Diastereoselective construction of carbazole-based spirooxindoles via Levy three-component Reaction

Shao-Cong Zhan, Jing Sun, Ru-Zhang Liu, Chao-Guo Yan*

Supporting Information

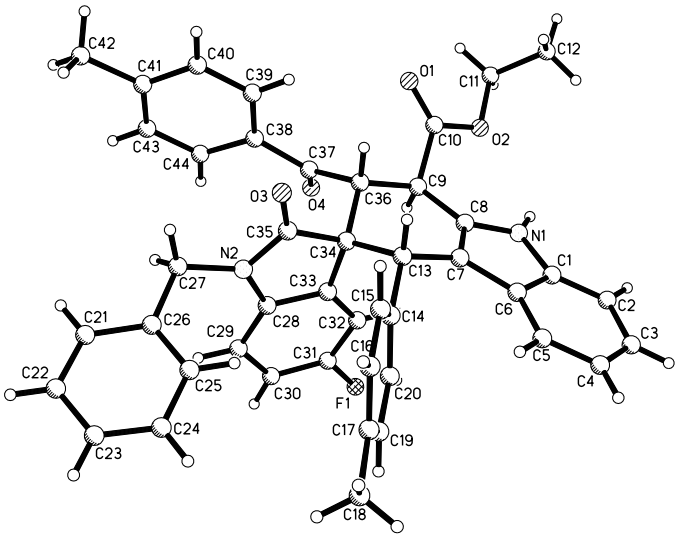


Fig. s1 Single crystal structure of the spiro compound **1e**

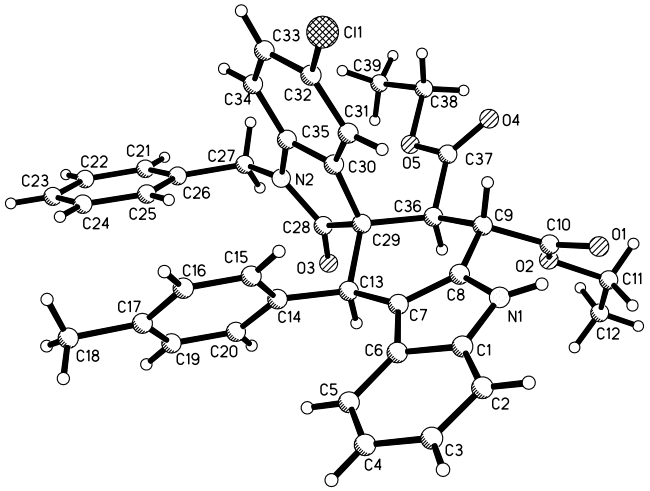


Fig. s2 Single crystal structure of the spiro compound **1g**

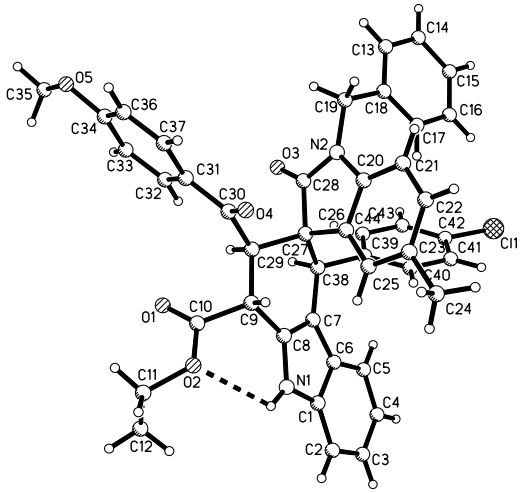


Fig. s3 Single crystal structure of the spiro compound **1k**

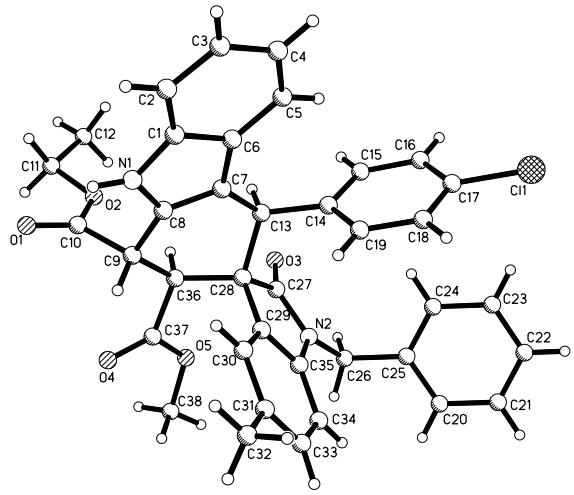


Fig. s4 Single crystal structure of the spiro compound **1l**

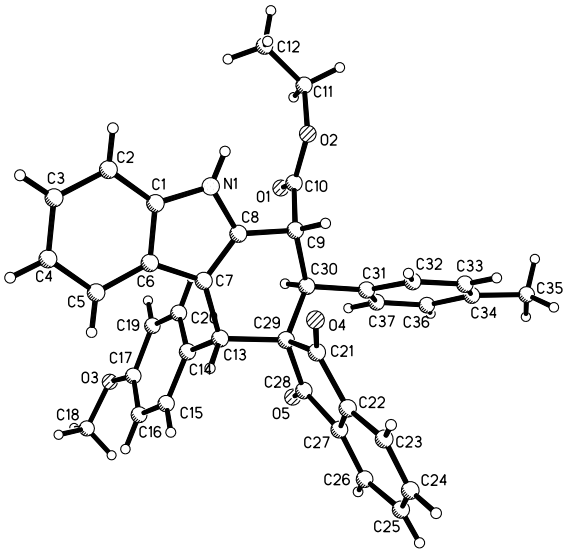


Fig. s5 Single crystal structure of the spiro compound **2a**

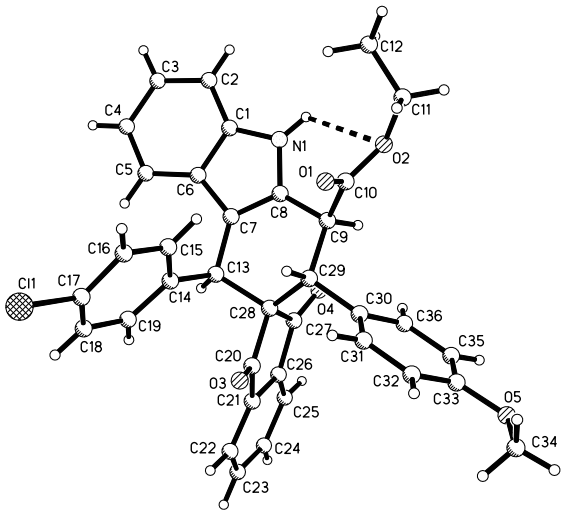


Fig. s6 Single crystal structure of the spiro compound **2h**

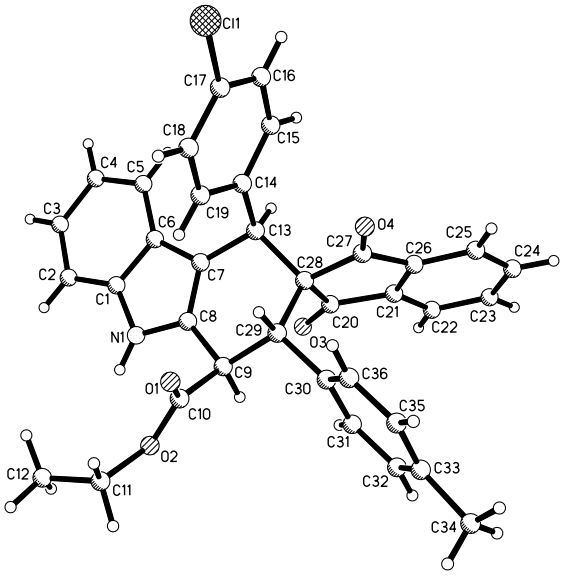


Fig. s7 Single crystal structure of the spiro compound **2j**

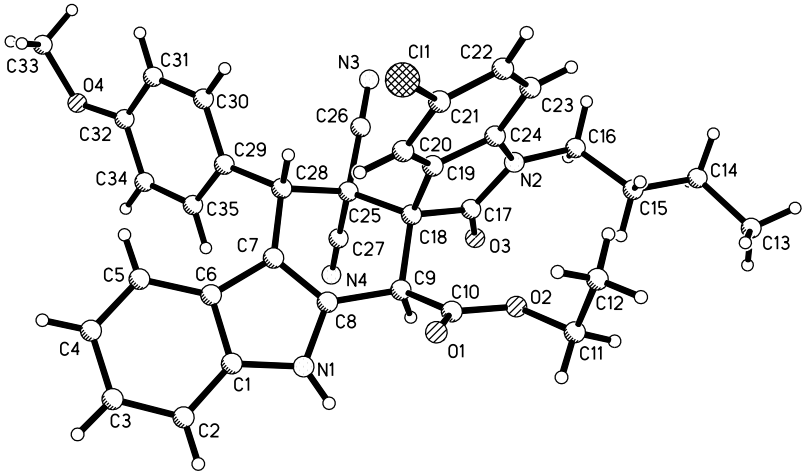


Fig. s8 Single crystal structure of the spiro compound **3f**

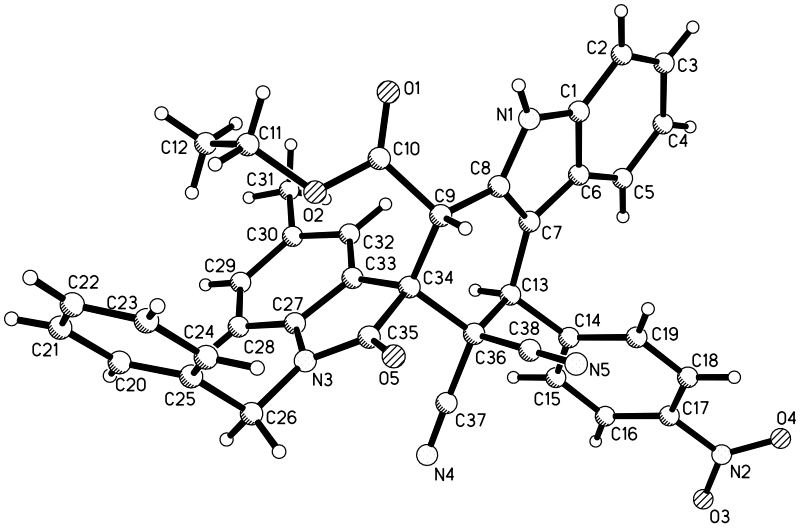


Fig. s9 Single crystal structure of the spiro compound **3h**

Experimental section

1. General procedure for the preparation of spiro[carbazole-3,3'-indolines] 1a-1m: In a Shlenck tube and in a nitrogen atmosphere, a mixture of ethyl indole-2-acetate (0.5 mmol), aromatic aldehyde (0.6 mmol), 3-phencylideneoxindole (0.5 mmol), and $CuSO_45H_2O$ (0.2 mmol) in toluene (6.0 mL) was heated at 130 ºC for 16 h. Then, the solvent was removed by rotatory evaporation at reduced pressure. The residue was subjected to silica chromatography with light petroleum and ethyl acetate (V/V = 6:1) as eluent to give the product for analysis.

Ethyl

1'-benzyl-5'-methyl-3-(4-methylbenzoyl)-2'-oxo-4-phenyl-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1a): yellow solid, 0.204 g, 60%, m.p. 218-220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.10 (s, 1H, NH), 7.89 (d, *J* = 7.6 Hz, 2H, ArH), 7.45-7.39 (m, 2H, ArH), 7.45-7.39 (m, 2H, ArH), 7.23-7.19 (m, 1H, ArH), 7.16-7.12 (m, 2H, ArH), 7.08-7.05 (m, 1H, ArH), 7.01-6.97 (m, 3H, ArH), 6.82-6.76 (m, 3H, ArH), 6.53 (d, *J* = 8.0 Hz, 1H, ArH), 6.37-6.32 (m, 3H, ArH), 6.02 (d, *J* = 8.0 Hz, 1H, ArH), 5.20-5.17 (m, 2H, CH_2), 5.16 (s, 1H, CH), 4.24 (d, *J* = 16.0 Hz, 1H, CH), 4.14 (q, *J* = 7.2 Hz, 2H, CH_2), 4.01 (d, *J* = 16.0 Hz, 1H, CH), 2.42 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 1.06 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 197.2, 175.3, 170.9, 144.0, 140.1, 136.5, 136.5, 134.8, 134.5, 131.3, 131.3, 130.2, 129.2, 128.9, 128.7, 128.7, 128.6, 128.2, 127.7, 127.0, 126.8, 126.8, 126.5, 126.4, 121.9, 120.5, 119.2, 111.0, 110.8, 108.7, 62.3, 57.6, 48.5, 48.4, 43.1, 41.8, 21.7, 21.4, 13.7; IR(KBr) υ: 3300, 3031, 2912, 1714, 1664, 1605, 1491, 1451, 1355, 1261, 1190, 1022, 979, 853, 805, 742, 700 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{38}N_2O_4$ ([M+Na]$^+$): 681.2724, found: 681.2668.

Ethyl

1'-benzyl-5'-fluoro-3-(4-methylbenzoyl)-2'-oxo-4-phenyl-1,3,4,9-tetrahydrospiro[carbazole-2, 3'-indoline]-1-carboxylate (1b): yellow solid, 0.213g, 62%, m.p. 222-224 ºC;^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.09 (s, 1H, NH), 9.92 (d, *J* = 7.2 Hz, 2H, ArH), 7.45-7.40 (m, 2H, ArH), 7.26-7.21 (m, 3H, ArH), 7.19-7.13 (m, 2H, ArH), 7.11-7.07 (m, 1H, ArH), 7.02-6.99 (m, 2H, ArH), 6.93-6.91 (m, 1H, ArH), 6.82-6.79 (m, 2H, ArH), 6.73-6.68 (m, 1H, ArH), 6.54 (d, *J* = 7.2 Hz, 1H, ArH), 6.36-6.32 (m, 3H, ArH), 6.13-6.09 (m, 1H, ArH), 5.21-5.17 (m, 2H, CH_2), 5.10 (s, 1H, CH), 4.24 (d, *J* = 16.0 Hz, 1H, CH), 4.15 (q, *J* = 8.0 Hz, 2H, CH_2), 4.06 (d, *J* = 16.0 Hz, 1H, CH), 2.43 (s, 3H, CH_3), 1.07 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 197.0, 170.5, 157.3,

144.3, 138.6, 138.5, 136.5, 136.1, 134.4, 134.2, 131.3, 130.0, 129.3, 128.7, 128.4, 128.3, 127.9, 127.2, 127.0, 126.3, 126.3, 122.1, 120.5, 119.3, 114.9, 114.7, 114.3, 114.1, 111.0, 110.4, 109.5, 62.4, 57.9, 48.5, 48.2, 43.3, 41.8, 21.7, 13.7; IR(KBr) υ: 3293, 3055, 2911, 1717, 1667, 1604, 1487, 1450, 1362, 1261, 1099, 1021, 967, 887, 853, 804, 739, 665 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{43}H_{35}FN_2O_4$ ($[M+Na]^+$): 685.2473, found: 685.2427.

Diethyl

1'-benzyl-5'-chloro-2'-oxo-4-phenyl-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1,3-dicarboxylate (1c): yellow solid, 0.197g, 60%, m.p. 170-172 ^oC;^1H NMR (400 MHz, $CDCl_3$) δ: 8.75 (s, 1H, NH), 7.44 (d, J = 8.0 Hz, 1H, ArH), 7.36-7.34 (m, 1H, ArH), 7.26-7.16 (m, 6H, ArH), 6.92 (d, J = 8.0 Hz, 1H, ArH), 6.84-6.78 (m, 3H, ArH), 6.71-6.69 (m, 2H, ArH), 6.44-6.42 (m, 1H, ArH), 6.25-6.23 (m, 1H, ArH), 6.18-6.16 (m, 1H, ArH), 4.97 (d, J = 16.0 Hz, 1H, CH), 4.83-4.82 (m, 1H, CH_2), 4.78 (s, 1H, CH), 4.57 (d, J = 16.0 Hz, 1H, CH), 4.29-4.23 (m, 1H, CH_2), 4.18-4.12 (m, 2H, CH_2), 4.12-4.04 (m, 2H, CH_2), 1.26-1.18 (m, 3H, CH_3), 1.18-1.16 (m, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 178.1, 169.7, 169.5, 143.1, 137.1, 135.8, 135.1, 131.0, 130.0, 128.9, 128.5, 128.2, 128.0, 127.9, 127.3, 127.0, 126.9, 126.6, 126.5, 126.0, 125.8, 122.5, 120.9, 119.3, 112.0, 111.0, 109.9, 62.4, 60.9, 54.6, 50.4, 48.6, 44.3, 40.7, 14.0, 13.8; IR(KBr) υ: 3200, 3059, 2980, 1712, 1607, 1485, 1452, 1369, 1193, 1103, 1052, 1023, 959, 813, 742, 700 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{38}H_{33}ClN_2O_5$ ($[M+Na]^+$): 655.1970, found: 655.1955.

Ethyl

1'-benzyl-3-(4-methoxybenzoyl)-5'-methyl-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1d): yellow solid, 0.202g, 57%, m.p. 220-223 ^oC;^1H NMR (400 MHz, $CDCl_3$) δ: 9.08 (s, 1H, NH), 8.00 (d, *J* = 8.0 Hz, 2H, ArH), 7.43 (d, *J* = 8.0 Hz, 1H, ArH), 7.34-7.25 (m, 2H, ArH), 7.16-7.12 (m, 1H, ArH), 7.09-7.06 (m, 1H, ArH), 7.03-6.93 (m, 6H, ArH), 6.84-6.79 (m, 2H, ArH), 6.69 (d, *J* = 8.0 Hz, 1H, ArH), 6.39-6.38 (m, 3H, ArH), 6.11 (d, *J* = 8.0 Hz, 1H, ArH), 5.18-5.13 (m, 2H, CH_2), 5.12 (s, 1H, CH), 4.32 (d, *J* = 16.0 Hz, 1H, CH), 4.13 (q, *J* = 7.2 Hz, 2H, CH_2), 4.12 (d, *J* = 16.0 Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 2.26 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 1.06 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 195.9, 171.0, 163.7, 140.2, 136.4, 134.9, 131.5, 128.5, 127.7, 126.5, 121.9, 119.1, 113.1, 111.0, 108.7, 62.2, 57.7, 55.4, 48.3, 43.1, 42.0, 21.4, 21.2, 13.9; IR(KBr) υ: 3462, 3181, 2922, 1736, 1703, 1596, 1498, 1453, 1360, 1304, 1258, 1226, 1100, 985, 805, 750, 658 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for

$C_{45}H_{40}N_2O_5$ ([M+Na]$^+$): 711.2829, found: 711.2781.

Ethyl

1'-benzyl-5'-fluoro-3-(4-methylbenzoyl)-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1e): yellow solid, 0.227g, 65%, m.p. 230-232 ^oC;^1H NMR (400 MHz, $CDCl_3$) δ: 9.07 (s, 1H, NH), 7.90 (d, *J* = 7.2 Hz, 2H, ArH), 7.43 (d, *J* = 8.0 Hz, 1H, ArH), 7.28-7.26 (m, 3H, ArH), 7.19-7.08 (m, 3H, ArH), 7.05-6.98 (m, 3H, ArH), 6.90 (d, *J* = 8.0 Hz, 1H, ArH), 6.84-6.80 (m, 3H, ArH), 6.73-6.69 (m, 1H, ArH), 6.63 (d, *J* = 8.0 Hz, 1H, ArH), 6.42-6.37 (m, 4H, ArH), 6.13-6.11 (m, 1H, ArH), 5.19 (s, 1H, CH), 5.13-5.09 (m, 2H, CH_2), 4.31 (d, *J* = 16.0 Hz, 1H, CH), 4.15 (q, *J* = 8.0 Hz, 2H, CH_2), 4.00 (d, *J* = 16.0 Hz, 1H, CH), 2.42 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 1.07 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 197.1, 170.6, 157.3, 144.2, 138.6, 136.7, 136.5, 134.4, 134.3, 133.0, 131.3, 131.3, 129.2, 129.2, 128.7, 128.7, 128.5, 128.3, 128.2, 127.0, 126.4, 126.3, 122.1, 119.2, 114.9, 114.6, 114.3, 114.1, 111.0, 110.6, 109.4, 62.3, 57.9, 48.1, 43.2, 41.8, 21.7, 21.7, 21.1, 13.7; IR(KBr) υ: 3261, 3054, 2975, 1721, 1671, 1606, 1488, 1452, 1351, 1298, 1234, 1180, 958, 855, 809, 739, 694, 627 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{44}H_{37}FN_2O_4$ ([M+Na]$^+$): 699.2630, found: 699.2568.

Ethyl

1'-benzyl-5'-chloro-3-(4-methylbenzoyl)-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1f): white solid, 0.207g, 58%, m.p. 217-219 ^oC;^1H NMR (400 MHz, $CDCl_3$) δ: 8.75 (s, 1H, NH), 7.71 (d, *J* = 7.2 Hz, 2H, ArH), 7.43 (d, *J* = 8.0 Hz, 1H, ArH), 7.27-7.25 (m, 1H, ArH), 7.21-7.19 (m, 2H, ArH), 7.18-7.12 (m, 4H, ArH), 7.06-7.04 (m, 1H, ArH), 6.95-6.91 (m, 2H, ArH), 6.83-6.79 (m, 1H, ArH), 6.73 (d, *J* = 7.2 Hz, 2H, ArH), 6.64 (d, *J* = 8.0 Hz, 1H, ArH), 6.30 (d, *J* = 7.2 Hz, 2H, ArH), 6.21 (d, *J* = 8.0 Hz, 1H, ArH), 4.99 (d, *J* = 16.0 Hz, 1H, CH), 4.85-4.84 (m, 2H, CH_2), 4.82 (s, 1H, CH), 4.56 (d, *J* = 16.0 Hz, 1H, CH), 4.00 (q, *J* = 8.0 Hz, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 1.05 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 197.3, 178.5, 169.3, 143.2, 137.3, 136.8, 134.7, 132.7, 131.0, 129.9, 128.6, 126.7, 125.9, 121.0, 119.2, 112.7, 111.0, 105.0, 62.5, 55.1, 52.6, 50.4, 44.3, 42.1, 21.6, 21.3, 13.5; IR(KBr) υ: 3330, 3034, 2947, 2860, 1876, 1685, 1485, 1450, 1375, 1342, 1219, 1174, 1104, 951, 818, 779, 695, 627 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{44}H_{37}ClN_2O_4$ ([M+Na]$^+$): 715.2334, found: 715.2281.

Diethyl

1'-benzyl-5'-chloro-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1,3-dic arboxylate (1g): yellow solid, 0.171g, 51%, m.p. 160-162 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (s, 1H, NH), 7.39 (d, *J* = 8.0 Hz, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 1H, ArH), 7.16-7.07 (m, 5H, ArH), 6.99-6.97 (m, 2H, ArH), 6.80-6.77 (m, 1H, ArH), 6.66-6.62 (m, 3H, ArH), 6.27 (d, *J* = 8.0 Hz, 1H, ArH), 6.21 (d, *J* = 8.0 Hz, 2H, ArH), 5.07 (d, *J* = 16.0 Hz, 1H, CH), 4.97 (s, 1H, CH), 4.80 (d, *J* = 16.0 Hz, 1H, CH), 4.40-4.35 (m, 2H, CH_2), 4.33 (q, *J* = 7.2 Hz, 2H, CH_2), 3.94 (q, *J* = 7.2 Hz, 2H, CH_2), 2.32 (s, 3H, CH_3), 1.34 (t, *J* = 7.2 Hz, 3H, CH_3), 1.00 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 176.8, 170.7, 170.0, 142.3, 136.9, 136.7, 134.7, 132.9, 131.3, 129.6, 129.0, 128.8, 128.6, 128.4, 128.0, 127.4, 127.2, 126.8, 126.4, 125.4, 122.3, 120.6, 119.4, 111.2, 111.0, 110.0, 62.3, 61.4, 56.3, 48.4, 48.4, 44.1, 41.6, 21.3, 14.2, 13.9; IR(KBr) υ: 3100, 3060, 2973, 2895, 1719, 1606, 1483, 1455, 1354, 1251, 1184, 1120, 1021, 859, 811, 737, 699, 640 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{39}H_{35}ClN_2O_5$ ([M+Na]$^{+}$): 669.2127, found: 669.2090.

Diethyl

1'-benzyl-5'-chloro-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1,3-dic arboxylate (1g'): yellow solid, 0.033g, 10%, m.p. 165-167 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 (s, 1H, NH), 7.44 (d, *J* = 8.0 Hz, 1H, ArH), 7.25-7.23 (m, 1H, ArH), 7.16-7.12 (m, 4H, ArH), 7.04-7.02 (m, 1H, ArH), 6.93 (d, *J* = 8.0 Hz, 1H, ArH), 6.84-6.78 (m, 2H, ArH), 6.70-6.93 (m, 3H, ArH), 6.31-6.26 (m, 2H, ArH), 6.19 (d, *J* = 7.2 Hz, 1H, ArH), 5.08 (d, *J* = 16.4 Hz, 1H, CH), 4.82-4.80 (m, 1H, CH), 4.75 (s, 1H, CH), 4.52 (d, *J* = 16.4 Hz, 1H, CH), 4.28-4.22 (m, 1H, CH), 4.19-4.11 (m, 2H, CH_2), 4.09-3.99 (m, 2H, CH_2), 2.31 (s, 3H, CH_3), 1.26-1.19 (m, 3H, CH_3), 1.17-1.15 (m, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 178.2, 169.7, 169.5, 143.1, 137.1, 136.7, 135.1, 132.7, 131.0, 129.8, 129.0, 128.6, 128.3, 128.0, 127.8, 127.7, 127.0, 126.7, 126.4, 126.0, 125.7, 122.4, 120.9, 119.1, 112.1, 110.9, 109.8, 62.3, 60.9, 54.6, 50.0, 48.6, 44.3, 44.2, 40.7, 21.2, 14.0; IR(KBr) υ: 3100, 3060, 2983, 2909, 1720, 1607, 1485, 1451, 1370, 1297, 1201, 1108, 1023, 961, 813, 739 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{39}H_{35}ClN_2O_5$ ([M+Na]$^{+}$): 669.2127, found: 669.2096.

Ethyl

1'-benzyl-4-(4-methoxyphenyl)-3-(4-methylbenzoyl)-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole -2,3'-indoline]-1-carboxylate (1h): yellow solid, 0.209g, 60%, m.p. 215-217 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.07 (s, 1H, NH), 7.90 (d, *J* = 7.2 Hz, 2H, ArH), 7.42 (d, *J* = 8.0 Hz, 1H, ArH),

7.32 (d, *J* = 8.0 Hz, 1H, ArH), 7.27-7.25 (m, 2H, ArH), 7.15-7.07 (m, 3H, ArH), 7.03-6.98 (m, 3H, ArH), 6.89-6.86 (m, 1H, ArH), 6.83-6.79 (m, 1H, ArH), 6.75-6.73 (m, 1H, ArH), 6.39-6.35 (m, 4H, ArH), 6.32-6.30 (m, 1H, ArH), 6.23 (d, *J* = 8.0 Hz, 1H, ArH), 5.19-5.14 (m, 2H, CH_2), 5.11 (s, 1H, CH), 4.32 (d, *J* = 16.0 Hz, 1H, CH), 4.15 (q, *J* = 8.0 Hz, 2H, CH_2), 4.03 (d, *J* = 16.0 Hz, 1H, CH), 3.72 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3), 1.07 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 197.2, 170.8, 158.6, 144.0, 142.5, 136.5, 134.7, 134.5, 132.4, 131.0, 129.2, 128.7, 128.4, 128.1, 126.9, 126.6, 126.4, 126.4, 126.4, 126.4, 126.1, 122.0, 121.9, 119.2, 112.7, 112.7, 112.5, 111.1, 110.9, 109.1, 62.2, 57.6, 54.9, 48.5, 48.0, 47.9, 43.0, 21.7, 13.8; IR(KBr) υ: 3281, 3033, 2960, 1734, 1705, 1670, 1605, 1506, 1457, 1356, 1247, 1178, 1023, 981, 841, 794, 750, 688, 644 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{44}H_{38}N_2O_5$ ($[M+Na]^+$): 697.2673, found: 697.2613.

Ethyl

1'-benzyl-3-(4-methoxybenzoyl)-4-(4-methoxyphenyl)-5'-methyl-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1i): yellow solid, 0.207g, 57%, m.p. 210-212 ^oC;^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.07 (s, 1H, NH), 8.00 (d, *J* = 8.0 Hz, 2H, ArH), 7.44 (d, *J* = 7.2 Hz, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 1H, ArH), 7.17-7.13 (m, 1H, ArH), 7.09-7.06 (m, 1H, ArH), 7.01-6.98 (m, 2H, ArH), 6.95-6.93 (m, 3H, ArH), 6.83-6.79 (m, 2H, ArH), 6.74-6.72 (m, 1H, ArH), 6.42-6.33 (m, 5H, ArH), 6.12 (d, *J* = 8.0 Hz, 1H, ArH), 5.18-5.13 (m, 2H, CH_2), 5.09 (s, 1H, CH), 4.31 (d, *J* = 16.0 Hz, 1H, CH), 4.14 (q, *J* = 7.2 Hz, 2H, CH_2), 4.06 (d, *J* = 16.0 Hz, 1H, CH), 3.88 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 2.20 (s, 3H, CH_3), 1.07 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 195.8, 170.9, 163.6, 140.2, 136.5, 134.8, 132.4, 131.5, 131.2, 131.1, 129.9, 128.8, 128.6, 128.1, 126.8, 126.8, 126.7, 126.5, 126.4, 121.8, 120.5, 119.1, 113.1, 112.8, 112.4, 111.1, 110.9, 108.8, 62.2, 57.7, 55.4, 48.2，48.0, 47.9, 43.0, 41.9, 21.4, 13.7; IR(KBr) υ: 3181, 3033, 2922, 1735, 1705, 1664, 1599, 1503, 1459, 1356, 1303, 1254, 1176, 1095, 1027, 853, 806, 750, 653 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{45}H_{40}N_2O_6$ ($[M+Na]^+$): 727.2779, found: 727.2717.

Ethyl

1'-benzyl-3-(4-methoxybenzoyl)-4-(4-methoxyphenyl)-5'-methyl-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1i'): yellow solid, 0.025 g, 7%, m.p. 215-217 ^oC;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.76 (s, 1H, NH), 7.80 (d, *J* = 8.0 Hz, 2H, ArH), 7.42 (d, *J* = 8.0 Hz, 1H, ArH), 7.30-7.27 (m, 1H, ArH), 7.16-7.13 (m, 4H, ArH), 6.89 (d, *J* = 8.0 Hz, 2H, ArH),

6.82-6.74 (m, 3H, ArH), 6.73-6.69 (m, 3H, ArH), 6.34-6.31 (m, 2H, ArH), 6.26-6.20 (m, 2H, ArH), 5.02 (d, *J* = 16.0 Hz, 1H, CH), 4.87-4.83 (m, 2H, CH_2), 4.81 (s, 1H, CH), 4.56 (d, *J* = 16.0 Hz, 1H, CH), 3.93 (q, *J* = 7.2 Hz, 2H, CH_2), 3.85 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 2.06 (s, 3H, CH_3), 0.97 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 195.8, 170.9, 158.5, 140.2, 136.5, 134.8, 132.4, 131.5, 131.2, 131.1, 129.9, 128.8, 128.6, 128.1, 126.8, 126.7, 126.7, 126.5, 126.4, 121.8, 120.5, 119.1, 113.1, 112.8, 112.4, 111.1, 110.9, 109.9, 108.8, 62.2, 57.7, 55.9, 55.4, 48.1, 47.9, 43.0, 41.9, 21.4, 13.7; IR(KBr) υ: 3130, 3052, 2962, 1704, 1598, 1510, 1458, 1354, 1301, 1253, 1226, 1175, 1030, 807, 749, 595 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{45}H_{40}N_2O_6$ ($[M+Na]^+$): 727.2779, found: 727.2755.

1-Ethyl-3-methyl

1'-benzyl-5'-fluoro-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1,3-dic arboxylate (1j): yellow solid, 0.176g, 55%, m.p. 160-162 ^oC;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.75 (s, 1H, NH), 7.43 (d, *J* = 8.0 Hz, 1H, ArH), 7.25-7.24 (m, 1H, ArH), 7.18-7.13 (m, 4H, ArH), 7.06-7.04 (m, 1H, ArH), 6.80-6.77 (m, 1H, ArH), 6.74-6.72 (m, 2H, ArH), 6.66-6.60 (m, 3H, ArH), 6.27 (d, *J* = 8.0 Hz, 2H, ArH), 6.19-6.16 (m, 1H, ArH), 5.02 (d, *J* = 16.0 Hz, 1H, CH_2), 4.81-4.79 (m, 1H, CH), 4.79-4.75 (m, 1H, CH), 4.55 (d, *J* = 16.0 Hz, 1H, CH_2), 4.27-4.21 (m, 1H, CH_2), 4.12 (q, *J* = 8.0 Hz, 2H, CH_2), 3.63 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3), 1.17 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 178.3, 170.3, 156.8, 140.6, 137.1, 136.8, 135.3, 132.6, 131.1, 129.7, 128.6, 128.3, 127.9, 127.7, 127.0, 126.7, 126.1, 122.4, 121.0, 119.2, 114.3, 114.3, 114.1, 112.2, 110.9, 109.4, 109.3, 62.3, 54.8, 51.9, 50.1, 48.5, 44.3, 40.7, 21.2, 13.8; IR(KBr) υ: 3090, 3022, 2980, 1748, 1691, 1617, 1489, 1453, 1372, 1346, 1201, 1021, 821, 740, 697, 629, 546, 433 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{38}H_{33}FN_2O_5$ ($[M+Na]^+$): 639.2266, found: 639.2253.

Ethyl

1'-benzyl-4-(4-chlorophenyl)-3-(4-methoxybenzoyl)-5'-methyl-2'-oxo-1,3,4,9-tetrahydrospiro [carbazole-2,3'-indoline]-1-carboxylate (1k): white solid, 0.201g, 55%, m.p. 220-222 ^oC;^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.11 (s, 1H, NH), 7.99 (d, *J* = 8.0 Hz, 2H, ArH), 7.45 (d, *J* = 8.0 Hz, 1H, ArH), 7.32 (d, *J* = 8.0 Hz, 1H, ArH), 7.17-7.15 (m, 2H, ArH), 7.18-7.05 (m, 3H, ArH), 6.95-6.93 (m, 3H, ArH), 6.87-6.82 (m, 2H, ArH), 6.77 (d, *J* = 8.0 Hz, 1H, ArH), 6.47 (d, *J* = 8.0 Hz, 1H, ArH), 6.41-6.35 (m, 3H, ArH), 6.16 (d, *J* = 8.0 Hz, 1H, ArH), 5.17-5.13 (m, 2H, CH_2),

5.12-5.09 (m, 1H, CH), 4.30 (d, *J* = 16.0 Hz, 1H, CH), 4.16-4.11 (m, 2H, CH_2), 4.06 (d, *J* = 16.0 Hz, 1H, CH), 3.89 (s, 3H, OCH_3), 2.19 (s, 3H, CH_3), 1.06 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 195.6, 170.7, 163.7, 140.1, 136.5, 135.2, 134.7, 132.9, 132.6, 131.5, 131.4, 129.8, 129.1, 129.1, 128.9, 128.3, 127.9, 127.1, 127.1, 127.0, 126.7, 126.4, 126.3, 126.2, 122.0, 120.2, 119.3, 113.1, 111.1, 111.1, 110.1, 109.9, 108.9, 62.3, 57.5, 55.4, 55.3, 48.0, 43.1, 41.8, 21.4, 13.7; IR(KBr) υ: 3120, 3070, 2972, 1712, 1598, 1492, 1471, 1452, 1362, 1309, 1261, 1220, 1172, 1087, 1020, 982, 808, 743, 702, 659 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{44}H_{37}ClN_2O_5$ ($[M+Na]^+$): 731.2283, found: 731.2264.

1-Ethyl-3-methyl 1'-benzyl-4-(4-chlorophenyl)-5'-methyl-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1,3-dicarboxylate (1l): yellow solid, 0.187g, 57%, m.p. 172-174 ^oC;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (s, 1H, NH), 7.41-7.36 (m, 2H, ArH), 7.25-7.21 (m, 4H, ArH), 7.16-7.12 (m, 1H, ArH), 6.85-6.73 (m, 6H, ArH), 6.32-6.23 (m, 3H, ArH), 4.97-4.92 (m, 2H, CH_2), 4.86 (d, *J* = 10.4 Hz, 1H, CH), 4.47 (d, *J* = 10.4 Hz, 1H, CH), 4.40-4.34 (m, 1H, CH), 4.30-4.26 (m, 2H, CH_2), 3.39 (s, 3H, OCH_3), 2.15 (s, 3H, CH_3), 1.33 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 176.8, 170.8, 170.7, 141.0, 136.6, 135.2, 135.0, 133.1, 132.7, 131.5, 131.1, 129.3, 128.5, 128.1, 127.8, 127.3, 127.1, 126.9, 126.4, 126.2, 125.9, 122.2, 120.3, 119.5, 111.1, 110.5, 109.0, 62.3, 56.1, 52.3, 48.2, 43.9, 41.5, 21.3, 14.2; IR(KBr) υ: 3396, 3073, 2941, 1710, 1610, 1492, 1447, 1353, 1261, 1203, 1069, 1018, 807, 737, 701, 659 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{38}H_{33}ClN_2O_5$ ($[M+Na]^+$): 655.1940, found: 655.1959.

Ethyl 1'-benzyl-5'-chloro-3-(4-methoxybenzoyl)-4-(4-nitrophenyl)-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1m): yellow solid, 0.222g, 60%, m.p. 232-234 ^oC;^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.22 (s, 1H, NH), 8.11 (d, *J* = 8.0 Hz, 1H, ArH), 7.89 (d, *J* = 8.0 Hz, 1H, ArH), 7.69 (d, *J* = 8.0 Hz, 1H, ArH), 7.45-7.41 (m, 2H, ArH), 7.18-7.12 (m, 2H, ArH), 7.09-7.01 (m, 3H, ArH), 6.89 (d, *J* = 8.0 Hz, 1H, ArH), 6.82 (d, *J* = 8.0 Hz, 2H, ArH), 6.59-6.54 (m, 3H, ArH), 6.47 (d, *J* = 8.0 Hz, 1H, ArH), 6.34 (d, *J* = 8.0 Hz, 1H, ArH), 5.98 (d, *J* = 8.0 Hz, 1H, CH), 5.71 (s, 1H, CH), 4.43 (d, *J* = 16.0 Hz, 1H, CH), 4.07-4.04 (m, 2H, CH_2), 3.94 (d, *J* = 16.0 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 0.93-0.92 (m, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 173.6, 163.2, 147.9, 146.4, 142.2, 139.8, 134.5, 131.9, 131.0, 130.5, 130.1, 128.8, 128.6, 128.5,

127.9, 127.4, 124.2, 123.4, 122.4, 121.0, 113.5, 110.7, 110.2, 59.5, 59.0, 55.4, 43.8, 18.4, 14.0, 13.9; IR(KBr) υ: 3100, 3073, 2976, 1696, 1603, 1519, 1471, 1347, 1247, 1213, 1171, 1103, 978, 939, 844, 806, 748 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{43}H_{34}ClN_3O_7$ ($[M+H]^+$): 740.2158, found: 740.1977.

2. General procedure for the preparation of spiro[carbazole-3,2'-indenes] 2a-2l: In a Shlenck tube and in a nitrogen atmosphere, a mixture of ethyl indole-2-acetate (0.5 mmol), aromatic aldehyde (0.6 mmol), 2-arylidene-1,3-indanedione (0.5 mmol), and $CuSO_45H_2O$ (0.2 mmol) in toluene (6.0 mL) was heated at 120-130 ºC for 16 h. Then, the solvent was removed by rotatory evaporation at reduced pressure. The residue was subjected to silica chromatography with light petroleum and ethyl acetate (V/V = 6:1) as eluent to give the product for analysis.

Ethyl

4-(4-methoxyphenyl)-1',3'-dioxo-3-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2a): yellow solid, 0.163g, 55%, m.p. 250-252 ºC;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (s, 1H, NH), 7.91-7.89 (m, 1H, ArH), 7.76-7.71 (m, 3H, ArH), 7.35 (d, *J* = 8.0 Hz, 1H, ArH), 7.11-7.09 (m, 1H, ArH), 7.04 (d, *J* = 8.0 Hz, 2H, ArH), 6.96-6.94 (m, 2H, ArH), 6.91-6.84 (m, 4H, ArH), 6.77-6.75 (m, 2H, ArH), 4.96-4.93 (m, 1H, CH), 4.38-4.36 (m, 2H, CH_2), 4.18 (q, *J* = 7.2 Hz, 2H, CH_2), 3.76 (s, 3H, OCH_3), 2.14 (s, 3H, CH_3), 1.23 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 201.1, 171.2, 158.7, 141.7, 141.1, 136.7, 136.5, 135.5, 135.3, 131.7, 130.8, 130.6, 129.5, 128.9, 126.5, 123.5, 123.2, 122.1, 119.5, 118.6, 113.5, 110.9, 109.9, 62.4, 61.6, 55.0, 45.7, 41.5, 20.9, 14.2; IR(KBr) υ: 2979, 1731, 1704, 1592, 1510, 1460, 1247, 1178, 1155, 1032, 818, 748, 598 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{37}H_{33}NO_5$ ($[M+Na]^+$): 592.2094, found: 592.2072.

Ethyl

4-(4-methoxyphenyl)-1',3'-dioxo-3-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2b): yellow solid, 0.159g, 55%, m.p. 244-246 ºC;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43 (s, 1H, NH), 7.91-7.89 (m, 1H, ArH), 7.74-7.69 (m, 3H, ArH), 7.35 (d, *J* = 8.0 Hz, 1H, ArH), 7.17-7.16 (m, 2H, ArH), 7.12-7.04 (m, 4H, ArH), 6.96 (d, *J* = 8.0 Hz, 2H, ArH), 6.92-6.87 (m, 2H, ArH), 6.76 (d, *J* = 8.0 Hz, 2H, ArH), 4.99-4.97 (m, 1H, CH), 4.42-4.39 (m, 2H, CH_2), 4.19 (q, *J* = 8.0 Hz, 2H, CH_2), 3.76 (s, 3H, OCH_3), 1.21 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 201.0, 171.2, 158.7, 141.7, 141.1, 138.5, 136.5, 135.5, 135.3, 131.7, 130.8, 130.6, 129.7,

128.1, 127.2, 126.5, 123.5, 123.2, 122.2, 119.5, 118.6, 113.5, 110.9, 109.9, 62.3, 61.7, 55.0, 45.6, 42.0, 14.1; IR(KBr) υ: 2976, 2838, 1729, 1702, 1592, 1509, 1458, 1330, 1247, 1203, 1176, 1154, 1031, 969, 929, 819, 801, 748, 701, 595 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{31}NO_5$ ($[M+Na]^+$): 578.1938, found: 578.1936.

Ethyl 4-(4-methoxyphenyl)-1',3'-dioxo-3-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2b'): yellow solid, 0.028g, 10%, m.p. 245-249 ^oC;^1H NMR (400 MHz, $CDCl_3$) δ: 8.47 (s, 1H, NH), 7.53-7.51 (m, 1H, ArH), 7.49-7.41 (m, 3H, ArH), 7.36 (d, *J* = 8.0 Hz, 1H, ArH), 7.12-7.08 (m, 3H, ArH), 7.05-6.95 (m, 4H, ArH), 6.80 (d, *J* = 8.0 Hz, 2H, ArH), 6.52-6.45 (m, 2H, ArH), 6.41 (d, *J* = 8.0 Hz, 1H, ArH), 5.19 (d, *J* = 11.2 Hz, 1H, CH), 5.03 (s, 1H, CH), 4.31 (d, *J* = 11.2 Hz, 1H, CH), 4.15-4.10 (m, 1H, CH), 4.05-4.01 (m, 1H, CH), 3.61 (s, 3H, OCH_3), 1.08 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 202.7, 171.0, 158.5, 143.3, 142.3, 137.2, 136.2, 135.0, 134.7, 131.0, 130.7, 130.2, 129.3, 129.1, 128.1, 127.3, 126.5, 122.1, 122.0, 121.6, 120.3, 119.1, 113.5, 112.8, 110.8, 109.9, 63.8, 61.5, 55.0, 47.7, 47.0, 44.5, 13.9; IR(KBr) υ: 3063, 2831, 2363, 1740, 1701, 1593, 1511, 1455, 1366, 1342, 1293, 1249, 1179, 1155, 1039, 926, 806, 767, 745, 701 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{31}NO_5$ ($[M+Na]^+$): 578.1938, found: 578.1937.

Ethyl 3-(4-chlorophenyl)-4-(4-methoxyphenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2c): yellow solid, 0.184g, 60%, m.p. 243-244 ^oC;^1H NMR (400 MHz, $CDCl_3$) δ: 8.48 (s, 1H, NH), 7.51-7.48 (m, 4H, ArH), 7.35 (d, *J* = 8.0 Hz, 1H, ArH), 7.08 (d, *J* = 8.0 Hz, 3H, ArH), 7.02-6.98 (m, 3H, ArH), 6.79-6.76 (m, 2H, ArH), 6.50 (d, *J* = 8.0 Hz, 1H, ArH), 6.46 (d, *J* = 8.0 Hz, 1H, ArH), 6.39 (d, *J* = 8.0 Hz, 1H, ArH), 5.15 (d, *J* = 11.2 Hz, 1H, CH), 4.99 (s, 1H, CH), 4.30 (d, *J* = 11.2 Hz, 1H, CH), 4.14-4.13 (m, 1H, CH_2), 4.08-4.06 (m, 1H, CH_2), 3.61 (s, 3H, OCH_3), 1.12 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 202.5, 170.7, 158.6, 143.2, 142.3, 136.2, 136.1, 135.3, 135.0, 133.1, 130.9, 130.6, 129.9, 129.0, 128.3, 126.4, 122.3, 122.1, 121.7, 120.3, 119.2, 113.5, 112.9, 110.8, 109.9, 63.6, 61.7, 55.0, 47.3, 46.8, 44.5, 14.0; IR(KBr) υ: 3062, 2927, 2831, 1739, 1701, 1595, 1511, 1455, 1343, 1249, 1178, 1156, 1041, 1018, 929, 806, 767, 746, 701 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{28}ClNO_5$ ($[M+Na]^+$): 612.1548, found: 612.1538.

Ethyl

3-(4-chlorophenyl)-4-(4-methoxyphenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2c'): white solid, 0.025g, 8%, m.p. 245-147 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.43 (s, 1H, NH), 7.92-7.91 (m, 1H, ArH), 7.78-7.73 (m, 3H, ArH), 7.37-7.35 (m, 1H, ArH), 7.13-7.12 (m, 3H, ArH), 7.04 (d, *J* = 8.0 Hz, 2H, ArH), 6.94-6.88 (m, 4H, ArH), 6.77 (d, *J* = 8.0 Hz, 2H, ArH), 4.97-4.95 (m, 1H, CH_2), 4.40-4.38 (m, 2H, CH_2), 4.21 (q, *J* = 8.0 Hz, 2H, CH_2), 3.76 (s, 3H, OCH_3), 1.24 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 200.8, 170.9, 158.8, 141.6, 141.0, 137.1, 136.5, 135.8, 135.5, 133.1, 131.4, 131.1, 130.5, 130.4, 128.4, 126.4, 123.6, 123.3, 122.3, 119.6, 118.6, 113.6, 110.9, 109.7, 62.4, 58.5, 55.0, 45.4, 41.2, 18.4, 14.2; IR(KBr) υ: 3062, 2971, 1740, 1699, 1593, 1510, 1490, 1460, 1332, 1300, 1250, 1202, 1174, 1091, 1033, 968, 823, 782, 743, 688 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{28}ClNO_5$ ($[M+Na]^+$): 612.1548, found: 612.1541.

Ethyl

3-(4-fluorophenyl)-1',3'-dioxo-4-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2d): yellow solid, 0.180g, 62%, m.p. 255-257 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (s, 1H, NH), 7.92-7.90 (m, 1H, ArH), 7.76-7.71 (m, 3H, ArH), 7.34 (d, *J* = 8.0 Hz, 1H, ArH), 7.17-7.08 (m, 3H, ArH), 7.06-7.04 (m, 2H, ArH), 6.92-6.87 (m, 4H, ArH), 6.76-6.71 (m, 2H, ArH), 4.99 (t, *J* = 10.4 Hz, 1H, CH), 4.43 (d, *J* = 10.4 Hz, 1H, CH), 4.38 (s, 1H, CH), 4.20 (q, *J* = 7.2 Hz, 2H, CH_2), 2.31 (s, 3H, CH_3), 1.22 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 200.9, 171.0, 162.6, 141.7, 141.0, 137.0, 136.5, 135.7, 135.5, 131.4, 131.4, 130.5, 129.3, 129.0, 126.5, 123.6, 123.3, 122.2, 119.6, 118.5, 115.1, 115.0, 110.9, 109.6, 62.4, 61.7, 45.6, 41.1, 21.2, 14.2; IR(KBr) υ: 3010, 2914, 2827, 1728, 1500, 1428, 1459, 1229, 1200, 1140, 1122, 1091, 1034, 921, 803, 750, 727 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{28}FNO_4$ ($[M+Na]^+$): 580.1895, found: 580.1891.

Ethyl

3-(3-nitrophenyl)-1',3'-dioxo-4-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2e): yellow solid, 0.161g, 53%, m.p. 260-262 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (s, 1H, NH), 8.08 (s, 1H, ArH), 7.96-7.91 (m, 2H, ArH), 7.81-7.70 (m, 3H, ArH), 7.57 (d, *J* = 8.0 Hz, 1H, ArH), 7.37 (d, *J* = 8.0 Hz, 1H, ArH), 7.26-7.24 (m, 1H, ArH), 7.14-7.11 (m, 1H, ArH), 7.07-7.06 (m, 2H, ArH), 6.93-6.88 (m, 4H, ArH), 5.07 (d, *J* = 10.4 Hz, 1H, CH), 4.56 (d, *J* = 10.4

Hz, 1H, CH), 4.42 (s, 1H, CH), 4.20 (q, *J* = 8.0 Hz, 2H, CH_2), 2.32 (s, 3H, CH_3), 1.24 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 200.2, 198.1, 170.5, 148.0, 141.6, 141.0, 140.9, 137.3, 136.5, 136.1, 135.9, 135.8, 129.9, 129.3, 129.1, 126.4, 124.8, 123.9, 123.4, 122.5, 122.4, 119.7, 118.6, 111.0, 109.5, 62.0, 45.3, 41.4, 21.2, 14.2; IR(KBr) υ: 3090, 3015, 2904, 2799, 1726, 1504, 1450, 1419, 1228, 1200, 1152, 1121, 1090, 1040, 901, 822, 720, 705 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{28}N_2O_6$ ($[M+Na]^+$): 607.1840, found: 607.1833.

