

Supporting Information for

Catalytic Asymmetric Povarov Reaction of Isatin-derived 2-Azadienes with 3-Vinylindoles

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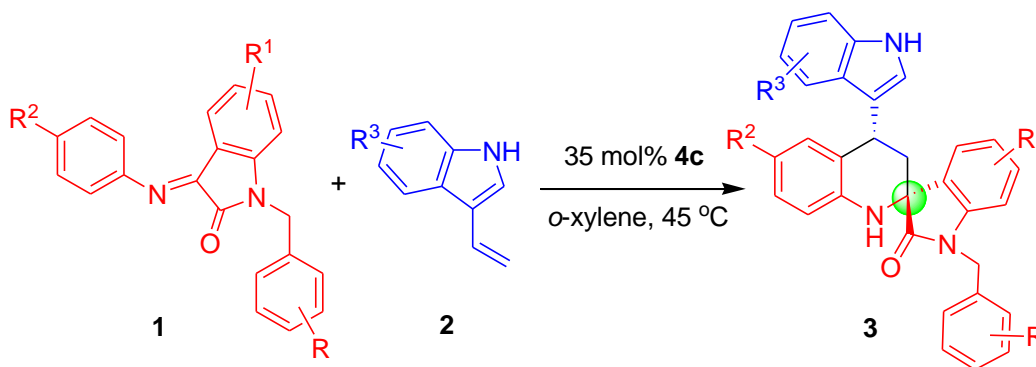
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General information:

NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was CDCl₃, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a micrOTOF-Q II HRMS/MS instrument (Bruker). Enantiomeric ratios (*er*) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of enantiomeric excesses by chiral HPLC were Chiralpak AD-H 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. Analytic grade solvents for the column chromatography and commercially available reagents were used as received. All starting materials commercially available were used directly. Substrates **1** and **2** were synthesized according to the literature methods.¹

General procedure for the catalytic asymmetric Povarov reaction:

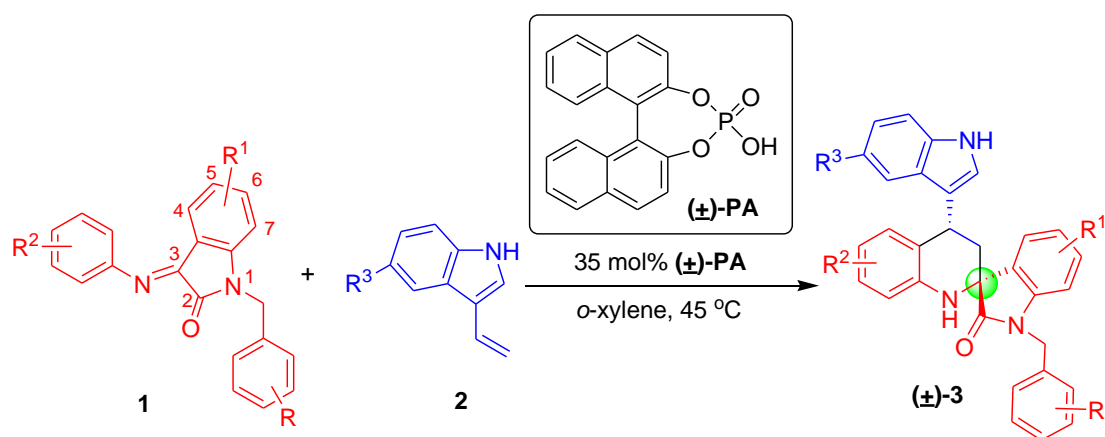


To the stirred solution of isatin-derived 2-azadienes **1** (0.1 mmol) and the catalyst **4c** (0.035 mmol) in *o*-xylene (2 mL) at 45 °C, the solution of 3-vinylindoles **2** (0.3 mmol) in a mixed solvent of *o*-xylene (0.8 mL) and 1,4-dioxane (0.2 mL) was added dropwise by syringe pump for 10 h. After completing the addition of 3-vinylindoles **2**, the reaction mixture was stirred for another one hour. The resultant

1. a) Sun, C.; Lin, X.; Weinreb, S. M. *J. Org. Chem.* 2006, 71, 3159; b) Gioia, C.; Hauville, A.; Bernardi, L.; Fini, F.; Ricci, A. *Angew. Chem. Int. Ed.* 2008, 47, 9236; c) Scott, M. S.; Lucas, A. C.; Luckhurst, C. A.; Prodger, J. C.; Dixon, D. J. *Org. Biomol. Chem.* 2006, 4, 1313.

solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography on silica gel to afford pure spiro-product **3**.

General procedure for the racemic Povarov reaction:



To the stirred solution of isatin-derived 2-azadienes **1** (0.1 mmol) and the racemic phosphoric acid (0.035 mmol) in *o*-xylene (2 mL) at 45 °C, the solution of 3-vinylindoles **2** (0.3 mmol) in a mixed solvent of *o*-xylene (0.8 mL) and 1,4-dioxane (0.2 mL) was added dropwise by syringe pump for 10 h. After completing the addition of 3-vinylindoles **2**, the reaction mixture was stirred for another one hour. 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 spiro-product **(±)-3**. These products were used as racemic standards for HPLC determination.

Characterization of compounds **3**:

(2'R,4'S)-1-benzyl-4'-(1H-indol-3-yl)-6'-methoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3aa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 68% (33.1 mg); >95:5 dr; yellow solid; $[\alpha]_D^{20} = +132.7$ (c 0.59, Acetone); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 8.06 (s, 1H), 7.46 (d, $J = 7.8$ Hz, 1H), 7.39 – 7.36 (m, 2H), 7.33 (d, $J = 4.3$ Hz, 4H), 7.31 – 7.26 (m, 1H), 7.20 – 7.15 (m, 3H), 7.07 – 7.00 (m, 2H), 6.72 (d, $J = 7.8$ Hz,

1H), 6.66 (dd, $J = 8.5, 2.9$ Hz, 1H), 6.61 – 6.54 (m, 2H), 5.17 (dd, $J = 12.6, 5.2$ Hz, 1H), 5.00 – 4.81 (m, 2H), 4.03 (s, 1H), 3.55 (s, 3H), 2.68 (t, $J = 13.1$ Hz, 1H), 2.20 (dd, $J = 13.7, 5.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 179.1, 152.4, 142.1, 136.7, 136.3, 136.0, 132.0, 129.3, 128.9, 127.7, 127.4, 125.4, 123.6, 123.0, 122.8, 121.9, 119.9, 119.3, 117.8, 114.7, 113.2, 111.3, 109.2, 60.1, 55.8, 43.7, 39.0, 30.7; IR (KBr): 3646, 3309, 2922, 2360, 1702, 1607, 1497, 1351, 1289, 1231, 1173, 1098, 1037, 986, 858, 808, 741, 697, 669 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{32}\text{H}_{27}\text{N}_3\text{O}_2\text{-H})^-$ requires m/z 484.2020, found m/z 484.2026; Enantiomeric ratio: 84:16, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 9.21$ min (minor), $t_R = 10.37$ min (major).

(2'R,4'S)-1-(4-(tert-butyl)benzyl)-4'-(1H-indol-3-yl)-6'-methoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3ba): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 50% (27.1 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20} = +167.9$ (c 0.32, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.12 (s, 1H), 7.47 (d, $J = 7.9$ Hz, 1H), 7.36 (dd, $J = 9.4, 6.1$ Hz, 4H), 7.28 (s, 2H), 7.23 – 7.16 (m, 2H), 7.14 (d, $J = 2.5$ Hz, 1H), 7.07 – 7.00 (m, 2H), 6.77 (d, $J = 7.8$ Hz, 1H), 6.67 (dd, $J = 8.5, 2.6$ Hz, 1H), 6.61 – 6.55 (m, 2H), 5.18 (dd, $J = 12.5, 5.1$ Hz, 1H), 4.93 (d, $J = 15.5$ Hz, 1H), 4.82 (d, $J = 15.5$ Hz, 1H), 3.55 (s, 3H), 2.68 (t, $J = 13.1$ Hz, 1H), 2.21 (dd, $J = 13.7, 5.3$ Hz, 1H), 1.61 (s, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 179.0, 152.4, 150.6, 142.3, 136.7, 136.3, 132.9, 132.0, 129.2, 127.2, 125.7, 123.5, 122.9, 122.6, 121.9, 120.0, 119.3, 118.0, 114.7, 114.6, 113.2, 111.2, 109.2, 60.1, 55.8, 43.3, 39.0, 34.5, 31.3, 30.7, 29.7; IR (KBr): 3651, 3298, 2959, 2360, 1704, 1605, 1628, 1498, 1353, 1264, 1290, 1237, 1174, 1097, 1038, 987, 861, 806, 742 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{36}\text{H}_{35}\text{N}_3\text{O}_2\text{-H})^-$ requires m/z 540.2646, found m/z 540.2673; Enantiomeric ratio: 84:16, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 7.27$ min (minor), $t_R = 9.24$ min (major).

(2'R,4'S)-4'-(1H-indol-3-yl)-6'-methoxy-1-(3-methylbenzyl)-3',4'-dihydro-1'H-spi

ro[indoline-3,2'-quinolin]-2-one (3ca): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 73% (36.7 mg); 81:19 dr; yellow sticky oil; $[\alpha]_D^{20} = +197.7$ (c 0.31, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.11 (s, 1H), 7.46 (d, $J = 7.9$ Hz, 1H), 7.40 – 7.34 (m, 2H), 7.25 – 7.12 (m, 6H), 7.12 – 7.07 (m, 1H), 7.06 – 7.00 (m, 2H), 6.74 (d, $J = 7.8$ Hz, 1H), 6.70 – 6.64 (m, 1H), 6.62 – 6.54 (m, 2H), 5.18 (dd, $J = 12.5, 5.1$ Hz, 1H), 4.93 (d, $J = 15.5$ Hz, 1H), 4.81 (d, $J = 15.5$ Hz, 1H), 4.05 (s, 1H), 3.55 (s, 3H), 2.68 (t, $J = 13.1$ Hz, 1H), 2.33 (s, 3H), 2.21 (dd, $J = 13.7, 5.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 179.0, 152.4, 142.2, 138.6, 136.7, 136.3, 135.9, 132.0, 129.3, 128.7, 128.5, 128.2, 126.7, 125.4, 124.5, 123.5, 122.9, 122.6, 121.9, 119.9, 119.3, 118.0, 114.7, 114.6, 113.2, 111.2, 109.2, 60.1, 55.8, 43.7, 39.1, 30.7, 21.5; IR (KBr): 3651, 3319, 2922, 2361, 1698, 1603, 1628, 1499, 1437, 1344, 1291, 1235, 1177, 1098, 1035, 811, 745, 696 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{33}\text{H}_{29}\text{N}_3\text{O}_2\text{-H})^-$ requires m/z 498.2176, found m/z 498.2195; Enantiomeric ratio: 84:16, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 $^\circ\text{C}$, 254 nm): $t_R = 9.23$ min (minor), $t_R = 12.72$ min (major).

(2'R,4'S)-1-(3-chlorobenzyl)-4'-(1H-indol-3-yl)-6'-methoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3da): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 60% (31.2 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20} = +43.3$ (c 0.80, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.11 (s, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.41 – 7.34 (m, 2H), 7.29 (dd, $J = 7.9, 5.5$ Hz, 4H), 7.23 – 7.16 (m, 2H), 7.14 (dd, $J = 6.5, 1.6$ Hz, 1H), 7.07 – 7.02 (m, 2H), 6.73 – 6.63 (m, 2H), 6.61 – 6.55 (m, 2H), 5.15 (dd, $J = 12.5, 5.1$ Hz, 1H), 4.92 (d, $J = 15.6$ Hz, 1H), 4.81 (d, $J = 15.6$ Hz, 1H), 4.08 (s, 1H), 3.54 (s, 3H), 2.68 (t, $J = 13.1$ Hz, 1H), 2.18 (dd, $J = 13.7, 5.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 178.8, 152.5, 143.4, 136.7, 136.0, 135.4, 130.9, 129.0, 127.9, 127.4, 126.6, 125.9, 125.3, 125.0, 122.8, 122.7, 122.0, 119.9, 119.3, 117.7, 114.9, 114.6, 113.2, 112.5, 111.3, 59.9, 55.7, 43.7, 38.9, 30.6; IR (KBr): 3651, 3525, 3441, 3274, 2923, 1705, 1629, 1490, 1353, 1235, 1173, 1095, 1013.99 1037, 987, 801, 743, 567 cm^{-1} ;

ESI FTMS exact mass calcd for $(C_{32}H_{26}ClN_3O_2-H)^-$ requires m/z 518.1630, found m/z 518.1631; Enantiomeric ratio: 83:17, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 10.57 min (minor), t_R = 15.83 min (major).

(2'R,4'S)-1-(4-chlorobenzyl)-4'-(1H-indol-3-yl)-6'-methoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3ea): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 50% (26.1 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20}$ = +226.3 (c 0.31, Acetone); 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.10 (s, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.32 – 7.26 (m, 4H), 7.22 – 7.13 (m, 3H), 7.06 – 7.01 (m, 2H), 6.71 – 6.64 (m, 2H), 6.61 – 6.54 (m, 2H), 5.15 (dd, J = 12.5, 5.1 Hz, 1H), 4.92 (d, J = 15.6 Hz, 1H), 4.81 (d, J = 15.6 Hz, 1H), 4.03 (s, 1H), 3.54 (s, 3H), 2.68 (t, J = 13.1 Hz, 1H), 2.21 – 2.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 179.0, 152.4, 141.8, 136.7, 136.2, 134.5, 133.6, 132.0, 129.3, 129.0, 128.8, 126.6, 125.3, 123.7, 123.2, 122.6, 122.0, 119.9, 119.3, 117.9, 114.7, 114.6, 113.2, 111.2, 109.0, 60.1, 55.8, 43.0, 39.0, 30.7; IR (KBr): 3659, 3525, 3443, 3043, 2360, 1629, 1538, 1353, 568 cm^{-1} ; ESI FTMS exact mass calcd for $(C_{32}H_{26}ClN_3O-H)^-$ requires m/z 518.1630, found m/z 518.1630; Enantiomeric ratio: 83:17, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 10.73 min (minor), t_R = 16.07 min (major).

(2'R,4'S)-1-(4-bromobenzyl)-4'-(1H-indol-3-yl)-6'-methoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3fa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 55% (31.2 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20}$ = +449.5 (c 0.41, Acetone); 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11 (s, 1H), 7.45 (d, J = 8.3 Hz, 3H), 7.37 (t, J = 8.4 Hz, 2H), 7.24 – 7.12 (m, 5H), 7.07 – 7.00 (m, 2H), 6.72 – 6.62 (m, 2H), 6.61 – 6.53 (m, 2H), 5.15

(dd, $J = 12.6, 5.1$ Hz, 1H), 4.90 (d, $J = 15.7$ Hz, 1H), 4.79 (d, $J = 15.7$ Hz, 1H), 4.06 (s, 1H), 3.54 (s, 3H), 2.68 (t, $J = 13.1$ Hz, 1H), 2.18 (dd, $J = 13.7, 5.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 179.0, 152.4, 141.8, 136.7, 136.2, 135.0, 132.0, 129.3, 129.2, 125.3, 123.7, 123.2, 122.6, 122.0, 121.6, 119.9, 119.3, 117.9, 114.7, 114.6, 113.2, 111.3, 109.0, 60.1, 55.8, 43.1, 39.0, 30.7; IR (KBr): 3659, 3525, 3441, 3292, 2923, 1707, 1629, 1488, 1352, 1291, 1235, 1173, 1071, 1097, 1011, 1038, 799, 743, 580 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{32}\text{H}_{26}\text{BrN}_3\text{O}_2\text{-H})^-$ requires m/z 564.1110, found m/z 564.1086; Enantiomeric ratio: 83:17, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_{\text{R}} = 10.74$ min (minor), $t_{\text{R}} = 16.07$ min (major).

(2'R,4'S)-1-(3,4-dichlorobenzyl)-4'-(1H-indol-3-yl)-6'-methoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3ga): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 51% (28.3 mg); >95:5 dr; yellow sticky oil; $[\alpha]_{\text{D}}^{20} = +146.0$ (c 0.35, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.11 (s, 1H), 7.47 – 7.42 (m, 2H), 7.41 – 7.34 (m, 3H), 7.22 (td, $J = 7.8, 1.3$ Hz, 1H), 7.19 – 7.13 (m, 3H), 7.08 – 7.01 (m, 2H), 6.72 – 6.64 (m, 2H), 6.61 – 6.55 (m, 2H), 5.14 (dd, $J = 12.6, 5.2$ Hz, 1H), 4.89 (d, $J = 15.8$ Hz, 1H), 4.79 (d, $J = 15.7$ Hz, 1H), 4.05 (s, 1H), 3.55 (s, 3H), 2.68 (t, $J = 13.2$ Hz, 1H), 2.23 – 2.16 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 179.0, 152.4, 141.5, 136.7, 136.3, 136.1, 133.0, 131.9, 130.9, 129.4, 126.8, 126.6, 125.3, 123.8, 123.4, 122.6, 122.0, 119.9, 119.3, 117.8, 114.8, 114.6, 113.3, 111.3, 108.8, 60.1, 55.8, 42.7, 39.1, 30.7; IR (KBr): 3666, 3525, 3441, 3273, 2923, 2360, 1707, 1629, 1498, 1354, 1236, 1173, 1097, 1031, 988, 872, 806, 742, 567 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{32}\text{H}_{25}\text{Cl}_2\text{N}_3\text{O}_2\text{-H})^-$ requires m/z 552.1240, found m/z 552.1230; Enantiomeric ratio: 81:19, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_{\text{R}} = 9.92$ min (minor), $t_{\text{R}} = 14.61$ min (major).

(2'R,4'S)-1-benzyl-4'-(1H-indol-3-yl)-6'-methoxy-5-methyl-3',4'-dihydro-1'H-spir

o[indoline-3,2'-quinolin]-2-one (3ha): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 75% (37.5 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20} = +60.5$ (c 0.56, Acetone); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 8.15 (s, 1H), 7.47 (d, $J = 7.9$ Hz, 1H), 7.34 (dd, $J = 11.2, 6.3$ Hz, 5H), 7.28 (dd, $J = 8.4, 4.5$ Hz, 1H), 7.23 – 7.20 (m, 1H), 7.16 (t, $J = 7.3$ Hz, 1H), 7.11 (d, $J = 2.3$ Hz, 1H), 7.04 (t, $J = 7.3$ Hz, 1H), 6.99 (d, $J = 7.8$ Hz, 1H), 6.67 (dd, $J = 8.5, 2.7$ Hz, 1H), 6.64 – 6.54 (m, 3H), 5.17 (dd, $J = 12.5, 5.2$ Hz, 1H), 4.96 (d, $J = 15.6$ Hz, 1H), 4.84 (d, $J = 15.6$ Hz, 1H), 3.54 (s, 3H), 2.68 (t, $J = 13.1$ Hz, 1H), 2.28 (s, 3H), 2.20 (dd, $J = 13.7, 5.2$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm): 179.1, 152.3, 139.6, 136.8, 136.4, 136.1, 132.7, 132.0, 129.5, 128.8, 127.6, 127.4, 126.6, 125.5, 124.4, 122.7, 121.9, 120.0, 119.2, 118.0, 114.7, 113.2, 111.3, 109.0, 60.2, 55.8, 43.7, 39.1, 30.8, 21.0; IR (KBr): 3553, 3482, 3416, 3234, 2920, 1701, 1617, 1637, 1497, 1438, 1455, 1383, 1342, 1265, 1288, 1242, 1149, 1182, 1011, 1038, 988, 809, 742, 697, 620 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{33}\text{H}_{29}\text{N}_3\text{O}_2\text{-H})^-$ requires m/z 498.2176, found m/z 498.2176; Enantiomeric ratio: 72:28, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 $^\circ\text{C}$, 254 nm): $t_R = 9.21$ min (minor), $t_R = 10.37$ min (major).

(2'R,4'S)-1-benzyl-4'-(1H-indol-3-yl)-6'-methoxy-6-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3ia): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 65% (32.7 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20} = +192.6$ (c 0.39, Acetone); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 8.08 (s, 1H), 7.46 (d, $J = 7.9$ Hz, 1H), 7.38 – 7.32 (m, 5H), 7.29 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H), 7.19 – 7.13 (m, 3H), 7.05 – 7.01 (m, 1H), 6.84 (d, $J = 7.5$ Hz, 1H), 6.65 (dd, $J = 8.4, 2.7$ Hz, 1H), 6.57 – 6.54 (m, 2H), 5.16 (dd, $J = 12.5, 5.1$ Hz, 1H), 4.96 (d, $J = 15.6$ Hz, 1H), 4.81 (d, $J = 15.6$ Hz, 1H), 3.54 (s, 3H), 2.67 (t, $J = 13.1$ Hz, 1H), 2.28 (s, 3H), 2.18 (dd, $J = 13.7, 5.2$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm): 179.3, 152.3, 142.2, 139.6, 136.7, 136.4, 136.1, 129.0, 128.8, 127.6, 127.3, 125.4, 123.5, 123.3, 122.6, 121.9, 120.0, 119.3, 118.1, 114.7, 114.6, 113.2, 111.2, 110.0, 59.9, 55.8, 43.6, 39.0, 30.7, 21.9; IR (KBr): 3347, 3030, 2921, 2851,

1706, 1619, 1497, 1455, 1378, 1341, 1289, 1261, 1239, 1208, 1151, 1096, 1029, 806, 739 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{33}\text{H}_{29}\text{N}_3\text{O}_2\text{-H})^-$ requires m/z 498.2177, found m/z 498.2178; Enantiomeric ratio: 87:13, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 9.52 min (minor), t_R = 13.64 min (major).

(2'R,4'S)-1-benzyl-4'-(1H-indol-3-yl)-6'-methoxy-7-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3ja): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 51% (25.6 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20}$ = +193.1 (c 0.38, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.13 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.33 (dd, J = 16.0, 7.9 Hz, 3H), 7.30 – 7.26 (m, 2H), 7.17 (dd, J = 15.6, 7.3 Hz, 3H), 7.11 (d, J = 2.2 Hz, 1H), 7.05 – 7.00 (m, 1H), 6.96 (d, J = 4.9 Hz, 2H), 6.66 (dd, J = 8.9, 2.5 Hz, 1H), 6.61 – 6.55 (m, 2H), 5.27 (d, J = 16.8 Hz, 1H), 5.19 – 5.08 (m, 2H), 4.05 (s, 1H), 3.54 (s, 3H), 2.67 (t, J = 13.1 Hz, 1H), 2.28 (s, 3H), 2.22 (dd, J = 13.7, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 175.3, 175.0, 166.9, 165.9, 144.5, 143.0, 136.5, 136.2, 130.8, 130.4, 130.2, 128.9, 128.7, 128.1, 127.9, 126.5, 125.1, 123.9, 122.9, 122.3, 119.6, 119.5, 111.2, 109.6, 109.0, 107.4, 71.3, 61.9, 61.7, 61.0, 53.6, 44.2, 26.6, 13.8, 13.4; IR (KBr): 3651, 3298, 2924, 2360, 1701, 1600, 1629, 1497, 1353, 1235, 1177, 1094, 1039, 988, 862, 781 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{33}\text{H}_{29}\text{N}_3\text{O}_2\text{-H})^-$ requires m/z 498.2176, found m/z 498.2189; Enantiomeric ratio: 87:13, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 9.11 min (minor), t_R = 14.23 min (major).

(2'R,4'S)-1-benzyl-4'-(1H-indol-3-yl)-6,6'-dimethoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3ka): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 67% (34.8 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20}$ = +232.7 (c 0.45, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.13 (s, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.37 – 7.31 (m, 5H), 7.31 – 7.26 (m, 2H), 7.18 – 7.14 (m, 1H), 7.11 (d, J = 2.3 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.66 (dd, J =

8.3, 2.6 Hz, 1H), 6.59 – 6.54 (m, 2H), 6.52 (dd, $J = 8.3, 2.2$ Hz, 1H), 6.32 (d, $J = 2.2$ Hz, 1H), 5.17 (dd, $J = 12.5, 5.1$ Hz, 1H), 4.93 (d, $J = 15.5$ Hz, 1H), 4.82 (d, $J = 15.5$ Hz, 1H), 4.01 (s, 1H), 3.73 (s, 3H), 3.54 (s, 3H), 2.66 (t, $J = 13.1$ Hz, 1H), 2.18 (dd, $J = 13.7, 5.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 179.5, 160.9, 152.3, 143.4, 136.7, 136.4, 135.9, 128.9, 127.7, 127.4, 125.4, 124.3, 123.9, 122.7, 121.9, 120.0, 119.2, 118.0, 114.7, 113.2, 111.3, 106.4, 97.4, 59.7, 55.8, 55.5, 43.7, 39.1, 30.8; IR (KBr): 3356, 2923, 2834, 1706, 1625, 1501, 1377, 1340, 1264, 1230, 1201, 1159, 1102, 1032, 985, 907, 804, 740, 698 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{33}\text{H}_{29}\text{N}_3\text{O}_3\text{-H})^-$ requires m/z 514.2126, found m/z 514.2130; Enantiomeric ratio: 89:11, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 12.58$ min (minor), $t_R = 18.99$ min (major).

(2'R,4'S)-1-benzyl-6-bromo-4'-(1H-indol-3-yl)-6'-methoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3la): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 81% (45.9 mg); 85:15 dr; yellow sticky oil; $[\alpha]_D^{20} = +171.2$ (c 0.52, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.12 (s, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 7.39 – 7.29 (m, 6H), 7.23 (d, $J = 7.9$ Hz, 1H), 7.20 – 7.14 (m, 2H), 7.12 (d, $J = 2.3$ Hz, 1H), 7.06 – 7.01 (m, 1H), 6.87 (d, $J = 1.5$ Hz, 1H), 6.67 (dd, $J = 8.5, 2.6$ Hz, 1H), 6.57 (d, $J = 8.7$ Hz, 2H), 5.14 (dd, $J = 12.5, 5.2$ Hz, 1H), 4.94 (d, $J = 15.6$ Hz, 1H), 4.79 (d, $J = 15.6$ Hz, 1H), 3.54 (s, 3H), 2.65 (t, $J = 13.1$ Hz, 1H), 2.18 (dd, $J = 13.7, 5.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 179.1, 152.4, 141.8, 136.7, 136.2, 134.5, 133.6, 132.0, 129.3, 129.1, 128.8, 126.6, 125.3, 123.7, 123.2, 122.6, 122.0, 119.9, 119.3, 117.9, 114.7, 114.6, 113.2, 111.3, 109.0, 60.1, 55.8, 43.0, 39.0, 30.7; IR (KBr): 3294, 2923, 2360, 1712, 1603, 1497, 1427, 1369, 1289, 1233, 1173, 1107, 1059, 1037, 985, 867, 810, 742 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{32}\text{H}_{26}\text{BrN}_3\text{O}_2\text{-H})^-$ requires m/z 564.1110, found m/z 564.1102; Enantiomeric ratio: 85:15, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 9.24$ min (minor), $t_R = 10.33$ min (major).

(2'R,4'S)-1-benzyl-7-bromo-4'-(1H-indol-3-yl)-6'-methoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3ma): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 60% (33.6 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20} = +200.0$ (c 0.52, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.11 (s, 1H), 7.40 (d, $J = 7.9$ Hz, 1H), 7.36 (dd, $J = 8.0, 3.7$ Hz, 3H), 7.31 (d, $J = 6.1$ Hz, 2H), 7.29 – 7.25 (m, 3H), 7.19 – 7.13 (m, 1H), 7.09 (d, $J = 2.4$ Hz, 1H), 7.05 – 7.00 (m, 1H), 6.92 (t, $J = 7.8$ Hz, 1H), 6.67 (dd, $J = 8.5, 2.5$ Hz, 1H), 6.58 (d, $J = 8.5$ Hz, 2H), 5.41 (s, 2H), 5.09 (dd, $J = 12.4, 5.1$ Hz, 1H), 4.04 (s, 1H), 3.54 (s, 3H), 2.63 (t, $J = 13.1$ Hz, 1H), 2.20 (dd, $J = 13.7, 5.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 179.7, 152.5, 139.6, 137.6, 136.7, 136.1, 135.4, 135.2, 128.6, 127.2, 126.5, 125.3, 124.3, 122.8, 122.7, 122.0, 119.8, 119.3, 117.6, 114.9, 114.6, 113.3, 111.3, 102.5, 59.6, 55.8, 44.2, 39.5, 30.7; IR (KBr): 3552, 3475, 3415, 3237, 3031, 2924, 1714, 1617, 1637, 1497, 1451, 1341, 1270.63 1289, 1229, 1157, 1113, 1038, 737, 624 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{32}\text{H}_{26}\text{BrN}_3\text{O}_2\text{-H})^-$ requires m/z 564.1110, found m/z 564.1073; Enantiomeric ratio: 85:15, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 $^\circ\text{C}$, 254 nm): $t_R = 8.85$ min (minor), $t_R = 10.90$ min (major).

