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

Molecular diversity of TEMPO-mediated cycloaddition of ketohydrazones and 3-Phenacylideneoxindoles

Rong Ye, Jing Sun, Ying Han, Chao-Guo Yan*

Supporting Information

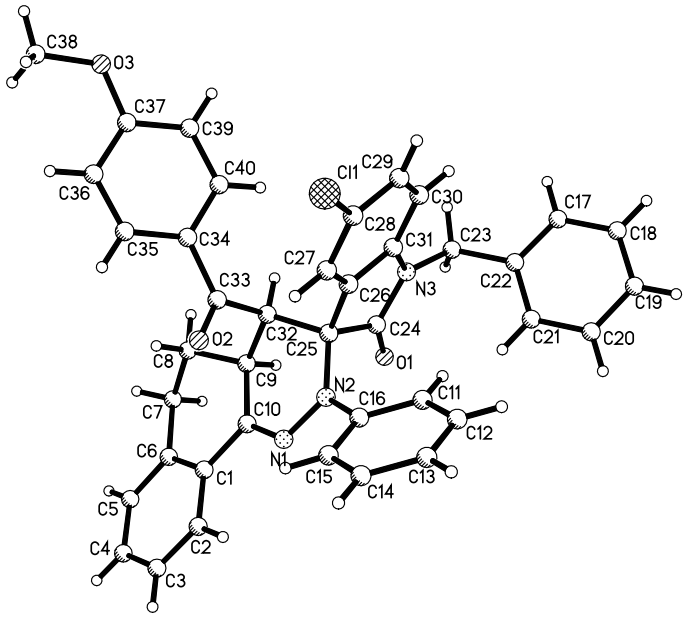


Fig. s1 Single crystal structure of the compound **1g**

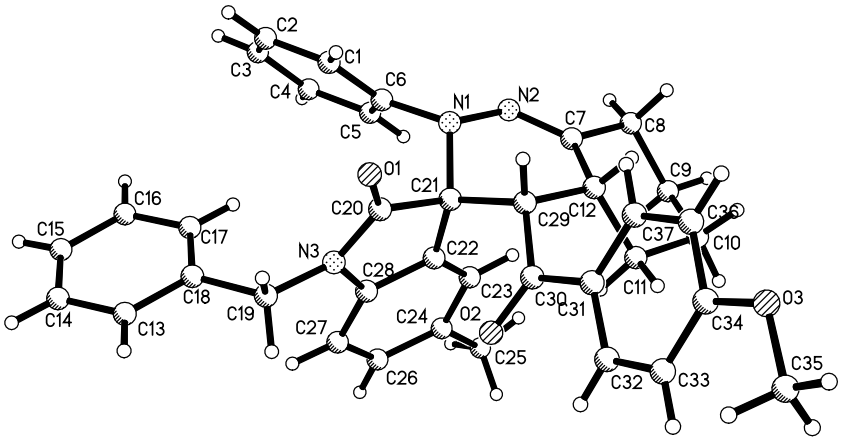


Fig. s2 Single crystal structure of the compound **2b**

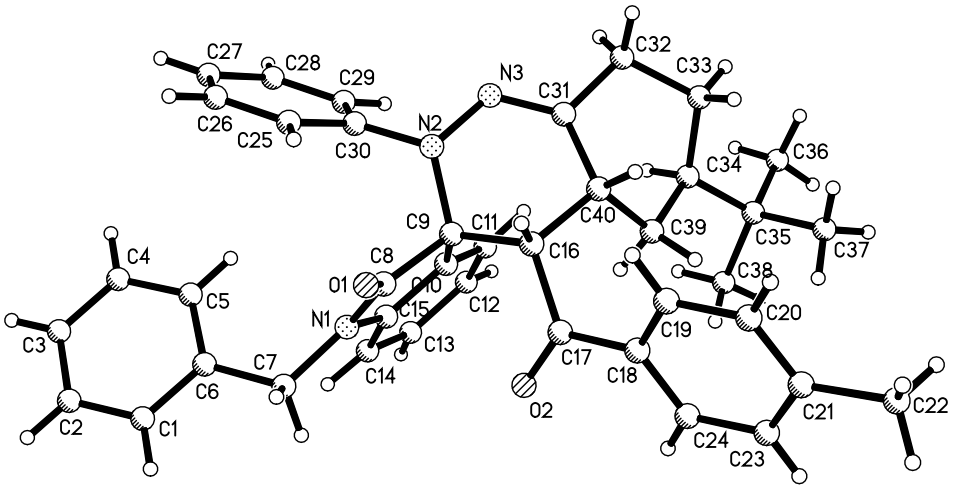


Fig. s3 Single crystal structure of the compound **2d**

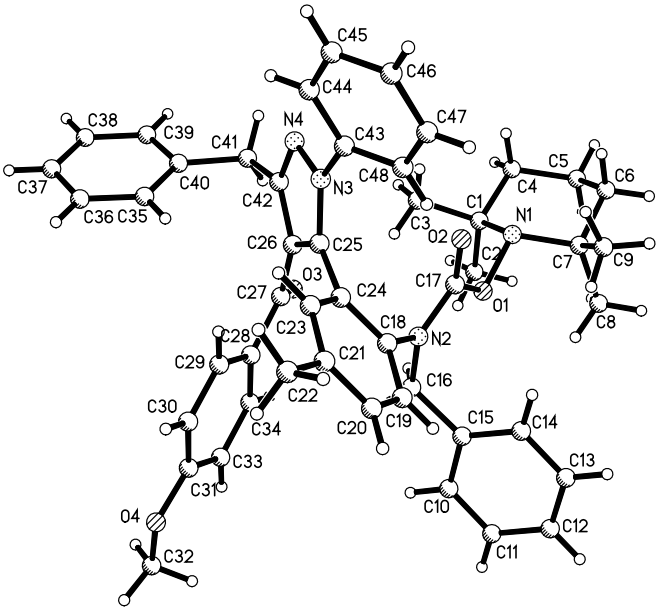


Fig. s4 Single crystal structure of the spiro compound **3c**

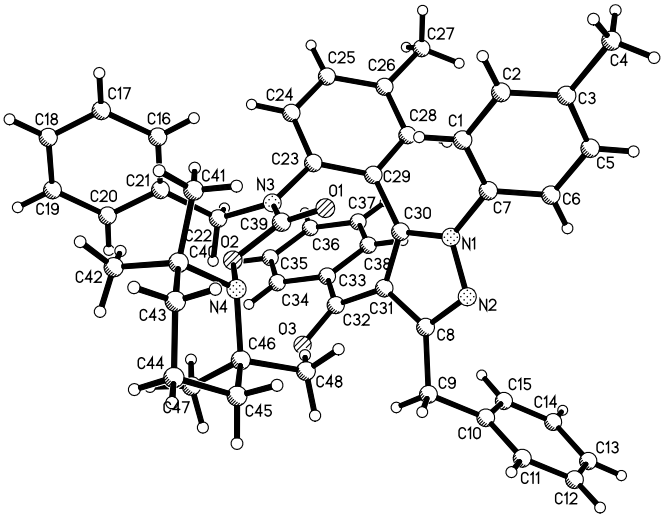


Fig. s5 Single crystal structure of the spiro compound **3d**

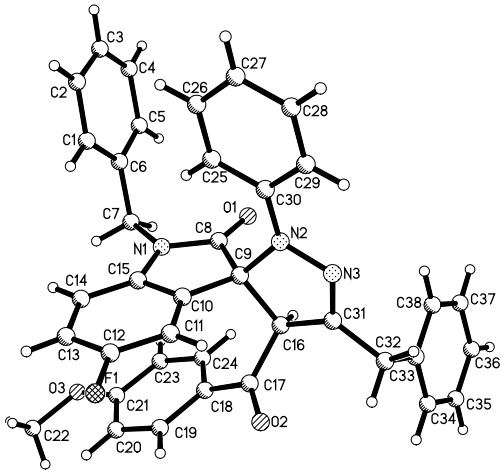


Fig. s6 Single crystal structure of the spiro compound **4e**

1. General procedure for the synthesis of spiro compounds 1a-1k and 2a-2i:

To a Schlenk tube was added ketohydrazone (1.0 mmol), 3-methyleneoxindole (0.5 mmol), TEMPO (1.5 mmol) and acetonitrile (2.0 mL). The mixture was heated at 80 ^{o}C for 48 hours under nitrogen atmosphere. After removing the solvent by rotatory evaporation under reduced pressure, the residue was subjected to column with a mixture of ethyl acetate and light petroleum (V/V = 1:3) as eluent to give the pure product for analysis.

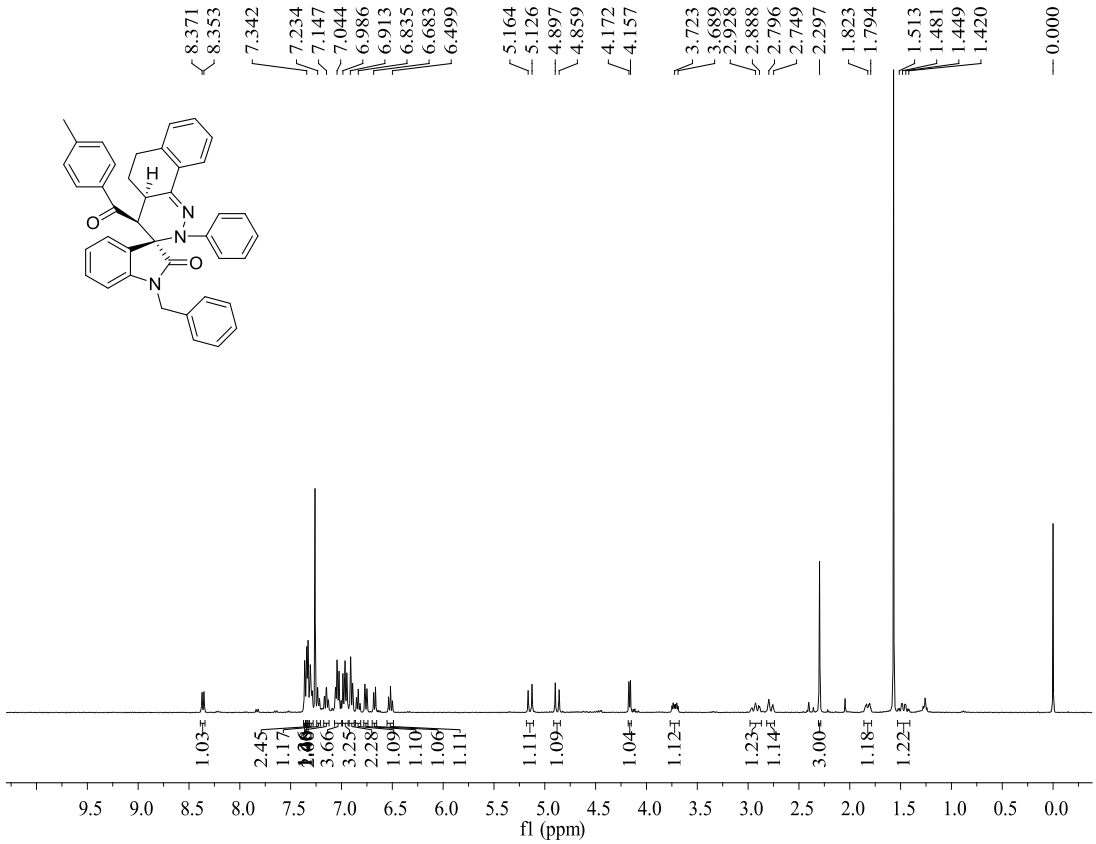
2. General procedure for the synthesis of spiro compounds 3a-3h:

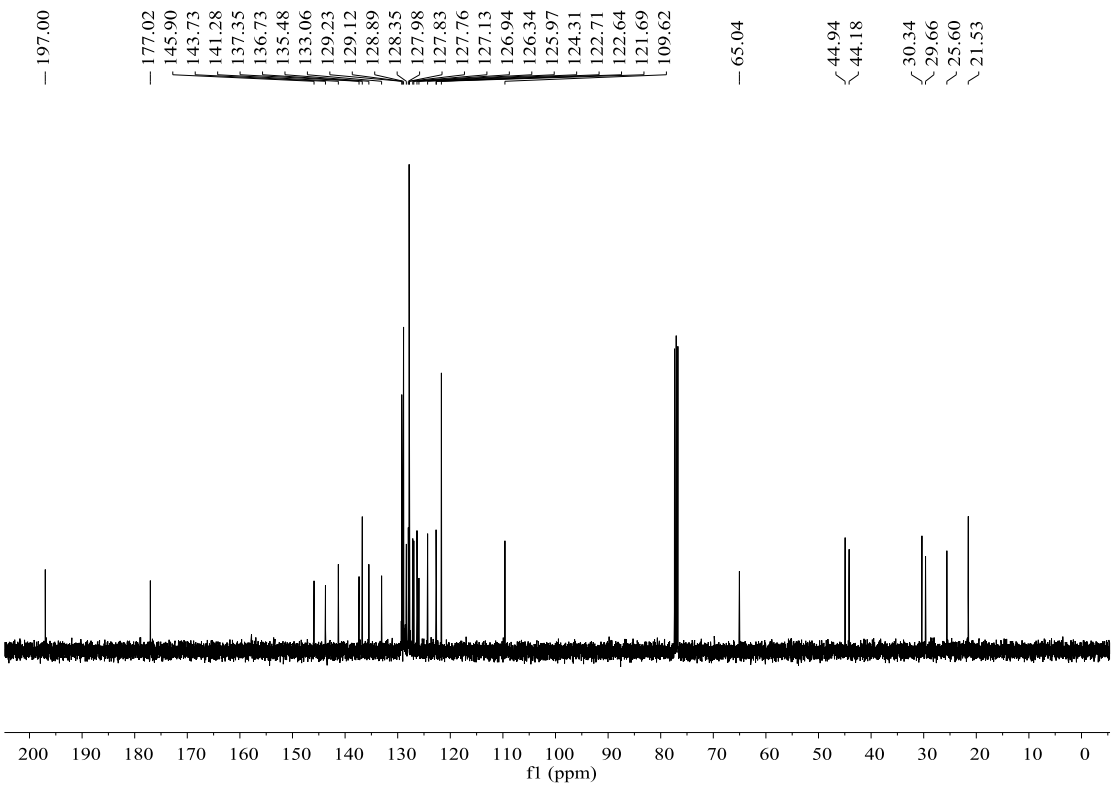
To a Schlenk tube was added ketohydrazone (1.0 mmol), 3-methyleneoxindole (0.5 mmol), TEMPO (1.5 mmol) and acetonitrile (2.0 mL). The mixture was heated at 80 ^{o}C for 48 hours under nitrogen atmosphere. After removing the solvent by rotatory evaporation under reduced pressure, the residue was subjected to column with a mixture of ethyl acetate and light petroleum (V/V = 1:3) as eluent to give the pure product for analysis.

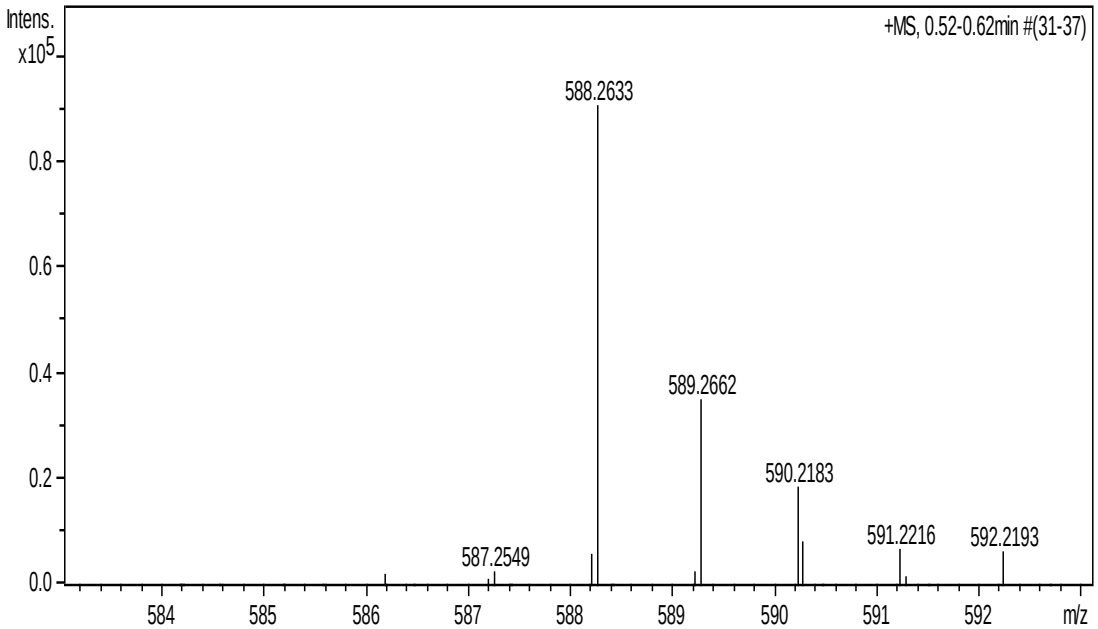
3. General procedure for the synthesis of spiro compounds 4a-4j:

To a Schlenk tube was added ketohydrazone (1.0 mmol), 3-methyleneoxindole (0.5 mmol), TEMPO (1.5 mmol) and acetonitrile (2.0 mL). The mixture was heated at 80 ^{o}C for 48 hours under nitrogen atmosphere. After removing the solvent by rotatory evaporation under reduced pressure, the residue was subjected to column with a mixture of ethyl acetate and light petroleum (V/V = 1:3) as eluent to give the pure product for analysis.

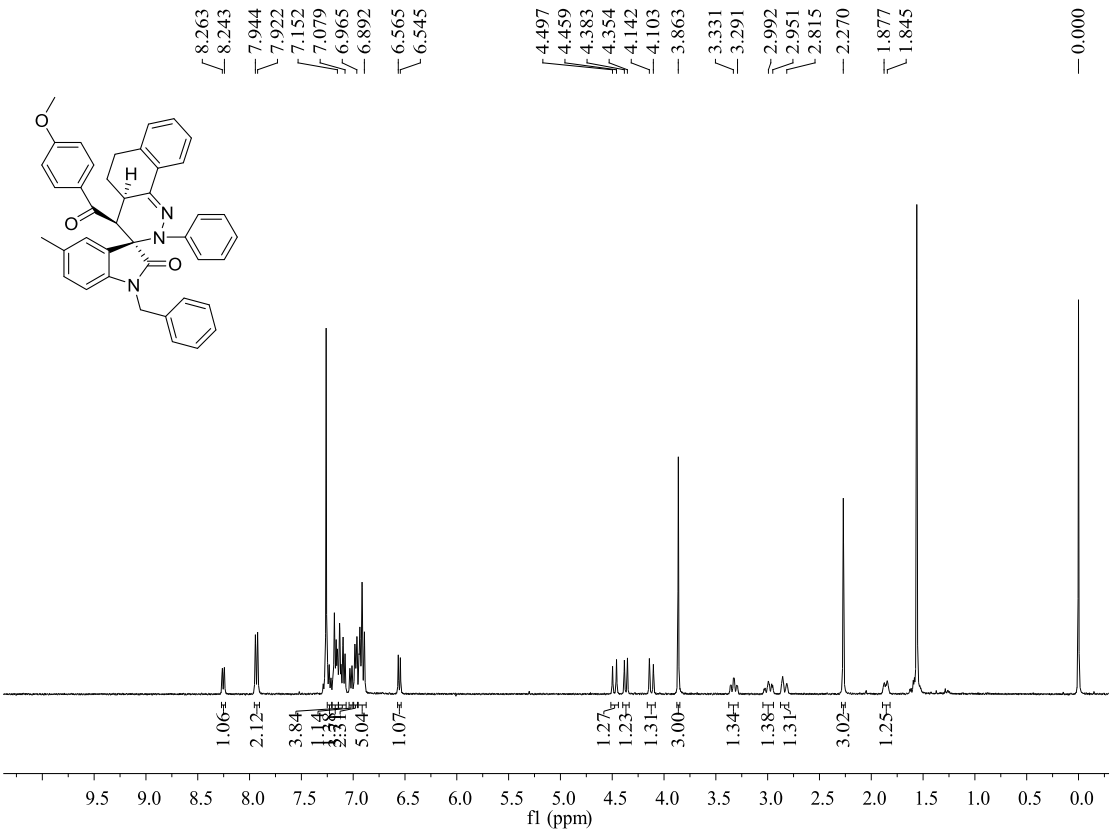
1'-benzyl-4-(4-methylbenzoyl)-2-phenyl-4,4a,5,6-tetrahydro-2*H*-spiro[benzo[h]cinnoline-3,3'-indolin]-2'-one (1a): pink solid, 0.323g, 55%, m.p. 223-225 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, *J* = 7.2 Hz, 1H, ArH), 7.36-7.36 (m, 1H, ArH), 7.34-7.34 (m, 1H, ArH), 7.33-7.32 (m, 2H, ArH), 7.32-7.28 (m, 2H, ArH), 7.23-7.22 (m, 1H, ArH), 7.17-7.13 (m, 1H, ArH), 7.06-7.00 (m, 4H, ArH), 6.99-6.94 (m, 3H, ArH), 6.91-6.89 (m, 2H, ArH), 6.85-6.82 (m, 1H, ArH), 6.77-6.75 (m, 1H, ArH), 6.68-6.67 (m, 1H, ArH), 6.54-6.50 (m, 1H, ArH), 5.14 (d, *J* = 15.2 Hz, 1H, CH), 4.88 (d, *J* = 15.2 Hz, 1H, CH), 4.16 (d, *J* = 6.0 Hz, 1H, CH), 3.75-3.69 (m, 1H, CH), 2.97-2.89 (m, 1H, CH), 2.81-2.75 (m, 1H, CH), 2.30 (s, 3H, CH_3), 1.85-1.80 (m, 1H, CH), 1.52-1.42 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.0, 177.0, 145.9, 143.7, 141.3, 137.4, 136.7, 135.5, 133.1, 129.2, 129.1, 128.9, 128.4, 128.0, 127.8, 127.8, 127.1, 126.9, 126.3, 126.0, 124.3, 122.7, 122.6, 121.7, 109.6, 65.0, 44.9, 44.2, 30.3, 29.7, 25.6, 21.5; IR (KBr) υ : 3031, 2930, 1709, 1601, 1485, 1344, 1265, 1179, 1072, 1009, 797, 757 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{40}H_{34}N_3O_2$ ($[M+H]^+$):588.2646, Found: 588.2633.

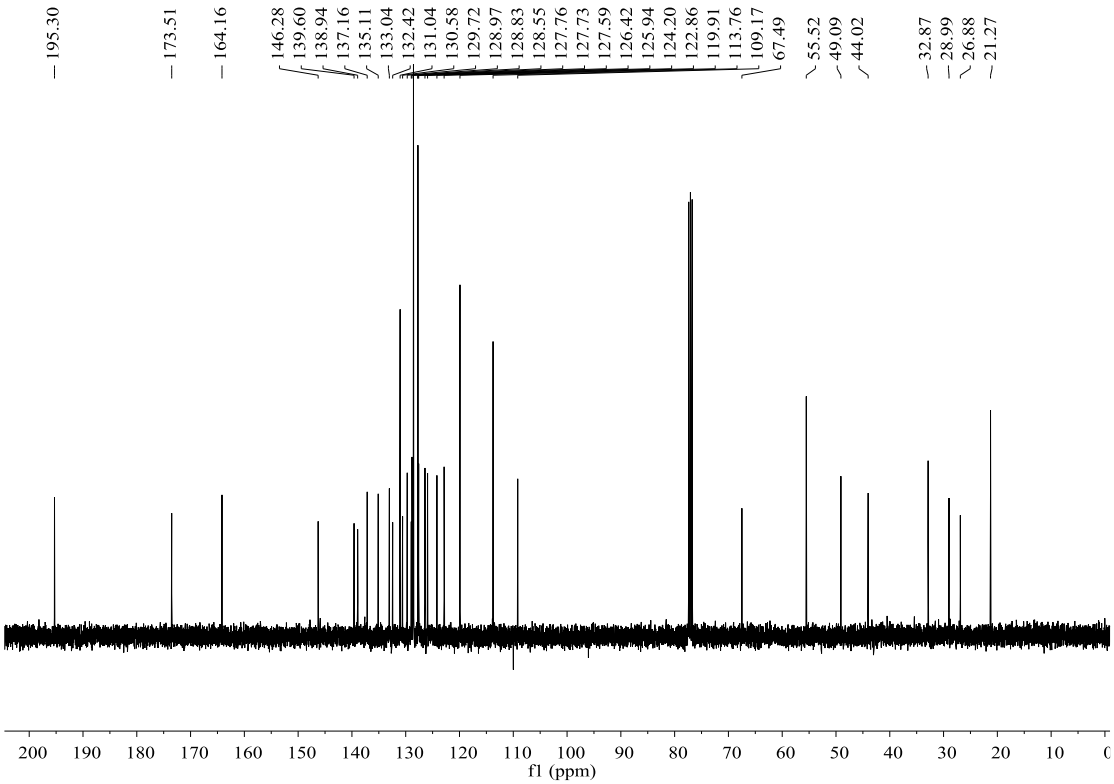


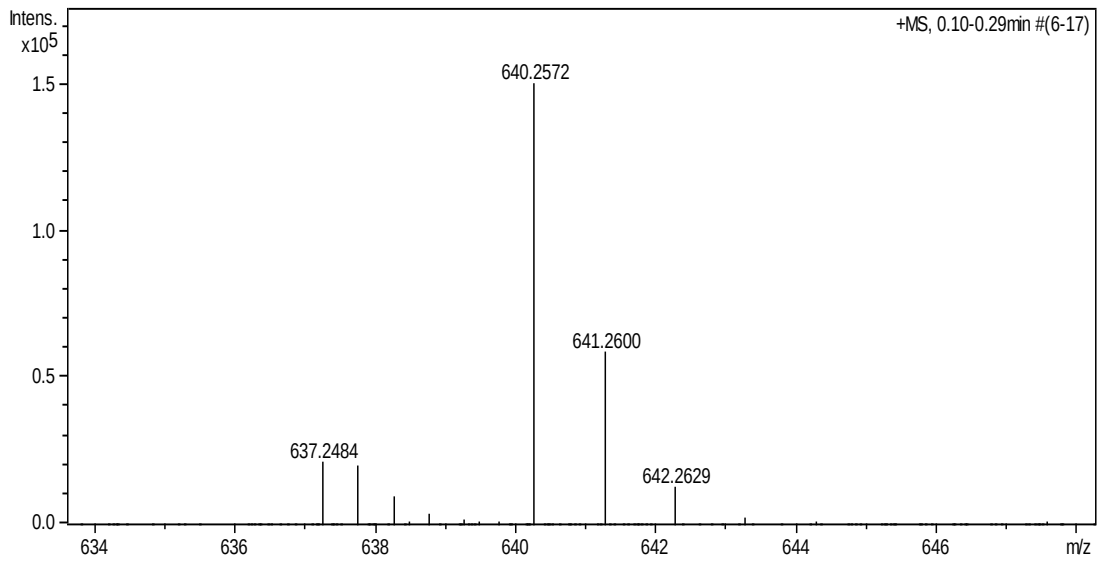

197.00
177.02
145.90
143.73
141.28
137.35
136.73
135.48
133.06
129.23
129.12
128.89
128.35
127.98
127.83
127.76
127.13
126.94
126.34
125.97
124.31
122.71
122.64
121.69
109.62
65.04
44.94
44.18
30.34
29.66
25.60
21.53
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.52-0.62min #(31-37)
588.2633
589.2662
590.2183
591.2216
592.2193
587.2549
0.0
0.2
0.4
0.6
0.8
584 585 586 587 588 589 590 591 592
m/z

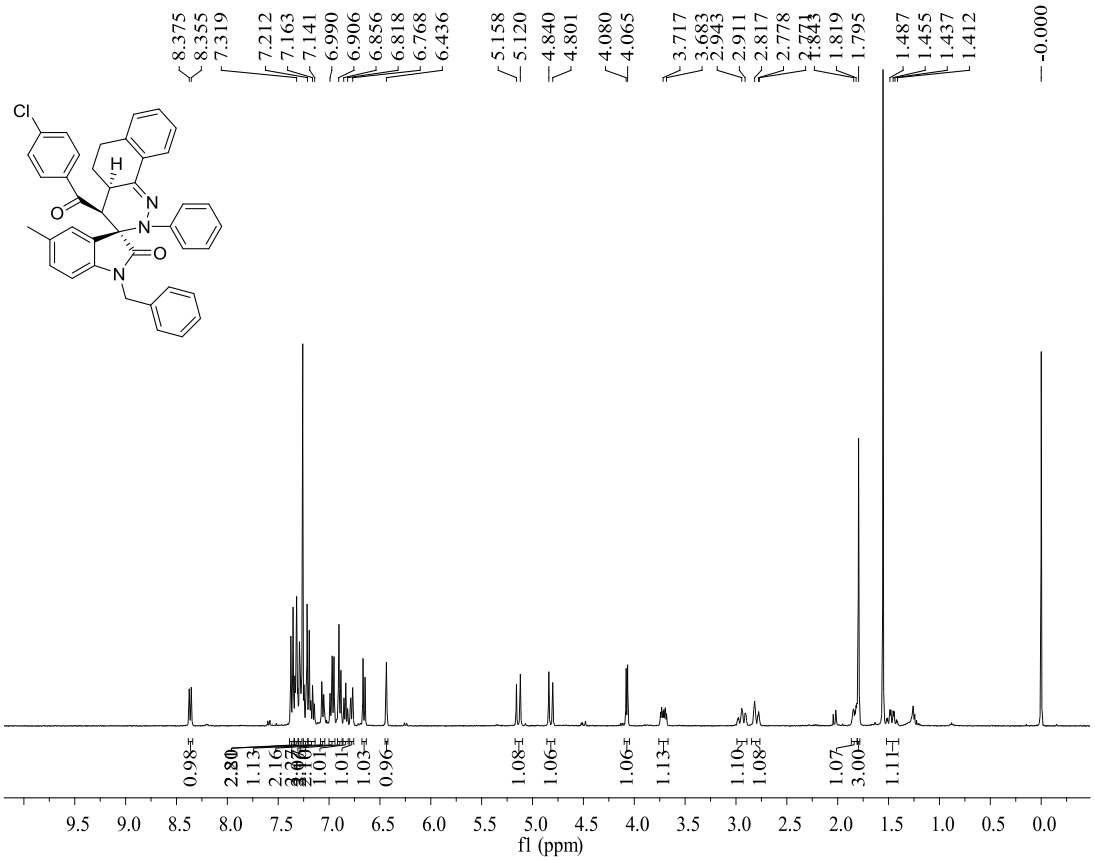
1'-benzyl-4-(4-methoxybenzoyl)-5'-methyl-2-phenyl-4,4a,5,6-tetrahydro-2*H*-spiro[benzo[h]cinnoline-3,3'-indolin]-2'-one (1b): pink solid, 0.321g, 52%, m.p. 215-217 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.25 (d, *J* = 8.0 Hz, 1H, ArH), 7.93 (d, *J* = 8.8 Hz, 1H, ArH), 7.25-7.21 (m, 1H, ArH), 7.20-7.15 (m, 4H, ArH), 7.13-7.08 (m, 4H, ArH), 7.03-7.01 (m, 1H, ArH), 6.98-6.97 (m, 2H, ArH), 6.95-6.89 (m, 5H, ArH), 6.55 (d, *J* = 8.0 Hz, 1H, ArH), 4.48 (d, *J* = 15.2 Hz, 1H, CH), 4.37 (d, *J* = 11.6 Hz, 1H, CH), 4.12 (d, *J* = 15.6 Hz, 1H, CH), 3.86 (s, 3H, OCH_3), 3.36-3.29 (m, 1H, CH), 3.04-2.95 (m, 1H, CH), 2.86-2.82 (m, 1H, CH), 2.27 (s, 3H, CH_3), 1.88-1.86 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.3, 173.5, 164.2, 146.3, 139.6, 138.9, 137.2, 135.1, 133.0, 132.4, 131.0, 130.6, 129.7, 129.0, 128.8, 128.6, 127.8, 127.7, 127.6, 126.4, 125.9, 124.2, 122.9, 119.9, 113.8, 109.2, 67.5, 55.5, 49.1, 44.0, 32.9, 29.0, 26.9, 21.3; IR (KBr) υ : 3024, 2925, 2843, 1719, 1664, 1596, 1492, 1453, 1345, 1312, 1263, 1218, 1177, 1122, 1084, 1028, 848, 807, 757, 735 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{41}H_{35}N_3O_3Na$ ($[M+Na]^+$):640.2571, Found: 640.2572.

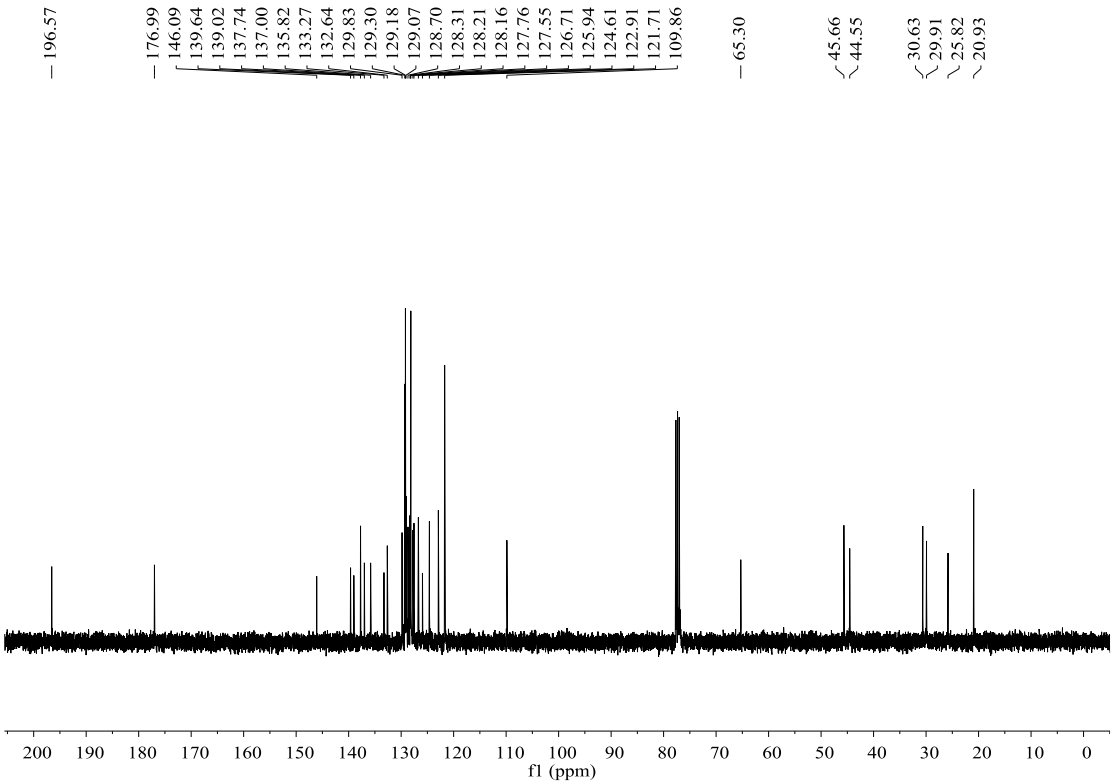


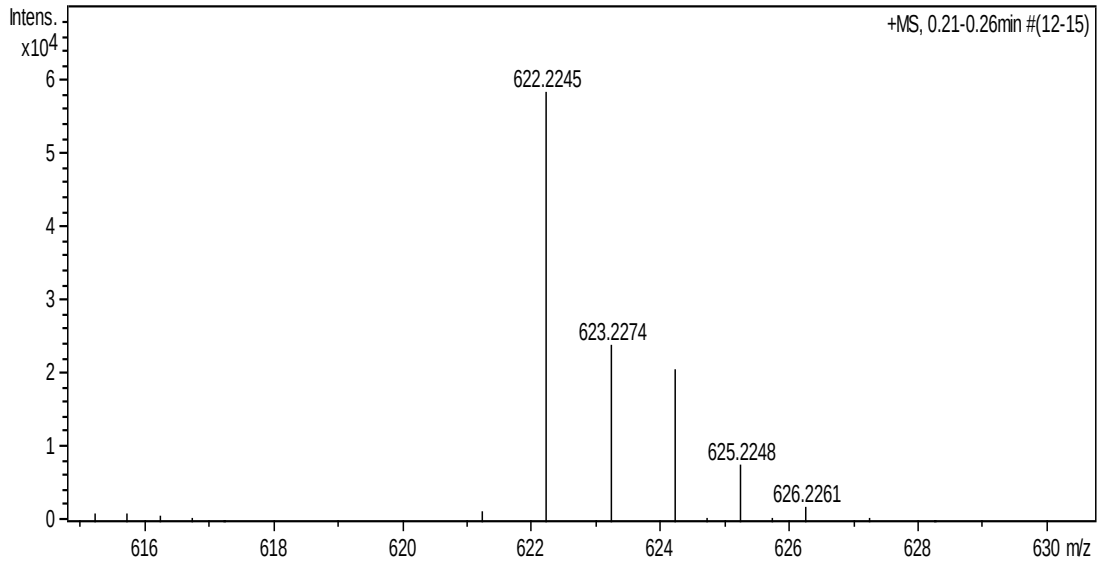

195.30
173.51
164.16
146.28
139.60
138.94
137.16
135.11
133.04
132.42
131.04
130.58
129.72
128.97
128.83
128.55
127.76
127.73
127.59
126.42
125.94
124.20
122.86
119.91
113.76
109.17
67.49
55.52
49.09
44.02
32.87
28.99
26.88
21.27
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
x10^5
+MS, 0.10-0.29min #(6-17)
640.2572
641.2600
637.2484
642.2629
1.5
1.0
0.5
0.0
634 636 638 640 642 644 646
m/z

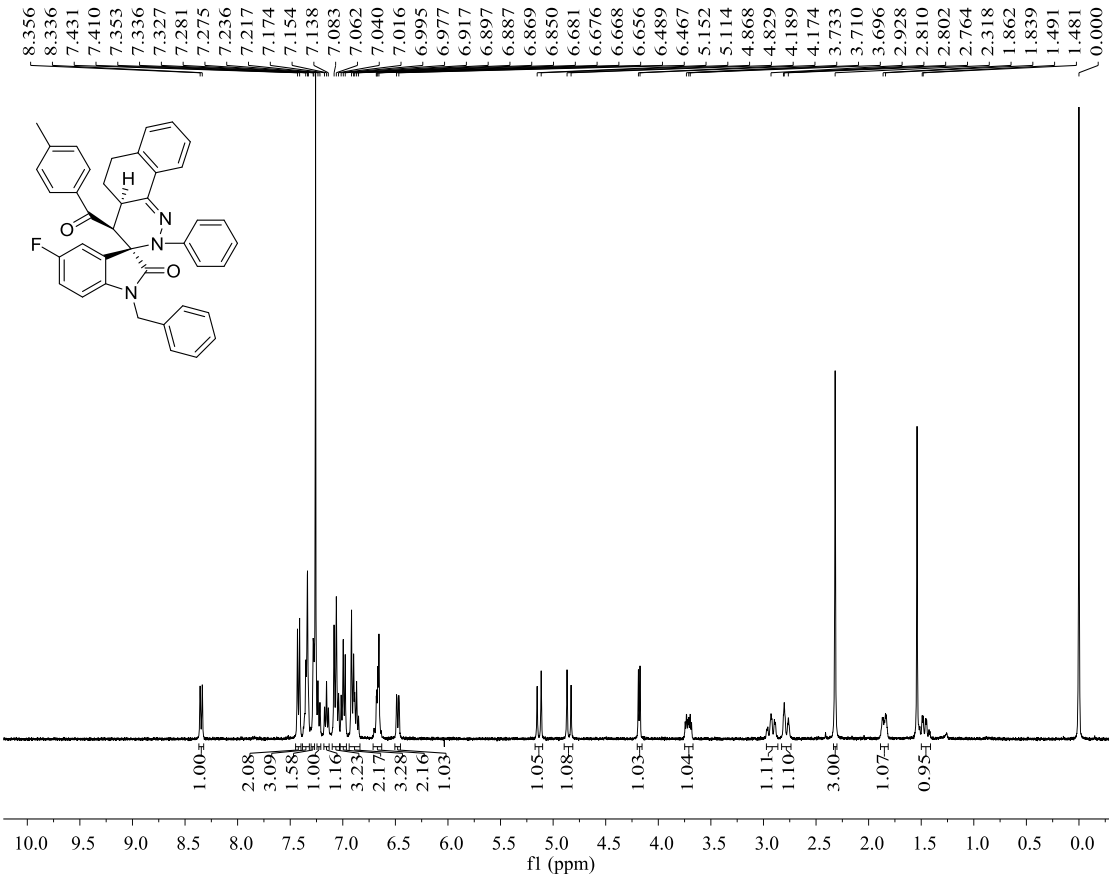
1'-benzyl-4-(4-chlorobenzoyl)-5'-methyl-2-phenyl-4,4a,5,6-tetrahydro-2*H*-spiro[benzo[h]cinnoline-3,3'-indolin]-2'-one (1c): yellow solid, 0.329g, 53%, m.p. 228-230 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.36 (d, *J* = 8.0 Hz, 1H, ArH), 7.38-7.35 (m, 2H, ArH), 7.34-7.31 (m, 3H, ArH), 7.29-7.27 (m, 2H, ArH), 7.25-7.21 (m, 2H, ArH), 7.20-7.14 (m, 2H, ArH), 7.07-7.05 (m, 1H, ArH), 6.99-6.95 (m, 2H, ArH), 6.91-6.88 (m, 2H, ArH), 6.86-6.82 (m, 1H, ArH), 6.79-6.77 (m, 1H, ArH), 6.66 (d, *J* = 8.0 Hz, 1H, ArH), 6.44 (s, 1H, ArH), 5.14 (d, *J* = 15.2 Hz, 1H, CH), 4.82 (d, *J* = 15.6 Hz, 1H, CH), 4.07 (d, *J* = 6.0 Hz, 1H, CH), 3.74-3.68 (m, 1H, CH), 2.99-2.91 (m, 1H, CH), 2.82-2.77 (m, 1H, CH), 1.86-1.81 (m, 1H, CH), 1.80 (s, 3H, CH_3), 1.52-1.41 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.6, 177.0, 146.1, 139.6, 139.0, 137.7, 137.0, 135.8, 133.3, 132.6, 129.8, 129.3, 129.2, 129.0, 128.7, 128.3, 128.2, 128.2, 127.8, 127.6, 126.7, 125.9, 124.6, 122.9, 121.7, 109.9, 65.3, 45.7, 44.6, 30.6, 29.9, 25.8, 20.9; IR (KBr) υ : 3032, 2925, 1714, 1592, 1492, 1447, 1337, 1277, 1180, 1088, 1007, 953, 760 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{40}H_{33}ClN_3O_2$ ([M+H]$^{+}$):622.2256, Found: 622.2245.

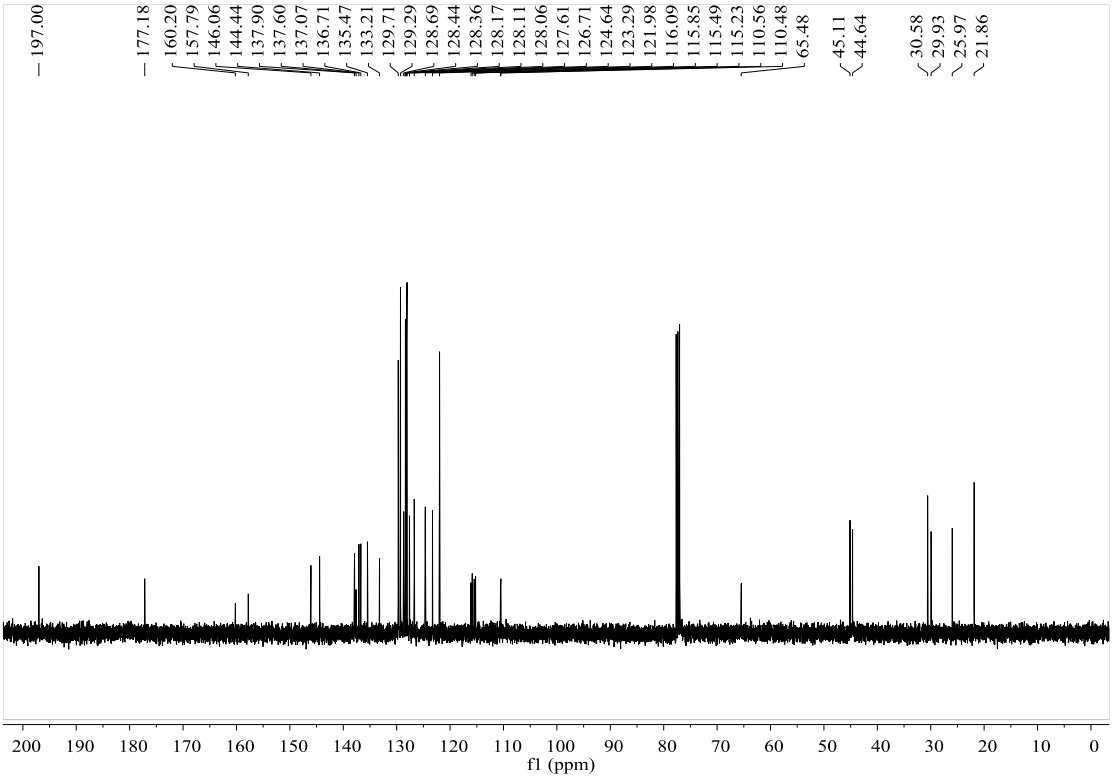


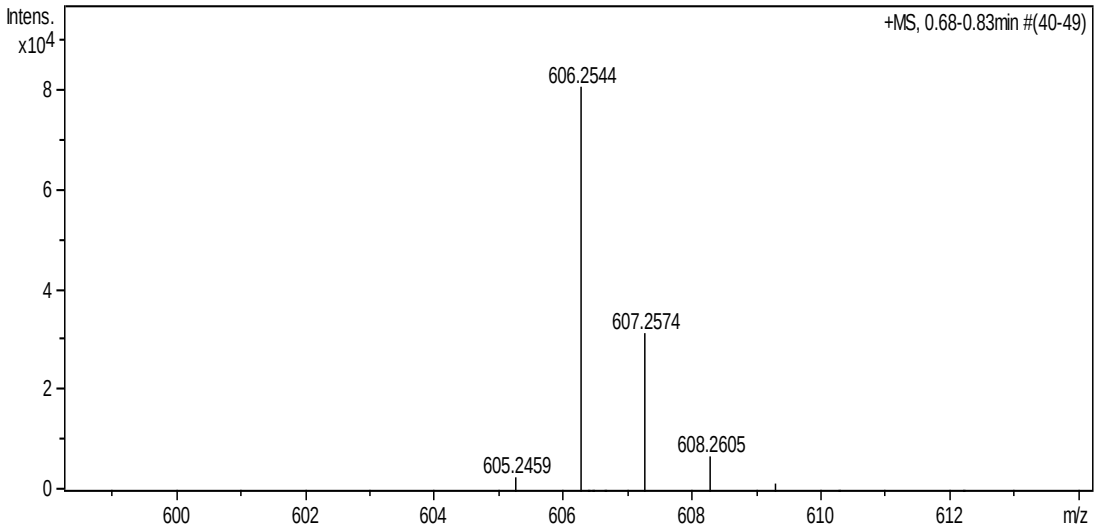

196.57
176.99
146.09
139.64
139.02
137.74
137.00
135.82
133.27
132.64
129.83
129.30
129.18
129.07
128.70
128.31
128.21
128.16
127.76
127.55
126.71
125.94
124.61
122.91
121.71
109.86
65.30
45.66
44.55
30.63
29.91
25.82
20.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^4
+MS, 0.21-0.26min #(12-15)
622.2245
623.2274
625.2248
626.2261
0 1 2 3 4 5 6
616 618 620 622 624 626 628 630 m/z

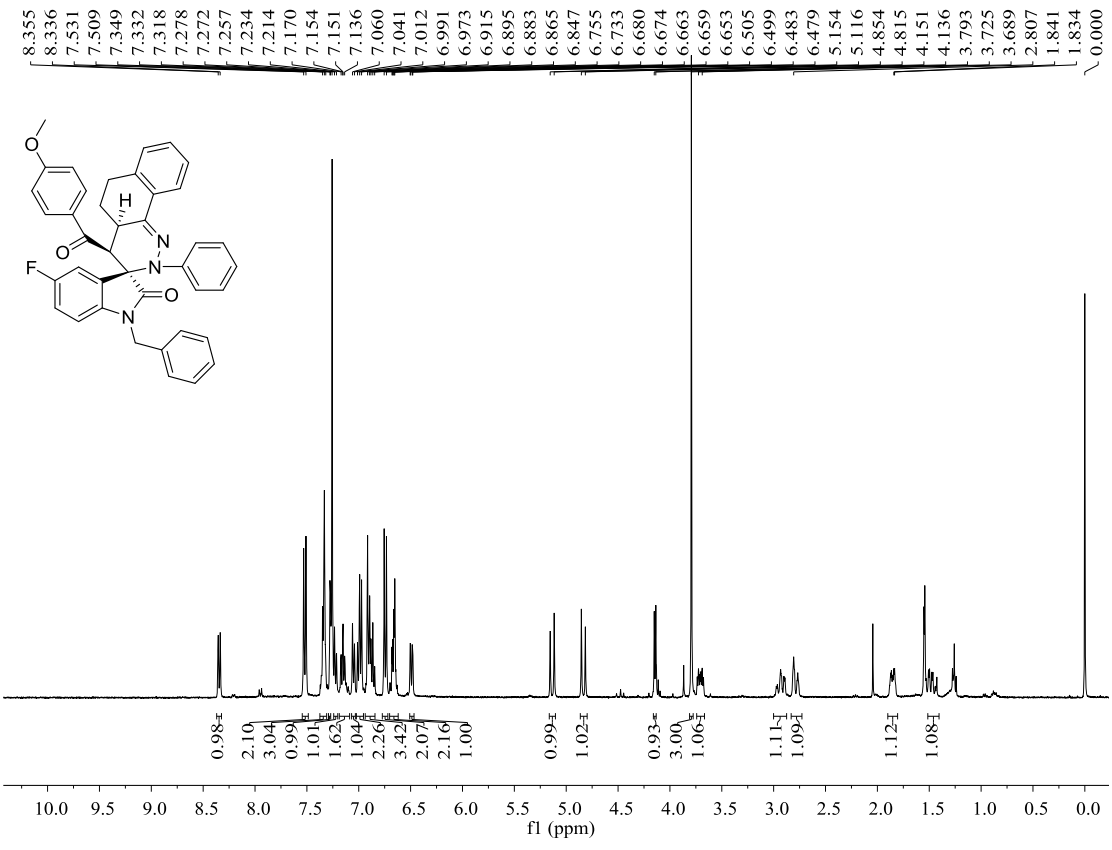
1'-benzyl-5'-fluoro-4-(4-methylbenzoyl)-2-phenyl-4,4a,5,6-tetrahydro-2*H*-spiro[benzo[h]cinnoline-3,3'-indolin]-2'-one (1d): red solid, 0.309 g, 51%, m.p. 224-226 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35 (d, *J* = 8.0 Hz, 1H, ArH), 7.43-7.41 (m, 2H, ArH), 7.37-7.33 (m, 3H, ArH), 7.28-7.28 (m, 2H, ArH), 7.24-7.22 (m, 1H, ArH), 7.17-7.14 (m, 1H, ArH), 7.08-7.04 (m, 3H, ArH), 7.02-6.98 (m, 2H, ArH), 6.92-6.85 (m, 3H, ArH), 6.70-6.64 (m, 2H, ArH), 6.49-6.47 (m, 1H, ArH), 5.13 (d, *J* = 15.2 Hz, 1H, CH), 4.85 (d, *J* = 15.6 Hz, 1H, CH), 4.18 (d, *J* = 6.0 Hz, 1H, CH), 3.74-3.68 (m, 1H, CH), 2.96-2.90 (m, 1H, CH), 2.81-2.75 (m, 1H, CH), 2.32 (s, 3H, CH_3), 1.88-1.82 (m, 1H, CH), 1.49-1.42 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.0, 177.2, 159.0 (d, *J* = 241.7 Hz), 146.1, 144.4, 137.9, 137.6, 137.1, 136.7, 135.5, 133.2, 129.7, 129.3, 128.7, 128.4, 128.4, 128.2, 128.1, 128.1, 127.6, 126.7, 124.6, 123.3, 122.0, 115.9 (d, *J* = 13.7 Hz), 115.3 (d, *J* = 25.7 Hz), 110.5 (d, *J* = 7.8 Hz), 65.5, 45.1, 44.6, 30.6, 29.9, 26.0, 21.9; IR (KBr) υ : 3061, 2928, 1717, 1677, 1601, 1487, 1449, 1331, 1266, 1172, 1070, 1012, 950, 877, 821, 761 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{40}H_{33}FN_3O_2$ ([M+H]$^{+}$):606.2551, Found: 606.2544.