Ethyl

3-(4-chlorophenyl)-4-(4-fluorophenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2f): yellow solid, 0.165g, 55%, m.p. 245-247 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.46 (s, 1H, NH), 7.92-7.91 (m, 1H, ArH), 7.82-7.71 (m, 3H, ArH), 7.36 (d, J = 8.0 Hz, 1H, ArH), 7.14-7.10 (m, 3H, ArH), 7.05-7.03 (m, 2H, ArH), 7.01-6.98 (m, 2H, ArH), 6.95-6.88 (m, 4H, ArH), 4.95 (d, J = 10.0 Hz, 1H, CH), 4.41 (s, 1H, CH), 4.36 (d, J = 10.0 Hz, 1H, CH), 4.21 (q, J = 7.2 Hz, 2H, CH_2), 1.24 (t, J = 7.2 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 200.5, 198.4, 170.8, 141.5, 140.9, 136.8, 136.5, 135.9, 135.7, 133.2, 131.1, 131.0, 131.0, 130.5, 128.4, 126.2, 123.7, 123.3, 122.4, 119.7, 118.5, 115.3, 115.1, 111.1, 109.3, 61.9, 45.3, 41.3, 14.2; IR(KBr) υ: 3052, 2927, 2831, 1726, 1701, 1592, 1509, 1455, 1342, 1240, 1173, 1152, 1038, 1018, 920, 803, 762, 741, 712 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{35}H_{25}ClFNO_4$ ($[M+Na]^+$): 600.1348, found: 600.1347.

Ethyl

4-(4-chlorophenyl)-3-(3-methoxyphenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2g): yellow solid, 0.153g, 50%, m.p. 255-257 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (s, 1H, NH), 7.92-7.90 (m, 1H, ArH), 7.79-7.72 (m, 3H, ArH), 7.36 (d, *J* = 8.0 Hz, 1H, ArH), 7.21 (d, *J* = 8.0 Hz, 2H, ArH), 7.14-7.11 (m, 1H, ArH), 6.99-6.95 (m, 3H, ArH), 6.92-6.84 (m, 2H, ArH), 6.74-6.72 (m, 2H, ArH), 6.68 (s, 1H, ArH), 6.59-6.57 (m, 1H, ArH), 4.95 (d, *J* = 10.0 Hz, 1H, CH), 4.38 (s, 1H, CH), 4.34 (d, *J* = 10.0 Hz, 1H, CH), 4.21 (q, *J* = 8.0 Hz, 2H, CH_2), 3.62 (s, 3H, OCH_3), 1.24 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 200.6, 171.0, 159.2, 141.5, 141.0, 139.6, 138.3, 136.5, 135.7, 135.6, 133.2, 130.9, 129.2, 128.4, 126.2, 123.6, 123.3, 122.3, 121.9, 119.7, 118.4, 115.2, 113.3, 111.0, 109.1, 61.8, 55.1, 45.5, 42.2, 14.2; IR(KBr) υ: 3022, 2929, 1733, 1703, 1595, 1490, 1459, 1330, 1290, 1251, 1153, 1094, 933, 848, 814, 780, 754, 698 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{28}ClNO_5$ ($[M+Na]^+$): 612.1548,

found: 612.1543.

Ethyl

4-(4-chlorophenyl)-3-(4-methoxyphenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2h): white solid, 0.168g, 55%, m.p. 257-259 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.45 (s, 1H, NH), 7.92-7.90 (m, 1H, ArH), 7.76-7.71 (m, 3H, ArH), 7.35 (d, *J* = 8.0 Hz, 1H, ArH), 7.21 (d, *J* = 8.0 Hz, 2H, ArH), 7.13-7.10 (m, 1H, ArH), 7.06 (d, *J* = 8.0 Hz, 2H, ArH), 6.99 (d, *J* = 8.0 Hz, 2H, ArH), 6.91-6.88 (m, 2H, ArH), 6.58 (d, *J* = 8.0 Hz, 2H, ArH), 4.94-4.89 (m, 1H, CH), 4.38 (s, 1H, CH), 4.34-4.31 (m, 1H, CH), 4.22 (q, *J* = 8.0 Hz, 2H, CH_2), 3.64 (s, 3H, OCH_3), 1.23 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 200.8, 171.1, 158.6, 130.9, 130.0, 128.4, 126.3, 123.6, 123.3, 122.4, 119.7, 118.5, 113.6, 111.1, 109.2, 61.9, 61.7, 55.0, 45.6, 41.3, 14.2; IR(KBr) υ: 3059, 2934, 2837, 1731, 1592, 1512, 1488, 1459, 1329, 1300, 1253, 1178, 1155, 1091, 1034, 931, 883, 780, 747 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{28}ClNO_5$ ($[M+Na]^+$): 612.1548, found: 612.1540.

Ethyl

4-(4-chlorophenyl)-1',3'-dioxo-3-(m-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2i): yellow solid, 0.170g, 57%, m.p. 250-252 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.45 (s, 1H, NH), 7.92-7.91 (m, 1H, ArH), 7.75-7.70 (m, 3H, ArH), 7.35 (d, *J* = 8.0 Hz, 1H, ArH), 7.25-7.20 (m, 2H, ArH), 7.12-7.10 (m, 1H, ArH), 7.05-6.98 (m, 2H, ArH), 6.95-6.84 (m, 6H, ArH), 4.96 (d, *J* = 10.0 Hz, 1H, CH), 4.38 (s, 1H, CH), 4.33 (d, *J* = 10.0 Hz, 1H, CH), 4.20 (q, *J* = 8.0 Hz, 2H, CH_2), 2.13 (s, 3H, CH_3), 1.21 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 200.7, 198.5, 171.1, 141.5, 141.0, 138.4, 137.9, 137.7, 136.5, 135.7, 135.5, 133.2, 131.1, 130.9, 130.9, 128.4, 128.1, 128.1, 126.3, 126.2, 123.6, 123.3, 122.3, 119.7, 118.4, 111.0, 109.1, 61.7, 45.5, 44.9, 42.1, 21.3, 14.1; IR(KBr) υ: 3100, 3025, 2914, 2800, 1756, 1514, 1478, 1429, 1228, 1200, 1150, 1123, 1095, 1044, 911, 823, 740, 720 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{28}ClNO_4$ ($[M+Na]^+$): 596.1599, found: 596.1623.

Ethyl

4-(4-chlorophenyl)-1',3'-dioxo-3-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2j): yellow solid, 0.179g, 60%, m.p. 240-242 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.46 (s, 1H, NH), 7.92-7.90 (m, 1H, ArH), 7.75-7.70 (m, 3H, ArH), 7.35 (d, *J* = 8.0 Hz, 1H, ArH), 7.20 (d, *J* = 8.0 Hz, 2H, ArH), 7.13-7.09 (m, 1H, ArH), 7.03-6.98 (m, 4H, ArH), 6.89-6.85 (m, 4H,

ArH), 4.93 (d, *J* = 9.6 Hz, 1H, CH), 4.38 (s, 1H, CH), 4.34 (d, *J* = 9.6 Hz, 1H, CH), 4.18 (q, *J* = 7.2 Hz, 2H, CH_2), 2.14 (s, 3H, CH_3), 1.22 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 200.7, 198.6, 171.0, 141.6, 141.0, 138.3, 136.9, 136.5, 135.7, 135.5, 134.9, 133.2, 131.1, 130.9, 129.5, 128.9, 128.4, 126.3, 123.6, 123.3, 122.3, 119.6, 118.5, 111.0, 109.2, 61.9, 61.7, 45.6, 41.7, 20.9, 14.2; IR(KBr) υ: 3010, 2920, 2814, 1712, 1504, 1432, 1218, 1200, 1172, 1141, 1070, 1020, 921, 905, 832, 750, 725 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{28}ClNO_4$ ([M+Na]$^+$): 596.1599, found: 596.1607.

Ethyl

3-(4-nitrophenyl)-1',3'-dioxo-4-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2k): yellow solid, 0.158g, 52%, m.p. 255-257 ^{o}C;^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (s, 1H, NH), 7.94-7.91 (m, 3H, ArH), 7.94-7.71 (m, 3H, ArH), 7.41-7.35 (m, 3H, ArH), 7.14-7.10 (m, 1H, ArH), 7.07-7.05 (m, 2H, ArH), 6.93-6.88 (m, 4H, ArH), 5.07 (d, *J* = 10.0 Hz, 1H, CH), 4.56 (d, *J* = 10.0 Hz, 1H, CH), 4.42 (s, 1H, CH), 4.20 (q, *J* = 8.0 Hz, 2H, CH_2), 2.31 (s, 3H, CH_3), 1.24 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 200.3, 198.0, 170.5, 147.1, 146.4, 141.5, 140.8, 137.3, 136.5, 136.0, 135.8, 130.9, 129.8, 129.3, 129.1, 126.4, 123.9, 123.4, 123.3, 122.5, 119.7, 118.6, 111.0, 109.5, 62.5, 62.0, 45.9, 45.1, 41.5, 21.2, 14.2; IR(KBr) υ: 3052, 2918, 2810, 1703, 1511, 1410, 1201, 1178, 1145, 1100, 1070, 1020, 921, 905, 832, 800, 743, 722 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{28}N_2O_6$ ([M+Na]$^+$): 607.1840, found: 607.1836.

Ethyl

3-(4-nitrophenyl)-1',3'-dioxo-4-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2k'): yellow solid, 0.030g, 10%, m.p. 253-255 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55 (s, 1H, NH), 7.90 (d, *J* = 8.0 Hz, 2H, ArH), 7.51-7.47 (m, 4H, ArH), 7.38-7.34 (m, 3H, ArH), 7.13-7.09 (m, 1H, ArH), 6.97-6.95 (m, 1H, ArH), 6.82-6.75 (m, 2H, ArH), 6.72-6.67 (m, 2H, ArH), 6.40 (d, *J* = 8.0 Hz, 1H, ArH), 5.26 (d, *J* = 11.6 Hz, 1H, CH), 5.01 (s, 1H, CH), 4.46 (d, *J* = 11.6 Hz, 1H, CH), 4.18-4.05 (m, 2H, CH_2), 2.08 (s, 3H, CH_3), 1.13 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 202.0, 201.7, 170.3, 147.0, 145.4, 143.0, 142.0, 137.0, 136.2, 135.5, 135.2, 133.4, 130.2, 130.1, 129.8, 129.2, 128.8, 128.4, 126.4, 123.3, 122.3, 122.2, 121.9, 120.4, 119.3, 110.9, 109.7, 63.5, 61.9, 48.0, 47.1, 44.1, 20.9, 14.0; IR(KBr) υ: 3074, 2917, 2831, 1732, 1701, 1590, 1511, 1450, 1342, 1248, 1140, 1040, 1012, 935, 806, 767, 756, 701 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{28}N_2O_6$ ([M+Na]$^+$): 607.1840, found: 607.1831.

Ethyl

3-(4-methoxyphenyl)-4-(4-nitrophenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2l): yellow solid, 0.165g, 53%, m.p. 255-257 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (s, 1H, NH), 8.11 (d, *J* = 8.0 Hz, 2H, ArH), 7.93 (d, *J* = 8.0 Hz, 1H, ArH), 7.81-7.69 (m, 3H, ArH), 7.38 (d, *J* = 8.0 Hz, 1H, ArH), 7.25-7.23 (m, 2H, ArH), 7.15-7.11 (m, 1H, ArH), 7.09-7.01 (m, 2H, ArH), 6.91-6.88 (m, 1H, ArH), 6.83-6.81 (m, 1H, ArH), 6.58 (d, *J* = 8.0 Hz, 2H, ArH), 4.94 (d, *J* = 10.0 Hz, 1H, CH), 4.49 (s, 1H, CH), 4.32 (d, *J* = 10.0 Hz, 1H, CH), 4.24-4.20 (m, 2H, CH_2), 3,64 (s, 3H, OCH_3), 1.24 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 200.4, 170.9, 158.7, 147.6, 147.2, 141.4, 141.0, 136.6, 136.0, 135.9, 131.3, 130.6, 130.5, 126.0, 123.7, 123.4, 123.3, 122.6, 119.9, 118.1, 113.7, 111.2, 108.3, 61.9, 61.5, 55.0, 45.5, 41.6, 14.2; IR(KBr) υ: 3059, 2932, 2830, 1722, 1703, 1578, 1507, 1488, 1459, 1322, 1253, 1170, 1149, 1050, 1022, 933, 853, 826, 780, 743 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{28}N_2O_7$ ($[M+Na]^+$): 623.1789, found: 623.1781.

3. General procedure for the preparation of spiro[carbazole-2,3'-indolines] 3a-3m: In a Shlenck tube and in a nitrogen atmosphere, a mixture of ethyl indole-2-acetate (0.5 mmol), aromatic aldehyde (0.6 mmol), isatylidene malononitrile (0.5 mmol), and $CuSO_45H_2O$ (0.2 mmol) in toluene (6.0 mL) was heated at 120-130 ^{o}C for 16 h. Then, the solvent was removed by rotatory evaporation at reduced pressure. The residue was subjected to silica chromatography with light petroleum and ethyl acetate (V/V = 6:1) as eluent to give the product for analysis.

Ethyl

1'-benzyl-3,3-dicyano-2'-oxo-4-phenyl-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3a): white solid, 0.180g, 60%, m.p. 212-214 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.96 (s, 1H, NH), 7.73 (d, *J* = 7.6 Hz, 2H, ArH), 7.68-7.66 (m, 1H, ArH), 7.51-7.46 (m, 4H, ArH), 7.41-7.31 (m, 7H, ArH), 7.17-7.16 (m, 2H, ArH), 6.91-6.84 (m, 2H, ArH), 6.44 (d, *J* = 7.2 Hz, 1H, ArH), 5.46 (s, 1H, CH), 5.14 (s, 1H, CH), 5.07 (d, *J* = 15.2 Hz, 1H, CH), 4.97 (d, *J* = 16.0 Hz, 1H, CH), 4.19-4.16 (m, 1H, CH), 3.94-3.90 (m, 1H, CH), 0.97 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (600 MHz, $CDCl_3$) δ: 171.8, 166.9, 143.9, 136.3, 135.0, 134.3, 131.6, 130.9, 130.3, 129.3, 128.8, 128.6, 127.9, 126.0, 125.7, 125.7, 123.5, 123.4, 122.6, 120.6, 119.9, 112.9, 112.2, 111.1, 110.0, 108.3, 62.8, 52.0, 49.7, 45.6, 45.3, 45.1, 13.7; IR(KBr) υ: 3059, 2932, 2830, 1719, 1611, 1491, 1456, 1366, 1300, 1238, 1217, 1179, 1136, 1079, 1051, 995, 847, 752, 713, 696, 656 cm^{-1}; MS (*m/z*):

HRMS (ESI) Calcd. for $C_{38}H_{29}N_3O_3$ ([M+Na]$^+$): 599.2054, found: 599.2078.

Ethyl

1'-benzyl-3,3-dicyano-5'-methyl-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3b): white solid, 0.223g, 71%, m.p. 205-207 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.49 (s, 1H, NH), 7.55 (d, *J* = 7.2 Hz, 2H, ArH), 7.45 (d, *J* = 8.0 Hz, 1H, ArH), 7.36-7.28 (m, 5H, ArH), 7.25-7.20 (m, 2H, ArH), 7.14 (d, *J* = 8.0 Hz, 2H, ArH), 6.94-6.87 (m, 2H, ArH), 6.70 (s, 1H, ArH), 6.55 (d, *J* = 8.0 Hz, 1H, ArH), 5.19 (s, 1H, CH), 5.06 (d, *J* = 15.2 Hz, 1H, CH), 4.99 (d, *J* = 15.2 Hz, 1H, CH), 4.78 (s, 1H, CH), 3.95-3.91 (m, 1H, CH), 3.74-3.69 (m, 1H, CH), 3.63-3.59 (m, 1H, CH), 2.40 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 0.60 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 173.1, 167.8, 142.3, 139.3, 136.9, 135.1, 133.1, 131.5, 131.1, 130.4, 130.2, 129.4, 129.0, 128.7, 128.5, 128.0, 127.9, 125.4, 125.0, 122.8, 120.7, 119.8, 112.3, 111.4, 109.9, 107.7, 62.2, 53.6, 48.0, 45.2, 43.5, 21.2, 21.1, 13.3; IR(KBr) υ: 3040, 2983, 1739, 1711, 1600, 1495, 1441, 1372, 1348, 1303, 1285, 1243, 1198, 1114, 1023, 855, 808, 741, 710, 655 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{40}H_{33}N_3O_3$ ([M+Na]$^+$): 627.2367, found: 627.2395.

Ethyl

1'-benzyl-3,3-dicyano-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3c): white solid, 0.192g, 63%, m.p. 220-222 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.64 (s, 1H, NH), 7.72 (d, *J* = 7.2 Hz, 1H, ArH), 7.51-7.45 (m, 4H, ArH), 7.38-7.34 (m, 2H, ArH), 7.26 (s, 1H, ArH), 7.15-7.08 (m, 3H, ArH), 6.95-6.93 (m, 1H, ArH), 6.80-6.69 (m, 4H, ArH), 6.38 (d, *J* = 7.2 Hz, 1H, ArH), 5.42-5.39 (m, 1H, CH), 5.35-5.30 (m, 1H, CH), 5.02 (s, 1H, CH), 4.09 (q, *J* = 8.0 Hz, 2H, CH_2), 2.06 (s, 3H, CH_3), 1.02 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 202.1, 170.7, 150.6, 143.2, 141.9, 136.8, 136.2, 135.0, 134.9, 133.4, 132.1, 130.1, 129.9, 128.4, 126.3, 125.4, 122.4, 121.7, 120.3, 119.1, 110.8, 109.8, 63.6, 61.8, 48.6, 44.7, 40.4, 20.8, 13.6; IR(KBr) υ: 3122, 2984, 2810, 1722, 1698, 1591, 1525, 1456, 1355, 1316, 1246, 1196, 1164, 1035, 924, 853, 804, 775, 742, 711, 670, 581, 491 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{38}H_{29}FN_4O_3$ ([M+Na]$^+$): 609.2296, found: 609.1904.

Ethyl

3-(4-methoxyphenyl)-4-(4-nitrophenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (3d): white solid, 0.190g, 62%, m.p. 232-234 ^{o}C; ^{1}H NMR (400 MHz,

$CDCl_3$) δ: 9.49 (s, 1H, NH), 7.44-7.37 (m, 4H, ArH), 7.25-7.24 (m, 2H, ArH), 7.15-7.14 (m, 1H, ArH), 6.95-6.86 (m, 3H, ArH), 6.55-6.54 (m, 1H, ArH), 5.17 (s, 1H, CH), 4.75 (s, 1H, CH), 4.07-4.02 (m, 2H, CH_2), 3.99-3.97 (m, 1H, CH), 3.74-3.60 (m, 1H, CH), 2.40 (s, 3H, CH_3), 1.77-1.76 (m, 2H, CH_2), 1.51-1.49 (m, 2H, CH_2), 0.99-0.98 (m, 3H, CH_3), 0.96-0.92 (m, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 172.4, 167.3, 143.7, 139.5, 136.8, 131.2, 130.3, 129.9, 129.0, 128.4, 127.1, 125.2, 124.9, 124.6, 123.0, 120.7, 120.0, 111.8, 111.4, 111.0, 110.1, 107.5, 62.5, 53.4, 47.8, 46.8, 43.4, 40.9, 29.2, 21.2, 20.4, 13.6, 13.5; IR(KBr) υ: 3011, 2963, 2875, 1737, 1717, 1607, 1512, 1483, 1455, 1351, 1306, 1242, 1196, 1113, 1023, 893, 851, 822, 760, 740, 667, 618, 554, 492 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{35}H_{31}ClN_4O_3$ ($[M+Na]^+$): 613.1977, found: 613.1981.

Ethyl

1'-benzyl-3,3-dicyano-5'-fluoro-4-(4-methoxyphenyl)-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3e): white solid, 0.188g, 58%, m.p. 210-212 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.95 (s, 1H, NH), 7.59-7.57 (m, 1H, ArH), 7.51-7.45 (m, 3H, ArH), 7.38-7.30 (m, 5H, ArH), 7.17-7.13 (m, 1H, ArH), 7.08-7.00 (m, 2H, ArH), 6.89-6.86 (m, 2H, ArH), 6.81-6.77 (m, 1H, ArH), 6.51 (d, *J* = 8.0 Hz, 1H, ArH), 5.42-5.41 (m, 1H, CH), 5.06-5.02 (m, 2H, CH_2), 4.96-4.92 (m, 1H, CH), 4.21-4.14 (m, 1H, CH), 3.99-3.94 (m, 1H, CH), 3.84 (s, 3H, OCH_3), 1.02 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 171.5, 166.7, 139.9, 136.3, 134.7, 132.7, 131.4, 128.8, 128.0, 127.8, 125.9, 125.6, 125.2, 122.7, 120.6, 119.9, 117.3, 117.1, 114.3, 113.7, 112.8, 112.1, 112.1, 111.8, 111.1, 110.8, 110.7, 108.5, 62.9, 55.2, 52.2, 49.7, 45.6, 45.1, 44.6, 13.8; IR(KBr) υ: 3065, 2981, 2838, 1719, 1611, 1584, 1512, 1493, 1452, 1350, 1327, 1305, 1255, 1217, 1179, 1134, 1029, 962, 933, 860, 838, 813, 756, 741, 694 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{39}H_{30}FN_3O_4$ ($[M+Na]^+$): 647.2065, found: 647.2089.

Ethyl

1'-butyl-3,3-dicyano-4-(4-methoxyphenyl)-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3f): white solid, 0.198g, 63%, m.p. 235-237 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.49 (s, 1H, NH), 7.47-7.41 (m, 3H, ArH), 7.29-7.27 (m, 1H, ArH), 7.25-7.21 (m, 1H, ArH), 6.97-6.92 (m, 3H, ArH), 6.87-6.86 (m, 2H, ArH), 6.56 (d, *J* = 8.0 Hz, 1H, ArH), 5.17 (s, 1H, CH), 4.75 (s, 1H, CH), 4.11-4.05 (m, 1H, CH), 4.03-3.92 (m, 2H, CH_2), 3.84 (s, 3H, OCH_3), 3.66-3.60 (m, 1H, CH), 1.77 (q, *J* = 7.2 Hz, 2H, CH_2), 1.50 (q, *J* = 8.0 Hz, 2H, CH_2), 0.99 (t, *J* = 8.0 Hz, 3H,

CH_3), 0.92 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 172.4, 167.3, 143.7, 136.8, 132.3, 131.7, 131.2, 128.4, 127.1, 125.2, 124.9, 123.0, 120.7, 114.2, 113.6, 111.9, 111.5, 111.1, 110.1, 107.6, 62.5, 55.2, 53.4, 47.9, 46.5, 43.4, 40.9, 29.2, 20.4, 13.6, 13.5; IR(KBr) υ: 2956, 2933, 2871, 1749, 1722, 1609, 1585, 1511, 1481, 1454, 1352, 1304, 1268, 1245, 1188, 1144, 1027, 841, 814, 743, 673, 616, 557 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{36}H_{33}N_3O_4$ ($[M+Na]^+$): 629.1926, found: 629.1927.

Ethyl

1'-benzyl-3,3-dicyano-4-(4-fluorophenyl)-5'-methyl-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3g): white solid, 0.193g, 61%, m.p. 210-212 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.97 (s, 1H, NH), 7.66-7.65 (m, 1H, ArH), 7.51-7.47 (m, 3H, ArH), 7.39-7.29 (m, 5H, ArH), 7.21-7.15 (m, 3H, ArH), 7.07-7.03 (m, 1H, ArH), 6.90-6.86 (m, 1H, ArH), 6.78 (d, *J* = 8.0 Hz, 1H, ArH), 6.45 (d, *J* = 8.0 Hz, 1H, ArH), 5.47 (s, 1H, CH), 5.09 (s, 1H, CH), 5.04 (d, *J* = 15.6 Hz, 1H, CH), 4.93 (d, *J* = 15.2 Hz, 1H, CH), 4.19-4.11 (m, 1H, CH), 3.97-3.90 (m, 1H, CH), 2.36 (s, 3H, CH_3), 0.99 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 171.6, 166.8, 141.3, 136.3, 135.0, 133.2, 132.2, 131.2, 130.2, 128.7, 127.8, 125.9, 125.5, 124.1, 122.7, 120.3, 119.9, 115.8, 115.6, 115.6, 115.4, 112.7, 112.1, 111.1, 109.7, 107.9, 62.7, 51.9, 49.7, 45.5, 45.0, 44.6, 21.2, 13.7; IR(KBr) υ: 3061, 2912, 2790, 1740, 1707, 1604, 1503, 1450, 1370, 1351, 1325, 1300, 1222, 1185, 1165, 1137, 1116, 1050, 1019, 859, 840, 814, 760, 738, 693, 661, 589 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{39}H_{30}FN_3O_3$ ($[M+Na]^+$): 631.2116, found: 631.2142.

Ethyl

3-(4-methoxyphenyl)-4-(4-nitrophenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (3h): white solid, 0.209g, 66%, m.p. 208-210 ^oC; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (s, 1H, NH), 7.71 (d, *J* = 7.2 Hz, 2H, ArH), 7.61 (d, *J* = 7.2 Hz, 1H, ArH), 7.49-7.47 (m, 3H, ArH), 7.39-7.30 (m, 7H, ArH), 7.19-7.15 (m, 2H, ArH), 6.91-6.88 (m, 2H, ArH), 6.47 (d, *J* = 8.0 Hz, 1H, ArH), 5.46-5.45 (m, 1H, CH), 5.11-5.10 (m, 1H, CH), 5.05 (d, *J* = 15.2 Hz, 1H, CH), 4.96 (d, *J* = 15.2 Hz, 1H, CH), 4.17-4.13 (m, 1H, CH), 3.95-3.87 (m, 1H, CH), 0.96 (t, *J* = 8.0 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 171.6, 166.7, 143.8, 136.3, 135.4, 134.9, 132.9, 132.7, 131.6, 130.9, 128.9, 128.8, 128.8, 127.9, 127.8, 125.8, 125.4, 123.4, 122.7, 120.3, 120.0, 112.6, 112.0, 111.2, 110.0, 107.6, 62.7, 51.8, 49.5, 45.5, 45.0, 44.7, 13.7; IR(KBr) υ: 3059, 2981, 2938, 2855, 1738, 1707, 1612, 1490, 1466, 1370, 1326, 1299, 1238, 1217, 1179, 1133, 1088,

1049, 1015, 951, 910, 840, 799, 759, 732, 697, 656, 587, 457 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{38}H_{28}ClN_3O_3$ ($[M+Na]^+$): 633.1664, found: 633.1689.

Ethyl

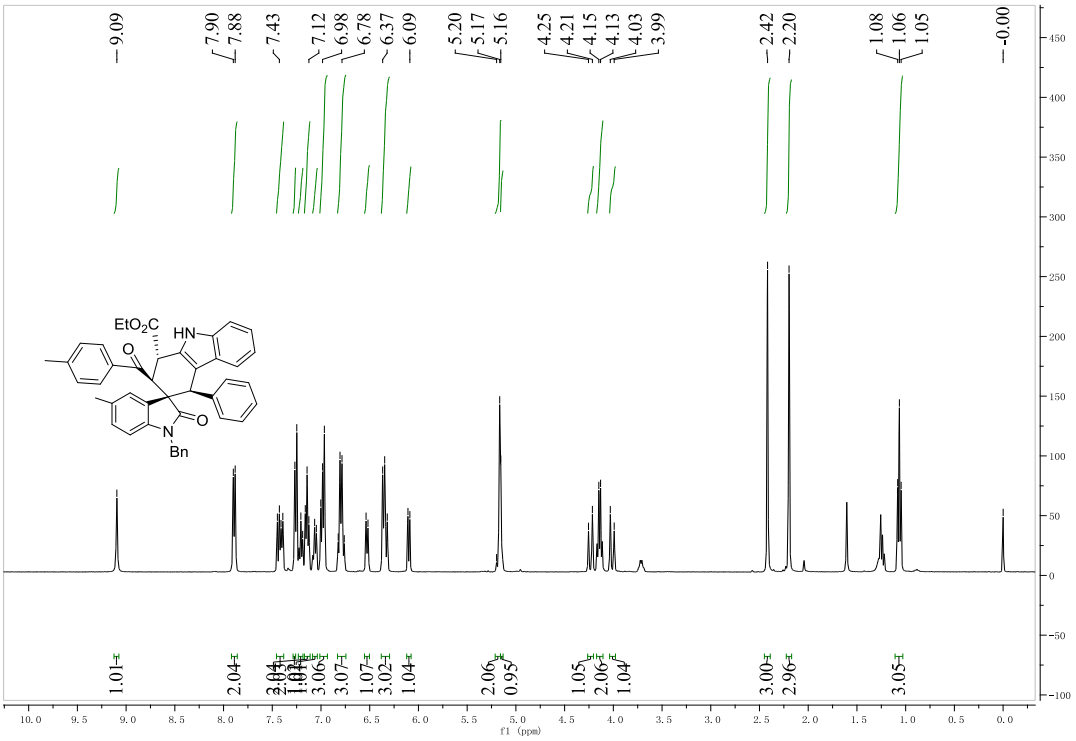
1'-benzyl-3,3-dicyano-5'-methyl-4-(4-nitrophenyl)-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3i): white solid, 0.171g, 52%, m.p. 222-224 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.04 (s, 1H, NH), 8.38-8.35 (m, 1H, ArH), 8.22-8.19 (m, 1H, ArH), 7.87-7.85 (m, 1H, ArH), 7.61-7.59 (m, 1H, ArH), 7.50-7.46 (m, 3H, ArH), 7.40 (d, *J* = 8.0 Hz, 1H, ArH), 7.36-7.27 (m, 3H, ArH), 7.19-7.16 (m, 2H, ArH), 6.90-6.86 (m, 1H, ArH), 6.79 (d, *J* = 8.0 Hz, 1H, ArH), 6.35 (d, *J* = 8.0 Hz, 1H, ArH), 5.61 (s, 1H, CH), 5.09 (s, 1H, CH), 5.03 (d, *J* = 15.6 Hz, 1H, CH), 4.94 (d, *J* = 15.6 Hz, 1H, CH), 4.20-4.14 (m, 1H, CH), 3.97-3.91 (m, 1H, CH), 2.36 (s, 3H, CH_3), 0.99 (t, *J* = 7.2 Hz, 3H, CH_3);^{13}C NMR (400 MHz, $CDCl_3$) δ: 171.4, 166.6, 148.6, 141.7, 141.3, 136.3, 134.9, 133.4, 132.5, 131.5, 131.5, 128.8, 127.9, 127.8, 126.3, 125.5, 125.1, 124.1, 123.8, 123.6, 122.9, 120.2, 119.8, 112.3, 111.8, 111.4, 109.9, 106.6, 62.9, 51.7, 49.0, 45.4, 45.1, 45.0, 21.2, 13.7; IR(KBr) υ: 2956, 2933, 2871, 1749, 1722, 1609, 1585, 1511, 1481, 1454, 1352, 1304, 1268, 1245, 1188, 1144, 1027, 841, 814, 743, 673, 616, 557 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{39}H_{30}N_4O_5$ ($[M+Na]^+$): 658.2061, found: 658.2091.

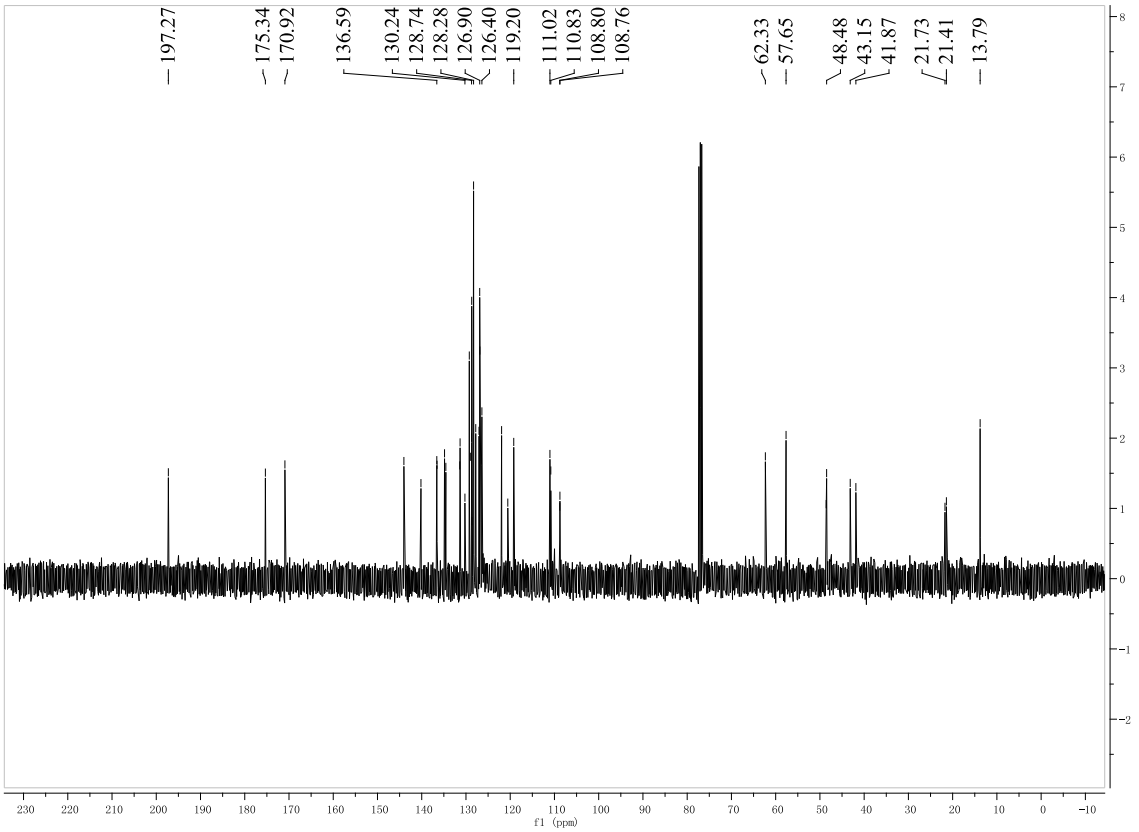
Ethyl

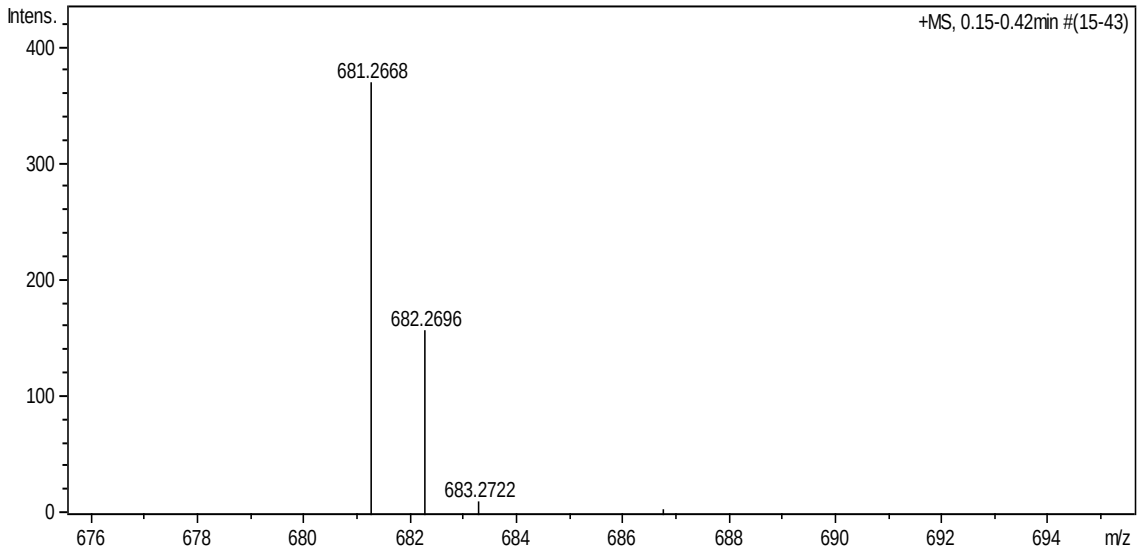
1'-benzyl-3,3-dicyano-5'-methyl-4-(4-nitrophenyl)-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3i'): white solid, 0.032g, 10%, m.p. 220-222 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.61 (s, 1H, NH), 8.30 (d, *J* = 8.0 Hz, 1H, ArH), 8.18 (d, *J* = 8.0 Hz, 1H, ArH), 7.67 (d, *J* = 8.0 Hz, 1H, ArH), 7.59-7.53 (m, 3H, ArH), 7.49 (d, *J* = 8.0 Hz, 1H, ArH), 7.36-7.30 (m, 3H, ArH), 7.26-7.23 (m, 1H, ArH), 7.17 (d, *J* = 8.0 Hz, 1H, ArH), 6.96-6.91 (m, 2H, ArH), 6.66 (s, 1H, ArH), 6.41 (d, *J* = 8.0 Hz, 1H, ArH), 5.19 (s, 1H, CH), 5.06 (d, *J* = 15.2 Hz, 1H, CH), 5.01 (s, 1H, CH), 4.95 (d, *J* = 13.6 Hz, 1H, CH), 3.96-3.92 (m, 1H, CH), 3.66-3.59 (m, 1H, CH), 2.13 (s, 3H, CH_3), 0.59 (t, *J* = 7.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 172.7, 167.4, 148.7, 142.3, 140.7, 136.9, 134.9, 133.3, 132.2, 131.9, 128.7, 128.5, 128.1, 125.2, 124.3, 123.6, 123.3, 122.3, 120.3, 119.9, 111.9, 111.8, 111.0, 110.1, 105.8, 62.4, 53.5, 47.3, 46.8, 45.2, 43.4, 21.1, 13.2; IR(KBr) υ: 3080, 2980, 1724, 1600, 1523, 1493, 1456, 1346, 1244, 1190, 1139, 1115, 1019, 852, 811, 741, 694, 654, 556, 489 cm^{-1}; MS (*m/z*): HRMS (ESI) Calcd. for $C_{39}H_{30}N_4O_5$ ($[M+Na]^+$): 658.2061, found: 658.2091.

Ethyl

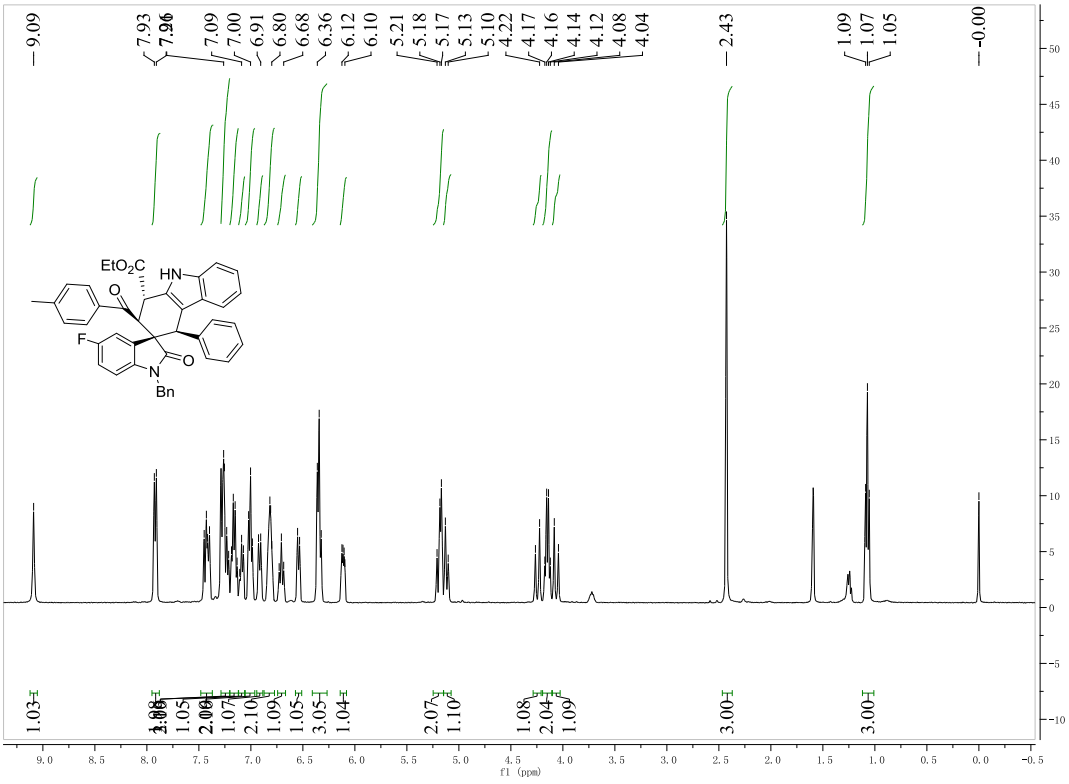
1'-benzyl-5'-methyl-3-(4-methylbenzoyl)-2'-oxo-4-phenyl-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1a):

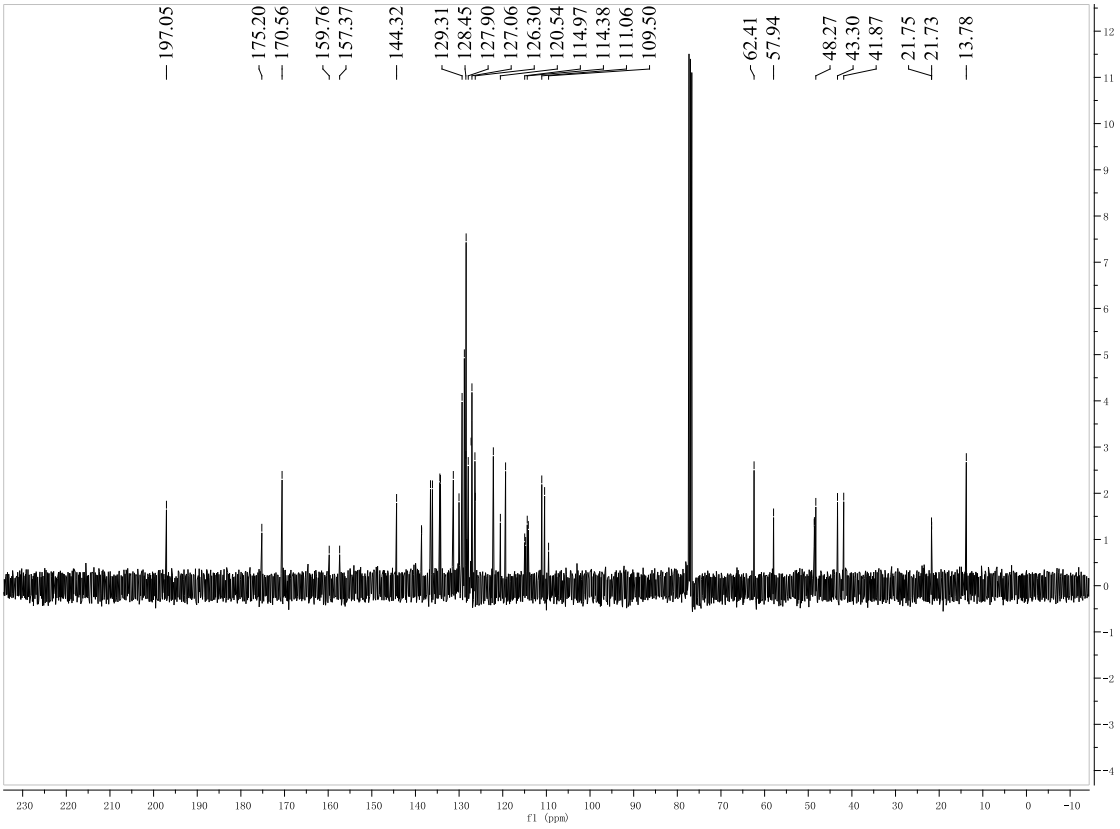


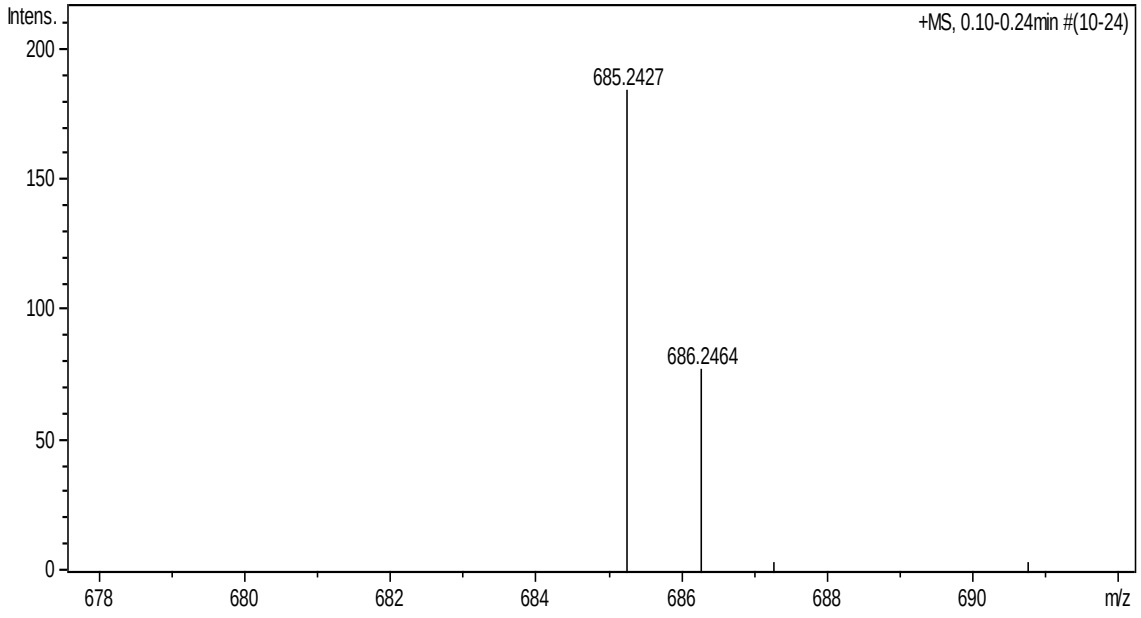




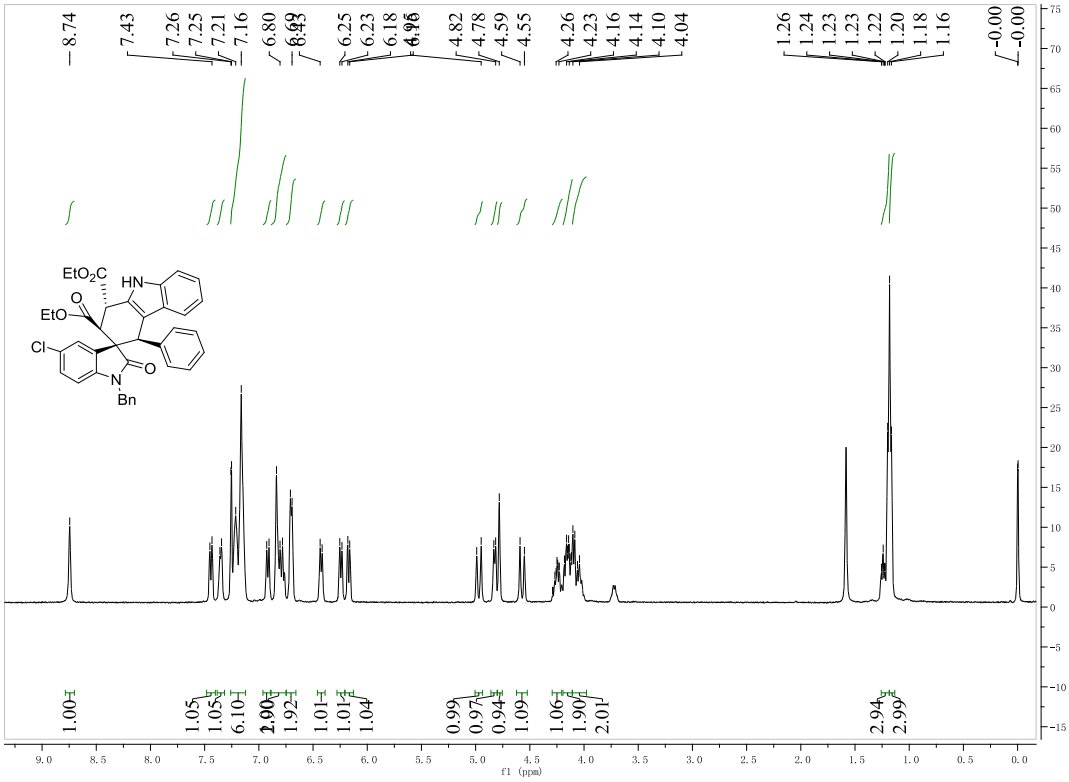
Ethyl-1'-benzyl-5'-fluoro-3-(4-methylbenzoyl)-2'-oxo-4-phenyl-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1b):

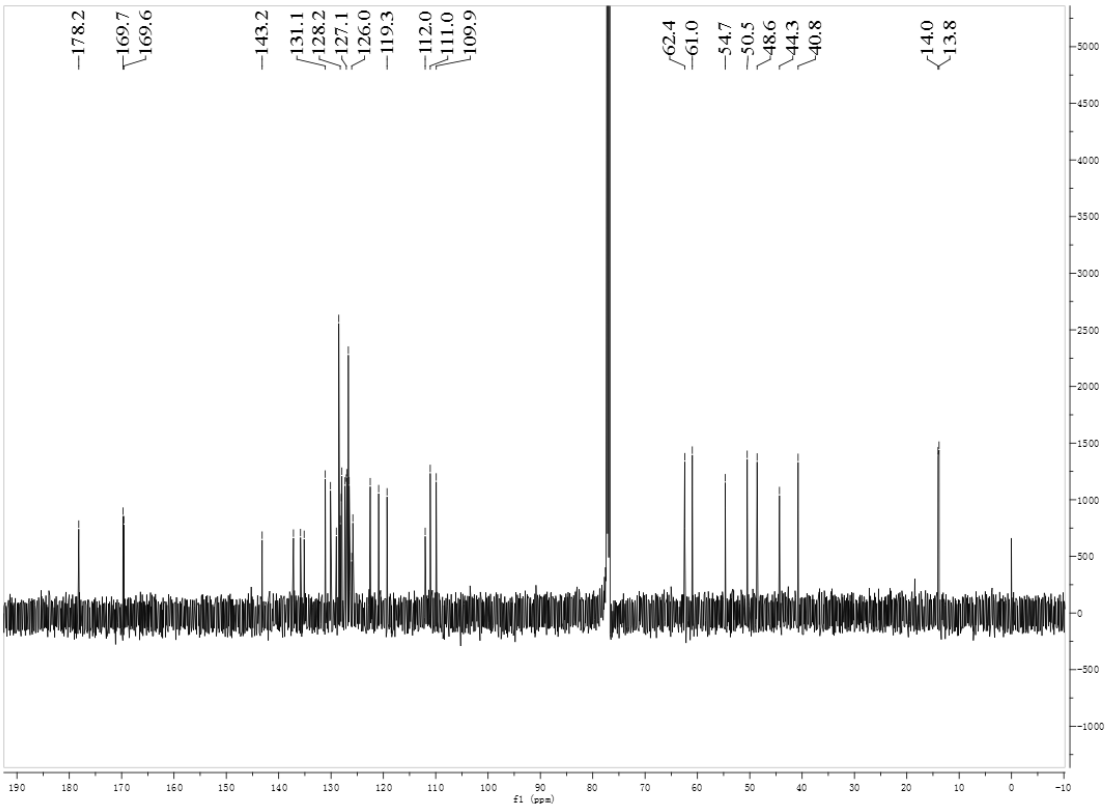


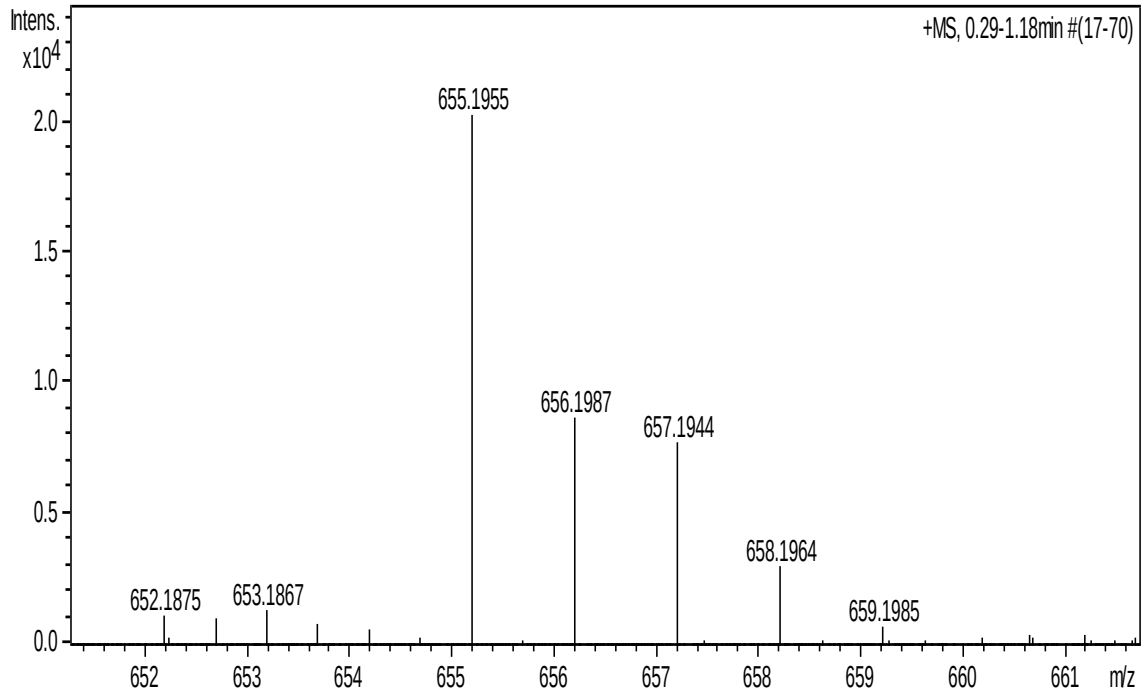

197.05
175.20
170.56
159.76
157.37
144.32
129.31
128.45
127.90
127.06
126.30
120.54
114.97
114.38
111.06
109.50
62.41
57.94
48.27
43.30
41.87
21.75
21.73
13.78
f1 (ppm)


