Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Domino aza/oxa-hetero-Diels-Alder reaction for construction of novel spiro[pyrido[3',2':5,6]pyrano[2,3-*d*]pyrimidine-7,5'-pyrimidine]

Wen-Juan Yan, Qiu Sun, Jing Sun, Chao-Guo Yan*

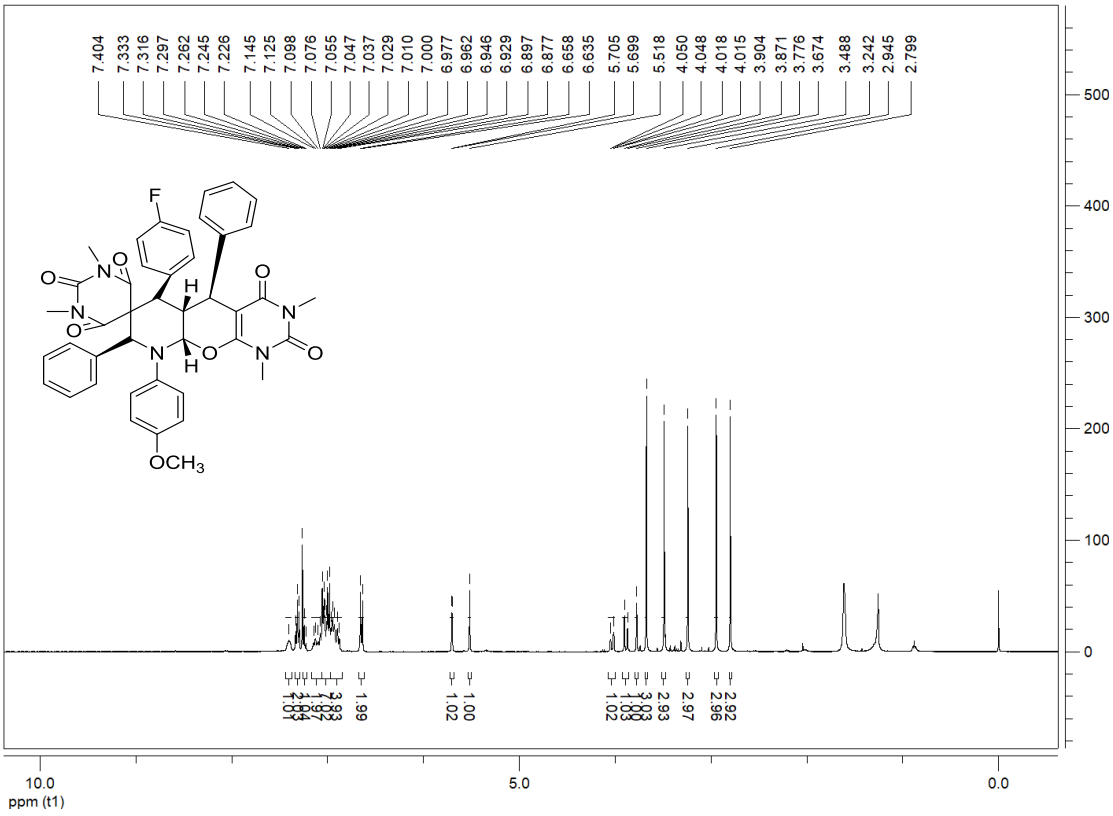
Supporting Information

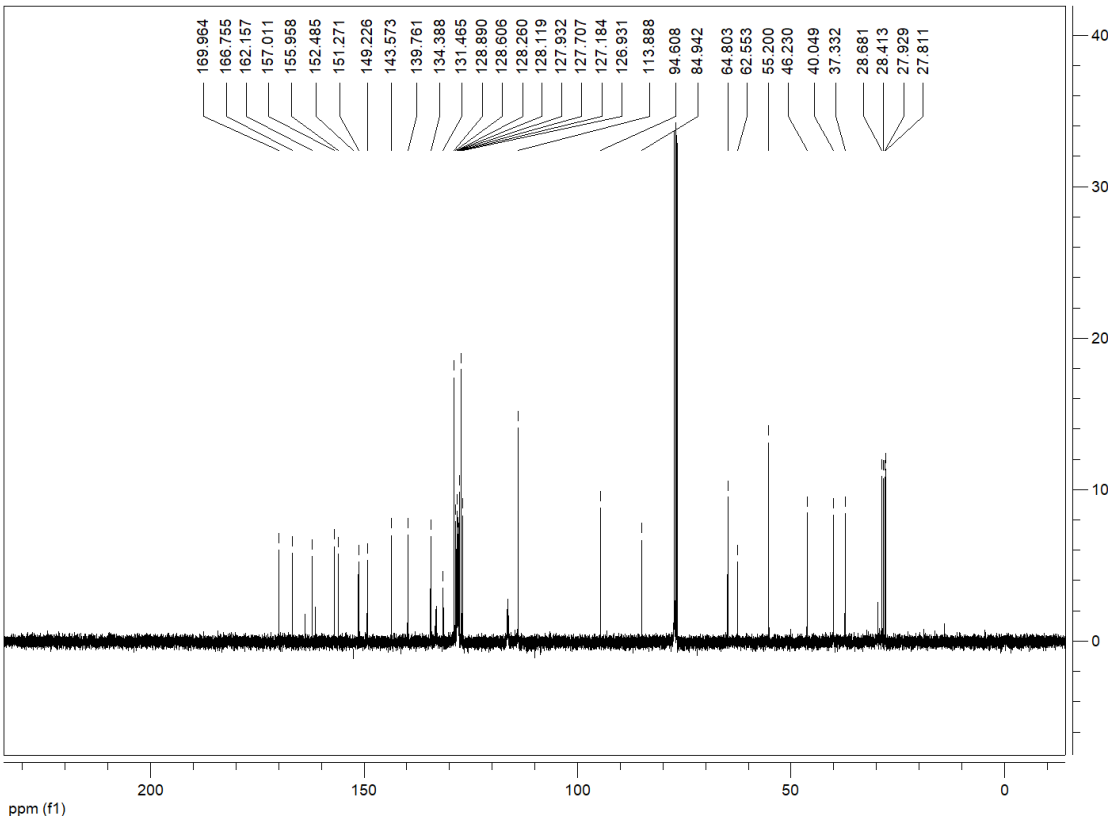
Experimental section

General procedure for the synthesis of polycyclic compounds 3-5 via annulation reaction: Under N_2 atmosphere, a mixture of *α,β*-unsaturated *N*-arylaldimine (0.5 mmol), 2-arylidene-1,3-dimethylbarbituric acid (1.5 mmol) and CH_2Cl_2 (10.0 mL) was added in a Schlenk tube. The mixture was stirred at room temperature for six hours. The solvent was removed by rotatory evaporation at reduced pressure. The residue was subjected with silicon column chromatography with mixed petroleum ether and ethyl acetate (V/V = 2:1) as eluent to give pure product for analysis.

***rel*-(5S,5aS,6S,8R,9aS)-6-(4-fluorophenyl)-9-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-5,8-diphenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3a):**

yellow solid, 80%, m.p.152-154℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (brs, 1H, ArH), 7.32 (t, *J* = 14.4 Hz, 2H, ArH), 7.26 -7.23 (m, 1H, ArH), 7.14-7.08 (m, 2H, ArH), 7.06-6.98 (m, 7H, ArH), 6.96-6.88 (m, 4H, ArH), 6.65 (d, *J* = 9.2 Hz, 2H, ArH), 5.70 (d, *J* = 2.4 Hz, 1H, CH), 5.52 (s, 1H, CH), 4.05-4.02 (m, 1H, CH), 3.88 (d, *J* = 13.2 Hz, 1H, CH), 3.78 (s, 1H, CH), 3.67 (s, 3H, OCH_3), 3.49 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 2.94 (s, 3H, NCH_3), 2.80 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 166.7, 162.1, 157.0, 155.9, 151.2, 149.2, 143.5, 139.7, 134.3, 131.4, 128.8, 128.6, 128.2, 128.1, 127.9, 127.7, 127.1, 126.9, 113.8, 94.6, 84.9, 64.8, 62.5, 55.1, 46.2, 40.0, 37.3, 28.6, 28.4, 27.9, 27.8; IR(KBr) υ: 3032, 2958, 1687, 1642, 1487, 1381, 1272, 1166, 1016, 914, 829, 781, 703, 643 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{42}H_{39}FN_5O_7$([M+H]$^+$): 744.2834, found: 744.2799.

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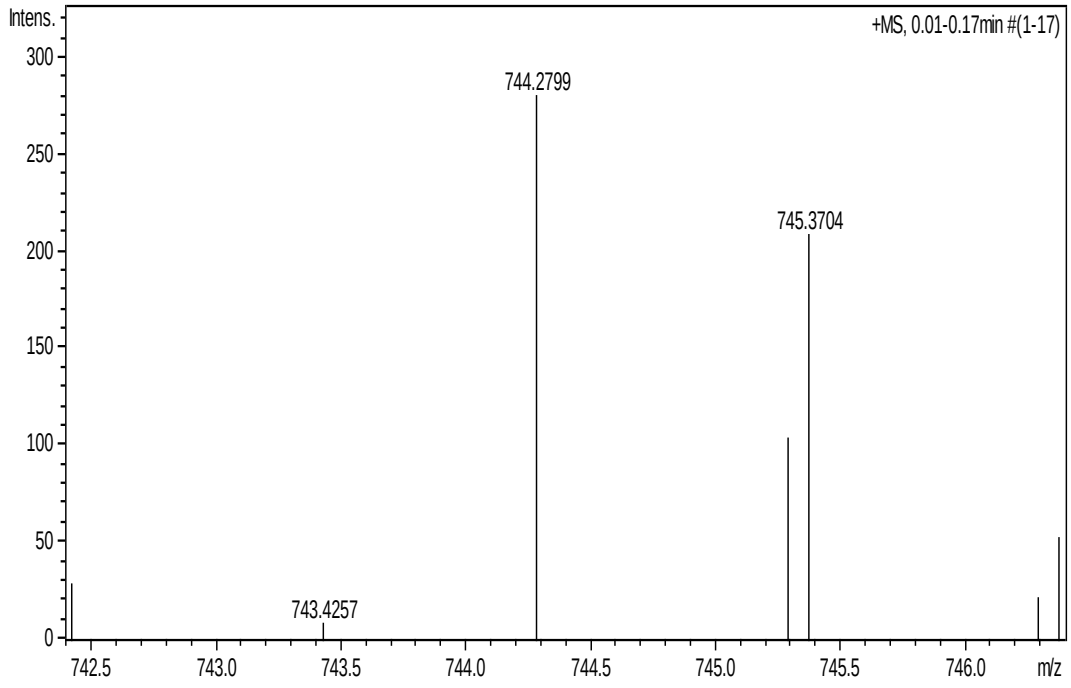
ppm (f1)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743.5
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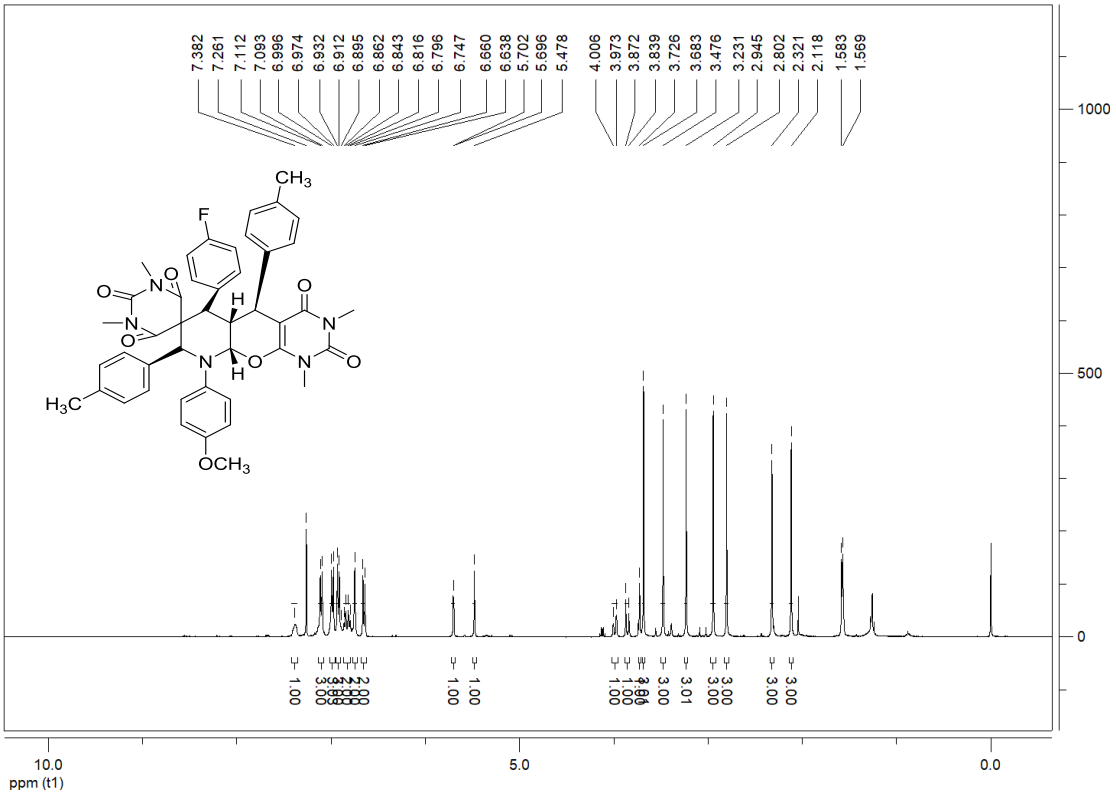
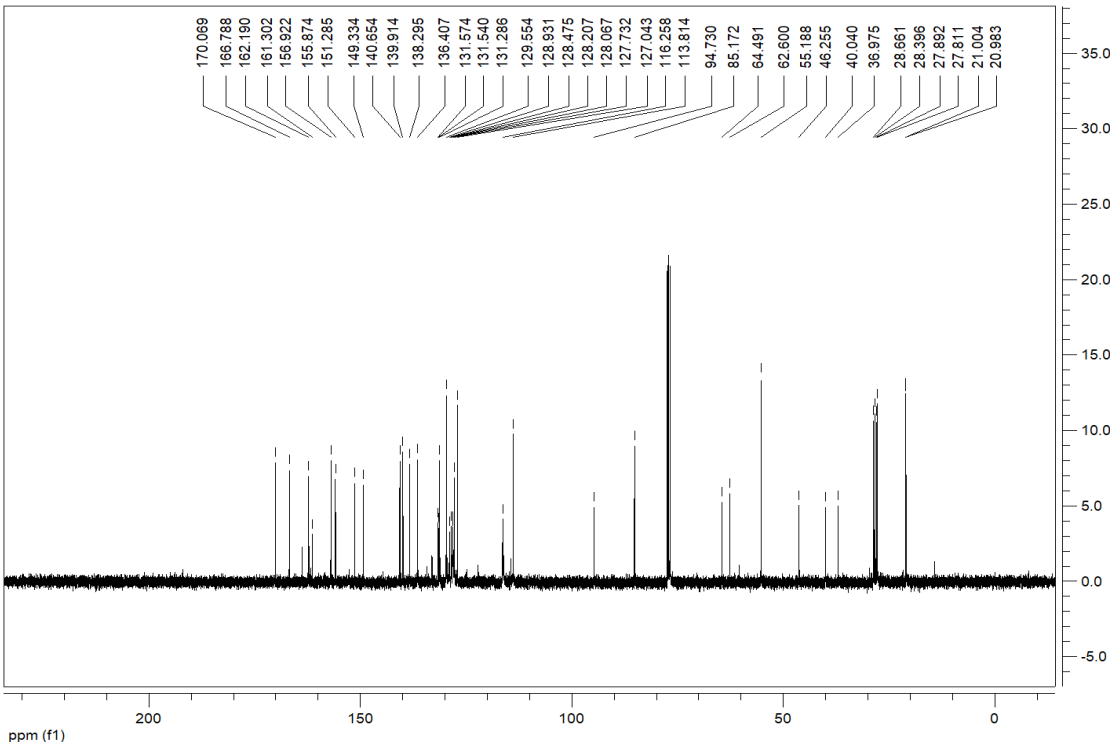
744.5
745.0
745.5
746.0
m/z

***rel*-(5S,5aS,6S,8R,9aS)-6-(4-fluorophenyl)-9-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-5,8-di-p-tolyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3b):**

Yellow solid, 73%, m.p.150-152℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (brs, 1H, ArH), 7.10 (d, *J* = 7.6 Hz, 3H, ArH), 6.98 (d, *J* = 8.8 Hz, 3H, ArH), 6.92 (d, *J* = 8.0 Hz, 3H, ArH), 6.86-6.80 (m, 2H, ArH), 6.75 (s, 2H, ArH), 6.65 (d, *J* = 8.8 Hz, 2H, ArH), 5.70 (d, *J* = 3.2 Hz, 1H, CH), 5.48 (s, 1H, CH), 4.99 (d, *J* = 13.2 Hz, 1H, CH), 3.86 (d, *J* = 13.2 Hz, 1H, CH), 3.73 (s, 1H, CH), 3.68 (s, 3H, OCH_3), 3.48 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.94 (s, 3H, NCH_3), 2.80 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 166.7, 162.1, 161.3, 156.9, 155.8, 151.2, 149.3, 140.6, 139.9, 138.2, 136.4, 131.5, 131.5, 131.2, 129.5, 128.9, 128.4, 128.2, 128.0, 127.7, 127.0, 116.2, 113.8, 94.7, 85.1, 64.4, 62.5, 55.1, 46.2, 40.0, 36.9, 28.6, 28.3, 27.8, 27.8, 21.0, 20.9; IR(KBr) υ: 2963, 1651, 1505, 1430, 1379, 1241, 1168, 909, 823, 762 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{43}FN_5O_7$([M+H]$^+$): 772.3147, found: 772.3129.

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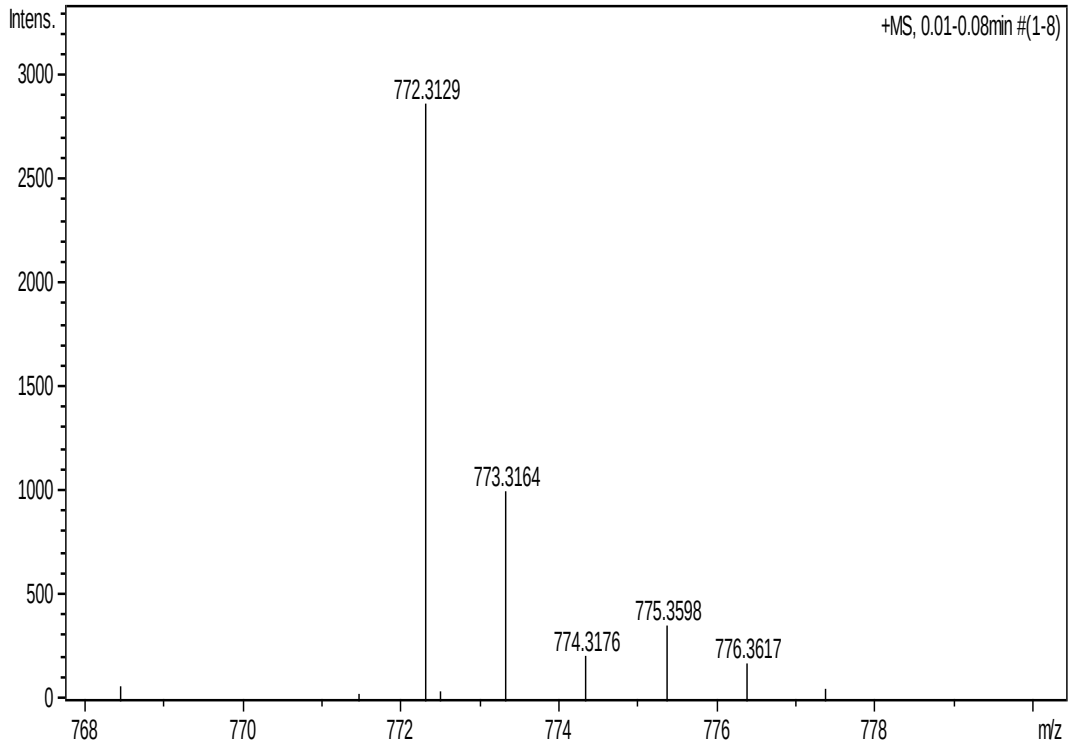
ppm (f1)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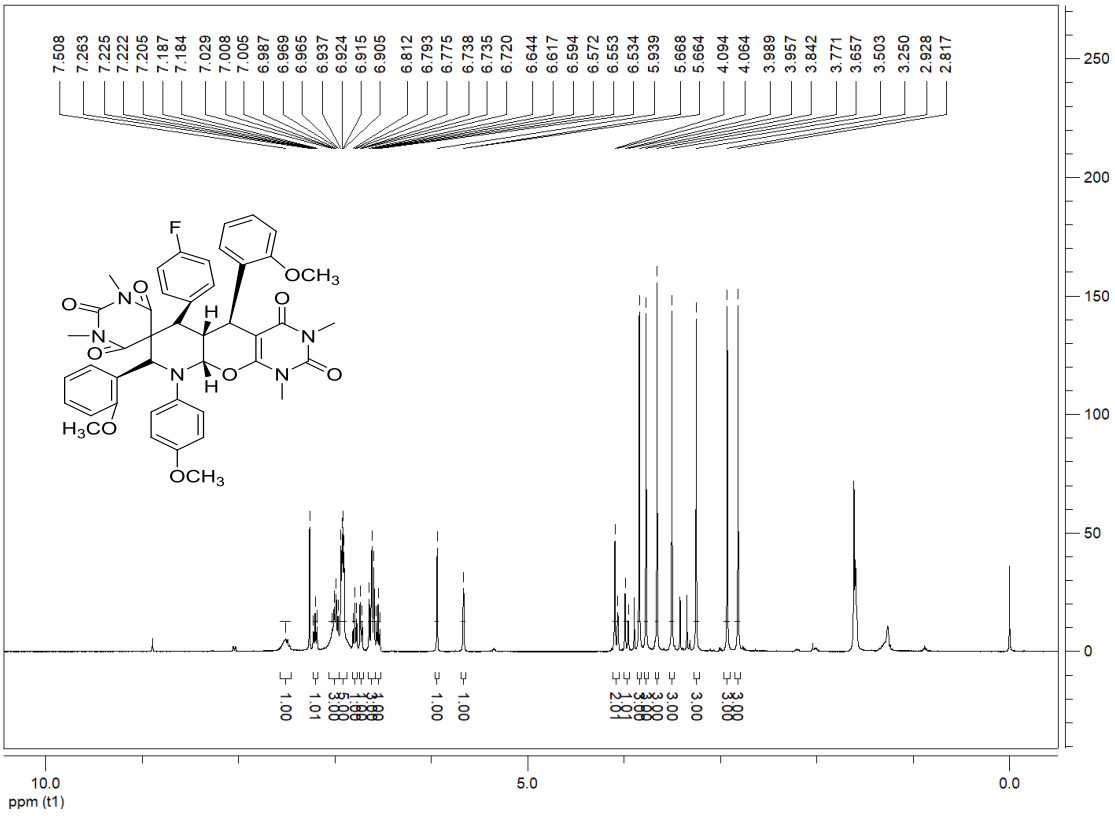
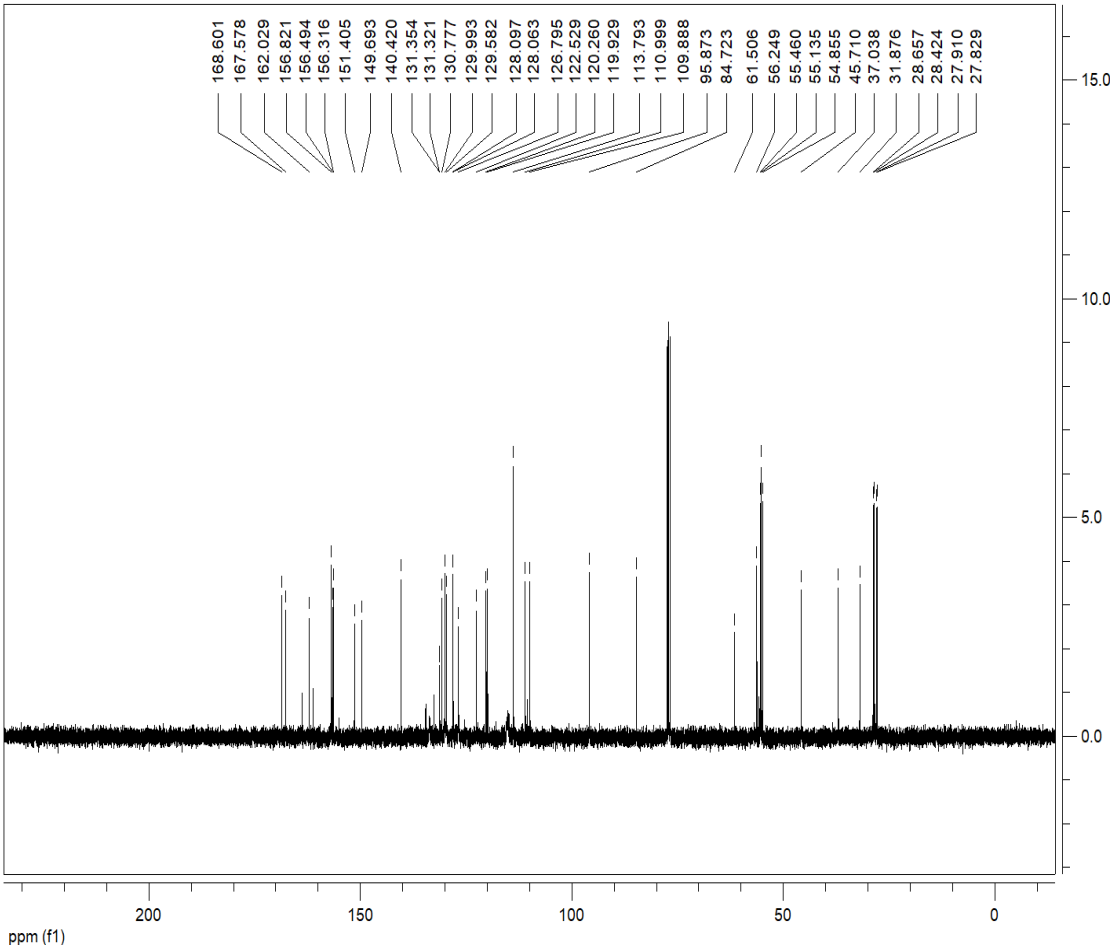
770
772
774
776
778
m/z

***rel*-(5S,5aS,6S,8R,9aS)-6-(4-fluorophenyl)-5,8-bis(2-methoxyphenyl)-9-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3c):**

Yellow solid, 46%, m.p.147-149℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (brs, 1H, ArH), 7.22-7.18 (m, 1H, ArH), 7.03 -6.96 (m, 3H, ArH), 6.94-6.90 (m, 5H, ArH), 6.79 (t, *J* = 7.4 Hz, 1H, ArH), 6.74-6.72 (m, 1H, ArH), 6.64-6.59 (m, 3H, ArH), 6.55 (t, *J* = 7.6 Hz, 1H, ArH), 5.94 (s, 1H, CH), 5.67 (d, *J* = 2.4 Hz, 1H, ArH), 4.09-4.06 (m, 2H, CH), 3.97 (d, *J* = 12.8 Hz, 1H, CH), 3.77 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.50 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 2.93 (s, 3H, NCH_3), 2.82 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.6, 167.5, 162.0, 156.8, 156.4, 156.3, 151.4, 149.6, 140.4, 131.3, 131.3, 130.7, 129.9, 129.5, 128.0, 128.0, 126.7, 122.5, 120.2, 119.9, 113.7, 110.9, 109.8, 95.8, 84.7, 61.5, 56.2, 55.4, 55.1, 54.8, 45.7, 37.0, 31.8, 28.6, 28.4, 27.9, 27.8; IR(KBr) υ: 3008, 2952, 2837, 1653, 1500, 1377, 1291, 1245, 1169, 1032, 908, 836, 757, 641 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{43}FN_5O_9$([M+H]$^+$): 804.3045, found: 804.3029.

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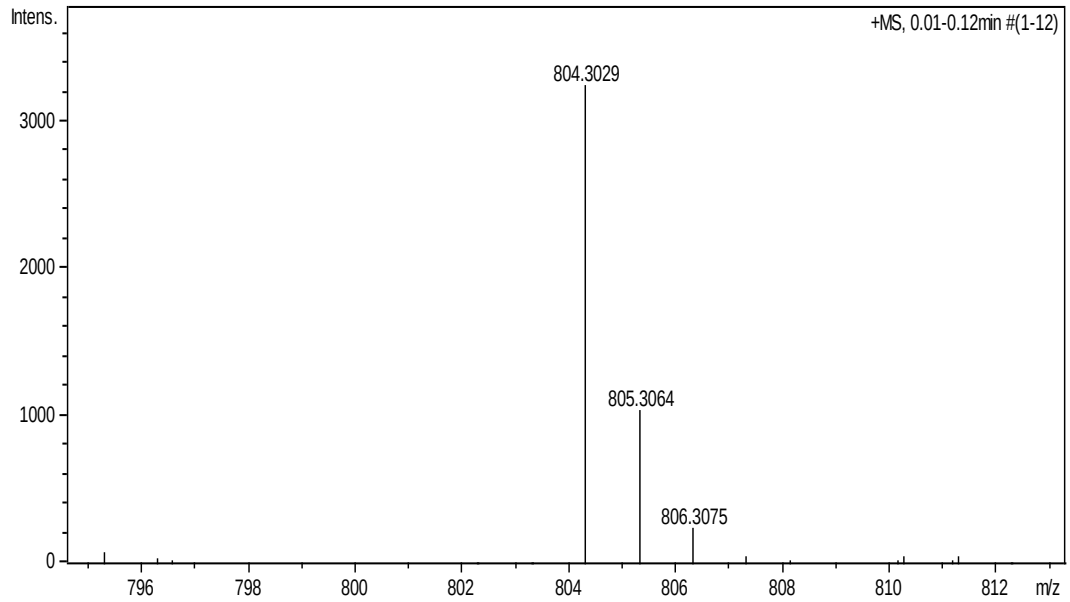
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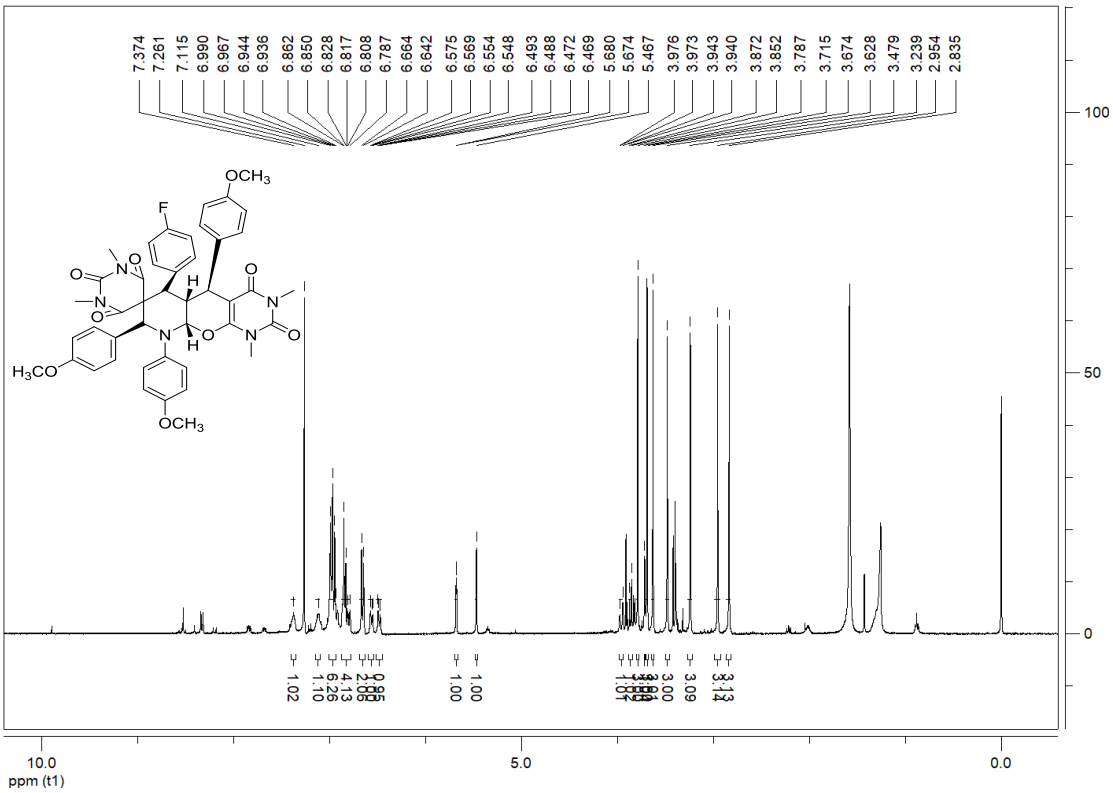
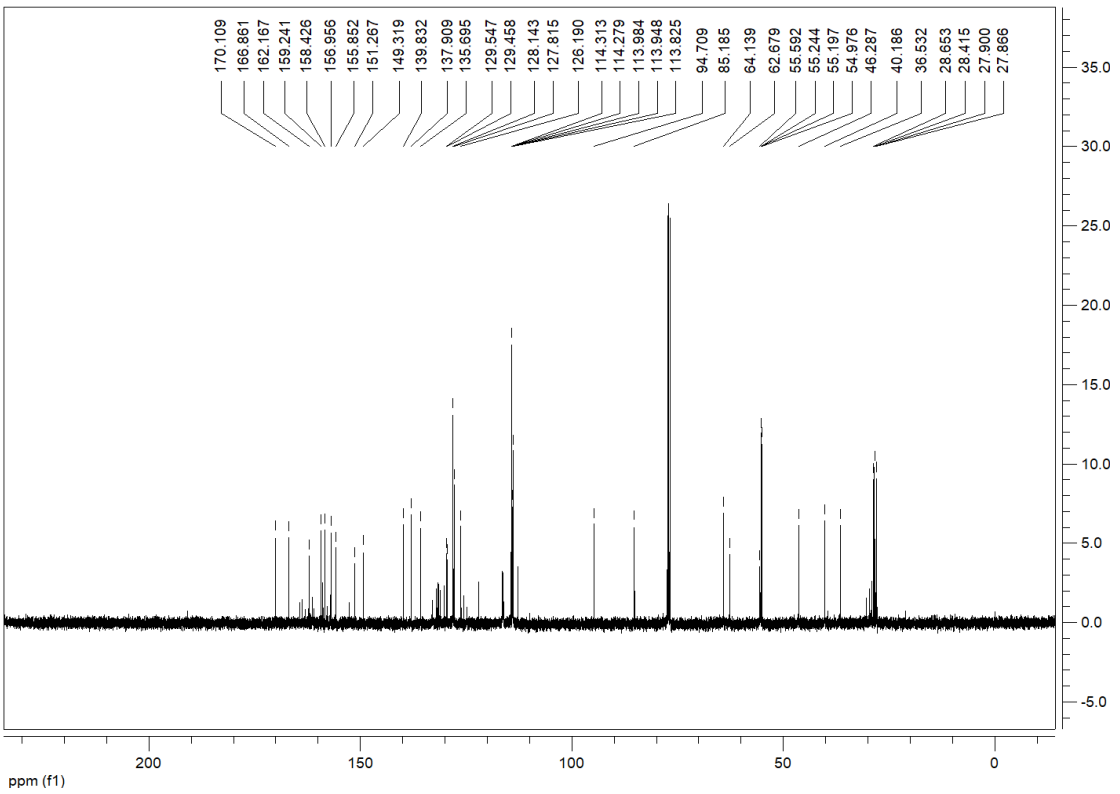
802
804
806
808
810
812
m/z

***rel*-(5S,5aS,6S,8R,9aS)-6-(4-fluorophenyl)-5,8,9-tris(4-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3d)**:

Yellow solid, 43%, m.p.112-114℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (brs, 1H, ArH), 7.12 (brs, 1H, ArH), 6.99-6.94 (m, 6H, ArH), 6.86-6.79 (m, 4H, ArH), 6.65 (d, *J* = 8.8 Hz, 2H, ArH), 6.58-6.55 (m, 1H, ArH), 6.49-6.47 (m, 1H, ArH), 5.68 (d, *J* = 2.4 Hz, 1H, CH), 5.47 (s, 1H, CH), 3.98-3.94 (m, 1H, CH), 3.86 (d, *J* = 8.0 Hz, 1H, CH), 3.79 (s, 3H, OCH_3), 3.72 (s, 1H, CH), 3.67 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.48 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 2.95 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.1, 166.8, 162.1, 159.2, 158.4, 156.9, 155.8, 151.2, 149.3, 139.8, 137.9, 135.6, 129.5, 129.4, 128.1, 127.8, 126.1, 114.3, 114.2, 113.9, 113.9, 113.8, 94.7, 85.1, 64.1, 62.6, 55.5, 55.2, 55.1, 54.9, 46.2, 40.1, 36.5, 28.6, 28.4, 27.8, 27.8; IR(KBr) υ: 2953, 2841, 1646, 1506, 1456, 1380, 1251, 1170, 1030, 910, 831, 763, 672, 631 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{43}FN_5O_9$([M+H]$^+$): 804.3045, found: 804.3020.

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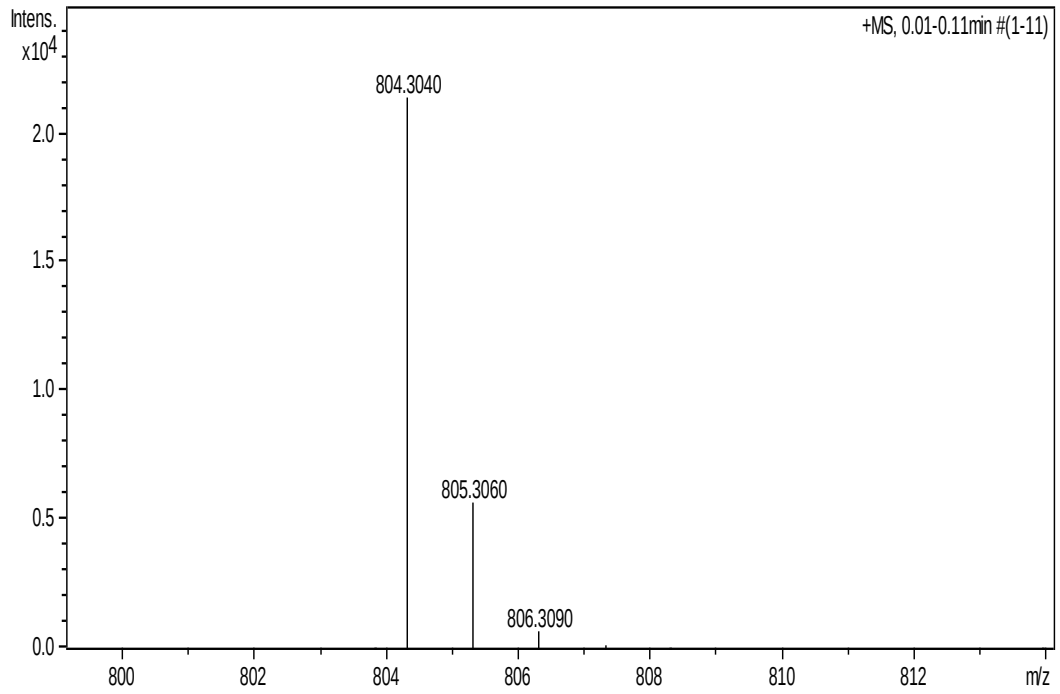
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1.0
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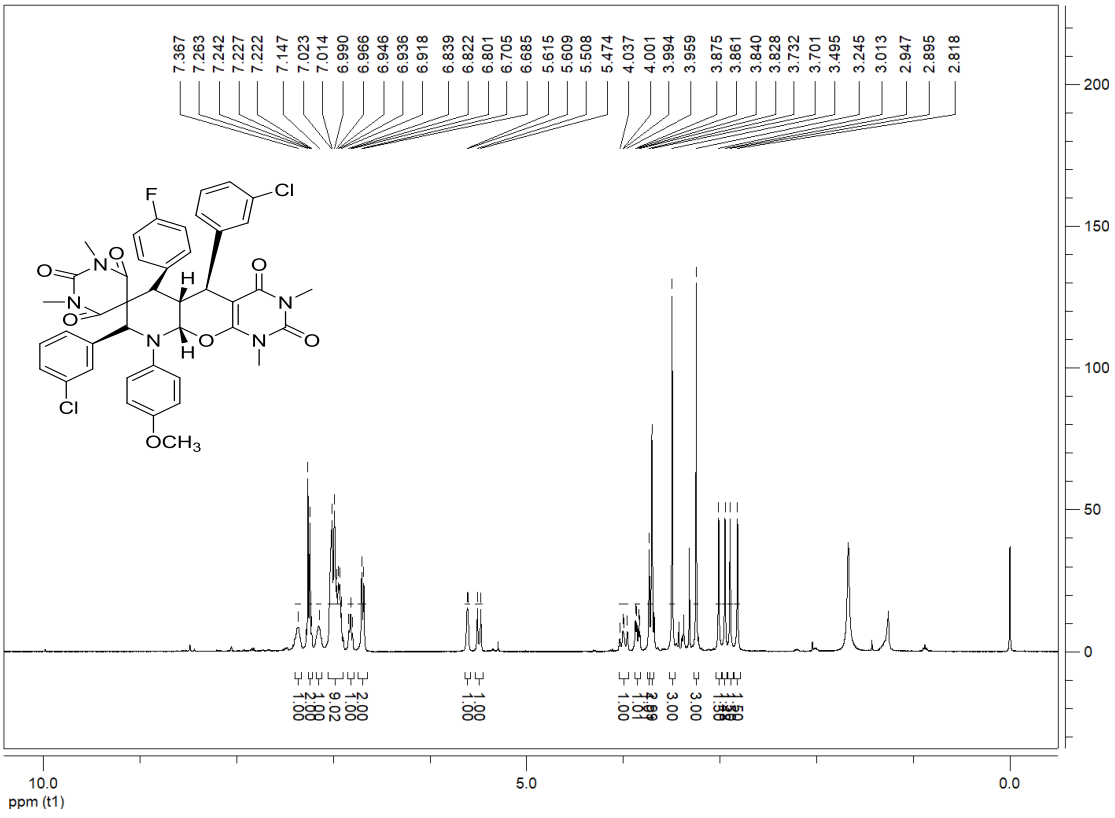
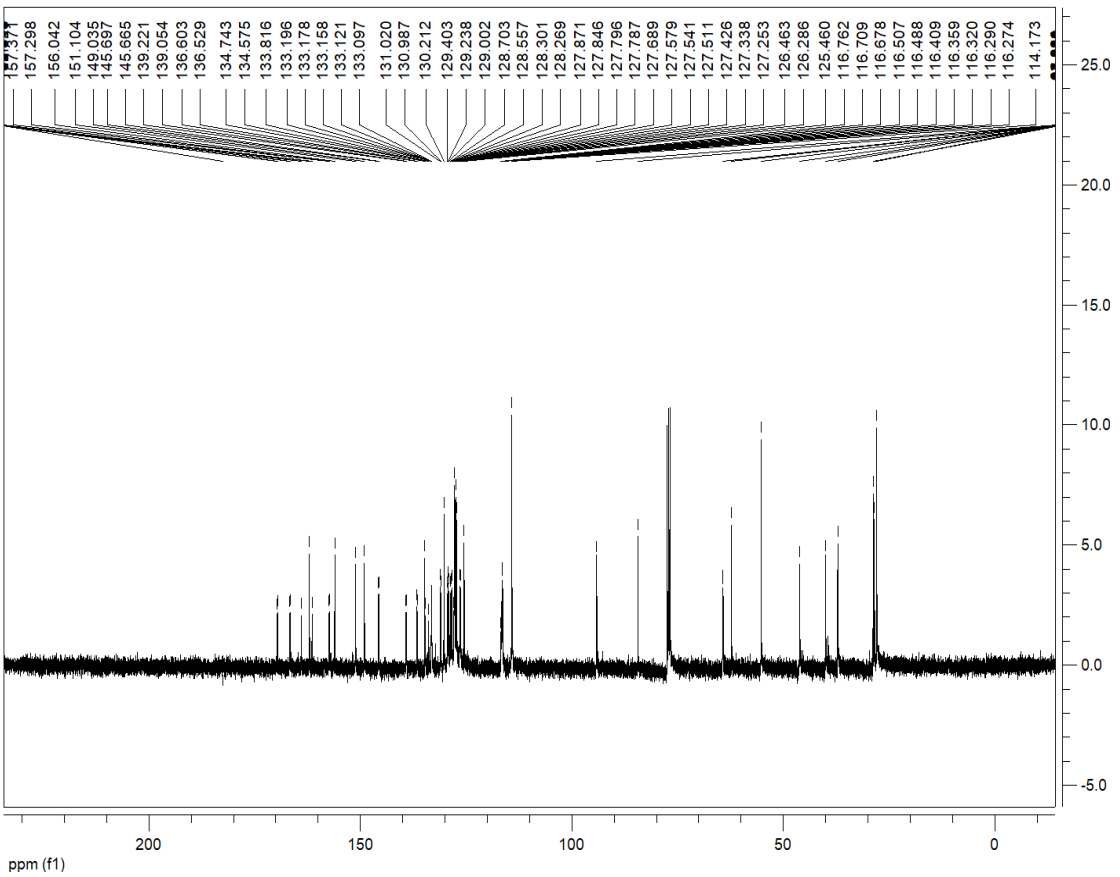
0.0
800
802
804
806
808
810
812
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(3-chlorophenyl)-6-(4-fluorophenyl)-9-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3e):**

white solid, 93%, m.p.128-130℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (brs, 1H, ArH), 7.26-7.22 (m, 2H, ArH), 7.15 (brs, 1H, ArH), 7.02-6.92 (m, 9H, ArH), 6.82 (t, *J* = 7.6 Hz, 1H, ArH), 6.70 (d, *J* = 8.0 Hz, 2H, ArH), 5.61 (d, *J* = 2.4 Hz, 1H, CH), 5.49 (d, *J* = 13.6 Hz, 1H, CH), 4.04-3.96 (m, 1H, CH), 3.88-3.83 (m, 1H, CH), 3.73 (s, 1H, CH), 3.70 (s, 3H, OCH_3), 3.50 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 3.01-2.82 (s, s, s, s, 6H, $2NCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.6, 169.5, 166.6, 166.5, 163.8, 162.0, 161.4, 157.3, 157.2, 156.0, 151.1, 149.0, 145.6, 145.6, 139.2, 139.0, 136.6, 136.5, 134.7, 134.5, 133.8, 133.1, 133.1, 133.1, 133.1, 133.0, 131.0, 130.9, 130.2, 129.4, 129.2, 129.0, 128.7, 128.5, 128.3, 128.2, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.5, 127.5, 127.4, 127.3, 127.2, 126.4, 126.2, 125.4, 116.7, 116.7, 116.6, 116.5, 116.4, 116.4, 116.3, 116.3, 116.2, 116.2, 114.1, 94.1, 94.1, 84.3, 64.3, 64.2, 62.2, 55.2, 46.1, 46.0, 40.0, 39.9, 37.1, 28.7, 28.4, 27.9; IR(KBr) υ: 2957, 1685, 1646, 1503, 1379, 1242, 1169, 1029, 900, 838, 788, 700, 643 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{42}H_{37}Cl_2FN_5O_7$([M+H]$^+$): 812.2054, found: 812.2058.

