

Supporting Information for

**A Catalytic Asymmetric Isatin-involved Povarov Reaction:
Diastereo- and Enantioselective Construction of
Spiro[indolin-3,2'-quinoline] Scaffold**

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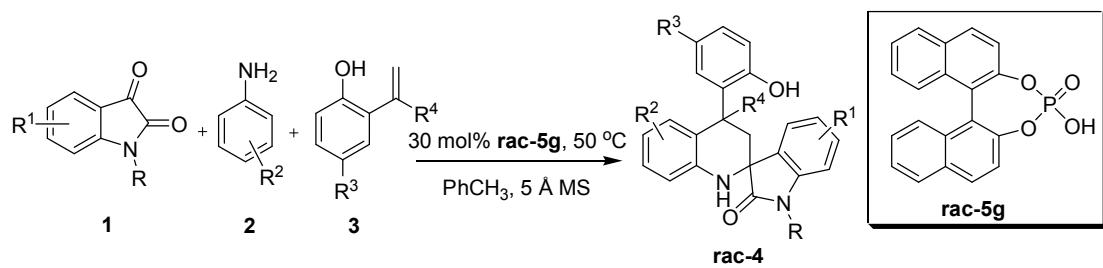
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General information: NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was CDCl_3 , using tetramethylsilane as the internal reference. HRMS spectra were recorded on a LTQ-Orbitrap mass spectrometer (ionization mode: ESI $^+$). Enantiomeric excesses (*ee*) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of enantiomeric excesses by chiral HPLC were Chiraldak IC and IA columns. Optical rotation values were measured with instruments operating at $\lambda = 589$ nm, corresponding to the sodium D line at the temperatures indicated. The relative and absolute configurations of **4had** were assigned by the X-ray analysis.

Analytical grade solvents for the column chromatography and commercially available reagents were used as received. Toluene was dried over Na and distilled prior to use. All starting materials commercially available were used directly. Substrates **1a-1d**, **1f-1p** and **3a-3d** were synthesized according to the literature methods.¹ Catalysts **5a-5f** were prepared according to previously described procedures.²

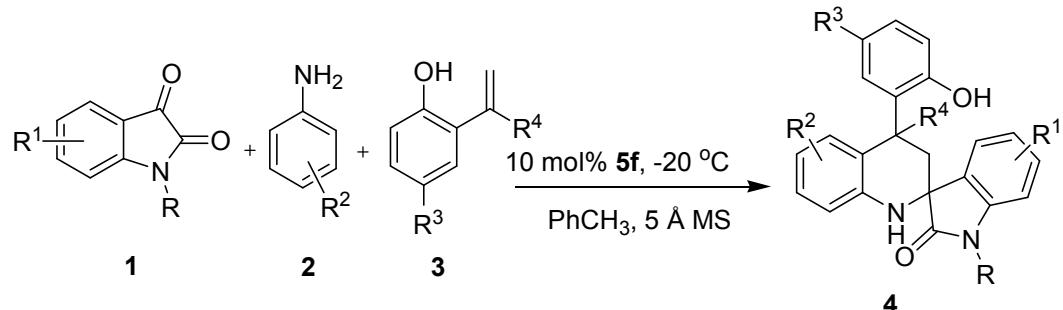
General procedure for the preparation of racemic products:



After a solution of isatin **1** (0.12 mmol), anilines **2** (0.1 mmol), the catalyst **rac-5g** (0.03 mmol), and 5 \AA molecular sieves (100 mg) in toluene (0.5 mL) was stirred at room temperature for 20 mins, the solution of styrenes **3** (0.36 mmol) in toluene (0.5 mL) was added. After being stirred at 50 °C for 48 h, the reaction mixture was filtered to remove molecular sieves and the solid powder was washed with ethyl acetate. The resultant solution was concentrated under the reduced pressure to give the residue,

which was purified through flash column chromatography on silica gel to afford pure products.

General procedure for the asymmetric isatin-involved Povarov reaction:



After a solution of isatin **1** (0.12 mmol), anilines **2** (0.1 mmol), the catalyst **5f** (0.01 mmol), and 5Å molecular sieves (100 mg) in toluene (0.5 mL) was stirred at room temperature for 20 mins then cooled to -20 °C, the solution of styrenes **3** (0.36 mmol) in toluene (0.5 mL) was added. After being stirred at -20 °C for 84 h, the reaction mixture was filtered to remove molecular sieves and the solid powder was washed with ethyl acetate. The resultant solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography on silica gel to afford pure products. In some cases as indicated in Table 2-3, the reaction temperature was increased to 50 °C and carbon tetrachloride was utilized as solvent.

1-benzyl-4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4aaa): dr > 99:1; yield: 99%; colorless sticky oil; $[\alpha]_D^{20} = -298.8$ (c 0.6, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.33-7.26 (m, 6H), 7.13-7.11 (m, 2H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.89 (td, *J* = 7.6, 1.0 Hz, 2H), 6.76 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.62 (dd, *J* = 5.4, 2.6 Hz, 2H), 5.78 (s, 1H), 4.98 (d, *J* = 15.5 Hz, 1H), 4.64 (d, *J* = 15.5 Hz, 1H), 4.05 (s, 1H), 3.66 (s, 3H), 2.96 (d, *J* = 14.8 Hz, 1H), 2.10 (d, *J* = 14.7 Hz, 1H), 1.98 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 179.0, 154.0, 153.7, 141.8, 135.9, 135.4, 135.1, 132.2, 129.2, 128.8, 128.2, 127.7, 127.4, 127.2, 124.3, 122.9, 120.4, 117.9, 116.2, 113.9, 113.7, 108.9, 60.5, 55.6, 44.9, 43.7, 39.6, 29.1; IR (KBr): γ 3375, 3059, 3031, 2928, 2854, 1702, 1609, 1498, 1463, 1444, 1356, 1293, 1261, 1217, 1173, 1125,

934, 904, 852, 809, 751, 698; ESI FTMS exact mass calcd for ($C_{31}H_{28}N_2O_3+H$)⁺ requires m/z 477.2178, found m/z 477.2174; Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.234 min (minor), t_R = 20.164 min (major).

1-(4-tert-butylbenzyl)-4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4baa): dr > 99:1; yield: 90%; colorless sticky oil; [α]_D²⁰ = -262.5 (c 0.7, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.34-7.31 (m, 3H), 7.24-7.21 (m, 2H), 7.13 (tdd, *J* = 7.8, 3.7, 1.5 Hz, 2H), 6.95 (d, *J* = 7.1 Hz, 1H), 6.88 (m, 2H), 6.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.70 (dd, *J* = 8.7, 2.8 Hz, 2H), 6.62 (m, 2H), 5.82 (s, 1H), 4.95 (d, *J* = 15.4 Hz, 1H), 4.61 (d, *J* = 15.4 Hz, 1H), 4.05 (s, 1H), 3.66 (s, 3H), 2.96 (d, *J* = 14.8 Hz, 1H), 2.10 (d, *J* = 14.7 Hz, 1H), 1.98 (s, 3H), 1.29 (s, 9H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 178.9, 154.0, 153.7, 150.6, 142.0, 135.5, 132.9, 129.2, 128.1, 127.2, 127.1, 125.7, 124.2, 122.9, 120.3, 117.9, 116.2, 113.9, 113.7, 109.0, 60.5, 55.6, 44.9, 43.4, 39.5, 34.5, 31.3, 29.1; IR (KBr): γ 3381, 3092, 3057, 2961, 2868, 1699, 1644, 1609, 1499, 1464, 1443, 1364, 1293, 1263, 1217, 1172, 1105, 1043, 933, 807, 751; ESI FTMS exact mass calcd for ($C_{35}H_{36}N_2O_3+H$)⁺ requires m/z 533.2804, found m/z 533.2799; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.913 min (minor), t_R = 14.122 min (major).

4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-1-(perfluorobenzyl)-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4caa): dr > 99:1; total yield: 99%; colorless sticky oil; [α]_D²⁰ = -234.9 (c 0.9, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.33 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.20 (td, *J* = 7.7, 1.2 Hz, 1H), 7.14 (td, *J* = 7.9, 1.5 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.88 (td, *J* = 7.8, 1.1 Hz, 1H), 6.76 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.72-6.67 (m, 2H), 6.62-6.59 (m, 2H), 5.73 (s, 1H), 5.14 (d, *J* = 15.4 Hz, 1H), 4.73 (d, *J* = 15.5 Hz, 1H), 4.04 (s, 1H), 3.66 (s, 3H), 2.91 (d, *J* = 14.8 Hz, 1H), 2.03 (d, *J* = 14.8 Hz, 1H), 1.95 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ

(ppm): 178.3, 153.9, 153.8, 140.7, 135.2, 135.1, 132.1, 129.4, 128.8, 128.2, 127.2, 124.6, 123.4, 120.4, 117.9, 116.2, 113.9, 113.7, 107.7, 60.3, 55.6, 44.8, 39.5, 32.0, 29.0; IR (KBr): γ 3384, 3059, 3030, 2926, 2853, 1713, 1649, 1609, 1502, 1465, 1446, 1352, 1218, 1124, 1041, 1002, 808, 752; ESI FTMS exact mass calcd for ($C_{31}H_{23}F_5N_2O_3+H$)⁺ requires m/z 567.1707, found m/z 567.1709; Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.455 min (minor), t_R = 7.990 min (major).

4'-(2-hydroxyphenyl)-1-isopropyl-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4daa): dr > 99:1; total yield: 41%; colorless sticky oil; $[\alpha]_D^{20} = -398.5$ (c 0.1, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.32 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.21 (td, *J* = 7.8, 1.4 Hz, 1H), 7.14 (td, *J* = 7.9, 1.6 Hz, 1H), 7.00 (d, *J* = 7.1 Hz, 1H), 6.94-6.86 (m, 3H), 6.77 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.62-6.59 (m, 2H), 5.78 (s, 1H), 4.57-4.47 (m, 1H), 4.00 (s, 1H), 3.66 (s, 3H), 2.88 (d, *J* = 14.8 Hz, 1H), 2.02 (d, *J* = 14.6 Hz, 1H), 1.94 (s, 3H), 1.46 (dd, *J* = 7.0, 4.0 Hz, 6H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 178.6, 154.0, 153.7, 141.4, 135.6, 135.3, 132.6, 129.0, 128.8, 128.1, 127.1, 124.4, 122.3, 120.3, 117.9, 116.1, 113.8, 113.7, 109.5, 60.2, 55.6, 45.1, 43.8, 39.4, 29.1, 19.5, 19.1; IR (KBr): γ 3360, 3056, 2974, 2932, 2854, 1694, 1606, 1500, 1484, 1444, 1355, 1263, 1225, 1154, 1128, 1094, 1044, 809, 753, 700; ESI FTMS exact mass calcd for ($C_{27}H_{28}N_2O_3+H$)⁺ requires m/z 429.2178, found m/z 429.2172; Enantiomeric excess: 88%, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 4.895 min (minor), t_R = 6.528 min (major).

4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-1-phenyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4eaa): dr > 99:1; yield: 31%; colorless sticky oil; $[\alpha]_D^{20} = -245.2$ (c 0.2, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.51-7.48 (m, 2H), 7.43-7.34 (m, 4H), 7.21-7.15 (m, 2H), 7.08 (d, *J* = 7.3 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.93-6.89 (m, 1H), 6.82-6.79 (m, 2H), 6.71 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.65 (d, *J* =

8.6 Hz, 1H), 6.61 (d, J = 2.7 Hz, 1H), 5.78 (s, 1H), 4.17 (s, 1H), 3.67 (s, 3H), 3.02 (d, J = 14.8 Hz, 1H), 2.21 (d, J = 14.8 Hz, 1H), 1.97 (s, 3H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 178.0, 154.0, 153.8, 142.5, 135.2, 134.3, 131.9, 129.5, 129.2, 128.8, 128.2, 127.9, 127.1, 126.3, 124.6, 123.4, 120.4, 117.9, 116.2, 113.9, 113.7, 109.3, 60.5, 55.6, 45.1, 39.5, 29.2; IR (KBr): γ 3378, 3060, 2924, 2853, 1708, 1607, 1499, 1462, 1445, 1369, 1329, 1293, 1262, 1221, 1102, 1043, 807, 754, 698; ESI FTMS exact mass calcd for $(\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}_3+\text{H})^+$ requires m/z 463.2022, found m/z 463.2011; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak IA, hexane/isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.69 min (minor), t_R = 8.55 min (major).

1-benzyl-5-chloro-4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4faa): dr > 99:1; yield: 65%; colorless sticky oil; $[\alpha]_D^{20} = -171.8$ (c 0.2, CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 7.34-7.29 (m, 2H), 7.27-7.24 (m, 3H), 7.18 (td, J = 7.9, 1.6 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 7.04 (dd, J = 8.3, 2.1 Hz, 1H), 6.90-6.86 (m, 1H), 6.76-6.72 (m, 3H), 6.64 (d, J = 8.4 Hz, 1H), 6.55 (d, J = 8.3 Hz, 1H), 6.43 (s, 1H), 5.32 (s, 1H), 4.99 (d, J = 15.6 Hz, 1H), 4.64 (d, J = 15.6 Hz, 1H), 3.96 (s, 1H), 3.71 (s, 3H), 3.04 (d, J = 14.4 Hz, 1H), 2.13 (d, J = 14.4 Hz, 1H), 1.95 (s, 3H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 179.3, 154.2, 153.6, 140.2, 135.6, 135.4, 134.3, 133.7, 129.1, 128.9, 128.8, 128.5, 128.2, 128.0, 127.8, 127.2, 125.2, 120.7, 117.6, 116.0, 113.8, 113.5, 109.8, 61.3, 55.7, 53.4, 43.9, 40.0, 28.2; IR (KBr): γ 3412, 3069, 3031, 2961, 2924, 2853, 1709, 1698, 1645, 1607, 1478, 1447, 1440, 1340, 1297, 1258, 1216, 1157, 1116, 1078, 1044, 808, 736, 698; ESI FTMS exact mass calcd for $(\text{C}_{31}\text{H}_{27}\text{ClN}_2\text{O}_3+\text{H})^+$ requires m/z 511.1788, found m/z 511.1783; Enantiomeric excess: 81%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.237 min (minor), t_R = 10.316 min (major).

1-benzyl-6-fluoro-4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4gaa): dr > 99:1; yield: 76%; colorless sticky

oil; $[\alpha]_D^{20} = -240.5$ (c 0.4, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.29-7.16 (m, 6H), 7.07 (td, *J* = 7.8, 1.5 Hz, 1H), 6.81 (td, *J* = 7.7, 1.2 Hz, 1H), 6.68-6.63 (m, 3H), 6.58-6.55 (m, 2H), 6.45 (td, *J* = 9.5, 2.3 Hz, 1H), 6.32 (dd, *J* = 8.8, 2.2 Hz, 1H), 5.54 (s, 1H), 4.89 (d, *J* = 15.6 Hz, 1H), 4.55 (d, *J* = 15.6 Hz, 1H), 3.92 (s, 1H), 3.61 (s, 3H), 2.90 (d, *J* = 14.6 Hz, 1H), 2.03 (d, *J* = 14.6 Hz, 1H), 1.89 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 178.3, 162.4 (*J* = 245 Hz), 153.0, 152.7, 142.4, 142.3, 134.3, 133.7, 127.9, 127.2, 126.9, 126.6, 126.4, 126.3, 124.7, 124.6, 119.5, 116.8, 115.1, 112.9, 112.7, 108.0, 107.8, 96.8, 96.5, 59.3, 54.6, 43.7, 42.9, 38.6, 27.8; IR (KBr): γ 3364, 3060, 3031, 2960, 2925, 2854, 1710, 1612, 1497, 1448, 1376, 1344, 1292, 1260, 1218, 1156, 1102, 1039, 937, 904, 833, 806, 737, 699; ESI FTMS exact mass calcd for (C₃₁H₂₇FN₂O₃+H)⁺ requires m/z 495.2084, found m/z 495.2070; Enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.067 min (minor), t_R = 8.975 min (major).

1-benzyl-6-chloro-4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4haa): dr > 99:1; yield: 95%; colorless sticky oil; $[\alpha]_D^{20} = -241.1$ (c 0.7, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.28-7.24 (m, 2H), 7.22-7.17 (m, 3H), 7.09-7.03 (m, 2H), 6.79 (td, *J* = 7.7, 1.1 Hz, 1H), 6.70 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.66-6.61 (m, 2H), 6.60 (d, *J* = 2.7 Hz, 1H), 6.57-6.53 (m, 2H), 6.46 (d, *J* = 7.6 Hz, 1H), 5.55 (s, 1H), 4.88 (d, *J* = 15.6 Hz, 1H), 4.50 (d, *J* = 15.6 Hz, 1H), 3.91 (s, 1H), 3.61 (s, 3H), 2.92 (d, *J* = 14.5 Hz, 1H), 2.02 (d, *J* = 14.5 Hz, 1H), 1.86 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 178.2, 153.0, 152.6, 142.0, 134.4, 134.3, 133.7, 133.3, 129.8, 128.0, 127.9, 127.2, 126.9, 126.7, 126.2, 124.5, 121.6, 119.5, 116.7, 115.0, 112.8, 112.6, 108.4, 59.5, 54.6, 43.4, 42.8, 38.8, 27.5; IR (KBr): γ 3363, 3061, 3029, 2961, 2925, 2853, 1708, 1606, 1500, 1440, 1371, 1339, 1261, 1216, 1107, 1076, 1040, 929, 905, 839, 803, 755, 699; ESI FTMS exact mass calcd for (C₃₁H₂₇ClN₂O₃+H)⁺ requires m/z 511.1788, found m/z 511.1784; Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20,

flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.466 min (minor), t_R = 10.821 min (major).

1-benzyl-6-bromo-4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4iaa): dr > 99:1; yield: 99%; colorless sticky oil; [α]_D²⁰ = -220.2 (c 0.9, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.35-7.24 (m, 5H), 7.16-7.11 (m, 2H), 6.94 (dd, J = 8.0, 1.6 Hz, 1H), 6.86 (td, J = 7.6, 1.2 Hz, 1H), 6.79 (d, J = 1.6 Hz, 1H), 6.73-6.67 (m, 3H), 6.62 (d, J = 8.6 Hz, 1H), 6.46 (d, J = 7.6 Hz, 1H), 5.59 (s, 1H), 4.95 (d, J = 15.6 Hz, 1H), 4.56 (d, J = 15.6 Hz, 1H), 3.98 (s, 1H), 3.68 (s, 3H), 2.99 (d, J = 14.5 Hz, 1H), 2.10 (d, J = 14.5 Hz, 1H), 1.93 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 179.3, 154.2, 153.6, 143.1, 135.5, 135.3, 134.2, 131.5, 129.1, 129.0, 128.2, 127.9, 127.8, 127.3, 126.0, 125.6, 122.5, 120.6, 117.7, 116.1, 113.8, 113.6, 112.1, 60.7, 55.6, 44.2, 43.8, 39.9, 28.4; IR (KBr): γ 3390, 3064, 3031, 2969, 2925, 2854, 1710, 1602, 1498, 1443, 1370, 1293, 1265, 1216, 1111, 1043, 928, 903, 843, 812, 737, 698; ESI FTMS exact mass calcd for (C₃₁H₂₇BrN₂O₃+H)⁺ requires m/z 555.1283, found m/z 555.1282; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.580 min (minor), t_R = 11.024 min (major).

1-benzyl-4'-(2-hydroxyphenyl)-6'-methoxy-4',6-dimethyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4jaa): dr > 99:1; yield: 99%; colorless sticky oil; [α]_D²⁰ = -338.5 (c 0.5, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.33-7.26 (m, 6H), 7.14 (td, J = 7.9, 1.6 Hz, 1H), 6.91-6.84 (m, 2H), 6.77 (dd, J = 8.0, 1.2 Hz, 1H), 6.72-6.68 (m, 2H), 6.62-6.60 (m, 2H), 6.50 (s, 1H), 5.84 (s, 1H), 4.98 (d, J = 15.6 Hz, 1H), 4.63 (d, J = 15.6 Hz, 1H), 4.01 (s, 1H), 3.66 (s, 3H), 2.94 (d, J = 14.8 Hz, 1H), 2.24 (s, 3H), 2.08 (d, J = 14.8 Hz, 1H), 1.97 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 179.1, 154.0, 153.7, 142.0, 139.5, 136.1, 135.4, 135.2, 129.2, 128.9, 128.8, 128.1, 127.6, 127.3, 127.1, 124.0, 123.5, 120.3, 117.9, 116.1, 113.9, 113.8, 109.7, 60.3, 55.6, 45.1, 43.6, 39.5, 29.2, 21.8; IR (KBr): γ 3363, 3059, 3029, 2960, 2924, 2854, 1699, 1619, 1499, 1445, 1377, 1348, 1292, 1261, 1217, 1151, 1111, 1081, 1042,

934, 808, 753, 698; ESI FTMS exact mass calcd for ($C_{32}H_{30}N_2O_3+H$)⁺ requires m/z 491.2335, found m/z 491.2328; Enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 8.459 min (minor), t_R = 13.191 min (major).

1-benzyl-7-fluoro-4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4kaa): dr > 99:1; yield: 99%; colorless sticky oil; $[\alpha]_D^{20} = -286.7$ (c 0.8, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.35-7.25 (m, 6H), 7.13 (td, *J* = 7.9, 1.6 Hz, 1H), 6.92-6.85 (m, 2H), 6.83-6.78 (m, 1H), 6.74-6.68 (m, 3H), 6.62-6.60 (m, 2H), 5.67 (s, 1H), 5.03 (d, *J* = 15.2 Hz, 1H), 4.88 (d, *J* = 15.3 Hz, 1H), 4.03 (s, 1H), 3.66 (s, 3H), 2.93 (d, *J* = 14.7 Hz, 1H), 2.07 (d, *J* = 14.7 Hz, 1H), 1.95 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 178.9, 154.0, 153.8, 147.1, (*J* = 242 Hz) 137.1, 135.3, 135.2, 134.8, 128.9, 128.6, 128.4, 128.3, 128.2, 127.7, 127.7, 127.6, 127.4, 123.6, 123.5, 120.4, 120.2, 120.2, 117.8, 117.3, 117.1, 116.2, 113.9, 113.7, 60.8, 55.6, 45.3, 44.8, 39.6, 28.9; IR (KBr): γ 3380, 3063, 3032, 2962, 2926, 2854, 1705, 1629, 1600, 1497, 1446, 1349, 1261, 1183, 1104, 1080, 1043, 875, 802, 735, 699; ESI FTMS exact mass calcd for ($C_{31}H_{27}FN_2O_3+H$)⁺ requires m/z 495.2084, found m/z 495.2074; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.952 min (minor), t_R = 8.306 min (major).

1-benzyl-7-bromo-4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4laa): dr > 99:1; yield: 99%; colorless sticky oil; $[\alpha]_D^{20} = -256.8$ (c 0.6, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.32-7.28 (m, 4H), 7.26-7.20 (m, 3H), 7.14 (td, *J* = 7.8, 1.6 Hz, 1H), 6.94-6.87 (m, 2H), 6.79-6.74 (m, 2H), 6.70 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.63-6.59 (m, 2H), 5.61 (s, 1H), 5.38-5.28 (m, 2H), 4.04 (s, 1H), 3.66 (s, 3H), 2.93 (d, *J* = 14.7 Hz, 1H), 2.08 (d, *J* = 14.7 Hz, 1H), 1.92 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 179.8, 153.9, 153.8, 139.4, 137.5, 135.7, 135.2, 135.0, 134.9, 128.7, 128.6, 128.2, 127.3, 127.2, 126.5, 124.2, 123.6, 120.5, 117.9, 116.2, 113.9, 113.7, 60.1, 55.6, 45.2, 44.2, 39.7, 28.9; IR

(KBr): γ 3360, 3061, 3030, 2961, 2925, 2853, 1708, 1603, 1581, 1499, 1448, 1350, 1262, 1214, 1157, 1112, 1040, 1018, 803, 737, 699; ESI FTMS exact mass calcd for ($C_{31}H_{27}BrN_2O_3+H$)⁺ requires m/z 555.1283, found m/z 555.1276; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.752 min (minor), t_R = 11.020 min (major).

1-benzyl-4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-7-(trifluoromethyl)-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4maa): dr > 99:1; yield: 89%; colorless sticky oil; $[\alpha]_D^{20}$ = -265.6 (c 0.8, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.50 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.30-7.26 (m, 3H), 7.23-7.20 (m, 1H), 7.17-7.11 (m, 4H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.89 (td, *J* = 7.8, 1.2 Hz, 1H), 6.75-6.69 (m, 2H), 6.63-6.59 (m, 2H), 5.55 (s, 1H), 5.19 (d, *J* = 16.8 Hz, 1H), 5.03 (d, *J* = 16.8 Hz, 1H), 4.03 (s, 1H), 3.65 (s, 3H), 2.96 (d, *J* = 14.7 Hz, 1H), 2.08 (d, *J* = 14.6 Hz, 1H), 1.86 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 180.5, 153.9, 153.8, 140.2, 136.5, 135.2, 135.2, 134.8, 128.7, 128.4, 128.3, 127.8 (*J* = 76.6 Hz), , 127.3 (*J* = 6.0 Hz), 127.0, 125.8, 124.7, 122.4, 122.0, 119.3 (*J* = 268.0 Hz), 116.3, 114.0, 113.7, 112.6 (*J* = 32.6 Hz), 59.0, 55.6, 45.5, 45.5 (*J* = 4.8 Hz), 39.8, 28.8; IR (KBr): γ 3412, 3089, 3065, 3033, 2925, 2854, 1715, 1596, 1499, 1447, 1333, 1296, 1270, 1232, 1157, 1122, 1097, 1042, 843, 802, 749, 698; ESI FTMS exact mass calcd for ($C_{32}H_{27}F_3N_2O_3+H$)⁺ requires m/z 545.2052, found m/z 545.2043; Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 4.915 min (minor), t_R = 6.436 min (major).

1-benzyl-4'-(2-hydroxyphenyl)-6'-methoxy-4',7-dimethyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4naa): dr > 99:1; yield: 60%; colorless sticky oil; $[\alpha]_D^{20}$ = -252.6 (c 0.2, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.33 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.26-7.23 (m, 2H), 7.20-7.16 (m, 1H), 7.11-7.07 (m, 3H), 6.98 (d, *J* = 6.8 Hz, 1H), 6.87-6.79 (m, 3H), 6.74 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.63 (dd, *J* = 8.7, 2.8

Hz, 1H), 6.56 (d, J = 8.6 Hz, 1H), 6.50 (d, J = 2.7 Hz, 1H), 5.76 (s, 1H), 5.18 (d, J = 16.7 Hz, 1H), 4.92 (d, J = 16.7 Hz, 1H), 4.01 (s, 1H), 3.58 (s, 3H), 2.86 (d, J = 14.9 Hz, 1H), 2.18 (s, 3H), 2.04 (d, J = 14.8 Hz, 1H), 1.90 (s, 3H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 178.7, 152.9, 152.8, 138.9, 136.7, 134.6, 134.3, 132.2, 131.8, 127.8, 127.5, 127.1, 126.2, 125.8, 122.1, 121.1, 119.3, 118.7, 117.0, 115.2, 112.9, 112.8, 58.6, 54.5, 44.8, 43.7, 38.4, 28.4, 17.7; IR (KBr): γ 3357, 3058, 3029, 2961, 2925, 2853, 1697, 1600, 1499, 1445, 1353, 1262, 1224, 1182, 1157, 1101, 1043, 860, 802, 750, 698; ESI FTMS exact mass calcd for ($\text{C}_{32}\text{H}_{30}\text{N}_2\text{O}_3+\text{H}$) $^+$ requires m/z 491.2335, found m/z 491.2324; Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_{R} = 6.963 min (minor), t_{R} = 9.588 min (major).

1-benzyl-5,6-difluoro-4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4oaa): dr > 99:1; yield: 87%; colorless sticky oil; $[\alpha]_D^{20} = -157.1$ (c 0.8, CHCl_3); ^1H -NMR (CDCl_3 , 400 MHz) δ (ppm): 7.27-7.15 (m, 5H), 7.07 (td, J = 7.9, 1.5 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 6.78 (td, J = 7.8, 0.9 Hz, 1H), 6.68-6.66 (m, 2H), 6.61 (d, J = 7.9 Hz, 1H), 6.57-6.54 (m, 1H), 6.34 (dd, J = 10.0, 6.3 Hz, 1H), 6.01 (s, 1H), 5.39 (s, 1H), 4.87 (d, J = 15.6 Hz, 1H), 4.48 (d, J = 15.6 Hz, 1H), 3.85 (s, 1H), 3.64 (s, 3H), 2.98 (d, J = 14.2 Hz, 1H), 2.05 (d, J = 14.2 Hz, 1H), 1.85 (s, 3H); ^{13}C -NMR (CDCl_3 , 100 MHz) δ (ppm): 178.7, 153.3, 152.5, 150.7 (J = 13.5 Hz), 148.2 (J = 14.1 Hz), 146.6 (J = 12.8 Hz), 144.2 (J = 13.1 Hz), 136.9 (J = 7.6 Hz), 134.6, 134.0, 130.1 (J = 380.8 Hz), 128.0, 127.4, 127.3, 126.9, 126.2, 118.1 (J = 326.1 Hz), 114.9, 113.8, 113.6, 112.7, 112.4, 97.9 (J = 22.9 Hz), 60.4, 54.6, 43.0, 42.7, 39.1, 26.7; IR (KBr): γ 3385, 3064, 3032, 2925, 2855, 1709, 1624, 1499, 1448, 1399, 1346, 1294, 1270, 1239, 1212, 1168, 1110, 1042, 800, 740, 697; ESI FTMS exact mass calcd for ($\text{C}_{31}\text{H}_{26}\text{F}_2\text{N}_2\text{O}_3+\text{H}$) $^+$ requires m/z 513.1990, found m/z 513.1988; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_{R} = 6.345 min (minor), t_{R} = 8.988 min (major).

