



Supporting Information

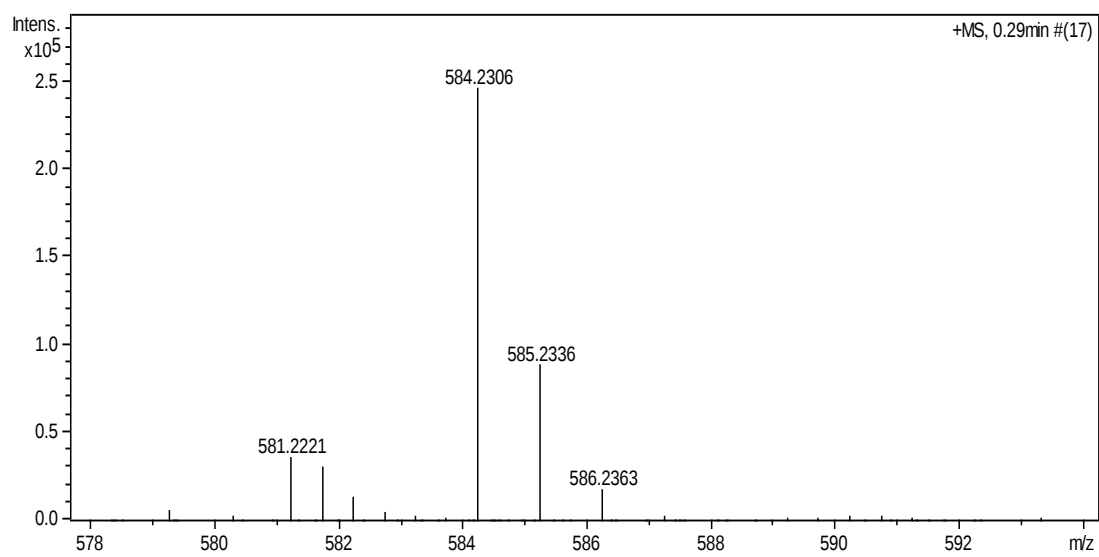
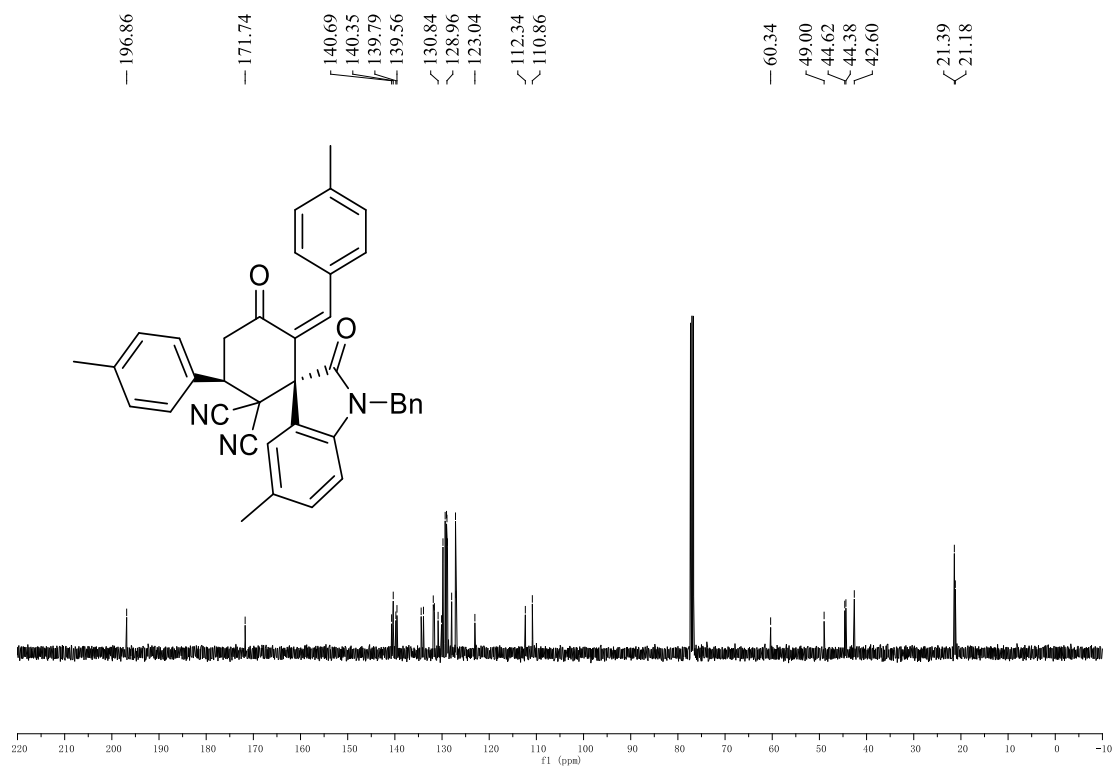
for

Tri(*n*-butyl)phosphine-promoted domino reaction for the efficient construction of spiro[cyclohexane-1,3'-indolines] and spiro[indoline-3,2'-furan-3',3''-indolines]

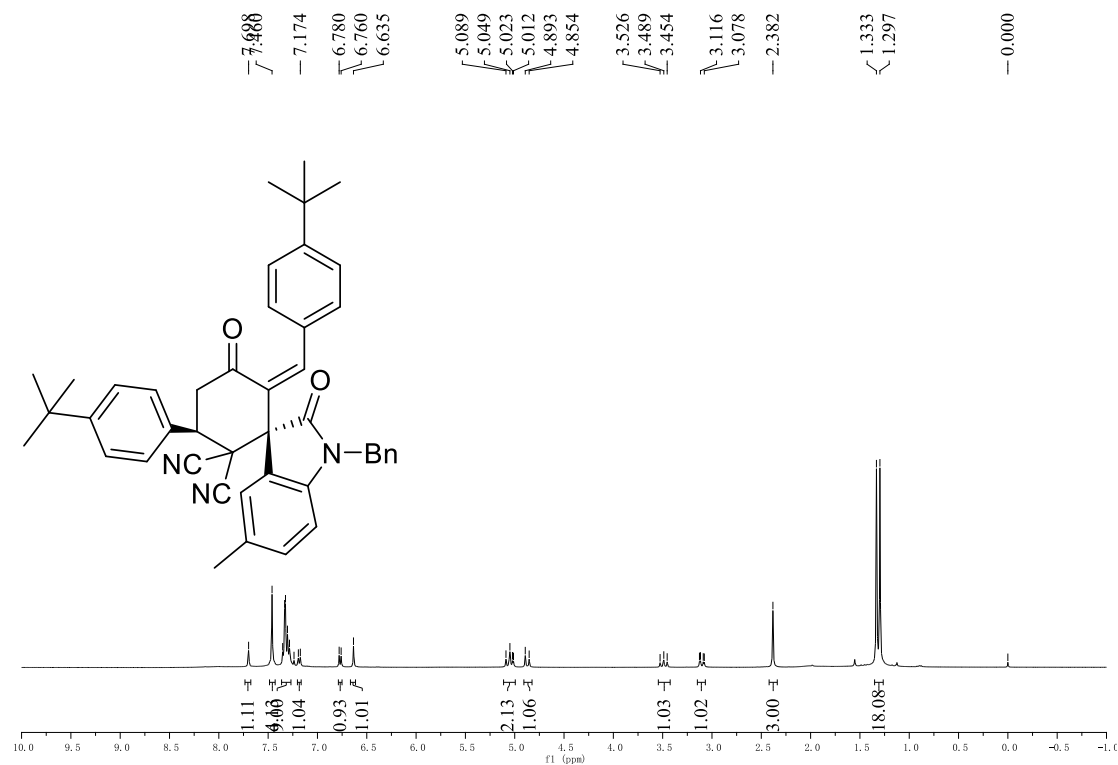
Hui Zheng, Ying Han, Jing Sun and Chao-Guo Yan

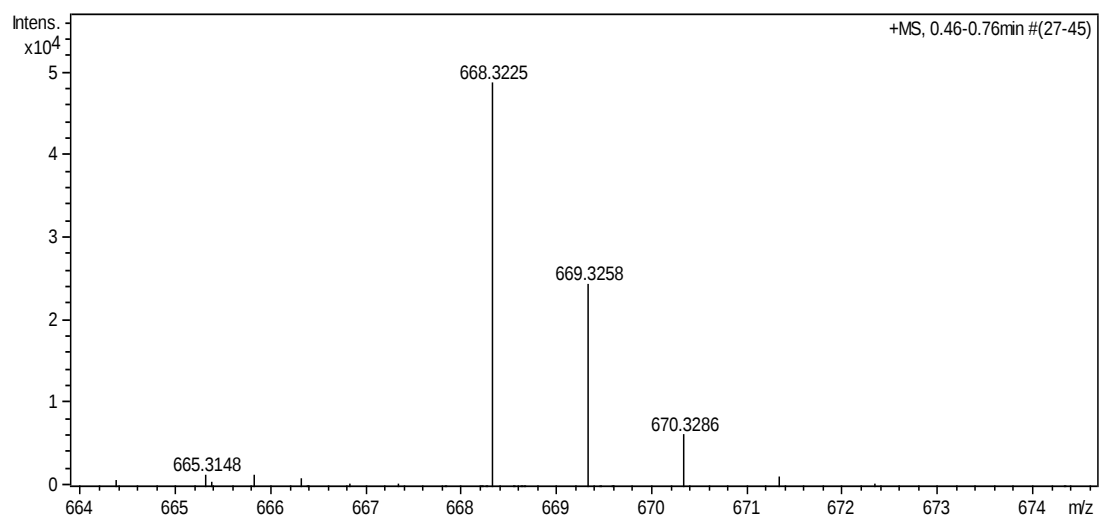
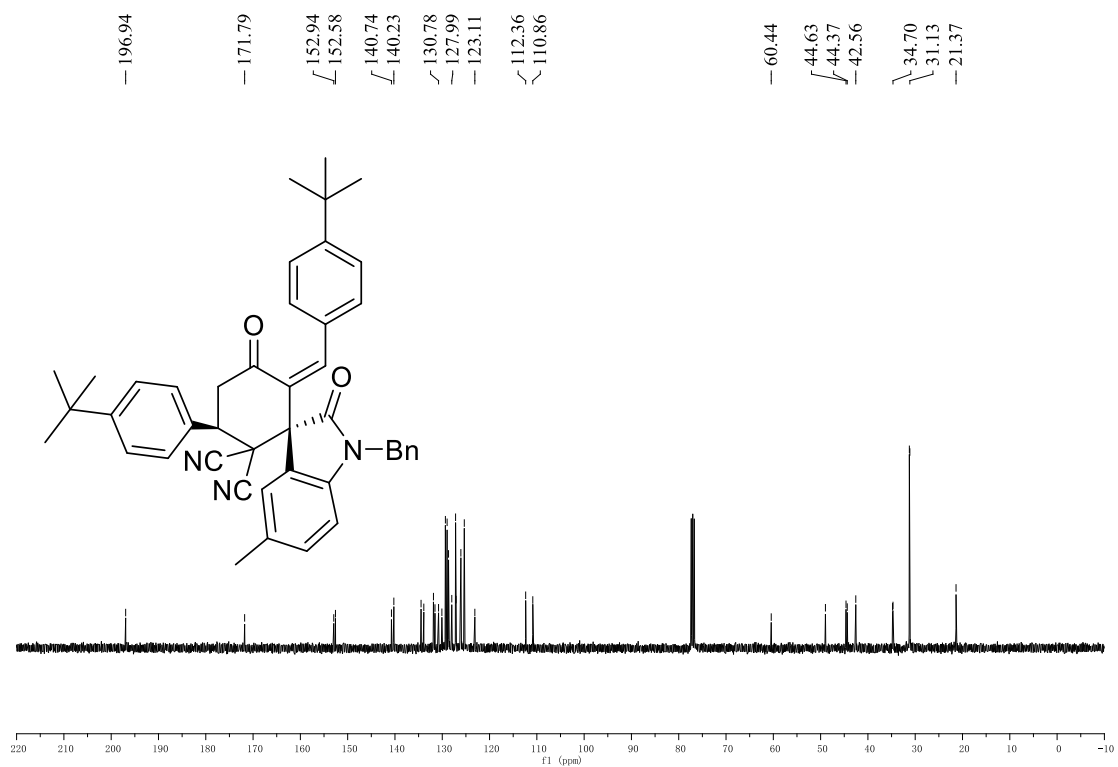
Beilstein J. Org. Chem. **2022**, *18*, 669–679. doi:10.3762/bjoc.18.68

Characterization data and copies of NMR and HRMS spectra

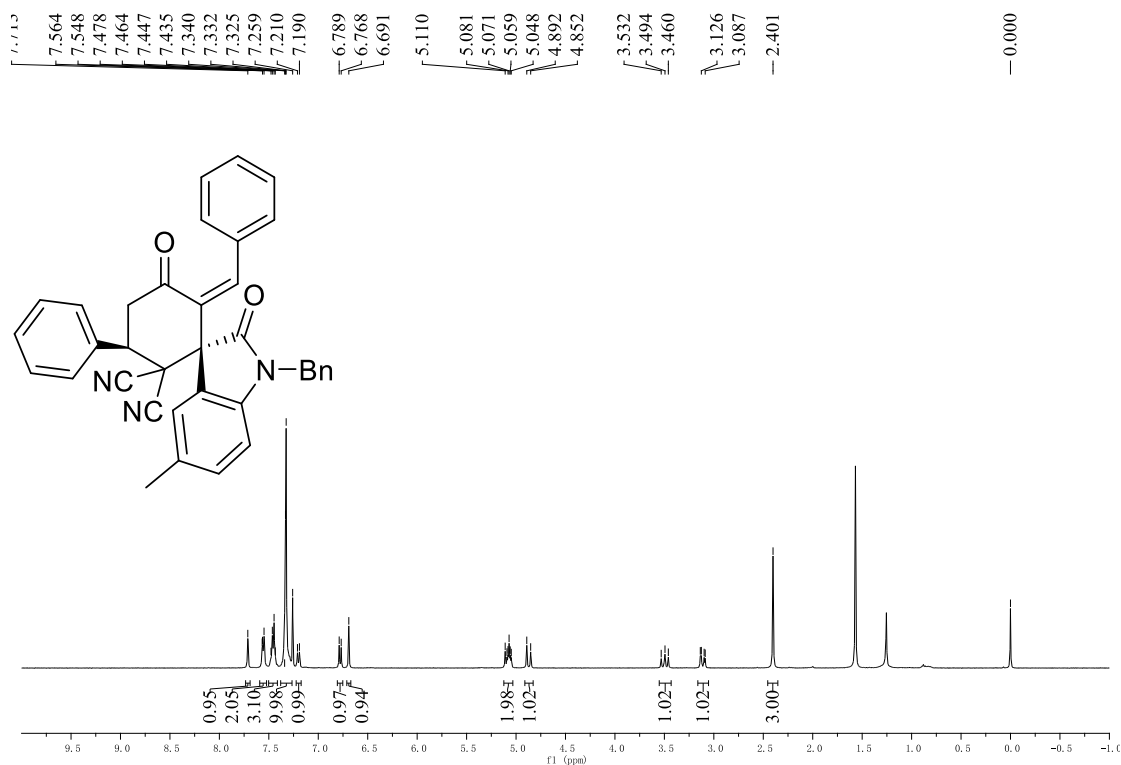


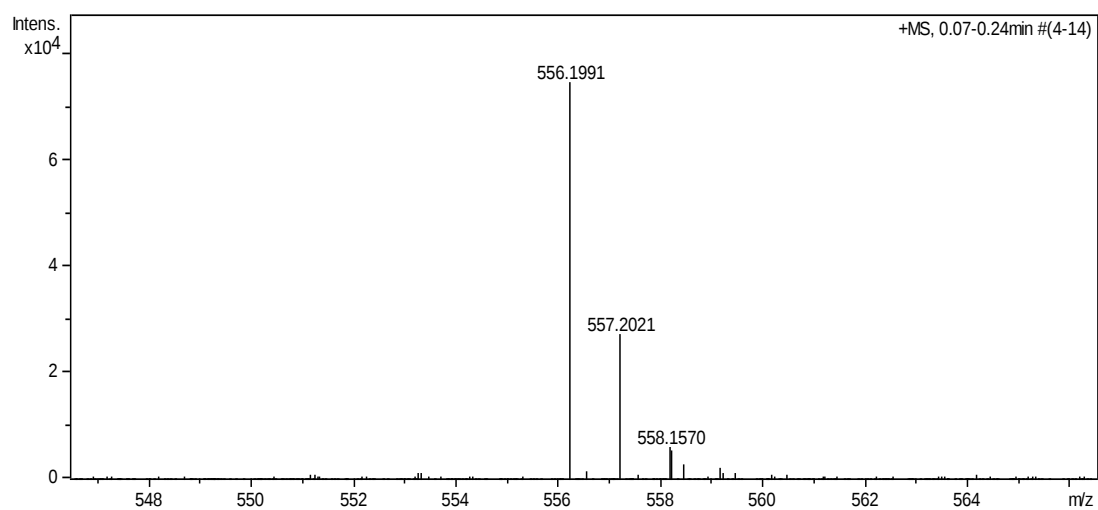
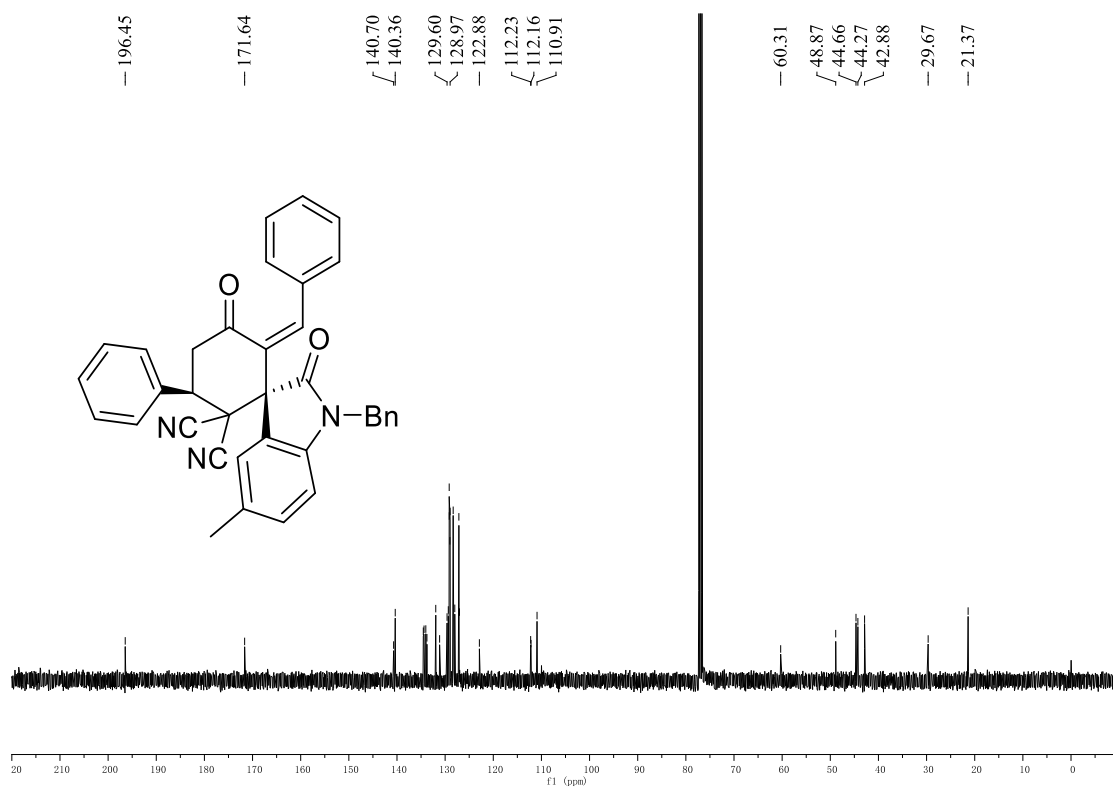
***rel*-(1*R*,3*R*)-1'-Benzyl-6-((*Z*)-4-(*tert*-butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-5'-methyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3b):** white solid, 64%, m.p. 173-175 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 1H, ArH), 7.46 (s, 4H, ArH), 7.35-7.28 (m, 9H, ArH), 7.18 (d, *J* = 8.0 Hz, 1H, ArH), 6.77 (d, *J* = 8.0 Hz, 1H, ArH), 6.64 (s, 1H, CH), 5.09-5.01 (m, 2H, CH₂), 4.87 (d, *J* = 15.6 Hz, 1H, CH₂), 3.49 (t, *J* = 14.0 Hz, 1H, CH), 3.13-3.08 (m, 1H, CH₂), 2.38 (s, 3H, CH₃), 1.33 (s, 9H, (CH₃)₃), 1.30 (s, 3H, (CH₃)₃). ¹³C NMR (100 MHz, CDCl₃) δ 196.9, 171.8, 152.9, 152.6, 140.7, 140.2, 134.5, 133.9, 131.9, 131.5, 130.8, 130.1, 129.3, 129.0, 128.7, 128.0, 127.2, 127.1, 126.1, 125.3, 123.1, 112.4, 110.9, 60.4, 49.0, 44.6, 44.4, 42.6, 34.8, 34.7, 31.2, 31.1, 21.4. IR (KBr) ν: 3288, 2963, 1728, 1614, 1499, 1358, 1306, 1266, 1207, 1112, 1058, 1021, 968, 829 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₄H₄₃NaN₃O₂ ([M+Na]⁺): 668.3253, found: 668.3225.



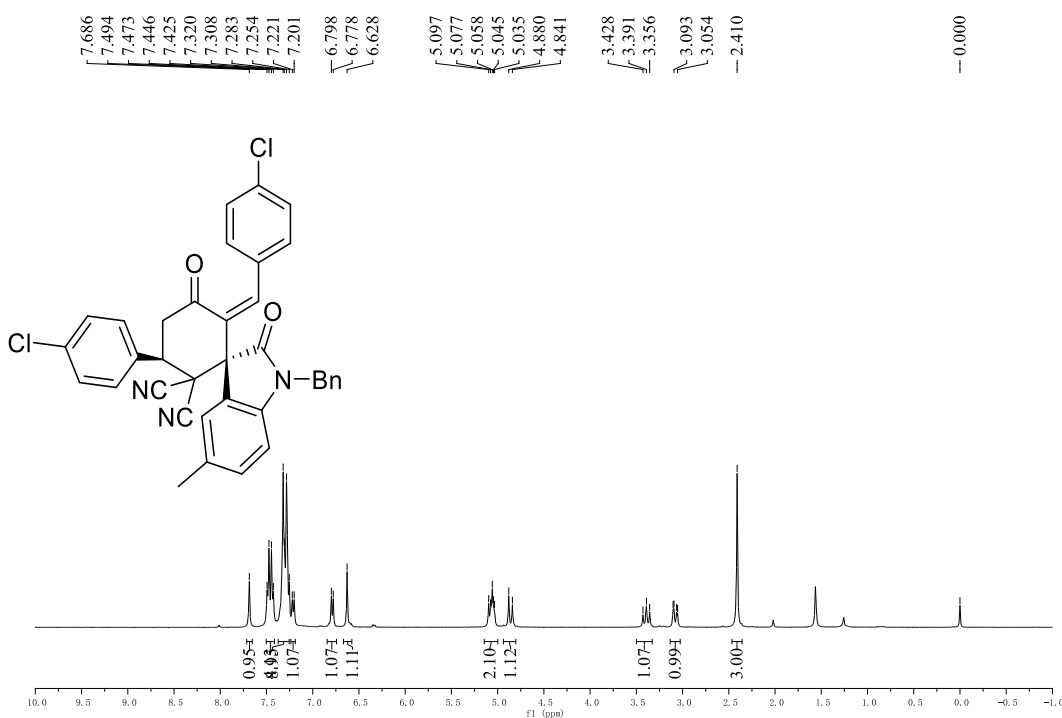


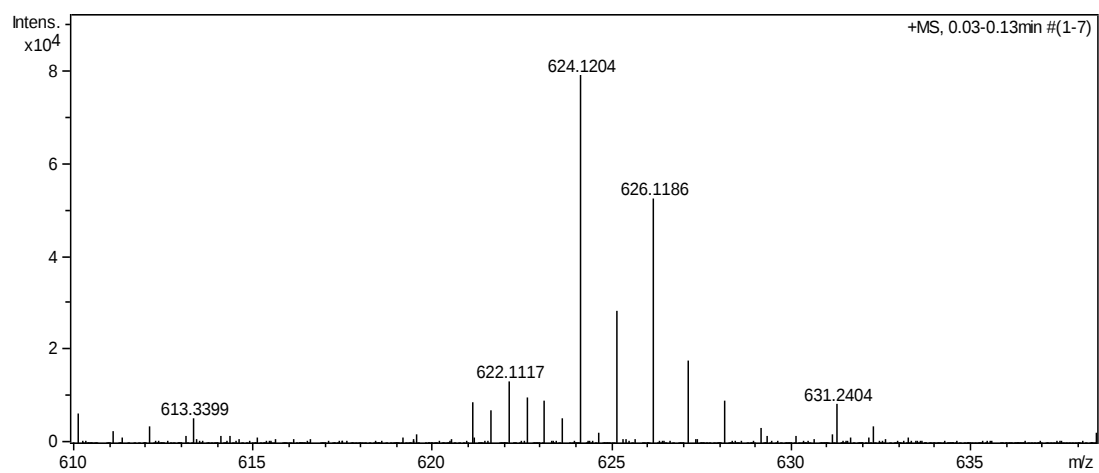
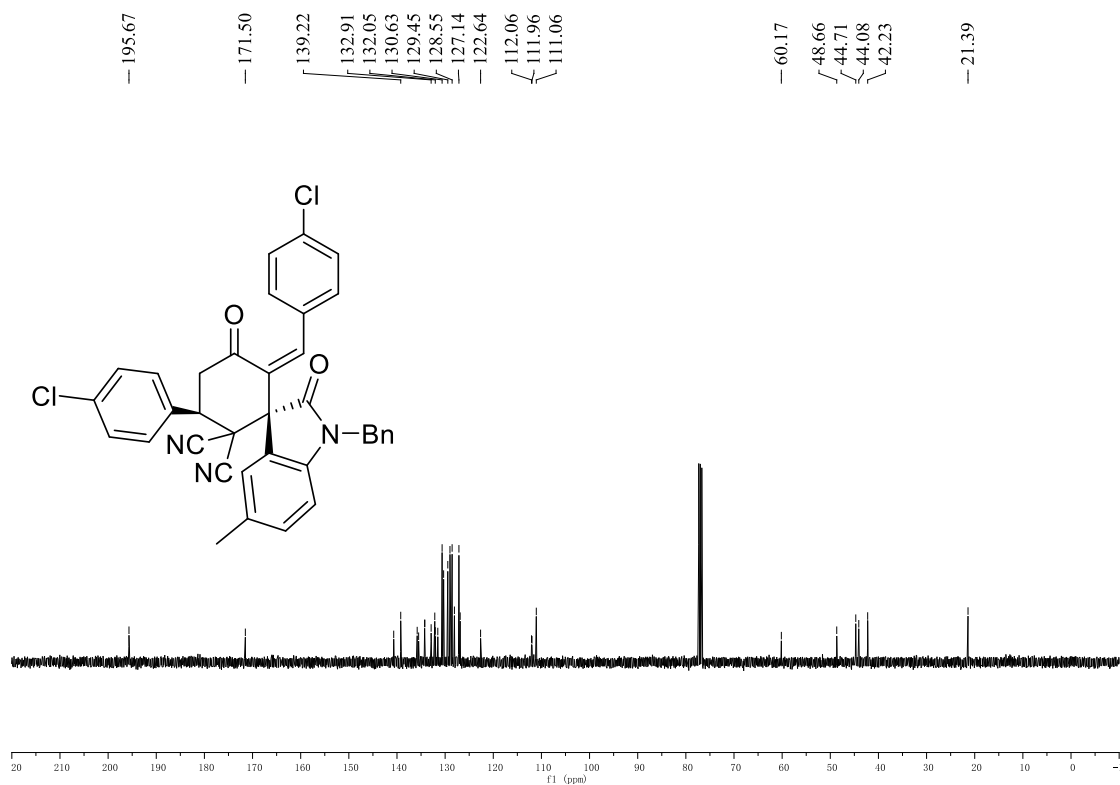
***rel*-(1*R*,3*R*)-1'-Benzyl-6-((*Z*)-benzylidene)-5'-methyl-2',5-dioxo-3-phenylspiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3c)**: white solid, 64%, m.p. 162-164 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.71 (s, 1H, ArH), 7.57-7.55 (m, 2H, ArH), 7.48-7.44 (m, 3H, ArH), 7.34-7.33 (m, 10H, ArH), 7.20 (d, *J* = 8.0 Hz, 1H, ArH), 6.78 (d, *J* = 8.4 Hz, 1H, ArH), 6.69 (s, 1H, CH), 5.11-5.05 (m, 2H, CH₂), 4.87 (d, *J* = 16.0 Hz, 1H, CH₂), 3.49 (t, *J* = 13.6 Hz, 1H, CH), 3.14-3.09 (m, 1H, CH₂), 2.40 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 196.5, 171.6, 140.7, 140.4, 134.5, 134.4, 134.0, 133.8, 132.0, 131.2, 129.6, 129.3, 129.2, 129.1, 129.0, 128.9, 128.3, 128.0, 127.2, 127.0, 122.9, 112.2, 112.1, 110.9, 60.3, 48.9, 44.7, 44.3, 42.9, 29.7, 21.4. IR (KBr) ν: 3728, 3399, 3032, 2918, 2852, 2319, 1948, 1882, 1709, 1609, 1492, 1441, 1348, 1189, 1064, 1018, 926, 811, 772, 733 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₆H₂₇NaN₃O₂ ([M+Na]⁺): 556.2001, found: 556.1991.



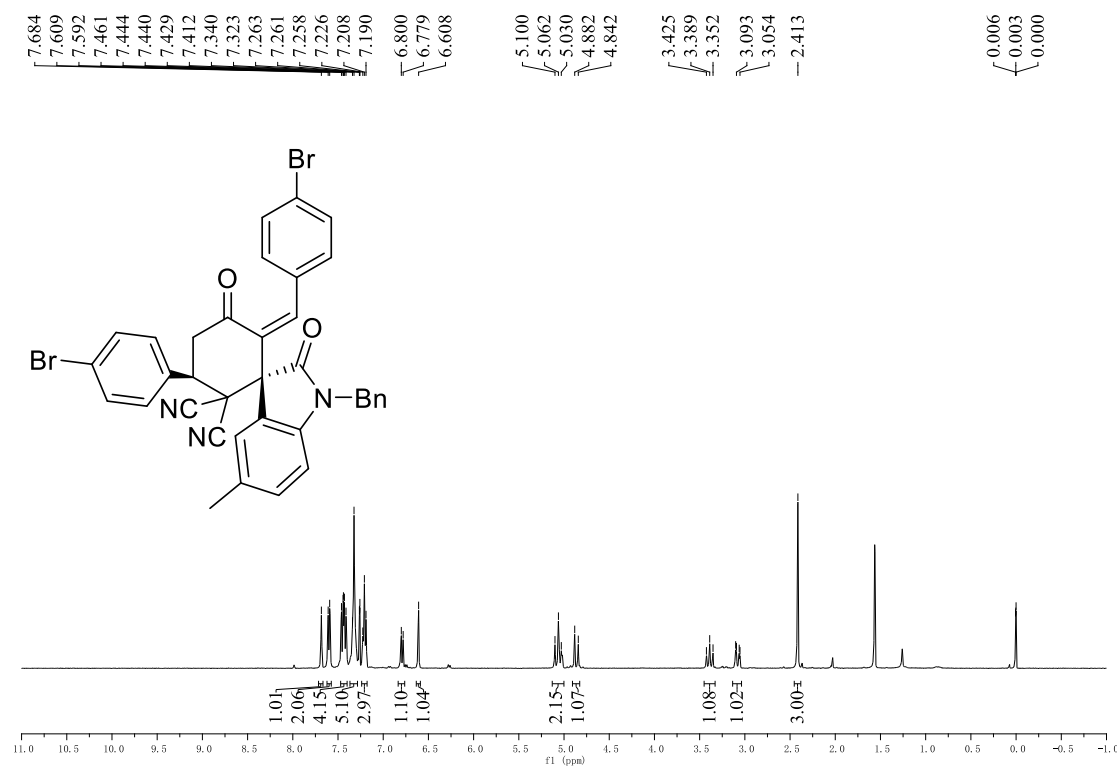


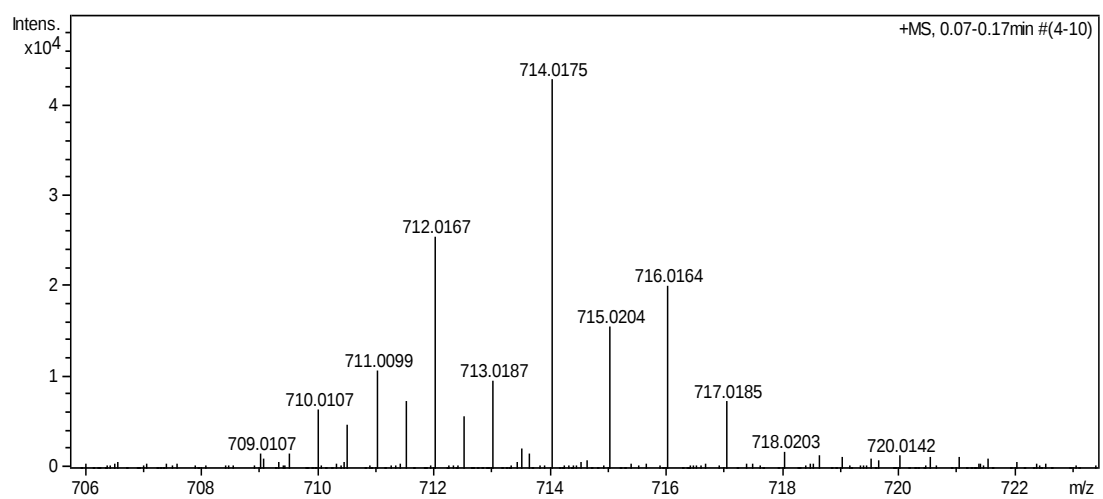
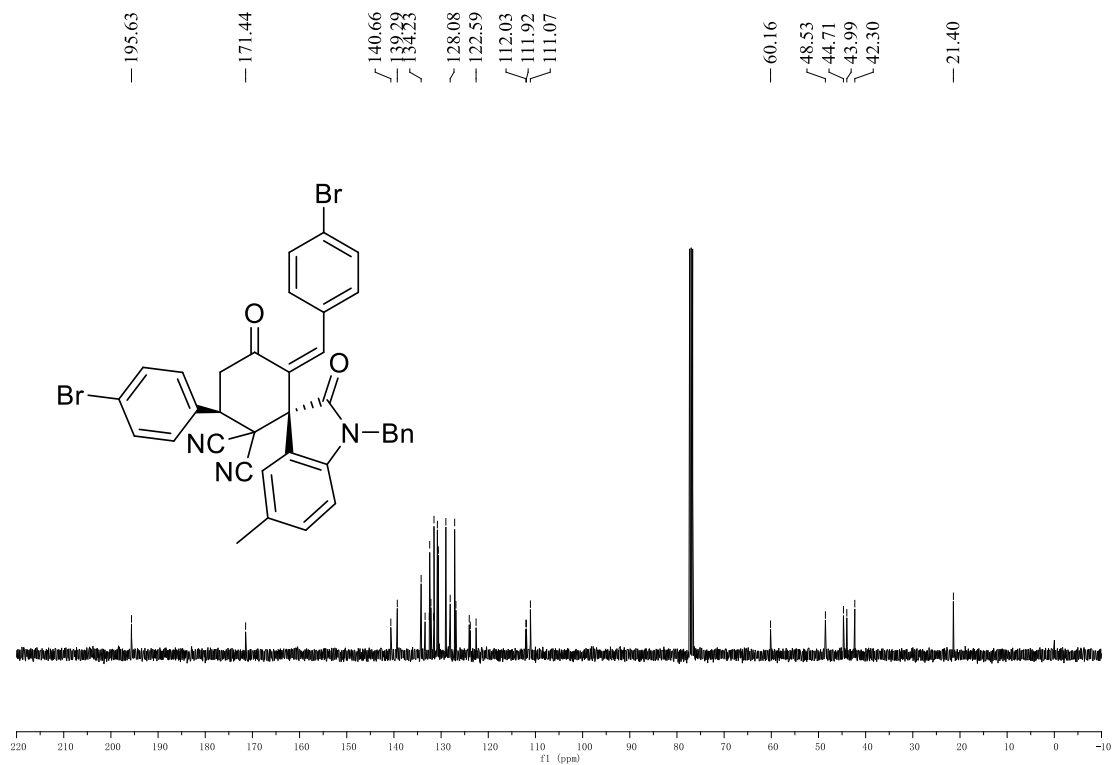
rel-(1*R*,3*R*)-1'-Benzyl-6-((*Z*)-4-chlorobenzylidene)-3-(4-chlorophenyl)-5'-methyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3d): pole pink solid, 58%, m.p. 244-246 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.69 (s, 1H, ArH), 7.49-7.43 (m, 4H, ArH), 7.32-7.28 (m, 9H, ArH), 7.21 (d, *J* = 8.0 Hz, 1H, ArH), 6.80 (d, *J* = 8.0 Hz, 1H, ArH), 6.63 (s, 1H, CH), 5.10-5.04 (m, 2H, CH₂), 4.86 (d, *J* = 15.6 Hz, 1H, CH₂), 3.39 (t, *J* = 14.0 Hz, 1H, CH), 3.10-3.05 (m, 1H, CH₂), 2.41 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 195.7, 171.5, 140.7, 139.2, 135.8, 135.5, 134.3, 134.2, 132.9, 132.2, 132.1, 131.5, 130.6, 130.3, 129.5, 129.0, 128.6, 128.1, 127.1, 126.9, 122.6, 112.1, 112.0, 111.1, 60.2, 48.7, 44.7, 44.1, 42.2, 21.4. IR (KBr) ν: 3726, 3630, 3405, 3065, 2925, 2316, 1903, 1708, 1610, 1494, 1443, 1414, 1357, 1291, 1187, 1091, 1059, 1013, 917, 824, 732 cm⁻¹ MS (*m/z*): HRMS (ESI) Calcd. for C₃₆H₂₅NaCl₂N₃O₂ ([M+Na]⁺): 624.1222, found: 624.1204.



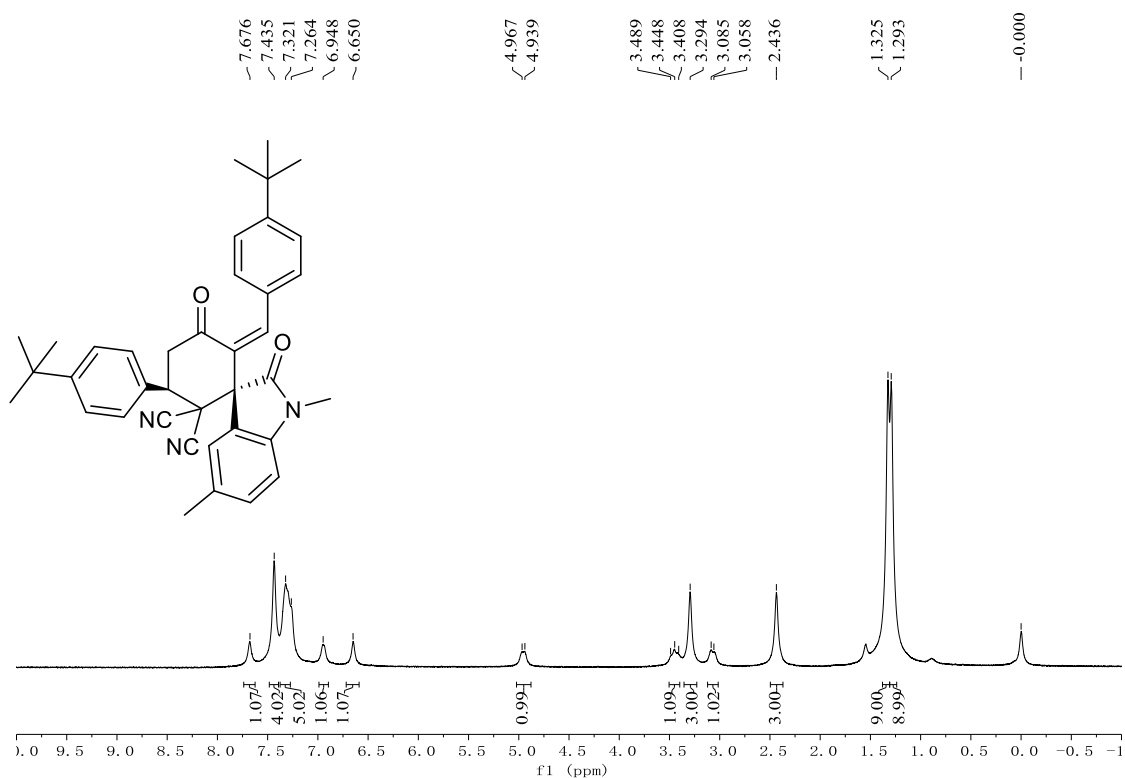


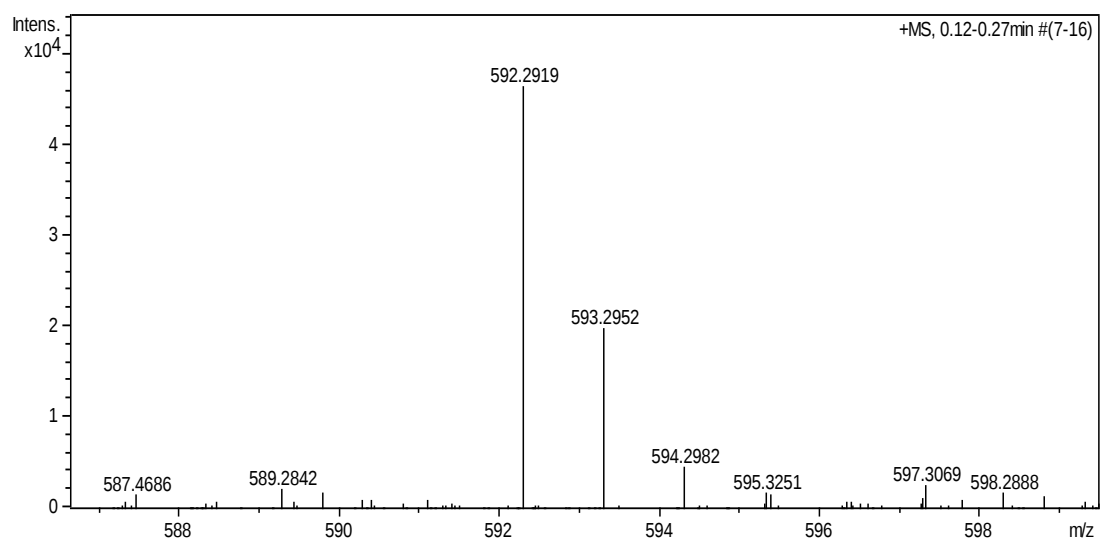
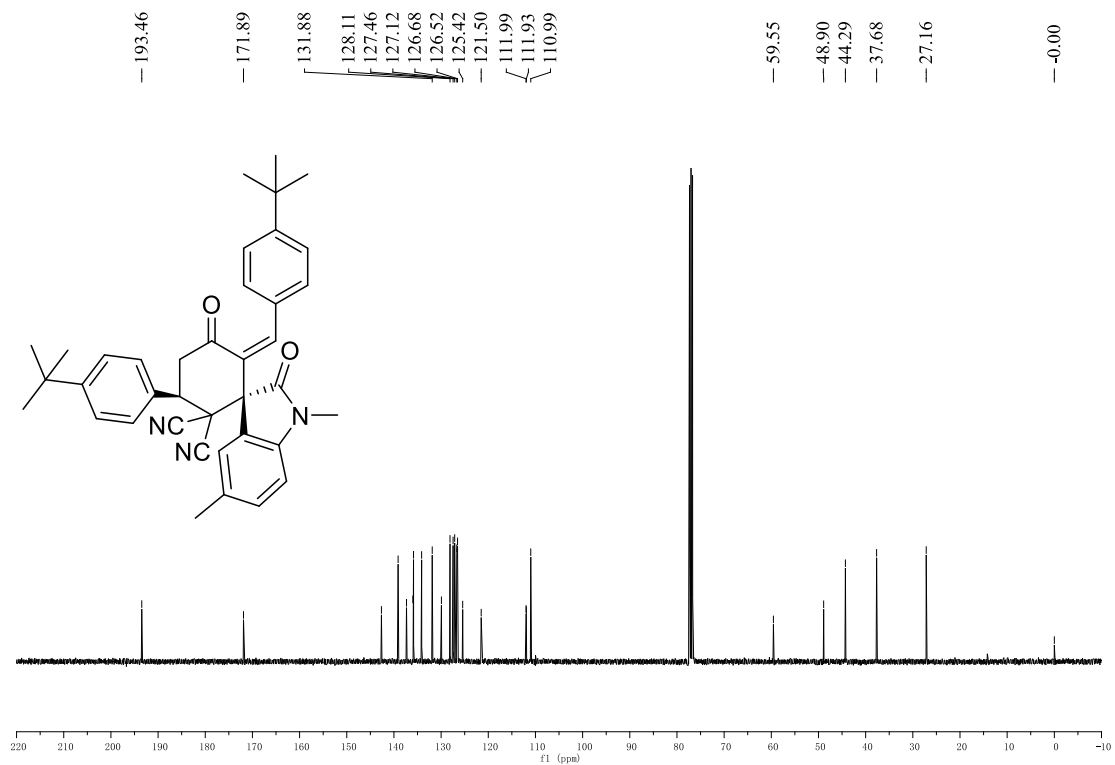
***rel*-(1*R*,3*R*)-1'-Benzyl-6-((*Z*)-4-bromobenzylidene)-3-(4-bromophenyl)-5'-methyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (**3e**):** white solid, 62%, m.p. 233-234 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.68 (s, 1H, ArH), 7.60 (d, *J* = 6.8 Hz, 2H, ArH), 7.46-7.41 (m, 4H, ArH), 7.36-7.30 (m, 5H, ArH), 7.23-7.19 (m, 3H, ArH), 6.79 (d, *J* = 8.4 Hz, 1H, ArH), 6.61 (s, 1H, CH), 5.10-5.02 (m, 2H, CH₂), 4.86 (d, *J* = 16.0 Hz, 1H, CH₂), 3.39 (t, *J* = 14.8 Hz, 1H, CH), 3.10-3.05 (m, 1H, CH₂), 2.41 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 195.6, 171.4, 140.7, 139.3, 134.2, 133.4, 132.5, 132.4, 132.2, 131.6, 131.5, 130.8, 130.6, 129.0, 128.1, 127.1, 126.9, 124.0, 123.8, 122.6, 112.0, 111.9, 111.1, 60.2, 48.5, 44.7, 44.0, 42.3, 21.4. IR (KBr) ν: 3725, 3627, 3401, 3065, 2924, 2316, 1902, 1708, 1613, 1493, 1443, 1411, 1357, 1291, 1187, 1110, 1070, 1009, 959, 917, 821, 733 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₆H₂₅NaBr₂N₃O₂ ([M+Na]⁺): 712.0211, found: 712.0167.



