



Supporting Information

for

Construction of diazepine-containing spiroindolines via annulation reaction of α -halogenated *N*-acylhydrazones and isatin-derived MBH carbonates

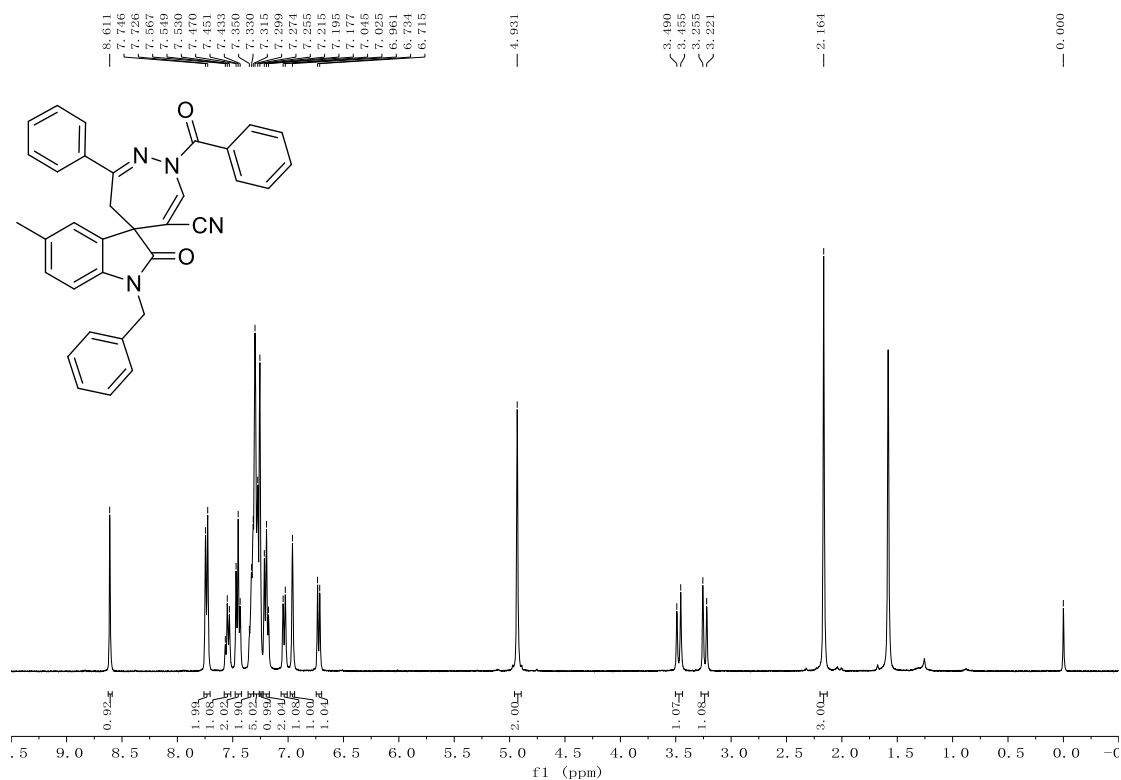
Xing Liu, Wenjing Shi, Jing Sun and Chao-Guo Yan

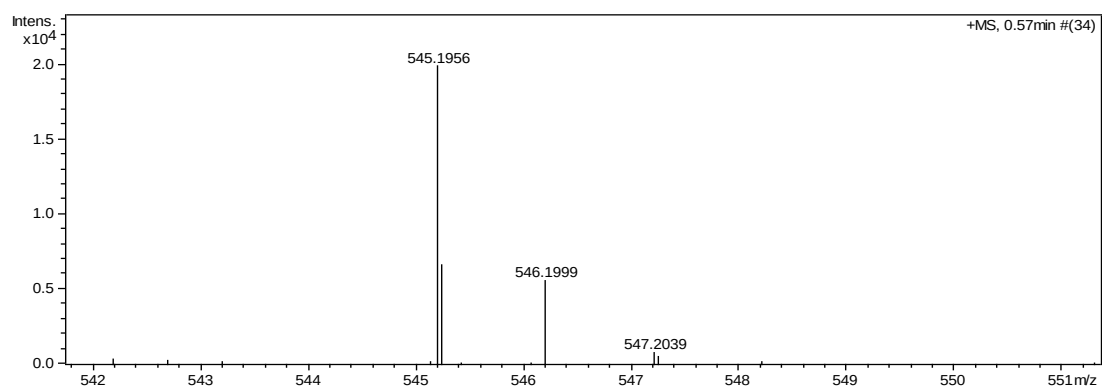
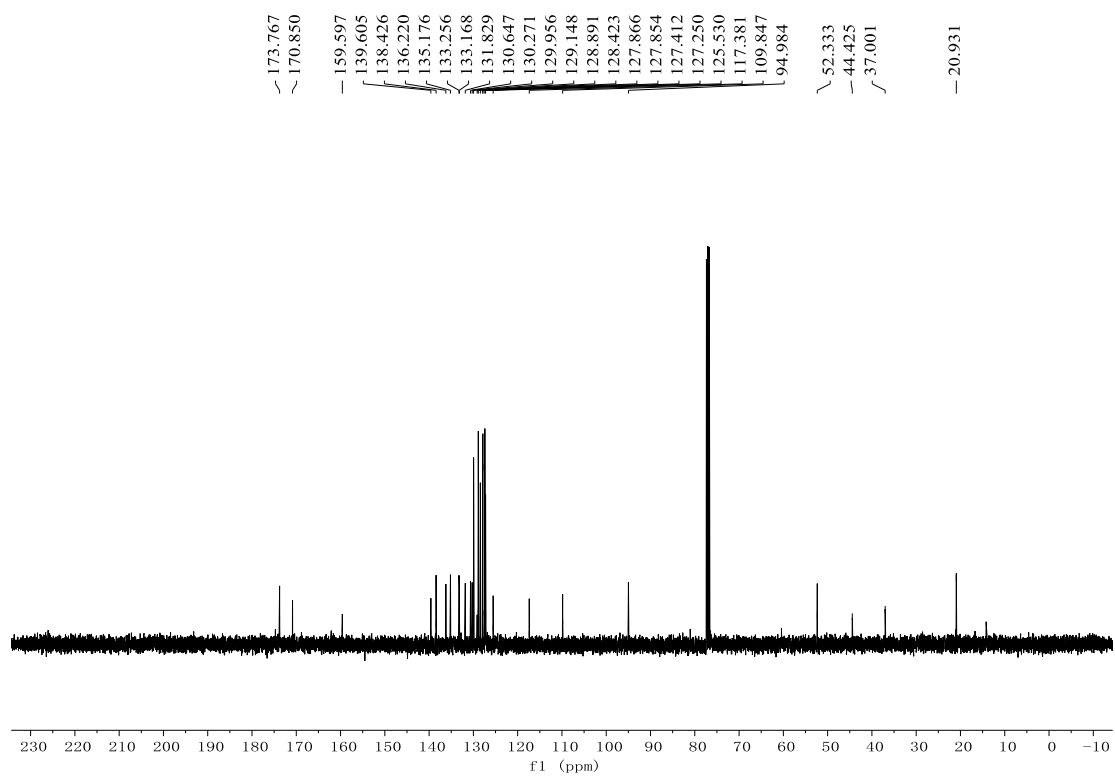
Beilstein J. Org. Chem. **2023**, *19*, 1923–1932. doi:10.3762/bjoc.19.143

Characterization data and ^1H , ^{13}C NMR, and HRMS spectra for all new compounds

1'-Benzoyl-1-benzyl-5-methyl-2-oxo-3'-phenyl-1',4'-dihydrospiro[indoline-3,5'-

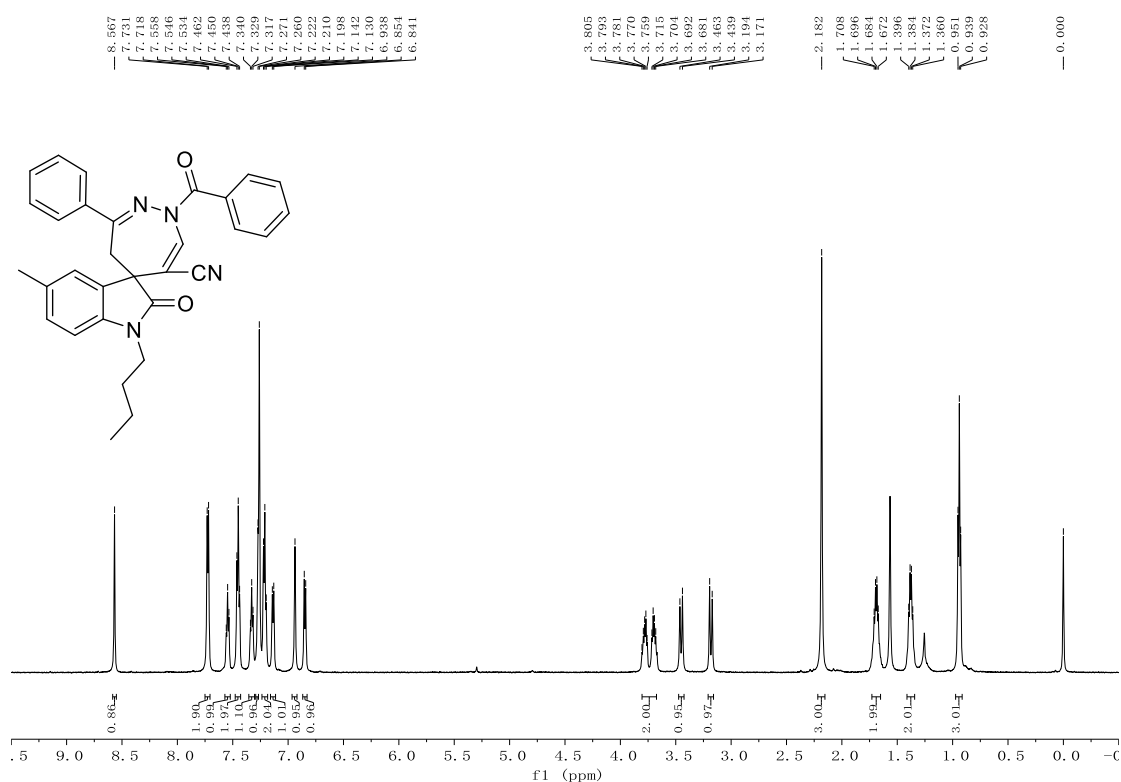
[1,2]diazepine]-6'-carbonitrile (3a): yellow solid, 0.370 g, 71%, m.p. 186-187 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.61 (s, 1H, ArH), 7.74 (d, *J* = 8.0 Hz, 2H, ArH), 7.57-7.53 (m, 1H, ArH), 7.47-7.43 (m, 2H, ArH), 7.35-7.31 (m, 2H, ArH), 7.30-7.27 (m, 5H, ArH), 7.26-7.23 (m, 1H, ArH), 7.22-7.18 (m, 2H, ArH), 7.05-7.02 (m, 1H, ArH), 6.96 (s, 1H, ArH), 6.73 (d, *J* = 8.0 Hz, 1H, ArH), 4.93 (s, 2H, CH₂), 3.47 (d, *J* = 14.0 Hz, 1H, CH), 3.24 (d, *J* = 14.0 Hz, 1H, CH), 2.16 (s, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 173.8, 170.9, 159.6, 139.6, 138.4, 136.2, 135.2, 133.3, 133.2, 131.8, 130.7, 130.3, 130.0, 129.2, 128.9, 128.4, 127.9, 127.8, 127.4, 127.3, 125.5, 117.4, 109.9, 95.0, 52.3, 44.4, 37.0, 20.9 ppm. IR (KBr) ν: 2960, 2936, 2870, 2211, 1717, 1626, 1498, 1445, 1367, 1268, 1193, 1112, 1090, 1009, 903, 868, 815 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₄H₂₆N₄O₂Na ([M+Na]⁺): 545.1956, Found: 545.1948.

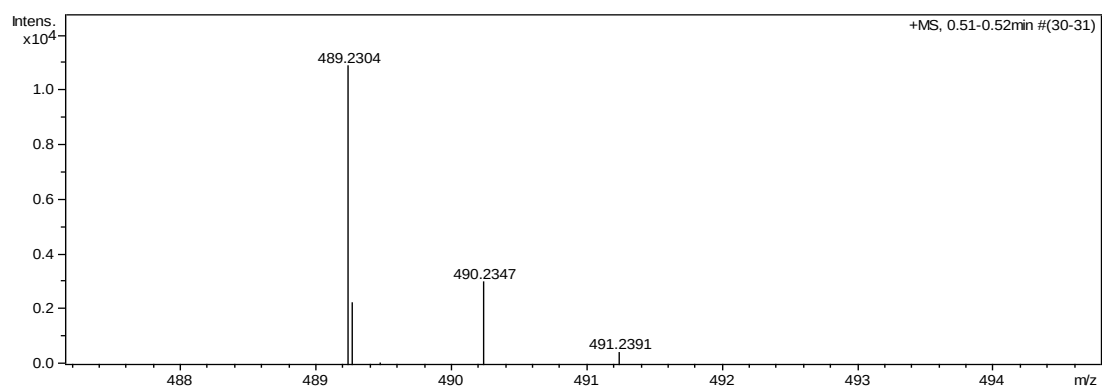
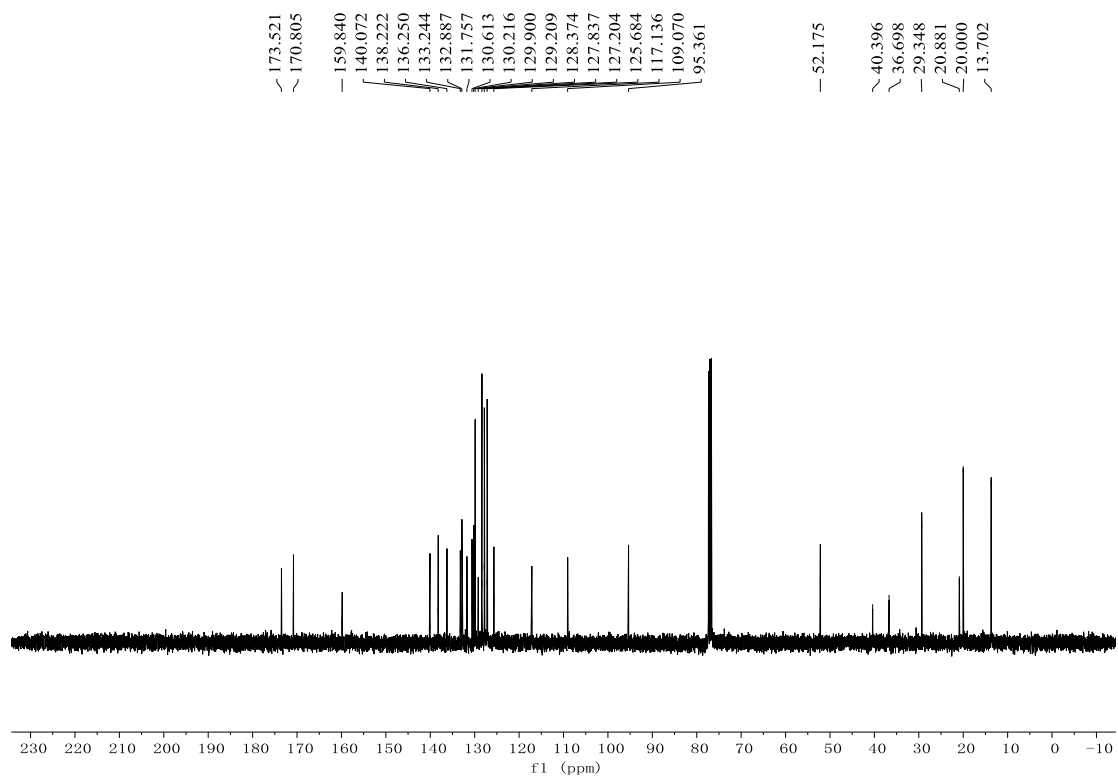




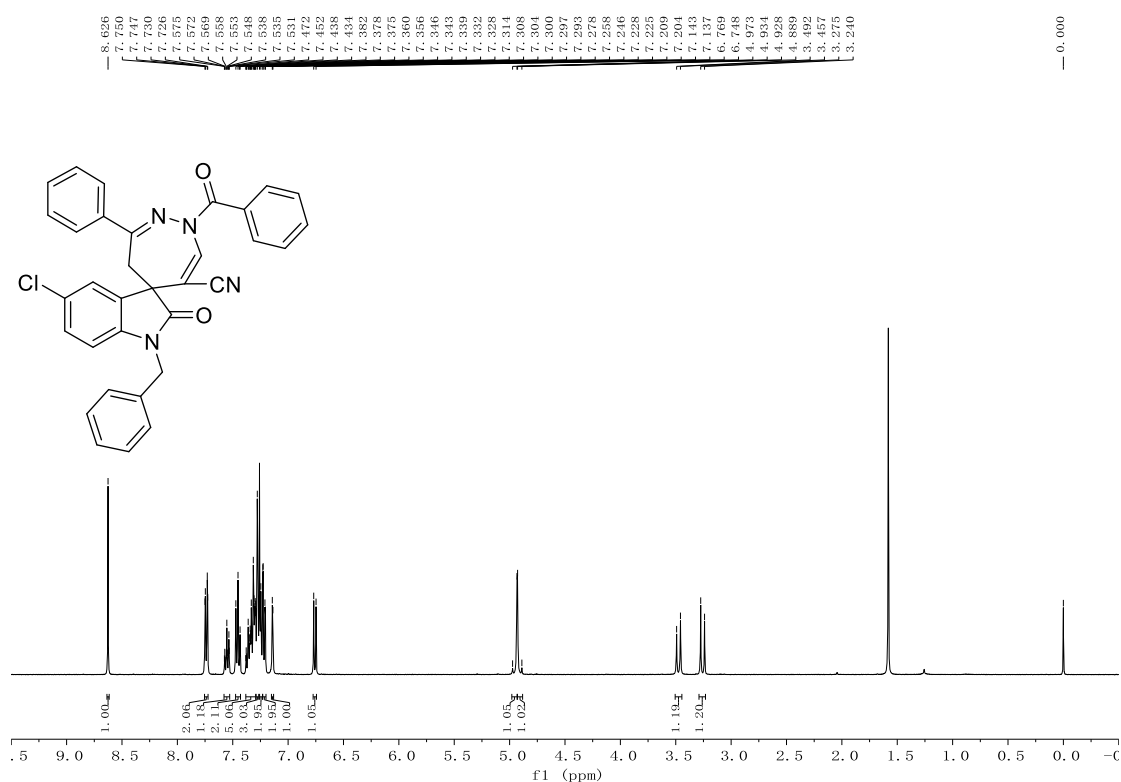
1'-Benzoyl-1-butyl-5-methyl-2-oxo-3'-phenyl-1',4'-dihydrospiro[indoline-3,5']-

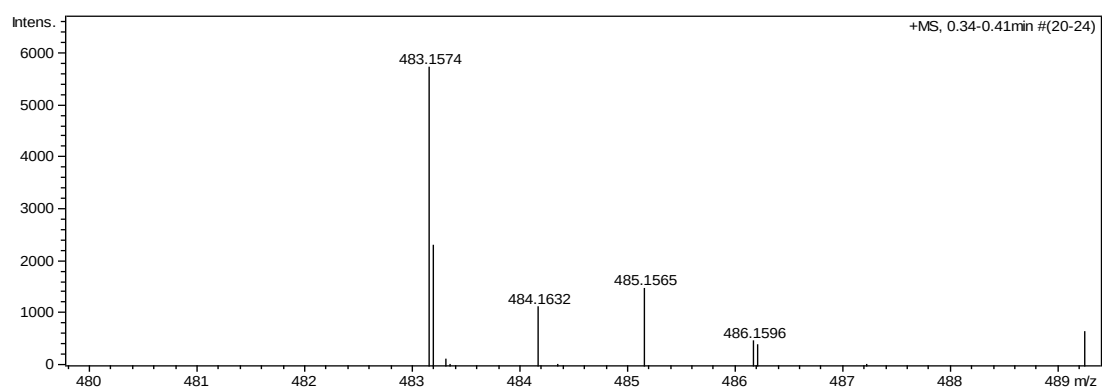
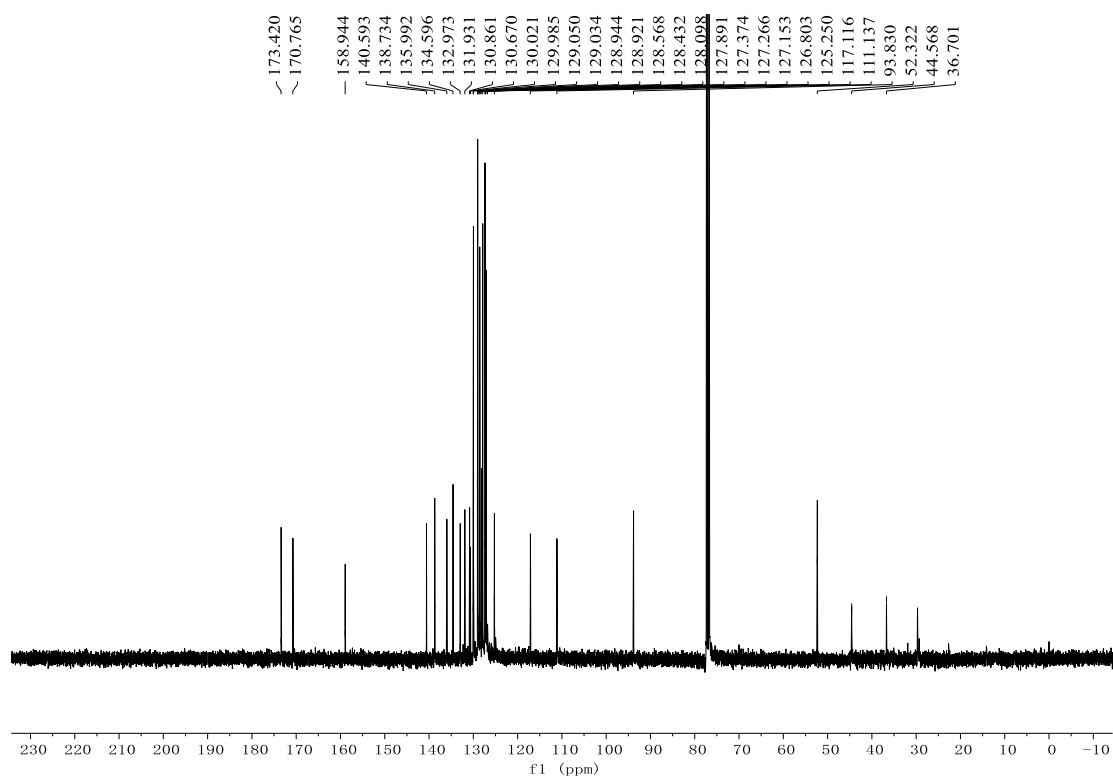
[1,2]diazepine]-6'-carbonitrile (3b): yellow solid, 0.345 g, 74%, m.p. 191-193 °C; ¹H NMR (600 MHz, CDCl₃) δ: 8.57 (s, 1H, ArH), 7.73 (d, *J* = 7.8 Hz, 2H, ArH), 7.55 (t, *J* = 7.2 Hz, 1H, ArH), 7.45 (t, *J* = 7.2 Hz, 2H, ArH), 7.34-7.32 (m, 1H, ArH), 7.27 (m, 1H, ArH), 7.21 (t, *J* = 7.2 Hz, 2H, ArH), 7.14 (d, *J* = 7.2 Hz, 1H, ArH), 6.94 (s, 1H, ArH), 6.85 (d, *J* = 7.8 Hz, 1H, ArH), 3.81-3.68 (m, 2H, CH₂), 3.45 (d, *J* = 14.4 Hz, 1H, CH), 3.18 (d, *J* = 13.8 Hz, 1H, CH), 2.18 (s, 3H, CH₃), 1.71-1.67 (m, 2H, CH₂), 1.40-1.36 (m, 2H, CH₂), 0.94 (t, *J* = 7.2 Hz, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 173.5, 170.8, 159.8, 140.1, 138.2, 136.3, 133.2, 132.9, 131.8, 130.6, 130.2, 129.9, 129.2, 128.4, 127.8, 127.2, 125.7, 117.1, 109.1, 95.4, 52.2, 40.4, 36.7, 29.4, 20.9, 20.0, 13.7 ppm; IR (KBr) ν: 2917, 1752, 1735, 1719, 1654, 1577, 1561, 1495, 1114, 957, 902, 855, 816 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₁H₂₉N₄O₂ ([M+H]⁺): 489.2285, Found: 489.2304.



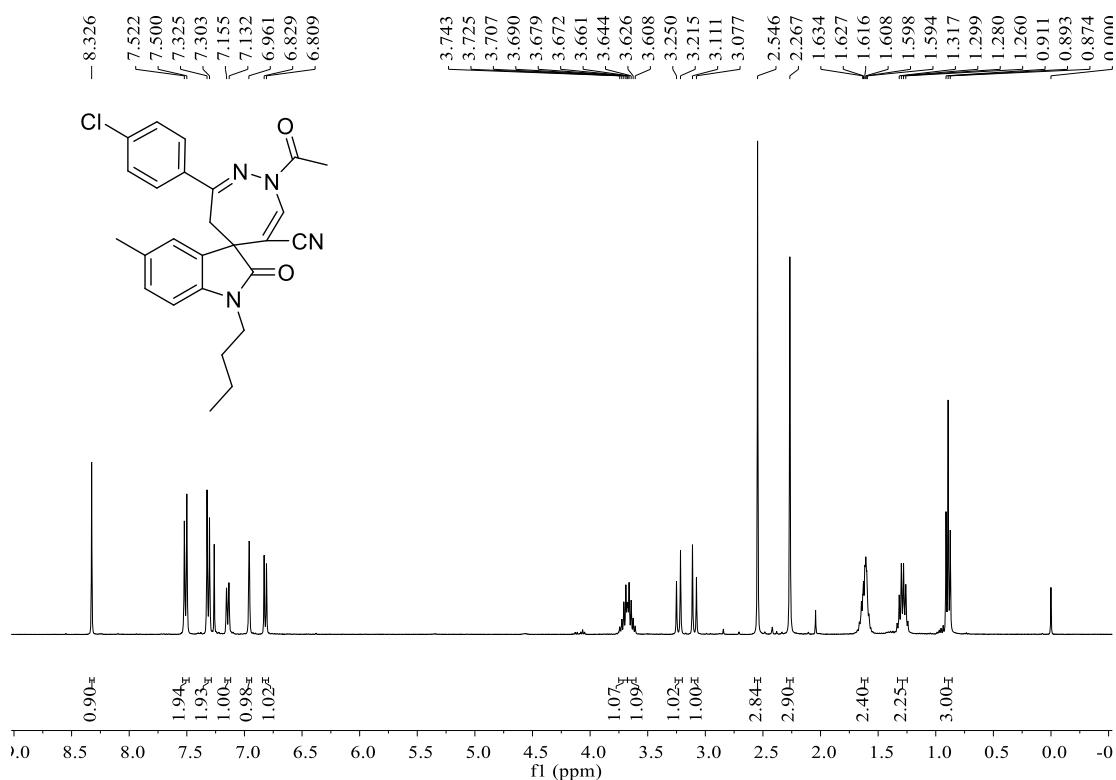


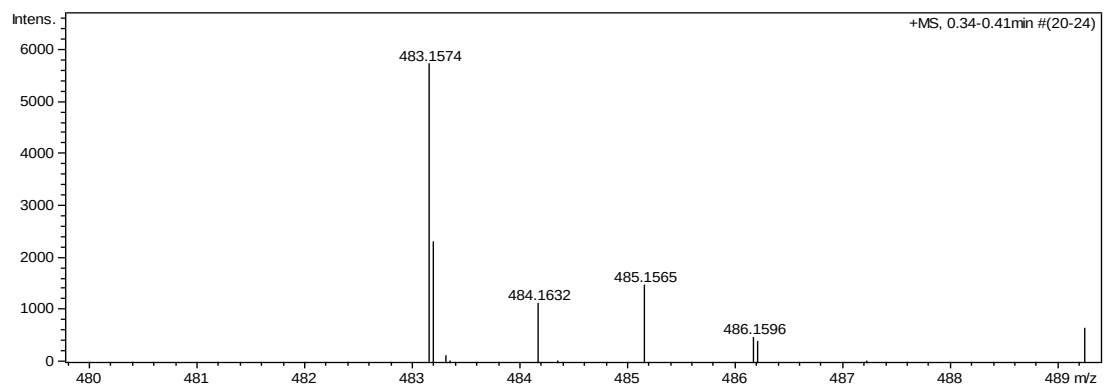
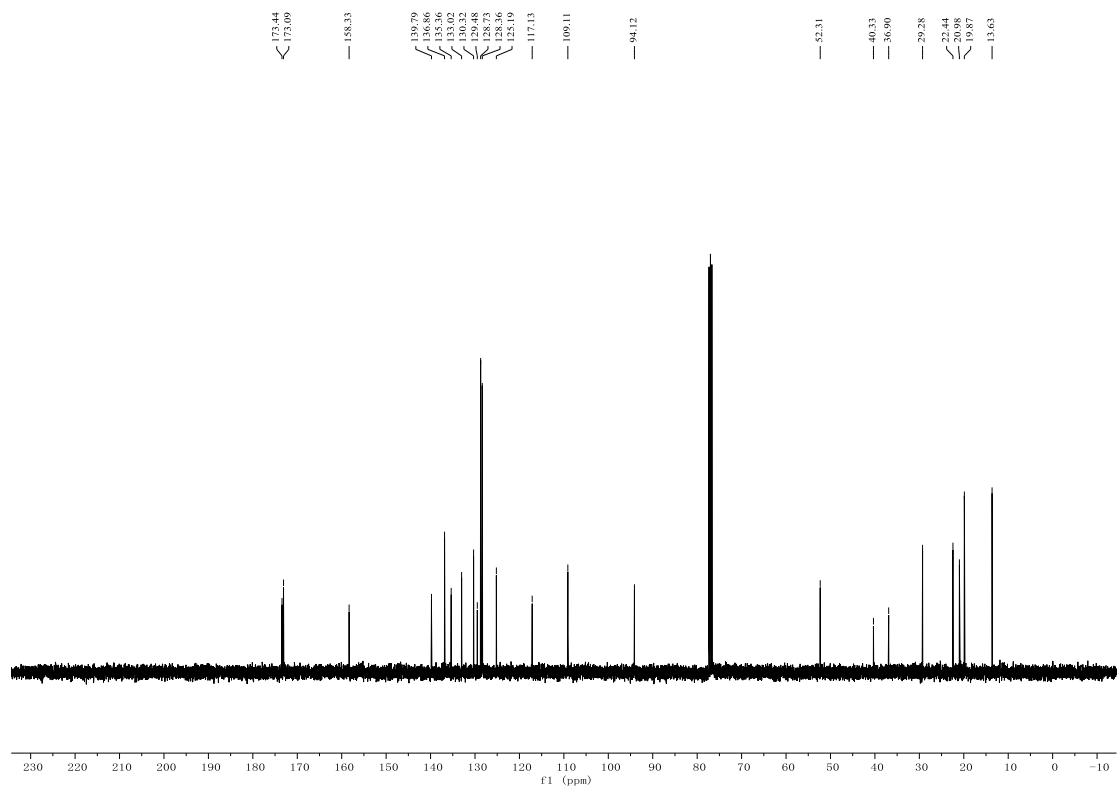
[1,2]diazepine]-6'-carbonitrile (3c): yellow solid, 0.317 g, 69%, m.p. 195-196 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.63 (s, 1H, ArH), 7.75-7.73 (m, 2H, ArH), 7.57-7.53 (m, 1H, ArH), 7.47-7.43 (m, 2H, ArH), 7.38-7.29 (m, 5H, ArH), 7.28-7.27 (m, 3H, ArH), 7.25-7.24 (m, 2H, ArH), 7.21-7.20 (m, 2H, ArH), 7.14 (d, *J* = 2.4 Hz, 1H, ArH), 6.76 (d, *J* = 8.4 Hz, 1H, ArH), 4.95 (d, *J* = 15.6 Hz, 1H, CH), 4.91 (d, *J* = 15.6 Hz, 1H, CH), 3.47 (d, *J* = 13.6 Hz, 1H, CH), 3.26 (d, *J* = 13.6 Hz, 1H, CH) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 173.4, 170.7, 158.9, 140.6, 138.7, 136.0, 134.6, 133.0, 131.9, 130.9, 130.7, 130.0, 130.0, 129.1, 129.0, 128.9, 128.9, 128.6, 128.4, 128.1, 127.9, 127.4, 127.3, 127.2, 126.8, 125.3, 117.1, 111.1, 93.8, 52.3, 36.7 ppm; IR (KBr) ν: 2959, 2928, 2871, 2215, 1712, 1632, 1492, 1438, 1360, 1269, 1194, 1197, 1091, 1013, 905, 863, 811 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₂₆H₂₅ClN₄O₂Na ([M+Na]⁺): 483.1574, Found: 483.1558.



