Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Regioselective and diastereoselective synthesis of two functionalized 1,5-methanoindeno[1,2-*d*]azocines via three-component reaction

Jun Cao, Jing Sun, Chao-Guo Yan*

Supporting Information

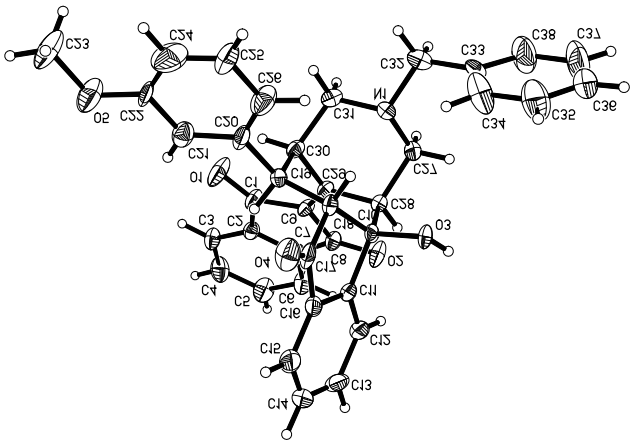


Fig. s1 Molecular structure of the compound **1c**

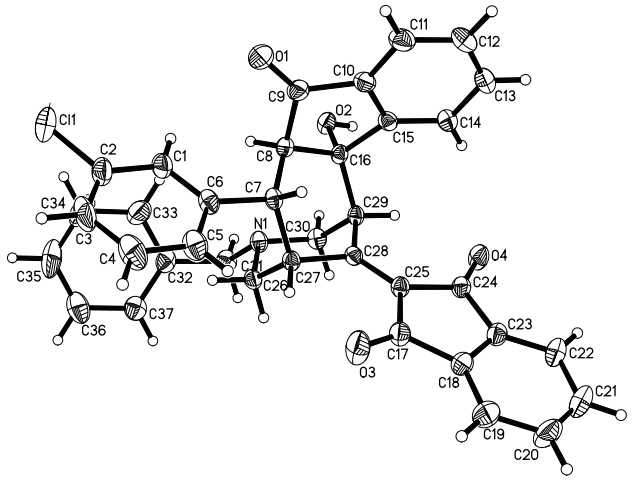


Fig. s2 Molecular structure of the compound **1e**

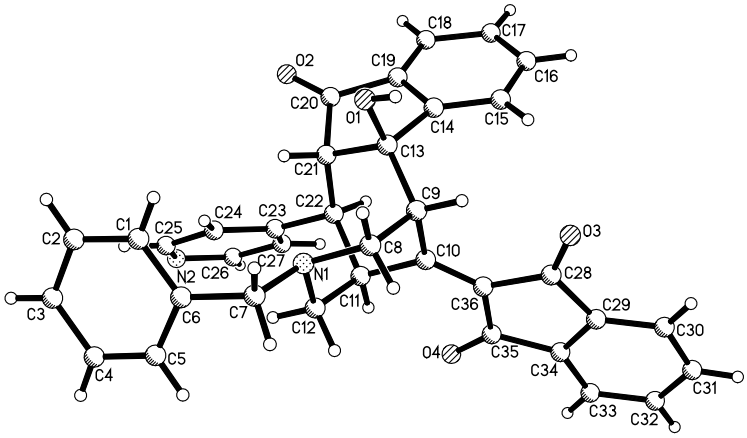


Fig. s3 Molecular structure of the compound **1k**

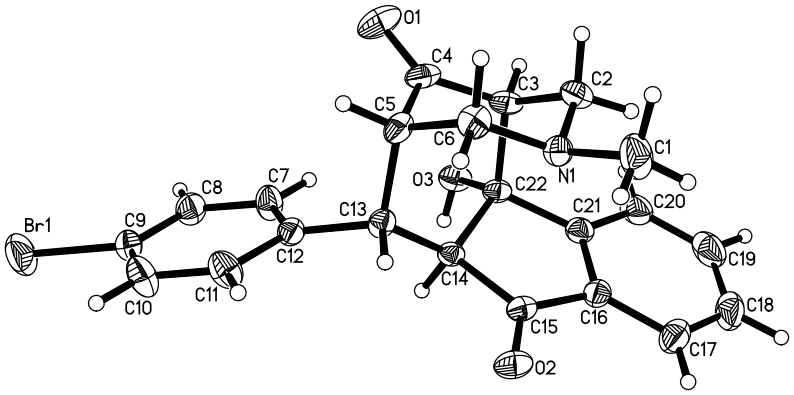


Fig. s4 Molecular structure of the compound **2c**

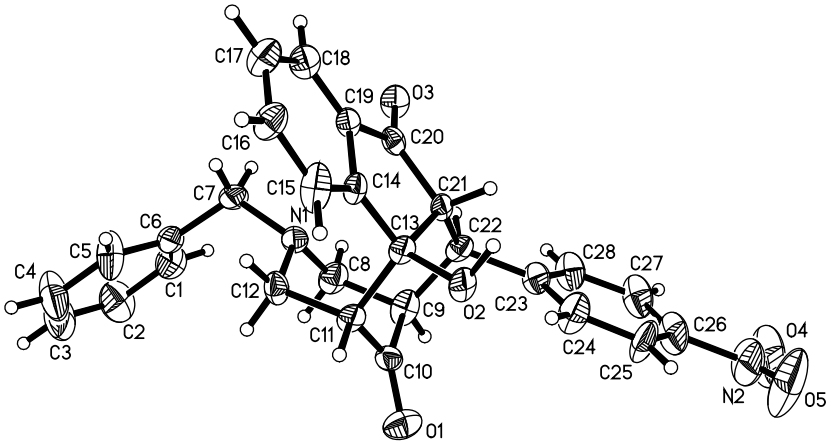


Fig. s5 Molecular structure of the compound **2d**

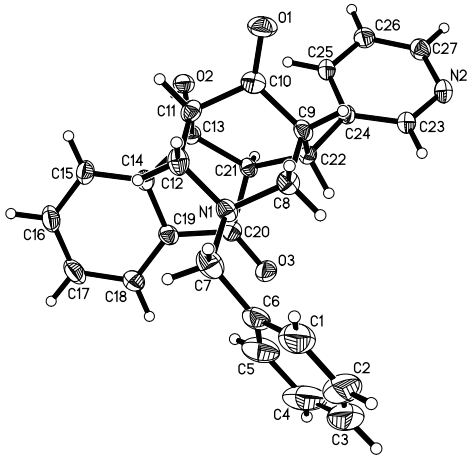


Fig. s6 Molecular structure of the compound **2e**

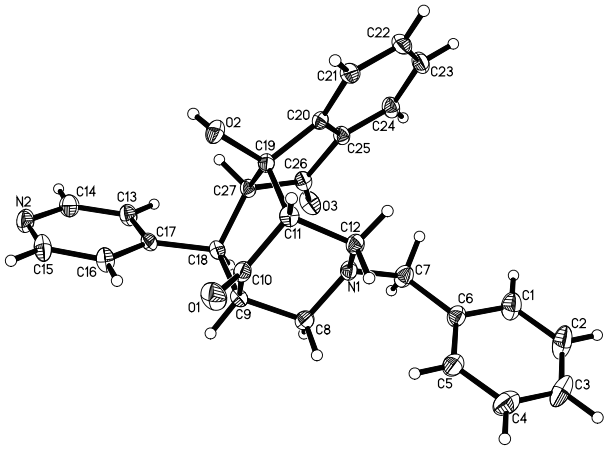


Fig. s7 Molecular structure of the compound **2f**

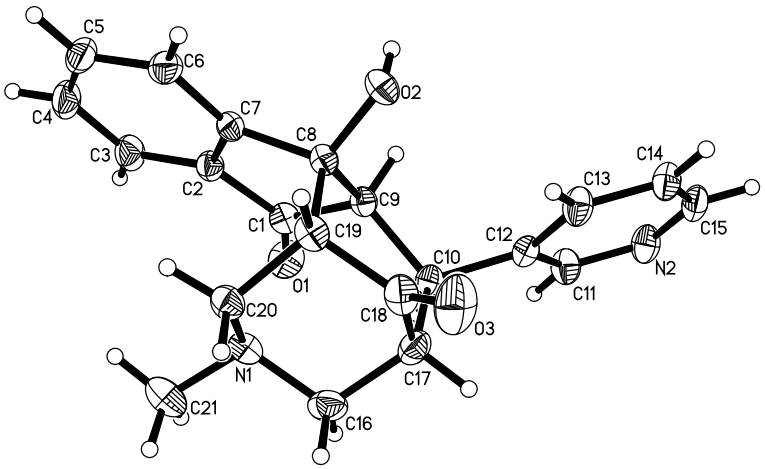
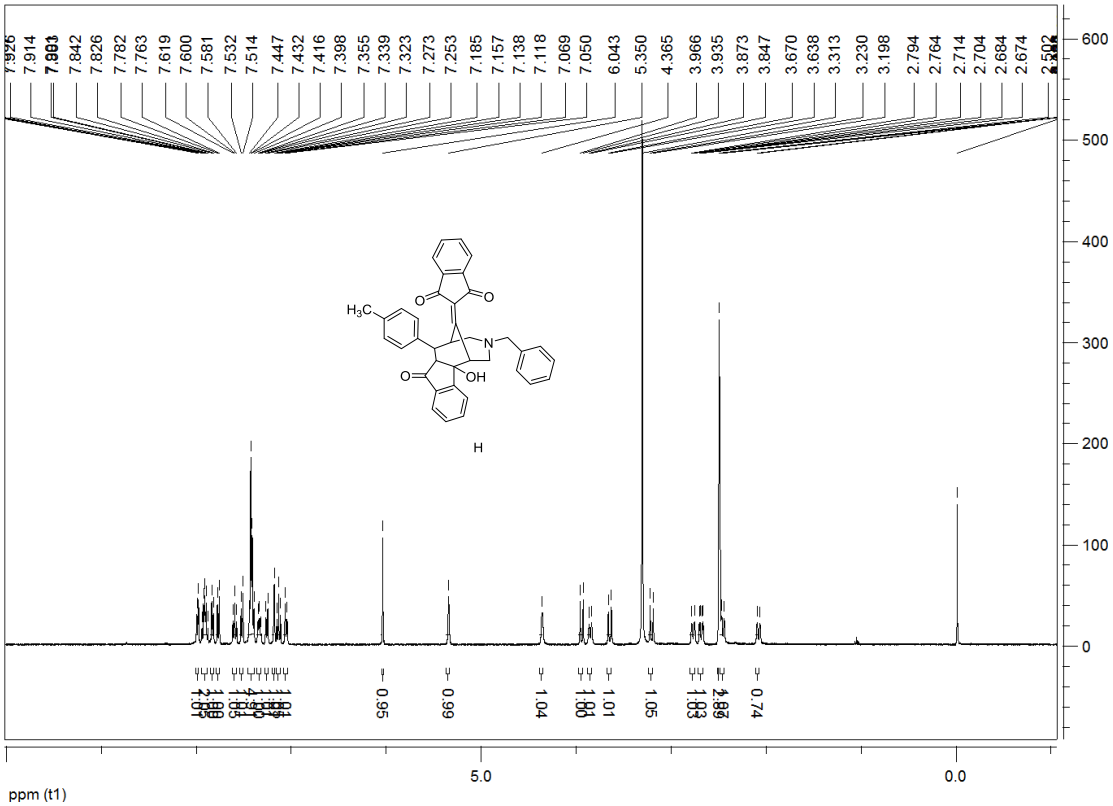
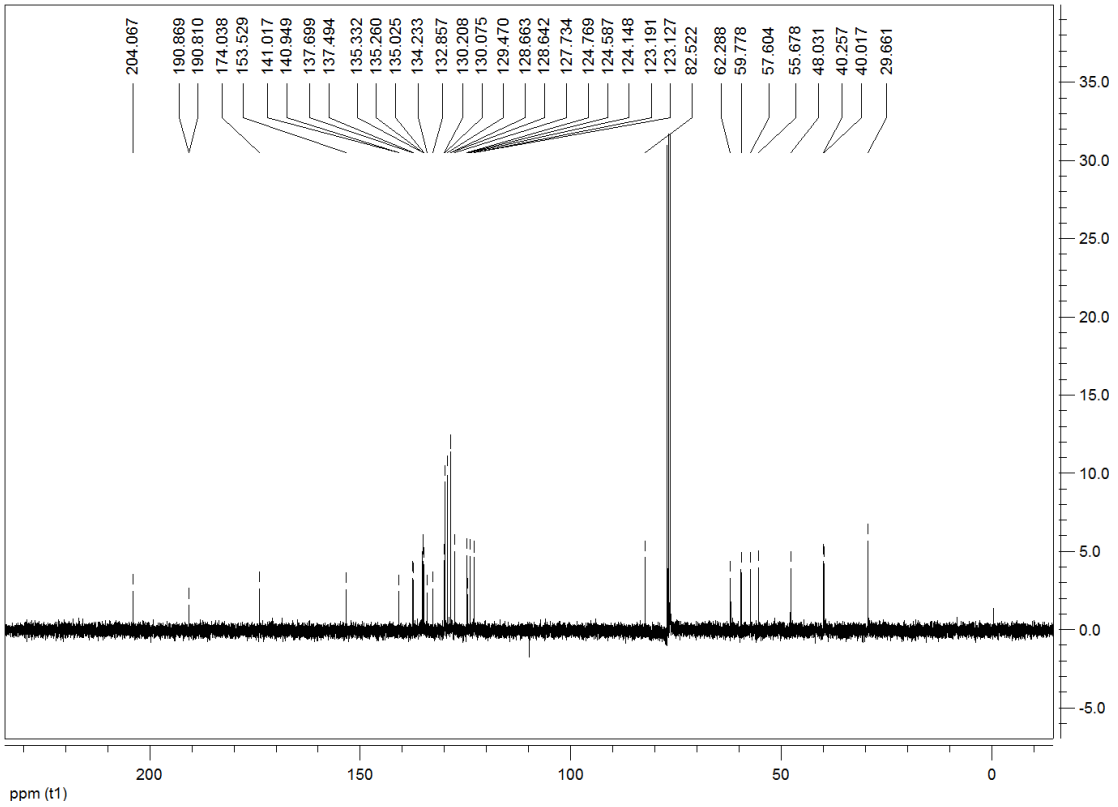


Fig. s8 Molecular structure of the compound **2i**

2-(-3-benzyl-11b-hydroxy-7-oxo-6-(p-tolyl)-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1a): yellow solid, 71%, m.p. 179-181℃; ^{1}H NMR (400 MHz, DMSO) δ: 7.99 (d, *J* = 6.4 Hz, 1H, ArH), 7.94-7.88 (m, 2H, ArH), 7.83 (d, *J* = 6.4 Hz, 1H, ArH), 7.77 (d, *J* = 7.6 Hz, 1H, ArH), 7.60 (t, *J* = 7.6 Hz, 1H, ArH), 7.52 (d, *J* = 7.2 Hz, 1H, ArH), 7.45-7.40 (m, 5H, ArH),7.36-7.32 (m, 1H, ArH), 7.26 (d, *J* = 8.0 Hz, 1H, ArH), 7.18-7.12 (m, 2H, ArH), 7.06 (d, *J* = 7.6 Hz, 1H, ArH), 6.04 (s, 1H, CH),5.35 (s, 1H, CH),4.36 (s, 1H, CH), 3.95 (d, *J* = 12.4 Hz, 1H, CH), 3.86 (d, *J* = 10.4 Hz, 1H, CH), 3.65 (d, *J* = 12.8Hz, 1H, CH), 3.11 (d, *J* = 12.8 Hz, 1H, CH), 2.78 (d, *J* = 12.0 Hz, 1H, CH), 2.71-2.67 (m, 1H, CH), 2.50 (s, 3H, CH_3), 2.48-2.45 (m, 1H, CH), 2.09 (d, *J* = 10.8 Hz, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 204.0, 190.9, 190.8, 174.0, 153.5, 141.0, 140.9, 137.7, 137.5, 135.3, 135.3, 135.0, 134.2, 132.9, 130.2, 130.1, 129.6, 128.7, 128.6, 127.7, 124.8, 124.6, 124.1, 123.2, 123.1, 82.5, 62.3, 59.8, 57.6, 55.7, 48.0, 40.3, 40.0, 29.7; IR(KBr) υ: 3436, 3031, 2940, 2820, 1722, 1675, 1602, 1466, 1352, 1227, 1047, 1002, 750, 706 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{38}H_{32}NO_4$([M+H]$^+$): 566.2331, found: 566.2346.

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134.233
132.857
130.208
130.075
129.470
128.663
128.642
127.734
124.769
124.587
124.148
123.191
123.127
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57.604
55.678
48.031
40.257
40.017
29.661
35.0
30.0
25.0
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10.0
5.0
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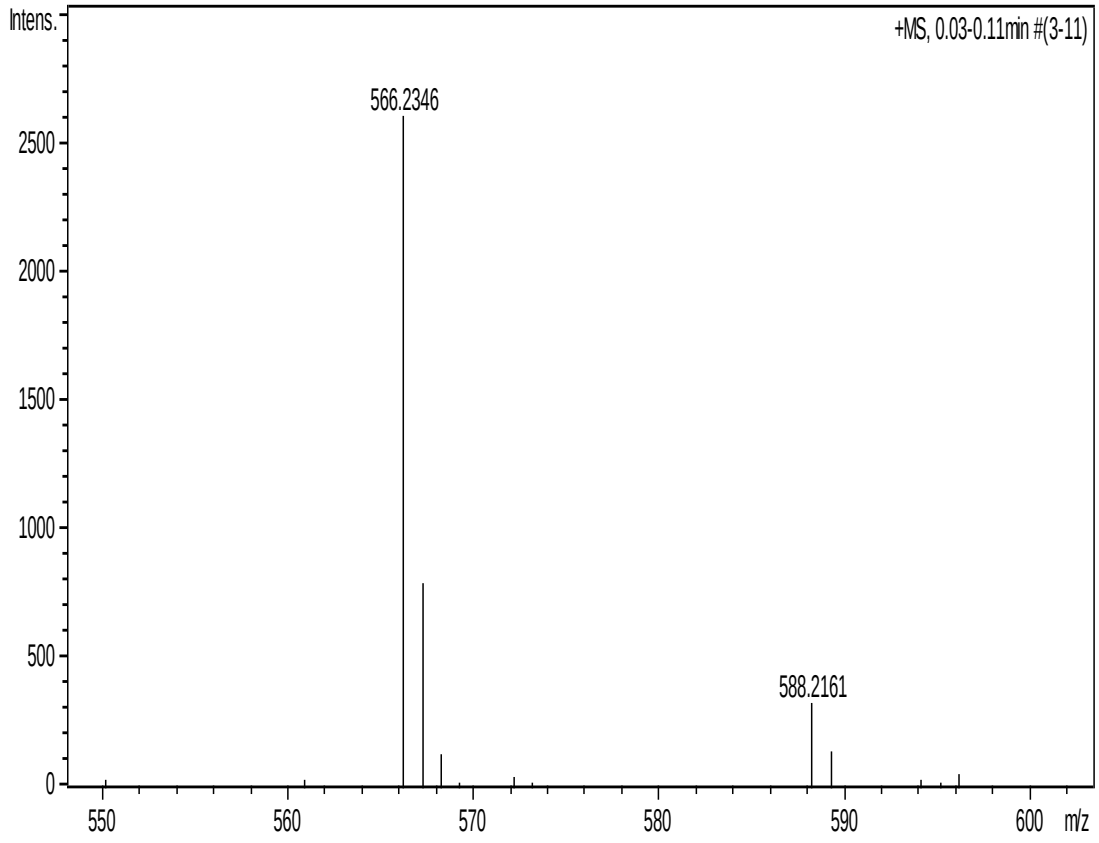
150
100
50
0
ppm (t1)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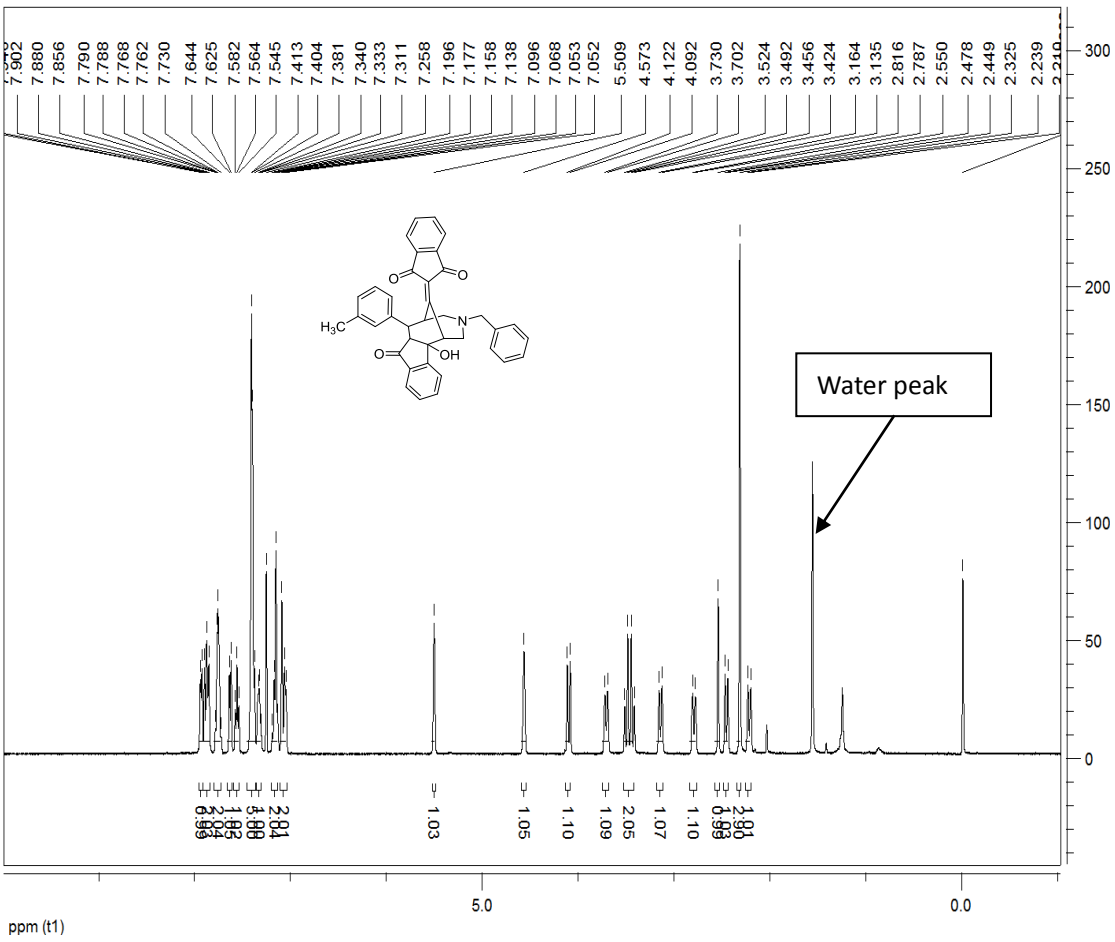
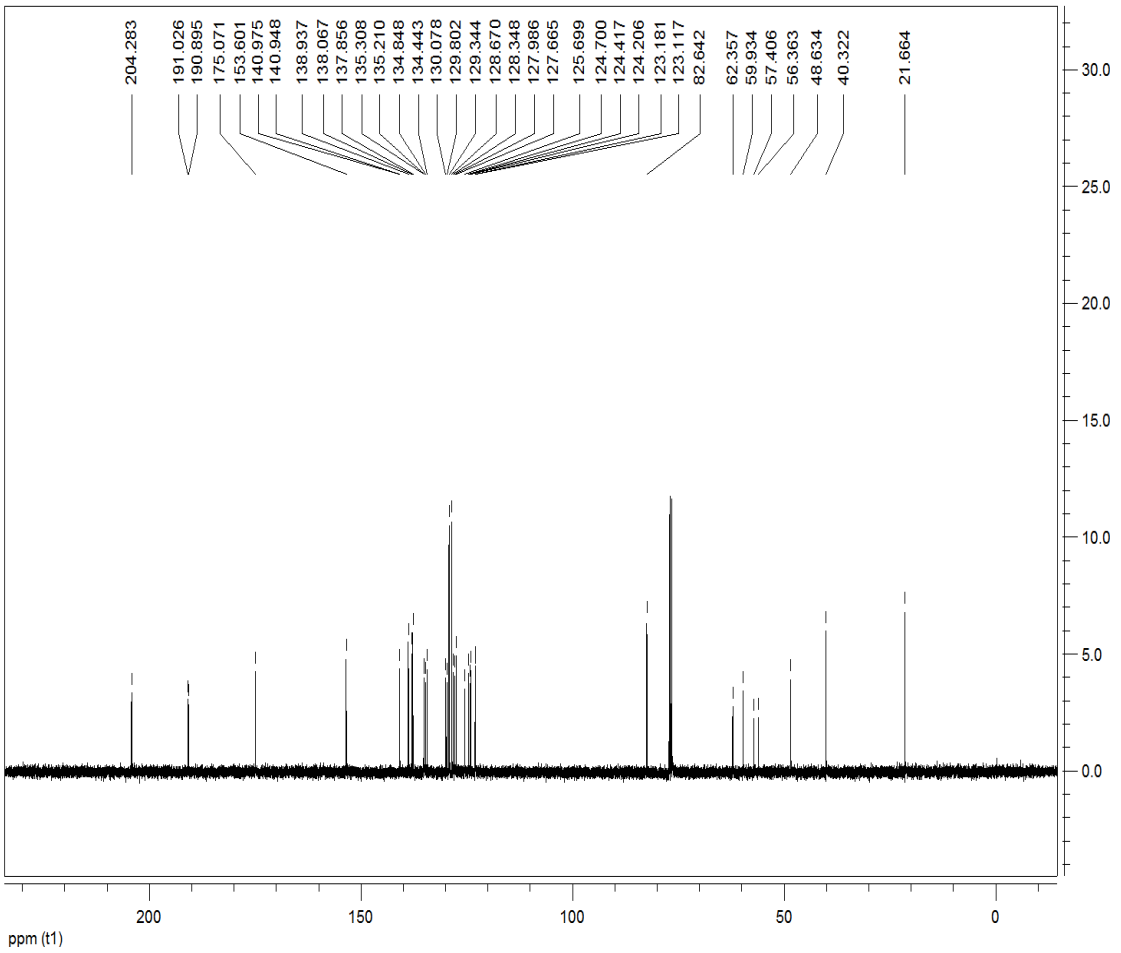
2000
1500
1000
500
0
550
560
570
580
590
600
m/z

2-(3-benzyl-11b-hydroxy-7-oxo-6-(*m*-tolyl)-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1b): yellow solid, 77%, m.p. 181-183℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94-7.93 (m, 1H, ArH), 7.90-7.86 (m, 2H, ArH), 7.79-7.73 (m, 2H, ArH), 7.63 (d, *J* = 7.6 Hz, 1H, ArH), 7.56 (t, *J* = 7.2 Hz, 1H, ArH), 7.41-7.38 (m, 5H, ArH), 7.34-7.31 (m, 1H, ArH), 7.20-7.14 (m, 2H, ArH), 7.10-7.05 (m, 2H, ArH), 5.51 (s, 1H, CH), 4.57 (s, 1H, CH), 4.11 (d, *J* = 12.0 Hz, 1H, CH), 3.72 (d, *J* = 11.2 Hz, 1H, CH), 3.52-3.42 (m, 2H, CH), 3.15 (d, *J* = 11.6 Hz, 1H, CH), 2.80 (d, *J* = 11.6 Hz, 1H, CH), 2.55 (s, 1H, CH), 2.46 (d, *J* = 11.6 Hz, 1H, CH), 2.32 (s, 3H, CH_3), 2.22 (d, *J* = 11.6 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ:204.3, 191.0, 190.9, 175.1, 153.6, 141.0, 140.9, 138.9, 138.1, 137.9, 135.3, 135.2, 134.8, 134.4, 130.1, 129.8, 129.3, 128.7, 128.3, 128.0, 127.7, 125.7, 124.7, 124.4, 124.2, 123.2, 123.1, 82.6, 62.4, 59.9, 57.4, 56.4, 48.6, 40.3, 21.7; IR(KBr) υ: 3416, 3028, 2926, 2788, 2751, 1720, 1670, 1619, 1593, 1458, 746, 701 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{38}H_{32}NO_4$ ($[M+H]^+$): 566.2331, found: 566.2351.

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123.117
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62.357
59.934
57.406
56.363
48.634
40.322
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20.0
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10.0
5.0
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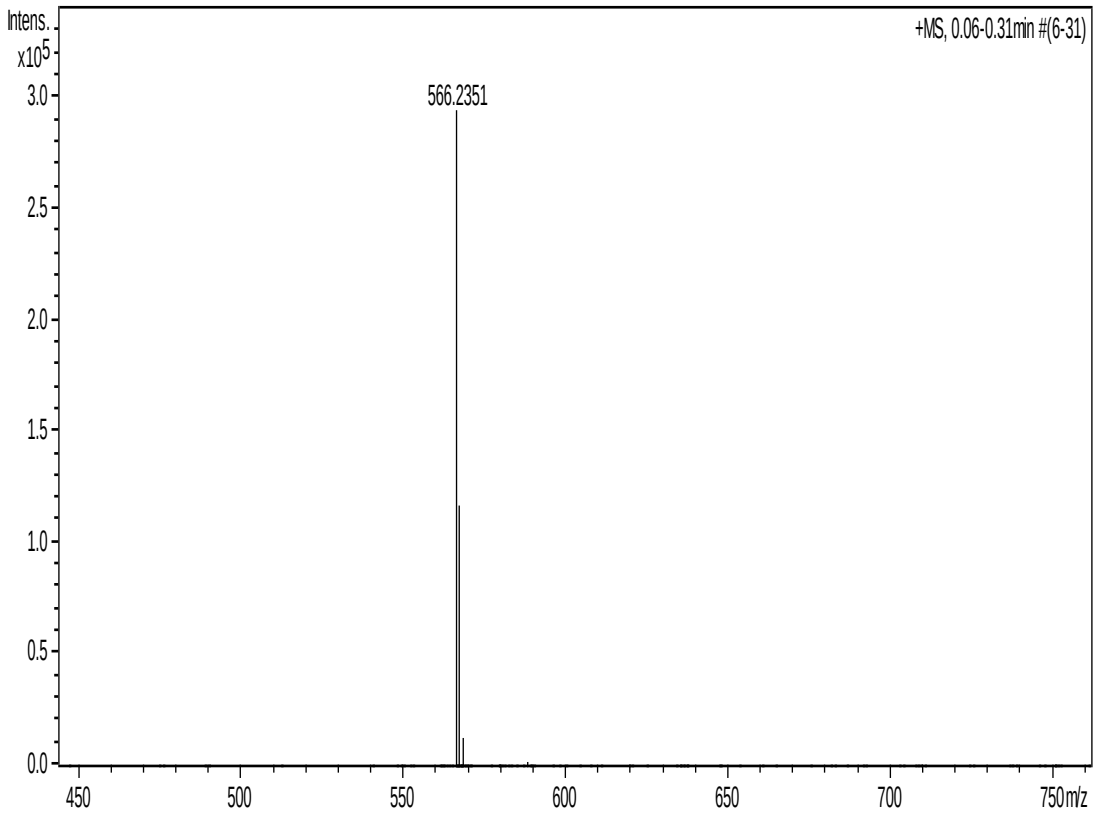
100
50
0
ppm (t1)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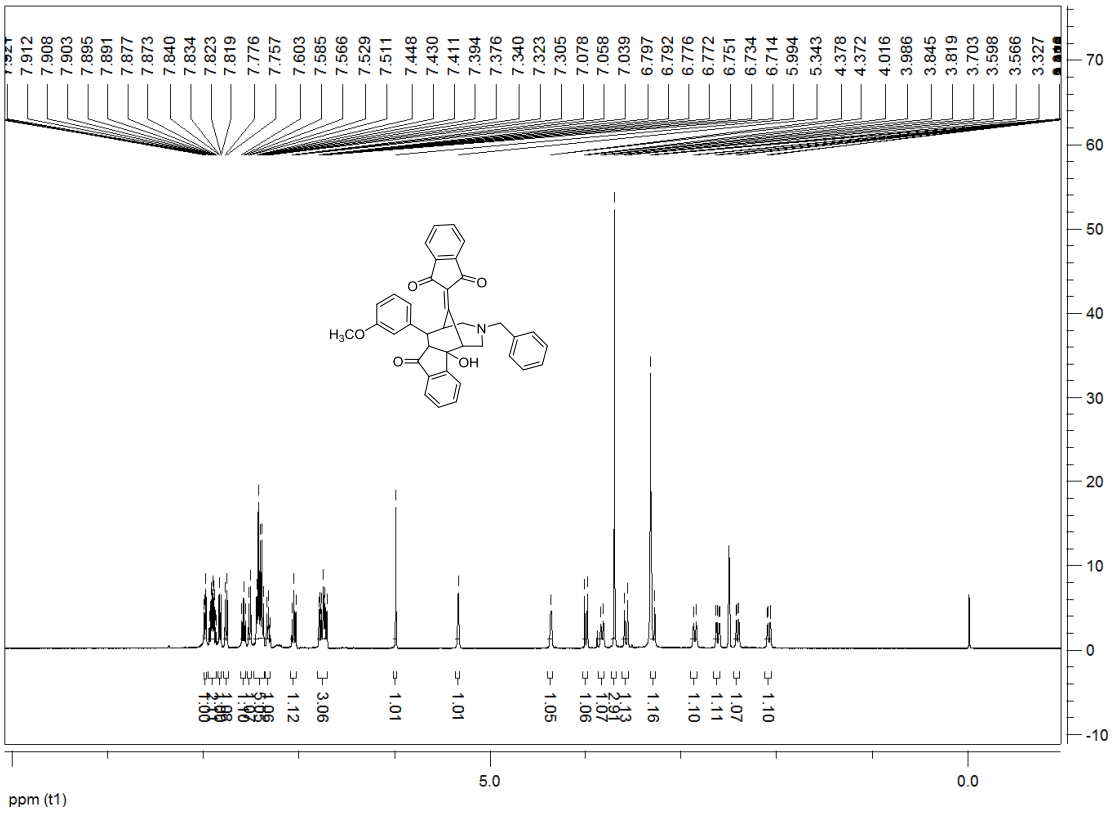
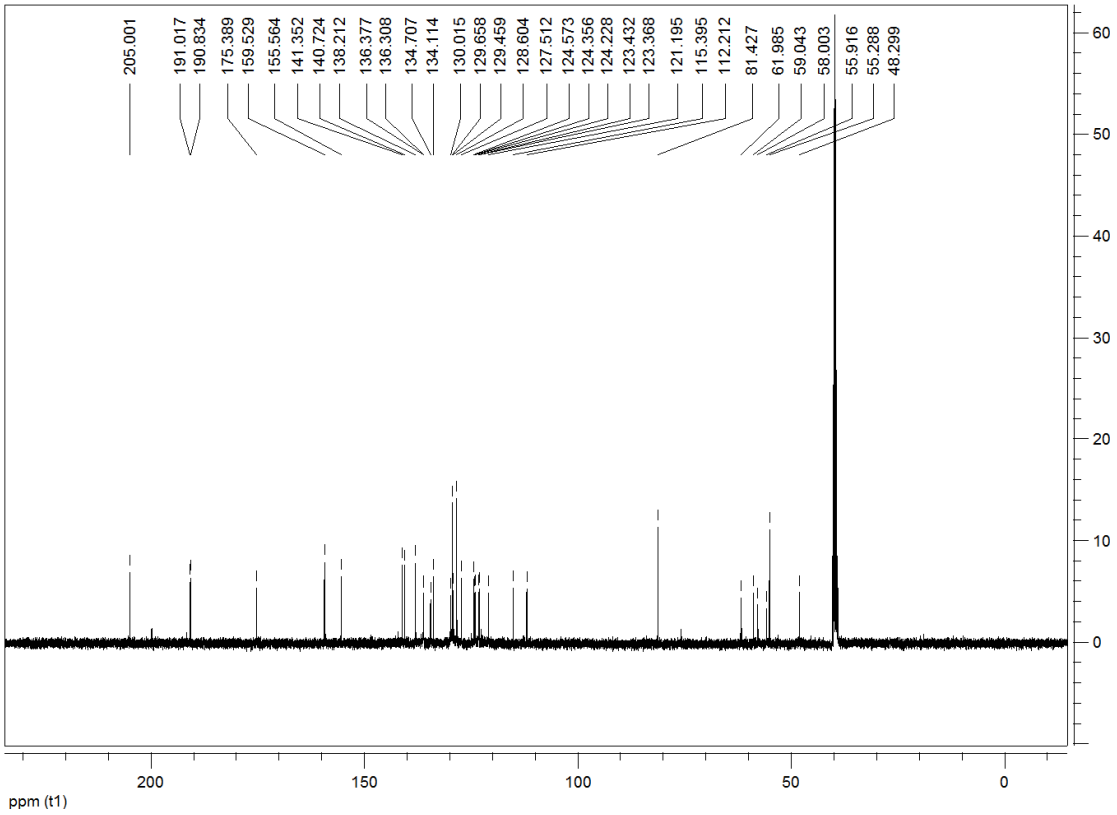
2.0
1.5
1.0
0.5
0.0
450
500
550
600
650
700
750 m/z

2-((5S,6aR,11bR)-3-benzyl-11b-hydroxy-6-(3-methoxyphenyl)-7-oxo-2,3,4,5,6,6a,7,11b-octahydro-1H-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1c): yellow solid, 68%, m.p. 177-179℃; ^{1}H NMR (400 MHz, DMSO) δ: 8.00-7.98 (m, 1H, ArH), 7.94-7.87 (m, 2H, ArH), 7.84-7.82 (m, 1H, ArH), 7.77 (d, *J* = 7.6 Hz, 1H, ArH), 7.58 (t, *J* = 7.2 Hz, 1H, ArH), 7.52 (d, *J* = 7.2 Hz, 1H, ArH), 7.45-7.38 (m, 5H, ArH), 7.34-7.30 (m, 1H, ArH), 7.06 (t, *J* = 8.0Hz, 1H, ArH), 6.80-6.71 (m, 3H, ArH), 6.00 (s, 1H, CH), 5.34 (s, 1H, CH), 4.38 (d, *J* = 2.4 Hz, 1H, CH), 4.00 (d, *J* = 12.0 Hz, 1H, CH), 3.83 (d, *J* = 10.4 Hz, 1H, CH), 3.70 (s, 3H, OCH_3), 3.58 (d, *J* = 12.8 Hz, 1H, CH), 3.32-3.28 (m, 1H, CH), 2.86 (d, *J* = 11.2 Hz, 1H, CH), 2.64-2.60 (m, 1H, CH), 2.43-2.41 (m, 1H, CH), 2.11-2.08 (m, 1H, CH); ^{13}C NMR (100 MHz, DMSO) δ: 205.0, 191.0, 190.8, 175.4, 159.5, 155.6, 141.4, 140.7, 138.2, 136.4, 136.3, 134.7, 134.1, 130.0, 129.7, 129.5, 128.6, 127.5, 124.6, 124.4, 124.2, 123.4, 123.4, 121.2, 115.4, 112.2, 81.4, 62.0, 59.0, 58.0, 55.9, 55.3, 48.3; IR(KBr) υ: 3420, 2786, 2750, 1719, 1670, 1617, 1591, 1453, 1349, 1225, 1148, 1042, 770, 701 cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{38}H_{32}NO_5$([M+H]+): 582.2280, found:582.2326.