(2'R,4'S)-1-benzyl-7-fluoro-4'-(1H-indol-3-yl)-6'-methoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3na): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 56% (28.1 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20} = +194.9$ (c 0.30, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.10 (s, 1H), 7.47 – 7.36 (m, 4H), 7.36 – 7.33 (m, 1H), 7.33 – 7.27 (m, 2H), 7.20 – 7.11 (m, 3H), 7.06 – 7.01 (m, 1H), 7.00 – 6.95 (m, 2H), 6.67 (dd, $J = 8.4, 2.6$ Hz, 1H), 6.62 – 6.53 (m, 2H), 5.13 (dd, $J = 12.5, 5.2$ Hz, 1H), 5.05 (s, 2H), 4.02 (s, 1H), 3.55 (s, 3H), 2.62 (t, $J = 13.1$ Hz, 1H), 2.18 (dd, $J = 8.7, 4.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 178.7, 152.5, 148.5, 146.0, 137.2, 136.7, 136.0, 128.7, 127.7, 125.3, 122.7, 122.0, 119.9, 119.3, 117.8, 117.5, 117.3, 114.8, 114.6, 113.3, 60.3, 55.8, 45.2, 39.2, 30.6; IR (KBr): 3666, 3525, 3440, 3299, 2926, 2360,

1713, 1629, 1497, 1342, 1235, 1178, 1039, 980, 877, 782, 810, 701, 590 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{32}\text{H}_{26}\text{FN}_3\text{O}_2\text{-H})^-$ requires m/z 502.1925, found m/z 502.1925; Enantiomeric ratio: 82:18, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.90 min (minor), t_R = 10.72 min (major).

(2'R,4'S)-1-benzyl-4'-(1H-indol-3-yl)-6'-methoxy-7-(trifluoromethyl)-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (30a): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 55% (30.4 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20} = +168.5$ (c 0.44, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.12 (s, 1H), 7.63 (d, $J = 6.7$ Hz, 1H), 7.57 (d, $J = 8.1$ Hz, 1H), 7.36 (t, $J = 8.4$ Hz, 2H), 7.30 (dd, $J = 7.2, 5.7$ Hz, 2H), 7.23 (d, $J = 7.4$ Hz, 1H), 7.20 – 7.12 (m, 4H), 7.08 (d, $J = 2.1$ Hz, 1H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.67 (dd, $J = 8.5, 2.9$ Hz, 1H), 6.58 (d, $J = 8.7$ Hz, 2H), 5.26 (d, $J = 16.9$ Hz, 1H), 5.15 (d, $J = 16.9$ Hz, 1H), 5.06 (dd, $J = 12.5, 5.2$ Hz, 1H), 4.03 (s, 1H), 3.54 (s, 3H), 2.65 (t, $J = 13.1$ Hz, 1H), 2.21 (dd, $J = 13.7, 5.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 180.1, 152.6, 140.4, 136.7, 136.6, 136.0, 134.8, 128.5, 127.5, 127.0, 125.8, 125.2, 122.7, 122.6, 122.0, 119.7, 119.3, 117.5, 115.0, 114.6, 113.3, 111.3, 58.4, 55.8, 45.3, 45.3, 39.6, 30.6; IR (KBr): 3651, 3293, 2925, 2361, 1720, 1595, 1498, 1335, 1241, 1180, 1098, 1039, 976, 851, 800, 744, 696 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{33}\text{H}_{26}\text{F}_3\text{N}_3\text{O}_2\text{-H})^-$ requires m/z 552.1893, found m/z 552.1893; Enantiomeric ratio: 82:18, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.93 min (minor), t_R = 7.74 min (major).

(2'R,4'S)-1-benzyl-6'-ethoxy-4'-(1H-indol-3-yl)-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3pa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 50% (24.2 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20} = +127.4$ (c 0.32, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.09 (s, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.39 – 7.35 (m, 2H), 7.33 (d, $J = 4.5$ Hz,

4H), 7.28 (dd, $J = 8.4, 4.4$ Hz, 1H), 7.21 – 7.14 (m, 3H), 7.06 – 7.00 (m, 2H), 6.72 (d, $J = 7.8$ Hz, 1H), 6.68 – 6.64 (m, 1H), 6.59 – 6.54 (m, 2H), 5.16 (dd, $J = 12.5, 5.2$ Hz, 1H), 4.97 (d, $J = 15.5$ Hz, 1H), 4.84 (d, $J = 15.5$ Hz, 1H), 4.03 (s, 1H), 3.81 – 3.71 (m, 2H), 2.68 (t, $J = 13.1$ Hz, 1H), 2.23 – 2.17 (m, 1H), 1.22 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 179.1, 151.6, 142.1, 136.3, 136.0, 129.2, 128.8, 127.7, 127.4, 125.3, 123.5, 123.0, 122.7, 121.9, 120.0, 119.3, 115.5, 114.7, 114.1, 111.2, 109.2, 64.0, 60.1, 43.6, 39.1, 30.7, 14.9; IR (KBr): 3666, 3524, 3440, 3296, 2922, 2360, 1704, 1628, 1497, 1352, 1264, 1173, 1098, 1046, 973, 808, 742, 697 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{34}\text{H}_{31}\text{N}_3\text{O}_3\text{-H})^-$ requires m/z 498.2176, found m/z 498.2177; Enantiomeric ratio: 82:18, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 8.95$ min (minor), $t_R = 13.30$ min (major).

(2'R,4'S)-1-benzyl-4'-(1H-indol-3-yl)-6'-phenoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3qa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 69% (37.6 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20} = +231.4$ (c 0.43, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.00 (s, 1H), 7.44 – 7.39 (m, 2H), 7.36 – 7.32 (m, 5H), 7.22 – 7.17 (m, 2H), 7.17 – 7.10 (m, 4H), 7.07 – 7.02 (m, 2H), 6.90 – 6.86 (m, 1H), 6.81 – 6.70 (m, 5H), 6.66 – 6.58 (m, 1H), 5.18 (dd, $J = 12.6, 5.1$ Hz, 1H), 4.97 (d, $J = 15.6$ Hz, 1H), 4.87 (d, $J = 15.6$ Hz, 1H), 4.21 (s, 1H), 2.72 (t, $J = 13.2$ Hz, 1H), 2.20 (dd, $J = 13.7, 5.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 179.0, 159.1, 147.5, 142.1, 138.9, 136.8, 135.9, 131.7, 129.4, 129.2, 128.9, 127.7, 127.4, 125.3, 123.5, 123.1, 122.0, 121.4, 121.2, 119.5, 119.3, 117.6, 116.6, 114.8, 111.3, 109.3, 60.0, 43.7, 38.7, 30.7; IR (KBr): 3355, 3055, 2962, 2919, 2850, 2361, 1702, 1612, 1486, 1351, 1290, 1261, 1225, 1164, 1096, 1022, 907, 801, 741, 692 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{37}\text{H}_{29}\text{N}_3\text{O}_2\text{-H})^-$ requires m/z 546.2177, found m/z 546.2170; Enantiomeric ratio: 71:29, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 38.43$ min (minor), $t_R = 43.31$ min (major).

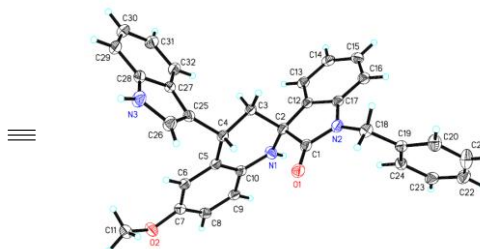
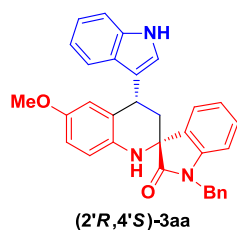
(2'R,4'S)-1-benzyl-4'-(1H-indol-3-yl)-6'-methyl-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3ra): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 54% (25.6 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20} = +202.7$ (c 0.18, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.08 (s, 1H), 7.49 (d, $J = 7.9$ Hz, 1H), 7.41 – 7.36 (m, 2H), 7.32 (d, $J = 4.5$ Hz, 4H), 7.30 – 7.27 (m, 1H), 7.21 – 7.15 (m, 3H), 7.07 – 7.00 (m, 2H), 6.87 – 6.83 (m, 1H), 6.76 (s, 1H), 6.72 (d, $J = 7.8$ Hz, 1H), 6.54 (d, $J = 8.0$ Hz, 1H), 5.17 (dd, $J = 12.5, 5.0$ Hz, 1H), 4.97 (d, $J = 15.5$ Hz, 1H), 4.84 (d, $J = 15.6$ Hz, 1H), 4.10 (s, 1H), 2.68 (t, $J = 13.1$ Hz, 1H), 2.24 – 2.18 (m, 1H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 175.3, 175.0, 166.9, 165.9, 144.5, 143.0, 136.5, 136.2, 130.8, 130.4, 130.2, 128.9, 128.7, 128.1, 127.9, 126.5, 125.1, 123.9, 122.9, 122.3, 119.6, 119.5, 111.2, 109.6, 109.0, 107.4, 71.3, 61.9, 61.7, 61.0, 53.6, 44.2, 26.6, 13.8, 13.4; IR (KBr): 3665, 3525, 3442, 3272, 2922, 2360, 1705, 1629, 1586, 1504, 1351, 1260, 1293, 1175, 1097, 986, 815, 746, 694 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{32}\text{H}_{27}\text{N}_3\text{O}-\text{H})^-$ requires m/z 468.2070, found m/z 468.2084; Enantiomeric ratio: 79:21, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 8.21$ min (minor), $t_R = 10.16$ min (major).

(2'R,4'S)-1-benzyl-4'-(1H-indol-3-yl)-5',6',7'-trimethoxy-3',4'-dihydro-1'H-spiro[indoline-3,2'-quinolin]-2-one (3sa): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 67% (36.8 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20} = +132.7$ (c 0.34, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.98 (s, 1H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.32 (q, $J = 5.2, 4.2$ Hz, 5H), 7.30 – 7.27 (m, 1H), 7.14 – 7.09 (m, 2H), 7.04 – 6.98 (m, 3H), 6.87 (t, $J = 7.5$ Hz, 1H), 6.68 (d, $J = 7.8$ Hz, 1H), 6.03 (s, 1H), 5.00 – 4.90 (m, 2H), 4.83 (d, $J = 15.5$ Hz, 1H), 4.02 (s, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 3.19 (s, 3H), 2.69 (dd, $J = 13.9, 9.9$ Hz, 1H), 2.34 (dd, $J = 13.9, 6.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 152.9, 152.6, 142.1, 139.3, 136.5, 135.9, 135.2, 131.6, 129.1, 128.8, 127.7, 127.4, 126.4, 124.0, 122.8, 121.6, 121.3, 120.7, 119.5, 119.0, 111.1, 110.7, 109.1, 94.2, 60.8, 60.1, 59.7, 55.6,

43.6, 40.5, 28.0; IR (KBr): 3348, 3055, 2928, 1707, 1609, 1486, 1466, 1432, 1395, 1348, 1262, 1237, 1196, 1173, 1110, 1014, 908, 804, 740, 697 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{34}\text{H}_{31}\text{N}_3\text{O}_4\text{-H})^-$ requires m/z 544.2232, found m/z 544.2239; Enantiomeric ratio: 84:16, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 16.36 min (minor), t_R = 11.80 min (major).

(2'R,4'S)-1-benzyl-4'-(5-bromo-1H-indol-3-yl)-6'-methoxy-3',4'-dihydro-1'H-spir o[indoline-3,2'-quinolin]-2-one (3ab): Flash column chromatography eluent, petroleum ether/ethyl acetate = 6/1; Reaction time = 11 h; yield: 57% (32.1 mg); >95:5 dr; yellow sticky oil; $[\alpha]_D^{20}$ = +138.4 (c 0.51, Acetone); ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.26 (s, 1H), 7.58 (s, 1H), 7.40 (d, J = 7.4 Hz, 1H), 7.33 (d, J = 4.3 Hz, 4H), 7.30 – 7.26 (m, 1H), 7.24 – 7.16 (m, 3H), 7.05 (dd, J = 16.7, 9.1 Hz, 2H), 6.74 (d, J = 7.8 Hz, 1H), 6.70 – 6.64 (m, 1H), 6.57 (d, J = 8.6 Hz, 1H), 6.53 – 6.49 (m, 1H), 5.13 (dd, J = 12.6, 5.2 Hz, 1H), 4.97 (d, J = 15.5 Hz, 1H), 4.85 (d, J = 15.5 Hz, 1H), 4.05 (s, 1H), 3.57 (s, 3H), 2.61 (t, J = 13.1 Hz, 1H), 2.23 – 2.15 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 179.0, 152.3, 142.1, 136.3, 135.9, 135.3, 131.8, 129.4, 128.9, 127.7, 127.4, 124.9, 124.0, 123.6, 123.1, 122.2, 117.7, 114.8, 114.6, 113.2, 112.8, 112.6, 109.3, 60.0, 55.8, 43.7, 38.9, 30.5; IR (KBr): 3652, 3310, 2924, 2360, 1704, 1608, 1499, 1348, 1291, 1237, 1175, 1099, 1032, 987, 862, 883, 796, 750, 697 cm^{-1} ; ESI FTMS exact mass calcd for $(\text{C}_{32}\text{H}_{26}\text{BrN}_3\text{O}_2\text{-H})^-$ requires m/z 564.1110, found m/z 564.1114; Enantiomeric ratio: 80:20, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 8.12 min (minor), t_R = 11.01 min (major).

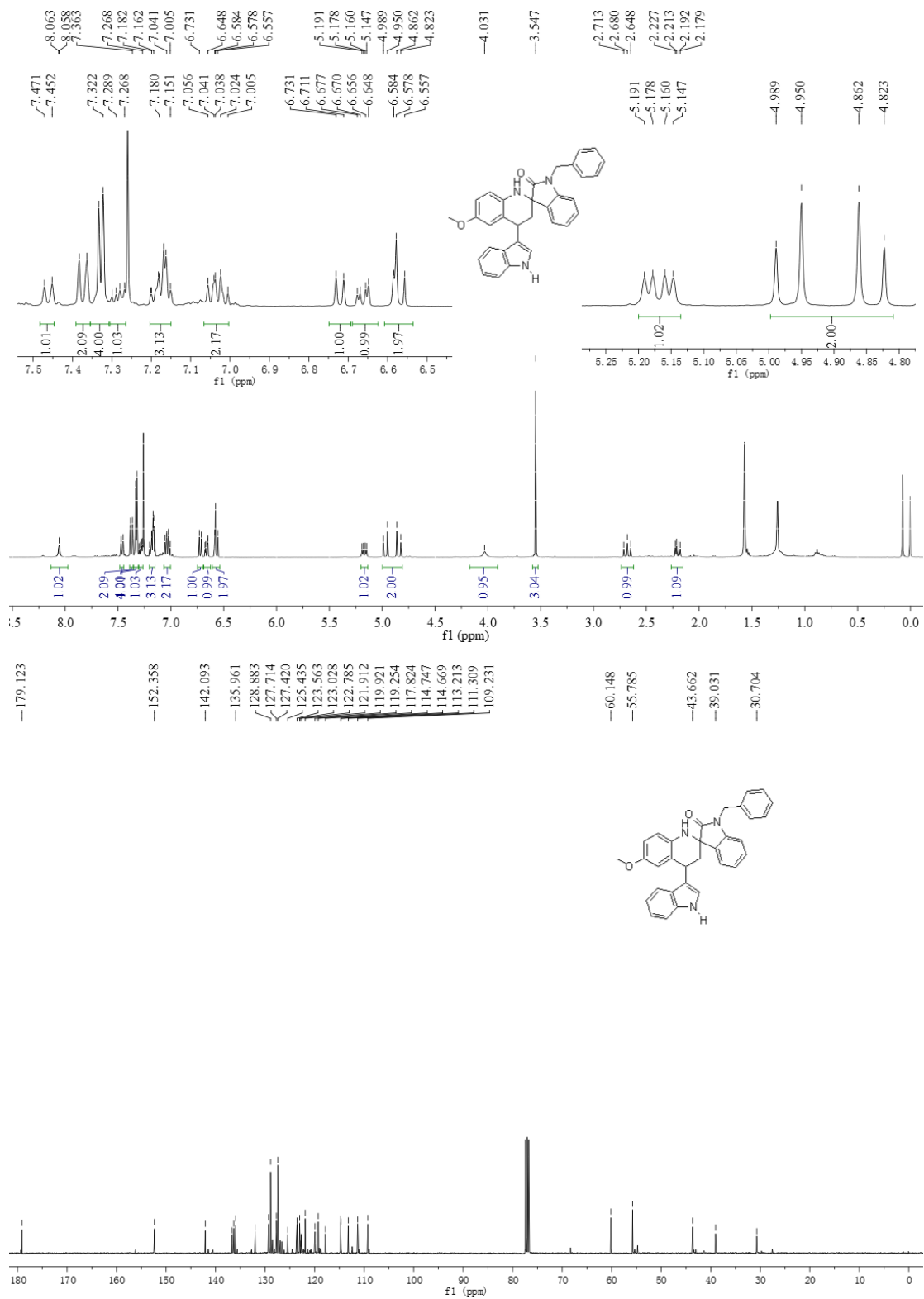
X-ray single crystal data for compound 3aa



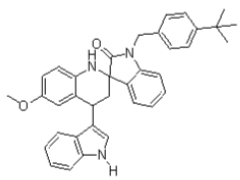
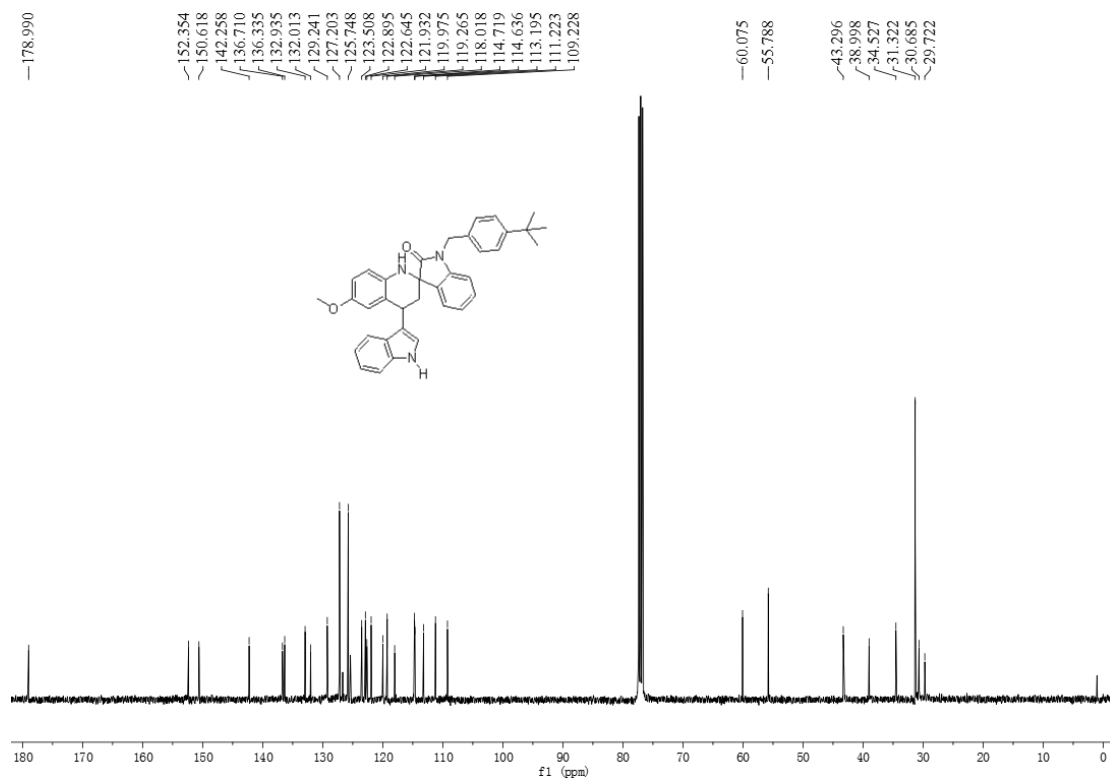
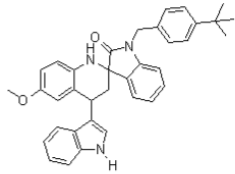
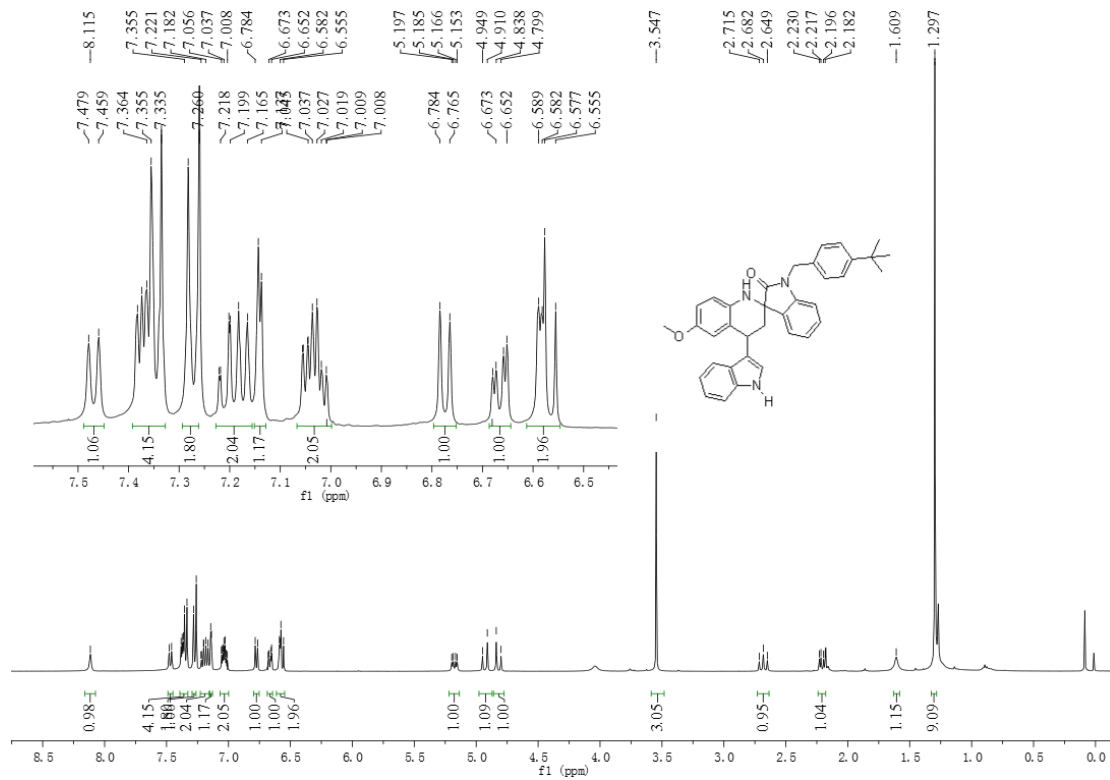
Identification code	cu_dm14304_0m	
Empirical formula	C ₃₂ H ₂₇ N ₃ O ₂	
Formula weight	485.56	
Temperature	140(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 17.5165(3) Å	α = 90 °
	b = 5.88650(10) Å	β = 94.9970(10) °
	c = 23.6140(4) Å	γ = 90 °
Volume	2425.61(7) Å ³	
Z	4	
Density (calculated)	1.330 Mg/m ³	
Absorption coefficient	0.663 mm ⁻¹	
F(000)	1024	
Crystal size	0.250 x 0.080 x 0.030 mm ³	
Theta range for data collection	1.878 to 69.992 °	
Index ranges	-21 ≤ h ≤ 17, -5 ≤ k ≤ 6, -28 ≤ l ≤ 28	
Reflections collected	5722	
Independent reflections	3102 [R(int) = 0.0332]	
Completeness to theta = 67.679 °	96.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7532 and 0.4726	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3102 / 1 / 335	
Goodness-of-fit on F ²	1.105	
Final R indices [I > 2σ(I)]	R1 = 0.0441, wR2 = 0.1239	
R indices (all data)	R1 = 0.0487, wR2 = 0.1322	
Absolute structure parameter	0.2(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.310 and -0.348 e.Å ⁻³	