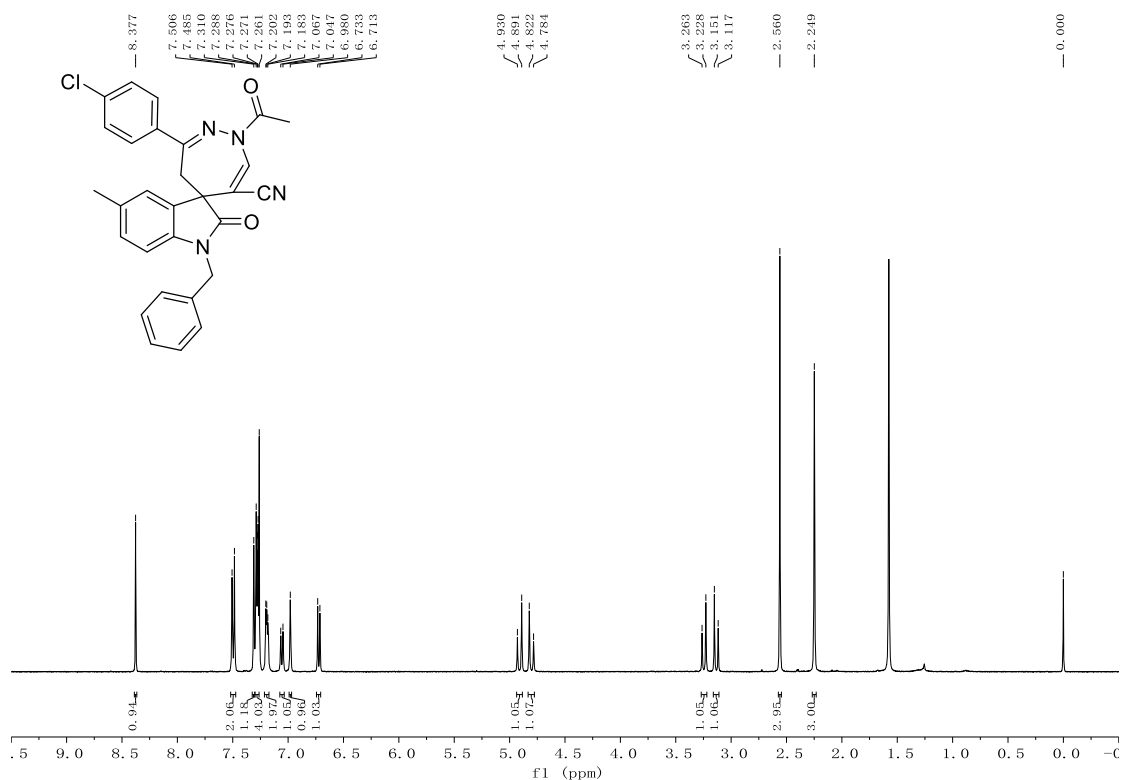


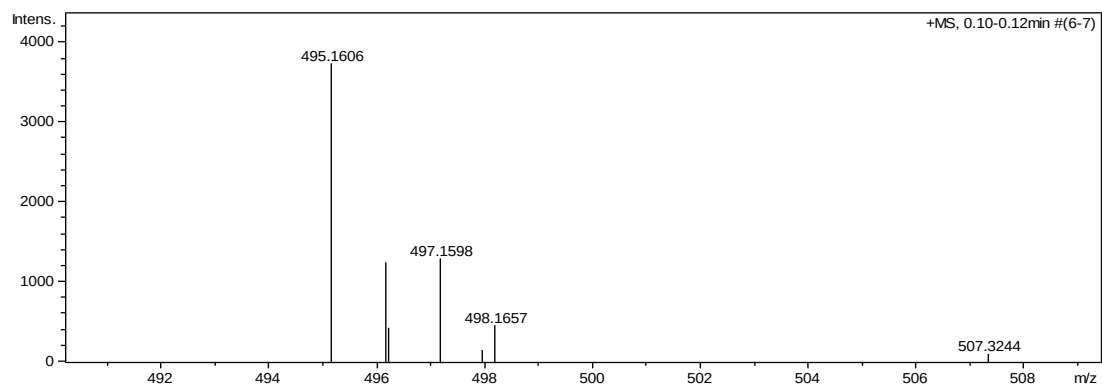
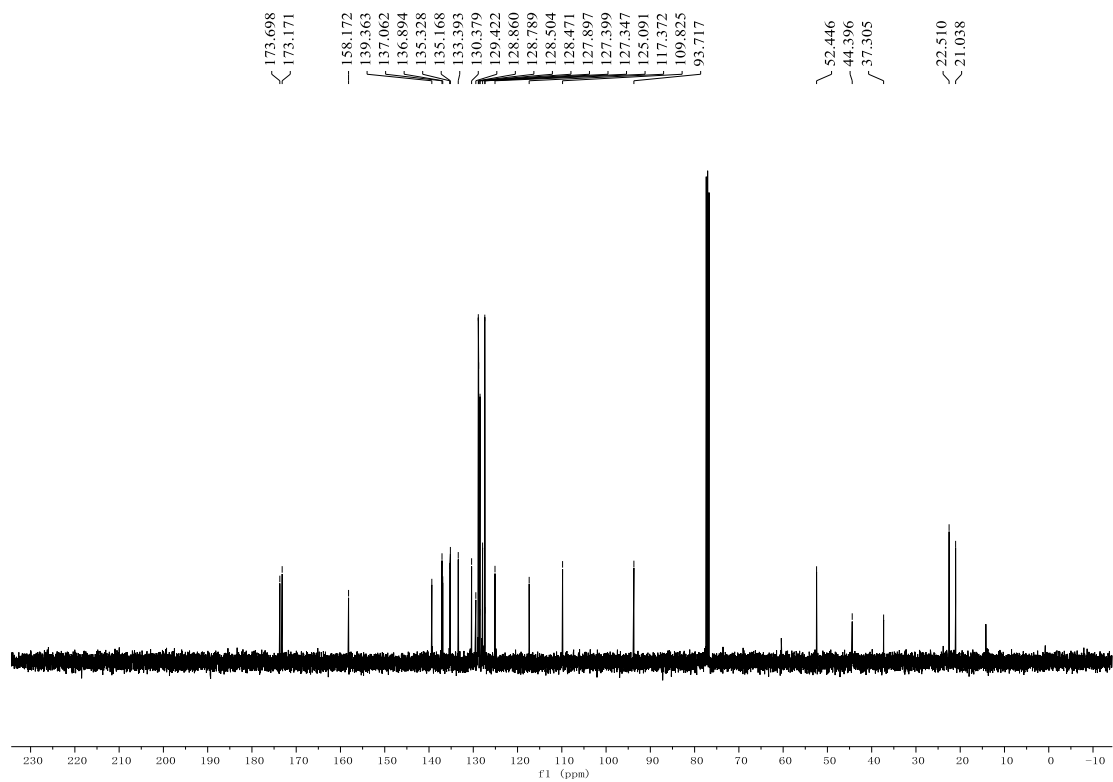
1'-Acetyl-1-butyl-3'-(4-chlorophenyl)-5-methyl-2-oxo-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carbonitrile (3d): yellow solid, 0.386 g, 84%, m.p. 132-133 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.33 (s, 1H, ArH), 7.52-7.50 (m, 2H, ArH), 7.33-7.30 (m, 2H, ArH), 7.16-7.13 (m, 1H, ArH), 6.96 (s, 1H, ArH), 6.83-6.81 (m, 1H, ArH), 3.74-3.68 (m, 1H, CH), 3.67-3.61 (m, 1H, CH), 3.23 (d, *J* = 14.0 Hz, 1H, CH), 3.09 (d, *J* = 13.6 Hz, 1H, CH), 2.55 (s, 3H, CH₃), 2.27 (s, 3H, CH₃), 1.65-1.59 (m, 2H, CH₂), 1.32-1.26 (m, 2H, CH₂), 0.91-0.87 (m, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 173.4, 173.1, 158.3, 139.8, 136.9, 135.4, 133.0, 130.3, 129.5, 128.7, 128.4, 125.2, 117.1, 109.1, 94.1, 52.3, 40.3, 36.9, 29.3, 22.4, 21.0, 19.9, 13.6 ppm; IR (KBr) ν: 2959, 2932, 2872, 2215, 1716, 1626, 1495, 1443, 1364, 1268, 1197, 1111, 1093, 1012, 900, 867, 812 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₂₆H₂₅ClN₄O₂Na ([M+Na]⁺): 483.1558, Found: 483.1574.





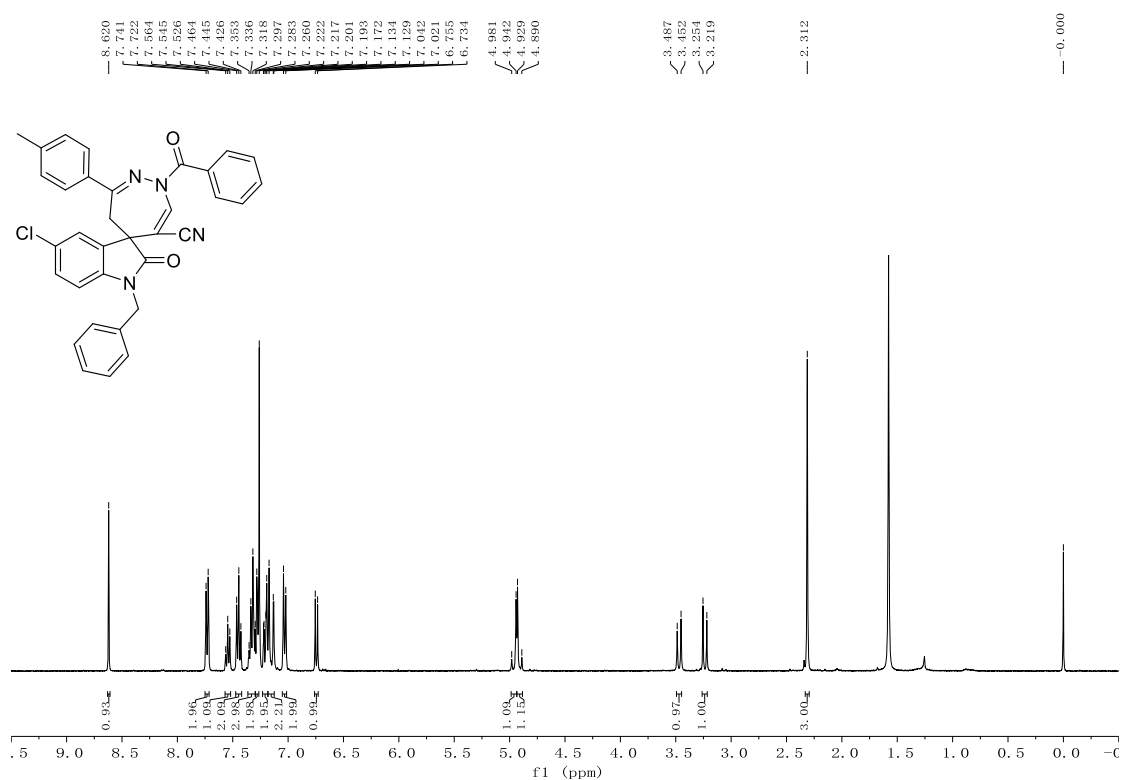
1'-Acetyl-1-benzyl-3'-(4-chlorophenyl)-5-methyl-2-oxo-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carbonitrile (3e): yellow solid, 0.400 g, 81%, m.p. 174-175 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.38 (s, 1H, ArH), 7.50 (d, *J* = 8.4 Hz, 2H, ArH), 7.31 (s, 1H, ArH), 7.30-7.26 (m, 4H, ArH), 7.21-7.18 (m, 2H, ArH), 7.06 (d, *J* = 8.0 Hz, 1H, ArH), 6.98 (s, 1H, ArH), 6.72 (d, *J* = 8.0 Hz, 1H, ArH), 4.92 (d, *J* = 15.6 Hz, 1H, CH), 4.80 (d, *J* = 15.6 Hz, 1H, CH), 3.24 (d, *J* = 14.8 Hz, 1H, CH), 3.13 (d, *J* = 14.4 Hz, 1H, CH), 2.56 (s, 3H, CH₃), 2.25 (s, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 173.7, 173.2, 158.2, 139.4, 137.1, 136.9, 135.3, 135.2, 133.4, 130.4, 129.4, 128.9, 128.8, 128.5, 128.4, 127.9, 127.4, 127.3, 125.1, 117.4, 109.8, 93.7, 52.5, 44.4, 37.3, 22.5, 21.0 ppm; IR (KBr) ν: 2923, 2853, 1716, 1666, 1602, 1496, 1456, 1364, 1268, 1170, 1093, 809 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₂₉H₂₅ClN₄O₂Na ([M+H]⁺): 495.1606, Found: 495.1582.

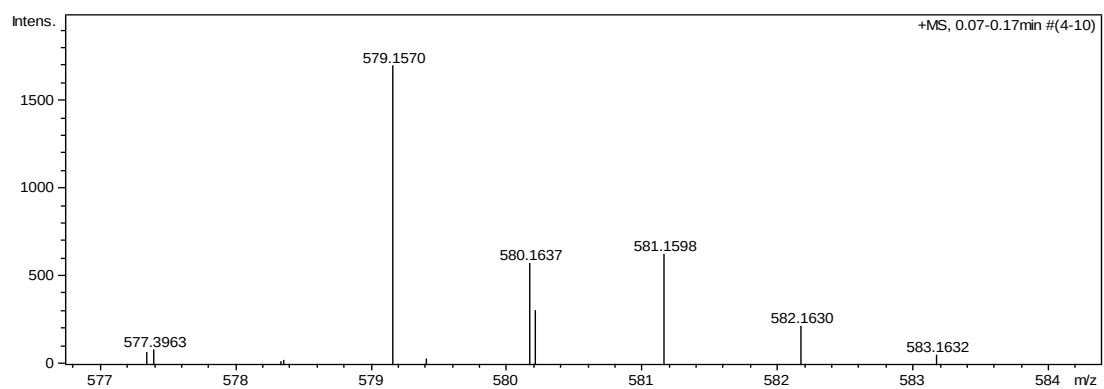
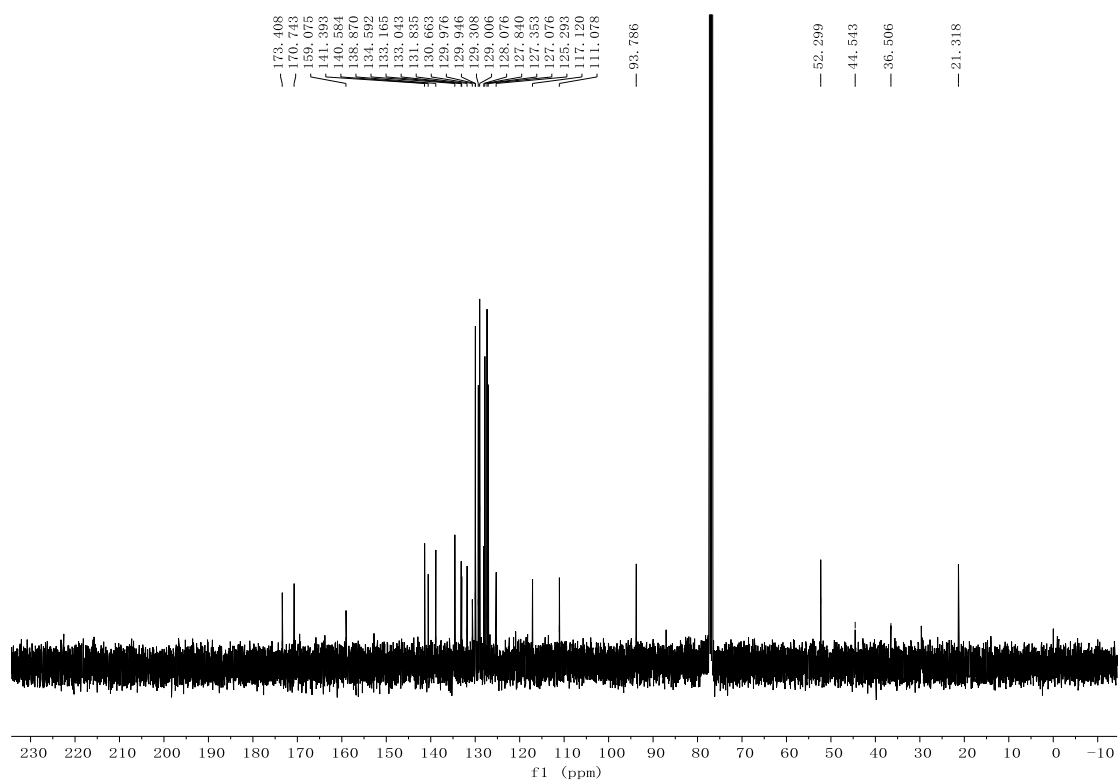




1'-Benzoyl-1-benzyl-5-chloro-2-oxo-3'-(p-tolyl)-1',4'-dihydrospiro[indoline-3,5']-

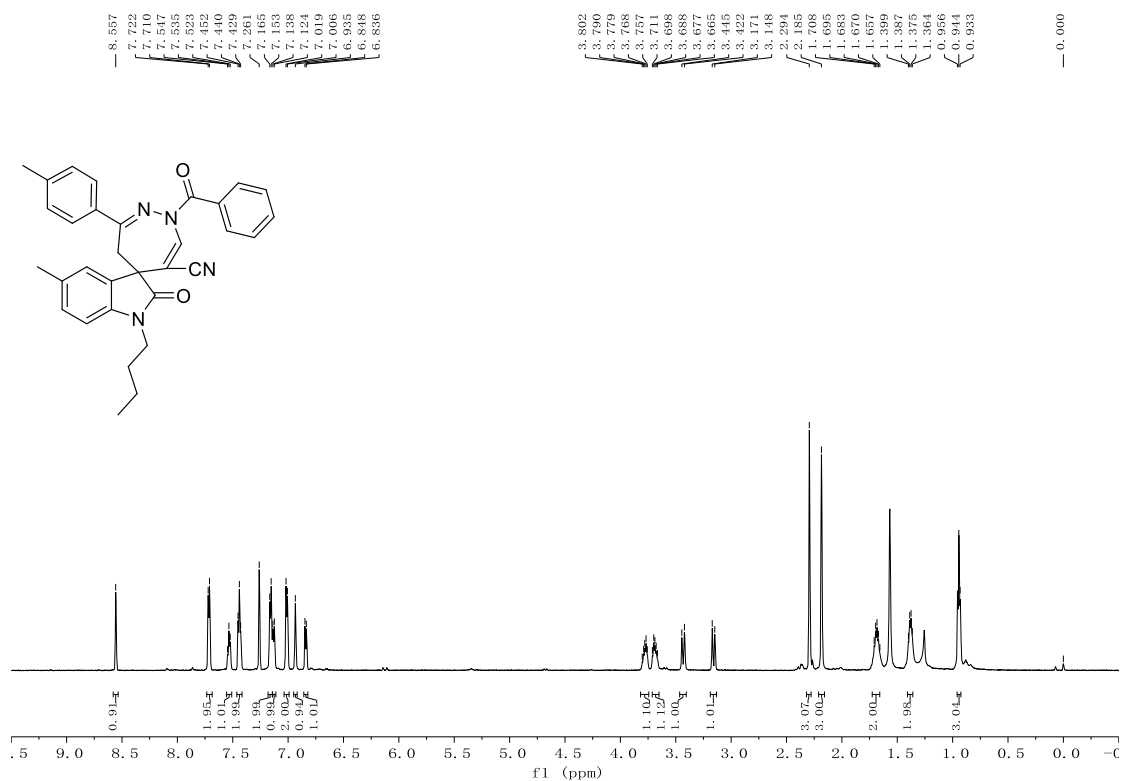
[1,2]diazepine]-6'-carbonitrile (3f): yellow solid, 0.372 g, 67%, m.p. 213-214 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.62 (s, 1H, ArH), 7.74-7.72 (m, 2H, ArH), 7.56-7.53 (m, 1H, ArH), 7.46-7.43 (m, 2H, ArH), 7.35-7.30 (m, 3H, ArH), 7.28-7.26 (m, 2H, ArH), 7.22-7.19 (m, 2H, ArH), 7.17-7.13 (m, 3H, ArH), 7.04-7.02 (d, $J = 8.4$ Hz, 2H, ArH), 6.74 (m, $J = 8.4$ Hz, 1H, ArH), 4.96 (d, $J = 15.6$ Hz, 1H, CH), 4.91 (d, $J = 15.2$ Hz, 1H, CH), 3.47 (d, $J = 14.0$ Hz, 1H, CH), 3.23 (d, $J = 14.0$ Hz, 1H, CH), 2.31 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 173.4, 170.7, 159.1, 141.4, 140.6, 138.9, 134.6, 133.2, 133.0, 131.8, 130.7, 130.0, 130.0, 129.3, 129.0, 128.1, 127.8, 127.4, 127.1, 125.3, 117.1, 111.1, 93.8, 52.3, 36.5, 21.3 ppm; IR (KBr) ν : 2943, 2879, 2197, 1867, 1791, 1698, 1568, 1488, 1374, 1339, 1280, 1171, 968, 902, 846, 809 cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{34}\text{H}_{25}\text{ClN}_4\text{O}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$): 579.1570, Found: 579.1558.

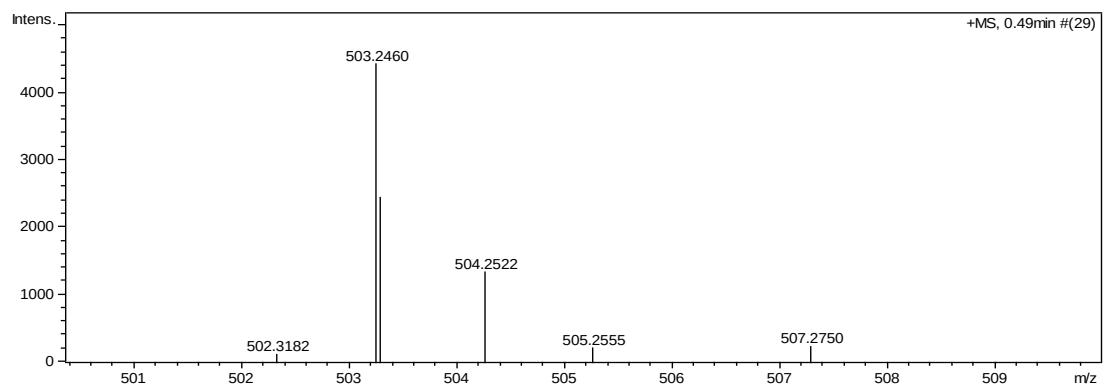
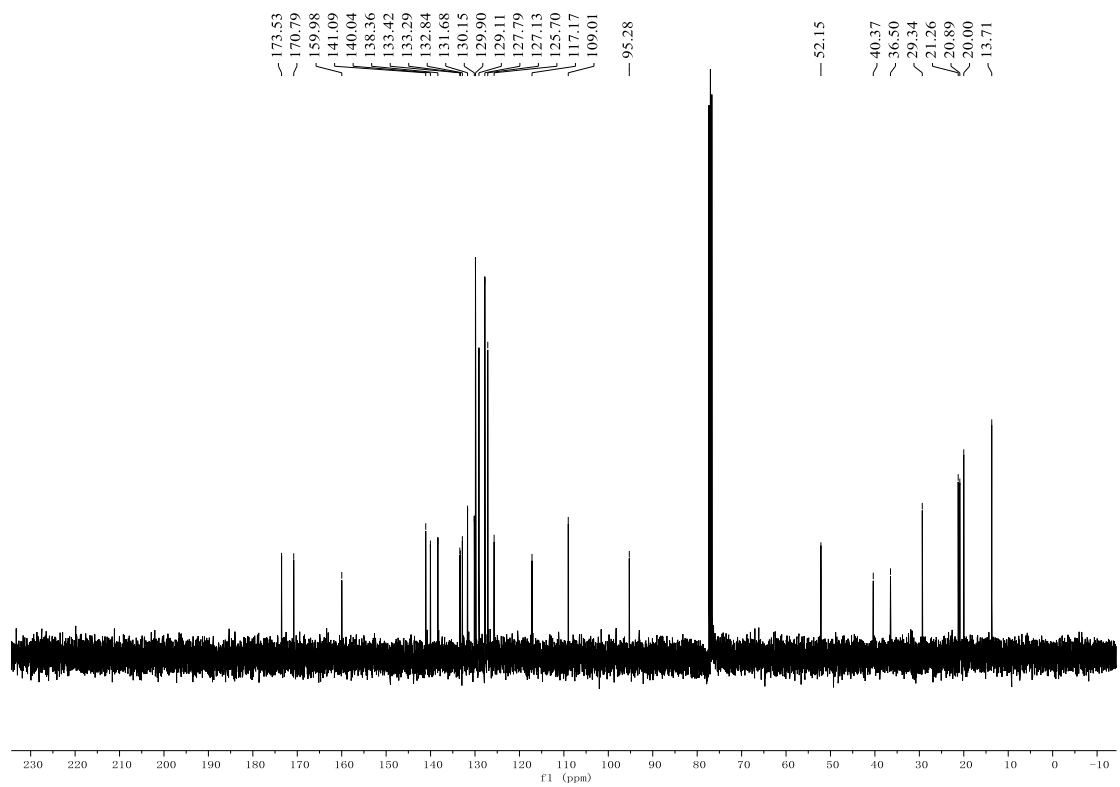




1'-Benzoyl-1-butyl-5-methyl-2-oxo-3'-(p-tolyl)-1',4'-dihydrospiro[indoline-3,5'-

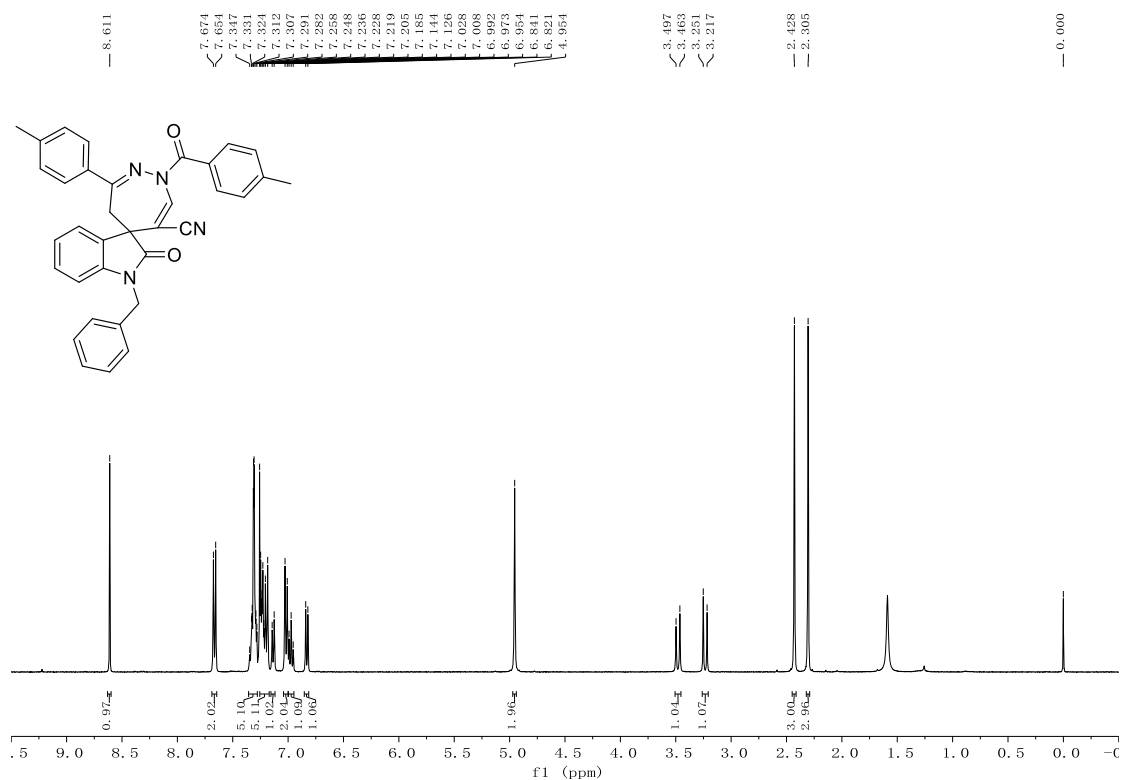
[1,2]diazepine]-6'-carbonitrile (3g): yellow solid, 0.412 g, 82%, m.p. 131-133 °C; ¹H NMR (600 MHz, CDCl₃) δ: 8.56 (s, 1H, ArH), 7.71 (d, *J* = 7.2 Hz, 2H, ArH), 7.55-7.52 (m, 1H, ArH), 7.45-7.42 (m, 2H, ArH), 7.16 (d, *J* = 7.8 Hz, 2H, ArH), 7.13 (d, *J* = 8.4 Hz, 1H, ArH), 7.01 (d, *J* = 7.8 Hz, 2H, ArH), 6.94 (s, 1H, ArH), 6.84 (d, *J* = 7.2 Hz, 1H, ArH), 3.80-3.75 (m, 1H, CH), 3.71-3.66 (m, 1H, CH), 3.43 (d, *J* = 13.8 Hz, 1H, CH), 3.16 (d, *J* = 13.8 Hz, 1H, CH), 2.29 (s, 3H, CH₃), 2.18 (s, 3H, CH₃), 1.71-1.66 (m, 2H, CH₂), 1.40-1.36 (m, 2H, CH₂), 0.94 (t, *J* = 7.2 Hz, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 173.5, 170.8, 160.0, 141.1, 140.0, 138.4, 133.4, 133.3, 132.8, 131.7, 130.2, 129.9, 129.1, 127.8, 127.1, 125.7, 117.2, 109.0, 95.3, 52.2, 40.4, 36.5, 29.3, 21.3, 20.9, 20.0, 13.7 ppm; IR (KBr) ν: 2930, 2871, 2211, 1715, 1625, 1600, 1495, 1446, 1348, 1279, 1189, 1113, 1062, 1027, 958, 900, 857, 815 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₂H₃₁N₄O₂ ([M+H]⁺): 503.2460, Found: 503.2442.

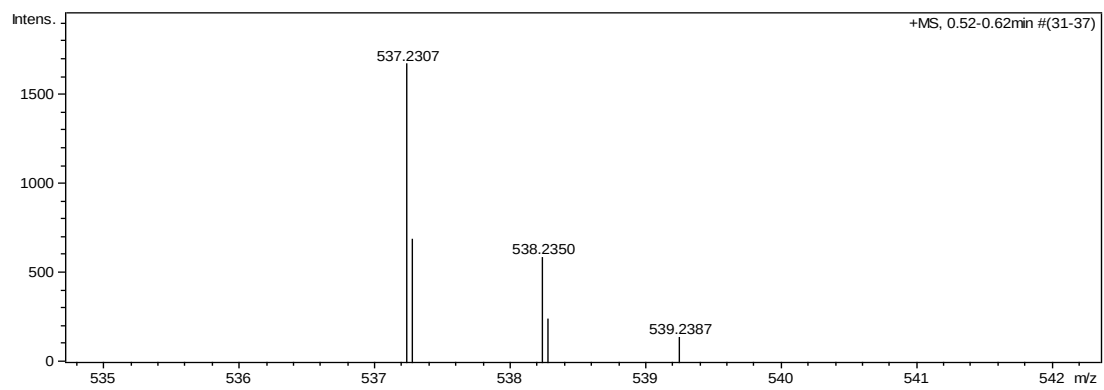
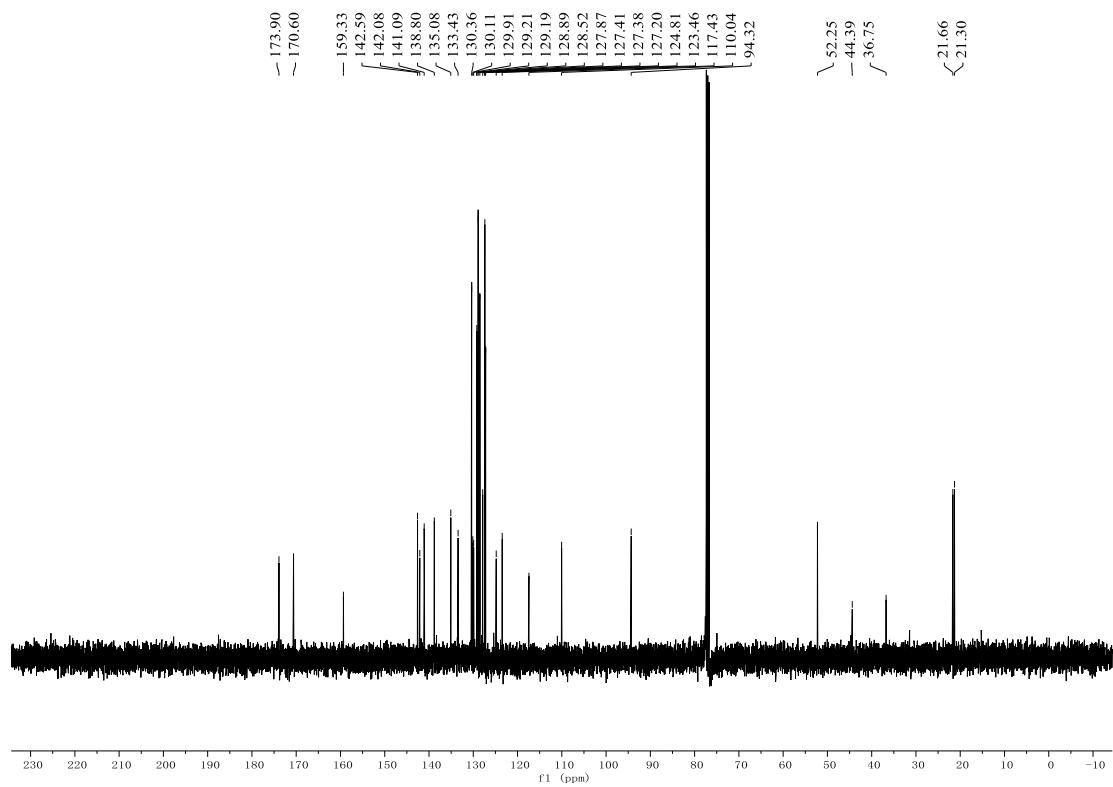




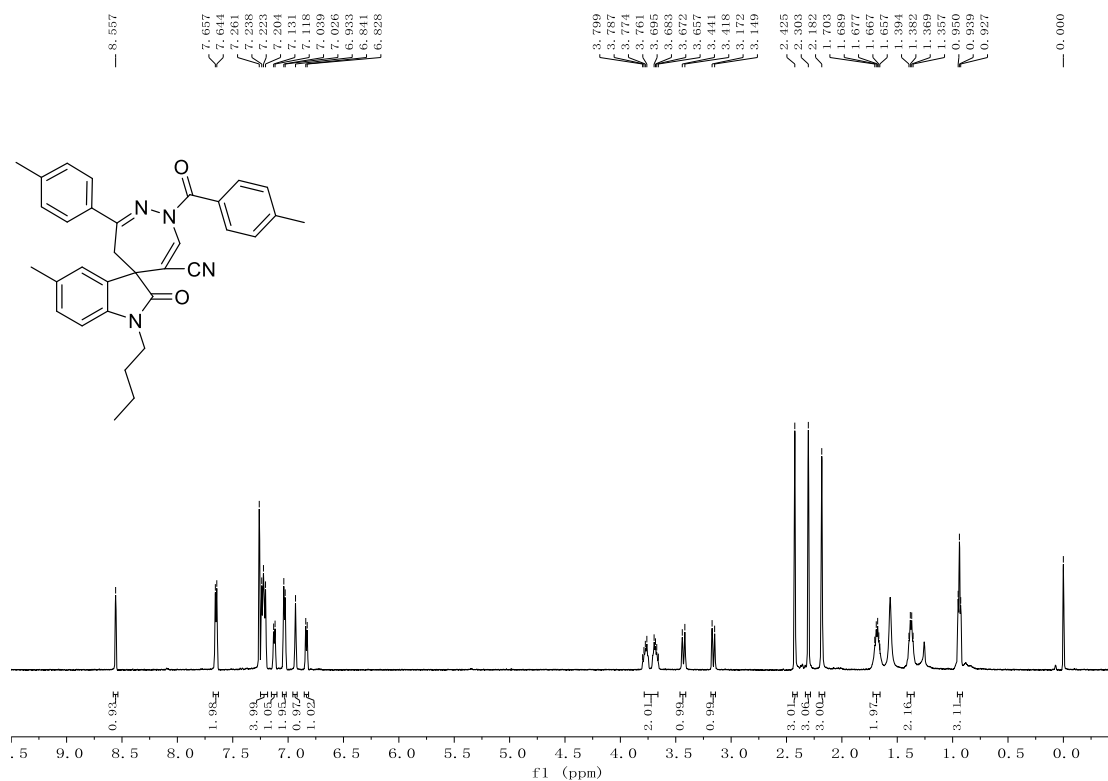
1-Benzyl-1'-(4-methylbenzoyl)-2-oxo-3'-(p-tolyl)-1',4'-dihydrospiro[indoline-3,5'-

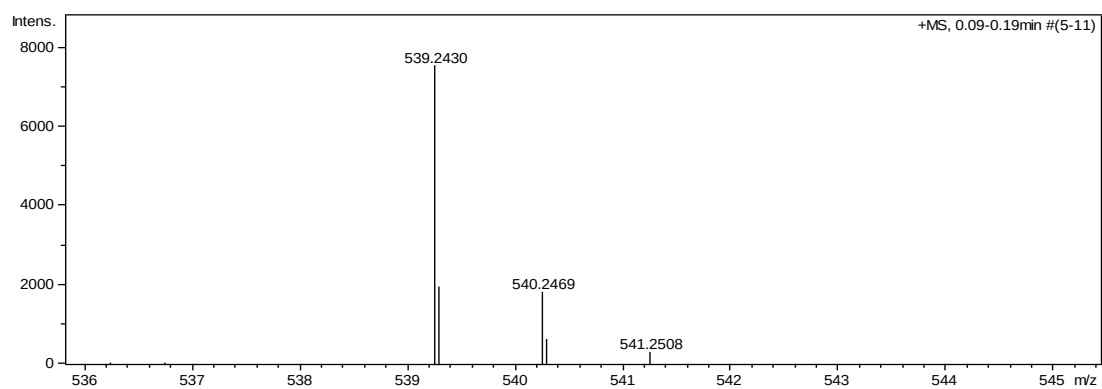
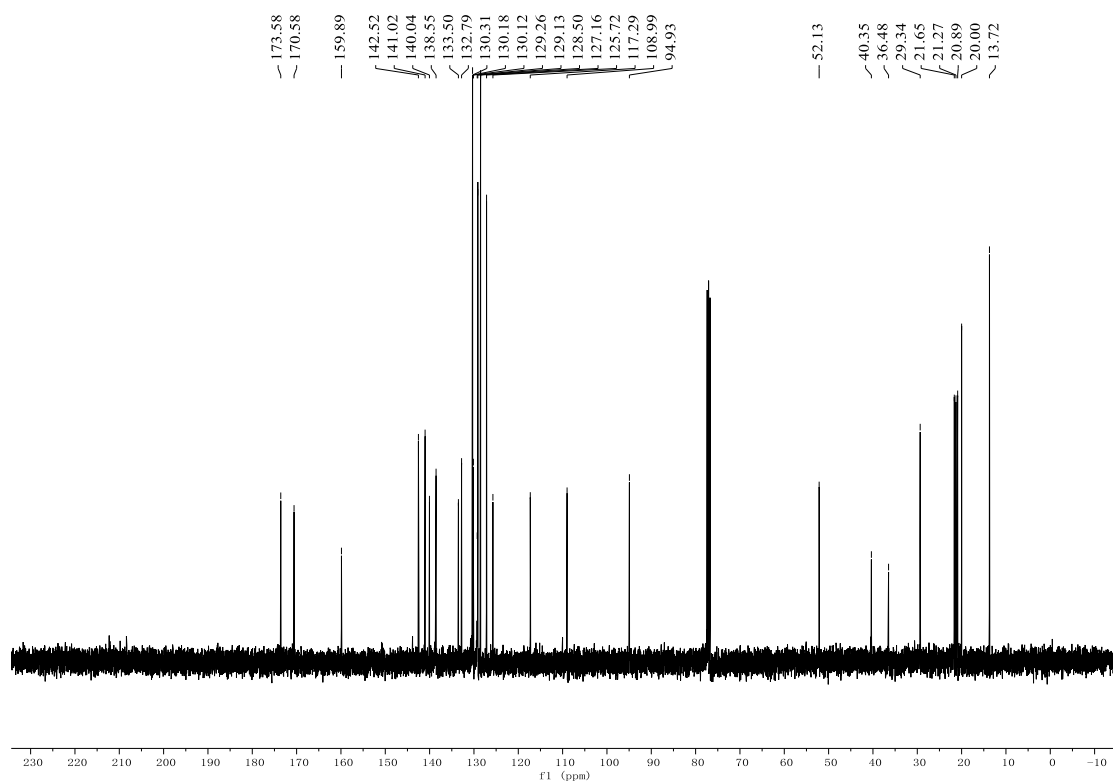
[1,2]diazepine]-6'-carbonitrile (3h): yellow solid, 0.386 g, 72%, m.p. 245-246 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.61 (s, 1H, ArH), 7.66 (d, *J* = 8.0 Hz, 2H, ArH), 7.34-7.28 (m, 5H, ArH), 7.25-7.18 (m, 6H, ArH), 7.13 (d, *J* = 7.2 Hz, 1H, ArH), 7.02 (m, *J* = 8.0 Hz, 2H, ArH), 6.97 (t, *J* = 7.6 Hz, 1H, ArH), 6.83 (d, *J* = 8.0 Hz, 1H, ArH), 4.95 (s, 2H, CH₂), 3.48 (d, *J* = 13.6 Hz, 1H, CH), 3.23 (d, *J* = 14.0 Hz, 1H, CH), 2.43 (s, 3H, CH₃), 2.31 (s, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 173.9, 170.6, 159.3, 142.6, 142.1, 141.1, 138.8, 135.1, 133.4, 130.4, 130.1, 129.9, 129.2, 129.2, 128.9, 128.5, 127.9, 127.4, 127.4, 127.2, 124.8, 123.5, 117.4, 110.0, 94.3, 52.3, 44.4, 36.8, 21.7, 21.3 ppm; IR (KBr) ν : 2921, 2868, 2209, 1748, 1715, 1698, 1682, 1568, 1516, 1507, 1489, 1471, 1287, 1029, 900, 857, 819 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₅H₂₉N₄O₂ ([M+H]⁺): 537.2307, Found: 537.2285.