7-bromo-1-(4-tert-butylbenzyl)-4'-(2-hydroxyphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4paa): dr > 99:1; yield: 63%; colorless sticky oil; $[\alpha]_D^{20} = -232.1$ (c 0.5, CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 7.33-7.30 (m, 4H), 7.18-7.14 (m, 3H), 6.97 (d, $J = 7.0$ Hz, 1H), 6.90 (td, $J = 7.7, 1.3$ Hz, 1H), 6.78 (t, $J = 7.8$ Hz, 2H), 6.71 (dd, $J = 8.7, 2.8$ Hz, 1H), 6.63 (d, $J = 8.6$ Hz, 1H), 6.59 (d, $J = 2.7$ Hz, 1H), 5.55 (s, 1H), 5.37-5.25 (m, 2H), 4.02 (s, 1H), 3.67 (s, 3H), 2.91 (d, $J = 14.7$ Hz, 1H), 2.08 (d, $J = 14.7$ Hz, 1H), 1.94 (s, 3H), 1.30 (s, 9H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 179.7, 153.8, 150.0, 141.9, 139.5, 135.6, 135.2, 135.1, 134.4, 128.6, 128.2, 127.2, 126.3, 125.4, 124.1, 123.5, 120.5, 117.9, 116.2, 114.0, 113.7, 102.2, 59.9, 55.6, 45.3, 43.9, 39.7, 34.4, 31.3, 29.0; IR (KBr): γ 3416, 2964, 2924, 2855, 1706, 1667, 1644, 1606, 1501, 1449, 1415, 1352, 1268, 1213, 1157, 1112, 1045, 878, 806, 742; ESI FTMS exact mass calcd for $(\text{C}_{35}\text{H}_{35}\text{BrN}_2\text{O}_3+\text{H})^+$ requires m/z 611.1909, found m/z 611.1902; Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): $t_R = 6.091$ min (minor), $t_R = 7.138$ min (major).

1-benzyl-6'-ethoxy-4'-(2-hydroxyphenyl)-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4aba): dr > 99:1; yield: 70%; colorless sticky oil; $[\alpha]_D^{20} = -306.9$ (c 0.4, CHCl_3); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 7.27-7.19 (m, 6H), 7.09-7.03 (m, 2H), 6.92 (d, $J = 7.2$ Hz, 1H), 6.85-6.80 (m, 2H), 6.70 (dd, $J = 8.0, 1.1$ Hz, 1H), 6.64-6.58 (m, 2H), 6.54 (s, 2H), 5.65 (s, 1H), 4.92 (d, $J = 15.5$ Hz, 1H), 4.59 (d, $J = 15.5$ Hz, 1H), 3.97 (s, 1H), 3.80 (s, 2H), 2.87 (d, $J = 14.8$ Hz, 1H), 2.02 (d, $J = 14.7$ Hz, 1H), 1.91 (s, 3H), 1.24 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ (ppm): 177.9, 153.0, 152.0, 140.8, 134.9, 134.3, 128.1, 127.8, 127.1, 126.6, 126.3, 126.1, 123.2, 121.9, 119.3, 116.9, 115.1, 113.5, 107.9, 62.8, 59.4, 43.9, 42.7, 38.5, 28.1, 13.8; IR (KBr): γ 3412, 3061, 2971, 2925, 1696, 1644, 1610, 1496, 1464, 1358, 1262, 1212, 1154, 1085, 1046, 955, 877, 801, 747, 699; ESI FTMS exact mass calcd for $(\text{C}_{32}\text{H}_{30}\text{N}_2\text{O}_3+\text{H})^+$ requires m/z 491.2335, found m/z 491.2321; Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20,

flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.961 min (minor), t_R = 10.914 min (major).

1-benzyl-6-chloro-6'-ethoxy-4'-(2-hydroxyphenyl)-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4hba): dr > 99:1; yield: 99%; colorless sticky oil; [α]_D²⁰ = -262.6 (c 0.8, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.35-7.31 (m, 2H), 7.29-7.25 (m, 3H), 7.18 (d, J = 7.8 Hz, 1H), 7.13 (td, J = 7.8, 1.6 Hz, 1H), 6.86 (td, J = 7.7, 1.2 Hz, 1H), 6.78 (dd, J = 8.0, 1.8 Hz, 1H), 6.71 (m, 2H), 6.67 (d, J = 2.6 Hz, 1H), 6.64-6.60 (m, 2H), 6.57 (d, J = 7.5 Hz, 1H), 5.60 (s, 1H), 4.96 (d, J = 15.6 Hz, 1H), 4.57 (d, J = 15.6 Hz, 1H), 3.98 (s, 1H), 3.98-3.84 (m, 2H), 2.98 (d, J = 14.5 Hz, 1H), 2.09 (d, J = 14.5 Hz, 1H), 1.94 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 178.2, 157.6, 152.9, 148.1, 140.7, 137.2, 134.8, 131.2, 128.4, 128.1, 128.0, 127.8, 127.2, 126.7, 126.5, 126.3, 123.3, 121.9, 120.9, 119.5, 119.0, 118.9, 116.7, 116.0, 115.2, 107.9, 59.7, 43.2, 42.8, 38.7, 27.7; IR (KBr): γ 3369, 3062, 3030, 2974, 2925, 2855, 1709, 1606, 1498, 1441, 1371, 1292, 1249, 1212, 1111, 1076, 1047, 840, 814, 754, 699; ESI FTMS exact mass calcd for (C₃₂H₂₉ClN₂O₃+H)⁺ requires m/z 525.1945, found m/z 525.1946; Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.821 min (minor), t_R = 9.522 min (major).

1-benzyl-4'-(2-hydroxyphenyl)-4'-methyl-6'-phenoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4aca): dr > 99:1; yield: 99%; colorless sticky oil; [α]_D²⁰ = -223.4 (c 0.5, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.27-7.21 (m, 4H), 7.19-7.15 (m, 4H), 7.08-7.03 (m, 2H), 6.92-6.88 (m, 1H), 6.84-6.74 (m, 7H), 6.67 (dd, J = 8.0, 1.2 Hz, 1H), 6.61-6.58 (m, 2H), 5.36 (s, 1H), 4.94 (d, J = 15.6 Hz, 1H), 4.59 (d, J = 15.6 Hz, 1H), 4.10 (s, 1H), 2.95 (d, J = 14.7 Hz, 1H), 2.07 (d, J = 14.7 Hz, 1H), 1.88 (s, 3H). ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 178.2, 157.6, 152.9, 148.1, 140.7, 137.2, 134.8, 131.2, 128.4, 128.1, 128.0, 127.8, 127.2, 126.7, 126.5, 126.3, 123.3, 121.9, 120.9, 119.5, 119.0, 118.9, 116.7, 116.0, 115.2, 107.9, 59.7, 43.2, 42.8, 38.7, 27.7; IR (KBr): γ 3352, 3059, 3029, 2957, 2922, 2854, 1695, 1604, 1485, 1453, 1363,

1259, 1214, 1168, 1098, 1077, 1025, 802, 750, 694; ESI FTMS exact mass calcd for ($C_{36}H_{30}N_2O_3+H$)⁺ requires m/z 539.2335, found m/z 539.2322; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.592 min (minor), t_R = 7.473 min (major).

1-benzyl-6-chloro-4'-(2-hydroxyphenyl)-4'-methyl-6'-phenoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4hca): dr > 99:1; yield: 99%; colorless solid, m.p. 161-163 °C; [α]_D²⁰ = -164.8 (c 0.9, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.37-7.34 (m, 2H), 7.31-7.24 (m, 5H), 7.17-7.09 (m, 2H), 6.99 (t, J = 7.4 Hz, 1H), 6.93-6.83 (m, 5H), 6.76 (dd, J = 8.0, 1.7 Hz, 1H), 6.71-6.65 (m, 3H), 6.42 (d, J = 7.5 Hz, 1H), 5.19 (s, 1H), 5.00 (d, J = 15.6 Hz, 1H), 4.63 (d, J = 15.6 Hz, 1H), 4.09 (s, 1H), 3.06 (d, J = 14.4 Hz, 1H), 2.15 (d, J = 14.4 Hz, 1H), 1.93 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 179.5, 158.7, 154.0, 149.2, 143.0, 138.2, 135.3, 134.7, 130.9, 129.5, 129.2, 129.0, 128.3, 128.1, 127.9, 127.3, 125.6, 122.6, 122.0, 120.8, 120.0, 119.8, 117.6, 117.1, 116.1, 109.4, 60.8, 44.0, 43.7, 40.0, 28.2; IR (KBr): γ 3374, 3063, 3031, 2922, 2853, 1707, 1605, 1485, 1441, 1371, 1344, 1293, 1221, 1165, 1109, 1075, 1002, 817, 753, 694; ESI FTMS exact mass calcd for ($C_{36}H_{29}ClN_2O_3+H$)⁺ requires m/z 573.1945, found m/z 573.1946; Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 4.788 min (minor), t_R = 6.438 min (major).

1-benzyl-6'-fluoro-4'-(2-hydroxyphenyl)-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4ada): dr > 99:1; yield: 44%; colorless sticky oil; [α]_D²⁰ = -176.0 (c 0.2, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.28-7.16 (m, 6H), 7.11-7.04 (m, 2H), 6.85-6.81 (m, 1H), 6.79-6.77 (m, 1H), 6.76-6.72 (m, 2H), 6.70-6.67 (m, 1H), 6.61 (d, J = 7.8 Hz, 1H), 6.55 (m, 1H), 5.39 (s, 1H), 4.93 (d, J = 15.5 Hz, 1H), 4.60 (d, J = 15.5 Hz, 1H), 4.06 (s, 1H), 2.96 (d, J = 14.7 Hz, 1H), 2.05 (d, J = 14.7 Hz, 1H), 1.90 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 178.0, 156.2 (J = 236.0 Hz), 152.9, 140.8, 136.8, 134.8, 133.3, 131.0, 128.5 (J = 6.2 Hz), 128.2, 127.8, 127.3, 126.7, 126.4, 126.3, 123.3, 121.9, 119.6, 116.8, 115.0 (J = 7.6

Hz), 113.6 (J = 19.0 Hz), 107.9, 59.6, 43.2, 42.8, 38.6, 27.7; IR (KBr): γ 3359, 3060, 3031, 2962, 2922, 2853, 1698, 1608, 1497, 1464, 1446, 1371, 1296, 1261, 1201, 1175, 1151, 1102, 1082, 1022, 938, 803, 754, 699; ESI FTMS exact mass calcd for ($C_{30}H_{25}FN_2O_2+H$)⁺ requires m/z 465.1978, found m/z 465.1976; Enantiomeric excess: 78%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 4.861 min (minor), t_R = 5.823 min (major).

1-benzyl-6-chloro-4'-(2-hydroxy-5-methylphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4hab): dr > 99:1; yield: 99%; colorless sticky oil; $[\alpha]_D^{20}$ = -265.8 (c 0.8, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.36-7.25 (m, 5H), 7.02 (s, 1H), 6.93 (dd, J = 8.1, 1.6 Hz, 1H), 6.82 (dd, J = 8.0, 1.7 Hz, 1H), 6.72-6.70 (m, 2H), 6.65-6.61 (m, 4H), 5.39 (s, 1H), 4.96 (d, J = 15.6 Hz, 1H), 4.58 (d, J = 15.6 Hz, 1H), 4.00 (s, 1H), 3.68 (s, 3H), 2.95 (d, J = 14.6 Hz, 1H), 2.26 (s, 3H), 2.06 (d, J = 14.6 Hz, 1H), 1.93 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 179.2, 153.7, 151.7, 143.0, 135.4, 134.7, 134.2, 130.9, 129.5, 129.0, 129.0, 128.6, 128.1, 127.9, 127.3, 125.5, 122.7, 117.6, 116.1, 113.8, 113.7, 109.4, 60.5, 55.6, 44.6, 43.8, 39.7, 28.8, 20.9; IR (KBr): γ 3363, 3069, 3030, 2925, 2855, 1711, 1606, 1497, 1442, 1370, 1341, 1255, 1215, 1182, 1134, 1074, 1040, 814, 736, 700; ESI FTMS exact mass calcd for ($C_{32}H_{29}ClN_2O_3+H$)⁺ requires m/z 525.1945, found m/z 525.1936; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 6.207 min (minor), t_R = 9.744 min (major).

1-benzyl-6-chloro-4'-(2-hydroxy-5-methoxyphenyl)-6'-methoxy-4'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4hac): dr > 99:1; yield: 86%; colorless sticky oil; $[\alpha]_D^{20}$ = -247.9 (c 0.7, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.28-7.18 (m, 5H), 6.77-6.75 (m, 2H), 6.68-6.53 (m, 7H), 5.08 (s, 1H), 4.89 (d, J = 15.6 Hz, 1H), 4.52 (d, J = 15.6 Hz, 1H), 3.93 (s, 1H), 3.65 (s, 3H), 3.60 (s, 3H), 2.90 (d, J = 14.6 Hz, 1H), 1.99 (d, J = 14.6 Hz, 1H), 1.86 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 179.1, 153.7, 153.5, 147.9, 143.0, 136.0, 135.3, 135.3, 134.8,

130.8, 129.0, 128.4, 127.9, 127.3, 125.4, 122.7, 118.3, 116.1, 114.4, 114.1, 113.5, 112.0, 109.4, 60.3, 55.7, 55.6, 44.4, 43.9, 39.9, 28.7; IR (KBr): γ 3364, 3062, 3030, 2927, 2853, 2833, 1712, 1607, 1499, 1439, 1421, 1370, 1287, 1213, 1176, 1112, 1041, 811, 737, 699; ESI FTMS exact mass calcd for $(C_{32}H_{29}ClN_2O_4+H)^+$ requires m/z 541.1894, found m/z 541.1890; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.234 min (minor), t_R = 12.239 min (major).

1-benzyl-6-chloro-4'-ethyl-4'-(2-hydroxyphenyl)-6'-methoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (4had): dr > 99:1; yield: 87%; colorless solid; m.p. 115-117 °C; $[\alpha]_D^{20}$ = -70.9 (c 0.6, CHCl₃); ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.37-7.28 (m, 5H), 7.16-7.11 (m, 1H), 6.98 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.87-6.84 (m, 1H), 6.77-6.75 (m, 2H), 6.68-6.62 (m, 4H), 6.15 (d, *J* = 8.1 Hz, 1H), 5.08 (s, 1H), 5.00 (d, *J* = 15.6 Hz, 1H), 4.63 (d, *J* = 15.6 Hz, 1H), 3.82 (s, 1H), 3.74 (s, 3H), 2.94 (d, *J* = 14.3 Hz, 1H), 2.64 (dt, *J* = 14.6, 7.3 Hz, 1H), 2.36-2.27 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ (ppm): 180.0, 154.5, 153.1, 142.9, 136.5, 135.3, 134.2, 131.9, 131.8, 129.4, 128.9, 128.1, 127.8, 127.4, 127.3, 125.8, 122.5, 120.9, 117.6, 116.2, 114.1, 113.5, 109.3, 61.3, 55.8, 44.3, 44.0, 40.3, 29.7, 10.1; IR (KBr): γ 3371, 3062, 3030, 2960, 2925, 2854, 1708, 1605, 1495, 1443, 1370, 1347, 1261, 1215, 1144, 1103, 1077, 1041, 804, 739, 699; ESI FTMS exact mass calcd for $(C_{32}H_{29}ClN_2O_3+H)^+$ requires m/z 525.1945, found m/z 525.1942; Enantiomeric excess: 89%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.355 min (minor), t_R = 7.924 min (major).

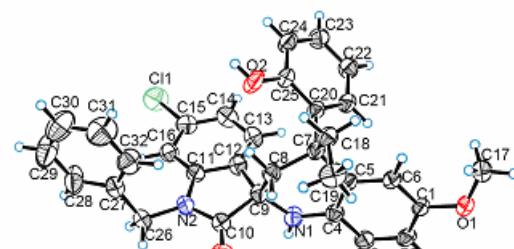
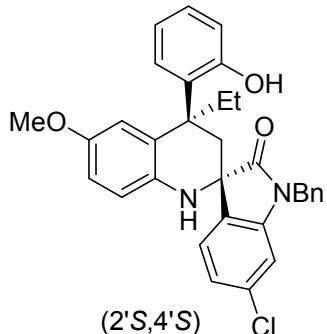
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1. (a) Shi, F.; Tao, Z.-L.; Luo, S.-W.; Tu, S.-J.; Gong, L.-Z. *Chem. Eur. J.* **2012**, *18*, 6885; (b) X. Elias, R. Pleixats, M. W. C. Man, *Tetrahedron*, **2008**, *64*, 6770; (c) J. L. R. Williams, D. G. Borden, T. M. Laasko, *J. Org. Chem.* **1956**, *21*, 1461; (d) V. V. Dhekne, B. D. Kulkarni, A. S. Rao, *Indian J. Chem. B.* **1977**, *15*, 755; (e) R. A. Smith,

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2. (a) Uraguchi, D.; Terada, M. *J. Am. Chem. Soc.* **2004**, *126*, 5356; (b) Akiyam, T.; Morita, H.; Itoh, J.; Fuchibe, K. *Org. Lett.* **2005**, *7*, 2583; (c) Storer, R. I.; Carrera, D. E.; Ni, Y.; Macmillan, D. W. C. *J. Am. Chem. Soc.* **2006**, *128*, 84; (d) Uraguchi, D.; Sorimachi, K.; Terada, M. *Angew. Chem. Int. Ed.* **2006**, *45*, 2254; (e) Itoh, K.; Fuchibe, K.; Akiyama, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 4796; (f) Yamanaka, M.; Junji Itoh; Fuchibe, K.; Akiyama, T. *J. Am. Chem. Soc.* **2007**, *129*, 6756; (g) Guo, Q.-X.; Liu, H.; Guo, C.; Luo, S.-W.; Gu, Y.; Gong, L.-Z. *J. Am. Chem. Soc.* **2007**, *129*, 3790; (h) Jiang, J.; Yu, J.; Sun, X.-X.; Rao, Q.-Q.; Gong, L.-Z. *Angew. Chem. Int. Ed.* **2008**, *47*, 2458; (i) Chen, X.-H.; Zhang, W.-Q.; Gong, L.-Z. *J. Am. Chem. Soc.* **2008**, *130*, 5652.

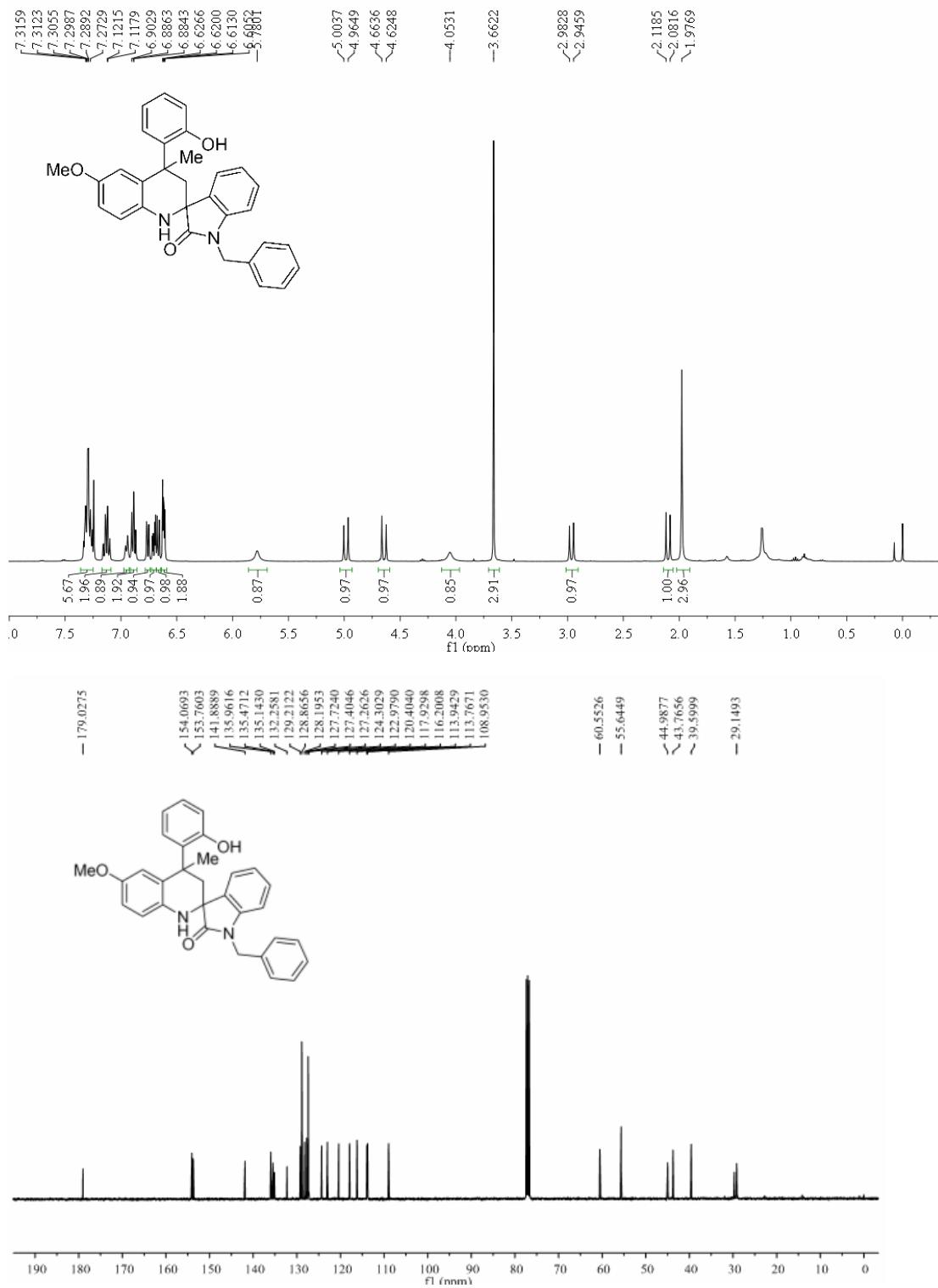
Absolute configuration of 4had:



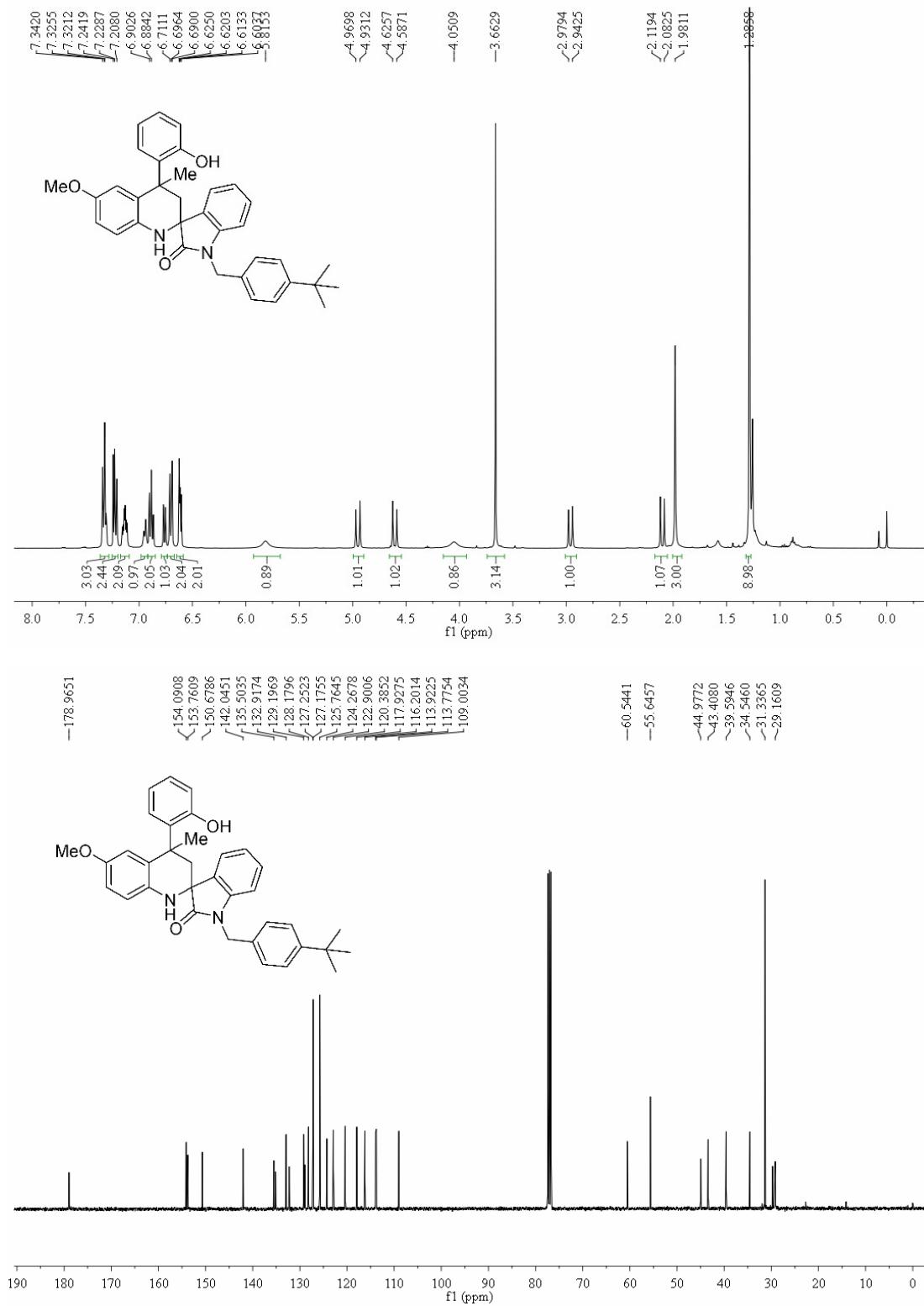
Empirical formula	C ₃₂ H ₂₉ ClN ₂ O ₃
Formula weight	525.02
Temperature	290(2) K
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	$a = 8.37710(10)$ Å $\alpha = 90.00^\circ$ $b = 10.2900(2)$ Å $\beta = 90.00^\circ$ $c = 31.1680(4)$ Å $\gamma = 90.00^\circ$
Volume	2686.69(7) Å ³
Z	4
Density (calculated)	1.298 mg/mm ³
$F(000)$	1104.0
Crystal size	0.37 × 0.32 × 0.31
Theta range for data collection	9.06 to 134.8°
Index ranges	-9 ≤ h ≤ 10, -12 ≤ k ≤ 11, -37 ≤ l ≤ 37
Reflections collected	21252
Independent reflections	4779[R(int) = 0.0238]
Data / restraints / parameters	4779/0/347
Goodness-of-fit on F^2	1.033
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0306$, $wR_2 = 0.0882$
R indices (all data)	$R_1 = 0.0336$, $wR_2 = 0.0904$
Largest diff. peak and hole	0.15/-0.21