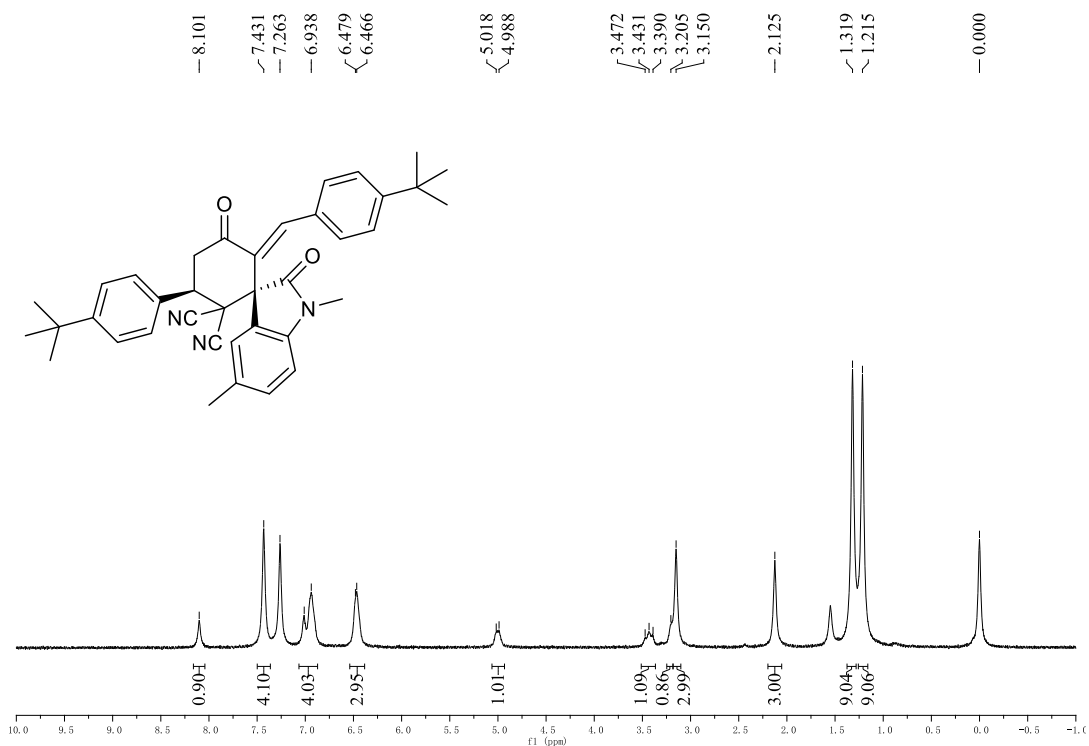


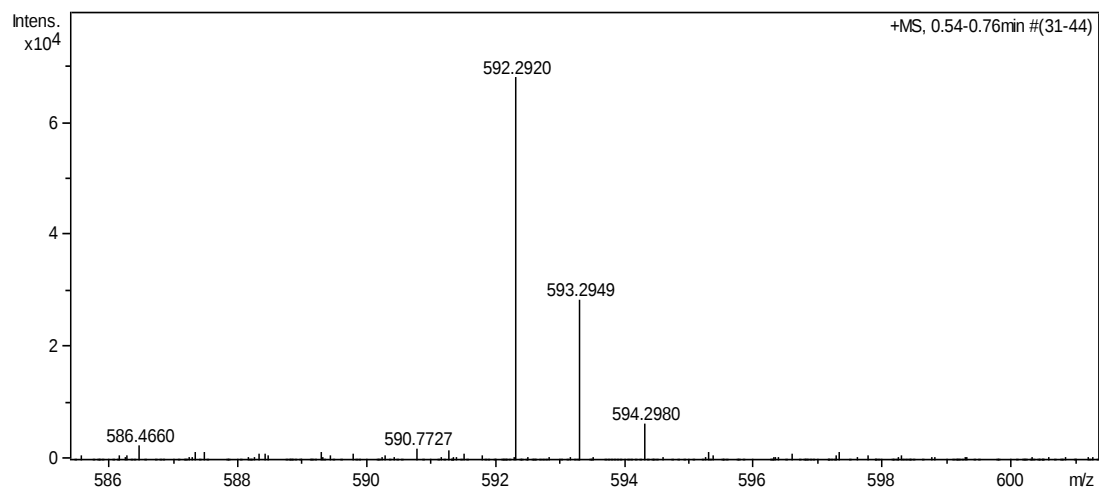
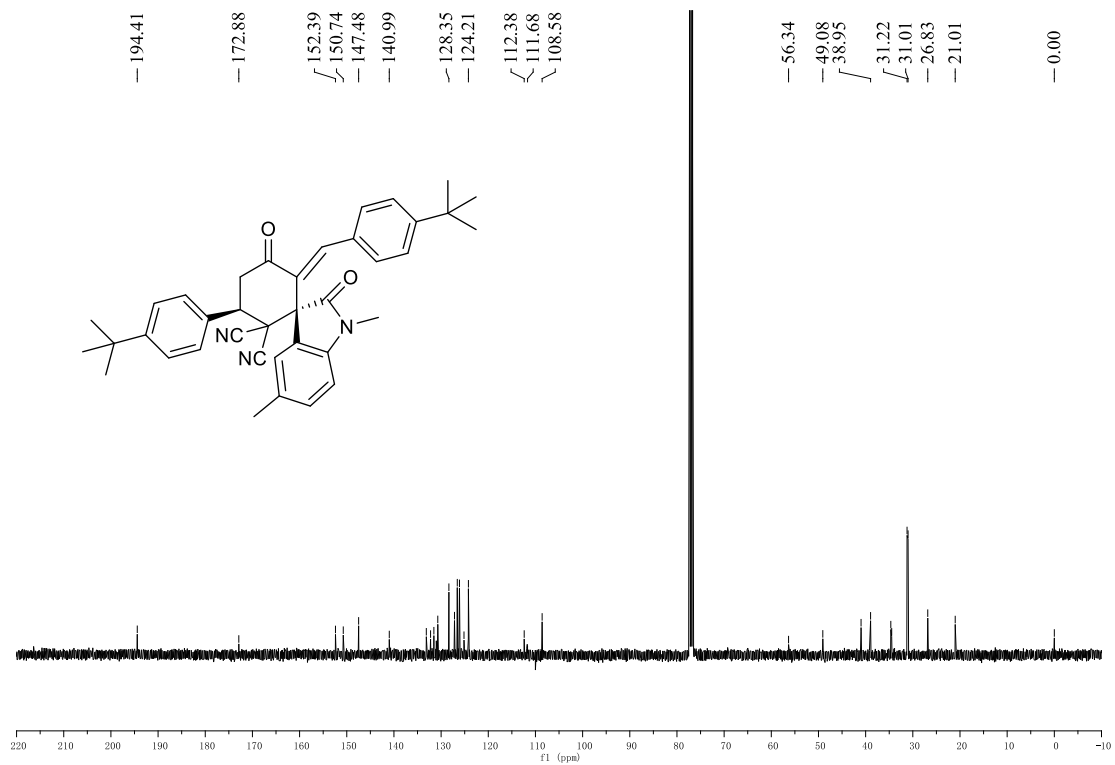
***rel*-(1*R*,3*R*)-6-((*Z*)-4-(*tert*-Butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-1',5'-dimethyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3f)**: yellow solid, 42%, m.p. 212-214 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.68 (s, 1H, ArH), 7.43 (s, 4H, ArH), 7.32-7.26 (m, 5H, ArH), 6.95 (s, 1H, ArH), 6.65 (s, 1H, CH), 4.96 (d, *J* = 11.2 Hz, 1H, CH₂), 3.45 (t, *J* = 16.0 Hz, 1H, CH), 3.29 (s, 3H, CH₃), 3.07 (d, *J* = 10.8 Hz, 1H, CH₂), 2.44 (s, 3H, CH₃), 1.32 (s, 9H, (CH₃)₃), 1.29 (s, 9H, (CH₃)₃). ¹³C NMR (100 MHz, CDCl₃) δ 193.5, 171.9, 142.7, 139.1, 137.3, 136.0, 135.9, 134.1, 131.9, 129.9, 128.1, 127.5, 127.1, 126.7, 126.5, 125.4, 121.5, 112.0, 111.9, 111.0, 59.6, 48.9, 44.3, 37.7, 27.2. IR (KBr) ν: 3030, 2956, 2869, 1710, 1611, 1502, 1424, 1358, 1195, 1149, 1052, 939, 817, 738 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₈H₃₉NaN₃O₂ ([M+Na]⁺): 592.2940, found: 592.2919.



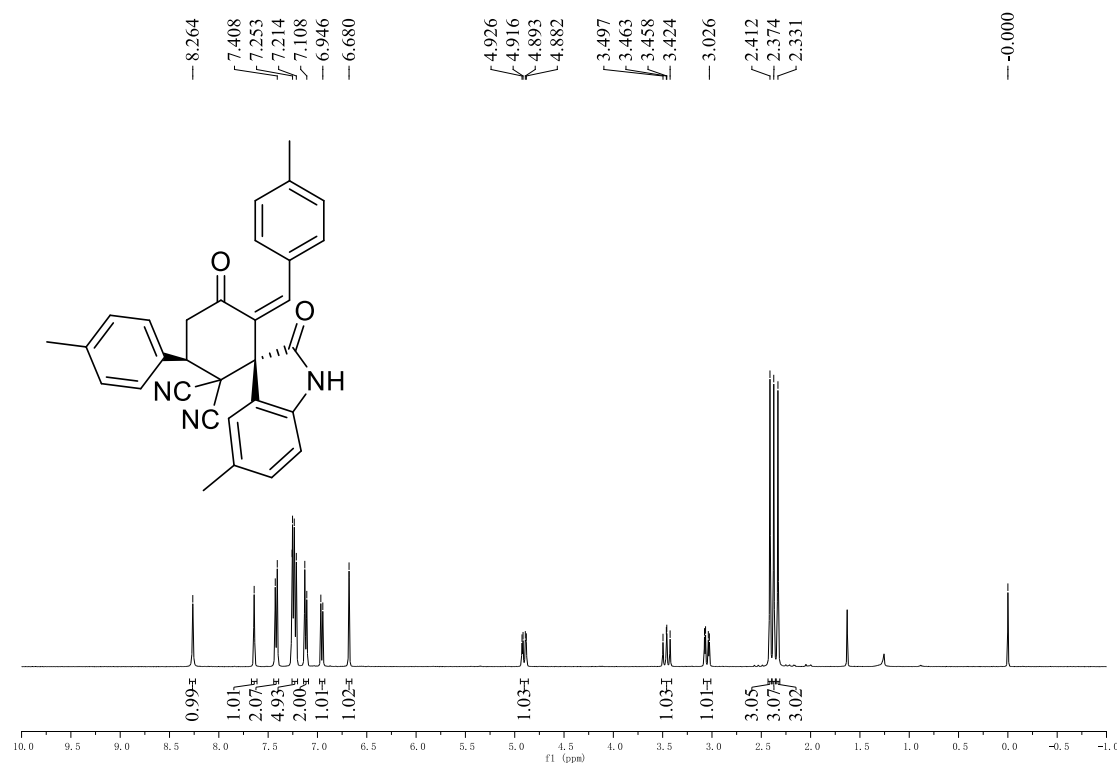


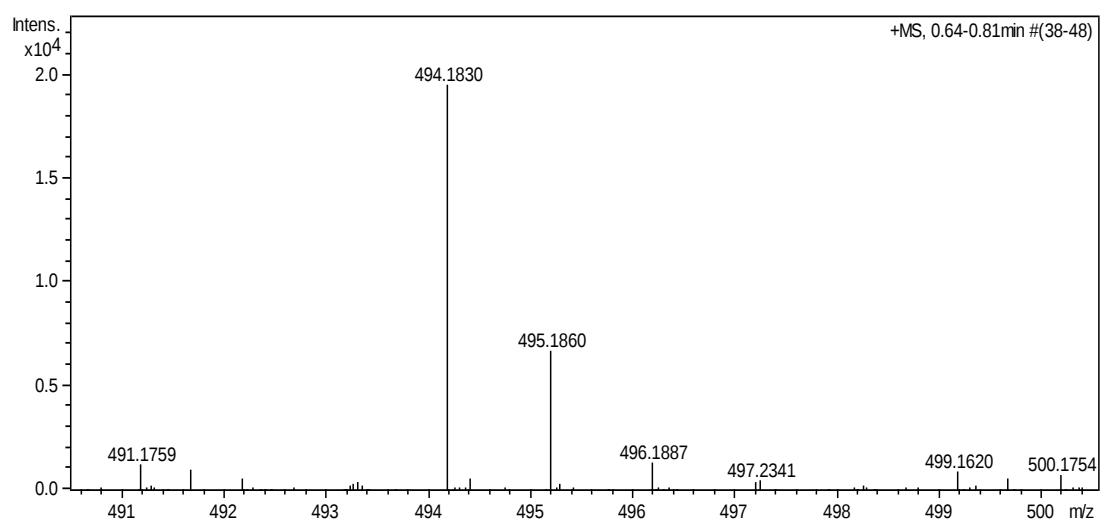
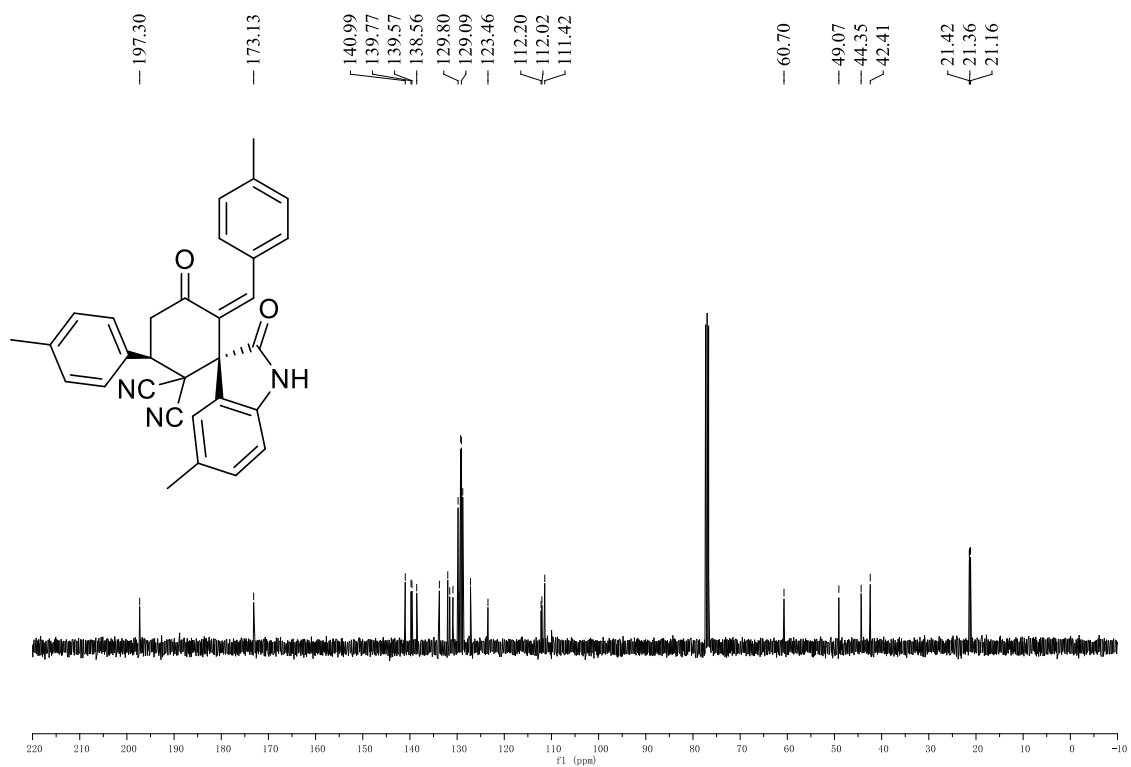
***rel*-(1*R*,3*R*)-6-((*E*)-4-(*tert*-Butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-1',5'-dimethyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3f')**: yellow solid, 14%, m.p. 172-174 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H, ArH), 7.43 (s, 4H, ArH), 7.01-6.94 (m, 4H, ArH), 6.48-6.47 (m, 3H, ArH), 5.02-4.99 (m, 1H, CH₂), 3.43 (m, 1H, CH), 3.21 (s, 1H, CH₂), 3.15 (s, 3H, CH₃), 2.13 (s, 3H, CH₃), 1.32 (s, 9H, (CH₃)₃), 1.22 (s, 9H, (CH₃)₃). ¹³C NMR (100 MHz, CDCl₃) δ 194.4, 172.9, 152.4, 150.7, 147.5, 141.0, 133.1, 132.2, 131.5, 130.7, 128.4, 127.2, 126.6, 126.1, 125.2, 124.2, 112.4, 111.7, 108.6, 56.3, 49.1, 41.0, 39.0, 34.7, 34.5, 31.2, 31.0, 26.8, 21.0; IR (KBr) ν: 3125, 3021, 2764, 1715, 1610, 1531, 1415, 1342, 1143, 1121, 1035, 940, 815, 732 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₈H₃₉NaN₃O₂ ([M+Na]⁺): 592.2940, found: 592.2920.



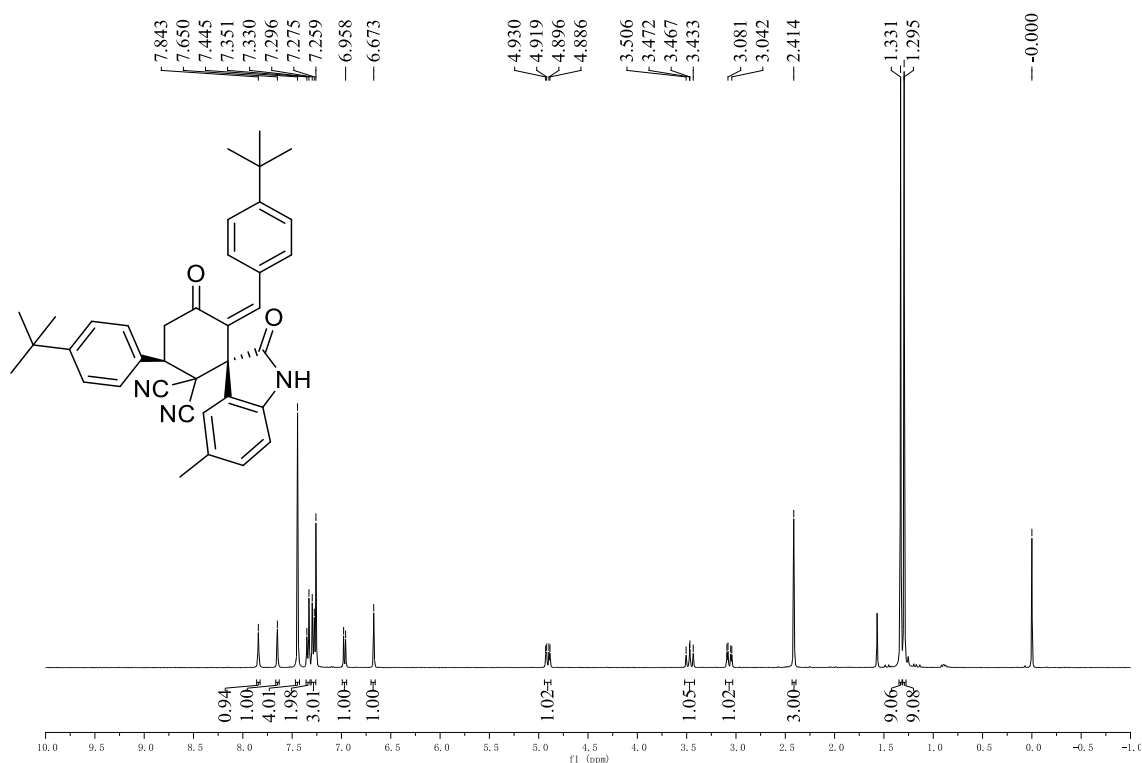


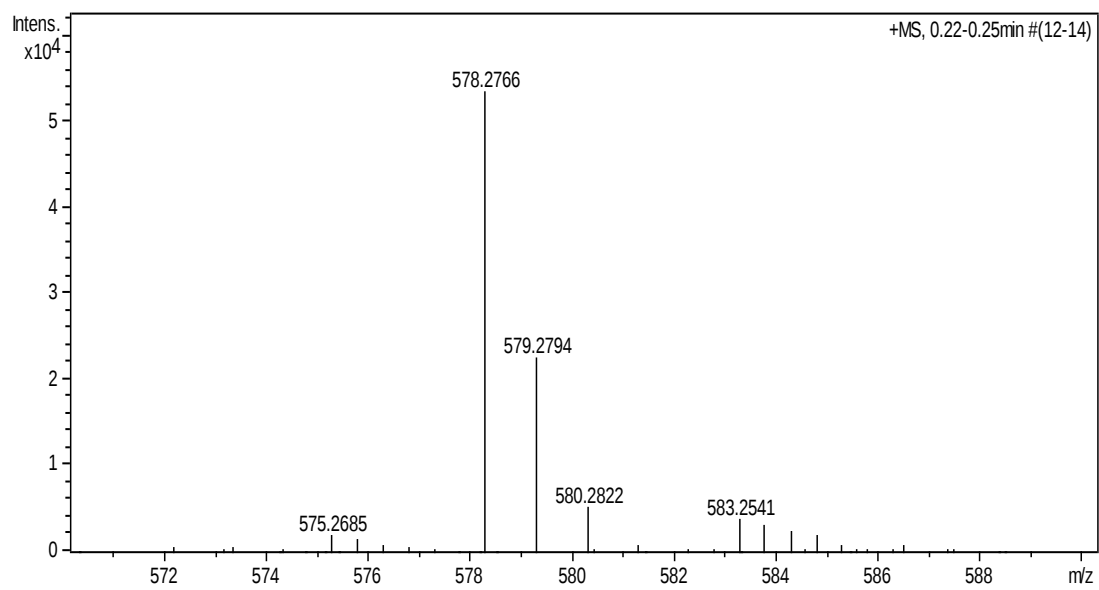
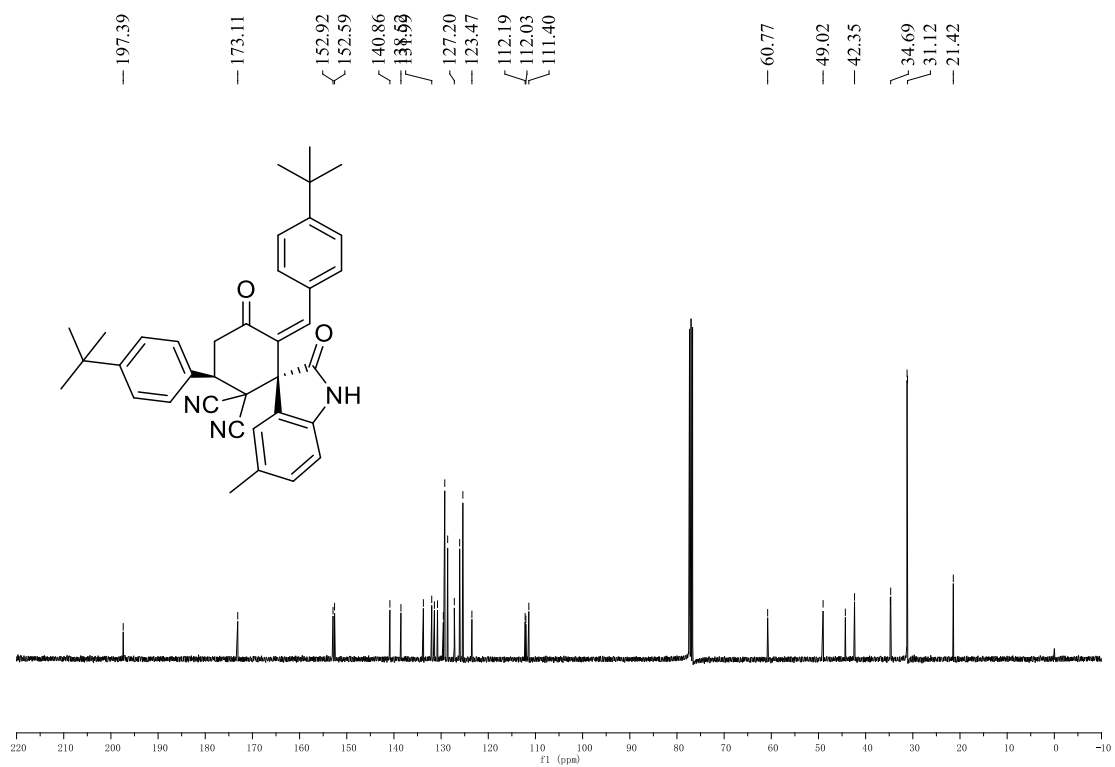
***rel*-(1*R*,3*R*)-5'-Methyl-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (**3g**):** white solid, 45%, m.p. 252-254 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 1H, NH), 7.64 (s, 1H, ArH), 7.42 (d, *J* = 8.0 Hz, 2H, ArH), 7.25-7.21 (m, 5H, ArH), 7.12 (d, *J* = 8.0 Hz, 2H, ArH), 6.96 (d, *J* = 8.0 Hz, 1H, ArH), 6.68 (s, 1H, CH), 4.93-4.88 (m, 1H, CH₂), 3.50-3.42 (m, 1H, CH), 3.08-3.03 (m, 1H, CH₂), 2.41 (s, 3H, CH₃), 2.37 (s, 3H, CH₃), 2.33 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 197.3, 173.1, 141.0, 139.8, 139.6, 138.6, 133.8, 132.0, 131.6, 130.9, 129.8, 129.6, 129.2, 129.1, 128.8, 127.2, 123.5, 112.2, 112.0, 111.4, 60.7, 49.1, 44.4, 42.4, 21.4, 21.4, 21.2. IR (KBr) ν: 3311, 3035, 2920, 1901, 1726, 1615, 1450, 1449, 1419, 1359, 1305, 1197, 1052, 959, 888, 818, 746 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₁H₂₅NaN₃O₂ ([M+Na]⁺): 494.1844, found: 494.1830.



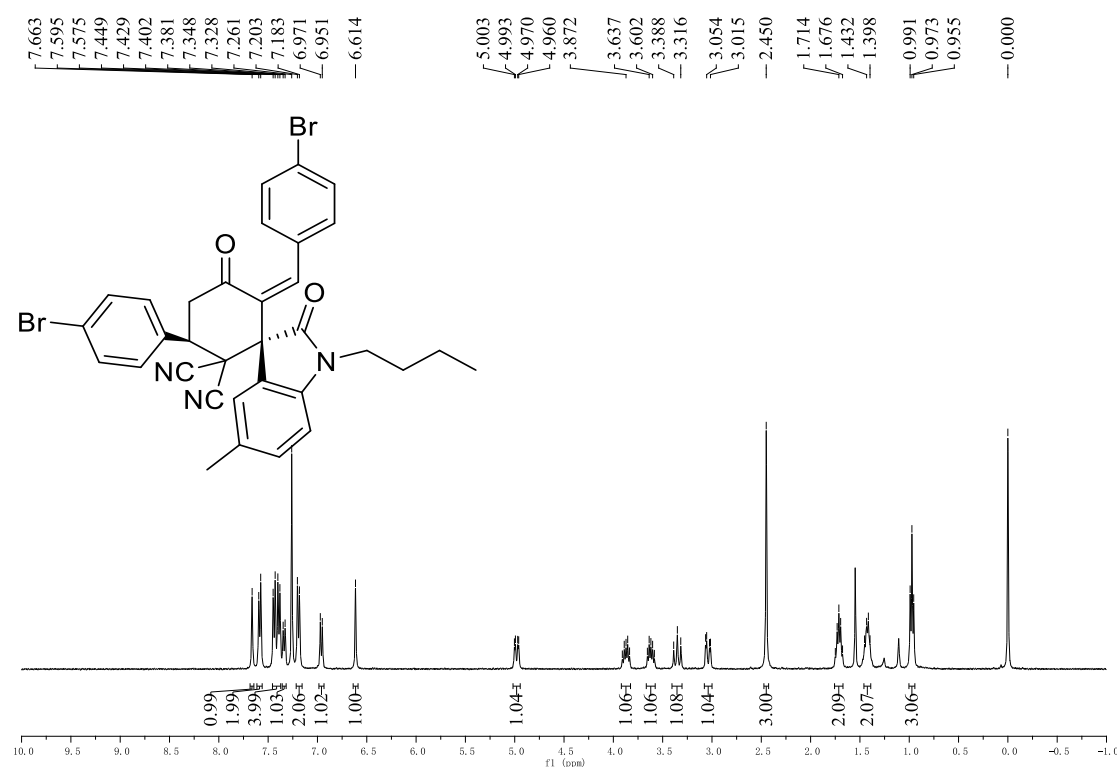


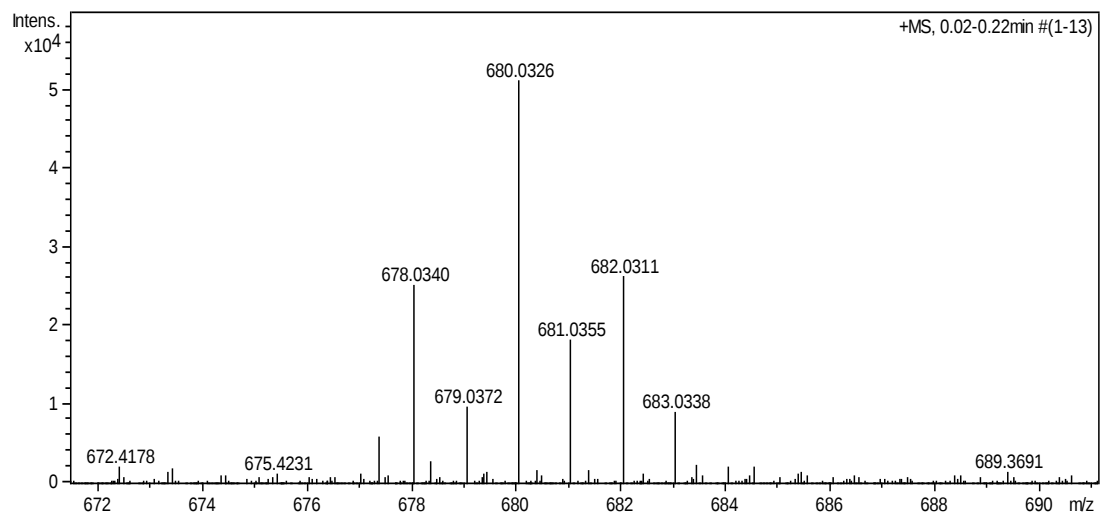
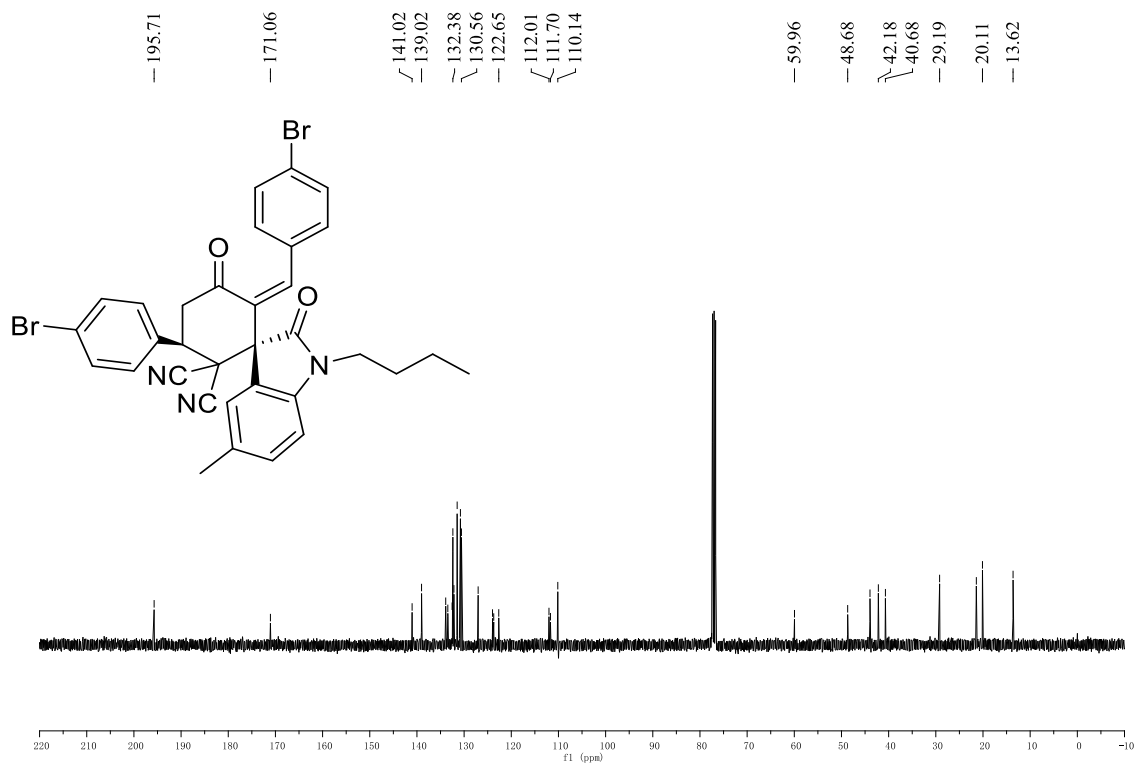
***rel*-(1*R*,3*R*)-6-((*Z*)-4-(*tert*-Butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-5'-methyl-2',5'-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (**3h**):** pale yellow solid, 49%, m.p. 238-240 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.84 (s, 1H, NH), 7.65 (s, 1H, ArH), 7.45 (s, 4H, ArH), 7.34 (d, *J* = 8.4 Hz, 2H, ArH), 7.29 (d, *J* = 8.4 Hz, 3H, ArH), 6.97 (d, *J* = 8.0 Hz, 1H, ArH), 6.67 (s, 1H, CH), 4.93-4.89 (m, 1H, CH₂), 3.51-3.43 (m, 1H, CH), 3.09-3.04 (m, 1H, CH₂), 2.41 (s, 3H, CH₃), 1.33 (s, 9H, (CH₃)₃), 1.30 (s, 3H, (CH₃)₃). ¹³C NMR (100 MHz, CDCl₃) δ 197.4, 173.1, 152.9, 152.6, 140.9, 138.5, 133.8, 132.0, 131.4, 130.8, 129.5, 129.2, 128.6, 127.2, 126.1, 125.4, 123.5, 112.2, 112.0, 111.4, 60.8, 49.0, 44.3, 42.4, 34.8, 34.7, 31.2, 31.1, 21.4. IR (KBr) ν: 3684, 3288, 2964, 1728, 1614, 1500, 1358, 1307, 1266, 1207, 1112, 1058, 1021, 968, 830 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₇H₃₇NaN₃O₂ ([M+Na]⁺): 578.2783, found: 578.2766.



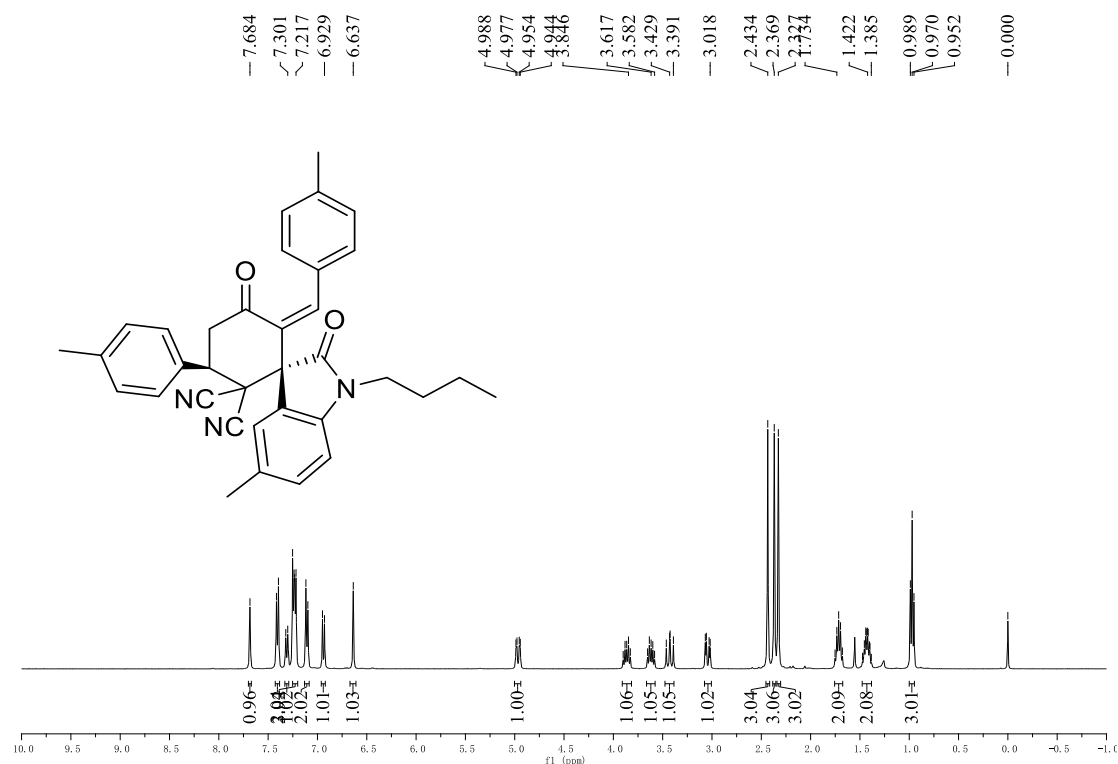


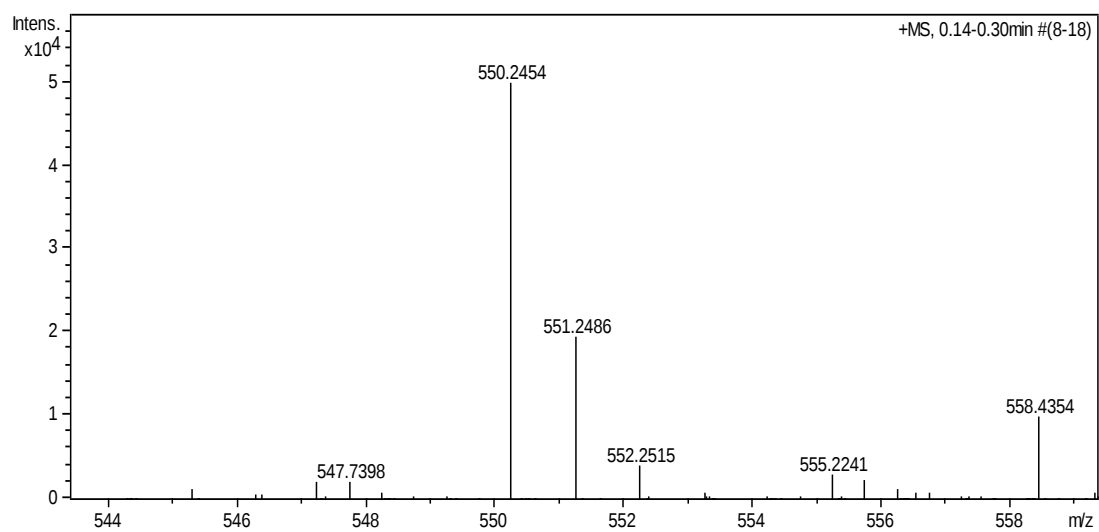
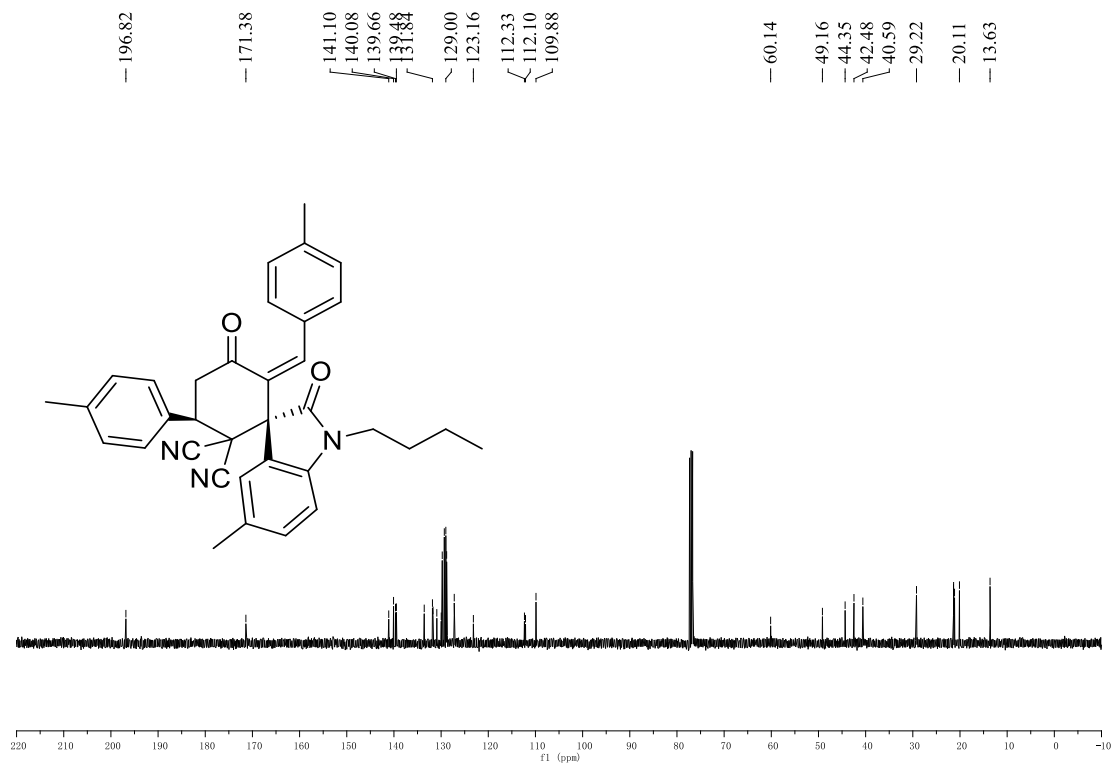
***rel*-(1*R*,3*R*)-6-((*Z*)-4-Bromobenzylidene)-3-(4-bromophenyl)-1'-butyl-5'-methyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3i)**: white solid, 54%, m.p. 170-172 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 1H, ArH), 7.59 (d, *J* = 8.0 Hz, 2H, ArH), 7.43-7.38 (m, 4H, ArH), 7.34 (d, *J* = 8.0 Hz, 1H, ArH), 7.19 (d, *J* = 8.0 Hz, 2H, ArH), 6.96 (d, *J* = 8.0 Hz, 1H, ArH), 6.61 (s, 1H, CH), 5.00-4.96 (m, 1H, CH₂), 3.91-3.84 (m, 1H, CH₂), 3.66-3.58 (m, 1H, CH₂), 3.35 (t, *J* = 14.0 Hz, 1H, CH), 3.07-3.02 (m, 1H, CH₂), 2.45 (s, 3H, CH₃), 1.75-1.68 (m, 2H, CH₂), 1.45-1.40 (m, 2H, CH₂), 0.97 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 195.7, 171.1, 141.0, 139.0, 133.9, 133.5, 132.6, 132.4, 132.2, 131.5, 130.8, 130.6, 127.0, 124.0, 123.7, 122.7, 112.0, 111.7, 110.1, 60.0, 48.7, 44.0, 42.2, 40.7, 29.2, 21.4, 20.1, 13.6. IR (KBr) ν: 3094, 2934, 2868, 1701, 1615, 1592, 1495, 1436, 1352, 1329, 1271, 1238, 1198, 1164, 1120, 1079, 1055, 991, 916, 857, 837, 815, 736, 713 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₃H₂₇NaBr₂N₃O₂ ([M+Na]⁺): 678.0368, found: 678.0340.