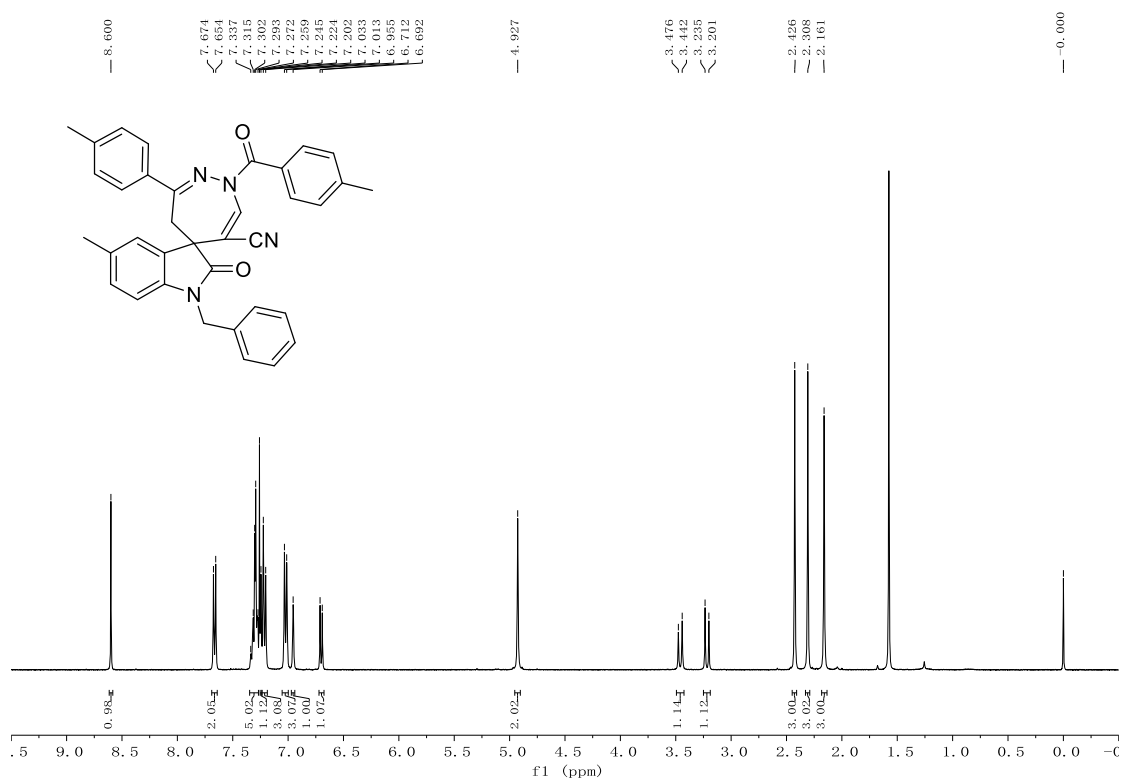


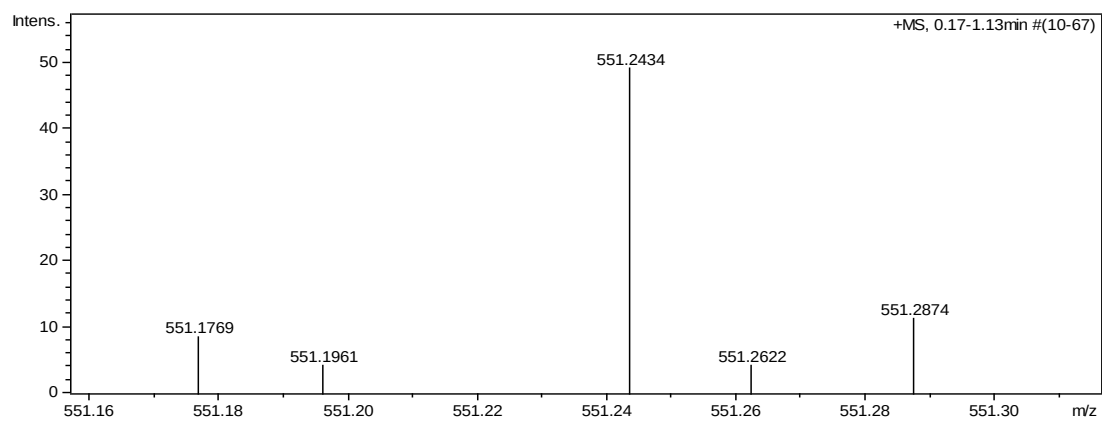
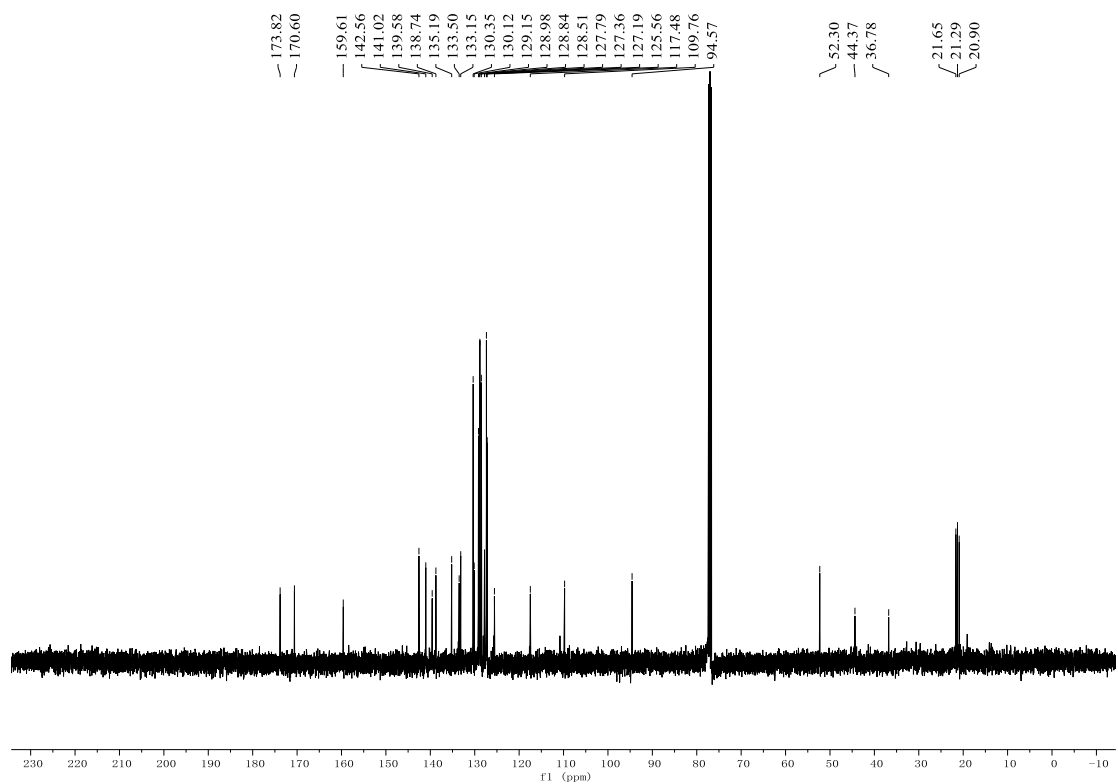
1-Butyl-5-methyl-1'-(4-methylbenzoyl)-2-oxo-3'-(p-tolyl)-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carbonitrile (3i): yellow solid, 0.382 g, 74%, m.p. 147-148 °C; ¹H NMR (600 MHz, CDCl₃) δ: 8.56 (s, 1H, ArH), 7.65 (d, *J* = 7.8 Hz, 2H, ArH), 7.26-7.20 (m, 4H, ArH), 7.12 (d, *J* = 7.8 Hz, 1H, ArH), 7.03 (d, *J* = 7.8 Hz, 2H, ArH), 6.93 (s, 1H, ArH), 6.83 (d, *J* = 7.8 Hz, 1H, ArH), 3.80-3.76 (m, 1H, CH), 3.70-3.66 (m, 1H, CH), 3.43 (d, *J* = 13.2 Hz, 1H, CH), 3.16 (d, *J* = 13.2 Hz, 1H, CH), 2.43 (s, 3H, CH₃), 2.30 (s, 3H, CH₃), 2.18 (s, 3H, CH₃), 1.70-1.66 (m, 2H, CH₂), 1.39-1.36 (m, 2H, CH₂), 0.94 (t, *J* = 7.2 Hz, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 173.6, 170.6, 159.9, 142.5, 141.0, 140.0, 138.6, 133.5, 132.8, 130.3, 130.2, 130.1, 129.3, 129.1, 128.5, 127.2, 125.7, 117.3, 109.0, 94.9, 52.1, 40.4, 36.5, 29.3, 21.7, 21.3, 20.9, 20.0, 13.7 ppm; IR (KBr) ν : 2931, 2875, 2212, 1711, 1627, 1603, 1497, 1442, 1349, 1278, 1189, 1110, 1063, 1028, 956, 907, 862, 818 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₃H₃₂N₄O₂Na ([M+Na]⁺): 539.2417, Found: 539.2430.



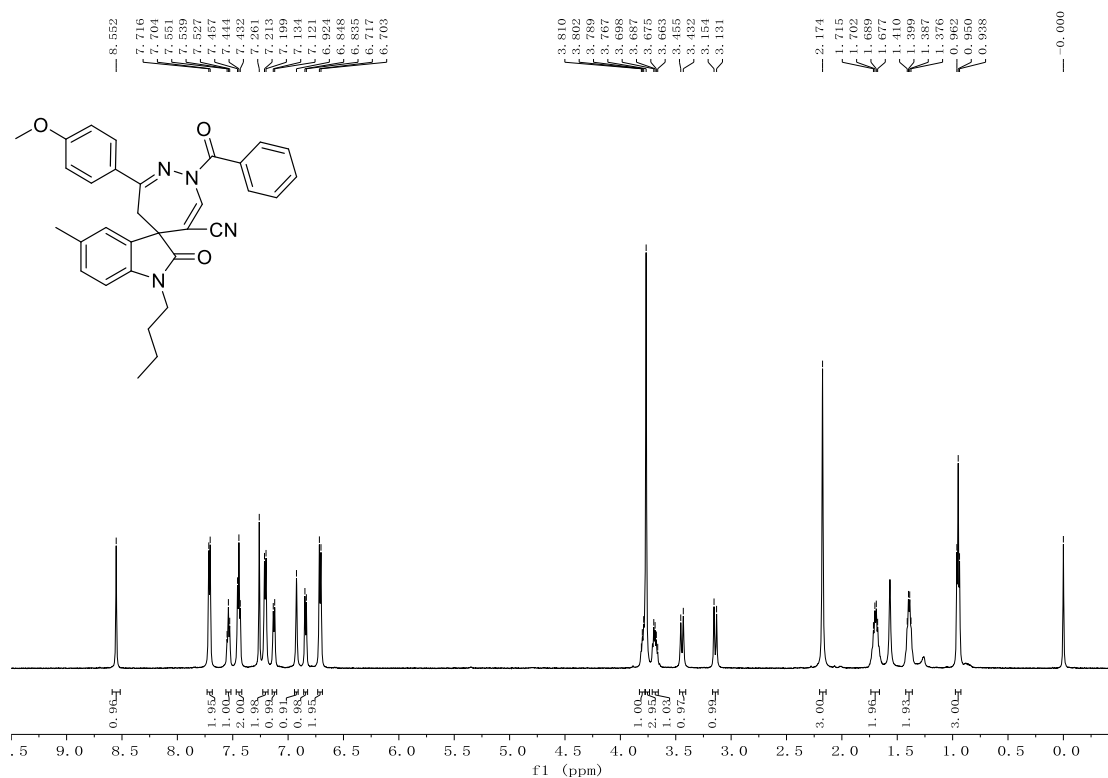


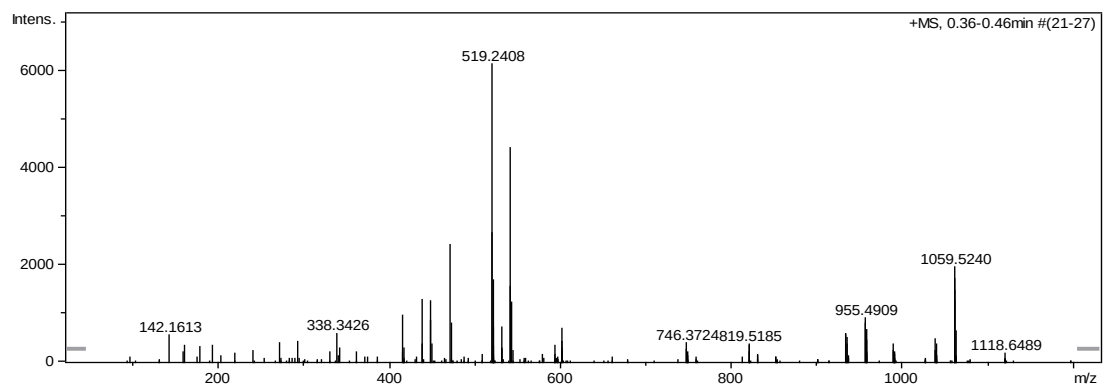
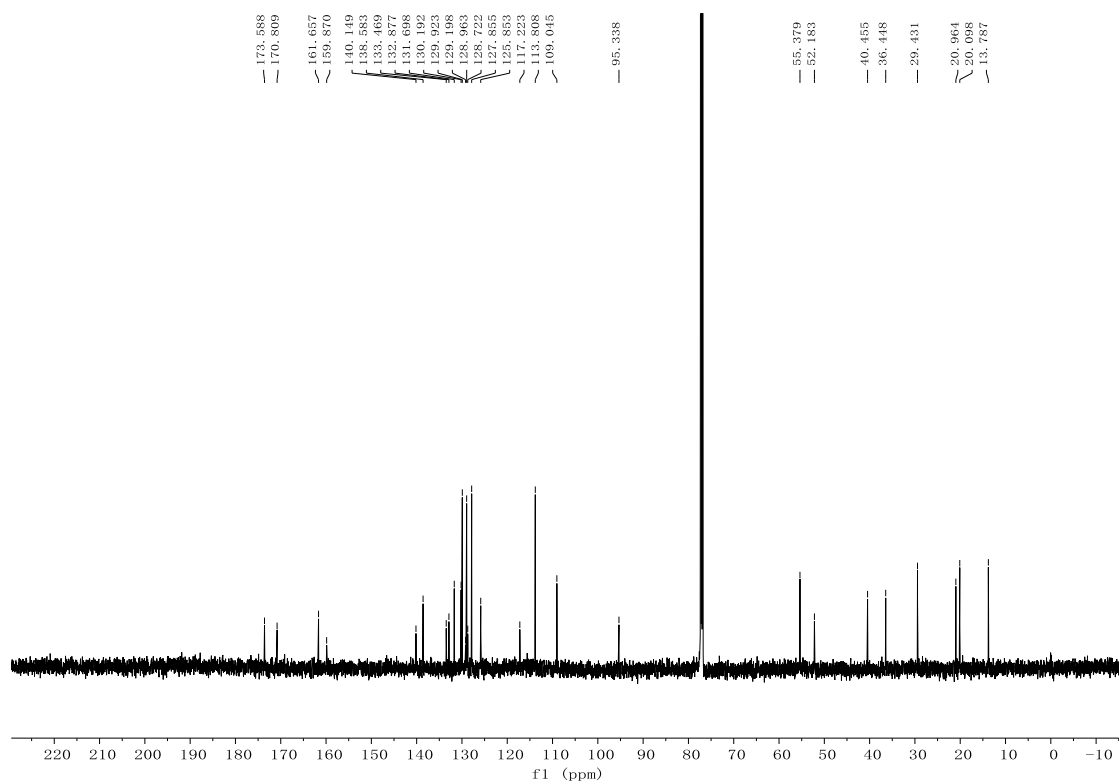
1-Benzyl-5-methyl-1'-(4-methylbenzoyl)-2-oxo-3'-(p-tolyl)-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carbonitrile (3j): yellow solid, 0.374 g, 68%, m.p. 232-233 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.60 (s, 1H, ArH), 7.66 (d, *J* = 8.0 Hz, 2H, ArH), 7.34-7.27 (m, 5H, ArH), 7.25 (s, 1H, ArH), 7.21 (d, *J* = 8.8 Hz, 3H, ArH), 7.02 (d, *J* = 8.0 Hz, 3H, ArH), 6.96 (s, 1H, ArH), 6.70 (d, *J* = 8.0 Hz, 1H, ArH), 4.93 (s, 2H, CH₂), 3.46 (d, *J* = 13.6 Hz, 1H, CH), 3.22 (d, *J* = 13.6 Hz, 1H, CH), 2.43 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 2.16 (s, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 173.8, 170.6, 159.6, 142.6, 141.0, 139.6, 138.7, 135.2, 133.5, 133.2, 130.4, 130.1, 129.2, 129.0, 128.8, 128.5, 127.8, 127.4, 127.2, 125.6, 117.5, 109.8, 94.6, 52.3, 44.4, 36.8, 21.7, 21.3, 20.9 ppm; IR (KBr) ν: 2957, 2931, 2868, 2213, 1721, 1628, 1495, 1443, 1368, 1270, 1194, 1110, 1087, 1007, 907, 867, 821 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₆H₃₁N₄O₂ ([M+H]⁺): 551.2442, Found: 551.2434.



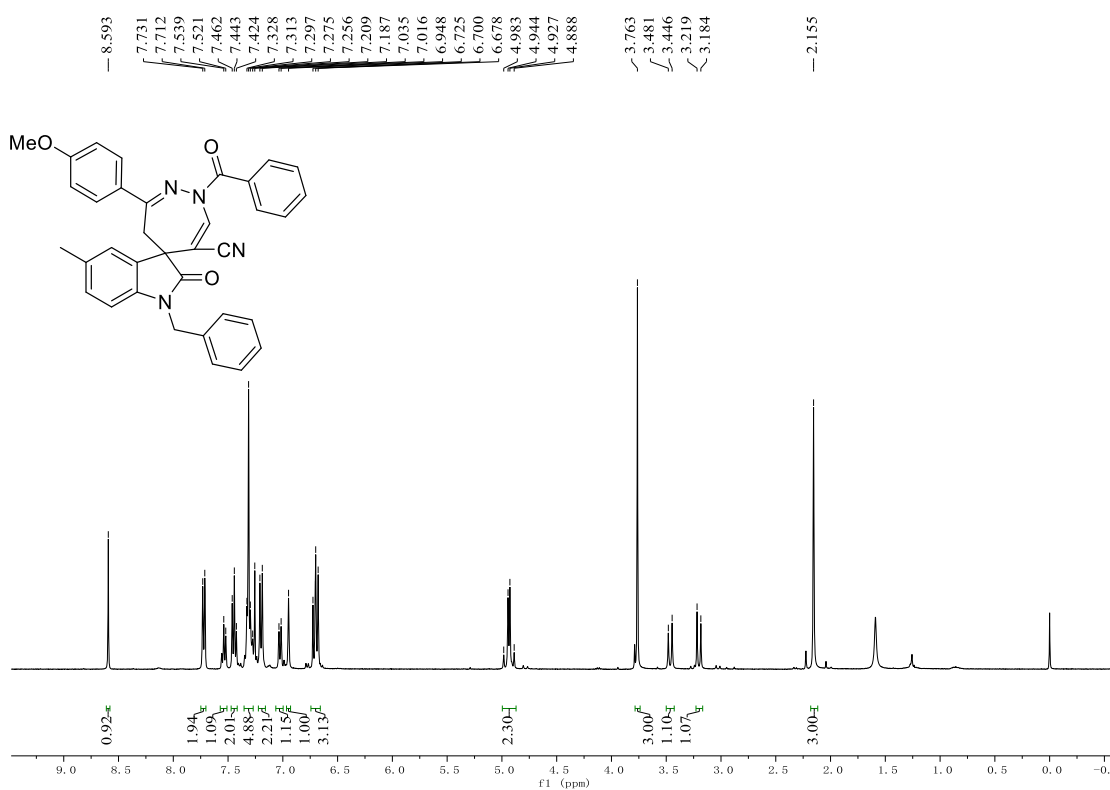


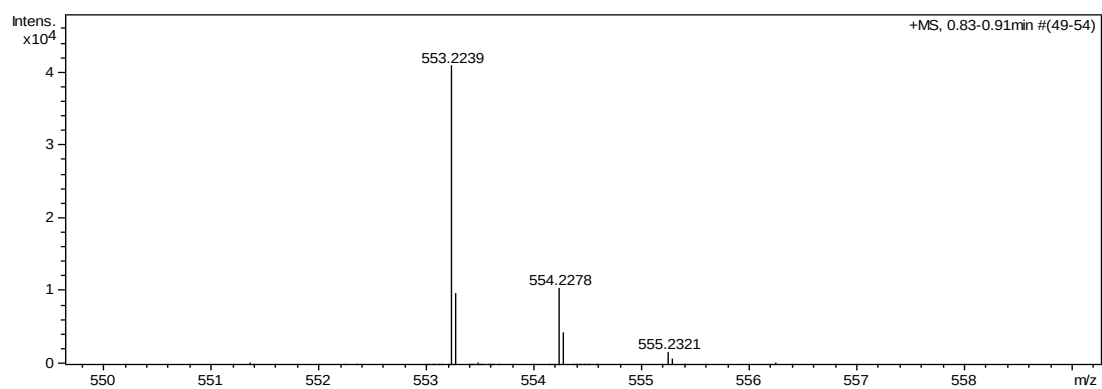
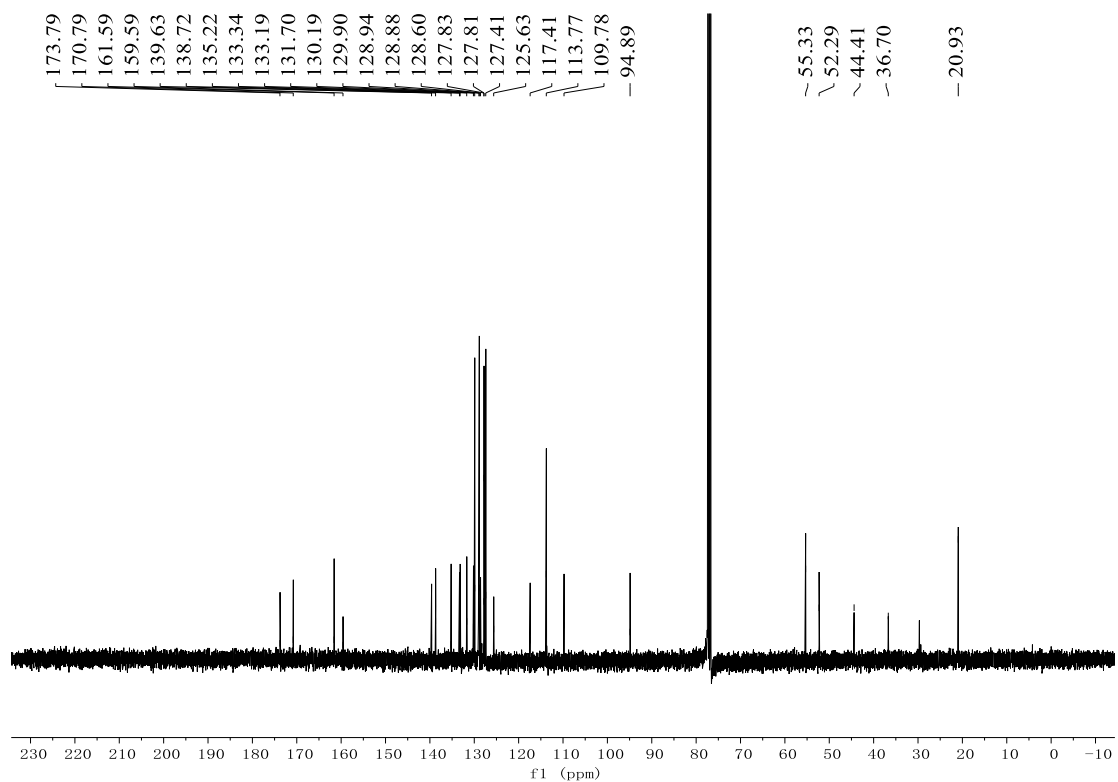
1'-Benzoyl-1-butyl-3'-(4-methoxyphenyl)-5-methyl-2-oxo-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carbonitrile (3k): yellow solid, 0.388 g, 75%, m.p. 176-177 °C; ¹H NMR (600 MHz, CDCl₃) δ: 8.55 (s, 1H, ArH), 7.70 (d, *J* = 7.2 Hz, 2H, ArH), 7.54 (t, *J* = 7.2 Hz, 1H, ArH), 7.46-7.42 (m, 2H, ArH), 7.21 (d, *J* = 8.4 Hz, 2H, ArH), 7.13 (d, *J* = 7.8 Hz, 1H, ArH), 6.92 (s, 1H, ArH), 6.84 (d, *J* = 7.8 Hz, 1H, ArH), 6.71 (d, *J* = 8.4 Hz, 2H, ArH), 3.81-3.66 (m, 2H, CH₂), 3.77 (s, 3H, OCH₃), 3.44 (d, *J* = 13.8 Hz, 1H, CH), 3.14 (d, *J* = 13.8 Hz, 1H, CH), 2.17 (s, 3H, CH₃), 1.72-1.67 (m, 2H, CH₂), 1.41-1.38 (m, 2H, CH₂), 0.95 (t, *J* = 7.2 Hz, 3H, CH₃) ppm; ¹³C NMR (151 MHz, CDCl₃) δ: 173.6, 170.8, 161.7, 159.9, 140.1, 138.6, 133.5, 132.9, 131.7, 130.2, 129.9, 129.2, 128.9, 128.7, 127.8, 125.8, 117.2, 113.8, 109.0, 95.3, 55.4, 52.2, 40.5, 36.4, 29.4, 21.0, 20.1, 13.8.cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₂H₃₁N₄O₃ ([M+H]⁺): 519.2408, Found: 519.2391.





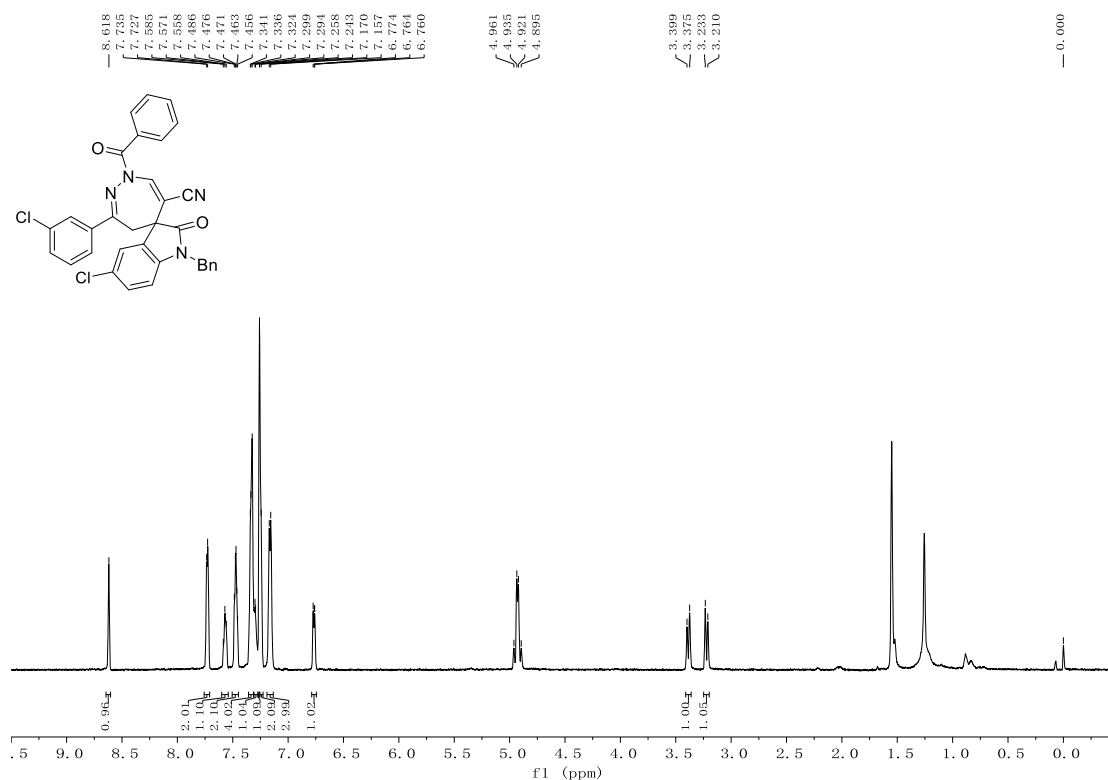
1'-Benzoyl-1-benzyl-3'-(4-methoxyphenyl)-5-methyl-2-oxo-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carbonitrile (3l): yellow solid, 0.381 g, 72%, m.p. 200-201 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.59 (s, 1H, ArH), 7.73-7.71 (m, 2H, ArH), 7.56-7.52 (m, 1H, ArH), 7.46-7.42 (m, 2H, ArH), 7.35-7.27 (m, 5H, ArH), 7.21-7.19 (m, 2H, ArH), 7.04-7.02 (m, 1H, ArH), 6.95 (s, 1H, ArH), 6.72-6.68 (m, 3H, ArH), 4.98-4.89 (m, 2H, CH₂), 3.76 (s, 3H, OCH₃), 3.46 (d, *J* = 14.0 Hz, 1H, CH), 3.20 (d, *J* = 13.6 Hz, 1H, CH), 2.16 (s, 3H, CH₃) ppm; ¹³C NMR (100 MHz, CDCl₃) δ: 173.8, 170.8, 161.6, 159.6, 139.6, 138.7, 135.2, 133.3, 133.2, 131.7, 130.2, 129.9, 128.9, 128.9, 128.6, 127.8, 127.8, 127.4, 125.6, 117.4, 113.8, 109.8, 94.9, 55.3, 52.3, 44.4, 36.7, 20.9 ppm; IR (KBr) ν: 2923, 2852, 1752, 1686, 1561, 1512, 1496, 1438, 1383, 1345, 1283, 1257, 1179, 1115, 985, 892, 757 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₅H₂₉N₄O₃H ([M+Na]⁺): 553.2239, Found: 553.2234.