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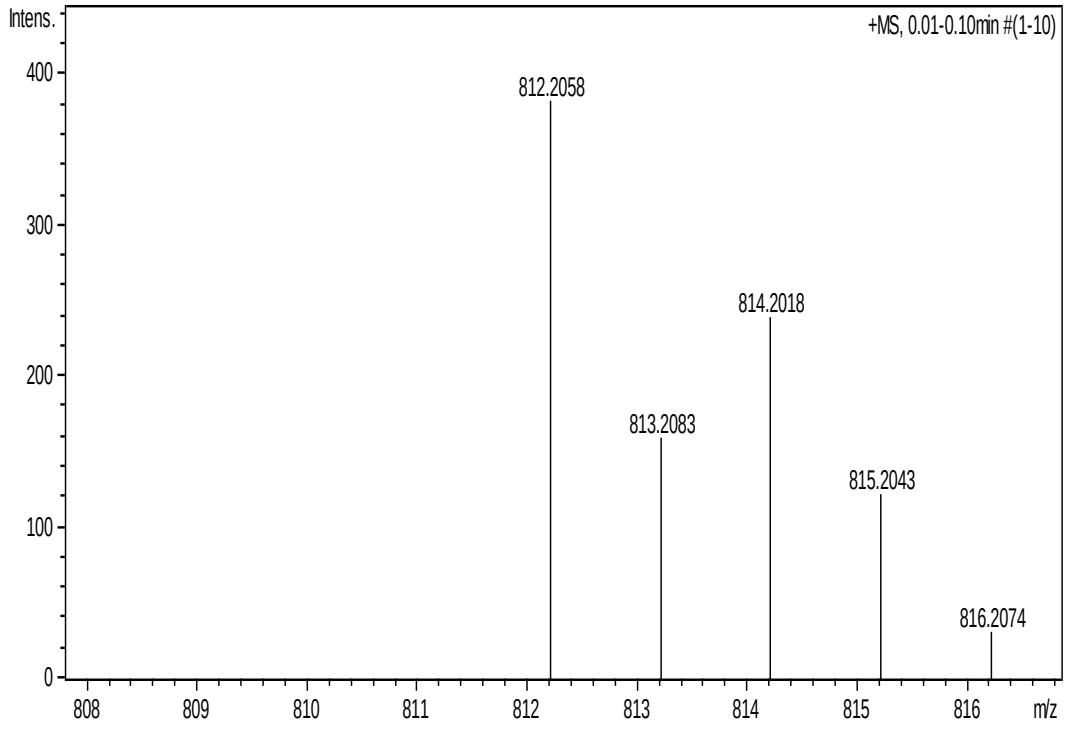
ppm (f1)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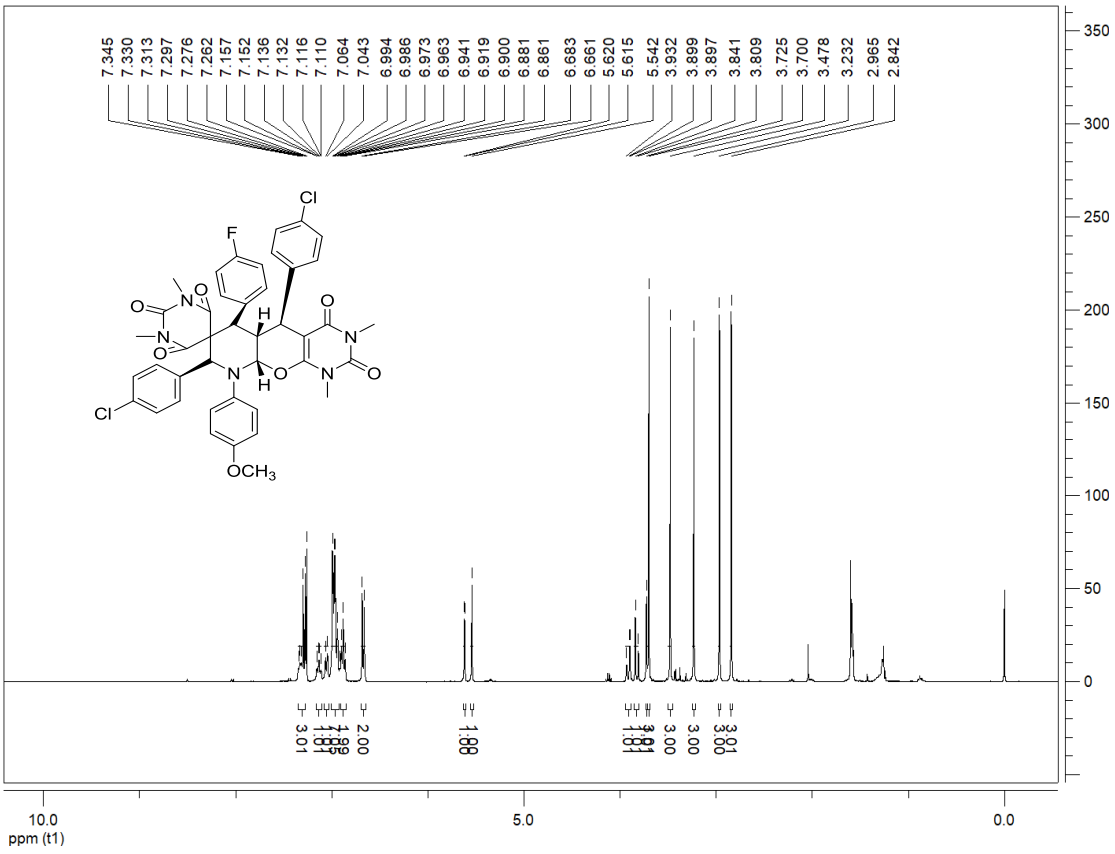
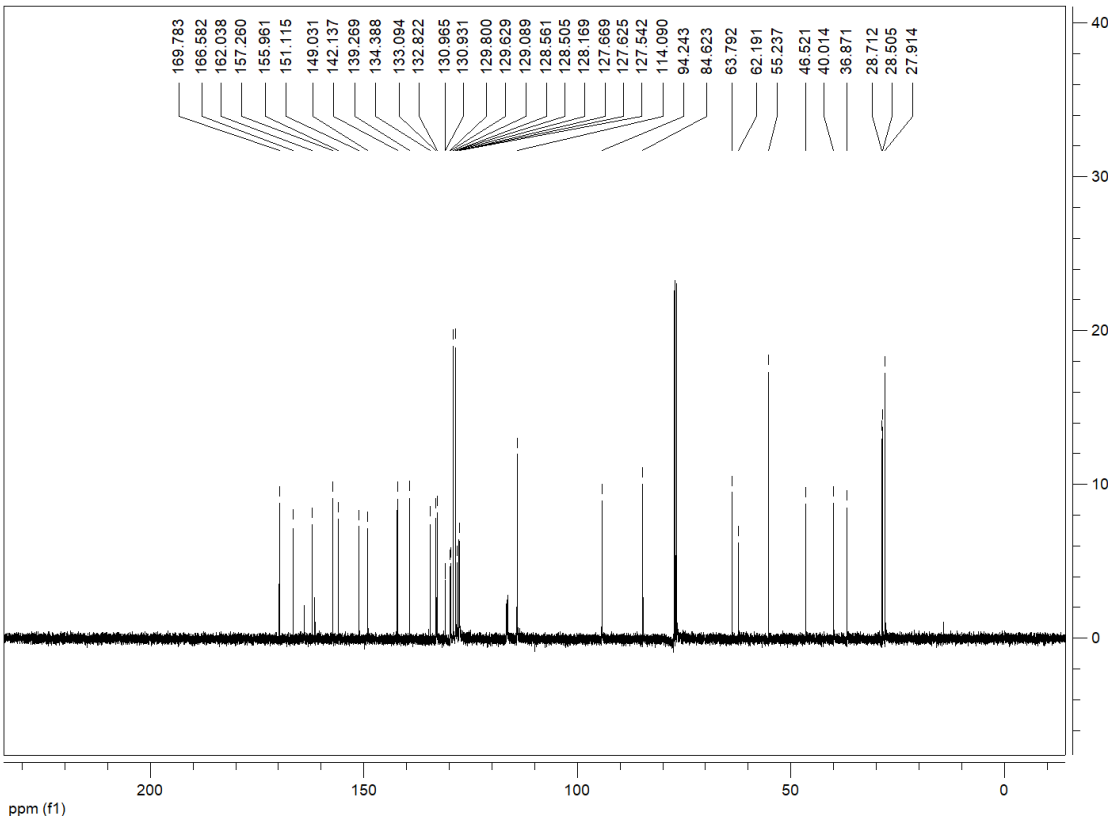
809
810
811
812
813
814
815
816
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(4-chlorophenyl)-6-(4-fluorophenyl)-9-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3f):**

white solid, 91%, m.p.172-174℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34-7.30 (m, 3H, ArH), 7.16-7.11 (m, 1H, ArH), 7.05 (d, *J* = 8.4 Hz, 1H, ArH), 6.99-6.94 (m, 7H, ArH), 6.88 (t, *J* = 7.8 Hz, 2H, ArH), 6.67 (d, *J* = 8.8 Hz, 2H, ArH), 5.62 (d, *J* = 2.0 Hz, 1H, CH), 5.54 (s, 1H, CH), 3.93-3.90 (m, 1H, CH), 3.82 (d, *J* = 12.8 Hz, 1H, CH), 3.72 (s, 1H, CH), 3.70 (s, 3H, OCH_3), 3.48 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.96 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.7, 166.5, 162.0, 157.2, 155.9, 151.1, 149.0, 142.1, 139.2, 134.3, 133.0, 132.8, 130.9, 130.9, 129.8, 129.6, 129.0, 128.5, 128.5, 128.1, 127.6, 127.6, 127.5, 114.0, 94.2, 84.6, 63.7, 62.1, 55.2, 46.5, 40.0, 36.8, 28.7, 28.5, 27.9; IR(KBr) υ: 2957, 2358, 1680, 1646, 1499, 1377, 1239, 1171, 1096, 1022, 907, 830, 752, 714, 666 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{42}H_{37}Cl_2FN_5O_7$ ($[M+H]^+$): 812.2054, found: 812.2034.

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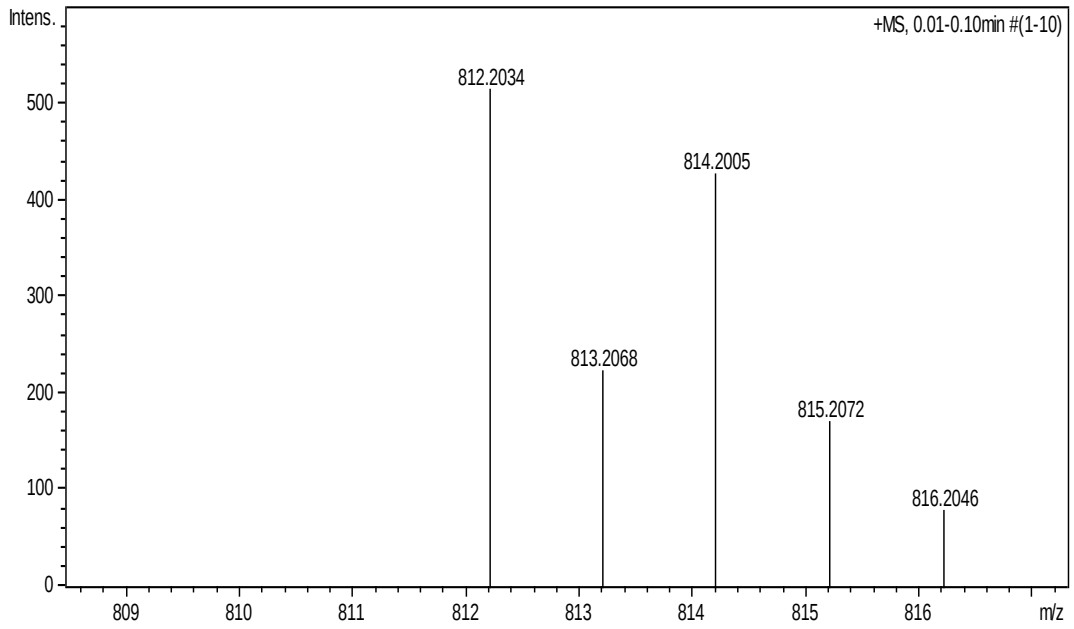
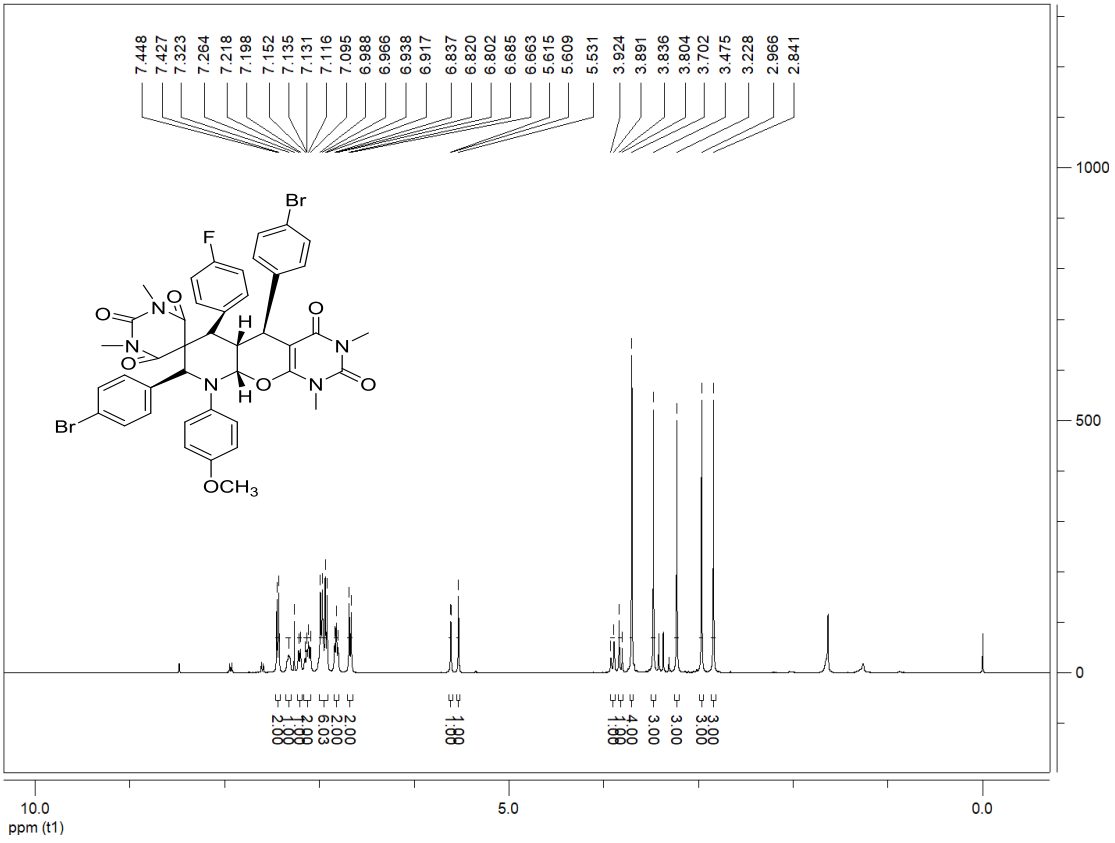
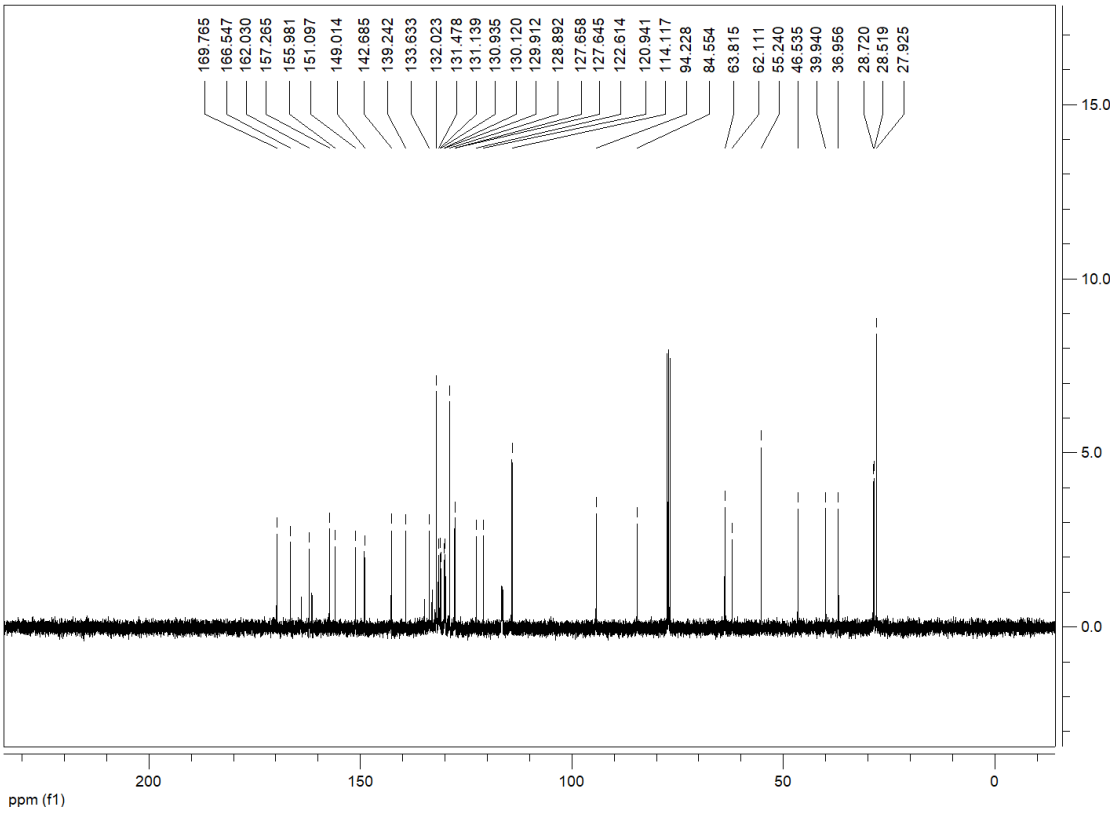
166.582
162.038
157.260
155.961
151.115
149.031
142.137
139.269
134.388
133.094
132.822
130.965
130.931
129.800
129.629
129.089
128.561
128.505
128.169
127.669
127.625
127.542
114.090
94.243
84.623
63.792
62.191
55.237
46.521
40.014
36.871
28.712
28.505
27.914
40
30
20
10
0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.01-0.10min #(1-10)
812.2034
814.2005
813.2068
815.2072
816.2046
500
400
300
200
100
0
809
810
811
812
813
814
815
816
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(4-bromophenyl)-6-(4-fluorophenyl)-9-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3g):**

white solid, 94%, m.p.175-177℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (d, *J* = 7.6 Hz, 2H, ArH), 7.32 (brs, 1H, ArH), 7.21 (d, *J* = 8.0 Hz, 1H, ArH), 7.15-7.10 (m, 2H, ArH), 6.99-6.92 (m, 6H, ArH), 6.82 (t, *J* = 7.0 Hz, 2H, ArH), 6.67 (d, *J* = 8.8 Hz, 2H, ArH), 5.61 (d, *J* = 2.4 Hz, 1H, CH), 5.53 (s, 1H, CH), 3.91 (d, *J* = 13.2 Hz, 1H, CH), 3.82 (d, *J* = 12.8 Hz, 1H, CH), 3.70 (s, 4H, CH, OCH_3), 3.70 (s, 3H, OCH_3), 3.48 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.7, 166.5, 162.0, 157.2, 155.9, 151.0, 149.0, 142.6, 139.2, 133.6, 132.0, 131.4, 131.1, 130.9, 130.1, 129.9, 128.8, 127.6, 127.6, 122.6, 120.9, 114.1, 94.2, 84.5, 63.8, 62.1, 55.2, 46.5, 39.9, 36.9, 28.7, 28.5, 27.9; IR (KBr) υ: 2957, 1678, 1647, 1478, 1376, 1239, 1171, 1019, 908, 827, 758, 657 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{42}H_{37}Br_2FN_5O_7$ ($[M+H]^+$): 902.1023, found: 902.1021.

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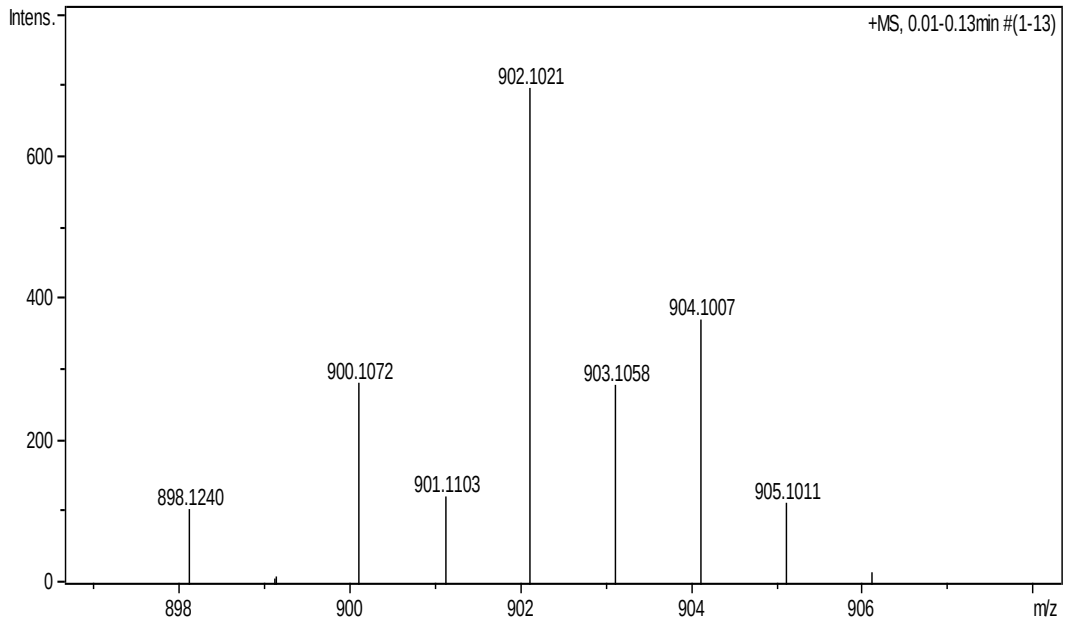
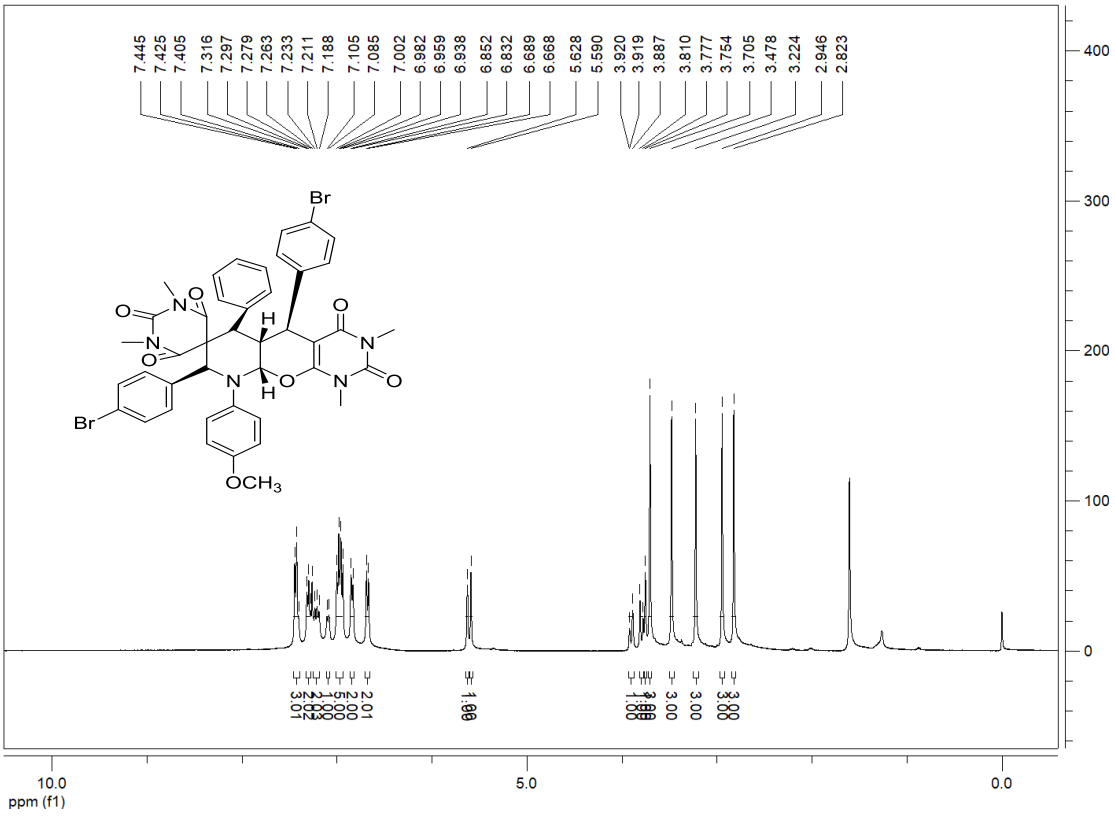
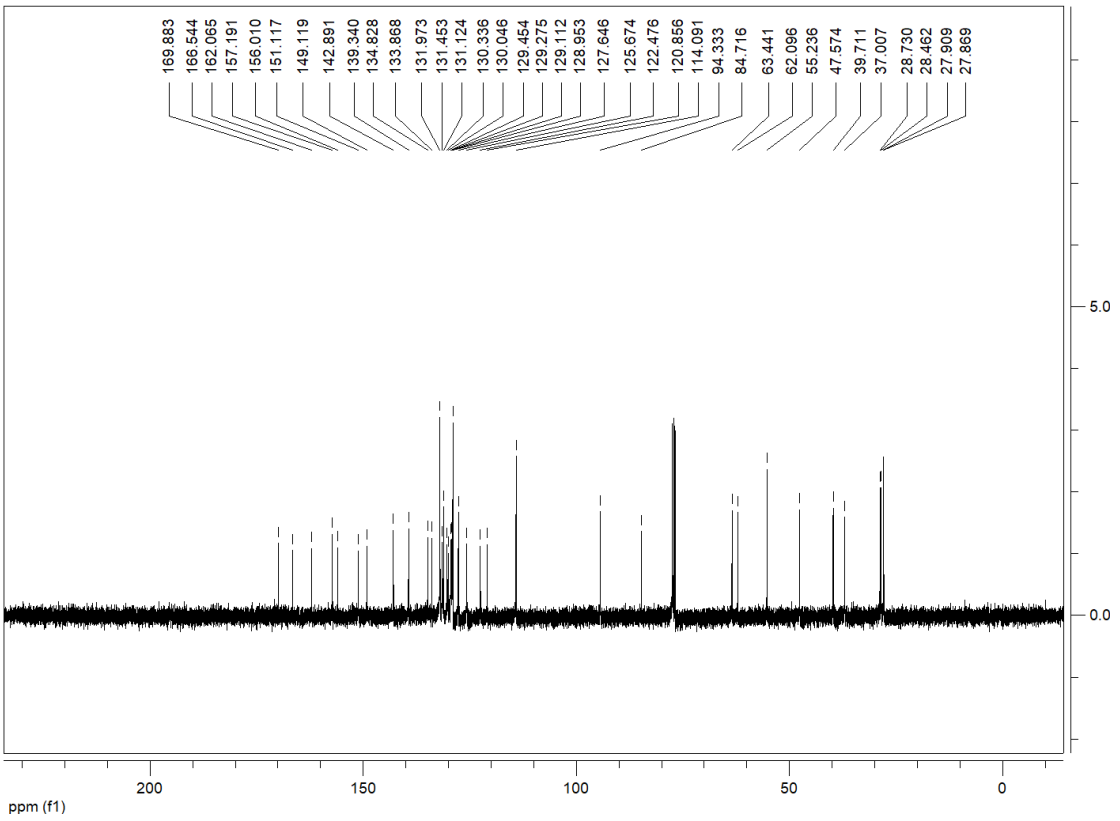
166.547
162.030
157.265
155.981
151.097
149.014
142.685
139.242
133.633
132.023
131.478
131.139
130.935
130.120
129.912
128.892
127.658
127.645
122.614
120.941
114.117
94.228
84.554
63.815
62.111
55.240
46.535
39.940
36.956
28.720
28.519
27.925
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

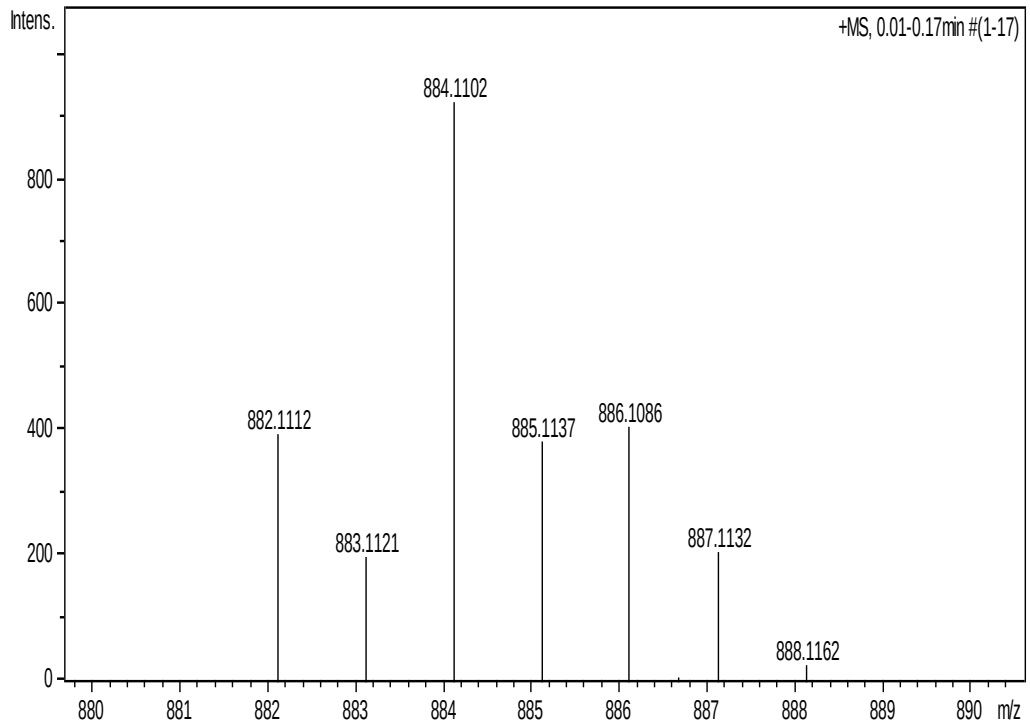

Intens.
+MS, 0.01-0.13min #(1-13)
902.1021
600
400
904.1007
900.1072
903.1058
200
898.1240
901.1103
905.1011
0
898
900
902
904
906
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(4-bromophenyl)-9-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-6-phenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3h):**

white solid, 93%, m.p.167-169℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.40 (m, 3H, ArH), 7.32-7.28 (m, 2H, ArH), 7.23-7.19 (m, 2H, ArH), 7.09 (d, *J* = 8.0 Hz, 1H, ArH), 7.00-6.94 (m, 5H, ArH), 6.84 (d, *J* = 8.0 Hz, 2H, ArH), 6.68 (d, *J* = 8.4 Hz, 2H, ArH), 5.63 (s, 1H, CH), 5.59 (s, 1H, CH), 3.92-3.89 (m, 1H, CH), 3.79 (d, *J* = 13.2 Hz, 1H, CH), 3.75 (s, 1H, CH), 3.70 (s, 3H, OCH_3), 3.48 (s, 3H, NCH_3), 3.22 (s, 3H, NCH_3), 2.95 (s, 3H, NCH_3), 2.82 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.8, 166.5, 162.0, 157.1, 156.0, 151.1, 149.1, 142.8, 139.3, 134.8, 133.8, 131.9, 131.4, 131.1, 130.3, 130.0, 129.4, 129.2, 129.1, 128.9, 127.6, 125.6, 122.4, 120.8, 114.0, 94.3, 84.7, 63.4, 62.0, 55.2, 47.5, 39.7, 37.0, 28.7, 28.4, 27.9, 27.8; IR(KBr) υ: 3046, 2954, 1749, 1648, 1479, 1378, 1246, 1173, 1022, 907, 830, 758, 708, 661 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{42}H_{38}Br_2N_5O_7$([M+H]$^+$): 884.1118, found: 884.1102.

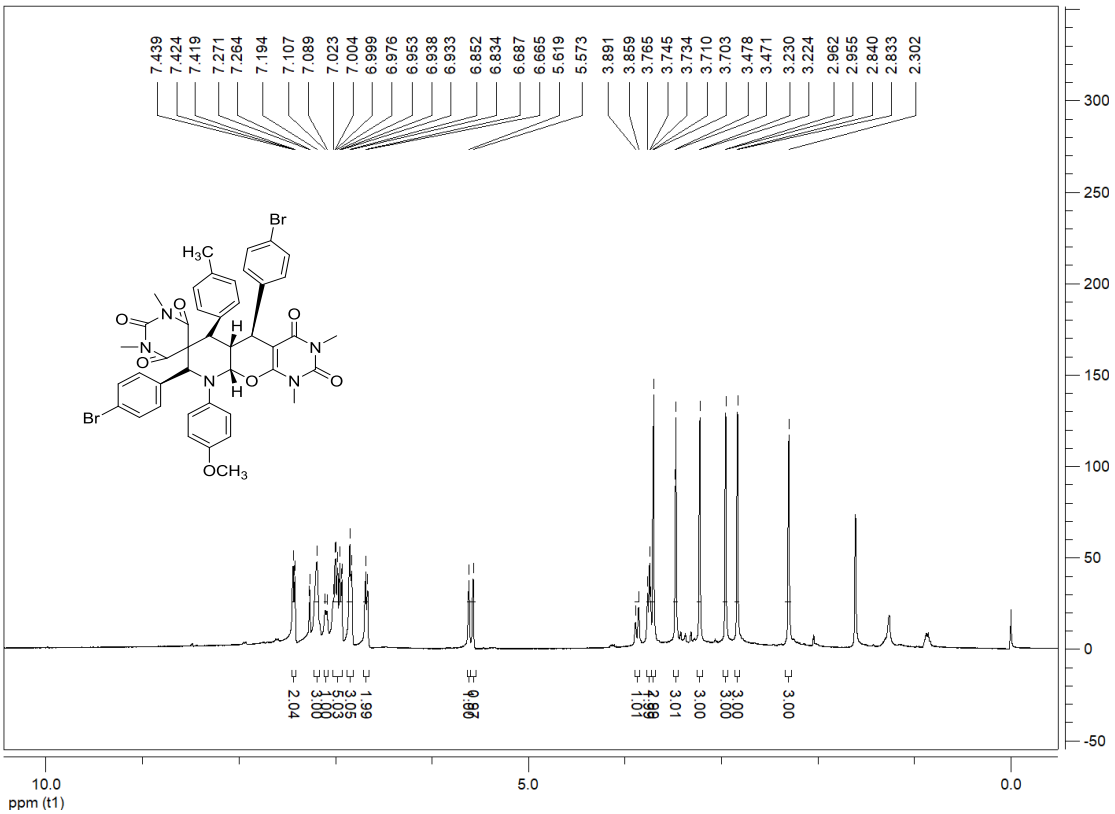


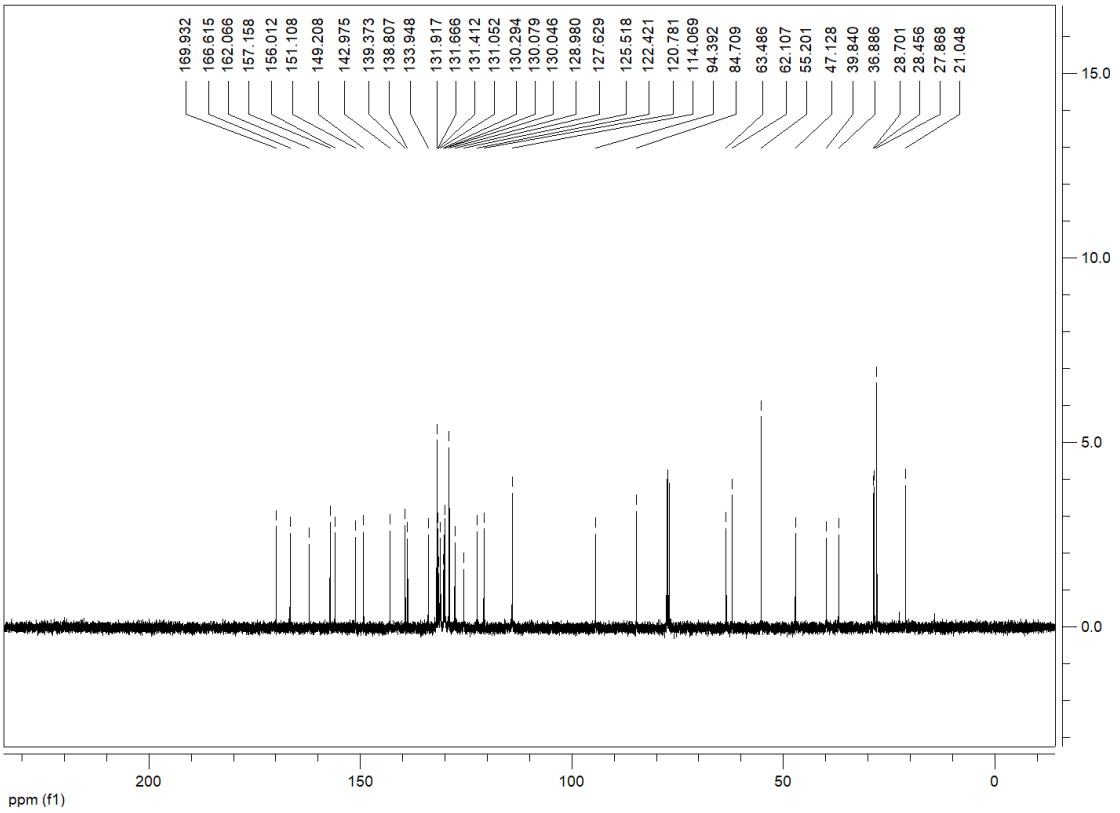

169.883
166.544
162.065
157.191
156.010
151.117
149.119
142.891
139.340
134.828
133.868
131.973
131.453
131.124
130.336
130.046
129.454
129.275
129.112
128.953
127.646
125.674
122.476
120.856
114.091
94.333
84.716
63.441
62.096
55.236
47.574
39.711
37.007
28.730
28.462
27.909
27.869
5.0
0.0
200
150
100
50
0
ppm (f1)

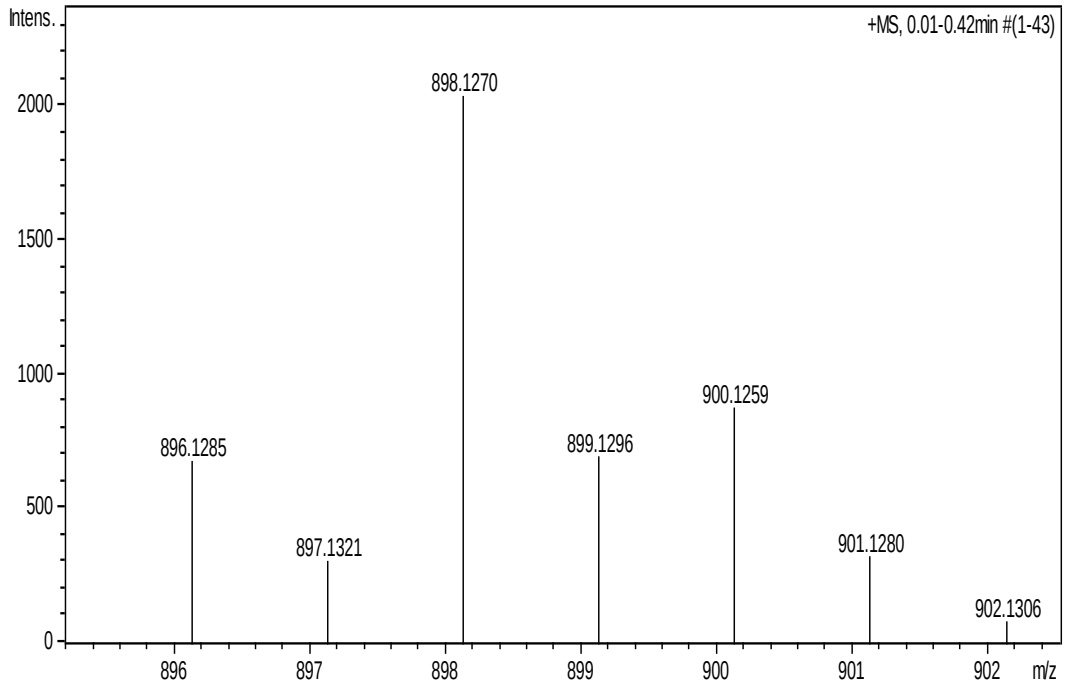

Intens.
+MS, 0.01-0.17min #(1-17)
884.1102
882.1112
883.1121
885.1137
886.1086
887.1132
888.1162
800
600
400
200
0
880
881
882
883
884
885
886
887
888
889
890
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(4-bromophenyl)-9-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-6-(p-tolyl)-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3i):**

Yellow solid, 90%, m.p.160-162℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.42 (m, 2H, ArH), 7.19 (brs, 3H, ArH), 7.10 (d, *J* = 7.2 Hz, 1H, ArH), 7.02-6.93 (m, 5H, ArH), 6.85-6.83 (m, 3H, ArH), 6.69-6.66 (m, 2H, ArH), 5.62 (s, 1H, CH), 5.57 (s, 1H, CH), 3.88 (d, *J* = 12.8 Hz, 1H, CH), 3.76-3.73 (m, 2H, 2CH), 3.70 (s, 3H, OCH_3), 3.47 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.96 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 166.6, 162.0, 157.1, 156.0, 151.1, 149.2, 142.9, 139.3, 138.8, 133.9, 131.9, 131.6, 131.4, 131.0, 130.2, 130.0, 130.0, 128.9, 127.6, 125.5, 122.4, 120.7, 114.0, 94.3, 84.7, 63.4, 62.1, 55.2, 47.1, 39.8, 36.8, 28.7, 28.4, 27.8, 21.0; IR(KBr) υ: 2956, 1651, 1480, 1378, 1251, 1173, 1023, 908, 818, 754, 715, 659 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{40}Br_2N_5O_7$([M+H]$^+$): 898.1274, found: 898.1270.

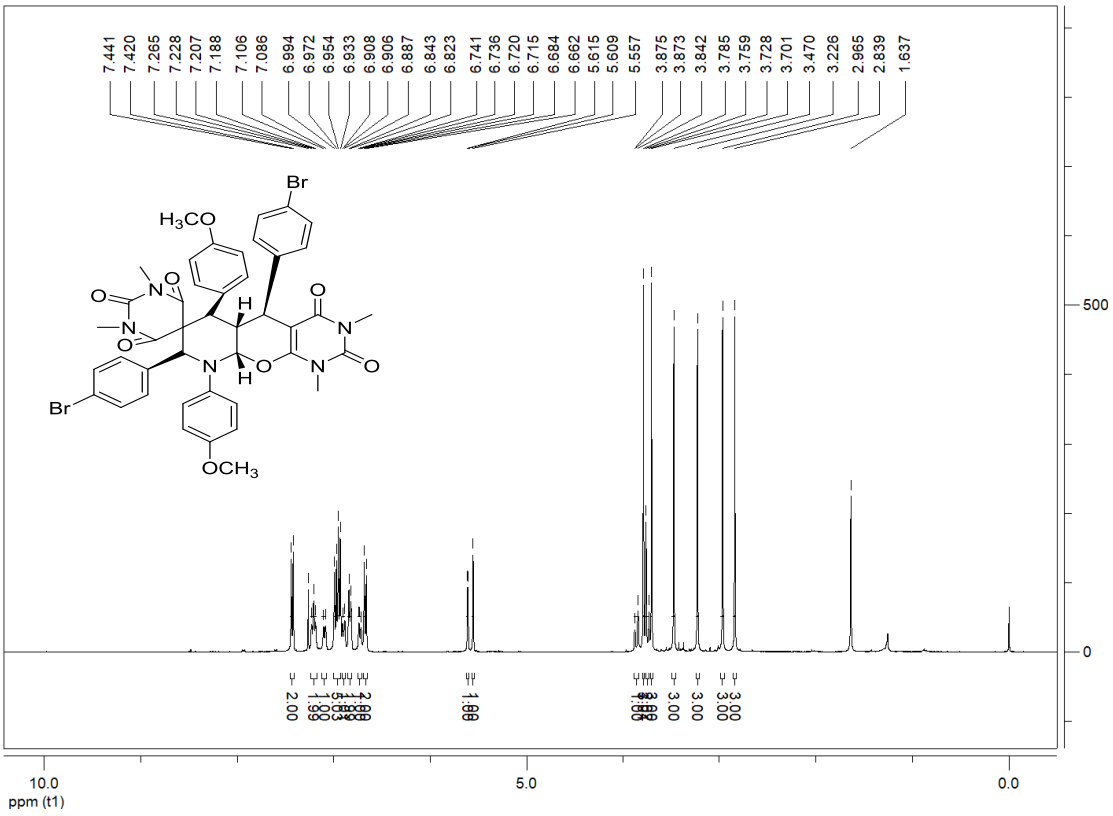


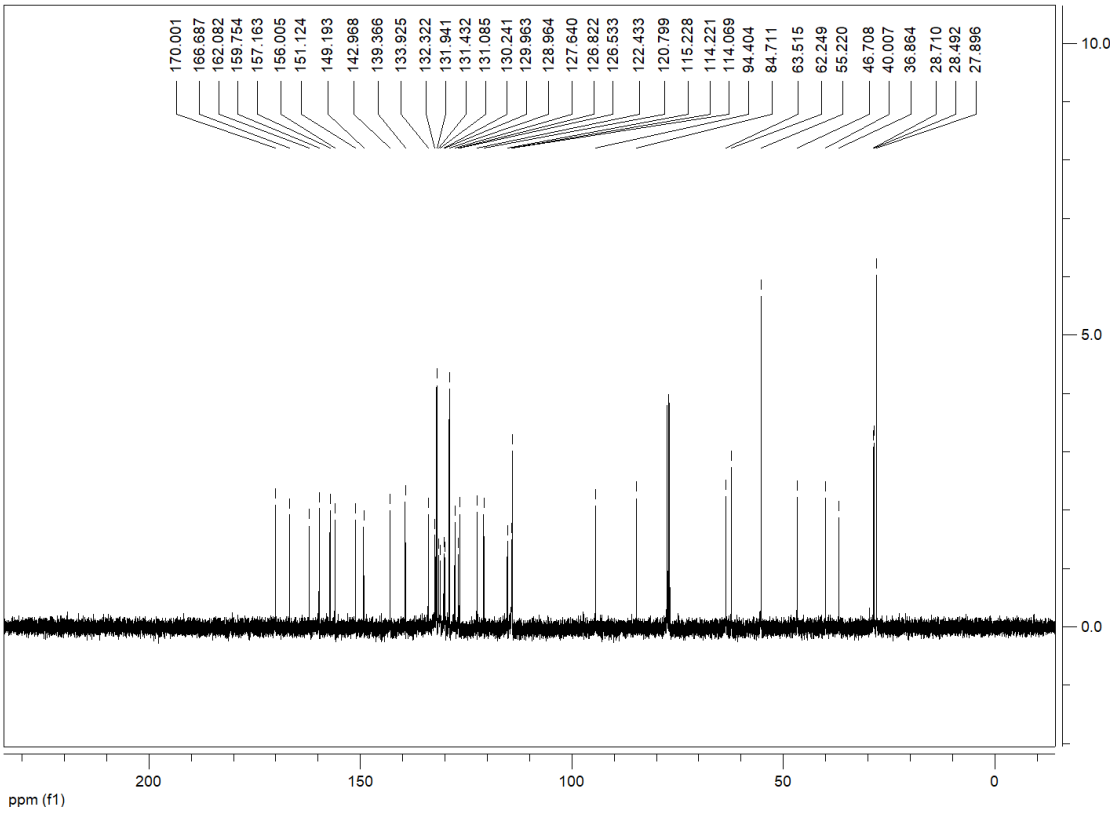

169.932
166.615
162.066
157.158
156.012
151.108
149.208
142.975
139.373
138.807
133.948
131.917
131.666
131.412
131.052
130.294
130.079
130.046
128.980
127.629
125.518
122.421
120.781
114.069
94.392
84.709
63.486
62.107
55.201
47.128
39.840
36.886
28.701
28.456
27.868
21.048
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.01-0.42min #(1-43)
2000
1500
1000
500
0
898.1270
900.1259
896.1285
899.1296
897.1321
901.1280
902.1306
896
897
898
899
900
901
902
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(4-bromophenyl)-6,9-bis(4-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3j):**

Yellow solid, 78%, m.p.153-155℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 8.4 Hz, 2H, ArH), 7.21 (t, *J* = 8.0 Hz, 2H, ArH), 7.10 (t, *J* = 8.0 Hz, 1H, ArH), 6.99-6.93 (m, 5H, ArH), 6.91-6.89 (m, 1H, ArH), 6.83 (d, *J* = 8.0 Hz, 2H, ArH), 6.74-6.72 (m, 1H, ArH), 6.67 (d, *J* = 8.8 Hz, 2H, ArH), 5.61 (d, *J* = 2.4 Hz, 1H, CH), 5.56 (s, 1H, CH), 3.88-3.84 (m, 1H, CH), 3.78 (s, 3H, OCH_3), 3.76-3.73 (m, 2H, 2CH), 3.70 (s, 3H, OCH_3), 3.47 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.96 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 166.6, 162.0, 159.7, 157.1, 156.0, 151.1, 149.1, 142.9, 139.3, 133.9, 132.3, 131.9, 131.4, 131.0, 130.2, 129.9, 128.9, 127.6, 126.8, 126.5, 122.4, 120.7, 115.2, 114.2, 114.0, 94.4, 84.7, 63.5, 62.2, 55.2, 46.7, 40.0, 36.8, 28.7, 28.4, 27.8; IR(KBr) υ: 2954, 2838, 1650, 1503, 1378, 1252, 1173, 1024, 909, 821, 754, 657 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{40}Br_2N_5O_8$([M+H]$^+$): 914.1223, found: 914.1219.