¹H and ¹³C NMR Spectra

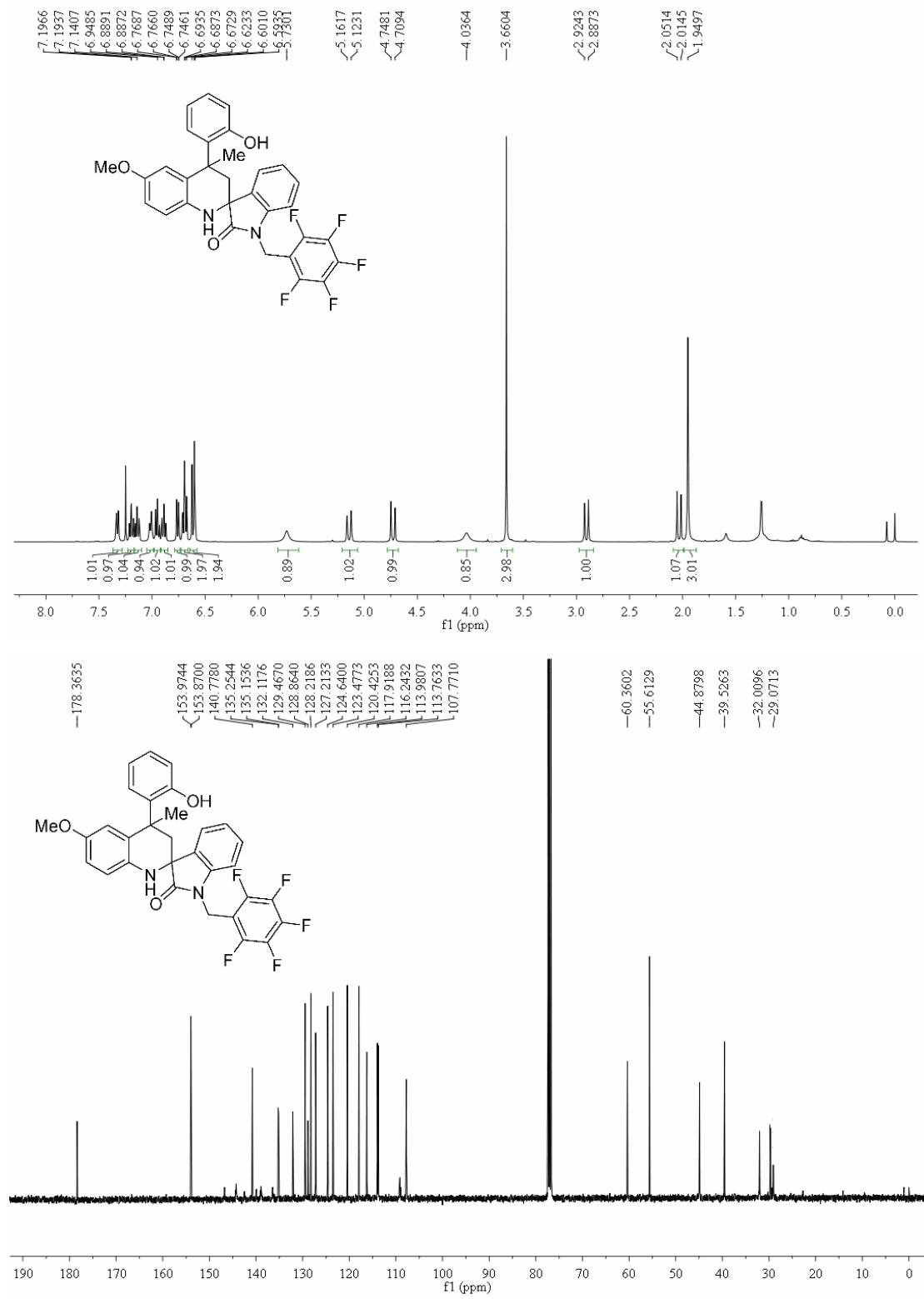
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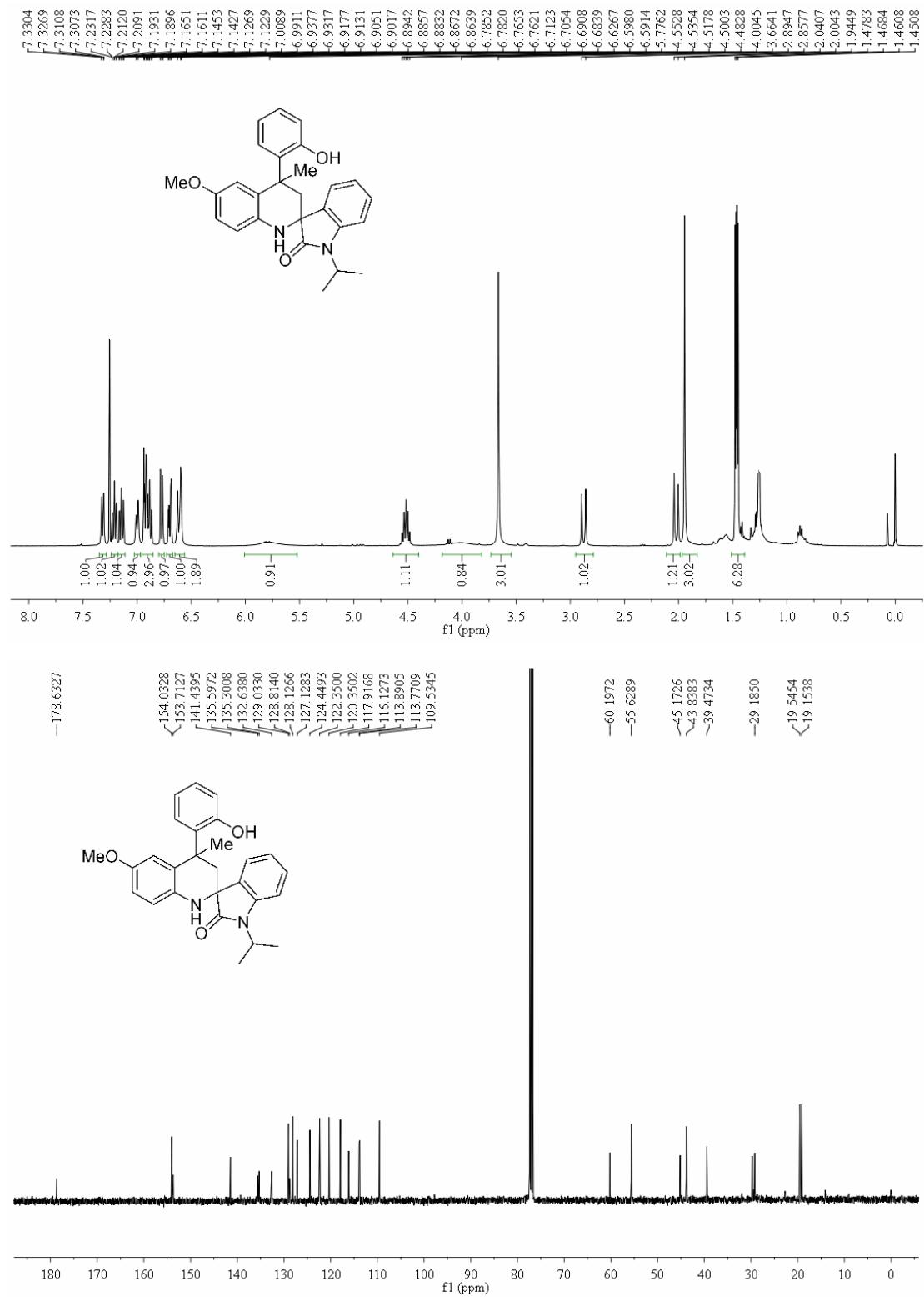
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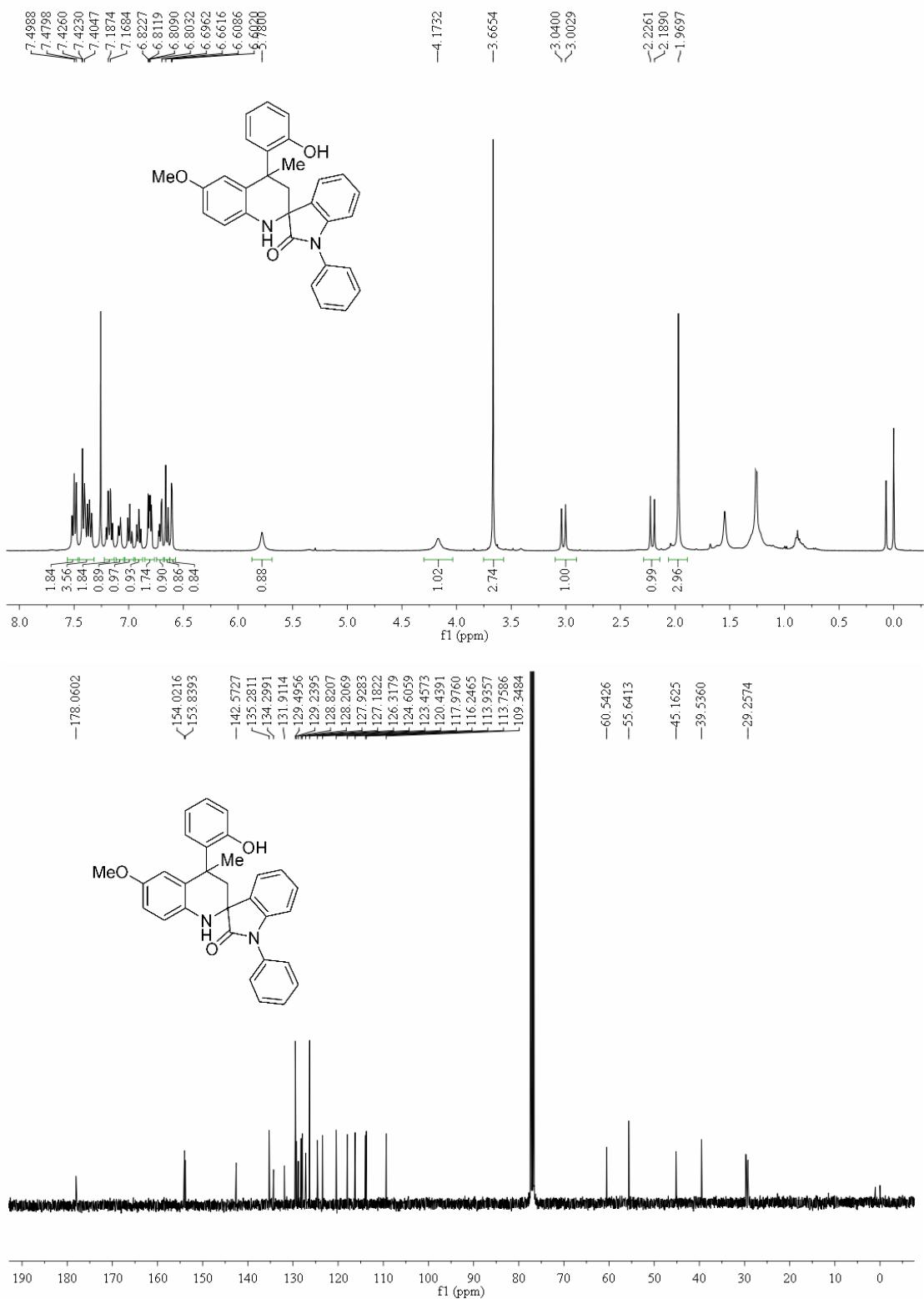
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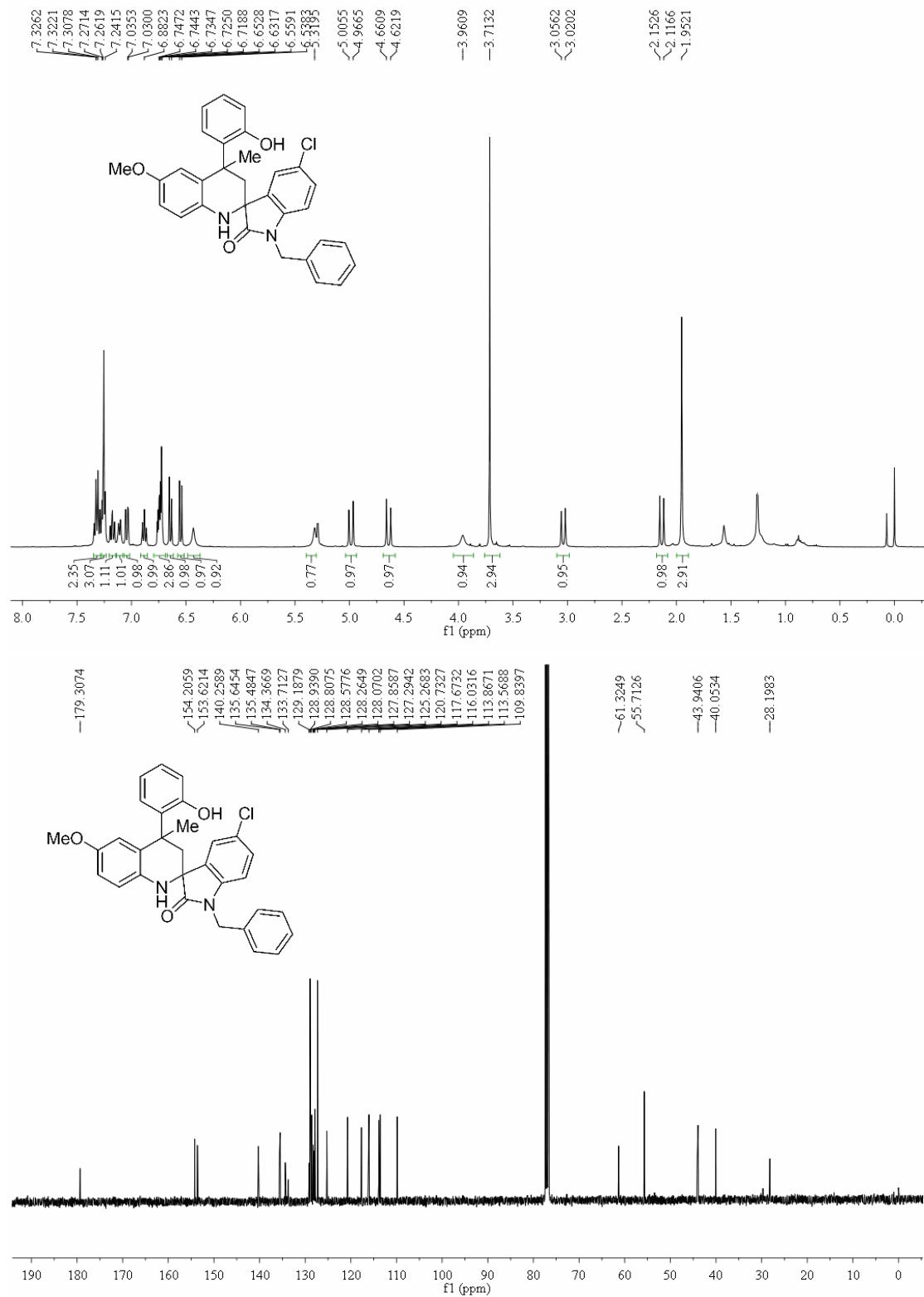
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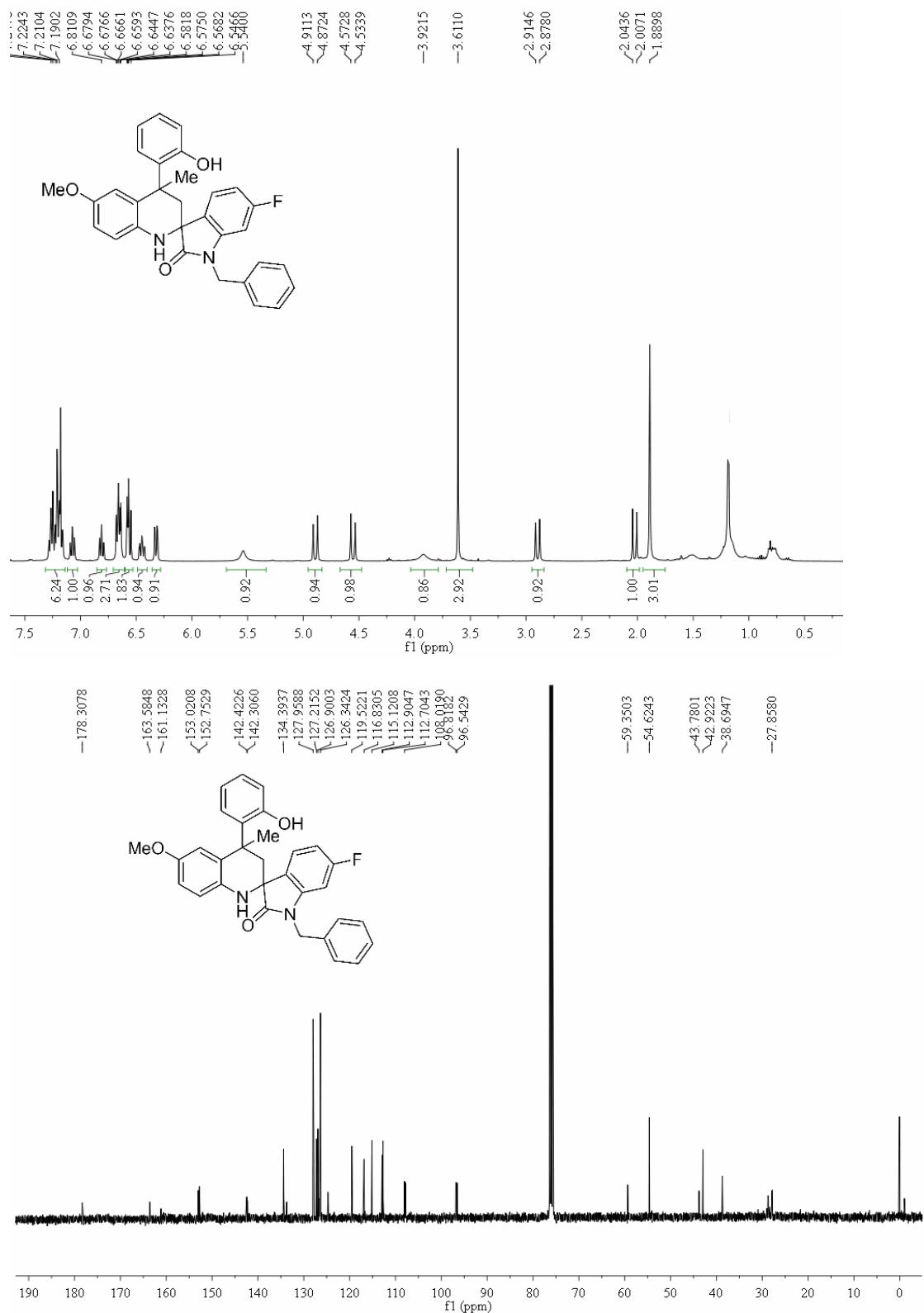
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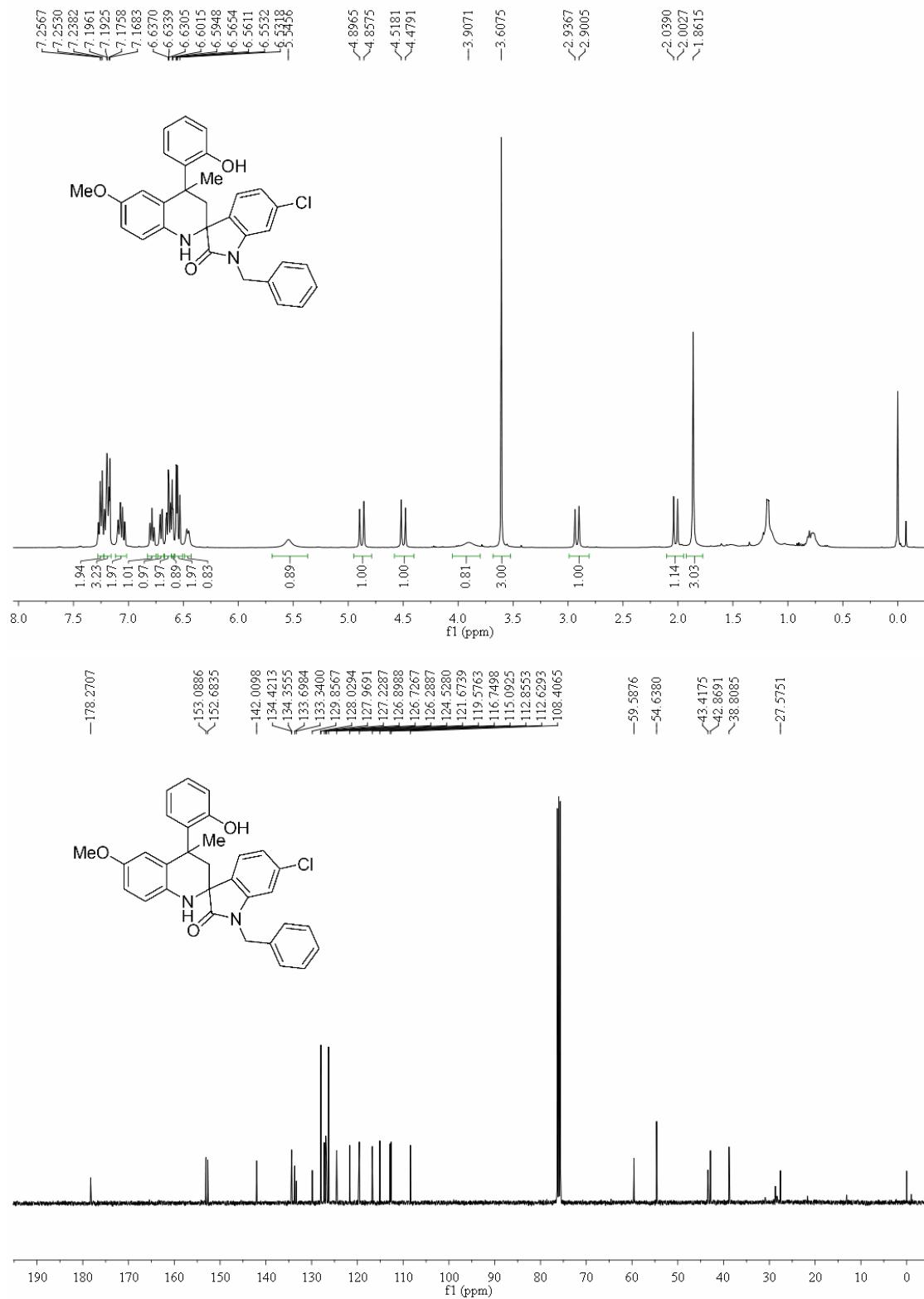
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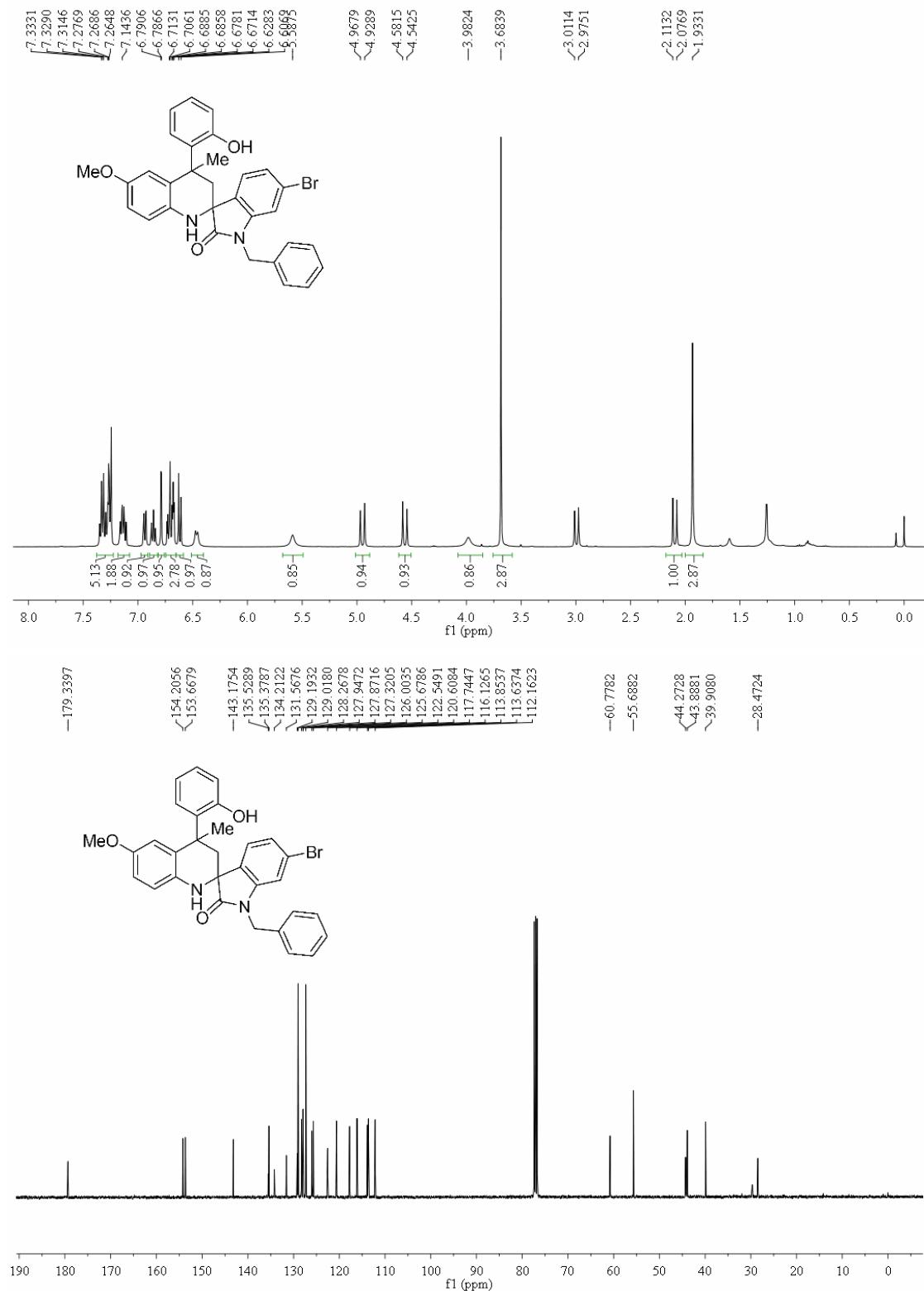
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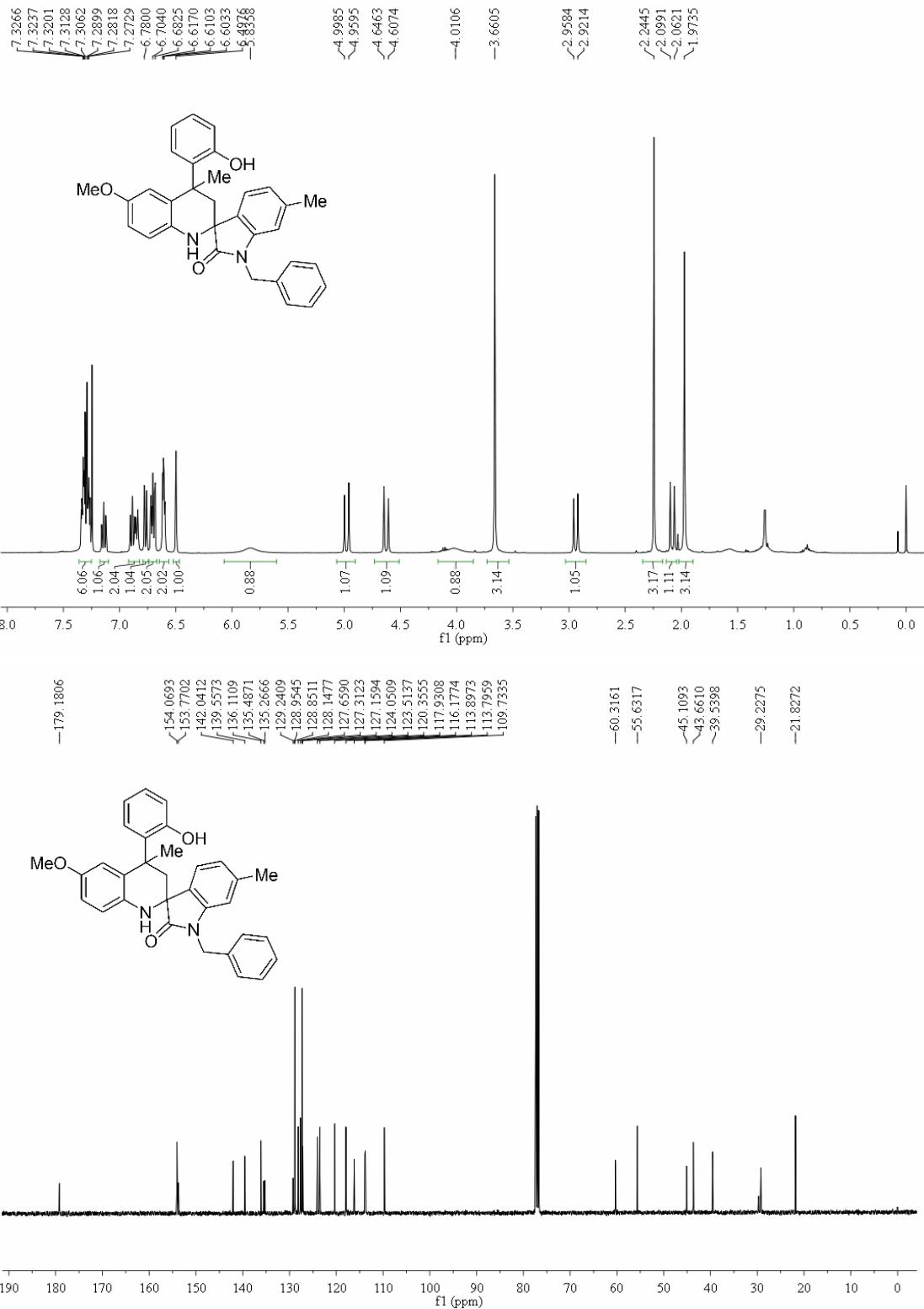
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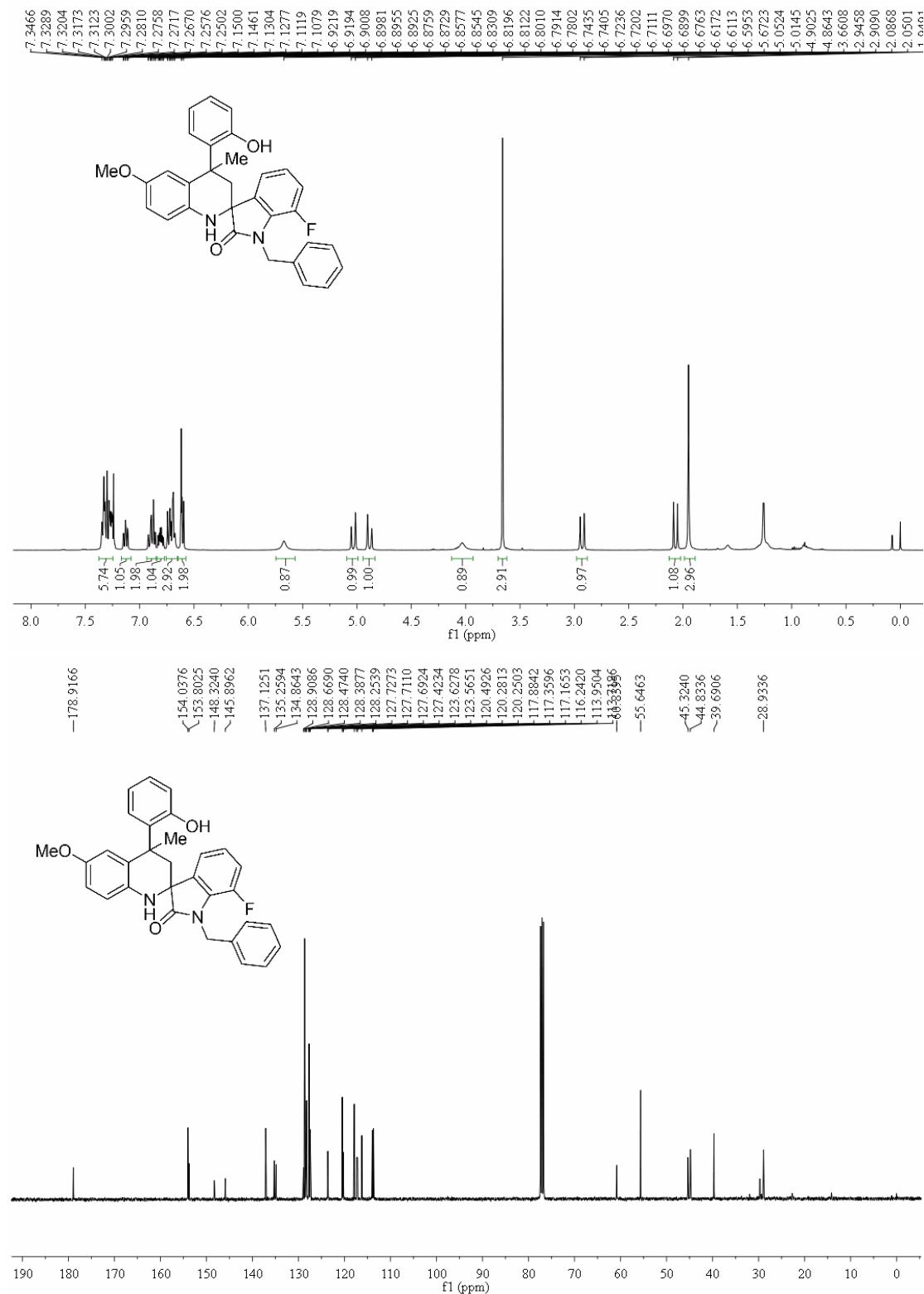
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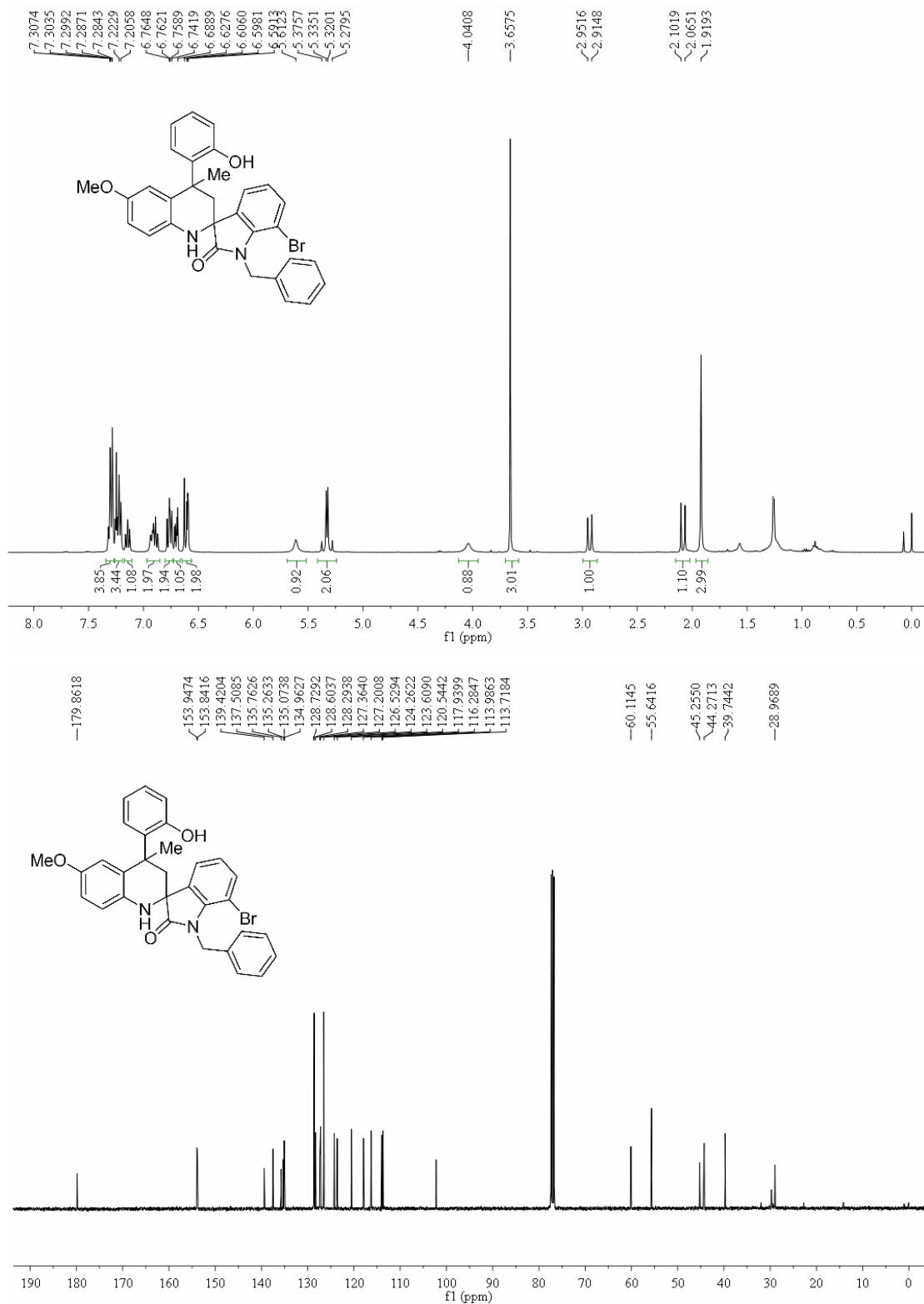
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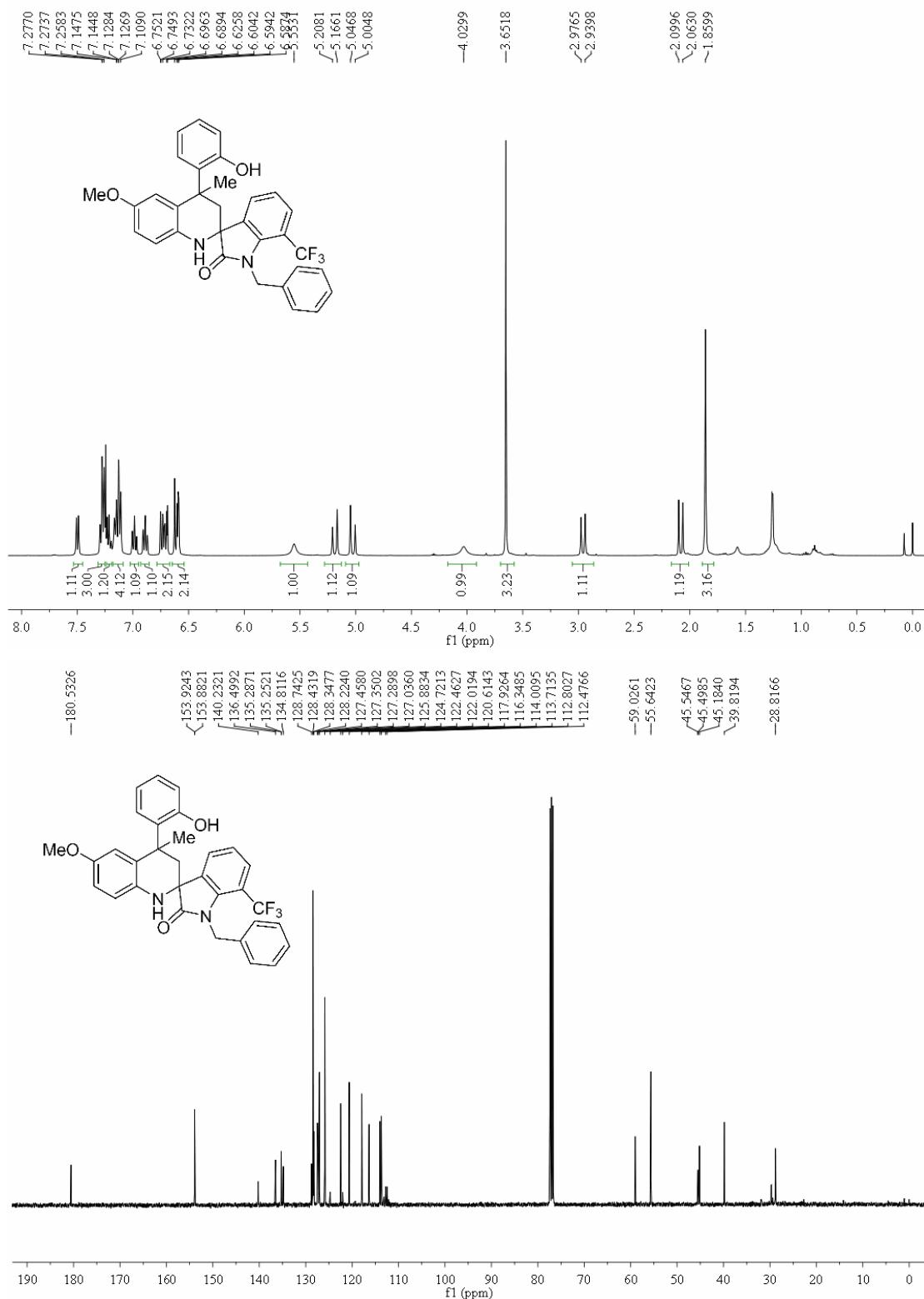
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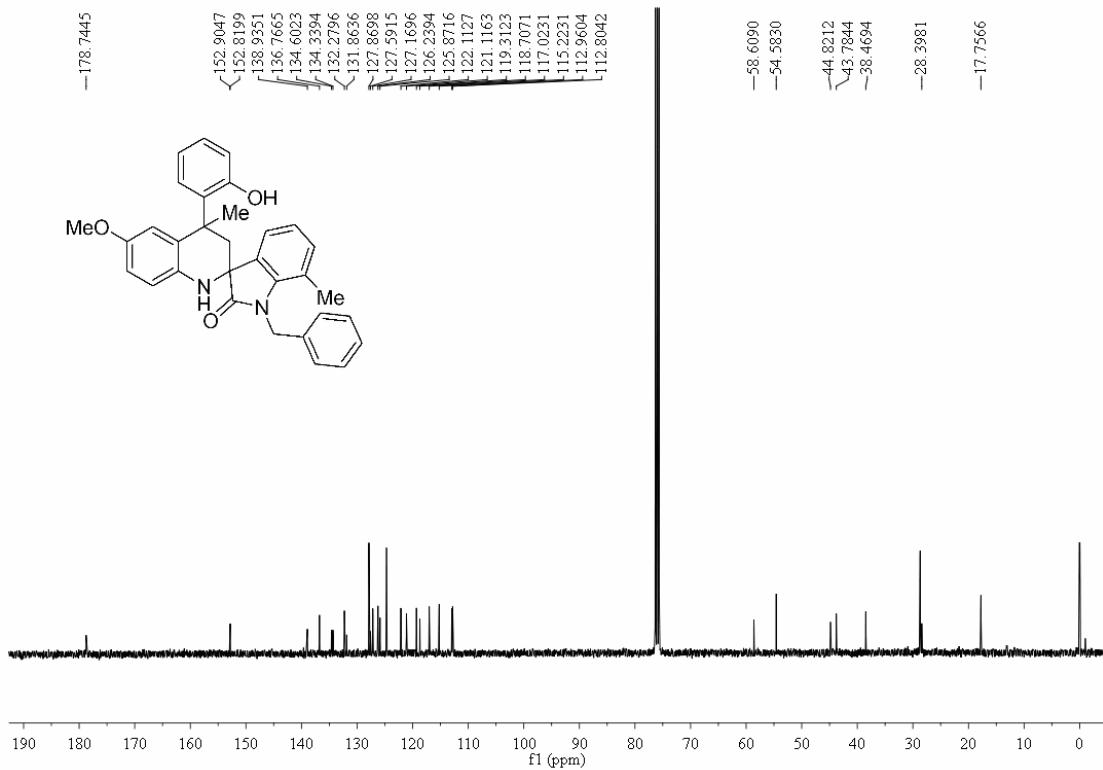
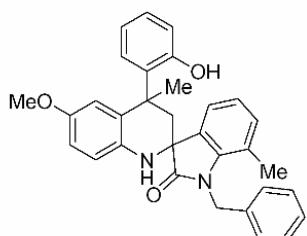
