Efficient Construction of Spirocyclopentane-1,3-dioxindoles via annulation reaction of isocyanides and 3-methyleneoxindoles

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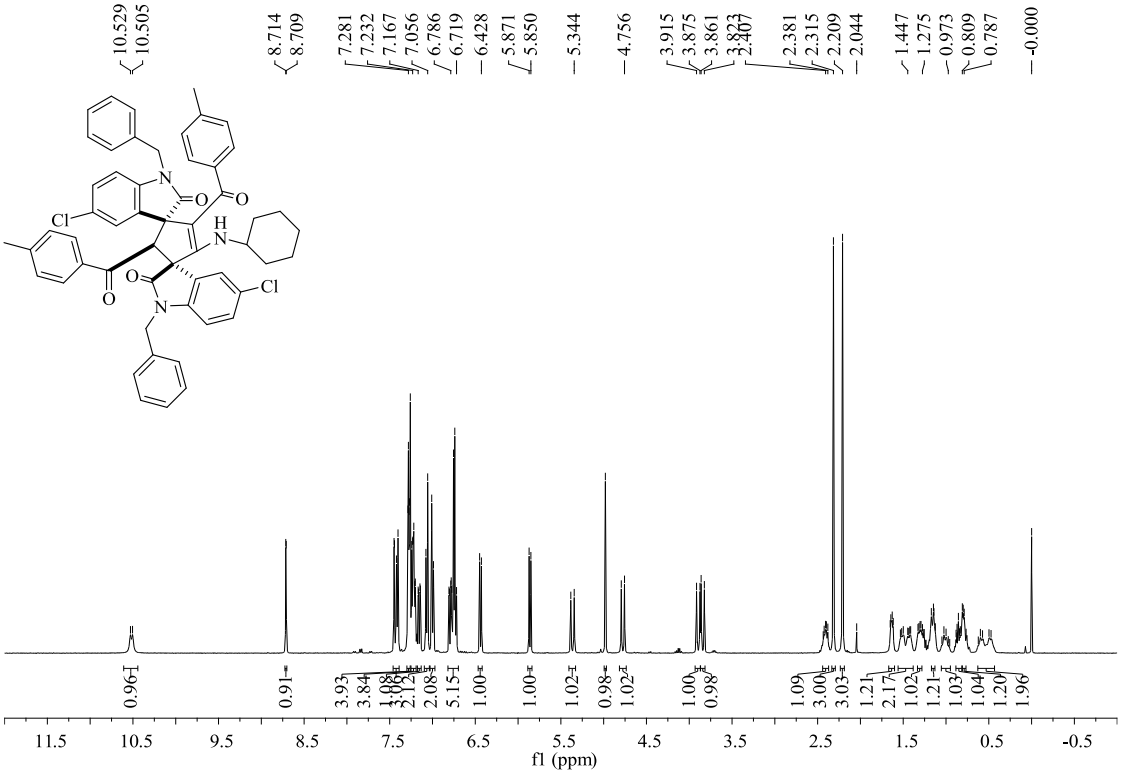
Supporting Information

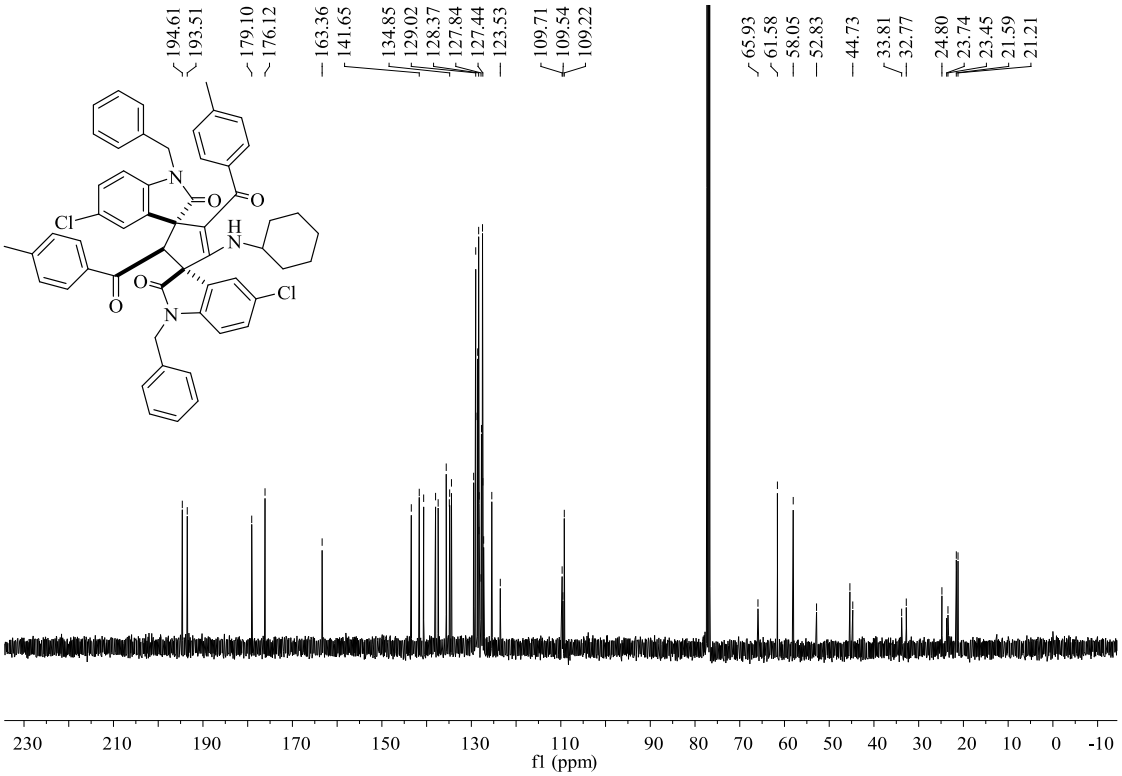
Experimental section

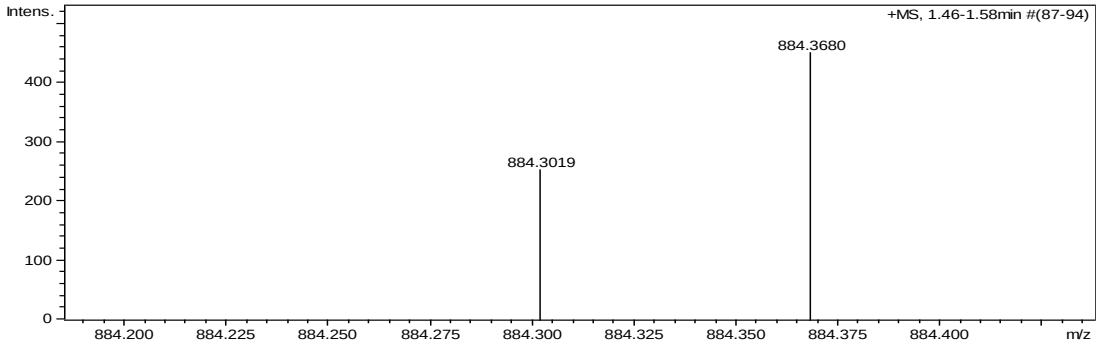
1. General procedure for the reactions of alkyl isocyanides and 3-methyleneoxindoles: A mixture of alkyl isocyanide (0.5 mmol), 3-methyleneoxindole (1.0 mmol), and DABCO (0.5 mmol) in acetonitrile (10 mL) was stirred at 80 ^{o}C for 12 hours. After removing the solvent at reduce pressure by rotatory evaporation, the resulting residue was purified by column chromatography on silica gel with ethyl acetate and petroleum ether (V/V = 1:8) as eluent to afford the desired products **3a-3p** and **3a'-3p'**.

2. General procedure for the reaction of (2-isocyanoethyl)indole and 3-methyleneoxindoles: A mixture of (2-isocyanoethyl)indole (0.2 mmol), 3-methyleneoxindole (0.2 mmol), and DABCO (0.2 mmol) in toluene (10.0 mL) was heated at 110 ^{o}C for 12 hours. After removing the solvent at reduce pressure by rotatory evaporation, the resulting residue was purified by column chromatography on silica gel with ethyl acetate and petroleum ether (V/V = 1:1) as eluent to afford the desired products **5a-5n**.

***rel*-(2'*S*,3*R*,3'*R*)-1,1''-dibenzyl-5,5''-dichloro-4'-(cyclohexylamino)-2',5'-bis(4-methylbenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3a):** white solid, 52%, m.p. 190-192 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.52 (d, *J* = 9.6 Hz, 1H, NH), 8.71 (d, *J* = 2.0 Hz, 1H, ArH), 7.45-7.40 (m, 3H, ArH), 7.29-7.27 (m, 4H, ArH), 7.24-7.20 (m, 4H, ArH), 7.15 (dd, *J*=2.0 Hz, *J*=8.0 Hz 1H, ArH) 7.07 (d, *J* = 8.4 Hz, 2H, ArH), 7.00 (d, *J*=8.4 Hz 2H, ArH), 6.81-6.72 (m, 5H, ArH), 6.44 (d, *J* = 8.4 Hz, 1H, ArH), 5.86 (d, *J* = 8.4 Hz, 1H, ArH), 5.36 (d, *J* = 16.0 Hz, 1H, CH_2), 4.98 (s, 1H, CH), 4.78 (d, *J* = 15.2 Hz, 1H, CH_2), 3.89 (d, *J* = 24.0 Hz, 1H, CH_2), 3.84 (d, *J* = 23.2 Hz, 1H, CH_2), 2.44-2.38 (m, 1H, CH), 2.32 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 1.65-1.62 (m, 1H, CH), 1.53-1.41 (m, 2H, CH_2), 1.33-1.28 (m, 1H, CH_2), 1.17-1.13 (m, 1H, CH_2), 1.05-0.96 (m, 1H, CH_2), 0.87-0.83 (m, 1H, CH_2), 0.79-0.77 (m, 1H, CH_2), 0.62-0.47 (m, 2H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 194.6, 193.5, 179.1, 176.1, 163.4, 143.4, 141.7, 140.7, 138.0, 137.4, 135.6, 134.9, 134.9, 134.4, 129.5, 129.0, 128.7, 128.6, 128.4, 128.3, 128.3, 127.8, 127.7, 127.5, 127.4, 127.3, 125.4, 123.5, 109.7, 109.5, 109.2, 65.9, 61.6, 58.1, 52.8, 45.4, 44.7, 33.8, 32.8, 24.8, 23.7, 23.5, 21.6, 21.2 ppm; IR (KBr) υ: 3061, 2933, 2854, 1718, 1682, 1611, 1568, 1479, 1454, 1427 ,1376, 1329, 1319, 1301, 1264, 1230, 1182, 1171, 1110, 1080, 1016, 973, 911, 844, 818, 808, 789, 750, 732, 721 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{55}H_{48}Cl_2N_3O_4$ ($[M+H]^+$): 884.3016, found: 884.3019.




194.61
193.51
179.10
176.12
163.36
141.65
134.85
129.02
128.37
127.84
127.44
123.53
109.71
109.54
109.22
65.93
61.58
58.05
52.83
44.73
33.81
32.77
24.80
23.74
23.45
21.59
21.21
Cl
Cl
O
O
O
O
N
N
H
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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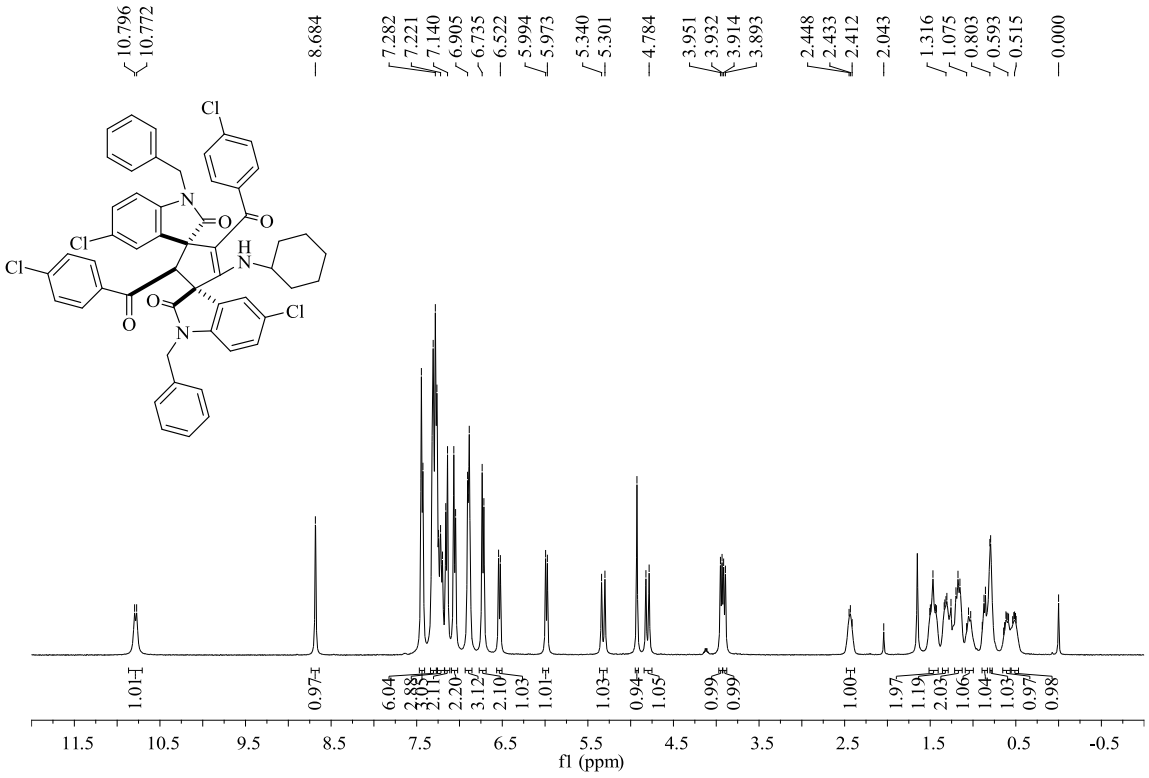
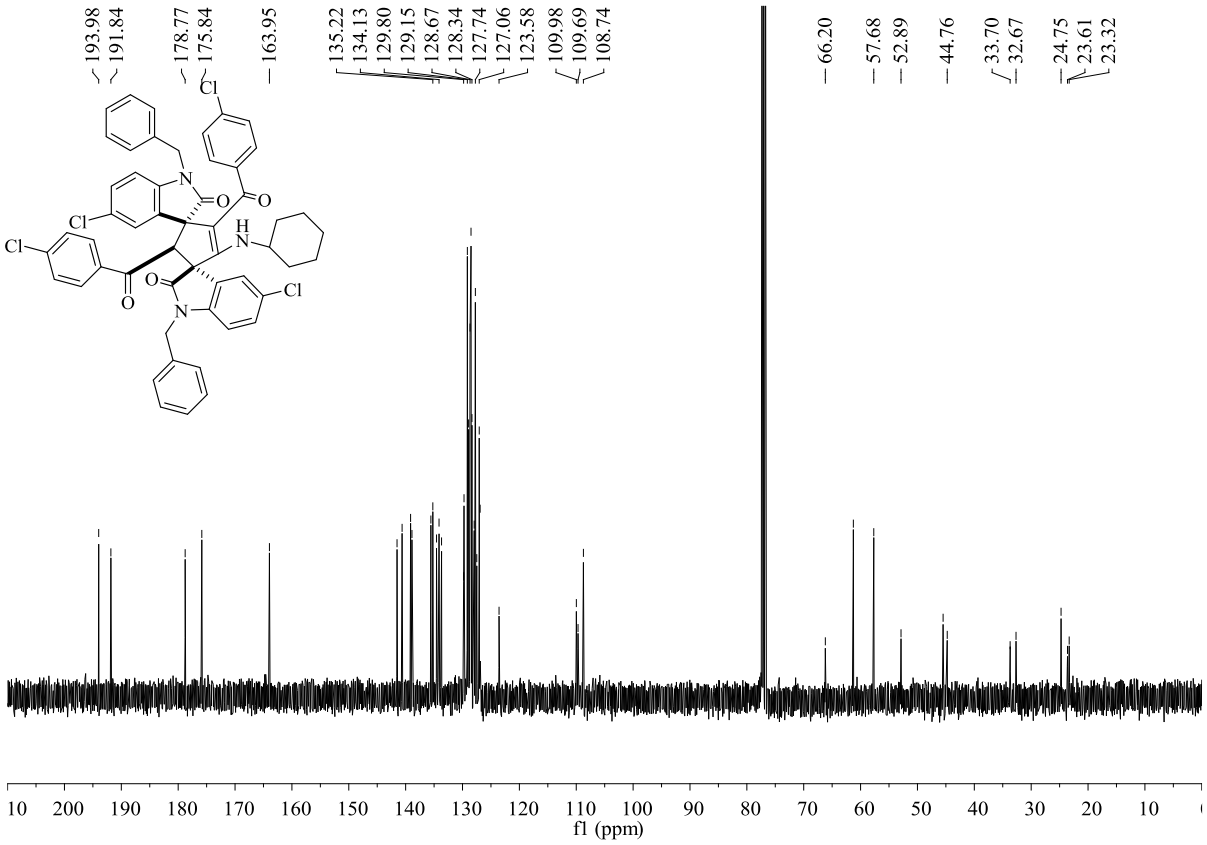
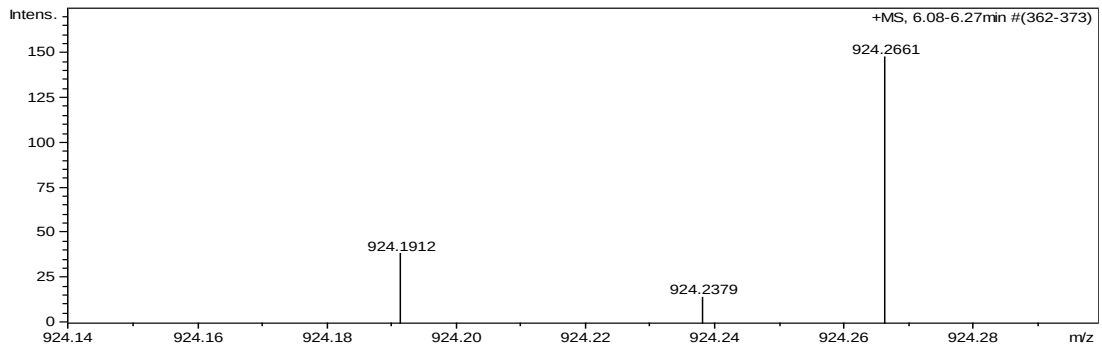
+MS, 1.46-1.58min #(87-94)
884.3680
884.3019
400
300
200
100
0
884.200
884.225
884.250
884.275
884.300
884.325
884.350
884.375
884.400
m/z

***rel*-(2'*S*,3*R*,3'*R*)-1,1''-dibenzyl-5,5''-dichloro-2',4'-bis(4-chlorobenzoyl)-5'-(cyclohexylamino)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3b):** white solid, 37%, m.p. 256-258 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.78 (d, *J* = 9.6 Hz, 1H, NH), 8.68 (s, 1H, ArH), 7.44 (d, *J* = 7.2 Hz, 3H, ArH), 7.31-7.28 (m, 6H, ArH), 7.25-7.20 (m, 3H, ArH), 7.15 (d, *J*=8.0 Hz 2H, ArH) 7.06 (d, *J* = 8.0 Hz, 2H, ArH), 6.91-6.89 (m, 3H, ArH), 6.73 (d, *J*=8.0 Hz, 2H, ArH), 6.53 (d, *J*=8.4 Hz, 1H, ArH), 5.98 (d, *J* = 8.4 Hz, 1H, ArH), 5.32 (d, *J* = 15.6 Hz, 1H, CH_2), 4.93 (s, 1H, CH), 4.80 (d, *J* = 15.2 Hz, 1H, CH_2), 3.94 (d, *J* = 7.6 Hz, 1H, CH_2), 3.90 (d, *J* = 8.4 Hz, 1H, CH_2), 2.45-2.41 (m, 1H, CH), 1.51-1.43 (m, 2H, CH_2), 1.34-1.31 (m, 1H, CH_2), 1.20-1.15 (m, 2H, CH_2), 1.08-1.03 (m, 1H, CH_2), 0.89-0.86(m, 1H, CH_2), 0.80-0.79 (m, 1H, CH_2), 0.64-0.59 (m, 1H, CH_2), 0.54-0.50 (m, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 194.0, 191.8, 178.8, 175.8, 164.0, 141.5, 140.6, 139.1, 138.9, 135.6, 135.2, 134.6, 134.1, 133.7, 129.8, 129.7, 129.2, 128.9, 128.7, 128.5, 128.3, 128.0, 127.7, 127.5, 127.1, 126.9, 123.6, 110.0, 109.7, 108.7, 66.2, 61.3, 57.7, 52.9, 45.5, 44.8, 33.7, 32.7, 24.8, 23.6, 23.3 ppm; IR (KBr) υ: 3061, 2933, 2854, 1720, 1684, 1612, 1566, 1484, 1455, 1428, 1398, 1376, 1328, 1318, 1302, 1227, 1172, 1112, 1085, 1037, 1014, 983, 892, 848, 831, 808, 780, 752, 738, 721 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{42}Cl_4N_3O_4$ ([M+H]$^{+}$): 924.1924, found: 924.1912.




193.98
191.84
178.77
175.84
163.95
135.22
134.13
129.80
129.15
128.67
128.34
127.74
127.06
123.58
109.98
109.69
108.74
66.20
57.68
52.89
44.76
33.70
32.67
24.75
23.61
23.32
Cl
Cl
Cl
Cl
N
O
O
H
N
O
O
N
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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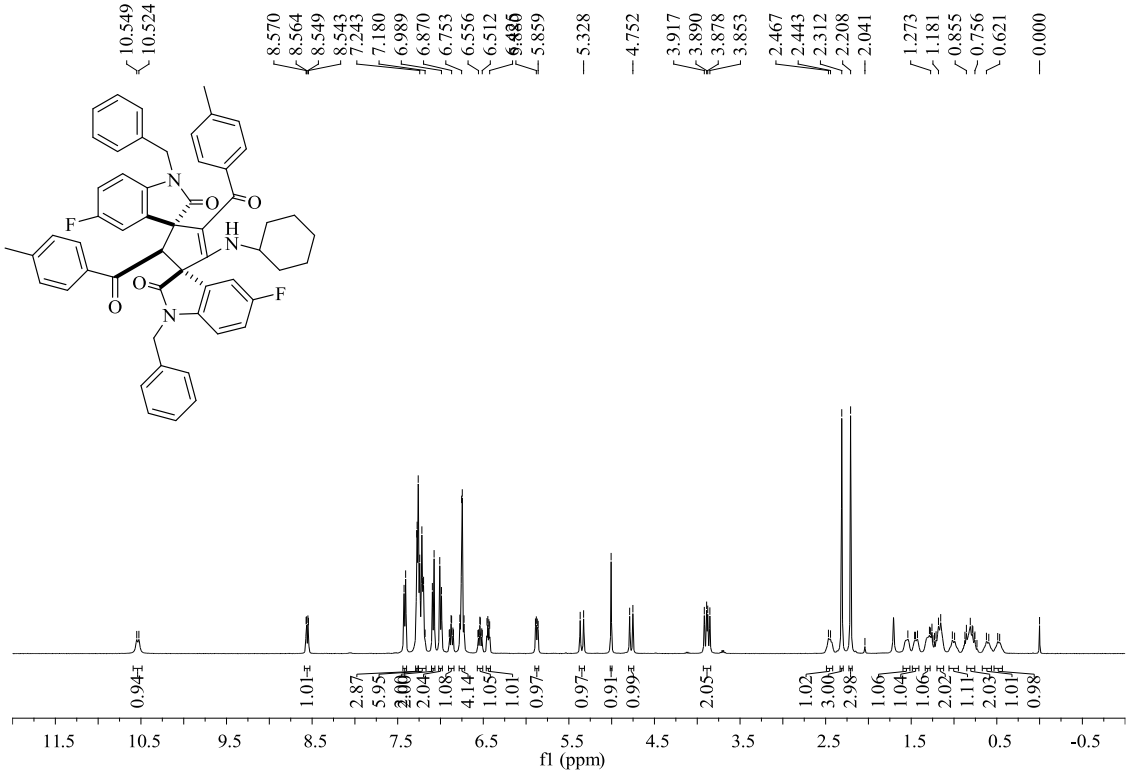
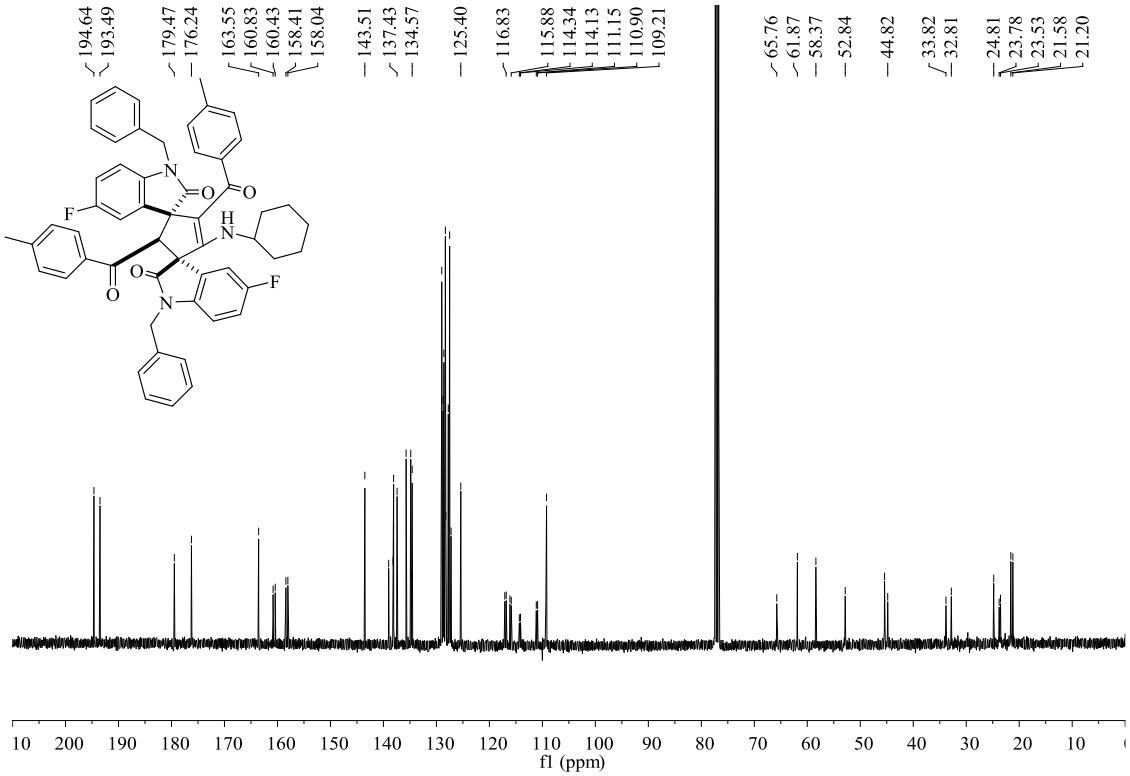
924.2661
924.1912
924.2379
150
125
100
75
50
25
0
924.14
924.16
924.18
924.20
924.22
924.24
924.26
924.28
m/z

***rel*-(2'*S*,3*R*,3'*R*)-1,1''-dibenzyl-4'-(cyclohexylamino)-5,5''-difluoro-2',5'-bis(4-methylbenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3c):** white solid, 31%, m.p. 218-220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.54 (d, *J* = 10.0 Hz, 1H, NH), 8.56 (dd, *J*=8.4 Hz, *J*=2.4 Hz, 1H, ArH), 7.42 (d, *J*=7.6 Hz 2H, ArH), 7.28 (d, *J* = 1.6 Hz, 3H, ArH), 7.24-7.18 (m, 6H, ArH), 7.08 (d, *J* = 8.0 Hz, 2H, ArH), 7.00 (d, *J*=8.0 Hz 2H, ArH), 6.90-6.85 (m, 1H, ArH), 6.77-6.73 (m, 4H, ArH), 6.56-6.51 (m, 1H, ArH), 6.46-6.43 (m, 1H, ArH), 5.89-5.86 (m, 1H, ArH), 5.35 (d, *J* = 16.0 Hz, 1H, CH_2), 5.01 (s, 1H, CH), 4.77 (d, *J* = 15.2 Hz, 1H, CH_2), 3.90 (d, *J* = 10.8 Hz, 1H, CH_2), 3.87 (d, *J* = 10.0 Hz, 1H, CH_2), 2.45 (d, *J* = 9.6 Hz, 1H, CH), 2.31 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 1.56-1.54 (m, 1H, CH), 1.46-1.43 (m, 1H, CH_2), 1.32-1.27 (m, 1H, CH_2), 1.18-1.16 (m, 2H, CH_2), 1.04-0.99 (m, 1H, CH_2), 0.86-0.76 (m, 2H, CH_2), 0.65-0.56 (m, 1H, CH_2), 0.52-0.43 (m, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 194.6, 193.5, 179.5, 176.2, 163.6, 160.8, 160.4, 158.4, 158.0, 143.5, 139.0, 138.2, 138.1, 138.1, 137.4, 135.7, 134.8, 134.8, 134.6, 129.0, 128.8, 128.6, 128.3, 128.2, 127.8, 127.5, 127.2, 125.4, 117.1, 116.8, 116.1, 115.9, 114.3, 114.1, 111.2, 110.9, 109.2, 65.8, 61.9, 58.4, 52.8, 45.4, 44.8, 33.8, 32.8, 24.8, 23.8, 23.5, 21.6, 21.2 ppm; IR (KBr) υ: 3064, 2933, 2854, 1717, 1678, 1604, 1545, 1488, 1449, 1330, 1296, 1262, 1242, 1206, 1178, 1151, 1121, 1078, 1037, 1017, 980, 911, 886, 834, 809, 750, 737 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{55}H_{47}F_2N_3NaO_4$ ([M+Na]$^+$): 874.3427, found: 874.3420.




194.64
193.49
179.47
176.24
163.55
160.83
160.43
158.41
158.04
143.51
137.43
134.57
125.40
116.83
115.88
114.34
114.13
111.15
110.90
109.21
65.76
61.87
58.37
52.84
44.82
33.82
32.81
24.81
23.78
23.53
21.58
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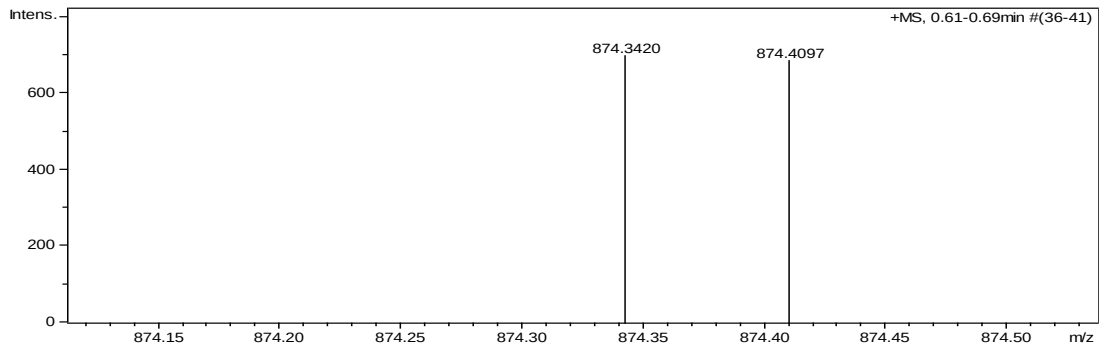
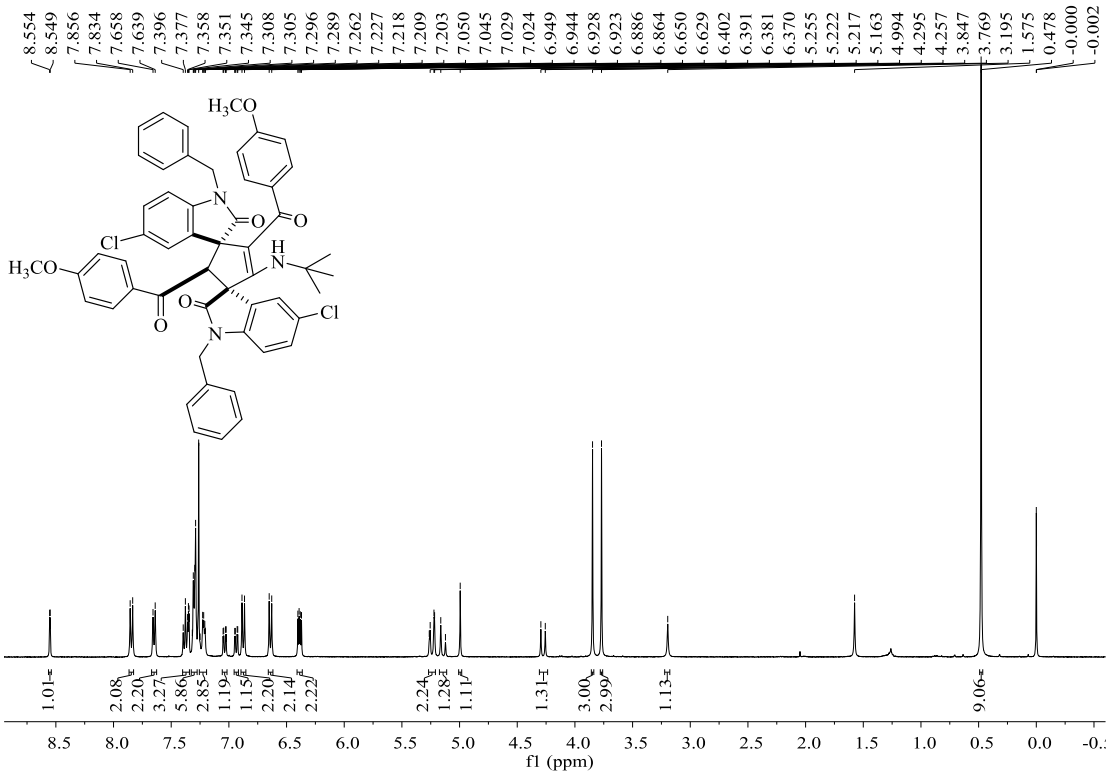
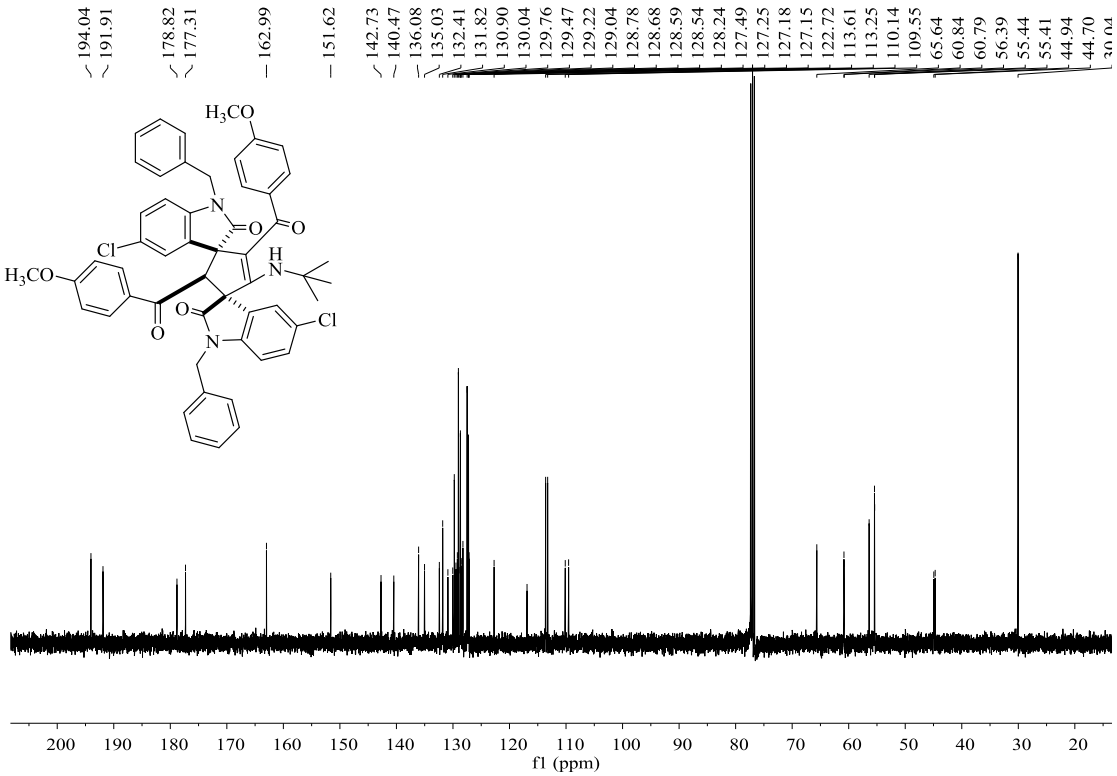
O
N
F
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 0.61-0.69min #(36-41)
874.3420
874.4097
600
400
200
0
874.15
874.20
874.25
874.30
874.35
874.40
874.45
874.50
m/z

***rel*-(2'*S*,3*R*,3'*R*)-1,1''-dibenzyl-4'-(*tert*-butylamino)-5,5''-dichloro-2',5'-bis(4-methoxybenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3d):** white solid, 37%, m.p. 277-279 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55-8.54 (m, 1H, NH), 7.84 (d, *J* = 8.8 Hz, 2H, ArH), 7.65 (d, *J* = 7.6 Hz, 2H, ArH), 7.40-7.35 (m, 3H, ArH), 7.32-7.29 (m, 6H, ArH), 7.25-7.20 (m, 3H, ArH), 7.05-7.02 (m, 1H, ArH), 6.95-6.92 (m, 1H, ArH), 6.88 (d, *J* = 8.8 Hz, 1H, ArH), 6.64 (d, *J* = 8.4 Hz, 2H, ArH), 6.40-6.37 (m, 2H, ArH), 5.26-5.25 (m, 2H, CH_2), 5.14 (d, *J* =16.4 Hz, 1H, CH_2), 4.99 (s, 1H, CH), 4.28 (d, *J* =15.2 Hz, 1H, CH_2), 3.85 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 0.48 (s, 9H, CH_3) ppm;^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 194.0, 191.9, 178.8, 177.3, 163.0, 151.6, 142.7, 140.5, 136.1, 135.0, 132.4, 131.8, 130.9, 130.0, 129.8, 129.5, 129.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.2, 127.5, 127.3, 127.2, 127.1, 122.7, 116.9, 113.6, 113.3, 110.1, 109.6, 65.6, 60.8, 60.7, 56.4, 55.4, 55.3, 44.9, 44.7, 30.0 ppm; IR (KBr) υ: 3363, 3062, 3034, 2994, 2952, 2867, 2360, 1712, 1691, 1619, 1568, 1522, 1487, 1450, 1409, 1360, 1333, 1277, 1258, 1222, 1174, 1125, 1083, 1030, 986, 921, 899, 854, 829, 805, 766, 737, 701, 653, 611 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{45}Cl_2N_3NaO_6$ ([M+Na]$^{+}$): 912.2583, found: 912.2602.




194.04
191.91
178.82
177.31
162.99
151.62
142.73
140.47
136.08
135.03
132.41
131.82
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130.04
129.76
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60.79
56.39
55.44
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Cl
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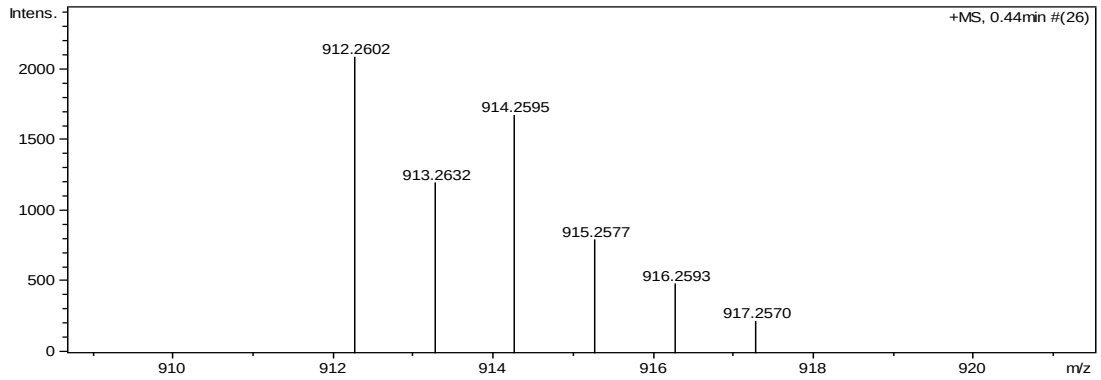
f1 (ppm)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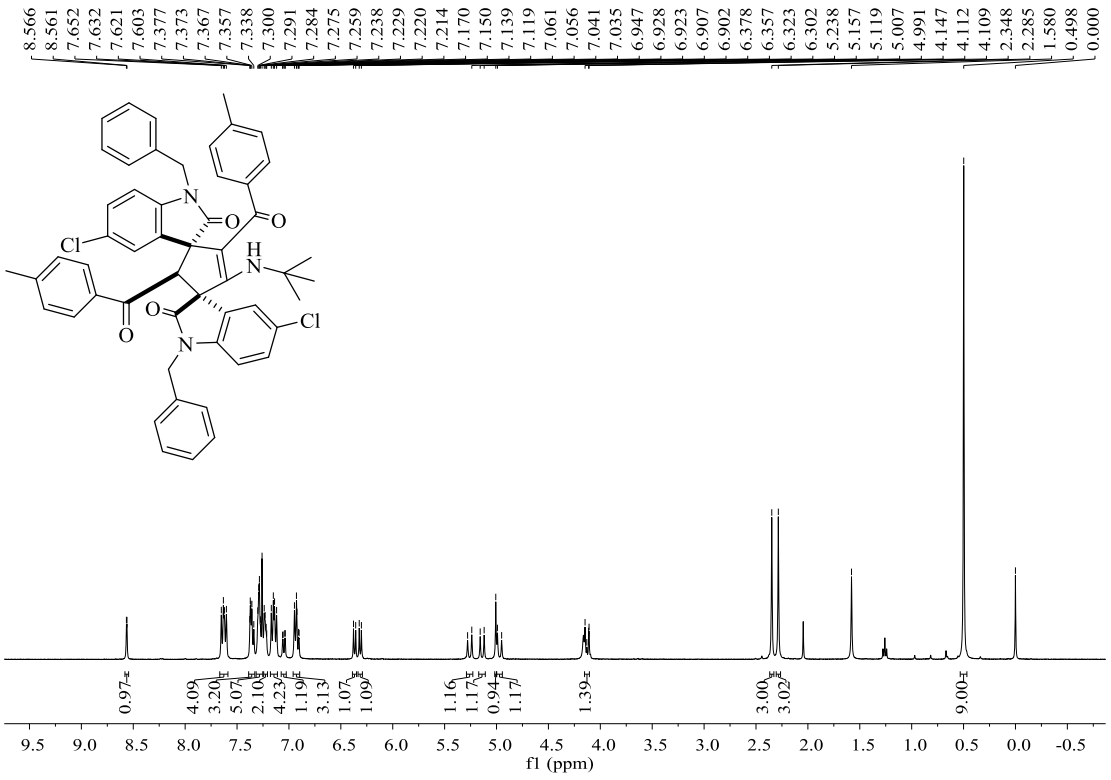
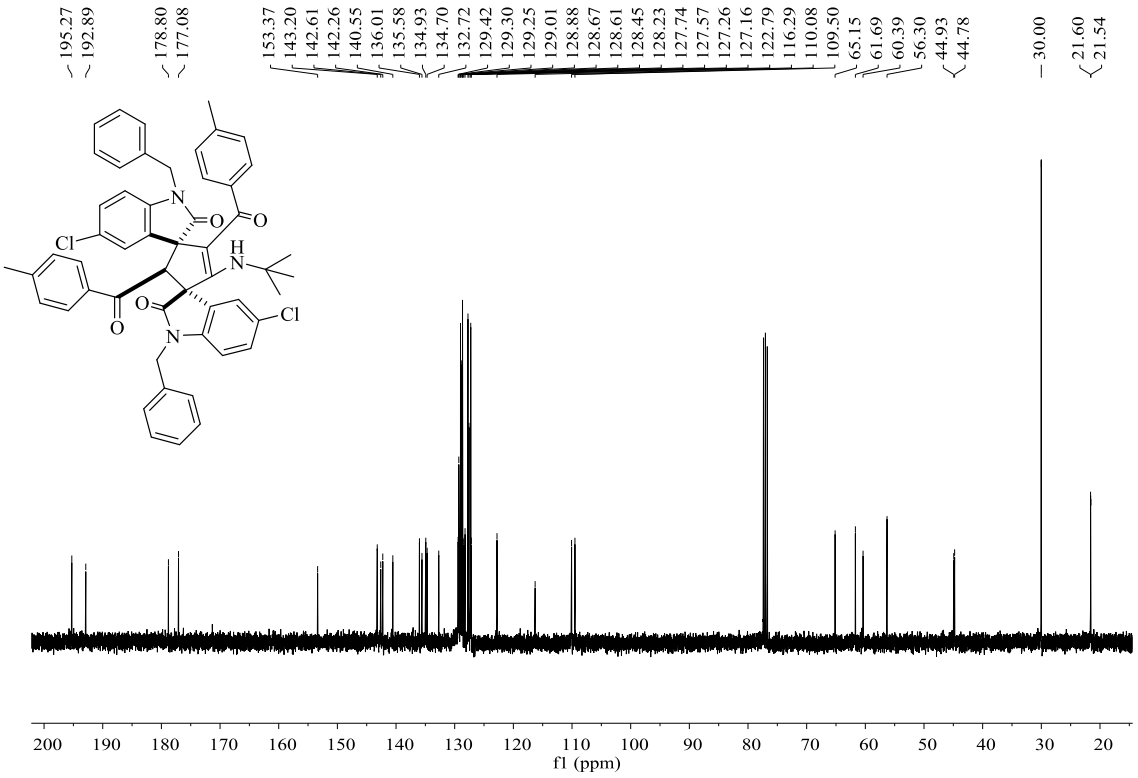
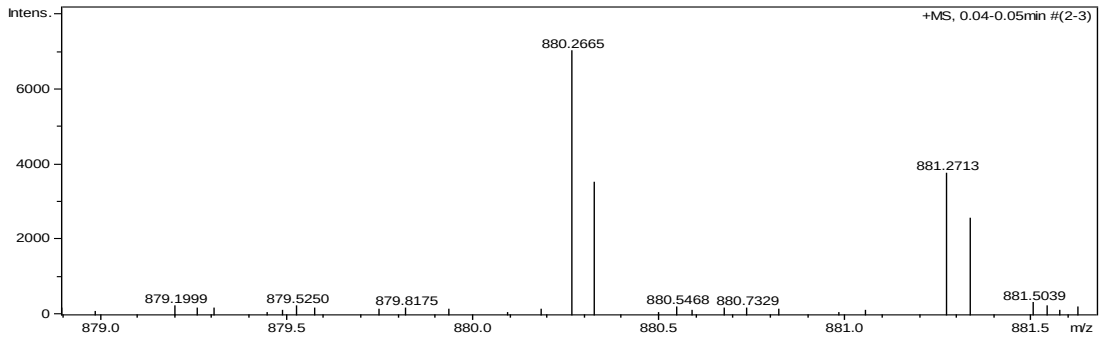
+MS, 0.44min #(26)
912.2602
914.2595
913.2632
915.2577
916.2593
917.2570
2000
1500
1000
500
0
910
912
914
916
918
920
m/z

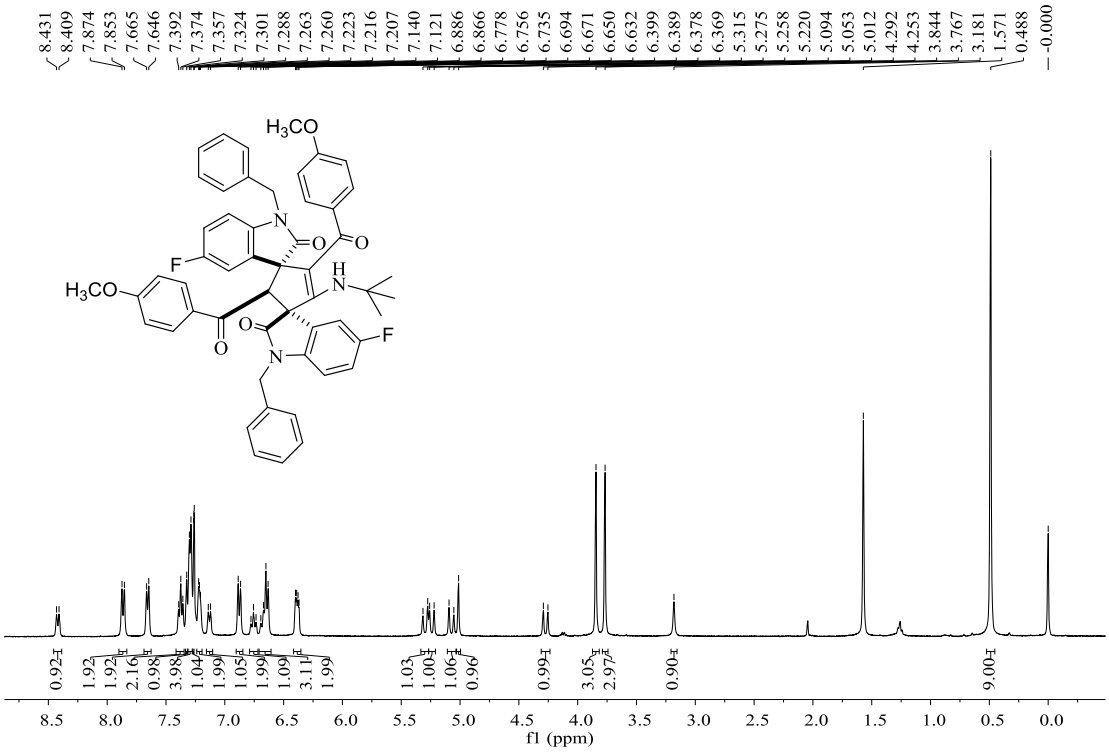
***rel*-(2'*S*,3*R*,3'*R*)-1,1''-dibenzyl-4'-(*tert*-butylamino)-5,5''-dichloro-2',5'-bis(4-methylbenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3e):** white solid, 48%, m.p. 275-277 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57-8.56 (m, 1H, NH), 7.65-7.60 (m, 4H, ArH), 7.38-7.34 (m, 3H, ArH), 7.30-7.26 (m, 5H, ArH), 7.24-7.21 (m, 2H, ArH), 7.17-7.12 (m, 4H, ArH), 7.07-7.04 (m, 1H, ArH), 6.95-6.90 (m, 3H, ArH), 6.37 (d, *J* = 8.4 Hz, 1H, ArH), 6.31 (d, *J* = 8.4 Hz, 1H, ArH), 5.26 (d, *J* = 16.4 Hz, 1H, CH_2), 5.16-5.12 (d, *J* =15.2 Hz, 1H, CH_2), 5.01 (s, 1H, CH), 4.97 (d, *J* =16.0 Hz, 1H, CH_2), 4.15-4.11 (m, 1H, CH_2), 2.35 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 0.50 (s, 9H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 195.3, 192.9, 178.8, 177.1, 153.4, 143.2, 142.6, 142.3, 140.6, 136.0, 135.6, 134.9, 134.7, 132.7, 129.4, 129.3, 129.2, 129.0, 128.9, 128.7, 128.6, 128.5, 128.2, 127.7, 127.6, 127.3, 127.2, 122.8, 116.3, 110.1, 109.5, 65.2, 61.7, 60.4, 56.3, 44.9, 44.8, 30.0, 21.6, 21.5 ppm; IR (KBr) υ: 3467, 3063, 3035, 2990, 2919, 2205, 1739, 1706, 1632, 1602, 1496, 1454, 1434, 1408, 1381, 1361, 1333, 1293, 1258, 1216, 1199, 1186, 1167, 1133, 1089, 1070, 1026, 997, 962, 932, 911, 895, 875, 836, 818, 776, 748, 726, 695, 650, 627 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{45}Cl_2N_3NaO_4$ ([M+Na]$^{+}$): 880.2679, found: 880.2665.