Intens.
+MS, 0.10-0.24min #(10-24)
685.2427
686.2464
m/z

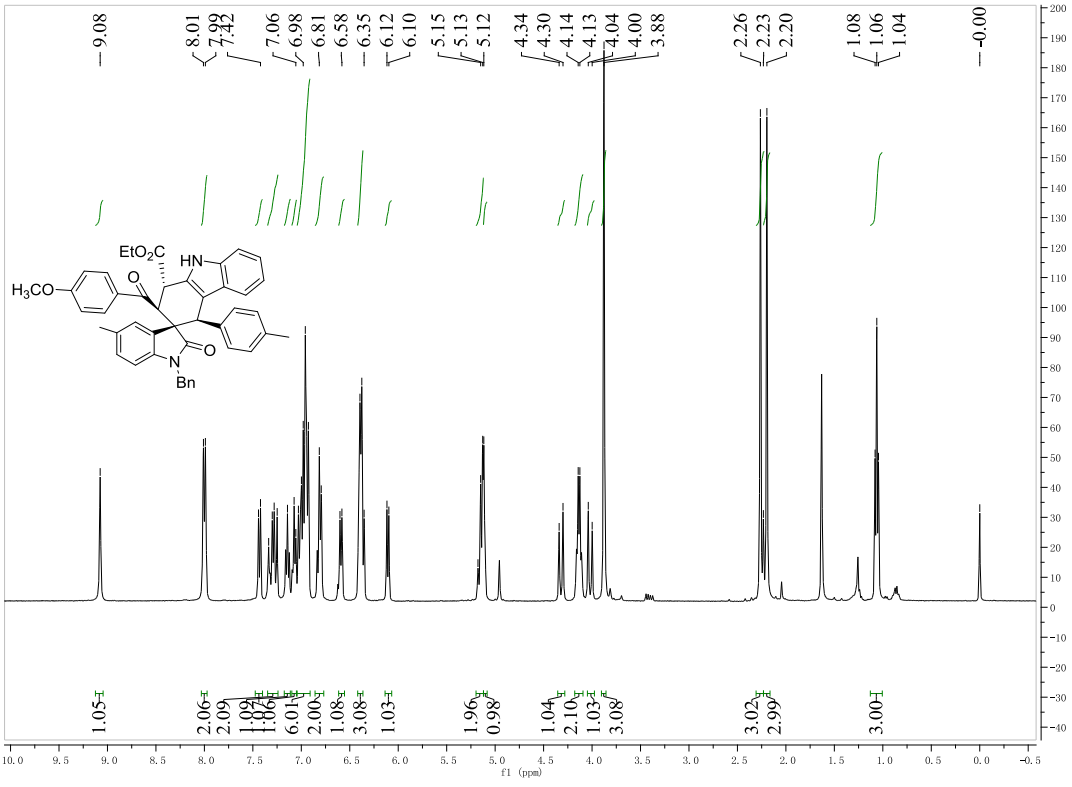
Diethyl
1'-benzyl-5'-chloro-2'-oxo-4-phenyl-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1,3-dicarboxylate (1c):

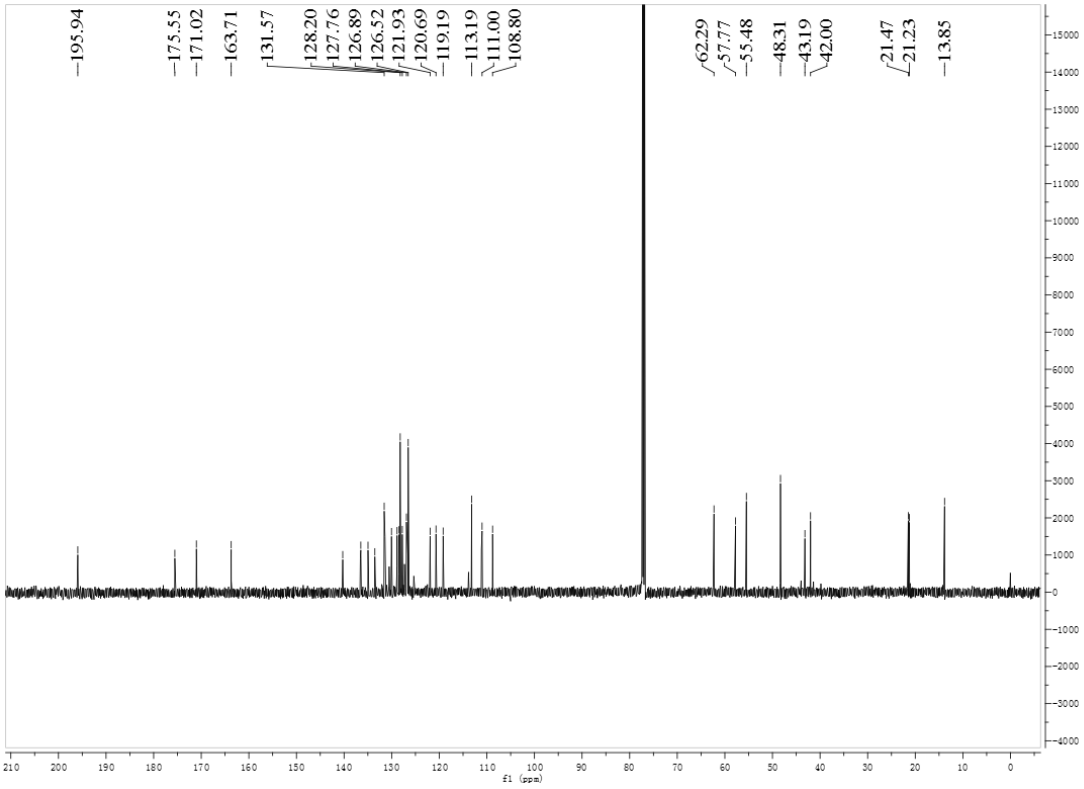


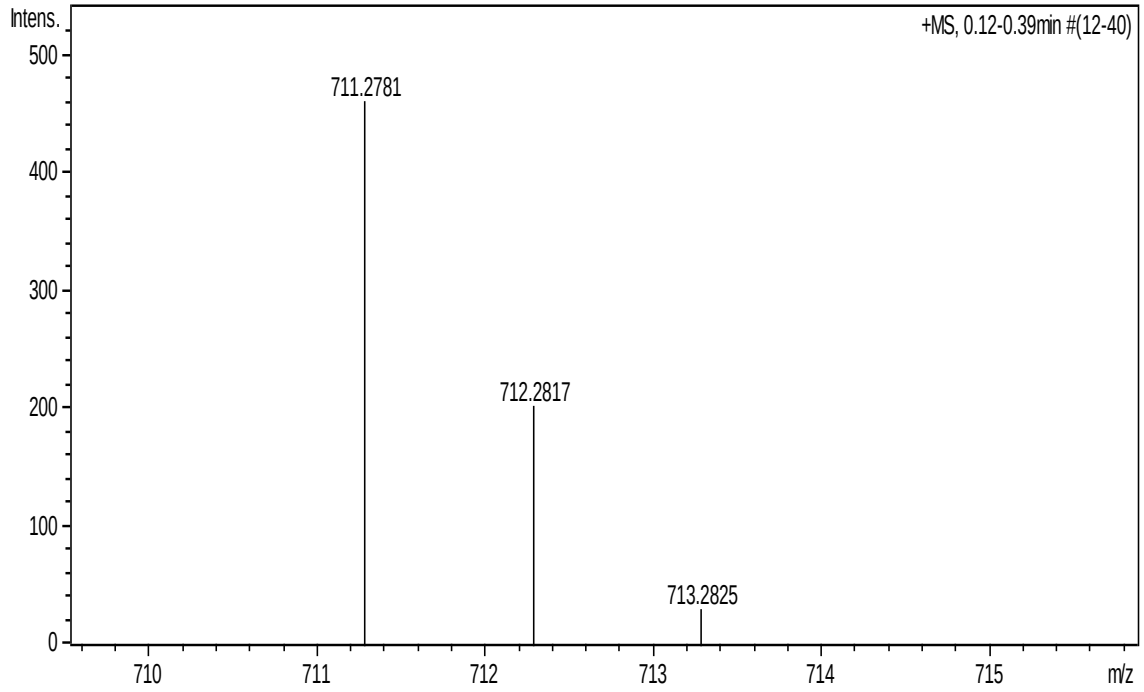




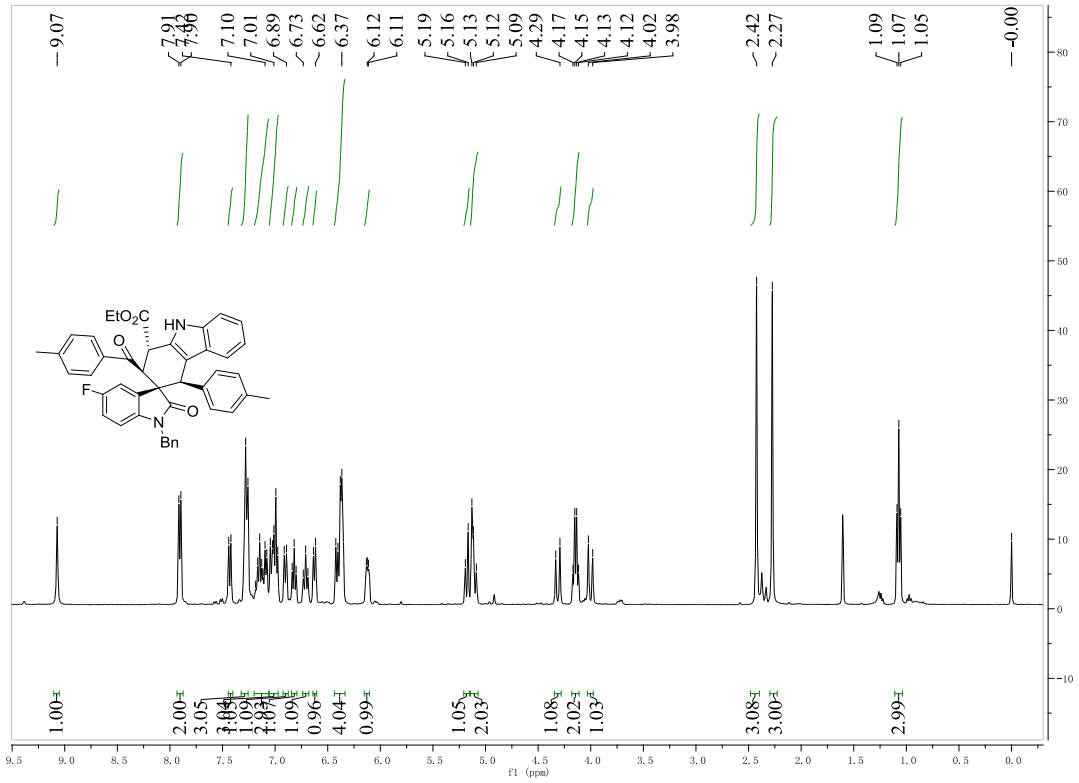
Ethyl-1'-benzyl-3-(4-methoxybenzoyl)-5'-methyl-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1d):

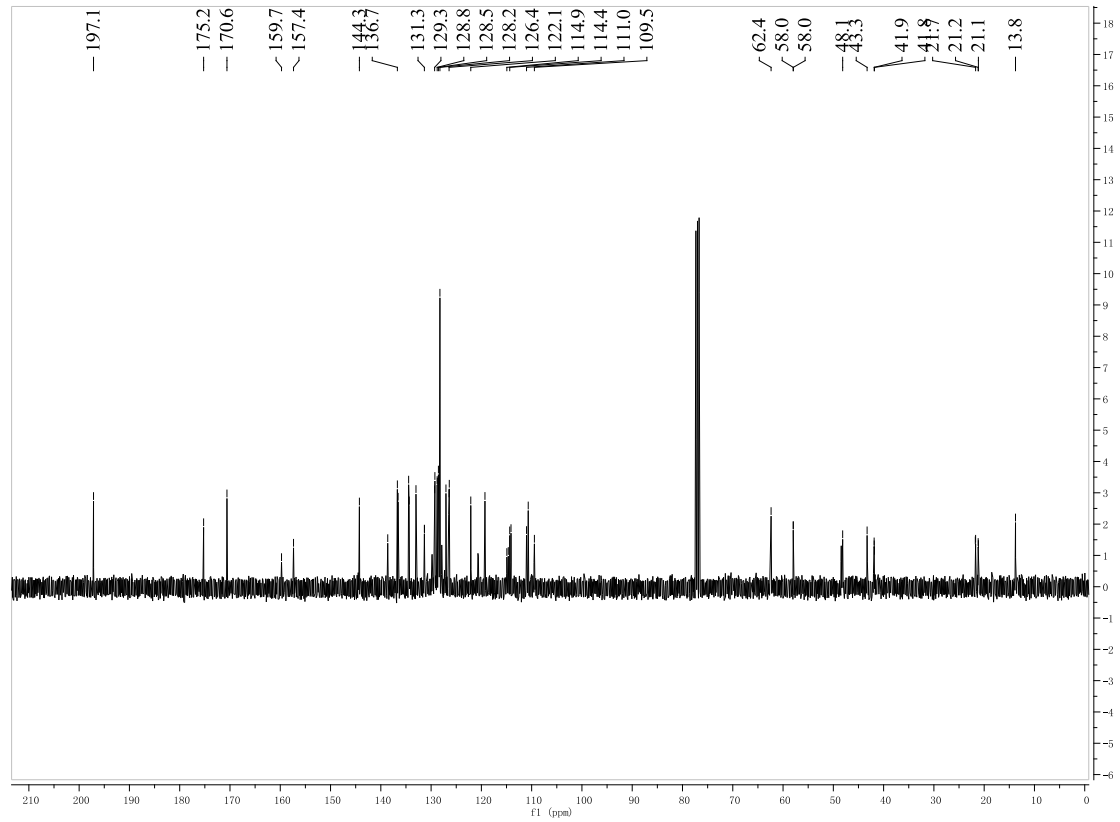


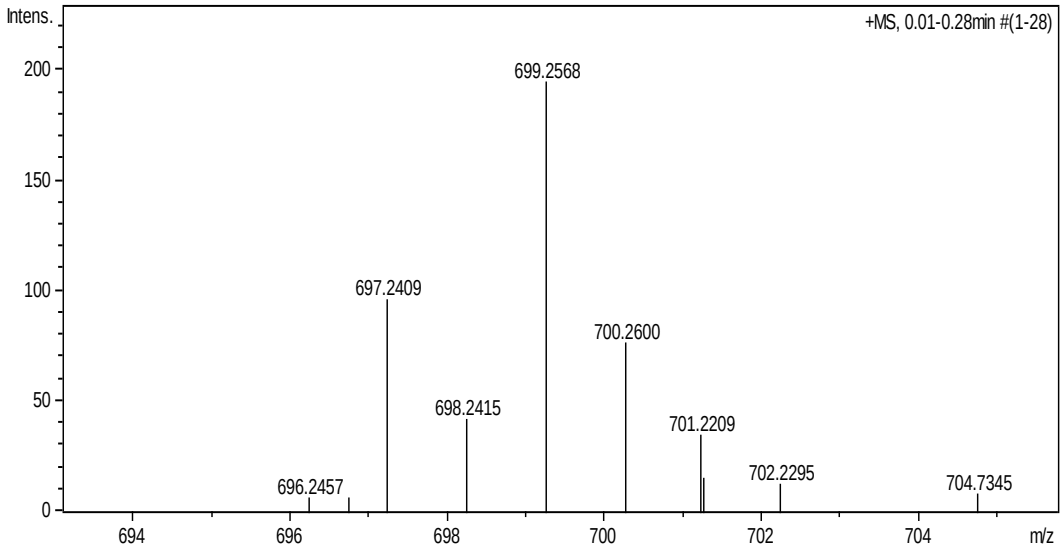

195.94
175.55
171.02
163.71
131.57
128.20
127.76
126.89
126.52
121.93
120.69
119.19
113.19
111.00
108.80
62.29
57.77
55.48
48.31
43.19
42.00
21.47
21.23
13.85
f1 (ppm)


Intens.
+MS, 0.12-0.39min #(12-40)
711.2781
712.2817
713.2825
m/z

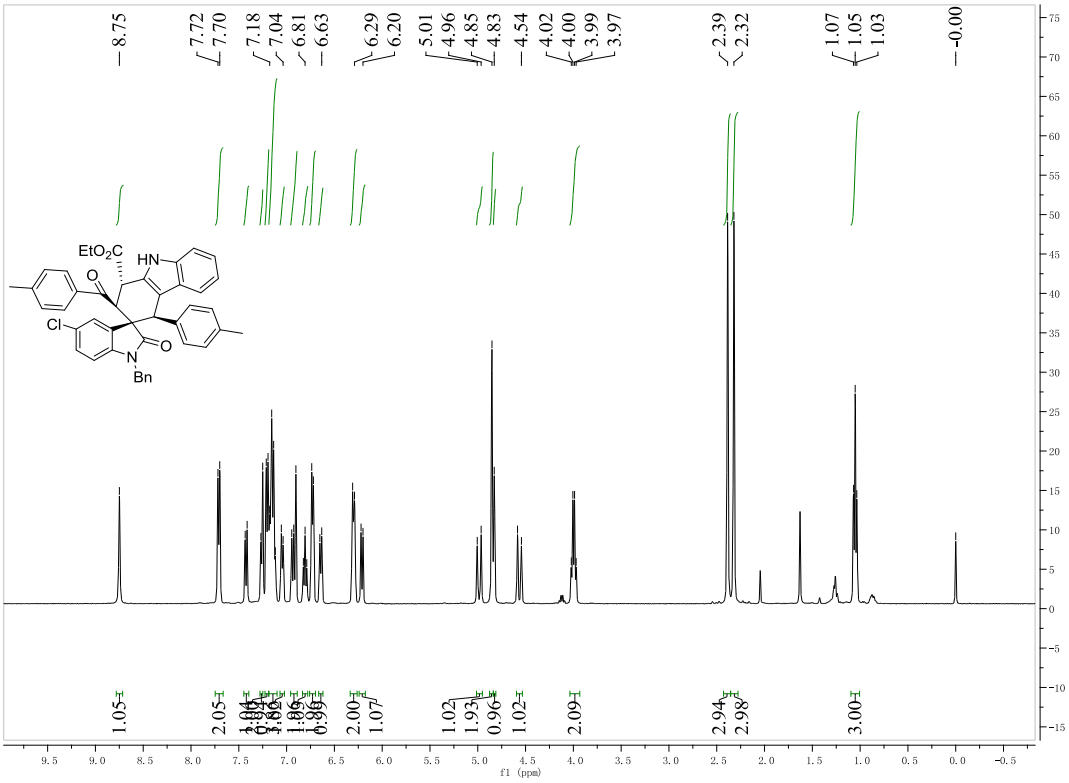
Ethyl-1'-benzyl-5'-fluoro-3-(4-methylbenzoyl)-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1e):

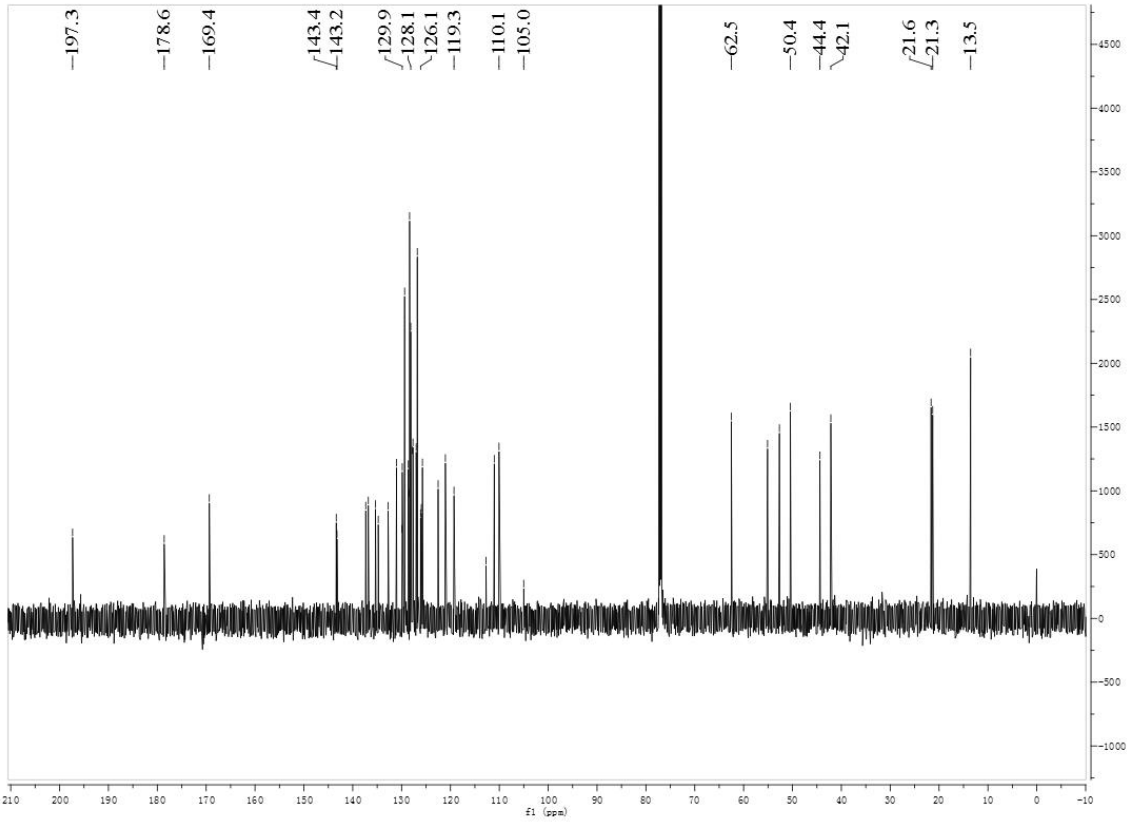


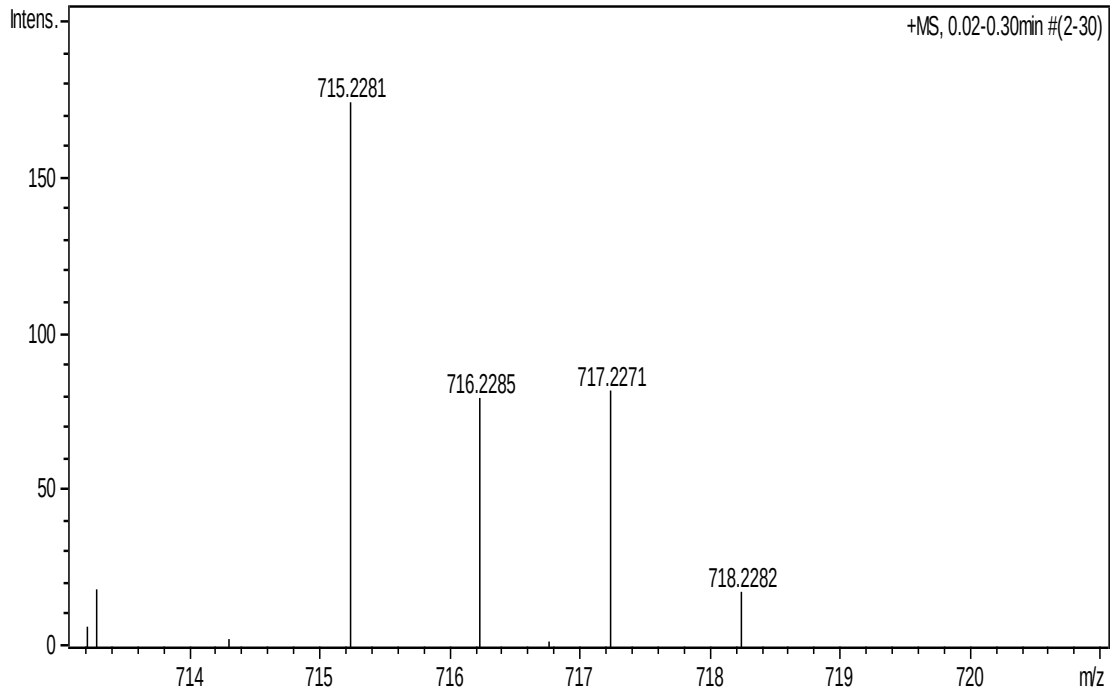




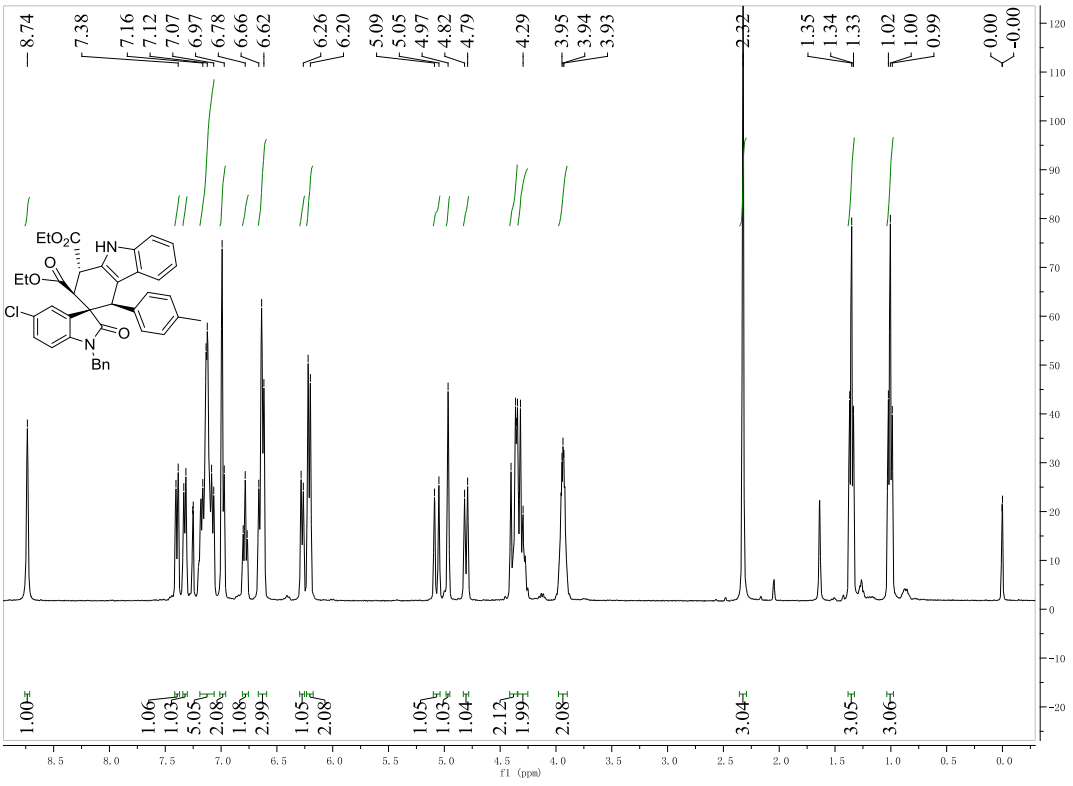
Ethyl-1'-benzyl-5'-chloro-3-(4-methylbenzoyl)-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1f):

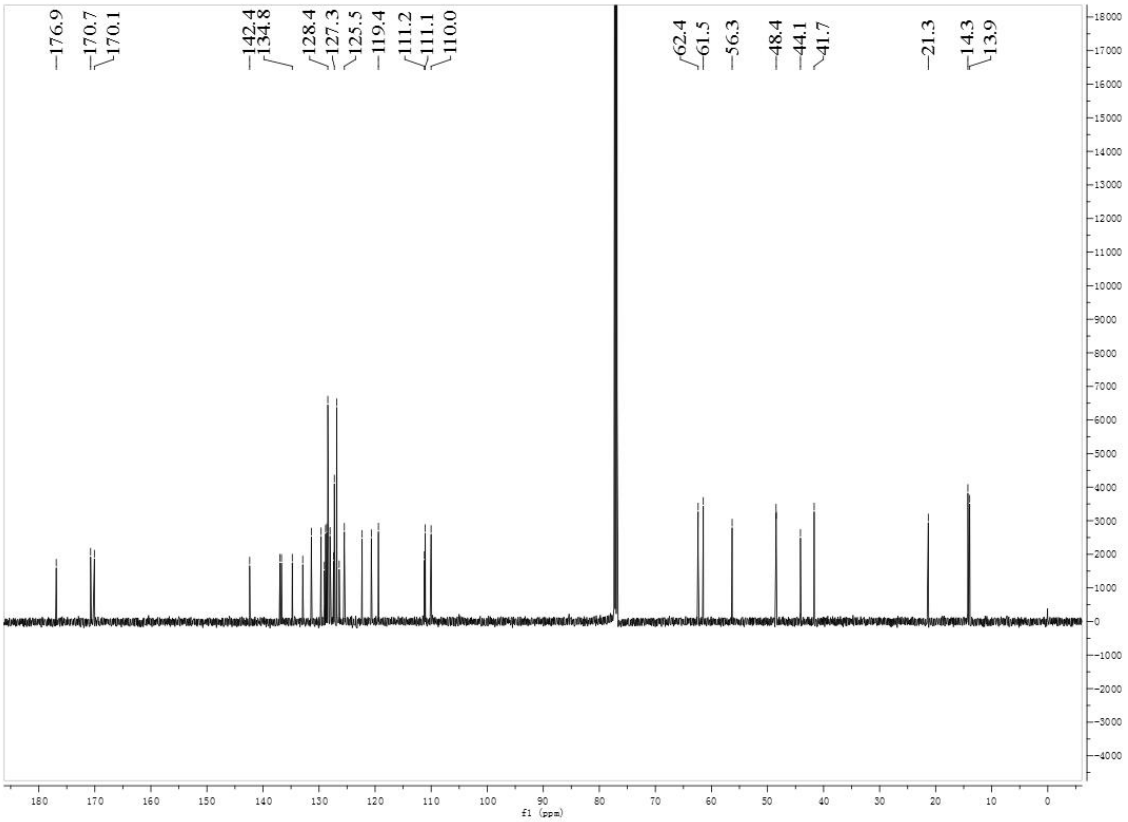


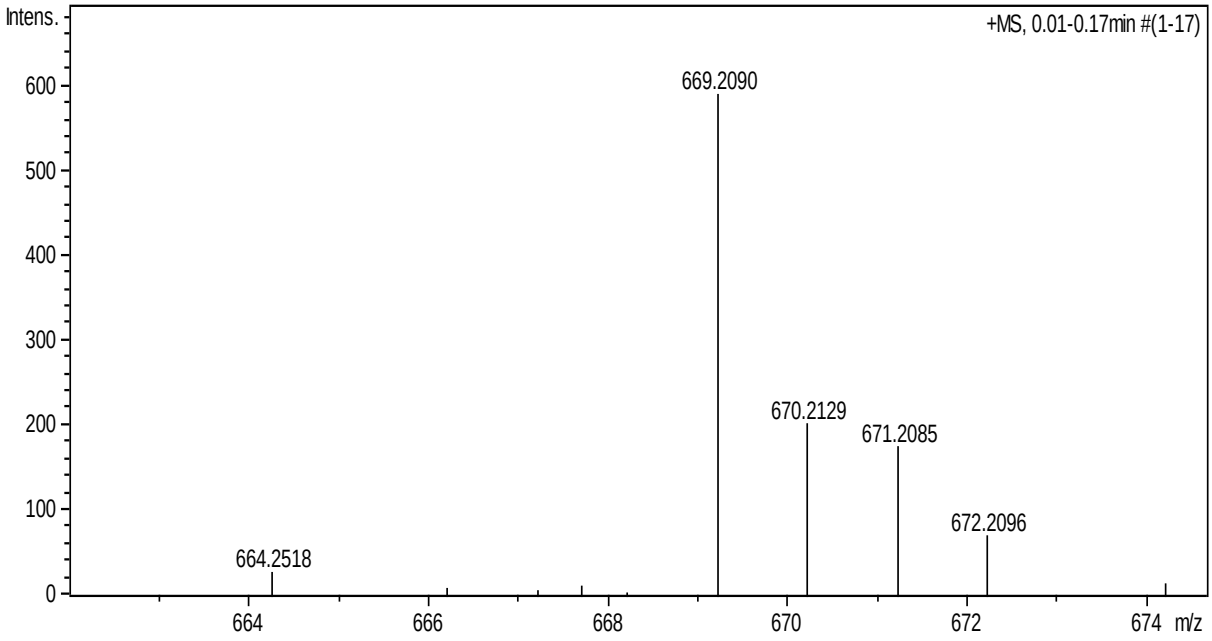

197.3
178.6
169.4
143.4
143.2
129.9
128.1
126.1
119.3
110.1
105.0
62.5
50.4
44.4
42.1
21.6
21.3
13.5
f1 (ppm)


Intens.
+MS, 0.02-0.30min #(2-30)
715.2281
716.2285
717.2271
718.2282
m/z

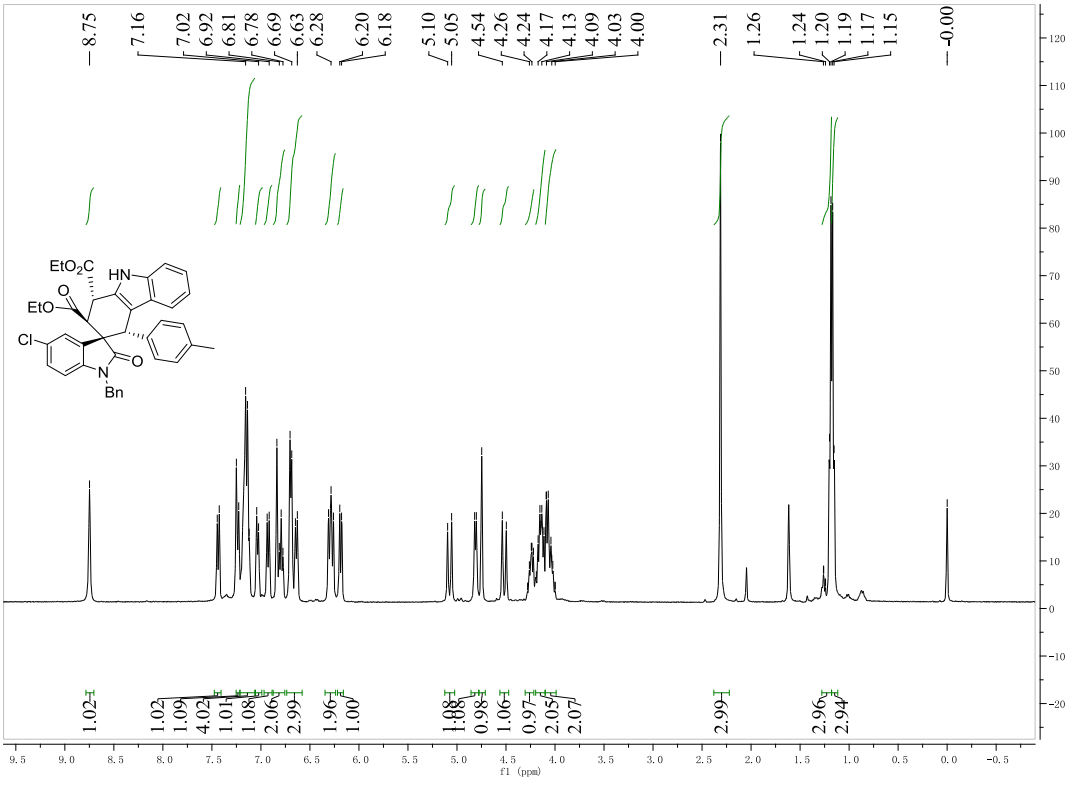
Diethyl-1'-benzyl-5'-chloro-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1,3-dicarboxylate (1g):

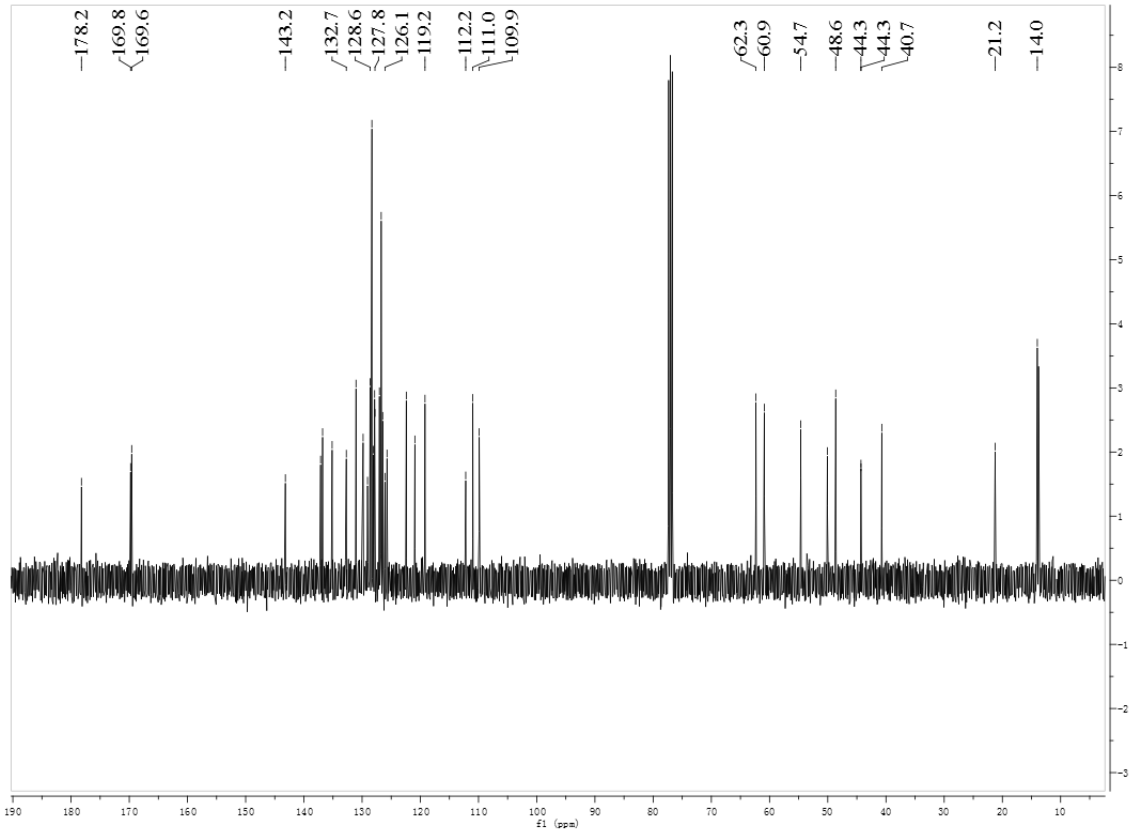


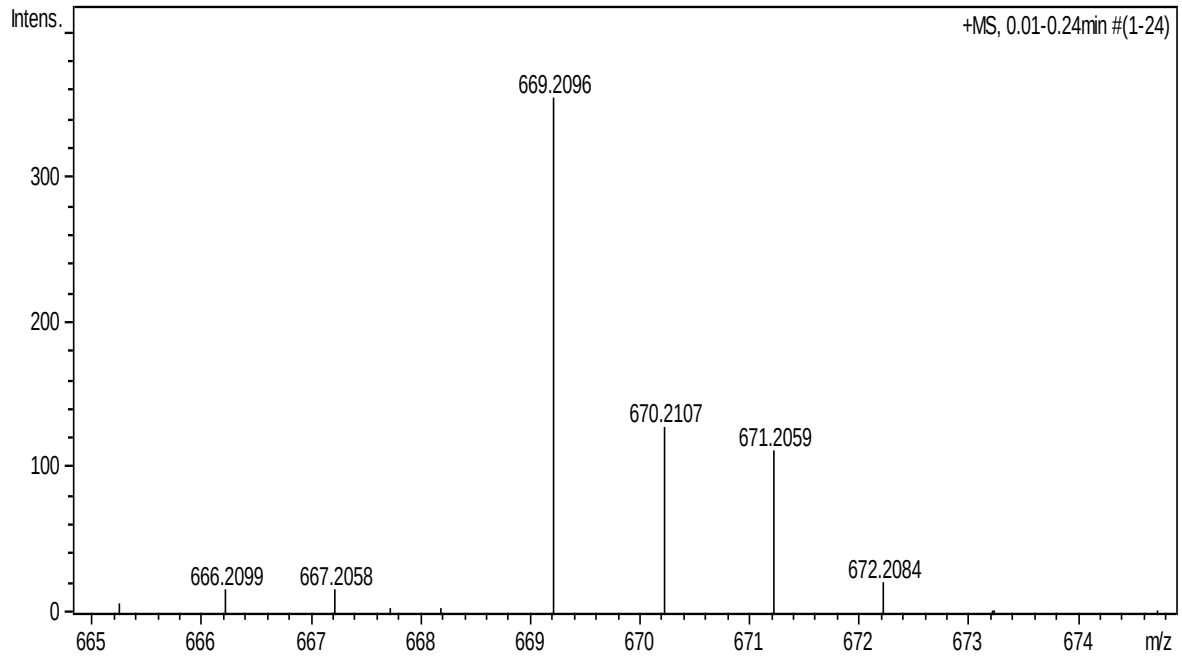




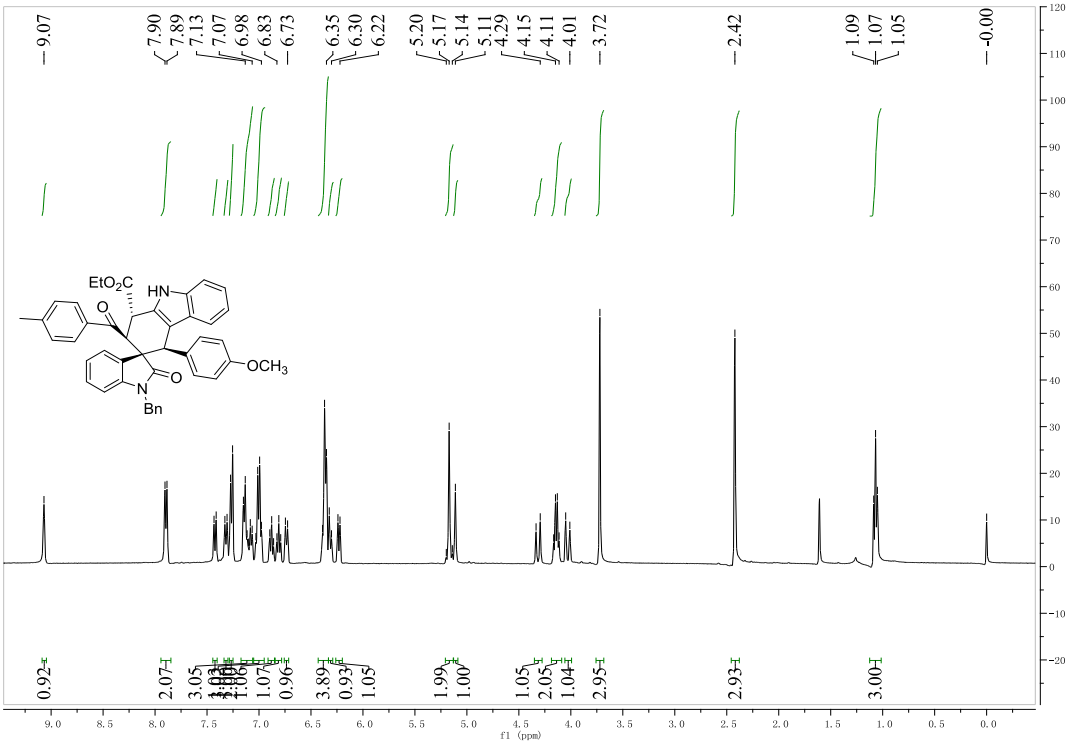
Diethyl-1'-benzyl-5'-chloro-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1,3-dicarboxylate (1g'):

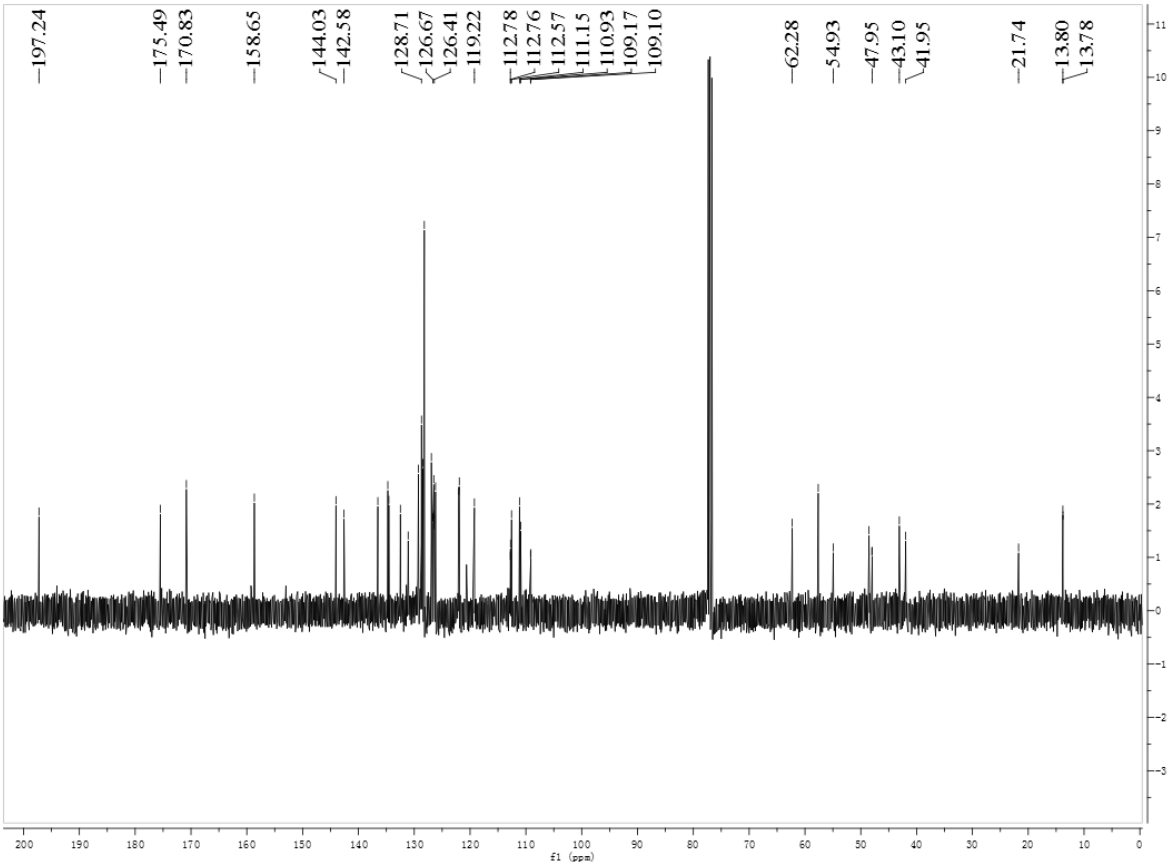


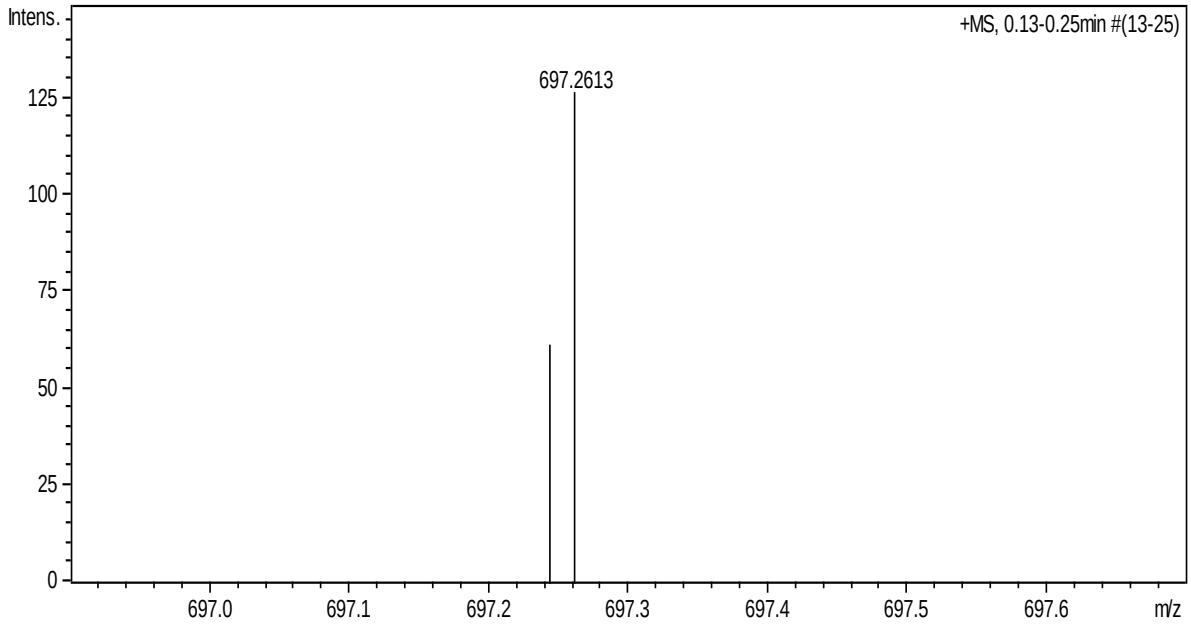

178.2
169.8
169.6
143.2
132.7
128.6
127.8
126.1
119.2
112.2
111.0
109.9
62.3
60.9
54.7
48.6
44.3
44.3
40.7
21.2
14.0
f1 (ppm)


Intens.
+MS, 0.01-0.24min #(1-24)
669.2096
670.2107
671.2059
666.2099
667.2058
672.2084
m/z