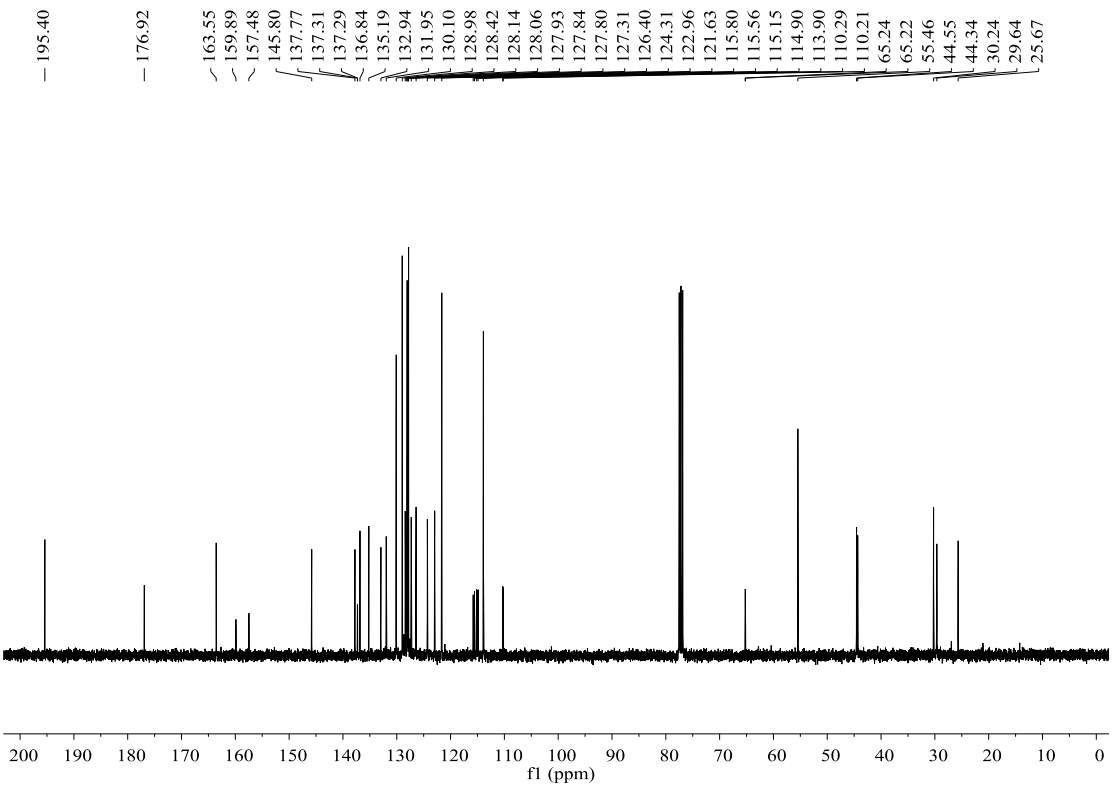


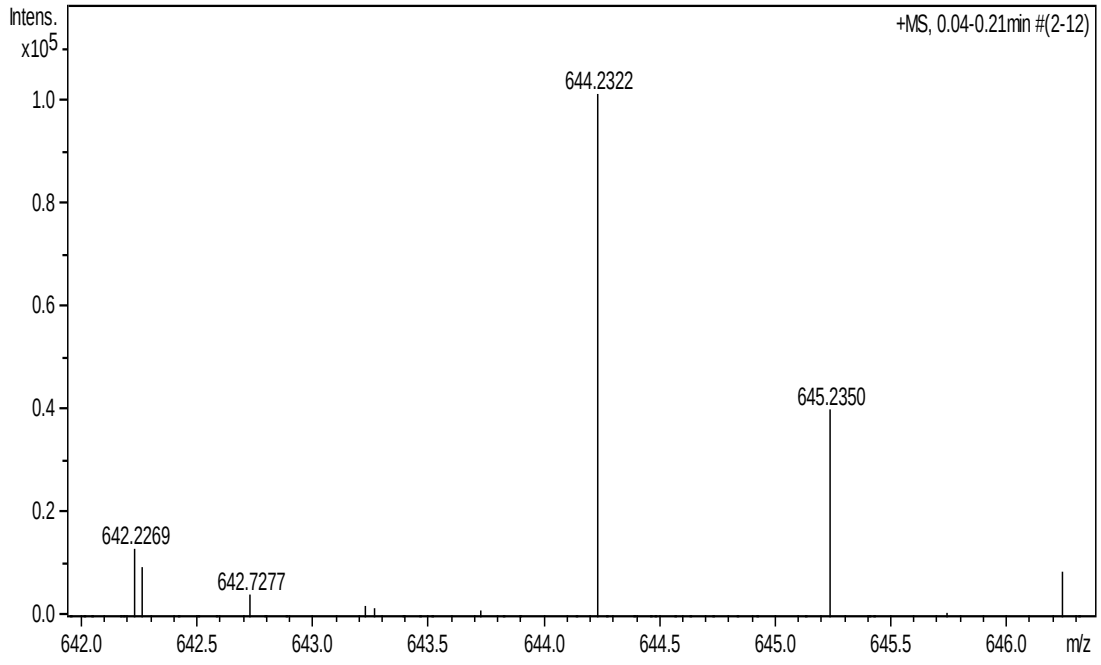

197.00
177.18
160.20
157.79
146.06
144.44
137.90
137.60
137.07
136.71
135.47
133.21
129.71
129.29
128.69
128.44
128.36
128.17
128.11
128.06
127.61
126.71
124.64
123.29
121.98
116.09
115.85
115.49
115.23
110.56
110.48
65.48
45.11
44.64
30.58
29.93
25.97
21.86
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^4
+MS, 0.68-0.83min #(40-49)
606.2544
607.2574
608.2605
605.2459
0
2
4
6
8
600
602
604
606
608
610
612
m/z

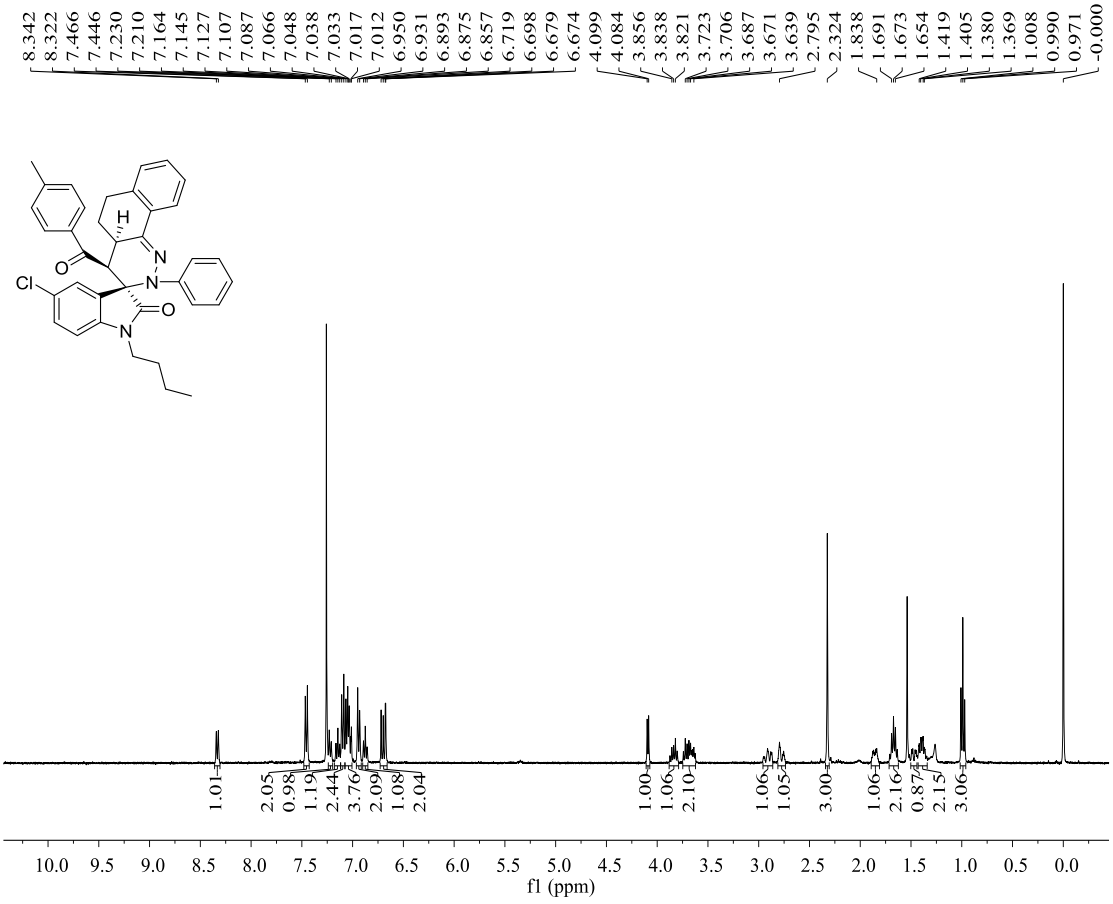
1'-benzyl-5'-fluoro-4-(4-methoxybenzoyl)-2-phenyl-4,4a,5,6-tetrahydro-2*H*-spiro[benzo[h]cinnoline-3,3'-indolin]-2'-one (1e): red solid, 0.310g, 50%, m.p. 225-227 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (d, *J* = 7.6 Hz, 1H, ArH), 7.53-7.51 (m, 1H, ArH), 7.37-7.32 (m, 3H, ArH), 7.28-7.27 (m, 1H, ArH), 7.23-7.21 (m, 1H, ArH), 7.17-7.10 (m, 2H, ArH), 7.06-7.04 (m, 1H, ArH), 7.01-6.97 (m, 2H, ArH), 6.93-6.85 (m, 3H, ArH), 6.76-6.73 (m, 2H, ArH), 6.70-6.63 (m, 2H, ArH) , 6.51-6.48 (m, 1H, ArH), 5.13 (d, *J* = 15.2 Hz, 1H, CH), 4.83 (d, *J* = 15.6 Hz, 1H, CH), 4.15-4.14 (m, 1H, CH), 3.79 (s, 3H, OCH_3), 3.74-3.68 (m, 1H, CH), 2.97-2.90 (m, 1H, CH), 2.81-2.77 (m, 1H, CH), 1.88-1.83 (m, 1H, CH) , 1.51-1.43 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.4, 176.9, 163.6, 158.7 (d, *J* = 241.3 Hz), 145.8, 137.8, 137.3, 137.3, 136.8, 135.2, 132.9, 131.9, 130.1, 129.0, 128.4, 128.1, 128.1, 127.9, 127.8, 127.8, 127.3, 126.4, 124.3, 122.9, 121.6, 115.6 (d, *J* = 23.7 Hz), 115. 0 (d, *J* = 25.8 Hz), 113.9, 110.2 (d, *J* = 8.0 Hz),, 65.2, 65.2, 55.5, 44.6, 44.3, 30.2, 29.6, 25.7; IR (KBr) υ : 2934, 1740, 1703, 1608, 1511, 1459, 1423, 1377, 1349, 1303, 1243, 1174, 1119, 1091, 1029, 888, 827, 742, 702 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{40}H_{32}FN_3O_3Na$ ($[M+Na]^+$):644.2320, Found: 644.2322.

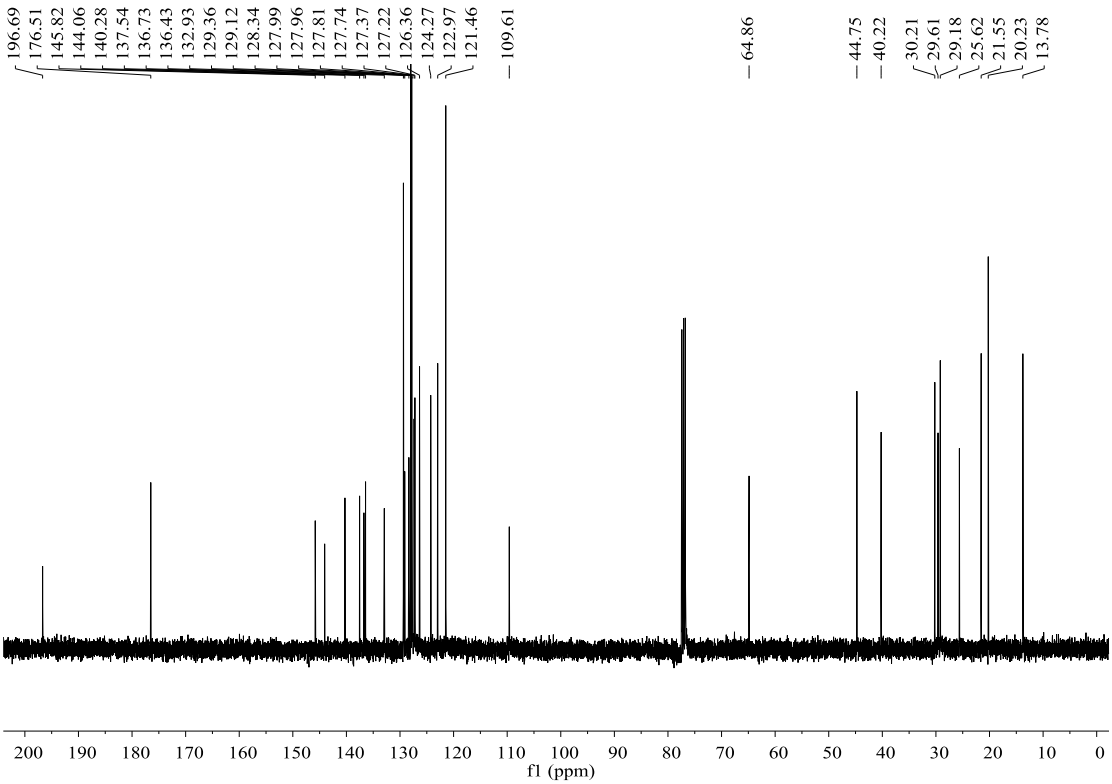


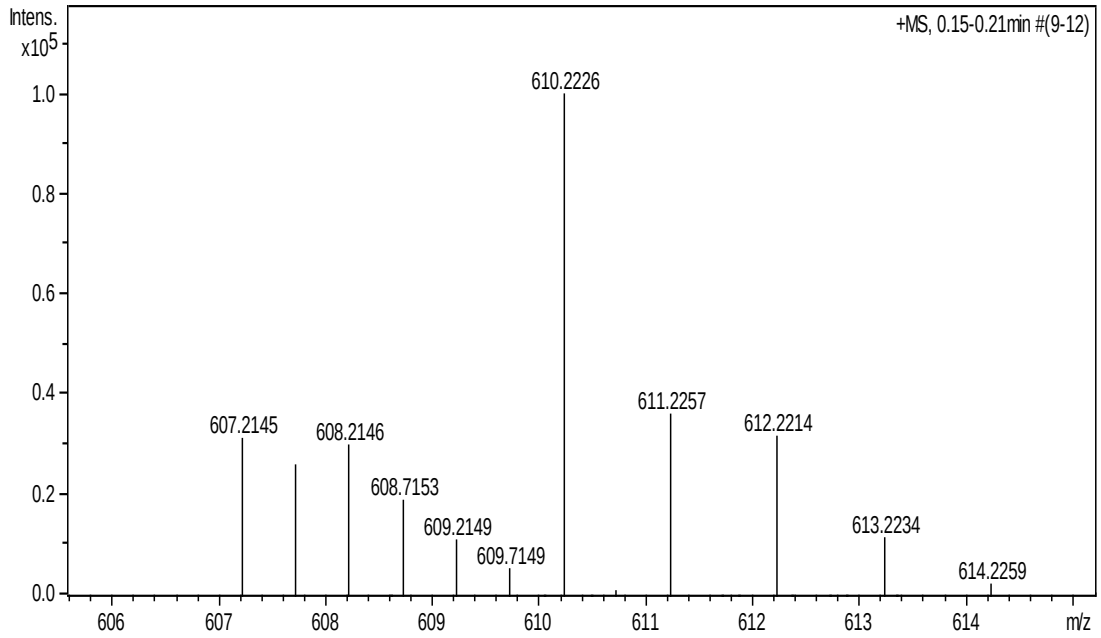

195.40
176.92
163.55
159.89
157.48
145.80
137.77
137.31
137.29
136.84
135.19
132.94
131.95
130.10
128.98
128.42
128.14
128.06
127.93
127.84
127.80
127.31
126.40
124.31
122.96
121.63
115.80
115.56
115.15
114.90
113.90
110.29
110.21
65.24
65.22
55.46
44.55
44.34
30.24
29.64
25.67
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.04-0.21min #(2-12)
644.2322
645.2350
642.2269
642.7277
1.0
0.8
0.6
0.4
0.2
0.0
642.0 642.5 643.0 643.5 644.0 644.5 645.0 645.5 646.0 m/z

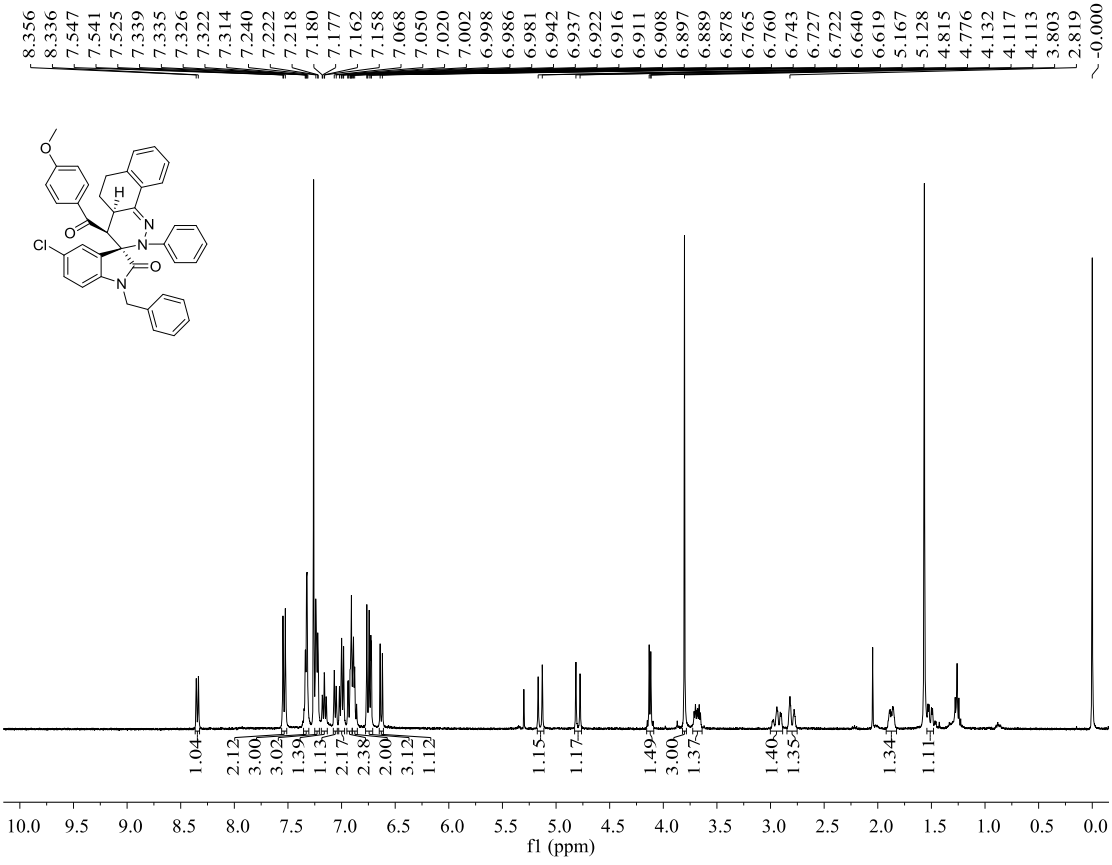
1'-butyl-5'-chloro-4-(4-methylbenzoyl)-2-phenyl-4,4a,5,6-tetrahydro-2*H*-spiro[benzo[h]cinnoline-3,3'-indolin]-2'-one (1f): red solid, 0.258g, 44%, m.p. 228-230 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, *J* = 8.0 Hz, 1H, ArH), 7.46 (d, *J* = 8.0 Hz, 1H, ArH), 7.23-7.21 (m, 1H, ArH), 7.16-7.13 (m, 1H, ArH), 7.11-7.09 (m, 2H, ArH), 7.07-7.01 (m, 4H, ArH), 6.95-6.93 (m, 2H, ArH), 6.89-6.86 (m, 1H, ArH), 6.72-6.67 (m, 2H, ArH), 4.09 (d, *J* = 6.0 Hz, 1H, CH), 3.86-3.80 (m, 1H, CH), 3.74-3.64 (m, 2H, CH), 2.95-2.87 (m, 1H, CH), 2.80-2.76 (m, 1H, CH), 2.32 (s, 3H, CH_3), 1.89-1.83 (m, 1H, CH), 1.71-1.64 (m, 2H, CH), 1.49-1.45 (m, 1H, CH), 1.42-1.35 (m, 2H, CH), 0.99 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ:: 196.7, 176.5, 145.8, 144.1, 140.3, 137.5, 136.7, 136.4, 132.9, 129.4, 129.1, 128.3, 128.0, 128.0, 127.8, 127.7, 127.4, 127.2, 126.4, 124.3, 123.0, 121.5, 109.6, 64.9, 44.8, 40.2, 30.2, 29.6, 29.2, 25.6, 21.6, 20.2, 13.8; IR (KBr) υ : 2926, 2319, 1721, 1673, 1599, 1485, 1456, 1429, 1328, 1257, 1220, 1174, 1080, 1020, 949, 881, 820, 794, 758, 732 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{37}H_{34}ClN_3O_2Na$ ($[M+Na]^+$):610.2232, Found: 610.2226.

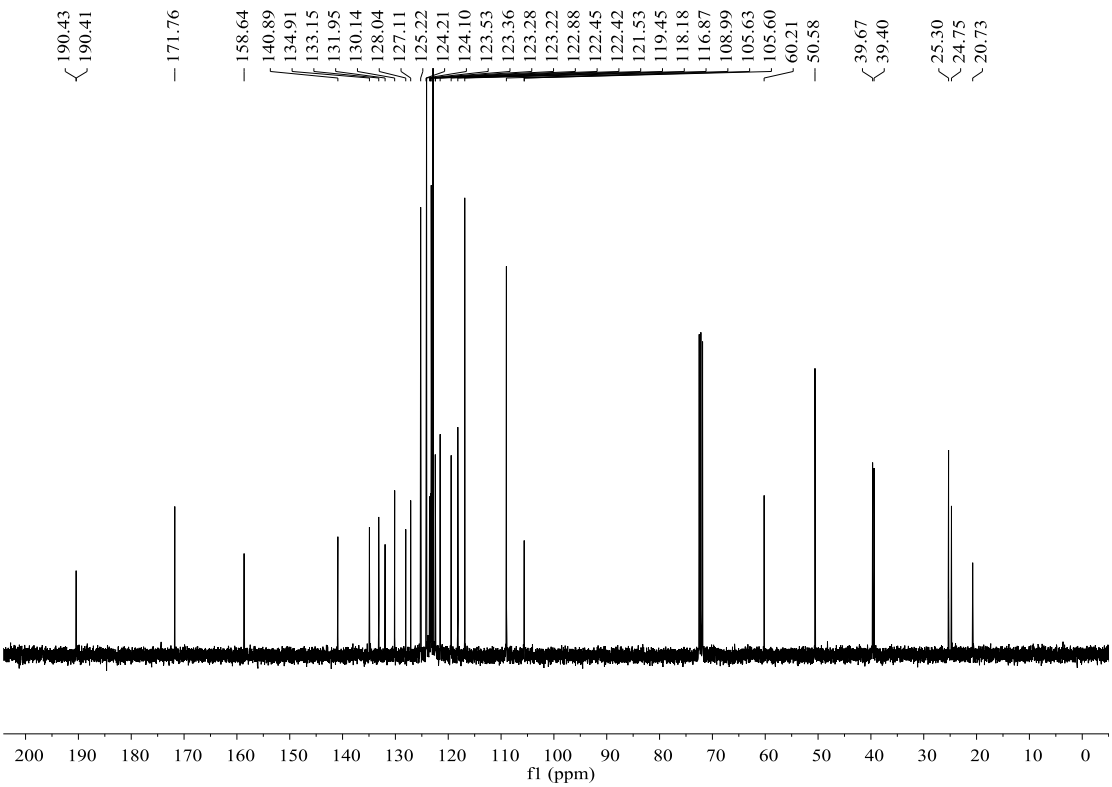


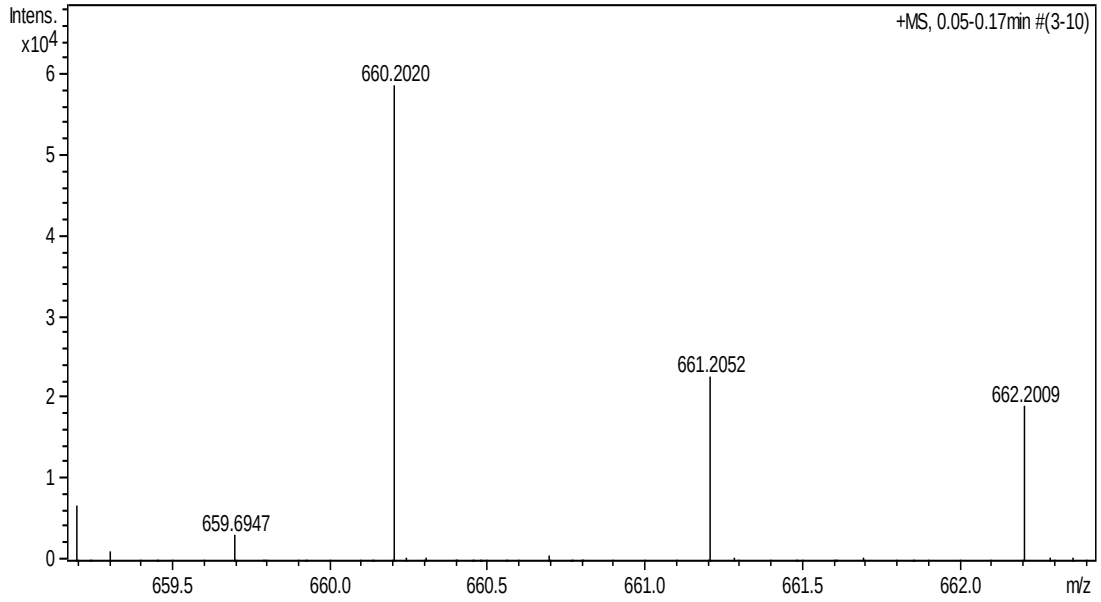

196.69
176.51
145.82
144.06
140.28
137.54
136.73
136.43
132.93
129.36
129.12
128.34
127.99
127.96
127.81
127.74
127.37
127.22
126.36
124.27
122.97
121.46
109.61
64.86
44.75
40.22
30.21
29.61
29.18
25.62
21.55
20.23
13.78
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.15-0.21min #(9-12)
610.2226
611.2257
612.2214
607.2145
608.2146
608.7153
609.2149
609.7149
613.2234
614.2259
1.0
0.8
0.6
0.4
0.2
0.0
606 607 608 609 610 611 612 613 614 m/z

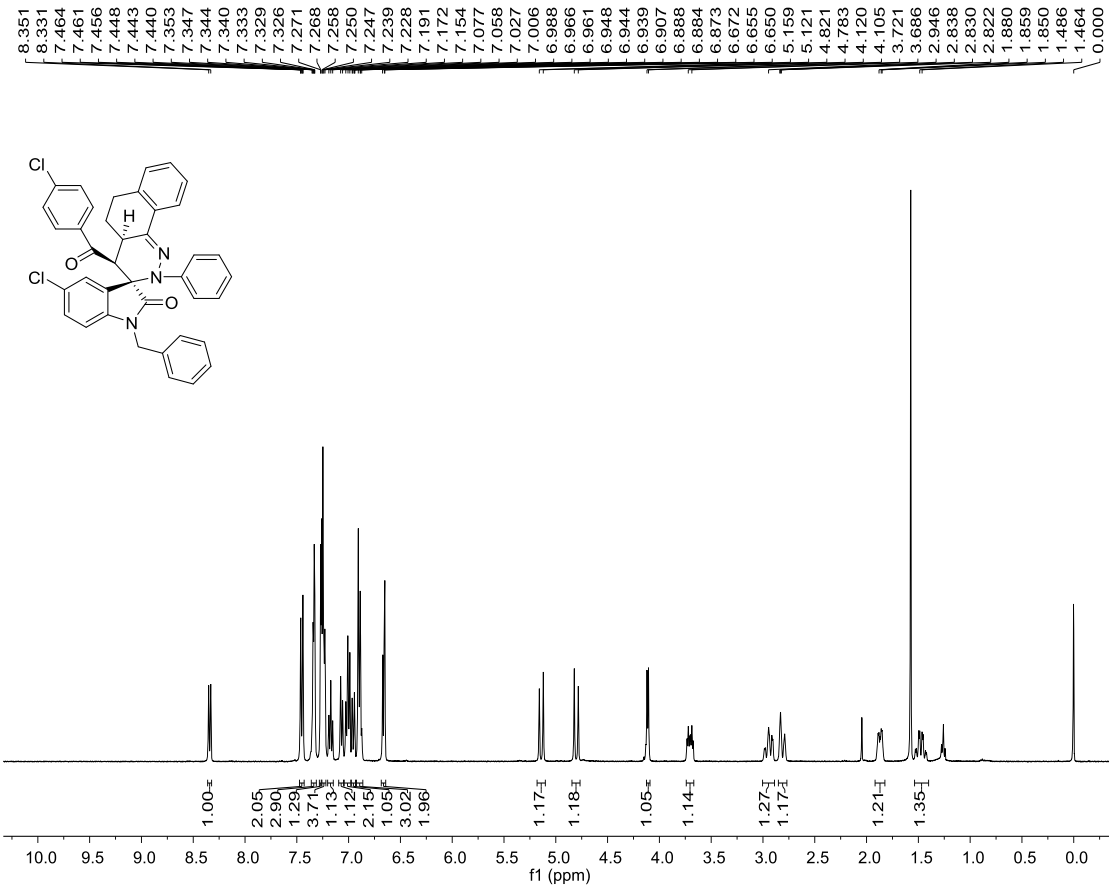
1'-benzyl-5'-chloro-4-(4-methoxybenzoyl)-2-phenyl-4,4a,5,6-tetrahydro-2*H*-spiro[benzo[h]cinnoline-3,3'-indolin]-2'-one (1g): orange solid, 0.261g, 41%, m.p. 233-235 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (d, J = 8.0 Hz, 1H, ArH), 7.55-7.53 (m, 2H, ArH), 7.35-7.31 (m, 3H, ArH), 7.24-7.22 (m, 3H, ArH), 7.18-7.14 (m, 1H, ArH), 7.07-7.05 (m, 1H, ArH), 7.02-6.98 (m, 2H, ArH), 6.94-6.91 (m, 2H, ArH), 6.90-6.86 (m, 2H, ArH), 6.77-6.72 (m, 3H, ArH), 6.64-6.62 (m, 1H, ArH), 5.15 (d, J = 15.6 Hz, 1H, CH), 4.80 (d, J = 15.6 Hz, 1H, CH), 4.15-4.11 (m, 1H, CH), 3.80 (s, 3H, OCH3), 3.71-3.65 (m, 1H, CH), 2.98-2.90 (m, 1H, CH), 2.83-2.77 (m, 1H, CH), 1.90-1.84 (m, 1H, CH), 1.53-1.49 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 190.4, 190.4, 171.8, 158.6, 140.9, 134.9, 133.1, 131.9, 130.1, 128.0, 127.1, 125.2, 124.2, 124.1, 123.5, 123.4, 123.3, 123.2, 122.9, 122.5, 122.4, 121.5, 119.5, 118.2, 116.9, 109.0, 105.6, 105.6, 60.2, 50.6, 39.7, 39.4, 25.3, 24.8, 20.7; IR (KBr) υ : 2927, 1724, 1672, 1606, 1492, 1466, 1346, 1302, 1268, 1242, 1170, 1077, 1013, 960, 881, 794, 764, 744 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{40}H_{32}ClN_3O_3Na$ ([M+Na]$^{+}$):660.2024, Found: 660.2020.

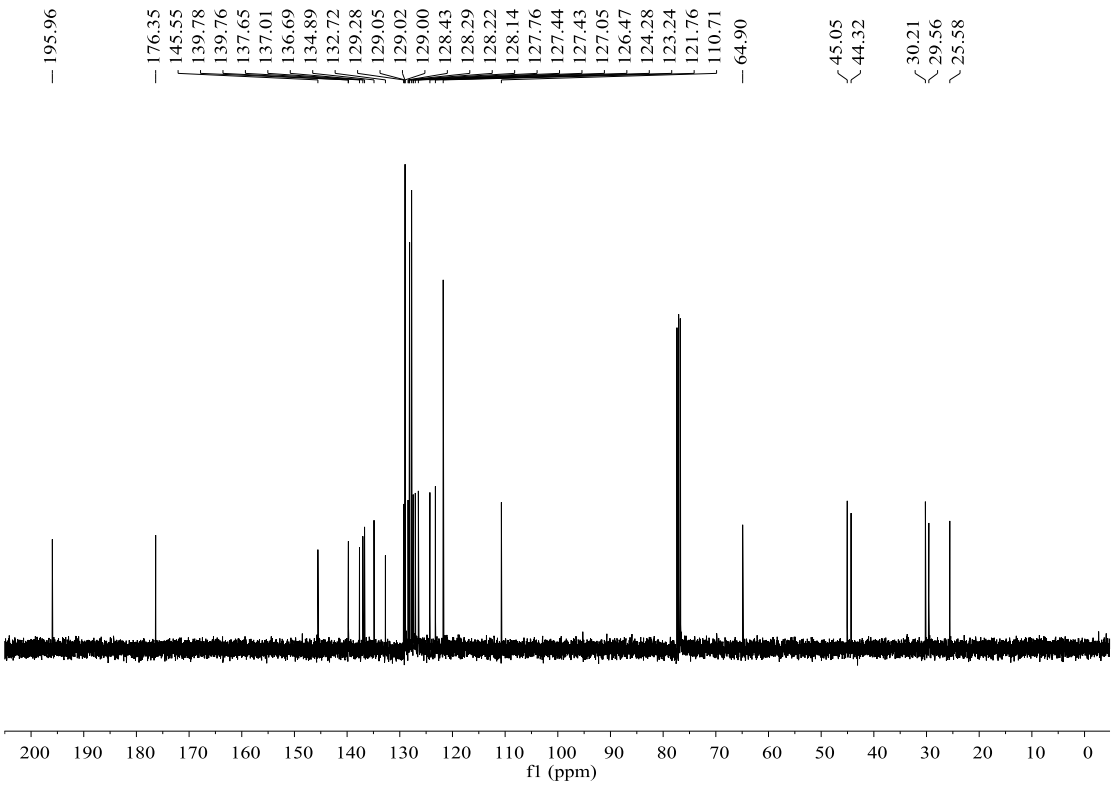


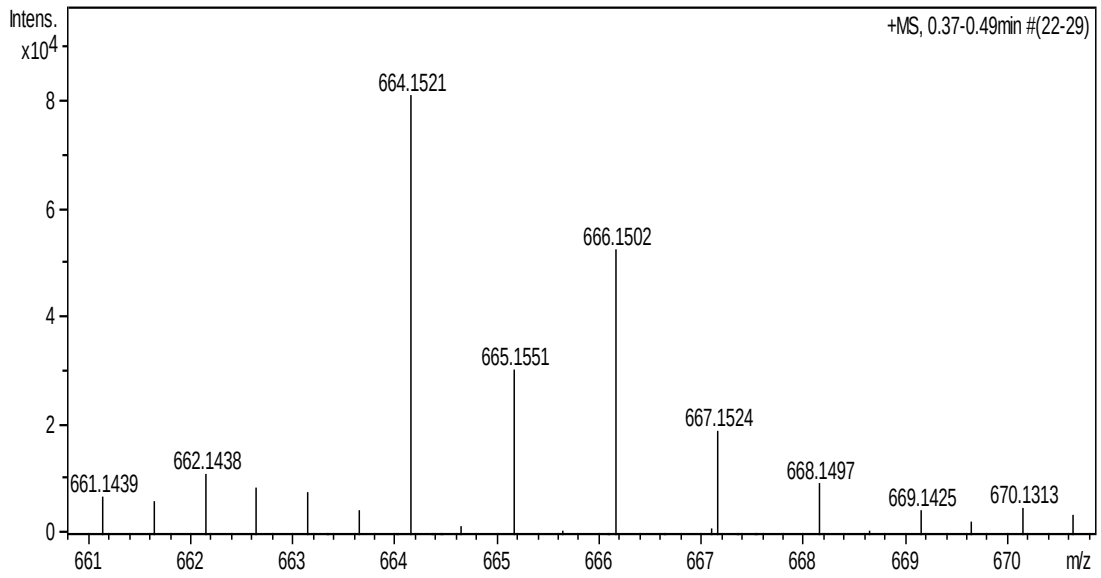

190.43
190.41
171.76
158.64
140.89
134.91
133.15
131.95
130.14
128.04
127.11
125.22
124.21
124.10
123.53
123.36
123.28
123.22
122.88
122.45
122.42
121.53
119.45
118.18
116.87
108.99
105.63
105.60
60.21
50.58
39.67
39.40
25.30
24.75
20.73
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^4
+MS, 0.05-0.17min #(3-10)
660.2020
661.2052
662.2009
659.6947
0 1 2 3 4 5 6
659.5 660.0 660.5 661.0 661.5 662.0
m/z

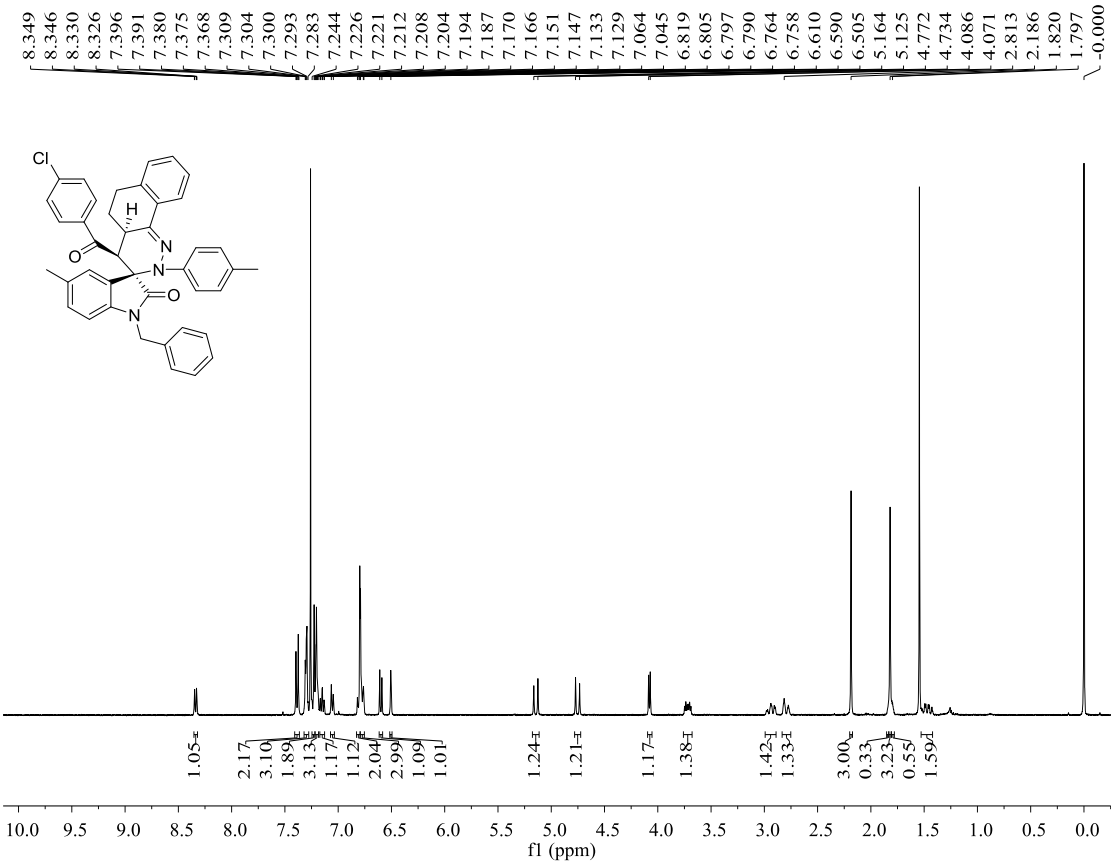
1'-benzyl-5'-chloro-4-(4-chlorobenzoyl)-2-phenyl-4,4a,5,6-tetrahydro-2*H*-spiro[benzo[h]cinnoline-3,3'-indolin]-2'-one (1h): yellow solid, 0.269 g, 42 %, m.p. 238-240 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.34 (d, J = 8.0 Hz, 1H, ArH), 7.46-7.43 (m, 2H, ArH), 7.35-7.33 (m, 3H, ArH), 7.27-7.27 (m, 1H, ArH), 7.26-7.23 (m, 4H, ArH), 7.19-7.15 (m, 1H, ArH), 7.08-7.06 (m, 1H, ArH), 7.03-6.99 (m, 2H, ArH), 6.97-6.94 (m, 1H, ArH), 6.91-6.87 (m, 3H, ArH), 6.67-6.65 (m, 2H, ArH), 5.14 (d, J = 15.2 Hz, 1H, CH), 4.80 (d, J = 15.2 Hz, 1H, CH), 4.11 (d, J = 6.0 Hz, 1H, CH), 3.73-3.67 (m, 1H, CH), 2.99-2.90(m, 1H, CH), 2.84-2.79 (m, 1H, CH), 1.89-1.85 (m, 1H, CH), 1.53-1.42 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.0, 176.4, 145.6, 139.8, 139.8, 137.7, 137.0, 136.7, 134.9, 132.7, 129.3, 129.1, 129.0, 129.0, 128.4, 128.3, 128.2, 128.1, 127.8, 127.4, 127.4, 127.1, 126.5, 124.3, 123.2, 121.8, 110.7, 64.9, 45.1, 44.3, 30.2, 29.6, 25.6; IR (KBr) υ : 3063, 2928, 2852, 1722, 1594, 1485, 1330, 1252, 1175, 1083, 1011, 948, 886, 825, 760 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{39}H_{29}Cl_2N_3O_2Na$ ([M+Na]$^{+}$):664.1529, Found: 664.1521.

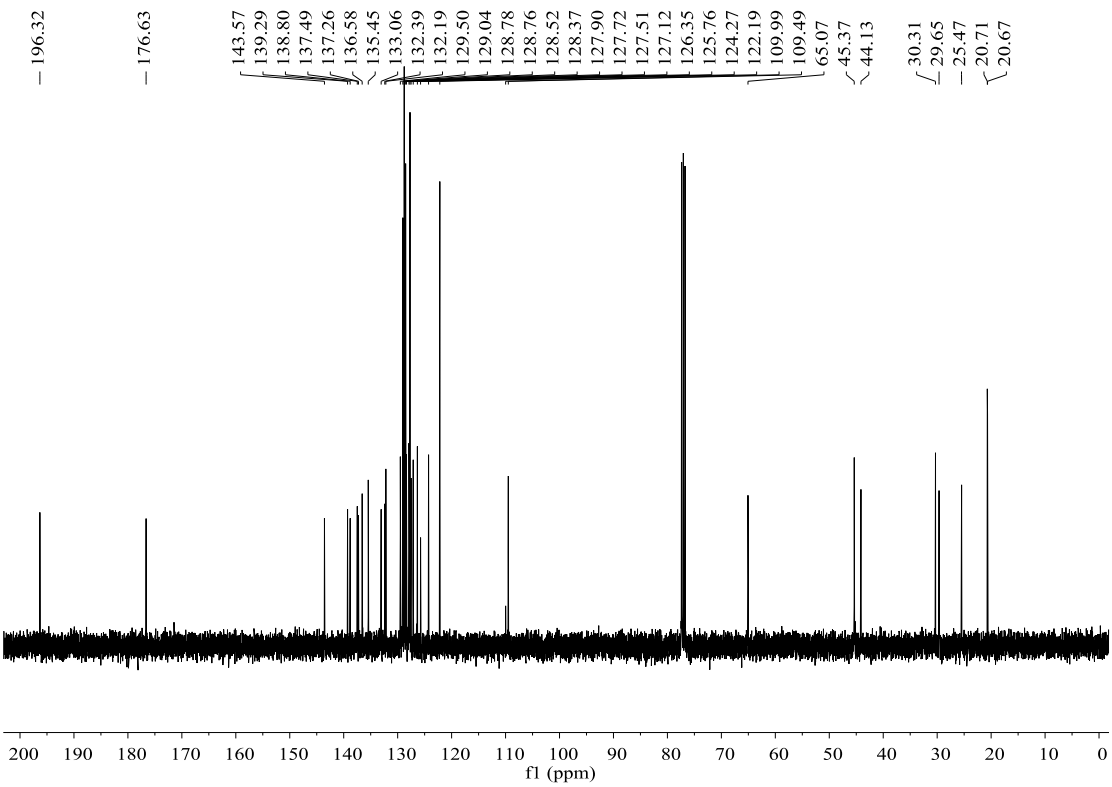


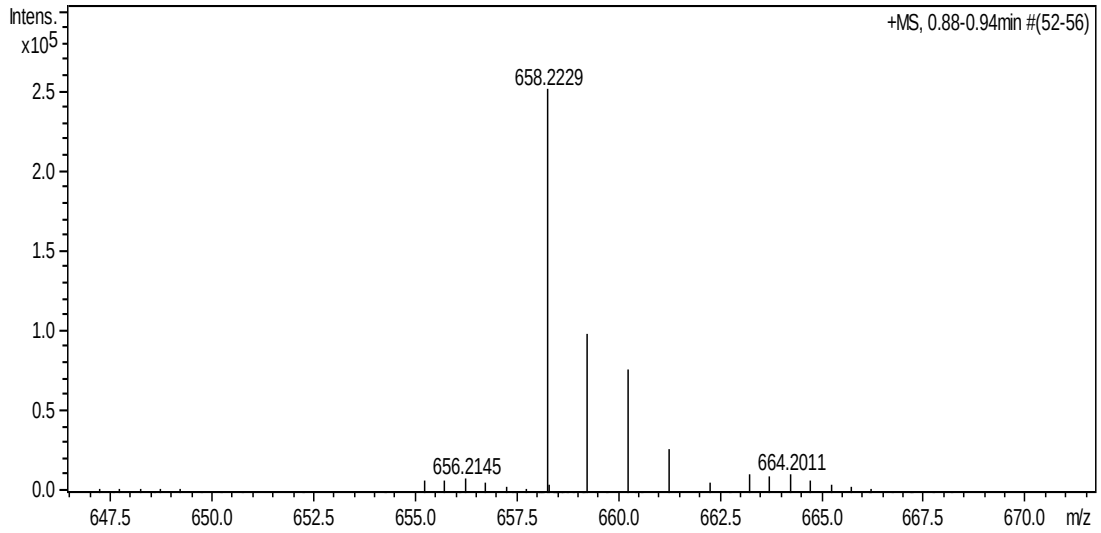

195.96
176.35
145.55
139.78
139.76
137.65
137.01
136.69
134.89
132.72
129.28
129.05
129.02
129.00
128.43
128.29
128.22
128.14
127.76
127.44
127.43
127.05
126.47
124.28
123.24
121.76
110.71
64.90
45.05
44.32
30.21
29.56
25.58
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^4
+MS, 0.37-0.49min #(22-29)
664.1521
666.1502
665.1551
667.1524
662.1438
661.1439
668.1497
669.1425
670.1313
0
2
4
6
8
661
662
663
664
665
666
667
668
669
670
m/z

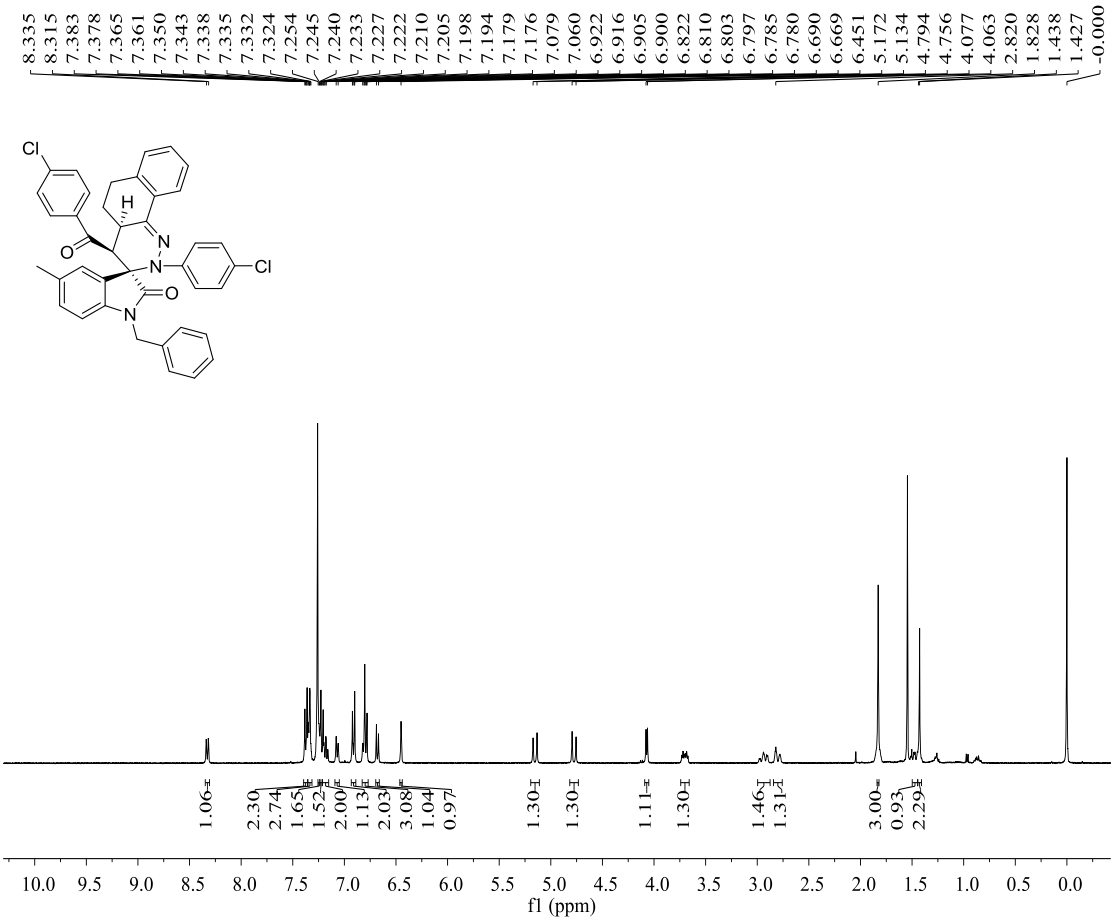
1'-benzyl-4-(4-chlorobenzoyl)-5'-methyl-2-(p-tolyl)-4,4a,5,6-tetrahydro-2*H*-spiro[benzo[h]cinnoline-3,3'-indolin]-2'-one (1i): yellow solid, 0.400g, 63%, m.p. 169-171 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.35-8.33 (m, 1H, ArH), 7.40-7.37 (m, 2H, ArH), 7.31-7.28 (m, 3H, ArH), 7.24-7.22 (m, 2H, ArH), 7.21-7.19 (m, 3H, ArH), 7.17-7.13 (m, 1H, ArH), 7.06-7.05 (m, 1H, ArH), 6.82-6.81 (m, 2H, ArH), 6.79-6.76 (m, 3H, ArH), 6.61-6.59 (m, 1H, ArH) , 6.51 (s, 1H, ArH), 5.14 (d, J = 15.6 Hz, 1H, CH), 4.75 (d, J = 15.2 Hz, 1H, CH), 4.08 (d, J = 6.0 Hz, 1H, CH), 3.75-3.69 (m, 1H, CH), 2.97-2.90(m, 1H, CH), 2.81-2.77 (m, 1H, CH), 2.19 (s, 3H, CH_3), 1.84-1.80 (m, 1H, CH), 1.82 (s, 3H, CH_3), 1.53-1.43 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: δ: 196.3, 176.6, 143.6, 139.3, 138.8, 137.5, 137.3, 136.6, 135.5, 133.1, 132.4, 132.2, 129.5, 129.0, 128.8, 128.8, 128.5, 128.4, 127.9, 127.7, 127.5, 127.1, 126.4, 125.8, 124.3, 122.2, 110.0, 109.5, 65.1, 45.4, 44.1, 30.3, 29.7, 25.5, 20.7, 20.7; IR (KBr) υ : 2928, 1723, 1654, 1599, 1489, 1476, 1430, 1355, 1257, 1238, 1172, 1073, 1014, 955, 883, 802, 763 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{41}H_{34}ClN_3O_2Na$ ([M+Na]$^{+}$):658.2232, Found: 658.2229.