NMR Spectra of products 3

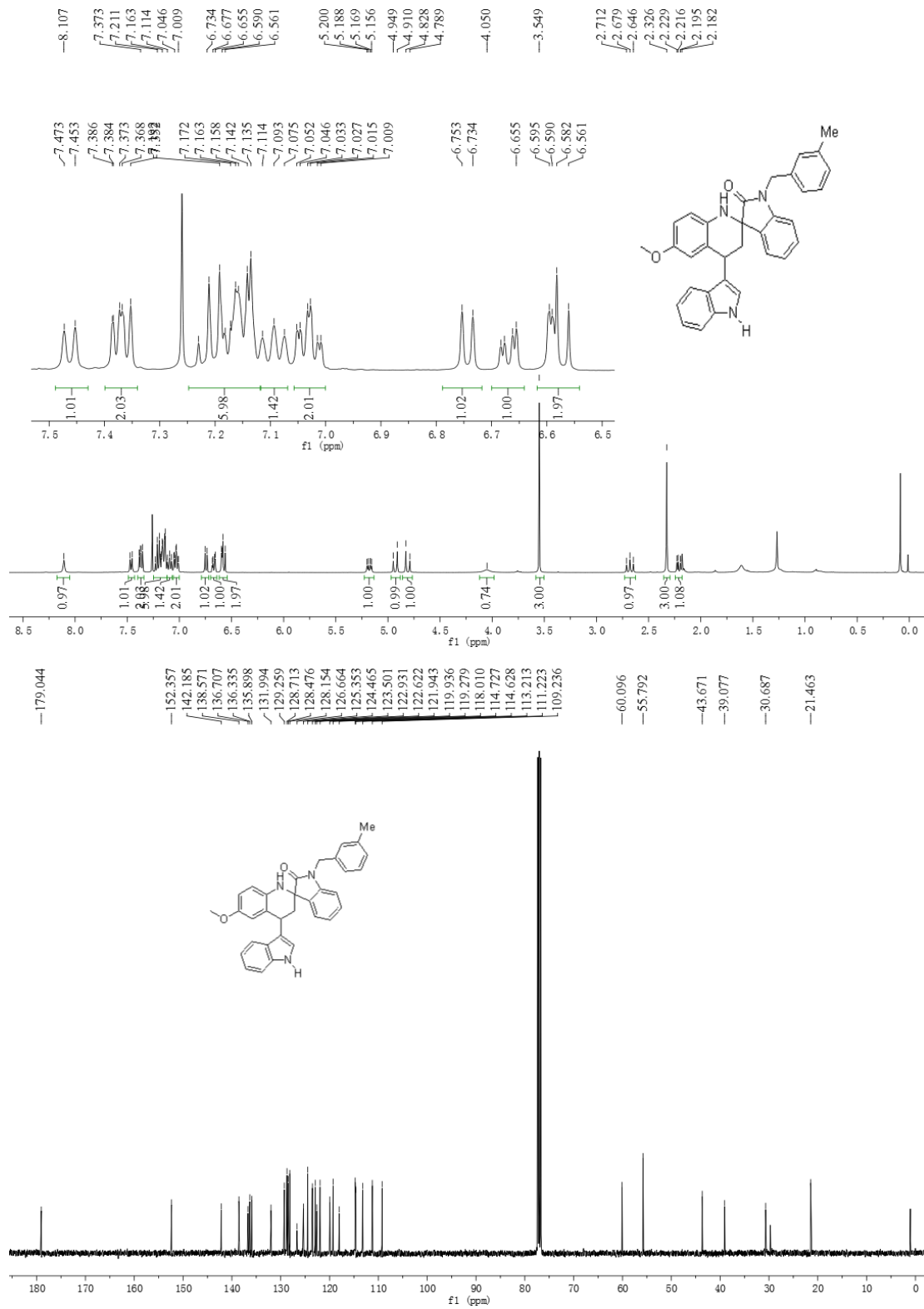
3aa



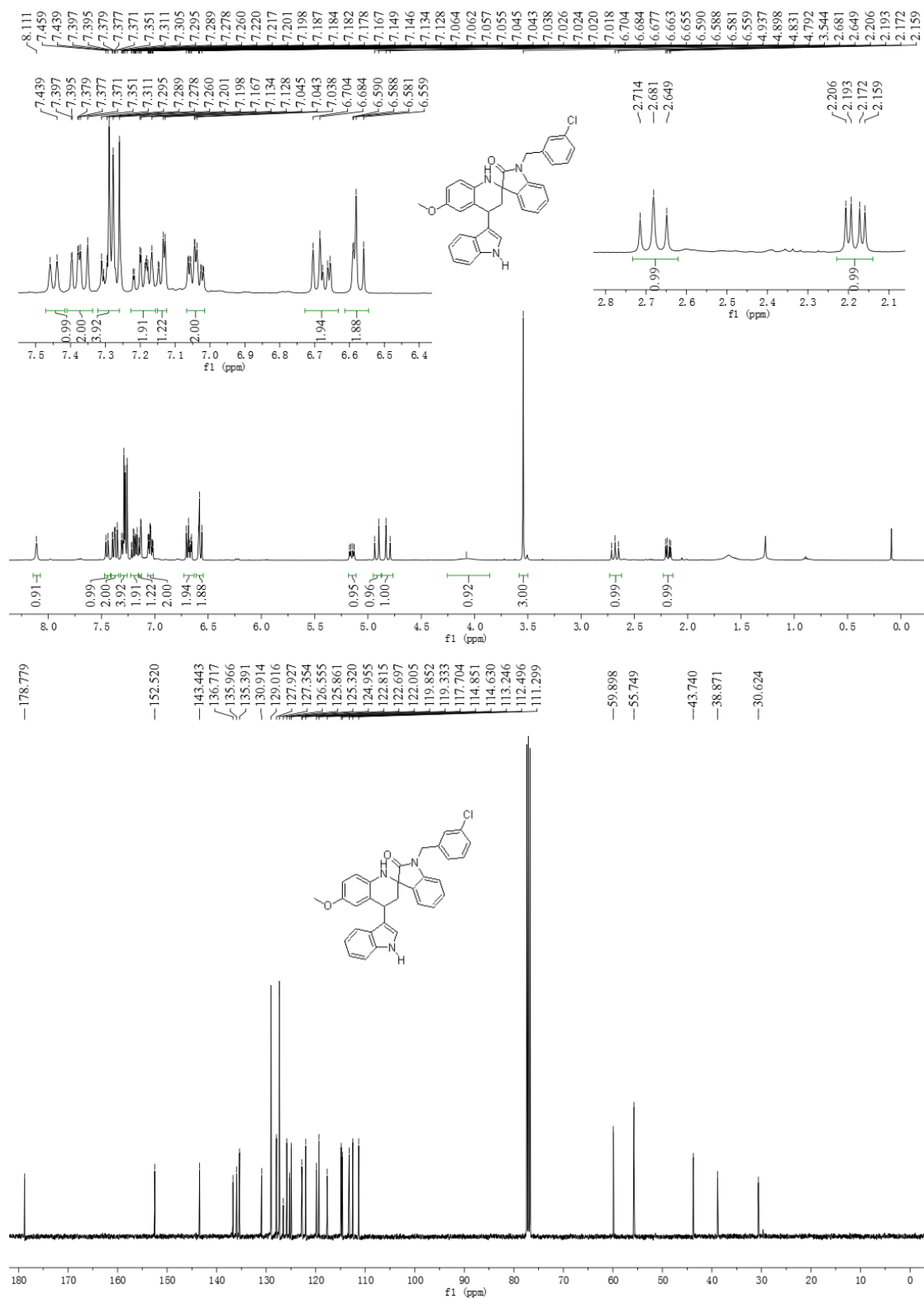
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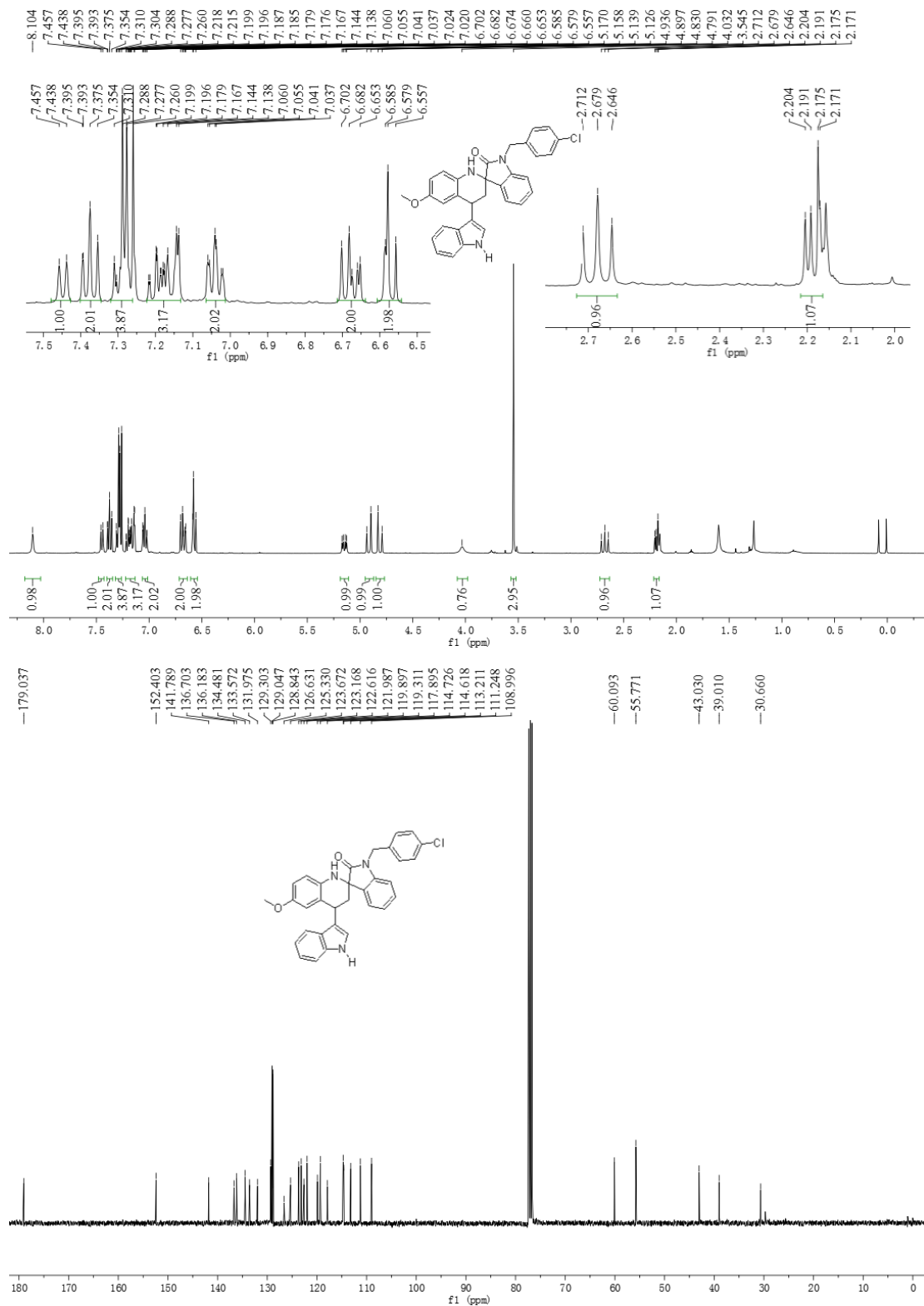
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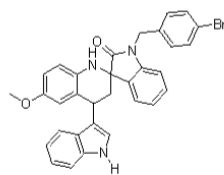
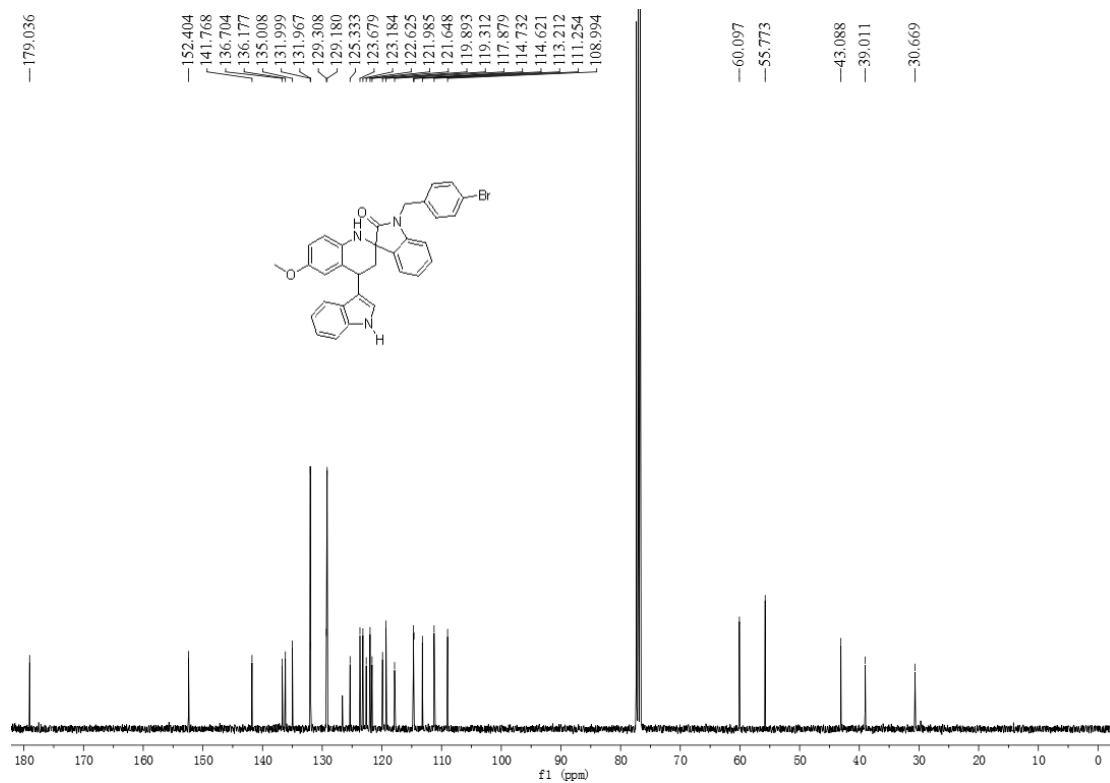
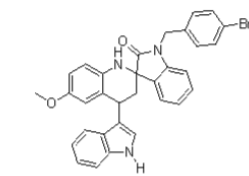
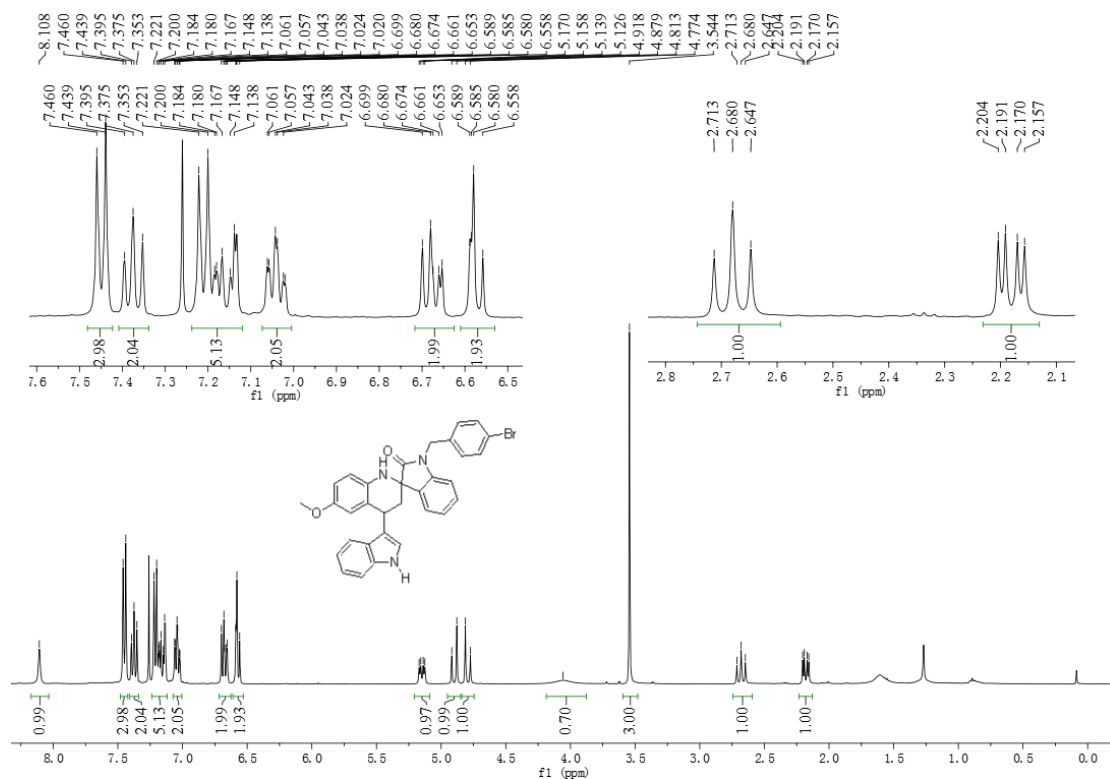
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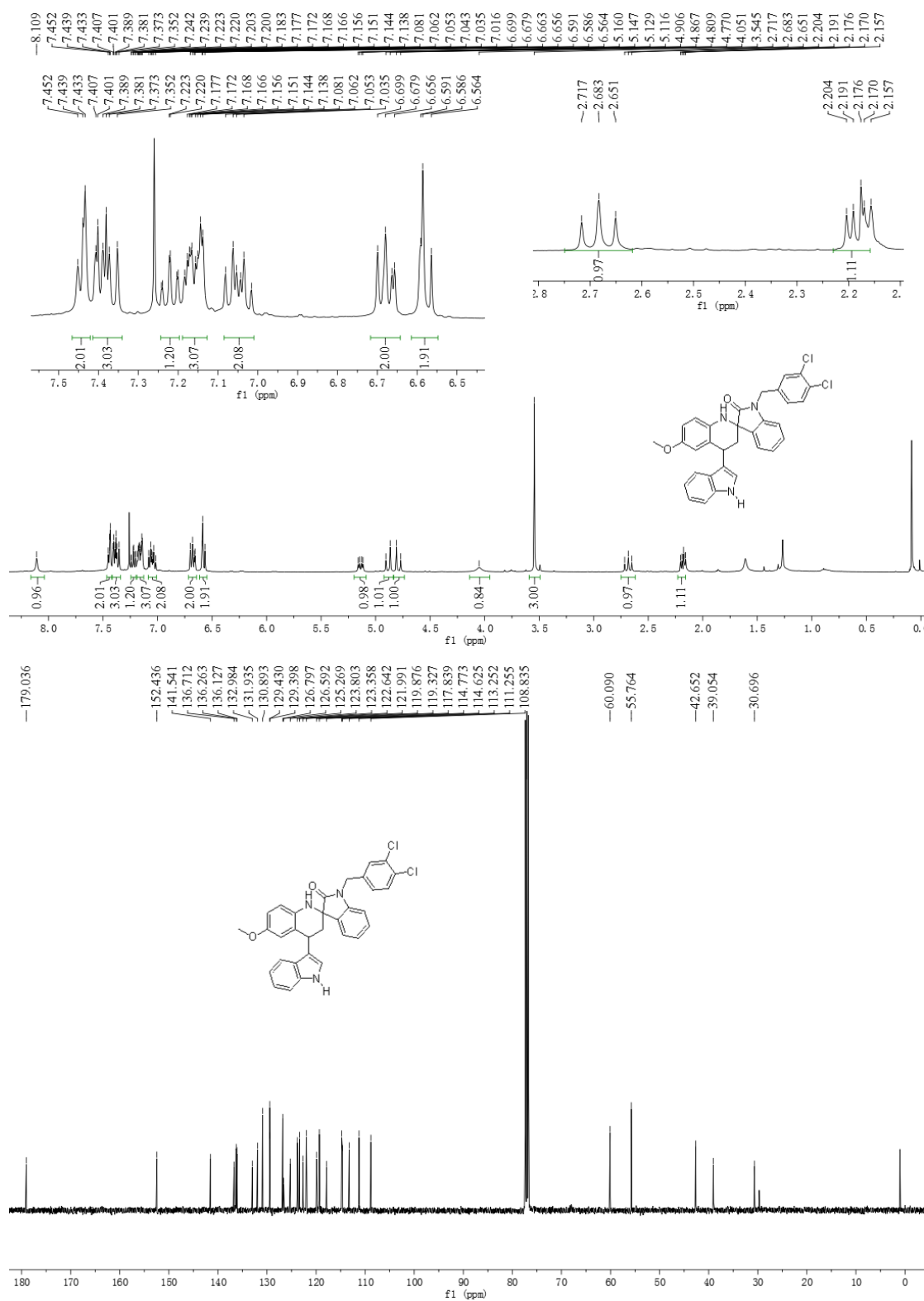
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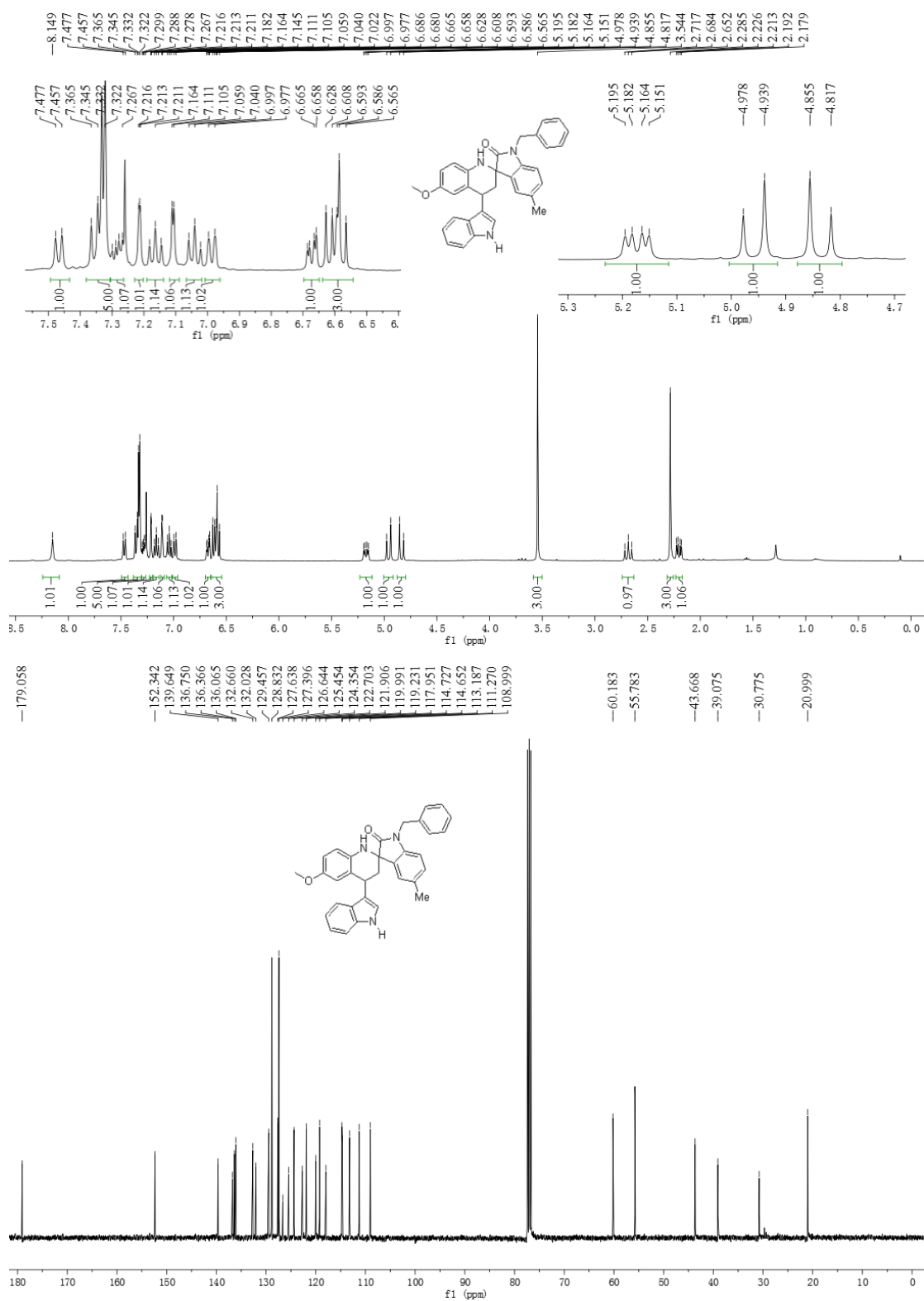
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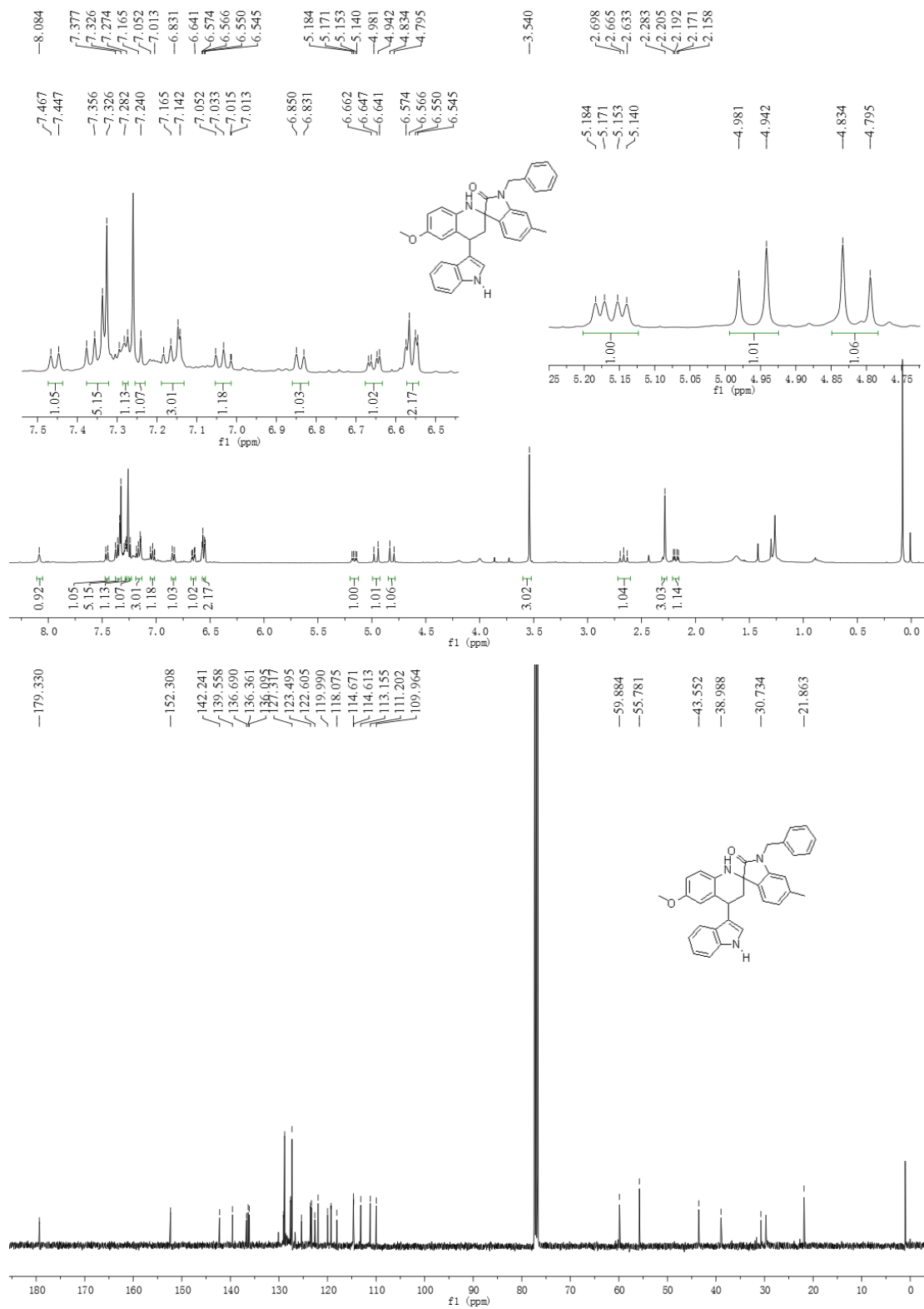
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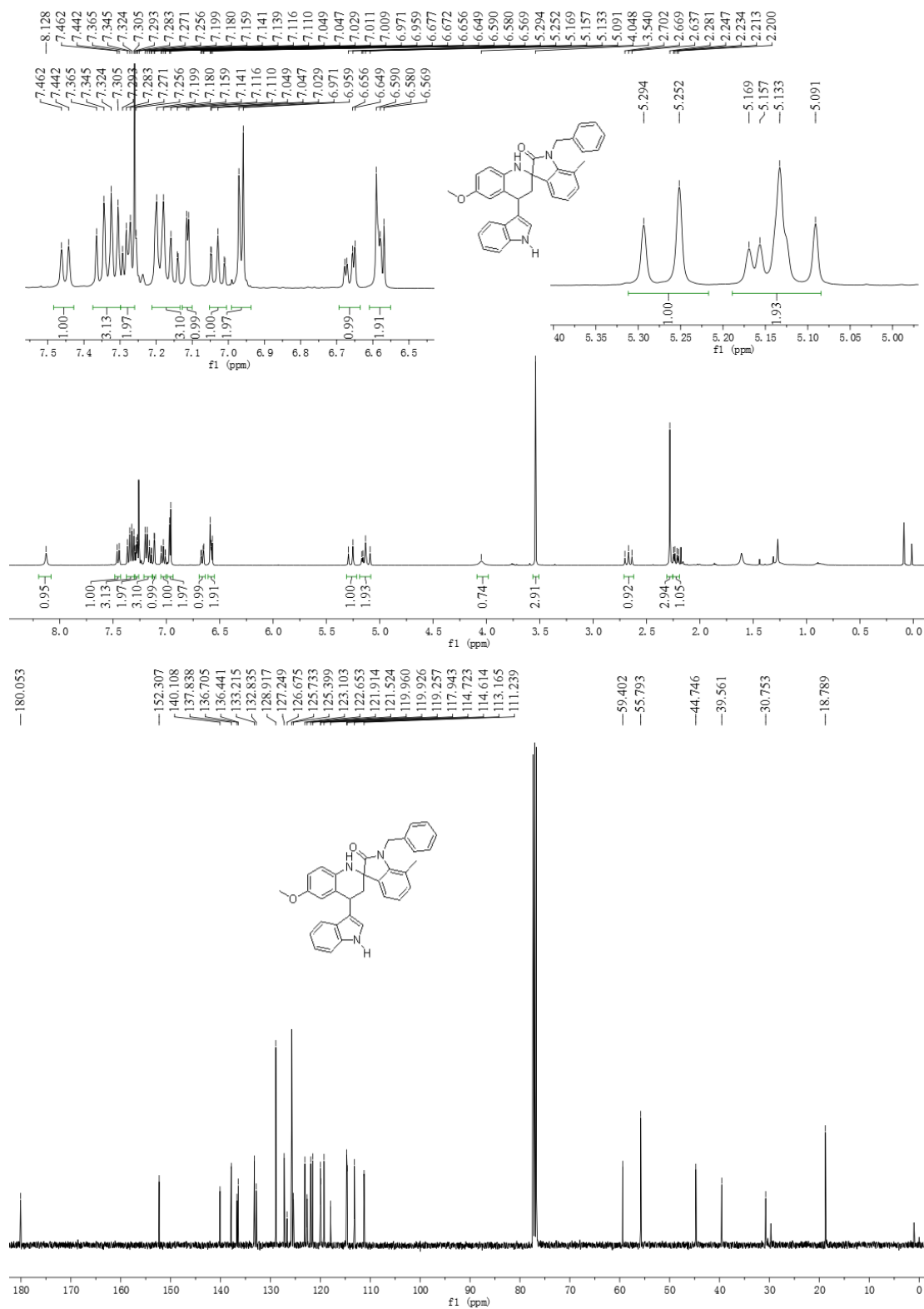
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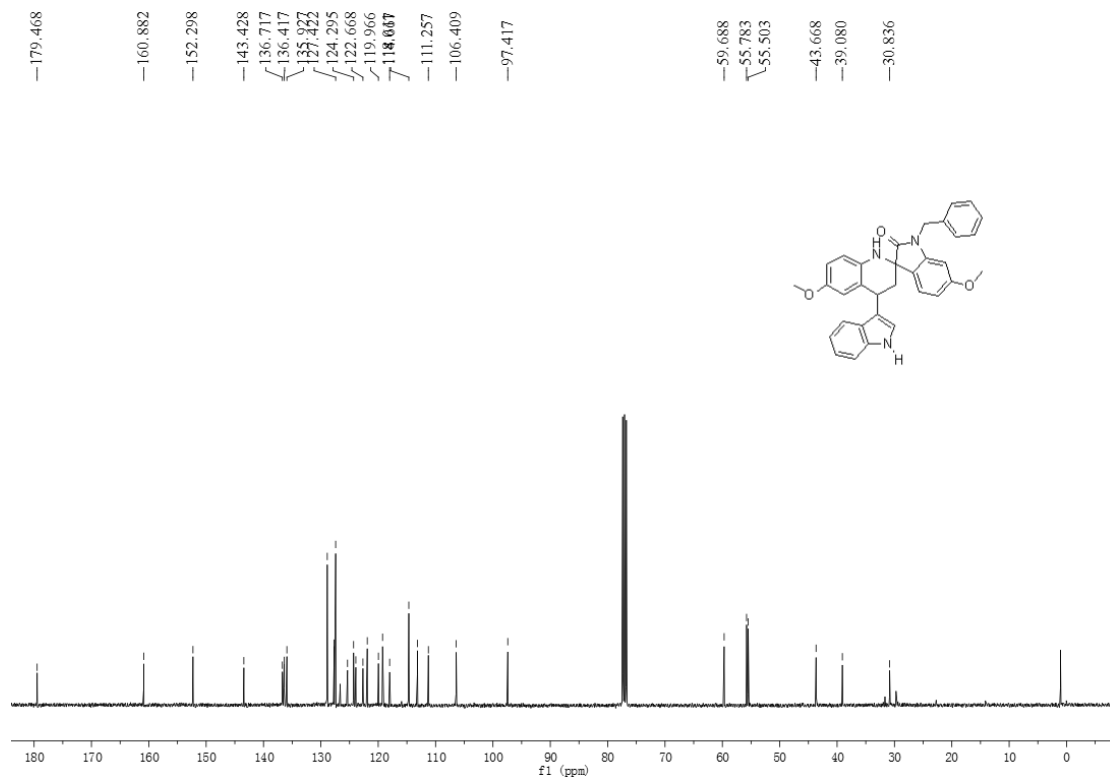
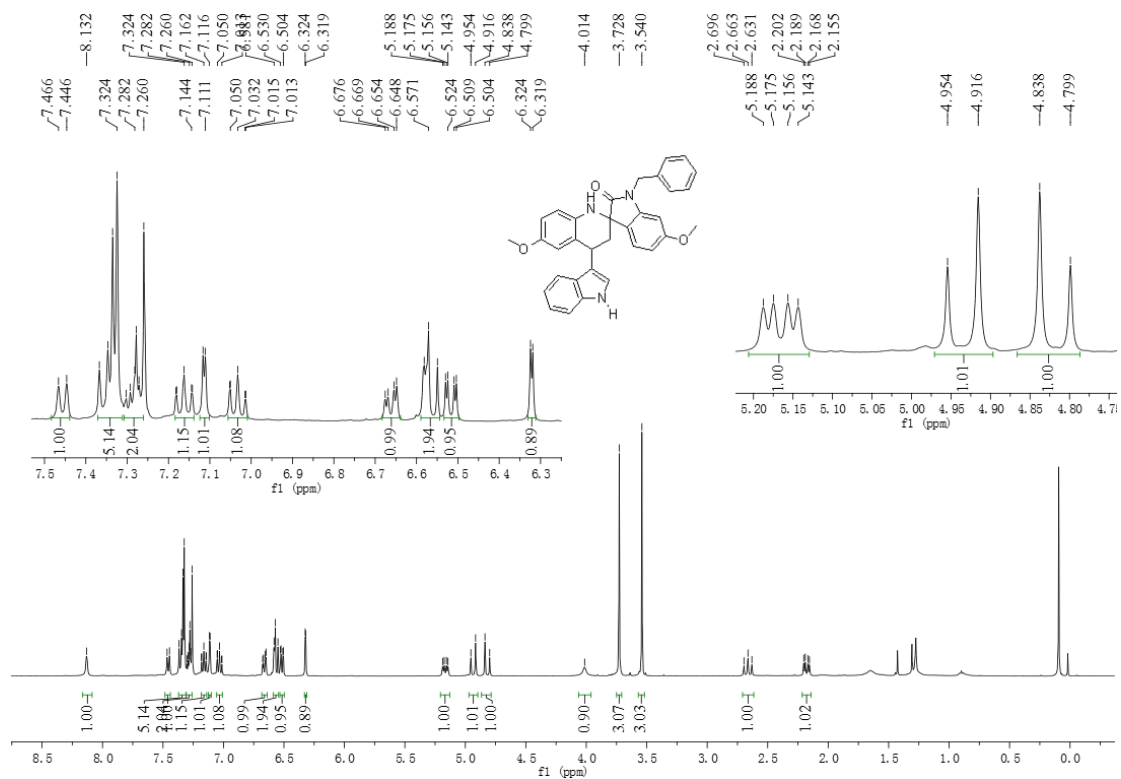
