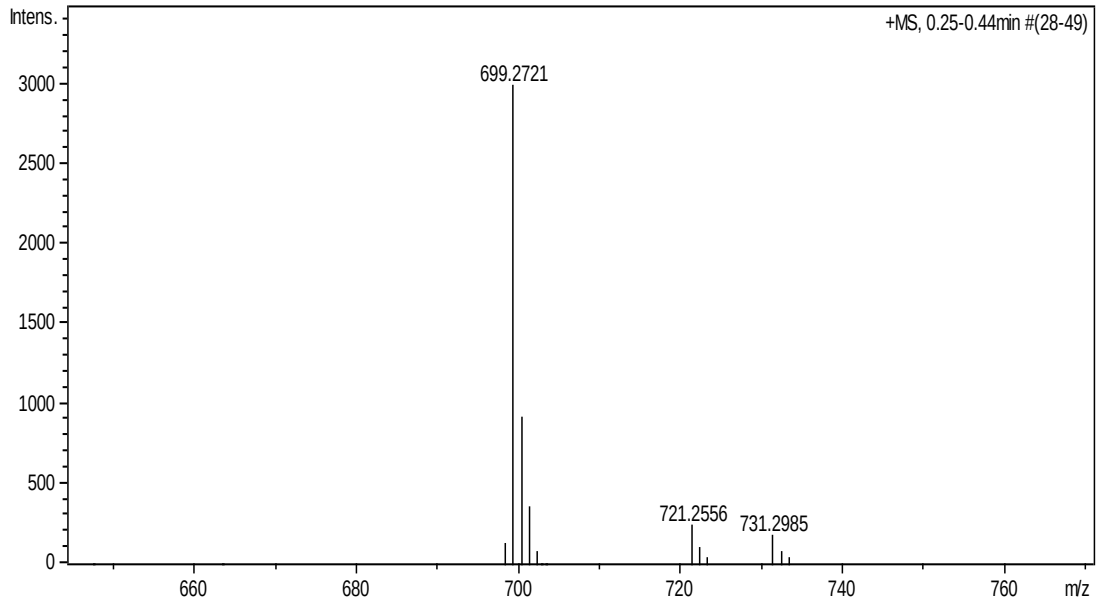
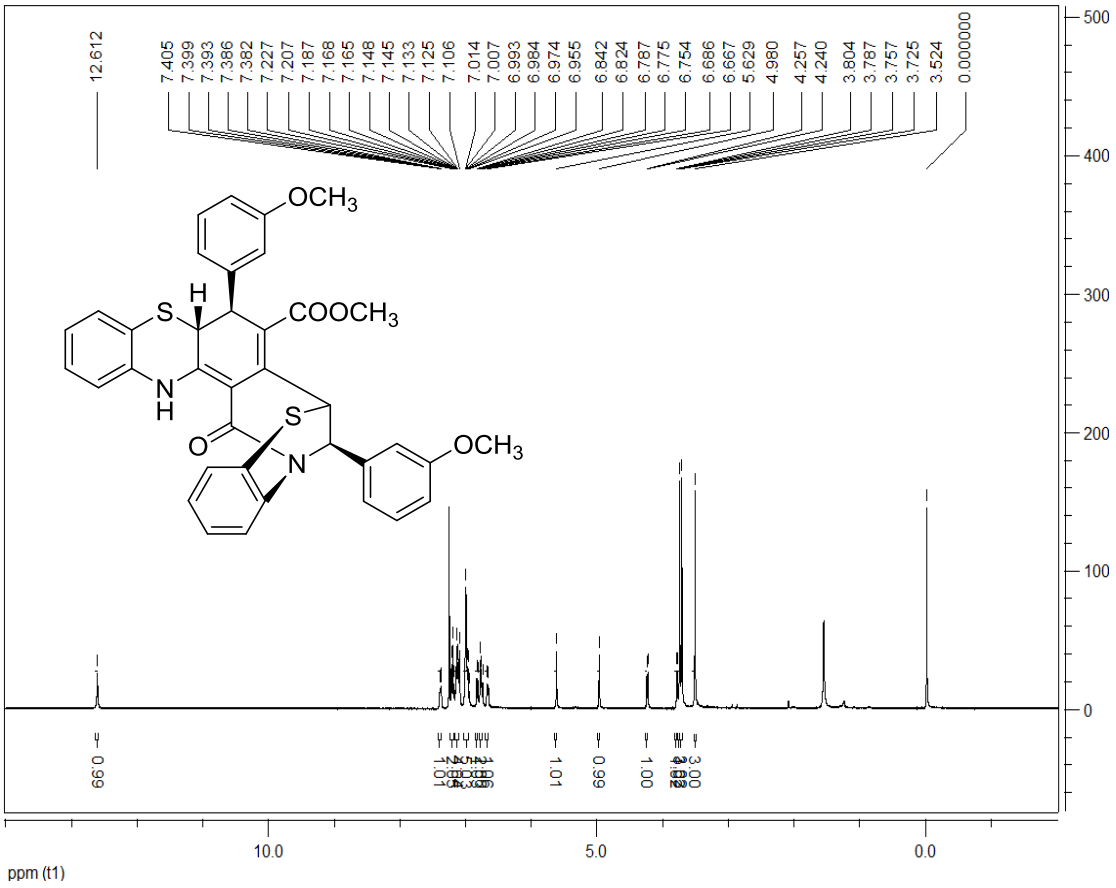
167.473
151.346
150.352
150.105
144.740
141.261
137.931
134.955
131.761
130.777
129.894
127.720
127.433
126.892
126.836
126.741
125.878
125.381
125.057
124.673
124.566
123.936
118.994
113.152
91.929
55.285
51.442
43.819
43.714
39.110
34.468
34.400
31.310
31.199
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

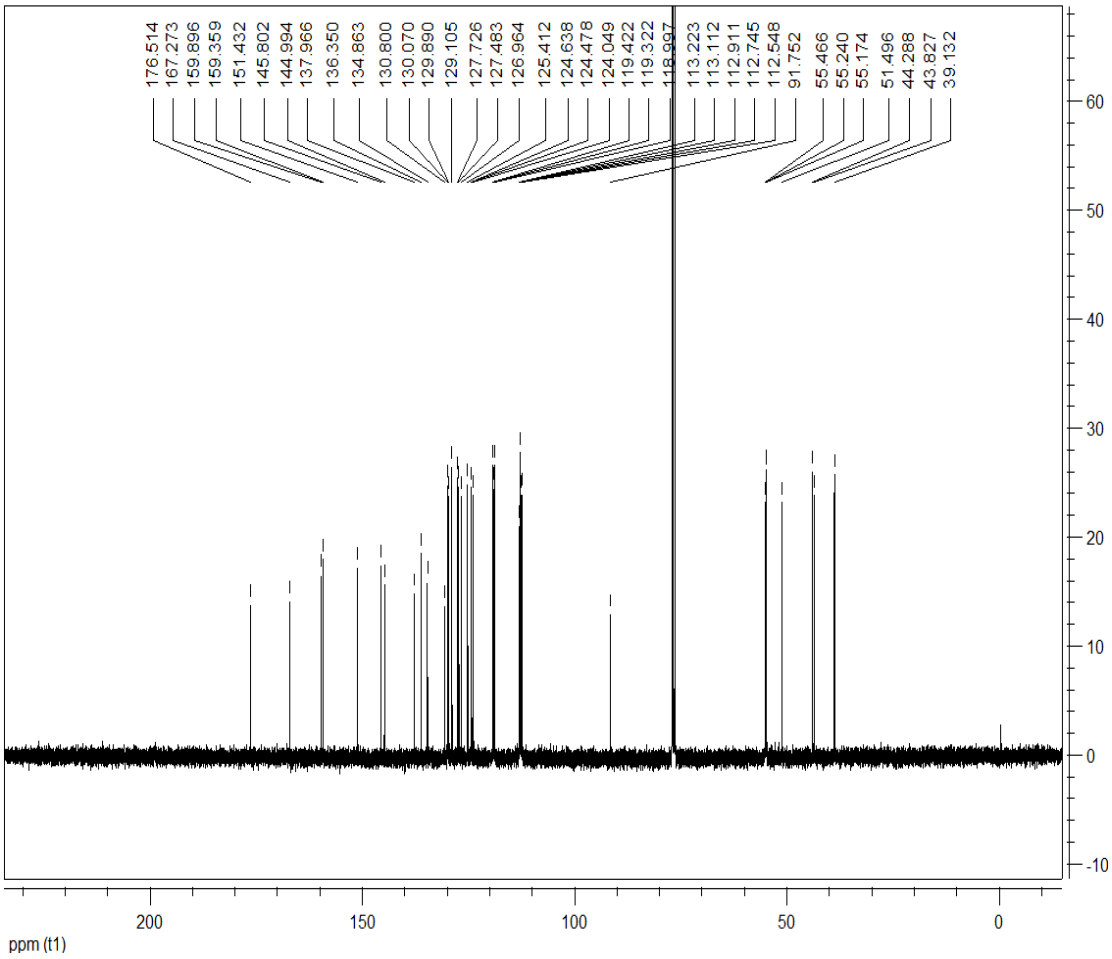

Intens.
+MS, 0.25-0.44min #(28-49)
699.2721
721.2556
731.2985
3000
2500
2000
1500
1000
500
0
660
680
700
720
740
760
m/z

Methyl

6,17-bis(3-methoxyphenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5f):

yellow solid, 87%, m.p. 198~201℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.61 (s, 1H, NH), 7.41~7.38 (m, 1H, ArH), 7.23~7.19 (m, 2H, ArH), 7.17~7.11 (m, 4H, ArH), 7.01~6.96 (m, 5H, ArH), 6.83 (d, *J* =7.2 Hz, 1H, ArH), 6.79~6.75 (m, *2*H, ArH), 6.68 (d, *J* = 7.8 Hz, 1H, ArH), 5.63 (s, 1H, CH), 4.98 (s, 1H, CH), 4.25 (d, *J* = 6.8 Hz, 1H, CH), 3.80 (d, *J* = 6.8 Hz, 1H, CH), 3.76 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.52 (s, 3H, OCH_3) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.9, 149.0, 136.2, 135.9, 133.6, 132.1, 130.0, 129.9, 128.9, 127.2, 127.1, 126.9, 126.4, 126.3, 125.8, 123.4, 122.6, 120.6, 118.8, 116.2, 107.2, 72.6, 51.5, 29.7, 25.0; IR (KBr) υ: 3849, 2958, 1700, 1642, 1611, 1576, 1551, 1513, 1468, 1433, 1351, 1265, 1233, 1126, 1056, 1020, 981, 895, 832, 817, 794, 776, 755 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{31}N_2O_5S_2$ ([M+H]$^+$): 647.1674. Found: 647.1681.

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159.359
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145.802
144.994
137.966
136.350
134.863
130.800
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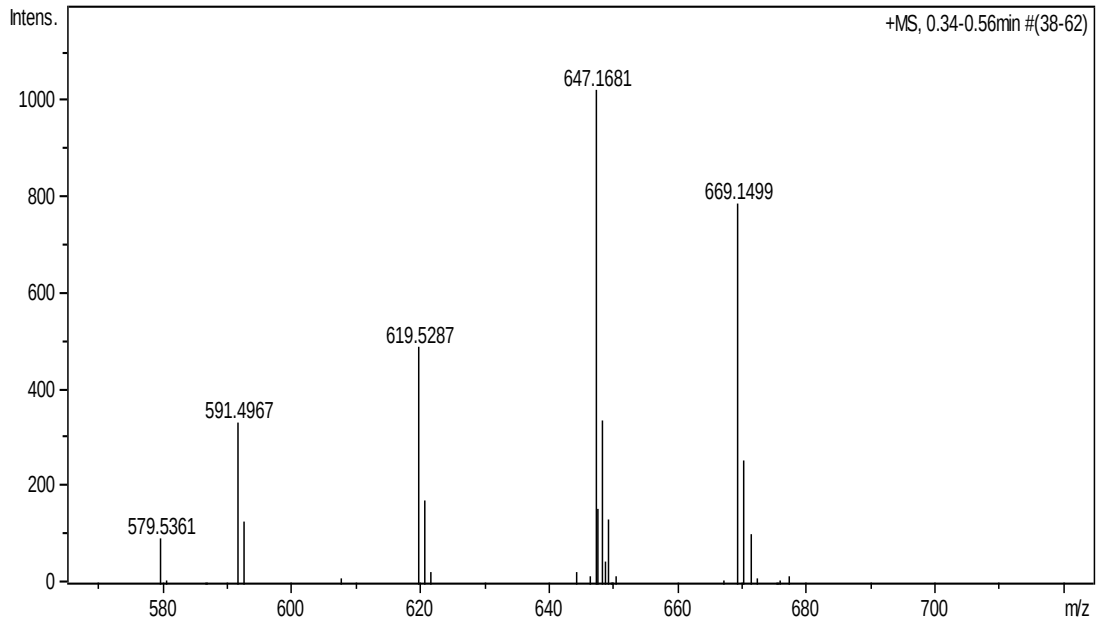
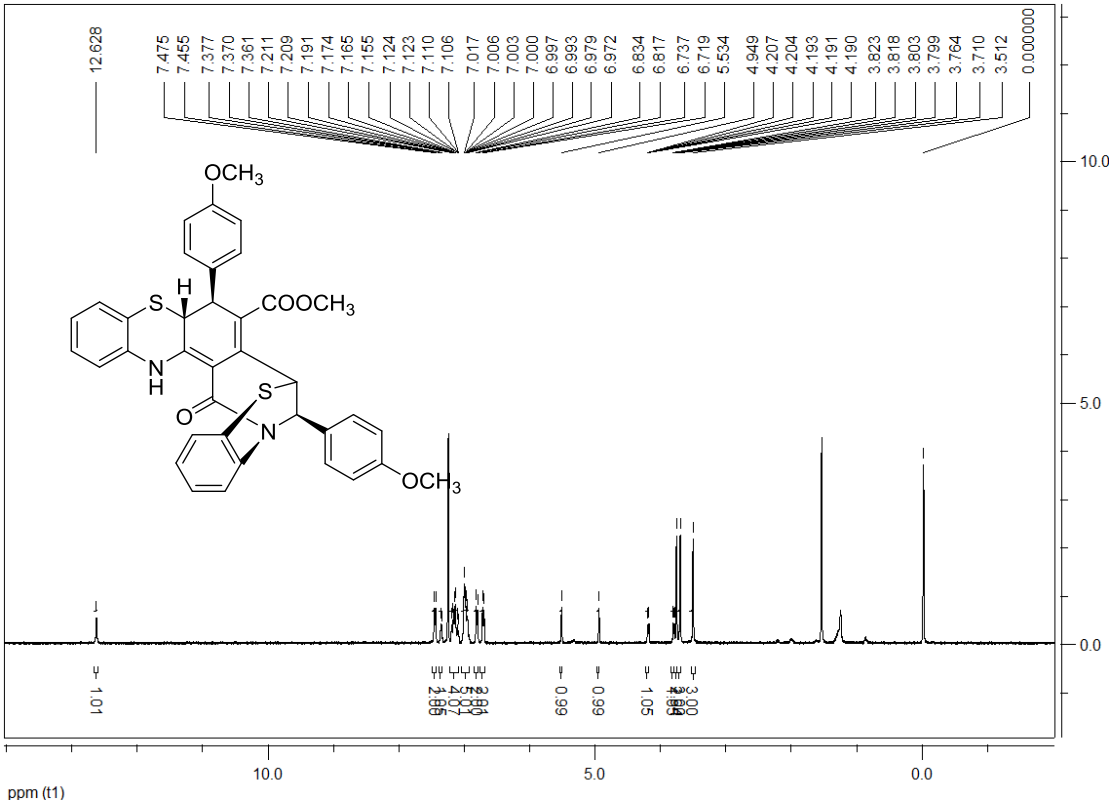
129.105
127.726
127.483
126.964
125.412
124.638
124.478
124.049
119.422
119.322
118.997
113.223
113.112
112.911
112.745
112.548
91.752
55.466
55.240
55.174
51.496
44.288
43.827
39.132
60
50
40
30
20
10
0
-10
200
150
100
50
0
ppm (t1)

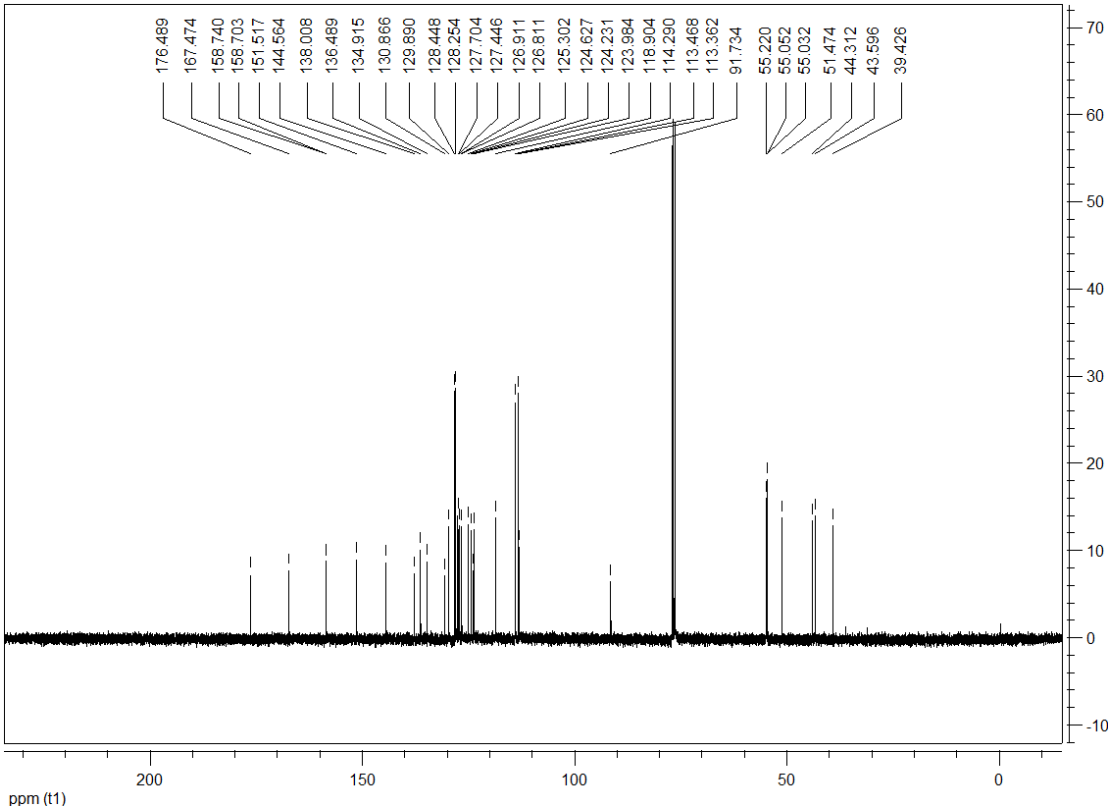

Intens.
+MS, 0.34-0.56min #(38-62)
647.1681
669.1499
619.5287
591.4967
579.5361
1000
800
600
400
200
0
580
600
620
640
660
680
700
m/z

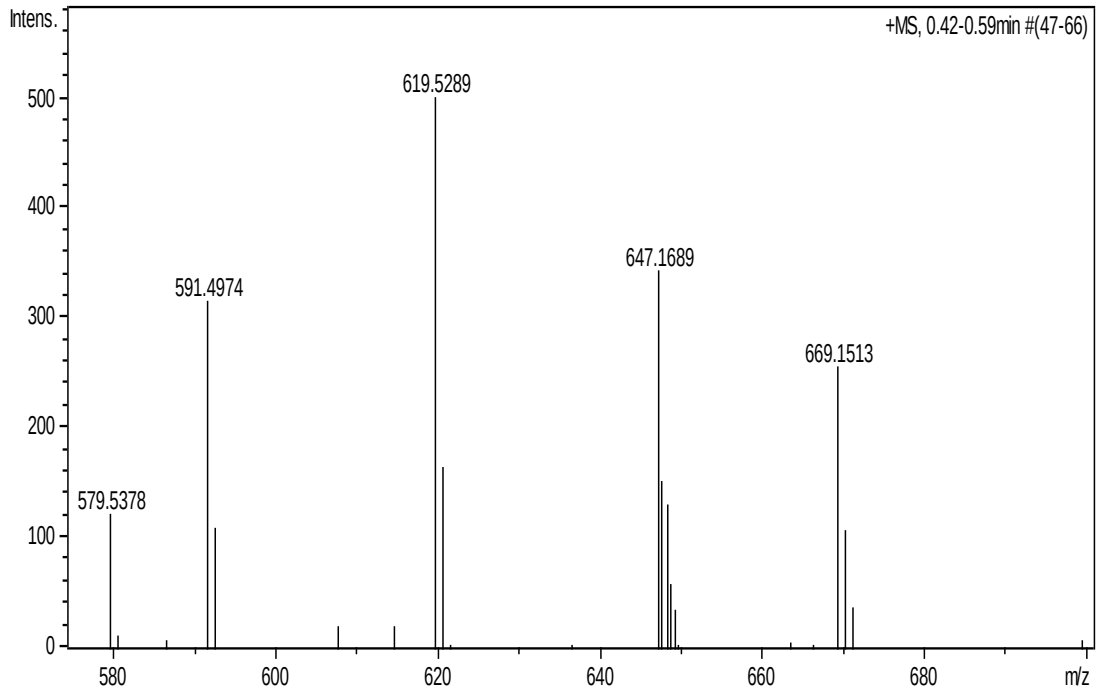
Methyl

6,17-bis(4-methoxyphenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5g):

yellow solid, 86%, m.p. 260~264℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.63 (s, 1H, NH), 7.60 (d, *J* = 8.0 Hz, 2H, ArH), 7.38~7.36 (m, 1H, ArH), 7.21~7.11 (m, 4H, ArH), 7.02~6.97 (m, 5H, ArH), 6.83 (d, *J* = 6.8 Hz, 2H, ArH), 6.73 (d, *J* = 7.2 Hz, 2H, ArH), 5.53 (s, 1H, CH), 4.95 (s, 1H, CH), 4.21~4.19 (m, 1H, CH), 3.82~3.80 (m, 1H, CH), 3.76 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.5 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4, 150.8, 138.7, 135.2, 134.6, 133.9, 129.6, 129.5, 128.7, 128.3, 127.4, 126.8, 126.4, 126.2, 126.0, 121.8, 121.4, 117.7, 116.8, 107.2, 73.1, 51.4, 25.0, 21.2; IR (KBr) υ: 3060, 2962, 2902, 2867, 1700, 1643, 1611, 1576, 1550, 1470, 1433, 1352, 1292, 1265, 1234, 1215, 1128, 1116, 1058, 1019, 894, 833, 794, 755, 745, 712cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{31}N_2O_5S_2$ ($[M+H]^+$): 647.1674. Found: 647.1689.



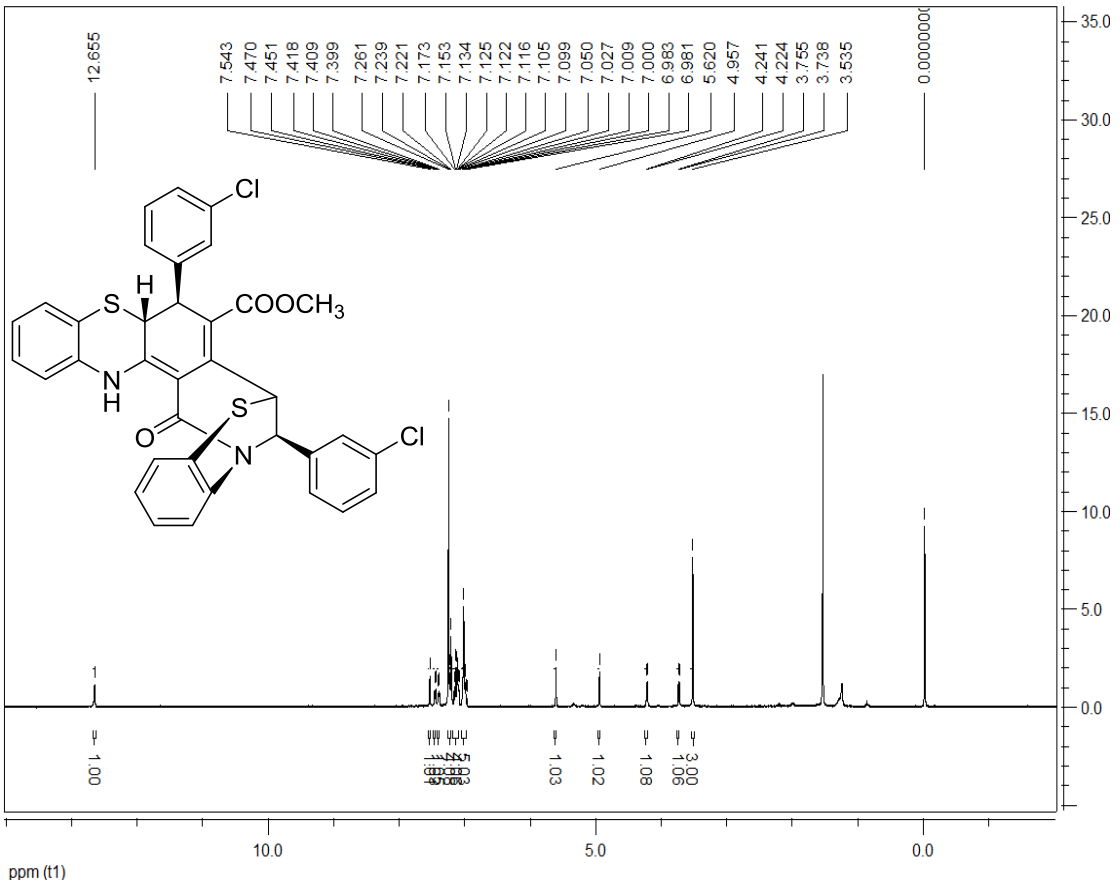

176.489
167.474
158.740
158.703
151.517
144.564
138.008
136.489
134.915
130.866
129.890
128.448
128.254
127.704
127.446
126.911
126.811
125.302
124.627
124.231
123.984
118.904
114.290
113.468
113.362
91.734
55.220
55.052
55.032
51.474
44.312
43.596
39.426
70
60
50
40
30
20
10
0
-10
200
150
100
50
0
ppm (t1)

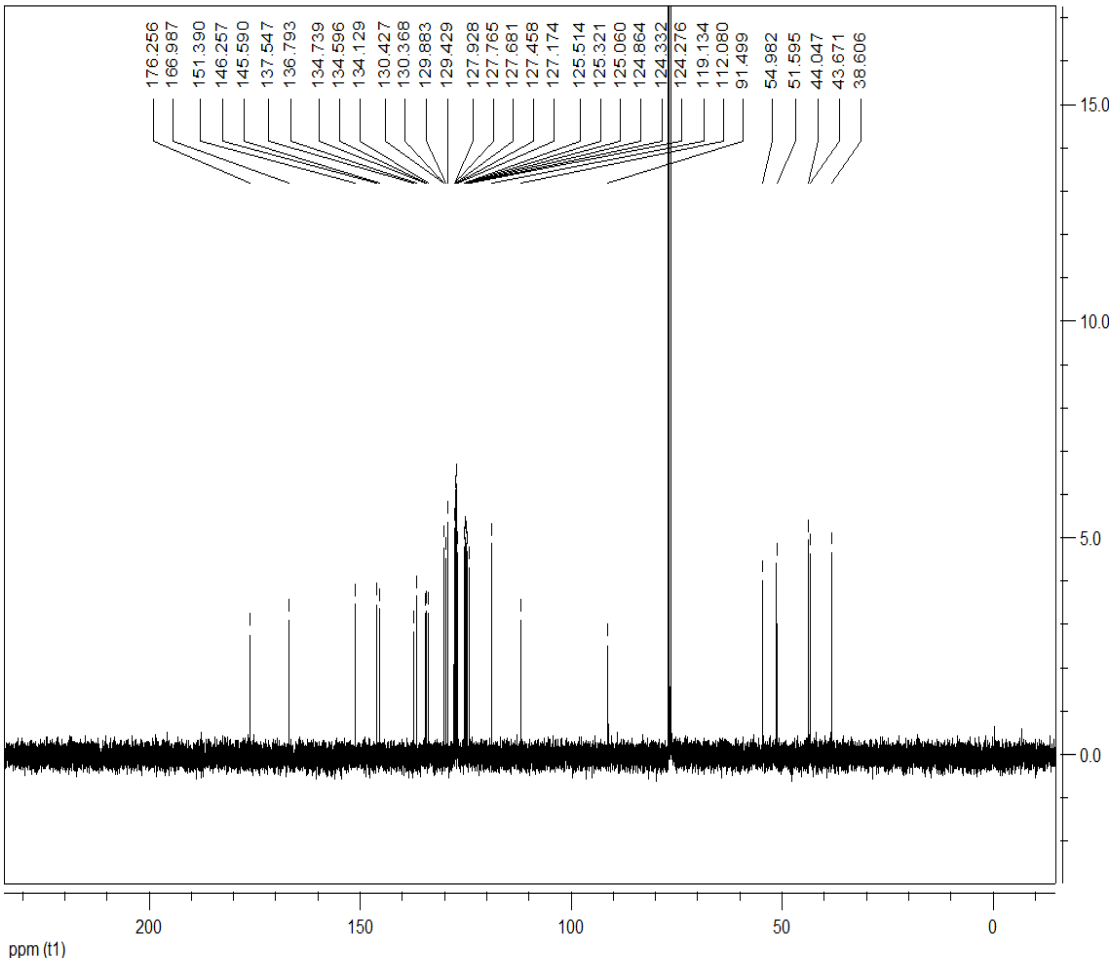

Intens.
+MS, 0.42-0.59min #(47-66)
619.5289
591.4974
647.1689
669.1513
579.5378
500
400
300
200
100
0
580
600
620
640
660
680
m/z

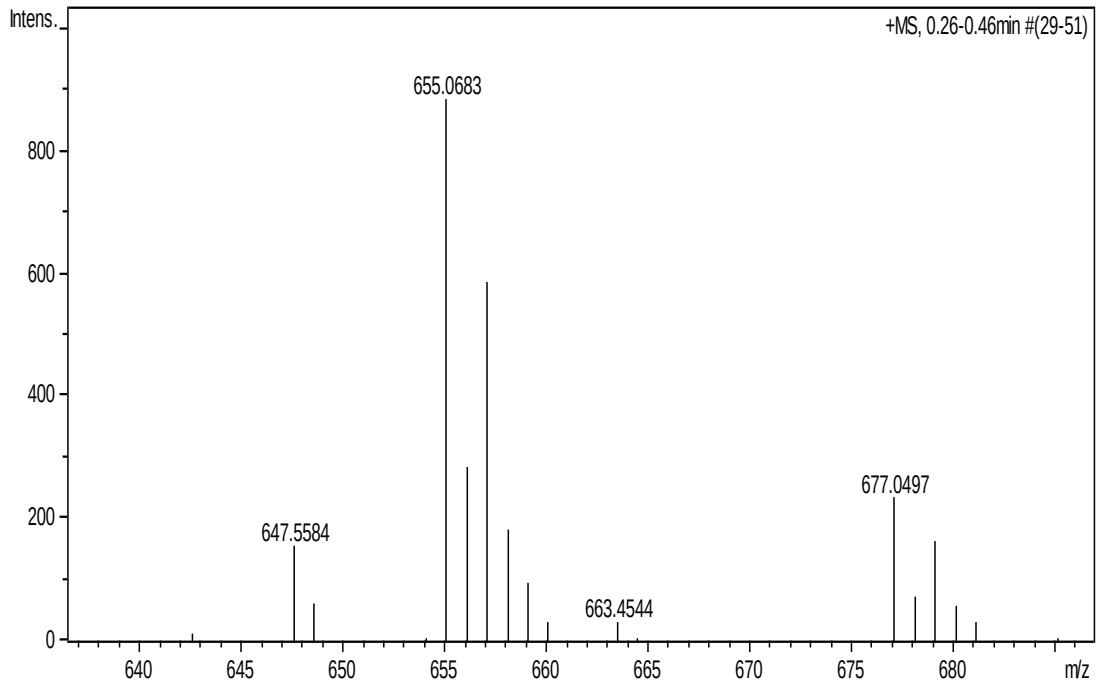
Methyl

6,17-bis(3-chlorophenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5h):

yellow solid, 87%, m.p. 210~213℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.66 (s, 1H, NH), 7.54 (s, 1H, ArH), 7.46 (d, *J* = 7.8 Hz, 1H, ArH), 7.42~7.40 (m, 1H, ArH), 7.26~7.22 (m, 4H, ArH), 7.17~7.10 (m, 4H, ArH), 7.05~6.98 (m, 5H, ArH), 5.62 (s, 1H, CH), 4.96 (s, 1H, CH), 4.23 (d, *J* = 6.8 Hz, 1H, CH), 3.75 (d, *J* = 6.8 Hz, 1H, CH), 3.54 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.1, 149.4, 139.0, 135.6, 134.2, 133.7, 129.7, 129.6, 128.8, 128.3, 127.0, 126.9, 126.8, 126.7, 126.2, 126.2, 122.9, 120.9, 118.8, 116.0, 107.1, 73.2, 51.4, 24.9, 21.2; IR (KBr) υ: 3861, 3849, 3732, 3708, 3625, 2951, 2834, 2351, 1700, 1609, 1579, 1551, 1513, 1467, 1431, 1347, 1271, 1251, 1231, 1179, 1128, 1032,898, 822, 782, 756, 744cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{25}Cl_2N_2O_3S_2$ ([M+H]$^{+}$): 655.0684. Found: 655.0696.