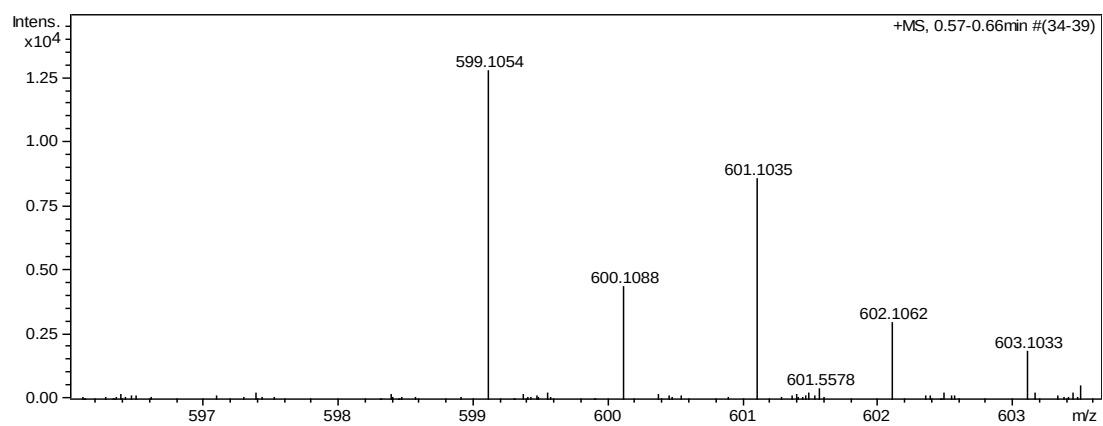
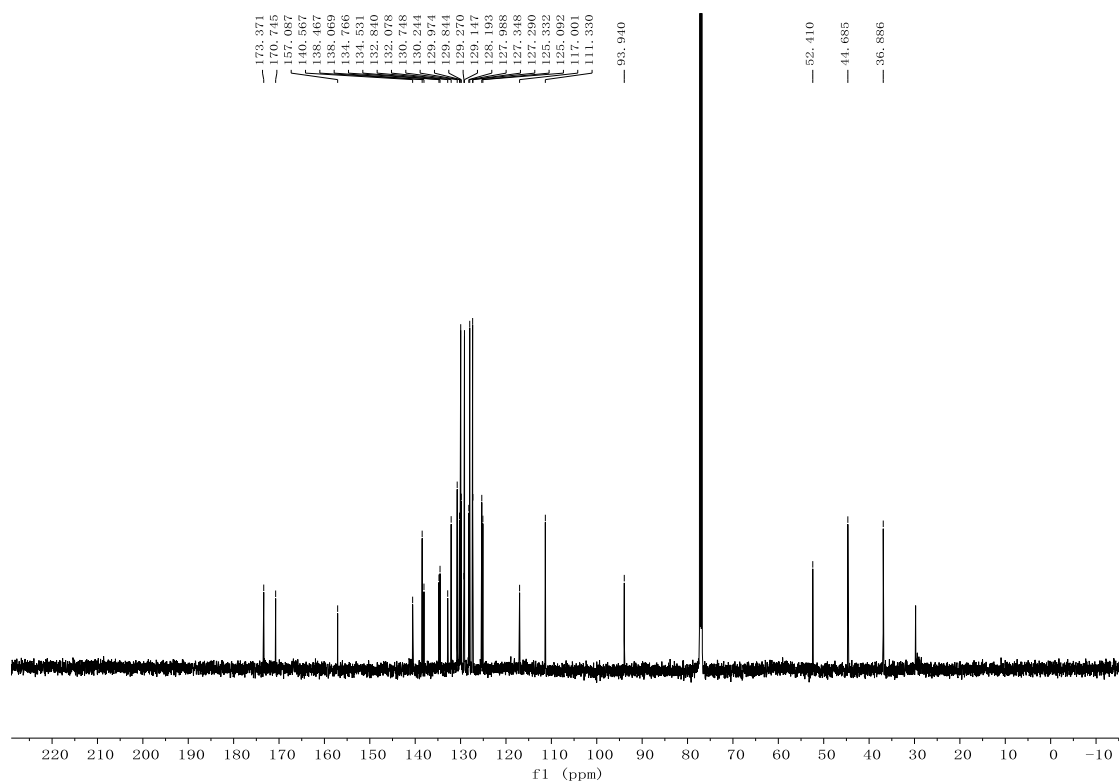




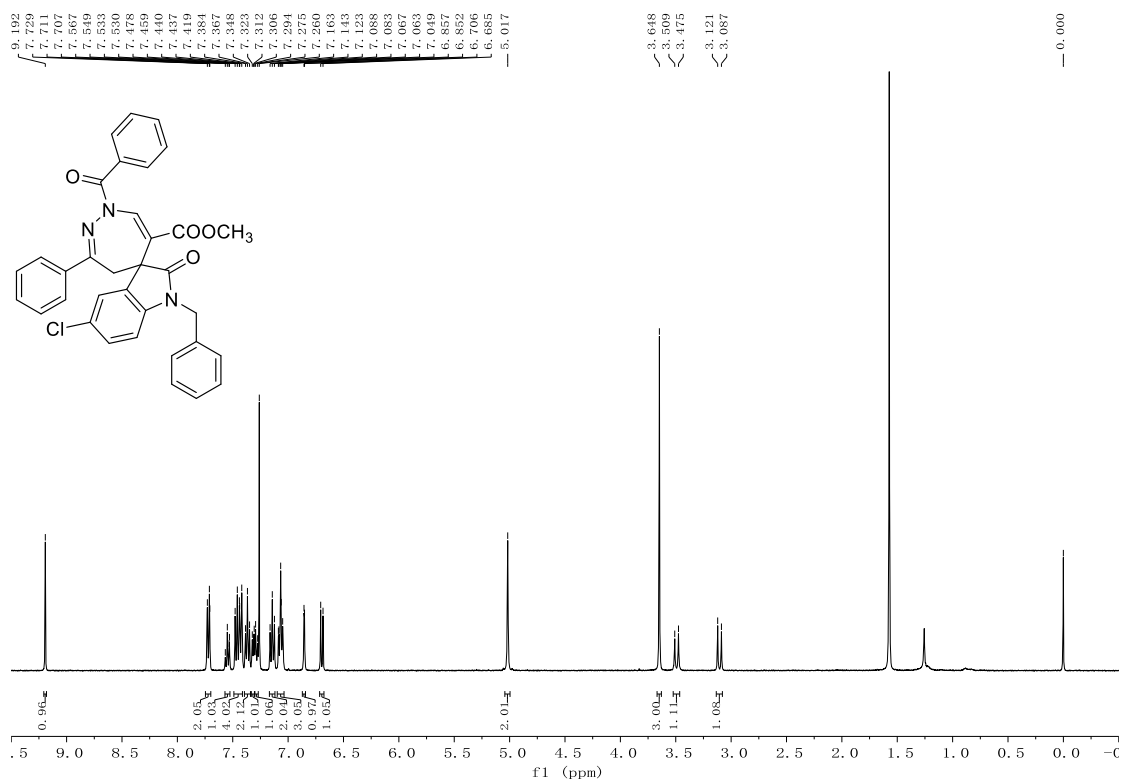
1'-Benzoyl-1-benzyl-5-chloro-3'-(3-chlorophenyl)-2-oxo-1',4'-dihydrospiro[indoline-3,5'-

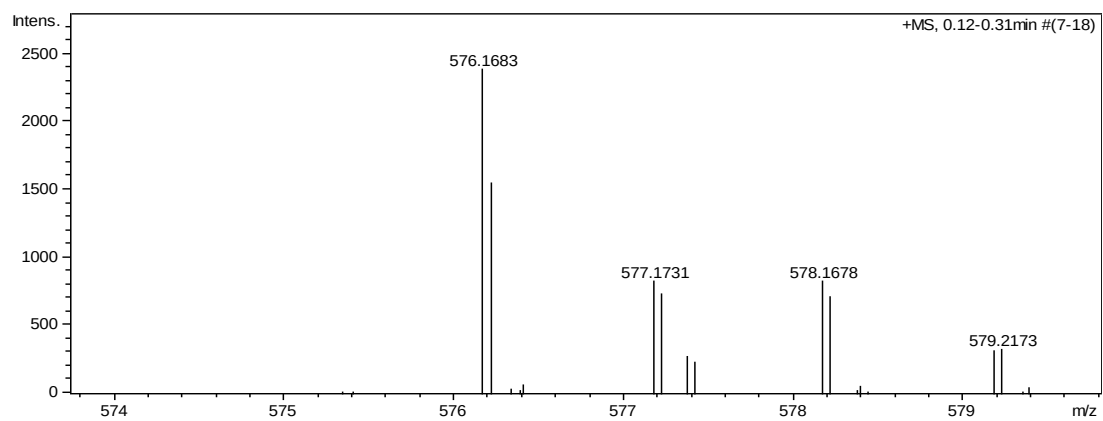
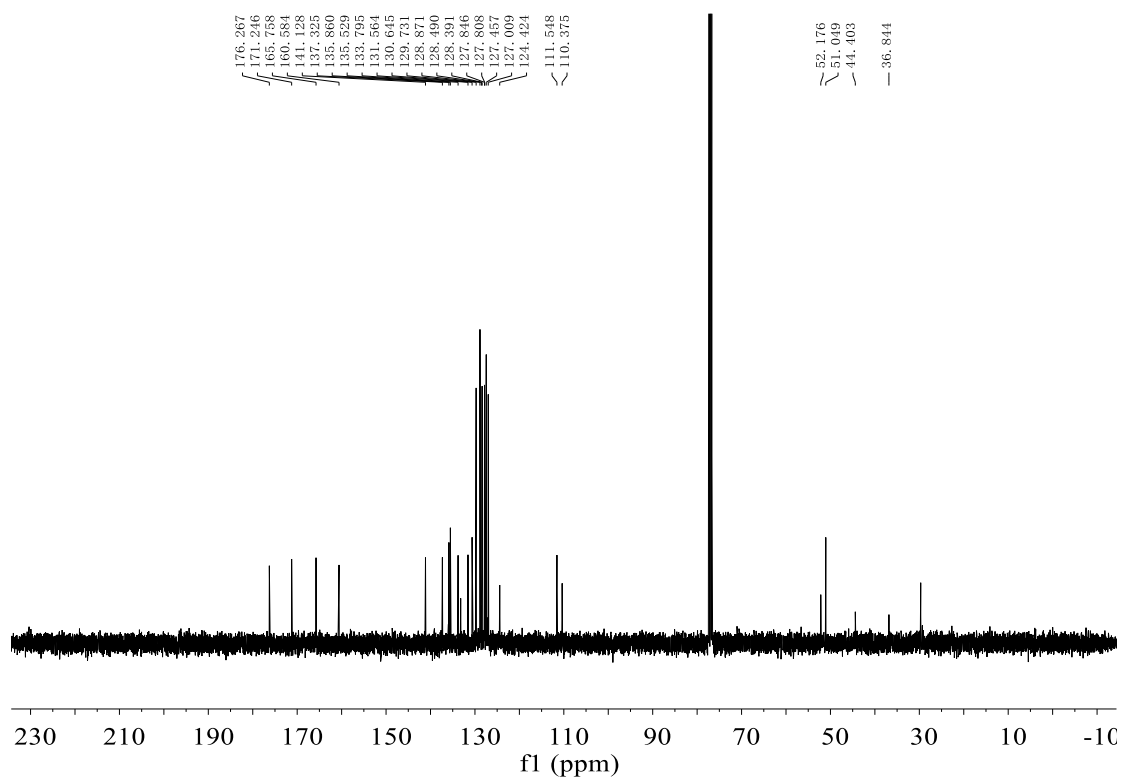
[1,2]diazepine]-6'-carbonitrile (3m): white solid, 0.355 g, 62%, m.p. 208-211 °C; ^1H NMR (600 MHz, CDCl_3) δ : 8.62 (s, 1H, ArH), 7.74-7.71 (m, 2H, ArH), 7.59-7.56 (m, 1H, ArH), 7.49-7.46 (m, 2H, ArH), 7.34-7.33 (m, 4H, ArH), 7.32-7.29 (m, 1H, ArH), 7.27-7.26 (m, 1H, ArH), 7.25-7.24 (m, 2H, ArH), 7.17-7.16 (m, 3H, ArH), 6.77-6.76 (m, 1H, ArH), 4.96-4.90 (m, 2H, CH_2), 3.39 (d, $J = 14.4$ Hz, 1H, CH), 3.22 (d, $J = 13.8$ Hz, 1H, CH) ppm; ^{13}C NMR (151 MHz, CDCl_3) δ : 173.4, 170.8, 157.1, 140.6, 138.5, 138.1, 134.8, 134.5, 132.8, 132.1, 130.8, 130.2, 129.9, 129.8, 129.3, 129.1, 128.2, 128.0, 127.3, 127.3, 125.3, 125.1, 117.0, 111.3, 93.9, 52.4, 44.7, 36.9 ppm; IR (KBr) ν : 3085, 2190, 1825, 1755, 1678, 1568, 1482, 1319, 1280, 1173, 966, 905, 842, 805 cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{33}\text{H}_{22}\text{Cl}_2\text{N}_4\text{O}_2\text{Na}$ ($[\text{M}+\text{Na}]^+$): 599.1012, Found: 599.1054.





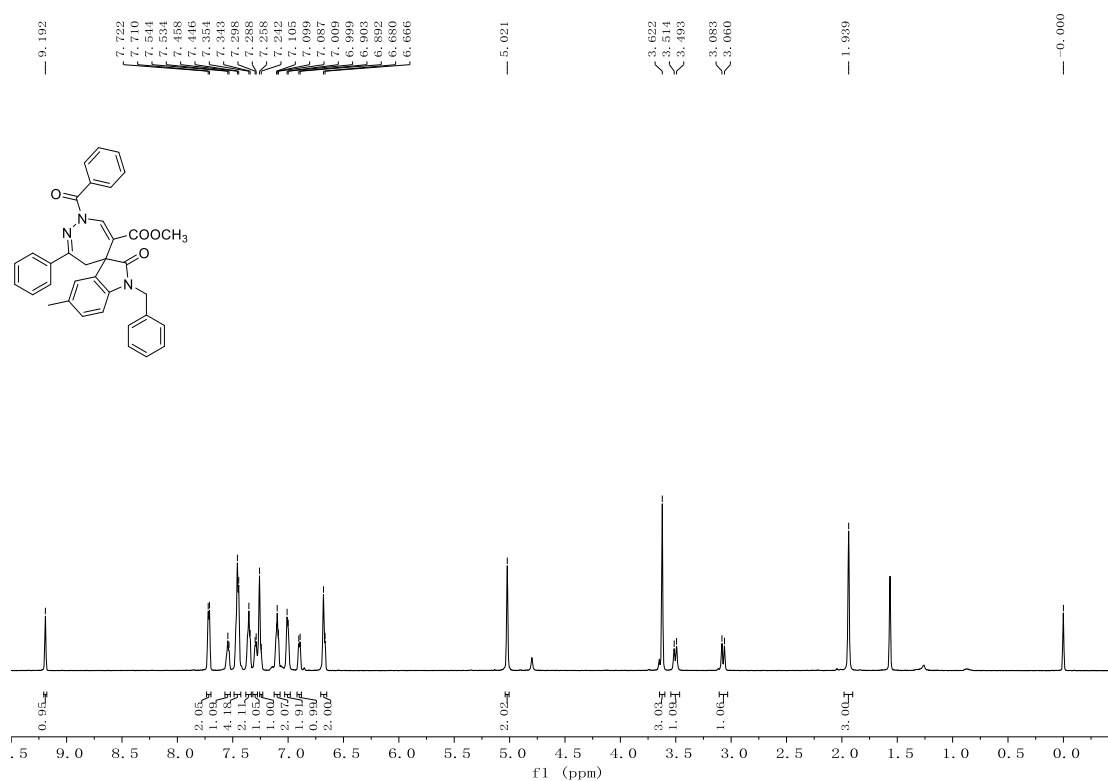
Methyl 1'-benzoyl-1-benzyl-5-chloro-2-oxo-3'-phenyl-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carboxylate (5a): yellow solid, 0.391 g, 68%, m.p. 189-191 °C; ^1H NMR (400 MHz, CDCl_3) δ : 9.19 (s, 1H, ArH), 7.73-7.71 (m, 2H, ArH), 7.56-7.53 (m, 1H, ArH), 7.48-7.42 (m, 4H, ArH), 7.38-7.35 (m, 2H, ArH), 7.32-7.31 (m, 1H, ArH), 7.29-7.27 (m, 1H, ArH), 7.14 (t, $J = 8.0$ Hz, 2H, ArH), 7.09-7.05 (m, 3H, ArH), 6.86-6.85 (m, 1H, ArH), 6.70 (d, $J = 8.4$ Hz, 1H, ArH), 5.02 (s, 2H, CH_2), 3.65 (s, 3H, OCH_3), 3.49 (d, $J = 13.6$ Hz, 1H, CH), 3.10 (d, $J = 13.6$ Hz, 1H, CH) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 176.3, 171.3, 165.8, 160.6, 141.1, 137.3, 135.9, 135.5, 133.8, 131.6, 130.6, 129.7, 128.9, 128.5, 128.4, 127.9, 127.8, 127.5, 127.0, 124.4, 111.6, 110.4, 52.2, 51.1, 44.4, 36.8 ppm; IR (KBr) ν : 2924, 2853, 1721, 1608, 1484, 1456, 1430, 1340, 1170, 812 cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{34}\text{H}_{27}\text{ClN}_3\text{O}_4$ ($[\text{M}+\text{H}]^+$): 576.1685, Found: 576.1683.

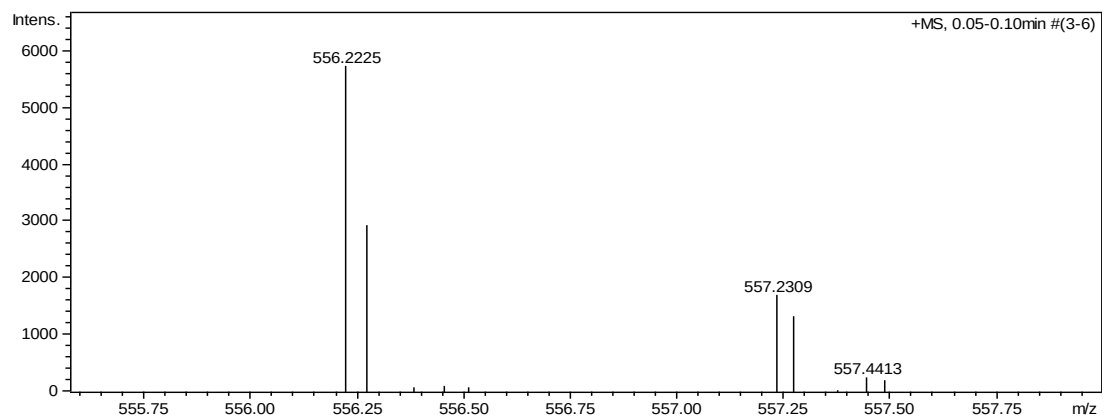
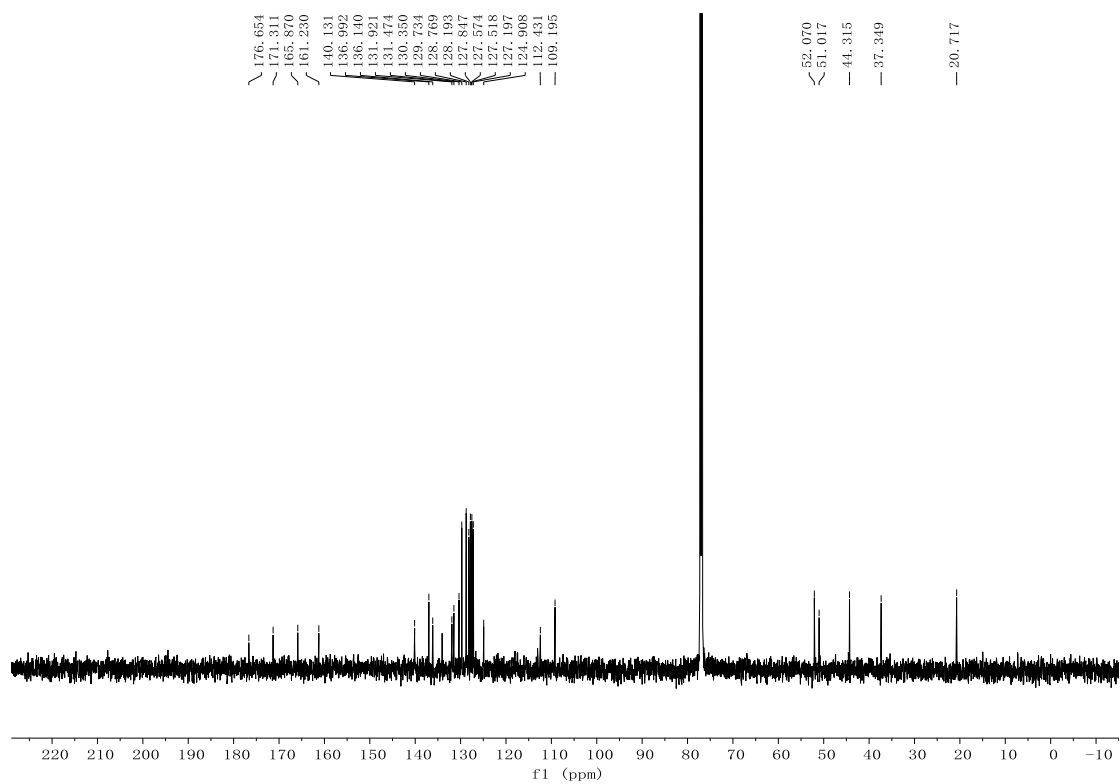




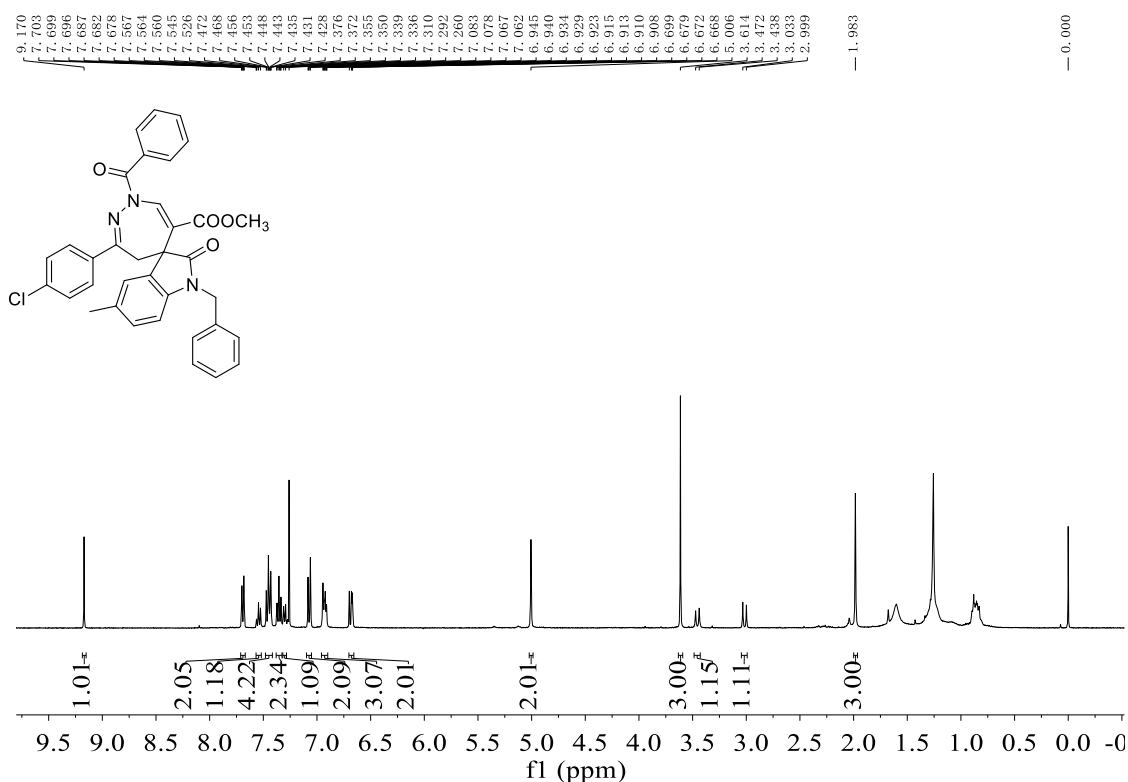
Methyl 1'-benzoyl-1-benzyl-5-methyl-2-oxo-3'-phenyl-1',4'-dihydrospiro[indoline-3,5'-

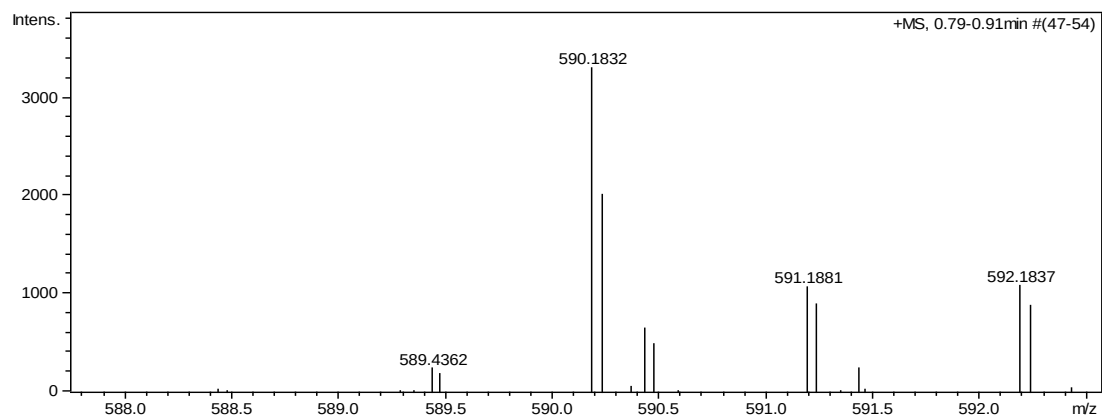
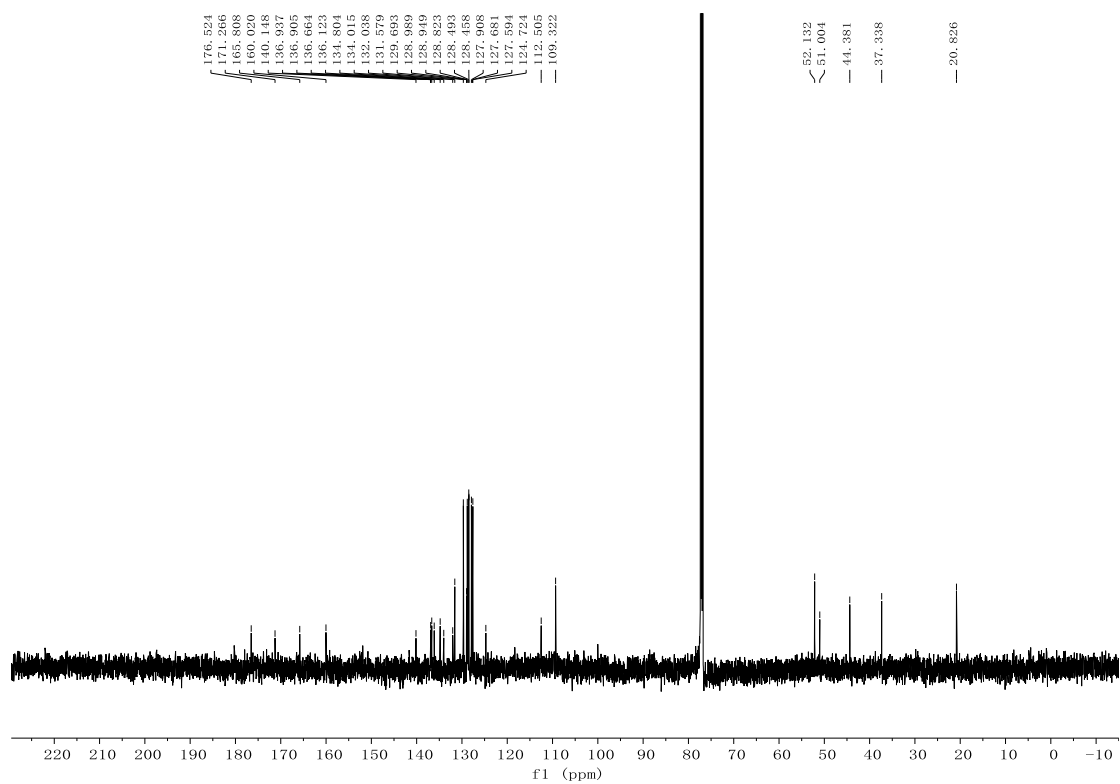
[1,2]diazepine]-6'-carboxylate (5b): yellow solid, 0.416 g, 75%, m.p. 165-167 °C; ¹H NMR (600 MHz, CDCl₃) δ: 9.19 (s, 1H, ArH), 7.72 (d, *J* = 7.2 Hz, 2H, ArH), 7.55-7.53 (m, 1H, ArH), 7.48-7.44 (m, 4H, ArH), 7.36-7.34 (m, 2H, ArH), 7.30-7.29 (m, 1H, ArH), 7.25-7.23 (m, 1H, ArH), 7.11-7.09 (m, 2H, ArH), 7.01-6.99 (m, 2H, ArH), 6.90-6.89 (m, 1H, ArH), 6.68-6.66 (m, 2H, ArH), 5.02 (s, 2H, CH₂), 3.62 (s, 3H, OCH₃), 3.50 (d, *J* = 12.6 Hz, 1H, CH), 3.07 (d, *J* = 13.8 Hz, 1H, CH), 1.94 (s, 3H, CH₃) ppm; ¹³C NMR (151 MHz, CDCl₃) δ: 176.6, 171.3, 165.9, 161.2, 140.1, 137.0, 136.1, 131.9, 131.5, 130.3, 129.7, 128.8, 128.2, 127.8, 127.6, 127.5, 127.2, 124.9, 112.4, 109.2, 52.1, 51.0, 44.3, 37.3, 20.7 ppm; IR (KBr) ν : 2924, 2853, 1715, 1601, 1496, 1447, 1349, 1280, 1188, 1140, 859, 785 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₅H₃₀N₃O₄ ([M+H]⁺): 556.2231, Found: 556.2225.



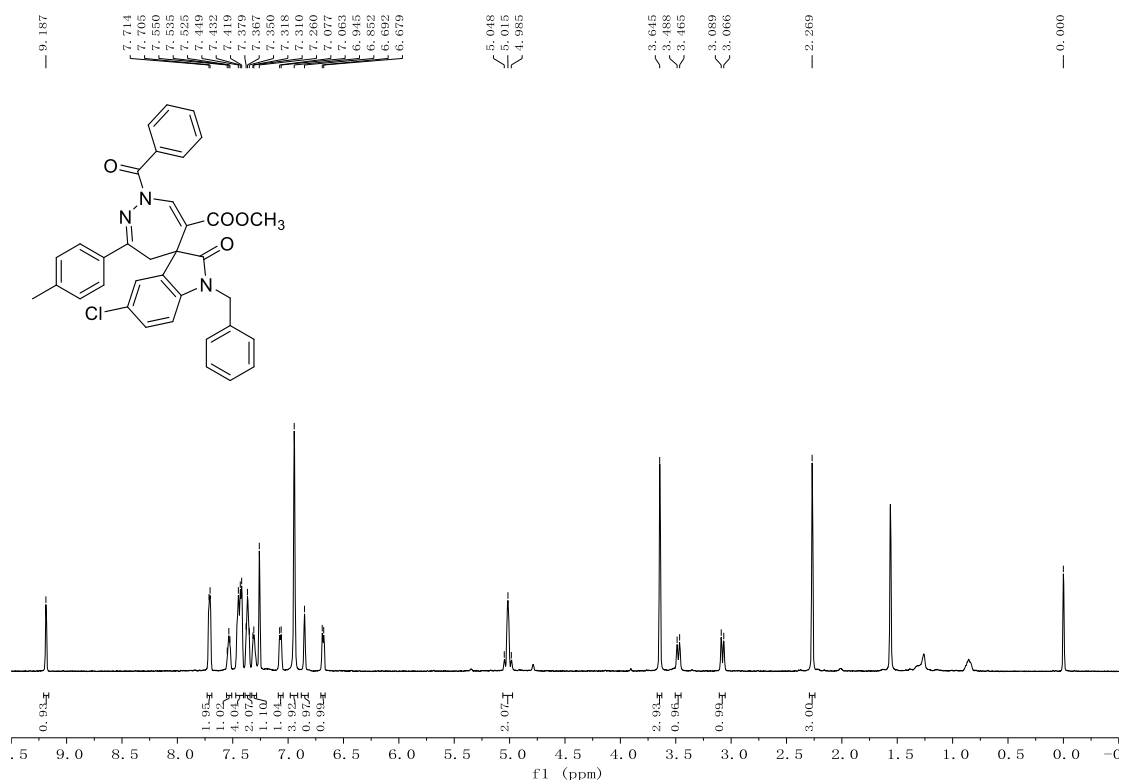


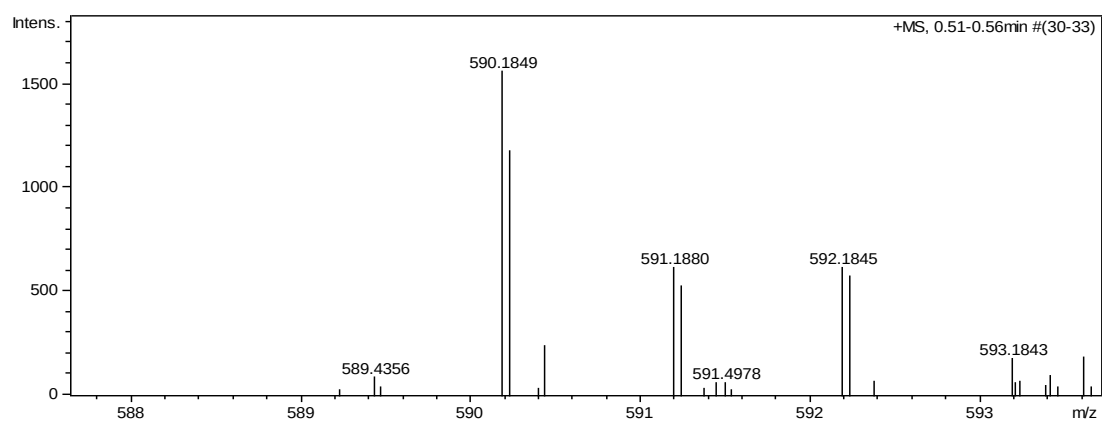
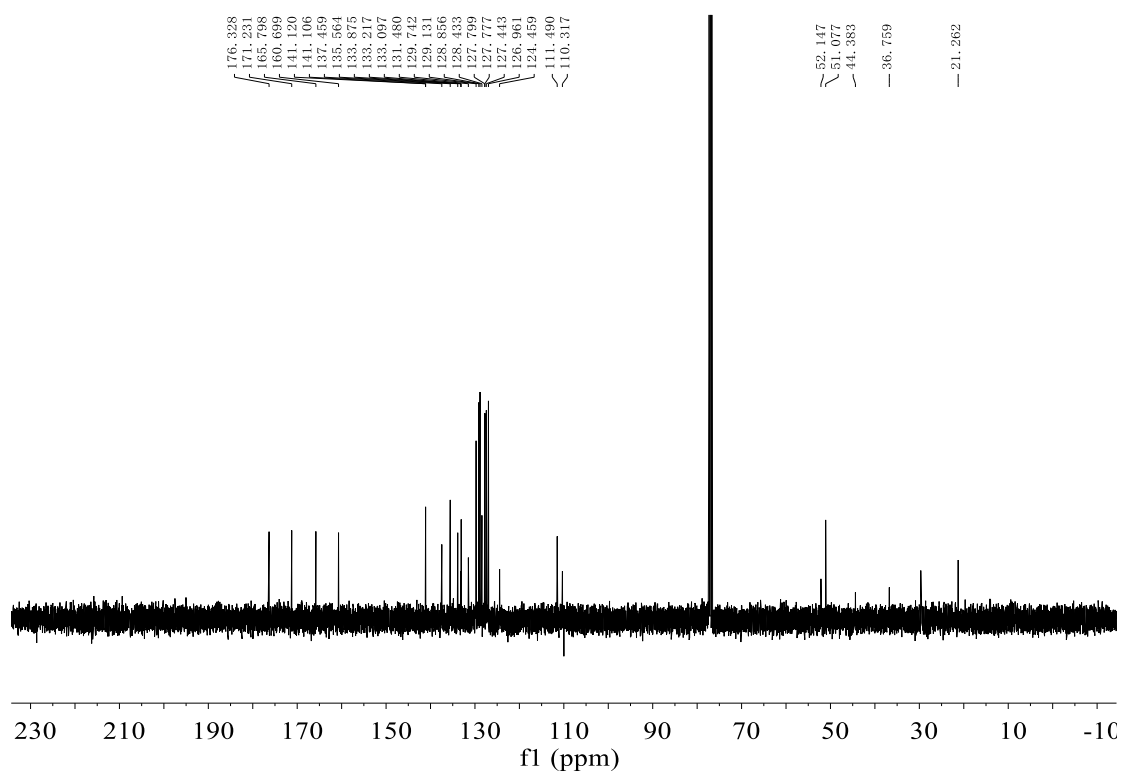
Methyl 1'-benzoyl-1-benzyl-3'-(4-chlorophenyl)-5-methyl-2-oxo-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carboxylate (5c): yellow solid, 0.400 g, 68%, m.p. 213-214 °C; ¹H NMR (400 MHz, CDCl₃) δ: 9.17 (s, 1H, ArH), 7.70-7.68 (m, 2H, ArH), 7.57-7.53 (m, 1H, ArH), 7.47-7.43 (m, 4H, ArH), 7.38-7.34 (m, 2H, ArH), 7.31-7.29 (m, 1H, ArH), 7.08-7.06 (m, 2H, ArH), 6.95-6.91 (m, 3H, ArH), 6.70-6.67 (m, 2H, ArH), 5.01 (s, 2H, CH₂), 3.61 (s, 3H, OCH₃), 3.45 (d, *J* = 13.6 Hz, 1H, CH), 3.02 (d, *J* = 13.6 Hz, 1H, CH), 1.98 (s, 3H, CH₃) ppm; ¹³C NMR (151 MHz, CDCl₃) δ: 176.5, 171.3, 165.8, 160.0, 140.1, 136.9, 136.9, 136.7, 136.1, 134.8, 134.0, 132.0, 131.6, 129.7, 129.0, 128.9, 128.8, 128.5, 128.5, 127.9, 127.7, 127.6, 124.7, 112.5, 109.3, 52.1, 51.0, 44.4, 37.3, 20.8 ppm; IR (KBr) ν: 2923, 2852, 1716, 1609, 1499, 1457, 1378, 1274, 1189, 1126, 1030, 855, 776 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₅H₂₉ClN₃O₃ ([M+H]⁺):590.1841, Found: 590.1832.