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112.212
81.427
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59.043
58.003
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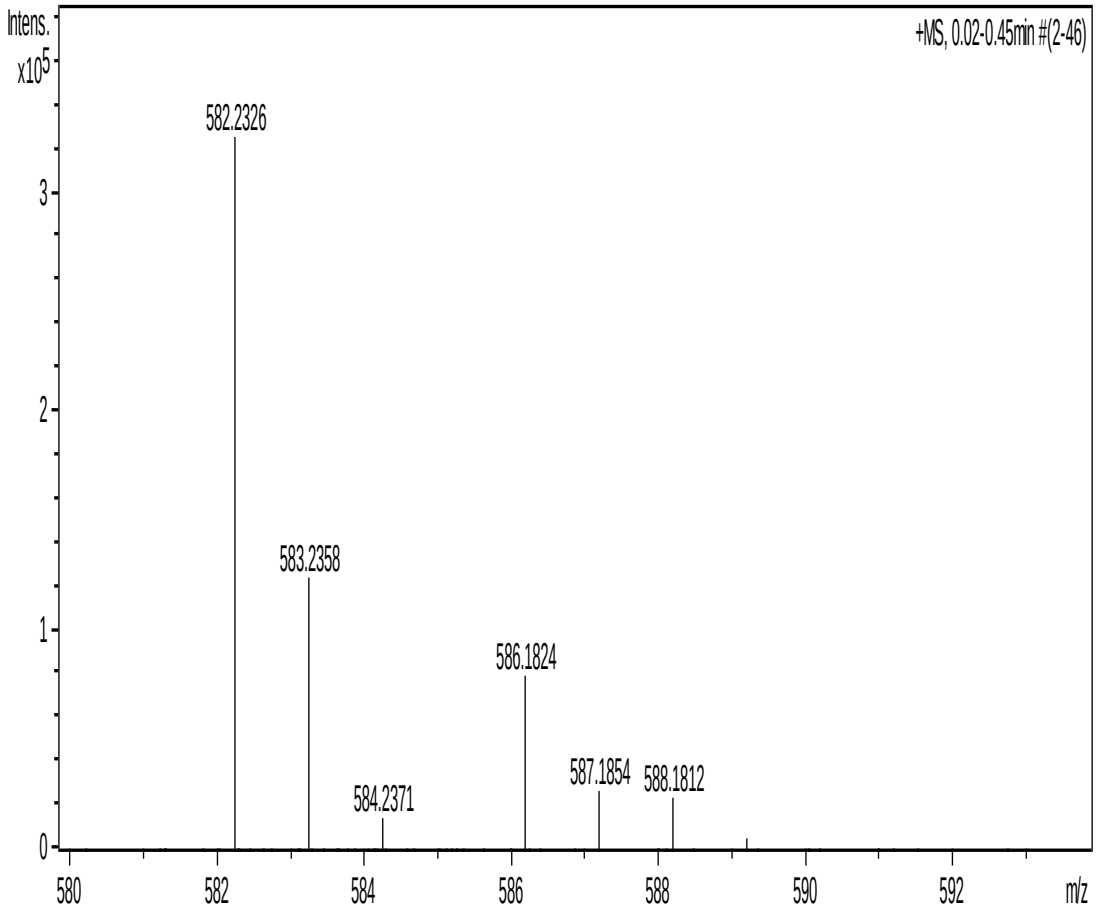
100
50
0
ppm (t1)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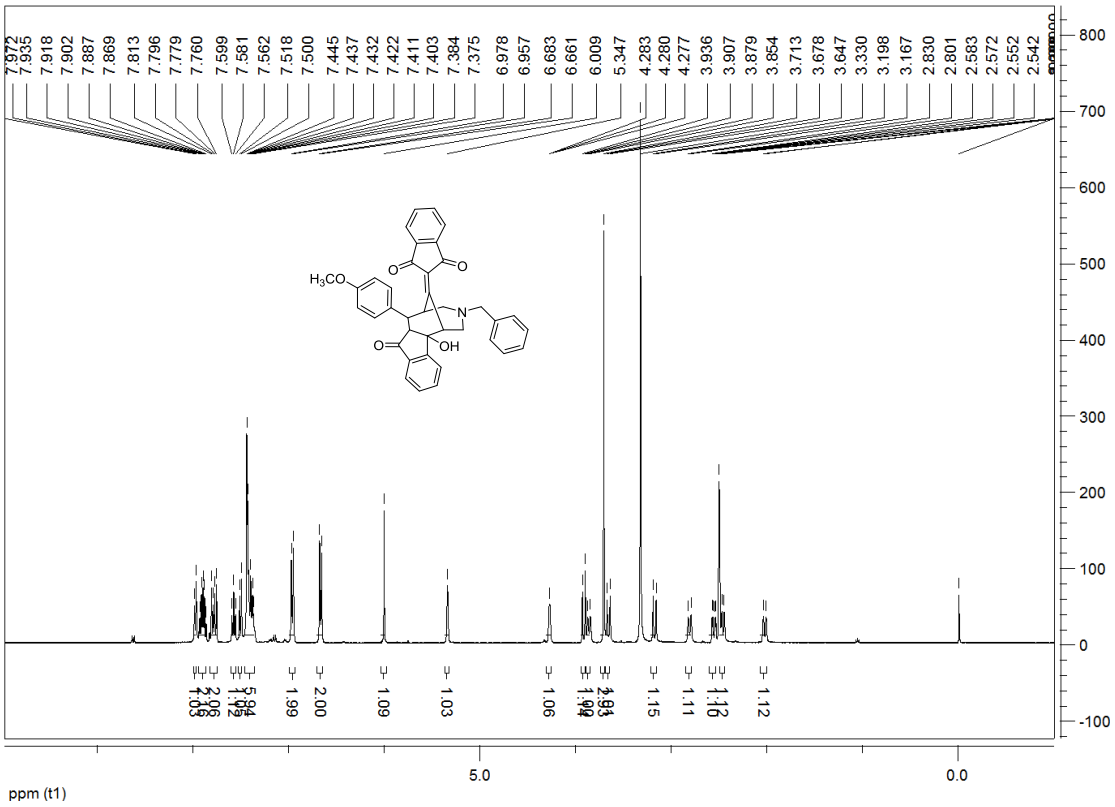
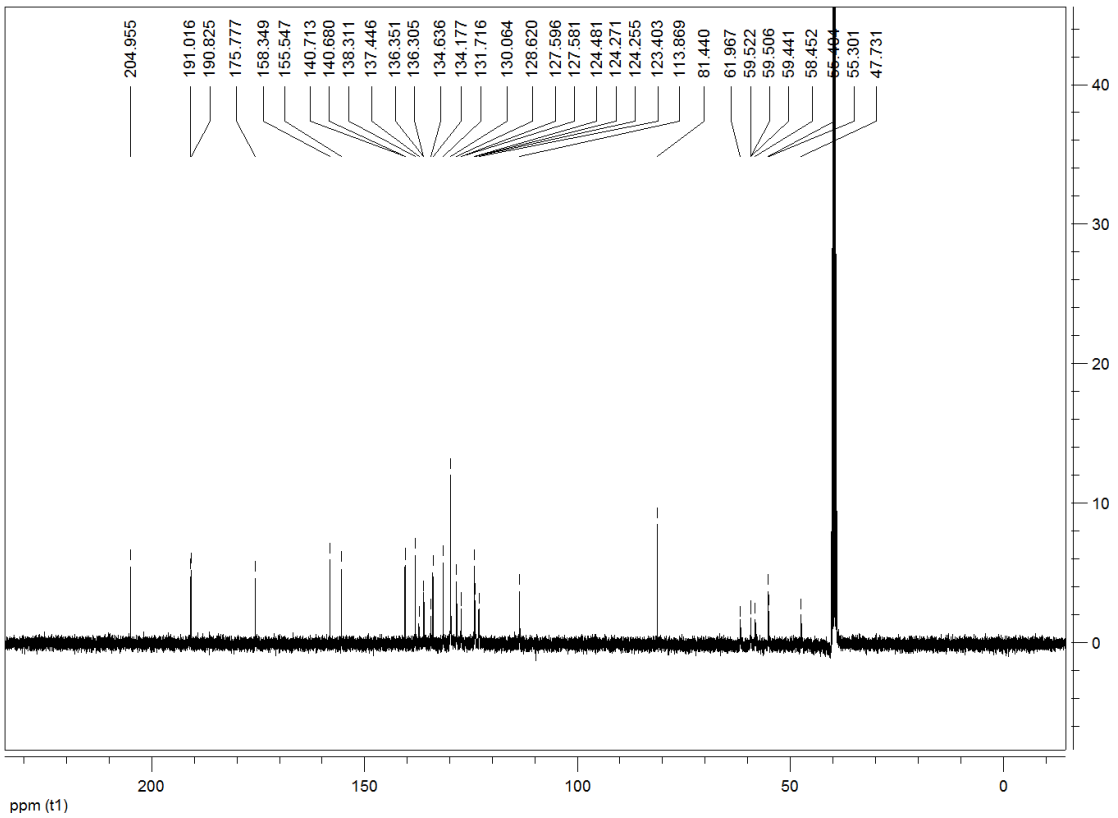
588.1812
3
2
1
0
580
582
584
586
588
590
592
m/z

2-((5S,6aR,11bR)-3-benzyl-11b-hydroxy-6-(4-methoxyphenyl)-7-oxo-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1d): yellow solid, 65%, m.p. 188-190℃; 1H NMR (400 MHz, CDCl3) δ: 7.96-7.94 (m, 1H, ArH), 7.90-7.86 (m, 2H, ArH), 7.80-7.74 (m, 2H, ArH), 7.64 (d, J = 7.6 Hz, 1H, ArH), 7.60-7.56 (m, 1H, ArH), 7.43-7.39 (m, 5H, ArH), 7.37-7.32 (m, 2H, ArH), 7.24-7.21 (m, 1H, ArH), 7.20-7.16 (m, 2H, ArH), 5.50 (s, 1H, CH), 4.59-4.58 (m, 1H, CH), 4.05 (d, J = 12.0 Hz, 1H, CH), 3.76-3.71 (m, 1H, CH), 3.48 (s, 2H, CH), 3.06 (d, J = 12.0 Hz, 1H, CH), 2.81 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H, CH), 2.53 (s, 1H, CH), 2.48 (dd, J_1 = 11.6 Hz, J_2 = 2.0 Hz, 1H, CH), 2.23 (dd, J_1 = 12.0 Hz, J_2 = 3.2 Hz, 1H, CH); 13C NMR (100 MHz, DMSO) δ: 205.0, 191.0, 190.8, 175.8, 158.3, 155.5, 140.7, 140.7, 138.3, 137.4, 136.4, 136.3, 134.6, 134.2, 131.7, 130.1, 128.6, 127.6, 127.6, 124.5, 124.3, 124.3, 123.4, 113.9, 81.4, 62.0, 59.5, 59.5, 59.4, 58.5, 55.4, 55.3, 47.7; IR(KBr) υ: 3404, 3004, 2949, 2870, 2781, 1719, 1670, 1618, 1508, 1456, 1395, 1350, 1252, 1222, 1041, 767, 743 cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for C38H32NO5([M+H]+): 582.2280, found:582.2270.

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124.255
123.403
113.869
81.440
61.967
59.522
59.506
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58.452
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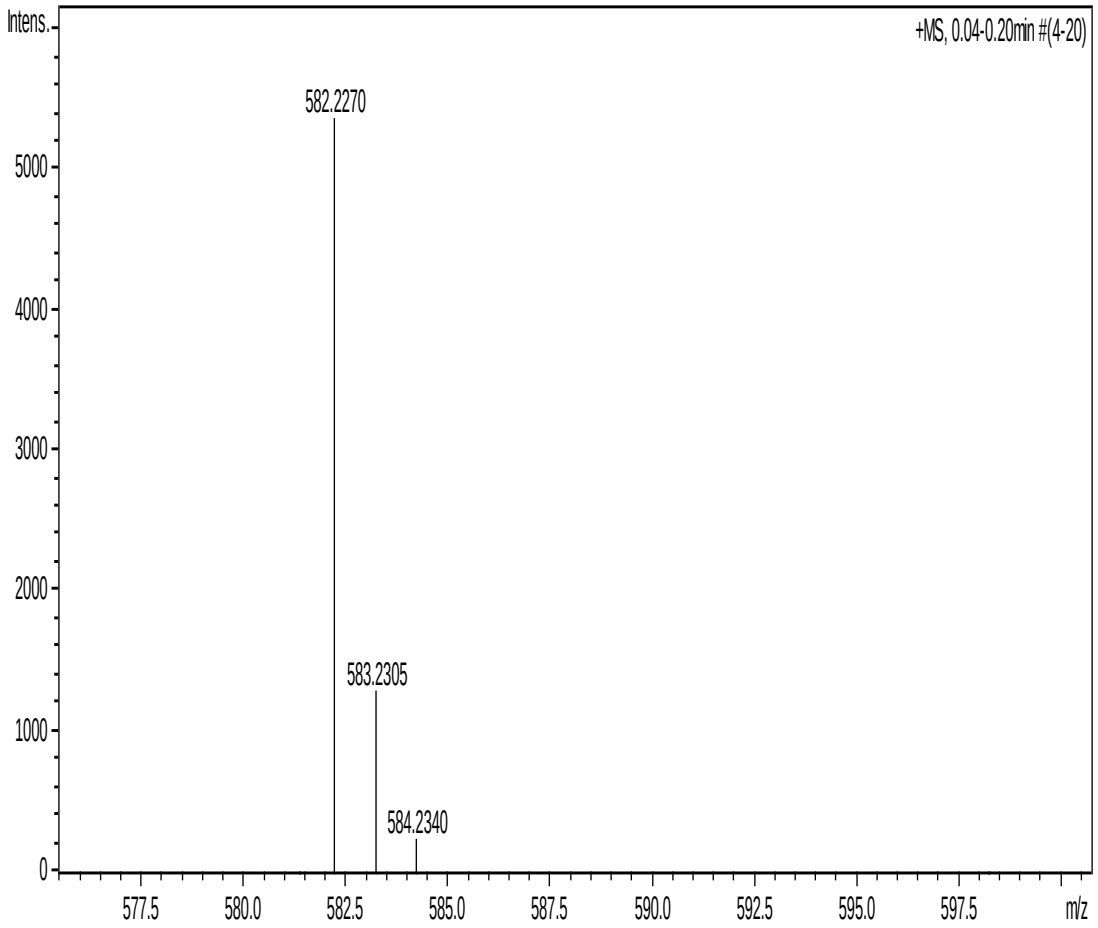
200
150
100
50
0
ppm (t1)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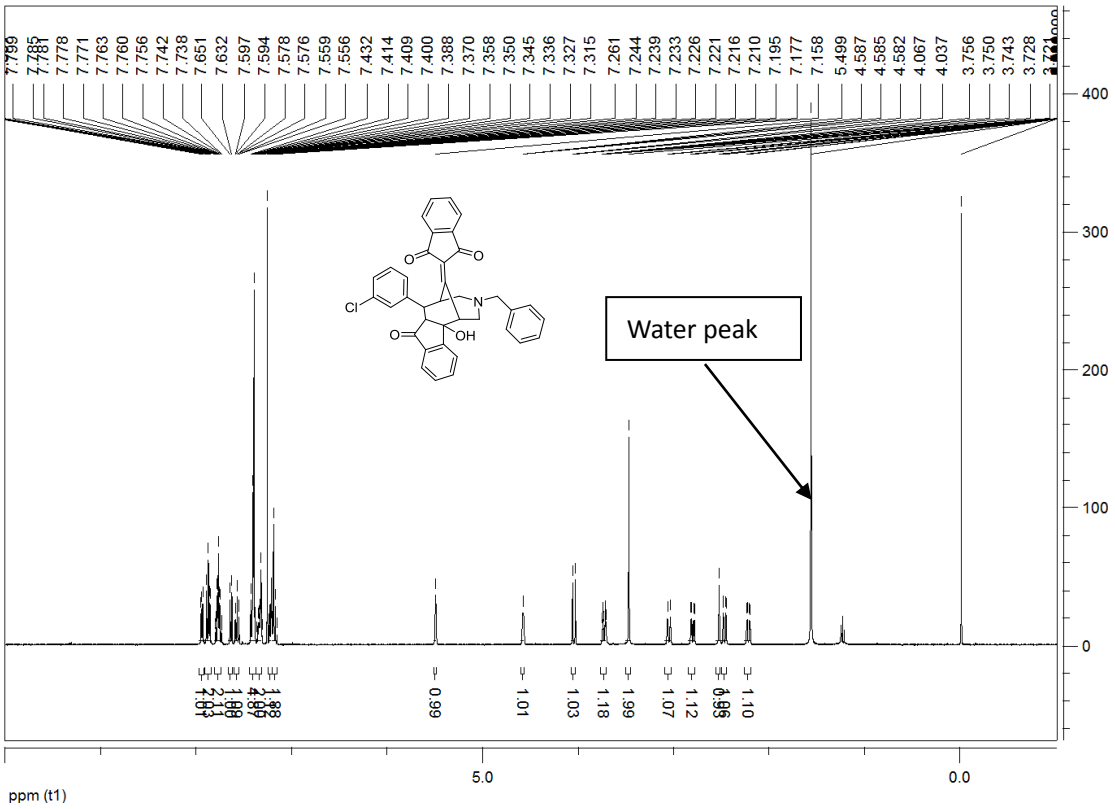
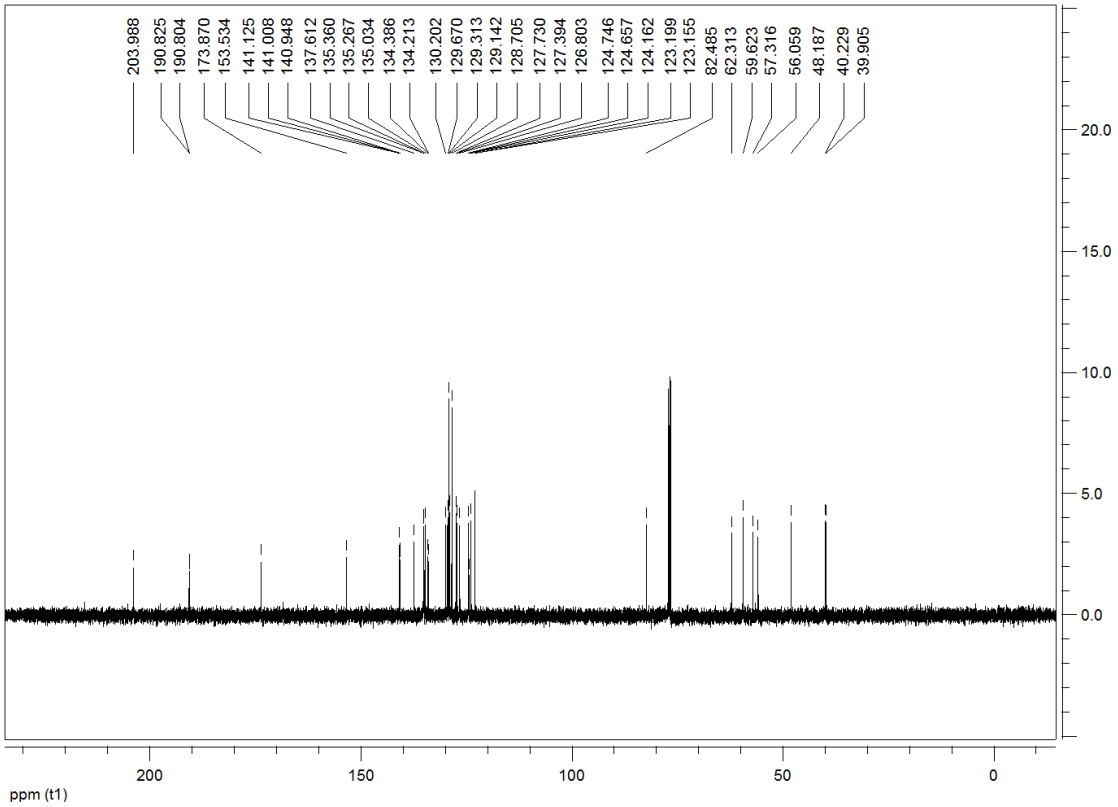
4000
3000
2000
1000
0
577.5
580.0
582.5
585.0
587.5
590.0
592.5
595.0
597.5
m/z

2-((5S,6aR,11bR)-3-benzyl-6-(3-chlorophenyl)-11b-hydroxy-7-oxo-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1e): yellow solid, 71%, m.p. 177-179℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95-7.93 (m, 1H, ArH), 7.89 (d, *J* = 8.0Hz, 1H, ArH), 7.86-7.84 (m, 1H, ArH), 7.79-7.73 (m, 2H, ArH), 7.63 (d, *J* = 7.2 Hz, 1H, ArH), 7.56 (t, *J* = 7.6 Hz, 1H, ArH), 7.42-7.32 (m, 6H, ArH), 7.20 (d, *J* = 8.4 Hz, 2H, ArH), 6.80 (d, *J* = 8.4 Hz, 2H, ArH), 5.50 (s, 1H, CH), 4.54-4.53 (m, 1H, CH), 4.05 (d, *J* = 12.4 Hz, 1H, CH), 3.75-3.71 (m, 1H, CH), 3.47 (s, 2H, CH), 3.12 (d, *J* = 11.6 Hz, 1H, CH), 2.78 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H, CH), 2.50-2.46 (m, 2H, CH), 2.21 (dd, J_1 = 12.0 Hz, J_2 = 3.2 Hz, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 204.0, 190.8, 190.8, 173.9, 153.5, 141.1, 141.0, 140.9, 137.6, 135.3, 135.3, 135.0, 134.4, 134.2, 130.2, 129.7, 129.3, 129.1, 128.7, 127.7, 127.4, 126.8, 124.7, 124.7, 124.2, 123.2, 123.2, 82.5, 62.3, 59.6, 57.3, 56.1, 48.2, 40.2, 39.9; IR(KBr) υ: 3402, 2781, 2752, 1719, 1670, 1619, 1508, 1456, 1351, 1253, 1221, 1042, 767, 743 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{29}ClNO_4$([M+H]$^+$): 586.1785, found: 586.1831.

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153.534
141.125
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134.213
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127.730
127.394
126.803
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124.657
124.162
123.199
123.155
82.485
62.313
59.623
57.316
56.059
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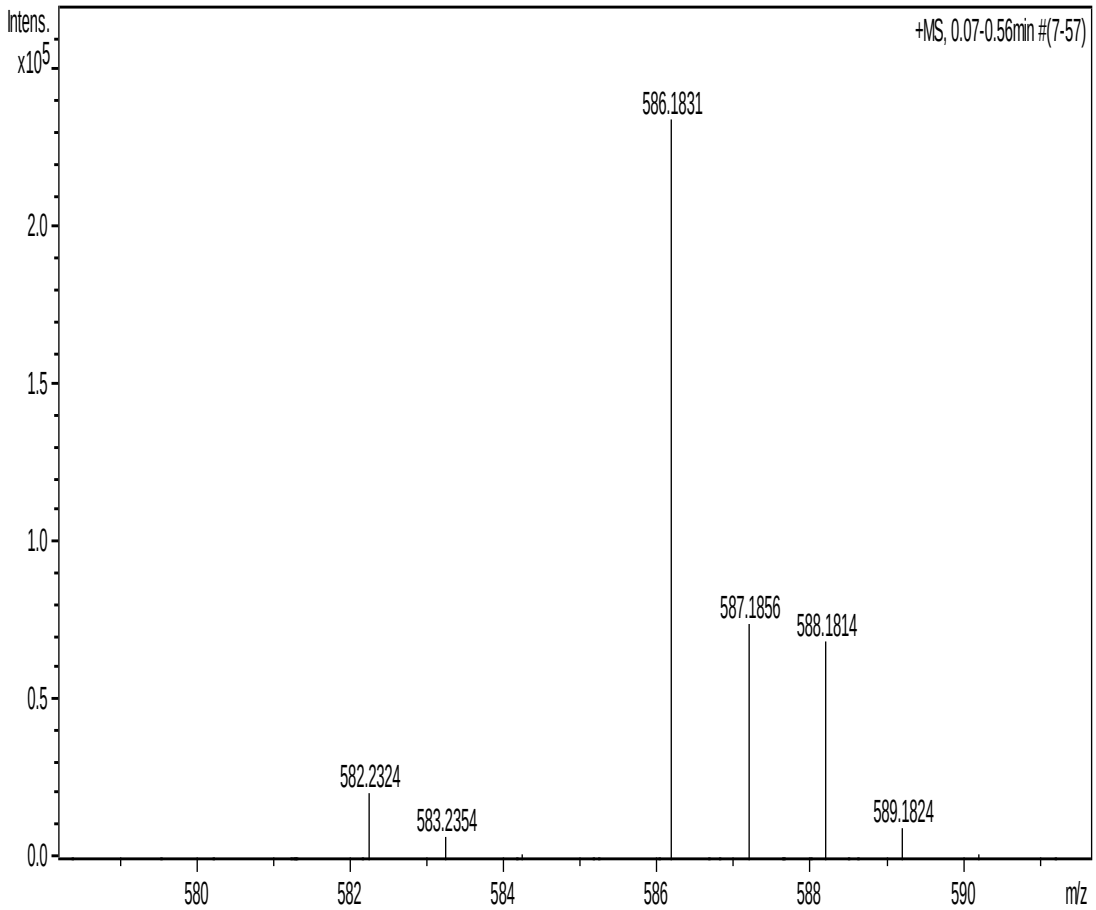
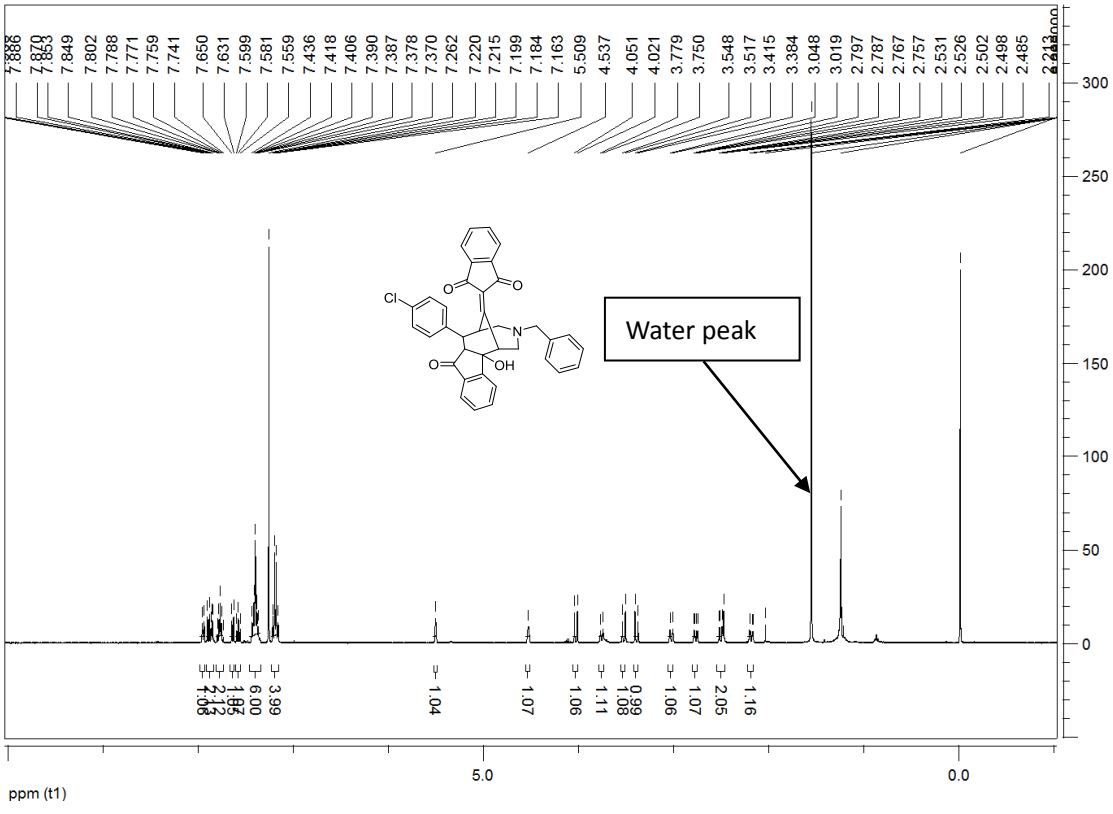
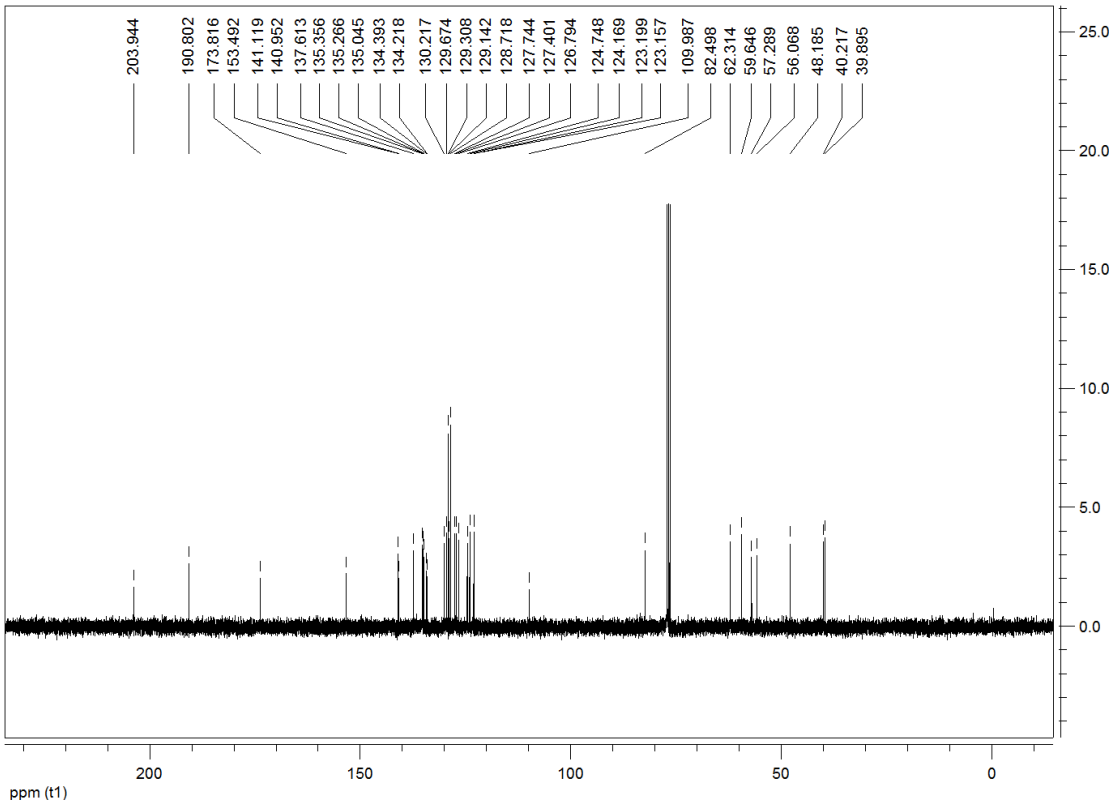
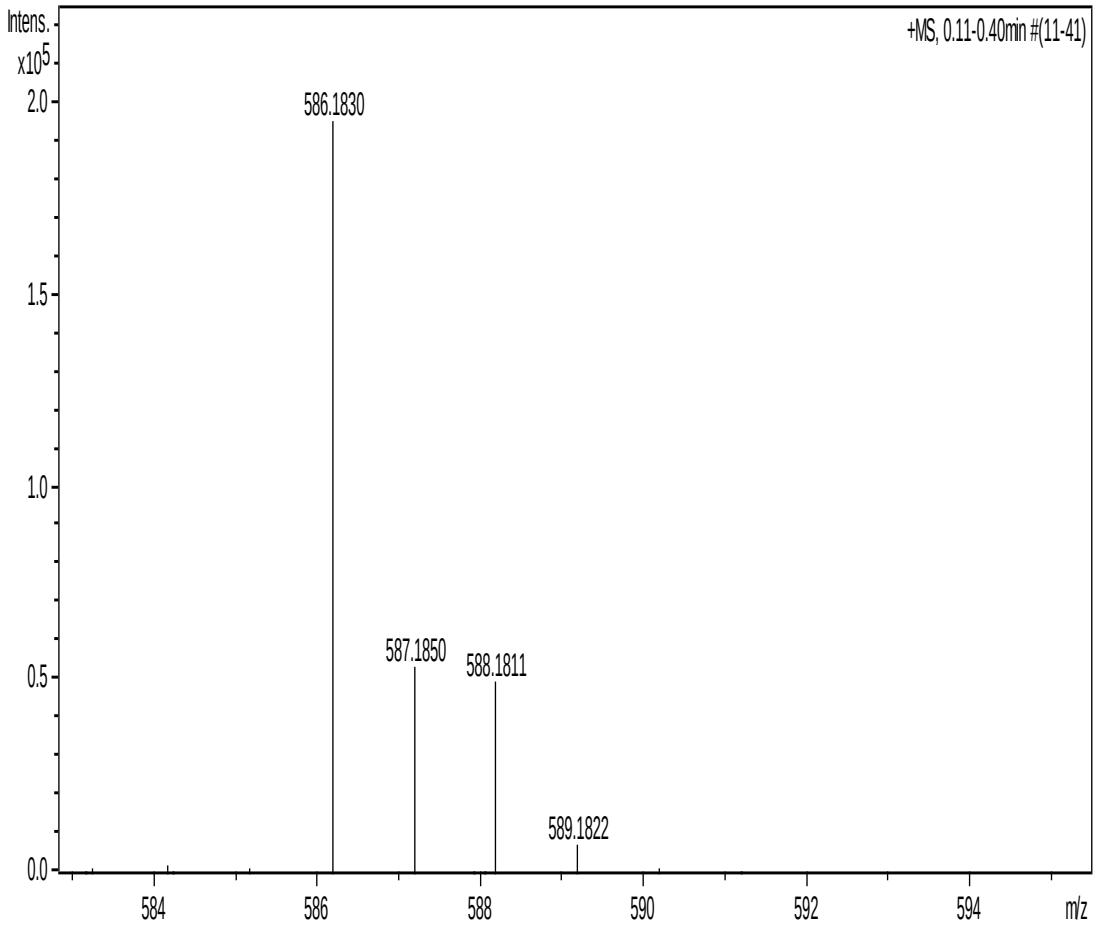
40.229
39.905
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)


Intens.
x10^5
+MS, 0.07-0.56min #(7-57)
586.1831
587.1856
588.1814
582.2324
583.2354
589.1824
2.0
1.5
1.0
0.5
0.0
580
582
584
586
588
590
m/z

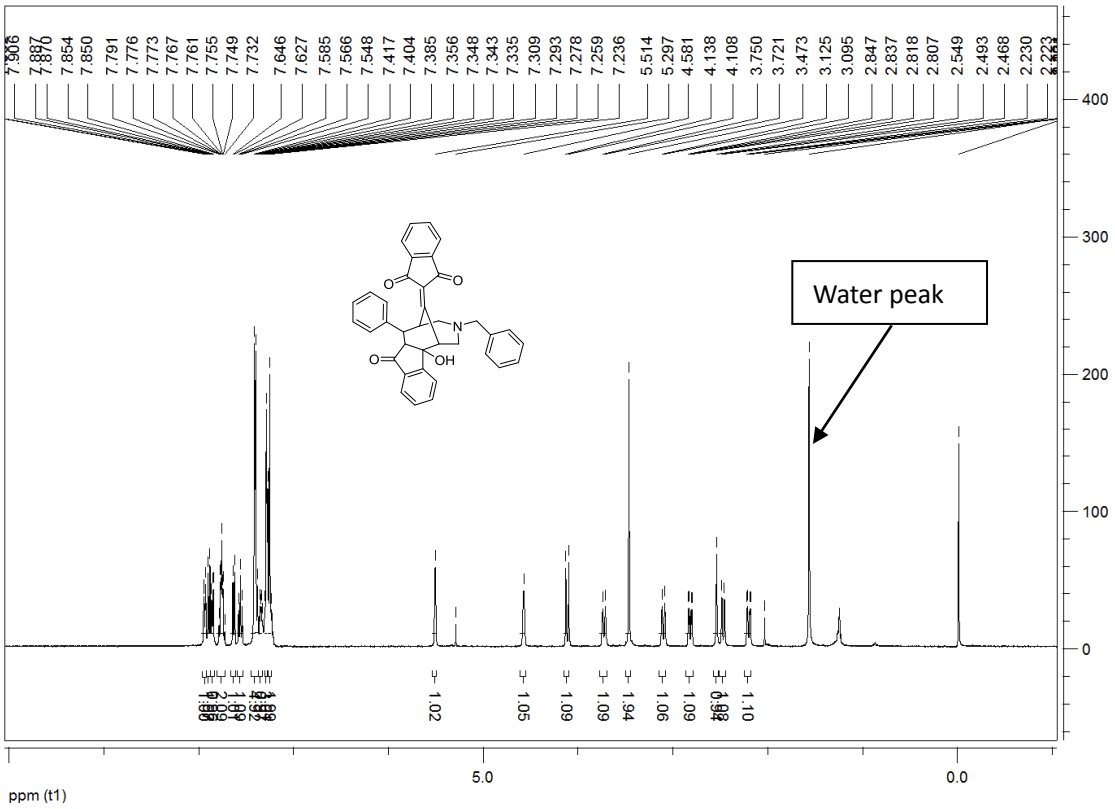
2-((5S,6aR,11bR)-3-benzyl-6-(4-chlorophenyl)-11b-hydroxy-7-oxo-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1f): yellow solid, 72%, m.p. 179-181℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96-7.94 (m, 1H, ArH), 7.90-7.85 (m, 2H, ArH), 7.80-7.74 (m, 2H, ArH), 7.64 (d, *J* = 7.6 Hz, 1H, ArH), 7.60-7.56 (m, 1H, ArH), 7.44-7.37 (m, 6H, ArH), 7.22-7.16 (m, 4H, ArH), 5.51 (s, 1H, CH), 4.54 (s, 1H, CH), 4.04(d, *J* = 12.0 Hz, 1H, CH), 3.76 (d, *J* = 11.6 Hz, 1H, CH), 3.53 (d, *J* = 12.4 Hz, 1H, CH), 3.40 (d, *J* = 12.4Hz, 1H, CH), 3.03 (d, *J* = 11.6 Hz, 1H, CH), 2.80-2.76 (m, 1H, CH), 2.53-2.48 (m, 2H, CH), 2.21-2.18 (m, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 203.9, 190.8, 173.8, 153.5, 141.1, 141.0, 137.6, 135.4, 135.3, 135.0, 134.4, 134.2, 130.2, 12.7, 129.3, 129.1, 128.7, 127.7, 127.4, 126.8, 124.7, 124.2, 123.2, 123.2, 110.0, 82.5, 62.3, 59.6, 57.3, 56.1, 48.2, 40.2, 39.9; IR(KBr) υ: 3383, 2919, 2854, 2786, 2753, 1722, 1668, 1624, 1591, 1351, 1228, 747, 701 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{29}ClNO_4$([M+H]$^+$): 586.1785, found: 586.1830.