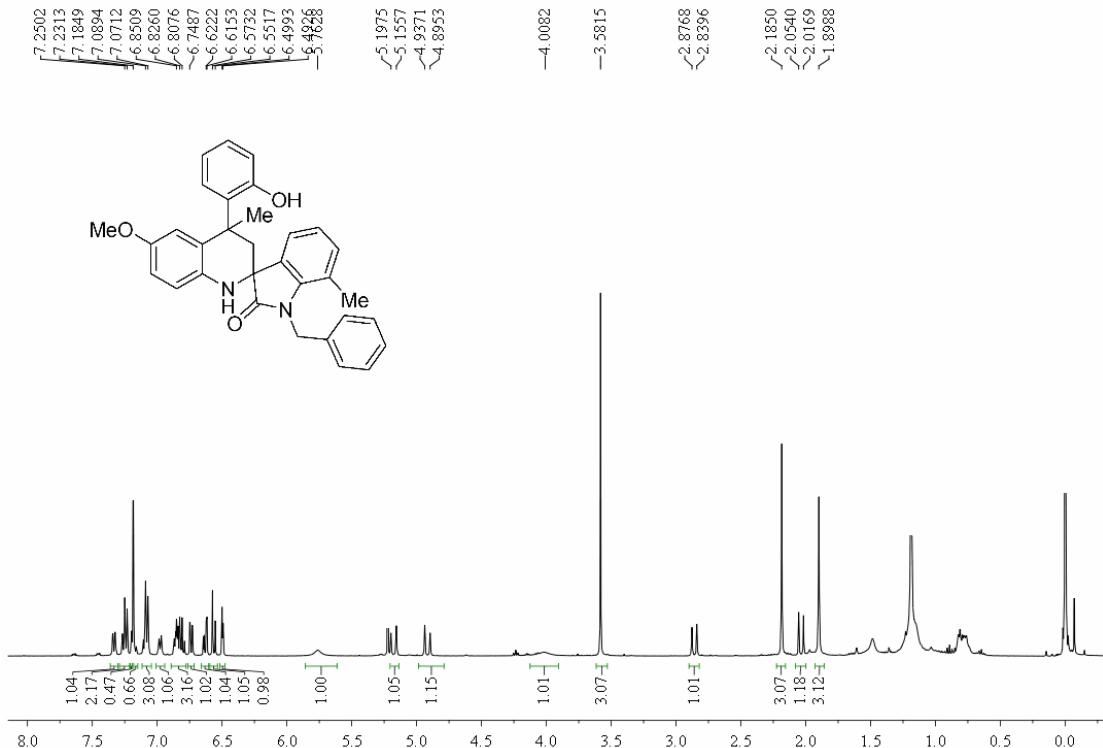
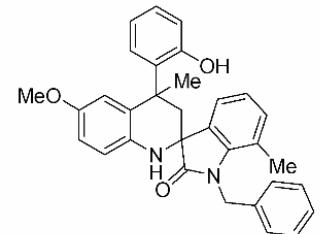
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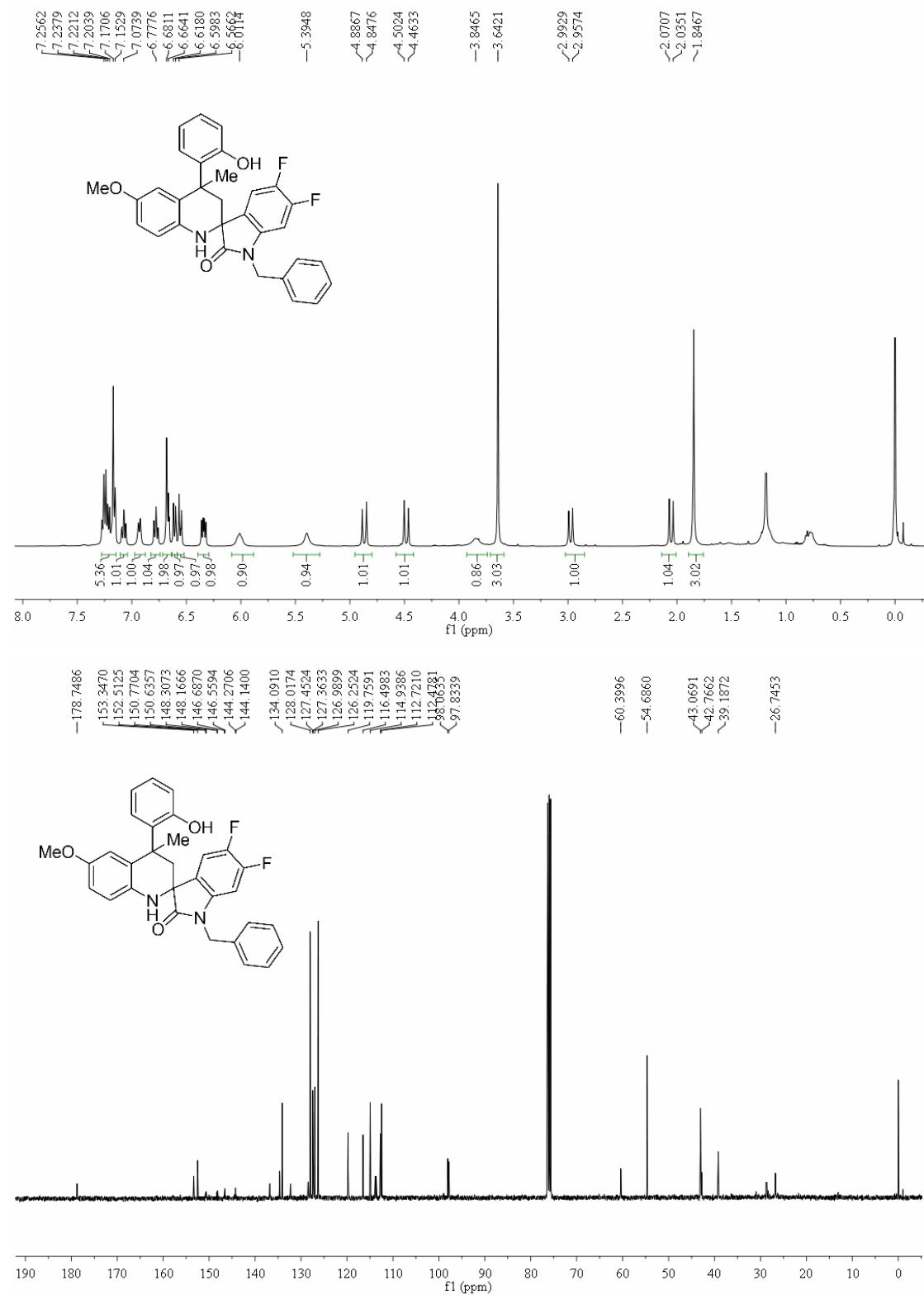
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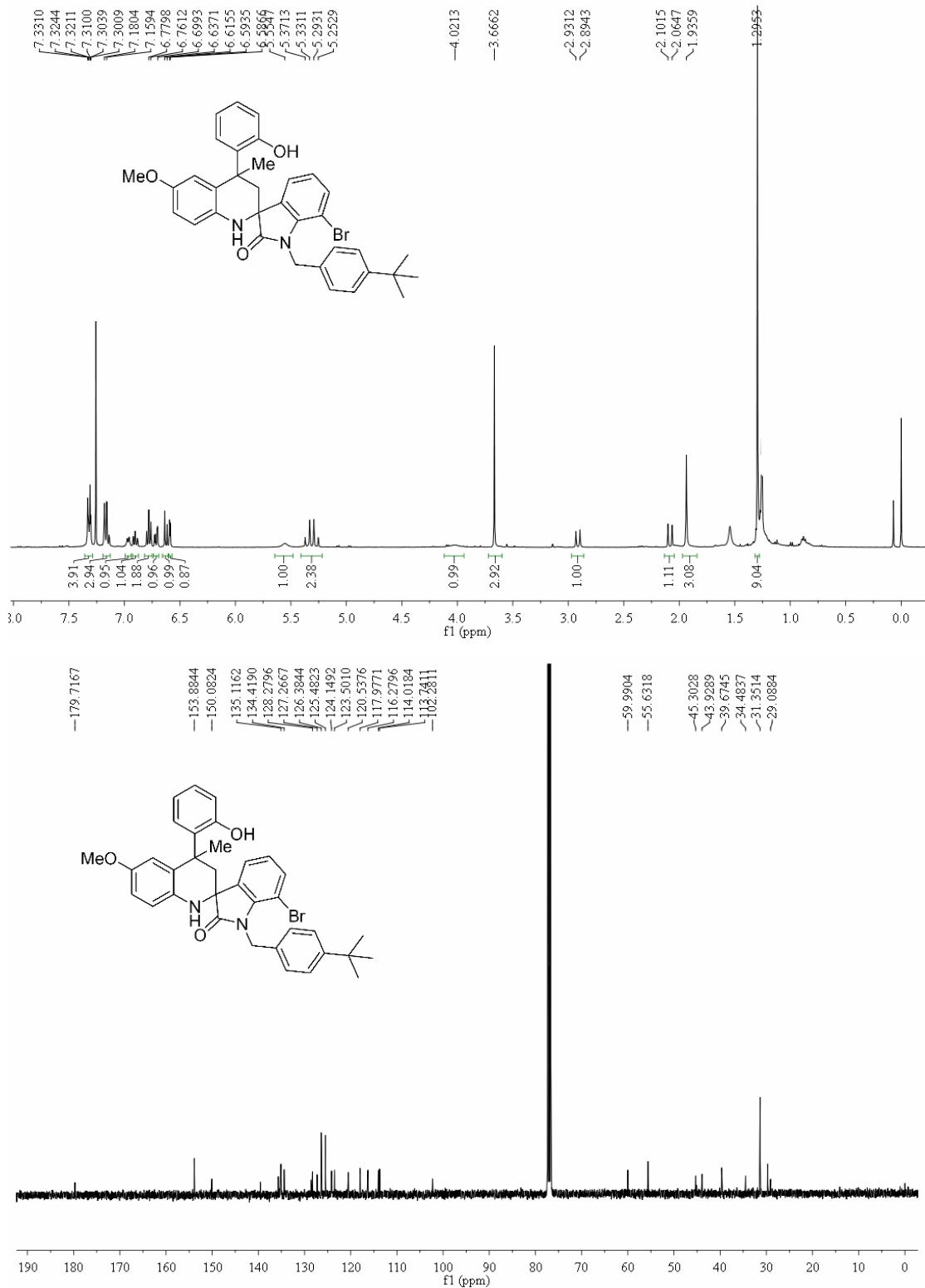
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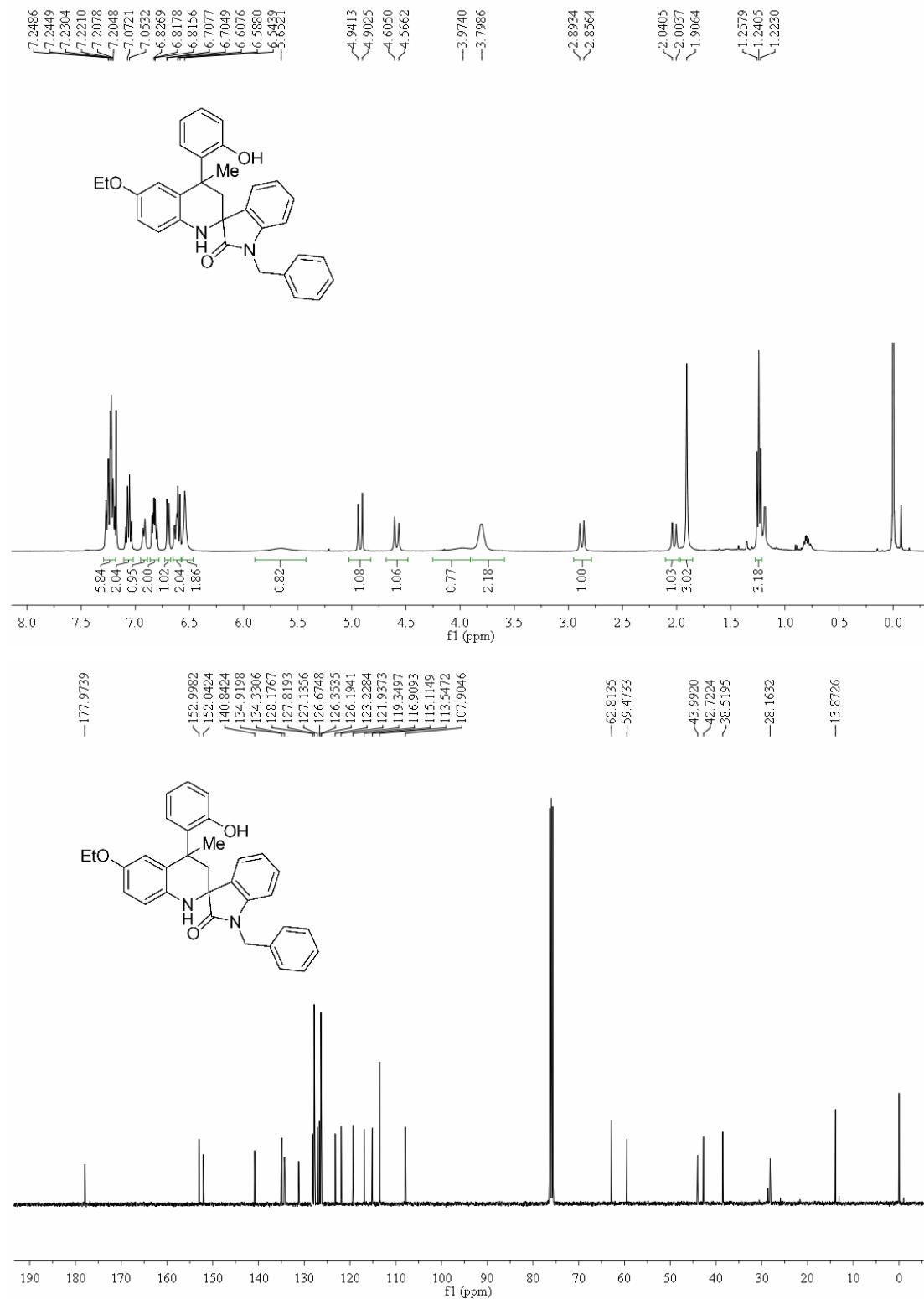
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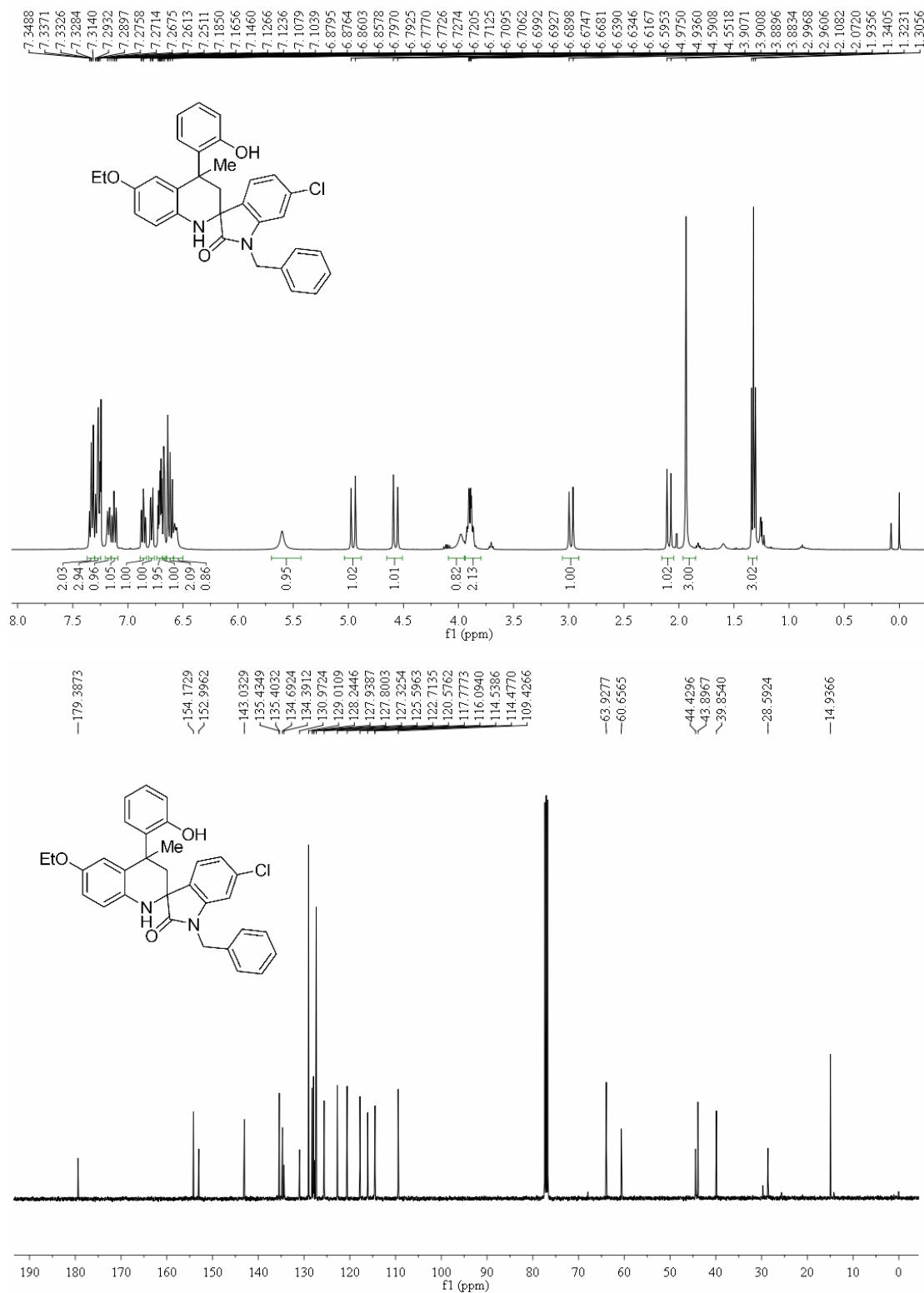
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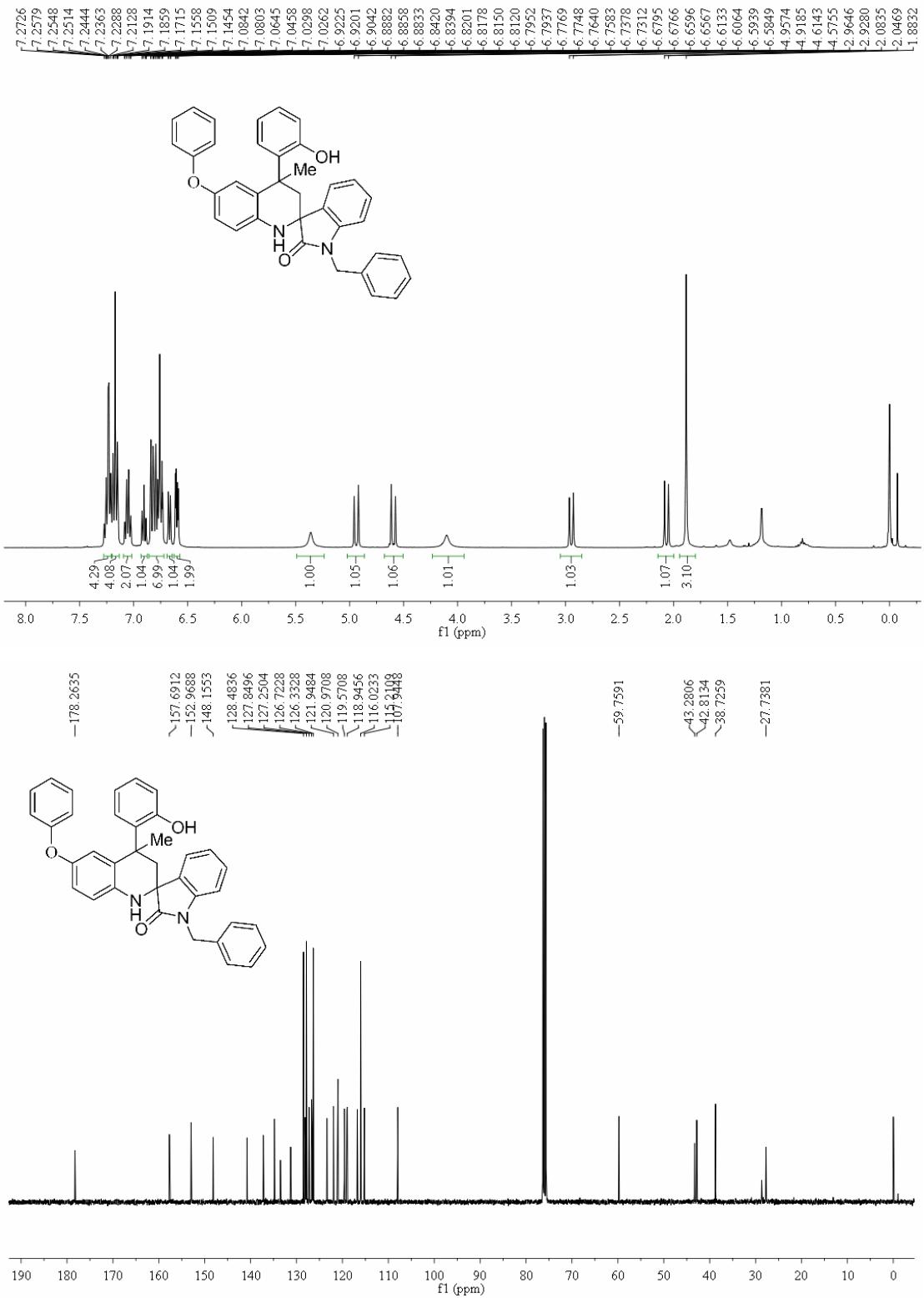
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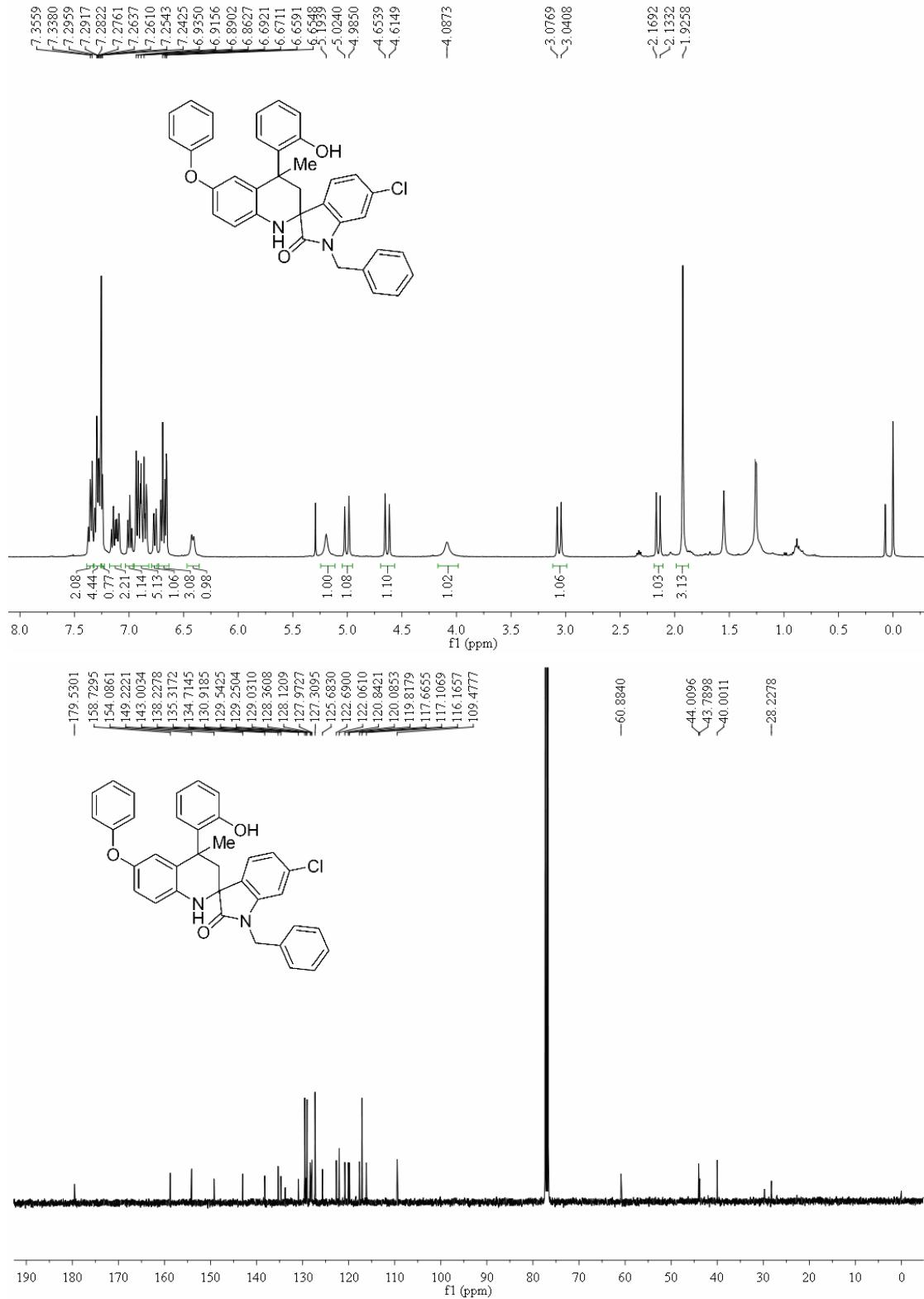
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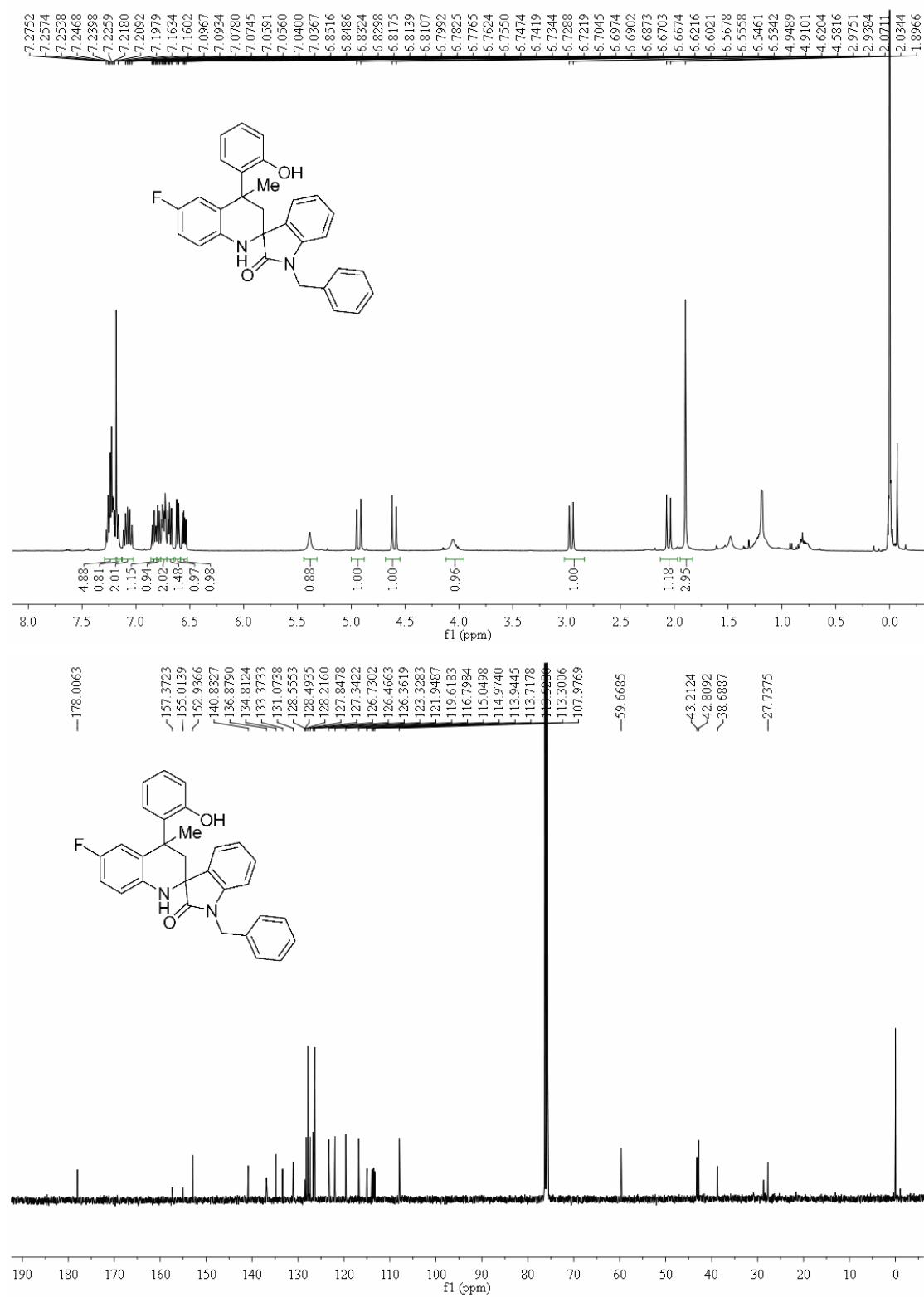
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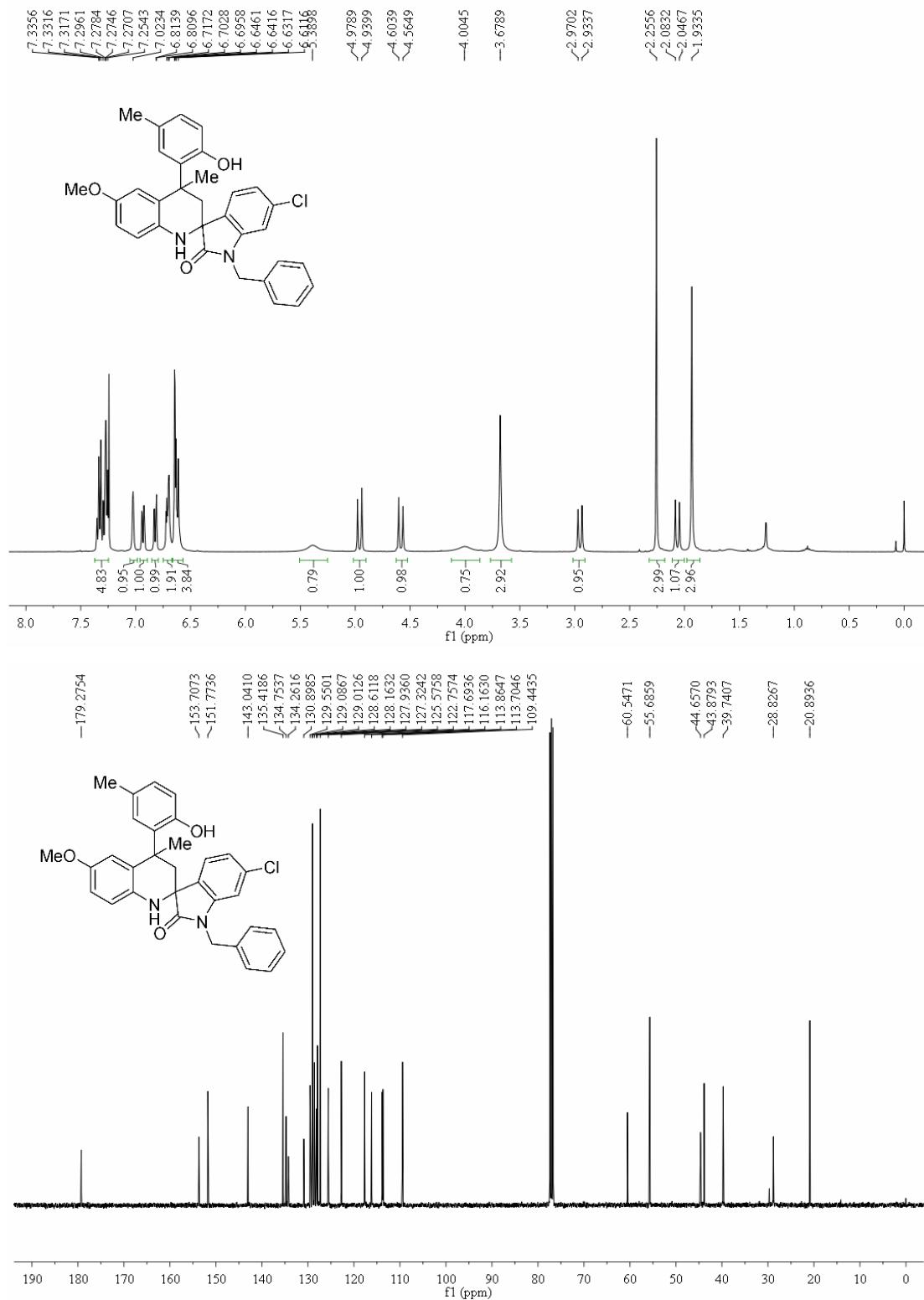
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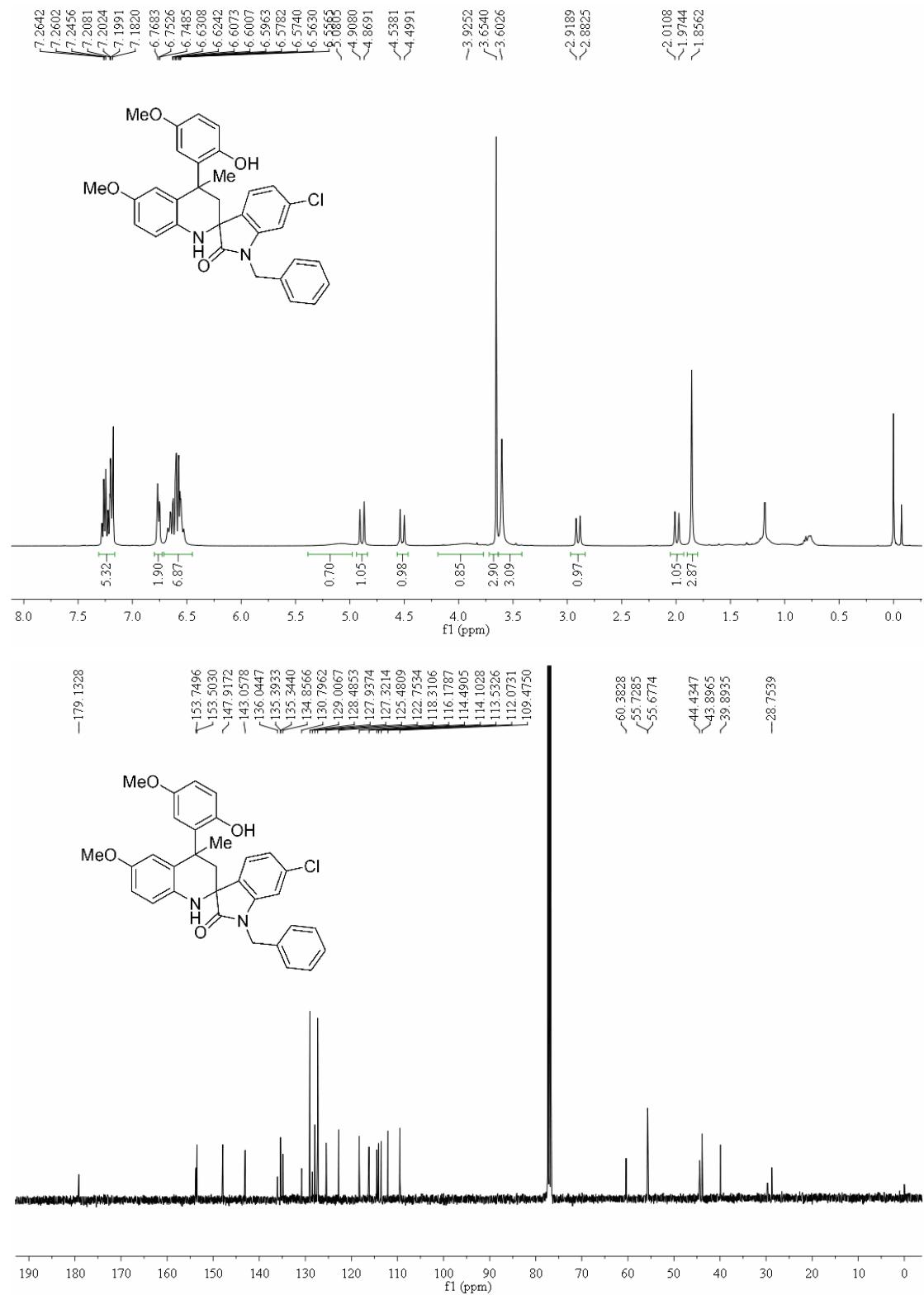
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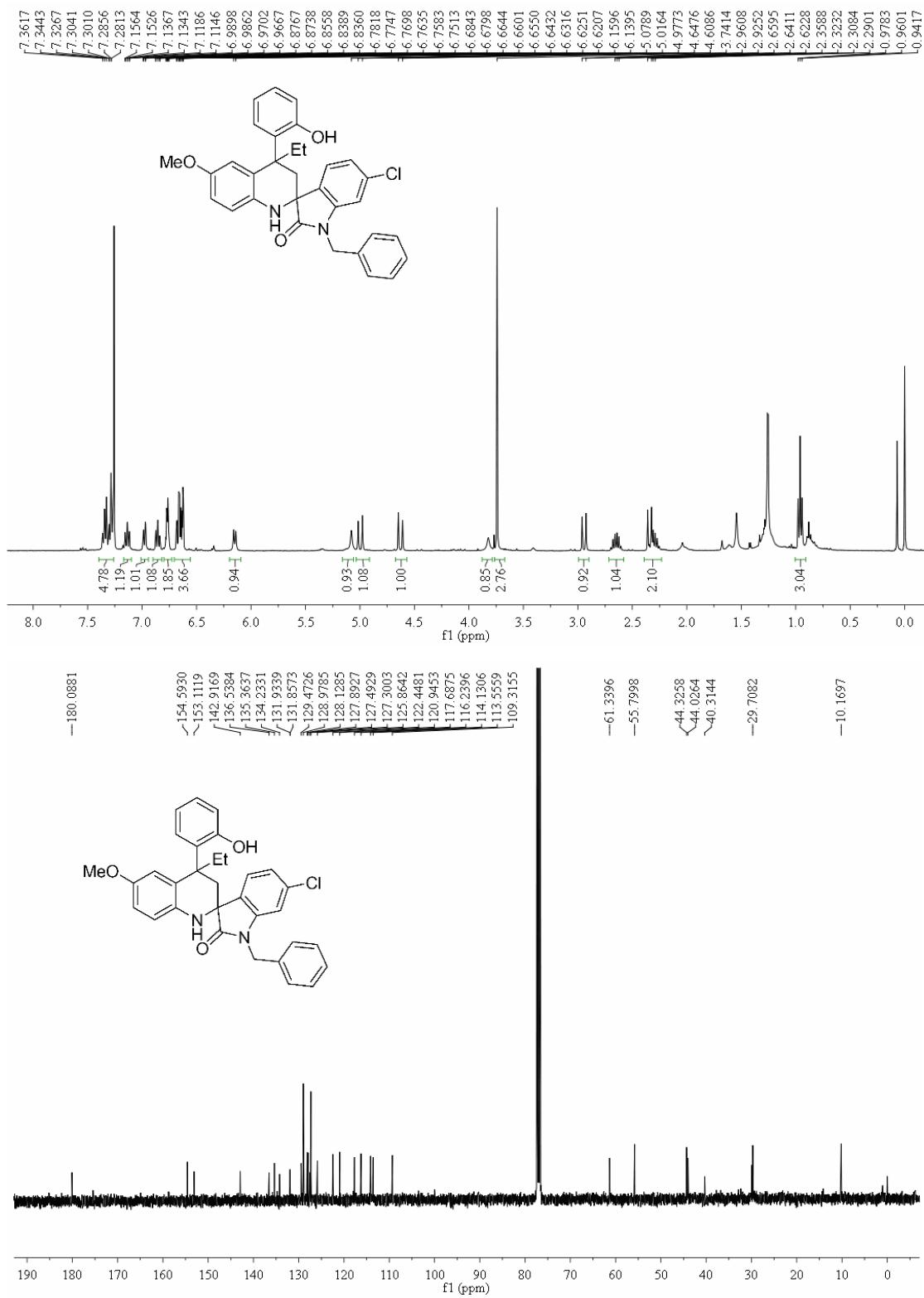
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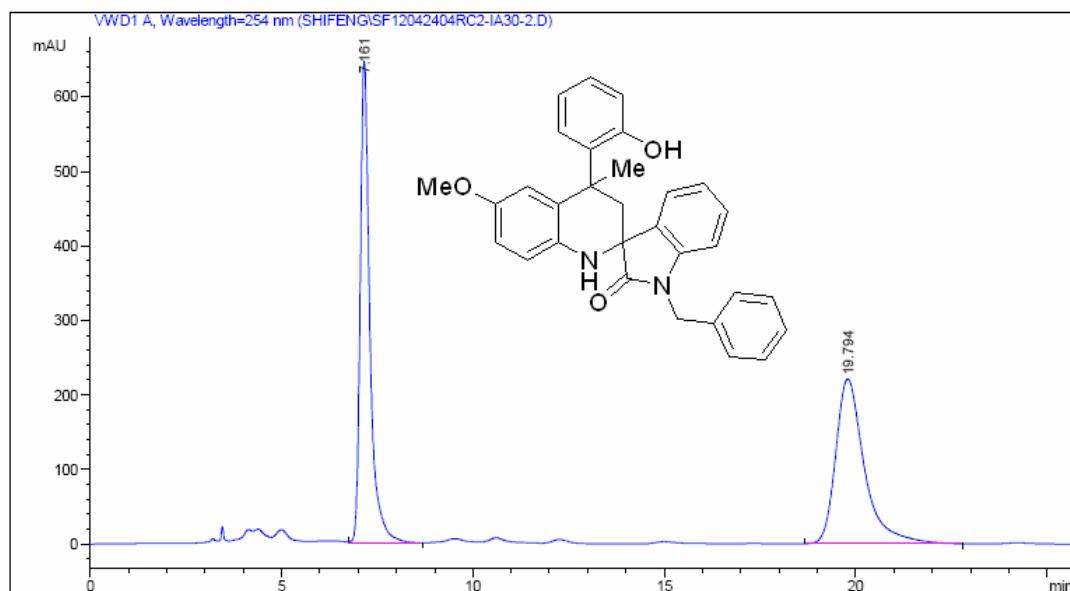