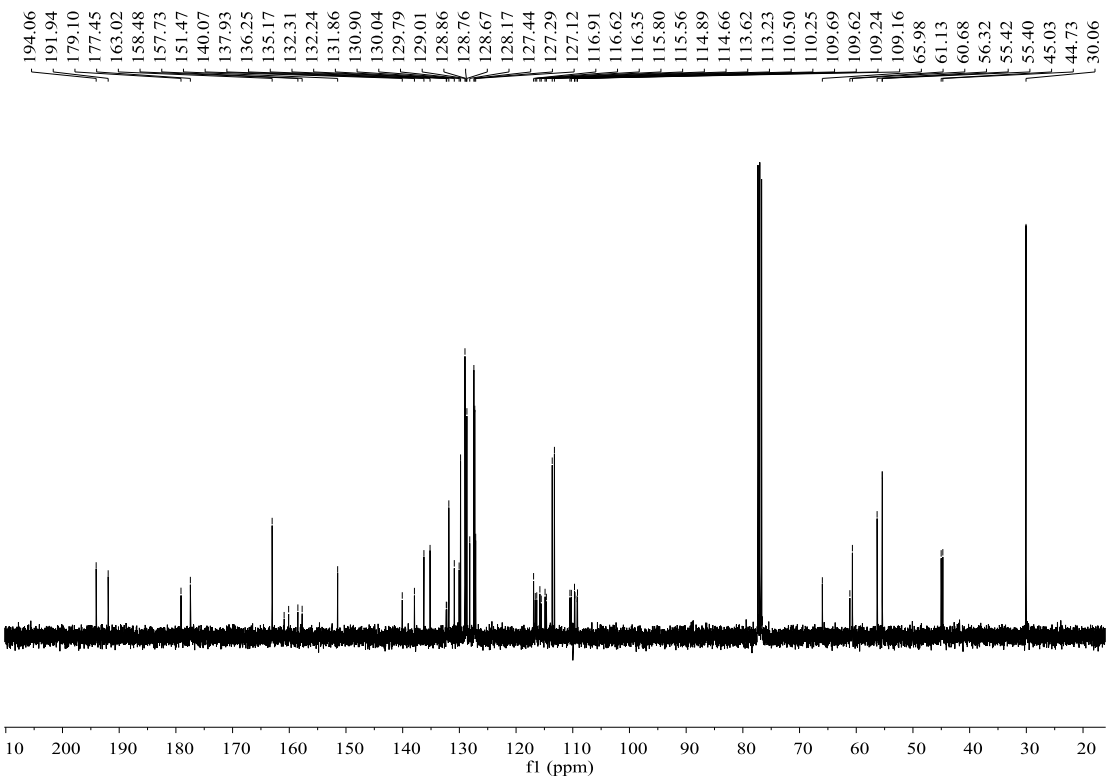


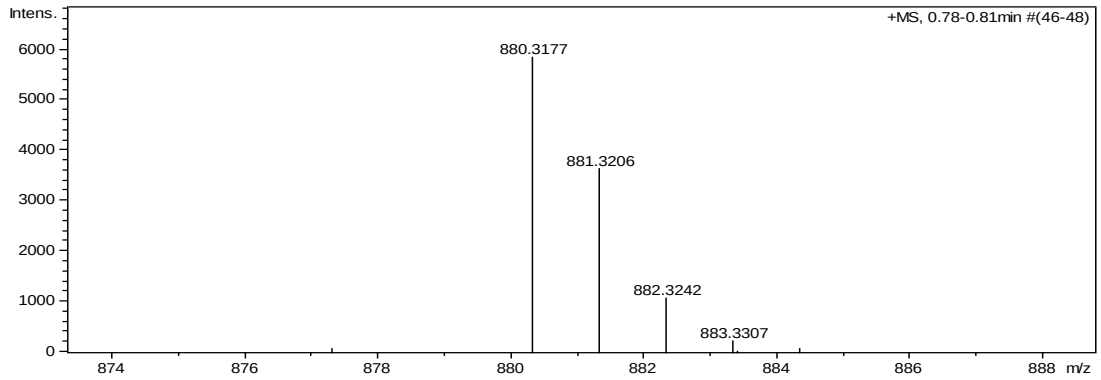

195.27
192.89
178.80
177.08
153.37
143.20
142.61
142.26
140.55
136.01
135.58
134.93
134.70
132.72
129.42
129.30
129.25
129.01
128.88
128.67
128.61
128.45
128.23
127.74
127.57
127.26
127.16
122.79
116.29
110.08
109.50
65.15
61.69
60.39
56.30
44.93
44.78
30.00
21.60
21.54
Cl
Cl
O
O
O
O
N
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
+MS, 0.04-0.05min #(2-3)
880.2665
881.2713
879.1999
879.5250
879.8175
880.5468
880.7329
881.5039
6000
4000
2000
0
879.0
879.5
880.0
880.5
881.0
881.5
m/z

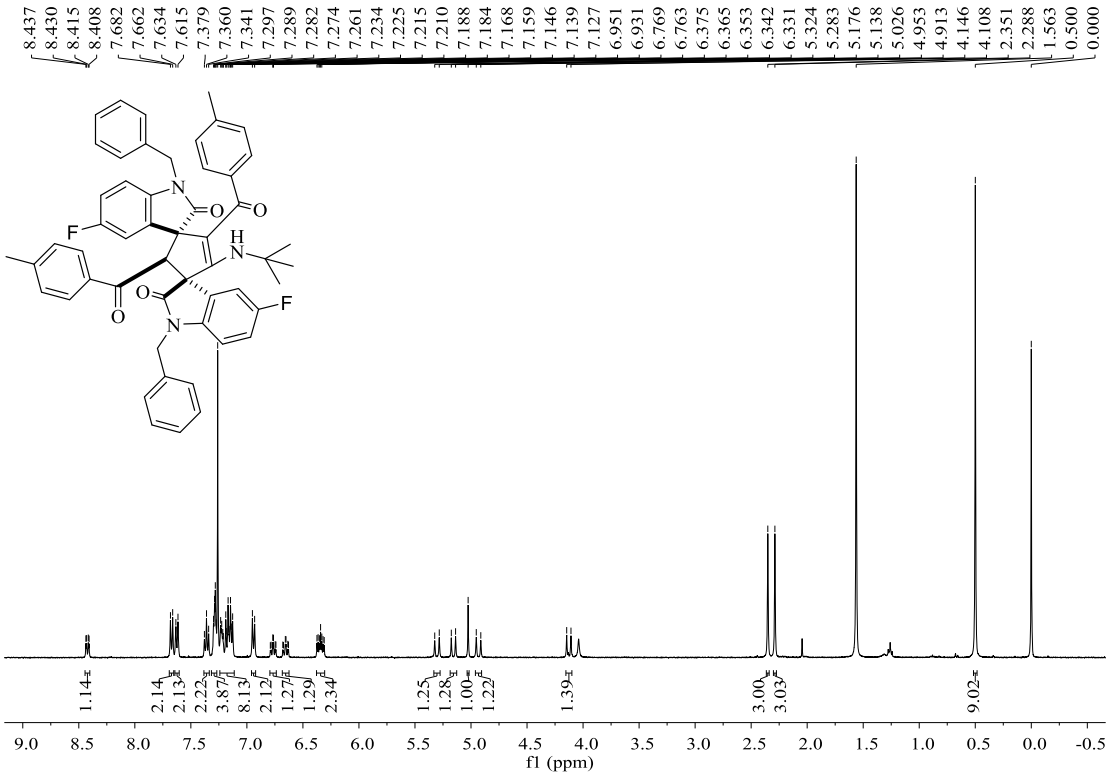
***rel*-(2'*S*,3*R*,3'*R*)-1,1''-dibenzyl-4'-(*tert*-butylamino)-5,5''-difluoro-2',5'-bis(4-methoxybenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3f):** white solid, 40%, m.p. 270-272 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.42 (d, *J* = 8.8 Hz, 1H, ArH), 7.86 (d, *J* = 8.4 Hz, 2H, ArH), 7.66 (d, *J* = 7.6 Hz, 2H, ArH), 7.37 (d, *J* = 7.0 Hz, 2H, ArH), 7.32 (s, 1H, ArH), 7.30-7.29 (m, 4H, ArH), 7.26 (s, 1H, ArH), 7.22-7.21 (m, 2H, ArH), 7.14-7.12 (m, 1H, ArH), 6.88 (d, *J* = 8.0 Hz, 2H, ArH), 6.76 (t, *J* = 8.6 Hz, 1H, ArH), 6.69-6.63 (m, 3H, ArH), 6.40-6.37 (m, 2H, ArH), 5.30 (d, *J* = 16.0 Hz, 1H, CH_2), 5.24 (d, *J* = 15.2 Hz, 1H, CH_2), 5.07 (d, *J* = 16.4 Hz, 1H, CH_2), 5.01 (s, 1H, CH), 4.27 (d, *J* = 15.6 Hz, 1H, CH_2), 3.84 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.18 (s, 1H, NH), 0.49 (s, 9H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 194.1, 191.9, 179.1, 177.5, 163.0, 160.5 (d, *J* = 79.8 Hz), 158.1 (d, *J* = 79.8 Hz), 151.5, 140.1, 137.9, 136.3, 135.2, 132.3 (d, *J* = 7.4 Hz), 131.9, 130.9, 130.0, 129.8, 129.0, 128.9, 128.8, 128.7, 128.2, 127.4, 127.3, 127.1, 116.9, 116.6, 116.4, 115.7 (d, *J* = 24.2 Hz), 114.9, 114.7, 113.6, 113.2, 110.4 (d, *J* = 24.7 Hz), 109.7 (d, *J* = 7.8 Hz), 109.2 (d, *J* = 8.1 Hz), 66.0, 61.1, 60.7, 56.3, 55.4, 55.3, 45.0, 44.7, 30.1 ppm; IR (KBr) υ: 3574, 3506, 3378, 3084, 3065, 3032, 2977, 2959, 2917, 2863, 1713, 1683, 1606, 1572, 1528, 1491, 1452, 1398, 1367, 1344, 1329, 1259, 1227, 1173, 1135, 1080, 1029, 976, 942, 897, 855, 814, 767, 738, 720, 662 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{45}F_2N_3NaO_6$ ([M+Na]$^+$): 880.3174, found: 880.3177.

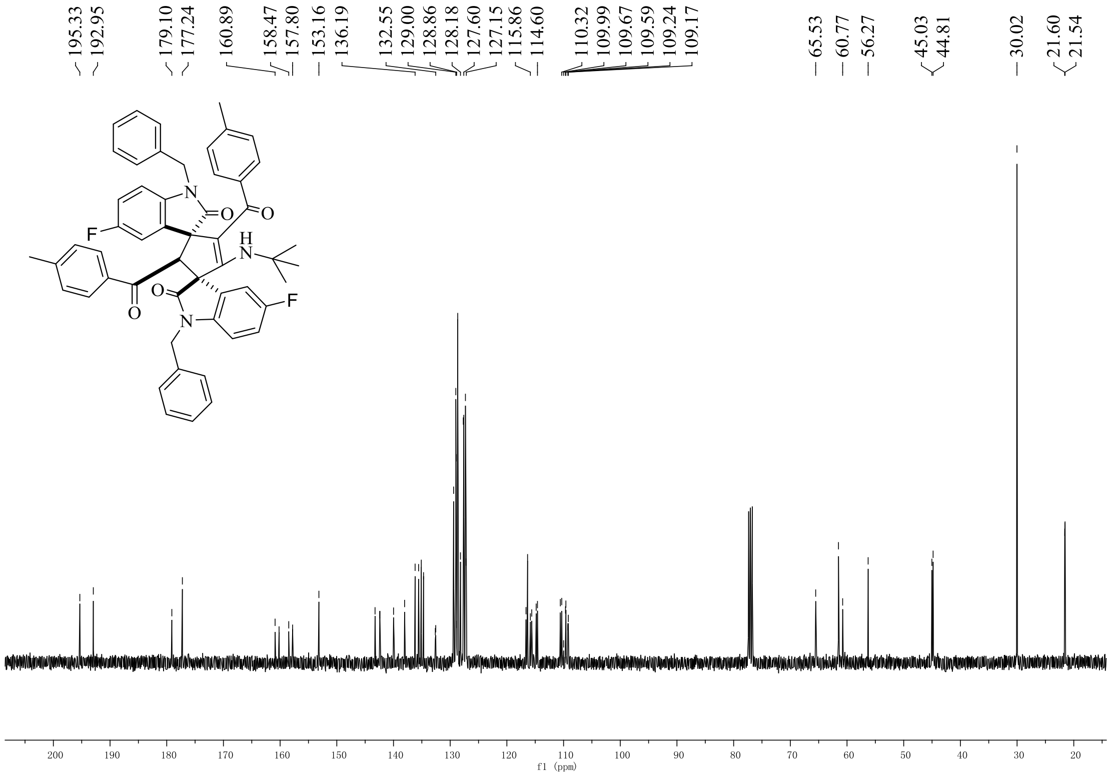


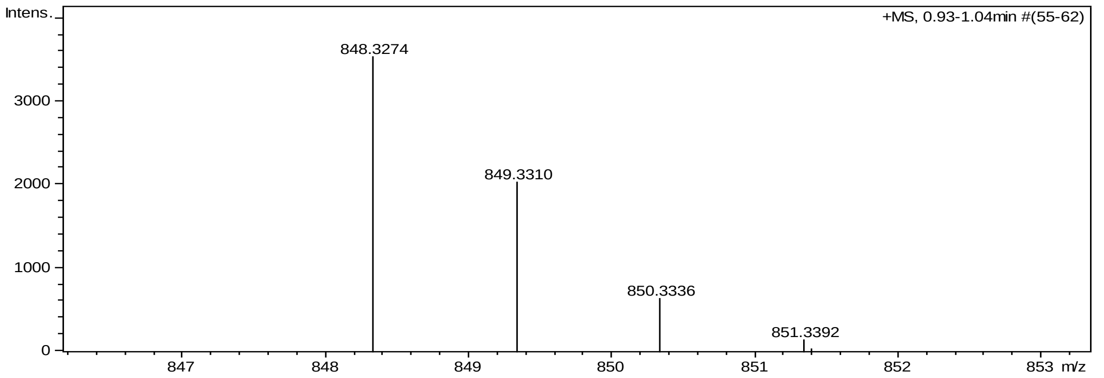

194.06
191.94
179.10
177.45
163.02
158.48
157.73
151.47
140.07
137.93
136.25
135.17
132.31
132.24
131.86
130.90
130.04
129.79
129.01
128.86
128.76
128.67
128.17
127.44
127.29
127.12
116.91
116.62
116.35
115.80
115.56
114.89
114.66
113.62
113.23
110.50
110.25
109.69
109.62
109.24
109.16
65.98
61.13
60.68
56.32
55.42
55.40
45.03
44.73
30.06
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
+MS, 0.78-0.81min #(46-48)
6000
5000
4000
3000
2000
1000
0
880.3177
881.3206
882.3242
883.3307
874 876 878 880 882 884 886 888 m/z

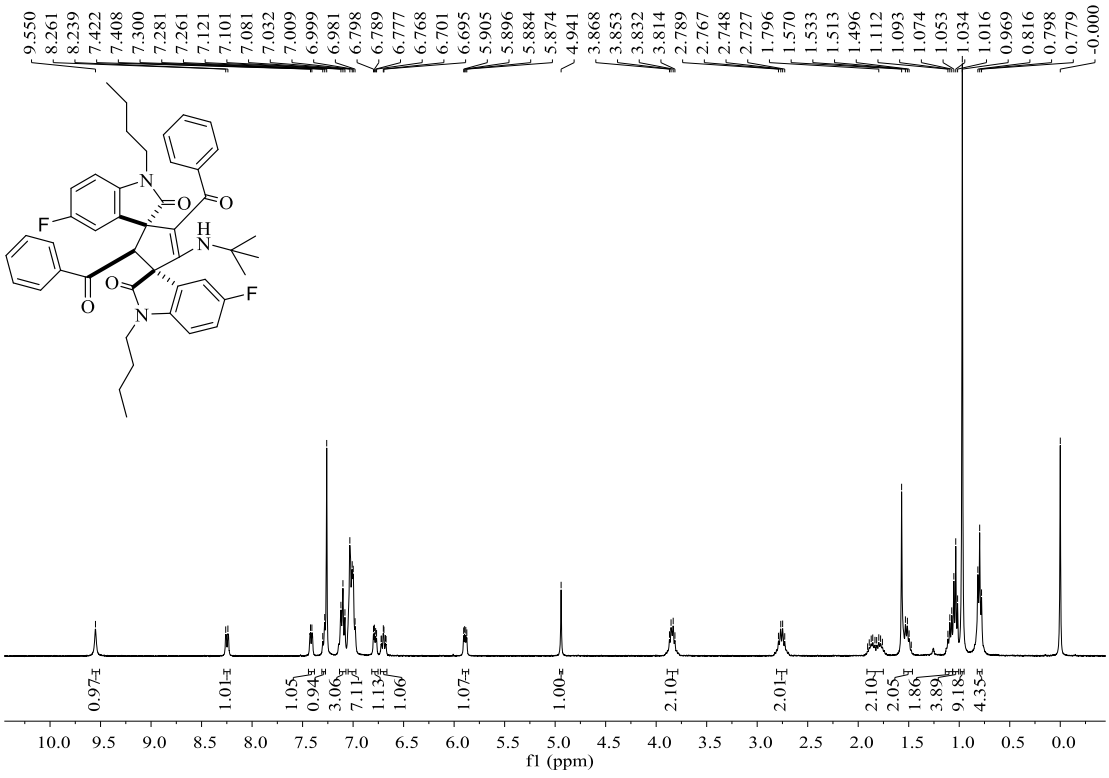
***rel*-(2'*S*,3*R*,3'*R*)-1,1''-dibenzyl-4'-(*tert*-butylamino)-5,5''-difluoro-2',5'-bis(4-methylbenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3g):** white solid, 44%, m.p. 241-243 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44-8.41 (m, 1H, NH), 7.67 (d, *J* = 8.0 Hz, 2H, ArH), 7.62 (d, *J* = 7.6 Hz, 2H, ArH), 7.36 (t, *J* = 7.6 Hz, 2H, ArH), 7.30-7.27 (m, 4H, ArH), 7.23-7.13 (m, 8H, ArH), 6.94 (d, *J* = 8.0 Hz, 2H, ArH), 6.79-6.74 (m, 1H, ArH), 6.68-6.63 (m, 1H, ArH), 6.38-6.31 (m, 2H, ArH), 5.30 (d, *J* = 16.4 Hz, 1H, CH_2), 5.16 (d, *J* = 15.2 Hz, 1H, CH_2), 5.03 (s, 1H, CH), 4.93 (d, *J* = 16.0 Hz, 1H, CH_2), 4.13 (d, *J* = 15.2 Hz, 1H, CH_2), 2.35 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 0.50 (s, 9H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 195.3, 193.0, 179.1, 177.2, 160.5 (d, *J* = 70.0 Hz), 158.1 (d, *J* = 67.6 Hz), 153.2, 143.3, 142.4, 140.0, 138.0, 136.2, 135.6, 135.1, 134.7, 132.6 (d, *J* = 7.4 Hz), 129.4, 129.0, 128.9, 128.8, 128.7, 128.2, 127.7, 127.6, 127.3, 127.2, 116.6, 116.4, 115.7 (d, *J* = 23.9 Hz), 114.7 (d, *J* = 23.1 Hz), 110.5 (d, *J* = 24.6 Hz), 109.6 (d, *J* = 7.6 Hz), 109.2 (d, *J* = 7.9 Hz), 65.5, 61.5, 60.8, 56.3, 45.0, 44.8, 30.0, 21.6, 21.5, 14.2 ppm; IR (KBr) υ: 3684, 3494, 3375, 3075, 2960, 2933, 2872, 2360, 1713, 1593, 1573, 1529, 1489, 1452, 1397, 1339, 1274, 1215, 1186, 1138, 1102, 1063, 1033, 1000, 939, 907, 870, 839, 813, 794, 758, 738, 698, 641, 613 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{45}F_2N_3NaO_4$ ([M+Na]$^+$): 848.3276, found: 848.3274.

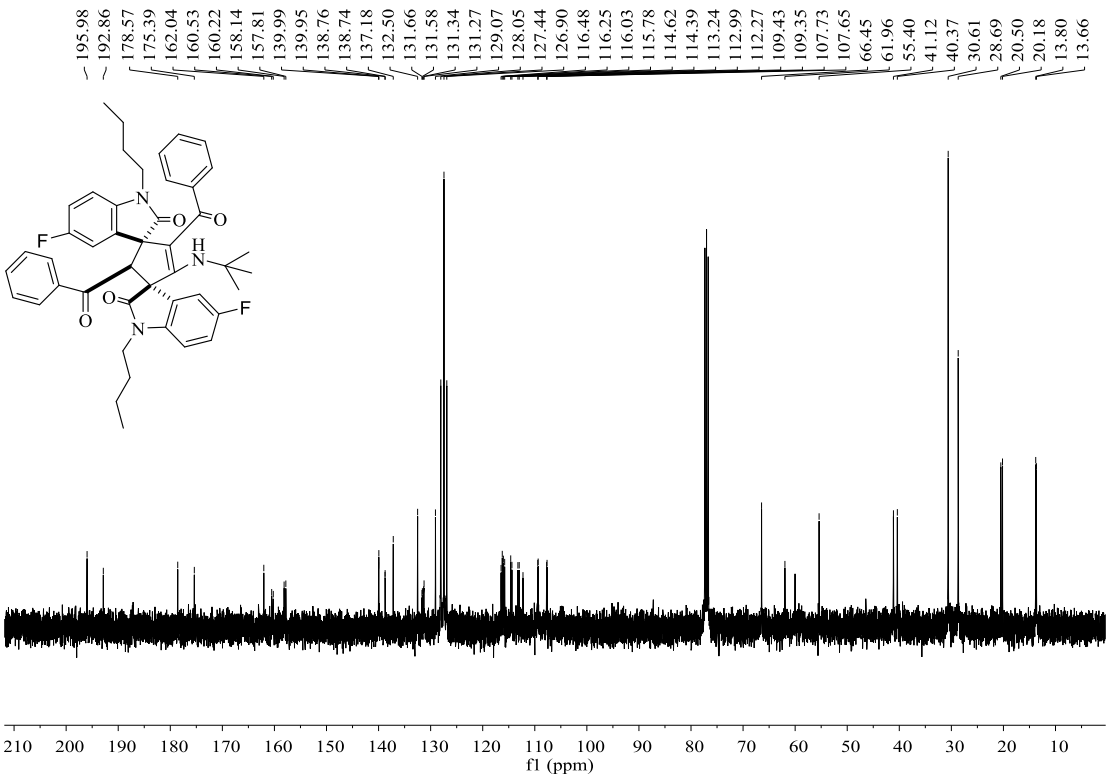


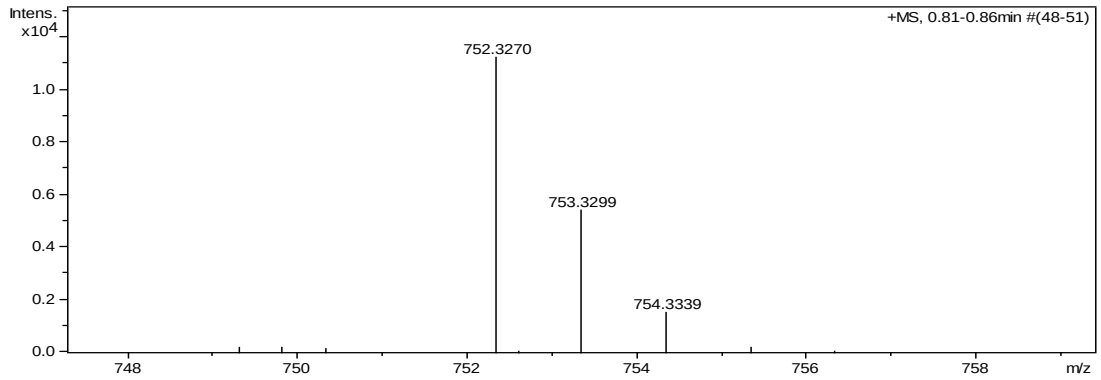

195.33
192.95
179.10
177.24
160.89
158.47
157.80
153.16
136.19
132.55
129.00
128.86
128.18
127.60
127.15
115.86
114.60
110.32
109.99
109.67
109.59
109.24
109.17
65.53
60.77
56.27
45.03
44.81
30.02
21.60
21.54
F
N
O
H
N
O
F
O
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


Intens.
+MS, 0.93-1.04min #(55-62)
848.3274
849.3310
850.3336
851.3392
3000
2000
1000
0
847
848
849
850
851
852
853 m/z

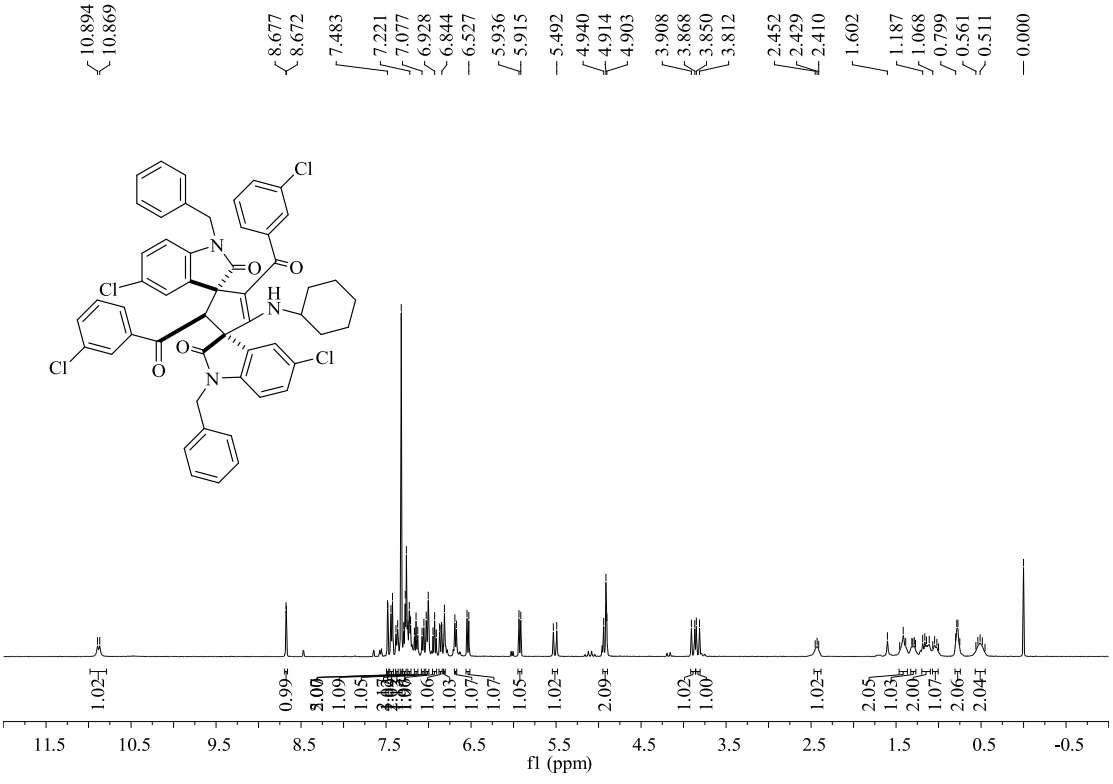
***rel*-(2'*S*,3*R*,3'*R*)-2',4'-dibenzoyl-1,1''-dibutyl-5'-(*tert*-butylamino)-5,5''-difluorodispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3h):** white solid, 34%, m.p. 193-195 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.55 (s, 1H, NH), 8.25 (d, *J* = 8.8 Hz, 1H, ArH), 7.41 (d, *J* = 5.6 Hz, 1H, ArH), 7.30-7.28 (m, 1H, ArH), 7.10 (t, *J* = 8.0 Hz, 3H, ArH), 7.03-6.98 (m, 7H, ArH), 6.80-6.77 (m, 1H, ArH), 6.72-6.67 (m, 1H, ArH), 5.91-5.87 (m, 1H, ArH), 4.94 (s, 1H, CH), 3.87-3.81 (m, 2H, CH_2), 2.79-2.73 (m, 2H, CH_2), 1.91-1.76 (m, 2H, CH_2), 1.53-1.48 (m, 2H, CH_2), 1.11-1.07 (m, 2H, CH_2), 1.03 (t, *J* = 7.4 Hz, 4H, CH_3, CH_2), 0.97 (s, 9H, CH_3), 0.80 (t, *J* = 7.4 Hz, 4H, CH_3, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 196.0, 192.9, 178.6, 175.4, 162.0, 160.4 (d, *J* = 30.6 Hz), 158.0 (d, *J* = 33.3 Hz), 140.0, 138.8, 138.7, 137.2, 132.5, 131.6 (d, *J* = 8.3 Hz), 131.3 (d, *J* = 7.8 Hz), 129.1, 128.1, 127.4, 126.9, 116.5, 116.3, 116.0, 115.8, 114.5 (d, *J* = 23.3 Hz), 113.1 (d, *J* = 25.0 Hz), 112.3, 109.4 (d, *J* = 7.7 Hz), 107.7 (d, *J* = 8.0 Hz), 66.5, 62.0, 55.4, 41.1, 40.4, 30.6, 28.7, 20.5, 20.2, 13.8, 13.7 ppm; IR (KBr) υ: 3362, 3066, 2964, 1711, 1680, 1600, 1568, 1511, 1491, 1450, 1396, 1341, 1259, 1224, 1171, 1081, 1026, 988, 897, 843, 819, 774, 737, 697, 648, 611 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{45}H_{45}F_2N_3NaO_4$ ([M+Na]$^{+}$): 752.3276, found: 752.3270.

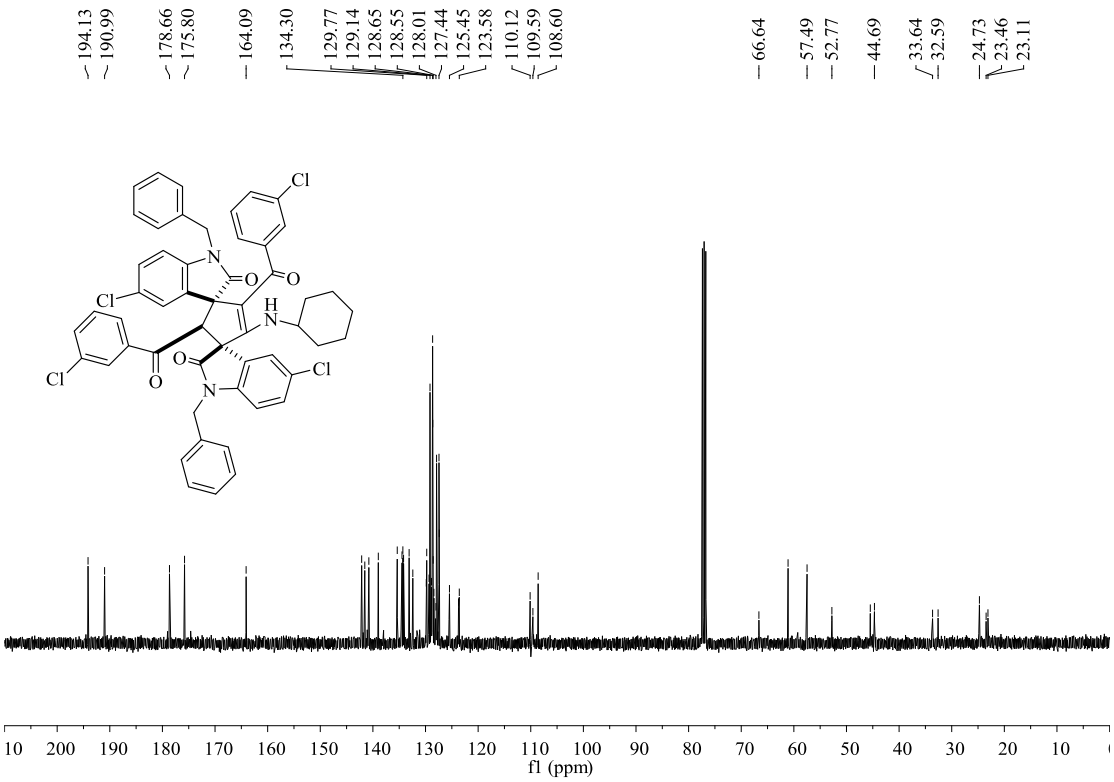


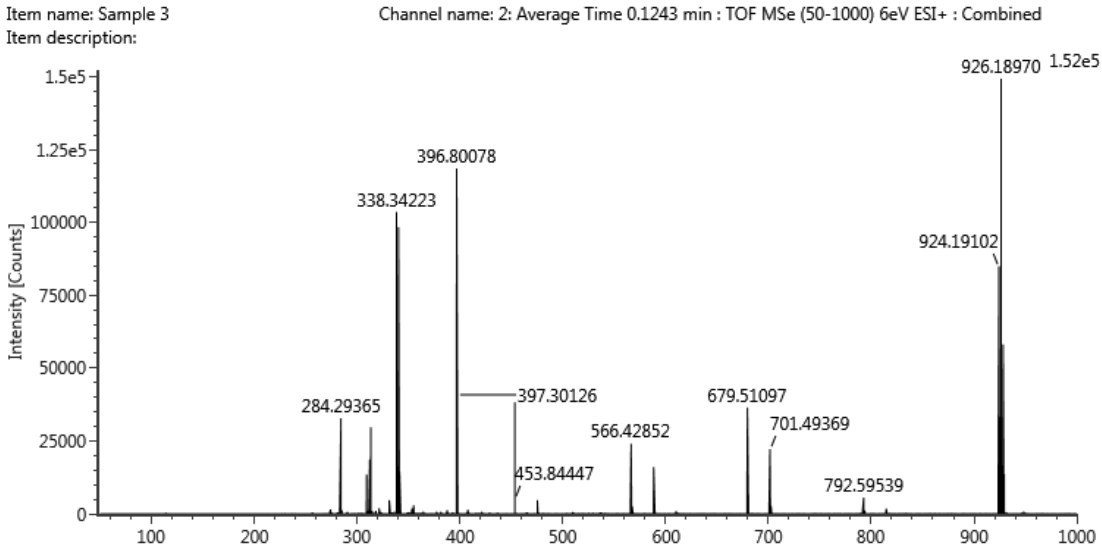

195.98
192.86
178.57
175.39
162.04
160.53
160.22
158.14
157.81
139.99
139.95
138.76
138.74
137.18
132.50
131.66
131.58
131.34
131.27
129.07
128.05
127.44
126.90
116.48
116.25
116.03
115.78
114.62
114.39
113.24
112.99
112.27
109.43
109.35
107.73
107.65
66.45
61.96
55.40
41.12
40.37
30.61
28.69
20.50
20.18
13.80
13.66
F
O
O
H
N
O
O
N
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
x10^4
+MS, 0.81-0.86min #(48-51)
752.3270
753.3299
754.3339
1.0
0.8
0.6
0.4
0.2
0.0
748
750
752
754
756
758
m/z

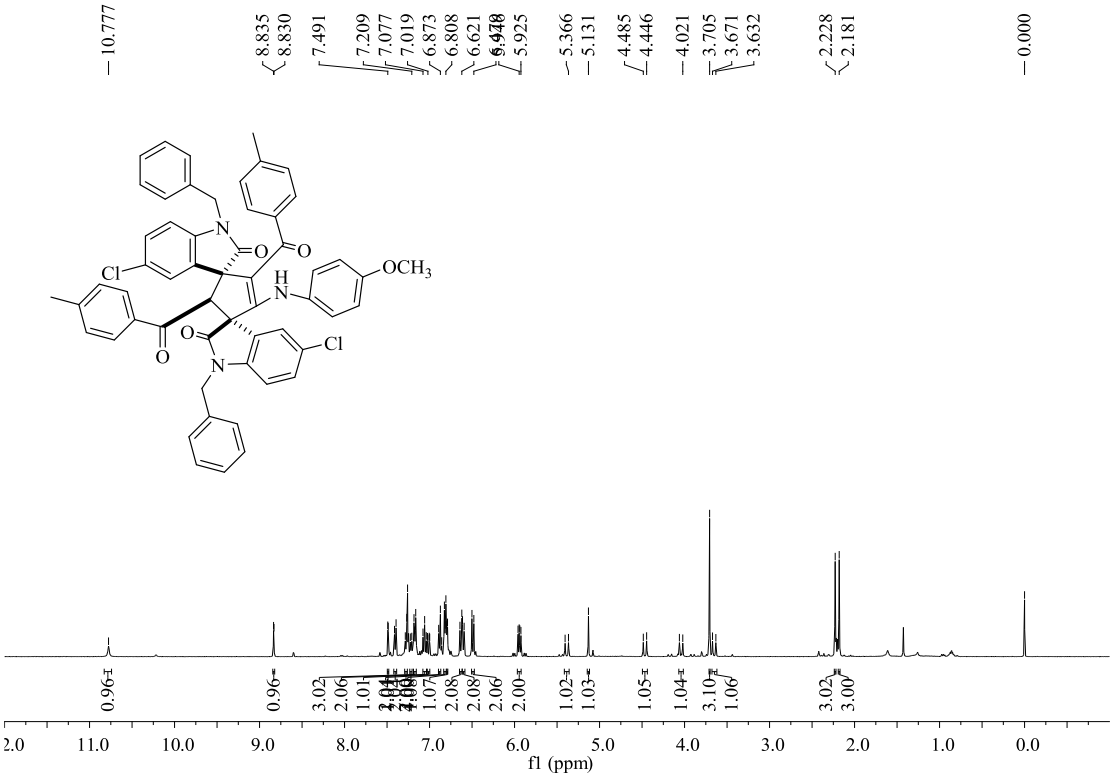
***rel*-(2'*S*,3*R*,3'*R*)-1,1''-dibenzyl-5,5''-dichloro-2',4'-bis(3-chlorobenzoyl)-5'-(cyclohexylamino)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3i):** white solid, 43%, m.p. 229-231 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.88 (d, *J* = 10.0 Hz, 1H, NH), 8.67 (d, *J* = 2.0 Hz, 1H, ArH), 7.48 (d, *J* = 1.6 Hz, 1H, ArH), 7.43 (d, *J* = 7.6 Hz, 2H, ArH), 7.37 (d, *J* = 8.0 Hz, 1H, ArH), 7.32 (s, 5H, ArH), 7.28 (d, *J* = 7.2 Hz, 2H, ArH), 7.24-7.21 (m, 2H, ArH), 7.15 (t, *J*=7.6 Hz, 1H, ArH) 7.07 (d, *J* = 8.8 Hz, 1H, ArH), 7.02 (d, *J* = 9.2 Hz, 2H, ArH), 6.93 (t, *J*=7.6 Hz, 1H, ArH), 6.86 (dd, J_1 =8.4 Hz, J_2 =1.6 Hz, 1H, ArH), 6.81 (s, 1H, ArH), 6.68 (d, *J*=7.6 Hz, 1H, ArH), 6.54 (d, *J*=8.4 Hz, 1H, ArH), 5.93 (d, *J*=8.4 Hz, 1H, ArH), 5.51 (d, *J* = 16.0 Hz, 1H, CH_2), 4.94-4.90 (m, 2H, CH, CH_2), 3.89 (d, *J* = 16.0 Hz, 1H, CH_2), 3.83 (d, *J* = 15.2 Hz, 1H, CH_2), 2.45-2.41 (m, 1H, CH), 1.46-1.39 (m, 2H, CH_2), 1.32-1.27 (m, 1H, CH_2), 1.19-1.11 (m, 2H, CH_2), 1.07-1.00 (m, 1H, CH_2), 0.80-0.75 (m, 2H, CH_2), 0.56-0.45 (m, 2H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 194.1, 191.0, 178.7, 175.8, 164.1, 142.1, 141.5, 140.8, 139.0, 135.4, 134.5, 134.3, 134.2, 133.1, 132.4, 129.9, 129.8, 129.3, 129.1, 128.9, 128.7, 128.6, 128.6, 128.4, 128.0, 127.9, 127.4, 127.4, 125.5, 123.7, 123.6, 110.1, 109.6, 108.6, 66.6, 61.1, 57.5, 52.8, 45.5, 44.7, 33.6, 32.6, 24.7, 23.5, 23.1 ppm; IR (KBr) υ: 3064, 2934, 2853, 2364, 1722, 1609, 1558, 1487, 1454, 1428, 1378, 1340, 1313, 1263, 1228, 1172, 1080, 995, 890, 812, 786, 747, 728, 716, 701 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{42}Cl_4N_3O_4$ ([M+H]$^+$): 924.1924, found: 924.1910.

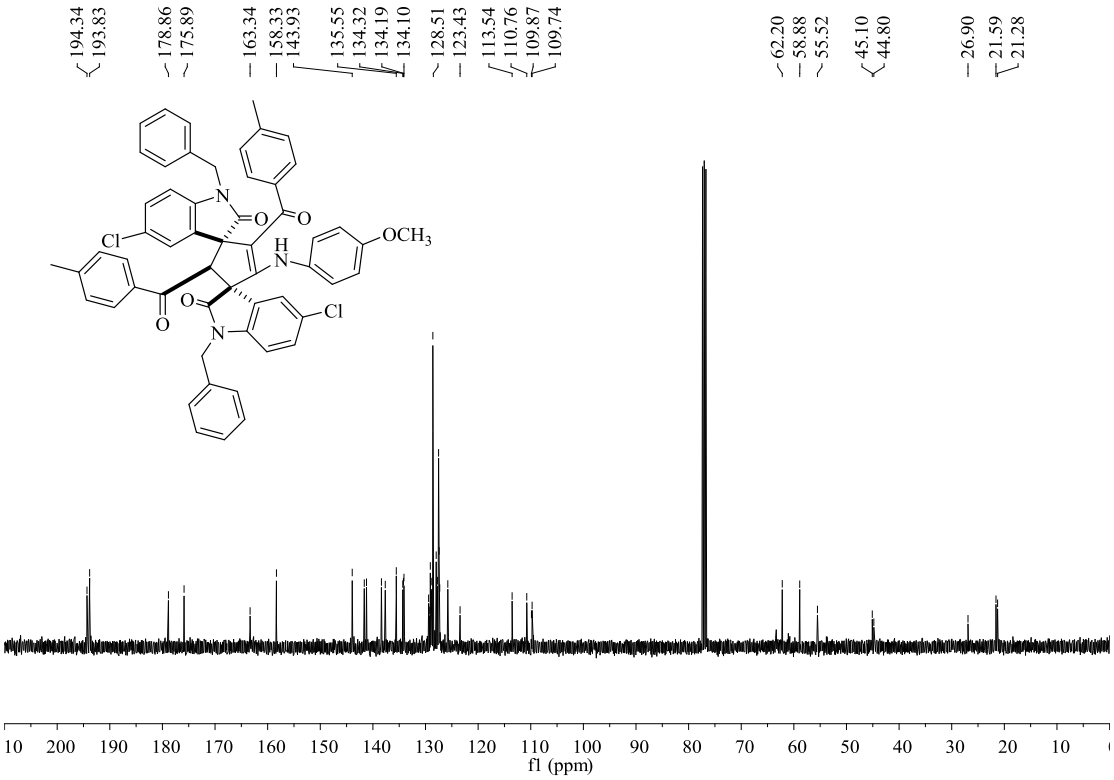


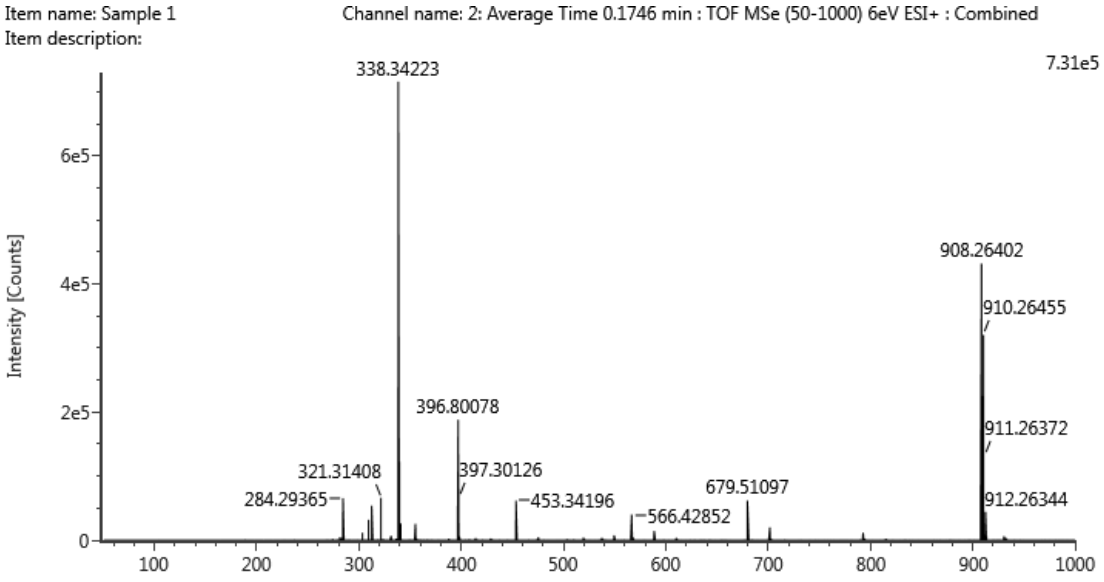

194.13
190.99
178.66
175.80
164.09
134.30
129.77
129.14
128.65
128.55
128.01
127.44
125.45
123.58
110.12
109.59
108.60
66.64
57.49
52.77
44.69
33.64
32.59
24.73
23.46
23.11
Cl
Cl
Cl
Cl
O
O
O
O
N
N
H
N
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Item name: Sample 3
Item description:
Channel name: 2: Average Time 0.1243 min : TOF MSe (50-1000) 6eV ESI+ : Combined
Intensity [Counts]
1.5e5
1.25e5
100000
75000
50000
25000
0
926.18970
1.52e5
396.80078
338.34223
924.19102
397.30126
679.51097
284.29365
566.42852
701.49369
453.84447
792.59539
100
200
300
400
500
600
700
800
900
1000

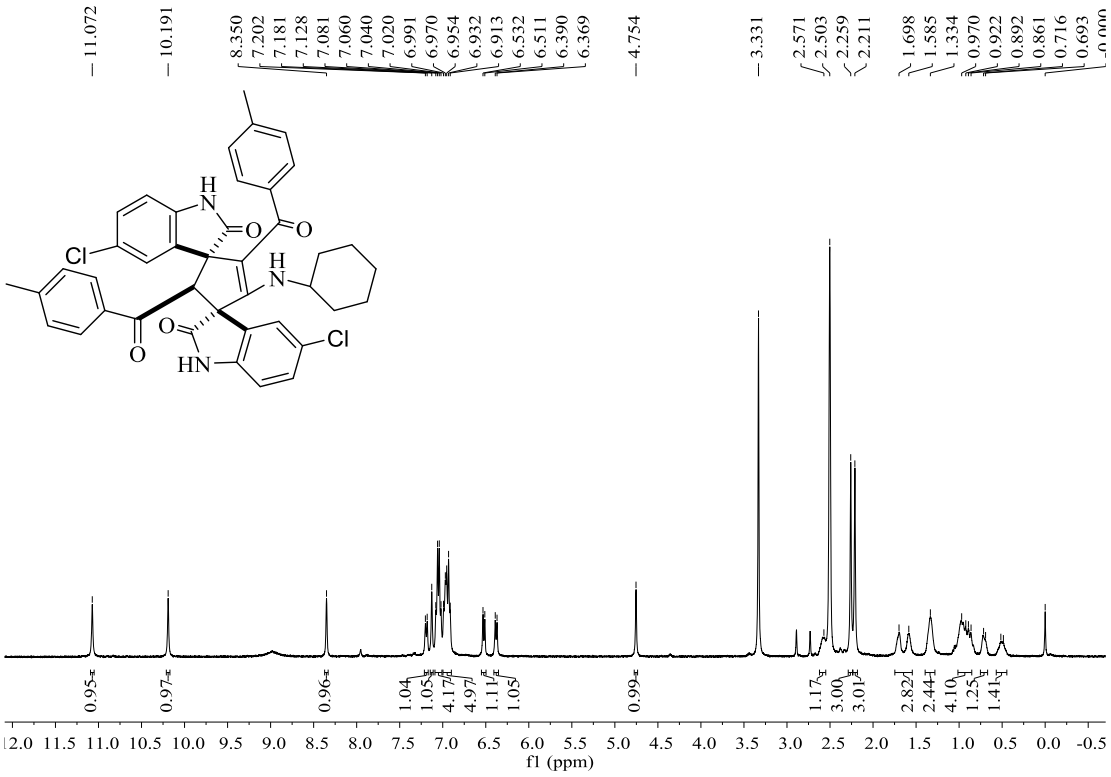
***rel*-(2'*S*,3*R*,3'*R*)-1,1''-dibenzyl-5,5''-dichloro-4'-((4-methoxyphenyl)amino)-2',5'-bis(4-methylbenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3j):** white solid, 28%, m.p. 164-166 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.78 (s, 1H, NH), 8.83 (d, *J* = 2.0 Hz, 1H, ArH), 7.49 (d, *J* = 2.0 Hz, 1H, ArH), 7.40 (d, *J* = 7.2 Hz, 2H, ArH), 7.28 (d, *J* = 6.8 Hz, 2H, ArH), 7.22 (d, *J* = 7.2 Hz, 1H, ArH), 7.18-7.16 (m, 3H, ArH), 7.06 (t, *J* = 7.6 Hz, 2H, ArH), 7.01 (dd, J_1 =8.4 Hz, J_2 =2.4 Hz, 1H, ArH), 6.88 (d, *J* = 8.0 Hz, 2H, ArH), 6.83-6.81 (m, 4H, ArH), 6.79 (d, *J*=2.4 Hz, 1H, ArH), 6.63 (d, *J*=8.8 Hz, 2H, ArH), 6.60 (d, *J*=7.6 Hz, 2H, ArH), 6.49 (d, *J* = 8.8 Hz, 2H, ArH), 5.94 (dd, J_1 =8.4 Hz, J_2 =5.2 Hz, 2H, ArH), 5.39 (d, *J* = 15.6 Hz, 1H, CH_2), 5.13 (s, 1H, CH), 4.47 (d, *J* = 15.6 Hz, 1H, CH_2), 4.04 (d, *J* = 16.0 Hz, 1H, CH_2), 3.71 (s, 3H, OCH_3), 3.65 (d, *J* = 15.6 Hz, 1H, CH_2), 2.23 (s, 3H, CH_3), 2.18 (s, 3H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 194.3, 193.8, 178.9, 175.9, 163.3, 158.3, 143.9, 141.6, 141.2, 138.4, 137.7, 135.6, 134.3, 134.2, 134.1, 129.4, 129.2, 129.1, 128.9, 128.8, 128.6, 128.5, 128.0, 127.7, 127.5, 127.4, 127.3, 125.8, 123.4, 113.5, 110.8, 109.9, 109.7, 62.2, 58.9, 55.5, 45.1, 44.8, 26.9, 21.6, 21.3 ppm; IR (KBr) υ: 3688, 3545, 3401, 3065, 3035, 2914, 1719, 1609, 1511, 1485, 1429, 1337, 1294, 1247, 1178, 1108, 1081, 1030, 981, 808, 789, 750, 737 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{56}H_{44}Cl_2N_3O_5$ ([M+H]$^+$): 908.2653, found: 908.2640.

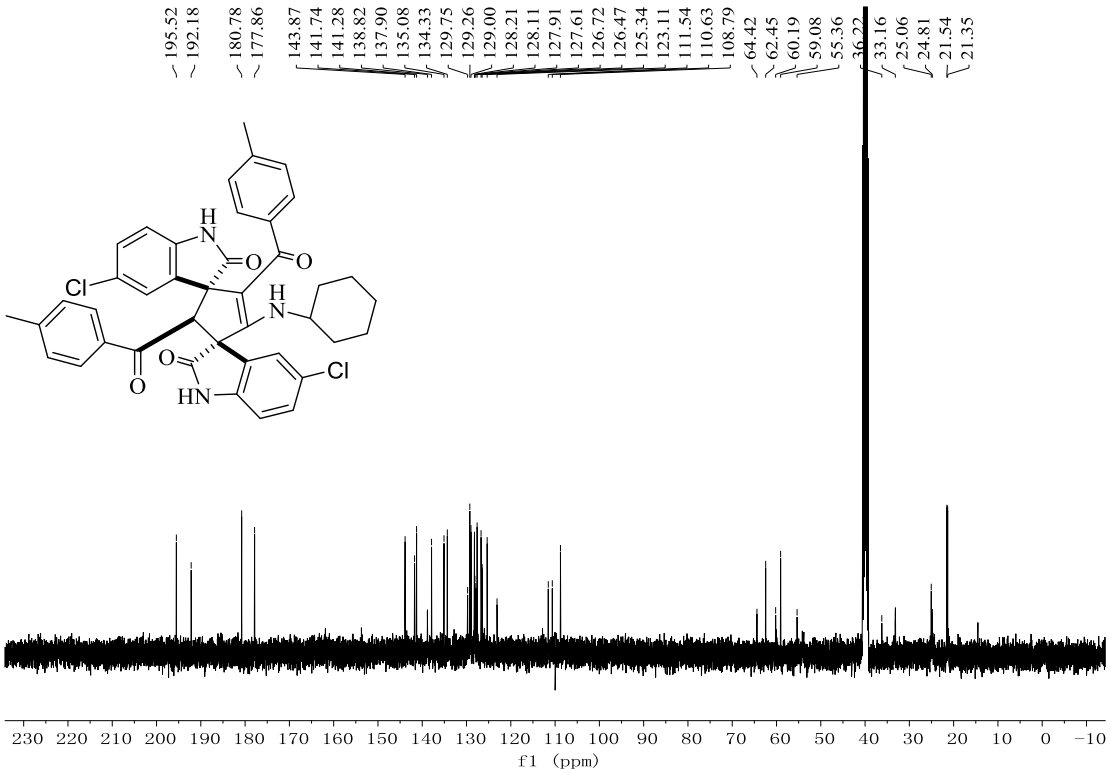


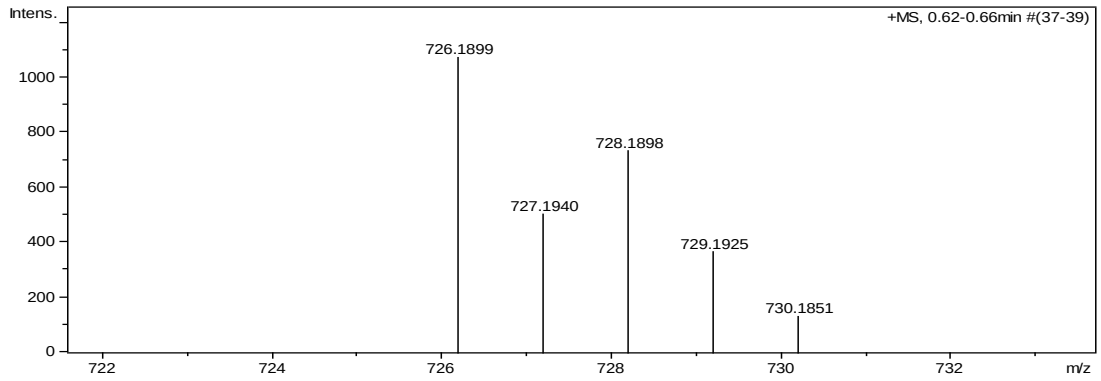

194.34
193.83
178.86
175.89
163.34
158.33
143.93
135.55
134.32
134.19
134.10
128.51
123.43
113.54
110.76
109.87
109.74
62.20
58.88
55.52
45.10
44.80
26.90
21.59
21.28
Cl
OCH3
H
N
O
Cl
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Item name: Sample 1
Item description:
Channel name: 2: Average Time 0.1746 min : TOF MSe (50-1000) 6eV ESI+ : Combined
7.31e5
Intensity [Counts]
6e5
4e5
2e5
0
338.34223
908.26402
910.26455
911.26372
912.26344
396.80078
397.30126
321.31408
284.29365
453.34196
566.42852
679.51097
100 200 300 400 500 600 700 800 900 1000

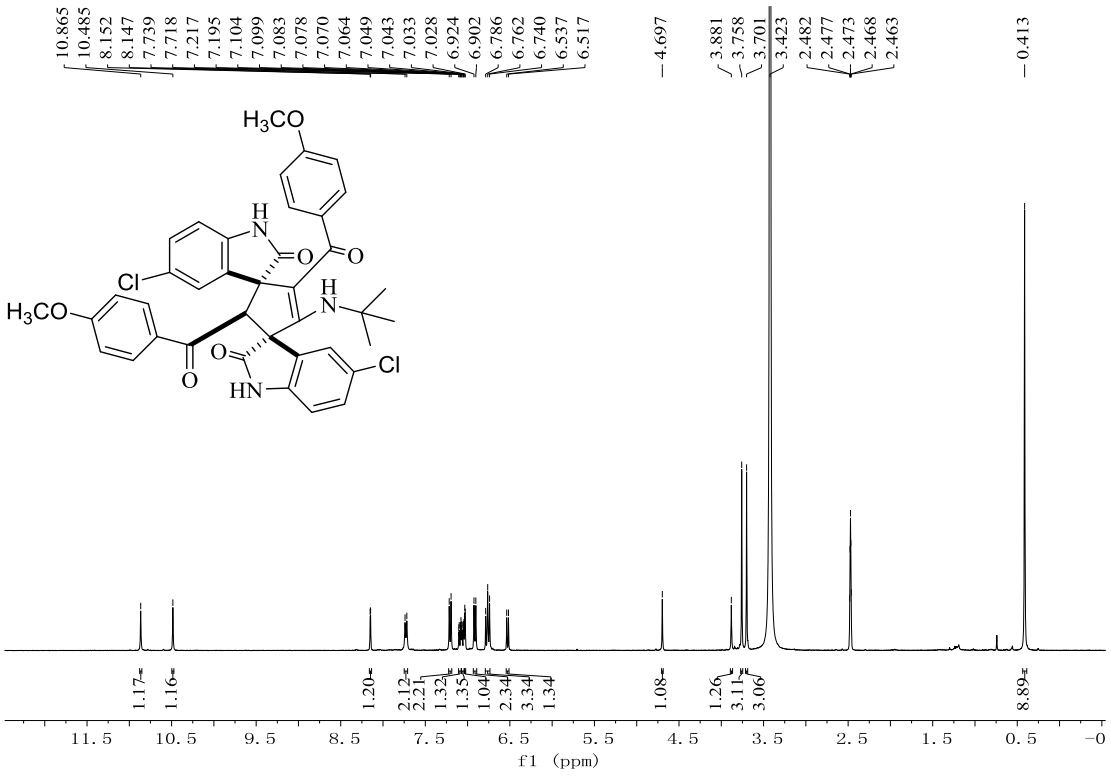
***rel*-(2'*S*,3*S*,3'*S*)-4,5''-dichloro-4'-(cyclohexylamino)-2',5'-bis(4-methylbenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3k):** ethyl acetate and petroleum ether (v/v = 1:3) as the eluent, pale yellow solid, 183 mg, 52%, m.p. 242-244 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.07 (s, 1H, NH), 10.19 (s, 1H, NH), 8.35 (s, 1H, ArH), 7.19 (d, *J* = 8.4 Hz, 1H, ArH), 7.13 (s, 1H, ArH), 7.08-7.02 (m, 4H, ArH), 6.99-6.91 (m, 5H, ArH), 6.92 (d, *J* = 8.4 Hz, 1H, ArH), 6.38 (d, *J* = 8.4 Hz, 1H, ArH), 4.75 (s, 1H, CH), 2.57 (s, 1H, CH), 2.26 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 1.70 (s, 1H, CH_2), 1.59 (s, 1H, CH_2), 1.33 (s, 2H, CH_2), 0.97-0.86 (m, 4H, CH_2), 0.72-0.69 (m, 1H, CH_2), 0.52-0.49 (m, 1H, CH_2); ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 195.5, 192.2, 180.8, 177.9, 143.9, 141.7, 141.3, 138.8, 137.9, 135.1, 134.3, 129.8, 129.3, 129.0, 128.2, 128.1, 127.9, 127.6, 126.7, 126.5, 125.3, 123.1, 111.5, 110.6, 108.8, 64.4, 62.5, 60.2, 59.1, 55.4, 36.2, 33.2, 25.1, 24.8, 21.5, 21.4; IR (KBr) υ: 3696, 3644, 3525, 3432, 3296, 3079, 2974, 2903, 2881, 2366, 1889, 1615, 1452, 1370, 1305, 1148, 1069, 987, 830, 723 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{41}H_{35}Cl_2N_3NaO_4$ ([M+Na]$^+$): 726.1897, found: 726.1899.