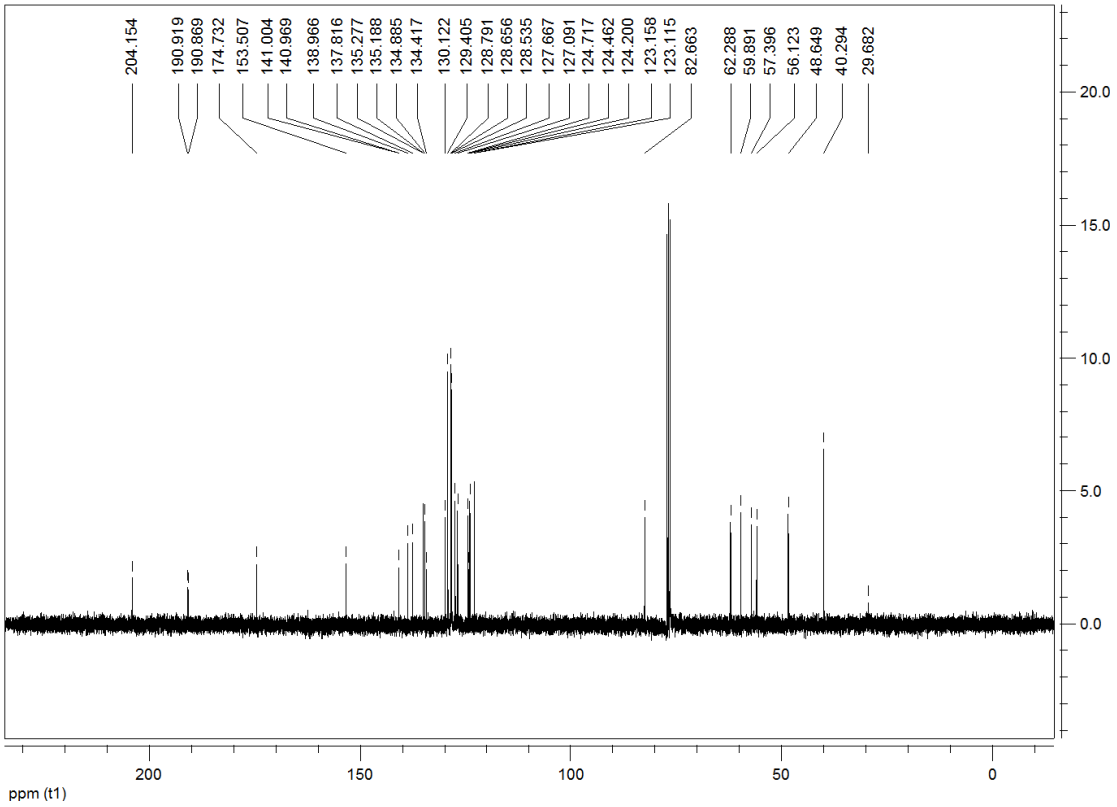


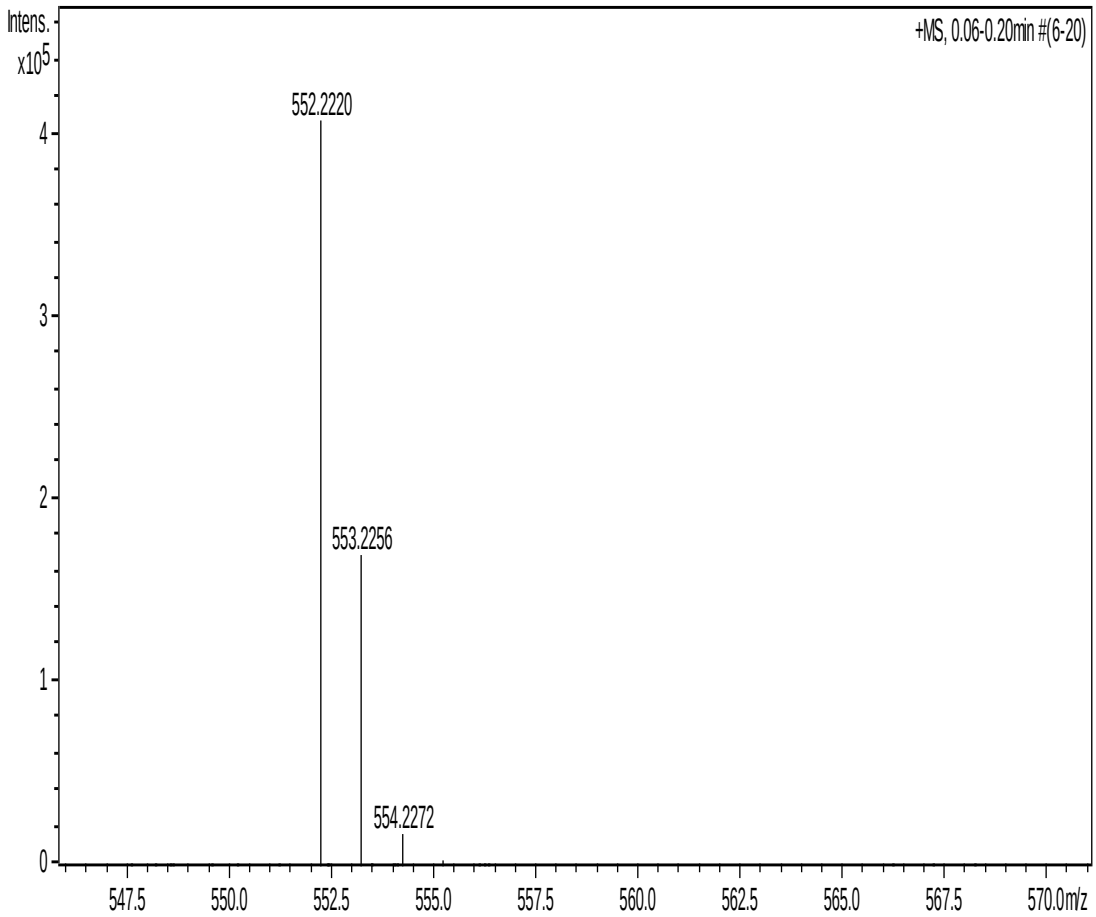

203.944
190.802
173.816
153.492
141.119
140.952
137.613
135.356
135.266
135.045
134.393
134.218
130.217
129.674
129.308
129.142
128.718
127.744
127.401
126.794
124.748
124.169
123.199
123.157
109.987
82.498
62.314
59.646
57.289
56.068
48.185
40.217
39.895
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)


Intens.
x10^5
+MS, 0.11-0.40min #(11-41)
2.0
1.5
1.0
0.5
0.0
586.1830
587.1850
588.1811
589.1822
584
586
588
590
592
594
m/z

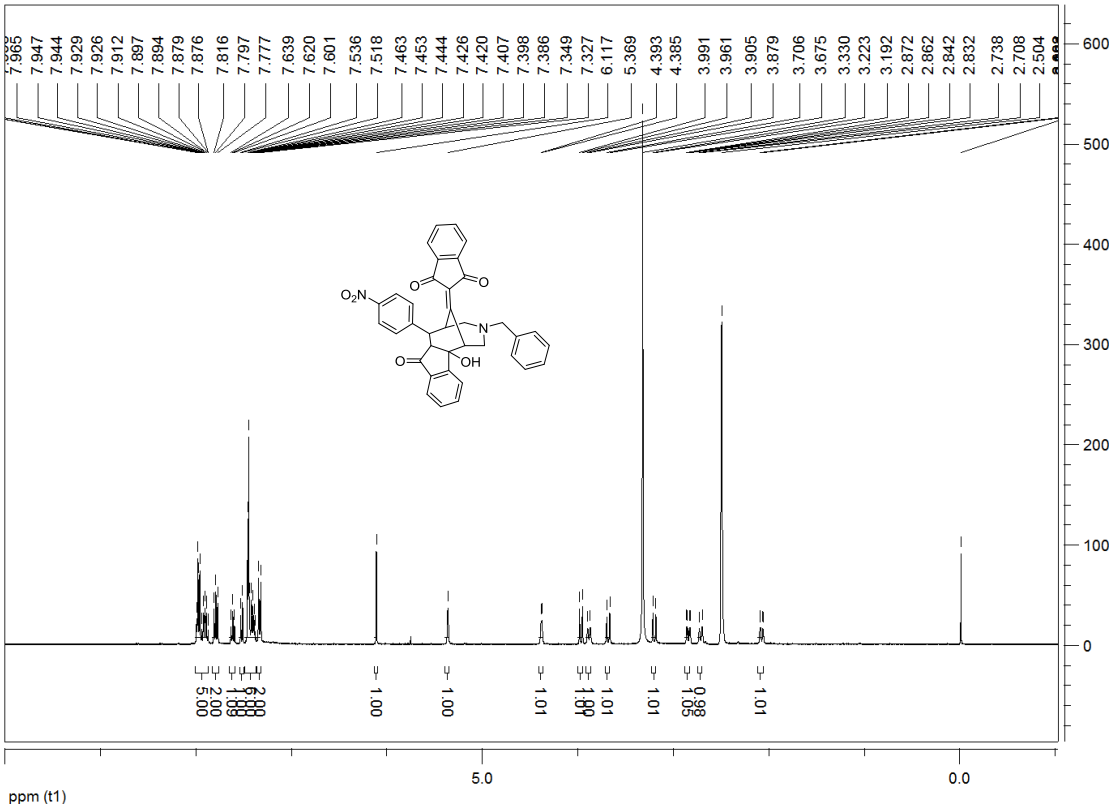
2-((5S,6aR,11bR)-3-benzyl-11b-hydroxy-7-oxo-6-phenyl-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1g): yellow solid, 68%, m.p. 183-185℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.95-7.93 (m, 1H, ArH), 7.90 (d, *J* = 7.6 Hz, 1H, ArH), 7.87-7.85 (m, 1H, ArH), 7.79-7.73 (m, 2H, ArH), 7.64 (d, *J* = 7.6 Hz, 1H, ArH), 7.60 (t, *J* = 7.2 Hz, 1H, ArH), 7.42-7.38 (m, 5H, ArH), 7.36-7.34 (m, 1H, ArH), 7.31-7.28 (m, 3H, ArH), 7.25 (d, *J* = 9.2 Hz, 2H, ArH), 5.51 (s, 1H, CH), 4.58 (s, 1H, CH), 4.12 (d, *J* = 12.0 Hz, 1H, CH), 3.74 (d, *J* = 11.6 Hz, 1H, CH), 3.47 (s, 2H, CH), 3.11 (d, *J* = 12.0 Hz, 1H, C), 2.83 (dd, J_1 = 11.6 Hz, J_2 = 4.0 Hz, 1H, CH), 2.55 (s, 1H, CH), 2.48 (d, *J* = 10.0 Hz, 1H, CH), 2.21 (dd, J_1 = 11.6 Hz, J_2 = 2.8 Hz, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.2, 190.9, 190.9, 174.7, 153.5, 141.0, 141.0, 139.0, 137.8, 135.3, 135.2, 134.9, 134.4, 130.1, 129.4, 12.8, 128.7, 128.5, 127.7, 127.1, 124.7, 124.5, 124.2, 123.2, 123.1, 82.7, 62.3, 59.9, 57.4, 56.1, 48.6, 40.3, 29.7; IR(KBr) υ: 3408, 2790, 2752, 1720, 1671, 1622, 1457, 1352, 1227, 1146, 1043, 767, 700 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{30}NO_4$([M+H]$^+$): 552.2175, found: 552.2220.

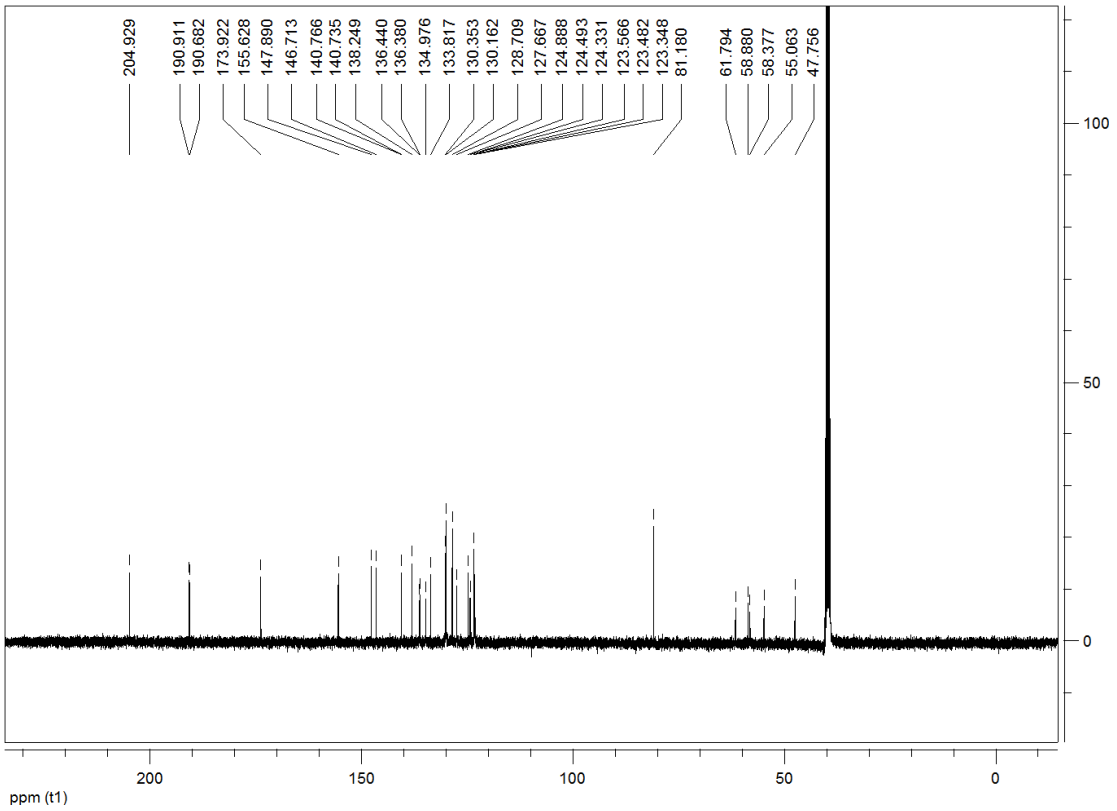


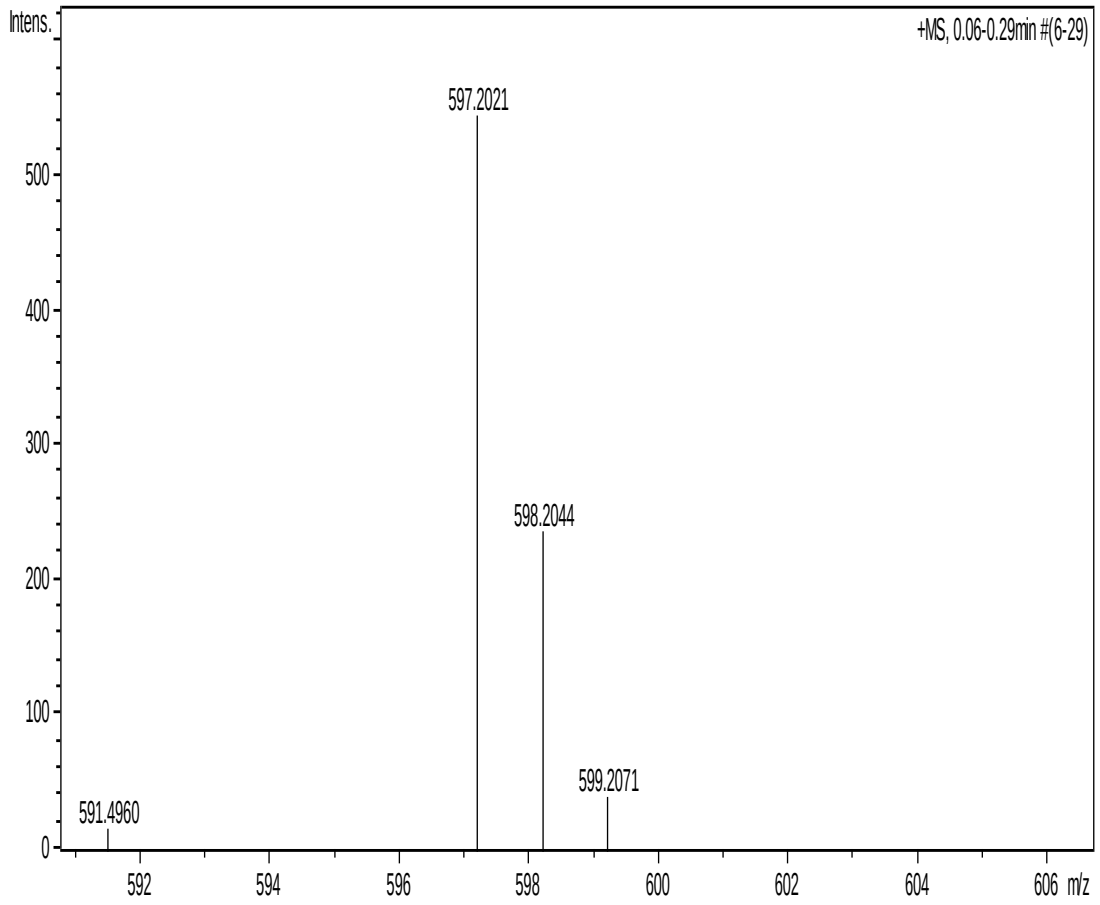

204.154
190.919
190.869
174.732
153.507
141.004
140.969
138.966
137.816
135.277
135.188
134.885
134.417
130.122
129.405
128.791
128.656
128.535
127.667
127.091
124.717
124.462
124.200
123.158
123.115
82.663
62.288
59.891
57.396
56.123
48.649
40.294
29.682
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)


Intens.
x10^5
+MS, 0.06-0.20min #(6-20)
552.2220
553.2256
554.2272
4
3
2
1
0
547.5
550.0
552.5
555.0
557.5
560.0
562.5
565.0
567.5
570.0m/z

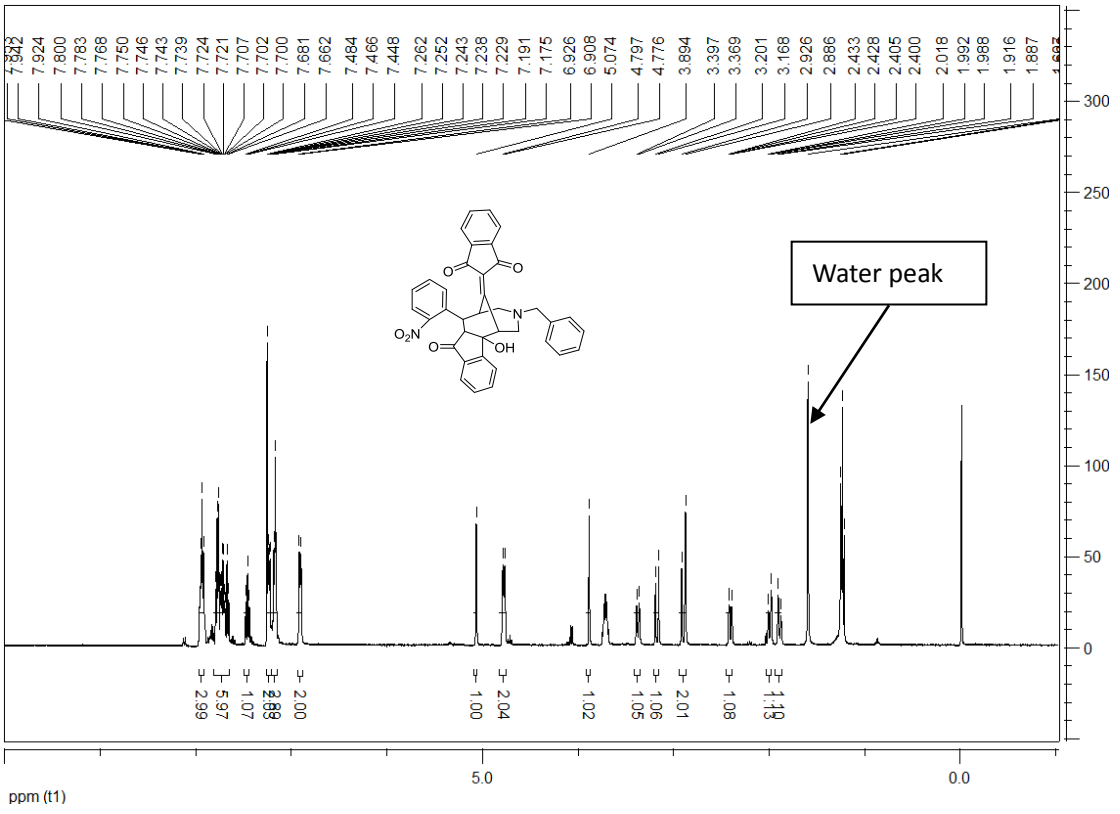
2-((5S,6aR,11bR)-3-benzyl-11b-hydroxy-6-(4-nitrophenyl)-7-oxo-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1h): yellow solid, 72%, m.p. 198-200℃; ^{1}H NMR (400 MHz, DMSO) δ: 8.00-7.88 (m, 5H, ArH), 7.82-7.78 (m, 2H, ArH), 7.62 (t, *J* = 7.6 Hz, 1H, ArH), 7.53 (d, *J* = 7.2 Hz, 1H, ArH), 7.46-7.39 (m, 6H, ArH), 7.34 (d, *J* = 8.8 Hz, 2H, ArH), 6.12 (s, 1H, CH), 5.37 (s, 1H, CH), 4.39 (d, *J* = 3.2 Hz, 1H, CH), 3.98 (d, *J* = 12.0 Hz, 1H, CH), 3.89 (d, *J* = 10.4 Hz, 1H, CH), 3.89 (d, *J* = 10.4 Hz, 1H, CH), 3.69 (d, *J* = 12.4 Hz, 1H, CH), 3.21 (d, *J* = 12.4 Hz, 1H, CH), 2.85 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H, CH), 2.72 (d, *J* = 12.0 Hz, 1H, CH), 2.09 (dd, J_1 = 11.6 Hz, J_2 = 2.0 Hz, 1H, CH); ^{13}C NMR (100 MHz, DMSO) δ: 204.9, 190.9, 190.7, 173.9, 155.6, 147.9, 146.7, 140.8, 140.7, 138.2, 136.4, 136.4, 135.0, 133.8, 130.4, 130.2, 128.7, 127.7, 124.9, 124.5, 124.3, 123.6, 123.5, 123.3, 81.2, 61.8, 58.9, 58.4, 55.1, 47.8; IR(KBr) υ: 3409, 2805, 1717, 1674, 1595, 1517, 1397, 1339, 1220, 1045, 742, 700 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{29}N_2O_6$([M+H]$^+$): 597.2026, found: 597.2021.

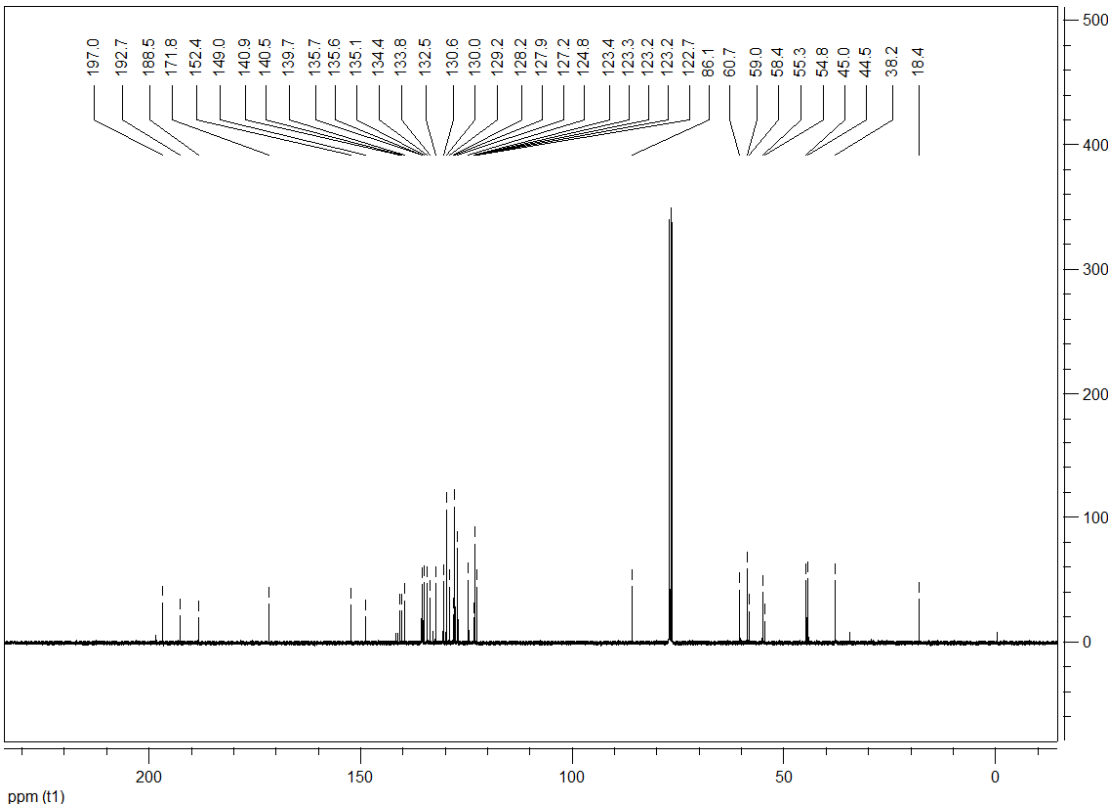


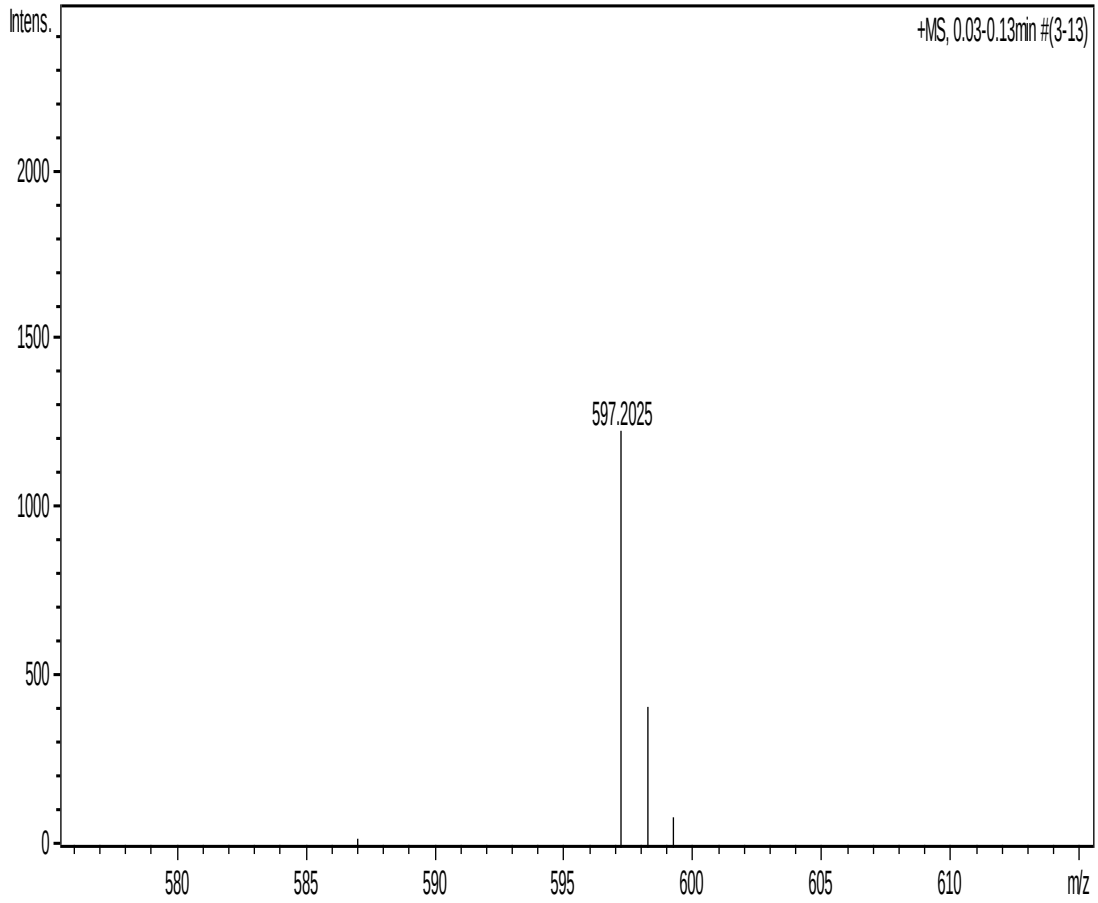

204.929
190.911
190.682
173.922
155.628
147.890
146.713
140.766
140.735
138.249
136.440
136.380
134.976
133.817
130.353
130.162
128.709
127.667
124.888
124.493
124.331
123.566
123.482
123.348
81.180
61.794
58.880
58.377
55.063
47.756
100
50
0
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.06-0.29min #(6-29)
597.2021
598.2044
599.2071
591.4960
500
400
300
200
100
0
592
594
596
598
600
602
604
606 m/z

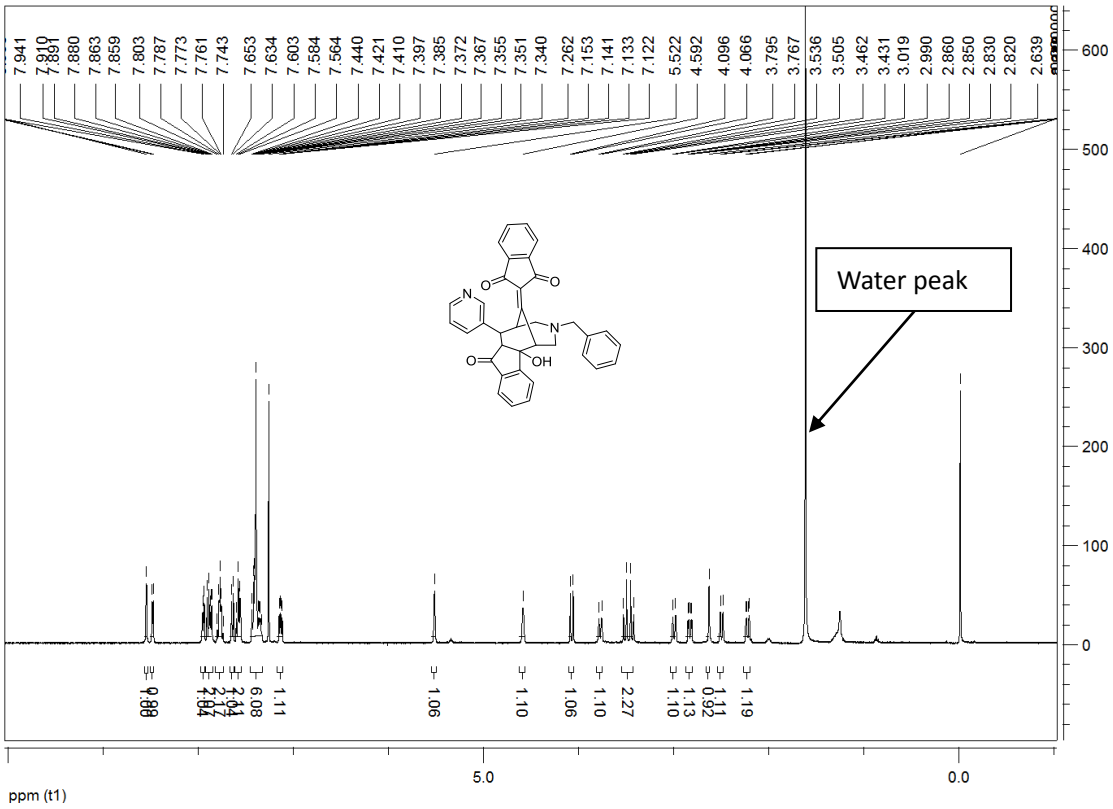
2-((5S,6aR,11bR)-3-benzyl-11b-hydroxy-6-(2-nitrophenyl)-7-oxo-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1i): white solid, 70%, m.p. 219-221℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97-7.92 (m, 3H, ArH), 7.80-7.66 (m, 6H, ArH), 7.47 (t, *J* = 7.2 Hz, 1H, ArH), 7.26-7.23 (m, 2H, ArH), 6.92 (d, *J* = 7.2 Hz, 2H, ArH), 5.08 (s, 1H, CH), 4.79 (d, *J* = 8.4 Hz, 2H, CH), 3.90 (s, 1H, CH), 3.38 (d, *J* = 11.2 Hz, 1H, CH), 3.18 (d, *J* = 13.2 Hz, 1H, CH), 2.91 (d, *J* = 16.0 Hz, 2H, CH), 2.42 (dd, J_1 = 11.2 Hz, J_2 = 2.0 Hz, 1H, CH), 2.00 (d, *J* = 10.4 Hz, 1H, CH), 1.90 (d, *J* = 11.6 Hz, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 197.0, 192.7, 188.5, 171.8, 152.4, 149.0, 140.9, 140.5, 139.7, 135.7, 135.6, 135.1, 134.4, 133.8, 132.5, 130.6, 130.0, 129.2, 128.2, 127.9, 127.2, 124.8, 123.4, 123.3, 123.2, 123.2, 122.7, 86.1, 60.7, 59.0, 58.4, 55.3, 54.8, 45.0, 44.5, 38.2, 18.4,; IR(KBr) υ: 3348, 2807, 1717, 1680, 1623, 1520, 1350, 1233, 739 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{36}H_{29}N_2O_4$([M+H]$^+$): 597.2026, found:597.2025.

