Supporting Information

Synthesis of Polycyclic Spirooxindoles via Asymmetric Catalytic One-pot Stepwise Aldol/ Chloroetherification/Aromatization Procedure

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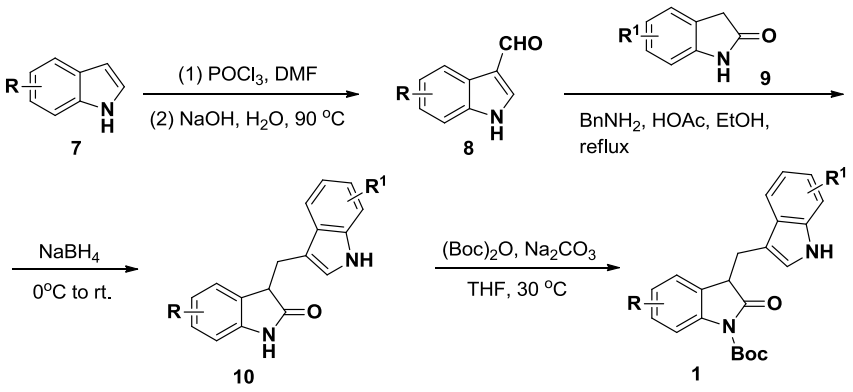
General Information.

All starting materials were of the highest commercially available grade and used without further purification. All solvents used in the reactions were distilled from appropriate drying agents prior to use. Reactions were monitored by thin layer chromatography using silica gel HSGF254 plates. Flash chromatography (FC) was performed using silica gel HG/T2354-2010. ^{1}H and ^{13}C NMR (300 and 75 MHz or 400 and 100 MHz or 600 MHz and 151 MHz respectively) spectra were recorded in DMSO-d_6 and $CDCl_3$. ^{1}H NMR chemical shifts are reported in ppm ($\boldsymbol{\delta}$) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, $\boldsymbol{\delta}$ = 7.26 ppm; DMSO-d_6, $\boldsymbol{\delta}$ = 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, $\boldsymbol{\delta}$ = 77.16 ppm; DMSO-d_6, $\boldsymbol{\delta}$ = 39.52 ppm). ESI HRMS spectra were recorded on BioTOF Q.

General procedure for preparation of the substrates 1 **[1, 2, 3, 4]**



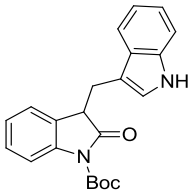
*T*o a solution of $POCl_3$ (0.93 mL, 10 mmol) in DMF (15 mL) was added indole **7** (5 mmol) at 0°C, the reaction was performed at room temperature until indole **7** disappeared. Then the solution was cooled to 0℃, neutralized with aq NaOH to pH = 7, and the reaction mixture was stirred at 90℃ for 2 h later. The resulting mixture was poured into ice water (150 mL) and solid precipitated, filtered, dried to get pure indole-3-carbaldehyde **8**.

*I*ndole-3-carbaldehyde **8** (4 mmol), $BnNH_2$ (44 μL, 0.4 mmol), HOAc (23 μL, 0.4 mmol) and oxindole **9** (4 mmol) were reflux in EtOH (20 mL) for 5-12 h. The resulting mixture was cooled to 0 °C, $NaBH_4$ (0.76 g, 20 mmol) was added, and the mixture was stirred at room temperature overnight. The reaction was quenched with a saturated aqueous solution of NH_4Cl, and extracted with EtOAc for three times, washed with brine, dried over anhydrous Na_2SO_4, evaporated and the residue was purified by recrystallization or column chromatography (silica gel, hexane/EtOAc =

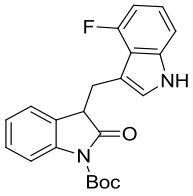
5/1 to 3/1) to afford **10**.

3-((1H-indol-3-yl)methyl)indolin-2-one **10** (3 mmol), $(Boc)_2O$ (2.76 mL, 12 mmol) and Na_2CO_3 (2.54 g, 24 mmol) were stirred in THF at 30 ºC for 5-12 h. The resulting mixture was filtrated, evaporated and purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 30/1) to afford **1**.

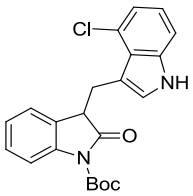
Experiment data for the substrates 1



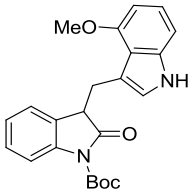
Tert-butyl 3-((1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1a): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.03 (br s, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.17-7.23 (m, 2H), 7.09-7.12 (m, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 2.2 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 3.92 (dd, *J* = 8.8, 4.5 Hz, 1H), 3.62 (dd, *J* = 14.5, 4.5 Hz, 1H), 3.17 (dd, *J* = 14.5, 8.8 Hz, 1H), 1.61 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 176.08, 149.40, 140.25, 136.33, 128.16, 128.13, 127.28, 124.56, 124.00, 123.16, 122.31, 119.69, 119.05, 114.87, 111.89, 111.26, 84.32, 46.68, 28.21, 27.87. ESI HRMS exact mass calcd. for $(C_{22}H_{22}N_2O_3 + Na)^+$ requires m/z 385.1523, found m/z 385.1520.



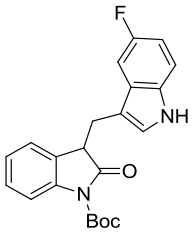
Tert-butyl 3-((4-fluoro-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1b): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.38 (br s, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.07 (td, *J* = 8.0, 5.0 Hz, 1H), 6.99 (td, *J* = 7.5, 0.7 Hz, 1H), 6.88 (dd, *J* = 11.7, 4.8 Hz, 2H), 6.75 (dd, *J* = 11.1, 7.8 Hz, 1H), 3.97 (dd, *J* = 8.1, 5.9 Hz, 1H), 3.67 (dd, *J* = 14.5, 5.8 Hz, 1H), 3.22 (dd, *J* = 14.5, 8.3 Hz, 1H), 1.64 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 176.10, 157.41 (d, *J* = 245.6 Hz), 149.53, 140.01, 139.24 (d, *J* = 11.7 Hz), 128.08, 128.05, 124.61, 124.04, 123.48, 122.70 (d, *J* = 7.7 Hz), 116.14 (d, *J* = 19.8 Hz), 114.79, 110.94, 107.58, 104.84 (d, *J* = 19.7 Hz), 84.39, 47.04, 28.90, 28.25. ESI HRMS exact mass calcd. for $(C_{22}H_{21}FN_2O_3 + Na)^+$ requires m/z 403.1428, found m/z 403.1430.



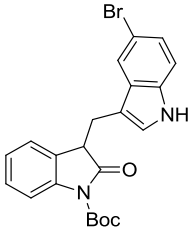
Tert-butyl 3-((4-chloro-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1c): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.37 (br s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.21-7.37 (m, 2H), 7.05-7.15 (m, 2H), 6.92-7.03 (m, 2H), 6.80 (d, *J* = 7.5 Hz, 1H), 4.09 (dd, *J* = 8.7, 6.1 Hz, 1H), 3.85 (dd, *J* = 14.6, 6.1 Hz, 1H), 3.25 (dd, *J* = 14.6, 8.9 Hz, 1H), 1.66 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 175.89, 149.63, 140.02, 138.10, 128.16, 128.08, 126.52, 125.19, 124.71, 124.16, 123.93, 122.82, 120.81, 114.88, 112.60, 110.31, 84.38, 47.32, 29.26, 28.28. ESI HRMS exact mass calcd. for $(C_{22}H_{21}ClN_2O_3 + Na)^+$ requires m/z 419.1133, found m/z 419.1141.



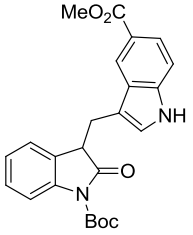
Tert-butyl 3-((4-methoxy-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1d): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.01 (br s, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 1.9 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 4.13 (dd, *J* = 9.6, 5.1 Hz, 1H), 3.93 (s, 3H), 3.83 (dd, *J* = 13.9, 5.1 Hz, 1H), 3.00 (dd, *J* = 13.9, 9.7 Hz, 1H), 1.65 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 176.29, 154.98, 149.71, 140.03, 138.41, 128.71, 127.79, 124.81, 123.68, 123.25, 122.09, 117.33, 114.70, 113.20, 104.68, 99.69, 84.18, 55.26, 47.23, 29.97, 28.29. ESI HRMS exact mass calcd. for $(C_{23}H_{24}N_2O_4 + Na)^+$ requires m/z 415.1628, found m/z 415.1641.



Tert-butyl 3-((5-fluoro-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1e): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.01 (br s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.21-7.24 (m, 3H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.90-6.94 (m, 3H), 3.87 (dd, *J* = 7.9, 4.6 Hz, 1H), 3.51 (dd, *J* = 14.6, 4.5 Hz, 1H), 3.22 (dd, *J* = 14.6, 8.0 Hz, 1H), 1.59 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 175.83, 157.79 (d, *J* = 234.5 Hz), 149.21, 140.22, 132.56, 128.12, 127.80, 127.60 (d, *J* = 9.8 Hz), 124.86, 124.21, 123.96, 114.81, 111.71, 111.64, 110.54 (d, *J* = 26.4 Hz), 103.91 (d, *J* = 23.4 Hz), 84.22, 46.58, 28.04, 27.52. ESI HRMS exact mass calcd. for $(C_{22}H_{21}FN_2O_3 + Na)^+$ requires m/z 403.1428, found m/z 403.1421.

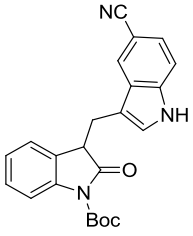


Tert-butyl 3-((5-bromo-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1f): yellow solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.11 (br s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 1.5 Hz, 1H), 7.23-7.25 (m, 2H), 7.19-7.21 (m, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 2.2 Hz, 1H), 3.88 (dd, *J* = 8.0, 4.6 Hz, 1H), 3.51 (dd, *J* = 14.6, 4.6 Hz, 1H), 3.21 (dd, *J* = 14.6, 8.1 Hz, 1H), 1.60 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 175.89, 149.33, 140.33, 134.85, 129.05, 128.33, 127.88, 125.14, 124.48, 124.38, 124.12, 121.68, 114.99, 112.98, 112.69, 111.41, 84.41, 46.68, 28.20, 27.59. ESI HRMS exact mass calcd. for $(C_{22}H_{21}BrN_2O_3 + Na)^+$ requires m/z 463.0628, found m/z 463.0632.

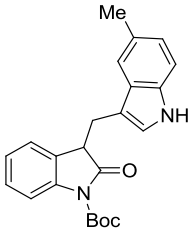


Methyl 3-((1-(tert-butoxycarbonyl)-2-oxoindolin-3-yl)methyl)-1H-indole-5-carboxylate (1g): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.34 (br s, 2H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 1.5 Hz, 1H), 6.91 (d, *J* = 7.4 Hz, 1H), 3.95 (dd, *J* = 8.1, 4.8 Hz, 1H), 3.92 (s, 3H), 3.61 (dd, *J* = 14.7, 4.8 Hz, 1H), 3.27 (dd, *J* =

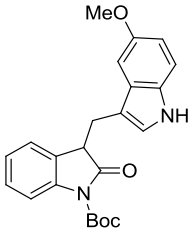
14.7, 8.3 Hz, 1H), 1.60 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 175.89, 168.22, 149.33, 140.24, 138.84, 128.30, 127.82, 126.95, 124.53, 124.44, 124.15, 123.74, 122.00, 121.81, 114.94, 113.21, 111.01, 84.42, 51.99, 46.65, 28.19, 27.45. ESI HRMS exact mass calcd. for $(C_{24}H_{24}N_2O_5 + Na)^+$ requires m/z 443.1577, found m/z 443.1585.



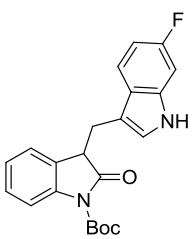
Tert-butyl 3-((5-cyano-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1h): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.45 (br s, 1H), 7.84 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.37 (s, 2H), 7.24-7.27 (m, 1H), 7.09-7.11 (m, 2H), 6.98 (d, *J* = 2.1 Hz, 1H), 3.88-3.90 (m, 1H), 3.49 (dd, *J* = 14.7, 4.8 Hz, 1H), 3.40 (dd, *J* = 14.7, 7.0 Hz, 1H), 1.57 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 175.78, 149.21, 140.42, 137.71, 128.56, 127.57, 127.25, 125.49, 125.11, 124.87, 124.33, 124.14, 120.77, 115.11, 112.39, 112.12, 102.82, 84.54, 46.87, 28.17, 27.12. ESI HRMS exact mass calcd. for $(C_{23}H_{21}N_3O_3 + Na)^+$ requires m/z 410.1475, found m/z 410.1476.



Tert-butyl 3-((5-methyl-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1i): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 7.96 (br s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.42 (s, 1H), 7.20-7.28 (m, 2H), 7.02 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 2.1 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 3.92 (dd, *J* = 9.2, 4.3 Hz, 1H), 3.58-3.65 (m, 1H), 3.09 (dd, *J* = 14.5, 9.3 Hz, 1H), 2.44 (s, 3H), 1.62 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 176.12, 149.43, 140.21, 134.74, 128.92, 128.29, 128.09, 127.43, 124.66, 123.94, 123.33, 118.67, 114.85, 111.42, 110.96, 84.30, 46.55, 28.22, 28.08, 21.62. ESI HRMS exact mass calcd. for $(C_{23}H_{24}N_2O_3 + Na)^+$ requires m/z 399.1679, found m/z 399.1686.

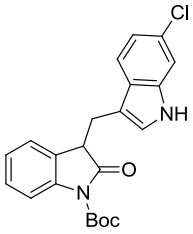


Tert-butyl 3-((5-methoxy-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1j): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 7.93 (br s, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 2H), 6.96 -7.06 (m, 2H), 6.85 (dt, *J* = 8.8, 4.9 Hz, 3H), 3.90 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.84 (s, 3H), 3.58 (dd, *J* = 14.6, 4.4 Hz, 1H), 3.16 (dd, *J* = 14.6, 8.8 Hz, 1H), 1.61 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 176.13, 154.22, 149.37, 140.32, 131.41, 128.15, 127.65, 124.60, 124.01, 124.00, 114.91, 112.75, 111.99, 111.55, 111.54, 100.63, 84.32, 56.02, 46.65, 28.20, 27.95. ESI HRMS exact mass calcd. for $(C_{23}H_{24}N_2O_4 + Na)^+$ requires m/z 415.1628, found m/z 415.1625.

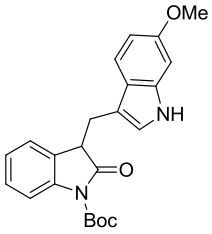


Tert-butyl 3-((6-fluoro-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1k): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.02 (br s, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.50 (dd, *J* = 8.7, 5.3 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.98-7.06 (m, 2H), 6.90 (d, *J* = 7.4 Hz, 1H), 6.81-6.88 (m, 2H), 3.88 (dd, *J* = 8.2, 4.5 Hz,

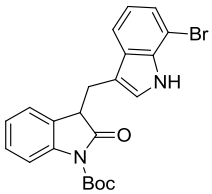
1H), 3.56 (dd, *J* = 14.6, 4.5 Hz, 1H), 3.21 (dd, *J* = 14.6, 8.3 Hz, 1H), 1.60 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 176.00, 160.17 (d, *J* = 237.5 Hz), 149.32, 140.33, 136.16 (d, *J* = 12.4 Hz), 128.24, 127.98, 124.41, 124.07, 123.92, 123.38 (d, *J* = 3.3 Hz), 119.85 (d, *J* = 10.4 Hz), 114.94, 111.88, 108.45 (d, *J* = 24.5 Hz), 97.52 (d, *J* = 26.2 Hz), 84.37, 46.76, 28.20, 27.68. ESI HRMS exact mass calcd. for $(C_{22}H_{21}FN_2O_3 + Na)^+$ requires m/z 403.1428, found m/z 403.1423.



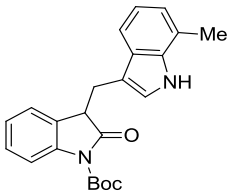
Tert-butyl 3-((6-chloro-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1l): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.05 (br s, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.32 (d, *J* = 1.7 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 6.98-7.08 (m, 2H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 2.3 Hz, 1H), 3.87 (dd, *J* = 8.1, 4.6 Hz, 1H), 3.54 (ddd, *J* = 14.6, 4.6, 0.7 Hz, 1H), 3.23 (dd, *J* = 14.6, 8.2 Hz, 1H), 1.60 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 175.98, 149.28, 140.33, 136.56, 128.27, 128.21, 127.90, 125.94, 124.37, 124.10, 123.83, 120.42, 119.99, 114.96, 111.89, 111.17, 84.41, 46.78, 28.19, 27.57. ESI HRMS exact mass calcd. for $(C_{22}H_{21}ClN_2O_3 + Na)^+$ requires m/z 419.1133, found m/z 419.1124.