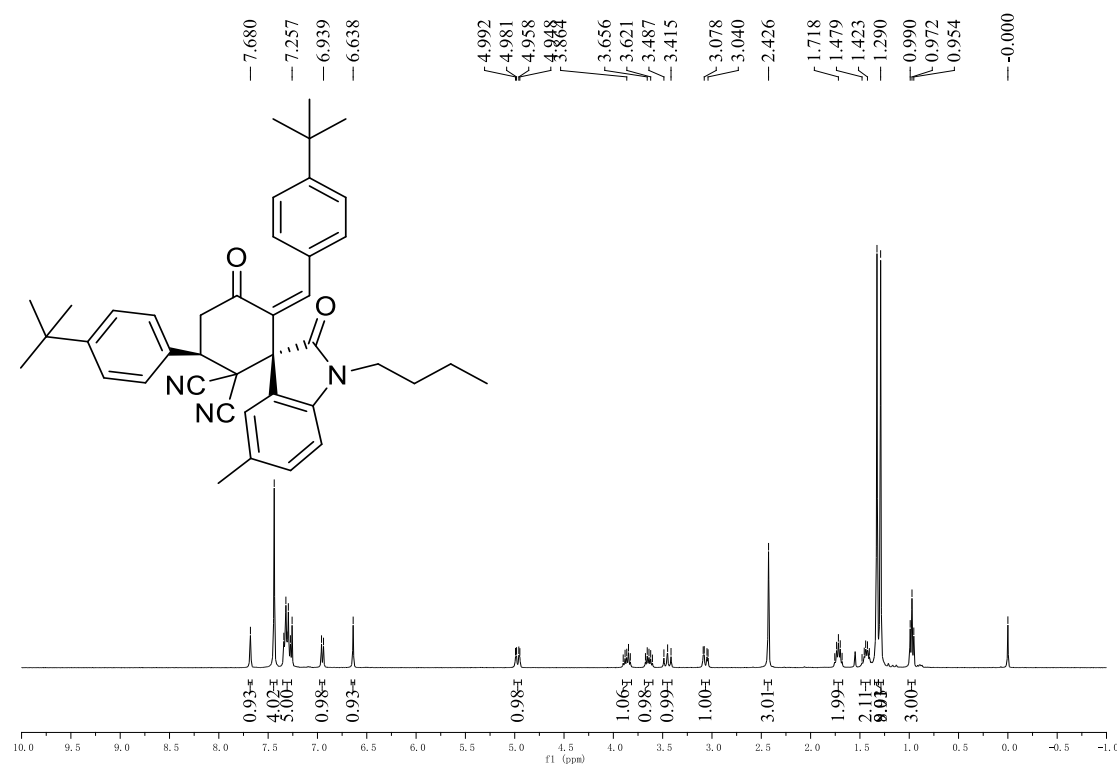


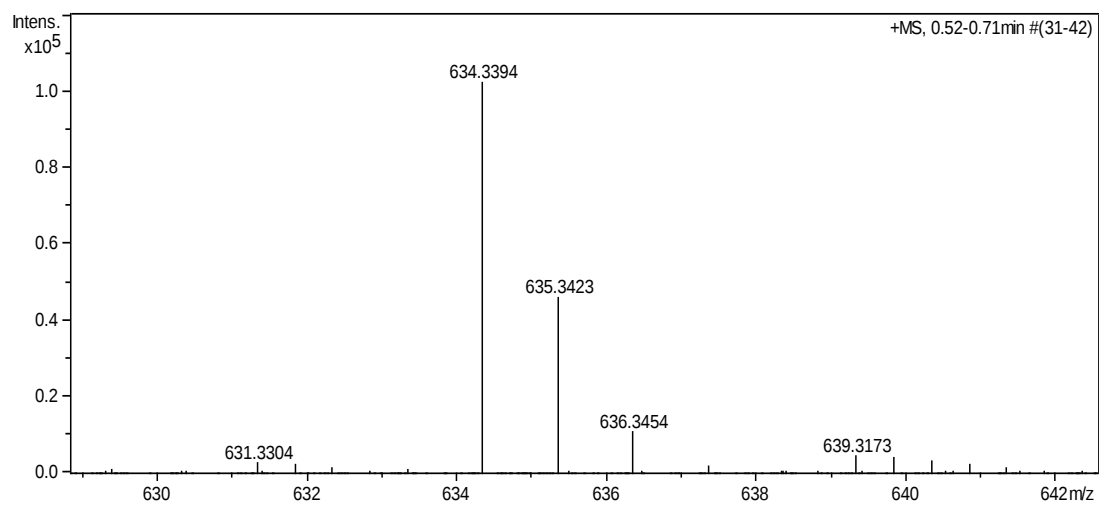
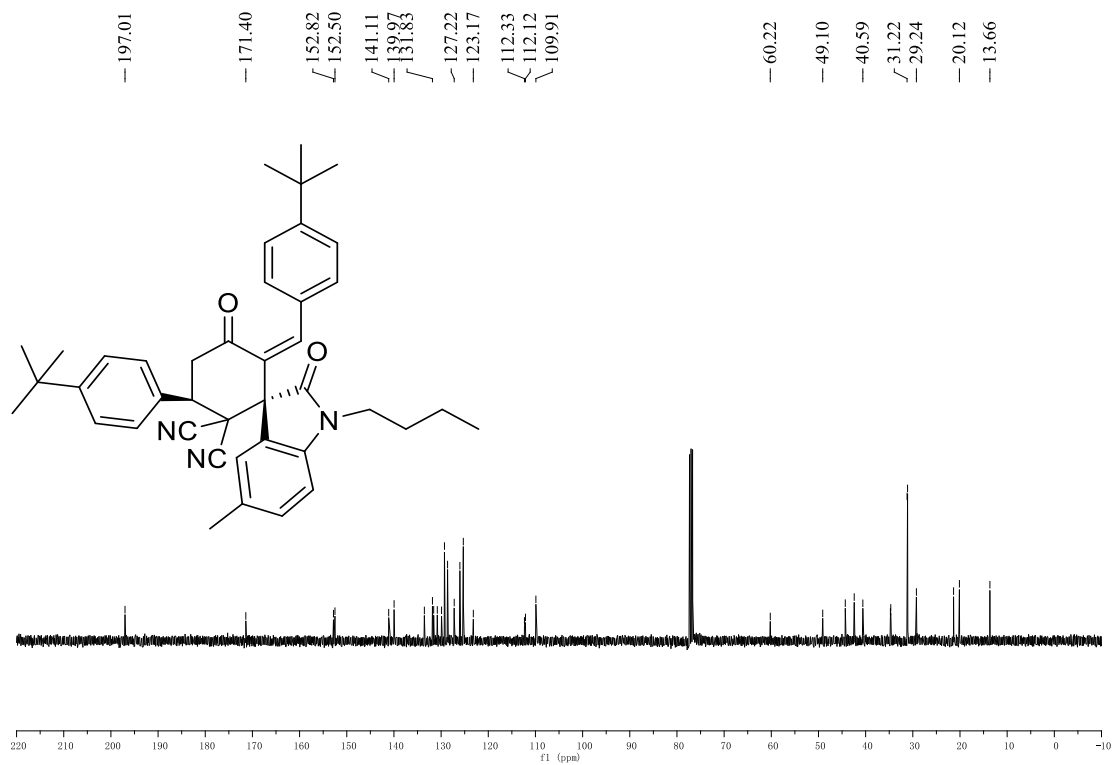
***rel*-(1*R*,3*R*)-1'-Butyl-5'-methyl-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3j)**: white solid, 54%, m.p. 214-216 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.68 (s, 1H, ArH), 7.41 (d, *J* = 8.4 Hz, 2H, ArH), 7.31 (d, *J* = 8.0 Hz, 1H, ArH), 7.24-7.22 (m, 4H, ArH), 7.11 (d, *J* = 8.0 Hz, 2H, ArH), 6.94 (d, *J* = 8.0 Hz, 1H, ArH), 6.64 (s, 1H, CH), 4.99-4.94 (m, 1H, CH₂), 3.90-3.83 (m, 1H, CH₂), 3.65-3.58 (m, 1H, CH₂), 3.46-3.39 (m, 1H, CH), 3.07-3.02 (m, 1H, CH₂), 2.43 (s, 3H, CH₃), 2.37 (s, 3H, CH₃), 2.33 (s, 3H, CH₃), 1.75-1.68 (m, 2H, CH₂), 1.46-1.39 (m, 2H, CH₂), 0.97 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 196.8, 171.4, 141.1, 140.1, 139.7, 139.5, 133.6, 131.8, 131.7, 130.9, 130.0, 129.8, 129.3, 129.0, 128.8, 127.2, 123.2, 112.3, 112.1, 109.9, 60.1, 49.2, 44.4, 42.5, 40.6, 29.2, 21.4, 21.3, 21.2, 20.1, 13.6. IR (KBr) ν: 3030, 2956, 2869, 1710, 1611, 1502, 1424, 1358, 1195, 1149, 1052, 939, 817, 738 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₅H₃₃NaN₃O₂ ([M+Na]⁺): 550.2470, found: 550.2454.



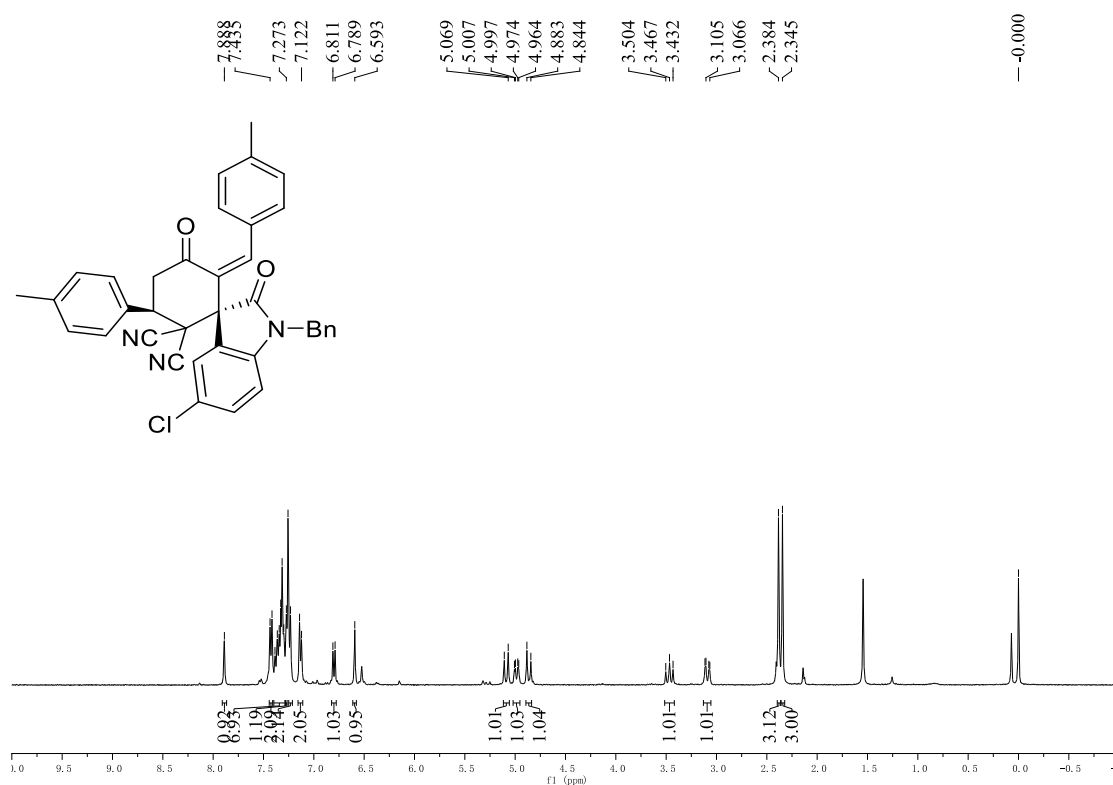


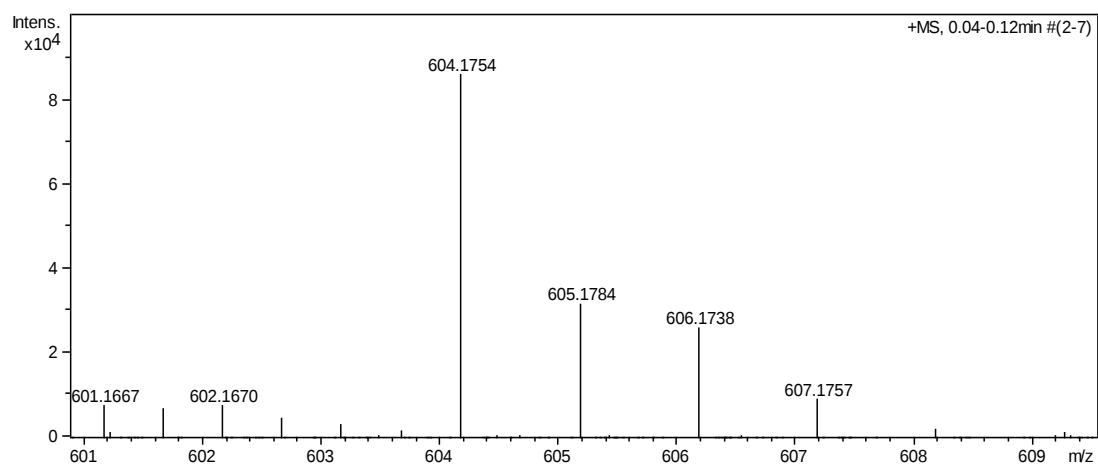
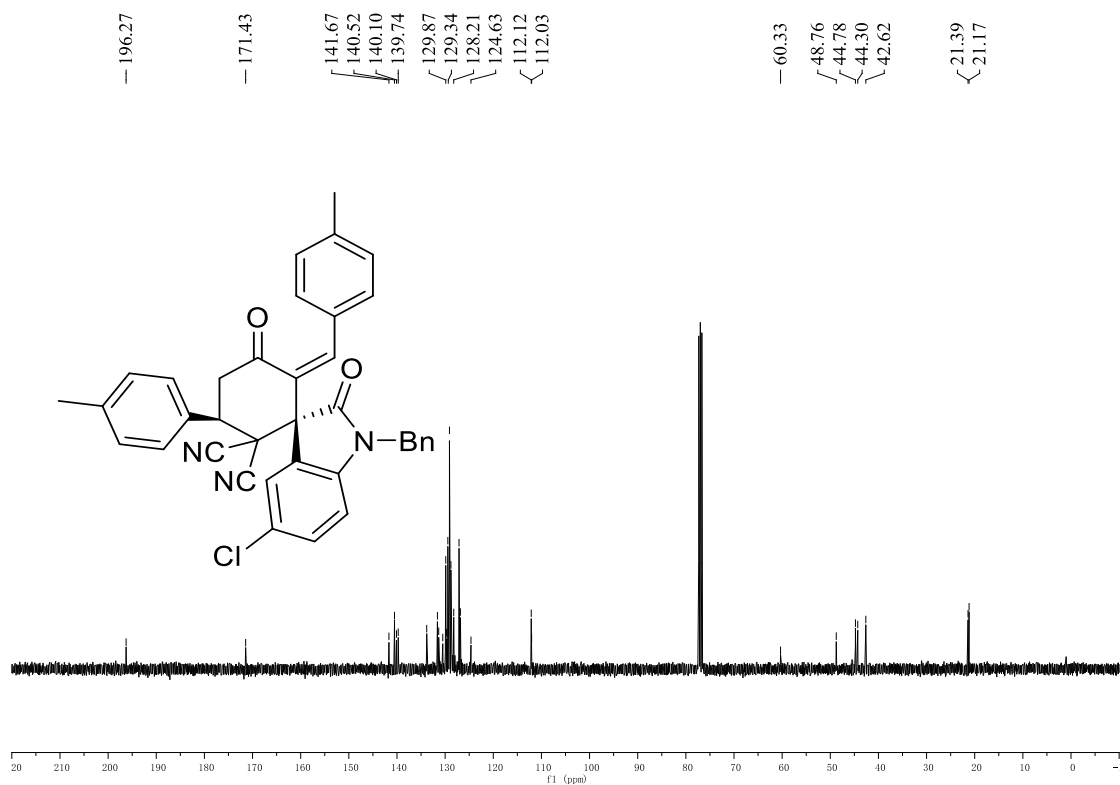
***rel*-(1*R*,3*R*)-1'-Butyl-6-((*Z*)-4-(*tert*-butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-5'-methyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (**3k**):** white solid, 58%, m.p. 143-145 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.68 (s, 1H, ArH), 7.44 (s, 4H, ArH), 7.34-7.27 (m, 5H, ArH), 6.95 (d, *J* = 8.0 Hz, 1H, ArH), 6.64 (s, 1H, CH), 4.99-4.95 (m, 1H, CH₂), 3.90-3.83 (m, 1H, CH₂), 3.67-3.60 (m, 1H, CH₂), 3.49-3.42 (m, 1H, CH), 3.09-3.04 (m, 1H, CH₂), 2.43 (s, 3H, CH₃), 1.76-1.68 (m, 2H, CH₂), 1.48-1.40 (m, 2H, CH₂), 1.33 (s, 9H, (CH₃)₃), 1.29 (s, 9H, (CH₃)₃), 0.97 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 197.0, 171.4, 152.8, 152.5, 141.1, 140.0, 133.6, 131.8, 131.6, 130.8, 130.0, 129.3, 128.6, 127.2, 126.0, 125.3, 123.2, 112.3, 112.1, 109.9, 60.2, 49.1, 44.3, 42.4, 40.6, 34.8, 34.7, 31.2, 31.1, 29.2, 21.4, 20.1, 13.7. IR (KBr) ν: 2963, 2872, 1711, 1608, 1500, 1462, 1423, 1360, 1264, 1197, 1151, 1114, 1058, 932, 831 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₁H₄₅NaN₃O₂ ([M+Na]⁺): 634.3409, found: 634.3394.



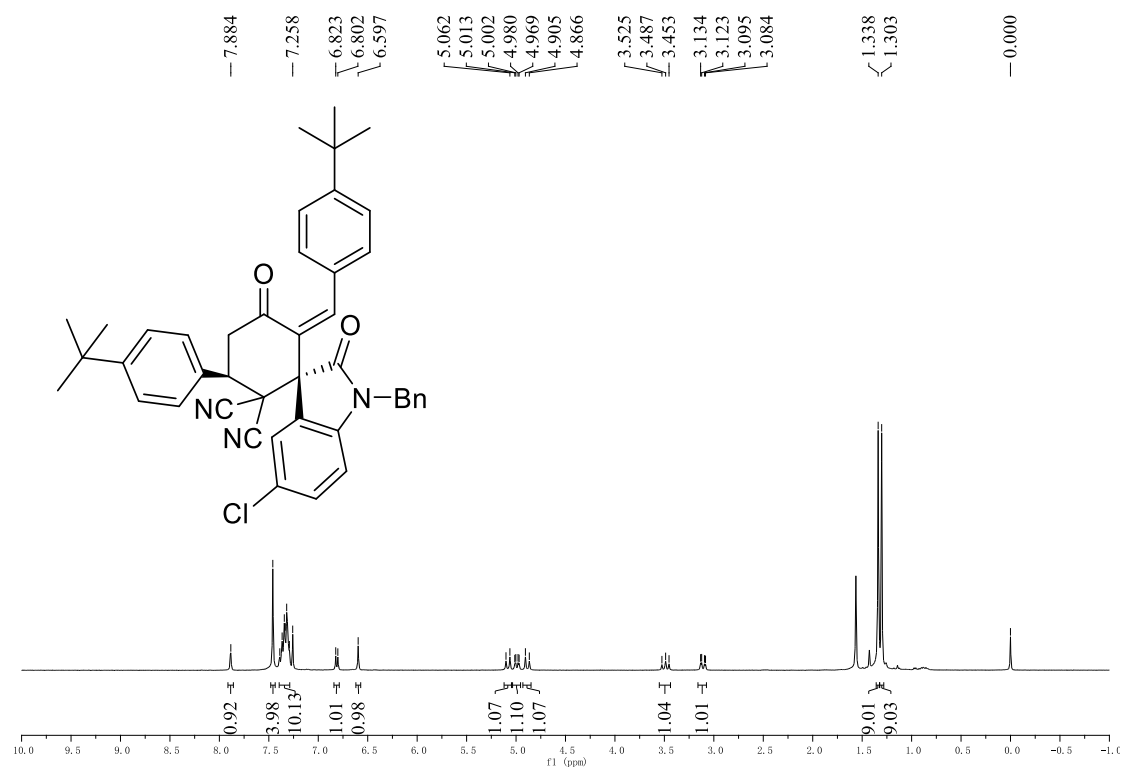


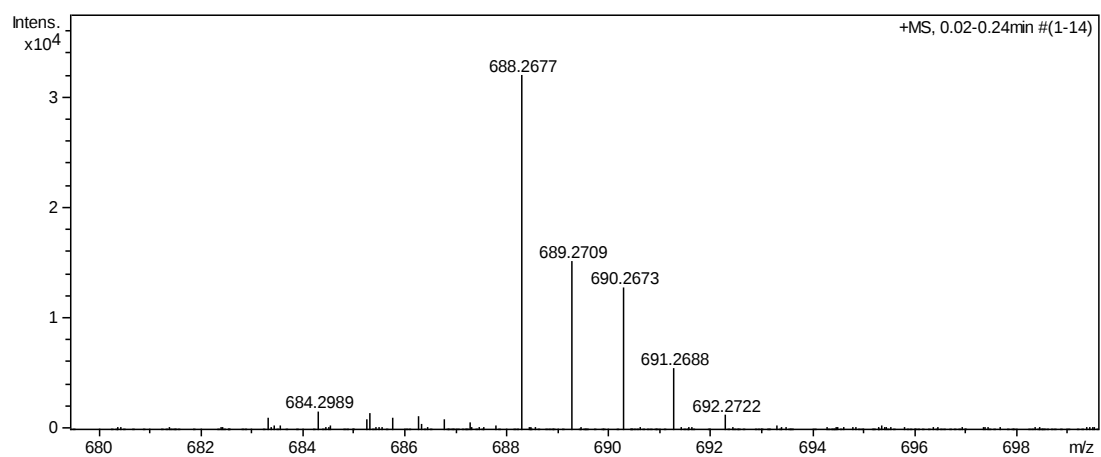
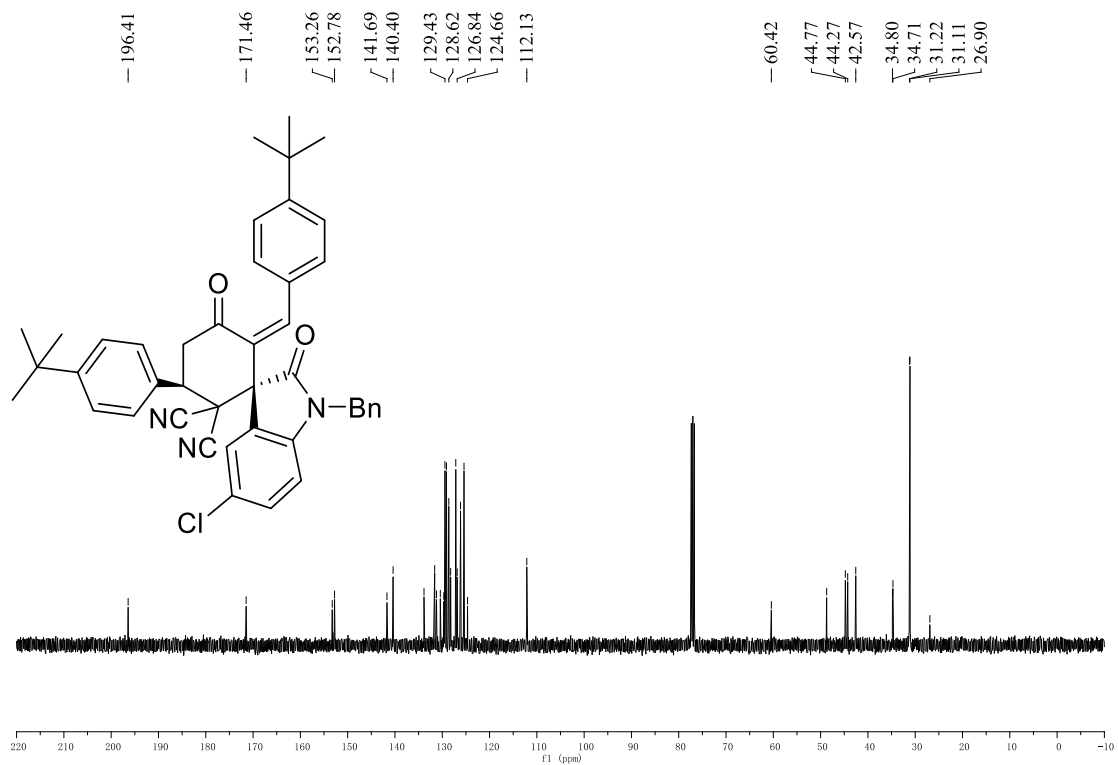
***rel*-(1*R*,3*R*)-1'-Benzyl-5'-chloro-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3l)**: white solid, 54%, m.p. 235-237 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (s, 1H, ArH), 7.42 (d, *J* = 8.0 Hz, 2H, ArH), 7.39-7.30 (m, 7H, ArH), 7.27 (s, 1H, ArH), 7.23 (s, 2H, ArH), 7.13 (d, *J* = 8.0 Hz, 2H, ArH), 6.80 (d, *J* = 8.8 Hz, 1H, ArH), 6.60 (s, 1H, CH), 5.09 (d, *J* = 15.6 Hz, 1H, CH₂), 5.01-4.96 (m, 1H, CH₂), 4.86 (d, *J* = 15.6 Hz, 1H, CH₂), 3.47 (t, *J* = 14.0 Hz, 1H, CH), 3.12-3.07 (m, 1H, CH₂), 2.38 (s, 3H, CH₃), 2.35 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 171.4, 141.7, 140.5, 140.1, 139.7, 133.8, 131.6, 131.3, 130.5, 129.9, 129.7, 129.4, 129.3, 129.1, 128.8, 128.2, 127.1, 126.83, 124.6, 112.1, 112.0, 60.3, 48.8, 44.8, 44.3, 42.6, 21.4, 21.2. IR (KBr) ν: 3728, 3407, 3033, 2919, 2318, 1899, 1776, 1717, 1611, 1485, 1425, 1349, 1259, 1188, 1083, 1020, 957, 883, 816, 724 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₇H₂₈NaClN₃O₂ ([M+Na]⁺): 604.1768, found: 604.1754.



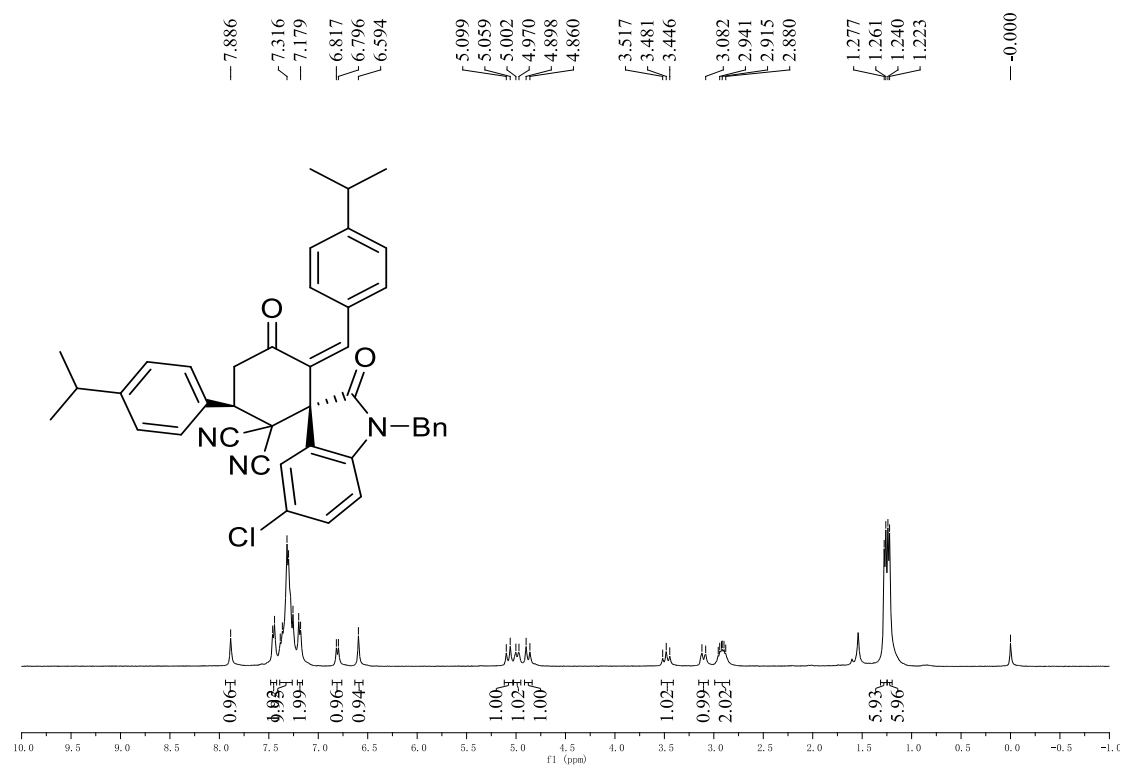


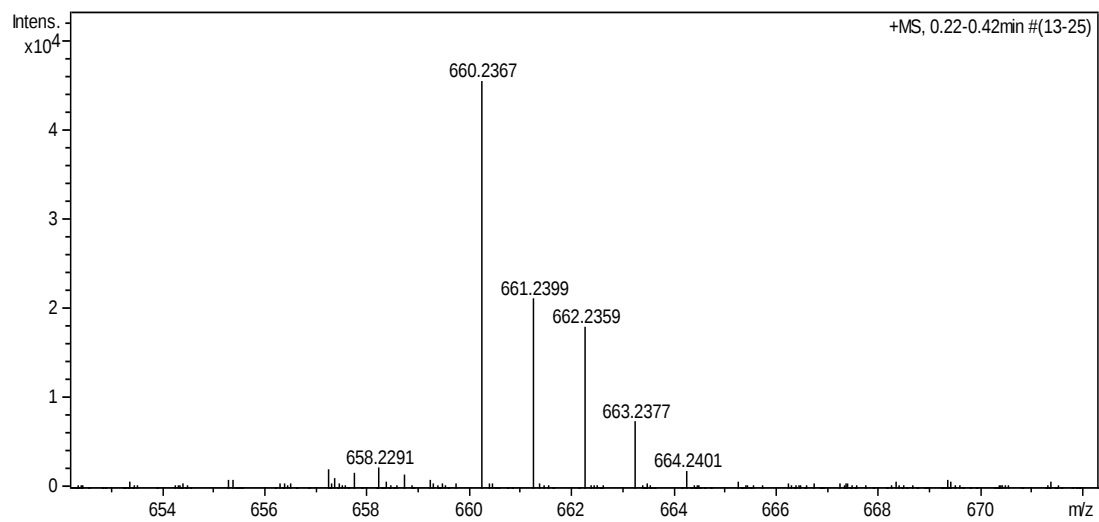
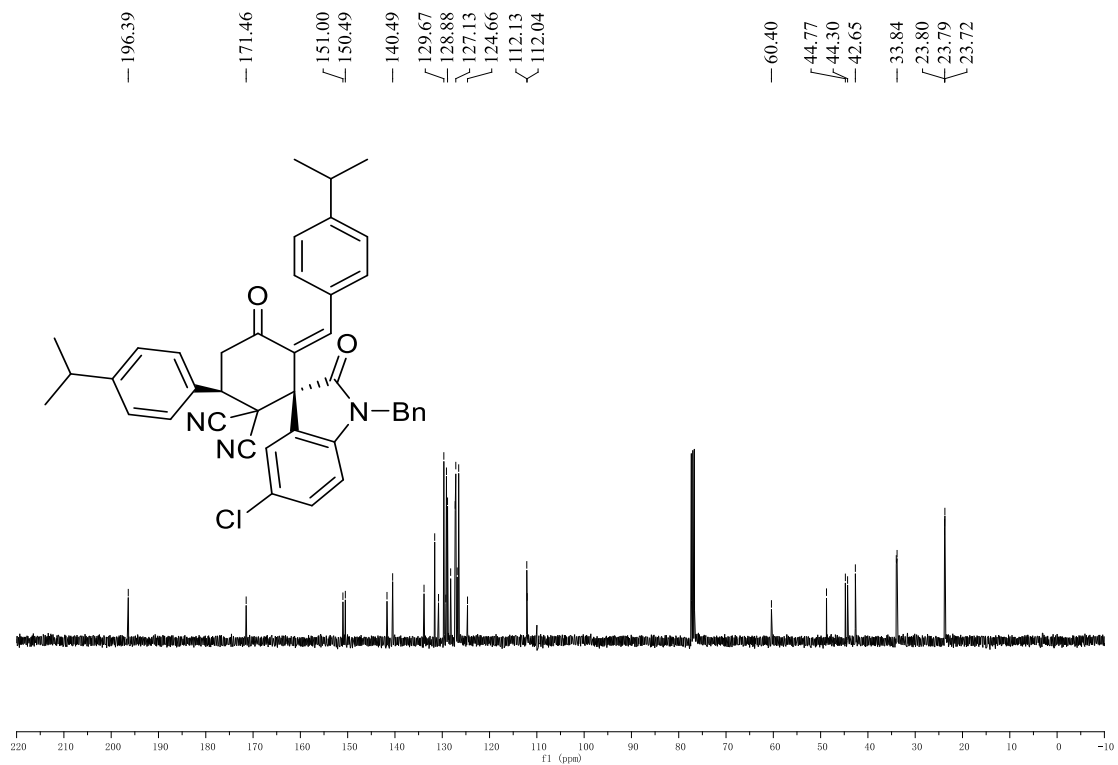
***rel*-(1*R*,3*R*)-1'-Benzyl-6-((*Z*)-4-(*tert*-butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-5'-chloro-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (**3m**):** white solid, 60%, m.p. 184-186 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H, ArH), 7.46 (s, 4H, ArH), 7.39-7.29 (m, 10H, ArH), 6.81 (d, *J* = 8.4 Hz, 1H, ArH), 6.60 (s, 1H, CH), 5.08 (d, *J* = 16.0 Hz, 1H, CH₂), 5.01-4.97 (m, 1H, CH₂), 4.99 (d, *J* = 15.6 Hz, 1H, CH₂), 3.49 (t, *J* = 13.6 Hz, 1H, CH), 3.13-3.08 (m, 1H, CH₂), 1.34 (s, 9H, (CH₃)₃), 1.30 (s, 9H, (CH₃)₃). ¹³C NMR (100 MHz, CDCl₃) δ 196.4, 171.5, 153.3, 152.8, 141.7, 140.4, 133.9, 131.6, 131.2, 130.4, 129.7, 129.4, 129.3, 129.1, 128.6, 128.2, 127.1, 126.8, 126.1, 125.4, 124.7, 112.1, 60.4, 48.7, 44.8, 44.3, 42.6, 34.8, 34.7, 31.2, 31.1, 26.9. IR (KBr) ν: 3685, 3062, 2962, 1718, 1607, 1486, 1424, 1354, 1265, 1189, 1114, 1019, 958, 832 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₃H₄₀NaClN₃O₂ ([M+Na]⁺): 688.2707, found: 688.2677.



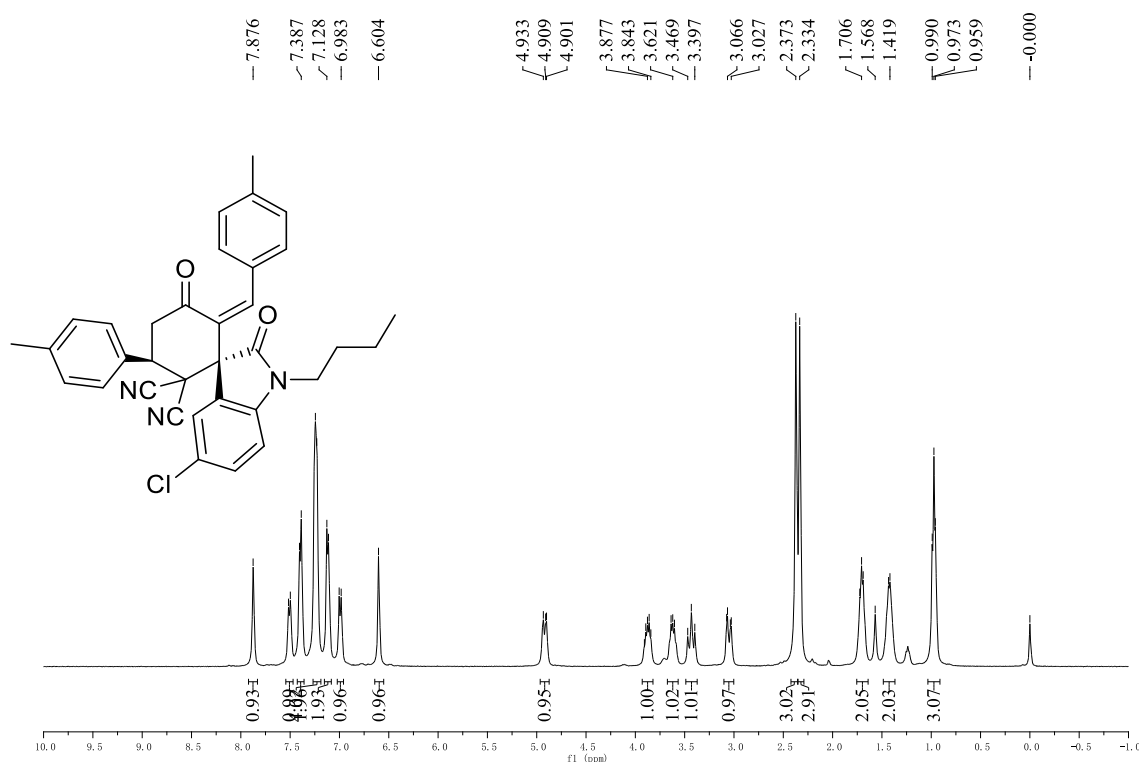


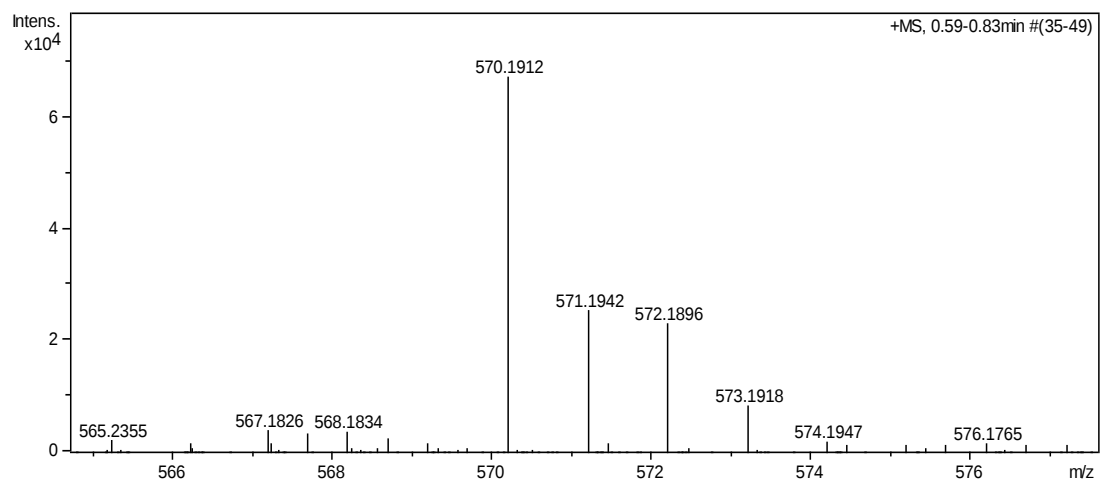
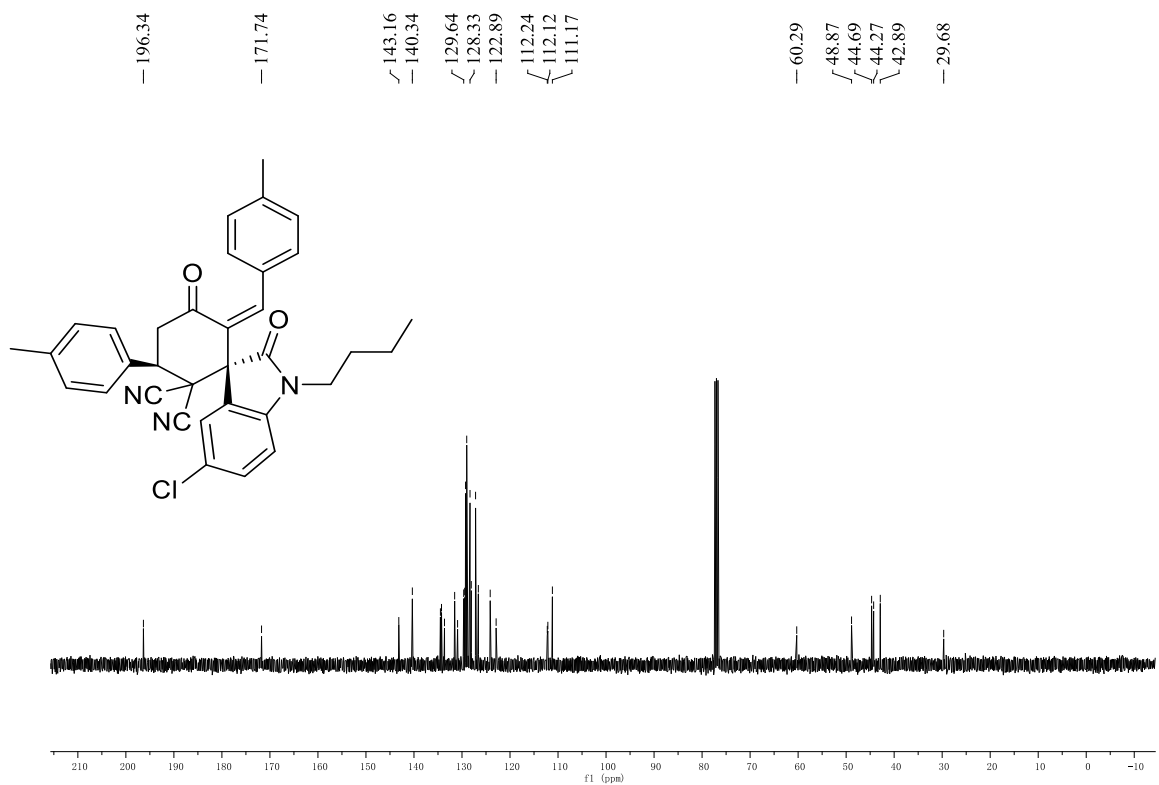
***rel*-(1*R*,3*R*)-1'-Benzyl-5'-chloro-6-((*Z*)-4-isopropylbenzylidene)-3-(4-isopropylphenyl)-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3n)**: white solid, 56%, m.p. 242-244 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.89 (s, 1H, ArH), 7.45 (d, *J* = 7.6 Hz, 2H, ArH), 7.38-7.30 (m, 10H, ArH), 7.19 (d, *J* = 7.6 Hz, 2H, ArH), 6.81 (d, *J* = 8.4 Hz, 1H, ArH), 6.59 (s, 1H, CH), 5.08 (d, *J* = 16.0 Hz, 1H, CH₂), 4.99 (d, *J* = 12.8 Hz, 1H, CH₂), 4.88 (d, *J* = 15.2 Hz, 1H, CH₂), 3.48 (t, *J* = 14.4 Hz, 1H, CH), 3.10 (d, *J* = 15.2 Hz, 1H, CH₂), 2.96-2.88 (m, 2H, CH), 1.27 (d, *J* = 6.4 Hz, 6H, (CH₃)₂), 1.23 (d, *J* = 6.8 Hz, 6H, (CH₃)₂). ¹³C NMR (100 MHz, CDCl₃) δ 196.4, 171.5, 151.0, 150.5, 141.7, 140.5, 133.9, 131.6, 130.8, 129.7, 129.2, 129.1, 128.9, 128.2, 127.3, 127.1, 126.8, 126.5, 124.7, 112.1, 112.0, 60.4, 48.8, 44.8, 44.3, 42.7, 34.0, 33.8, 23.8, 23.8, 23.7. IR (KBr) ν: 3035, 2965, 1718, 1610, 1483, 1423, 1351, 1188, 1056, 1016, 958, 921, 887, 831, 721 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₁H₃₆NaClN₃O₂ ([M+Na]⁺): 660.2394, found: 660.2367.



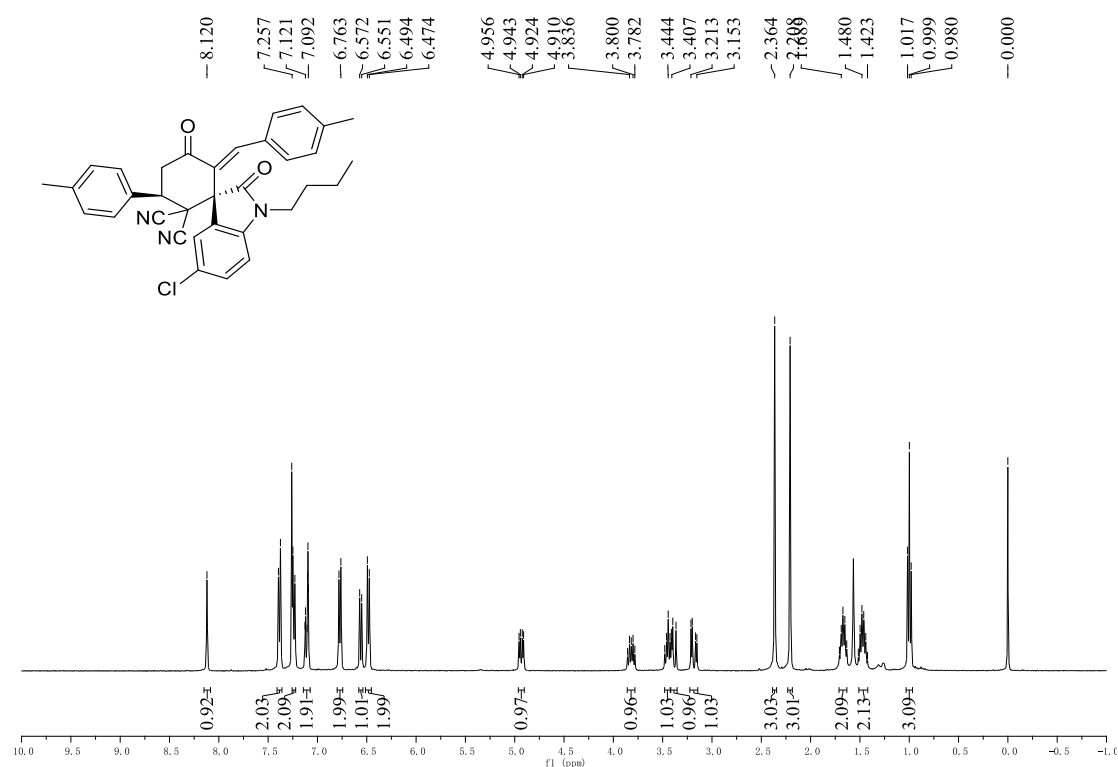


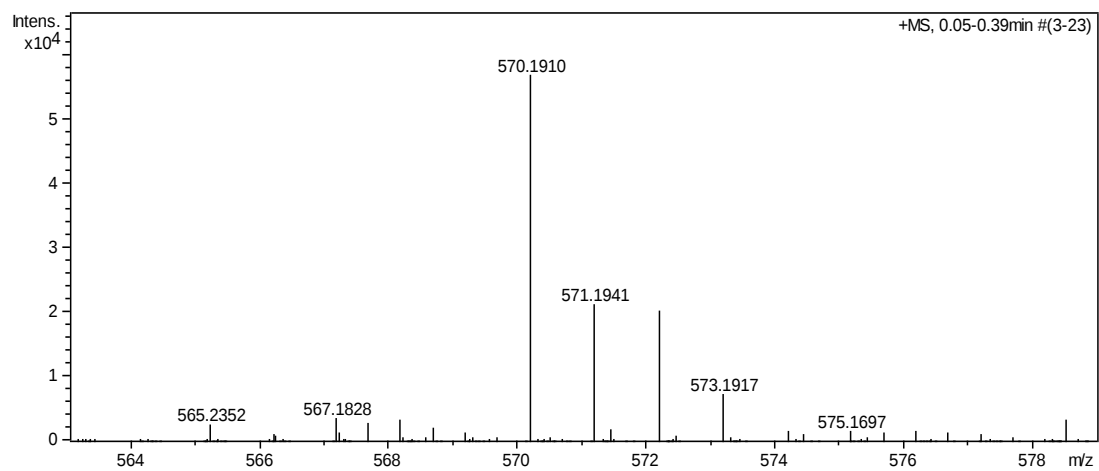
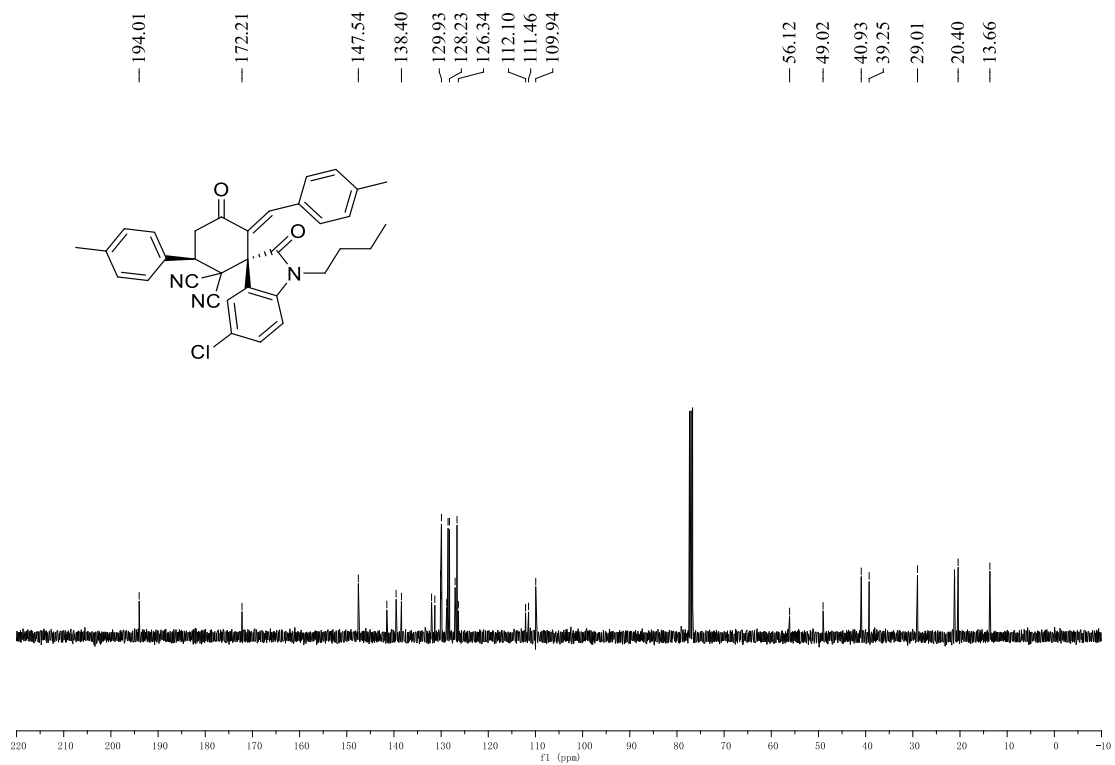
***rel*-(1*R*,3*R*)-1'-Butyl-5'-chloro-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3o)**: white solid, 42%, m.p. 225-227 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H, ArH), 7.51 (d, *J* = 7.2 Hz, 1H, ArH), 7.40 (d, *J* = 7.2 Hz, 2H, ArH), 7.24-7.23 (m, 4H, ArH), 7.12 (d, *J* = 6.8 Hz, 2H, ArH), 6.99 (d, *J* = 8.0 Hz, 1H, ArH), 6.60 (s, 1H, CH), 4.93-4.90 (m, 1H, CH₂), 3.91-3.84 (m, 1H, CH₂), 3.64-3.60 (m, 1H, CH₂), 3.47-3.40 (m, 1H, CH), 3.07-3.03 (m, 1H, CH₂), 2.37-2.33 (s, 3H, CH₃), 1.72-1.69 (m, 2H, CH₂), 1.43-1.42 (m, 2H, CH₂), 0.97 (d, *J* = 5.6 Hz, 1H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 171.1, 142.1, 140.3, 140.0, 139.7, 131.6, 131.4, 130.5, 129.9, 129.4, 129.3, 129.2, 129.1, 128.8, 127.0, 124.7, 112.2, 111.9, 111.1, 60.1, 48.9, 44.3, 42.5, 40.8, 29.1, 21.4, 21.2, 20.1, 13.6. IR (KBr) ν: 3689, 2962, 2317, 1713, 1595, 1501, 1468, 1388, 1354, 1324, 1271, 1244, 1212, 1161, 1135, 1047, 882, 831 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₃₀ClN₃O₂ ([M+Na]⁺): 570.1924, found: 570.1912.