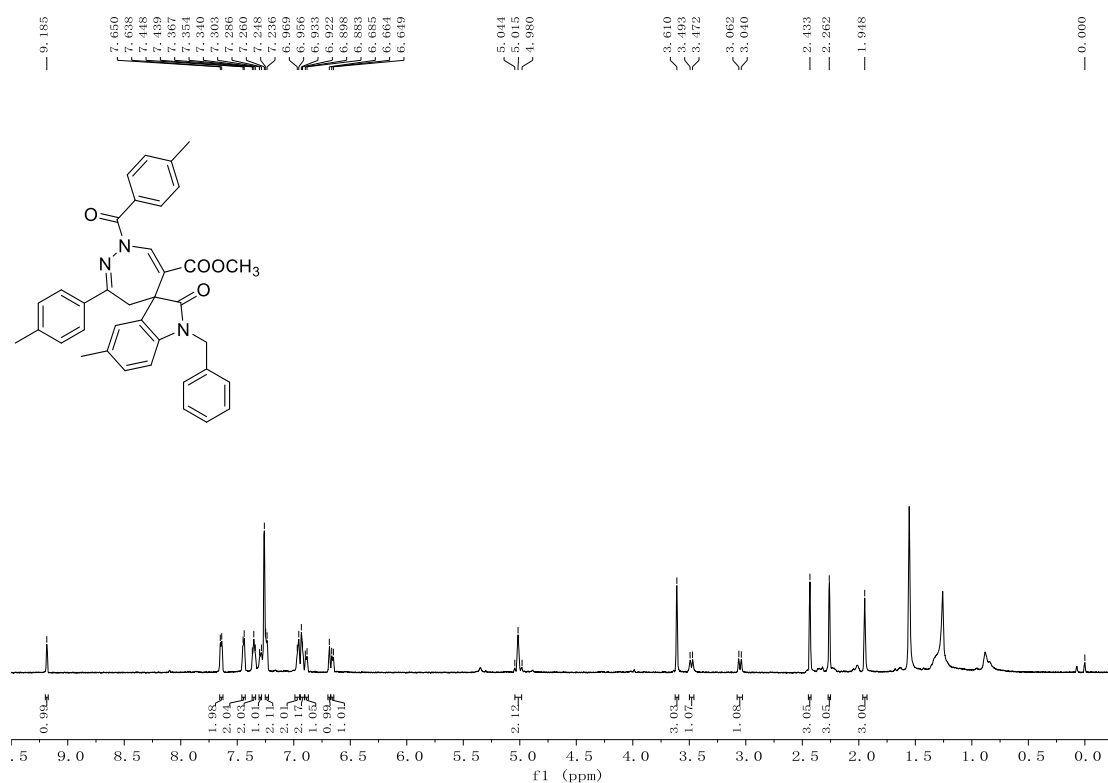
Methyl 1'-benzoyl-1-benzyl-5-chloro-2-oxo-3'-(p-tolyl)-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carboxylate (5d): yellow solid, 0.365 g, 65%, m.p. 152-154 °C; ^1H NMR (600 MHz, CDCl_3) δ : 9.19 (s, 1H, ArH), 7.71-7.70 (m, 2H, ArH), 7.55-7.52 (m, 1H, ArH), 7.46-7.41 (m, 4H, ArH), 7.39-7.35 (m, 2H, ArH), 7.32-7.29 (m, 1H, ArH), 7.08-7.06 (m, 1H, ArH), 6.95 (s, 4H, ArH), 6.85 (s, 1H, ArH), 6.69-6.68 (m, 1H, ArH), 5.05-4.99 (m, 2H, CH_2), 3.65 (s, 3H, OCH_3), 3.48 (d, $J = 13.8$ Hz, 1H, CH), 3.08 (d, $J = 13.8$ Hz, 1H, CH), 2.27 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 176.3, 171.2, 165.8, 160.7, 141.2, 141.1, 137.5, 135.6, 133.9, 133.2, 133.1, 131.5, 129.7, 129.1, 128.9, 128.4, 127.8, 127.7, 127.5, 127.0, 124.5, 111.5, 110.3, 52.2, 51.1, 44.4, 36.8, 21.3 ppm; IR (KBr) ν : 2925, 2854, 1721, 1608, 1483, 1436, 1342, 1171, 812cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{35}\text{H}_{29}\text{ClN}_3\text{O}_4$ ($[\text{M}+\text{H}]^+$): 590.1841, Found: 590.1849.

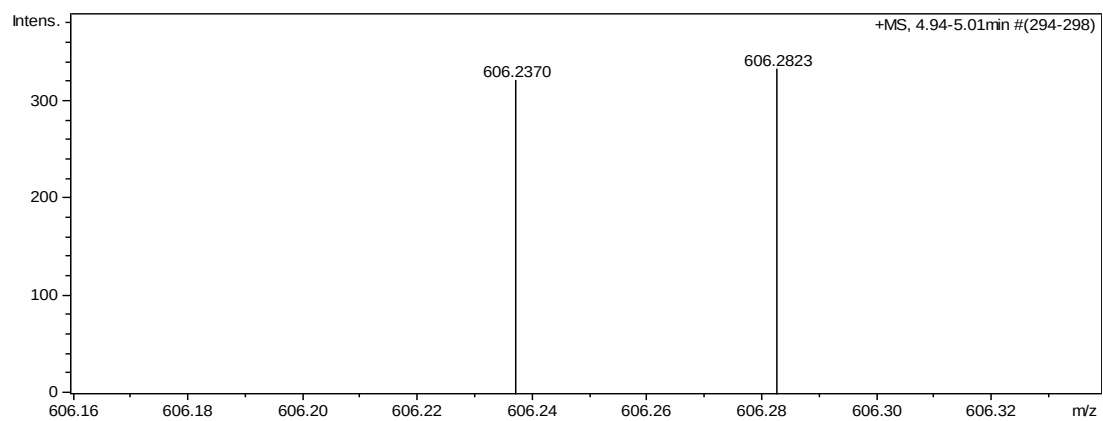
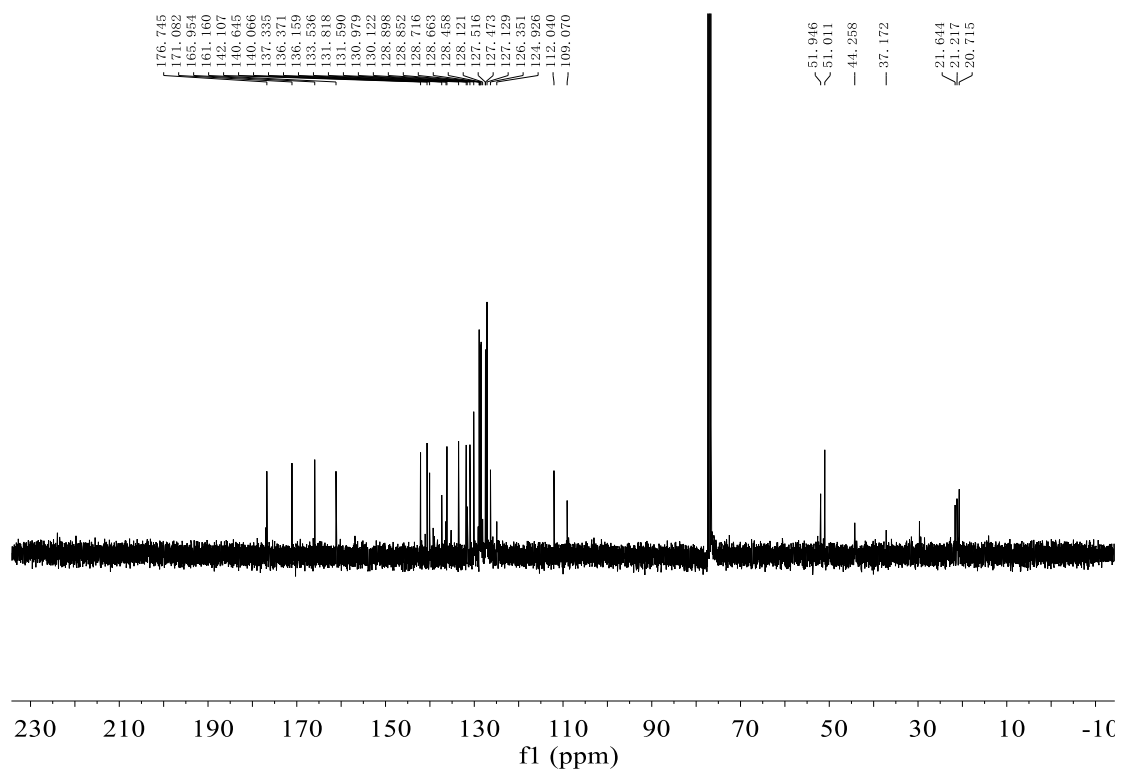




Methyl 1-benzyl-5-methyl-1'-(4-methylbenzoyl)-2-oxo-3'-(p-tolyl)-1',4'-

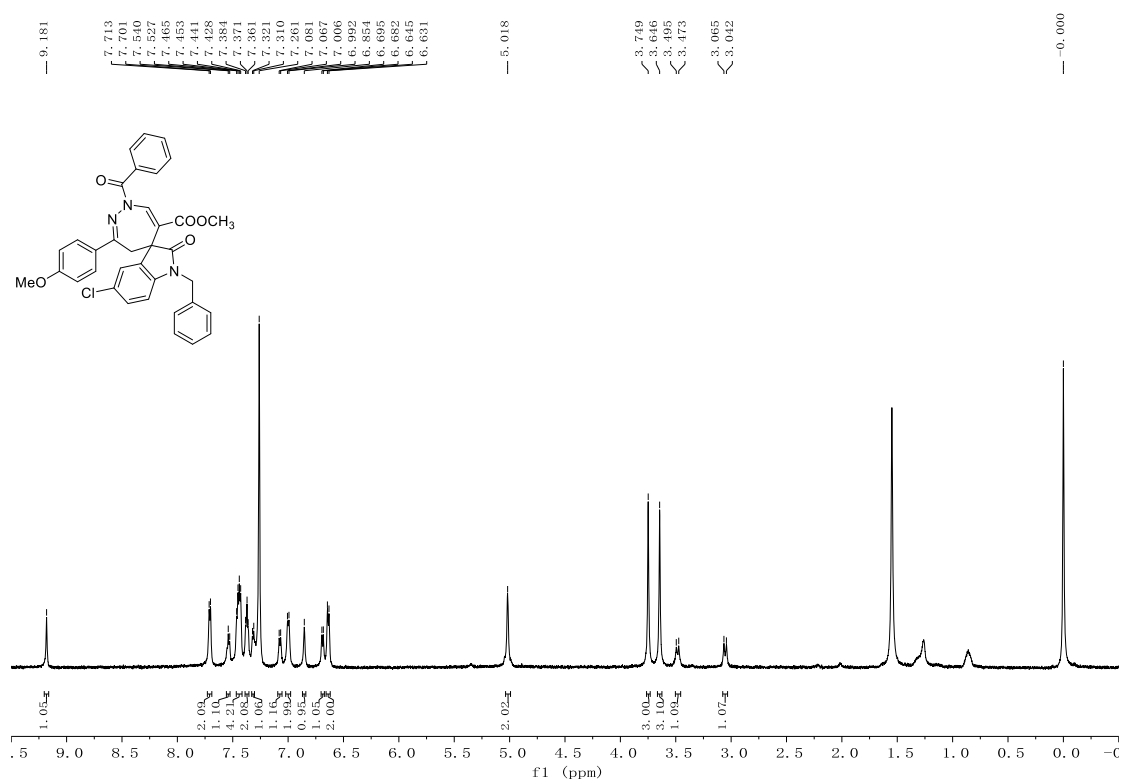
dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carboxylate (5e): yellow solid, 0.426 g, 73%, m.p. 201-202 °C; ^1H NMR (600 MHz, CDCl_3) δ : 9.18 (s, 1H, ArH), 7.64 (d, $J = 7.2$ Hz, 2H, ArH), 7.45-7.43 (m, 2H, ArH), 7.37-7.32 (m, 2H, ArH), 7.30-7.28 (m, 1H, ArH), 7.26-7.24 (m, 2H, ArH), 6.97-6.95 (m, 2H, ArH), 6.94-6.92 (m, 2H, ArH), 6.90-6.88 (m, 1H, ArH), 6.69 (s, 1H, ArH), 6.66-6.65 (m, 1H, ArH), 5.05-4.98 (m, 2H, CH_2), 3.61 (s, 3H, OCH_3), 3.48 (d, $J = 12.6$ Hz, 1H, CH), 3.05 (d, $J = 13.2$ Hz, 1H, CH), 2.43 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.95 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 176.74, 171.08, 165.95, 161.16, 142.11, 140.65, 140.07, 137.34, 136.37, 136.16, 133.54, 131.82, 131.59, 130.98, 130.12, 128.90, 128.85, 128.72, 128.66, 128.46, 128.12, 127.52, 127.47, 127.13, 126.35, 124.93, 112.04, 109.07, 51.95, 51.01, 44.26, 37.17, 21.64, 21.22, 20.72 ppm; IR (KBr) ν : 2925, 2855, 1716, 1602, 1497, 1449, 1347, 1281, 1189, 1138, 857, 786cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{37}\text{H}_{33}\text{N}_3\text{O}_4\text{Na}$ ($[\text{M}+\text{Na}]^+$): 606.2363, Found: 606.2370.

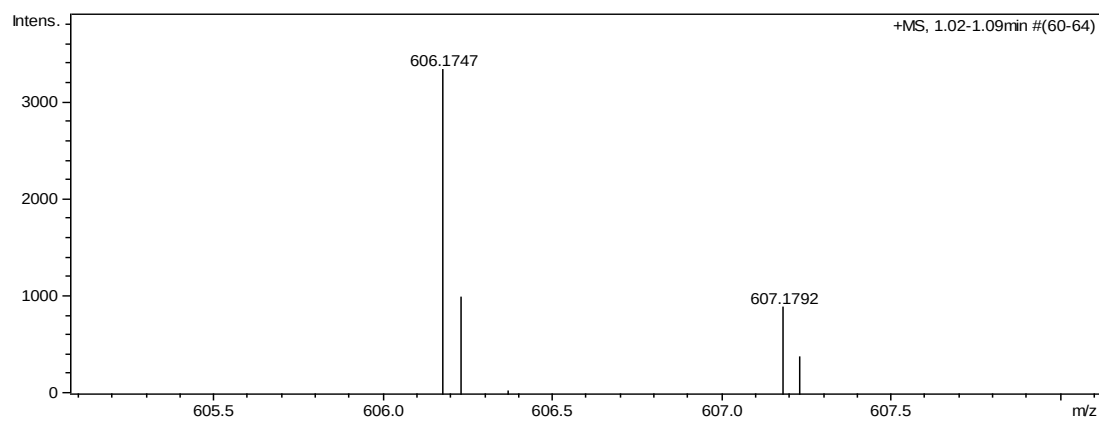
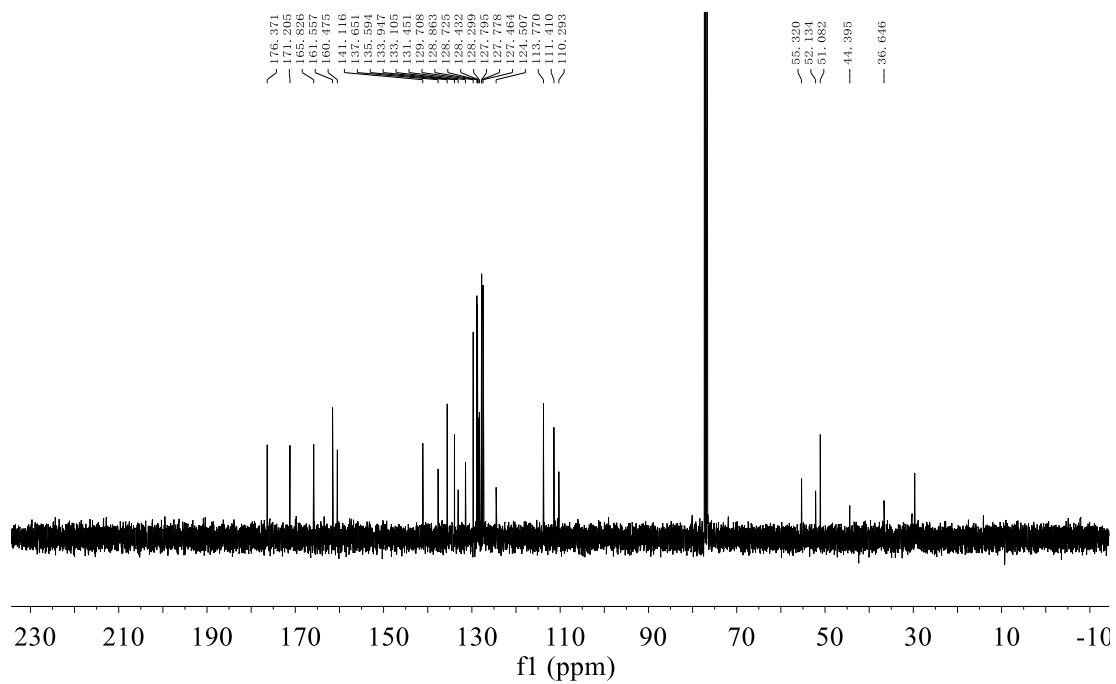




Methyl 1'-benzoyl-1-benzyl-5-chloro-3'-(4-methoxyphenyl)-2-oxo-1',4'-

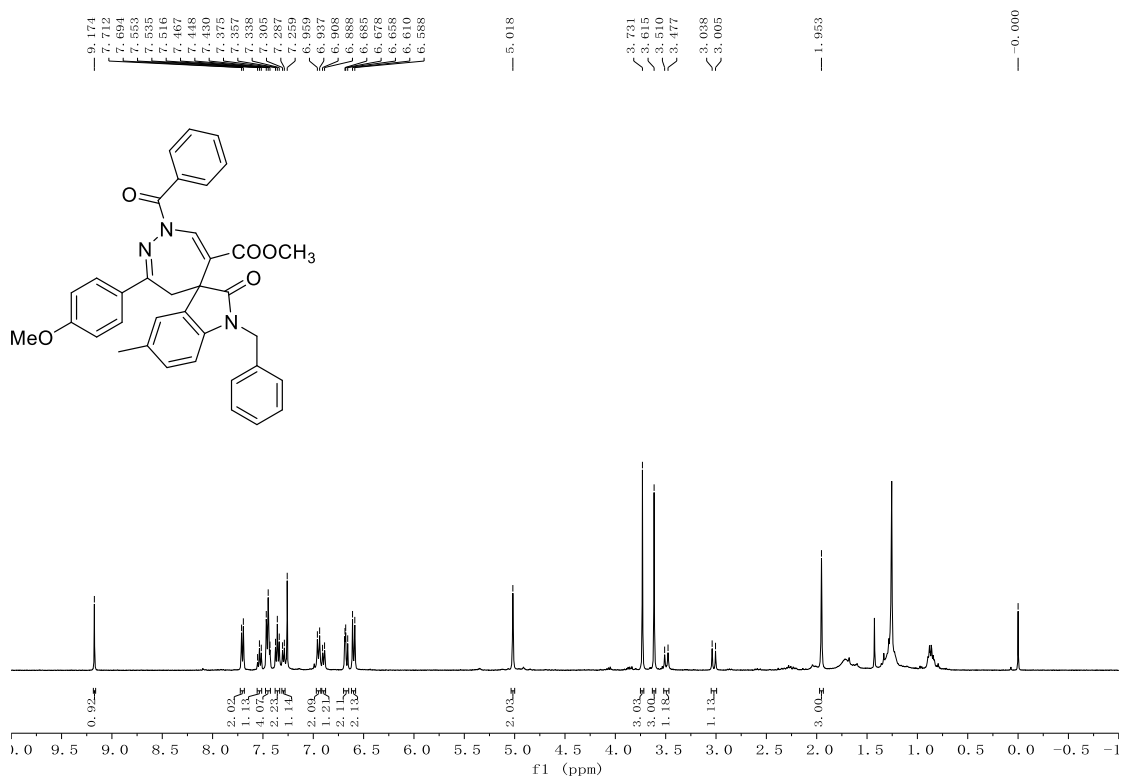
dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carboxylate (5f): yellow solid, 0.466 g, 77%, m.p. 136-137 °C; ^1H NMR (600 MHz, CDCl_3) δ : 9.18 (s, 1H, ArH), 7.71 (d, $J = 7.2\text{ Hz}$, 2H, ArH), 7.54-7.52 (m, 1H, ArH), 7.47-7.42 (m, 4H, ArH), 7.38-7.36 (m, 2H, ArH), 7.33-7.31 (m, 1H, ArH), 7.08-7.06 (m, 1H, ArH), 7.01-6.99 (m, 2H, ArH), 6.85 (s, 1H, ArH), 6.69 (d, $J = 7.8\text{ Hz}$, 1H, ArH), 6.64 (d, $J = 8.4\text{ Hz}$, 2H, ArH), 5.02 (s, 2H, CH_2), 3.75 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.48 (d, $J = 13.2\text{ Hz}$, 1H, CH), 3.05 (d, $J = 13.8\text{ Hz}$, 1H, CH) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 176.4, 171.2, 165.8, 161.6, 160.5, 141.1, 137.7, 135.6, 134.0, 133.1, 131.5, 129.7, 128.9, 128.7, 128.4, 128.3, 127.8, 127.7, 127.5, 124.5, 113.8, 111.4, 110.3, 55.3, 52.1, 51.1, 44.4, 29.7 ppm; IR (KBr) ν : 2927, 2851, 1718, 1600, 1498, 1444, 1351, 1282, 1189, 1143, 857, 788 cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{35}\text{H}_{29}\text{ClN}_3\text{O}_5$ ($[\text{M}+\text{H}]^+$): 606.1790, Found: 606.1747.

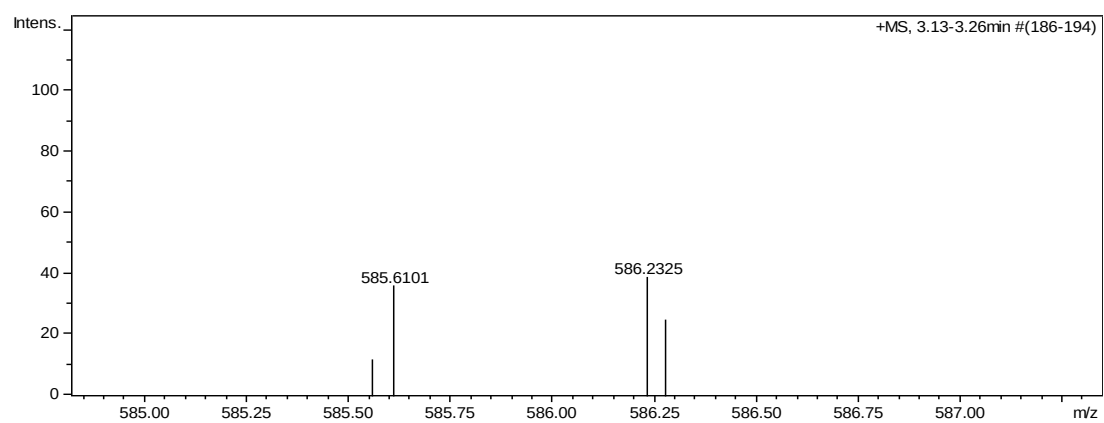
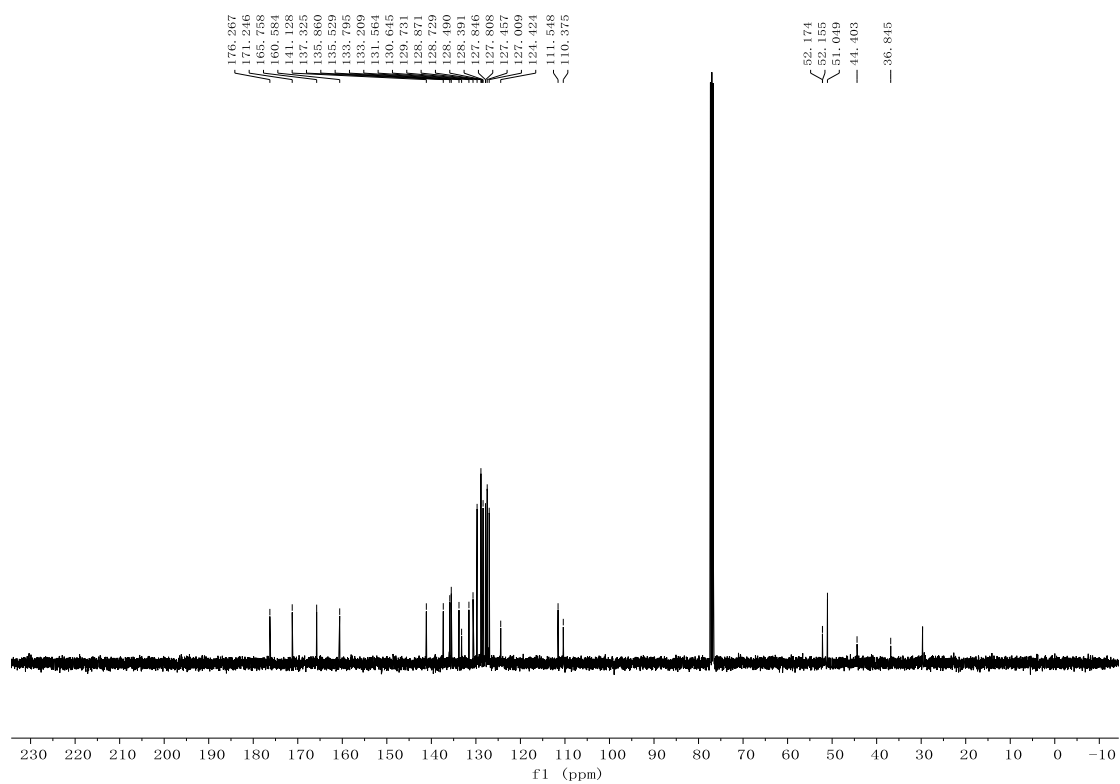




Methyl 1'-benzoyl-1-benzyl-3'-(4-methoxyphenyl)-5-methyl-2-oxo-1',4'-

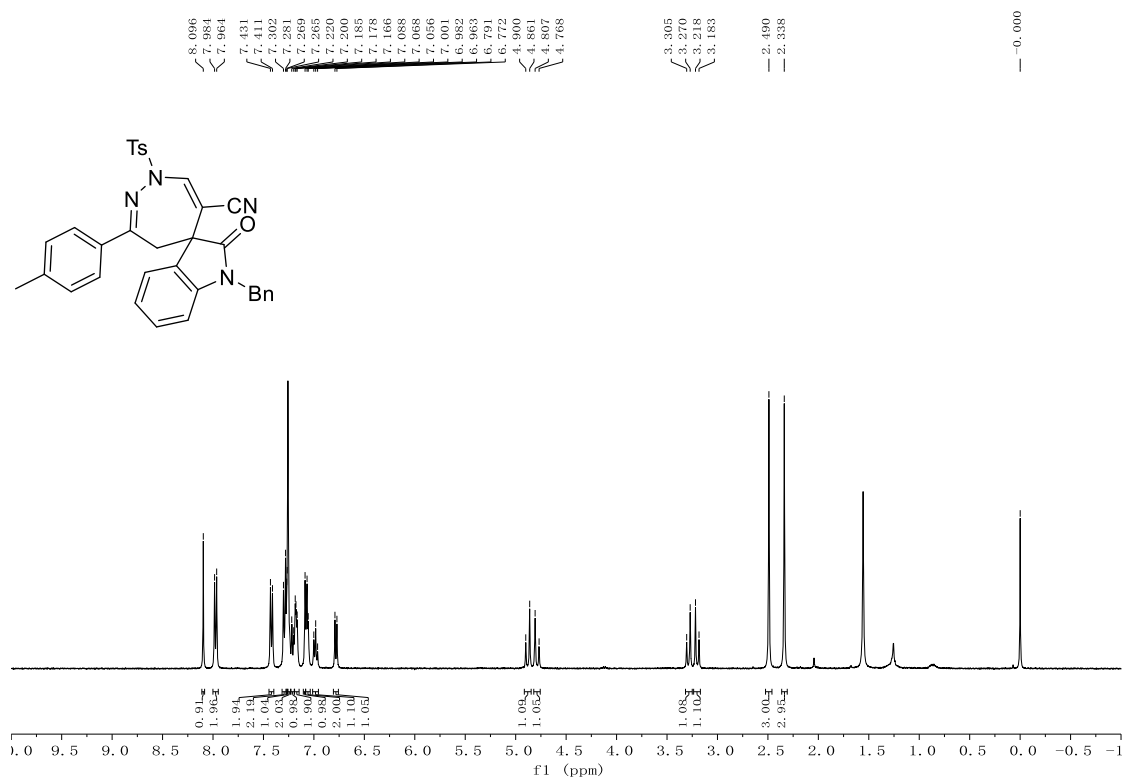
dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carboxylate (5g): yellow solid, 0.356 g, 63%, m.p. 184-187 °C; ^1H NMR (400 MHz, CDCl_3) δ : 9.17 (s, 1H, ArH), 7.71-7.69 (m, 2H, ArH), 7.55-7.52 (m, 1H, ArH), 7.47-7.44 (m, 4H, ArH), 7.38-7.34 (m, 2H, ArH), 7.31-7.29 (m, 1H, ArH), 6.95 (d, $J = 8.8$ Hz, 2H, ArH), 6.90 (d, $J = 8.0$ Hz, 1H, ArH), 6.69-6.66 (m, 2H, ArH), 6.60 (d, $J = 8.8$ Hz, 2H, ArH), 5.02 (s, 2H, CH_2), 3.73 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.50 (d, $J = 13.2$ Hz, 1H, CH), 3.03 (d, $J = 13.2$ Hz, 1H, CH), 1.95 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ : 176.3, 171.3, 165.8, 160.6, 141.1, 137.3, 135.9, 135.5, 133.8, 133.2, 131.6, 130.6, 129.7, 128.9, 128.7, 128.5, 128.4, 127.9, 127.8, 127.5, 127.0, 124.4, 111.6, 110.4, 52.2, 52.2, 51.1, 44.4, 36.9 ppm; IR (KBr) ν : 2923, 2851, 1716, 1603, 1497, 1438, 1348, 1282, 1189, 1142, 857, 783 cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{36}\text{H}_{32}\text{N}_3\text{O}_5$ ($[\text{M}+\text{H}]^+$): 586.2336, Found: 586.2325.