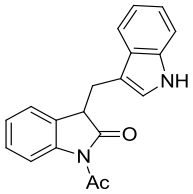
Tert-butyl 3-((6-methoxy-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1m): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 7.89 (br s, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.83-6.85 (m, 2H), 6.76-6.77 (m, 2H), 3.89 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.83 (s, 3H), 3.58 (dd, *J* = 14.5, 4.4 Hz, 1H), 3.13 (dd, *J* = 14.6, 8.8 Hz, 1H), 1.61 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 176.08, 156.74, 149.40, 140.25, 137.11, 128.17, 128.11, 124.57, 123.99, 121.90, 121.71, 119.70, 114.85, 111.88, 109.62, 94.78, 84.30, 55.78, 46.72, 28.22, 27.94. ESI HRMS exact mass calcd. for $(C_{23}H_{24}N_2O_4 + Na)^+$ requires m/z 415.1628, found m/z 415.1621.



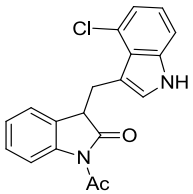
Tert-butyl 3-((7-bromo-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1n): yellow solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.17 (br s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.9 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 3.89 (dd, *J* = 8.3, 4.5 Hz, 1H), 3.57 (dd, *J* = 14.6, 4.5 Hz, 1H), 3.22 (dd, *J* = 14.7, 8.3 Hz, 1H), 1.60 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 175.89, 149.28, 140.33, 134.93, 128.52, 128.29, 127.86, 124.65, 124.40, 124.10, 123.73, 120.89, 118.39, 114.98, 113.09, 104.84, 84.38, 46.70, 28.20, 27.79. ESI HRMS exact mass calcd. for $(C_{22}H_{21}BrN_2O_3 + Na)^+$ requires m/z 463.0628, found m/z 463.0614.



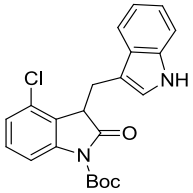
Tert-butyl 3-((7-methyl-1H-indol-3-yl)methyl)-2-oxoindoline-1-carboxylate (1o): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 7.94 (br s, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H), 6.96-7.02 (m, 2H), 6.92 (d, J = 2.2 Hz, 1H), 6.84 (d, J = 7.5 Hz, 1H), 3.92 (dd, J = 9.0, 4.4 Hz, 1H), 3.60-3.69 (m, 1H), 3.14 (dd, J = 14.6, 9.0 Hz, 1H), 2.49 (s, 3H), 1.62 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 176.07, 149.43, 140.24, 135.96, 128.22, 128.12, 126.83, 124.61, 123.99, 122.88, 122.85, 120.40, 119.93, 116.79, 114.87, 112.51, 84.31, 46.65, 28.22, 28.02, 16.73. ESI HRMS exact mass calcd. for $(C_{23}H_{24}N_2O_3 + Na)^+$ requires m/z 399.1679, found m/z 399.1683.



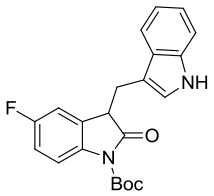
3-((1H-indol-3-yl)methyl)-1-acetylindolin-2-one (1p): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.13 (d, *J* = 8.2 Hz, 1H), 7.98 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.23-7.29 (m, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.06-7.15 (m, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 1.8 Hz, 1H), 3.98 (dd, *J* = 7.8, 4.6 Hz, 1H), 3.56 (dd, *J* = 14.6, 4.5 Hz, 1H), 3.34 (dd, *J* = 14.6, 7.9 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 178.34, 171.07, 140.78, 136.16, 128.35, 127.19, 124.84, 124.20, 123.03, 122.38, 119.71, 118.97, 116.45, 111.29, 111.19, 46.88, 27.76, 26.69. ESI HRMS exact mass calcd. for $(C_{19}H_{16}N_2O_2 + Na)^+$ requires m/z 327.1104, found m/z 327.1100.



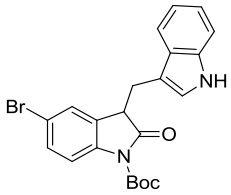
1-acetyl-3-((4-chloro-1H-indol-3-yl)methyl)indolin-2-one (1q): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.22-8.24 (m, 2H), 7.27-7.33 (m, 2H), 7.08-7.15 (m, 2H), 7.05 (td, *J* = 7.5, 0.9 Hz, 1H), 6.92 (d, *J* = 2.3 Hz, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 4.15 (dd, *J* = 8.8, 6.1 Hz, 1H), 3.84 (ddd, *J* = 14.5, 6.0, 0.6 Hz, 1H), 3.29 (dd, *J* = 14.5, 8.8 Hz, 1H), 2.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 178.06, 171.28, 140.40, 138.05, 128.36, 128.29, 126.50, 124.91, 124.72, 124.44, 124.10, 123.03, 121.00, 116.50, 112.48, 110.33, 47.41, 29.33, 26.91. ESI HRMS exact mass calcd. for $(C_{19}H_{15}ClN_2O_2 + Na)^+$ requires m/z 361.0714, found m/z 361.0709.



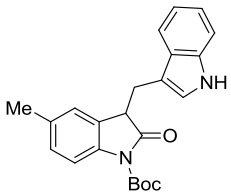
Tert-butyl 3-((1H-indol-3-yl)methyl)-4-chloro-2-oxoindoline-1-carboxylate (1r): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 7.85 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.47 (dd, *J* = 6.0, 3.0 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.10-7.15 (m, 2H), 7.05-7.10 (m, 1H), 6.98-7.03 (m, 1H), 6.76 (d, *J* = 2.3 Hz, 1H), 3.94 (dd, *J* = 5.4, 3.9 Hz, 1H), 3.78 (dd, *J* = 14.7, 5.5 Hz, 1H), 3.70 (dd, *J* = 14.6, 3.8 Hz, 1H), 1.48 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 175.31, 148.82, 142.11, 135.77, 130.44, 129.39, 127.51, 125.69, 124.62, 123.29, 121.88, 119.53, 119.23, 113.32, 110.79, 110.11, 84.35, 47.78, 28.04, 25.20. ESI HRMS exact mass calcd. for $(C_{22}H_{21}ClN_2O_3 + Na)^+$ requires m/z 419.1133, found m/z 419.1128.



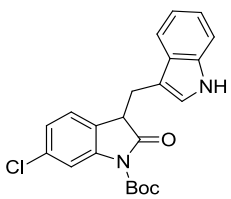
Tert-butyl 3-((1H-indol-3-yl)methyl)-5-fluoro-2-oxoindoline-1-carboxylate (1s): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.07 (s, 1H), 7.73 (dd, *J* = 8.9, 4.6 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.18-7.24 (m, 1H), 7.15-7.10 (m, 1H), 6.88-6.96 (m, 2H), 6.53 (dd, *J* = 8.0, 2.6 Hz, 1H), 3.90 (dd, *J* = 9.1, 4.4 Hz, 1H), 3.64 (ddd, *J* = 14.5, 4.4, 0.8 Hz, 1H), 3.14 (dd, *J* = 14.6, 9.1 Hz, 1H), 1.61 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 175.54, 159.58 (d, *J* = 242.5 Hz), 149.33, 136.41, 136.21, 129.93 (d, *J* = 8.6 Hz), 127.05, 123.20, 122.50, 119.85, 118.93, 116.05 (d, *J* = 8.0 Hz), 114.54 (d, *J* = 23.0 Hz), 112.09 (d, *J* = 24.9 Hz), 111.46, 111.40, 84.52, 46.72, 28.20, 27.89. ESI HRMS exact mass calcd. for $(C_{22}H_{21}FN_2O_3 + Na)^+$ requires m/z 403.1428, found m/z 403.1429.



Tert-butyl 3-((1H-indol-3-yl)methyl)-5-bromo-2-oxoindoline-1-carboxylate (1t): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.06 (s, 1H), 7.64 (t, *J* = 9.0 Hz, 2H), 7.33-7.40 (m, 2H), 7.21 (dd, *J* = 11.2, 3.9 Hz, 1H), 7.13 (dd, *J* = 11.0, 3.9 Hz, 1H), 6.96 (d, *J* = 0.7 Hz, 1H), 6.91 (d, *J* = 1.9 Hz, 1H), 3.88 (dd, *J* = 8.7, 4.4 Hz, 1H), 3.61 (dd, *J* = 14.5, 4.4 Hz, 1H), 3.16 (dd, *J* = 14.6, 8.8 Hz, 1H), 1.60 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 175.09, 149.18, 139.33, 136.37, 131.05, 130.26, 127.63, 127.04, 123.20, 122.49, 119.85, 118.94, 117.01, 116.51, 111.37, 84.69, 46.52, 28.18, 27.90. ESI HRMS exact mass calcd. for $(C_{22}H_{21}BrN_2O_3 + Na)^+$ requires m/z 463.0628, found m/z 463.0620.



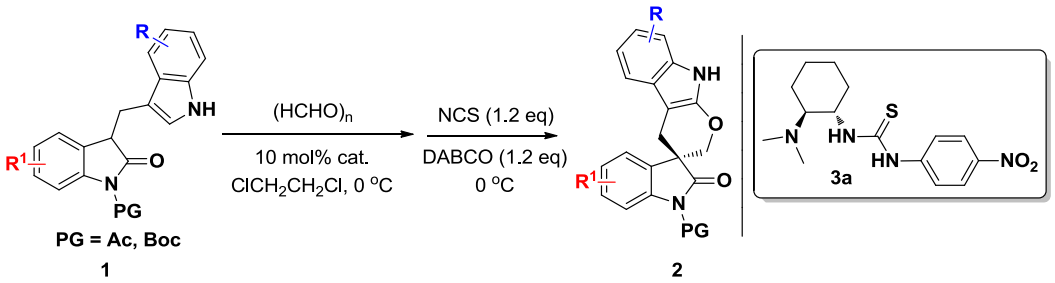
Tert-butyl 3-((1H-indol-3-yl)methyl)-5-methyl-2-oxoindoline-1-carboxylate (1u): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.02 (s, 1H), 7.61 (t, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 2.1 Hz, 1H), 6.71 (s, 1H), 3.87 (dd, *J* = 8.4, 4.5 Hz, 1H), 3.59 (dd, *J* = 14.6, 4.5 Hz, 1H), 3.19 (dd, *J* = 14.6, 8.5 Hz, 1H), 2.21 (s, 3H), 1.60 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 176.25, 149.44, 137.86, 136.30, 133.58, 128.53, 128.17, 127.37, 125.22, 123.03, 122.27, 119.62, 119.08, 114.63, 112.05, 111.23, 84.13, 46.78, 28.22, 27.81, 21.14. ESI HRMS exact mass calcd. for $(C_{23}H_{24}N_2O_3 + Na)^+$ requires m/z 399.1679, found m/z 399.1674.



Tert-butyl 3-((1H-indol-3-yl)methyl)-6-chloro-2-oxoindoline-1-carboxylate (1v): white solid, ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 8.06 (s, 1H), 7.82 (d, *J* = 1.8 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.96 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.88 (d, *J* = 2.0 Hz, 1H), 6.71 (d, *J* =

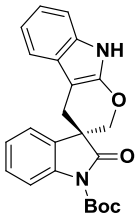
8.0 Hz, 1H), 3.88 (dd, *J* = 8.9, 4.5 Hz, 1H), 3.61 (dd, *J* = 14.5, 4.5 Hz, 1H), 3.14 (dd, *J* = 14.5, 8.9 Hz, 1H), 1.61 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 175.53, 149.12, 141.15, 136.34, 133.90, 127.12, 126.43, 125.38, 124.01, 123.17, 122.45, 119.82, 118.96, 115.65, 111.50, 111.35, 84.85, 46.38, 28.16, 27.86. ESI HRMS exact mass calcd. for $(C_{22}H_{21}ClN_2O_3 + Na)^+$ requires m/z 419.1133, found m/z 419.1127.

General procedure for the one-pot stepwise Aldol/Chloroetherification/Aromatization reaction

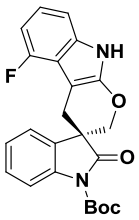


3-(3-indolomethyl)oxindole **1** (0.1 mmol), paraformaldehyde (18 mg, 0.6 mmol) and catalyst **3a** (3.2 mg, 0.01 mmol) were stirred in $ClCH_2CH_2Cl$ at 0˚C until the reaction finished. Then, DABCO (13.5 mg, 0.12 mmol) and NCS (16 mg, 0.12 mmol) were added and the reaction mixture was vigorously stirred at 0˚C for 30 min. The crude reaction mixture was directly loaded on a silica-gel column and next chromatograph afforded the corresponding product **2**.

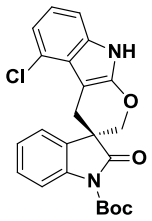
Experiment data for the products 2



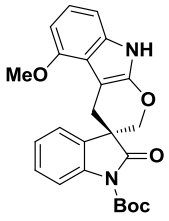
(R)-tert-butyl 2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2a): white solid, 31 mg, 79% yield, 95% ee, mp 142.8-144.5 °C; ^{1}H NMR (300 MHz, DMSO-d_6): ***δ*** 11.20 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.21-7.24 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.90-6.97 (m, 3H), 4.42 (d, *J* = 10.6 Hz, 1H), 4.30 (d, *J* = 10.6 Hz, 1H), 3.11 (d, *J* = 15.0 Hz, 1H), 2.82 (d, *J* = 15.0 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): ***δ*** 174.53, 148.61, 148.09, 138.69, 130.93, 130.06, 128.49, 126.87, 124.45, 123.50, 119.22, 118.95, 116.25, 114.50, 110.49, 84.07, 83.88, 71.06, 45.23, 28.06, 27.68; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak OD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 20.21 min, t_{minor} = 12.28 min); $[\alpha]_D^{20}$ = +33.3 (c = 1.25, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{22}N_2O_4 + H)^+$ requires m/z 391.1652, found m/z 391.1649.



(R)-tert-butyl 5'-fluoro-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2b): white solid, 24.5 mg, 60% yield, 89% ee, mp 177.0-178.3 °C; ^{1}H NMR (300 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 11.49 (s, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.02-7.08 (m, 2H), 6.94-6.96 (m, 1H), 6.87-6.89 (m, 1H), 6.63-6.70 (m, 1H), 4.40 (d, J = 10.7 Hz, 1H), 4.28 (d, J = 10.7 Hz, 1H), 3.21 (d, J = 15.2 Hz, 1H), 2.95 (d, J = 15.3 Hz, 1H), 1.54 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 174.25, 155.15 (d, J = 238 Hz), 148.63, 147.81, 138.84, 133.43 (d, J = 12.6 Hz), 129.81, 128.56, 124.47, 123.45, 119.47 (d, J = 7.8 Hz), 114.93 (d, J = 20.1 Hz), 114.58, 107.18, 104.34 (d, J = 18.0 Hz), 83.79, 82.09, 70.98, 45.10, 28.90, 27.67; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 10.97 min, t_{minor} = 10.23 min); $[\alpha]_D^{20}$ = +4.7 (c = 1.0, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{21}FN_2O_4 + H)^+$ requires m/z 409.1558, found m/z 409.1565.

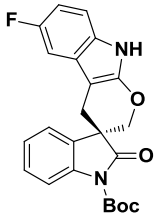


(R)-tert-butyl 5'-chloro-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2c): white solid, 24.2 mg, 57% yield, 87% ee, mp 188.1-189.7 °C; ^{1}H NMR (300 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 11.59 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.34-7.39 (m, 1H), 7.18-7.21 (m, 1H), 7.08-7.13 (m, 1H), 7.01 (d, J = 6.8 Hz, 1H), 6.92-6.94 (m, 2H), 4.45 (d, J = 10.7 Hz, 1H), 4.32 (d, J = 10.7 Hz, 1H), 3.36 (d, J = 15.4 Hz, 1H), 3.18 (d, J = 15.4 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 174.27, 148.83, 148.62, 138.84, 132.02, 129.83, 128.60, 124.51, 124.12, 123.50, 122.49, 119.99, 119.26, 114.59, 109.63, 84.08, 83.81, 70.78, 45.07, 29.47, 27.68; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 6.18 min, t_{minor} = 7.47 min); $[\alpha]_D^{20}$ = -9.3 (c = 0.9, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{21}ClN_2O_4 + H)^+$ requires m/z 425.1263, found m/z 425.1245.