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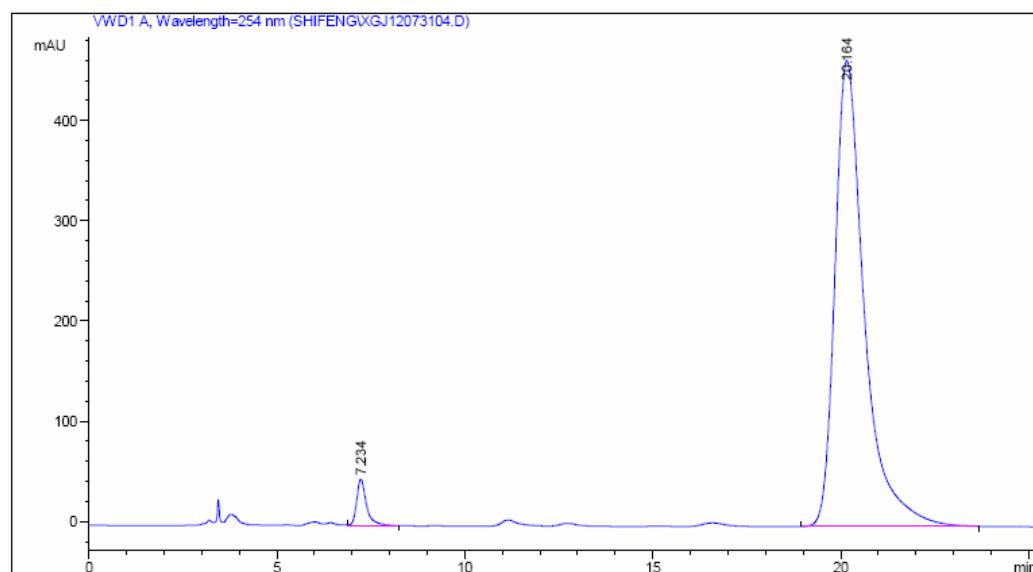


HPLC spectra:

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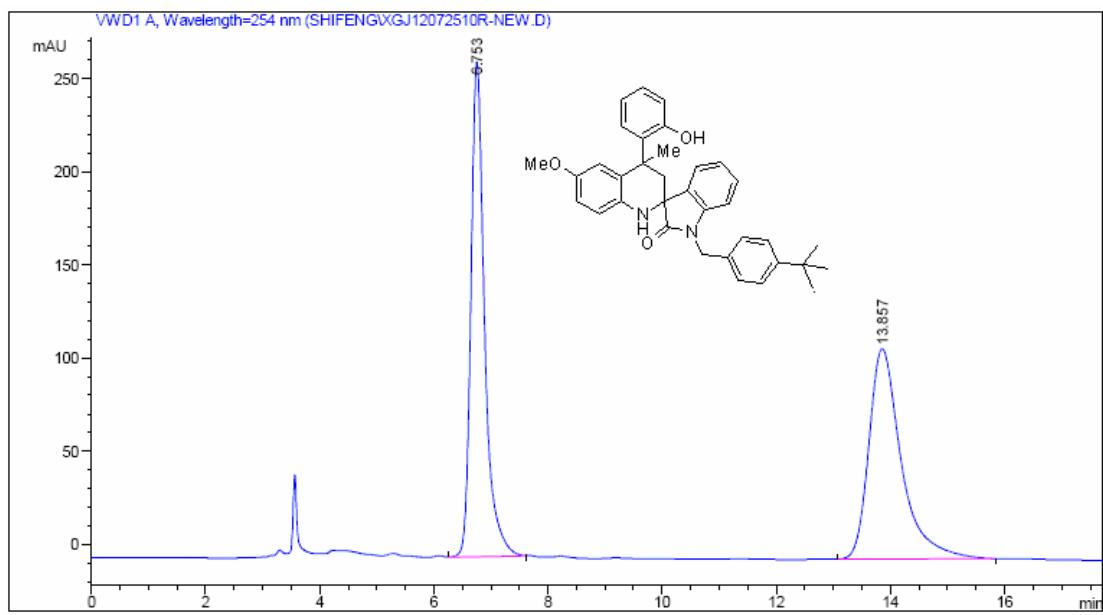


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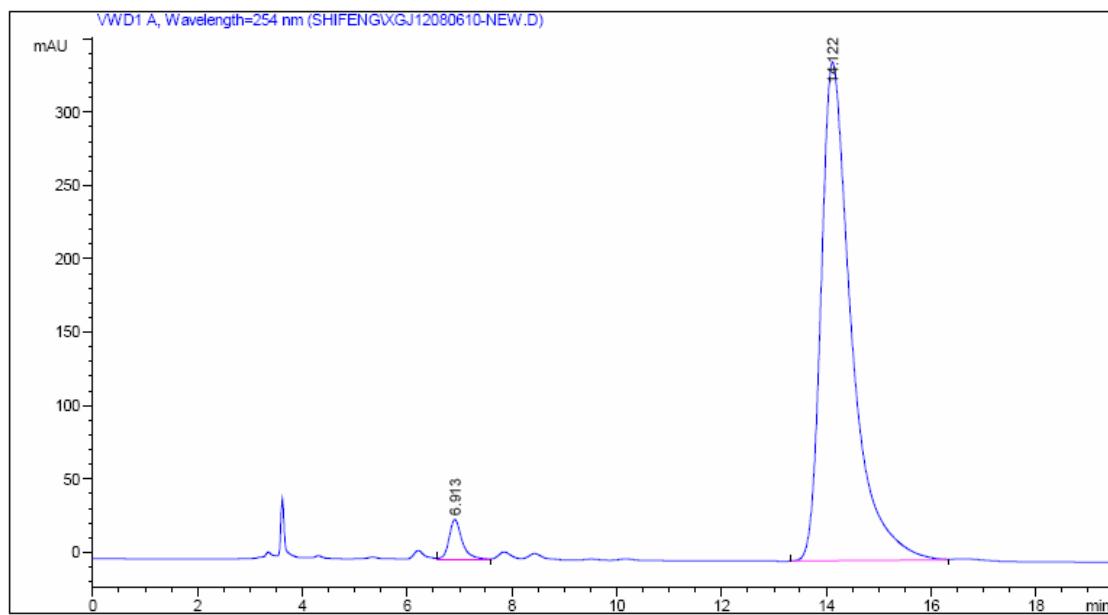


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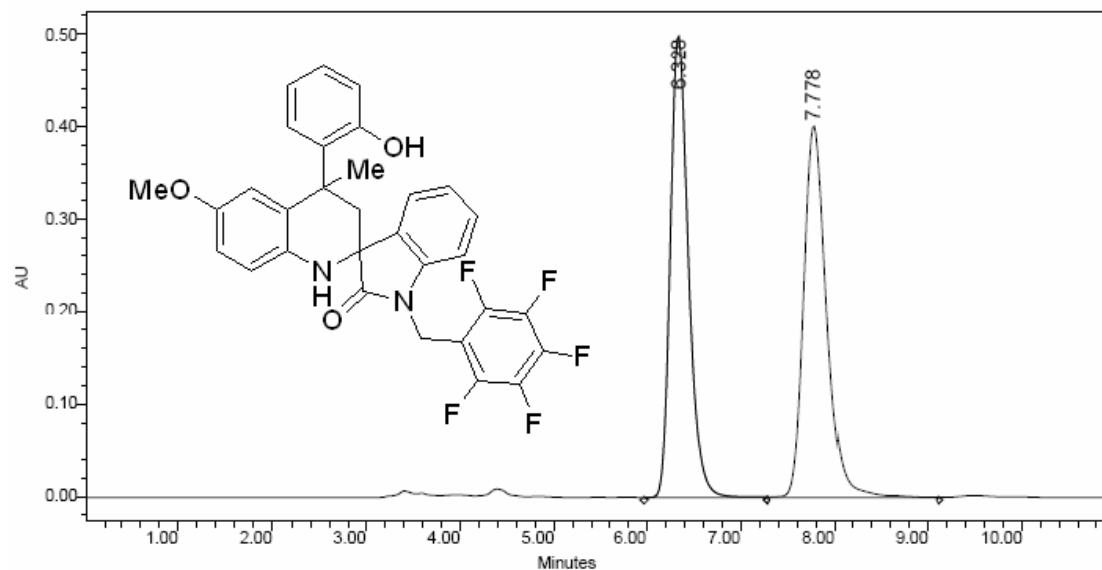