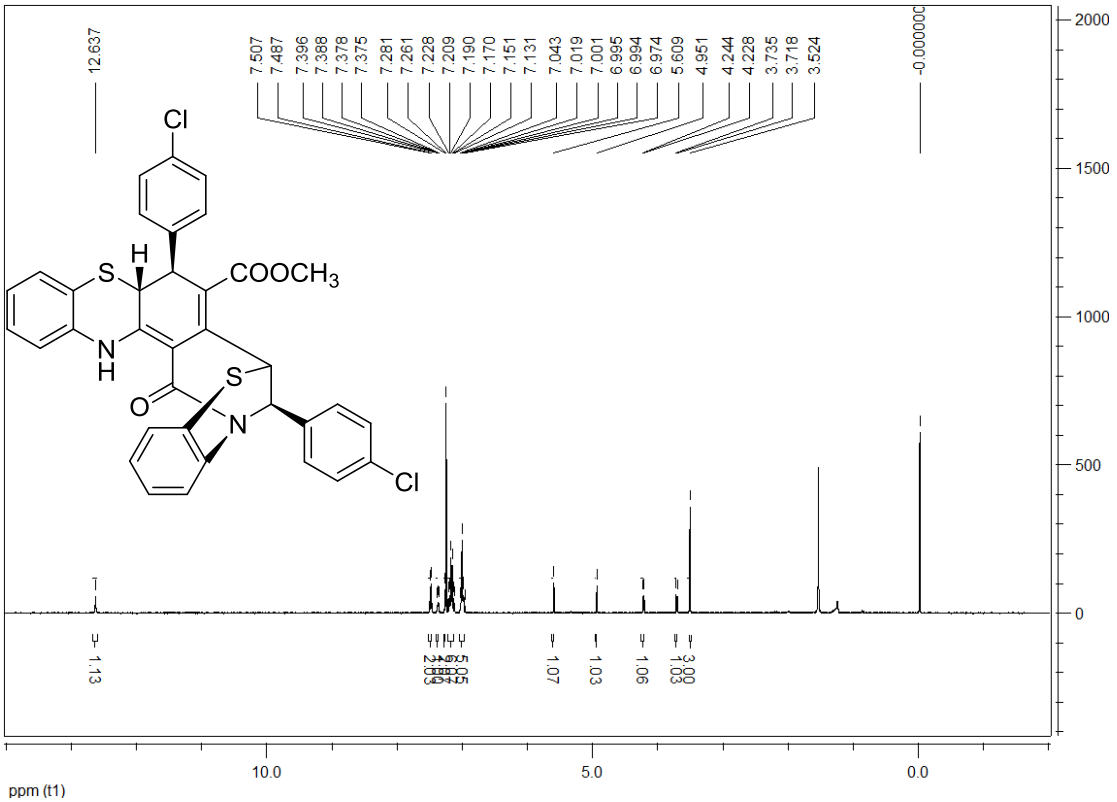

176.256
166.987
151.390
146.257
145.590
137.547
136.793
134.739
134.596
134.129
130.427
130.368
129.883
129.429
127.928
127.765
127.681
127.458
127.174
125.514
125.321
125.060
124.864
124.332
124.276
119.134
112.080
91.499
54.982
51.595
44.047
43.671
38.606
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

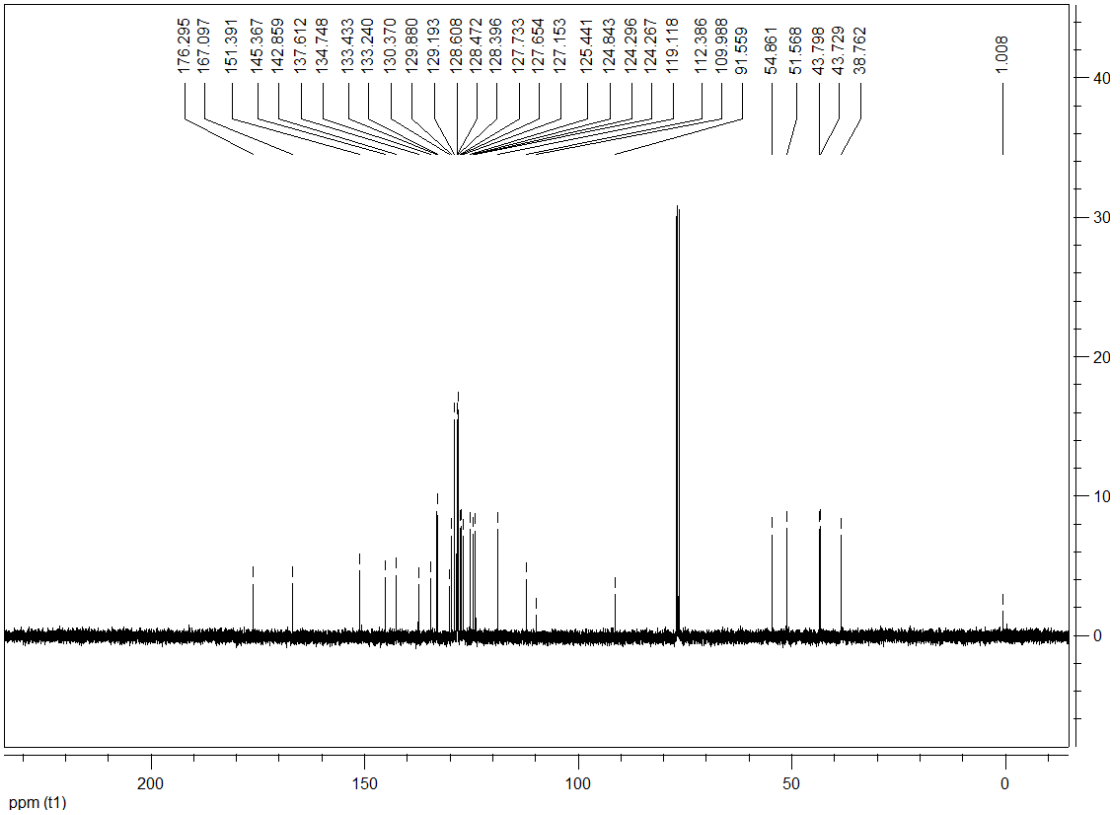

Intens.
+MS, 0.26-0.46min #(29-51)
655.0683
677.0497
647.5584
663.4544
800
600
400
200
0
640
645
650
655
660
665
670
675
680
m/z

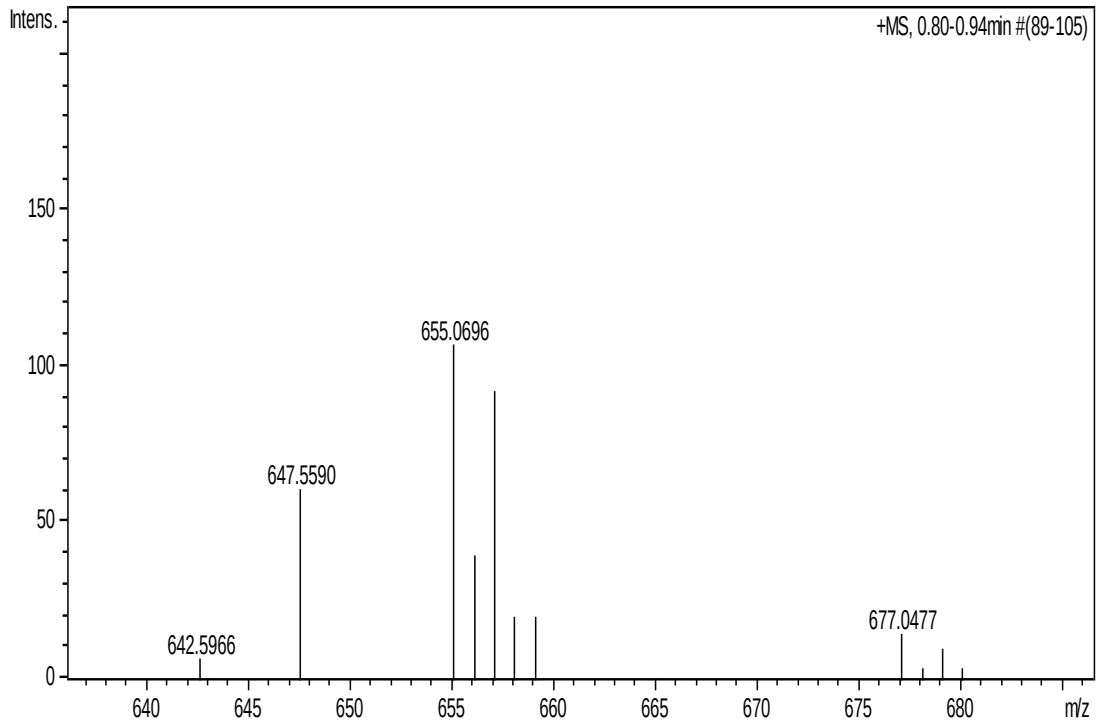
Methyl

6,17-bis(4-chlorophenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5i):

yellow solid, 71%, m.p. 231~235℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.64 (s, 1H, NH), 7.50 (d, *J* = 8.0 Hz, 2H, ArH), 7.40~7.38 (m, 1H, ArH), 7.27 (d, *J* = 8.0 Hz, 2H, ArH), 7.23~7.13 (m, 6H, ArH), 7.04~6.97 (m, 5H, ArH), 5.61 (s, 1H, CH), 4.95 (s, 1H, CH), 4.24 (d, *J* = 6.4Hz, 1H, CH), 3.73 (d, *J* = 6.8 Hz, 1H, CH), 3.52 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.8, 149.2, 148.6, 139.6, 136.4, 134.1, 133.4, 130.4, 130.1, 130.0, 129.5, 129.1, 126.9, 126.6, 124.2, 123.2, 122.9, 120.3, 119.1, 116.4, 115.0, 107.4, 72.1, 51.6, 29.7, 25.0; IR (KBr) υ: 3666, 1702, 1637, 1610, 1579, 1551, 1491, 1466, 1430, 1347, 1268, 1231, 1125, 1092, 1015, 978, 898, 813, 793, 742, 706cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{31}H_{24}BrN_2O_4S$ ($[M+H]^+$): $C_{35}H_{25}Cl_2N_2O_3S_2$ ($[M+H]^+$): 655.0684. Found: 655.0696.



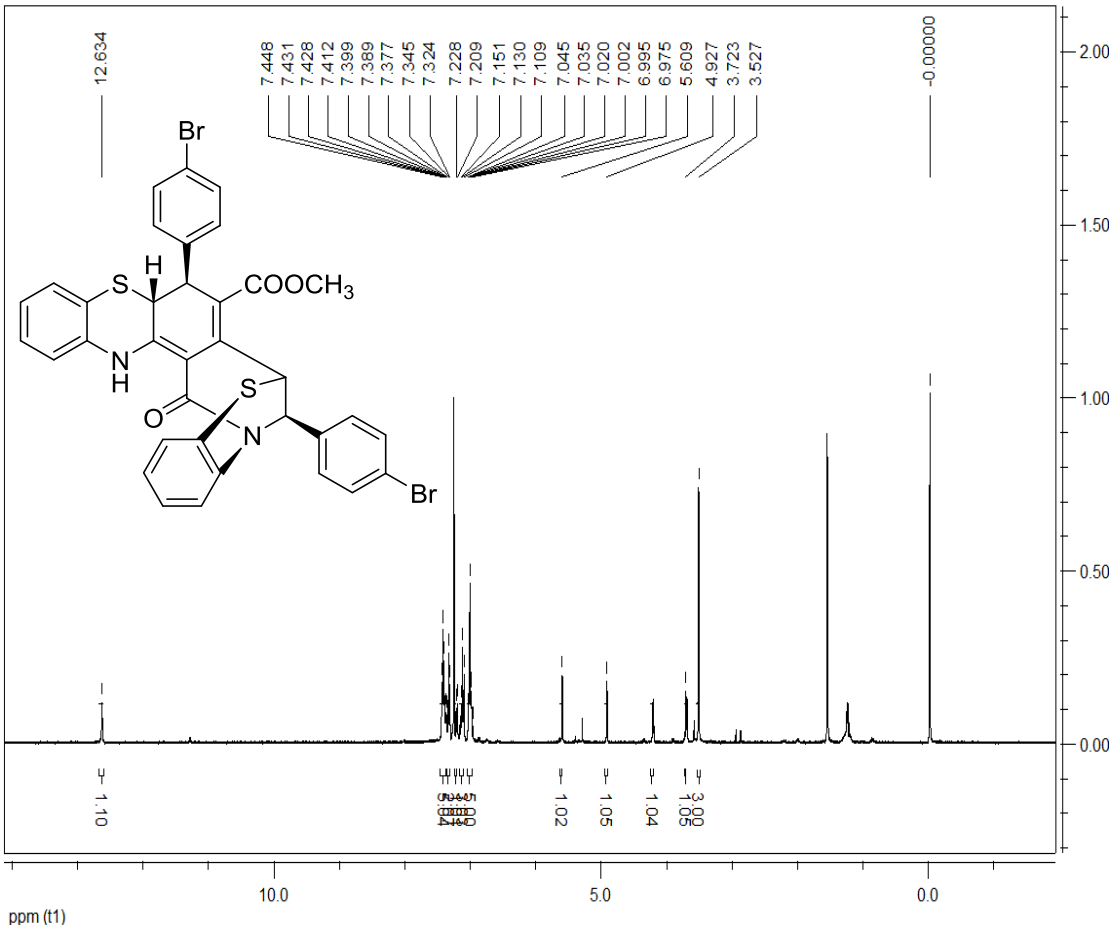

176.295
167.097
151.391
145.367
142.859
137.612
134.748
133.433
133.240
130.370
129.880
129.193
128.608
128.472
128.396
127.733
127.654
127.153
125.441
124.843
124.296
124.267
119.118
112.386
109.988
91.559
54.861
51.568
43.798
43.729
38.762
1.008
40
30
20
10
0
200
150
100
50
0
ppm (t1)

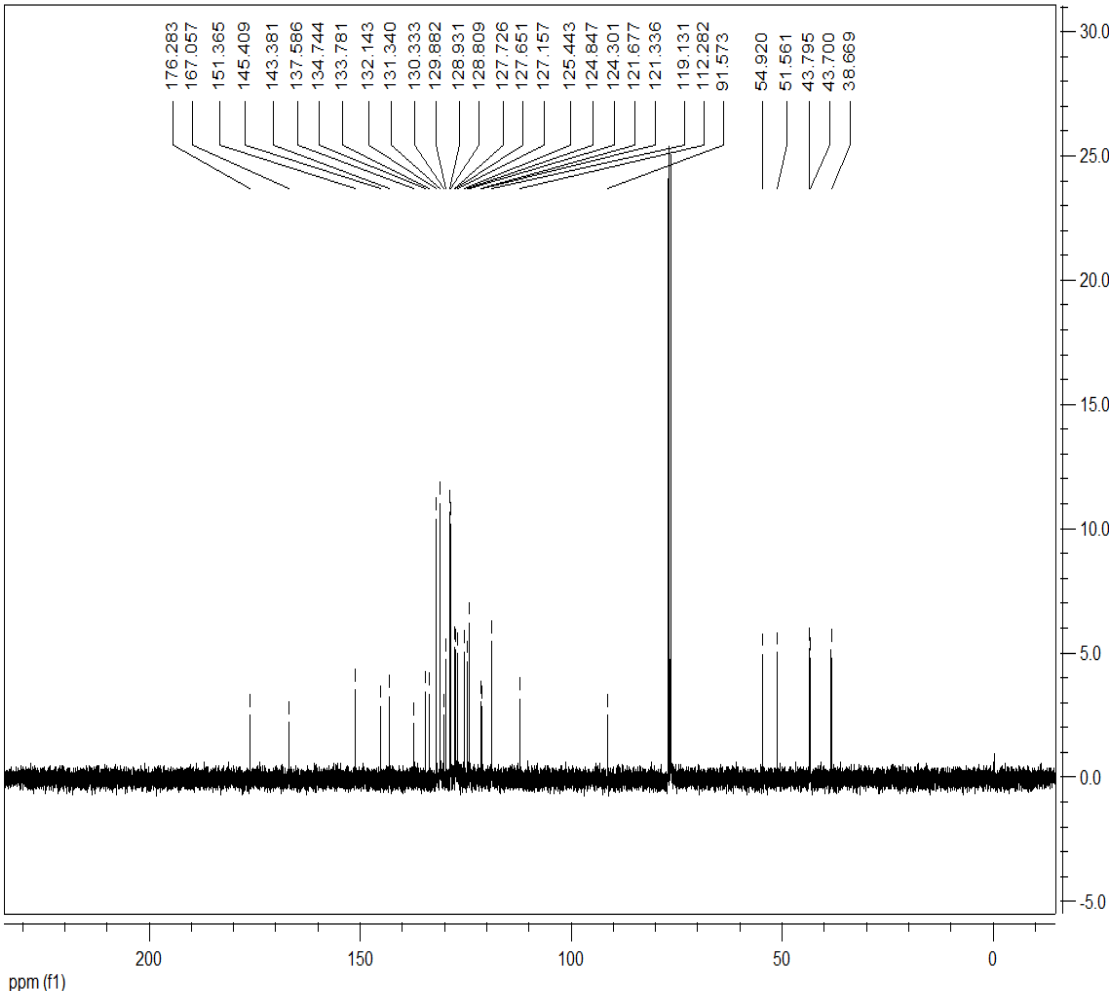

Intens.
+MS, 0.80-0.94min #(89-105)
150
100
50
0
655.0696
647.5590
642.5966
677.0477
640
645
650
655
660
665
670
675
680
m/z

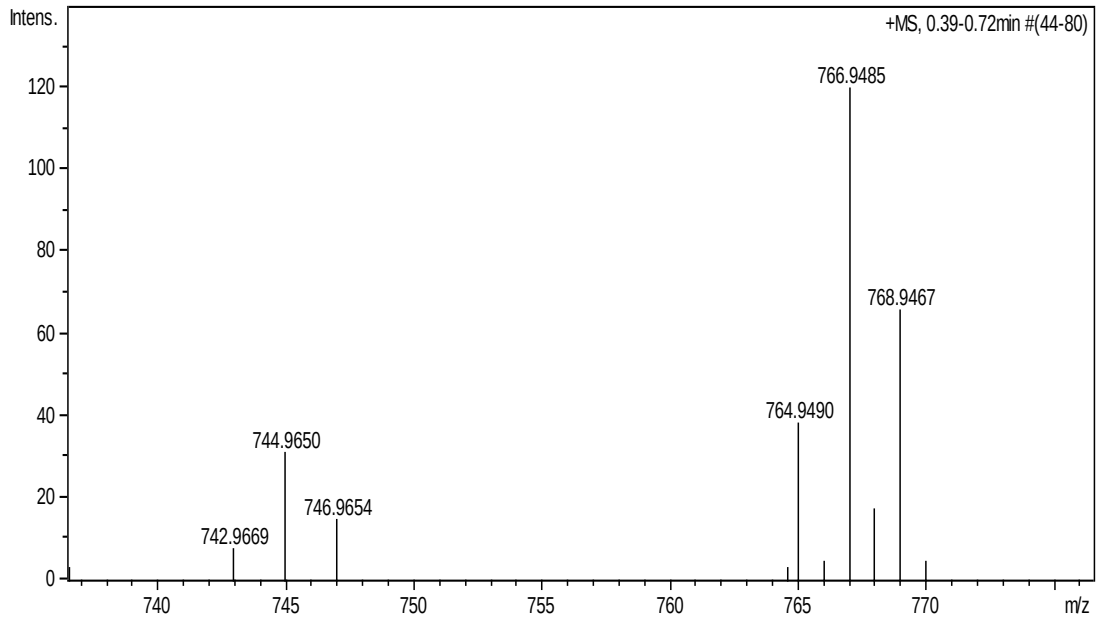
Methyl

6,17-bis(4-bromophenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5j):

yellow solid, 83%, m.p. 240~243℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.63 (s, 1H, NH), 7.45~7.38 (m, 5H, ArH), 7.33 (d, *J* = 8.4 Hz, 2H, ArH), 7.22 (d, *J* = 7.6 Hz, 1H, ArH), 7.15~7.11 (m, 3H, ArH), 7.05~6.98 (m, 5H, ArH), 5.61 (s, 1H, CH), 4.93 (s, 1H, CH), 4.22 (d, *J* = 6.8 Hz, 1H, CH), 3.71 (d, *J* = 6.8 Hz, 1H, CH), 3.53 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.0, 149.8, 137.1, 135.8, 133.7, 130.0, 129.7, 129.2, 129.1, 128.9, 128.8, 128.4, 126.9, 126.4, 126.3, 126.2, 123.3, 120.8, 119.2, 115.9, 114.4, 107.1, 73.3, 51.4, 24.9; IR (KBr) υ: 3072, 2999, 1699, 1584, 1533, 1483, 1444, 1407, 1331, 1288, 1195, 1149, 1063, 982, 917, 848, 806, 761cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{24}Br_2NaO_3S_2$ ([M+Na]$^+$): 764.9493. Found: 764.9490.



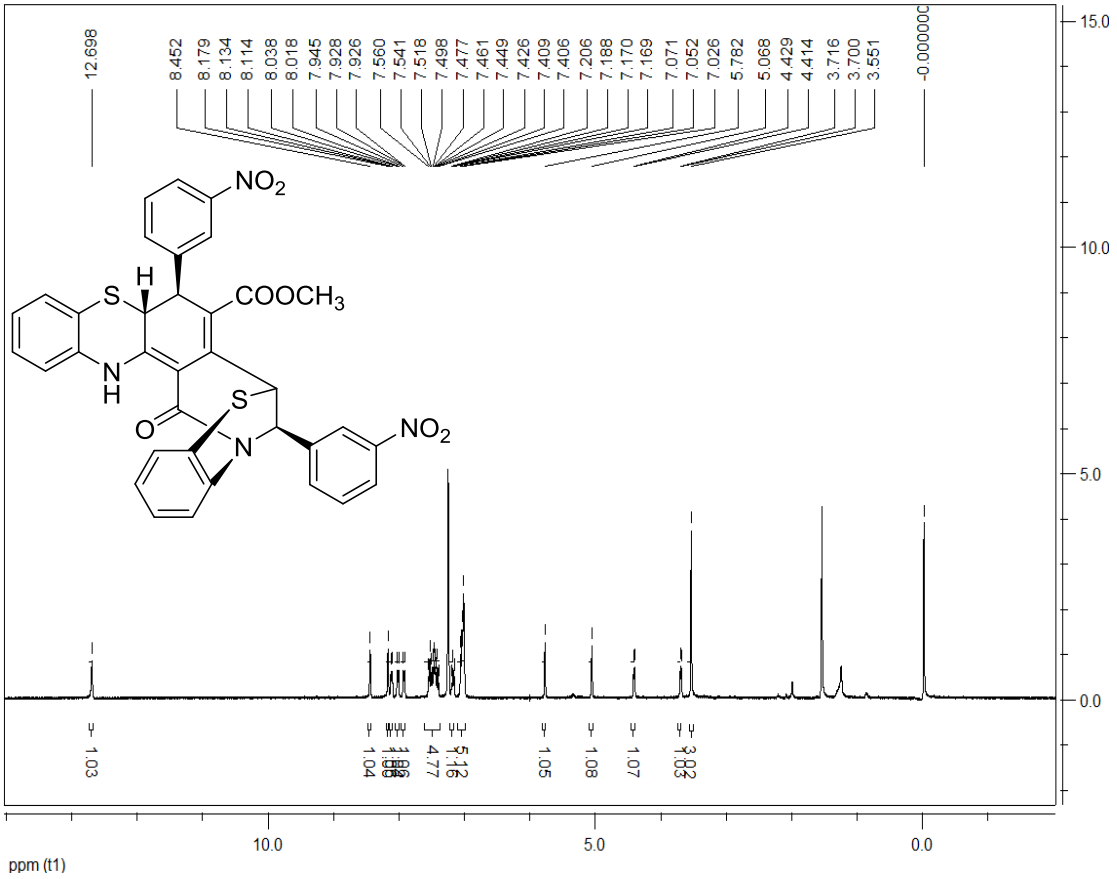

176.283
167.057
151.365
145.409
143.381
137.586
134.744
133.781
132.143
131.340
130.333
129.882
128.931
128.809
127.726
127.651
127.157
125.443
124.847
124.301
121.677
121.336
119.131
112.282
91.573
54.920
51.561
43.795
43.700
38.669
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (f1)

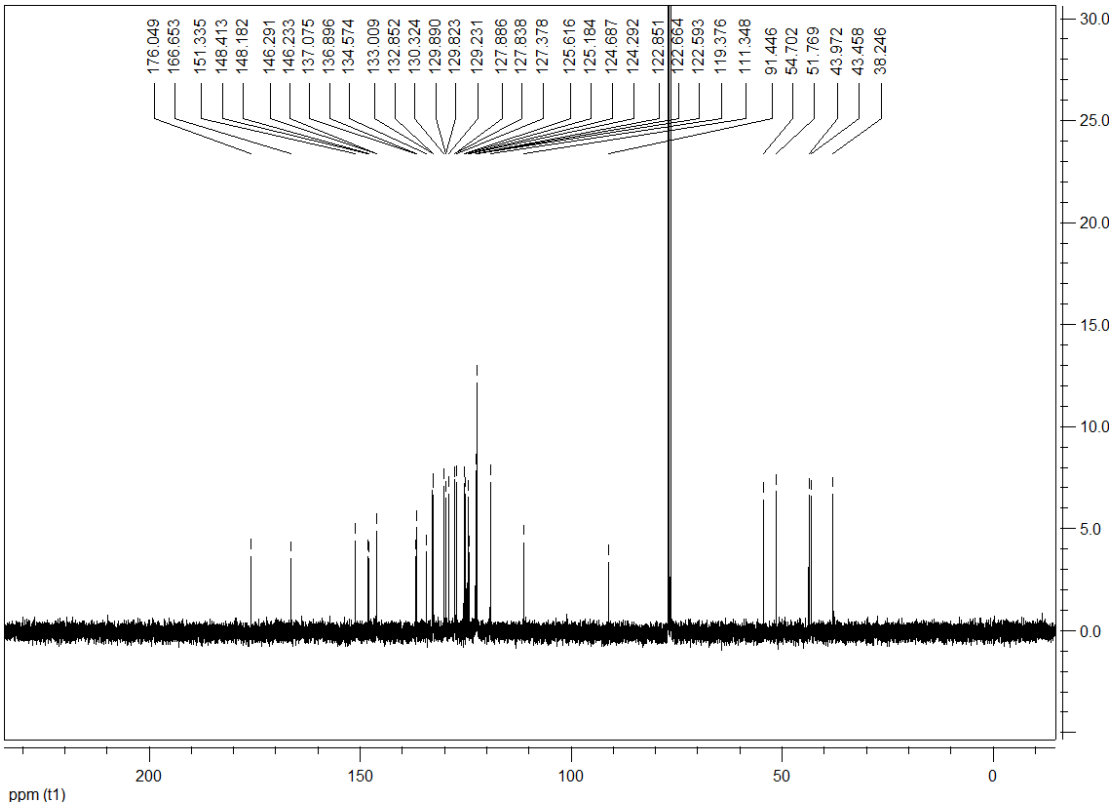

Intens.
+MS, 0.39-0.72min #(44-80)
766.9485
768.9467
764.9490
744.9650
746.9654
742.9669
120
100
80
60
40
20
0
740
745
750
755
760
765
770
m/z

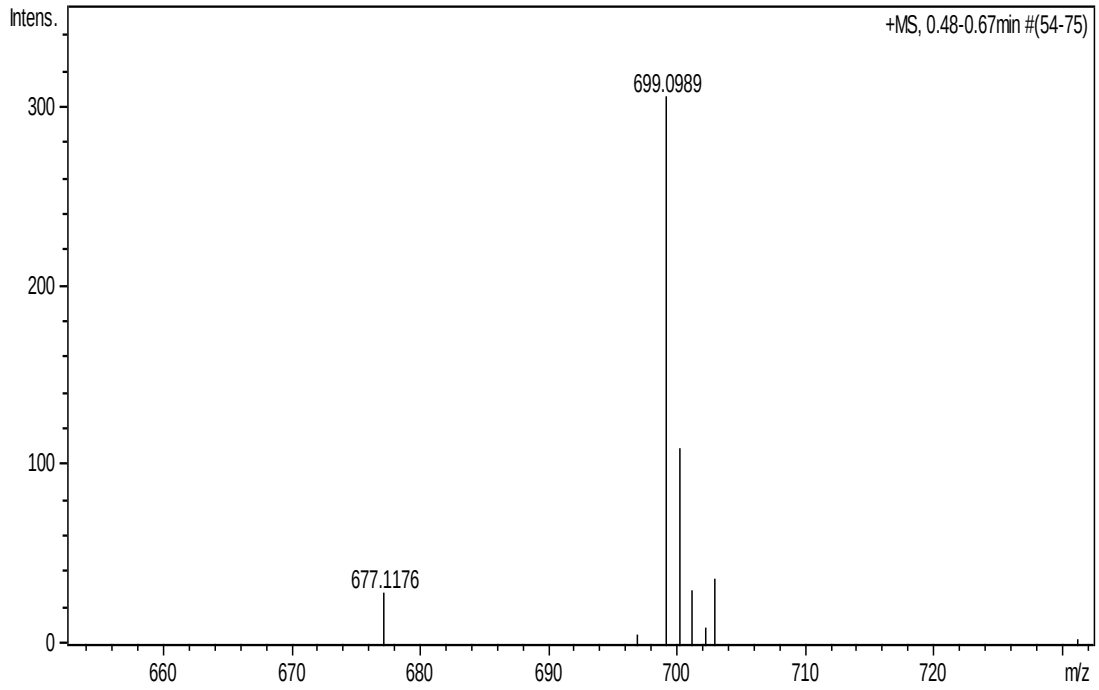
Methyl

6,17-bis(3-nitrophenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5k):

yellow solid, 77%, m.p. 204~206℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.70 (s, 1H, NH), 8.45 (s, 1H, ArH), 8.18 (s, 1H, ArH), 8.12 (d, *J* = 8.0 Hz, 1H, ArH), 8.03 (d, *J* = 8.0 Hz, 1H, ArH), 7.94 (d, *J* = 7.6 Hz, 1H, ArH), 7.56~7.41 (m, 5H, ArH), 7.21~7.17 (m, 1H, ArH), 7.07~7.03 (m, 5H, ArH), 5.78 (s, 1H, CH), 5.07 (s, 1H, CH), 4.42 (d, *J* = 6.0 Hz, 1H, CH), 3.71 (d, *J* = 6.4 Hz, 1H, CH), 3.55 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4, 159.9, 135.2, 133.9, 129.7, 129.6, 128.7, 127.4, 126.8, 126.5, 126.1, 126.0, 121.8, 121.4, 120.9, 117.7, 116.8, 114.1, 107.2, 72.9, 55.1, 51.4, 29.7, 25.0; IR (KBr) υ: 3849, 2949, 1701, 1609, 1580, 1552, 1467, 1432, 1348, 1272, 1226, 1127, 1082, 1022, 980, 922, 876, 839, 799, 780, 755, 736, 701 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{24}N_4NaO_7S_2$ ([M+Na]$^+$): 699.0984. Found: 699.0989.