170.001
166.687
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159.754
157.163
156.005
151.124
149.193
142.968
139.366
133.925
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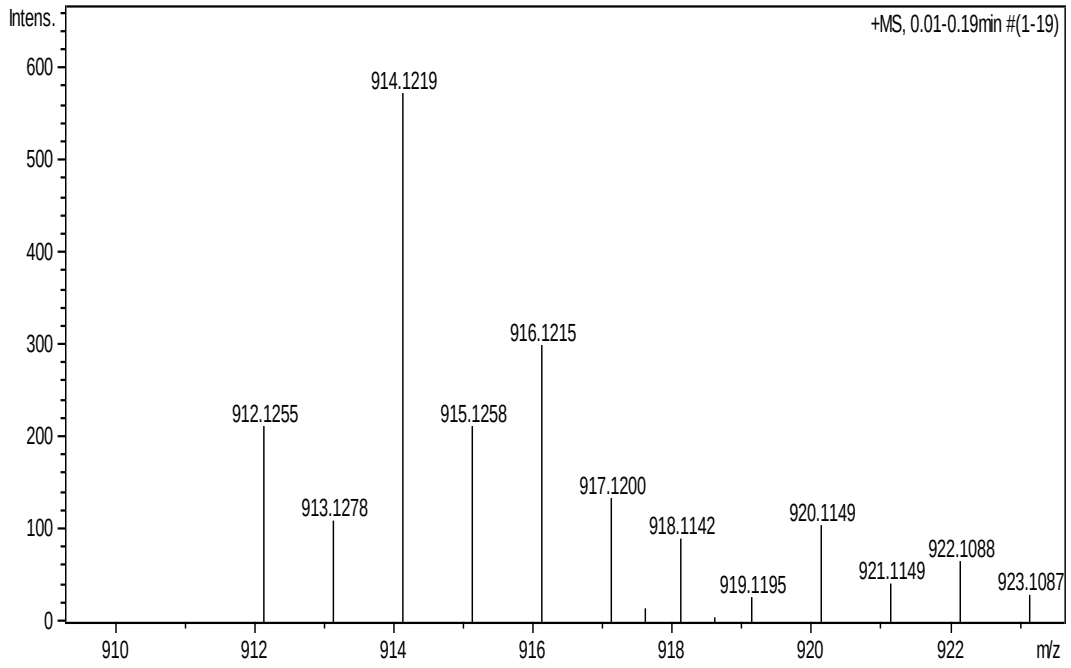
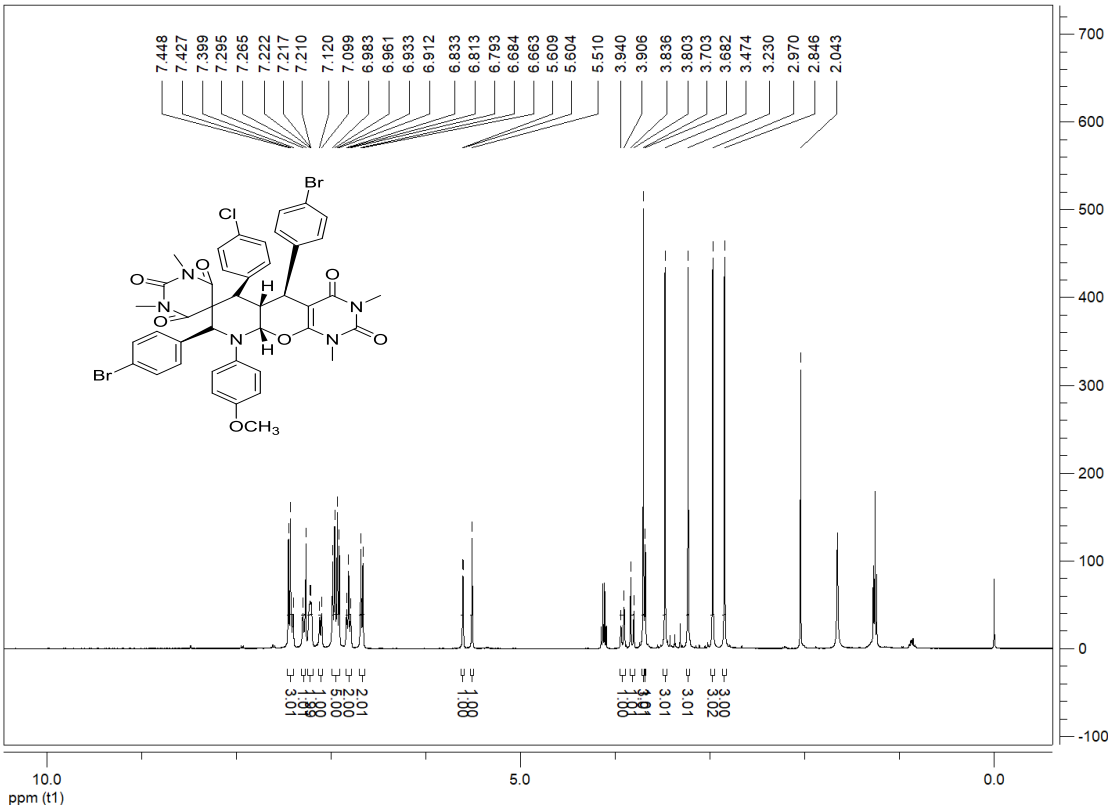
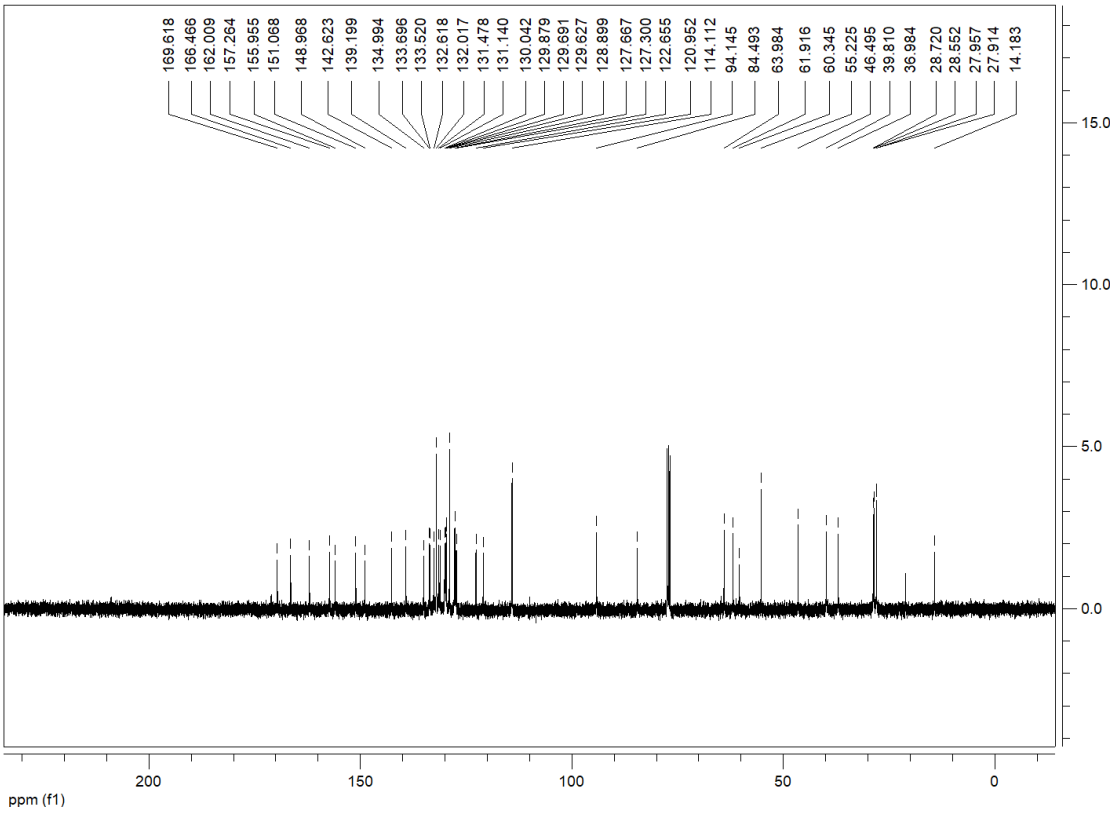
131.432
131.085
130.241
129.963
128.964
127.640
126.822
126.533
122.433
120.799
115.228
114.221
114.069
94.404
84.711
63.515
62.249
55.220
46.708
40.007
36.864
28.710
28.492
27.896
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.01-0.19min #(1-19)
600
500
400
300
200
100
0
914.1219
916.1215
912.1255
915.1258
917.1200
913.1278
918.1142
920.1149
922.1088
921.1149
919.1195
923.1087
910
912
914
916
918
920
922
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(4-bromophenyl)-6-(4-chlorophenyl)-9-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3k):**

white solid, 89%, m.p.184-186℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.40 (m, 3H, ArH), 7.30-7.26 (m, 1H, ArH), 7.22-7.21 (m, 2H, ArH), 7.11 (d, *J* = 8.4 Hz, 1H, ArH), 6.98-6.91 (m, 5H, ArH), 6.81 (t, *J* = 8.0 Hz, 1H, ArH), 6.67 (d, *J* = 8.4 Hz, 2H, ArH), 5.61 (d, *J* = 2.0 Hz, 1H, CH), 5.51 (s, 1H, CH), 3.92 (d, *J* = 13.6 Hz, 1H, CH), 3.82 (d, *J* = 13.2 Hz, 1H, CH), 3.70 (s, 3H, OCH_3), 3.68 (s, 1H, CH), 3.47 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3), 2.85 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.6, 166.4, 162.0, 157.2, 155.9, 151.0, 148.9, 142.6, 139.1, 134.9, 133.6, 133.5, 132.6, 132.0, 131.4, 131.1, 130.0, 129.8, 129.6, 129.6, 128.8, 127.6, 127.2, 122.6, 120.9, 114.1, 94.1, 84.4, 63.9, 61.9, 60.3, 55.2, 46.4, 39.8, 36.9, 28.7, 28.5, 27.9, 27.9, 14.1; IR(KBr) υ: 2961, 1681, 1647, 1481, 1376, 1247, 1171, 1105, 1018, 916, 825 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{42}H_{37}Br_2ClN_5O_7$([M+H]$^+$): 918.0728, found: 918.0725.




169.618
166.466
162.009
157.264
155.955
151.068
148.968
142.623
139.199
134.994
133.696
133.520
132.618
132.017
131.478
131.140
130.042
129.879
129.691
129.627
128.899
127.667
127.300
122.655
120.952
114.112
94.145
84.493
63.984
61.916
60.345
55.225
46.495
39.810
36.984
28.720
28.552
27.957
27.914
14.183
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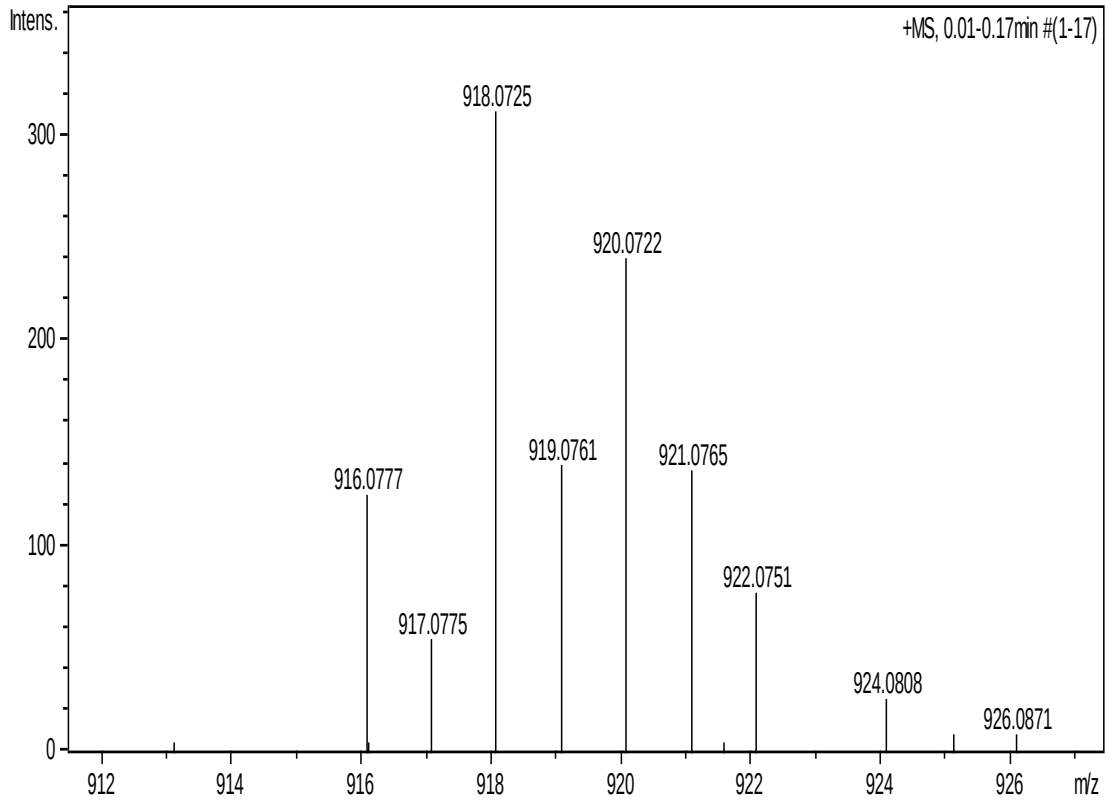
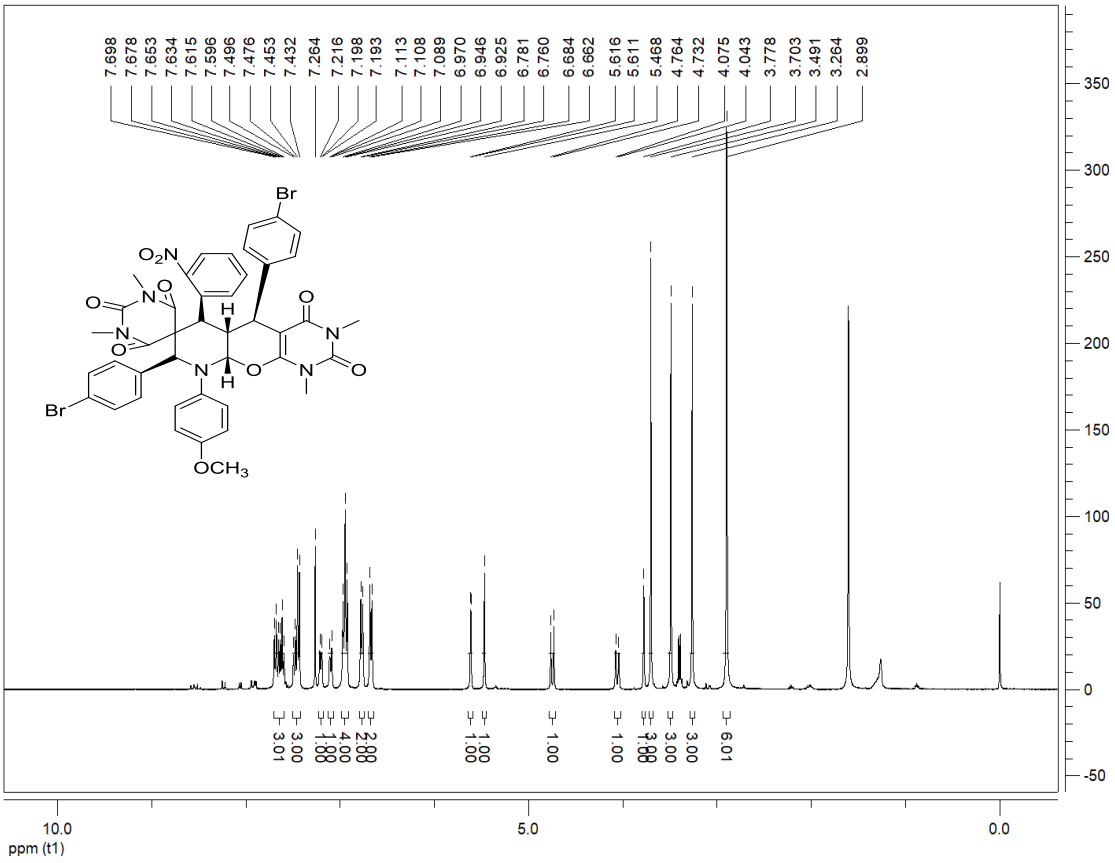
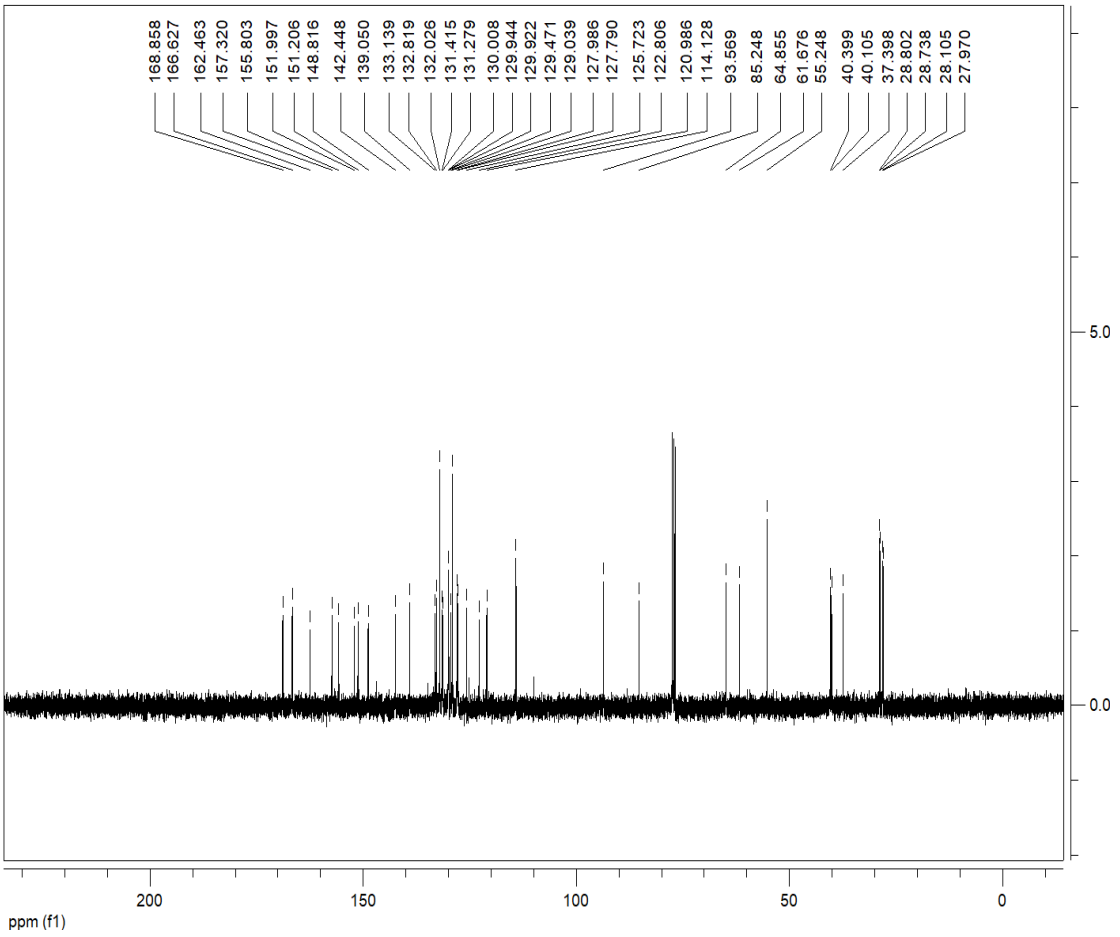
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.01-0.17min #(1-17)
918.0725
920.0722
916.0777
919.0761
921.0765
922.0751
917.0775
924.0808
926.0871
300
200
100
0
912
914
916
918
920
922
924
926
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(4-bromophenyl)-9-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-6-(2-nitrophenyl)-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (3l):**

white solid, 88%, m.p.154-156℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70-7.60 (m, 3H, ArH), 7.50-7.43 (m, 3H, ArH), 7.22-7.19 (m, 1H, ArH), 7.11-7.09 (m, 1H, ArH), 6.97-6.92 (m, 4H, ArH), 6.77 (d, *J* = 8.4 Hz, 2H, ArH), 6.67 (d, *J* = 8.8 Hz, 2H, ArH), 5.61 (d, *J* = 2.0 Hz, 1H, CH), 5.47 (s, 1H, CH), 4.74 (d, *J* = 12.8 Hz, 1H, CH), 4.06 (d, *J* = 12.8 Hz, 1H, CH), 3.78 (s, 1H, CH), 3.70 (s, 3H, OCH_3), 3.49 (s, 3H, NCH_3), 3.26 (s, 3H, NCH_3), 2.90 (s, 6H, $2NCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.8, 166.6, 162.4, 157.3, 155.8, 151.9, 151.2, 148.8, 142.4, 139.0, 133.1, 132.8, 132.0, 131.4, 131.2, 130.0, 129.9, 129.9, 129.4, 129.0, 127.9, 127.7, 125.7, 122.8, 120.9, 114.1, 93.5, 85.2, 64.8, 61.6, 55.2, 40.3, 40.1, 37.3, 28.8, 28.7, 28.1, 27.9; IR(KBr) υ: 2955, 1681, 1647, 1523, 1479, 1379, 1247, 1173, 1002, 907, 828, 781 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{42}H_{37}Br_2N_6O_9$([M+H]$^+$): 929.0968, found: 929.0980.

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155.803
151.997
151.206
148.816
142.448
139.050
133.139
132.819
132.026
131.415
131.279
130.008
129.944
129.922
129.471
129.039
127.986
127.790
125.723
122.806
120.986
114.128
93.569
85.248
64.855
61.676
55.248
40.399
40.105
37.398
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28.738
28.105
27.970
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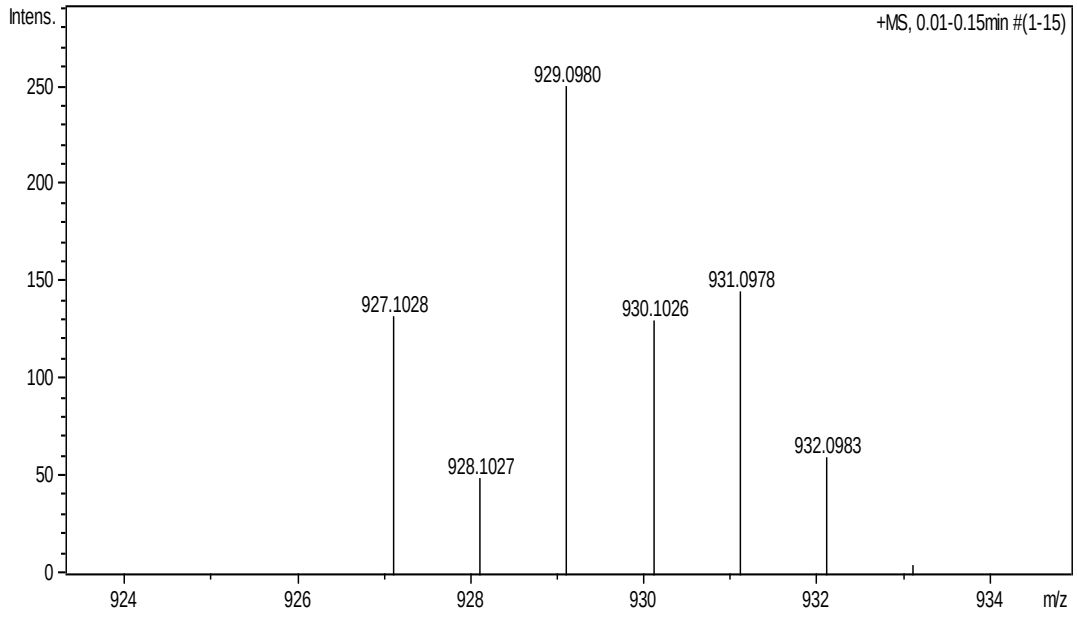
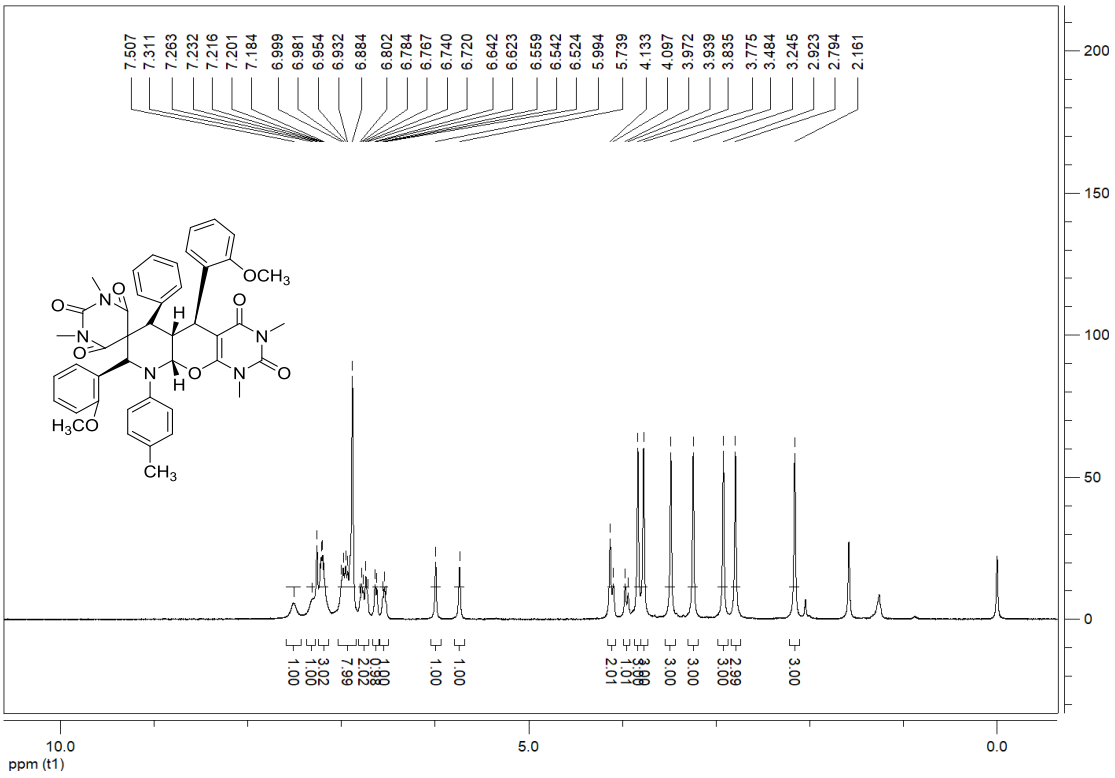
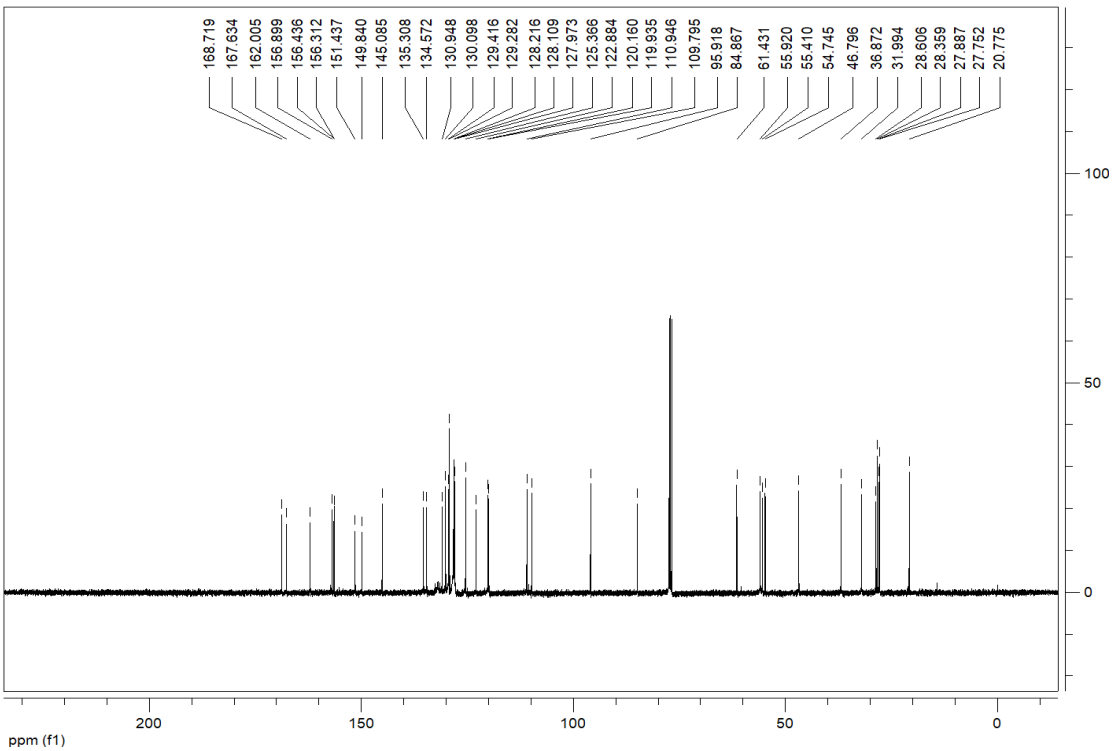
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.01-0.15min #(1-15)
929.0980
927.1028
930.1026
931.0978
928.1027
932.0983
250
200
150
100
50
0
924
926
928
930
932
934
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(2-methoxyphenyl)-1,1',3,3'-tetramethyl-6-phenyl-9-(p-tolyl)-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone (4a):**

white solid, 47%, m.p.140-143℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (brs, 1H, ArH), 7.31 (brs, 1H, ArH), 7.23 -7.18 (m, 3H, ArH), 7.00-6.88 (m, 8H, ArH), 6.80-6.72 (m, 2H, ArH), 6.63 (d, *J* = 7.6 Hz, 1H, ArH), 6.54 (t, *J* = 7.0 Hz, 1H, ArH), 5.99 (s, 1H, CH), 5.74 (s, 1H, CH), 4.13-4.10 (m, 2H, CH), 3.96 (d, *J* = 13.2 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.48 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 2.92 (s, 3H, NCH_3), 2.79 (s, 3H, NCH_3), 2.16 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.7, 167.6, 162.0, 156.8, 156.4, 156.3, 151.4, 149.8, 145.0, 135.3, 134.5, 130.9, 130.0, 129.4, 129.2, 128.2, 128.1, 127.9, 125.3, 122.8, 120.1, 119.9, 110.9, 109.7, 95.9, 84.8, 61.4, 55.9, 55.4, 54.7, 46.7, 36.8, 31.9, 28.6, 28.3, 27.8, 27.7, 20.7; IR(KBr) υ:3031, 2954, 2838, 1744, 1680, 1650, 1599, 1585, 1513, 1492, 1456, 1419, 1379, 1316, 1288, 1243, 1197, 1172, 1136, 1112, 1021, 986, 915, 893, 821, 798, 784, 756, 703, 673, 646 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{44}N_5O_8$([M+H]$^+$): 770.3190, found: 770.3206.

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162.005
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135.308
134.572
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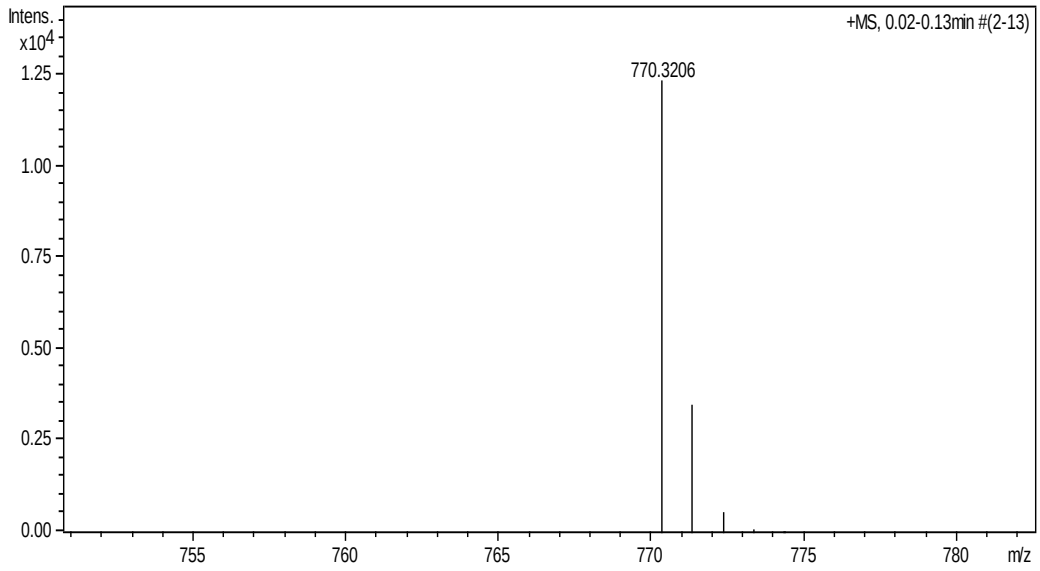
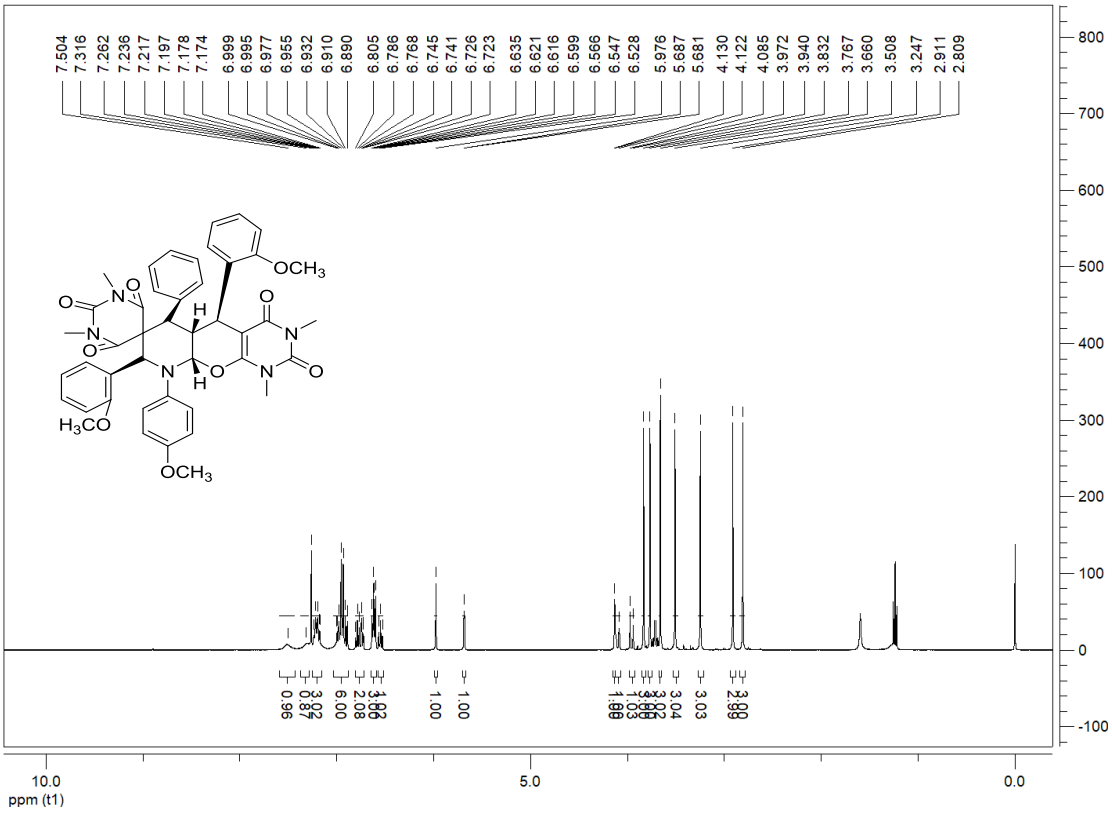
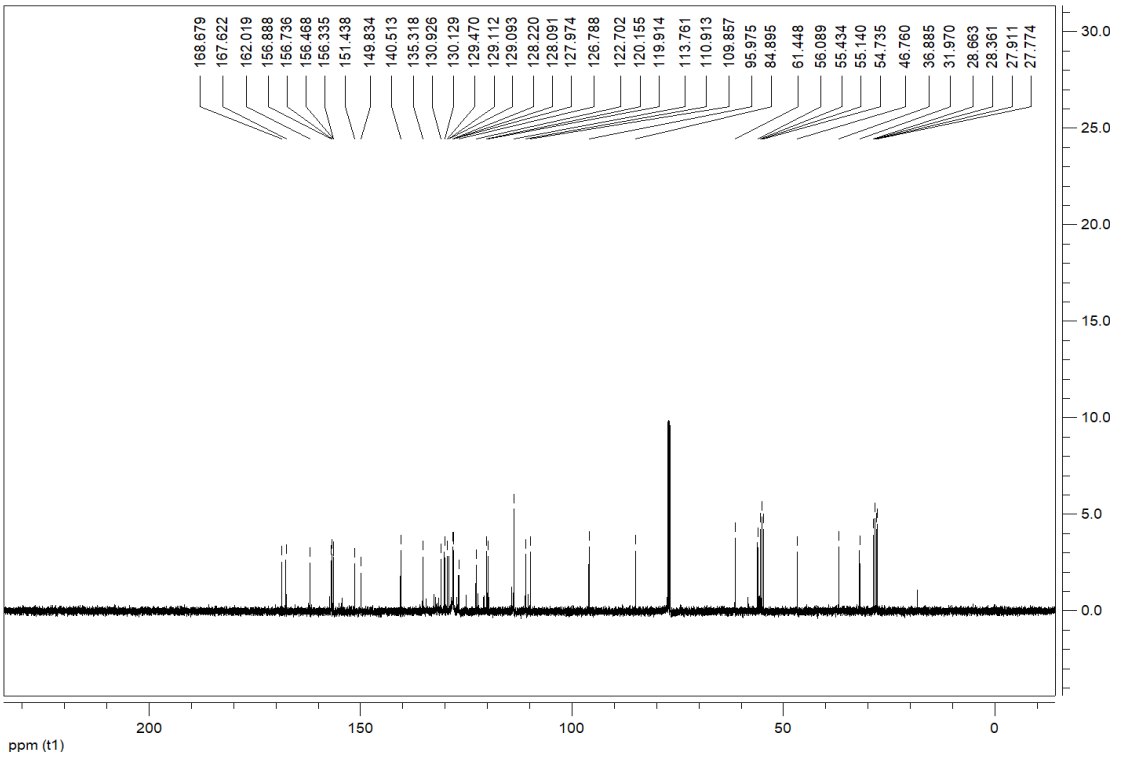
130.098
129.416
129.282
128.216
128.109
127.973
125.366
122.884
120.160
119.935
110.946
109.795
95.918
84.867
61.431
55.920
55.410
54.745
46.796
36.872
31.994
28.606
28.359
27.887
27.752
20.775
100
50
0
200
150
100
50
0
ppm (f1)


Intens.
x10^4
1.25
1.00
0.75
0.50
0.25
0.00
+MS, 0.02-0.13min #(2-13)
770.3206
755
760
765
770
775
780
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(2-methoxyphenyl)-9-(4-methoxyphenyl)-1,1',3,3'-tetramethyl-6-phenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4b)**:

white solid, 47%, m.p.136-138℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (brs, 1H, ArH), 7.32 (brs, 1H, ArH), 7.24 -7.17 (m, 3H, ArH), 7.00-6.89 (m, 6H, ArH), 6.80-6.72 (m, 2H, ArH), 6.64-6.60 (m, 3H, ArH), 6.55 (t, *J* = 7.6 Hz, 1H, ArH), 5.98 (s, 1H, CH), 5.68 (d, *J* = 2.4 Hz, 1H, CH), 4.13 (s, 1H, CH), 4.10 (d, *J* = 14.8 Hz, 1H, CH), 3.96 (d, *J* = 12.8 Hz, 1H, CH), 3.83 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.51 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 2.91 (s, 3H, NCH_3), 2.81 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.6, 167.6, 162.0, 156.8, 156.7, 156.4, 156.3, 151.4, 149.8, 140.5, 135.3, 130.9, 130.1, 129.4, 129.1, 129.0, 128.2, 128.0, 127.9, 126.7, 122.7, 120.1, 119.9, 113.7, 110.9, 109.8, 95.9, 84.8, 61.4, 56.0, 55.4, 55.1, 54.7, 46.7, 36.8, 31.9, 28.6, 28.3, 27.9, 27.7; IR(KBr) υ: 3065, 2962, 2840, 1701, 1679, 1640, 1600, 1586, 1512, 1492, 1464, 1419, 1377, 1277, 1250, 1170, 1111, 1028, 986, 913, 889, 837, 828, 813, 800, 785, 755, 702, 672, 647 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{44}N_5O_9$([M+H]$^+$): 786.3139, found: 786.3150.




168.679
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162.019
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156.335
151.438
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140.513
135.318
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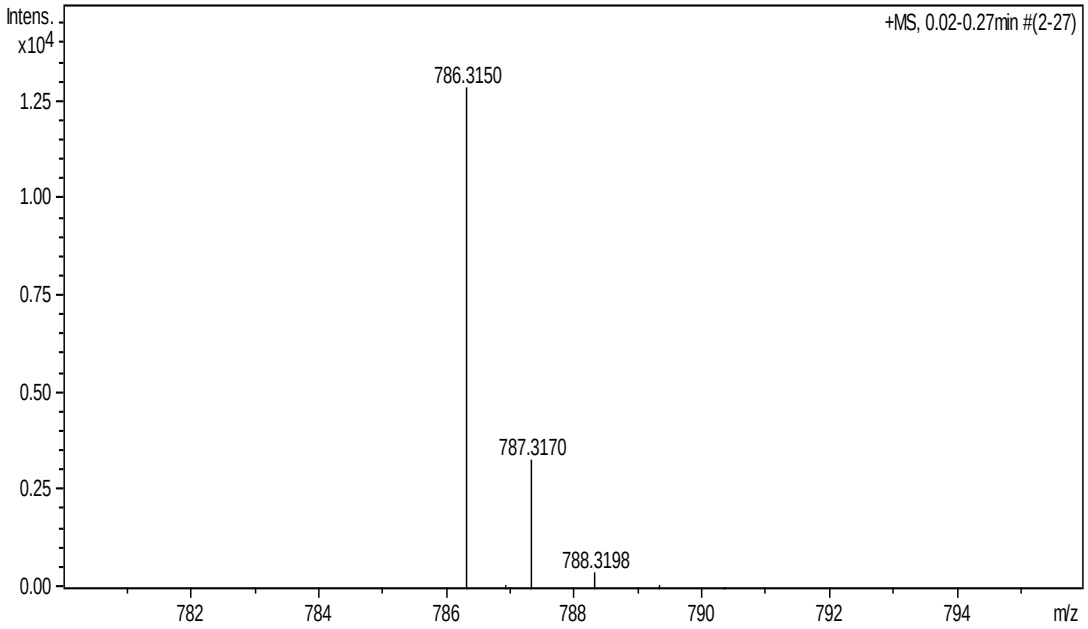
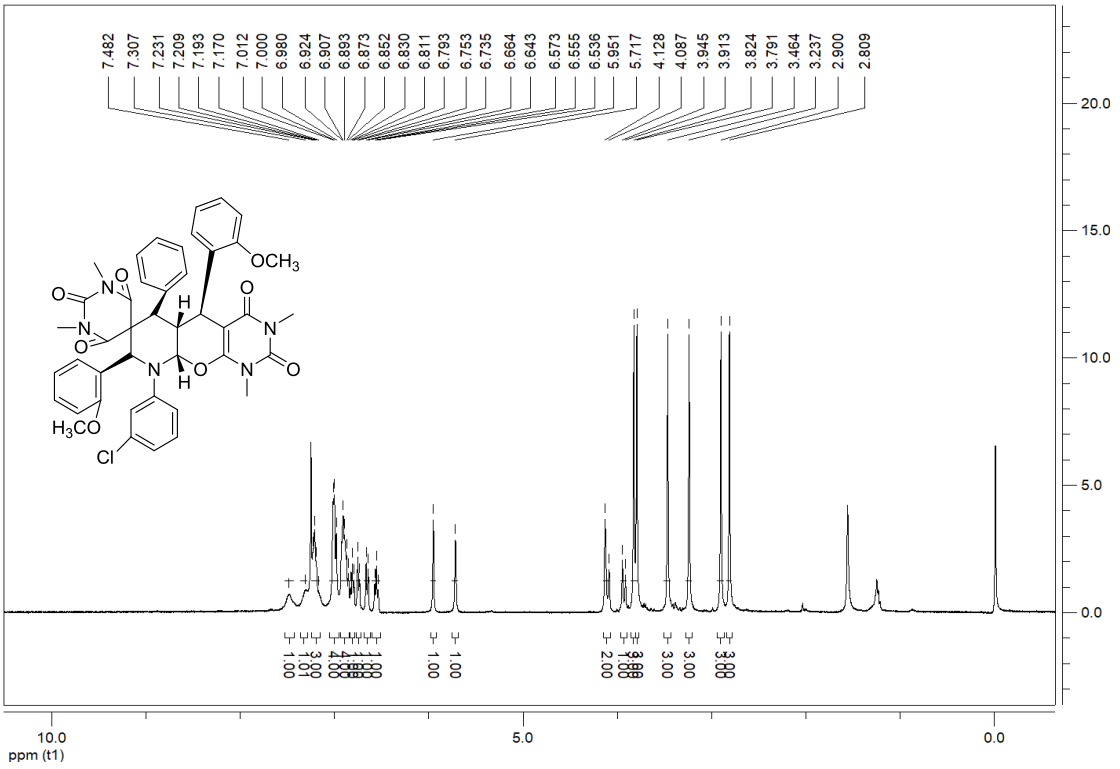
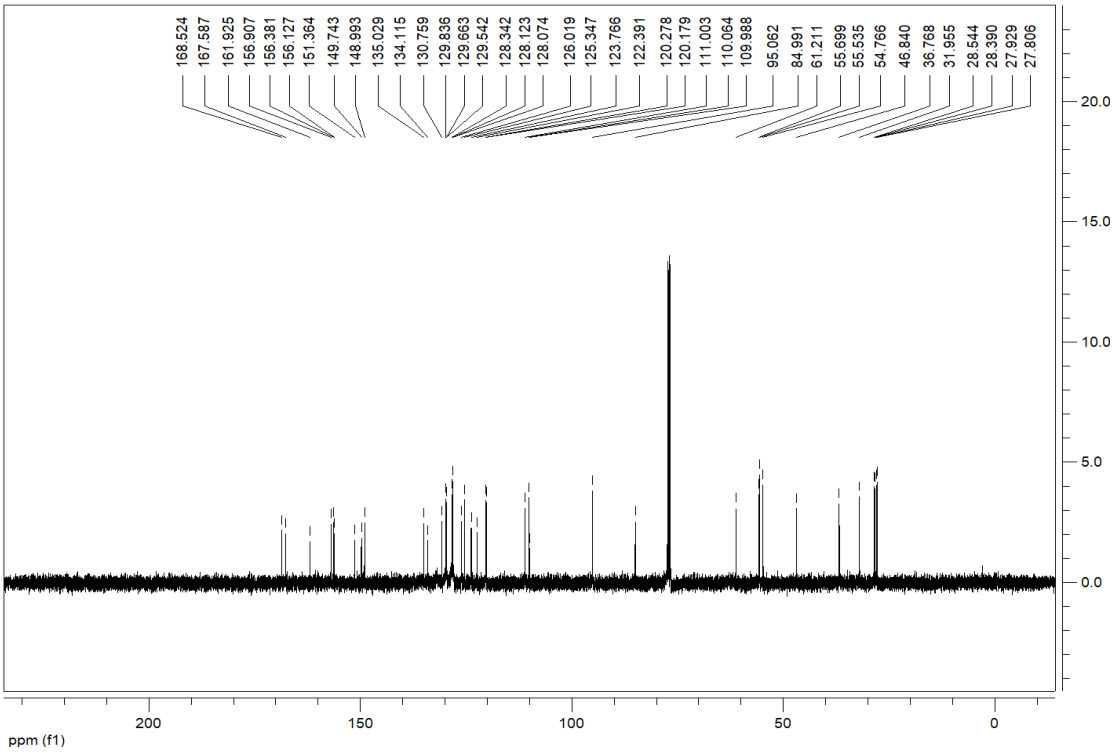
130.129
129.470
129.112
129.093
128.220
128.091
127.974
126.788
122.702
120.155
119.914
113.761
110.813
109.857
95.975
84.895
61.448
56.089
55.434
55.140
54.735
46.760
36.885
31.970
28.663
28.361
27.911
27.774
30.0
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)


Intens.
x10^4
+MS, 0.02-0.27min #(2-27)
786.3150
787.3170
788.3198
1.25
1.00
0.75
0.50
0.25
0.00
782
784
786
788
790
792
794
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(3-chlorophenyl)-5,8-bis(2-methoxyphenyl)-1,1',3,3'-tetramethyl-6-phenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4c):**

white solid, 43%, m.p.149-150℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (brs, 1H, ArH), 7.31 (brs, 1H, ArH), 7.23-7.17 (m, 3H, ArH), 7.01-6.98 (m, 4H, ArH), 6.92-6.85 (m, 4H, ArH), 6.81 (t, *J* = 7.4 Hz, 1H, ArH), 6.74 (d, *J* = 7.2 Hz, 1H, ArH), 6.65 (d, *J* = 8.4 Hz, 1H, ArH), 6.56 (t, *J* = 7.4 Hz, 1H, ArH), 5.95 (s, 1H, CH), 5.72 (s, 1H, CH), 4.13-4.09 (m, 2H, CH), 3.93 (d, *J* = 12.8 Hz, 1H, CH), 3.82 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.46 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 2.90 (s, 3H, NCH_3), 2.81 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5, 167.5, 161.9, 156.9, 156.3, 156.1, 151.3, 149.7, 148.9, 135.0, 134.1, 130.7, 129.8, 129.6, 129.5, 128.3, 128.1, 128.0, 126.0, 125.3, 123.7, 122.3, 120.2, 120.1, 111.0, 110.0, 109.9, 95.0, 84.9, 61.2, 55.6, 55.5, 54.7, 46.8, 36.7, 31.9, 28.5, 28.3, 27.9, 27.8; IR(KBr) υ: 3071, 3000, 2957, 2838, 1712, 1681, 1651, 1588, 1487, 1419, 1379, 1282, 1243, 1170, 1137, 1109, 1026, 986, 918, 867, 815, 798, 751, 702, 671, 646, cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{41}ClN_5O_8$([M+H]$^+$): 790.2644, found: 790.2649.