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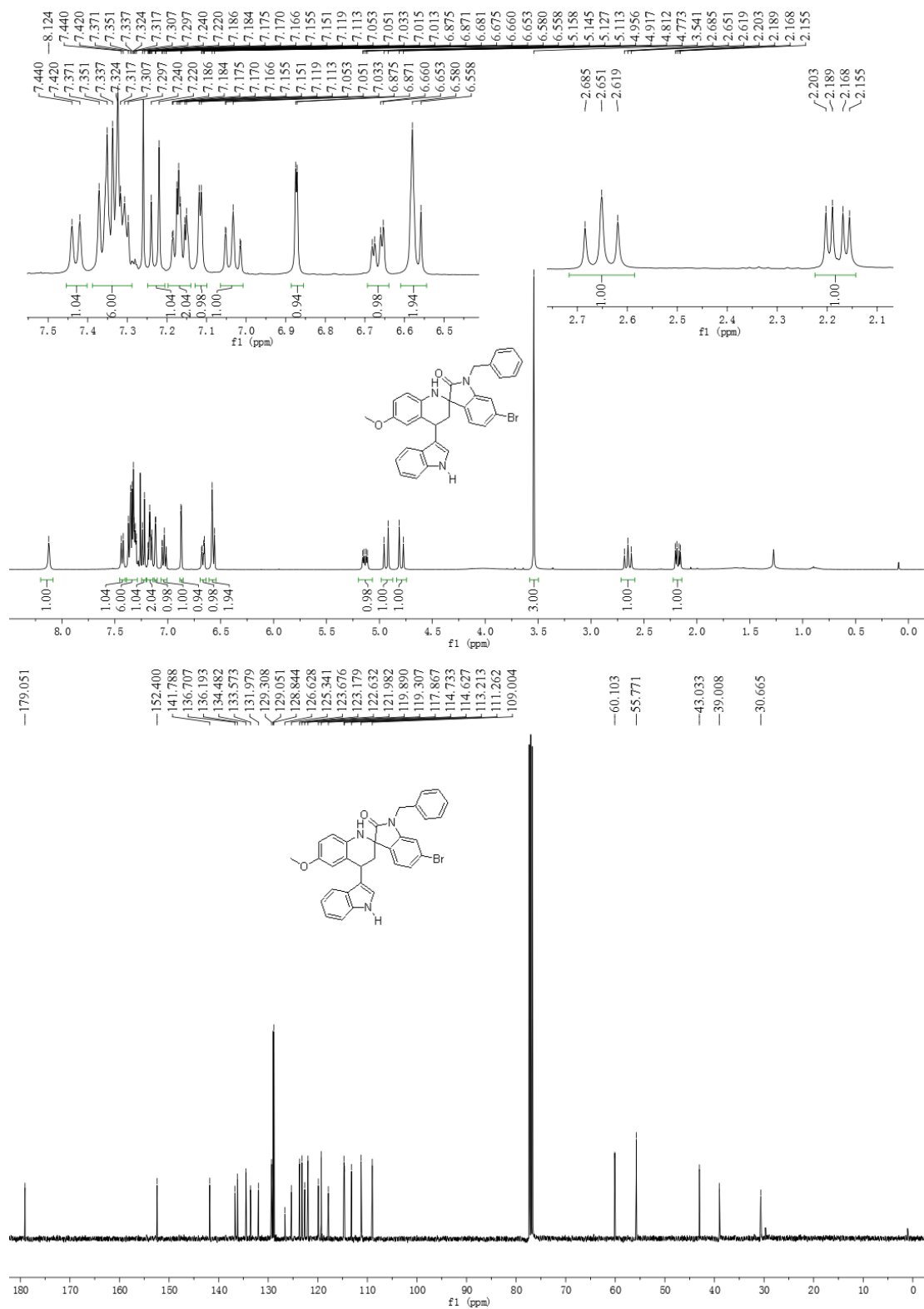
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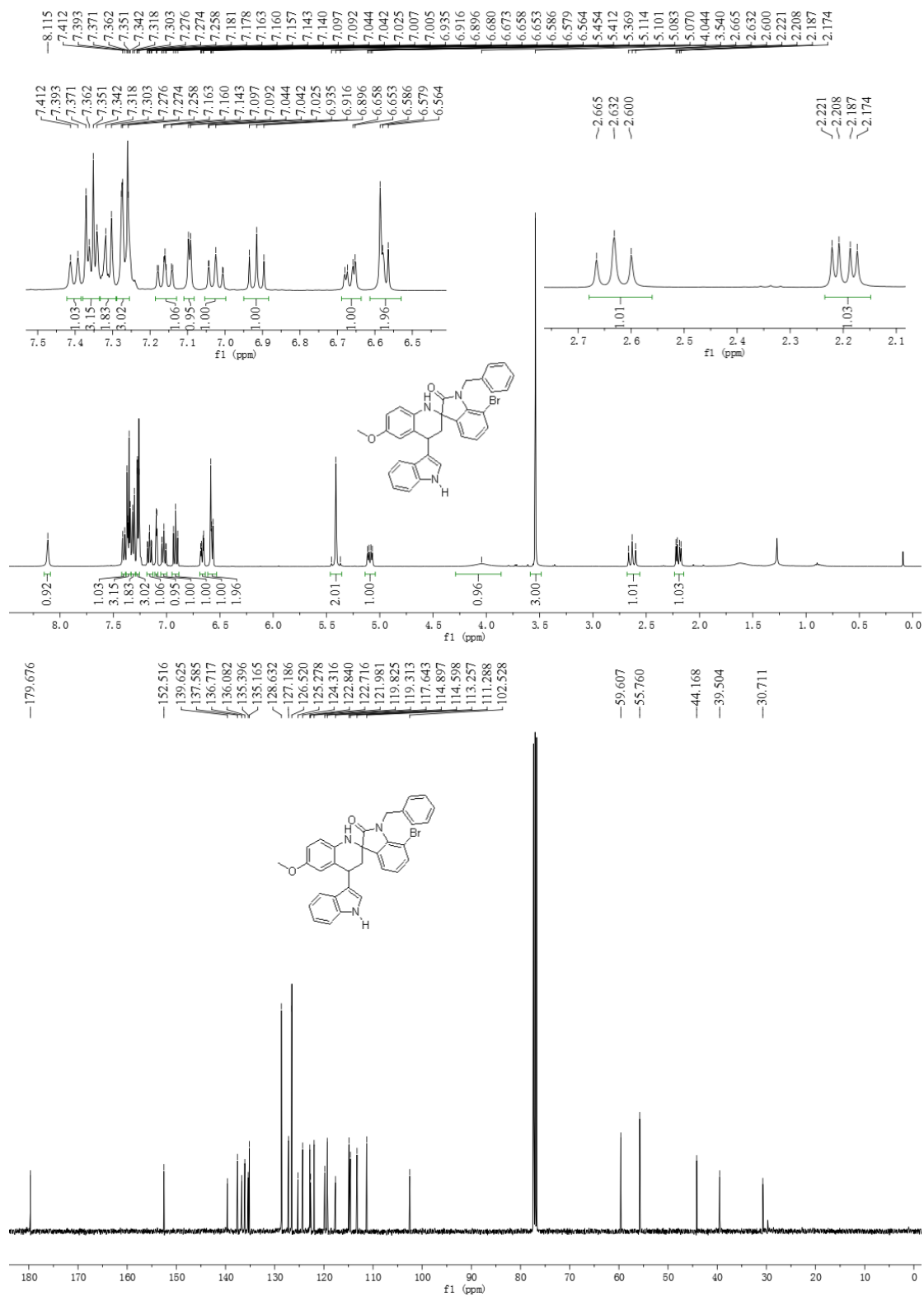
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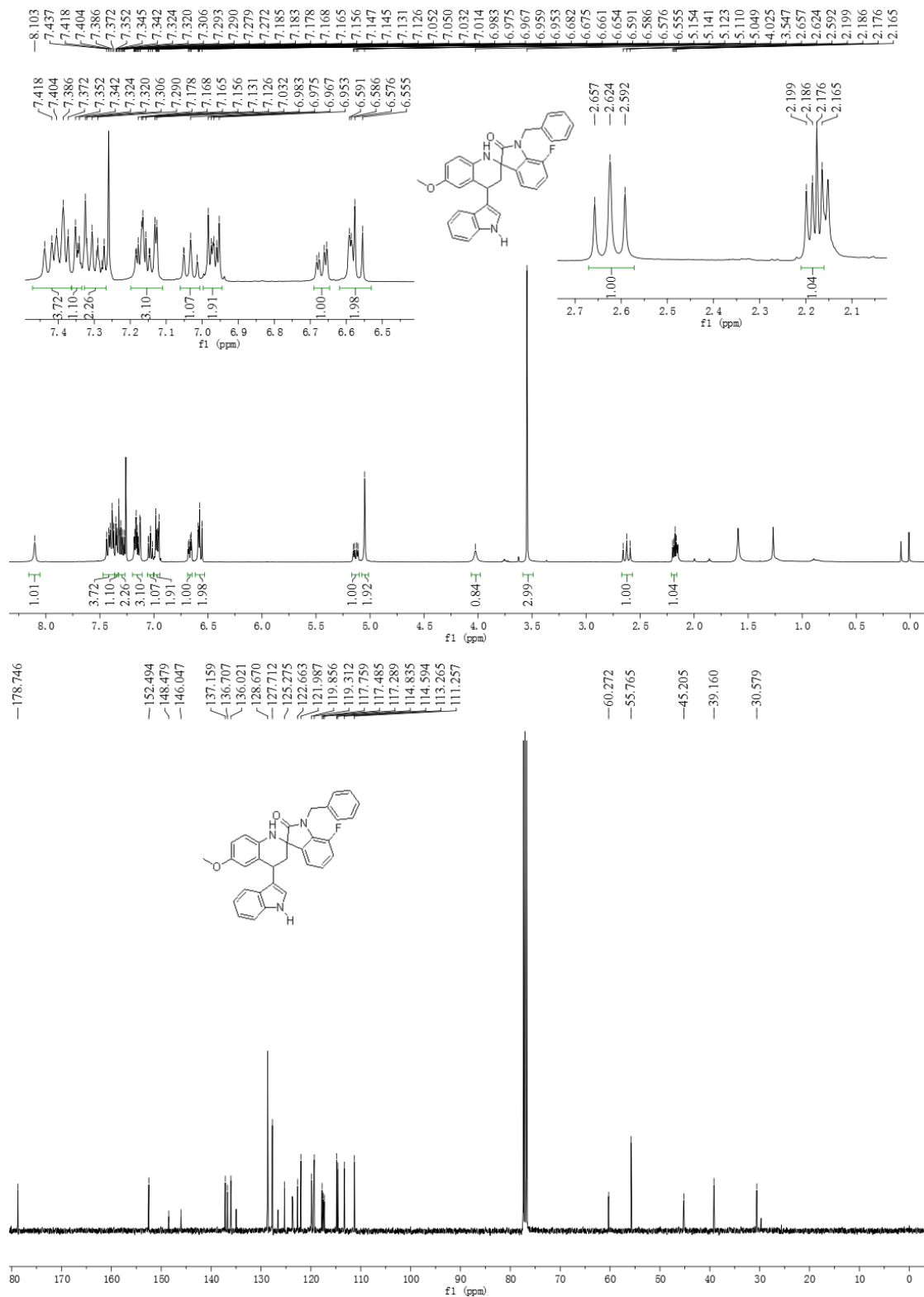
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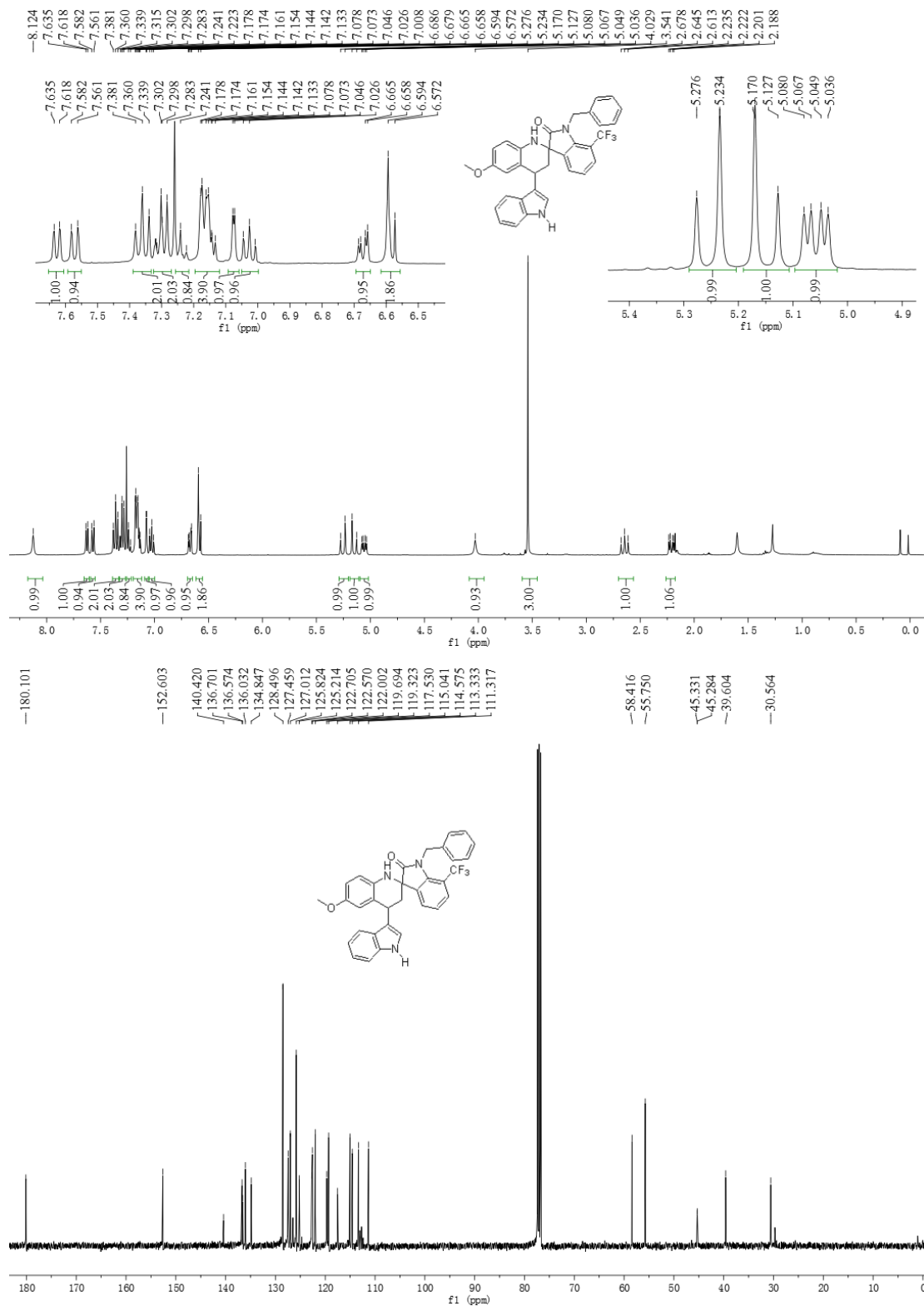
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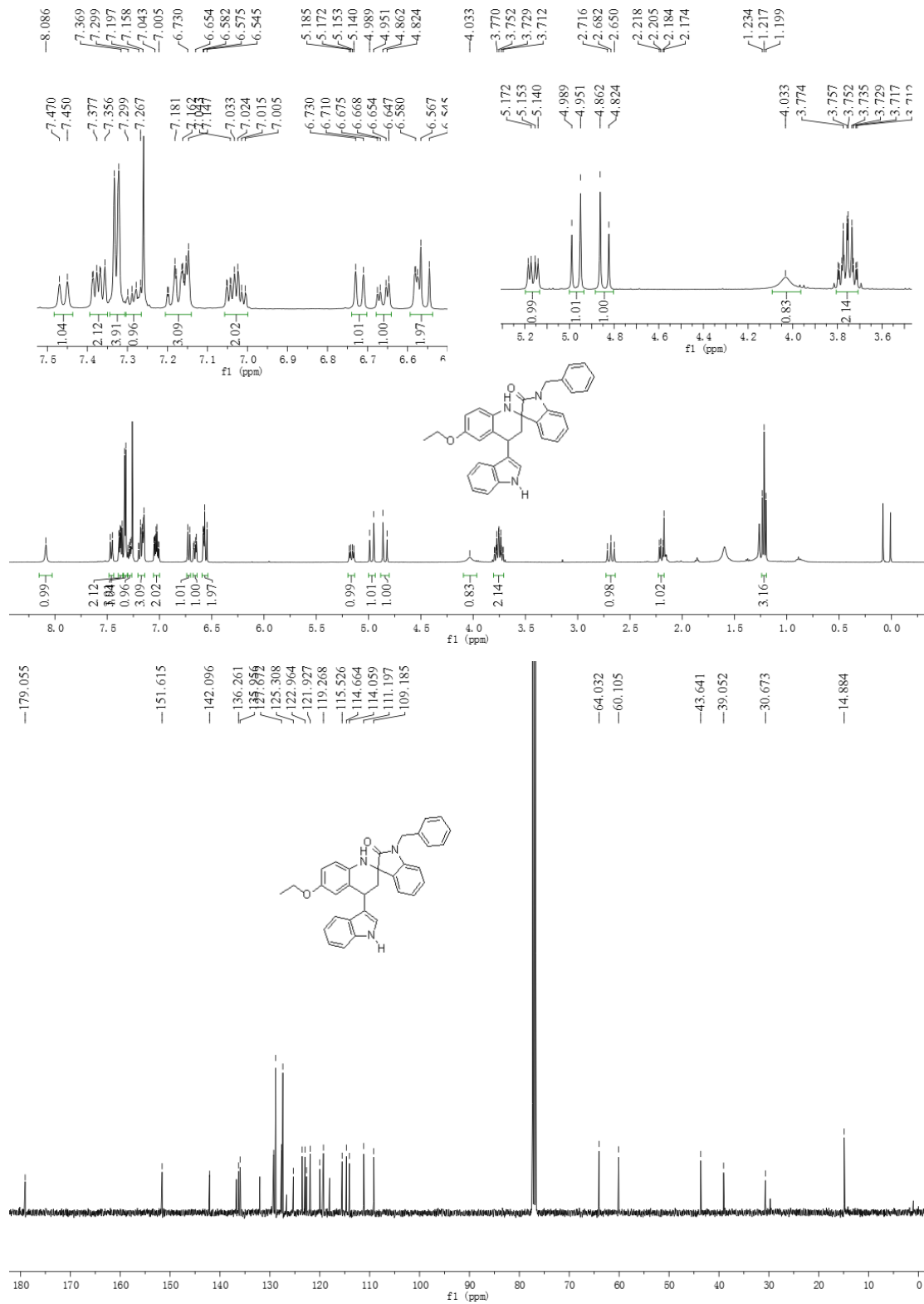
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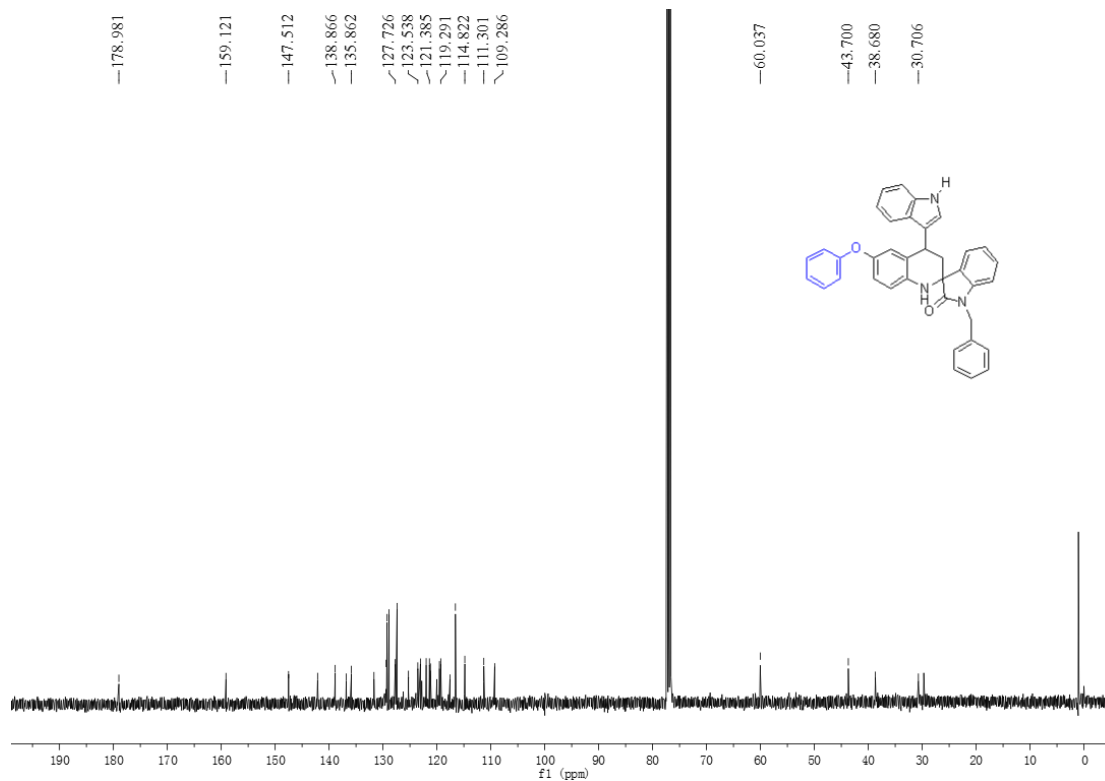
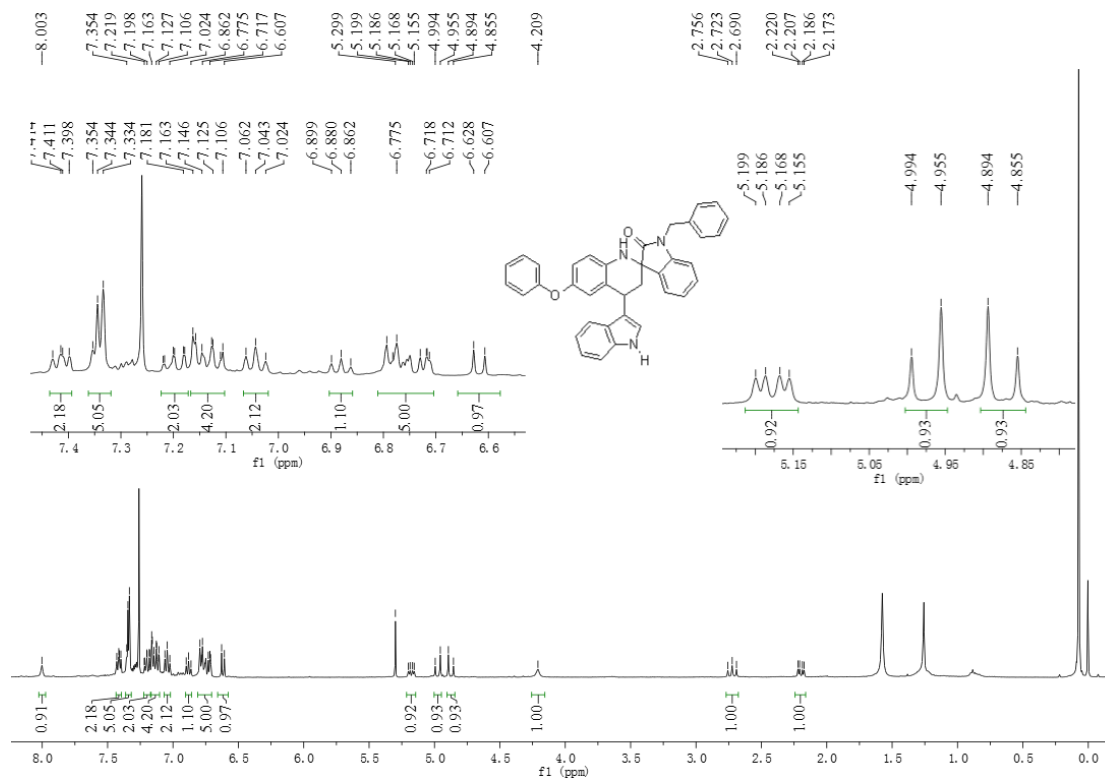
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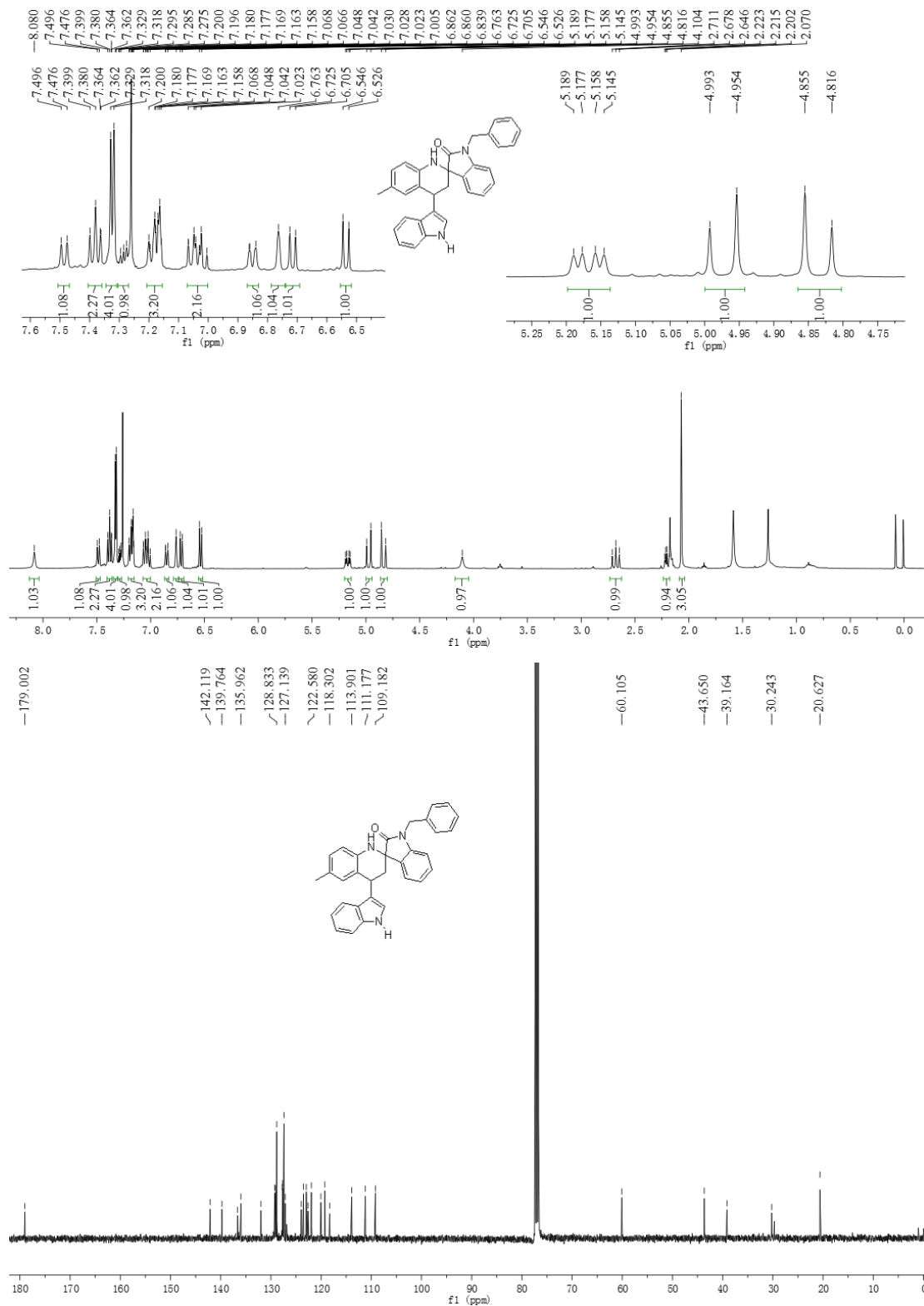
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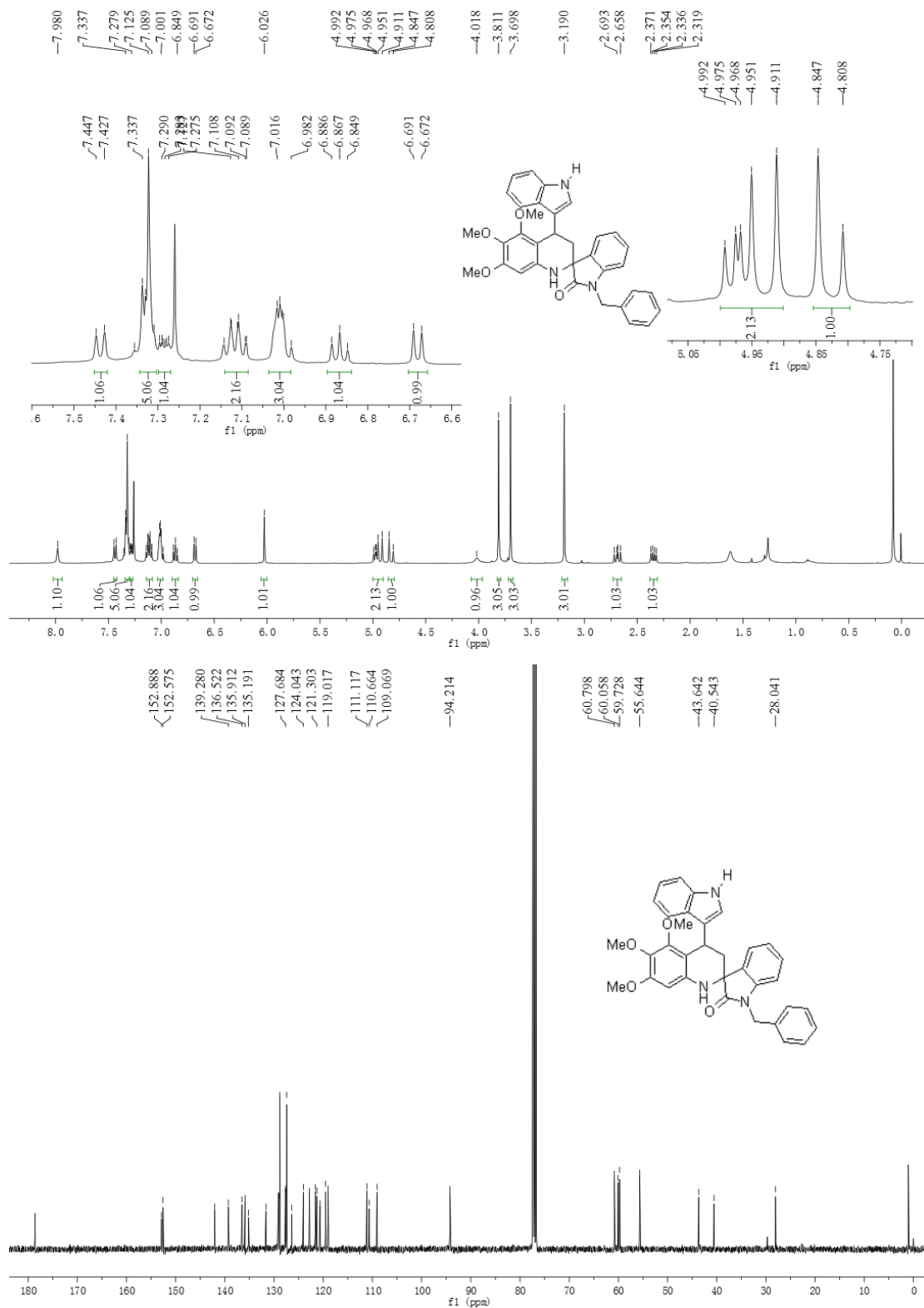
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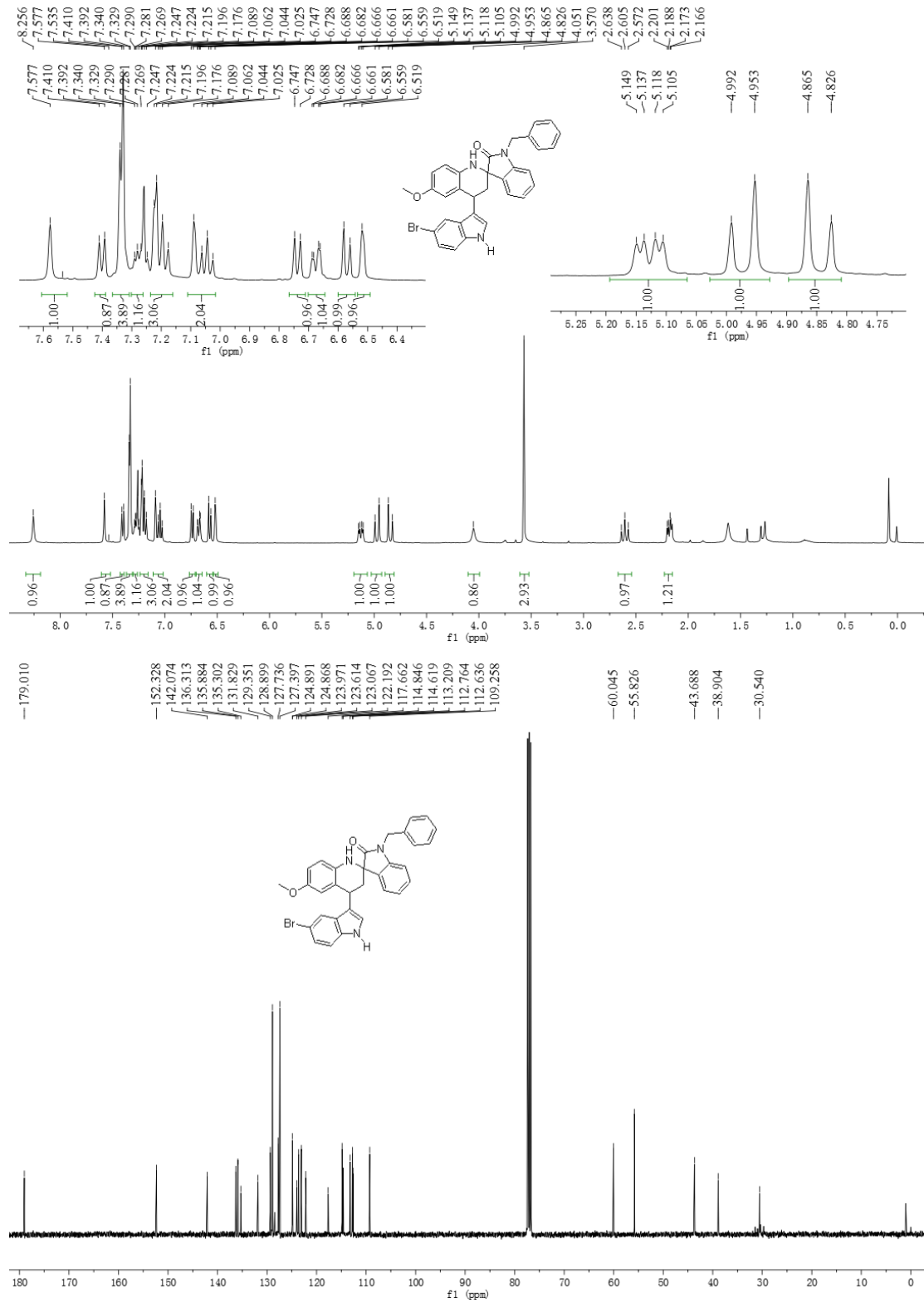
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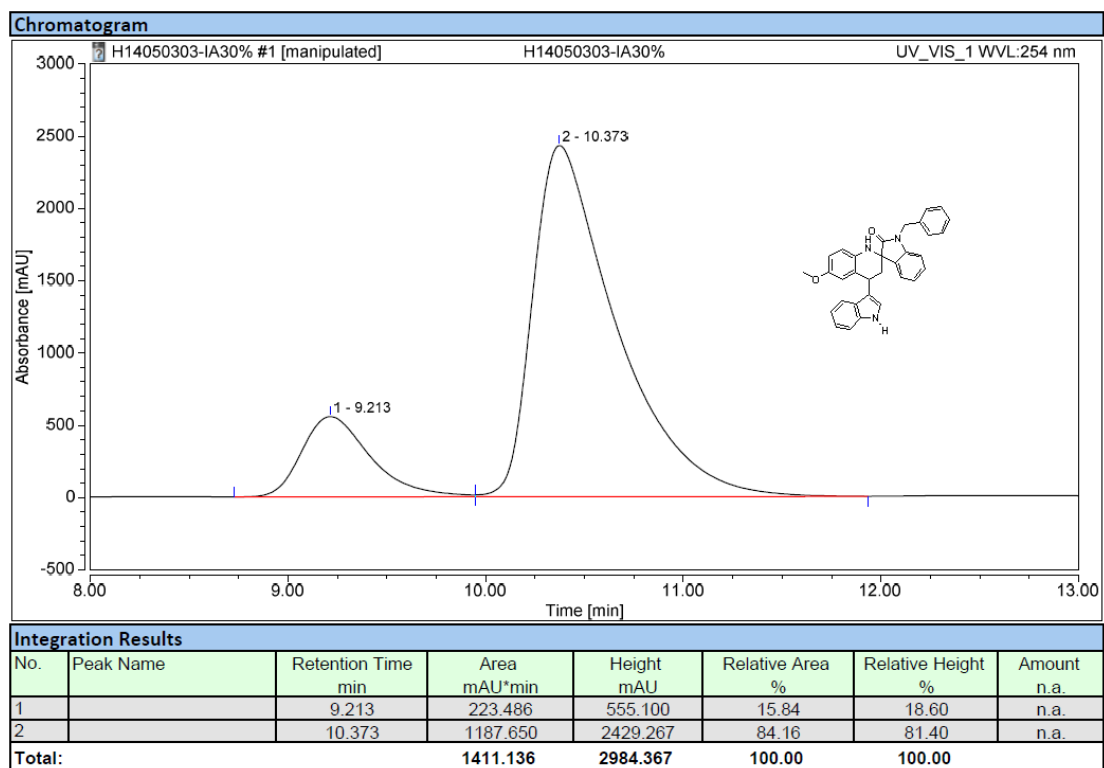
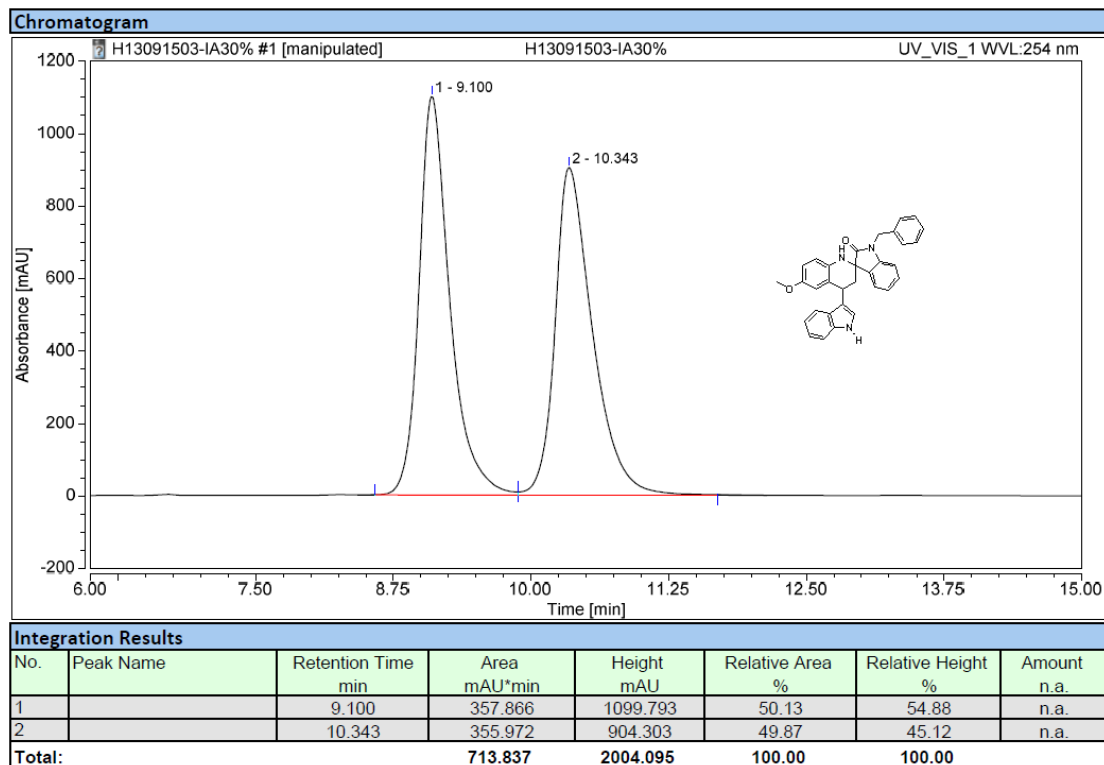