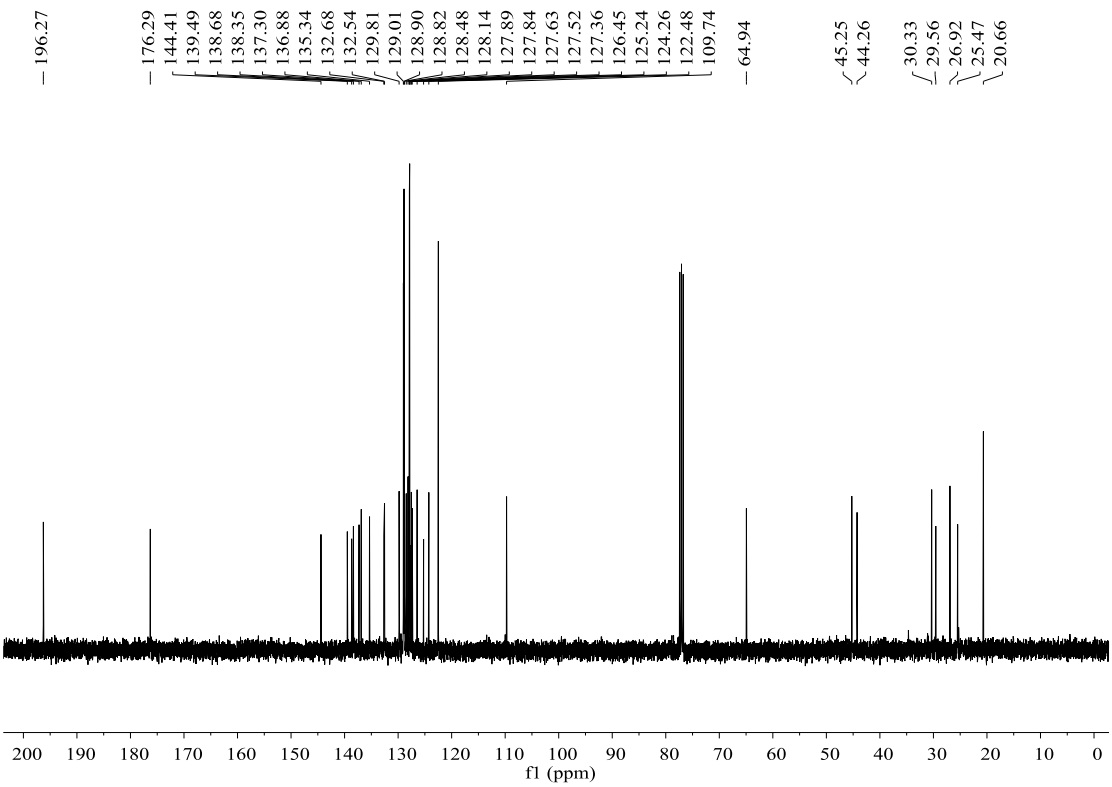


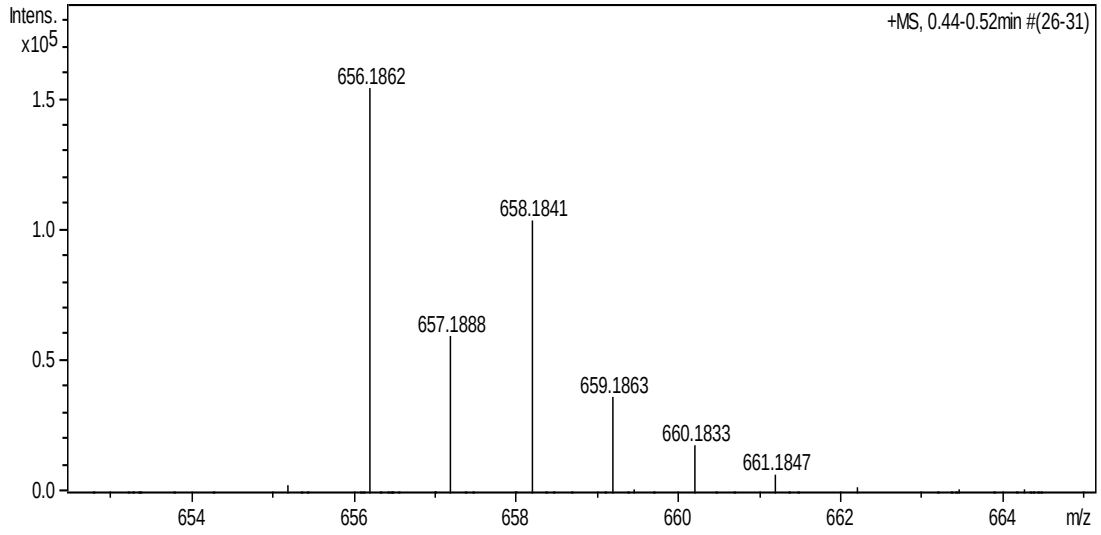

196.32
176.63
143.57
139.29
138.80
137.49
137.26
136.58
135.45
133.06
132.39
132.19
129.50
129.04
128.78
128.76
128.52
128.37
127.90
127.72
127.51
127.12
126.35
125.76
124.27
122.19
109.99
109.49
65.07
45.37
44.13
30.31
29.65
25.47
20.71
20.67
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.88-0.94min #(52-56)
658.2229
656.2145
664.2011
2.5
2.0
1.5
1.0
0.5
0.0
647.5 650.0 652.5 655.0 657.5 660.0 662.5 665.0 667.5 670.0 m/z

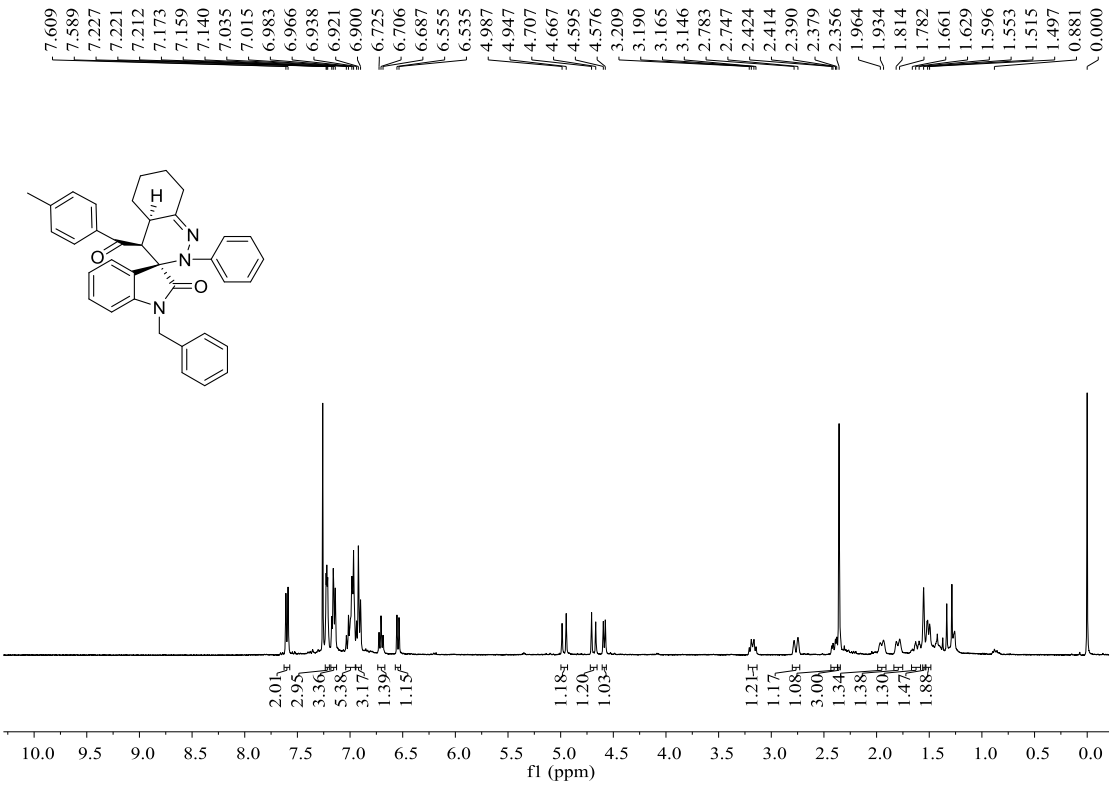
1'-benzyl-4-(4-chlorobenzoyl)-2-(4-chlorophenyl)-5'-methyl-4,4a,5,6-tetrahydro-2*H*-spiro[benzo[h]cinnoline-3,3'-indolin]-2'-one (1j): yellow solid, 0.282g, 43%, m.p. 172-174 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, J = 8.0 Hz, 1H, ArH), 7.38-7.36 (m, 2H, ArH), 7.35-7.32 (m, 3H, ArH), 7.25-7.24 (m, 2H, ArH), 7.23-7.22 (m, 2H, ArH), 7.21-7.16 (m, 2H, ArH), 7.08-7.06 (m, 1H, ArH), 6.92-6.89 (m, 2H, ArH), 6.82-6.77 (m, 3H, ArH), 6.69-6.67 (m, 1H, ArH), 6.45 (s, 1H, ArH), 5.15 (d, J = 15.2 Hz, 1H, CH), 4.78 (d, J = 15.2 Hz, 1H, CH), 4.07 (d, J = 5.6 Hz, 1H, CH), 3.73-3.67 (m, 1H, CH), 2.97-2.90(m, 1H, CH), 2.83-2.78 (m, 1H, CH), 1.83 (s, 3H, CH_3), 1.48-1.45 (m, 1H, CH), 1.44-1.43 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.3, 176.3, 144.4, 139.5, 138.7, 138.4, 137.3, 136.9, 135.3, 132.7 132.5, 129.8, 129.0, 128.9, 128.8, 128.5, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 126.5, 125.2, 124.3, 122.5, 109.7, 64.9, 45.3, 44.3, 30.3, 29.6, 26.9, 25.5, 20.7; IR (KBr) υ : 3053, 2926, 2854, 1709, 1673, 1586, 1491, 1445, 1334, 1265, 1180, 1091, 1008, 954, 811, 761 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{40}H_{32}Cl_2N_3O_2H$ ($[M+H]^+$):656.1866, Found: 656.1862.

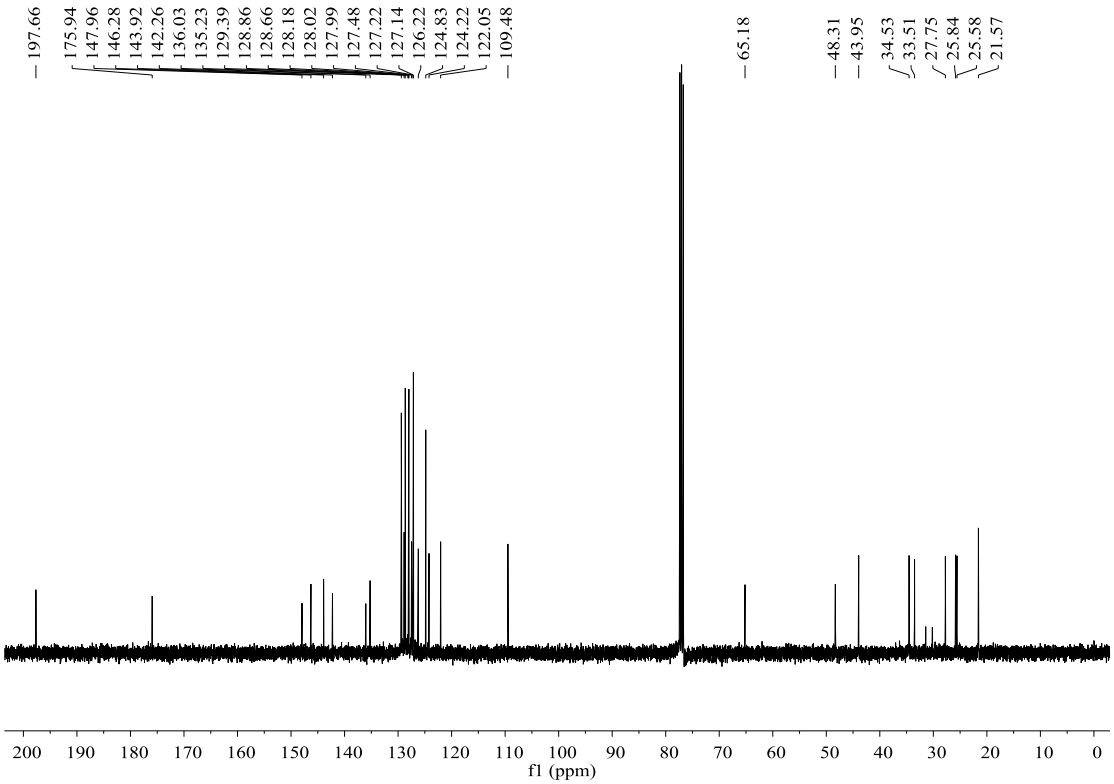


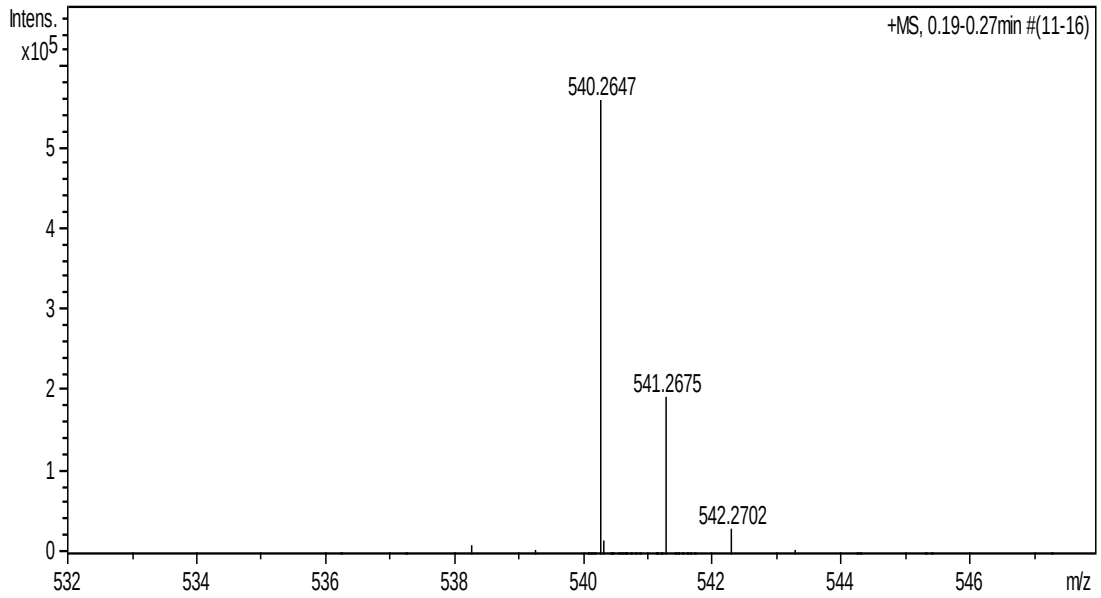

196.27
176.29
144.41
139.49
138.68
138.35
137.30
136.88
135.34
132.68
132.54
129.81
129.01
128.90
128.82
128.48
128.14
127.89
127.84
127.63
127.52
127.36
126.45
125.24
124.26
122.48
109.74
64.94
45.25
44.26
30.33
29.56
26.92
25.47
20.66
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.44-0.52min #(26-31)
656.1862
658.1841
657.1888
659.1863
660.1833
661.1847
1.5
1.0
0.5
0.0
654
656
658
660
662
664
m/z

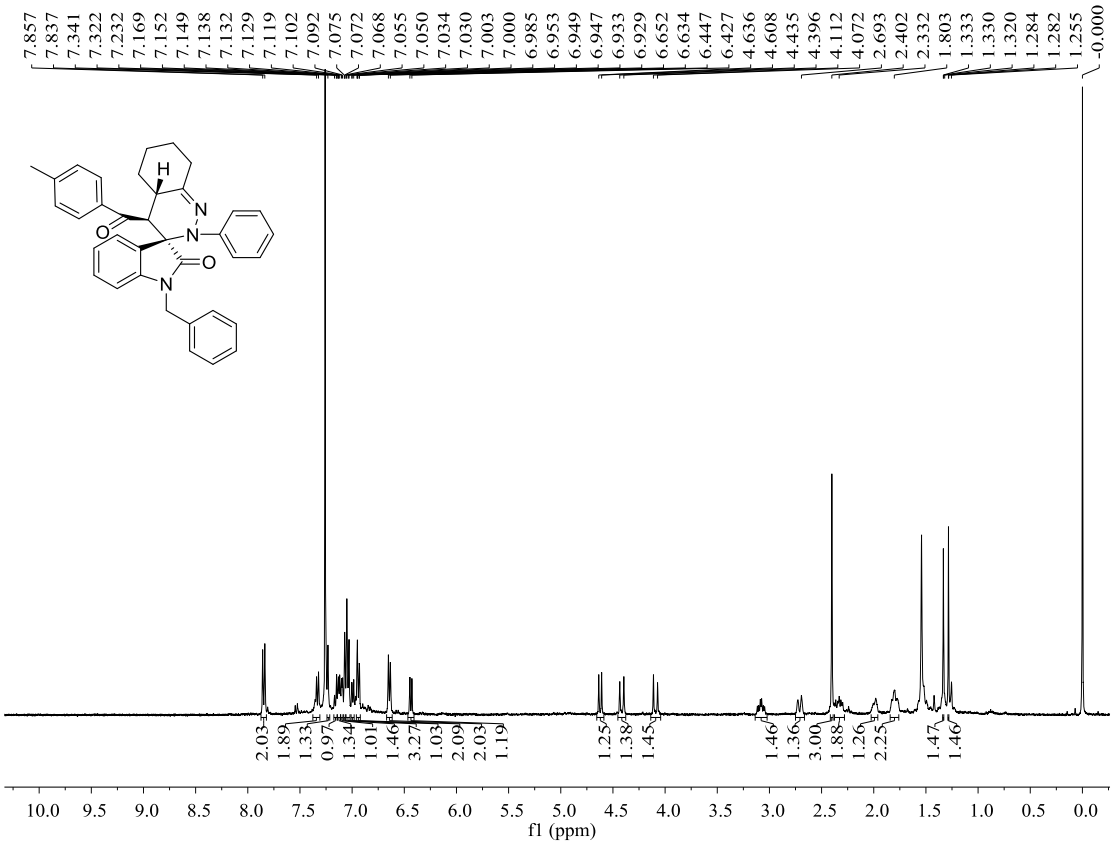
1'-benzyl-4-(4-methylbenzoyl)-2-phenyl-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2a): orange solid, 0.161g, 27%, m.p. 159-161 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61-7.59 (m, 2H, ArH), 7.23-7.21 (m, 3H, ArH), 7.17-7.14 (m, 3H, ArH), 7.04-6.97 (m, 5H, ArH), 6.94-6.90 (m, 3H, ArH), 6.73-6.69 (m, 1H, ArH), 6.55 (d, *J* = 8.0 Hz, 1H, ArH), 4.97 (d, *J* = 16.0 Hz, 1H, CH), 4.69 (d, *J* = 16.0 Hz, 1H, CH), 4.59 (d, *J* = 7.6 Hz, 1H, CH), 3.21-3.15 (m, 1H, CH), 2.78-2.75 (m, 1H, CH), 2.42-2.38 (m, 1H, CH), 2.36 (s, 3H, CH_3), 1.96-1.93 (m, 1H, CH), 1.81-1.78 (m, 1H, CH), 1.66-1.60 (m, 1H, CH), 1.55-1.55 (m, 1H, CH), 1.52-1.50 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.7, 175.9, 147.9, 146.3, 143.9, 142.3, 136.0, 135.2, 129.4, 128.9, 128.7, 128.2, 128.0, 128.0, 127.5, 127.2, 127.1, 126.2, 124.8, 124.2, 122.0, 109.5, 65.2, 48.3, 43.9, 34.5, 33.5, 27.7, 25.8, 25.6, 21.6; IR (KBr) υ : 3015, 2964, 2879, 1725, 1665, 1592, 1551, 1515, 1497, 1387, 1346, 1311, 1248, 1217, 1176, 1149, 1129, 1071, 1002, 939, 912, 875, 846, 827, 764, 729, 705 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{34}N_3O_2$ ($[M+H]^+$):540.2646, Found: 540.2647.

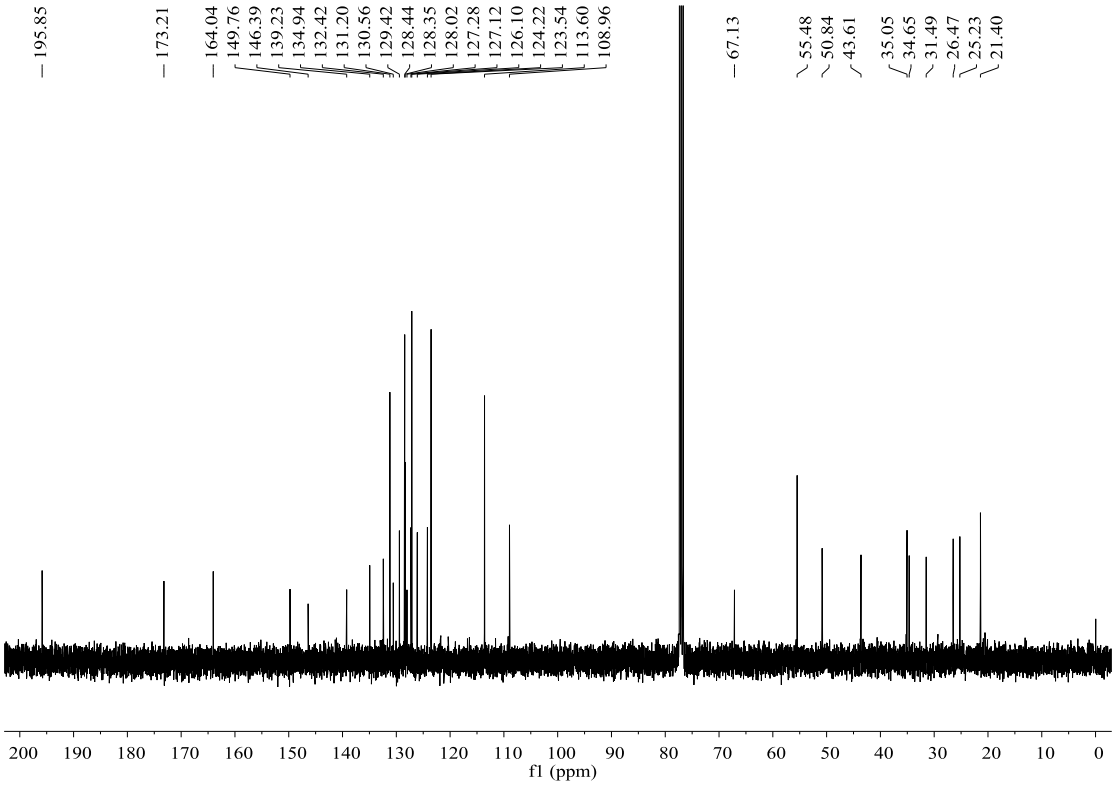


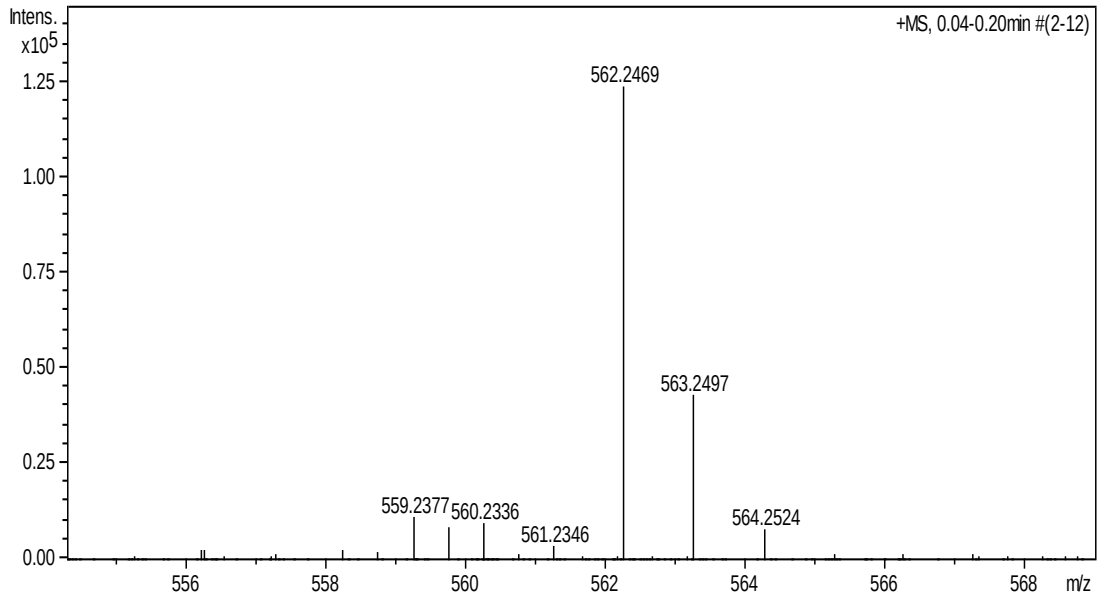

197.66
175.94
147.96
146.28
143.92
142.26
136.03
135.23
129.39
128.86
128.66
128.18
128.02
127.99
127.48
127.22
127.14
126.22
124.83
124.22
122.05
109.48
65.18
48.31
43.95
34.53
33.51
27.75
25.84
25.58
21.57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.19-0.27min #(11-16)
540.2647
541.2675
542.2702
0
1
2
3
4
5
532
534
536
538
540
542
544
546
m/z

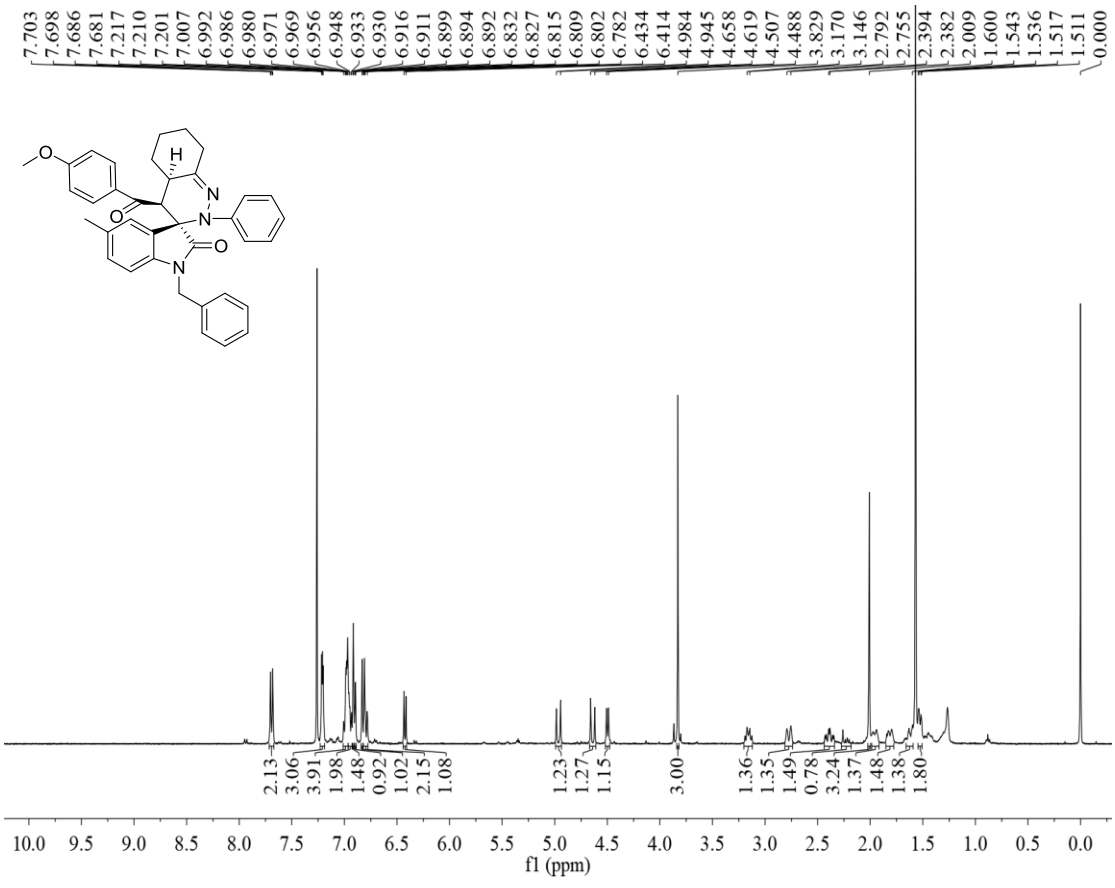
1'-benzyl-4-(4-methylbenzoyl)-2-phenyl-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2a'): orange solid, 0.119g, 22%, m.p. 150-152 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86-7.84 (m, 2H, ArH), 7.35-7.32 (m, 3H, ArH), 7.23-7.22 (m, 1H, ArH), 7.17-7.15 (m, 1H, ArH), 7.14-7.12 (m, 1H, ArH), 7.10-7.09 (m, 1H, ArH), 7.08-7.07 (m, 1H, ArH), 7.06-7.03 (m, 3H, ArH), 7.00-6.99 (m, 1H, ArH), 6.95-6.93 (m, 2H, ArH), 6.65-6.63 (m, 2H, ArH), 6.45-6.43 (m, 1H, ArH), 4.62 (d, *J* = 11.2 Hz, 1H, CH), 4.42 (d, *J* = 15.6 Hz, 1H, CH), 4.09 (d, *J* = 16.0 Hz, 1H, CH), 3.12-3.05 (m, 1H, CH), 2.71 (d, *J* = 14.0 Hz, 1H, CH), 2.40 (s, 3H, CH_3), 2.37-2.30 (m, 2H, CH), 2.01-1.98 (m, 1H, CH), 1.83-1.77 (m, 2H, CH), 1.32-1.33 (m, 1H, CH), 1.28-1.25 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.9, 173.2, 164.0, 149.8, 146.4, 139.2, 135.0, 132.4, 131.2, 130.6, 129.4, 128.4, 128.4, 128.0, 127.3, 127.1, 126.1, 124.2, 123.5, 113.6, 109.0, 67.1, 55.5, 50.8, 43.6, 35.1, 34.7, 31.5, 26.5, 25.2, 21.4; IR (KBr) υ : 2974, 2934, 1723, 1645, 1598, 1542, 1514, 144, 1377, 1334, 1311, 1251, 1208, 1182, 1158, 1127, 1075, 1002, 941, 912, 873, 847, 826, 764, 729, 701 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{33}N_2O_{32}Na$ ([M+H]$^{+}$):562.2465, Found: 562.2469.

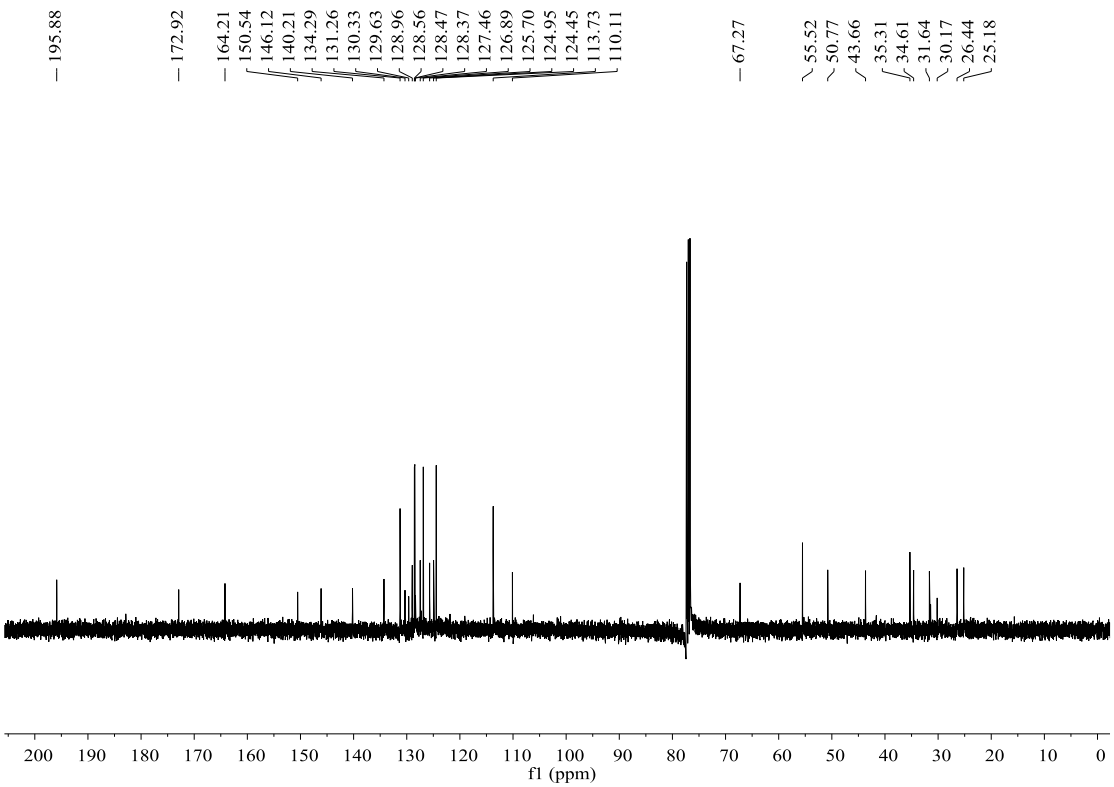


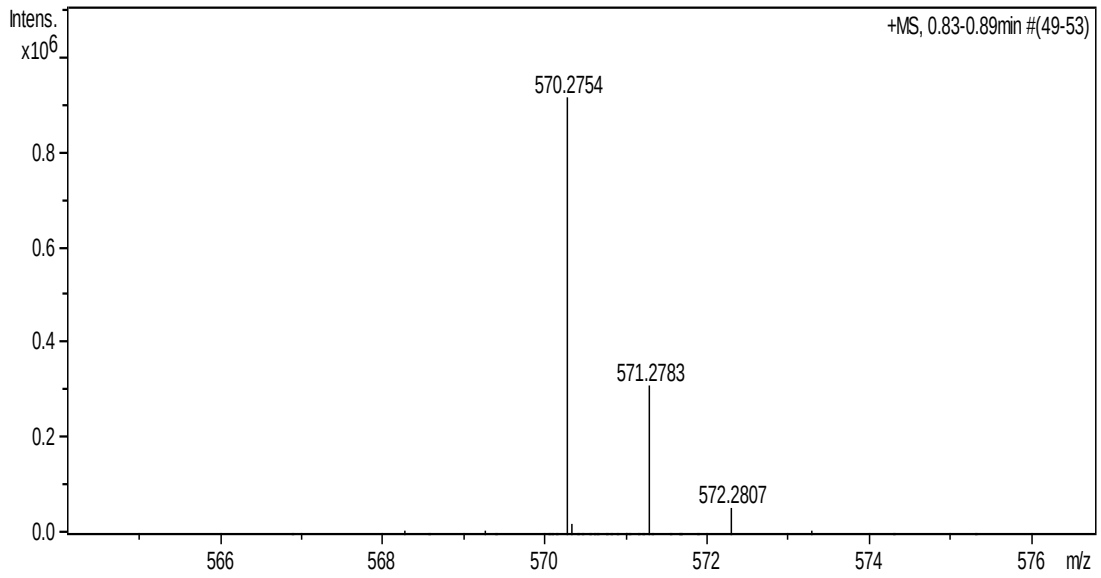

195.85
173.21
164.04
149.76
146.39
139.23
134.94
132.42
131.20
130.56
129.42
128.44
128.35
128.02
127.28
127.12
126.10
124.22
123.54
113.60
108.96
67.13
55.48
50.84
43.61
35.05
34.65
31.49
26.47
25.23
21.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.04-0.20min #(2-12)
562.2469
563.2497
559.2377
560.2336
561.2346
564.2524
1.25
1.00
0.75
0.50
0.25
0.00
556 558 560 562 564 566 568 m/z

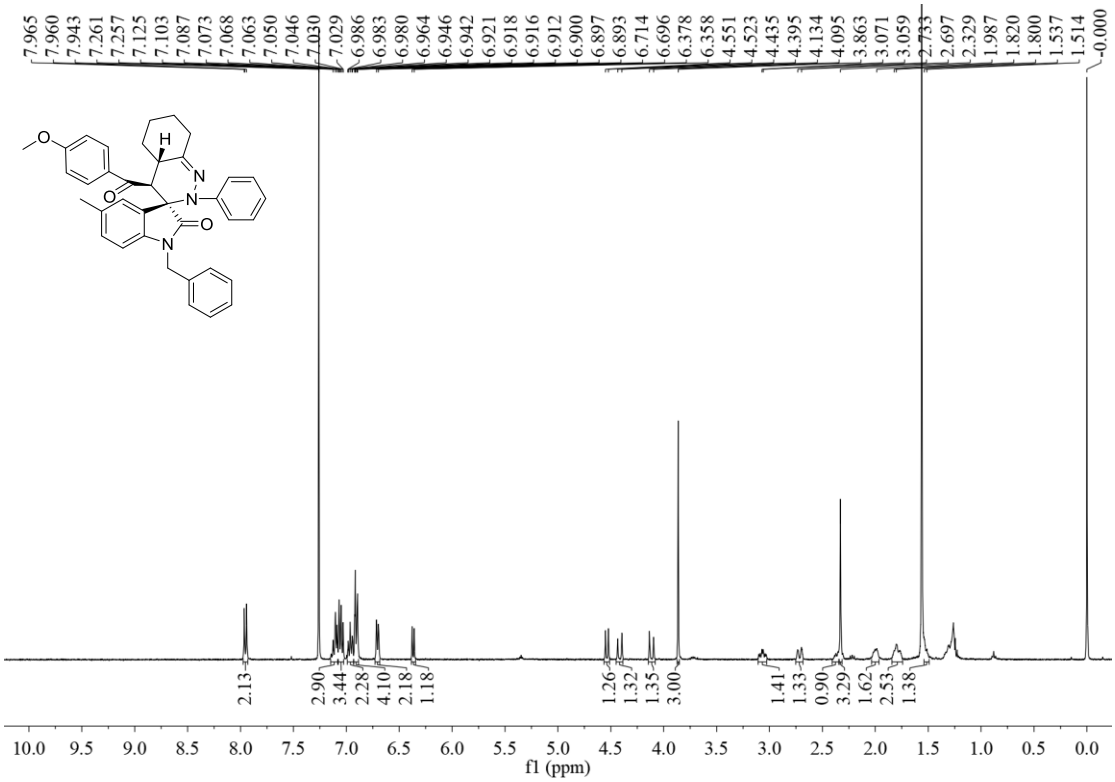
1'-benzyl-4-(4-methoxybenzoyl)-5'-methyl-2-phenyl-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2b): orange solid, 0.148g, 26%, m.p. 156-158 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70-7.68 (m, 2H, ArH), 7.22-7.20 (m, 3H, ArH), 7.01-6.97 (m, 4H, ArH), 6.96-6.93 (m, 2H, ArH), 6.92-6.91 (m, 1H, ArH), 6.90-6.89 (m, 1H, ArH), 6.83-6.83 (m, 1H, ArH), 6.82-6.78 (m, 3H, ArH), 6.42 (d, *J* = 8.0 Hz, 1H, ArH), 4.96 (d, *J* = 15.6 Hz, 1H, CH), 4.64 (d, *J* = 15.6 Hz, 1H, CH), 4.50 (d, *J* = 7.6 Hz, 1H, CH), 3.83 (s, 3H, OCH_3), 3.19-3.13 (m, 1H, CH), 2.79-2.76 (m, 1H, CH), 2.43-2.35 (m, 1H, CH), 2.26-2.10 (m, 1H, CH), 2.01 (s, 3H, CH_3), 1.97-1.94 (m, 1H, CH), 1.85-1.80 (m, 1H, CH), 1.65-1.60 (m, 1H, CH), 1.54-1.51 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.9, 172.9, 164.2, 150.5, 146.1, 140.2, 134.3, 131.3, 130.3, 129.6, 129.0, 128.6, 128.5, 128.4, 127.5, 126.9, 125.7, 125.0, 124.5, 113.7, 110.1, 67.3, 55.5, 50.8, 43.7, 35.3, 34.6, 31.6, 30.2, 26.4, 25.2.; IR (KBr) υ : 2992, 2945, 1721, 1662, 1598, 1543, 1452, 1375, 1364, 1315, 1258, 1210, 1181, 1159, 1127, 1076, 1000, 934, 874, 835, 816, 765, 724, cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{37}H_{36}N_3O_3$ ([M+H]$^{+}$):570.2751, Found: 570.2754.

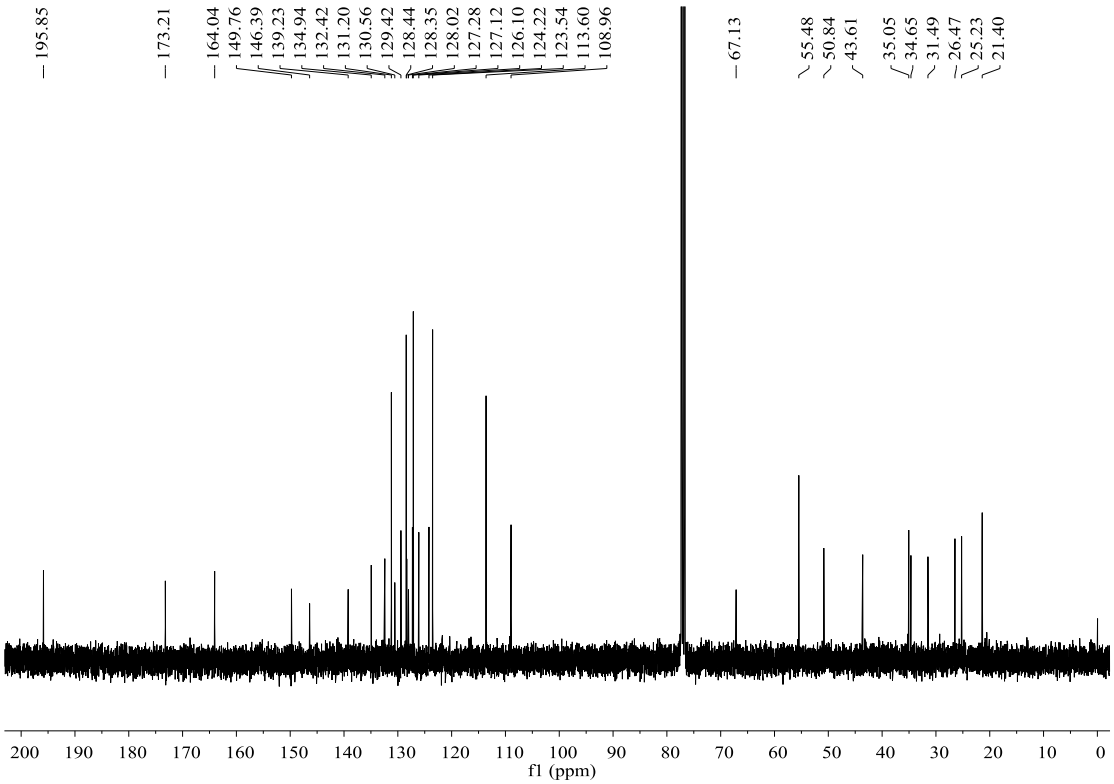


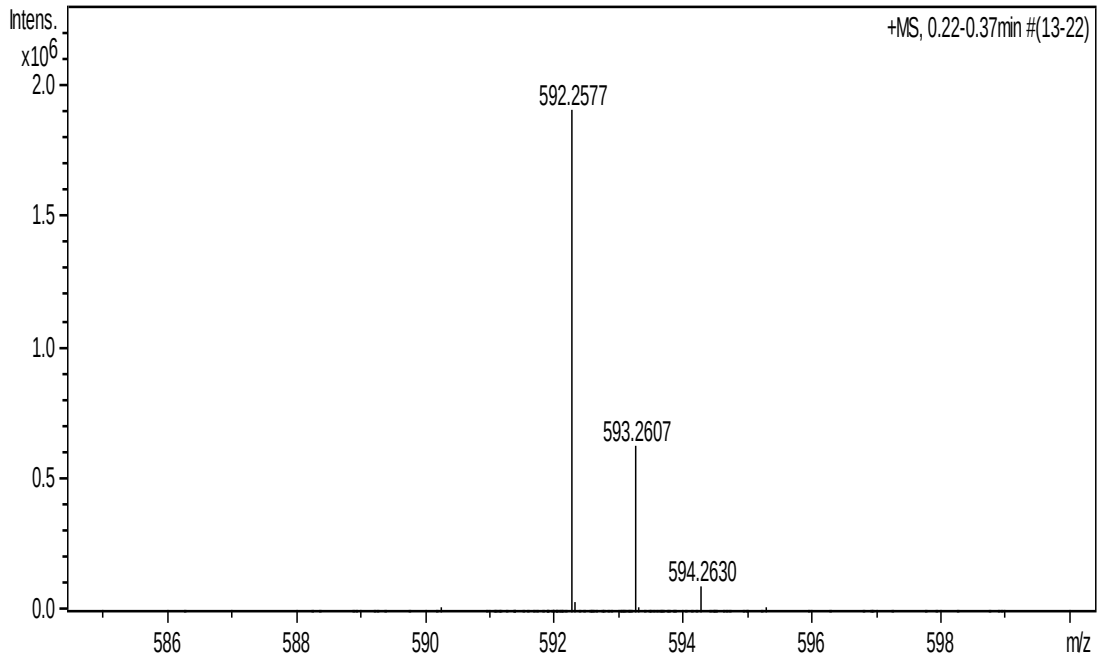

195.88
172.92
164.21
150.54
146.12
140.21
134.29
131.26
130.33
129.63
128.96
128.56
128.47
128.37
127.46
126.89
125.70
124.95
124.45
113.73
110.11
67.27
55.52
50.77
43.66
35.31
34.61
31.64
30.17
26.44
25.18
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^6
+MS, 0.83-0.89min #(49-53)
570.2754
571.2783
572.2807
0.0
0.2
0.4
0.6
0.8
566
568
570
572
574
576
m/z

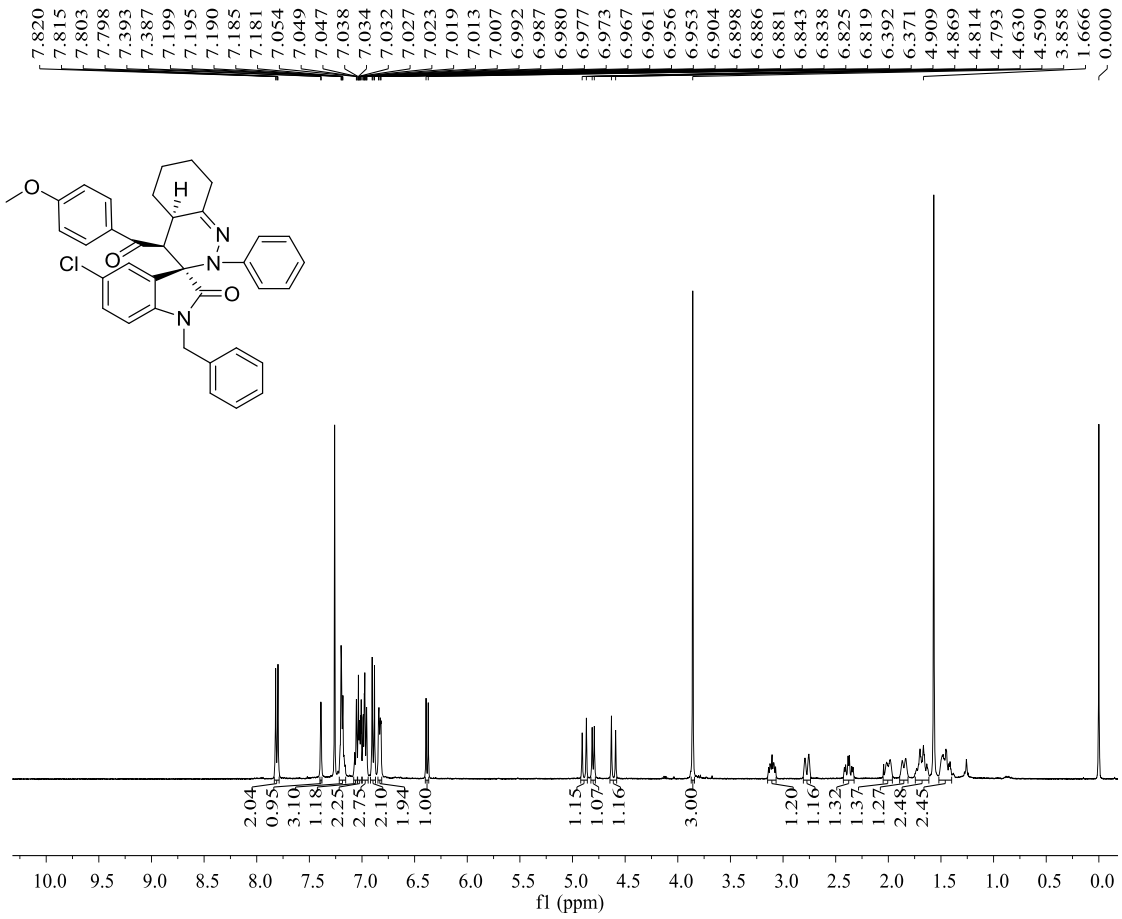
1'-benzyl-4-(4-methoxybenzoyl)-5'-methyl-2-phenyl-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2b'): white solid, 0.148g, 26%, m.p. 95-97 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70-7.68 (m, 2H, ArH), 7.22-7.20 (m, 3H, ArH), 7.01-6.97 (m, 4H, ArH), 6.96-6.93 (m, 2H, ArH), 6.92-6.91 (m, 1H, ArH), 6.90-6.89 (m, 1H, ArH), 6.83-6.83 (m, 1H, ArH), 6.82-6.78 (m, 3H, ArH), 6.42 (d, *J* = 8.0 Hz, 1H, ArH), 4.96 (d, *J* = 15.6 Hz, 1H, CH), 4.64 (d, *J* = 15.6 Hz, 1H, CH), 4.50 (d, *J* = 7.6 Hz, 1H, CH), 3.83 (s, 3H, OCH_3), 3.19-3.13 (m, 1H, CH), 2.79-2.76 (m, 1H, CH), 2.43-2.35 (m, 1H, CH), 2.26-2.10 (m, 1H, CH), 2.01 (s, 3H, CH_3), 1.97-1.94 (m, 1H, CH), 1.85-1.80 (m, 1H, CH), 1.65-1.60 (m, 1H, CH), 1.54-1.51 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.9, 173.2, 164.0, 149.8, 146.4, 139.2, 134.9, 132.4, 131.2, 130.6, 129.4, 128.4, 128.3, 128.0, 127.2, 127.1, 126.1, 124.2, 123.5, 113.6, 109.0, 67.1, 55.5, 50.8, 43.6, 35.1, 34.7, 31.5, 26.5, 25.2, 21.4; IR (KBr) υ : 2994, 2955, 1722, 1664, 1599, 1538, 1457, 1373, 1354, 1319, 1260, 1211, 1183, 1160, 1125, 1078, 958, 910, 869, 833, 826, 764, 727 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{37}H_{36}N_3O_3$ ([M+H]$^{+}$):592.2571, Found: 592.2577.