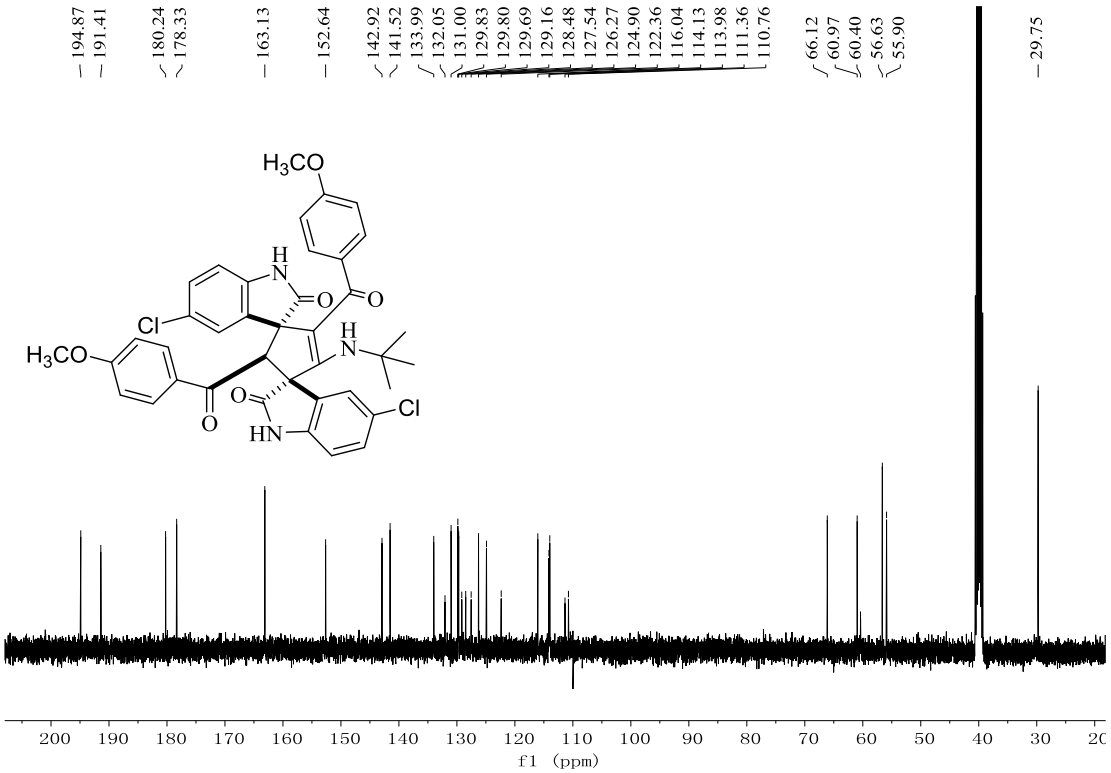


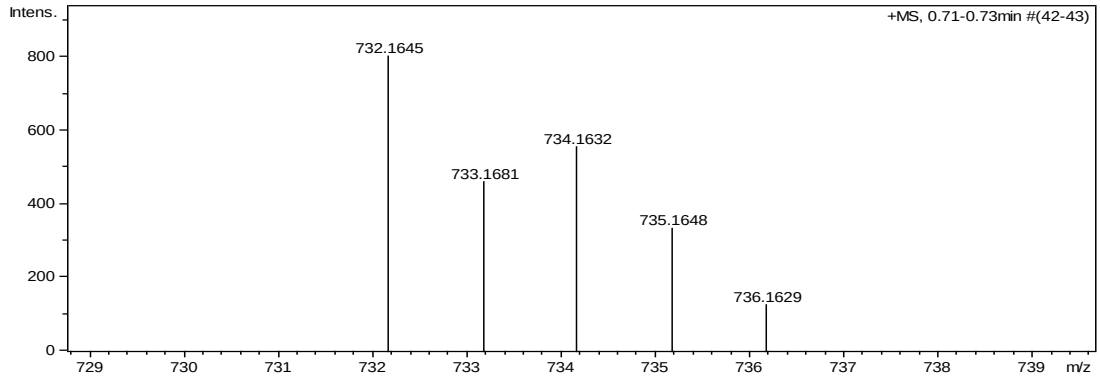

195.52
192.18
180.78
177.86
143.87
141.74
141.28
138.82
137.90
135.08
134.33
129.75
129.26
129.00
128.21
128.11
127.91
127.61
126.72
126.47
125.34
123.11
111.54
110.63
108.79
64.42
62.45
60.19
59.08
55.36
36.22
33.16
25.06
24.81
21.54
21.35
H
N
O
O
Cl
H
N
O
O
HN
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


Intens.
+MS, 0.62-0.66min #(37-39)
726.1899
728.1898
727.1940
729.1925
730.1851
1000
800
600
400
200
0
722
724
726
728
730
732
m/z

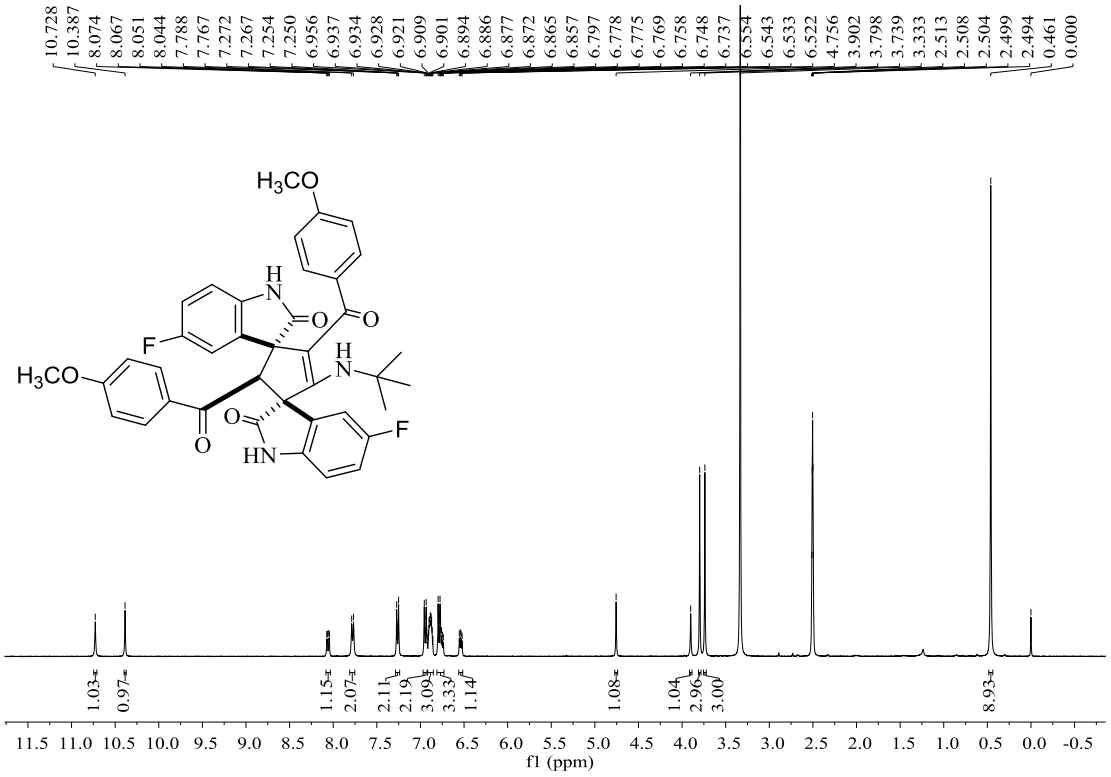
***rel*-(2'*S*,3*S*,3'*S*)-4'-(*tert*-butylamino)-4,5''-dichloro-2',5'-bis(4-methoxybenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3l):** ethyl acetate and petroleum ether (v/v = 1:3) as the eluent, pale yellow solid, 152 mg, 43%, m.p. 224-226 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.87 (s, 1H, NH), 10.49 (s, 1H, NH), 8.15-8.14 (m, 1H, ArH), 7.73 (d, *J* = 8.4 Hz, 2H, ArH), 7.21 (d, *J* = 8.8 Hz, 2H, ArH), 7.10-7.06 (m, 2H, ArH), 7.05-7.03 (m, 1H, ArH), 6.91 (d, *J* = 8.8 Hz, 1H, ArH), 6.79-6.74 (m, 3H, ArH), 6.53 (d, *J* = 8.0 Hz, 1H, ArH), 6.56 (d, *J* = 8.4 Hz, 1H, ArH), 4.70 (s, 1H, CH), 3.88 (s, 1H, NH), 3.76 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 0.41 (s, 9H, CH_3); ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 194.9, 191.4, 180.2, 178.3, 163.1, 152.6, 142.9, 141.5, 134.0, 132.1, 131.0, 129.8, 129.7, 129.2, 128.5, 127.5, 126.3, 124.9, 122.4, 116.0, 114.1, 114.0, 111.4, 110.8, 66.1, 61.0, 60.4, 56.6, 55.9, 29.8; IR (KBr) υ: 3770, 3649, 3522, 3431, 3298, 3078, 2977, 2905, 2866, 2340, 1705, 1612, 1445, 1376, 1324, 1176, 1071, 986, 804, 773 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{39}H_{33}Cl_2N_3NaO_6$ ([M+Na]$^+$): 732.1639, found: 732.1645.

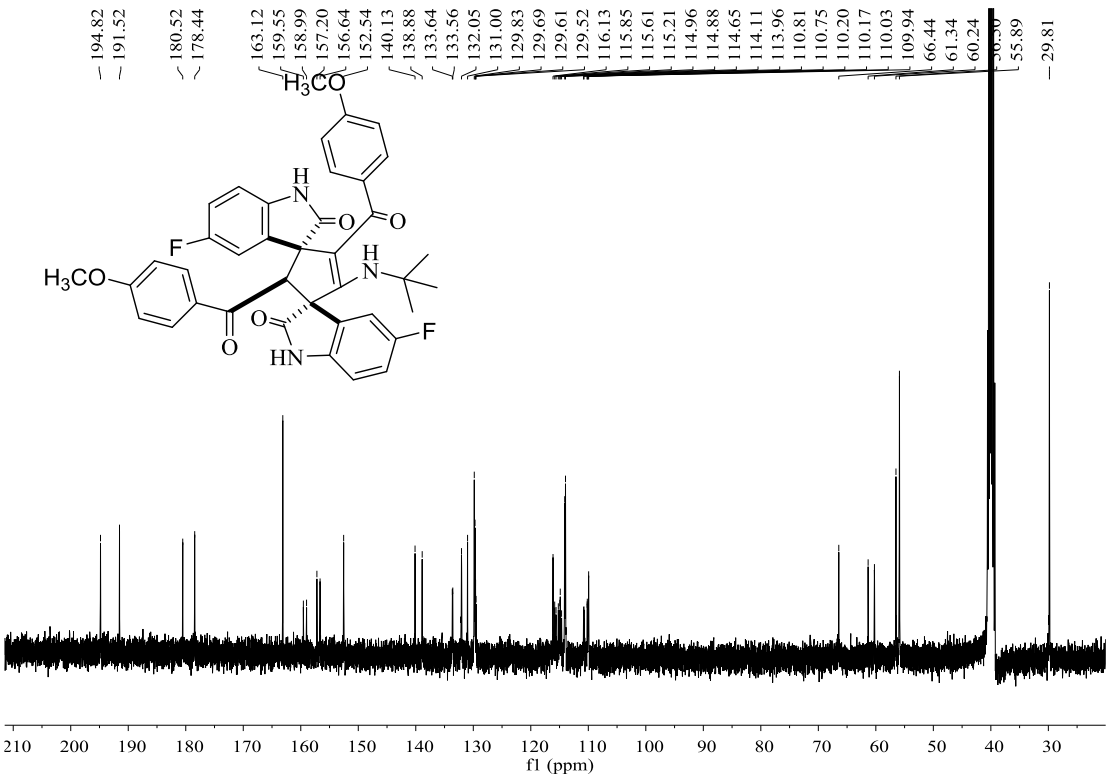


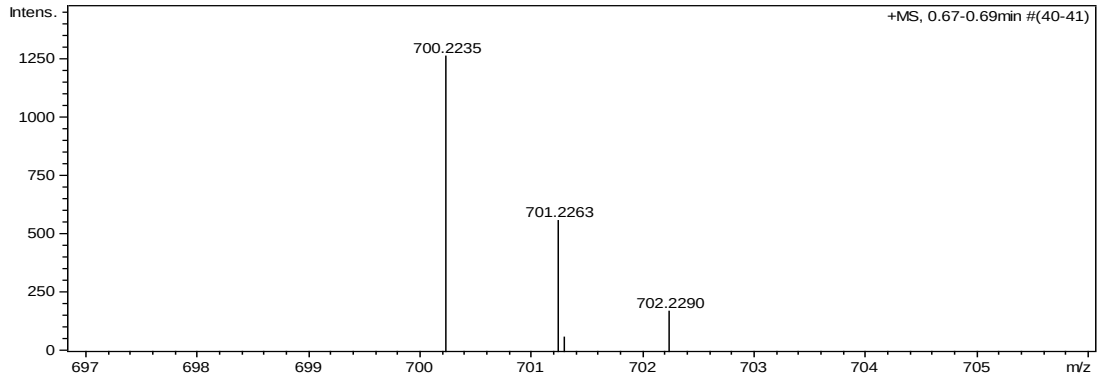

194.87
191.41
180.24
178.33
163.13
152.64
142.92
141.52
133.99
132.05
131.00
129.83
129.80
129.69
129.16
128.48
127.54
126.27
124.90
122.36
116.04
114.13
113.98
111.36
110.76
66.12
60.97
60.40
56.63
55.90
29.75
H3CO
H
N
O
O
Cl
H3CO
H
N
O
O
HN
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
+MS, 0.71-0.73min #(42-43)
732.1645
734.1632
733.1681
735.1648
736.1629
800
600
400
200
0
729 730 731 732 733 734 735 736 737 738 739 m/z

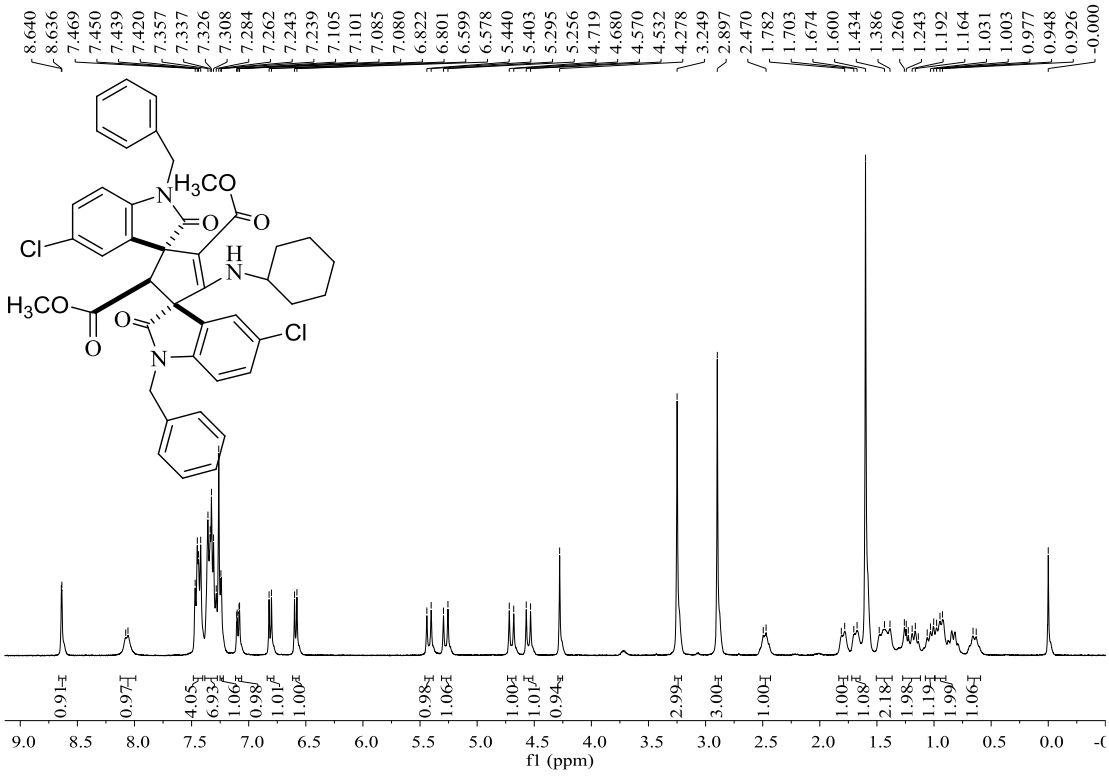
***rel*-(2'*S*,3*S*,3'*S*)-4'-(*tert*-butylamino)-4,5''-difluoro-2',5'-bis(4-methoxybenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3m):** ethyl acetate and petroleum ether (v/v = 1:3) as the eluent, pale yellow solid, 169 mg, 50%, m.p. 247-249 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.73 (s,1H, NH), 10.39 (s, 1H, NH), 8.07-8.04 (m, 1H, ArH), 7.78 (d, *J* = 8.4 Hz, 2H, ArH), 7.26 (d, *J* = 8.8 Hz, 2H, ArH), 6.96-6.93 (m, 2H, ArH), 6.91-6.86 (m, 3H, ArH), 6.80-6.74 (m, 3H, ArH), 6.55-6.52 (m, 1H, ArH), 4.76 (s, 1H, CH), 3.90 (s, 1H, NH), 3.80 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 0.46 (s, 9H, CH_3); ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ 194.8, 191.5, 180.5, 178.4, 163.1, 159.3 (d, *J* = 55.1 Hz), 156.9 (d, *J* = 55.0 Hz), 152.5, 140.1, 138.9, 133.6, 133.5, 132.1, 131.0, 129.8, 129.7, 129.6, 129.5, 116.1, 115.7 (d, *J* = 23.1 Hz), 115.2, 114.9 (d, *J* = 8.4 Hz), 114.7, 114.1, 114.0, 110.8, 110.7, 110.2, 110.1, 110.0, 109.9, 66.4, 61.3, 60.2, 56.5, 55.9, 29.8, 19.0; IR (KBr) υ: 3658, 3304, 3248, 3064, 2967, 2855, 1716, 1590, 1477, 1313, 1262, 1175, 1122, 1017, 904, 821, 759, 691 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{39}H_{33}F_2N_3NaO_6$ ([M+Na]$^+$): 700.2230, found: 700.2235.

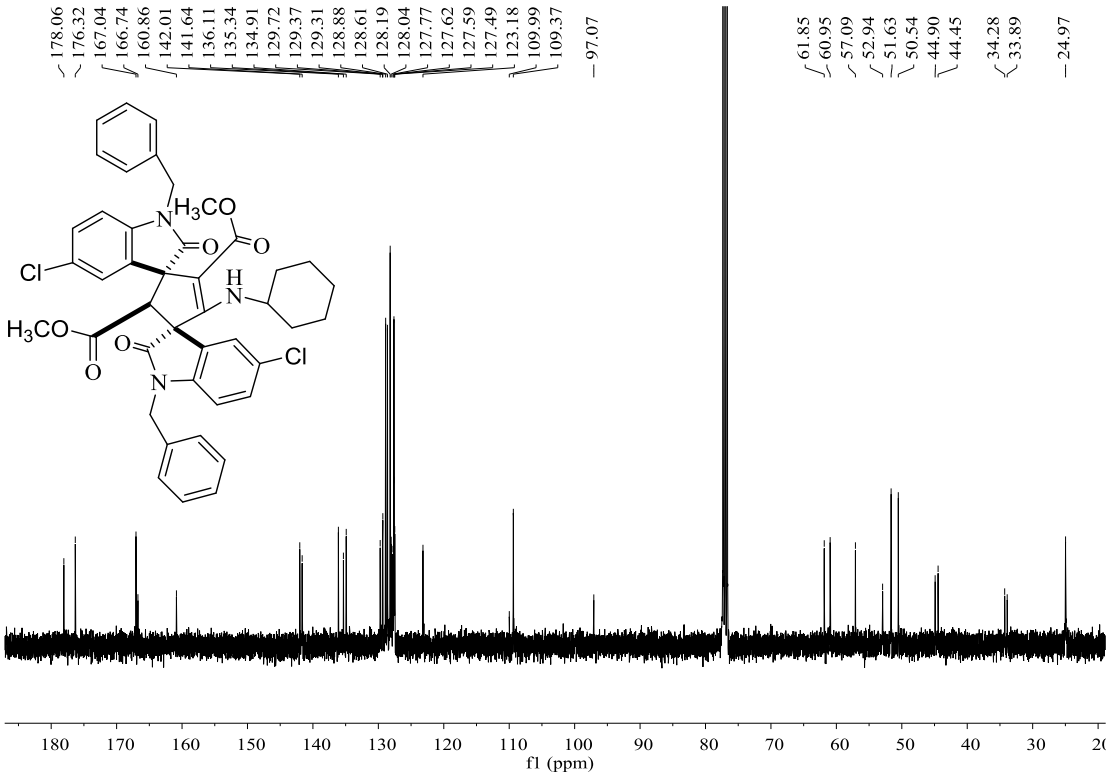



194.82
191.52
180.52
178.44
163.12
159.55
158.99
157.20
156.64
152.54
140.13
138.88
133.64
133.56
132.05
131.00
129.83
129.69
129.61
129.52
116.13
115.85
115.61
115.21
114.96
114.88
114.65
114.11
113.96
110.81
110.75
110.20
110.17
110.03
109.94
66.44
61.34
60.24
55.89
29.81
H3CO
H
N
O
O
F
H3CO
H
N
O
O
HN
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)


Intens.
+MS, 0.67-0.69min #(40-41)
700.2235
701.2263
702.2290
1250
1000
750
500
250
0
697 698 699 700 701 702 703 704 705 m/z

Dimethyl *rel*-(2'*S*,3*S*,3'*S*)-1,1''-dibenzyl-4'',5-dichloro-5'-(cyclohexylamino)-2,2''-dioxodispiro-[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2',4'-dicarboxylate (3n): ethyl acetate and petroleum ether (v/v = 1:8) as the eluent, white solid, 126 mg, 33%, m.p. 247-249 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64-8.63 (m, 1H, NH), 8.08-8.06 (m, 1H, ArH), 7.47-7.42 (m, 4H, ArH), 7.36-7.28 (m, 7H, ArH), 7.24-7.23 (m, 1H, ArH), 7.11-7.08 (m, 1H, ArH), 6.81 (d, *J* = 8.4 Hz, 1H, ArH), 6.59 (d, *J* = 8.4 Hz, 1H, ArH), 5.42 (d, *J* = 14.8 Hz, 1H, CH_2), 5.28 (d, *J* = 15.6 Hz, 1H, CH_2), 4.70 (d, *J* = 15.6 Hz, 1H, CH_2), 4.55 (d, *J* = 15.2 Hz, 1H, CH_2), 4.28 (s, 1H, CH), 3.25 (s, 3H, OCH_3), 2.90 (s, 3H, OCH_3), 2.50-2.47 (m, 1H, CH), 1.81-1.78 (m, 1H, CH_2), 1.70-1.67 (m, 1H, CH_2), 1.48-1.39 (m, 2H, CH_2), 1.26-1.14 (m, 2H, CH_2), 1.06-1.00 (m, 1H, CH_2), 0.98-0.93 (m, 2H, CH_2), 0.66-0.63 (m, 1H, CH_2); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 178.1, 176.3, 167.0, 166.7, 160.9, 142.0, 141.6, 136.1, 135.3, 134.9, 129.7, 129.4, 129.3, 128.9, 128.6, 128.2, 128.0, 127.8, 127.6, 127.5, 123.2, 110.0, 109.4, 97.1, 61.9, 61.0, 57.1, 52.9, 51.6, 50.5, 44.9, 44.5, 34.3, 33.9, 25.0; IR (KBr) υ: 3346, 3032, 2973, 1745, 1660, 1621, 1538, 1485, 1440, 1388, 1303, 1247, 1213, 1152, 1069, 998, 884, 868, 811, 767, 725, 683, 629 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{43}H_{39}Cl_2N_3NaO_6$ ([M+Na]$^+$): 786.2114, found: 786.2117.




178.06
176.32
167.04
166.74
160.86
142.01
141.64
136.11
135.34
134.91
129.72
129.37
129.31
128.88
128.61
128.19
128.04
127.77
127.62
127.59
127.49
123.18
109.99
109.37
97.07
61.85
60.95
57.09
52.94
51.63
50.54
44.90
44.45
34.28
33.89
24.97
H3CO
O
O
Cl
H
N
H3CO
O
O
Cl
N
180
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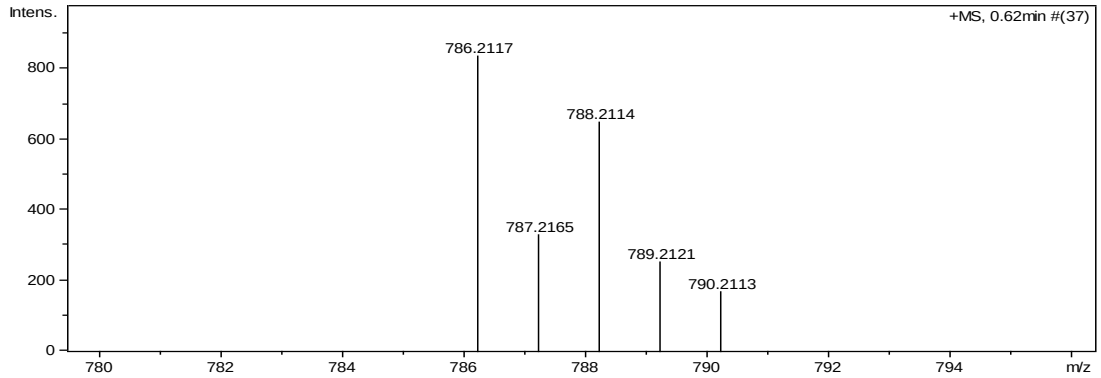
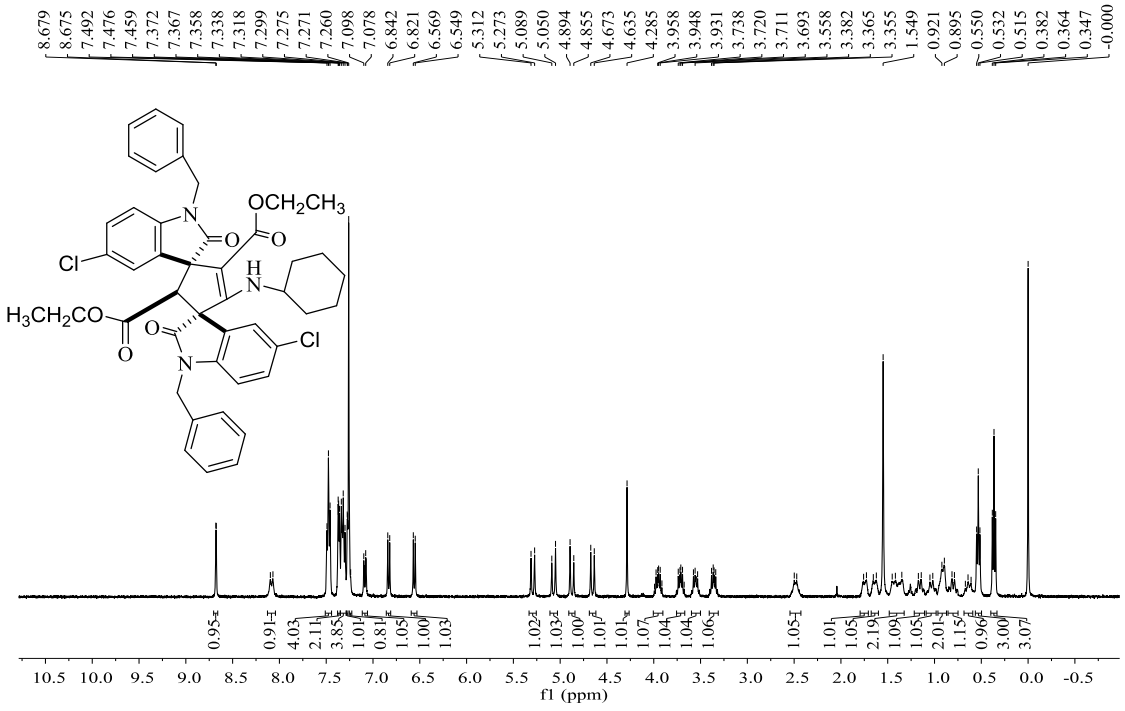
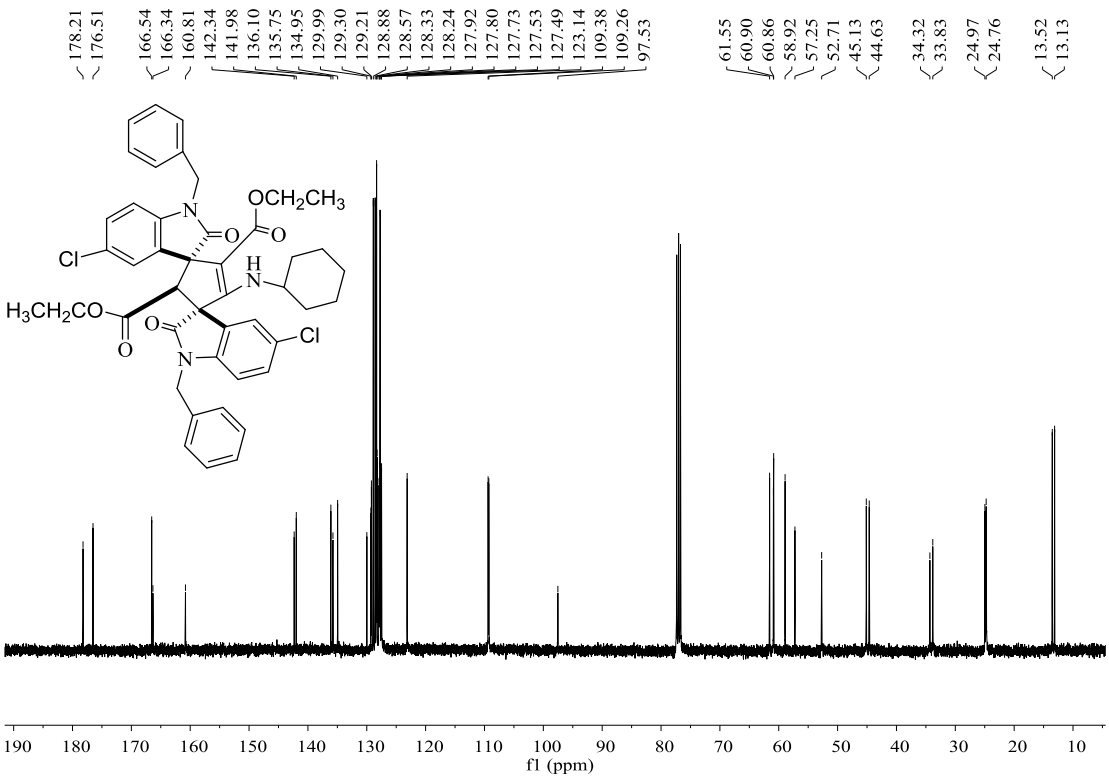
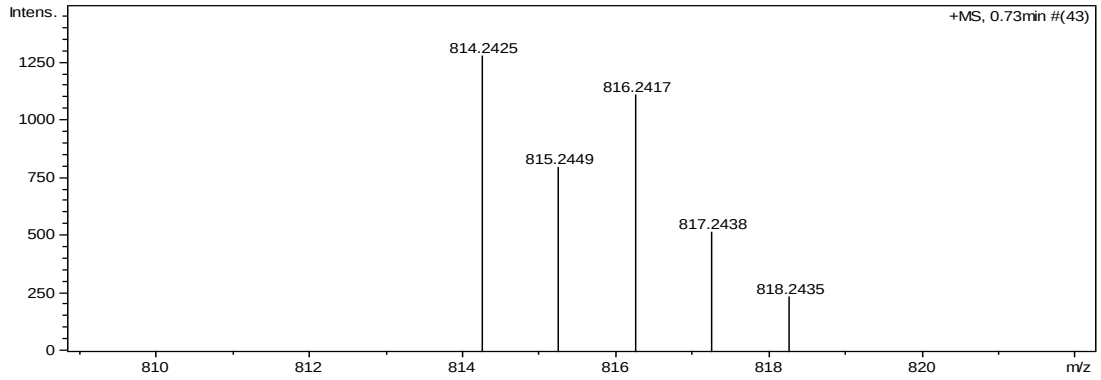
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


Intens.
+MS, 0.62min #(37)
786.2117
788.2114
787.2165
789.2121
790.2113
800
600
400
200
0
780
782
784
786
788
790
792
794
m/z

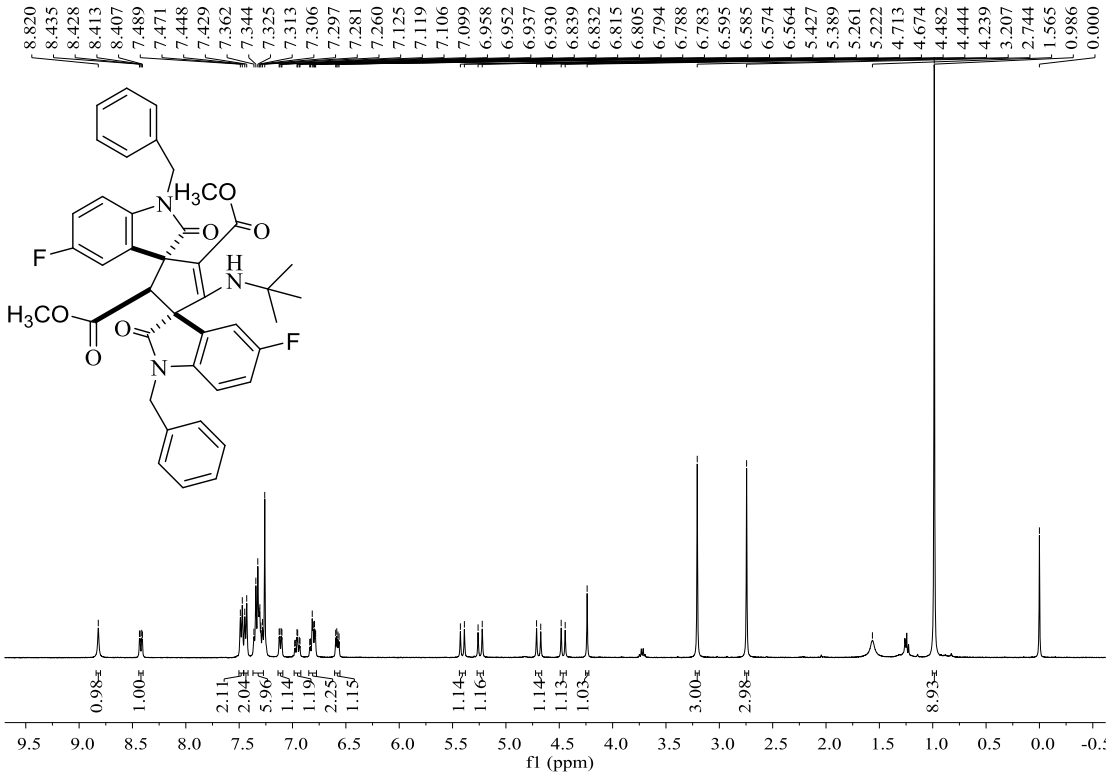
Diethyl *rel*-(2'*S*,3*S*,3'*S*)-1,1''-dibenzyl-4'',5-dichloro-5'-(cyclohexylamino)-2,2''-dioxodispiro-[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2',4'-dicarboxylate (3o): ethyl acetate and petroleum ether (v/v = 1:8) as the eluent, white solid, 119 mg, 30%, m.p. 218-220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68-8.67 (m, 1H, NH), 8.10-8.07 (m, 1H, ArH), 7.48 (t, *J* = 13.2 Hz, 4H, ArH), 7.37-7.36 (m, 2H, ArH), 7.34-7.30 (m, 4H, ArH), 7.28-7.27 (m, 1H, ArH), 7.24 (s, 1H, ArH), 7.10-7.07 (m, 2H, ArH), 6.83 (d, *J* = 8.4 Hz, 1H, ArH), 6.56 (d, *J* = 8.0 Hz, 1H, ArH), 5.29 (d, *J* = 15.6 Hz, 1H, CH_2), 5.07 (d, *J* = 15.6 Hz, 1H, CH_2), 4.87 (d, *J* = 15.6 Hz, 1H, CH_2), 4.65 (d, *J* = 15.2 Hz, 1H, CH_2), 4.29 (s, 1H, CH), 3.99-3.91 (m, 1H, CH_2), 3.74-3.68 (m, 1H, CH_2), 3.58-3.53 (m, 1H, CH_2), 3.38-3.34 (m, 1H, CH_2), 2.50-2.47 (m, 1H, CH), 1.76-1.73 (m, 1H, CH_2), 1.45-1.35 (m, 2H, CH_2), 1.17-1.14 (m, 1H, CH_2), 1.05-1.02 (m, 1H, CH_2), 0.92-0.90 (m, 2H, CH_2), 0.81-0.79 (m, 1H, CH_2), 0.67-0.61 (m, 1H, CH_2), 0.53 (t, *J* = 7.0 Hz, 3H, CH_3), 0.36 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 178.2, 176.5, 166.5, 166.3, 160.8, 142.3, 142.0, 136.1, 135.8, 135.0, 130.0, 129.3, 129.2, 128.9, 128.6, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5, 123.1, 109.4, 109.3, 97.5, 61.6, 60.9, 60.8, 58.9, 57.3, 52.7, 45.1, 44.6, 34.3, 33.8, 25.0, 24.8, 13.5, 13.1; IR (KBr) υ: 3362, 3069, 3009, 2965, 2837, 2361, 1876, 1714, 1675, 1608, 1567, 1512, 1484, 1455, 1427, 1395, 1340, 1258, 1172, 1154, 1109, 1086, 1025, 989, 937, 895, 876, 845, 819, 782, 742, 695, 649, 623, 610 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{45}H_{43}Cl_2N_3NaO_6$ ([M+Na]$^+$): 814.2427, found: 814.2425.

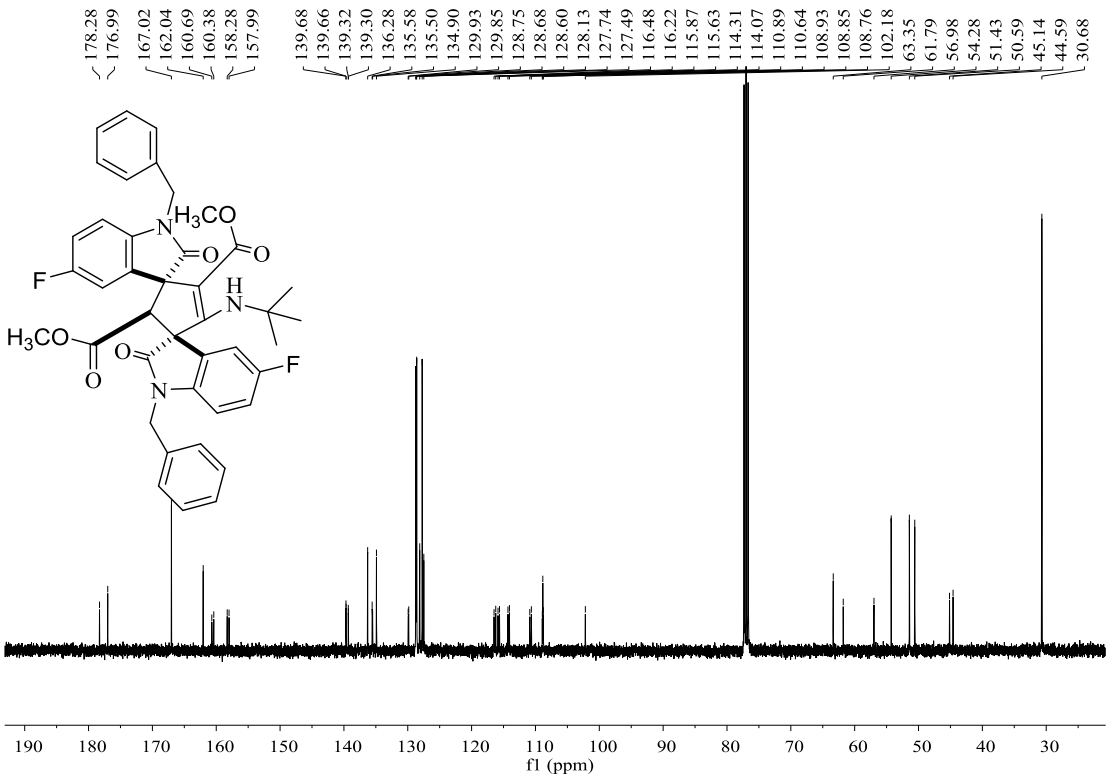



178.21
176.51
166.54
166.34
160.81
142.34
141.98
136.10
135.75
134.95
129.99
129.30
129.21
128.88
128.57
128.33
128.24
127.92
127.80
127.73
127.53
127.49
123.14
109.38
109.26
97.53
61.55
60.90
60.86
58.92
57.25
52.71
45.13
44.63
34.32
33.83
24.97
24.76
13.52
13.13
OCH2CH3
Cl
H3CH2CO
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 0.73min #(43)
814.2425
816.2417
815.2449
817.2438
818.2435
1250
1000
750
500
250
0
810
812
814
816
818
820
m/z

Dimethyl *rel*-(2'*S*,3*S*,3'*S*)-1,1''-dibenzyl-4'-(*tert*-butylamino)-4,5''-difluoro-2,2''-dioxodispiro-[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2',5'-dicarboxylate (3p): ethyl acetate and petroleum ether (v/v = 1:8) as the eluent, white solid, 102 mg, 29%, m.p. 211-213 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.82 (s, 1H, NH), 8.44-8.41 (m, 1H, ArH), 7.48 (d, *J* = 7.2 Hz, 2H, ArH), 7.44 (d, *J* = 7.6 Hz, 2H, ArH), 7.36-7.28 (m, 6H, ArH), 7.13-7.10 (m, 1H, ArH), 6.98-6.93 (m, 1H, ArH), 6.84-6.78 (m, 2H, ArH), 6.60-6.56 (m, 1H, ArH), 5.41 (d, *J* = 15.2 Hz, 1H, CH_2), 5.24 (d, *J* = 15.6 Hz, 1H, CH_2), 4.69 (d, *J* = 15.6 Hz, 1H, CH_2), 4.46 (d, *J* = 15.2 Hz, 1H, CH_2), 4.24 (s, 1H, CH), 3.21 (s, 3H, OCH_3), 2.74 (s, 3H, OCH_3), 0.99 (s, 9H, CH_3); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 178.3, 177.0, 167.0, 162.0, 160.5 (d, *J* = 30.8 Hz), 158.1 (d, *J* = 28.5 Hz), 139.7, 139.7, 139.3, 139.2, 136.3, 135.6, 135.5, 134.9, 129.9 (d, *J* = 8.9 Hz), 128.8, 128.7, 128.6, 128.1, 127.7, 127.5, 116.4 (d, *J* = 26.3 Hz), 115.8 (d, *J* = 23.8 Hz), 114.2 (d, *J* = 23.4 Hz), 110.8 (d, *J* = 24.7 Hz), 108.9, 108.8, 102.2, 63.4, 61.8, 57.0, 54.3, 51.4, 50.6, 45.1, 44.6, 30.7; IR (KBr) υ: 3271, 3189, 3063, 2977, 2932, 2852, 2361, 1735, 1666, 1608, 1483, 1454, 1430, 1364, 1334, 1303, 1224, 1194, 1162, 1135, 1112, 1079, 1034, 961, 903, 887, 871, 852, 805, 789, 743, 701, 630, 608 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{41}H_{37}F_2N_3NaO_6$ ([M+Na]$^{+}$): 728.2548, found: 728.2549.




178.28
176.99
167.02
162.04
160.69
160.38
158.28
157.99
139.68
139.66
139.32
139.30
136.28
135.58
135.50
134.90
129.93
129.85
128.75
128.68
128.60
128.13
127.74
127.49
116.48
116.22
115.87
115.63
114.31
114.07
110.89
110.64
108.93
108.85
108.76
102.18
63.35
61.79
56.98
54.28
51.43
50.59
45.14
44.59
30.68
H3CO
O
O
F
H
N
H3CO
O
O
F
N
190
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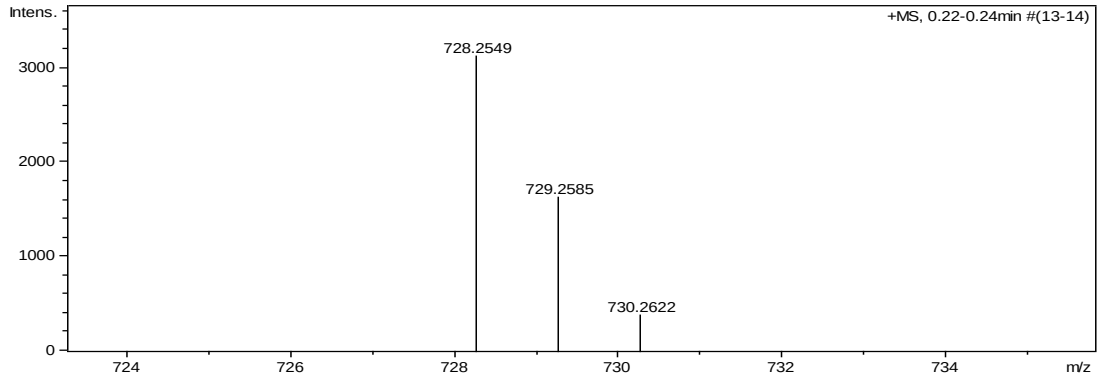
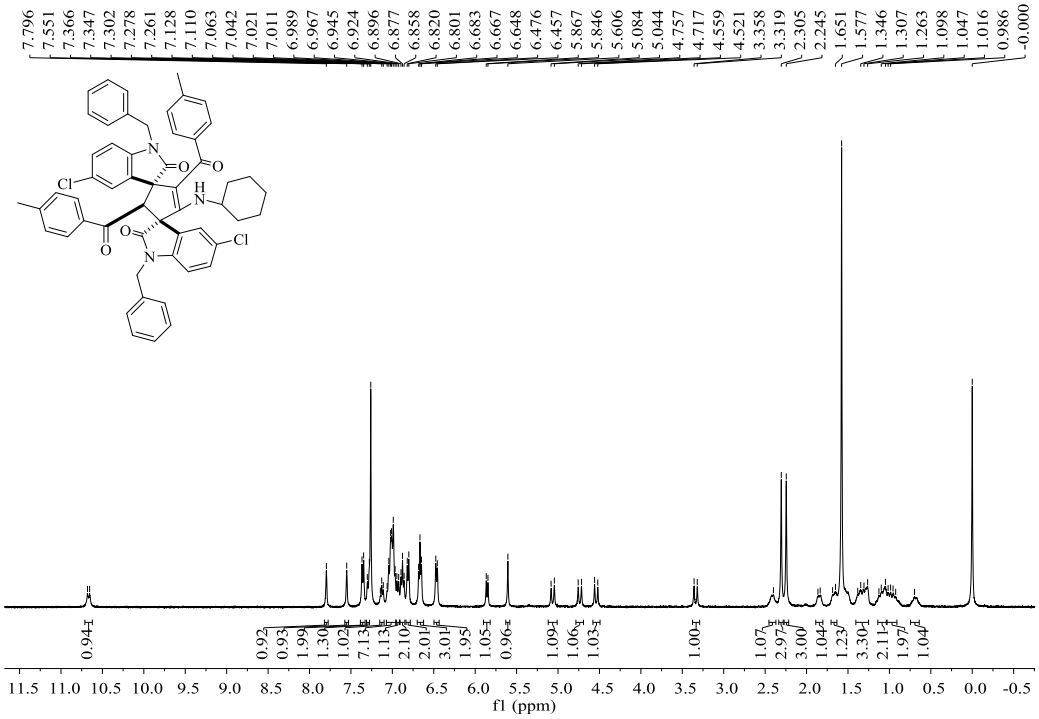
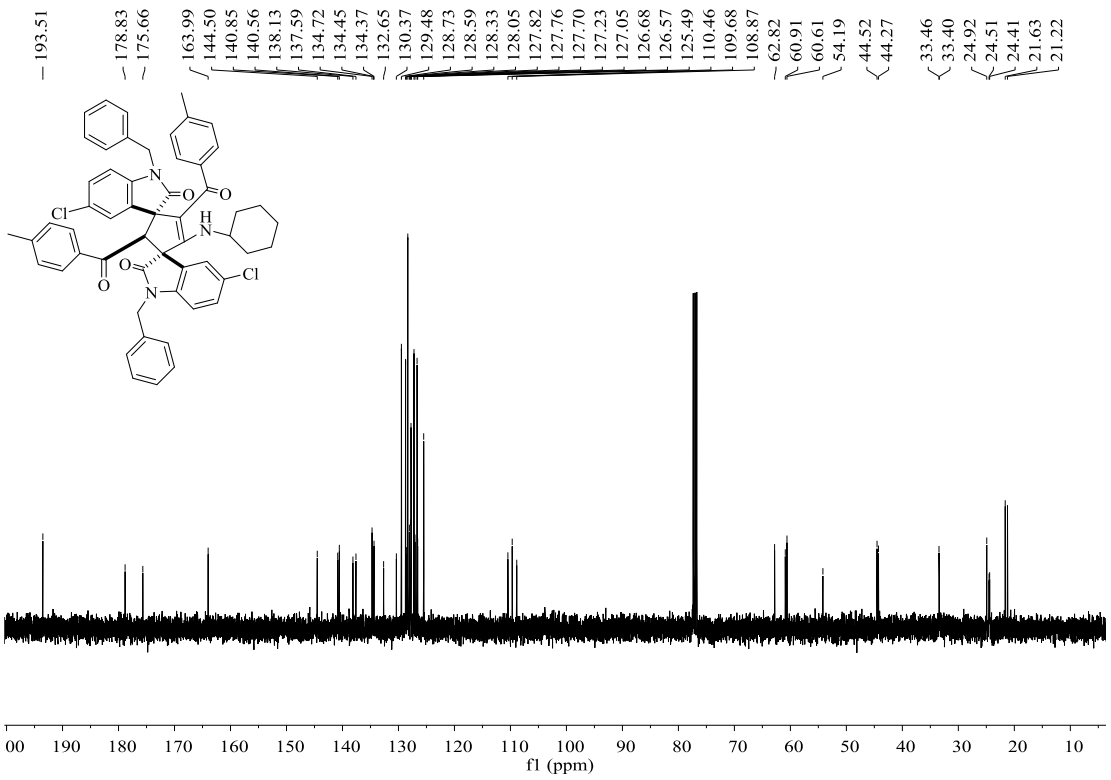
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


Intens.
+MS, 0.22-0.24min #(13-14)
728.2549
729.2585
730.2622
3000
2000
1000
0
724
726
728
730
732
734
m/z

***rel*-(2'*S*,3*R*,3'*S*)-1,1''-dibenzyl-5,5''-dichloro-4'-(cyclohexylamino)-2',5'-bis(4-methylbenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3a'):**

white solid, 36%, m.p. 253-255 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.67 (d, *J* = 10.4 Hz, 1H, NH), 7.80 (s, 1H, ArH), 7.55 (s, 1H, ArH), 7.36 (d, *J* = 7.6 Hz, 2H, ArH), 7.29 (d, *J* = 9.6 Hz 1H, ArH), 7.13 (t, *J* = 7.0 Hz, 1H, ArH), 7.06-6.97 (m, 7H, ArH), 6.93 (d, *J* = 8.4 Hz, 1H, ArH), 6.88 (t, *J* = 7.6 Hz, 2H, ArH), 6.81 (d, *J* = 7.6 Hz, 2H, ArH), 6.67 (t, *J* = 7.0 Hz, 3H, ArH), 6.47 (d, *J* = 7.6 Hz, 2H, ArH), 5.86 (d, *J* = 8.4 Hz, 1H, ArH), 5.61 (s, 1H, CH), 5.06 (d, *J* = 16.0 Hz, 1H, CH_2), 4.74 (d, *J* = 16.0 Hz, 1H, CH_2), 4.54 (d, *J* = 15.2 Hz, 1H, CH_2), 3.34 (d, *J* = 15.6 Hz, 1H, CH_2), 2.40 (s, 1H, CH), 2.31 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 1.85 (d, *J* = 11.2 Hz, 1H, CH_2), 1.67 (d, *J* = 14.0 Hz, 1H, CH_2), 1.38-1.26 (m, 3H, CH_2), 1.13-1.05 (m, 2H, CH_2), 1.02-0.92 (m, 2H, CH_2), 0.70 (s, 1H, CH_2); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 193.5, 178.8, 175.7, 164.0, 144.5, 140.9, 140.6, 138.1, 137.6, 134.7, 134.5, 134.4, 132.7, 130.4, 129.5, 128.7, 128.6, 128.3, 128.1, 127.8, 127.7, 127.2, 127.1, 126.7, 126.6, 125.5, 110.5, 109.7, 108.9, 62.8, 60.9, 60.6, 54.2, 44.5, 44.3, 33.5, 33.4, 24.9, 24.5, 24.4, 21.6, 21.2; IR (KBr) υ: 3645, 3148, 3072, 3030, 2955, 2899, 2360, 1746, 1721, 1660, 1616, 1489, 1449, 1333, 1295, 1264, 1237, 1222, 1196, 1174, 1124, 1081, 1030, 989, 939, 914, 892, 811, 775, 737, 701, 653, 619 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{55}H_{47}Cl_2N_3NaO_4$ ([M+Na]$^+$): 906.2841, found: 906.2823.