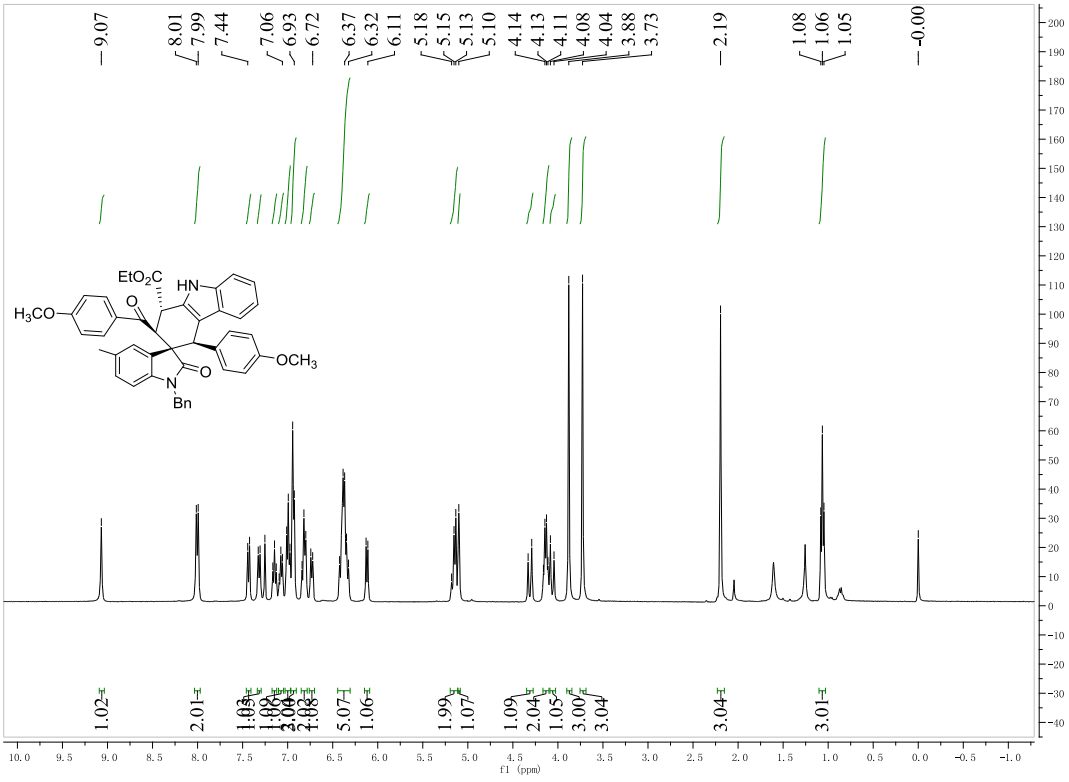
Ethyl-1'-benzyl-4-(4-methoxyphenyl)-3-(4-methylbenzoyl)-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1h):

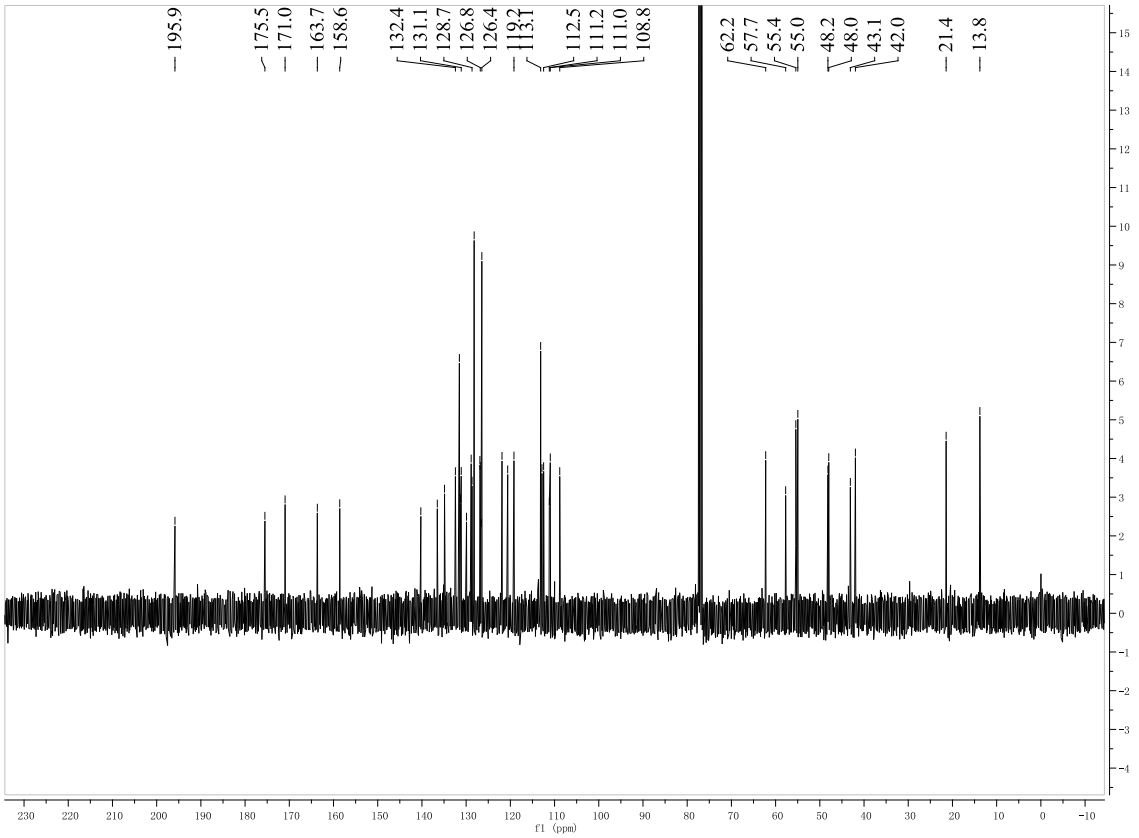


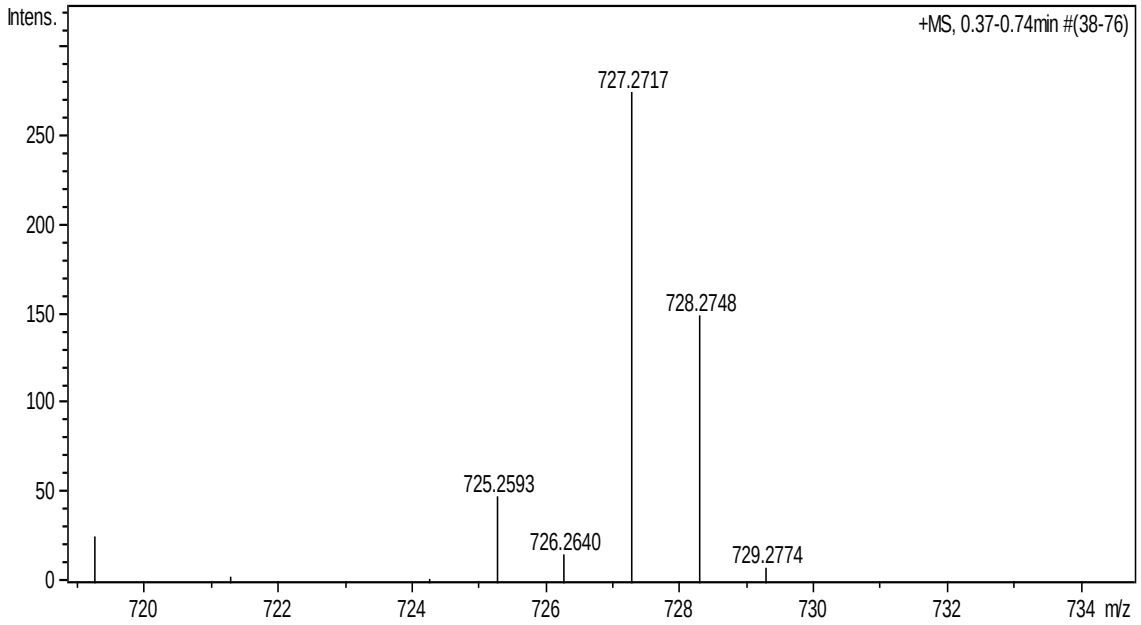




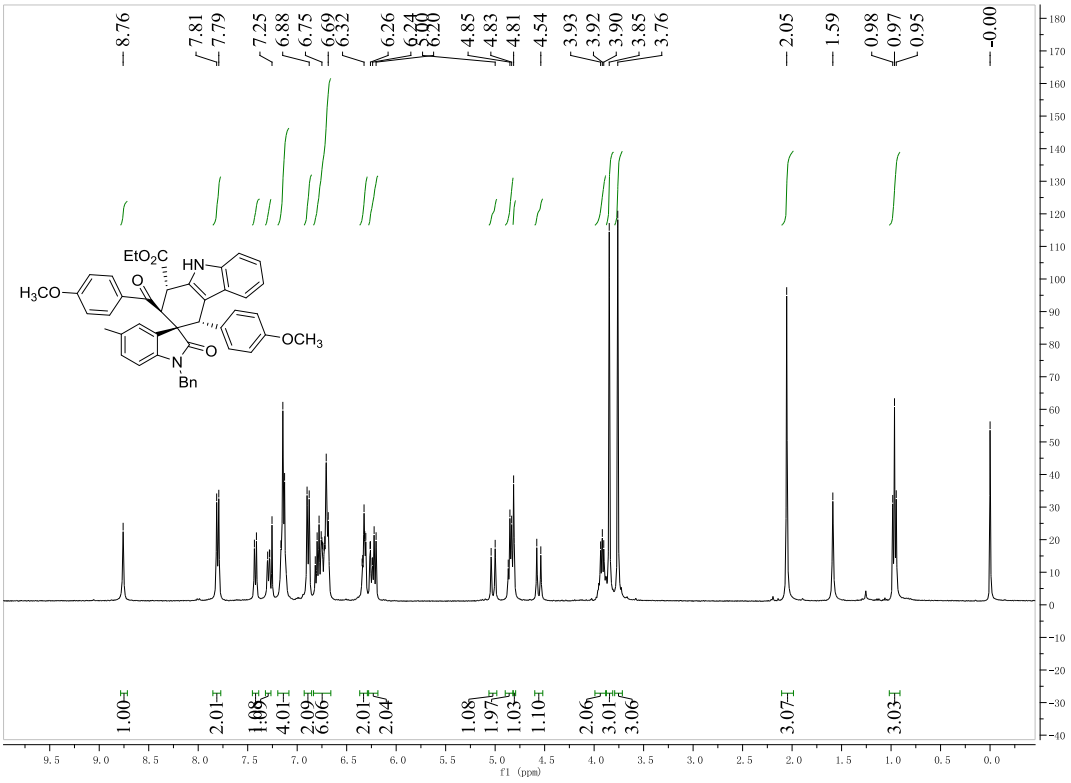
Ethyl-1'-benzyl-3-(4-methoxybenzoyl)-4-(4-methoxyphenyl)-5'-methyl-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1i):

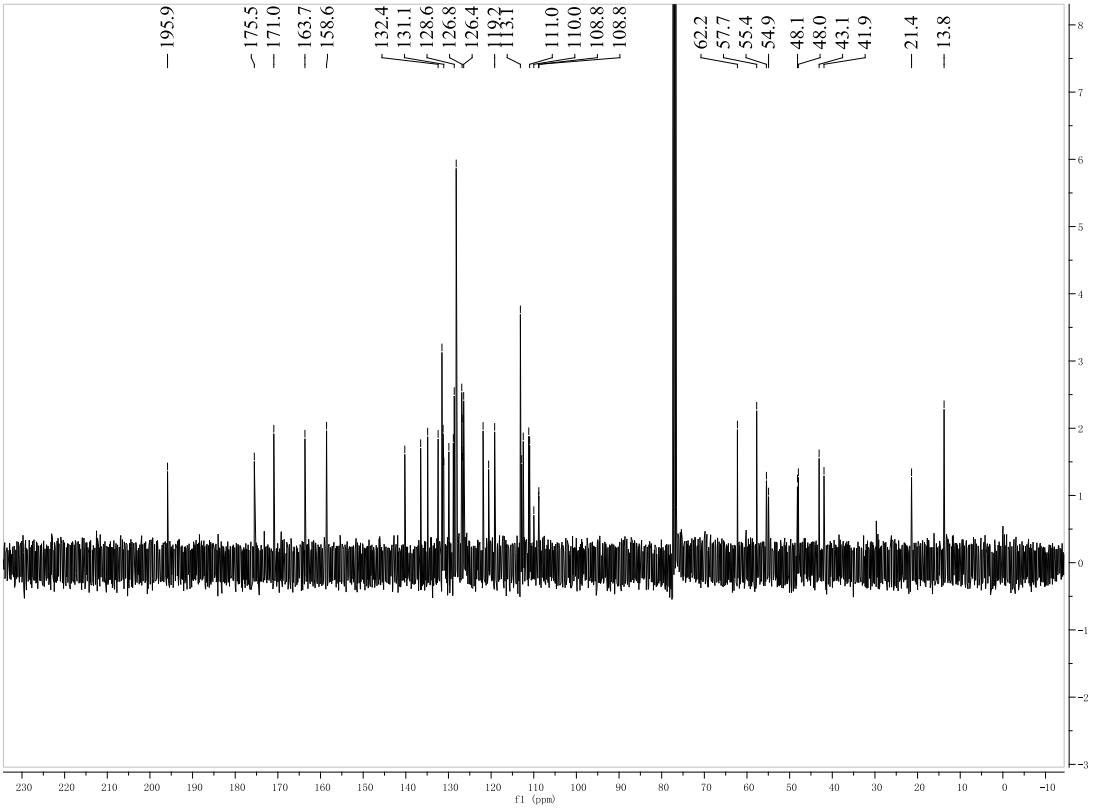


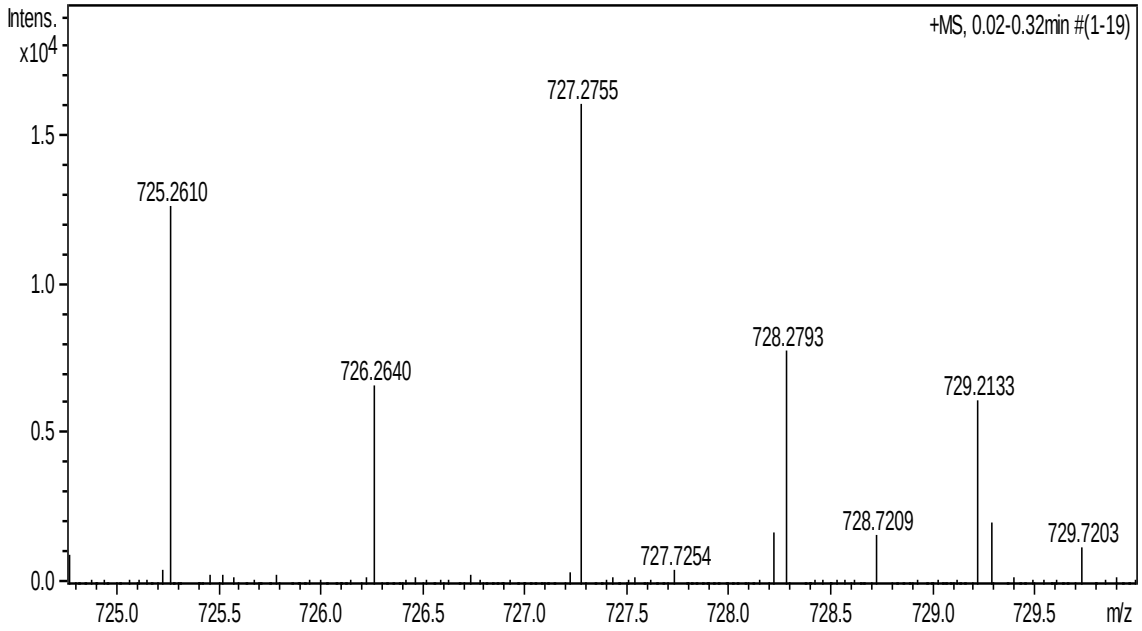

195.9
175.5
171.0
163.7
158.6
132.4
131.1
128.7
126.8
126.4
112.5
111.2
111.0
108.8
62.2
57.7
55.4
55.0
48.2
48.0
43.1
42.0
21.4
13.8
f1 (ppm)


Intens.
+MS, 0.37-0.74min #(38-76)
727.2717
728.2748
725.2593
726.2640
729.2774
m/z

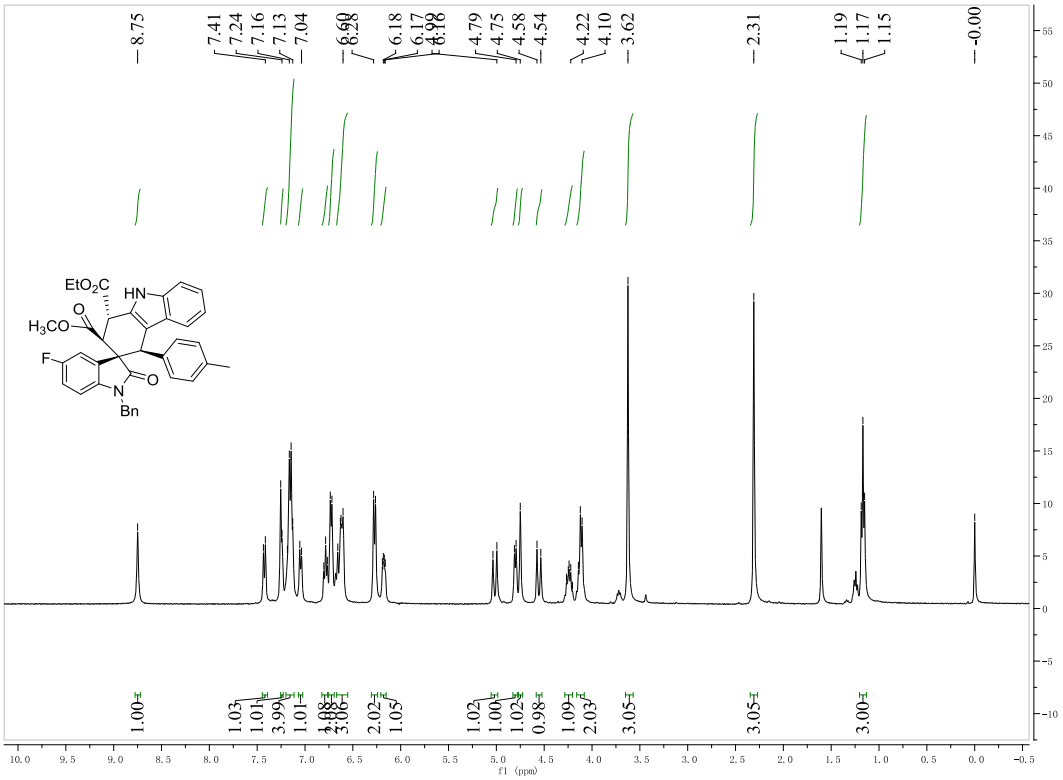
Ethyl-1'-benzyl-3-(4-methoxybenzoyl)-4-(4-methoxyphenyl)-5'-methyl-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1i'):

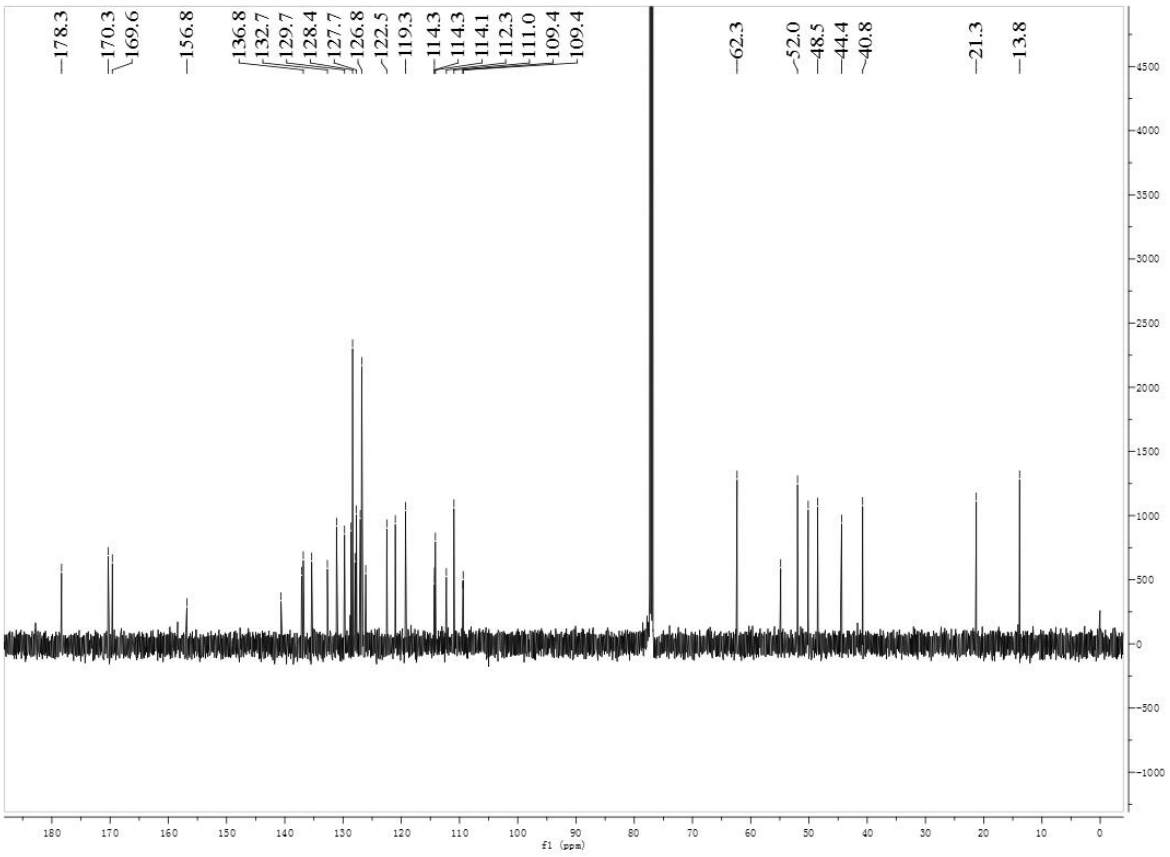


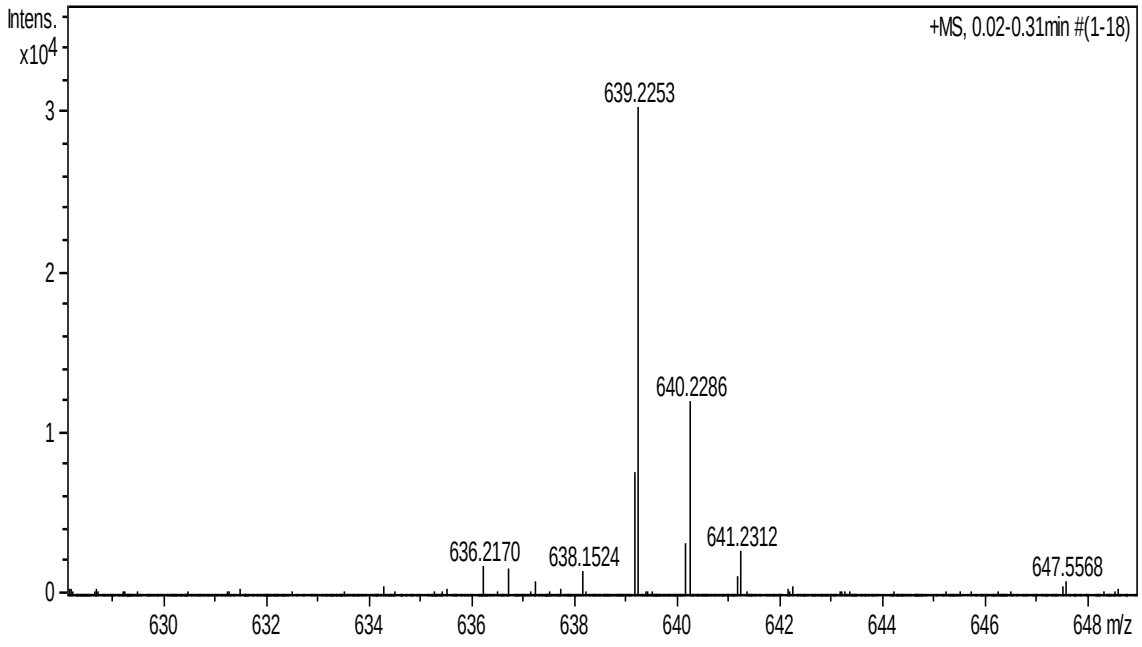




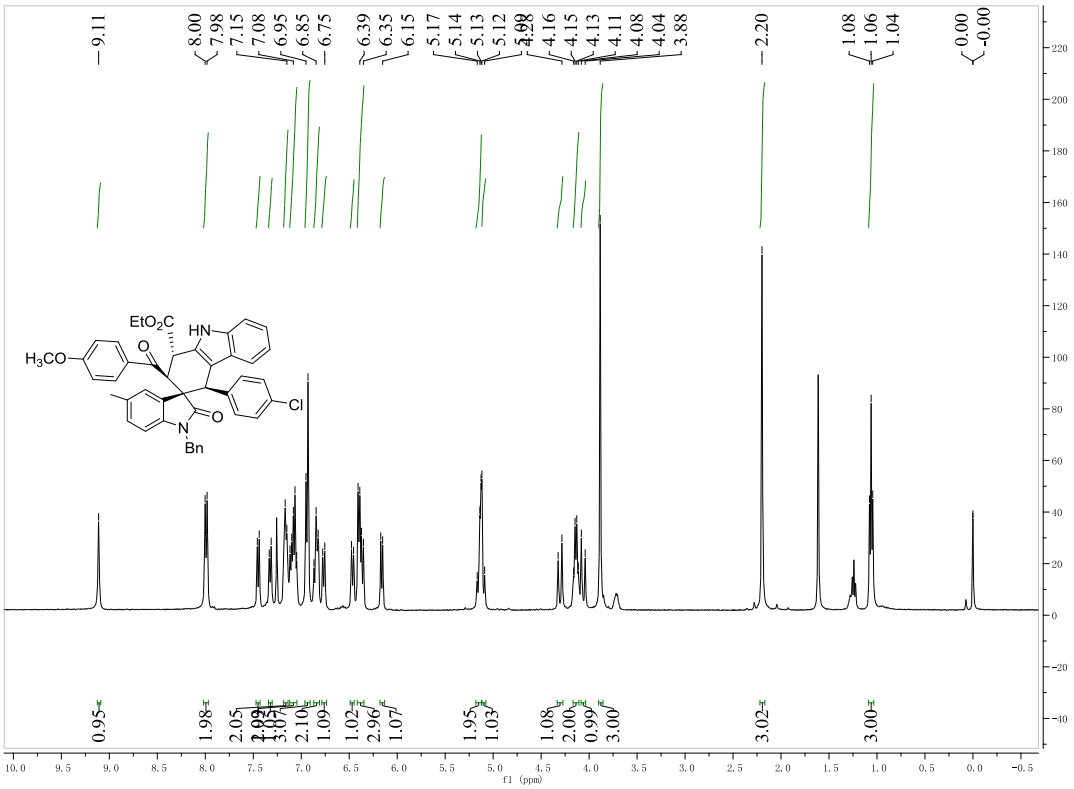
1-ethyl-3-methyl-1'-benzyl-5'-fluoro-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1,3-dicarboxylate (1j):

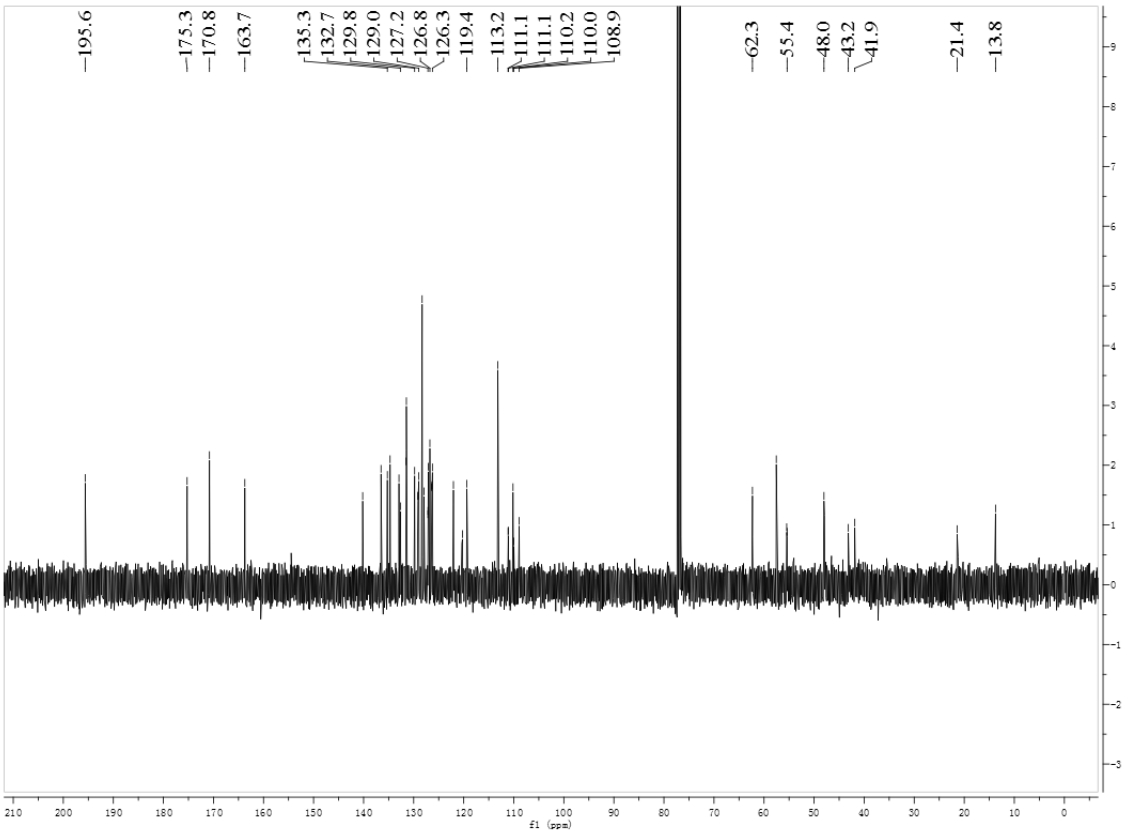


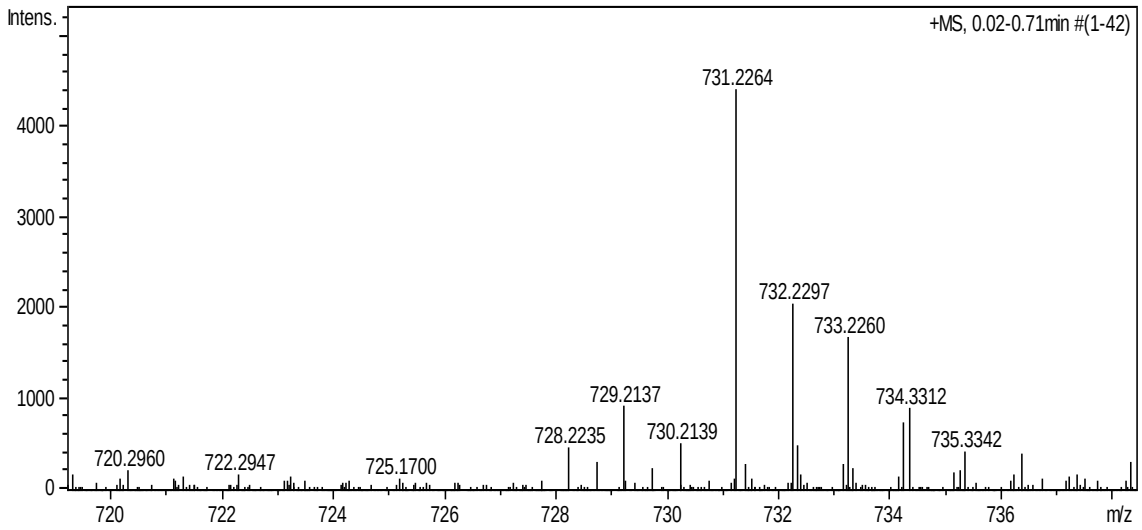

178.3
170.3
169.6
156.8
136.8
132.7
129.7
128.4
127.7
126.8
122.5
119.3
114.3
114.3
114.1
112.3
111.0
109.4
109.4
62.3
52.0
48.5
44.4
40.8
21.3
13.8
f1 (ppm)


Intens.
x10^4
+MS, 0.02-0.31min #(1-18)
639.2253
640.2286
641.2312
636.2170
638.1524
647.5568
m/z

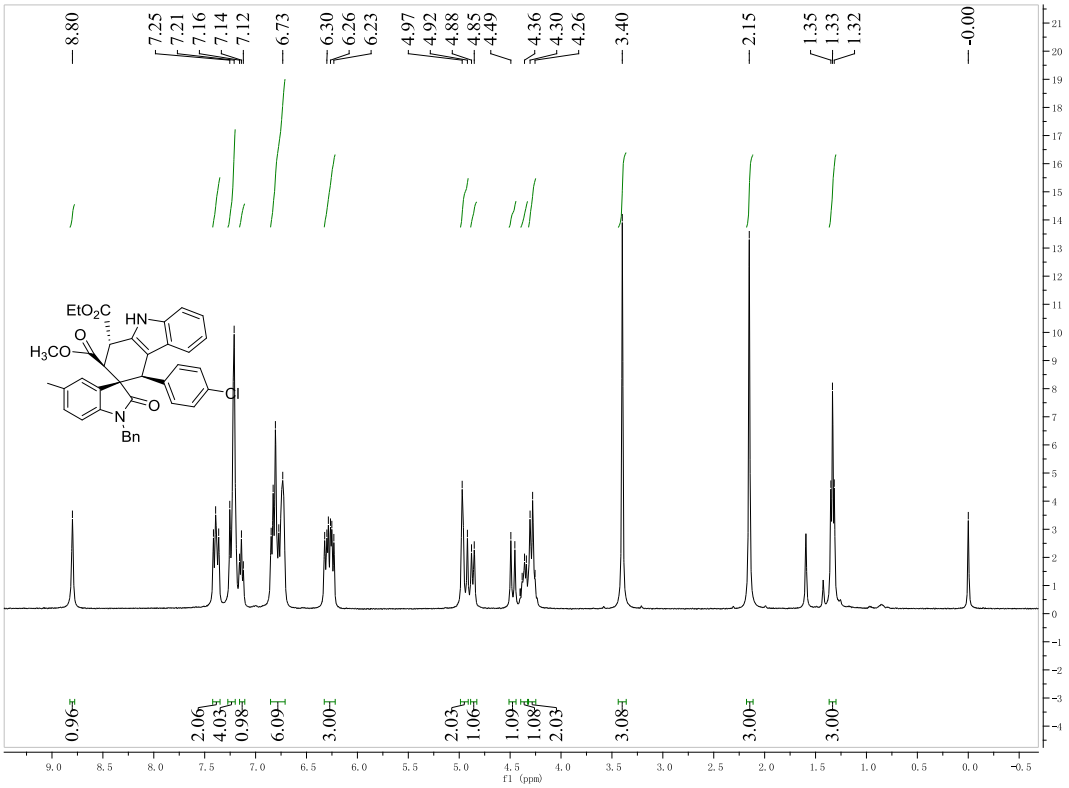
Ethyl-1'-benzyl-4-(4-chlorophenyl)-3-(4-methoxybenzoyl)-5'-methyl-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (1k):

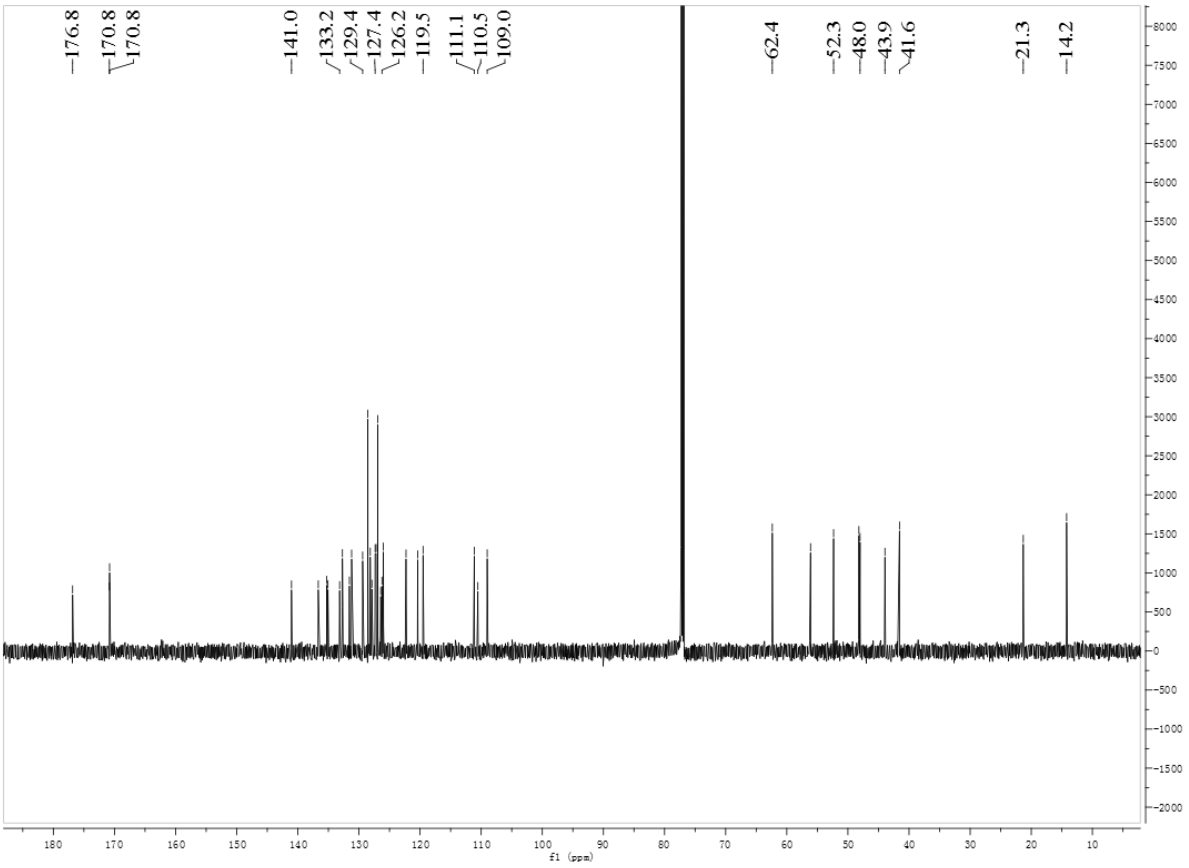


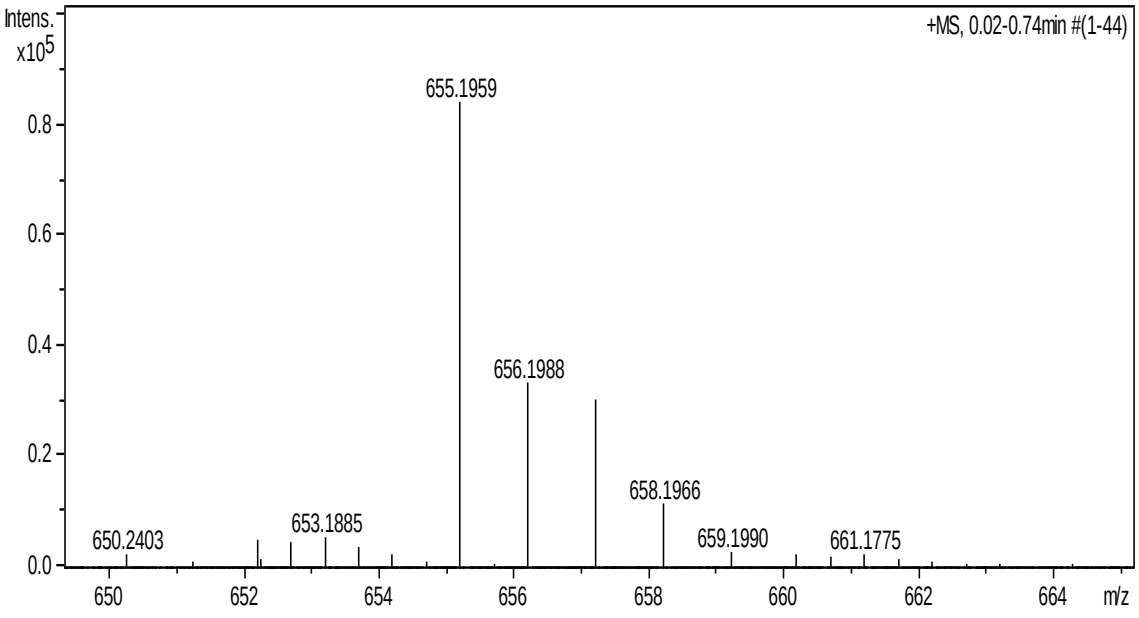




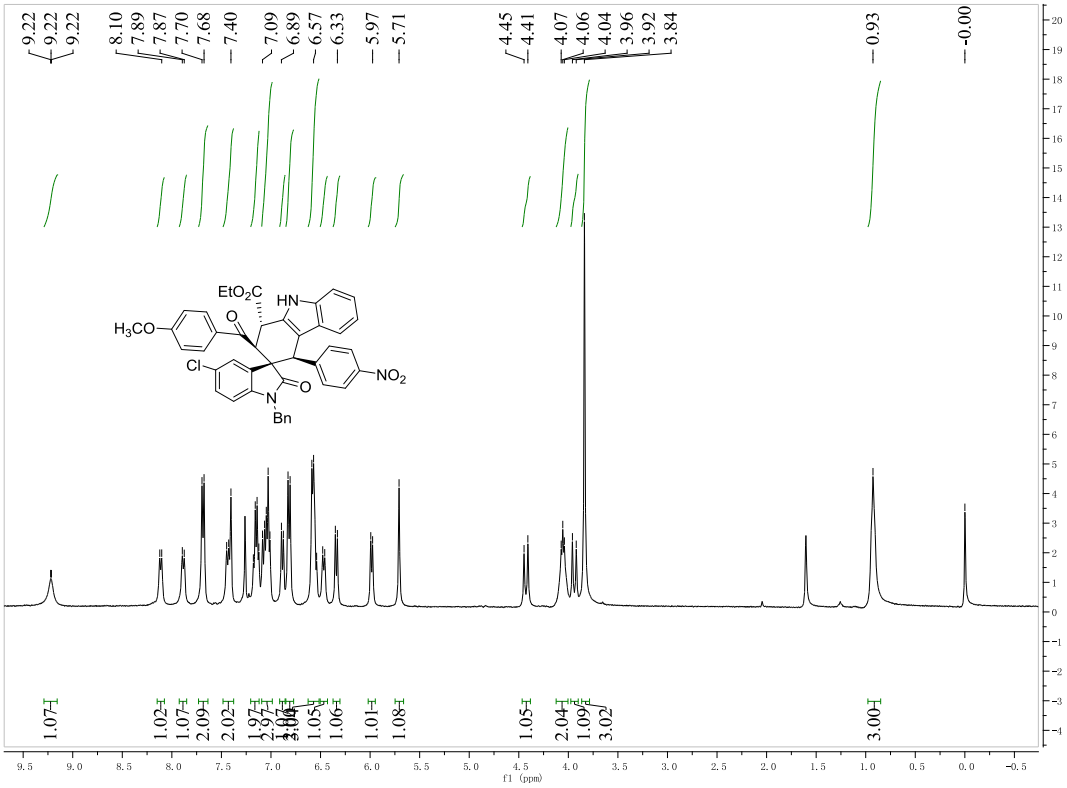
1-ethyl-3-methyl-1'-benzyl-4-(4-chlorophenyl)-5'-methyl-2'-oxo-1,3,4,9-tetrahydrospiro[carb azole-2,3'-indoline]-1,3-dicarboxylate (1l):

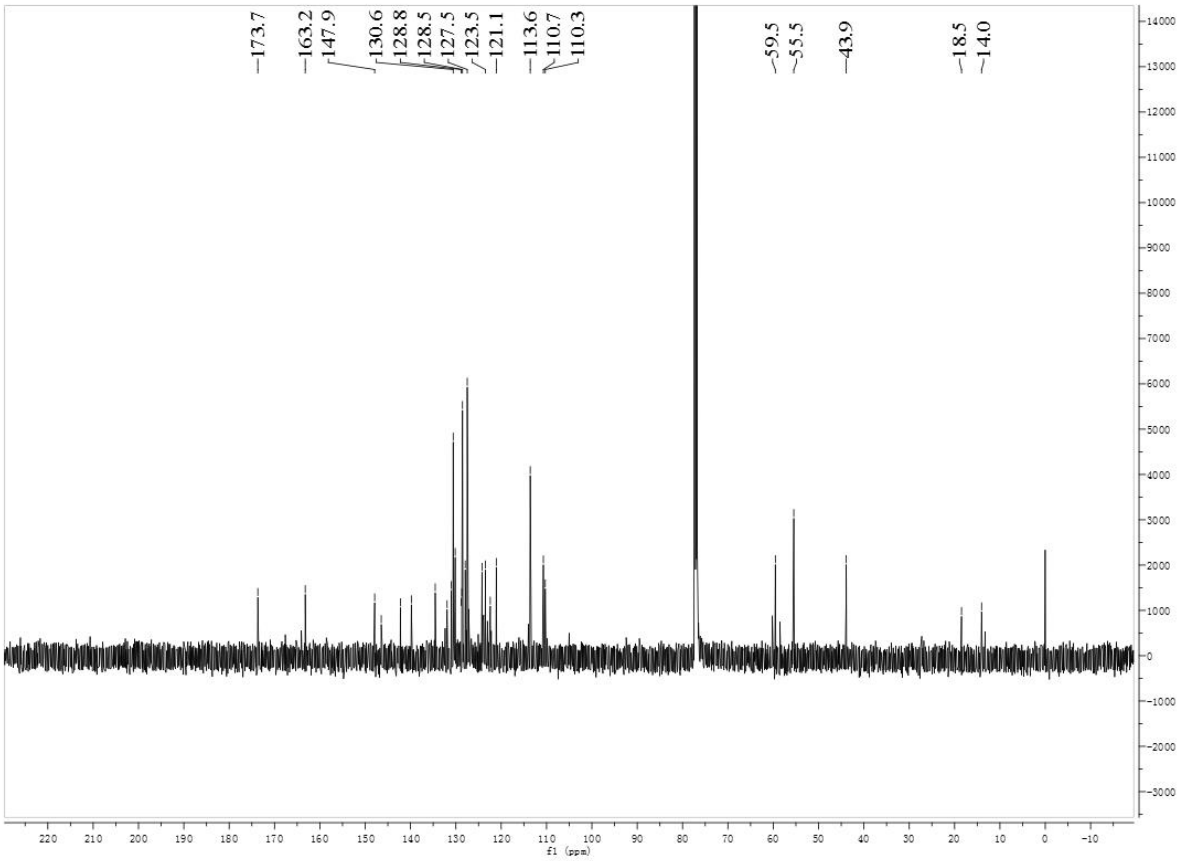


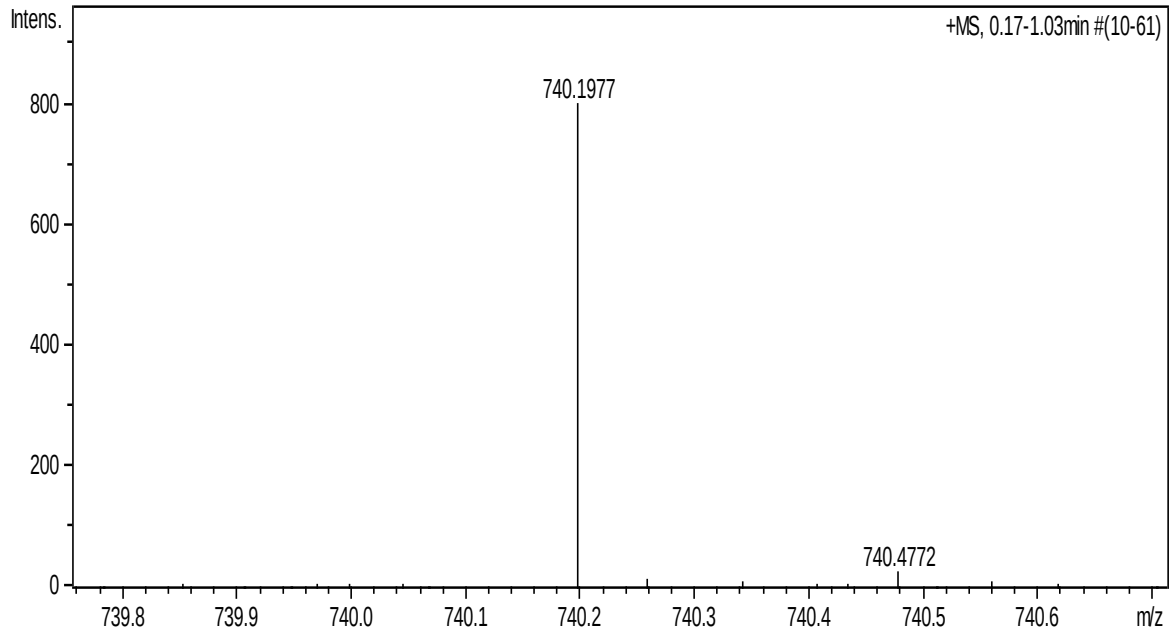

176.8
170.8
170.8
141.0
133.2
129.4
127.4
126.2
119.5
111.1
110.5
109.0
62.4
52.3
48.0
43.9
41.6
21.3
14.2
f1 (ppm)


Intens.
x10^5
+MS, 0.02-0.74min #(1-44)
655.1959
656.1988
658.1966
653.1885
650.2403
659.1990
661.1775
m/z

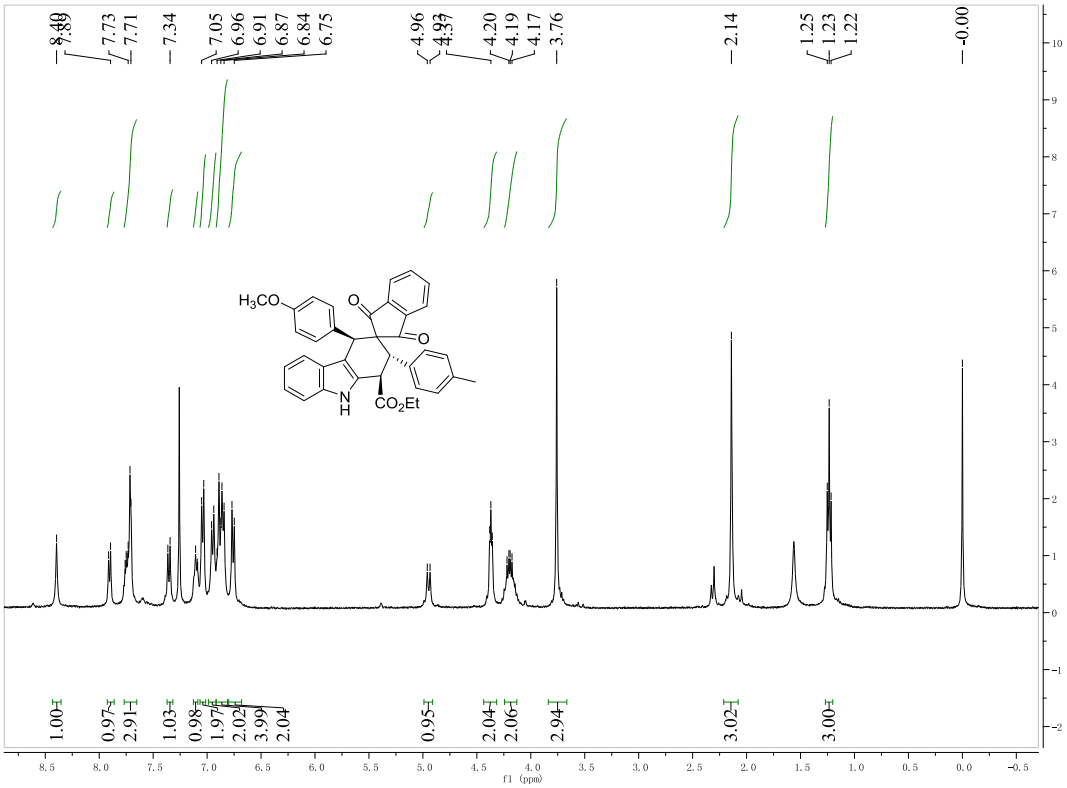
Ethyl-1'-benzyl-5'-chloro-3-(4-methoxybenzoyl)-4-(4-nitrophenyl)-2'-oxo-1,3,4,9-tetrahydros piro[carbazole-2,3'-indoline]-1-carboxylate (1m):