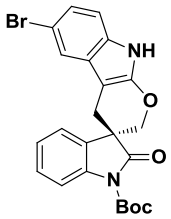


(R)-tert-butyl 5'-methoxy-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2d): white solid, 24.0 mg, 57% yield, 88% ee, mp 168.3-169.9 °C; ^{1}H NMR (300 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 11.17 (s, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.35 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.82-6.94 (m, 3H), 6.43-6.46 (m, 1H), 4.38 (d, J = 10.3 Hz, 1H), 4.25 (d, J = 10.5 Hz, 1H), 3.71 (s, 3H), 3.25 (d, J = 15.5 Hz, 1H), 2.99 (d, J = 15.2 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 174.56, 152.51, 148.62, 146.39, 138.72, 131.77, 130.16, 128.45, 124.43, 123.51, 119.88, 116.27, 114.49, 104.34, 100.05, 83.81, 83.45, 70.71, 54.97, 45.31, 30.18, 27.69; The enantiomeric ratio was determined by HPLC

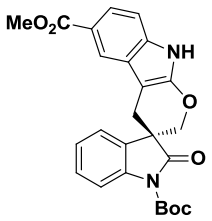
analysis using Daicel Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 8.11 min, t_{minor} = 10.25 min); $[\alpha]_D^{20}$ = +19.0 (c = 1.0, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{24}H_{24}N_2O_5 + Na)^+$ requires m/z 443.1577, found m/z 443.1566.



(R)-tert-butyl 6'-fluoro-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2e): white solid, 28.1 mg, 69% yield, 95% ee, mp 180.3-181.3 °C; ^{1}H NMR (300 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 11.31 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.18-7.22 (m, 1H), 7.05-7.09 (m, 1H), 7.01 (dd, *J* = 2.5 and 9.9 Hz, 1H), 6.92-6.95 (m, 1H), 6.77 (t, *J* = 7.8 Hz, 1H), 4.44 (d, *J* = 10.7 Hz, 1H), 4.32 (d, *J* = 10.7 Hz, 1H), 3.09 (d, *J* = 15.1 Hz, 1H), 2.82 (d, *J* = 15.1 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 174.40, 157.25 (d, *J* = 229 Hz), 149.61, 148.63, 138.74, 129.89, 128.58, 127.47 (d, *J* = 6.6 Hz), 127.37, 124.50, 123.50, 114.56, 111.22 (d, *J* = 9.6 Hz), 106.39 (d, *J* = 25.1 Hz), 101.78 (d, *J* = 23.9 Hz), 84.92 (d, *J* = 4.0 Hz), 83.91, 71.11, 45.11, 27.96, 27.68; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak OD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 13.44 min, t_{minor} = 11.48 min); $[\alpha]_D^{20}$ = +38.4 (c = 1.2, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{21}FN_2O_4 + H)^+$ requires m/z 409.1558, found m/z 409.1559.

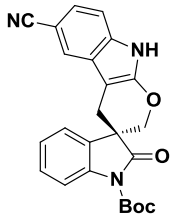


(R)-tert-butyl 6'-bromo-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2f): yellow solid, 33.8 mg, 72% yield, 95% ee, mp 163.4-165.4 °C; ^{1}H NMR (300 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 11.44 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.34-7.39 (m, 2H), 7.18 (d, *J* = 8.5 Hz, 1H), 7.06-7.11 (m, 2H), 6.91-6.93 (m, 1H), 4.45 (d, *J* = 10.5 Hz, 1H), 4.32 (d, *J* = 10.7 Hz, 1H), 3.08 (d, *J* = 15.3 Hz, 1H), 2.84 (d, 15.1 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 174.31, 149.15, 148.59, 138.71, 129.80, 129.65, 128.78, 128.60, 124.52, 123.47, 121.46, 118.55, 114.54, 112.39, 111.59, 84.32, 83.92, 71.11, 44.99, 27.77, 27.68; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak OD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 14.55 min, t_{minor} = 12.81 min); $[\alpha]_D^{20}$ = +48.5 (c = 0.73, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{21}BrN_2O_4 + H)^+$ requires m/z 469.0757, found m/z 469.0748.

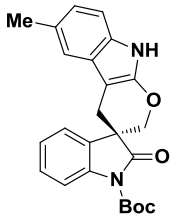


(R)-1-tert-butyl 6'-methyl 2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1,6'-dicarboxylate (2g): white solid, 22.8 mg, 51% yield, 90% ee, mp 187.8-189.5 °C; ^{1}H NMR (300 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 11.71 (s, 1H), 7.93 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.31-7.38 (m, 2H), 7.09 (t, *J* = 7.5 Hz,

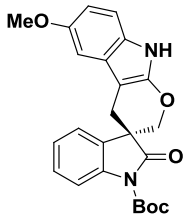
1H), 6.95 (d, *J* = 7.4 Hz, 1H), 4.47 (d, *J* = 10.7 Hz, 1H), 4.35 (d, *J* = 10.7 Hz, 1H), 3.80 (s, 3H), 3.16 (d, *J* = 15.2 Hz, 1H), 2.93 (d, *J* = 15.2 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): ***δ*** 174.31, 167.33, 149.30, 148.63, 138.77, 133.99, 129.82, 128.58, 126.51, 124.51, 123.46, 120.73, 120.44, 118.32, 114.57, 110.33, 85.37, 83.89, 71.24, 51.59, 45.05, 27.67, 27.57; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak OD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 32.04 min, t_{minor} = 29.60 min); $[\alpha]_D^{20}$ = +41.3 (c = 0.35, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{25}H_{24}N_2O_6 + Na)^+$ requires m/z 471.1527, found m/z 471.1525.



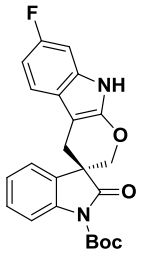
(R)-tert-butyl 6'-cyano-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2h): white solid, 24.9 mg, 60% yield, 95% ee, mp 188.5-190.2 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): ***δ*** 11.90 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.74 (s, 1H), 7.32-7.40 (m, 3H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.4 Hz, 1H), 4.50 (d, *J* = 10.7 Hz, 1H), 4.36 (d, *J* = 10.8 Hz, 1H), 3.11 (d, *J* = 15.3 Hz, 1H), 2.90 (d, *J* = 15.3 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): ***δ*** 174.20, 149.89, 148.59, 138.79, 133.15, 129.59, 128.70, 126.85, 124.58, 123.47, 122.55, 121.05, 120.93, 114.59, 111.50, 100.95, 85.27, 83.95, 71.22, 44.80, 27.68, 27.60; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak OD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 26.02 min, t_{minor} = 22.55 min); $[\alpha]_D^{20}$ = +45.7 (c = 0.5, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{24}H_{21}N_3O_4 + Na)^+$ requires m/z 438.1424, found m/z 438.1407.



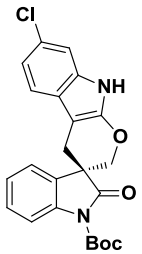
(R)-tert-butyl 6'-methyl-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2i): white solid, 29.1 mg, 72% yield, 96% ee, mp 176.9-179.2 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): ***δ*** 10.99 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.96-7.07 (m, 3H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 4.21-4.34 (m, 2H), 3.04 (d, *J* = 15.2 Hz, 1H), 2.74 (d, *J* = 15.3 Hz, 1H), 2.27 (s, 3H), 1.54 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): ***δ*** 174.59, 148.61, 148.20, 138.67, 130.12, 129.13, 128.49, 127.39, 127.08, 124.46, 123.50, 120.49, 116.28, 114.51, 110.22, 83.91, 83.67, 71.05, 45.30, 28.05, 27.70, 21.34; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 7.45 min, t_{minor} = 13.54 min); $[\alpha]_D^{20}$ = +56.2 (c = 0.9, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{24}H_{24}N_2O_4 + Na)^+$ requires m/z 427.1628, found m/z 427.1610.



(R)-tert-butyl 6'-methoxy-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2j): white solid, 26 mg, 62% yield, 94% ee, mp 180.5-182.3 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 10.99 (s, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.05-7.33 (m, 2H), 6.91 (d, J = 7.5 Hz, 1H), 6.77 (d, J = 2.3 Hz, 1H), 6.59 (dd, J = 8.6 and 2.4 Hz, 1H), 4.41 (d, J = 10.7 Hz, 1H), 4.28 (d, J = 10.7 Hz, 1H), 3.69 (s, 3H), 3.09 (d, J = 15.0 Hz, 1H), 2.80 (d, J = 15.0 Hz, 1H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 174.56, 153.54, 148.69, 148.62, 138.69, 130.07, 128.51, 127.46, 125.68, 124.47, 123.53, 114.51, 111.06, 107.76, 99.89, 84.29, 83.91, 71.02, 55.32, 45.27, 28.20, 27.70; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90/10 hexane/i-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 12.43 min, t_{minor} = 19.61 min); $[\alpha]_D^{20}$ = +56.6 (c = 1.25, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{24}H_{24}N_2O_5 + Na)^+$ requires m/z 443.1577, found m/z 443.1572.

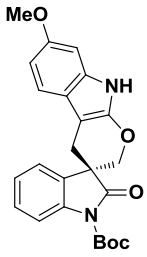


(R)-tert-butyl 7'-fluoro-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2k): white solid, 25.7 mg, 63% yield, 95% ee, mp 185.4-186.3 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 11.34 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 6.9 Hz, 1H), 7.17-7.21 (m, 1H), 7.00-7.08 (m, 2H), 6.93 (d, J = 6.7 Hz, 1H), 6.77-6.81 (m, 1H), 4.41 (d, J = 10.6 Hz, 1H), 4.28 (d, J = 10.6 Hz, 1H), 3.08 (d, J = 15.1 Hz, 1H), 2.82 (d, J = 15.0 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 174.46, 157.70 (d, J = 230 Hz), 148.61, 148.27 (d, J = 2.7 Hz), 138.72, 130.82 (d, J = 12.4 Hz), 129.97, 128.56, 124.51, 123.56, 123.50, 116.91 (d, J = 9.6 Hz), 114.53, 106.62 (d, J = 23.3 Hz), 97.32 (d, J = 26.0 Hz), 84.08, 83.90, 70.98, 45.12, 27.94, 27.69; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90/10 hexane/i-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 8.66 min, t_{minor} = 13.37 min); $[\alpha]_D^{20}$ = -15.2 (c = 0.65, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{21}FN_2O_4 + Na)^+$ requires m/z 431.1378, found m/z 431.1365.

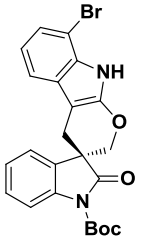


(R)-tert-butyl 7'-chloro-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2l): white solid, 29.3 mg, 69% yield, 93% ee, mp 128.0-130.2 ^{o}C; ^{1}H NMR (300 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 11.42 (s, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.21-7.24 (m, 2H), 7.09 (t, J = 7.6 Hz, 1H), 6.91-6.97 (m, 2H), 4.44 (d, J = 10.6 Hz, 1H), 4.31 (d, J = 10.8 Hz, 1H), 3.08 (d, J = 15.1 Hz, 1H), 2.85 (d, J = 15.0 Hz, 1H), 1.57 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 174.37, 148.76, 148.61, 138.75, 131.40, 129.84, 128.61, 125.69, 124.52, 123.50, 119.10, 117.52, 114.55, 110.23, 84.50, 83.91, 71.06, 45.01, 27.83,

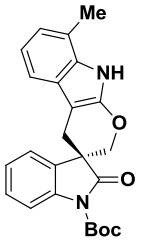
27.69; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 9.15 min, t_{minor} = 13.78 min); $[\alpha]_D^{20}$ = +0.9 (c = 1.0, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{21}ClN_2O_4 + Na)^+$ requires m/z 447.1082, found m/z 447.1070.



(R)-tert-butyl 7'-methoxy-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2m): white solid, 6.3 mg, 15% yield, 95% ee, mp 261.9-263.4 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.90 (d, *J* = 6.4 Hz, 1H), 7.79 (s, 1H), 7.30 (t, *J* = 6.4 Hz, 1H), 7.16 (d, *J* = 6.8 Hz, 1H), 6.99 (t, *J* = 6.0 Hz, 1H), 6.93-6.94 (m, 1H), 6.84 (s, 1H), 6.75 (d, *J* = 6.4 Hz, 1H), 4.40 (d, *J* = 8.4 Hz, 1H), 4.12 (d, *J* = 8.4 Hz, 1H), 3.83 (s, 3H), 3.35 (d, *J* = 12 Hz, 1H), 2.76 (d, *J* = 12 Hz, 1H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): ***δ*** 175.65, 155.30, 149.09, 146.59, 138.61, 131.58, 130.32, 128.60, 124.85, 124.07, 121.62, 117.40, 114.86, 108.50, 95.99, 85.30, 84.86, 72.00, 55.94, 46.40, 28.32, 28.13; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak OD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 14.49 min, t_{minor} = 13.10 min); $[\alpha]_D^{20}$ = +23.1 (c = 0.55, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{24}H_{24}N_2O_5 + H)^+$ requires m/z 421.1758, found m/z 421.1755.

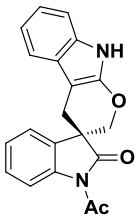


(R)-tert-butyl 8'-bromo-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2n): white solid, 17.8 mg, 38% yield, 93% ee, mp 178.8-180.5 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): ***δ*** 11.52 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.07-7.17 (m, 2H), 6.86-6.96 (m, 2H), 4.47 (d, *J* = 10.5 Hz, 1H), 4.33 (d, *J* = 10.7 Hz, 1H), 3.10 (d, *J* = 15.1 Hz, 1H), 2.86 (d, *J* = 15.3 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): ***δ*** 174.32, 149.10, 148.60, 138.75, 129.79, 129.46, 128.58, 124.53, 123.49, 121.79, 120.53, 115.67, 114.53, 103.28, 85.62, 83.89, 71.12, 44.93, 27.92, 27.68; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 7.56 min, t_{minor} = 9.66 min); $[\alpha]_D^{20}$ = -14.7 (c = 0.85, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{21}BrN_2O_4 + Na)^+$ requires m/z 491.0577, found m/z 491.0573.

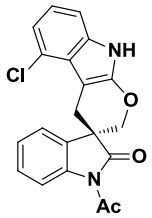


(R)-tert-butyl 8'-methyl-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2o): white solid, 27 mg, 67% yield, 95% ee, mp 161.9-163.5 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): ***δ*** 11.10 (s, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.03-7.32 (m, 2H), 6.75-6.92 (m, 3H), 4.42 (d, *J* = 10.6 Hz, 1H), 4.29

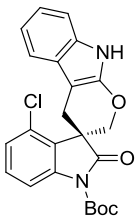
(d, J = 10.6 Hz, 1H), 3.10 (d, J = 15.0 Hz, 1H), 2.80 (d, J = 15.0 Hz, 1H), 2.42 (s, 3H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 174.61, 148.62, 148.20, 138.69, 130.21, 130.14, 128.50, 126.53, 124.47, 123.52, 120.28, 119.64, 119.16, 114.52, 113.95, 84.44, 83.90, 71.07, 45.29, 28.19, 27.70, 16.85; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 6.44 min, t_{minor} = 9.83 min); $[\alpha]_D^{20}$ = +7.0 (c = 1.0, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{24}H_{24}N_2O_4 + Na)^+$ requires m/z 427.1628, found m/z 427.1623.



(R)-1-acetyl-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indol]-2-one (2p): white solid, 21.9 mg, 66% yield, 81% ee, mp 196.8-198.3 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 11.16 (s, 1H), 8.15 (d, J = 7.9 Hz, 1H), 7.30-7.33 (m, 1H), 7.17-7.20 (m, 2H), 7.06-7.09 (m, 1H), 6.89-6.93 (m, 3H), 4.41 (d, J = 10.5 Hz, 1H), 4.30 (d, J = 10.6 Hz, 1H), 3.11 (d, J = 15.0 Hz, 1H), 2.83 (d, J = 15.3 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 177.19, 170.72, 148.13, 139.39, 130.92, 130.47, 128.47, 126.85, 125.06, 123.38, 119.25, 118.98, 116.24, 115.71, 110.50, 84.08, 71.03, 45.37, 28.05, 26.52; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak OD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 26.92 min, t_{minor} = 22.25 min); $[\alpha]_D^{20}$ = +60.7 (c = 0.75, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{20}H_{16}N_2O_3 + H)^+$ requires m/z 333.1234, found m/z 333.1243.