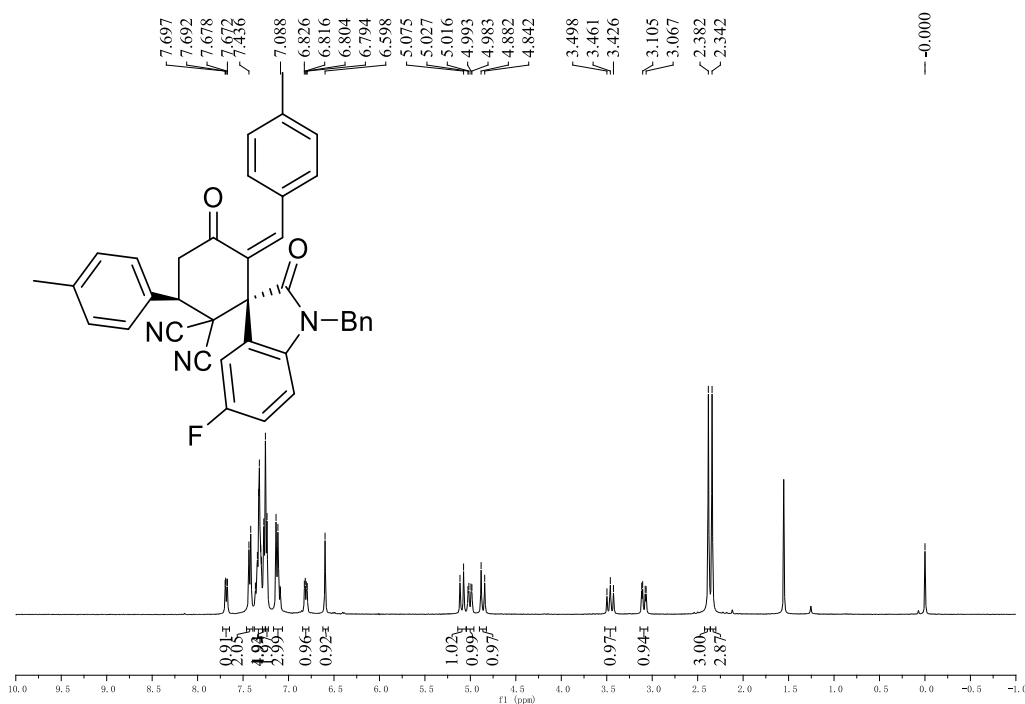


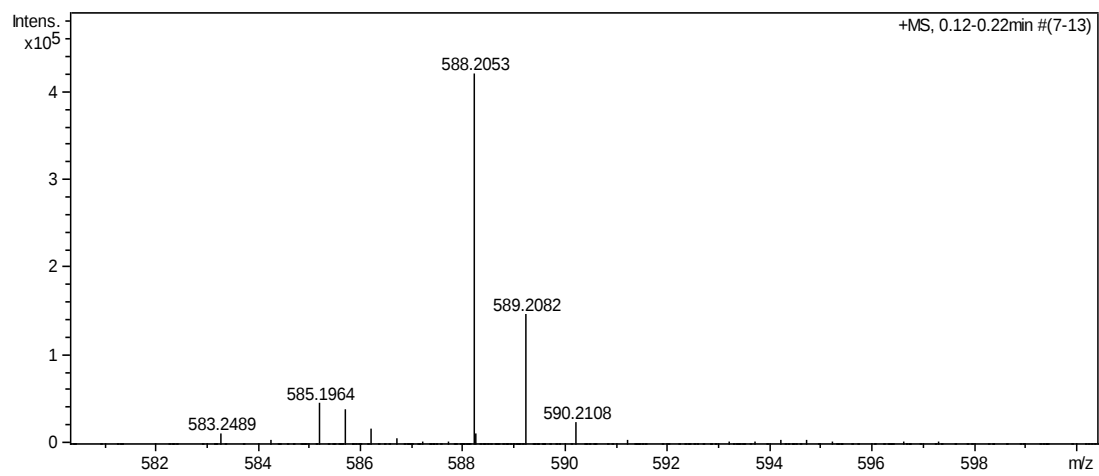
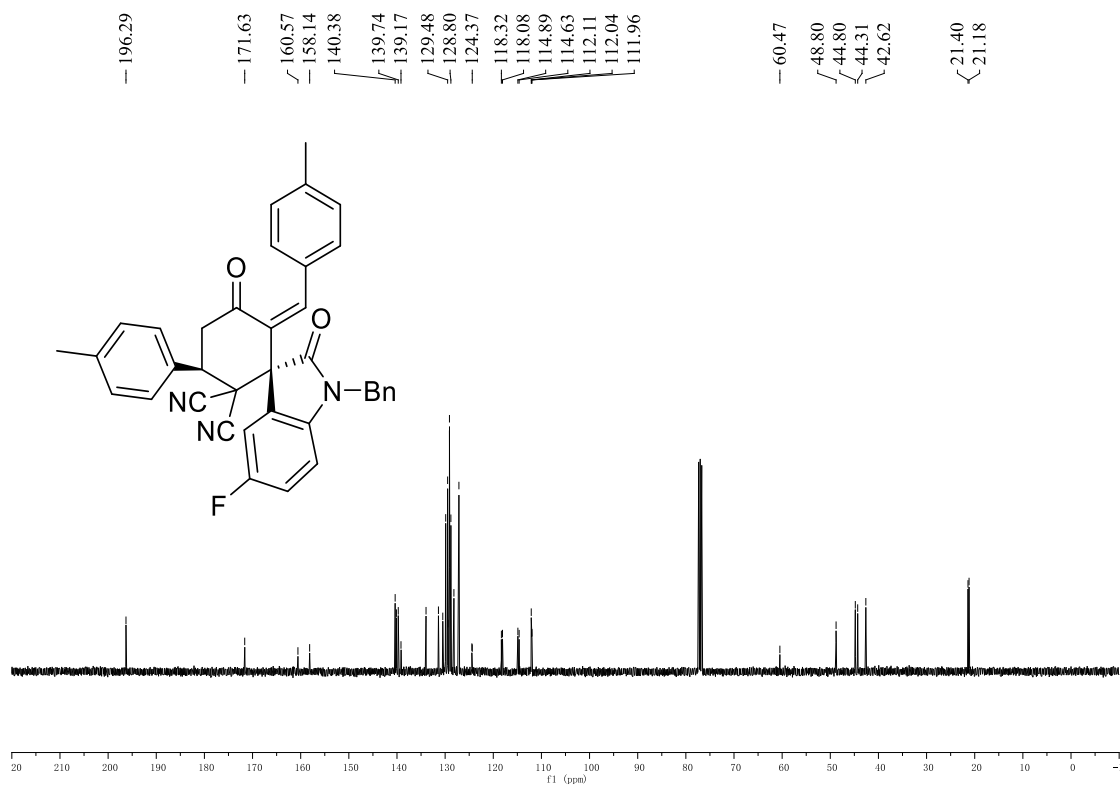
***rel*-(1*R*,3*R*)-1'-Butyl-5'-chloro-6-((*E*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3o')**: lilac solid, 8%, m.p. 167-169 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.12 (s, 1H, ArH), 7.39 (d, *J* = 8.4 Hz, 2H, ArH), 7.26-7.23 (m, 2H, ArH), 7.13-7.09 (m, 2H, ArH), 6.77 (d, *J* = 7.6 Hz, 2H, ArH), 6.56 (d, *J* = 8.4 Hz, 1H, CH), 6.48 (d, *J* = 8.0 Hz, 2H, ArH), 4.96-4.91 (m, 1H, CH₂), 3.86-3.78 (m, 1H, CH₂), 3.48-3.43 (m, 1H, CH₂), 3.41-3.37 (m, 1H, CH), 3.21-3.15 (m, 1H, CH₂), 2.36 (s, 3H, CH₃), 2.21 (s, 3H, CH₃), 1.71-1.63 (m, 2H, CH₂), 1.52-1.42 (m, 2H, CH₂), 1.00 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 194.0, 172.2, 147.5, 141.5, 139.5, 138.4, 132.0, 131.3, 130.1, 130.0, 129.9, 128.8, 128.5, 128.2, 127.0, 126.6, 126.3, 112.1, 111.5, 109.9, 56.1, 49.0, 40.9, 39.3, 29.0, 21.2, 21.1, 20.4, 13.7; IR (KBr) ν: 3628, 3413, 3041, 2910, 2832, 1958, 1845, 1813, 1710, 1543, 1483, 1342, 1231, 1123, 1043, 1010, 945, 821, 753, 721 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₄H₃₀ClNaN₃O₂ ([M+Na]⁺): 570.1924, found: 570.1910.



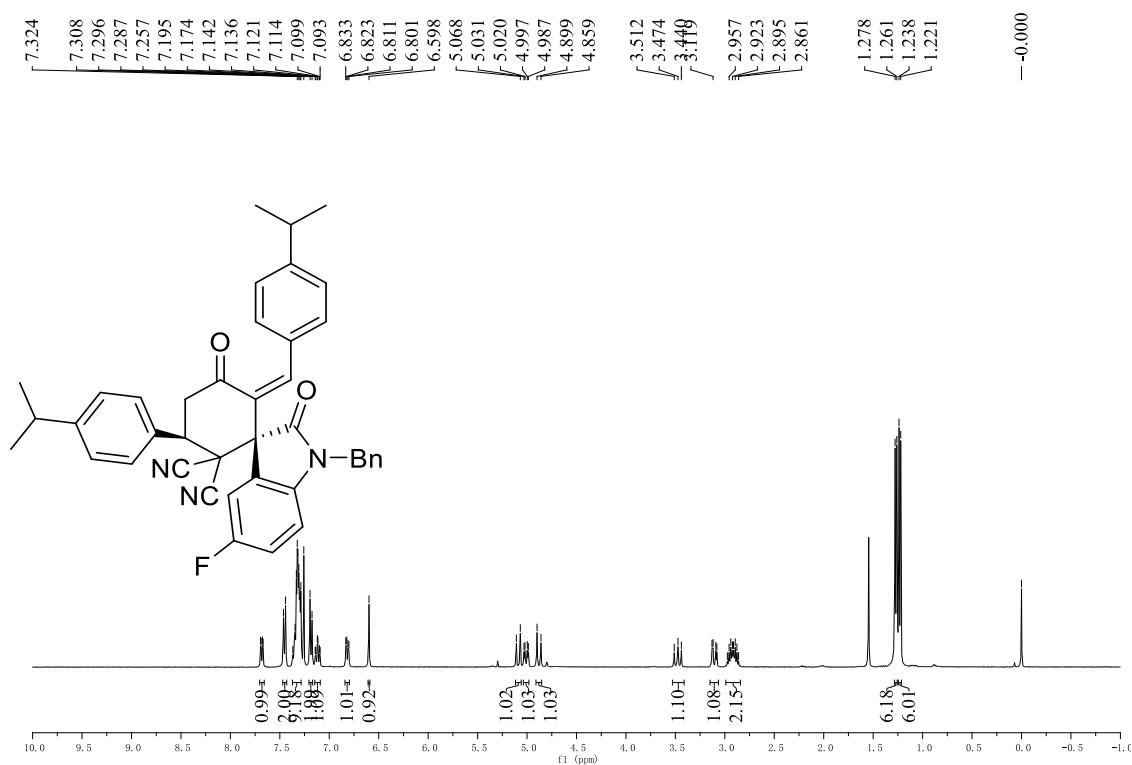


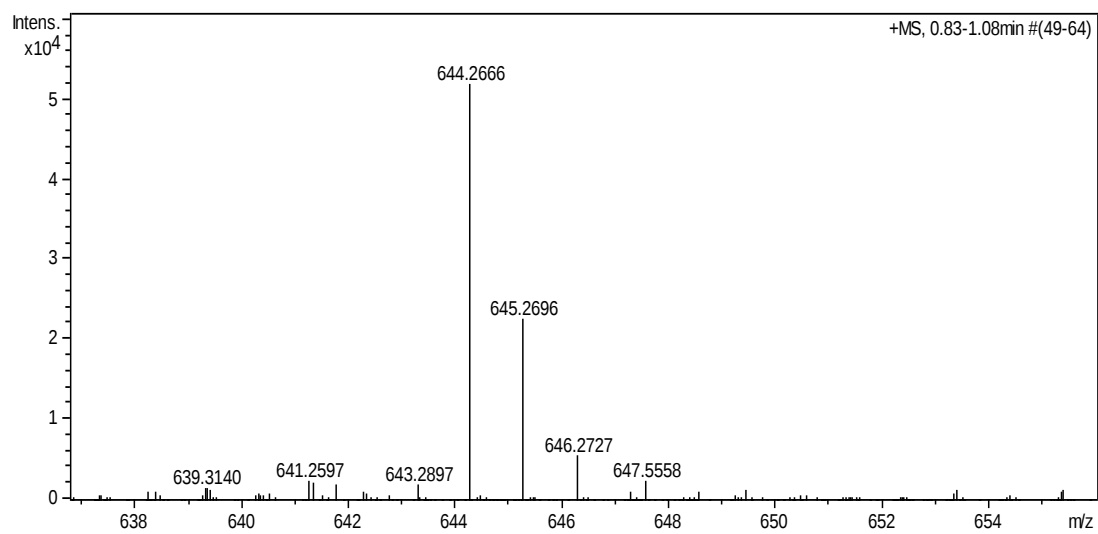
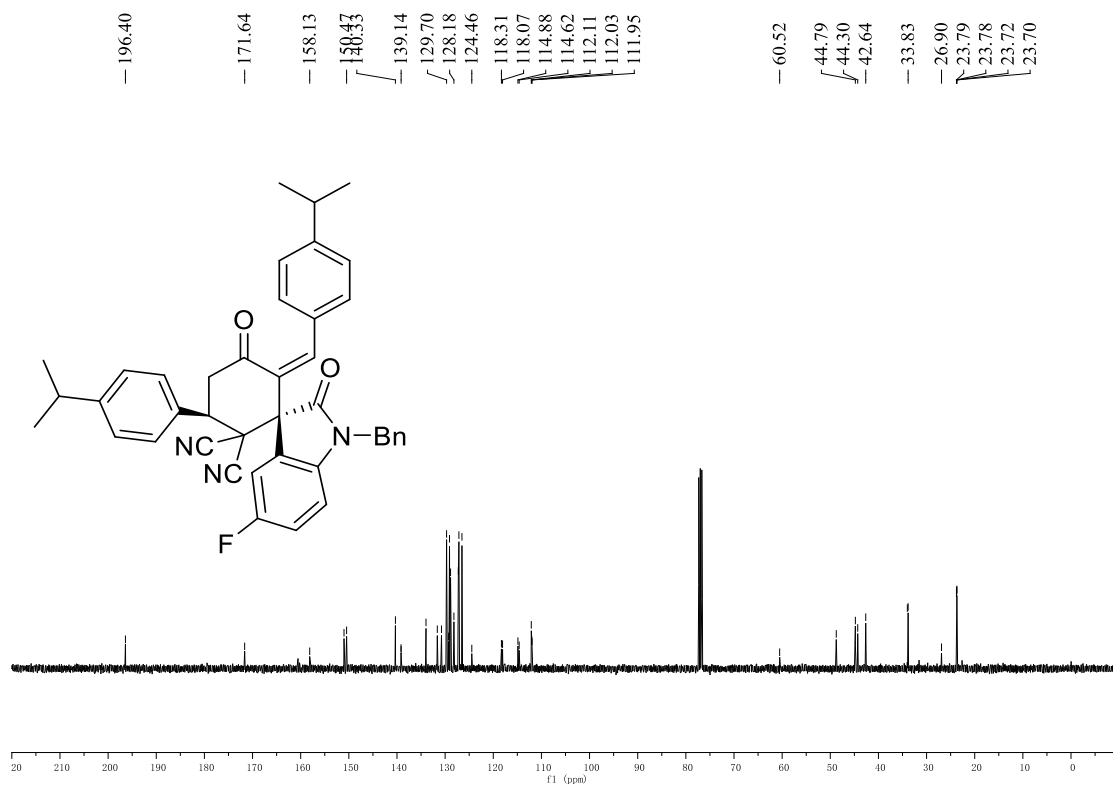
***rel*-(1*R*,3*R*)-1'-Benzyl-5'-fluoro-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3p)**: white solid, 53%, m.p. 223-225 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.70-7.67 (m, 1H, ArH), 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 7.36-7.30 (m, 5H, ArH), 7.27 (s, 2H, ArH), 7.24 (s, 2H, ArH), 7.14-7.09 (m, 3H, ArH), 6.83-6.79 (m, 1H, ArH), 6.60 (s, 1H, CH), 5.09 (d, *J* = 15.6 Hz, 1H, CH₂), 5.03-4.98 (m, 1H, CH₂), 4.86 (d, *J* = 16.0 Hz, 1H, CH₂), 3.46 (t, *J* = 14.8 Hz, 1H, CH), 3.12-3.07 (m, 1H, CH₂), 2.38 (s, 3H, CH₃), 2.34 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 171.6, 160.6, 158.1, 140.4, 140.1, 139.7, 139.2, 134.0, 131.4, 130.5, 129.9, 129.5, 129.4, 129.1, 129.1, 128.8, 128.2, 127.1, 124.5, 124.4, 118.3, 118.1, 114.9, 114.6, 112.1, 112.0, 112.0, 60.5, 48.8, 44.8, 44.3, 42.6, 21.4, 21.2. IR (KBr) ν: 3725, 3407, 3031, 2917, 2319, 1881, 1715, 1614, 1494, 1452, 1421, 1352, 1270, 1185, 1145, 1021, 965, 928, 875, 819, 731 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₇H₂₈NaFN₃O₂ ([M+Na]⁺): 588.2063, found: 588.2053.



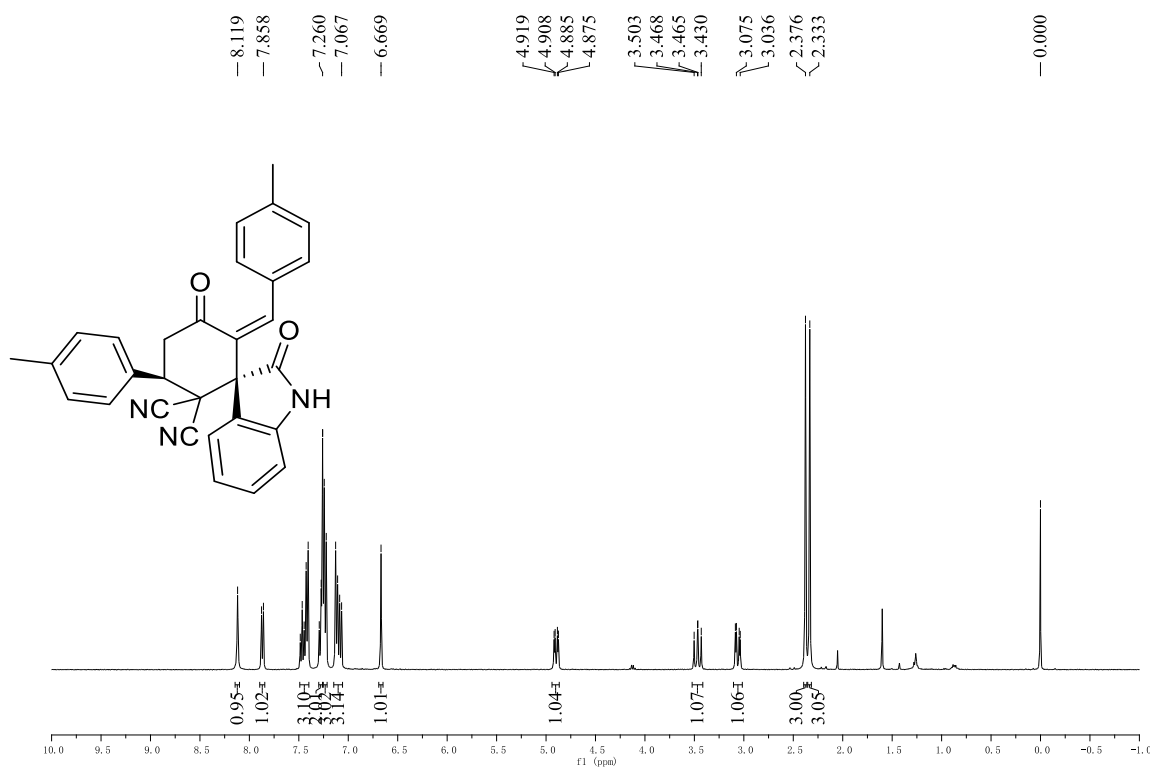


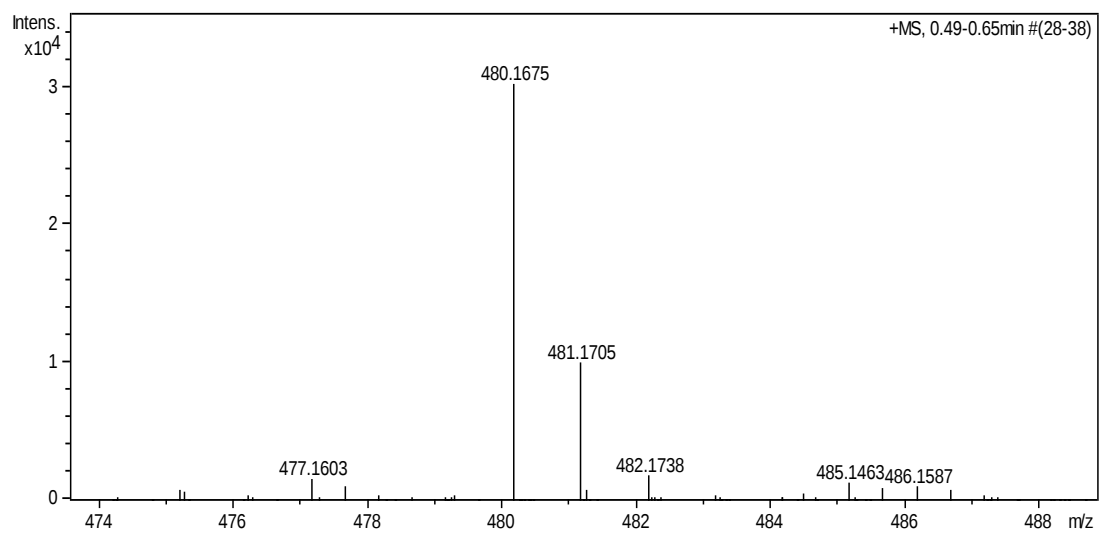
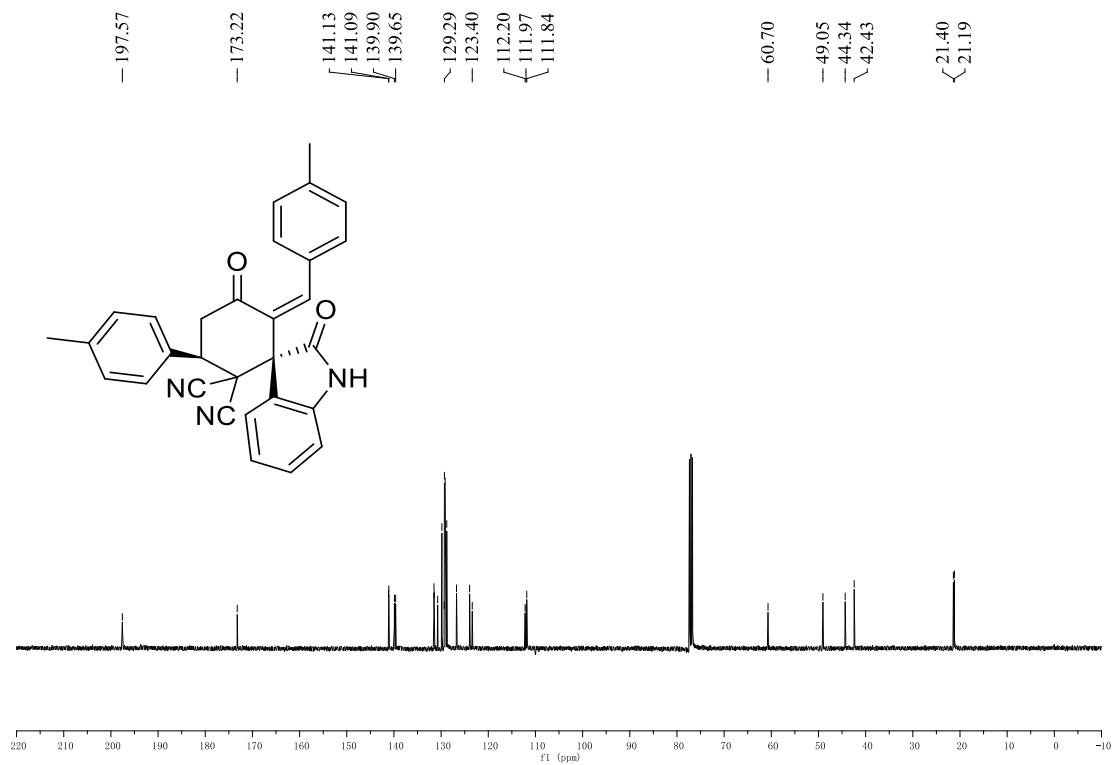
rel-(1R,3R)-1'-Benzyl-5'-fluoro-6-((Z)-4-isopropylbenzylidene)-3-(4-isopropylphenyl)-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3q): white solid, 58%, m.p. 195-197 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.70-7.67 (m, 1H, ArH), 7.45 (d, $J = 8.4$ Hz, 2H, ArH), 7.37-7.29 (m, 9H, ArH), 7.18 (d, $J = 8.4$ Hz, 2H, ArH), 7.14-7.09 (m, 1H, ArH), 6.83-6.80 (m, 1H, ArH), 6.60 (s, 1H, CH), 5.09 (d, $J = 16.0$ Hz, 1H, CH_2), 5.03-4.99 (m, 1H, CH_2), 4.88 (d, $J = 16.0$ Hz, 1H, CH_2), 3.47 (t, $J = 15.2$ Hz, 1H, CH), 3.13-3.08 (m, 1H, CH_2), 2.97-2.86 (m, 2H, CH), 1.27 (d, $J = 6.8$ Hz, 6H, $(\text{CH}_3)_2$), 1.23 (d, $J = 6.8$ Hz, 6H, $(\text{CH}_3)_2$). ^{13}C NMR (100 MHz, CDCl_3) δ 196.4, 171.6, 158.1, 151.0, 150.5, 140.3, 139.2, 139.1, 134.0, 131.6, 130.8, 129.7, 129.3, 129.1, 128.9, 128.2, 127.3, 127.1, 126.5, 124.5, 118.3, 118.1, 114.9, 114.6, 112.1, 112.0, 111.9, 60.5, 48.8, 44.8, 44.3, 42.6, 34.0, 33.8, 26.9, 23.8, 23.8, 23.7, 23.7. IR (KBr) ν : 3059, 2961, 1715, 1612, 1492, 1454, 1420, 1353, 1270, 1185, 1058, 1018, 966, 926, 831, 727 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{41}\text{H}_{36}\text{NaFN}_3\text{O}_2$ ($[\text{M}+\text{Na}]^+$): 644.2689, found: 644.2666.



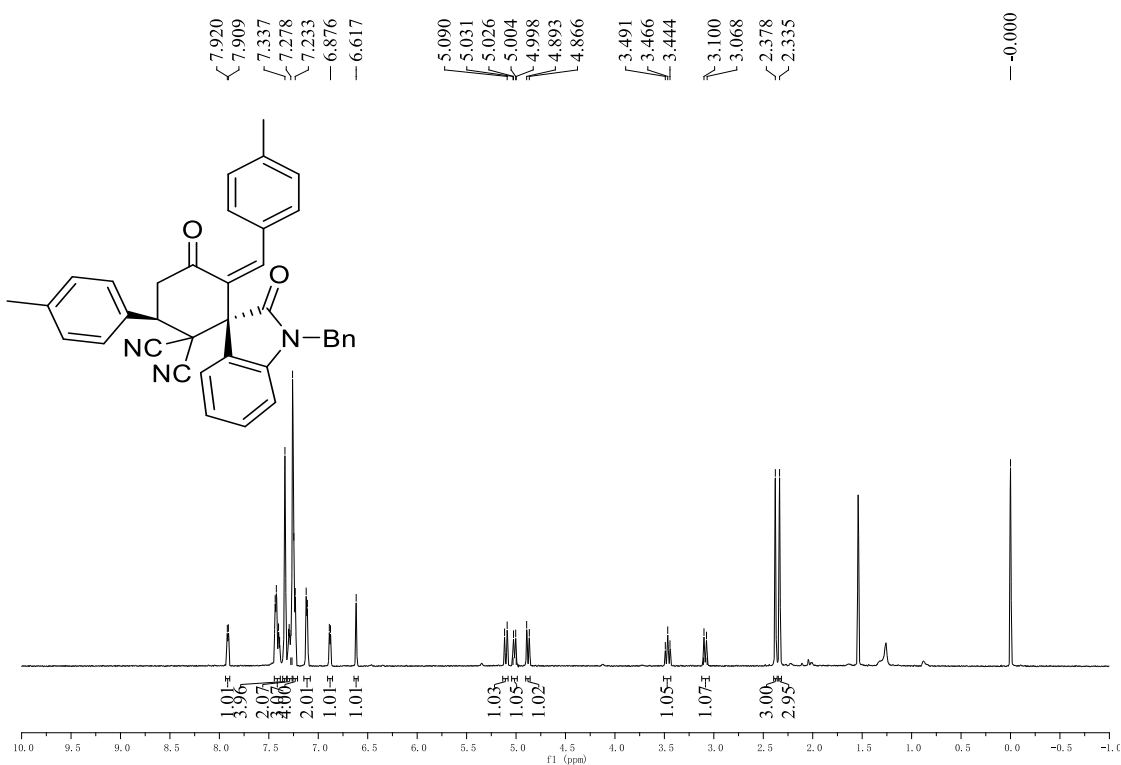


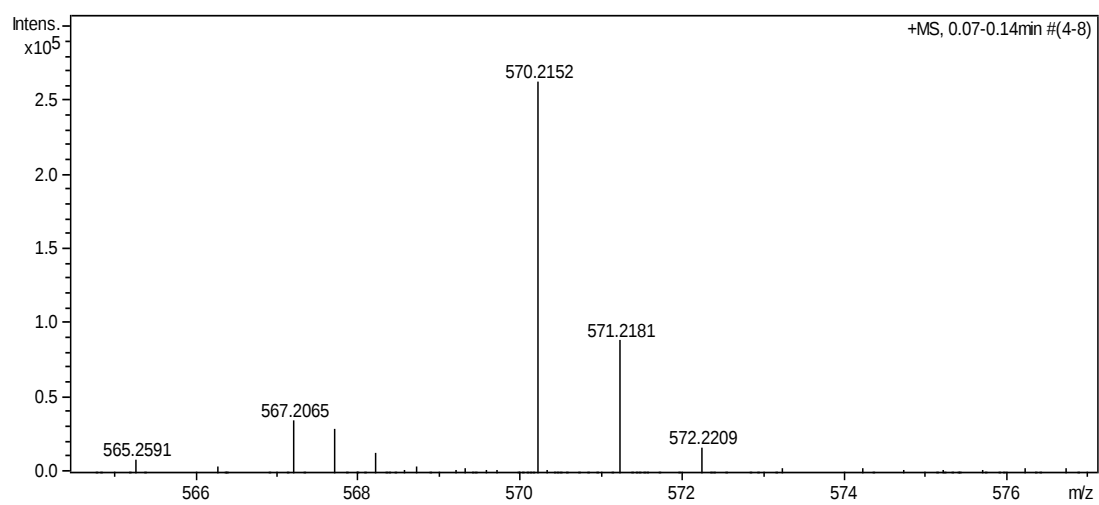
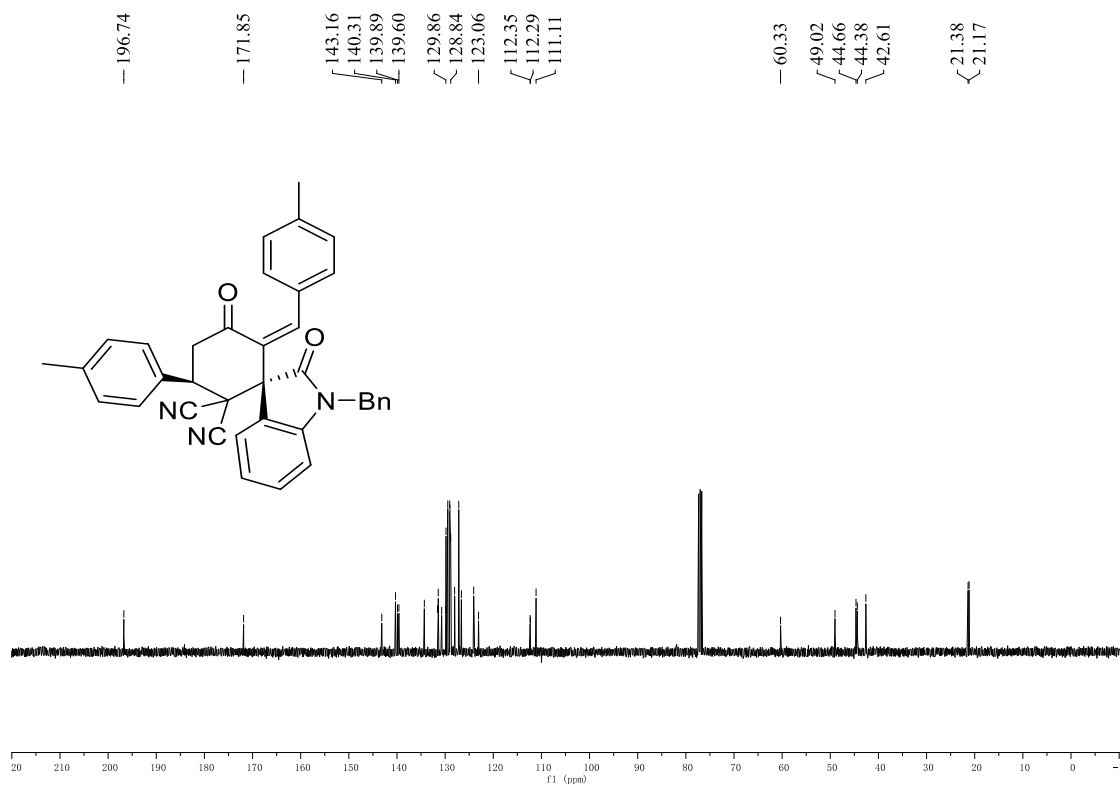
***rel*-(1*R*,3*R*)-6-((*Z*)-4-Methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3r)**: pale pink solid, 48%, m.p. 252-254 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.12 (s, 1H, NH), 7.87 (d, *J* = 7.6 Hz, 1H, ArH), 7.49-7.41 (m, 3H, ArH), 7.29-7.27 (m, 2H, ArH), 7.26-7.22 (m, 3H, ArH), 6.67 (s, 1H, CH), 4.92 (m, 1H, CH₂), 3.50-3.43 (m, 1H, CH), 3.09-3.04 (m, 1H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 197.6, 173.2, 141.1, 141.0, 139.9, 139.7, 131.5, 131.4, 130.7, 129.8, 129.2, 129.3, 129.1, 128.8, 126.7, 124.0, 123.4, 112.2, 112.0, 111.8, 60.7, 49.1, 44.3, 42.4, 21.4, 21.2. IR (KBr) ν: 3686, 3067, 1723, 1567, 1514, 1474, 1420, 1381, 1323, 1191, 1045, 821, 759 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₀H₂₃NaN₃O₂ ([M+Na]⁺): 480.1688, found: 480.1675.



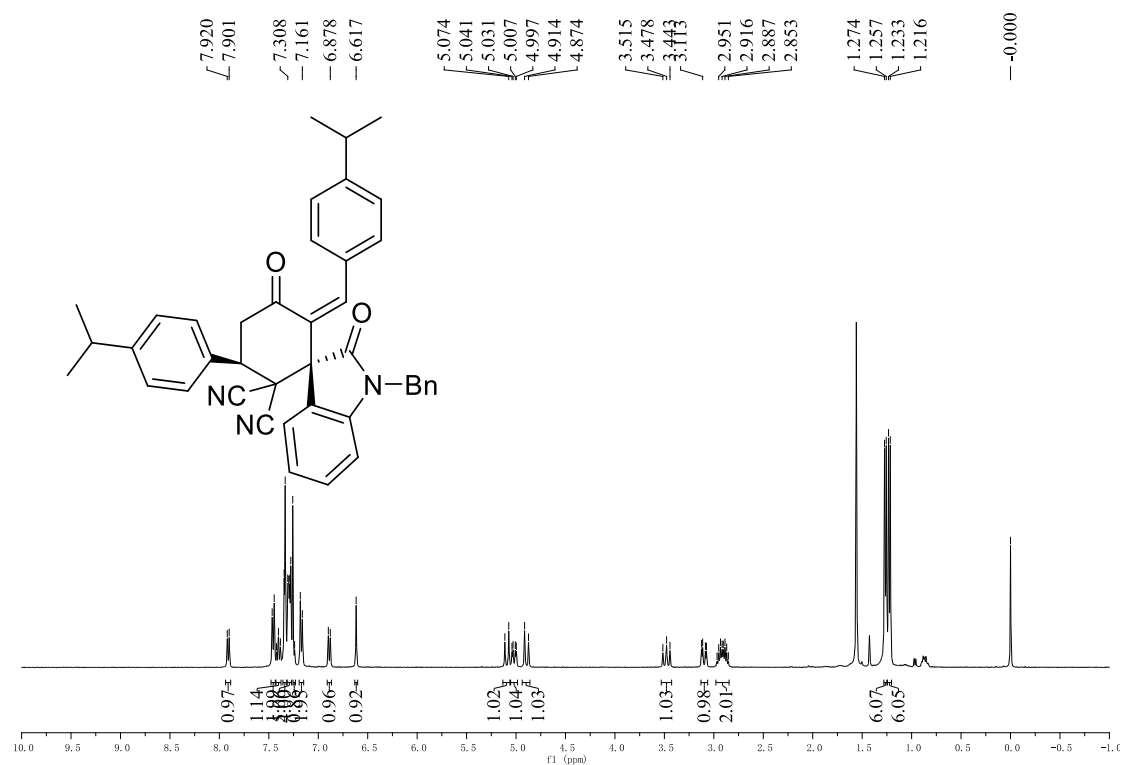


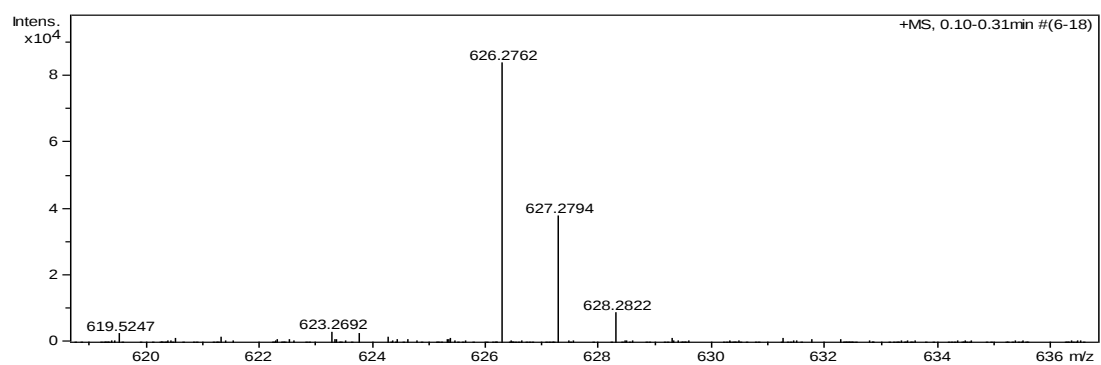
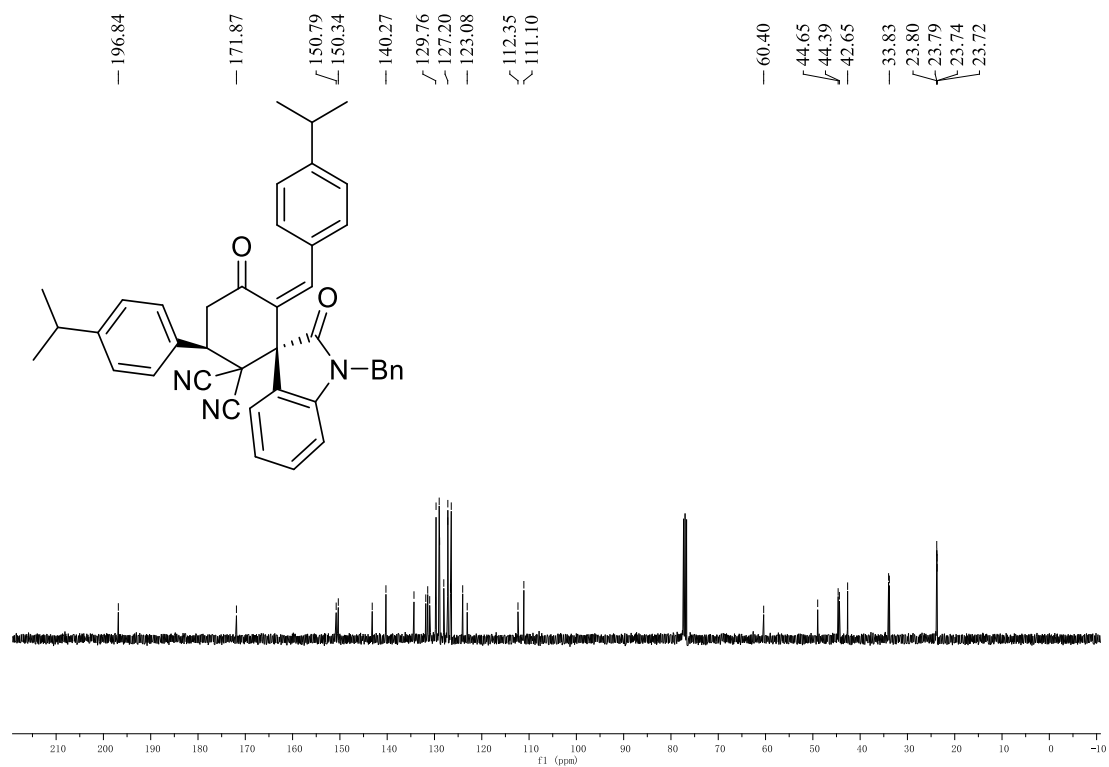
***rel*-(1*R*,3*R*)-1'-Benzyl-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3s):** pale yellow solid, 58%, m.p. 212-214 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.91 (d, *J* = 6.6 Hz, 1H, ArH), 7.44-7.39 (m, 3H, ArH), 7.34 (s, 4H, ArH), 7.30-7.27 (m, 2H, ArH), 7.25-7.23 (m, 4H, ArH), 7.11 (d, *J* = 7.2 Hz, 2H, ArH), 6.88 (d, *J* = 7.2 Hz, 1H, ArH), 6.62 (s, 1H, CH), 5.10 (d, *J* = 15.6 Hz, 1H, CH₂), 5.03-5.00 (m, 1H, CH₂), 4.88 (d, *J* = 16.2 Hz, 1H, CH₂), 3.47 (t, *J* = 13.2 Hz, 1H, CH), 3.11-3.07 (m, 1H, CH₂), 2.38 (s, 3H, CH₃), 2.34 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 196.7, 171.9, 143.2, 140.3, 139.9, 139.6, 134.3, 131.6, 131.4, 130.7, 129.9, 129.8, 129.5, 129.1, 129.0, 128.8, 128.0, 127.2, 126.6, 124.1, 123.1, 112.2, 112.3, 111.1, 60.3, 49.0, 44.7, 44.4, 42.6, 21.4, 21.2. IR (KBr) ν: 3729, 3407, 3029, 2965, 2922, 2859, 2319, 1980, 1903, 1805, 1710, 1607, 1482, 1362, 1298, 1183, 1153, 1120, 1045, 953, 894, 812, 763, 733 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₇H₂₉NaN₃O₂ ([M+Na]⁺): 570.2157, found: 570.2152.