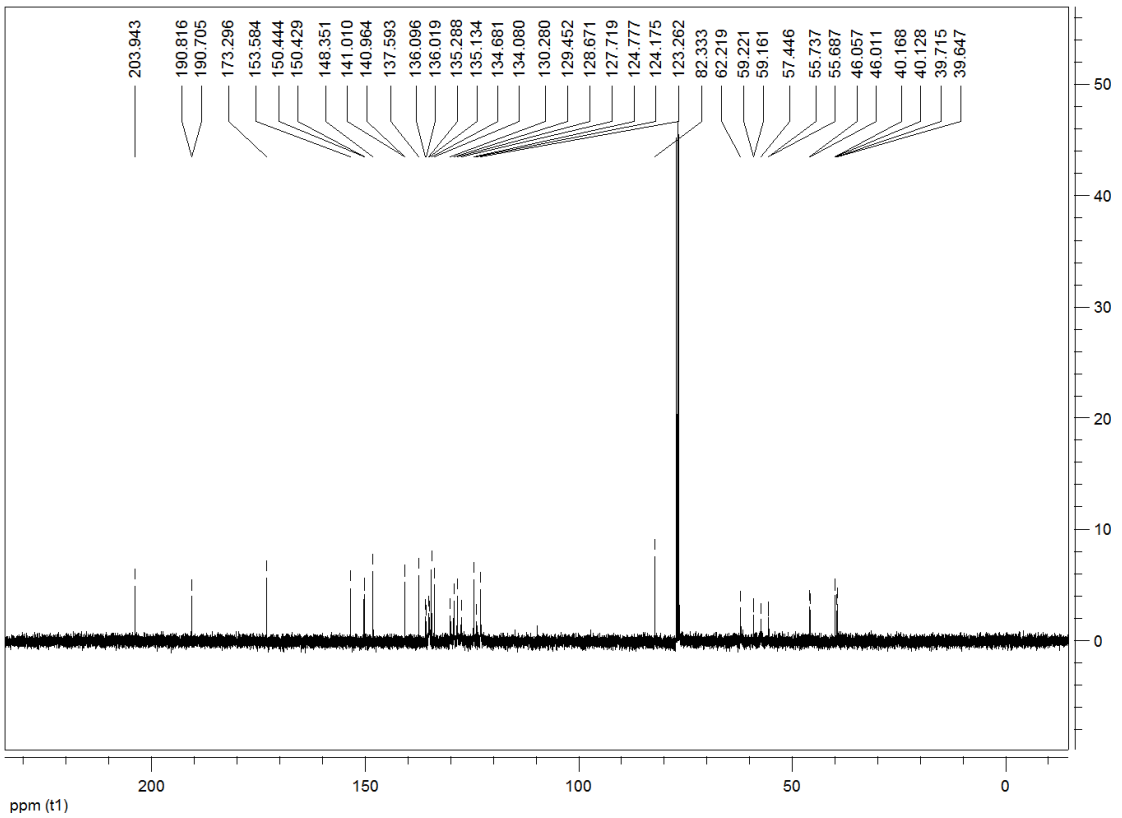


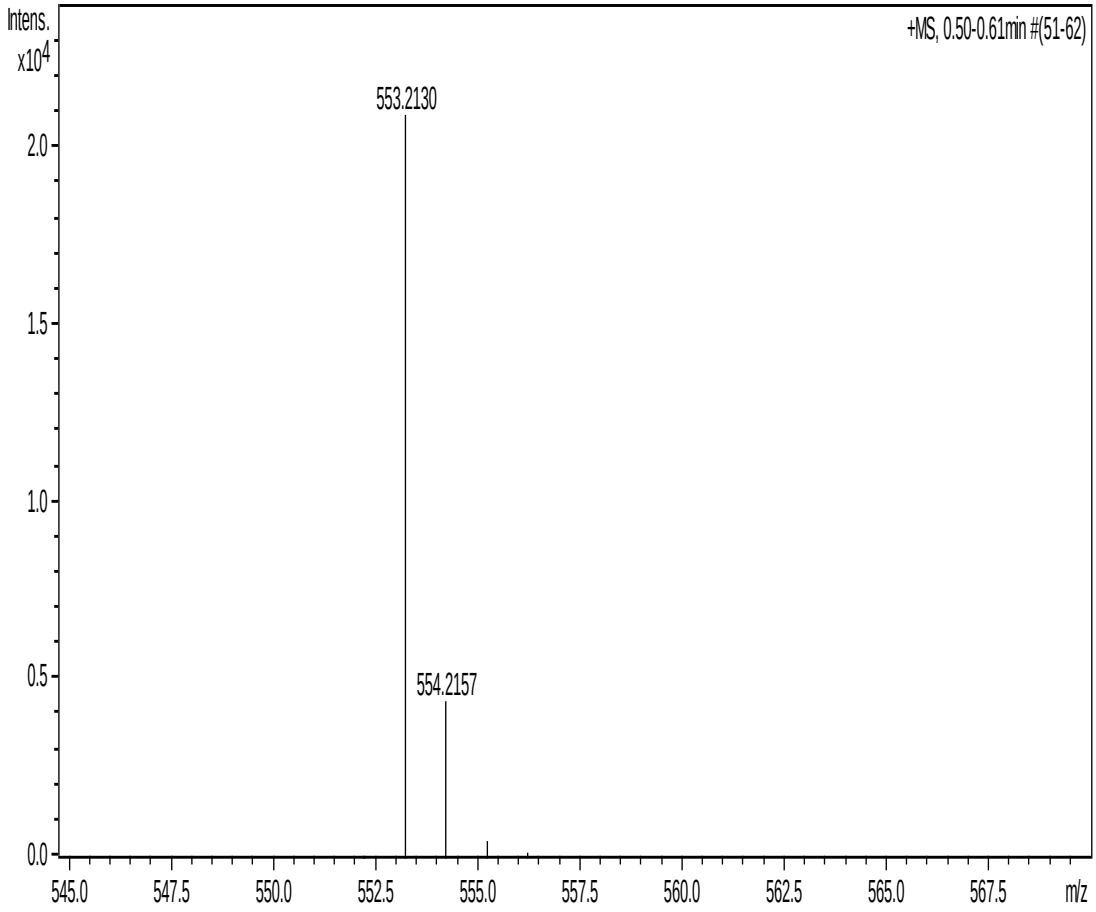

197.0
192.7
188.5
171.8
152.4
149.0
140.9
140.5
139.7
135.7
135.6
135.1
134.4
133.8
132.5
130.6
130.0
129.2
128.2
127.9
127.2
124.8
123.4
123.3
123.2
123.2
122.7
86.1
60.7
59.0
58.4
55.3
54.8
45.0
44.5
38.2
18.4
500
400
300
200
100
0
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.03-0.13min #(3-13)
2000
1500
1000
500
0
597.2025
580
585
590
595
600
605
610
m/z

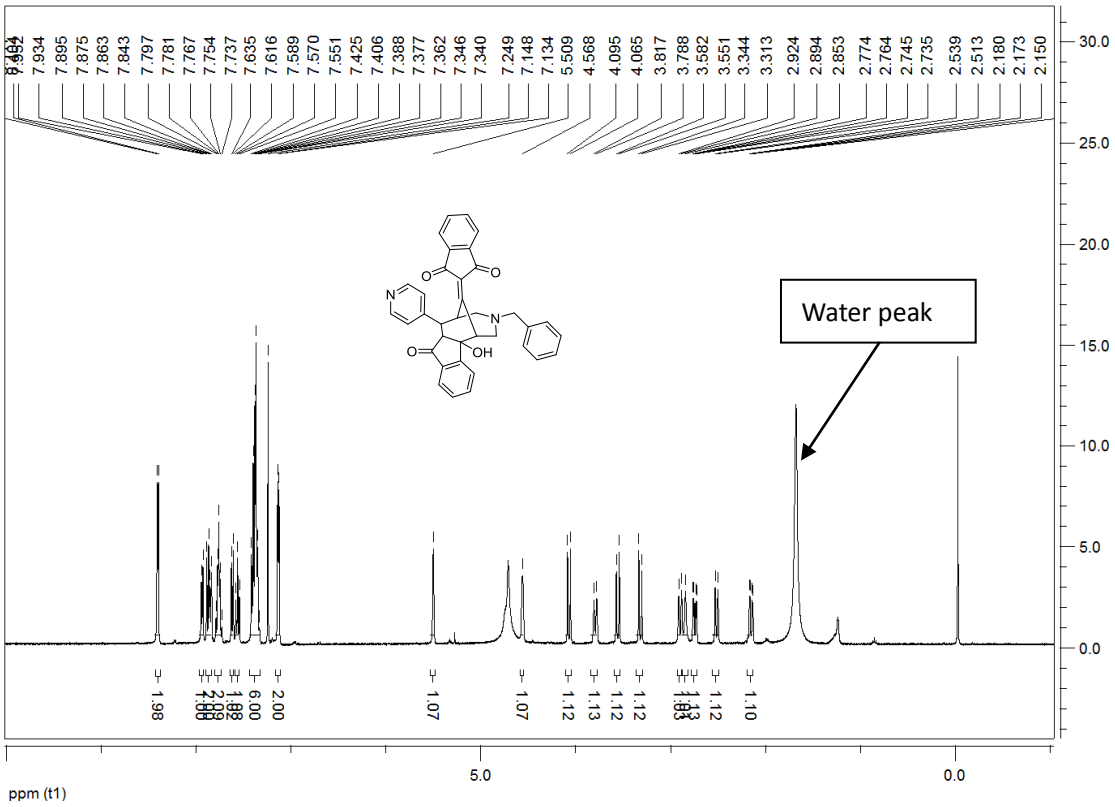
2-((5S,6aR,11bR)-3-benzyl-11b-hydroxy-7-oxo-6-(pyridin-3-yl)-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1j): yellow solid, 66%, m.p. 179-181℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (s, 1H, ArH), 8.48 (d, *J* = 4.8 Hz, 1H, ArH), 7.96-7.94 (m, 1H, ArH), 7.91-7.86 (m, 2H, ArH), 7.80-7.74 (m, 2H, ArH), 7.64 (d, *J* = 7.6 Hz, 1H, ArH), 7.58 (t,*J* = 8.0 Hz, 2H, ArH), 7.44-7.34 (m, 6H, ArH), 7.14 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 1H, ArH), 5.52 (s, 1H, CH), 4.60 (s, 1H, CH), 4.08 (d, *J* = 12.0 Hz, 1H, CH), 3.78 (d, *J* = 11.2 Hz, 1H, CH), 3.54-3.43 (m, 2H, CH), 3.01 (d, *J* = 11.6 Hz, 1H, CH), 2.84 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H, CH), 2.64 (s, 1H, CH), 2.51 (d, *J* = 10.0 Hz, 1H, CH), 2.23 (dd, J_1 = 12.0 Hz, J_2 = 2.4 Hz, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 203.9, 190.8, 190.7, 173.3, 153.6, 150.4, 150.4, 148.4, 141.0, 141.0, 137.6, 136.1, 136.0, 135.3, 135.1, 134.7, 134.1, 130.3, 129.5, 128.7, 127.7, 124.8, 124.2, 123.3, 82.3, 62.2, 59.2, 59.2, 57.4, 55.7, 55.7, 46.1, 46.0, 40.2, 40.1, 39.7, 39.6; IR(KBr) υ: 3416, 2791, 2755, 1723, 1673, 1625, 1587, 1224, 802, 774 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{36}H_{29}N_2O_4$([M+H]$^+$): 553.2127, found:553.2130.

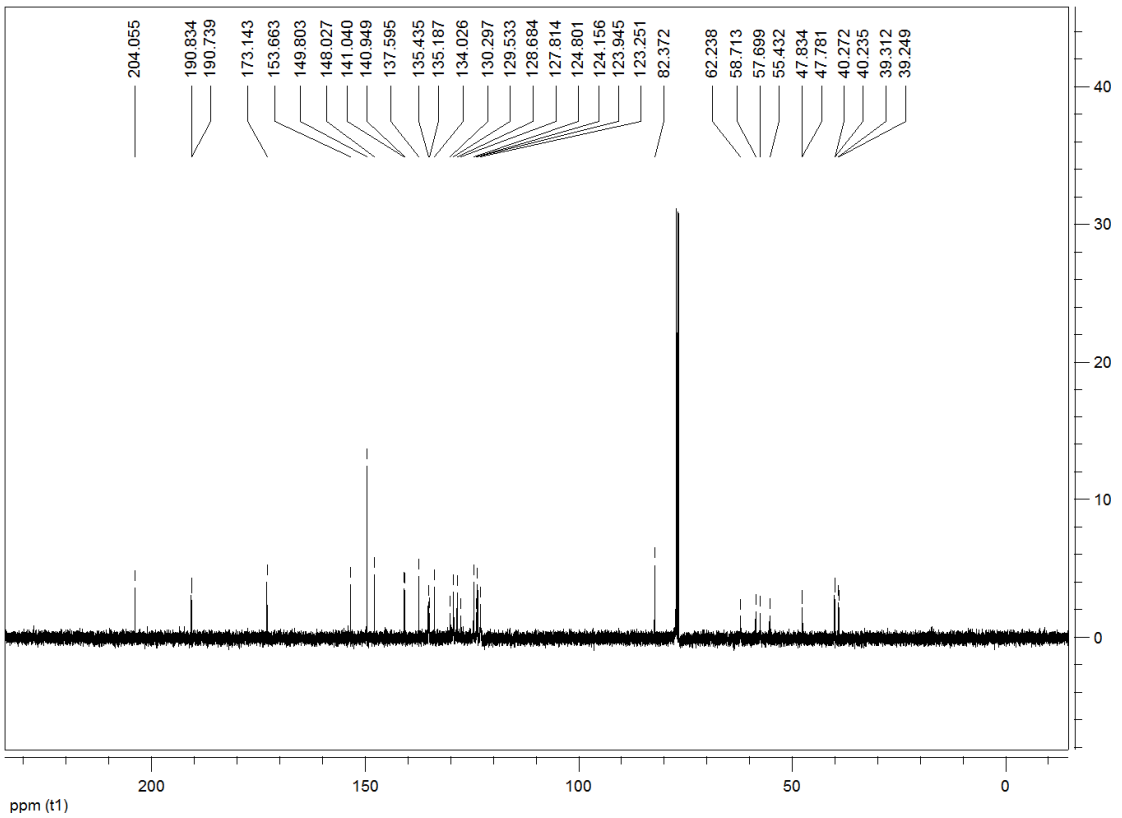


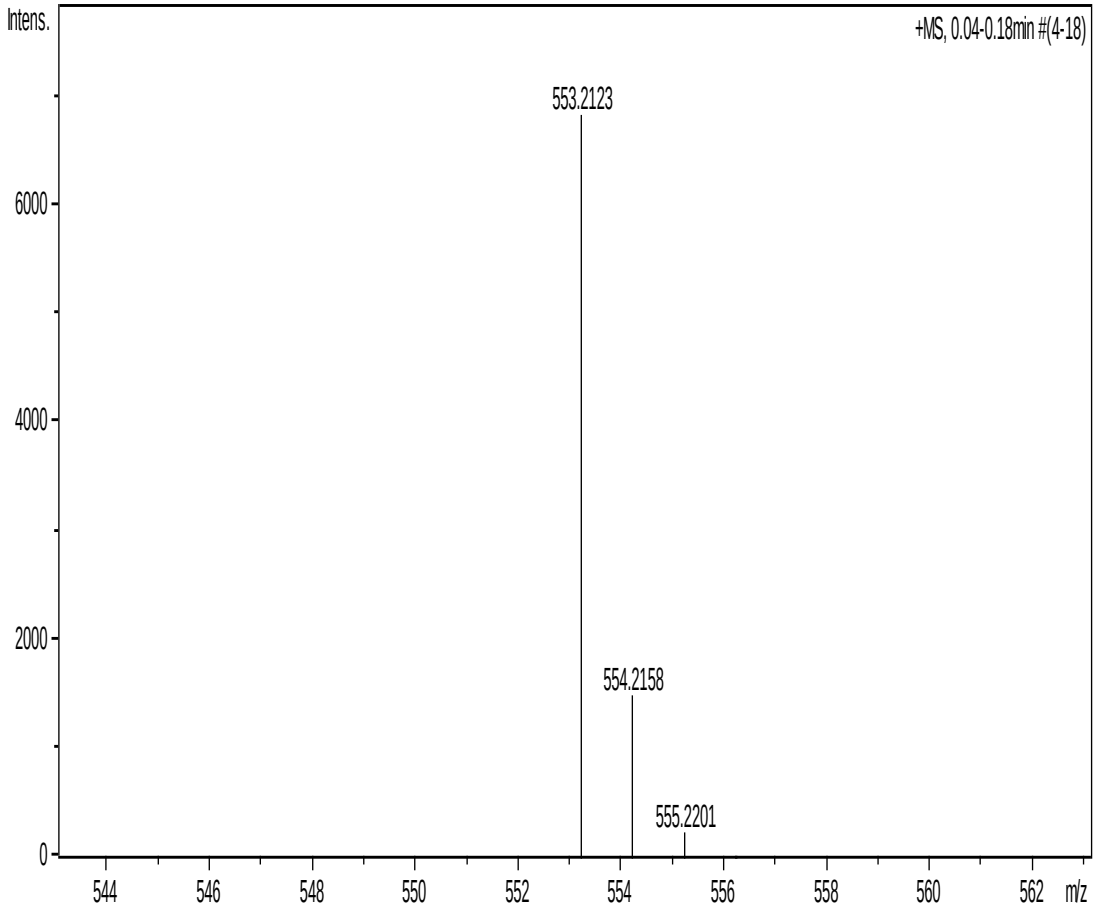

203.943
190.816
190.705
173.296
153.584
150.444
150.429
148.351
141.010
140.964
137.593
136.096
136.019
135.288
135.134
134.681
134.080
130.280
129.452
128.671
127.719
124.777
124.175
123.262
82.333
62.219
59.221
59.161
57.446
55.737
55.687
46.057
46.011
40.168
40.128
39.715
39.647
50
40
30
20
10
0
200
150
100
50
0
ppm (t1)


Intens.
x10^4
+MS, 0.50-0.61min #(51-62)
553.2130
554.2157
2.0
1.5
1.0
0.5
0.0
545.0
547.5
550.0
552.5
555.0
557.5
560.0
562.5
565.0
567.5
m/z

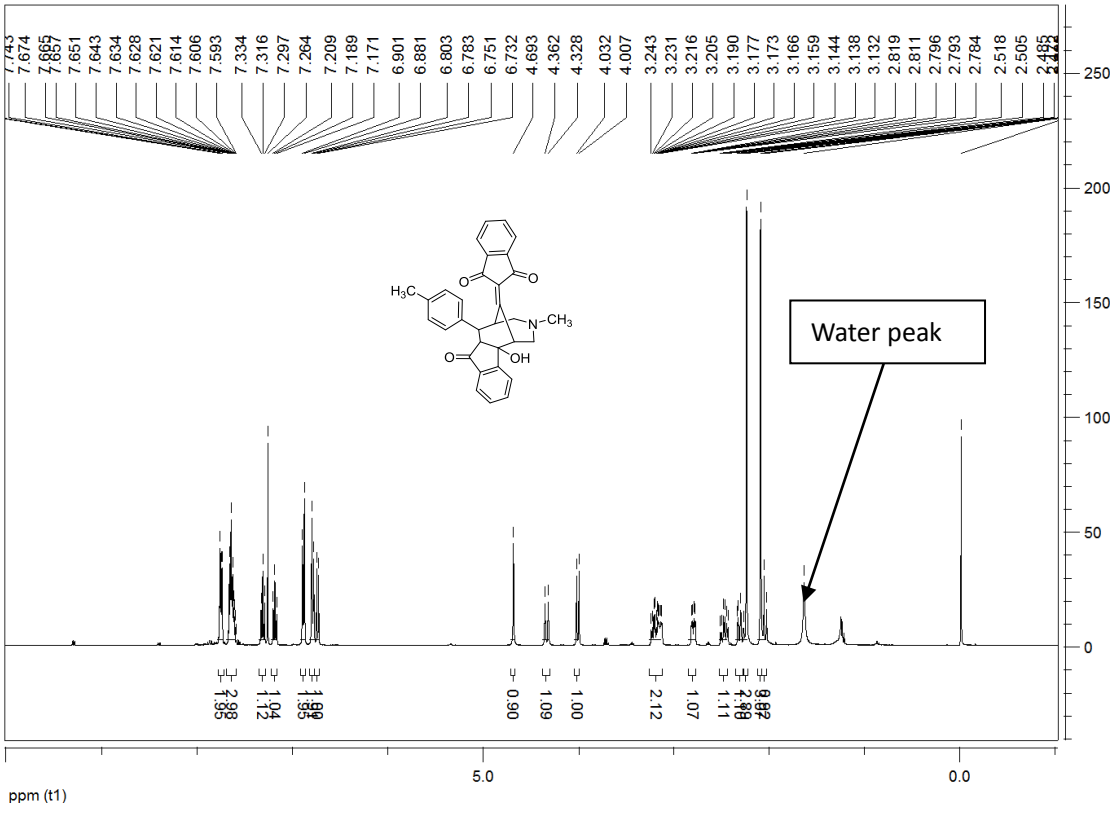
2-((5S,6aR,11bR)-3-benzyl-11b-hydroxy-7-oxo-6-(pyridin-4-yl)-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1k): yellow solid, 58%, m.p. 172-174℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (d, *J* = 5.2 Hz, 2H, ArH), 7.94 (d, *J* = 7.2 Hz, 1H, ArH), 7.90-7.84 (m, 2H, ArH), 7.80-7.74 (m, 2H, ArH), 7.63 (d, *J* = 7.6 Hz, 1H, ArH), 7.57(t,*J* = 7.6 Hz, 1H, ArH), 7.42-7.34 (m, 6H, ArH), 7.14 (d, *J* = 5.6 Hz, 2H, ArH), 5.51 (s, 1H, CH), 4.57 (s, 1H, CH), 4.08 (d, *J* = 12.0 Hz, 1H, CH), 3.80 (d, *J* = 11.6 Hz, 1H, CH), 3.57 (d, *J* = 12.4 Hz, 1H, CH), 3.33 (d, *J* = 12.4 Hz, 1H, CH), 2.91 (d, *J* = 12.0 Hz, 1H, CH), 2.85 (s, 1H, CH), 2.75 (dd, J_1 = 11.6 Hz, J_2 = 4.0 Hz, 1H, CH), 2.53 (d, *J* = 10.4 Hz, 1H, CH), 2.16 (dd, J_1 = 12.0 Hz, J_2 = 2.8 Hz, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 204.1, 190.8, 190.7, 173.1, 153.7, 149.8, 148.0, 141.0, 140.9, 137.6, 135.4, 13.2, 134.0, 130.3, 129.5, 128.7, 127.8, 124.8, 124.2, 123.9, 123.3, 82.4, 62.2, 58.7, 57.7, 55.4, 47.8, 47.8, 40.3, 40.2, 39.3, 39.2; IR(KBr) υ: 3422, 2815, 1721, 1682, 1625, 1596, 1347, 1223, 833, 768 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{36}H_{29}N_2O_4$ ($[M+H]^+$): 553.2127, found:553.2123.

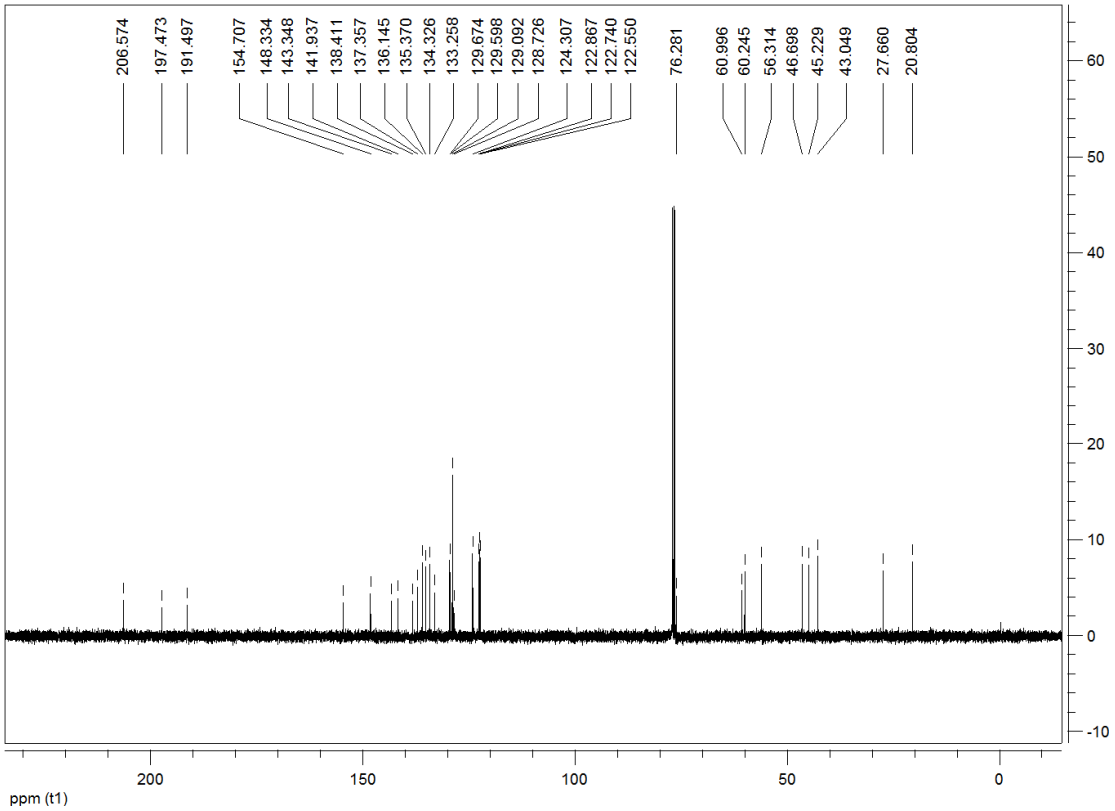


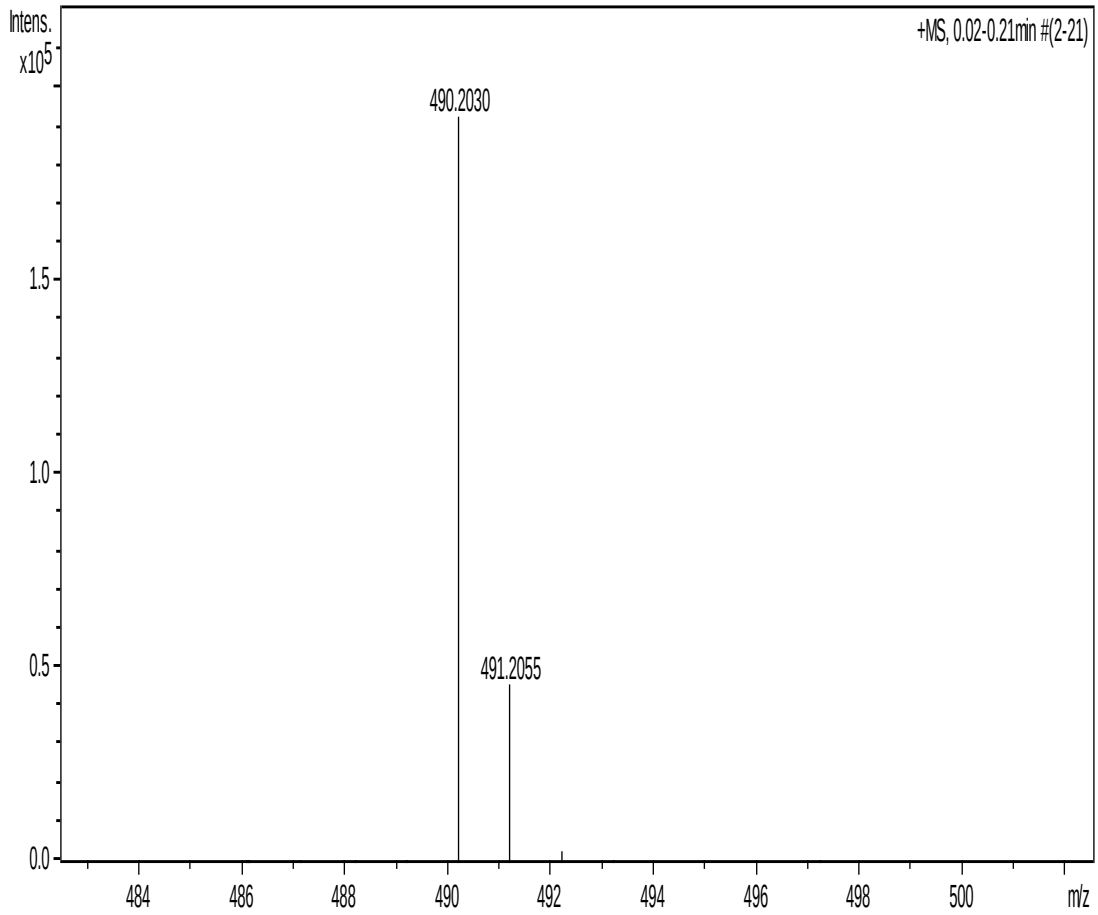

204.055
190.834
190.739
173.143
153.663
149.803
148.027
141.040
140.949
137.595
135.435
135.187
134.026
130.297
129.533
128.684
127.814
124.801
124.156
123.945
123.251
82.372
62.238
58.713
57.699
55.432
47.834
47.781
40.272
40.235
39.312
39.249
40
30
20
10
0
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.04-0.18min #(4-18)
553.2123
554.2158
555.2201
6000
4000
2000
0
544
546
548
550
552
554
556
558
560
562
m/z

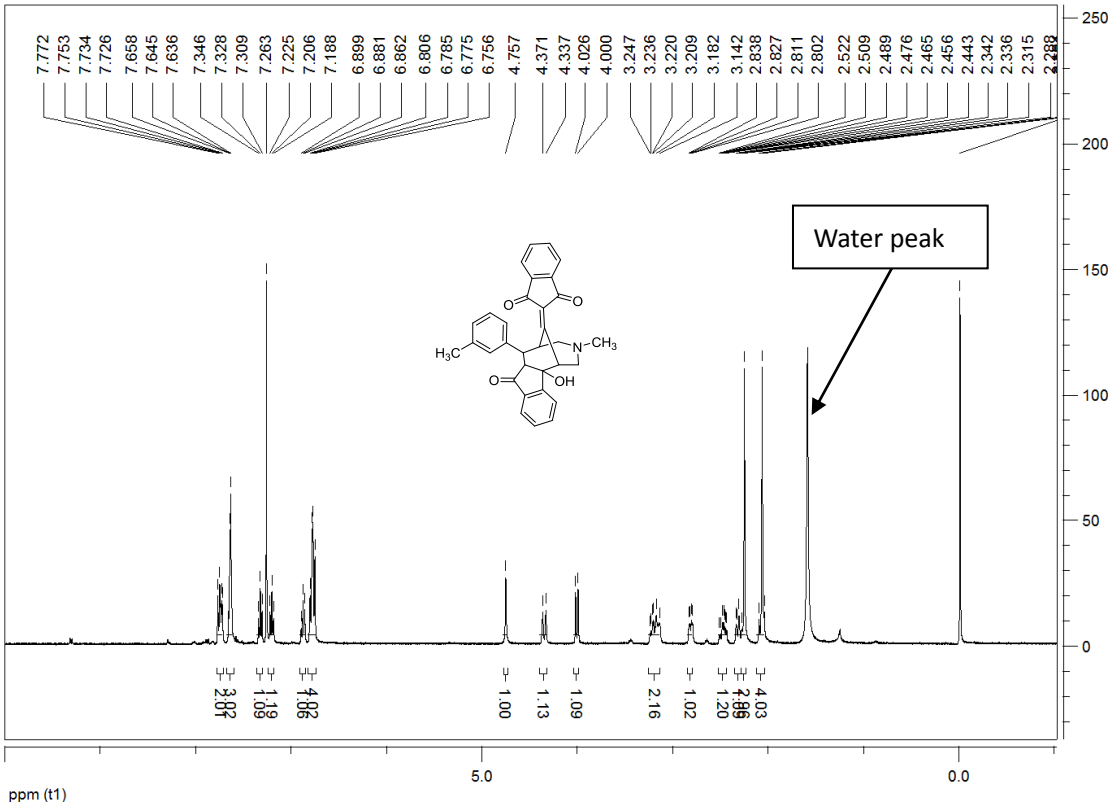
2-((5S,6aR,11bR)-11b-hydroxy-3-methyl-7-oxo-6-(p-tolyl)-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1l): yellow solid, 66%, m.p. 181-183℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77-7.74 (m, 2H, ArH), 7.67-7.59 (m, 3H, ArH), 7.32 (t, *J* = 7.2 Hz, 1H, ArH), 7.21-7.17 (m, 1H, ArH), 6.89 (d, *J* = 8.0 Hz, 2H, ArH), 6.79 (d, *J* = 8.0 Hz, 2H, ArH), 6.74 (d, *J* = 7.6 Hz, 1H, ArH), 4.69 (s, 1H, CH), 4.35 (d, *J* = 13.6 Hz, 1H, CH), 4.02 (d, *J* = 10.0 Hz, 1H, CH), 3.24-3.13 (m, 2H, CH), 2.82-2.78 (m, 1H, CH), 2.52-2.44 (m, 1H, CH), 2.34-2.27 (m, 1H, CH), 2.24 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.05 (d, *J* = 10.8 Hz, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 206.6, 197.5, 191.5, 154.7, 148.3, 143.3, 141.9, 138.4, 137.4, 136.1, 135.4, 134.3, 133.3, 129.7, 129.6, 129.1, 128.7, 124.3, 122.9, 122.7, 122.6, 76.3, 61.0, 60.2, 56.3, 46.7, 45.2, 43.0, 27.7, 20.8; IR(KBr) υ: 3407, 2933, 2792, 1697, 1653, 1594, 1371, 1258, 1033, 767 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{32}H_{28}NO_4$([M+H]$^+$): 490.2018, found: 490.2030.