193.51
178.83
175.66
163.99
144.50
140.85
140.56
138.13
137.59
134.72
134.45
134.37
132.65
130.37
129.48
128.73
128.59
128.33
128.05
127.82
127.76
127.70
127.23
127.05
126.68
126.57
125.49
110.46
109.68
108.87
62.82
60.91
60.61
54.19
44.52
44.27
33.46
33.40
24.92
24.51
24.41
21.63
21.22
Cl
Cl
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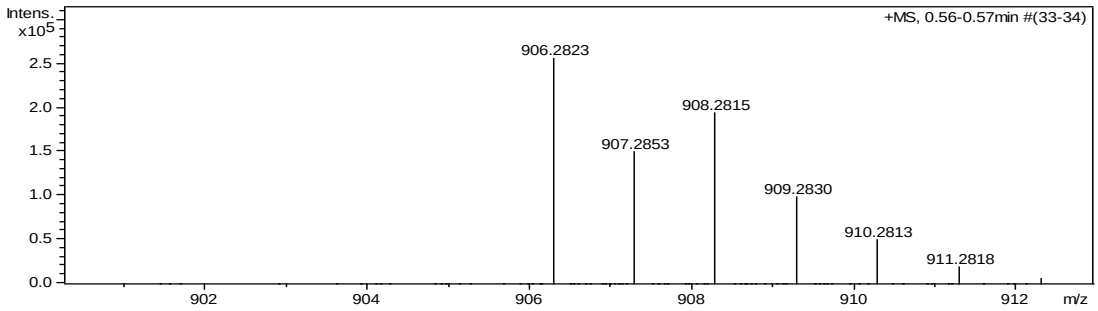
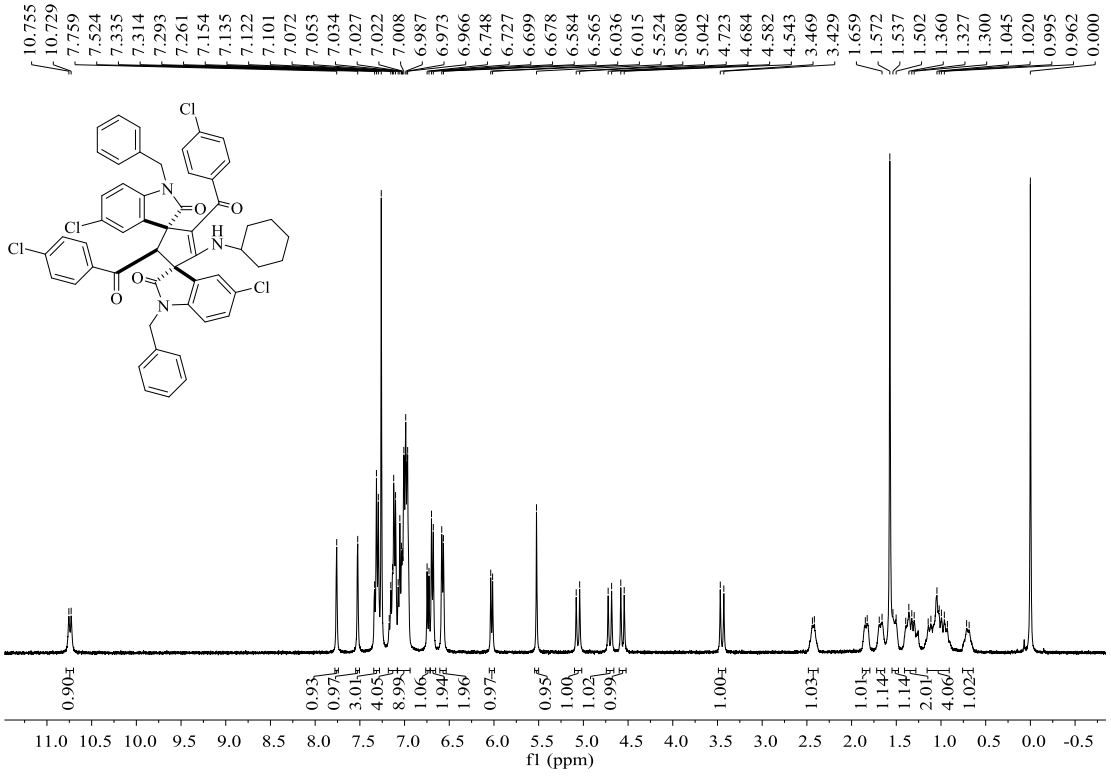
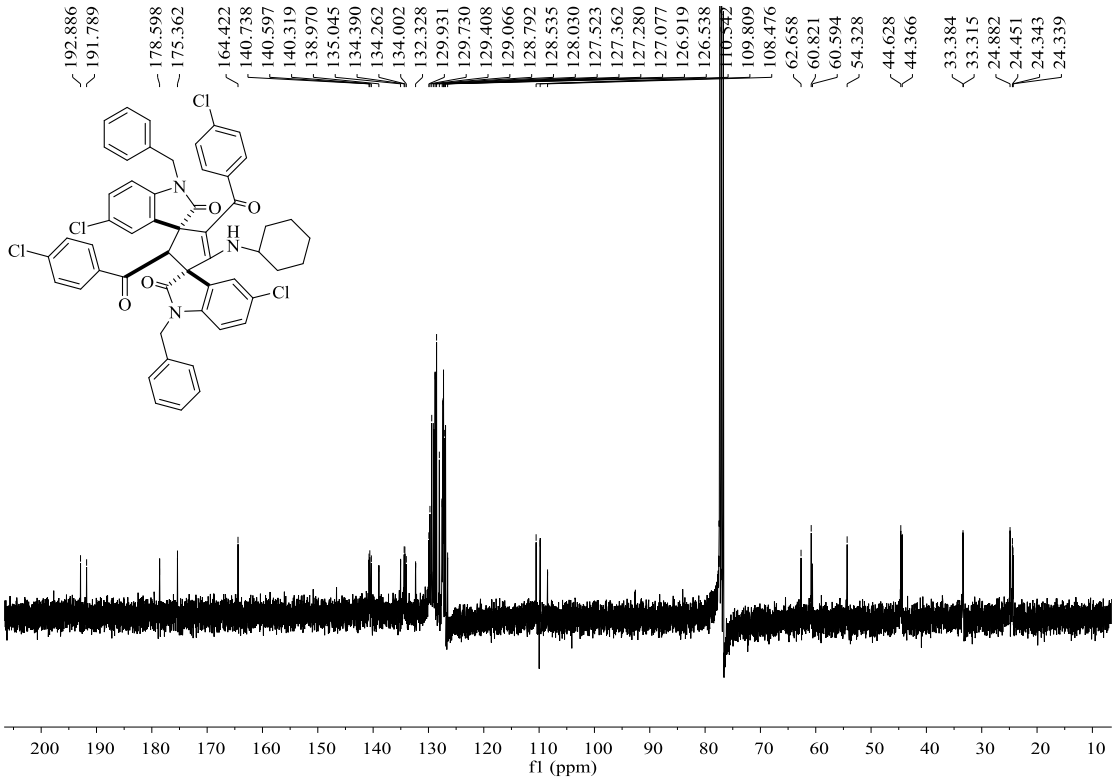
O
O
O
N
N
H
N
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
x10^5
2.5
2.0
1.5
1.0
0.5
0.0
+MS, 0.56-0.57min #(33-34)
906.2823
908.2815
907.2853
909.2830
910.2813
911.2818
902
904
906
908
910
912
m/z

***rel*-(2'*S*,3*S*,3'*S*)-1,1''-dibenzyl-4'',5-dichloro-2',4'-bis(4-chlorobenzoyl)-5'-(cyclohexylamineo)-dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3b'):** white solid, 28%, m.p. 262-264 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.74 (d, *J* = 10.4 Hz, 1H, NH), 7.76 (s, 1H, ArH), 7.52 (s, 1H, ArH), 7.34-7.29 (m, 3H, ArH), 7.17-7.10 (m, 4H, ArH), 7.07-6.97 (m, 9H, ArH), 6.74 (d, *J* = 8.4 Hz, 1H, ArH), 6.69 (d, *J* = 8.4 Hz, 2H, ArH), 6.57 (d, *J* = 7.6 Hz, 2H, ArH), 6.03 (d, *J* = 8.4 Hz, 1H, ArH), 5.52 (s, 1H, CH), 5.06 (d, *J* = 15.2 Hz, 1H, CH_2), 4.70 (d, *J* = 15.6 Hz, 1H, CH_2), 4.56 (d, *J* = 15.6 Hz, 1H, CH_2), 3.45 (d, *J* = 16.0 Hz, 1H, CH_2), 2.44-2.42 (m, 1H, CH), 1.85-1.83 (m, 1H, CH_2), 1.69-1.66 (m, 1H, CH_2), 1.54-1.50 (m, 1H, CH_2), 1.40-1.30 (m, 2H, CH_2), 1.14-0.93 (m, 4H, CH_2), 0.71-0.69 (m, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 192.9, 191.8, 178.6, 175.4, 164.4, 140.7, 140.6, 140.3, 139.0, 135.1, 134.4, 134.3, 134.0, 132.3, 129.9, 129.7, 129.4, 129.1, 128.8, 128.5, 128.0, 127.5, 127.4, 127.3, 127.1, 126.9, 126.5, 110.5, 109.8, 108.5, 62.7, 60.8, 60.6, 54.3, 44.6, 44.4, 33.4, 33.3, 24.9, 24.5, 24.3, 24.3 ppm; IR (KBr) υ: 3514, 3059, 2934, 2860, 1723, 1678, 1610, 1562, 1489, 1449, 1340, 1303, 1265, 1215, 1184, 1136, 1105, 1050, 1021, 1001, 979, 937, 865, 811, 767, 702, 686, 655, 631 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{41}Cl_4N_3NaO_4$ ([M+Na]$^+$): 946.1749, found: 946.1732.




192.886
191.789
178.598
175.362
164.422
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140.597
140.319
138.970
135.045
134.390
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134.002
132.328
129.931
129.730
129.408
129.066
128.792
128.535
128.030
127.523
127.362
127.280
127.077
126.919
126.538
110.342
109.809
108.476
62.658
60.821
60.594
54.328
44.628
44.366
33.384
33.315
24.882
24.451
24.343
24.339
Cl
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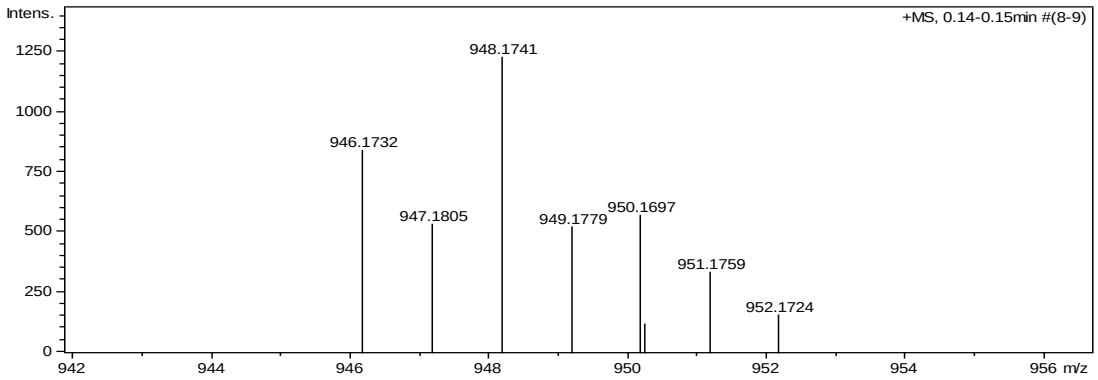
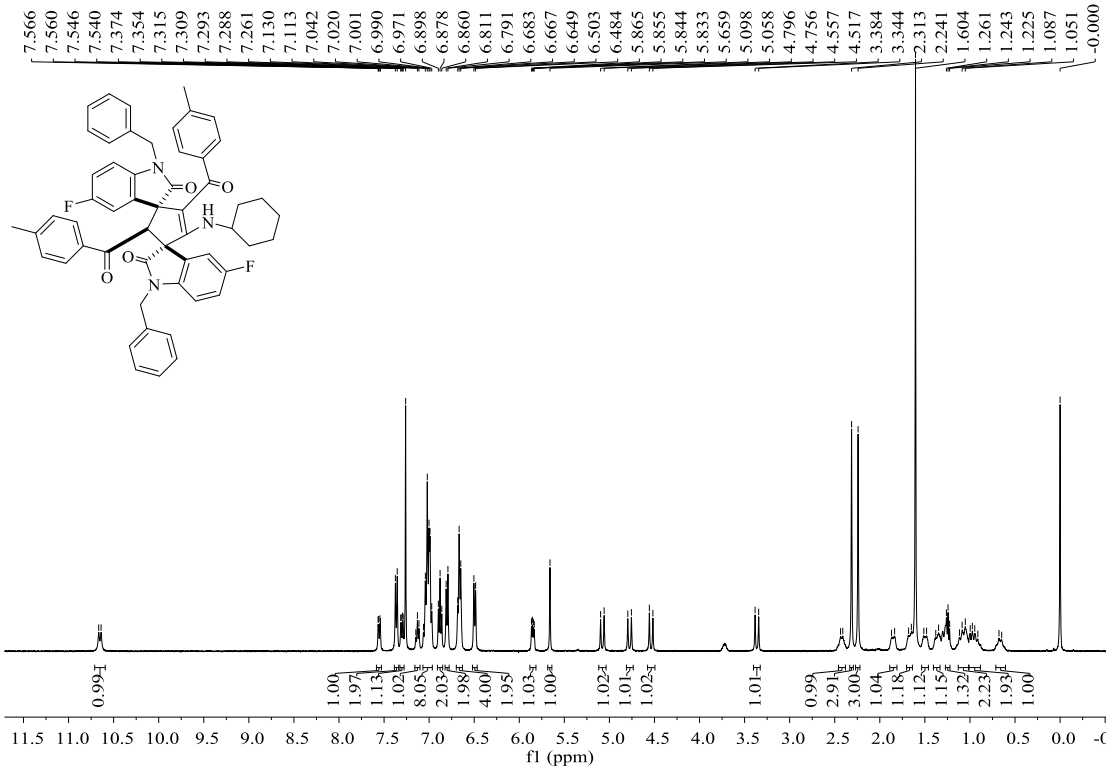
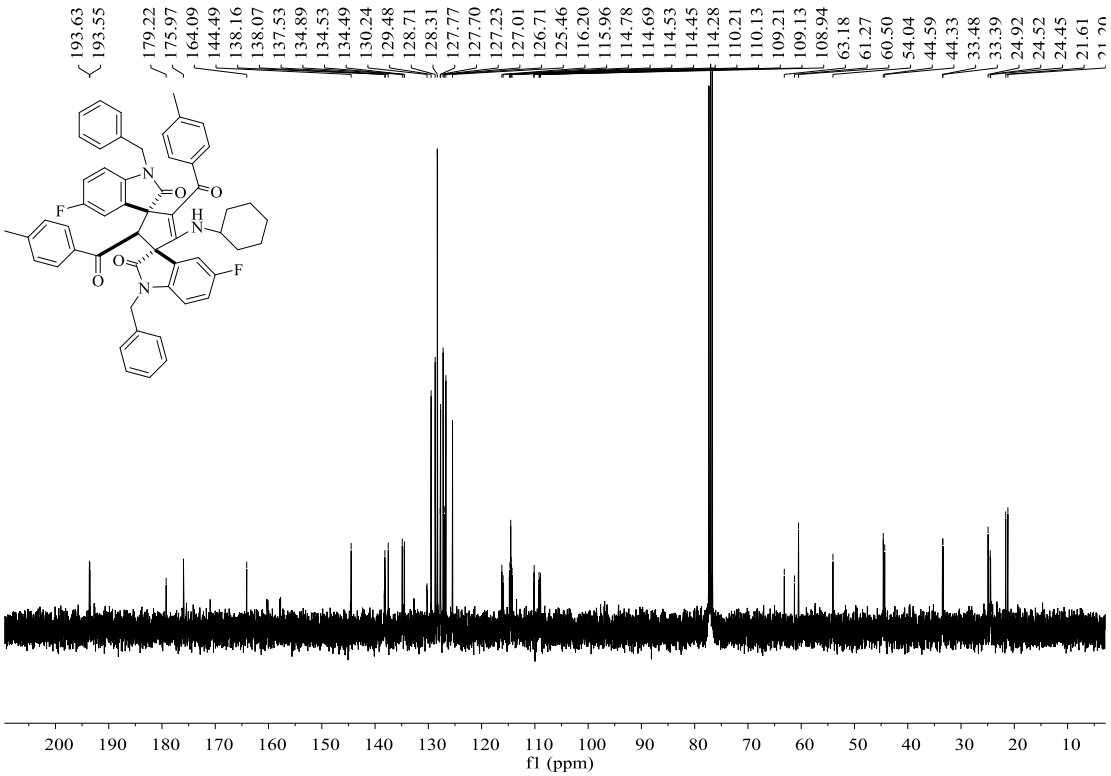
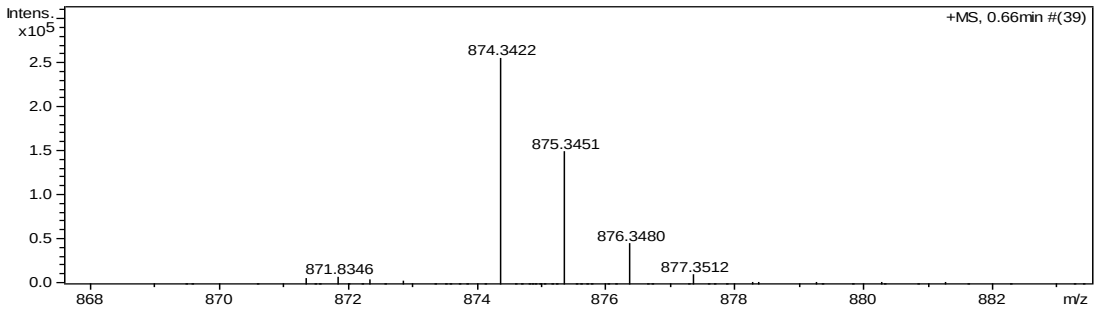
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 0.14-0.15min #(8-9)
1250
1000
750
500
250
0
948.1741
946.1732
947.1805
949.1779
950.1697
951.1759
952.1724
942
944
946
948
950
952
954
956 m/z

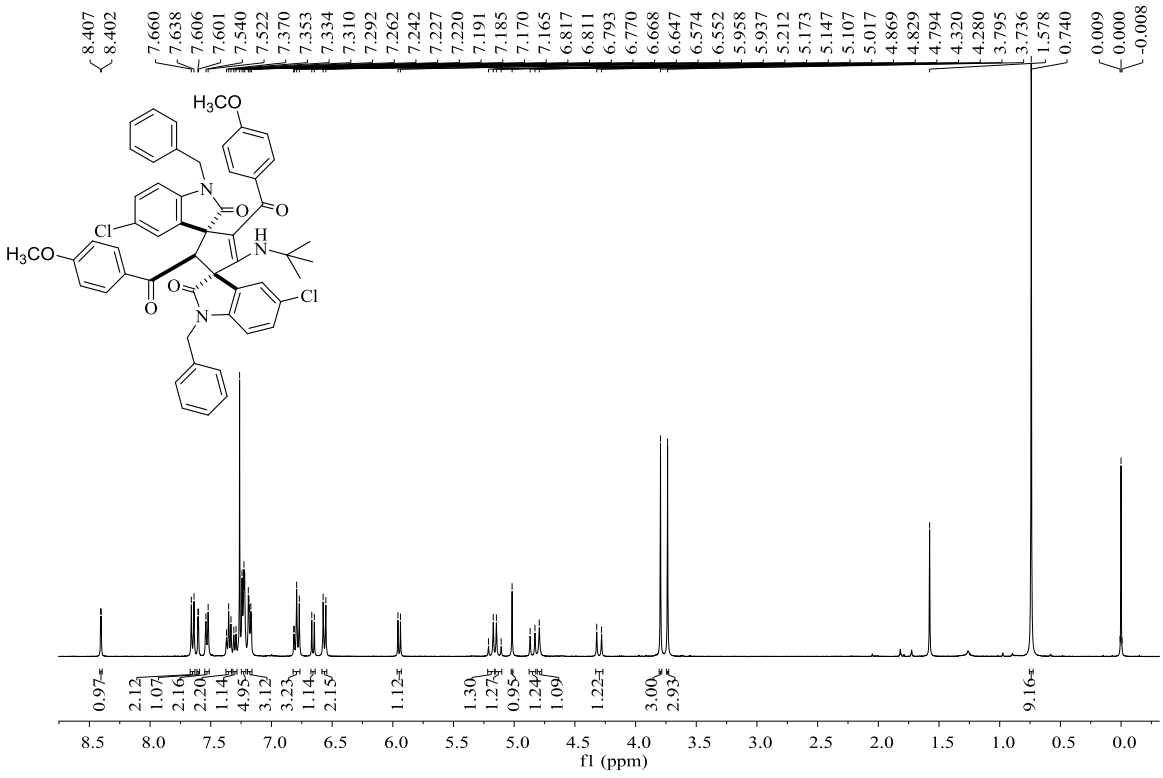
***rel*-(2'*S*,3*S*,3'*S*)-1,1''-dibenzyl-4'-(cyclohexylamino)-4,5''-difluoro-2',5'-bis(4-methyl-benzoyl)dispiro-[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3c'):** white solid, 18%, m.p. 221-223 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.65 (d, *J* = 10.8 Hz, 1H, NH), 7.57-7.54 (m, 1H, ArH), 7.36 (d, *J* = 8.0 Hz, 2H, ArH), 7.32-7.29 (m, 1H, ArH), 7.13 (t, *J* = 6.8 Hz, 1H, ArH), 7.06-6.97 (m, 8H, ArH), 6.88 (t, *J* = 7.6 Hz, 2H, ArH), 6.80 (d, *J* = 8.0 Hz, 2H, ArH), 6.68-6.65 (m, 4H, ArH), 6.49 (d, *J* = 7.6 Hz, 2H, ArH), 5.87-5.83 (m, 1H, ArH), 5.66 (s, 1H, CH), 5.08 (d, *J* = 16.0 Hz, 1H, CH_2), 4.78 (d, *J* = 16.0 Hz, 1H, CH_2), 4.54 (d, *J* = 16.0 Hz, 1H, CH_2), 3.36 (d, *J* = 16.0 Hz, 1H, CH_2), 2.44-2.41 (m, 1H, CH), 2.31 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 1.87-1.84 (m, 1H, CH_2), 1.68-1.65 (m, 1H, CH_2), 1.51-1.48 (m, 1H, CH_2), 1.38-1.35 (m, 1H, CH_2), 1.26-1.23 (m, 1H, CH_2), 1.12-1.05 (m, 2H, CH_2), 1.00-0.91 (m, 2H, CH_2), 0.68-0.65 (m, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 193.6, 193.5, 179.2, 176.0, 164.1, 160.2 (d, *J* = 18.5 Hz), 157.8 (d, *J* = 15.3 Hz), 144.5, 138.2 (d, *J* = 19.7 Hz), 137.5, 134.9, 134.5, 134.4, 130.3, 130.2, 129.5, 128.7, 128.3, 127.8, 127.7, 127.2, 127.0, 126.7, 125.5, 116.1 (d, *J* = 23.9 Hz), 114.8, 114.7, 114.5, 114.3, 110.2 (d, *J* = 7.5 Hz), 109.2 (d, *J* = 8.1 Hz), 108.9, 63.2, 61.3, 60.5, 54.0, 44.6, 44.3, 33.5, 33.4, 24.9, 24.5, 24.4, 21.6, 21.2 ppm; IR (KBr) υ: 3671, 3064, 2933, 2853, 2361, 1719, 1674, 1602, 1511, 1489, 1451, 1338, 1301, 1265, 1246, 1174, 1079, 1027, 982, 949, 873, 840, 808, 777, 735, 697, 656, 603 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{55}H_{47}F_2N_3NaO_4$ ([M+Na]$^+$): 874.3432, found: 874.3422.

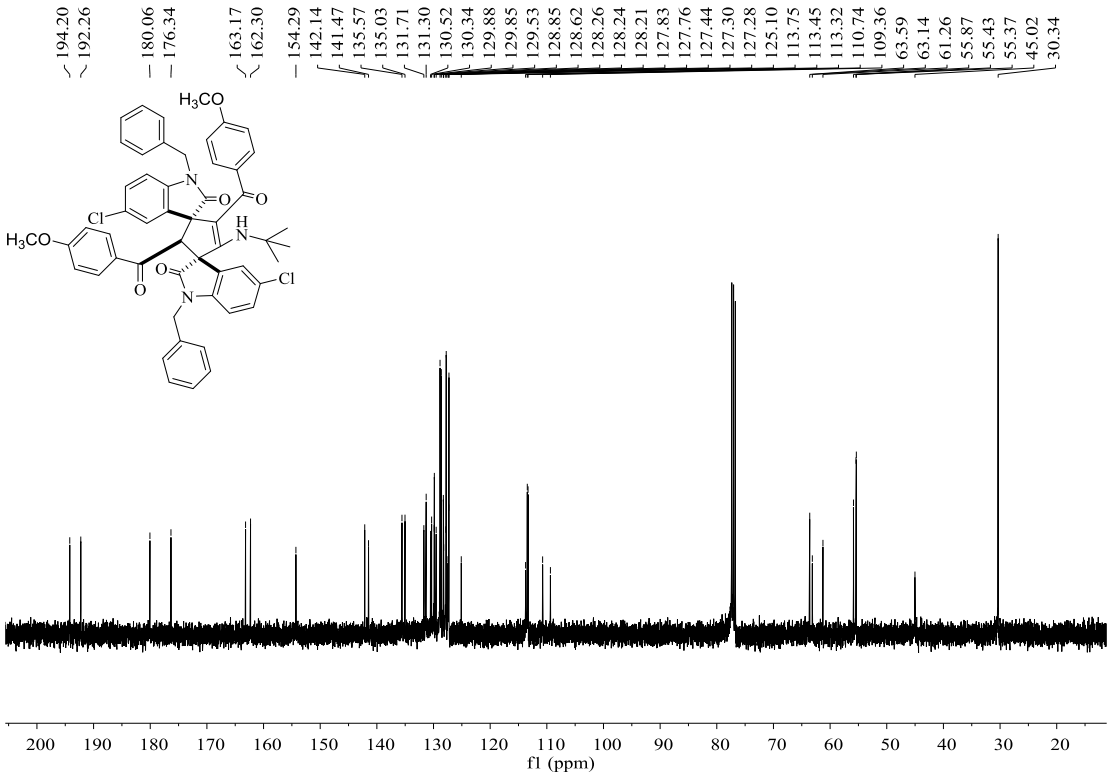


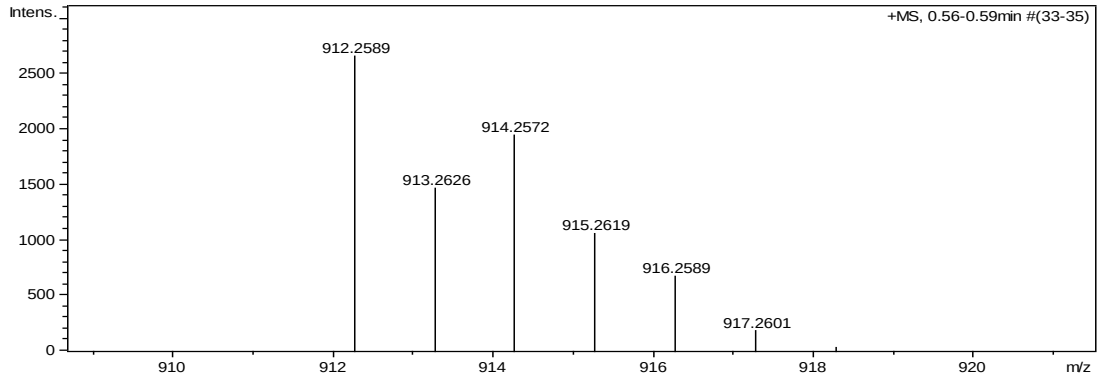

193.63
193.55
179.22
175.97
164.09
144.49
138.16
138.07
137.53
134.89
134.53
134.49
130.24
129.48
128.71
128.31
127.77
127.70
127.23
127.01
126.71
125.46
116.20
115.96
114.78
114.69
114.53
114.45
114.28
110.21
110.13
109.21
109.13
108.94
63.18
61.27
60.50
54.04
44.59
44.33
33.48
33.39
24.92
24.52
24.45
21.61
F
O
O
N
H
N
O
O
F
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
x10^5
2.5
2.0
1.5
1.0
0.5
0.0
+MS, 0.66min #(39)
874.3422
875.3451
876.3480
877.3512
871.8346
868
870
872
874
876
878
880
882
m/z

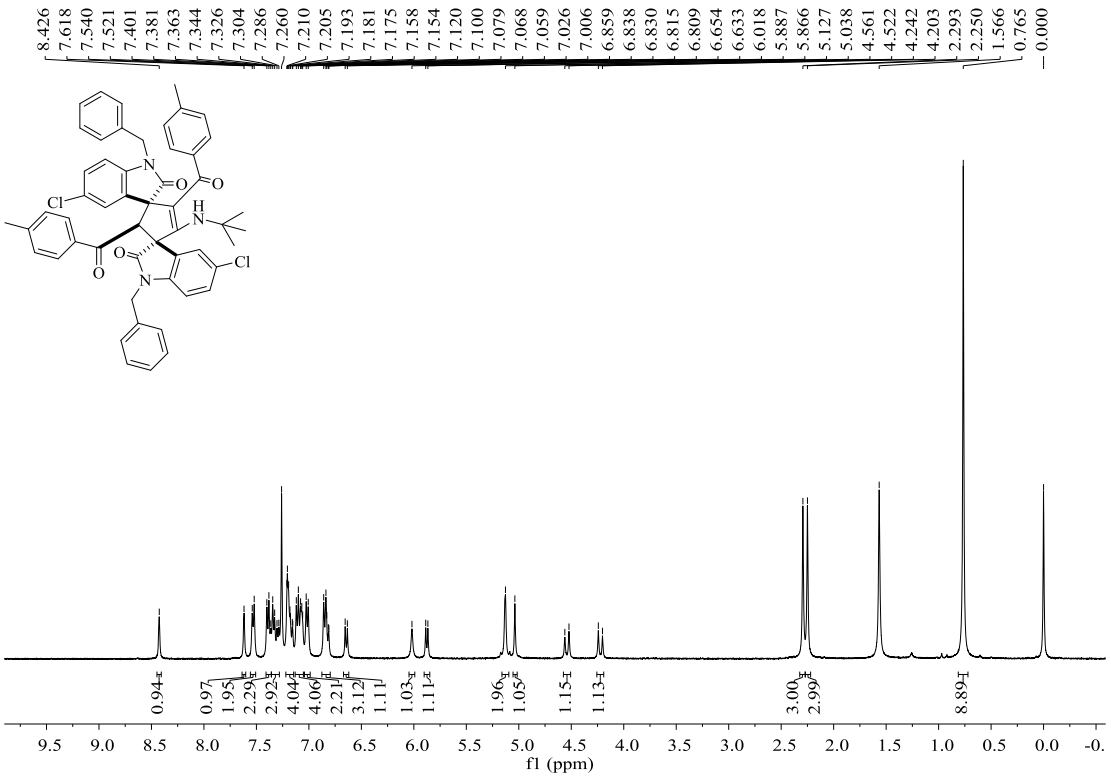
***rel*-(2'*S*,3*R*,3'*S*)-1,1''-dibenzyl-4'-(*tert*-butylamino)-5,5''-dichloro-2',5'-bis(4-methoxybenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3d'):** white solid, 30%, m.p. 273-275 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41-8.40 (m, 1H, ArH), 7.65 (d, *J* = 8.8 Hz, 2H, ArH), 7.61-7.60 (m, 1H, ArH), 7.53 (d, *J* = 7.2 Hz, 2H, ArH), 7.35 (t, *J* = 7.2 Hz, 2H, ArH), 7.30 (d, *J* = 8.0 Hz, 1H, ArH), 7.24-7.22 (m, 5H, ArH), 7.19-7.17 (m, 3H, ArH), 6.82-6.77 (m, 3H, ArH), 6.66 (d, *J* = 8.4 Hz, 1H, ArH), 6.56 (d, *J* = 8.8 Hz, 2H, ArH), 5.95 (d, *J* = 8.4 Hz, 1H, CH_2), 5.21-5.17 (m, 1H, CH_2), 5.15-5.11 (m, 1H, CH_2), 5.02 (s, 1H, CH), 4.85 (d, *J* =16.0 Hz, 1H, CH_2), 4.79 (s, 1H, NH), 4.30 (d, *J* = 16.0 Hz, 1H, CH_2), 3.79 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 0.74 (s, 9H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 194.2, 192.3, 180.1, 176.3, 163.2, 162.3, 154.3, 142.1, 141.5, 135.6, 135.0, 131.7, 131.3, 130.5, 130.3, 129.9, 129.8, 129.5, 128.9, 128.6, 128.3, 128.2, 128.1, 127.8, 127.7, 127.4, 127.3, 127.2, 125.1, 113.8, 113.5, 113.3, 110.7, 109.4, 63.6, 63.1, 61.3, 55.9, 55.4, 55.3, 45.0, 30.3 ppm; IR (KBr) υ: 3376, 2935, 2289, 2108, 2082, 1893, 1717, 1598, 1510, 1484, 1427, 1326, 1254, 1224, 1171, 1118, 1078, 1013, 848, 808, 738, 692, 644 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{45}Cl_2N_3NaO_6$ ([M+Na]$^+$): 912.2583, found: 912.2589.

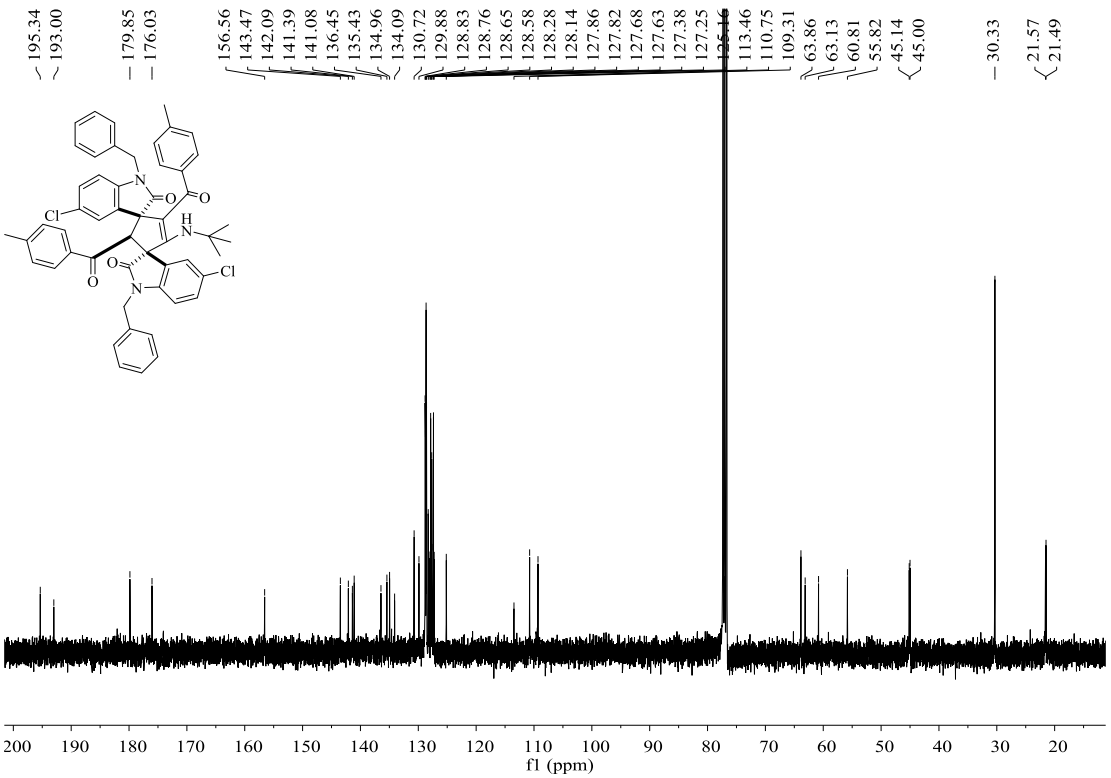



194.20
192.26
180.06
176.34
163.17
162.30
154.29
142.14
141.47
135.57
135.03
131.71
131.30
130.52
130.34
129.88
129.85
129.53
128.85
128.62
128.26
128.24
128.21
127.83
127.76
127.44
127.30
127.28
125.10
113.75
113.45
113.32
110.74
109.36
63.59
63.14
61.26
55.87
55.43
55.37
45.02
30.34
H3CO
Cl
H3CO
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
+MS, 0.56-0.59min #(33-35)
912.2589
914.2572
913.2626
915.2619
916.2589
917.2601
2500
2000
1500
1000
500
0
910
912
914
916
918
920
m/z

***rel*-(2'*S*,3*R*,3'*S*)-1,1''-dibenzyl-4'-(*tert*-butylamino)-5,5''-dichloro-2',5'-bis(4-methylbenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3e'):** white solid, 33%, m.p. 274-276 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43 (s, 1H, ArH), 7.62 (s, 1H, ArH), 7.53 (d, *J* = 7.6 Hz, 2H, ArH), 7.40-7.36 (m, 2H, ArH), 7.34-7.29 (m, 3H, ArH), 7.21-7.15 (m, 4H, ArH), 7.12-7.06 (m, 4H, ArH), 7.02 (d, *J* = 8.0 Hz, 2H, ArH), 6.86-6.81 (m, 3H, ArH), 6.64 (d, *J* = 8.4 Hz, 1H, ArH), 6.02 (s, 1H, ArH), 5.88 (d, *J* = 8.4 Hz, 1H, NH), 5.13 (s, 2H, CH_2), 5.04 (s, 1H, CH), 4.54 (d, *J* =15.6 Hz, 1H, CH_2), 4.22 (d, *J* =15.6 Hz, 1H, CH_2), 2.29 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 0.76 (s, 9H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 195.3, 193.0, 179.9, 176.0, 156.6, 143.5, 142.1, 141.4, 141.1, 136.5, 135.4, 135.0, 134.1, 130.7, 129.9, 128.8, 128.7, 128.6, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.4, 127.3, 125.2, 113.5, 110.8, 109.3, 63.9, 63.1, 60.8, 55.8, 45.1, 45.0, 30.3, 21.6, 21.5 ppm; IR (KBr) υ: 3367, 2960, 2162, 1702, 1605, 1524, 1474, 1427, 1387, 1329, 1254, 1174, 1081, 1014, 995, 813, 755, 736, 691 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{45}Cl_2N_3NaO_4$ ([M+Na]$^{+}$): 880.2679, found: 880.2708.




195.34
193.00
179.85
176.03
156.56
143.47
142.09
141.39
141.08
136.45
135.43
134.96
134.09
130.72
129.88
128.83
128.76
128.65
128.58
128.28
128.14
127.86
127.82
127.68
127.63
127.38
127.25
125.16
113.46
110.75
109.31
63.86
63.13
60.81
55.82
45.14
45.00
30.33
21.57
21.49
Cl
Cl
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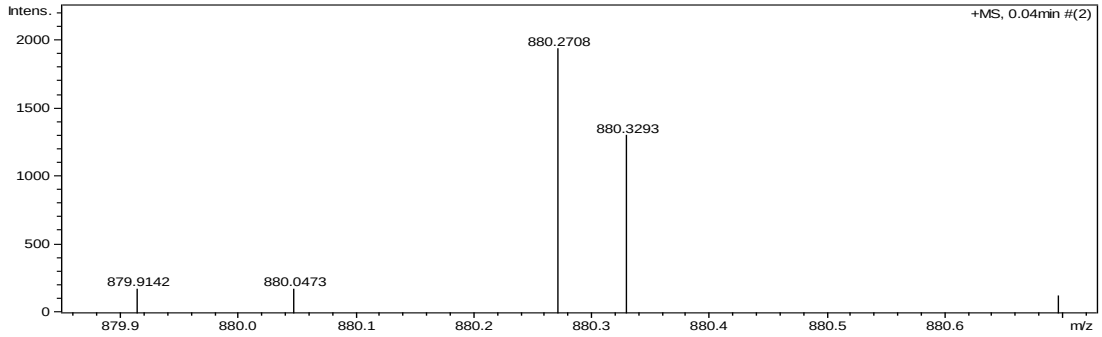
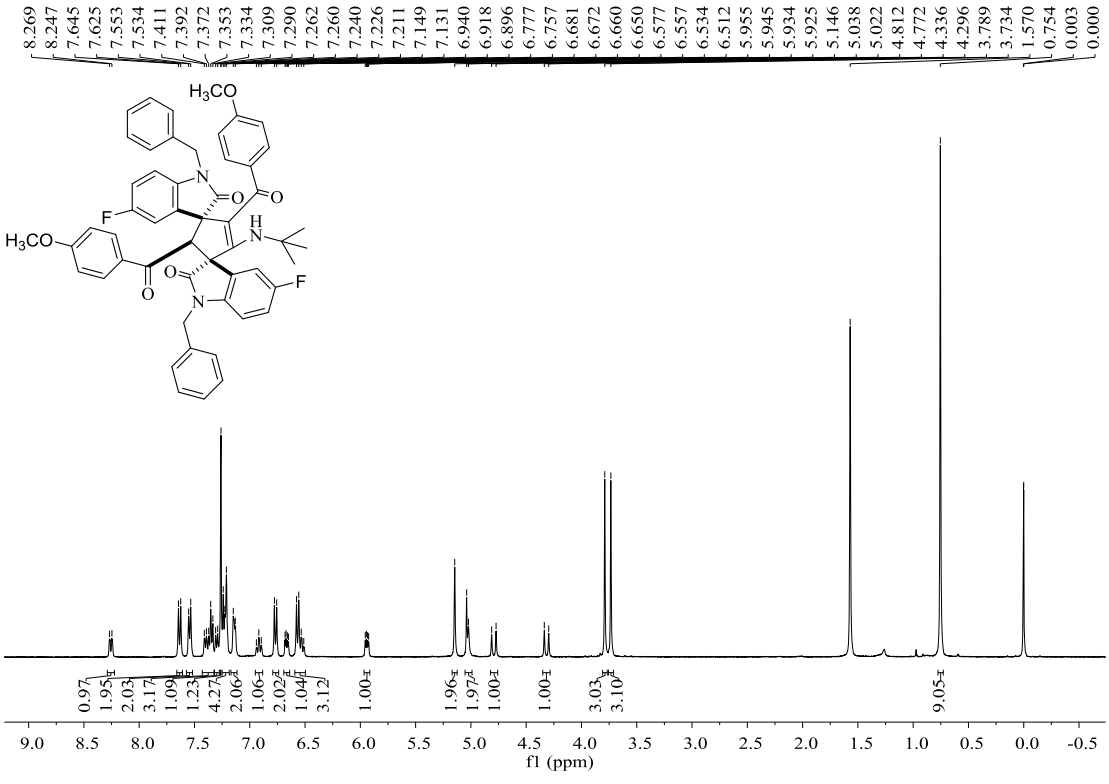
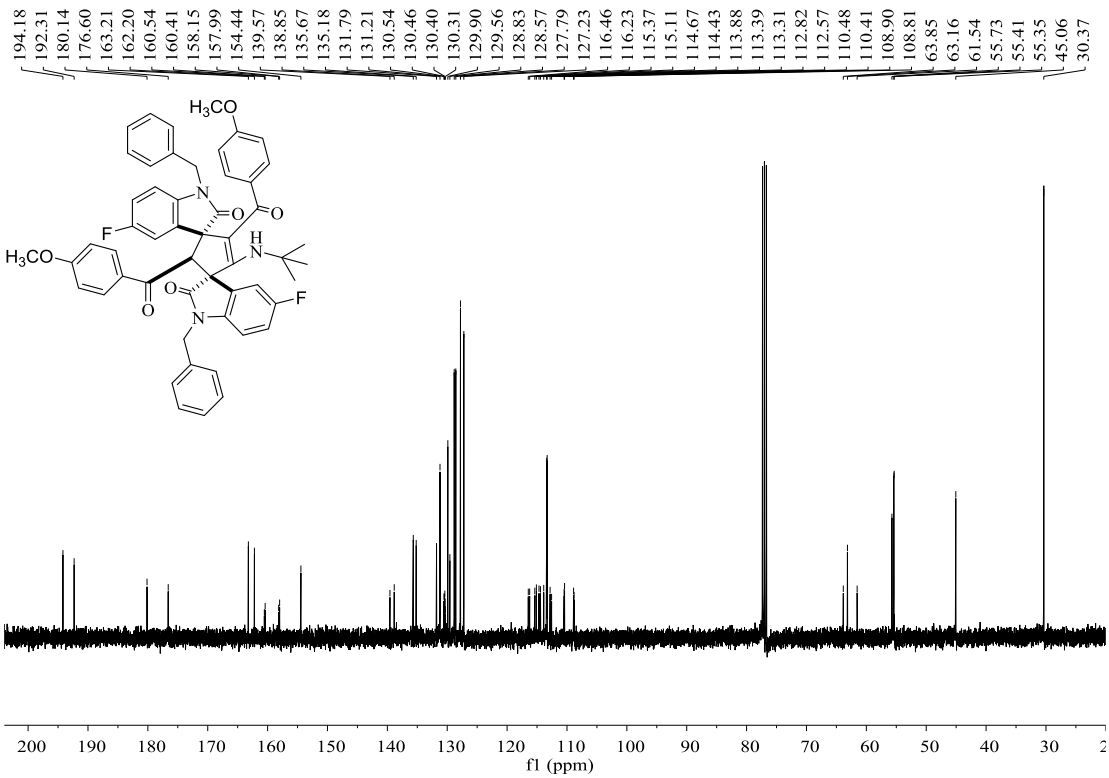
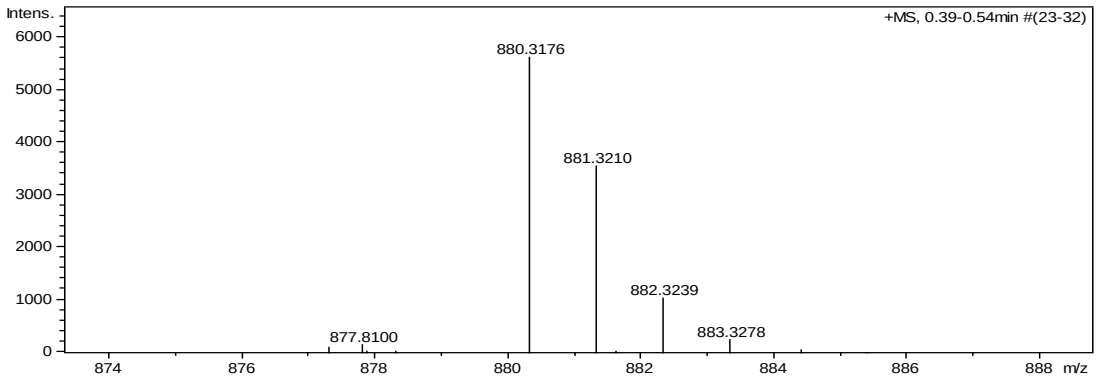
O
O
H
N
O
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
+MS, 0.04min #(2)
2000
1500
1000
500
0
880.2708
880.3293
879.9142
880.0473
879.9 880.0 880.1 880.2 880.3 880.4 880.5 880.6
m/z

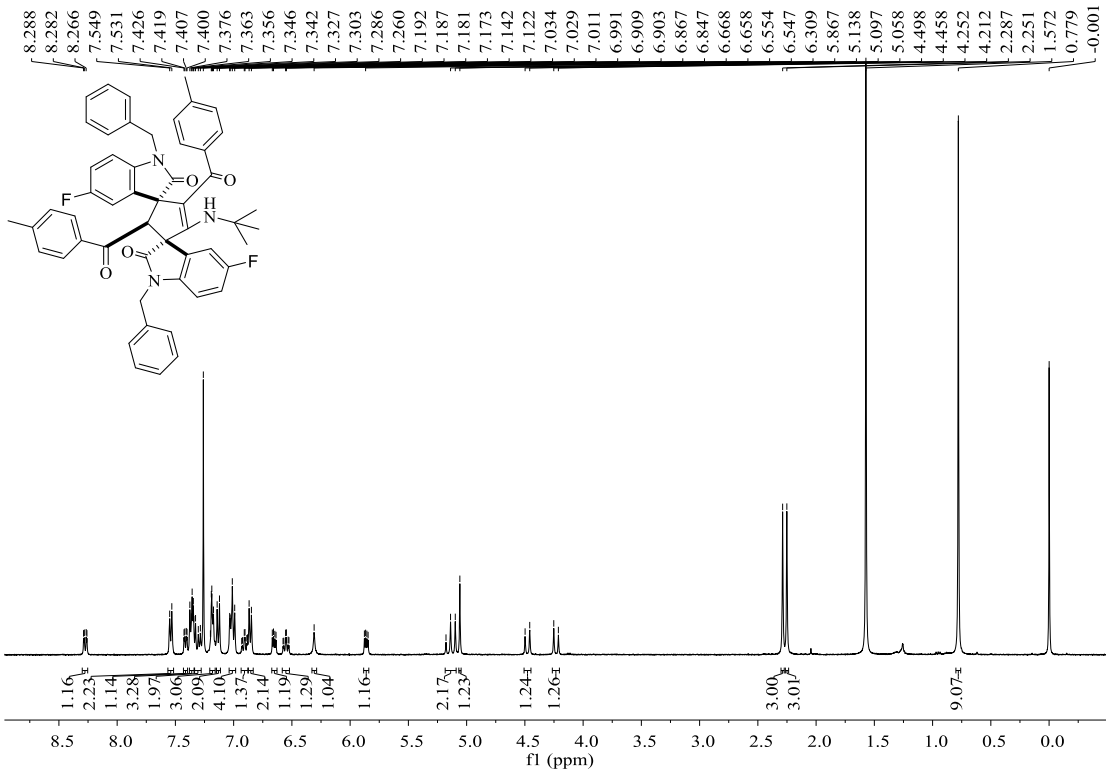
***rel*-(2'*S*,3*R*,3'*S*)-1,1''-dibenzyl-4'-(*tert*-butylamino)-5,5''-difluoro-2',5'-bis(4-methoxybenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3f'):** white solid, 37%, m.p. 230-232 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (d, *J* = 8.8 Hz, 1H, ArH), 7.63 (d, *J* = 8.0 Hz, 2H, ArH), 7.54 (d, *J* = 7.6 Hz, 2H, ArH), 7.41-7.33 (m, 3H, ArH), 7.31-7.29 (m, 1H, ArH), 7.26 (s, 1H, ArH), 7.24-7.21 (m, 4H, ArH), 7.15-7.13 (m, 2H, ArH), 6.92 (t, *J* = 8.8 Hz, 1H, ArH), 6.77 (d, *J* = 8.0 Hz, 2H, ArH), 6.68-6.65 (m, 1H, ArH), 6.58-6.51 (m, 3H, ArH), 5.96-5.93 (m, 1H, ArH), 5.15 (s, 2H, CH_2), 5.04-5.02 (m, 2H, CH, NH), 4.79 (d, *J* = 16.0 Hz, 1H, CH_2), 4.32 (d, *J* = 16.0 Hz, 1H, CH_2), 3.79 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 0.75 (s, 9H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 194.2, 192.3, 180.1, 176.6, 163.2, 162.2, 160.5 (d, *J* = 13.7 Hz), 158.1 (d, *J* = 16.1 Hz), 154.4, 139.6, 138.9, 135.7, 135.2, 131.8, 131.2, 130.5 (d, *J* = 7.7 Hz), 130.4, 130.3, 129.9, 129.6, 128.8, 128.6, 127.8, 127.2, 116.5, 116.2, 115.2 (d, *J* = 26.1 Hz), 114.7, 114.4, 113.9, 113.4, 113.3, 112.7 (d, *J* = 24.8 Hz), 110.4 (d, *J* = 7.5 Hz), 108.9 (d, *J* = 8.4 Hz), 63.9, 63.2, 61.5, 55.7, 55.4, 55.4, 45.1, 30.4 ppm; IR (KBr) υ: 3361, 3069, 2953, 2909, 2864, 1935, 1869, 1812, 1720, 1682, 1608, 1520, 1486, 1453, 1429, 1360, 1339, 1282, 1240, 1218, 1176, 1155, 1109, 1080, 1029, 989, 912, 895, 875, 834, 816, 777, 755, 736, 695, 649, 623, 606 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{45}F_2N_3NaO_6$ ([M+Na]$^{+}$): 880.3174, found: 880.3176.

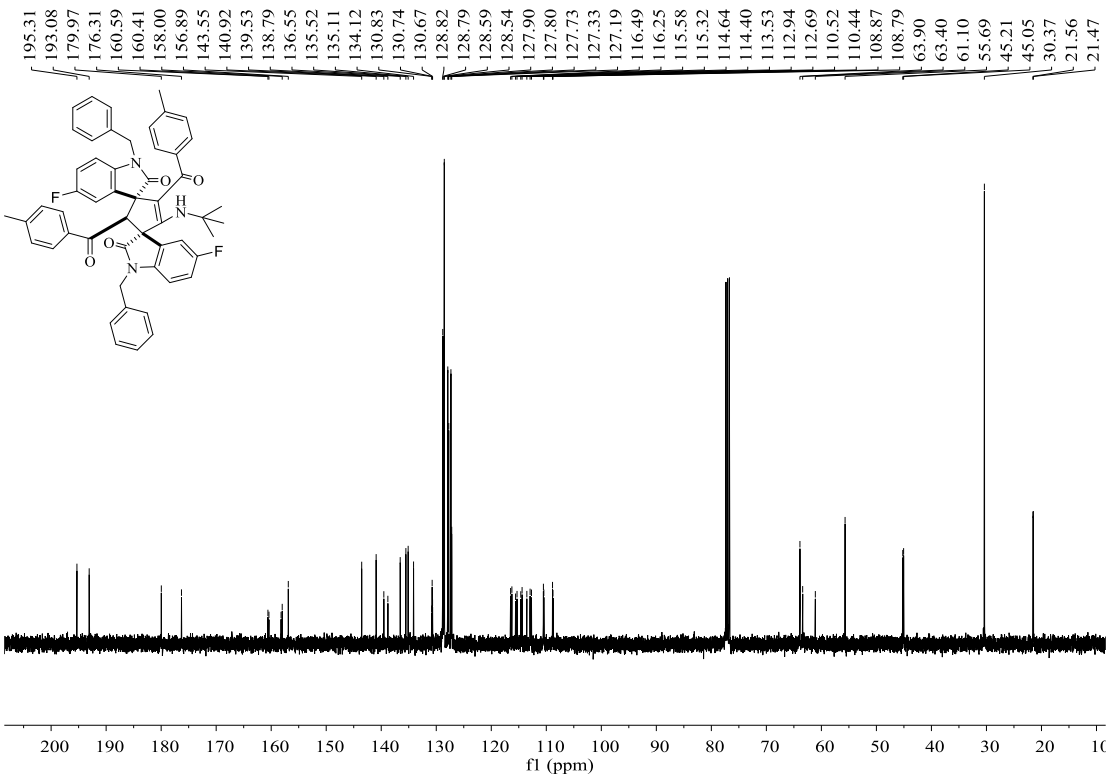


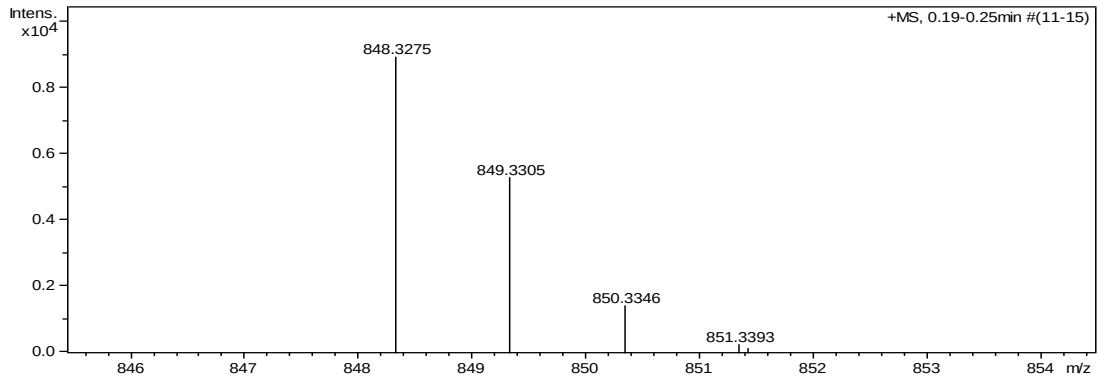

194.18
192.31
180.14
176.60
163.21
162.20
160.54
160.41
158.15
157.99
154.44
139.57
138.85
135.67
135.18
131.79
131.21
130.54
130.46
130.40
130.31
129.90
129.56
128.83
128.57
127.79
127.23
116.46
116.23
115.37
115.11
114.67
114.43
113.88
113.39
113.31
112.82
112.57
110.48
110.41
108.90
108.81
63.85
63.16
61.54
55.73
55.41
55.35
45.06
30.37
H3CO
F
H3CO
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)


Intens.
+MS, 0.39-0.54min #(23-32)
6000
5000
4000
3000
2000
1000
0
880.3176
881.3210
882.3239
883.3278
877.8100
874 876 878 880 882 884 886 888 m/z

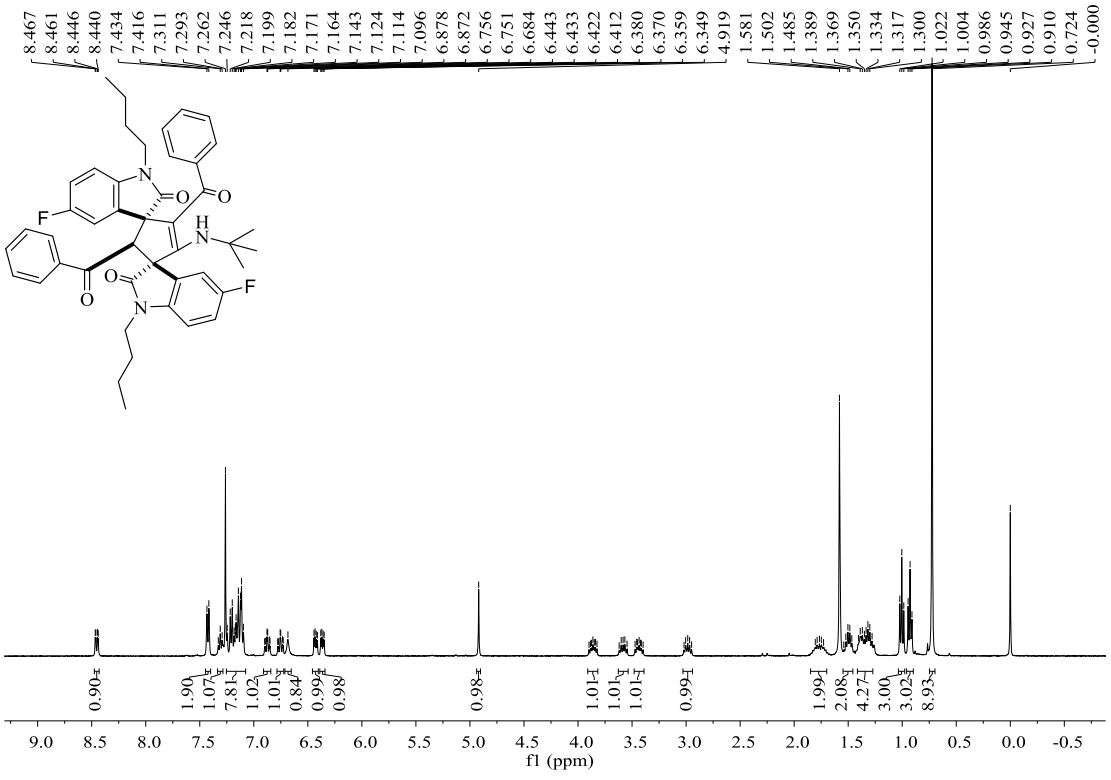
***rel*-(2'*S*,3*R*,3'*S*)-1,1''-dibenzyl-4'-(*tert*-butylamino)-5,5''-difluoro-2',5'-bis(4-methylbenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3g'):** white solid, 34%, m.p. 257-259 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.29-8.26 (m, 1H, NH), 7.54 (d, *J* = 7.2 Hz, 2H, ArH), 7.43-7.40 (m, 1H, ArH), 7.38-7.34 (m, 3H, ArH), 7.33-7.29 (m, 2H, ArH), 7.20-7.17 (m, 3H, ArH), 7.13 (d, *J* = 8.0 Hz, 2H, ArH), 7.03-6.99 (m, 4H, ArH), 6.93-6.88 (m, 1H, ArH), 6.86 (d, *J* = 8.0 Hz, 2H, ArH), 6.67-6.64 (m, 1H, ArH), 6.58-6.53 (m, 1H, ArH), 6.31 (s, 1H, ArH), 5.86 (m, 1H, ArH), 5.18-5.10 (m, 2H, CH_2), 5.06 (s, 1H, CH), 4.48 (d, *J* = 16.0 Hz, 1H, CH_2), 4.23 (d, *J* = 16.0 Hz, 1H, CH_2), 2.29 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 0.78 (s, 9H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 195.3, 193.1, 180.0, 176.3, 160.5 (d, *J* = 18.4 Hz), 158.1 (d, *J* = 20.9 Hz), 156.9, 143.6, 140.9, 139.5, 138.8, 136.6 135.5, 135.1, 134.1, 130.7 (d, *J* = 16.0 Hz), 128.8, 128.7, 128.6, 128.5, 127.9, 127.8, 127.7, 127.3, 127.2, 116.4 (d, *J* = 23.4 Hz), 115.4 (d, *J* = 26.2 Hz), 114.6, 114.4, 113.5, 112.8 (d, *J* = 25.0 Hz), 110.5 (d, *J* = 7.9 Hz), 108.8 (d, *J* = 7.9 Hz), 63.9, 63.4, 61.1, 55.7, 45.2, 45.1, 30.4, 21.6, 21.5 ppm; IR (KBr) υ: 3365, 3072, 2923, 2844, 1714, 1667, 1618, 1600, 1491, 1451, 1393, 1368, 1343, 1314, 1257, 1221, 1166, 1133, 1079, 1024, 995, 972, 897, 880, 846, 825, 810, 772, 740, 726, 697, 647, 618, 603 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{45}F_2N_3NaO_4$ ([M+Na]$^+$): 848.3276, found: 848.3275.