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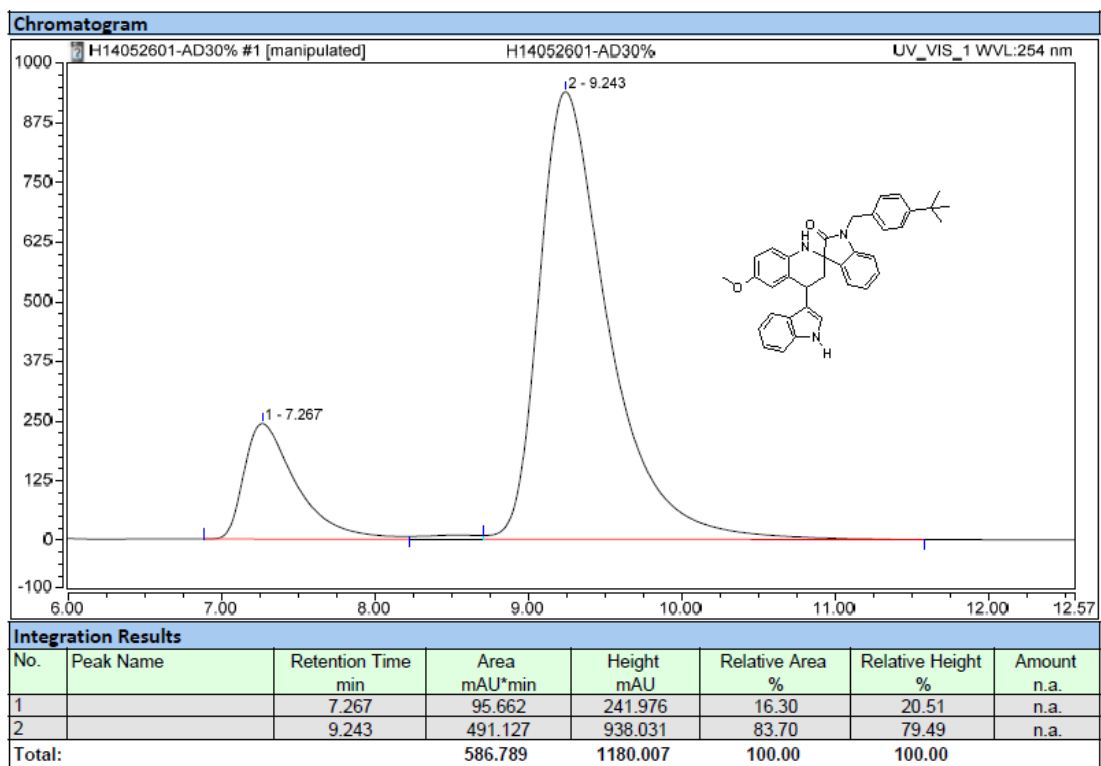
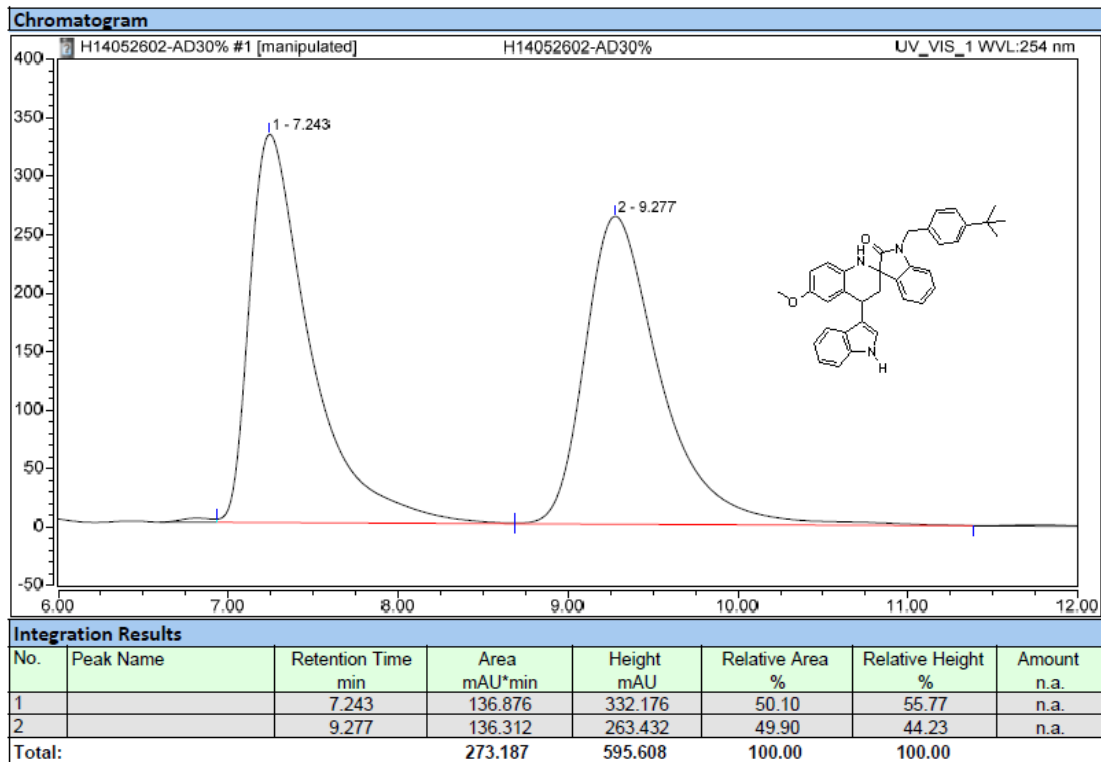