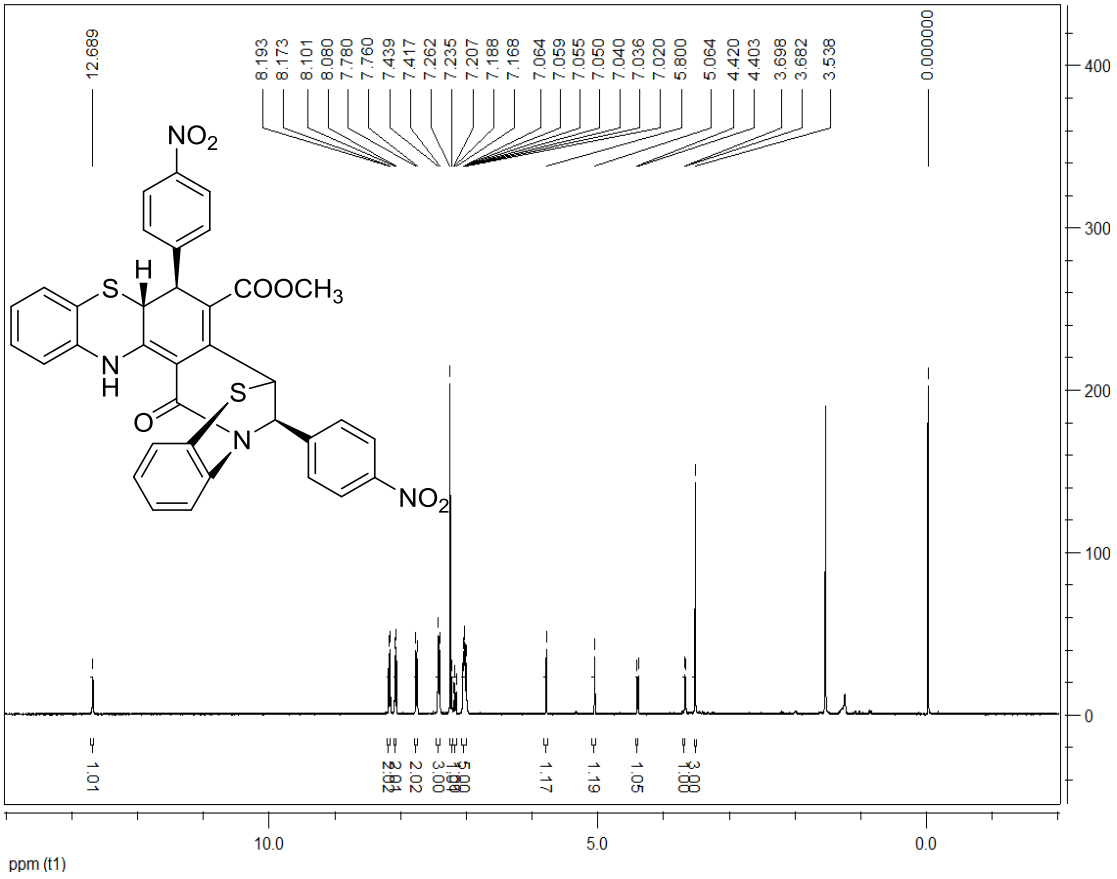

176.049
166.653
151.335
148.413
148.182
146.291
146.233
137.075
136.896
134.574
133.009
132.852
130.324
129.890
129.823
129.231
127.886
127.838
127.378
125.616
125.184
124.687
124.292
122.851
122.664
122.593
119.376
111.348
91.446
54.702
51.769
43.972
43.458
38.246
30.0
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

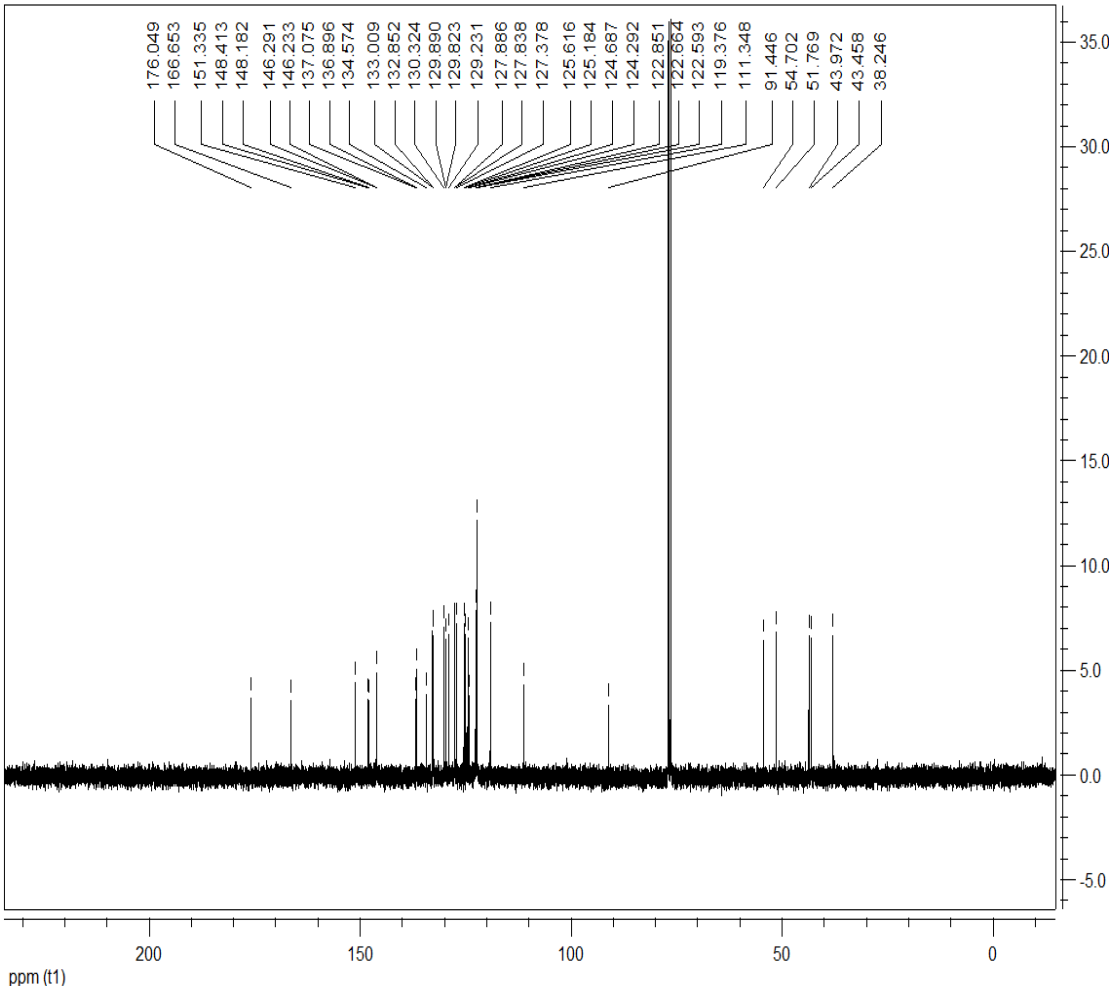

Intens.
+MS, 0.48-0.67min #(54-75)
699.0989
677.1176
300
200
100
0
660
670
680
690
700
710
720
m/z

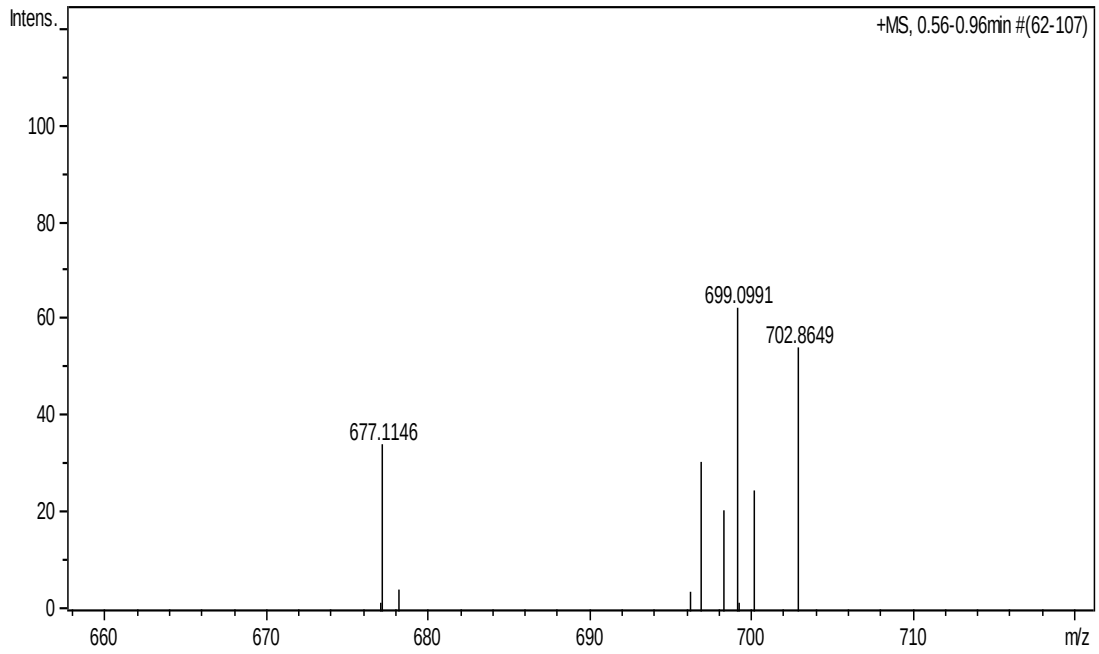
Methyl

6,17-bis(4-nitrophenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5l):

yellow solid, 85%, m.p. 249~252℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.69 (s, 1H, NH), 8.18 (d, *J* = 8.0 Hz, 2H, ArH), 8.09 (d, *J* = 8.4 Hz, 2H, ArH), 7.77 (d, *J* = 8.0 Hz, 2H, ArH), 7.43 (d, *J* = 8.8 Hz, 2H, ArH), 7.22 (d, *J* = 11.2 Hz, 1H, ArH), 7.18 (d, *J* = 8.0 Hz, 1H, ArH), 7.06~7.02 (m, 5H, ArH), 5.80 (s, 1H, CH), 5.06 (s, 1H, CH), 4.41 (d, *J* = 6.8 Hz, 1H, CH), 3.68 (d, *J* = 7.2 Hz, 1H, CH), 3.54 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4, 159.9, 135.2, 133.9, 129.7, 129.6, 128.7, 127.4, 126.8, 126.5, 126.1, 126.0, 121.8, 121.4, 120.9, 117.7, 116.8, 114.1, 107.2, 72.9, 55.1, 51.4, 29.7, 25.0; IR (KBr) υ: 3732, 3057, 2947, 1704, 1638, 1612, 1579, 1551, 1487, 1467, 1431, 1404, 1349, 1269, 1232, 1198, 1127, 1074, 1011, 979, 899, 833, 813, 792, 755, 742, 709cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{24}N_4NaO_7S_2$ ([M+Na]$^+$): 699.0984. Found: 699.0991.



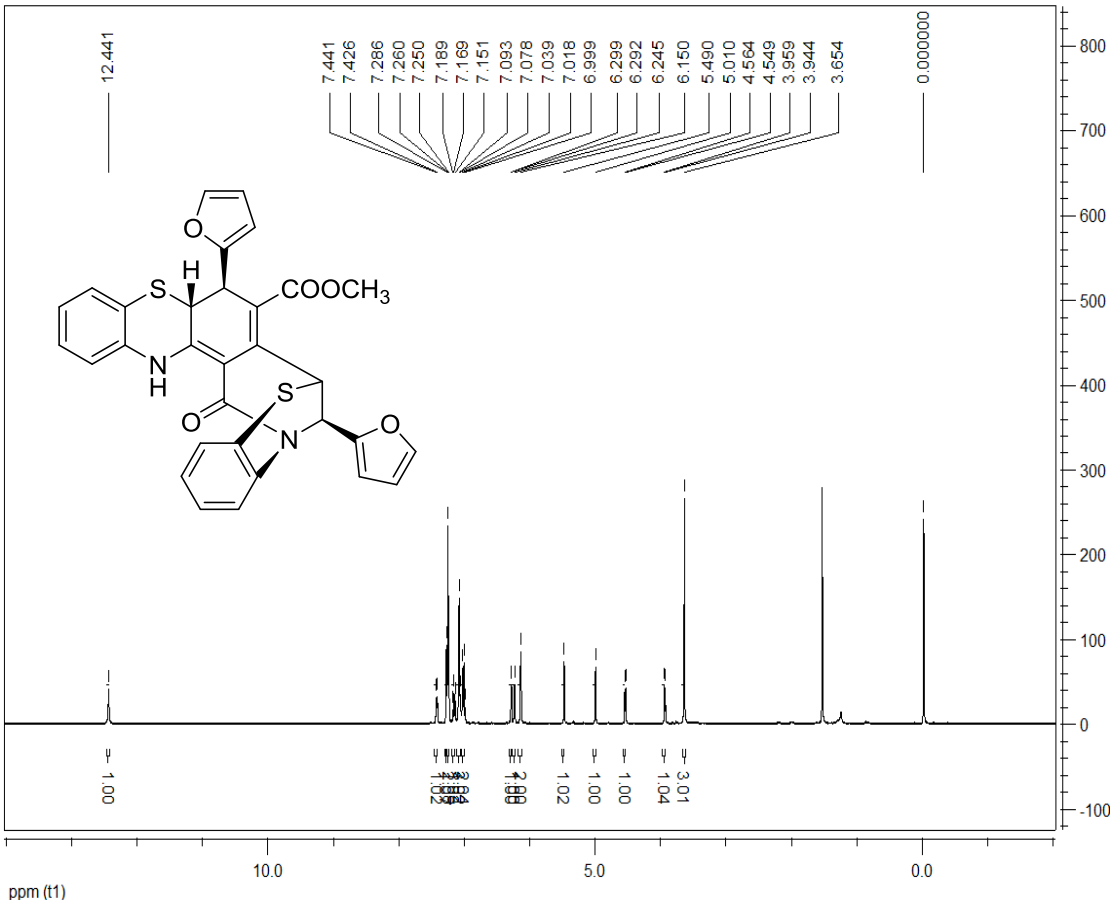

176.049
166.653
151.335
148.413
148.182
146.291
146.233
137.075
136.896
134.574
133.009
132.852
130.324
129.890
129.823
129.231
127.886
127.838
127.378
125.616
125.184
124.687
124.292
122.851
122.664
122.593
119.376
111.348
91.446
54.702
51.769
43.972
43.458
38.246
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (t1)

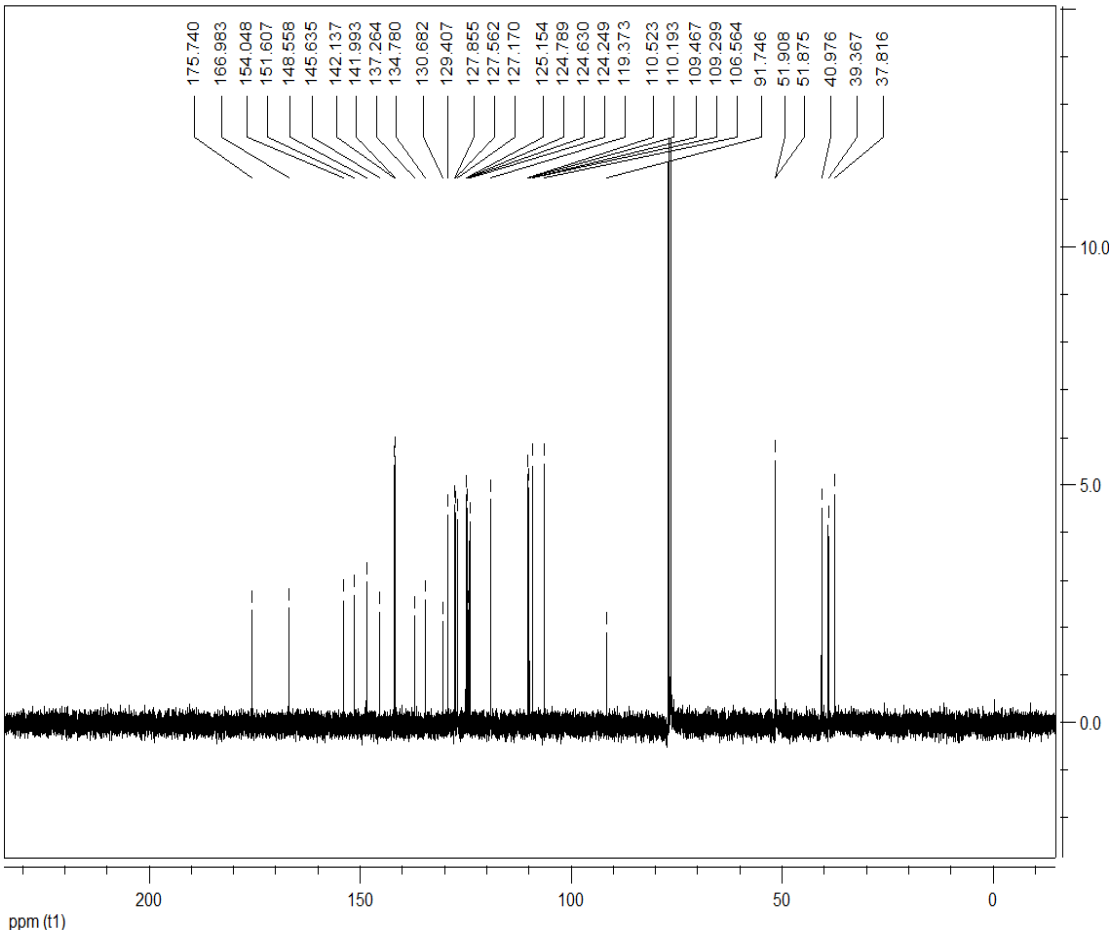

Intens.
+MS, 0.56-0.96min #(62-107)
100
80
60
40
20
0
699.0991
702.8649
677.1146
660
670
680
690
700
710
m/z

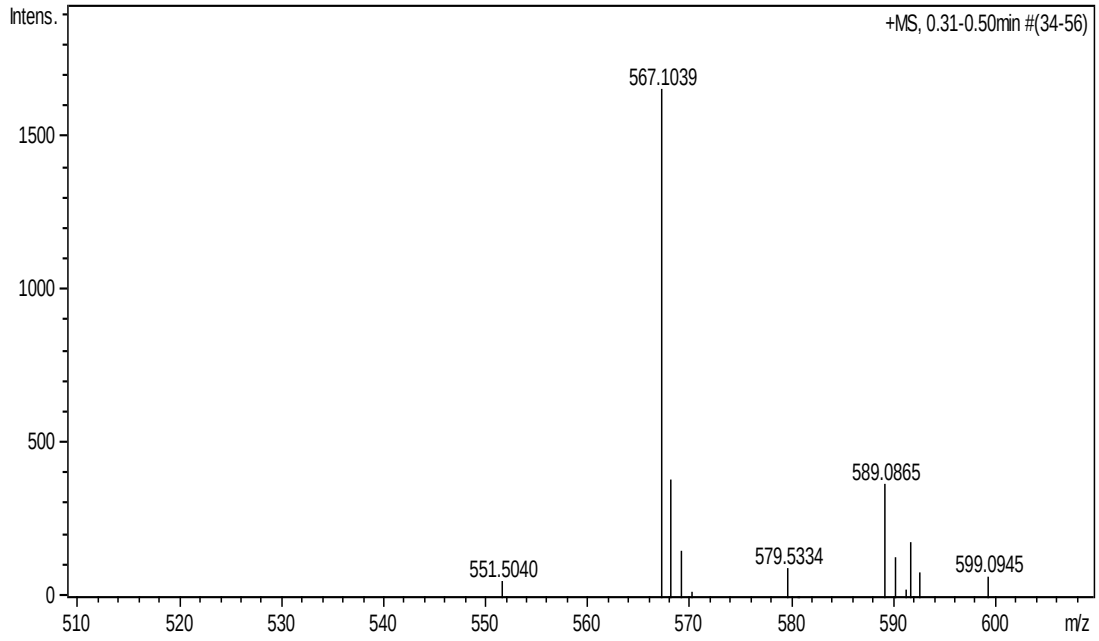
Methyl

6,17-di(furan-2-yl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5m):

yellow solid, 69%, m.p. 165~168℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.44 (s, 1H, NH), 7.43 (d, *J* = 6.0 Hz, 1H, ArH), 7.29 (s, 1H, ArH), 7.26 (d, *J* = 4.0 Hz, 1H, ArH), 7.19~7.15 (m, 1H, ArH), 7.09~7.07 (m, 3H, ArH), 7.04~7.00 (m, 2H, ArH), 6.30 (d, *J* = 2.4 Hz, 1H, ArH), 6.25 (s, 1H, ArH), 6.15 (s, 2H, ArH), 5.49 (s, 1H, CH), 5.01 (s, 1H, CH), 4.56 (d, *J* = 6.0 Hz, 1H, CH), 3.95 (d, *J* = 6.0 Hz, 1H, CH), 3.65 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.7, 167.0, 154.0, 151.6, 148.6, 145.6, 142.1, 142.0, 137.3, 134.8, 130.7, 129.4, 127.9, 127.6, 127.2, 125.2, 124.8, 124.6, 124.2, 119.4, 110.5, 110.2, 109.5, 109.3, 106.6, 91.7, 51.9, 51.9, 41.0, 39.4, 37.8; IR (KBr) υ: 3861, 3849, 3728, 3708, 3625, 3604, 3060, 2947, 2351, 2323, 1695, 1607, 1580, 1551, 1503, 1467, 1433, 1352, 1280, 1261, 1239, 1198, 1132, 1012, 949, 926, 900, 885, 837, 785, 744cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{31}H_{23}N_2O_5S_2$ ([M+H]$^+$): 567.1048. Found: 567.1039.



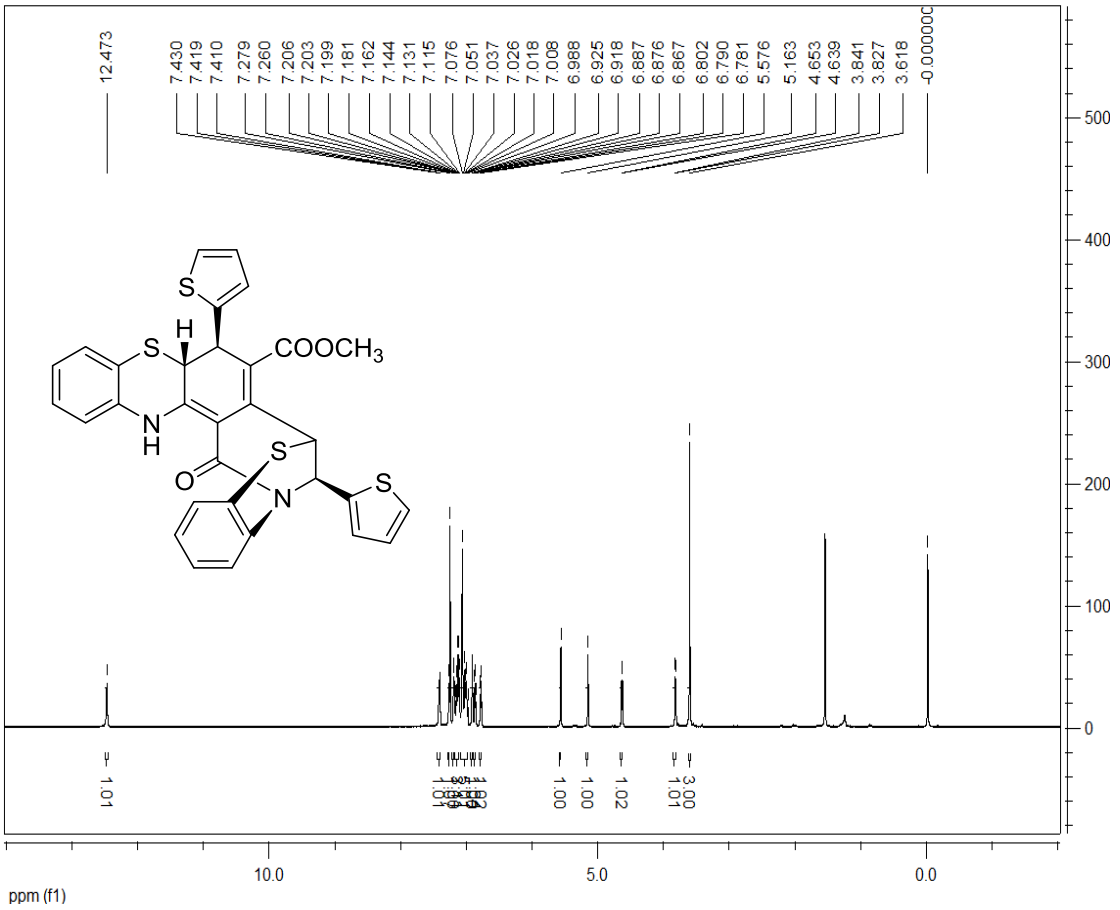

175.740
166.983
154.048
151.607
148.558
145.635
142.137
141.993
137.264
134.780
130.682
129.407
127.855
127.562
127.170
125.154
124.789
124.630
124.249
119.373
110.523
110.193
109.467
109.299
106.564
91.746
51.908
51.875
40.976
39.367
37.816
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

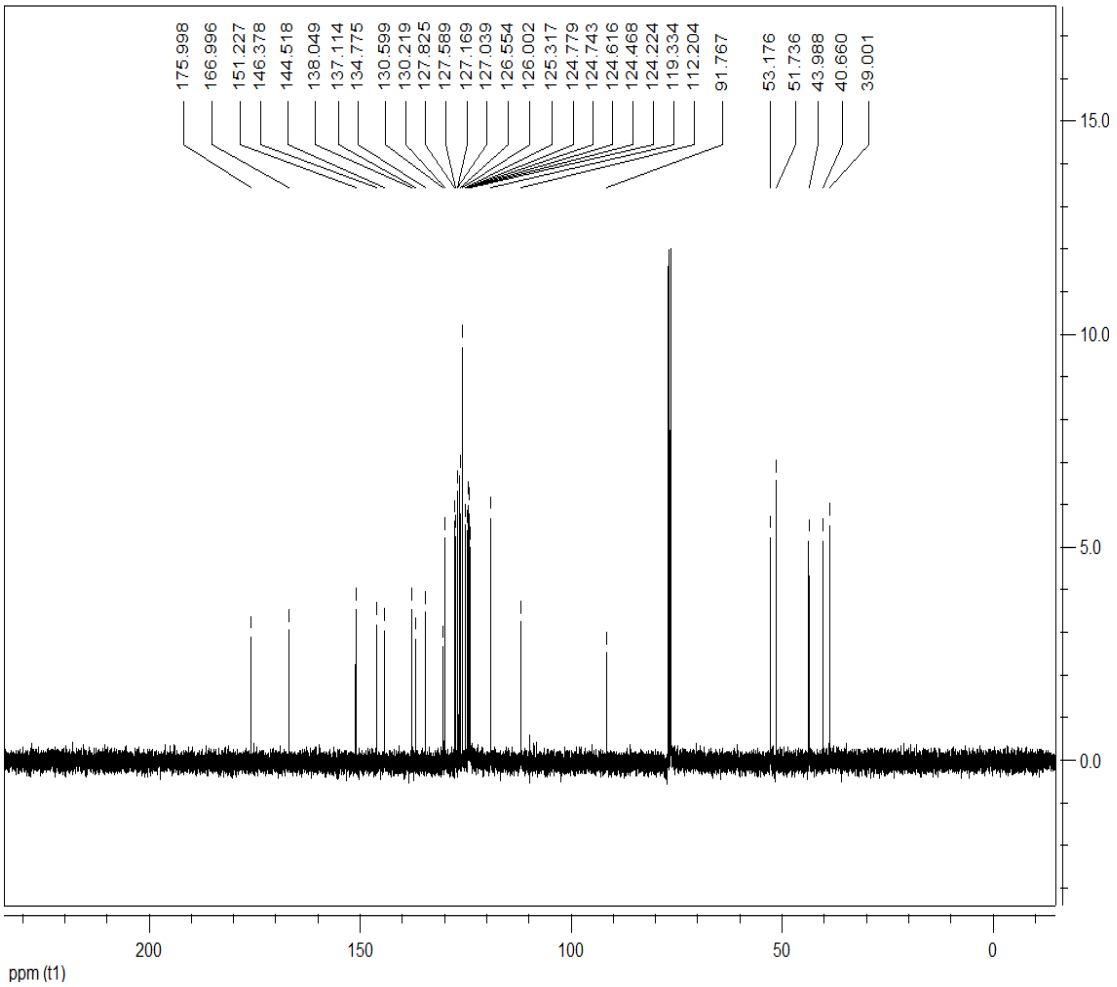

Intens.
+MS, 0.31-0.50min #(34-56)
567.1039
1500
1000
500
0
589.0865
551.5040
579.5334
599.0945
510
520
530
540
550
560
570
580
590
600
m/z

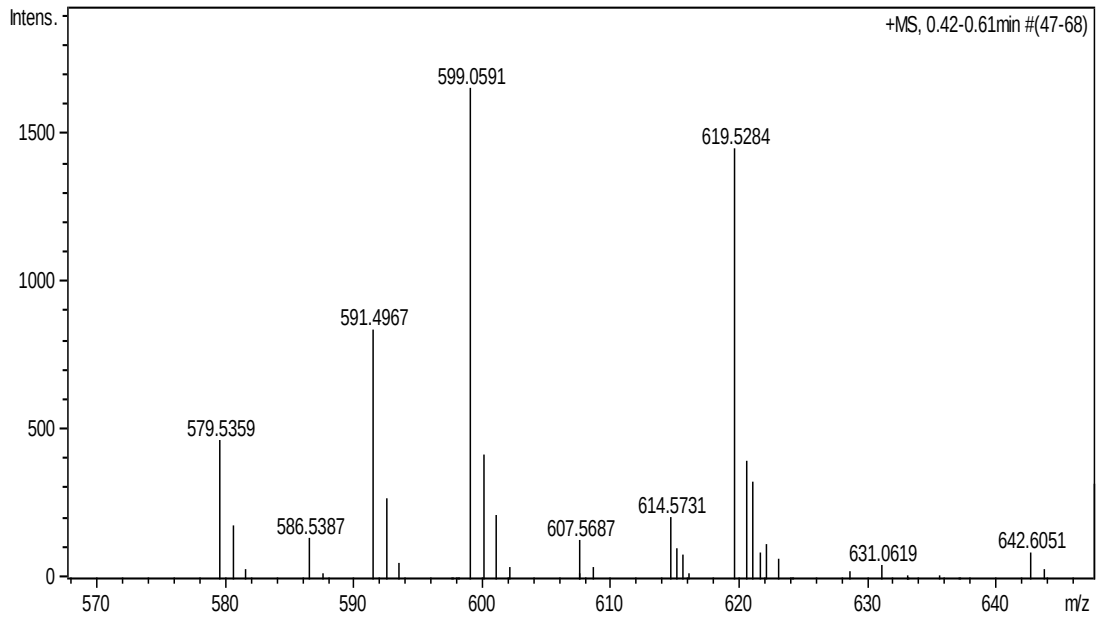
Methyl

15-oxo-6,17-di(thiophen-2-yl)-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5n):

yellow solid, 71%, m.p. 171~175℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.47 (s, 1H, NH), 7.43~7.41 (m, 1H, ArH), 7.27 (d, *J* = 6.8 Hz, 1H, ArH), 7.21~7.20 (m, 1H, ArH), 7.18~7.12 (m, 3H, ArH), 7.08~6.99 (m, 2H, ArH), 6.92 (d, *J* = 2.8 Hz, 1H, ArH), 6.89~6.87 (m, 1H, ArH), 6.80~6.78 (m, 1H, ArH), 5.58 (s, 1H, CH), 5.16 (s, 1H, CH), 4.65 (d, *J* = 5.6 Hz, 1H, CH), 3.83 (d, *J* = 5.6 Hz, 1H, CH), 3.62 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.0, 167.0, 151.2, 146.4, 144.5, 138.0, 137.1, 134.8, 130.6, 130.2, 127.8, 127.6, 127.2, 127.0, 126.6, 126.0, 125.3, 124.8, 124.7, 124.6, 124.5, 124.2, 119.3, 112.2, 91.8, 53.2, 51.7, 44.0, 40.7, 39.0; IR (KBr) υ: 3861, 3834, 3727, 3708, 3625, 3599, 3450, 3061, 2946, 2350, 2323, 1695, 1607, 1579, 1550, 1467, 1433, 1348, 1281, 1260, 1238, 1161, 1129, 1047, 999, 974, 899, 835, 782, 751cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{31}H_{23}N_2O_3S_4$ ($[M+H]^+$): 599.0591. Found: 599.0592.