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135.029
134.115
130.759
129.836
129.663
129.542
128.342
128.123
128.074
126.019
125.347
123.766
122.391
120.278
120.179
111.003
110.064
109.988
95.062
84.991
61.211
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55.535
54.766
46.840
36.768
31.955
28.544
28.390
27.929
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20.0
15.0
10.0
5.0
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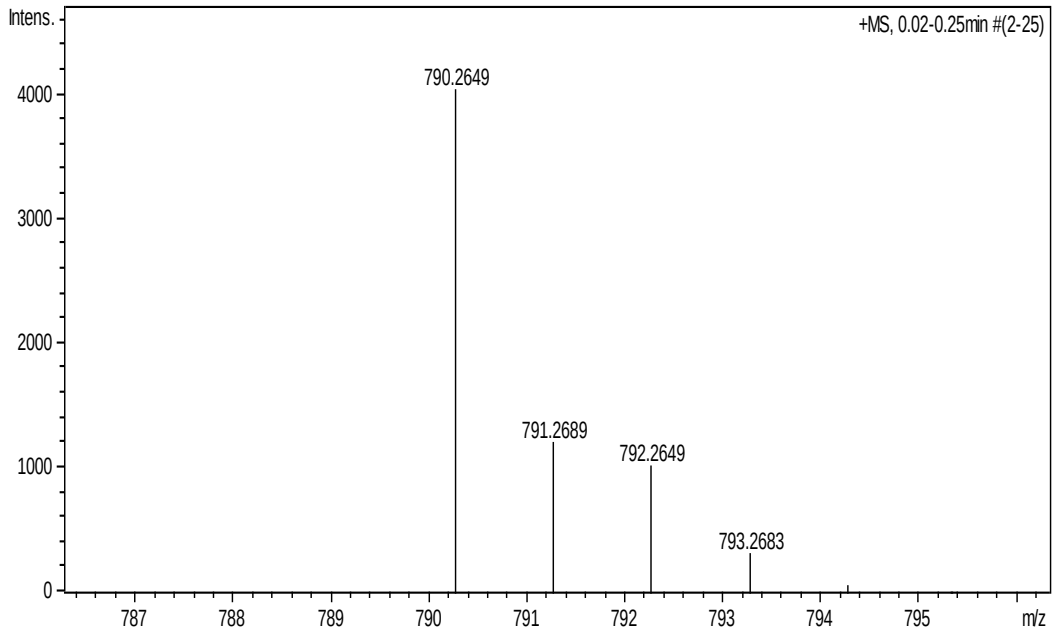
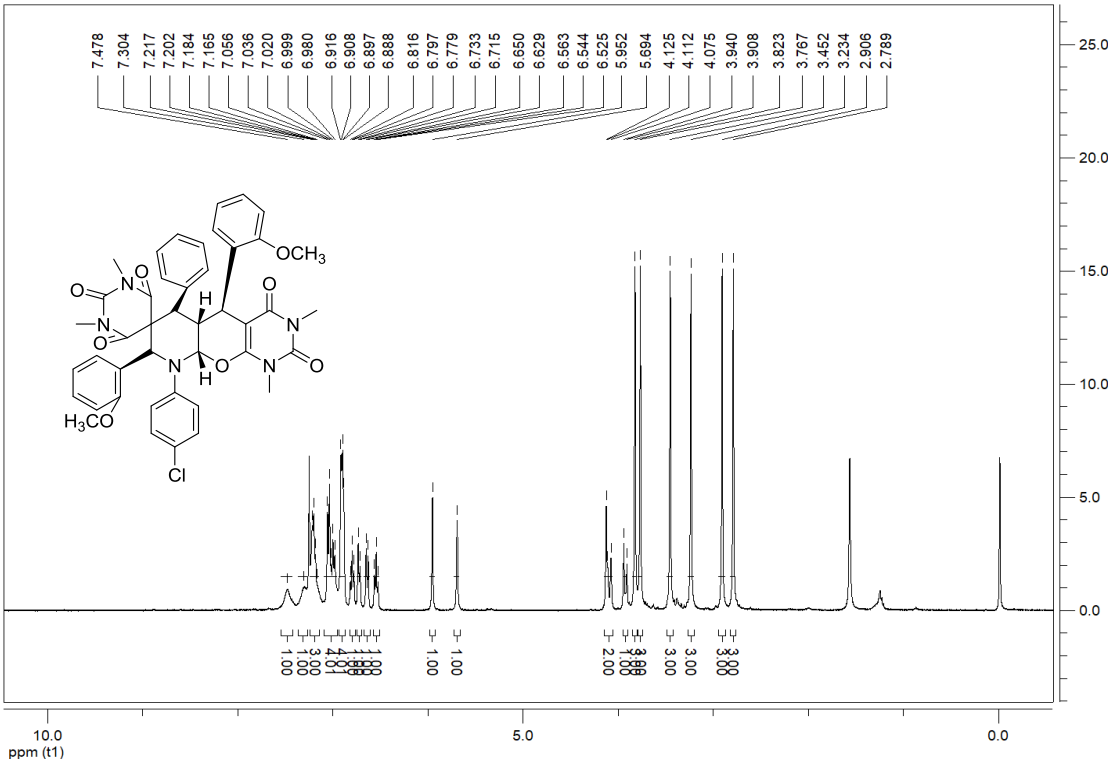
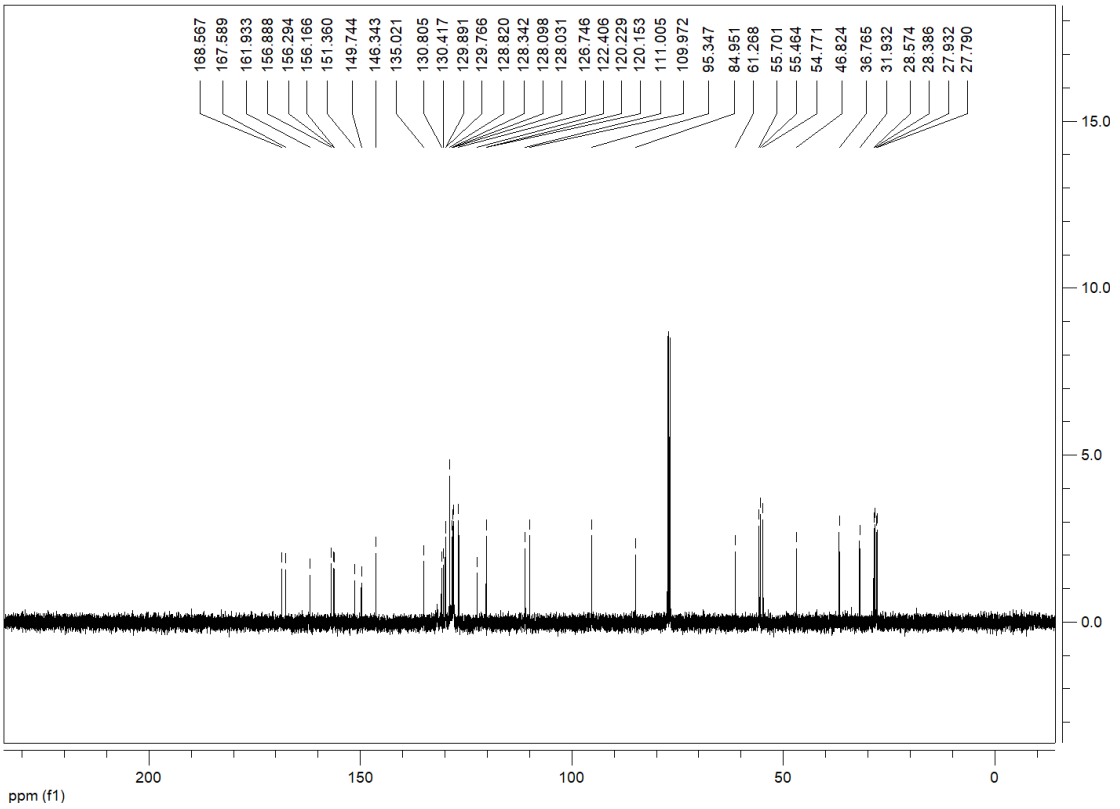
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.25min #(2-25)
790.2649
791.2689
792.2649
793.2683
4000
3000
2000
1000
0
787
788
789
790
791
792
793
794
795
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(4-chlorophenyl)-5,8-bis(2-methoxyphenyl)-1,1',3,3'-tetramethyl-6-phenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4d)**:

white solid, 57%, m.p.139-140℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ:7.48 (brs, 1H, ArH), 7.30 (brs, 1H, ArH), 7.22-7.16 (m, 3H, ArH), 7.06-6.98 (m, 4H, ArH), 6.92-6.89 (m, 4H, ArH), 6.80 (t, *J* = 7.4 Hz, 1H, ArH), 6.72 (d, *J* = 7.2 Hz, 1H, ArH), 6.64 (d, *J* = 8.4 Hz, 1H, ArH), 6.54 (t, *J* = 7.6 Hz, 1H, ArH), 5.95 (s, 1H, CH), 5.69 (s, 1H, CH), 4.12-4.08 (m, *2*H, CH), 3.92 (d, *J* =12.8 Hz,1H, CH), 3.82 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.45 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.91 (s, 3H, NCH_3), 2.79 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5, 167.5, 161.9, 156.8, 156.2, 156.1, 151.3, 149.7, 146.3, 135.0, 130.8, 130.4, 129.8, 129.7, 128.8, 128.3, 128.0, 128.0, 126.7, 122.4, 120.2, 120.1, 111.0, 109.9, 95.3, 84.9, 61.2, 55.7, 55.4, 54.7, 46.8, 36.7, 31.9, 28.5, 28.3, 27.9, 27.7; IR(KBr) υ: 2951, 2836, 1707, 1682, 1649, 1600, 1492, 1461, 1419, 1380, 1286, 1243, 1171, 1138, 1111, 1090, 1050, 1029, 987, 917, 894, 821, 800, 786, 758, 703, 673, 659, 644, cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{41}ClN_5O_8$([M+H]$^+$): 790.2644, found: 790.2638.

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167.589
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149.744
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130.417
129.891
129.766
128.820
128.342
128.098
128.031
126.746
122.406
120.229
120.153
111.005
109.972
95.347
84.951
61.268
55.701
55.464
54.771
46.824
36.765
31.932
28.574
28.386
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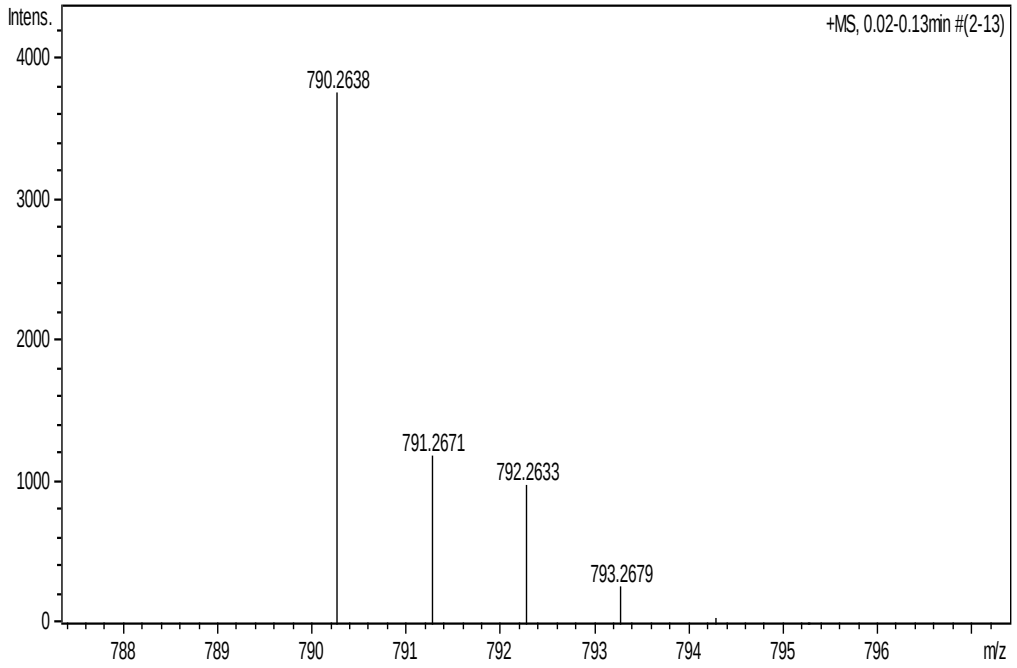
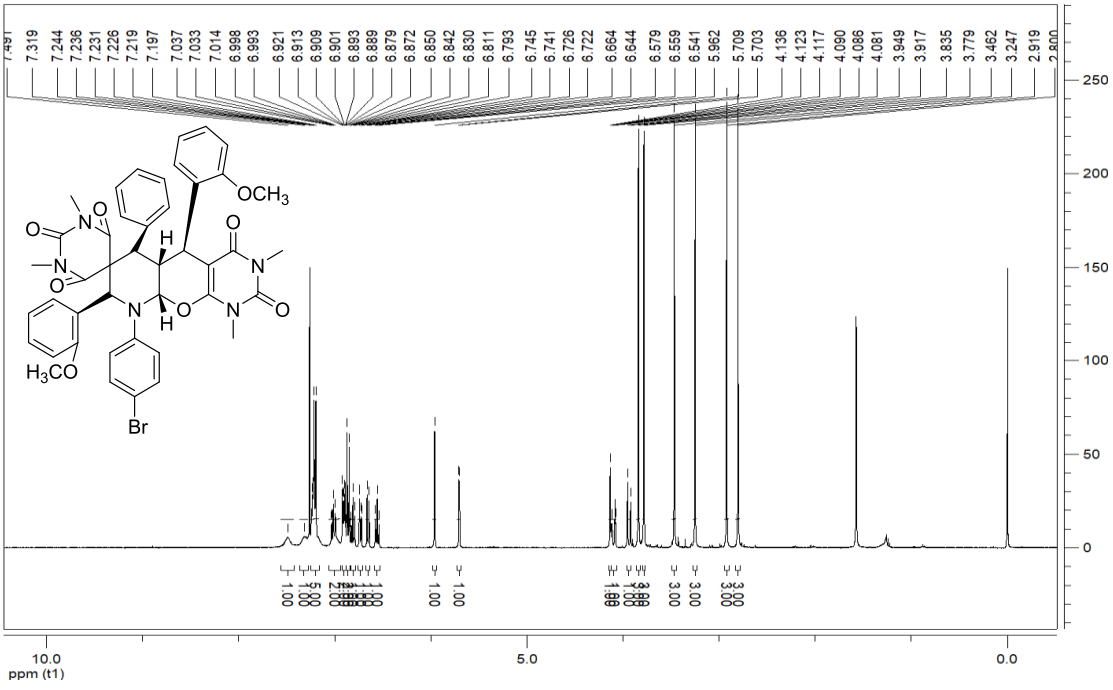
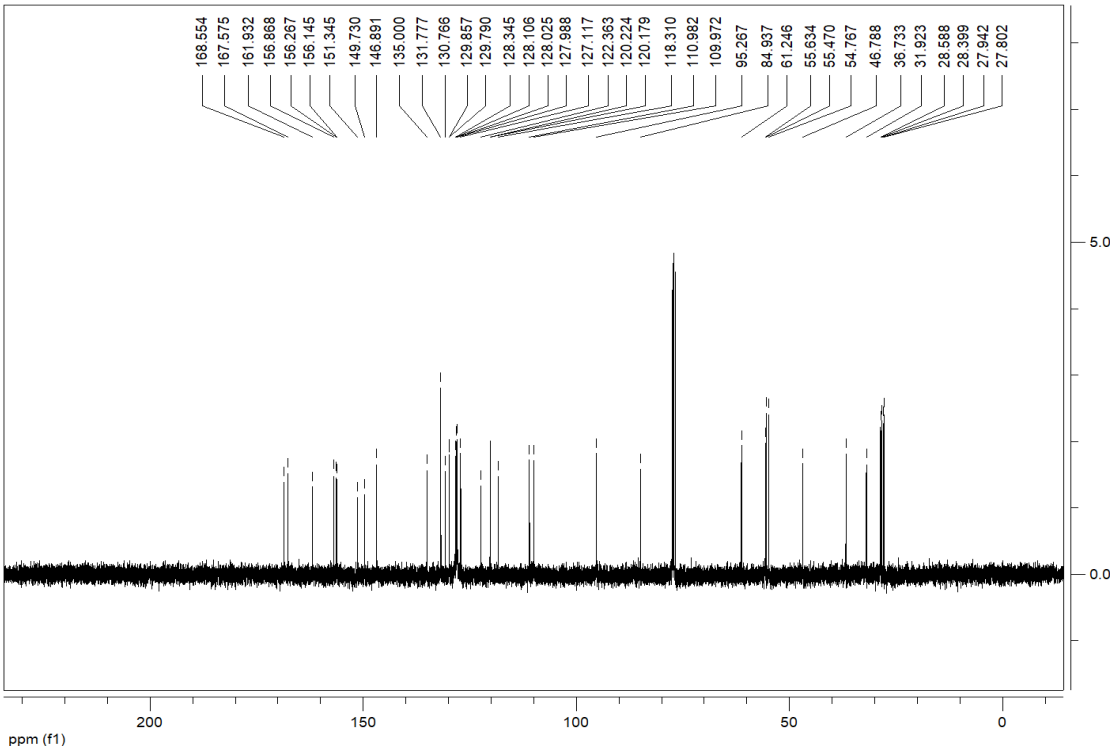
27.790
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.13min #(2-13)
4000
3000
2000
1000
0
790.2638
791.2671
792.2633
793.2679
788
789
790
791
792
793
794
795
796
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(4-bromophenyl)-5,8-bis(2-methoxyphenyl)-1,1',3,3'-tetramethyl-6-phenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4e):**

white solid, 46%, m.p.137-138℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (brs, 1H, ArH), 7.32 (brs, 1H, ArH), 7.24-7.20 (m, 5H, ArH), 7.04-6.99 (m, 2H, ArH), 6.92-6.89 (m, 2H, ArH), 6.88-6.84 (m, 2H, ArH), 6.81 (t, *J* = 7.4 Hz, 1H, ArH), 6.74-6.72 (m, 1H, ArH), 6.65 (d, *J* = 8.0 Hz, 1H, ArH), 6.56 (t, *J* = 7.6 Hz, 1H, ArH), 5.96 (s, 1H, CH), 5.71 (d, *J* = 2.4 Hz, 1H, CH), 4.14 (s, 1H, CH), 4.12-4.08 (m, 1H, CH), 3.93 (d, *J* = 12.8 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.46 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 2.92 (s, 3H, NCH_3), 2.80 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.5, 167.5, 161.9, 156.8, 156.2, 156.1, 151.3, 149.7, 146.8, 135.0, 131.7, 130.7, 129.8, 129.7, 128.3, 128.1, 128.0, 127.9, 127.1, 122.3, 120.2, 120.1, 118.3, 110.9, 109.9, 95.2, 84.9, 61.2, 55.6, 55.4, 54.7, 46.7, 36.7, 31.9, 28.5, 28.3, 27.9, 27.8; IR(KBr) υ: 3065, 3032, 2957, 2839, 1746, 1689, 1676, 1658, 1640, 1600, 1586, 1491, 1419, 1379, 1287, 1243, 1198, 1172, 1137, 1110, 1075, 1051, 1027, 987, 938, 916, 892, 815, 799, 785, 756, 704, 672, 653, 638, 605 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{41}BrN_5O_8$([M+H]$^+$): 834.2139, found: 834.2151.

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151.345
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135.000
131.777
130.766
129.857
129.790
128.345
128.106
128.025
127.988
127.117
122.363
120.224
120.179
118.310
110.982
109.972
95.267
84.937
61.246
55.634
55.470
54.767
46.788
36.733
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28.399
27.942
27.802
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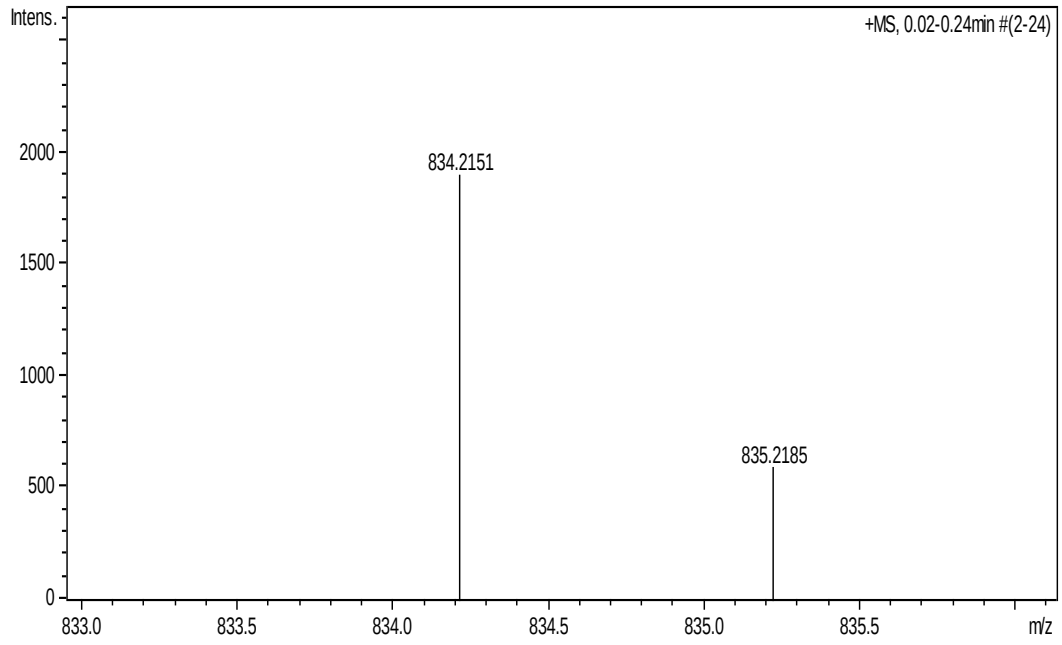
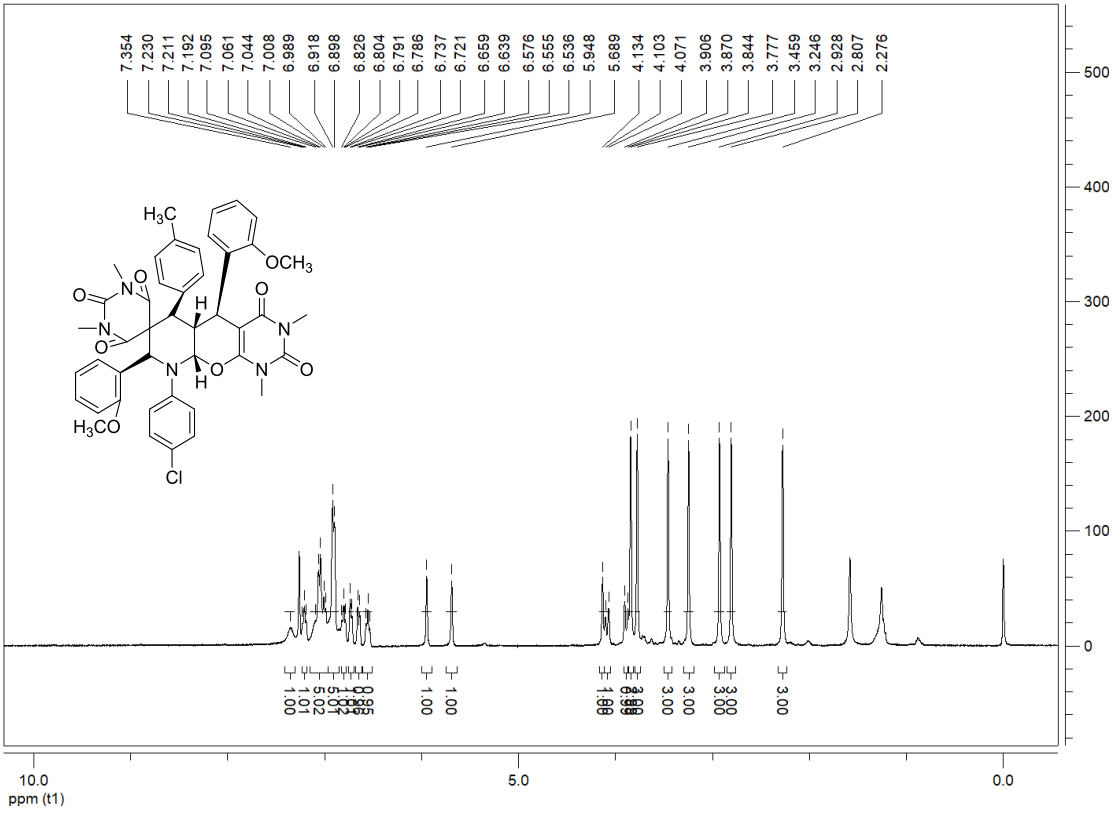
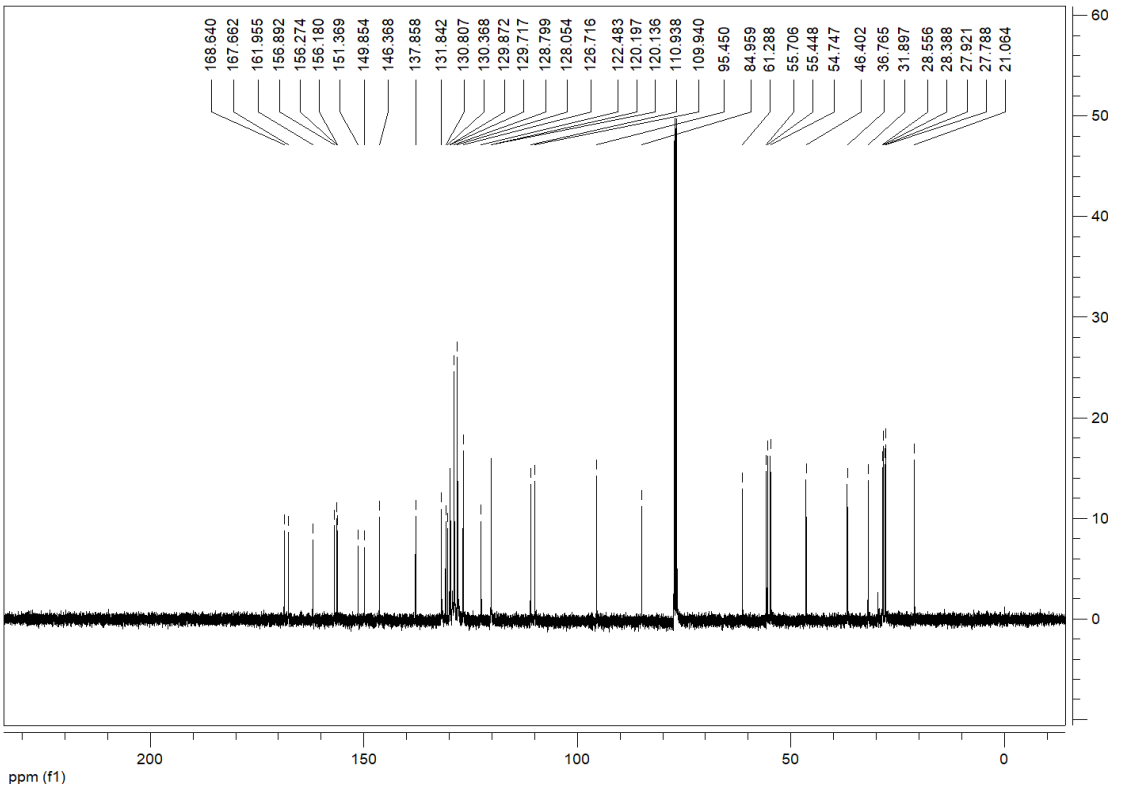
0.0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.24min #(2-24)
2000
1500
1000
500
0
834.2151
835.2185
833.0
833.5
834.0
834.5
835.0
835.5
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(4-chlorophenyl)-5,8-bis(2-methoxyphenyl)-1,1',3,3'-tetramethyl-6-(p-tolyl)-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4f)**:

white solid, 43%, m.p.132-135℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (brs, 1H, ArH), 7.21 (t, *J* = 7.4 Hz, 1H, ArH), 7.10 -6.99 (s, *J* = 8.0 Hz, 5H, ArH), 6.91 (d, *J* = 2.4 Hz, 5H, ArH), 6.83-6.79 (m, 1H, ArH), 6.65 (d, *J* = 8.0 Hz, 1H, ArH), 6.56 (t, *J* = 8.0 Hz, 1H, ArH), 5.95 (s, 1H, CH), 5.69 (s, 1H, CH), 4.13 (s, 1H, CH), 4.09 (d, *J* = 12.8 Hz, 1H, CH), 3.89 (d, *J* = 14.4 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.46 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 2.93 (s, 3H, NCH_3), 2.81 (s, 3H, NCH_3), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.6, 167.6, 161.9, 156.8, 156.2, 156.1, 151.3, 149.8, 146.3, 137.8, 131.8, 130.8, 130.3, 129.8, 129.7, 128.7, 128.0, 126.7, 122.4, 120.1, 120.1, 110.9, 109.9, 95.4, 84.9, 61.2, 55.7, 55.4, 54.7, 46.4, 36.7, 31.8, 28.5, 28.3, 27.9, 27.7, 21.0; IR(KBr) υ:2954, 2837, 2097, 1747, 1707, 1682, 1649, 1492, 1462, 1419, 1380, 1285, 1243, 1172, 1138, 1108, 1090, 1051, 1026, 988, 963, 917, 895, 824, 802, 783, 763, 721, 694, cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{43}ClN_5O_8$([M+H]$^+$): 804.2800, found: 804.2806.




168.640
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156.892
156.274
156.180
151.369
149.854
146.368
137.858
131.842
130.807
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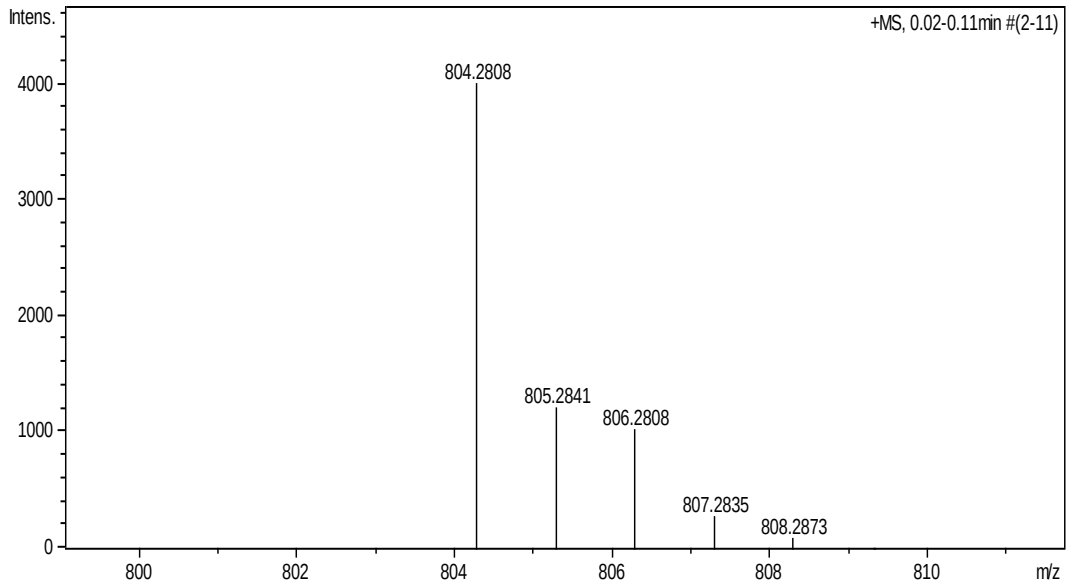
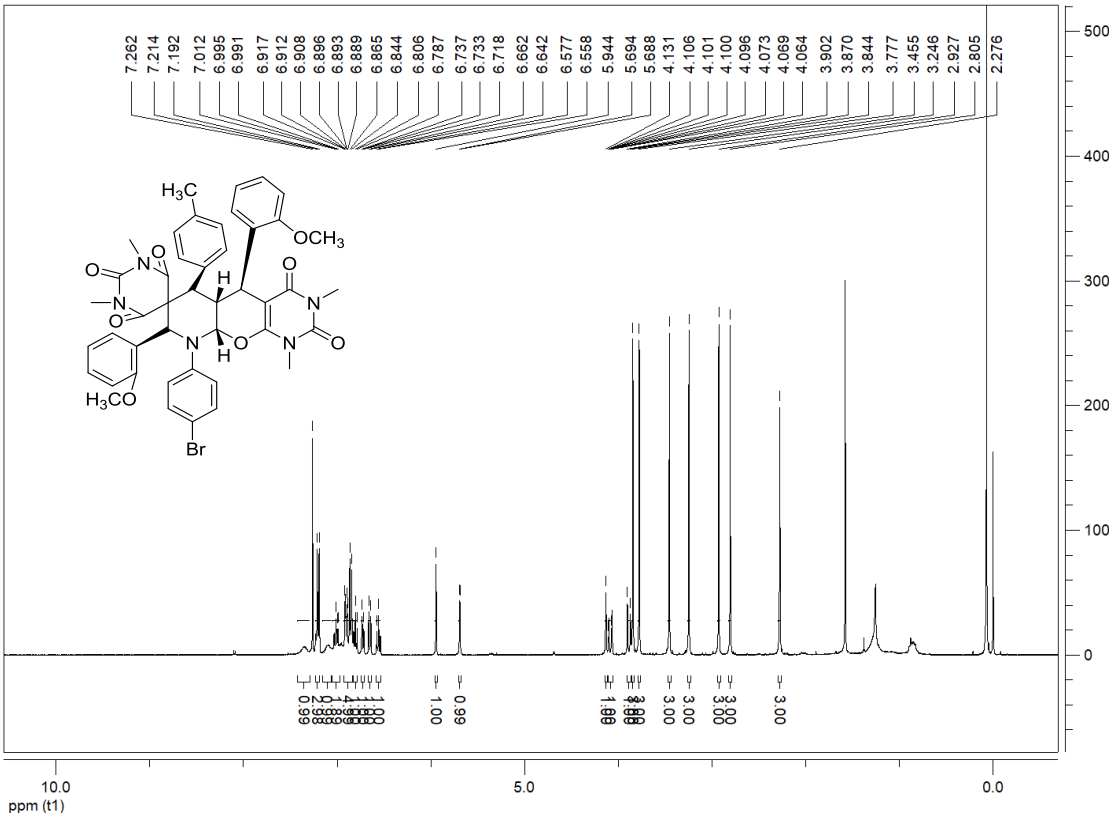
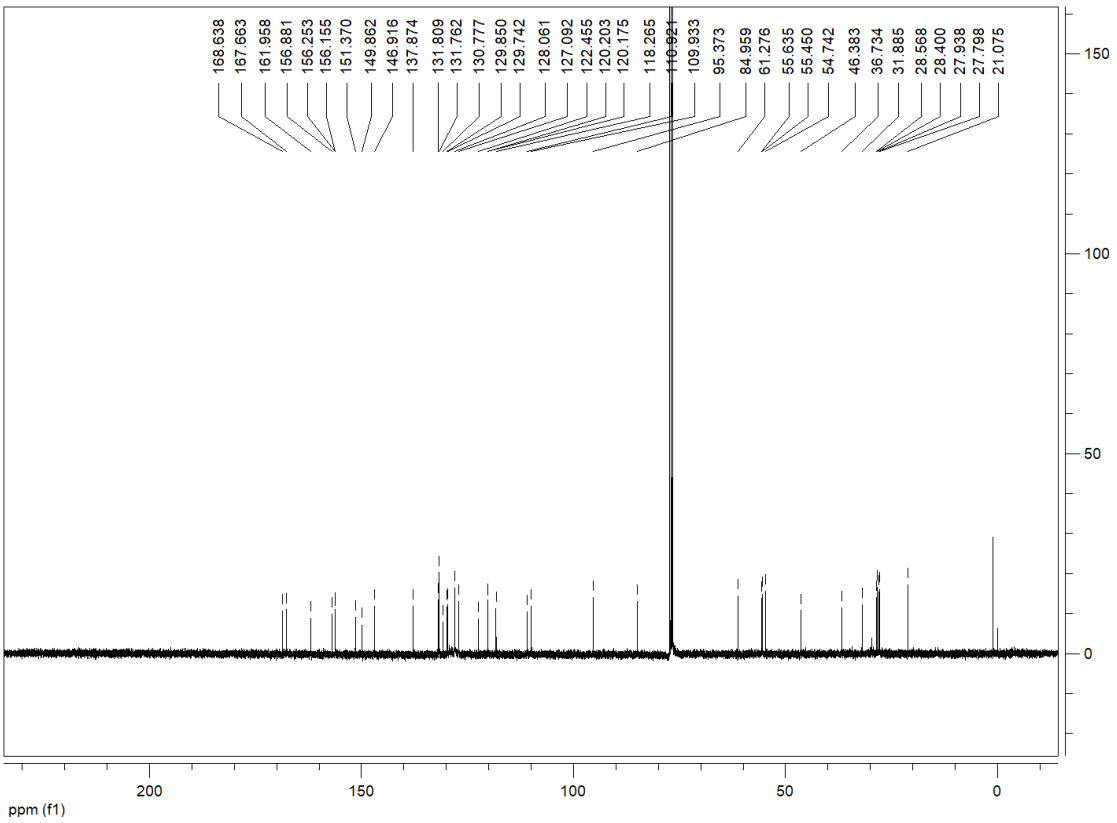
129.872
129.717
128.799
128.054
126.716
122.483
120.197
120.136
110.938
109.940
95.450
84.959
61.288
55.706
55.448
54.747
46.402
36.765
31.897
28.556
28.388
27.921
27.788
21.064
60
50
40
30
20
10
0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.11min #(2-11)
804.2808
805.2841
806.2808
807.2835
808.2873
4000
3000
2000
1000
0
800
802
804
806
808
810
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(4-bromophenyl)-5,8-bis(2-methoxyphenyl)-1,1',3,3'-tetramethyl-6-(p-tolyl)-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4g):**

white solid, 51%, m.p.139-141℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (brs, 1H, ArH), 7.23-7.19 (m, 3H, ArH), 7.09 (brs, 1H, ArH), 7.03-6.99 (m, 2H, ArH), 6.92-6.84 (m, 5H, ArH), 6.81 (t, *J* = 7.6 Hz, 1H, ArH), 6.74-6.72 (m, 1H, CH), 6.65 (d, *J* = 8.0 Hz, 1H, ArH), 6.56 (t, *J* = 7.6 Hz, 1H, ArH), 5.94 (s, 1H, CH), 5.69 (d, *J* = 2.4 Hz, 1H, CH), 4.13 (s, 1H, CH), 4.11-4.06 (m, 1H, CH), 3.89 (d, *J* = 12.8 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.46 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 2.93 (s, 3H, NCH_3), 2.80 (s, 3H, NCH_3), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.6, 167.6, 161.9, 156.8, 156.2, 156.1, 151.3, 149.8, 146.9, 137.8, 131.8, 131.7, 130.7, 129.8, 129.7, 128.0, 127.0, 122.4, 120.2, 120.1, 118.2, 110.9, 109.9, 95.3, 84.9, 61.2, 55.6, 55.4, 54.7, 46.3, 36.7, 31.8, 28.5, 28.4, 27.9, 27.7, 21.0; IR(KBr) υ: 2953, 2839, 1747, 1705, 1682, 1650, 1600, 1587, 1490, 1463, 1417, 1379, 1287, 1246, 1172, 1138, 1109, 1052, 1027, 987, 916, 895, 824, 800, 782, 756, 720, 664 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{43}BrN_5O_8$([M+H]$^+$): 848.2295, found: 848.2317.

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151.370
149.862
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130.777
129.850
129.742
128.061
127.092
122.455
120.203
120.175
118.265
110.921
109.933
95.373
84.959
61.276
55.635
55.450
54.742
46.383
36.734
31.885
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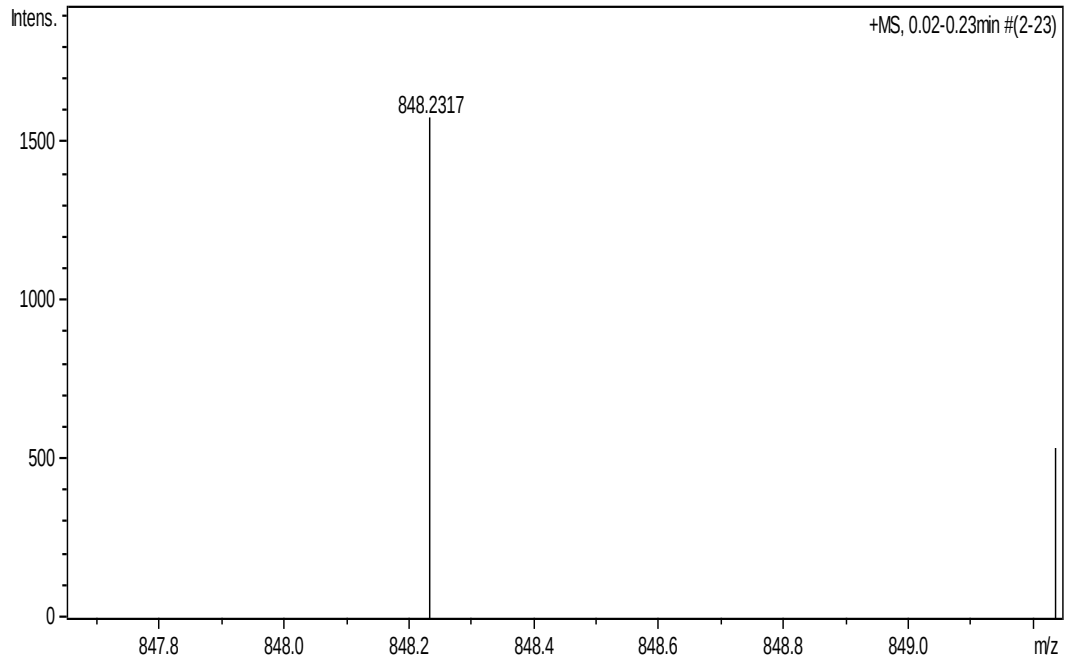
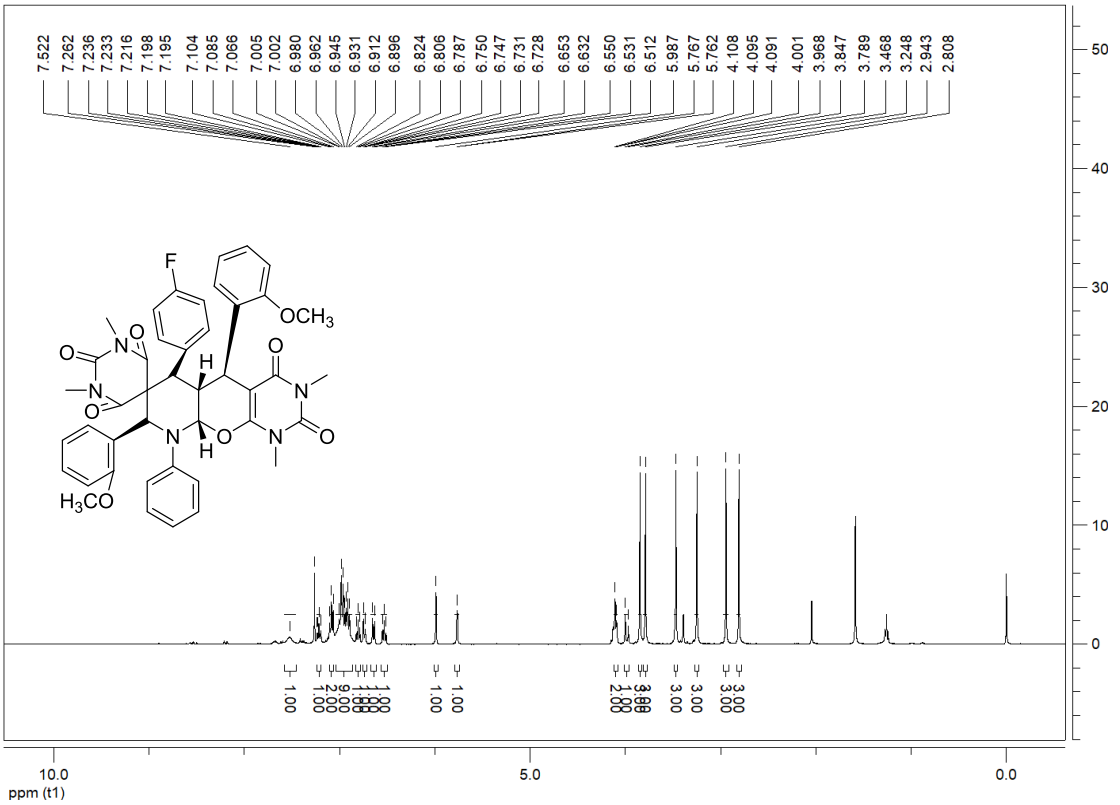
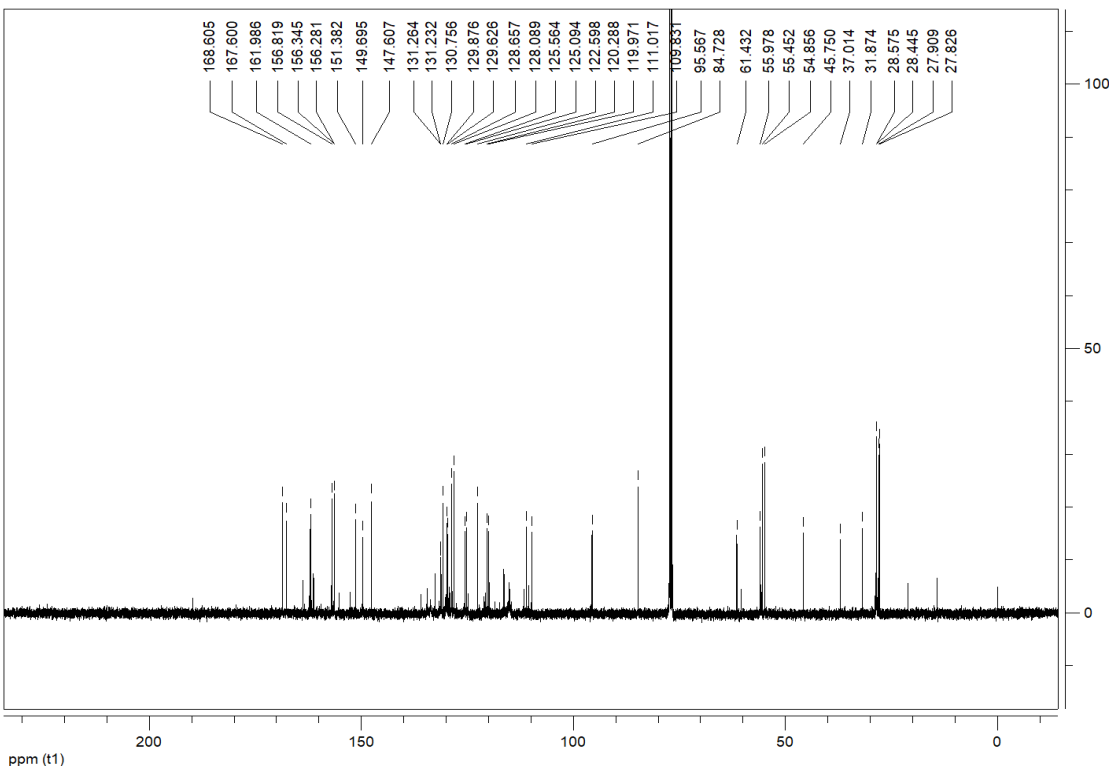
28.400
27.938
27.798
21.075
150
100
50
0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.23min #(2-23)
848.2317
1500
1000
500
0
847.8
848.0
848.2
848.4
848.6
848.8
849.0
m/z

***rel*-(5S,5aS,6S,8R,9aS)-6-(4-fluorophenyl)-5,8-bis(2-methoxyphenyl)-1,1',3,3'-tetramethyl-9-phenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4h):**

white solid, 38%, m.p.131-133℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (brs, 1H, ArH), 7.24-7.20 (m, 1H, ArH), 7.08 (t, *J* = 7.6 Hz, 2H, ArH), 7.00-6.90 (m, 9H, ArH), 6.81 (t, *J* = 7.4 Hz, 1H, ArH), 6.75-6.73 (m, 1H, ArH), 6.64 (d, *J* = 7.6 Hz, 1H, ArH), 6.53 (t, *J* = 7.6 Hz, 1H, ArH), 5.99 (s, 1H, CH), 5.76 (d, *J* = 2.8 Hz, 1H, CH), 4.11-4.09 (m, 2H, CH), 4.98 (d, *J* = 13.2 Hz, 1H, CH), 3.85 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.47 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 2.94 (s, 3H, NCH_3), 2.81 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.6, 167.6, 161.9, 156.8, 156.3, 156.2, 151.3, 149.6, 147.6, 131.2, 131.2, 130.7, 129.8, 129.6, 128.6, 128.0, 125.5, 125.0, 122.5, 120.2, 119.9, 111.0, 109.8, 95.5, 84.7, 61.4, 55.9, 55.4, 54.8, 45.7, 37.0, 31.8, 28.5, 28.4, 27.9, 27.8; IR(KBr) υ:2956, 2839, 1710, 1680, 1656, 1599, 1510, 1491, 1458, 1418, 1376, 1243, 1219, 1163, 1110, 1028, 987, 916, 837, 785, 754, 720, 701, 648 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{41}FN_5O_8$([M+H]$^+$): 774.2939, found: 774.2953.