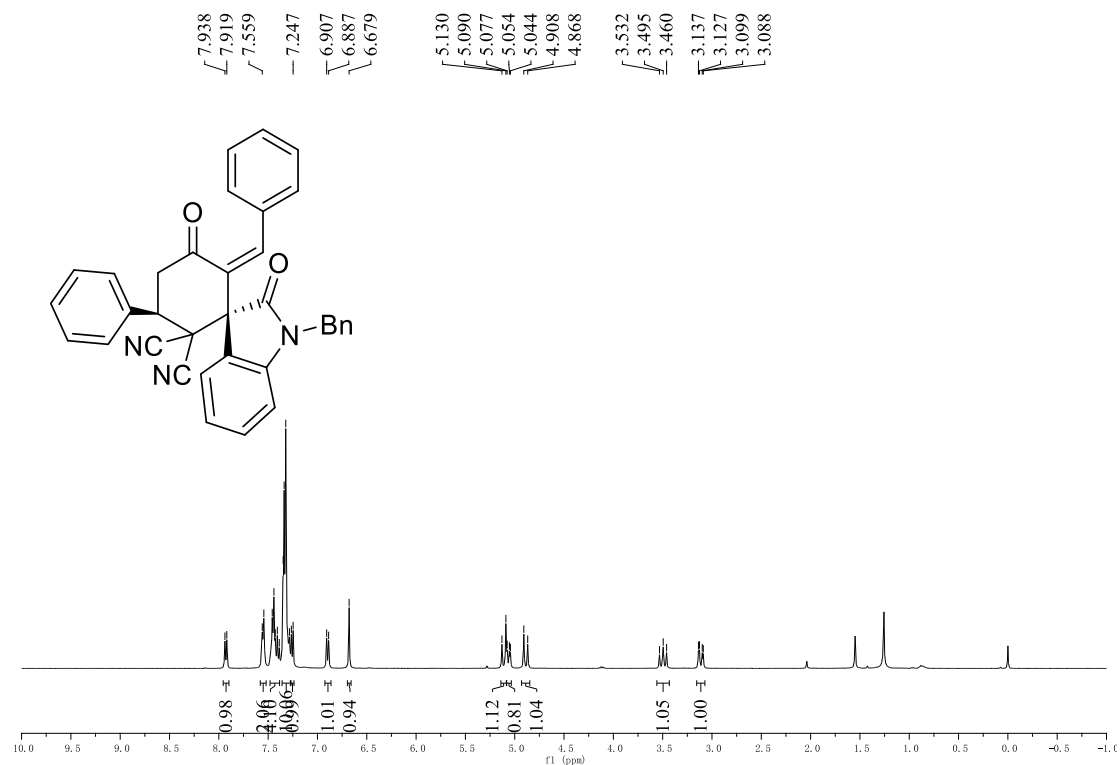


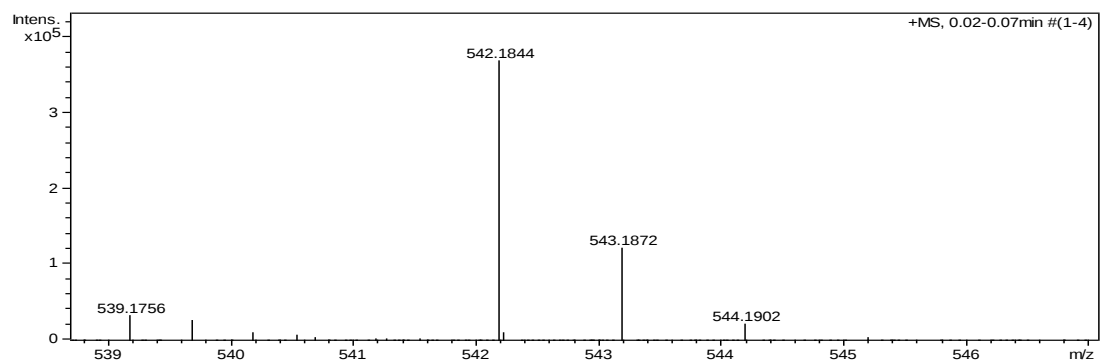
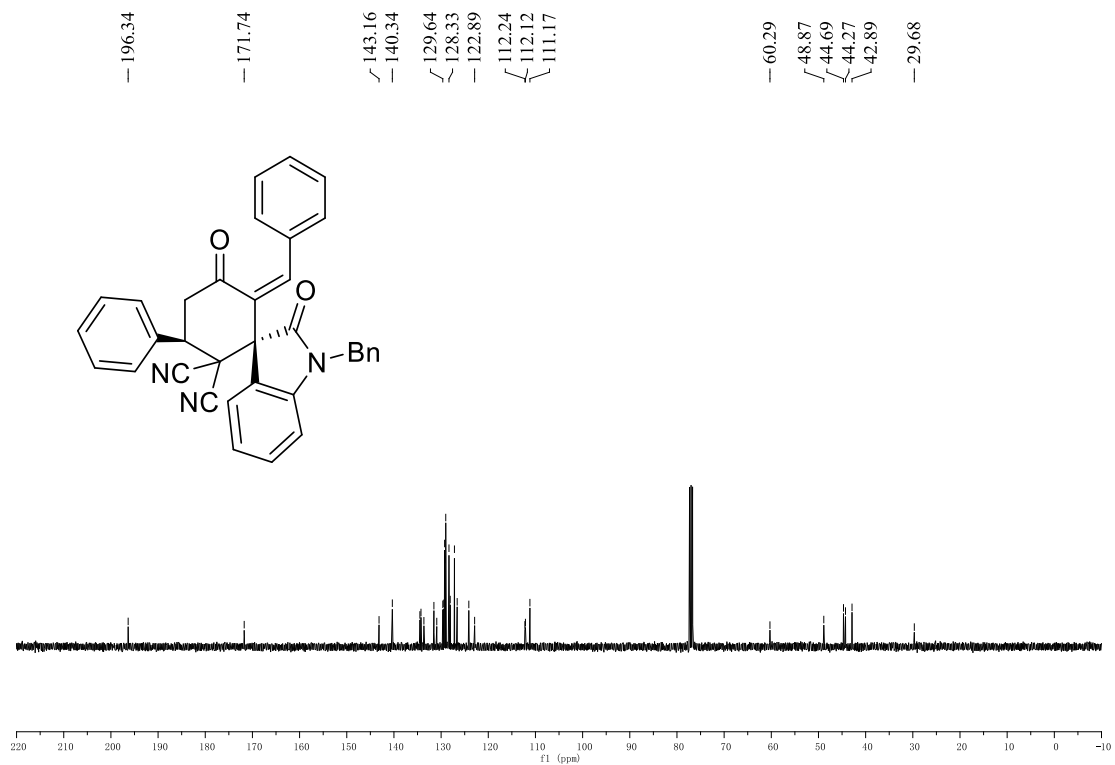
***rel*-(1*R*,3*R*)-1'-Benzyl-6-((*Z*)-4-isopropylbenzylidene)-3-(4-isopropylphenyl)-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3t)**: white solid, 57%, m.p. 168-170 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 7.6 Hz, 1H, ArH), 7.46 (d, *J* = 8.0 Hz, 2H, ArH), 7.40 (d, *J* = 8.0 Hz, 1H, ArH), 7.35-7.33 (m, 4H, ArH), 7.35-7.33 (m, 4H, ArH), 7.31-7.28 (m, 5H, ArH), 7.24 (s, 1H, ArH), 7.17 (d, *J* = 8.0 Hz, 2H, ArH), 6.89 (d, *J* = 8.0 Hz, 1H, ArH), 6.62 (s, 1H, CH), 5.09 (d, *J* = 15.6 Hz, 1H, CH₂), 5.04-5.00 (m, 1H, CH₂), 4.89 (d, *J* = 16.0 Hz, 1H, CH₂), 3.48 (t, *J* = 14.0 Hz, 1H, CH), 3.12-3.07 (m, 1H, CH₂), 2.97-2.85 (m, 2H, CH), 1.26 (d, *J* = 6.8 Hz, 6H, (CH₃)₂), 1.22 (d, *J* = 6.8 Hz, 6H, (CH₃)₂). ¹³C NMR (100 MHz, CDCl₃) δ 196.8, 171.9, 150.8, 150.3, 143.2, 140.3, 134.3, 131.8, 131.4, 131.0, 129.8, 129.7, 129.0, 128.9, 128.0, 127.2, 127.1, 126.6, 126.5, 124.0, 123.1, 112.2, 111.1, 60.4, 49.0, 44.7, 44.4, 42.7, 34.0, 33.8, 23.8, 23.8, 23.7, 23.6. IR (KBr) ν: 3685, 3057, 2962, 1711, 1609, 1479, 1420, 1364, 1191, 1056, 1014, 957, 845, 754 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₄₁H₃₇NaN₃O₂ ([M+Na]⁺): 626.2783, found: 626.2762.





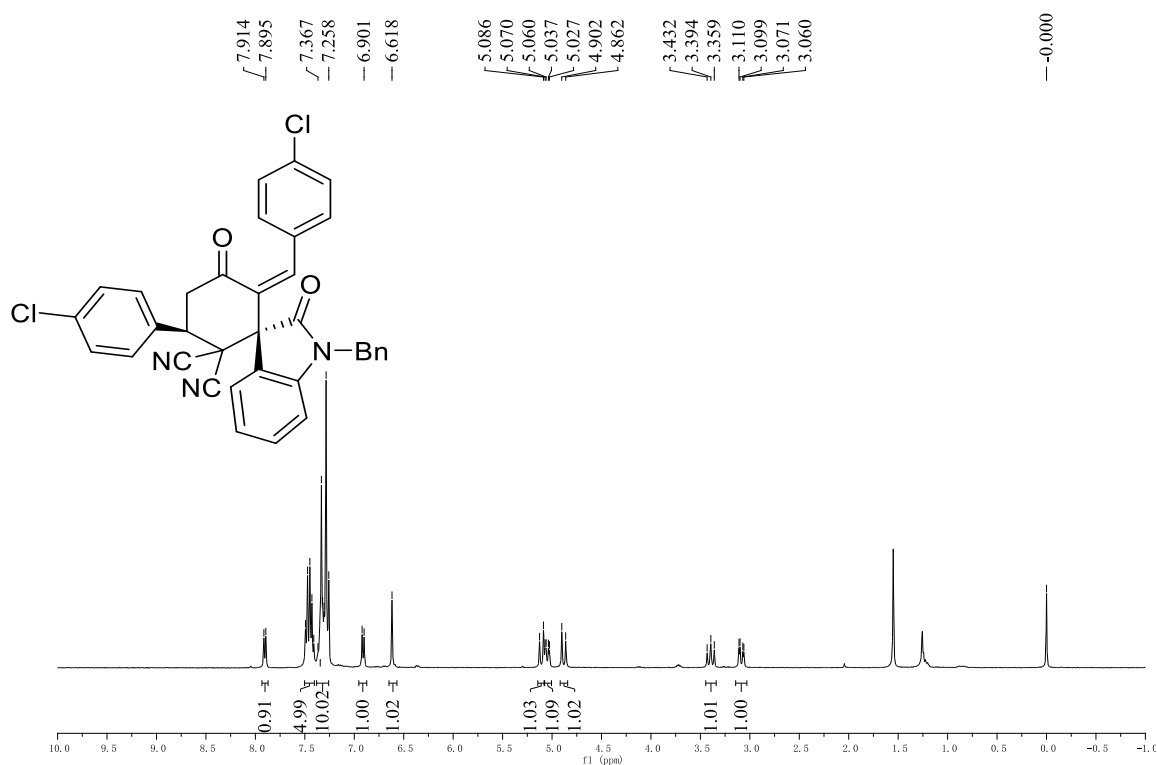
***rel*-(1*R*,3*R*)-1'-Benzyl-6-((*Z*)-benzylidene)-2',5-dioxo-3-phenylspiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3u)**: pale yellow solid, 42%, m.p. 211-213 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 7.6 Hz, 1H, ArH), 7.56-7.54 (m, 2H, ArH), 7.46-7.39 (m, 4H, ArH), 7.35-7.27 (m, 10H, ArH), 7.25 (d, *J* = 7.2 Hz, 1H, ArH), 6.90 (d, *J* = 8.0 Hz, 1H, ArH), 6.68 (s, 1H, CH), 5.11 (d, *J* = 16.0 Hz, 1H, CH₂), 5.08-5.04 (m, 1H, CH₂), 4.89 (d, *J* = 16.0 Hz, 1H, CH₂), 3.50 (t, *J* = 14.0 Hz, 1H, CH), 3.14-3.09 (m, 1H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 171.7, 143.2, 140.3, 134.5, 134.3, 133.7, 131.5, 130.9, 129.6, 129.4, 129.3, 129.2, 129.0, 128.3, 128.1, 127.2, 126.6, 124.1, 122.9, 112.2, 112.1, 111.2, 60.3, 48.9, 44.7, 44.3, 42.9, 29.7. IR (KBr) ν: 3728, 3413, 3040, 2919, 2852, 2317, 1958, 1888, 1813, 1711, 1607, 1483, 1457, 1356, 1231, 1187, 1069, 1009, 951, 835, 784, 746 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₅H₂₅NaN₃O₂ ([M+Na]⁺): 542.1844, found: 542.1844.

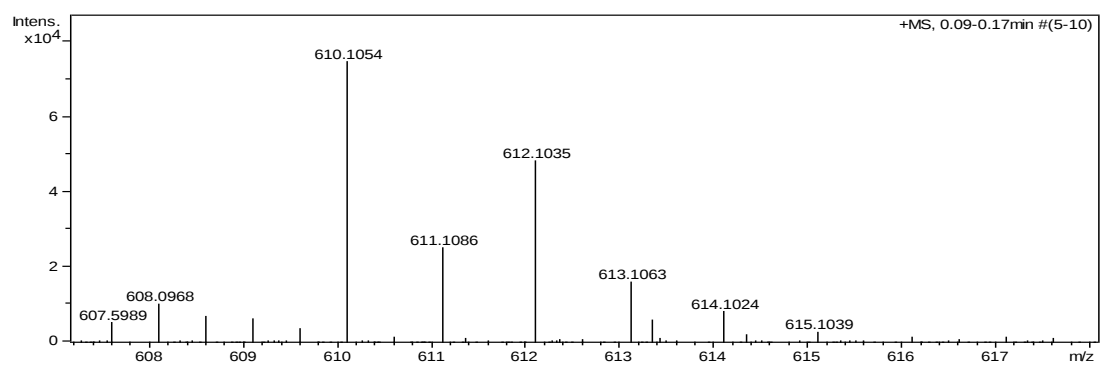
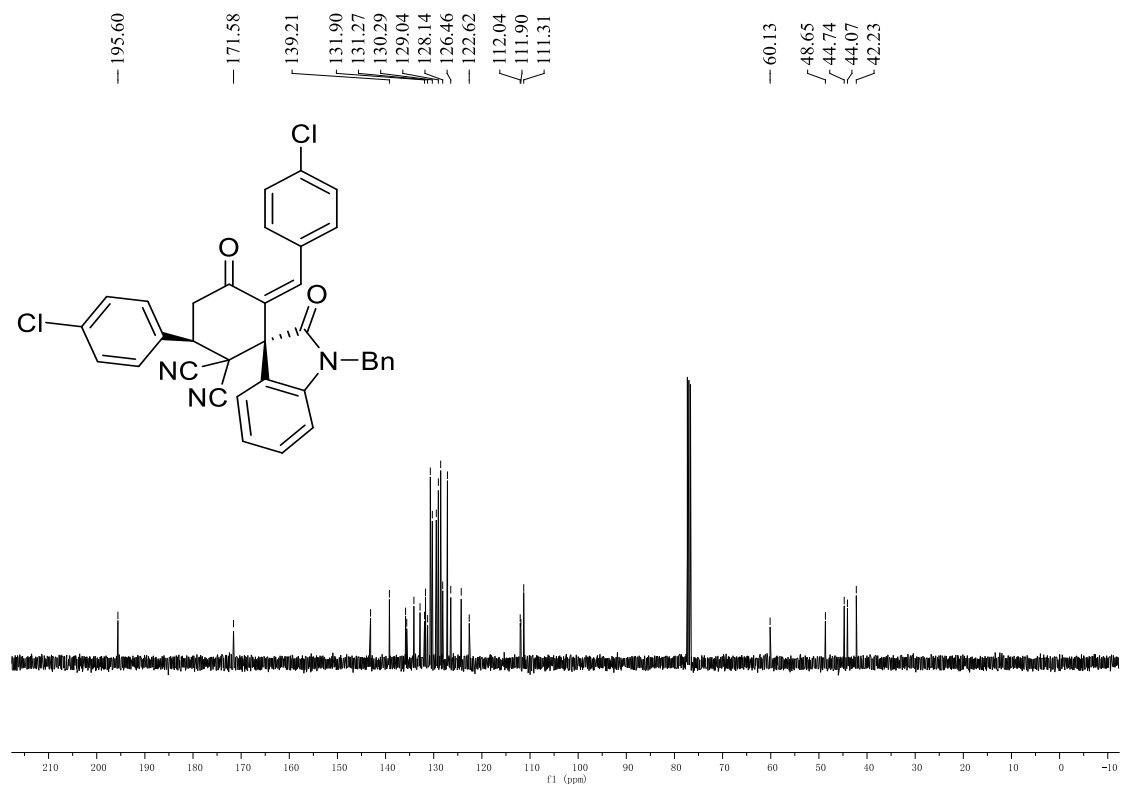




***rel*-(1*R*,3*R*)-1'-Benzyl-6-((*Z*)-4-chlorobenzylidene)-3-(4-chlorophenyl)-2',5-**

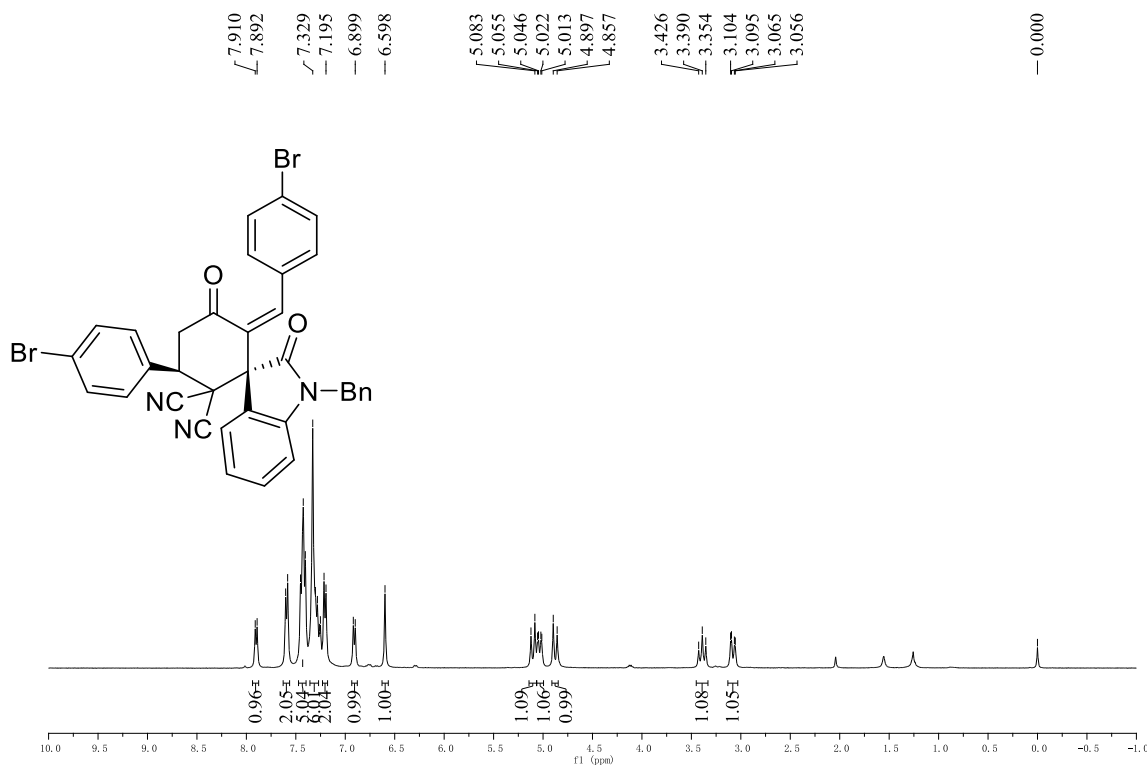
dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3v): white solid, 45%, m.p. 222-224 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 7.6 Hz, 1H, ArH), 7.49-7.41 (m, 5H, ArH), 7.37-7.29 (m, 10H, ArH), 6.91 (d, *J* = 8.0 Hz, 1H, ArH), 6.62 (s, 1H, CH), 5.11 (d, *J* = 16.0 Hz, 1H, CH₂), 5.07-5.03 (m, 1H, CH₂), 4.88 (d, *J* = 16.0 Hz, 1H, CH₂), 3.39 (t, *J* = 15.2 Hz, 1H, CH), 3.11-3.06 (m, 1H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 195.6, 171.6, 143.1, 139.2, 135.9, 135.6, 134.1, 132.8, 131.9, 131.7, 131.3, 130.7, 130.3, 129.5, 129.0, 128.6, 128.1, 127.2, 126.5, 124.3, 122.6, 112.0, 111.9, 111.3, 60.1, 48.65, 44.7, 44.1, 42.2. IR (KBr) ν: 3726, 3629, 3405, 3063, 2973, 2924, 2853, 2343, 1896, 1709, 1610, 1486, 1410, 1363, 1293, 1187, 1152, 1092, 1049, 1011, 953, 893, 826, 756, 734 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₅H₂₃NaClN₃O₂ ([M+Na]⁺): 610.1065, found: 610.1054.

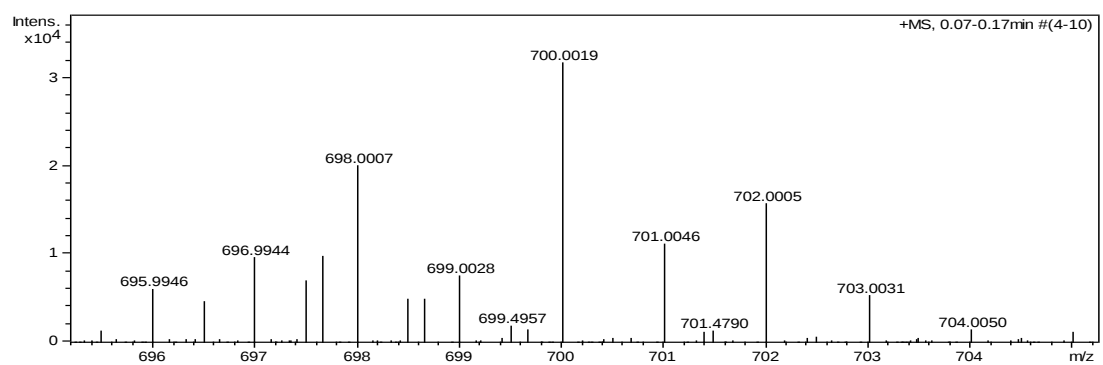
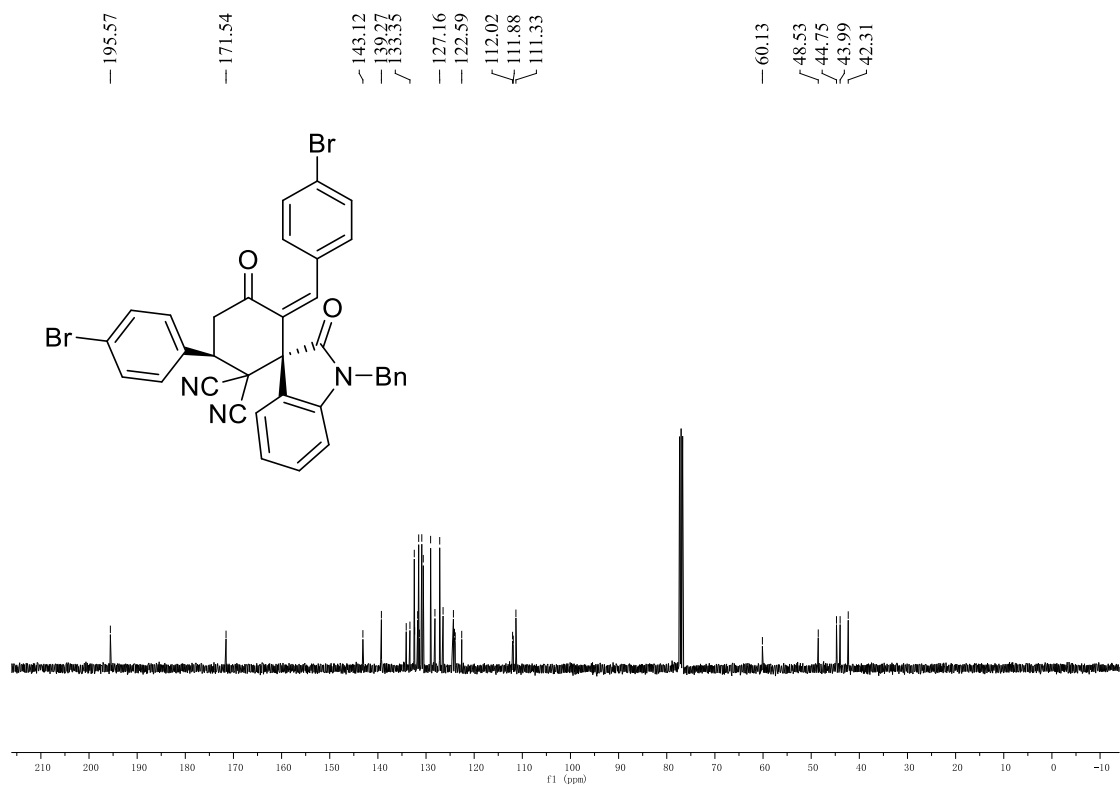




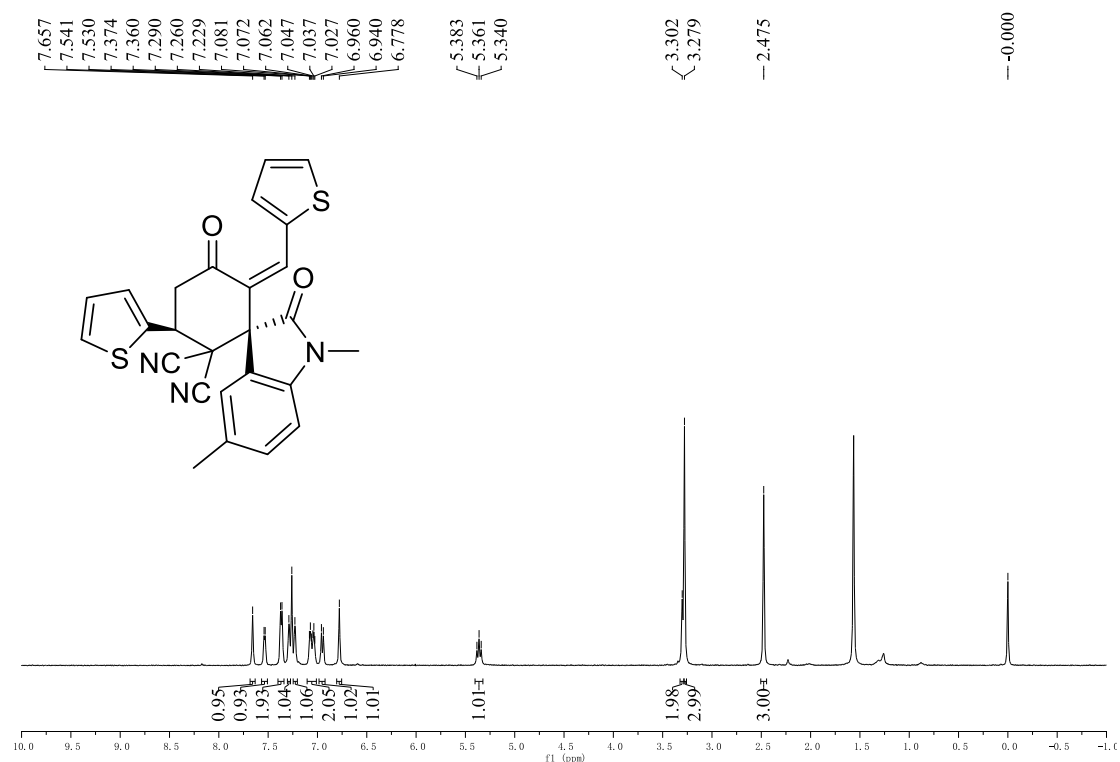
***rel*-(1*R*,3*R*)-1'-Benzyl-6-((*Z*)-4-bromobenzylidene)-3-(4-bromophenyl)-2',5-**

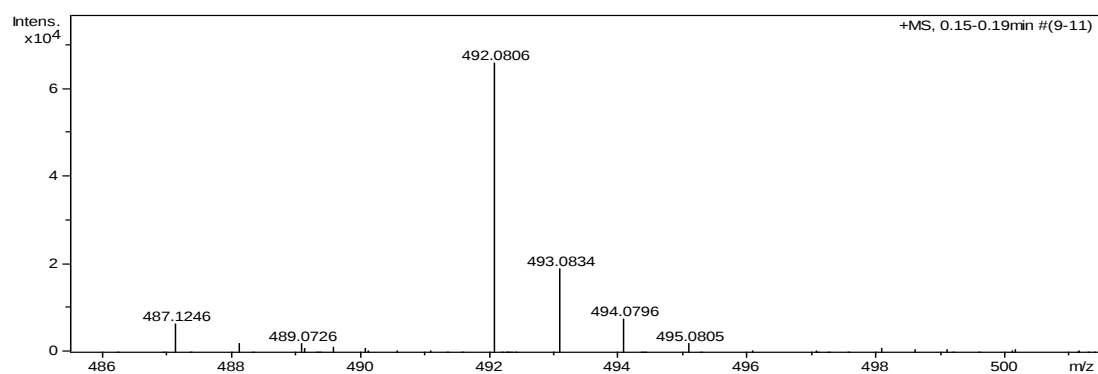
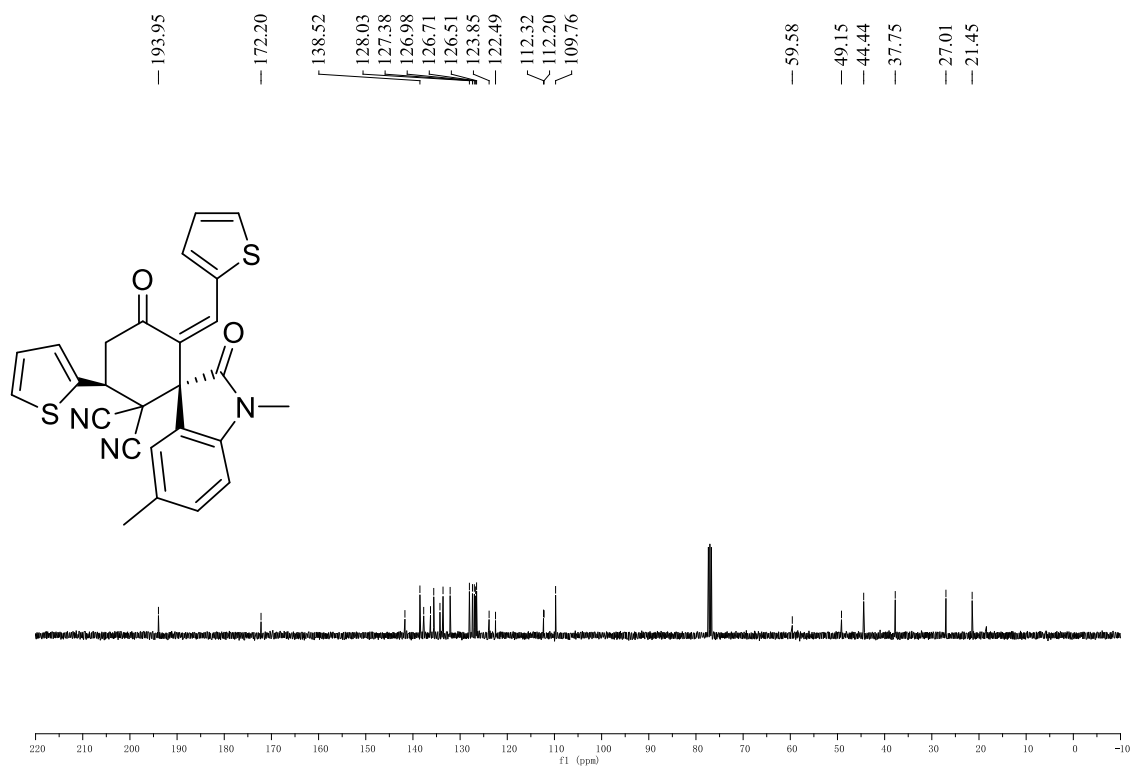
dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3w): white solid, 47%, m.p. 221-223 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 7.2 Hz, 1H, ArH), 7.59 (d, *J* = 8.0 Hz, 2H, ArH), 7.45-7.40 (m, 5H, ArH), 7.33-7.28 (m, 6H, ArH), 7.21 (d, *J* = 8.0 Hz, 2H, ArH), 6.91 (d, *J* = 8.0 Hz, 1H, ArH), 6.60 (s, 1H, CH), 5.10 (d, *J* = 15.6 Hz, 1H, CH₂), 5.06-5.01 (m, 1H, CH₂), 4.88 (d, *J* = 16.0 Hz, 1H, CH₂), 3.39 (t, *J* = 14.4 Hz, 1H, CH), 3.10-3.06 (m, 1H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 195.6, 171.5, 143.1, 139.3, 134.1, 133.4, 132.4, 132.3, 131.7, 131.5, 131.4, 130.9, 130.6, 129.1, 128.2, 127.2, 126.5, 124.3, 124.1, 123.9, 122.6, 112.0, 111.9, 111.3, 60.1, 48.5, 44.8, 44.0, 42.3. IR (KBr) ν: 3727, 3632, 3404, 3063, 2971, 2928, 2344, 1896, 1709, 1610, 1483, 1409, 1361, 1292, 1186, 1152, 1118, 1069, 1005, 951, 893, 821, 753 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₅H₂₃NaBr₂N₃O₂ ([M+Na]⁺): 698.0055, found: 698.0007.



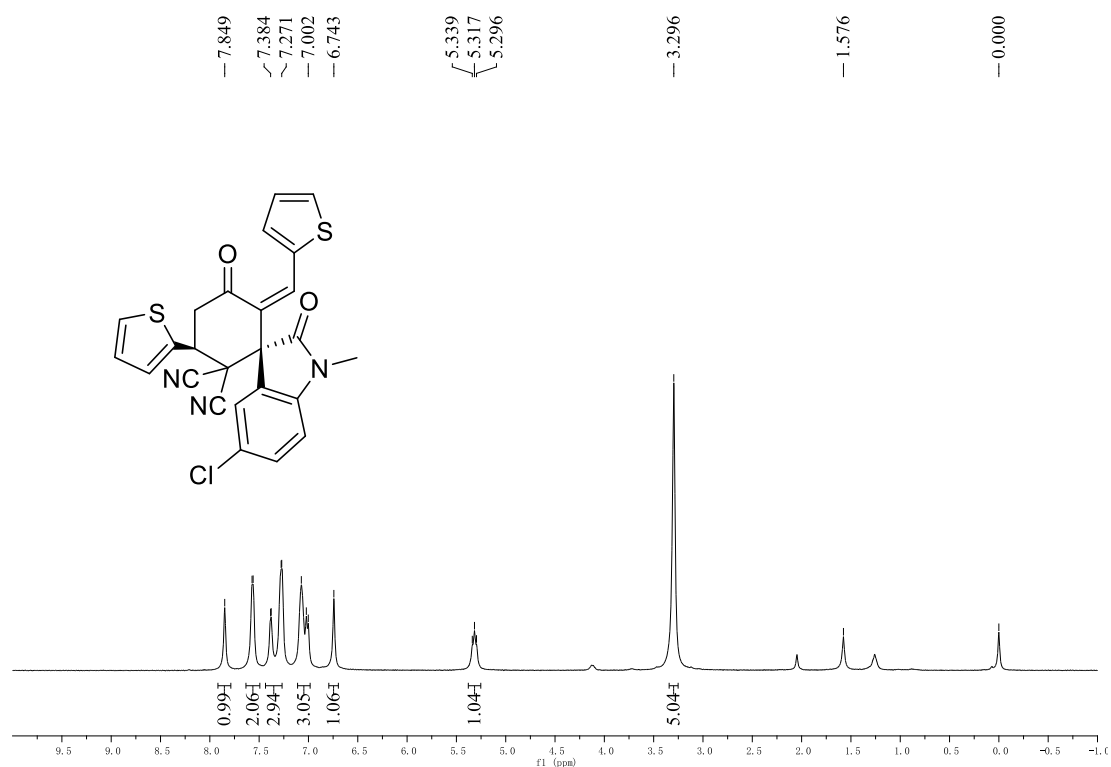


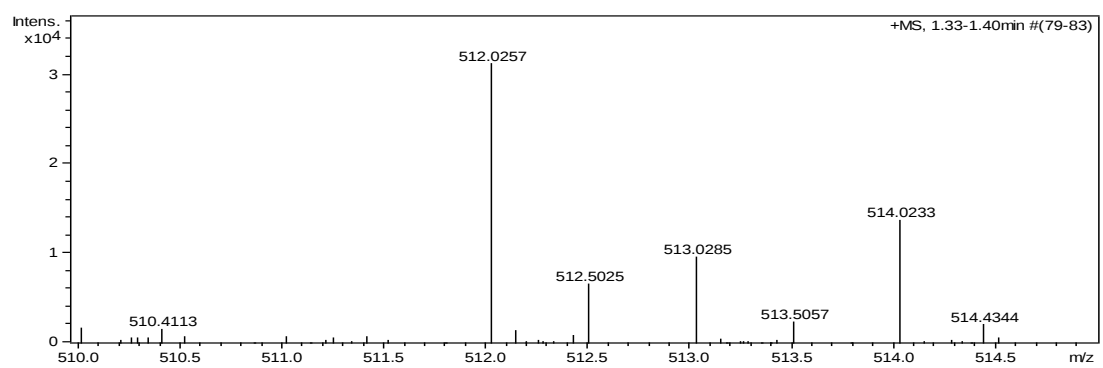
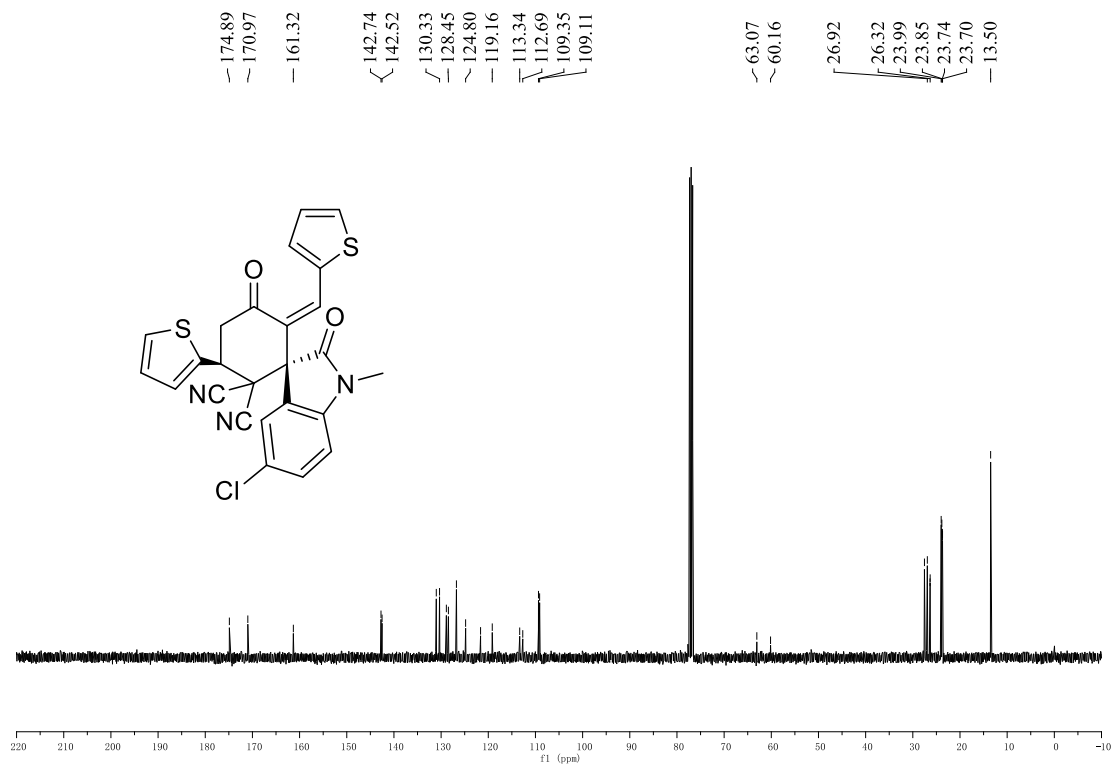
***rel*-(1*R*,3*S*,*Z*)-1',5'-Dimethyl-2',5-dioxo-3-(thiophen-2-yl)-6-(thiophen-2-ylmethylene)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3x)**: yellow solid, 52%, m.p. 154-156 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 1H, ArH), 7.54 (d, *J* = 4.4 Hz, 1H, ArH), 7.37 (d, *J* = 5.6 Hz, 2H, ArH), 7.30 (s, 1H, ArH), 7.23 (s, 1H, ArH), 7.07-7.03 (m, 2H, ArH), 6.95 (d, *J* = 8.0 Hz, 1H, ArH), 6.78 (s, 1H, CH), 5.36 (t, *J* = 8.4 Hz, 1H, CH), 3.30 (s, 2H, CH₂), 3.28 (s, 3H, CH₃), 2.48 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 194.0, 172.2, 141.7, 138.5, 137.7, 136.3, 135.6, 134.3, 133.6, 132.1, 128.0, 127.4, 127.0, 126.7, 126.5, 123.9, 122.5, 112.3, 112.2, 109.8, 59.6, 49.2, 44.4, 37.8, 27.0, 21.5. IR (KBr) ν: 3458, 3108, 2905, 2352, 2318, 1707, 1610, 1587, 1490, 1464, 1424, 1388, 1355, 1328, 1264, 1105, 1063, 856, 812, 779, 706 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₂₆H₁₉NaN₃O₂S₂ ([M+Na]⁺): 492.0816, found: 492.0806.



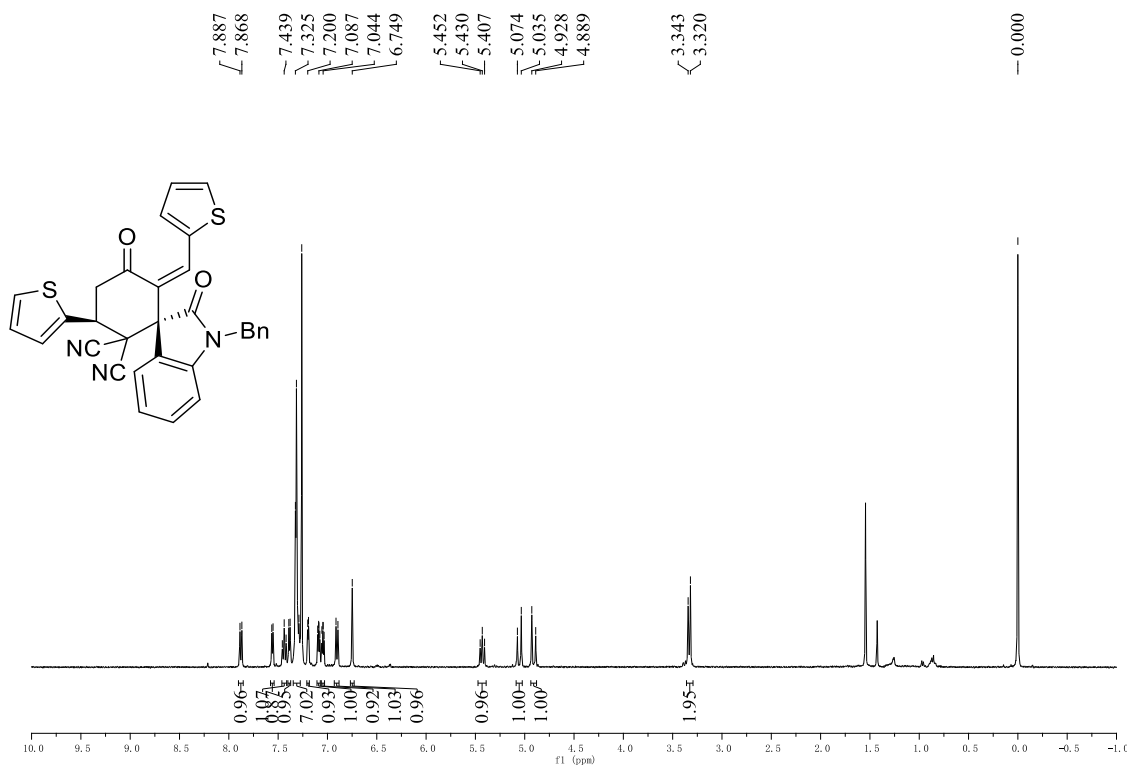


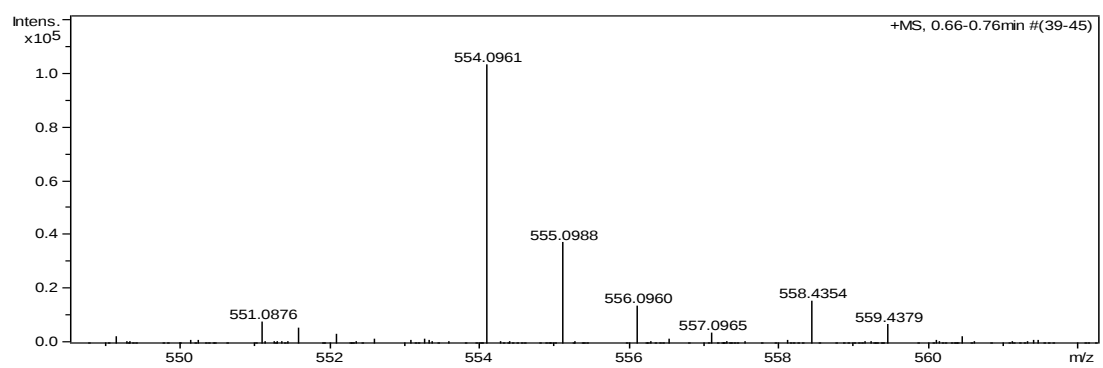
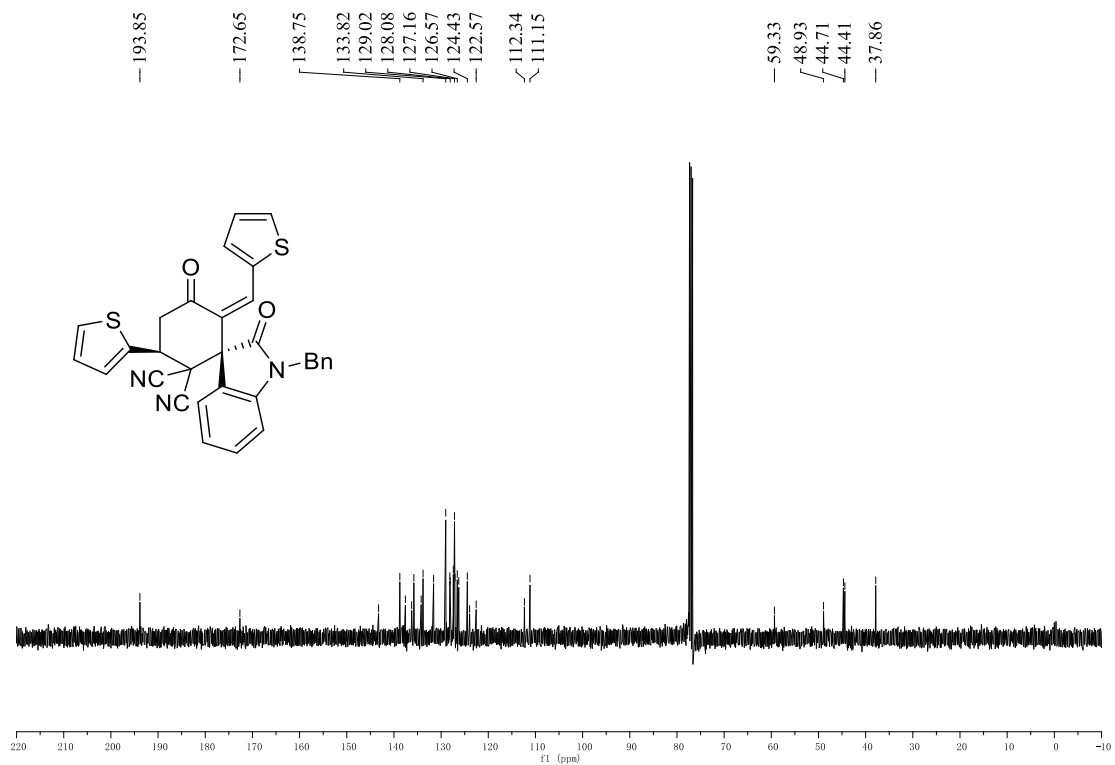
***rel*-(1*R*,3*S*,*Z*)-5'-Chloro-1'-methyl-2',5-dioxo-3-(thiophen-2-yl)-6-(thiophen-2-ylmethylene)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3y)**: pale yellow solid, 45%, m.p. 160-162 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H, ArH), 7.56 (d, *J* = 4.4 Hz, 2H, ArH), 7.38-7.28 (m, 3H, ArH), 7.07-7.00 (m, 3H, ArH), 6.74 (s, 1H, CH), 5.32 (t, *J* = 8.4 Hz, 1H, CH), 3.30 (s, 5H, CH₃, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 174.9, 171.0, 161.3, 142.7, 142.5, 131.0, 130.3, 128.9, 128.5, 126.8, 124.8, 121.6, 119.2, 113.3, 112.7, 109.4, 109.1, 63.1, 60.2, 27.5, 26.9, 26.4, 26.3, 24.0, 23.9, 23.7, 23.7, 13.5. IR (KBr) ν: 3458, 3108, 2905, 2352, 2318, 1707, 1610, 1587, 1490, 1464, 1424, 1388, 1355, 1328, 1264, 1105, 1063, 856, 812, 779, 706 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₂₅H₁₆ClNaN₃O₂S₂ ([M+Na]⁺): 512.0270, found: 512.0257.