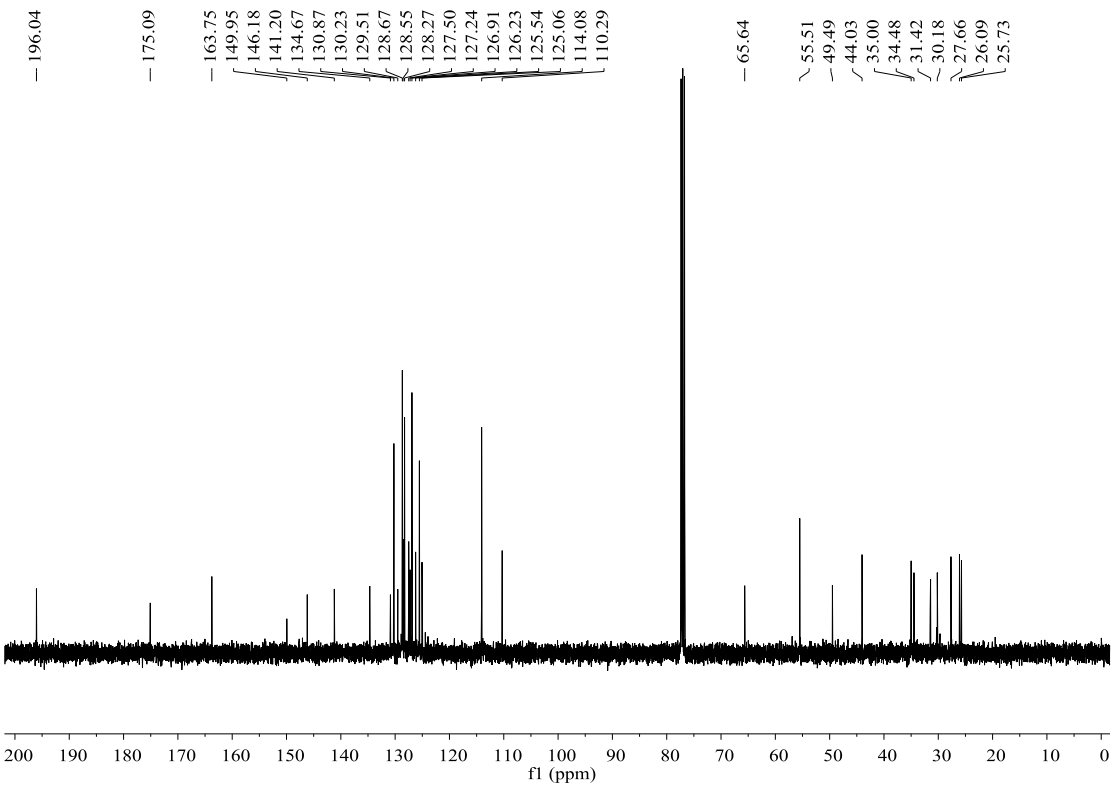


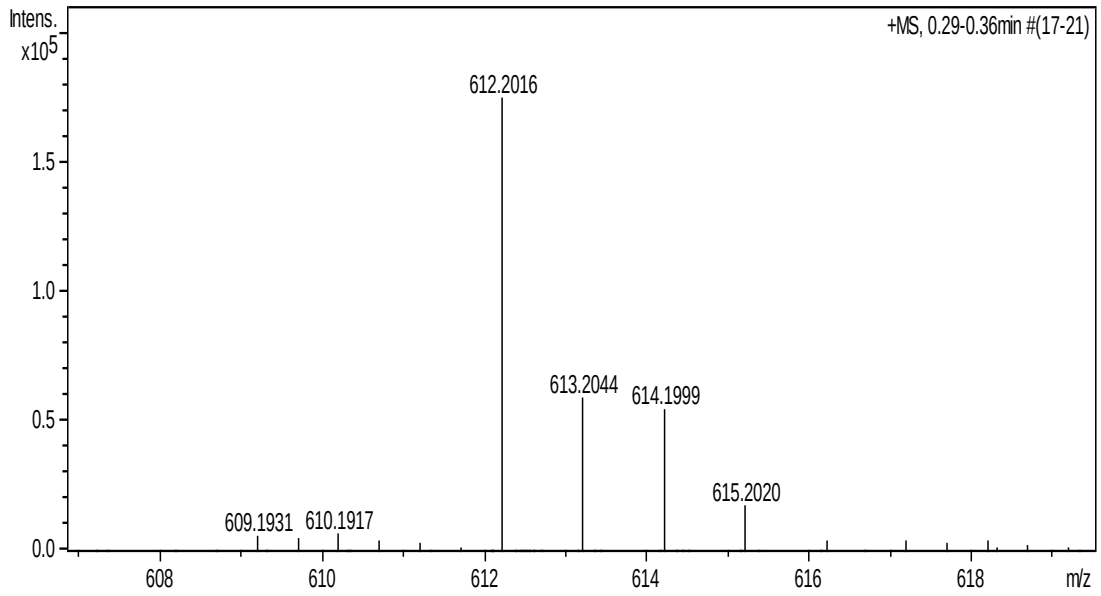

195.85
173.21
164.04
149.76
146.39
139.23
134.94
132.42
131.20
130.56
129.42
128.44
128.35
128.02
127.28
127.12
126.10
124.22
123.54
113.60
108.96
67.13
55.48
50.84
43.61
35.05
34.65
31.49
26.47
25.23
21.40
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^6
2.0
1.5
1.0
0.5
0.0
+MS, 0.22-0.37min #(13-22)
592.2577
593.2607
594.2630
586 588 590 592 594 596 598
m/z

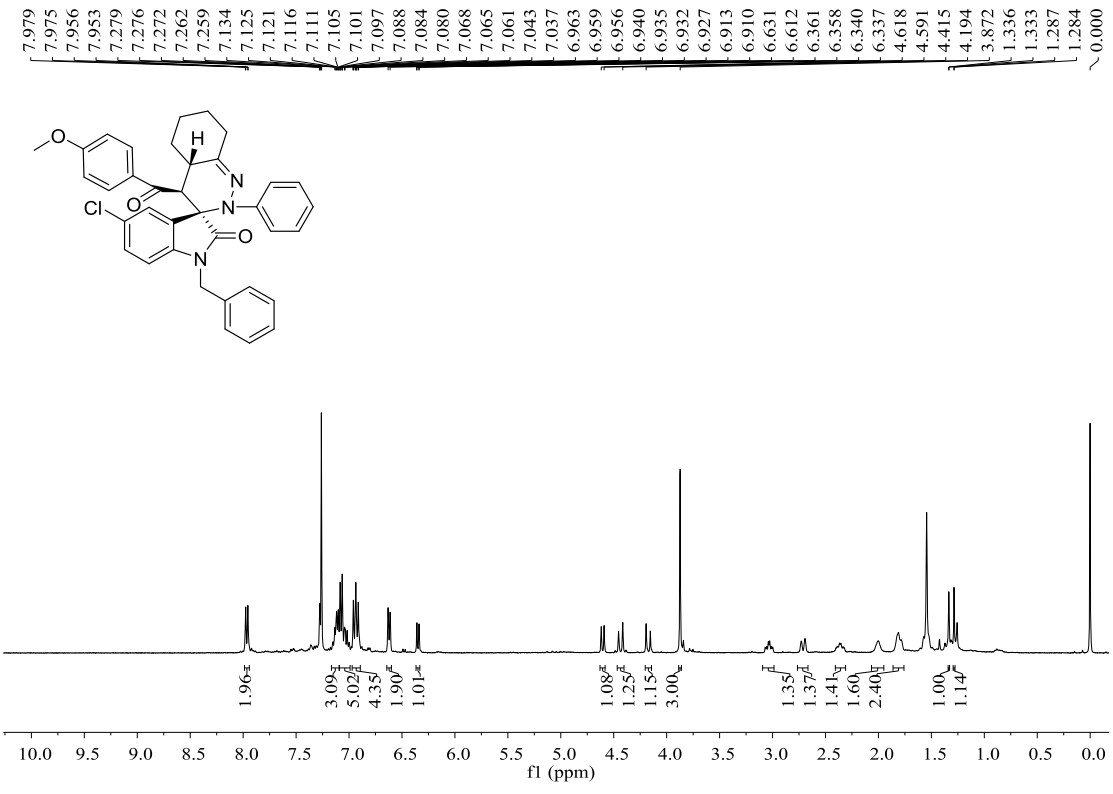
1'-benzyl-5'-chloro-4-(4-methoxybenzoyl)-2-phenyl-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2c): orange solid, 0.141g, 24%, m.p. 124-126 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.83-7.79 (m, 2H, ArH), 7.39-7.39 (m, 1H, ArH), 7.21-7.16 (m, 3H, ArH), 7.07-7.05 (m, 1H, ArH), 7.04-7.01 (m, 2H, ArH), 6.99-6.95 (m, 3H, ArH), 6.91-6.87 (m, 2H, ArH), 6.84-6.82 (m, 2H, ArH), 6.38 (d, *J* = 8.4 Hz, 1H, ArH), 4.89 (d, *J* = 16.0 Hz, 1H, CH), 4.80 (d, *J* = 8.4 Hz, 1H, CH), 4.61 (d, *J* = 16.0 Hz, 1H, CH), 3.86 (s, 3H, OCH_3), 3.14-3.07 (m, 1H, CH), 2.79-2.76 (m, 1H, CH), 2.42-2.34 (m, 1H, CH), 2.05-1.98 (m, 1H, CH), 1.87-1.84 (m, 1H, CH), 1.73-1.63 (m, 2H, CH), 1.49-1.41 (m, 2H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.0, 175.1, 163.8, 150.0, 146.2, 141.2, 134.7, 130.9, 130.2, 129.5, 128.7, 128.6, 128.3, 127.5, 127.2, 126.9, 126.2, 125.5, 125.1, 114.1, 110.3, 65.6, 55.5, 49.5, 44.0, 35.0, 34.5, 31.4, 30.2, 27.7, 26.1, 25.7; IR (KBr) υ : 3031, 2964, 1721, 1677, 1610, 1489, 1464, 1372, 1321, 1265, 1202, 1180, 1082, 1017, 964, 907, 830, 763, 725 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{32}ClN_3O_3$ ($[M+H]^+$):612.2024, Found: 612.2016.

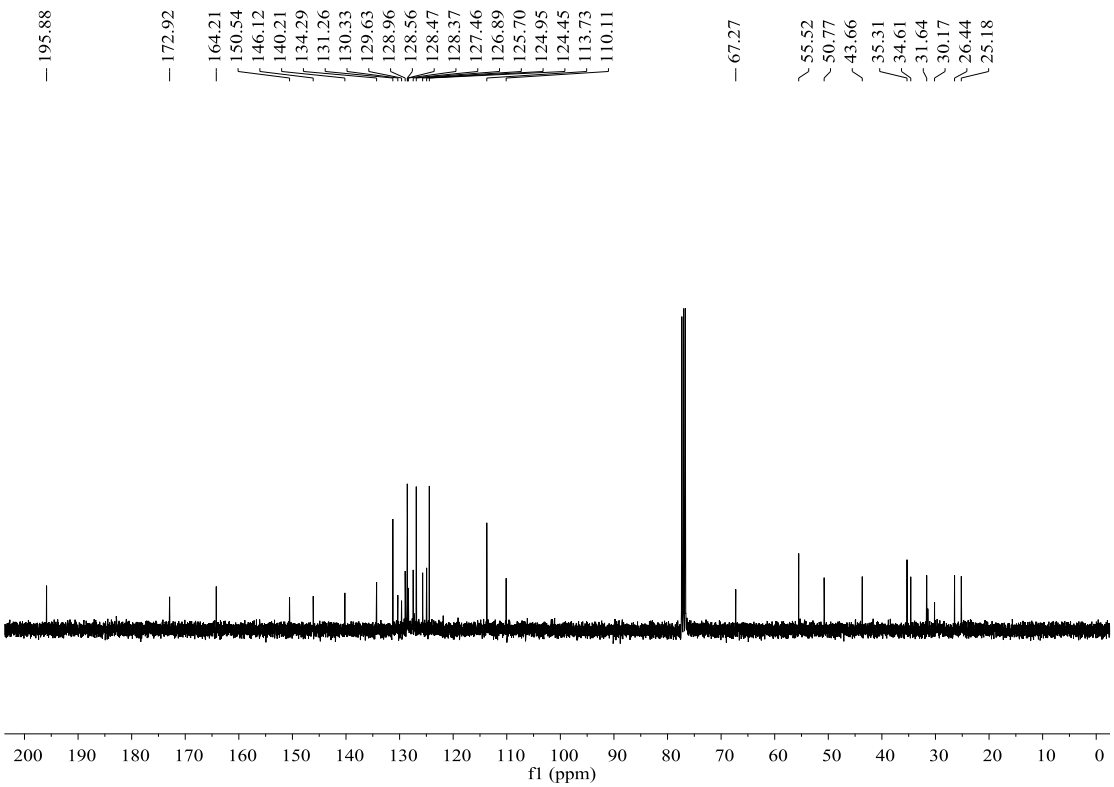


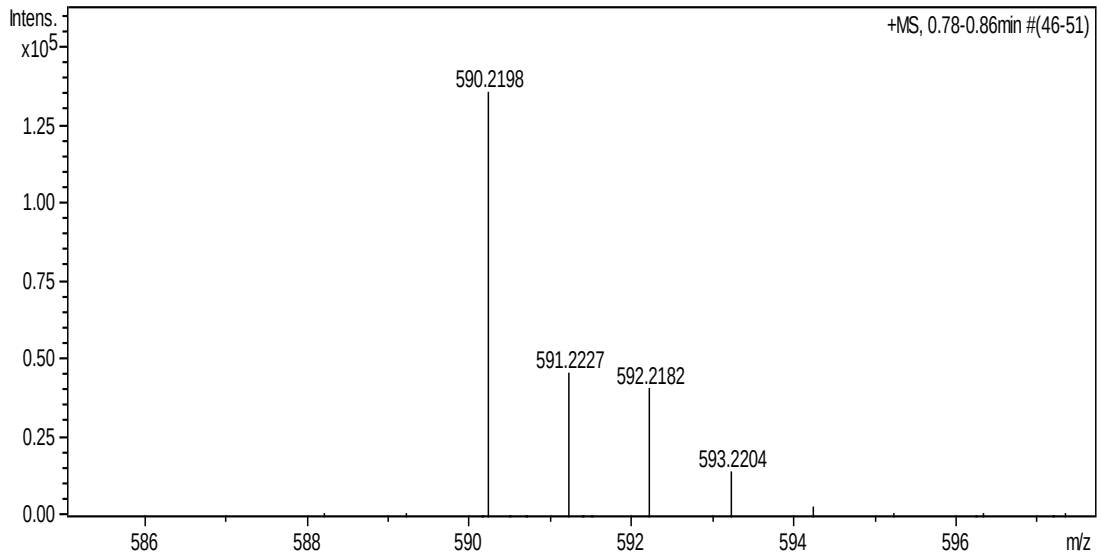

196.04
175.09
163.75
149.95
146.18
141.20
134.67
130.87
130.23
129.51
128.67
128.55
128.27
127.50
127.24
126.91
126.23
125.54
125.06
114.08
110.29
65.64
55.51
49.49
44.03
35.00
34.48
31.42
30.18
27.66
26.09
25.73
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.29-0.36min #(17-21)
612.2016
613.2044
614.1999
615.2020
609.1931
610.1917
1.5
1.0
0.5
0.0
608
610
612
614
616
618
m/z

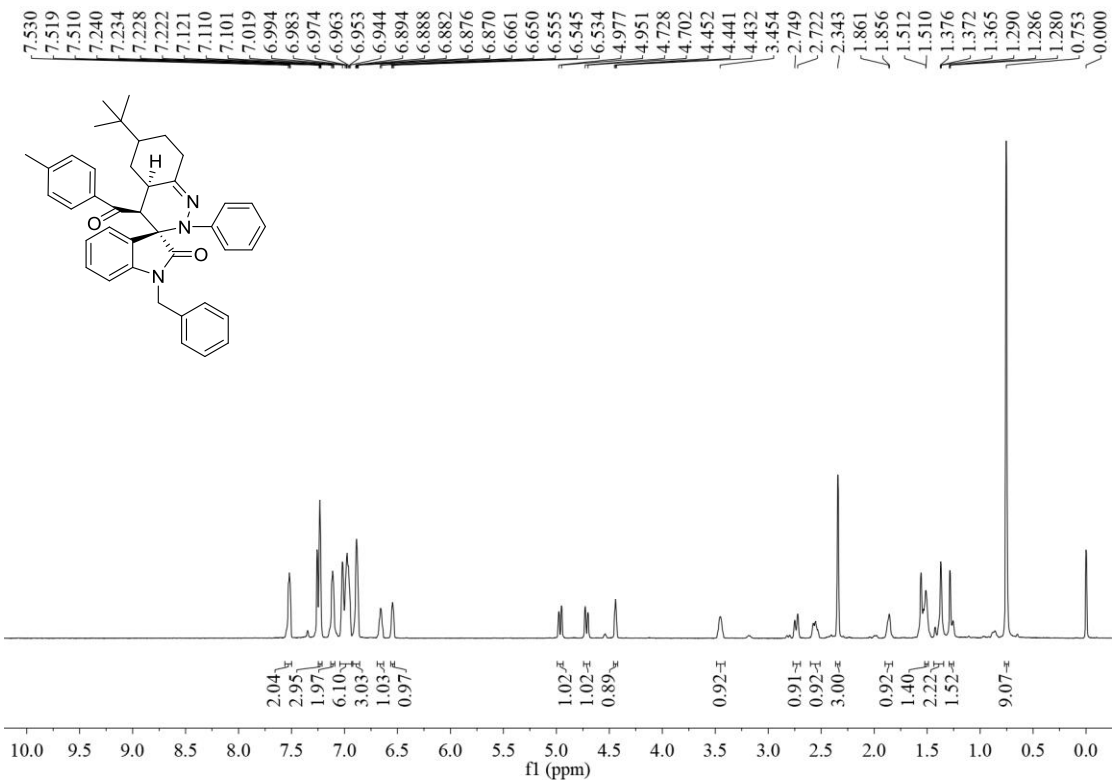
1'-benzyl-5'-chloro-4-(4-methoxybenzoyl)-2-phenyl-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2c'): orange solid, 0.106g, 18%, m.p. 124-126 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.98-7.95 (m, 2H, ArH), 7.15-7.10 (m, 3H, ArH), 7.09-7.00 (m, 5H, ArH), 6.96-6.90 (m, 4H, ArH), 6.63-6.61 (m, 2H, ArH), 6.36-6.34 (m, 1H, ArH), 4.61 (d, *J* = 10.8 Hz, 1H, CH), 4.43 (d, *J* = 15.6 Hz, 1H, CH), 4.17 (d, *J* = 16.0 Hz, 1H, CH), 3.87 (s, 3H, OCH_3), 3.04-3.03 (m, 1H, CH), 2.73-2.69 (m, 1H, CH), 2.37-2.35 (m, 1H, CH), 2.00 (s, 2H, CH), 1.81-1.78 (m, 2H, CH), 1.34-1.33 (m, 1H, CH), 1.29-1.28 (m, 1H, CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 13C NMR (101 MHz, cdcl3) δ 195.9, 172.9, 164.2, 150.5, 146.1, 140.2, 134.3, 131.3, 130.3, 129.6, 128.9, 128.6, 128.5, 128.4, 127.5, 126.9, 125.70 124.9, 124.5, 113.7, 110.1, 67.3, 55.5, 50.7, 43.6, 35.3, 34.6, 31.6, 30.2, 26.4, 25.2; IR (KBr) υ : 3034, 2960, 1718, 1681, 1606, 1490, 1465, 1369, 1300, 1255, 1206, 1182, 1078, 1020, 958, 906, 834, 759, 730 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{36}H_{33}ClN_3O_3$ ($[M+H]^+$):590.2205, Found: 590.2198.

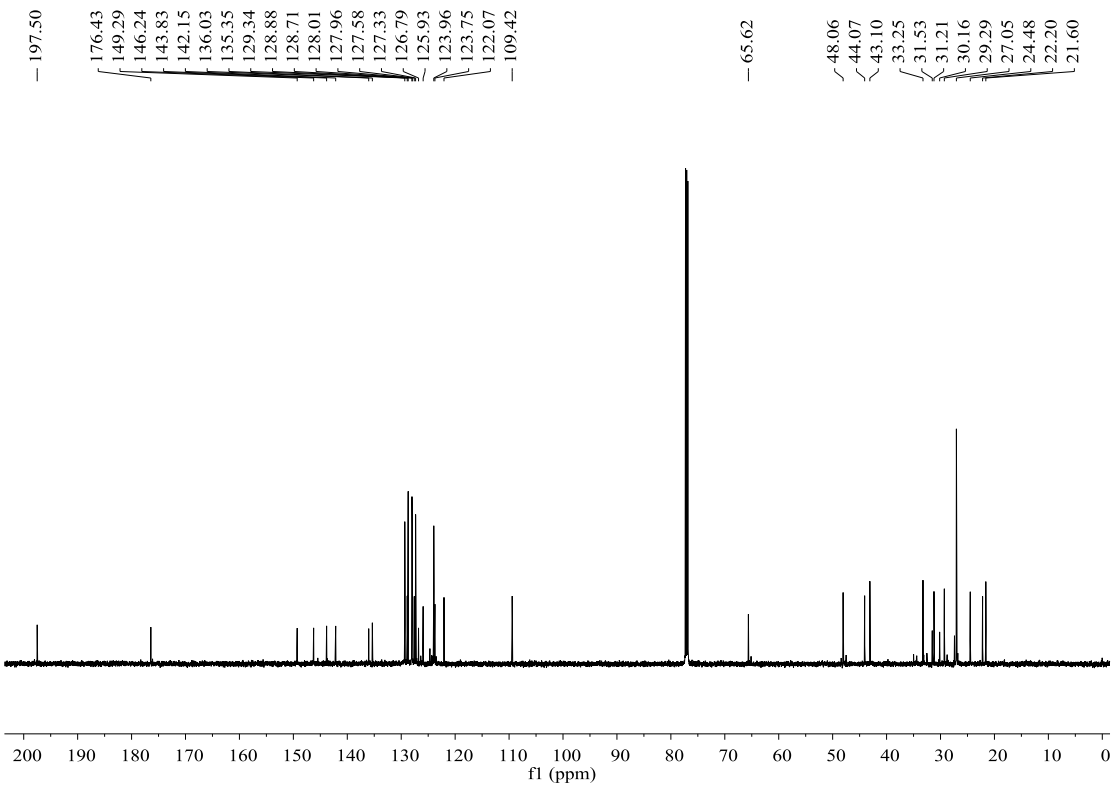


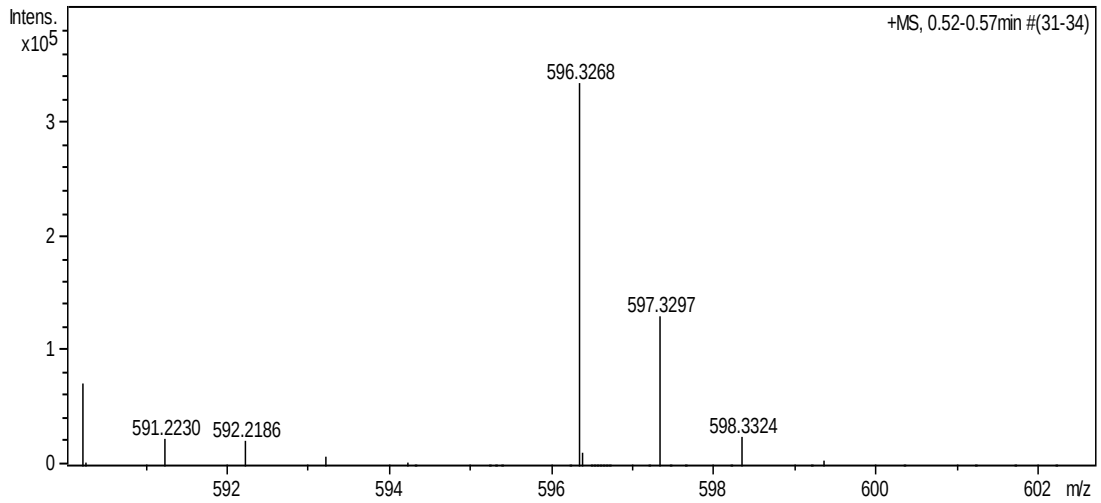

195.88
172.92
164.21
150.54
146.12
140.21
134.29
131.26
130.33
129.63
128.96
128.56
128.47
128.37
127.46
126.89
125.70
124.95
124.45
113.73
110.11
67.27
55.52
50.77
43.66
35.31
34.61
31.64
30.17
26.44
25.18
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.78-0.86min #(46-51)
590.2198
591.2227
592.2182
593.2204
1.25
1.00
0.75
0.50
0.25
0.00
586
588
590
592
594
596
m/z

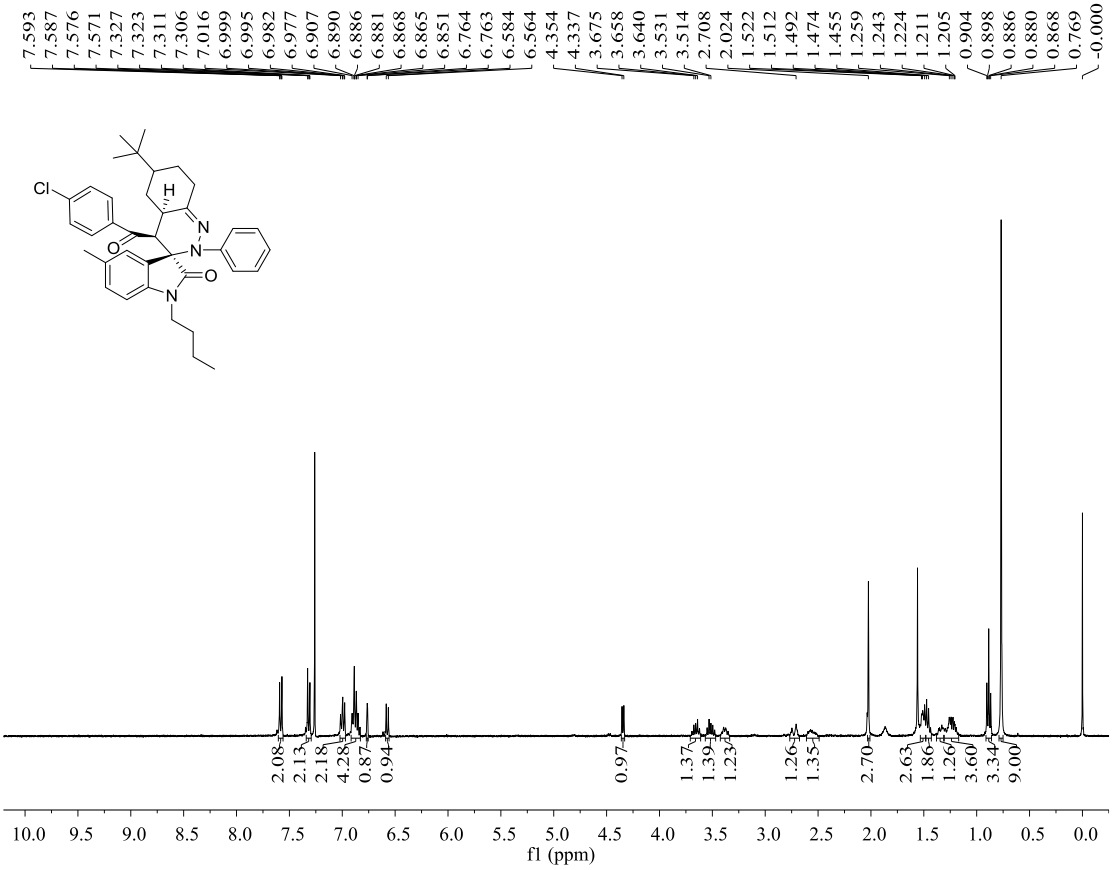
1'-benzyl-5'-chloro-4-(4-methoxybenzoyl)-2-phenyl-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2d): yellow solid, 0.323g, 55%, m.p. 213-215 ^{o}C; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.53-7.51 (m, 2H, ArH), 7.24-7.22 (m, 3H, ArH), 7.12-7.10 (m, 2H, ArH), 7.02-6.94 (m, 6H, ArH), 6.89-6.87 (m, 3H, ArH), 6.67-6.65 (m, 1H, ArH), 6.56-6.53 (m, 1H, ArH), 4.96 (d, *J* = 15.6 Hz, 1H, CH), 4.71 (d, *J* = 15.6 Hz, 1H, CH), 4.45-4.43 (m, 1H, CH), 3.47-3.43 (m, 1H, CH), 2.75-2.72 (m, 1H, CH), 2.57-2.53 (m, 1H, CH), 2.34 (s, 3H, CH_3), 1.86-1.86 (m, 1H, CH), 1.51-1.51 (m, 1H, CH), 1.43-1.37 (m, 2H, CH), 1.29-1.25 (m, 1H, CH), 0.75 (s, 9H, $3CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 197.5, 176.4, 149.3, 146.2, 143.8, 142.2, 136.0, 135.4, 129.3, 128.9, 128.7, 128.0, 128.0, 127.6, 127.3, 126.8, 125.9, 124.0, 123.8, 122.1, 109.4, 65.6, 48.1, 44.1, 43.1, 33.3, 31.5, 31.2, 30.2, 29.3, 27.1, 24.5, 22.2, 21.6; IR (KBr) υ : 3034, 2960, 1719, 1681, 1606, 1490, 1466, 1369, 1301, 1255, 1207, 1182, 1078, 1021, 958, 906, 834, 759, 730 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{40}H_{42}N_3O_2$ ($[M+H]^+$):596.3272, Found: 596.3268.

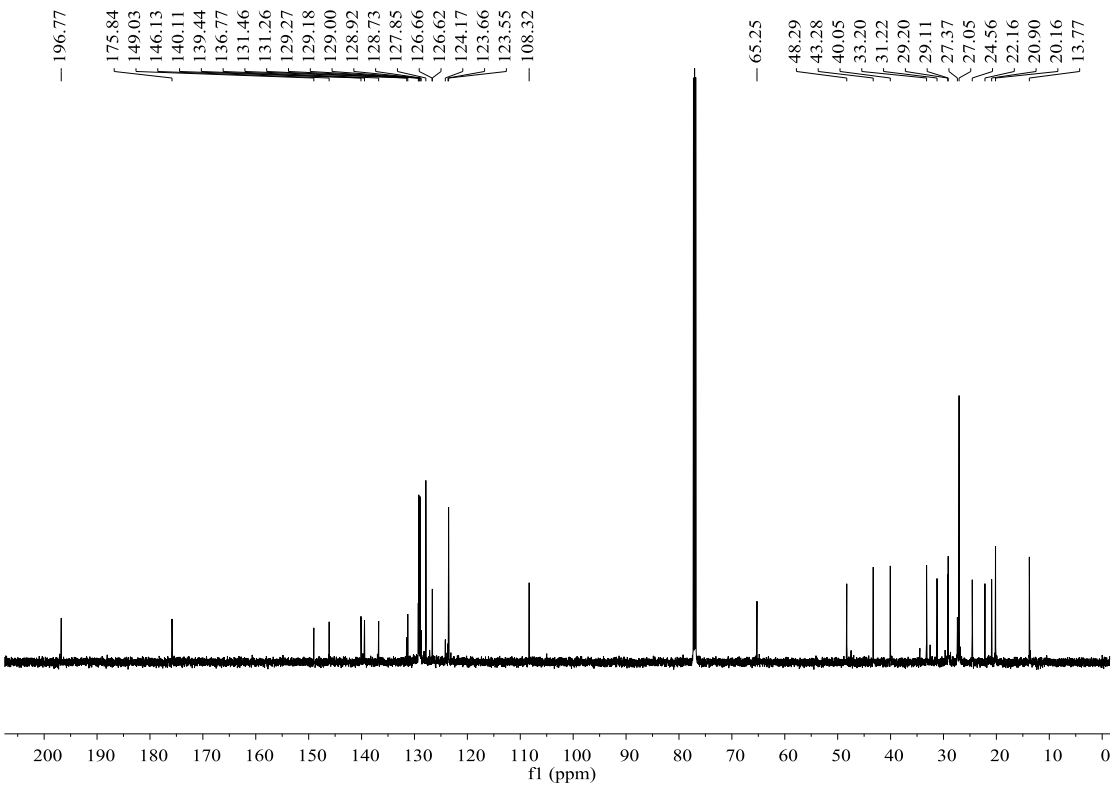


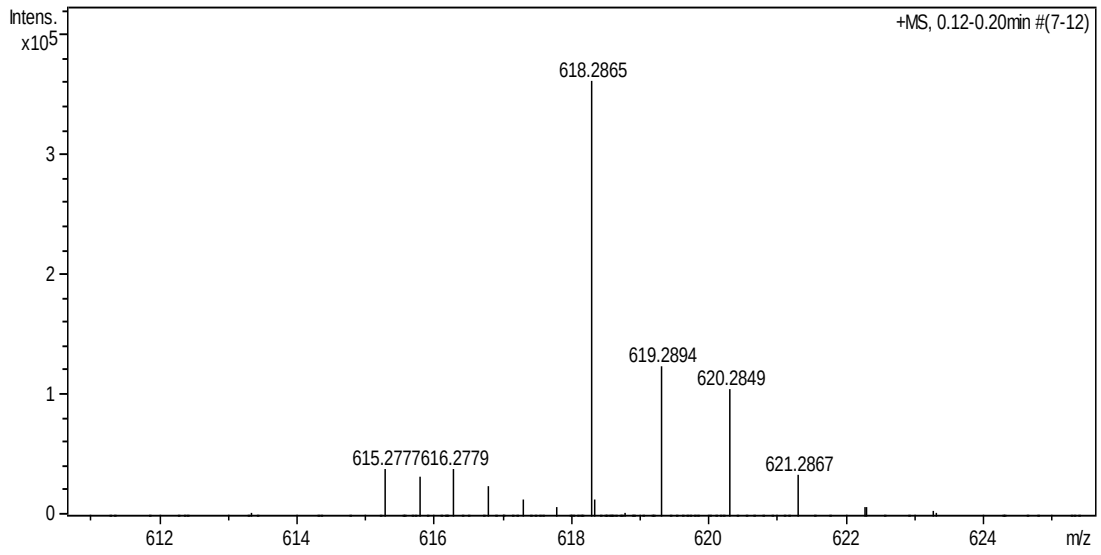

197.50
176.43
149.29
146.24
143.83
142.15
136.03
135.35
129.34
128.88
128.71
128.01
127.96
127.58
127.33
126.79
125.93
123.96
123.75
122.07
109.42
65.62
48.06
44.07
43.10
33.25
31.53
31.21
30.16
29.29
27.05
24.48
22.20
21.60
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.52-0.57min #(31-34)
596.3268
597.3297
591.2230
592.2186
598.3324
0
1
2
3
592
594
596
598
600
602
m/z

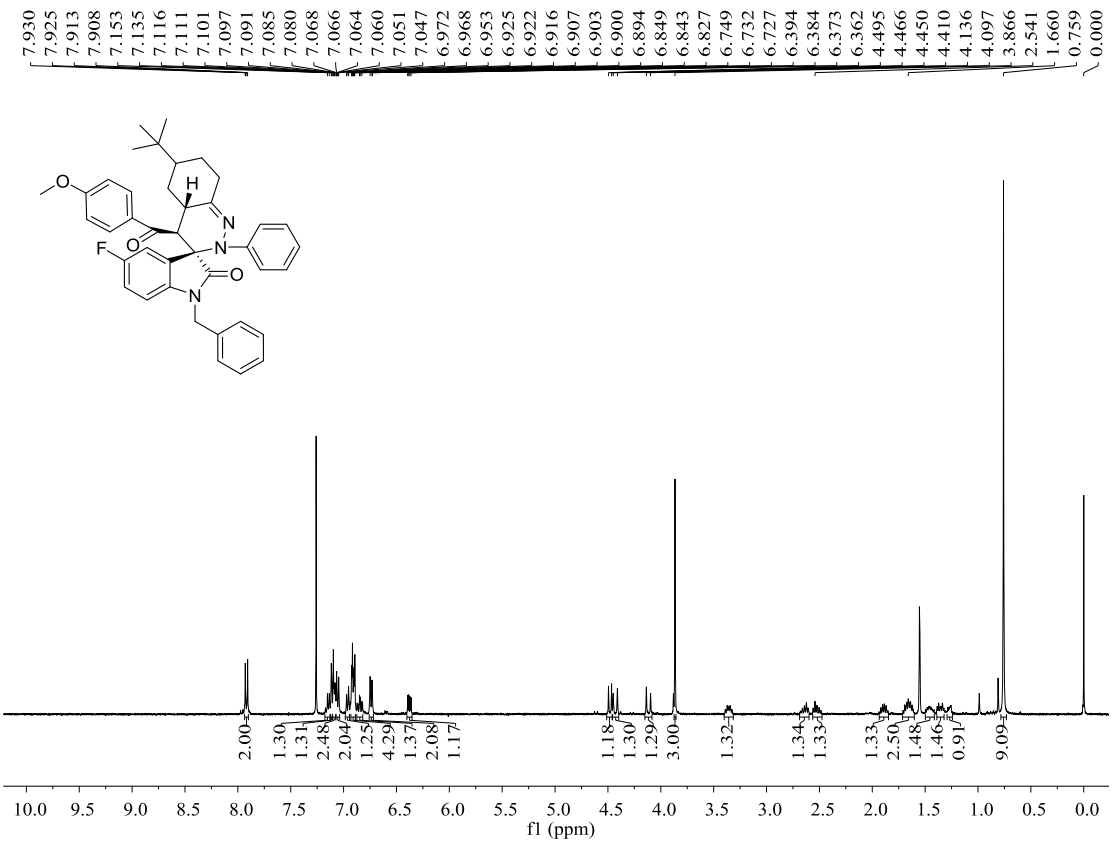
1'-benzyl-6-(tert-butyl)-4-(4-methylbenzoyl)-2-phenyl-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2e): yellow solid, 0.416g, 70%, m.p. 129-131 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59-7.57 (m, 2H, ArH), 7.33-7.31 (m, 2H, ArH), 7.02-6.98 (m, 2H, ArH), 6.91-6.83 (m, 4H, ArH), 6.76-6.76 (m, 1H, ArH), 6.57 (d, *J* = 8.0 Hz, 1H, ArH), 4.35 (d, *J* = 6.8 Hz, 1H, CH), 3.70-3.62 (m, 1H, CH), 3.55-3.48 (m, 1H, CH), 3.41-3.37 (m, 1H, CH), 2.75-2.71 (m, 1H, CH), 2.57-2.53 (m, 1H, CH), 2.02 (s, 3H, CH_3), 1.52-1.49 (m, 3H, CH), 1.47-1.44 (m, 2H, CH), 1.36-1.33 (m, 1H, CH), 1.29-1.19 (m, 4H, CH), 0.90-0.87 (m, 3H, CH_3), 0.77 (s, 9H, $3CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 196.8, 175.8, 149.0, 146.1, 140.1, 139.4, 136.8, 131.5, 131.3, 129.3, 129.2, 129.0, 128.9, 128.7, 127.9, 126.7, 126.6, 124.2, 123.7, 123.6, 108.3, 65.3, 48.3, 43.3, 40.1, 33.2, 31.2, 29.2, 29.1, 27.4, 27.1, 24.6, 22.2, 20.9, 20.2, 13.8; IR (KBr) υ : 3035, 2953, 1715, 1669, 1598, 1489, 1453, 1340, 1308, 1263, 1174, 1055, 1030, 943, 883, 846, 803, 769, 745 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{37}H_{42}ClN_3O_2$ ([M+H]$^{+}$):618.2858, Found: 618.2865.

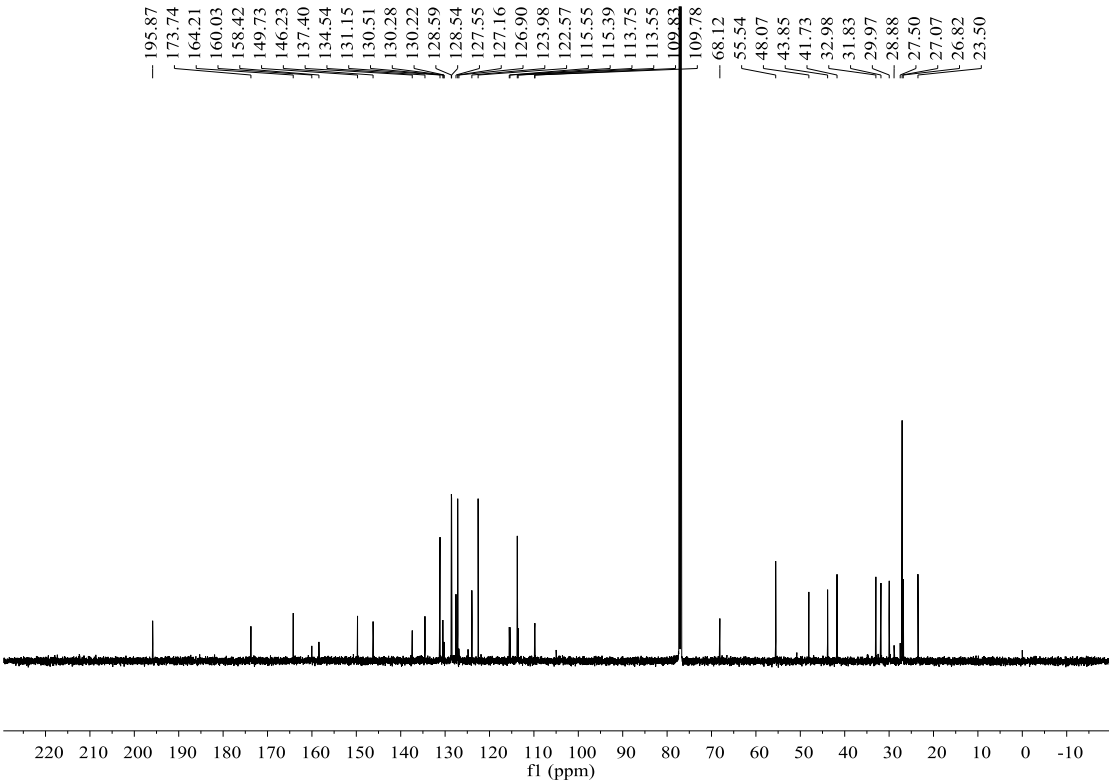


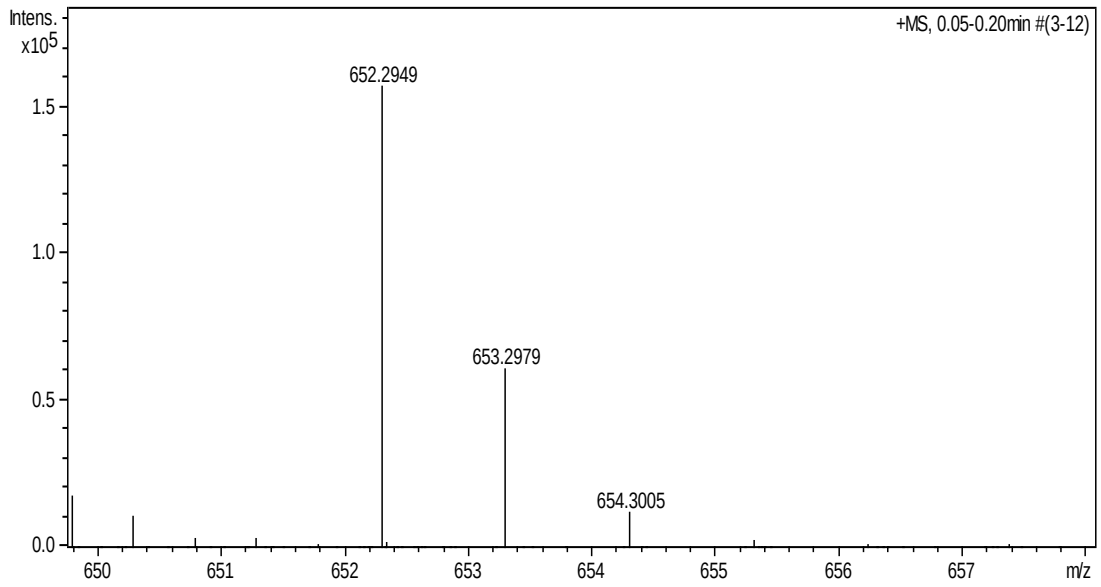

196.77
175.84
149.03
146.13
140.11
139.44
136.77
131.46
131.26
129.27
129.18
129.00
128.92
128.73
127.85
126.66
126.62
124.17
123.66
123.55
108.32
65.25
48.29
43.28
40.05
33.20
31.22
29.20
29.11
27.37
27.05
24.56
22.16
20.90
20.16
13.77
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.12-0.20min #(7-12)
618.2865
619.2894
620.2849
615.2777
616.2779
621.2867
0
1
2
3
612
614
616
618
620
622
624
m/z

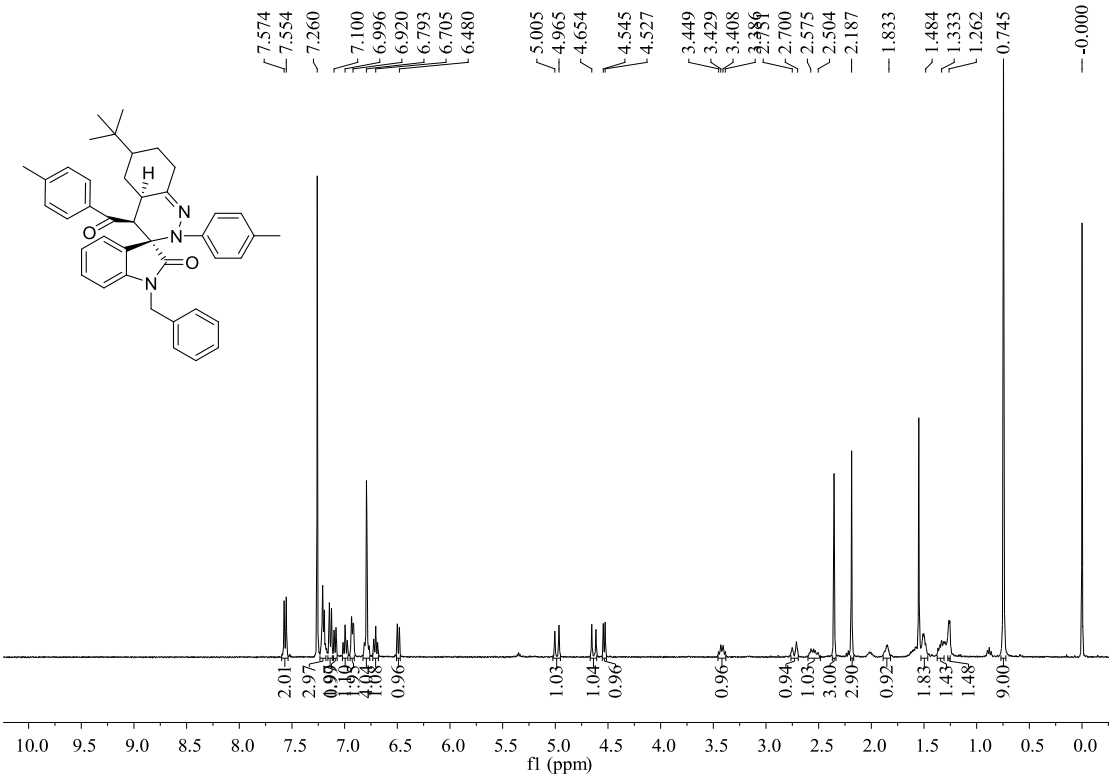
1'-benzyl-6-(tert-butyl)-5'-fluoro-4-(4-methoxybenzoyl)-2-phenyl-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2f): yellow solid, 0.440g, 72%, m.p. 217-219 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93-7.91 (m, 2H, ArH), 7.17-7.14 (m, 1H, ArH), 7.12-7.11 (m, 1H, ArH), 7.10-7.08 (m, 2H, ArH), 7.07-7.05 (m, 2H, ArH), 6.97 -6.95 (m, 1H, ArH), 6.94-6.89 (m, 4H, ArH), 6.87-6.82 (m, 1H, ArH), 6.75-6.73 (m, 2H, ArH), 6.39-6.36 (m, 1H, ArH), 4.47 (d, *J* = 11.6 Hz, 1H, CH), 4.43 (d, *J* = 16.0 Hz, 1H, CH), 4.12 (d, *J* = 15.6 Hz, 1H, CH), 3.87 (s, 3H, OCH_3), 3.39-3.33 (m, 1H, CH), 2.68-2.61 (m, 1H, CH), 2.56-2.50 (m, 1H, CH), 1.92-1.85 (m, 1H, CH), 1.69-1.62 (m, 1H, CH), 1.50-1.42 (m, 1H, CH), 1.39-1.32 (m, 1H, CH), 1.28-1.26 (m, 1H, CH), 0.76 (s, 9H, $3CH_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 195.9, 173.7, 164.2, 159.2 (d, *J* = 160.2 Hz), 149.7, 146.2, 137.4, 134.5, 131.2, 130.5, 130.2 (d, *J* = 5.3 Hz),, 128.6, 128.5, 127.6, 127.2, 126.9, 124.0, 122.6, 115.4 (d, *J* = 15.6 Hz),, 113.8, 113.6, 109.8 (d, *J* = 5.4 Hz), 68.1, 55.5, 48.1, 43.9, 41.7, 33.0, 31.8, 30.0, 28.9, 27.5, 27.1, 26.8, 23.5; IR (KBr) υ : 3064, 2925, 1719, 1673, 1600, 1489, 1453, 1329, 1260, 1223, 1170, 1136, 1101, 1078, 1021, 952, 869, 847, 824, 796, 761, 730 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{40}H_{40}FN_3O_3$ ($[M+H]^+$):652.2946, Found: 652.2949.