HPLC Spectra of products 3

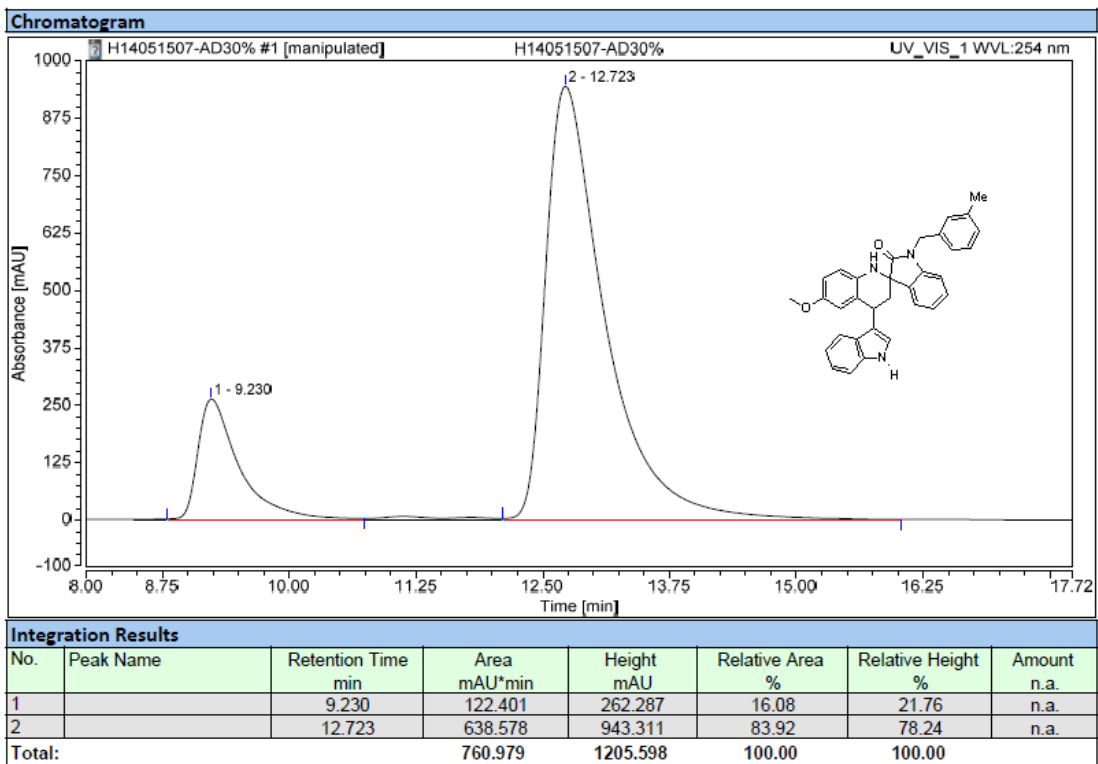
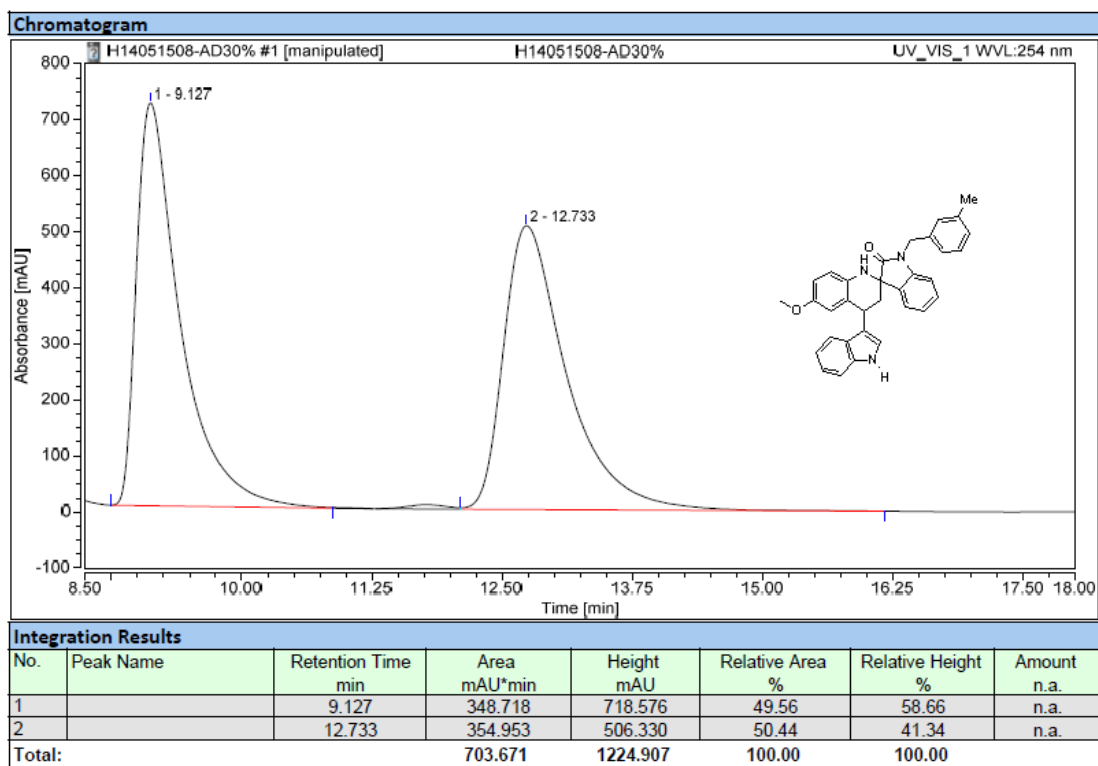
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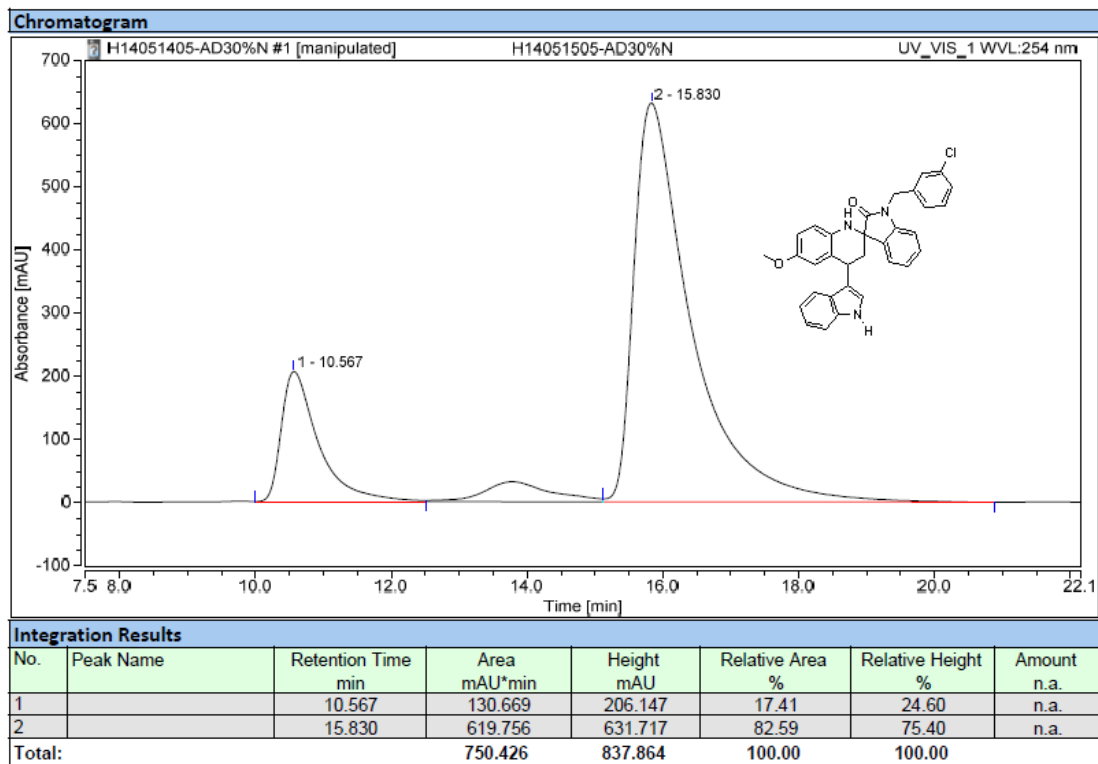
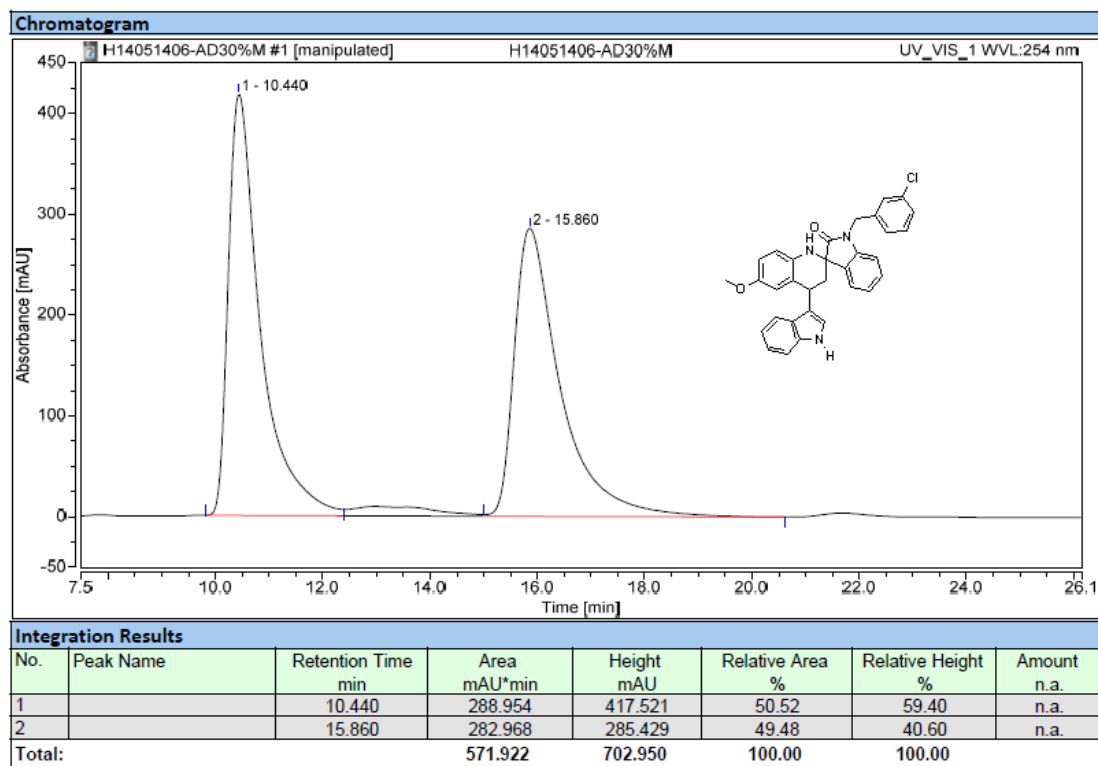
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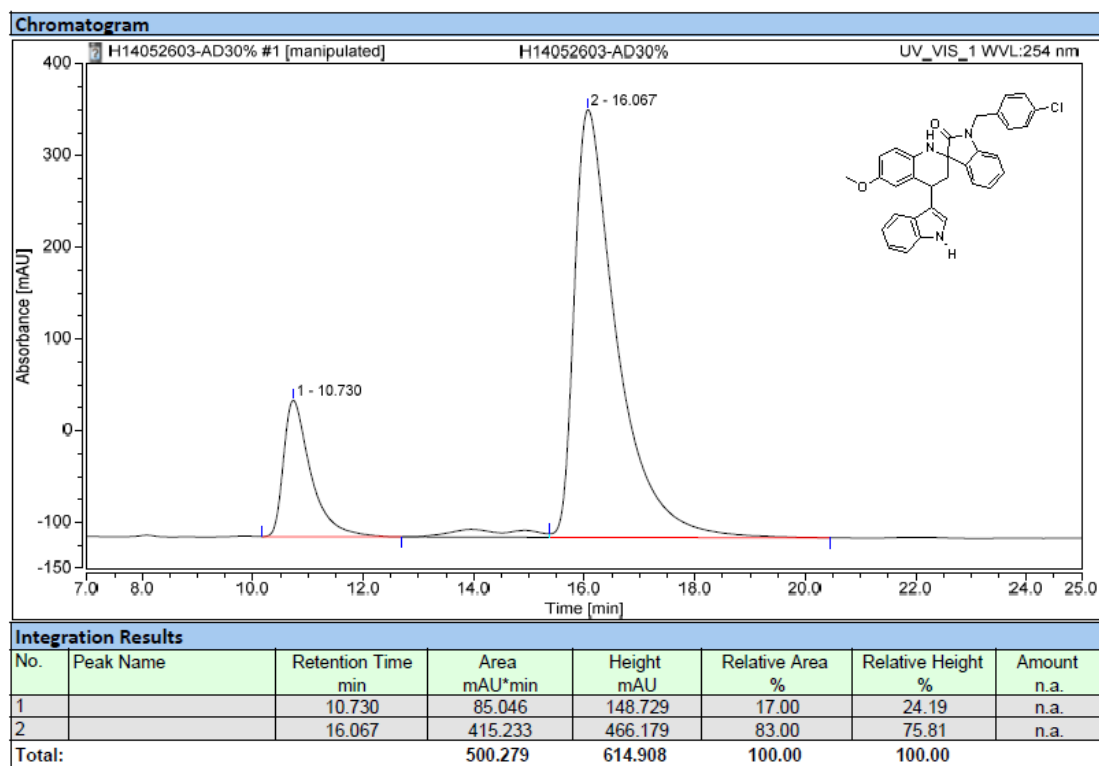
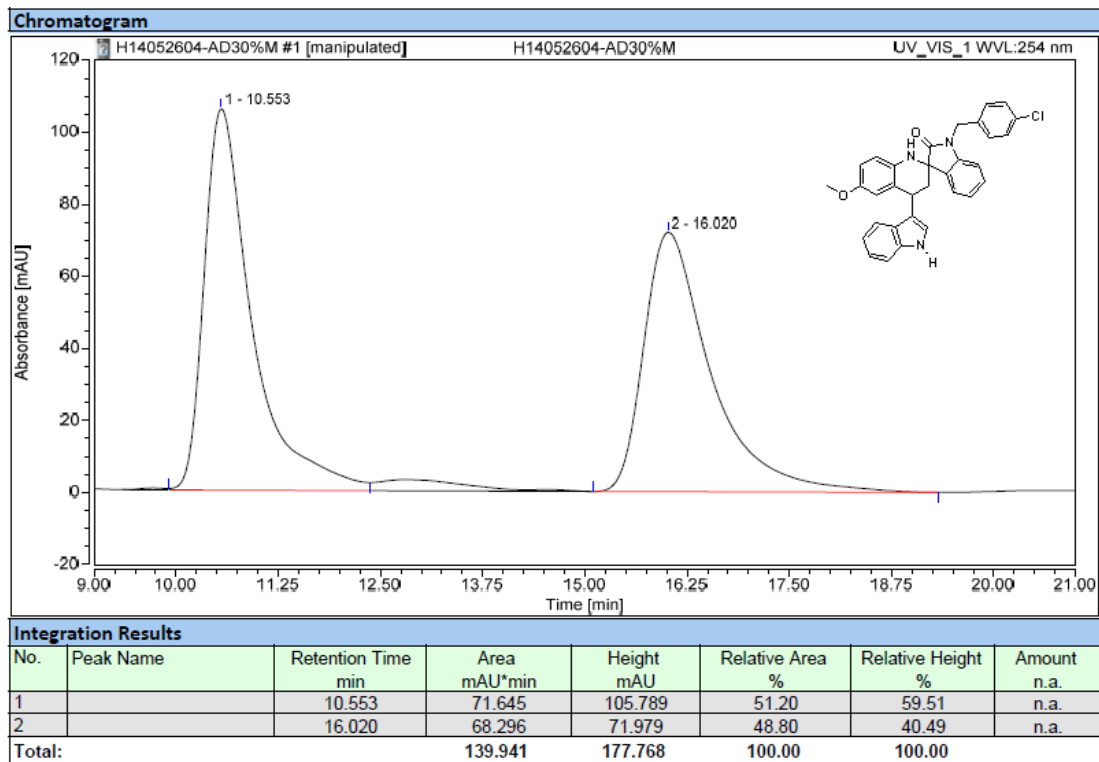
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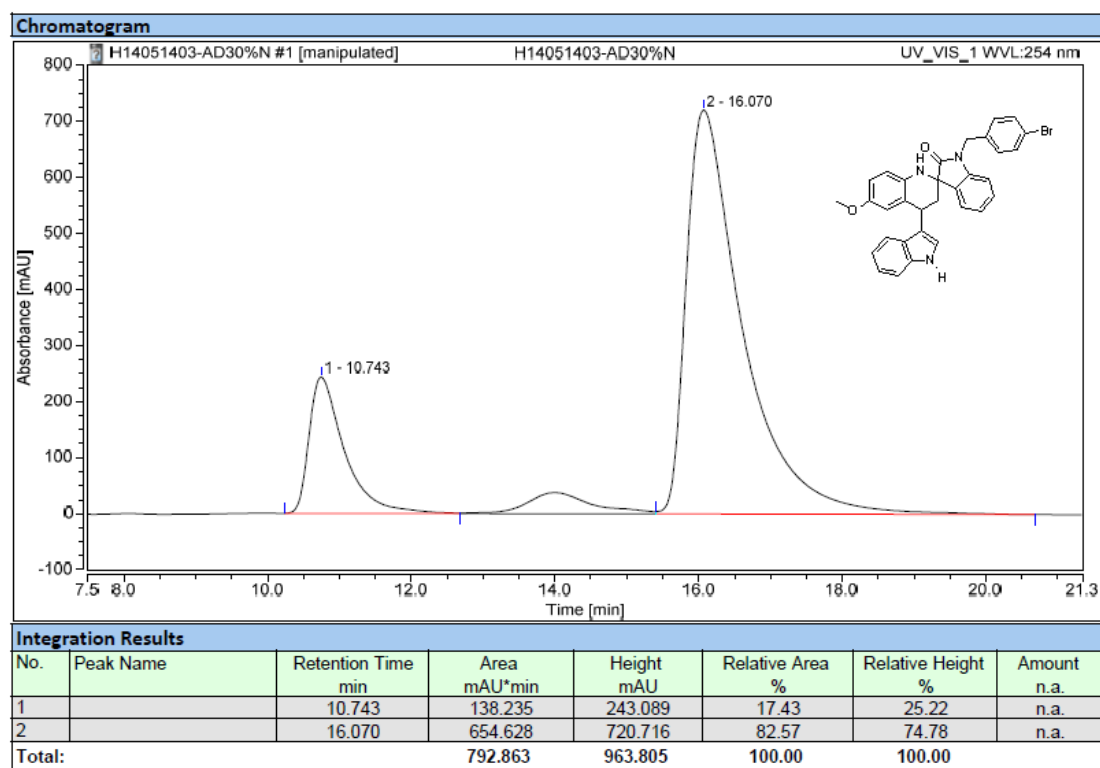
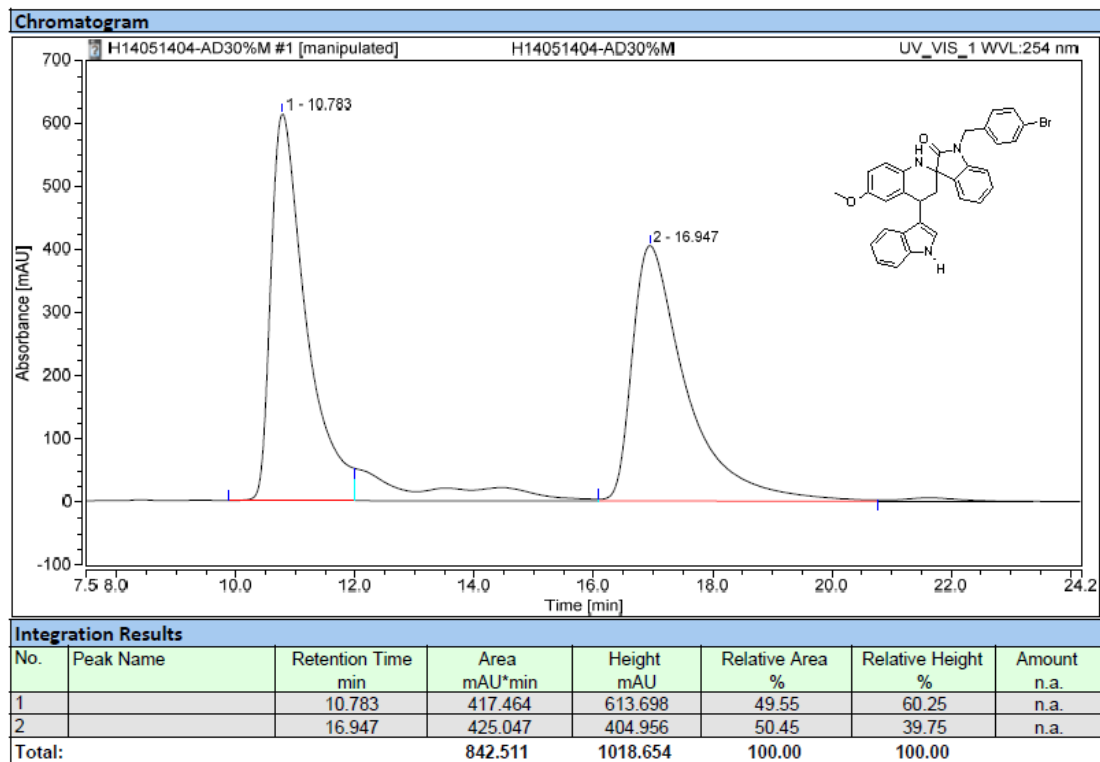
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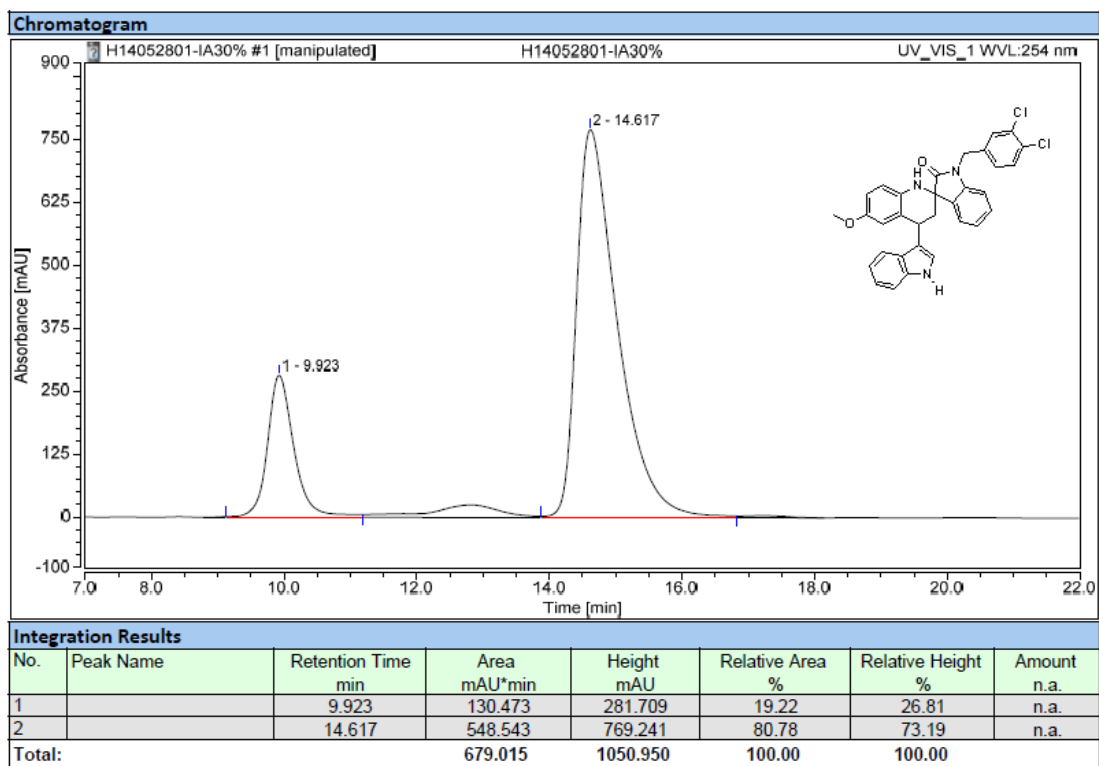
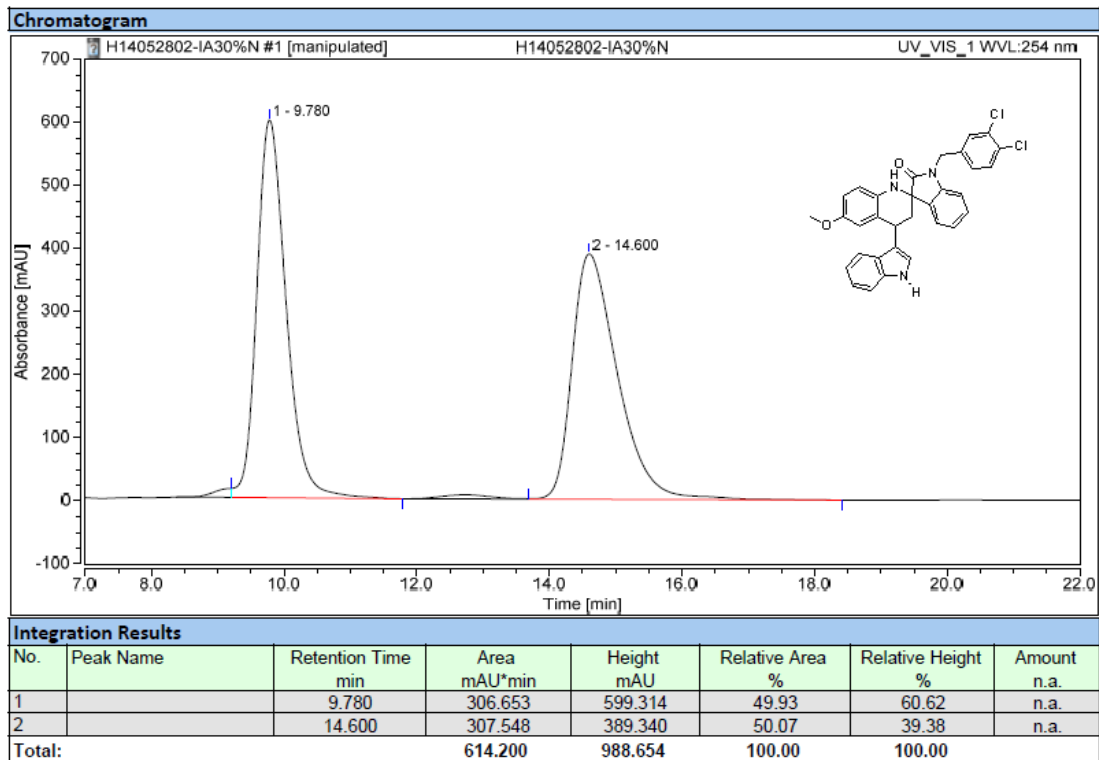
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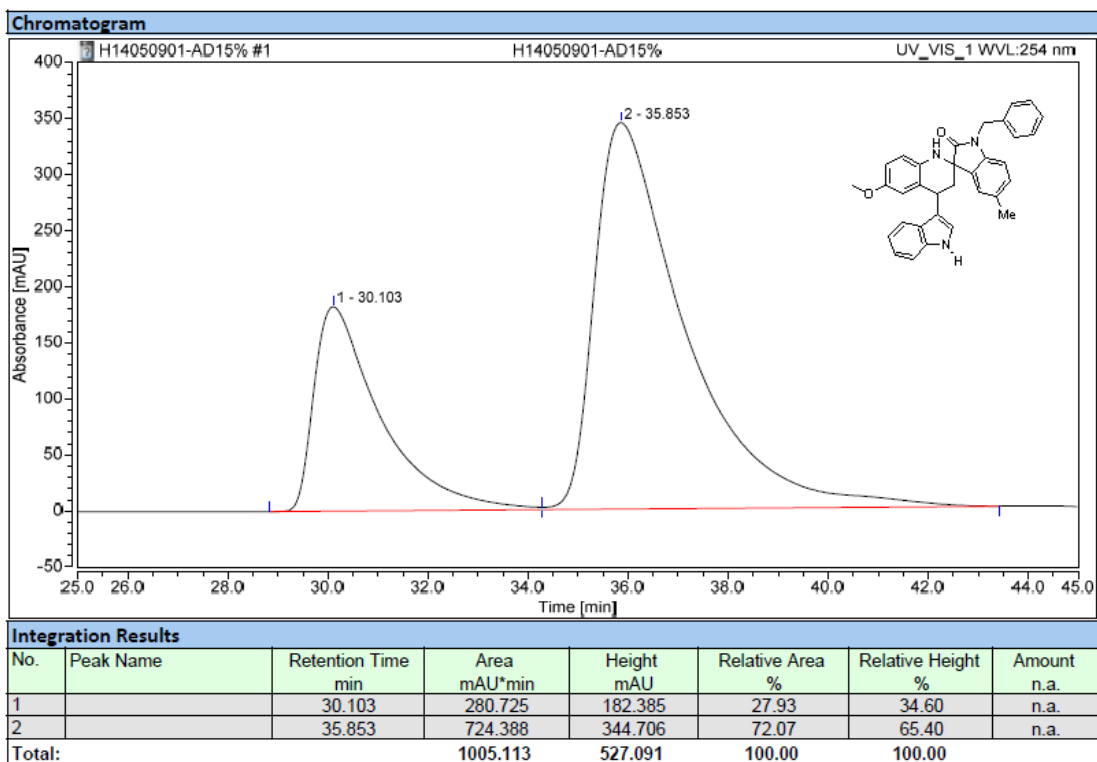
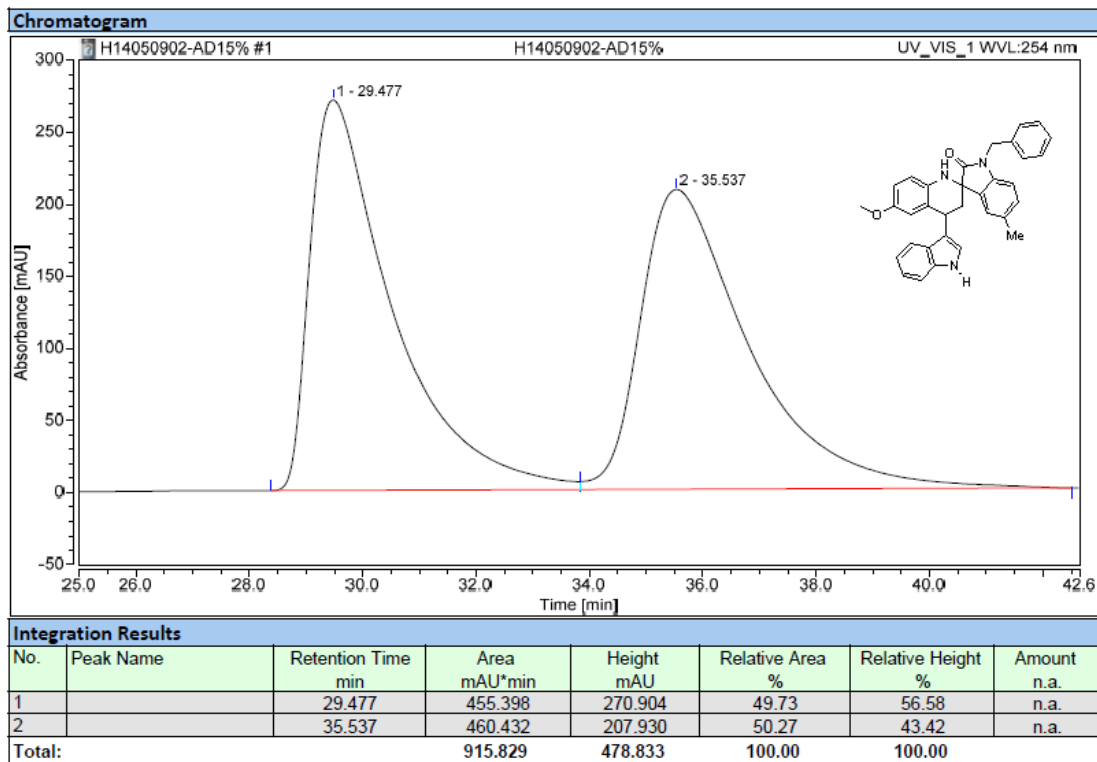
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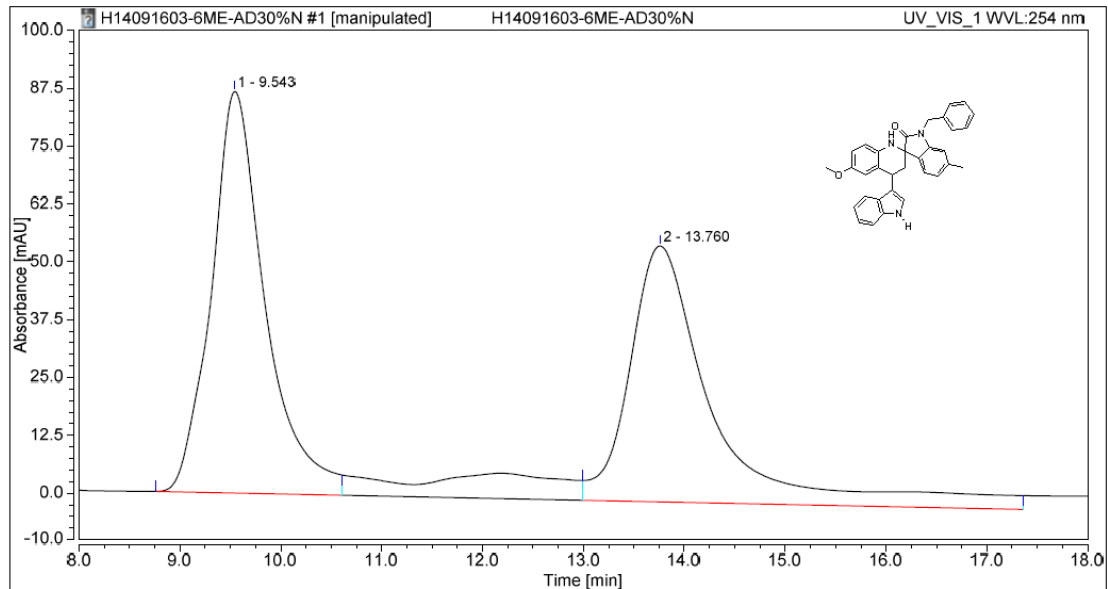
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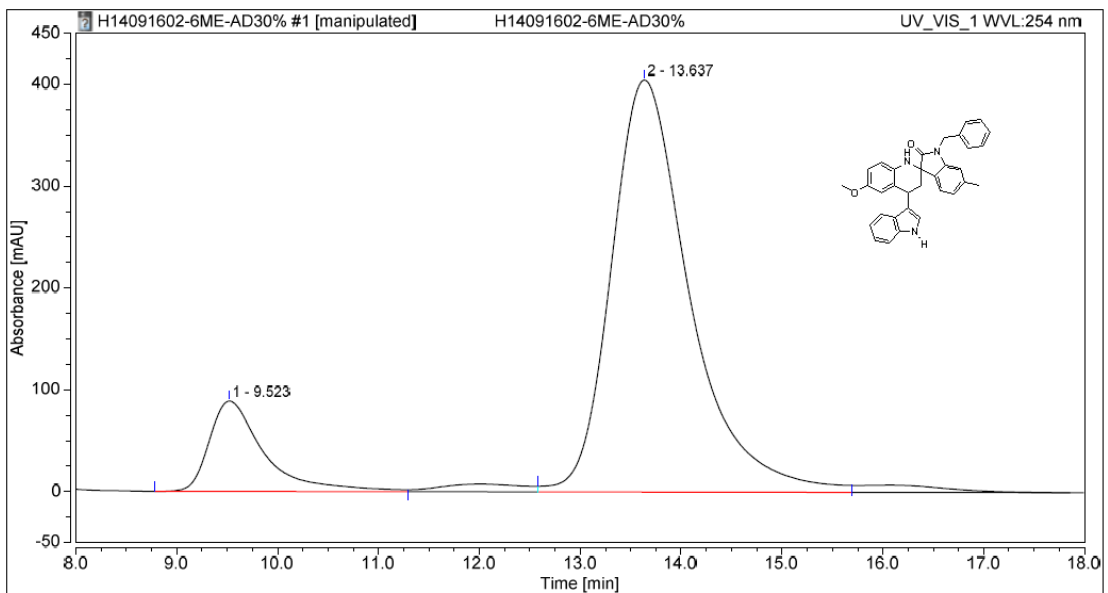
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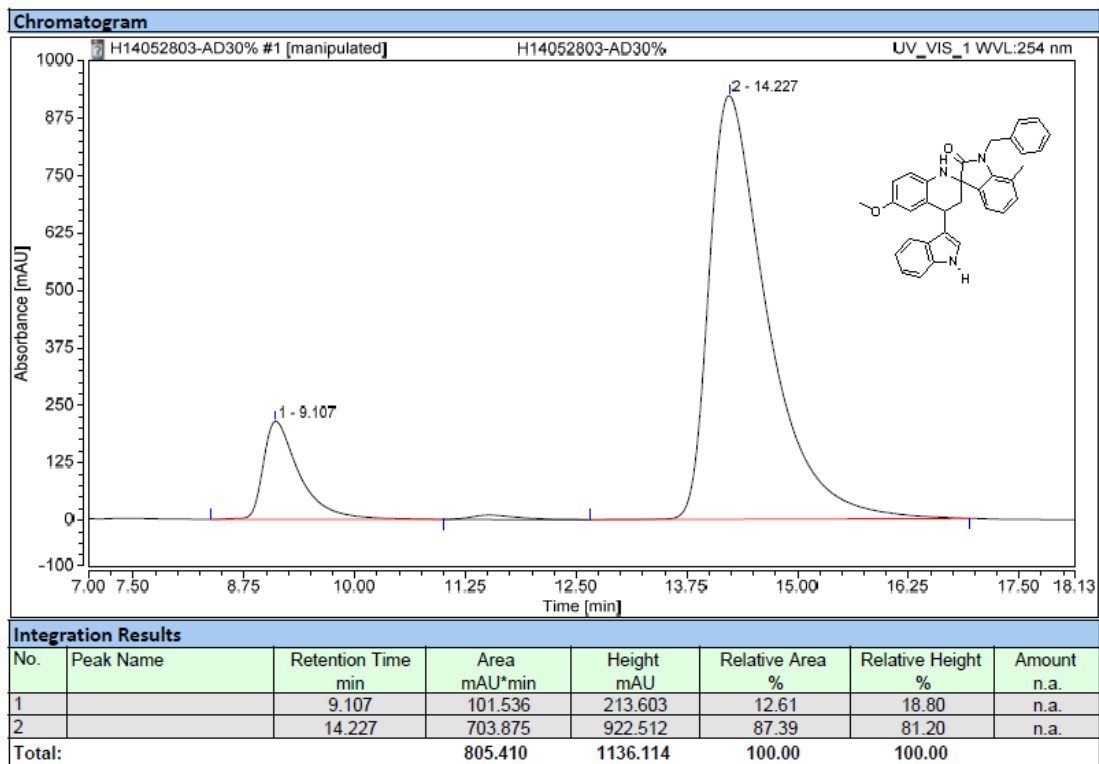
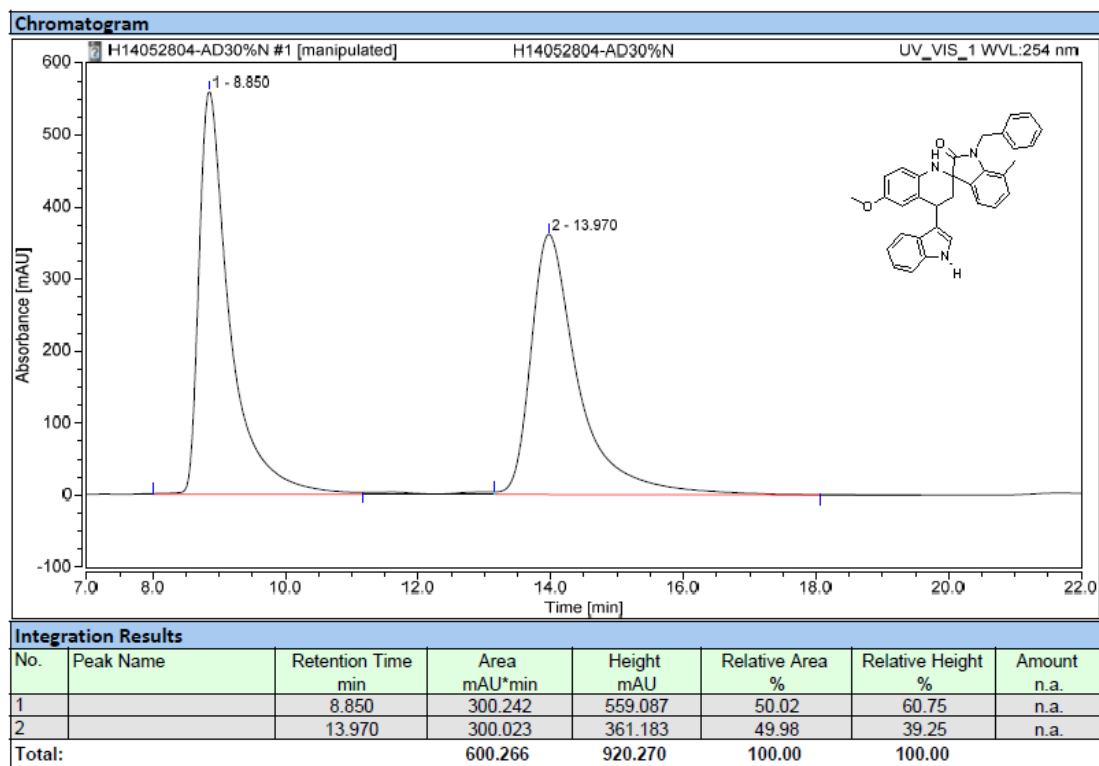