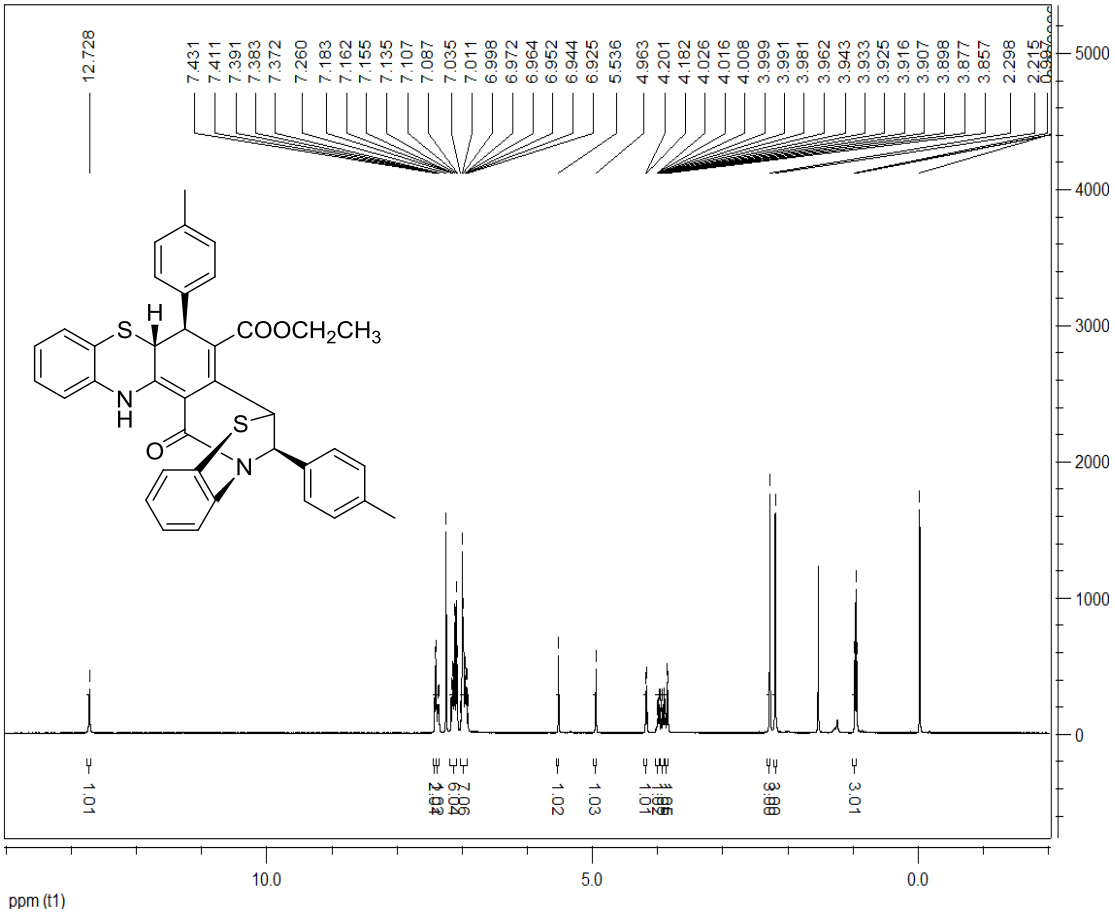

175.998
166.996
151.227
146.378
144.518
138.049
137.114
134.775
130.599
130.219
127.825
127.589
127.169
127.039
126.554
126.002
125.317
124.779
124.743
124.616
124.468
124.224
119.334
112.204
91.767
53.176
51.736
43.988
40.660
39.001
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

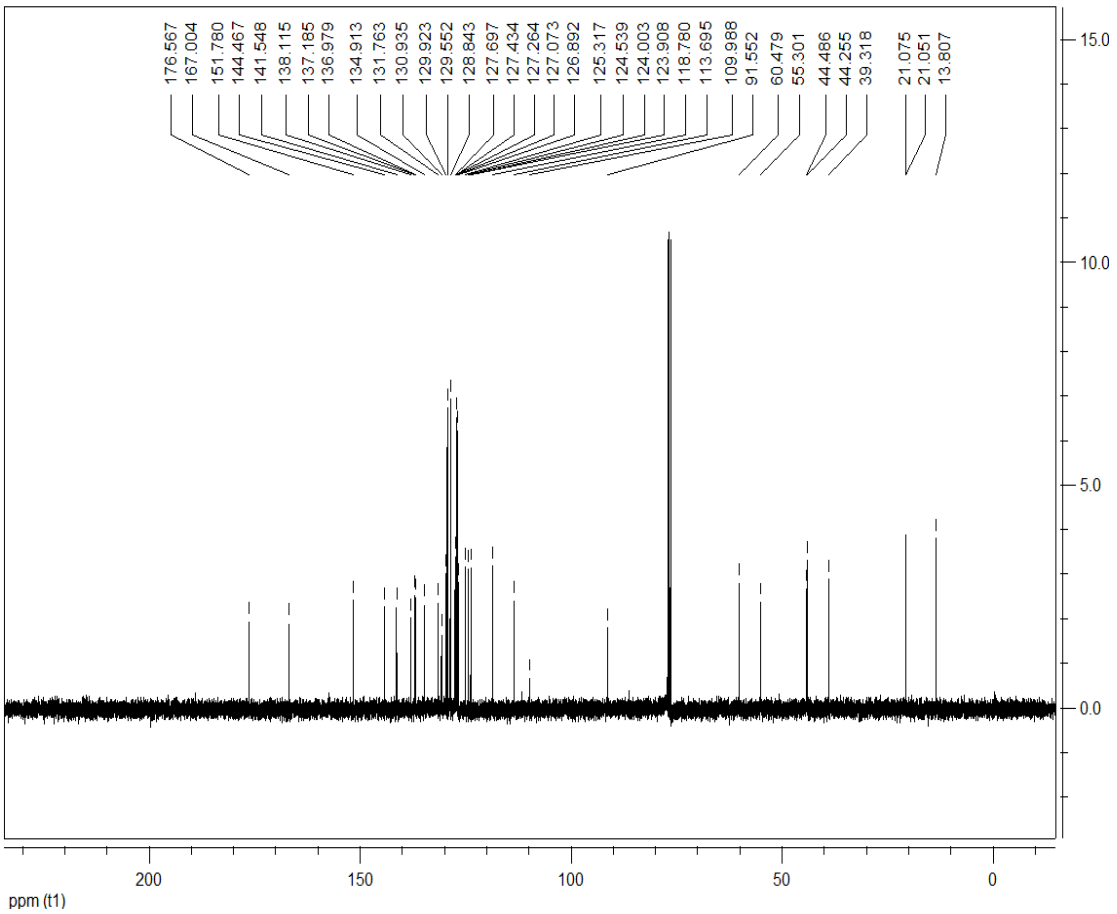

Intens.
+MS, 0.42-0.61min #(47-68)
599.0591
619.5284
591.4967
579.5359
586.5387
607.5687
614.5731
631.0619
642.6051
1500
1000
500
0
570
580
590
600
610
620
630
640
m/z

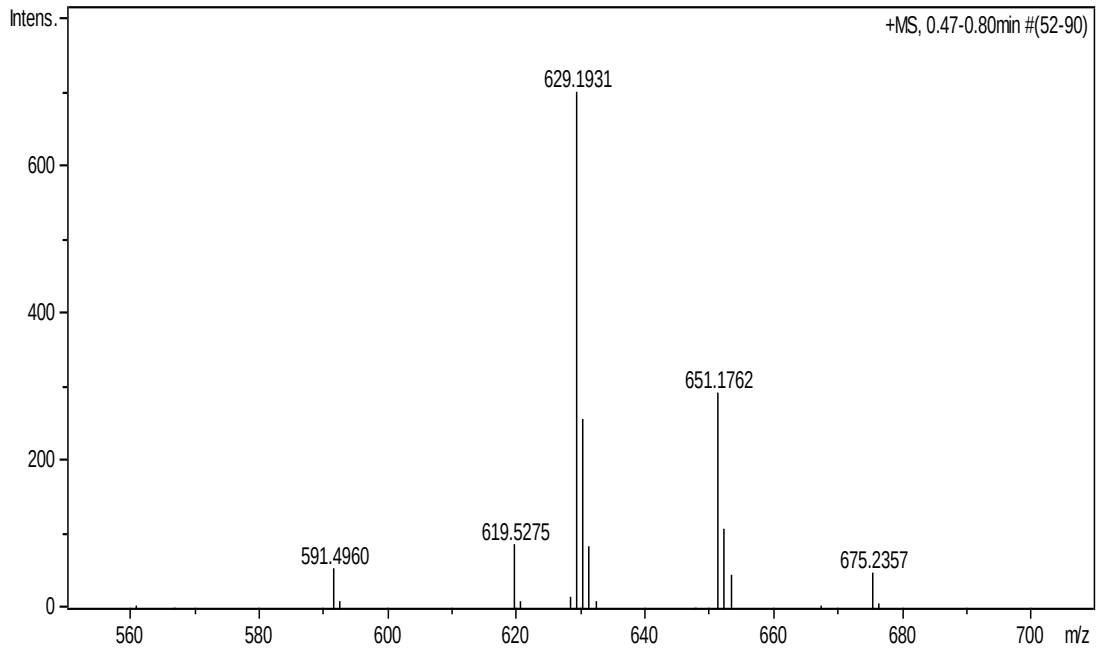
Ethyl

15-oxo-6,17-di-p-tolyl-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5o):

yellow solid, 82%, m.p. 235~237℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.73 (s, 1H, NH), 7.39~7.37 (m, 1H, ArH), 7.18~7.09 (m, 6H, ArH), 7.04~6.93 (m, 7H, ArH), 5.54 (s, 1H, CH), 4.96 (s, 1H, CH), 4.19 (d, *J* = 6.8 Hz, 1H, CH), 4.03~3.98 (m, 1H, ArH), 3.94~3.89 (m, 1H, ArH), 3.87 (d, *J* = 8.0 Hz, 1H, CH), 2.30 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 0.98 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.6, 167.0, 151.8, 144.5, 141.5, 138.1, 137.2, 137.0, 134.9, 131.8, 130.9, 129.9, 129.6, 128.8, 127.7, 127.4, 127.3, 127.1, 126.9, 125.3, 124.5, 124.0, 123.9, 118.8, 113.7, 110.0, 91.6, 60.5, 55.3, 44.5, 44.3, 39.3, 21.1, 21.1, 13.8; IR (KBr) υ: 3850, 3732, 3459, 2983, 2351, 1696, 1638, 1611, 1578, 1553, 1514, 1467, 1444, 1420, 1348, 1325,1269, 1232, 1127, 1112, 1058, 1031, 928, 892, 811, 781, 754, 742, 711cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{28}N_2NaO_3S_2$ ([M+Na]$^{+}$): 635.1432. Found: 635.1439.



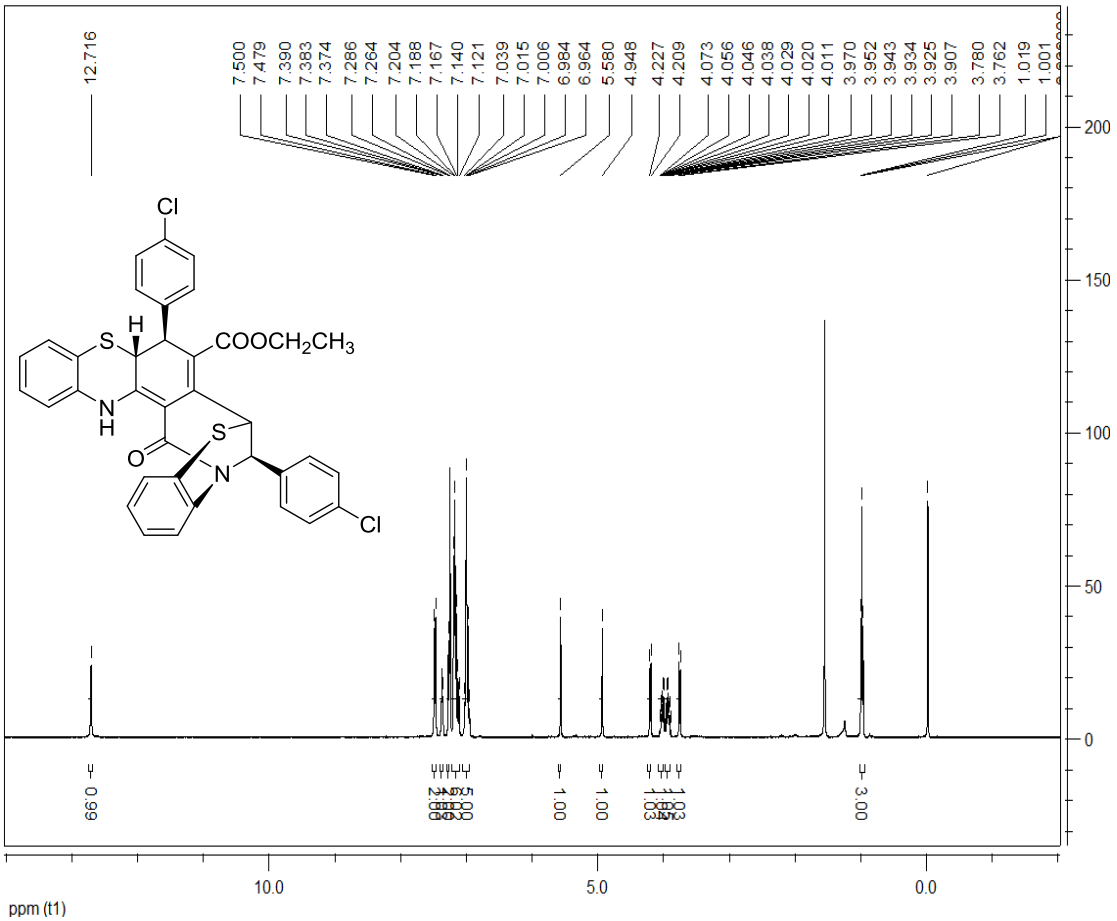

176.567
167.004
151.780
144.467
141.548
138.115
137.185
136.979
134.913
131.763
130.935
129.923
129.552
128.843
127.697
127.434
127.264
127.073
126.892
125.317
124.539
124.003
123.908
118.780
113.695
109.988
91.552
60.479
55.301
44.486
44.255
39.318
21.075
21.051
13.807
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

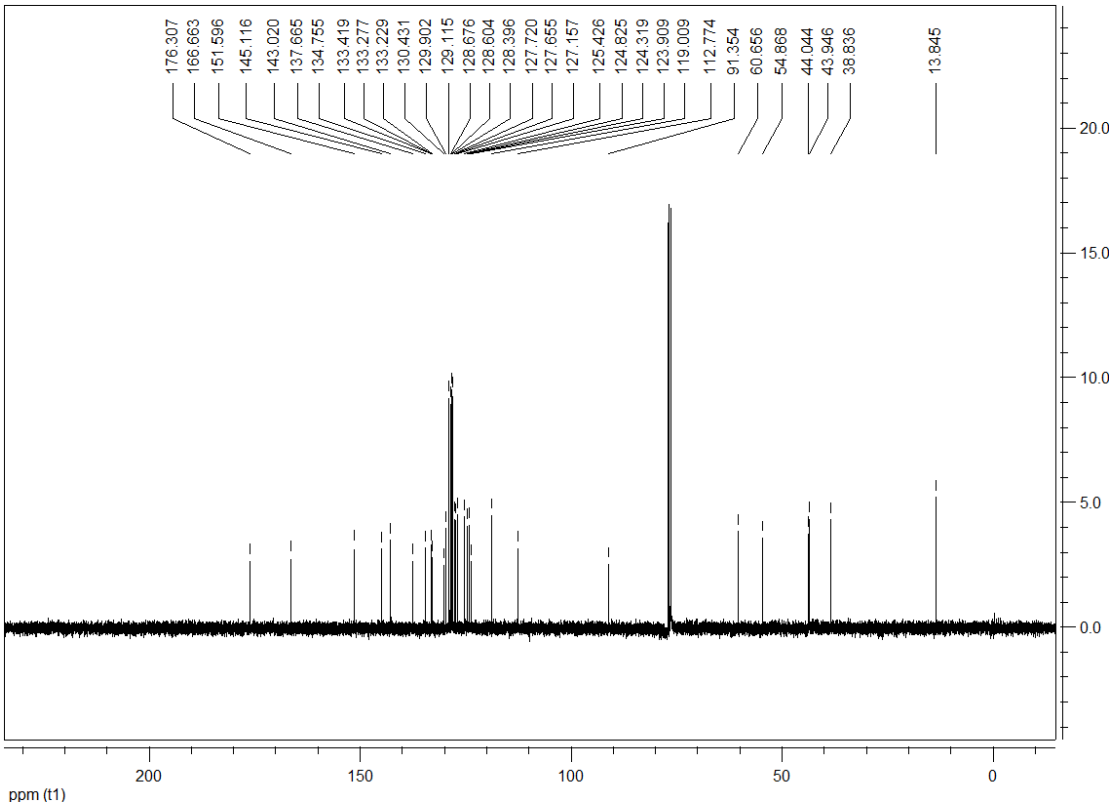

Intens.
+MS, 0.47-0.80min #(52-90)
629.1931
651.1762
591.4960
619.5275
675.2357
600
400
200
0
560
580
600
620
640
660
680
700
m/z

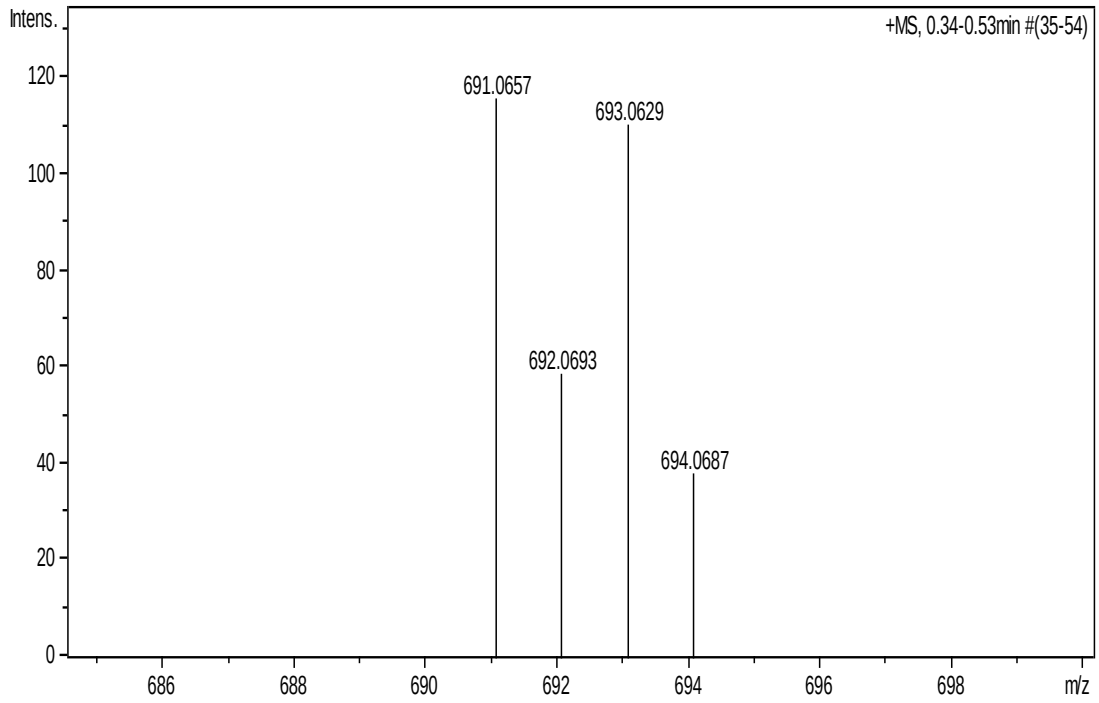
Ethyl

6,17-bis(4-chlorophenyl)-15-oxo-5a,6,15,16-tetrahydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (5p):

yellow solid, 86%, m.p. 221~255℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 12.72 (s, 1H, NH), 7.48 (d, *J* = 8.4 Hz, 2H, ArH), 7.39~7.34 (m, 1H, ArH), 7.28 (d, *J* = 8.8 Hz, 2H, ArH), 7.20~7.12 (m, 6H, ArH), 7.04~6.96 (m, 5H, ArH), 5.58 (s, 1H, CH), 4.95 (s, 1H, CH), 4.22 (d, *J* = 6.8 Hz, 1H, CH), 4.07~4.01 (m, 1H, ArH), 3.97~3.91 (m, 1H, ArH), 3.77 (d, *J* = 8.0 Hz, 1H, CH), 2.30 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 1.00 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.3, 166.7, 151.6, 145.1, 143.0, 137.7, 134.8, 133.4, 133.3, 133.2, 130.4, 129.9, 129.1, 128.7, 128.6, 128.4, 127.7, 127.7, 127.2, 125.4, 124.8, 124.3, 123.9, 119.0, 112.8, 91.4, 60.7, 54.9, 44.0, 43.9, 38.8, 13.8; IR (KBr) υ: 3483, 2981, 1696, 1639, 1611, 1579, 1552, 1491, 1467, 1444, 1422, 1407, 1348, 1325, 1268, 1248, 1232, 1199, 1128, 1093, 1028, 1015, 928, 892, 823, 793, 755, 743, 707cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{36}H_{26}Cl_2N_2NaO_3S_2$ ([M+Na]$^{+}$): 692.0660. Found: 692.0657.



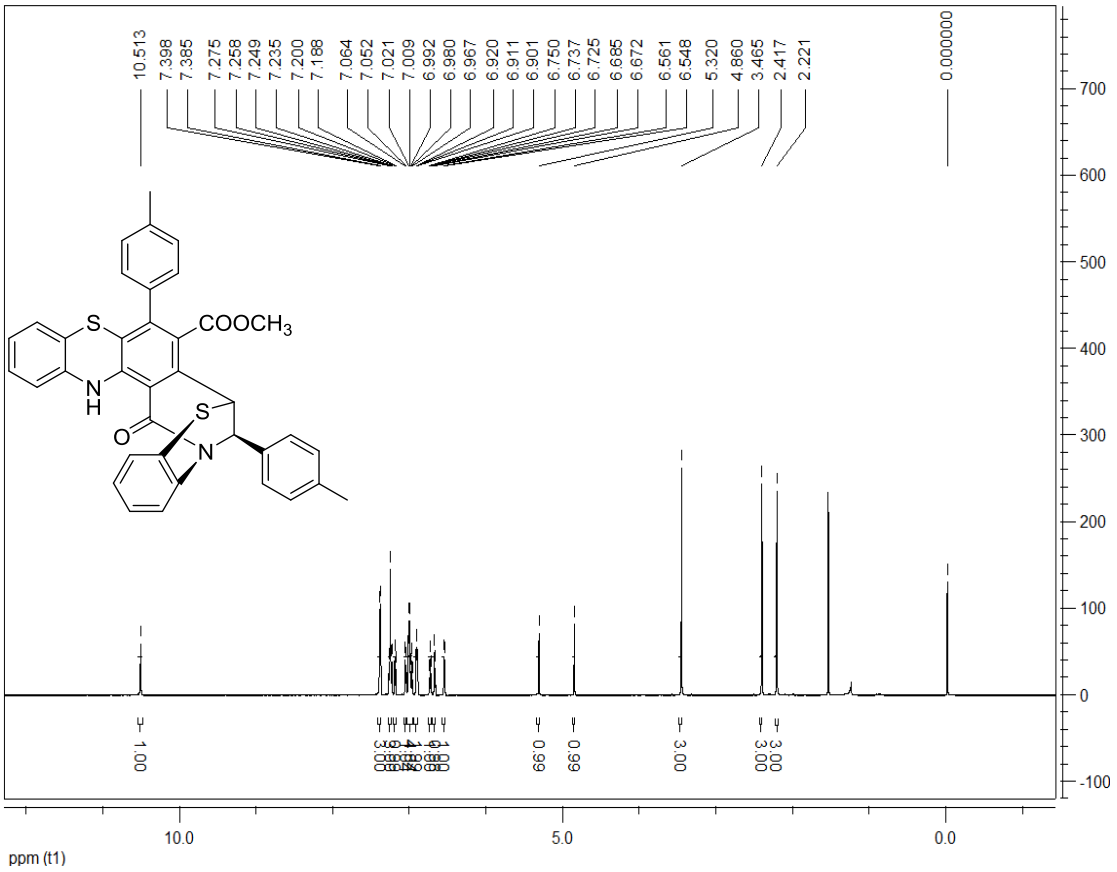

176.307
166.663
151.596
145.116
143.020
137.665
134.755
133.419
133.277
133.229
130.431
129.902
129.115
128.676
128.604
128.396
127.720
127.655
127.157
125.426
124.825
124.319
123.909
119.009
112.774
91.354
60.656
54.868
44.044
43.946
38.836
13.845
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

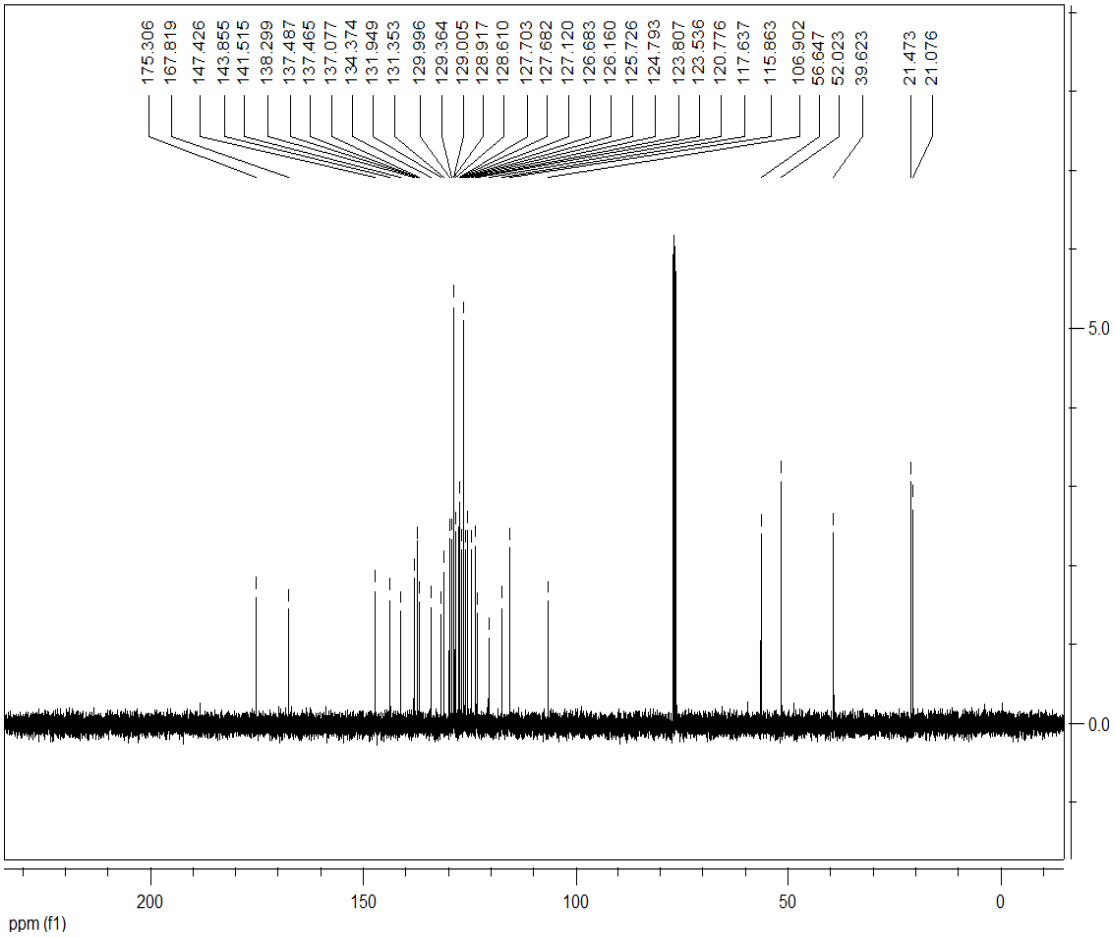

Intens.
+MS, 0.34-0.53min #(35-54)
691.0657
693.0629
692.0693
694.0687
120
100
80
60
40
20
0
686
688
690
692
694
696
698
m/z

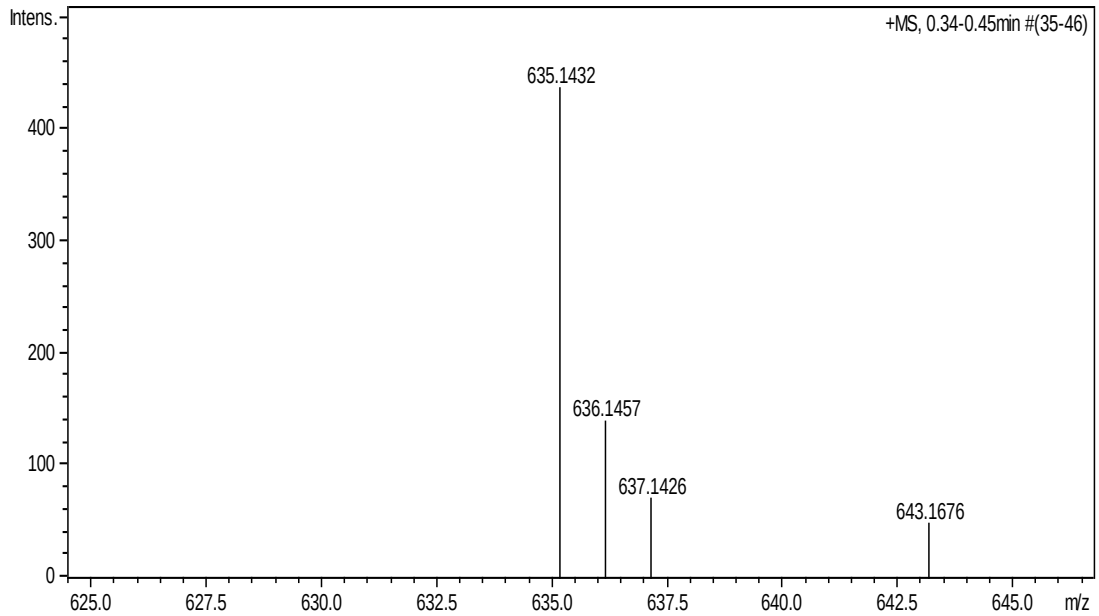
Methyl

15-oxo-6,17-di-p-tolyl-15,16-dihydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]pheno thiazine-7-carboxylate (6a):

yellow solid, 64%, m.p. 238~241℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.51 (s, 1H, NH), 7.39 (d, *J* = 5.2 Hz, 3H, ArH), 7.28~7.24 (m, 3H, ArH), 7.19 (d, *J* = 4.8 Hz, 1H, ArH), 7.06 (d, *J* = 4.8 Hz, 1H, ArH), 7.02~6.97 (m, 4H, ArH), 6.92~6.90 (m, 2H, ArH), 6.68 (d, *J* = 5.2 Hz, 1H, ArH), 6.65 (d, *J* = 5.2 Hz, 1H, ArH), 5.32 (s, 1H, CH), 4.86 (s, 1H, CH), 3.47 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3), 2.22 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.3, 167.8, 147.4, 143.9, 141.5, 138.3, 137.5, 137.5, 137.1, 134.4, 131.9, 131.4, 130.0, 129.4, 129.0, 128.9, 128.6, 127.7, 127.7, 127.1, 126.7, 126.2, 125.7, 124.8, 123.8, 123.5, 120.8, 117.6, 115.9, 106.9, 56.6, 52.0, 39.6, 21.5, 21.1; IR (KBr) υ: 3728, 3272, 3021, 2948, 1905, 1713, 1653, 1587, 1538, 1473, 1417, 1347, 1270, 1240, 1141, 1062, 1024, 977, 920, 877, 812, 748 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{28}N_2NaO_3S_2$ ([M+Na]$^+$): 635.1439. Found: 635.1432.