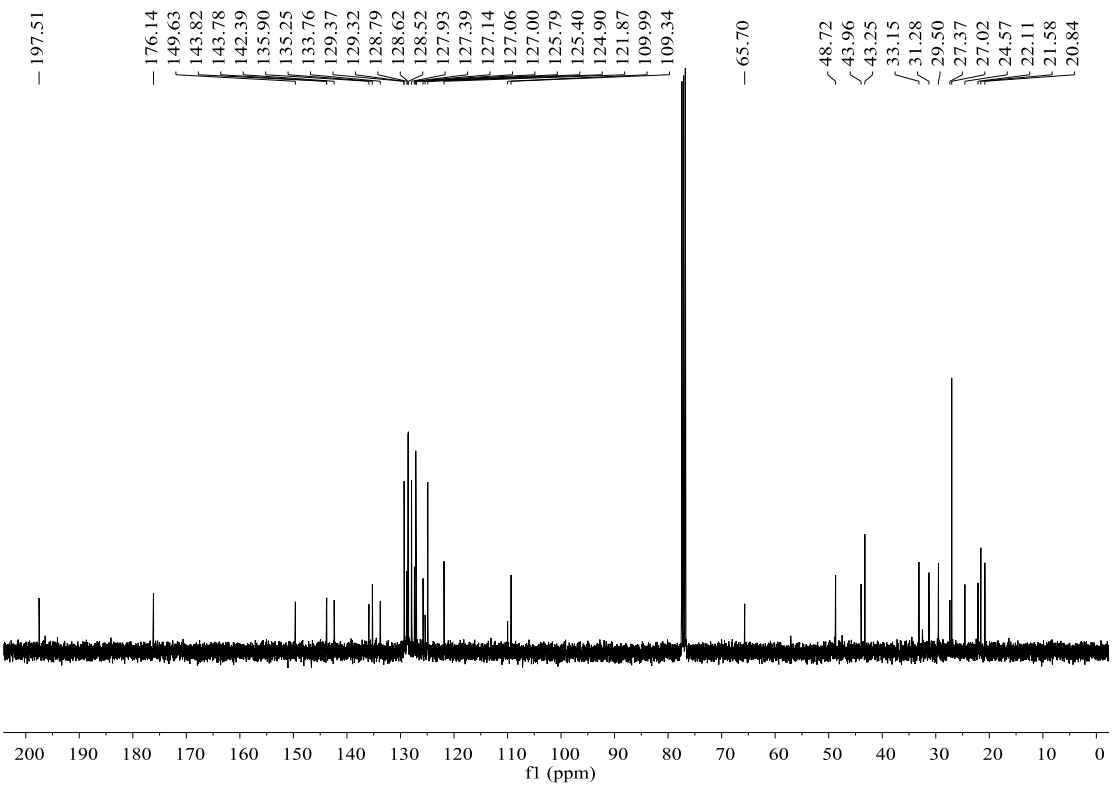


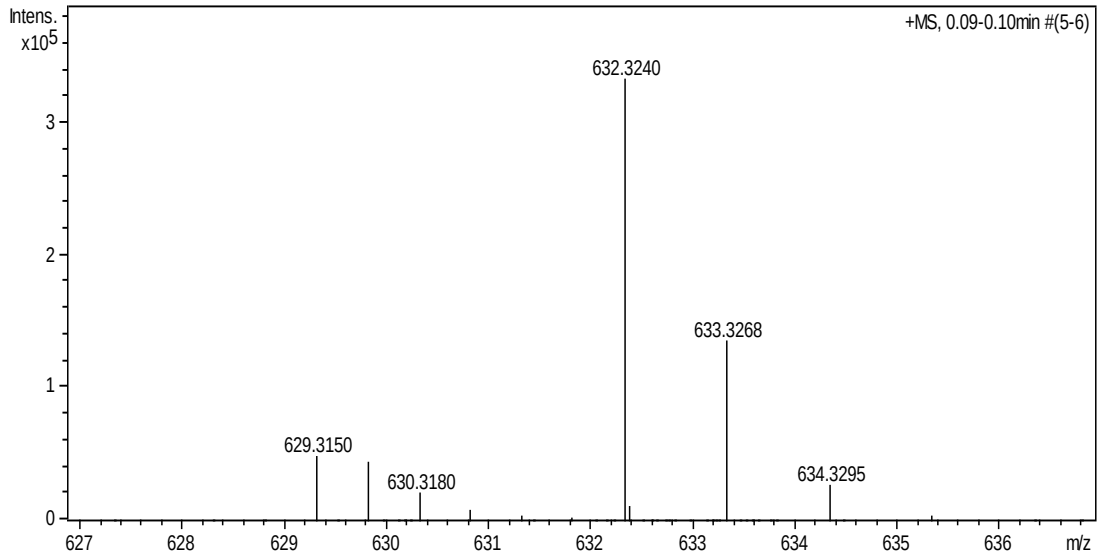

195.87
173.74
164.21
160.03
158.42
149.73
146.23
137.40
134.54
131.15
130.51
130.28
130.22
128.59
128.54
127.55
127.16
126.90
123.98
122.57
115.55
115.39
113.75
113.55
109.83
109.78
68.12
55.54
48.07
43.85
41.73
32.98
31.83
29.97
28.88
27.50
27.07
26.82
23.50
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.05-0.20min #(3-12)
652.2949
653.2979
654.3005
1.5
1.0
0.5
0.0
650
651
652
653
654
655
656
657
m/z

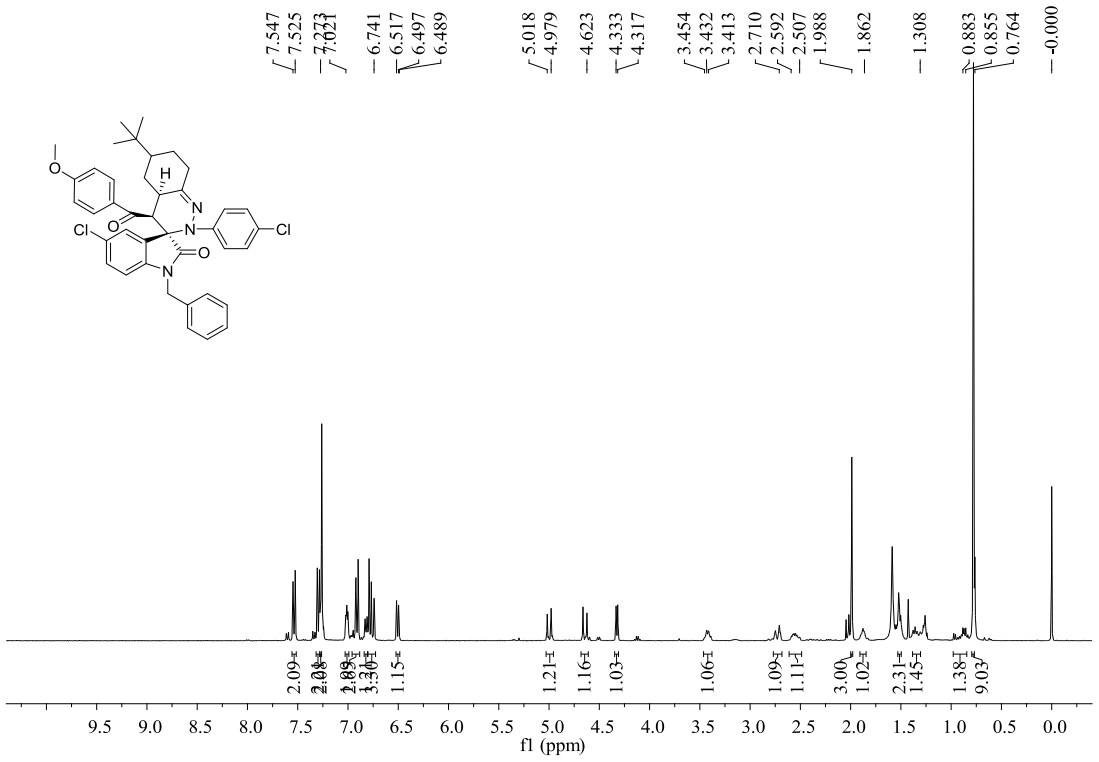
1'-benzyl-6-(tert-butyl)-4-(4-methylbenzoyl)-2-(p-tolyl)-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2g): yellow solid, 0.323g, 80%, m.p. 148-150 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57-7.55 (m, 2H, ArH), 7.23-7.19 (m, 3H, ArH), 7.15-7.13 (m, 2H, ArH), 7.10-7.08 (m, 1H, ArH), 7.02-6.98 (m, 1H, ArH), 6.93 -6.92 (m, 2H, ArH), 6.81-6.77 (m, 4H, ArH), 6.72-6.69 (m, 1H, ArH), 6.50-6.48 (m, 1H, ArH), 4.97 (d, *J* = 16.0 Hz, 1H, CH), 4.63 (d, *J* = 16.0 Hz, 1H, CH), 4.54 (d, *J* = 7.2 Hz, 1H, CH), 3.45-3.39 (m, 1H, CH), 2.76-2.70 (m, 1H, CH), 2.59-2.50 (m, 1H, CH), 2.35 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 1.88-1.83 (m, 1H, CH), 1.52-1.48 (m, 2H, CH), 1.37-1.31 (m, 1H, CH), 1.27-1.26 (m, 1H, CH), 0.75 (s, 9H, CH_3[3]); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 197.5, 176.1, 149.6, 143.8, 143.8, 142.4, 135.9, 135.3, 133.8, 129.4, 129.3, 128.8, 128.6, 128.5, 127.9, 127.4, 127.1, 127.1, 127.0, 125.8, 125.4, 124.9, 121.9, 110.0, 109.3, 65.7, 48.7, 44.0, 43.3, 33.2, 31.3, 29.5, 27.4, 27.0, 24.6, 22.1, 21.6, 20.8**;** IR (KBr) υ : 3032, 2958, 2869, 1719, 1678, 1608, 1509, 1487, 1467, 1366, 1301, 1207, 1181, 1105, 1038, 958, 824, 752 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{41}H_{43}N_3O_2$ ([M+H]$^{+}$):632.3247, Found: 632.3240.

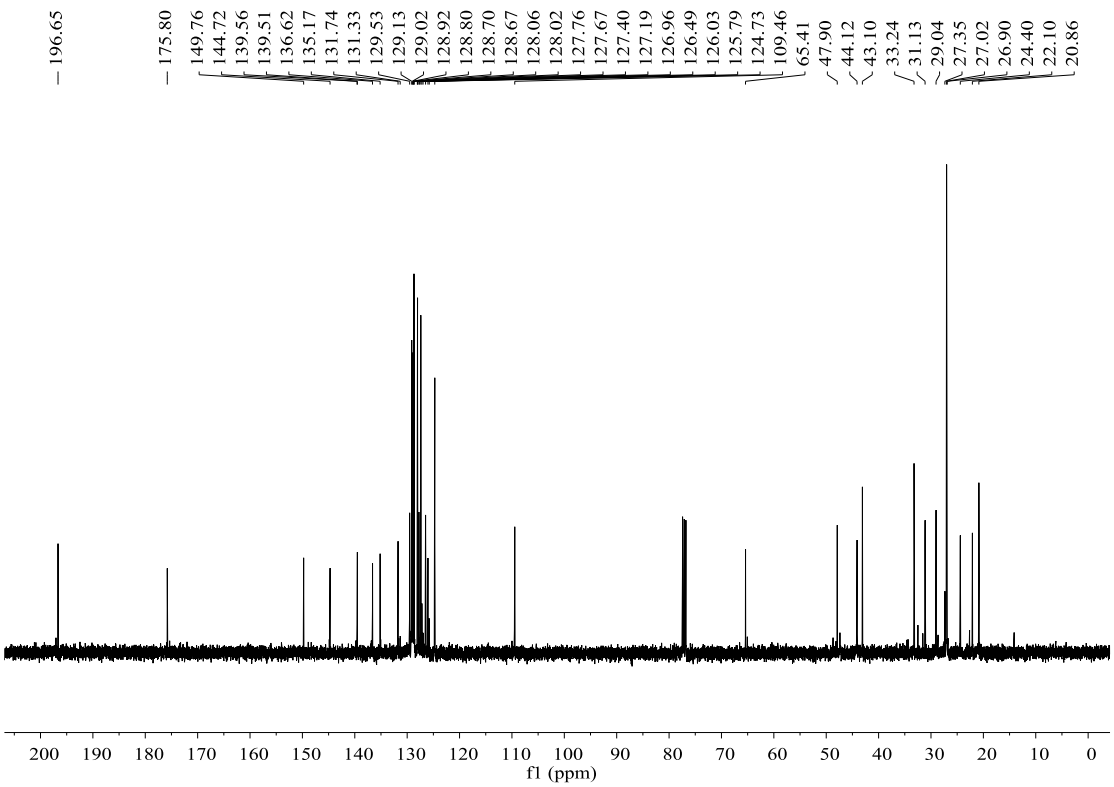


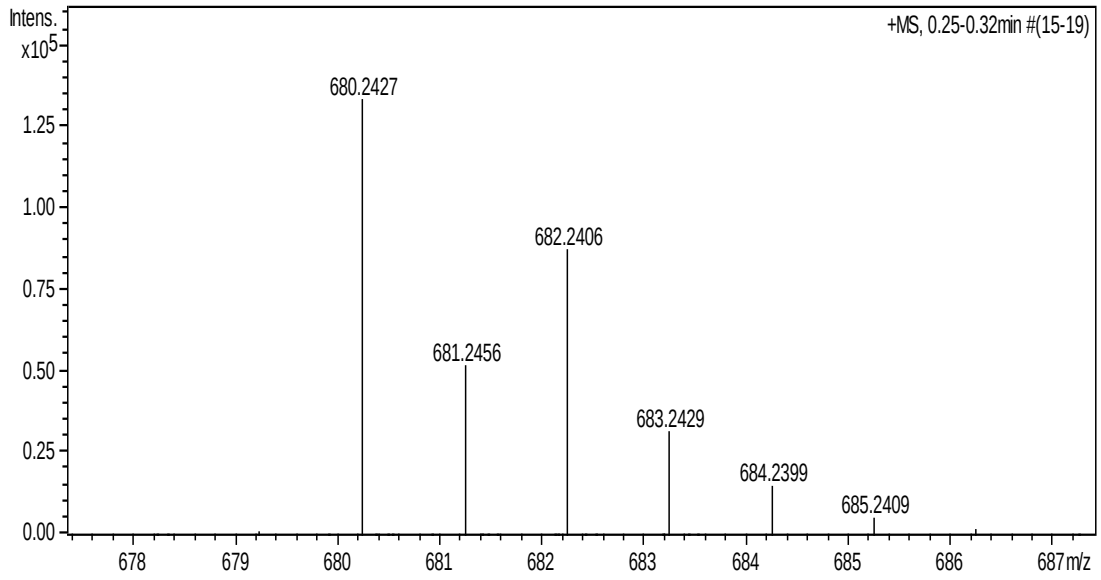

197.51
176.14
149.63
143.82
143.78
142.39
135.90
135.25
133.76
129.37
129.32
128.79
128.62
128.52
127.93
127.39
127.14
127.06
127.00
125.79
125.40
124.90
121.87
109.99
109.34
65.70
48.72
43.96
43.25
33.15
31.28
29.50
27.37
27.02
24.57
22.11
21.58
20.84
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.09-0.10min #(5-6)
632.3240
633.3268
629.3150
630.3180
634.3295
0
1
2
3
627 628 629 630 631 632 633 634 635 636
m/z

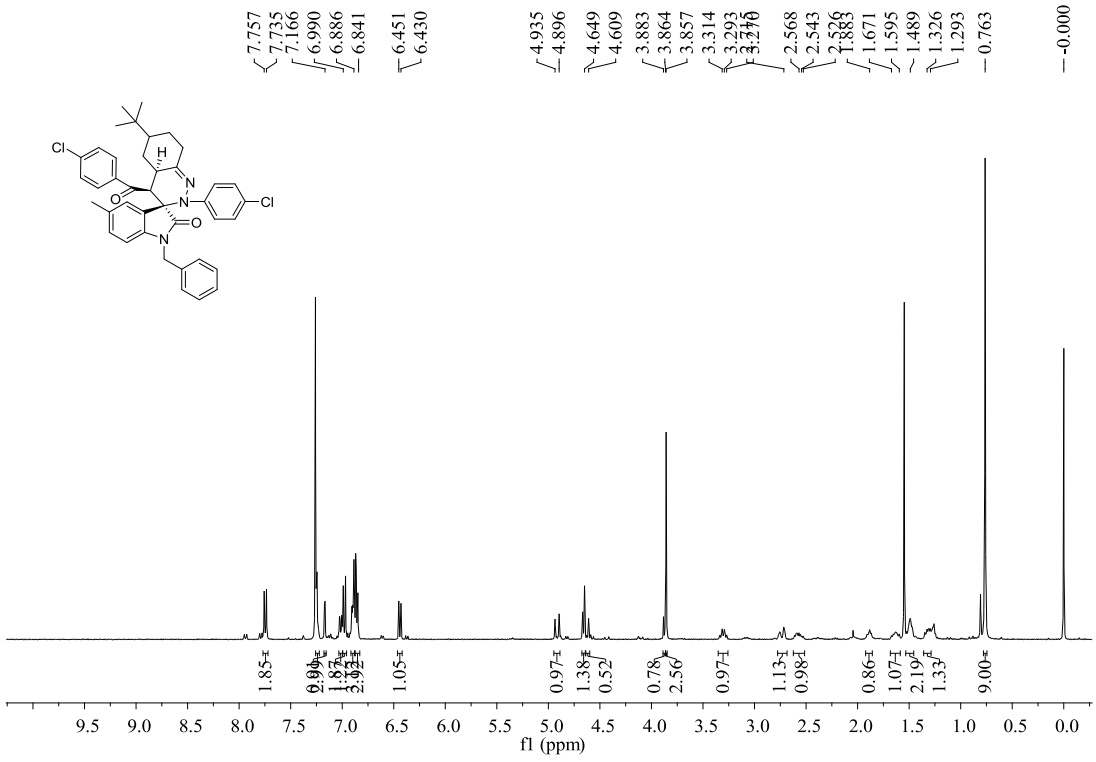
1'-benzyl-6-(tert-butyl)-5'-chloro-2-(4-chlorophenyl)-4-(4-methoxybenzoyl)-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2h): white solid, 0.408g, 60%, m.p. 186-188 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.53 (m, 2H, ArH), 7.31-7.28 (m, 2H, ArH), 7.28-7.27 (m, 2H, ArH), 7.02-7.00 (m, 2H, ArH), 6.95-6.89 (m, 3H, ArH), 6.83 -6.81 (m, 1H, ArH), 6.80-6.74 (m, 3H, ArH), 6.52-6.49 (m, 1H, ArH), 5.00 (d, *J* = 15.6 Hz, 1H, CH), 4.64 (d, *J* = 15.6 Hz, 1H, CH), 4.32 (d, *J* = 6.4 Hz, 1H, CH), 3.45-3.41 (m, 1H, CH), 2.75-2.70 (m, 1H, CH), 2.59-2.51 (m, 1H, CH), 1.99 (s, 3H, CH_3), 1.90-1.86 (m, 1H, CH), 1.52-1.50 (m, 2H, CH), 1.38-1.31 (m, 1H, CH), 0.97-0.86 (m, 1H, CH), 0.78 (s, 9H, $3CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 196.7, 175.8, 149.8, 144.7, 139.6, 139.5, 136.6, 135.2, 131.7, 131.3, 129.5, 129.1, 129.0, 128.9, 128.8, 128.7, 128.7, 128.1, 128.0, 127.8, 127.7, 127.4, 127.2, 127.0, 126.5, 126.0, 125.8, 124.8, 109.5, 65.4, 47.9, 44.1, 43.1, 33.2, 31.1, 29.0, 27.4, 27.0, 26.9, 24.4, 22.1, 20.9; IR (KBr) υ : 3028, 2956, 2870, 1716, 1670, 1612, 1505, 1482, 1457, 1364, 1309, 1205, 1171, 1108, 1042, 960, 821, 757 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{40}H_{40}Cl_2N_3O_3$ ($[M+H]^+$):680.2441, Found: 680.2427.

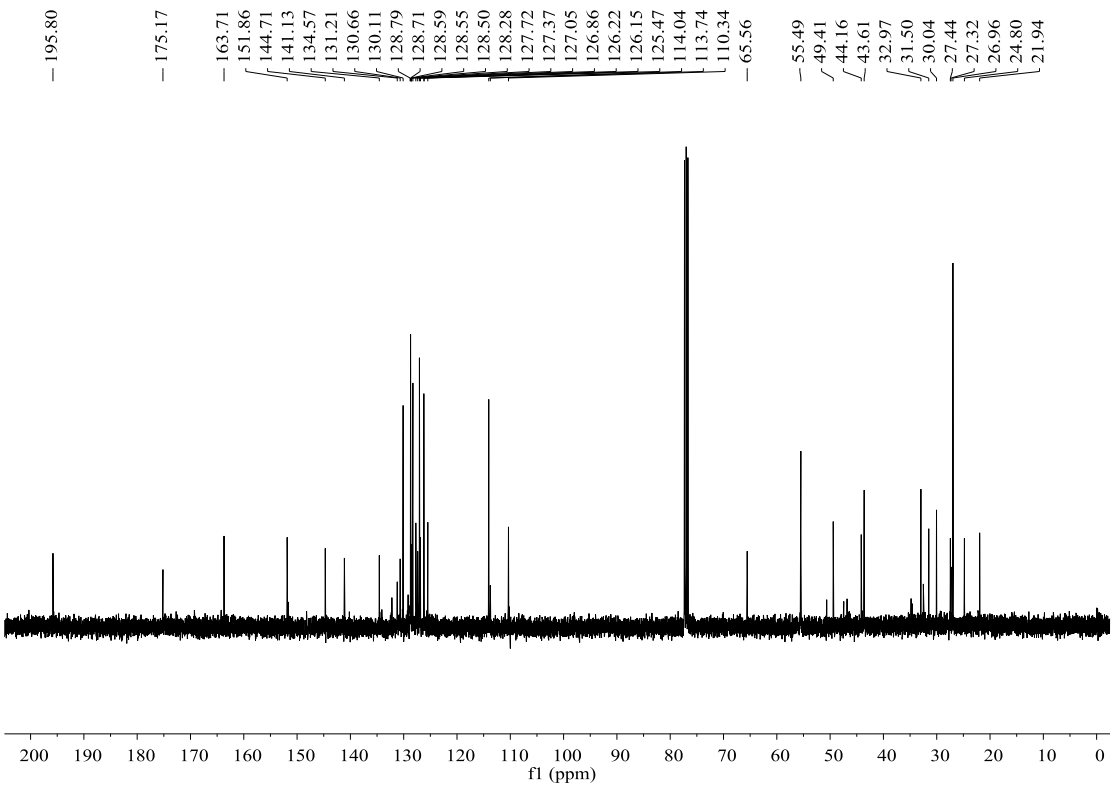


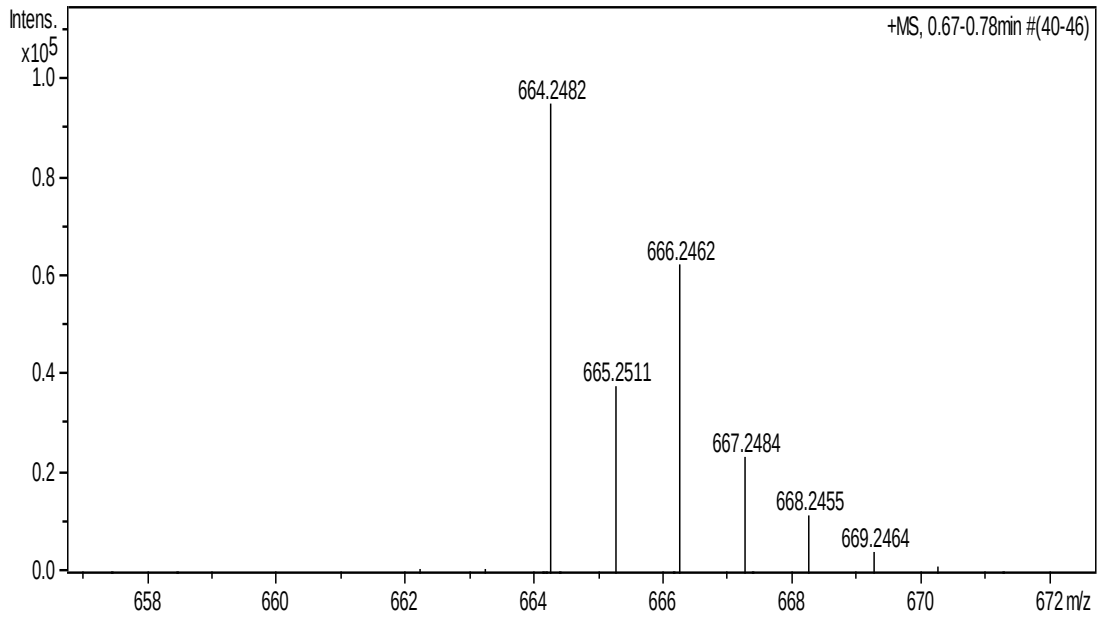

196.65
175.80
149.76
144.72
139.56
139.51
136.62
135.17
131.74
131.33
129.53
129.13
129.02
128.92
128.80
128.70
128.67
128.06
128.02
127.76
127.67
127.40
127.19
126.96
126.49
126.03
125.79
124.73
109.46
65.41
47.90
44.12
43.10
33.24
31.13
29.04
27.35
27.02
26.90
24.40
22.10
20.86
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.25-0.32min #(15-19)
680.2427
682.2406
681.2456
683.2429
684.2399
685.2409
1.25
1.00
0.75
0.50
0.25
0.00
678 679 680 681 682 683 684 685 686 687 m/z

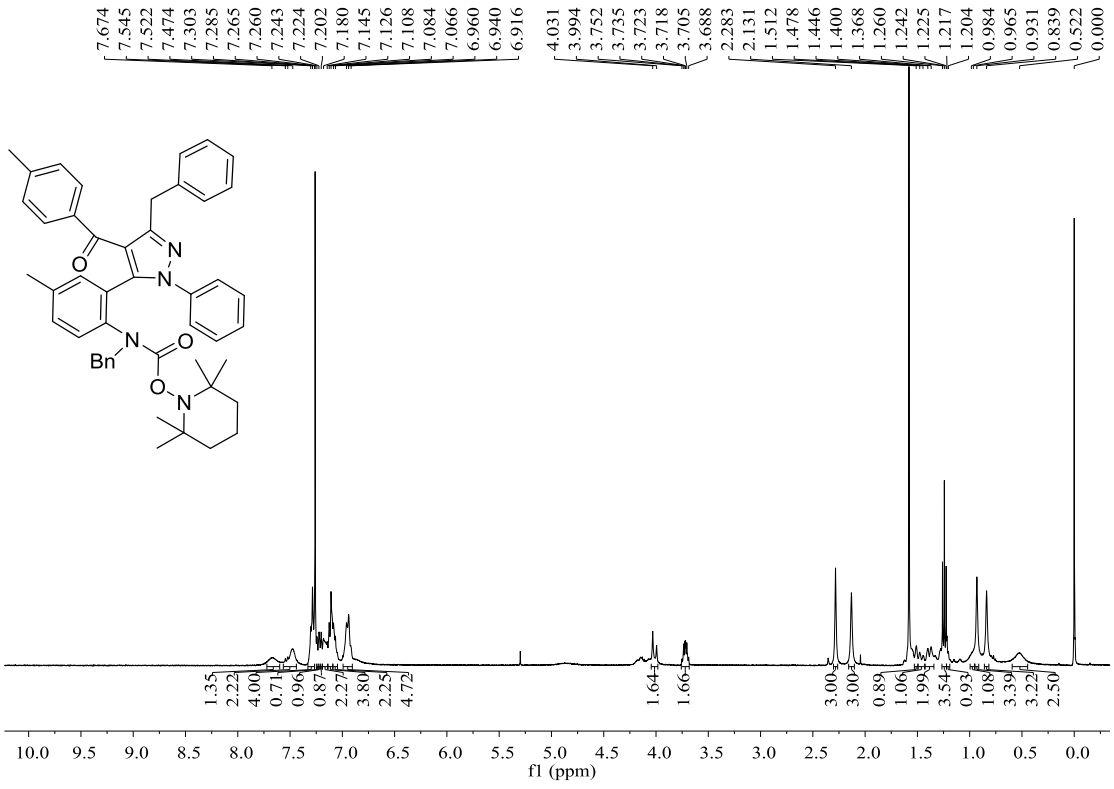
1'-benzyl-6-(tert-butyl)-4-(4-chlorobenzoyl)-2-(4-chlorophenyl)-5'-methyl-4,4a,5,6,7,8-hexahydro-2*H*-spiro[cinnoline-3,3'-indolin]-2'-one (2i): yellow solid, 0.438g, 66%, m.p. 214-216 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76-7.74 (m, 2H, ArH), 7.25-7.23 (m, 3H, ArH), 7.17-7.17 (m, 1H, ArH), 7.03-7.00 (m, 1H, ArH), 6.99-6.96 (m, 2H, ArH), 6.91 -6.89 (m, 3H, ArH), 6.87-6.84 (m, 3H, ArH), 6.45-6.43 (m, 1H, ArH), 4.92 (d, *J* = 15.6 Hz, 1H, CH), 4.66 (d, *J* = 7.2 Hz, 1H, CH), 4.62 (d, *J* = 7.6 Hz, 1H, CH), 3.88-3.86 (m, 1H, CH), 3.86 (s, 3H, OCH_3), 3.34-3.27 (m, 1H, CH), 2.75-2.72 (m, 1H, CH), 2.61-2.53 (m, 1H, CH), 1.91-1.87 (m, 1H, CH), 1.67-1.59 (m, 1H, CH), 1.52-1.47 (m, 2H, CH), 1.33-1.29 (m, 1H, CH), 0.76 (s, 9H, $3CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 195.8, 175.2, 163.7, 151.9, 144.7, 141.1, 134.6, 131.2, 130.7, 130.1, 128.8, 128.7, 128.6, 128.6, 128.5, 128.3, 127.7, 127.4, 127.1, 126.9, 126.2, 126.2, 125.5, 114.0, 113.7, 110.3, 65.6, 55.5, 49.4, 44.2, 43.6, 33.0, 31.5, 30.0, 27.4, 27.3, 27.0, 24.8, 21.9; IR (KBr) υ : 3022, 2952, 2872, 1720, 1675, 1608, 1501, 1480, 1458, 1358, 1310, 1206, 1174, 1110, 1039, 964, 819, 759 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{40}H_{40}Cl_2N_3O_2$ ($[M+H]^+$):664.2492, Found: 664.2482.

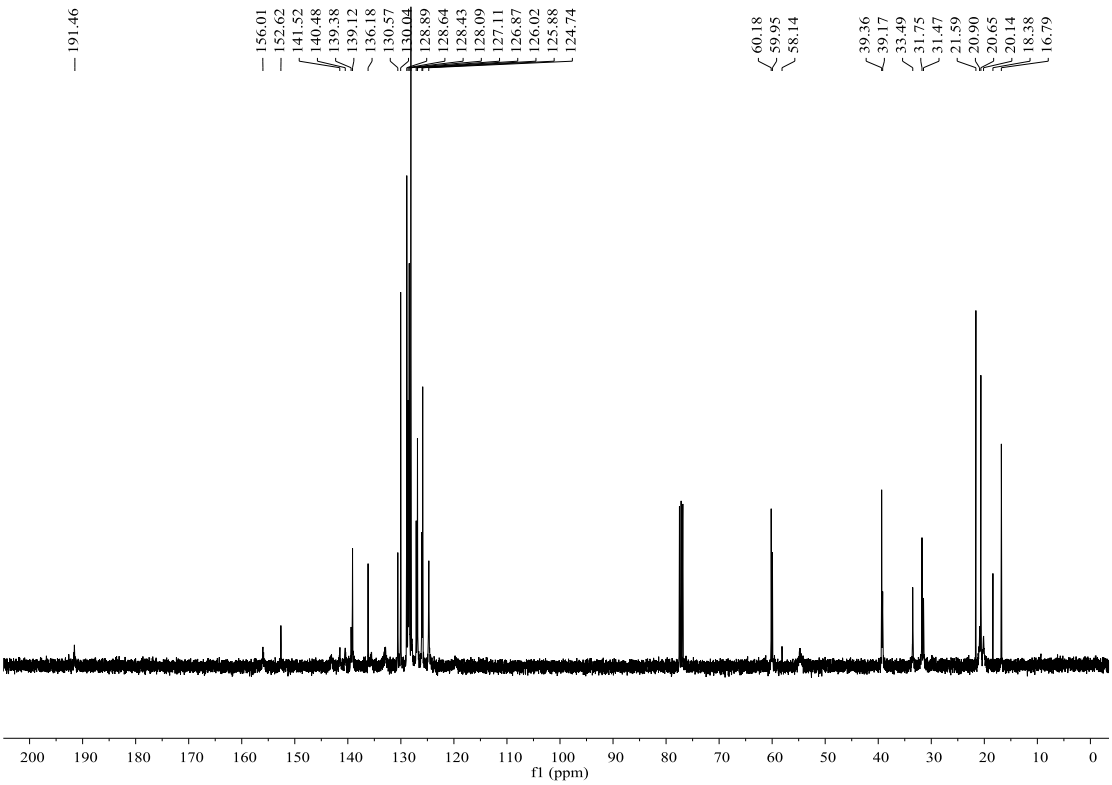


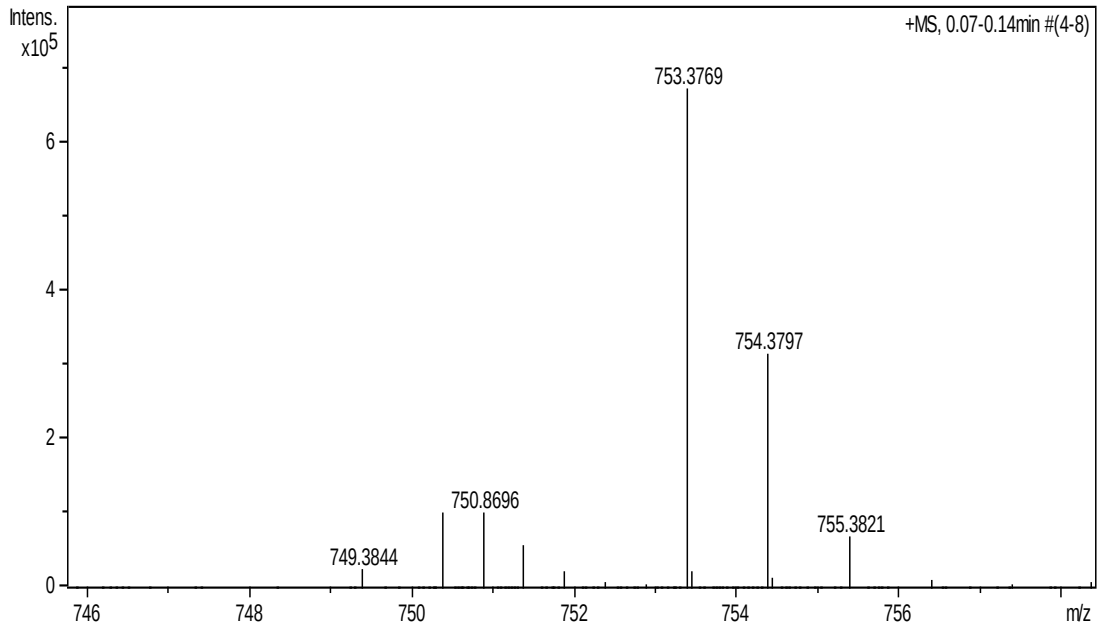

195.80
175.17
163.71
151.86
144.71
141.13
134.57
131.21
130.66
130.11
128.79
128.71
128.59
128.55
128.50
128.28
127.72
127.37
127.05
126.86
126.22
126.15
125.47
114.04
113.74
110.34
65.56
55.49
49.41
44.16
43.61
32.97
31.50
30.04
27.44
27.32
26.96
24.80
21.94
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
1.0
0.8
0.6
0.4
0.2
0.0
+MS, 0.67-0.78min #(40-46)
664.2482
666.2462
665.2511
667.2484
668.2455
669.2464
658
660
662
664
666
668
670
672 m/z

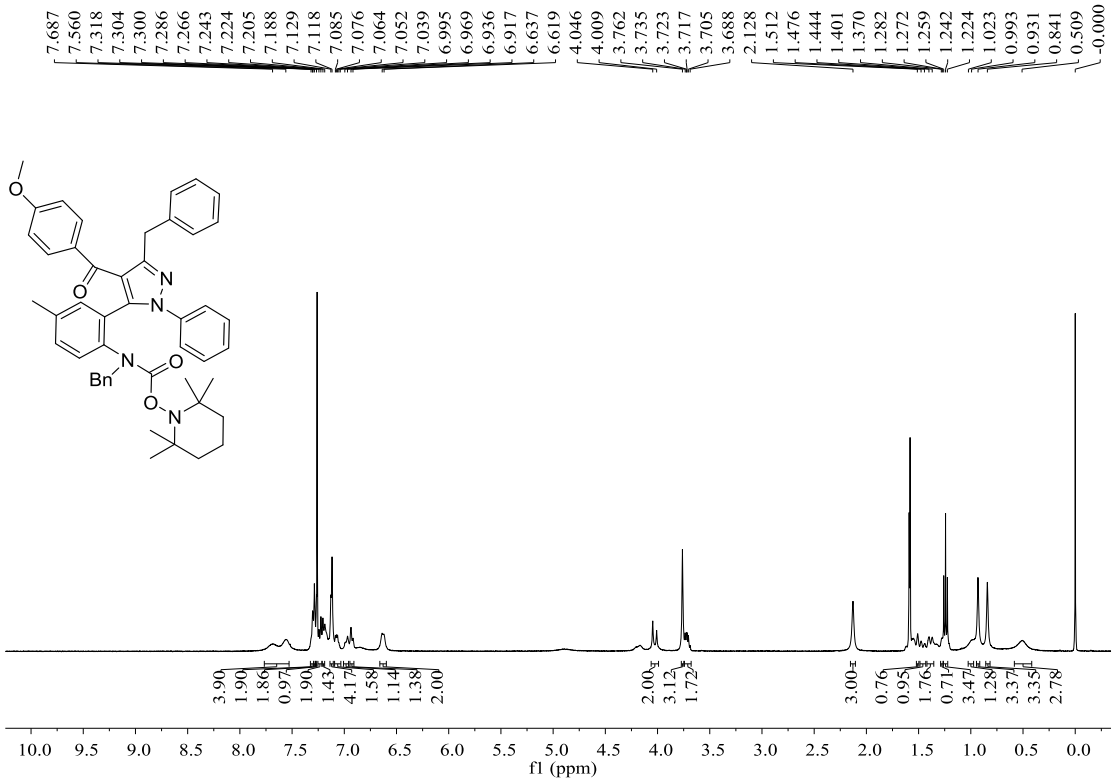
2,2,6,6-tetramethylpiperidin-1-yl benzyl(2-(3-benzyl-4-(4-methylbenzoyl)-1-phenyl-1*H*-pyrazol-5-yl)-4-methylphenyl)carbamate (3a): white solid, 0.423g, 58%, m.p. 107-109 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 1H, ArH), 7.55-7.47 (m, 2H, ArH), 7.30-7.27 (m, 4H, ArH), 7.24-7.24 (m, 1H, ArH), 7.22-7.22 (m, 1H, ArH), 7.20-7.20 (m, 1H, ArH), 7.18-7.15 (m, 2H, ArH), 7.13-7.11 (m, 4H, ArH), 7.08-7.07 (m, 2H, ArH), 6.96-6.92 (m, 5H, ArH), 4.01 (d, *J* = 14.8 Hz, 2H, CH), 3.75-3.69 (m, 2H, CH), 2.28 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.51-1.51 (m, 1H, CH), 1.48-1.45 (m, 1H, CH), 1.40-1.37 (m, 2H, CH), 1.26-1.23 (m, 3H, CH), 1.22-1.20 (m, 1H, CH), 0.98-0.97 (m, 1H, CH), 0.93 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 0.52 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.5, 156.0, 152.6, 141.5, 140.5, 139.4, 139.1, 136.2, 130.6, 130.0, 128.9, 128.6, 128.4, 128.1, 127.1, 126.9, 126.0, 125.9, 124.8, 60.2, 60.0, 58.1, 39.4, 39.2, 33.5, 31.8, 31.5, 21.6, 20.9, 20.7, 20.1, 18.4, 16.8; IR (KBr) υ : 2971, 2930, 2352, 1725, 1646, 1602, 1537, 1501, 1445, 1379, 1247, 1221, 1185, 1161, 1131, 1077, 1048, 1010940, 911, 830, 759, 728 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{48}H_{50}N_4O_3Na$ ([M+Na]$^{+}$):753.3775, Found: 753.3765.

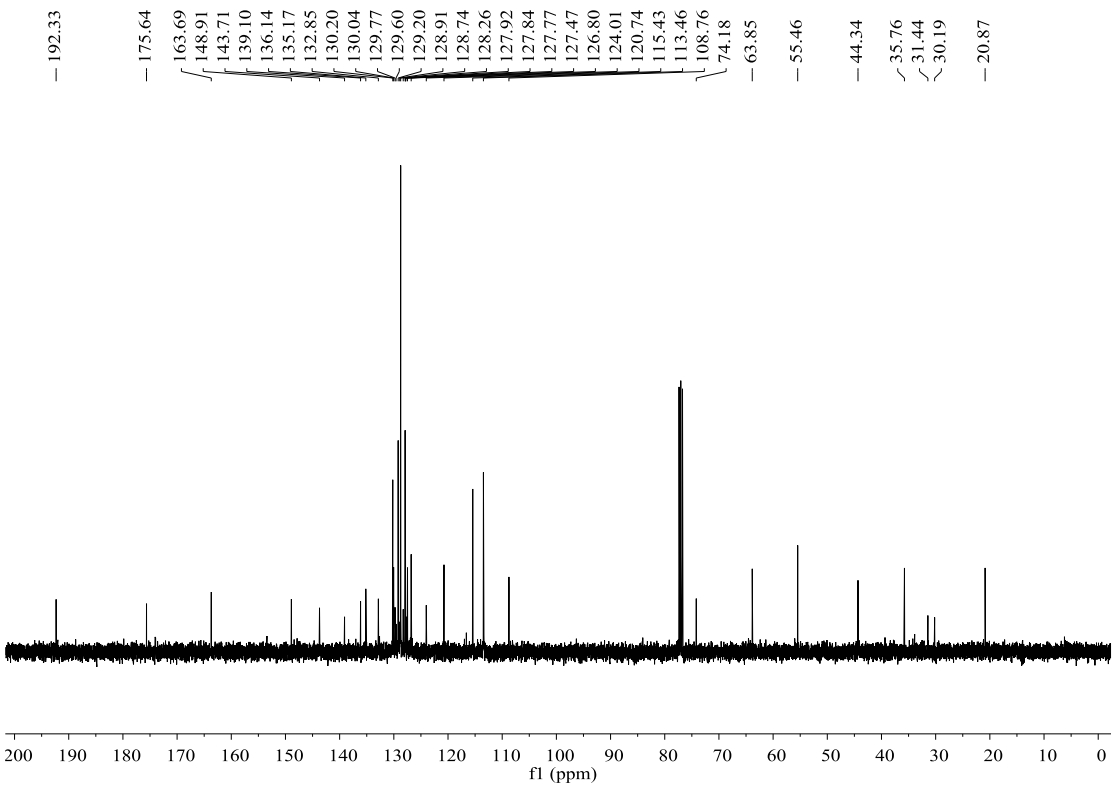


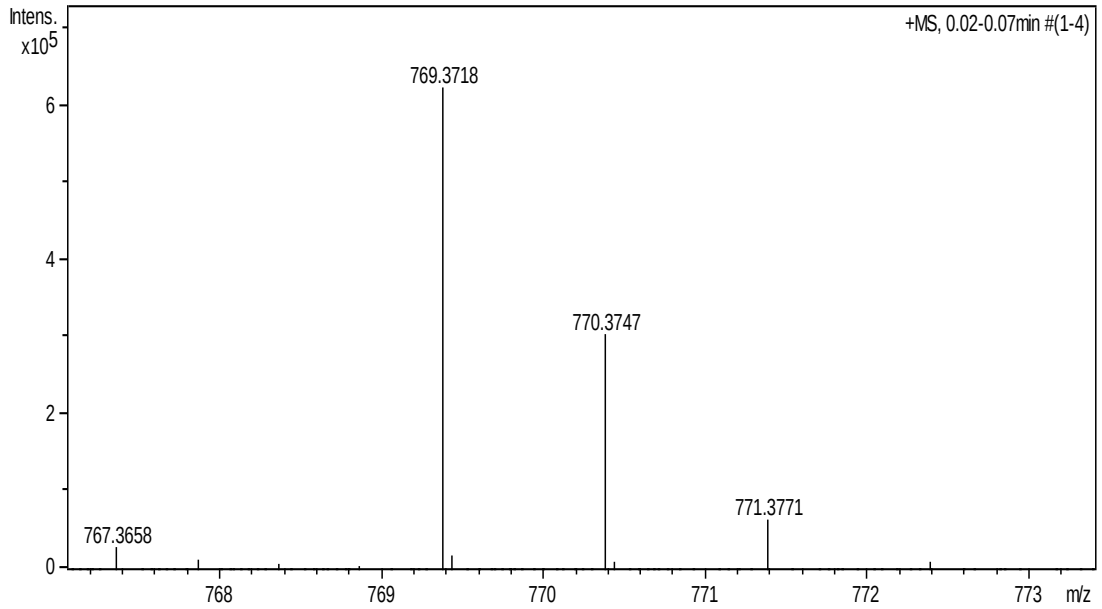

191.46
156.01
152.62
141.52
140.48
139.38
139.12
136.18
130.57
130.04
128.89
128.64
128.43
128.09
127.11
126.87
126.02
125.88
124.74
60.18
59.95
58.14
39.36
39.17
33.49
31.75
31.47
21.59
20.90
20.65
20.14
18.38
16.79
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.07-0.14min #(4-8)
753.3769
754.3797
750.8696
755.3821
749.3844
0
2
4
6
746
748
750
752
754
756
m/z

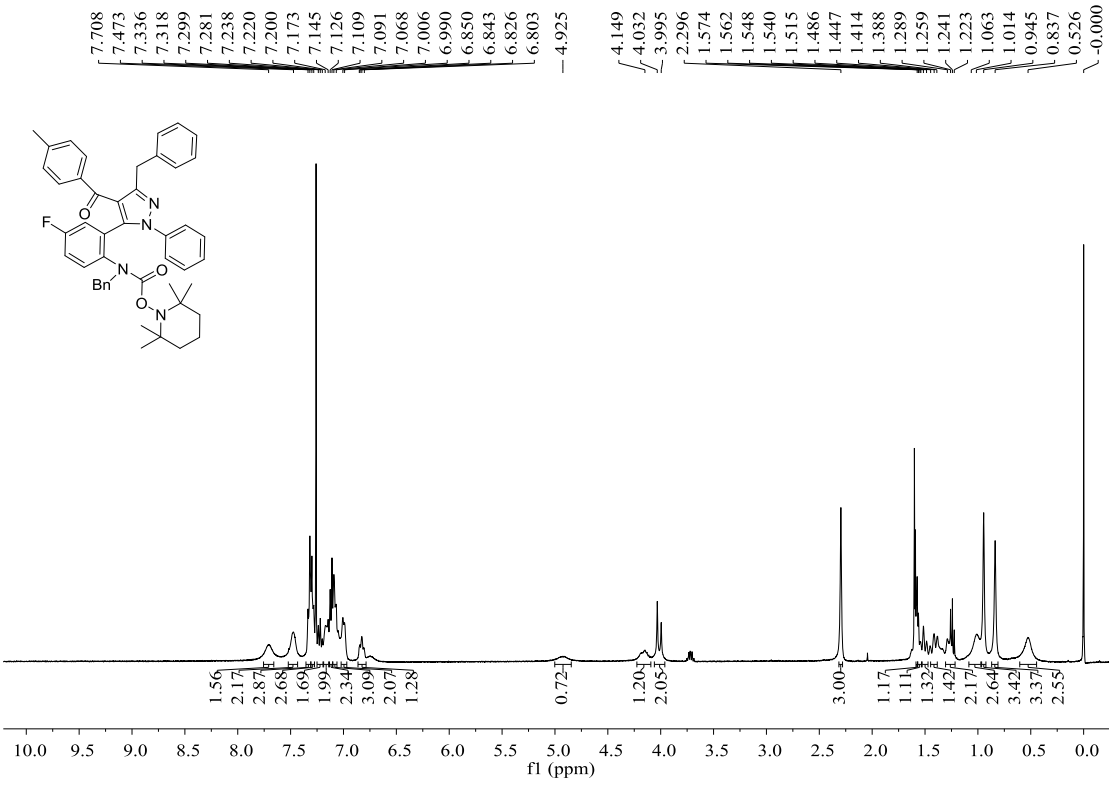
2,2,6,6-tetramethylpiperidin-1-yl benzyl(2-(3-benzyl-4-(4-methoxybenzoyl)-1-phenyl-1*H*-pyrazol-5-yl)-4-methylphenyl)carbamate (3b): white solid, 0.395g, 53%, m.p. 173-175 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69-7.56 (m, 4H, ArH), 7.32-7.30 (m, 2H, ArH), 7.29-7.29 (m, 2H, ArH), 7.27-7.27 (m, 1H, ArH), 7.24-7.22 (m, 2H, ArH), 7.21-7.19 (m, 1H, ArH), 7.13-7.12 (m, 4H, ArH), 7.09-7.04 (m, 2H, ArH), 7.00-6.97 (m, 1H, ArH), 6.94-6.92 (m, 1H, ArH), 6.64-6.62 (m, 2H, ArH), 4.03 (d, *J* = 14.8 Hz, 2H, CH), 3.76 (s, 3H, OCH_3), 3.74-3.69 (m, 2H, CH), 2.13 (s, 3H, CH_3), 1.51-1.51 (m, 2H, CH), 1.48-1.44 (m, 1H, CH), 1.40-1.37 (m, 2H, CH), 1.28-1.27 (m, 1H, CH), 1.26-1.22 (m, 3H, CH), 1.02-0.99 (m, 1H, CH), 0.93 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 0.51 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.3, 175.6, 163.7, 148.9, 143.7, 139.1, 136.1, 135.2, 132.8, 130.2, 130.0, 129.8, 129.6, 129.2, 128.9, 128.7, 128.3, 127.9, 127.8, 127.8, 127.5, 126.8, 124.0, 120.7, 115.4, 113.5, 108.8, 74.2, 63.9, 55.5, 44.3, 35.8, 31.4, 30.2, 20.9; IR (KBr) υ : 2971, 2932, 1725, 1646, 1596, 1538, 1502, 1445, 1378, 1309, 1249, 1222, 1184, 1159, 1129, 1077, 1030, 1009, 937, 911, 846, 828, 761, 730 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{48}H_{50}N_4O_4Na$ ($[M+Na]^+$):769.3724, Found: 769.3718.