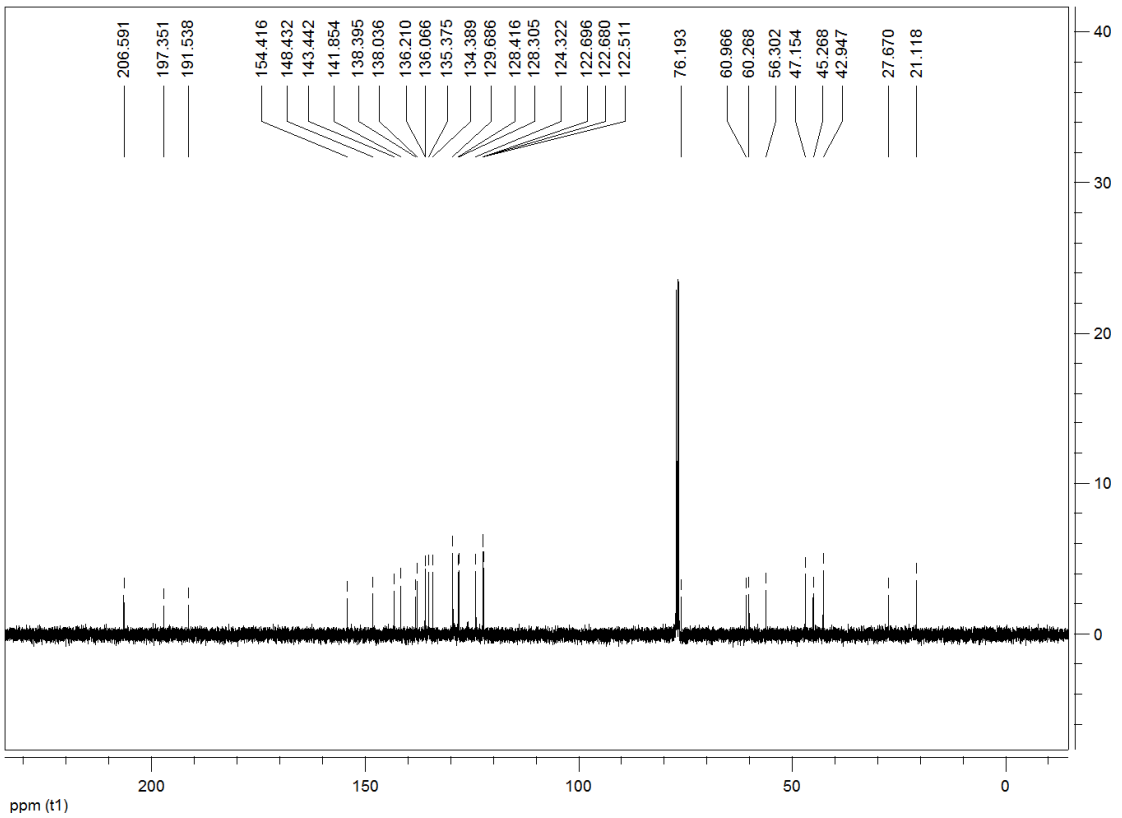


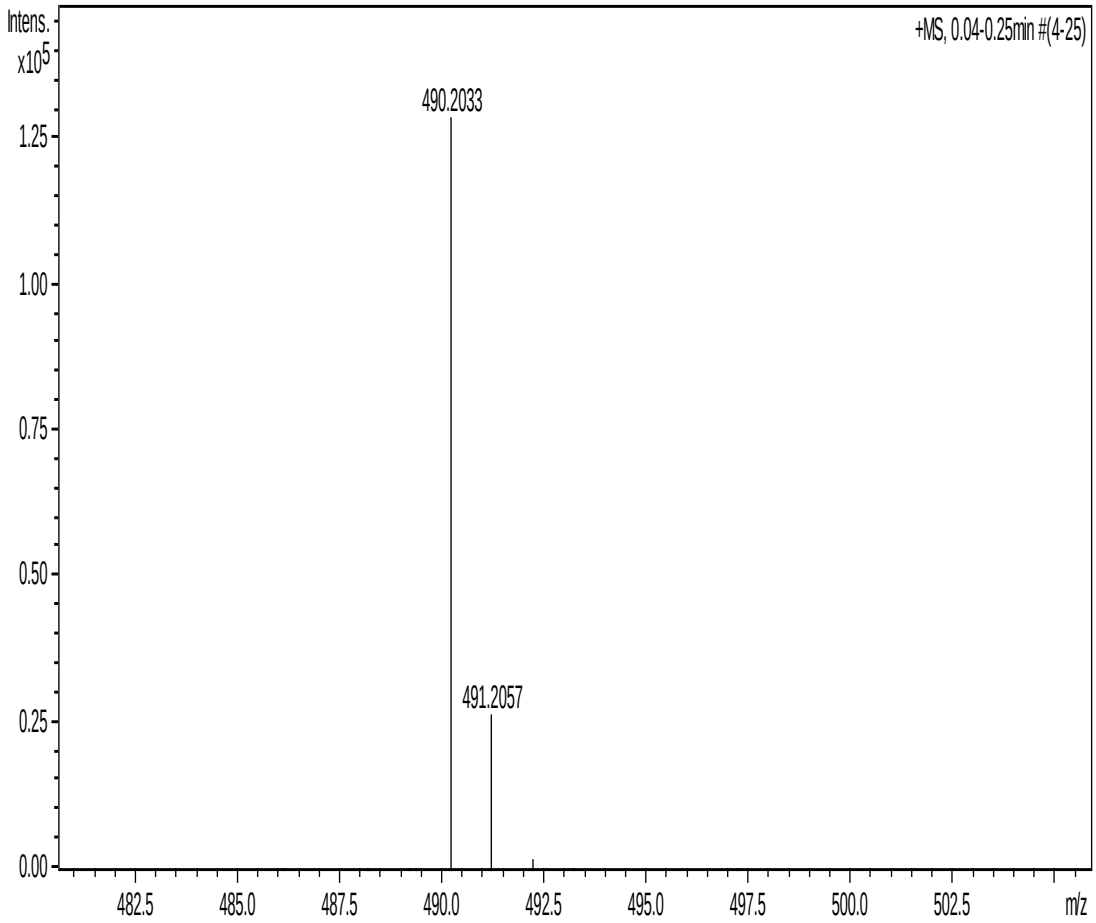

206.574
197.473
191.497
154.707
148.334
143.348
141.937
138.411
137.357
136.145
135.370
134.326
133.258
129.674
129.598
129.092
128.726
124.307
122.867
122.740
122.550
76.281
60.996
60.245
56.314
46.698
45.229
43.049
27.660
20.804
60
50
40
30
20
10
0
-10
200
150
100
50
0
ppm (t1)


Intens.
x10^5
+MS, 0.02-0.21min #(2-21)
490.2030
491.2055
1.5
1.0
0.5
0.0
484
486
488
490
492
494
496
498
500
m/z

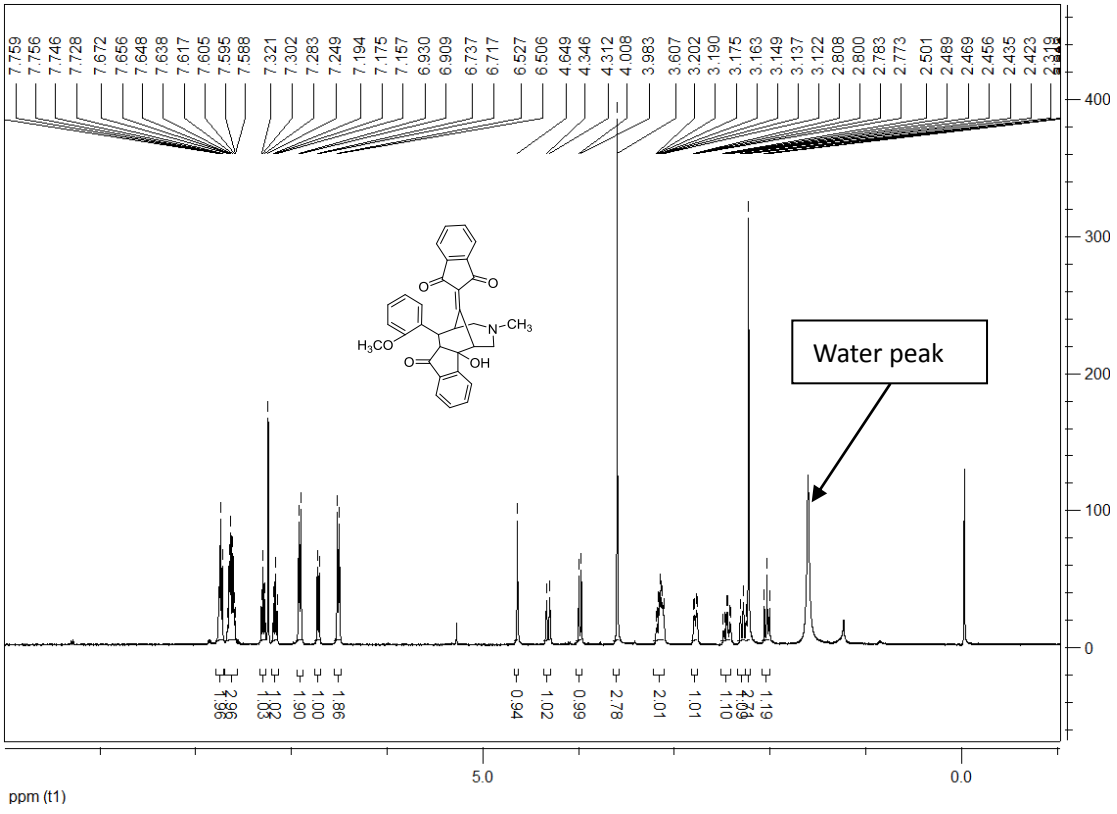
2-((5S,6aR,11bR)-11b-hydroxy-3-methyl-7-oxo-6-(m-tolyl)-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1m): yellow solid, 63%, m.p. 172-174℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77-7.73 (m, 2H, ArH), 7.66-7.64 (m, 3H, ArH), 7.33 (t, *J* = 7.2 Hz, 1H, ArH), 7.21 (t, *J* = 7.2 Hz, 1H, ArH), 6.90-6.86 (m, 1H, ArH), 6.81-6.76 (m, 4H, ArH), 4.76 (s, 1H, CH), 4.35 (d, *J* = 13.6 Hz, 1H, CH), 4.01 (d, *J* = 10.4 Hz, 1H, CH), 3.25-3.14 (m, 2H, CH), 2.84-2.80 (m, 1H, CH), 2.52-2.44 (m, 1H, CH), 2.34-2.29 (m, 1H, CH), 2.26 (s, 3H, CH_3), 2.10-2.05 (m, 4H, CH, CH_3); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 206.6, 197.4, 191.5, 154.4, 148.4, 143.4, 141.9, 138.4, 138.0, 136.2, 136.1, 135.4, 134.4, 129.7, 128.4, 128.3, 124.3, 122.7, 122.7, 122.5, 76.2, 61.0, 60.3, 56.3, 47.2, 45.3, 42.9, 27.7, 21.1; IR(KBr) υ: 3448, 2791, 1697, 1654, 1595, 1458, 1371, 1333, 1249, 775 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{32}H_{28}NO_4$([M+H]$^+$): 490.2018, found: 490.2033.

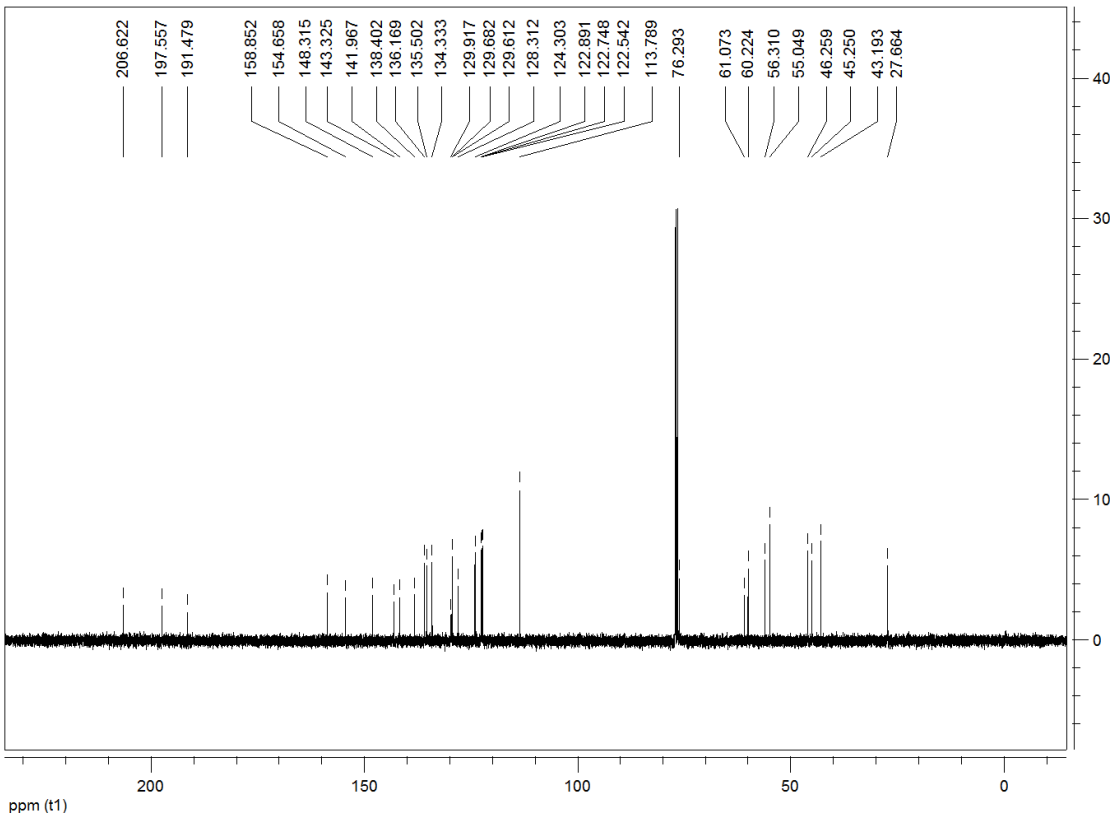


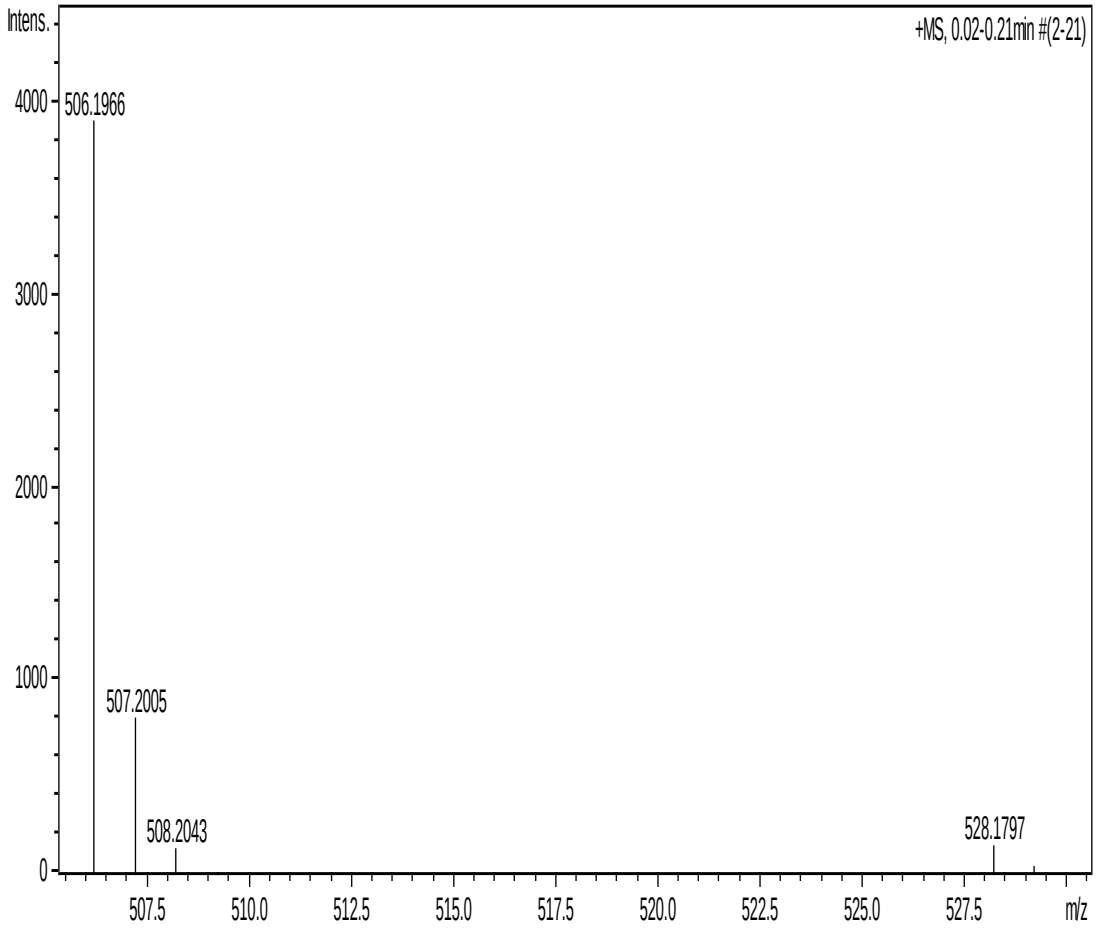

206.591
197.351
191.538
154.416
148.432
143.442
141.854
138.395
138.036
136.210
136.066
135.375
134.389
129.686
128.416
128.305
124.322
122.696
122.680
122.511
76.193
60.966
60.268
56.302
47.154
45.268
42.947
27.670
21.118
40
30
20
10
0
200
150
100
50
0
ppm (t1)


Intens.
x10^5
+MS, 0.04-0.25min #(4-25)
490.2033
491.2057
1.25
1.00
0.75
0.50
0.25
0.00
482.5
485.0
487.5
490.0
492.5
495.0
497.5
500.0
502.5
m/z

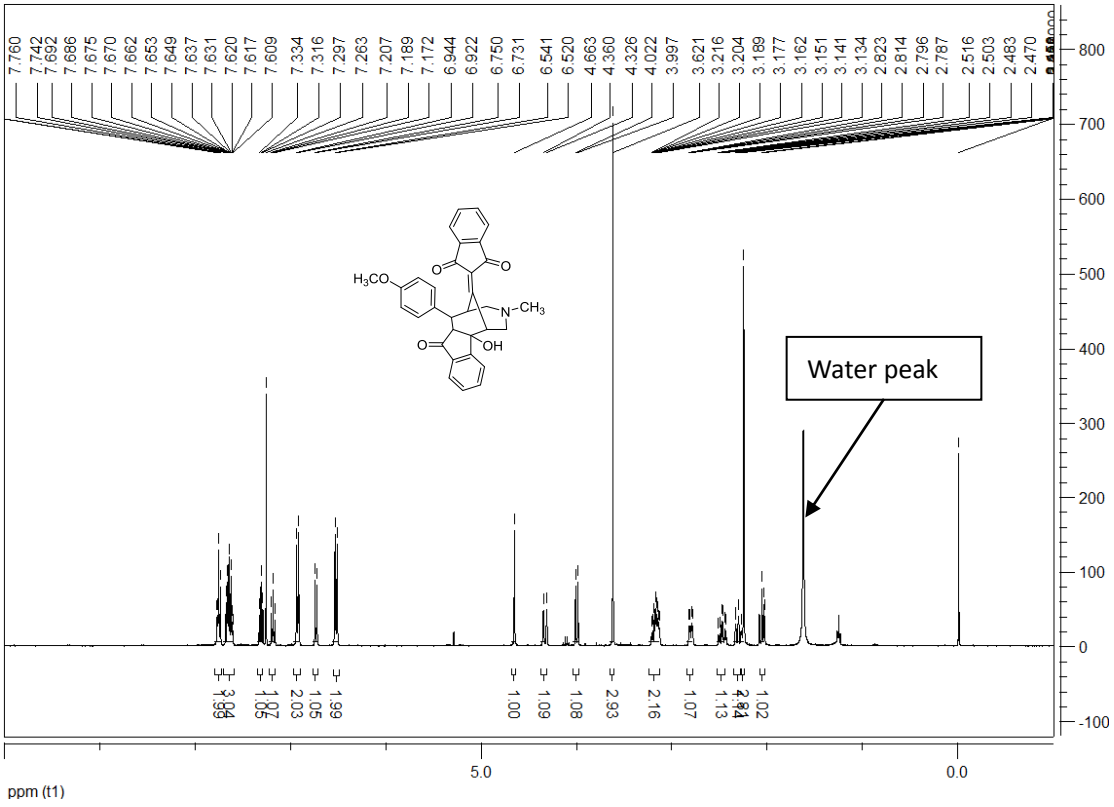
2-((5S,6aR,11bR)-11b-hydroxy-6-(2-methoxyphenyl)-3-methyl-7-oxo-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1n): yellow solid, 71%, m.p. 173-175℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77-7.73 (m, 2H, ArH), 7.67-7.59 (m, 3H, ArH), 7.30 (t, *J* = 7.6 Hz, 1H, ArH), 7.18 (t, *J* = 7.6 Hz, 1H, ArH), 6.92 (d, *J* = 8.4 Hz, 2H,, ArH), 6.73 (d, *J* = 8.0 Hz, 1H,, ArH), 6.52 (d, *J* = 8.4 Hz, 2H,, ArH), 4.65 (s, 1H, CH), 4.33(d, *J* = 13.6 Hz, 1H, CH), 3.99 (d, *J* = 10.0 Hz, 1H, CH), 3.61 (s, 3H, OCH_3), 3.20-3.12 (m, 2H, CH), 2.81-2.77 (m, 1H, CH), 2.50-2.42 (m, 1H, CH), 2.32-2.26 (m, 1H, CH), 2.24 (s, 3H, CH_3), 2.07-2.02 (m, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 206.6, 197.6, 191.5, 158.9, 154.7, 148.3, 143.3, 142.0, 138.4, 136.2, 135.5, 134.3, 129.9, 129.7, 129.6, 128.3, 124.3, 122.9, 122.7, 122.5, 113.8, 76.3, 61.1, 60.2, 56.3, 55.0, 46.3, 45.2, 43.2, 27.7; IR(KBr) υ: 3409, 2932, 2796, 1697,5 1654, 1598, 1511, 1458, 1259, 1036, 766 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{32}H_{28}NO_5$ ([M+H]$^{+}$): 506.1967, found: 506.1966.

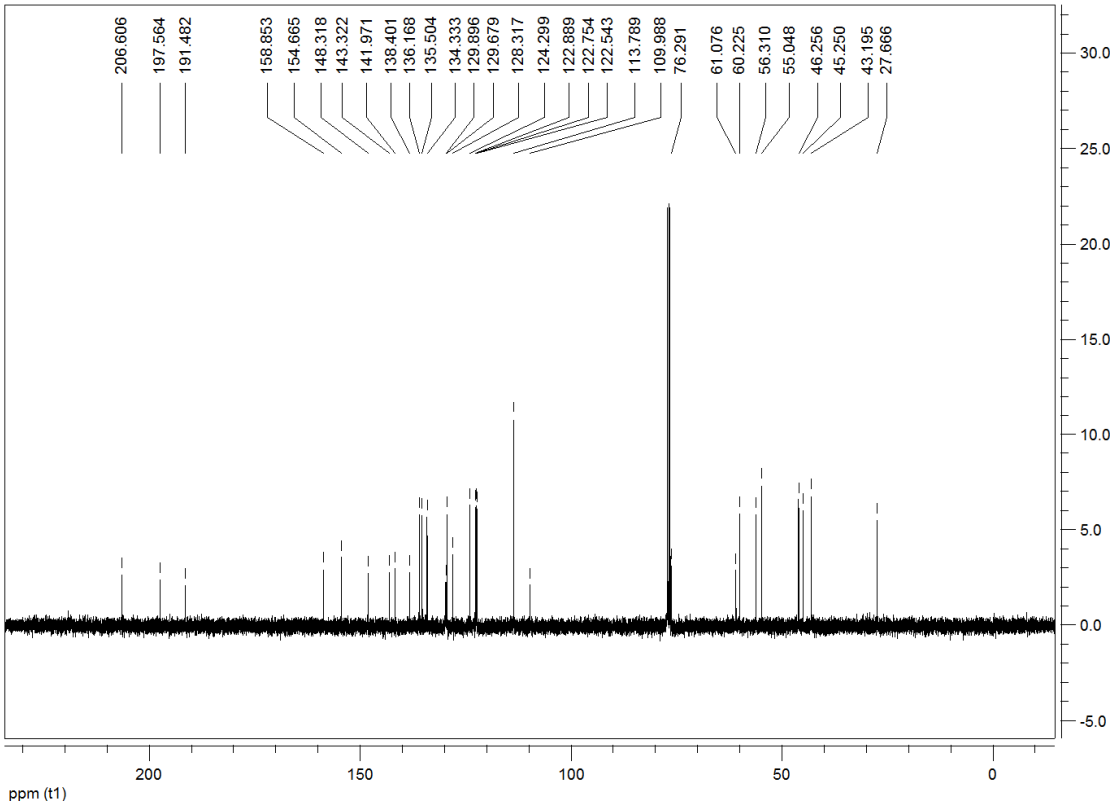


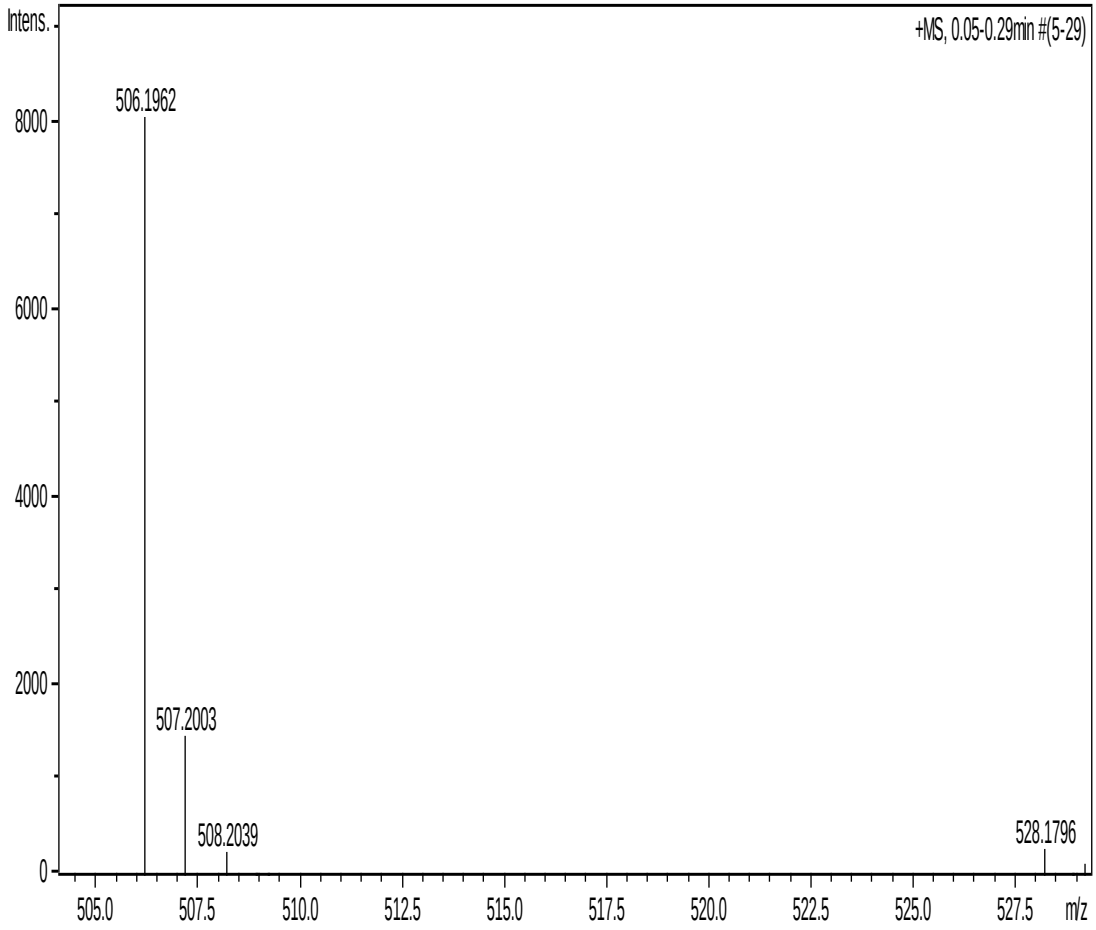

206.622
197.557
191.479
158.852
154.658
148.315
143.325
141.967
138.402
136.169
135.502
134.333
129.917
129.682
129.612
128.312
124.303
122.891
122.748
122.542
113.789
76.293
61.073
60.224
56.310
55.049
46.259
45.250
43.193
27.664
40
30
20
10
0
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.02-0.21min #(2-21)
4000
3000
2000
1000
0
506.1966
507.2005
508.2043
528.1797
507.5
510.0
512.5
515.0
517.5
520.0
522.5
525.0
527.5
m/z

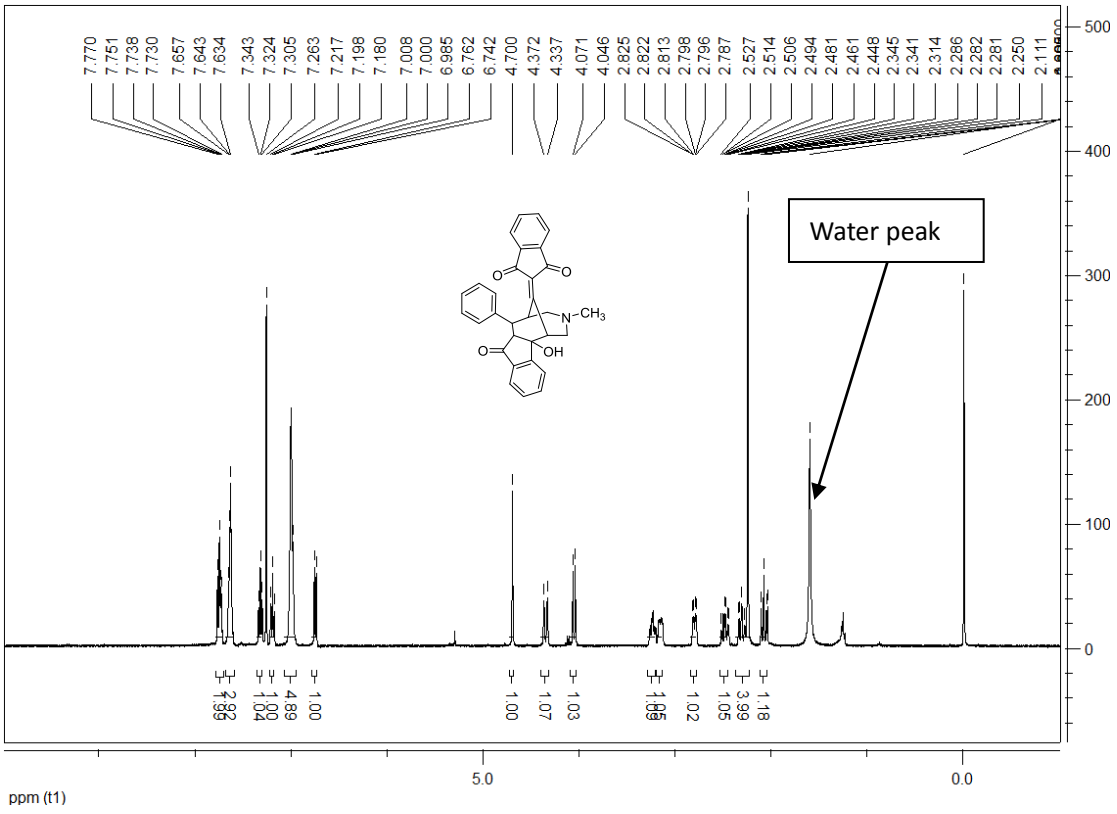
2-((5S,6aR,11bR)-11b-hydroxy-6-(4-methoxyphenyl)-3-methyl-7-oxo-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1o): yellow solid, 68%, m.p. 170-172℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78-7.74 (m, 2H, ArH), 7.70-7.61 (m, 3H, ArH), 7.32 (t, *J* = 7.2 Hz, 1H, ArH), 7.19 (t, *J* = 7.2 Hz, 1H, ArH), 6.93 (d, *J* = 8.8 Hz, 2H,, ArH), 6.74 (d, *J* = 7.6 Hz, 1H,, ArH), 6.53 (d, *J* = 8.4 Hz, 2H,, ArH), 4.66 (s, 1H, CH), 4.34 (d, *J* = 13.6 Hz, 1H, CH), 4.01 (d, *J* = 10.0 Hz, 1H, CH), 3.62 (s, 3H, OCH_3), 3.22-3.13 (m, 2H, CH), 2.82-2.78 (m, 1H, CH), 2.52-2.44 (m, 1H, CH), 2.34-2.27 (m, 1H, CH), 2.25 (s, 3H, CH_3), 2.06-2.03 (m, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 206.6, 197.5, 191.4, 158.8, 154.6, 148.3, 143.3, 141.9, 138.4, 136.1, 135.5, 134.3, 129.9, 129.7, 128.3, 124.3, 122.9, 122.8, 122.5, 113.8, 110.0, 76.3, 61.1, 60.2, 56.3, 55.0, 46.3, 45.2, 43.2, 27.7; IR(KBr) υ: 3408, 2931, 2796, 1697, 1654, 1599, 1511, 1458, 1258, 1036, 766 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{32}H_{28}NO_5$ ($[M+H]^+$): 506.1967, found: 506.1962.

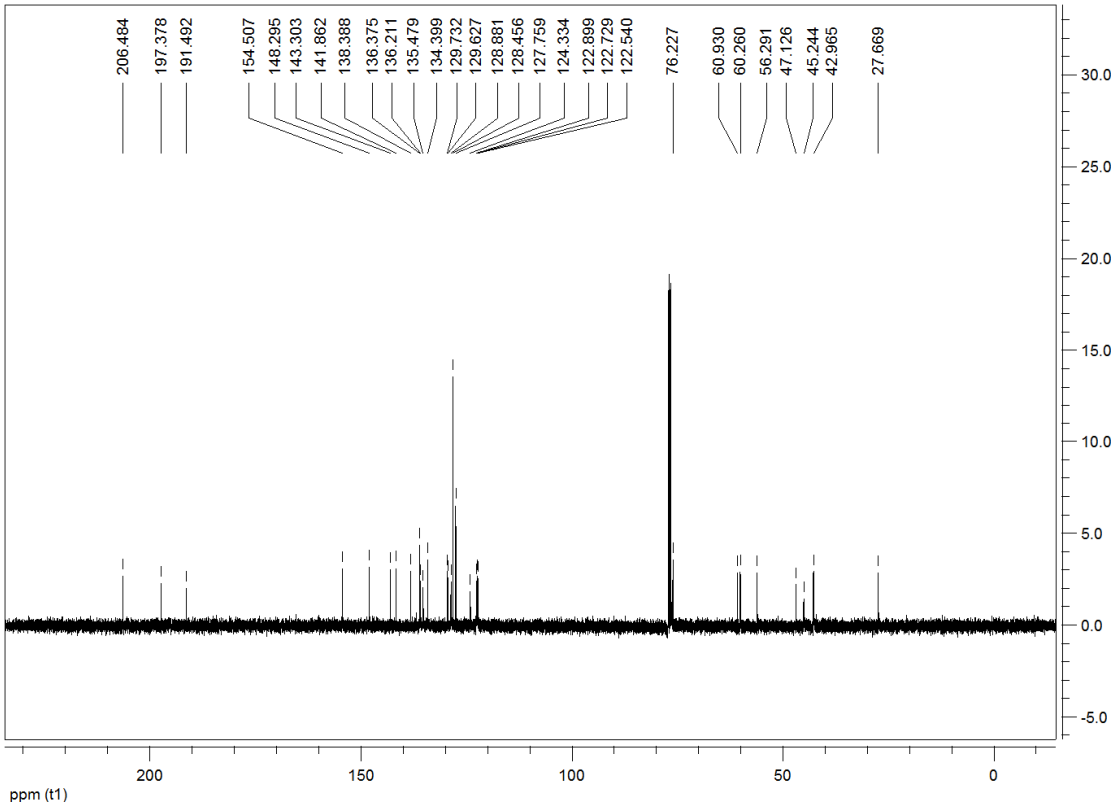


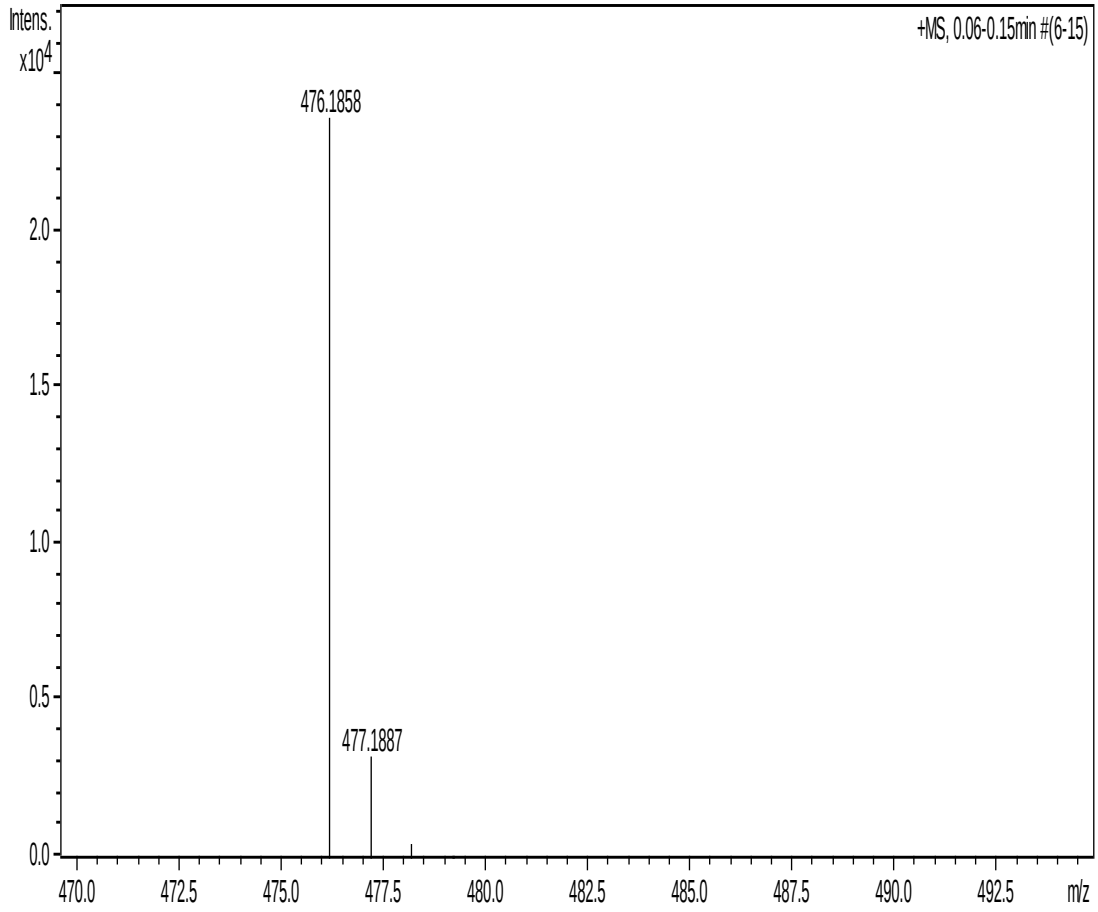

206.606
197.564
191.482
158.853
154.665
148.318
143.322
141.971
138.401
136.168
135.504
134.333
129.896
129.679
128.317
124.299
122.889
122.754
122.543
113.789
109.988
76.291
61.076
60.225
56.310
55.048
46.256
45.250
43.195
27.666
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.05-0.29min #(5-29)
506.1962
507.2003
508.2039
528.1796
8000
6000
4000
2000
0
505.0
507.5
510.0
512.5
515.0
517.5
520.0
522.5
525.0
527.5
m/z

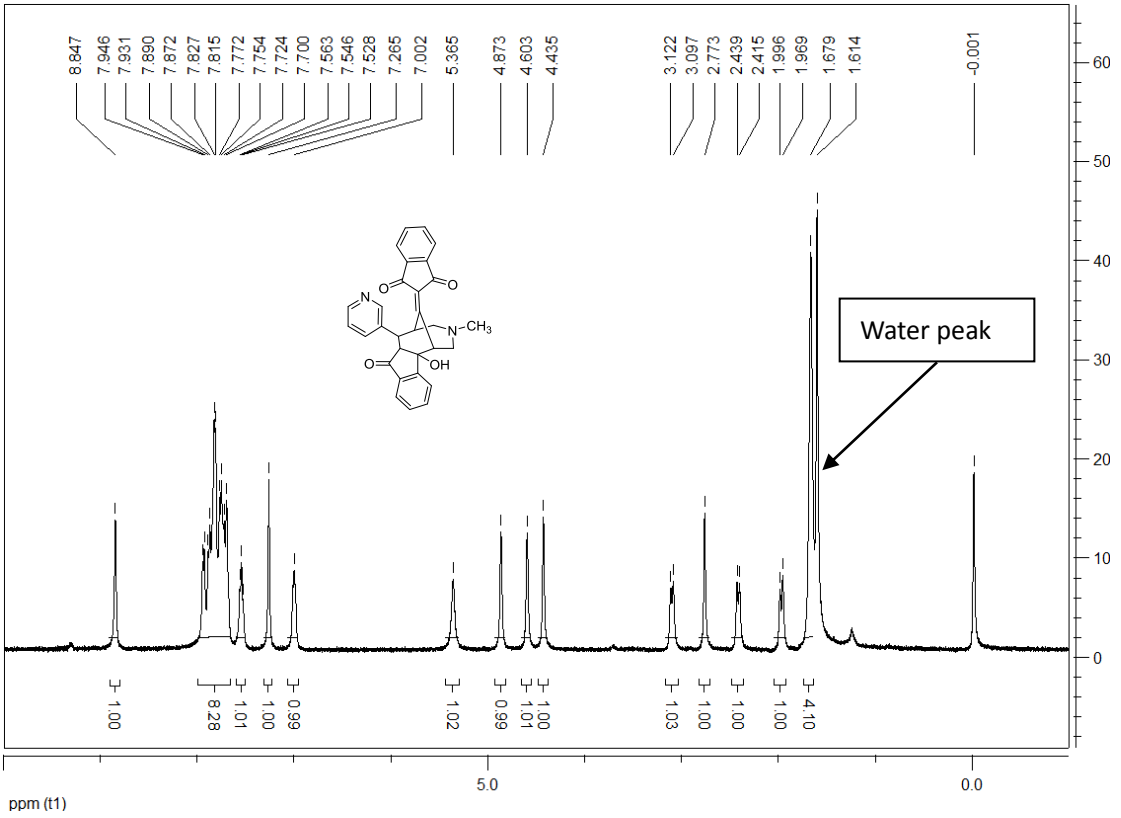
2-((5S,6aR,11bR)-11b-hydroxy-3-methyl-7-oxo-6-phenyl-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1p): yellow solid, 70%, m.p. 163-165℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77-7.72 (m, 2H, ArH), 7.66-7.61 (m, 3H, ArH), 7.32 (t, *J* = 7.6 Hz, 1H, ArH), 7.20 (t, *J* = 7.2 Hz, 1H, ArH), 7.01-6.98 (m, 5H, ArH), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 4.70 (s, 1H, CH), 4.35 (d, *J* = 14.0 Hz, 1H, CH), 4.06 (d, *J* = 10.0 Hz, 1H, CH), 3.27-3.21 (m, 1H, CH), 3.18-3.14 (m, 1H, CH), 2.81 (dd, J_1 = 10.8 Hz, J_2 = 4.8 Hz, 1H, CH_3), 2.53-2.45 (m, 1H, CH), 2.34-2.28 (m, 1H, CH), 2.25 (s, 3H, CH_3), 2.11-2.04 (m, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 206.5, 197.4, 191.5, 154.5, 148.3, 143.3, 141.9, 138.4, 136.4, 136.2, 135.5, 134.4, 129.7, 129.6, 128.9, 128.5, 127.8, 124.3, 122.9, 122.7, 122.5, 76.2, 60.9, 60.3, 56.3, 47.1, 45.2, 43.0, 27.7; IR(KBr) υ: 3625, 2948, 1703, 1646, 1594, 1553, 1452, 1264, 1223, 763 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{31}H_{26}NO_4$([M+H]$^+$): 476.1862, found: 476.1858.