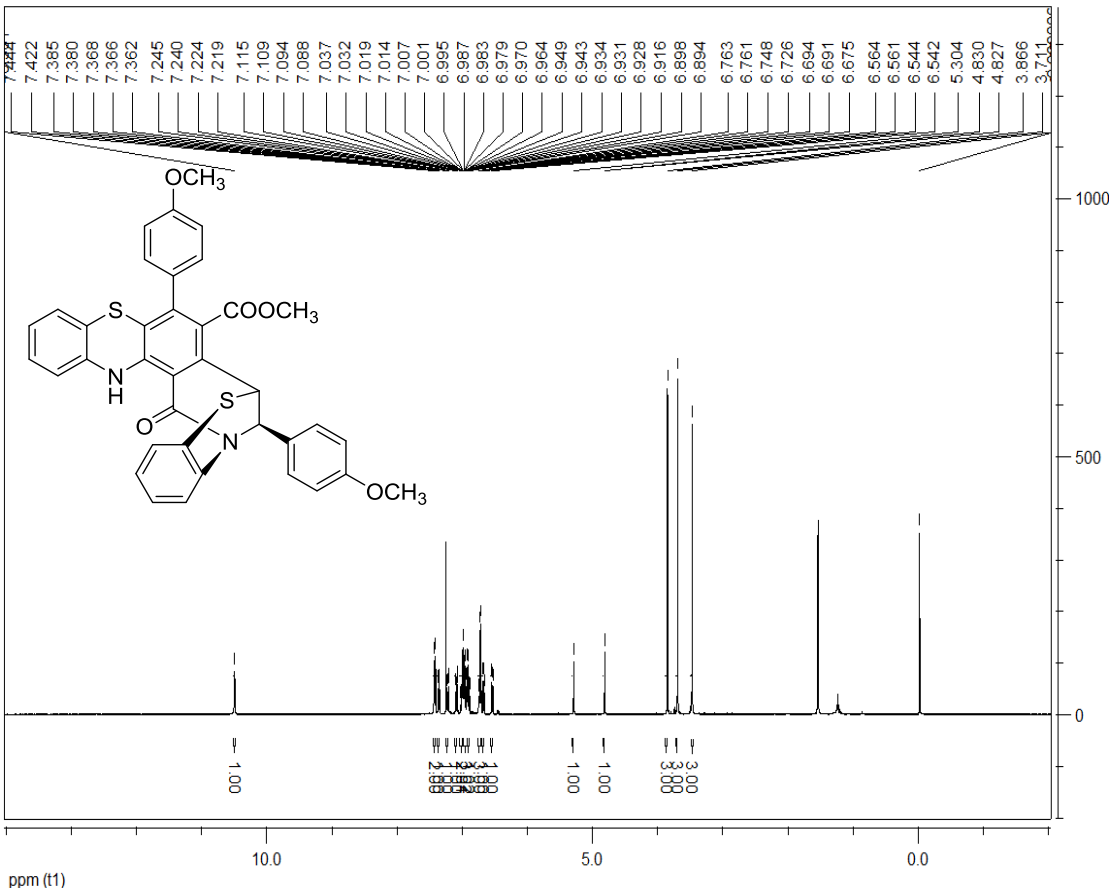

175.306
167.819
147.426
143.855
141.515
138.299
137.487
137.465
137.077
134.374
131.949
131.353
129.996
129.364
129.005
128.917
128.610
127.703
127.682
127.120
126.683
126.160
125.726
124.793
123.807
123.536
120.776
117.637
115.863
106.902
56.647
52.023
39.623
21.473
21.076
5.0
0.0
200
150
100
50
0
ppm (f1)

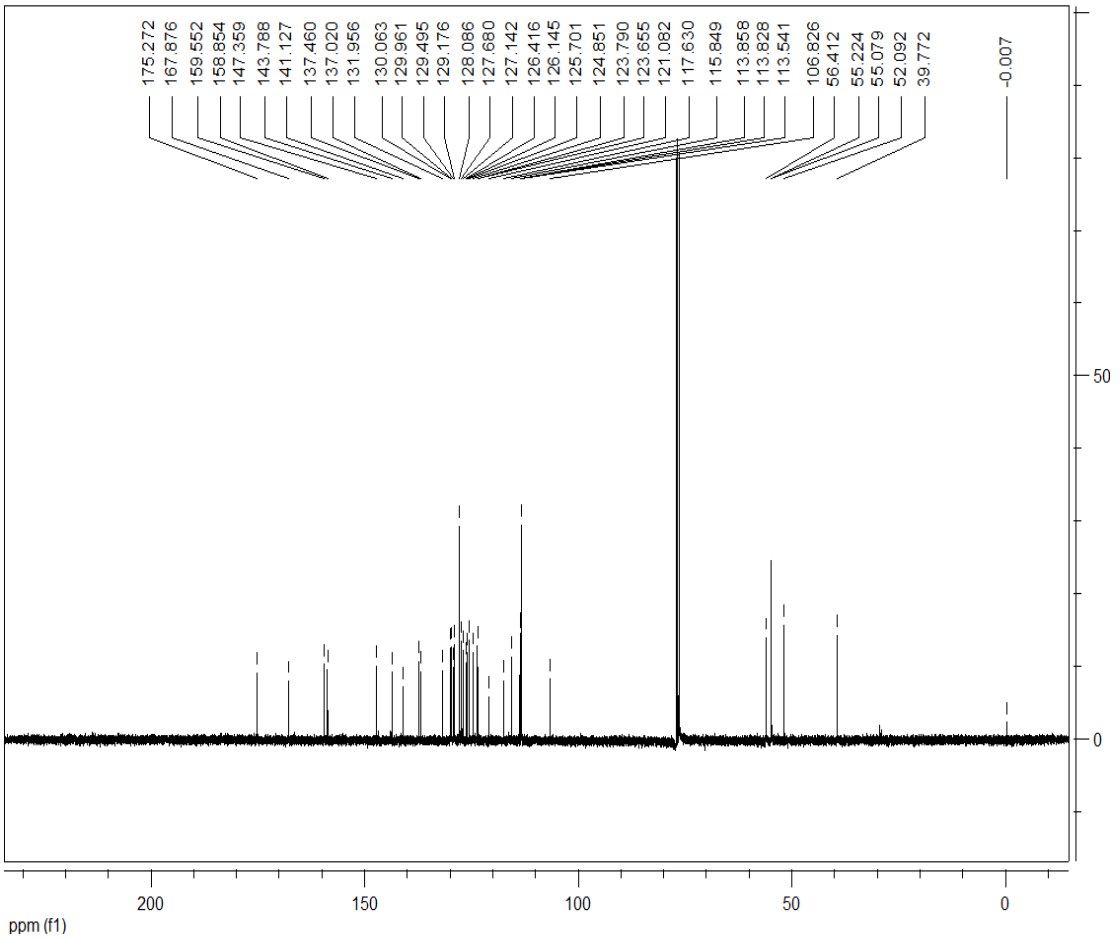

Intens.
+MS, 0.34-0.45min #(35-46)
635.1432
636.1457
637.1426
643.1676
400
300
200
100
0
625.0
627.5
630.0
632.5
635.0
637.5
640.0
642.5
645.0
m/z

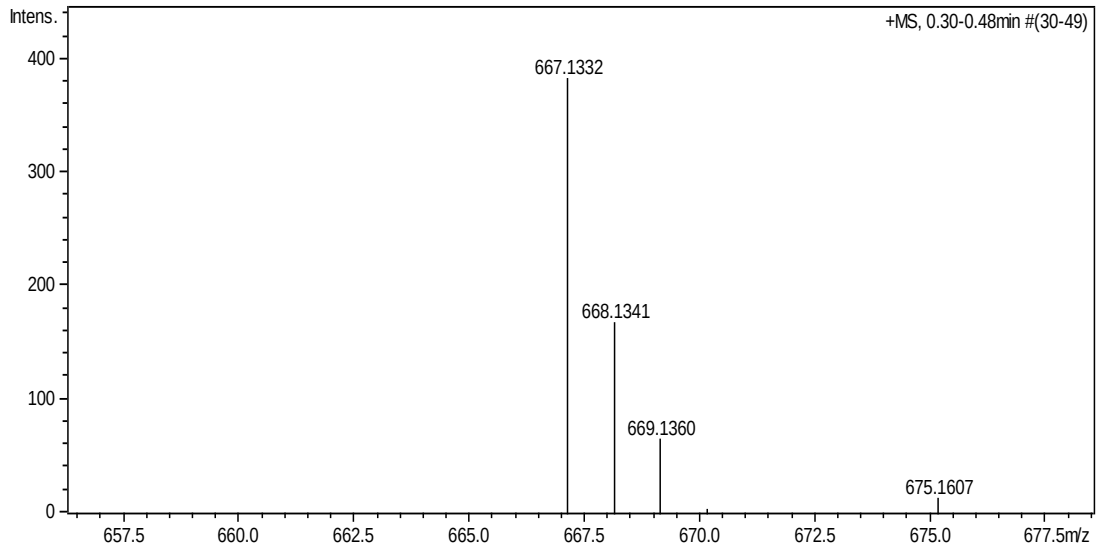
Methyl

6,17-bis(4-methoxyphenyl)-15-oxo-15,16-dihydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino [6,7-a]phenothiazine-7-carboxylate (6b):

red solid, 59%, m.p. 235~238℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.50 (s, 1H, NH), 7.33 (d, *J* = 5.2 Hz, 3H, ArH), 7.39~7.36 (m, 1H, ArH), 7.12~7.09 (m, 1H, ArH), 7.04~7.00 (m, 2H, ArH), 6.99~6.93 (m, 3H, ArH), 6.92~6.89 (m, 1H, ArH), 6.76~6.73 (m, 3H, ArH), 6.69~6.68 (m, 1H, ArH), 6.56~6.54 (m, 1H, ArH), 5.30 (s, 1H, CH), 4.83 (d, *J* = 1.2 Hz, 1H, CH), 3.87 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.3, 167.9, 159.6, 158.9, 147.4, 143.8, 141.1, 137.5, 137.0, 132.0, 130.1, 130.0, 129.5, 129.2, 128.1, 127.7, 127.1, 126.4, 126.1, 125.7, 124.9, 123.8, 123.7, 121.1, 117.6, 115.8, 113.9, 113.8, 113.5, 106.8, 56.4, 55.2, 55.1, 52.1, 39.8, 0.0; IR (KBr) υ: 3691, 3010, 2944, 2839, 1725, 1647, 1592, 1520, 1472, 1422, 1344, 1247, 1183, 1139, 1028, 976, 920, 872, 827, 751cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{40}N_2NaO_3S_2$ ([M+Na]$^{+}$): 667.1337. Found: 667.1332.



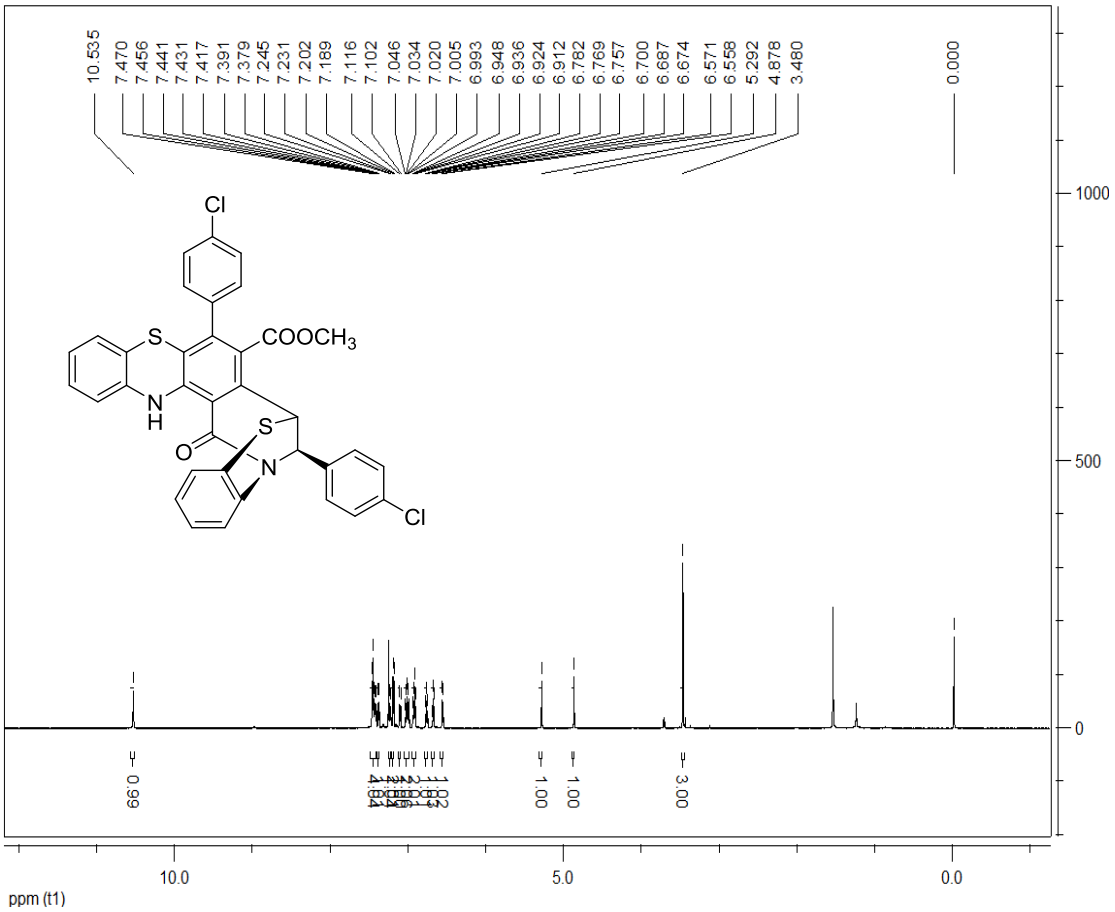

175.272
167.876
159.552
158.854
147.359
143.788
141.127
137.460
137.020
131.956
130.063
129.961
129.495
129.176
128.086
127.680
127.142
126.416
126.145
125.701
124.851
123.790
123.655
121.082
117.630
115.849
113.858
113.828
113.541
106.826
56.412
55.224
55.079
52.092
39.772
-0.007
50
0
200
150
100
50
0
ppm (f1)

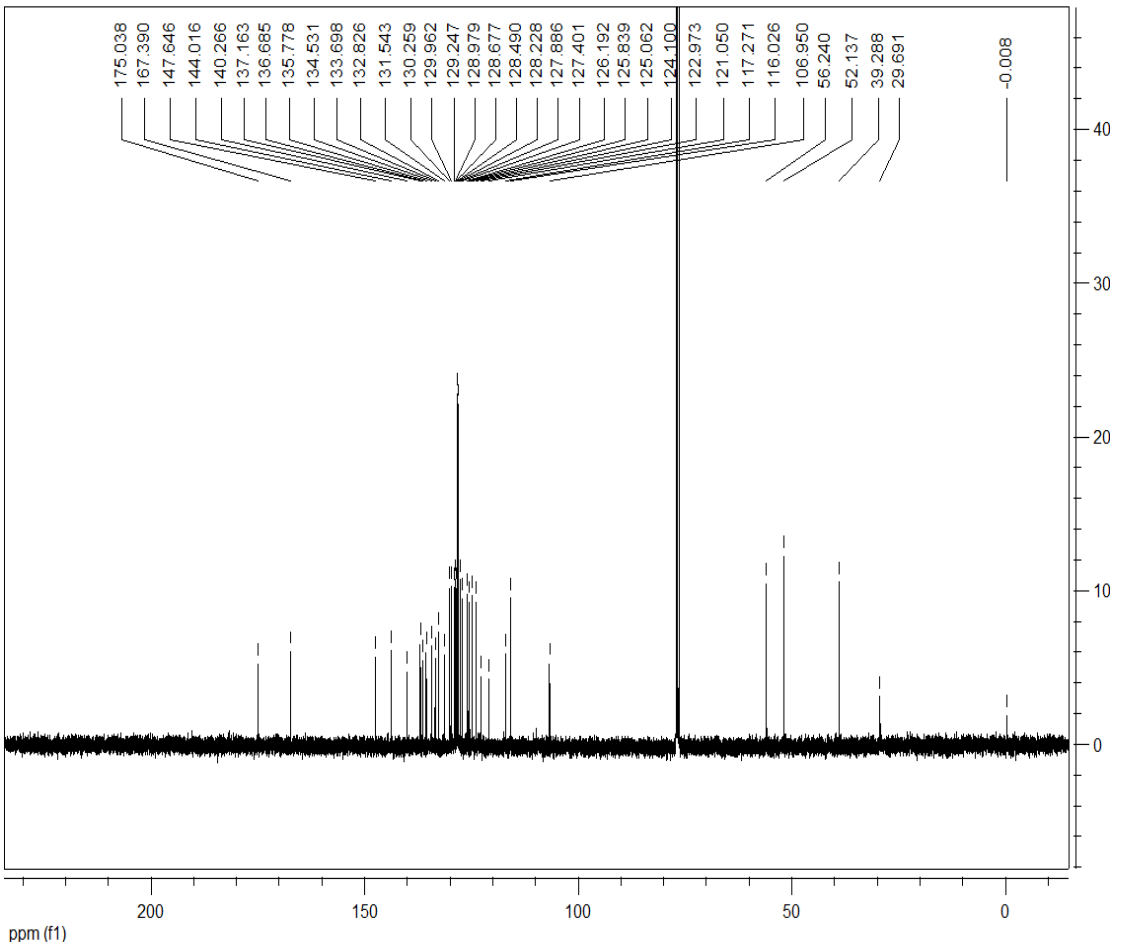

Intens.
+MS, 0.30-0.48min #(30-49)
400
300
200
100
0
667.1332
668.1341
669.1360
675.1607
657.5
660.0
662.5
665.0
667.5
670.0
672.5
675.0
677.5m/z

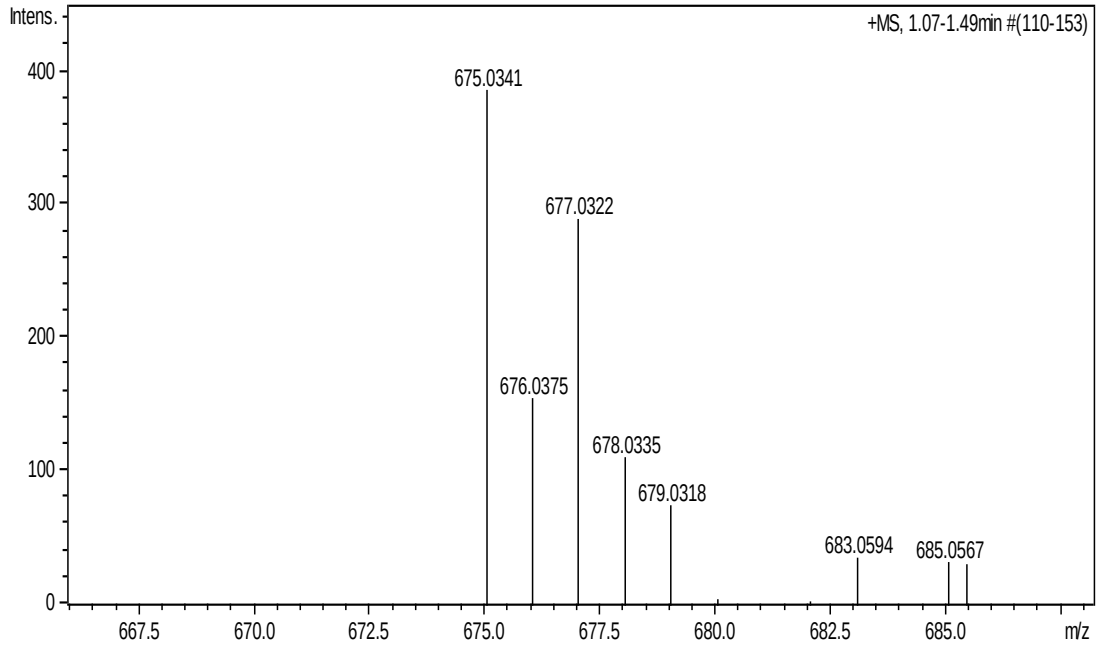
Methyl

6,17-bis(4-chlorophenyl)-15-oxo-15,16-dihydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (6c):

red solid, 54%, m.p. 251~255℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.54 (s, 1H, NH), 7.47~7.42 (m, 4H, ArH), 7.39 (d, *J* = 4.8 Hz, 1H, ArH), 7.24 (d, *J* = 5.6 Hz, 1H, ArH), 7.20 (d, *J* = 5.2 Hz, 2H, ArH), 7.10 (d, *J* = 5.6 Hz, 1H, ArH), 7.05~6.99 (m, 2H, ArH), 6.95~6.91 (m, 2H, ArH), 6.78~6.76 (m, 1H, ArH), 6.70~6.67 (m, 1H, ArH), 6.56 (d, *J* = 5.2 Hz, 1H, ArH), 5.29 (s, 1H, CH), 4.88 (s, 1H, CH), 3.48 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.0, 167.4, 147.6, 144.0, 140.3, 137.2, 136.7, 135.8, 134.5, 133.7, 132.8, 131.5, 130.3, 130.0, 129.2, 129.0, 128.7, 128.5, 128.2, 127.9, 127.4, 126.2, 125.8, 125.1, 124.1, 123.0, 121.0, 117.3, 116.0, 106.9, 56.2, 52.1, 39.3, 29.7, 0.0; IR (KBr) υ: 3683, 3063, 2931, 2851, 1908, 1710, 1648, 1590, 1542, 1482, 1424, 1351, 1268, 1237, 1142, 1092, 1015, 977, 916, 873, 825, 742, cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{22}Cl_2N_2NaO_3S_2$ ([M+Na]$^+$): 695.0347. Found: 697.0341.



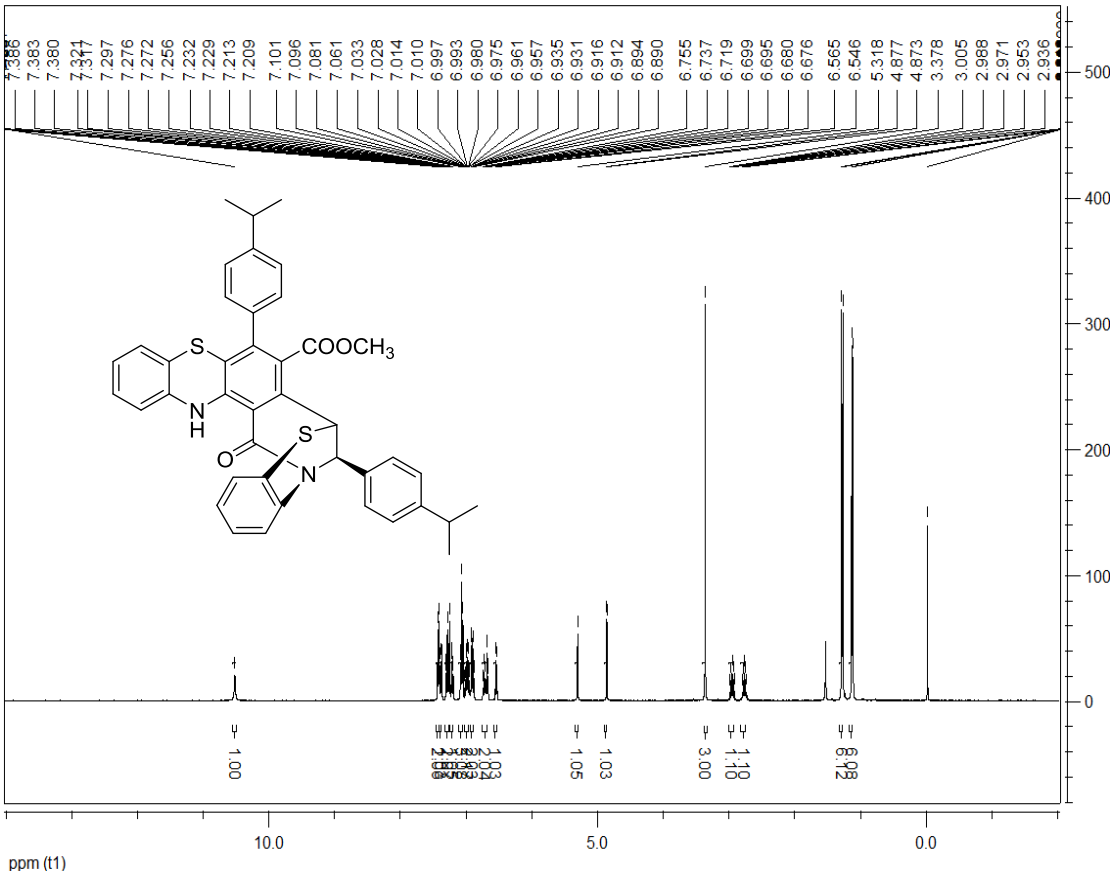

175.038
167.390
147.646
144.016
140.266
137.163
136.685
135.778
134.531
133.698
132.826
131.543
130.259
129.962
129.247
128.979
128.677
128.490
128.228
127.886
127.401
126.192
125.839
125.062
124.100
122.973
121.050
117.271
116.026
106.950
56.240
52.137
39.288
29.691
-0.008
40
30
20
10
0
200
150
100
50
0
ppm (f1)

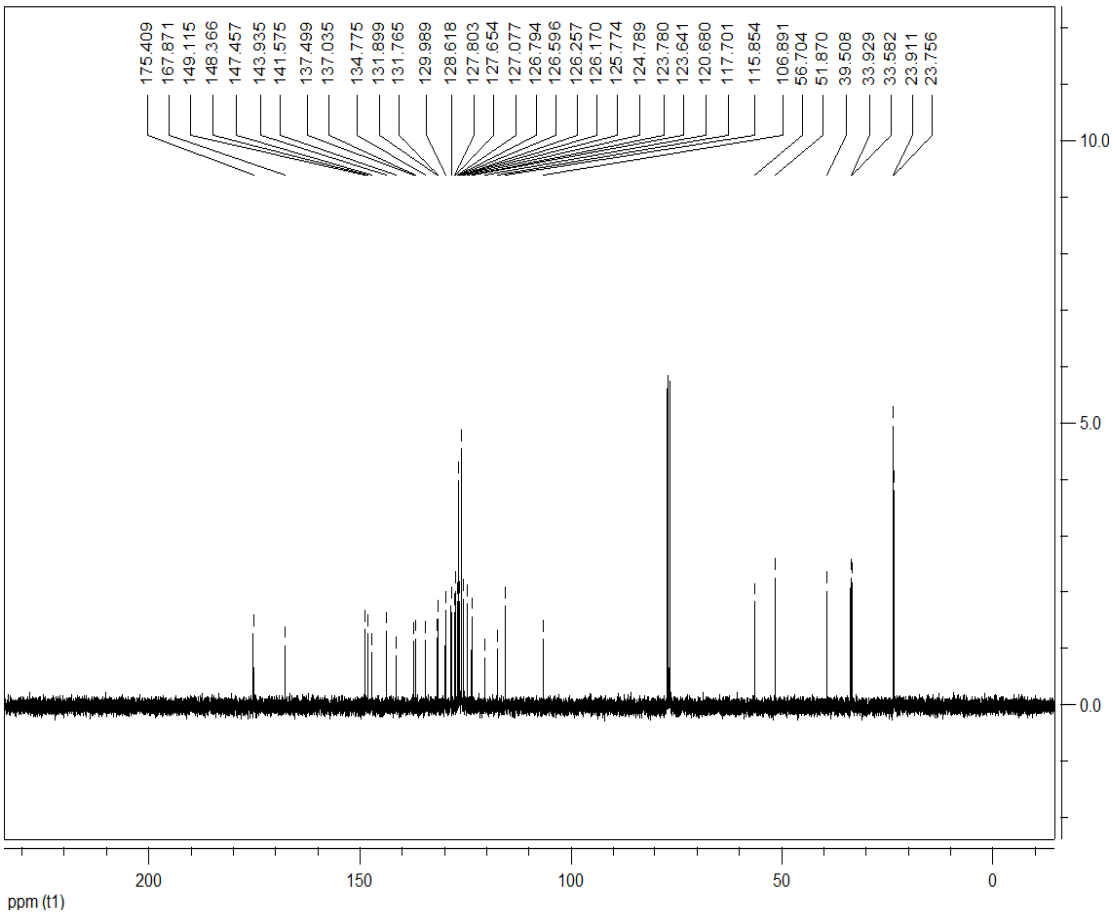

Intens.
+MS, 1.07-1.49min #(110-153)
400
300
200
100
0
675.0341
677.0322
676.0375
678.0335
679.0318
683.0594
685.0567
667.5
670.0
672.5
675.0
677.5
680.0
682.5
685.0
m/z

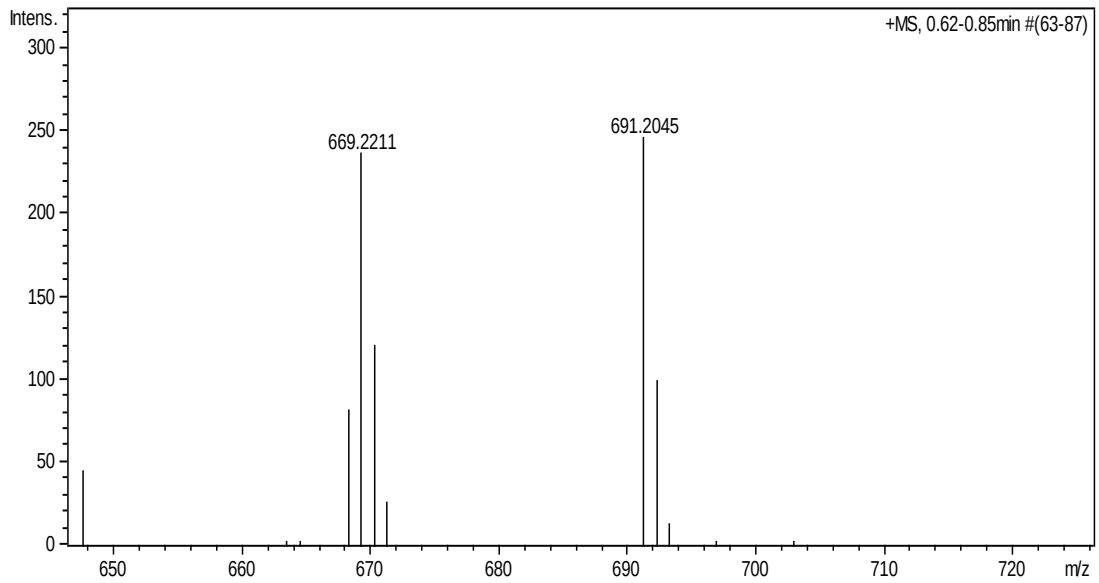
Methyl

6,17-bis(4-isopropylphenyl)-15-oxo-15,16-dihydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (6d):

yellow solid, 61%, m.p. 231~235℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.53 (s, 1H, NH), 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 7.40~7.38 (m, 1H, ArH), 7.32~7.27 (m, 2H, ArH), 7.23~7.21 (m, 1H, ArH),, 7.10~7.06 (m, 3H, ArH), 7.03~6.96 (m, 2H, ArH), 6.94~6.89 (m, 2H, ArH), 6.76~6.68 (m, 2H, ArH), 6.56 (d, *J* = 7.6 Hz, 1H, ArH), 5.32 (s, 1H, CH), 4.88 (d, *J* = 1.2 Hz, 1H, CH), 3.38 (s, 3H, OCH_3), 3.01~2.94 (m, 1H, CH), 2.82~2.75 (m, 1H, CH), 1.30 (d, *J* = 7.2 Hz, 6H, CH_3), 1.15 (d, *J* = 7.2 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.4, 167.9, 149.1, 148.4, 147.5, 143.9, 141.6, 137.5, 137.0, 134.8, 131.9, 131.8, 130.0, 128.6, 127.8, 127.7, 127.1, 126.8, 126.6, 126.3, 126.2, 125.8, 124.8, 123.8, 123.6, 120.7, 117.7, 115.9, 106.9, 56.7, 51.9, 39.5, 33.9, 33.6, 23.9, 23.8; IR (KBr) υ: 3810, 3214, 2946, 2865, 1723, 1642, 1576, 1523, 1498, 1412, 1298, 1215, 1133, 1075, 1002, 945, 867, 825, 817, 785, 765cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{36}N_2NaO_3S_2$ ([M+Na]$^{+}$): 691.2060. Found: 691.2045.