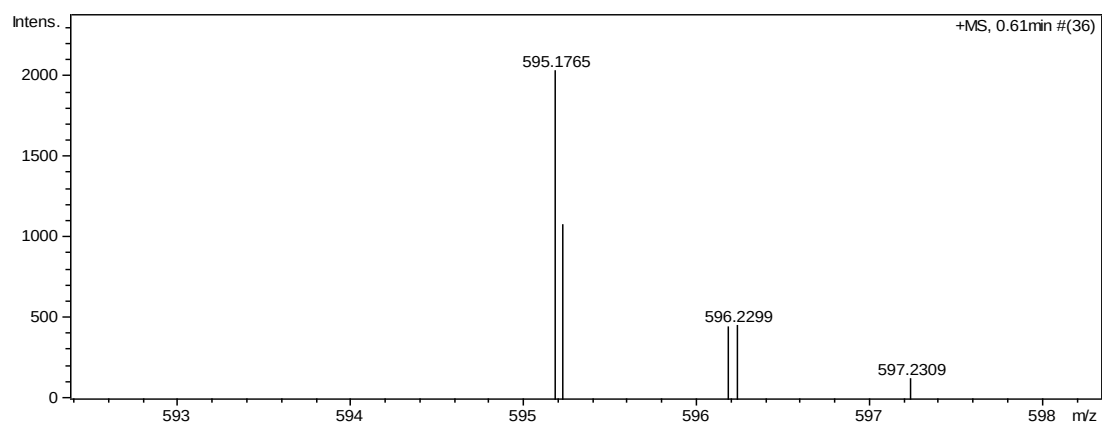
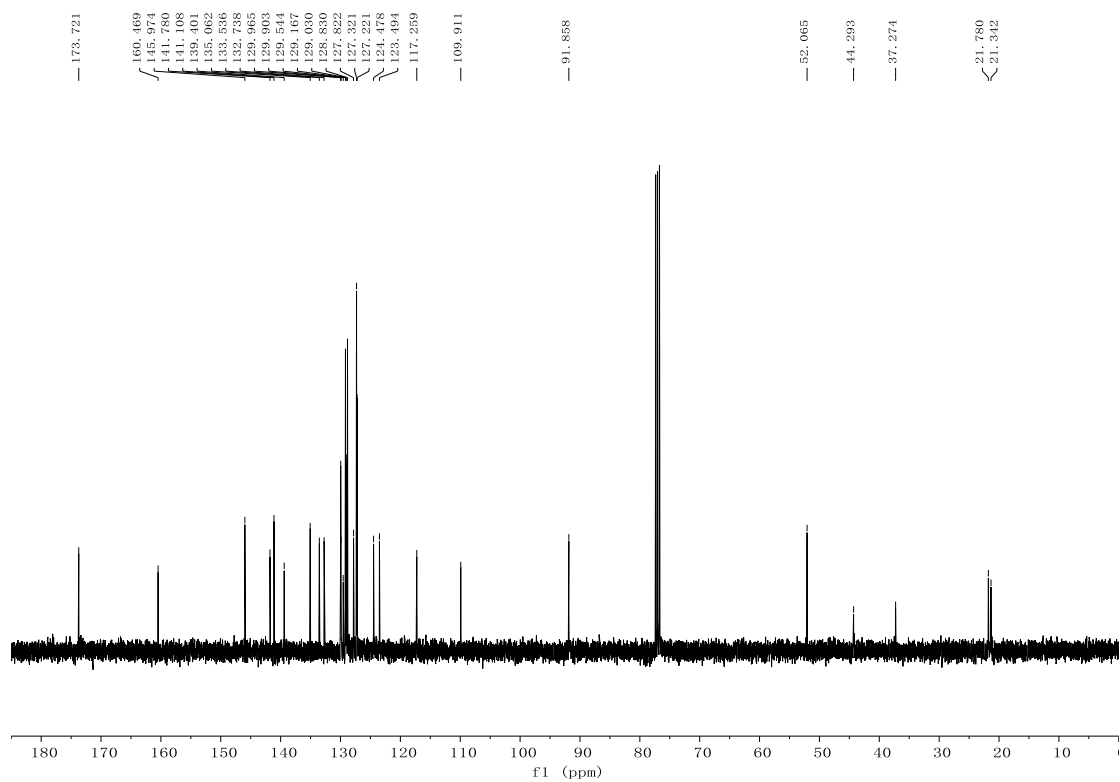




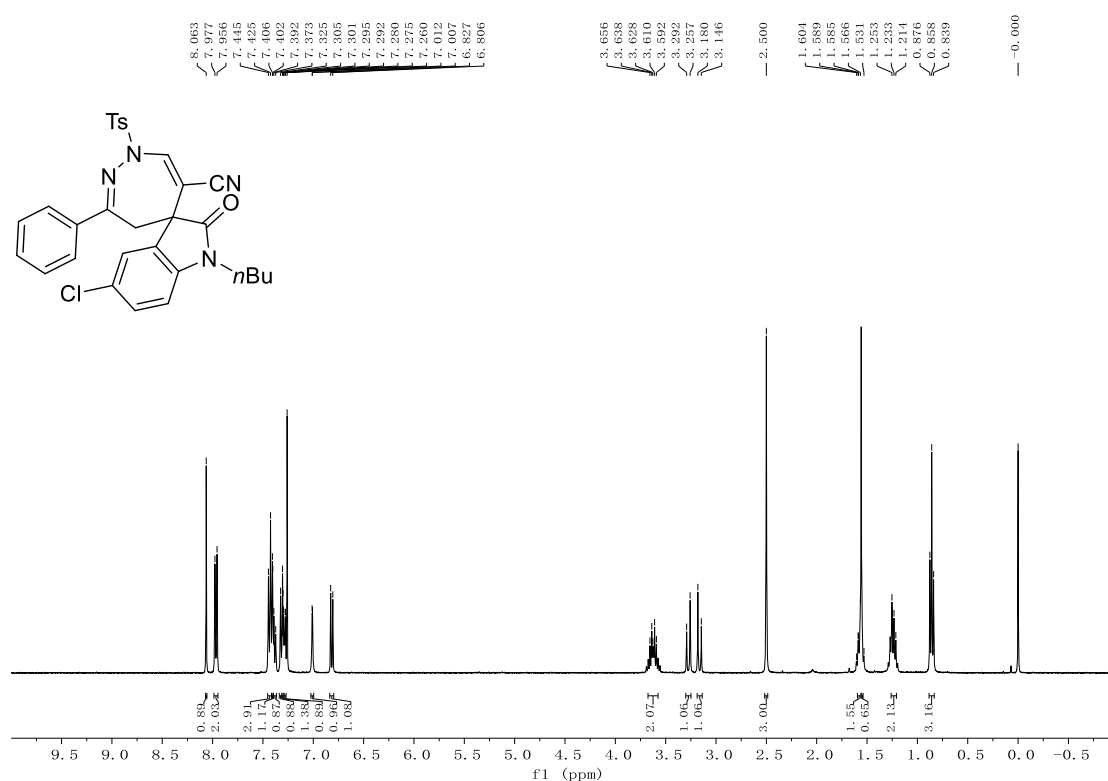
1-Benzyl-2-oxo-3'-(p-tolyl)-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-

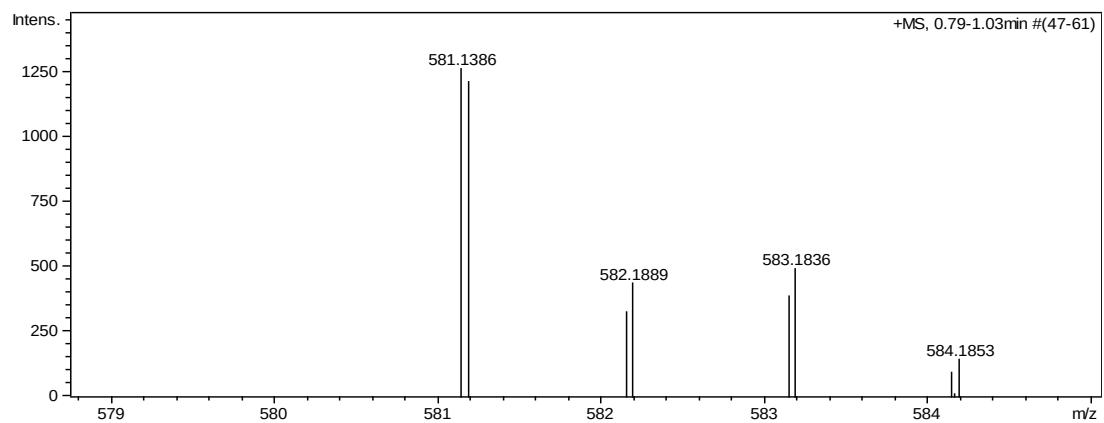
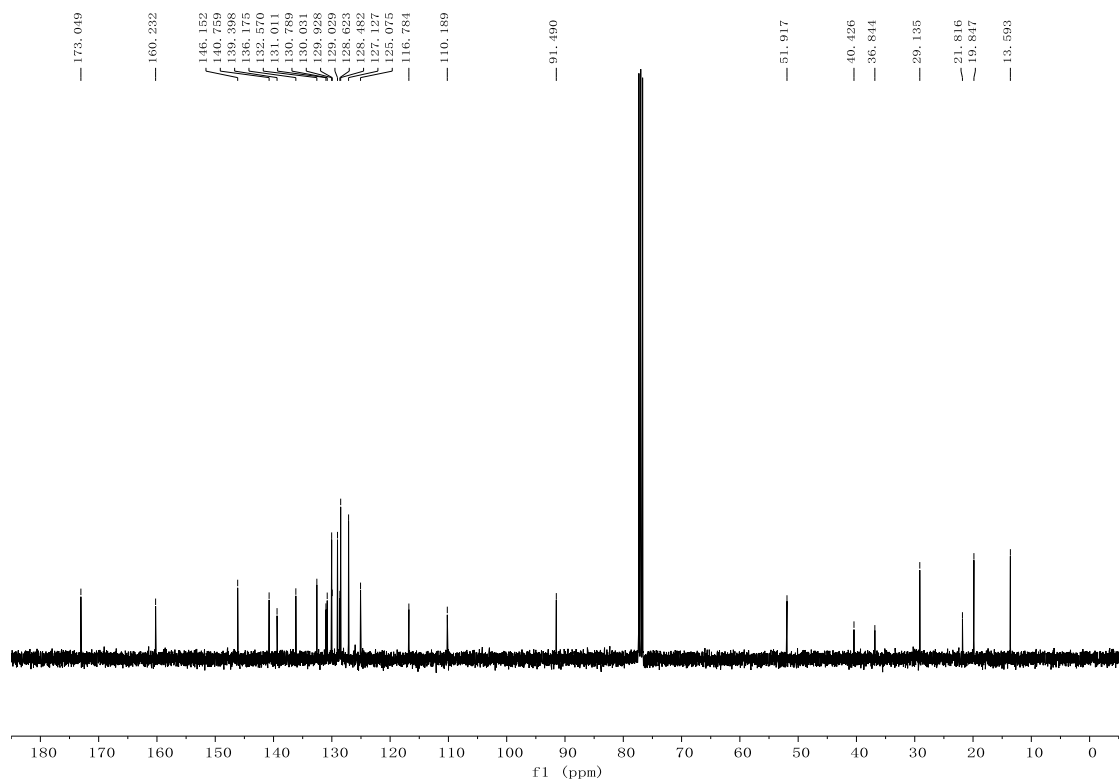
carbonitrile (7a): white solid, 64%, m.p. 226-230 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.10 (s, 1H, C=CH-N), 7.97 (d, J = 8.0 Hz, 2H, ArH), 7.42 (d, J = 8.0 Hz, 2H, ArH), 7.29 (d, J = 8.4 Hz, 2H, ArH), 7.28-7.26 (s, 1H, ArH), 7.26-7.24 (m, 2H, ArH), 7.22-7.20 (m, 1H, ArH), 7.19-7.16 (m, 2H, ArH), 7.09 (s, 1H, ArH), 7.06 (d, J = 4.8 Hz, 2H, ArH), 6.98 (t, J = 7.6 Hz, 1H, ArH), 6.78 (d, J = 7.6 Hz, 1H, ArH), 4.88 (d, J = 15.6 Hz, 1H, CH), 4.79 (d, J = 15.6 Hz, 1H, CH), 3.29 (d, J = 10.0 Hz, 1H, CH), 3.20 (d, J = 10.0 Hz, 1H, CH), 2.49 (s, 3H, CH_3), 2.34 (s, 3H, CH_3) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 173.7, 160.5, 145.9, 141.8, 141.1, 139.4, 135.1, 133.5, 132.7, 129.9, 129.9, 129.5, 129.2, 129.0, 128.8, 127.8, 127.3, 127.2, 124.5, 123.5, 117.3, 109.9, 91.9, 52.1, 44.3, 37.3, 21.8, 21.3 ppm; IR (KBr) ν : 3057, 3055, 2928, 2217, 1716, 1613, 1488, 1467, 1449, 1369, 1297, 1259, 1189, 1175, 1090, 1021, 999, 869, 804, 764, 754, 696, 667, 657, 639 cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{34}\text{H}_{28}\text{ClN}_4\text{O}_3\text{SNa}$ ($[\text{M}+\text{Na}]^+$): 595.1774, Found: 595.1765.





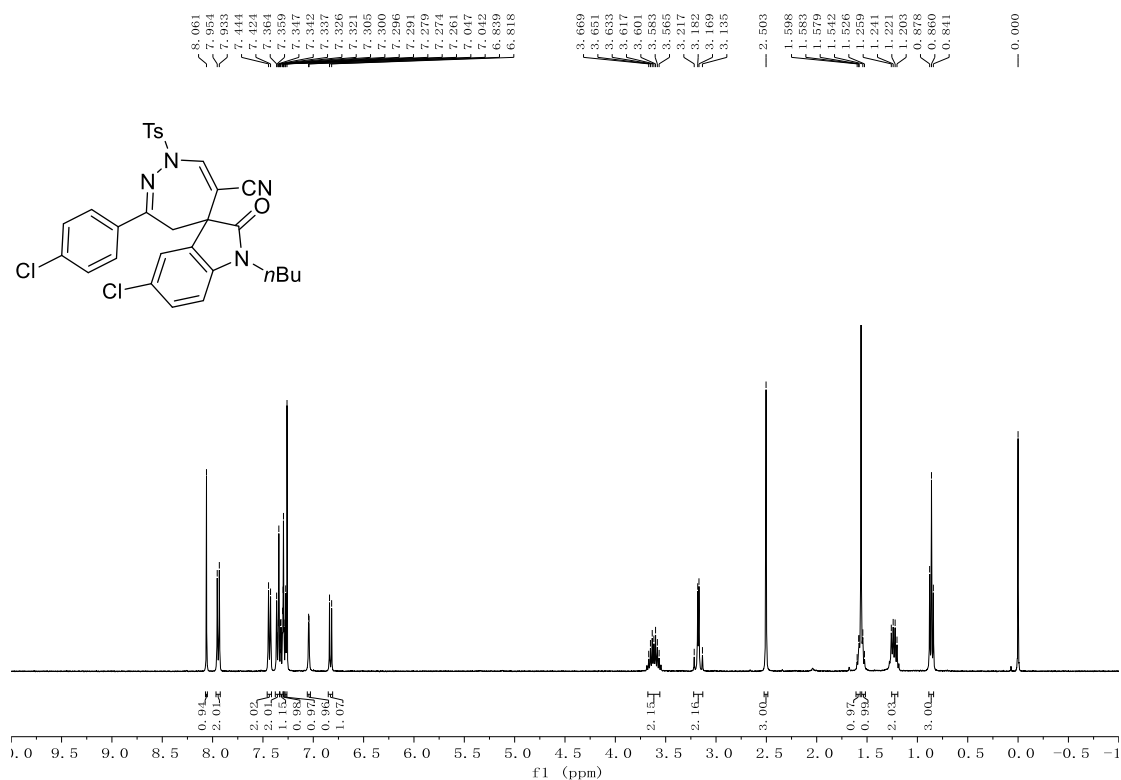
1-Butyl-5-chloro-2-oxo-3'-phenyl-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carbonitrile (7b): white solid, 76%, m.p. 224-228 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.06 (s, 1H, C=CH-N), 7.97 (d, J = 8.4 Hz, 2H, ArH), 7.45-7.42 (m, 3H, ArH), 7.41-7.40 (m, 1H, ArH), 7.39-7.37 (m, 1H, ArH), 7.33-7.31 (m, 1H, ArH), 7.30-7.29 (m, 1H, ArH), 7.28-7.27 (m, 1H, ArH), 7.10 (d, J = 2.0 Hz, 1H, ArH), 6.82 (d, J = 8.4 Hz, 1H, ArH), 3.65-3.60 (m, 2H, CH_2), 3.28 (d, J = 14.0 Hz, 1H, CH), 3.16 (d, J = 13.6 Hz, 1H, CH), 2.50 (s, 3H, CH_3), 1.60-1.53 (m, 2H, CH_2), 1.23 (t, J = 8.0 Hz, 2H, CH_2), 0.86 (t, J = 7.2 Hz, 3H, CH_3) ppm; ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ : 173.1, 160.2, 146.2, 140.8, 139.4, 136.2, 132.6, 131.0, 130.8, 130.0, 129.9, 129.0, 128.6, 128.5, 127.1, 125.1, 116.8, 110.2, 91.5, 51.9, 40.4, 36.8, 29.1, 21.8, 19.9, 13.6 ppm; IR (KBr) ν : 3061, 2957, 2932, 2872, 2215, 1719, 1618, 1595, 1483, 1446, 1428, 1370, 1296, 1189, 1174, 1109, 1088, 994, 886, 813, 759, 698, 658, 606 cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{30}\text{H}_{27}\text{ClN}_4\text{O}_3\text{SNa}$ ($[\text{M}+\text{Na}]^+$): 581.1385, Found: 581.1386.

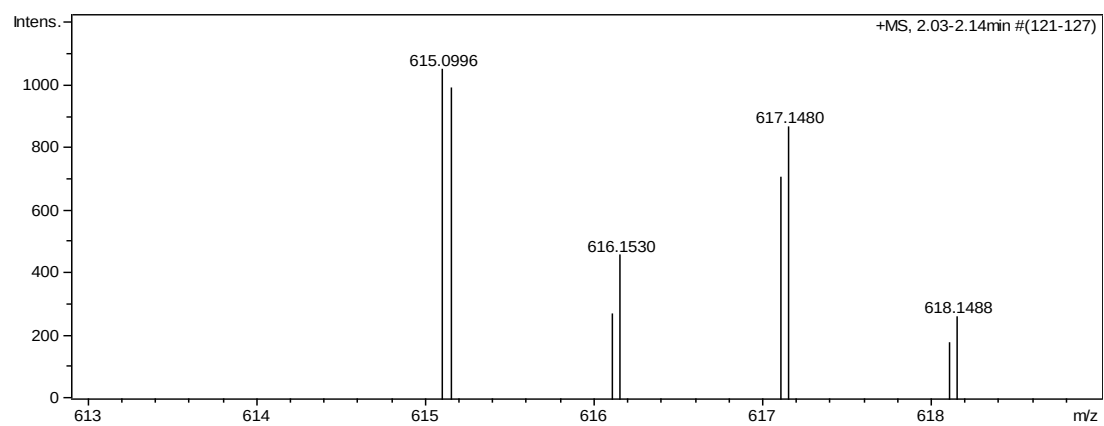
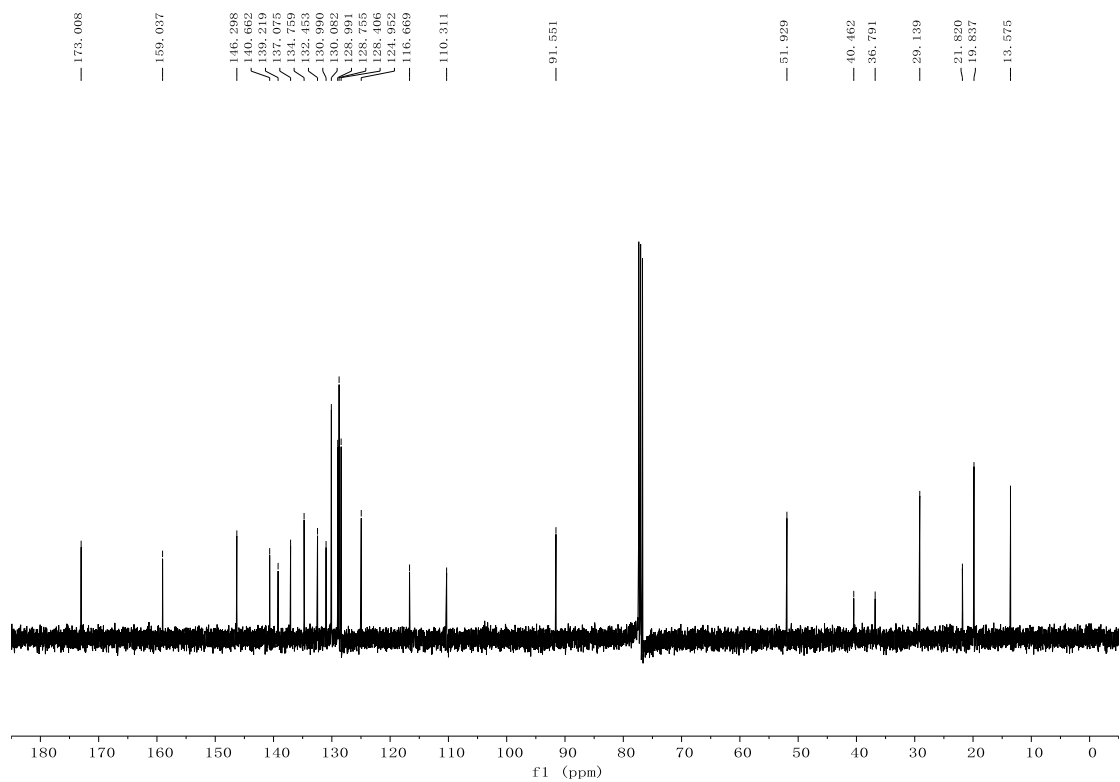




1-Butyl-5-chloro-3'-(4-chlorophenyl)-2-oxo-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-

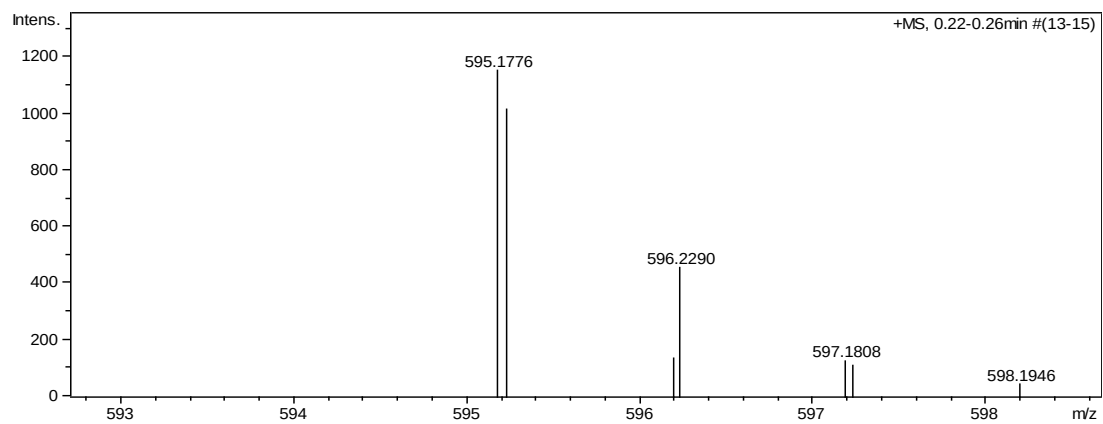
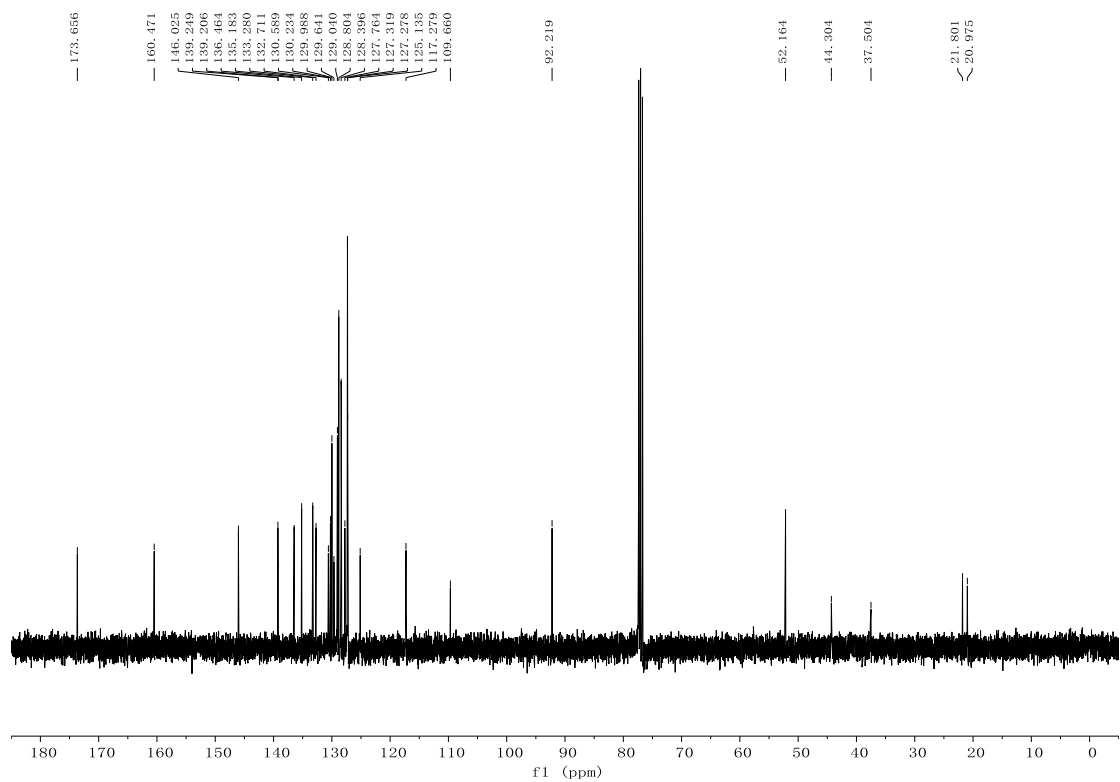
[1,2]diazepine]-6'-carbonitrile (7c): white solid, 83%, m.p. 208-213 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.06 (s, 1H, C=CH-N), 7.94 (d, *J* = 8.4 Hz, 2H, ArH), 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 7.36-7.34 (m, 2H, ArH), 7.33-7.31 (m, 1H, ArH), 7.30-7.29 (m, 1H, ArH), 7.28-7.27 (m, 1H, ArH), 7.04 (d, *J* = 2.0 Hz, 1H, ArH), 6.83 (d, *J* = 8.4 Hz, 1H, ArH), 3.67-3.57 (m, 2H, CH₂), 3.20 (d, *J* = 14.0 Hz, 1H, CH), 3.15 (d, *J* = 13.6 Hz, 1H, CH), 2.50 (s, 3H, CH₃), 1.60-1.53 (m, 2H, CH₂), 1.26-1.20 (m, 2H, CH₂), 0.86 (t, *J* = 7.6 Hz, 3H, CH₃) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃) δ: 173.0, 159.0, 146.3, 140.7, 139.2, 137.1, 134.8, 132.5, 131.0, 130.1, 129.0, 128.8, 128.4, 125.0, 116.7, 110.3, 91.6, 51.9, 40.5, 36.8, 29.1, 21.8, 19.8, 13.6 ppm; IR (KBr) ν: 3072, 2958, 2931, 2871, 2213, 1715, 1625, 1594, 1484, 1429, 1398, 1362, 1292, 1263, 1230, 1212, 1189, 1174, 1142, 1108, 1089, 1011, 999, 890, 831, 812, 761, 750, 728, 715, 701, 682, 660, 584 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₀H₂₆ClN₄O₃SNa ([M+Na]⁺): 615.0995, Found: 615.0996.





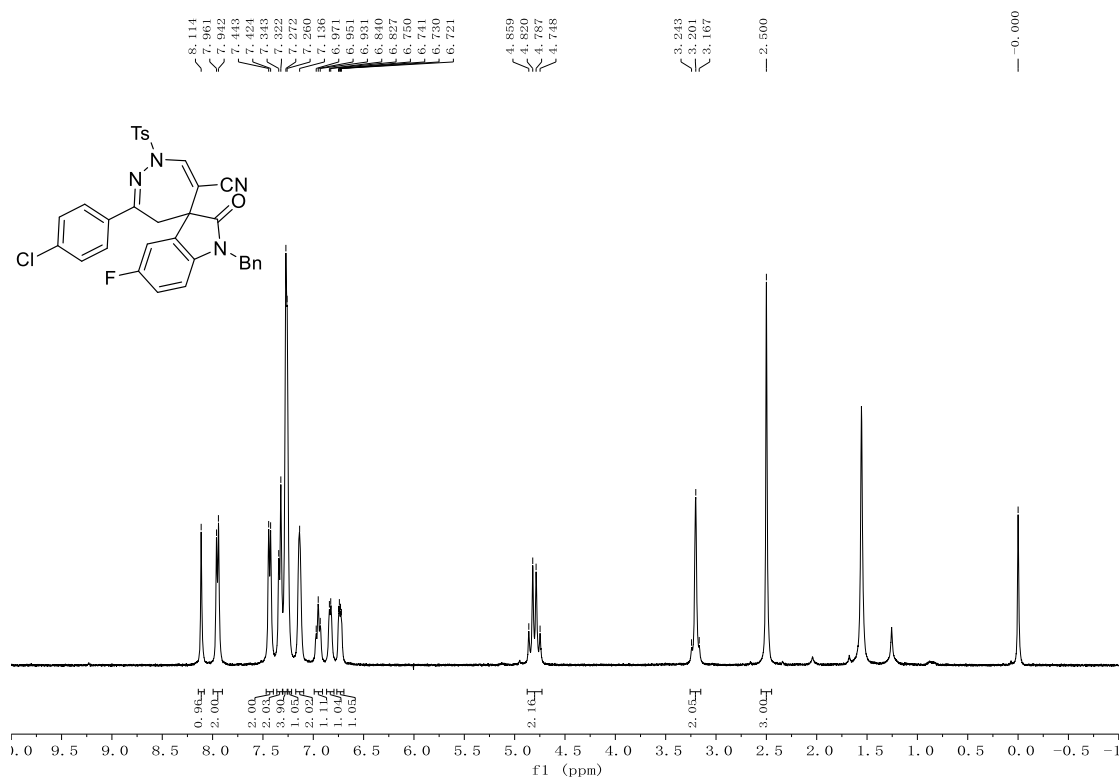
Chemical structure of compound 10 is shown above the spectrum. The spectrum displays peaks from 0 to 10 ppm. Aromatic and heterocyclic protons appear between 6.5 and 8.1 ppm. A methine proton is at 4.715 ppm. A methoxy singlet is at 3.233 ppm. A methyl singlet is at 2.211 ppm. Integration values are provided below the baseline.

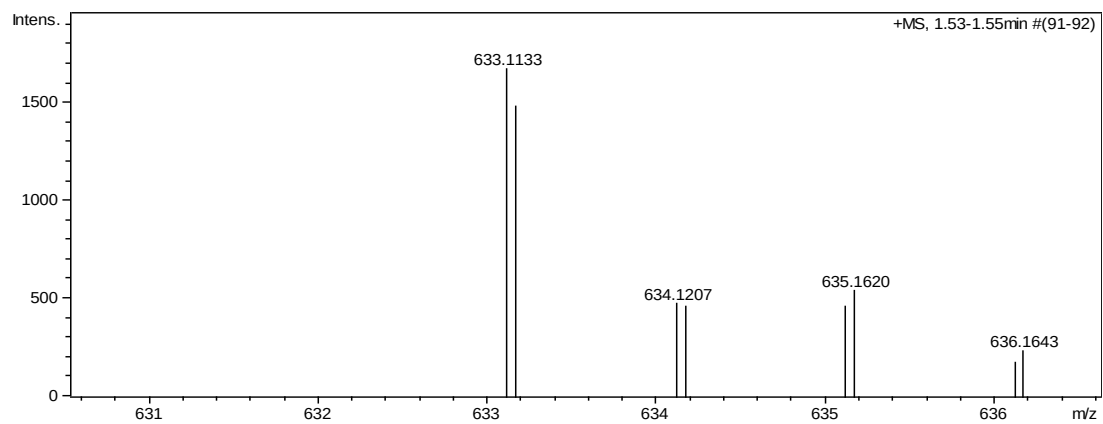
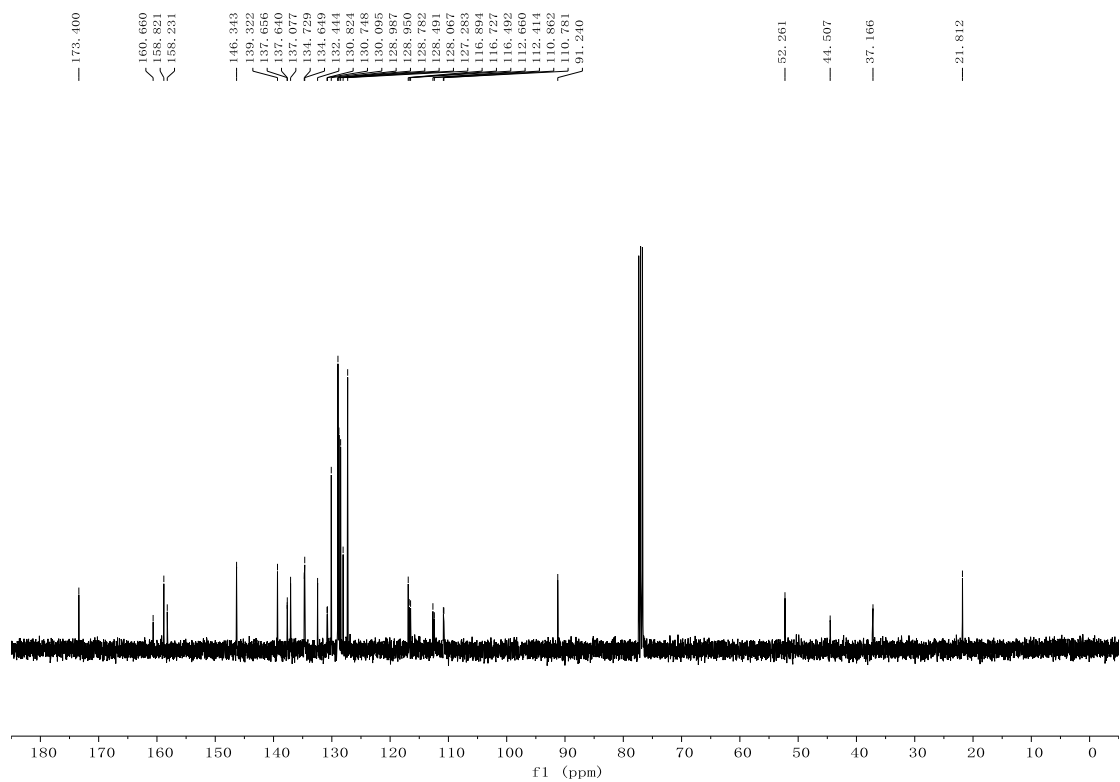
Chemical Shift (ppm)	Integration
8.098	0.93
7.989	1.95
7.437	4.00
7.418	0.92
7.401	1.93
7.382	2.92
7.300	2.01
7.257	1.06
7.234	1.00
7.151	1.00
7.144	1.00
7.133	1.00
7.025	1.00
6.912	1.00
6.877	1.00
6.657	1.00
4.871	1.06
4.832	1.07
4.753	1.07
4.715	1.07
3.275	0.91
3.239	0.96
3.233	0.96
3.197	0.96
2.491	2.94
2.211	3.00



1-Benzyl-3'-(4-chlorophenyl)-5-fluoro-2-oxo-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-

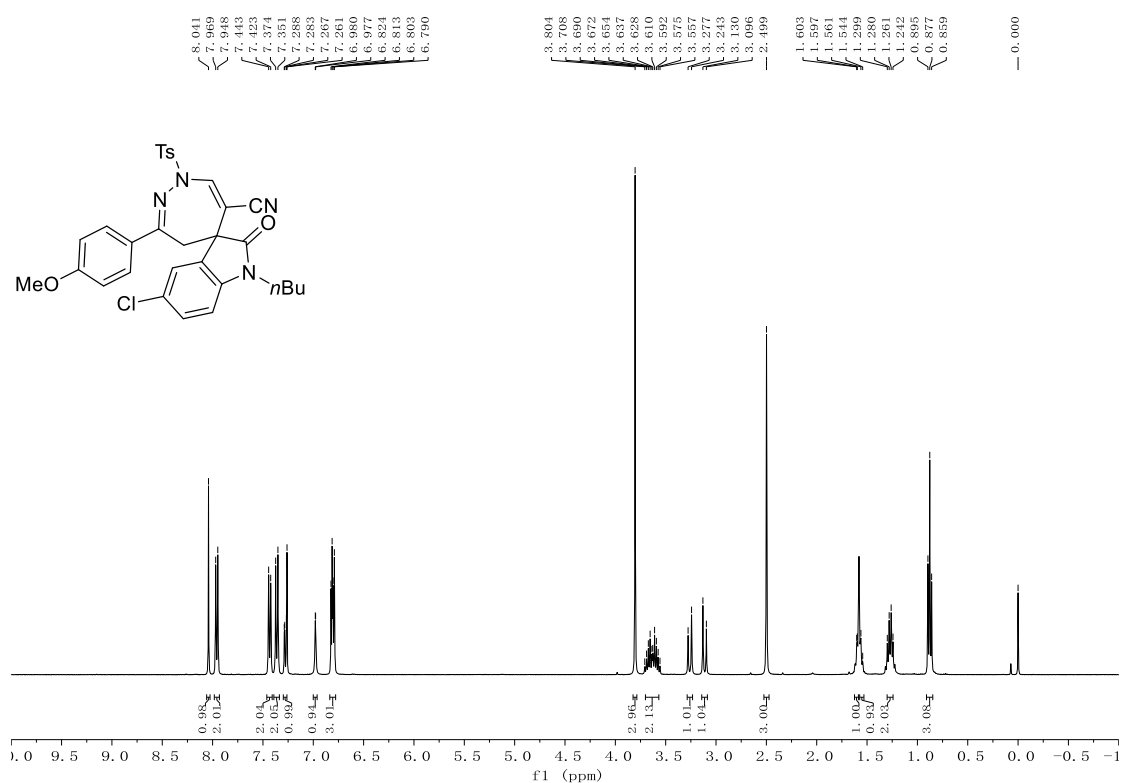
[1,2]diazepine]-6'-carbonitrile (7e): white solid, 60%, m.p. 175-179 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.11 (s, 1H, C=CH-N), 7.95 (d, *J* = 7.6 Hz, 2H, ArH), 7.43 (d, *J* = 7.6 Hz, 2H, ArH), 7.33 (d, *J* = 7.6 Hz, 2H, ArH), 7.27-7.26 (m, 4H, ArH), 7.25-7.24 (m, 1H, ArH), 7.14 (s, 2H, ArH), 6.95 (t, *J* = 8.0 Hz, 1H, ArH), 6.83 (d, *J* = 4.2 Hz, 1H, ArH), 6.75-6.73 (m, 1H, ArH), 4.85 (d, *J* = 15.6 Hz, 1H, CH), 4.77 (d, *J* = 15.6 Hz, 1H, CH), 3.24-3.17 (m, 2H, CH₂), 2.50 (s, 3H, CH₃) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃) δ: 173.4, 159.4 (d, *J* = 243 Hz), 158.2, 146.3, 139.3, 137.7, 137.6, 137.1, 134.7, 134.7, 132.4, 130.8 (d, *J* = 7.6 Hz), 130.1, 129.0, 129.0, 128.8, 128.5, 128.1, 127.3, 116.9, 116.7 (d, *J* = 23.5 Hz), 112.5 (d, *J* = 24.6 Hz), 110.8 (d, *J* = 8.1 Hz), 91.2, 52.3, 44.5, 37.2, 21.8 ppm; IR (KBr) ν: 3063, 2921, 2212, 1718, 1619, 1594, 1492, 1454, 1437, 1400, 1360, 1292, 1268, 1234, 1215, 1188, 1173, 1088, 1011, 1001, 991, 887, 839, 828, 812, 772, 729, 701, 687, 660 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₃H₂₄ClFN₄O₃SNa ([M+Na]⁺): 633.1134, Found: 633.1133.