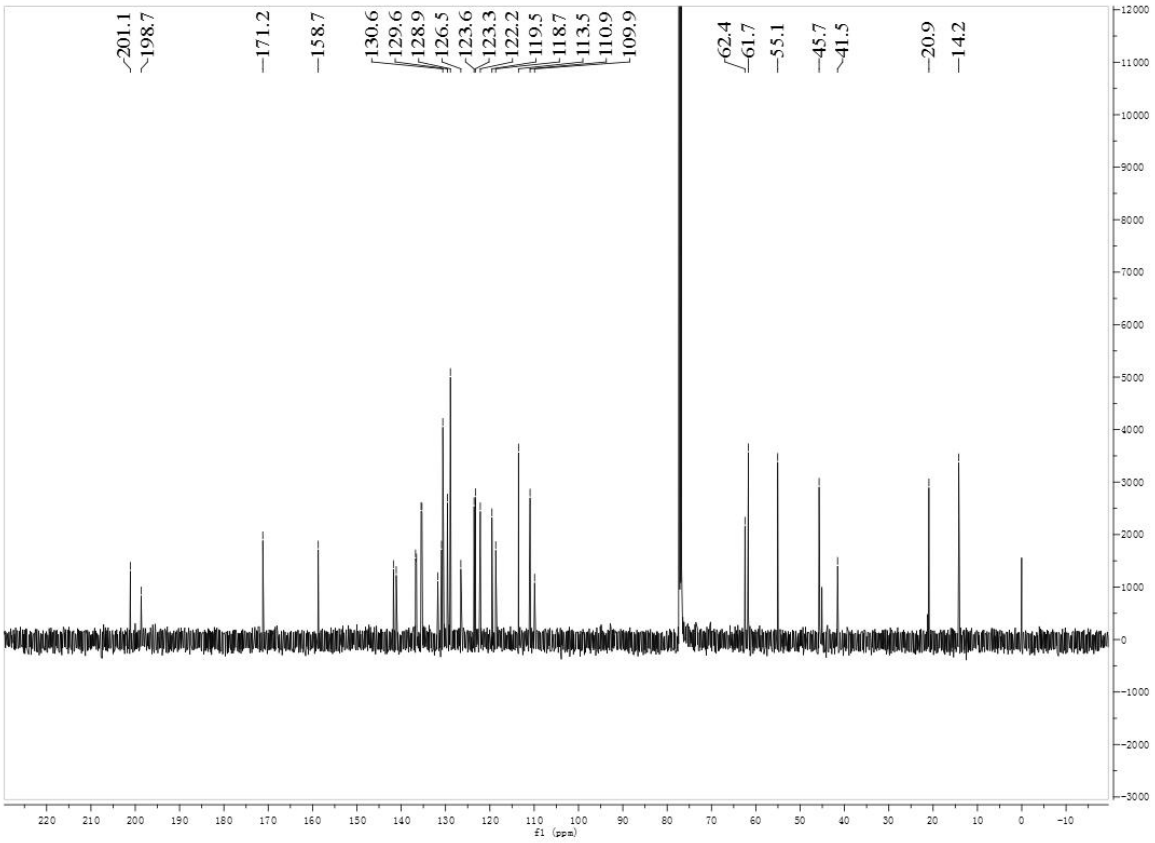


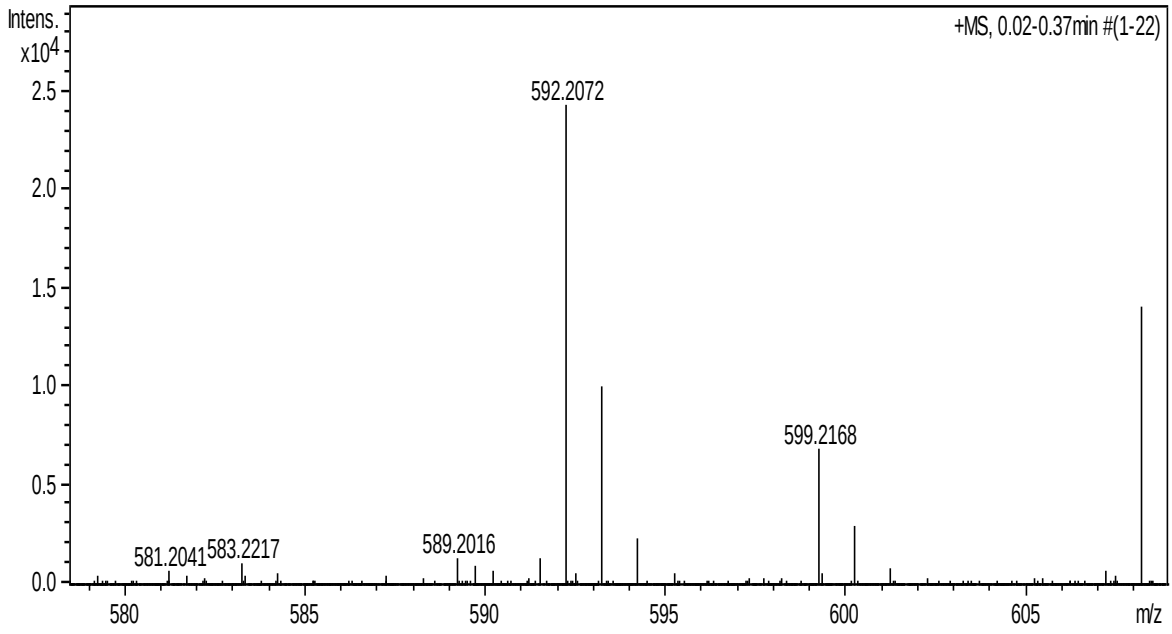




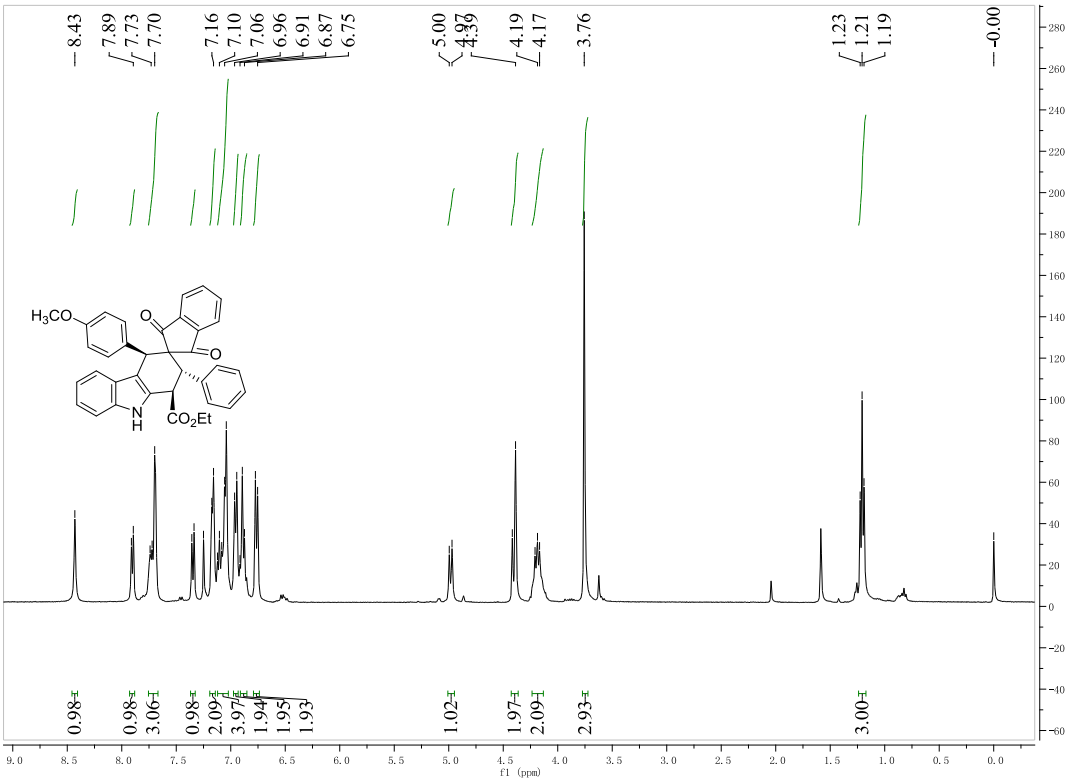
Ethyl-4-(4-methoxyphenyl)-1',3'-dioxo-3-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2a):

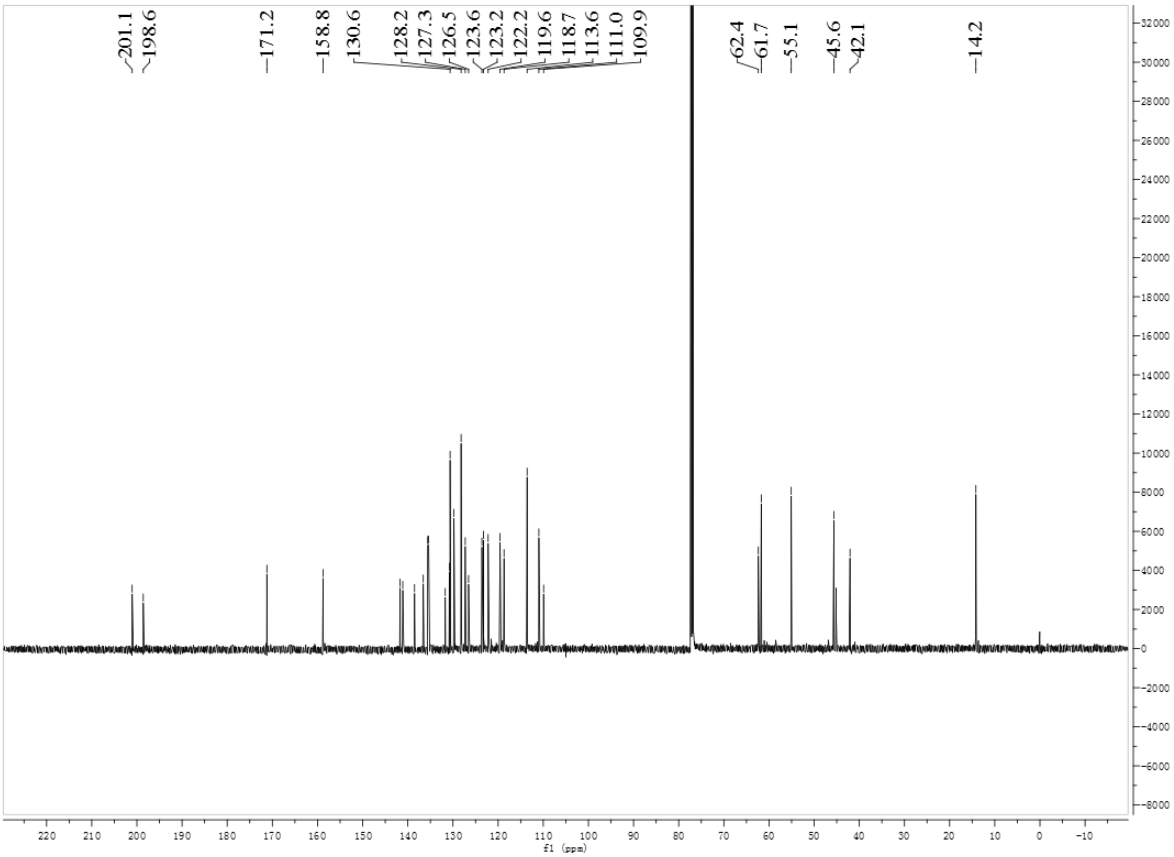


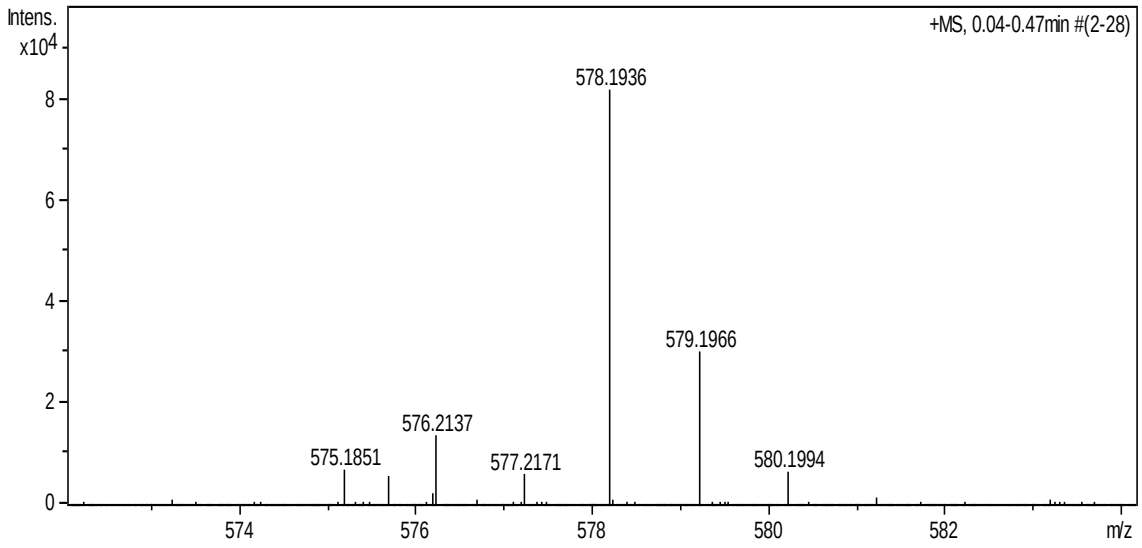

201.1
198.7
171.2
158.7
130.6
129.6
128.9
126.5
123.6
123.3
122.2
119.5
118.7
113.5
110.9
109.9
62.4
61.7
55.1
45.7
41.5
20.9
14.2
f1 (ppm)


Intens.
x10^4
+MS, 0.02-0.37min #(1-22)
592.2072
599.2168
581.2041
583.2217
589.2016
m/z

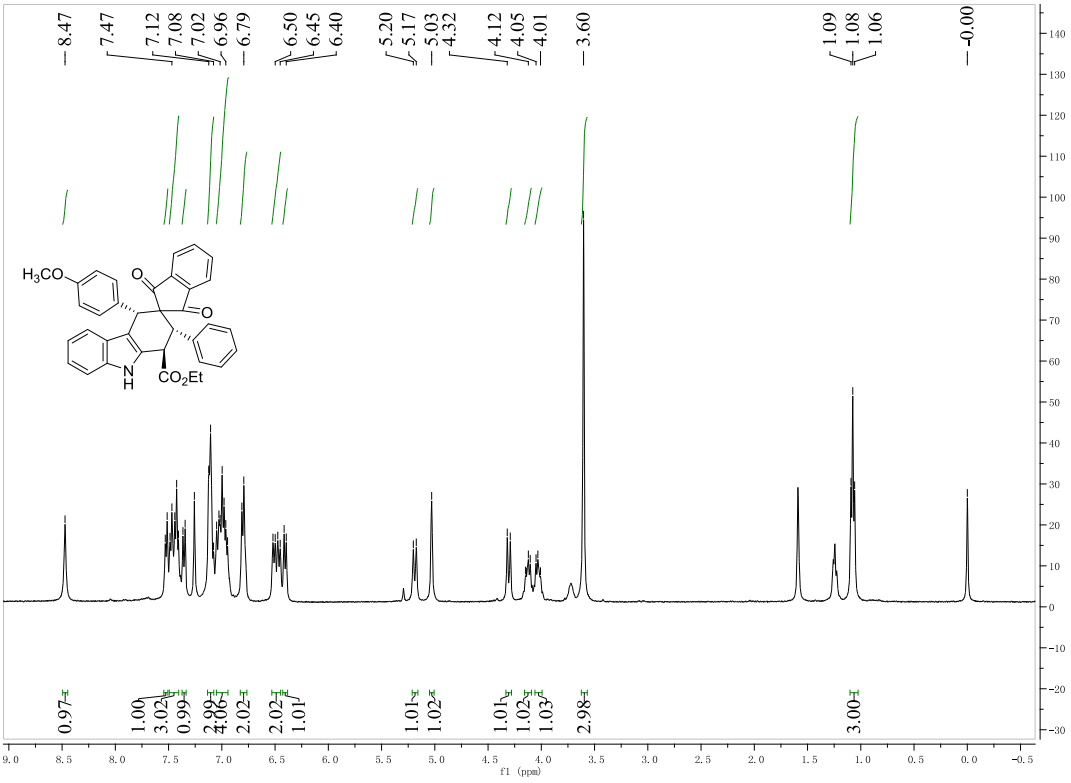
Ethyl-4-(4-methoxyphenyl)-1',3'-dioxo-3-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2b):

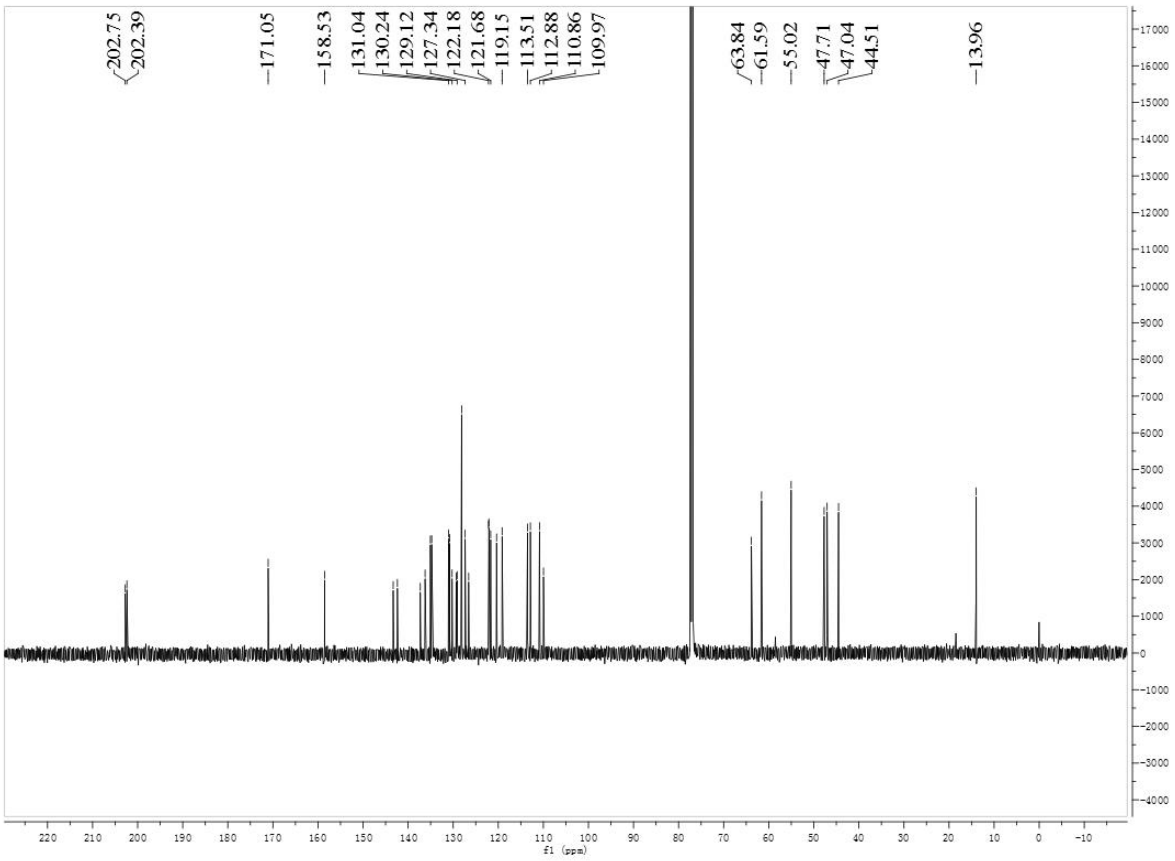


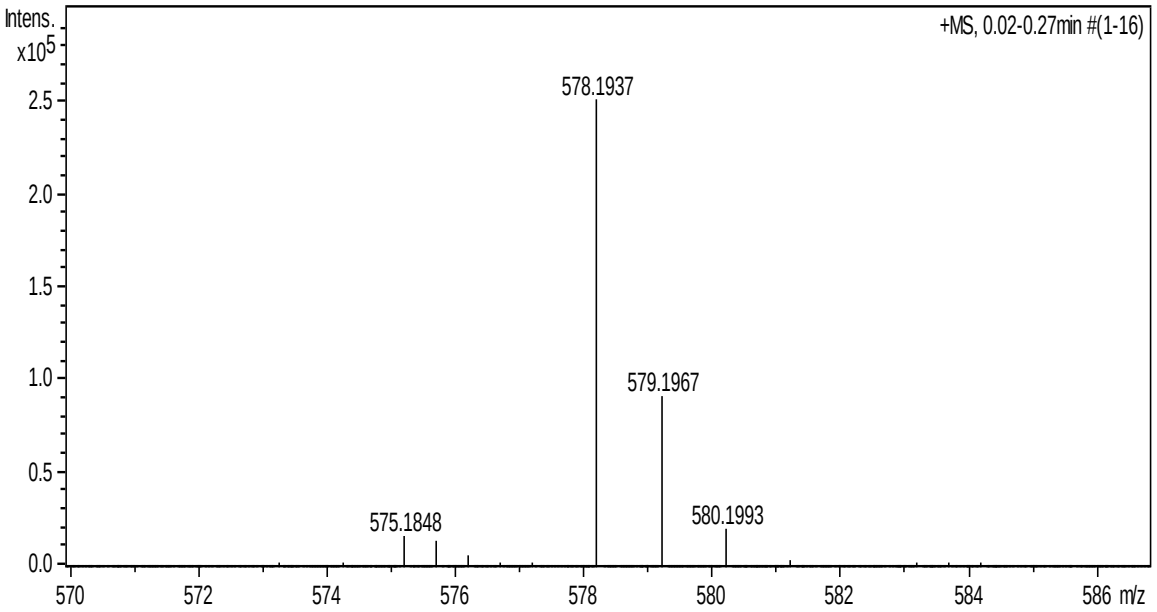




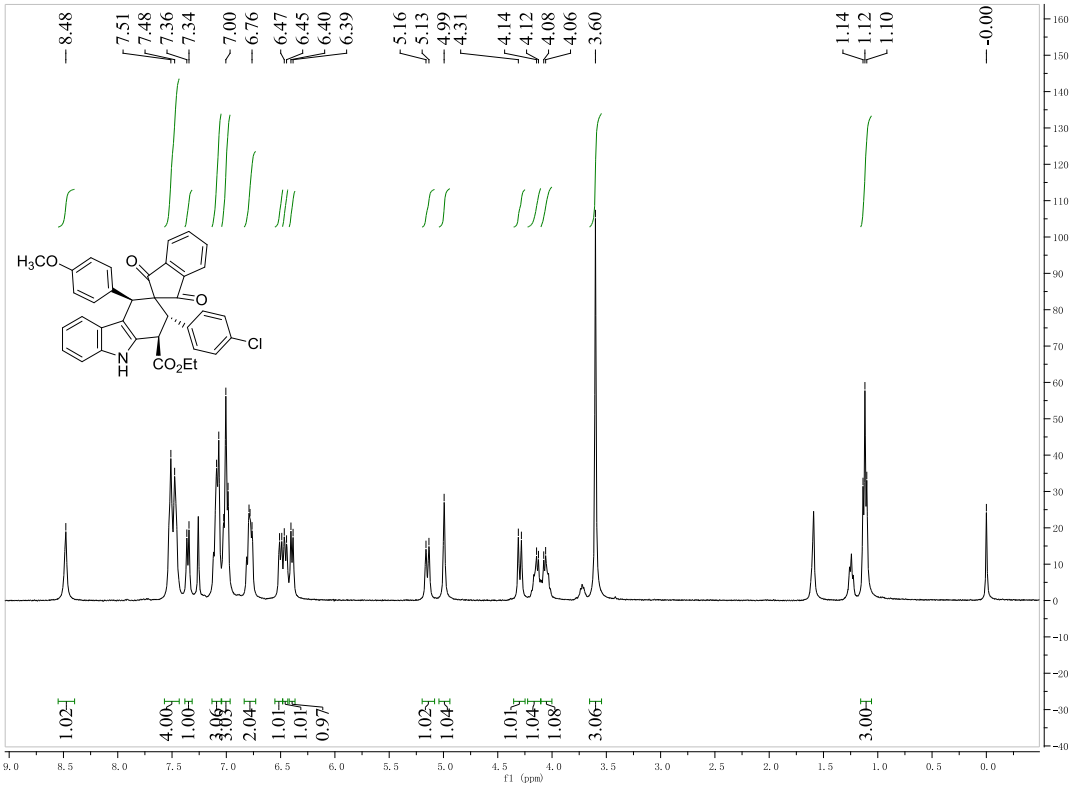
Ethyl-4-(4-methoxyphenyl)-1',3'-dioxo-3-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2b'):

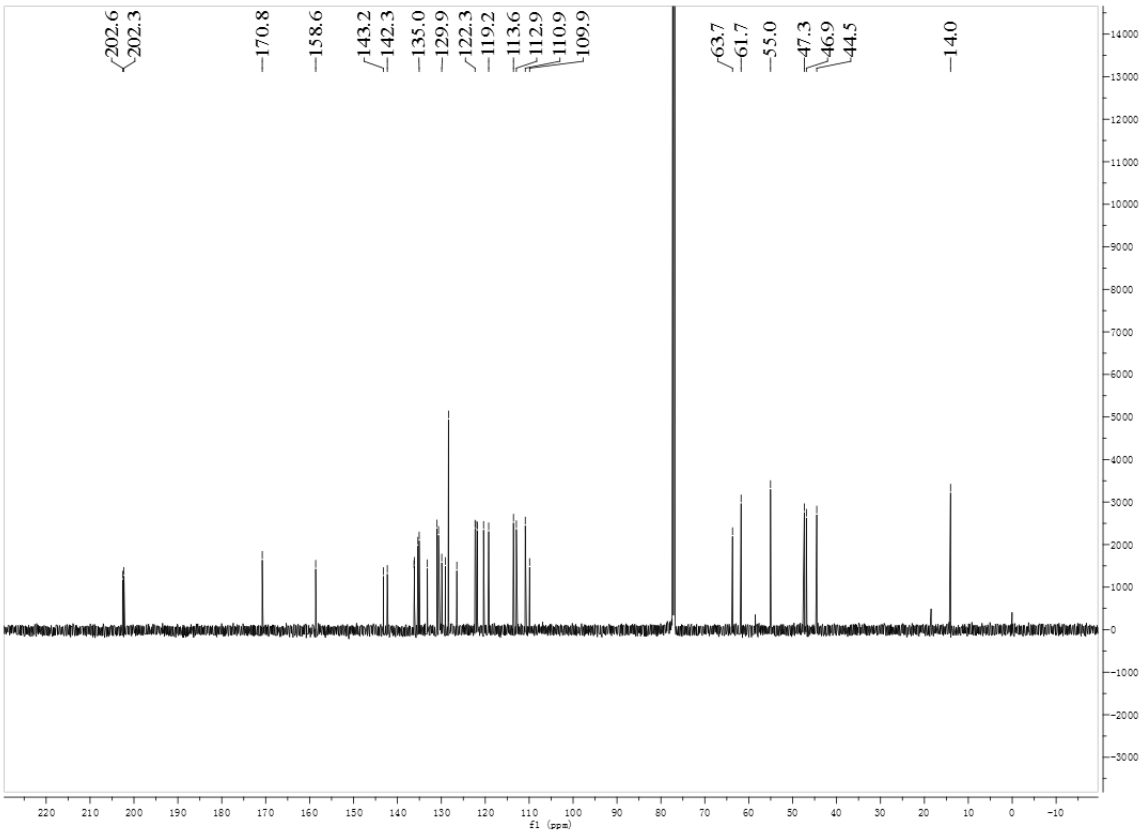


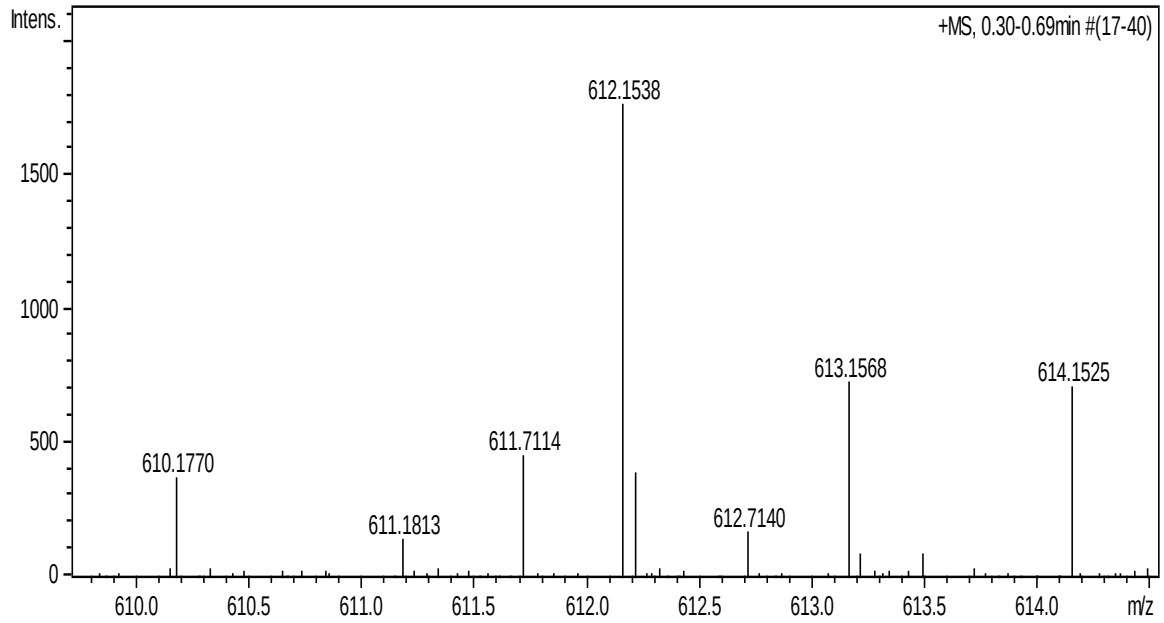

202.75
202.39
171.05
158.53
131.04
130.24
129.12
127.34
122.18
121.68
119.15
113.51
112.88
110.86
109.97
63.84
61.59
55.02
47.71
47.04
44.51
13.96
f1 (ppm)


Intens.
x10^5
+MS, 0.02-0.27min #(1-16)
578.1937
579.1967
575.1848
580.1993
m/z

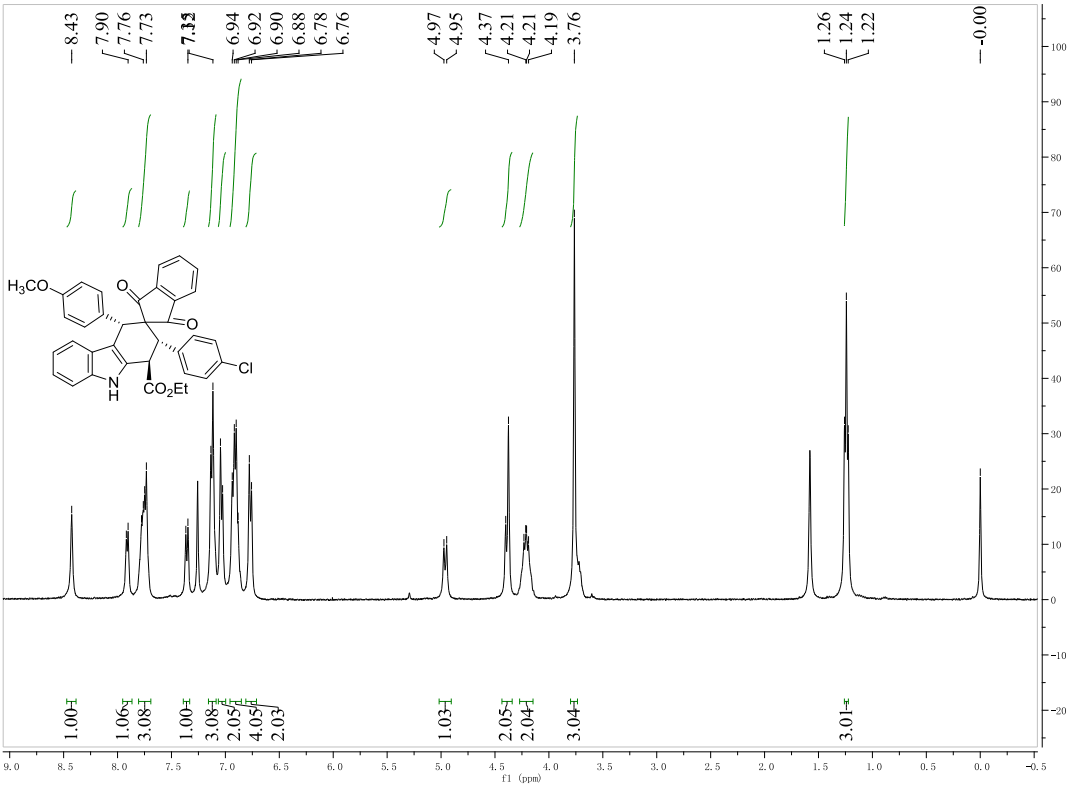
Ethyl-3-(4-chlorophenyl)-4-(4-methoxyphenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2c):

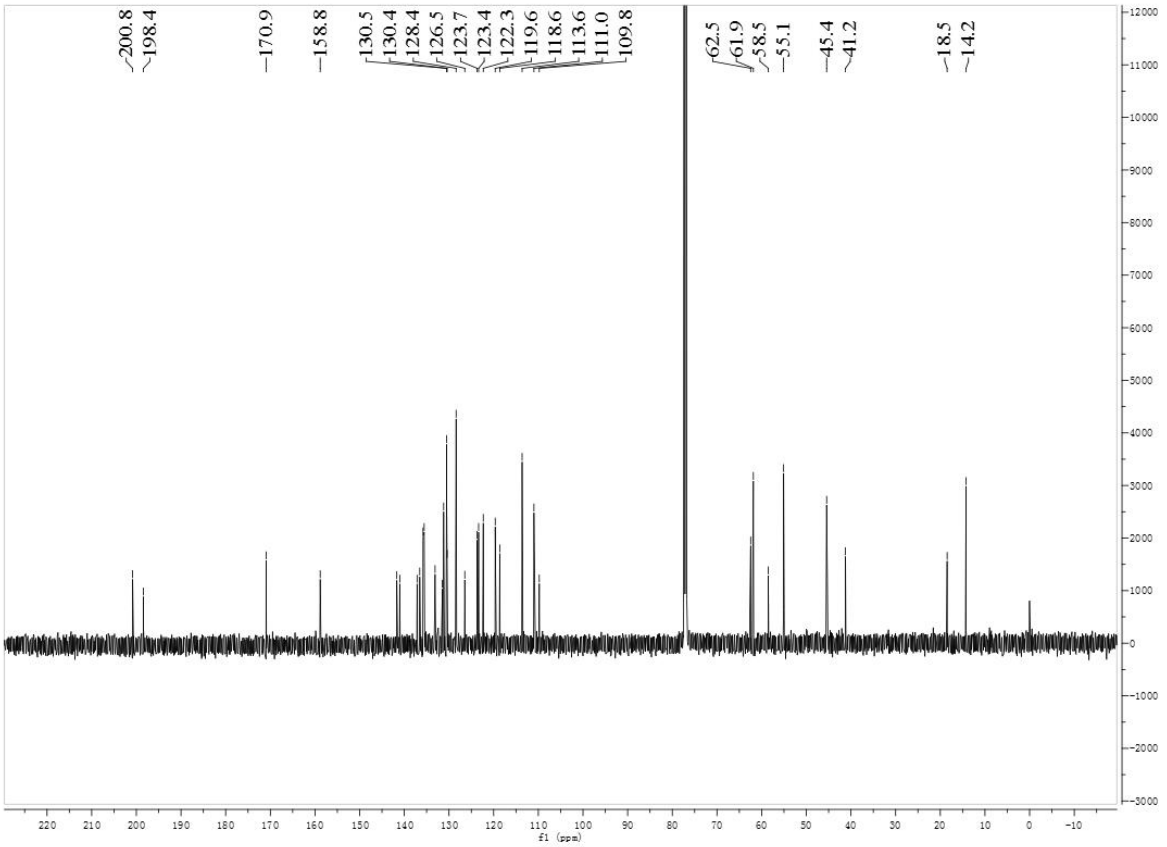


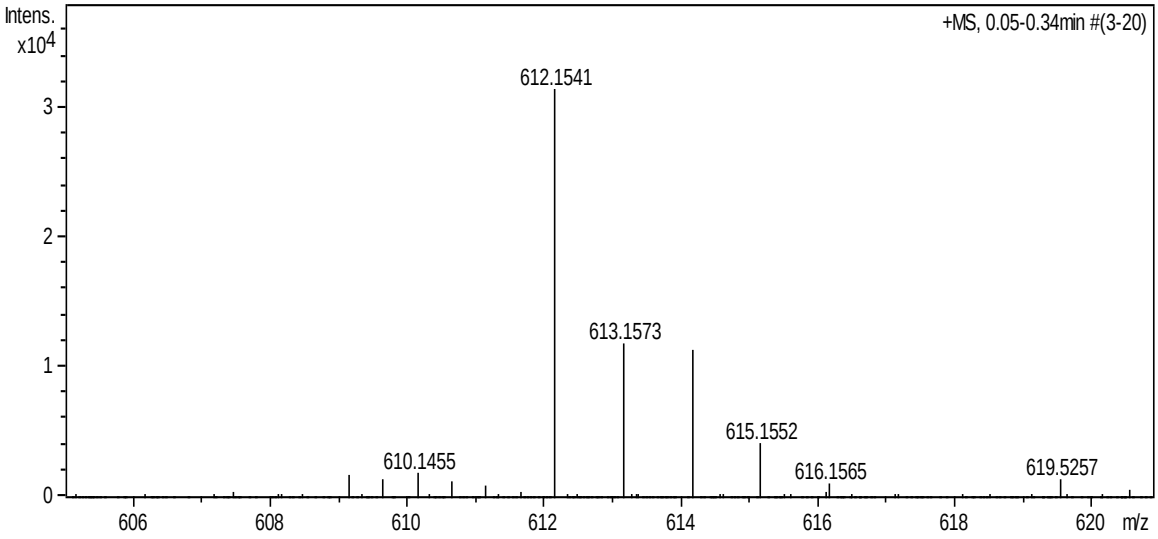




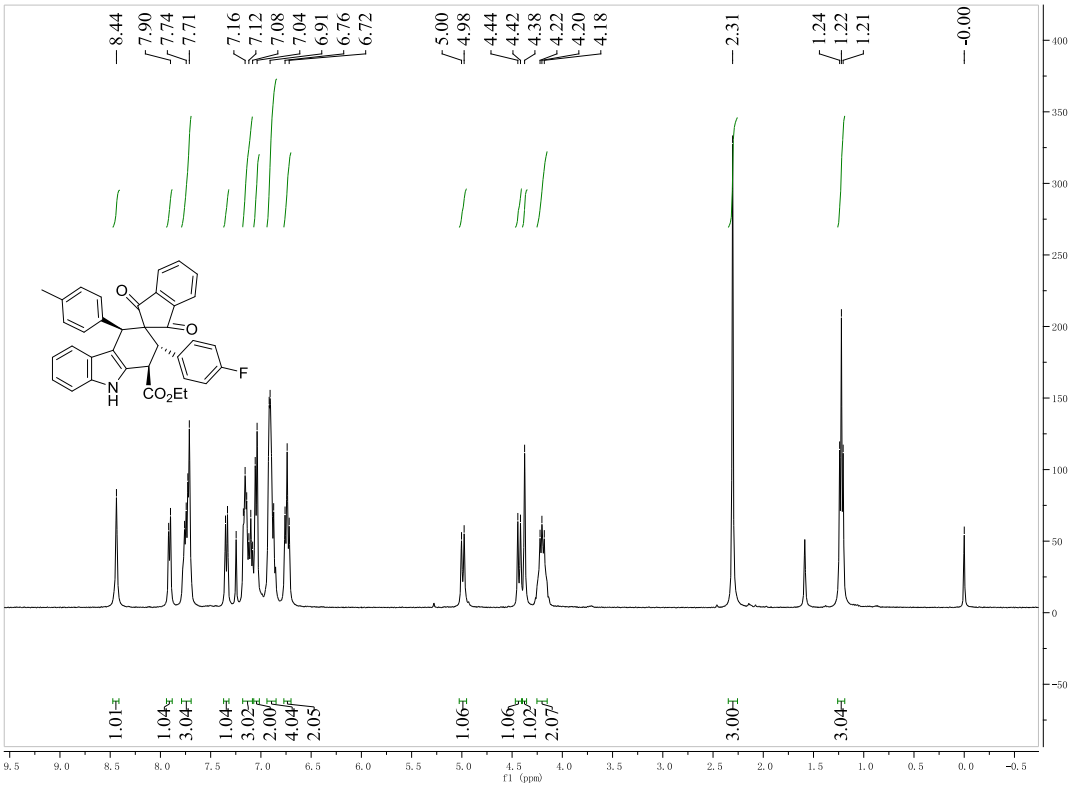
Ethyl-3-(4-chlorophenyl)-4-(4-methoxyphenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carb azole-2,2'-indene]-1-carboxylate (2c'):

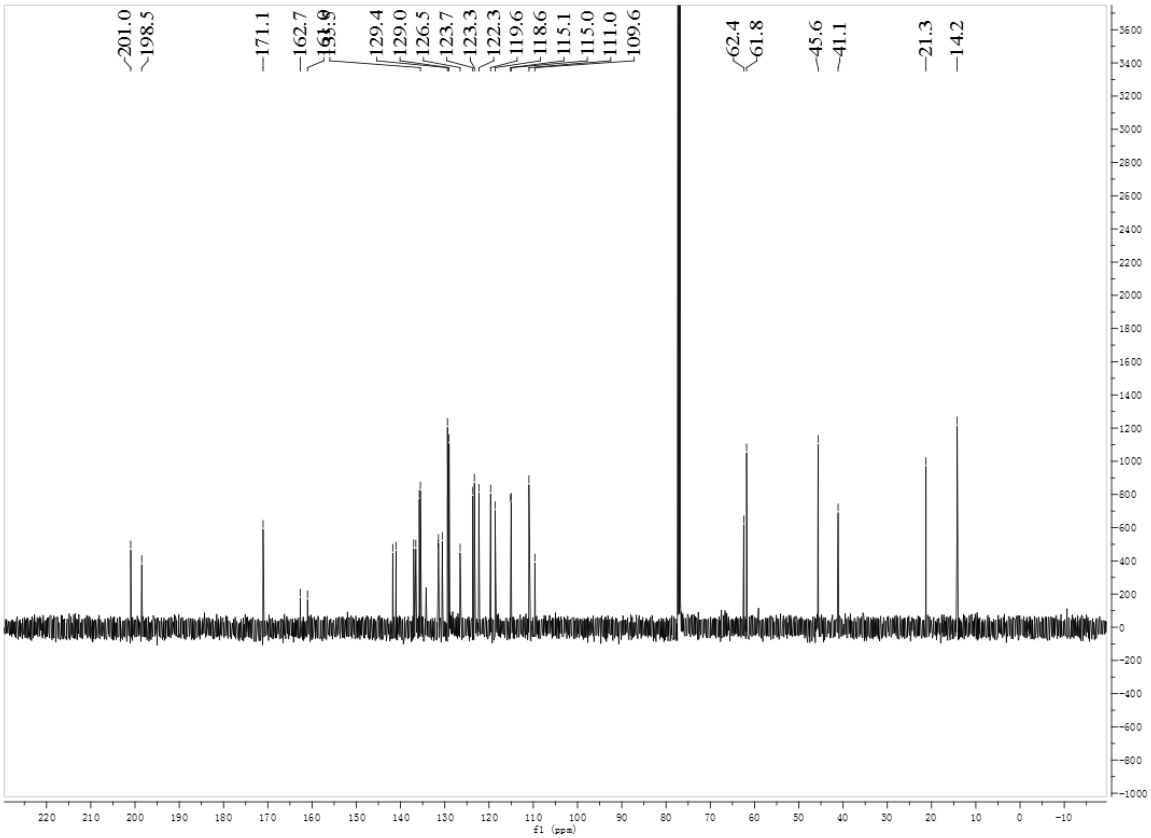


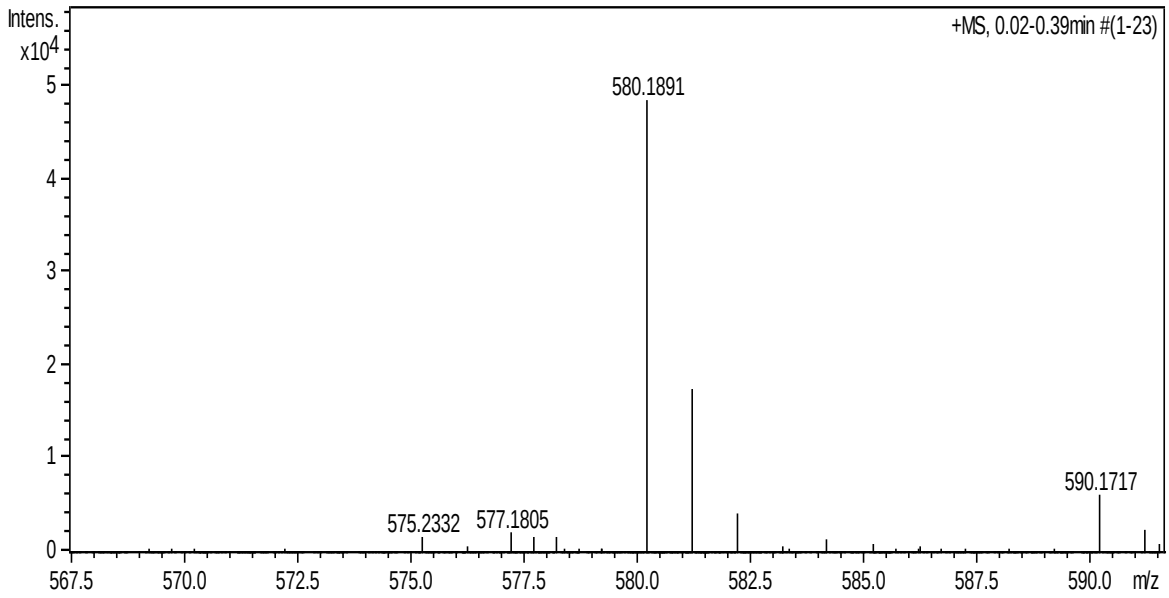

200.8
198.4
170.9
158.8
130.5
130.4
128.4
126.5
123.7
123.4
122.3
119.6
118.6
113.6
111.0
109.8
62.5
61.9
58.5
55.1
45.4
41.2
18.5
14.2
f1 (ppm)


Intens.
x10^4
+MS, 0.05-0.34min #(3-20)
612.1541
613.1573
615.1552
610.1455
616.1565
619.5257
m/z

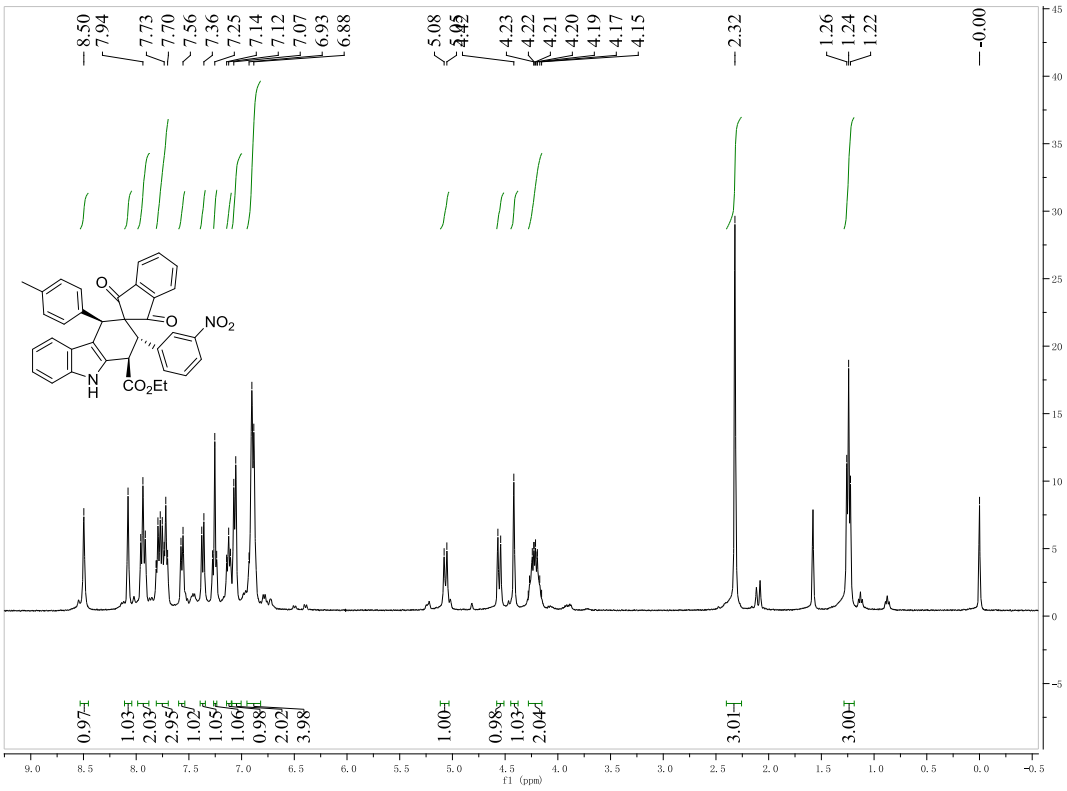
Ethyl-3-(4-fluorophenyl)-1',3'-dioxo-4-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2d):