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105.831
95.567
84.728
61.432
55.978
55.452
54.856
45.750
37.014
31.874
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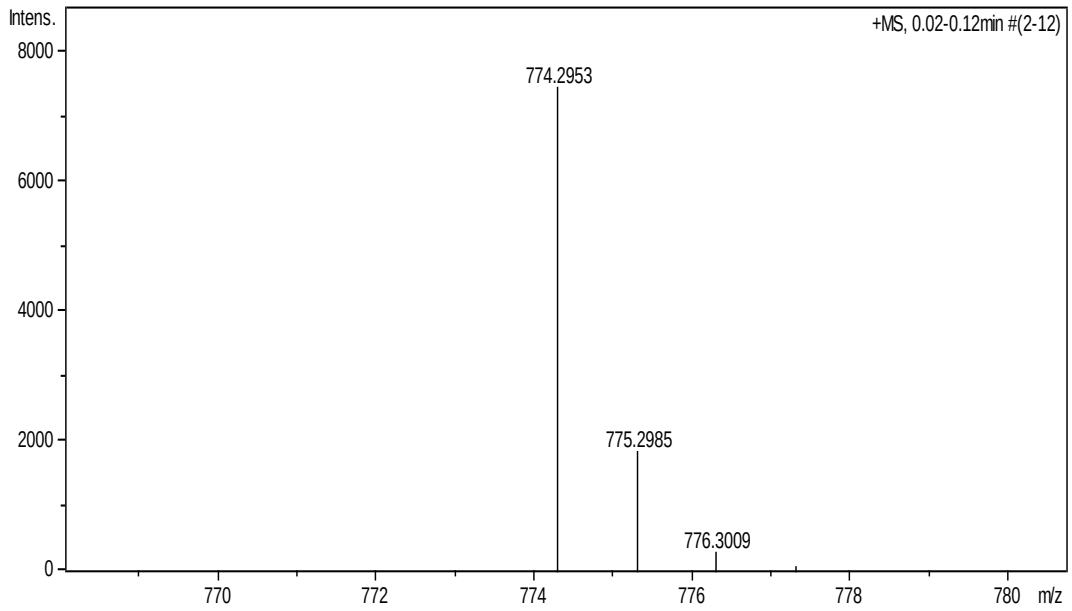
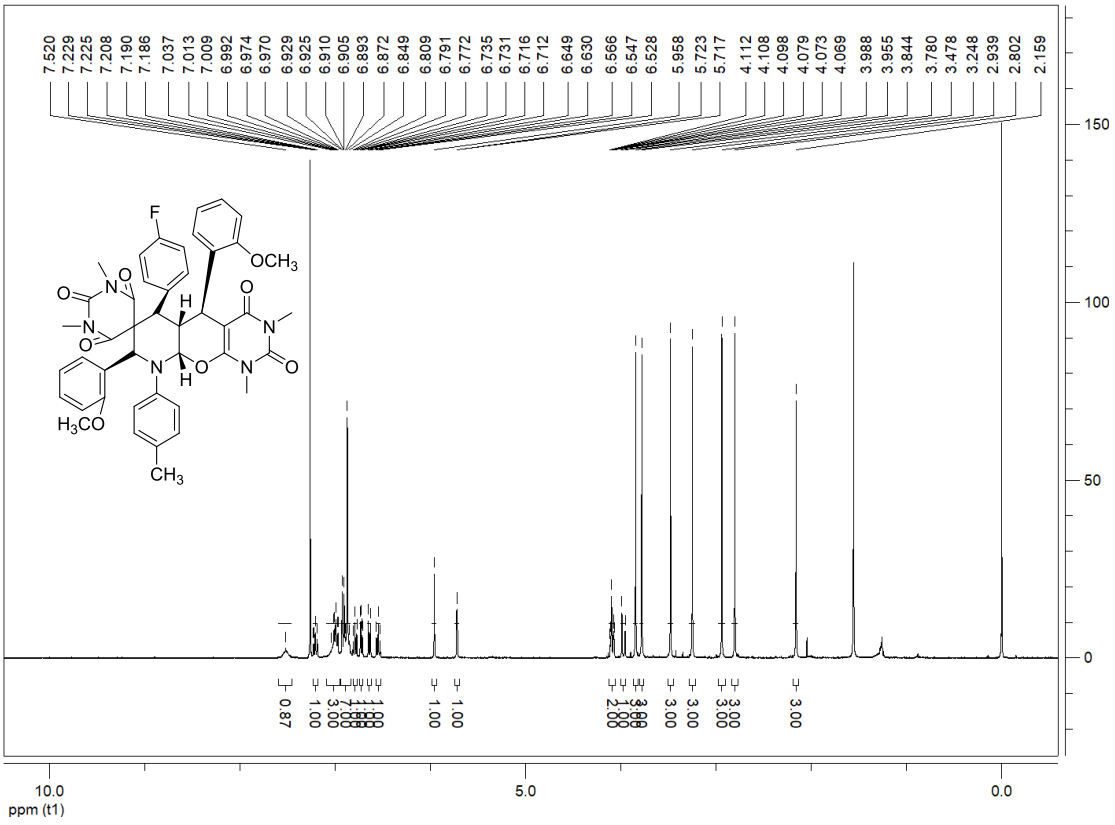
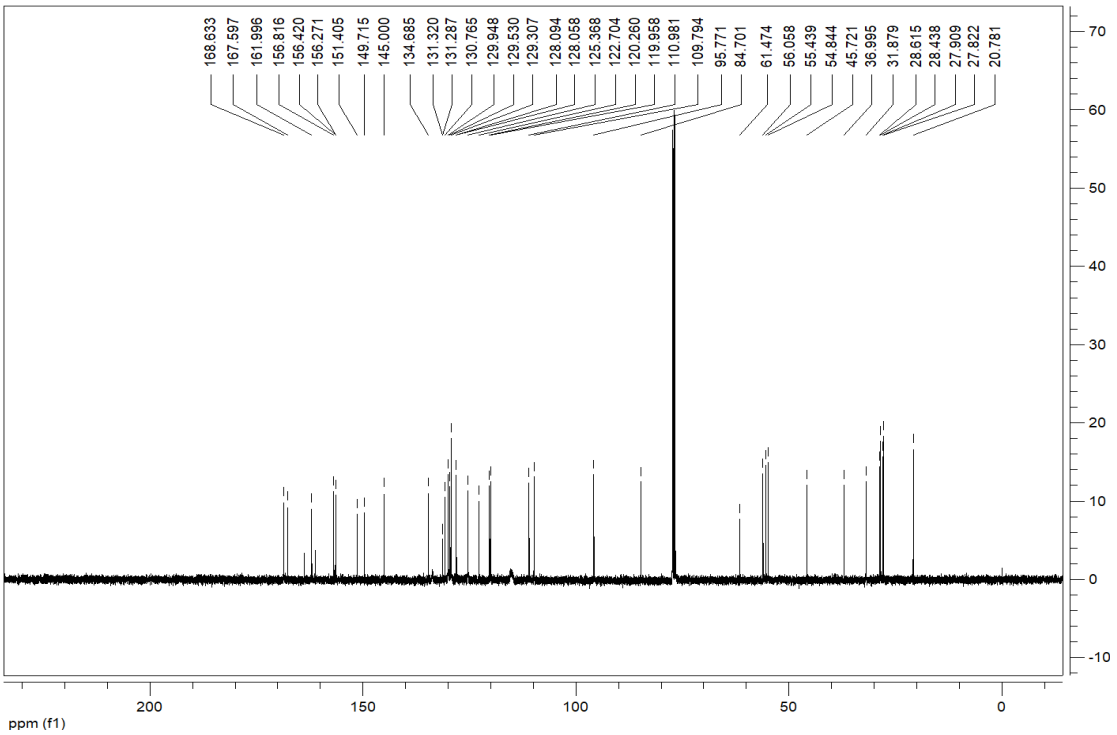
28.445
27.909
27.826
100
50
0
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.02-0.12min #(2-12)
8000
6000
4000
2000
0
774.2953
775.2985
776.3009
770
772
774
776
778
780
m/z

***rel*-(5S,5aS,6S,8R,9aS)-6-(4-fluorophenyl)-5,8-bis(2-methoxyphenyl)-1,1',3,3'-tetramethyl-9-(p-tolyl)-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4i):**

white solid, 43%, m.p.146-148℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (brs, 1H, ArH), 7.23-7.17 (m, 1H, ArH), 7.04-6.97 (m, 3H, ArH), 6.93-6.85 (m, 7H, ArH), 6.79 (t, *J* = 7.4 Hz, 1H, ArH), 6.74-6.71 (m, 1H, ArH), 6.64 (d, *J* = 7.6 Hz, 1H, ArH), 6.55 (t, *J* = 7.6 Hz, 1H, ArH), 5.96 (s, 1H, CH), 5.72 (d, *J* = 2.4 Hz, 1H, CH), 4.11-4.07 (m, 2H, CH), 3.97 (d, *J* = 13.2 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.48 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 2.94 (s, 3H, NCH_3), 2.80 (s, 3H, NCH_3), 2.16 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.6, 167.5, 161.9, 156.8, 156.4, 156.2, 151.4, 149.7, 145.0, 134.6, 131.3, 131.2, 130.7, 129.9, 129.5, 129.3, 128.0, 128.0, 125.3, 122.7, 120.2, 119.9, 110.9, 109.7, 95.7, 84.7, 61.4, 56.0, 55.4, 54.8, 45.7, 36.9, 31.8, 28.6, 28.4, 27.9, 27.8, 20.7; IR(KBr) υ: 2955, 2838, 1709, 1678, 1657, 1601, 1509, 1492, 1463, 1419, 1377, 1292, 1246, 1217, 1199, 1173, 1138, 1111, 1037, 987, 914, 892, 837, 810, 781, 759, 675, 645, cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{43}FN_5O_8$([M+H]$^+$): 788.3096, found: 788.3111.

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129.948
129.530
129.307
128.094
128.058
125.368
122.704
120.260
119.958
110.981
109.794
95.771
84.701
61.474
56.058
55.439
54.844
45.721
36.995
31.879
28.615
28.438
27.909
27.822
20.781
70
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50
40
30
20
10
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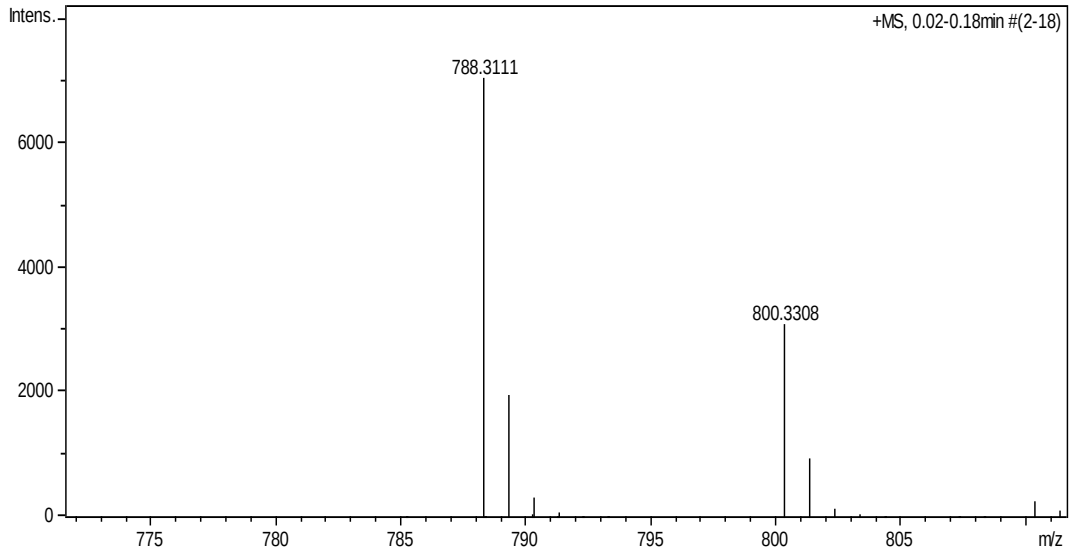
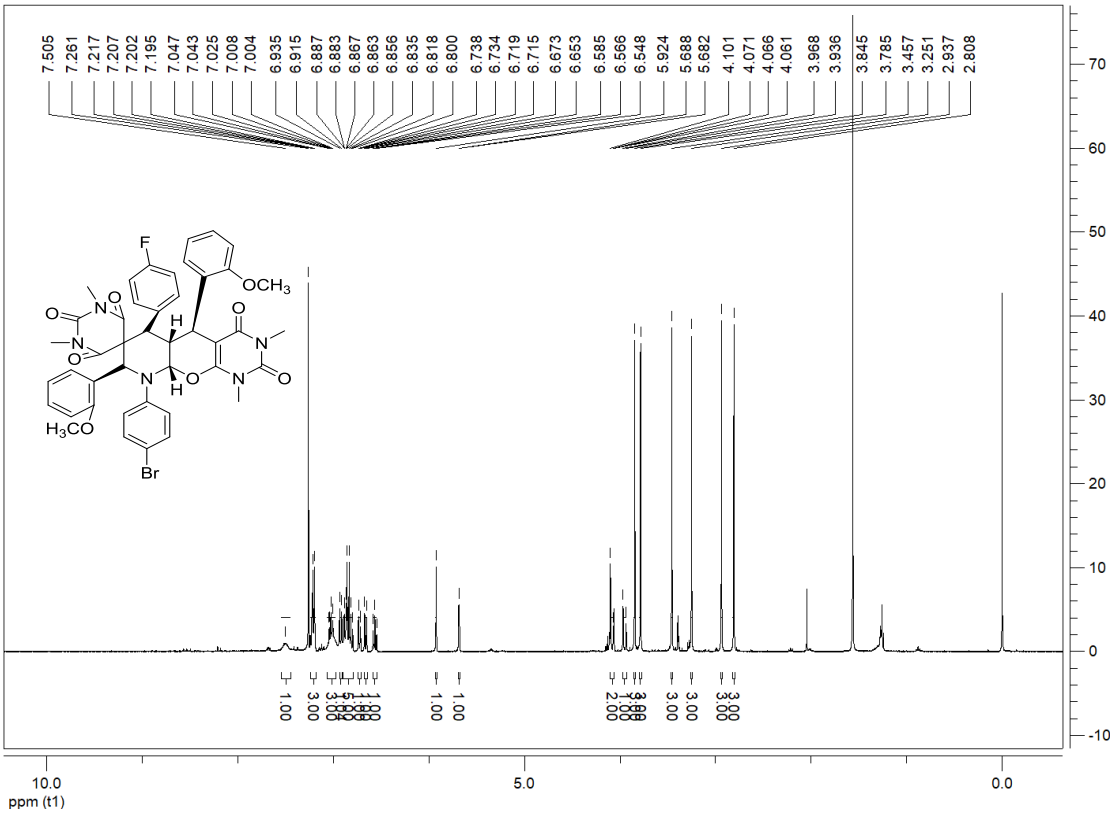
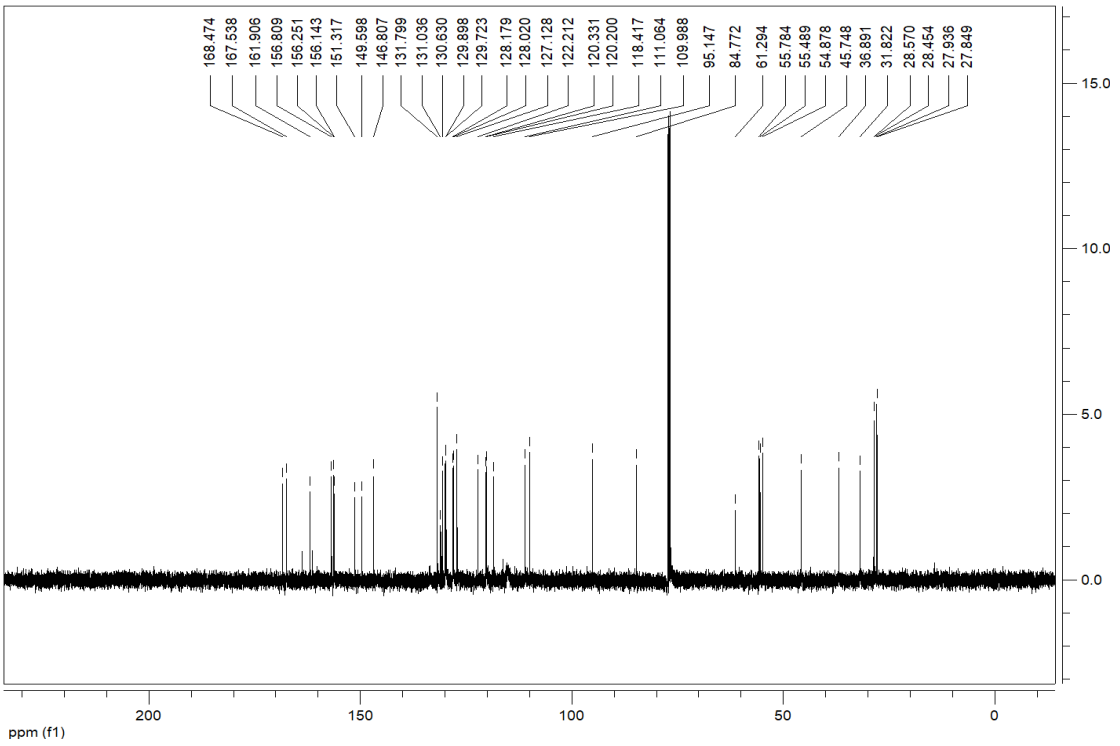
-10
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.18min #(2-18)
788.3111
800.3308
6000
4000
2000
0
775
780
785
790
795
800
805
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(4-bromophenyl)-6-(4-fluorophenyl)-5,8-bis(2-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone (4j):**

white solid, 52%, m.p.156-157℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (brs, 1H, ArH), 7.22-7.20 (m, 3H, ArH), 7.05 -7.00 (m, 3H, ArH), 6.93 (d, *J* = 8.0 Hz, 1H, ArH), 6.89-6.80 (m, 5H, ArH), 6.74-6.72 (m, 1H, ArH), 6.66 (d, *J* = 8.0 Hz, 1H, ArH), 6.57 (t, *J* = 7.4 Hz, 1H, ArH), 5.92 (s, 1H, CH), 5.68 (d, *J* = 2.4 Hz, 1H, CH), 4.10-4.06 (m, 2H, CH), 3.95 (d, *J* = 12.8 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.46 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 2.94 (s, 3H, NCH_3), 2.81 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.4, 167.5, 161.9, 156.8, 156.2, 156.1, 151.3, 149.5, 146.8, 131.7, 131.0, 130.6, 129.8, 129.7, 128.1, 128.0, 127.1, 122.2, 120.3, 120.2, 118.4, 111.0, 109.9, 95.1, 84.7, 61.2, 55.7, 55.4, 54.8, 45.7, 36.8, 31.8, 28.5, 28.4, 27.9, 27.8; IR(KBr) υ:1376, 1167, 1243, 3009, 2956, 2838, 1711, 1679, 1656, 1601, 1586, 1509, 1491, 1462, 1419, 1376, 1292, 1245, 1216, 1198, 1170, 1139, 1111, 1098, 1070, 1033, 1008, 987, 963, 915, 892, 837, 807, 783.28, 762.95, 719.31, 689.44, 665.41, 651.12, 601.07cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{40}BrFN_5O_8$([M+H]$^+$): 852.2044, found: 852.2055.

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156.809
156.251
156.143
151.317
149.598
146.807
131.799
131.036
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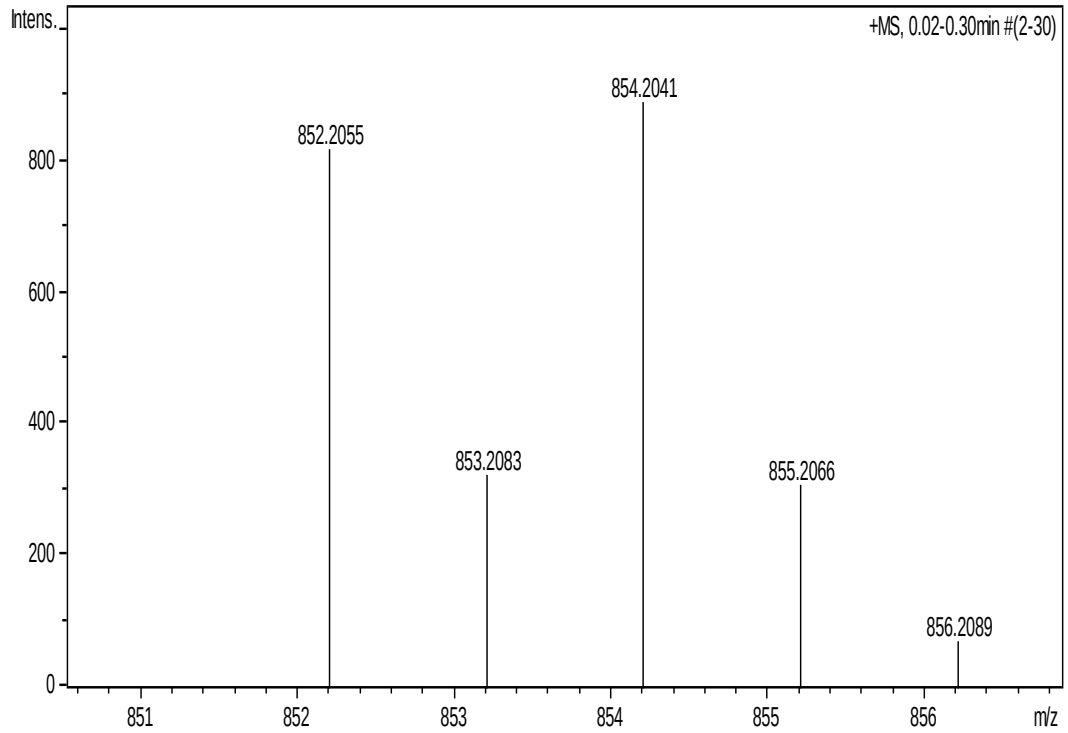
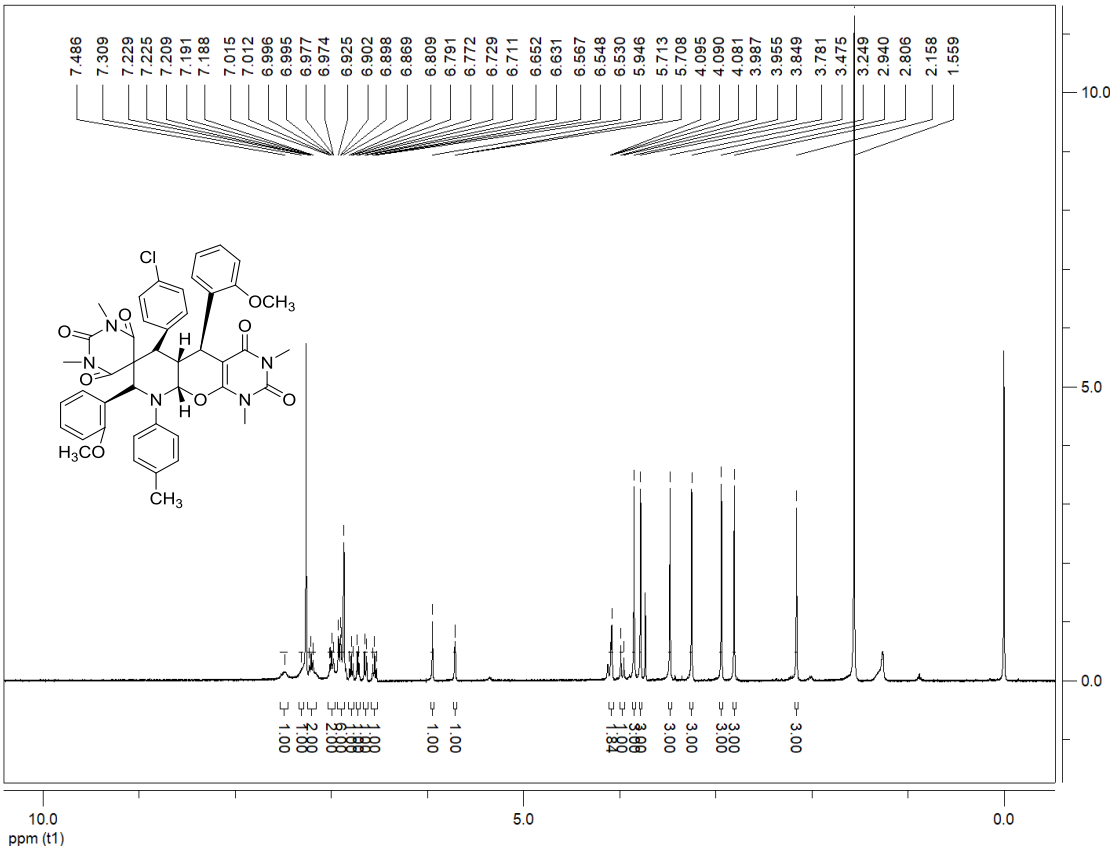
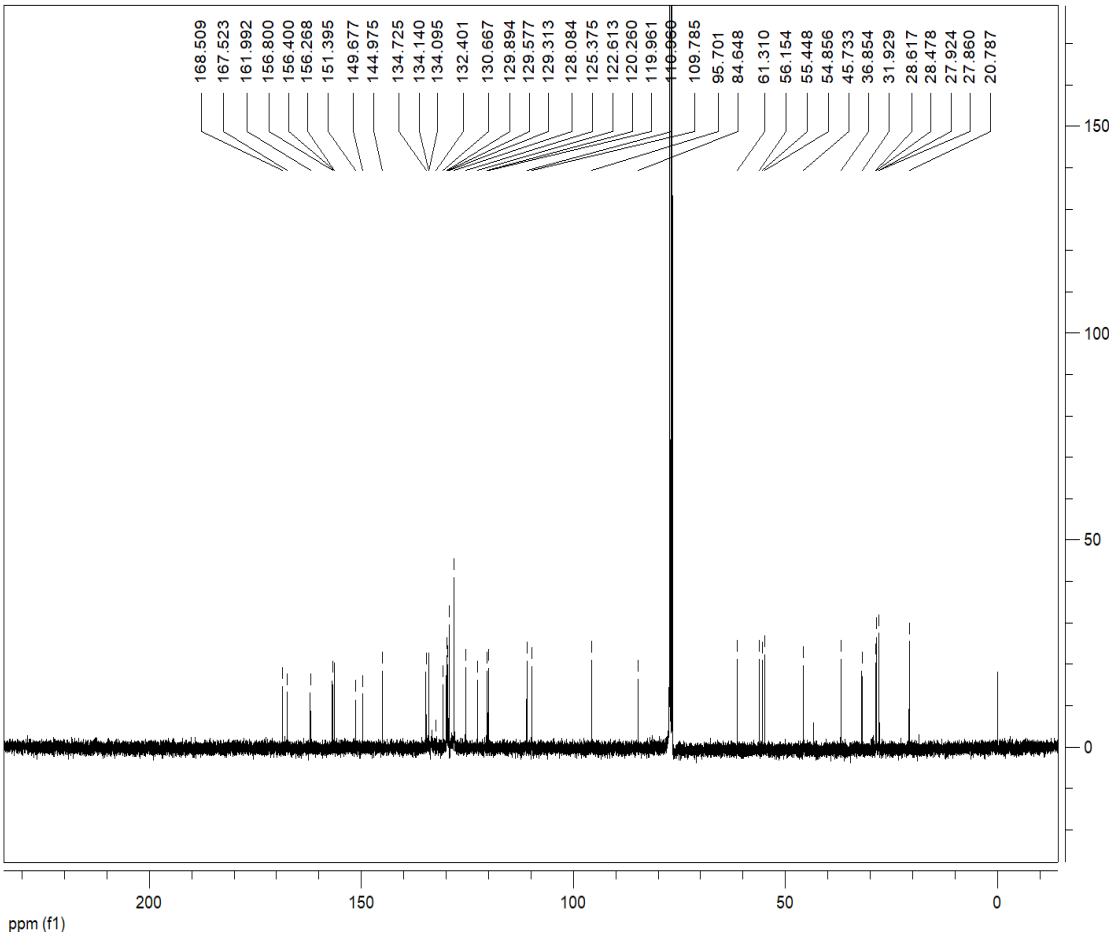
129.723
128.179
128.020
127.128
122.212
120.331
120.200
118.417
111.064
109.988
95.147
84.772
61.294
55.784
55.489
54.878
45.748
36.891
31.822
28.570
28.454
27.936
27.849
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

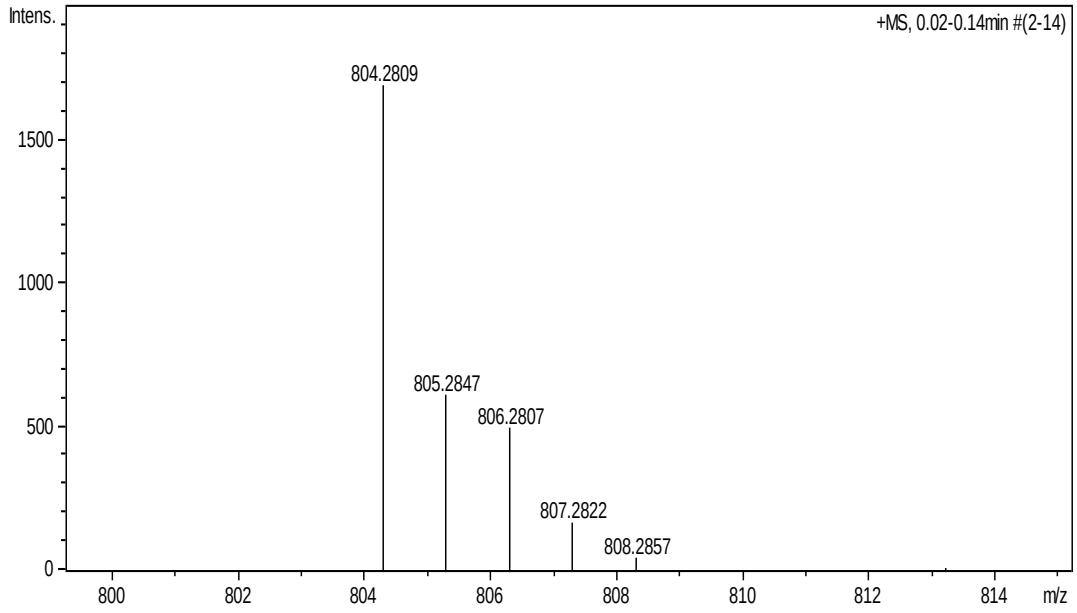

Intens.
+MS, 0.02-0.30min #(2-30)
854.2041
852.2055
853.2083
855.2066
856.2089
800
600
400
200
0
851
852
853
854
855
856
m/z

***rel*-(5S,5aS,6S,8R,9aS)-6-(4-chlorophenyl)-5,8-bis(2-methoxyphenyl)-1,1',3,3'-tetramethyl-9-(p-tolyl)-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4k)**:

white solid, 34%, m.p.129-131℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (brs, 1H, ArH), 7.31 (brs, 1H, ArH), 7.23 -7.19 (m, 2H, ArH), 7.02-6.97 (m, 2H, ArH), 6.92-6.87 (m, 6H, ArH), 6.79 (t, *J* = 7.4 Hz, 1H, ArH), 6.72 (t, *J* = 7.2 Hz, 1H, ArH), 6.64 (d, *J* = 8.4 Hz, 1H, ArH), 6.55 (t, *J* = 7.4 Hz, 1H, ArH), 5.95 (s, 1H, CH), 5.71 (d, *J* = 2.0 Hz, 1H, CH), 4.10-4.08 (m, 2H, CH), 3.97 (d, *J* = 12.8 Hz, 1H, CH), 3.85 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.48 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 2.94 (s, 3H, NCH_3), 2.81 (s, 3H, NCH_3), 2.16 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 234.3, 168.5, 167.5, 161.9, 156.7, 156.3, 156.2, 151.3, 149.6, 144.9, 134.7, 134.1, 134.0, 130.6, 129.8, 129.5, 129.3, 128.0, 125.3, 122.6, 120.2, 119.9, 110.9, 109.7, 95.7, 84.6, 61.3, 56.1, 55.4, 54.8, 45.7, 36.8, 31.9, 28.6, 28.4, 27.9, 27.8, 20.7, ; IR(KBr) υ:2957, 2350, 2324, 1704, 1682, 1646, 1586, 1512, 1491, 1463, 1419, 1379, 1287, 1242, 1198, 1168, 1115, 1025, 987, 914, 820, 758, 719, 697, 631 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{43}ClN_5O_8$([M+H]$^+$): 804.2800, found: 804.2809.

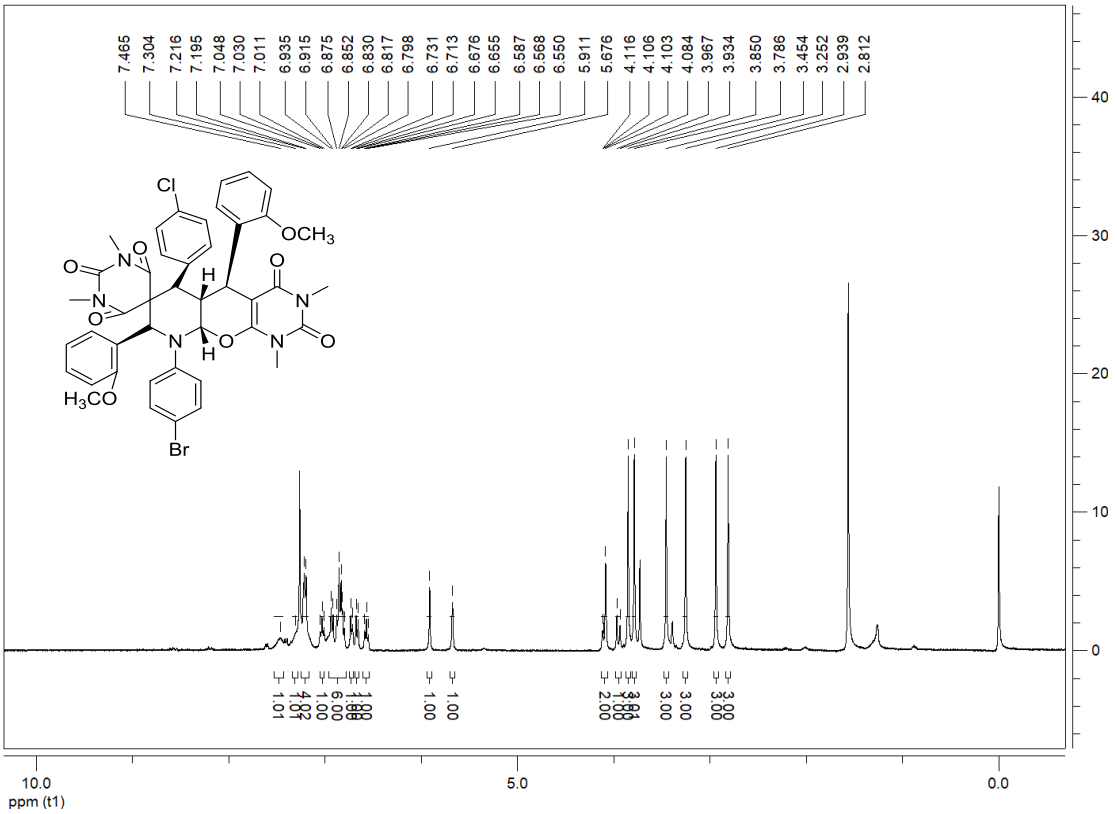


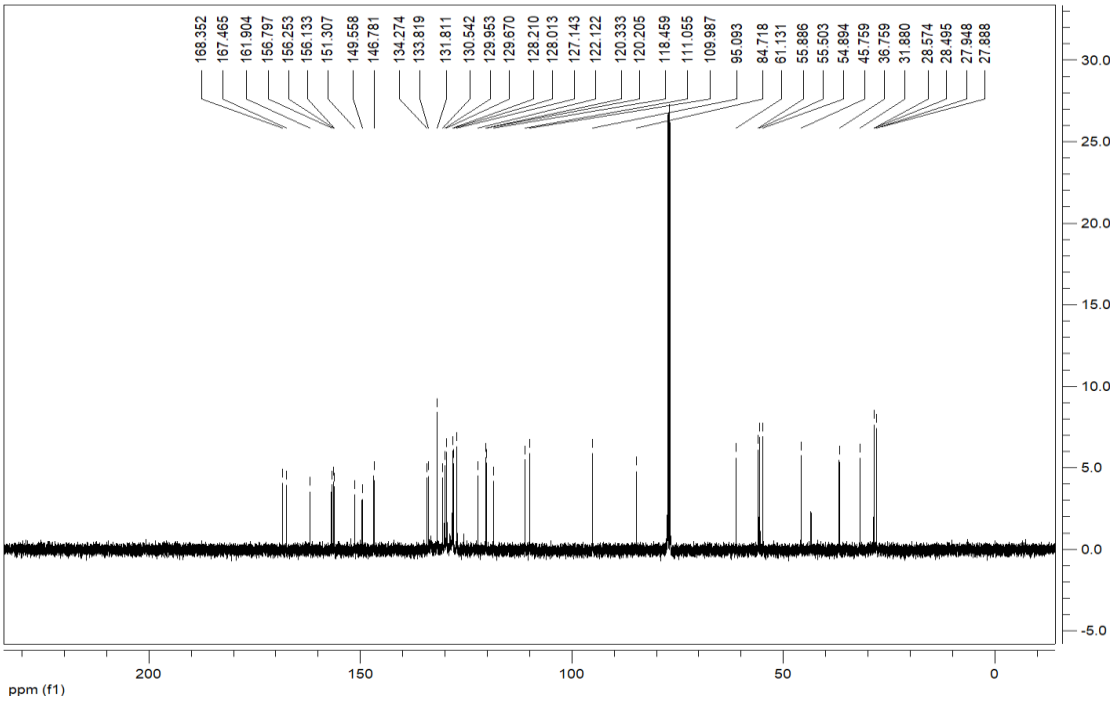

168.509
167.523
161.992
156.800
156.400
156.268
151.395
149.677
144.975
134.725
134.140
134.095
132.401
130.667
129.894
129.577
129.313
128.084
125.375
122.613
120.260
119.961
110.000
109.785
95.701
84.648
61.310
56.154
55.448
54.856
45.733
36.854
31.929
28.617
28.478
27.924
27.860
20.787
150
100
50
0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.14min #(2-14)
804.2809
805.2847
806.2807
807.2822
808.2857
1500
1000
500
0
800
802
804
806
808
810
812
814
m/z

***rel*-(5S,5aS,6S,8R,9aS)-6,9-bis(4-fluorophenyl)-5,8-bis(2-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4l)**:

white solid, 50%, m.p.135-137℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (brs, 1H, ArH), 7.30 (brs, 1H, ArH), 7.22 -7.19 (m, 4H, ArH), 7.03 (d, *J* = 7.4 Hz, 1H, ArH), 6.94-6.80 (m, 6H, ArH), 6.72 (d, *J* = 7.2 Hz, 1H, ArH), 6.67 (d, *J* = 8.4 Hz, 1H, ArH), 6.57 (t, *J* = 7.4 Hz, 1H, ArH), 5.91 (s, 1H, CH), 5.68 (s, 1H, CH), 4.12-4.08 (m, 2H, CH), 3.95 (d, *J* = 13.2 Hz, 1H, CH), 3.85 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.45 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 2.94 (s, 3H, NCH_3), 2.81 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.3, 167.4, 161.9, 156.7, 156.2, 156.1, 151.3, 149.5, 146.7, 134.2, 133.8, 131.8, 130.5, 129.9, 129.6, 128.2, 128.0, 127.1, 122.1, 120.3, 120.2, 118.4, 111.0, 109.9, 95.0, 84.7, 61.1, 55.8, 55.5, 54.8, 45.7, 36.7, 31.8, 28.5, 28.4, 27.9, 27.8; IR(KBr) υ:1292, 1110, 1222, 2962, 1704, 1682, 1648, 1599, 1491, 1463, 1419, 1380, 1286, 1242, 1198, 1167, 1110, 1026, 987, 914, 822, 798, 757, 698 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{40}BrClN_5O_8$ $[M+H]^+$): 868.1749, found: 868.1750.

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128.210
128.013
127.143
122.122
120.333
120.205
118.459
111.055
109.987
95.093
84.718
61.131
55.886
55.503
54.894
45.759
36.759
31.880
28.574
28.495
27.948
27.888
30.0
25.0
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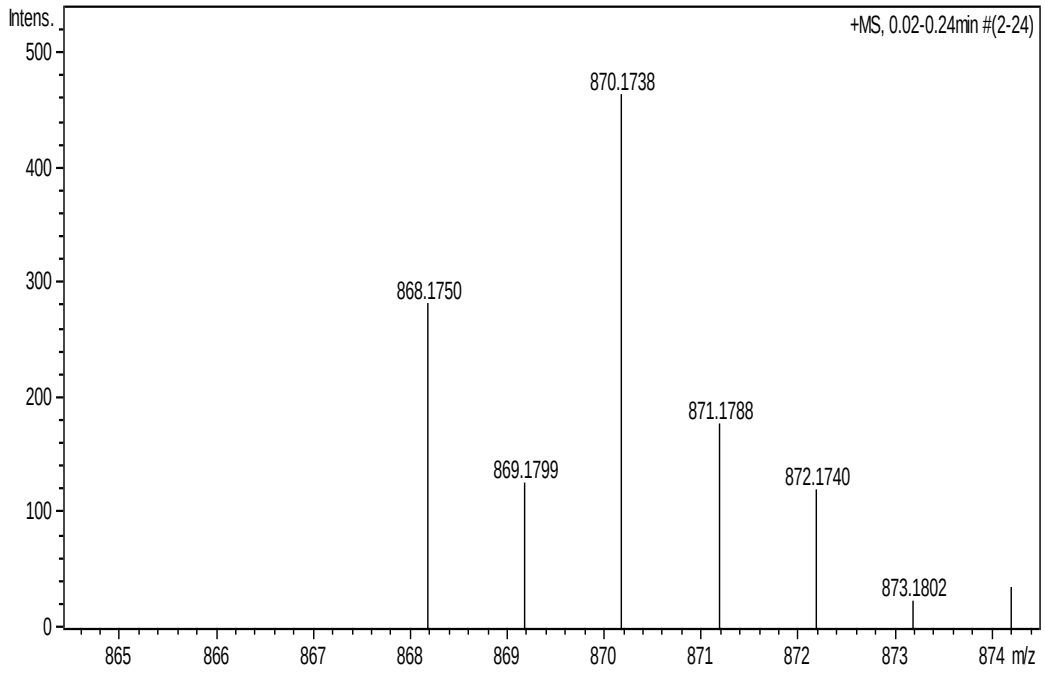
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.24min #(2-24)
500
400
300
200
100
0
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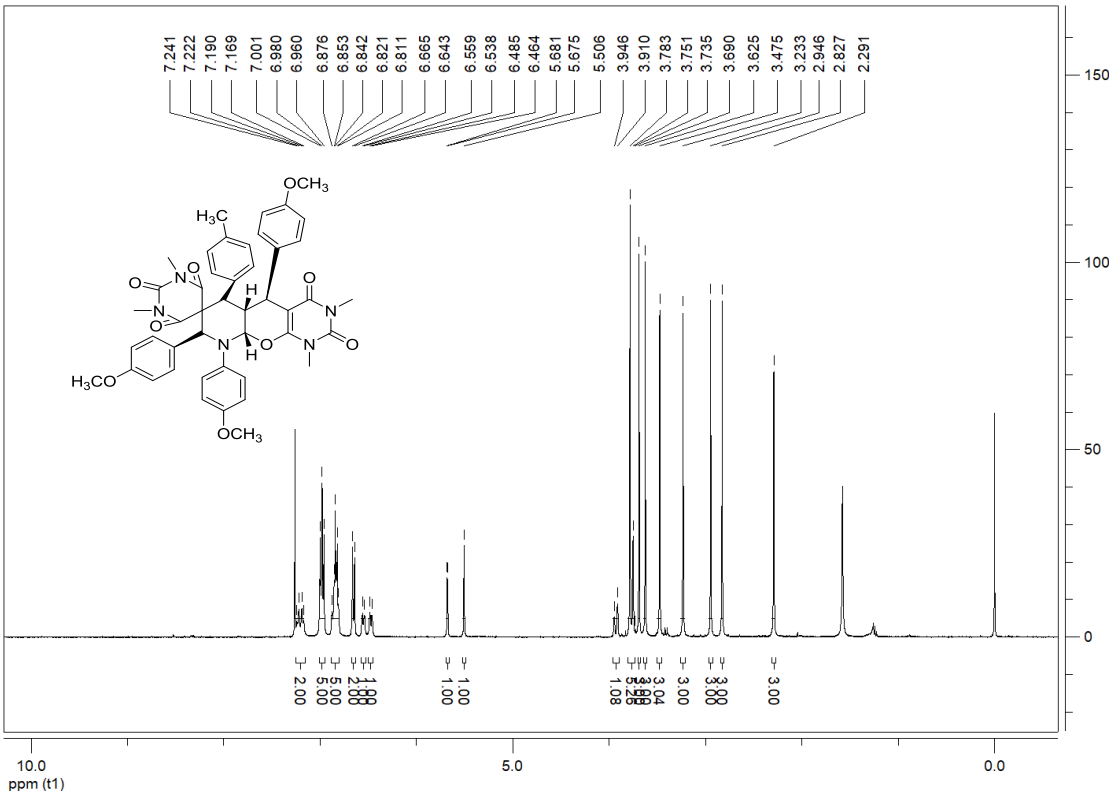
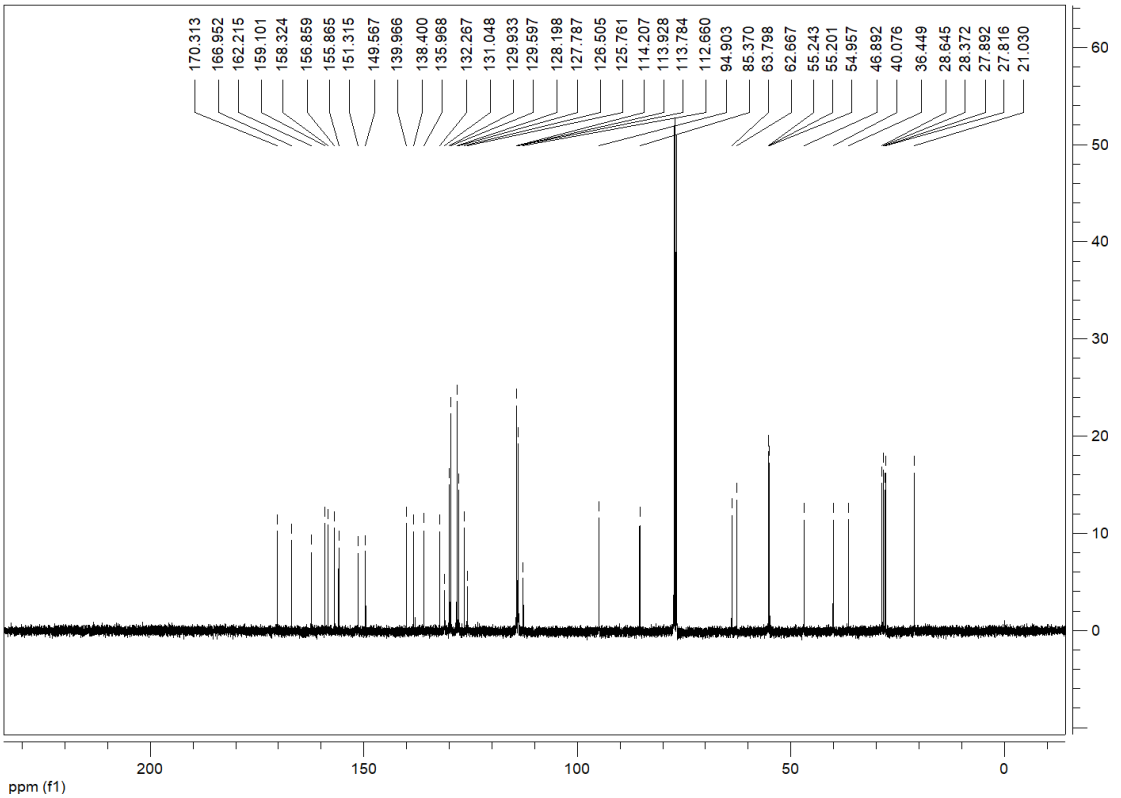
868.1750
871.1788
869.1799
872.1740
873.1802
865
866
867
868
869
870
871
872
873
874 m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8,9-tris(4-methoxyphenyl)-1,1',3,3'-tetramethyl-6-(p-tolyl)-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4m)**:

yellow solid, 46%, m.p.115-116℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24-7.17 (m, 2H, ArH), 6.98 (t, *J* = 8.2 Hz, 5H, ArH), 6.88-6.81 (m, 5H, ArH), 6.65 (d, *J* = 8.4 Hz, 2H, ArH), 6.55 (d, *J* = 8.4 Hz, 1H, ArH), 6.47 (t, *J* = 8.4 Hz, 1H, ArH), 5.68 (d, *J* = 2.4 Hz, 1H, CH), 5.51 (s, 1H, CH), 3.93 (d, *J* = 12.4 Hz, 1H, CH), 3.78-3.75 (m, 5H, OCH_3, CH), 3.69 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.48 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.95 (s, 3H, NCH_3), 2.83 (s, 3H, NCH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.3, 166.9, 162.2, 159.1, 158.3, 156.8, 155.8, 151.3, 149.5, 139.9, 138.3, 135.9, 132.2, 131.0, 129.9, 129.5, 128.1, 127.7, 126.5, 125.7, 114.2, 113.9, 113.7, 112.6, 94.9, 85.3, 63.7, 62.6, 55.2, 55.2, 54.9, 46.8, 40.0, 36.4, 28.6, 28.3, 27.8, 27.8, 21.0; IR(KBr) υ: 2955, 2836, 1747, 1703, 1679, 1647, 1611, 1584, 1511, 1456, 1423, 1381, 1343, 1294, 1244, 1175, 1112, 1034, 989, 918, 894, 863, 820, 779, 755, 726, 674, 627, cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{45}H_{46}N_5O_9$([M+H]$^+$): 800.3296, found: 800.3304.