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		9.543	53.593	86.811	50.08	61.07	n.a.
2		13.760	53.422	55.333	49.92	38.93	n.a.
Total:			107.014	142.144	100.00	100.00	

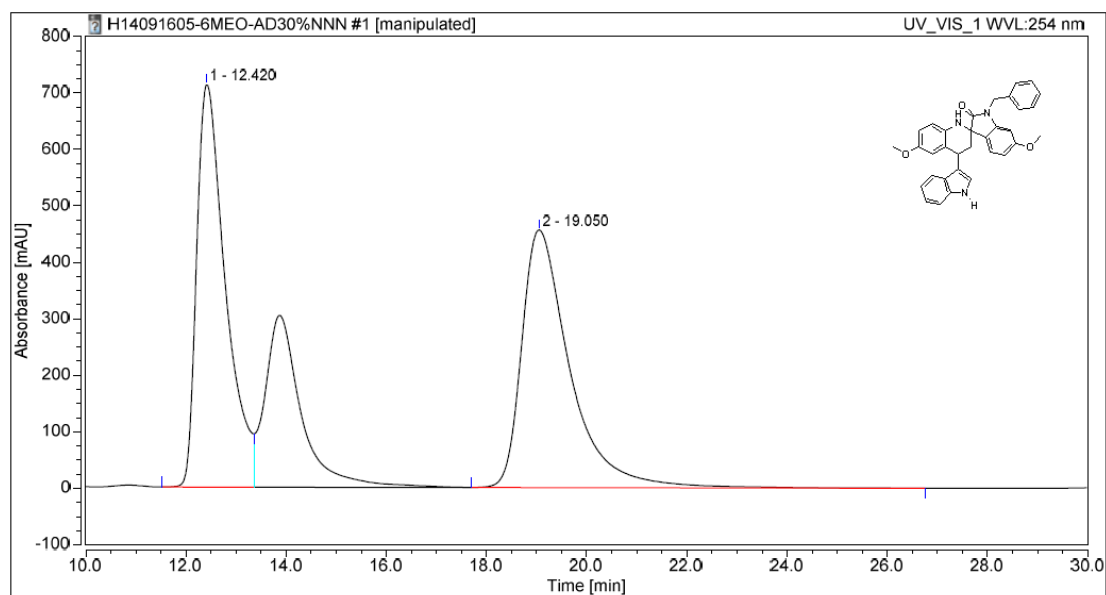


No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount
1		9.523	55.997	88.965	13.34	18.02	n.a.
2		13.637	363.845	404.759	86.66	81.98	n.a.
Total:			419.842	493.723	100.00	100.00	

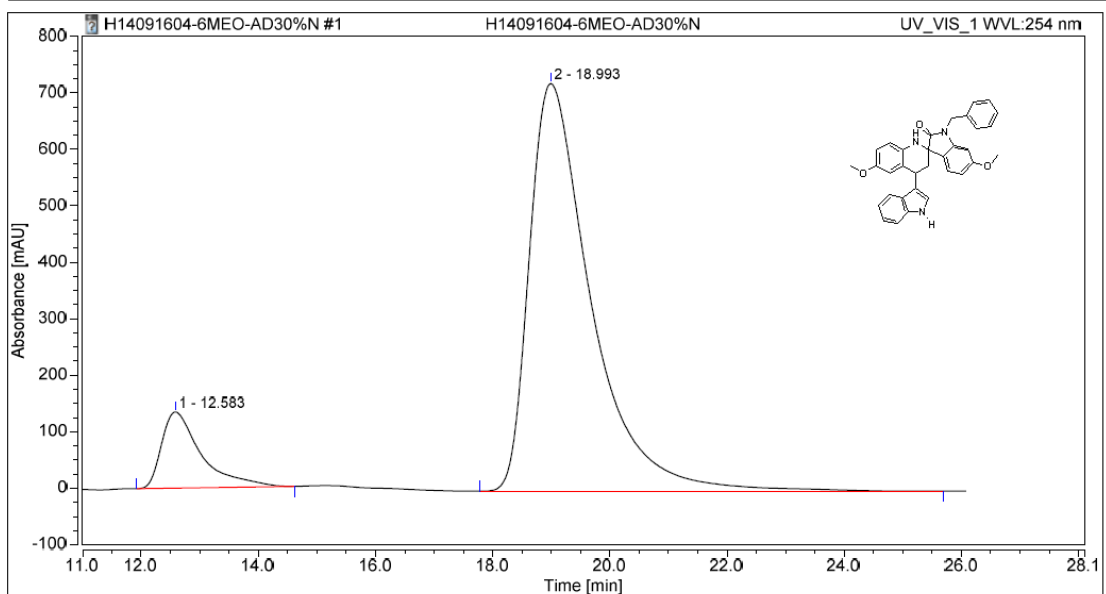
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3ka

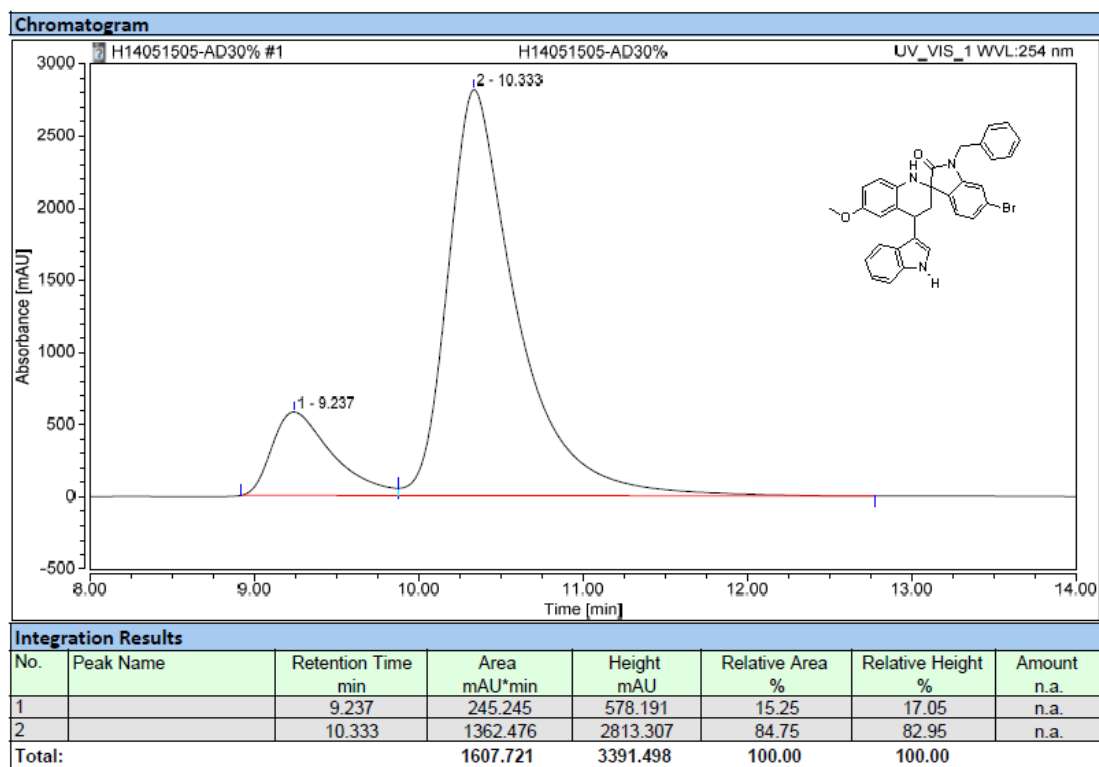
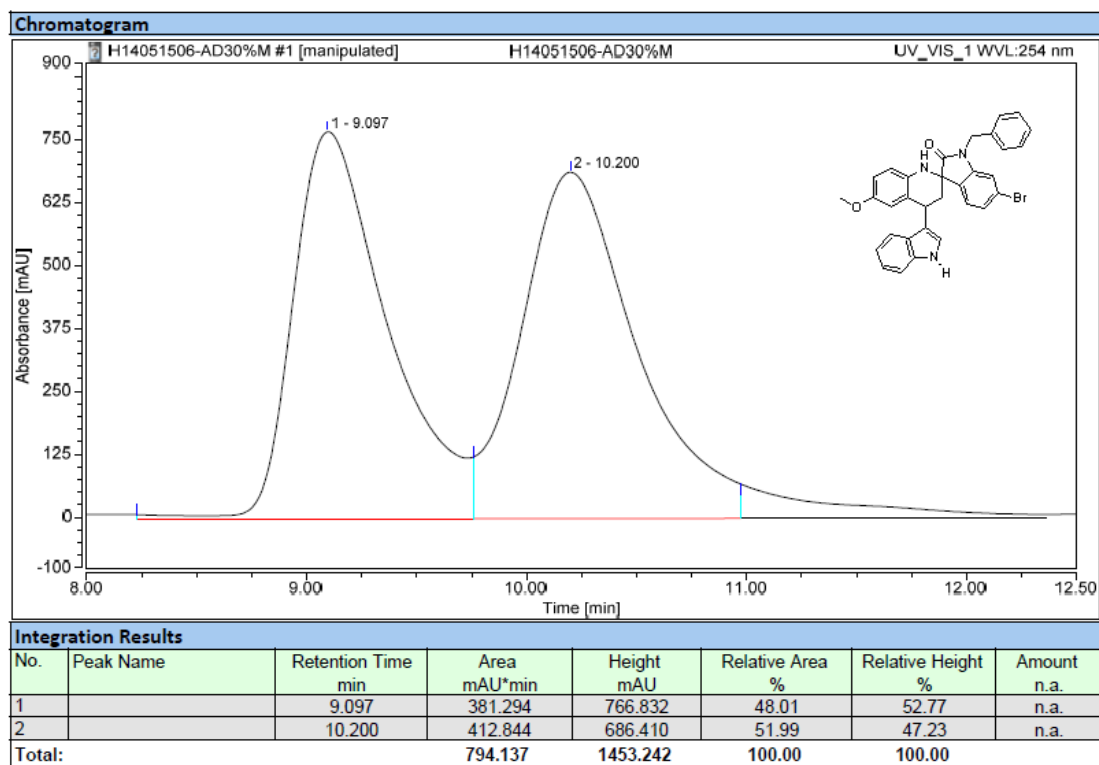


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.420	474.134	713.198	48.33	60.98	n.a.
2		19.050	506.905	456.374	51.67	39.02	n.a.
Total:			981.039	1169.572	100.00	100.00	

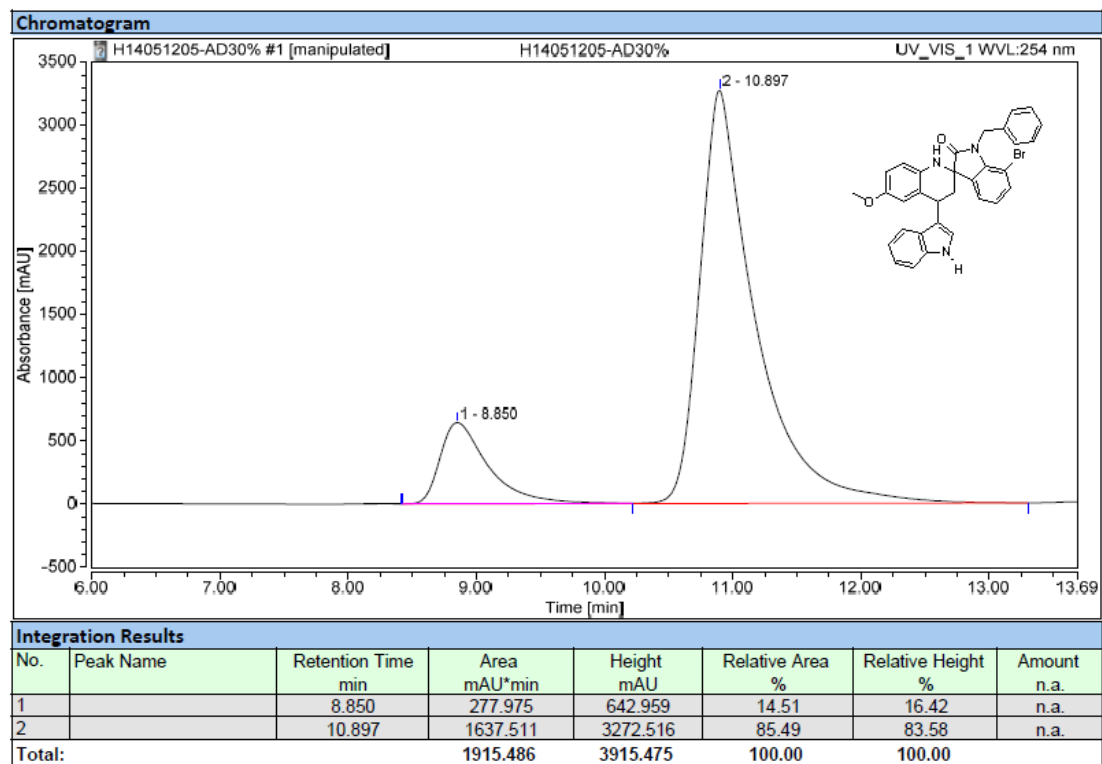
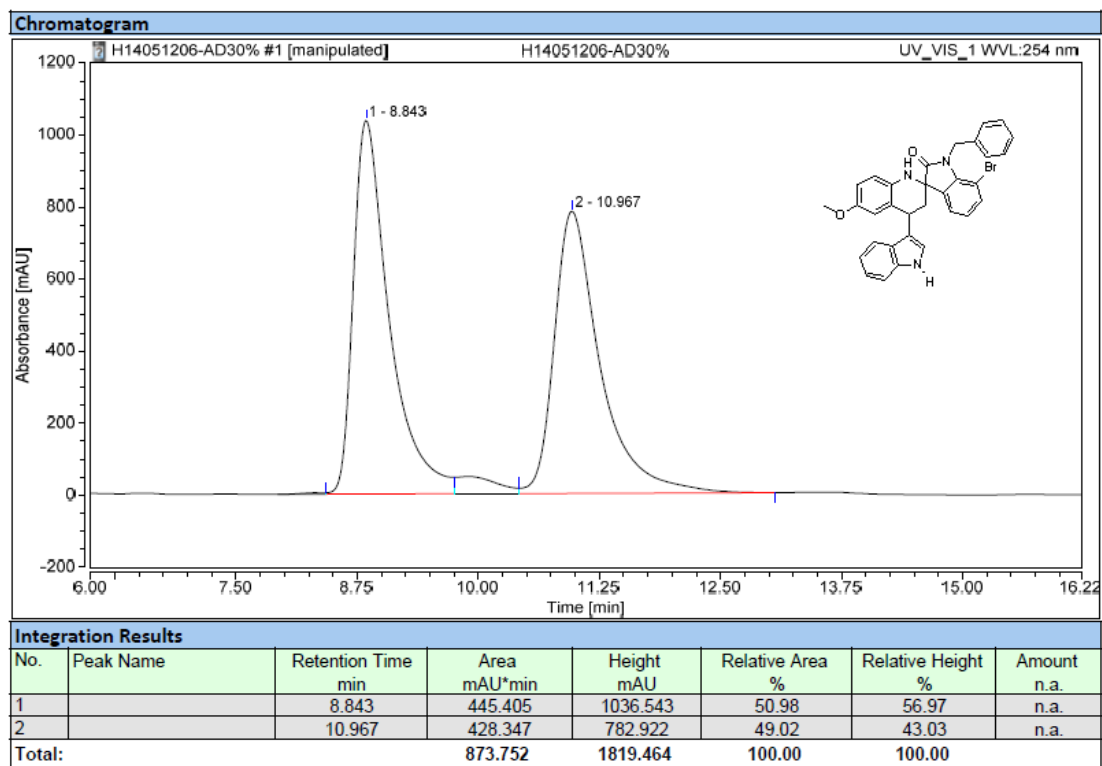


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.583	105.822	134.781	10.73	15.74	n.a.
2		18.993	880.716	721.714	89.27	84.26	n.a.
Total:			986.537	856.495	100.00	100.00	