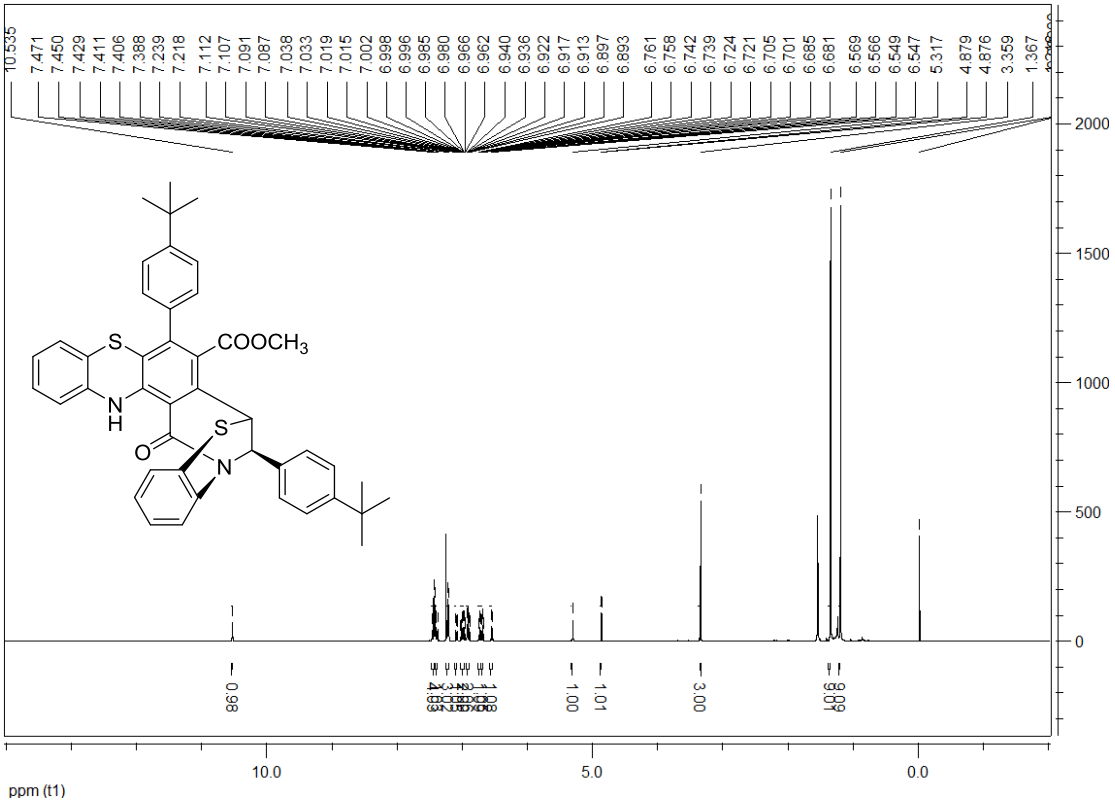

175.409
167.871
149.115
148.366
147.457
143.935
141.575
137.499
137.035
134.775
131.899
131.765
129.989
128.618
127.803
127.654
127.077
126.794
126.596
126.257
126.170
125.774
124.789
123.780
123.641
120.680
117.701
115.854
106.891
56.704
51.870
39.508
33.929
33.582
23.911
23.756
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

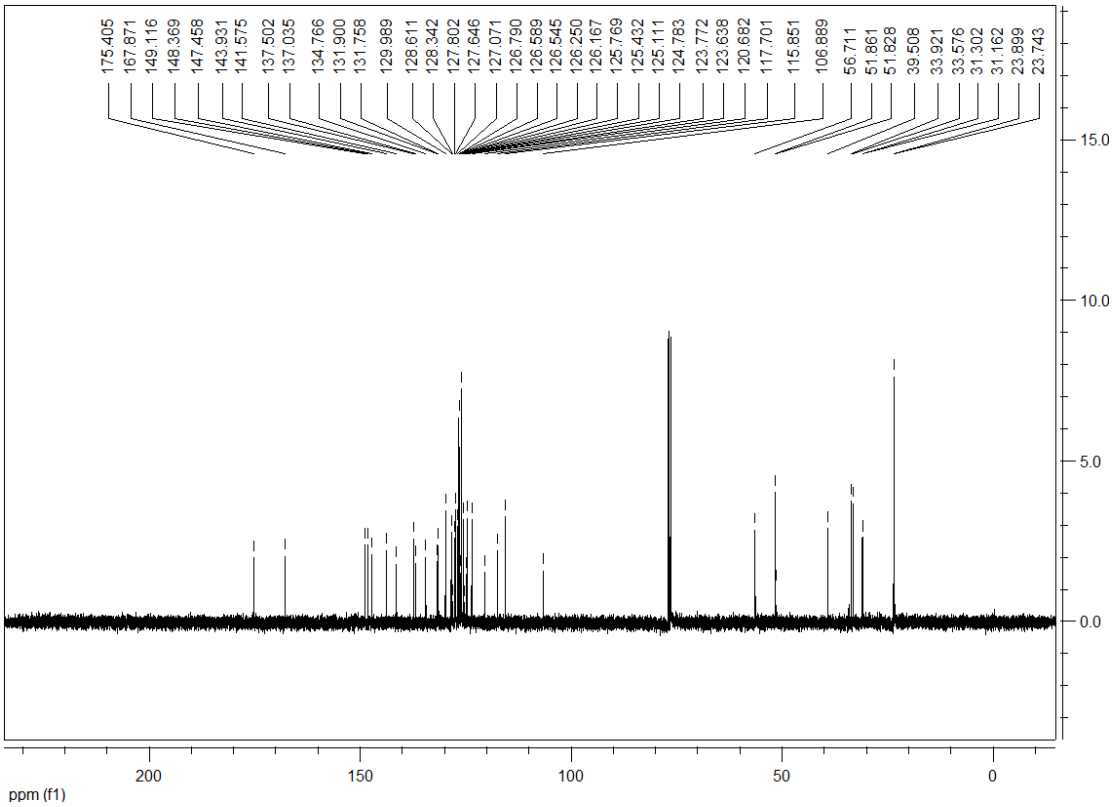

Intens.
+MS, 0.62-0.85min #(63-87)
669.2211
691.2045
300
250
200
150
100
50
0
650
660
670
680
690
700
710
720
m/z

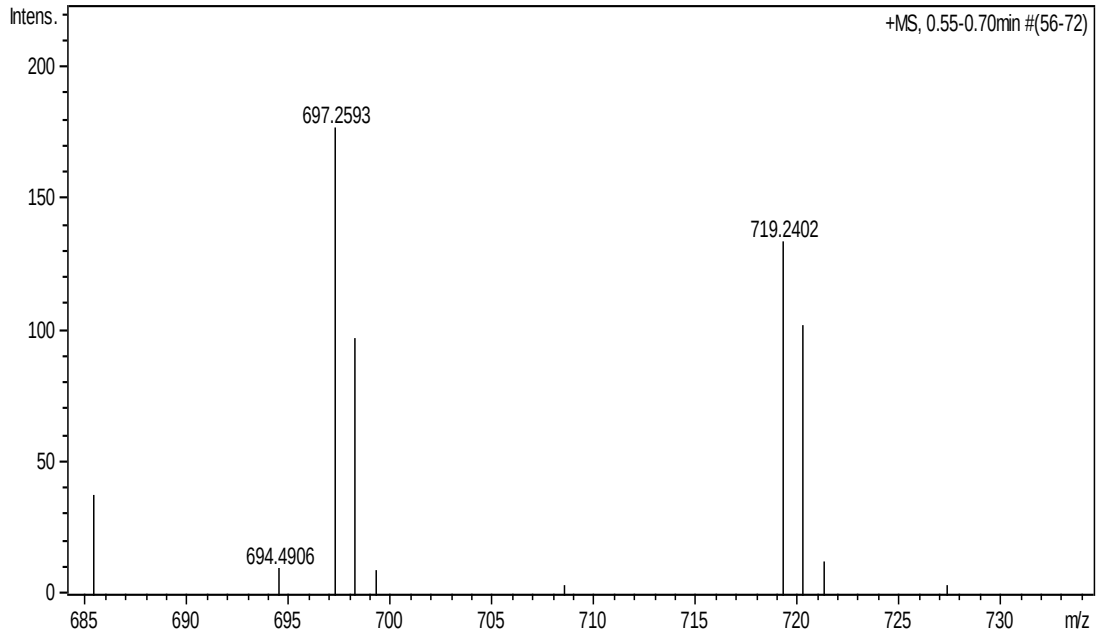
Methyl

6,17-bis(4-(tert-butyl)phenyl)-15-oxo-15,16-dihydro-8H-8,14-methanobenzo[2,3][1,4]thiazocino[6,7-a]phenothiazine-7-carboxylate (6e):

yellow solid, 56%, m.p. 224~227℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.54 (s, 1H, NH), 7.47~7.43 (m, 4H, ArH), 7.41~7.39 (m, 1H, ArH), 7.23 (d, *J* = 5.2 Hz, 3H, ArH), 7.11~7.09 (m, 1H, ArH), 7.04~6.96 (m, 2H, ArH), 6.94~6.89 (m, 2H, ArH), 6.76~6.72 (m, 1H, ArH), 6.71~6.68 (m, 1H, ArH), 6.57~6.55 (m, 1H, ArH), 5.32 (s, 1H, CH), 4.88 (d, *J* = 1.2 Hz, 1H, CH), 3.56 (s, 3H, OCH_3), 1.37 (s, 9H, CH_3), 1.22 (s, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.4, 167.9, 149.1, 148.4, 147.5, 143.9, 141.6, 137.5, 137.0, 134.8, 131.9, 131.8, 130.0, 128.6, 128.3, 127.8, 127.6, 127.1, 126.8, 126.6, 126.5, 126.3, 126.2, 125.8, 125.4, 125.1, 124.8, 123.8, 123.6, 120.7, 117.7, 115.9, 106.9, 56.7, 51.9, 51.8, 39.5, 33.9, 33.6, 31.3, 31.2, 23.9, 23.7; IR (KBr) υ: 3725, 3317, 3077, 2971, 2910, 2838, 1712, 1639, 1588, 1569, 1535, 1425, 1314, 1292, 1254, 1139, 1105, 1073, 1042, 905, 833, 782, 743, cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{43}H_{40}N_2NaO_3S_2$ ([M+Na]$^+$): 719.2378. Found: 719.2402.



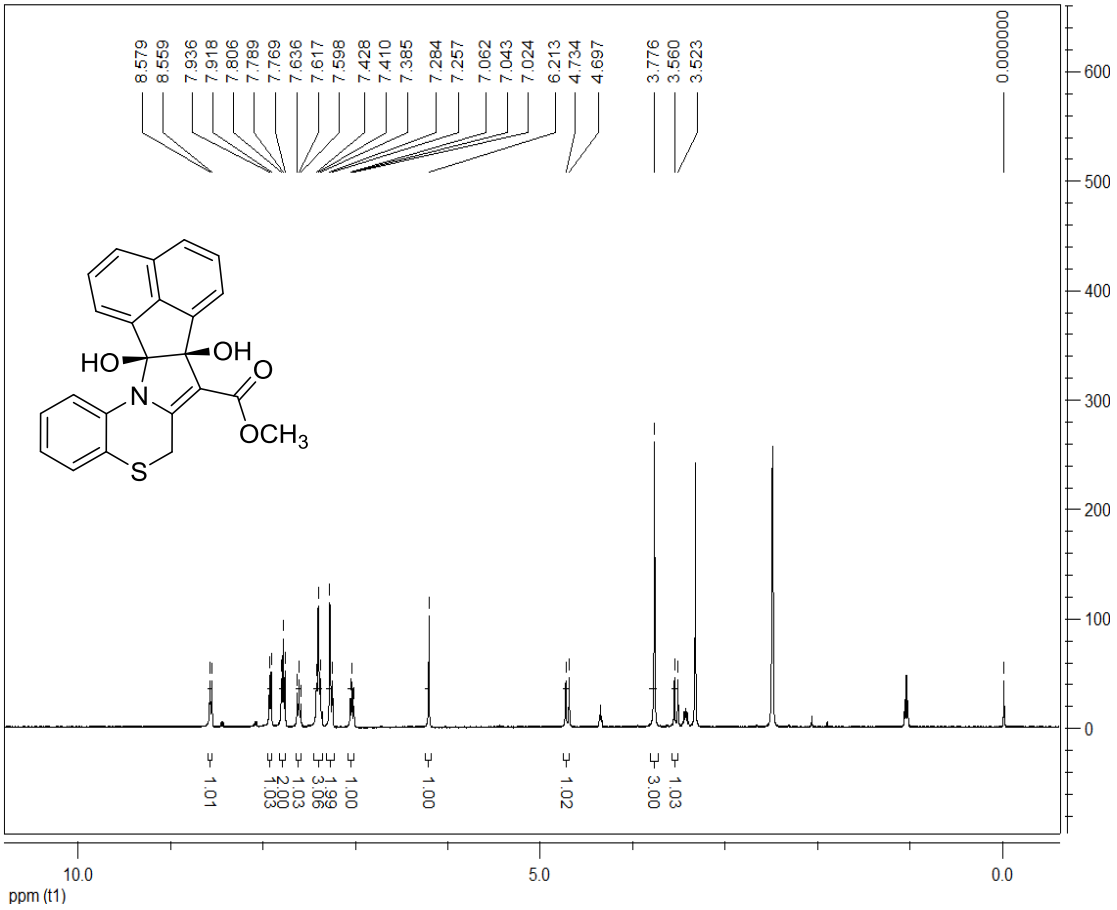

175.405
167.871
149.116
148.369
147.458
143.931
141.575
137.502
137.035
134.766
131.900
131.758
129.989
128.611
128.342
127.802
127.646
127.071
126.790
126.589
126.545
126.250
126.167
125.769
125.432
125.111
124.783
123.772
123.638
120.682
117.701
115.851
106.889
56.711
51.861
51.828
39.508
33.921
33.576
31.302
31.162
23.899
23.743
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

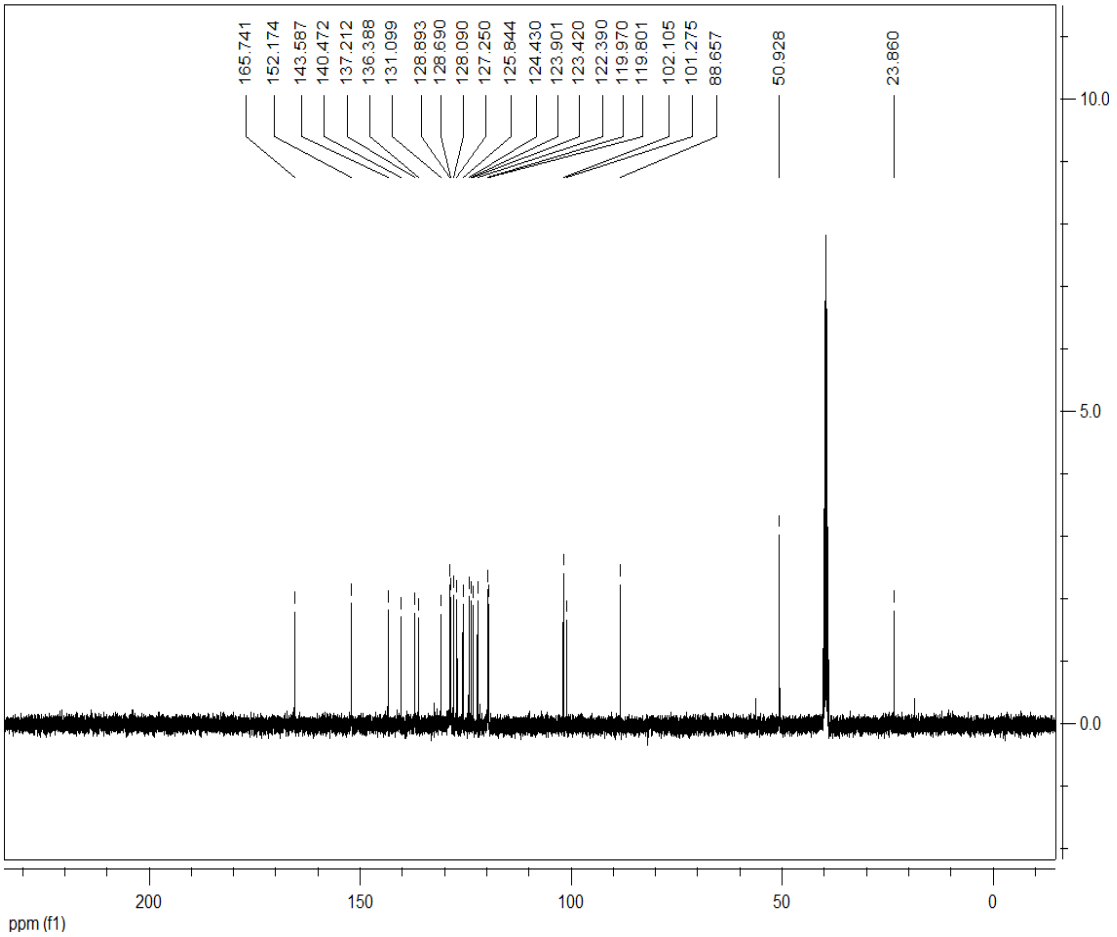

Intens.
+MS, 0.55-0.70min #(56-72)
200
150
100
50
0
697.2593
719.2402
694.4906
685
690
695
700
705
710
715
720
725
730
m/z

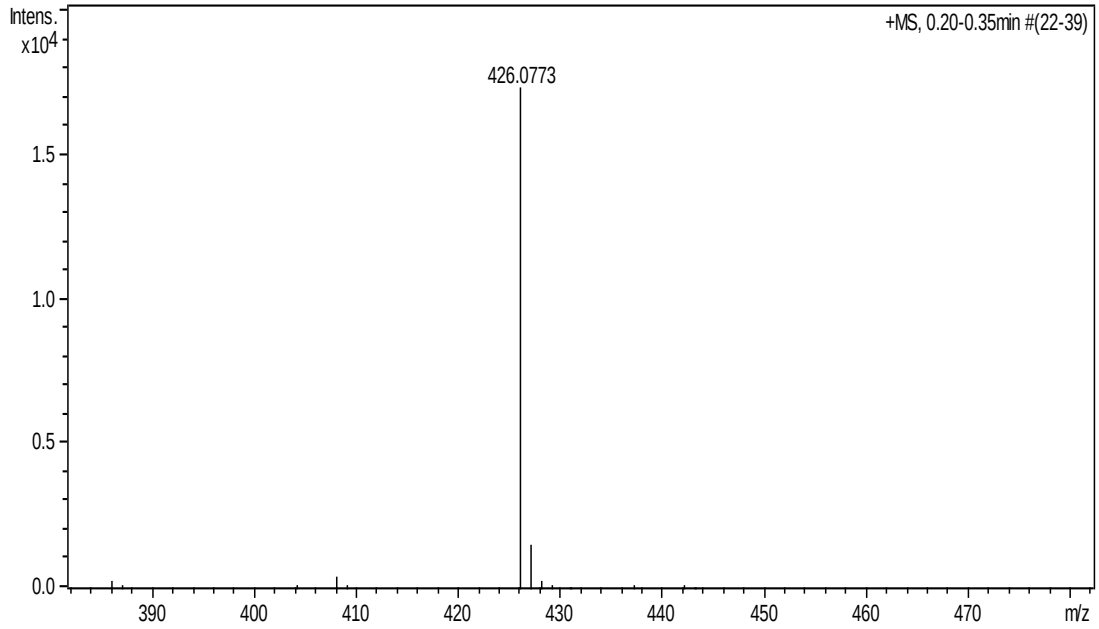
Methyl

7a,13b-dihydroxy-7a,13b-dihydro-6H-acenaphtho[1',2':4,5]pyrrolo[1,2-d]benzo[b][1,4]thiazine-7-carboxylate (7a):

white solid, 95%, m.p. 195~198℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57 (d, *J* = 8.0 Hz, 1H, ArH), 7.93 (d, *J* = 7.2 Hz, 1H, ArH), 7.81~7.77 (m, 2H, ArH), 7.64~7.60 (m, 1H, ArH), 7.43~7.37 (m, 3H, ArH), 7.27 (d, *J* = 10.8 Hz, 2H, ArH), 7.06~7.02 (m, 1H, ArH), 6.21 (s, 1H, OH), 6.72 (d, *J* = 14.8 Hz, 1H, CH), 3.78 (s, 3H, OCH_3) , 3.54 (d, *J* = 14.8 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.7, 152.2, 143.6, 140.5, 137.2, 136.4, 131.1, 128.9, 128.7, 128.1, 127.2, 125.8, 124.4, 123.9, 123.4, 122.4, 120.0, 119.8, 102.1, 101.3, 88.7, 50.9, 23.9; IR (KBr) υ: 3386, 3032, 2993, 2944, 1722, 1661, 1605, 1578, 1562, 1496, 1470, 1449, 1438, 1415, 1397, 1361, 1271, 1249, 1231, 1189, 1169, 1153, 1128, 1098, 1073, 1055, 1029, 1004, 988, 959, 920, 895, 833, 809, 784, 754, 730, 718cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{23}H_{17}NNaO_4S$ ([M+Na]$^{+}$): 426.0776. Found: 426.0773.



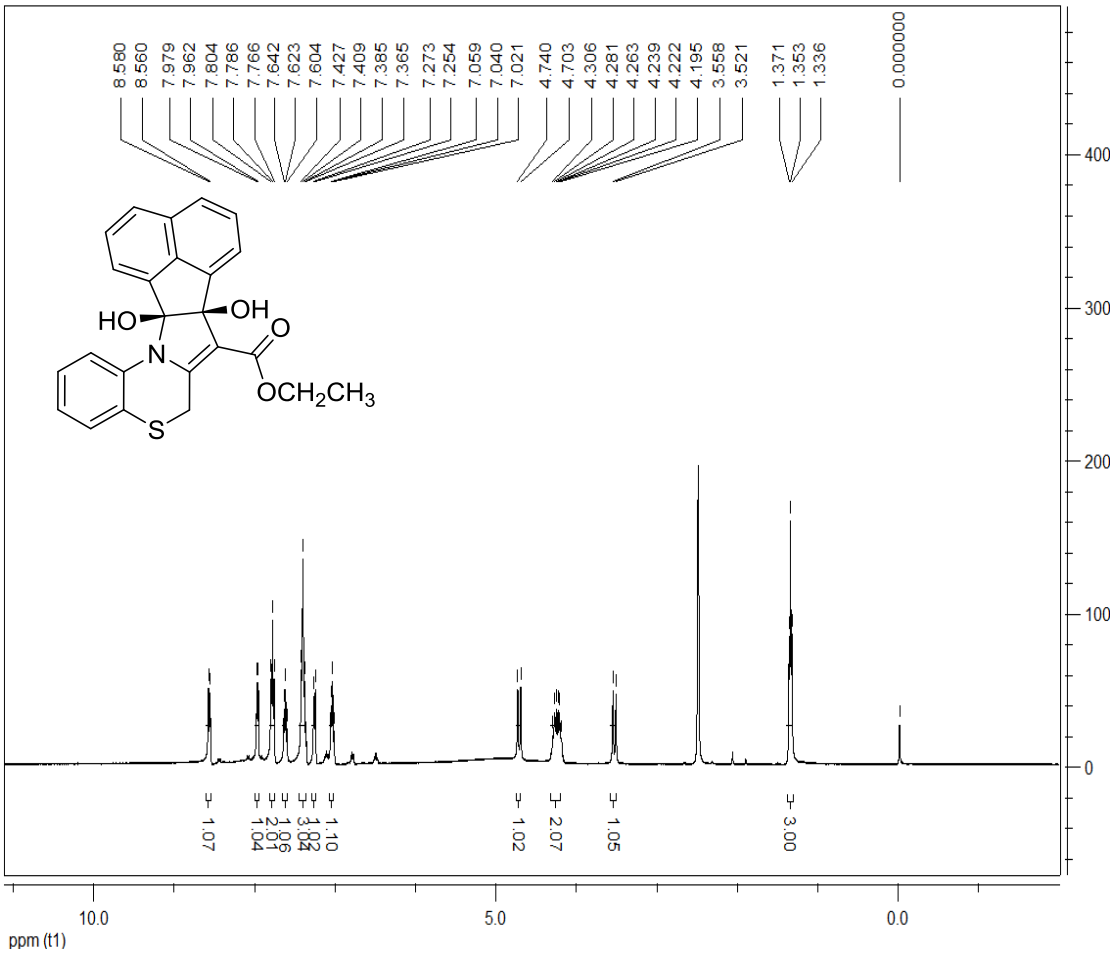

165.741
152.174
143.587
140.472
137.212
136.388
131.099
128.893
128.690
128.090
127.250
125.844
124.430
123.901
123.420
122.390
119.970
119.801
102.105
101.275
88.657
50.928
23.860
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

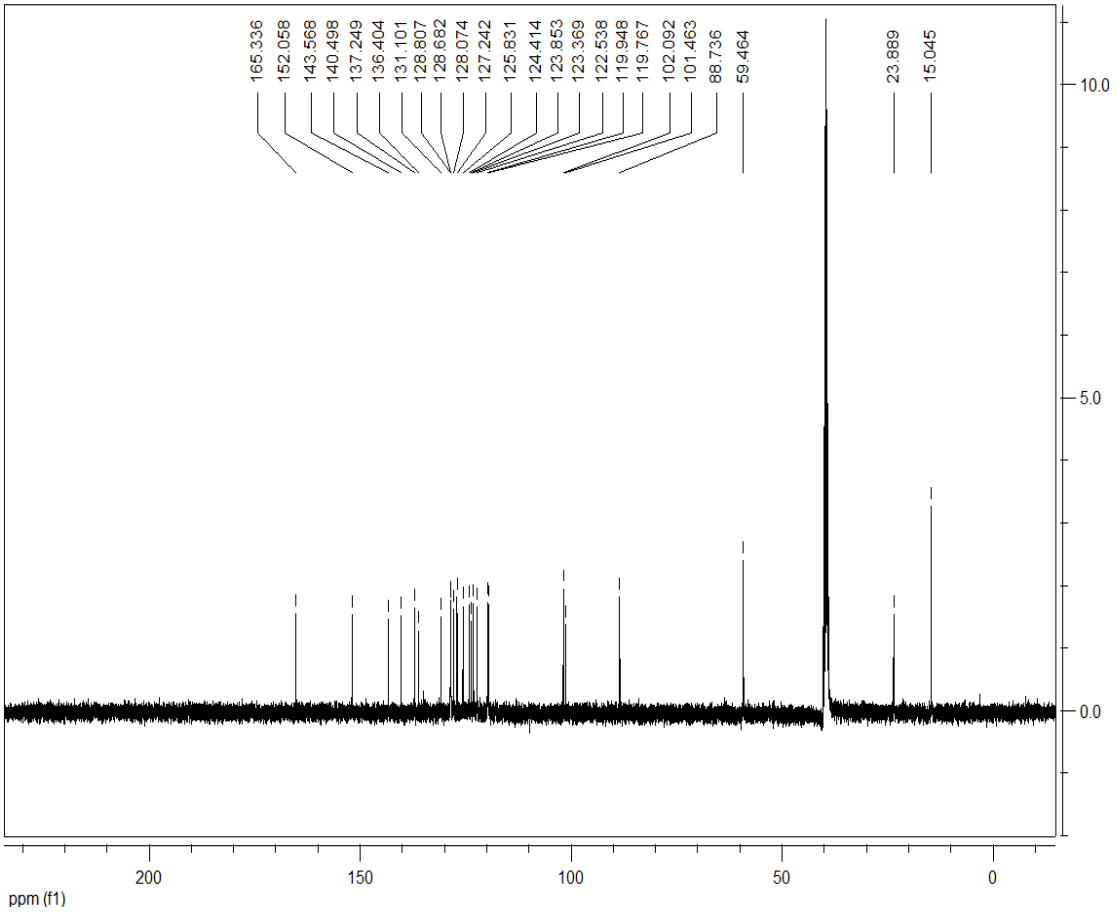

Intens.
x10^4
+MS, 0.20-0.35min #(22-39)
426.0773
1.5
1.0
0.5
0.0
390
400
410
420
430
440
450
460
470
m/z

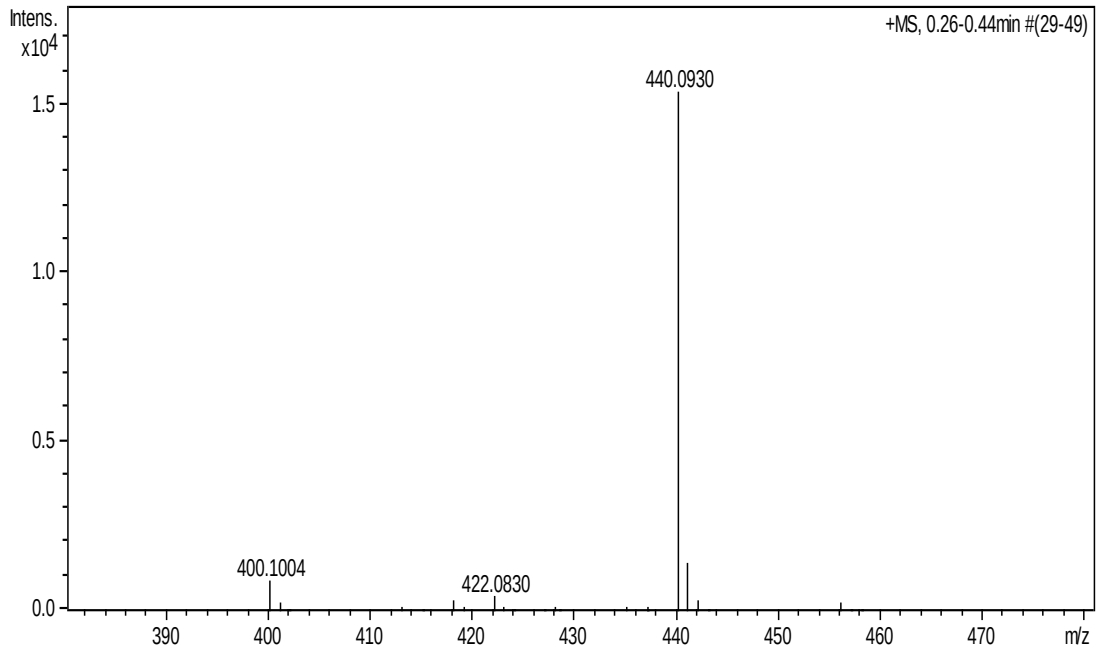
Ethyl

7a,13b-dihydroxy-7a,13b-dihydro-6H-acenaphtho[1',2':4,5]pyrrolo[1,2-d]benzo[b][1,4]thiazine-7-carboxylate (7b):

white solid, 89%, m.p. 164~167℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57 (d, *J* = 8.0 Hz, 1H, ArH), 7.97 (d, *J* = 6.8 Hz, 1H, ArH), 7.80~7.77 (m, 2H, ArH), 7.64~7.60 (m, 1H, ArH), 7.43~7.37 (m, 3H, ArH), 7.26 (d, *J* = 7.6 Hz, 2H, ArH), 7.06~7.02 (m, 1H, ArH), 4.72 (d, *J* = 14.8 Hz, 1H, CH), 4.31~4.20 (m, 2H, OCH_2), 3.54 (d, *J* = 14.8 Hz, 1H, CH) , 1.37~1.34 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.3, 152.1, 143.6, 140.5, 137.2, 136.4, 131.1, 128.8, 128.7, 128.1, 127.2, 125.8, 124.4, 123.9, 123.4, 122.5, 119.9, 119.8, 102.1, 101.5, 88.7, 59.5, 23.9, 15.0; IR (KBr) υ: 3444, 3371, 3014, 2950, 1722, 1661, 1608, 1578, 1497, 1474, 1443, 1394, 1376, 1352, 1250, 1234, 1187, 1167, 1155, 1120, 1099, 1073, 1058, 1034, 1018, 959, 942, 916, 847, 834, 809, 784, 752, 727cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{24}H_{19}NNaO_4S$ ([M+Na]$^{+}$): 440.0932. Found: 440.0932.