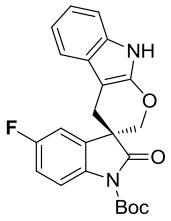


(R)-1-acetyl-5'-chloro-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indol]-2-one (2q): white solid, 31 mg, 84% yield, 76% ee, mp 223.8-225.1 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): $\boldsymbol{\delta}$ 8.30 (d, J = 6.4 Hz, 1H), 7.92 (s, 1H), 7.35 (t, J = 6.0 Hz, 1H), 7.16 (d, J = 6.0 Hz, 1H), 7.10 (t, J = 5.6 Hz, 1H), 6.99-7.02 (m, 3H), 4.41 (d, J = 8.0 Hz, 1H), 4.21 (d, J = 8.4 Hz, 1H), 3.60 (d, J = 12.4 Hz, 1H), 3.30 (d, J = 12.4 Hz, 1H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\boldsymbol{\delta}$ 177.66, 170.82, 147.82, 139.14, 131.67, 130.17, 128.99, 125.62, 124.96, 124.55, 123.63, 121.01, 120.76, 116.57, 109.09, 85.90, 71.75, 46.27, 29.85, 26.85; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak OD-H column (60/40 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 5.25 min, t_{minor} = 6.17 min); $[\alpha]_D^{20}$ = +27.3 (c = 1.0, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{20}H_{15}ClN_2O_3 + Na)^+$ requires m/z 389.0663, found m/z 389.0648;

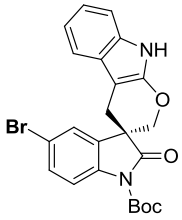


(R)-tert-butyl 4-chloro-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2r): white solid, 34 mg, 80% yield, 94% ee, mp 173.2-175.1 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): $\boldsymbol{\delta}$ 11.05 (s, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.45 (t, J = 8.2 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.17-7.23 (m, 2H), 6.92-6.95 (m, 2H), 4.81 (d,

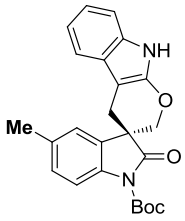
J = 11.1 Hz, 1H), 4.53 (d, *J* = 11.1 Hz, 1H), 3.58 (d, *J* = 15.8 Hz, 1H), 2.92 (d, *J* = 15.8 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): ***δ*** 172.32, 148.60, 148.37, 141.55, 130.78, 130.73, 129.43, 126.85, 125.71, 124.59, 118.98, 118.80, 116.10, 113.70, 110.32, 84.07, 83.03, 66.74, 45.62, 27.63, 22.94; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak OD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 12.66 min, t_{minor} = 8.47 min); $[\alpha]_D^{20}$ = +25.6 (c = 1.0, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{21}ClN_2O_4 + H)^+$ requires m/z 425.1263, found m/z 425.1254.



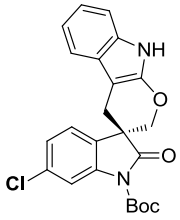
(R)-tert-butyl 5-fluoro-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2s): white solid, 24 mg, 59% yield, 92% ee, mp 187.3-189.7 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): ***δ*** 11.20 (s, 1H), 7.86 (dd, *J* = 8.8 and 4.7 Hz, 1H), 7.18-7.25 (m, 3H), 6.91-7.00 (m, 2H), 6.72 (dd, *J* = 8.1 and 2.7 Hz, 1H), 4.46 (d, *J* = 10.7 Hz, 1H), 4.31 (d, *J* = 10.8 Hz, 1H), 3.10 (d, *J* = 15.1 Hz, 1H), 2.88 (d, *J* = 15.1 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): ***δ*** 174.05, 159.05 (d, *J* = 238.8 Hz), 148.58, 147.97, 135.14, 131.88 (d, *J* = 8.5 Hz), 130.91, 126.76, 119.33, 119.02, 116.30, 116.07 (d, *J* = 8.2 Hz), 114.88 (d, *J* = 22.4 Hz), 110.84 (d, *J* = 24.6 Hz), 110.53, 83.99, 83.90, 70.65, 45.37, 27.85, 27.67; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 7.69 min, t_{minor} = 12.11 min); $[\alpha]_D^{20}$ = +34.9 (c = 0.88, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{21}FN_2O_4 + Na)^+$ requires m/z 431.1378, found m/z 431.1367.



(R)-tert-butyl 5-bromo-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2t): white solid, 22 mg, 47% yield, 92% ee, mp 262.0-264.4 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): ***δ*** 11.21 (s, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.55-7.58 (m, 1H), 7.23 (d, *J* = 7.1 Hz, 2H), 6.94-7.03 (m, 3H), 4.47 (d, *J* = 10.6 Hz, 1H), 4.30 (d, *J* = 10.6 Hz, 1H), 3.10 (d, *J* = 15.1 Hz, 1H), 2.88 (d, *J* = 15.3 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): ***δ*** 173.69, 148.47, 147.93, 138.26, 132.44, 131.25, 130.89, 126.73, 126.06, 119.38, 119.04, 116.64, 116.39, 116.34, 110.56, 84.17, 83.95, 70.69, 45.28, 27.85, 27.66; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 8.91 min, t_{minor} = 12.63 min); $[\alpha]_D^{20}$ = +110.8 (c = 0.65, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{21}BrN_2O_4 + Na)^+$ requires m/z 491.0577, found m/z 491.0571.

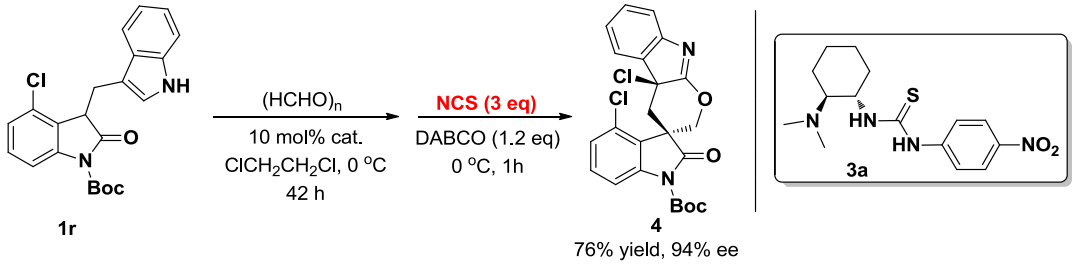


(R)-tert-butyl 5-methyl-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2u): white solid, 29 mg, 72% yield, 94% ee, mp 152.7-154.8 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): ***δ*** 11.17 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.15-7.23 (m, 3H), 6.91-6.99 (m, 2H), 6.77 (s, 1H), 4.39 (d, *J* = 10.6 Hz, 1H), 4.26 (d, *J* = 10.6 Hz, 1H), 3.08 (d, *J* = 15.1 Hz, 1H), 2.82 (d, *J* = 15.1 Hz, 1H), 2.16 (s, 3H), 1.56 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): ***δ*** 174.57, 148.66, 148.12, 136.37, 133.47, 130.89, 130.14, 128.89, 126.86, 123.95, 119.24, 118.96, 116.31, 114.36, 110.53, 84.17, 83.77, 71.11, 45.29, 27.97, 27.70, 20.75; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 7.99 min, t_{minor} = 10.20 min); $[\alpha]_D^{20}$ = +51.9 (c = 0.9, CH_2Cl_2); ESI HRMS exact mass calcd. for ($C_{24}H_{24}N_2O_4$ + Na)$^+$ requires m/z 427.1628, found m/z 427.1628.



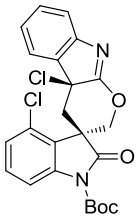
(R)-tert-butyl 6-chloro-2-oxo-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (2v): white solid, 21 mg, 59% yield, 93% ee, mp 185.0-186.1 ºC; ^{1}H NMR (300 MHz, DMSO-d_6): ***δ*** 11.21 (s, 1H), 7.87 (d, *J* = 1.9 Hz, 1H), 7.15-7.22 (m, 3H), 6.93-6.99 (m, 2H), 6.89 (d, *J* = 8.1 Hz, 1H), 4.44 (d, *J* = 10.5 Hz, 1H), 4.29 (d, *J* = 10.5 Hz, 1H), 3.10 (d, *J* = 15.1 Hz, 1H), 2.83 (d, *J* = 15.0 Hz, 1H), 1.58 (s, 9H); ^{13}C NMR (75 MHz, DMSO-d_6): ***δ*** 174.09, 148.49, 147.98, 140.09, 132.73, 130.91, 129.00, 126.77, 124.88, 124.22, 119.31, 119.00, 116.27, 114.72, 110.52, 84.32, 83.92, 70.80, 45.14, 27.94, 27.64; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak OD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 22.02 min, t_{minor} = 13.05 min); $[\alpha]_D^{20}$ = +49.4 (c = 0.85, CH_2Cl_2); ESI HRMS exact mass calcd. for ($C_{23}H_{21}ClN_2O_4$ + Na)$^+$ requires m/z 447.1082, found m/z 447.1080.

General procedure for the one-pot stepwise construction of 4



3-(3-indolomethyl)oxindole **1r** (0.1 mmol, 39.7 mg), paraformaldehyde (18 mg, 0.6 mmol) and catalyst **3a** (3.2 mg, 0.01 mmol) were stirred in $ClCH_2CH_2Cl$ at 0˚C for 42 h. Then, DABCO (13.5 mg, 0.12 mmol) and NCS (40 mg, 0.3 mmol) were added and the reaction mixture was

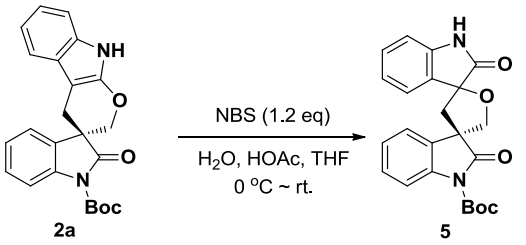
vigorously stirred at 0℃ for 30 min. The crude reaction mixture was directly loaded on a silica-gel column and next chromatograph (PE:EA = 5:1) afforded the corresponding product **4** (white solid, 35 mg) with 76% yield and 94% ee.



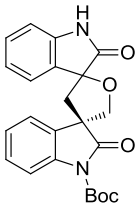
(3R,4a'S)-tert-butyl 4,4a'-dichloro-2-oxo-4',4a'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indole]-1-carboxylate (4): white solid, mp 171.4-172.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 7.90 (d, *J* = 6.8 Hz, 1H), 7.42 (d, *J* = 6.4 Hz, 1H), 7.32-7.37 (m, 3H), 7.21 (d, *J* = 6.4 Hz, 1H), 7.11 (t, *J* = 5.6 Hz, 1H), 5.87 (d, *J* = 9.2 Hz, 1H), 4.24 (d, *J* = 9.6 Hz, 1H), 3.84 (d, *J* = 12.8 Hz, 1H), 2.69 (d, *J* = 12.8 Hz, 1H), 1.57 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): ***δ*** 175.66, 173.99, 151.76, 148.76, 141.61, 138.86, 131.19, 130.72, 130.57, 126.33, 124.56, 122.07, 121.85, 120.35, 114.06, 85.69, 67.13, 61.96, 45.96, 36.16, 27.98; $[\alpha]_D^{20}$ = -86.4 (c = 1.5, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{20}Cl_2N_2O_4 + H)^+$ requires m/z 459.0873, found m/z 459.0878.

The enantiomeric ratio was determined by HPLC analysis of **4** after deprotection of Boc using Daicel Chiralpak OD-H column (70/30 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{major} = 7.40 min, t_{minor} = 10.63 min).

Synthesis of bispirooxindole 5



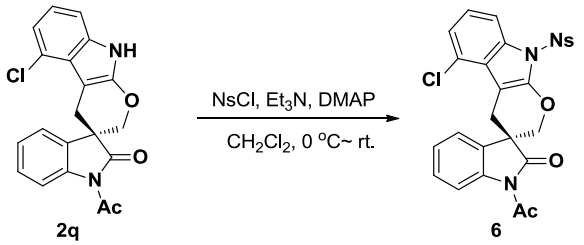
To the solution of **2a** (0.077 mmol, 30 mg) in THF (2 mL), H_2O (1 mL) and HOAc (1 mL) was added NBS (0.092 mmol, 16.4 mg) at 0℃, The resulting mixture was warmed to room temperature and vigorously stirred until the slightly red fade away. The mixture was extracted with CH_2Cl_2 three times, and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated under reduced pressure and the resulting crude mixture was purified by silica gel column chromatography (PE:EA = 3:1) to afford compound **5** (white solid, 15 mg) with 48% yield.



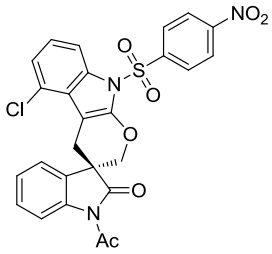
Tert*-buty(4'R)-2,2"-dioxo-3'H,5'H-dispiro[indoline-3,2'-furan-4'3"-indoline]-1"-carboxylate (5)**: white solid, ^{1}H NMR (400 MHz, $CDCl_3$): ***δ 8.18 (s, 0.4H), 8.03 (d, *J* = 10.0 Hz, 1H), 7.92 (d, *J* = 5.6 Hz, 0.7H), 7.78-7.85 (m, 2H), 7.41 (d, *J* = 6.8

Hz, 0.4H), 7.34 (m, 1H), 7.24-7.30 (m, 2H), 7.11-7.14 (m, 0.7H), 6.88 (d, *J* = 6.4 Hz, 0.7H), 6.78 (d, *J* = 6.4 Hz, 0.4H), 4.57-4.60 (m, 1H), 4.48-4.51 (m, 1H), 2.86-2.91 (m, 1H), 2.76-2.79 (m, 1H), 1.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): ***δ*** 179.11, 178.74, 178.38, 178.34, 149.11, 149.06, 140.81, 139.91, 139.43, 139.35, 133.22, 131.13, 130.29, 129.40, 129.35, 129.31, 128.98, 128.85, 126.32, 125.39, 124.17, 124.08, 123.74, 116.30, 114.96, 114.87, 111.59, 110.01, 84.94, 84.79, 84.33, 84.17, 78.78, 78.32, 55.54, 55.43, 46.70, 46.57, 28.16; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; *t* = 10.79, 12.15, 15.68, 18.41); $[\alpha]_D^{20}$ = -16.2 (c = 0.75, CH_2Cl_2); ESI HRMS exact mass calcd. for $(C_{23}H_{22}N_2O_5 + Na)^+$ requires m/z 429.1421, found m/z 429.1410.

Synthesis of compound 6



To the solution of **2q** (31 mg, 0.084 mmol) in CH_2Cl_2 (4 mL) were added Et_3N (70 μL, 0.5 mmol) and DMAP (2 mg, 0.2 eq), then *p*-nitrobenzene sulfonyl chloride (93 mg, 0.42 mmol) was added to the solution by portion under stirration at 0℃. The resulting mixture was warmed to room temperature and vigorously stirred until the reaction finished. The reaction was quenched with a saturated NH_4Cl solution, extracted with CH_2Cl_2 three times, and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated under reduced pressure and the resulting crude mixture was purified by silica gel column chromatography (PE:EA = 8:1) to afford compound **6** (yellow solid, 37 mg) with 80% yield.

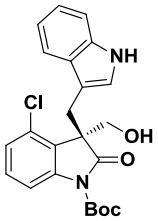


(R)-1-acetyl-5'-chloro-9'-((4-nitrophenyl)sulfonyl)-4',9'-dihydro-2'H-spiro[indoline-3,3'-pyrano[2,3-b]indol]-2-one (6): yellow solid, mp 171.5-173.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$): ***δ*** 8.28-8.32 (m, 3H), 8.14 (d, *J* = 6.4 Hz, 2H), 8.07 (d, *J* = 5.6 Hz, 1H), 7.37 (t, *J* = 6.4 Hz, 1H), 7.17-7.19 (m, 2H), 7.02 (t, *J* = 6.0 Hz, 1H), 6.77 (d, *J* = 7.2 Hz, 1H), 4.31-4.37 (m, 2H), 3.44 (d, *J* = 13.2 Hz, 1H), 3.20 (d, *J* = 13.2 Hz, 1H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): ***δ*** 176.68, 170.55, 150.99, 146.58, 143.33, 139.30, 132.33, 129.59, 128.88, 128.66, 126.11, 125.59, 125.41, 125.27, 124.60, 124.06, 122.98, 116.92, 112.61, 93.04, 72.41, 45.26, 29.52, 26.75; ESI HRMS exact mass calcd. for $(C_{26}H_{18}ClN_3O_7S +$

Na)$^+$ requires m/z 574.0446, found m/z 574.0462.

synthesis of 1r a

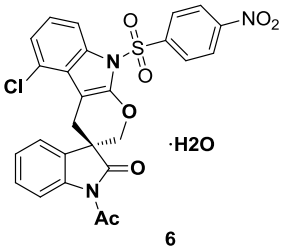
3-(3-indolomethyl)oxindole **1r** (0.1 mmol, 39.7 mg), paraformaldehyde (18 mg, 0.6 mmol) and catalyst **3a** (3.2 mg, 0.01 mmol) were stirred in DCE (2 mL) at 0℃ for 42 h. Purification of the crude product by flash column chromatography afforded the Aldol product **1r a** (petroleum ether/ethyl acetate as eluent (3:1)).