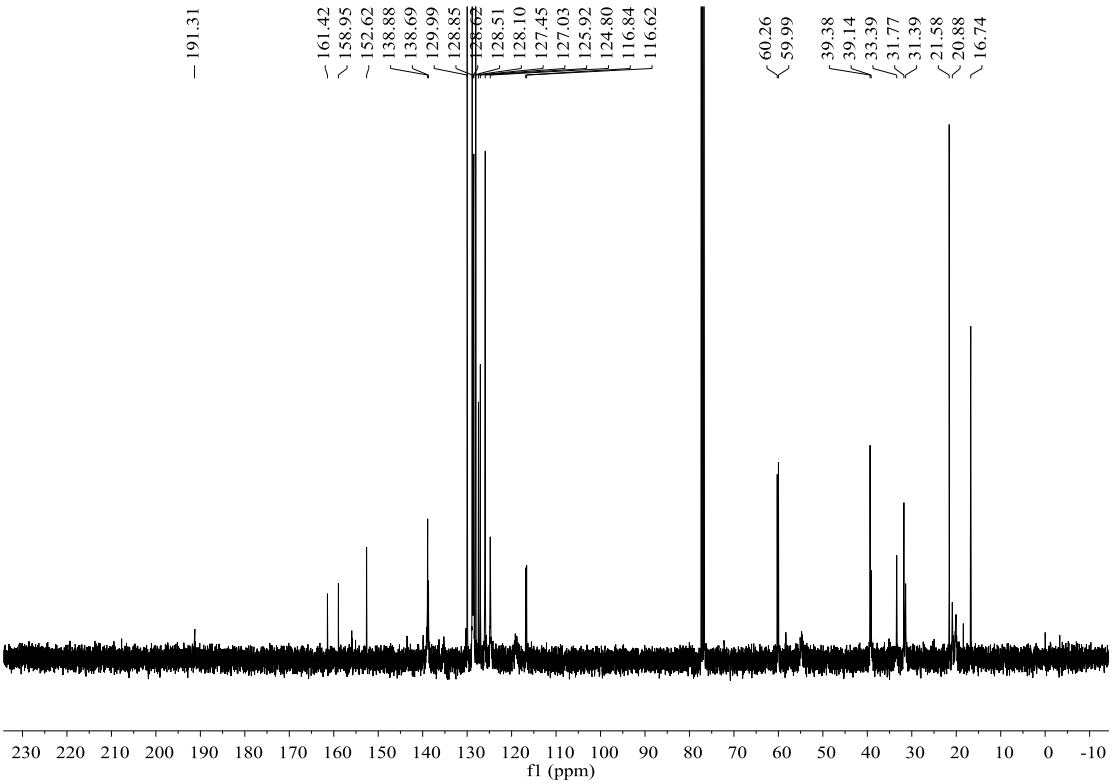


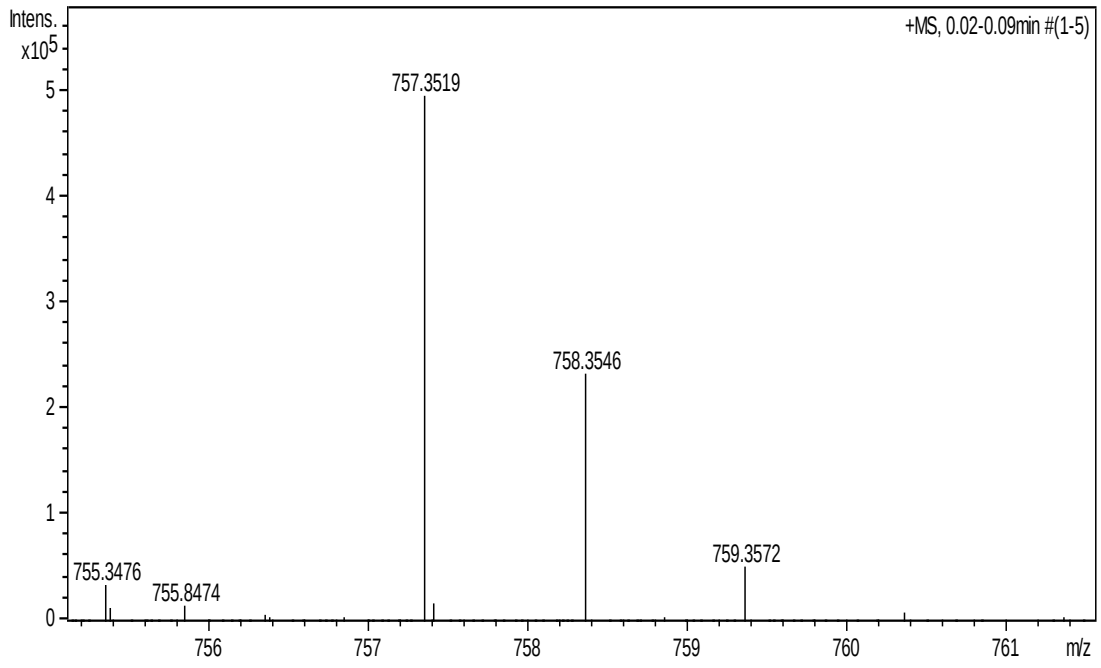

192.33
175.64
163.69
148.91
143.71
139.10
136.14
135.17
132.85
130.20
130.04
129.77
129.60
129.20
128.91
128.74
128.26
127.92
127.84
127.77
127.47
126.80
124.01
120.74
115.43
113.46
108.76
74.18
63.85
55.46
44.34
35.76
31.44
30.19
20.87
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.02-0.07min #(1-4)
769.3718
770.3747
771.3771
767.3658
6
4
2
0
768
769
770
771
772
773
m/z

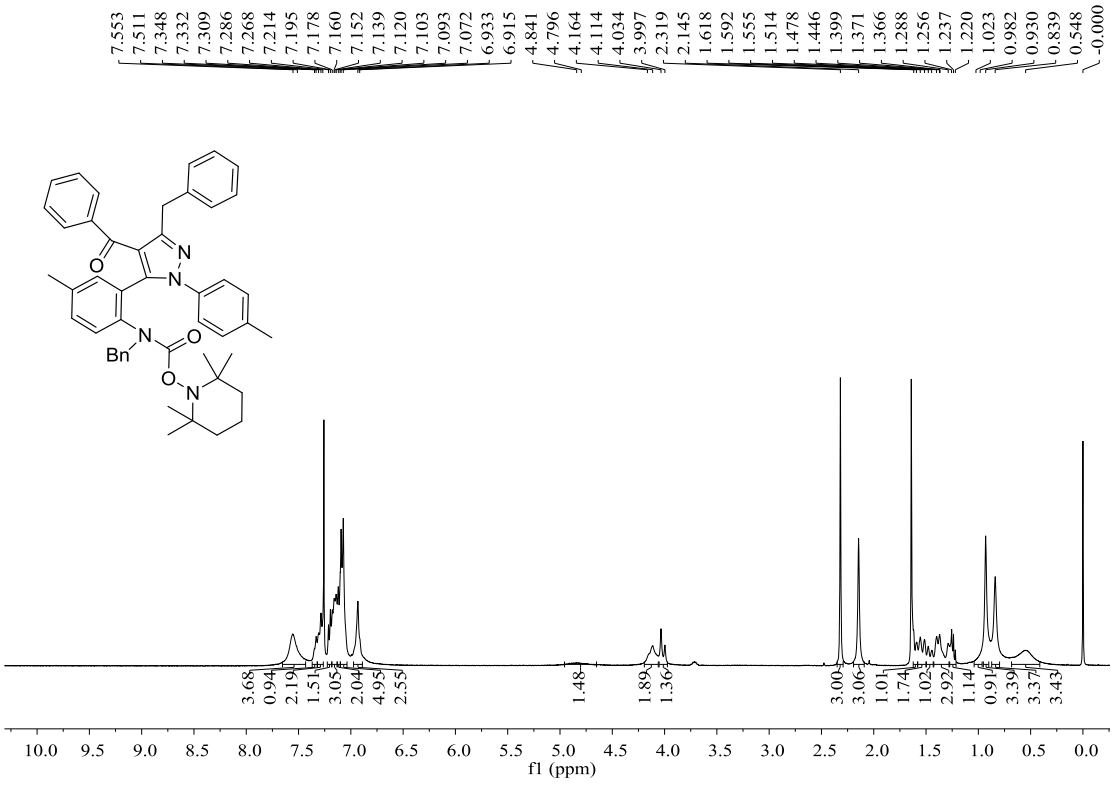
2,2,6,6-tetramethylpiperidin-1-ylbenzyl (2-(3-benzyl-4-(4-methylbenzoyl)-1-phenyl-1*H*-pyrazol-5-yl)-4-fluorophenyl)carbamate (3c): white solid, 0.374g, 51%, m.p. 170-172 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (s, 2H, ArH), 7.47 (s, 2H, ArH), 7.34-7.32 (m, 3H, ArH), 7.30-7.28 (m, 3H, ArH), 7.24-7.20 (m, 2H, ArH), 7.17-7.15 (m, 2H, ArH), 7.13-7.11 (m, 2H, ArH), 7.09-7.07 (m, 3H, ArH), 7.01-6.99 (m, 2H, ArH), 6.85-6.80 (m, 1H, ArH), 4.93 (s, 1H, CH), 4.15 (s, 1H, CH), 4.01 (d, *J* = 15.2 Hz, 2H, CH), 2.30 (s, 3H, CH_3), 1.57-1.56 (m, 1H, CH), 1.55-1.54 (m, 1H, CH), 1.52-1.49 (m, 1H, CH), 1.45-1.39 (m, 1H, CH), 1.29-1.22 (m, 2H, CH), 1.06-1.01 (m, 3H, CH), 0.95 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 0.53 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.3, 161.4, 159.0, 152.6, 138.8 (d, *J* = 18.6 Hz), 130.0, 128.9, 128.6, 128.5, 128.1, 127.5, 127.0, 125.9, 124.8, 116.7 (d, *J* = 21.8 Hz), 60.3, 60.0, 39.4, 39.1, 33.4, 31.8, 31.4, 21.6, 20.9, 16.7; IR (KBr) υ : 3028, 2972, 2930, 1739, 1651, 1601, 1547, 1501, 1446, 1378, 1314, 1247, 1204, 1131, 1074, 1005, 942, 916, 875, 840, 754, 724 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{47}H_{47}FN_4O_3Na$ ($[M+Na]^+$):757.3524, Found: 757.3519.

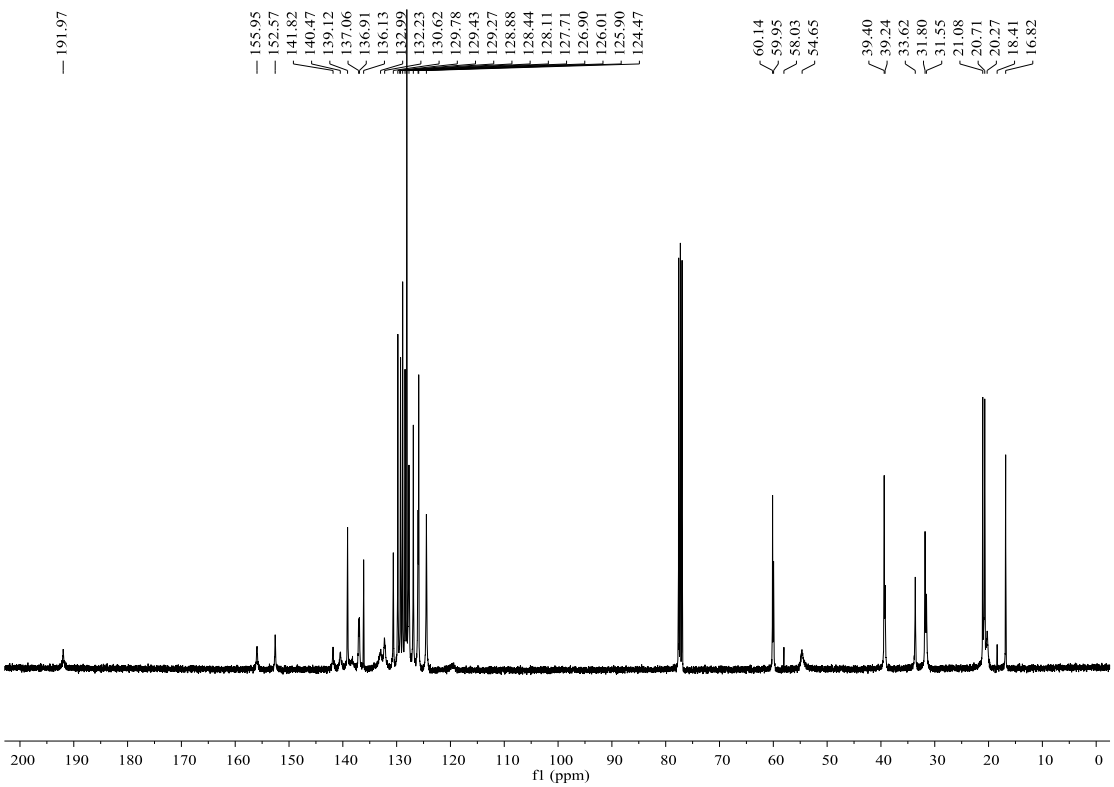


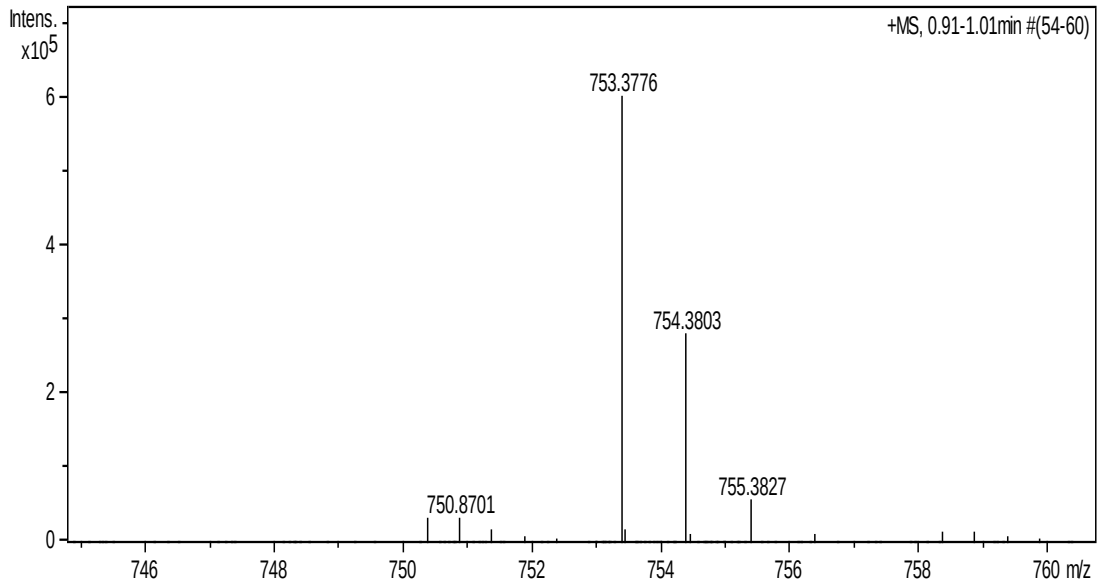

191.31
161.42
158.95
152.62
138.88
138.69
129.99
128.85
128.62
128.51
128.10
127.45
127.03
125.92
124.80
116.84
116.62
60.26
59.99
39.38
39.14
33.39
31.77
31.39
21.58
20.88
16.74
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^5
+MS, 0.02-0.09min #(1-5)
757.3519
758.3546
759.3572
755.3476
755.8474
0
1
2
3
4
5
756
757
758
759
760
761
m/z

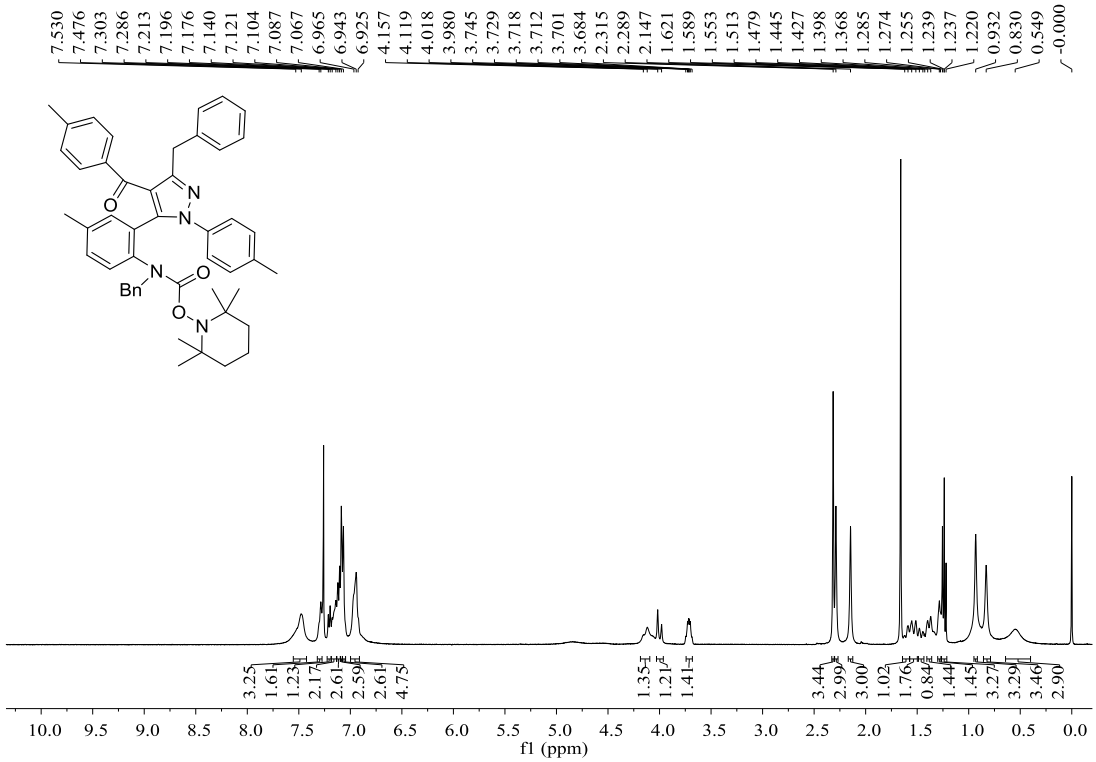
2,2,6,6-tetramethylpiperidin-1-yl (2-(4-benzoyl-3-benzyl-1-(p-tolyl)-1*H*-pyrazol-5-yl)-4-methylphenyl)(benzyl)carbamate (3d): white solid, 0.453g, 62%, m.p. 115-117 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.51 (m, 4H, ArH), 7.35-7.33 (m, 1H, ArH), 7.31-7.27 (m, 2H, ArH), 7.21-7.20 (m, 2H, ArH), 7.18-7.14 (m, 3H, ArH), 7.12-7.10 (m, 2H, ArH), 7.09-7.07 (m, 5H, ArH), 6.93-6.92 (m, 3H, ArH), 4.84-4.80 (m, 1H, CH), 4.16-4.11 (m, 2H, CH), 4.02 (d, *J* = 14.8 Hz, 1H, CH), 2.32 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.62-1.59 (m, 1H, CH), 1.56-1.51 (m, 2H, CH), 1.48-1.45 (m, 1H, CH), 1.40-1.29 (m, 3H, CH), 1.26-1.22 (m, 1H, CH), 1.02-0.98 (m, 1H, CH), 0.93 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 0.55 (s, 3H, CH_3; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.0, 155.9, 152.6, 141.8, 140.5, 139.1, 137.1, 136.9, 136.1, 133.0, 132.2, 130.6, 129.8, 129.4, 129.3, 128.9, 128.4, 128.1, 127.7, 126.9, 126.0, 125.9, 124.5, 60.1, 59.9, 58.0, 54.6, 39.4, 39.2, 33.6, 31.8, 31.5, 21.1, 20.7, 20.3, 18.4, 16.8; IR (KBr) υ : 2927, 1733, 1640, 1506, 1443, 1388, 1227, 1131, 996, 928, 901, 823, 740 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{48}H_{50}N_4O_3Na$ ([M+Na]$^{+}$):753.3956, Found: 753.3776.

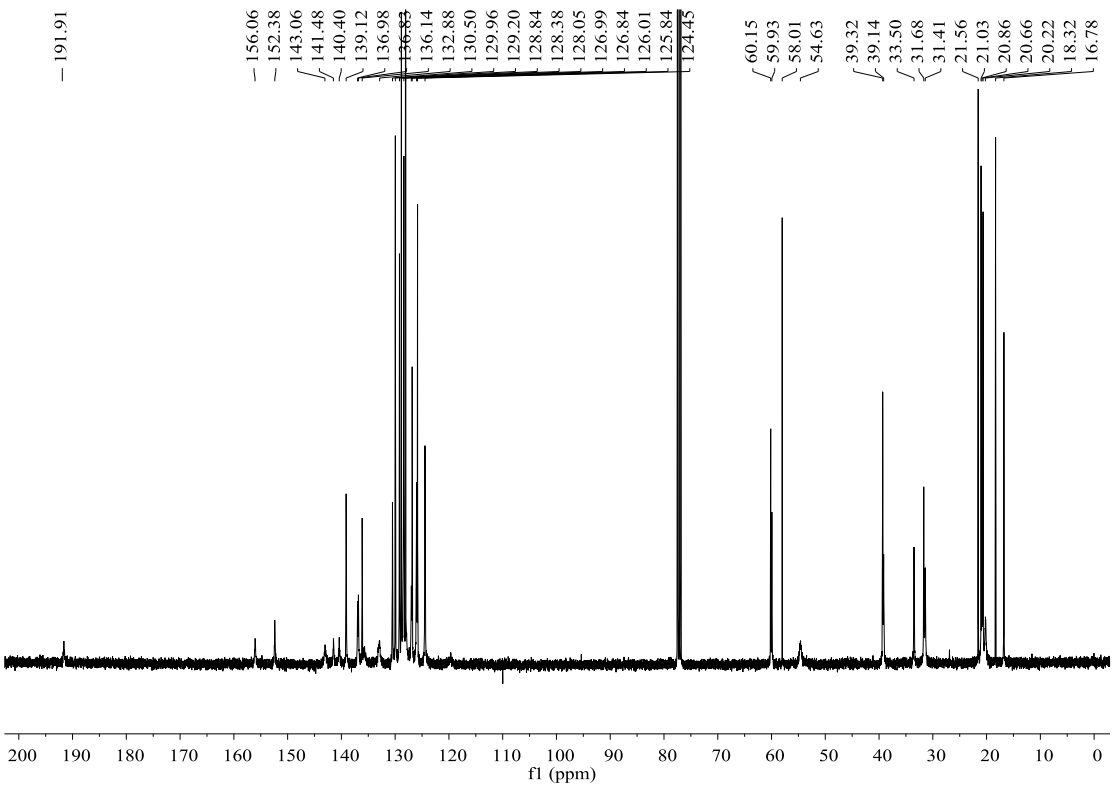


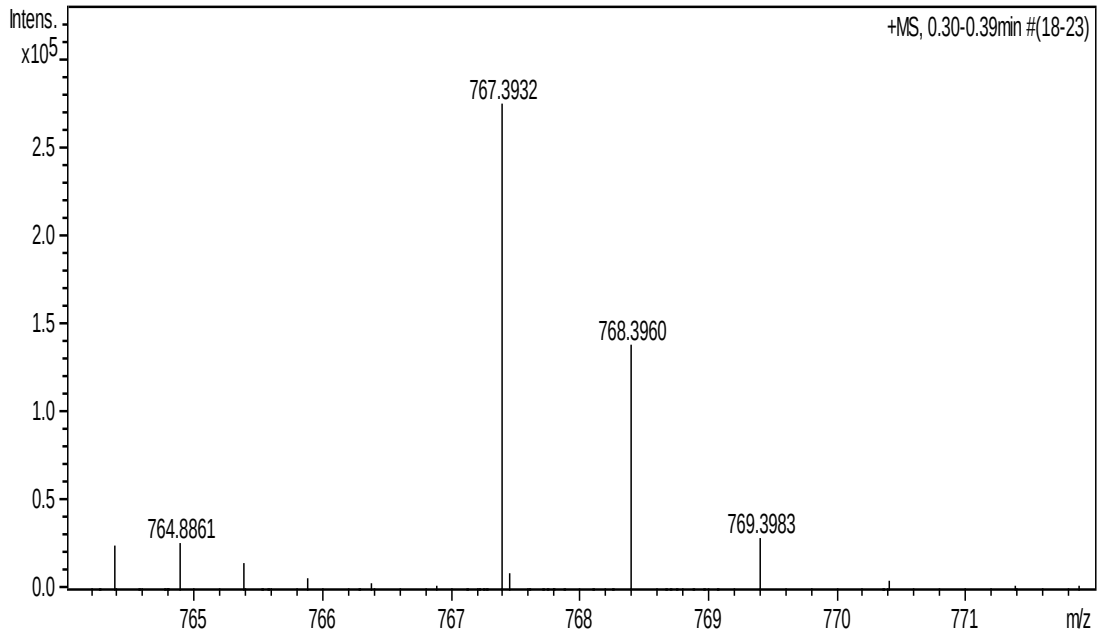

191.97
155.95
152.57
141.82
140.47
139.12
137.06
136.91
136.13
132.99
132.23
130.62
129.78
129.43
129.27
128.88
128.44
128.11
127.71
126.90
126.01
125.90
124.47
60.14
59.95
58.03
54.65
39.40
39.24
33.62
31.80
31.55
21.08
20.71
20.27
18.41
16.82
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.91-1.01min #(54-60)
753.3776
754.3803
755.3827
750.8701
0
2
4
6
746 748 750 752 754 756 758 760 m/z

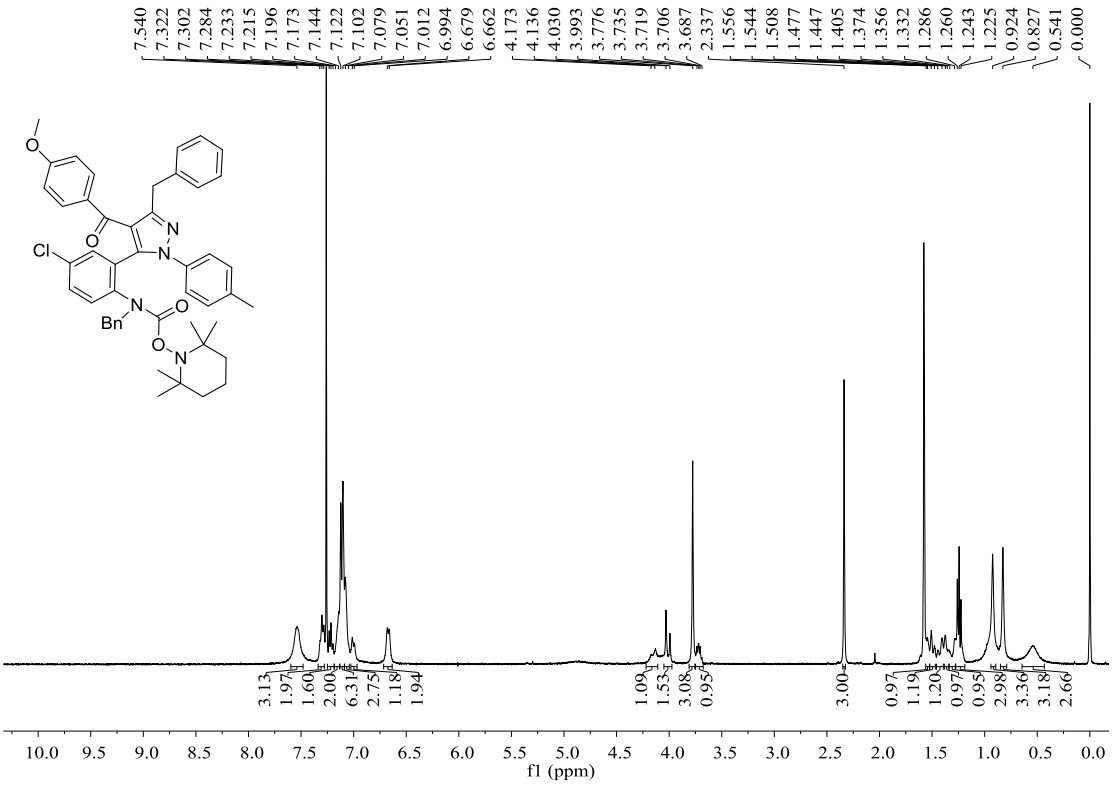
2,2,6,6-tetramethylpiperidin-1-yl benzyl (2-(3-benzyl-4-(4-methylbenzoyl)-1-(p-tolyl)-1*H*-pyrazol-5-yl)-4-methylphenyl)carbamate (3e): pink solid, 0.446g, 60%, m.p. 117-119 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.48 (m, 3H, ArH), 7.30-7.29 (m, 2H, ArH), 7.21-7.20 (m, 1H, ArH), 7.18-7.14 (m, 2H, ArH), 7.12-6.10 (m, 2H, ArH), 7.09-7.09 (m, 3H, ArH), 7.07-7.07 (m, 3H, ArH), 6.97-6.93 (m, 5H, ArH), 4.16-4.12 (m, 1H, CH), 4.00 (d, *J* = 15.2 Hz, 1H, CH), 3.75-3.68 (m, 1H, CH), 2.32 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.62-1.59 (m, 1H, CH), 1.55-1.51 (m, 2H, CH), 1.48-1.44 (m, 1H, CH), 1.40-1.37 (m, 1H, CH), 1.29-1.27 (m, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.9, 156.1, 152.4, 143.1, 141.5, 140.4, 139.1, 137.0, 136.8, 136.1, 132.9, 130.5, 130.0, 129.2, 128.8, 128.4, 128.1, 127.0, 126.8, 126.0, 125.8, 124.5, 60.2, 59.9, 58.0, 54.6, 39.3, 39.1, 33.5, 31.7, 31.4, 21.6, 21.0, 20.9, 20.7, 20.2, 18.3, 16.8; IR (KBr) υ : 2932, 1728, 1646, 1604, 1509, 1448, 1378, 1242, 1125, 1082, 1004, 944, 910, 826, 758, 726 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{49}H_{52}N_4O_3Na$ ([M+Na]$^{+}$):767.3932, Found: 767.3932.

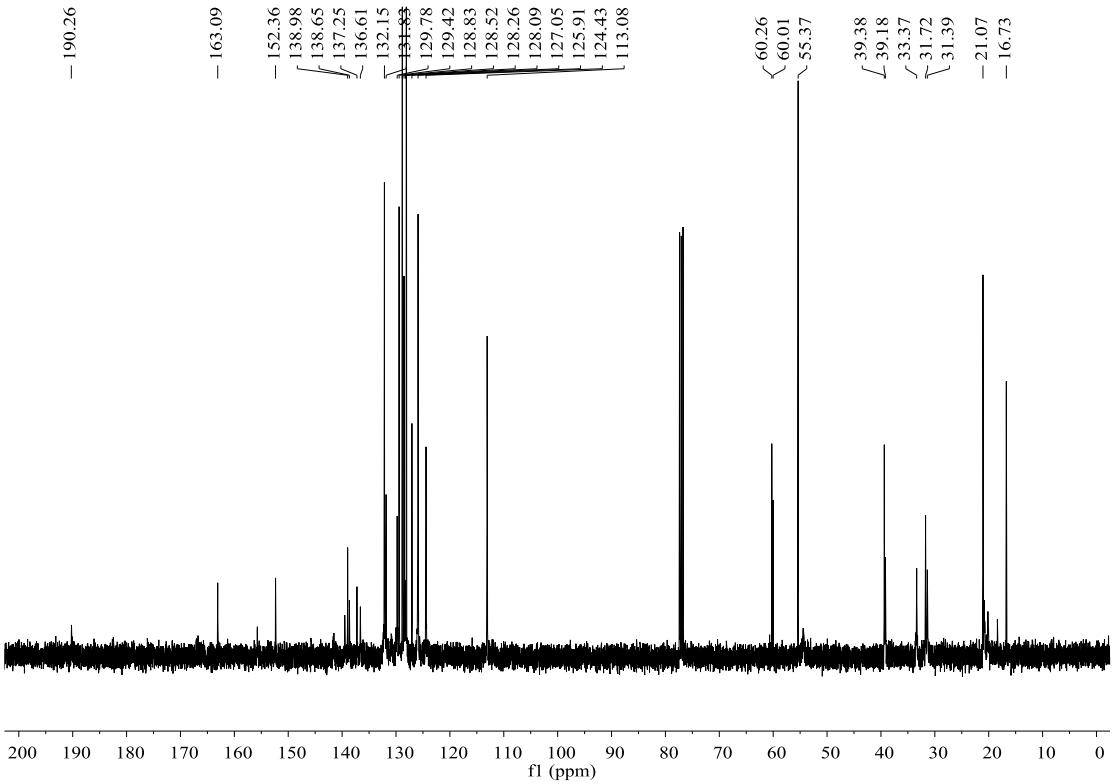


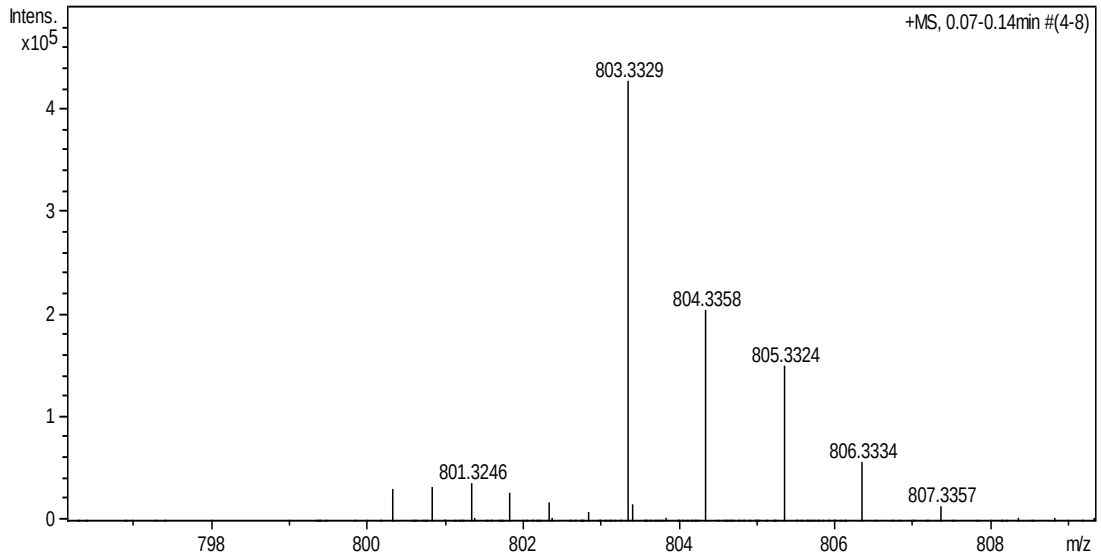

191.91
156.06
152.38
143.06
141.48
140.40
139.12
136.98
136.83
136.14
132.88
130.50
129.96
129.20
128.84
128.38
128.05
126.99
126.84
126.01
125.84
124.45
60.15
59.93
58.01
54.63
39.32
39.14
33.50
31.68
31.41
21.56
21.03
20.86
20.66
20.22
18.32
16.78
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.30-0.39min #(18-23)
767.3932
768.3960
764.8861
769.3983
2.5
2.0
1.5
1.0
0.5
0.0
765 766 767 768 769 770 771
m/z

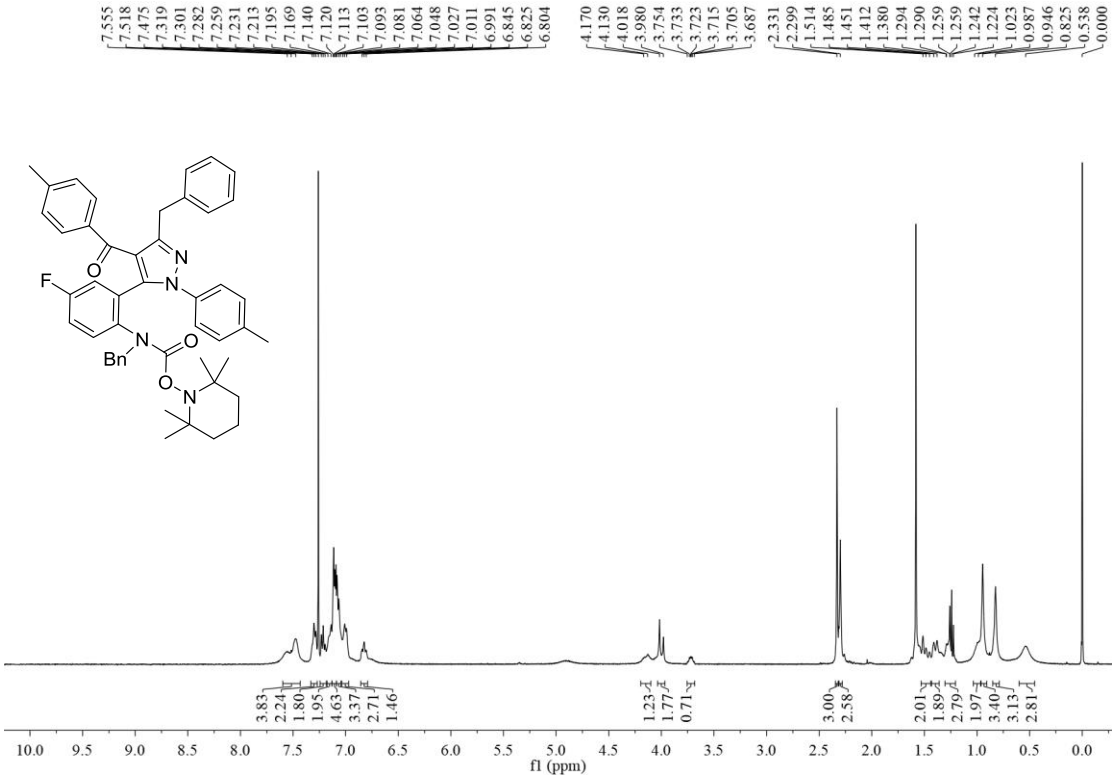
2,2,6,6-tetramethylpiperidin-1-yl benzyl(2-(3-benzyl-4-(4-methoxybenzoyl)-1-(p-tolyl)-1*H*-pyrazol-5-yl)-4-chlorophenyl)carbamate (3f): white solid, 0.507g, 65%, m.p. 109-111 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.54 (m, 3H, ArH), 7.32-7.28 (m, 2H, ArH), 7.23-7.20 (m, 2H, ArH), 7.17-7.14 (m, 2H, ArH), 7.12-6.10 (m, 6H, ArH), 7.08-7.05 (m, 3H, ArH), 7.01-6.99 (m, 1H, ArH), 6.68-6.66 (m, 2H, ArH), 4.17-4.14 (m, 1H, CH), 4.01 (d, *J* = 14.8 Hz, 2H, CH), 3.78 (s, 3H, OCH_3), 3.74-3.69 (m, 1H, CH), 2.34 (s, 3H, CH_3), 1.56-1.54 (m, 1H, CH), 1.51-1.48 (m, 1H, CH), 1.45-1.41 (m, 1H, CH), 1.37-1.36 (m, 1H, CH), 1.33-1.29 (m, 1H, CH), 1.26-1.23 (m, 3H, CH), 0.92 (s, 3H, CH_3), 0.83 (s, 3H, CH_3), 0.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.3, 163.1, 152.4, 139.0, 138.7, 137.3, 136.6, 132.2, 131.8, 129.8, 129.4, 128.8, 128.5, 128.3, 128.1, 127.1, 125.9, 124.4, 113.1, 60.3, 60.0, 55.4, 39.4, 39.2, 33.4, 31.7, 31.4, 21.1, 16.7; IR (KBr) υ : 2973, 2934, 1724, 1646, 1598, 1515, 1492, 1449, 1375, 1310, 1249, 1221, 1186, 1160, 1129, 1077, 1030, 1011, 989, 941, 912, 880, 825, 755, 726 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{48}H_{49}ClN_4O_4Na$ ([M+Na]$^{+}$):803.3325, Found: 803.3329.

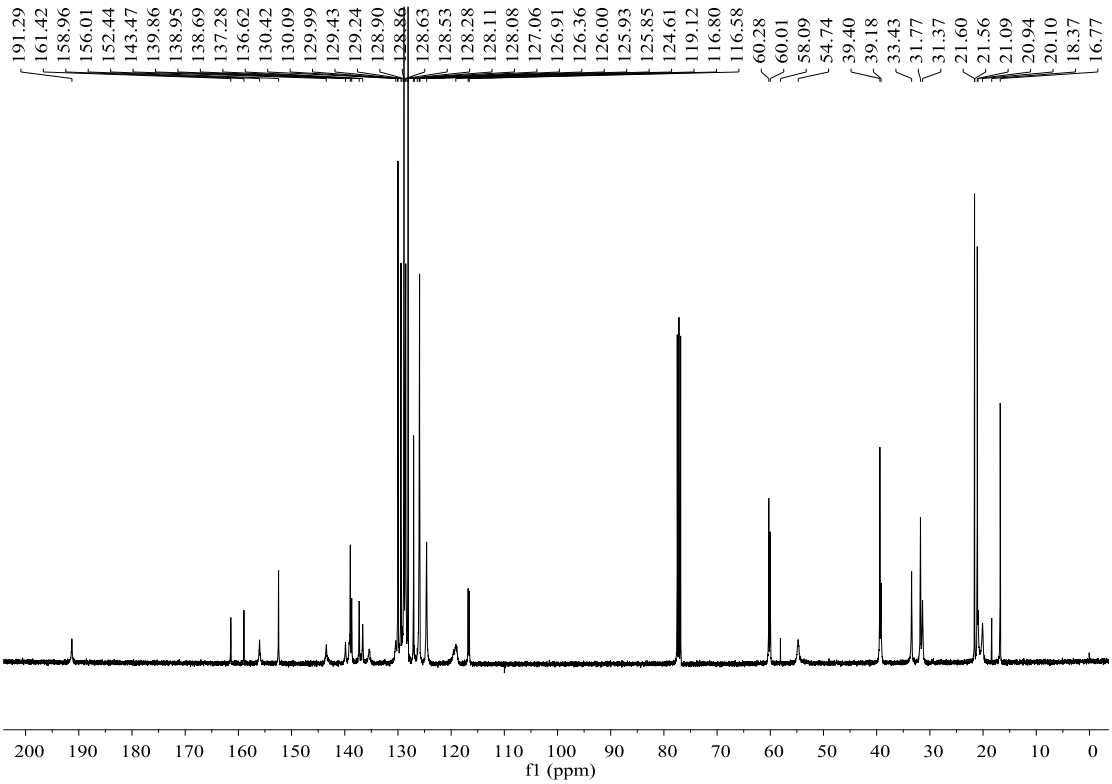


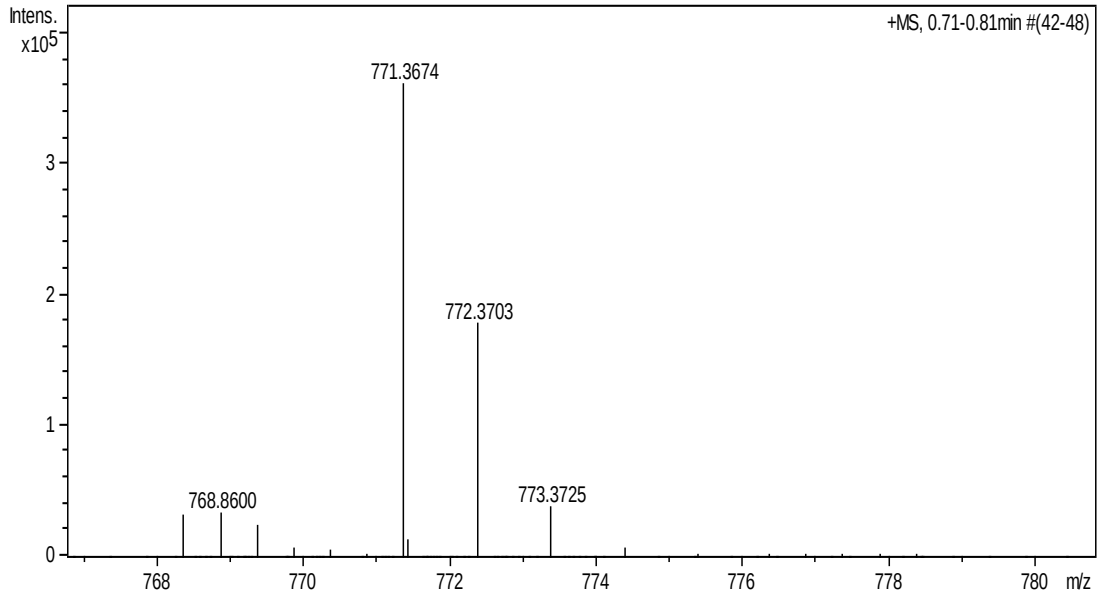

190.26
163.09
152.36
138.98
138.65
137.25
136.61
132.15
131.83
129.78
129.42
128.83
128.52
128.26
128.09
127.05
125.91
124.43
113.08
60.26
60.01
55.37
39.38
39.18
33.37
31.72
31.39
21.07
16.73
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.07-0.14min #(4-8)
803.3329
804.3358
805.3324
806.3334
807.3357
801.3246
0
1
2
3
4
798
800
802
804
806
808
m/z

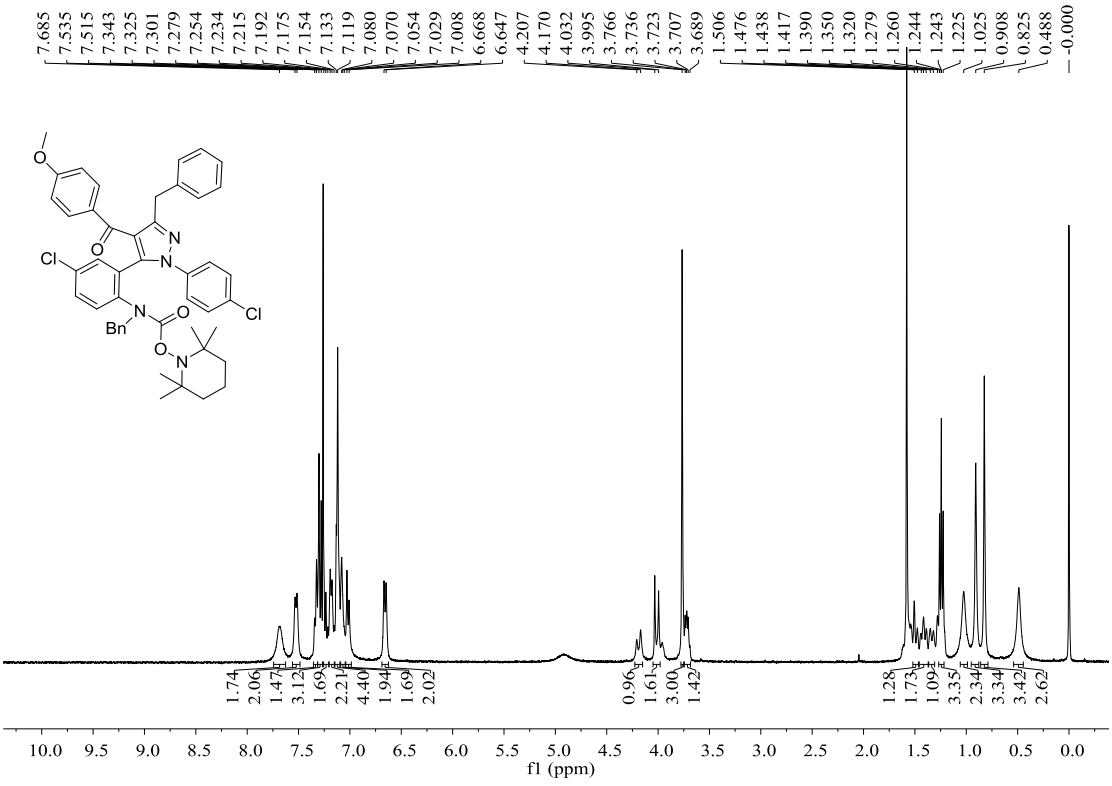
2,2,6,6-tetramethylpiperidin-1-yl benzyl(2-(3-benzyl-4-(4-methylbenzoyl)-1-(p-tolyl)-1*H*-pyrazol-5-yl)-4-fluorophenyl)carbamate (3g): yellow solid, 0.494g, 66%, m.p. 110-112 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56-7.48 (m, 4H, ArH), 7.32-7.28 (m, 2H, ArH), 7.23-7.20 (m, 2H, ArH), 7.17-7.14 (m, 2H, ArH), 7.12-7.09 (m, 5H, ArH), 7.08-7.05 (m, 3H, ArH), 7.03-6.99 (m, 3H, ArH), 6.85-6.80 (m, 1H, ArH), 4.17-4.13 (m, 1H, CH), 4.00 (d, *J* = 15.2 Hz, 2H, CH), 3.75-3.69 (m, 1H, CH), 2.33 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 1.51-1.45 (m, 2H, CH), 1.41-1.38 (m, 2H, CH), 1.29-1.22 (m, 3H, CH_3), 1.02-0.99 (m, 2H, CH), 0.95 (s, 3H, CH_3), 0.83 (s, 3H, CH_3), 0.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.3, 160.2 (d, *J* = 246.6 Hz), 156.0, 152.4, 143.5, 139.9, 139.0, 138.7, 137.3, 136.6, 135.4, 130.4, 130.1, 130.0, 129.4, 129.2, 128.9, 128.9, 128.6, 128.5, 128.3, 128.1, 128.1, 127.1, 126.9, 126.4, 126.0, 125.9, 125.9, 124.6, 119.1, 116.7 (d, *J* = 22.0 Hz), 60.3, 60.0, 58.1, 54.7, 39.4, 39.2, 33.4, 31.8, 31.4, 21.6, 21.6, 21.1, 20.9, 20.1, 18.4, 16.8; IR (KBr) υ : 3029, 2974, 2934, 1736, 1646, 1606, 1515, 1497, 1448, 1378, 1334, 1247, 1207, 1183, 1129, 1075, 1001, 941, 911, 872, 824, 757, 726 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{48}H_{49}ClN_4O_4Na$ ([M+Na]$^{+}$):771.3681, Found: 771.3674.