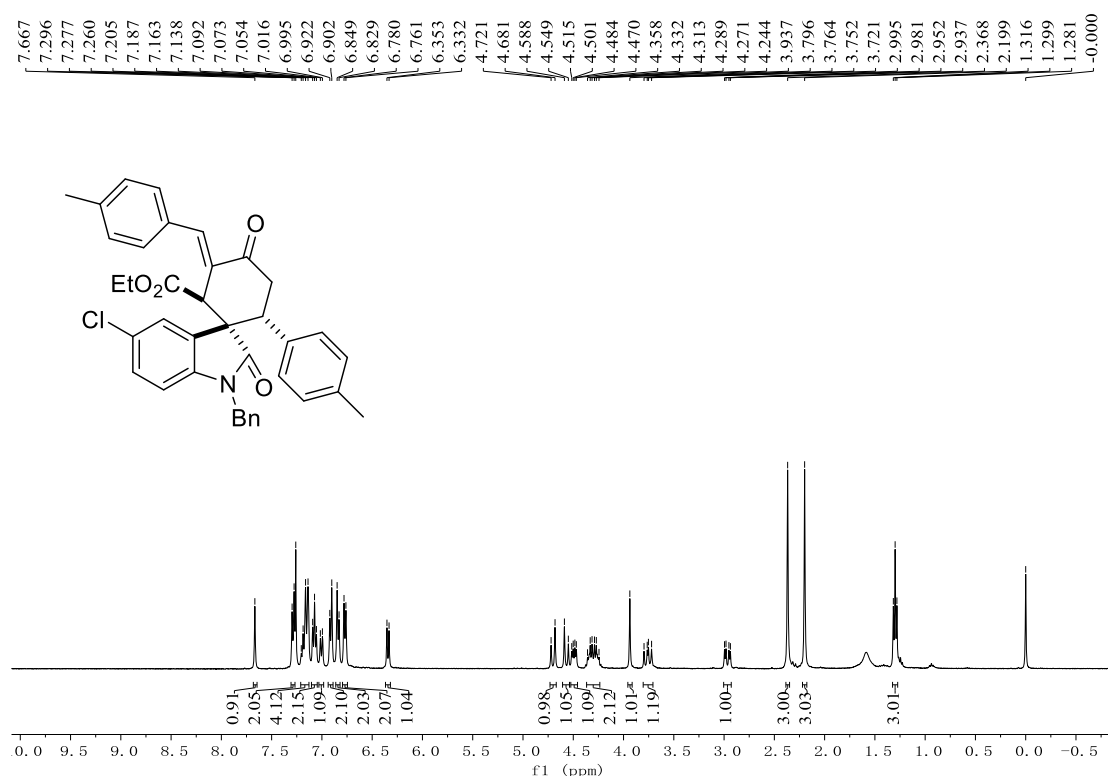


***rel*-(1*R*,3*S*,*Z*)-1'-Benzyl-2',5-dioxo-3-(thiophen-2-yl)-6-(thiophen-2-ylmethylene)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (**1z**):** yellow solid, 53%, m.p. 158-160 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 7.6 Hz, 1H, ArH), 7.55 (d, *J* = 4.8 Hz, 1H, ArH), 7.46-7.42 (m, 1H, ArH), 7.38 (d, *J* = 4.8 Hz, 1H, ArH), 7.33-7.29 (m, 7H, ArH), 7.19 (d, *J* = 3.2 Hz, 1H, ArH), 7.09-7.08 (m, 1H, ArH), 7.06-7.03 (m, 1H, ArH), 6.90 (d, *J* = 7.6 Hz, 1H, ArH), 6.75 (s, 1H, CH), 5.43 (t, *J* = 8.8 Hz, 1H, CH), 5.05 (d, *J* = 15.6 Hz, 1H, CH₂), 4.91 (d, *J* = 15.6 Hz, 1H, CH₂), 3.33 (d, *J* = 9.2 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 193.9, 172.7, 143.3, 138.8, 137.6, 136.3, 135.8, 134.2, 133.8, 131.6, 129.0, 128.2, 128.1, 127.4, 127.2, 127.1, 126.6, 126.3, 124.4, 124.0, 122.6, 112.3, 111.2, 59.3, 48.9, 44.7, 44.4, 37.9. IR (KBr) ν: 3095, 2914, 1708, 1604, 1488, 1466, 1417, 1366, 1271, 1233, 1188, 1059, 948, 894, 845, 756, 724 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₁H₂₁NaN₃O₂S₂ ([M+Na]⁺): 554.0973, found: 554.0961.

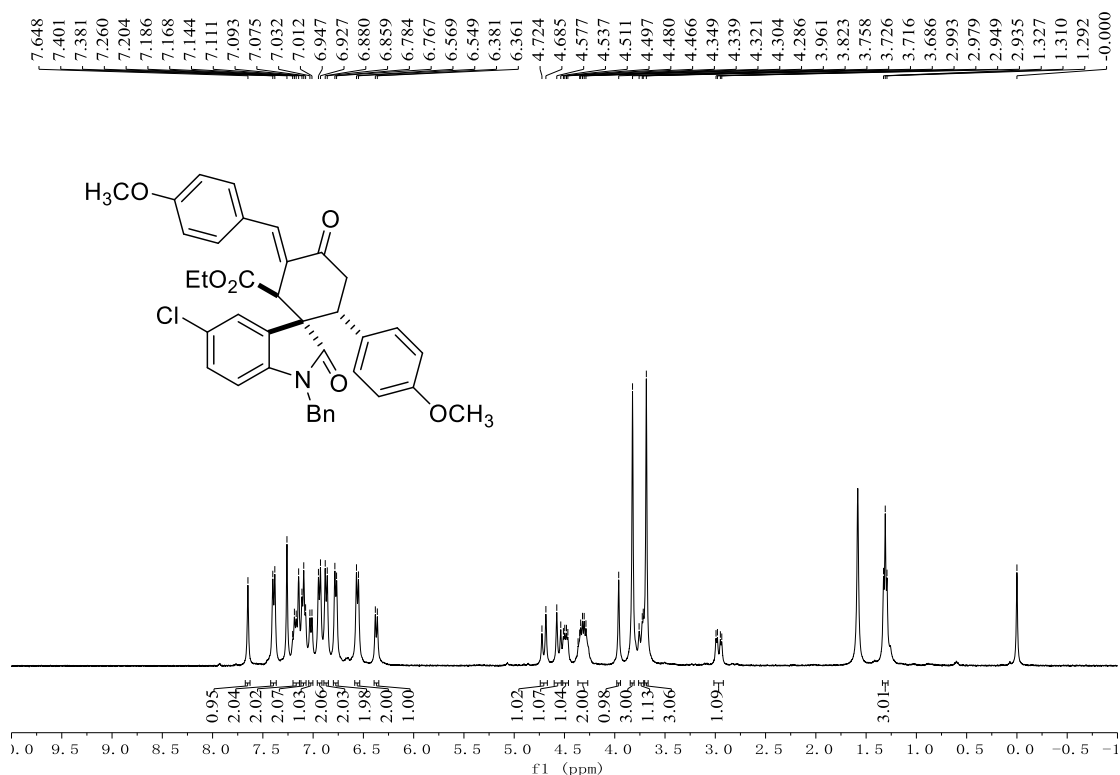


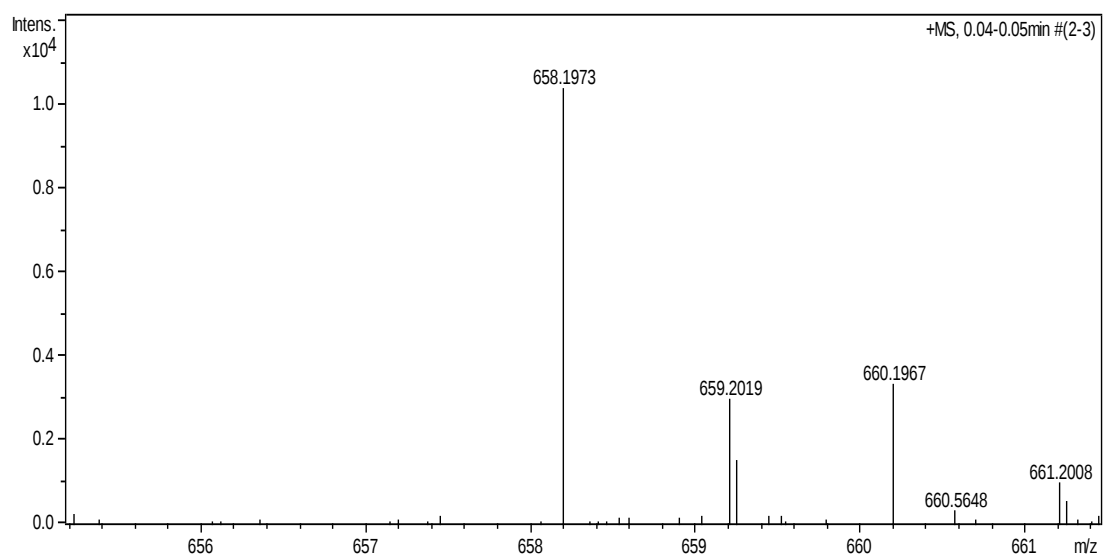
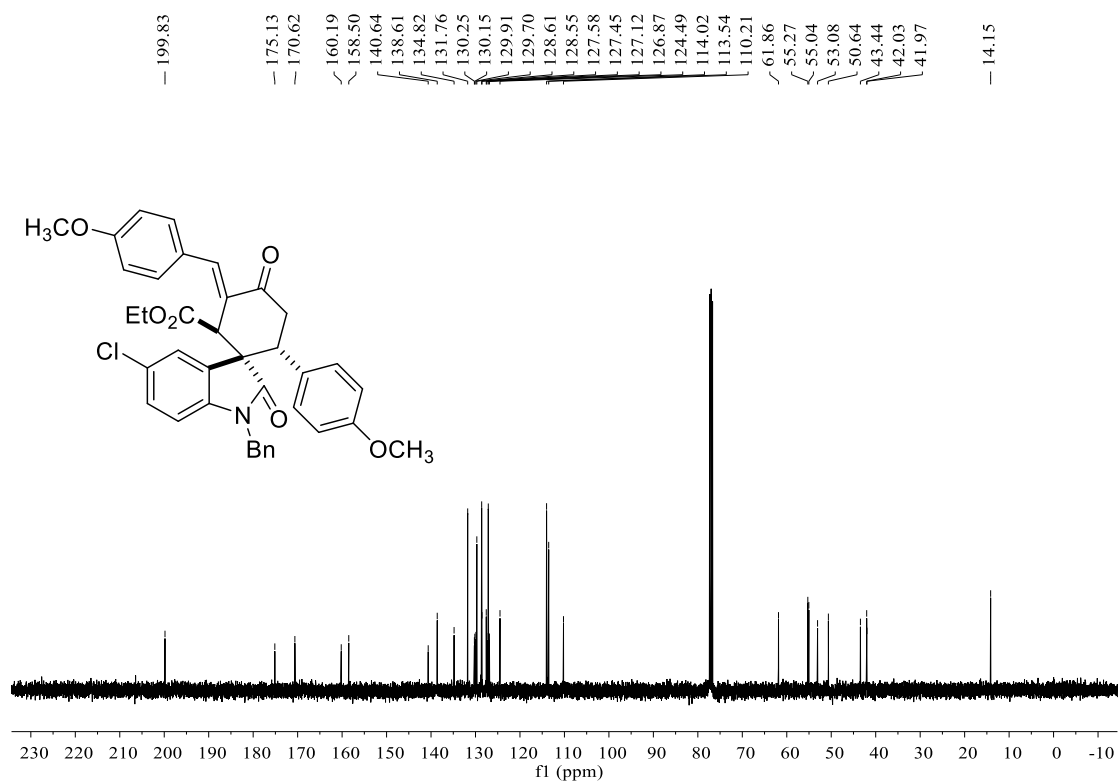


rel-Ethyl (1S,2S,6R)-1'-benzyl-5'-chloro-3-((E)-4-methylbenzylidene)-2',4-dioxo-6-(p-tolyl)spiro[cyclohexane-1,3'-indoline]-2-carboxylate (5a): white solid, 60%, m.p. 221-223 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (s, 1H, ArH), 7.29 (d, *J* = 7.6 Hz, 2H, ArH), 7.21-7.14 (m, 4H, ArH), 7.07 (t, *J* = 7.6 Hz, 2H, ArH), 7.01 (d, *J* = 8.4 Hz, 1H, ArH), 6.91 (d, *J* = 8.0 Hz, 2H, ArH), 6.84 (d, *J* = 8.0 Hz, 2H, ArH), 6.77 (d, *J* = 7.6 Hz, 2H, ArH), 6.34 (d, *J* = 8.4 Hz, 1H, CH), 4.70 (d, *J* = 16.0 Hz, 1H, CH₂), 4.57 (d, *J* = 15.6 Hz, 1H, CH₂), 4.52-4.47 (m, 1H, CH₂), 4.36-4.24 (m, 2H, OCH₂), 3.94 (s, 1H, CH), 3.80-3.72 (m, 1H, CH), 3.00-2.94 (m, 1H, CH₂), 2.37 (s, 3H, CH₃), 2.20 (s, 3H, CH₃), 1.30 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 200.0, 175.1, 170.6, 140.6, 139.0, 138.8, 136.8, 135.0, 134.8, 131.6, 131.2, 130.1, 129.8, 129.3, 129.0, 128.6, 128.5, 127.5, 127.4, 127.1, 124.5, 110.2, 61.8, 53.0, 50.7, 43.4, 42.5, 42.0, 21.4, 21.0, 14.1. IR (KBr) ν: 3723, 3412, 2933, 2871, 2324, 1925, 1817, 1703, 1604, 1474, 1442, 1339, 1172, 1091, 1010, 904, 824, 716 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₈H₃₄ClNaNO₄ ([M+Na]⁺): 626.2069, found: 626.2066.

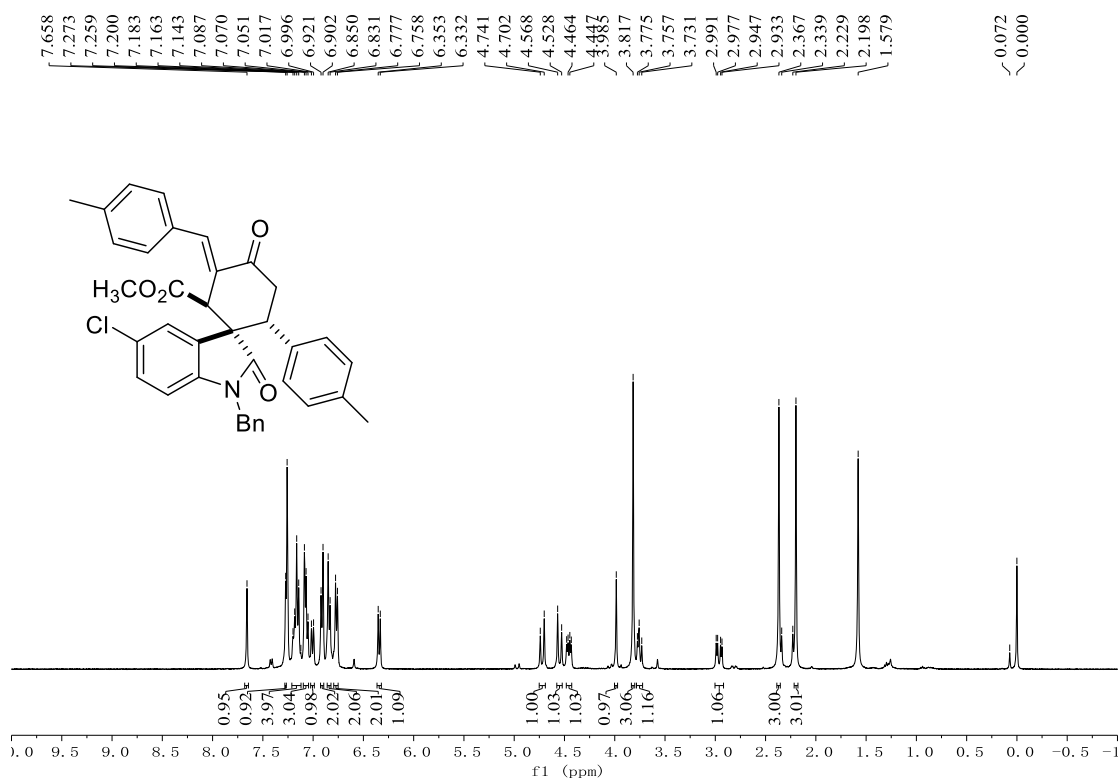


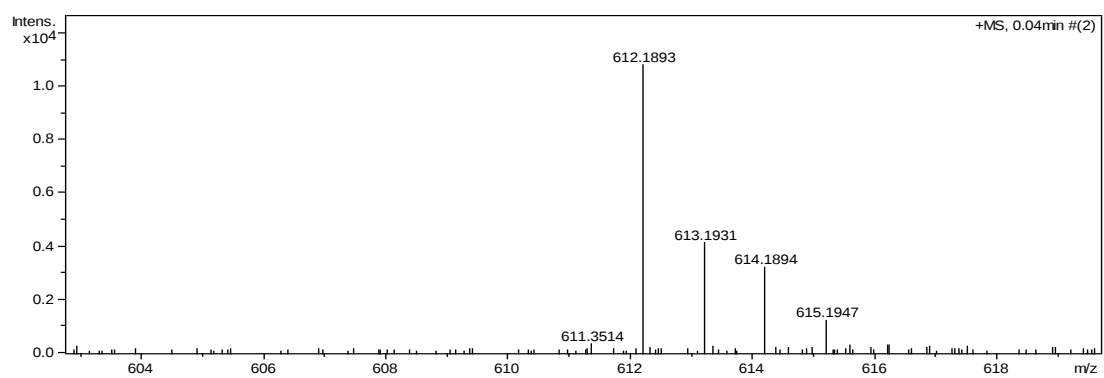
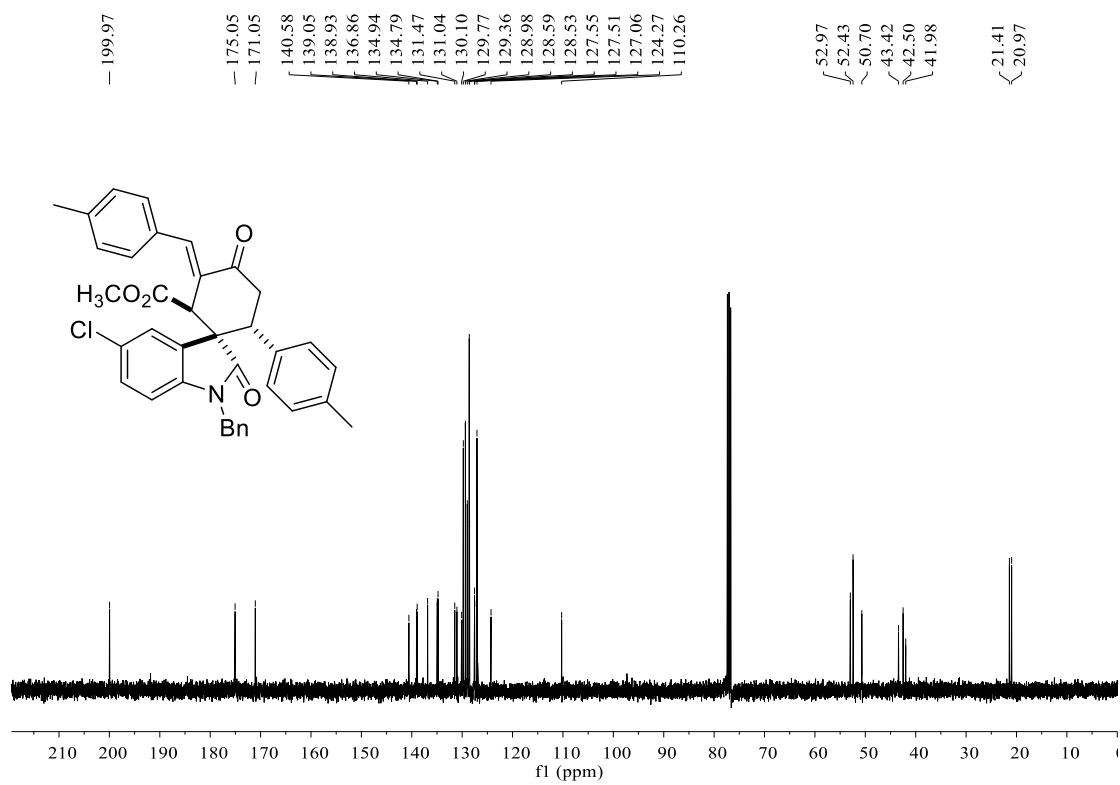
rel-Ethyl (1*S*,2*S*,6*R*)-1'-benzyl-5'-chloro-3-((*E*)-4-methoxybenzylidene)-6-(4-methoxyphenyl)-2',4'-dioxospiro[cyclohexane-1,3'-indoline]-2-carboxylate (5b): white solid, 57%, m.p. 231-233 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (s, 1H, ArH), 7.39 (d, *J* = 8.0 Hz, 2H, ArH), 7.20-7.14 (m, 2H, ArH), 7.09 (t, *J* = 7.2 Hz, 2H, ArH), 7.02 (d, *J* = 8.0 Hz, 1H, ArH), 6.94 (d, *J* = 8.0 Hz, 2H, ArH), 6.87 (d, *J* = 8.4 Hz, 2H, ArH), 6.77 (d, *J* = 6.8 Hz, 2H, ArH), 6.56 (d, *J* = 8.0 Hz, 2H, ArH), 6.37 (d, *J* = 8.0 Hz, 1H, CH), 4.70 (d, *J* = 15.6 Hz, 1H, CH₂), 4.56 (d, *J* = 16.0 Hz, 1H, CH₂), 4.51-4.47 (m, 1H, CH₂), 4.37-4.29 (m, 2H, OCH₂), 3.96 (s, 1H, CH), 3.82 (s, 3H, OCH₃), 3.76-3.72 (m, 1H, CH), 3.69 (s, 3H, OCH₃), 2.99-2.94 (m, 1H, CH₂), 1.31 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 199.8, 175.1, 170.6, 160.2, 158.5, 140.6, 138.6, 134.8, 131.8, 130.3, 130.2, 129.9, 129.7, 128.6, 128.6, 127.6, 127.5, 127.1, 126.9, 124.5, 114.0, 113.5, 110.2, 61.9, 55.3, 55.0, 53.1, 50.6, 43.4, 42.0, 41.9, 14.2. IR (KBr) ν: 3734, 3410, 2940, 2843, 2421, 1930, 1843, 1715, 1623, 1443, 1340, 1065, 1003, 876, 843, 721 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₈H₃₄ClNaNO₆ ([M+Na]⁺): 658.1967, found: 658.1973.



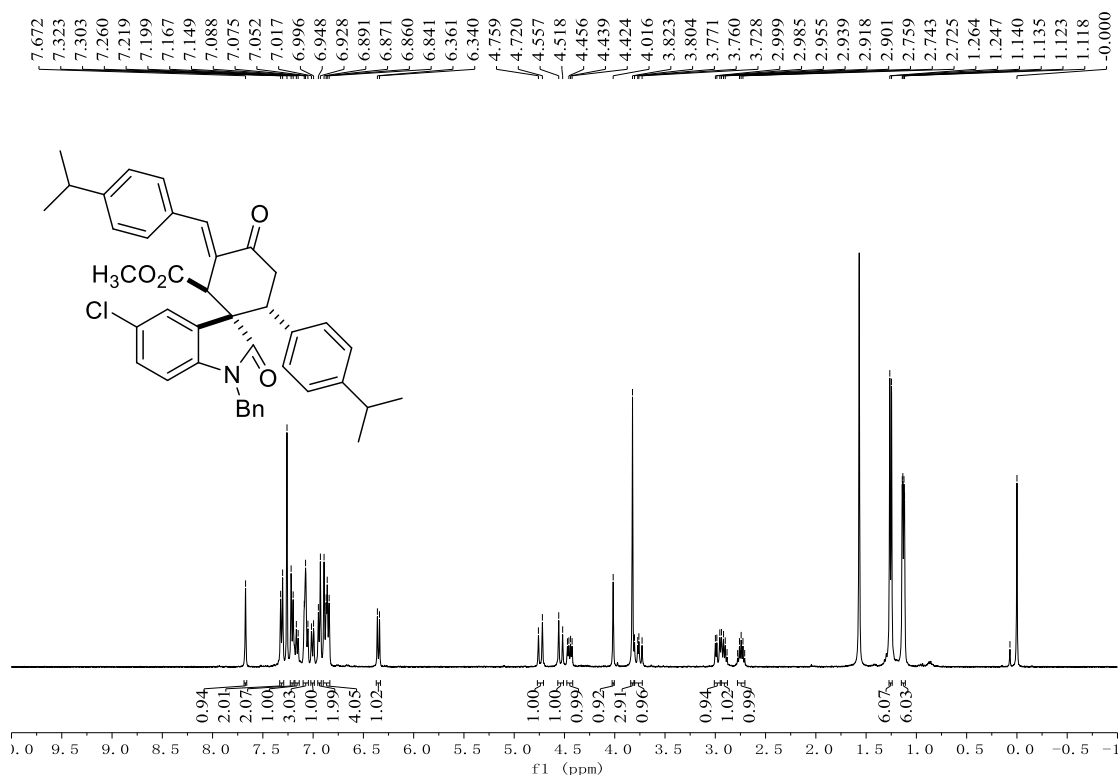


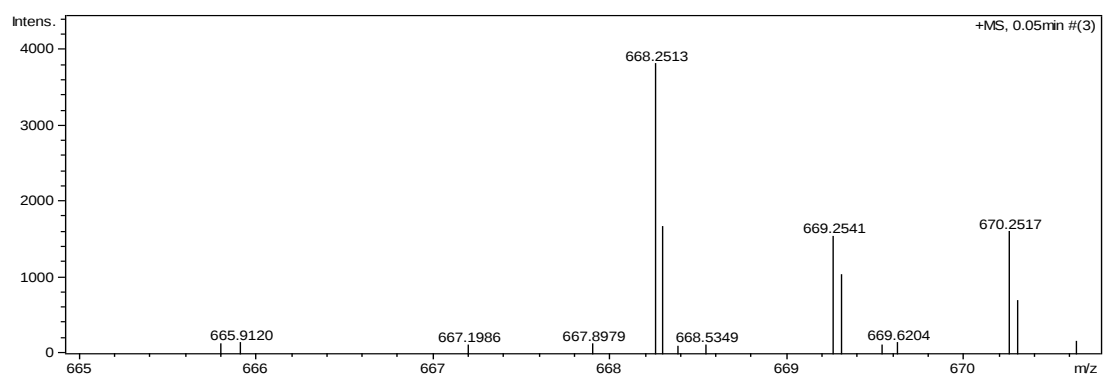
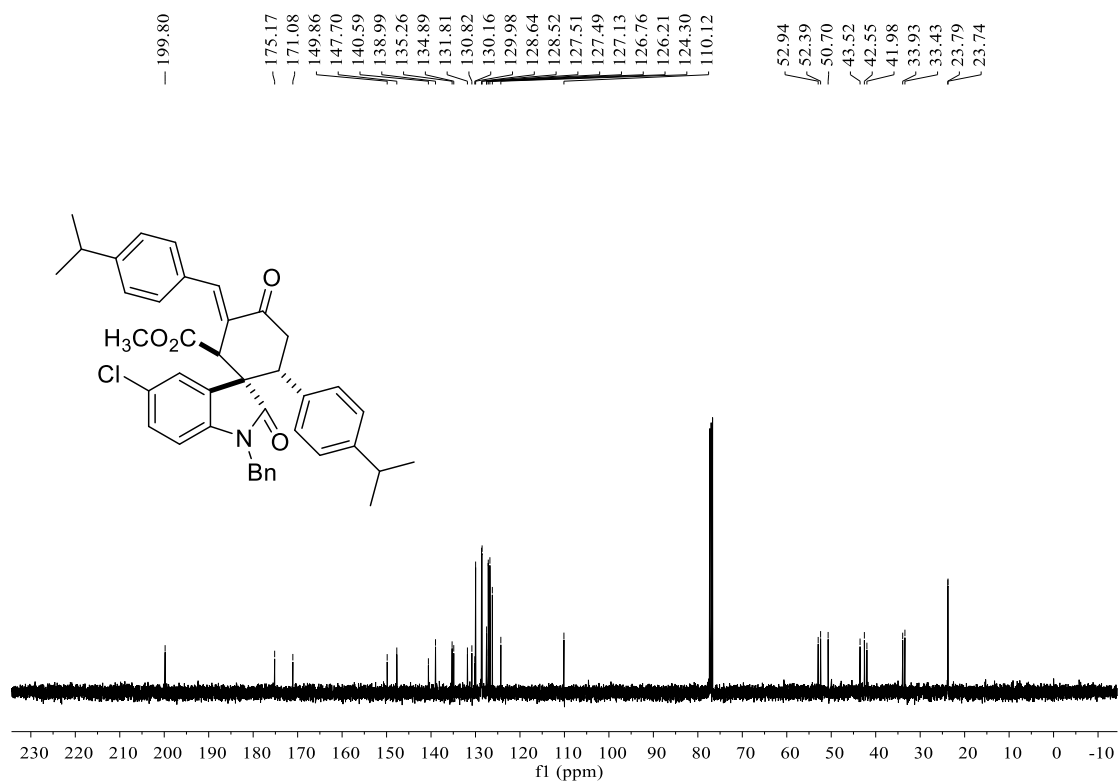
rel-Methyl (1S,2S,6R)-1'-benzyl-5'-chloro-3-((E)-4-methylbenzylidene)-2',4-dioxo-6-(p-tolyl)spiro[cyclohexane-1,3'-indoline]-2-carboxylate (5c): white solid, 42%, m.p. 225-227 °C; **ratio of major/minor = 10:1**, ^1H NMR (400 MHz, CDCl_3) δ 7.66 (s, 1H, ArH), 7.27 (s, 1H, ArH), 7.20-7.12 (m, 4H, ArH), 7.09-7.05 (m, 3H, ArH), 7.01 (d, J = 8.4 Hz, 1H, ArH), 6.91 (d, J = 7.6 Hz, 2H, ArH), 6.84 (d, J = 7.6 Hz, 2H, ArH), 6.77 (d, J = 7.6 Hz, 2H, ArH), 6.32 (d, J = 8.4 Hz, 1H, CH), 4.72 (d, J = 15.6 Hz, 1H, CH_2), 4.55 (d, J = 16.0 Hz, 1H, CH_2), 4.48-4.43 (m, 1H, CH_2), 3.99 (s, 1H, CH), 3.82 (s, 3H, OCH_3), 3.78-3.73 (m, 1H, CH), 2.99-2.93 (m, 1H, CH_2), 2.37 (s, 3H, CH_3), 2.20 (s, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ 200.0, 175.1, 171.1, 140.6, 139.1, 138.9, 136.9, 134.9, 134.8, 131.5, 131.0, 130.1, 129.8, 129.4, 129.0, 128.6, 128.5, 127.6, 127.5, 127.1, 124.3, 110.3, 53.0, 52.4, 50.7, 43.4, 42.5, 42.0, 21.4, 21.0. IR (KBr) ν : 3684, 3432, 2943, 2834, 2356, 1811, 1724, 1605, 1424, 1443, 1345, 1123, 1080, 904, 859, 746 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{37}\text{H}_{32}\text{ClNaNO}_4$ ($[\text{M}+\text{Na}]^+$): 612.1912, found: 612.1893.



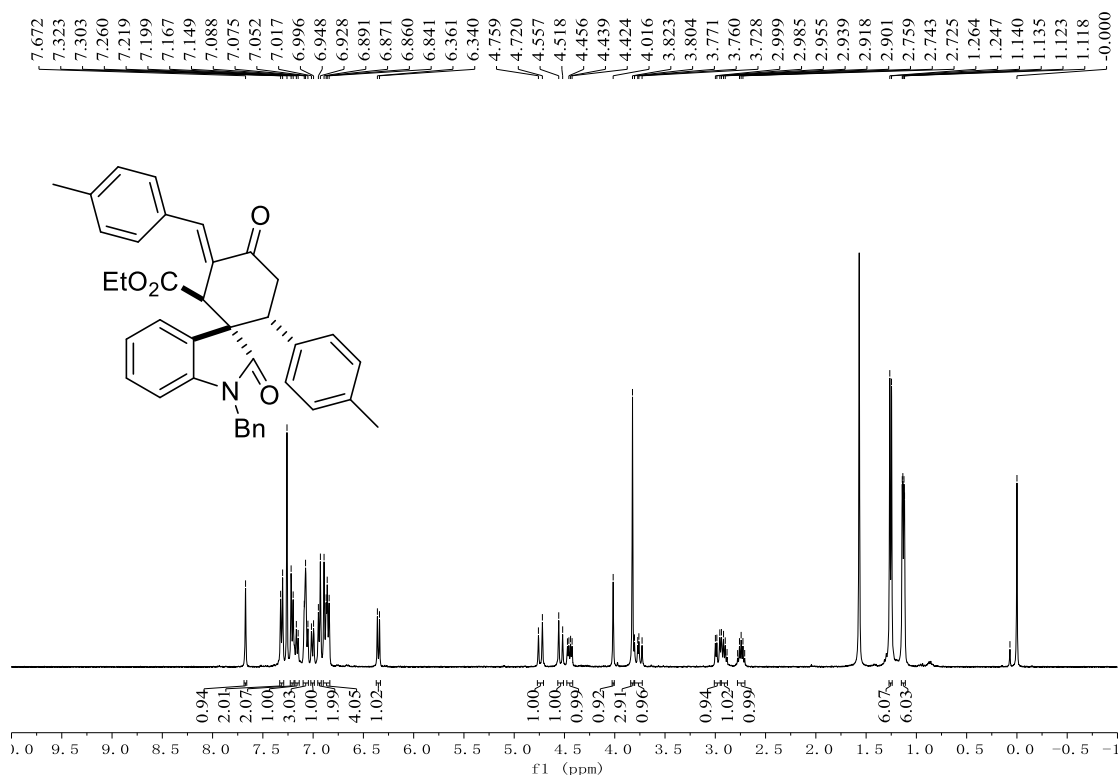


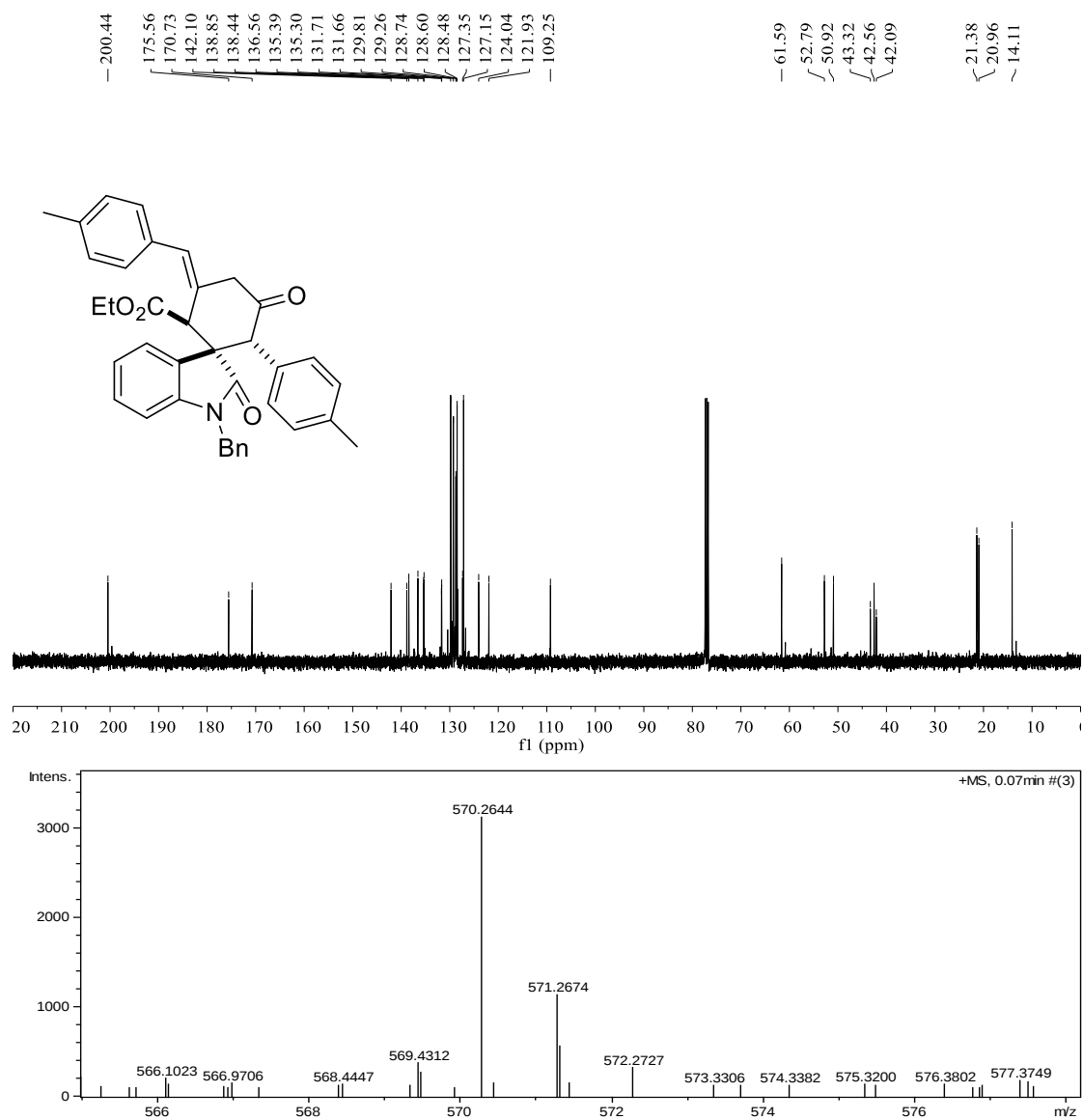
rel-Methyl (1S,2S,6R)-1'-benzyl-5'-chloro-3-((E)-4-isopropylbenzylidene)-6-(4-isopropylphenyl)-2',4-dioxospiro[cyclohexane-1,3'-indoline]-2-carboxylate (5d): white solid, 58%, m.p. 226-228 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (s, 1H, ArH), 7.31 (d, $J = 8.0$ Hz, 2H, ArH), 7.21 (d, $J = 8.0$ Hz, 2H, ArH), 7.16 (t, $J = 7.2$ Hz, 1H, ArH), 7.09-7.05 (m, 3H, ArH), 7.01 (d, $J = 8.4$ Hz, 1H, ArH), 6.94 (d, $J = 8.0$ Hz, 2H, ArH), 6.89-6.84 (m, 4H, ArH), 6.35 (d, $J = 8.0$ Hz, 1H, CH), 4.74 (d, $J = 15.6$ Hz, 1H, CH_2), 4.54 (d, $J = 15.6$ Hz, 1H, CH_2), 4.47-4.42 (m, 1H, CH_2), 4.02 (s, 1H, CH), 3.82 (s, 3H, OCH_3), 3.80-3.72 (m, 1H, CH), 3.00-2.96 (m, 1H, CH_2), 2.94-2.88 (m, 1H, CH), 2.78-2.71 (m, 1H, CH), 1.25 (d, $J = 6.8$ Hz, 6H, CH_3), 1.14-1.12 (m, 6H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ 199.8, 175.2, 171.1, 149.9, 147.7, 140.6, 139.0, 135.3, 134.9, 131.8, 130.8, 130.2, 130.0, 128.6, 128.5, 127.5, 127.5, 127.1, 126.8, 126.2, 124.3, 110.1, 52.9, 52.4, 50.7, 43.5, 42.6, 42.0, 33.9, 33.4, 23.8, 23.7. IR (KBr) ν : 3735, 3398, 2889, 2314, 1924, 1878, 1734, 1615, 1434, 1415, 1365, 1145, 1045, 904, 835, 745 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{41}\text{H}_{40}\text{ClNaNO}_4$ ($[\text{M}+\text{Na}]^+$): 668.2538, found: 668.2513.



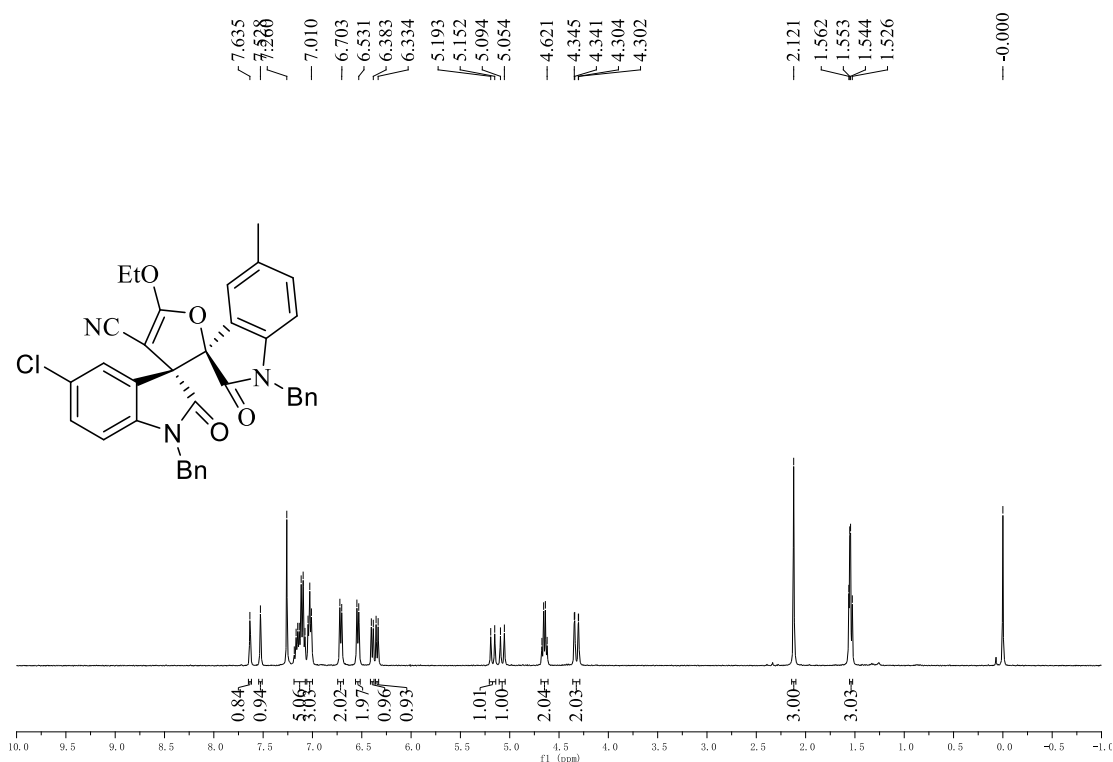


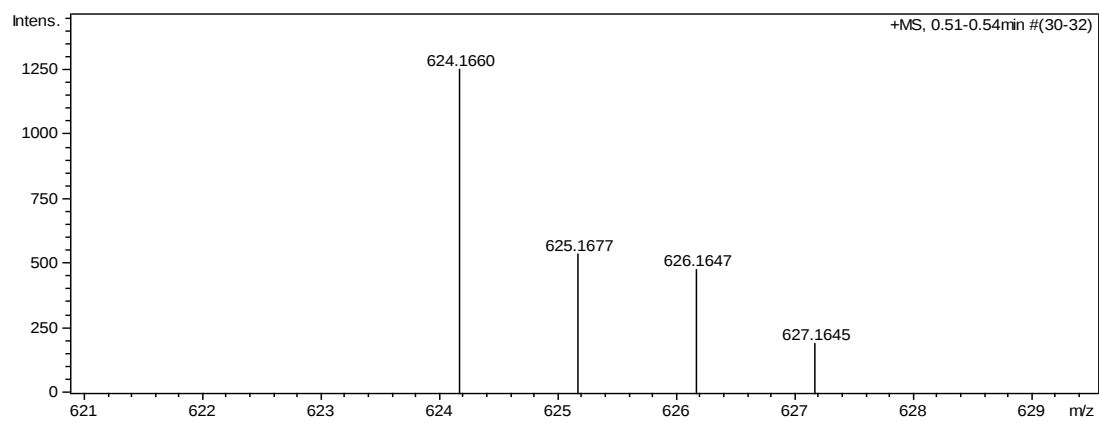
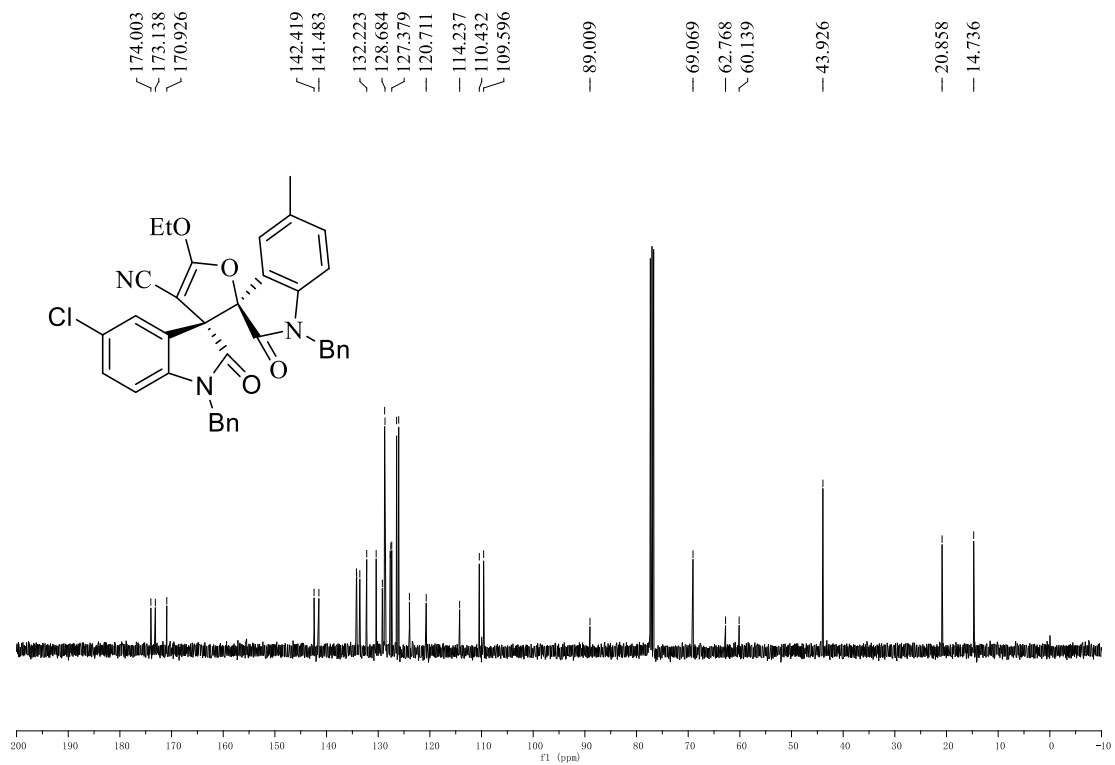
rel-Ethyl (1S,2S,6R)-1'-benzyl-3-((E)-4-methylbenzylidene)-2',4-dioxo-6-(p-tolyl)spiro[cyclohexane-1,3'-indoline]-2-carboxylate (5e): white solid, 56%, m.p. 236-238 °C; **ratio of major/minor = 9:1**, ^1H NMR (400 MHz, CDCl_3) δ 7.65 (s, 1H, ArH), 7.29 (d, $J = 7.6$ Hz, 2H, ArH), 7.19-7.13 (m, 5H, ArH), 7.08 (d, $J = 7.2$ Hz, 1H, ArH), 7.03 (d, $J = 8.0$ Hz, 1H, ArH), 6.95 (d, $J = 7.6$ Hz, 1H, ArH), 6.90 (d, $J = 7.6$ Hz, 2H, ArH), 6.81-6.78 (m, 4H, ArH), 6.44 (d, $J = 8.0$ Hz, 1H, CH), 4.72 (d, $J = 15.6$ Hz, 1H, CH_2), 4.57 (d, $J = 15.6$ Hz, 1H, CH_2), 4.55-4.52 (m, 1H, CH_2), 4.39-4.31 (m, 1H, OCH_2), 4.23-4.16 (m, 1H, OCH_2), 3.96 (s, 1H, CH), 3.83-3.75 (1, 1H, CH), 2.99-2.93 (m, 1H, CH_2), 2.36 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 1.27 (t, $J = 7.2$ Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ 200.4, 175.6, 170.7, 142.1, 138.9, 138.4, 136.6, 135.4, 135.3, 131.7, 131.7, 129.8, 129.3, 128.7, 128.6, 128.5, 127.4, 127.2, 124.0, 121.9, 109.3, 61.6, 52.8, 50.9, 43.3, 42.6, 42.1, 21.4, 21.0, 14.1. IR (KBr) ν : 3710, 2987, 2925, 1893, 1795, 1670, 1600, 1463, 1370, 1308, 1175, 1105, 1028, 900, 816, 744 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{38}\text{H}_{36}\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 570.2639, found: 570.2644.