(R)-tert-butyl 3-((1H-indol-3-yl)methyl)-4-chloro-3-(hydroxymethyl)-2-oxoindoline-1-carboxylate (1r a): white solid, 95% yield, 92% ee; ^{1}H NMR (600 MHz, $CDCl_3$): ***δ*** 7.83 (s, 1H), 7.52 (dd, *J* = 8.6, 5.3 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 4.2 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 1.6 Hz, 1H), 4.45 (dd, *J* = 10.9, 3.1 Hz, 1H), 4.30-4.40 (m, 1H), 3.63 (d, *J* = 14.3 Hz, 1H), 3.49 (d, *J* = 14.3 Hz, 1H), 2.04-2.05 (m, 1H), 1.44 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$): ***δ*** 177.68, 148.53, 142.70, 135.63, 130.29, 129.78, 127.33, 125.60, 125.46, 123.28, 121.88, 119.54, 119.21, 113.57, 110.75, 109.11, 84.50, 64.82, 59.15, 27.97, 27.50. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak OD-H column (90/10 hexane/*i*-PrOH; flow rate: 1.0 mL/min; λ = 254 nm; t_{minor} = *20.71 min*, t_{major} = *29.21 min*); $[\alpha]_D^{20}$ = +97.4 (c = 1.0, CH_2Cl_2); ESI HRMS exact mass calcd. for ($C_{23}H_{23}ClN_2O_4$ + Na)$^+$ requires m/z 449.1239, found m/z 449.1243.

X-ray crystal structure of compound 6 and 1r a

The chemical structure of pentacyclic spirooxindoles **2** has been confirmed by a single crystal X-ray analysis of **6**. And the absolute configuration of the chiral quaternary carbon has been confirmed by a single crystal X-ray analysis of **1ra** (the product of the first Aldol reaction of **1r**).



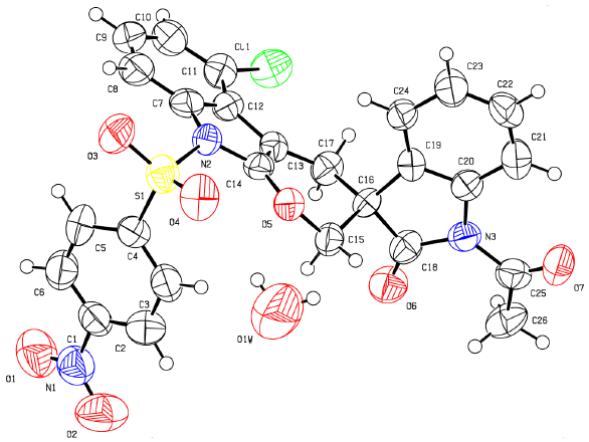
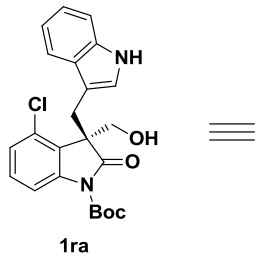


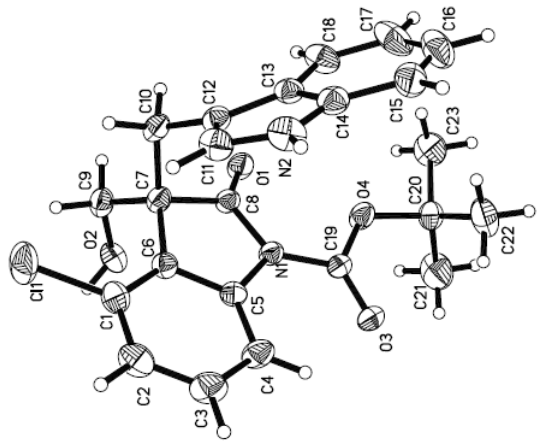
Table 1. Crystal data and structure refinement for 6.

Identification code	6
Empirical formula	C_{26} H_{20} Cl N_3 O_8 S

Formula weight	569.96
Temperature	296(2) K
Wavelength	0.71073A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 5.6165(18) A alpha = 65.52(3) deg. b = 13.983(2) A beta =88.60(3) deg. c = 16.7686(17) A gamma = 86.77(3) deg.
Volume	1196.6(4) A^3
Z, Calculated density	2, 1.582 Mg/m^3
Absorption coefficient	0.308 mm^-1
F(000)	588
Crystal size	0.26 x 0.21 x 0.17 mm
Theta range for data collection	1.60 to 25.00 deg.
Limiting indices	-6<=h<=6, -16<=k<=16, -19<=l<=11
Reflections collected / unique	6021 / 4185 [R(int) = 0.0828]
Completeness to theta = 25.00	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9496 and 0.9243
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4185 / 3 / 359
Goodness-of-fit on F^2	0.898
Final R indices [I>2sigma(I)]	R1 = 0.0706, wR2 = 0.1010
R indices (all data)	R1 = 0.2192, wR2 = 0.1237
Extinction coefficient	0.0039(8)
Largest diff. peak and hole	0.239 and -0.311 e.A^-3



1ra



C7R

Table 2. Crystal data and structure refinement for **1ra**.

Identification code	**1ra**
Empirical formula	$C_{23}H_{23}ClN_2O_4$
Formula weight	426.88
Temperature/K	293(2)
Crystal system	monoclinic

Space group	$P2_1$
a/Å	8.8442(2)
b/Å	10.8918(2)
c/Å	11.5077(3)
α/°	90
β/°	90.266(3)
γ/°	90
Volume/Å^3	1108.51(5)
Z	2
ρ_{calc}g/cm^3	1.279
μ/mm^{-1}	1.783
F(000)	448.0
Crystal size/mm^3	0.2 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.682 to 134.056
Index ranges	$-10 \leq h \leq 6$, $-13 \leq k \leq 13$, $-13 \leq l \leq 13$
Reflections collected	7923
Independent reflections	3966 [R_{int} = 0.0272, R_{sigma} = 0.0378]
Data/restraints/parameters	3966/1/275
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.0909
Final R indexes [all data]	R_1 = 0.0535, wR_2 = 0.0997
Largest diff. peak/hole / e Å^{-3}	0.13/-0.16
Flack parameter	0.019(11)

Reference

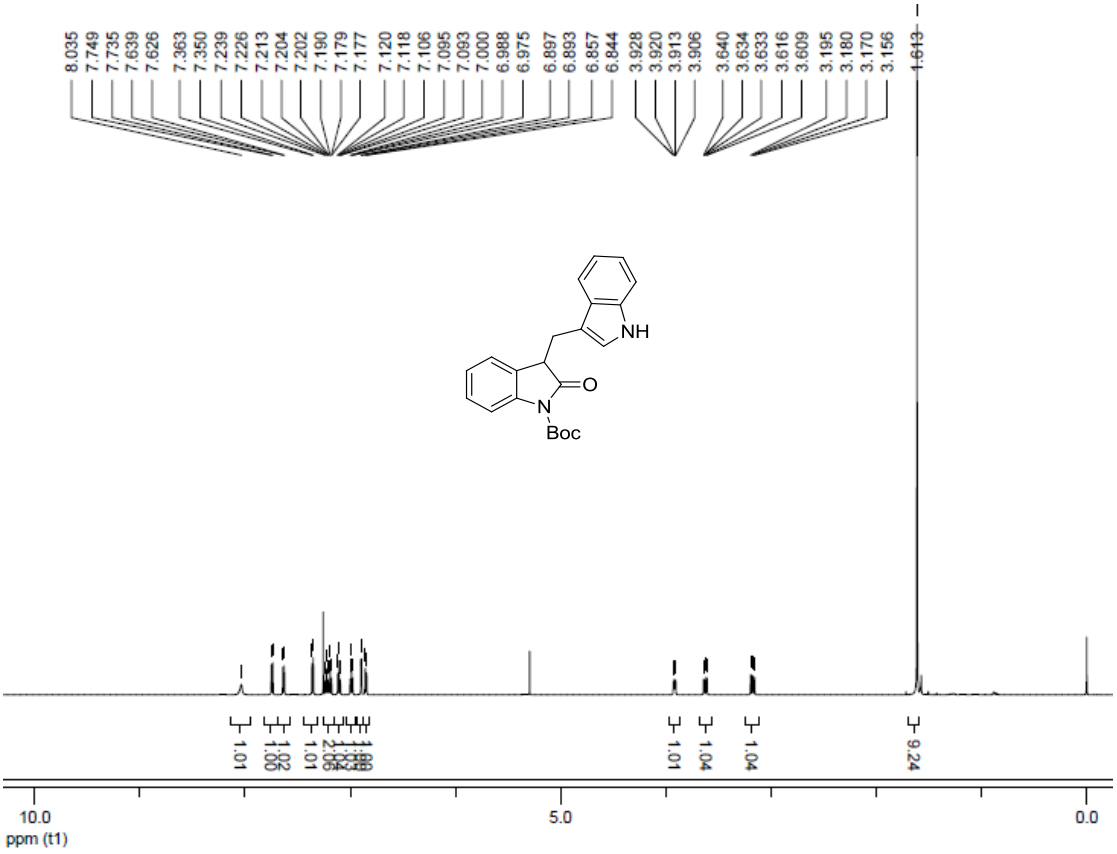
[1] V. Lanke, K. R. Prabhu, *Org. Lett.* **2013**, *15*, 6262–6265.

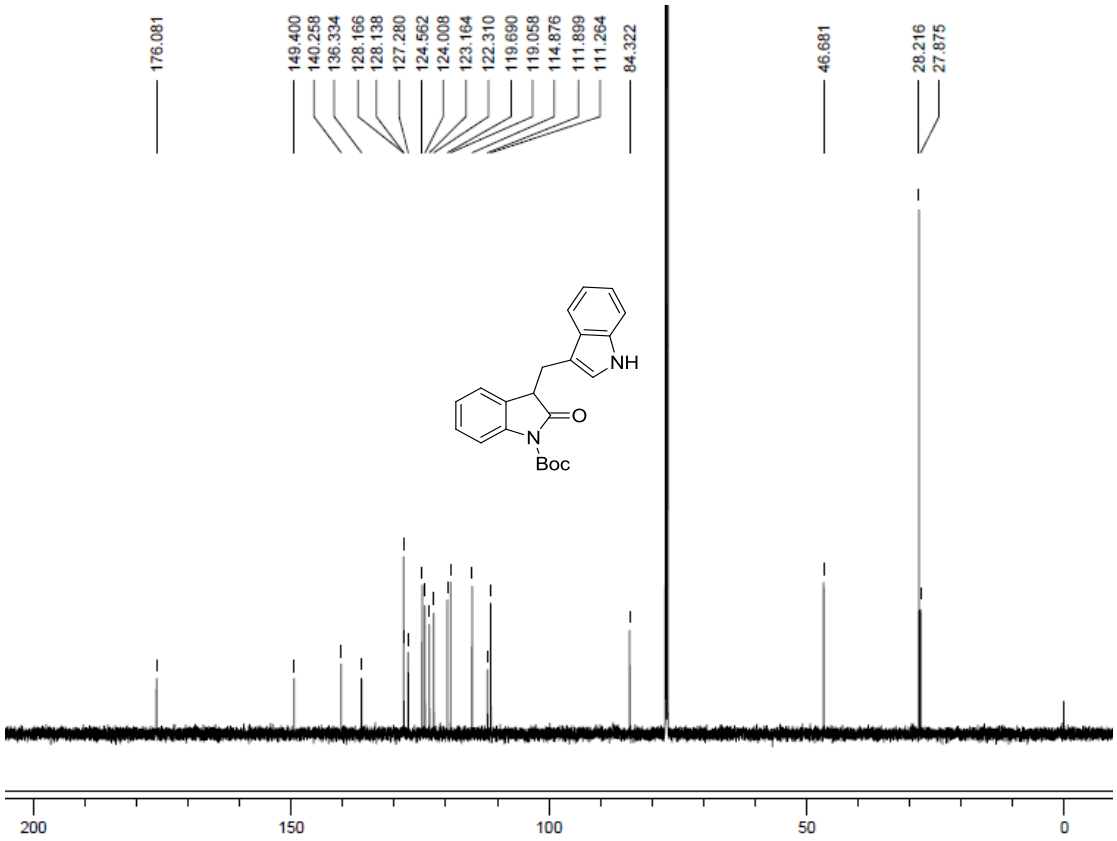
[2] W. Zhang, M.-L. Go, *Bioogan. Med. Chem*. **2009**, *17*, 2077–2090.

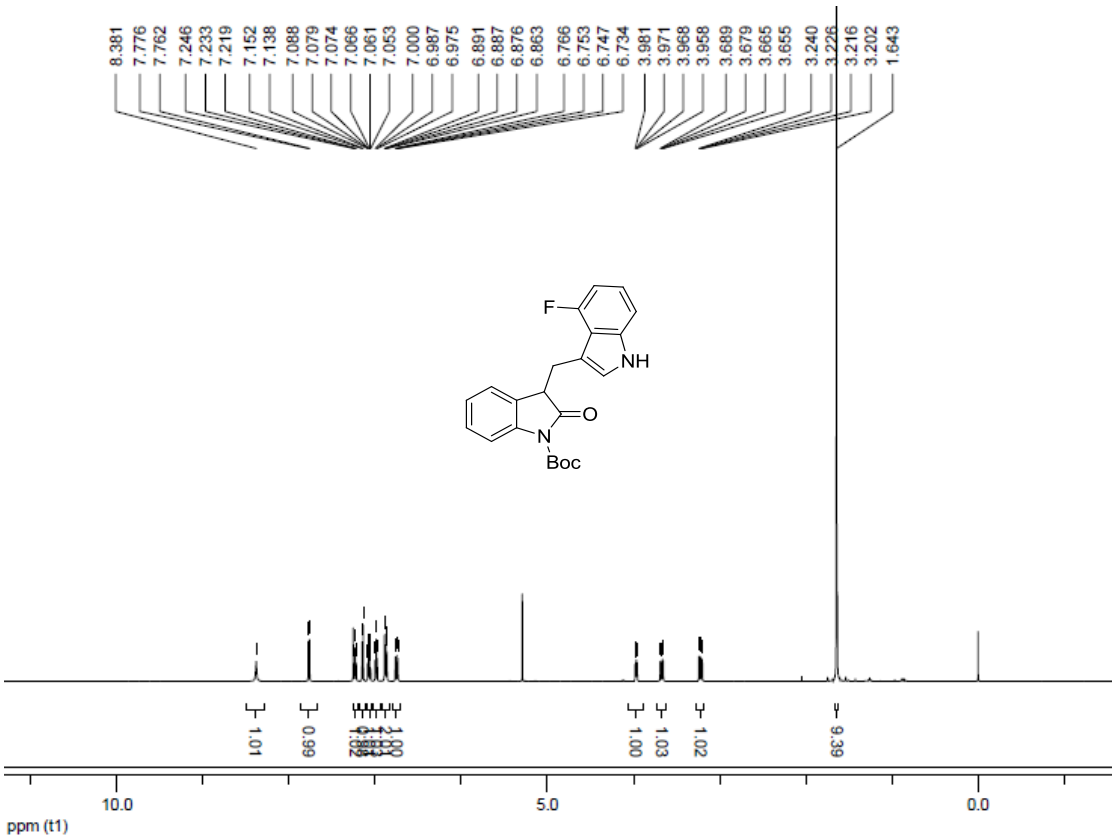
[3] L. Cheng, L. Liu, D. Wang, Y.-J. Chen, *Org. Lett.* **2009**, *11*, 3874–3877.

[4] W. G. Rajeswaran, L. A. Cohen, *Tetrahedron* **1998**, *54*, 11375-11380.