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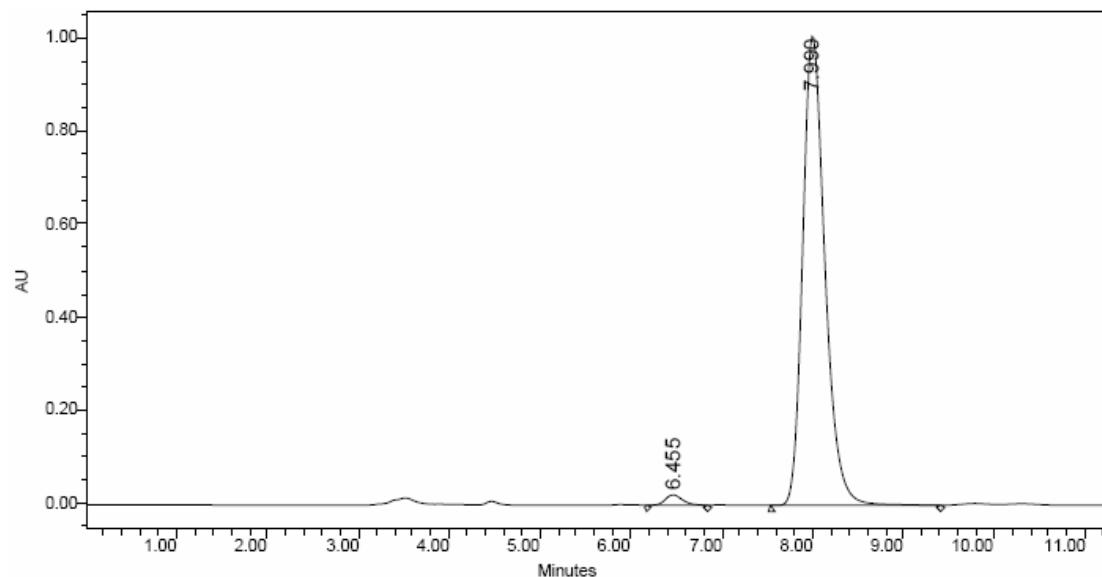


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4caa:

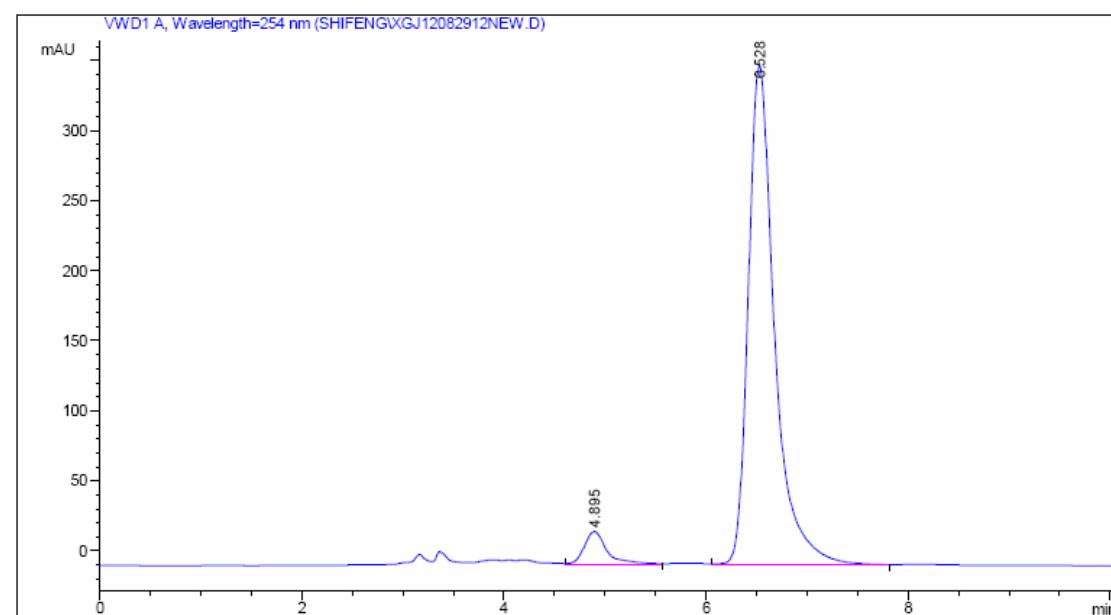
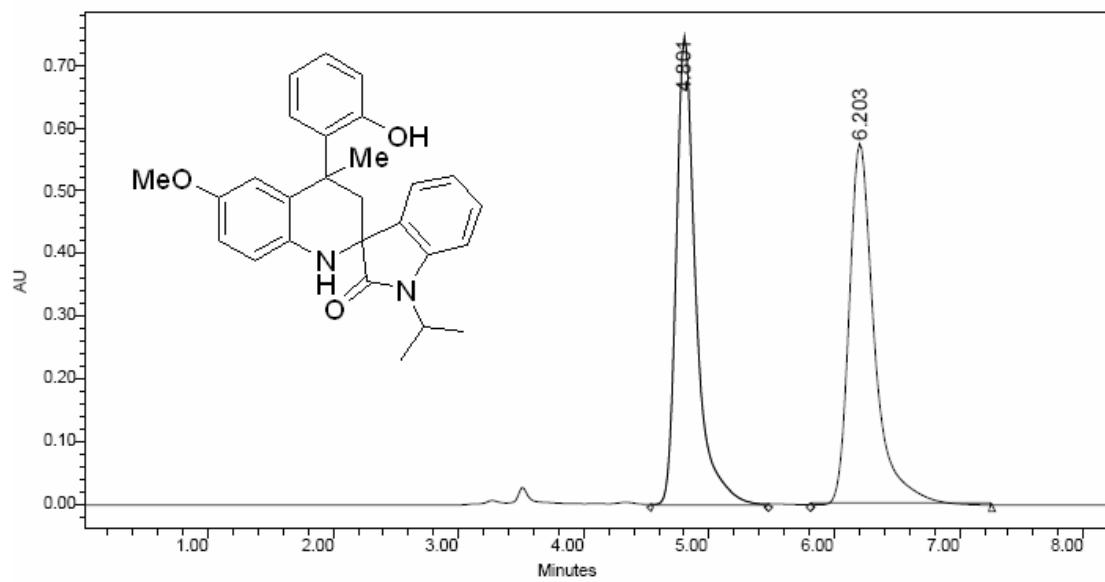


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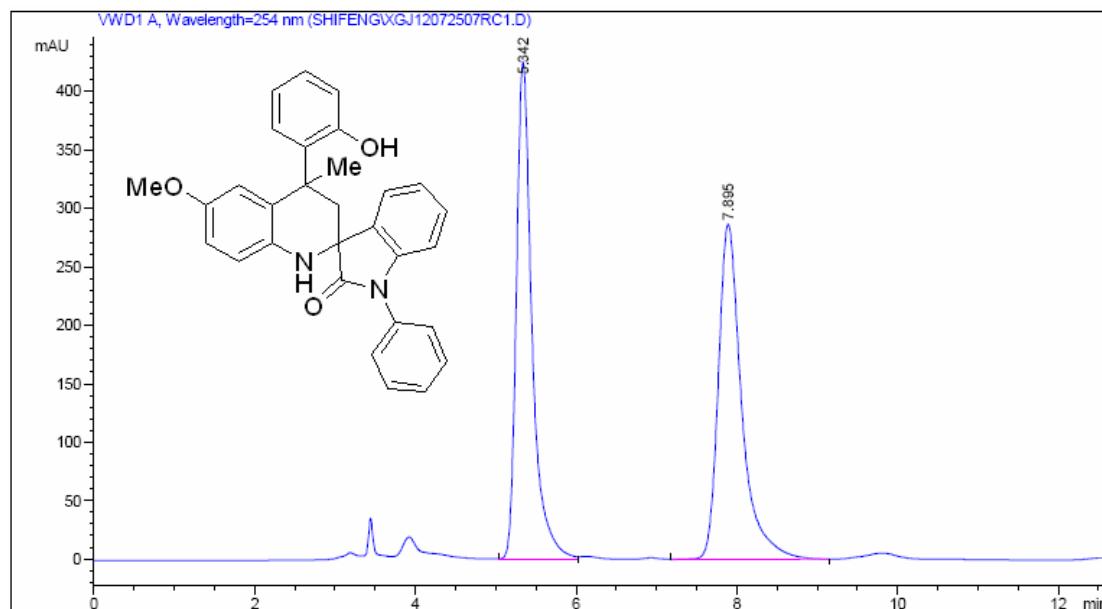


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.455	298993	1.71	22423	2.18
2	7.990	17173068	98.29	1008333	97.82

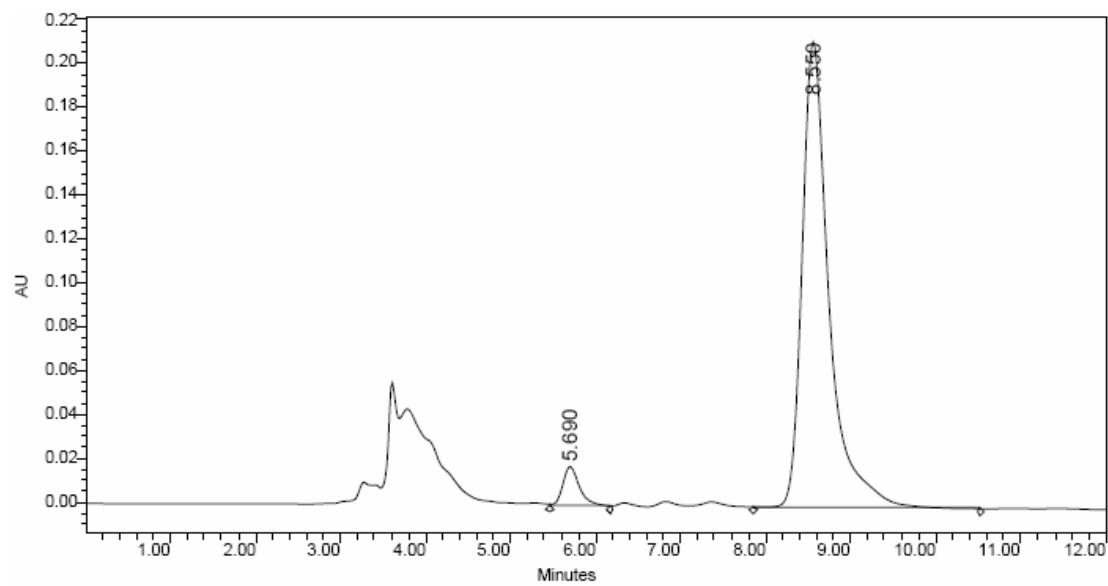
4daa:



4eaa:

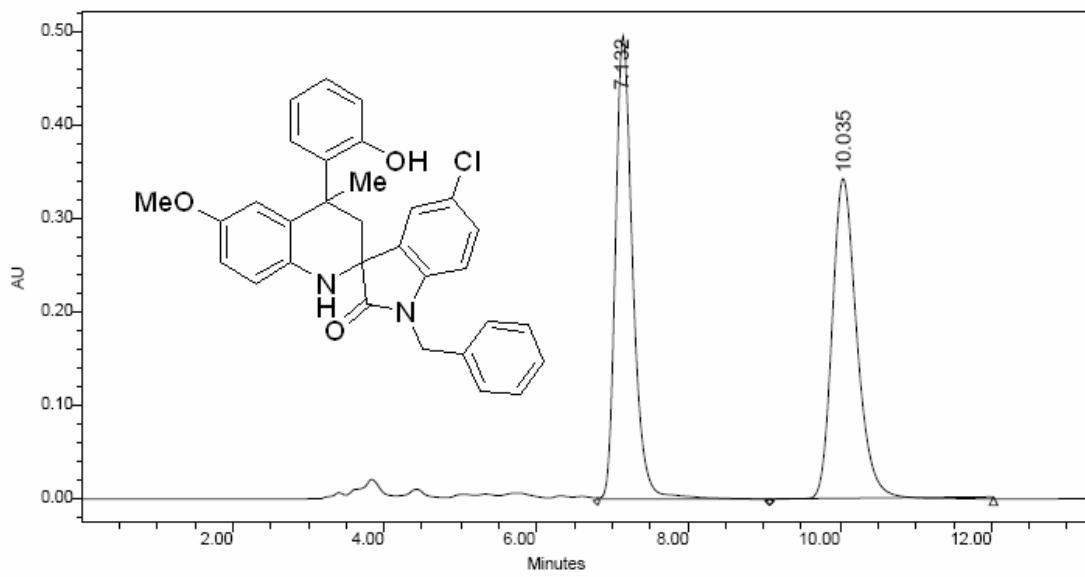


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	5.342	BV	0.2030	5755.00244	425.30197	425.30197	49.8734
2	7.895	VB	0.3027	5784.21533	286.22736	286.22736	50.1266

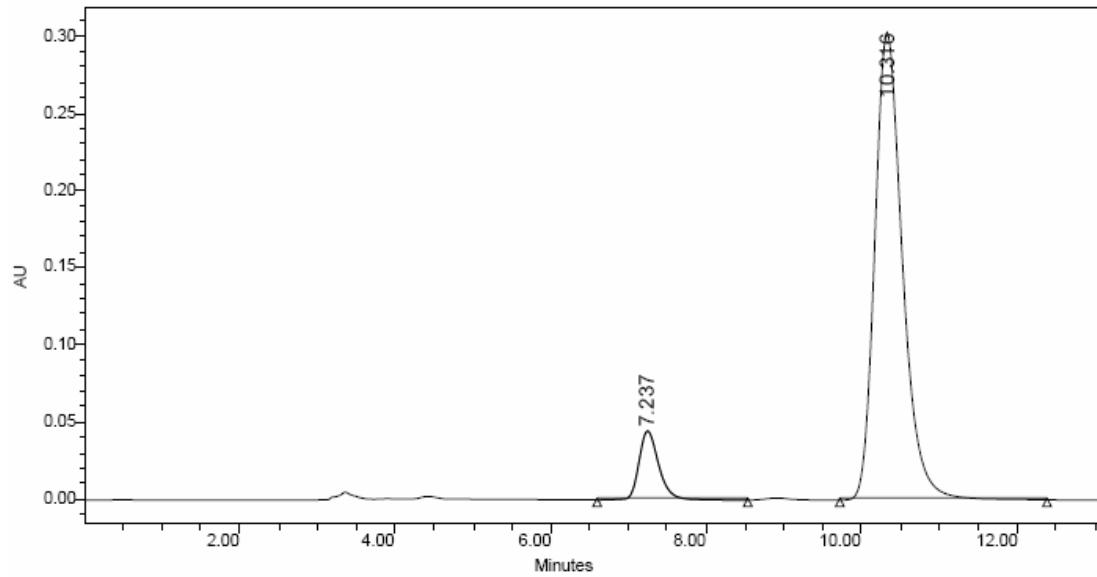


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.690	249682	5.04	17989	7.81
2	8.550	4702730	94.96	212361	92.19

4faa :

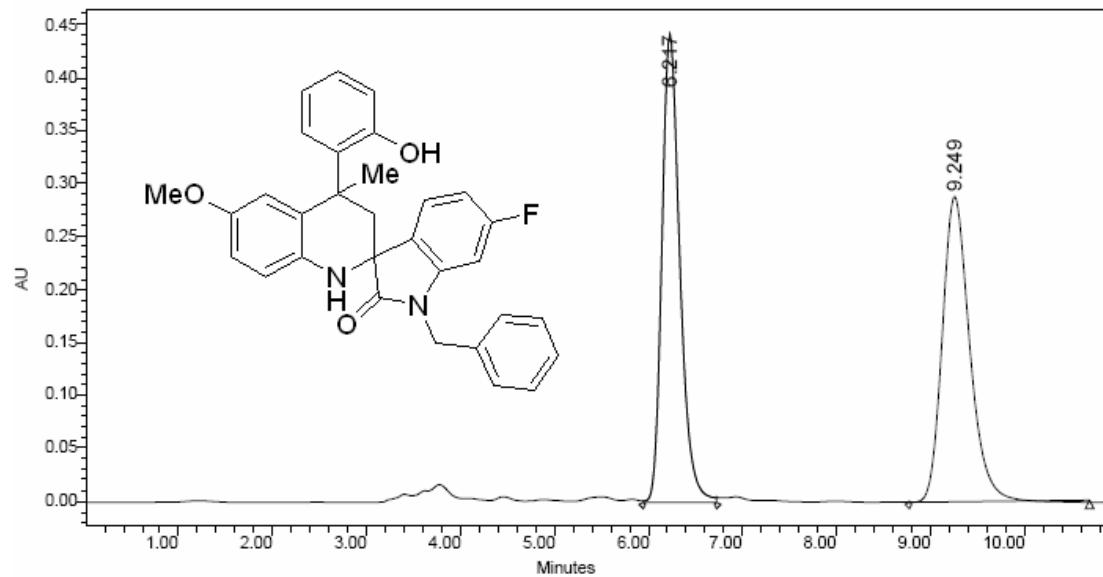


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.132	7864621	50.26	496061	59.08
2	10.035	7783909	49.74	343577	40.92

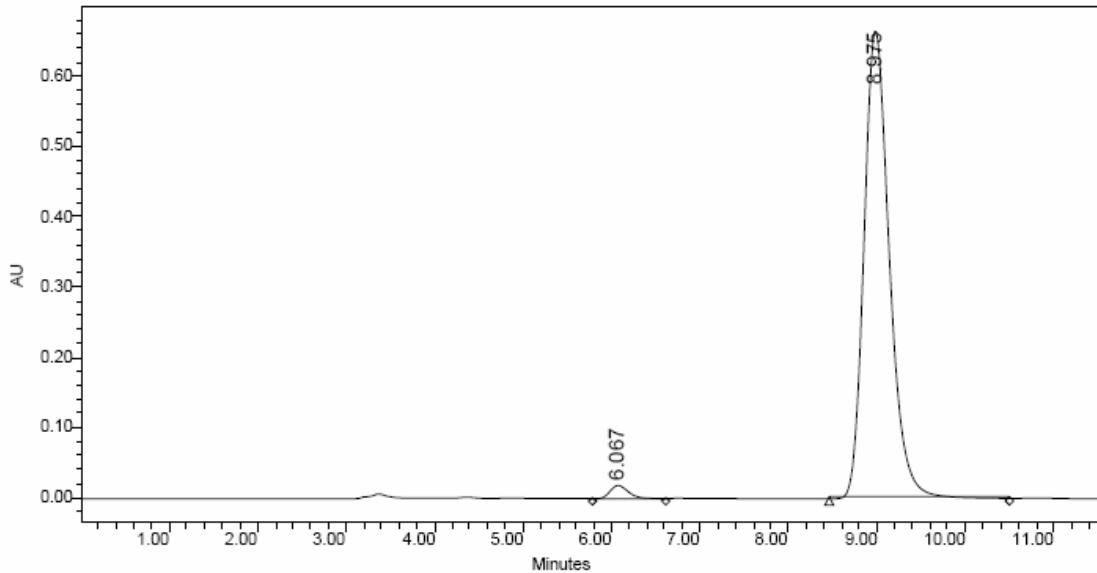


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.237	790576	9.52	44694	12.85
2	10.316	7511558	90.48	303050	87.15

4gaa :

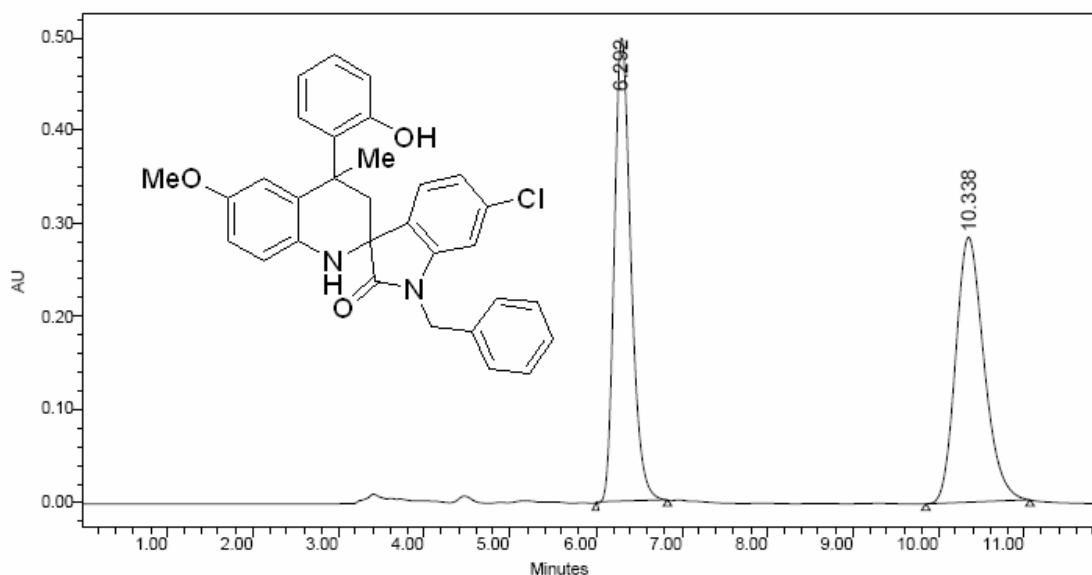


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.217	5873225	49.93	441767	60.48
2	9.249	5890138	50.07	288690	39.52

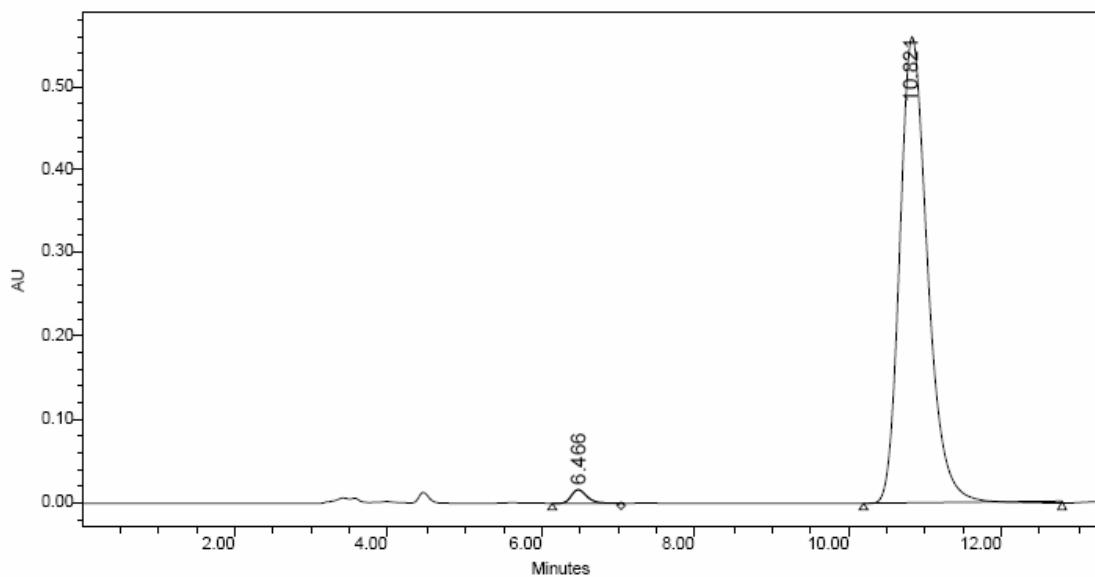


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.067	280912	2.07	18859	2.75
2	8.975	13313117	97.93	666514	97.25

4haa :

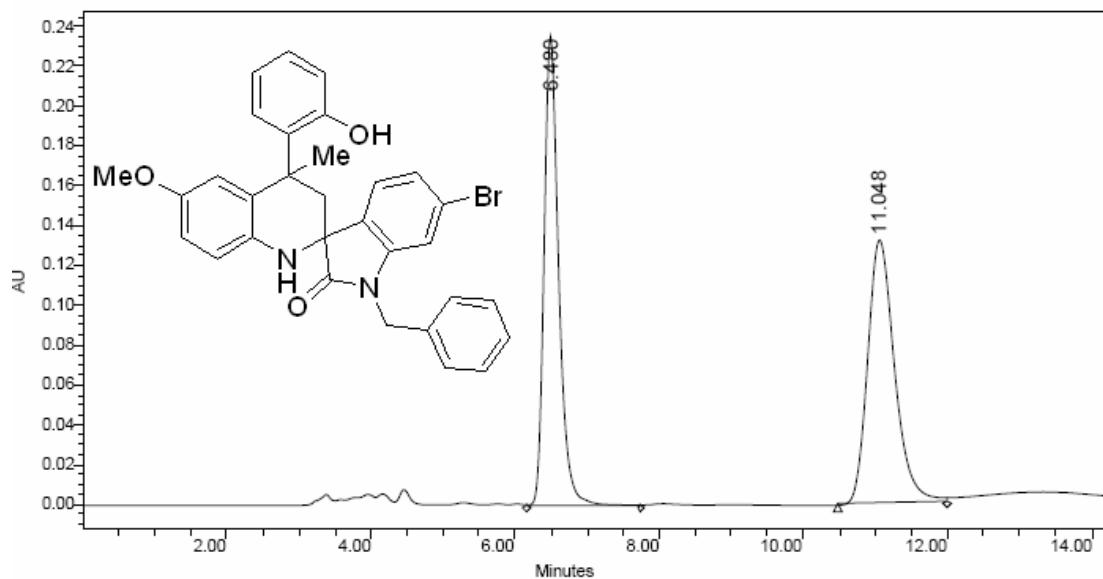


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.292	6734540	50.60	501018	63.70
2	10.338	6574040	49.40	285512	36.30

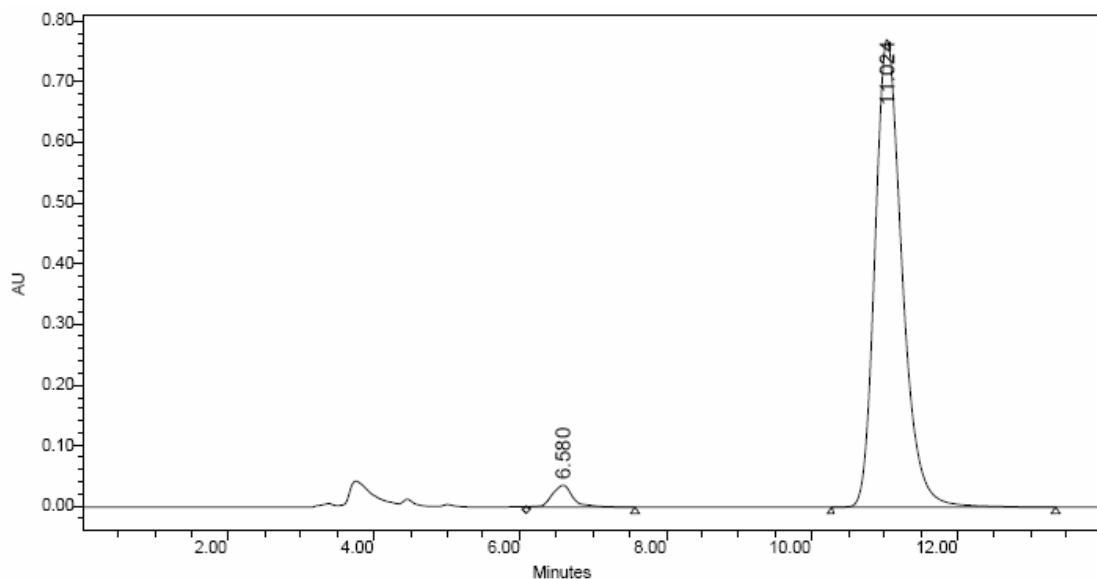


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.466	237407	1.65	16361	2.83
2	10.824	14170810	98.35	560888	97.17

4iaa:

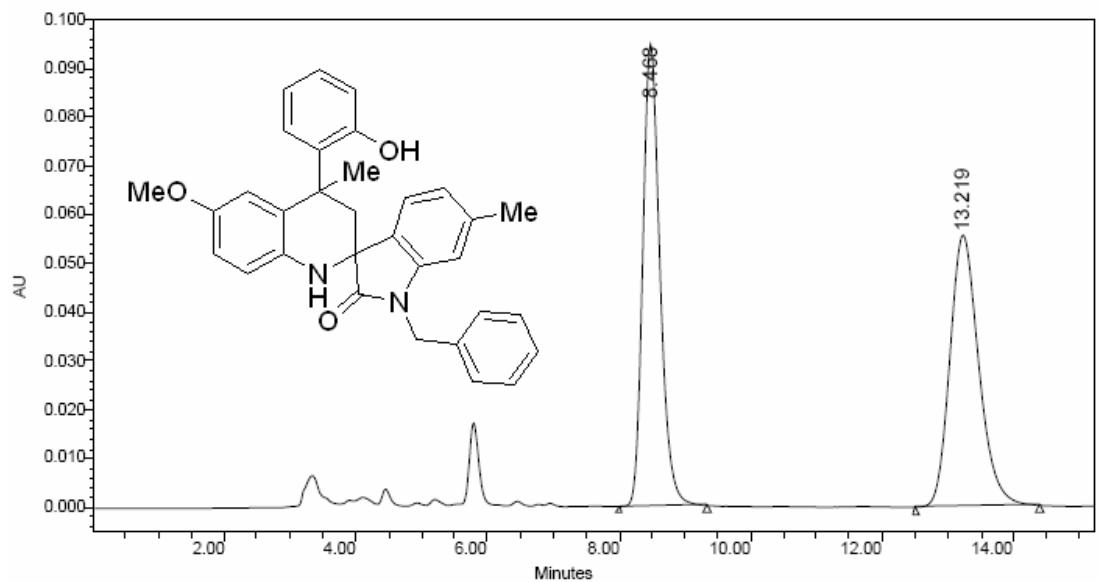


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.480	3319922	49.05	235869	64.01
2	11.048	3447835	50.95	132645	35.99