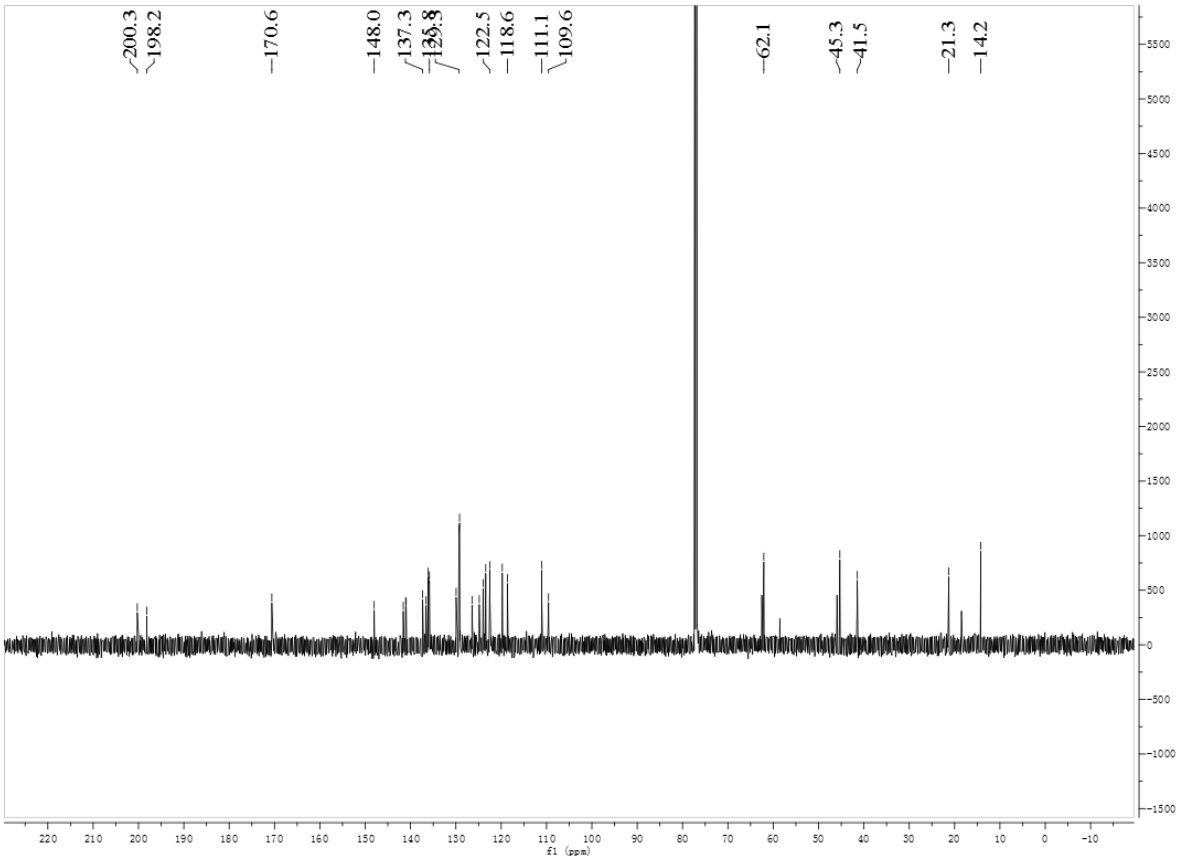


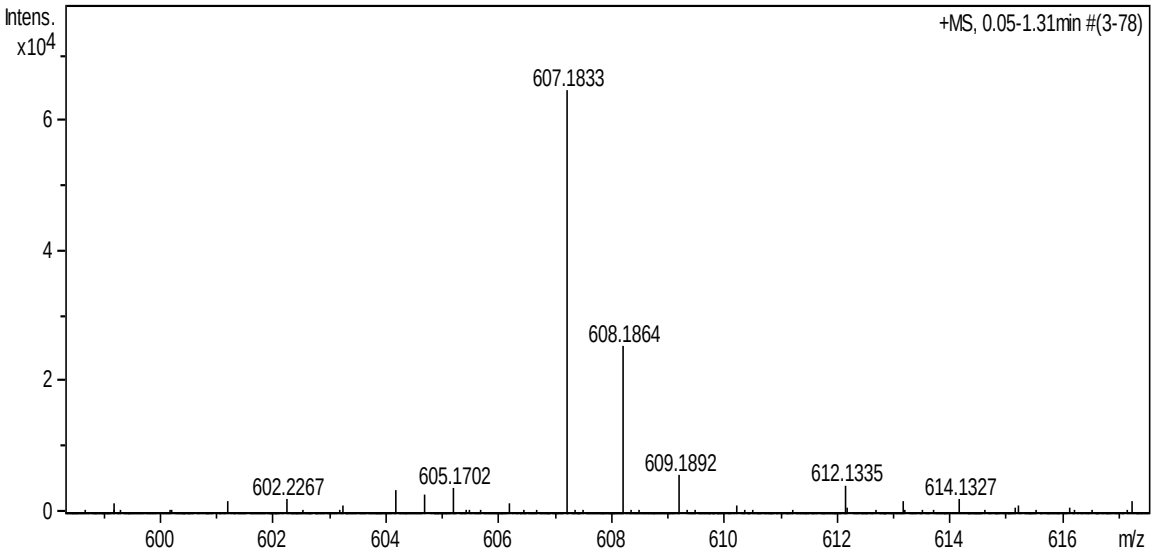




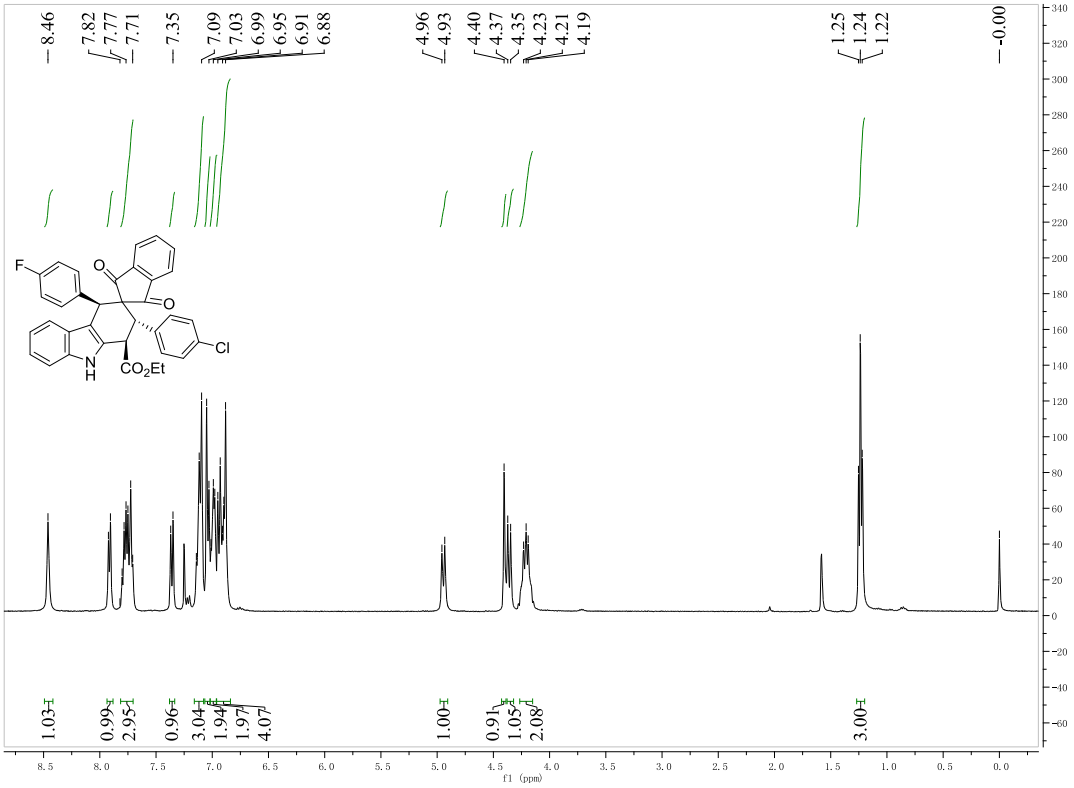
Ethyl-3-(3-nitrophenyl)-1',3'-dioxo-4-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-in dene]-1-carboxylate (2e):

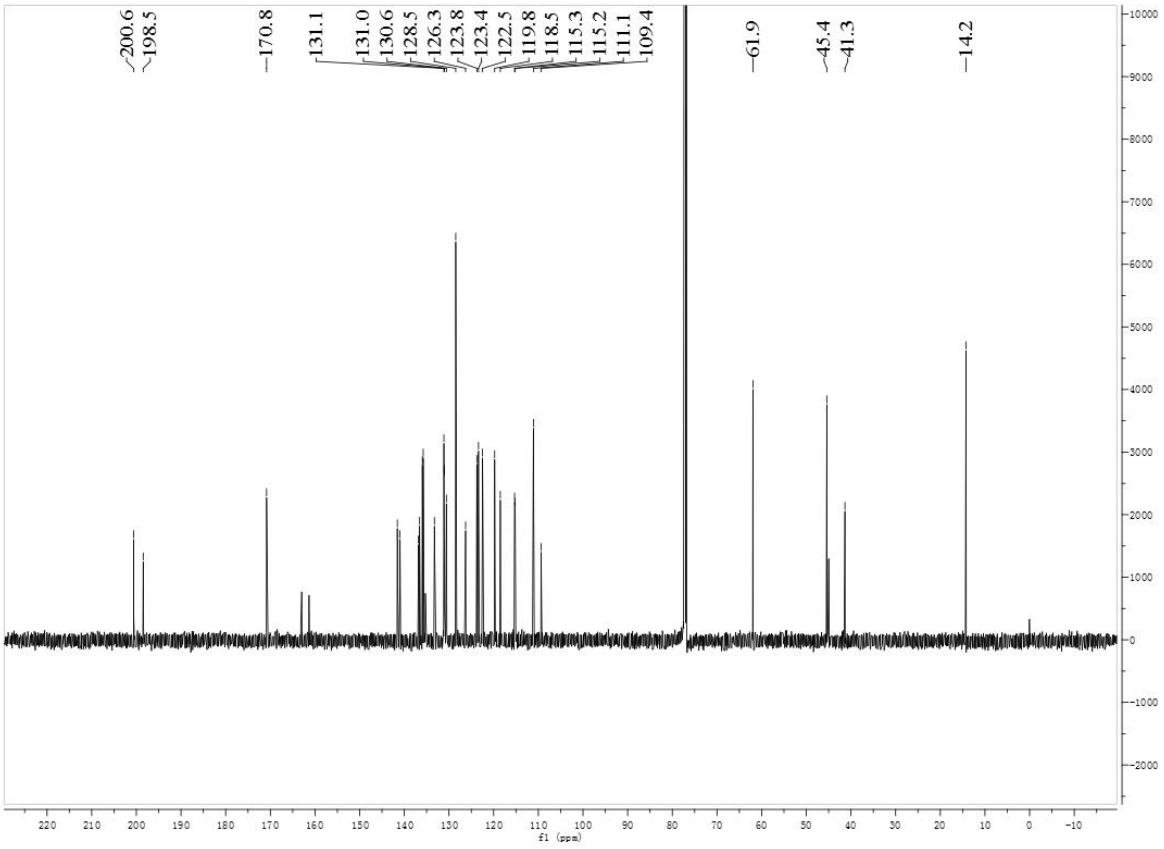


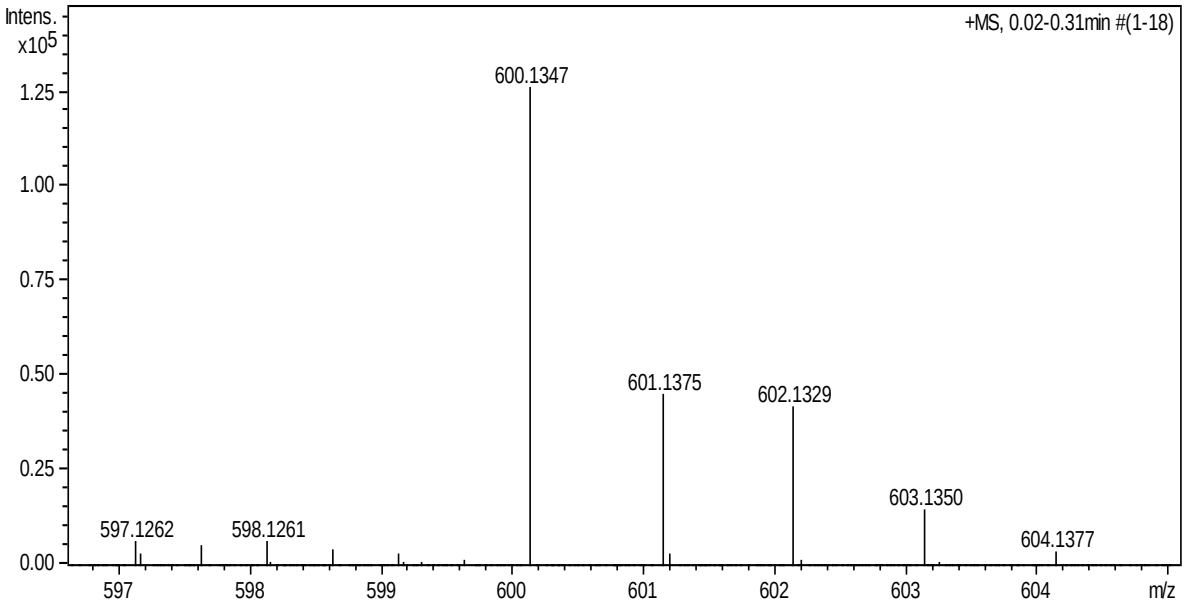

200.3
198.2
170.6
148.0
137.3
125.8
122.5
118.6
111.1
109.6
62.1
45.3
41.5
21.3
14.2
f1 (ppm)


Intens.
x10^4
+MS, 0.05-1.31min #(3-78)
607.1833
608.1864
609.1892
602.2267
605.1702
612.1335
614.1327
m/z

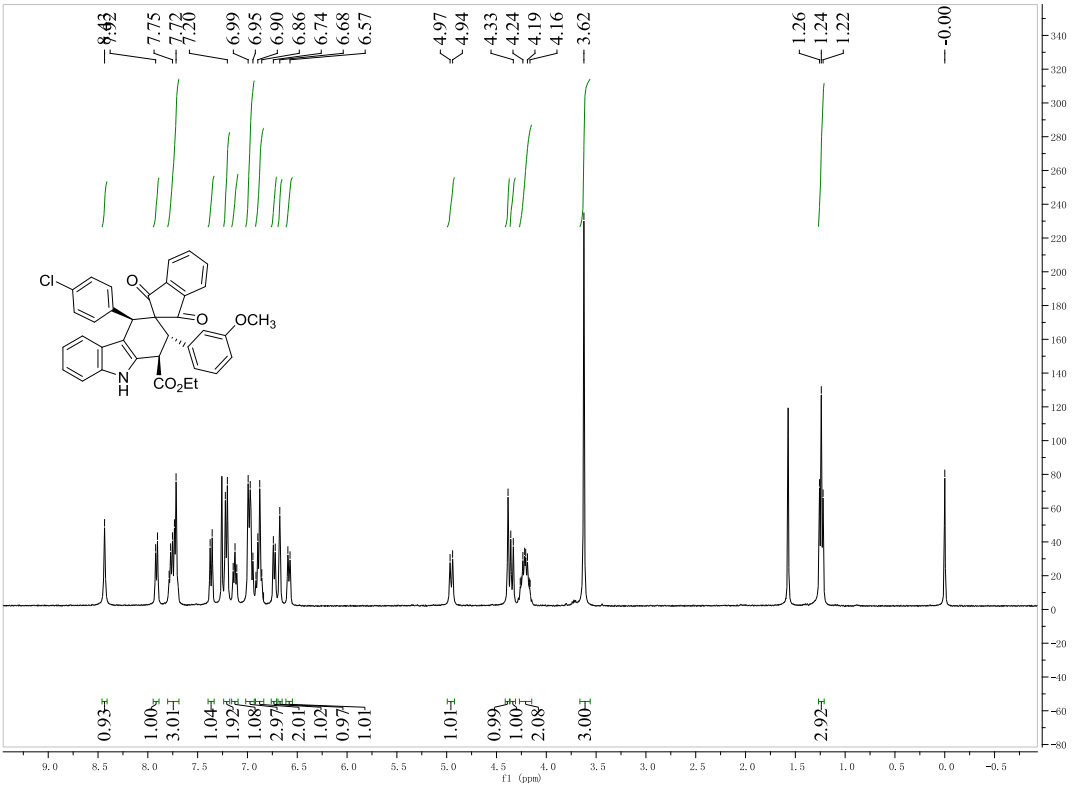
Ethyl-3-(4-chlorophenyl)-4-(4-fluorophenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2f):

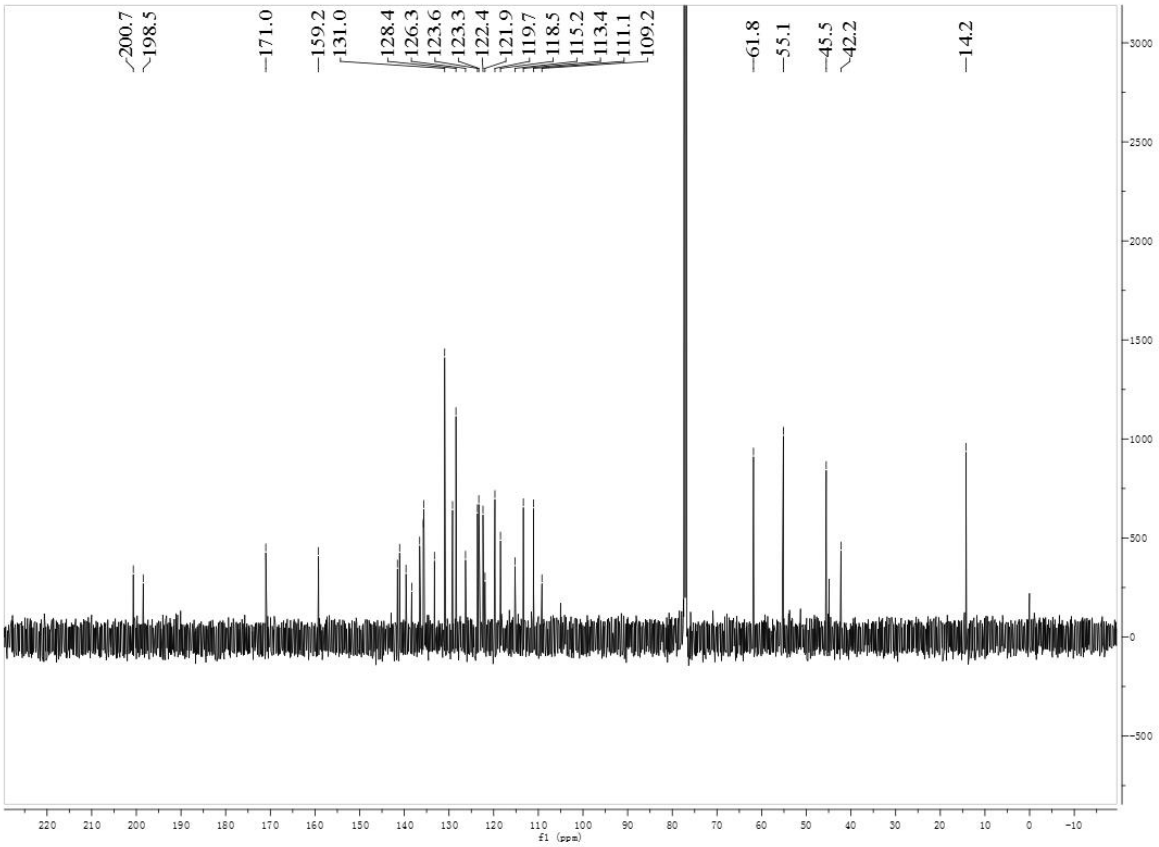


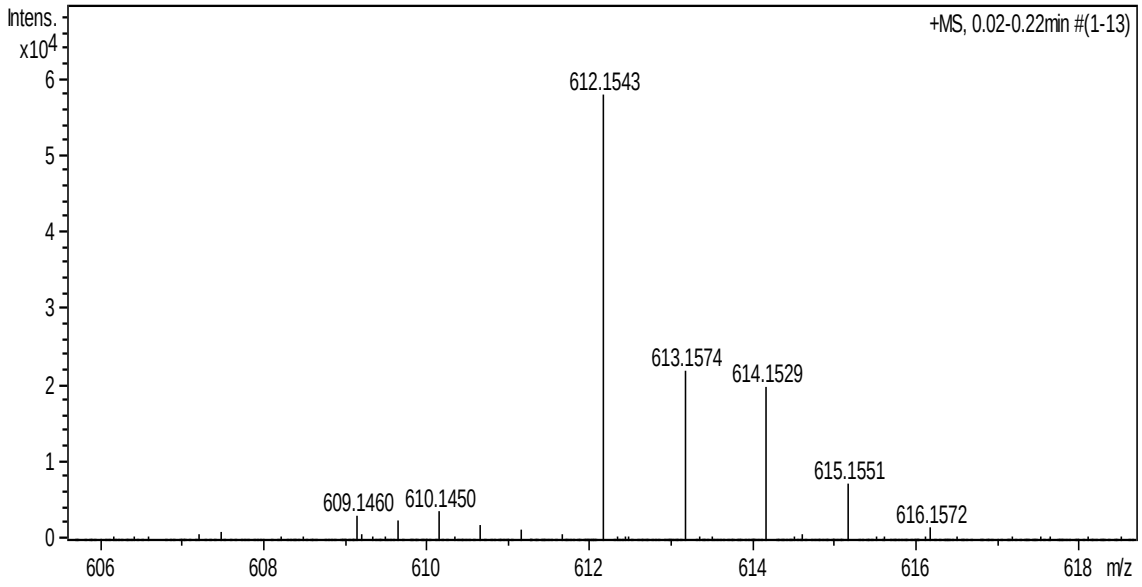




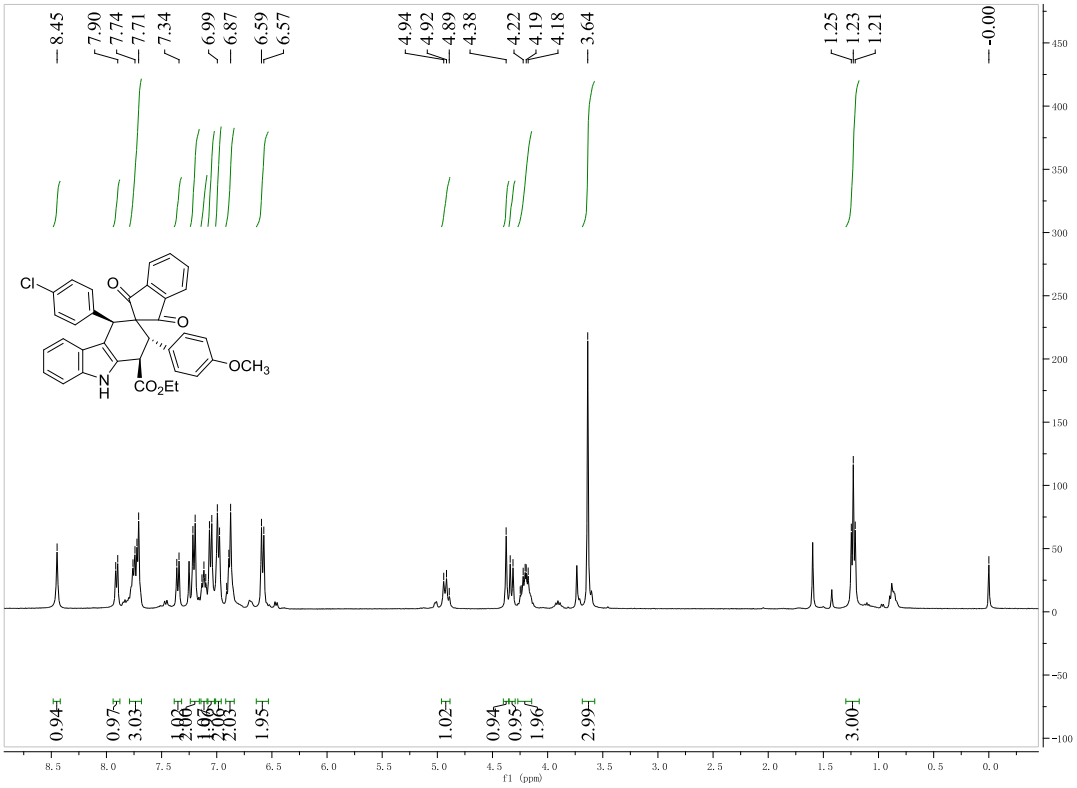
Ethyl-4-(4-chlorophenyl)-3-(3-methoxyphenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carb azole-2,2'-indene]-1-carboxylate (2g):

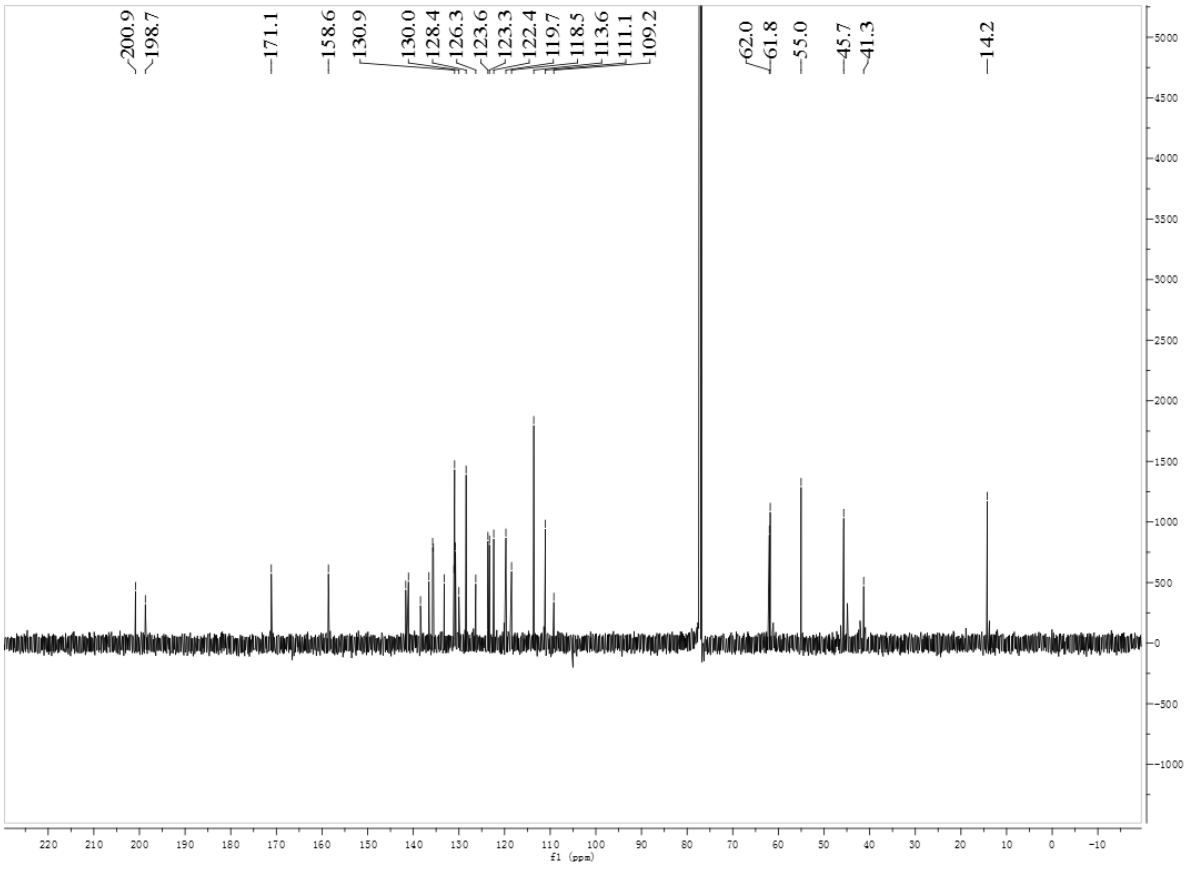


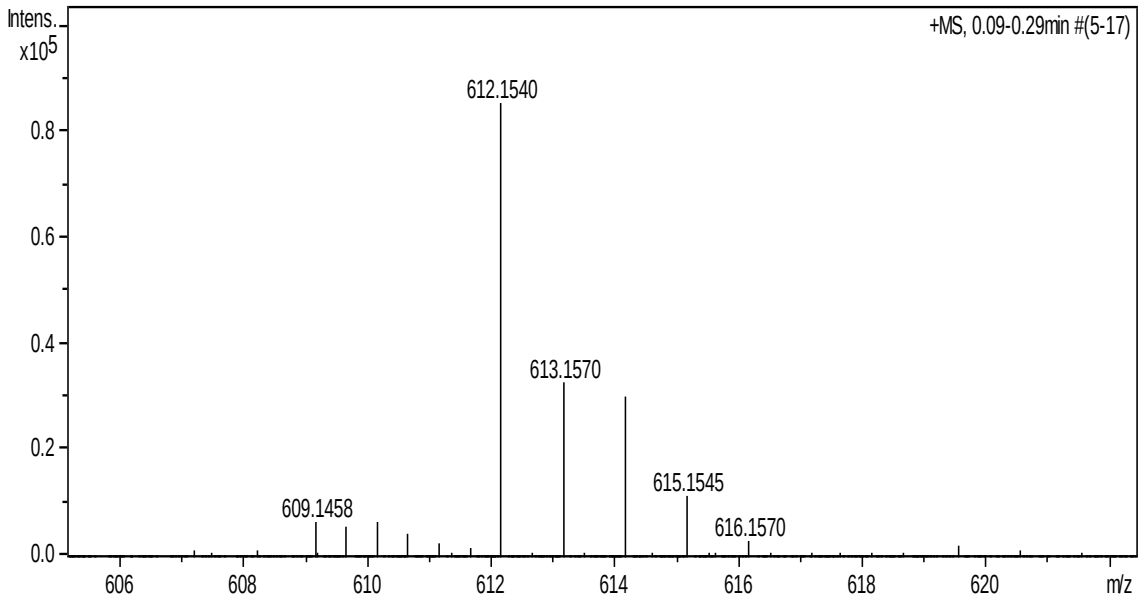

200.7
198.5
171.0
159.2
131.0
128.4
126.3
123.6
123.3
122.4
121.9
119.7
118.5
115.2
113.4
111.1
109.2
61.8
55.1
45.5
42.2
14.2
f1 (ppm)


Intens.
x10^4
+MS, 0.02-0.22min #(1-13)
612.1543
613.1574
614.1529
615.1551
616.1572
609.1460
610.1450
m/z

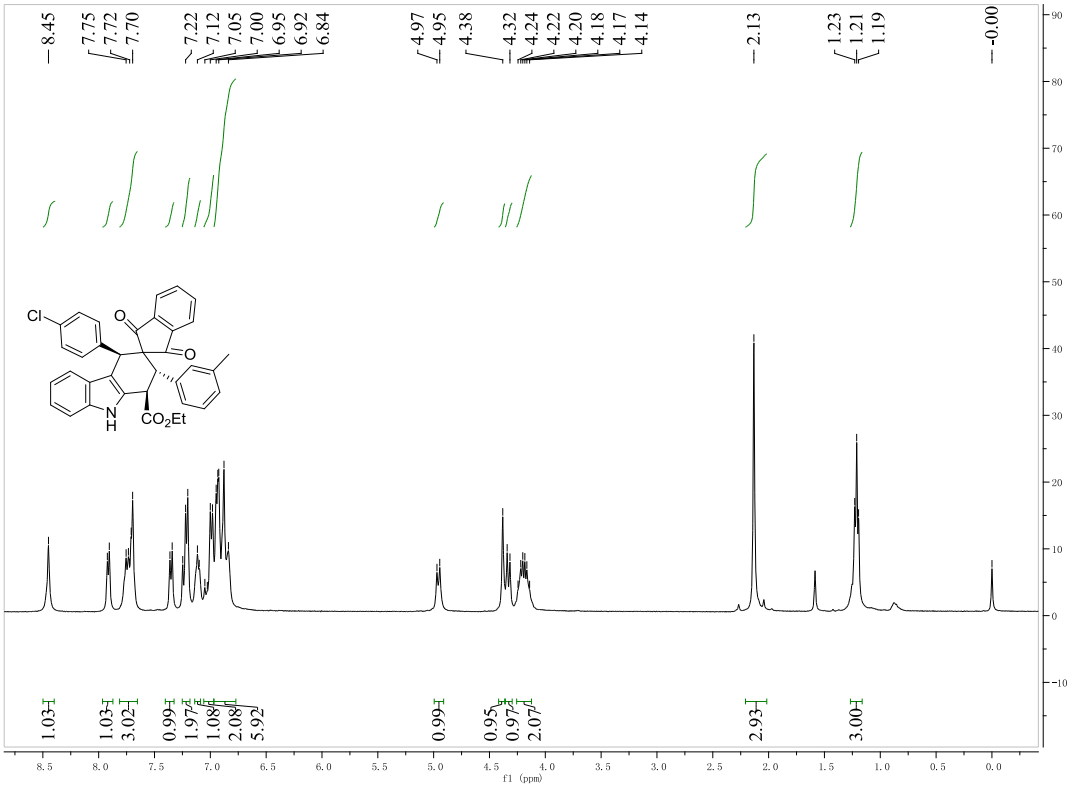
Ethyl-4-(4-chlorophenyl)-3-(4-methoxyphenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2h):

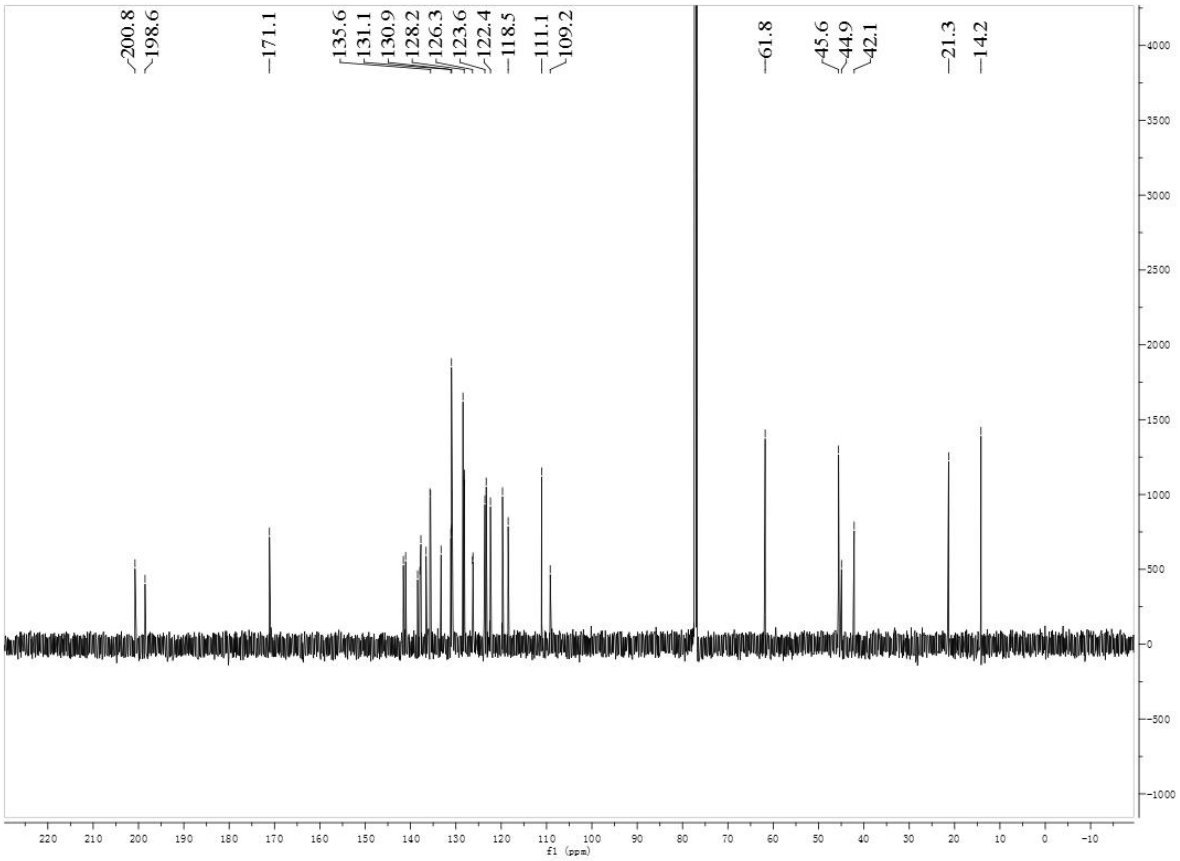


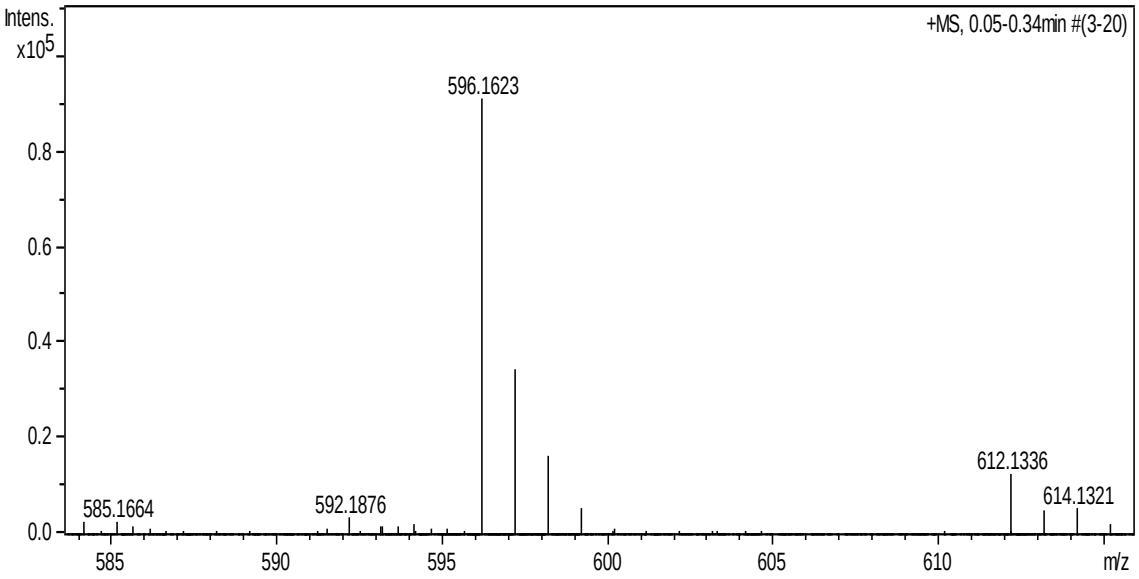




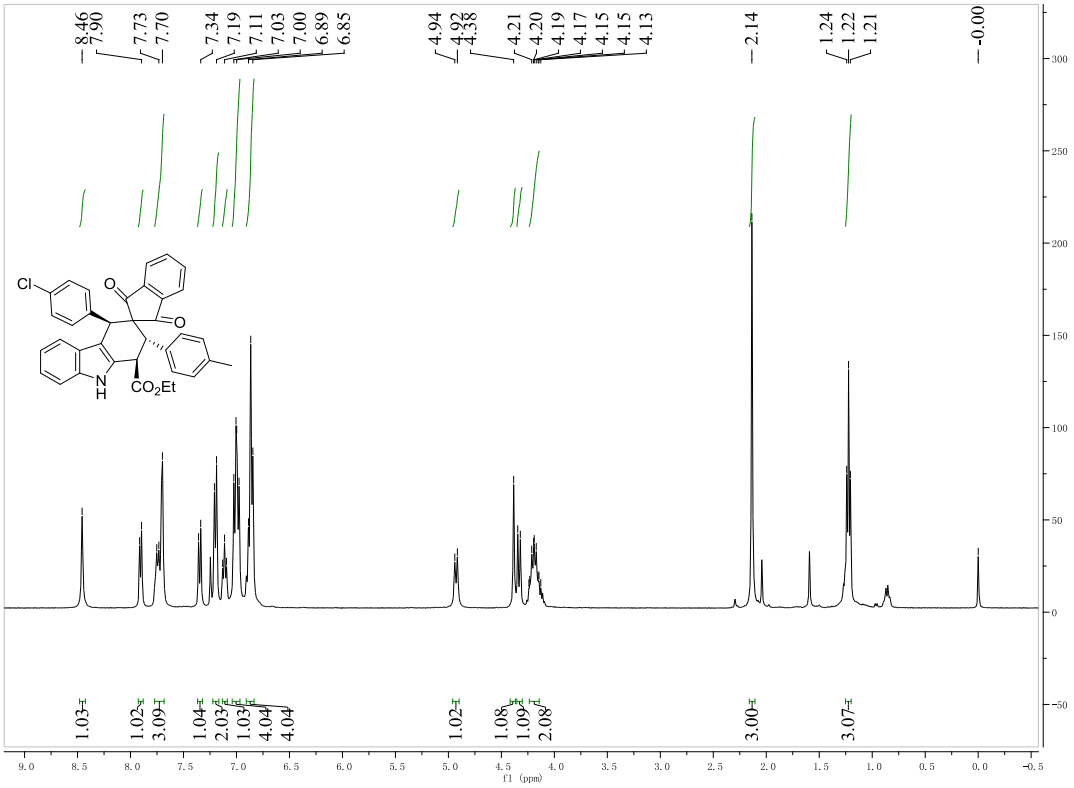
Ethyl-4-(4-chlorophenyl)-1',3'-dioxo-3-(m-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2i):

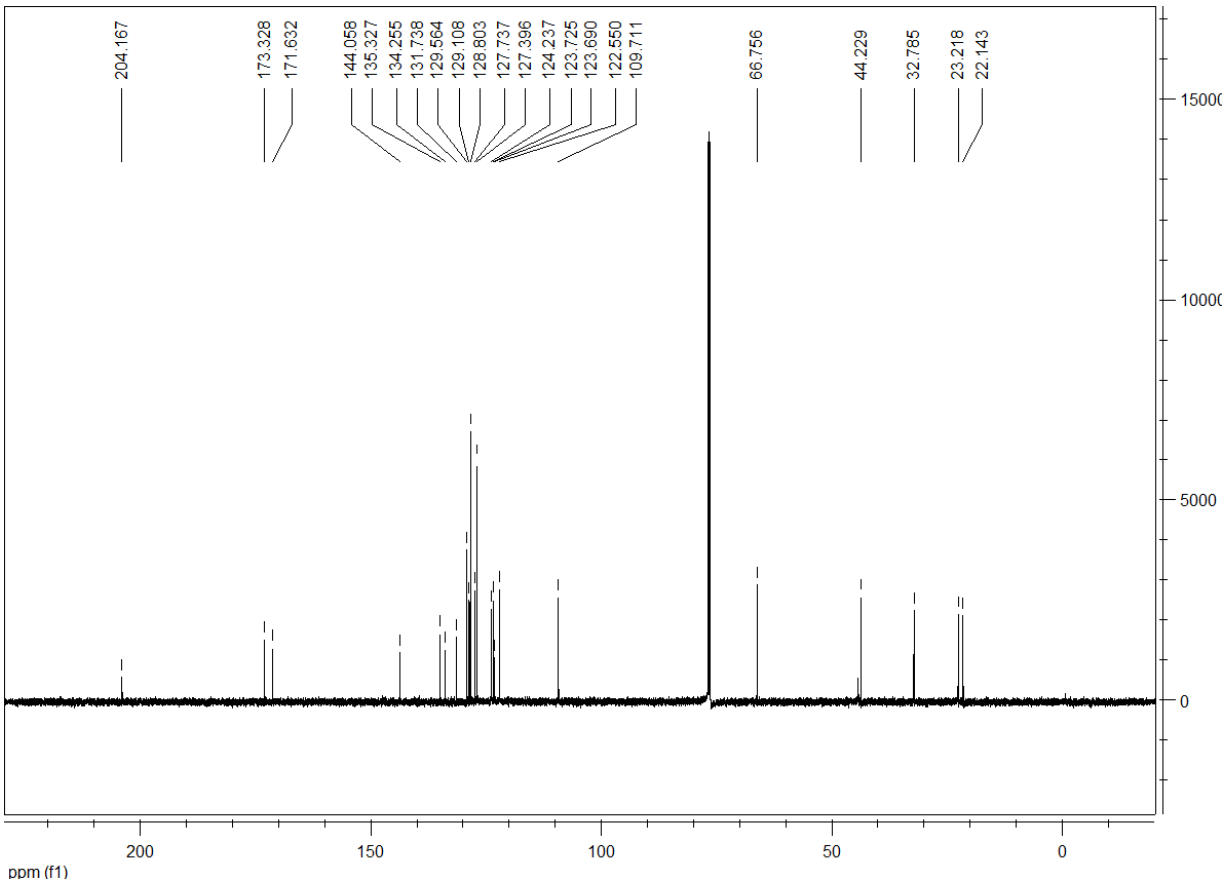


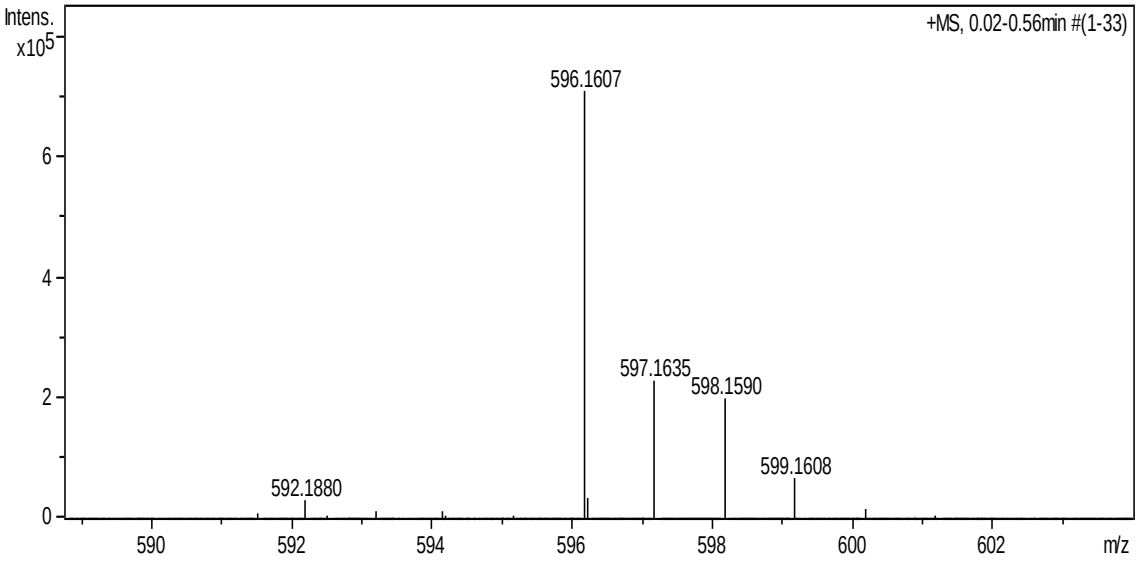

200.8
198.6
171.1
135.6
131.1
130.9
128.2
126.3
123.6
122.4
118.5
111.1
109.2
61.8
45.6
44.9
42.1
21.3
14.2
f1 (ppm)


Intens.
x10^5
+MS, 0.05-0.34min #(3-20)
596.1623
612.1336
614.1321
585.1664
592.1876
m/z

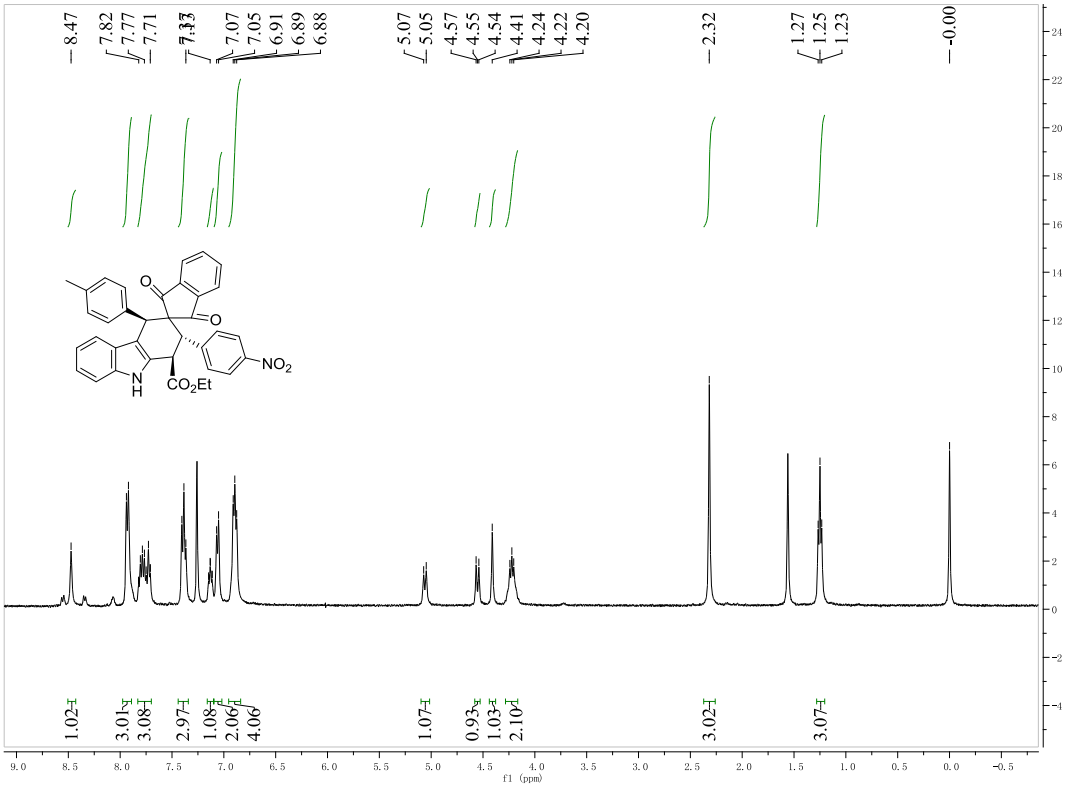
Ethyl-4-(4-chlorophenyl)-1',3'-dioxo-3-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2j):