Copies of NMR and HPLC spectra



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7.061
7.053
7.000
6.987
6.975
6.891
6.887
6.876
6.863
6.766
6.753
6.747
6.734
3.981
3.971
3.968
3.958
3.689
3.679
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3.655
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Boc
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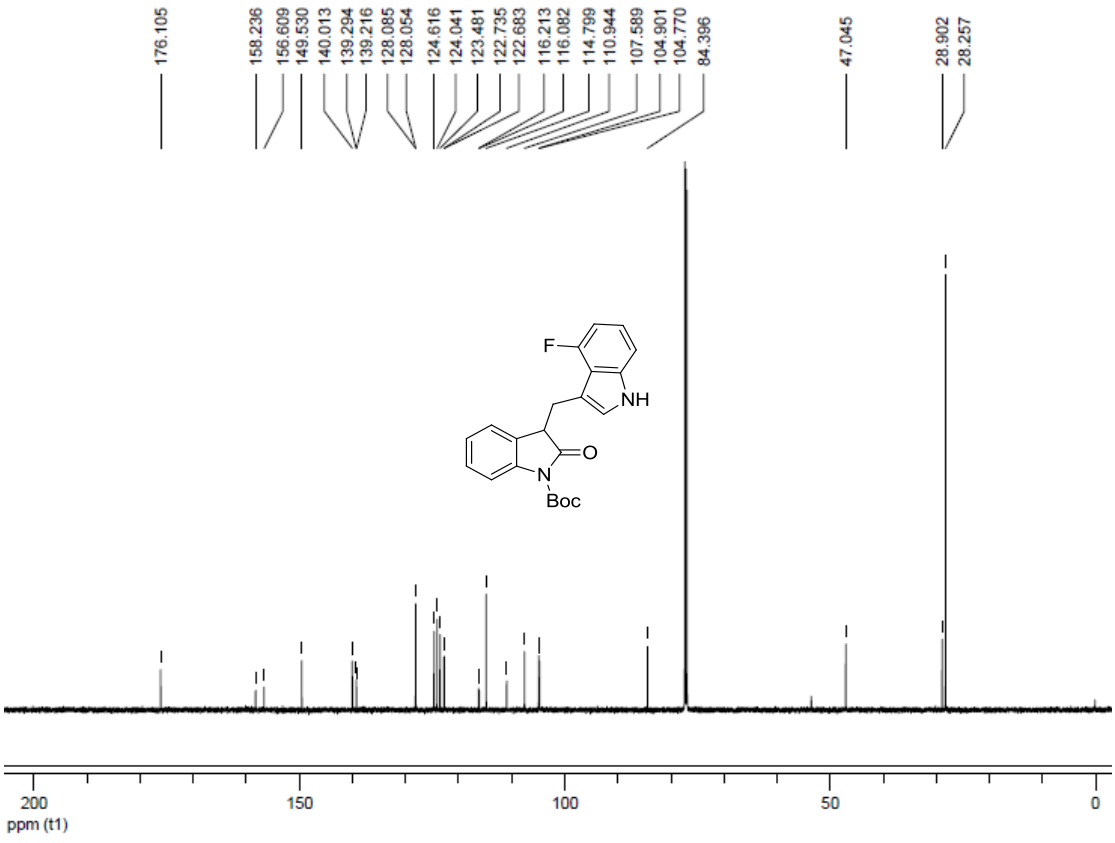
ppm (t1)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Boc
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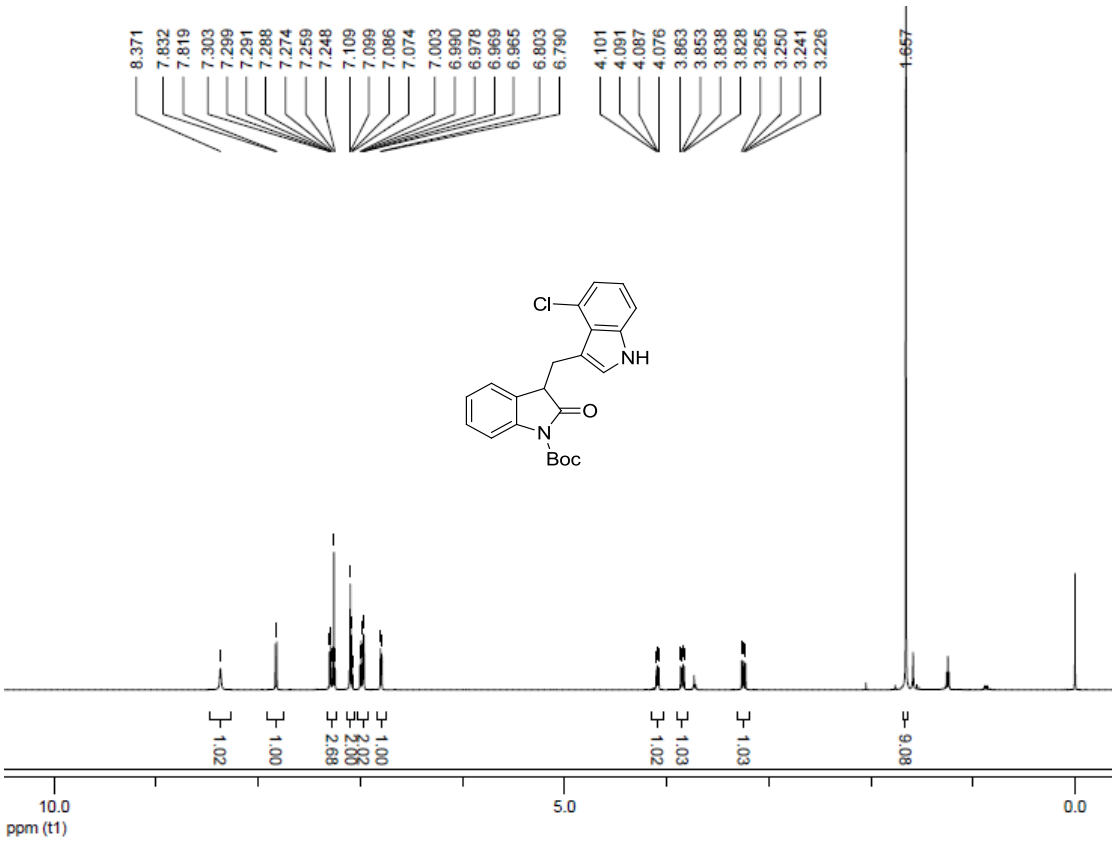
ppm (t1)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Boc
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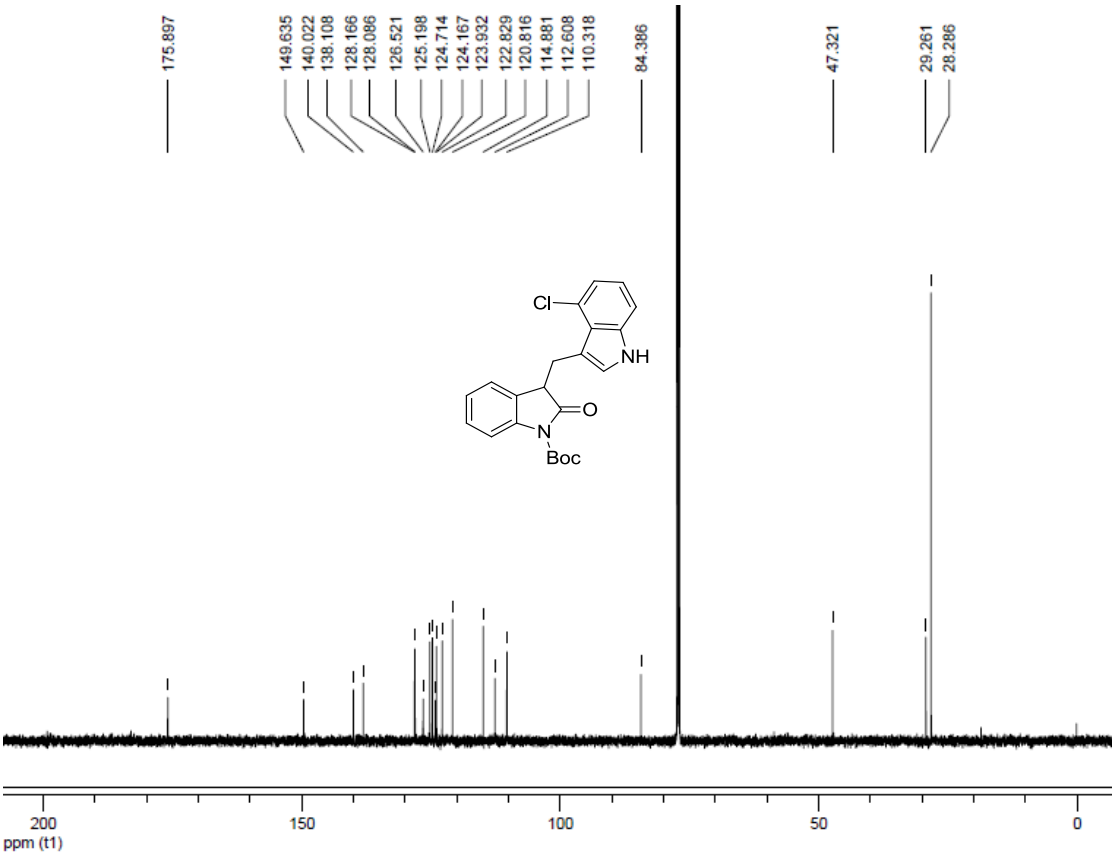
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114.881
112.608
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Boc
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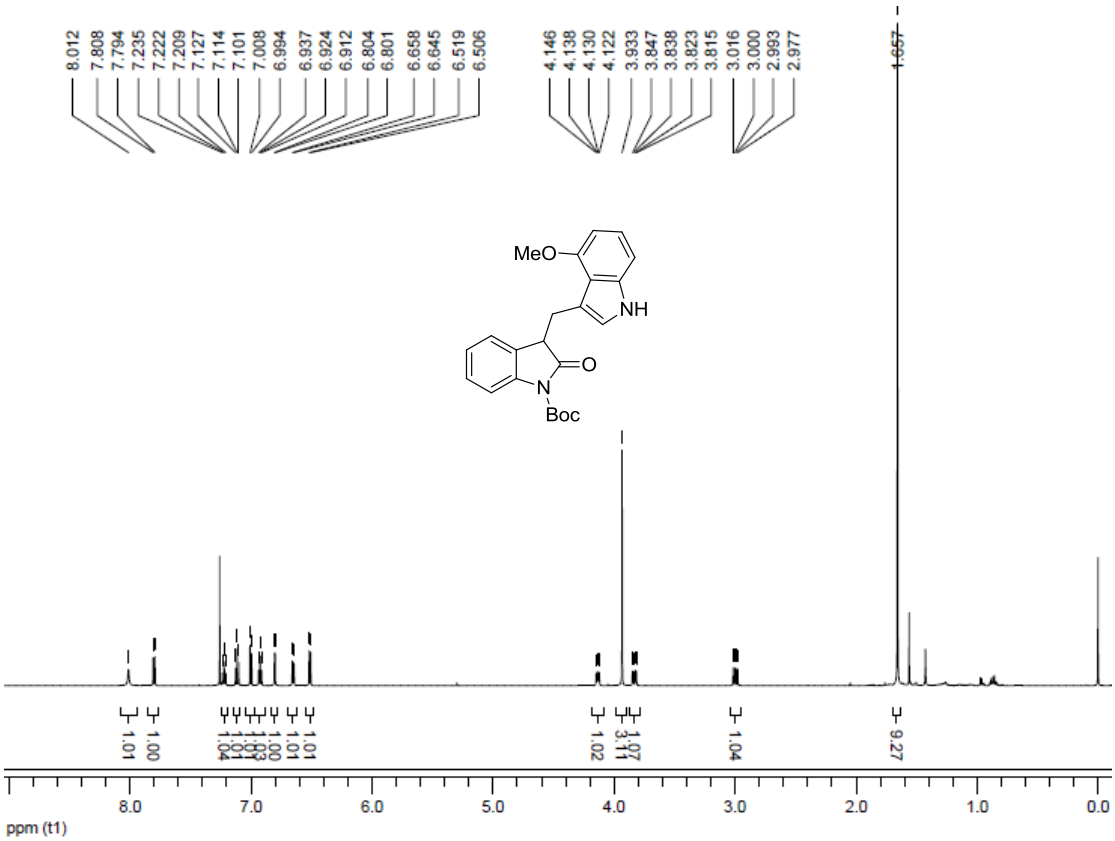
ppm (t1)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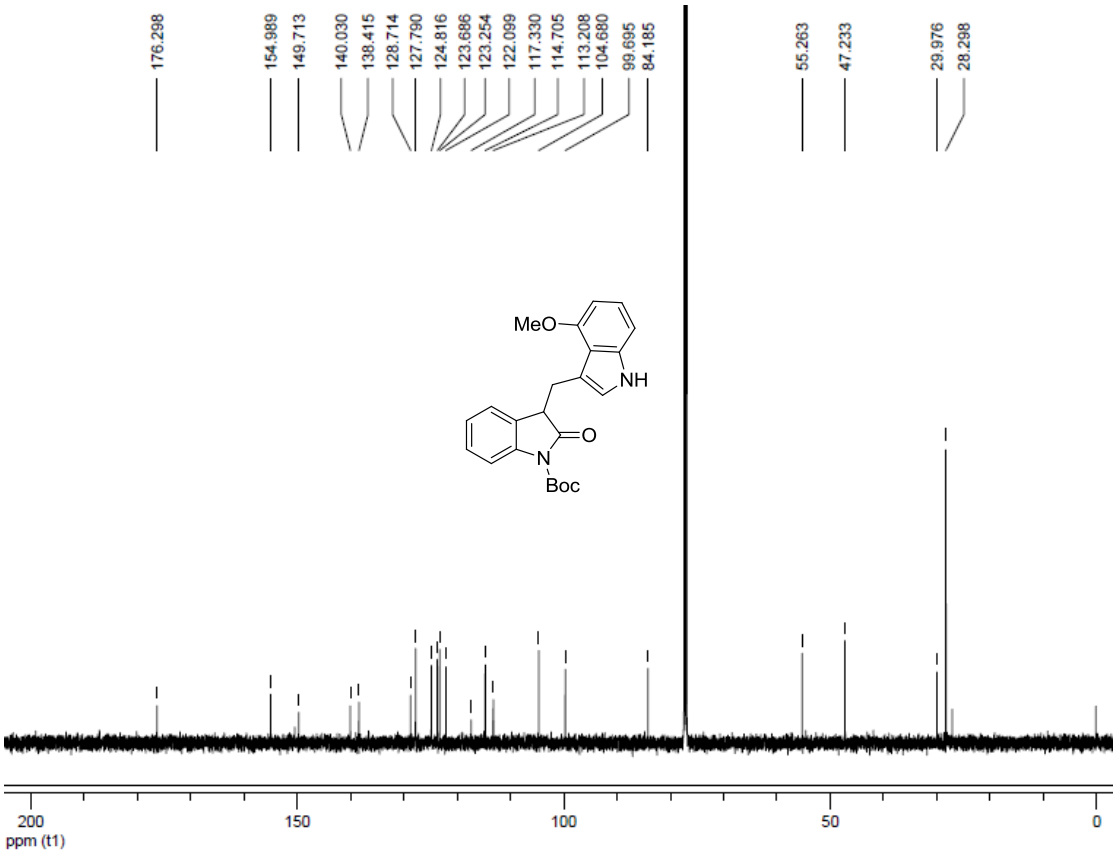
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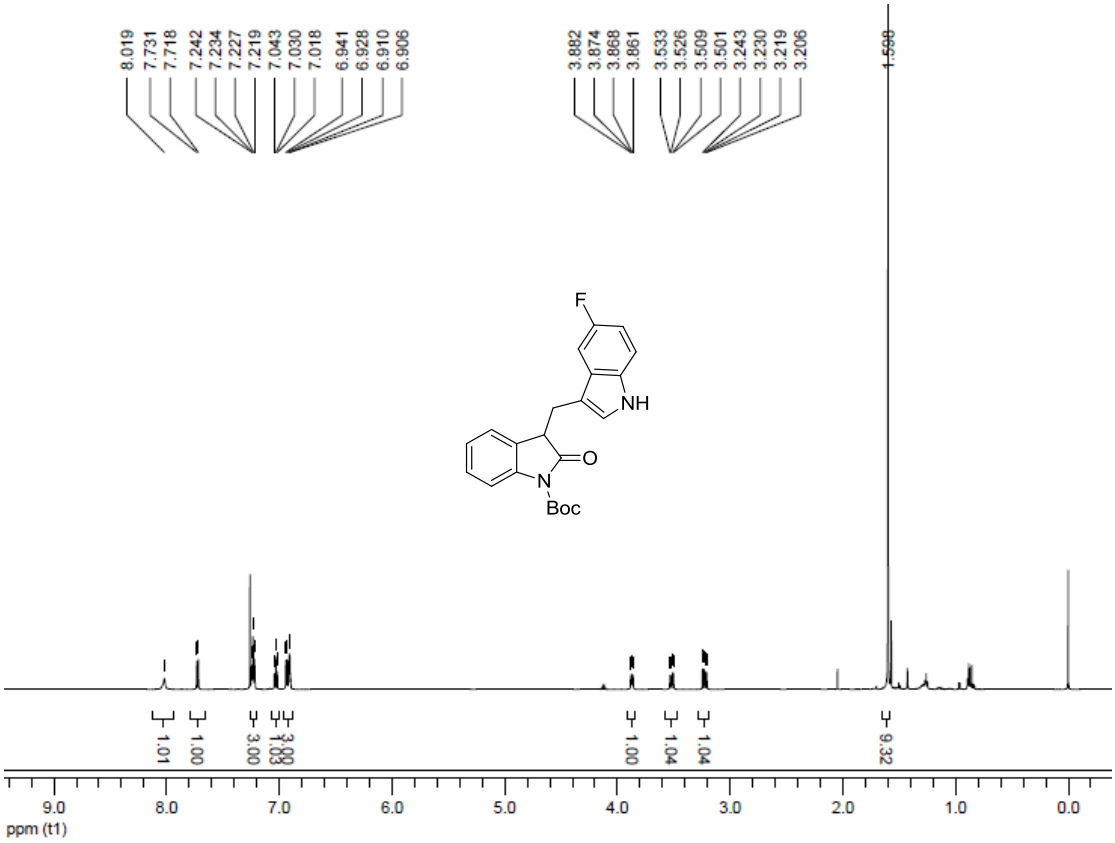
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6.910
6.906
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3.874
3.868
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3.526