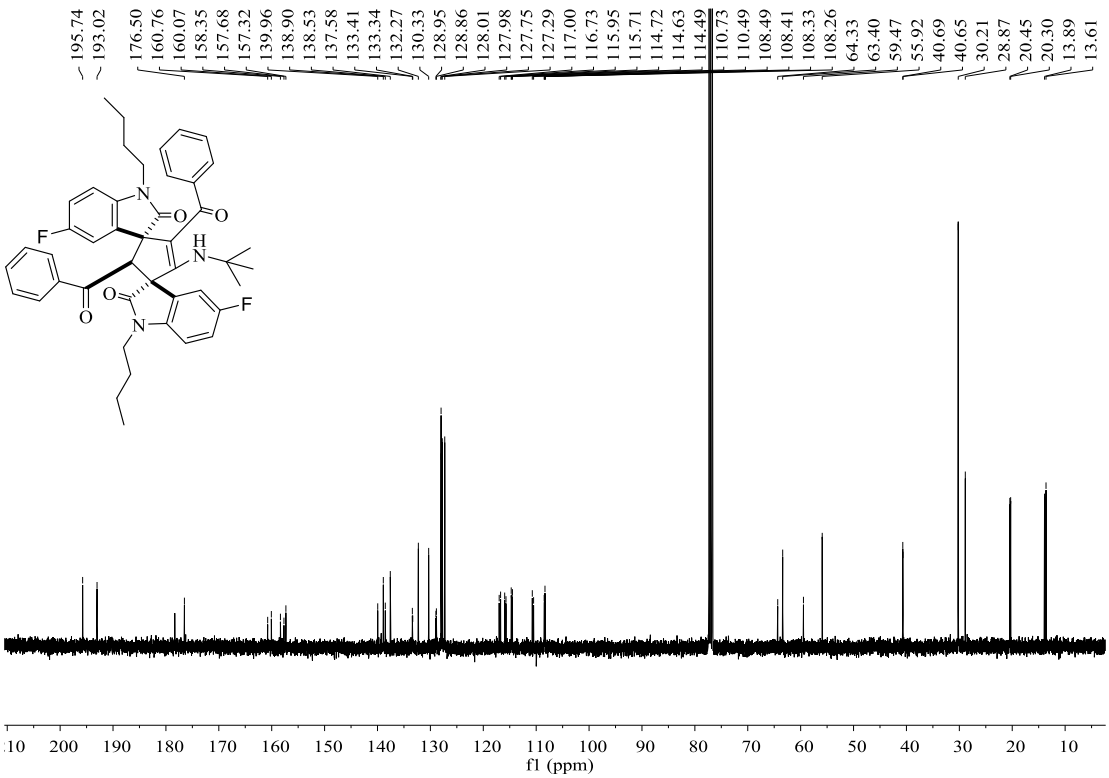



195.31
193.08
179.97
176.31
160.59
160.41
158.00
156.89
143.55
140.92
139.53
138.79
136.55
135.52
135.11
134.12
130.83
130.74
130.67
128.82
128.79
128.59
128.54
127.90
127.80
127.73
127.33
127.19
116.49
116.25
115.58
115.32
114.64
114.40
113.53
112.94
112.69
110.52
110.44
108.87
108.79
63.90
63.40
61.10
55.69
45.21
45.05
30.37
21.56
21.47
F
F
O
O
O
O
N
N
H
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
x10^4
+MS, 0.19-0.25min #(11-15)
848.3275
849.3305
850.3346
851.3393
0.0
0.2
0.4
0.6
0.8
846 847 848 849 850 851 852 853 854 m/z

***rel*-(2'*S*,3*S*,3'*R*)-2',4'-dibenzoyl-1,1''-dibutyl-5'-(*tert*-butylamino)-5,5''-difluorodispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3h'):** white solid, 27%, m.p. 227-229 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47-8.44 (m, 1H, NH), 7.42 (d, *J* = 7.2 Hz, 2H, ArH), 7.31 (t, *J* = 7.0 Hz, 1H, ArH), 7.25-7.10 (m, 8H, ArH), 6.90-6.85 (m, 1H, ArH), 6.78-6.73 (m, 1H, ArH), 6.68 (s, 1H, ArH), 6.44-6.41 (m, 1H, ArH), 6.38-6.35 (m, 1H, ArH), 4.92 (s, 1H, CH), 3.90-3.82 (m, 1H, CH_2), 3.62-3.55 (m, 1H, CH_2), 3.47-3.40 (m, 1H, CH_2), 3.02-2.95 (m, 1H, CH_2), 1.81-1.73 (m, 2H, CH_2), 1.54-1.47 (m, 2H, CH_2), 1.40-1.28 (m, 4H, CH_2), 1.00 (t, *J* = 7.2 Hz, 3H, CH_3), 0.93 (t, *J* = 7.0 Hz, 3H, CH_3), 0.72 (s, 9H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 195.7, 193.0, 176.5, 160.4 (d, *J* = 69.4 Hz), 158.0 (d, *J* = 66.6 Hz), 157.3, 140.0, 138.9, 138.5, 137.6, 133.4 (d, *J* = 7.3 Hz), 132.3, 130.3, 128.9 (d, *J* = 9.2 Hz), 128.0, 127.8, 127.3, 116.9 (d, *J* = 26.6 Hz), 115.8 (d, *J* = 24.1 Hz), 114.7, 114.6, 114.5, 110.6 (d, *J* = 24.4 Hz), 108.4 (d, *J* = 8.1 Hz), 108.3, 108.2, 64.3, 63.4, 59.5, 55.9, 40.7, 30.2, 28.9, 20.5, 20.3, 13.9, 13.6 ppm; IR (KBr) υ: 3356, 3012, 2945, 1688, 1673, 1595, 1555, 1466, 1442, 1389, 1332, 1244, 1220, 1166, 1088, 1015, 990, 906, 834, 809, 765, 723, 687, 638, 608 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{45}H_{45}F_2N_3NaO_4$ ($[M+Na]^+$): 752.3276, found: 752.3276.




195.74
193.02
176.50
160.76
160.07
158.35
157.68
157.32
139.96
138.90
138.53
137.58
133.41
133.34
132.27
130.33
128.95
128.86
128.01
127.98
127.75
127.29
117.00
116.73
115.95
115.71
114.72
114.63
114.49
110.73
110.49
108.49
108.41
108.33
108.26
64.33
63.40
59.47
55.92
40.69
40.65
30.21
28.87
20.45
20.30
13.89
13.61
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F
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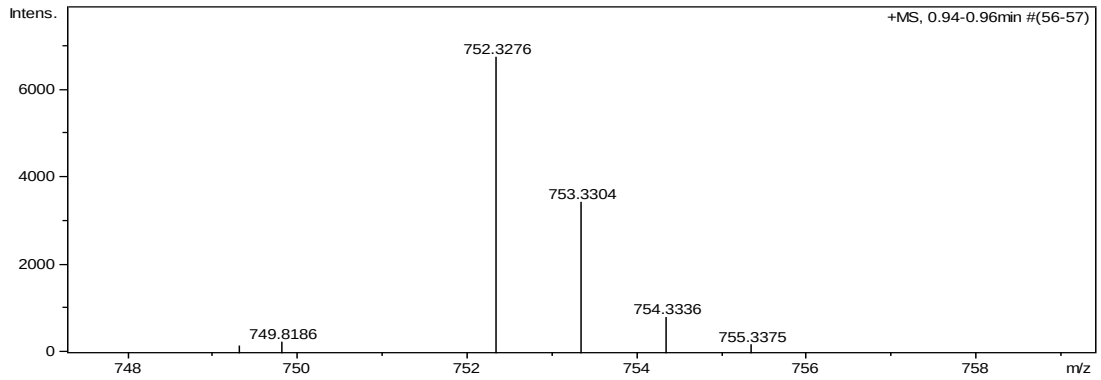
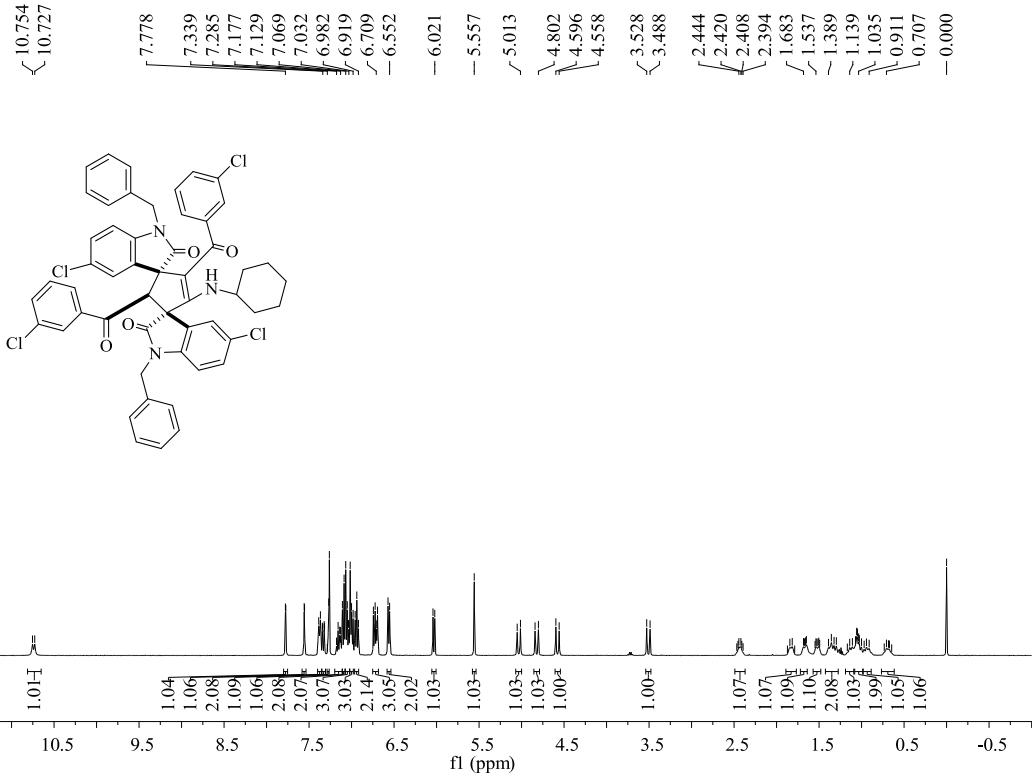
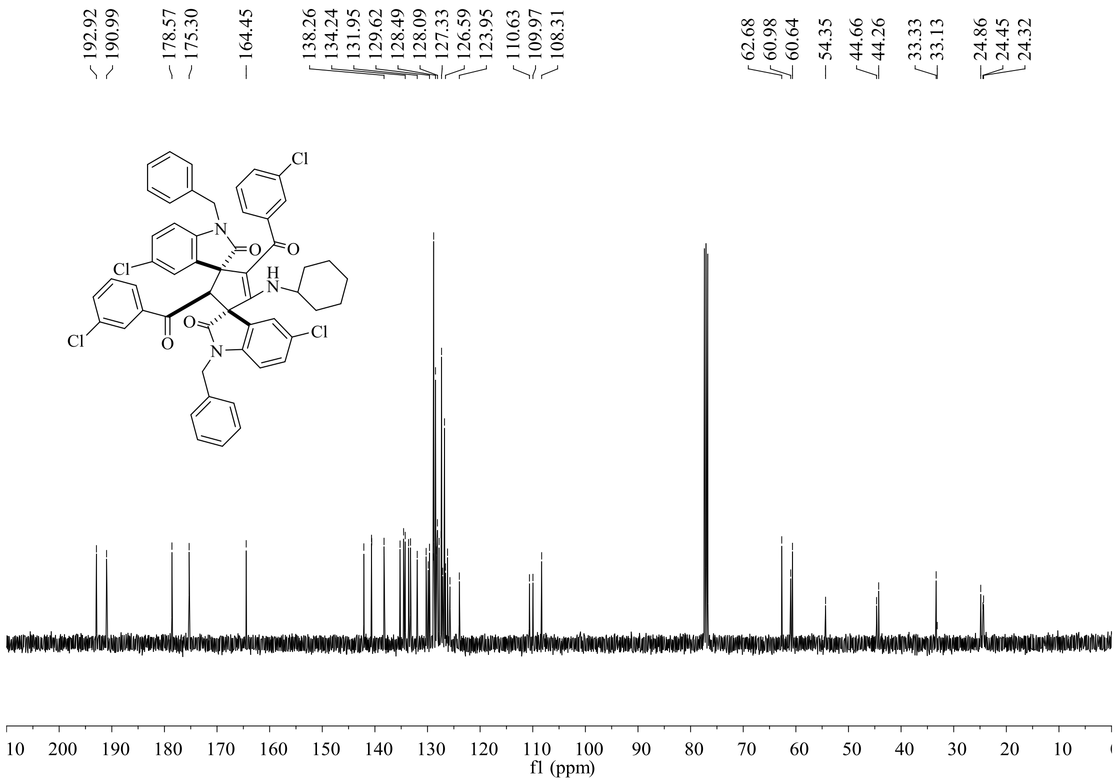
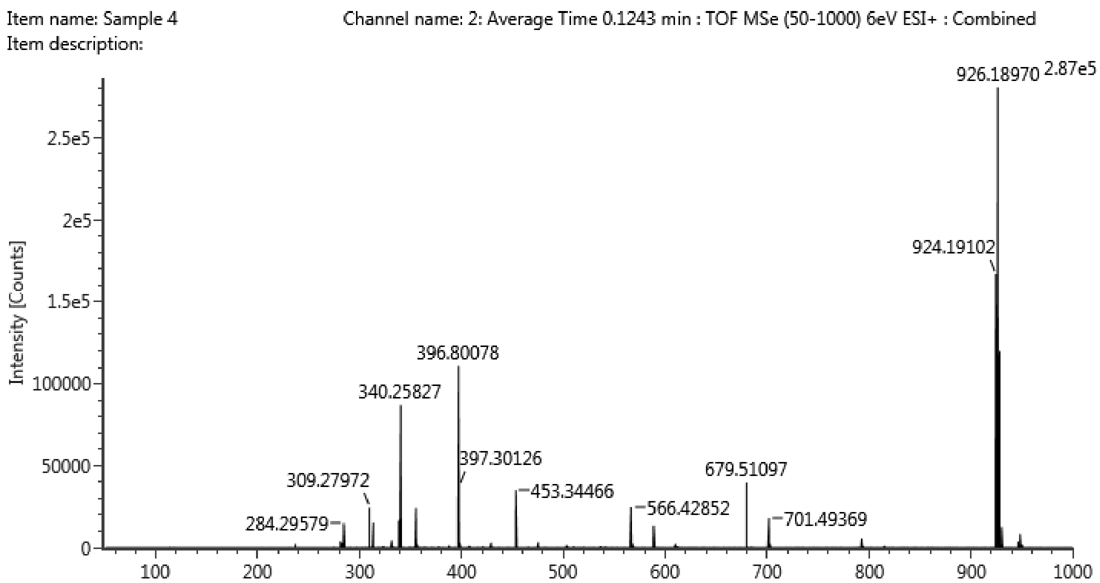
O
O
O
N
N
H
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 0.94-0.96min #(56-57)
752.3276
753.3304
754.3336
755.3375
749.8186
6000
4000
2000
0
748
750
752
754
756
758
m/z

***rel*-(2'*S*,3*S*,3'*R*)-1,1''-dibenzyl-5,5''-dichloro-2',4'-bis(3-chlorobenzoyl)-5'-(cyclohexylamino)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3i'):** white solid, 24%, m.p. 227-229 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.74 (d, *J* = 10.8 Hz, 1H, NH), 7.78 (d, *J* = 2.0 Hz, 1H, ArH), 7.56 (d, *J* = 2.0 Hz, 1H, ArH), 7.38 (d, *J* = 8.0 Hz, 2H, ArH), 7.33 (dd, J_1 =8.4 Hz, J_2 =1.6 Hz, 1H, ArH), 7.29-7.27 (m, 1H, ArH), 7.18-7.13 (m, 2H, ArH), 7.10 (d, *J* = 8.0 Hz, 2H, ArH), 7.07-7.03 (m, 3H, ArH), 7.02-6.98 (m, 3H, ArH), 6.94 (t, *J* = 8.0 Hz, 2H, ArH), 6.74-6.69 (m, 3H, ArH), 6.56 (d, *J* = 7.6 Hz, 2H, ArH), 6.03 (d, *J* = 8.4 Hz, 1H, ArH), 5.56 (s, 1H, CH), 5.03 (d, *J* = 15.6 Hz, 1H, CH_2), 4.82 (d, *J* = 15.6 Hz, 1H, CH_2), 4.58 (d, *J* = 15.2 Hz, 1H, CH_2), 3.51 (d, *J* = 16.0 Hz, 1H, CH_2), 2.47-2.39 (m, 1H, CH), 1.87-1.79 (m, 1H, CH_2), 1.68-1.65 (m, 1H, CH_2), 1.55-1.49 (m, 1H, CH_2), 1.39-1.30 (m, 2H, CH_2), 1.17-1.11 (m, 1H, CH_2), 1.07-1.00 (m, 2H, CH_2), 0.97-0.91 (m, 1H, CH_2), 0.73-0.65 (m, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 192.9, 191.0, 178.6, 175.3, 164.5, 142.1, 140.6, 140.6, 138.3, 135.2, 134.5, 134.2, 133.6, 133.2, 132.0, 130.3, 129.9, 129.6, 128.9, 128.8, 128.5, 128.3, 128.1, 128.1, 127.8, 127.4, 127.3, 127.1, 126.8, 126.6, 126.2, 125.7, 124.0, 110.6, 110.0, 108.3, 62.7, 61.0, 60.6, 54.4, 44.7, 44.3, 33.3, 33.1, 24.9, 24.5, 24.3 ppm; IR (KBr) υ: 3066, 3034, 2933, 2852, 2359, 1724, 1684, 1607, 1545, 1483, 1454, 1430, 1376, 1355, 1330, 1313, 1260, 1224, 1209, 1167, 1080, 1007, 810, 785, 752 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{53}H_{42}Cl_4N_3O_4$ ($[M+H]^+$): 924.1924, found: 924.1910.

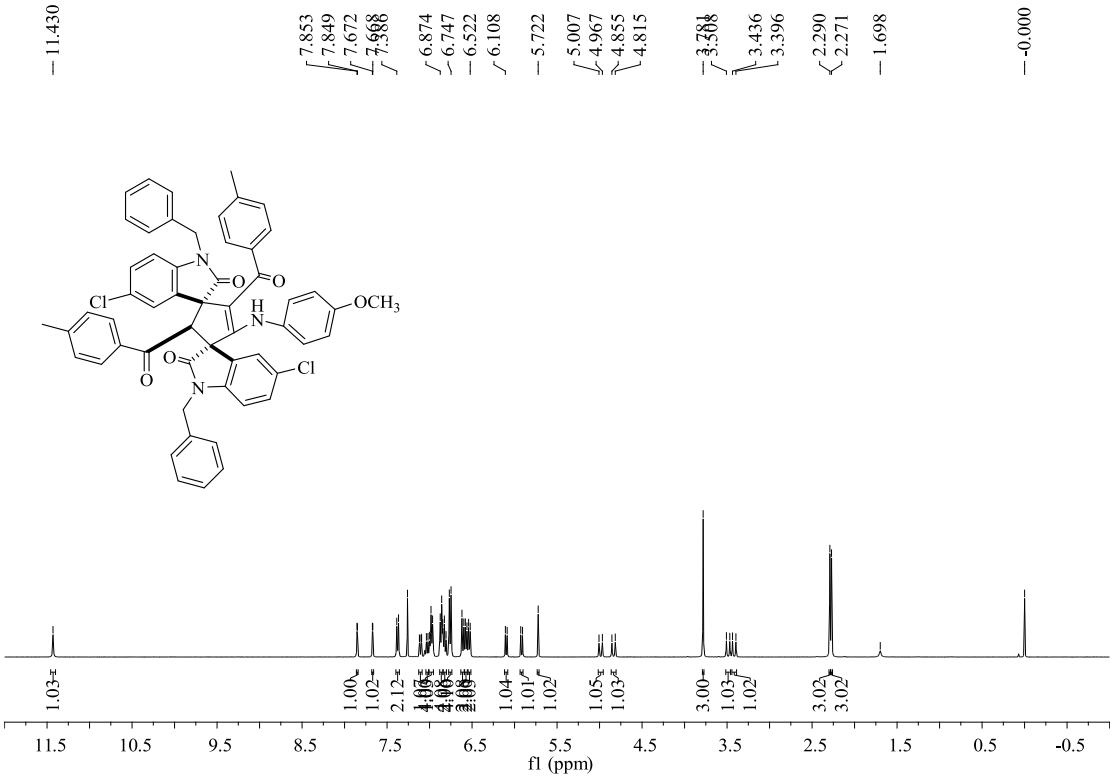


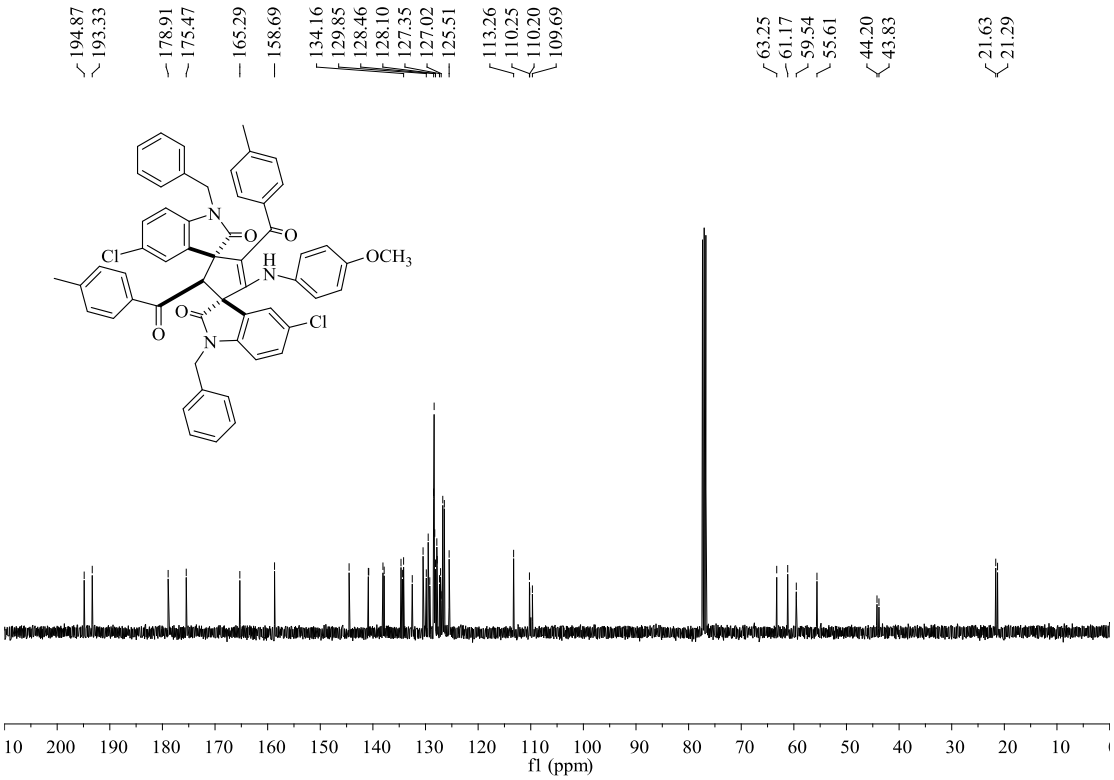

192.92
190.99
178.57
175.30
164.45
138.26
134.24
131.95
129.62
128.49
128.09
127.33
126.59
123.95
110.63
109.97
108.31
62.68
60.98
60.64
54.35
44.66
44.26
33.33
33.13
24.86
24.45
24.32
Cl
N
O
O
H
N
Cl
Cl
O
O
N
Cl
f1 (ppm)

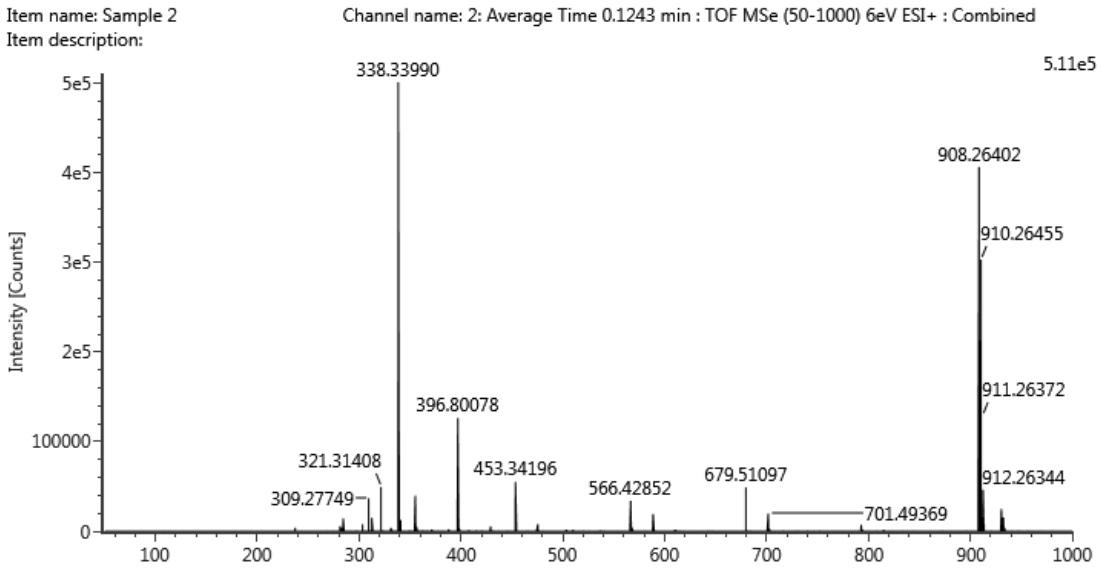

Item name: Sample 4
Item description:
Channel name: 2: Average Time 0.1243 min : TOF MSe (50-1000) 6eV ESI+ : Combined
926.18970 2.87e5
924.19102
396.80078
340.25827
397.30126
309.27972
453.34466
284.29579
566.42852
679.51097
701.49369
Intensity [Counts]

***rel*-(*2*'S,3*R*,3'*S*)-1,1''-dibenzyl-5,5''-dichloro-4'-((4-methoxyphenyl)amino)-2',5'-bis(4-methylbenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3j'):**

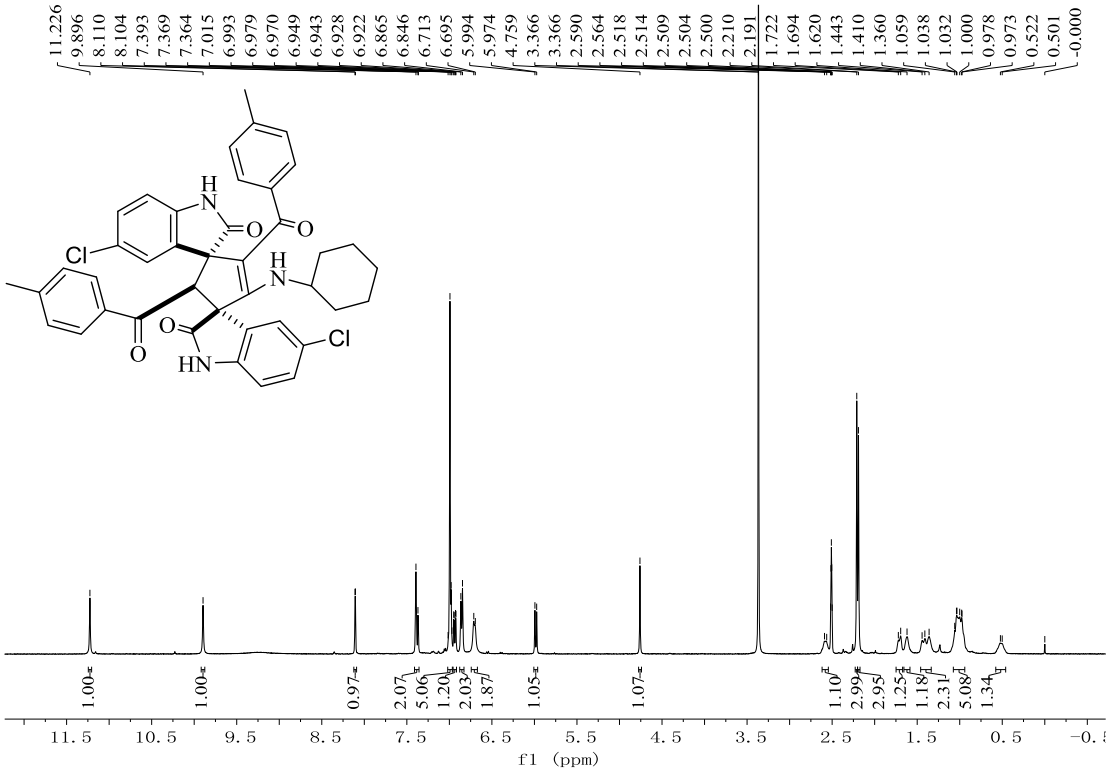
white solid, 20%, m.p. 247-249 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.43 (s, 1H, NH), 7.85 (d, *J* = 1.6 Hz, 1H, ArH), 7.67 (d, *J* = 1.6 Hz, 1H, ArH), 7.38 (d, *J* = 8.4 Hz, 2H, ArH), 7.11 (dd, J_1 =8.4 Hz, J_2 =2.0 Hz, 1H, ArH), 7.03 (d, *J* = 7.6 Hz 1H, ArH), 7.00-6.96 (m, 4H, ArH), 6.87-6.85 (m, 4H, ArH), 6.82 (d, *J* = 7.6 Hz, 2H, ArH), 6.76 (d, *J* = 8.4 Hz, 4H, ArH), 6.61 (d, *J* = 8.8 Hz, 2H, ArH), 6.57 (d, *J* = 7.6 Hz, 2H, ArH), 6.53 (d, *J* = 7.6 Hz, 2H, ArH), 6.10 (d, *J* = 8.4 Hz, 1H, ArH), 5.92 (d, *J* = 8.4 Hz, 1H, ArH), 5.72 (s, 1H, CH), 4.99 (d, *J* = 16.0 Hz, 1H, CH_2), 4.83 (d, *J* = 16.0 Hz, 1H, CH_2), 3.78 (s, 3H, OCH_3), 3.49 (d, *J* = 16.0 Hz, 1H, CH_2), 3.42 (d, *J* = 16.0 Hz, 1H, CH_2), 2.29 (s, 3H, CH_3), 2.27 (s, 3H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 194.9, 193.3, 178.9, 175.5, 165.3, 158.7, 144.5, 140.9, 140.8, 138.1, 137.9, 134.7, 134.4, 134.2, 132.5, 130.5, 129.9, 129.5, 129.2, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.4, 127.3, 127.1, 127.0, 126.7, 126.4, 125.5, 113.3, 110.3, 110.2, 109.7, 63.3, 61.2, 59.5, 55.6, 44.2, 43.8, 21.6, 21.3 ppm; IR (KBr) υ: 3531, 3514, 3497, 3034, 2914, 1726, 1676, 1610, 1551, 1511, 1484, 1454, 1431, 1339, 1296, 1250, 1183, 1030, 1011, 822, 807, 788, 752 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{56}H_{44}Cl_2N_3O_5$ ($[M+H]^+$): 908.2653, found: 908.2640.

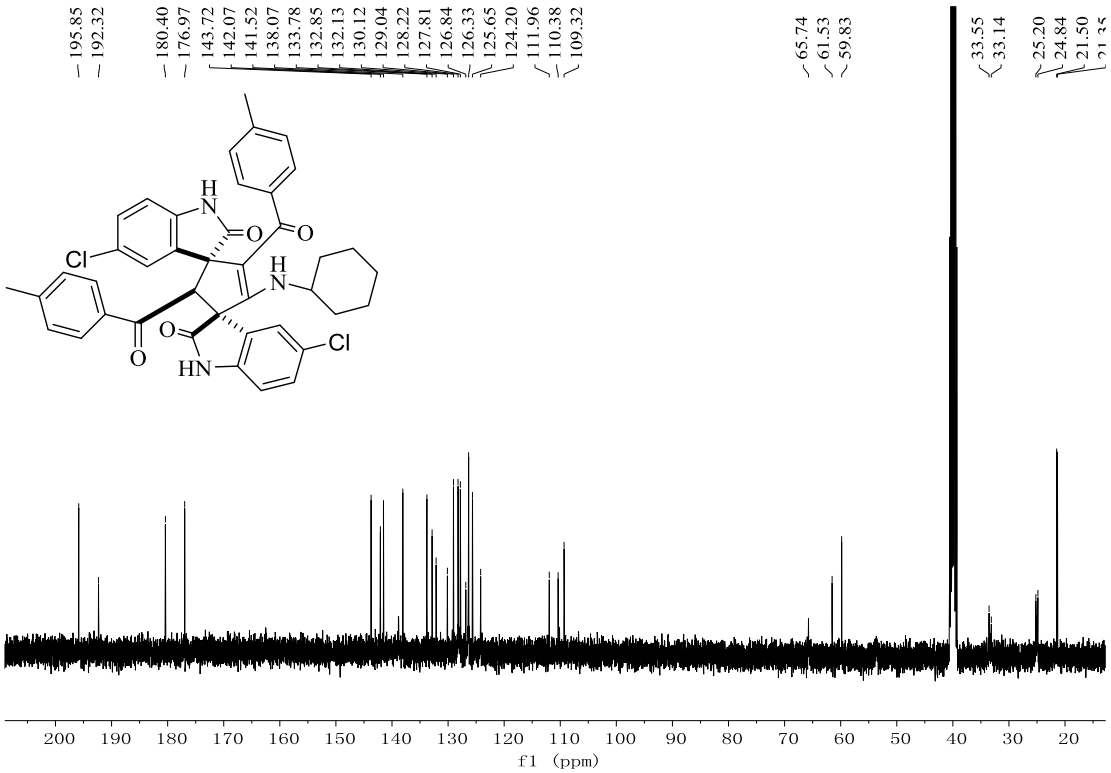


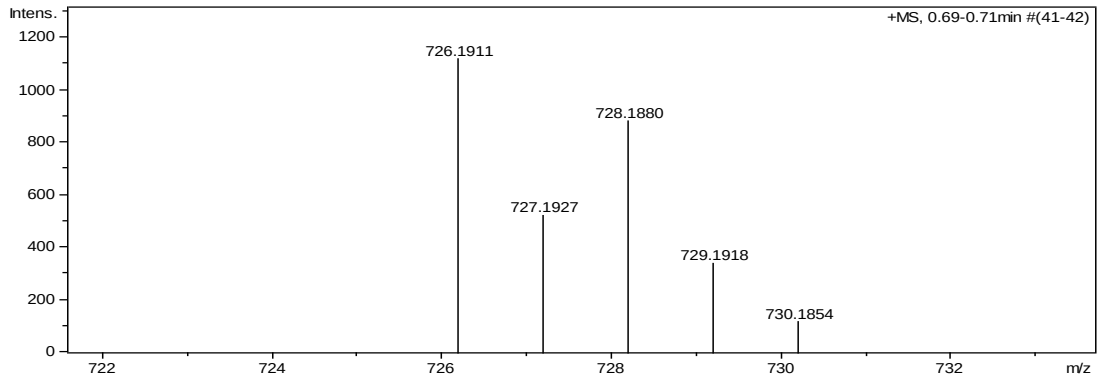

194.87
193.33
178.91
175.47
165.29
158.69
134.16
129.85
128.46
128.10
127.35
127.02
125.51
113.26
110.25
110.20
109.69
63.25
61.17
59.54
55.61
44.20
43.83
21.63
21.29
Cl
O
O
N
H
N
OCH3
O
O
N
Cl
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Item name: Sample 2
Item description:
Channel name: 2: Average Time 0.1243 min : TOF MSe (50-1000) 6eV ESI+ : Combined
5.11e5
Intensity [Counts]
5e5
4e5
3e5
2e5
100000
0
338.33990
908.26402
910.26455
911.26372
912.26344
396.80078
321.31408
309.27749
453.34196
566.42852
679.51097
701.49369
100 200 300 400 500 600 700 800 900 1000

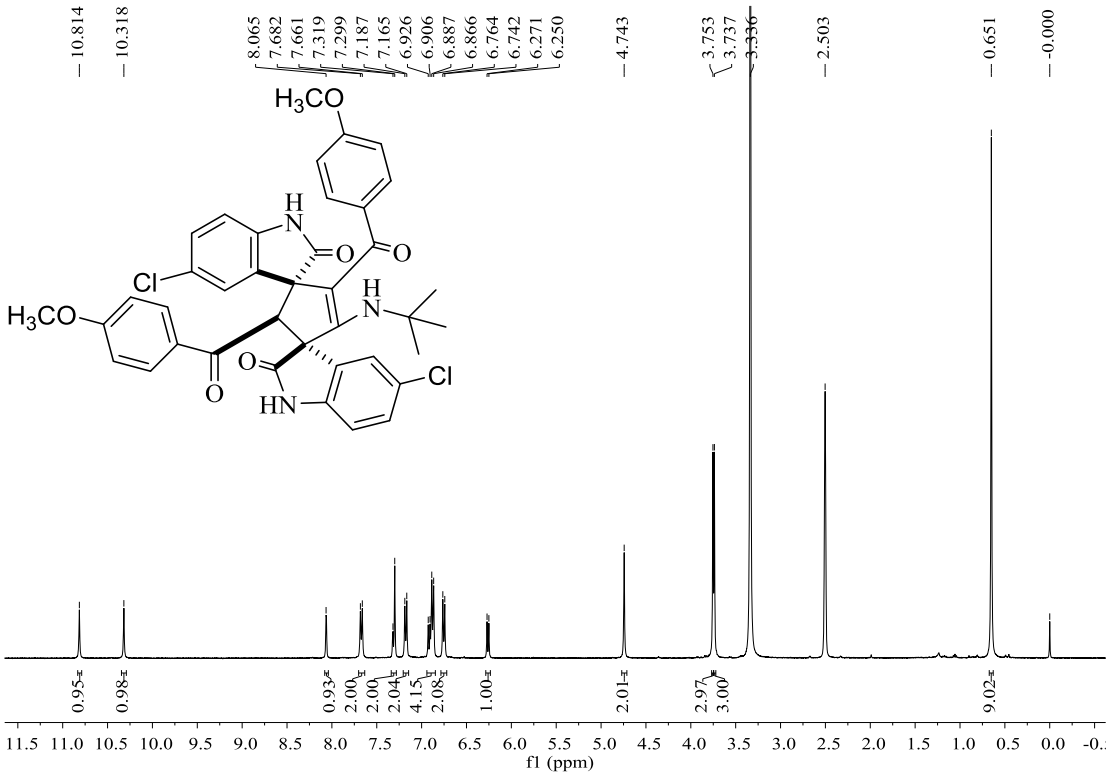
***rel*-(2'*S*,3*S*,3'*S*)-4,5''-dichloro-4'-(cyclohexylamino)-2',5'-bis(4-methylbenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3k'):** ethyl acetate and petroleum ether (v/v = 1:3) as the eluent, pale yellow solid, 112 mg, 32%, m.p. 231-233 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.23 (s, 1H, NH), 9.90 (s, 1H, NH), 8.11-8.10 (m, 1H, ArH), 7.39-7.36 (m, 2H, ArH), 7.02-6.97 (m, 5H, ArH), 6.95-6.92 (m, 1H, ArH), 6.86 (d, *J* = 7.6 Hz, 2H, ArH), 6.71-6.70 (m, 2H, ArH), 5.98 (d, *J* = 8.0 Hz, 1H, ArH), 4.76 (s, 1H, CH), 2.58 (d, *J* = 10.4 Hz, 1H, CH), 2.21 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 1.71 (d, *J* = 11.2 Hz, 1H, CH_2), 1.62 (s, 1H, CH_2), 1.44-1.36 (m, 2H, CH_2), 1.06-0.97 (m, 5H, CH_2), 0.51 (d, *J* = 8.4 Hz, 1H, CH_2); ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 195.9, 192.3, 180.4, 177.0, 143.7, 142.1, 141.5, 138.9, 138.1, 133.8, 132.9, 132.1, 130.1, 129.0, 128.2, 127.8, 126.8, 126.3, 125.7, 124.2, 112.0, 110.4, 109.3, 65.7, 61.5, 59.8, 33.6, 33.1, 25.2, 25.0, 24.8, 21.5, 21.4; IR (KBr) υ: 3643, 3323, 3217, 3045, 2946, 2828, 1806, 1599, 1463, 1320, 1278, 1184, 1102, 1021, 933, 854, 734, 663 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{41}H_{35}Cl_2N_3NaO_4$ ([M+Na]$^+$): 726.1897, found: 726.1911.

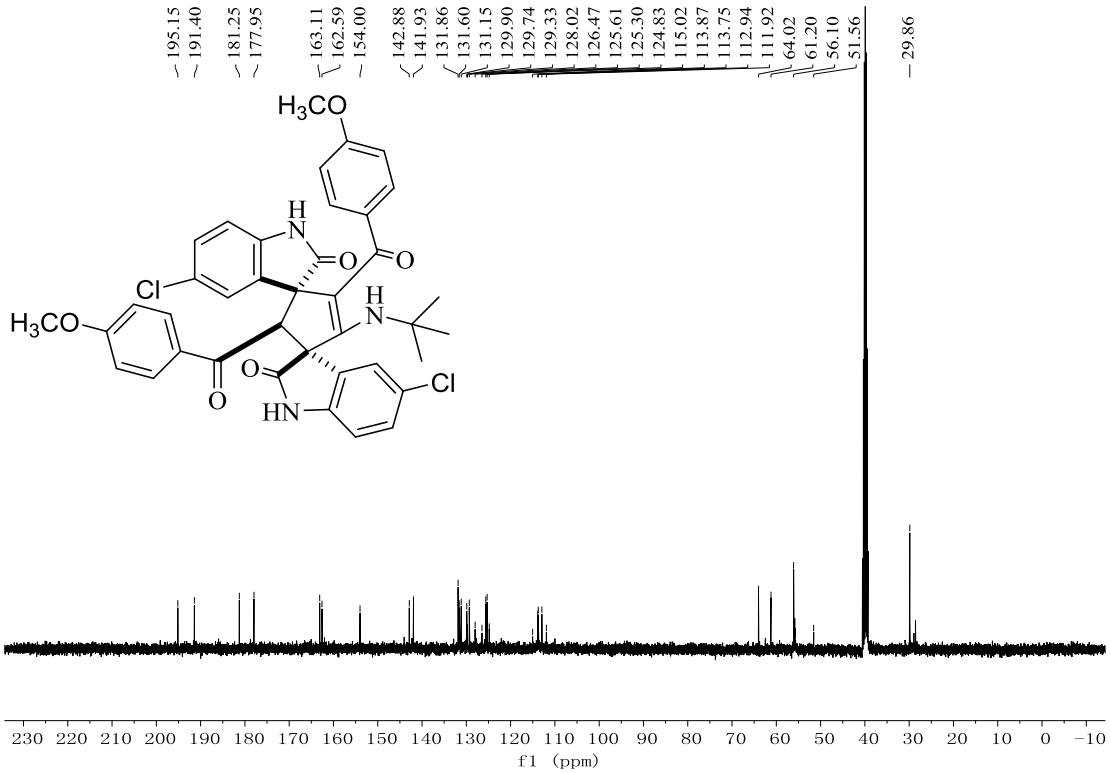


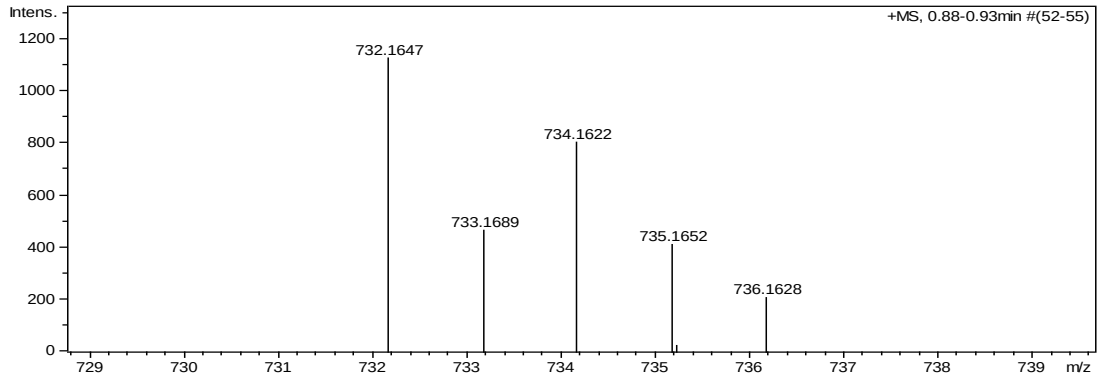

195.85
192.32
180.40
176.97
143.72
142.07
141.52
138.07
133.78
132.85
132.13
130.12
129.04
128.22
127.81
126.84
126.33
125.65
124.20
111.96
110.38
109.32
65.74
61.53
59.83
33.55
33.14
25.20
24.84
21.50
Cl
Cl
HN
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
+MS, 0.69-0.71min #(41-42)
726.1911
728.1880
727.1927
729.1918
730.1854
1200
1000
800
600
400
200
0
722
724
726
728
730
732
m/z

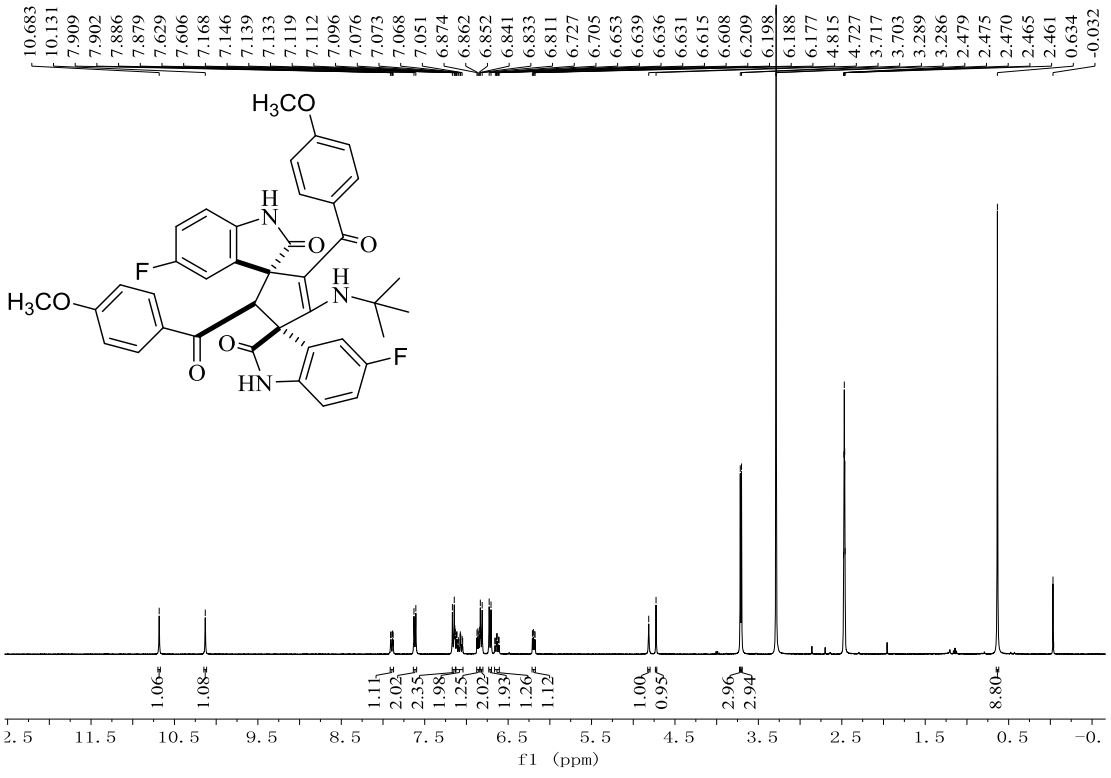
***rel*-(2'*S*,3*S*,3'*S*)-4'-(*tert*-butylamino)-4,5''-dichloro-2',5'-bis(4-methoxybenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3l'):** ethyl acetate and petroleum ether (v/v = 1:3) as the eluent, pale yellow solid, 82 mg, 23%, m.p. 248-250 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.81 (s, 1H, NH), 10.32 (s, 1H, NH), 8.06 (s, 1H, ArH), 7.67 (d, *J* = 8.4 Hz, 2H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.18 (d, *J* = 8.8 Hz, 2H, ArH), 6.93-6.87 (m, 4H, ArH), 6.75 (d, *J* = 8.8 Hz, 2H, ArH), 6.26 (d, *J* = 8.4 Hz, 1H, ArH), 4.74 (s, 2H, CH, NH), 3.75 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 0.65 (s, 9H, CH_3); ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 195.2, 191.4, 181.3, 178.0, 163.1, 162.6, 154.0, 142.9, 141.9, 131.9, 131.6, 131.2, 129.9, 129.7, 129.3, 128.0, 126.5, 125.6, 125.3, 124.8, 115.0, 113.9, 113.8, 112.9, 111.9, 64.0, 61.2, 56.1, 51.6, 29.9. IR (KBr) υ: 3655, 3403, 3242, 3053, 2956, 2843, 1787, 1626, 1533, 1324, 1273, 1185, 1110, 1002, 915, 832, 778, 682 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{39}H_{33}Cl_2N_3NaO_6$ ([M+Na]$^+$): 732.1639, found: 732.1647.