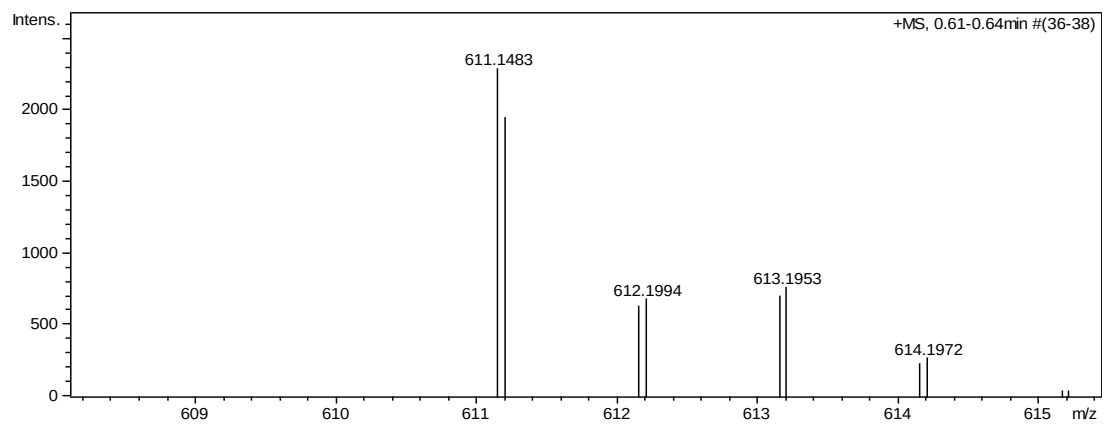
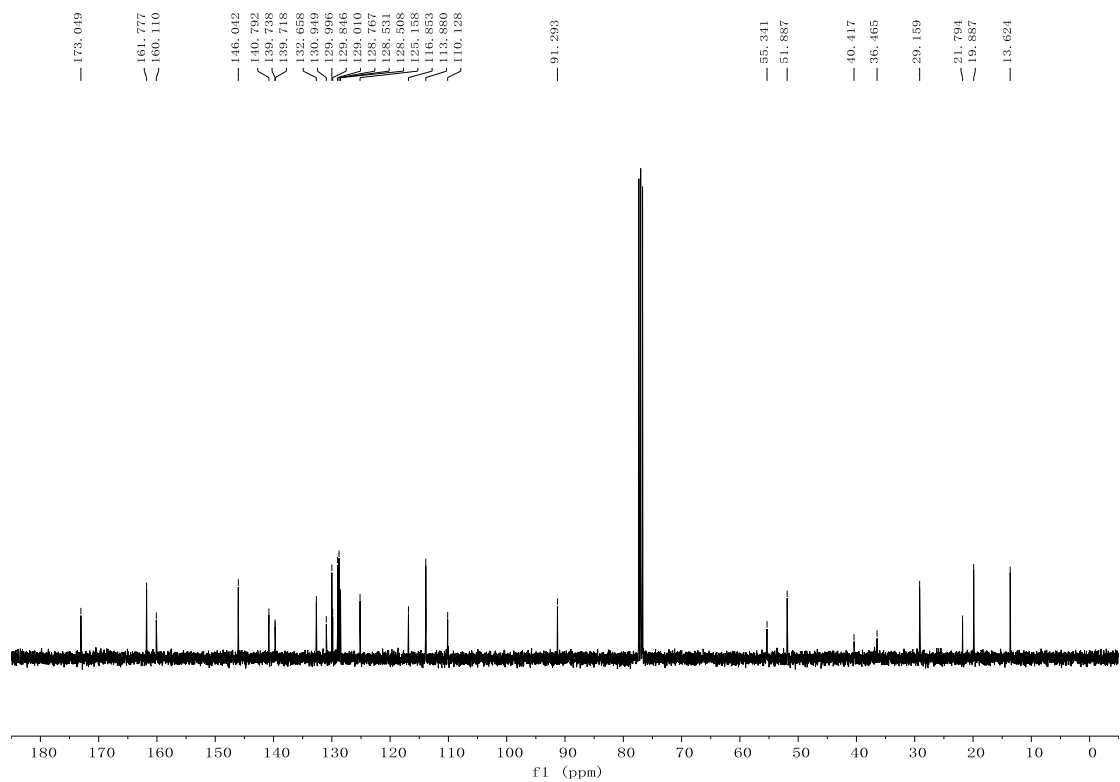




1-Butyl-5-chloro-3'-(4-methoxyphenyl)-2-oxo-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-

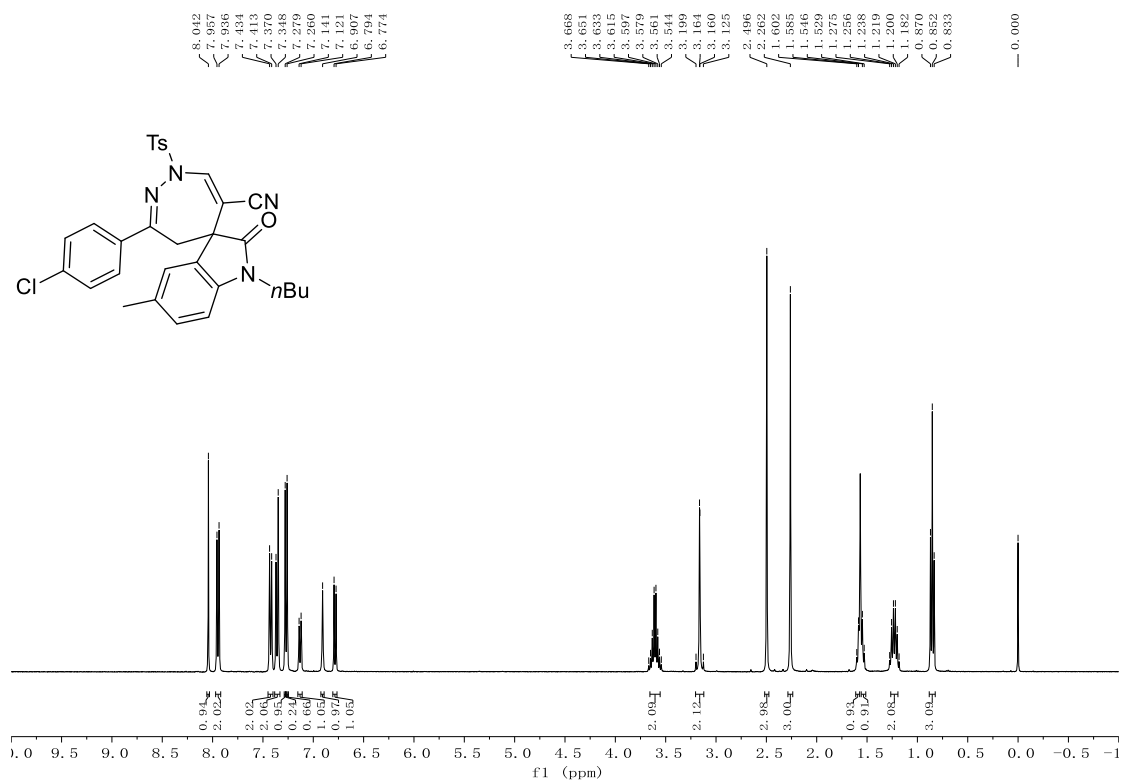
[1,2]diazepine]-6'-carbonitrile (7f): white solid, 79%, m.p. 223-227 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (s, 1H, C=CH-N), 7.96 (d, $J = 8.4$ Hz, 2H, ArH), 7.43 (d, $J = 8.0$ Hz, 2H, ArH), 7.36 (d, $J = 9.2$ Hz, 2H, ArH), 7.28-7.26 (m, 1H, ArH), 6.98-6.97 (m, 1H, ArH), 6.81 (d, $J = 8.4$ Hz, 1H, ArH), 6.80 (d, $J = 9.2$ Hz, 2H, ArH), 3.80 (s, 3H, OCH_3), 3.71-3.56 (m, 2H, CH_2), 3.26 (d, $J = 13.6$ Hz, 1H, CH), 3.11 (d, $J = 13.6$ Hz, 1H, CH), 2.50 (s, 3H, CH_3), 1.56-1.53 (m, 2H, CH_2), 1.30-1.24 (m, 2H, CH_2), 0.88 (t, $J = 7.2$ Hz, 3H, CH_3) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 173.1, 161.8, 160.1, 146.0, 140.8, 139.7, 139.7, 132.7, 131.0, 130.0, 129.9, 129.0, 128.8, 128.5, 128.5, 125.2, 116.9, 113.9, 110.1, 91.3, 55.3, 51.9, 40.4, 36.5, 29.2, 21.8, 19.9, 13.6 ppm; IR (KBr) ν : 302, 2962, 2928, 2871, 2827, 2213, 1715, 1614, 1592, 1481, 1441, 1422, 1370, 1292, 1185, 1173, 1088, 992, 884, 811, 756, 695, 656, 603 cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{31}\text{H}_{29}\text{ClN}_4\text{O}_4\text{SNa}$ ($[\text{M}+\text{Na}]^+$): 611.1490, Found: 611.1483.

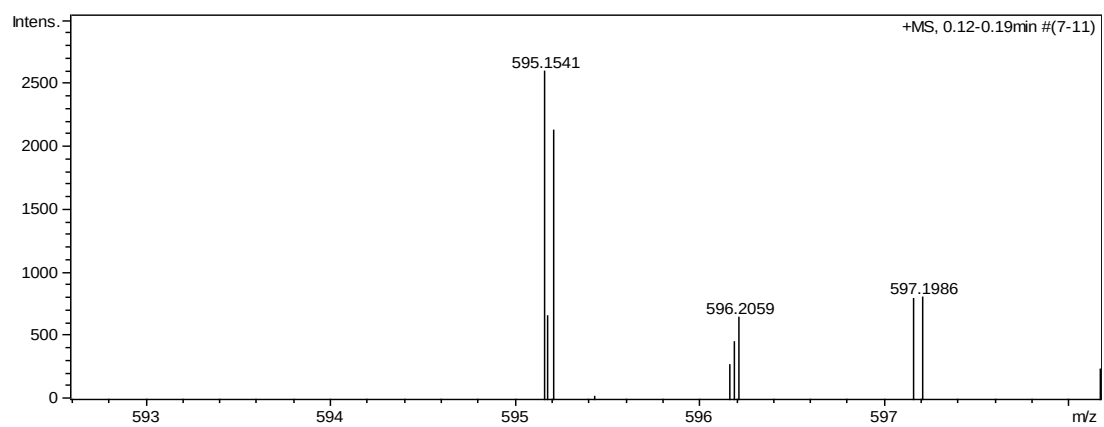
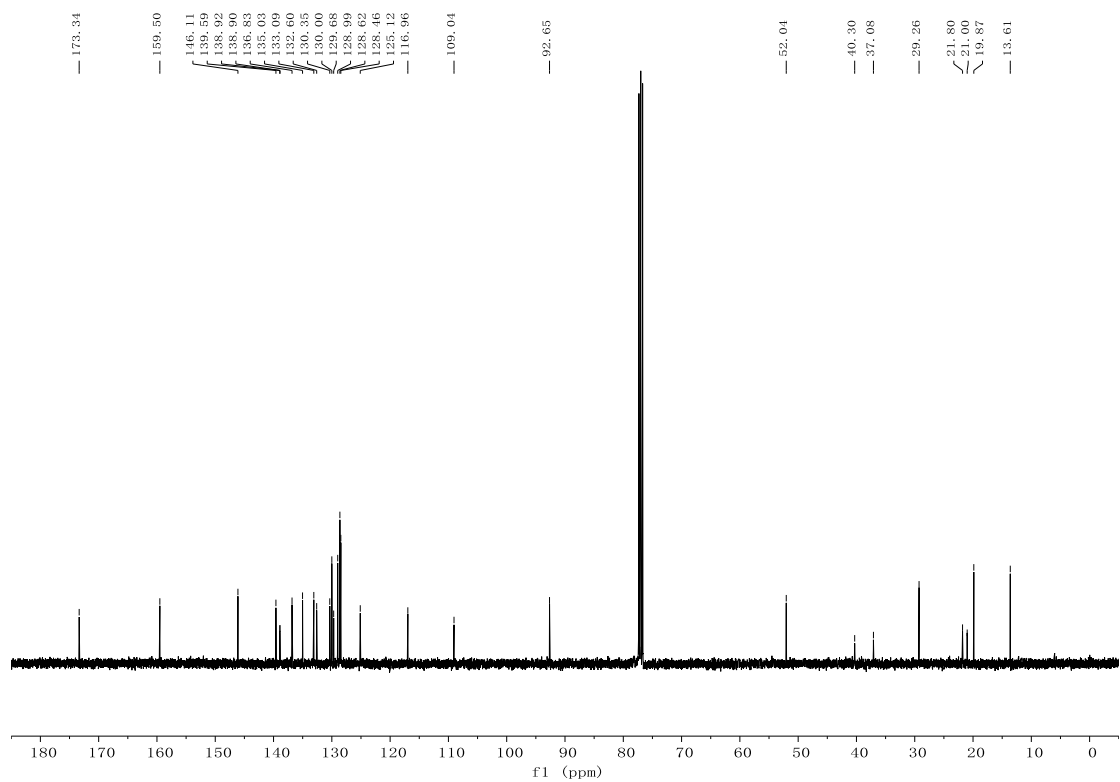




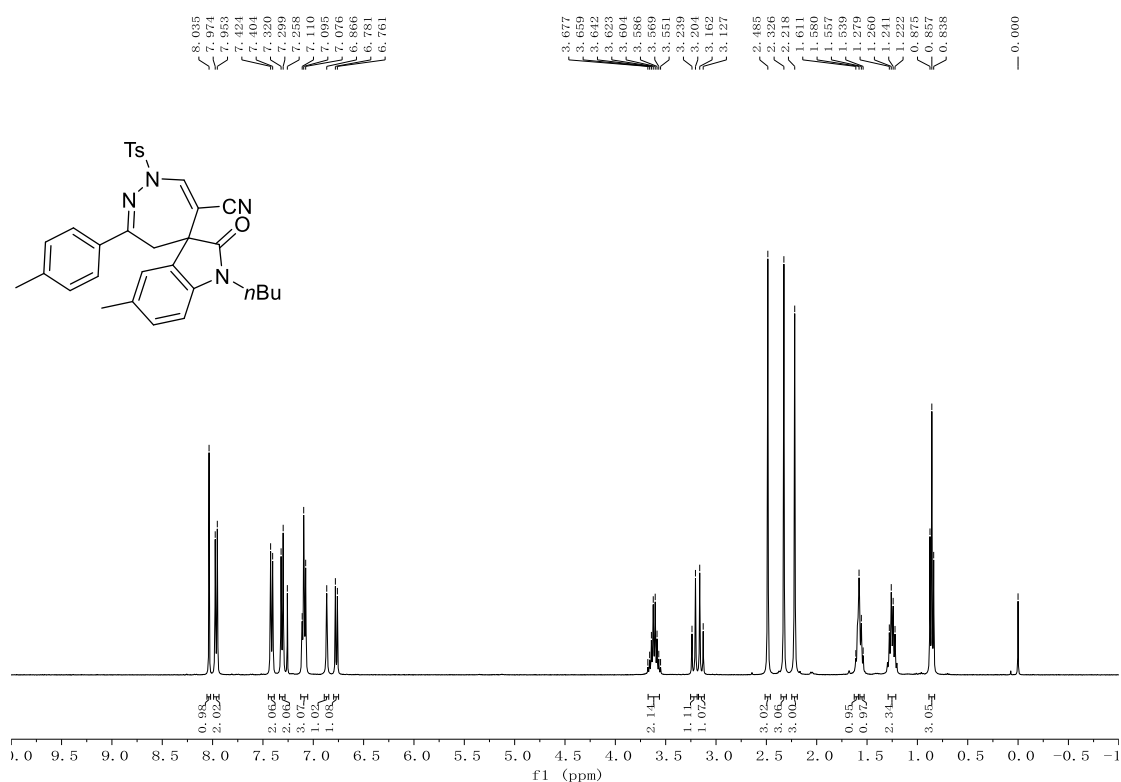
1-Butyl-3'-(4-chlorophenyl)-5-methyl-2-oxo-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-

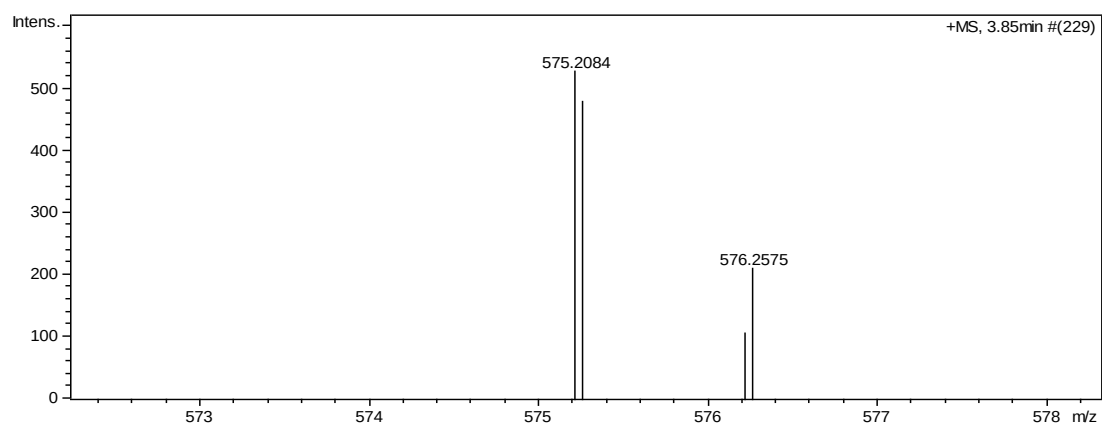
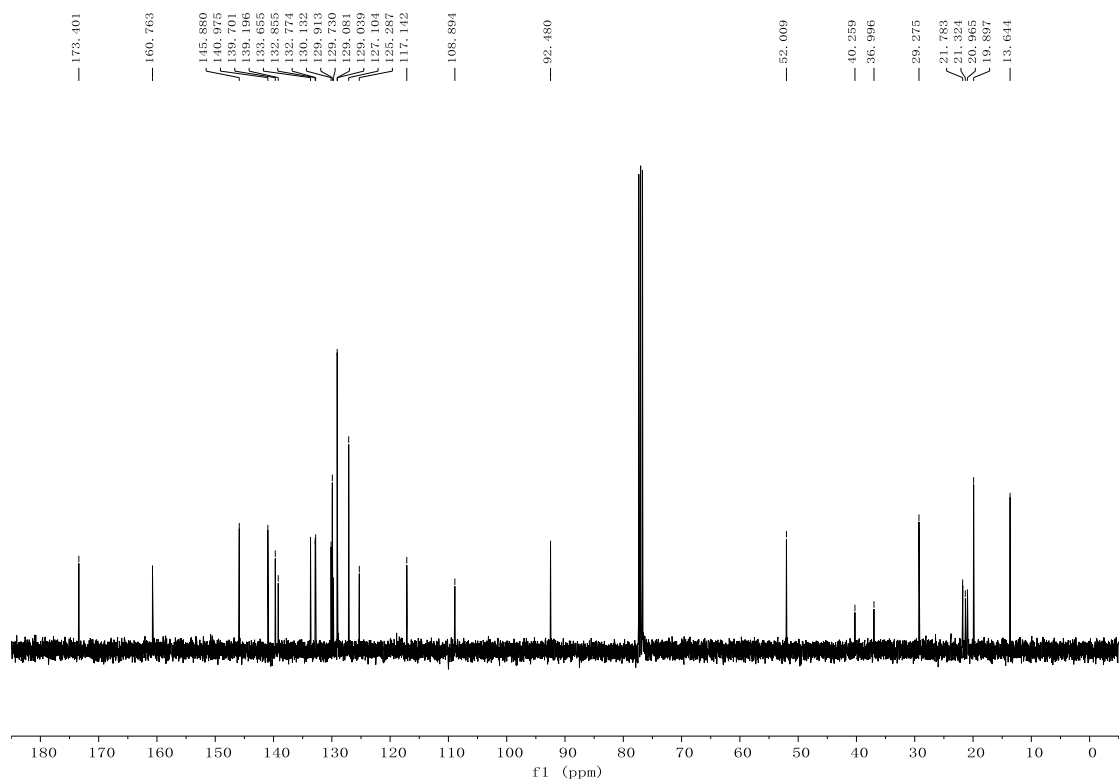
[1,2]diazepine]-6'-carbonitrile (7g): white solid, 63%, m.p. 214-217 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.04 (s, 1H, C=CH-N), 7.95 (d, *J* = 8.4 Hz, 2H, ArH), 7.42 (d, *J* = 8.0 Hz, 2H, ArH), 7.36 (d, *J* = 8.8 Hz, 2H, ArH), 7.27 (d, *J* = 7.6 Hz, 1H, ArH), 7.13 (d, *J* = 8.0 Hz, 1H, ArH), 6.91 (s, 1H, ArH), 6.78 (d, *J* = 8.4 Hz, 1H, ArH), 3.67-3.55 (m, 2H, CH₂), 3.18 (d, *J* = 14.0 Hz, 1H, CH), 3.14 (d, *J* = 14.0 Hz, 1H, CH), 2.50 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 1.60-1.53 (m, 2H, CH₂), 1.27-1.18 (m, 2H, CH₂), 0.85 (t, *J* = 7.6 Hz, 3H, CH₃) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃) δ: 173.3, 159.5, 146.1, 139.6, 138.9, 138.9, 136.8, 135.0, 133.1, 132.6, 130.4, 130.0, 129.7, 129.0, 128.6, 128.5, 125.1, 117.0, 109.0, 92.7, 52.0, 40.3, 37.1, 29.3, 21.8, 21.0, 19.9, 13.6 ppm; IR (KBr) ν: 3061, 3057, 2912, 2210, 1710, 1613, 1591, 1488, 1450, 1433, 1375, 1342, 1291, 1263, 1231, 1211, 1183, 1168, 1083, 1010, 985, 882, 833, 823, 810, 767, 722, 701, 683, 655 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₁H₂₉ClN₄O₃SNa ([M+Na]⁺): 595.1541, Found: 595.1541.





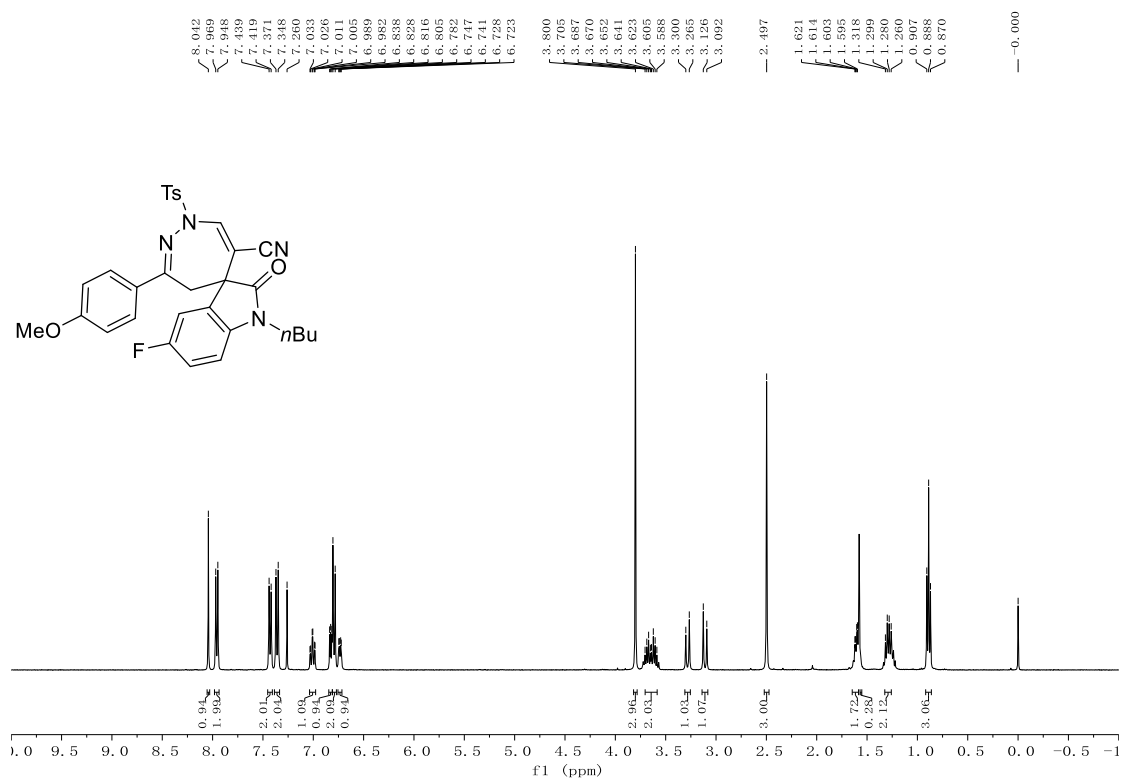
1-Butyl-5-methyl-2-oxo-3'-(p-tolyl)-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carbonitrile (7h): white solid, 58%, m.p. 185-188 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.04 (s, 1H, C=CH-N), 7.96 (d, J = 8.4 Hz, 2H, ArH), 7.41 (d, J = 8.0 Hz, 2H, ArH), 7.31 (d, J = 8.4 Hz, 2H, ArH), 7.11-7.08 (m, 3H, ArH), 6.87 (s, 1H, ArH), 6.77 (d, J = 8.0 Hz, 1H, ArH), 3.68-3.55 (m, 2H, CH_2), 3.22 (d, J = 14.0 Hz, 1H, CH), 3.14 (d, J = 14.0 Hz, 1H, CH), 2.49 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 1.61-1.54 (m, 2H, CH_2), 1.28-1.22 (m, 2H, CH_2), 0.86 (t, J = 7.6 Hz, 3H, CH_3) ppm; ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ : 173.4, 160.8, 145.9, 141.0, 139.7, 139.2, 133.7, 132.9, 132.8, 130.1, 129.9, 129.7, 129.1, 129.0, 127.1, 125.3, 117.1, 108.9, 92.5, 52.0, 40.2, 37.0, 29.3, 21.8, 21.3, 20.9, 19.9, 13.6 ppm; IR (KBr) ν : 3061, 3057, 2952, 2926, 2866, 2204, 1710, 1613, 1595, 1475, 1438, 1414, 1370, 1291, 1182, 1168, 1102, 1082, 988, 878, 810, 752, 692, 658, 600 cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{32}\text{H}_{32}\text{N}_4\text{O}_3\text{SNa}$ ($[\text{M}+\text{Na}]^+$): 575.2087, Found: 575.2084.

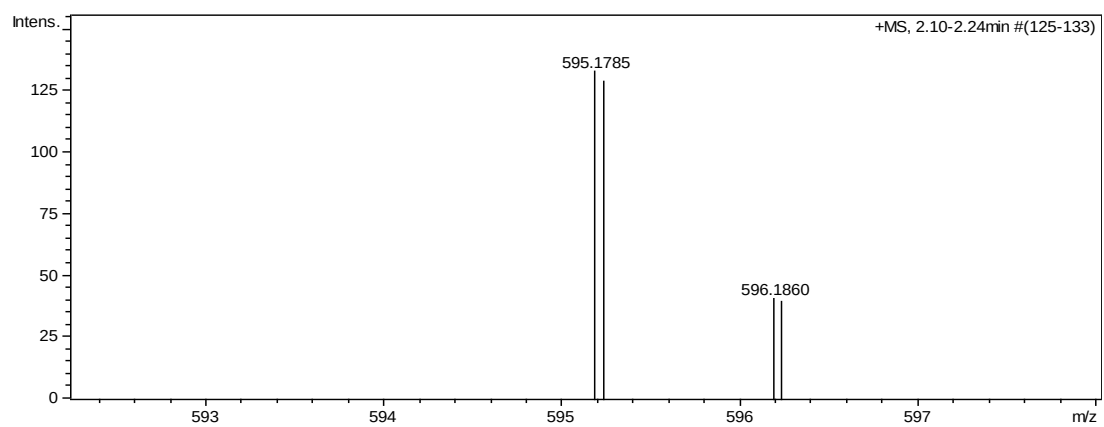
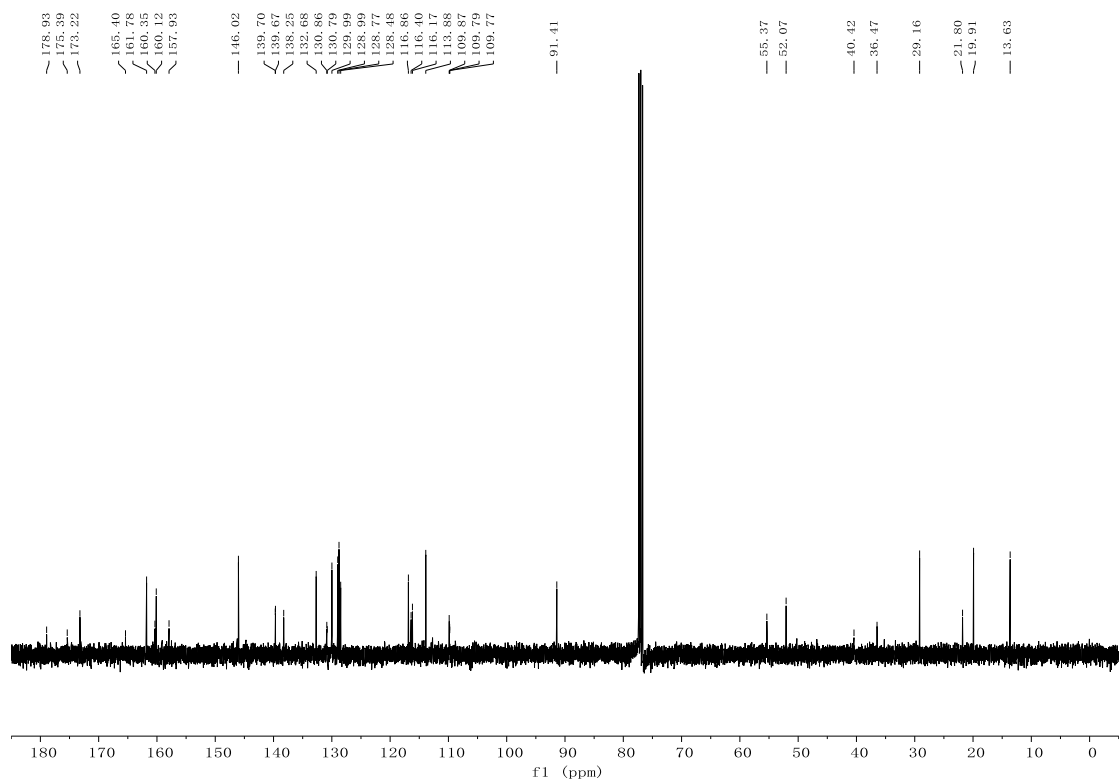




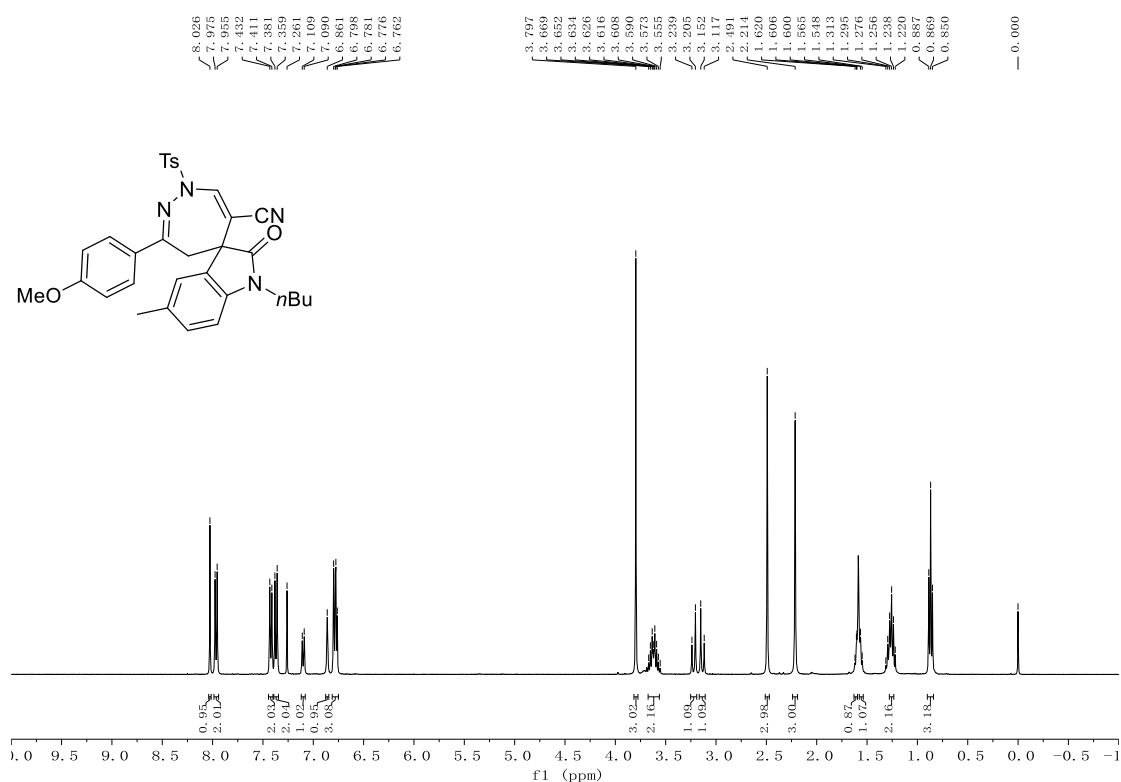
1-Butyl-5-fluoro-3'-(4-methoxyphenyl)-2-oxo-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-

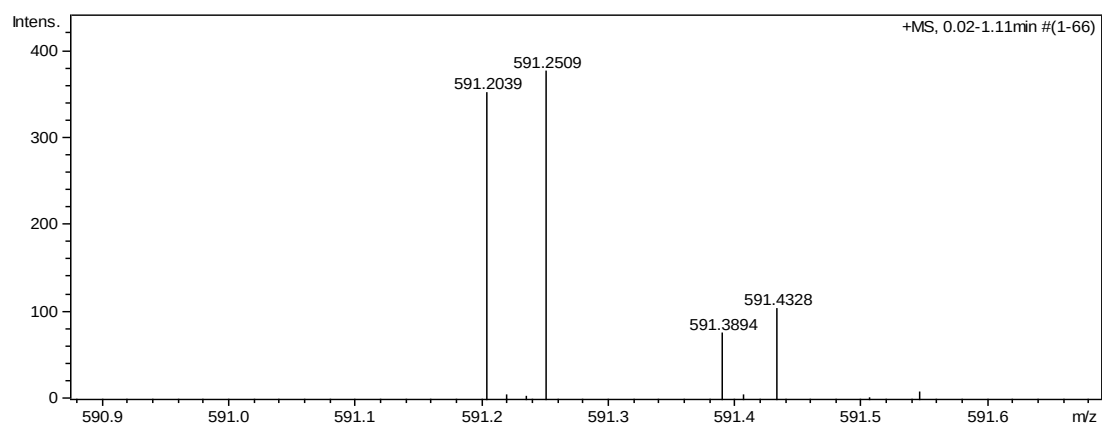
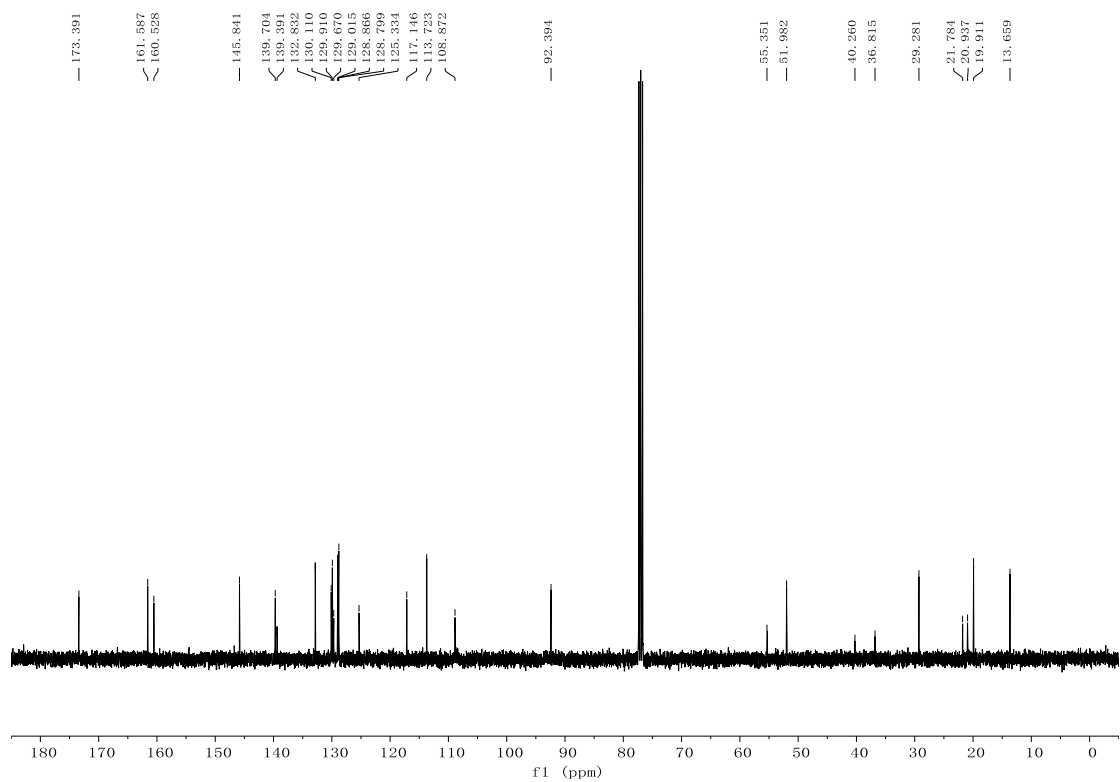
[1,2]diazepine]-6'-carbonitrile (7i): white solid, 82%, m.p. 263-265 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.04 (s, 1H, C=CH-N), 7.96 (d, *J* = 8.4 Hz, 2H, ArH), 7.42 (d, *J* = 8.0 Hz, 2H, ArH), 7.36 (d, *J* = 9.2 Hz, 2H, ArH), 7.03-6.98 (m, 1H, ArH), 6.84-6.82 (m, 1H, ArH), 6.79 (d, *J* = 9.2 Hz, 2H, ArH), 6.75-6.72 (m, 1H, ArH), 3.80 (s, 3H, OCH₃), 3.71-3.59 (m, 2H, CH₂), 3.28 (d, *J* = 14.0 Hz, 1H, CH), 3.11 (d, *J* = 13.6 Hz, 1H, CH), 2.50 (s, 3H, CH₃), 1.62-1.55 (m, 2H, CH₂), 1.32-1.26 (m, 2H, CH₂), 0.89 (t, *J* = 7.2 Hz, 3H, CH₃) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃) δ: 178.9, 175.4, 173.2, 165.4, 161.8, 160.1, 159.1 (d, *J* = 242 Hz), 146.0, 139.7 (d, *J* = 3.2 Hz), 138.2, 132.7, 130.8 (d, *J* = 7.0 Hz), 130.0, 129.9, 128.8, 128.5, 116.9, 116.3 (d, *J* = 23 Hz), 113.9, 109.9, 109.8, 109.8, 91.4, 55.4, 52.1, 40.4, 36.5, 29.2, 21.8, 19.9, 13.6 ppm; IR (KBr) ν: 3061, 2957, 2942, 2930, 2871, 2205, 1720, 1612, 1599, 1488, 1449, 1422, 1375, 1299, 1182, 1114, 1094, 998, 759, 698, 658, 606 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₁H₂₉FN₄O₄SN_a ([M+Na]⁺): 595.1786, Found: 595.1785.