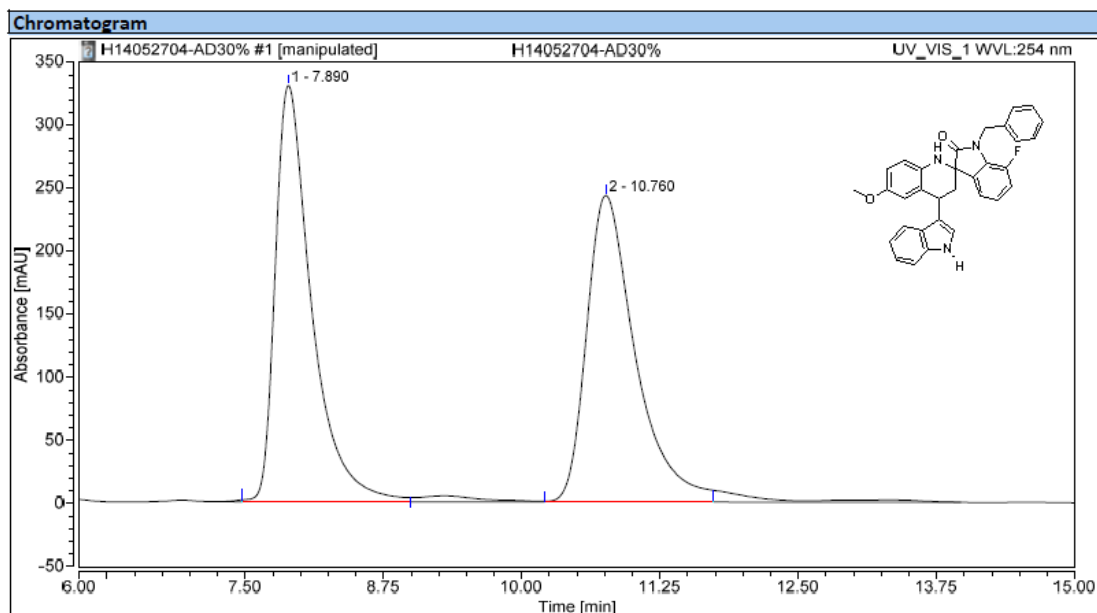
3la



3ma

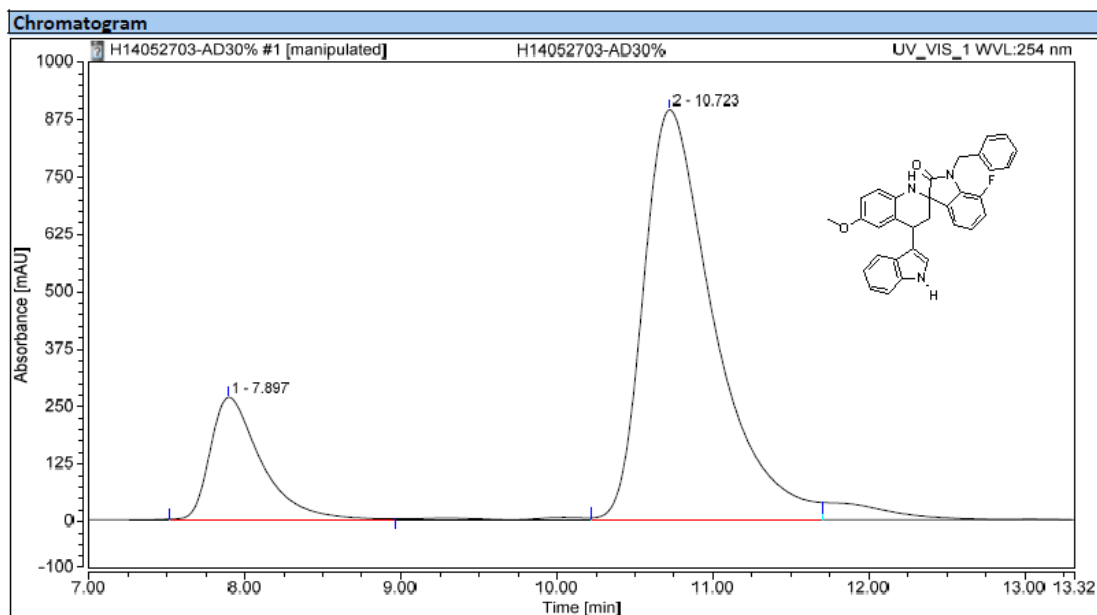


3na



Integration Results

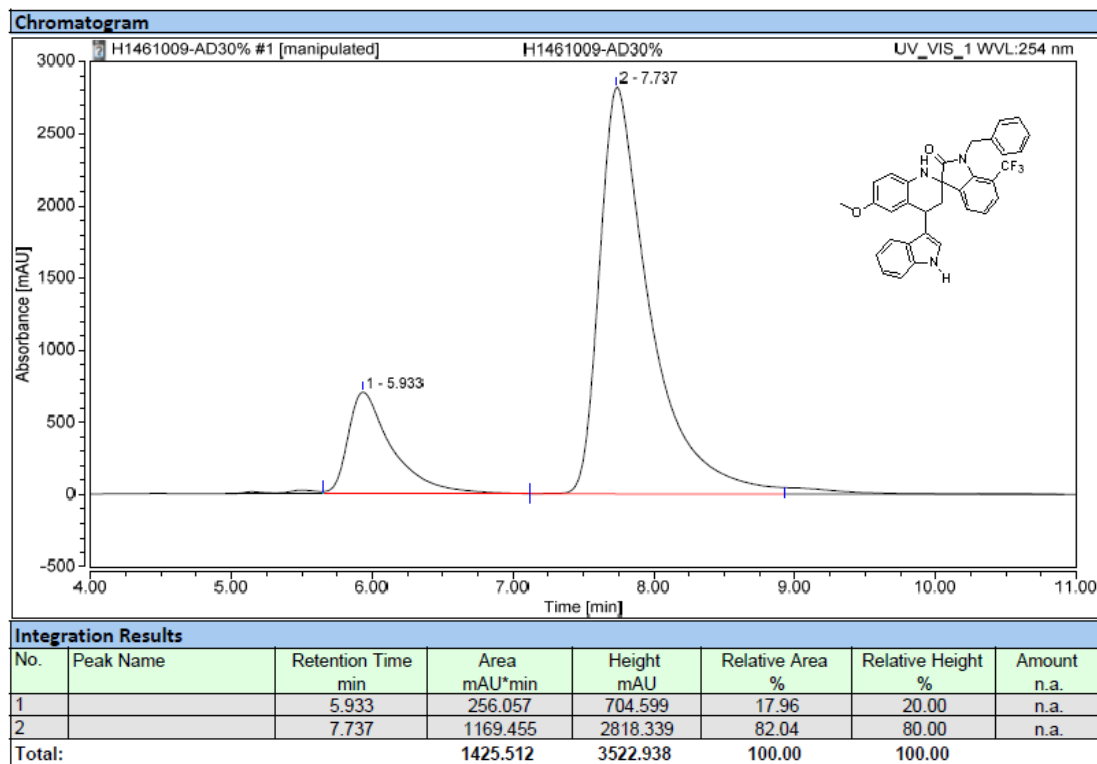
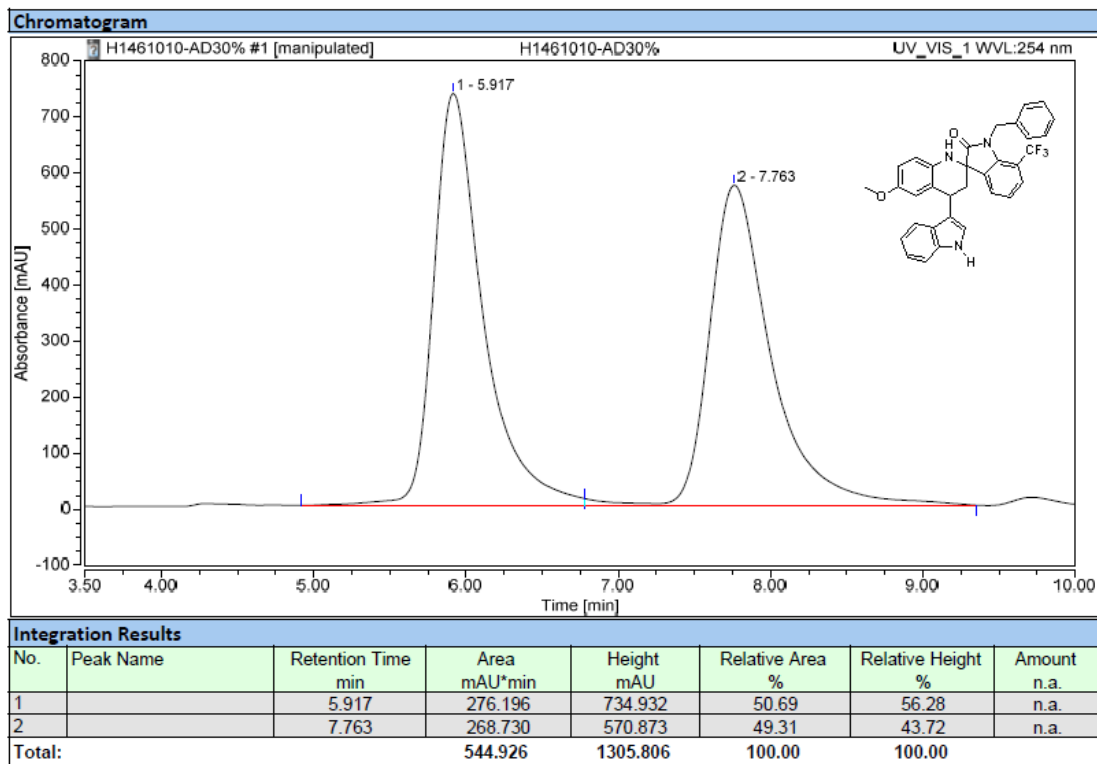
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.890	125.484	330.263	50.33	57.59	n.a.
2		10.760	123.853	243.162	49.67	42.41	n.a.
Total:			249.337	573.424	100.00	100.00	



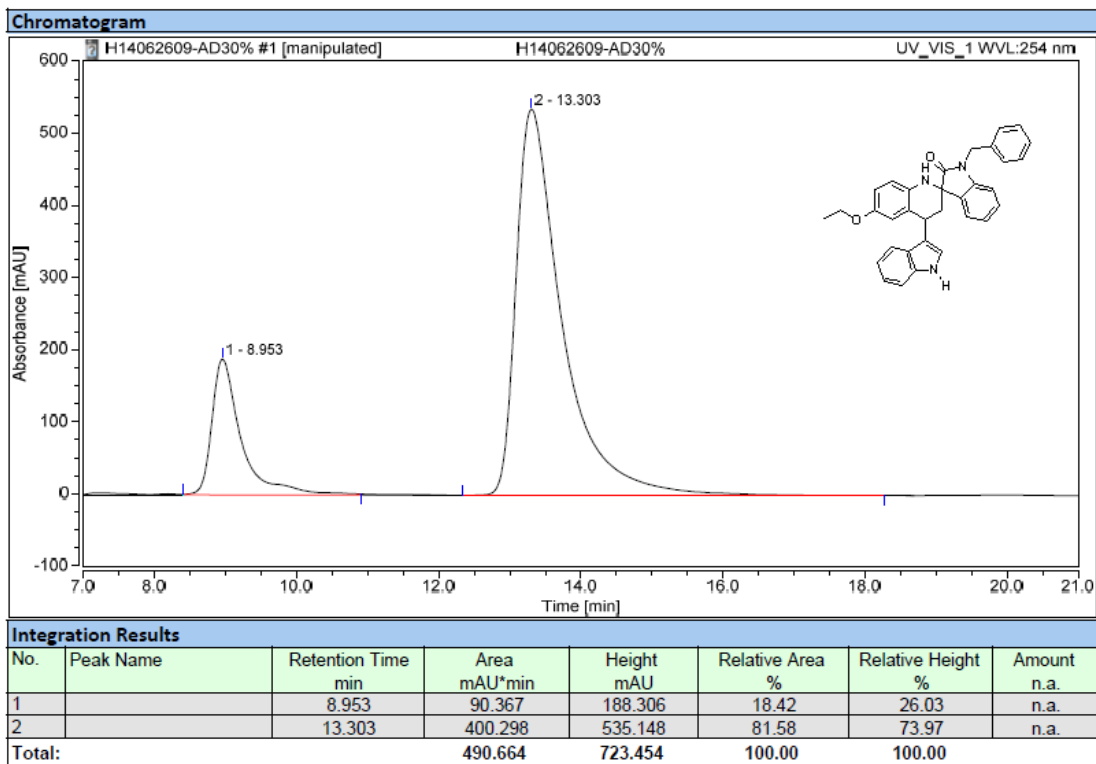
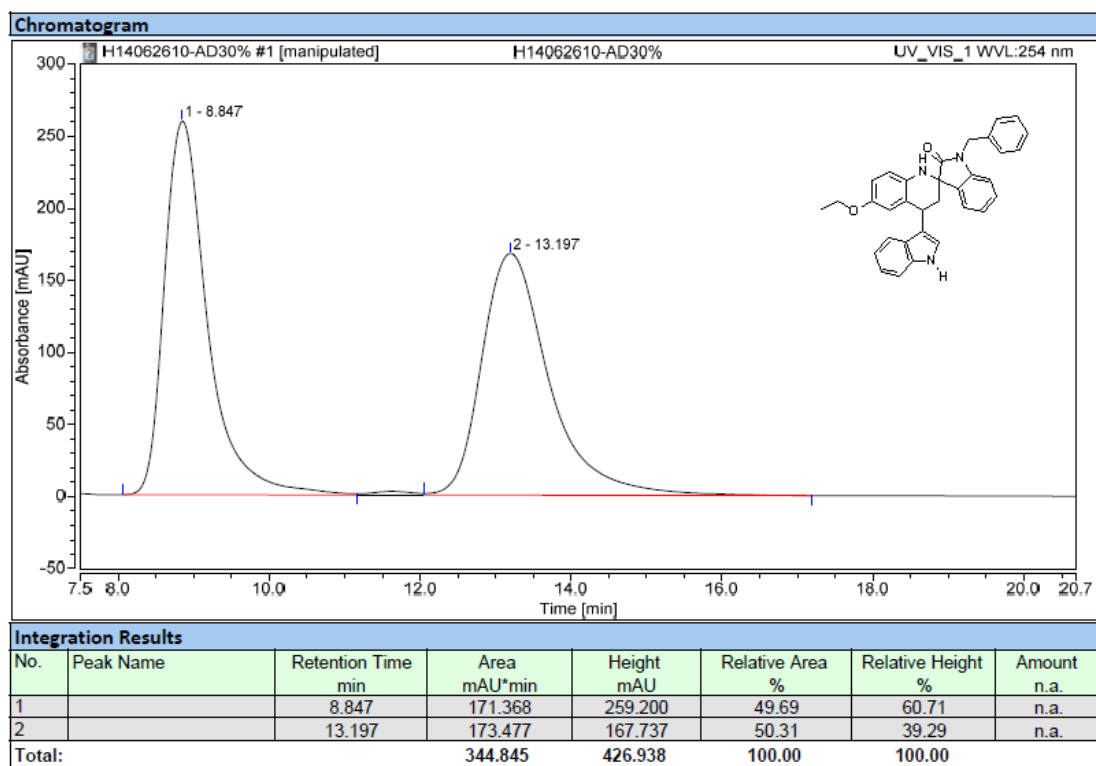
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.897	101.426	266.750	17.87	23.01	n.a.
2		10.723	466.203	892.567	82.13	76.99	n.a.
Total:			567.630	1159.318	100.00	100.00	

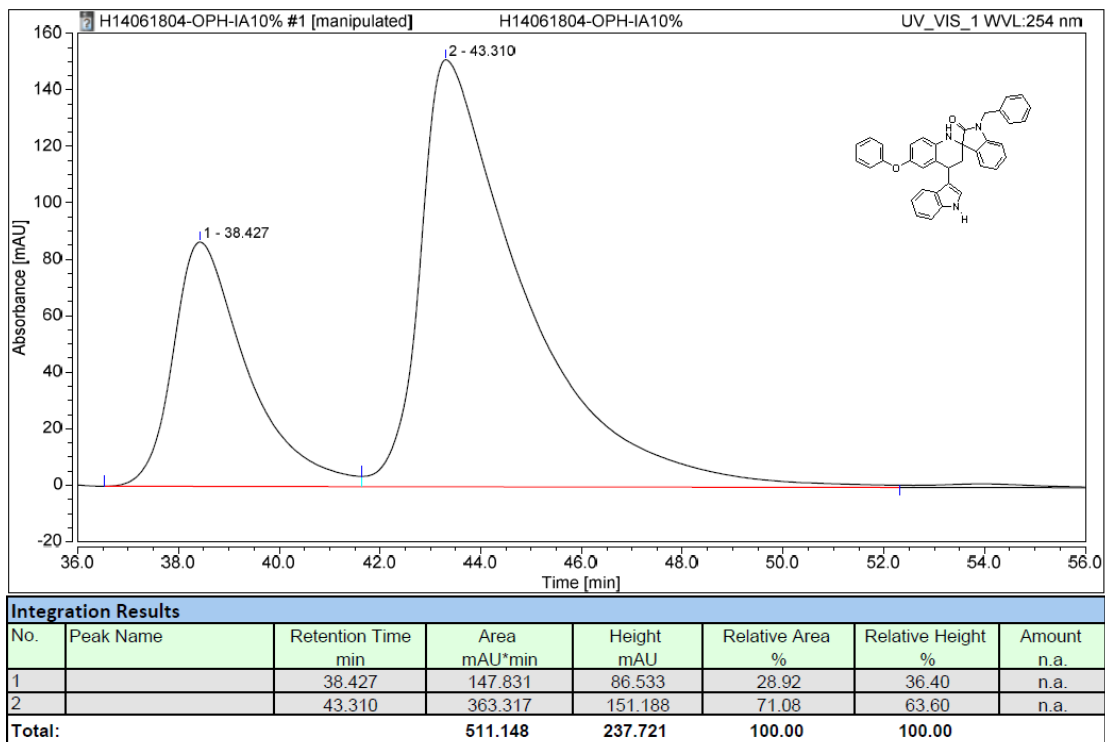
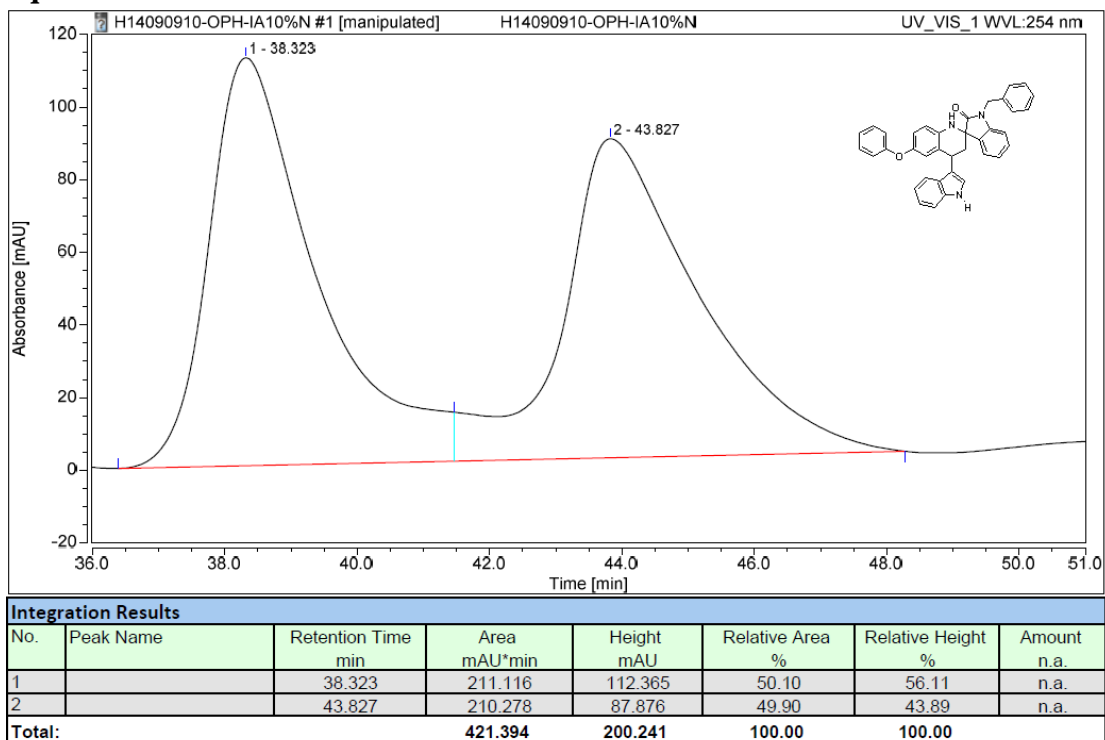
30a



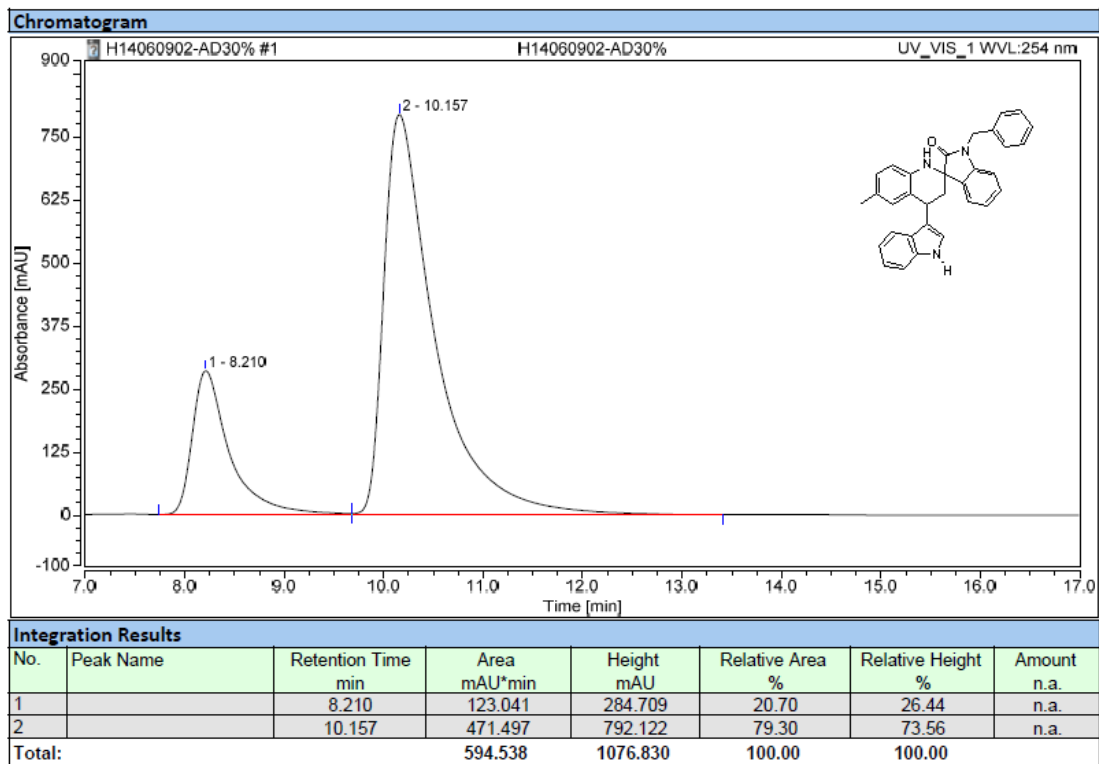
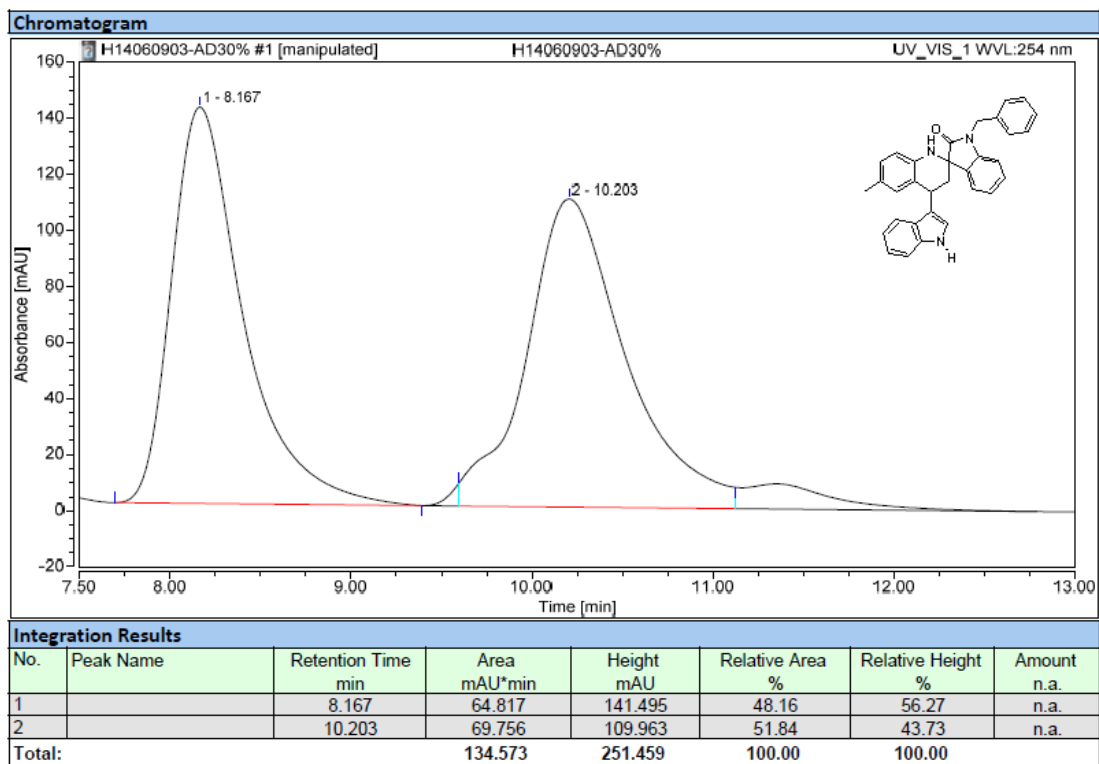
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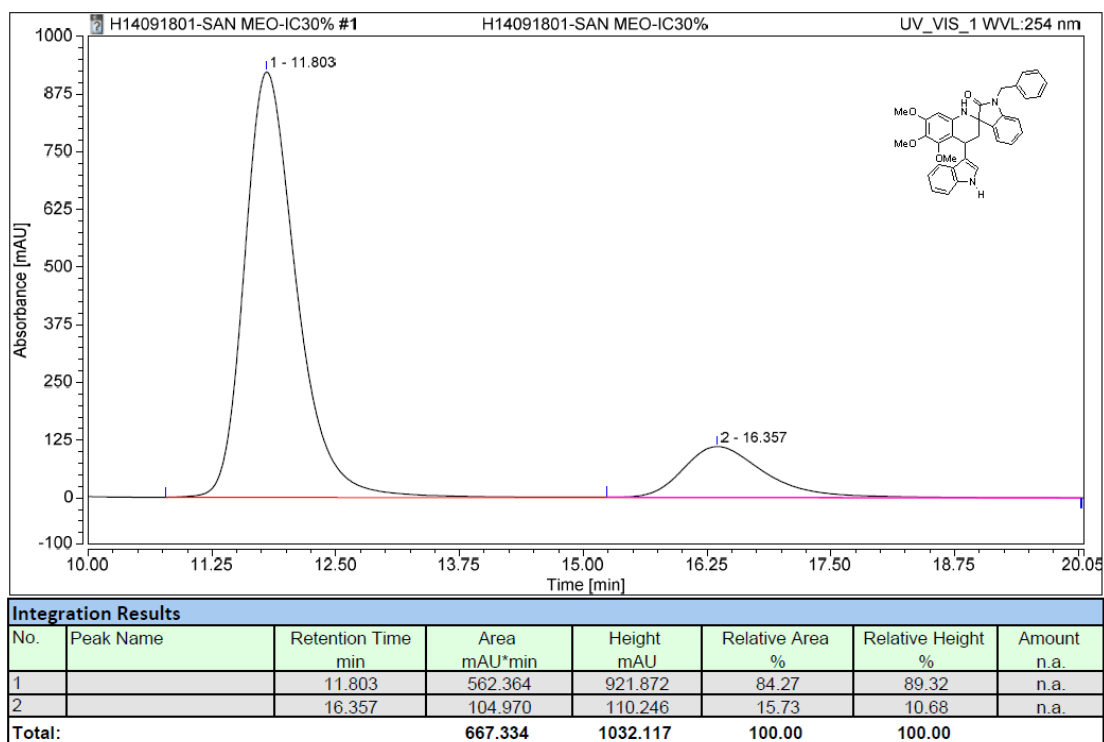
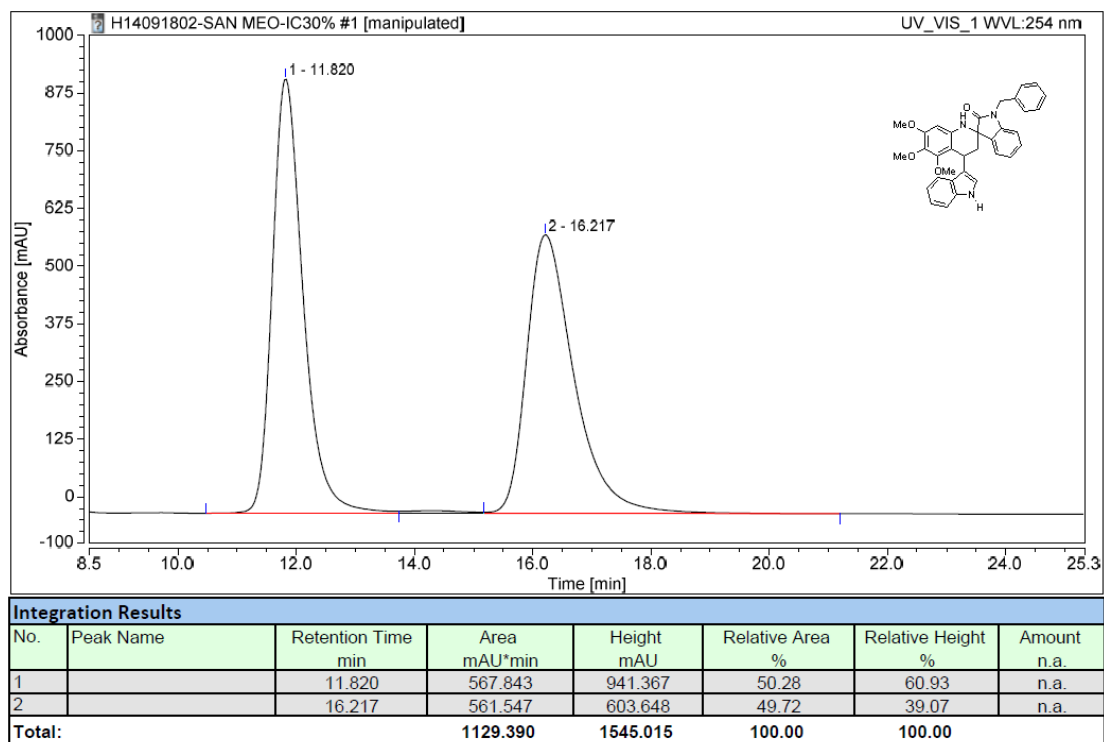
3qa



3ra



3sa



3ab