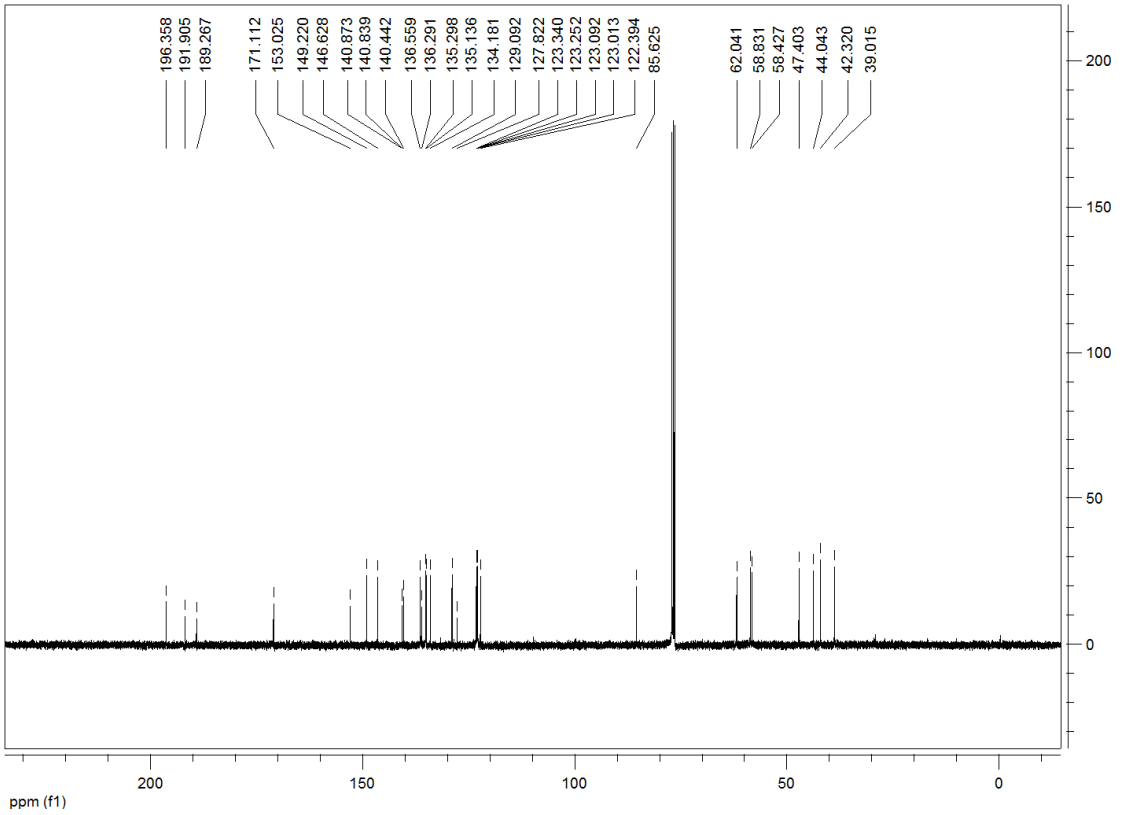


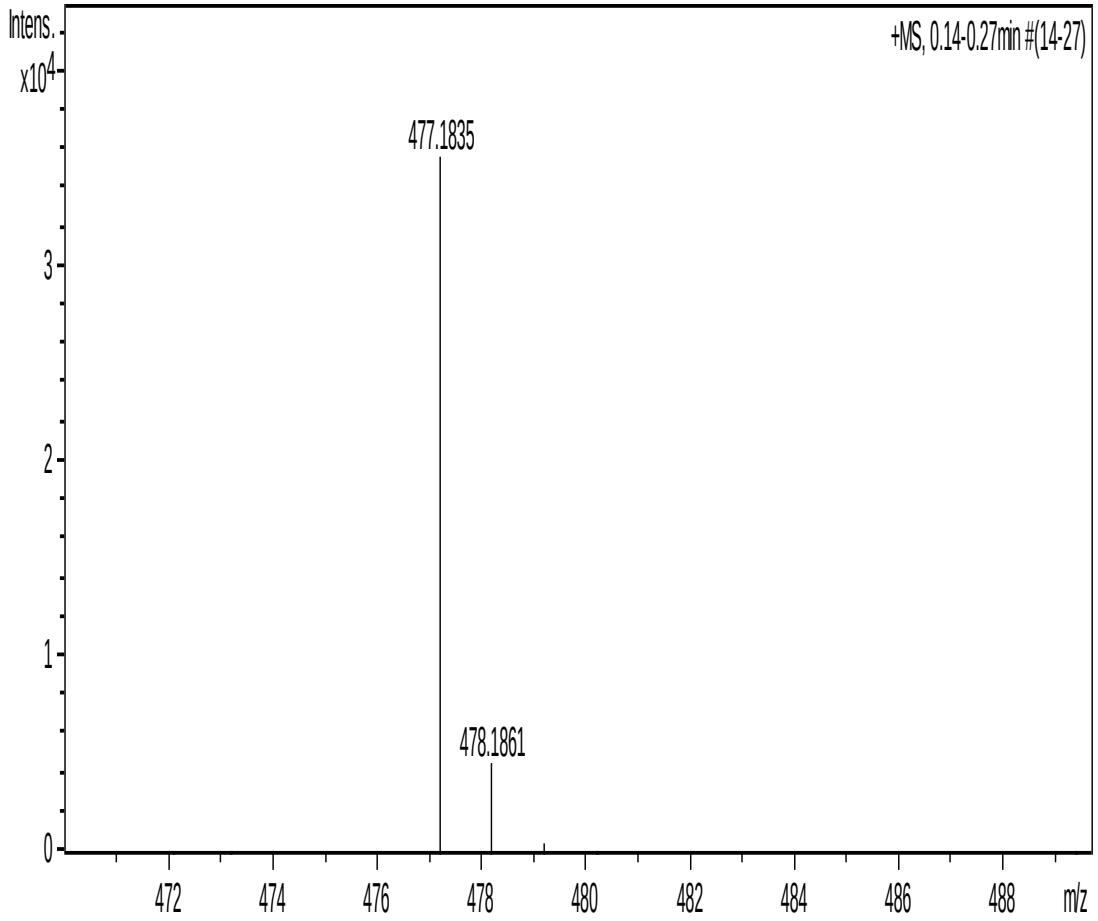

206.484
197.378
191.492
154.507
148.295
143.303
141.862
138.388
136.375
136.211
135.479
134.399
129.732
129.627
128.881
128.456
127.759
124.334
122.899
122.729
122.540
76.227
60.930
60.260
56.291
47.126
45.244
42.965
27.669
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (t1)


Intens.
x10^4
+MS, 0.06-0.15min #(6-15)
476.1858
477.1887
2.0
1.5
1.0
0.5
0.0
470.0
472.5
475.0
477.5
480.0
482.5
485.0
487.5
490.0
492.5
m/z

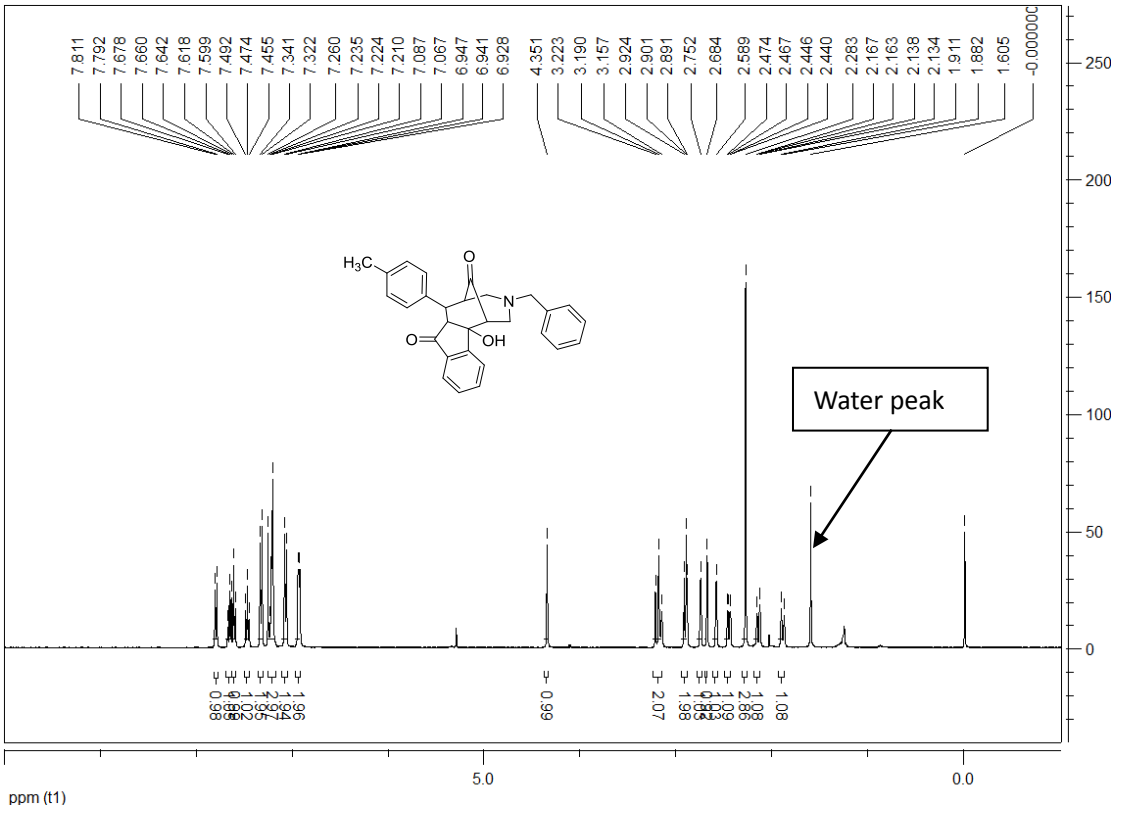
2-((5S,6aR,11bR)-11b-hydroxy-3-methyl-7-oxo-6-(pyridin-3-yl)-2,3,4,5,6,6a,7,11b-octahydro-1*H*-1,5-methanoindeno[1,2-*d*]azocin-12-ylidene)-1*H*-indene-1,3(2*H*)-dione (1q): yellow solid, 55%, m.p. 216-218℃; ^{1}H NMR (400 MHz, DMSO) δ: 8.85 (s, 1H, ArH), 7.90-7.27 (m, 8H, ArH), 7.56-7.53 (m, 1H, ArH), 7.26 (s, 1H, ArH), 7.00 (s, 1H, ArH), 5.36 (s, 1H, CH), 4.87 (s, 1H, CH), 4.60 (s, 1H, CH), 4.44 (s, 1H, CH), 3.11 (d, *J* = 10.0 Hz, 1H, CH), 2.77 (s, 1H, CH), 2.43 (d, *J* = 9.6 Hz, 1H, CH), 1.98 (d, *J* = 10.8 Hz, 1H, CH), 1.68 (s, 4H, CH, CH_3); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 196.4, 191.9, 189.1, 171.1, 153.0, 149.2, 146.6, 140.9, 140.8, 140.4, 136.6, 136.3, 135.3, 135.1, 134.2, 129.1, 127.8, 123.3, 123.3, 123.1, 123.0, 122.4, 85.6, 62.0, 58.8, 58.4, 47.4, 44.0, 42.3, 39.0; IR(KBr) υ: 3424, 2785, 1720, 1686, 1625, 1598, 1228, 1082, 818, 763 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{30}H_{25}N_2O_4$([M+H]$^{+}$): 477.1814, found: 477.1835.

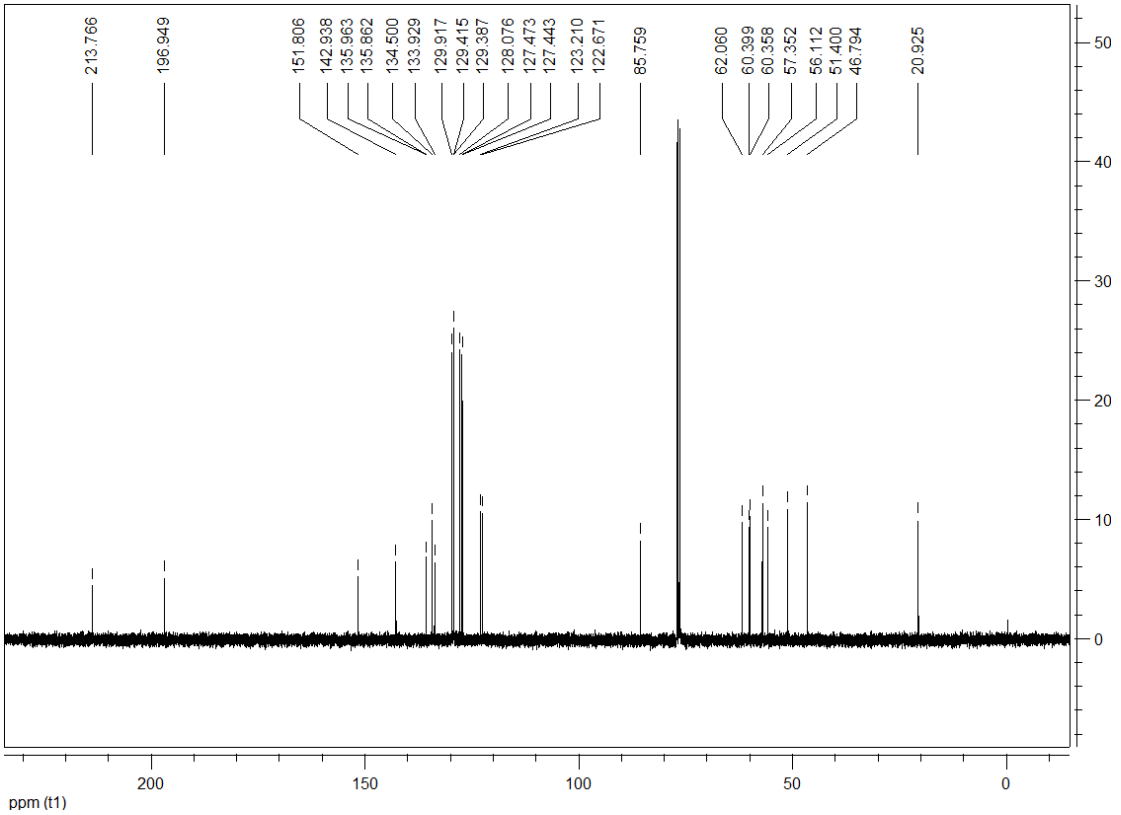


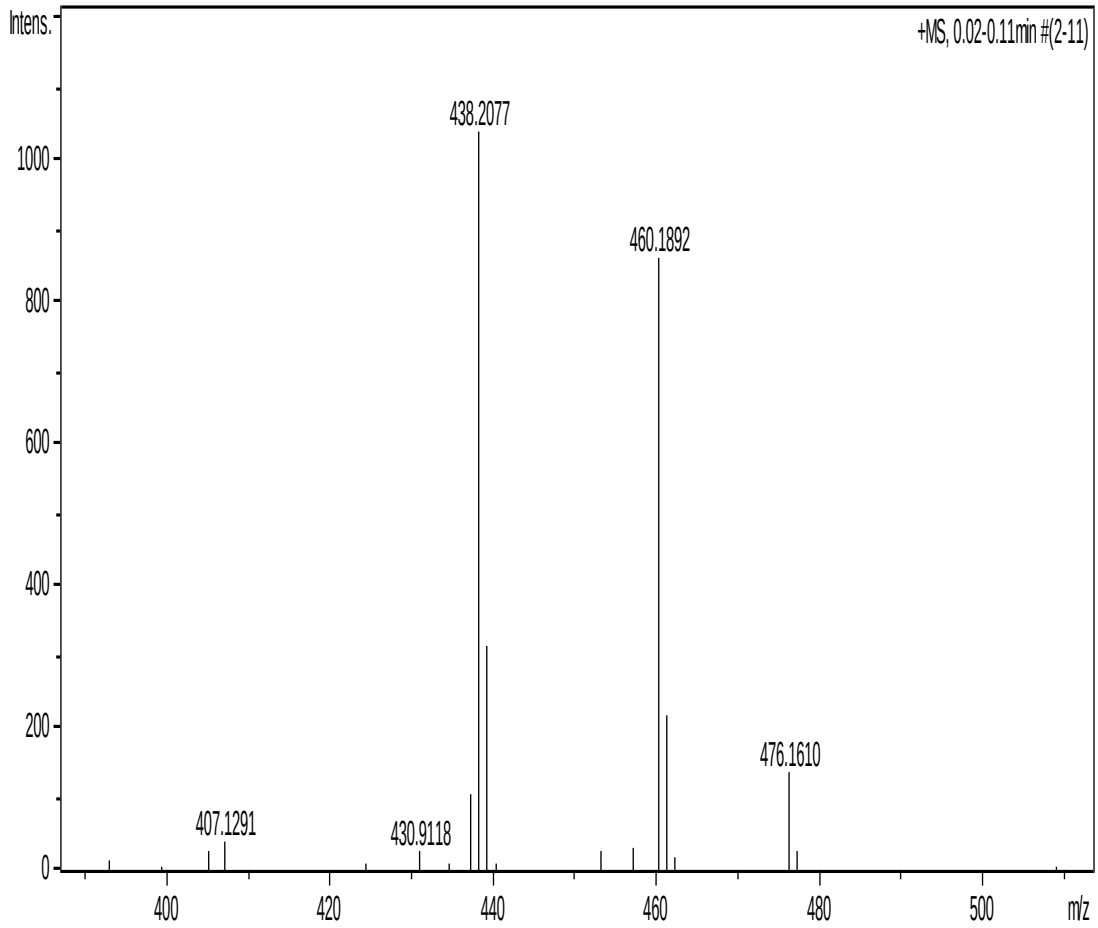

196.358
191.905
189.267
171.112
153.025
149.220
146.628
140.873
140.839
140.442
136.559
136.291
135.298
135.136
134.181
129.092
127.822
123.340
123.252
123.092
123.013
122.394
85.625
62.041
58.831
58.427
47.403
44.043
42.320
39.015
200
150
100
50
0
ppm (f1)


Intens.
x10^4
+MS, 0.14-0.27min #(14-27)
477.1835
478.1861
3
2
1
0
472
474
476
478
480
482
484
486
488
m/z

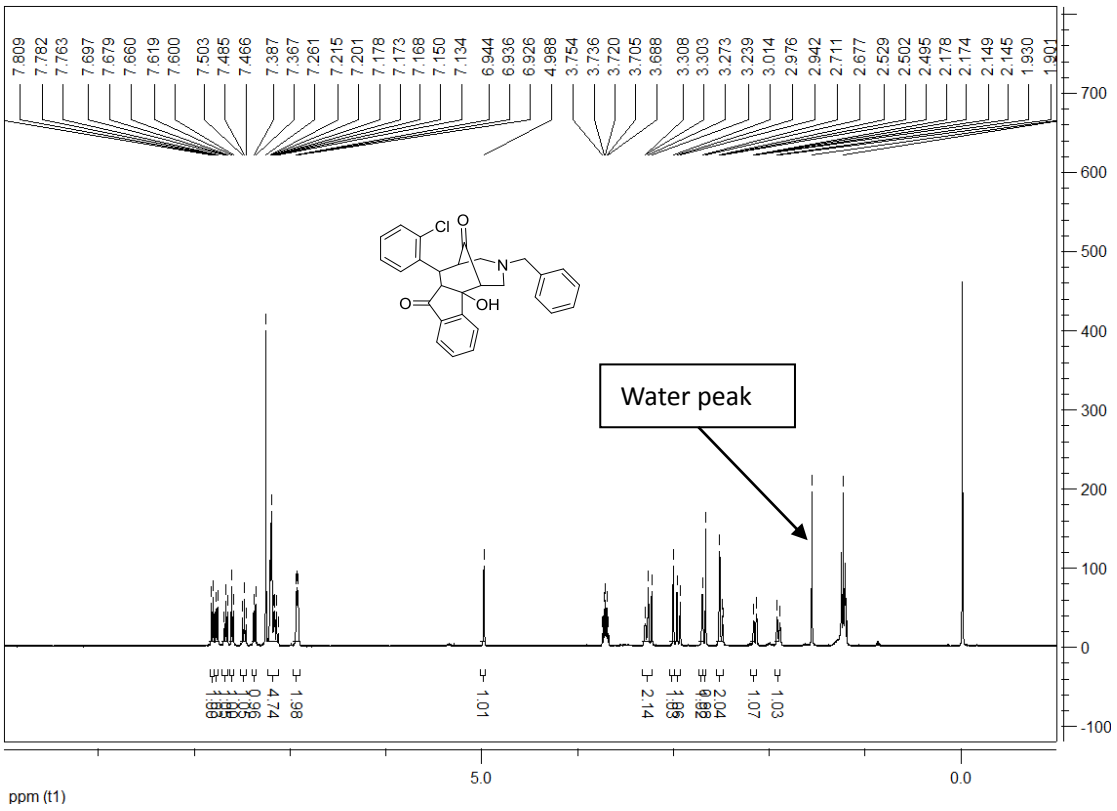
3-benzyl-11b-hydroxy-6-(p-tolyl)-1,2,3,4,5,6,6a,11b-octahydro-7H-1,5-methanoindeno[1,2-d] azocine-7,12-dione (2a): white solid, 68%, m.p. 213-215℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 7.6 Hz, 1H, ArH), 7.66 (t, *J* = 7.2 Hz, 1H, ArH), 7.61 (d, *J* = 7.6 Hz, 1H, ArH), 7.47 (t, *J* = 7.2 Hz, 1H, ArH), 7.33 (d, *J* = 7.6 Hz, 2H, ArH), 7.26-7.21 (m, 3H, ArH), 7.08 (d, *J* = 8.0 Hz, 2H, ArH), 6.95-6.93 (m, 2H, ArH), 4.35 (s, 1H, CH), 3.22-3.16 (t, *J* = 13.2 Hz, 2H, CH), 2.92-2.89 (m, 2H, CH), 2.75 (s, 1H, CH), 2.68 (s, 1H, CH), 2.59 (s, 1H, CH), 2.46 (dd, J_1 = 11.2 Hz, J_2 = 2.8 Hz, 1H, CH), 2.28 (s, 3H, CH_3), 2.15 (dd, J_1 = 11.6 Hz, J_2 = 1.6 Hz, 1H, CH), 1.90 (d, *J* = 11.6 Hz, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 213.8, 196.9, 151.8, 142.9, 136.0, 135.9, 134.5, 133.9, 129.9, 129.4, 129.4, 128.1, 127.5, 127.4, 123.2, 122.7, 85.8, 62.1, 60.4, 60.4, 57.4, 56.1, 51.4, 46.8, 20.9; IR(KBr) υ: 3374, 1715 1600, 1277, 1242 1116, 750 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{29}H_{28}NO_3$([M+H]$^+$): 438.2069, found: 438.2077.

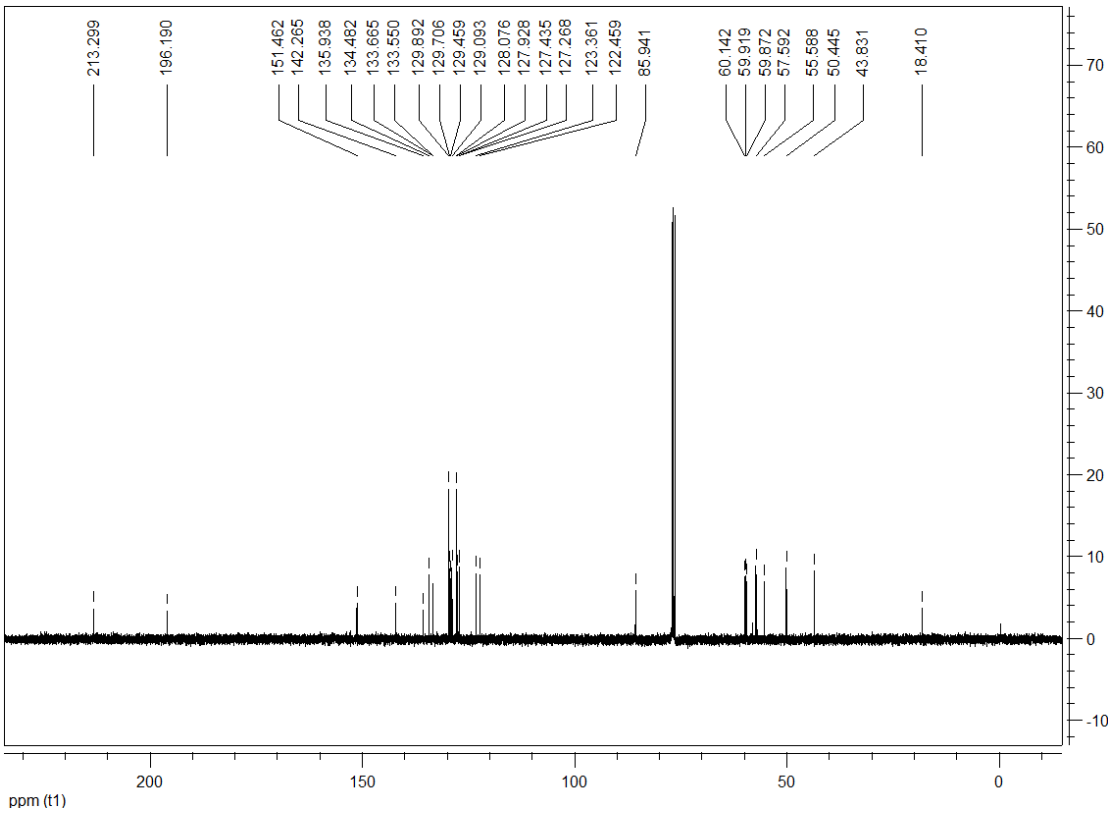


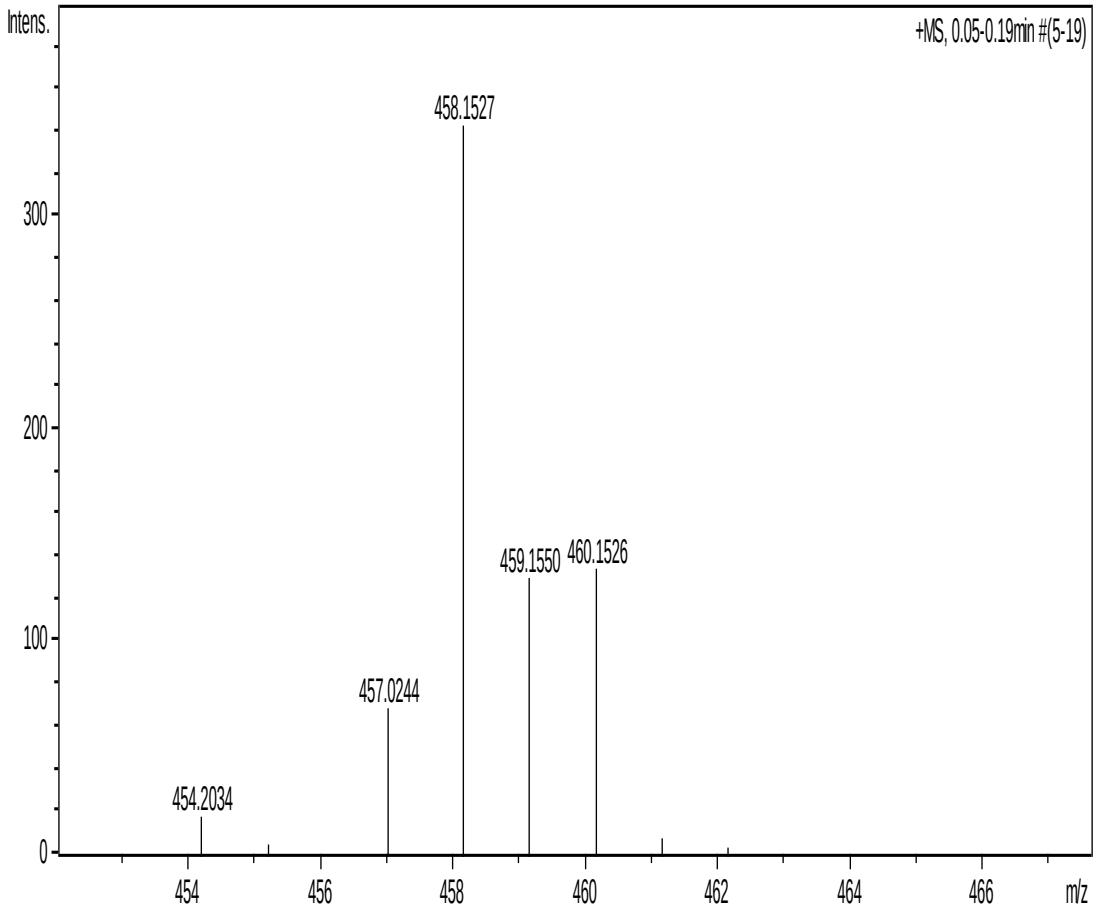

213.766
196.949
151.806
142.938
135.963
135.862
134.500
133.929
129.917
129.415
129.387
128.076
127.473
127.443
123.210
122.671
85.759
62.060
60.399
60.358
57.352
56.112
51.400
46.794
20.925
50
40
30
20
10
0
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.02-0.11min #(2-11)
438.2077
460.1892
476.1610
407.1291
430.9118
1000
800
600
400
200
0
400
420
440
460
480
500
m/z

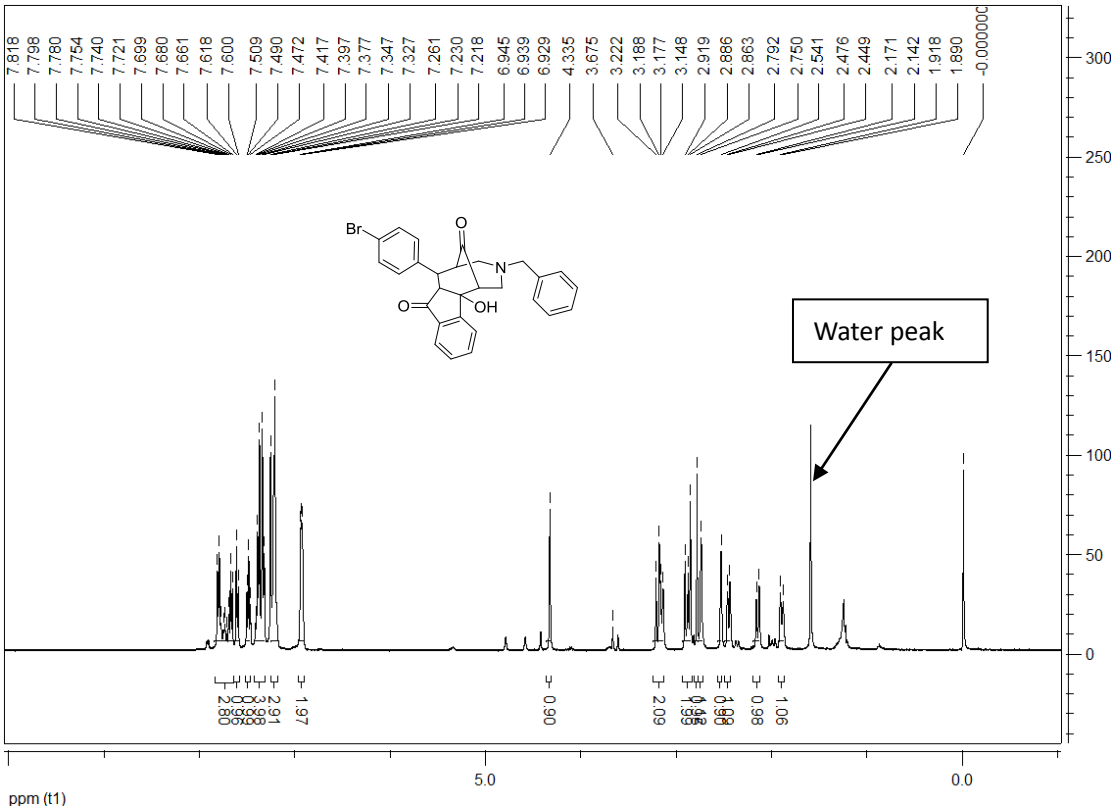
3-benzyl-6-(2-chlorophenyl)-11b-hydroxy-1,2,3,4,5,6,6a,11b-octahydro-7*H*-1,5-methanoinden o[1,2-*d*]azocine-7,12-dione (2b): white solid, 70%, m.p. 107-109℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 7.6 Hz, 1H, ArH), 7.77 (d, *J* = 7.6 Hz, 1H, ArH), 7.68 (t, *J* = 7.6 Hz, 1H, ArH), 7.61 (d, *J* = 7.6 Hz, 1H, ArH), 7.48 (t, *J* = 7.6 Hz, 1H, ArH), 7.38 (d, *J* = 8.0 Hz, 1H, ArH), 7.22-7.13 (m, 5H, ArH), 6.94-6.93 (m, 2H, ArH), 5.00 (s, 1H, CH), 3.31-3.24 (m, 2H, CH), 3.01 (s, 1H, CH), 2.96 (d, *J* = 13.6 Hz, 1H, CH), 2.71 (s, 1H, CH), 2.68 (s, 1H, CH), 2.53-2.50 (m, 2H, CH), 2.16 (dd, J_1 = 11.6 Hz, J_2 = 1.6 Hz, 1H, CH)), 1.92 (d, *J* = 11.6 Hz, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 213.2, 196.2, 151.5, 142.3, 135.9, 134.5, 133.7, 133.5, 129.9, 129.7, 129.5, 129.1, 128.1, 127.9, 127.4, 127.3, 123.4, 122.5, 85.9, 60.1, 59.9, 59.9, 57.6, 55.6, 50.4, 43.8, 18.4; IR(KBr) υ: 3490, 3323, 1703, 1601, 1464, 1036, 751, 704 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{28}H_{25}ClNO_3$([M+H]$^+$): 458.1523, found: 458.1527.