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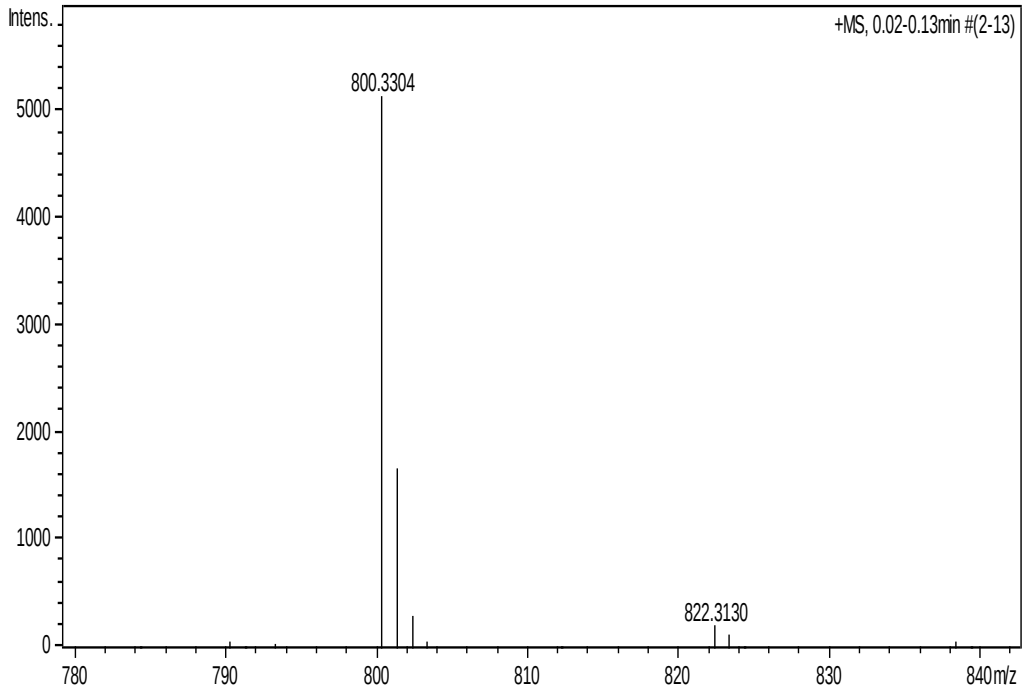
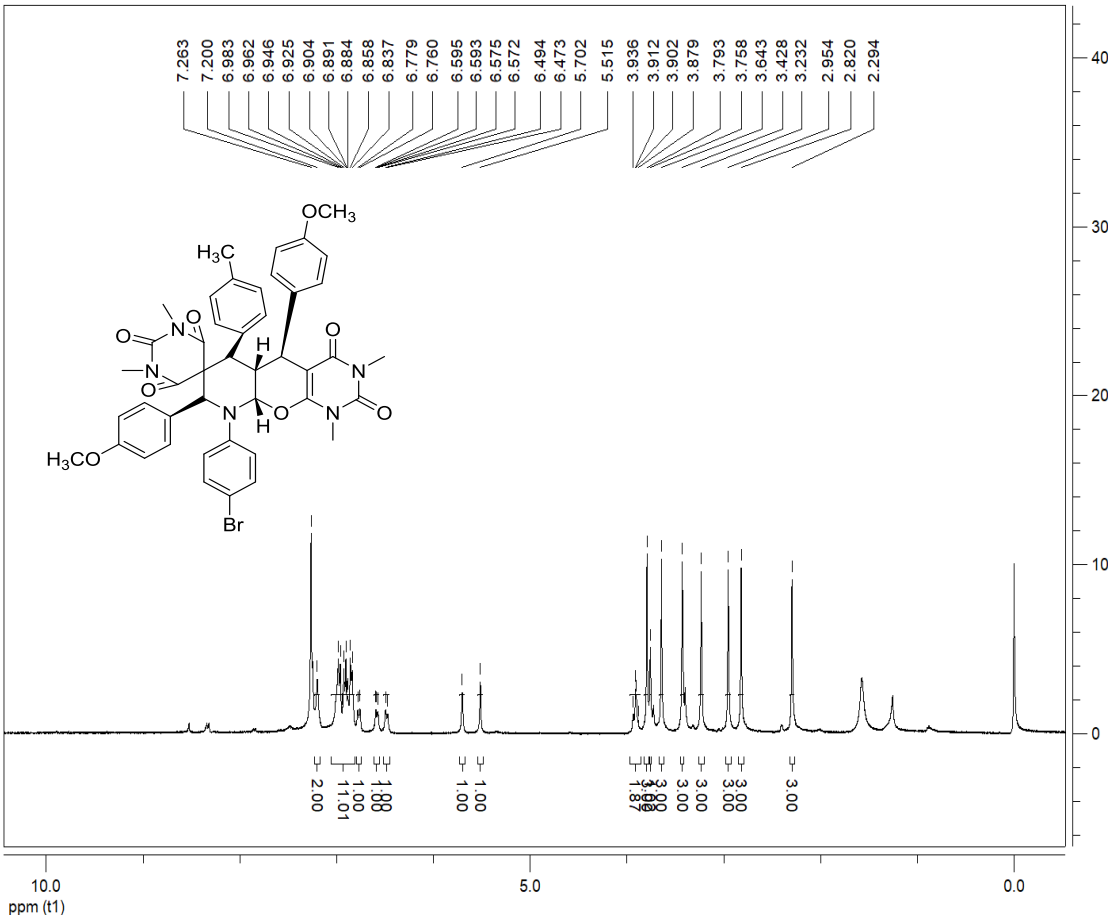
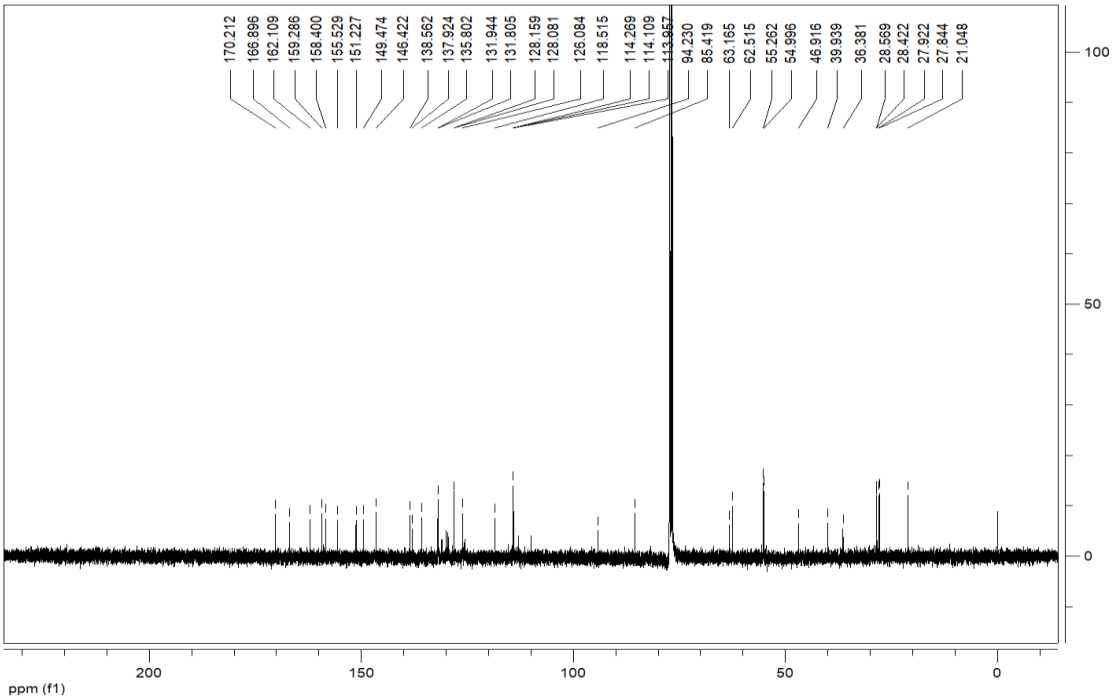
135.968
132.267
131.048
129.933
129.597
128.198
127.787
126.505
125.761
114.207
113.928
113.784
112.660
94.903
85.370
63.798
62.667
55.243
55.201
54.957
46.892
40.076
36.449
28.645
28.372
27.892
27.816
21.030
60
50
40
30
20
10
0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.13min #(2-13)
800.3304
822.3130
5000
4000
3000
2000
1000
0
780
790
800
810
820
830
840m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(4-bromophenyl)-5,8-bis(4-methoxyphenyl)-1,1',3,3'-tetramethyl-6-(p-tolyl)-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4n)**:

yellow solid, 32%, m.p.112-115℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (s, 2H, ArH), 6.98-6.76 (m, 11H, ArH), 6.77 (d, *J* = 7.6 Hz, 1H, ArH), 6.60-6.57 (m, 1H, ArH), 6.48 (d, *J* = 8.4 Hz, 1H, ArH), 5.70 (s, 1H, CH), 5.52 (s, 1H, CH), 3.94-3.88 (m, 2H, CH), 3.79 (s, 3H, OCH_3), 3.76 (s, 1H, CH), 3.64 (s, 3H, OCH_3), 3.43 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.95 (s, 3H, NCH_3), 2.82 (s, 3H, NCH_3), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.2, 166.8, 162.1, 159.2, 158.4, 155.5, 151.2, 149.4, 146.4, 138.5, 137.9, 135.8, 131.9, 131.8, 128.1, 128.0, 126.0, 118.5, 114.2, 114.1, 113.9, 94.2, 85.4, 63.1, 62.5, 55.2, 54.9, 46.9, 39.9, 36.3, 28.5, 28.4, 27.9, 27.8, 21.0; IR (KBr) υ:2954, 2837, 1747, 1706, 1680, 1650, 1611, 1583, 1511, 1488, 1459, 1421, 1381, 1302, 1251, 1168, 1084, 1033, 987, 916, 895, 822, 789, 776, 756, 719, 665 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{43}BrN_5O_8$ ($[M+H]^+$): 848.2295, found: 848.2298.




170.212
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162.109
159.286
158.400
155.529
151.227
149.474
146.422
138.562
137.924
135.802
131.944
131.805
128.159
128.081
126.084
118.515
114.269
114.109
113.957
94.230
85.419
63.165
62.515
55.262
54.996
46.916
39.939
36.381
28.569
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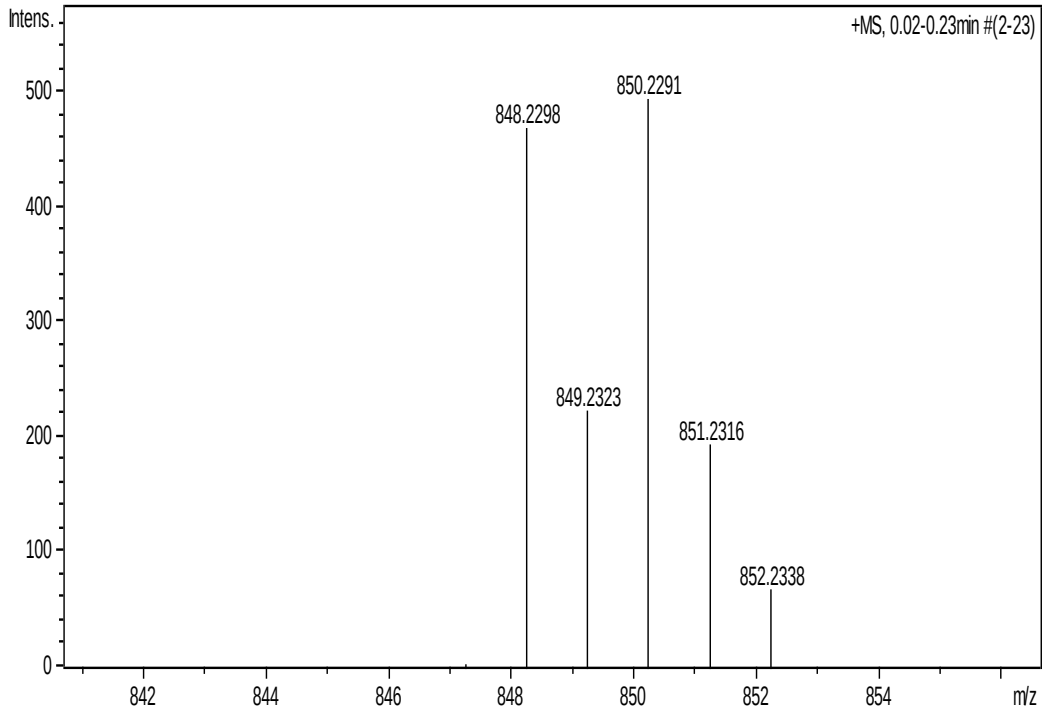
27.922
27.844
21.048
100
50
0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.23min #(2-23)
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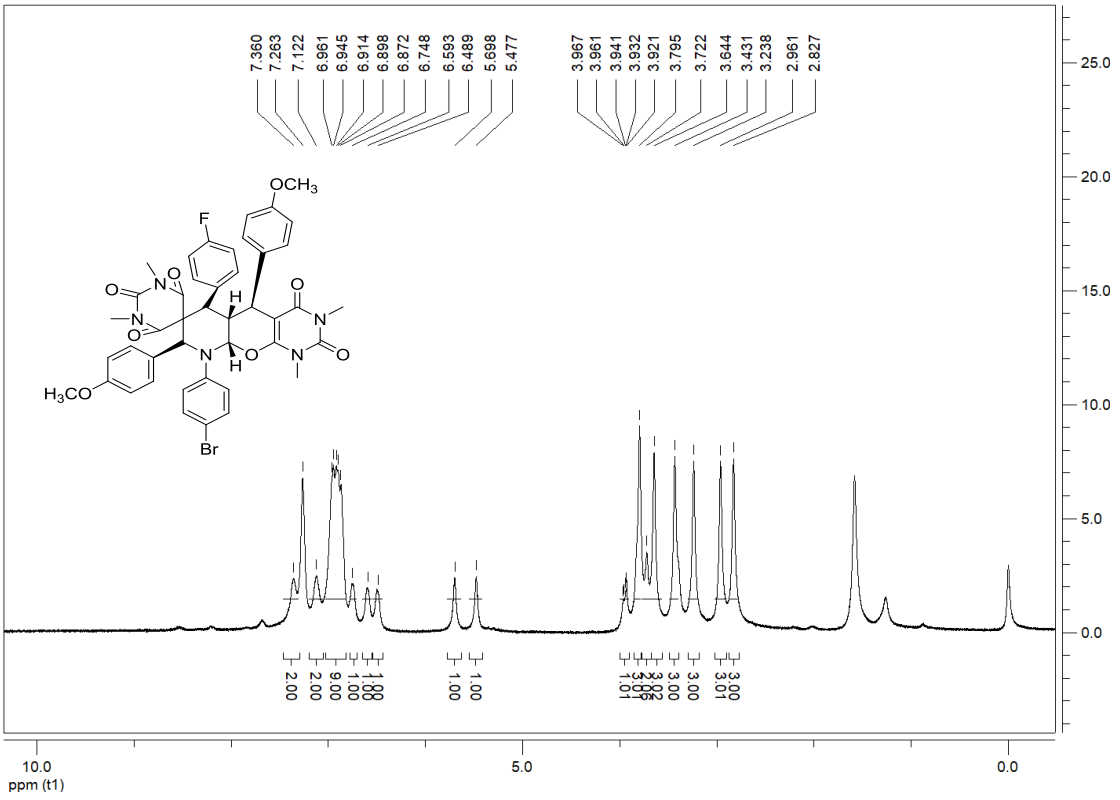
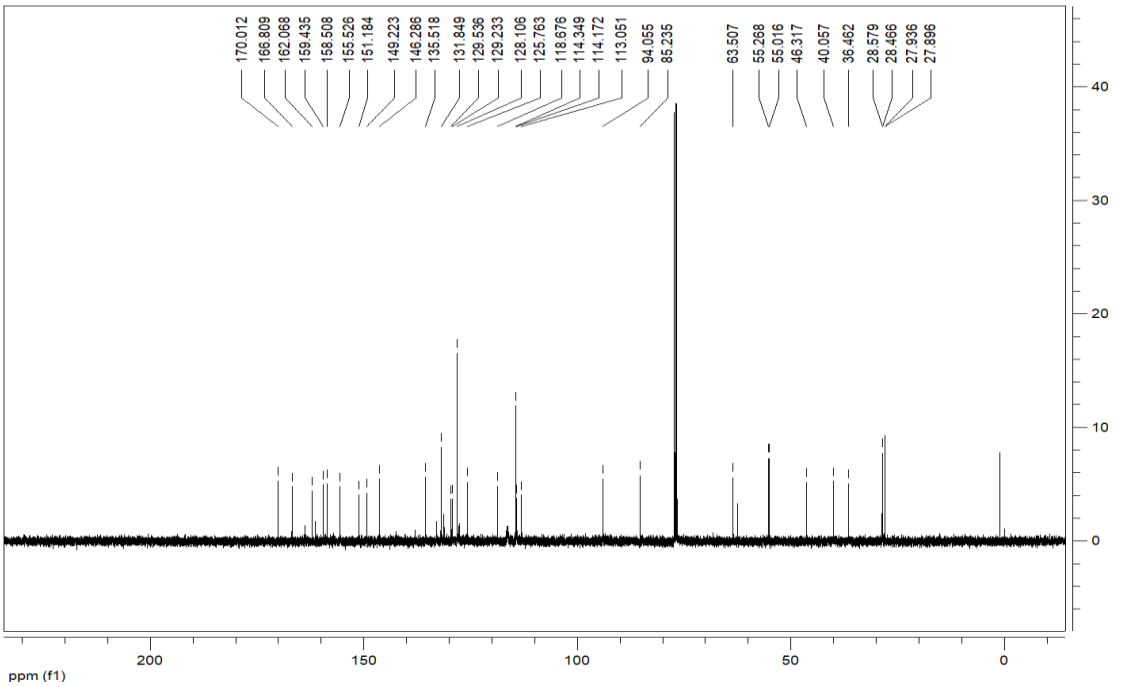
848.2298
849.2323
851.2316
852.2338
500
400
300
200
100
0
842
844
846
848
850
852
854
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(4-bromophenyl)-6-(4-fluorophenyl)-5,8-bis(4-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4o):**

white solid, 60%, m.p.124-126℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (brs, 2H, ArH), 7.12 (brs, 2H, ArH), 6.96-6.87 (m, 9H, ArH), 6.75 (brs, 1H, ArH), 6.59 (s, 1H, ArH), 6.49 (s, 1H, ArH), 5.70 (s, 1H, CH), 5.48 (s, 1H, CH), 3.97-3.92 (m, 1H, CH), 3.80 (s, 3H, OCH_3), 3.72 (brs, 2H, CH), 3.64 (s, 3H, OCH_3), 3.43 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 2.96 (s, 3H, NCH_3), 2.83 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 166.8, 162.0, 159.4, 158.5, 155.5, 151.1, 149.2, 146.2, 135.5, 131.8, 129.5, 129.2, 128.1, 125.7, 118.6, 114.3, 114.1, 113.0, 94.0, 85.2, 63.5, 55.2, 55.0, 46.3, 40.0, 36.4, 28.5, 28.4, 27.9, 27.8; IR(KBr) υ: 2955, 2836, 1747, 1706, 1681, 1647, 1610, 1585, 1511, 1489, 1462, 1423, 1382, 1302, 1250, 1167, 1113, 1036, 987, 917, 896, 832, 789, 777, 760, 716, 665, 622, cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{40}BrFN_5O_8$([M+H]$^+$): 852.2044, found: 852.2066.

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166.809
162.068
159.435
158.508
155.526
151.184
149.223
146.286
135.518
131.849
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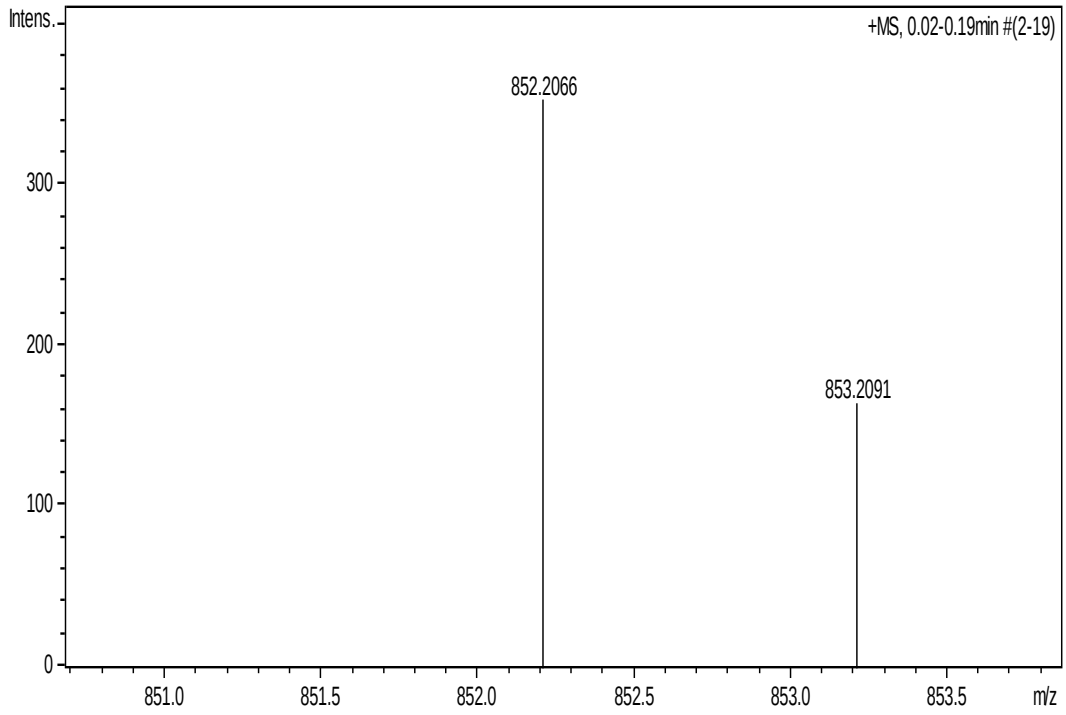
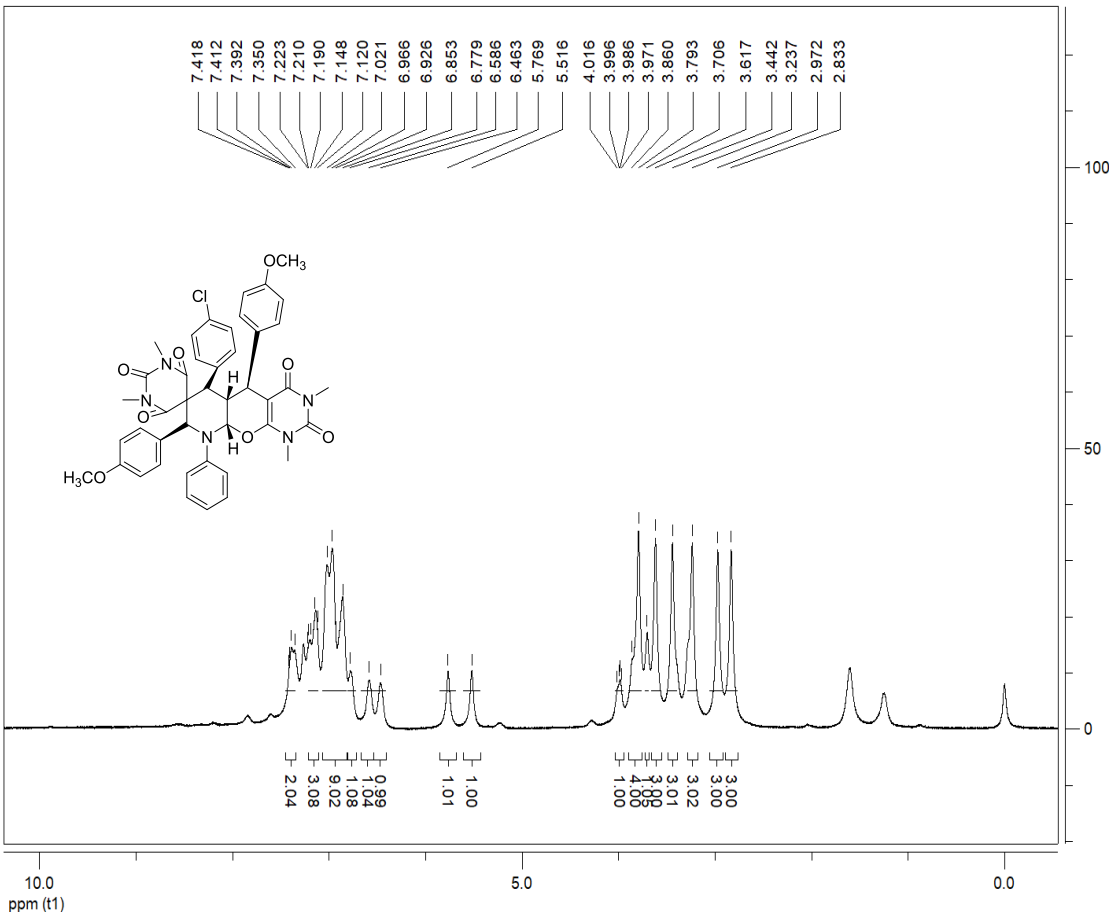
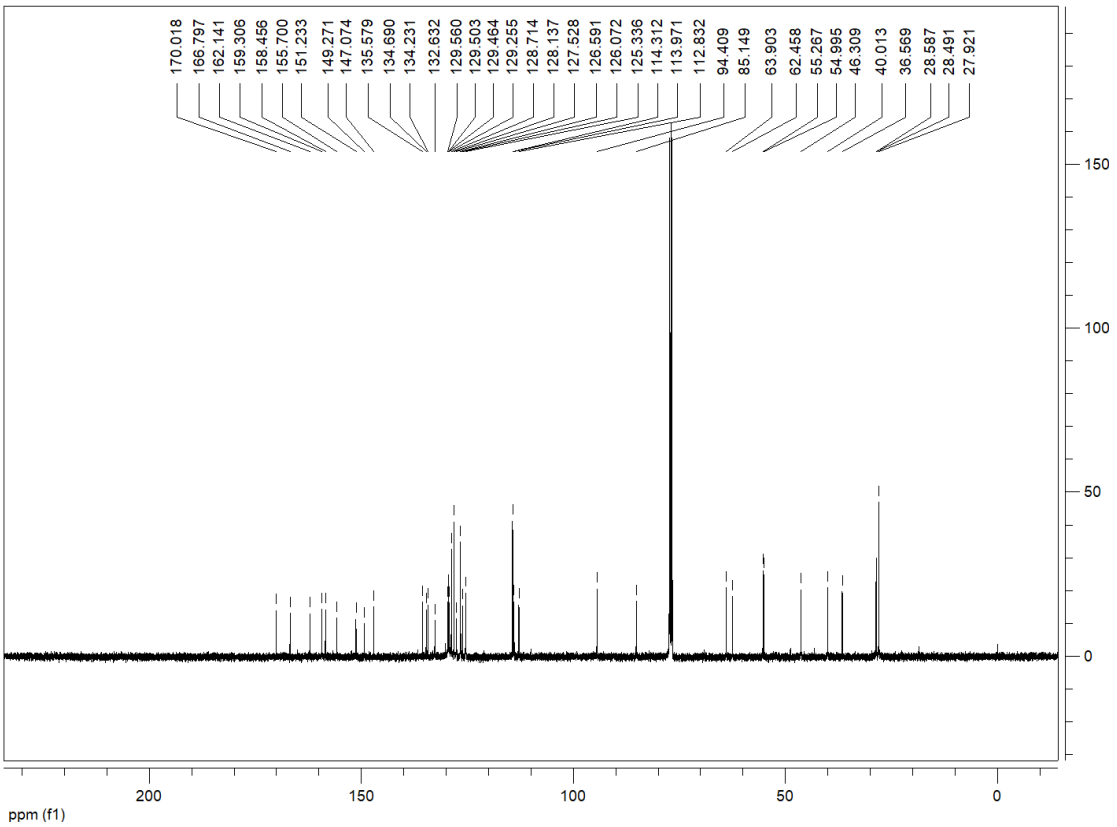
129.233
128.106
125.763
118.676
114.349
114.172
113.051
94.055
85.235
63.507
55.268
55.016
46.317
40.057
36.462
28.579
28.466
27.936
27.896
40
30
20
10
0
200
150
100
50
0
ppm (f1)

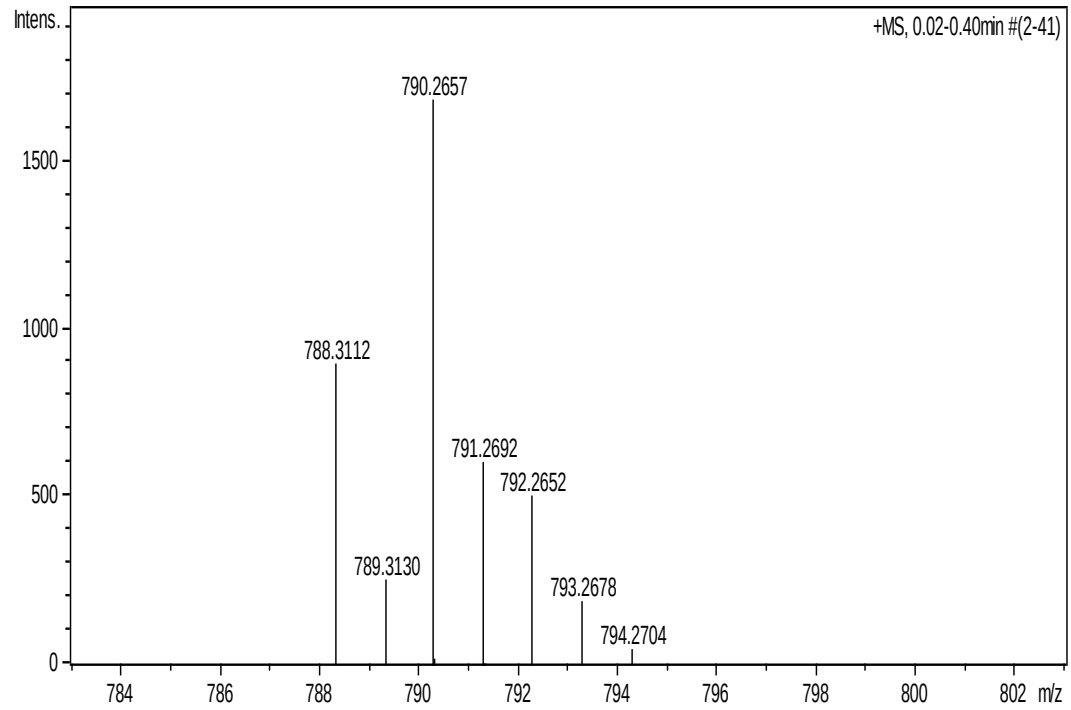

Intens.
+MS, 0.02-0.19min #(2-19)
852.2066
853.2091
300
200
100
0
851.0
851.5
852.0
852.5
853.0
853.5
m/z

***rel*-(5S,5aS,6S,8R,9aS)-6-(4-chlorophenyl)-5,8-bis(4-methoxyphenyl)-1,1',3,3'-tetramethyl-9-phenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'pentaone (4p)**:

white solid, 27%, m.p.117-120℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42-7.19 (m, 2H, ArH), 7.22-7.12 (m, 3H, ArH), 7.02-6.93 (m, 9H, ArH), 6.78 (s, 1H, ArH), 6.59 (s, 1H, ArH), 6.46 (s, 1H, ArH), 5.78 (s, 1H, CH), 5.52 (s, 1H, CH), 4.02-3.97 (m, 1H, CH), 3.86-3.79 (m, 4H, CH, OCH_3), 3.71 (s, 1H, CH), 3.62 (s, 3H, OCH_3), 3.44 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3), 2.80 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 166.7, 162.1, 159.3, 158.4, 155.6, 151.2, 149.2, 147.0, 135.5, 134.6, 134.2, 132.6, 129.5, 129.5, 129.4, 129.2, 128.7, 128.1, 127.5, 126.5, 126.0, 125.3, 114.3, 113.9, 112.8, 94.4, 85.1, 63.9, 62.4, 55.2, 54.9, 46.3, 40.0, 36.5, 28.5, 28.4, 27.9; IR(KBr) υ: 2956, 2835, 1747, 1705, 1681, 1644, 1511, 1493, 1454, 1422, 1382, 1298, 1248, 1167, 1092, 1036, 1015, 988, 918, 895, 863, 829, 811, 793, 759, 717, 699, 674, 642 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{41}ClN_5O_8$([M+H]$^+$): 790.2644, found: 790.2657.

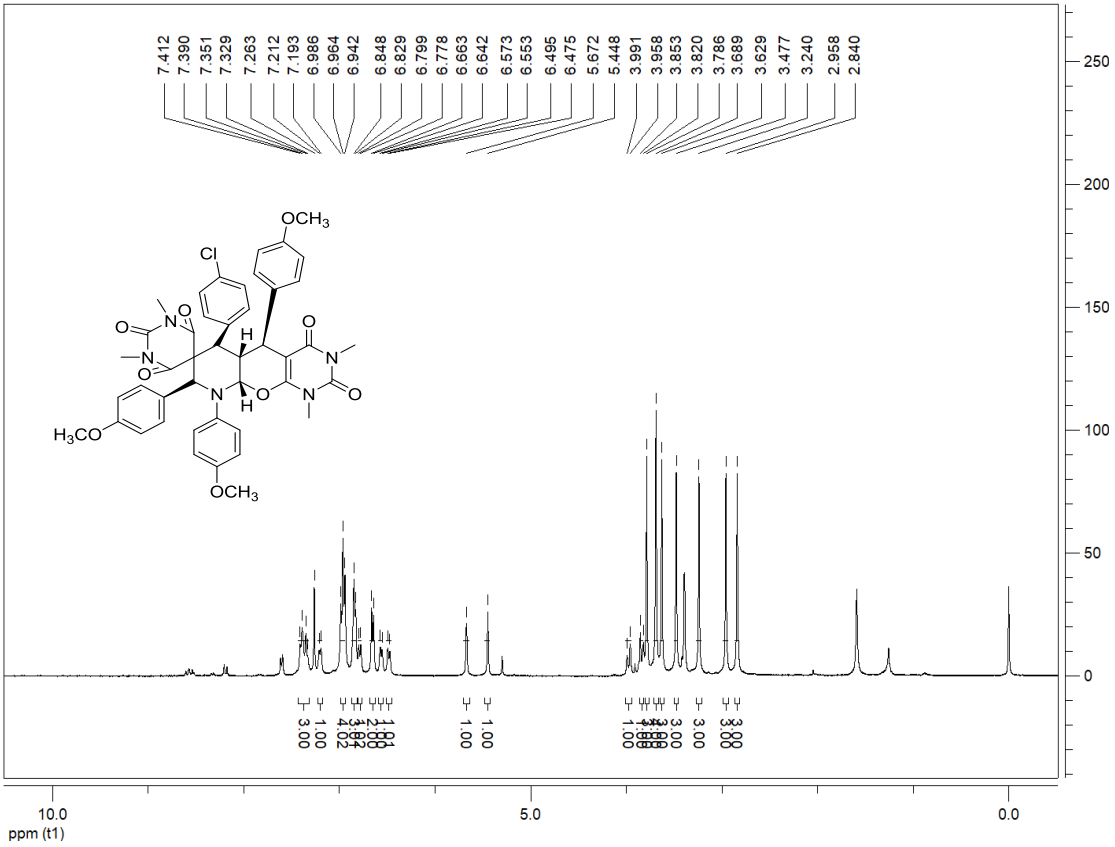


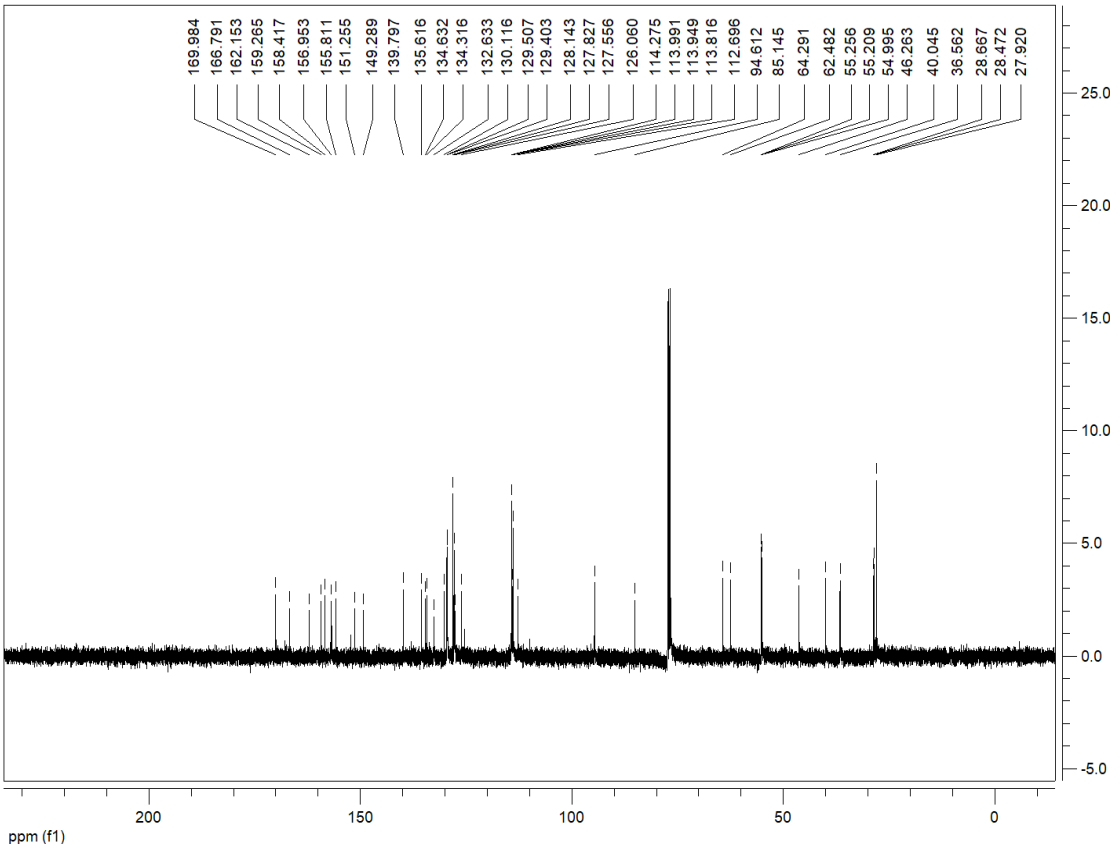

170.018
166.797
162.141
159.306
158.456
155.700
151.233
149.271
147.074
135.579
134.690
134.231
132.632
129.560
129.503
129.464
129.255
128.714
128.137
127.528
126.591
126.072
125.336
114.312
113.971
112.832
94.409
85.149
63.903
62.458
55.267
54.995
46.309
40.013
36.569
28.587
28.491
27.921
150
100
50
0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.40min #(2-41)
790.2657
1500
1000
788.3112
500
791.2692
792.2652
789.3130
793.2678
794.2704
0
784
786
788
790
792
794
796
798
800
802
m/z

***rel*-(5S,5aS,6S,8R,9aS)-6-(4-chlorophenyl)-5,8,9-tris(4-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4q):**

white solid, 34%, m.p.117-120℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.33 (m, 3H, ArH), 7.20 (d, *J* = 7.6 Hz, 1H, ArH), 6.99-6.94 (m, 4H, ArH), 6.85-6.83 (m, 3H, ArH), 6.79 (d, *J* = 8.4 Hz, 1H, ArH), 6.65 (d, *J* = 8.4 Hz, 1H, ArH), 6.56 (d, *J* = 8.0 Hz, 1H, CH), 6.49 (d, *J* = 8.0 Hz, 1H, ArH), 5.67 (s, 1H, CH), 5.45 (s, 1H, CH), 3.97 (d, *J* = 13.2 Hz, 1H, CH), 3.84 (d, *J* = 13.2 Hz, 1H, CH), 3.79 (s, 3H, OCH_3), 3.69 (s, 4H, CH, OCH_3), 3.63 (s, 3H, OCH_3), 3.48 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 2.96 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.9, 166.7, 162.1, 159.2, 158.4, 156.9, 155.8, 151.2, 149.2, 139.7, 135.6, 134.6, 134.3, 132.6, 130.1, 129.5, 129.4, 128.1, 127.8, 127.5, 126.0, 114.2, 113.9, 113.9, 113.8, 112.6, 94.6, 85.1, 64.2, 62.4, 55.2, 55.2, 54.9, 46.2, 40.0, 36.5, 28.6, 28.4, 27.9; IR(KBr) υ: 2954, 2835, 1747, 1704, 1678, 1655, 1611, 1573, 1510, 1492, 1454, 1423, 1380, 1342, 1325, 1294, 1244, 1175, 1113, 1085, 1034, 968, 918, 894, 862, 824, 803, 780, 754, 727, 698, 674, 627cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{43}ClN_5O_9$([M+H]$^+$): 820.2749, found: 820.2770.




169.984
166.791
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156.953
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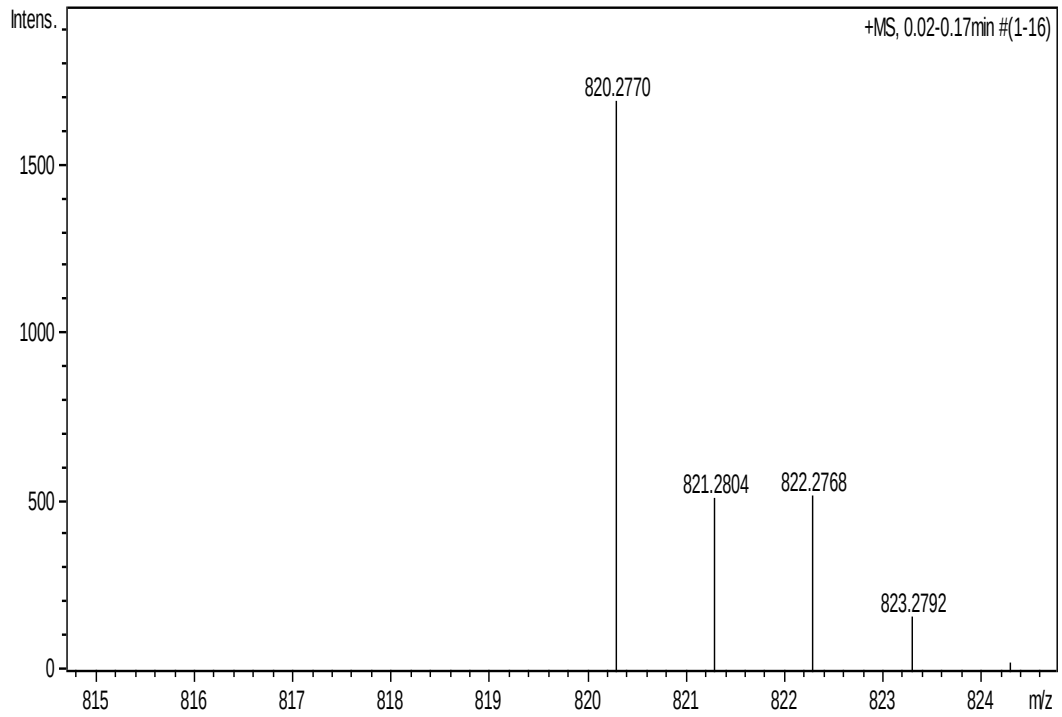
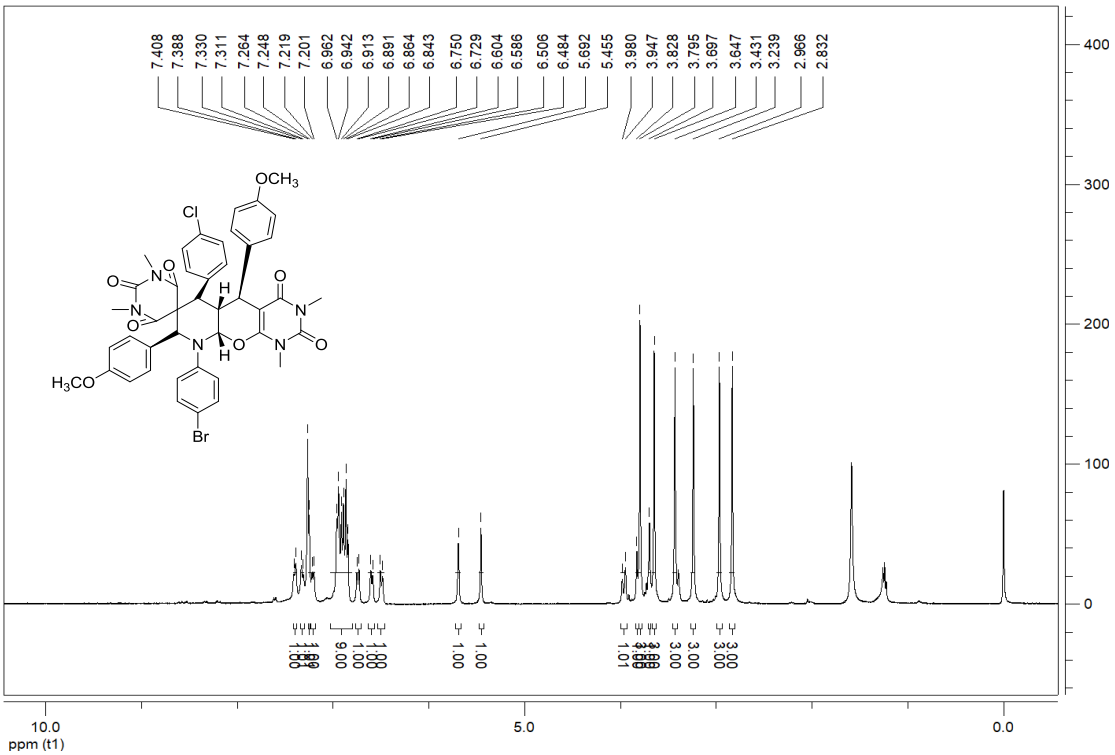
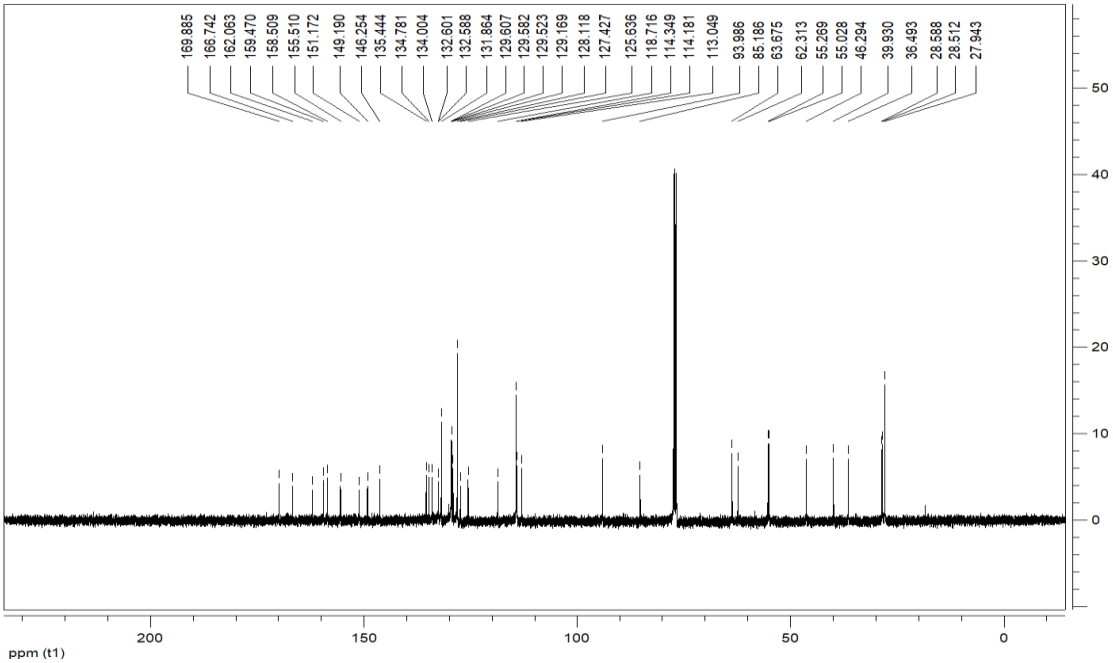
151.255
149.289
139.797
135.616
134.632
134.316
132.633
130.116
129.507
129.403
128.143
127.827
127.556
126.060
114.275
113.991
113.949
113.816
112.696
94.612
85.145
64.291
62.482
55.256
55.209
54.995
46.263
40.045
36.562
28.667
28.472
27.920
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.17min #(1-16)
820.2770
821.2804
822.2768
823.2792
1500
1000
500
0
815
816
817
818
819
820
821
822
823
824
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(4-bromophenyl)-6-(4-chlorophenyl)-5,8-bis(4-methoxyphenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (4r):**

white solid, 53%, m.p.122-125℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 8.0 Hz, 1H, ArH), 7.30 (d, *J* = 8.0 Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.21 (d, *J* = 7.2 Hz, 1H, ArH), 6.96-6.84 (m, 9H, ArH), 6.74 (d, *J* = 8.4 Hz, 1H, ArH), 6.60 (d, *J* = 7.2 Hz, 1H, ArH), 6.50 (d, *J* = 8.8 Hz, 1H, ArH), 5.69 (s, 1H, CH), 5.45 (s, 1H, CH), 3.96 (d, *J* = 13.2 Hz, 1H, CH), 3.83 (s, 1H, CH), 3.80 (s, 3H, OCH_3), 3.70(s, 1H, CH), 3.65 (s, 3H, OCH_3), 3.41 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3), 2.83 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.8, 166.7, 162.0, 159.4, 158.5, 155.5, 151.1, 149.1, 146.2, 135.4, 134.7, 134.0, 132.6, 132.5, 131.8, 129.6, 129.5, 129.5, 129.1, 128.1, 127.4, 125.6, 118.7, 114.3, 114.1, 113.0, 93.9, 85.1, 63.6, 62.3, 55.2, 55.0, 46.2, 39.9, 36.4, 28.5, 28.5, 27.9; IR(KBr) υ: 2955, 2836, 1747, 1682, 1644, 1511, 1490, 1463, 1423, 1381, 1351, 1329, 1300, 1251, 1167, 1092, 1036, 1012, 988, 966, 918, 896, 829, 791, 777, 758, 717, 697, 678, 657, 622 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{40}BrClN_5O_8$([M+H]$^+$): 868.1479, found: 868.1764.