3.509
3.501
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3.230
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O
N
Boc
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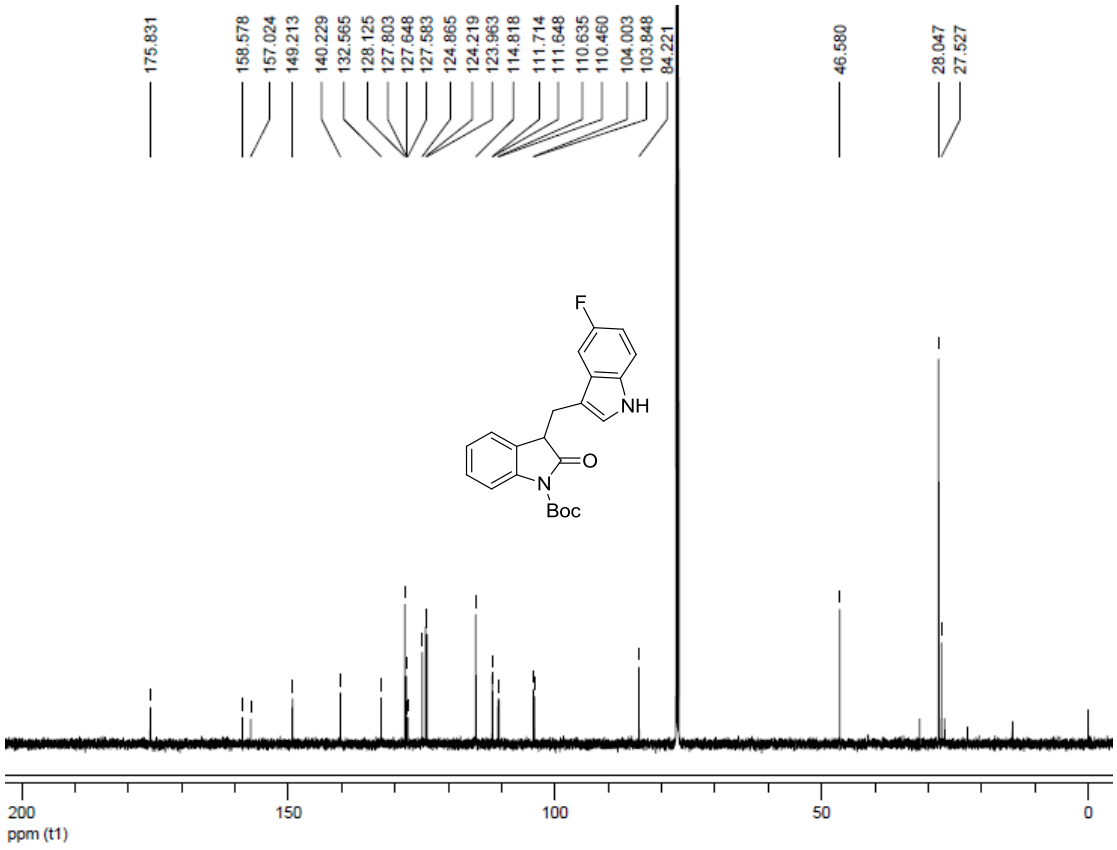
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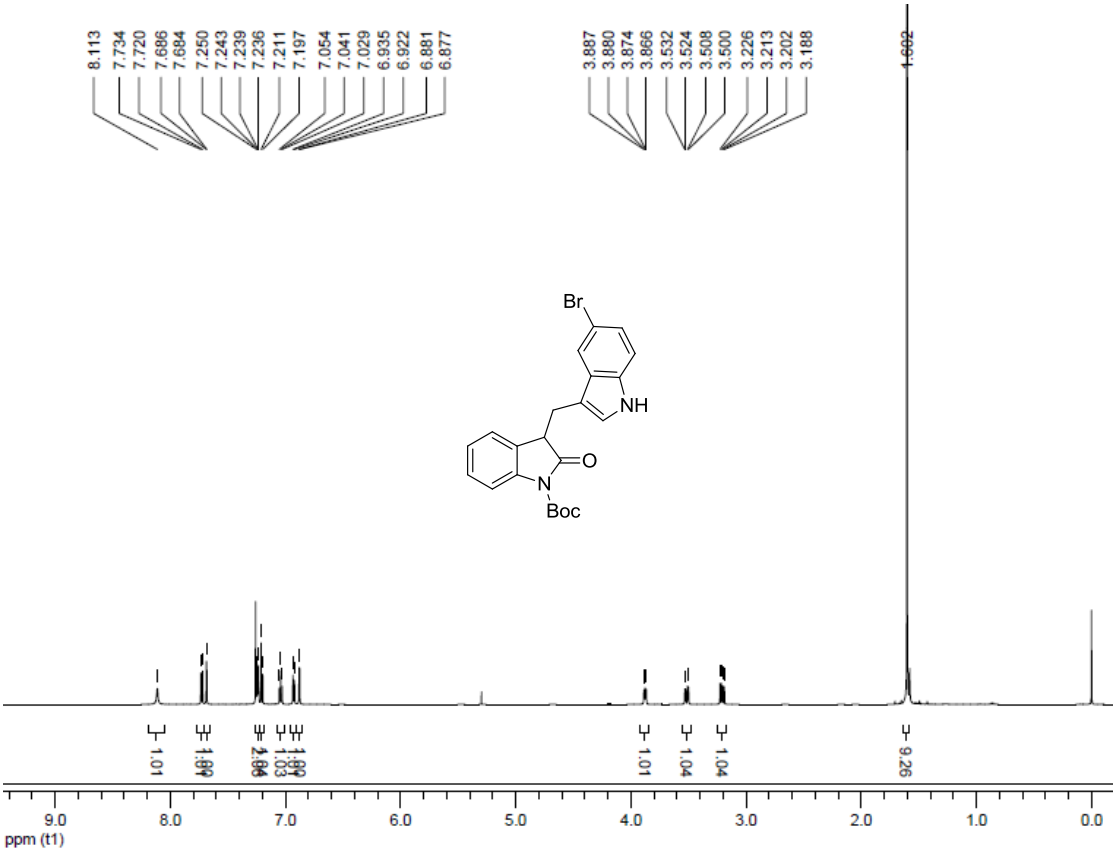
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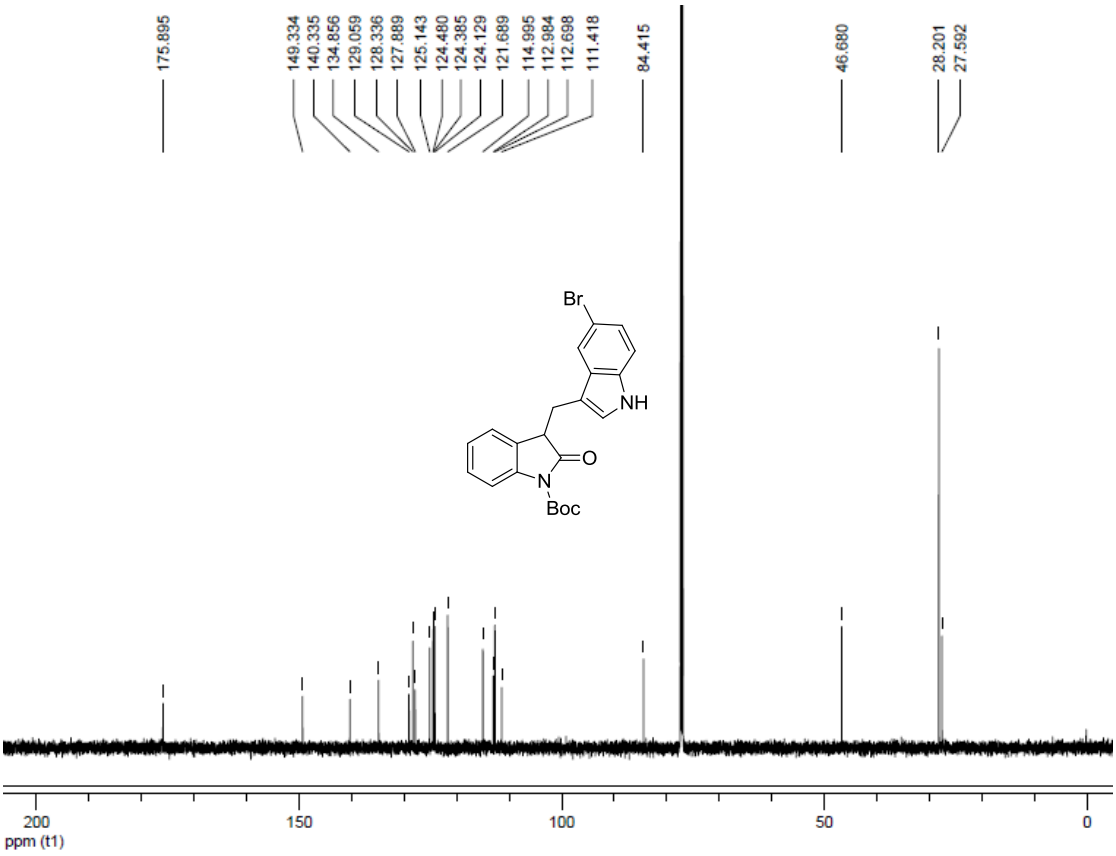
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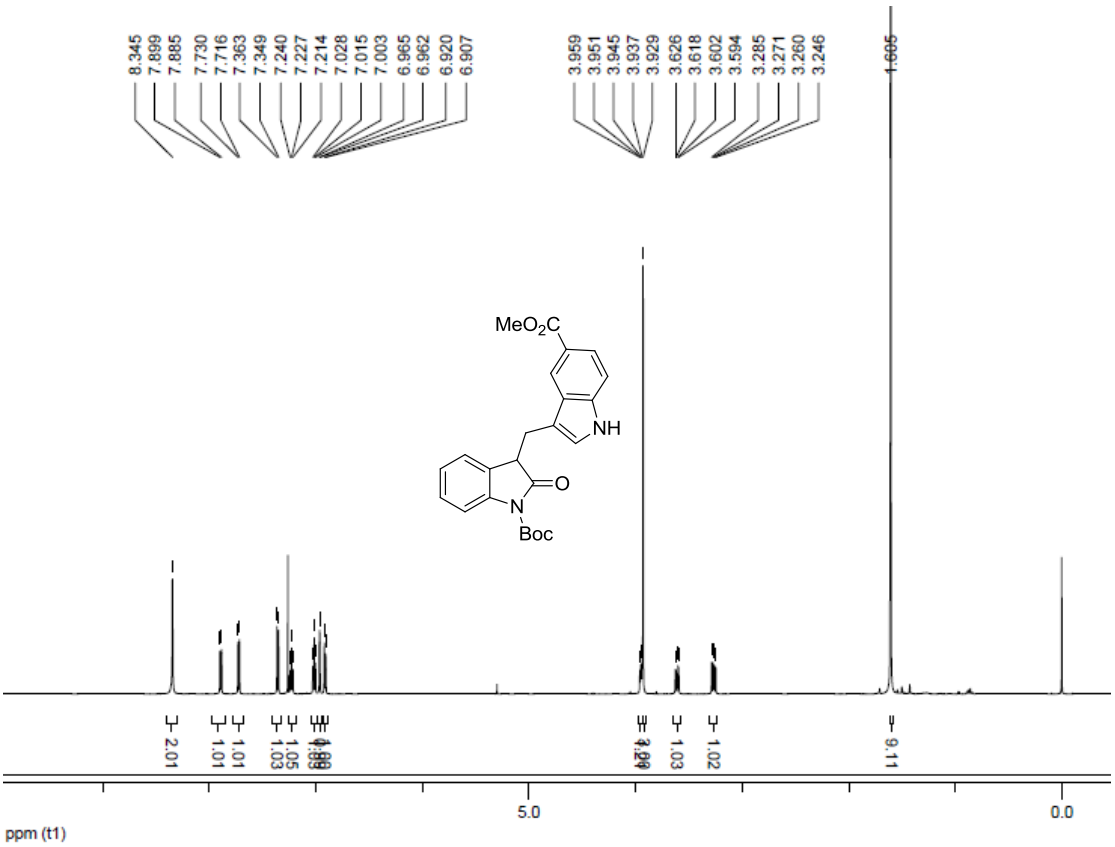
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3.951
3.945
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3.929
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3.260
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1.03
1.02
9.11
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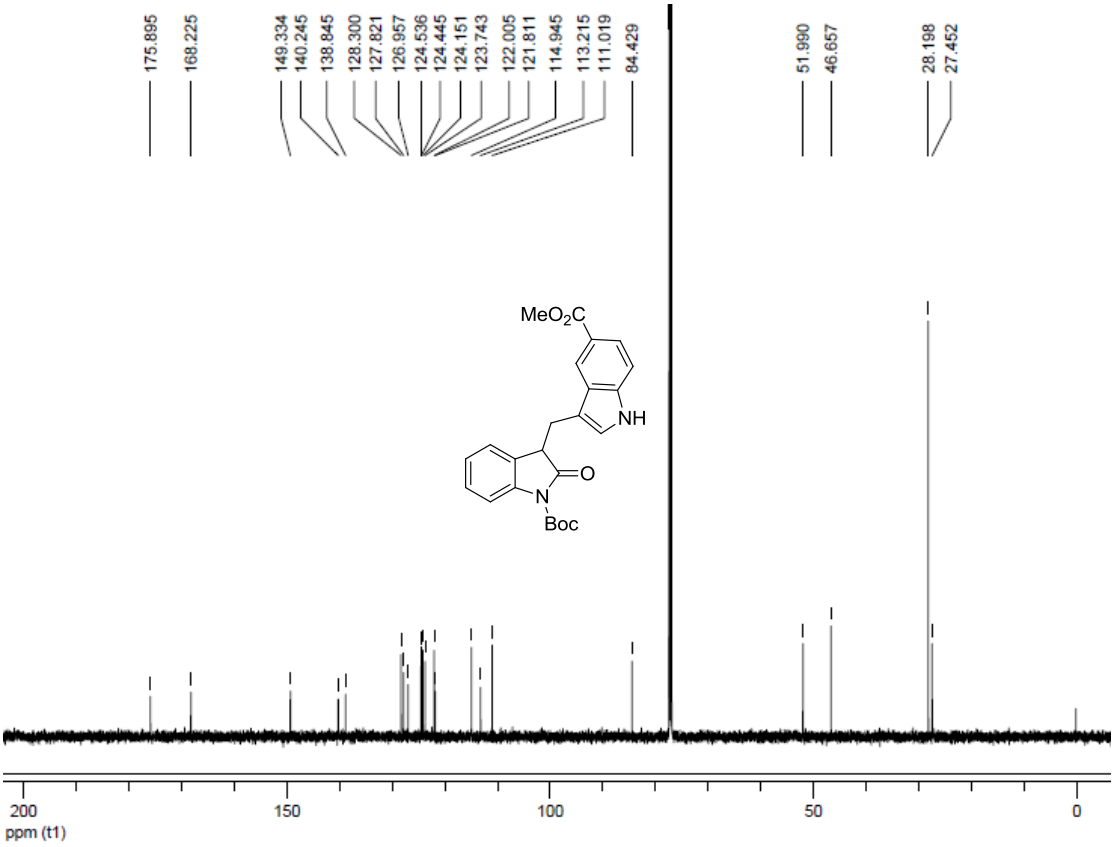
0.0
ppm (t1)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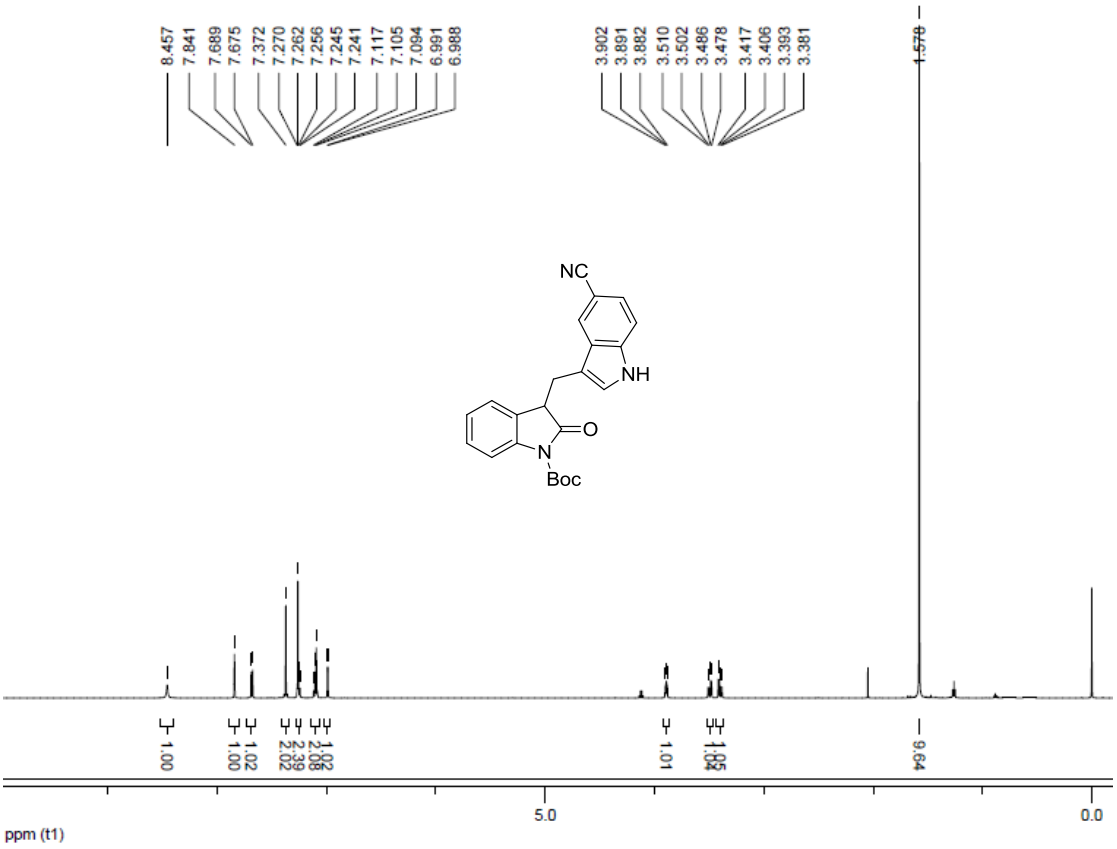
149.334
140.245
138.845
128.300
127.821
126.957
124.536
124.445
124.151
123.743
122.005
121.811
114.945
113.215
111.019
84.429
51.990
46.657
28.198
27.452
MeO2C
NH
O
N
Boc
200
150
100
50
0
ppm (t1)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7.689
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7.262
7.256
7.245