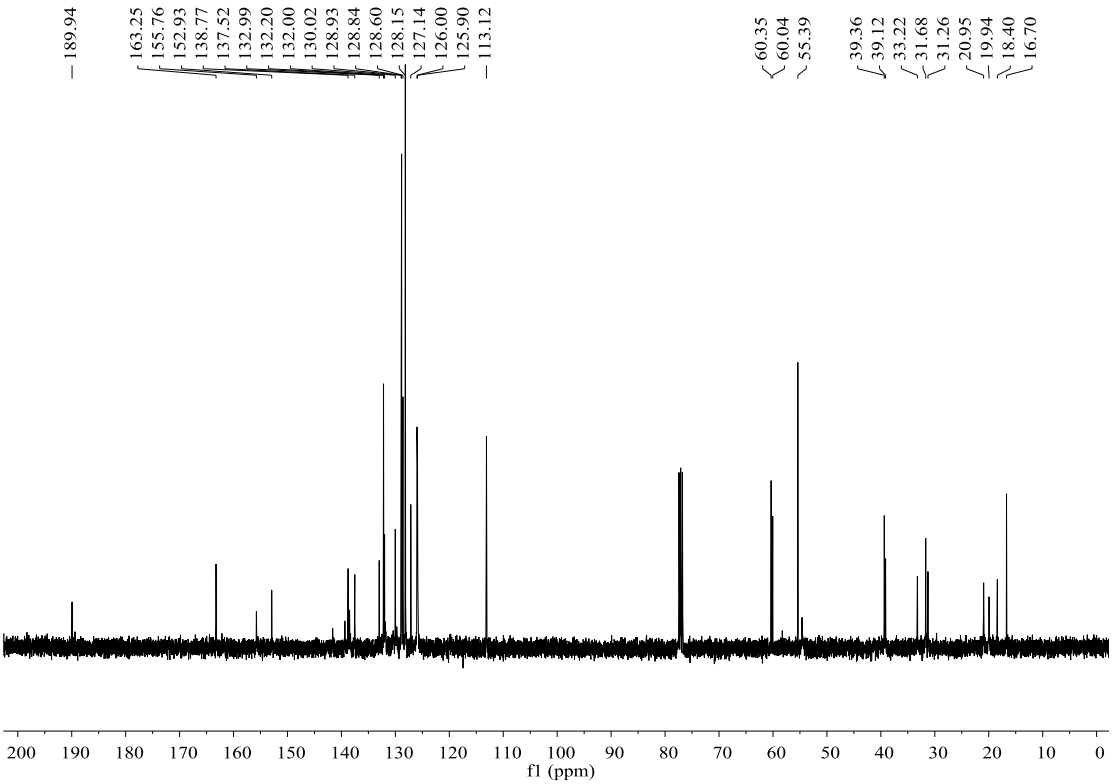


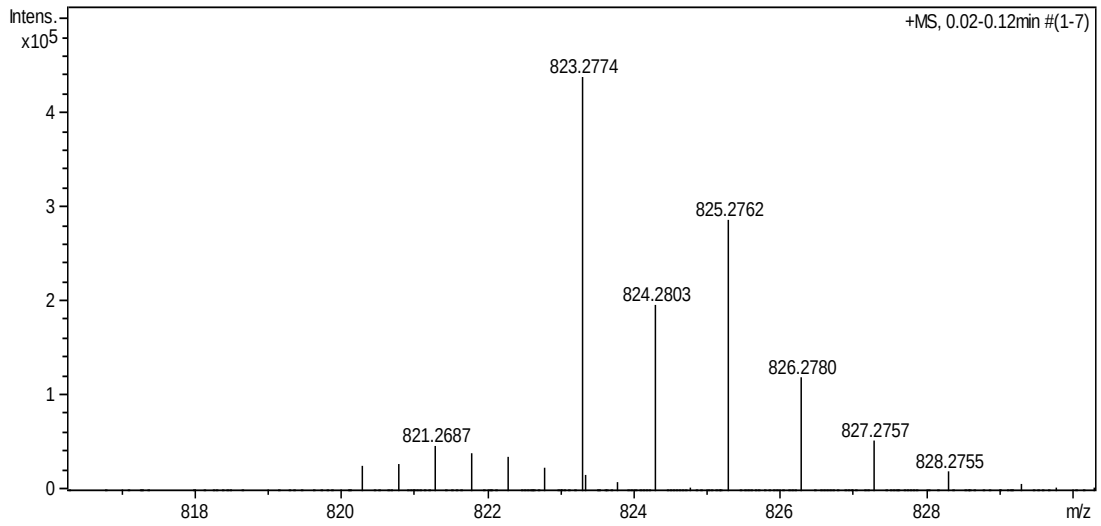

191.29
161.42
158.96
156.01
152.44
143.47
139.86
138.95
138.69
137.28
136.62
130.42
130.09
129.99
129.43
129.24
128.90
128.86
128.63
128.53
128.28
128.11
128.08
127.06
126.91
126.36
126.00
125.93
125.85
124.61
119.12
116.80
116.58
60.28
60.01
58.09
54.74
39.40
39.18
33.43
31.77
31.37
21.60
21.56
21.09
20.94
20.10
18.37
16.77
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.71-0.81min #(42-48)
771.3674
772.3703
768.8600
773.3725
0
1
2
3
768
770
772
774
776
778
780
m/z

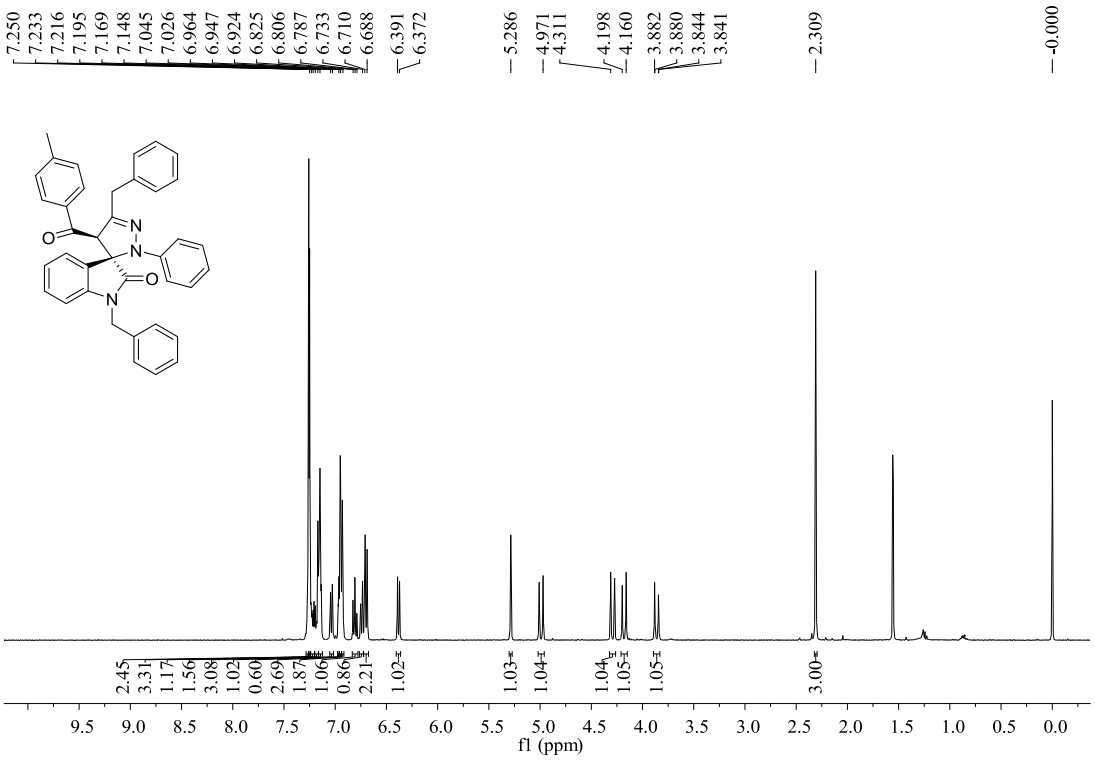
2,2,6,6-tetramethylpiperidin-1-yl benzyl(2-(3-benzyl-1-(4-chlorophenyl)-4-(4-methoxybenzoyl)-1H-pyrazol-5-yl)-4-chlorophenyl)carbamate (3h): yellow solid, 0.440g, 55%, m.p. 115-117 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (s, 2H, ArH), 7.54-7.52 (m, 2H, ArH), 7.34-7.33 (m, 1H, ArH), 7.30-7.28 (m, 3H, ArH), 7.25-7.22 (m, 2H, ArH), 7.19-7.15 (m, 2H, ArH), 7.13-7.12 (m, 4H, ArH), 7.08-7.05 (m, 2H, ArH), 7.03-7.01 (m, 2H, ArH), 6.67-6.65 (m, 2H, ArH), 4.21-4.17 (m, 1H, CH), 4.01 (d, *J* = 14.8 Hz, 2H, CH), 3.77 (s, 3H, OCH_3), 3.74-3.69 (m, 1H, CH), 1.51-1.48 (m, 1H, CH), 1.44-1.39 (m, 2H, CH), 1.35-1.32 (m, 1H, CH), 1.28-1.23 (m, 3H, CH), 1.03 (s, 2H, CH), 0.91 (s, 3H, CH_3), 0.83 (s, 3H, CH_3), 0.49 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.9, 163.3, 155.8, 152.9, 138.8, 137.5, 133.0, 132.2, 132.0, 130.0, 128.9, 128.8, 128.6, 128.2, 127.1, 126.0, 125.9, 113.1, 60.4, 60.0, 55.4, 39.4, 39.1, 33.2, 31.7, 31.3, 21.0, 19.9, 18.4, 16.7; IR (KBr) υ : 2972, 2934, 1721, 1646, 1597, 1539, 1499, 1451, 1374, 1334, 1250, 1223, 1185, 1160, 1129, 1093, 1031, 1012, 988, 940, 911, 880, 834, 755, 717 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{47}H_{46}Cl_2N_4O_4Na$ ([M+Na]$^{+}$):823.2788, Found: 823.2774.

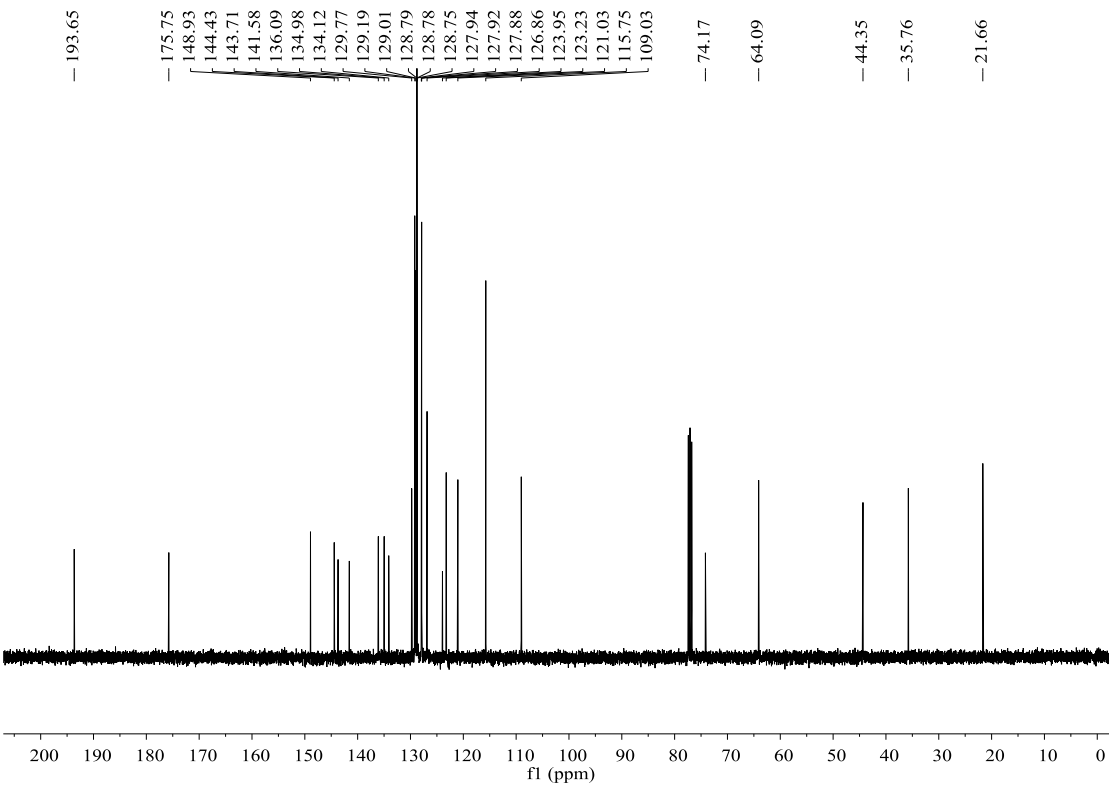


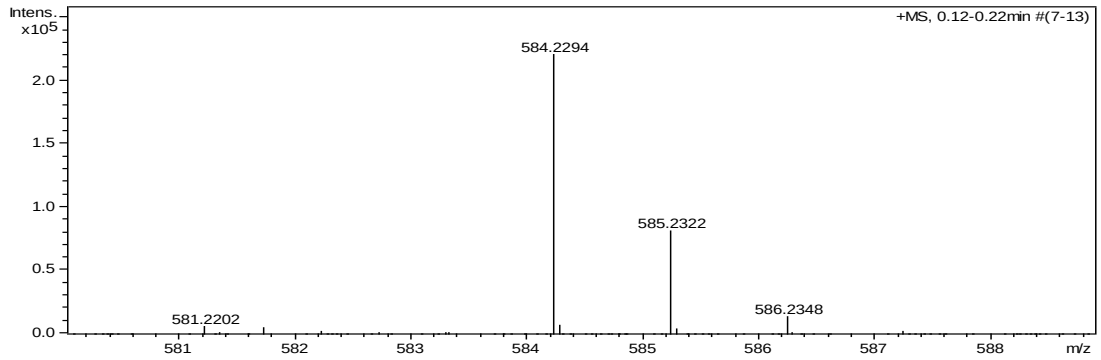

189.94
163.25
155.76
152.93
138.77
137.52
132.99
132.20
132.00
130.02
128.93
128.84
128.60
128.15
127.14
126.00
125.90
113.12
60.35
60.04
55.39
39.36
39.12
33.22
31.68
31.26
20.95
19.94
18.40
16.70
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.02-0.12min #(1-7)
823.2774
825.2762
824.2803
826.2780
821.2687
827.2757
828.2755
0
1
2
3
4
818
820
822
824
826
828
m/z

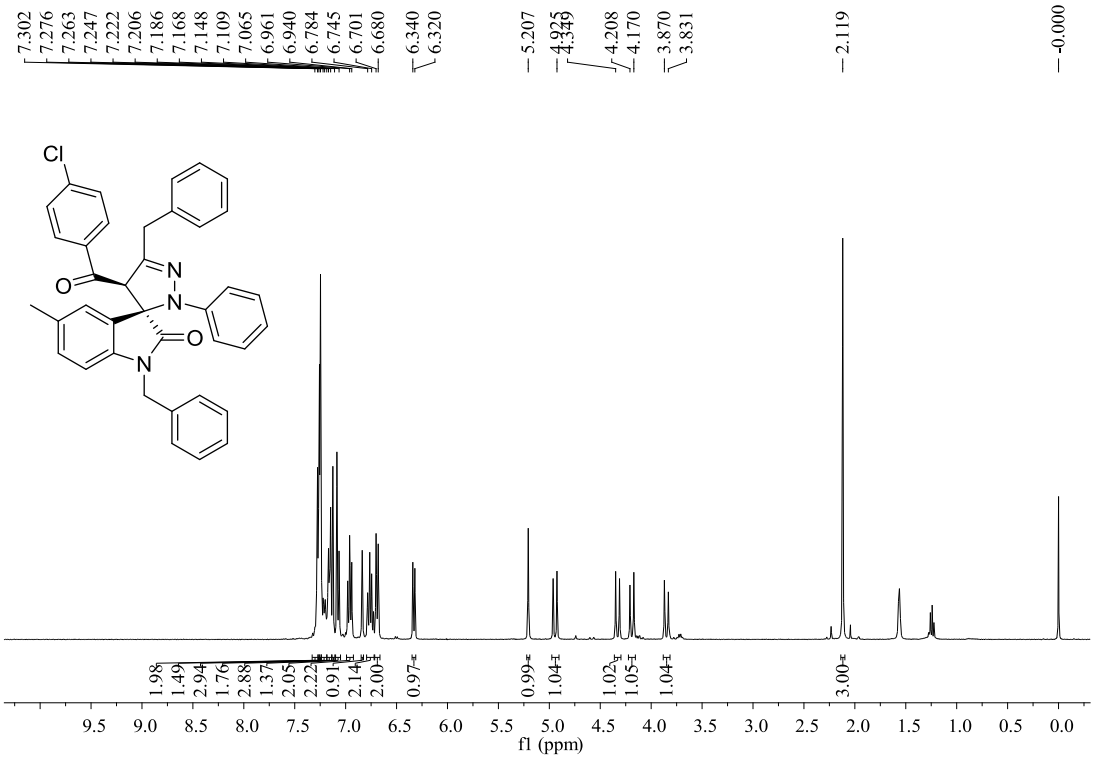
1,5'-dibenzyl-4'-(4-methylbenzoyl)-2'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (4a): yellow solid, 0.421g, 75%, m.p. 125-127 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.29-7.26 (m, 2H, ArH), 7.25-7.25 (m, 3H, ArH), 7.24-7.21 (m, 1H, ArH), 7.20-7.17 (m, 2H, ArH), 7.16-6.14 (m, 3H, ArH), 7.05-7.03 (m, 1H, ArH), 6.97-6.96 (m, 1H, ArH), 6.95-6.95 (m, 3H, ArH), 6.93-6.92 (m, 2H, ArH), 6.83-6.79 (m, 1H, ArH), 6.75-6.73 (m, 1H, ArH), 6.71-6.69 (m, 2H, ArH), 6.39-6.37 (m, 1H, ArH), 5.29 (s, 1H, CH), 4.99 (d, J = 15.2 Hz, 1H, CH), 4.39 (d, J = 15.6 Hz, 1H, CH), 4.18 (d, J = 15.2 Hz, 1H, CH), 3.86 (dd, J_1 = 0.8 Hz, J_2 = 15.2 Hz, 1H, CH), 2.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.7, 175.8, 148.9, 144.4, 143.7, 141.6, 136.1, 135.0, 134.1, 129.8, 129.2, 129.0, 128.8, 128.8, 128.8, 127.9, 127.9, 127.9, 126.9, 124.0, 123.2, 121.0, 115.8, 109.0, 74.2, 64.1, 44.4, 35.8, 21.7; IR (KBr) υ：3030, 1720, 1679, 1602, 1494, 1363, 1216, 1174, 1095, 1001, 877, 830, 755, 700 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{31}N_3O_2Na$ ([M+Na]$^{+}$):584.2308, Found: 584.2294.

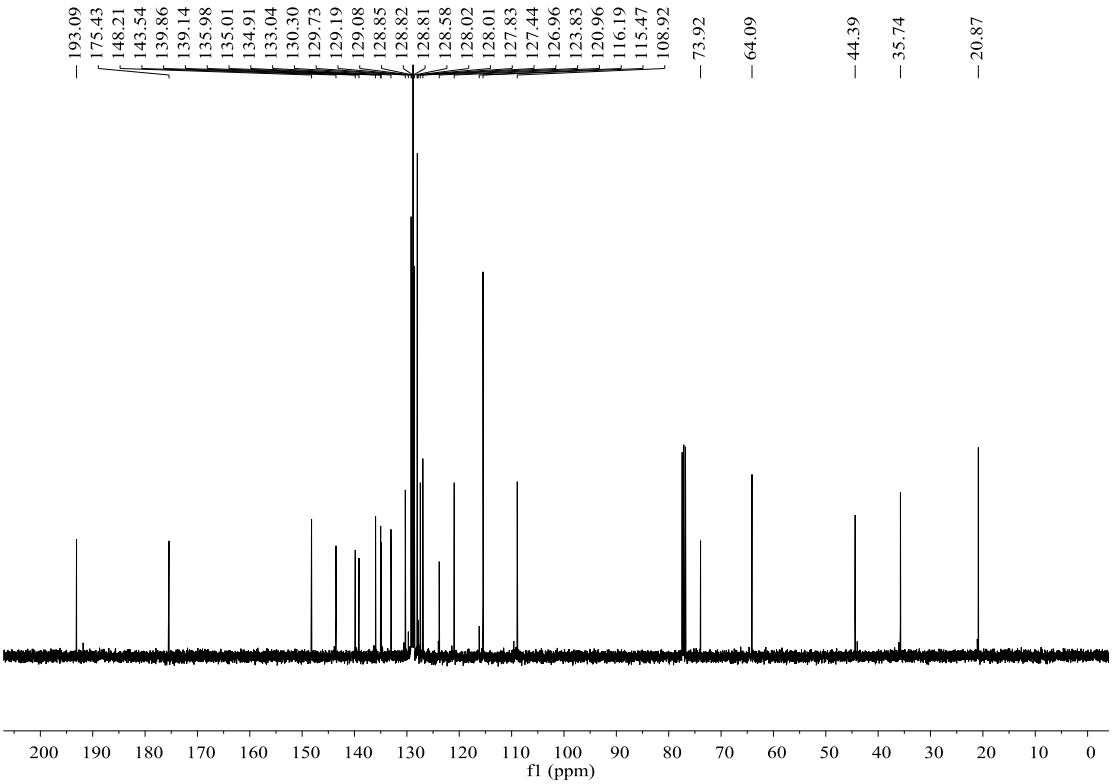


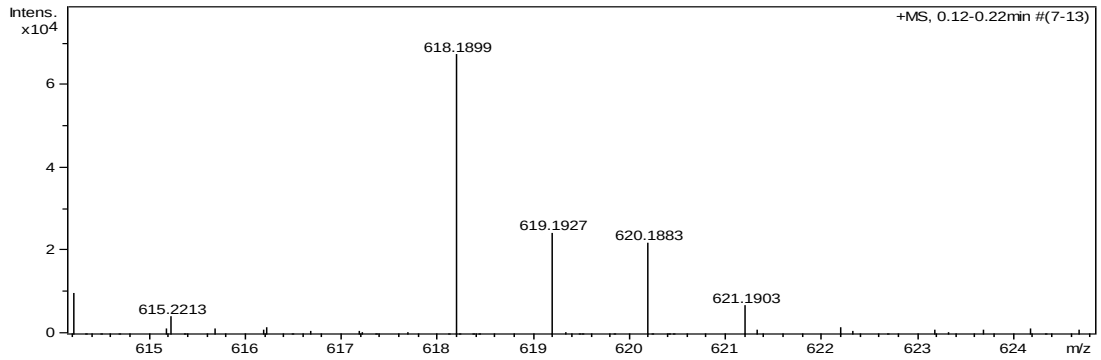

193.65
175.75
148.93
144.43
143.71
141.58
136.09
134.98
134.12
129.77
129.19
129.01
128.79
128.78
128.75
127.94
127.92
127.88
126.86
123.95
123.23
121.03
115.75
109.03
74.17
64.09
44.35
35.76
21.66
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.12-0.22min #(7-13)
584.2294
585.2322
581.2202
586.2348
0.0
0.5
1.0
1.5
2.0
581 582 583 584 585 586 587 588
m/z

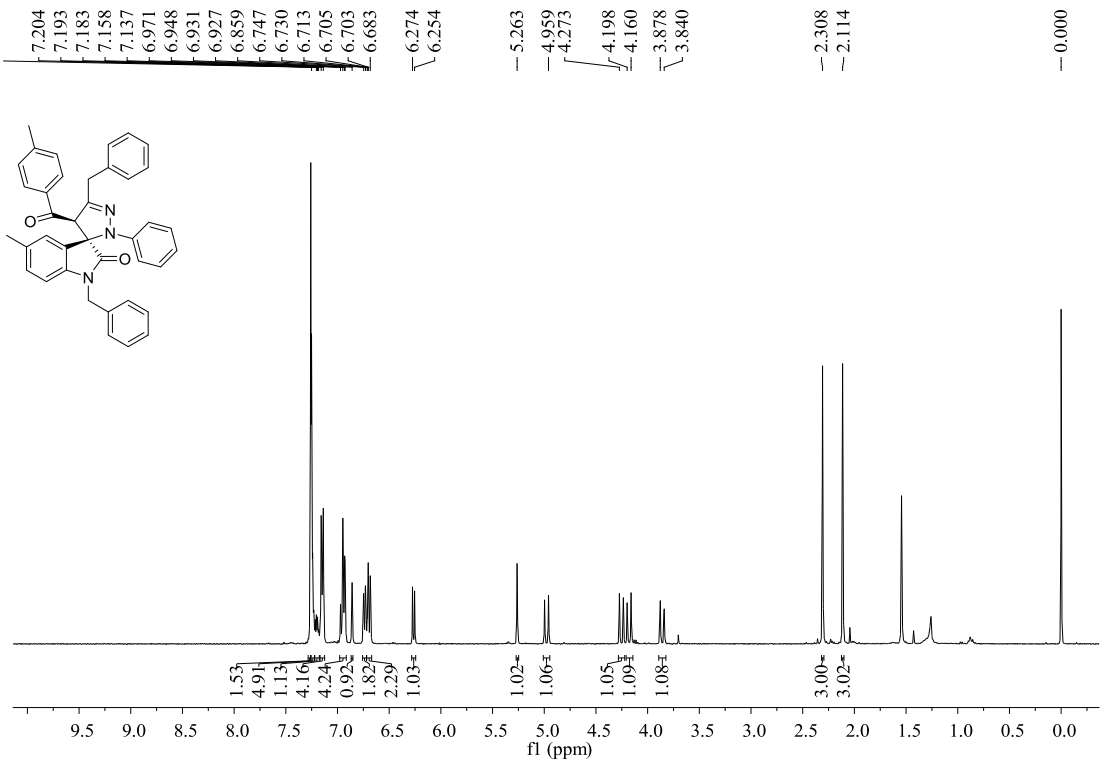
1,5'-dibenzyl-4'-(4-chlorobenzoyl)-5-methyl-2'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (4b): yellow solid, 0.452g, 76%, m.p. 163-165 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.28 (m, 2H, ArH), 7.27-7.26 (m, 1H, ArH), 7.25-7.25 (m, 3H, ArH), 7.23-7.19 (m, 2H, ArH), 7.17-7.15 (m, 3H, ArH), 7.13-7.11 (m, 1H, ArH), 7.09-7.07 (m, 2H, ArH), 6.98-6.94 (m, 2H, ArH), 6.84 (s, 1H, ArH), 6.78-6.73 (m, 2H, ArH), 6.70-6.68 (m, 2H, ArH), 6.34-6.32 (m, 1H, ArH), 5.21 (s, 1H, CH), 4.94 (d, *J* = 15.2 Hz, 1H, CH), 4.33 (d, *J* = 15.2 Hz, 1H, CH), 4.19 (d, *J* = 15.2 Hz, 1H, CH), 3.85 (d, *J* = 15.6 Hz, 1H, CH), 2.12 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.1, 175.4, 148.2, 143.5, 139.9, 139.1, 136.0, 135.0, 134.9, 133.0, 130.3, 129.7, 129.2, 129.1, 128.9, 128.8, 128.8, 128.6, 128.0, 128.0, 127.8, 127.4, 127.0, 123.8, 121.0, 116.2, 115.5, 108.9, 73.9, 64.1, 44.4, 35.7, 20.9; IR (KBr) υ : 3027., 1720, 1683, 1595, 1494, 1440, 1326, 1212, 1165, 1095, 1002, 878, 811, 740 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{30}ClN_3O_2Na$ ([M+Na]$^{+}$):618.1919, Found: 618.1899.

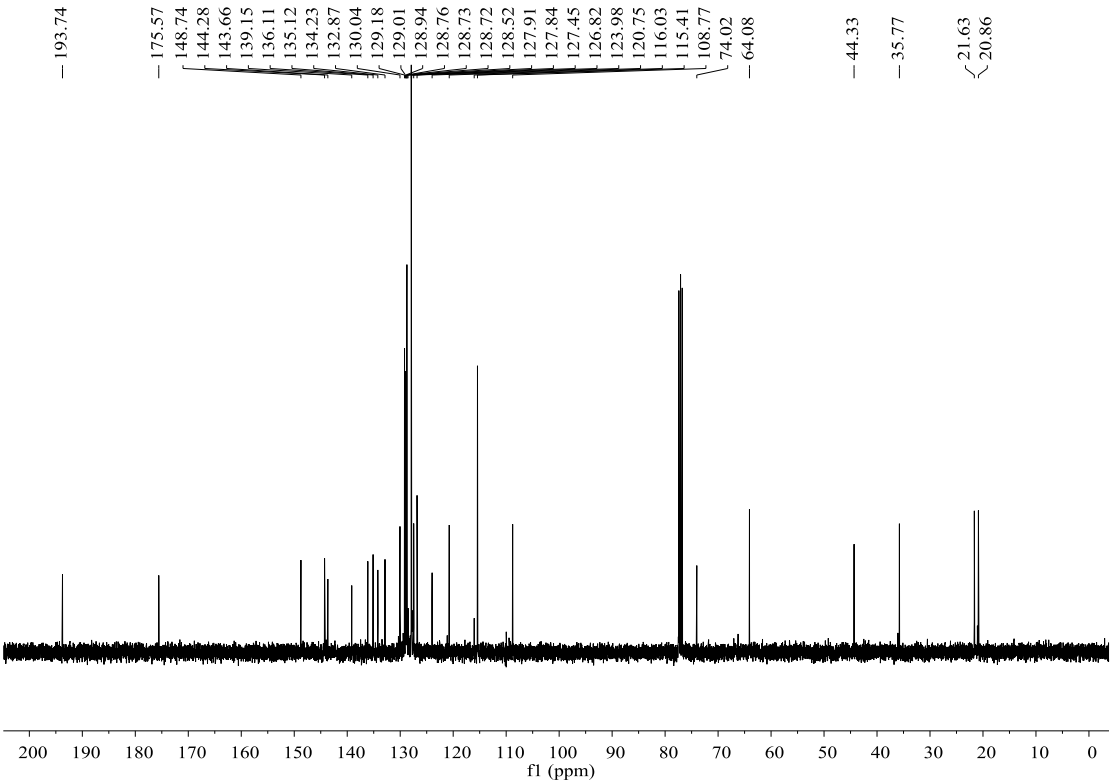



193.09
175.43
148.21
143.54
139.86
139.14
135.98
135.01
134.91
133.04
130.30
129.73
129.19
129.08
128.85
128.82
128.81
128.58
128.02
128.01
127.83
127.44
126.96
123.83
120.96
116.19
115.47
108.92
73.92
64.09
44.39
35.74
20.87
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

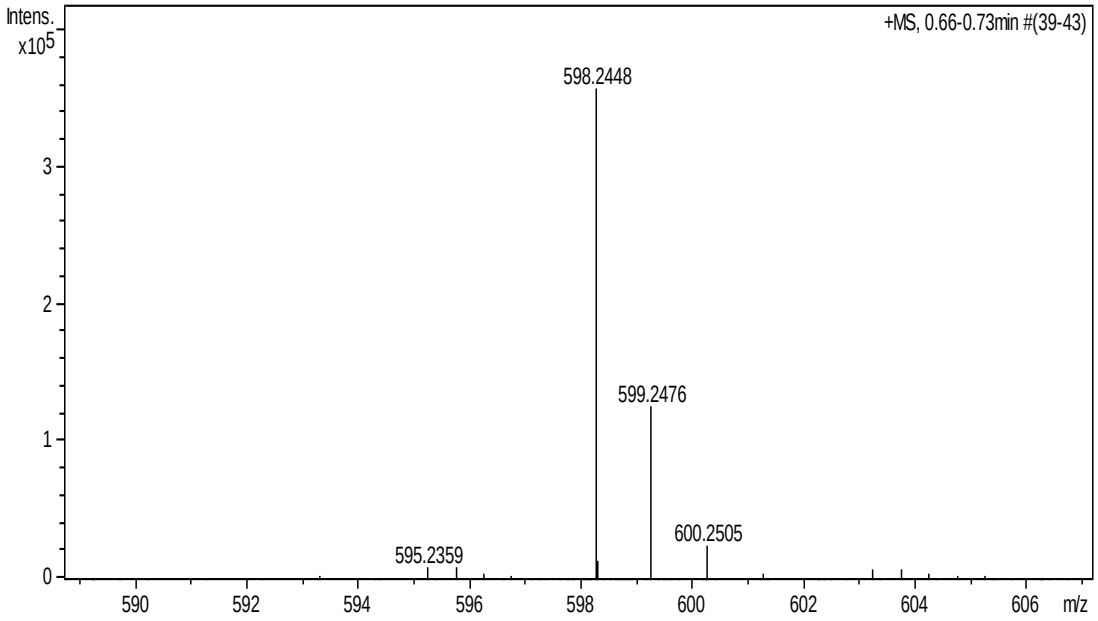

Intens.
x10^4
+MS, 0.12-0.22min #(7-13)
618.1899
619.1927
620.1883
615.2213
621.1903
0
2
4
6
615 616 617 618 619 620 621 622 623 624 m/z

1,5'-dibenzyl-5-methyl-4'-(4-methylbenzoyl)-2'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (4c): yellow solid, 0.448g, 78%, m.p. 174-176 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.28-7.26 (m, 2H, ArH), 7.25-7.23 (m, 5H, ArH), 7.21-7.18 (m, 1H, ArH), 7.16-7.14 (m, 4H, ArH), 6.97-6.93 (m, 4H, ArH), 6.86 (s, 1H, ArH), 6.75-6.73 (m, 2H, ArH), 6.71-6.68 (m, 2H, ArH), 6.27-6.25 (m, 1H, ArH), 5.26 (s, 1H, CH), 4.98 (d, *J* = 15.2 Hz, 1H, CH), 4.25 (d, *J* = 15.2 Hz, 1H, CH), 4.18 (d, *J* = 15.2 Hz, 1H, CH), 3.86 (d, *J* = 15.2 Hz, 1H, CH), 2.37 (s, 3H, CH_3) , 2.11 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.7, 175.6, 148.7, 144.3, 143.7, 139.2, 136.1, 135.1, 134.2, 132.9, 130.0, 129.2, 129.0, 128.9, 128.8, 128.7, 128.7, 128.5, 127.9, 127.8, 127.5, 126.8, 124.0, 120.8, 116.0, 115.4, 108.8, 74.0, 64.1, 44.3, 35.8, 21.6, 20.9; IR (KBr) υ : 3028, 2920, 1718, 1681, 1602, 1495, 1441, 1337, 1177, 1028, 881, 812, 740 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{39}H_{33}N_3O_2Na$ ([M+Na]$^{+}$):598.2465, Found: 598.2448.

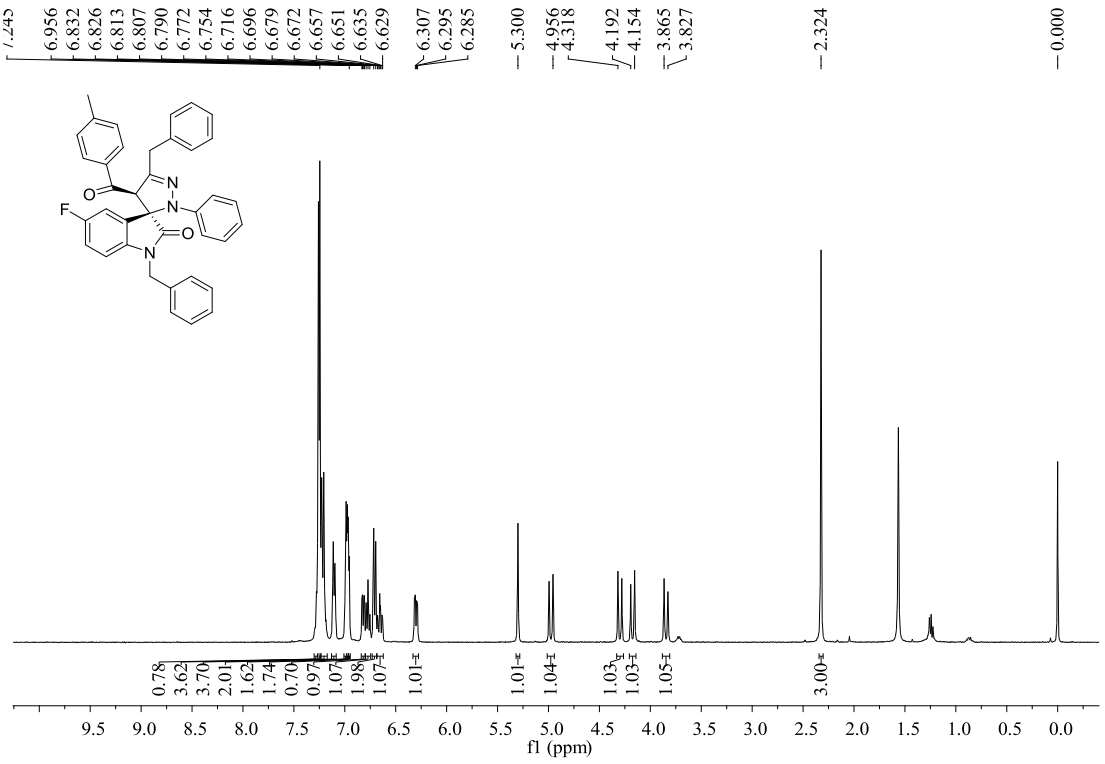


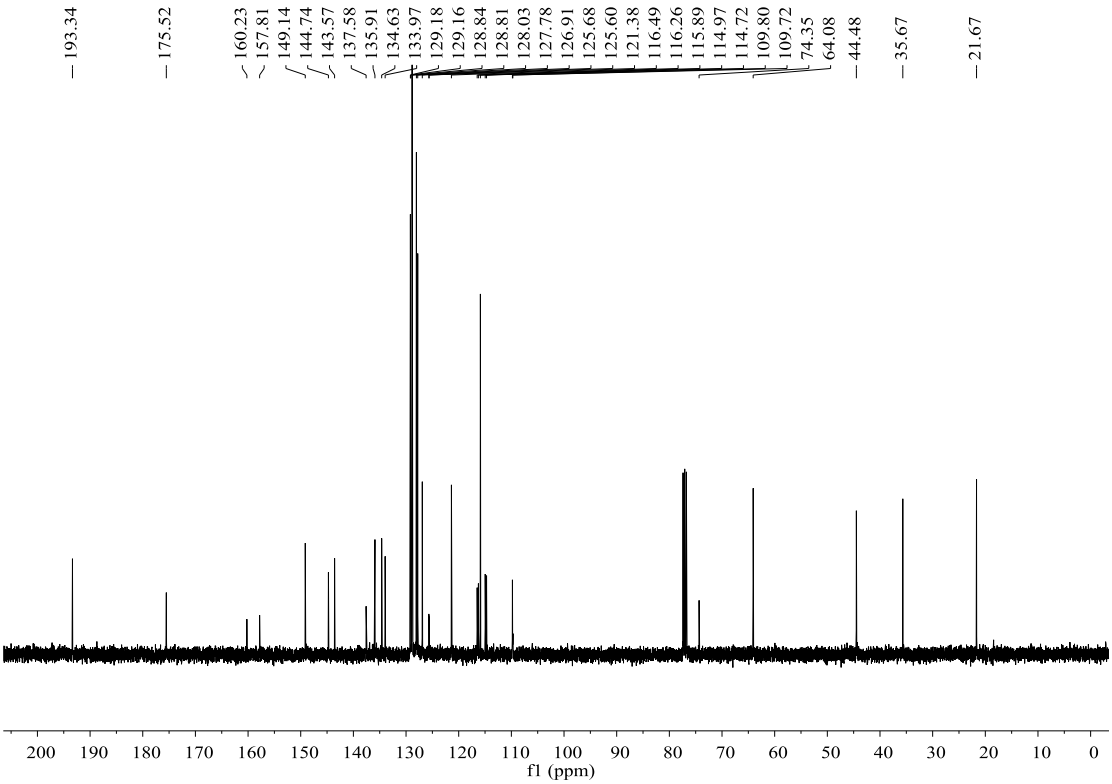

193.74
175.57
148.74
144.28
143.66
139.15
136.11
135.12
134.23
132.87
130.04
129.18
129.01
128.94
128.76
128.73
128.72
128.52
127.91
127.84
127.45
126.82
123.98
120.75
116.03
115.41
108.77
74.02
64.08
44.33
35.77
21.63
20.86
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

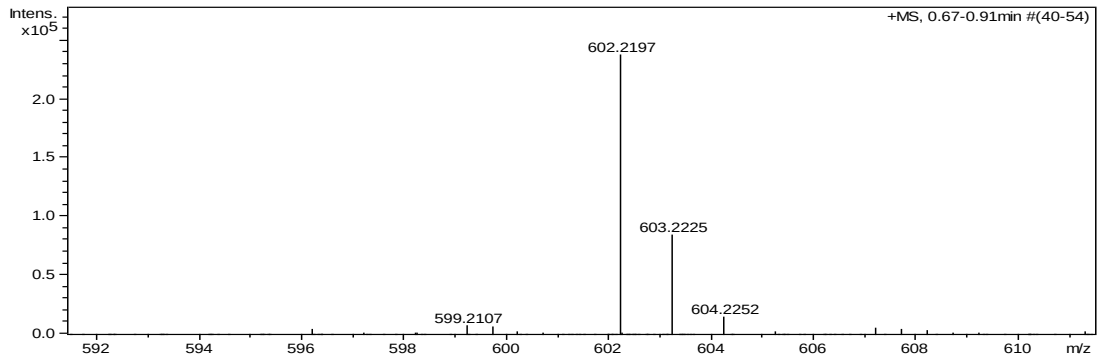
\


Intens.
x10^5
+MS, 0.66-0.73min #(39-43)
598.2448
599.2476
600.2505
595.2359
0
1
2
3
590 592 594 596 598 600 602 604 606 m/z

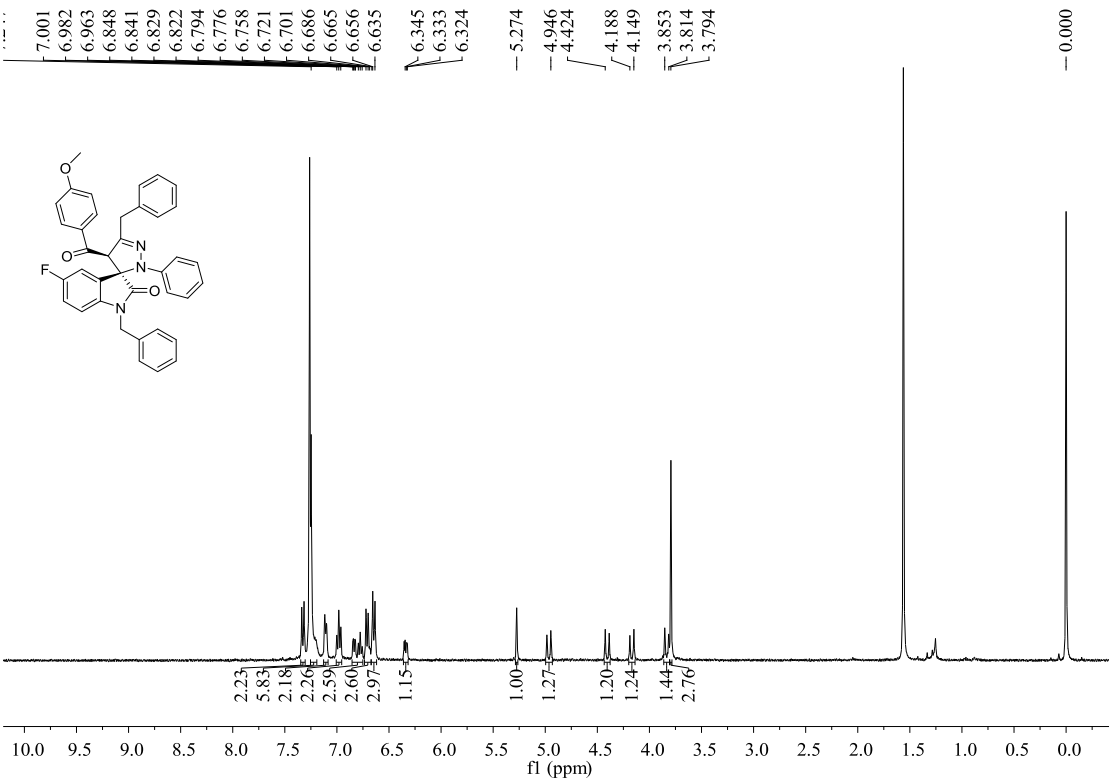
1,5'-dibenzyl-5-fluoro-4'-(4-methylbenzoyl)-2'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (4d): yellow solid, 0.448g, 80%, m.p. 132-134 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30-7.28 (m, 1H, ArH), 7.25-7.25 (m, 4H, ArH), 7.23-7.19 (m, 4H, ArH), 7.11-7.10 (m, 2H, ArH), 7.00-6.99 (m, 2H, ArH), 6.98-6.97 (m, 2H, ArH), 6.96-6.96 (m, 1H, ArH), 6.83-6.81 (m, 1H, ArH), 6.79-6.75 (m, 1H, ArH), 6.72-6.70 (m, 2H, ArH), 6.68-6.63 (m, 1H, ArH), 6.32-6.29 (m, 1H, ArH), 5.30 (s, 1H, CH), 4.97 (d, *J* = 15.2 Hz, 1H, CH), 4.30 (d, *J* = 15.2 Hz, 1H, CH), 4.17 (d, *J* = 15.2 Hz, 1H, CH), 3.85 (d, *J* = 15.2 Hz, 1H, CH), 2.32 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.3, 175.5, 159.0 (d, *J* = 242.2 Hz), 149.1, 144.7, 143.6, 137.6, 135.9, 134.6, 134.0, 129.2, 129.2, 128.8, 128.8, 128.0, 127.8, 126.9, 125.6 (d, *J* = 7.9 Hz), 121.4, 116.4 (d, *J* = 23.7 Hz), 115.9, 114.8 (d, *J* = 25.2 Hz), 109.7 (d, *J* = 7.8 Hz), 74.4, 64.1, 44.5, 35.7, 21.7; IR (KBr) υ : 3029, 2918, 1722, 1671, 1601, 1490, 1450, 1353, 1278, 1175, 1075, 1034, 994, 878, 818, 764 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{30}FN_3O_2Na$ ([M+Na]$^{+}$):602.2214, Found: 602.2197.

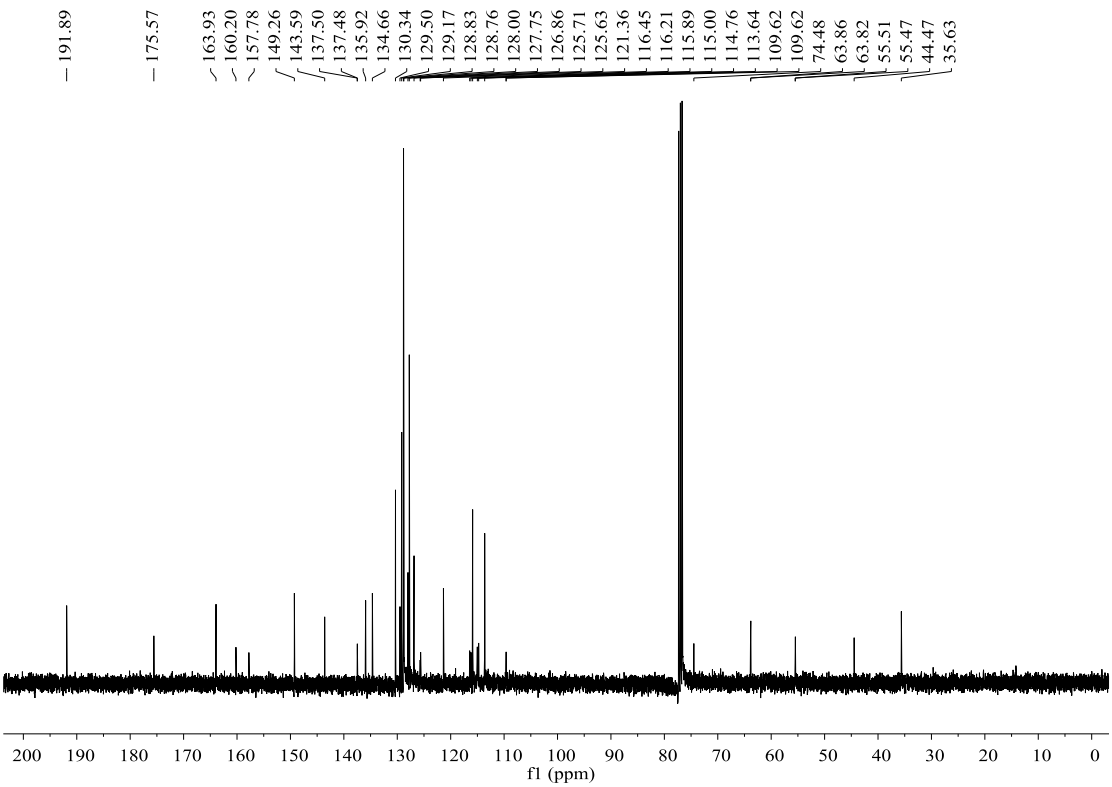


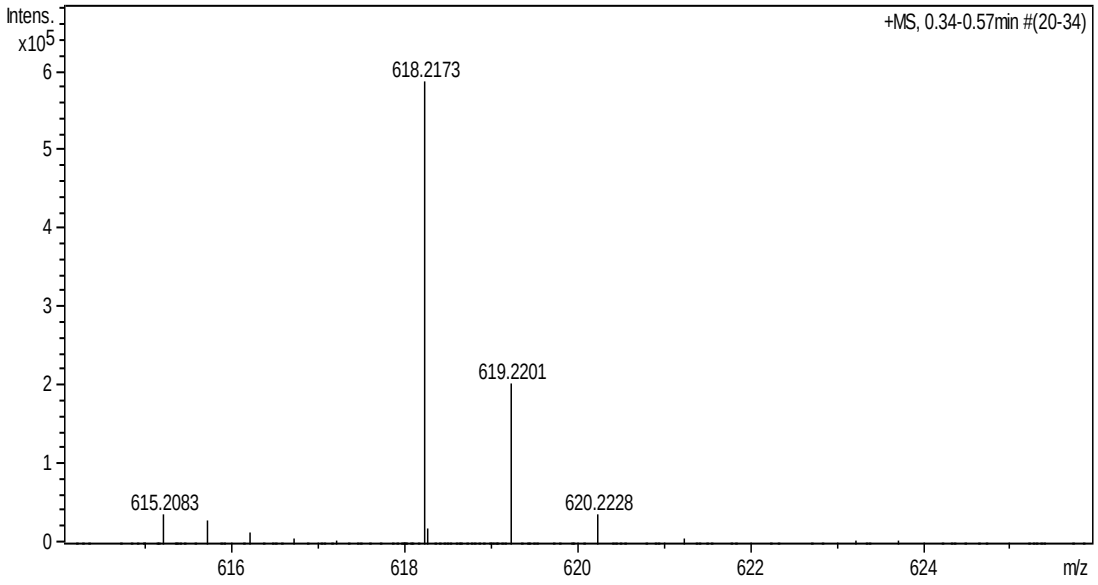

193.34
175.52
160.23
157.81
149.14
144.74
143.57
137.58
135.91
134.63
133.97
129.18
129.16
128.84
128.81
128.03
127.78
126.91
125.68
125.60
121.38
116.49
116.26
115.89
114.97
114.72
109.80
109.72
74.35
64.08
44.48
35.67
21.67
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.67-0.91min #(40-54)
602.2197
603.2225
604.2252
599.2107
2.0
1.5
1.0
0.5
0.0
592 594 596 598 600 602 604 606 608 610
m/z

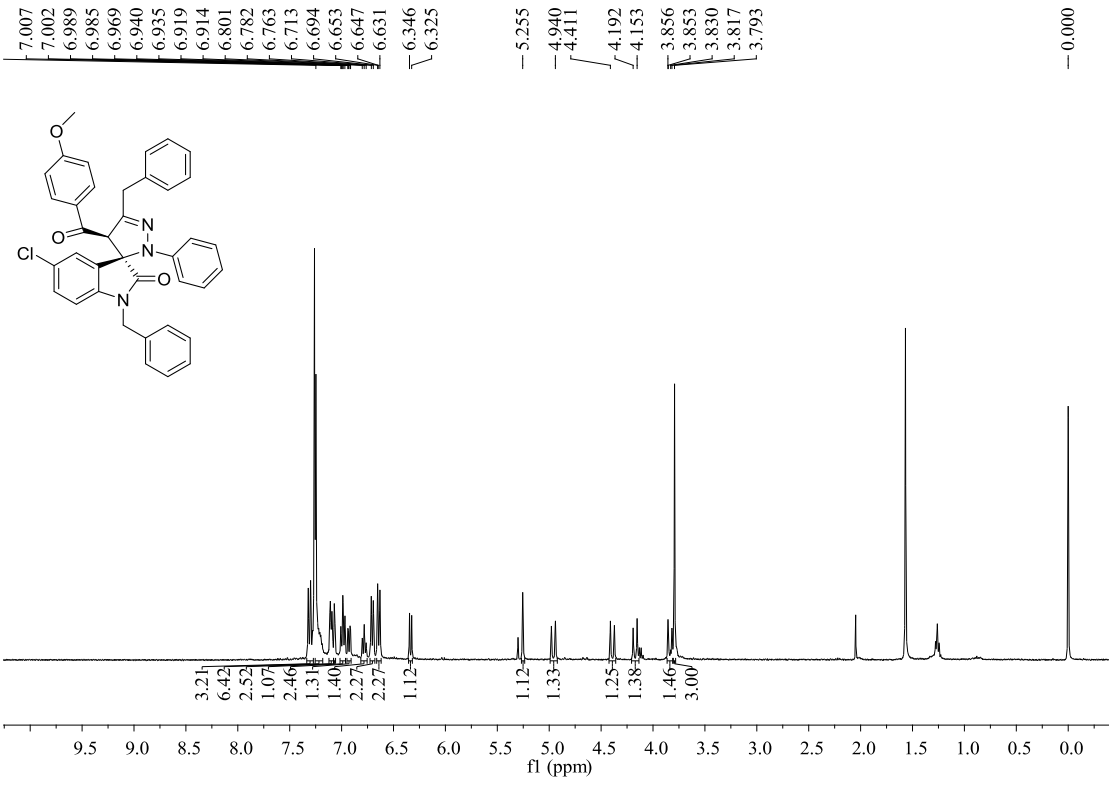
1,5'-dibenzyl-5-fluoro-4'-(4-methoxybenzoyl)-2'-phenyl-2',4'-dihydrospiro [indoline-3,3'-pyrazol]-2-one (4e): yellow solid, 0.458g, 77%, m.p. 120-122 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34-7.32 (m, 2H, ArH), 7.25-7.21 (m, 6H, ArH), 7.12-7.10 (m, 2H, ArH), 7.00-6.96 (m, 2H, ArH), 6.85-6.76 (m, 3H, ArH), 6.72-6.69 (m, 3H, ArH), 6.67-6.64 (m, 3H, ArH), 6.36-6.32 (m, 1H, ArH), 5.27 (s, 1H, CH), 4.97 (d, *J* = 15.6 Hz, 1H, CH), 4.40 (d, *J* = 15.2 Hz, 1H, CH), 4.17 (d, *J* = 15.6 Hz, 1H, CH), 3.83 (d, *J* = 15.6 Hz, 1H, CH), 3.80 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.9, 175.6, 163.9, 159.0 (d, *J* = 242.1 Hz), 149.3, 143.6, 137.5 (d, *J* = 1.9 Hz), 135.9, 134.7, 130.3, 129.5, 129.2, 128.8, 128.7, 128.0, 127.8, 126.9, 125.7 (d, *J* = 7.7 Hz), 121.4, 116.3 (d, *J* = 23.6 Hz), 115.9, 114.9 (d, *J* = 24.0 Hz), 113.6, 109.6, 74.5, 63.9, 63.8, 55.5, 55.5, 44.5, 35.6; IR (KBr) υ : 3025, 1729, 1676, 1596, 1492, 1455, 13729, 1320, 1267, 1215, 1166, 1024, 954, 883, 810, 753, 712 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{30}FN_3O_3Na$ ($[M+Na]^+$):618.2163, Found: 618.2173.