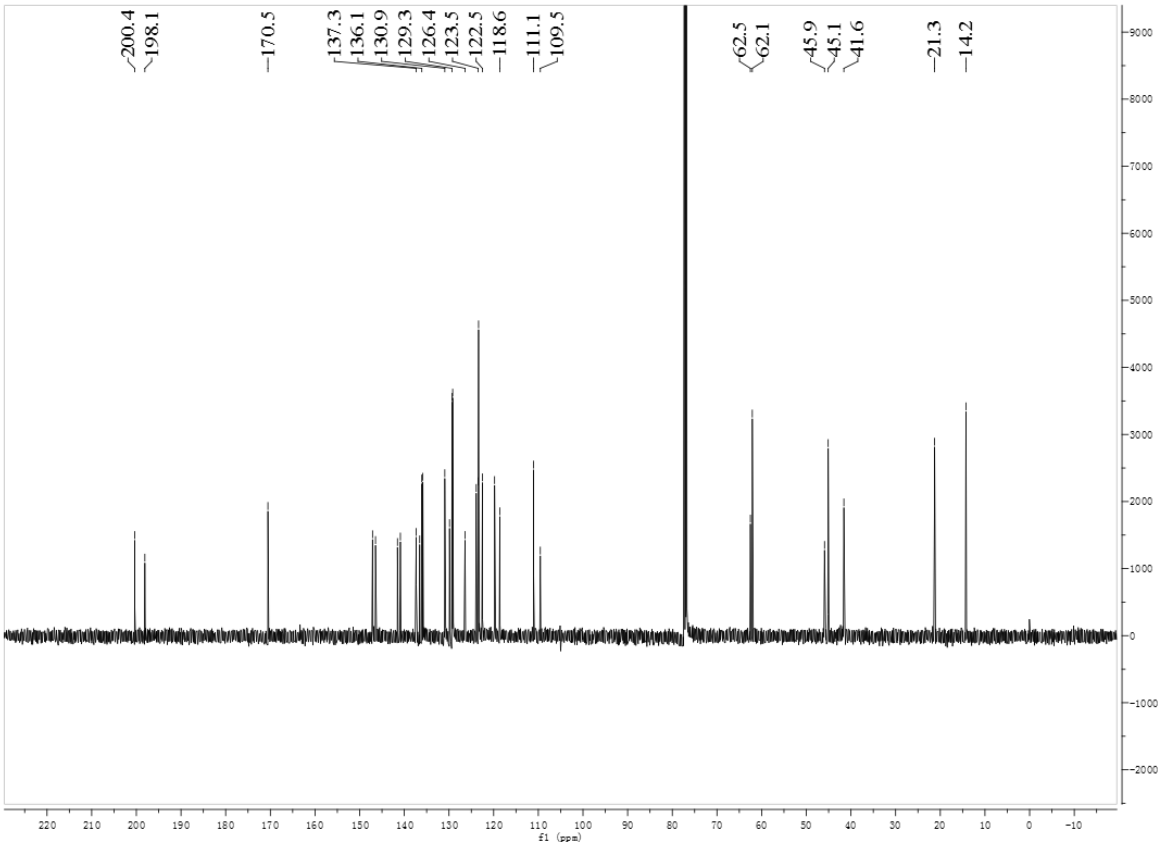


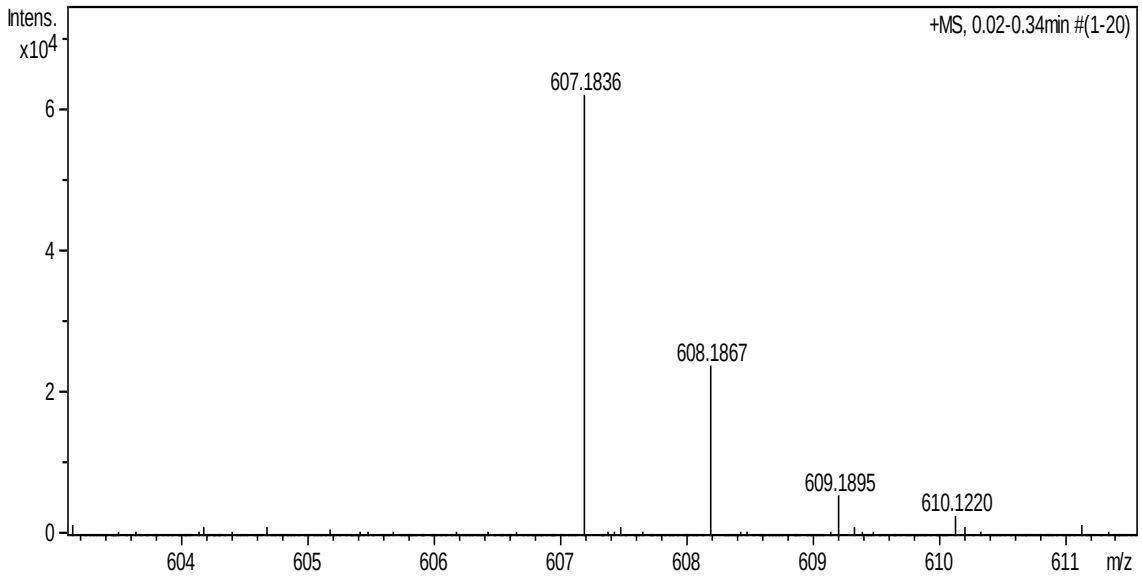




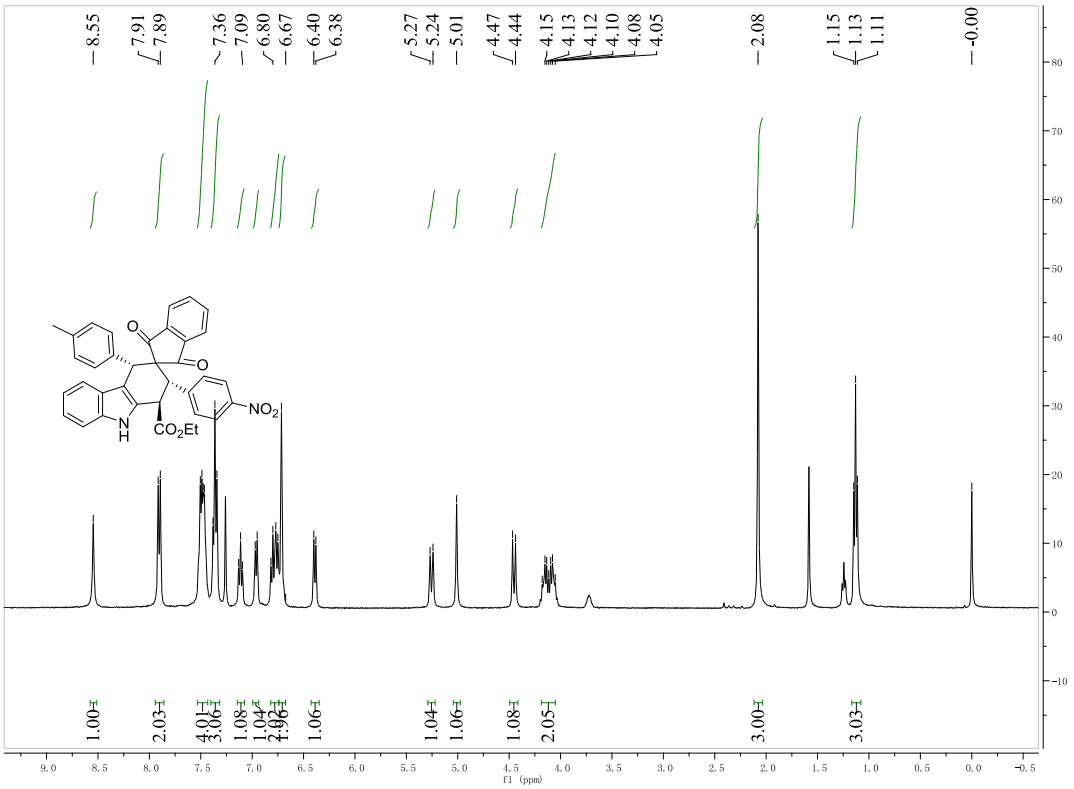
Ethyl-3-(4-nitrophenyl)-1',3'-dioxo-4-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2k):

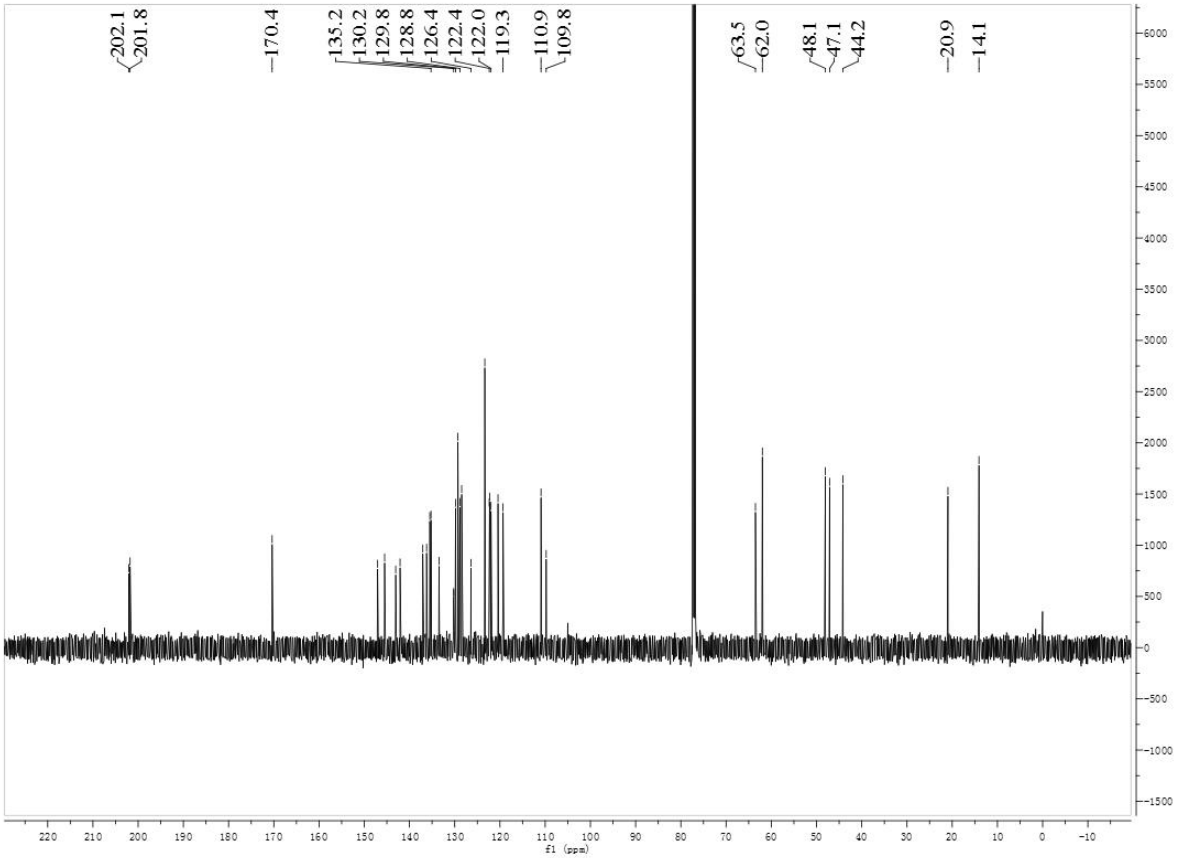


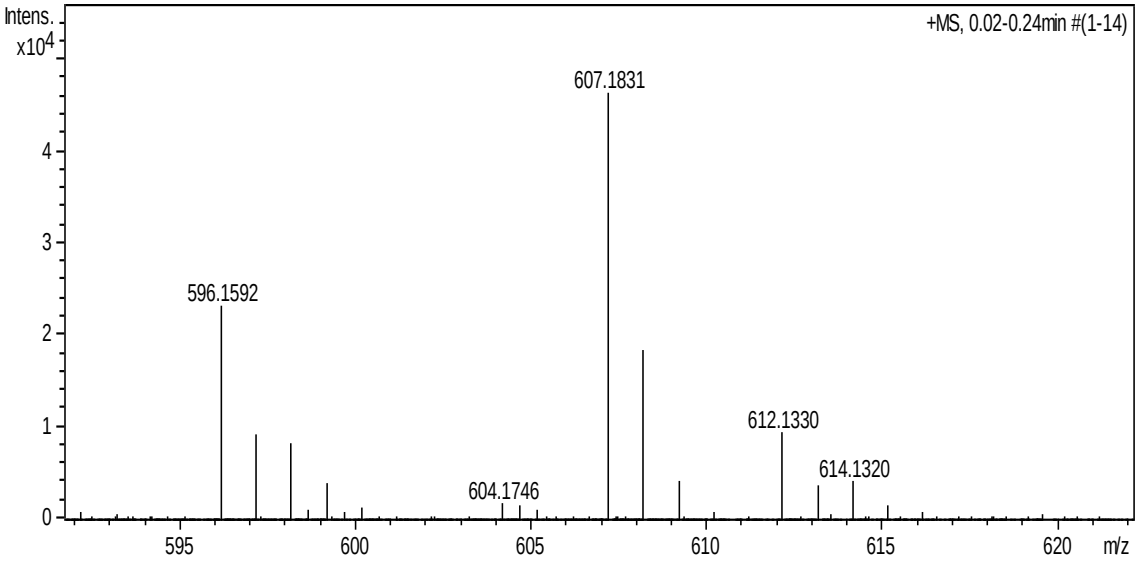

200.4
198.1
170.5
137.3
136.1
130.9
129.3
126.4
123.5
122.5
118.6
111.1
109.5
62.5
62.1
45.9
45.1
41.6
21.3
14.2
f1 (ppm)


Intens.
x10^4
+MS, 0.02-0.34min #(1-20)
607.1836
608.1867
609.1895
610.1220
m/z

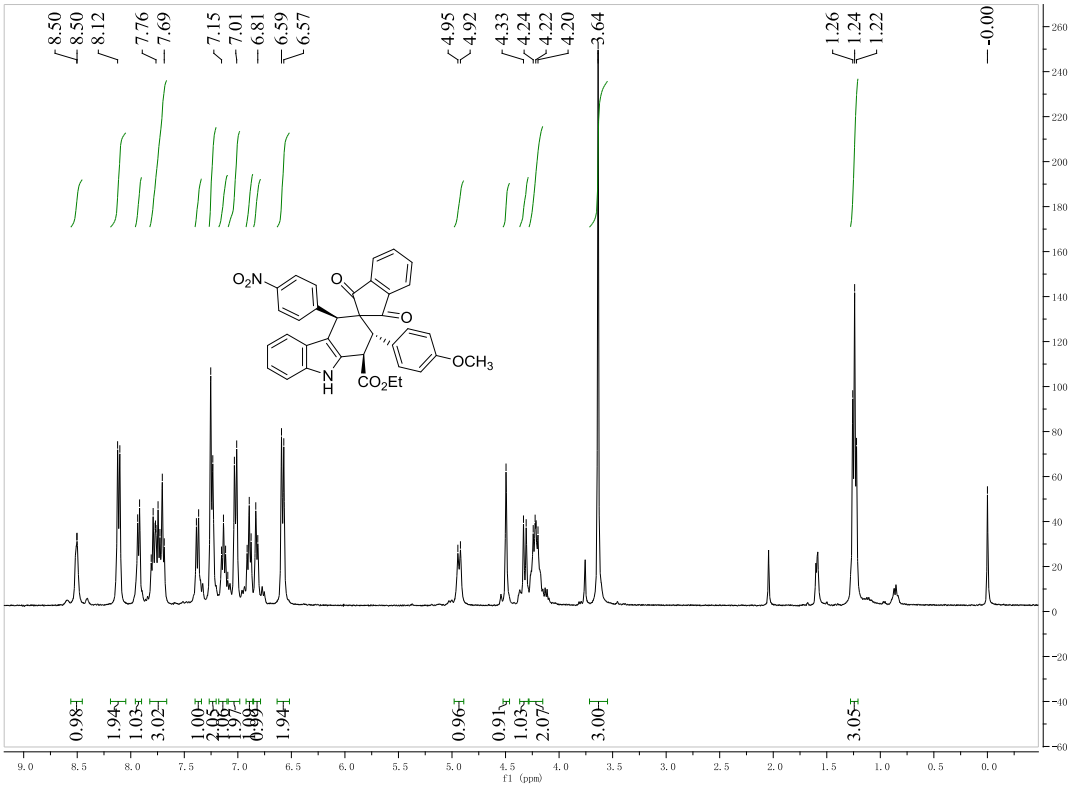
Ethyl-3-(4-nitrophenyl)-1',3'-dioxo-4-(p-tolyl)-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2k'):

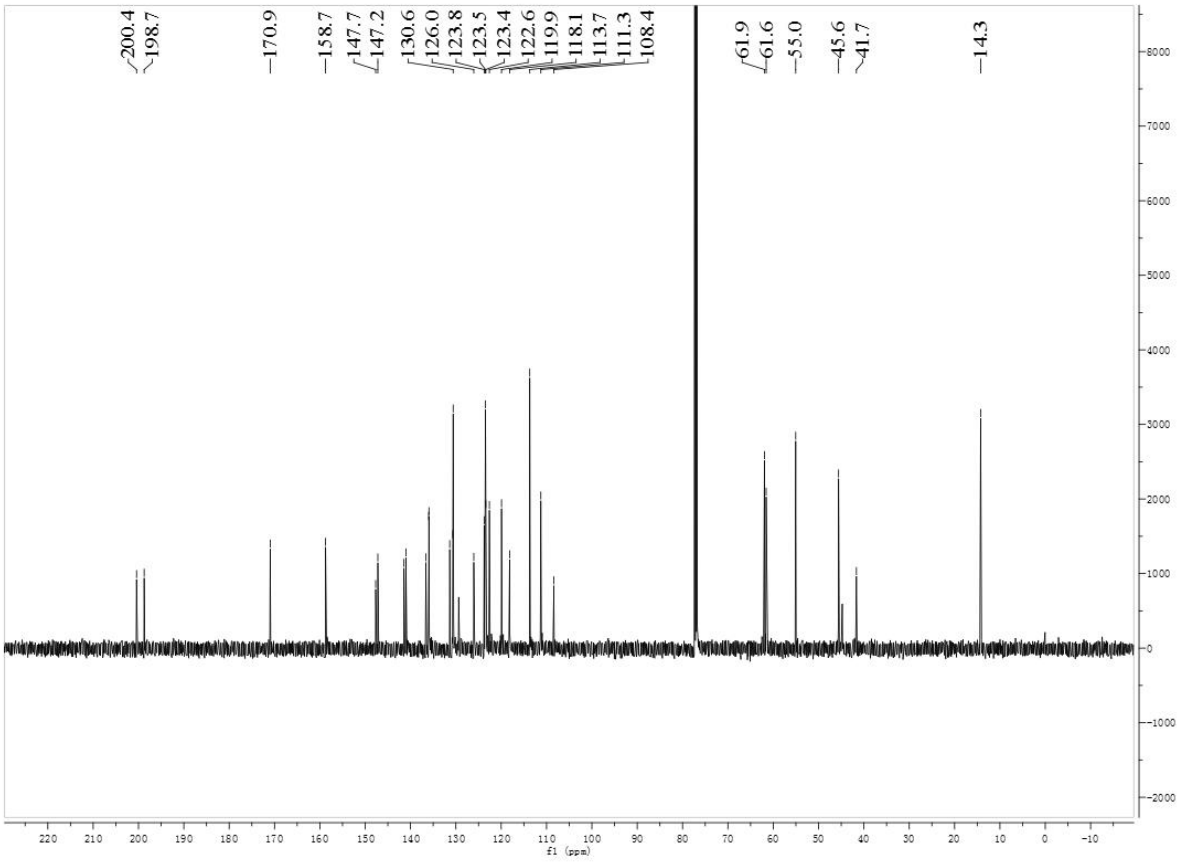


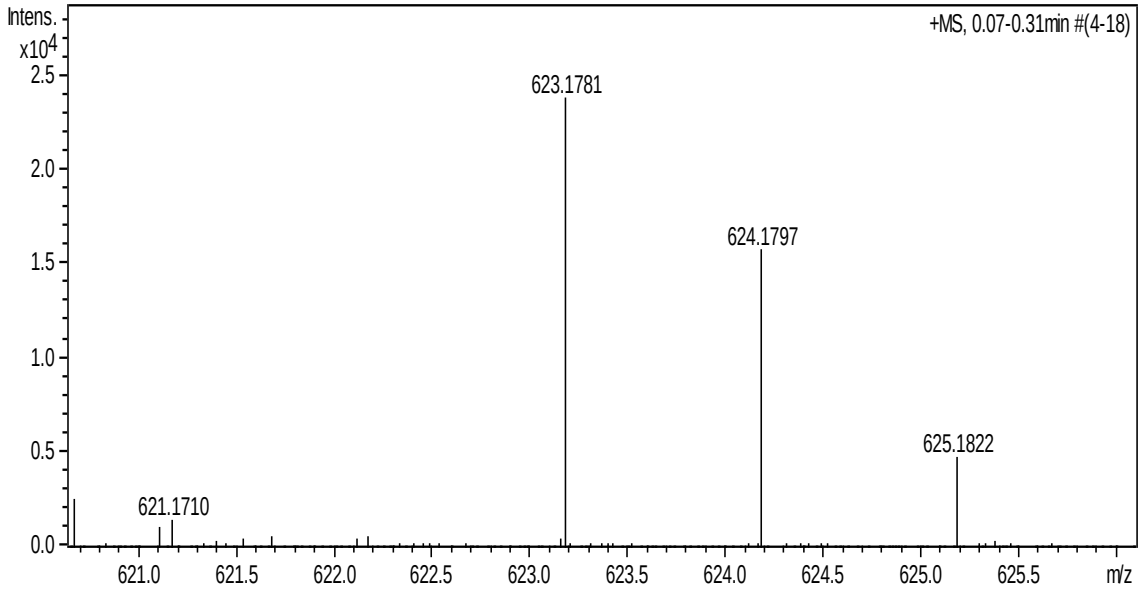




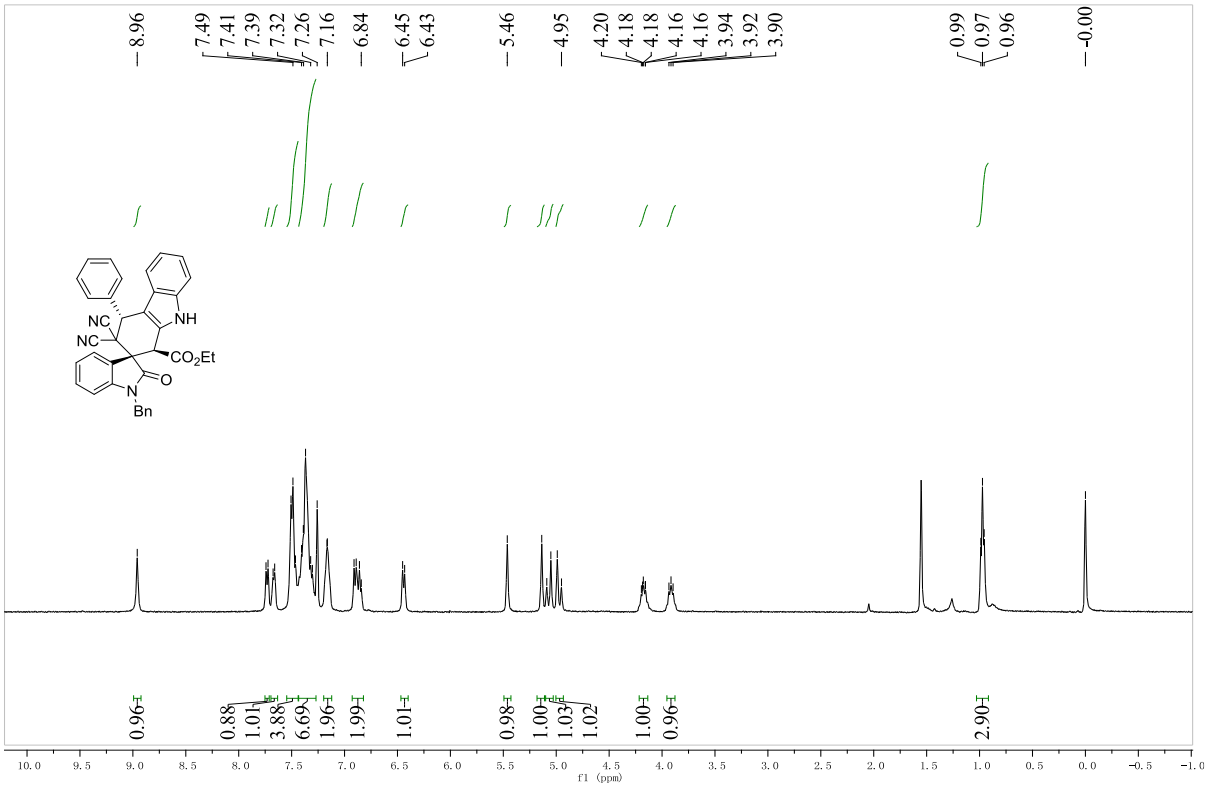
Ethyl-3-(4-methoxyphenyl)-4-(4-nitrophenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (2l):

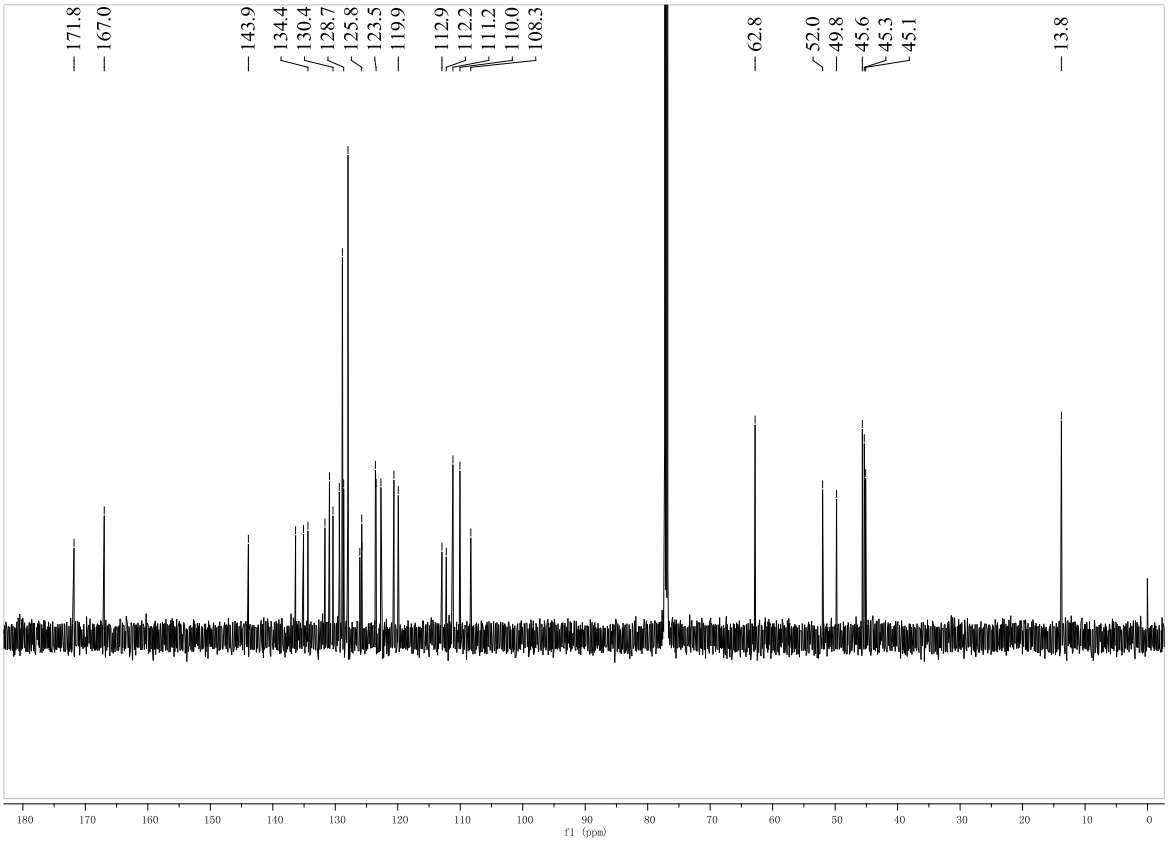


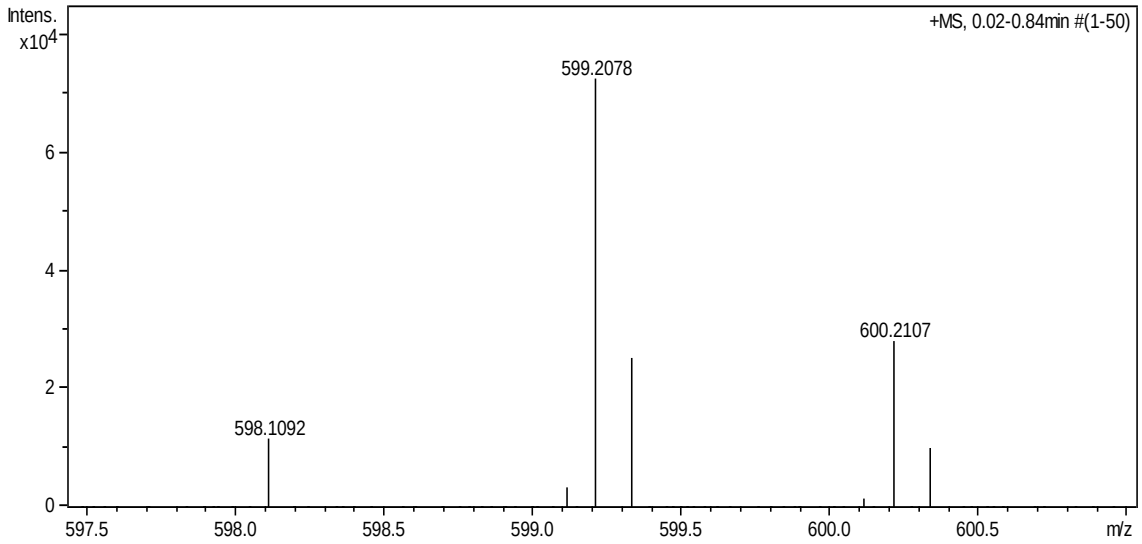

200.4
198.7
170.9
158.7
147.7
147.2
130.6
126.0
123.8
123.5
123.4
122.6
119.9
118.1
113.7
111.3
108.4
61.9
61.6
55.0
45.6
41.7
14.3
f1 (ppm)


Intens.
x10^4
+MS, 0.07-0.31min #(4-18)
623.1781
624.1797
625.1822
621.1710
m/z

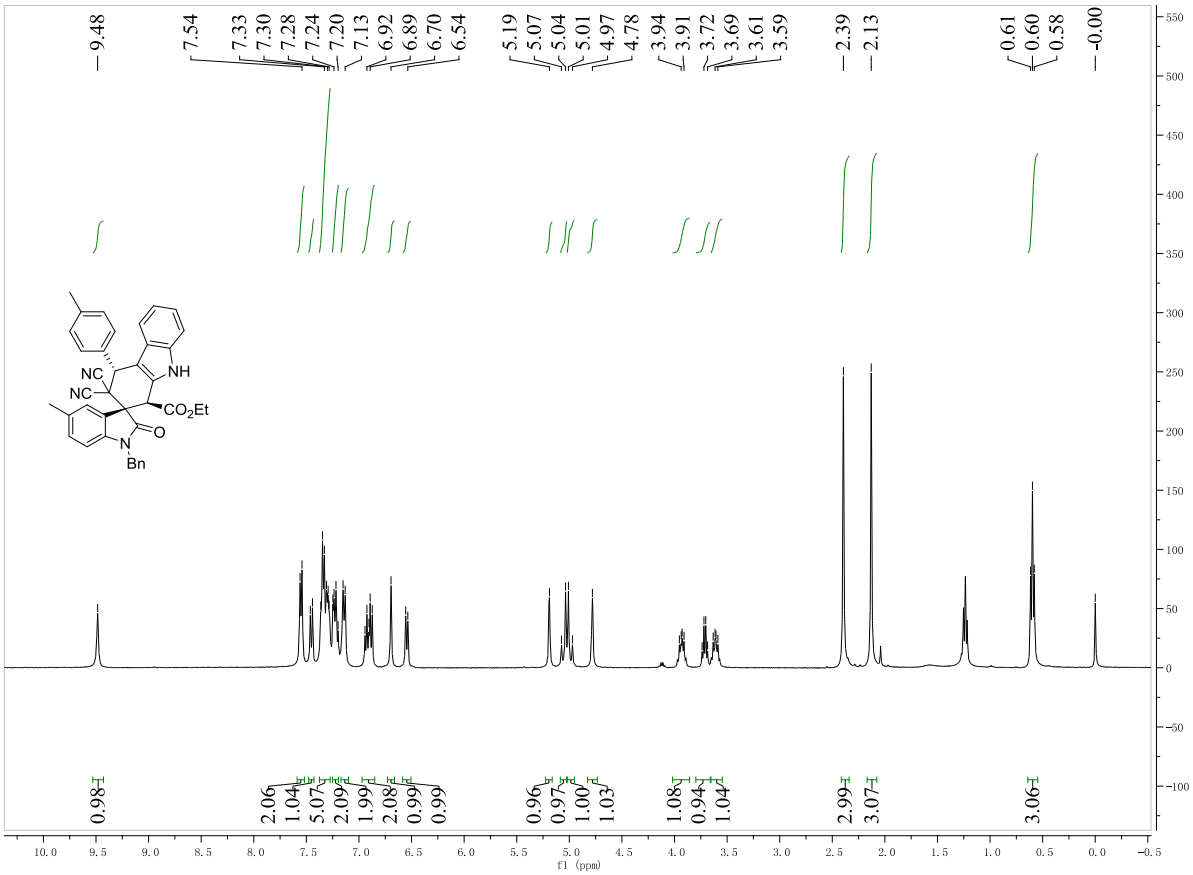
Ethyl-1'-benzyl-3,3-dicyano-2'-oxo-4-phenyl-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline] -1-carboxylate (3a):

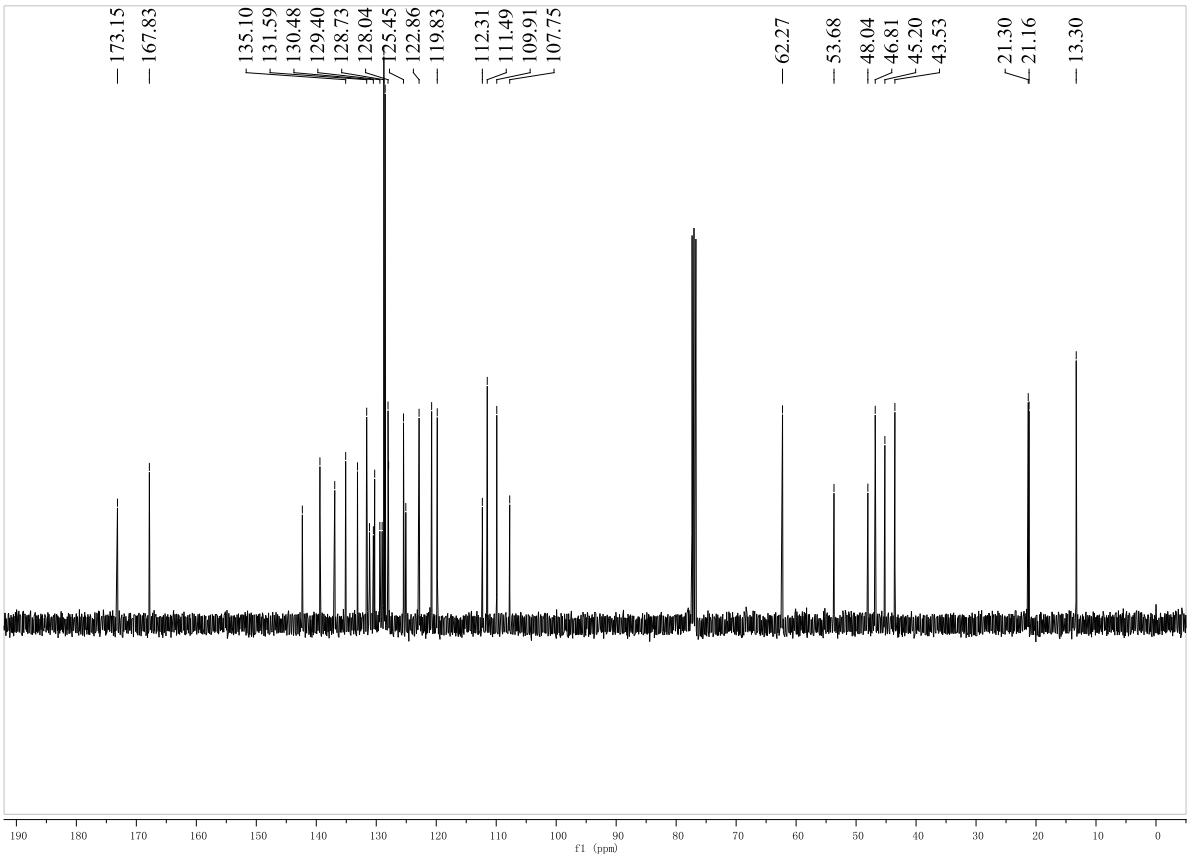


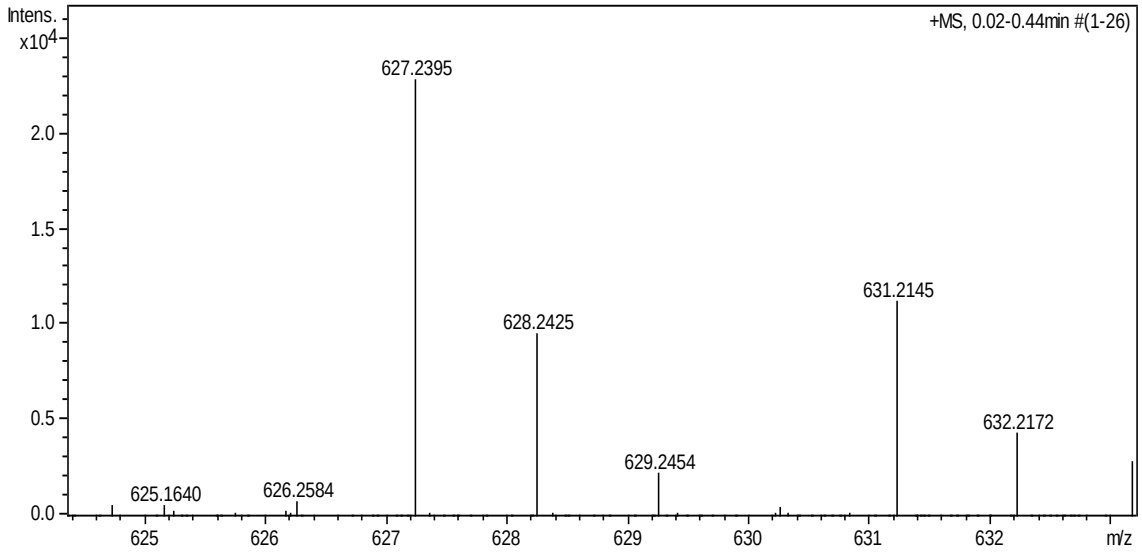




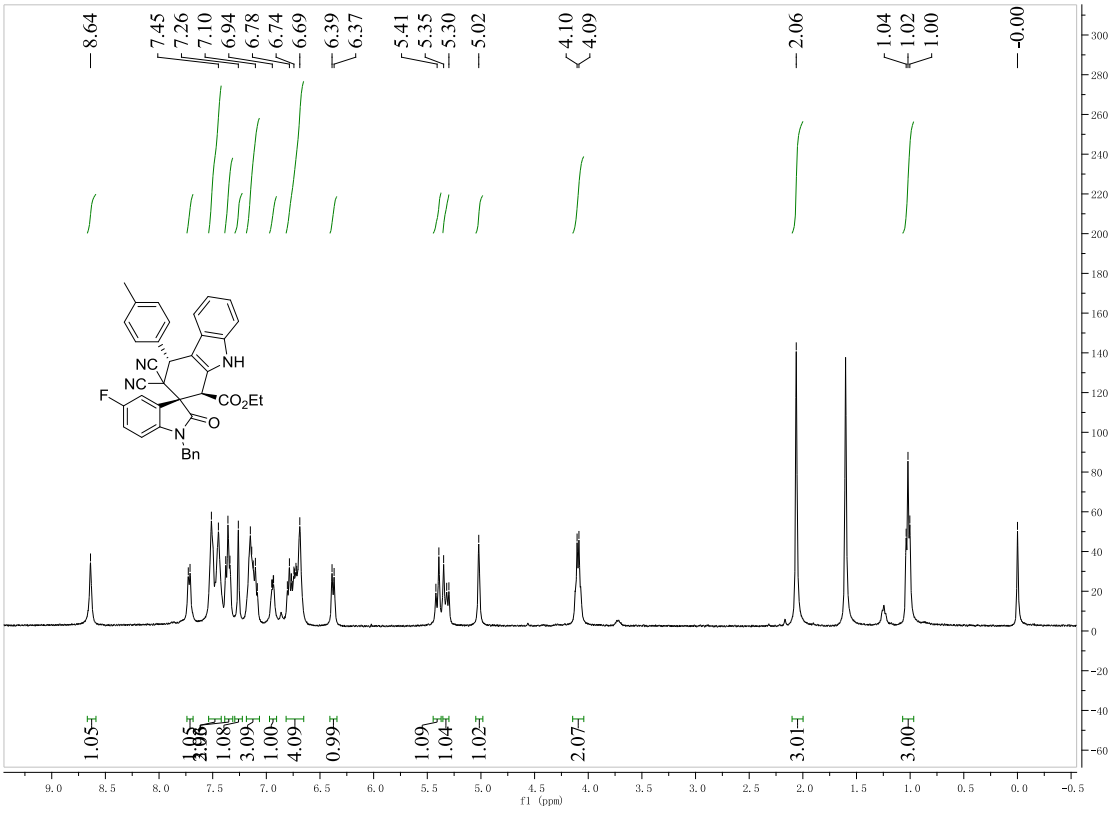
Ethyl-1'-benzyl-3,3-dicyano-5'-methyl-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2, 3'-indoline]-1-carboxylate (3b):

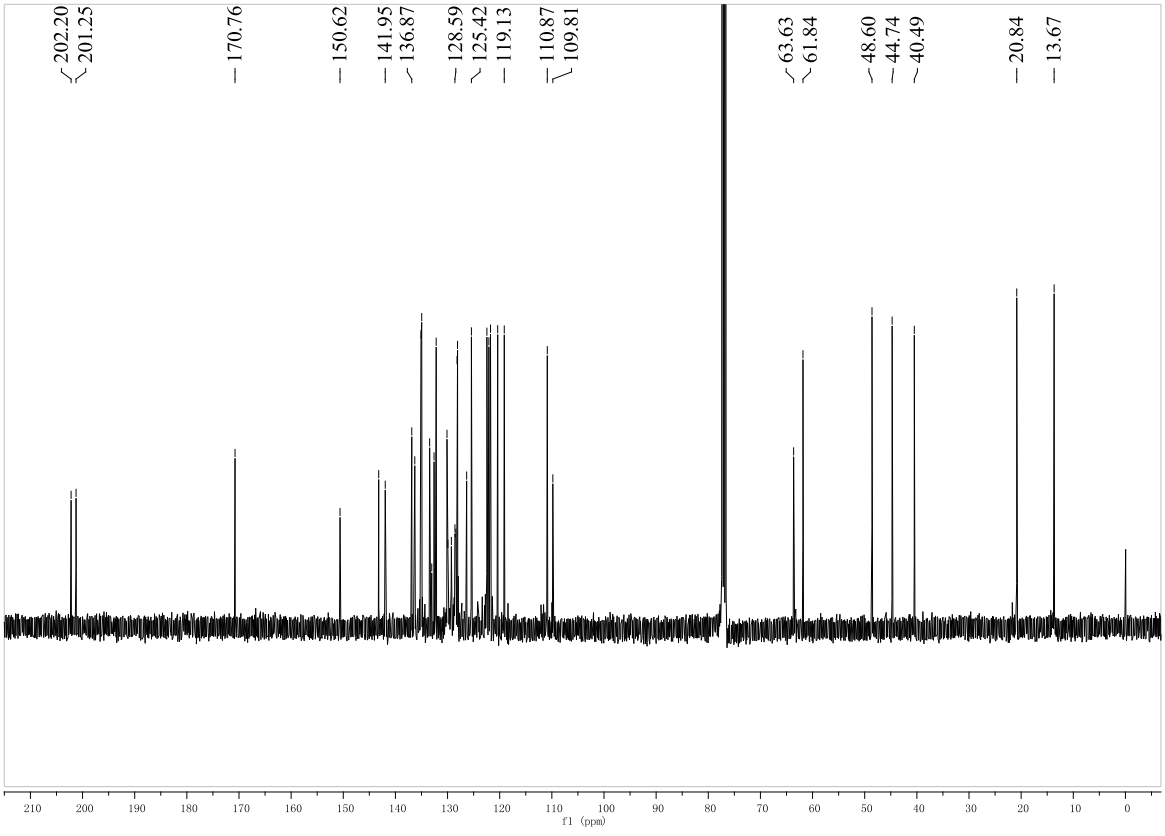


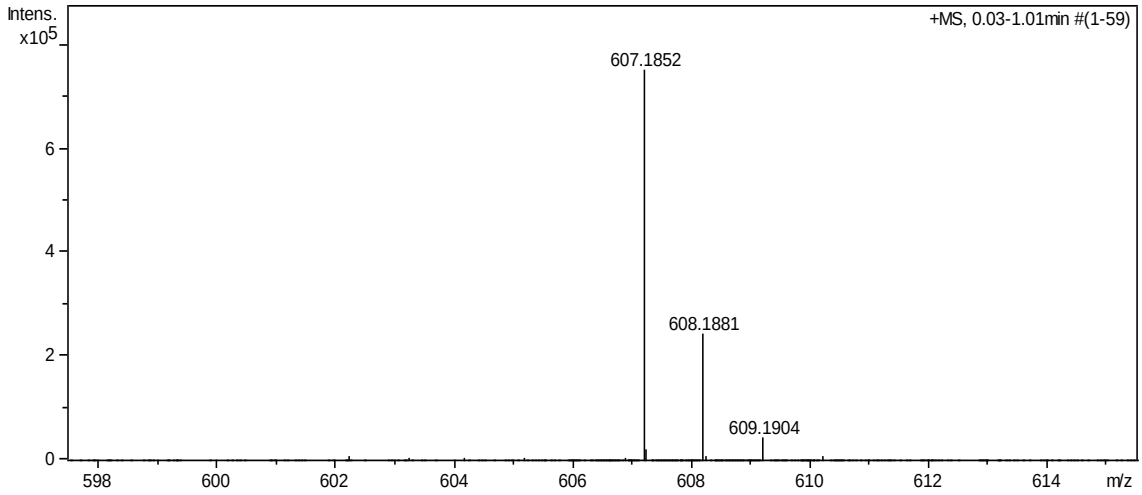

173.15
167.83
135.10
131.59
130.48
129.40
128.73
128.04
125.45
122.86
119.83
112.31
111.49
109.91
107.75
62.27
53.68
48.04
46.81
45.20
43.53
21.30
21.16
13.30
f1 (ppm)


Intens.
x10^4
+MS, 0.02-0.44min #(1-26)
627.2395
631.2145
628.2425
632.2172
629.2454
625.1640
626.2584
m/z

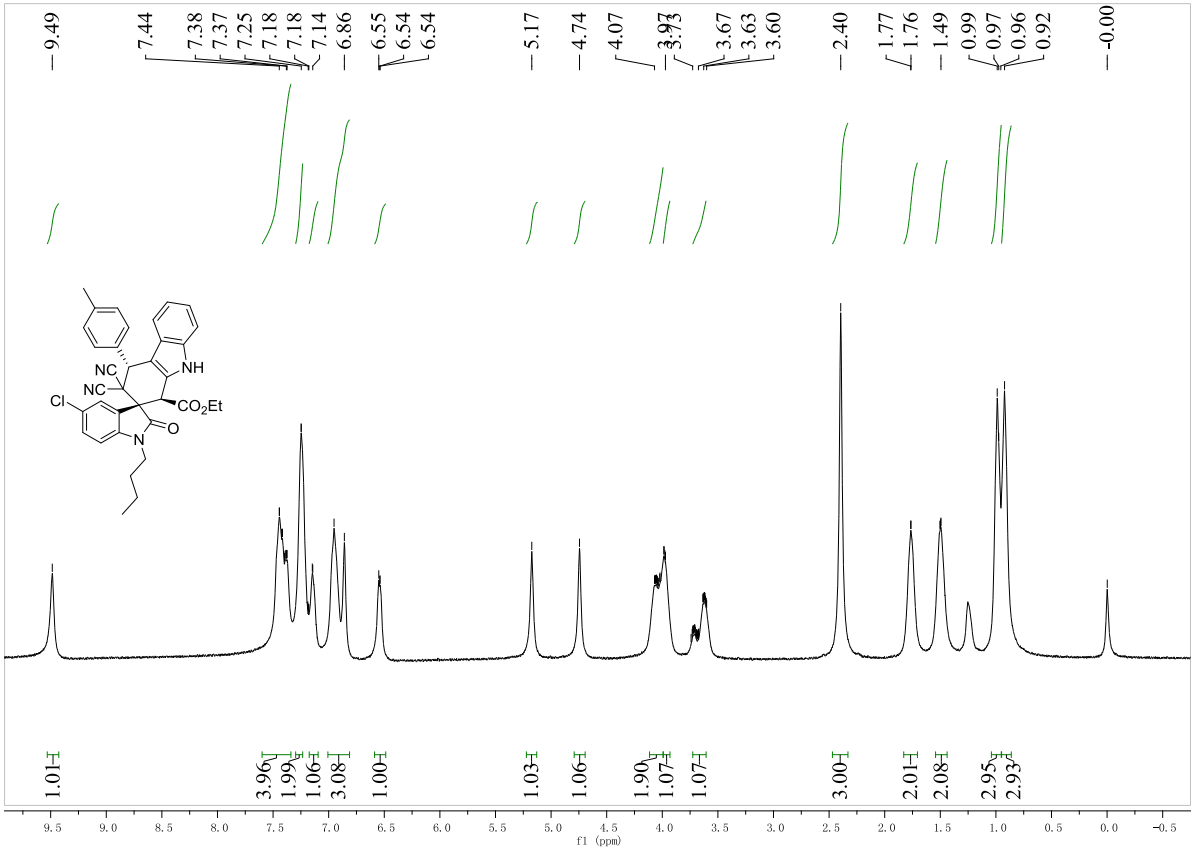
Ethyl-1'-benzyl-3,3-dicyano-2'-oxo-4-(p-tolyl)-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indolin e]-1-carboxylate (3c):