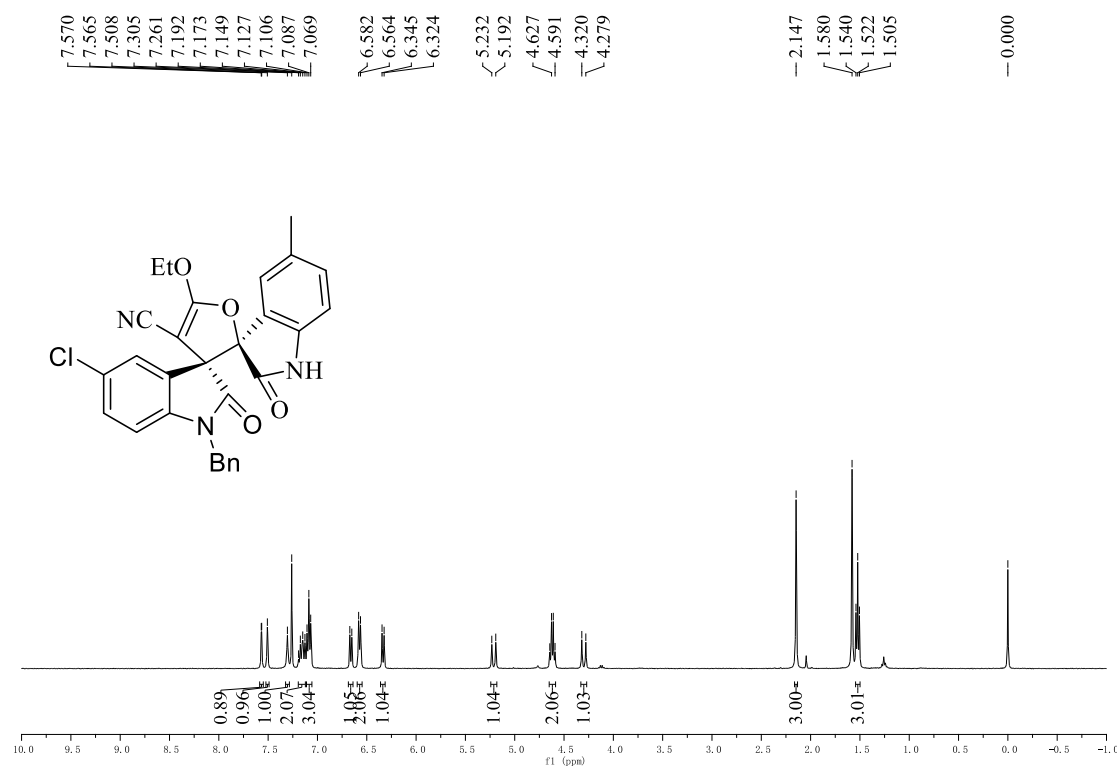


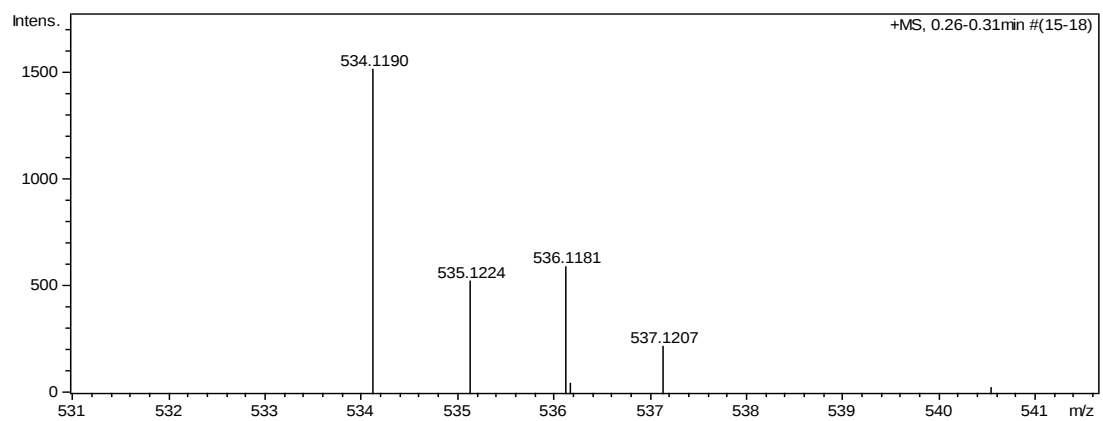
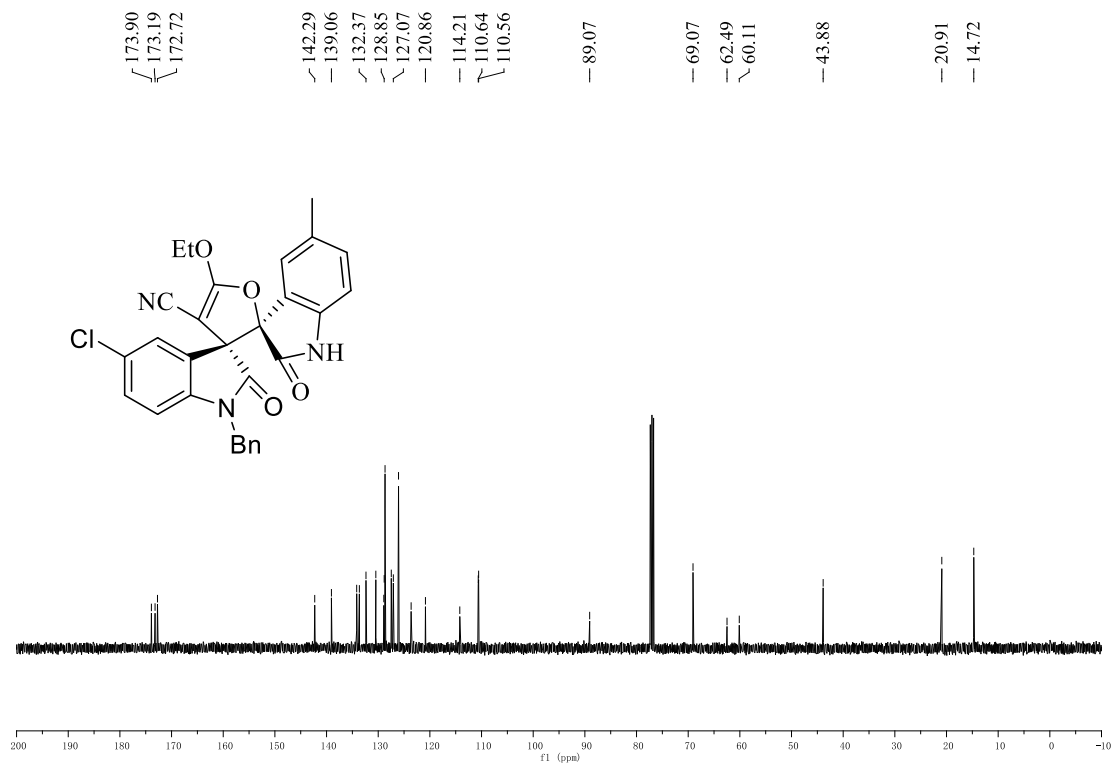
***rel*-(3*R*,3'*R*)-1,1''-Dibenzyl-5''-chloro-5'-ethoxy-5-methyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8a)**: white solid, 71%, m.p. 175-177 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H, ArH), 7.53 (s, 1H, ArH), 7.18-7.08 (m, 5H, ArH), 7.03 (t, *J* = 6.8 Hz, 3H, ArH), 6.71 (d, *J* = 7.6 Hz, 2H, ArH), 6.54 (d, *J* = 7.2 Hz, 2H, ArH), 6.39 (d, *J* = 8.0 Hz, 1H, ArH), 6.34 (d, *J* = 8.4 Hz, 1H, ArH), 5.17 (d, *J* = 16.4 Hz, 1H, CH₂), 5.07 (d, *J* = 16.0 Hz, 1H, CH₂), 4.65 (q, *J* = 7.2 Hz, 2H, CH₂), 4.35-4.30 (m, 2H, CH₂), 2.12 (s, 3H, CH₃), 1.54 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 174.0, 173.1, 170.9, 142.4, 141.5, 134.2, 134.2, 133.6, 132.2, 130.4, 129.2, 128.8, 128.7, 128.6, 127.7, 127.6, 127.4, 126.4, 126.0, 124.0, 120.7, 114.2, 110.4, 109.6, 89.0, 69.1, 62.8, 60.1, 43.9, 20.9, 14.7. IR (KBr) ν: 3467, 3063, 3035, 2990, 2919, 2205, 1739, 1706, 1632, 1602, 1496, 1454, 1434, 1408, 1381, 1361, 1333, 1293, 1258, 1215, 1199, 1186, 1167, 1133, 1089, 1070, 1026, 997, 962, 933, 911, 895, 875, 836, 818, 776, 747 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₆H₂₈NaClN₃O₄ ([M+Na]⁺): 624.1666, found: 624.1660.



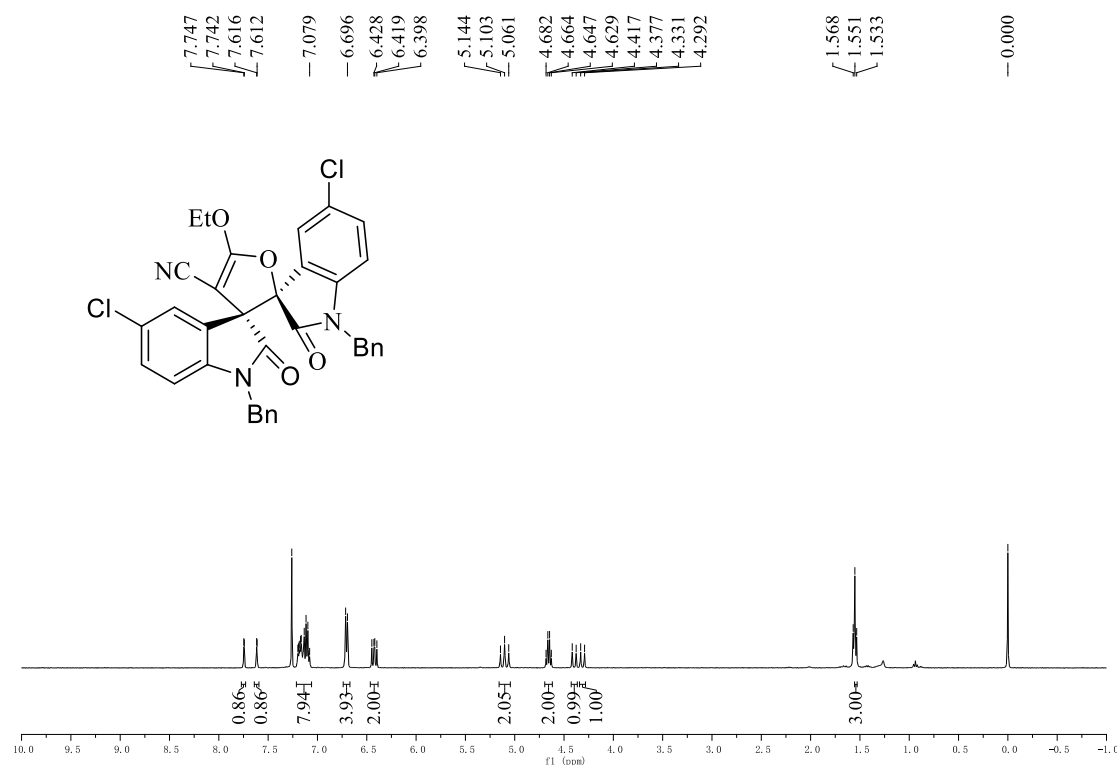


***rel*-(3*R*,3'*R*)-1''-Benzyl-5''-chloro-5'-ethoxy-5-methyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8b)**: white solid, 70%, m.p. 140-142 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 2.0 Hz, 1H, ArH), 7.51 (s, 1H, NH), 7.31 (s, 1H, ArH), 7.19-7.13 (m, 2H, ArH), 7.11-7.07 (m, 3H, ArH), 6.66 (d, *J* = 8.0 Hz, 1H, ArH), 6.57 (d, *J* = 7.2 Hz, 2H, ArH), 6.34 (d, *J* = 8.4 Hz, 1H, ArH), 5.21 (d, *J* = 16.0 Hz, 1H, CH₂), 4.62 (q, *J* = 7.2 Hz, 2H, CH₂), 4.30 (d, *J* = 16.4 Hz, 1H, CH₂), 2.15 (s, 3H, CH₃), 1.52 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 173.2, 172.7, 142.3, 139.1, 134.2, 133.7, 132.4, 130.5, 128.9, 128.9, 128.7, 127.5, 127.1, 126.1, 123.6, 120.9, 114.2, 110.6, 110.6, 89.1, 69.1, 62.5, 60.1, 43.9, 20.9, 14.7. IR (KBr) ν: 3610, 3281, 3087, 3032, 3005, 2920, 2862, 2206, 1743, 1724, 1700, 1628, 1481, 1454, 1430, 1406, 1380, 1342, 1260, 1214, 1169, 1150, 1115, 1064, 1033, 999, 951, 928, 897, 824, 791, 765, 744, 722 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₂₉H₂₂NaClN₃O₄ ([M+Na]⁺): 534.1197, found: 534.1190.

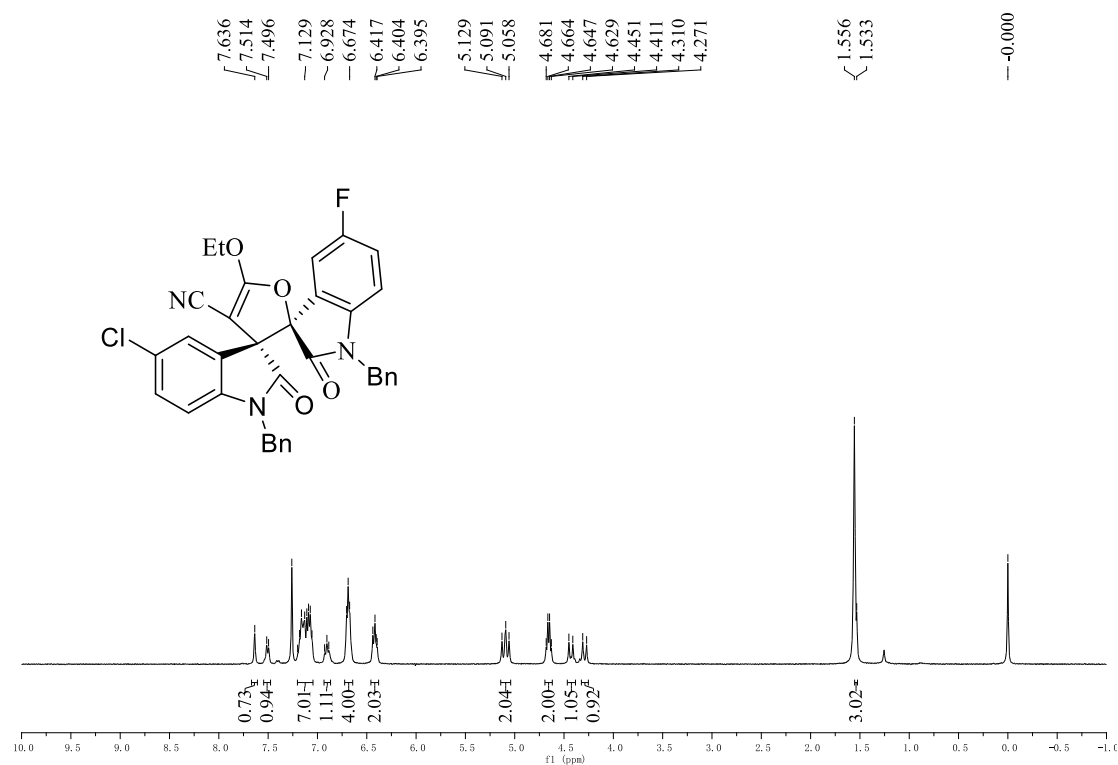


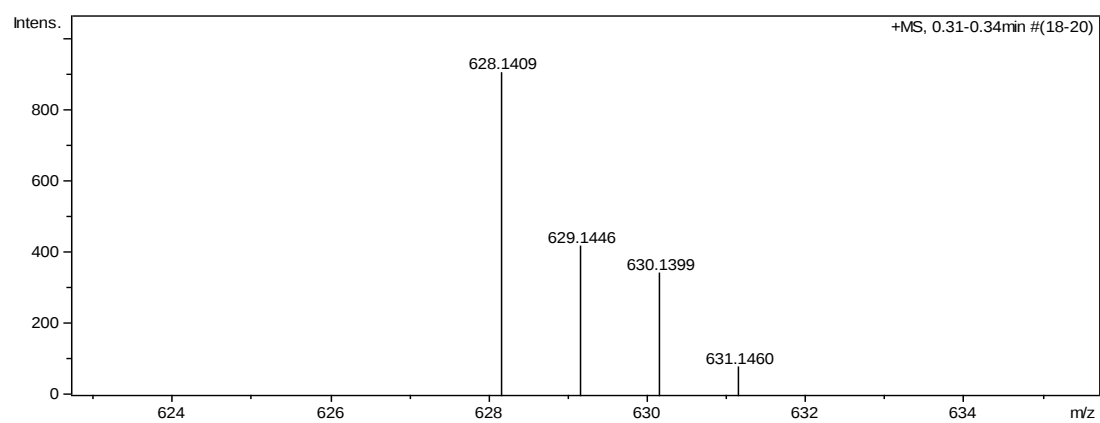
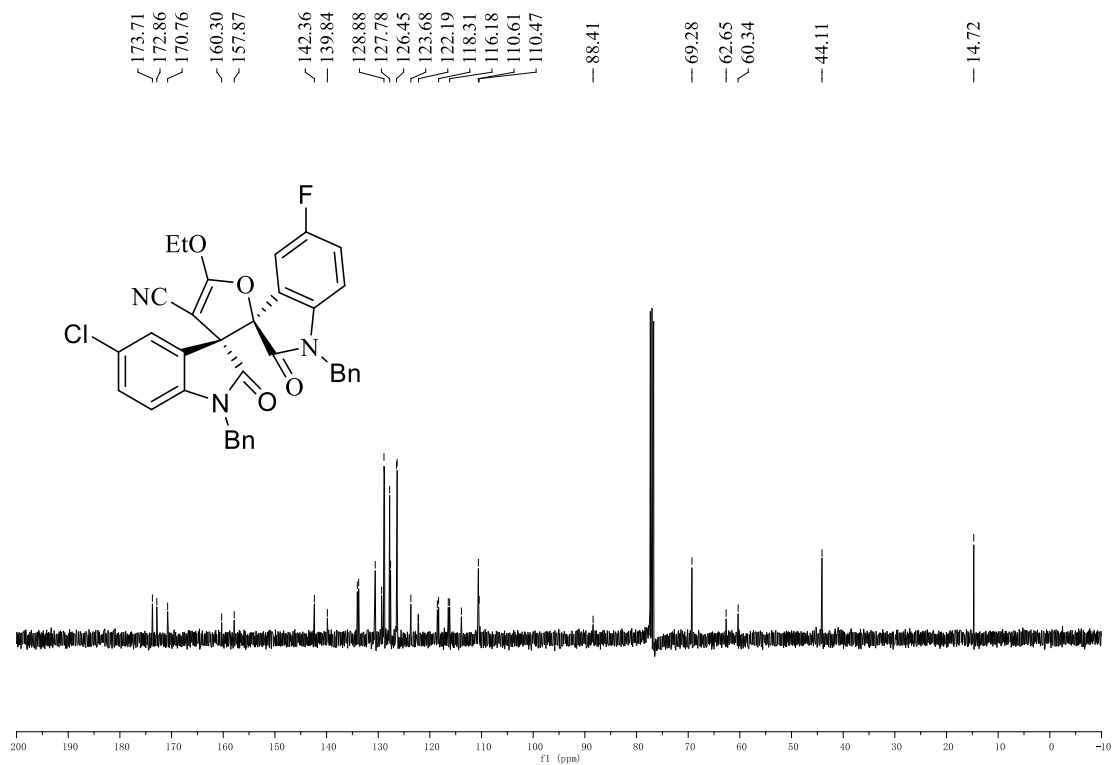


***rel*-(3*R*,3'*R*)-1,1''-Dibenzyl-5,5''-dichloro-5'-ethoxy-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8c)**: lilac solid, 57%, m.p. 168-170 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.75-7.74 (m, 1H, ArH), 7.62-7.61 (m, 1H, ArH), 7.19-7.08 (m, 8H, ArH), 6.70 (d, *J* = 7.2 Hz, 4H, ArH), 6.45-6.40 (m, 2H, ArH), 5.10 (t, *J* = 16.4 Hz, 2H, CH₂), 4.65 (q, *J* = 6.8 Hz, 2H, CH₂), 4.40 (d, *J* = 16.0 Hz, 1H, CH₂), 4.31 (d, *J* = 15.6 Hz, 1H, CH₂), 1.55 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 173.7, 172.9, 170.6, 142.4, 134.1, 133.7, 131.9, 130.6, 129.3, 129.3, 128.9, 128.8, 128.4, 127.9, 127.7, 127.6, 126.5, 126.4, 123.6, 122.4, 113.9, 110.8, 110.6, 110.0, 88.2, 69.3, 62.6, 60.4, 44.2, 44.1, 14.7. IR (KBr) ν: 3108, 3061, 3034, 2993, 2928, 2868, 2208, 1895, 1816, 1729, 1644, 1609, 1484, 1428, 1413, 1377, 1357, 1334, 1250, 1217, 1177, 1151, 1121, 1079, 995, 946, 903, 826, 752 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₅H₂₅NaCl₂N₃O₄ ([M+Na]⁺): 644.1120, found: 644.1128.

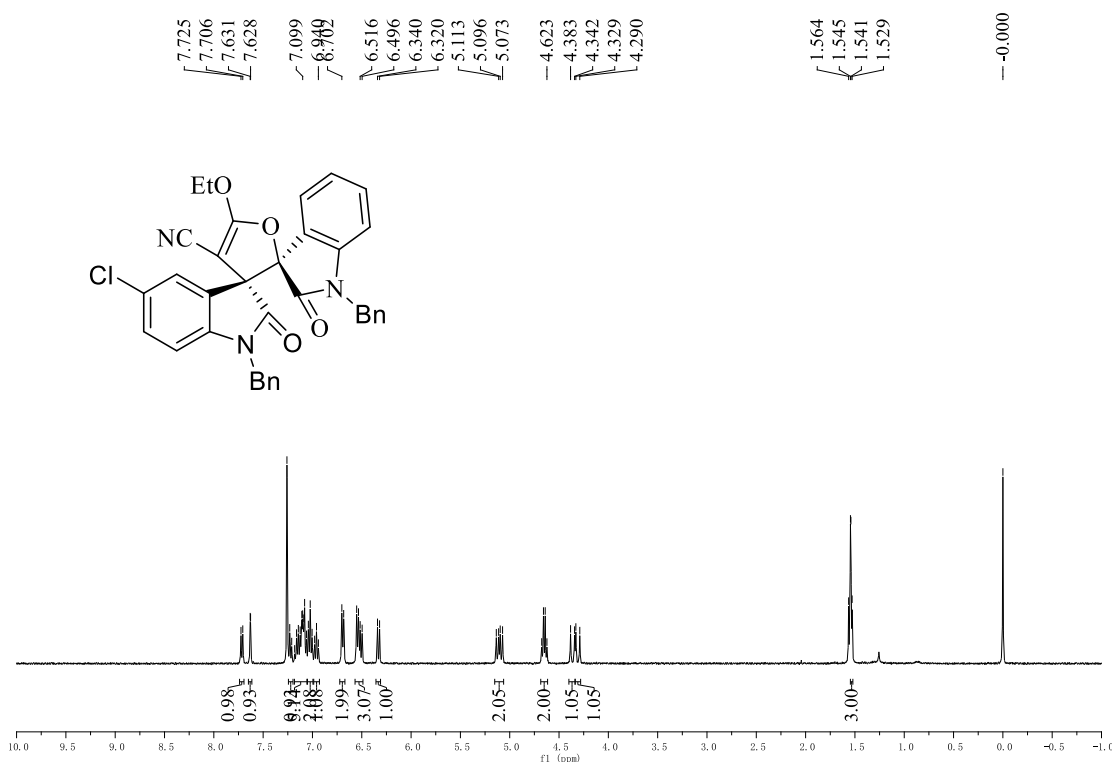


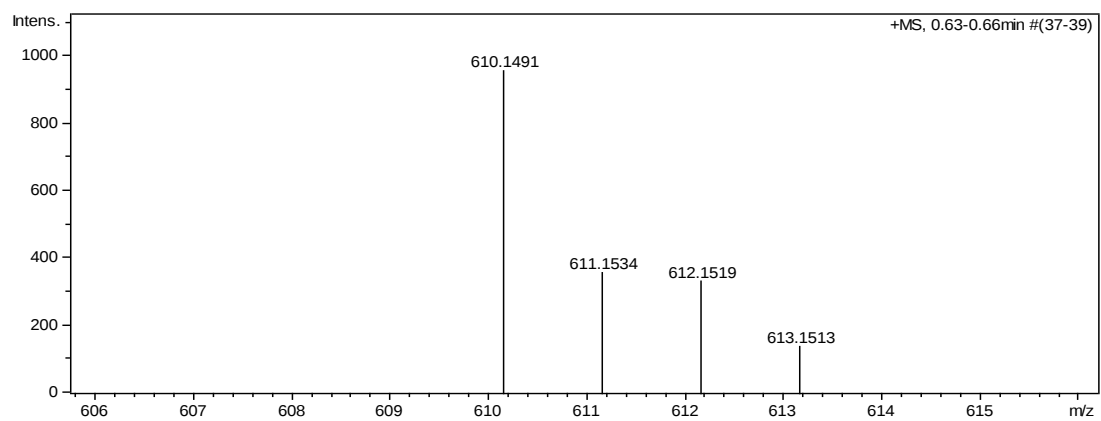
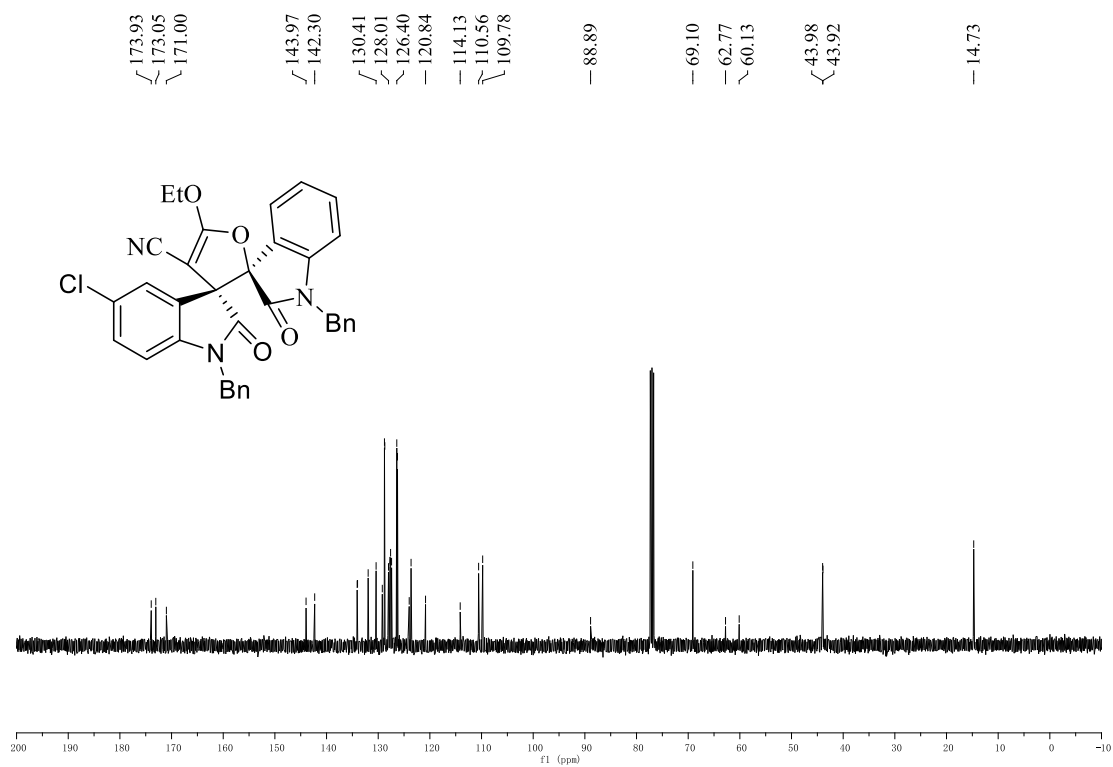
***rel*-(3*R*,3'*R*)-1,1''-Dibenzyl-5''-chloro-5'-ethoxy-5-fluoro-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8d)**: white solid, 56%, m.p. 137-139 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H, ArH), 7.50 (d, *J* = 7.2 Hz, 1H, ArH), 7.20-7.06 (m, 7H, ArH), 6.90 (t, *J* = 7.6 Hz, 1H, ArH), 6.70-6.67 (m, 4H, ArH), 6.44-6.40 (m, 2H, ArH), 5.09 (t, *J* = 15.2 Hz, 2H, CH₂), 4.65 (q, *J* = 6.8 Hz, 2H, CH₂), 4.43 (d, *J* = 16.0 Hz, 1H, CH₂), 4.29 (d, *J* = 15.6 Hz, 1H, CH₂), 1.55 (t, *J* = 9.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 173.7, 172.9, 170.8, 159.1 (d, *J* = 243.0 Hz), 142.4, 139.8, 134.0, 133.8, 130.6, 129.3, 128.9, 128.8, 127.8, 127.6, 126.5, 126.3, 123.7, 122.2 (d, *J* = 9.0 Hz), 118.4 (d, *J* = 24.0 Hz), 116.3 (d, *J* = 26.0 Hz), 113.9, 110.6, 110.5 (d, *J* = 8.0 Hz), 88.4, 69.3, 62.7, 60.3, 44.1, 14.7. IR (KBr) ν: 3062, 3036, 2993, 2929, 2868, 2209, 1883, 1728, 1643, 1489, 1453, 1412, 1378, 1336, 1273, 1217, 1178, 1152, 1117, 1078, 998, 954, 925, 899, 879, 846, 828, 785, 763, 748, 700 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₅H₂₅NaClFN₃O₄ ([M+Na]⁺): 628.1415, found: 628.1409.



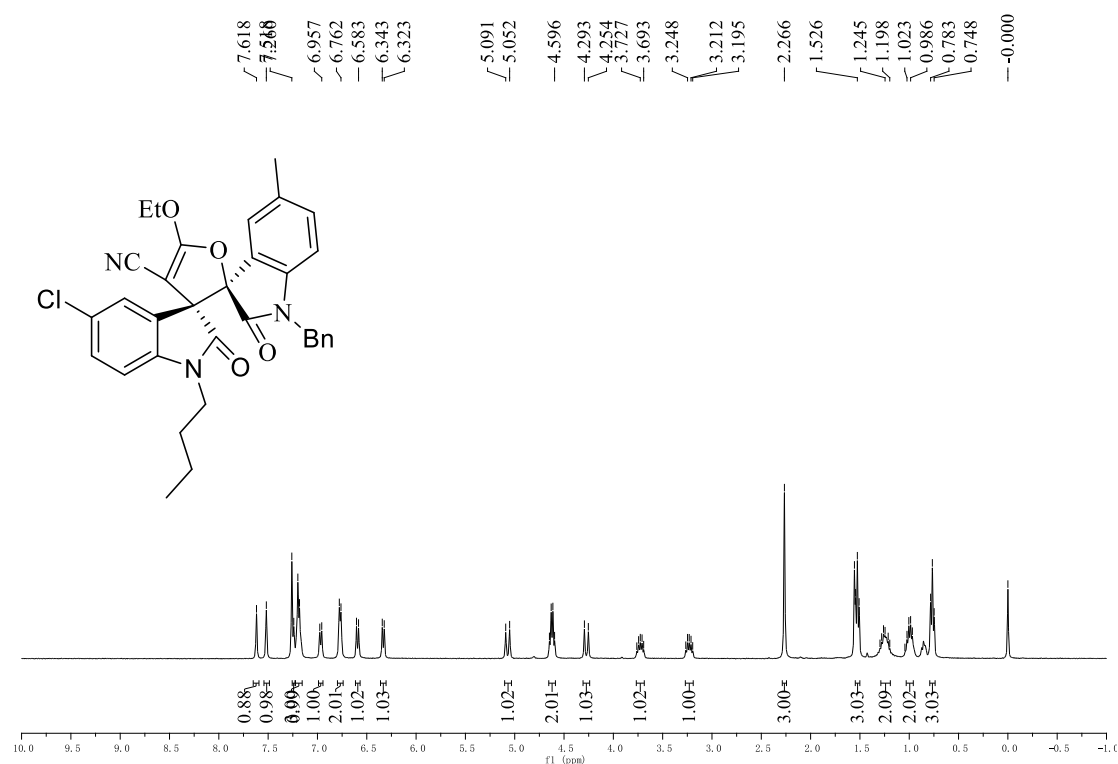


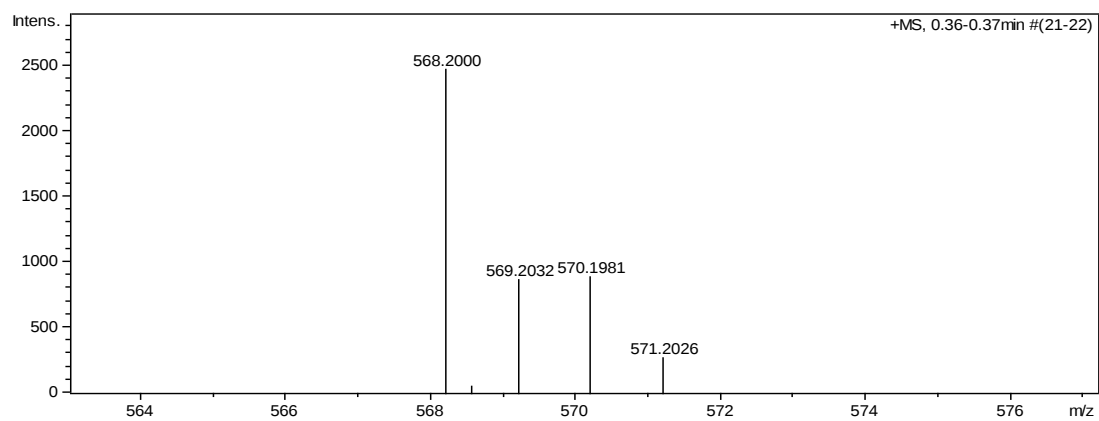
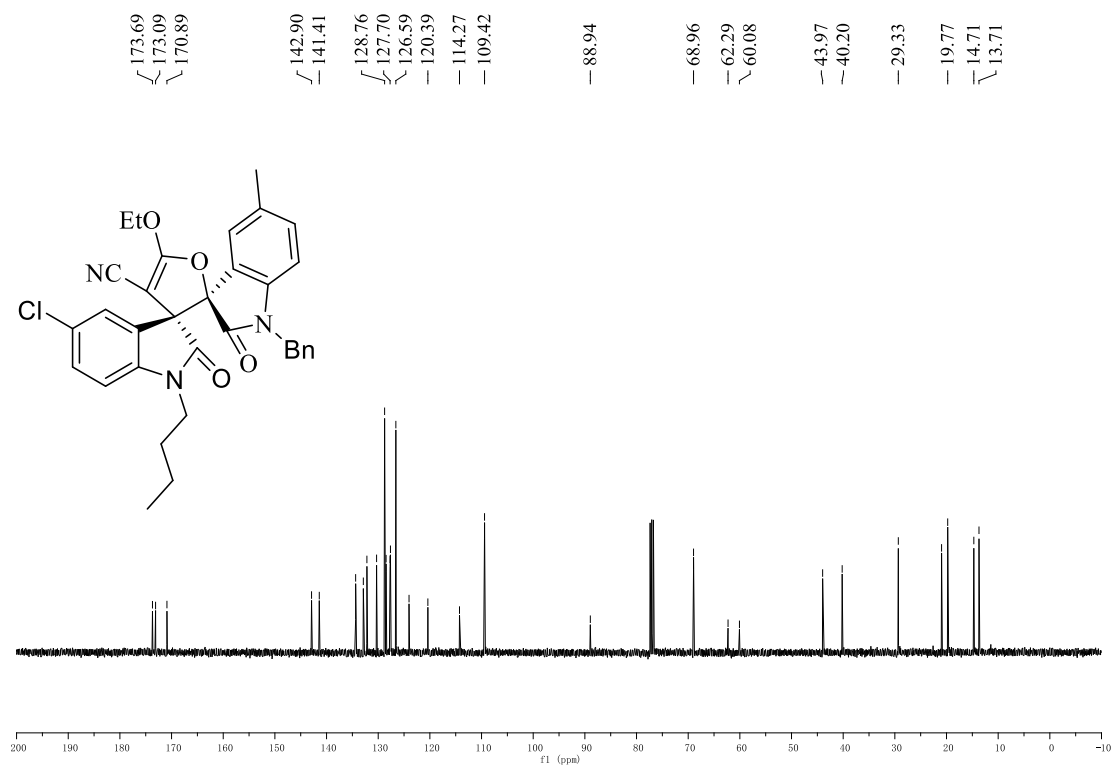
***rel*-(3*R*,3'*R*)-1,1''-Dibenzyl-5''-chloro-5'-ethoxy-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8e)**: white solid, 54%, m.p. 170-172 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 7.6 Hz, 1H, ArH), 7.63 (d, *J* = 1.2 Hz, 1H, ArH), 7.22 (d, *J* = 7.2 Hz, 1H, ArH), 7.18-7.06 (m, 5H, ArH), 7.02 (t, *J* = 7.6 Hz, 2H, ArH), 6.96 (t, *J* = 7.6 Hz, 1H, ArH), 6.69 (d, *J* = 7.6 Hz, 2H, ArH), 6.55-6.50 (m, 3H, ArH), 6.33 (d, *J* = 8.0 Hz, 1H, ArH), 5.14-5.07 (m, 2H, CH₂), 4.65 (q, *J* = 7.2 Hz, 2H, CH₂), 4.36 (d, *J* = 16.4 Hz, 1H, CH₂), 4.31 (d, *J* = 15.6 Hz, 1H, CH₂), 1.55 (t, *J* = 4.8 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 173.1, 171.0, 144.0, 142.3, 134.1, 134.0, 132.0, 130.4, 129.2, 128.8, 128.7, 128.0, 127.8, 127.6, 127.4, 126.4, 126.3, 124.0, 123.64, 120.8, 114.1, 110.6, 109.8, 88.9, 69.1, 62.8, 60.1, 44.0, 43.9, 14.7. IR (KBr) ν: 3063, 3034, 2986, 2936, 2207, 1727, 1641, 1611, 1484, 1467, 1429, 1412, 1378, 1336, 1251, 1213, 1178, 1150, 1112, 1079, 991, 942, 917, 904, 823, 769, 745 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₅H₂₆NaClN₃O₄ ([M+Na]⁺): 610.1510, found: 610.1491.



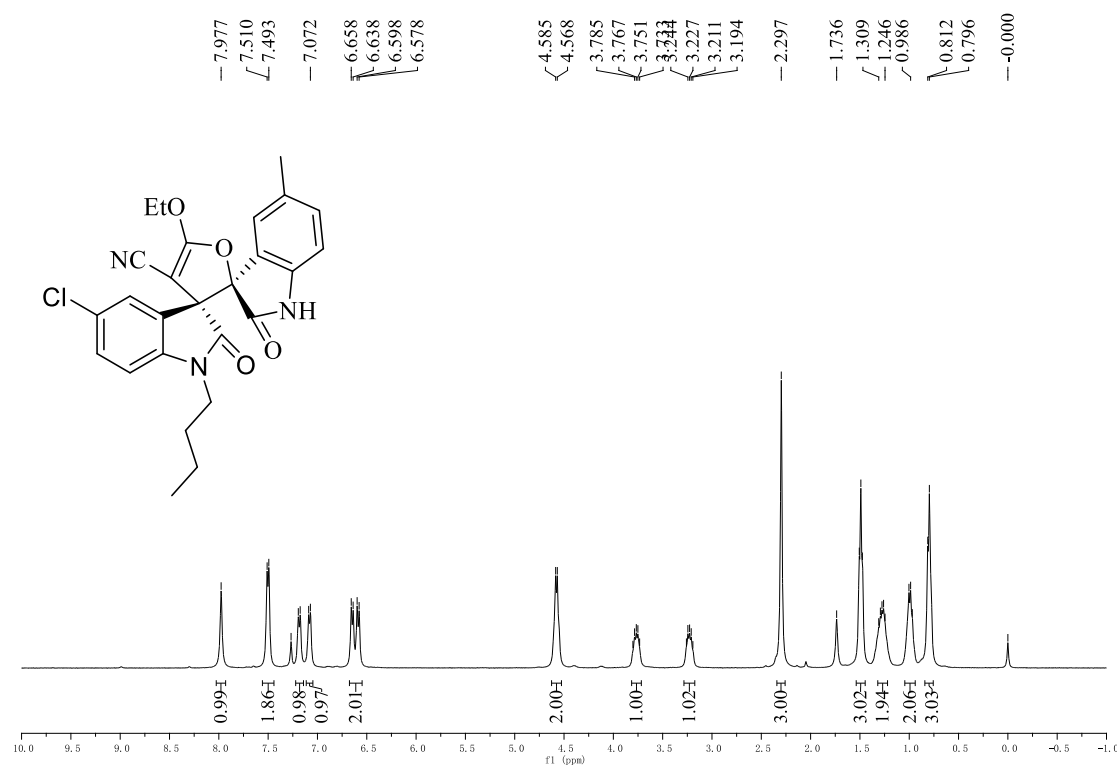


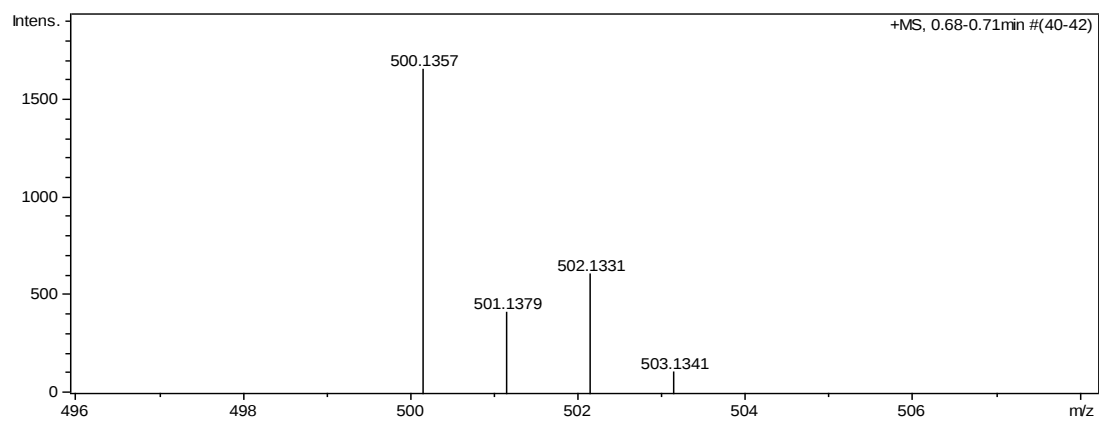
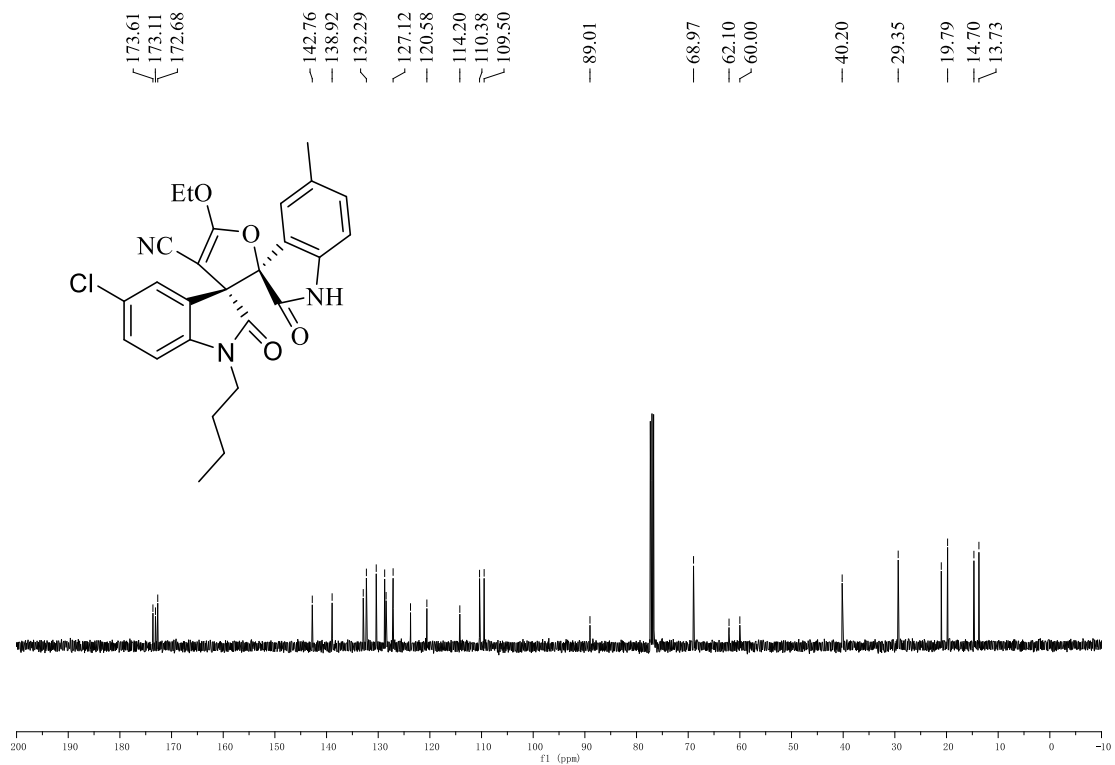
***rel*-(3*R*,3'*R*)-1-Benzyl-1''-butyl-5''-chloro-5'-ethoxy-5-methyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8f)**: white solid, 76%, m.p. 142-144 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (s, 1H, ArH), 7.52 (s, 1H, ArH), 7.24 (s, 1H, ArH), 7.20-7.18 (m, 3H, ArH), 6.97 (d, *J* = 7.6 Hz, 1H, ArH), 6.77 (d, *J* = 6.4 Hz, 2H, ArH), 6.59 (d, *J* = 8.4 Hz, 1H, ArH), 6.33 (d, *J* = 8.0 Hz, 1H, ArH), 5.07 (d, *J* = 15.6 Hz, 1H, CH₂), 4.62 (q, *J* = 6.8 Hz, 2H, CH₂), 4.27 (d, *J* = 15.6 Hz, 1H, CH₂), 3.76-3.69 (m, 1H, CH₂), 3.27-3.20 (m, 1H, CH₂), 2.27 (s, 3H, CH₃), 1.53 (t, *J* = 6.8 Hz, 3H, CH₃), 1.30-1.20 (m, 2H, CH₂), 1.04-0.97 (m, 2H, CH₂), 0.77 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 173.7, 173.1, 170.9, 142.9, 141.4, 134.4, 132.9, 132.2, 130.3, 128.8, 128.5, 127.7, 127.6, 126.6, 124.0, 120.4, 114.3, 109.4, 88.9, 69.0, 62.3, 60.1, 44.0, 40.2, 29.3, 21.0, 19.8, 14.7, 13.7. IR (KBr) ν: 3664, 3434, 3068, 3035, 2959, 2933, 2871, 2741, 2202, 1952, 1885, 1724, 1659, 1635, 1607, 1494, 1430, 1408, 1379, 1336, 1261, 1210, 1168, 1147, 1107, 1072, 997, 951, 928, 897, 846, 819, 729 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₃H₃₁ClN₃O₄ ([M+H]⁺): 568.2003, found: 568.2000.