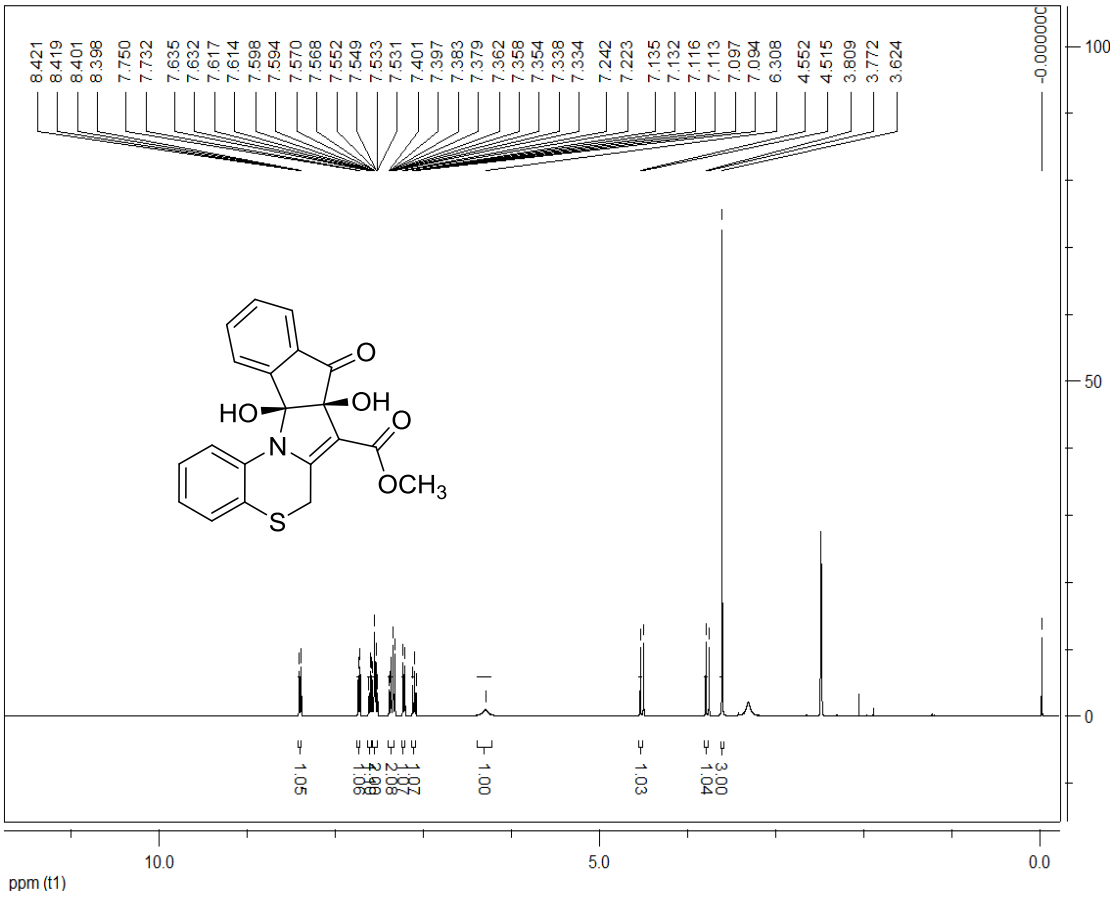

165.336
152.058
143.568
140.498
137.249
136.404
131.101
128.807
128.682
128.074
127.242
125.831
124.414
123.853
123.369
122.538
119.948
119.767
102.092
101.463
88.736
59.464
23.889
15.045
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

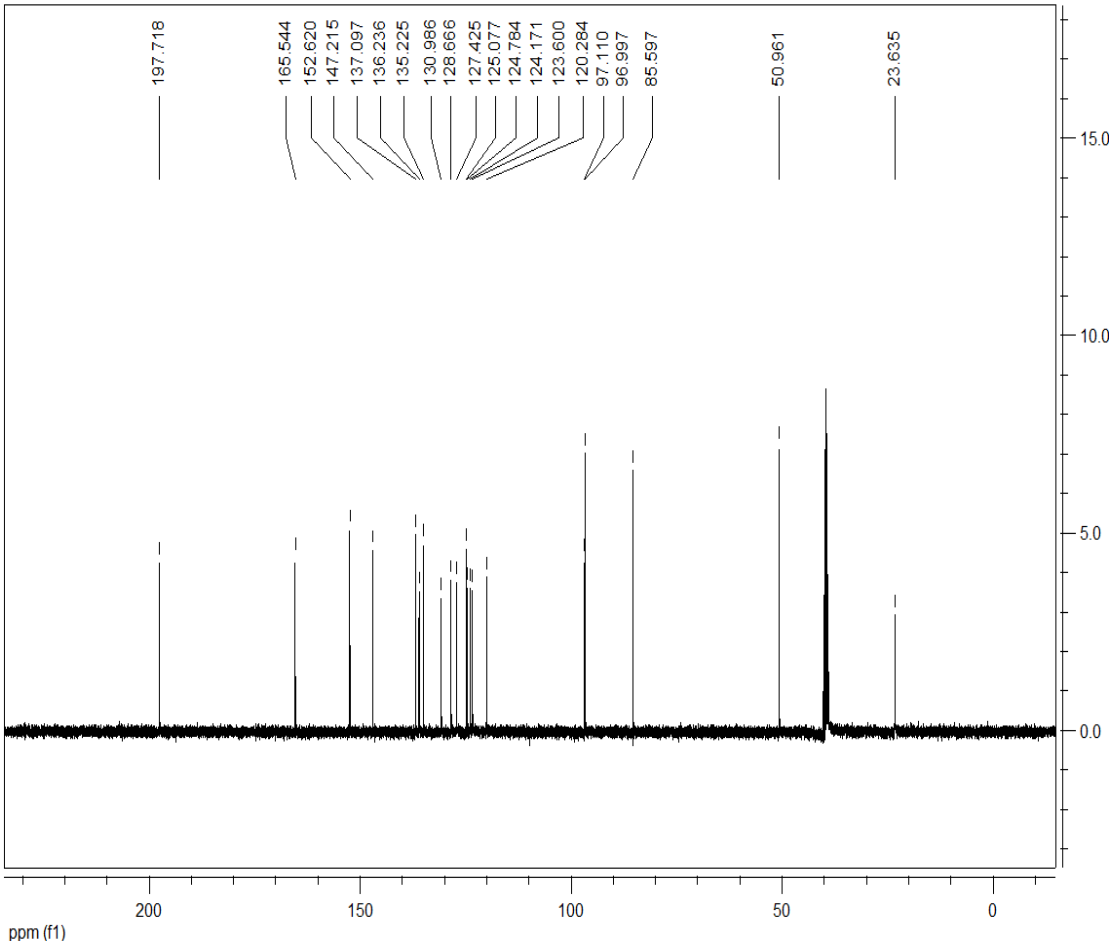

Intens.
x10^4
+MS, 0.26-0.44min #(29-49)
440.0930
400.1004
422.0830
1.5
1.0
0.5
0.0
390
400
410
420
430
440
450
460
470
m/z

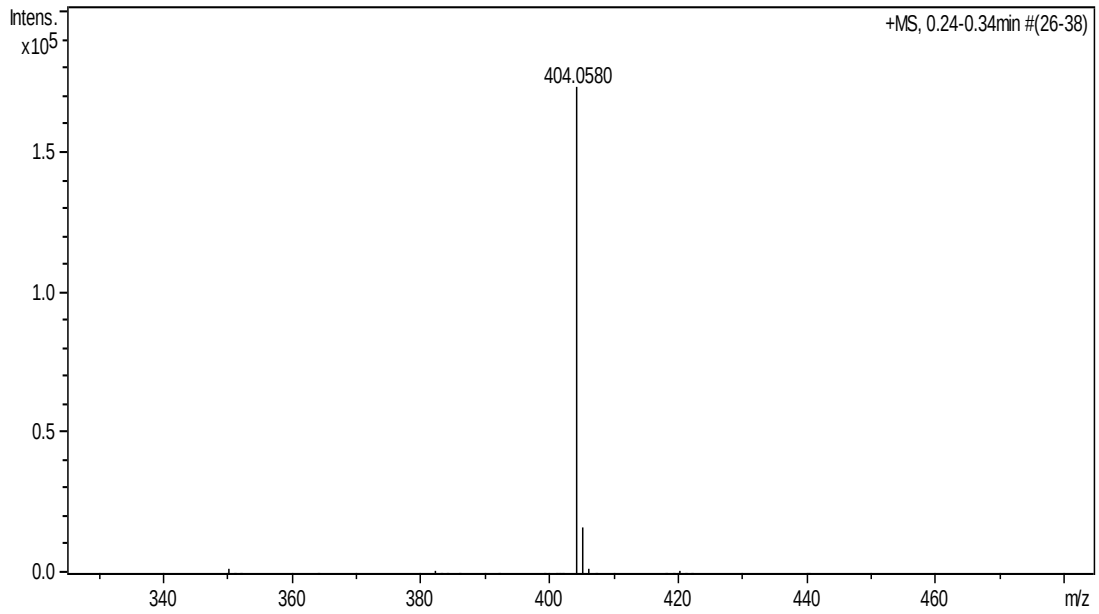
Methyl

7a,12b-dihydroxy-8-oxo-6,7a,8,12b-tetrahydrobenzo[b]indeno[2',1':4,5]pyrrolo[1,2-d][1,4]thiazine-7-carboxylate (8a):

white solid, 98%, m.p. 201~204℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42~8.40 (m, 1H, ArH), 7.74 (d, *J* = 7.2 Hz, 1H, ArH), 7.64~7.59 (m, 1H, ArH), 7.57~7.53 (m, 2H, ArH), 7.40~7.33 (m, 2H, ArH), 7.23 (d, *J* = 7.6 Hz, 1H, ArH), 7.14~7.09 (m, 1H, ArH), 6.31 (s, 1H, OH), 4.53 (d, *J* = 14.8 Hz, 1H, CH), 3.79 (d, *J* = 14.8 Hz, 1H, CH), 3.62 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.7, 165.5, 152.6, 147.2, 137.1, 136.2, 135.2, 131.0, 128.7, 127.4, 125.1, 124.8, 124.2, 123.6, 120.3, 97.1, 97.0, 85.6, 51.0, 23.6; IR (KBr) υ: 3466, 3193, 3027, 2944, 1721, 1641, 1587, 1572, 1558, 1468, 1439, 1388, 1273, 1250, 1216, 1187, 1160, 1138, 1107, 1088, 1071, 1029, 980, 946, 906, 834, 781, 756, 720cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{20}H_{15}NNaO_5S$ ([M+Na]$^{+}$): 404.0569. Found: 404.0580.



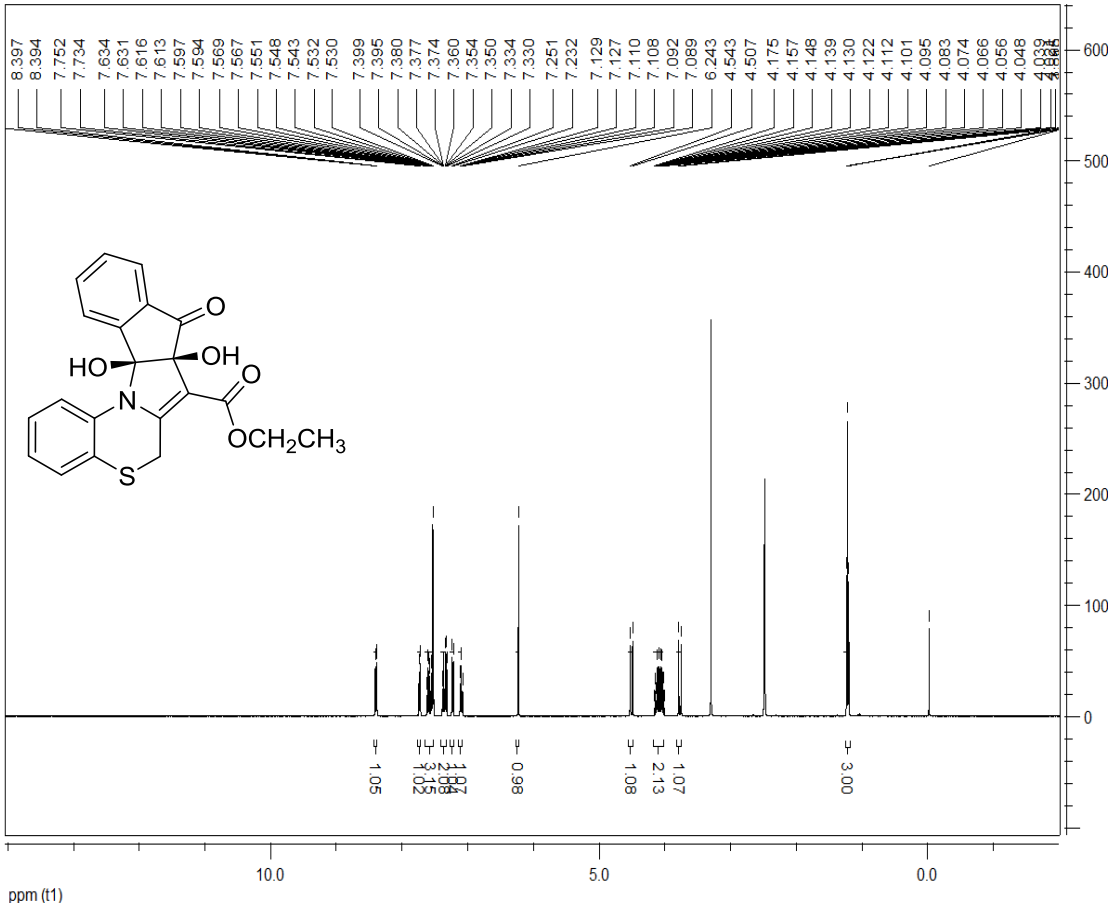

197.718
165.544
152.620
147.215
137.097
136.236
135.225
130.986
128.666
127.425
125.077
124.784
124.171
123.600
120.284
97.110
96.997
85.597
50.961
23.635
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

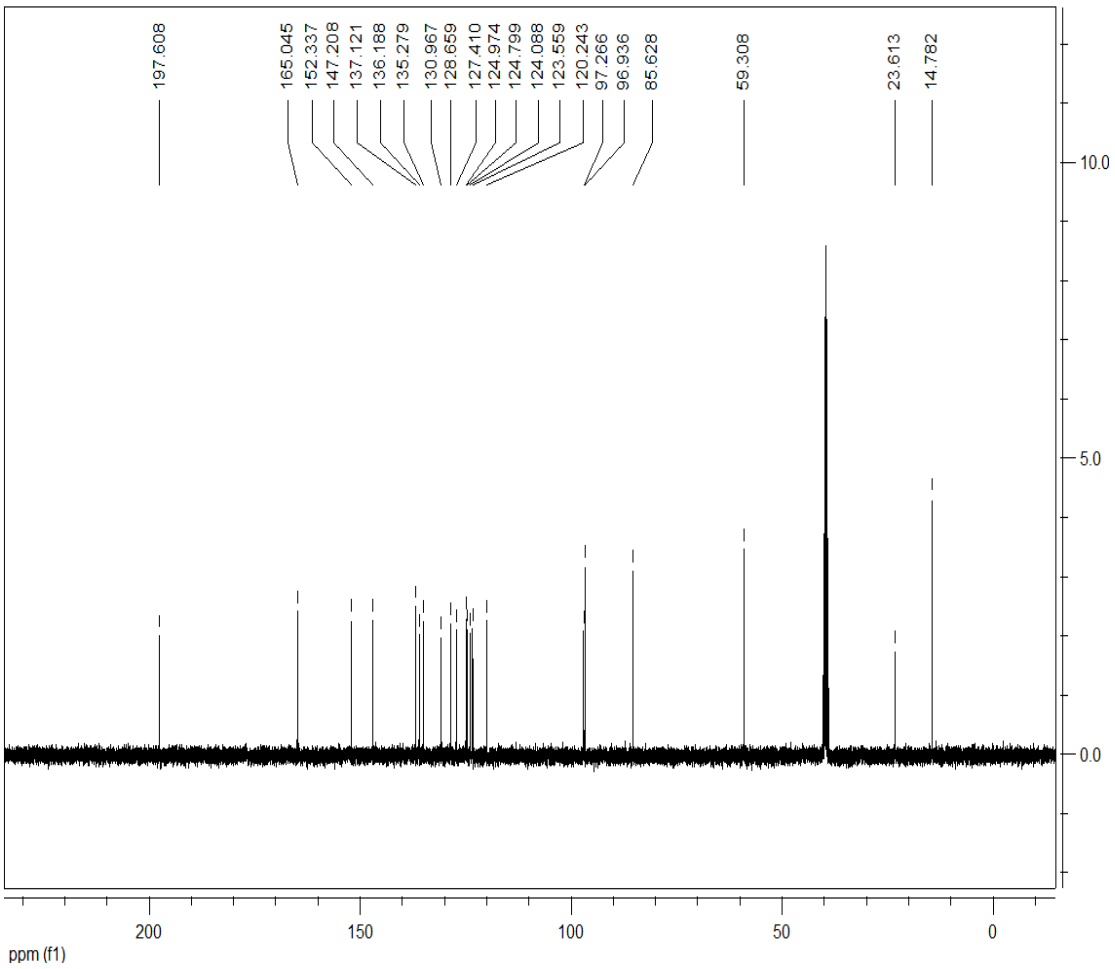

Intens.
x10^5
+MS, 0.24-0.34min #(26-38)
404.0580
1.5
1.0
0.5
0.0
340
360
380
400
420
440
460
m/z

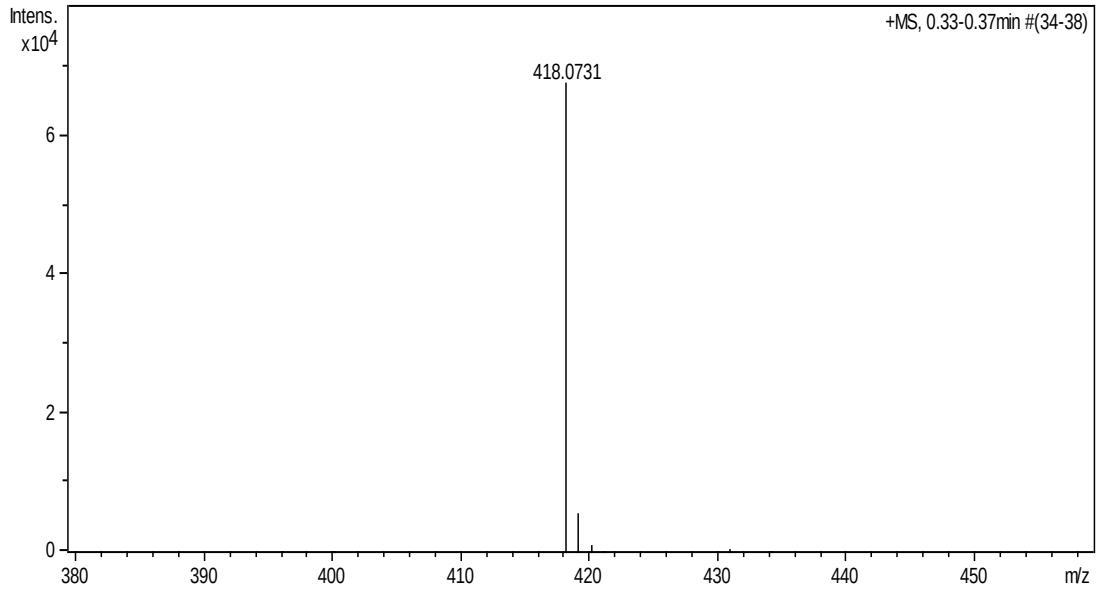
Ethyl

7a,12b-dihydroxy-8-oxo-6,7a,8,12b-tetrahydrobenzo[b]indeno[2',1':4,5]pyrrolo[1,2-d][1,4]thiazine-7-carboxylate (8b):

white solid, 75%, m.p. 185~189℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42~8.39 (m, 1H, ArH), 7.74 (d, *J* = 7.2 Hz, 1H, ArH), 7.63~7.53 (m, 3H, ArH), 7.40~7.33 (m, 2H, ArH), 7.24 (d, *J* = 7.6 Hz, 1H, ArH), 7.13~7.09 (m, 1H, ArH), 6.24 (s, 1H, OH), 4.53 (d, *J* = 14.8 Hz, 1H, CH), 4.18~4.02 (m, 2H, OCH_2)3.79 (d, *J* = 14.8 Hz, 1H, CH), 1.26~1.22 (m, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.6, 165.0, 152.3, 147.2, 137.1, 136.2, 135.3, 131.0, 128.7, 127.4, 125.0, 124.8, 124.1, 123.6, 120.2, 97.3, 96.9, 85.6, 59.3, 23.6, 14.8; IR (KBr) υ: 3355, 3061, 2971, 1721, 1678, 1591, 1458, 1406, 1373, 1243, 1186, 1141, 1098, 1029, 910, 867, 830, 758, 719cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{21}H_{17}NNaO_5S$ ([M+Na]$^{+}$): 418.0725. Found: 418.0731.



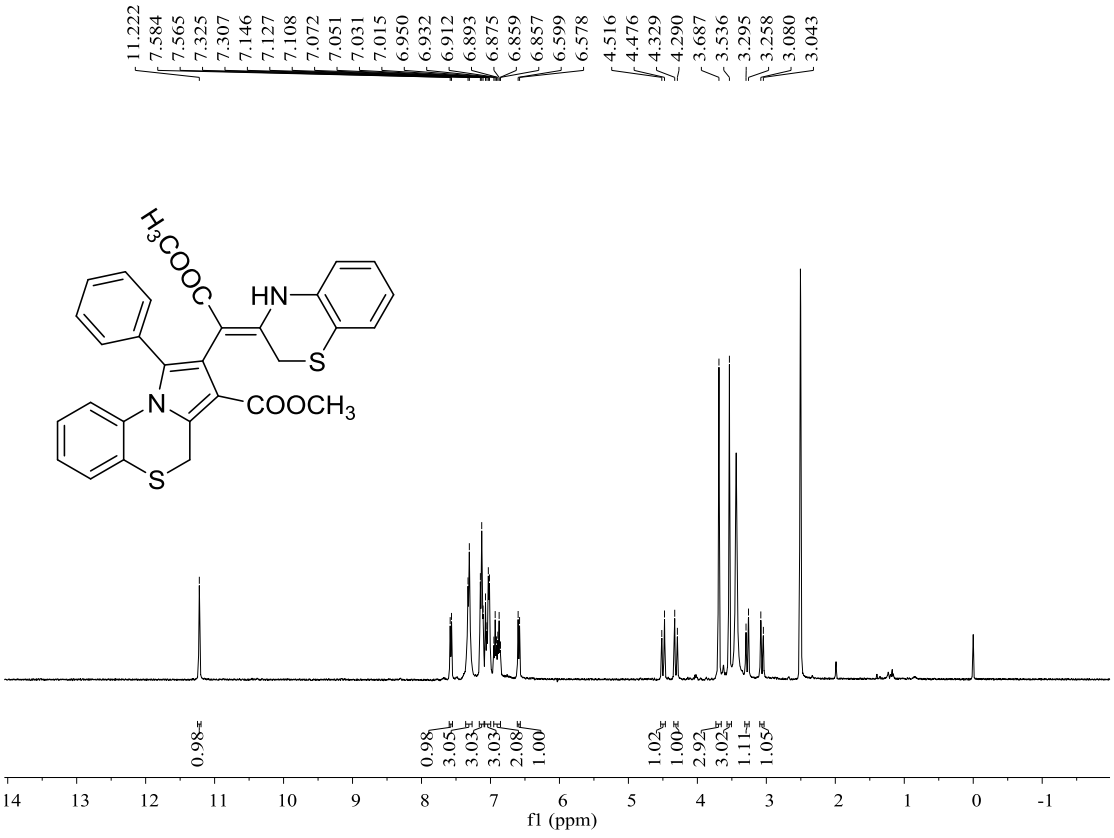

197.608
165.045
152.337
147.208
137.121
136.188
135.279
130.967
128.659
127.410
124.974
124.799
124.088
123.559
120.243
97.266
96.936
85.628
59.308
23.613
14.782
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

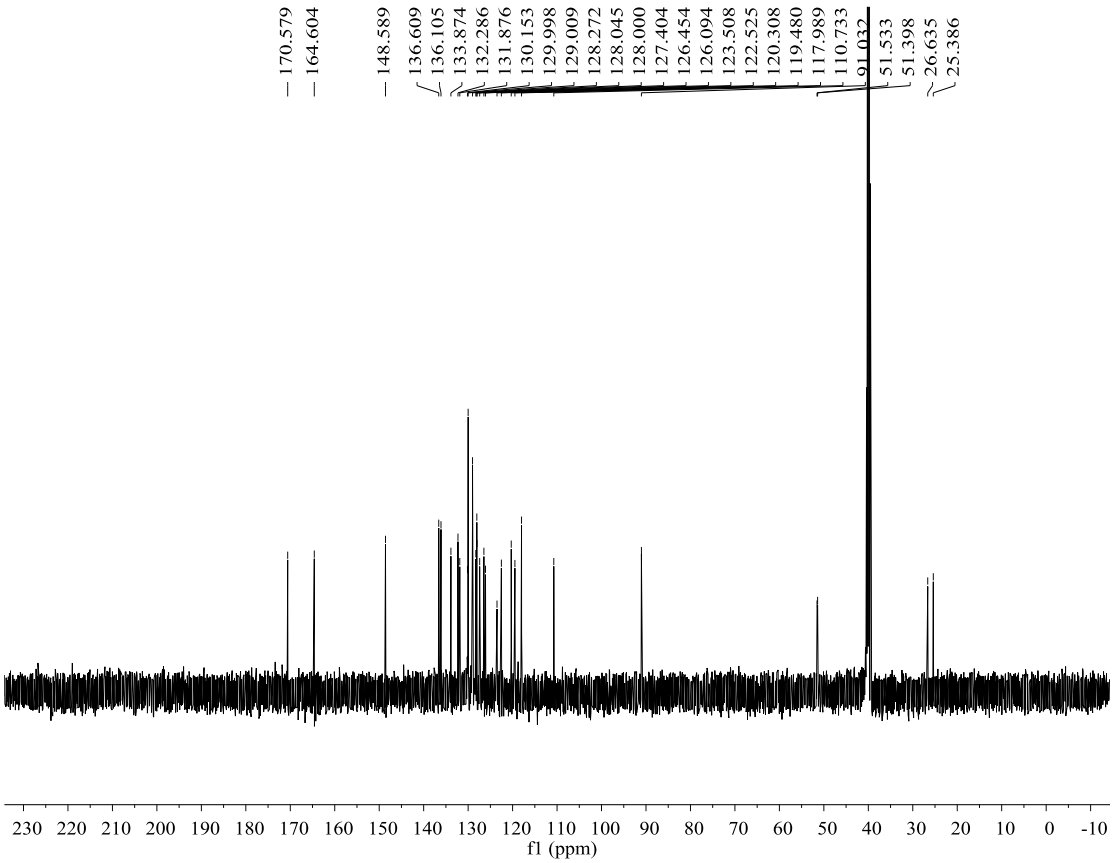

Intens.
x10^4
+MS, 0.33-0.37min #(34-38)
418.0731
6
4
2
0
380
390
400
410
420
430
440
450
m/z

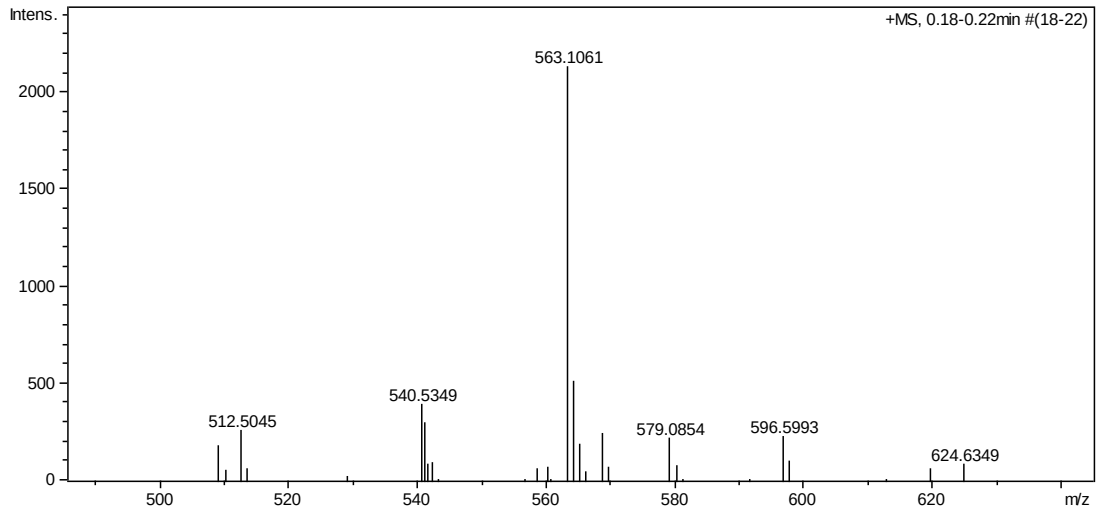
Methyl

(Z)-2-(1-(2H-benzo[b][1,4]thiazin-3(4H)-ylidene)-2-ethoxy-2-oxoethyl)-1-phenyl-4H-benzo[b] pyrrolo[1,2-d][1,4]thiazine-3-carboxylate (9a):

white solid, 75%, m.p. 129~131℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.22 (s, 1H, NH), 7.57 (d, *J* = 7.6 Hz, 1H, ArH), 7.33~7.30 (m, 3H, ArH), 7.15~7.11 (m, 3H, ArH), 7.07~7.02 (m, 3H, ArH), 6.95~6.86 (m, 2H, ArH), 6.59 (d, *J* = 8.4 Hz, 1H, ArH), 4.50 (d, *J* = 16.0 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H, CH), 3.69 (s, 3H, OCH_3) 3.54 (s, 3H, OCH_3) 3.28 (d, *J* = 16.0 Hz, 1H), 3.06 (d, *J* = 16.0 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.5, 164.6, 148.5, 136.6, 136.1, 133.8, 132.2, 131.8, 130.1, 129.9, 129.0, 128.2, 128.0, 128.0, 127.4, 126.4, 126.0, 123.5, 122.5, 120.3, 119.4, 117.9, 110.7, 91.0, 51.5, 51.3, 26.6, 25.3; IR (KBr) υ: 3458, 2945, 1704, 1660, 1607, 1479, 1441, 1386, 1239, 1133, 1087, 1044, 751 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{30}H_{24}N_2NaO_4S_2$ ($[M+Na]^+$): 563.1075. Found: 563.1061.