169.885
166.742
162.063
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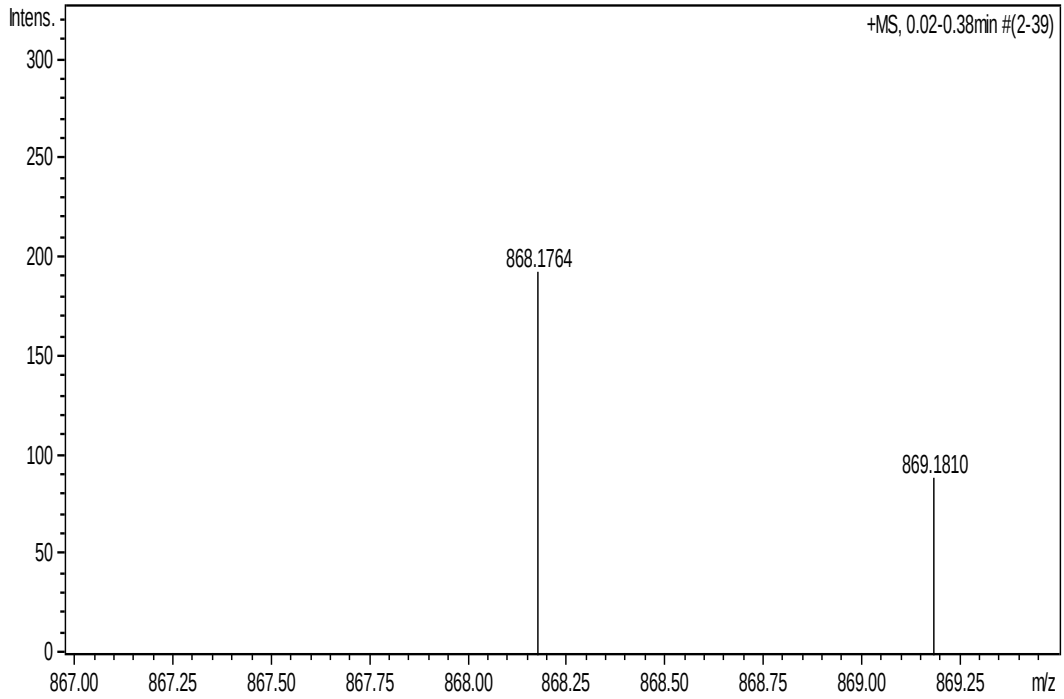
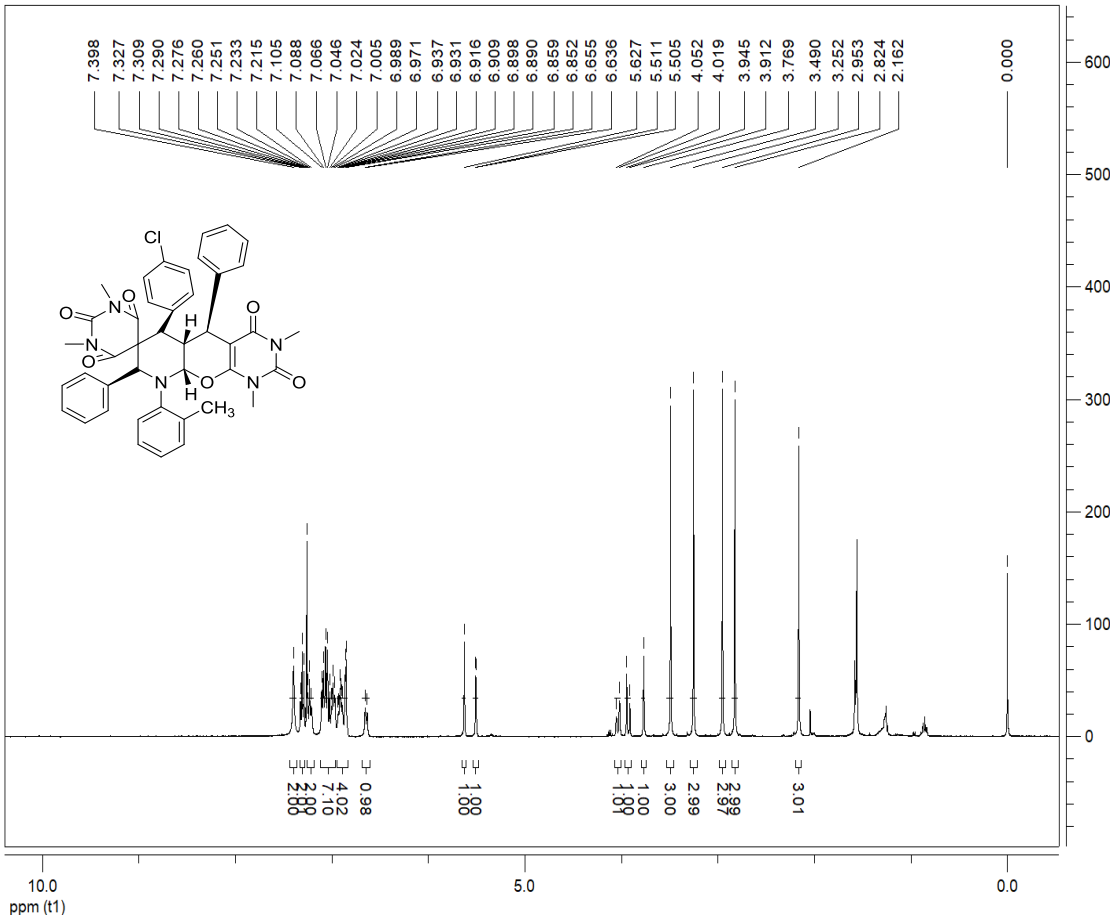
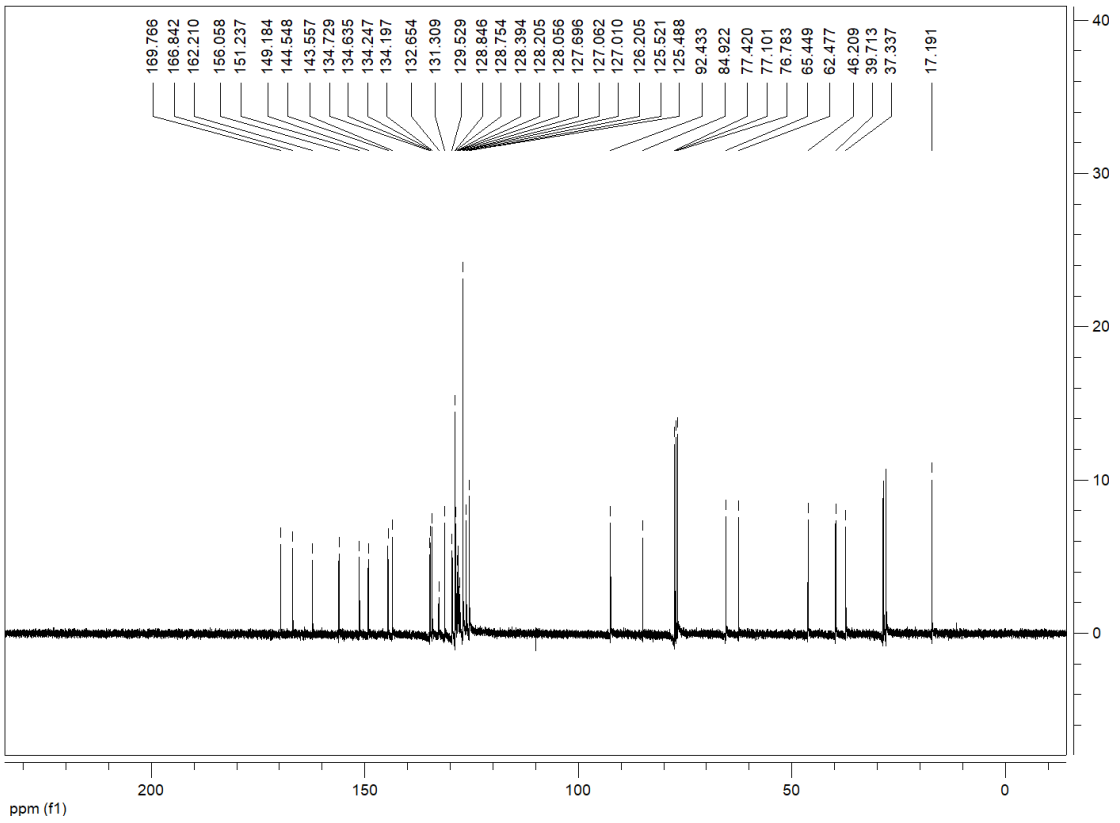
158.509
155.510
151.172
149.190
146.254
135.444
134.781
134.004
132.601
132.588
131.864
129.607
129.582
129.523
129.169
128.118
127.427
125.636
118.716
114.349
114.181
113.049
93.986
85.186
63.675
62.313
55.269
55.028
46.294
39.930
36.493
28.588
28.512
27.943
50
40
30
20
10
0
200
150
100
50
0
ppm (t1)


Intens.
+MS, 0.02-0.38min #(2-39)
300
250
200
150
100
50
0
868.1764
869.1810
867.00
867.25
867.50
867.75
868.00
868.25
868.50
868.75
869.00
869.25
m/z

***rel*-(5S,5aS,6S,8R,9aS)-6-(4-chlorophenyl)-1,1',3,3'-tetramethyl-5,8-diphenyl-9-(o-tolyl)-1,5,5a,8,9,9a-hexahydrospiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (5a):**

white solid, 88%, m.p.140-142℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (brs, 2H, ArH), 7.33-7.28 (m, 2H, ArH), 7.25 -7.22 (m, 2H, ArH), 7.10-6.97 (m, 7H, ArH), 6.94-6.85 (m, 4H, ArH), 6.65 (d, *J* = 8.4 Hz, 1H, ArH), 5.63 (s, 1H, CH), 5.51 (d, *J* = 2.4 Hz, 1H, CH), 4.04 (d, *J* = 13.2 Hz, 1H, CH), 3.93 (d, *J* = 13.2 Hz, 1H, CH), 3.77 (s, 1H, CH), 3.49 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 2.95 (s, 3H, NCH_3), 2.82 (s, 3H, NCH_3), 2.16 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.7, 166.8, 162.2, 156.0, 151.2, 149.1, 144.5, 143.5, 134.7, 134.6, 134.2, 134.1, 132.6, 131.3, 129.5, 128.8, 128.7, 128.3, 128.2, 128.0, 127.6, 127.0, 127.0, 126.2, 125.5, 125.4, 92.4, 84.9, 77.4, 77.1, 76.7, 65.4, 62.4, 46.2, 39.7, 37.3, 17.1; IR(KBr) υ: 2958, 1650, 1487, 1453, 1381, 1272, 1170, 997, 918, 826, 763, 704 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{42}H_{39}ClN_5O_6$([M+H]$^+$): 744.2589, found: 744.2813.




169.766
166.842
162.210
156.058
151.237
149.184
144.548
143.557
134.729
134.635
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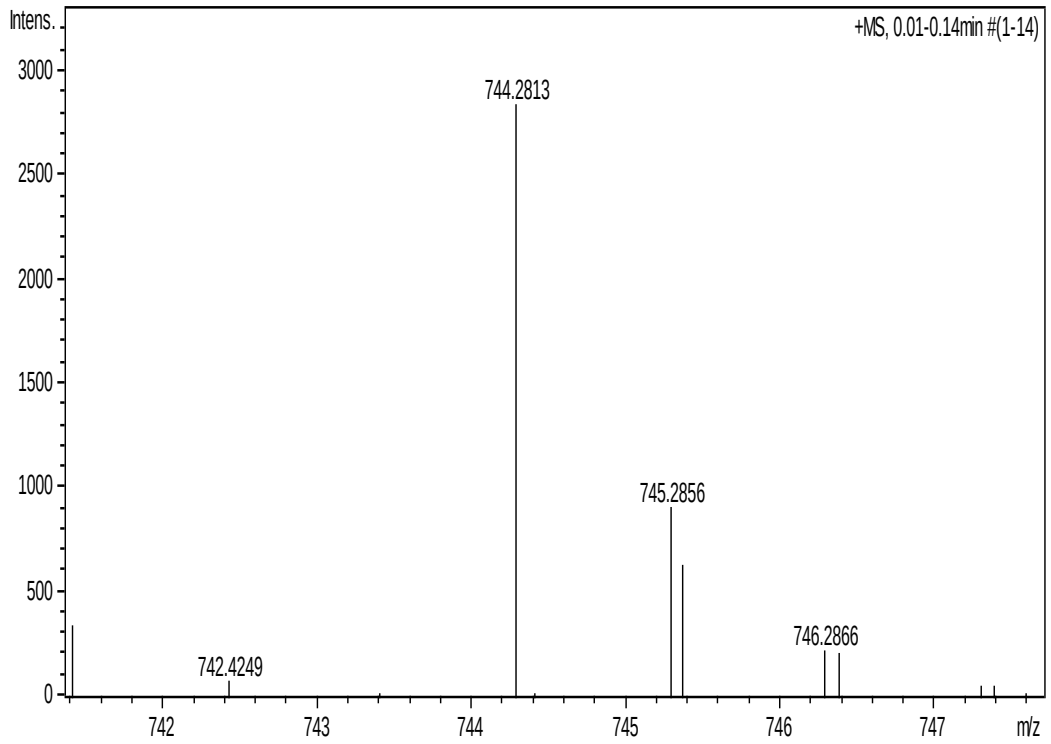
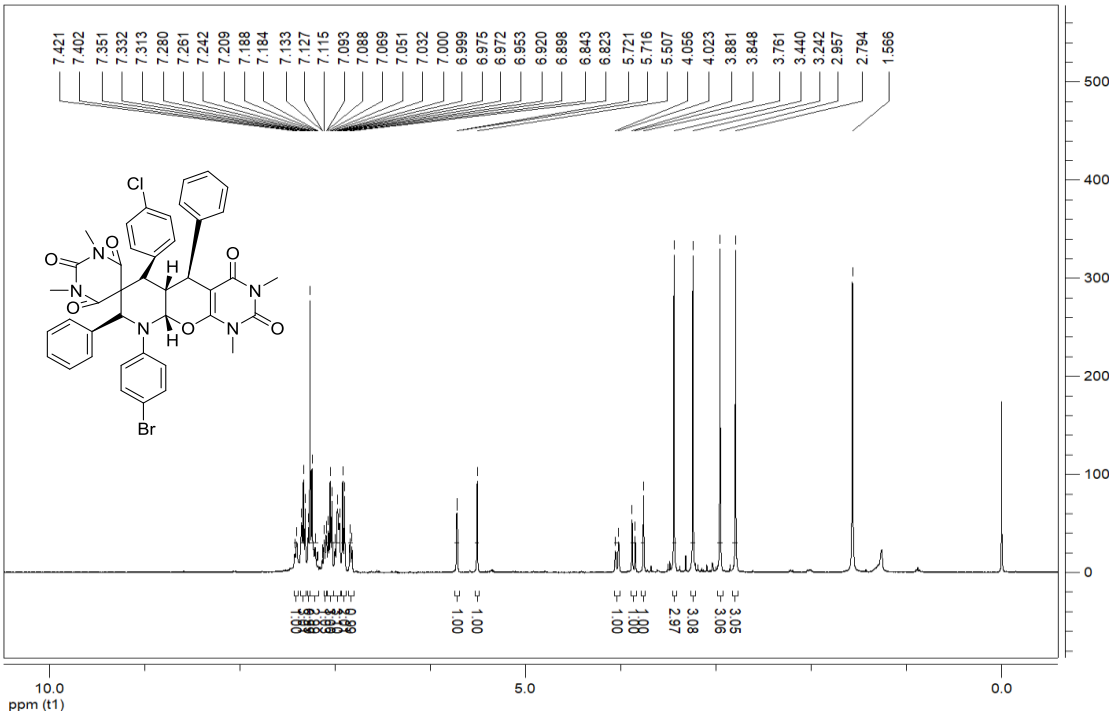
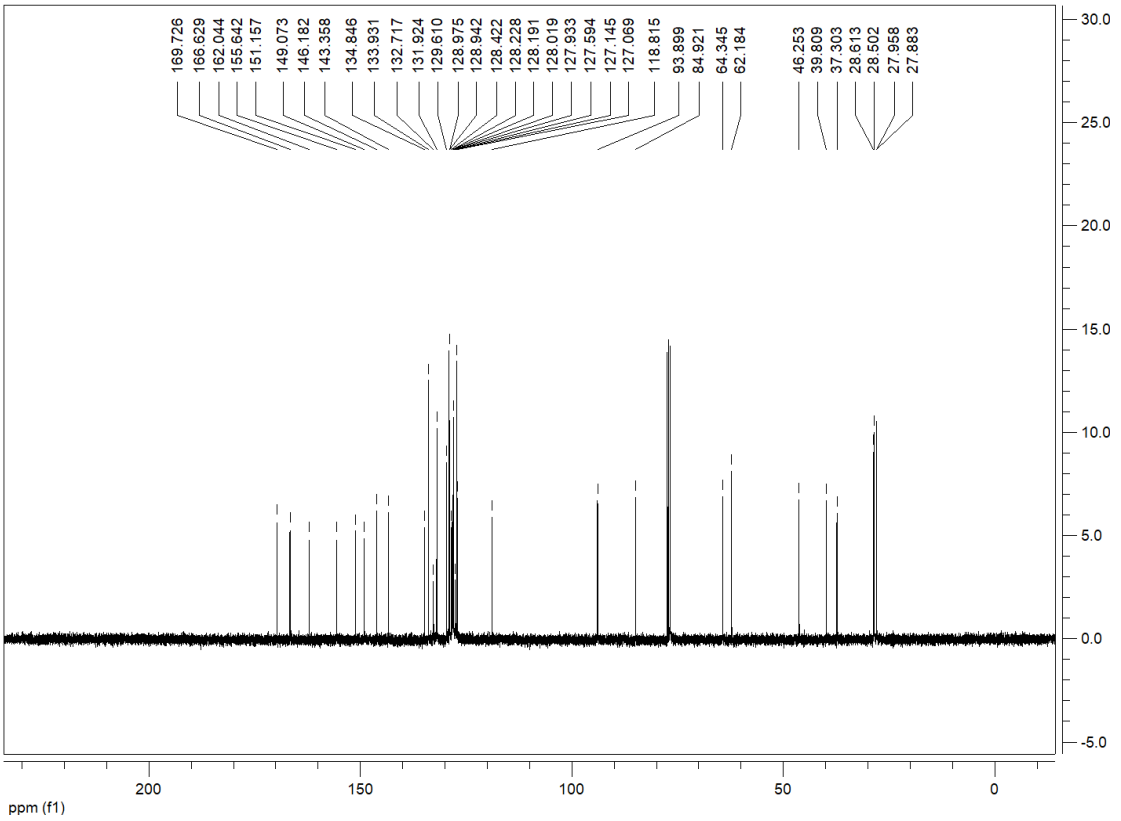
132.654
131.309
129.529
128.846
128.754
128.394
128.205
128.056
127.696
127.062
127.010
126.205
125.521
125.488
92.433
84.922
77.420
77.101
76.783
65.449
62.477
46.209
39.713
37.337
17.191
40
30
20
10
0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.01-0.14min #(1-14)
3000
2500
2000
1500
1000
500
0
744.2813
745.2856
746.2866
742.4249
742
743
744
745
746
747
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(4-bromophenyl)-6-(4-chlorophenyl)-1,1',3,3'-tetramethyl-5,8-diphenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (5b):**

white solid, 75%, m.p.142-144℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 7.6 Hz, 1H, ArH), 7.33 (t, *J* = 7.6 Hz, 3H, ArH), 7.28 -7.26 (m, 1H, ArH), 7.24-7.18 (m, 3H, ArH), 7.13-7.09 (m, 1H, ArH), 7.05 (t, *J* = 7.4 Hz, 3H, ArH), 7.00-6.95 (m, 3H, ArH), 6.91 (d, *J* = 8.8 Hz, 2H, ArH), 6.83 (d, *J* = 8.0 Hz, 1H, ArH), 5.72 (d, *J* = 2.0 Hz, 1H, CH), 5.51 (s, 1H, CH), 4.04 (d, *J* = 13.2 Hz, 1H, CH), 3.86 (d, *J* = 13.2 Hz, 1H, CH), 3.76 (s, 1H, CH), 3.44 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 2.96 (s, 3H, NCH_3), 2.79 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.7, 166.6, 162.0, 155.6, 151.1, 149.0, 146.1, 143.3, 134.8, 133.9, 132.7, 131.9, 129.6, 128.9, 128.9, 128.4, 128.2, 128.1, 128.0, 127.9, 127.5, 127.1, 127.0, 118.8, 93.8, 84.9, 64.3, 62.1, 46.2, 39.8, 37.3, 28.6, 28.5, 27.9, 27.8; IR(KBr) υ: 2957, 1650, 1503, 1455, 1381, 1240, 1169, 1034, 913, 833, 763, 708 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{36}BrClN_5O_6$([M+H]$^+$): 808.1537, found: 808.1530.

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166.629
162.044
155.642
151.157
149.073
146.182
143.358
134.846
133.931
132.717
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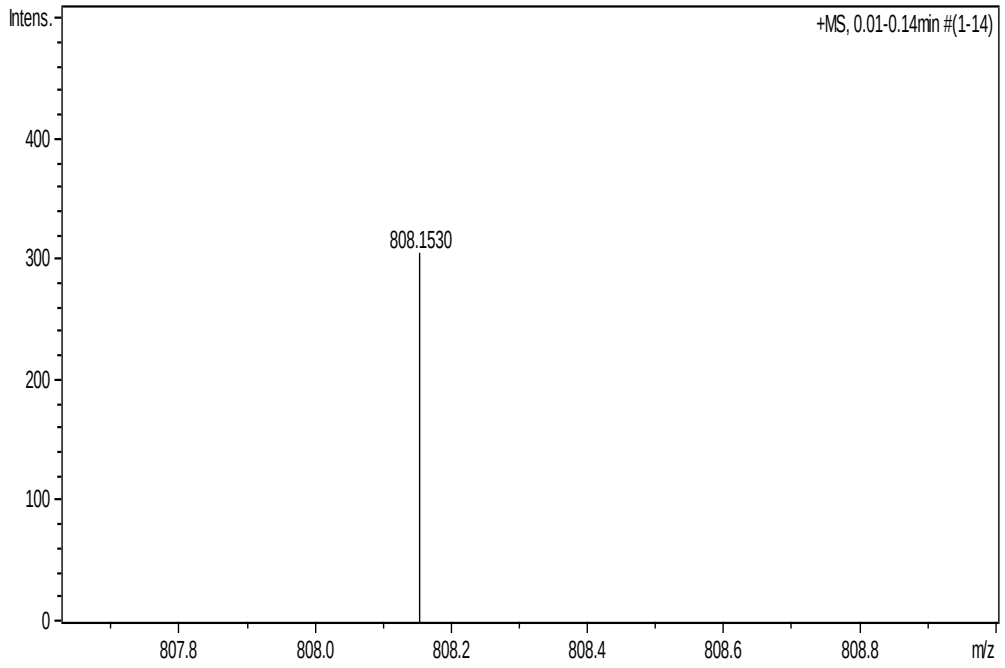
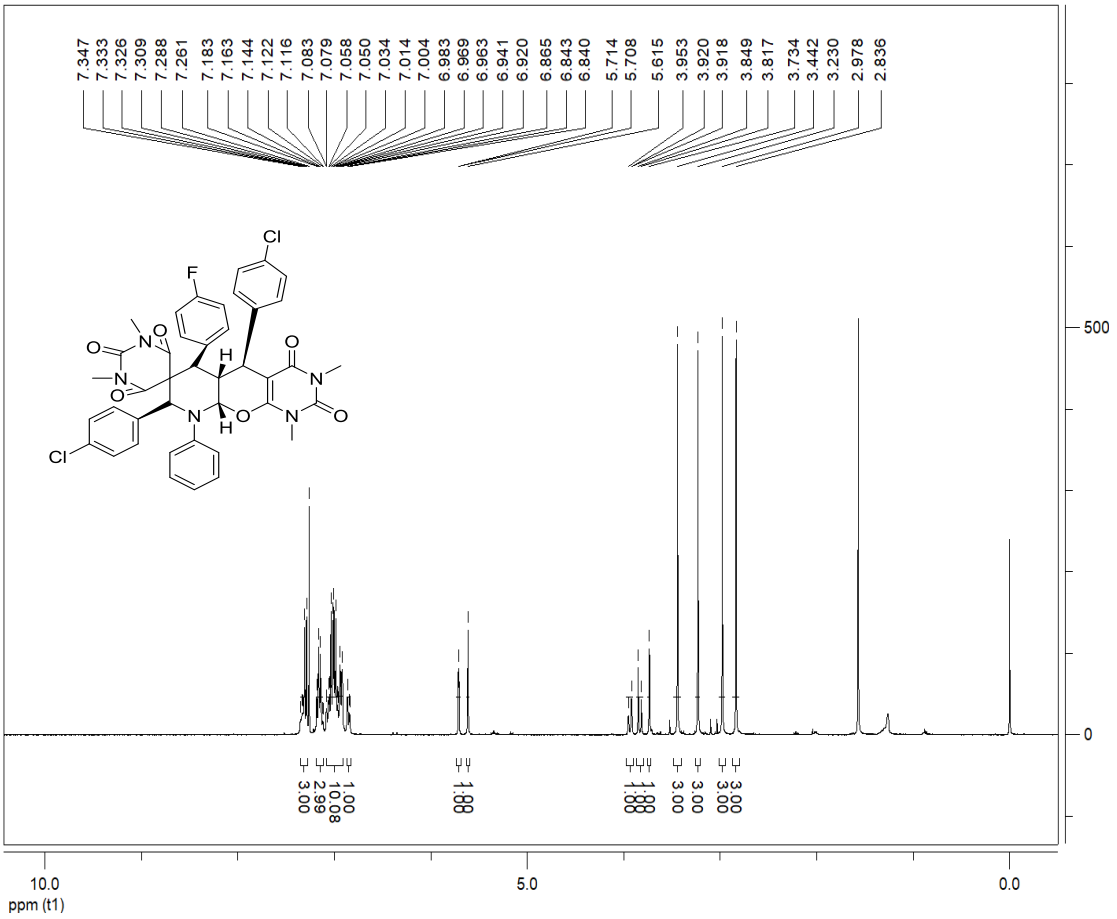
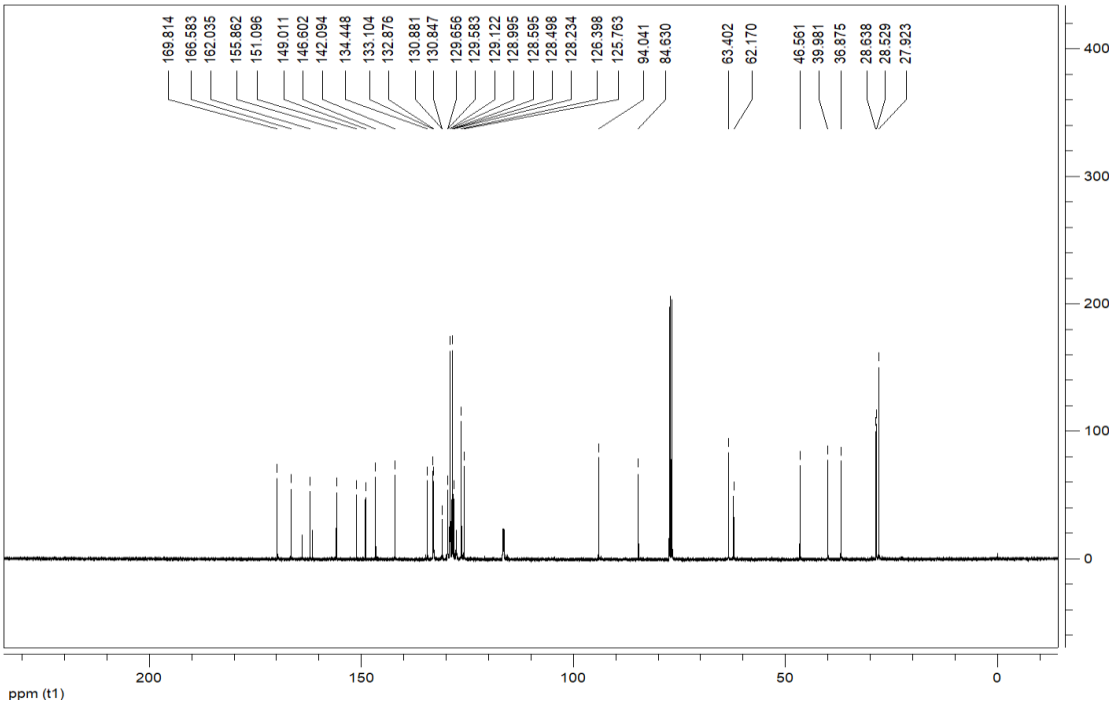
129.610
128.975
128.842
128.422
128.228
128.191
128.019
127.933
127.594
127.145
127.069
118.815
93.899
84.921
64.345
62.184
46.253
39.809
37.303
28.613
28.502
27.958
27.883
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.01-0.14min #(1-14)
808.1530
400
300
200
100
0
807.8
808.0
808.2
808.4
808.6
808.8
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(4-chlorophenyl)-6-(4-fluorophenyl)-1,1',3,3'-tetramethyl-9-phenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (5c)**:

white solid, 74%, m.p.170-172℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.29 (m, 3H, ArH), 7.18-7.12 (m, 3H, ArH), 7.08-6.92 (m, 10H, ArH), 6.86-6.74 (m, 1H, ArH), 5.71 (d, *J* = 2.4 Hz, 1H, CH), 5.62 (s, 1H, CH), 3.95-3.92 (m, 1H, CH), 3.83 (d, *J* = 12.8 Hz, 1H, CH), 3.73 (s, 1H, CH), 3.44 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.98 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.8, 166.5, 162.0, 155.8, 151.0, 149.0, 146.6, 142.0, 134.4, 133.1, 132.8, 130.8, 130.8, 129.6, 129.5, 129.1, 128.9, 128.5, 128.4, 128.2, 126.3, 125.7, 94.0, 84.6, 63.4, 62.1, 46.5, 39.9, 36.8, 28.6, 28.5, 27.9; IR(KBr) υ:3056, 1680, 1648, 1485, 1379, 1275, 1236, 1171, 1094, 1018, 910, 829, 752 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{35}Cl_2FN_5O_6$([M+H]$^+$): 782.1948, found: 782.1923.




169.814
166.583
162.035
155.862
151.096
149.011
146.602
142.094
134.448
133.104
132.876
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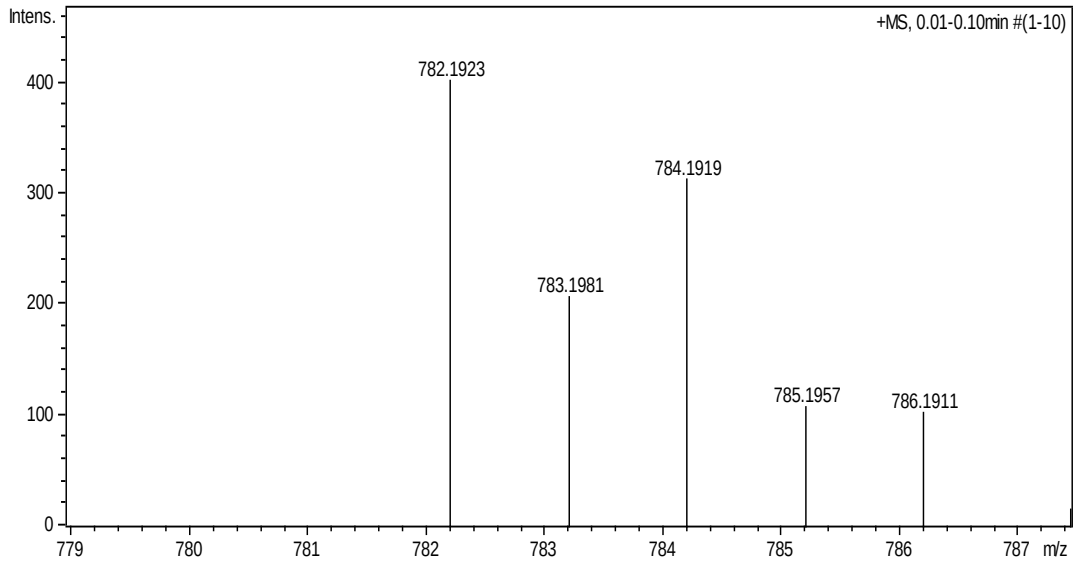
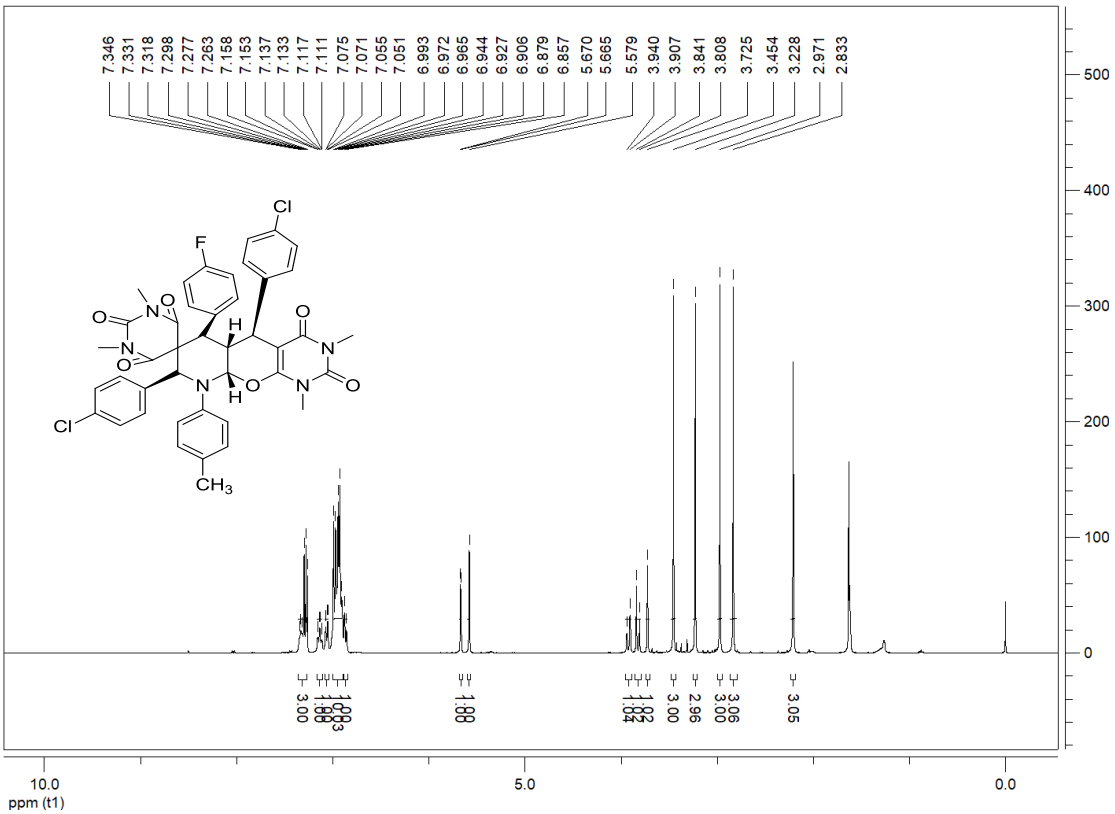
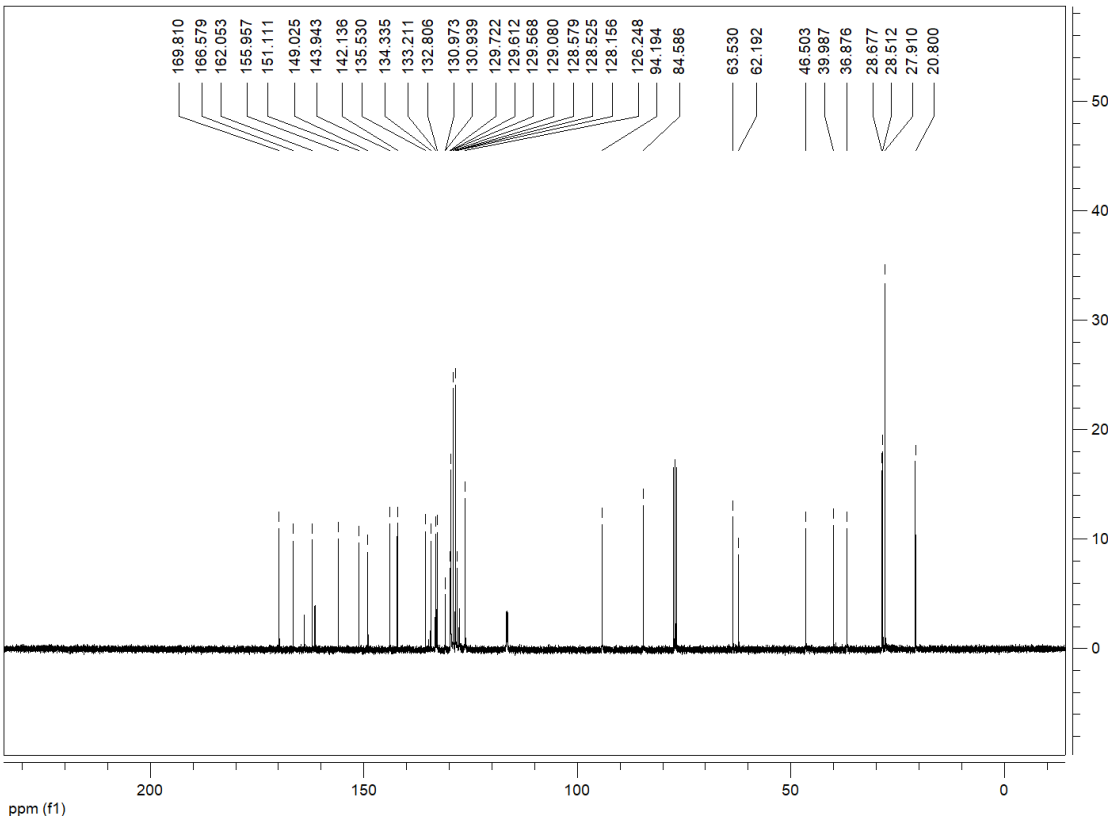
130.847
129.656
129.583
129.122
128.995
128.595
128.498
128.234
126.398
125.763
94.041
84.630
63.402
62.170
46.561
39.981
36.875
28.638
28.529
27.923
400
300
200
100
0
200
150
100
50
0
ppm (t1)

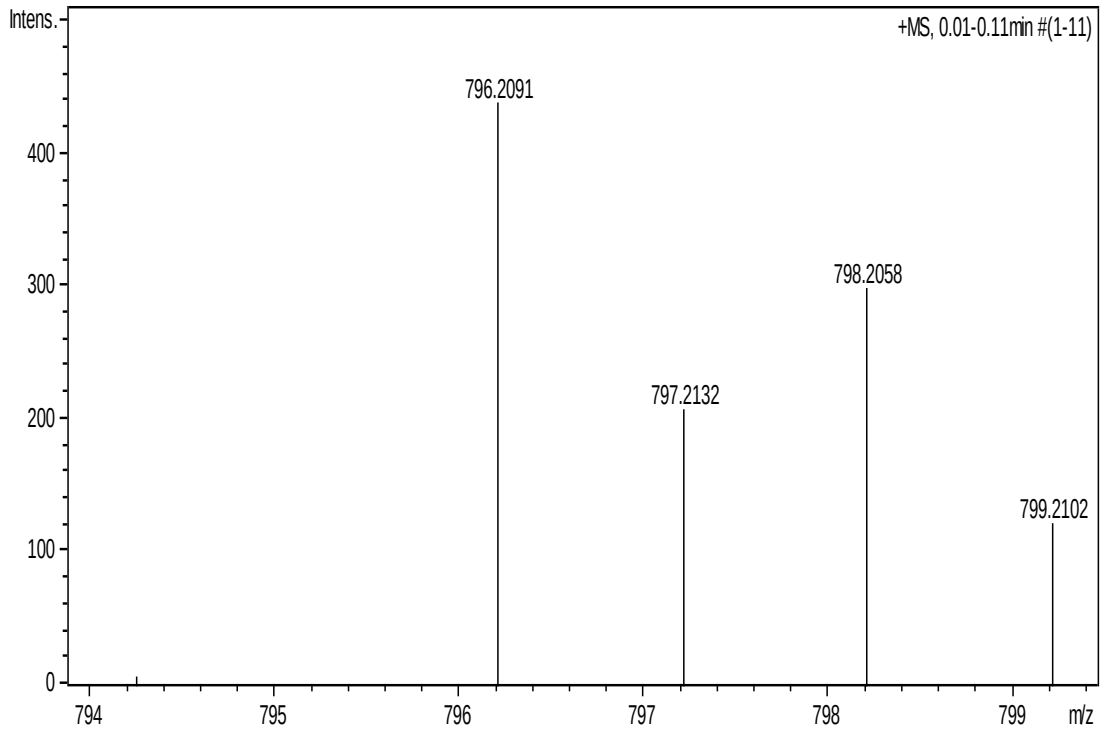

Intens.
+MS, 0.01-0.10min #(1-10)
782.1923
784.1919
783.1981
785.1957
786.1911
400
300
200
100
0
779
780
781
782
783
784
785
786
787
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(4-chlorophenyl)-6-(4-fluorophenyl)-1,1',3,3'-tetramethyl-9-(p-tolyl)-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (5d):**

white solid, 95%, m.p.163-165℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.28 (brs, 3H, ArH), 7.16-7.11 (m, 1H, ArH), 6.99-6.91 (m, 1H, ArH), 6.87 (d, *J* = 8.8 Hz, 1H, ArH), 5.67 (d, *J* = 2.0 Hz, 1H, CH), 5.58 (m, 1H, CH), 3.92 (d, *J* = 13.2 Hz, 1H, CH), 3.82 (d, *J* = 13.2 Hz, 1H, CH), 3.72 (s, 1H, CH), 3.45 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3), 2.83 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.8, 166.5, 162.0, 155.9, 151.1, 149.0, 143.9, 142.1, 135.5, 134.3, 133.2, 132.8, 130.9, 130.9, 129.7, 129.6, 129.5, 129.0, 128.5, 128.5, 128.1, 126.2, 94.1, 84.5, 63.5, 62.1, 46.5, 39.9, 36.8, 28.6, 28.5, 27.9, 20.8; IR(KBr) υ: 3028, 1685, 1647, 1483, 1424, 1377, 1272, 1172, 1095, 1016, 913, 826, 763, 669 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{42}H_{37}Cl_2FN_5O_6$([M+H]$^+$): 796.2105, found: 796.2091.

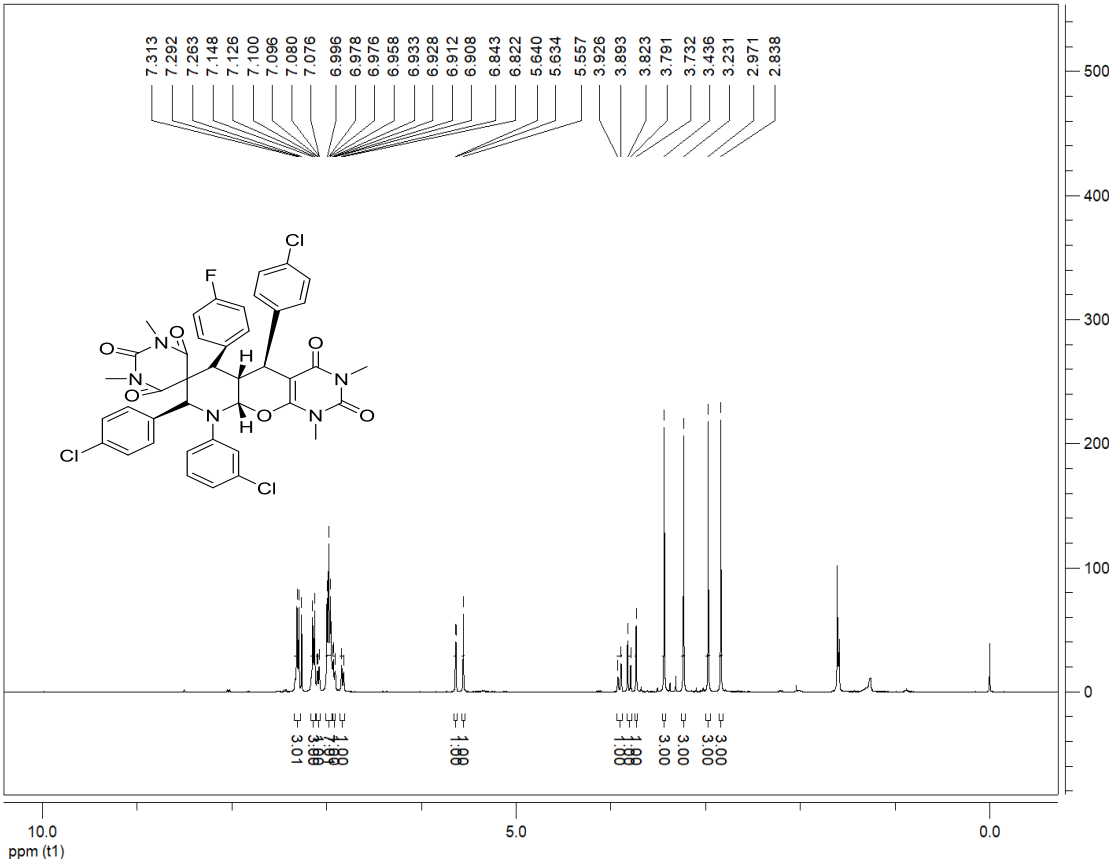


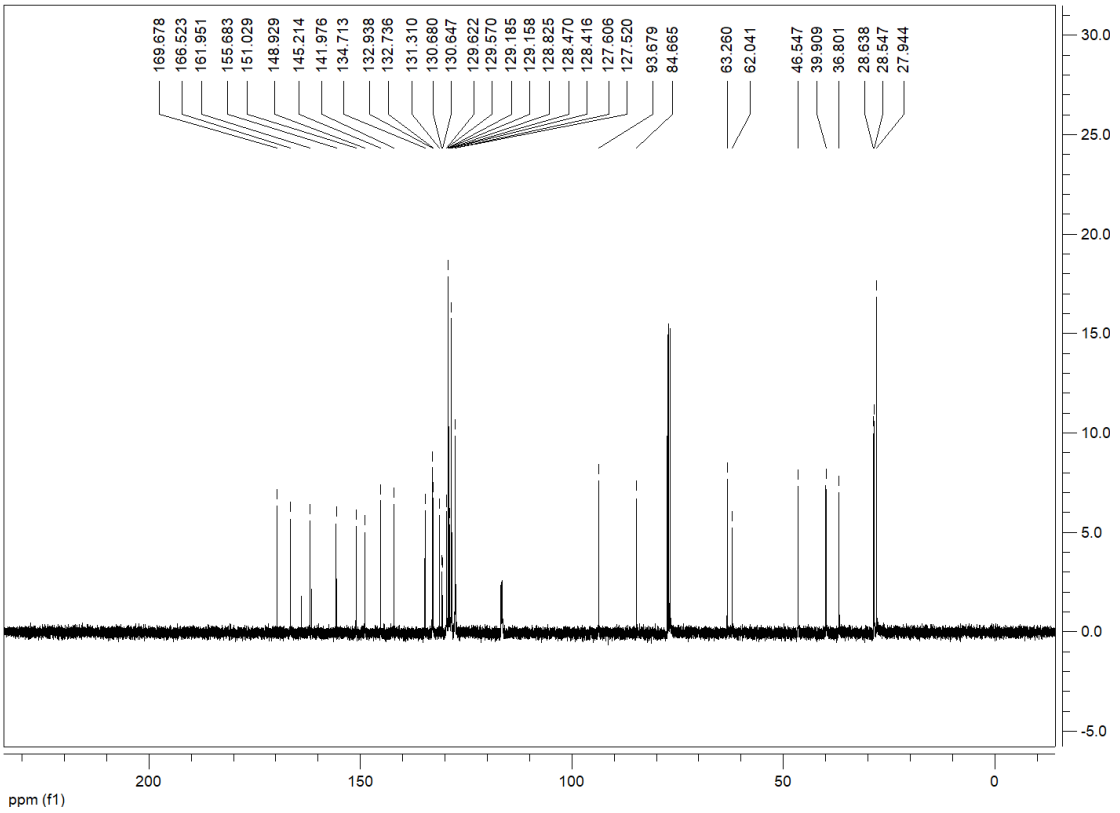

169.810
166.579
162.053
155.957
151.111
149.025
143.943
142.136
135.530
134.335
133.211
132.806
130.973
130.939
129.722
129.612
129.568
129.080
128.579
128.525
128.156
126.248
94.194
84.586
63.530
62.192
46.503
39.987
36.876
28.677
28.512
27.910
20.800
50
40
30
20
10
0
200
150
100
50
0
ppm (f1)

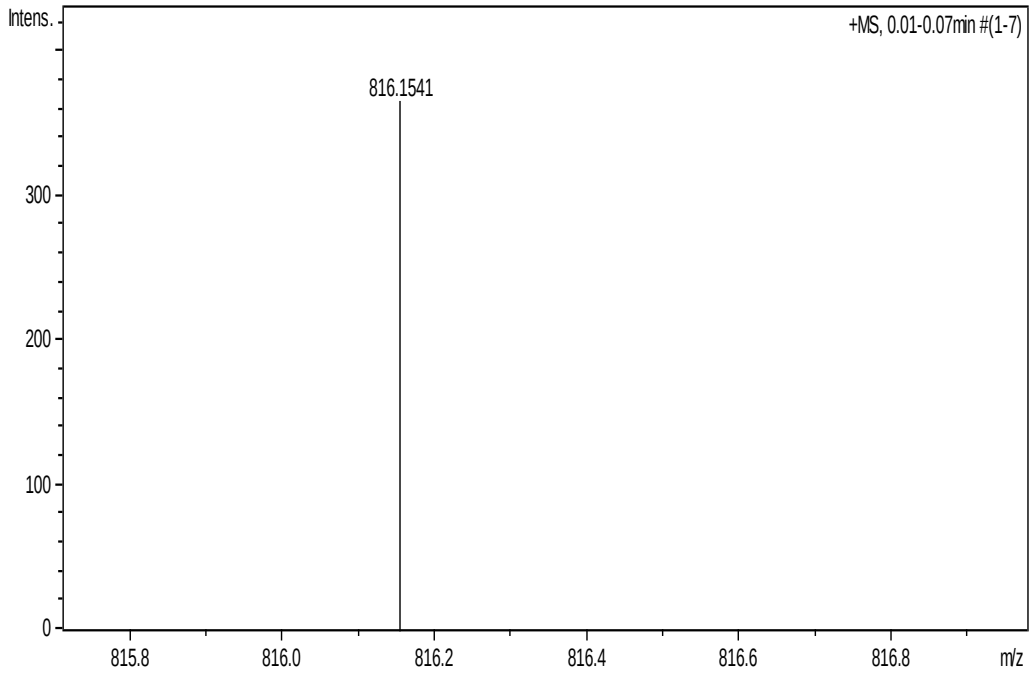

Intens.
+MS, 0.01-0.11min #(1-11)
796.2091
798.2058
797.2132
799.2102
400
300
200
100
0
794
795
796
797
798
799
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(3-chlorophenyl)-5,8-bis(4-chlorophenyl)-6-(4-fluorophenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (5e)**:

white solid, 87%, m.p.180-182℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31-7.29 (m, 3H, ArH), 7.15-7.13 (m, 3H, ArH), 7.10-7.08 (m, 1H, ArH), 7.00-6.96 (m, 7H, ArH), 6.93-6.91 (m, 1H, ArH), 6.83 (d, *J* = 8.4 Hz, 1H, ArH), 5.64 (d, *J* = 2.4 Hz, 1H, CH), 5.56 (s, 1H, CH), 3.91 (d, *J* = 13.2 Hz, 1H, CH), 3.81 (d, *J* = 12.8 Hz, 1H, CH), 3.73 (s, 1H, CH), 3.73 (s, 1H, CH), 3.44 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.6, 166.5, 161.9, 155.6, 151.0, 148.9, 145.2, 141.9, 134.7, 132.9, 132.7, 131.3, 130.6, 130.6, 129.6, 129.5, 129.1, 129.1, 128.8, 128.4, 128.4, 127.6, 127.5, 93.6, 84.6, 63.2, 62.0, 46.5, 39.9, 36.8, 28.6, 28.5, 27.9; IR(KBr) υ: 2957, 1651, 1484, 1377, 1273, 1232, 1171, 1094, 1019, 911, 829, 760, 717, 670 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{34}Cl_3FN_5O_6$([M+H]$^+$): 816.1559, found: 816.1541.