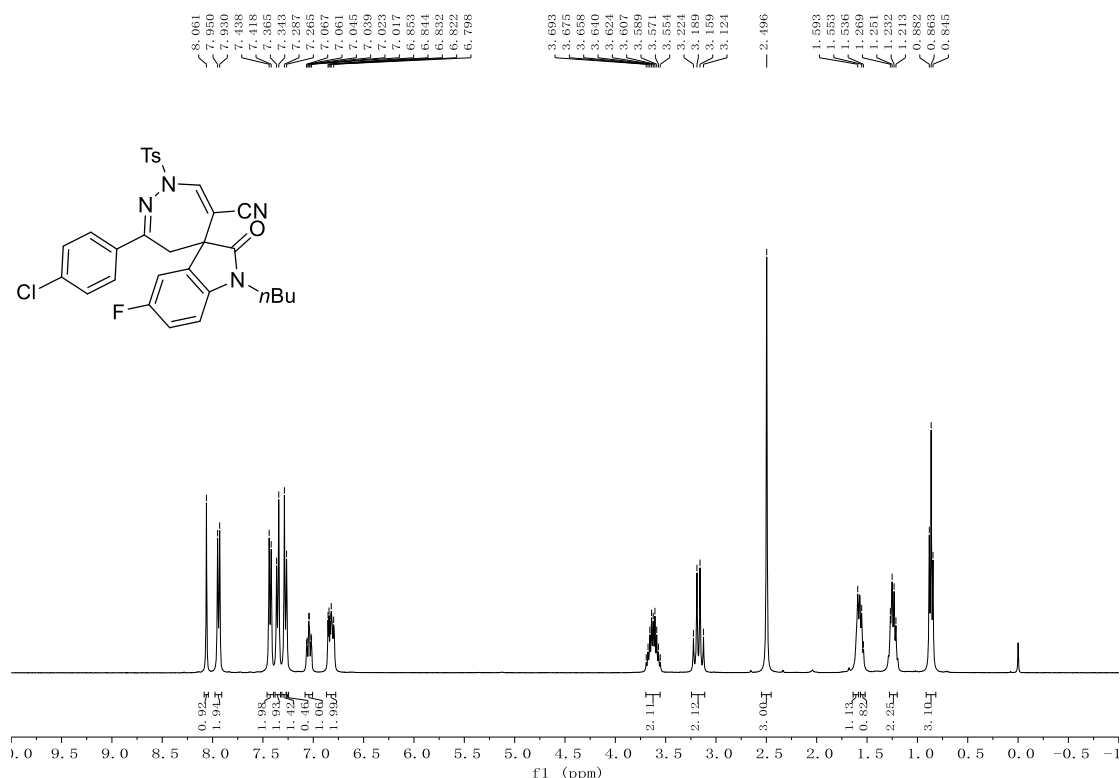
1-Butyl-3'-(4-methoxyphenyl)-5-methyl-2-oxo-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-carbonitrile (7j): white solid, 62%, m.p. 189-192 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.03 (s, 1H, C=CH-N), 7.97 (d, $J = 8.0$ Hz, 2H, ArH), 7.42 (d, $J = 8.4$ Hz, 2H, ArH), 7.37 (d, $J = 8.8$ Hz, 2H, ArH), 7.10 (d, $J = 7.6$ Hz, 1H, ArH), 6.86 (s, 1H, ArH), 6.80-6.76 (m, 3H, ArH), 3.80 (s, 3H, OCH_3), 3.67-3.56 (m, 2H, CH_2), 3.22 (d, $J = 13.6$ Hz, 1H, CH), 3.13 (d, $J = 14.0$ Hz, 1H, CH), 2.49 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 1.62-1.55 (m, 2H, CH_2), 1.31-1.22 (m, 2H, CH_2), 0.87 (t, $J = 7.6$ Hz, 3H, CH_3) ppm; ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ : 173.4, 161.6, 160.5, 145.8, 139.7, 139.4, 132.8, 130.1, 129.9, 129.7, 129.0, 128.9, 128.8, 125.3, 117.1, 113.7, 108.9, 92.4, 55.4, 52.0, 40.3, 36.8, 29.3, 21.8, 20.9, 19.9, 13.7 ppm; IR (KBr) ν : 3057, 2941, 2930, 2852, 2201, 1715, 1601, 1592, 1477, 1442, 1421, 1371, 1299, 1182, 1110, 1090, 991, 753, 694, 654, 601 cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{32}\text{H}_{32}\text{N}_4\text{O}_4\text{SNa}$ ($[\text{M}+\text{Na}]^+$): 591.2036, Found: 591.2039.

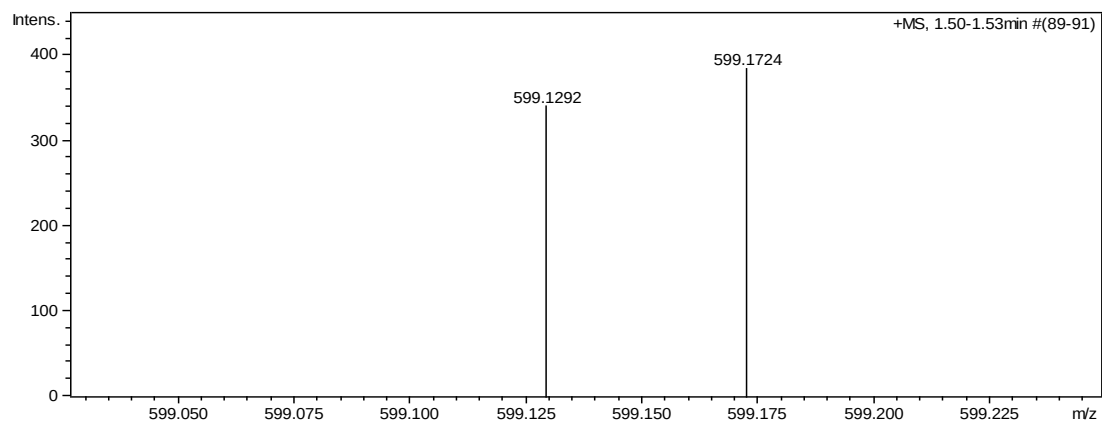
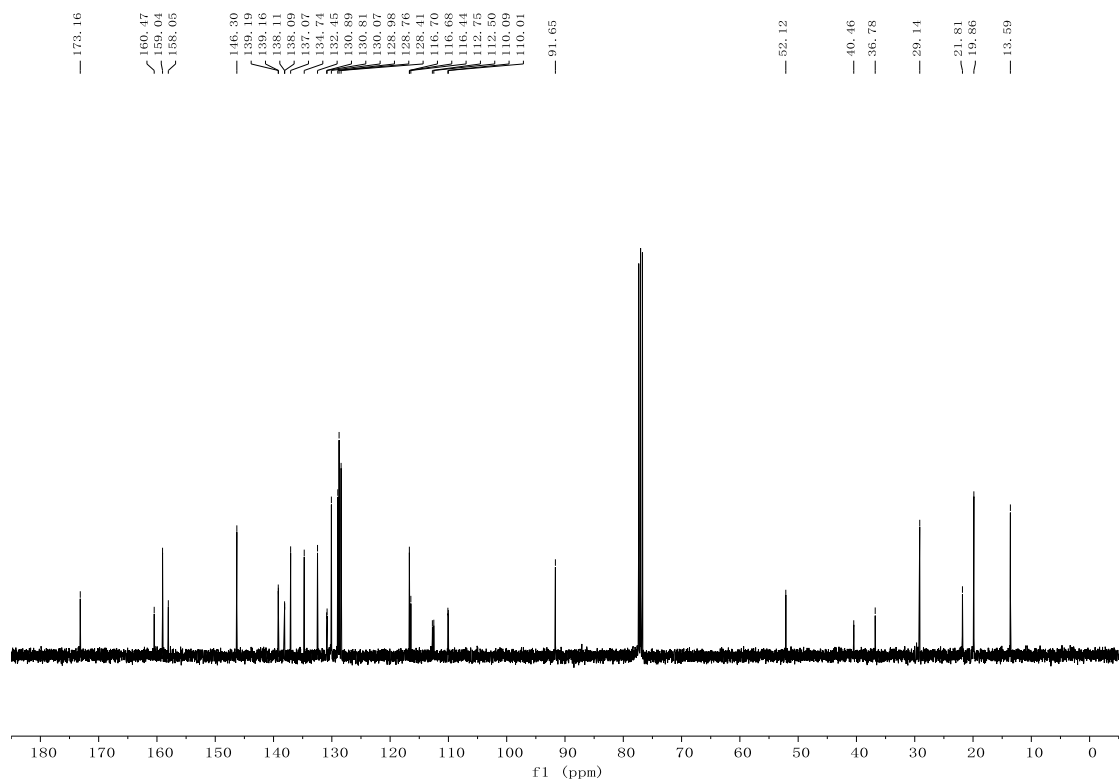




1-Butyl-3'-(4-chlorophenyl)-5-fluoro-2-oxo-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-

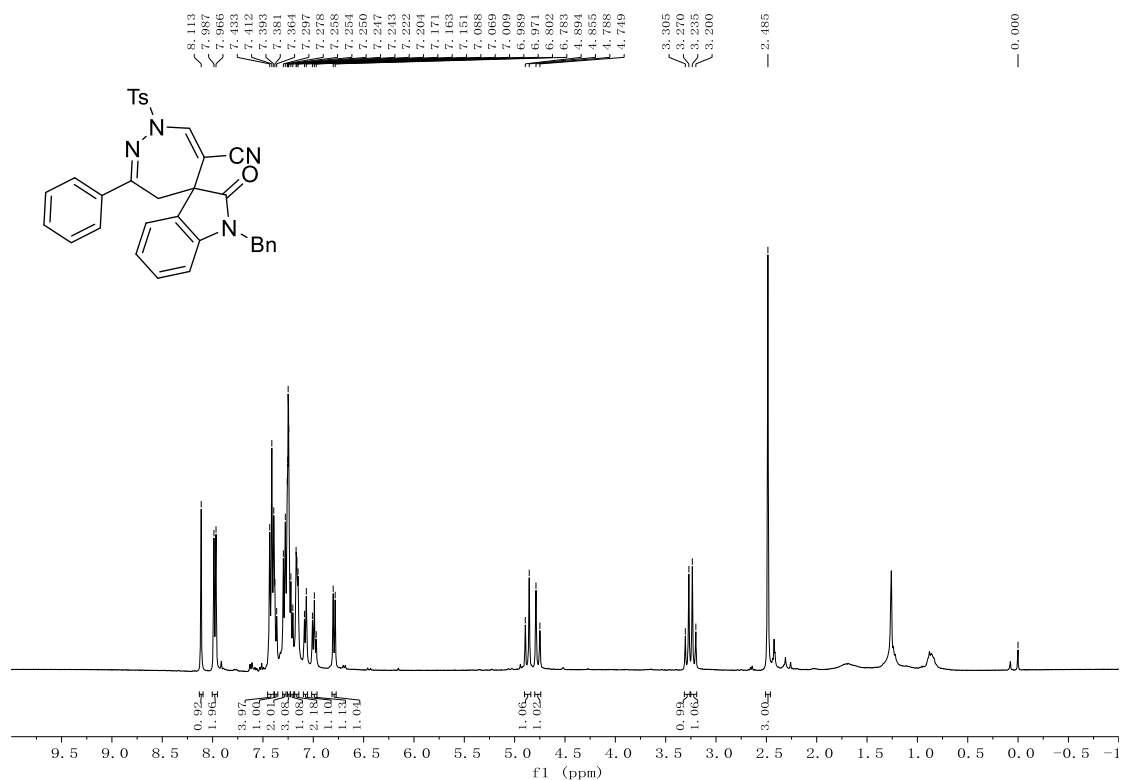
[1,2]diazepine]-6'-carbonitrile (7k): white solid, 65%, m.p. 242-244 °C; ¹H NMR (400 MHz, CDCl₃) δ: 8.06 (s, 1H, C=CH-N), 7.94 (d, *J* = 8.0 Hz, 2H, ArH), 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 7.35 (d, *J* = 8.8 Hz, 2H, ArH), 7.28-7.25 (m, 2H, ArH), 7.07-7.02 (m, 1H, ArH), 6.85-6.80 (m, 2H, ArH), 3.69-3.55 (m, 2H, CH₂), 3.20 (d, *J* = 14.0 Hz, 1H, CH), 3.14 (d, *J* = 14.0 Hz, 1H, CH), 2.50 (s, 3H, CH₃), 1.59-1.54 (m, 2H, CH₂), 1.27-1.21 (m, 2H, CH₂), 0.86 (t, *J* = 7.2 Hz, 3H, CH₃) ppm; ¹³C {¹H} NMR (100 MHz, CDCl₃) δ: 173.2, 159.5 (d, *J* = 242 Hz), 158.0, 146.3, 139.2 (d, *J* = 2.6 Hz), 138.1 (d, *J* = 2.1 Hz), 137.1, 134.7, 132.4, 130.8 (d, *J* = 7.8 Hz), 130.1, 129.0, 128.8, 128.4, 116.7 (d, *J* = 23.4 Hz), 116.4, 112.6 (d, *J* = 24.6 Hz), 110 (d, *J* = 7.8 Hz), 91.6, 52.1, 40.5, 36.8, 29.1, 21.8, 19.9, 13.6 ppm; IR (KBr) ν: 3072, 2959, 2931, 2921, 2872, 2216, 1719, 1623, 1599, 1482, 1457, 1447, 1409, 1370, 1295, 1273, 1239, 1219, 1189, 1177, 1089, 1009, 999, 889, 846, 831, 812, 782, 737, 709, 692, 672 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₀H₂₆ClFN₄O₃SNa ([M+Na]⁺): 599.1290, Found: 599.1292.

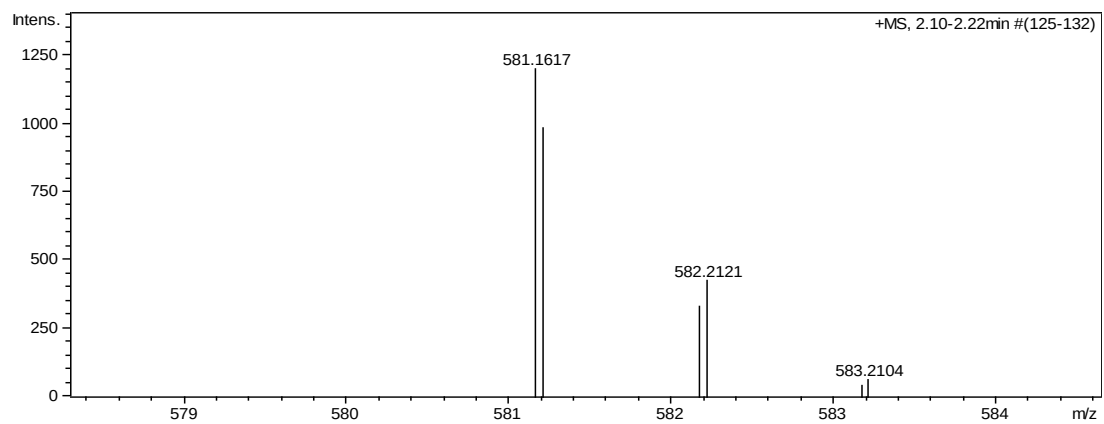
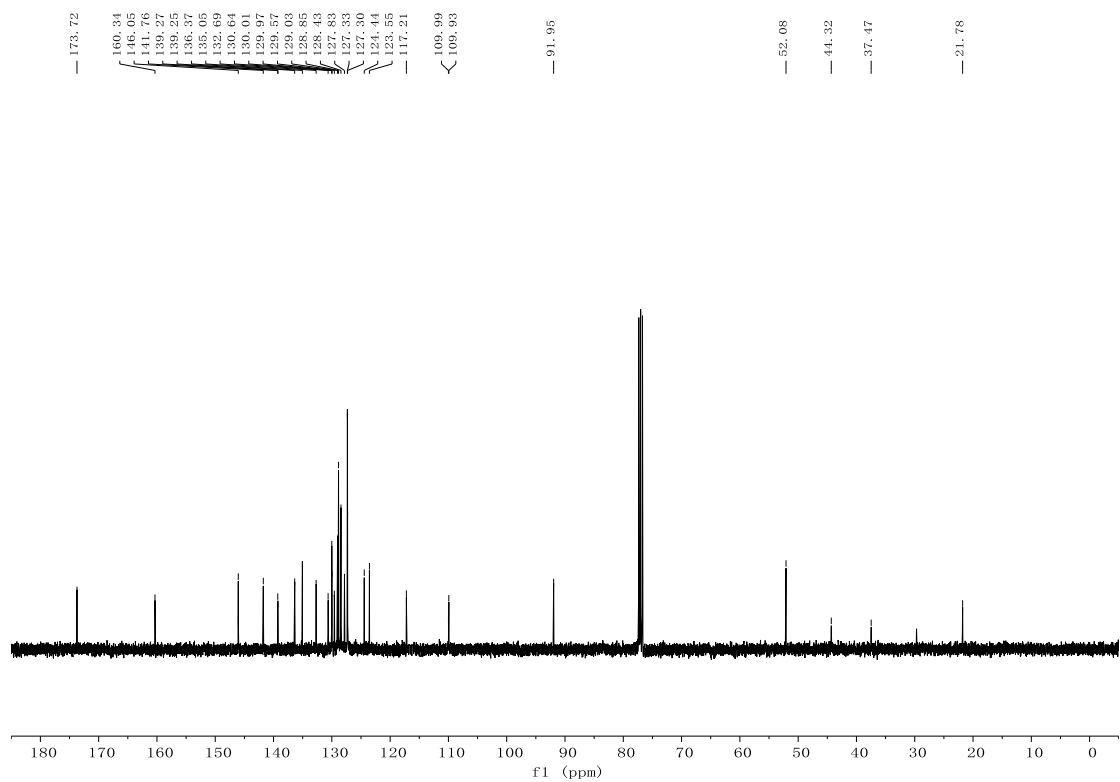




1-Benzyl-2-oxo-3'-phenyl-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-[1,2]diazepine]-6'-

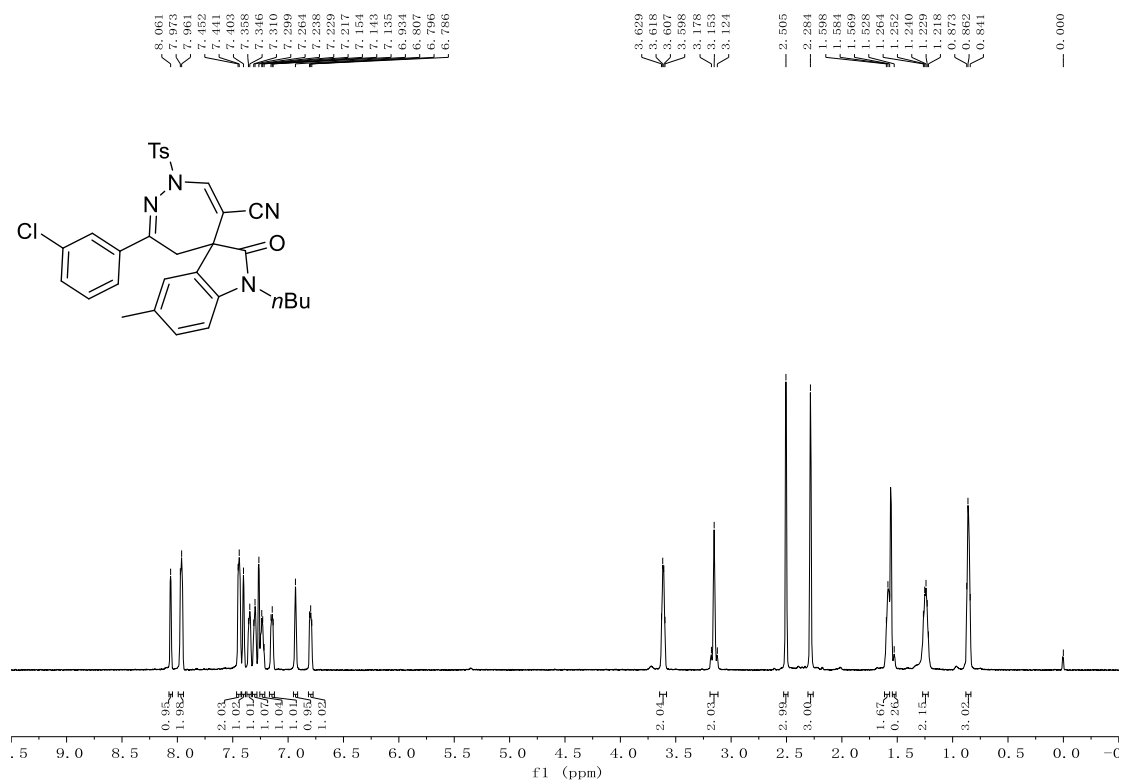
carbonitrile (7I): white solid, 75%, m.p. 208-211 °C; ^1H NMR (400 MHz, CDCl_3) δ : 8.11 (s, 1H, C=CH-N), 7.98 (d, J = 8.4 Hz, 2H, ArH), 7.43-7.39 (m, 3H, ArH), 7.37 (d, J = 6.8 Hz, 1H, ArH), 7.29 (d, J = 7.6 Hz, 2H, ArH), 7.26-7.25 (m, 3H, ArH), 7.21 (d, J = 7.2 Hz, 1H, ArH), 7.17-7.15 (m, 2H, ArH), 7.08 (d, J = 7.6 Hz, 1H, ArH), 7.01-6.97 (m, 1H, ArH), 6.79 (d, J = 7.2 Hz, 1H, ArH), 4.87 (d, J = 15.6 Hz, 1H, CH), 4.77 (d, J = 15.6 Hz, 1H, CH), 3.29 (d, J = 14.0 Hz, 1H, CH), 3.22 (d, J = 14.0 Hz, 1H, CH), 2.49 (s, 3H, CH_3) ppm; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 173.7, 160.3, 146.0, 141.8, 139.3, 139.2, 136.4, 135.0, 132.7, 130.6, 130.0, 130.0, 129.6, 129.0, 128.8, 128.4, 127.8, 127.3, 127.3, 124.4, 123.5, 117.2, 110.0, 109.9, 91.9, 52.1, 44.3, 37.5, 21.8 ppm; IR (KBr) ν : 3056, 2926, 2216, 1715, 1611, 1486, 1466, 1447, 1367, 1295, 1259, 1188, 1173, 1089, 1019, 997, 868, 802, 762, 753, 694, 665, 656, 638 cm^{-1} ; MS (m/z): HRMS (ESI-TOF) Calcd. for $\text{C}_{33}\text{H}_{26}\text{N}_4\text{O}_3\text{SNa}$ ($[\text{M}+\text{Na}]^+$): 581.1618, Found: 581.1617.

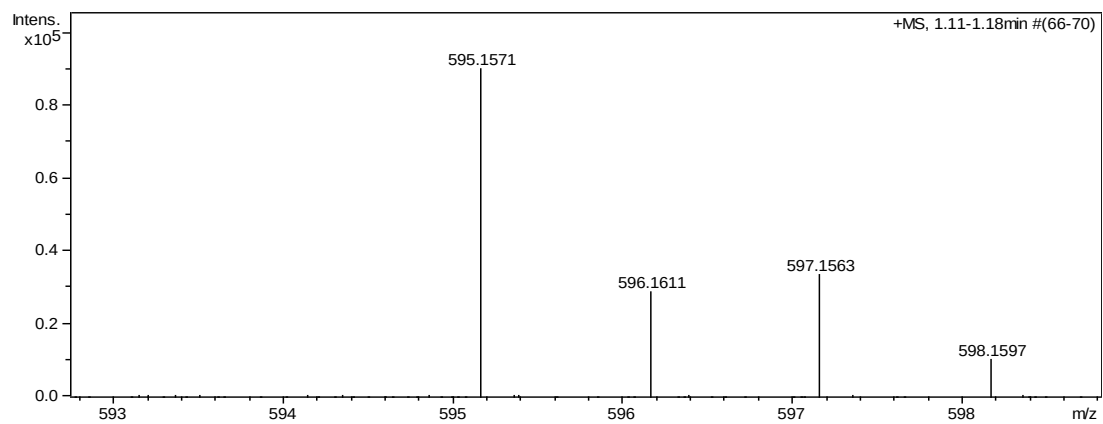
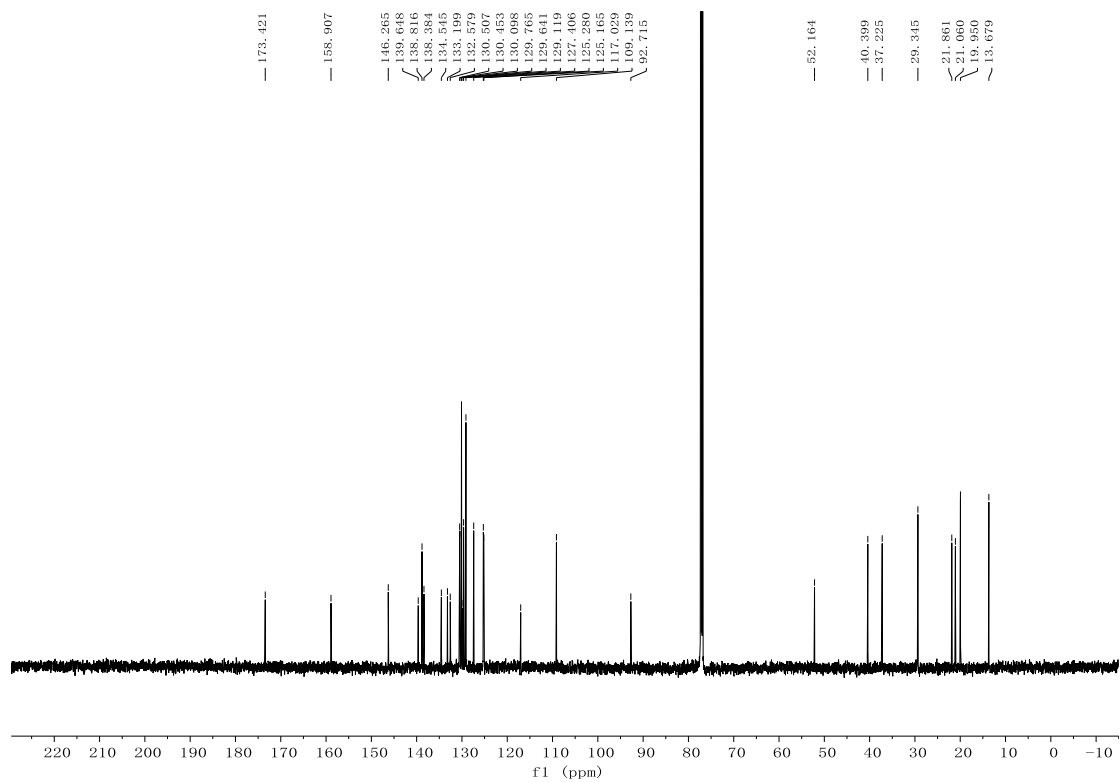




1-Butyl-3'-(3-chlorophenyl)-5-methyl-2-oxo-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-

[1,2]diazepine]-6'-carbonitrile (7m): white solid, 71%, m.p. 199-202 °C; ¹H NMR (600 MHz, CDCl₃) δ: 8.06 (s, 1H, C=CH-N), 7.97-7.96 (m, 2H, ArH), 7.45-7.44 (m, 2H, ArH), 7.40 (s, 1H, ArH), 7.36-7.34 (m, 1H, ArH), 7.32-7.29 (m, 1H, ArH), 7.24-7.21 (m, 1H, ArH), 7.15-7.13 (m, 1H, ArH), 6.93 (s, 1H, ArH), 6.81-6.78 (m, 1H, ArH), 3.63-3.60 (m, 2H, CH₂), 3.18-3.12 (m, 2H, CH₂), 2.51 (s, 3H, CH₃), 2.28 (s, 3H, CH₃), 1.60-1.52 (m, 2H, CH₂), 1.26-1.22 (m, 2H, CH₂), 0.87-0.84 (m, 3H, CH₃) ppm; ¹³C NMR (151 MHz, CDCl₃) δ: 173.4, 158.9, 146.3, 139.6, 138.8, 138.4, 134.5, 133.2, 132.6, 130.5, 130.4, 130.1, 129.8, 129.6, 129.1, 127.4, 125.3, 125.2, 117.0, 109.1, 92.7, 52.2, 40.4, 37.2, 29.3, 21.9, 21.1, 19.9, 13.7 ppm; IR (KBr) ν: 3064, 3052, 2922, 2213, 1715, 1611, 1597, 1489, 1445, 1428, 1375, 1341, 1281, 1258, 1222, 1207, 1181, 1162, 1075, 1009, 978, 878, 822, 762, 701, 683, 655 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₁H₂₉ClN₄O₃SNa ([M+Na]⁺): 595.1541, Found: 595.1571.





1-Butyl-3'-(2-chlorophenyl)-5-methyl-2-oxo-1'-tosyl-1',4'-dihydrospiro[indoline-3,5'-

[1,2]diazepine]-6'-carbonitrile (7n): white solid, 64%, m.p. 185-188 °C; ¹H NMR (600 MHz, CDCl₃) δ: 8.09 (s, 1H, C=CH-N), 7.88-7.87 (m, 2H, ArH), 7.38-7.37 (m, 2H, ArH), 7.34-7.33 (m, 1H, ArH), 7.30-7.26 (m, 2H, ArH), 7.22-7.20 (m, 1H, ArH), 7.12-7.10 (m, 1H, ArH), 7.03 (s, 1H, ArH), 6.71-6.70 (m, 1H, ArH), 3.56-3.51 (m, 2H, CH₂), 3.36 (d, *J* = 14.4 Hz, 1H, CH), 3.04 (d, *J* = 14.4 Hz, 1H, CH), 2.49 (s, 3H, CH₃), 2.34 (s, 3H, CH₃), 1.52-1.47 (m, 2H, CH₂), 1.06-1.03 (m, 2H, CH₂), 0.75-0.72 (m, 3H, CH₃) ppm; ¹³C NMR (151 MHz, CDCl₃) δ 173.9, 160.5, 145.9, 139.3, 138.5, 137.5, 133.2, 132.8, 132.4, 131.9, 130.5, 130.3, 130.2, 129.9, 129.5, 129.0, 126.6, 124.9, 117.2, 108.9, 92.2, 52.4, 41.2, 40.2, 29.2, 21.8, 21.1, 19.7, 13.6 ppm; IR (KBr) ν: 3073, 3058, 2932, 2215, 1725, 1621, 1599, 1491, 1448, 1425, 1377, 1328, 1221, 1203, 1191, 1157, 1082, 1001, 973, 871, 820, 772, 711, 689, 645 cm⁻¹; MS (*m/z*): HRMS (ESI-TOF) Calcd. for C₃₁H₂₉ClN₄O₃SNa ([M+Na]⁺): 595.1541, Found: 595.1570.