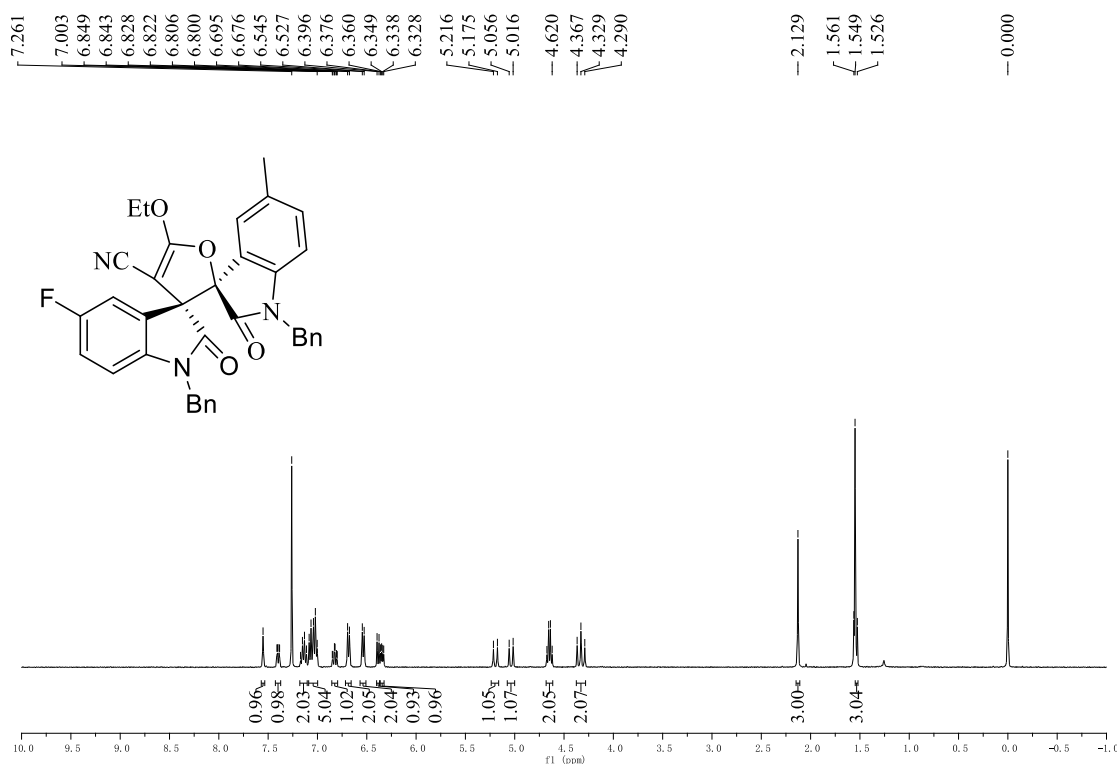
***rel*-(3*R*,3'*R*)-1''-Butyl-5''-chloro-5'-ethoxy-5-methyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8g)**: white solid, 73%, m.p. 189-191 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (s, 1H, NH), 7.50 (d, *J* = 6.8 Hz, 2H, ArH), 7.18 (d, *J* = 7.6 Hz, 1H, ArH), 7.08 (d, *J* = 6.8 Hz, 1H, ArH), 6.66-6.58 (m, 2H, ArH), 4.59-4.57 (m, 2H, CH₂), 3.80-3.73 (m, 1H, CH₂), 3.26-3.19 (m, 1H, CH₂), 2.30 (s, 3H, CH₃), 1.49 (t, *J* = 6.4 Hz, 3H, CH₃), 1.31-1.25 (m, 2H, CH₂), 1.00-0.97 (m, 2H, CH₂), 0.80 (t, *J* = 6.4 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 173.6, 173.1, 172.7, 142.8, 138.9, 132.9, 132.3, 130.4, 128.8, 128.5, 127.1, 123.8, 120.6, 114.2, 110.4, 109.5, 89.0, 69.0, 62.1, 60.0, 40.2, 29.4, 21.0, 19.8, 14.7, 13.7. IR (KBr) ν: 3236, 3072, 2968, 2935, 2864, 2208, 1748, 1719, 1643, 1606, 1487, 1411, 1382, 1347, 1301, 1266, 1244, 1208, 1188, 1166, 1150, 1106, 1075, 1045, 1000, 951, 923, 900, 879, 844, 814, 794, 715 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₂₆H₂₄NaClN₃O₄ ([M+Na]⁺): 500.1353, found: 500.1357.



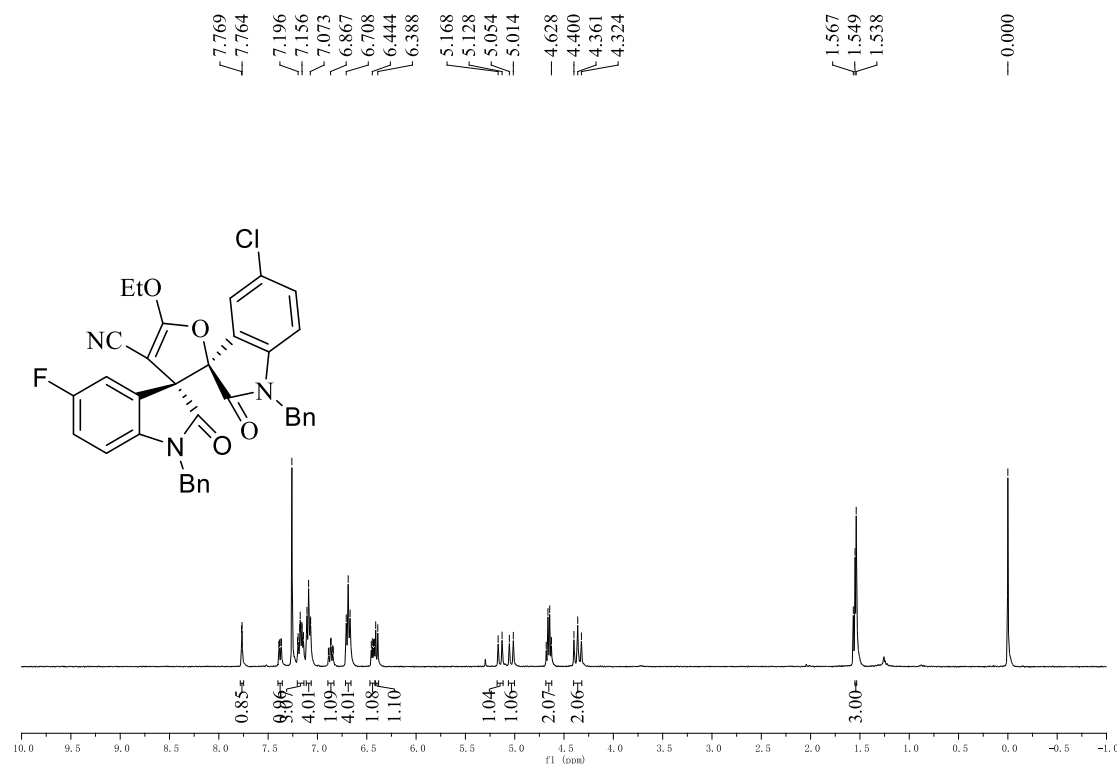


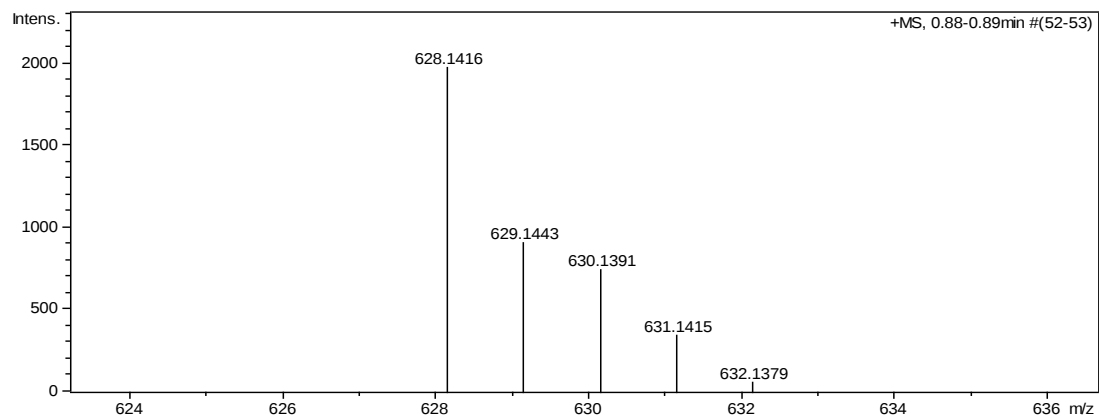
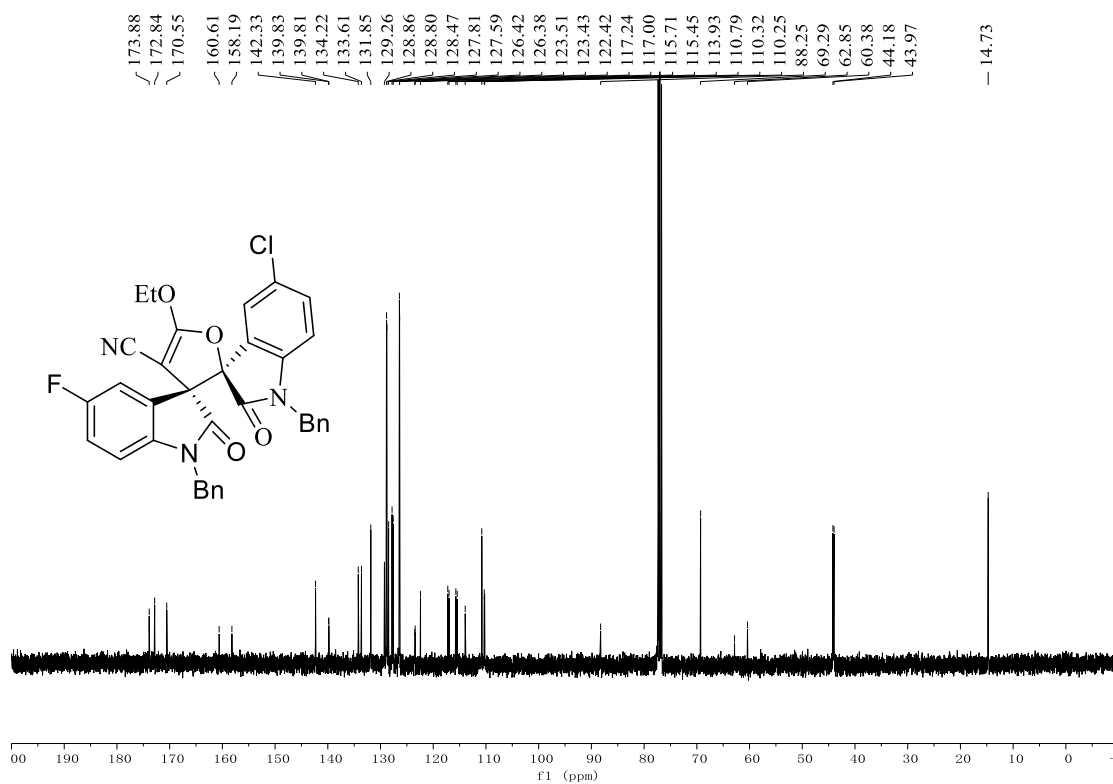
***rel*-(3*R*,3'*R*)-1,1''-Dibenzyl-5'-ethoxy-5''-fluoro-5-methyl-2,2''-dioxodispiro[indoline-3,2'-**

furan-3',3''-indoline]-4'-carbonitrile (8h): white solid, 69%, m.p. 158-160 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.55 (s, 1H, ArH), 7.40 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 7.17-7.11 (m, 2H, ArH), 7.08-7.00 (m, 5H, ArH), 6.85-6.80 (m, 1H, ArH), 6.69 (d, *J* = 7.6 Hz, 2H, ArH), 6.54 (d, *J* = 7.2 Hz, 2H, ArH), 6.39 (d, *J* = 8.0 Hz, 1H, ArH), 6.36-6.33 (m, 1H, ArH), 5.20 (d, *J* = 16.4 Hz, 1H, CH₂), 5.04 (d, *J* = 16.0 Hz, 1H, CH₂), 4.65 (q, *J* = 7.2 Hz, 2H, CH₂), 4.33 (t, *J* = 15.6 Hz, 2H, CH₂), 2.13 (s, 3H, CH₃), 1.55 (t, *J* = 9.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 174.2, 173.1, 170.9, 159.4 (d, *J* = 242.0 Hz), 141.4, 139.8, 134.3, 134.2, 133.6, 132.2, 128.7, 128.6, 127.5, 127.3, 126.4, 126.1, 123.9 (d, *J* = 9.0 Hz), 120.8, 116.9 (d, *J* = 23.0 Hz), 115.6 (d, *J* = 26.0 Hz), 114.3, 110.1 (d, *J* = 8.0 Hz), 109.6, 89.0, 69.0, 63.0, 60.2, 44.0, 43.8, 20.9, 14.7. IR (KBr) ν: 3064, 3033, 2989, 2918, 2208, 1723, 1633, 1491, 1453, 1411, 1378, 1337, 1281, 1261, 1224, 1167, 1131, 1079, 1027, 996, 965, 928, 888, 846, 819.63, 773, 732, 702 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₆H₂₈NaFN₃O₄ ([M+Na]⁺): 608.1962, found: 608.1960.

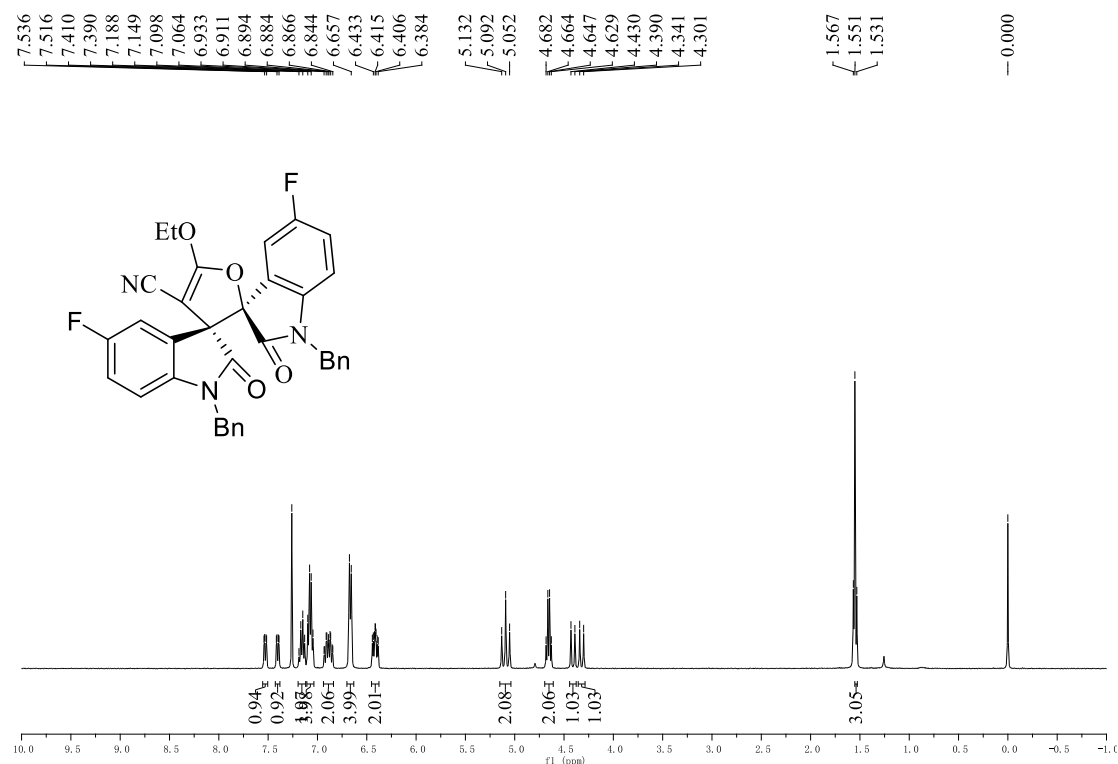


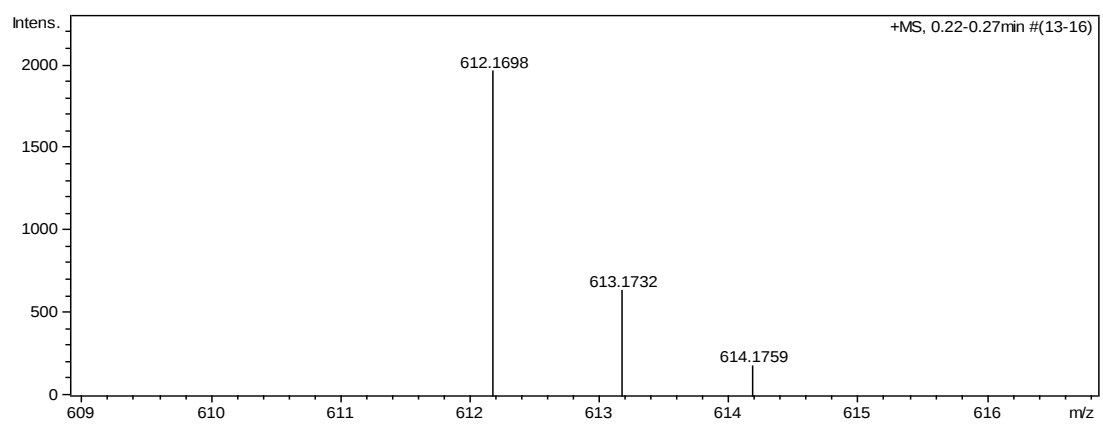
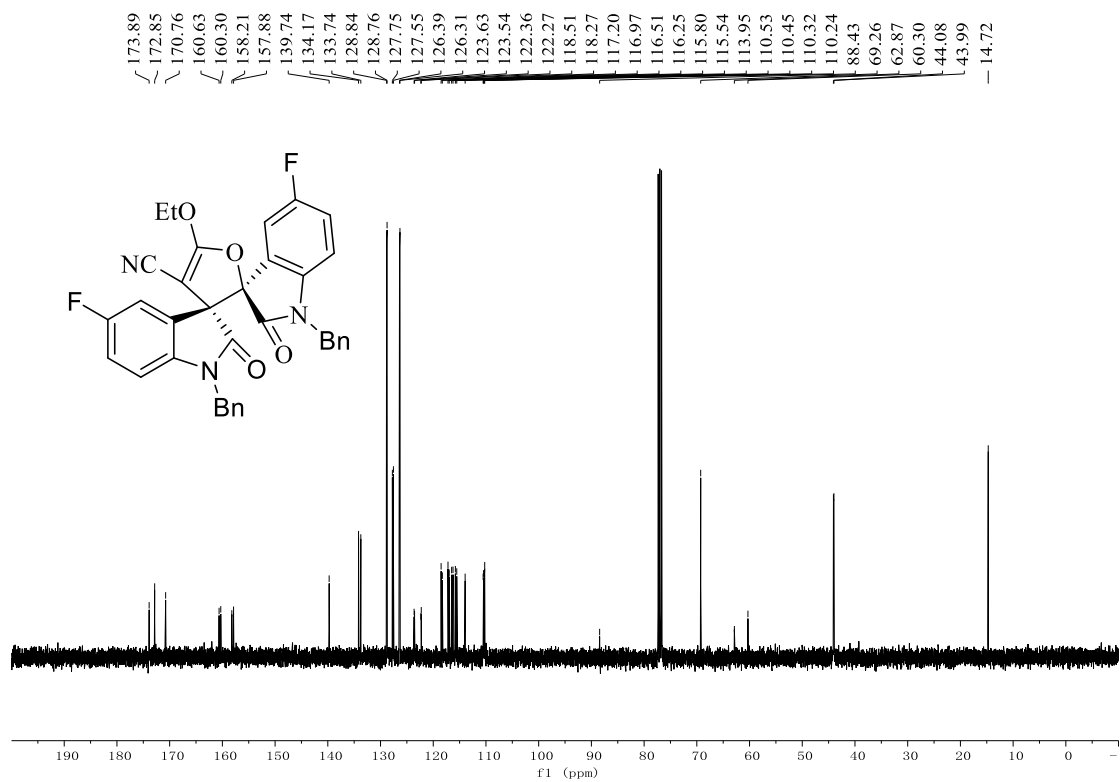
***rel*-(3*R*,3'*R*)-1,1''-Dibenzyl-5-chloro-5'-ethoxy-5''-fluoro-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8i)**: white solid, 47%, m.p. 150-152 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 2.0 Hz, 1H, ArH), 7.38 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 7.18-7.14 (m, 3H, ArH), 7.11-7.07 (m, 4H, ArH), 6.89-6.84 (m, 1H, ArH), 6.69 (t, *J* = 7.6 Hz, 4H, ArH), 6.45-6.42 (m, 1H, ArH), 6.40 (d, *J* = 8.8 Hz, 1H, ArH), 5.15 (d, *J* = 16.0 Hz, 1H, CH₂), 5.03 (d, *J* = 16.0 Hz, 1H, CH₂), 4.65 (q, *J* = 7.2 Hz, 2H, CH₂), 4.36 (t, *J* = 15.6 Hz, 2H, CH₂), 1.54 (t, *J* = 4.4 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 172.8, 170.6, 160.6, 158.2, 141.1 (d, *J* = 250.0 Hz), 139.8, 134.2, 133.6, 131.7, 129.3, 128.8, 128.5, 127.8, 127.6, 126.4, 126.3, 123.5 (d, *J* = 8.0 Hz), 122.4, 117.1 (d, *J* = 24.0 Hz), 115.6 (d, *J* = 26.0 Hz), 113.9, 110.8, 110.3 (d, *J* = 7.0 Hz), 88.3, 69.3, 62.9, 60.4, 44.2, 44.0, 14.7. IR (KBr) ν: 3082, 3032, 2980, 2936, 2361, 2206, 1885, 1724, 1637, 1612, 1487, 1452, 1437, 1408, 1379, 1334, 1263, 1222, 1178, 1130, 1078, 1029, 994, 963, 922, 902, 881, 841, 817, 746 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₅H₂₅NaClFN₃O₄ ([M+Na]⁺): 628.1415, found: 628.1416.



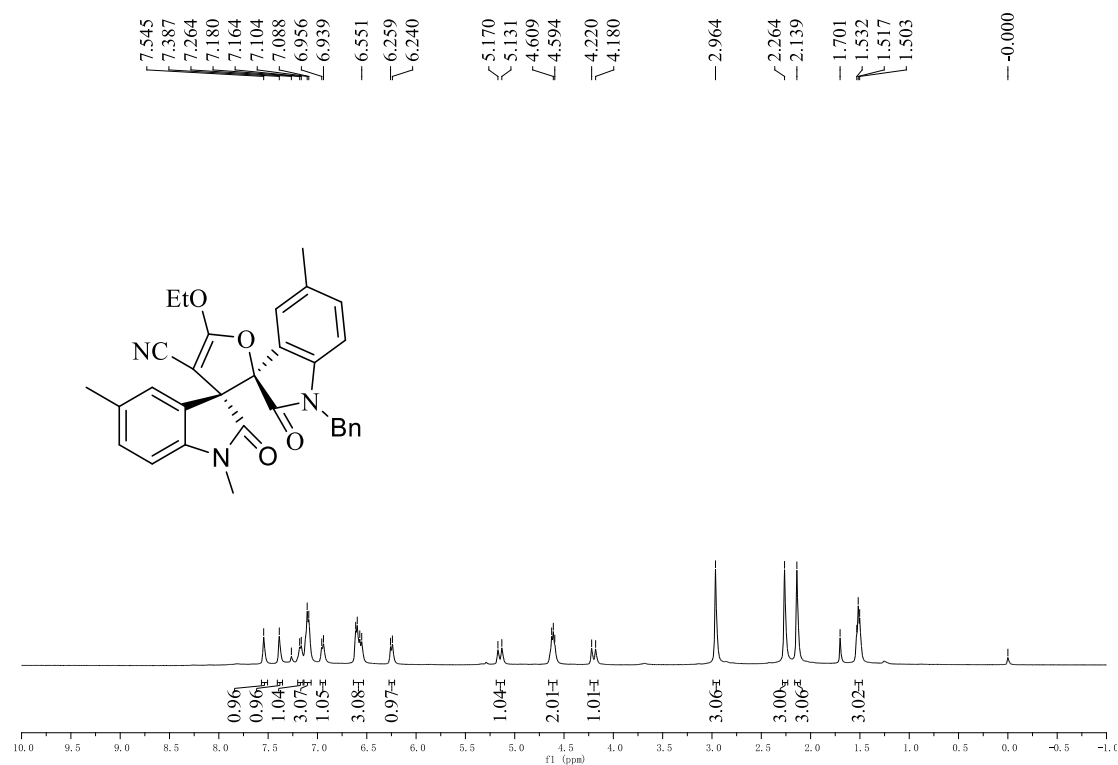


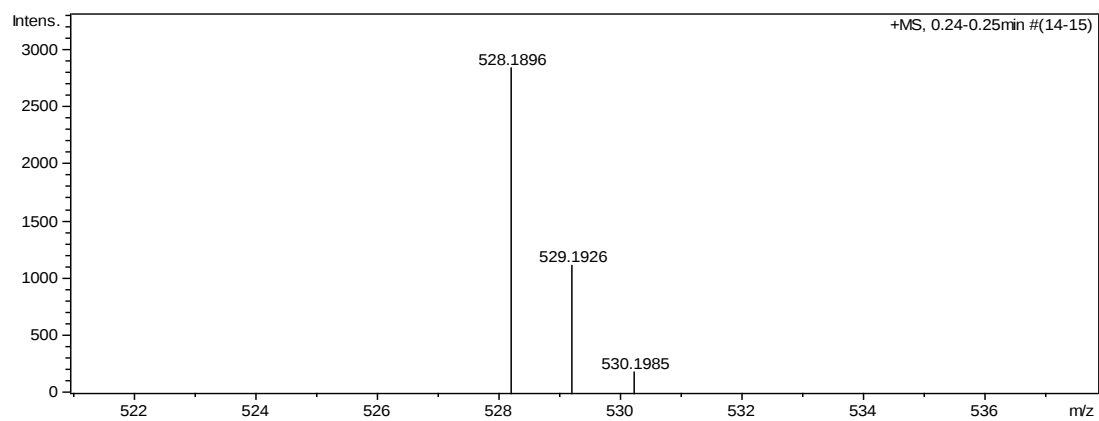
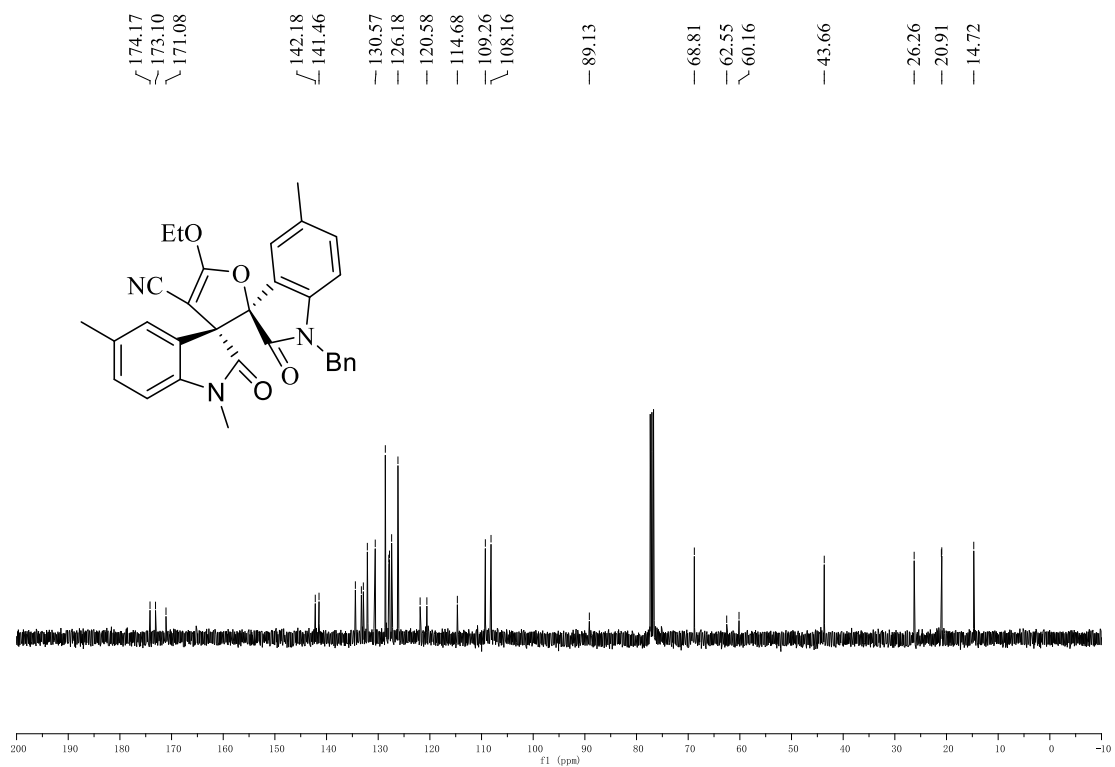
***rel*-(3*R*,3'*R*)-1,1''-Dibenzyl-5'-ethoxy-5,5''-difluoro-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8j)**: white solid, 35%, m.p. 168-170 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.4 Hz, 1H, ArH), 7.40 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.8 Hz, 1H, ArH), 7.19-7.13 (m, 2H, ArH), 7.10-7.05 (m, 4H, ArH), 6.93-6.84 (m, 2H, ArH), 6.67 (d, *J* = 7.6 Hz, 4H, ArH), 6.44-6.38 (m, 2H, ArH), 5.09 (t, *J* = 16.0 Hz, 2H, CH₂), 4.65 (q, *J* = 6.8 Hz, 2H, CH₂), 4.41 (d, *J* = 16.0 Hz, 1H, CH₂), 4.32 (d, *J* = 16.0 Hz, 1H, CH₂), 1.55 (t, *J* = 8.0 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 172.9, 170.8, 159.4 (d, *J* = 242.0 Hz), 159.1 (d, *J* = 242.0 Hz), 139.7, 134.2, 133.7, 128.8, 128.7, 127.8, 127.6, 126.4, 126.3, 123.6 (d, *J* = 9.0 Hz), 122.4 (d, *J* = 9.0 Hz), 118.4 (d, *J* = 24.0 Hz), 117.1 (d, *J* = 23.0 Hz), 116.4 (d, *J* = 26.0 Hz), 115.7 (d, *J* = 26.0 Hz), 114.0, 110.5 (d, *J* = 8.0 Hz), 110.3 (d, *J* = 8.0 Hz), 88.4, 69.3, 62.9, 60.3, 44.1, 44.0, 14.7. IR (KBr) ν: 3085, 3035, 2980, 2942, 2361, 2206, 1887, 1723, 1638, 1490, 1452, 1410, 1382, 1336, 1272, 1222, 1176, 1131, 1077, 1029, 997, 964, 930, 882, 846, 814, 776, 738, 701 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₅H₂₅NaF₂N₃O₄ ([M+Na]⁺): 612.1711, found: 612.1698.



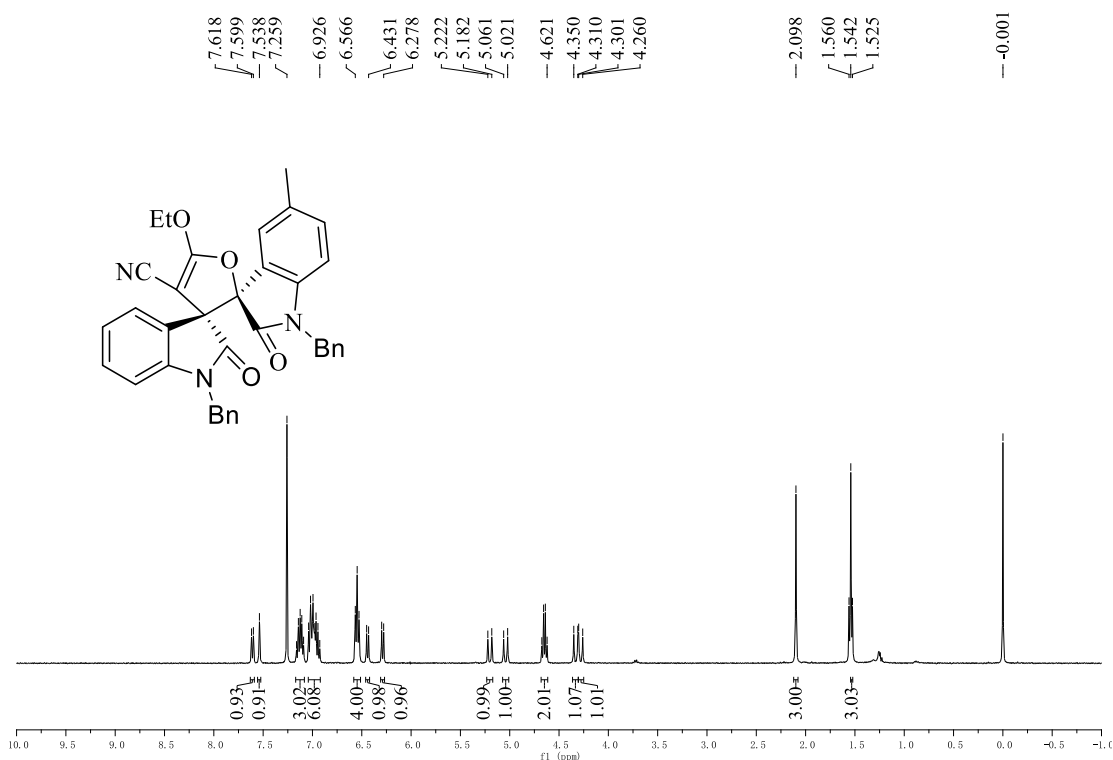


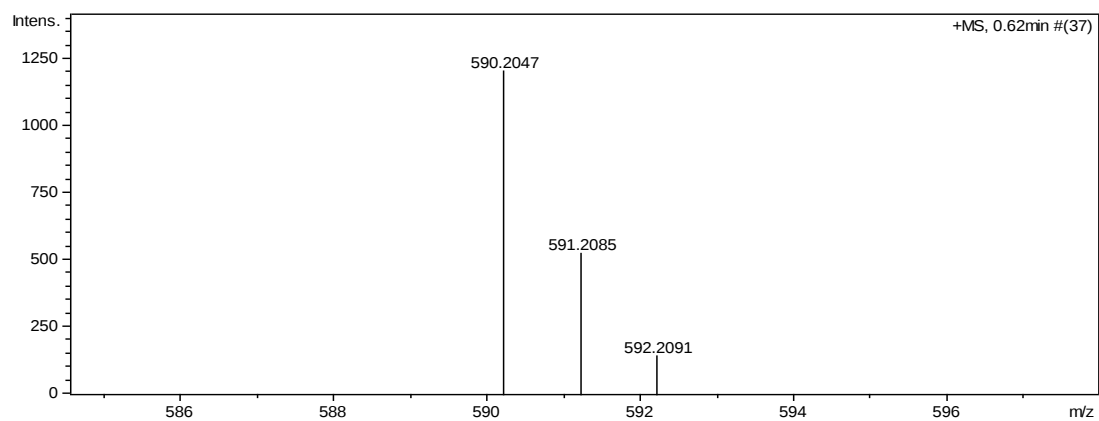
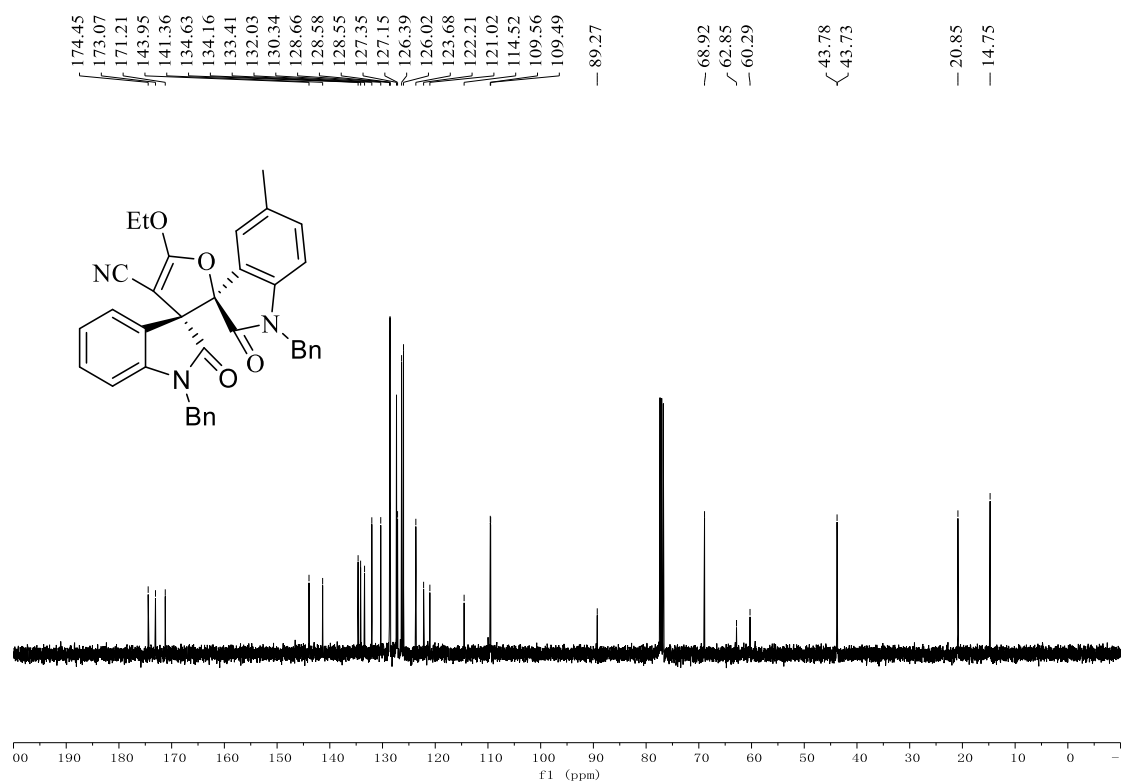
***rel*-(3*R*,3'*R*)-1-Benzyl-5'-ethoxy-1'',5,5''-trimethyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8k)**: white solid, 77%, m.p. 173-175 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.55 (s, 1H, ArH), 7.39 (s, 1H, ArH), 7.20-7.16 (m, 1H, ArH), 7.11 (t, *J* = 7.6 Hz, 3H, ArH), 6.95 (d, *J* = 8.0 Hz, 1H, ArH), 6.61 (d, *J* = 7.6 Hz, 2H, ArH), 6.56 (d, *J* = 8.0 Hz, 1H, ArH), 6.25 (d, *J* = 8.0 Hz, 1H, ArH), 5.15 (d, *J* = 16.0 Hz, 1H, CH₂), 4.63 (q, *J* = 7.2 Hz, 2H, CH₂), 4.20 (d, *J* = 16.4 Hz, 1H, CH₂), 2.97 (s, 3H, CH₃), 2.27 (s, 3H, CH₃), 2.14 (s, 3H, CH₃), 1.53 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 174.2, 173.1, 171.1, 142.2, 141.5, 134.4, 133.3, 132.9, 132.1, 130.6, 128.6, 128.0, 127.8, 127.4, 126.2, 121.9, 120.6, 114.7, 109.3, 108.2, 89.1, 68.8, 62.6, 60.2, 43.7, 26.3, 21.0, 20.9, 14.7. IR (KBr) ν: 3467, 3063, 3035, 2990, 2919, 2205, 1739, 1706, 1632, 1602, 1496, 1454, 1434, 1408, 1381, 1361, 1333, 1293, 1258, 1215, 1199, 1186, 1167, 1133, 1089, 1070, 1026, 997, 962, 933, 911, 895, 875, 836, 818, 776, 747 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₁H₂₇NaN₃O₄ ([M+Na]⁺): 528.1899, found: 528.1896.





***rel*-(3*R*,3'*R*)-1,1''-Dibenzyl-5'-ethoxy-5-methyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8l)**: white solid, 83%, m.p. 141-143 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 7.6$ Hz, 1H, ArH), 7.54 (s, 1H, ArH), 7.16-7.09 (m, 3H, ArH), 7.04-6.93 (m, 6H, ArH), 6.55 (d, $J = 7.6$ Hz, 4H, ArH), 6.44 (d, $J = 8.0$ Hz, 1H, ArH), 6.29 (d, $J = 8.0$ Hz, 1H, ArH), 5.20 (d, $J = 16.0$ Hz, 1H, CH_2), 5.04 (d, $J = 16.0$ Hz, 1H, CH_2), 4.65 (q, $J = 6.8$ Hz, 2H, CH_2), 4.33 (d, $J = 16.0$ Hz, 1H, CH_2), 4.28 (d, $J = 16.4$ Hz, 1H, CH_2), 2.10 (s, 3H, CH_3) 1.54 (t, $J = 6.8$ Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ 174.5, 173.1, 171.2, 144.0, 141.4, 134.6, 134.2, 133.4, 132.0, 130.3, 128.7, 128.6, 128.5, 127.4, 127.2, 126.4, 126.0, 123.7, 122.2, 121.0, 114.5, 109.6, 109.5, 89.3, 68.9, 62.9, 60.3, 43.8, 43.7, 20.9, 14.8. IR (KBr) ν : 3675, 3032, 2984, 2920, 2859, 2361, 2206, 1724, 1637, 1496, 1467, 1438, 1408, 1376, 1335, 1214, 1166, 1094, 1077, 1053, 1029, 994, 927, 902, 874, 848, 816, 779, 760, 737, 700 cm^{-1} ; MS (m/z): HRMS (ESI) Calcd. for $\text{C}_{36}\text{H}_{29}\text{NaN}_3\text{O}_4$ ($[\text{M}+\text{Na}]^+$): 590.2056, found: 590.2047.





***rel*-(3*R*,3'*R*)-1''-Benzyl-5'-ethoxy-1,5-dimethyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8m)**: white solid, 62%, m.p. 174-175 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 7.6 Hz, 1H, ArH), 7.53 (s, 1H, ArH), 7.19-7.15 (m, 2H, ArH), 7.11-7.08 (m, 3H, ArH), 7.00 (t, *J* = 8.0 Hz, 1H, ArH), 6.62 (d, *J* = 7.2 Hz, 2H, ArH), 6.55 (d, *J* = 8.0 Hz, 1H, ArH), 6.40 (d, *J* = 7.6 Hz, 1H, ArH), 5.21 (d, *J* = 16.0 Hz, 1H, CH₂), 4.62 (q, *J* = 6.8 Hz, 2H, CH₂), 4.32 (d, *J* = 16.0 Hz, 1H, CH₂), 2.92 (s, 3H, CH₃), 2.15 (s, 3H, CH₃), 1.52 (t, *J* = 7.2 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 173.2, 171.2, 143.7, 142.1, 134.8, 133.4, 132.0, 130.3, 128.6, 128.4, 127.3, 126.7, 126.2, 123.2, 121.8, 120.9, 115.5, 109.4, 108.4, 89.1, 68.9, 62.5, 60.6, 43.8, 26.1, 20.9, 14.7. IR (KBr) ν: 3057, 3029, 2987, 2964, 2927, 2360, 2204, 1955, 1731, 1650, 1609, 1499, 1465, 1410, 1380, 1343, 1293, 1242, 1214, 1179, 1136, 1097, 1063, 1006, 937, 906, 858, 815, 755, 739 cm⁻¹; MS (*m/z*): HRMS (ESI) Calcd. for C₃₀H₂₅NaN₃O₄ ([M+Na]⁺): 514.1743, found: 514.1744.