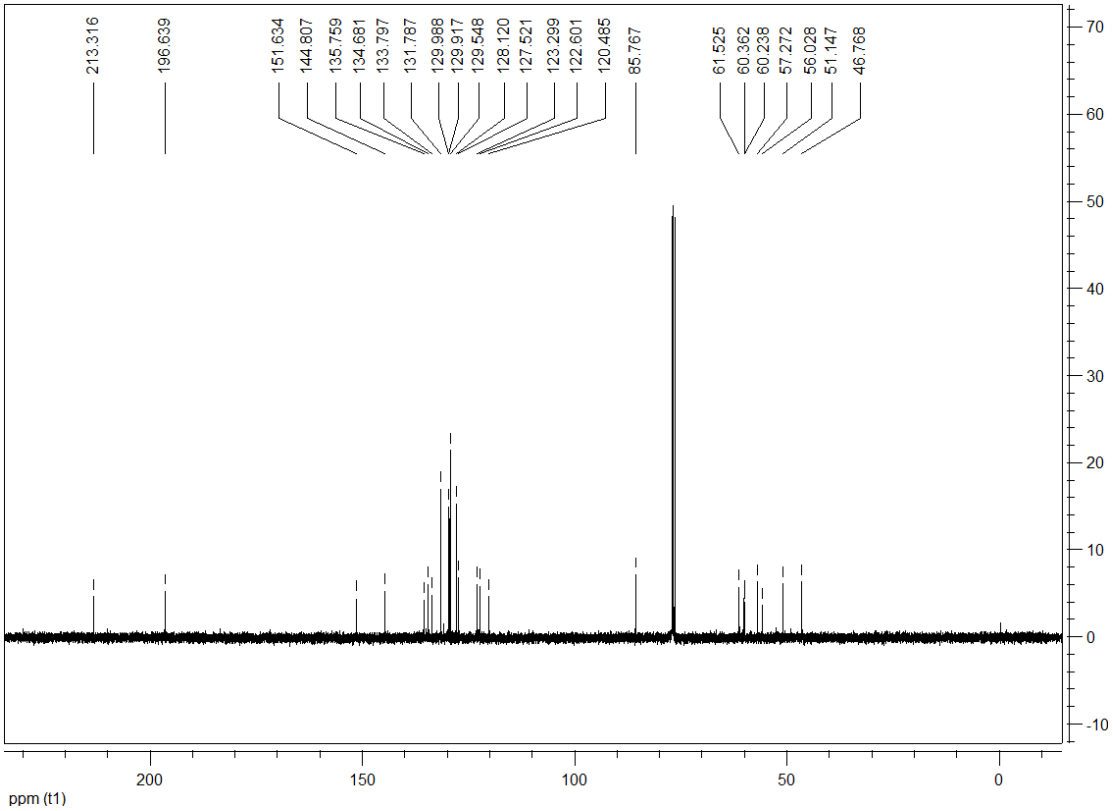


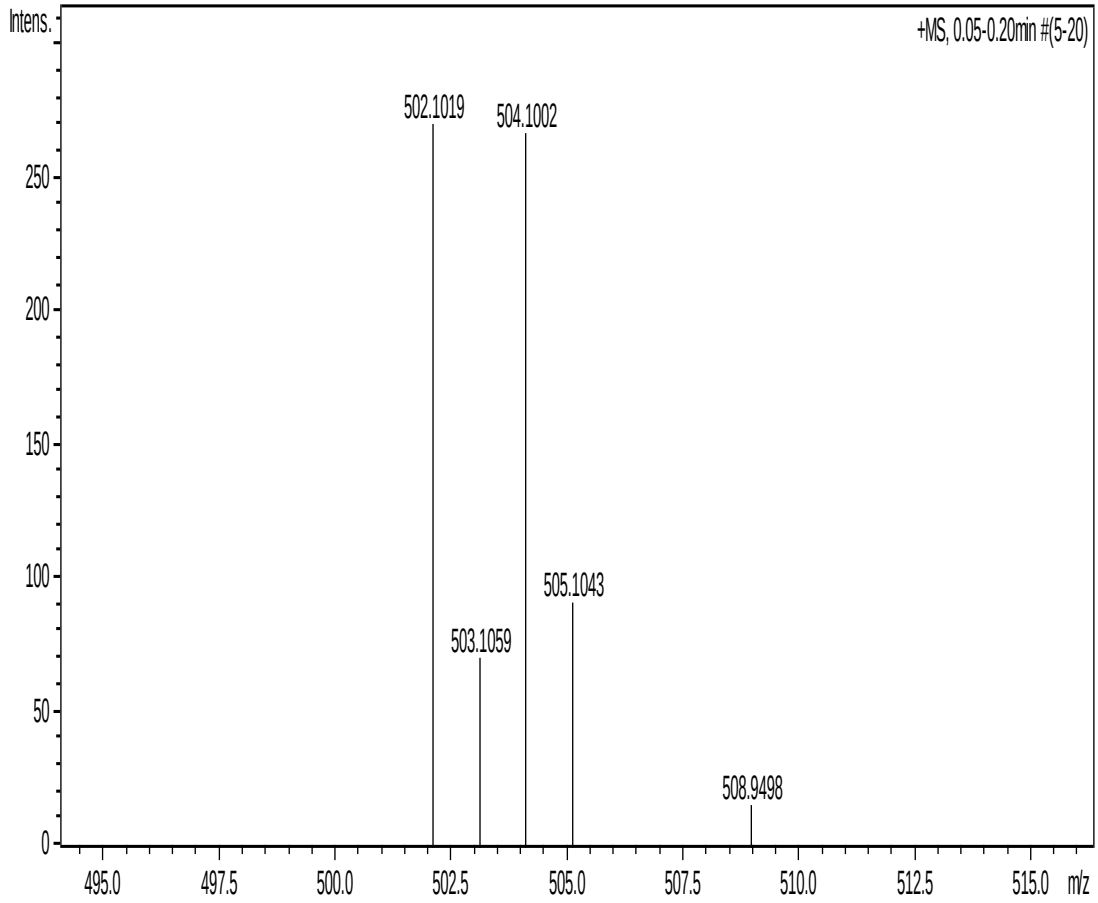

213.299
196.190
151.462
142.265
135.938
134.482
133.665
133.550
129.892
129.706
129.459
129.093
128.076
127.928
127.435
127.268
123.361
122.459
85.941
60.142
59.919
59.872
57.592
55.588
50.445
43.831
18.410
70
60
50
40
30
20
10
0
-10
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.05-0.19min #(5-19)
458.1527
459.1550
460.1526
457.0244
454.2034
300
200
100
0
454
456
458
460
462
464
466
m/z

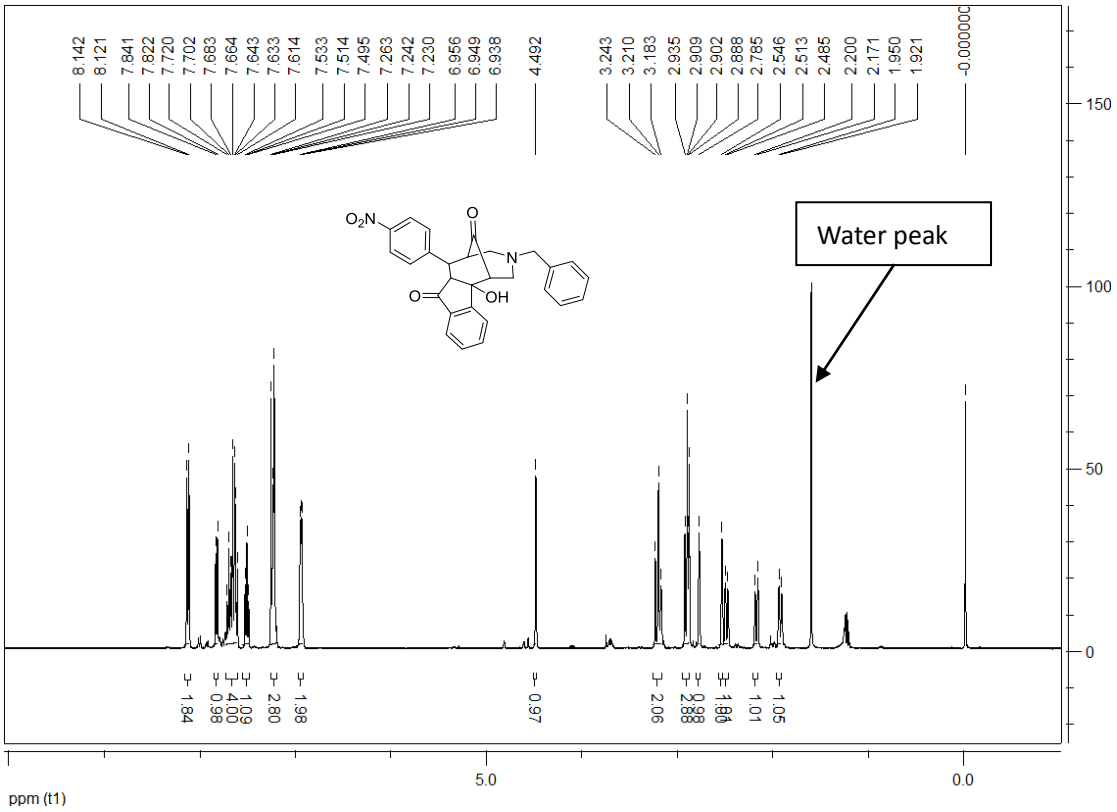
3-benzyl-6-(4-bromophenyl)-11b-hydroxy-1,2,3,4,5,6,6a,11b-octahydro-7*H*-1,5-methanoinde no[1,2-*d*]azocine-7,12-dione (2c): white solid, 56%, m.p. 200-202℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82-7.66 (m, 3H, ArH), 7.61 (d, *J* = 7.2 Hz, 1H, ArH), 7.49 (t, *J* = 7.6 Hz, 1H, ArH), 7.42-7.38 (m, 2H, ArH), 7.34 (d, *J* = 8.0 Hz, 2H, ArH), 7.23-7.22 (m, 3H, ArH), 6.94-6.93 (m, 2H, ArH), 4.34 (s, 1H, CH), 3.22-3.15 (m, 2H, CH), 2.92-2.86 (m, 2H, CH), 2.79 (s, 1H, CH), 2.75 (s, 1H, CH), 2.54 (s, 1H, CH), 2.46 (d, *J*= 10.8 Hz, 1H, CH), 2.16 (d, *J* = 11.6 Hz, 1H, CH), 1.90 (d, *J* = 11.2 Hz, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 213.3, 196.6, 151.6, 144.8, 135.8, 134.7, 133.8, 131.8, 130.0, 129.9, 129.5, 128.1, 127.5, 123.3, 122.6, 120.5, 85.8, 61.5, 60.4, 60.2, 57.3, 56.0, 51.1, 46.8,; IR(KBr) υ: 3374, 2814, 1599, 1483, 1404, 1243, 1019, 830, 746 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{28}H_{25}BrNO_3$([M+H]$^+$): 502.1018, found: 502.1019.

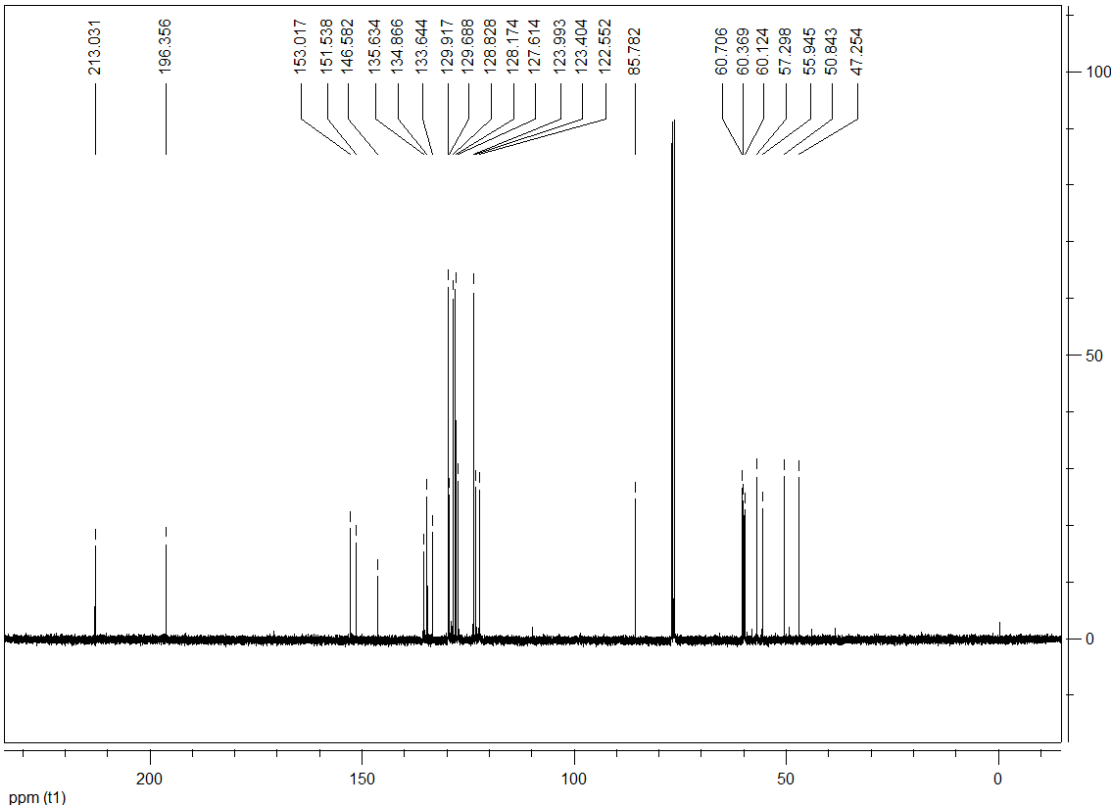


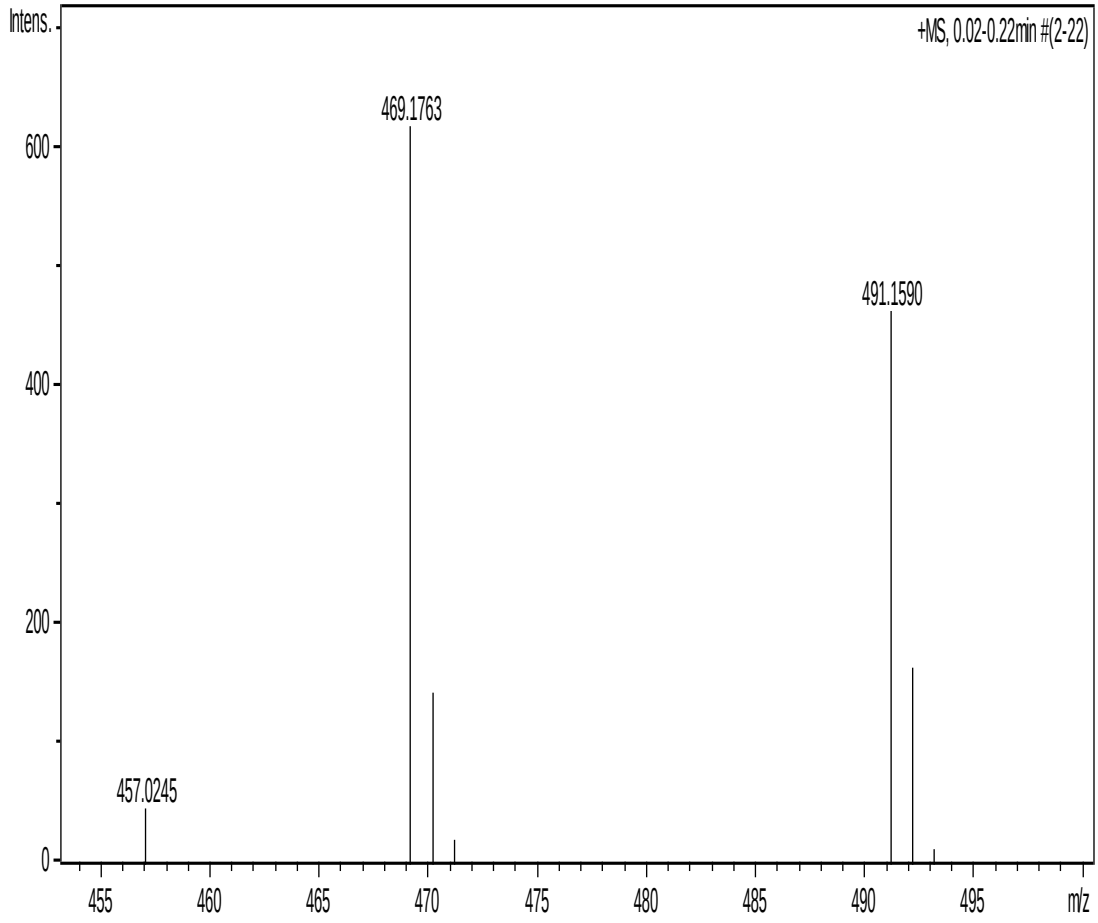

213.316
196.639
151.634
144.807
135.759
134.681
133.797
131.787
129.988
129.917
129.548
128.120
127.521
123.299
122.601
120.485
85.767
61.525
60.362
60.238
57.272
56.028
51.147
46.768
70
60
50
40
30
20
10
0
-10
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.05-0.20min #(5-20)
502.1019
504.1002
505.1043
503.1059
508.9498
250
200
150
100
50
0
495.0
497.5
500.0
502.5
505.0
507.5
510.0
512.5
515.0
m/z

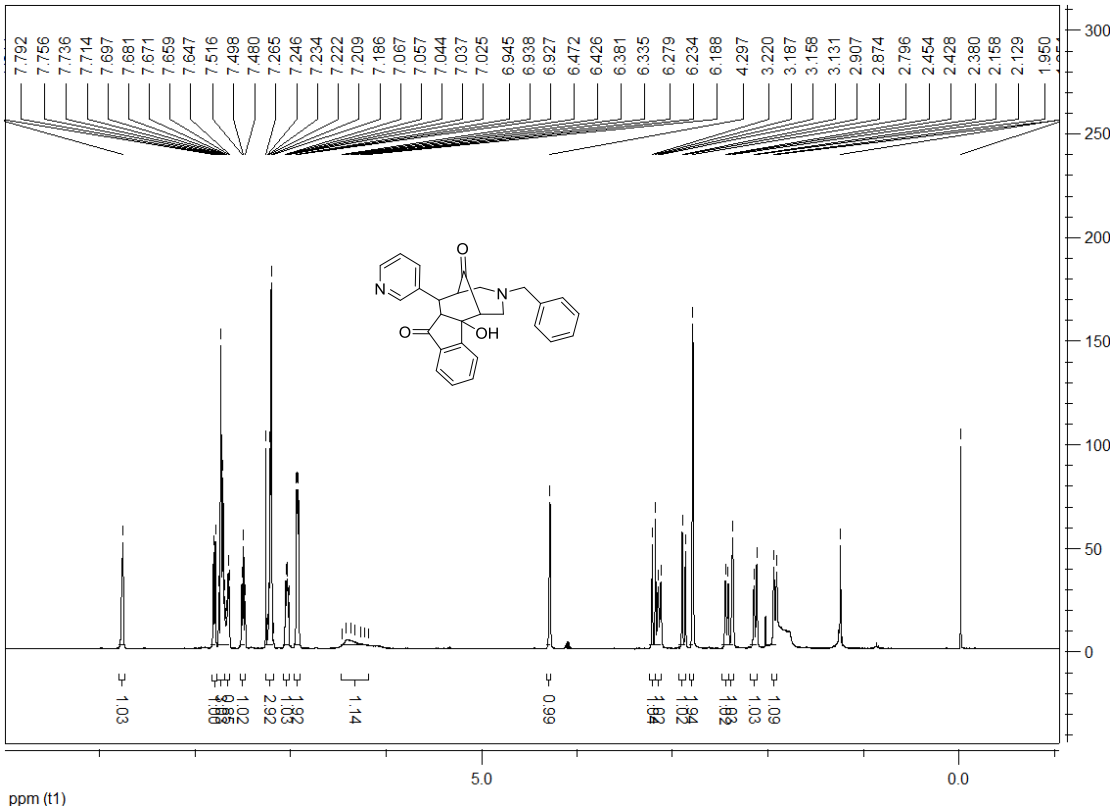
3-benzyl-11b-hydroxy-6-(4-nitrophenyl)-1,2,3,4,5,6,6a,11b-octahydro-7*H*-1,5-methanoindeno [1,2-*d*]azocine-7,12-dione (2d): white solid, 68%, m.p. 190-192℃;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.13 (d, *J* = 8.4 Hz, 2H, ArH), 7.83 (d, *J* = 7.6 Hz, 1H, ArH), 7.72-7.61 (m, 4H, ArH), 7.51 (t, *J* = 7.6 Hz, 1H, ArH), 7.24-7.23 (m, 3H, ArH), 7.00-6.94 (m, 2H, ArH), 4.49 (s, 1H, CH), 3.24-3.18 (m, 2H, CH), 2.94-2.89 (m, 3H, CH), 2.78 (s, 1H, CH), 2.55 (s, 1H, CH), 2.50 (d, *J* = 11.2 Hz, 1H, CH), 2.18 (d, *J* = 11.6 Hz, 1H, CH), 1.94 (d, *J* = 11.6 Hz, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 213.0, 196.4, 153.0, 151.5, 146.6, 135.6, 134.9, 133.6, 129.9, 129.7, 128.8, 128.2, 127.6, 124.0, 123.4, 122.6, 85.8, 60.7, 60.4, 60.1, 57.3, 55.9, 50.8, 47.3,; IR(KBr) υ: 3324, 2834, 1701, 1599, 1515, 1402, 1345, 1063, 844, 748, 701 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{29}H_{28}NO_3$([M+H]$^+$): 469.1763, found: 469.1763.

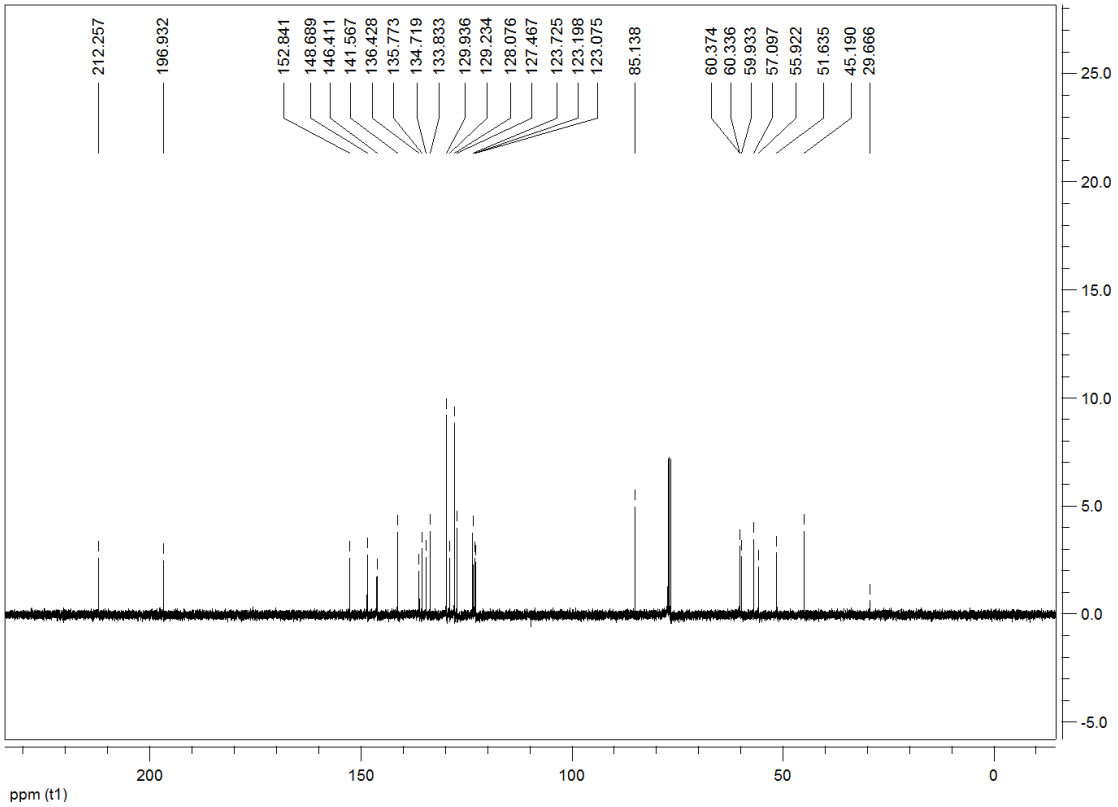


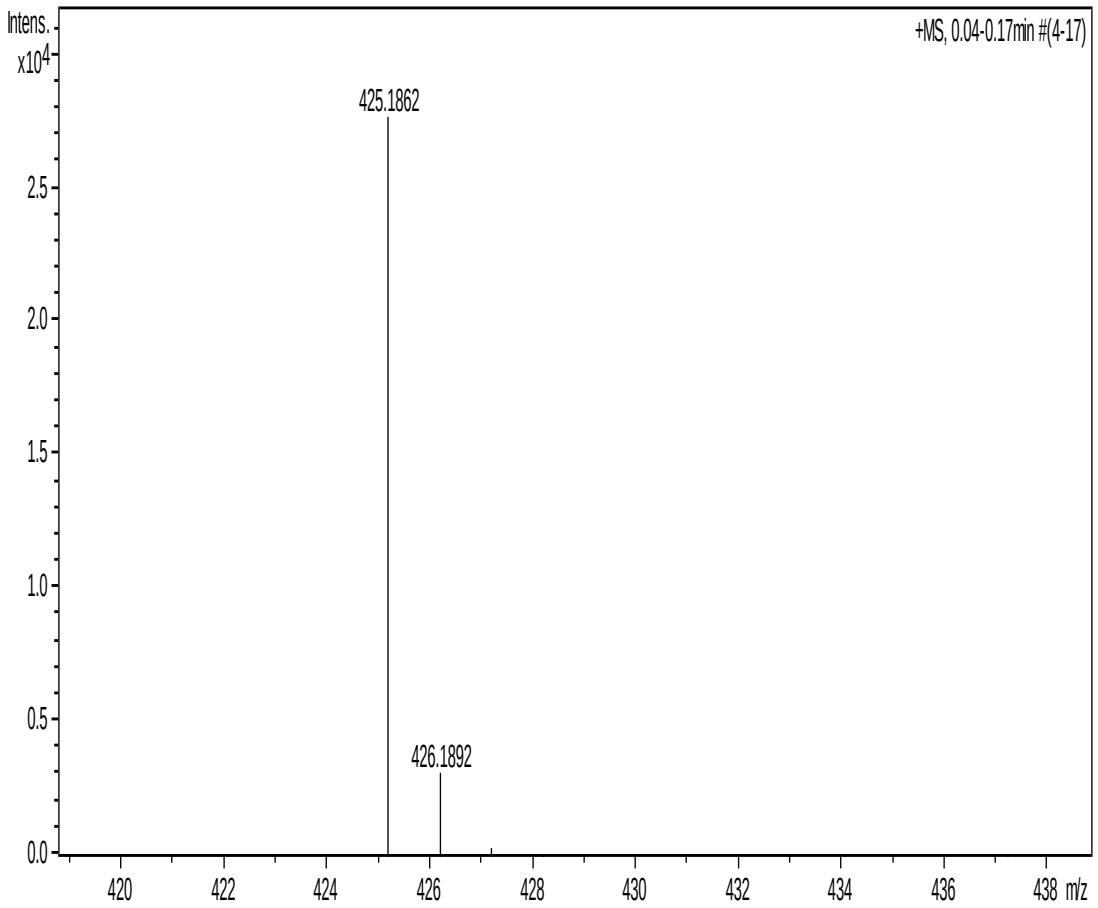

213.031
196.356
153.017
151.538
146.582
135.634
134.866
133.644
129.917
129.688
128.828
128.174
127.614
123.993
123.404
122.552
85.782
60.706
60.369
60.124
57.298
55.945
50.843
47.254
100
50
0
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.02-0.22min #(2-22)
469.1763
491.1590
457.0245
600
400
200
0
455
460
465
470
475
480
485
490
495
m/z

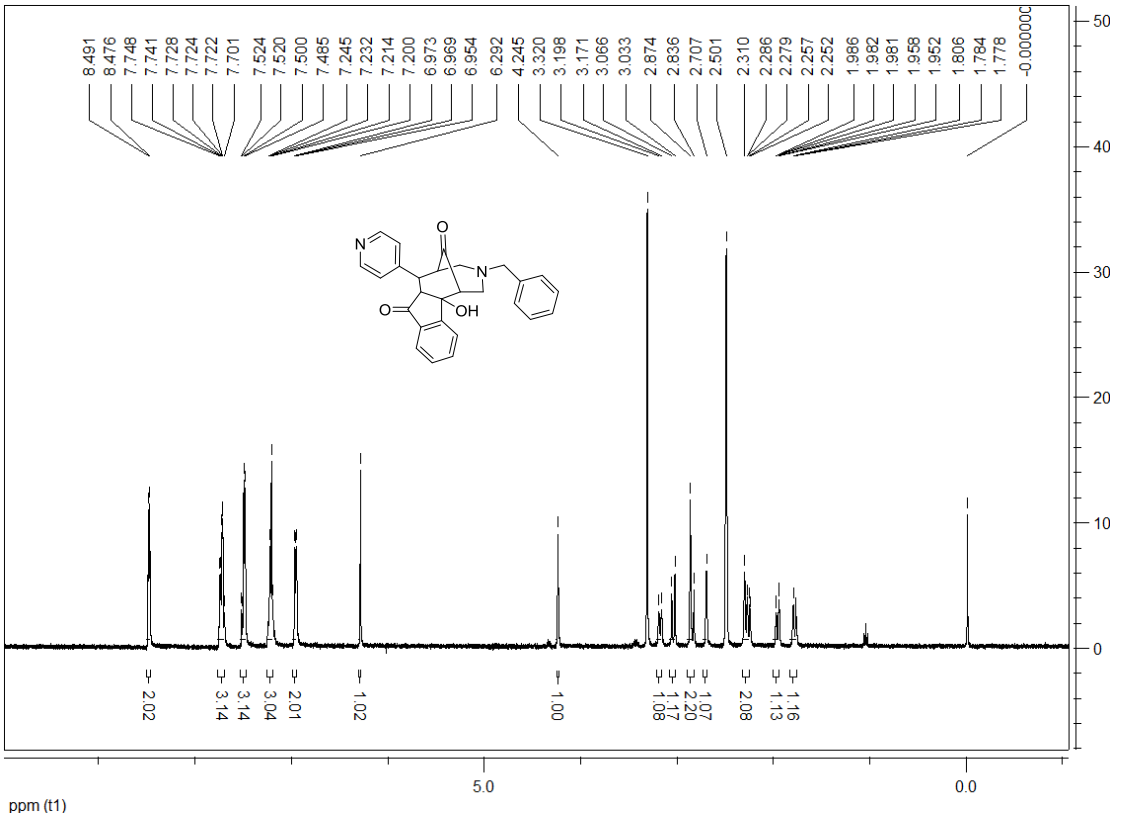
3-benzyl-11b-hydroxy-6-(pyridin-3-yl)-1,2,3,4,5,6,6a,11b-octahydro-7*H*-1,5-methanoindeno[1,2-*d*]azocine-7,12-dione (2e): white solid, 66%, m.p. 187-189℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 (s, 1H, ArH), 7.80 (t,*J* = 7.6 Hz, 1H, ArH), 7.76-7.70 (m, 3H, ArH), 7.68-7.65 (m, 1H, ArH), 7.50 (t,*J* = 7.2 Hz, 1H, ArH), 7.25-7.19 (m, 3H, ArH), 7.07-7.02 (m, 1H, ArH), 6.94-6.93 (m, 2H, ArH), 6.47-6.19 (m, 1H, ArH), 4.30 (s, 1H, CH), 3.20 (d, *J* = 13.2 Hz, 1H, CH), 3.14 (d, *J* = 10.8 Hz, 1H, CH), 2.89 (d, *J* = 13.2 Hz, 1H, CH), 2.80 (s, 2H, CH), 2.44 (d, *J* = 10.4 Hz, 1H, CH), 2.38 (s, 1H, CH), 2.14 (d, *J* = 11.6 Hz, 1H, CH), 1.94 (d, *J* = 12.0 Hz, 1H, CH, CH_3); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 212.3, 196.9, 152.8, 148.7, 146.4, 141.6, 136.4, 135.8, 134.7, 133.8, 129.9, 129.2, 128.1, 127.5, 123.7, 123.2, 123.1, 85.1, 60.4, 60.3, 59.9, 57.1, 55.9, 51.6, 45.2, 29.7; IR(KBr) υ: 3359, 2822, 2772, 1727, 1701, 1602, 1240 1062, 748, 706 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{27}H_{25}N_2O_3$([M+H]$^+$): 425.1865, found: 425.1862.