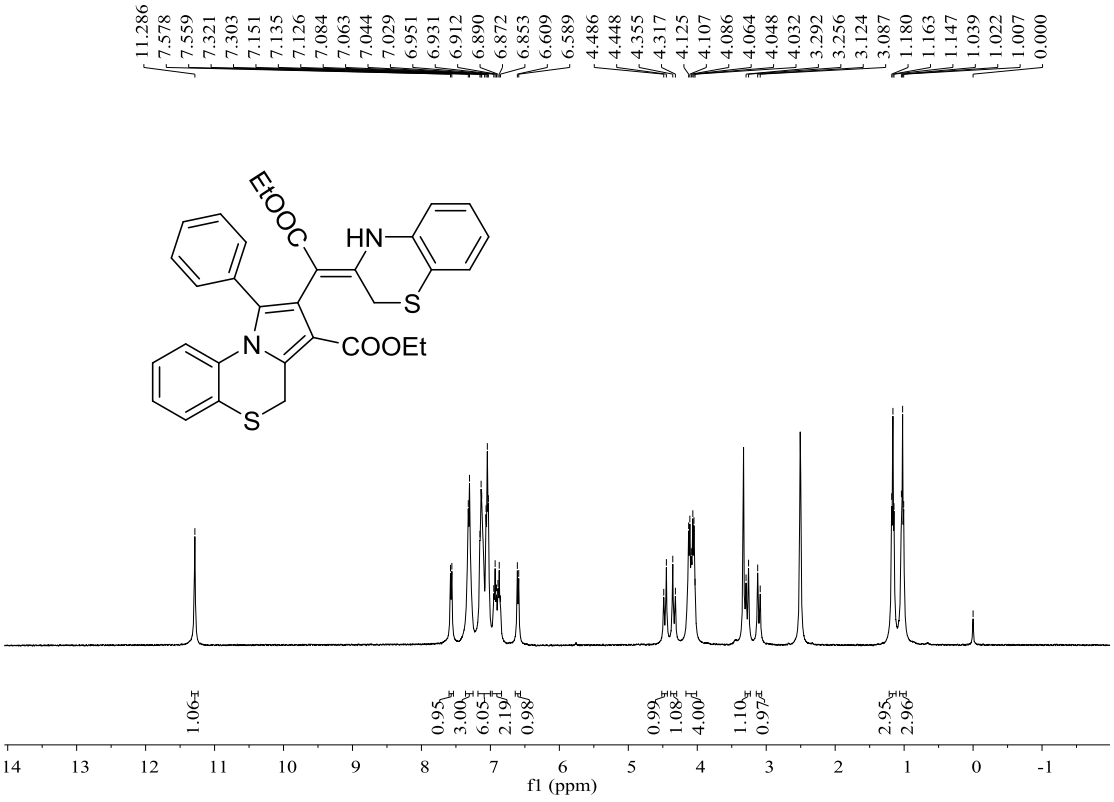

170.579
164.604
148.589
136.609
136.105
133.874
132.286
131.876
130.153
129.998
129.009
128.272
128.045
128.000
127.404
126.454
126.094
123.508
122.525
120.308
119.480
117.989
110.733
91.032
51.533
51.398
26.635
25.386
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

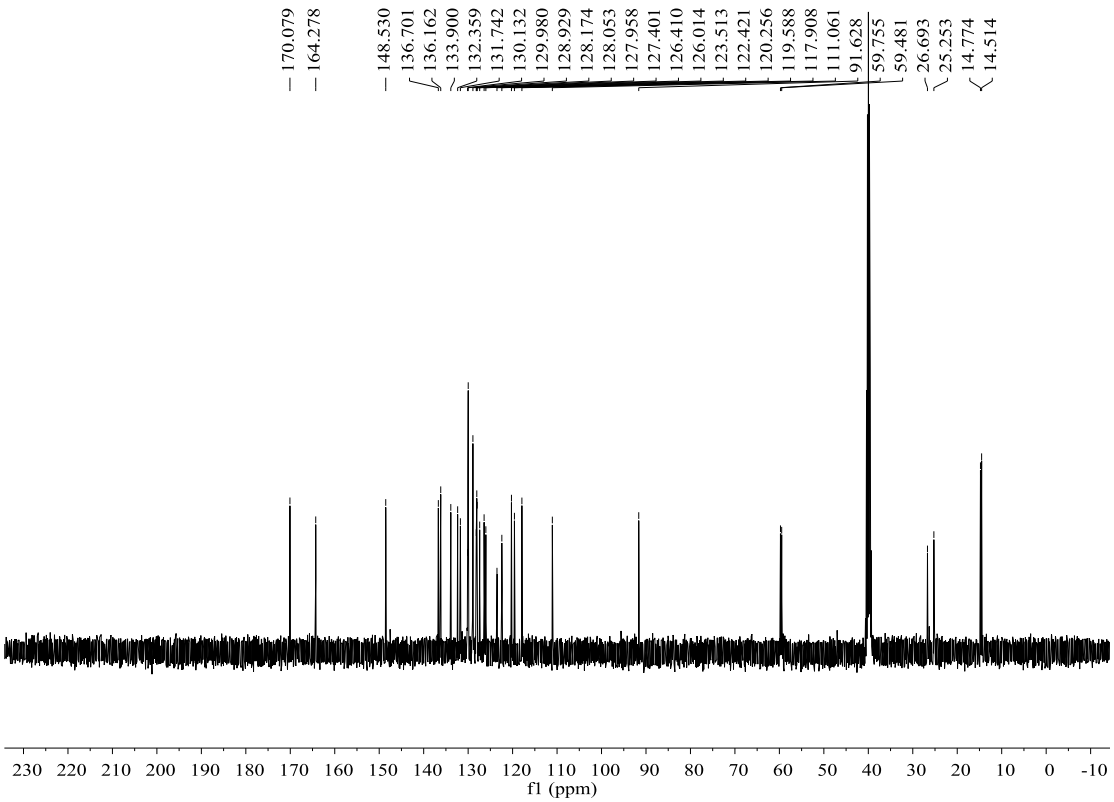

Intens.
+MS, 0.18-0.22min #(18-22)
563.1061
2000
1500
1000
500
0
540.5349
512.5045
579.0854
596.5993
624.6349
500
520
540
560
580
600
620
m/z

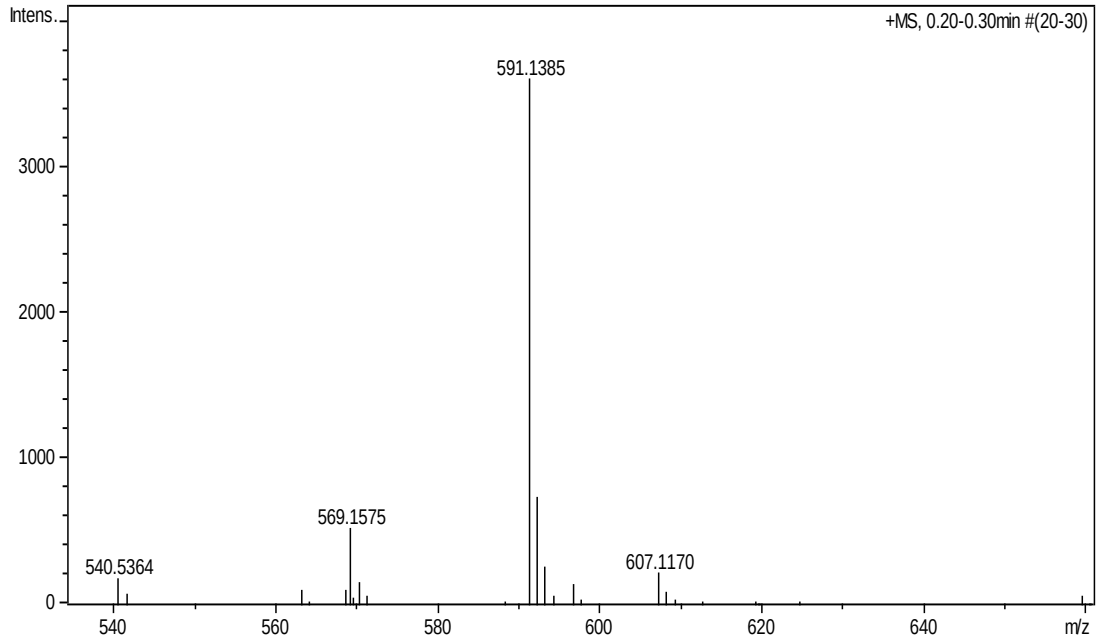
Ethyl

(Z)-2-(1-(2H-benzo[b][1,4]thiazin-3(4H)-ylidene)-2-ethoxy-2-oxoethyl)-1-phenyl-4H-benzo[b] pyrrolo[1,2-d][1,4]thiazine-3-carboxylate (9b):

white solid, 72%, m.p. 157~159℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.29 (s, 1H, NH), 7.57 (d, *J* = 7.6 Hz, 1H, ArH), 7.32~7.30 (m, 3H, ArH), 7.15~7.03 (m, 6H, ArH), 6.95~6.85 (m, 2H, ArH), 6.60 (d, *J* = 8.4 Hz, 1H, ArH), 4.47 (d, *J* = 15.2 Hz, 1H), 4.44 (d, *J* = 15.2 Hz, 1H, CH), 4.13~4.03 (m, 4H, OCH_2), 3.28 (d, *J* = 16.0 Hz, 1H), 3.06 (d, *J* = 16.0 Hz, 1H, CH_3) 1.16 (t, *J* = 6.8 Hz, 1H), 1.02 (t, *J* = 6.8 Hz, 1H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 164.2, 148.5, 136.7, 136.1, 133.8, 132.3, 131.7, 130.1, 129.9, 128.9, 128.1, 128.0, 127.9, 127.4, 126.4, 126.0, 123.5, 122.4, 120.2, 119.5, 117.9, 111.0, 91.6, 59.7, 59.4, 26.6, 25.2, 14.7, 14.5; IR (KBr) υ: 2975, 1692, 1653, 1609, 1478, 1380, 1237, 1177, 1132, 1101, 1045, 856, 752 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{32}H_{28}N_2NaO_4S_2$ ([M+Na]$^+$): 591.1388. Found: 591.1385.



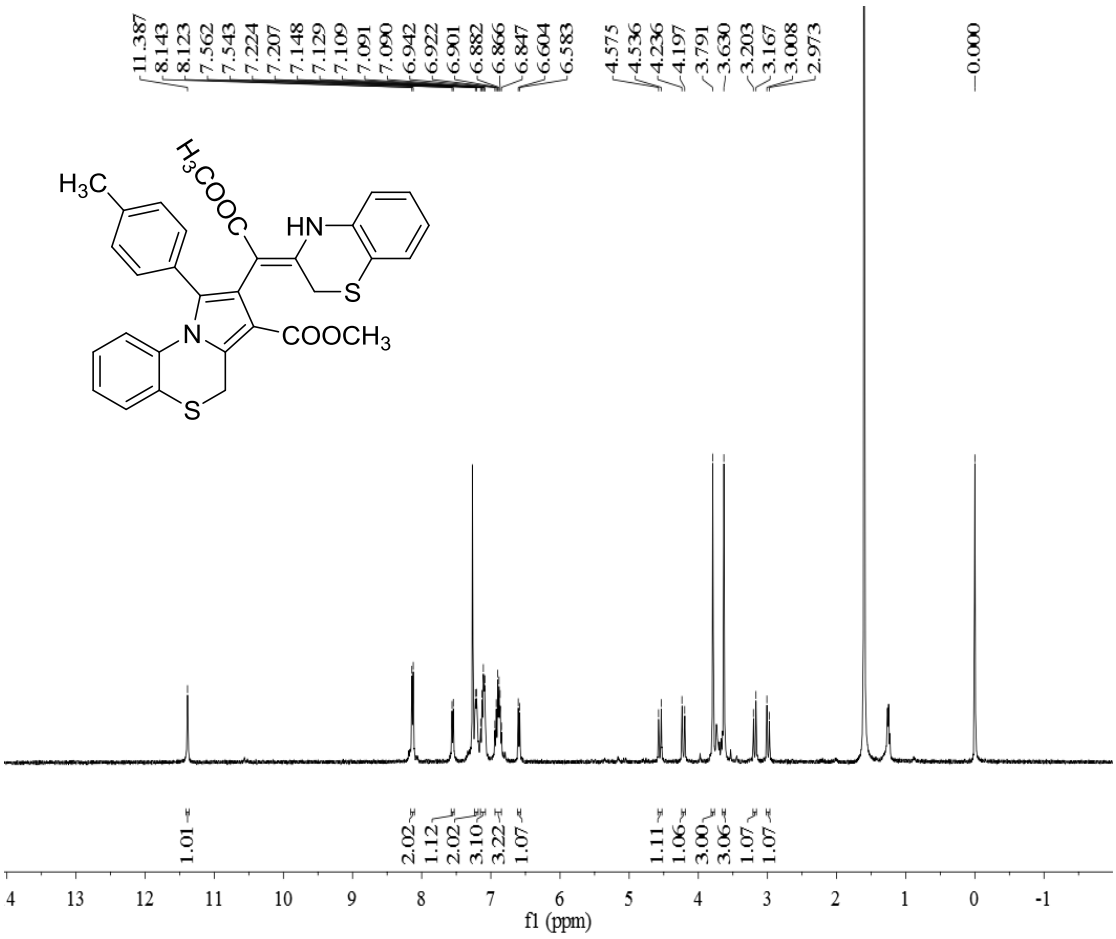

170.079
164.278
148.530
136.701
136.162
133.900
132.359
131.742
130.132
129.980
128.929
128.174
128.053
127.958
127.401
126.410
126.014
123.513
122.421
120.256
119.588
117.908
111.061
91.628
59.755
59.481
26.693
25.253
14.774
14.514
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

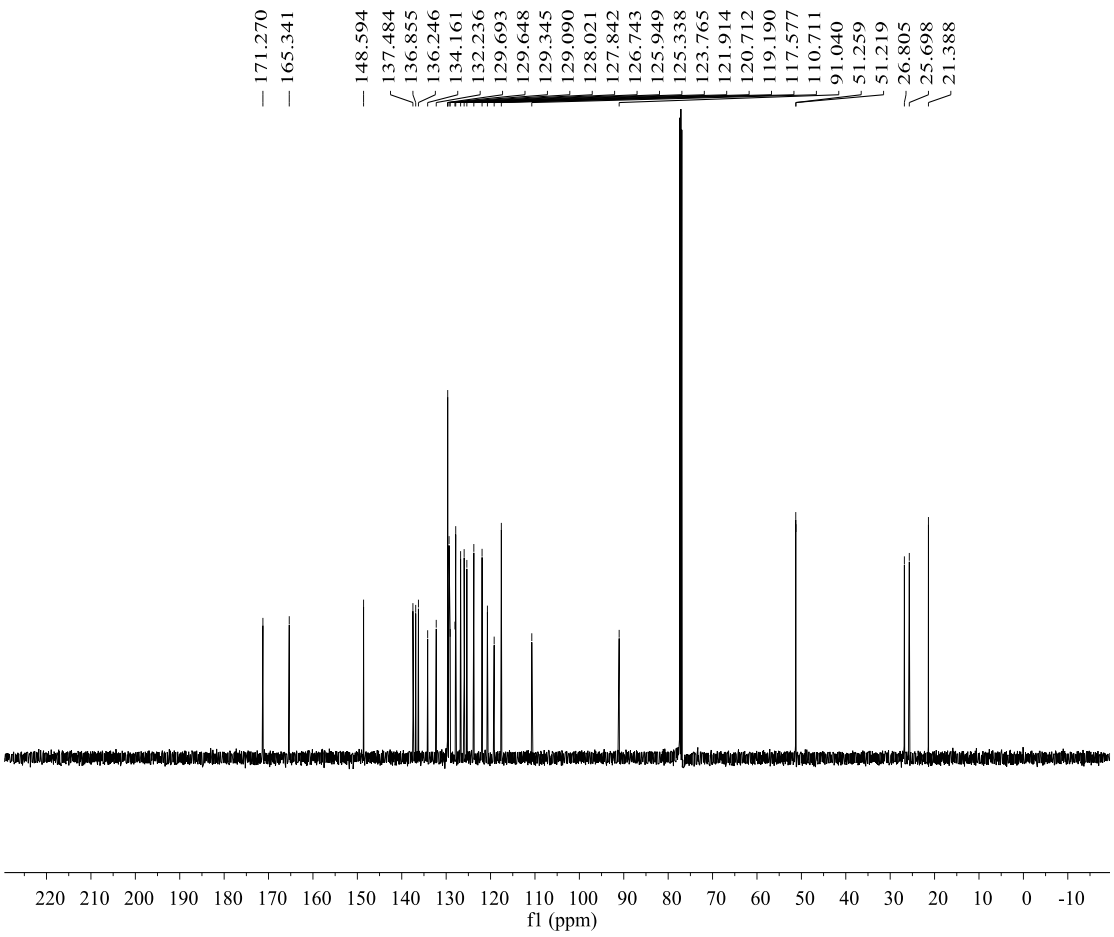

Intens.
+MS, 0.20-0.30min #(20-30)
591.1385
3000
2000
1000
0
569.1575
540.5364
607.1170
540
560
580
600
620
640
m/z

Methyl

(Z)-2-(1-(2H-benzo[b][1,4]thiazin-3(4H)-ylidene)-2-methoxy-2-oxoethyl)-1-(p-tolyl)-4H-benzo[b]pyrrolo[1,2-d][1,4]thiazine-3-carboxylate (9c):

white solid, 89%, m.p. 163~165℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.36 (s, 1H, NH), 7.48 (d, *J* = 8.0 Hz, 1H, ArH), 7.10~7.05 (m, 5H, ArH), 6.91~6.81 (m, 5H, ArH), 6.69 (d, *J* = 8.0 Hz, 1H, ArH), 4.63 (d, *J* = 15.6 Hz, 1H), 4.14 (d, *J* = 15.2 Hz, 1H, CH), 3.77 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.20 (d, *J* = 14.4 Hz, 1H), 2.96 (d, *J* = 14.8 Hz, 1H, CH), 2.30 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.2, 165.3, 148.5, 137.4, 136.8, 136.2, 134.1, 132.2, 129.6, 129.6, 129.3, 129.0, 128.0, 127.8, 126.7, 125.9, 125.3, 123.7, 121.9, 120.7, 119.1, 117.5, 110.7, 91.0, 51.2, 51.2, 26.8, 25.6, 21.3; IR (KBr) υ: 2946, 1714, 1657, 1601, 1570, 1510, 1477, 1437, 1339, 1263, 1236, 1190, 1150, 1130, 1079, 1053, 1034, 860, 748 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{31}H_{26}N_2NaO_4S_2$ ($[M+Na]^+$): 577.1232. Found: 577.1245.




171.270
165.341
148.594
137.484
136.855
136.246
134.161
132.236
129.693
129.648
129.345
129.090
128.021
127.842
126.743
125.949
125.338
123.765
121.914
120.712
119.190
117.577
110.711
91.040
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25.698
21.388
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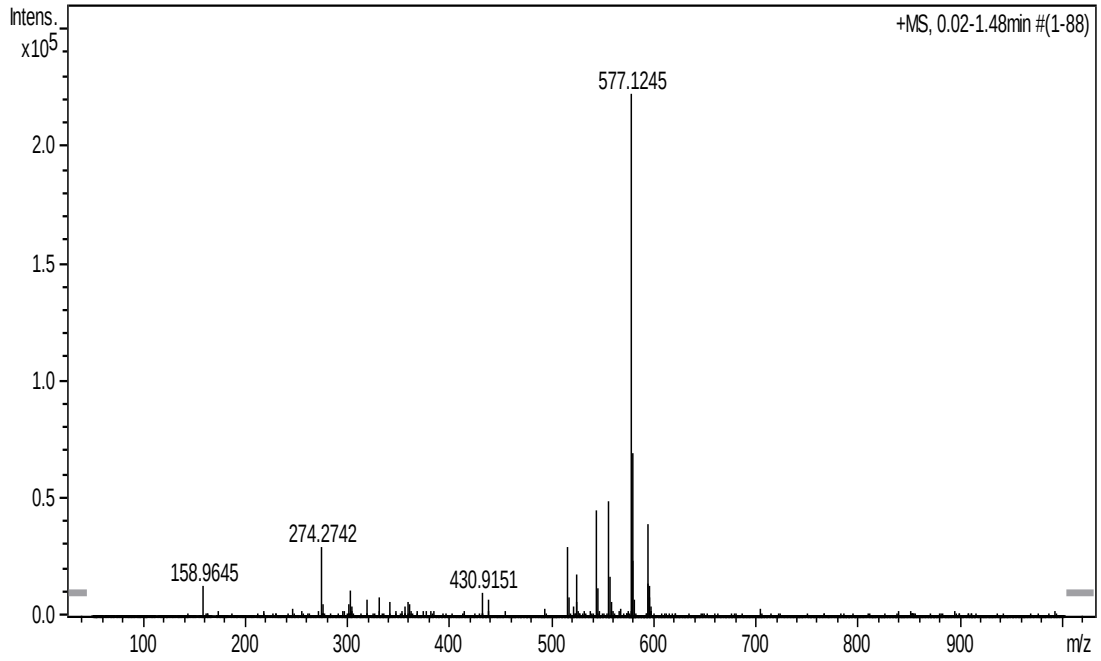
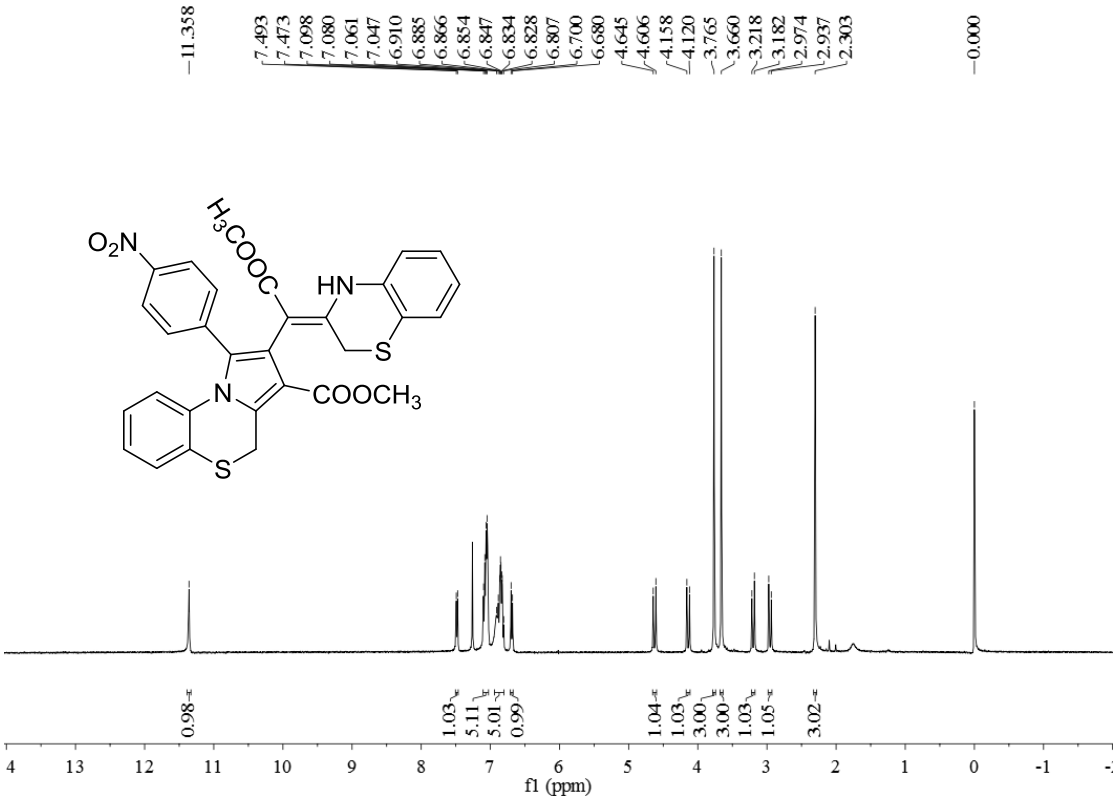
f1 (ppm)

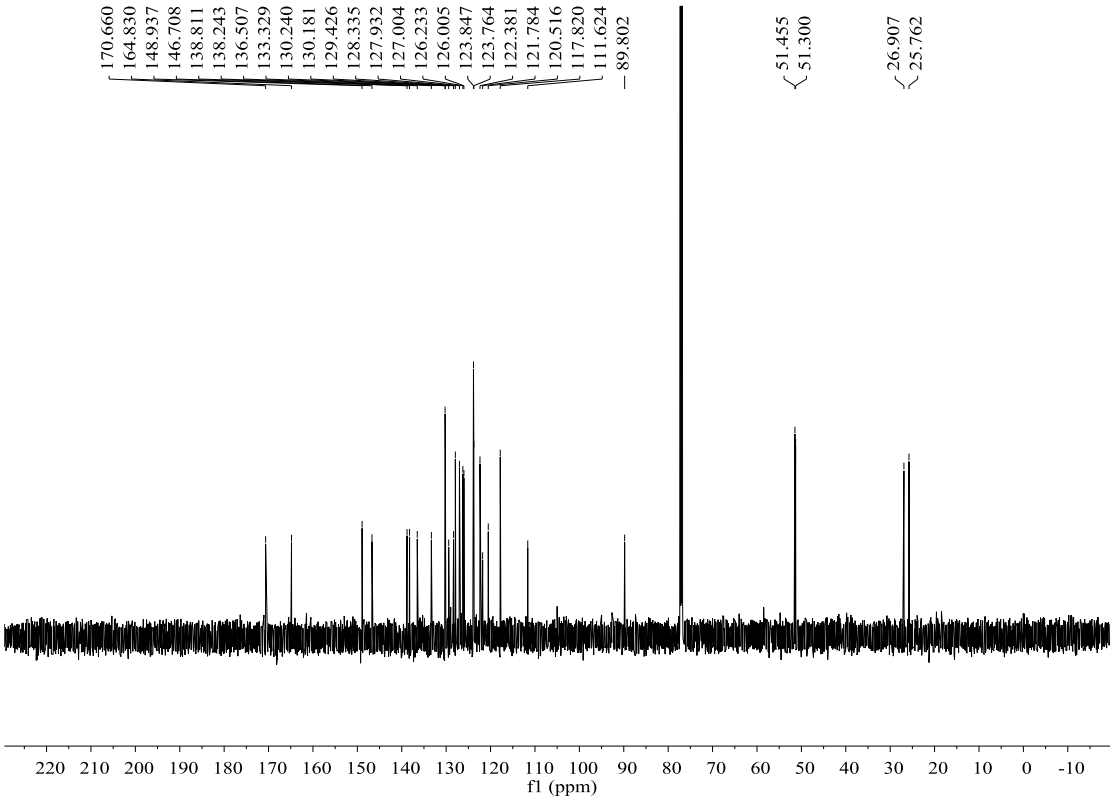

Intens.
x10^5
+MS, 0.02-1.48min #(1-88)
577.1245
274.2742
158.9645
430.9151
2.0
1.5
1.0
0.5
0.0
100 200 300 400 500 600 700 800 900
m/z

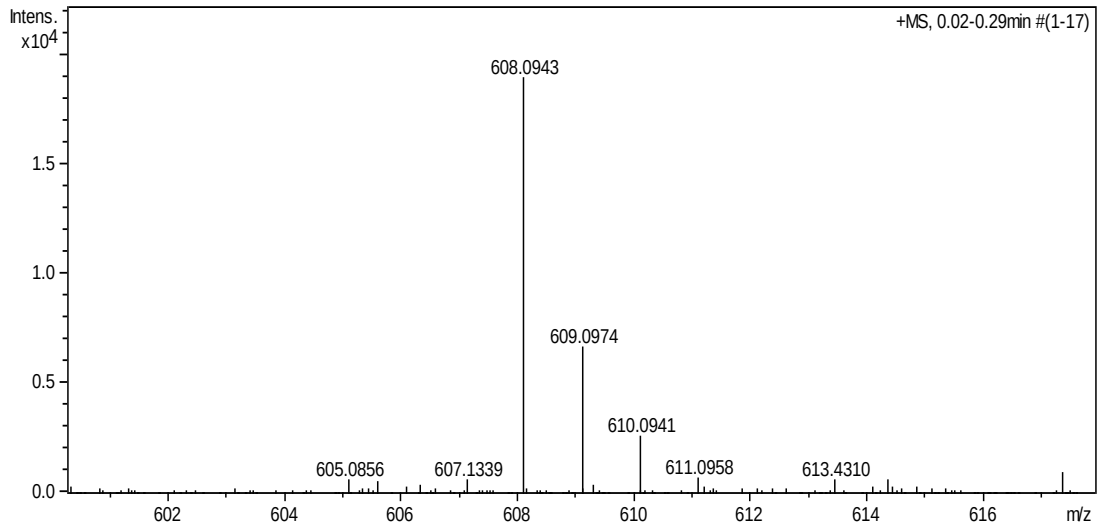
Methyl

(Z)-2-(1-(2H-benzo[b][1,4]thiazin-3(4H)-ylidene)-2-methoxy-2-oxoethyl)-1-(4-nitrophenyl)-4 H-benzo[b]pyrrolo[1,2-d][1,4]thiazine-3-carboxylate (9d):

yellow solid, 59%, m.p. 171~173℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.39 (s, 1H, NH), 8.13 (d, *J* = 8.0 Hz, 2H, ArH), 7.55 (d, *J* = 7.6 Hz, 1H, ArH), 7.22 (d, *J* = 6.8 Hz, 2H, ArH), 7.15~7.09 (m, 3H, ArH), 6.94~6.85 (m, 3H, ArH), 6.59 (d, *J* = 7.6 Hz, 1H, ArH), 4.56 (d, *J* = 15.6 Hz, 1H), 4.22 (d, *J* = 15.6 Hz, 1H, CH), 3.79 (s, 3H, OCH_3) 3.63 (s, 3H, OCH_3) 3.19 (d, *J* = 14.4 Hz, 1H), 2.99 (d, *J* = 14.0 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 229.5, 170.6, 164.8, 148.9, 146.7, 138.8, 138.2, 136.5, 133.3, 130.2, 130.1, 129.4, 128.3, 127.9, 127.0, 126.2, 126.0, 123.8, 123.7, 122.3, 121.7, 120.5, 117.8, 111.6, 89.8, 51.4, 51.3, 26.9, 25.7; IR (KBr) υ: 3521, 2953, 1682, 1649, 1611, 1546, 1452, 1439, 1371, 1317, 1157, 1065, 1037, 778 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{30}H_{23}N_3NaO_6S_2$ ([M+Na]$^+$): 608.0926. Found: 608.0943.




170.660
164.830
148.937
146.708
138.811
138.243
136.507
133.329
130.240
130.181
129.426
128.335
127.932
127.004
126.233
126.005
123.847
123.764
122.381
121.784
120.516
117.820
111.624
89.802
51.455
51.300
26.907
25.762
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.
x10^4
+MS, 0.02-0.29min #(1-17)
608.0943
609.0974
610.0941
605.0856
607.1339
611.0958
613.4310
1.5
1.0
0.5
0.0
602
604
606
608
610
612
614
616
m/z