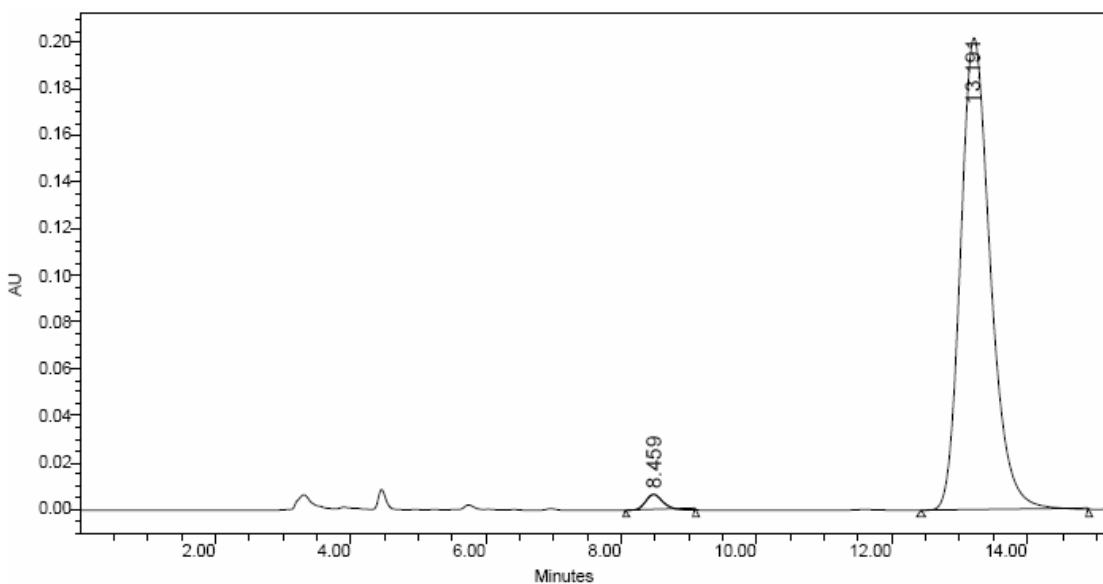


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.580	715957	3.47	36074	4.47
2	11.024	19900316	96.53	771004	95.53

4jaa :

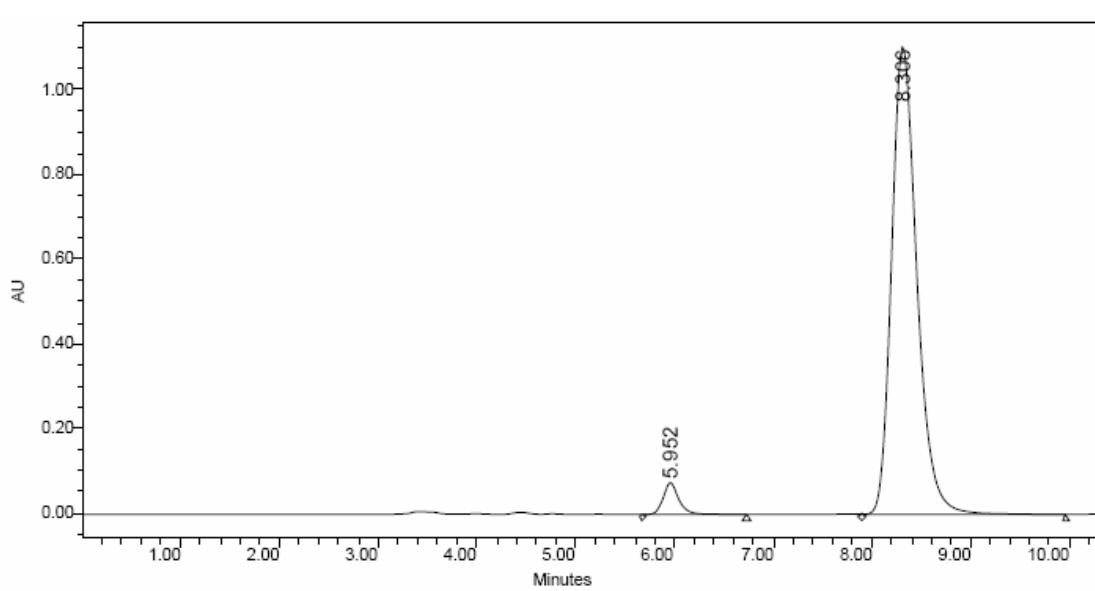
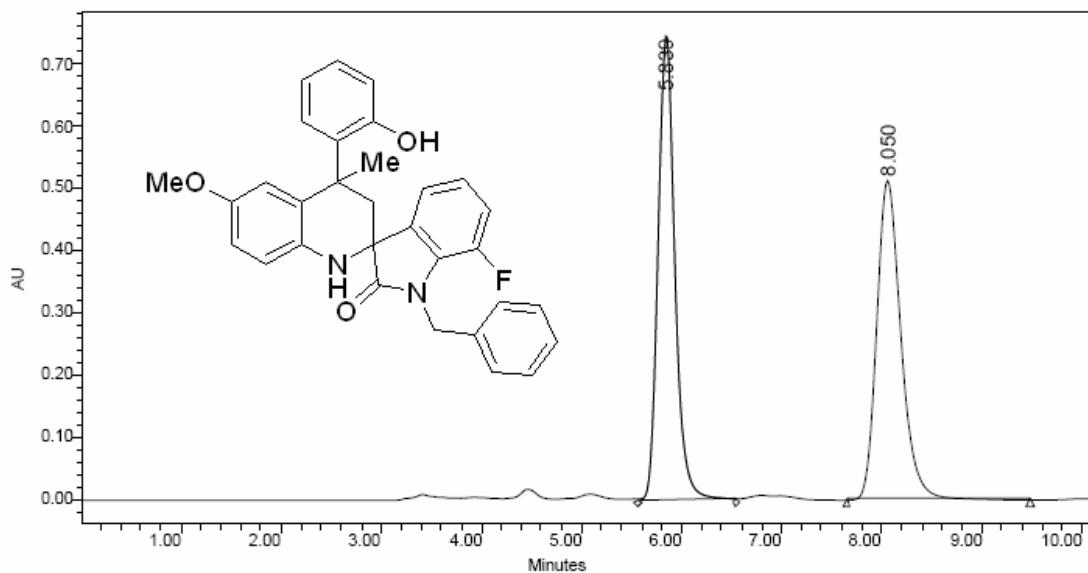


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.468	1711105	50.16	94723	63.00
2	13.219	1700112	49.84	55637	37.00

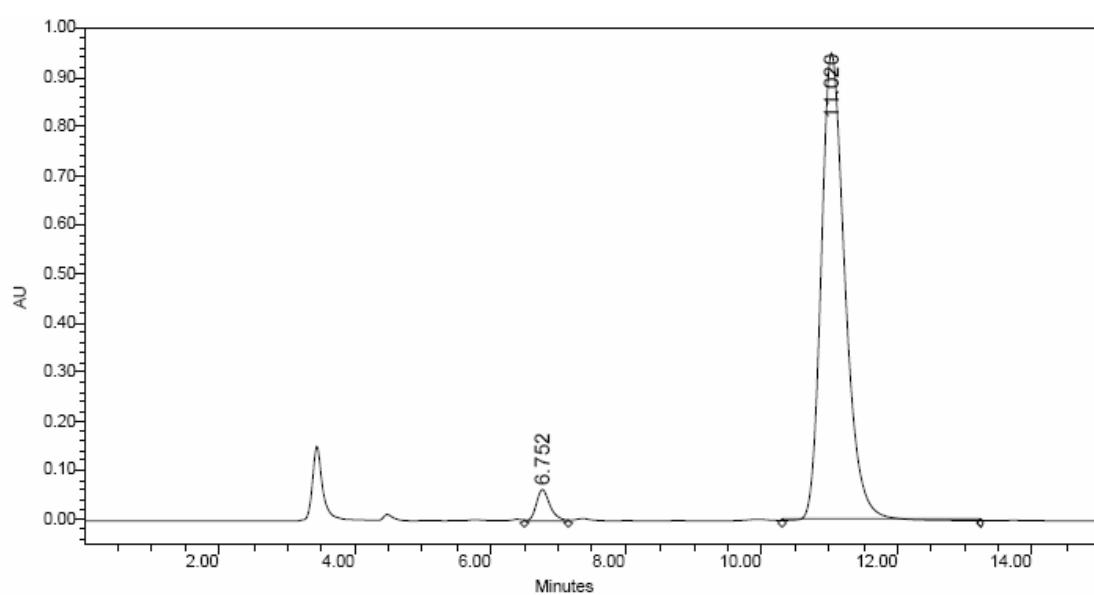
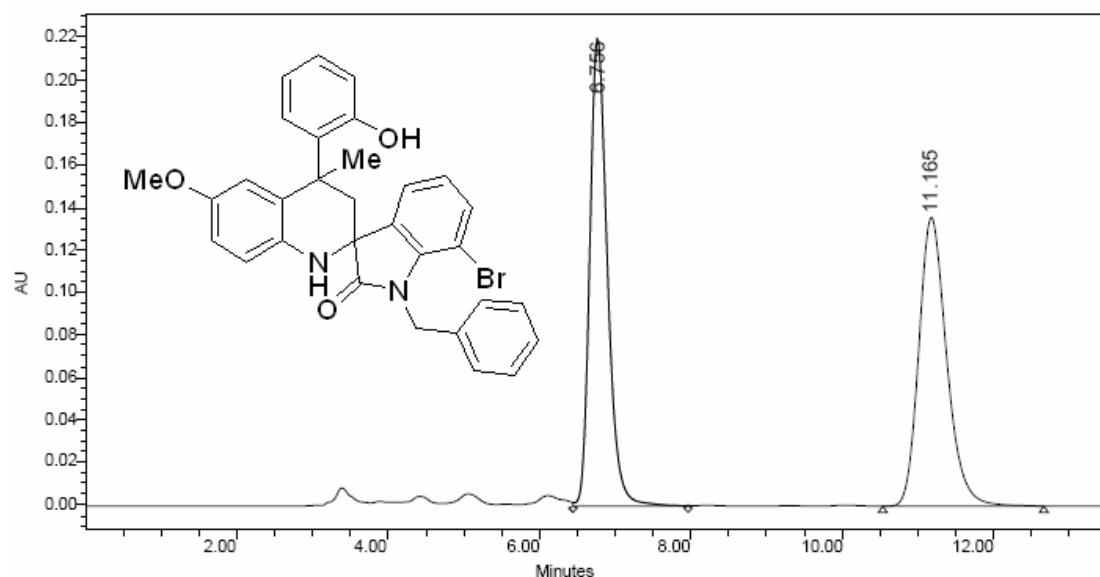


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.459	122448	1.94	6741	3.22
2	13.191	6195834	98.06	202431	96.78

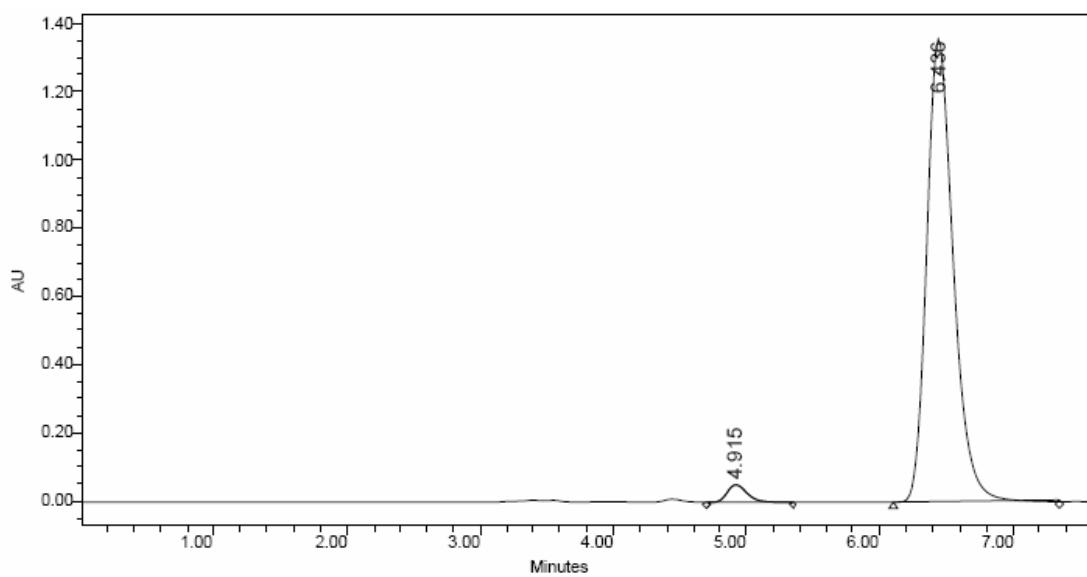
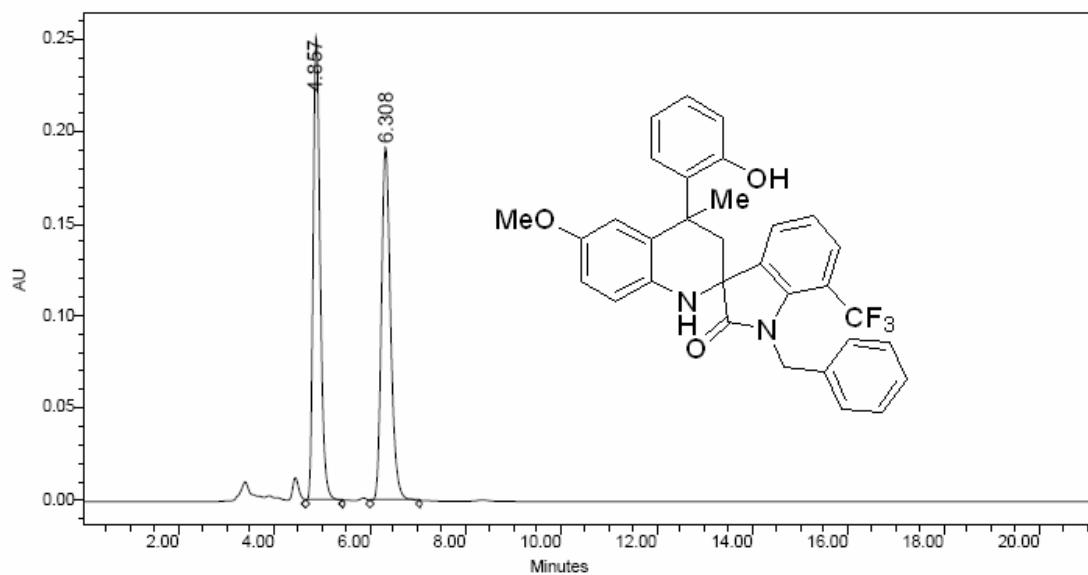
4kaa :



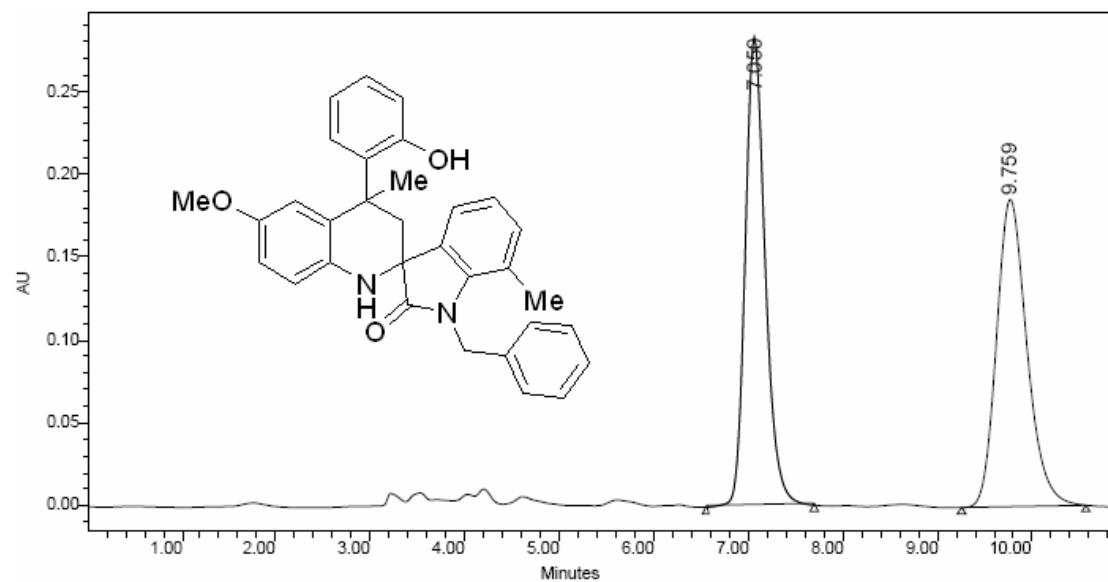
4laa :



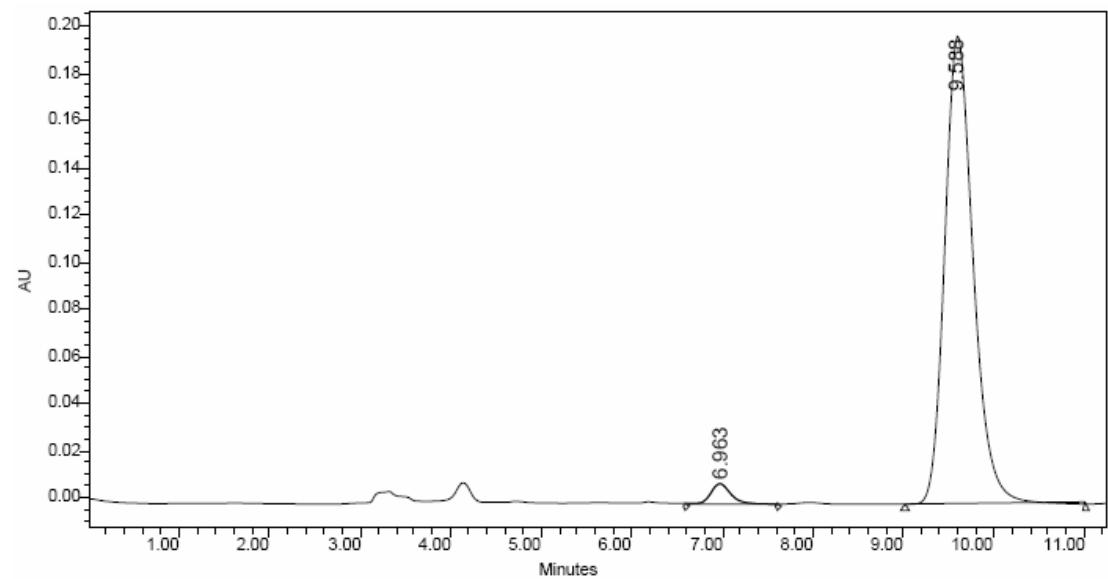
4maa :



4naa :

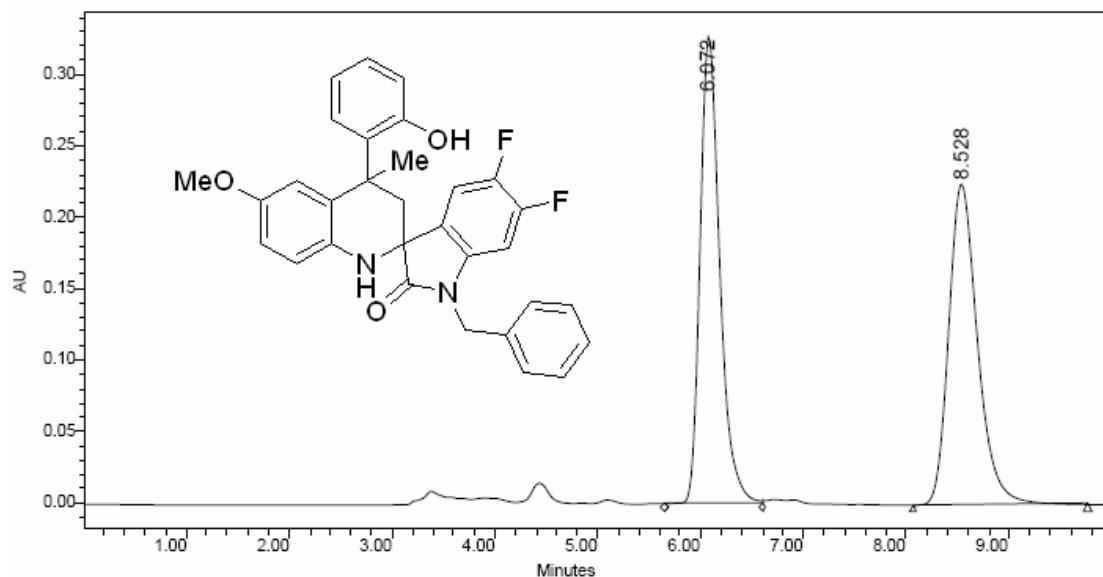


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.050	4160161	50.10	282727	60.38
2	9.759	4143628	49.90	185522	39.62

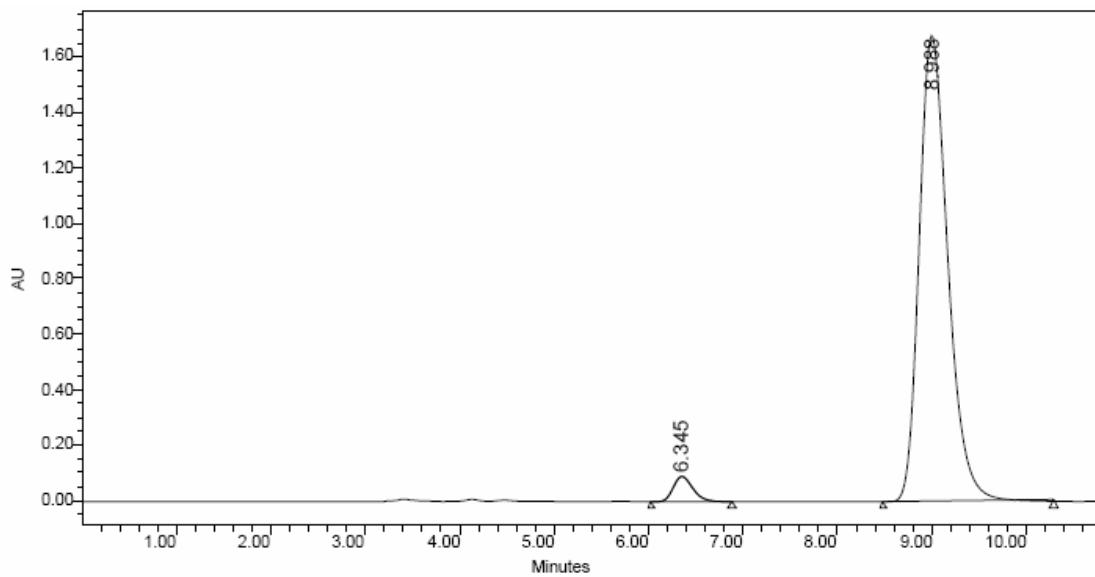


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.963	138249	3.08	8688	4.19
2	9.588	4344551	96.92	198440	95.81

4oaa :

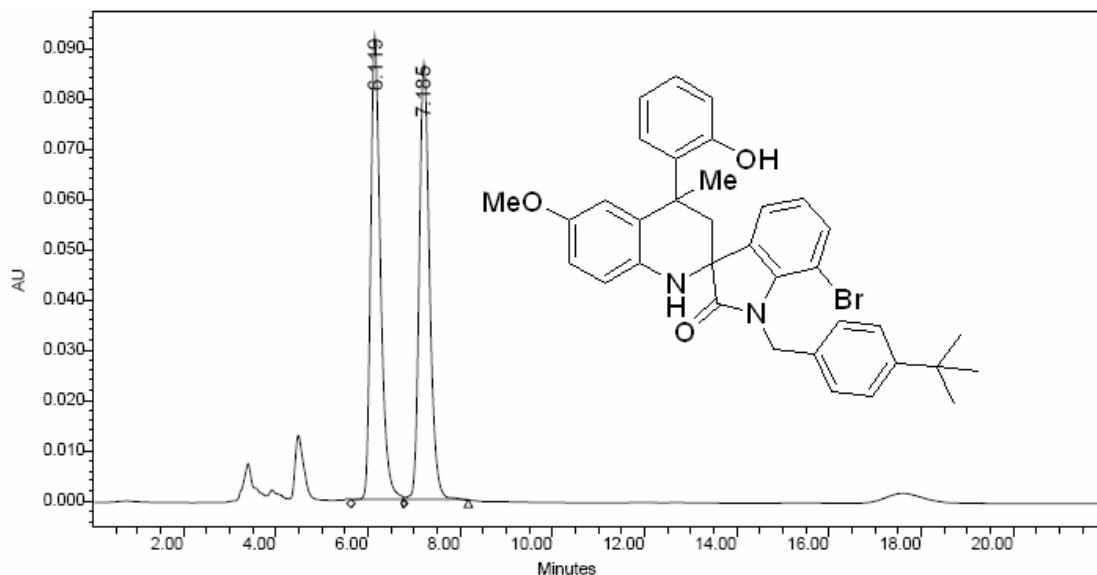


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.072	4369887	49.97	327431	59.32
2	8.528	4375065	50.03	224585	40.68

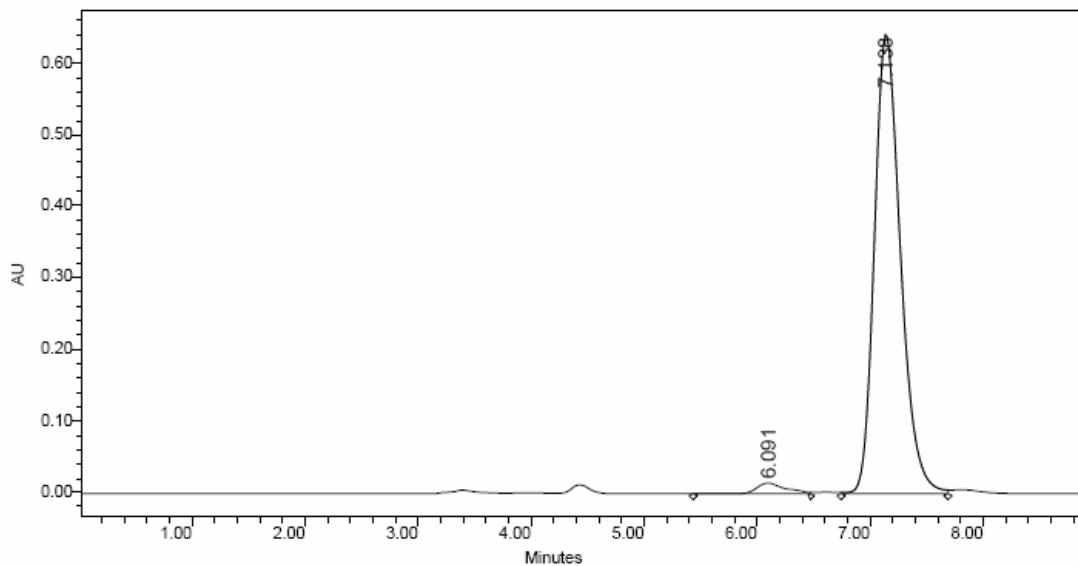


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.345	1309441	3.56	90788	5.12
2	8.988	35432731	96.44	1682118	94.88

4paa :

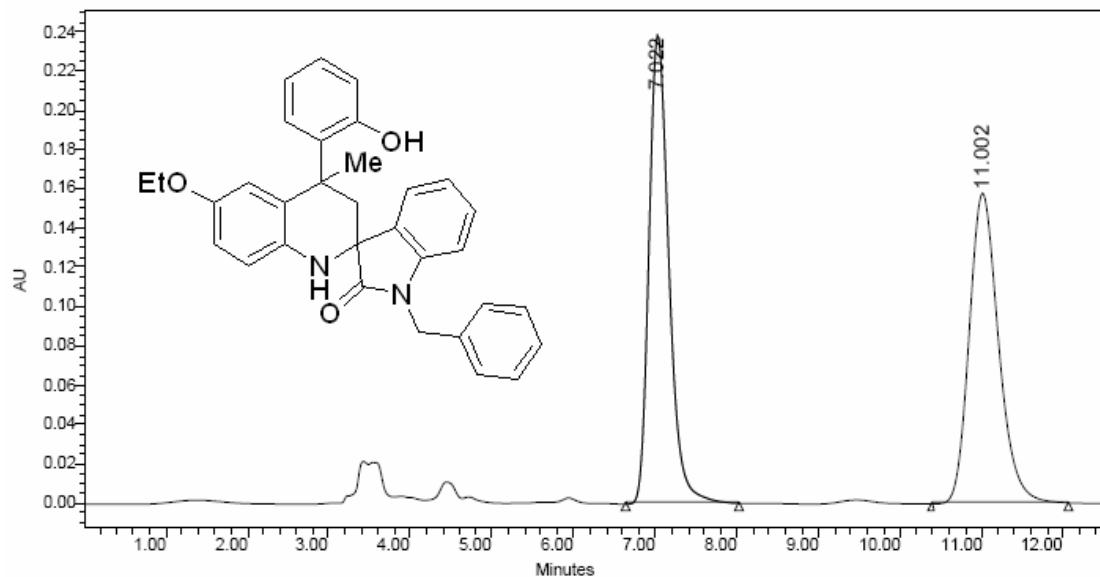


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.119	1377200	50.29	92137	51.51
2	7.185	1361143	49.71	86751	48.49

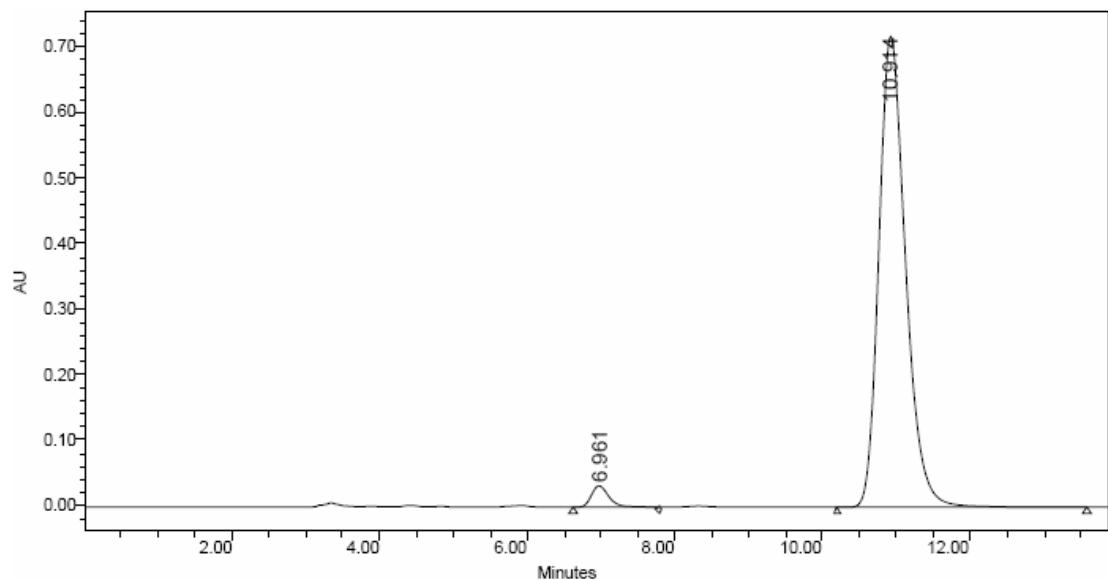


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.091	271189	2.56	14965	2.28
2	7.138	10327298	97.44	642131	97.72