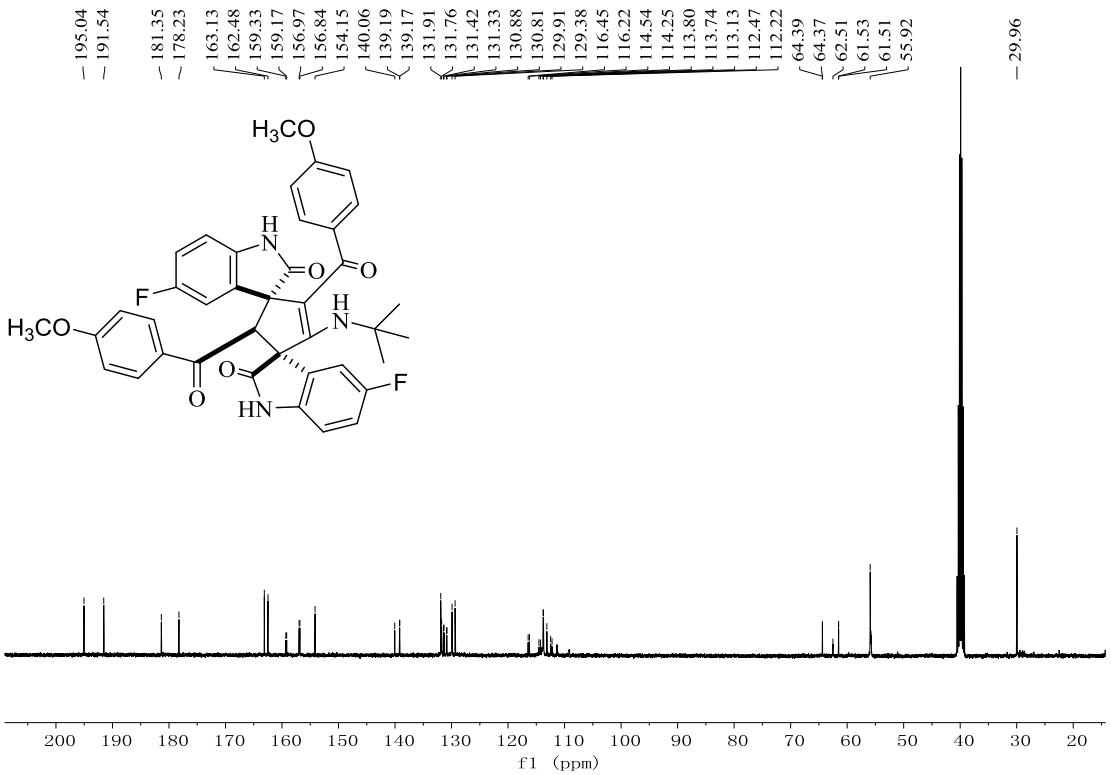


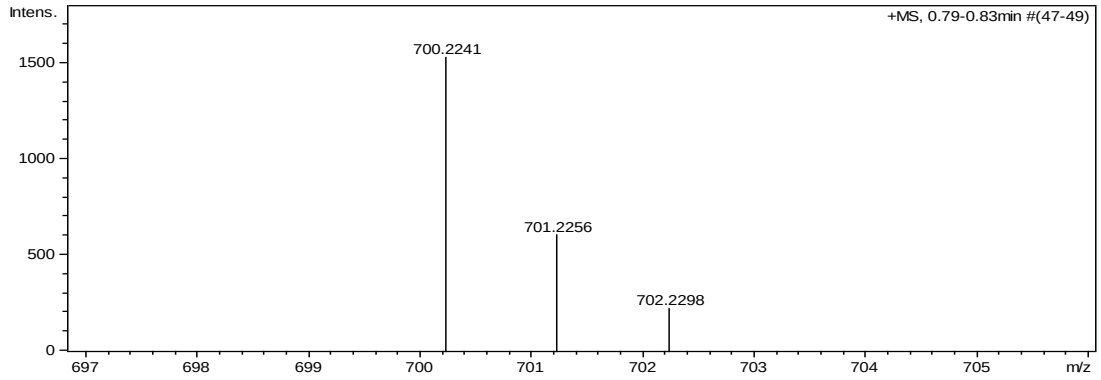

195.15
191.40
181.25
177.95
163.11
162.59
154.00
142.88
141.93
131.86
131.60
131.15
129.90
129.74
129.33
128.02
126.47
125.61
125.30
124.83
115.02
113.87
113.75
112.94
111.92
64.02
61.20
56.10
51.56
29.86
H3CO
H
N
O
O
Cl
H3CO
H
N
O
O
HN
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


Intens.
+MS, 0.88-0.93min #(52-55)
1200
1000
800
600
400
200
0
732.1647
734.1622
733.1689
735.1652
736.1628
729 730 731 732 733 734 735 736 737 738 739 m/z

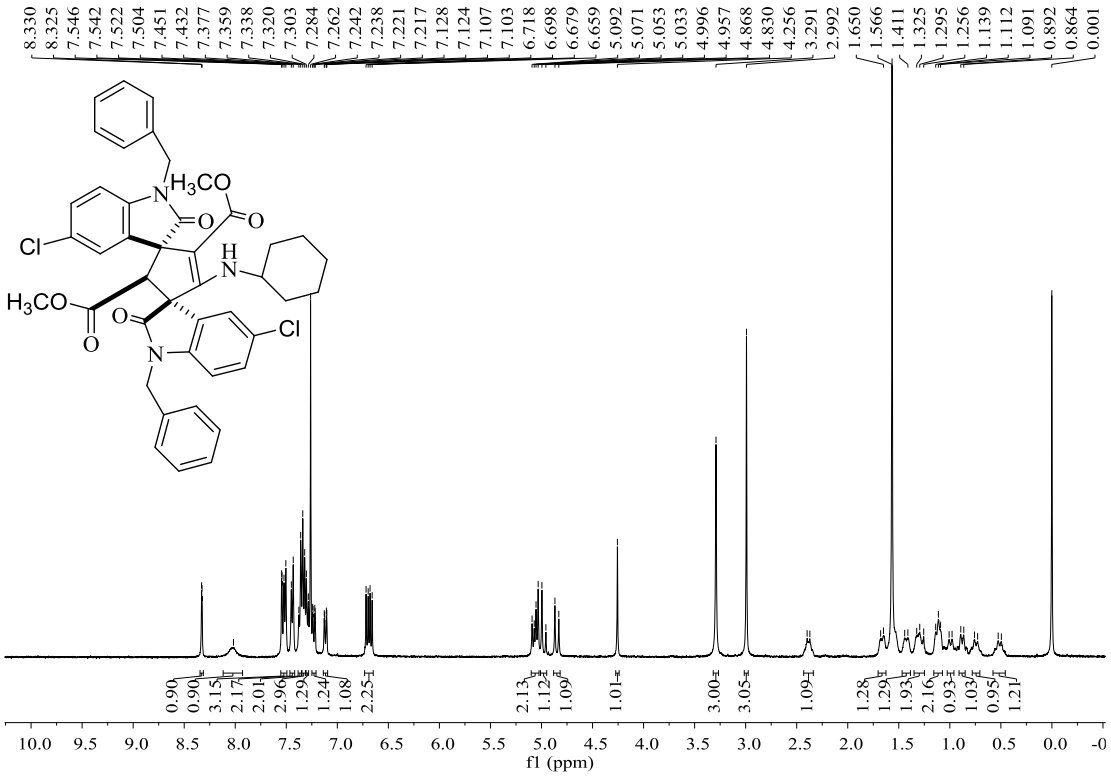
***rel*-(2'*S*,3*S*,3'*S*)-4'-(*tert*-butylamino)-4,5''-difluoro-2',5'-bis(4-methoxybenzoyl)dispiro[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2,2''-dione (3m'):** ethyl acetate and petroleum ether (v/v = 1:3) as the eluent, pale yellow solid, 74 mg, 22%, m.p. 234-236 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.68 (s,1H, NH), 10.13 (s, 1H, NH), 7.91-7.88 (m, 1H, ArH), 7.62 (d, *J* = 9.2 Hz, 2H, ArH), 7.17-7.13 (m, 2H, ArH), 7.12-7.05 (m, 2H, ArH), 6.87-6.84 (m, 1H, ArH), 6.82 (d, *J* = 8.8 Hz, 2H, ArH), 6.72 (d, *J* = 8.8 Hz, 2H, ArH), 6.66-6.61 (m, 1H, ArH), 6.21-6.18 (m, 1H, ArH), 4.82 (s, 1H, CH), 4.73 (s, 1H, NH), 3.72 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 0.63 (s, 9H, CH_3); ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 195.0, 191.5, 181.4, 178.2, 163.1, 162.5, 159.3 (d, *J* = 15.7 Hz), 156.9 (d, *J* = 13.0 Hz), 154.2, 140.1, 139.2, 139.2, 131.9, 131.8, 131.4 (d, *J* = 8.5 Hz), 130.8 (d, *J* = 7.6 Hz), 129.9, 129.4, 116.3 (d, *J* = 22.8 Hz), 114.5, 114.3, 113.8, 113.7, 113.1, 112.5, 112.2, 111.3, 111.3, 109.2, 64.4, 64.4, 62.5, 61.5, 61.5, 55.9, 29.9. IR (KBr) υ: 3544, 3315, 3257, 3106, 2947, 2844, 1826, 1578, 1466, 1322, 1240, 1183, 1104, 1020, 934, 841, 760, 681 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{39}H_{33}F_2N_3NaO_6$ ([M+Na]$^+$): 700.2230, found: 700.2241.

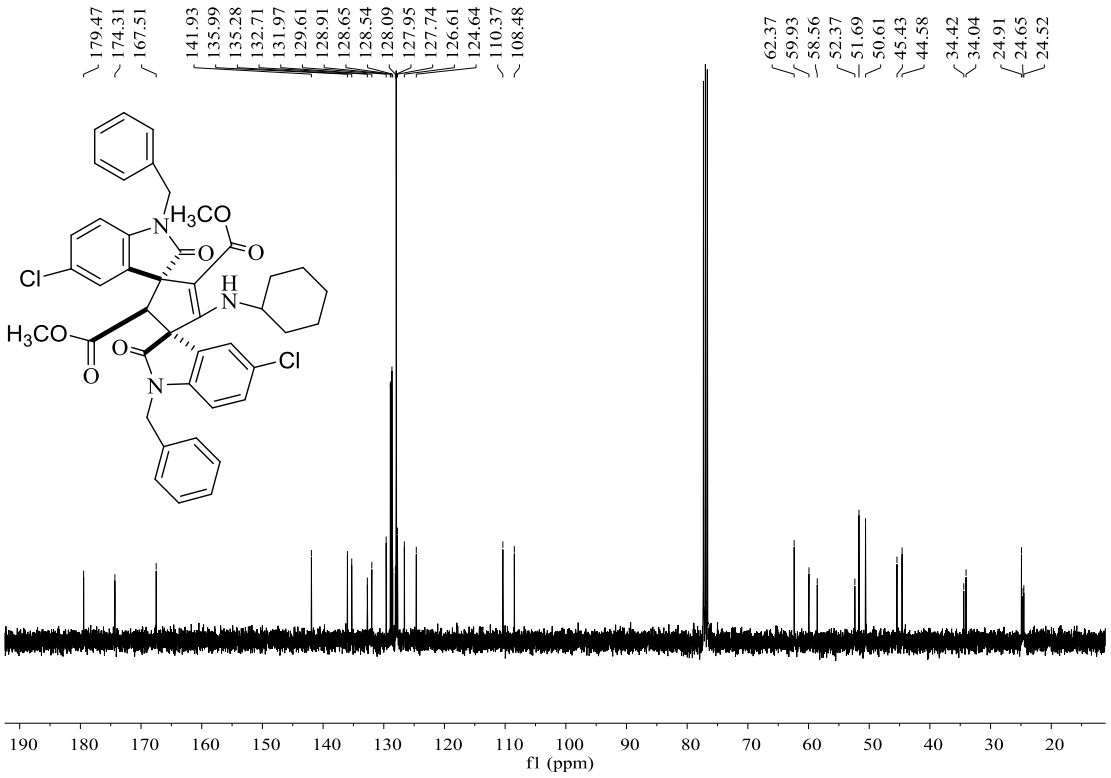


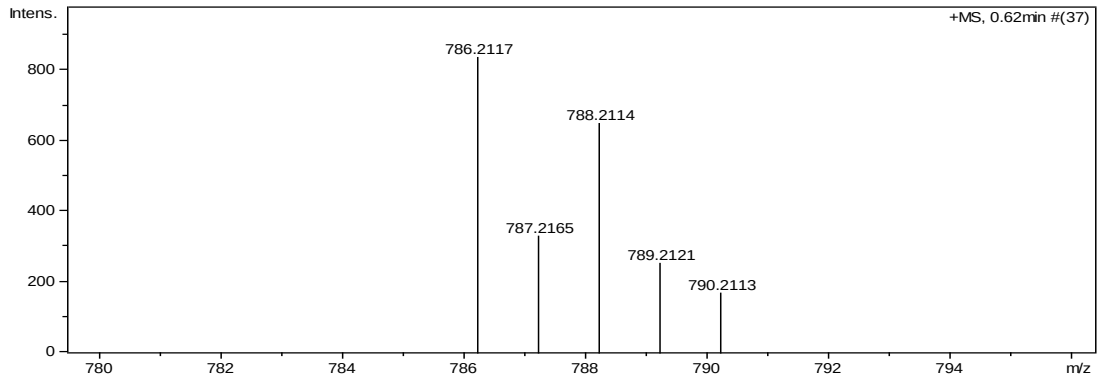

195.04
191.54
181.35
178.23
163.13
162.48
159.33
159.17
156.97
156.84
154.15
140.06
139.19
139.17
131.91
131.76
131.42
131.33
130.88
130.81
129.91
129.38
116.45
116.22
114.54
114.25
113.80
113.74
113.13
112.47
112.22
64.39
64.37
62.51
61.53
61.51
55.92
29.96
H3CO
H
N
O
O
F
H3CO
H
N
O
O
HN
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
+MS, 0.79-0.83min #(47-49)
700.2241
701.2256
702.2298
1500
1000
500
0
697 698 699 700 701 702 703 704 705 m/z

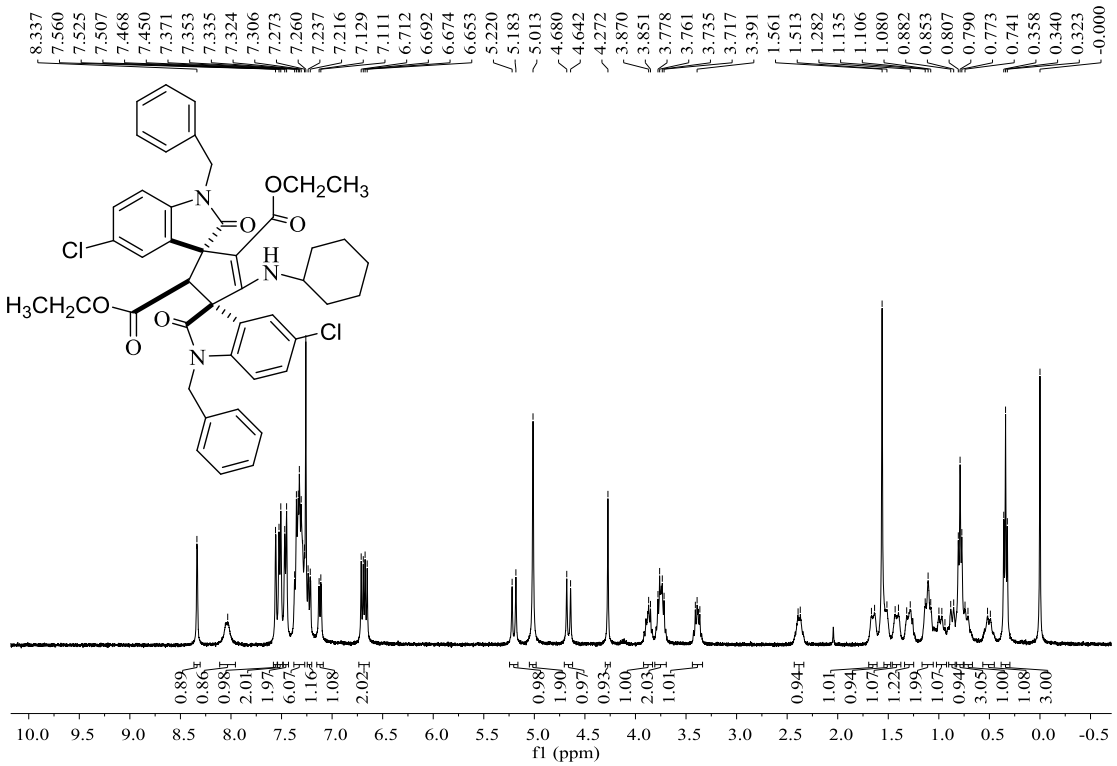
Dimethyl *rel*-(2'*S*,3*R*,3'*S*)-1,1''-dibenzyl-4'',5-dichloro-5'-(cyclohexylamino)-2,2''-dioxodispiro-[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2',4'-dicarboxylate (3n'): ethyl acetate and petroleum ether (v/v = 1:8) as the eluent, white solid, 99 mg, 26%, m.p. 186-188°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33-8.32 (m, 1H, NH), 8.02 (s, 1H, ArH), 7.55-7.50 (m, 3H, ArH), 7.44 (d, *J* = 7.6 Hz, 2H, ArH), 7.37 (d, *J* = 7.2 Hz, 2H, ArH), 7.33 (d, *J* = 7.2 Hz, 3H, ArH), 7.29 (d, *J* = 7.6 Hz, 1H, ArH), 7.24-7.22 (m, 1H, ArH), 7.13-7.10 (m, 1H, ArH), 6.72-6.66 (m, 2H, ArH), 5.09-5.03 (m, 2H, CH_2), 4.98 (d, *J* = 15.6 Hz, 1H, CH_2), 4.85 (d, *J* = 15.2 Hz, 1H, CH_2), 4.26 (s, 1H, CH), 3.29 (s, 3H, OCH_3), 2.99 (s, 3H, OCH_3), 2.40-2.37 (m, 1H, CH), 1.68-1.65 (m, 1H, CH_2), 1.44-1.41 (m, 1H, CH_2), 1.33-1.26 (m, 2H, CH_2), 1.14-1.09 (m, 2H, CH_2), 1.01-0.98 (m, 1H, CH_2), 0.89-0.86 (m, 1H, CH_2), 0.76-0.73 (m, 1H, CH_2); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 179.5, 174.3, 167.5, 141.9, 136.0, 135.3, 132.7, 132.0, 129.6, 128.9, 128.7, 128.5, 128.1, 128.0, 127.7, 126.6, 124.6, 110.4, 108.5, 62.4, 59.9, 58.6, 52.4, 51.7, 50.6, 45.4, 44.6, 34.4, 34.0, 24.9, 24.7, 24.5; IR (KBr) υ: 3421, 3260, 2933, 2851, 2291, 1860, 1722, 1667, 1605, 1482, 1428, 1347, 1302, 1201, 1143, 1078, 1031, 990, 882, 808, 746, 697 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{43}H_{39}Cl_2N_3NaO_6$ ($[M+Na]^+$): 786.2114, found: 786.2117.

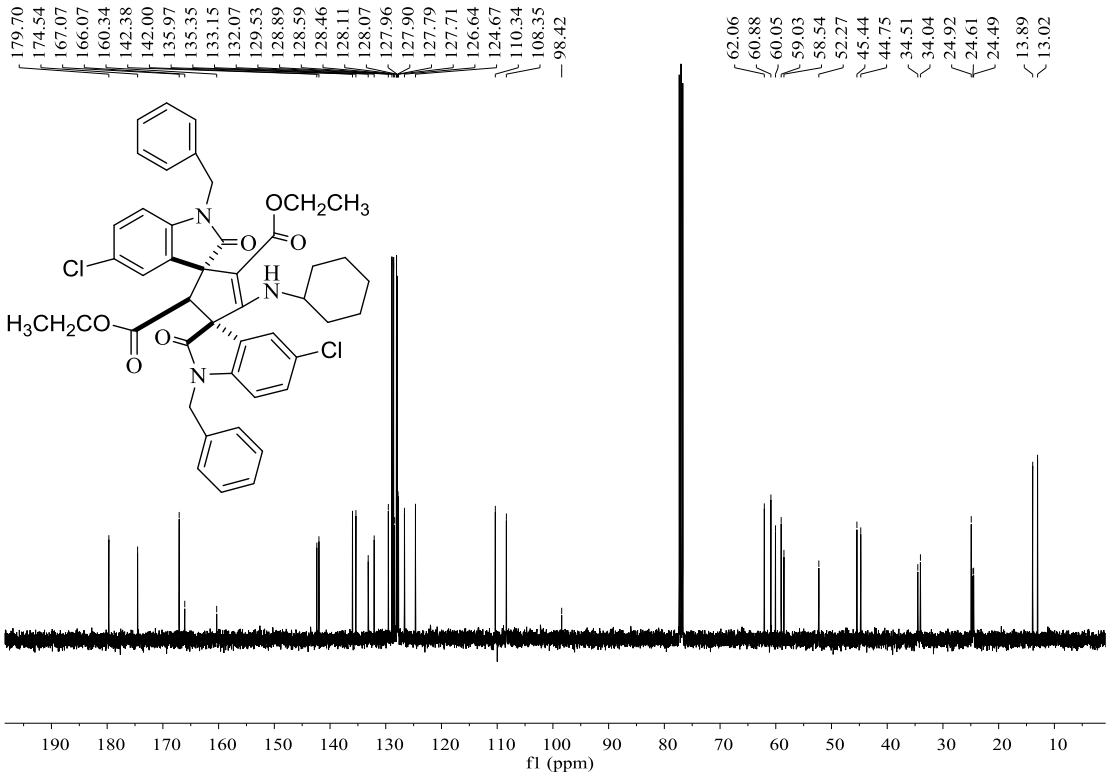


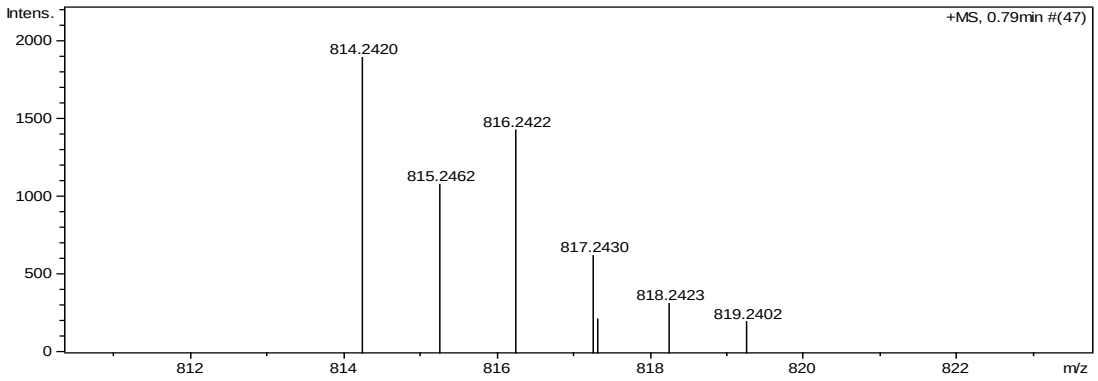

179.47
174.31
167.51
141.93
135.99
135.28
132.71
131.97
129.61
128.91
128.65
128.54
128.09
127.95
127.74
126.61
124.64
110.37
108.48
62.37
59.93
58.56
52.37
51.69
50.61
45.43
44.58
34.42
34.04
24.91
24.65
24.52
H3CO
O
O
Cl
H
N
H3CO
O
O
N
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


Intens.
+MS, 0.62min #(37)
786.2117
788.2114
787.2165
789.2121
790.2113
800
600
400
200
0
780 782 784 786 788 790 792 794
m/z

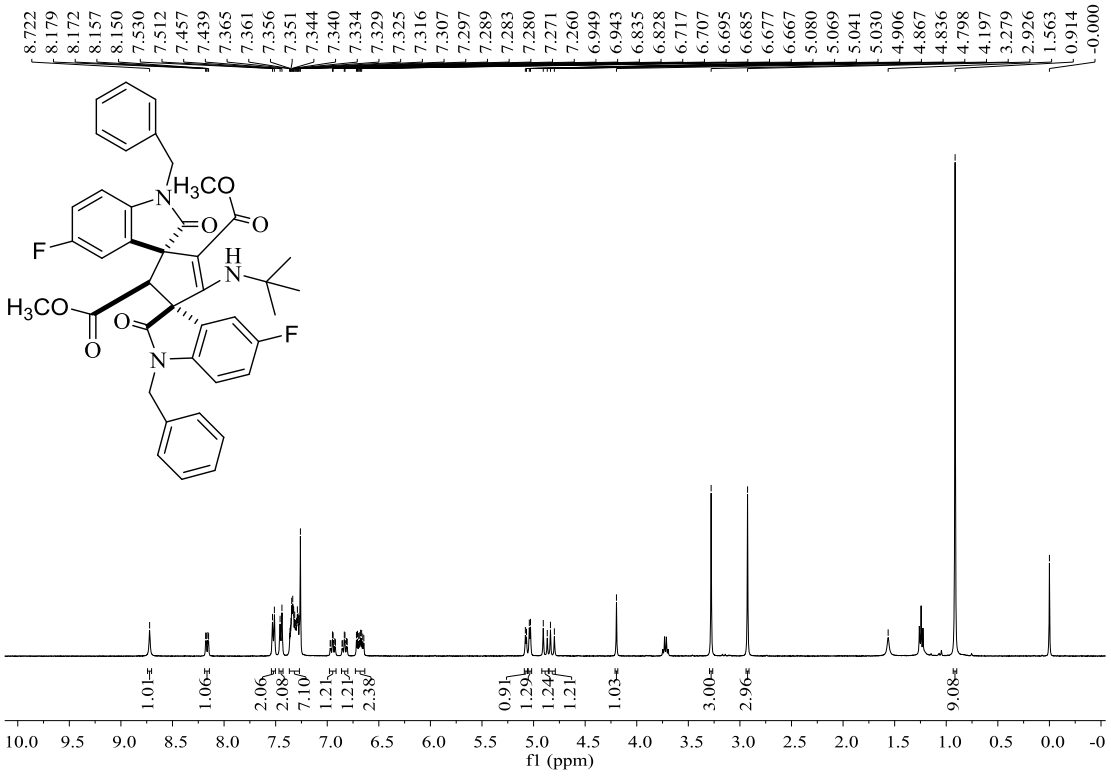
Diethyl *rel*-(2'*S*,3*R*,3'*S*)-1,1''-dibenzyl-4'',5-dichloro-5'-(cyclohexylamino)-2,2''-dioxodispiro-[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2',4'-dicarboxylate (3o'): ethyl acetate and petroleum ether (v/v = 1:8) as the eluent, white solid, 91 mg, 23%, m.p. 224-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (s, 1H, NH), 8.03 (s, 1H, ArH), 7.56 (s, 1H, ArH), 7.52 (d, *J* = 7.2 Hz, 2H, ArH), 7.46 (d, *J* = 7.2 Hz, 2H, ArH), 7.37-7.27 (m, 6H, ArH), 7.23 (d, *J* = 8.4 Hz, 1H, ArH), 7.12 (d, *J* = 7.2 Hz, 1H, ArH), 6.71-6.65 (m, 2H, ArH), 5.20 (d, *J* = 14.8 Hz, 1H, CH_2), 5.01 (s, 2H, CH_2), 4.66 (d, *J* = 15.2 Hz, 1H, CH_2), 4.27 (s, 1H, CH), 3.87-3.85 (m, 1H, CH_2), 3.78-3.72 (m, 2H, CH_2), 3.41-3.36 (m, 1H, CH_2), 2.39-2.37 (m, 1H, CH), 1.67-1.64 (m, 1H, CH_2), 1.51 (s, 1H, CH_2), 1.43-1.40 (m, 1H, CH_2), 1.32-1.28 (m, 1H, CH_2), 1.14-1.08 (m, 2H, CH_2), 1.00-0.94 (m, 1H, CH_2), 0.88-0.85 (m, 1H, CH_2), 0.79 (t, *J* = 6.8 Hz, 3H, CH_3), 0.74-0.71 (m, 1H, CH_2), 0.52-0.49 (m, 1H, CH_2), 0.34 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 179.7, 174.5, 167.1, 166.1, 160.3, 142.4, 142.0, 136.0, 135.4, 133.2, 132.1, 129.5, 128.9, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 126.6, 124.7, 110.3, 108.4, 98.4, 62.1, 60.9, 60.1, 59.0, 58.5, 52.3, 45.4, 44.8, 34.5, 34.0, 24.9, 24.6, 24.5, 13.9, 13.0; IR (KBr) υ: 3273, 3066, 2927, 2854, 2288, 1849, 1728, 1651, 1602, 1482, 1427, 1361, 1336, 1293, 1219, 1189, 1144, 1105, 1078, 1029, 969, 913, 809, 754, 702, 627 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{45}H_{43}Cl_2N_3NaO_6$ ([M+Na]$^+$): 814.2427, found: 814.2420.

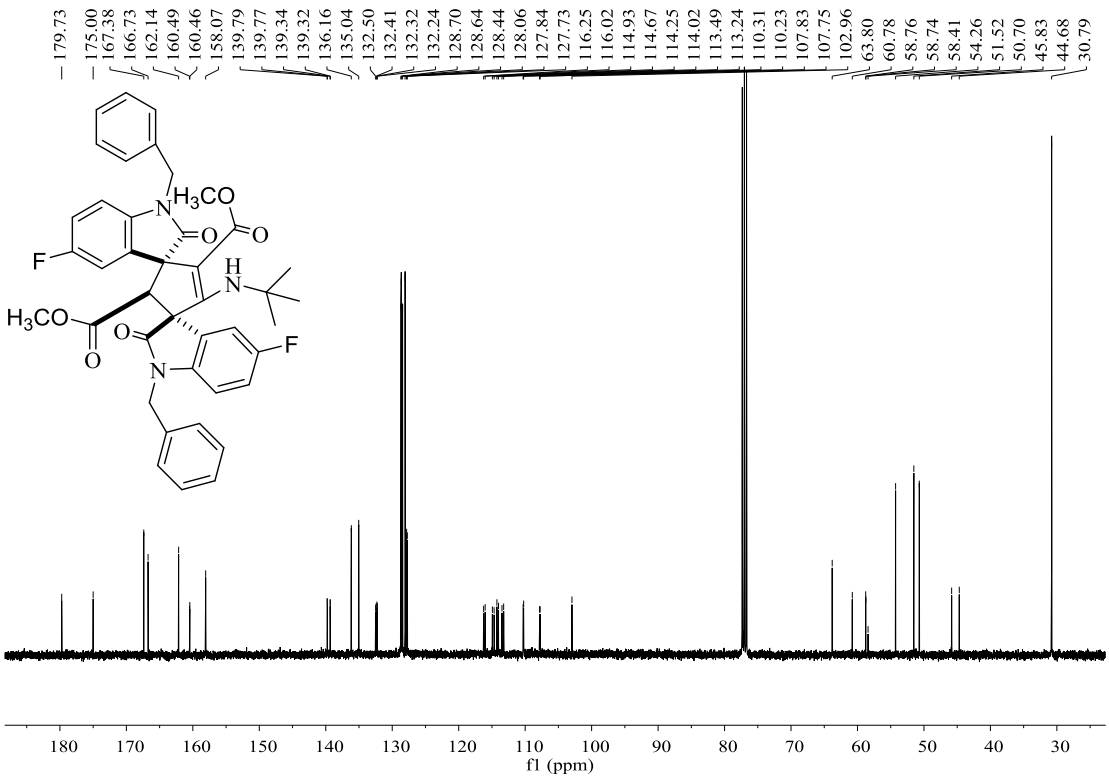



179.70
174.54
167.07
166.07
160.34
142.38
142.00
135.97
135.35
133.15
132.07
129.53
128.89
128.59
128.46
128.11
128.07
127.96
127.90
127.79
127.71
126.64
124.67
110.34
108.35
98.42
62.06
60.88
60.05
59.03
58.54
52.27
45.44
44.75
34.51
34.04
24.92
24.61
24.49
13.89
13.02
OCH2CH3
Cl
H3CH2CO
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 0.79min #(47)
2000
1500
1000
500
0
814.2420
816.2422
815.2462
817.2430
818.2423
819.2402
812
814
816
818
820
822
m/z

Dimethyl *rel*-(2'*S*,3*S*,3'*R*)-1,1''-dibenzyl-4'-(*tert*-butylamino)-4,5''-difluoro-2,2''-dioxodispiro-[indoline-3,1'-cyclopentane-3',3''-indolin]-4'-ene-2',5'-dicarboxylate (3p'): ethyl acetate and petroleum ether (v/v = 1:8) as the eluent, white solid, 85 mg, 24%, m.p. 166-168 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (s, 1H, NH), 8.18-8.15 (m, 1H, ArH), 7.52 (d, *J* = 7.2 Hz, 2H, ArH), 7.45 (d, *J* = 7.2 Hz, 2H, ArH), 7.37-7.27 (m, 7H, ArH), 6.97-6.92 (m, 1H, ArH), 6.86-6.81 (m, 1H, ArH), 6.72-6.65 (m, 2H, ArH), 5.07 (d, *J* = 8.0 Hz, 1H, CH_2), 5.04 (d, *J* = 4.4 Hz, 1H, CH_2), 4.89 (d, *J* = 15.6 Hz, 1H, CH_2), 4.82 (d, *J* = 15.2 Hz, 1H, CH_2), 4.20 (s, 1H, CH), 3.28 (s, 3H, OCH_3), 2.93 (s, 3H, OCH_3), 0.91 (s, 9H, CH_3); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 179.7, 175.0, 167.4, 166.7, 162.1, 160.5, 160.4, 158.1, 139.8, 139.8, 139.3, 139.3, 136.2, 135.0, 132.5 (d, *J* = 8.5 Hz), 132.3 (d, *J* = 7.9 Hz), 128.7, 128.6, 128.4, 128.1, 127.8, 127.7, 116.1 (d, *J* = 23.2 Hz), 114.8 (d, *J* = 26.0 Hz), 114.1 (d, *J* = 23.7 Hz), 113.4 (d, *J* = 25.0 Hz), 110.3 (d, *J* = 7.8 Hz), 107.8 (d, *J* = 7.9 Hz), 103.0, 63.8, 60.8, 58.8, 58.7, 58.4, 54.3, 51.5, 50.7, 45.8, 44.7, 30.8, 18.4; IR (KBr) υ: 3180, 3062, 2953, 1751, 1720, 1662, 1618, 1490, 1449, 1341, 1293, 1266, 1178, 1121, 1047, 983, 944, 887, 810, 738, 697, 649 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{41}H_{37}F_2N_3NaO_6$ ([M+Na]$^+$): 728.2548, found: 728.2543.




179.73
175.00
167.38
166.73
162.14
160.49
160.46
158.07
139.79
139.77
139.34
139.32
136.16
135.04
132.50
132.41
132.32
132.24
128.70
128.64
128.44
128.06
127.84
127.73
116.25
116.02
114.93
114.67
114.25
114.02
113.49
113.24
110.31
110.23
107.83
107.75
102.96
63.80
60.78
58.76
58.74
58.41
54.26
51.52
50.70
45.83
44.68
30.79
H3CO
O
O
F
H
N
H3CO
O
O
F
N
180
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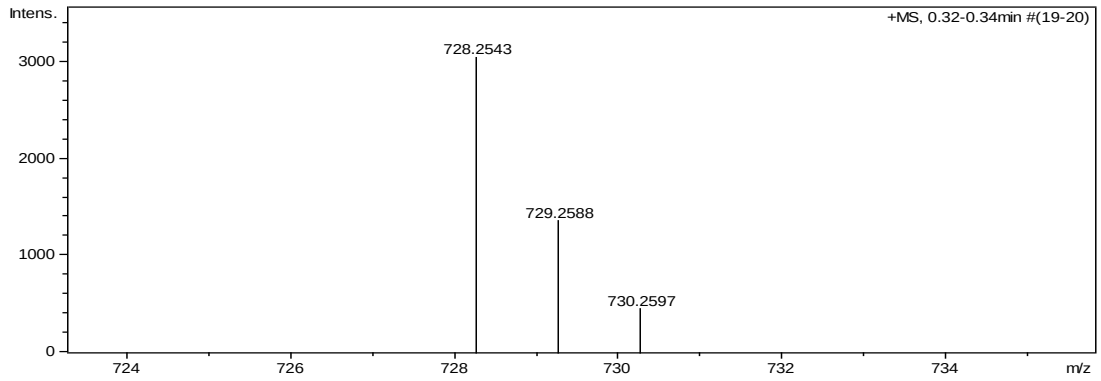
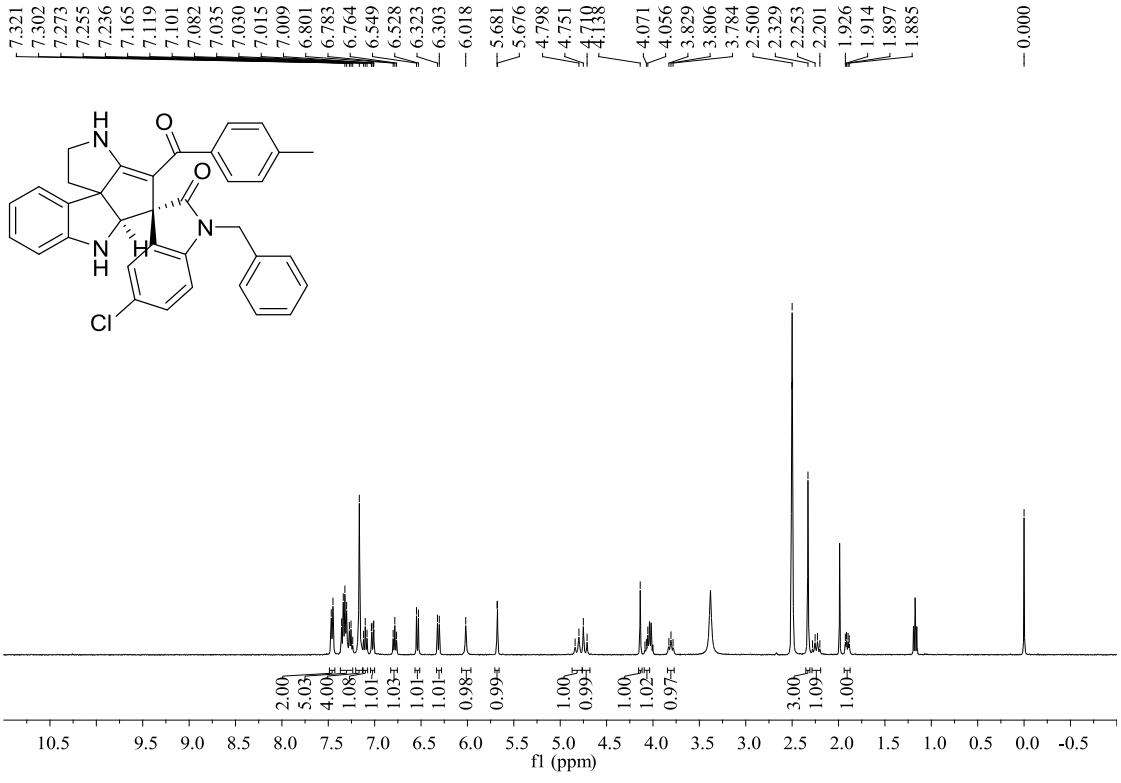
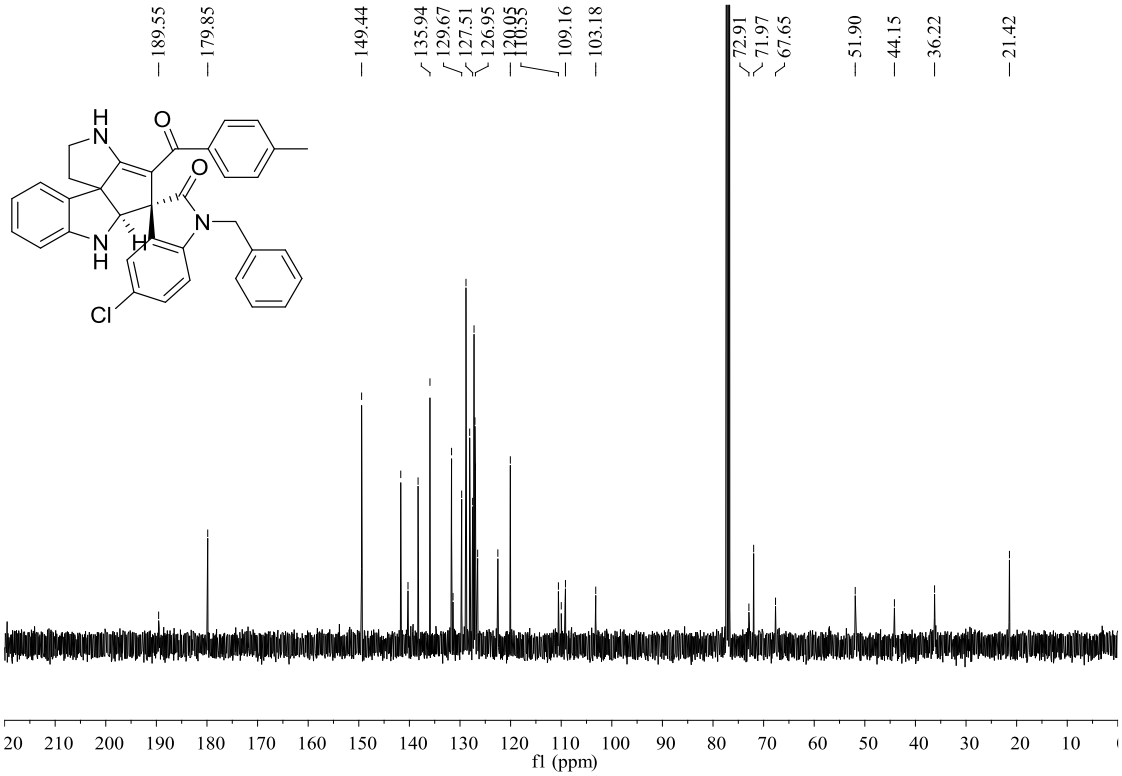
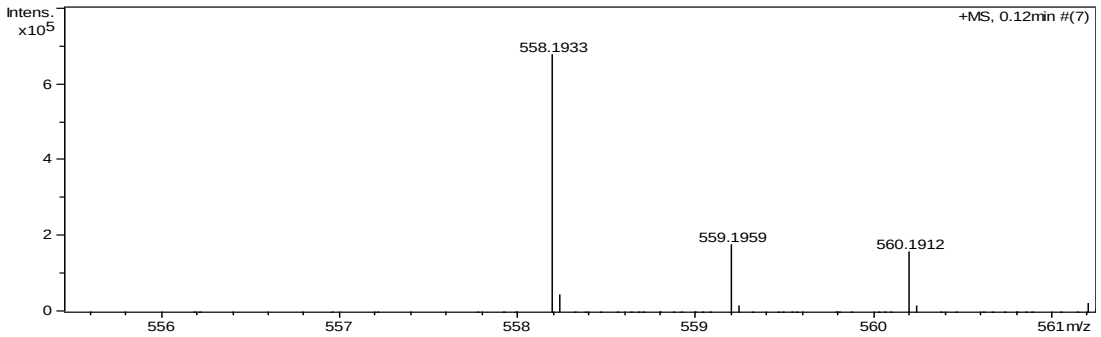
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)


Intens.
+MS, 0.32-0.34min #(19-20)
728.2543
729.2588
730.2597
3000
2000
1000
0
724
726
728
730
732
734
m/z

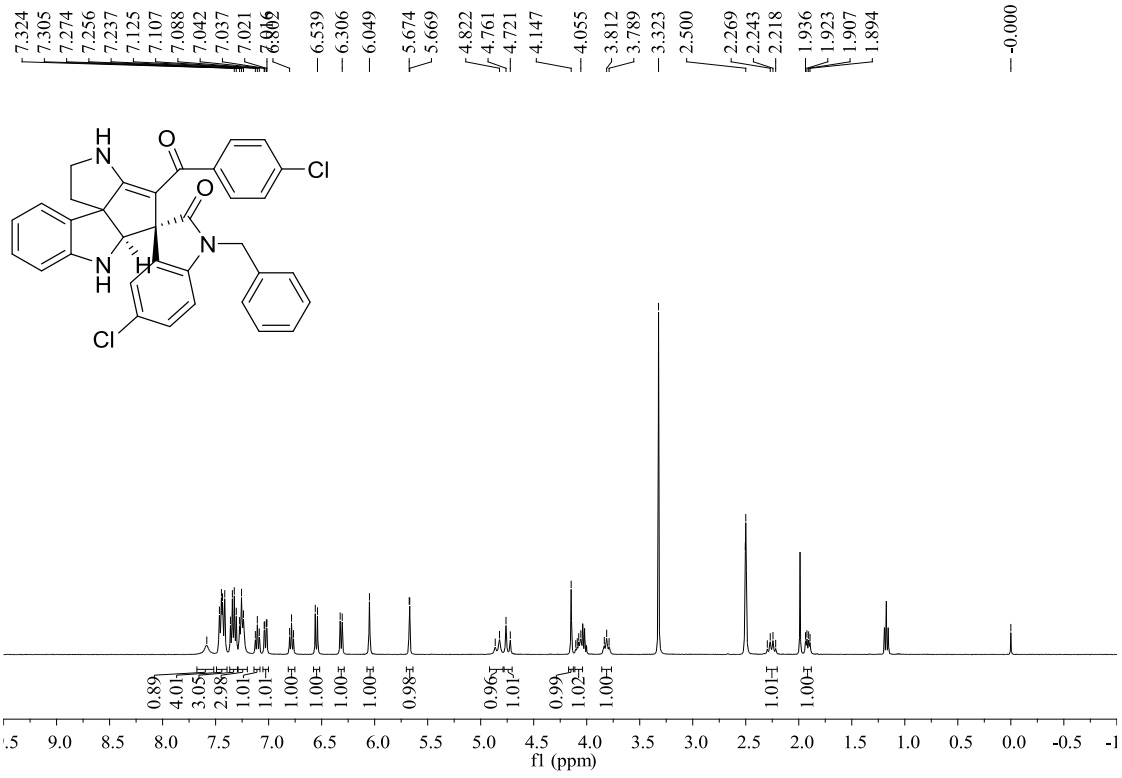
***rel*-(3*S*,5a'*S*)-1-benzyl-5-chloro-4'-(4-methylbenzoyl)-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5a):** white solid, 74%, m.p. 260-262 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.46 (d, J = 7.6 Hz, 1H, ArH), 7.36-7.24 (m, 5H, NH, ArH), 7.17 (s, 4H, ArH), 7.10 (t, J = 7.2 Hz, 1H, ArH), 7.02 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H, ArH), 6.78 (t, J = 7.2 Hz, 1H, ArH), 6.54 (d, J = 8.4 Hz, 1H, ArH), 6.31 (d, J = 8.0 Hz, 1H, ArH), 6.02 (s, 1H, NH), 5.68 (d, J = 2.0 Hz, 1H, ArH), 4.82 (d, J = 16.4 Hz, 1H, CH_2), 4.73 (d, J = 16.4 Hz, 1H, CH_2), 4.14 (s, 1H, CH), 4.09-4.06 (m, 1H, CH_2), 3.81 (t, J = 9.2 Hz, 1H, CH_2), 2.33 (s, 3H, CH_3), 2.28-2.20 (m, 1H, CH_2), 1.91 (dd, J_1 = 11.6 Hz, J_2 = 4.8 Hz, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 189.6, 179.9, 149.4, 141.7, 140.3, 138.3, 135.9, 131.7, 129.7, 128.8, 128.1, 127.5, 127.2, 127.1, 127.0, 126.5, 122.5, 120.1, 110.6, 109.2, 103.2, 72.9, 72.0, 67.7, 51.9, 44.2, 36.2, 21.4 ppm; IR (KBr) υ: 3839, 3746, 3673, 3648, 3612, 3320, 3030, 2941, 2876, 1737, 1698, 1633, 1607, 1583, 1551, 1479, 1426, 1374, 1342, 1326, 1277, 1247, 1177, 1100, 1075, 1000, 925, 824, 768, 727 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{35}H_{29}ClN_3O_2$ ([M+H]$^+$): 558.1943, found: 558.1933.

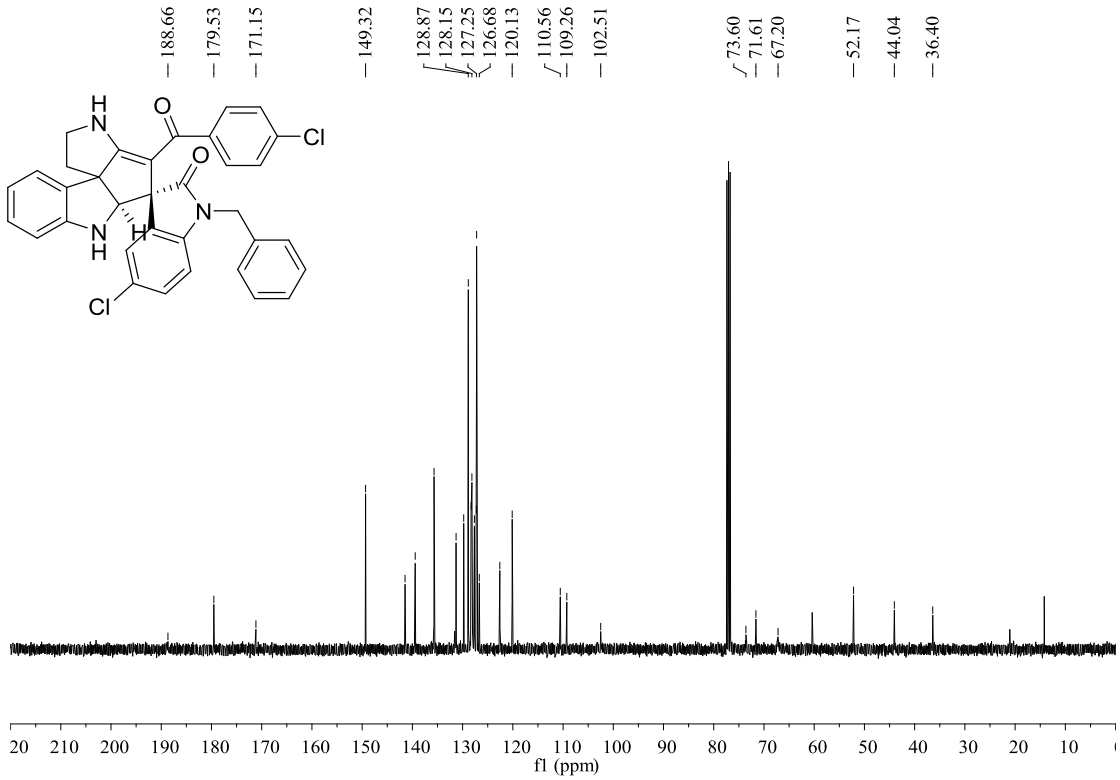


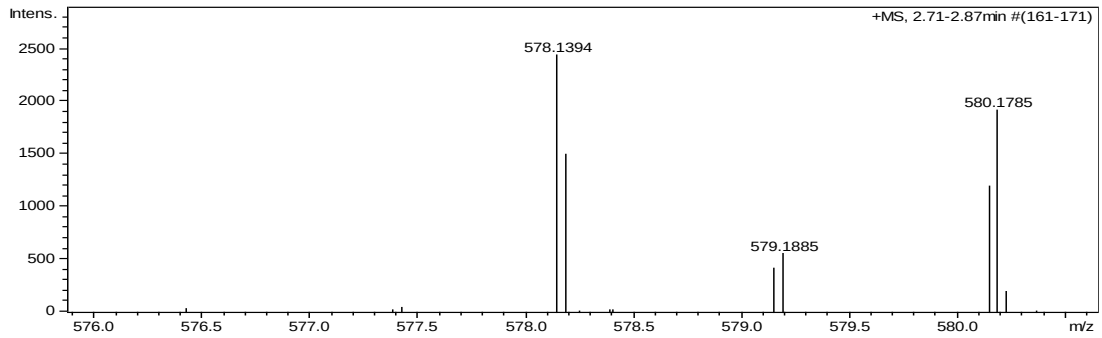

189.55
179.85
149.44
135.94
129.67
127.51
126.95
120.95
110.55
109.16
103.18
72.91
71.97
67.65
51.90
44.15
36.22
21.42
H
N
O
O
N
N
H
H
Cl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
x10^5
+MS, 0.12min #(7)
558.1933
559.1959
560.1912
0
2
4
6
556
557
558
559
560
561m/z

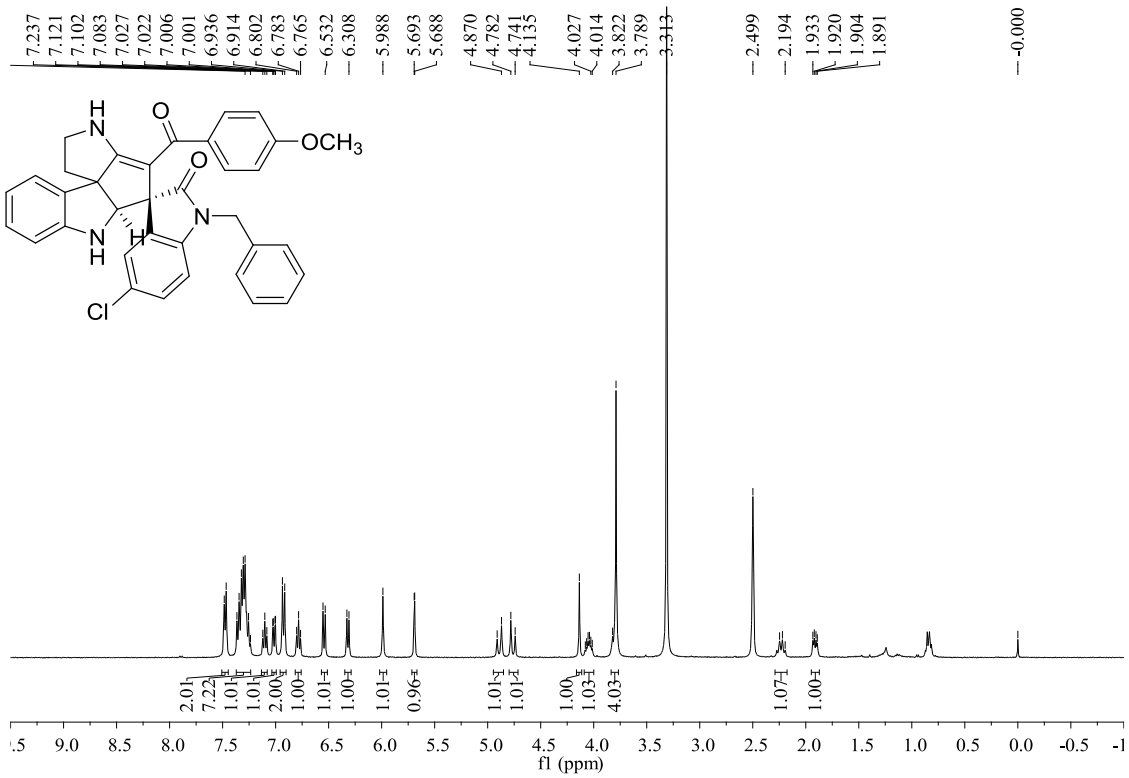
***rel*-(3*S*,5a'*S*)-1-benzyl-5-chloro-4'-(4-chlorobenzoyl)-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5b):** white solid, 69%, m.p. 259-261 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.58 (s, 1H, NH), 7.46-7.41 (m, 4H, ArH), 7.36-7.31 (m, 3H, ArH), 7.26 (t, J = 7.2 Hz, 3H, ArH), 7.11 (t, J = 7.2 Hz, 1H, ArH), 7.03 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H, ArH), 6.78 (t, J = 7.2 Hz, 1H, ArH), 6.55 (d, J = 8.4 Hz, 1H, ArH), 6.32 (d, J = 7.6 Hz, 1H, ArH), 6.05 (s, 1H, NH), 5.67 (d, J = 6.0 Hz, 1H, ArH), 4.84 (d, J = 16.4 Hz, 1H, CH_2), 4.74 (d, J = 16.0 Hz, 1H, CH_2), 4.15 (s, 1H, CH), 4.10-4.06 (m, 1H, CH_2), 3.81 (t, J = 8.8 Hz, 1H, CH_2), 2.30-2.22 (m, 1H, CH_2), 1.91 (dd, J_1 = 7.6 Hz, J_2 = 5.2 Hz, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 188.7, 179.5, 171.2, 149.3, 141.5, 139.4, 135.7, 131.3, 129.8, 128.9, 128.3, 128.2, 127.7, 127.3, 127.2, 126.7, 122.6, 120.1, 110.6, 109.3, 102.5, 73.6, 71.6, 67.2, 52.2, 44.0, 36.4 ppm; IR (KBr) υ: 3839, 3750, 3648, 3306, 3030, 2942, 2878, 1737, 1699, 1632, 1607, 1582, 1549, 1479, 1453, 1427, 1343, 1326, 1277, 1247, 1179, 1087, 1015, 1001, 844, 822, 768, 751, 728 cm^{-1}; MS (*m*/z): HRMS (ESI-TOF) Calcd. for $C_{34}H_{26}Cl_2N_3O_2$ ([M+H]$^+$): 578.1397, found: 578.1394.

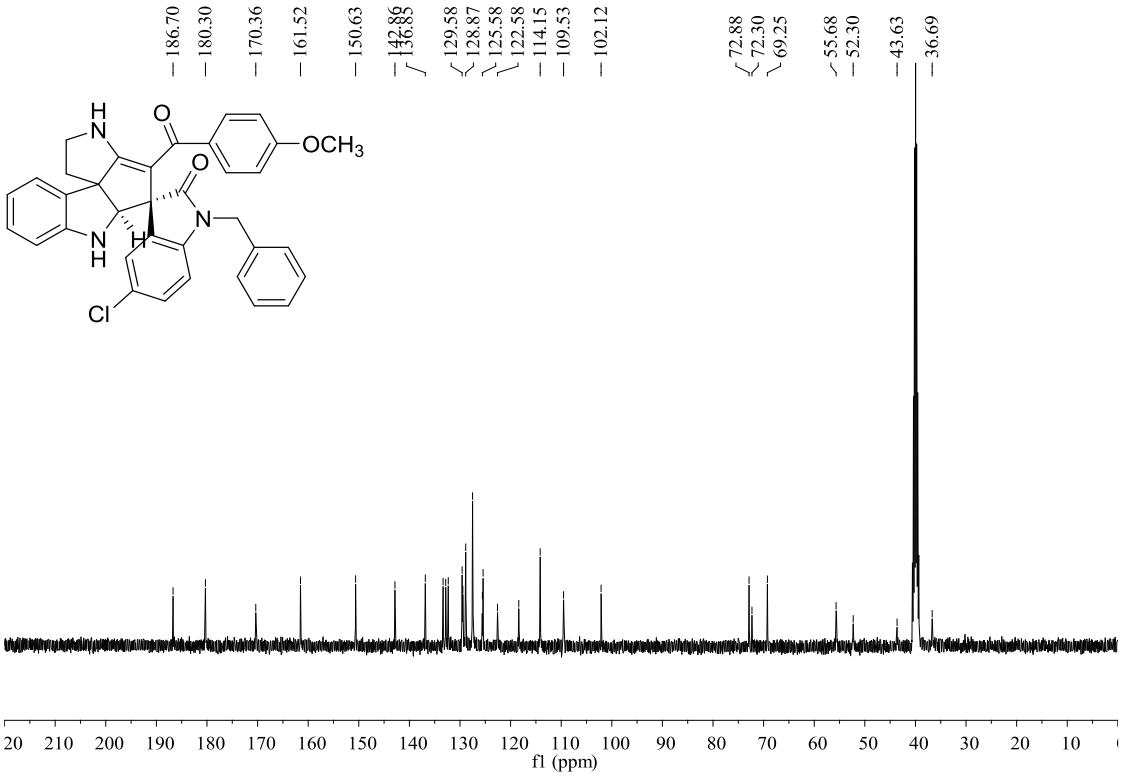



188.66
179.53
171.15
149.32
128.87
128.15
127.25
126.68
120.13
110.56
109.26
102.51
73.60
71.61
67.20
52.17
44.04
36.40
H
N
O
Cl
O
N
H
N
H
Cl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 2.71-2.87min #(161-171)
2500
2000
1500
1000
500
0
578.1394
580.1785
579.1885
576.0 576.5 577.0 577.5 578.0 578.5 579.0 579.5 580.0
m/z

***rel*-(3*S*,5a'*S*)-1-benzyl-5-chloro-4'-(4-methoxybenzoyl)-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5c):** white solid, 72%, m.p. 177-179 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.48 (d, J = 7.6 Hz, 2H, ArH), 7.37-7.24 (m, 7H, ArH, NH), 7.10 (t, J = 7.6 Hz, 1H, ArH), 7.01 (dd, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H, ArH), 6.92 (d, J = 8.8 Hz, 2H, ArH), 6.78 (t, J = 7.6 Hz, 1H, ArH), 6.54 (d, J = 8.4 Hz, 1H, ArH), 6.32 (d, J = 8.0 Hz, 1H, ArH), 5.99 (s, 1H, NH), 5.69 (d, J = 6.0 Hz, 1H, ArH), 4.89 (d, J = 16.4 Hz, 1H, CH_2), 4.76 (d, J = 16.0 Hz, 1H, CH_2), 4.14 (s, 1H, CH), 4.08-4.01 (m, 1H, CH_2), 3.82-3.79 (m, 4H, CH_2, OCH_3), 2.25-2.19 (m, 1H, CH_2), 1.91 (dd, J_1 = 7.6 Hz, J_2 = 5.2 Hz, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 186.7, 180.3, 170.4, 161.5, 150.6, 142.9, 136.9, 133.3, 132.8, 132.3, 129.6, 129.4, 128.9, 127.5, 125.6, 125.4, 122.6, 118.4, 114.2, 109.5, 102.1, 72.9, 72.3, 69.3, 55.7, 52.3, 43.6, 36.7 ppm; IR (KBr) υ: 3871, 3839, 3746, 3648, 3612, 3565, 3382, 3062, 2952, 1711, 1637, 1605, 1564, 1509, 1479, 1455, 1426, 1339, 1277, 1249, 1172, 1109, 1097, 1075, 1029, 996, 841, 808, 777, 744 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{35}H_{29}ClN_3O_3$ ([M+H]$^+$): 574.1892, found: 574.1884.