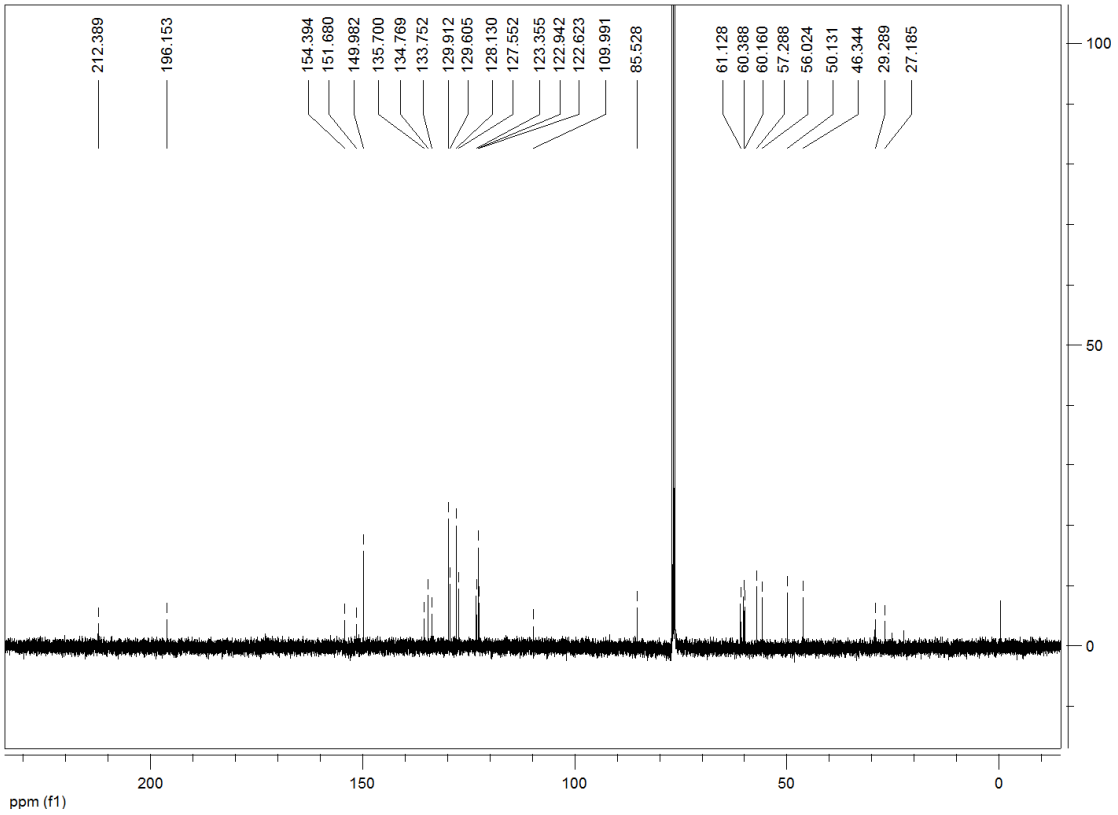


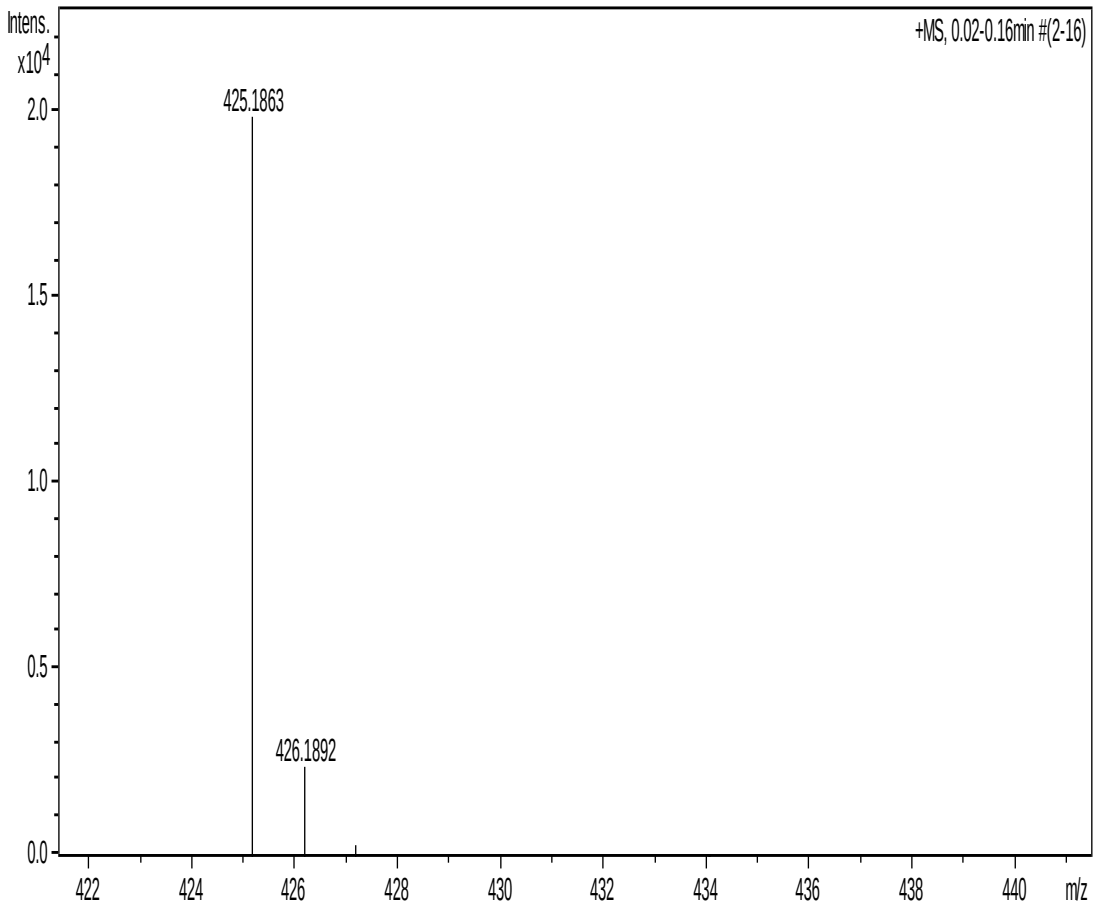

212.257
196.932
152.841
148.689
146.411
141.567
136.428
135.773
134.719
133.833
129.936
129.234
128.076
127.467
123.725
123.198
123.075
85.138
60.374
60.336
59.933
57.097
55.922
51.635
45.190
29.666
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (t1)


Intens.
x10^4
+MS, 0.04-0.17min #(4-17)
425.1862
426.1892
2.5
2.0
1.5
1.0
0.5
0.0
420
422
424
426
428
430
432
434
436
438 m/z

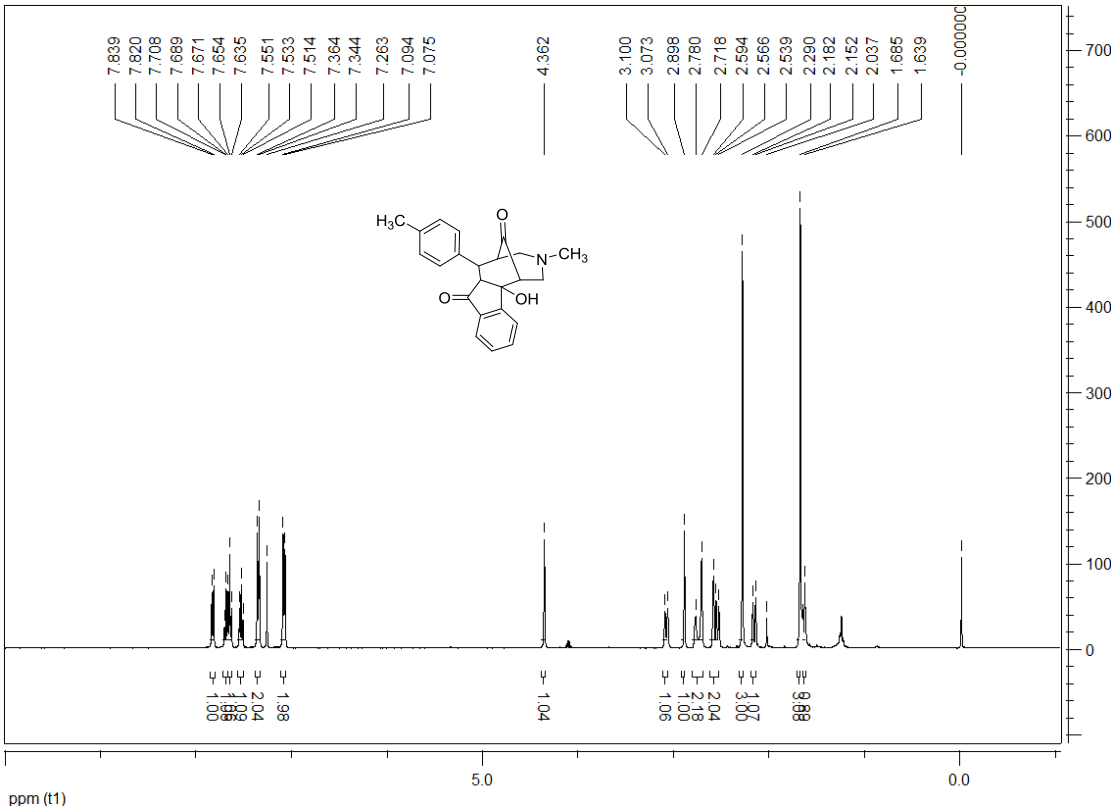
3-benzyl-11b-hydroxy-6-(pyridin-4-yl)-1,2,3,4,5,6,6a,11b-octahydro-7*H*-1,5-methanoindeno[1,2-*d*]azocine-7,12-dione (2f): white solid, 62%, m.p. 235-237℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29 (s, 2H, ArH), 7.82 (d, *J* = 7.6 Hz, 1H, ArH), 7.70 (t, *J* = 7.6 Hz, 1H, ArH), 7.64 (d, *J* = 7.6 Hz, 1H, ArH), 7.50 (t,*J* = 7.2 Hz, 1H, ArH), 7.36 (d, *J* = 5.2 Hz, 2H, ArH), 7.23-7.22 (m, 3H, ArH), 6.95-6.93 (m, 2H, ArH), 4.31 (s, 1H, CH), 3.21 (d, *J* = 13.6 Hz, 1H, CH), 3.15 (d, *J* = 10.8 Hz, 1H, CH), 2.91 (d, *J* = 13.6 Hz, 1H, CH), 2.82 (s, 1H, CH), 2.77 (s, 1H, CH), 2.54 (s, 1H, CH), 2.47 (d, *J* = 10.8 Hz, 1H, CH), 2.17 (d, *J* = 11.6 Hz, 1H, CH), 1.91 (d, *J* = 11.6 Hz, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 212.4, 196.2, 154.4, 151.7, 150.0, 135.7, 134.8, 133.8, 129.9, 129.6, 128.1, 127.6, 123.4, 122.9, 122.6, 110.0, 85.5, 61.1, 60.4, 60.2, 57.3, 56.0, 50.1, 46.3, 29.3, 27.2; IR(KBr) υ: 3123, 2799, 1723, 1602, 1456, 1067, 747, 704 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{27}H_{25}N_2O_3$ ($[M+H]^+$): 425.1865, found: 425.1863.

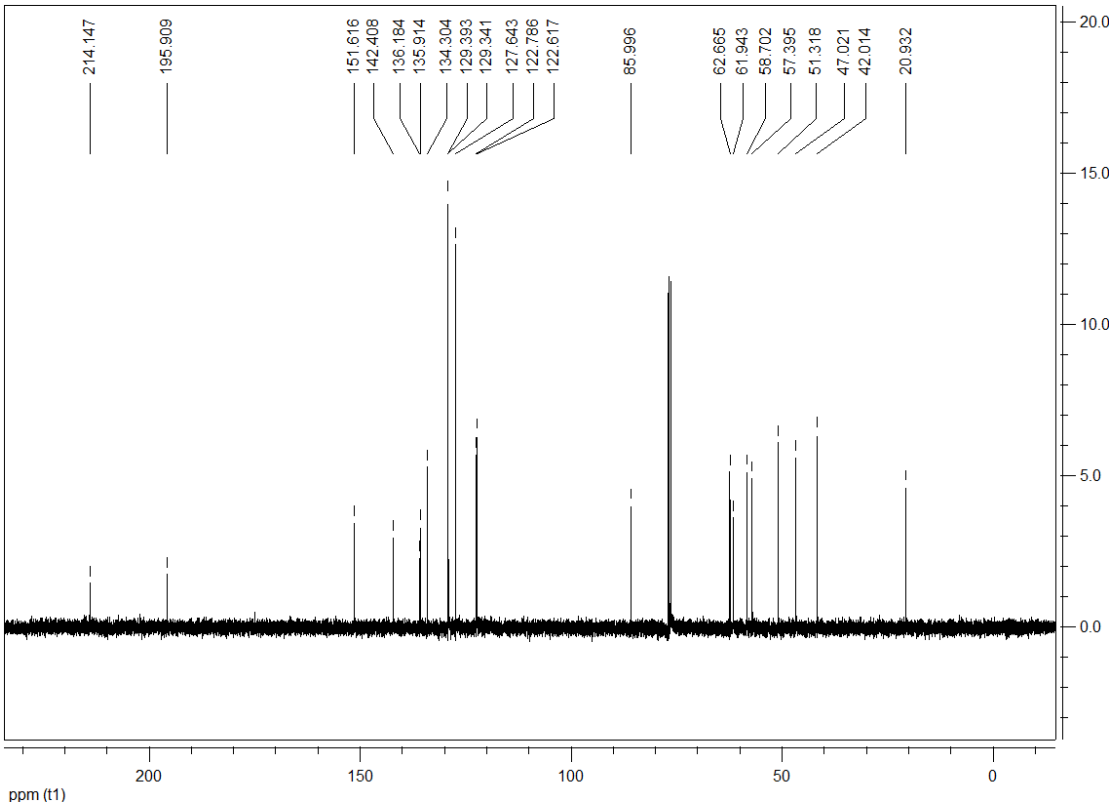


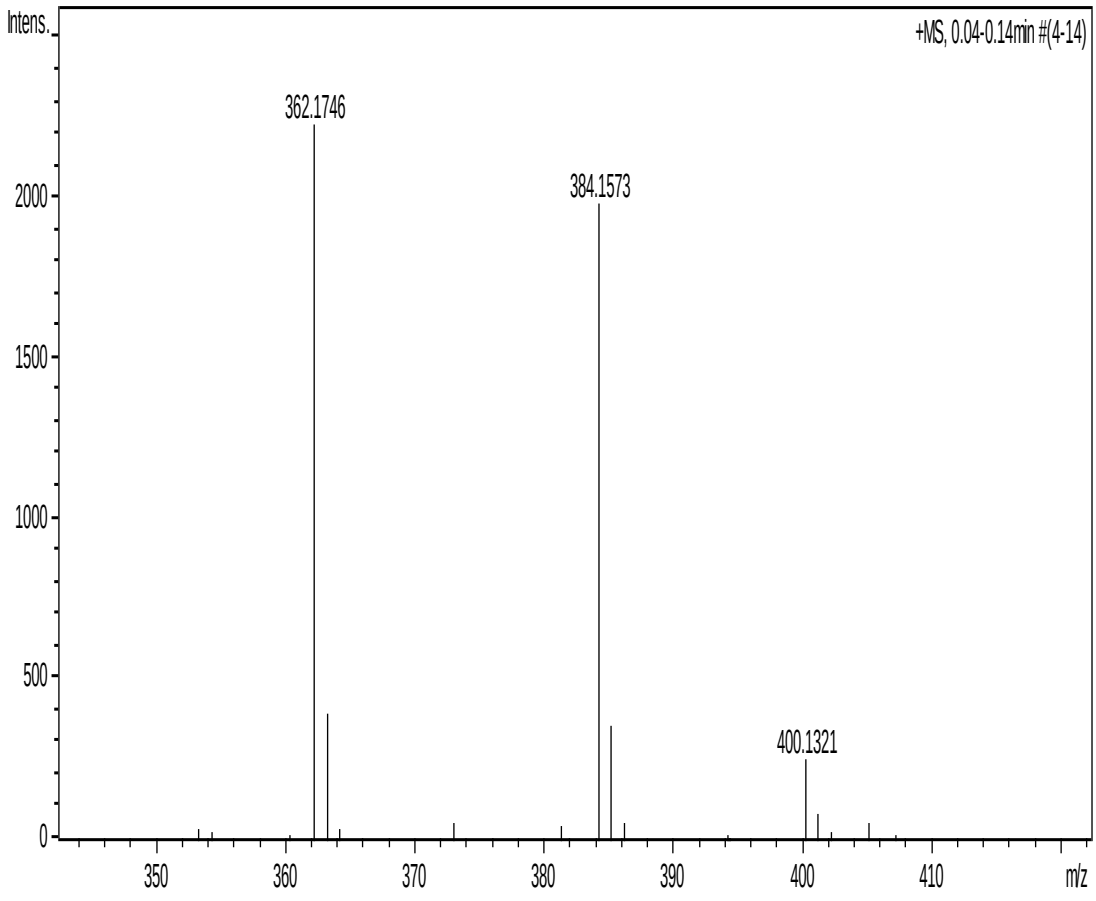

212.389
196.153
154.394
151.680
149.982
135.700
134.769
133.752
129.912
129.605
128.130
127.552
123.355
122.942
122.623
109.991
85.528
61.128
60.388
60.160
57.288
56.024
50.131
46.344
29.289
27.185
100
50
0
200
150
100
50
0
ppm (f1)


Intens.
x10^4
+MS, 0.02-0.16min #(2-16)
425.1863
426.1892
2.0
1.5
1.0
0.5
0.0
422
424
426
428
430
432
434
436
438
440
m/z

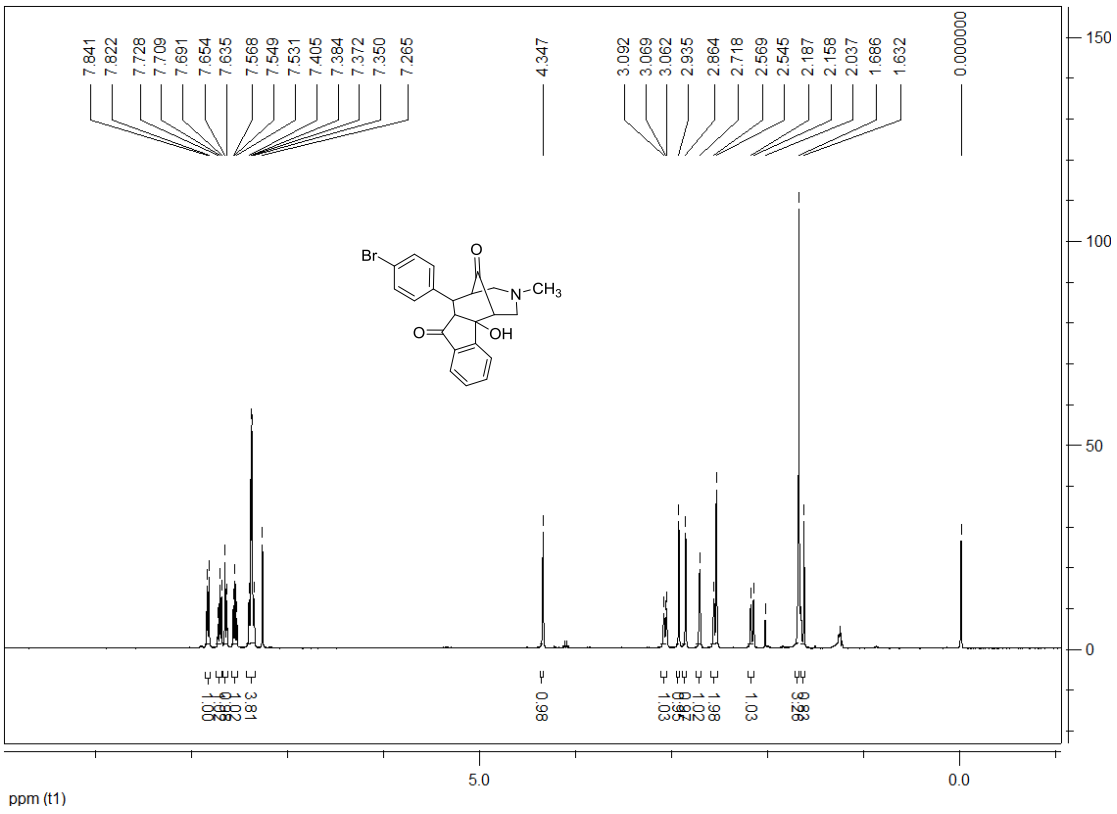
11b-hydroxy-3-methyl-6-(p-tolyl)-1,2,3,4,5,6,6a,11b-octahydro-7*H*-1,5-methanoindeno[1,2-*d*] azocine-7,12-dione (2g): white solid, 66%, m.p. 210-222℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 7.6 Hz, 1H, ArH), 7.69 (t, *J* = 7.6Hz, 1H, ArH), 7.64 (d, *J* = 7.6Hz, 1H, ArH), 7.53 (t, *J* = 7.6 Hz, 1H, ArH), 7.35 (d, *J* = 8.0 Hz, 2H, ArH), 7.08 (d, *J* = 7.6 Hz, 2H, ArH), 4.36 (s, 1H, CH), 3.08 (d, *J* = 10.8 Hz, 1H, CH), 2.90 (s, 1H, CH), 2.78-2.72 (m, 2H, CH), 2.59-2.54 (m, 2H, CH), 2.29 (s, 3H, CH_3), 2.17 (d, *J* = 12.0 Hz, 1H, CH), 1.68 (s, 3H, CH_3), 1.64 (s, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 214.1, 195.9, 151.6, 142.4, 136.2, 135.9, 134.3, 129.4, 129.3, 127.6, 122.8, 122.6, 86.0, 62.7, 61.9, 58.7, 57.4, 51.3, 47.0, 42.0, 20.9,; IR(KBr) υ: 3453, 2794, 1707, 1602, 1287, 1060, 765 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{23}H_{23}NO_3$([M+H]$^+$): 362.1756, found: 362.1746.

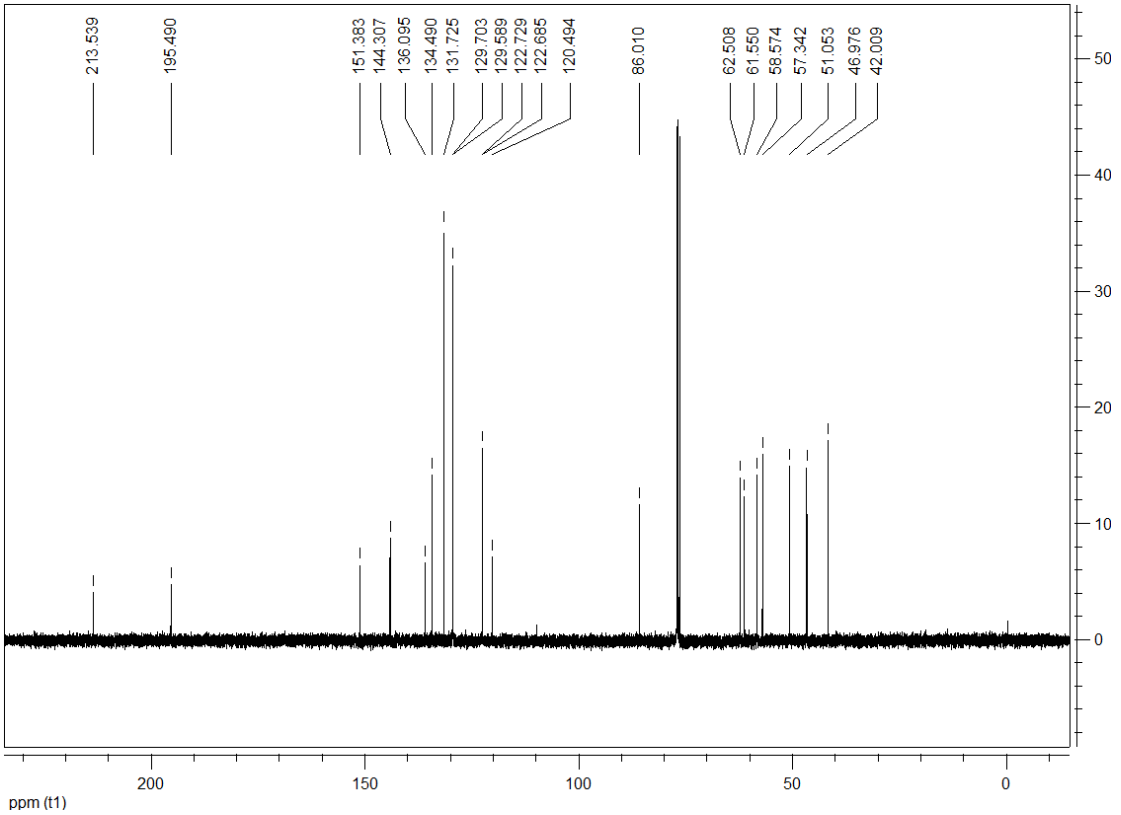


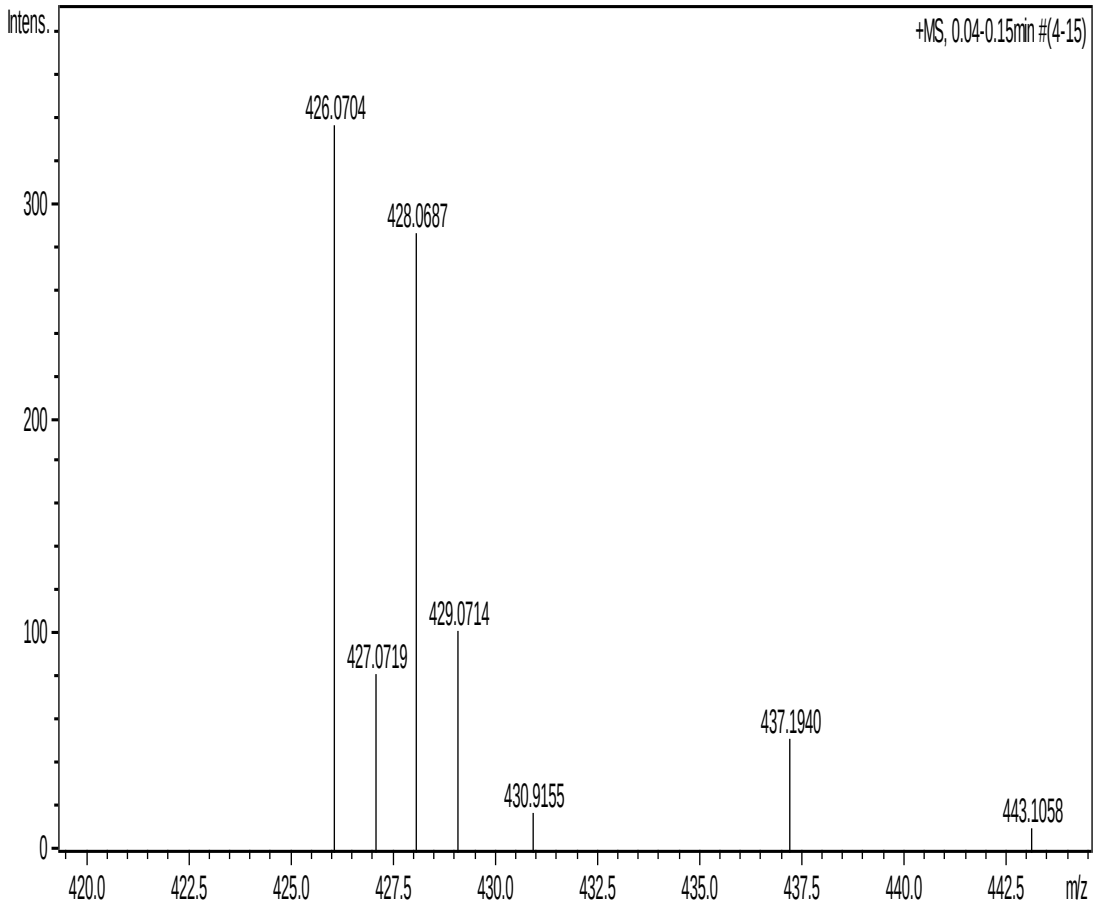

214.147
195.909
151.616
142.408
136.184
135.914
134.304
129.393
129.341
127.643
122.786
122.617
85.996
62.665
61.943
58.702
57.395
51.318
47.021
42.014
20.932
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.04-0.14min #(4-14)
362.1746
384.1573
400.1321
2000
1500
1000
500
0
350
360
370
380
390
400
410
m/z

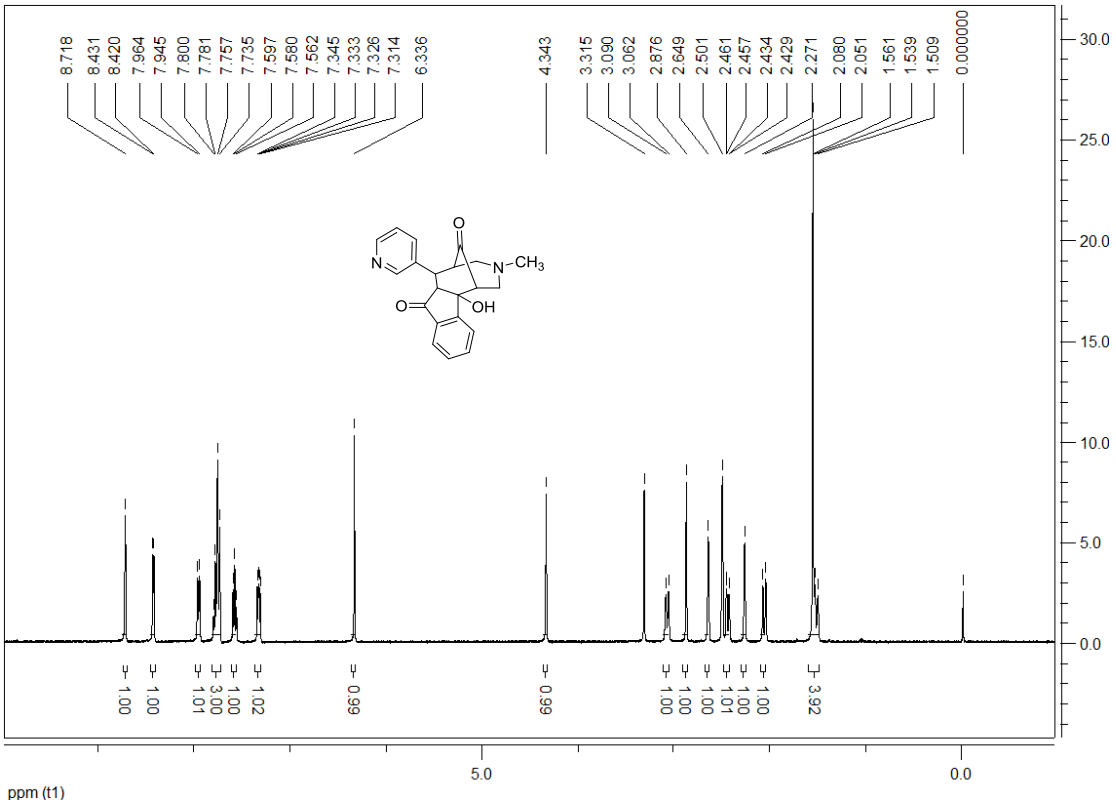
6-(4-bromophenyl)-11b-hydroxy-3-methyl-1,2,3,4,5,6,6a,11b-octahydro-7H-1,5-methanoindeno[1,2-d]azocine-7,12-dione (2h): white solid, 50%, m.p. 223-225℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 7.6 Hz, 1H, ArH), 7.71 (t, *J* = 7.6 Hz, 1H, ArH), 7.64 (d, *J* = 7.6 Hz, 1H, ArH), 7.55 (t, *J* = 7.6 Hz, 1H, ArH), 7.38 (m, 4H, ArH), 4.35 (s, 1H, CH), 3.08 (d, *J* = 12.0 Hz, 1H, CH), 2.94 (s, 1H, CH), 2.86 (s, 1H, CH), 2.72 (s, 1H, CH), 2.57-2.54 (m, 2H, CH), 2.18 (d, *J* = 11.6 Hz, 1H, CH), 1.69 (s, 3H, CH_3), 1.63 (s, 1H, CH); ^{13}C NMR (100 MHz,$CDCl_3$) δ: 213.5, 195.5, 151.4, 144.3, 136.1, 134.5, 131.7, 129.7, 129.6, 122.7, 122.7, 120.5, 86.0, 62.5, 61.5, 58.6, 57.3, 51.1, 47.0, 42.0,; IR(KBr) υ: 3498, 2941, 2787, 1703, 1597, 1293, 1239, 1140, 1064, 1015, 758 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{22}H_{21}BrNO_3$([M+H]$^+$): 426.0705, found: 426.0704.

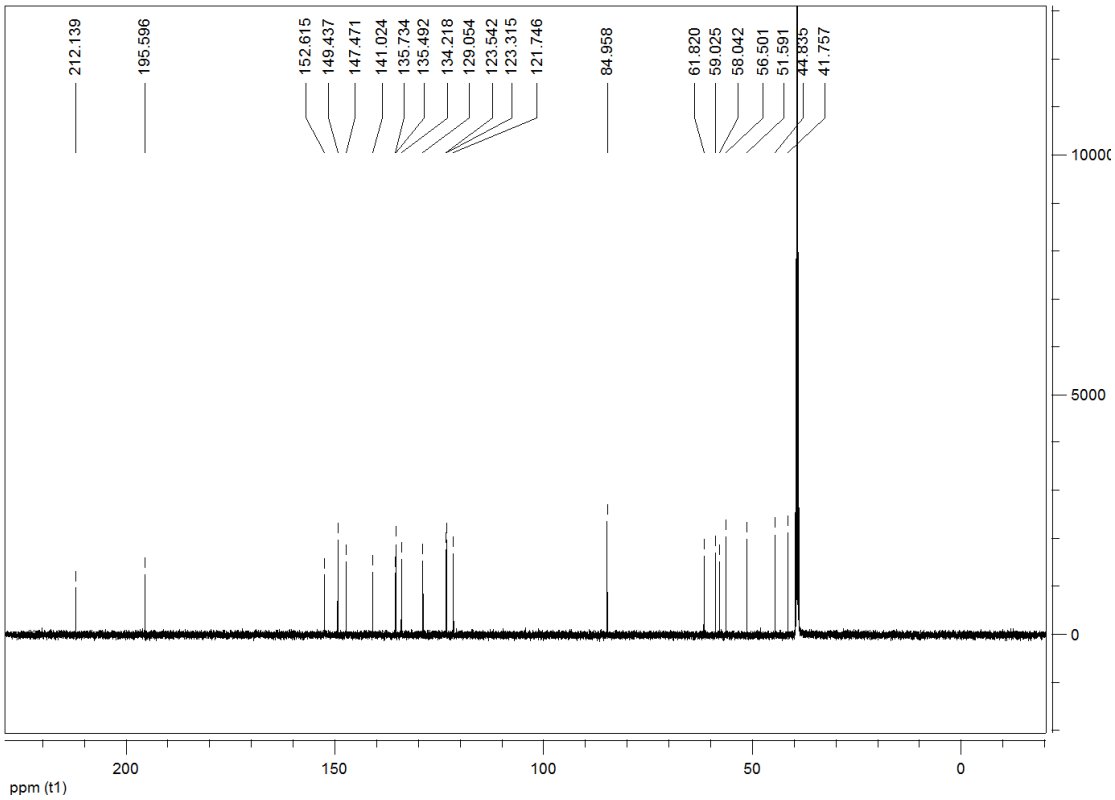


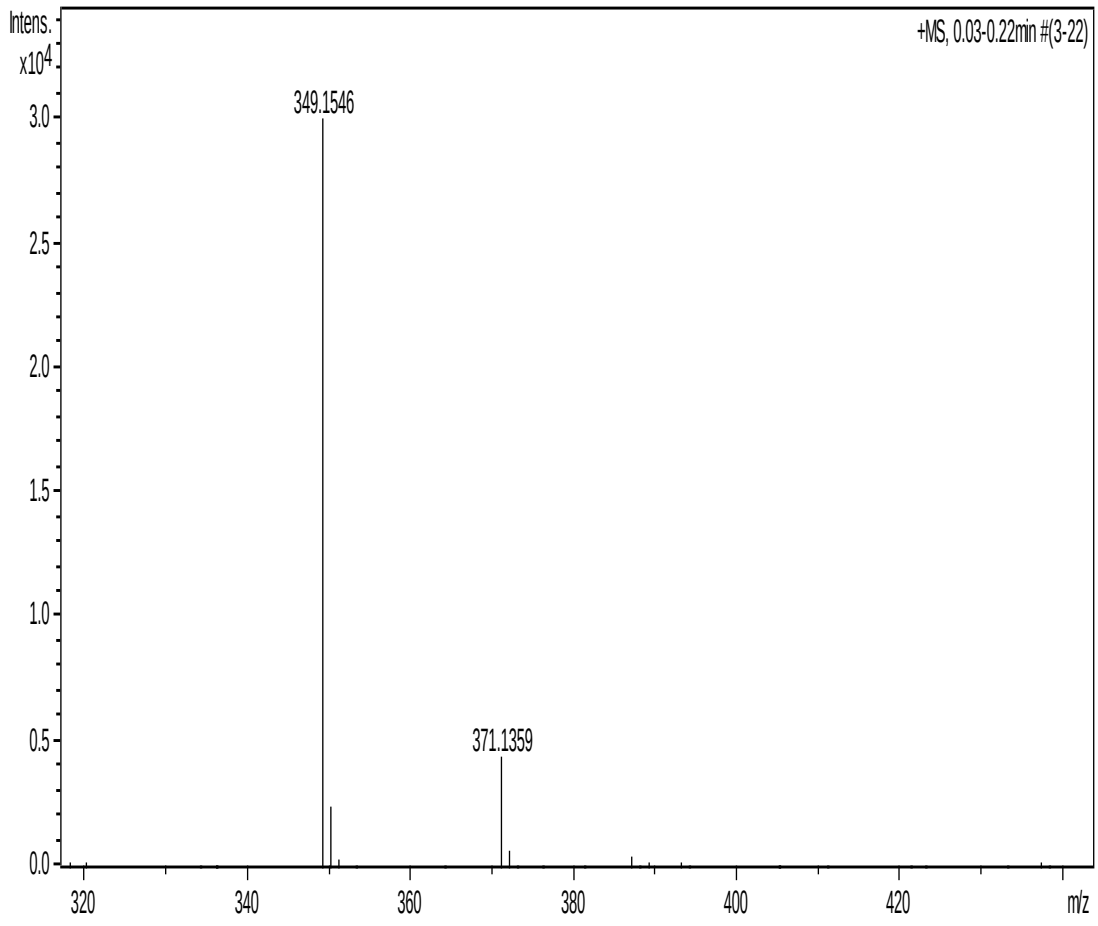

213.539
195.490
151.383
144.307
136.095
134.490
131.725
129.703
129.589
122.729
122.685
120.494
86.010
62.508
61.550
58.574
57.342
51.053
46.976
42.009
50
40
30
20
10
0
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.04-0.15min #(4-15)
426.0704
428.0687
429.0714
427.0719
437.1940
430.9155
443.1058
300
200
100
0
420.0
422.5
425.0
427.5
430.0
432.5
435.0
437.5
440.0
442.5
m/z

11b-hydroxy-3-methyl-6-(pyridin-3-yl)-1,2,3,4,5,6,6a,11b-octahydro-7*H*-1,5-methanoindeno[1,2-*d*]azocine-7,12-dione (2i): white solid, 59%, m.p. 248-250℃; ^{1}H NMR (400 MHz, DMSO) δ: 8.72 (s, 1H, ArH), 8.43 (d, *J* = 4.4 Hz, 1H, ArH), 7.95 (d, *J* = 7.6 Hz, 1H, ArH), 7.80-7.74 (m, 3H, ArH), 7.58 (t,*J* = 6.8 Hz, 1H, ArH), 7.33 (dd, J_1 = 7.6 Hz, J_2 = 4.8 Hz, 1H, ArH), 6.34 (s, 1H, CH), 4.34 (s, 1H, CH), 3.08 (d, *J* = 11.2 Hz, 1H, CH), 2.88 (s, 1H, CH), 2.65 (s, 1H, CH), 2.44 (dd, J_1 = 10.8 Hz, J_2 = 1.6 Hz, 1H, CH), 2.27 (s, 1H, CH), 2.07 (d, *J* = 11.6 Hz, 1H, CH), 1.56-1.51 (m, 4H, CH, CH_3); ^{13}C NMR (150 MHz,$CDCl_3$) δ: 212.1, 195.6, 152.6, 149.4, 147.5, 141.0, 135.7, 135.5, 134.2, 129.1, 123.5, 123.3, 121.7, 85.0, 61.8, 59.0, 58.0, 56.5, 51.6, 44.8, 41.8; IR(KBr) υ: 3421, 3121, 2801, 1720, 1601, 1468, 1428, 1283, 1061, 790, 762, 711 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{21}H_{21}NO_3$([M+H]$^+$): 349.1552, found: 349.1546.




212.139
195.596
152.615
149.437
147.471
141.024
135.734
135.492
134.218
129.054
123.542
123.315
121.746
84.958
61.820
59.025
58.042
56.501
51.591
44.835
41.757
10000
5000
0
200
150
100
50
0
ppm (t1)


Intens.
x10^4
+MS, 0.03-0.22min #(3-22)
349.1546
371.1359
3.0
2.5
2.0
1.5
1.0
0.5
0.0
320
340
360
380
400
420
m/z