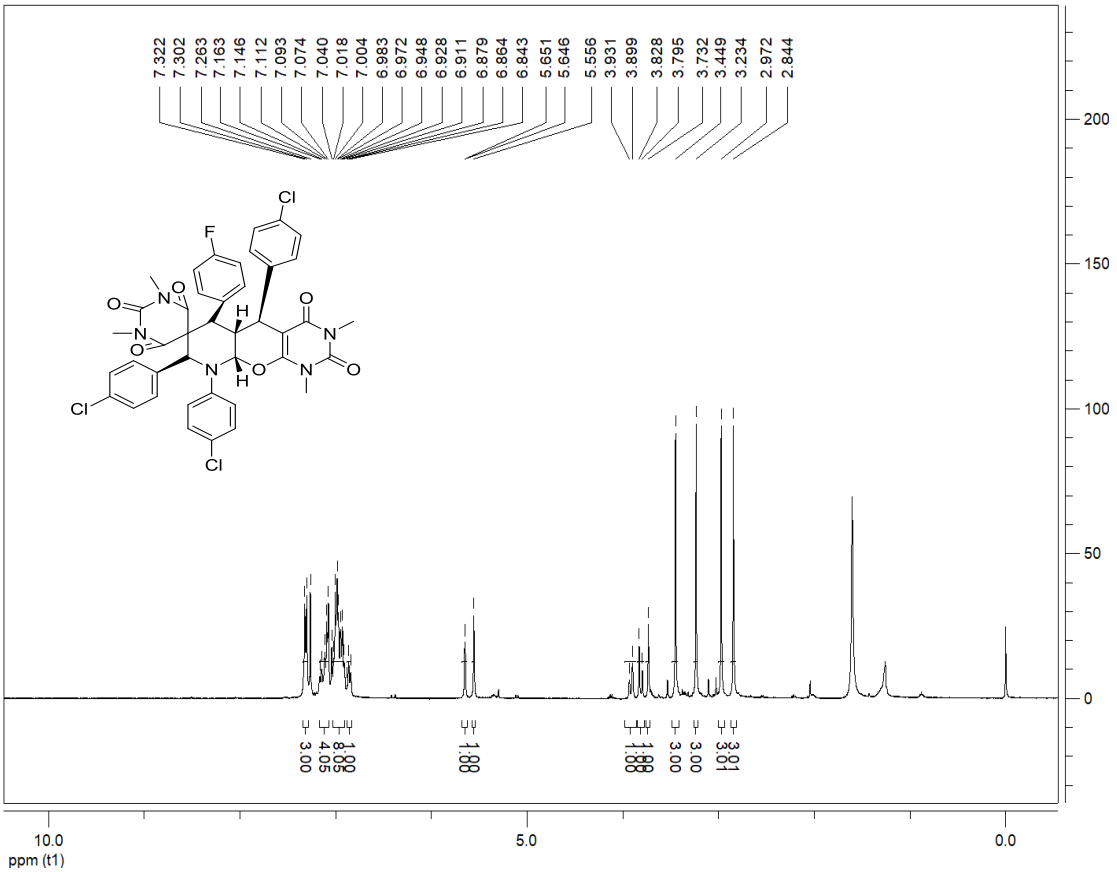


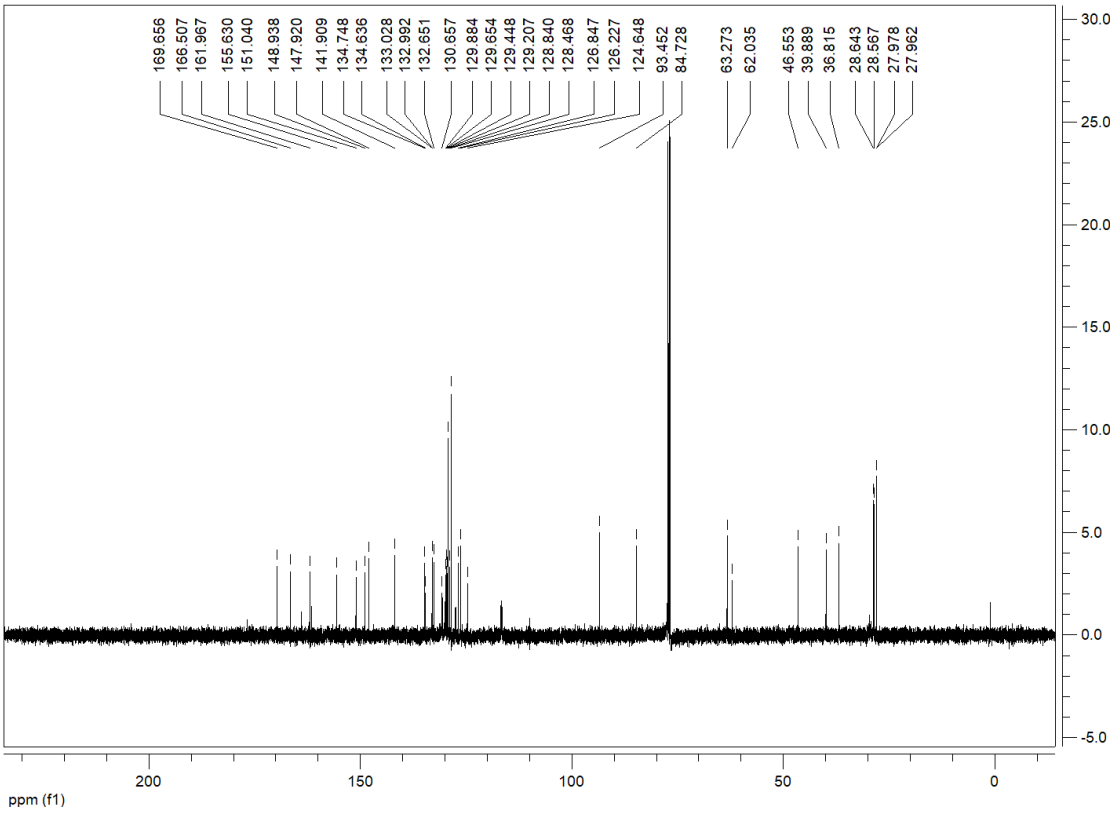

169.678
166.523
161.951
155.683
151.029
148.929
145.214
141.976
134.713
132.938
132.736
131.310
130.680
130.647
129.622
129.570
129.185
129.158
128.825
128.470
128.416
127.606
127.520
93.679
84.665
63.260
62.041
46.547
39.909
36.801
28.638
28.547
27.944
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (f1)

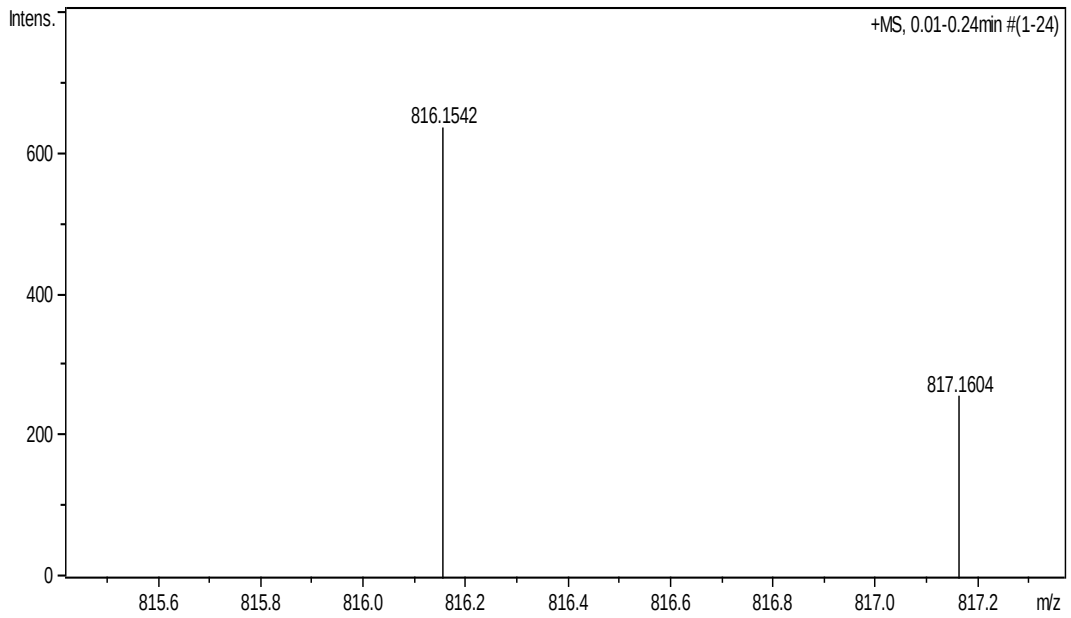

Intens.
+MS, 0.01-0.07min #(1-7)
816.1541
300
200
100
0
815.8
816.0
816.2
816.4
816.6
816.8
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8,9-tris(4-chlorophenyl)-6-(4-fluorophenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone (5f):**

white solid, 78%, m.p.190-192℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.30 (m, 3H, ArH), 7.16-7.07 (m, 4H, ArH), 7.04-6.91 (m, 8H, ArH), 6.88-6.84 (m, 1H, ArH), 5.65 (d, *J* = 2.0 Hz, 1H, CH), 5.56 (s, 1H, CH), 3.92 (d, *J* = 12.8 Hz, 1H, CH), 3.81 (d, *J* = 13.2 Hz, 1H, CH), 3.72 (s, 1H, CH), 3.45 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.6, 166.5, 161.9, 155.6, 151.0, 148.9, 147.9, 141.9, 134.7, 134.6, 133.0, 132.9, 132.6, 130.6, 129.8, 129.6, 129.4, 129.2, 128.8, 128.4, 126.8, 126.2, 124.6, 93.4, 84.7, 63.2, 62.0, 46.5, 39.8, 36.8, 28.6, 28.5, 27.9, 27.9; IR(KBr) υ: 3067, 1688, 1646, 1592, 1482, 1425, 1378, 1276, 1170, 1093, 1016, 915, 830, 765, 673 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{34}Cl_3FN_5O_6$([M+H]$^+$): 816.1559, found: 816.1542.

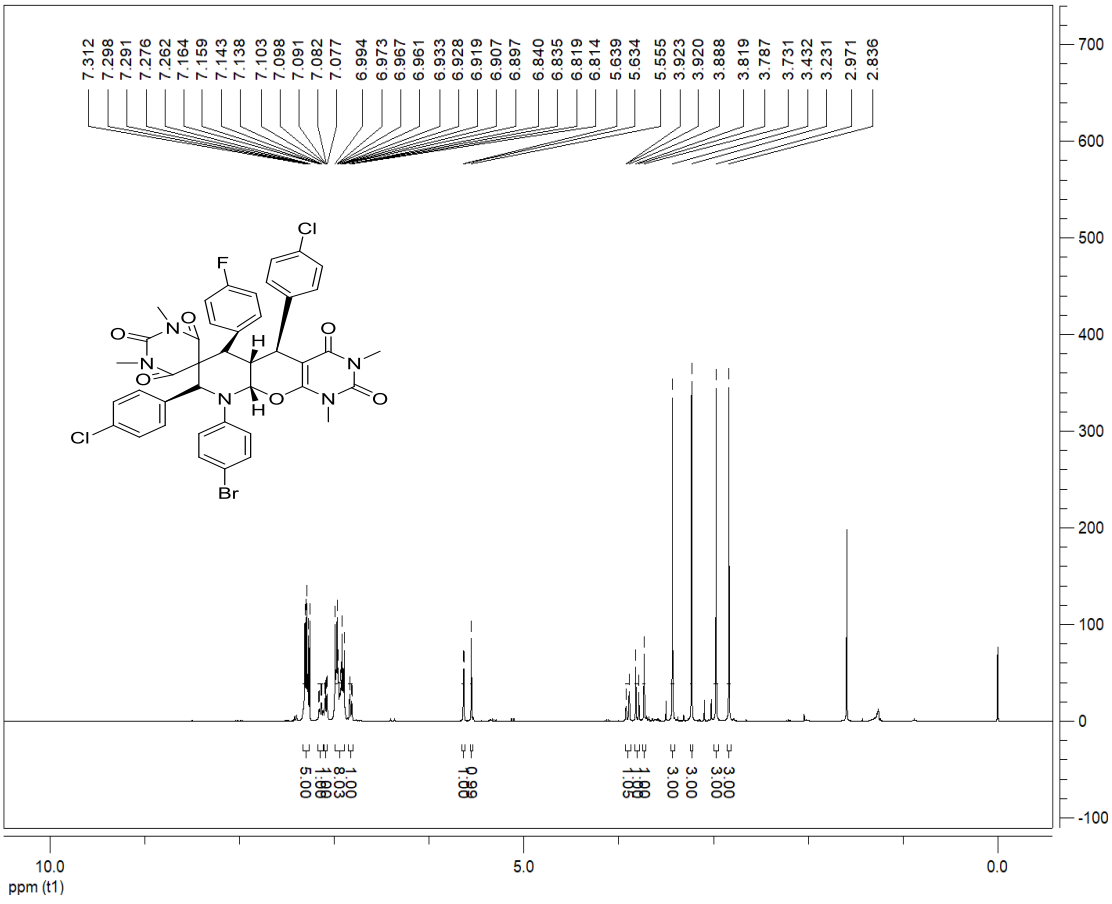


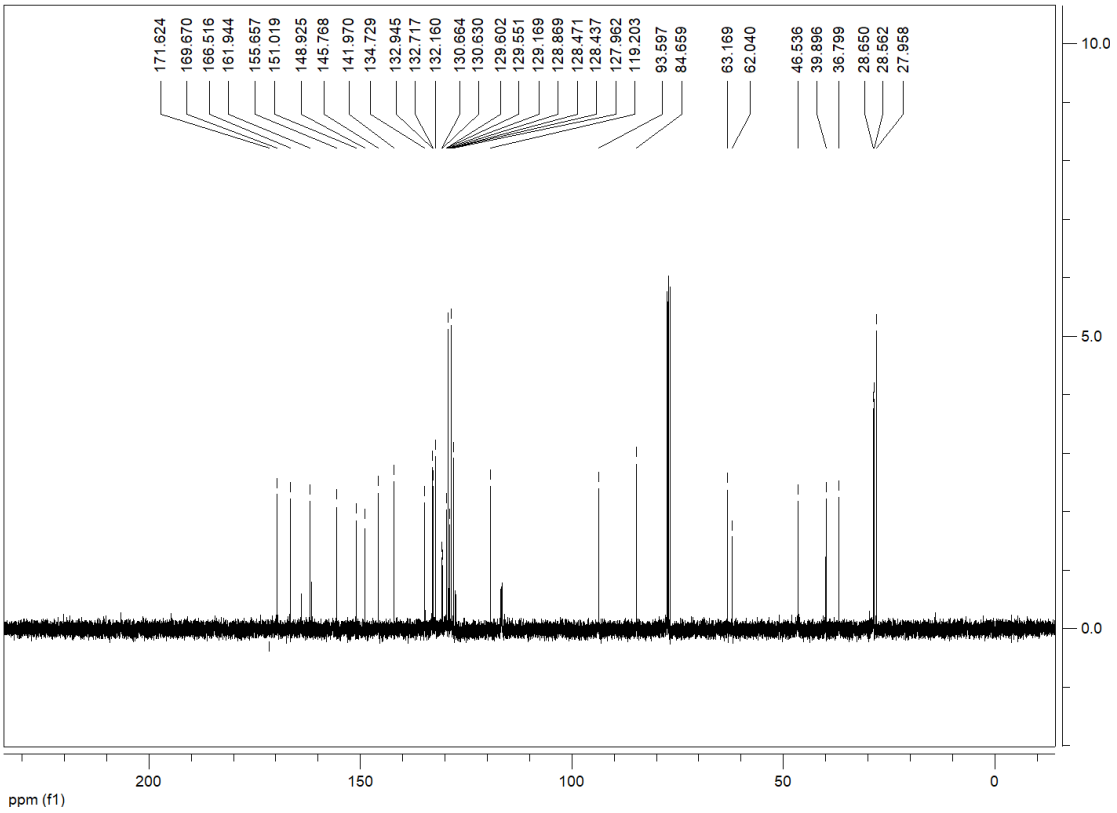

169.656
166.507
161.967
155.630
151.040
148.938
147.920
141.909
134.748
134.636
133.028
132.992
132.651
130.657
129.884
129.654
129.448
129.207
128.840
128.468
126.847
126.227
124.648
93.452
84.728
63.273
62.035
46.553
39.889
36.815
28.643
28.567
27.978
27.962
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
200
150
100
50
0
ppm (f1)

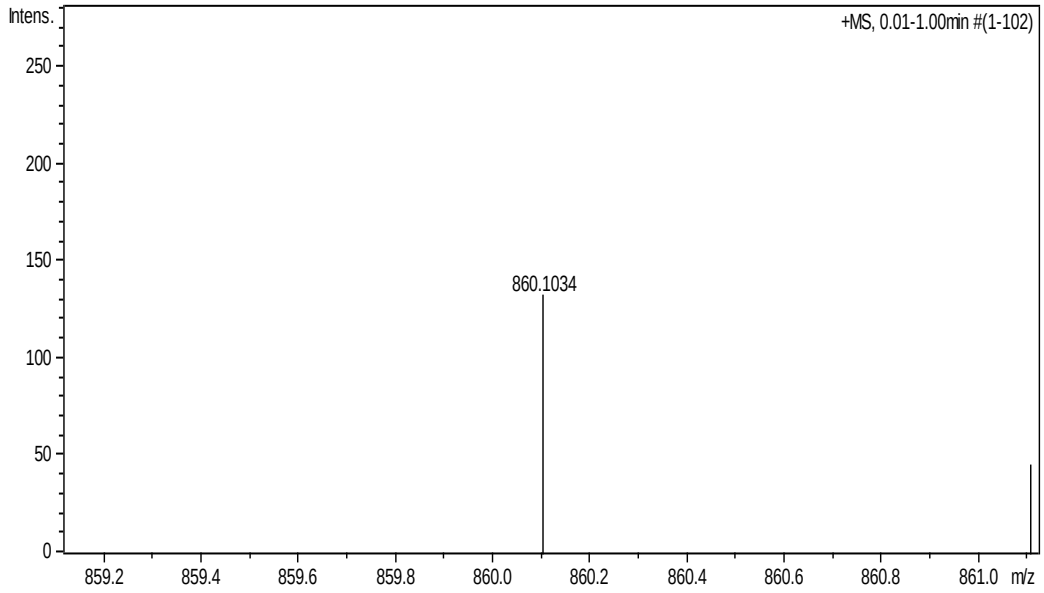

Intens.
+MS, 0.01-0.24min #(1-24)
816.1542
817.1604
600
400
200
0
815.6
815.8
816.0
816.2
816.4
816.6
816.8
817.0
817.2
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(4-bromophenyl)-5,8-bis(4-chlorophenyl)-6-(4-fluorophenyl)-1,1',3,3'-tetramethyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (5g)**:

white solid, 81%, m.p.195-197℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31-7.28 (m, 5H, ArH), 7.16 (m, 1H, ArH), 7.10-7.08 (m, 1H, ArH), 6.99-6.90 (m, 8H, ArH), 6.84-6.81 (m, 1H, ArH), 5.64 (d, *J* = 2.0 Hz, 1H, CH), 5.55 (s, 1H, CH), 3.92-3.89 (m, 1H, CH), 3.80 (d, *J* = 12.8 Hz, 1H, CH), 3.73 (s, 1H, CH), 3.43 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.97 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.6, 166.5, 161.9, 155.6, 151.0, 148.9, 145.7, 141.9, 134.7, 132.9, 132.7, 132.1, 130.6, 130.6, 129.6, 129.5, 129.1, 128.8, 128.4, 128.4, 127.9, 119.2, 93.5, 84.6, 63.1, 62.0, 46.5, 39.8, 36.7, 28.6, 28.5, 27.9; IR(KBr) υ: 2957, 1651, 1482, 1377, 1273, 1235, 1170, 1097, 1015, 910, 831, 759, 668 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{34}BrCl_2FN_5O_6$ ($[M+H]^+$): 860.1054, found: 860.1034.

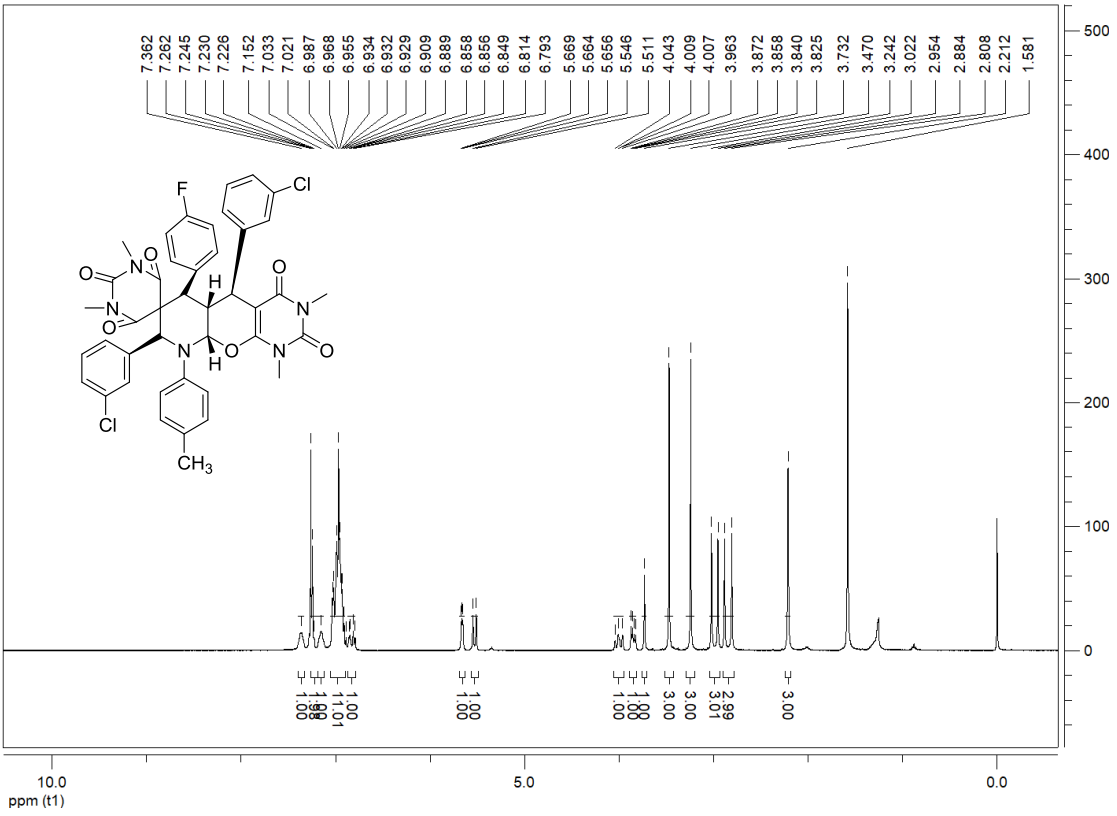


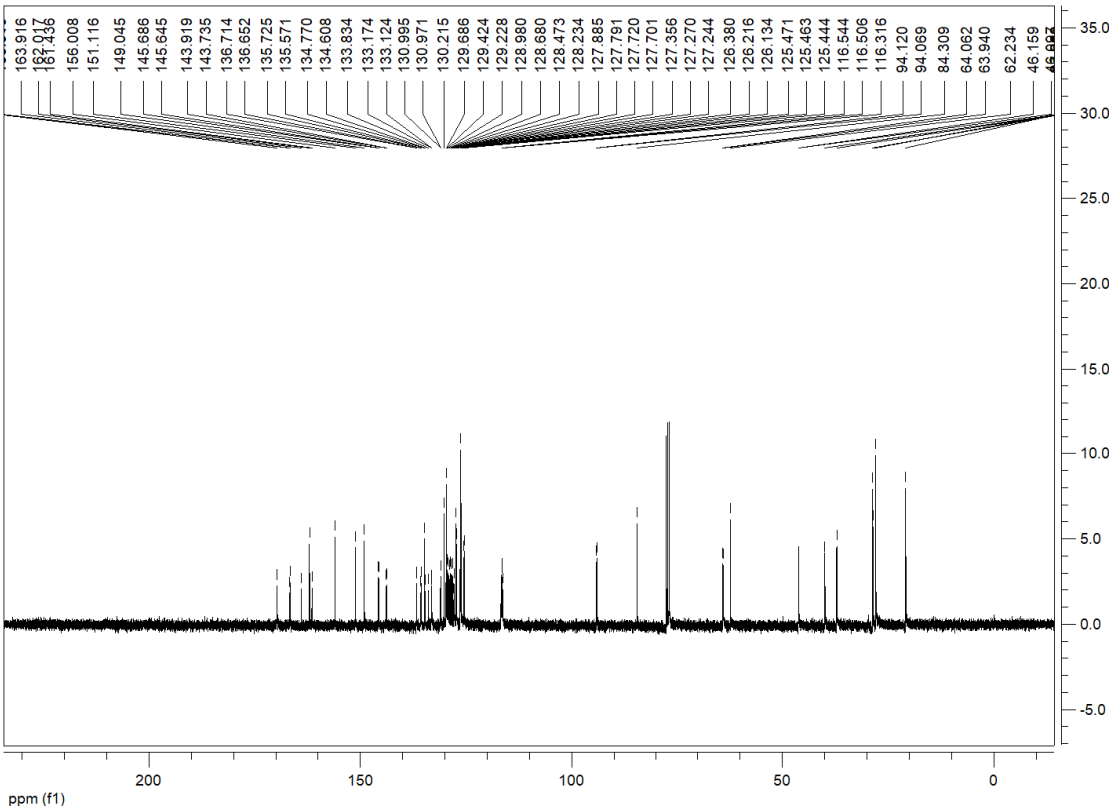

171.624
169.670
166.516
161.944
155.657
151.019
148.925
145.768
141.970
134.729
132.945
132.717
132.160
130.664
130.630
129.602
129.551
129.169
128.869
128.471
128.437
127.962
119.203
93.597
84.659
63.169
62.040
46.536
39.896
36.799
28.650
28.562
27.958
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.01-1.00min #(1-102)
250
200
150
100
50
0
860.1034
859.2
859.4
859.6
859.8
860.0
860.2
860.4
860.6
860.8
861.0
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8-bis(3-chlorophenyl)-6-(4-fluorophenyl)-1,1',3,3'-tetramethyl-9-(p-tolyl)-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (5h)**:

white solid, 84%, m.p.148-150℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (brs, 1H, ArH), 7.26-7.23 (m, 2H, ArH), 7.15 (s, 1H, ArH), 7.03-6.91 (m, 11H, ArH), 6.86-6.79 (m, 1H, ArH), 5.67-6.66 (m, 1H, CH), 5.53 (d, *J* = 14.0 Hz, 1H, CH), 4.04-3.96 (m, 1H, CH), 3.87-3.82 (m, 1H, CH), 3.73 (s, 1H, CH), 3.47 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 3.02-2.81 (s, s, s, s, 6H, $2NCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.7, 169.6, 166.6, 166.5, 163.9, 162.0, 161.4, 156.0, 151.1, 149.0, 145.6, 145.6, 143.9, 143.7, 136.7, 136.6, 135.7, 135.5, 134.7, 134.6, 133.8, 133.1, 133.1, 130.9, 130.9, 130.2, 129.6, 129.4, 129.2, 128.9, 128.6, 128.4, 128.2, 127.8, 127.7, 127.7, 127.7, 127.3, 127.2, 127.2, 126.3, 126.2, 126.1, 125.4, 125.4, 125.4, 116.5, 116.5, 116.3, 94.1, 94.0, 84.3, 64.0, 63.9, 62.2, 46.1, 46.0, 39.9, 39.9, 39.9, 37.1, 28.7, 28.5, 27.9, 27.9, 27.8, 20.8; IR(KBr) υ: 3061, 1685, 1650, 1476, 1431, 1381, 1273, 1171, 902, 841, 782, 700 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{42}H_{37}Cl_2FN_5O_6$ ($[M+H]^+$): 796.2105, found: 796.2097.

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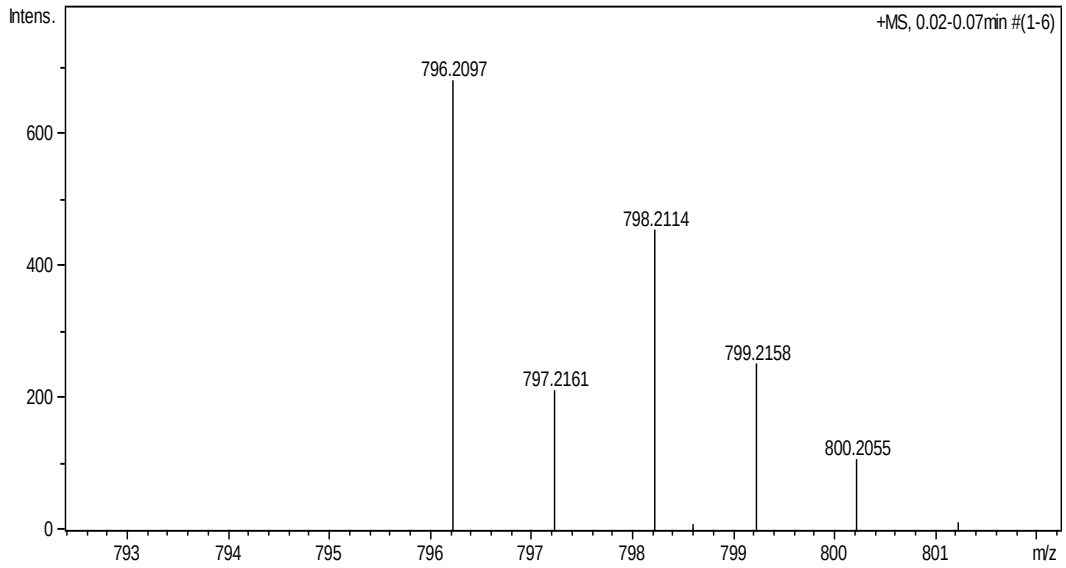
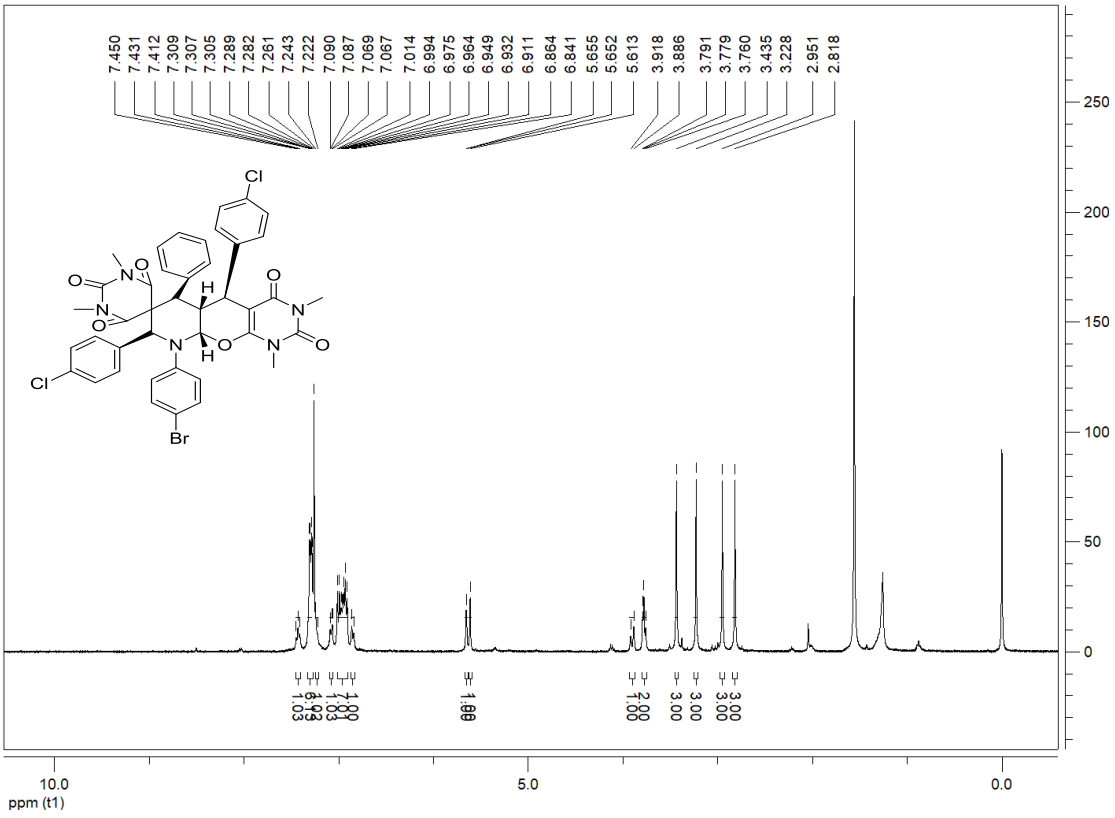
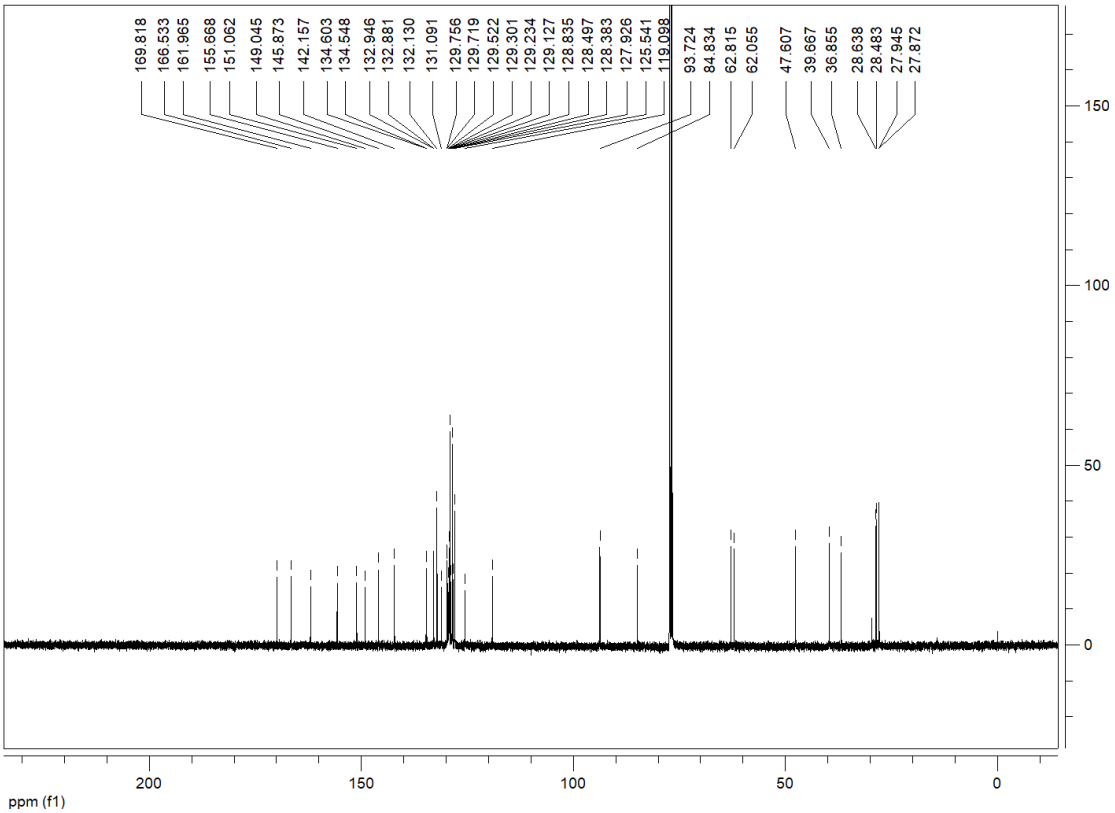
162.017
161.436
156.008
151.116
149.045
145.686
145.645
143.919
143.735
136.714
136.652
135.725
135.571
134.770
134.608
133.834
133.174
133.124
130.995
130.971
130.215
129.686
129.424
129.228
128.980
128.680
128.473
128.234
127.885
127.791
127.720
127.701
127.356
127.270
127.244
126.380
126.216
126.134
125.471
125.463
125.444
116.544
116.506
116.316
94.120
94.069
84.309
64.062
63.940
62.234
46.159
35.0
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, 0.02-0.07min #(1-6)
796.2097
798.2114
799.2158
797.2161
800.2055
600
400
200
0
793
794
795
796
797
798
799
800
801
m/z

***rel*-(5S,5aS,6S,8R,9aS)-9-(4-bromophenyl)-5,8-bis(4-chlorophenyl)-1,1',3,3'-tetramethyl-6-phenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'(1'H,3H,3'H)-pentaone (5i):**

white solid, 63%, m.p.127-129℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (t, *J* = 7.6 Hz, 1H, ArH), 7.31-7.28 (m, 6H, ArH), 7.24-7.22 (m, 1H, ArH), 7.09-7.07 (m, 1H, ArH), 7.01-6.91 (m, 7H, ArH), 6.85 (d, *J* = 9.2 Hz, 1H, ArH), 5.65 (d, *J* = 1.8 Hz, 1H, ArH), 5.61 (s, 1H, CH), 3.90 (d, *J* = 12.8 Hz, 1H, CH), 3.79-3.76 (m, 2H, CH), 3.44 (s, 3H, NCH_3), 3.23 (s, 3H, NCH_3), 2.95 (s, 3H, NCH_3), 2.82 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.8, 166.5, 161.9, 155.6, 151.0, 149.0, 145.8, 142.1, 134.6, 134.5, 132.9, 132.8, 132.1, 131.0, 129.7, 129.7, 129.5, 129.3, 129.2, 129.1, 128.8, 128.4, 128.3, 127.9, 125.5, 119.0, 93.7, 84.8, 62.8, 62.0, 47.6, 39.6, 36.8, 28.6, 28.4, 27.9, 27.8; IR(KBr) υ: 3062, 1685, 1649, 1484, 1377, 1278, 1170, 907, 831, 755 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{35}BrCl_2N_5O_6$([M+H]$^+$): 842.1148, found: 842.1137.

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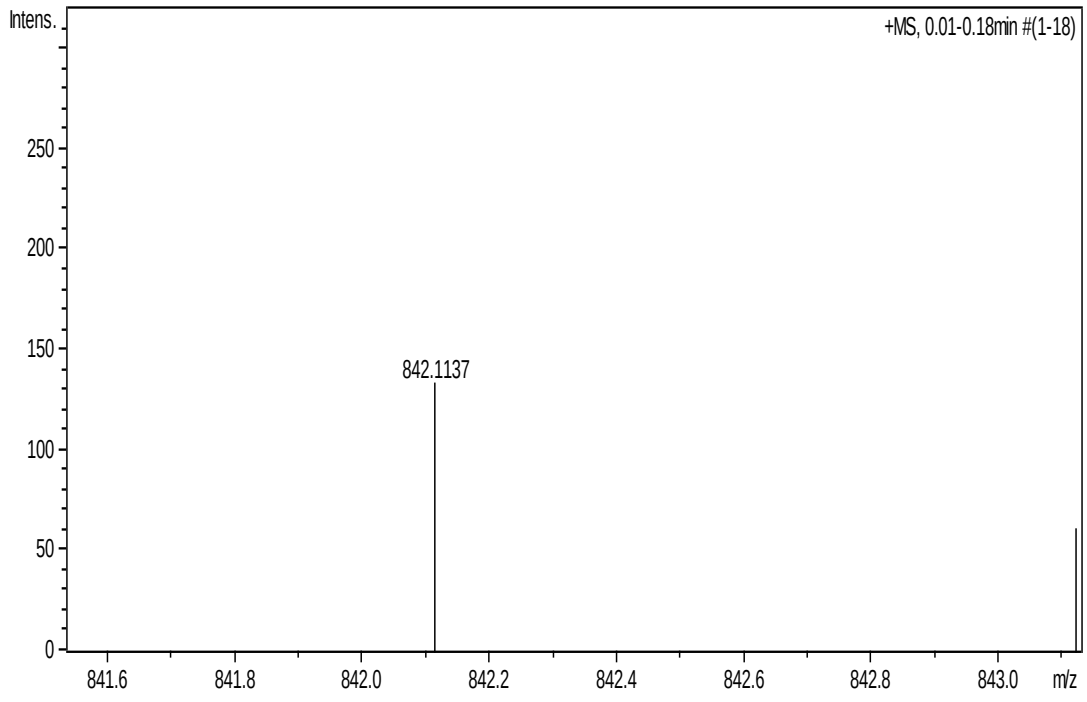
149.045
145.873
142.157
134.603
134.548
132.946
132.881
132.130
131.091
129.756
129.719
129.522
129.301
129.234
129.127
128.835
128.497
128.383
127.926
125.541
119.098
93.724
84.834
62.815
62.055
47.607
39.667
36.855
28.638
28.483
27.945
27.872
150
100
50
0
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.01-0.18min #(1-18)
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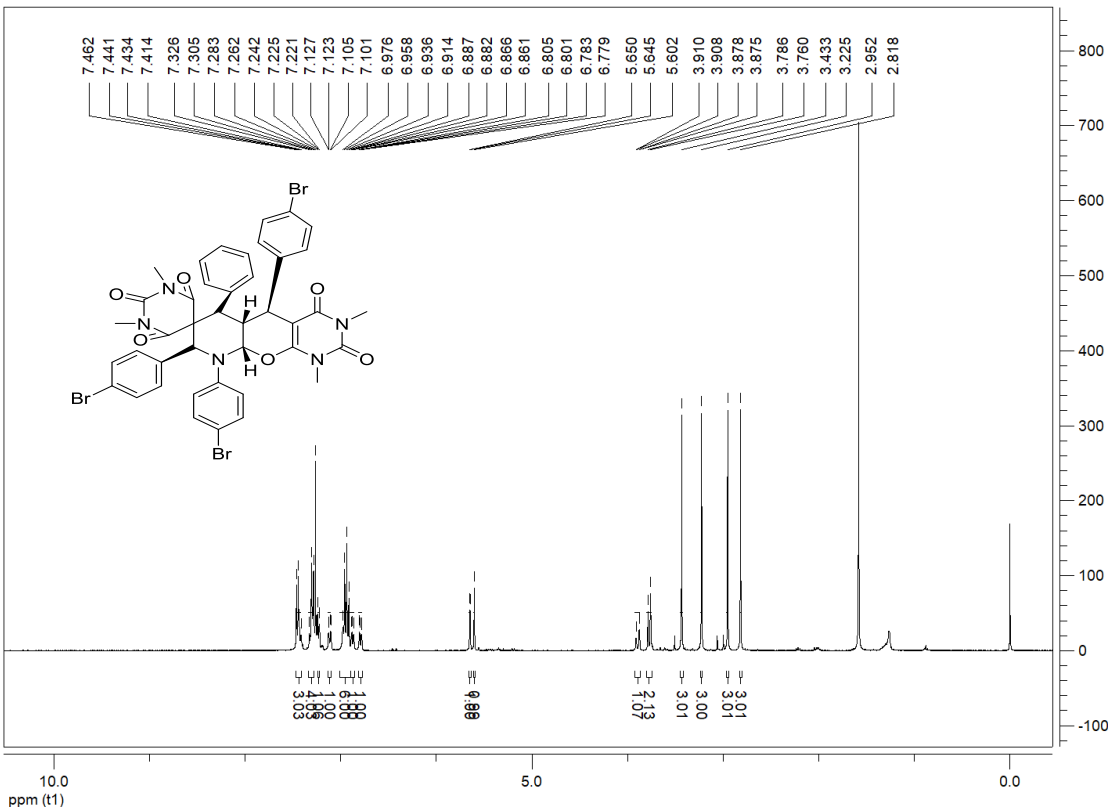
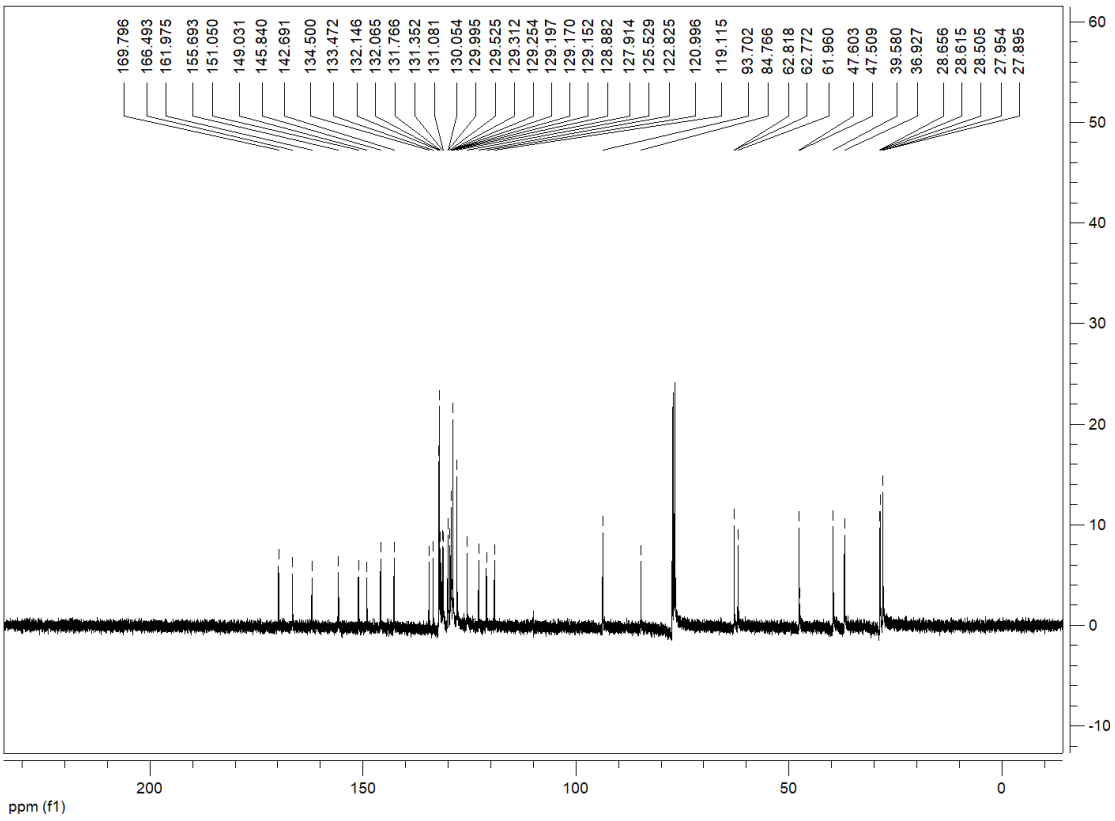
200
150
100
50
0
842.1137
841.6
841.8
842.0
842.2
842.4
842.6
842.8
843.0
m/z

***rel*-(5S,5aS,6S,8R,9aS)-5,8,9-tris(4-bromophenyl)-1,1',3,3'-tetramethyl-6-phenyl-1,5,5a,8,9,9a-hexahydro-2H,2'H,6H-spiro[pyrido[3',2':5,6]pyrano[2,3-d]pyrimidine-7,5'-pyrimidine]-2,2',4,4',6'-pentaone (5j)**:

white solid, 73%, m.p.159-161℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.41 (m, 3H, ArH), 7.33-7.28 (m, 4H, ArH), 7.24-7.22 (m, 1H, ArH), 7.13-7.10 (m, 1H, ArH), 6.98-6.91 (m, 6H, ArH), 6.89-6.86 (m, 1H, ArH), 6.80-6.78 (m, 1H, ArH), 5.67 (d, *J* = 2.0 Hz, 1H, CH), 5.60 (s, 1H, CH), 3.91-3.88 (m, 1H, CH), 3.79-3.76 (m, 2H, 2CH), 3.43 (s, 3H, NCH_3), 3.22 (s, 3H, NCH_3), 2.95 (s, 3H, NCH_3), 2.82 (s, 3H, NCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.7, 166.4, 161.9, 155.6, 151.0, 149.0, 145.8, 142.6, 134.4, 133.4, 132.1, 132.0, 131.7, 131.3, 131.0, 130.0, 129.9, 129.5, 129.3, 129.2, 129.1, 129.1, 129.1, 128.8, 127.9, 125.5, 122.8, 120.9, 119.1, 93.7, 84.7, 62.8, 62.7, 61.9, 47.6, 47.5, 39.5, 36.9, 28.6, 28.6, 28.5, 27.9, 27.8; IR(KBr) υ: 2961, 1690, 1646, 1483, 1380, 1274, 1169, 1065, 1011, 909, 824, 768, 709, 663 cm^{-1} ; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{35}Br_3N_5O_6$([M+H]$^+$): 932.0117, found: 932.0123.

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145.840
142.691
134.500
133.472
132.146
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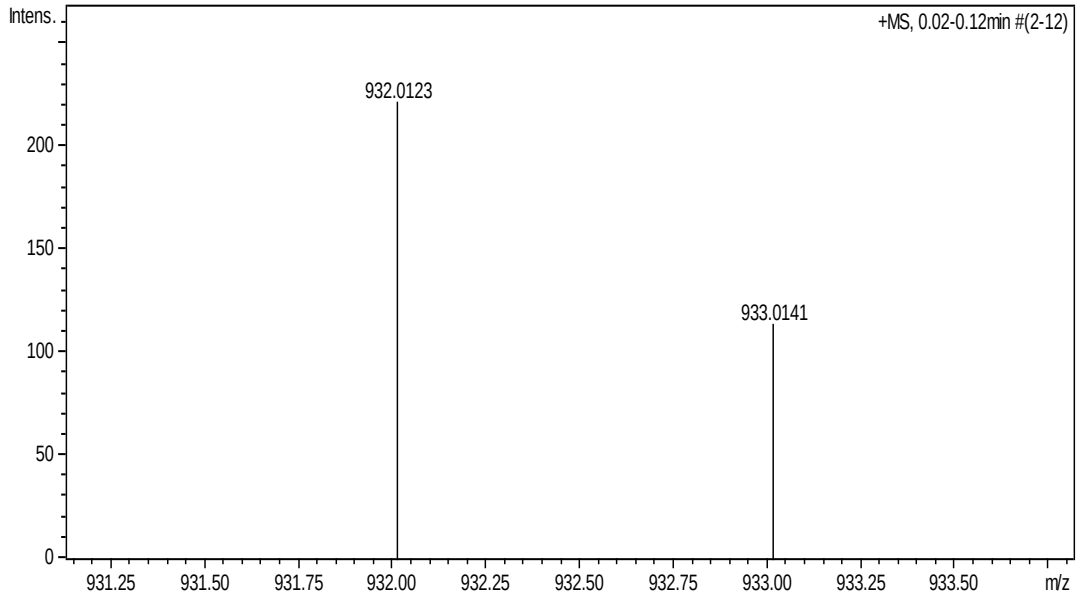
131.352
131.081
130.054
129.995
129.525
129.312
129.254
129.197
129.170
129.152
128.882
127.914
125.529
122.825
120.996
119.115
93.702
84.766
62.818
62.772
61.960
47.603
47.509
39.580
36.927
28.656
28.615
28.505
27.954
27.895
60
50
40
30
20
10
0
-10
200
150
100
50
0
ppm (f1)


Intens.
+MS, 0.02-0.12min #(2-12)
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100
50
0
931.25
931.50
931.75
932.00
932.25
932.50
932.75
933.00
933.25
933.50
m/z