186.70
180.30
170.36
161.52
150.63
142.86
136.85
129.58
128.87
125.58
122.58
114.15
109.53
102.12
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72.30
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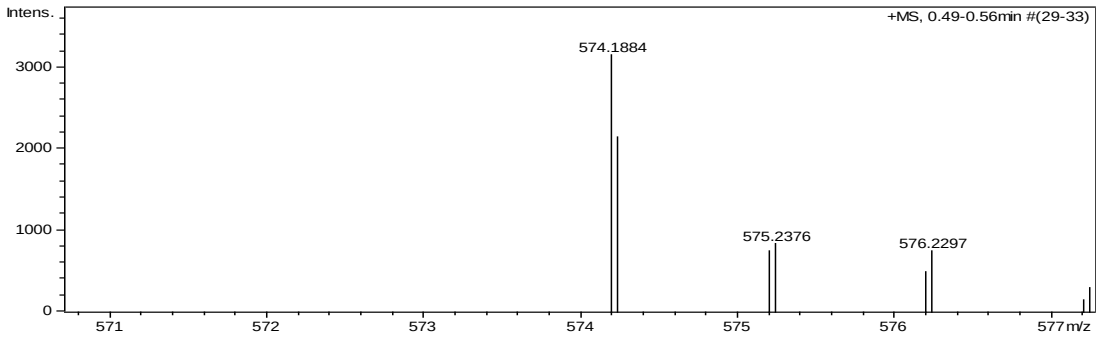
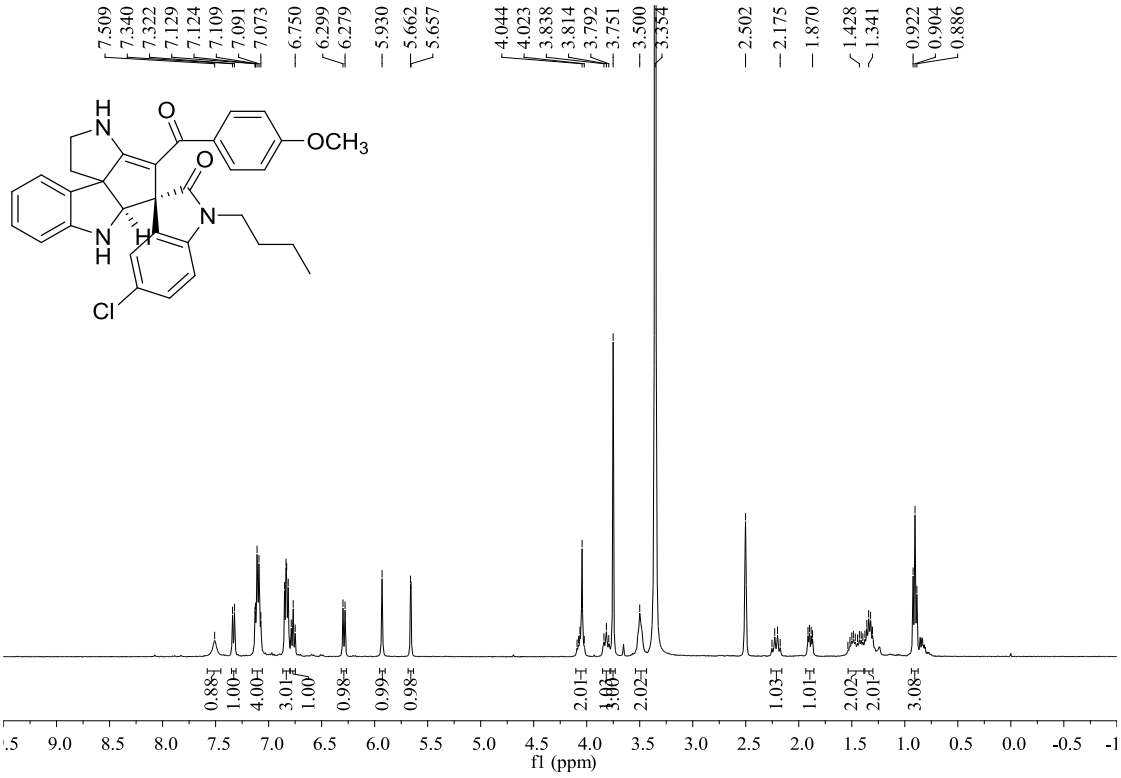
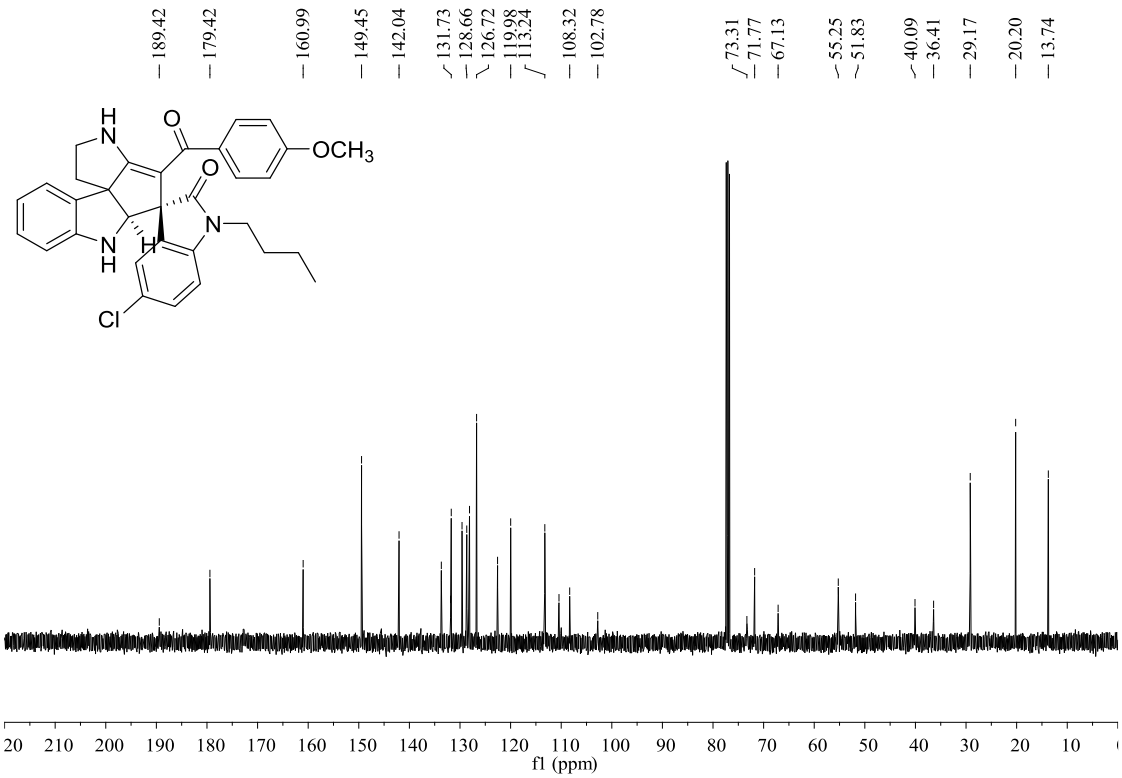
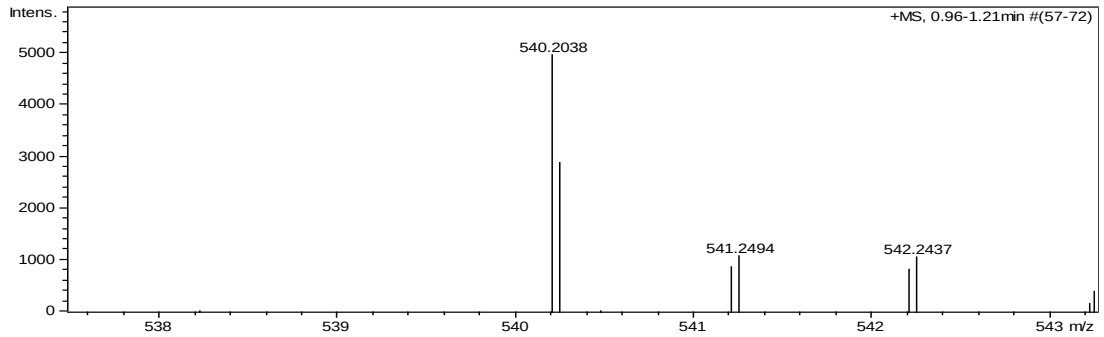
55.68
52.30
43.63
36.69
OCH3
Cl
f1 (ppm)


Intens.
+MS, 0.49-0.56min #(29-33)
574.1884
575.2376
576.2297
m/z

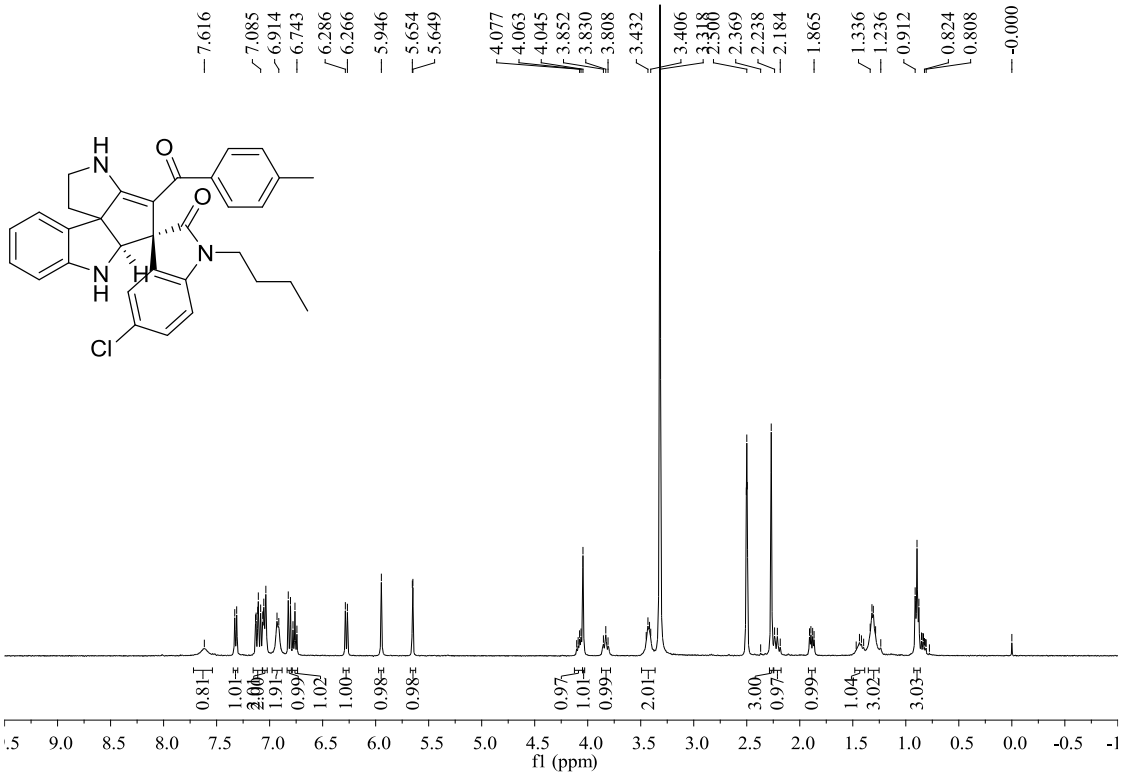
***rel*-(3*S*,5a'*S*)-1-butyl-5-chloro-4'-(4-methoxybenzoyl)-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5d):** white solid, 72%, m.p. 160-162 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.51 (s, 1H, NH), 7.33 (d, J = 7.2 Hz, 1H, ArH), 7.13-7.07 (m, 4H, ArH), 6.85-6.82 (m, 3H, ArH), 6.85-6.82 (m, 3H, ArH), 6.77 (t, J = 7.2 Hz, 1H, ArH), 6.29 (d, J = 8.0 Hz, 1H, ArH), 5.93 (s, 1H, NH), 5.66 (d, J = 2.0 Hz, 1H, ArH), 4.09-4.02 (m, 2H, CH_2, CH), 3.84-3.79 (m, 1H, CH_2), 3.75 (s, 3H, OCH_3), 3.51-3.48 (m, 2H, CH_2), 2.25-2.18 (m, 1H, CH_2), 1.89 (dd, J_1 = 12.0 Hz, J_2 = 5.6 Hz, 1H, CH_2), 1.54-1.40 (m, 2H, CH_2), 1.38-1.31 (m, 2H, CH_2), 0.90 (t, J = 7.2 Hz, 3H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 189.4, 179.4, 161.0, 149.5, 142.0, 133.7, 131.9, 131.7, 129.6, 128.7, 128.1, 126.7, 122.6, 120.0, 113.2, 110.4, 108.3, 102.8, 73.3, 71.8, 67.1, 55.3, 51.8, 40.1, 36.4, 29.2, 20.2, 13.7 ppm; IR (KBr) υ: 3839, 3746, 3648, 3612, 3381, 3053, 2957, 2933, 2872, 1709, 1640, 1605, 1565, 1532, 1510, 1479, 1427, 1346, 1282, 1250, 1172, 1107, 1075, 1023, 987, 952, 841, 808, 778, 746 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{32}H_{31}ClN_3O_3$ ([M+H]$^+$): 540.2048, found: 540.2038.

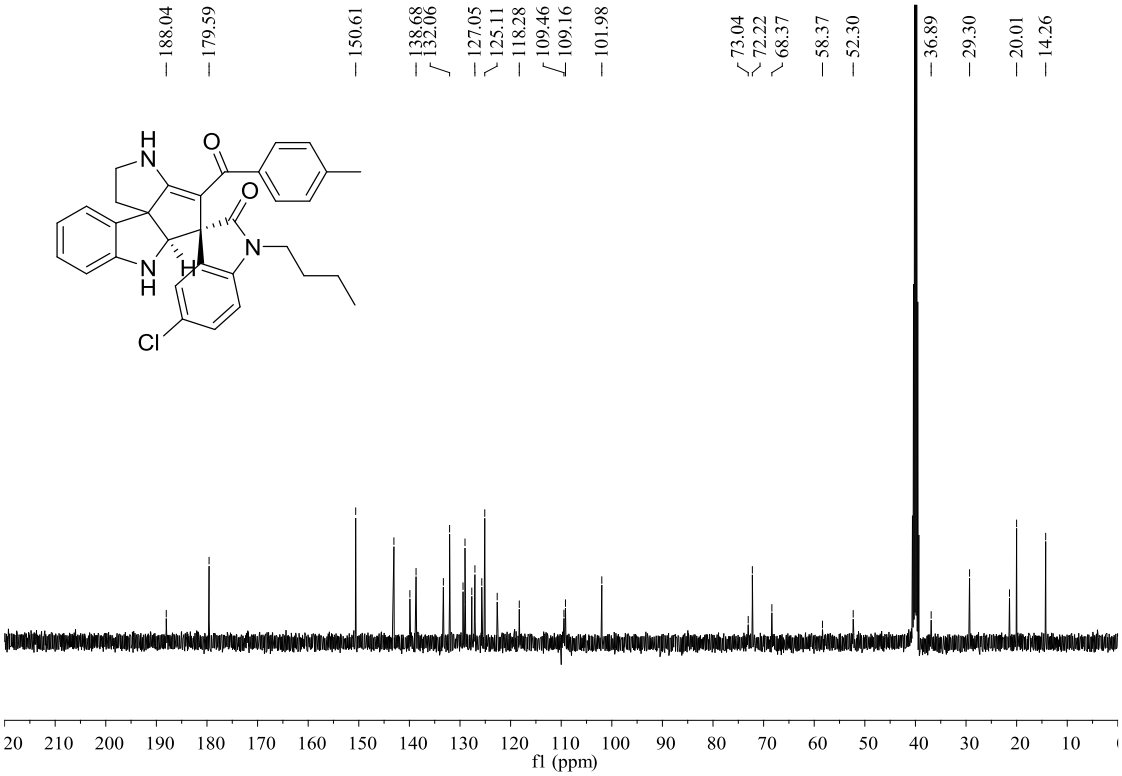


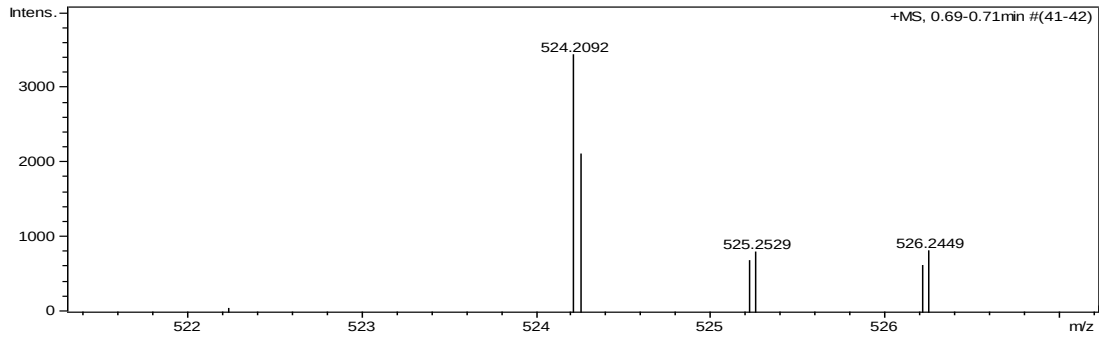

189.42
179.42
160.99
149.45
142.04
131.73
128.66
126.72
119.98
113.24
108.32
102.78
73.31
71.77
67.13
55.25
51.83
40.09
36.41
29.17
20.20
13.74
H
N
O
OCH3
O
N
N
H
H
Cl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 0.96-1.21min #(57-72)
5000
4000
3000
2000
1000
0
540.2038
541.2494
542.2437
538
539
540
541
542
543 m/z

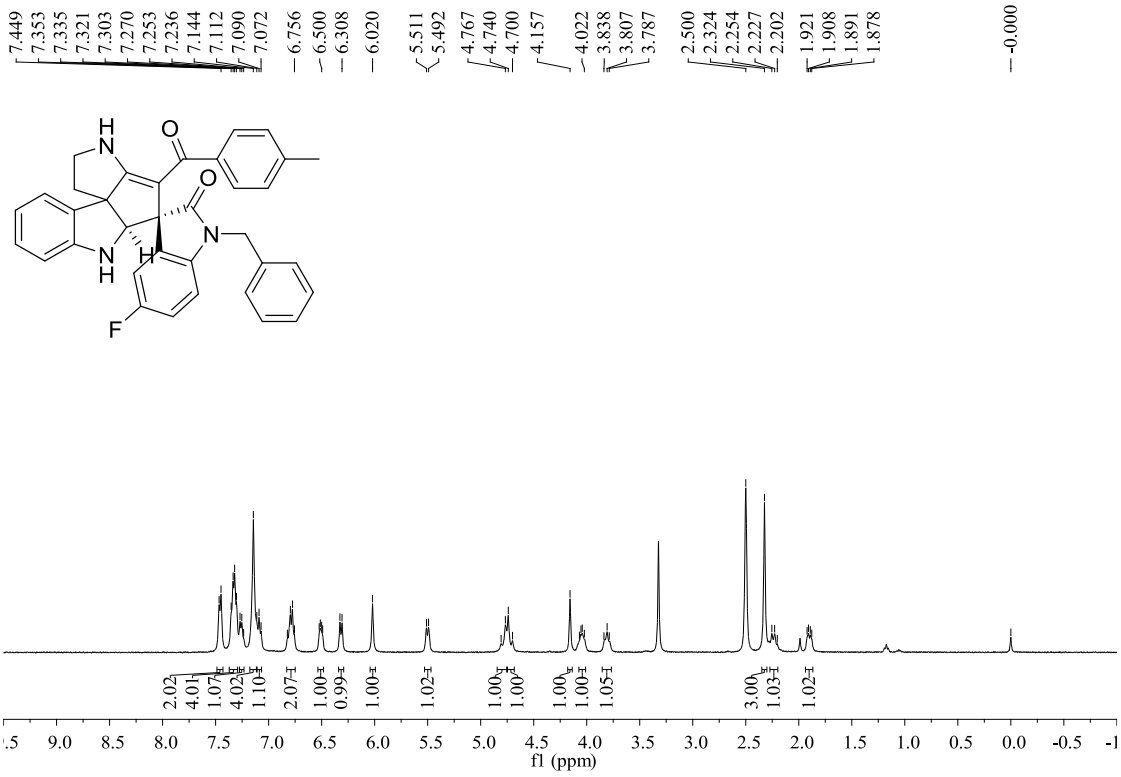
***rel*-(3*S*,5a'*S*)-1-butyl-5-chloro-4'-(4-methylbenzoyl)-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5e):** white solid, 82%, m.p. 164-166 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.62 (s, 1H, NH), 7.32 (d, J = 7.2 Hz, 1H, ArH), 7.13-7.09 (m, 2H, ArH), 7.07-7.04 (m, 2H, ArH), 6.92 (d, J = 6.4 Hz, 2H, ArH), 6.81 (d, J = 7.6 Hz , 1H, ArH), 6.76 (t, J = 7.6 Hz, 1H, ArH), 6.28 (d, J = 8.0 Hz, 1H, ArH), 5.95 (s, 1H, NH), 5.65 (d, J = 12.0 Hz, 1H, ArH), 4.10-4.06 (m, 1H, CH_2), 4.04 (s, 1H, CH), 3.86-3.80 (m, 1H, CH_2), 3.45-3.41 (m, 1H, CH_2), 2.27 (s, 3H, CH_3), 2.24-2.18 (m, 1H, CH_2), 1.89 (dd, J_1 = 12.0 Hz, J_2 = 5.2 Hz, 1H, CH_2), 1.47-1.40 (m, 1H, CH_2), 1.34-1.29 (m, 3H, CH_2), 0.89 (t, J = 7.2 Hz, 3H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 188.0, 179.6, 150.6, 143.1, 139.9, 138.7, 133.3, 132.1, 129.4, 129.0, 127.7, 127.1, 125.7, 125.1, 122.7, 118.3, 109.5, 109.2, 102.0, 73.0, 72.2, 68.4, 58.4, 52.3, 36.9, 29.3, 21.4, 20.0, 14.3 ppm; IR (KBr) υ: 3839, 3747, 3648, 3613, 3382, 2958, 2931, 2872, 1705, 1640, 1607, 1528, 1479, 1446, 1428, 1347, 1283, 1253, 1194, 1179, 1143, 1107, 1076, 1018, 988, 944, 828, 804, 771, 746 cm^{-1}; MS (*m*/z): HRMS (ESI-TOF) Calcd. for $C_{32}H_{31}ClN_3O_2$ ([M+H]$^+$): 524.2099, found: 524.2092.

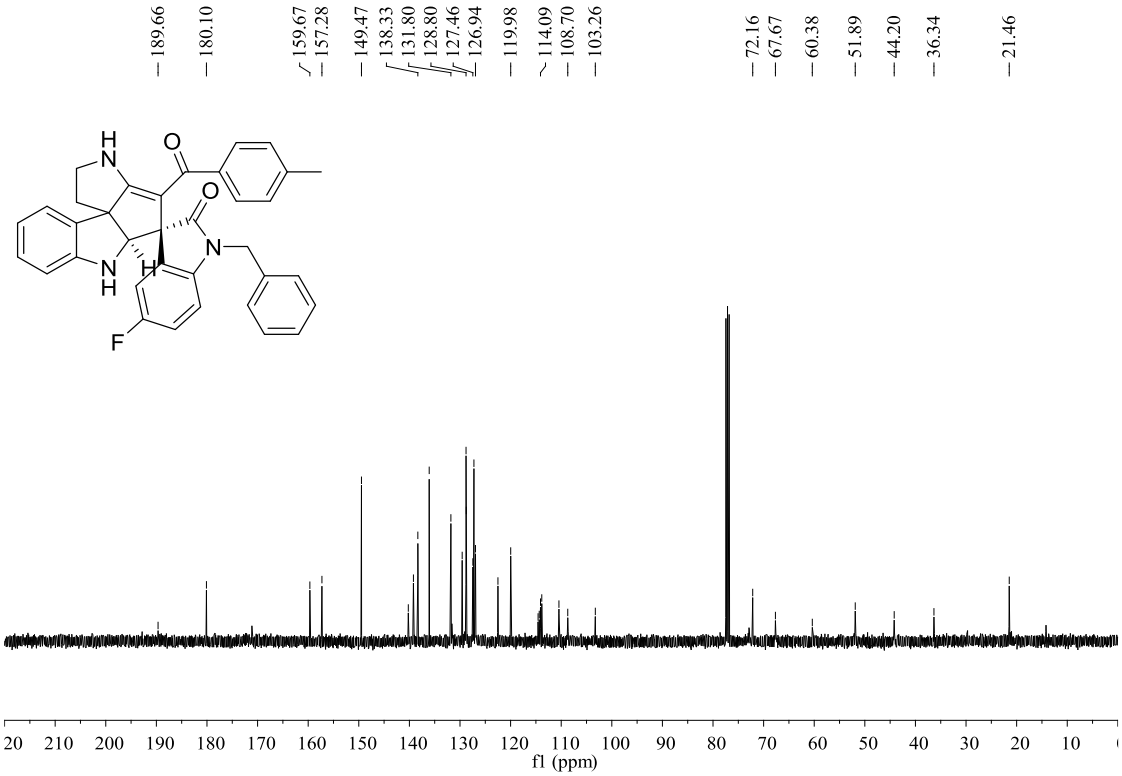


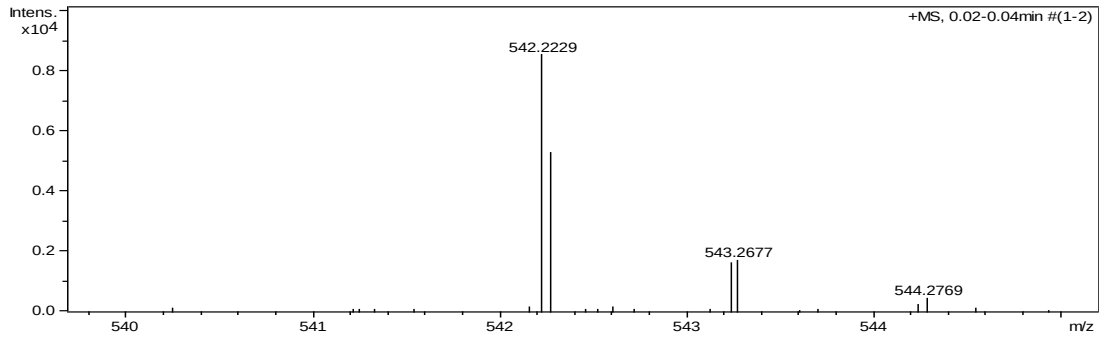

188.04
179.59
150.61
138.68
132.06
127.05
125.11
118.28
109.46
109.16
101.98
73.04
72.22
68.37
58.37
52.30
36.89
29.30
20.01
14.26
H
N
O
O
N
N
H
H
Cl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 0.69-0.71min #(41-42)
524.2092
525.2529
526.2449
3000
2000
1000
0
522
523
524
525
526
m/z

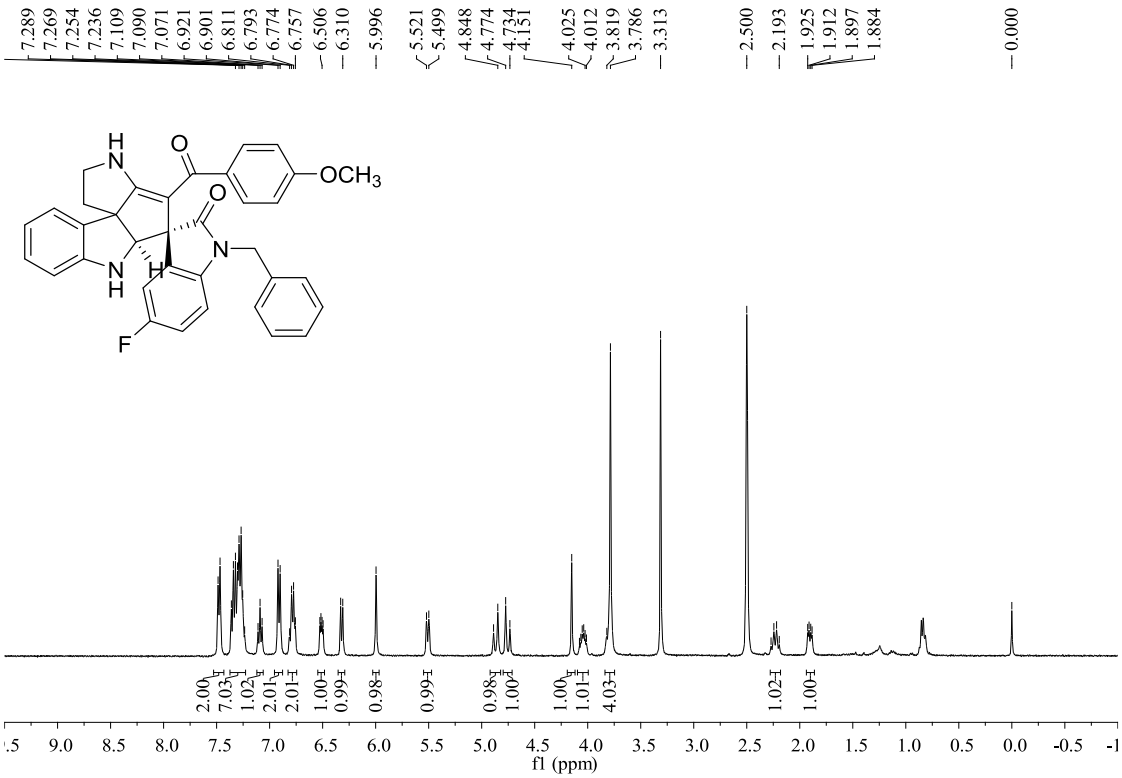
***rel*-(3*S*,5a'*S*)-1-benzyl-5-fluoro-4'-(4-methylbenzoyl)-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5f):** white solid, 85%, m.p. 218-220 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.46 (d, *J* = 7.2 Hz, 2H, ArH), 7.35-7.30 (m, 4H, ArH, NH), 7.27-7.24 (m, 1H, ArH), 7.14 (s, 4H, ArH), 7.11-7.07 (m, 1H, ArH), 6.82-6.76 (m, 2H, ArH), 6.52-6.49 (m, 1H, ArH), 6.32 (d, *J* = 7.6 Hz, 1H, ArH), 6.02 (s, 1H, NH), 5.50 (d, *J* = 7.6 Hz, 1H, ArH), 4.79 (d, *J* = 16.0 Hz, 1H, CH_2), 4.72 (d, *J* = 16.0 Hz, 1H, CH_2), 4.16 (s, 1H, CH), 4.07-4.02 (m, 1H, CH_2), 3.84-3.79 (m, 1H, CH_2), 2.32 (s, 1H, OCH_3), 2.25-2.20 (m, 1H, CH_2), 1.90 (dd, J_1 = 12.0 Hz, J_2 = 5.2 Hz, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 189.7, 180.1, 158.3 (*J* = 238.5 Hz), 149.5, 140.2, 139.2, 138.3, 136.1, 131.8, 129.6, 128.8, 128.8, 127.5, 127.3, 126.9, 122.5, 120.0, 114.5 (*J* = 22.7 Hz), 114. (*J* = 25.2 Hz), 110.5, 108.7, 103.3, 72.2, 67.7, 60.4, 51.9, 44.2, 36.3, 21.5 ppm; IR (KBr) υ: 3839, 3746, 3674, 3648, 3565, 3320, 3031, 2878, 1742, 1698, 1634, 1607, 1584, 1552, 1507, 1488, 1465, 1450, 1424, 1362, 1345, 1327, 1279, 1247, 1175, 821, 770, 753 cm^{-1}; MS (*m*/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{29}FN_3O_2$ ([M+H]$^+$): 542.2238, found: 542.2229.

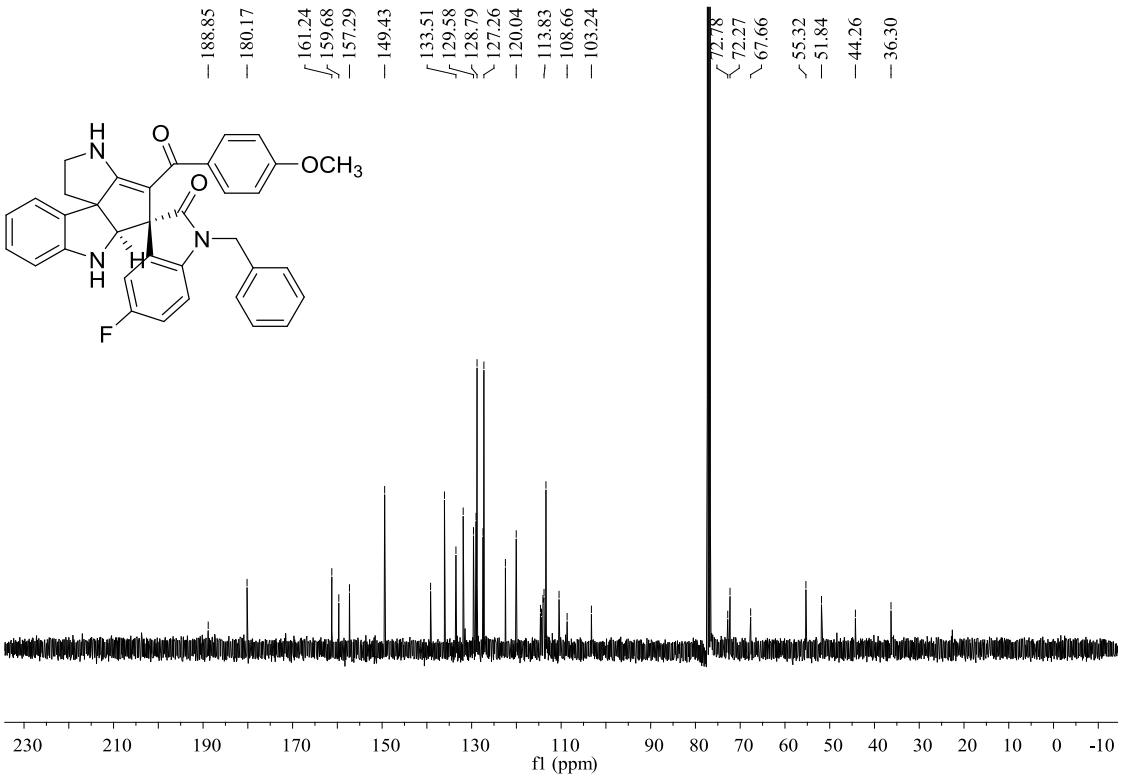


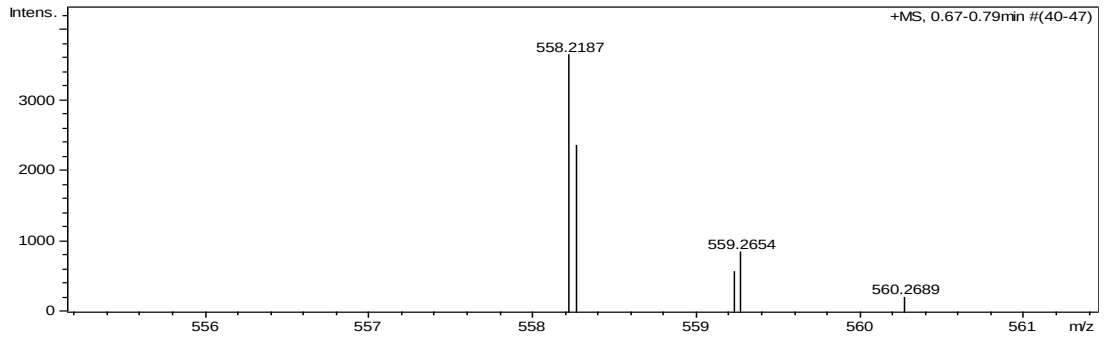

189.66
180.10
159.67
157.28
149.47
138.33
131.80
128.80
127.46
126.94
119.98
114.09
108.70
103.26
72.16
67.67
60.38
51.89
44.20
36.34
21.46
H
N
O
O
N
N
H
H
F
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
x10^4
+MS, 0.02-0.04min #(1-2)
542.2229
543.2677
544.2769
0.0
0.2
0.4
0.6
0.8
540
541
542
543
544
m/z

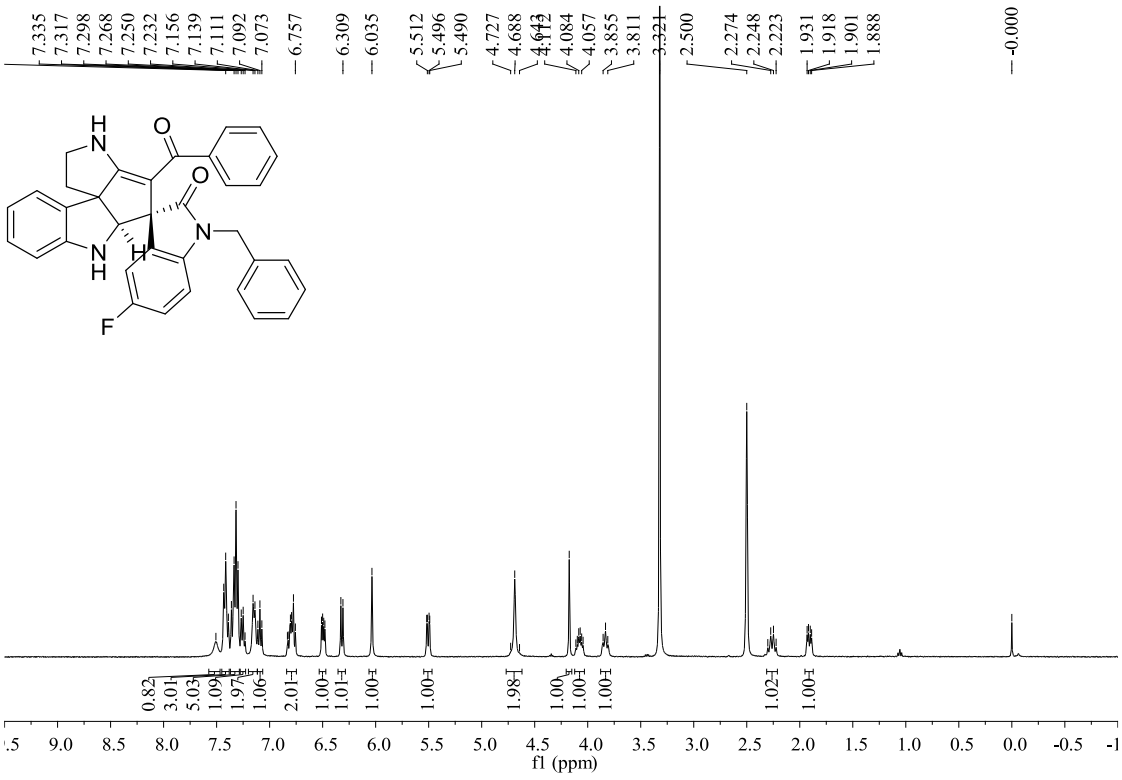
***rel*-(3*S*,5a'*S*)-1-benzyl-5-fluoro-4'-(4-methoxybenzoyl)-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5g):** white solid, 77%, m.p. 167-169 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.48 (d, J = 7.2 Hz, 2H, ArH), 7.36-7.24 (m, 7H, ArH, NH), 7.09 (d, J = 7.6 Hz, 1H, ArH), 6.91 (d, J = 8.0 Hz, 2H, ArH), 6.81-6.76 (m, 2H, ArH), 6.51 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H, ArH), 6.32 (d, J = 8.0 Hz, 1H, ArH), 6.00 (s, 1H, NH), 5.51 (d, J = 8.8 Hz, 1H, ArH), 4.87 (d, J = 16.0 Hz, 1H, CH_2), 4.75 (d, J = 16.0 Hz, 1H, CH_2), 4.15 (s, 1H, CH), 4.08-4.01 (m, 1H, CH_2), 3.82-3.79 (m, 4H, CH_2, CH_3), 2.27-2.19 (m, 1H, CH_2), 1.90 (dd, J_1 = 11.2 Hz, J_2 = 5.2 Hz, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 188.9, 180.2, 161.2, 158.5 (J = 238.7 Hz), 149.4, 139.2, 136.1, 133.5, 131.9, 129.6, 129.01, 128.8, 127.5, 127.3, 122.5, 120.0, 114.5 (J = 23.7 Hz), 114.1, 113.6 (J = 43.1 Hz), 110.5, 108.7, 103.2, 72.8, 72.3, 67.7, 55.3, 51.8, 44.3, 36.3 ppm; IR (KBr) υ: 3863, 3839, 3750, 3648, 3613, 3566, 3382, 2952, 1867, 1771, 1748, 1706, 1638, 1605, 1564, 1558, 1509, 1487, 1449, 1429, 1339, 1281, 1250, 1171, 1091, 1029, 846, 809, 777, 748 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{35}H_{29}FN_3O_3$ ([M+H]$^+$): 558.2187, found: 558.2187.

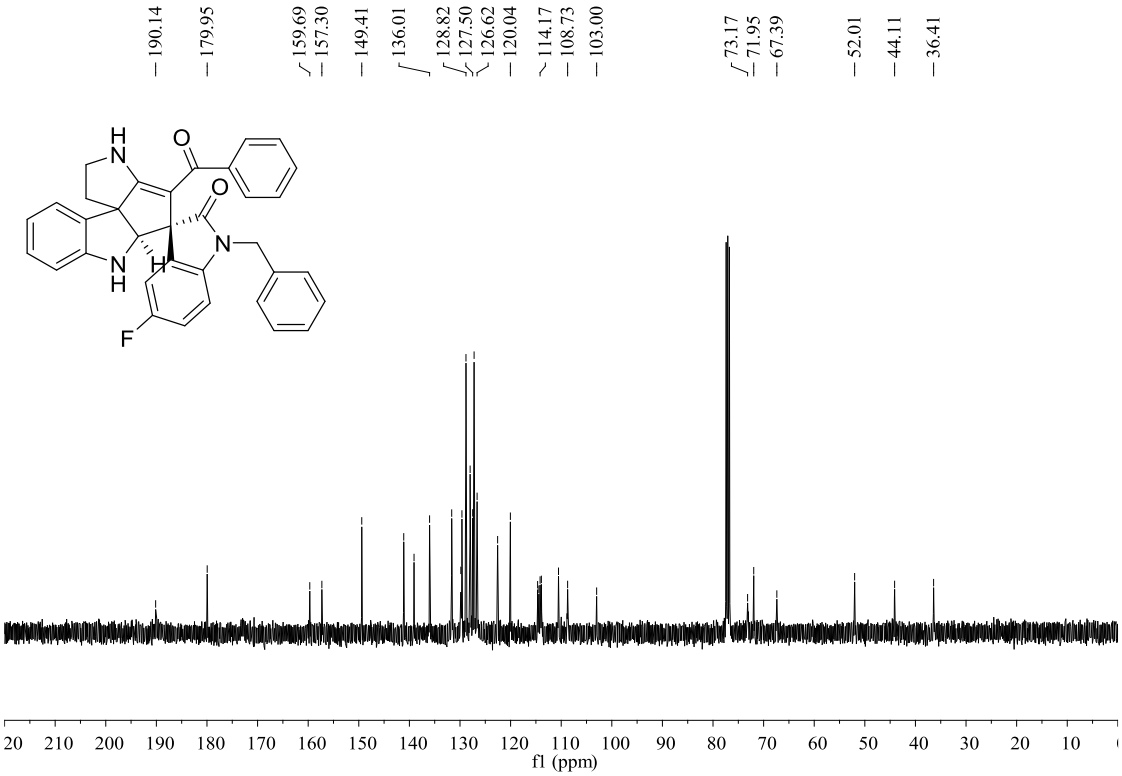


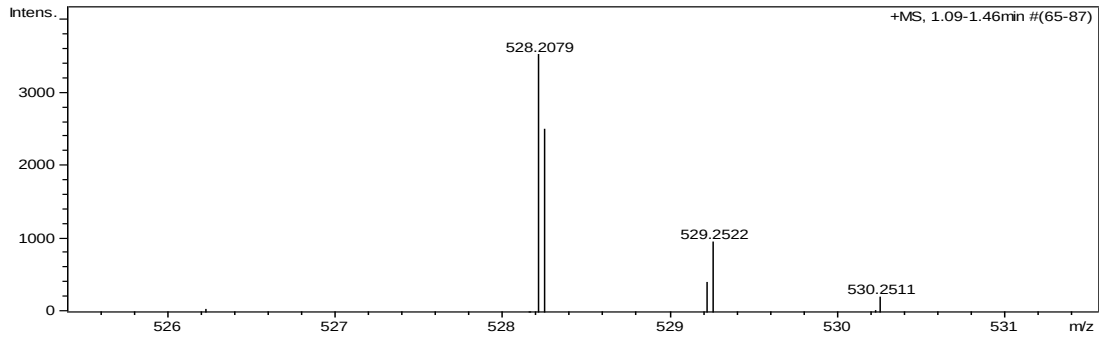

188.85
180.17
161.24
159.68
157.29
149.43
133.51
129.58
128.79
127.26
120.04
113.83
108.66
103.24
72.78
72.27
67.66
55.32
51.84
44.26
36.30
OCH3
O
O
N
H
N
H
N
H
F
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Intens.
+MS, 0.67-0.79min #(40-47)
558.2187
559.2654
560.2689
3000
2000
1000
0
556
557
558
559
560
561
m/z

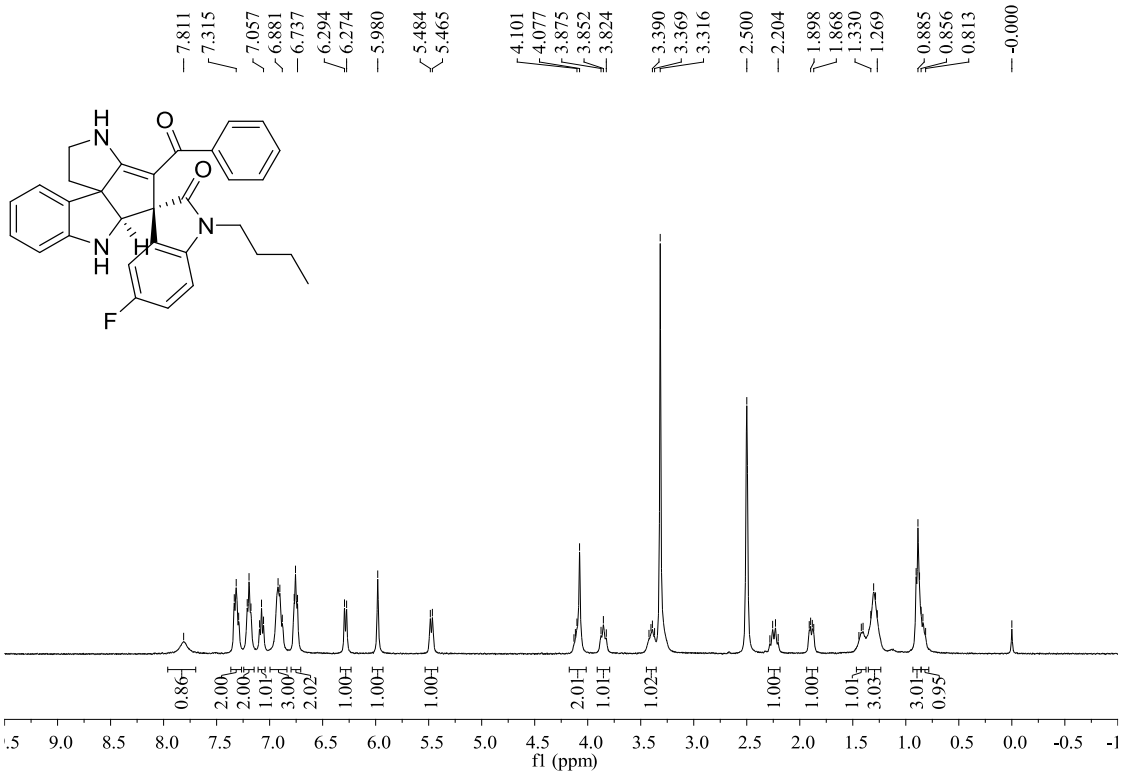
***rel*-(3*S*,5a'*S*)-4'-benzoyl-1-benzyl-5-fluoro-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5h):** white solid, 84%, m.p. 214-216 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.51 (s, 1H, NH), 7.43-7.39 (m, 3H, ArH), 7.36-7.30 (m, 5H, ArH), 7.25 (t, J = 7.2 Hz, 1H, ArH), 7.15 (d, J = 6.8 Hz, 2H, ArH), 7.09 (t, J = 7.6 Hz, 1H, ArH), 6.83-6.76 (m, 2H, ArH), 6.49 (dd, J_1 = 8.4 Hz, J_2 = 4.4 Hz, 1H, ArH), 6.32 (d, J = 7.6 Hz, 1H, ArH), 6.04 (s, 1H, NH), 5.50 (dd, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 1H, ArH), 4.73-4.64 (m, 2H, CH_2), 4.17 (s, 1H, CH), 4.11-4.04 (m, 1H, CH_2), 3.86-3.81 (m, 1H, CH_2), 2.30-2.22 (m, 1H, CH_2), 1.91 (dd, J_1 = 12.0 Hz, J_2 = 5.2 Hz, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 190.1, 180.0, 158.5 (J = 238.5 Hz), 149.4, 141.1, 139.1, 136.0, 131.6, 129.8, 129.6, 128.8, 128.0, 127.5, 127.2, 126.6, 122.6, 120.0, 114.5 (J = 25.2 Hz), 114.0 (J = 25.9 Hz), 110.5, 108.7, 103.0, 73.2, 72.0, 67.4, 52.0, 44.1, 36.4 ppm; IR (KBr) υ: 3839, 3648, 3365, 3292, 3031, 2934, 2886, 1698, 1639, 1605, 1568, 1542, 1488, 1470, 1448, 1427, 1344, 1280, 1258, 1171, 1137, 1003, 973, 950, 926, 844, 809, 753, 730, 700 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{34}H_{27}FN_3O_2$ ([M+H]$^+$): 528.2082, found: 528.2079.

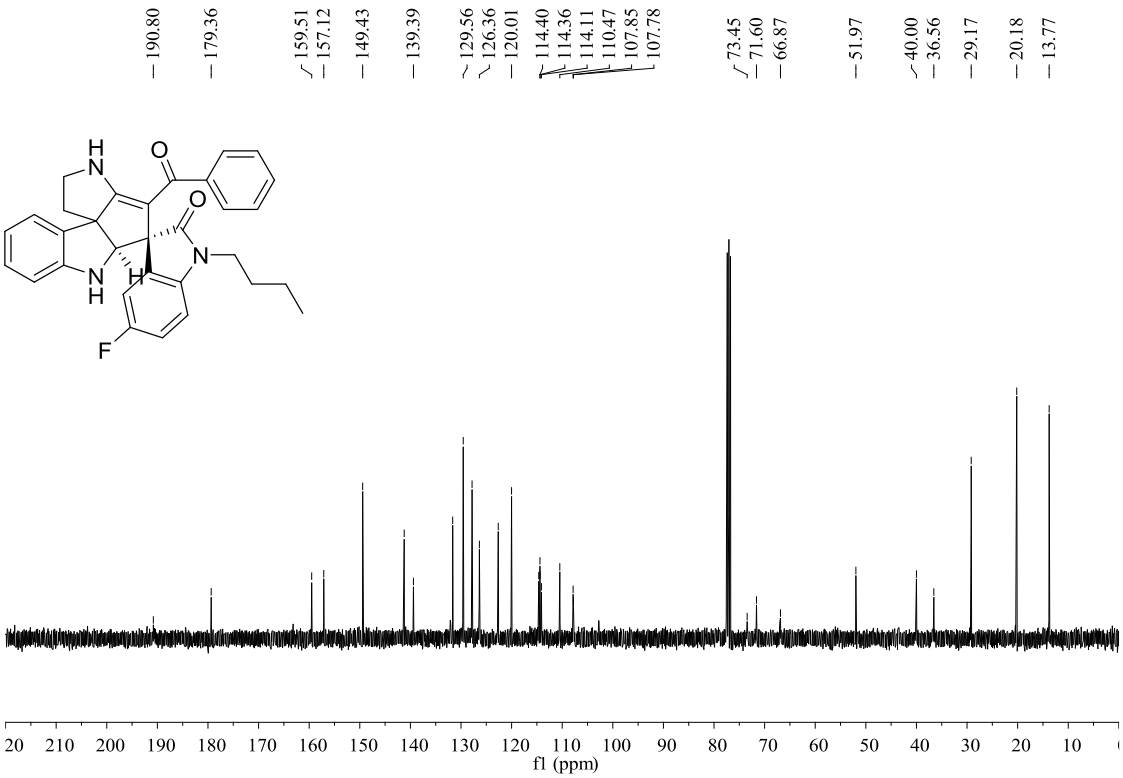


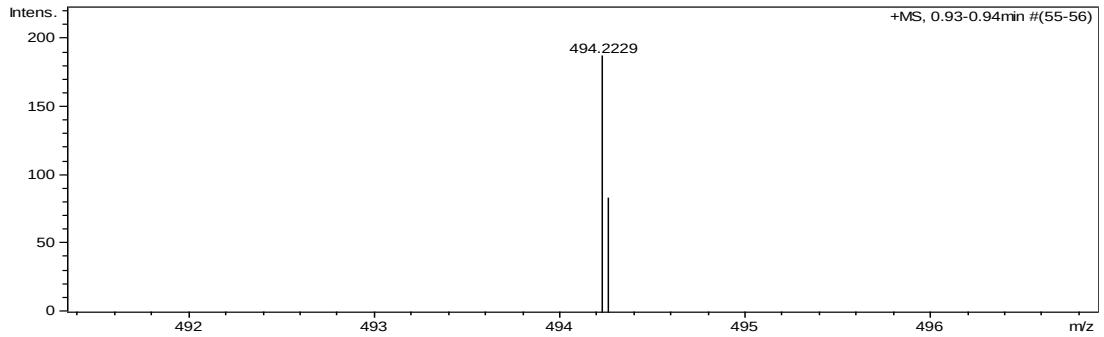

190.14
179.95
159.69
157.30
149.41
136.01
128.82
127.50
126.62
120.04
114.17
108.73
103.00
73.17
71.95
67.39
52.01
44.11
36.41
H
N
O
O
N
N
H
H
F
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 1.09-1.46min #(65-87)
528.2079
529.2522
530.2511
3000
2000
1000
0
526
527
528
529
530
531
m/z

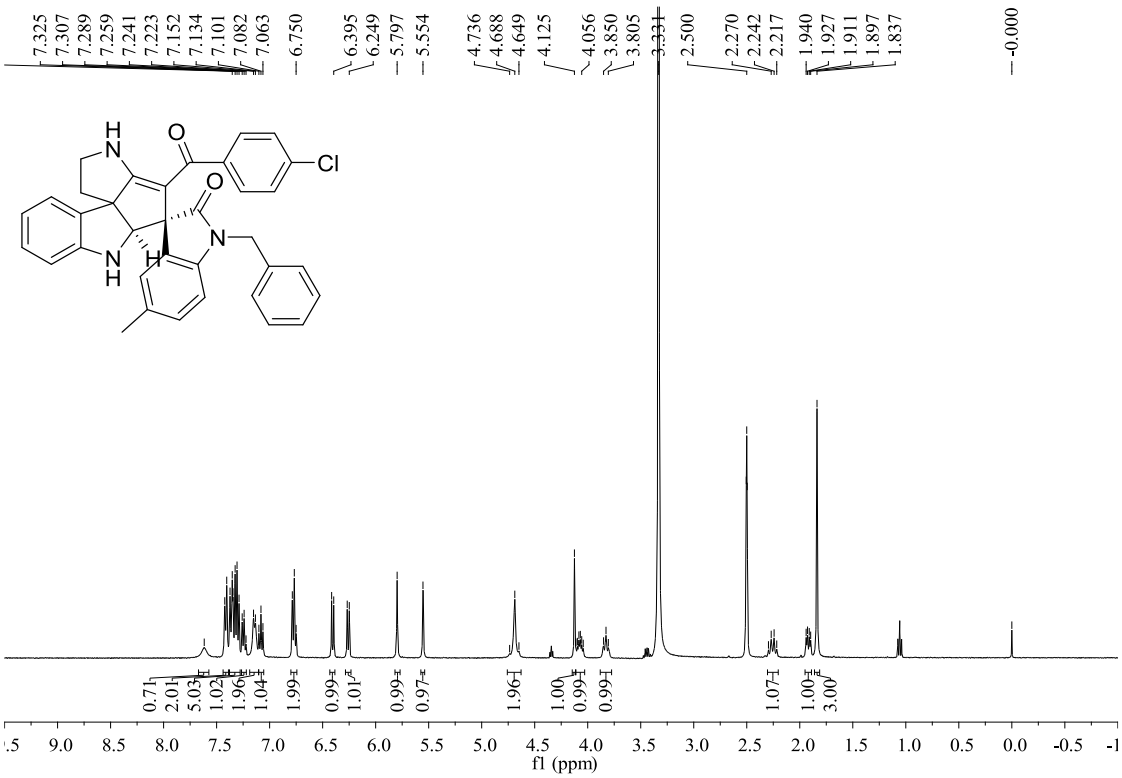
***rel*-(3*S*,5a'*S*)-4'-benzoyl-1-butyl-5-fluoro-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5i):** white solid, 74%, m.p. 147-149 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.81 (s, 1H, NH), 7.33-7.29 (m, 2H, ArH), 7.19 (t, J = 6.8 Hz, 2H, ArH), 7.08 (t, J = 7.2 Hz, 1H, ArH), 6.92-6.88 (m, 3H, ArH), 6.77-6.74 (m, 2H, ArH), 6.28 (d, J = 8.0 Hz, 1H, ArH), 5.98 (s, 1H, NH), 5.47 (d, J = 7.6 Hz, 1H, ArH), 4.13-4.08 (m, 2H, CH, CH_2), 3.85 (t, J = 9.2 Hz, 1H, CH_2), 3.42-3.37 (m, 1H, CH_2), 2.28-2.20 (m, 1H, CH_2), 1.89 (dd, J_1 = 11.6 Hz, J_2 = 5.2 Hz, 1H, CH_2), 1.44-1.40 (m, 1H, CH_2), 1.33-1.27 (m, 1H, CH_2), 0.89 (t, J = 6.8 Hz, 3H, CH_3), 0.86-0.81 (m, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 190.8, 179.4, 159.5, 157.1, 149.4, 141.2, 139.4, 131.6, 129.6, 127.8, 126.4, 122.6, 120.0, 114.6, 114.4, 114.4, 114.1, 110.5, 107.9, 107.8, 73.5, 71.6, 66.9, 52.0, 40.0, 36.6, 29.2, 20.2, 13.8 ppm; IR (KBr) υ: 3872, 3839, 3746, 3648, 3612, 3565, 3378, 3053, 2957, 2932, 2872, 1705, 1644, 1605, 1590, 1533, 1487, 1448, 1349, 1283, 1258, 1180, 1138, 1087, 1020, 964, 920, 843, 807, 752 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{31}H_{29}FN_3O_2$ ([M+H]$^{+}$): 494.2238, found: 494.2229.