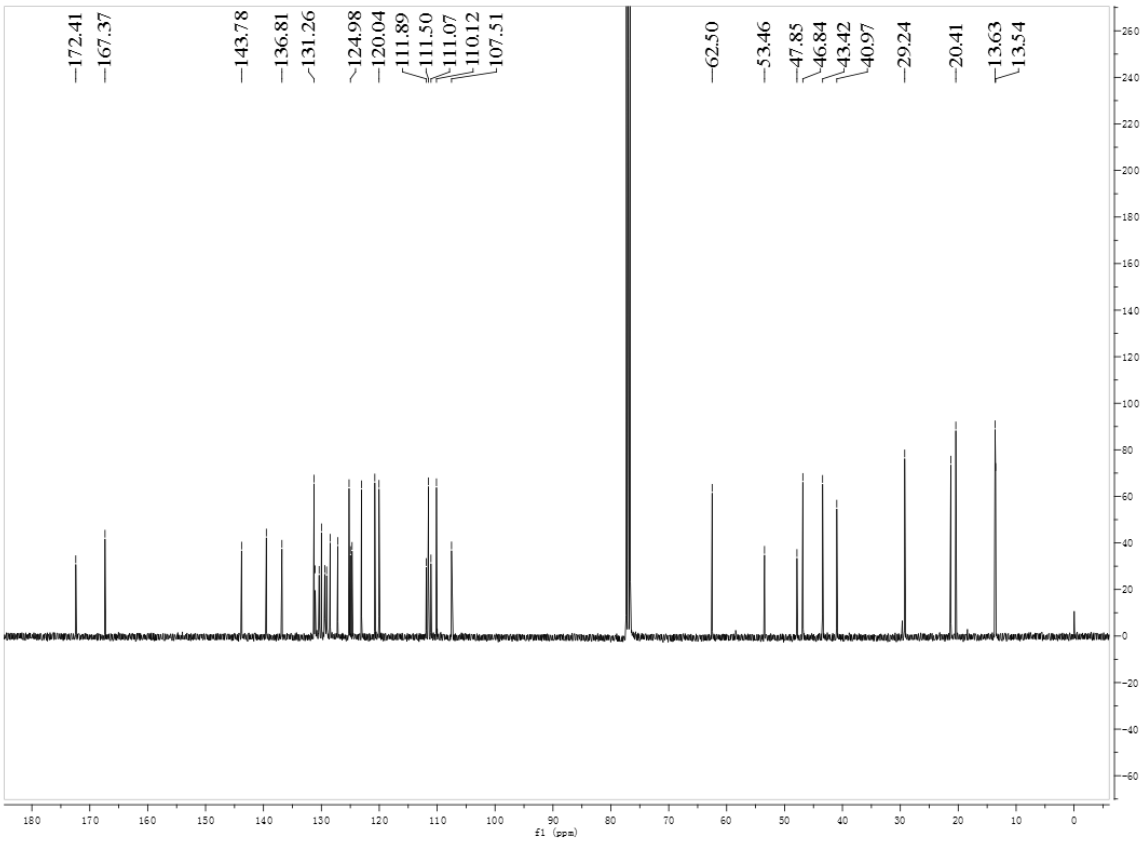


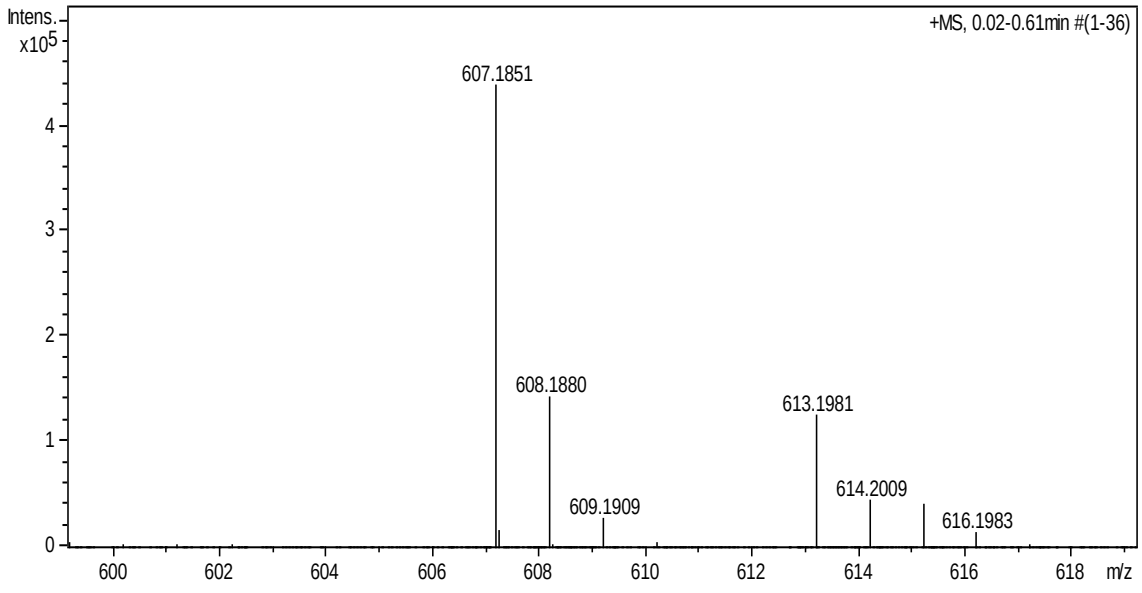




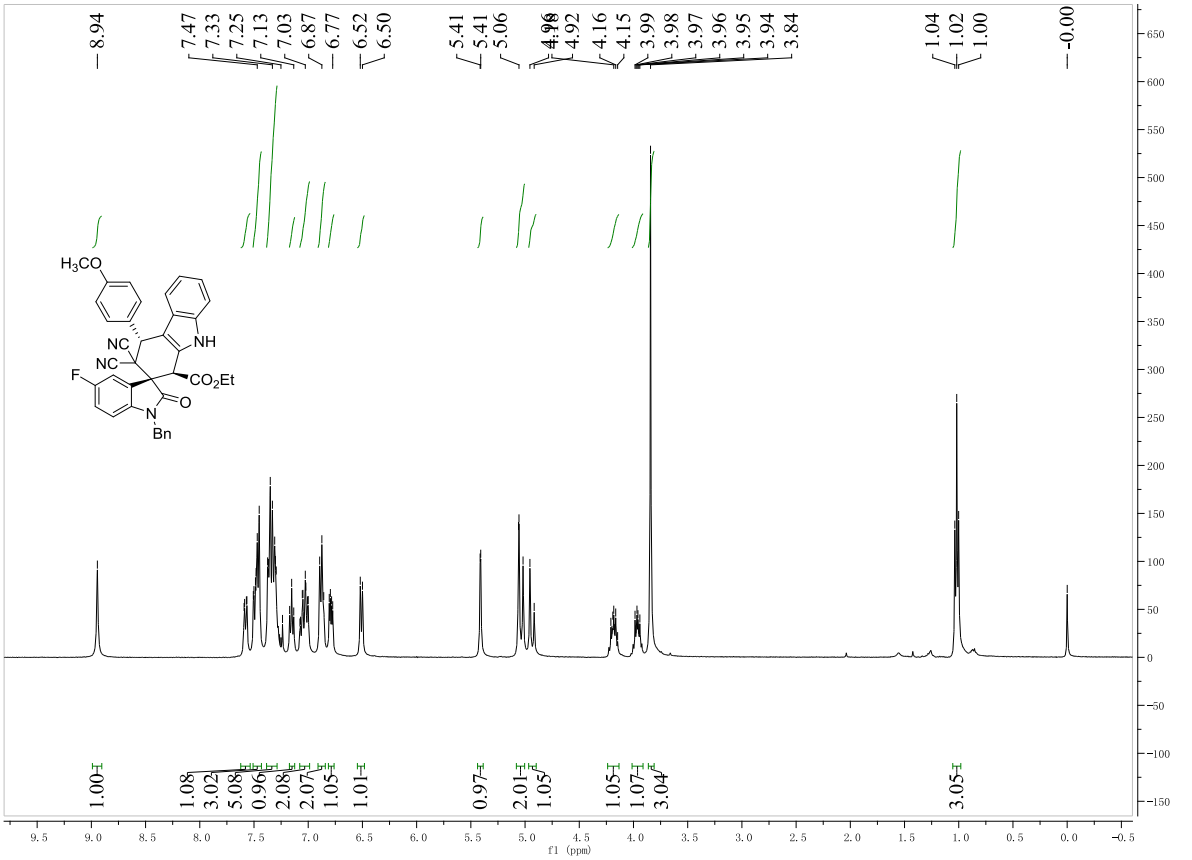
Ethyl-3-(4-methoxyphenyl)-4-(4-nitrophenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (3d):

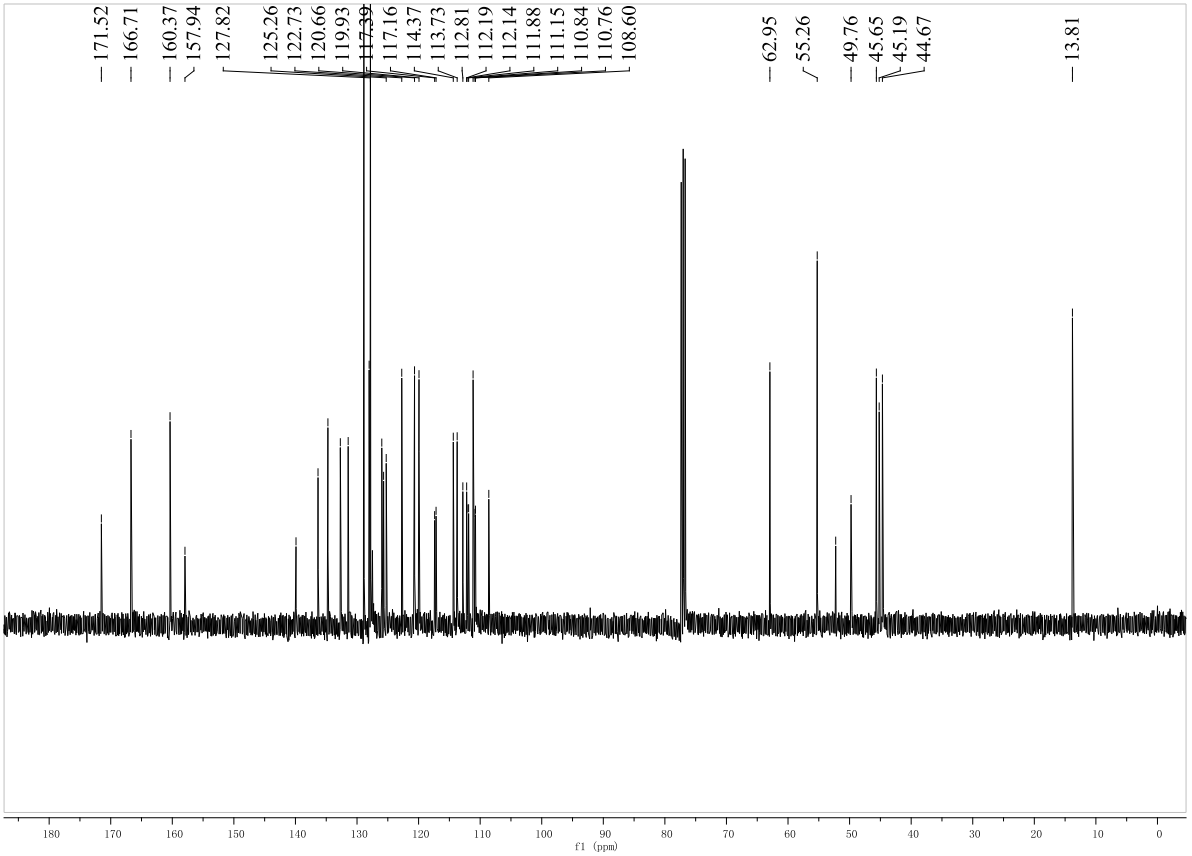


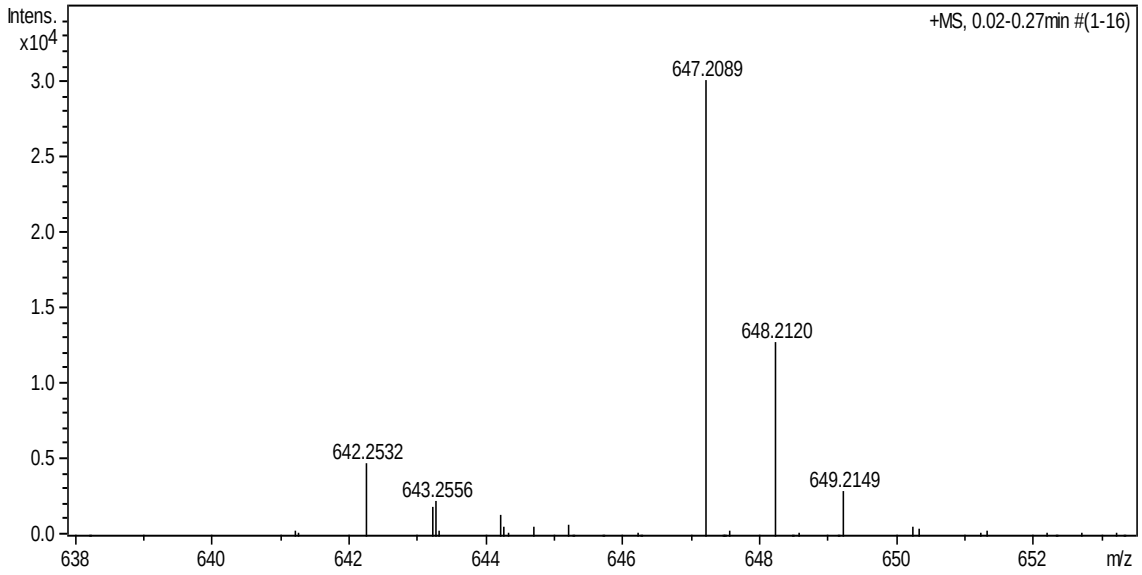

172.41
167.37
143.78
136.81
131.26
124.98
120.04
111.89
111.50
111.07
110.12
107.51
62.50
53.46
47.85
46.84
43.42
40.97
29.24
20.41
13.63
13.54
f1 (ppm)


Intens.
x10^5
+MS, 0.02-0.61min #(1-36)
607.1851
608.1880
609.1909
613.1981
614.2009
616.1983
m/z

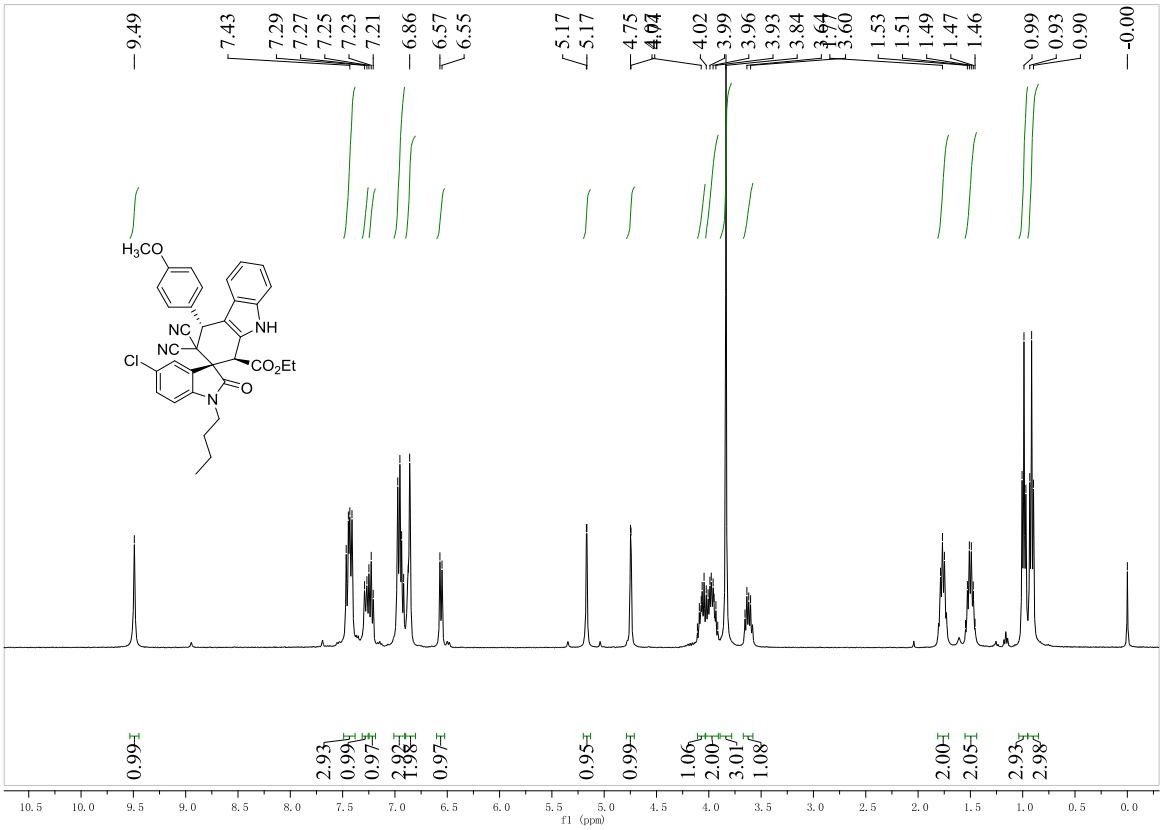
Ethyl-1'-benzyl-3,3-dicyano-5'-fluoro-4-(4-methoxyphenyl)-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3e):

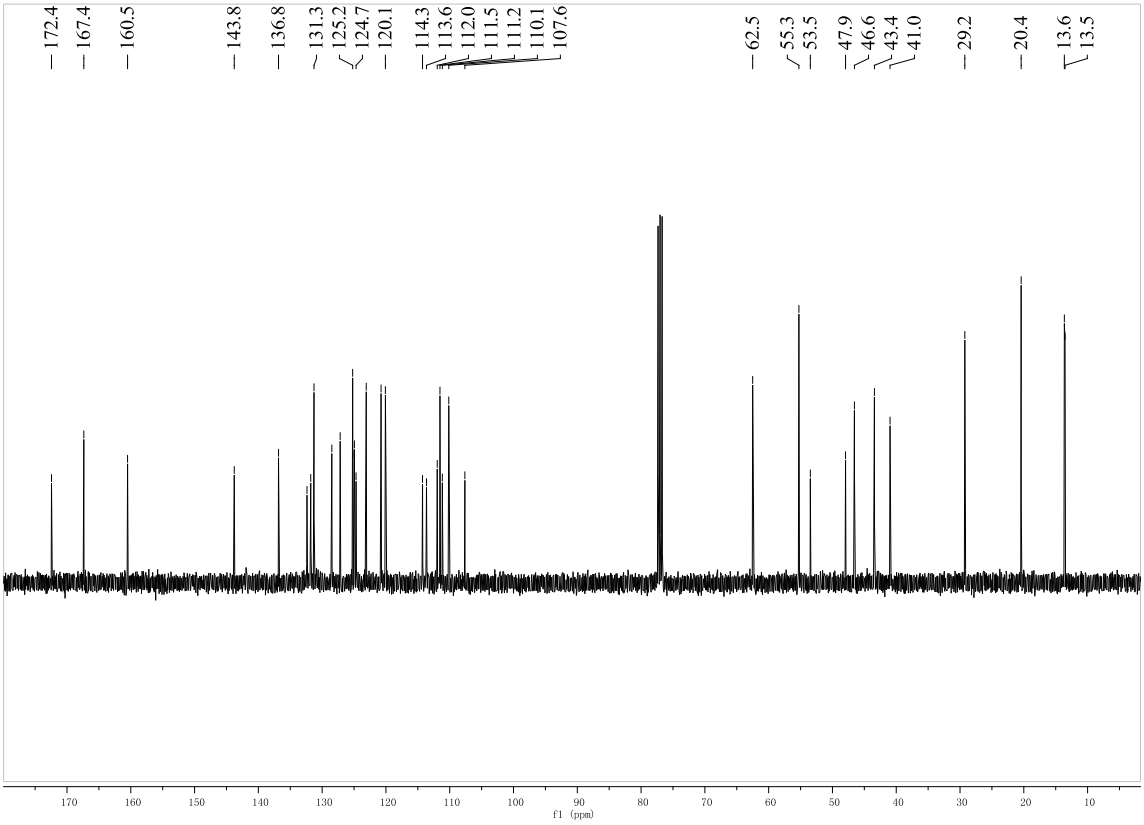


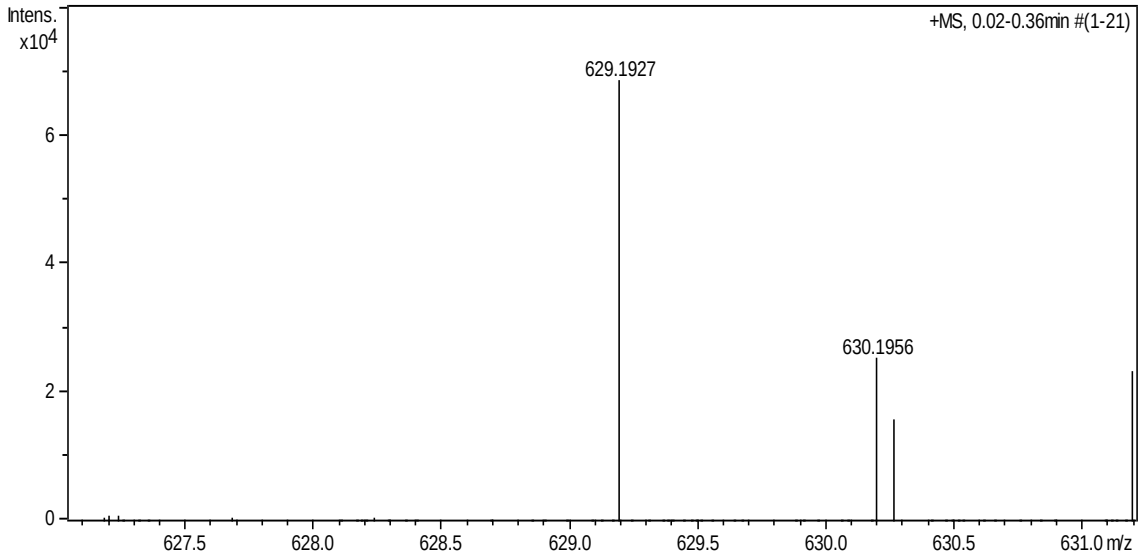




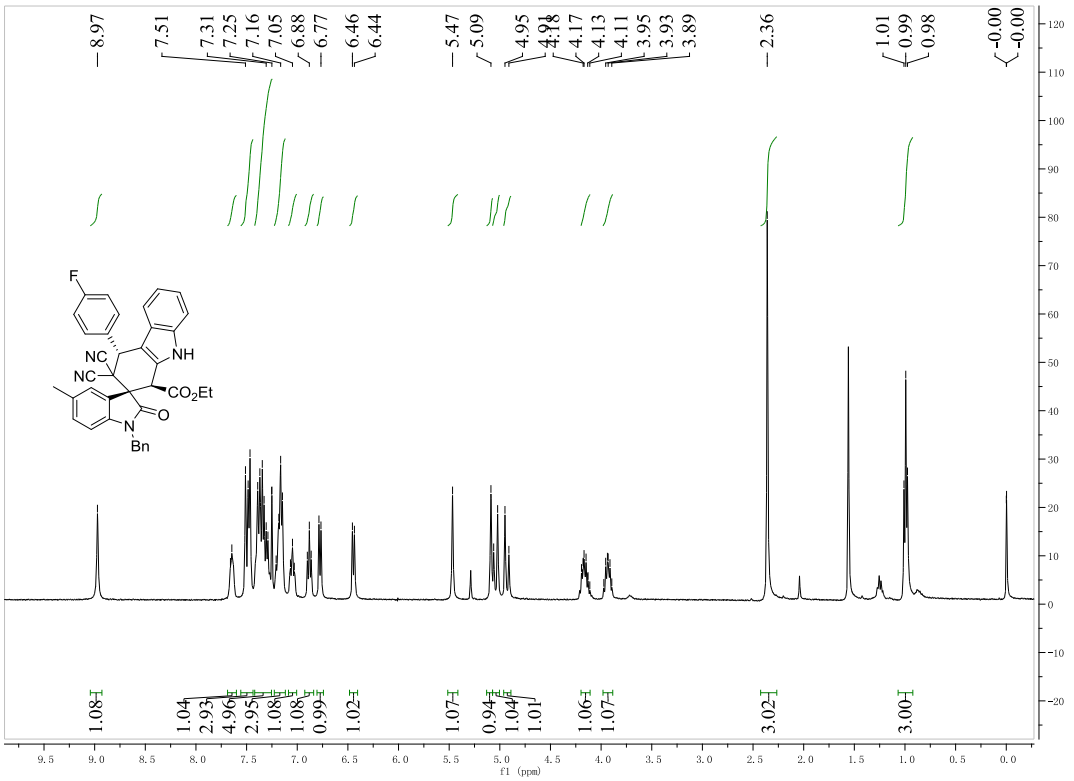
Ethyl-1'-butyl-3,3-dicyano-4-(4-methoxyphenyl)-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2, 3'-indoline]-1-carboxylate (3f):

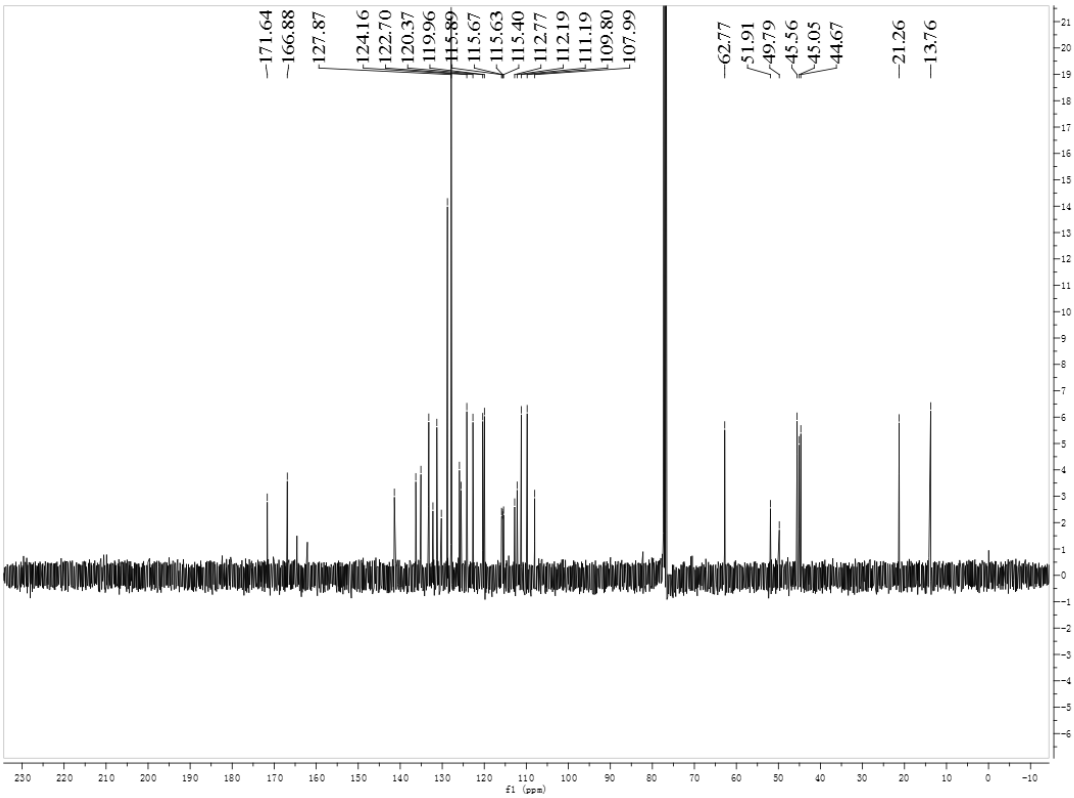


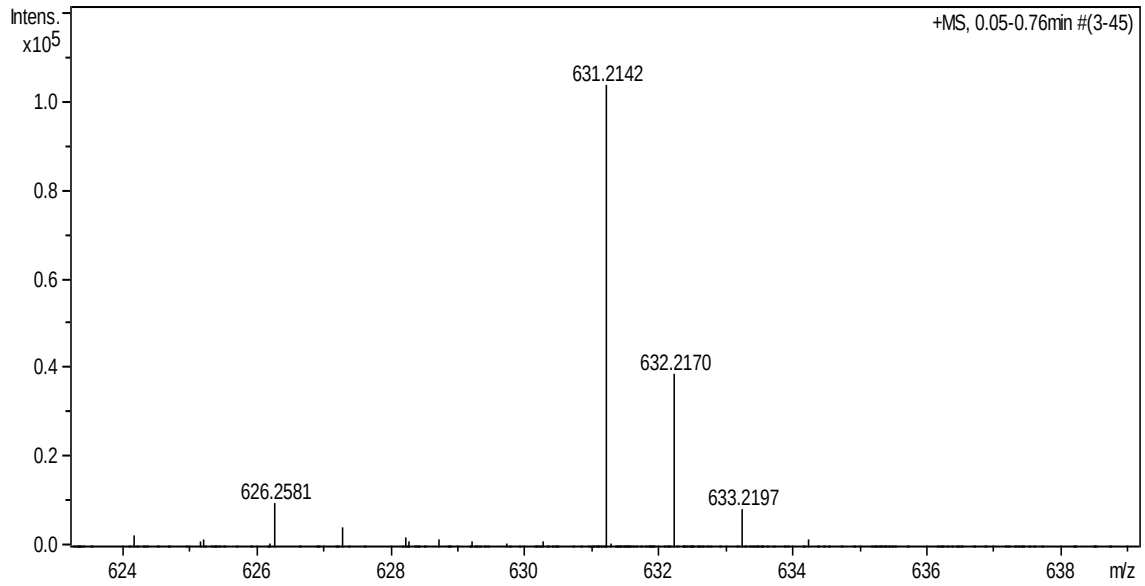

172.4
167.4
160.5
143.8
136.8
131.3
125.2
124.7
120.1
114.3
113.6
112.0
111.5
111.2
110.1
107.6
62.5
55.3
53.5
47.9
46.6
43.4
41.0
29.2
20.4
13.6
13.5
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
x10^4
+MS, 0.02-0.36min #(1-21)
629.1927
630.1956
6
4
2
0
627.5 628.0 628.5 629.0 629.5 630.0 630.5 631.0 m/z

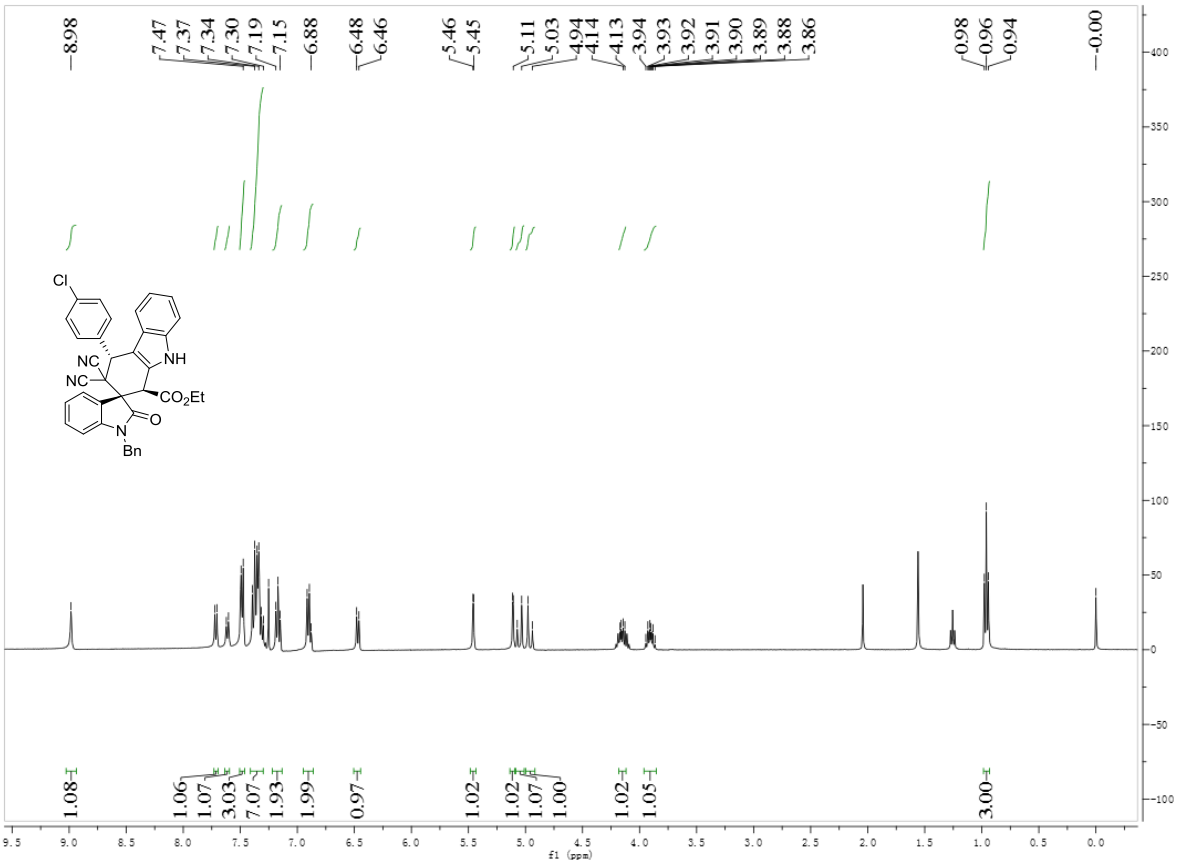
Ethyl-1'-benzyl-3,3-dicyano-4-(4-fluorophenyl)-5'-methyl-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3g):

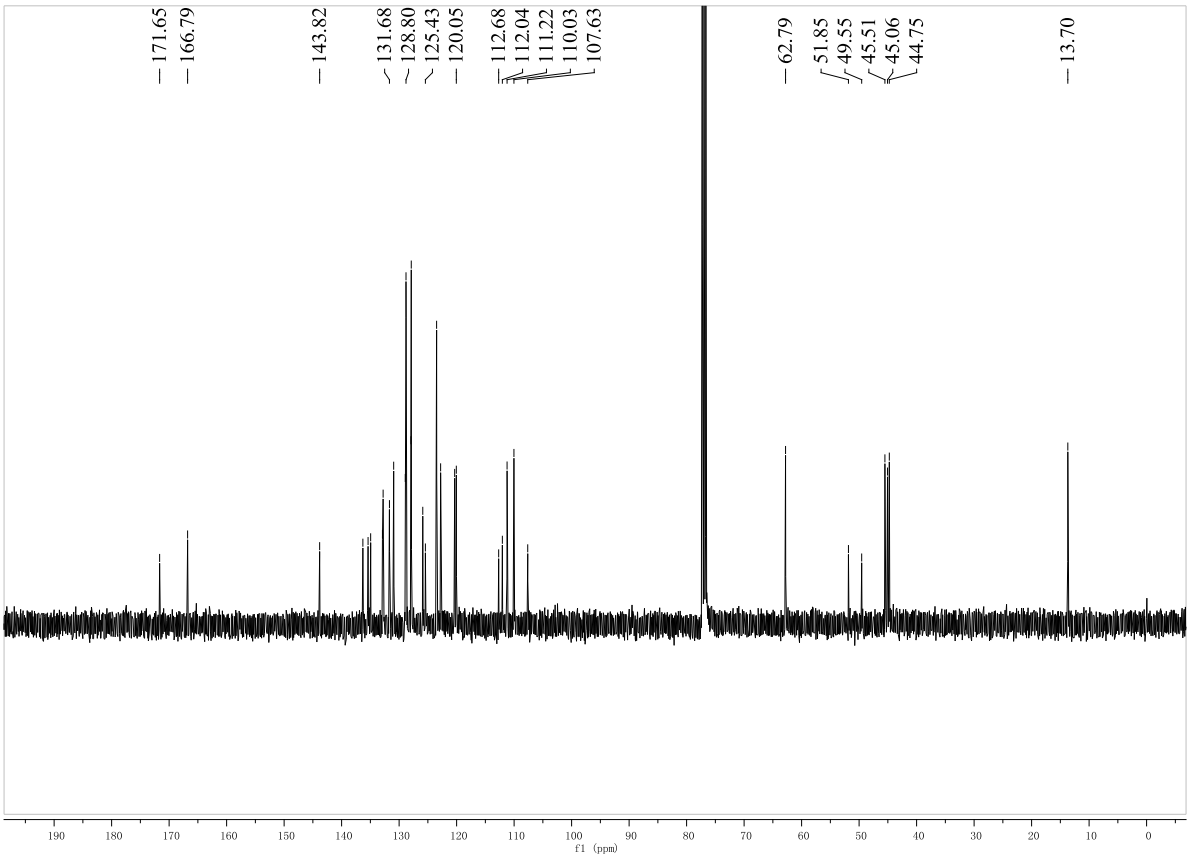


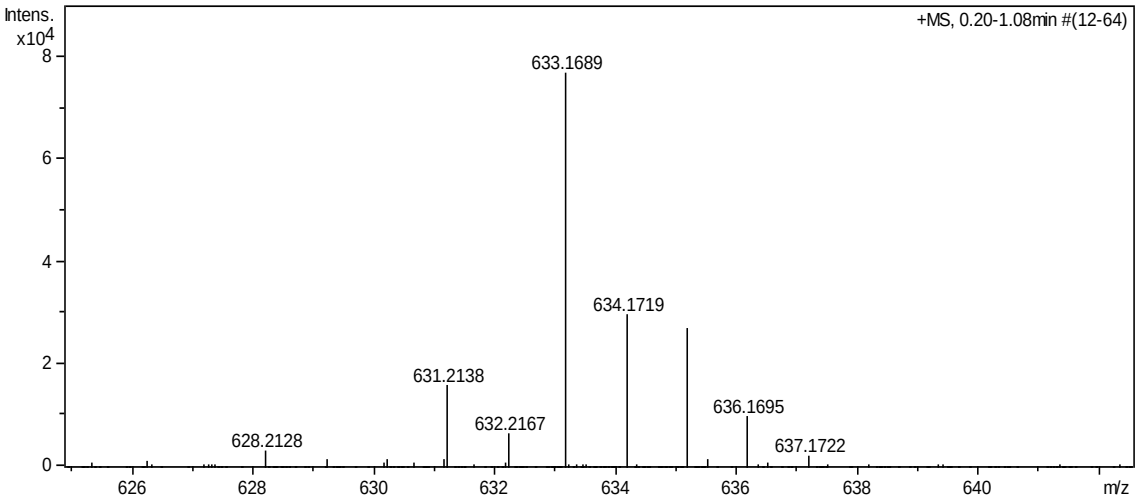




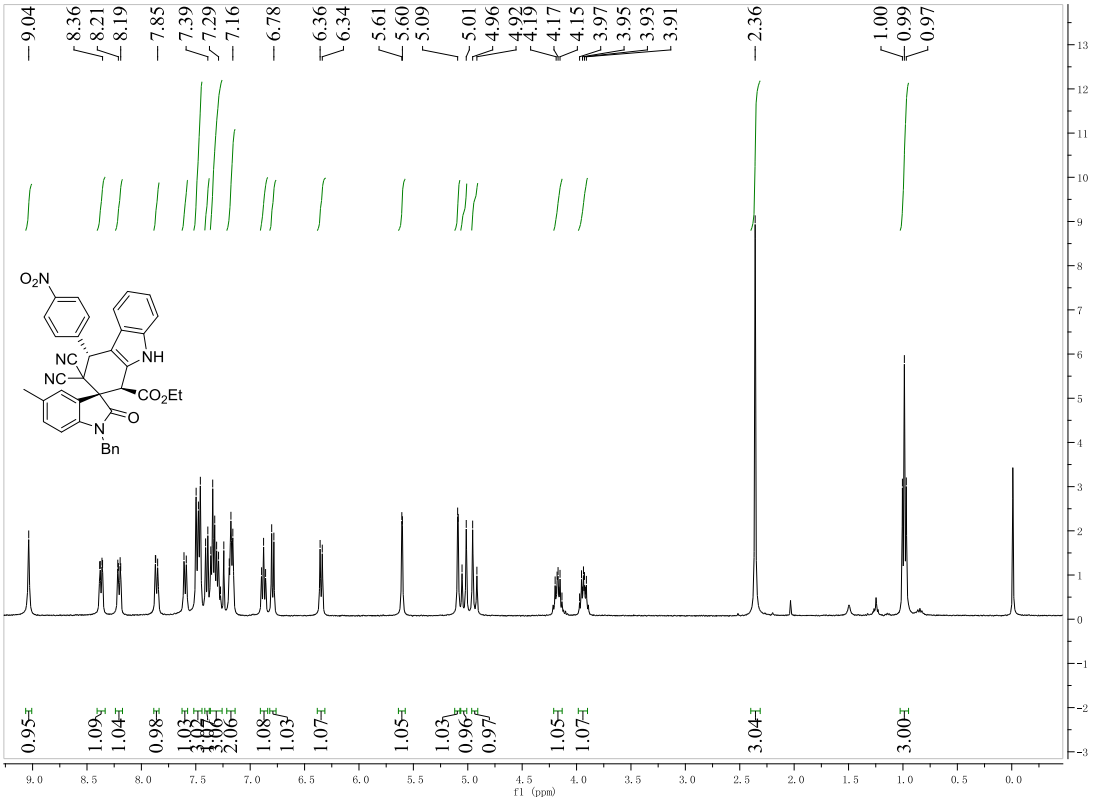
Ethyl-3-(4-methoxyphenyl)-4-(4-nitrophenyl)-1',3'-dioxo-1,1',3,3',4,9-hexahydrospiro[carbazole-2,2'-indene]-1-carboxylate (3h):

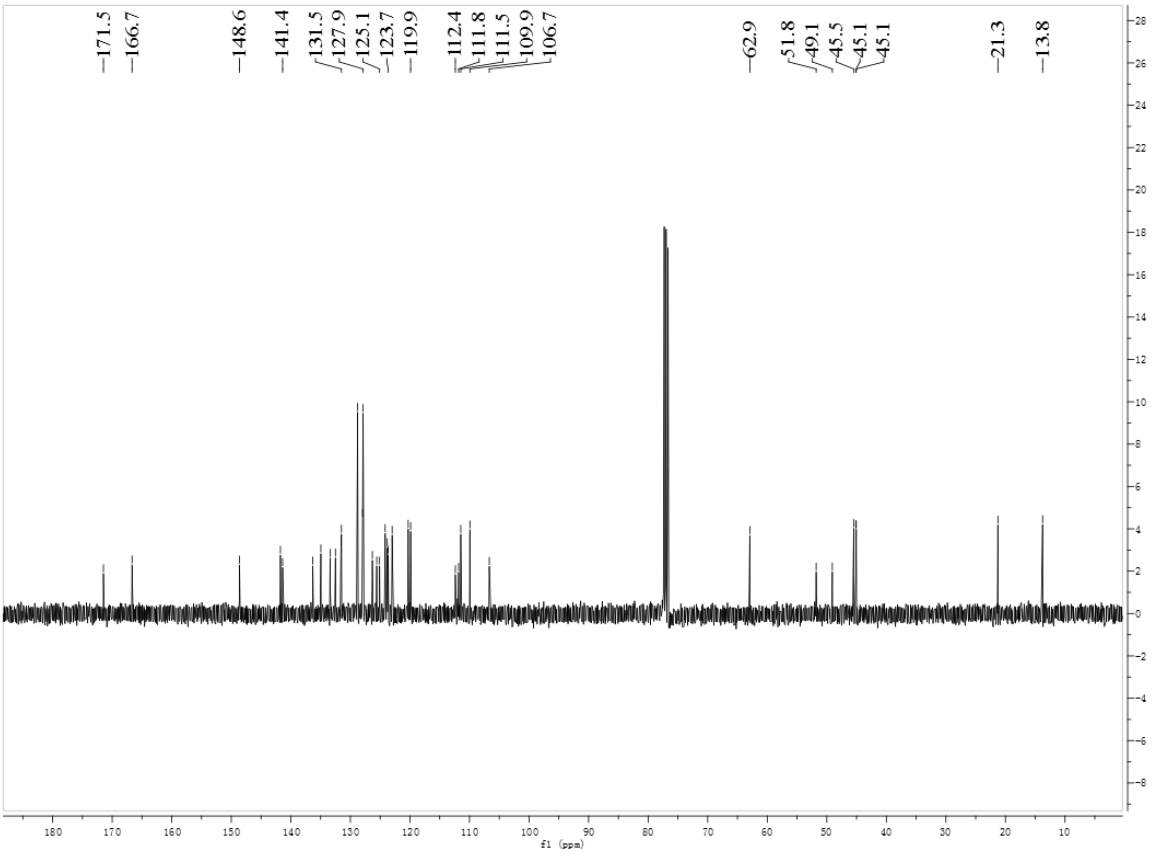


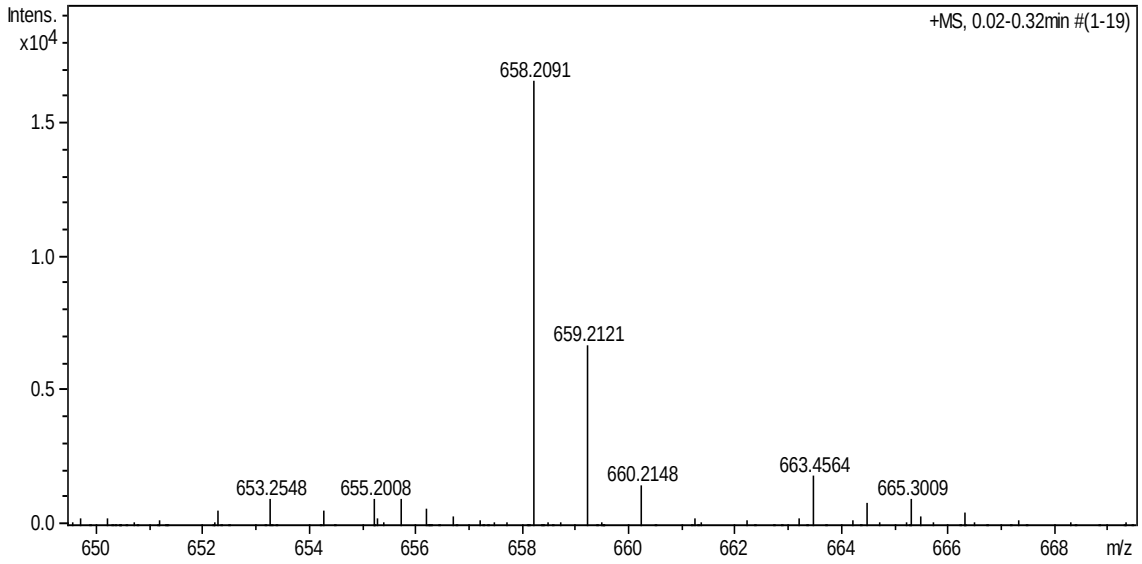

171.65
166.79
143.82
131.68
128.80
125.43
120.05
112.68
112.04
111.22
110.03
107.63
62.79
51.85
49.55
45.51
45.06
44.75
13.70
f1 (ppm)


Intens.
x10^4
+MS, 0.20-1.08min #(12-64)
633.1689
634.1719
631.2138
636.1695
632.2167
628.2128
637.1722
m/z

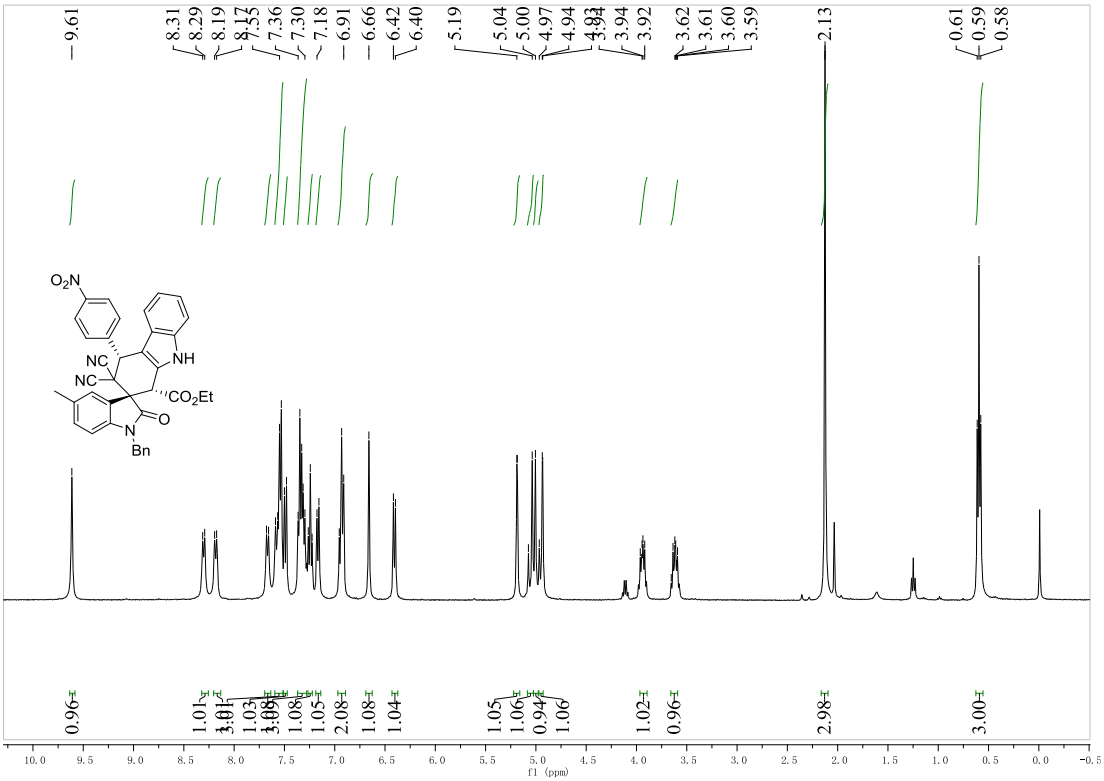
Ethyl-1'-benzyl-3,3-dicyano-5'-methyl-4-(4-nitrophenyl)-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3i):

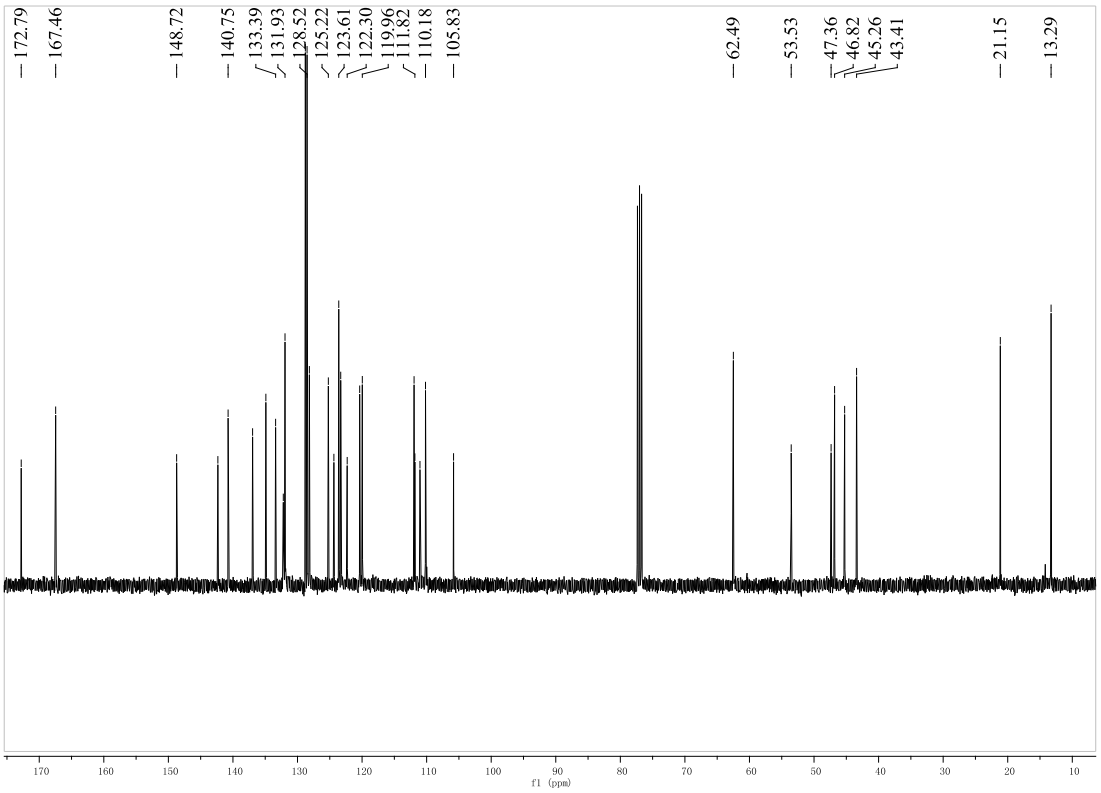


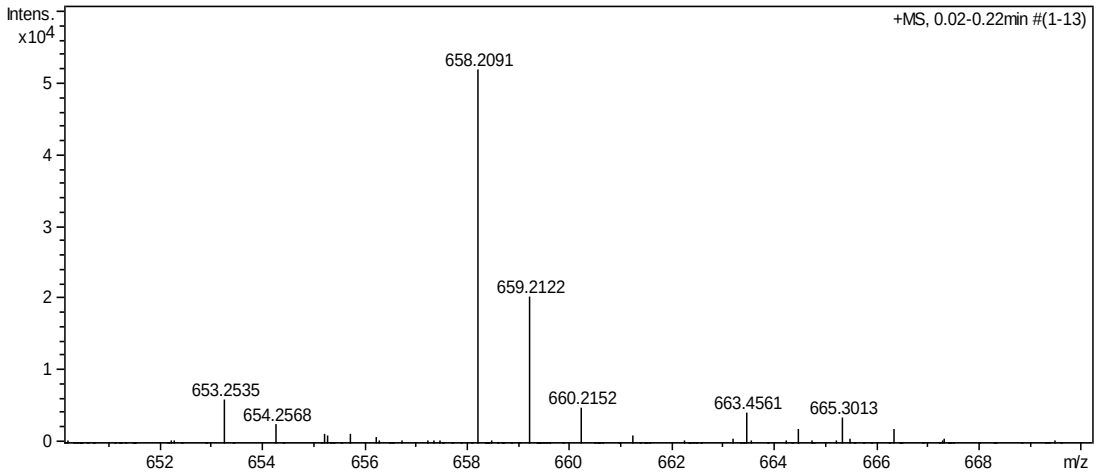




Ethyl-1'-benzyl-3,3-dicyano-5'-methyl-4-(4-nitrophenyl)-2'-oxo-1,3,4,9-tetrahydrospiro[carbazole-2,3'-indoline]-1-carboxylate (3i'):




172.79
167.46
148.72
140.75
133.39
131.93
128.52
125.22
123.61
122.30
119.96
111.82
110.18
105.83
62.49
53.53
47.36
46.82
45.26
43.41
21.15
13.29
f1 (ppm)


Intens.
x10^4
+MS, 0.02-0.22min #(1-13)
658.2091
659.2122
653.2535
654.2568
660.2152
663.4561
665.3013
m/z