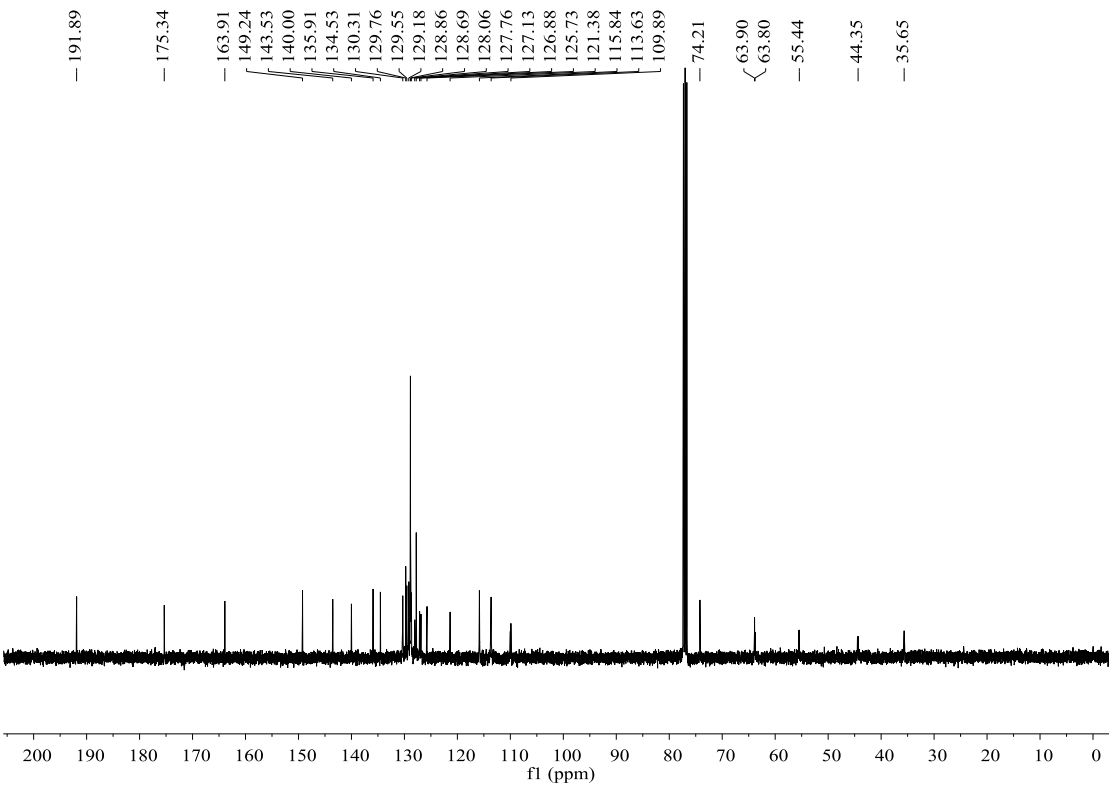


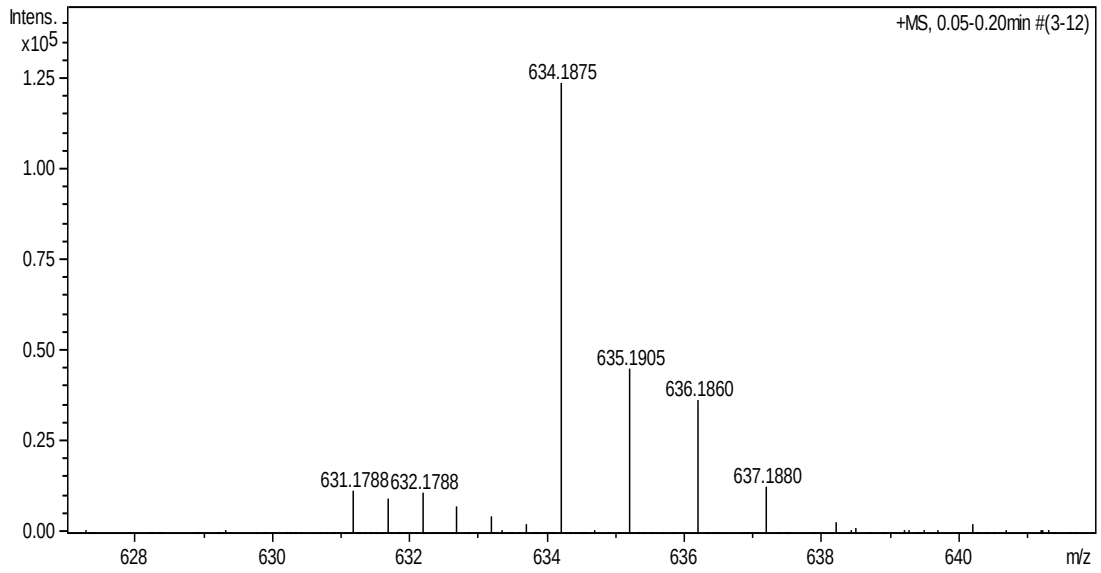

191.89
175.57
163.93
160.20
157.78
149.26
143.59
137.50
137.48
135.92
134.66
130.34
129.50
129.17
128.83
128.76
128.00
127.75
126.86
125.71
125.63
121.36
116.45
116.21
115.89
115.00
114.76
113.64
109.62
109.62
74.48
63.86
63.82
55.51
55.47
44.47
35.63
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.34-0.57min #(20-34)
618.2173
619.2201
615.2083
620.2228
0
1
2
3
4
5
6
616
618
620
622
624
m/z

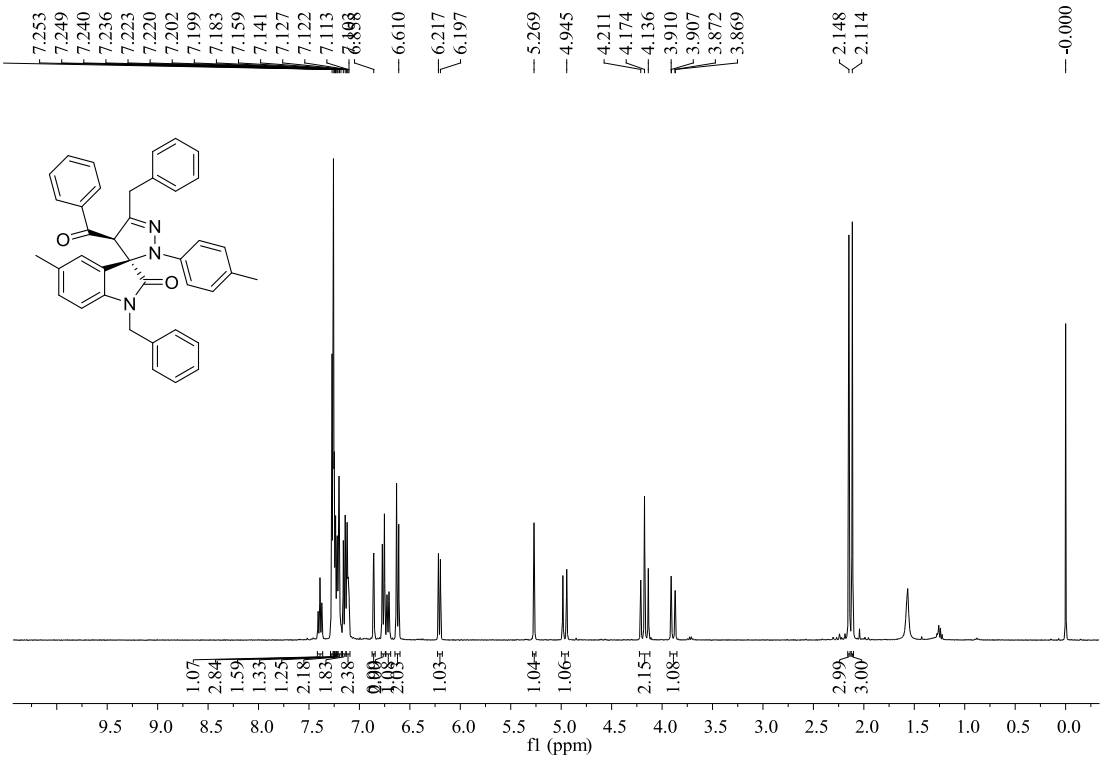
1,5'-dibenzyl-5-chloro-4'-(4-methoxybenzoyl)-2'-phenyl-2',4'-dihydrospiro [indoline-3,3'-pyrazol]-2-one (4f): yellow solid, 0.458g, 75%, m.p. 128-130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32-7.28 (m, 3H, ArH), 7.25-7.19 (m, 6H, ArH), 7.11-7.09 (m, 3H, ArH), 7.07-7.07 (m, 1H, ArH), 7.01-6.97 (m, 2H, ArH), 6.94-6.91 (m, 1H, ArH), 6.80-6.76 (m, 1H, ArH), 6.71-6.69 (m, 2H, ArH), 6.65-6.63 (m, 2H, ArH), 6.35-6.33 (m, 1H, ArH), 5.26 (s, 1H, CH), 4.96 (d, *J* = 15.6 Hz, 1H, CH), 4.39 (d, *J* = 15.6 Hz, 1H, CH), 4.17 (d, *J* = 15.6 Hz, 1H, CH), 3.86-3.82 (m, 1H, CH), 3.79 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.9, 175.3, 163.9, 149.2, 143.5, 140.0, 135.9, 134.5, 130.3, 129.8, 129.6, 129.2, 128.9, 128.7, 128.1, 127.8, 127.1, 126.9, 125.7, 121.4, 115.8, 113.6, 109.9, 74.2, 63.9, 63.8, 55.4, 44.4, 35.7; IR (KBr) υ : 3026, 1723, 1668, 1599, 1575, 1491, 1454, 1434, 1348, 1268, 1234, 1187, 1116, 1081, 1027, 992, 963, 892, 846, 822, 764, 725 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{30}ClN_3O_3Na$ ([M+Na]$^{+}$):634.1868, Found: 634.1875.

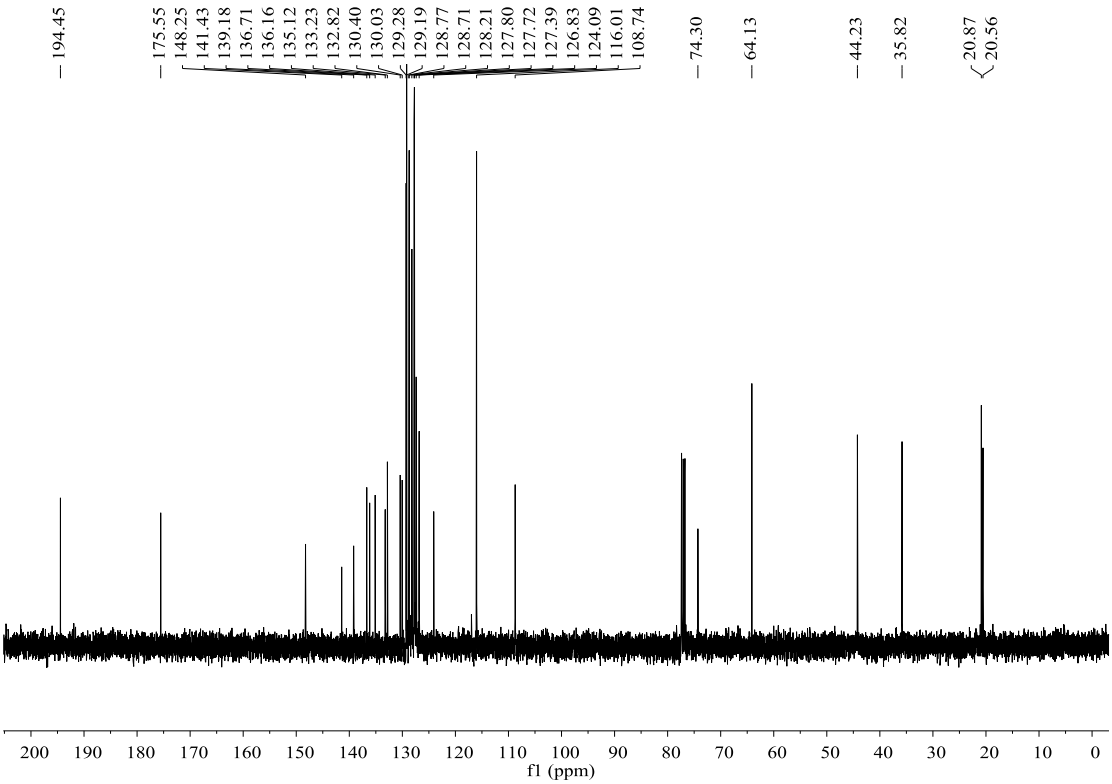


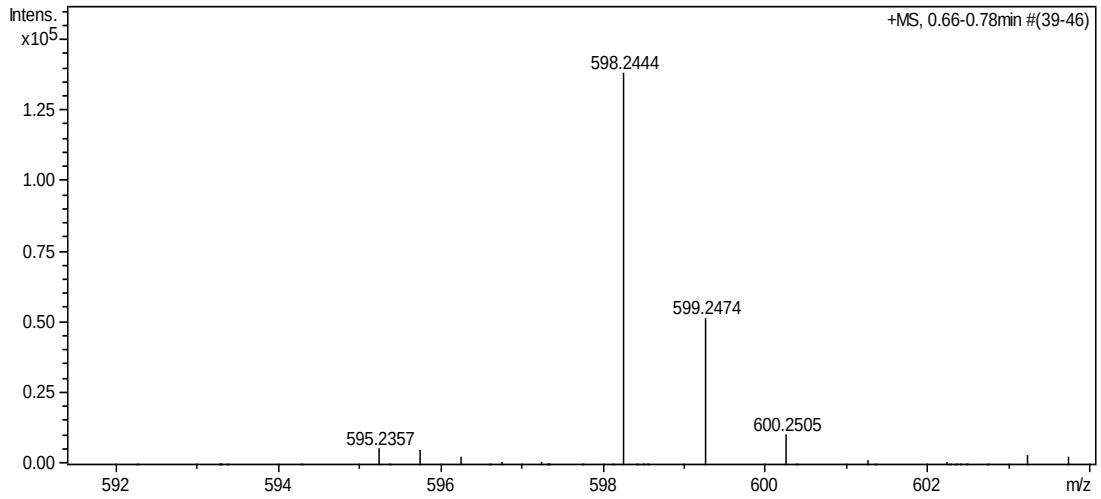

191.89
175.34
163.91
149.24
143.53
140.00
135.91
134.53
130.31
129.76
129.55
129.18
128.86
128.69
128.06
127.76
127.13
126.88
125.73
121.38
115.84
113.63
109.89
74.21
63.90
63.80
55.44
44.35
35.65
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
1.25
1.00
0.75
0.50
0.25
0.00
+MS, 0.05-0.20min #(3-12)
634.1875
635.1905
636.1860
631.1788
632.1788
637.1880
628
630
632
634
636
638
640
m/z

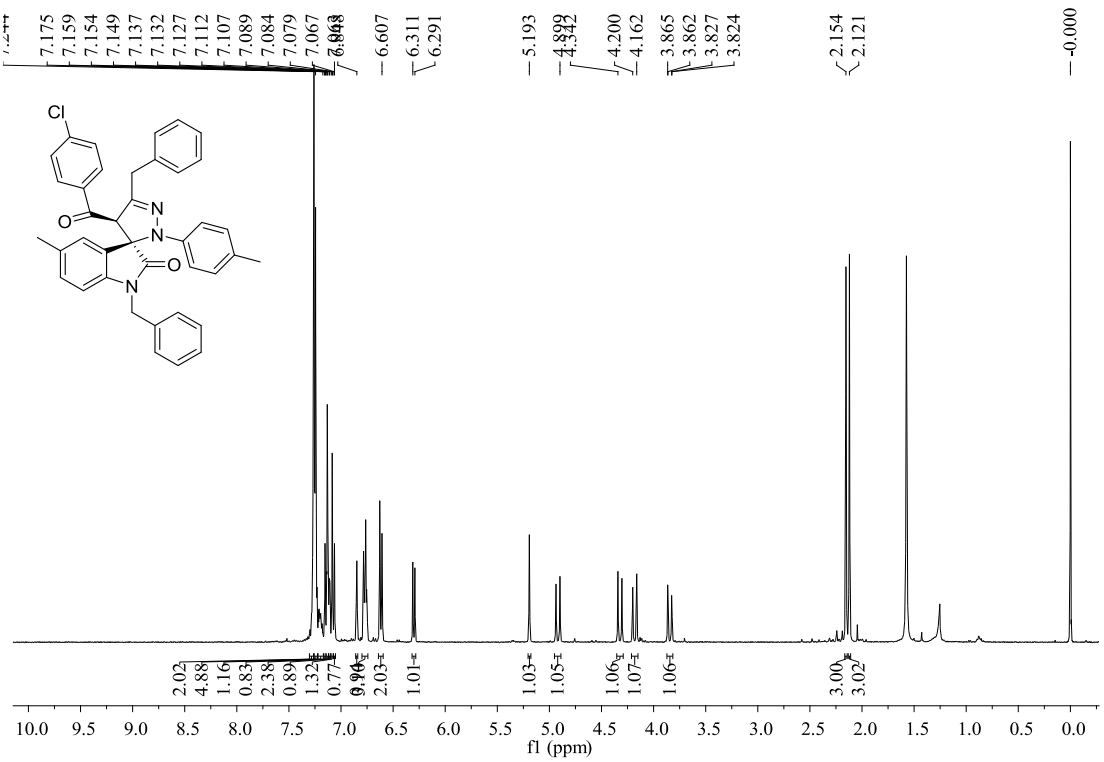
4'-benzoyl-1,5'-dibenzyl-5-methyl-2'-(p-tolyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (4g): yellow solid, 0.518g, 90%, m.p. 140-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.37 (m, 1H, ArH), 7.27-7.26 (m, 3H, ArH), 7.25-7.25 (m, 2H, ArH), 7.24-7.24 (m, 1H, ArH), 7.22-7.22 (m, 1H, ArH), 7.20-7.18 (m, 2H, ArH), 7.16-7.14 (m, 2H, ArH), 7.13-7.10 (m, 2H, ArH), 6.86 (s, 1H, ArH), 6.77-6.75 (m, 2H, ArH), 6.73-6.70 (m, 1H, ArH), 6.63-6.61 (m, 2H, ArH), 5.27 (s, 1H, CH), 4.96 (d, J = 15.2 Hz, 1H, CH), 4.17 (t, J_1 = 15.2 Hz, J_2 = 14.8 Hz, 2H, CH), 3.89 (dd, J_1 = 1.2 Hz, J_2 = 15.2 Hz, 1H, CH), 2.15 (s, 3H, CH_3), 2.11 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 194.5, 175.6, 148.3, 141.4, 139.2, 136.7, 136.2, 135.1, 133.2, 132.8, 130.4, 130.0, 129.3, 129.2, 128.8, 128.7, 128.2, 127.8, 127.7, 127.4, 126.8, 124.1, 116.0, 108.7, 74.3, 64.1, 44.2, 35.8, 20.9, 20.6; IR (KBr) υ : 3029, 2923, 1888, 1720, 1678, 1606, 1501, 1442, 1334, 1205, 1072, 994, 885, 814, 757 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{39}H_{33}N_3O_2Na$ ($[M+Na]^+$):598.2465, Found: 598.2444.

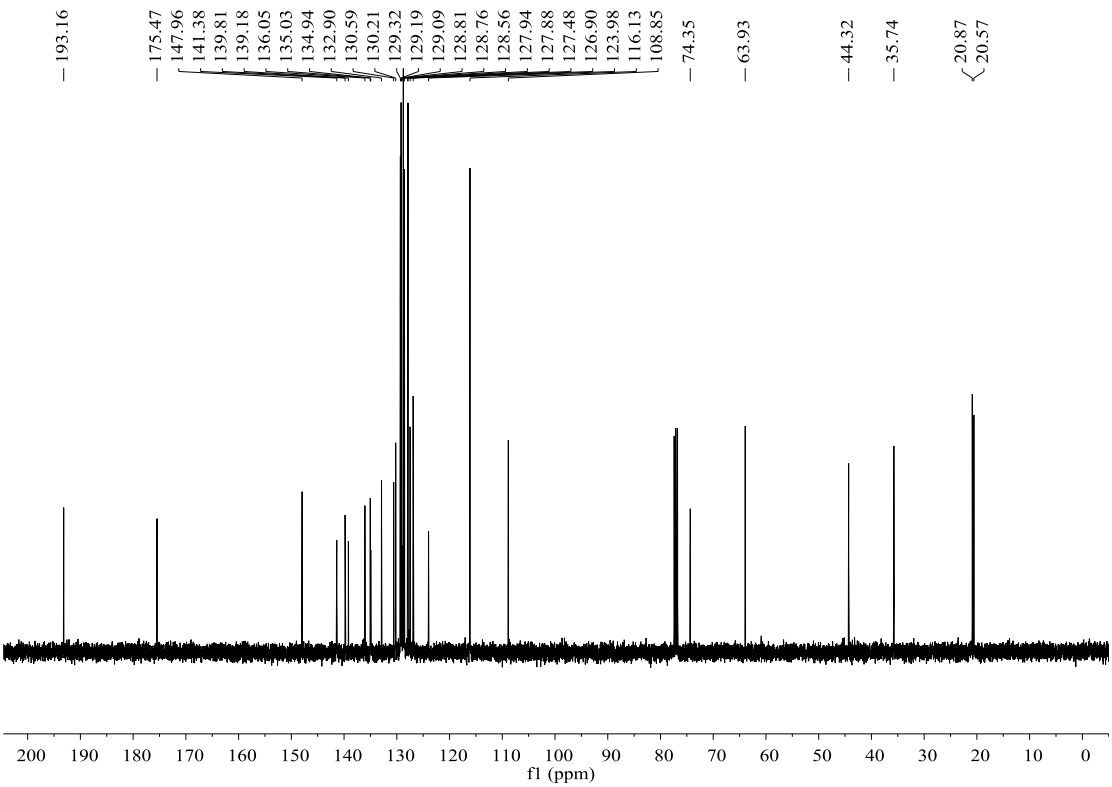


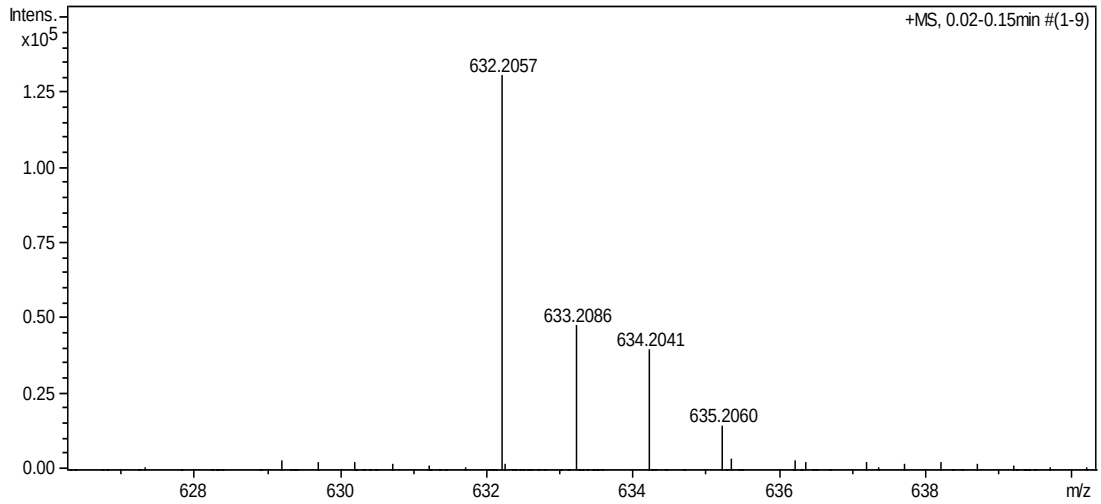

194.45
175.55
148.25
141.43
139.18
136.71
136.16
135.12
133.23
132.82
130.40
130.03
129.28
129.19
128.77
128.71
128.21
127.80
127.72
127.39
126.83
124.09
116.01
108.74
74.30
64.13
44.23
35.82
20.87
20.56
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.66-0.78min #(39-46)
598.2444
599.2474
595.2357
600.2505
1.25
1.00
0.75
0.50
0.25
0.00
592
594
596
598
600
602
m/z

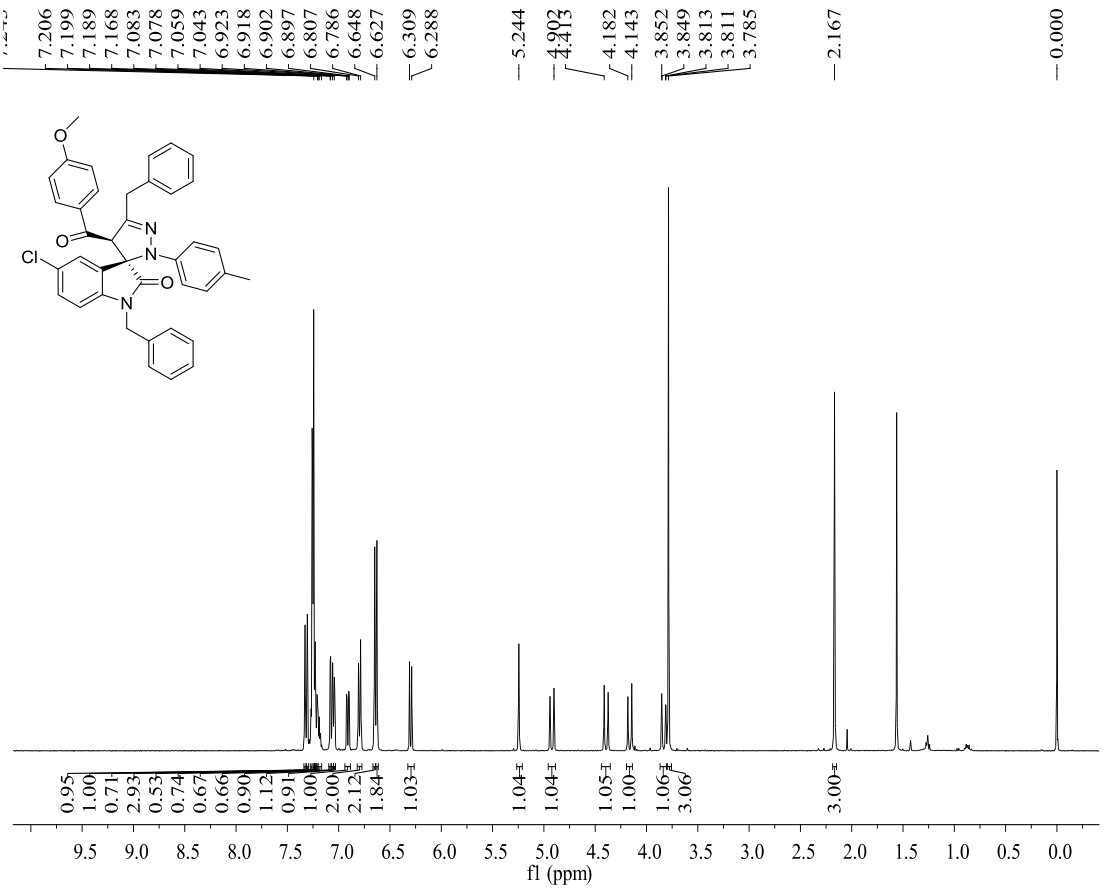
1,5'-dibenzyl-4'-(4-chlorobenzoyl)-5-methyl-2'-(p-tolyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (4h): yellow solid, 0.499g, 82%, m.p. 144-146 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30-7.27 (m, 2H, ArH), 7.25-7.23 (m, 5H, ArH), 7.22-7.18 (m, 1H, ArH), 7.16-7.15 (m, 1H, ArH), 7.14-7.13 (m, 2H, ArH), 7.11-7.11 (m, 1H, ArH), 7.09-7.08 (m, 1H, ArH), 7.07-7.06 (m, 1H, ArH), 6.85 (s, 1H, ArH), 6.78-6.75 (m, 3H, ArH), 6.63-6.61 (m, 2H, ArH), 6.31-6.29 (m, 1H, ArH), 5.19 (s, 1H, CH), 4.92 (d, *J* = 15.2 Hz, 1H, CH), 4.32 (d, *J* = 15.2 Hz, 1H, CH), 4.18 (d, *J* = 15.2 Hz, 1H, CH), 3.84 (dd, J_1 = 1.2 Hz, J_2 = 15.2 Hz, 1H, CH), 2.15 (s, 3H, CH_3) , 2.12 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 193.2, 175.5, 148.0, 141.4, 139.8, 139.2, 136.1, 135.0, 134.9, 132.9, 130.6, 130.2, 129.3, 129.2, 129.1, 128.8, 128.8, 128.6, 127.9, 127.9, 127.5, 126.9, 124.0, 116.1, 108.9, 74.4, 63.9, 44.3, 35.7, 20.9, 20.6; IR (KBr) υ : 3030, 2916, 1719, 1678, 1602, 1505, 1439, 1329, 1214, 1182, 1086, 1023, 883, 812, 721 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{39}H_{32}ClN_3O_2Na$ ([M+Na]$^{+}$):632.2075, Found: 632.2057.

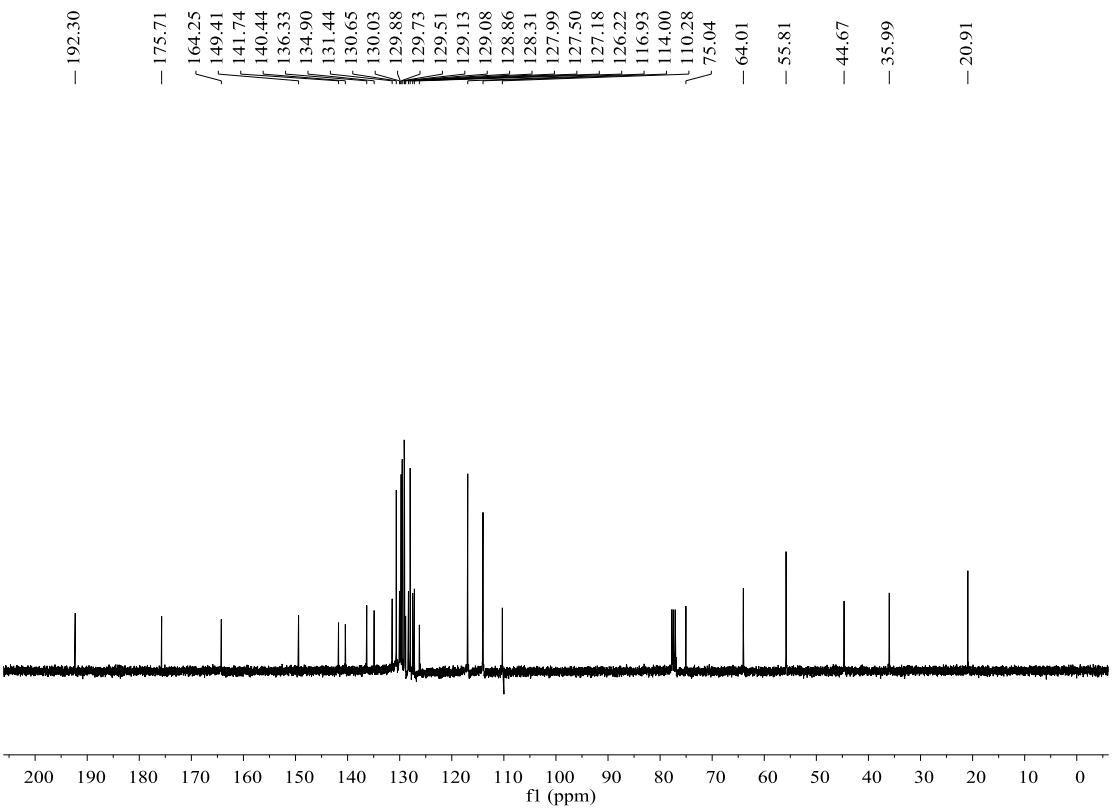


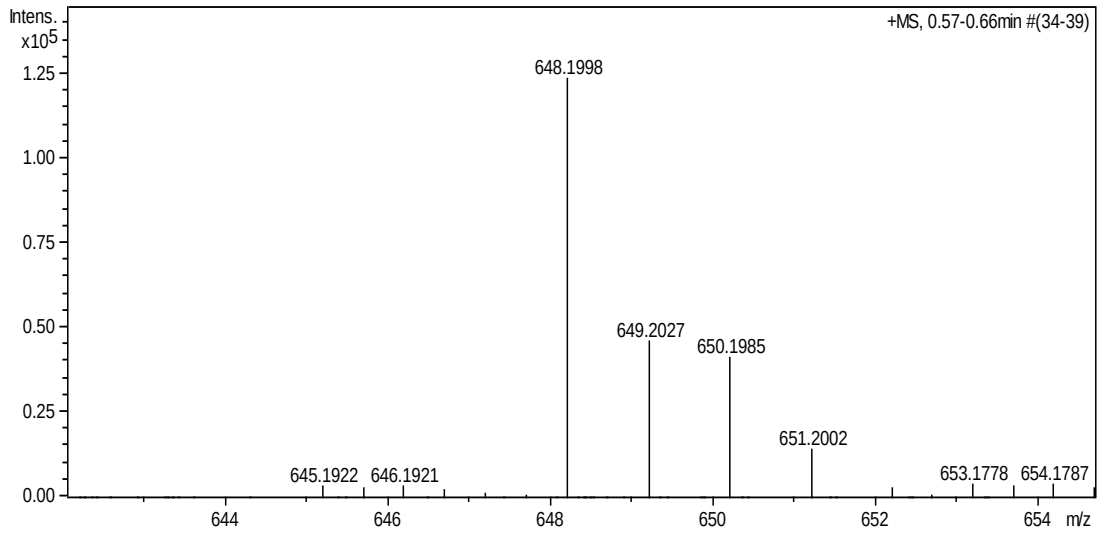

193.16
175.47
147.96
141.38
139.81
139.18
136.05
135.03
134.94
132.90
130.59
130.21
129.32
129.19
129.09
128.81
128.76
128.56
127.94
127.88
127.48
126.90
123.98
116.13
108.85
74.35
63.93
44.32
35.74
20.87
20.57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.02-0.15min #(1-9)
632.2057
633.2086
634.2041
635.2060
1.25
1.00
0.75
0.50
0.25
0.00
628
630
632
634
636
638
m/z

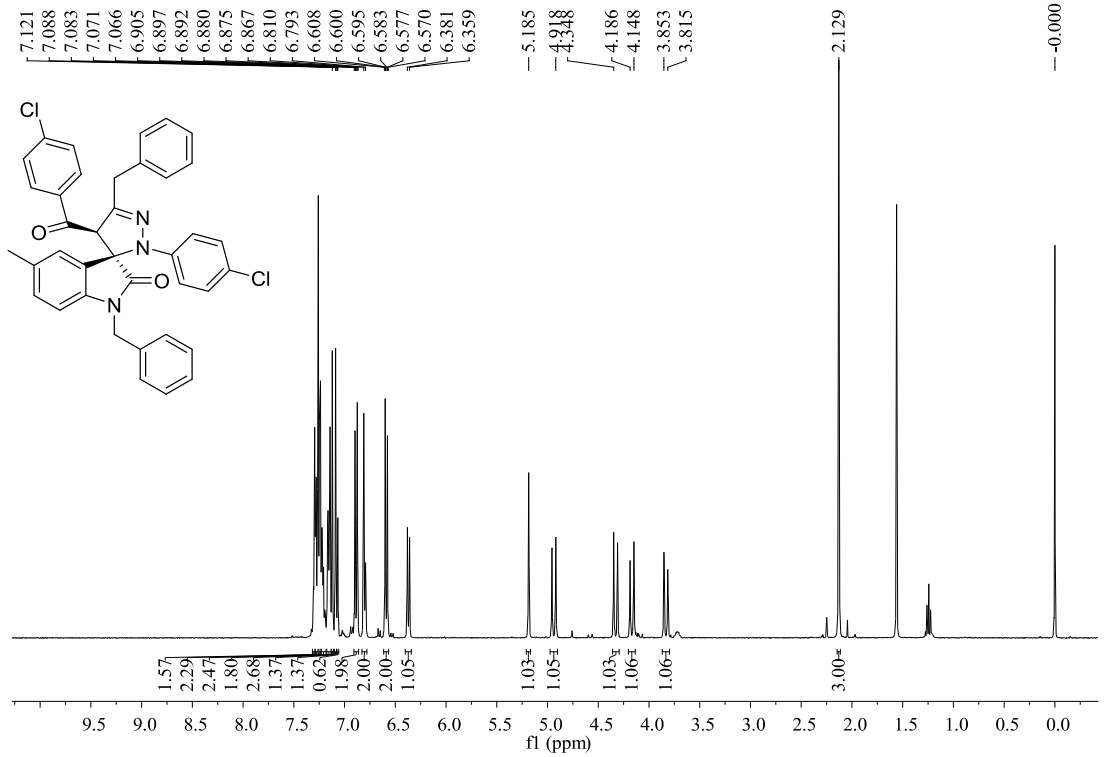
1,5'-dibenzyl-5-chloro-4'-(4-methoxybenzoyl)-2'-(p-tolyl)-2',4'-dihydrospiro [indoline-3,3'-pyrazol]-2-one (4i): yellow solid, 0.500g, 80%, m.p. 163-165 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34-7.32 (m, 1H, ArH), 7.31-7.30 (m, 1H, ArH), 7.27-7.27 (m, 1H, ArH), 7.25-7.24 (m, 5H, ArH), 7.23-7.22 (m, 1H, ArH), 7.22-7.21 (m, 1H, ArH), 7.20-7.17 (m, 1H, ArH), 7.08-7.08 (m, 1H, ArH), 7.06-7.04 (m, 2H, ArH), 7.02-6.90 (m, 1H, ArH), 6.81-6.79 (m, 2H, ArH), 6.65-6.63 (m, 4H, ArH), 6.31-6.29 (m, 1H, ArH), 5.24 (s, 1H, CH), 4.92 (d, J = 15.2 Hz, 1H, CH), 4.39 (d, J = 15.6 Hz, 1H, CH), 4.16 (d, J = 15.6 Hz, 1H, CH), 3.83 (dd, J_1 = 1.2 Hz, J_2 = 15.6 Hz, 1H, CH), 3.79 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.3, 175.7, 164.3, 149.4, 141.7, 140.4, 136.3, 134.9, 131.4, 130.7, 130.0, 129.9, 129.7, 129.5, 129.1, 129.1, 128.9, 128.3, 128.0, 127.5, 127.2, 126.2, 116.9, 114.0, 110.3, 75.0, 64.0, 55.8, 44.7, 36.0, 20.9; IR (KBr) υ : 3027, 2922, 1722, 1668, 1601, 1504, 1429, 1349, 1267, 1228, 1182, 1110, 1075, 1027, 885, 822, 712 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{39}H_{32}ClN_3O_3Na$ ([M+Na]$^{+}$):648.2024, Found: 648.1998.

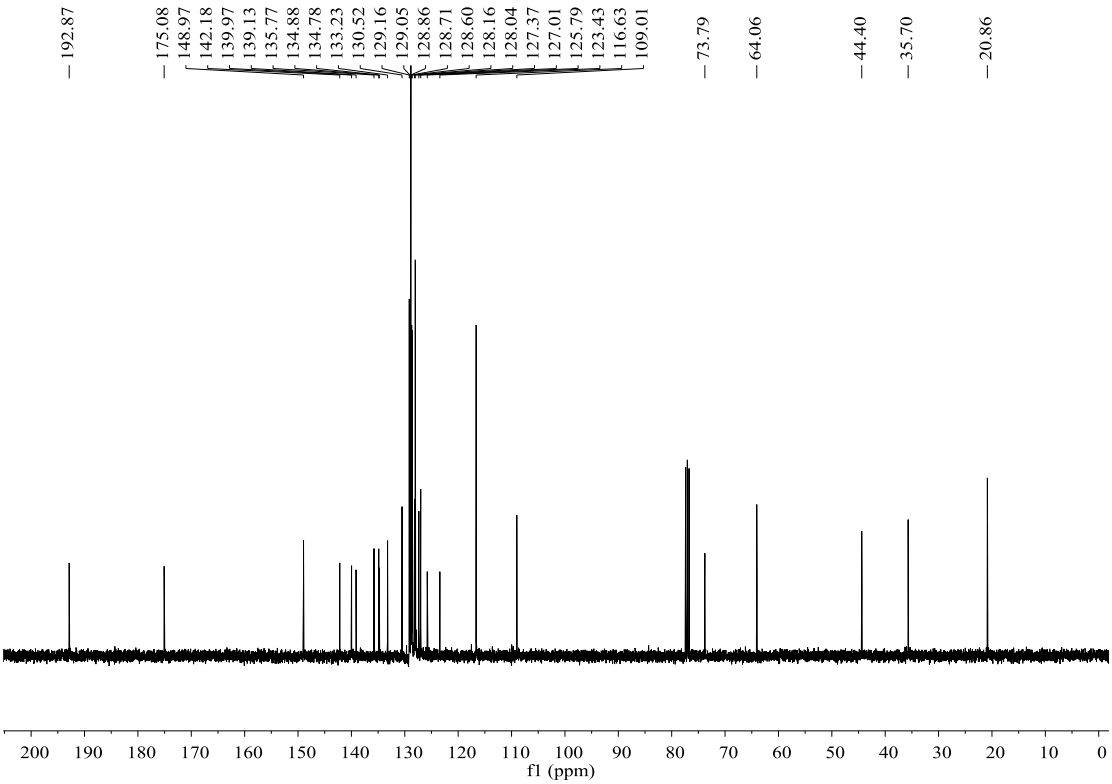


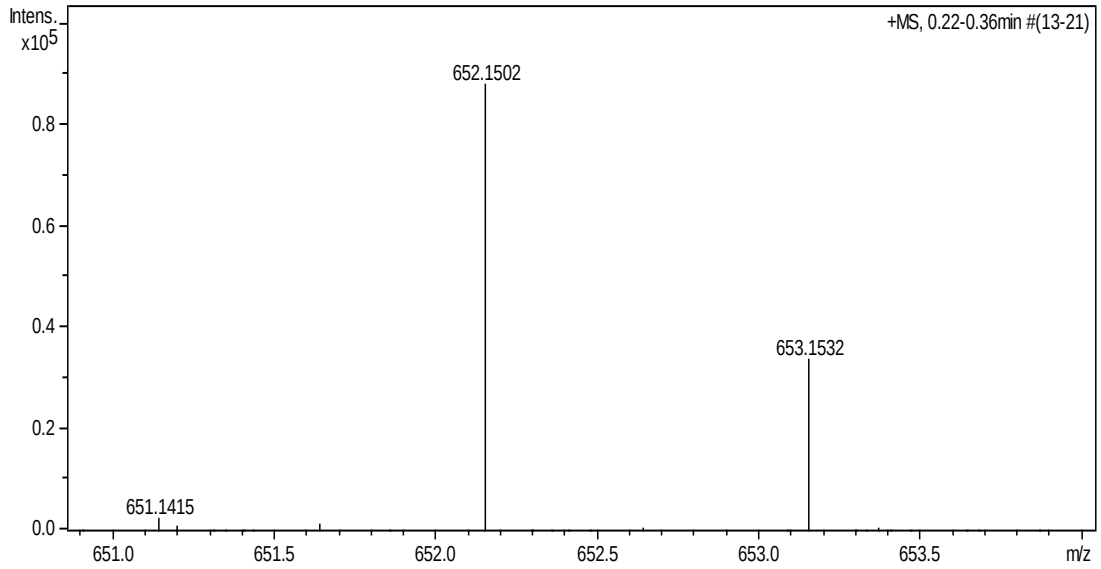

192.30
175.71
164.25
149.41
141.74
140.44
136.33
134.90
131.44
130.65
130.03
129.88
129.73
129.51
129.13
129.08
128.86
128.31
127.99
127.50
127.18
126.22
116.93
114.00
110.28
75.04
64.01
55.81
44.67
35.99
20.91
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.57-0.66min #(34-39)
1.25
1.00
0.75
0.50
0.25
0.00
648.1998
649.2027
650.1985
651.2002
645.1922
646.1921
653.1778
654.1787
644
646
648
650
652
654
m/z

1,5'-dibenzyl-4'-(4-chlorobenzoyl)-2'-(4-chlorophenyl)-5-methyl-2',4'-dihydrospiro [indoline-3,3'-pyrazol]-2-one (4j): yellow solid, 0.440g, 70%, m.p. 145-147 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31-7.30 (m, 2H, ArH), 7.29-7.27 (m, 2H, ArH), 7.25-7.24 (m, 2H, ArH), 7.23-7.19 (m, 2H, ArH), 7.17-7.14 (m, 3H, ArH), 7.13-7.12 (m, 1H, ArH), 7.09-7.08 (m, 1H, ArH), 7.07-7.07 (m, 1H, ArH), 6.91-6.87 (m, 2H, ArH), 6.81-6.79 (m, 2H, ArH), 6.61-6.57 (m, 2H, ArH), 6.38-6.36 (m, 1H, ArH), 5.19 (s, 1H, CH), 4.94 (d, *J* = 15.2 Hz, 1H, CH), 4.33 (d, *J* = 15.2 Hz, 1H, CH), 4.17 (d, *J* = 15.2 Hz, 1H, CH), 3.83 (d, *J* = 15.2 Hz, 1H, CH), 2.13 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 192.9, 175.1, 149.0, 142.2, 140.0, 139.1, 135.8, 134.9, 134.8, 133.2, 130.5, 129.2, 129.1, 128.9, 128.7, 128.6, 128.2, 128.0, 127.4, 127.0, 125.8, 123.4, 116.6, 109.0, 73.8, 64.1, 44.4, 35.7, 20.9; IR (KBr) υ : 3054, 1720, 1677, 1591, 1491, 1439, 1332, 1217, 1181, 1087, 1023, 885, 816, 719 cm^{-1}; MS (*m*/*z*): HRMS (ESI-TOF) Calcd. for $C_{38}H_{29}Cl_2N_3O_2Na$ ([M+Na]$^{+}$):652.1529, Found: 652.1502.




192.87
175.08
148.97
142.18
139.97
139.13
135.77
134.88
134.78
133.23
130.52
129.16
129.05
128.86
128.71
128.60
128.16
128.04
127.37
127.01
125.79
123.43
116.63
109.01
73.79
64.06
44.40
35.70
20.86
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Intens.
x10^5
+MS, 0.22-0.36min #(13-21)
652.1502
653.1532
651.1415
0.0
0.2
0.4
0.6
0.8
651.0
651.5
652.0
652.5
653.0
653.5
m/z