4aba :

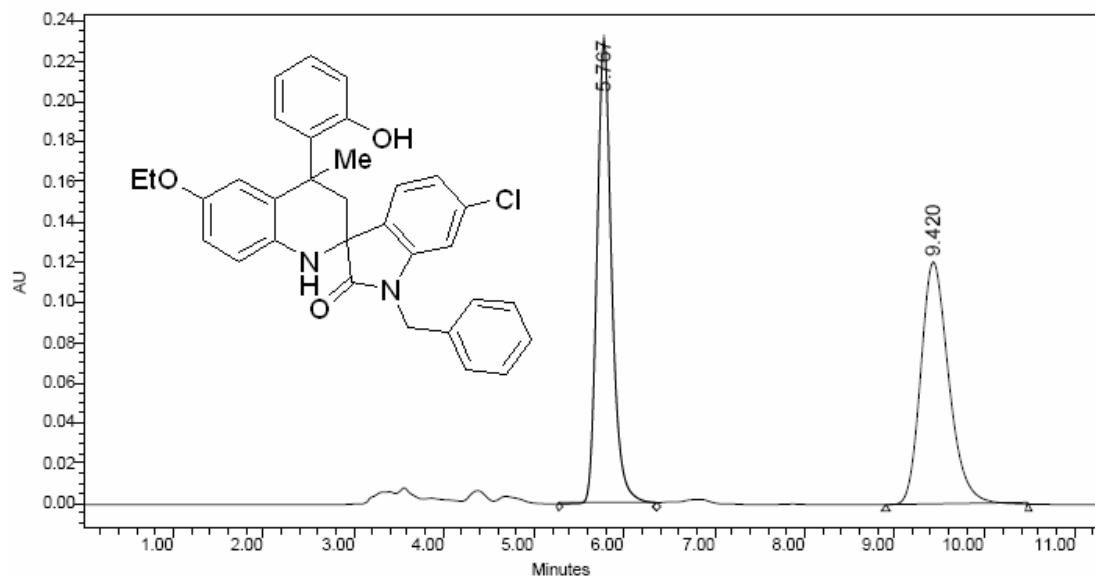


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.022	4046748	50.62	238748	60.17
2	11.002	3947958	49.38	158014	39.83

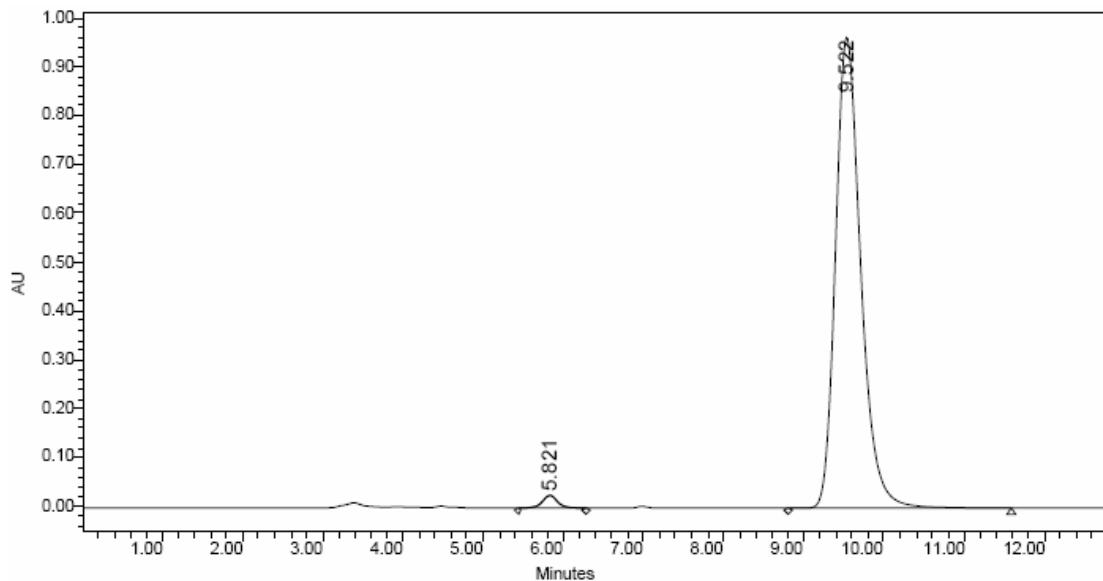


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.961	541509	2.91	32700	4.35
2	10.914	18069968	97.09	719353	95.65

4hba:

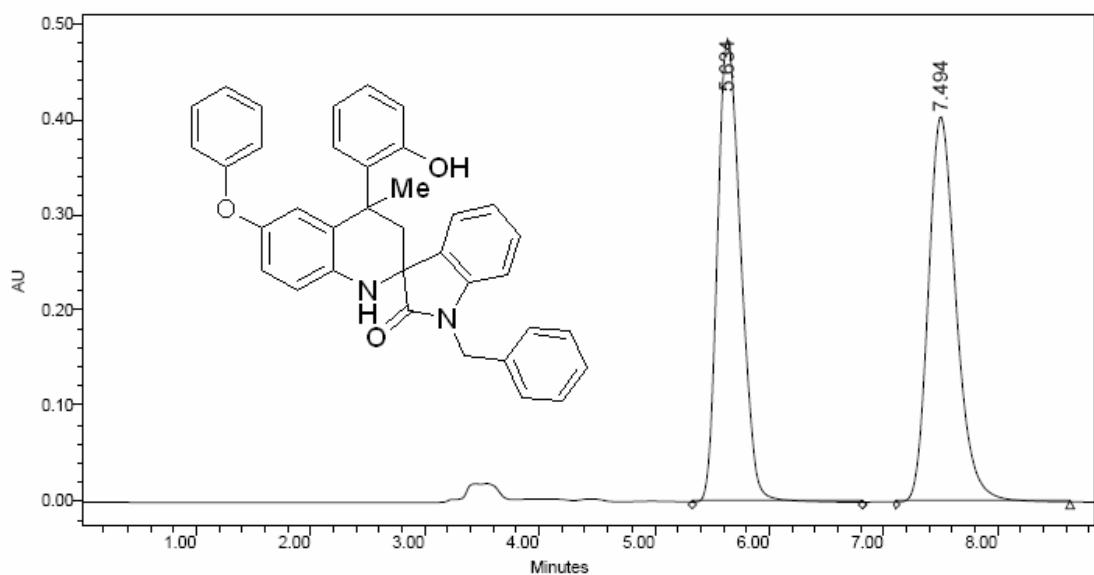


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.767	2639508	50.30	230902	65.67
2	9.420	2607779	49.70	120701	34.33

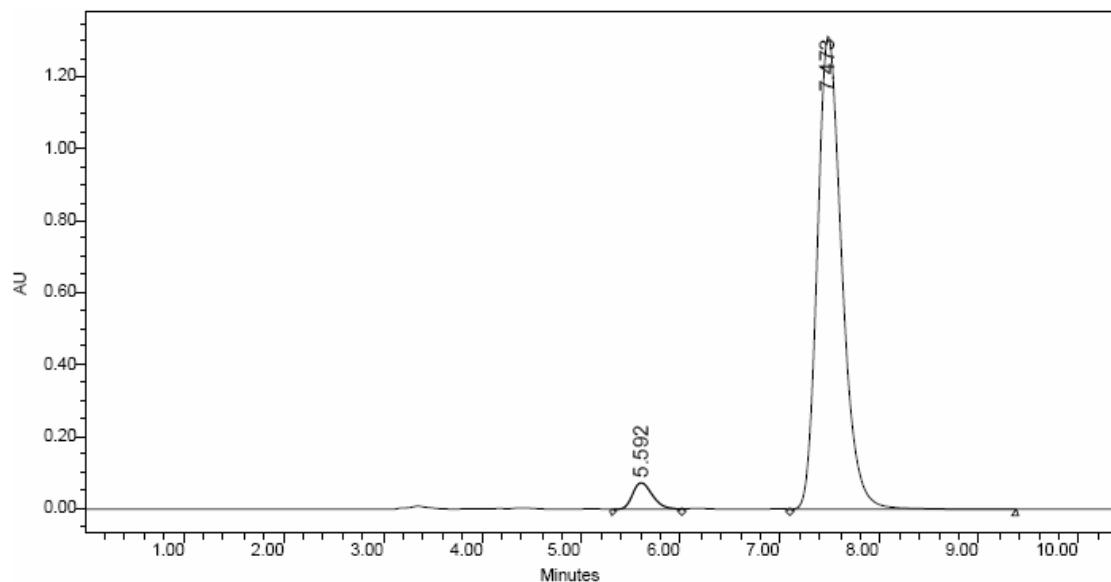


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.821	345499	1.61	25792	2.61
2	9.522	21068994	98.39	963837	97.39

4aca:

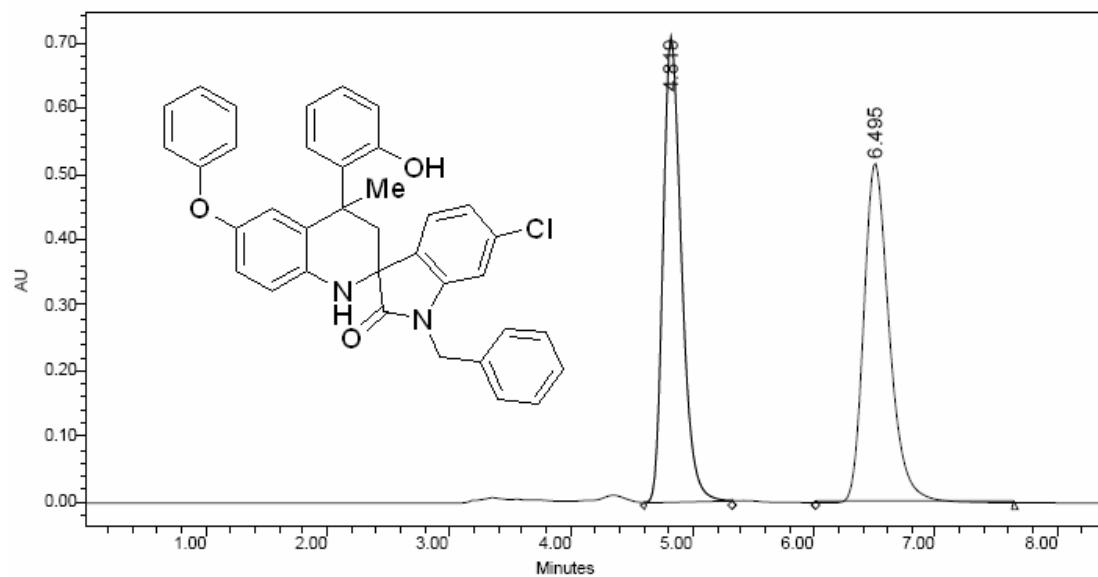


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.634	6873249	50.16	485446	54.56
2	7.494	6830161	49.84	404253	45.44

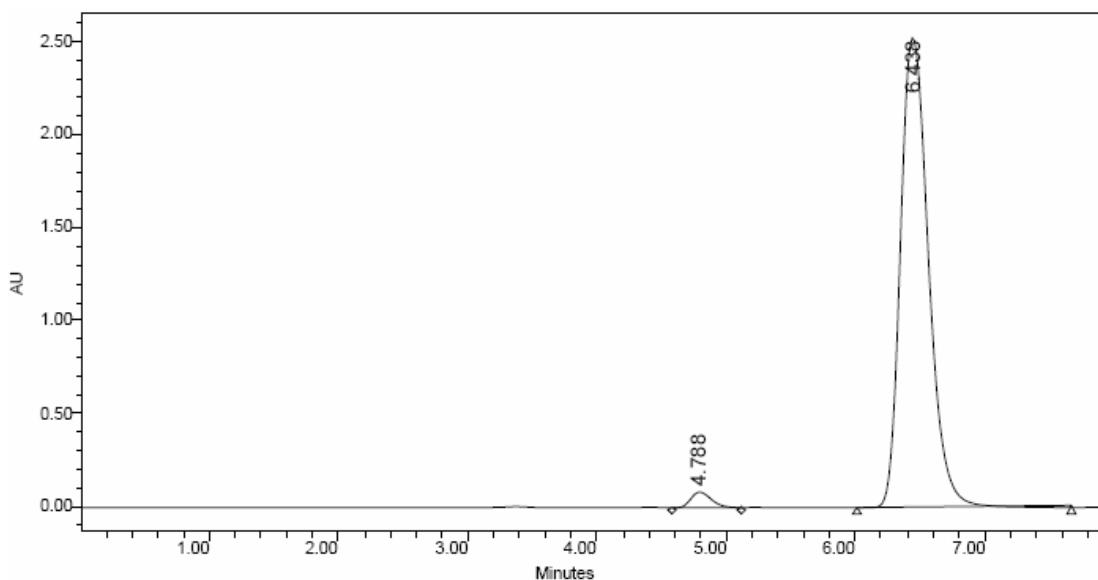


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.592	1039137	4.40	74131	5.32
2	7.473	22568345	95.60	1318296	94.68

4hca:

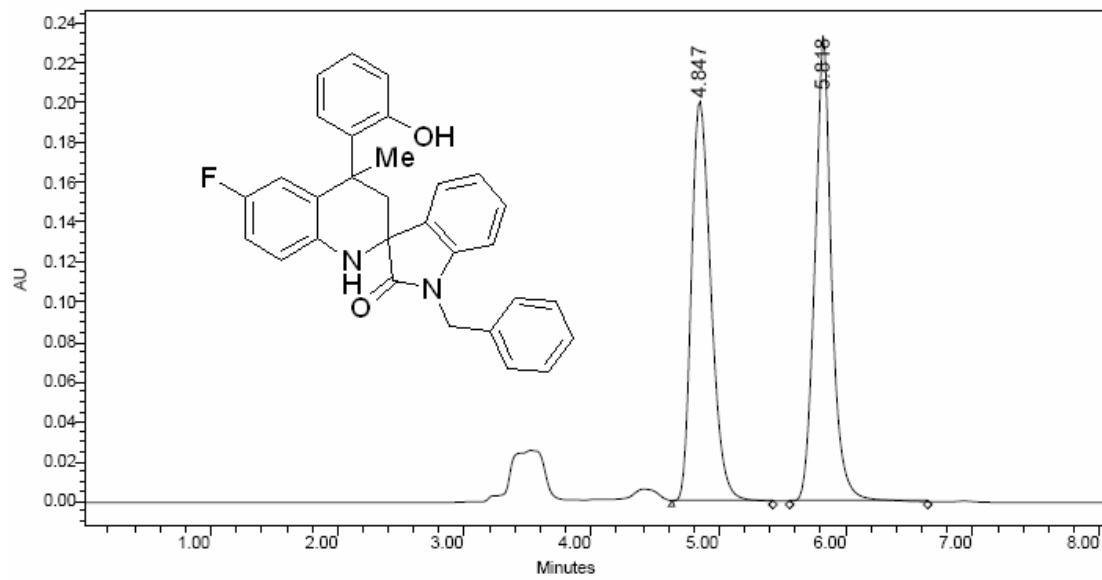


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.819	7554550	49.90	709805	57.82
2	6.495	7585606	50.10	517888	42.18

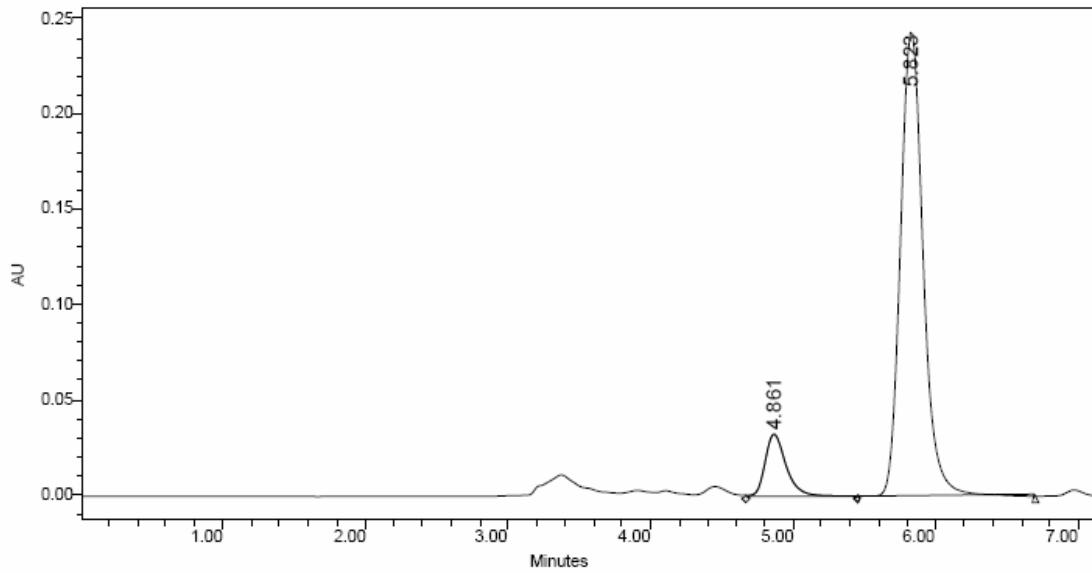


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.788	941508	2.41	84709	3.24
2	6.438	38158743	97.59	2531378	96.76

4ada:

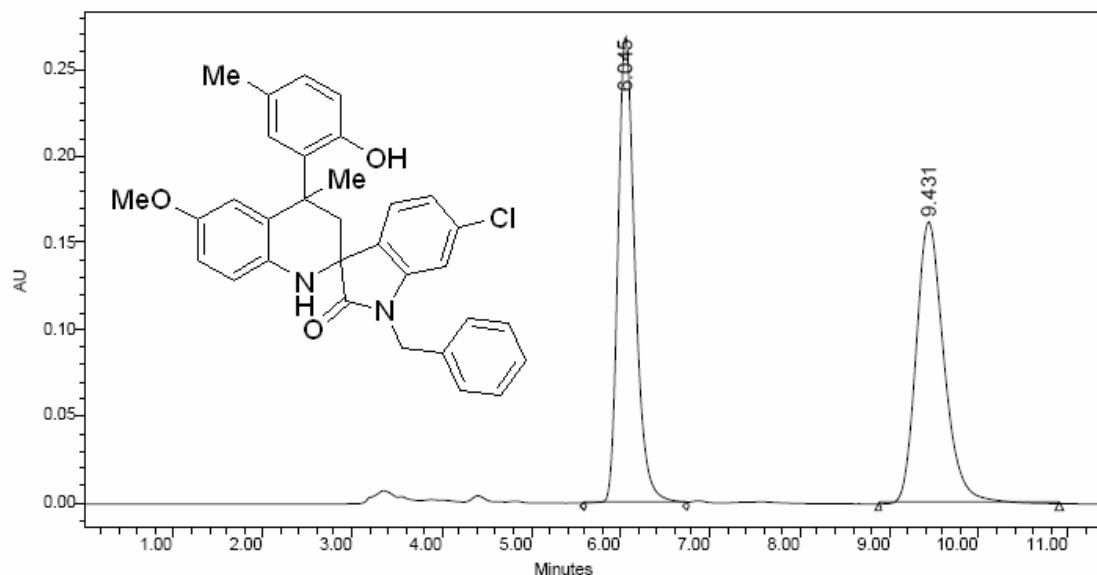


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.847	2154148	49.97	200711	46.28
2	5.818	2157148	50.03	232955	53.72

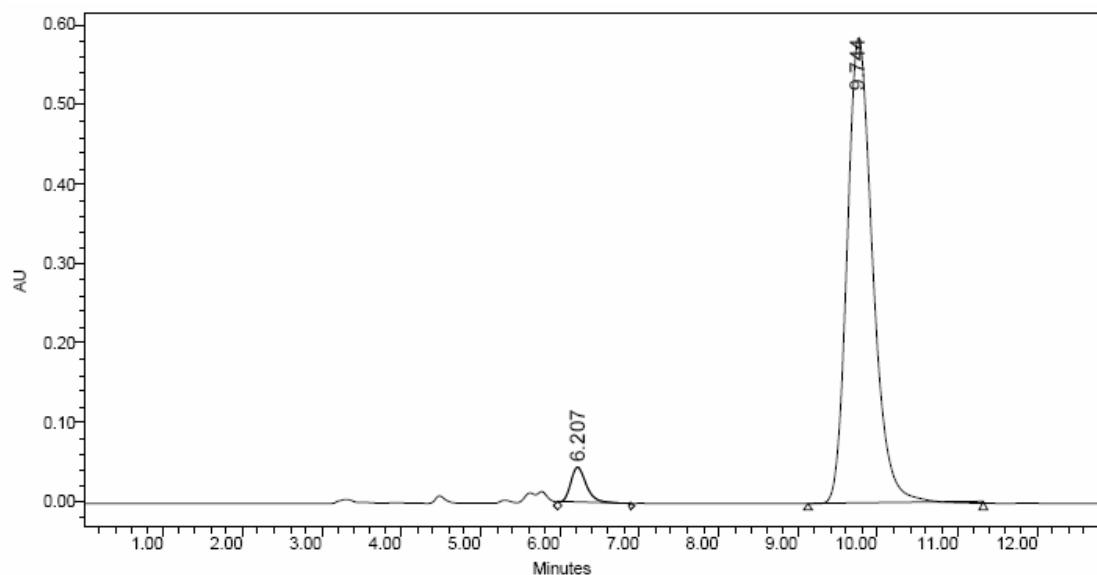


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	4.861	335980	11.05	32637	11.78
2	5.823	2703607	88.95	244405	88.22

4hab:

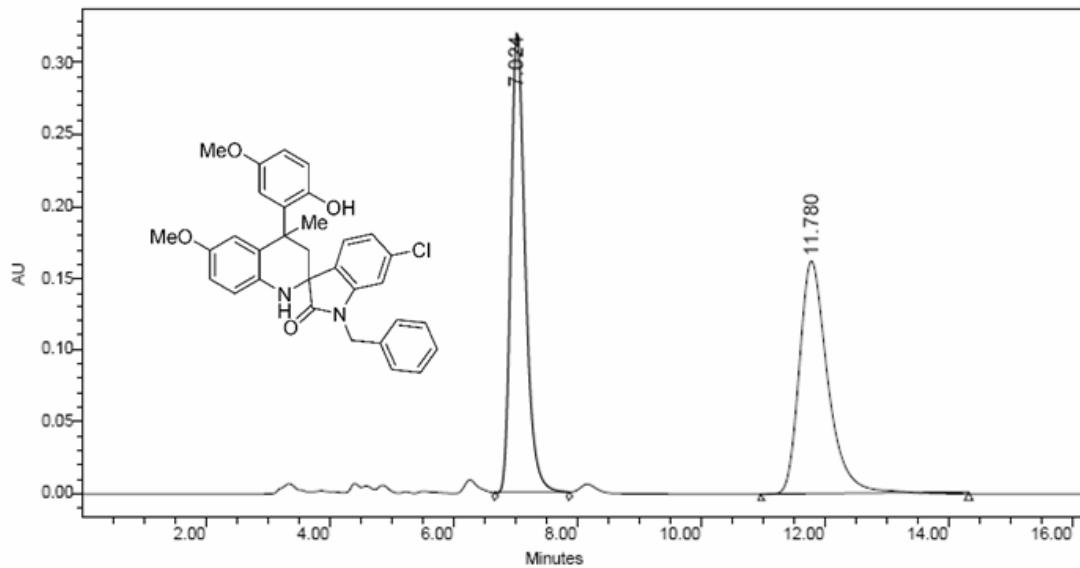


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.045	3571171	50.19	269316	62.35
2	9.431	3543925	49.81	162608	37.65

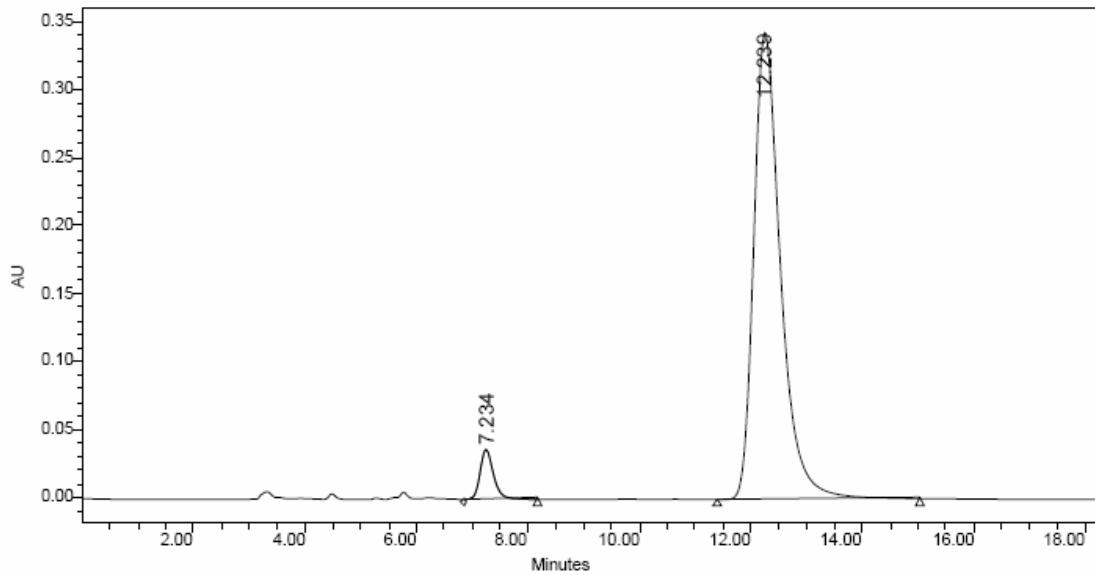


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	6.207	658698	4.76	45712	7.23
2	9.744	13182483	95.24	586948	92.77

4hac:

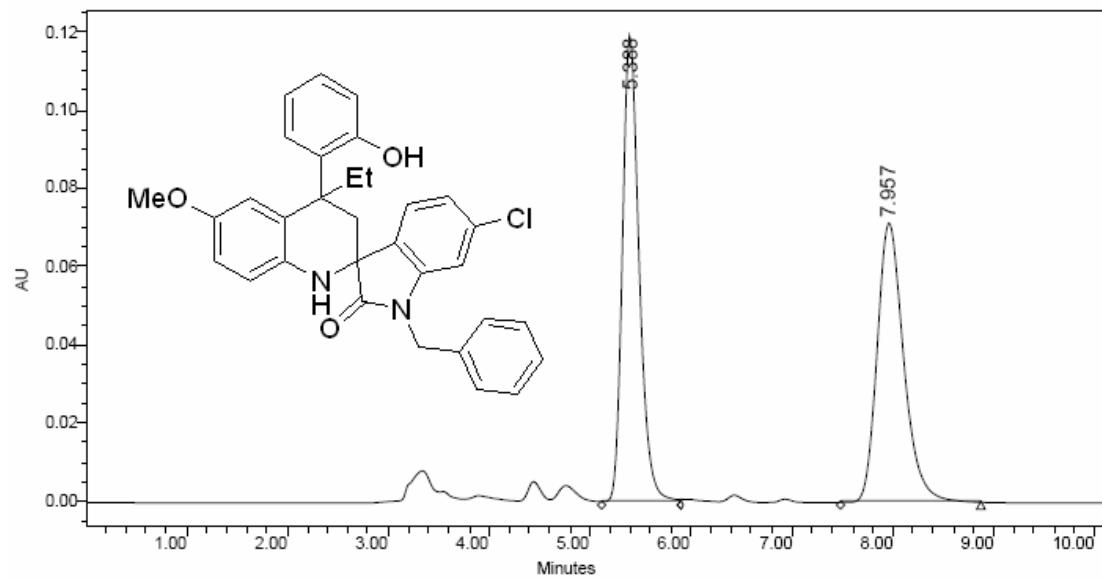


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.024	5242311	49.94	322128	66.44
2	11.780	5255537	50.06	162704	33.56

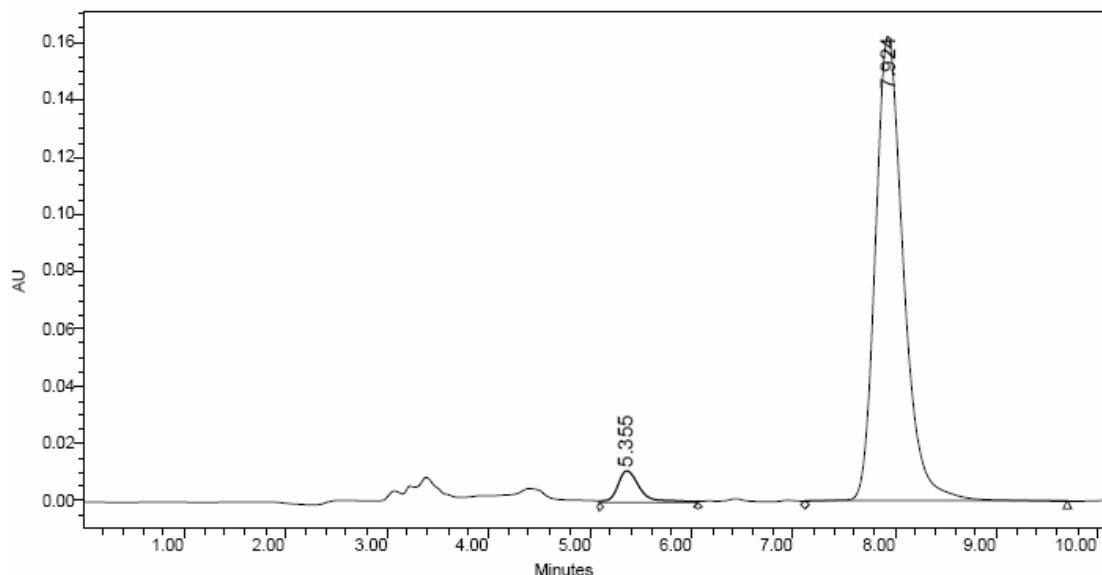


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.234	611009	5.05	36576	9.64
2	12.239	11483800	94.95	343010	90.36

4had:



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.388	1381295	51.26	119595	62.56
2	7.957	1313645	48.74	71564	37.44



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	5.355	190700	5.68	11424	6.56
2	7.924	3167749	94.32	162839	93.44