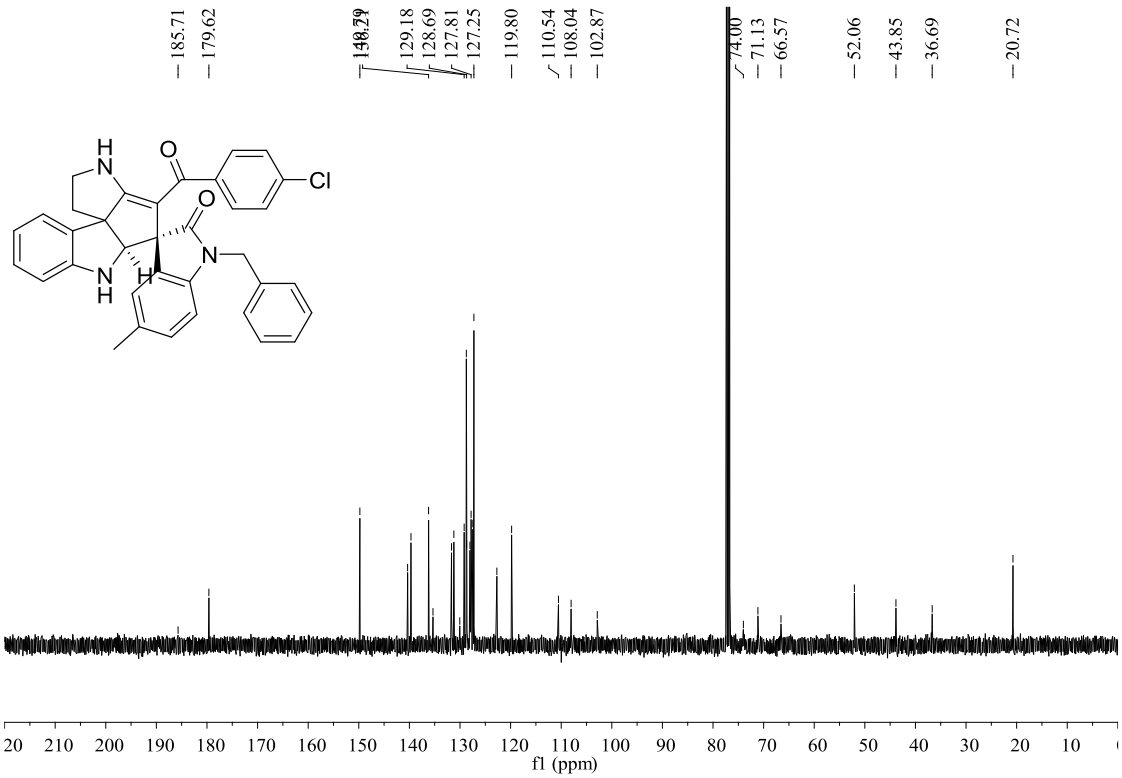


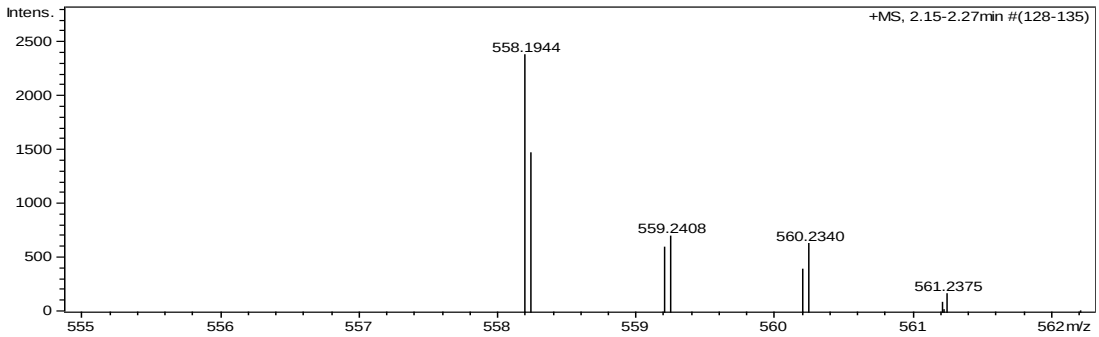

190.80
179.36
159.51
157.12
149.43
139.39
129.56
126.36
120.01
114.40
114.36
114.11
110.47
107.85
107.78
73.45
71.60
66.87
51.97
40.00
36.56
29.17
20.18
13.77
H
N
O
O
N
N
H
H
F
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 0.93-0.94min #(55-56)
494.2229
200
150
100
50
0
492
493
494
495
496
m/z

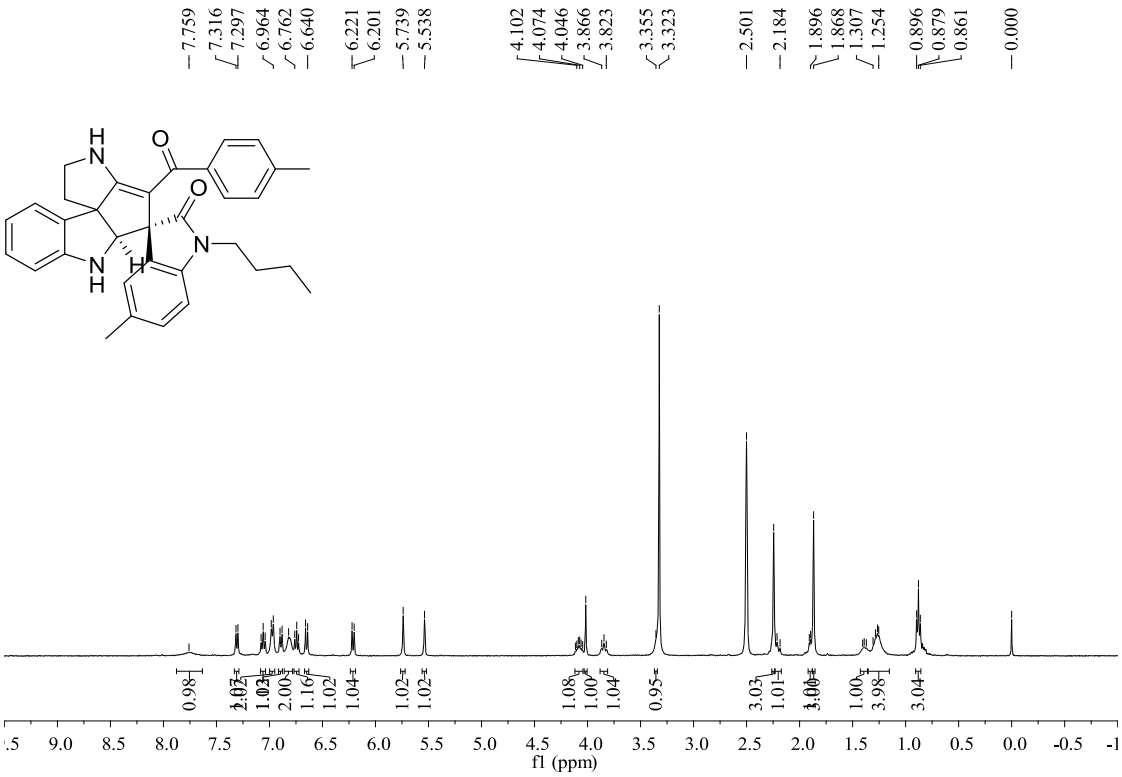
***rel*-(3*S*,5a'*S*)-1-benzyl-4'-(4-chlorobenzoyl)-5-methyl-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5j):** white solid, 41%, m.p. 238-240 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.62 (s, 1H, NH), 7.41 (d, J = 7.2 Hz, 2H, ArH), 7.37-7.29 (m, 5H, ArH), 7.24 (t, J = 7.2 Hz, 1H, ArH), 7.14 (d, J = 7.2 Hz, 2H, ArH), 7.08 (t, J = 7.6 Hz, 1H, ArH), 6.77 (t, J = 7.6 Hz, 2H, ArH), 6.41 (d, J = 8.0 Hz, 1H, ArH), 6.26 (d, J = 7.6 Hz, 1H, ArH), 5.80 (s, 1H, NH), 5.55 (s, 1H, ArH), 4.74-4.65 (m, 2H, CH_2), 4.13 (s, 1H, CH), 4.11-4.04 (m, 1H, CH_2), 3.85-3.81 (m, 1H, CH_2), 2.30-2.22 (m, 1H, CH_2), 1.92 (dd, J_1 = 11.6 Hz, J_2 = 5.2 Hz, 1H, CH_2), 1.84 (s, 3H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 185.7, 179.6, 149.8, 140.4, 139.7, 136.2, 135.3, 131.7, 131.2, 130.0, 129.2, 128.8, 128.7, 128.0, 127.8, 127.5, 127.3, 122.7, 119.8, 110.5, 108.0, 102.9, 74.0, 71.1, 66.6, 52.1, 43.9, 36.7, 20.7 ppm; IR (KBr) υ: 3871, 3839, 3818, 3746, 3673, 3648, 3296, 3030, 2939, 2879, 1694, 1633, 1583, 1551, 1507, 1495, 1425, 1348, 1326, 1278, 1248, 1178, 1086, 1016, 847, 820, 795, 772, 752, 726 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{35}H_{29}ClN_3O_2$ ([M+H]$^+$): 558.1943, found: 558.1944.

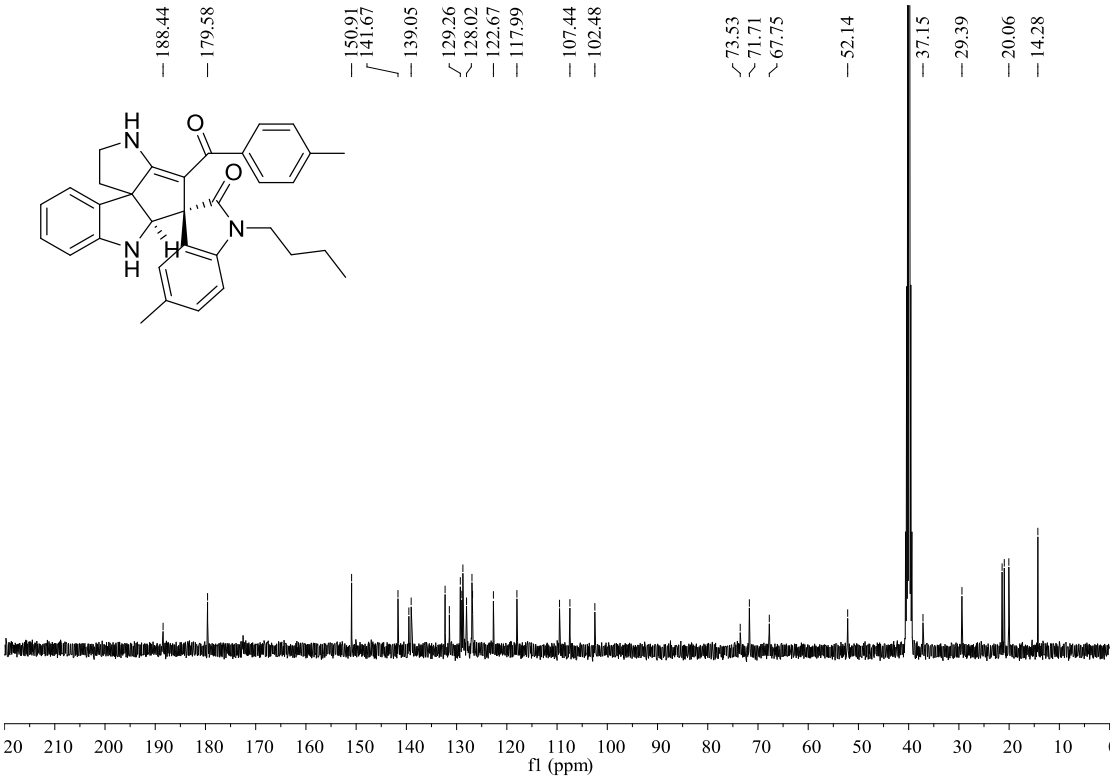


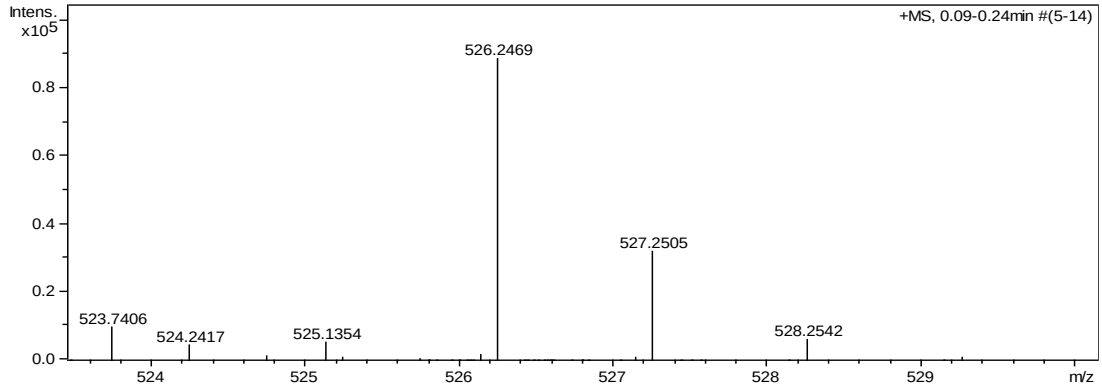

185.71
179.62
129.18
128.69
127.81
127.25
119.80
110.54
108.04
102.87
74.00
71.13
66.57
52.06
43.85
36.69
20.72
Cl
O
O
N
H
N
H
N
H
f1 (ppm)


Intens.
+MS, 2.15-2.27min #(128-135)
558.1944
559.2408
560.2340
561.2375
m/z

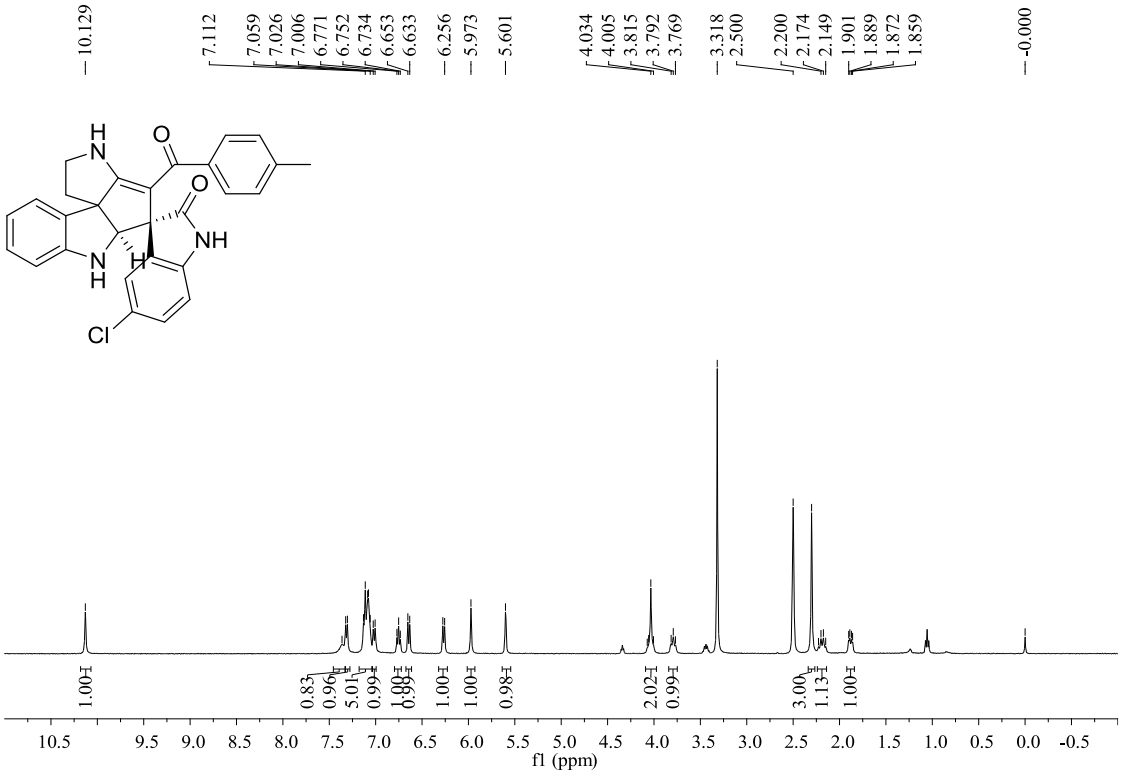
***rel*-(3*S*,5a'*S*)-1-butyl-5-methyl-4'-(4-methylbenzoyl)-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one(5k):** white solid, 48%, m.p. 168-170 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.76 (s, 1H, NH), 7.31 (d, *J* = 7.6 Hz, 1H, ArH), 7.06 (d, *J* = 8.0 Hz, 1H, ArH), 6.97 (d, *J* = 7.6 Hz, 2H, ArH), 6.89 (t, *J* = 7.6 Hz, 1H, ArH), 6.82 (s, 2H, ArH), 6.74 (t, *J* = 7.6 Hz, 1H, ArH), 6.65 (d, *J* = 8.0 Hz, 1H, ArH), 6.21 (d, *J* = 8.0 Hz, 1H, ArH), 5.74 (s, 1H, NH), 5.54 (s, 1H, ArH), 4.11-4.05 (m, 1H, CH_2), 4.02 (s, 1H, CH), 3.84 (t, *J* = 8.4 Hz, 1H, CH_2), 3.35 (s, 1H, CH_2), 2.24 (s, 3H, CH_3), 2.20 (d, *J* = 11.6 Hz, 1H, CH_2), 1.90 (d, *J* = 5.2 Hz, 1H, CH_2), 1.87 (s, 3H, CH_3), 1.41-1.37 (m, 1H, CH_2), 1.31-1.25 (m, 4H, CH_2), 0.88 (t, *J* = 6.8 Hz, 3H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 188.4, 179.6, 150.9, 141.7, 139.5, 139.1, 132.3, 131.4, 129.3, 129.0, 128.8, 128.0, 126.9, 126.8, 122.7, 118.0, 109.5, 107.4, 102.5, 73.5, 71.7, 67.8, 52.1, 37.2, 29.4, 21.4, 21.0, 20.1, 14.3 ppm; IR (KBr) υ: 3377, 3029, 2956, 2931, 2871, 1707, 1641, 1606, 1534, 1493, 1479, 1466, 1429, 1352, 1283, 1258, 1199, 1140, 1106, 1092, 1019, 984, 832, 804, 771, 745 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{33}H_{33}NaN_3O_2$ ([M+Na]$^+$): 526.2465, found: 526.2469.

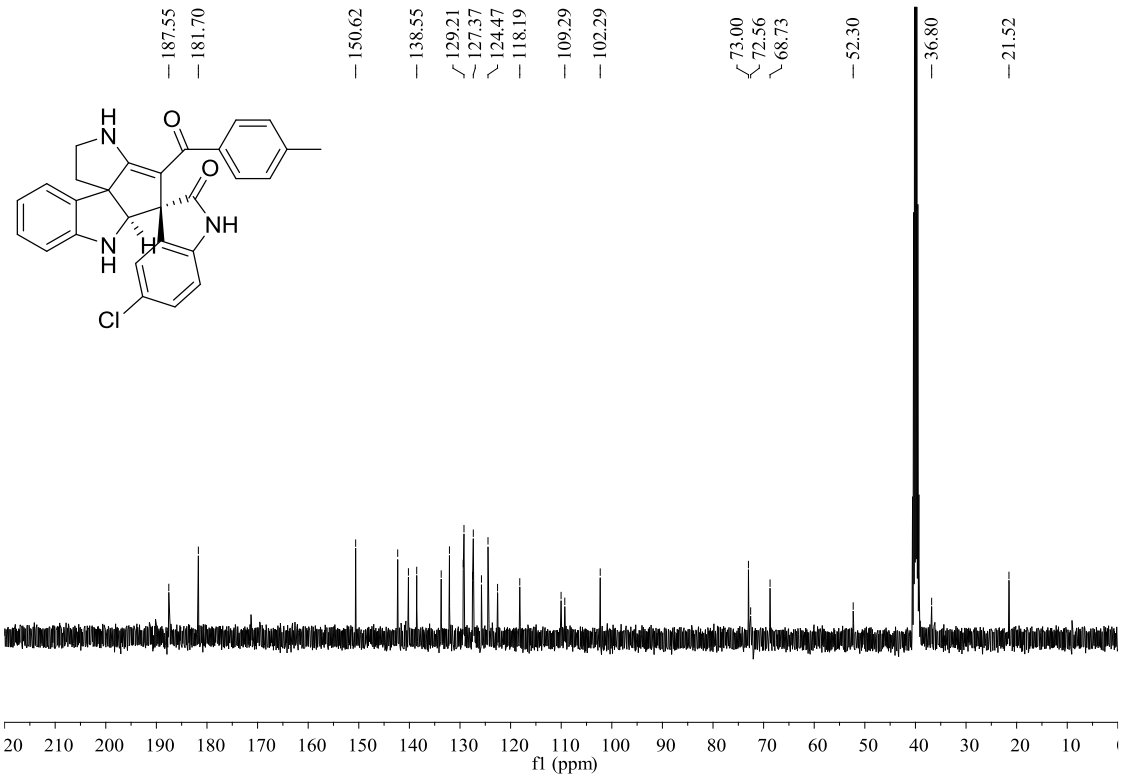


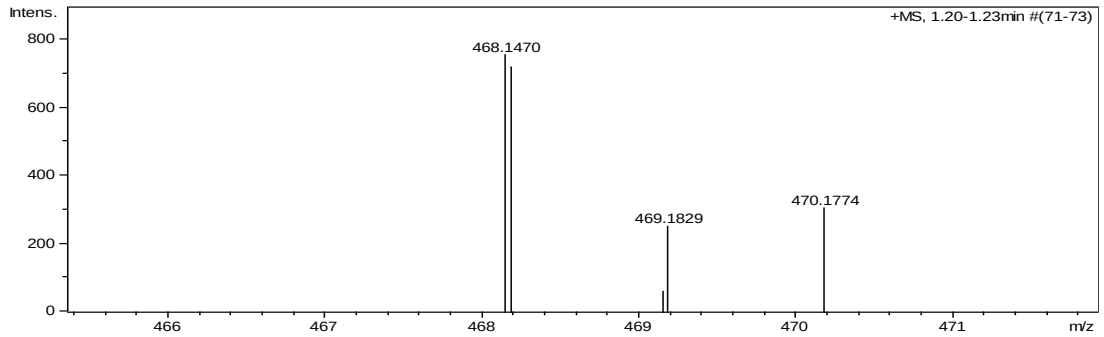

188.44
179.58
150.91
141.67
139.05
129.26
128.02
122.67
117.99
107.44
102.48
73.53
71.71
67.75
52.14
37.15
29.39
20.06
14.28
H
N
O
O
N
N
H
H
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
x10^5
+MS, 0.09-0.24min #(5-14)
526.2469
527.2505
523.7406
524.2417
525.1354
528.2542
0.0
0.2
0.4
0.6
0.8
524
525
526
527
528
529
m/z

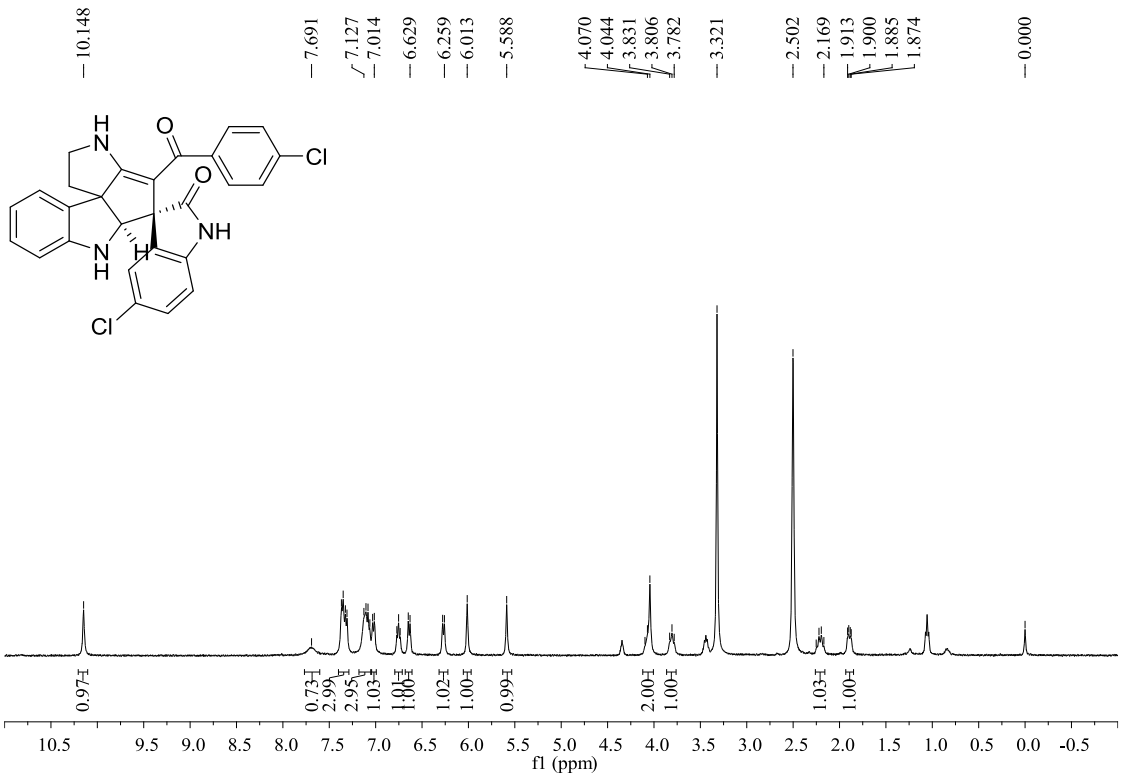
***rel*-(3*S*,5a'*S*)-5-chloro-4'-(4-methylbenzoyl)-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5l):** white solid, 62%, m.p. 259-261 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.13 (s, 1H, NH), 7.36 (s, 1H, NH), 7.31 (d, J = 7.2 Hz, 1H, ArH), 7.13-7.06 (m, 5H, ArH), 7.02 (d, J = 8.0 Hz, 1H, ArH), 6.75 (t, J = 7.6 Hz, 1H, ArH), 6.64 (d, J = 8.0 Hz, 1H, ArH), 6.27 (d, J = 8.0 Hz, 1H, ArH), 5.97 (s, 1H, NH), 5.60 (s, 1H, ArH), 4.07-4.01 (m, 2H, CH, CH_2), 3.79 (t, J = 9.2 Hz, 1H, CH_2), 2.30 (s, 3H, CH_3), 2.23-2.15 (m, 1H, CH_2), 1.88 (dd, J_1 = 11.6 Hz, J_2 = 4.8 Hz, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 187.6, 181.7, 150.6, 142.3, 140.2, 138.6, 133.7, 132.1, 129.4, 129.2, 127.5, 127.4, 125.8, 124.5, 122.6, 118.2, 110.0, 109.3, 102.3, 73.0, 72.6, 68.7, 52.3, 36.8, 21.5 ppm; IR (KBr) υ: 3872, 3839, 3750, 3648, 3613, 3565, 3427, 3378, 3324, 3252, 2973, 2885, 1714, 1633, 1607, 1578, 1555, 1474, 1446, 1427, 1374, 1308, 1255, 1196, 1179, 1106, 1075, 970, 810, 769 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{28}H_{23}ClN_3O_2$ ([M+H]$^+$): 468.1473, found: 468.1470.

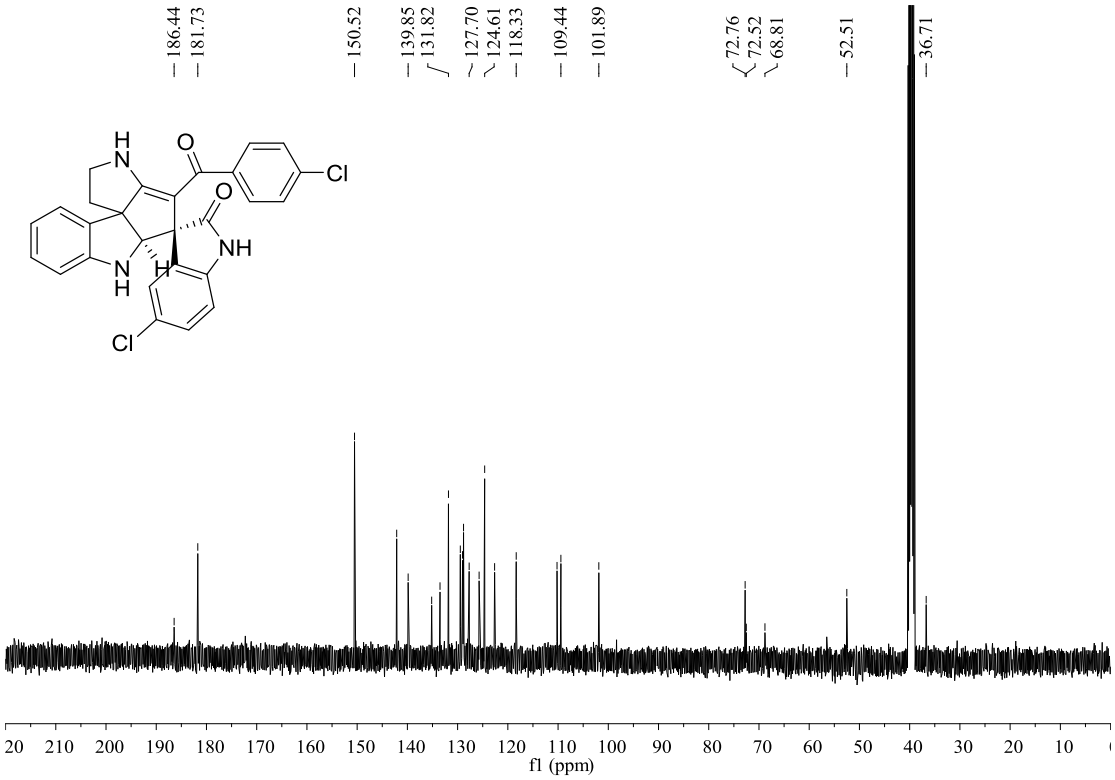


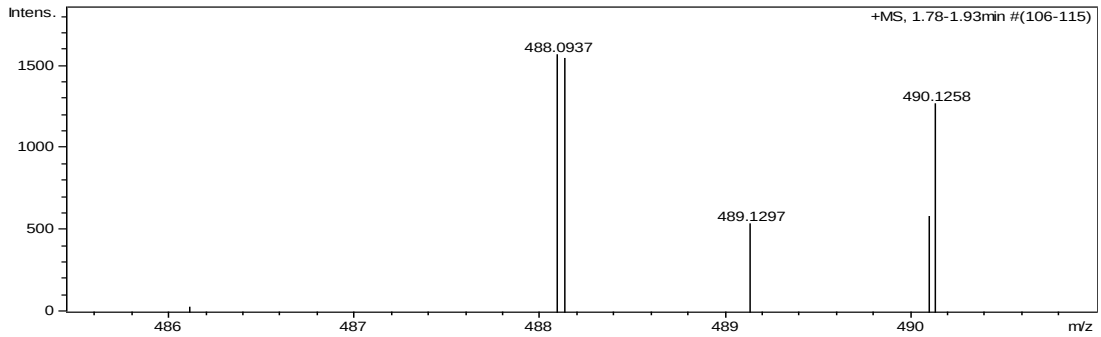

187.55
181.70
150.62
138.55
129.21
127.37
124.47
118.19
109.29
102.29
73.00
72.56
68.73
52.30
36.80
21.52
H
N
O
O
NH
N
H
H
Cl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 1.20-1.23min #(71-73)
800
600
400
200
0
468.1470
469.1829
470.1774
466
467
468
469
470
471
m/z

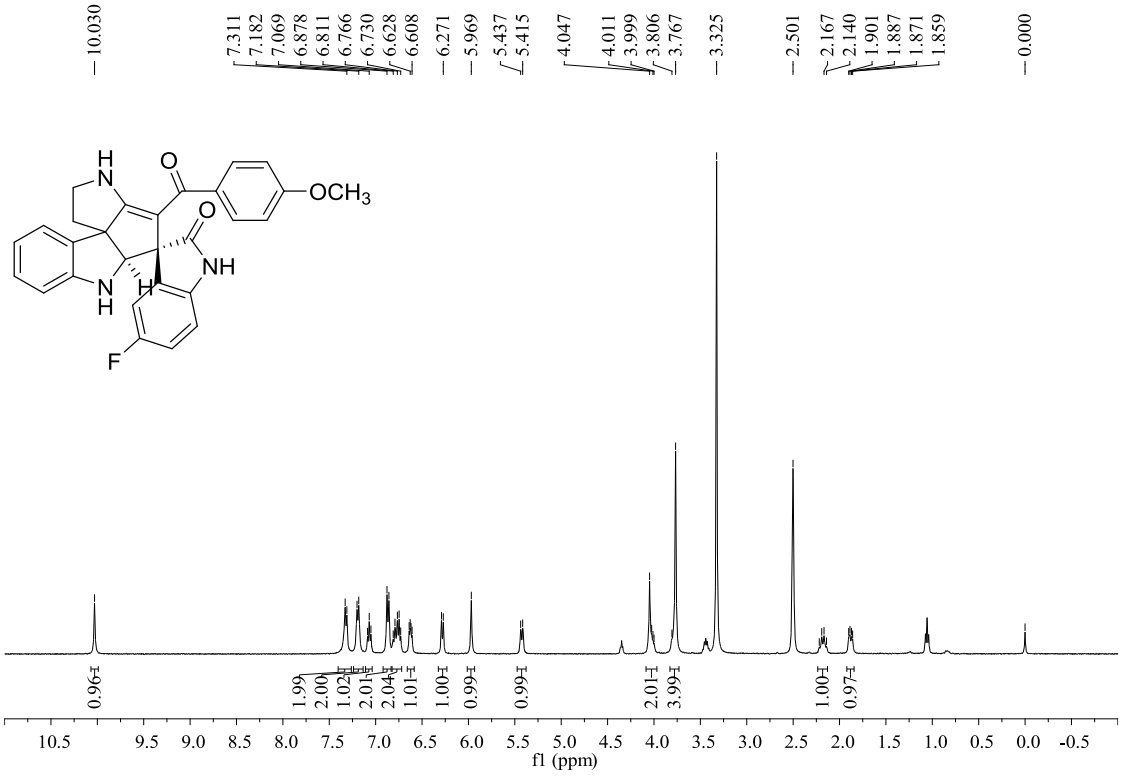
***rel*-(3*S*,5a'*S*)-5-chloro-4'-(4-chlorobenzoyl)-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5m):** white solid, 56%, m.p. 231-233 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.15 (s, 1H, NH), 7.69 (s, 1H, NH), 7.37-7.31 (m, 3H, ArH), 7.13-7.06 (m, 3H, ArH), 7.02 (d, J = 7.2 Hz, 1H, ArH), 6.75 (t, J = 7.6 Hz, 1H, ArH), 6.64 (d, J = 8.0 Hz, 1H, ArH), 6.27 (d, J = 7.6 Hz, 1H, ArH), 6.01 (s, 1H, NH), 5.59 (s, 1H, ArH), 4.10-4.04 (m, 2H, CH, CH_2), 3.81 (t, J = 10.0 Hz, 1H, CH_2), 2.25-2.17 (m, 1H, CH_2), 1.89 (dd, J_1 = 11.2 Hz, J_2 = 5.2 Hz, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 186.4, 181.7, 150.5, 142.1, 139.9, 135.2, 133.5, 131.8, 129.5, 129.0, 128.8, 127.7, 125.7, 124.6, 122.6, 118.3, 110.2, 109.4, 101.9, 72.8, 72.5, 68.8, 52.5, 36.7 ppm; IR (KBr) υ: 3872, 3839, 3747, 3648, 3613, 3332, 3248, 2971, 2888, 1716, 1626, 1606, 1582, 1550, 1506, 1472, 1446, 1429, 1307, 1255, 1197, 1159, 1089, 1054, 1013, 972, 822, 772, 743 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{27}H_{20}Cl_2N_3O_2$ ([M+H]$^+$): 488.0927, found: 488.0937.

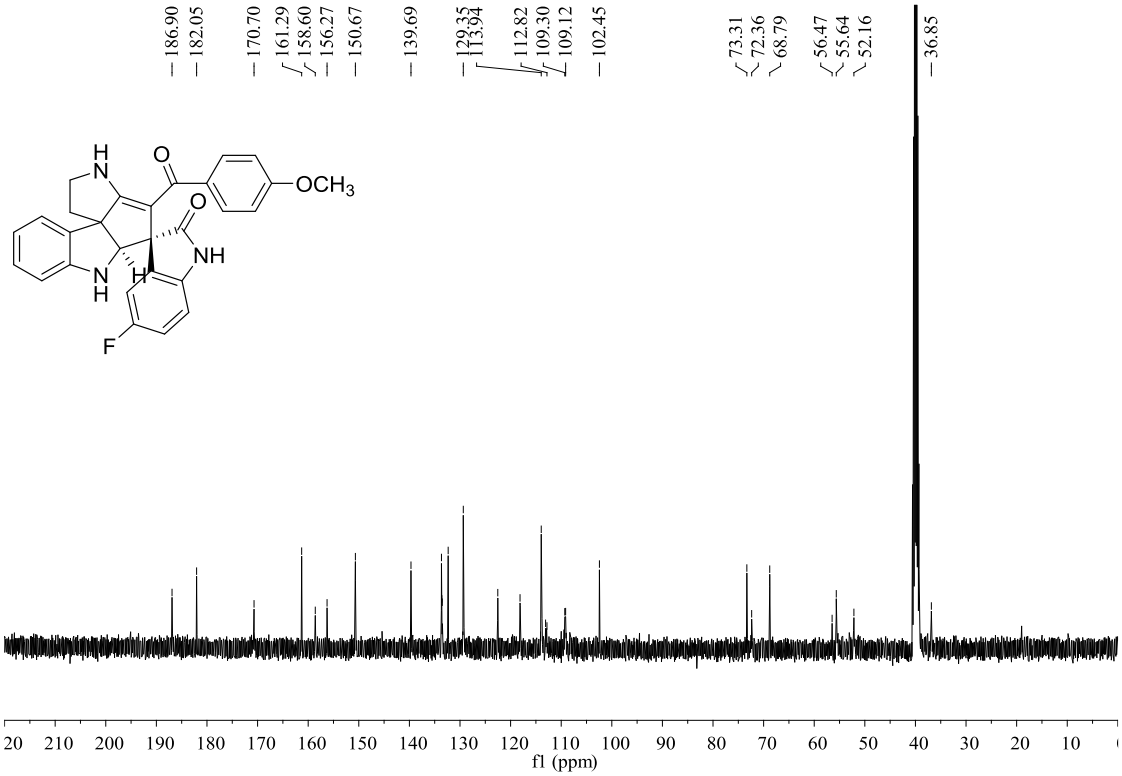


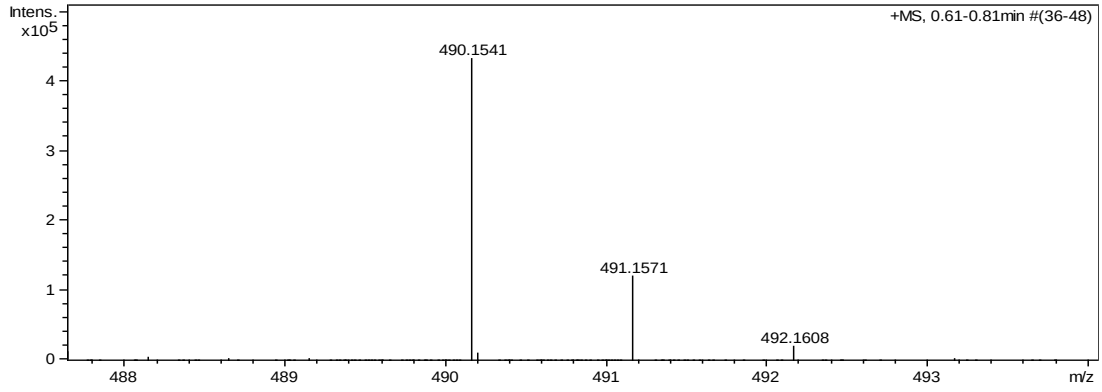

186.44
181.73
150.52
139.85
131.82
127.70
124.61
118.33
109.44
101.89
72.76
72.52
68.81
52.51
36.71
H
N
O
Cl
O
NH
N
H
H
Cl
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
+MS, 1.78-1.93min #(106-115)
1500
1000
500
0
488.0937
490.1258
489.1297
486
487
488
489
490
m/z

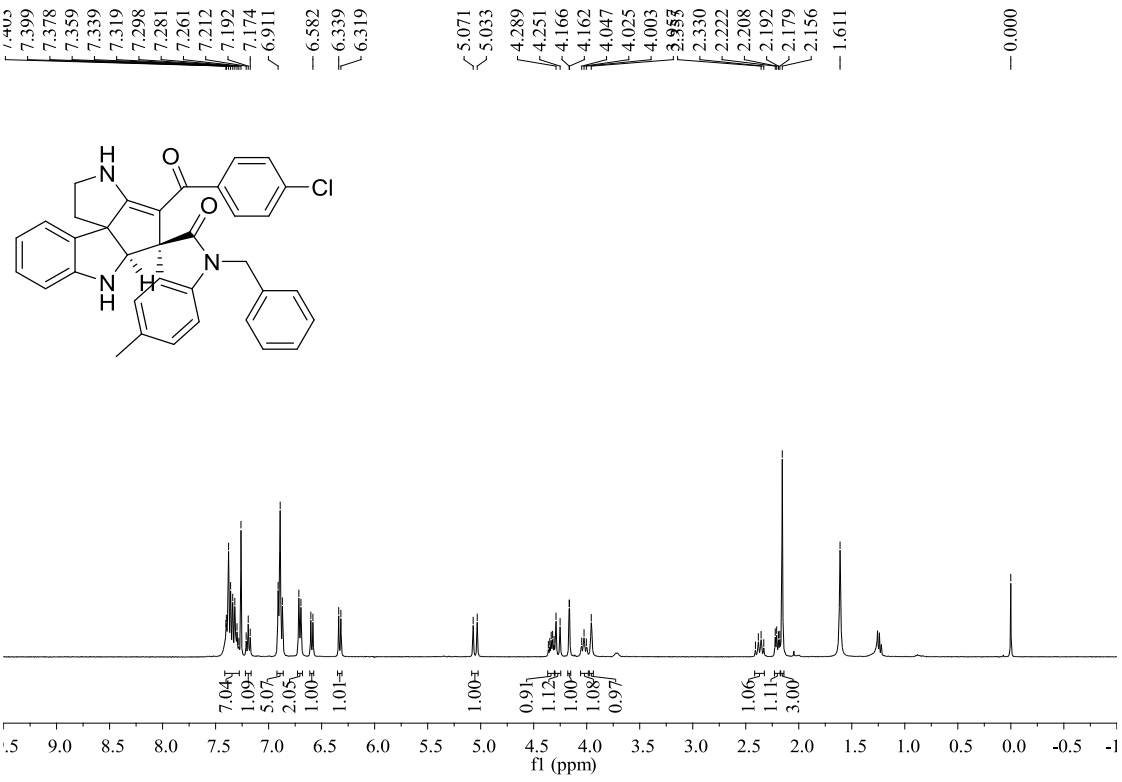
***rel*-(3*S*,5a'*S*)-5-fluoro-4'-(4-methoxybenzoyl)-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5n):** white solid, 49%, m.p. 280-282 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.03 (s, 1H, NH), 7.32 (d, J = 7.2 Hz, 2H, NH, ArH), 7.19 (d, J = 7.6 Hz, 2H, ArH), 7.07 (t, J = 7.2 Hz, 1H, ArH), 6.86 (d, J = 7.6 Hz, 2H, ArH), 6.81-6.73 (m, 2H, ArH), 6.64-6.61 (m, 1H, ArH), 6.28 (d, J = 7.6 Hz, 1H, ArH), 5.97 (s, 1H, NH), 5.43 (d, J = 8.8 Hz, 1H, ArH), 4.05-4.00 (m, 2H, CH, CH_2), 3.81-3.77 (m, 4H, CH_2, OCH_3), 2.22-2.14 (m, 1H, CH_2), 1.88 (dd, J_1 = 12.0 Hz, J_2 = 5.6 Hz, 1H, CH_2) ppm; ^{13}C{1H} NMR (100 MHz, DMSO-d_6) δ: 186.9, 182.1, 170.7, 161.3, 157.4 (J = 238.0 Hz), 150.7, 139.7, 133.7, 133.6, 133.5, 132.3, 129.4, 122.5, 118.1, 113.3 (J = 27.1 Hz), 112.8, 109.2 (J = 17.1 Hz), 102.5, 73.3, 72.4, 68.8, 56.5, 55.6, 52.2, 36.9 ppm; IR (KBr) υ: 3839, 3734, 3648, 3437, 3386, 3321, 3256, 2972, 2838, 1716, 1629, 1603, 1552, 1510, 1480, 1426, 1339, 1307, 1255, 1176, 1114, 1090, 1029, 981, 952, 851, 812, 778, 753 cm^{-1}; MS (m/z): HRMS (ESI-TOF) Calcd. for $C_{28}H_{22}FNaN_3O_3$ ([M+Na]$^+$): 490.1537, found: 490.1541.

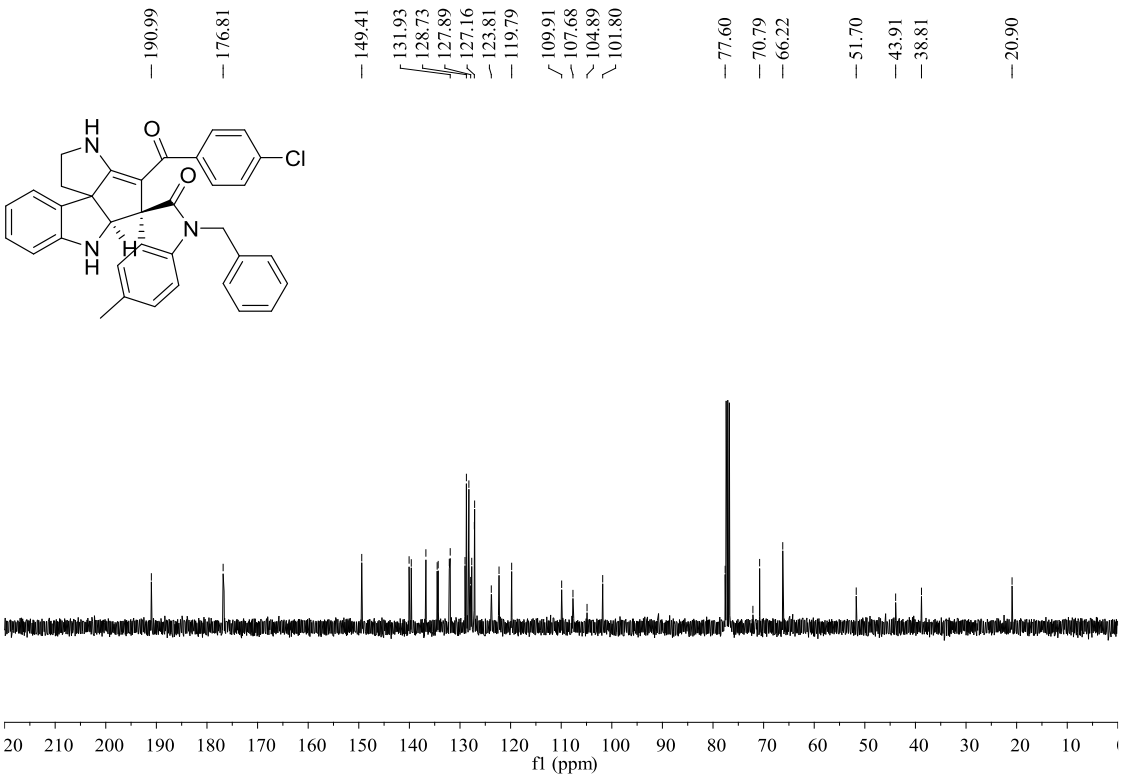


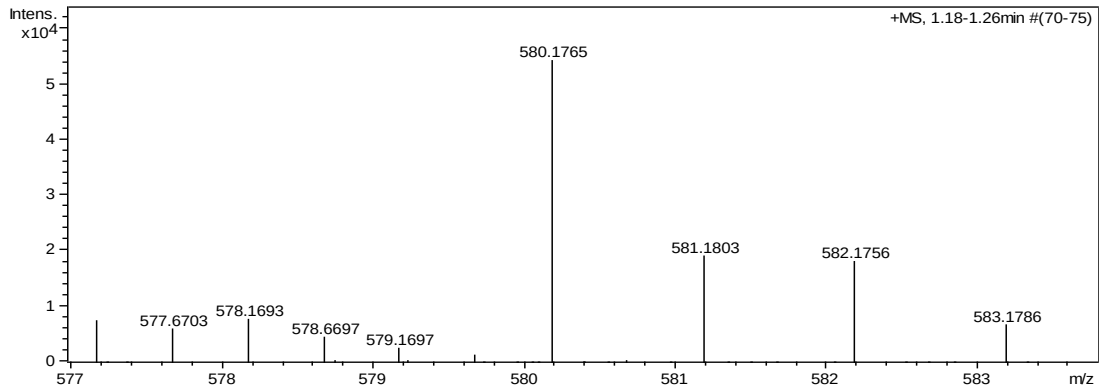

186.90
182.05
170.70
161.29
158.60
156.27
150.67
139.69
129.35
113.94
112.82
109.30
109.12
102.45
73.31
72.36
68.79
56.47
55.64
52.16
36.85
H
N
O
OCH3
O
NH
N
H
H
F
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
x10^5
+MS, 0.61-0.81min #(36-48)
490.1541
491.1571
492.1608
0
1
2
3
4
488
489
490
491
492
493
m/z

***rel*-(3*R*,5a'*S*)-1-benzyl-4'-(4-chlorobenzoyl)-5-methyl-2',3',5a',6'-tetrahydro-1'*H*-spiro[indoline-3,5'-pyrrolo[3',2':2,3]cyclopenta[1,2-*b*]indol]-2-one (5j'):** white solid,16%, m.p. 241-243 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40-7.28 (m, 7H, NH, ArH), 7.19 (t, *J* = 8.0 Hz, 1H, ArH), 6.89 (t, *J* = 8.0 Hz, 5H, ArH), 6.71 (d, *J* = 8.0 Hz, 2H, ArH), 6.59 (d, *J* = 8.0 Hz, 1H, ArH), 6.33 (d, *J* = 8.0 Hz, 1H, ArH), 5.05 (d, *J* = 15.2 Hz, 1H, CH_2), 4.36-4.31 (m, 1H, CH), 4.03 (t, *J* = 8.8 Hz, 1H, CH_2), 3.96 (s, 1H, NH), 2.41-2.33 (m, 1H, CH_2), 2.20 (dd, J_1 = 17.2 Hz, J_2 = 6.4 Hz, 1H, CH_2), 2.16 (s, 3H, CH_3) ppm; ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ: 191.0, 176.8, 149.4, 140.1, 139.6, 136.7, 134.5, 134.3, 132.1, 131.9, 129.0, 128.7, 128.2, 127.9, 127.7, 127.2, 127.1, 123.8, 122.3, 120.0, 109.9, 107.7, 104.9, 101.8, 77.6, 72.1, 70.8, 66.2, 51.7, 43.9, 38.8, 20.9 ppm; IR (KBr) υ: 3648, 3408, 3322, 3063, 3028, 2949, 2889, 1705, 1647, 1605, 1534, 1498, 1477, 1452, 1432, 1335, 1288, 1184, 1083, 1051, 1032, 1013, 987, 974, 836, 803, 781, 755, 745, 733, 720 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{35}H_{28}ClNaN_3O_2$ ([M+Na]$^+$): 580.1762, found: 580.1765.




190.99
176.81
149.41
131.93
128.73
127.89
127.16
123.81
119.79
109.91
107.68
104.89
101.80
77.60
70.79
66.22
51.70
43.91
38.81
20.90
H
N
O
Cl
O
N
N
H
H
f1 (ppm)


Intens.
x10^4
+MS, 1.18-1.26min #(70-75)
580.1765
581.1803
582.1756
583.1786
577.6703
578.1693
578.6697
579.1697
m/z