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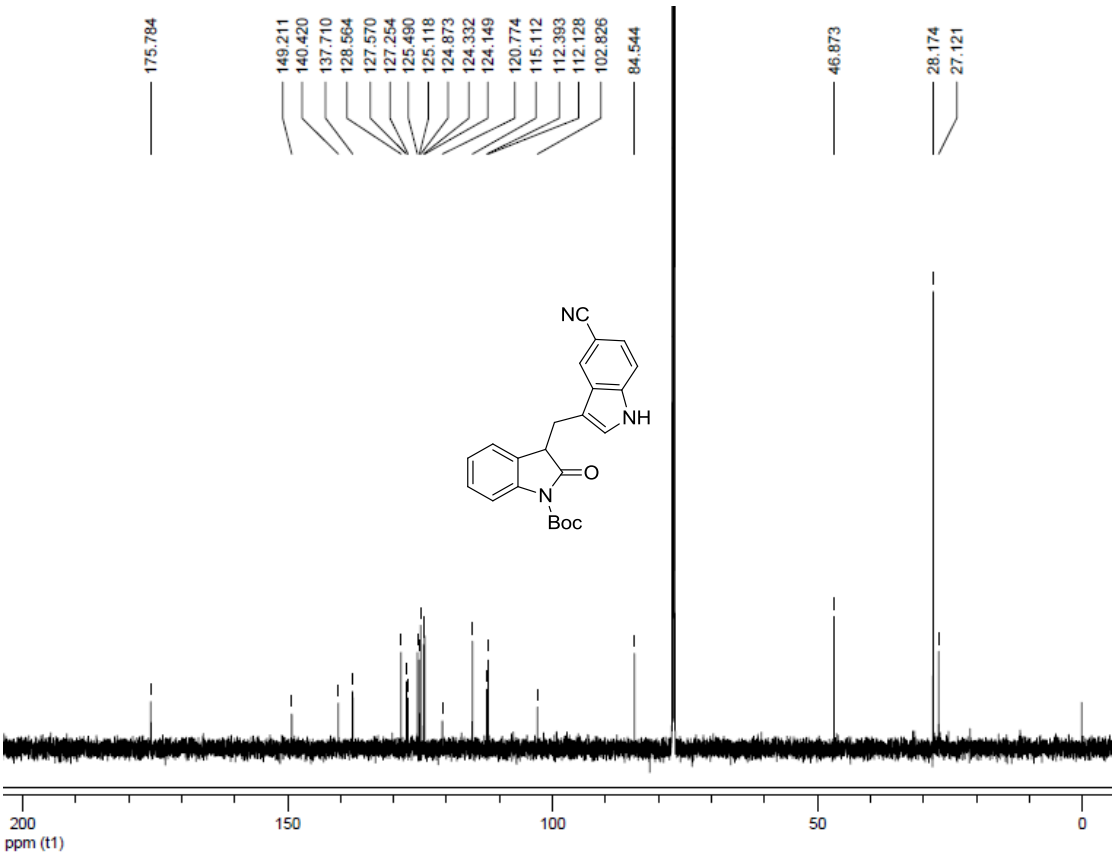
7.117
7.105
7.094
6.991
6.988
3.902
3.891
3.882
3.510
3.502
3.486
3.478
3.417
3.406
3.393
3.381
1.578
NC
NH
O
N
Boc
1.00
1.00
1.02
2.02
2.39
2.08
1.02
1.01
1.05
9.64
5.0
0.0
ppm (t1)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140.420
137.710
128.564
127.570
127.254
125.490
125.118
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124.332
124.149
120.774
115.112
112.393
112.128
102.826
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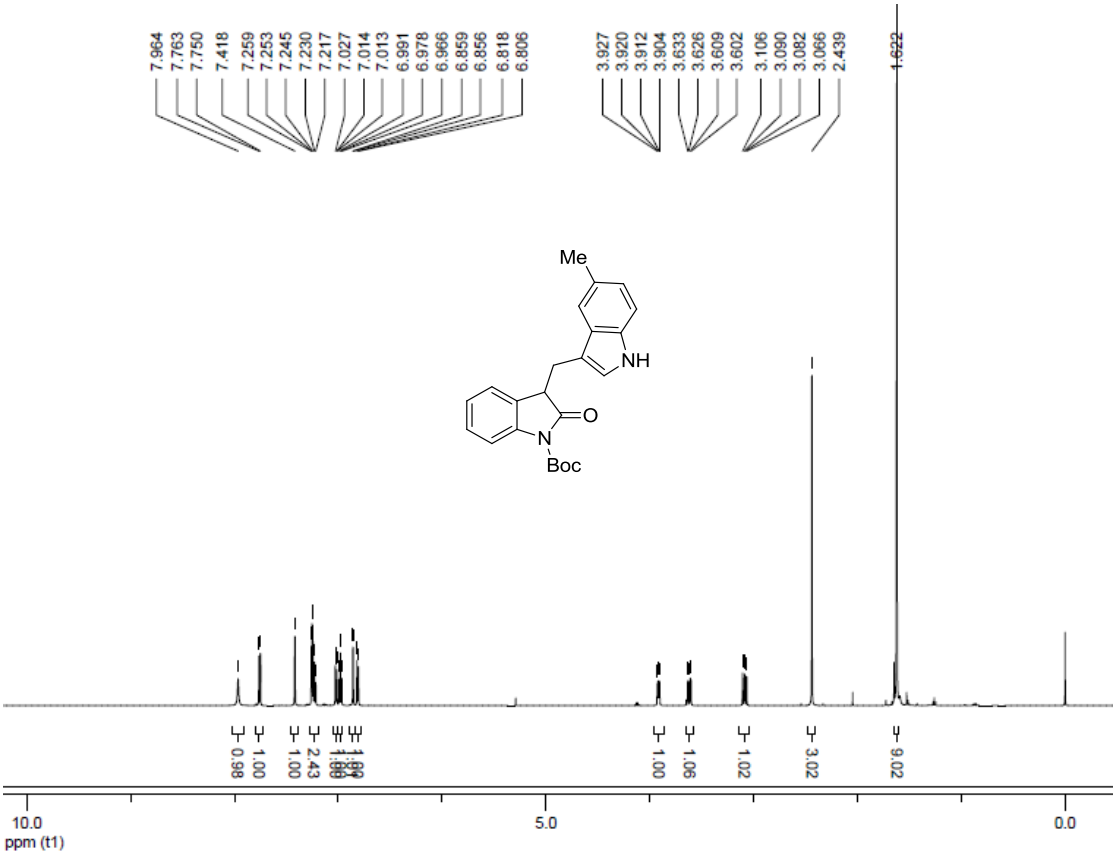
46.873
28.174
27.121
NC
NH
O
N
Boc
200
150
100
50
0
ppm (t1)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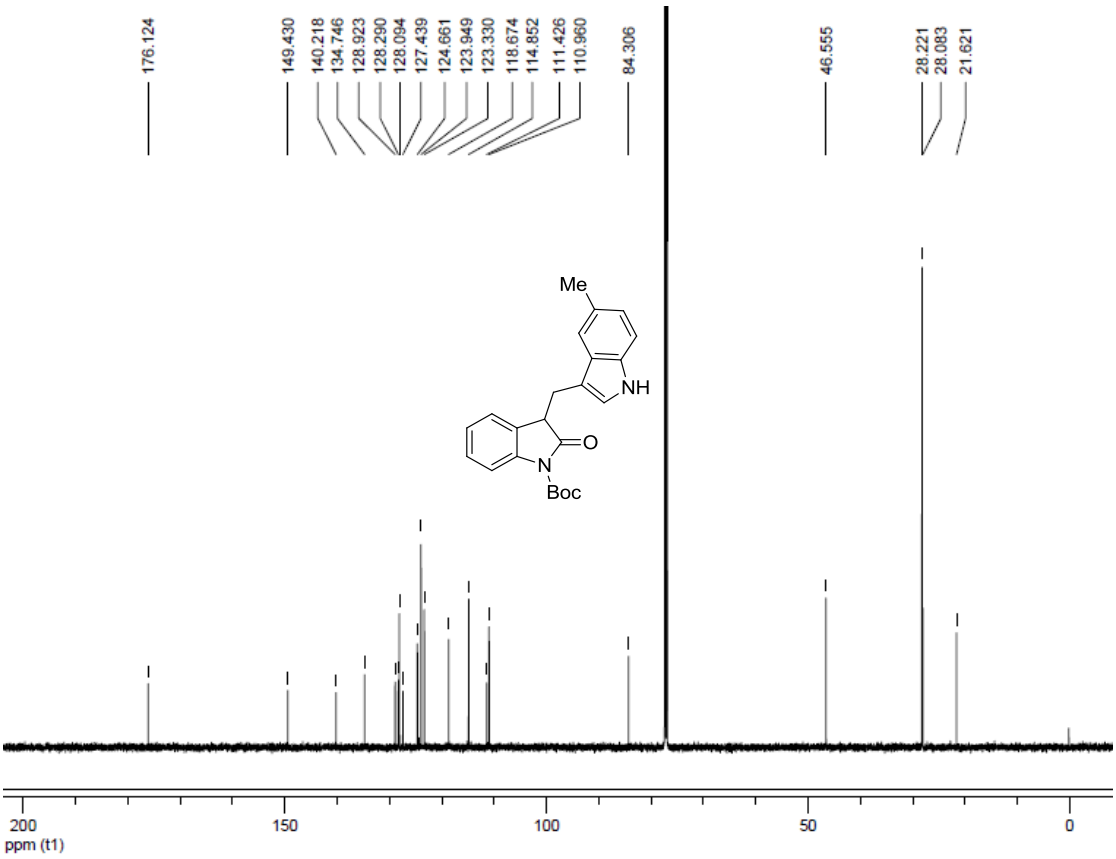
7.750
7.418
7.259
7.253
7.245
7.230
7.217
7.027
7.014
7.013
6.991
6.978
6.966
6.859
6.856
6.818
6.806
3.927
3.920
3.912
3.904
3.633
3.626
3.609
3.602
3.106
3.090
3.082
3.066
2.439
1.622
Me
NH
O
N
Boc
0.98
1.00
1.00
2.43
1.00
1.06
1.02
3.02
9.02
10.0
5.0
0.0
ppm (t1)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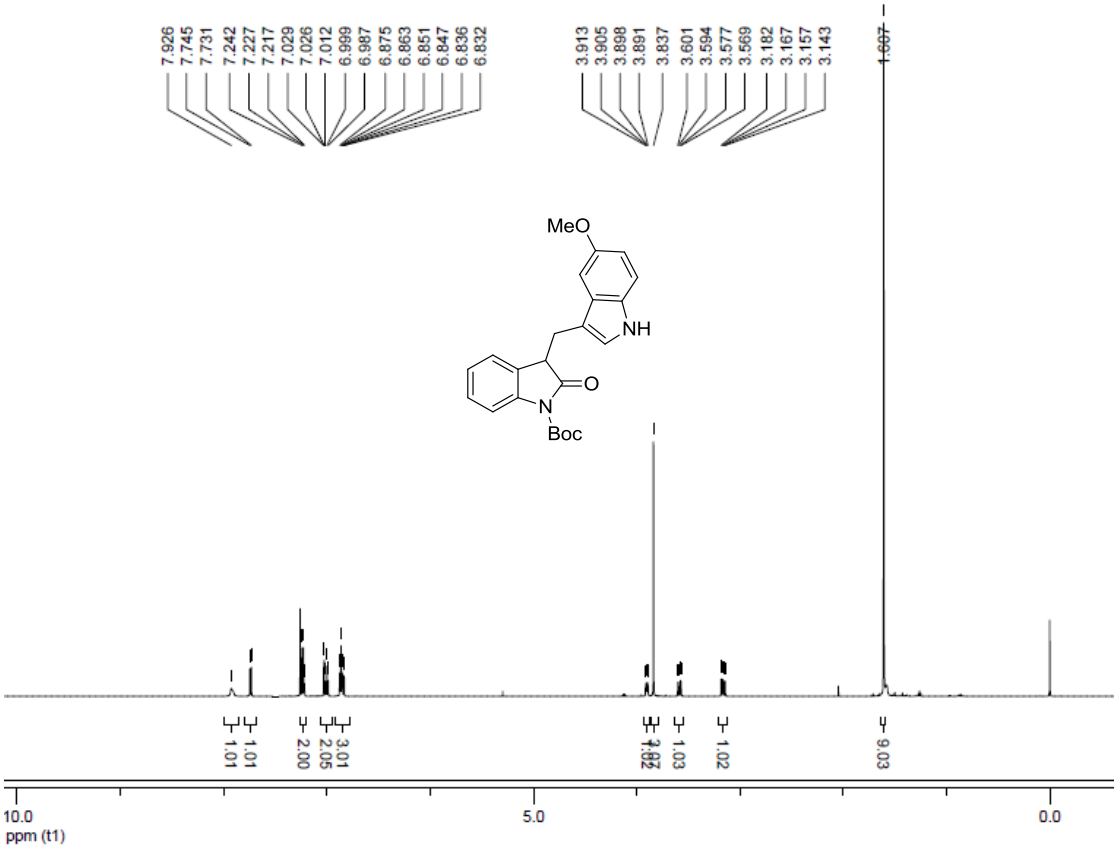
149.430
140.218
134.746
128.923
128.290
128.094
127.439
124.661
123.949
123.330
118.674
114.852
111.426
110.960
84.306
46.555
28.221
28.083
21.621
Me
NH
O
N
Boc
200
150
100
50
0
ppm (t1)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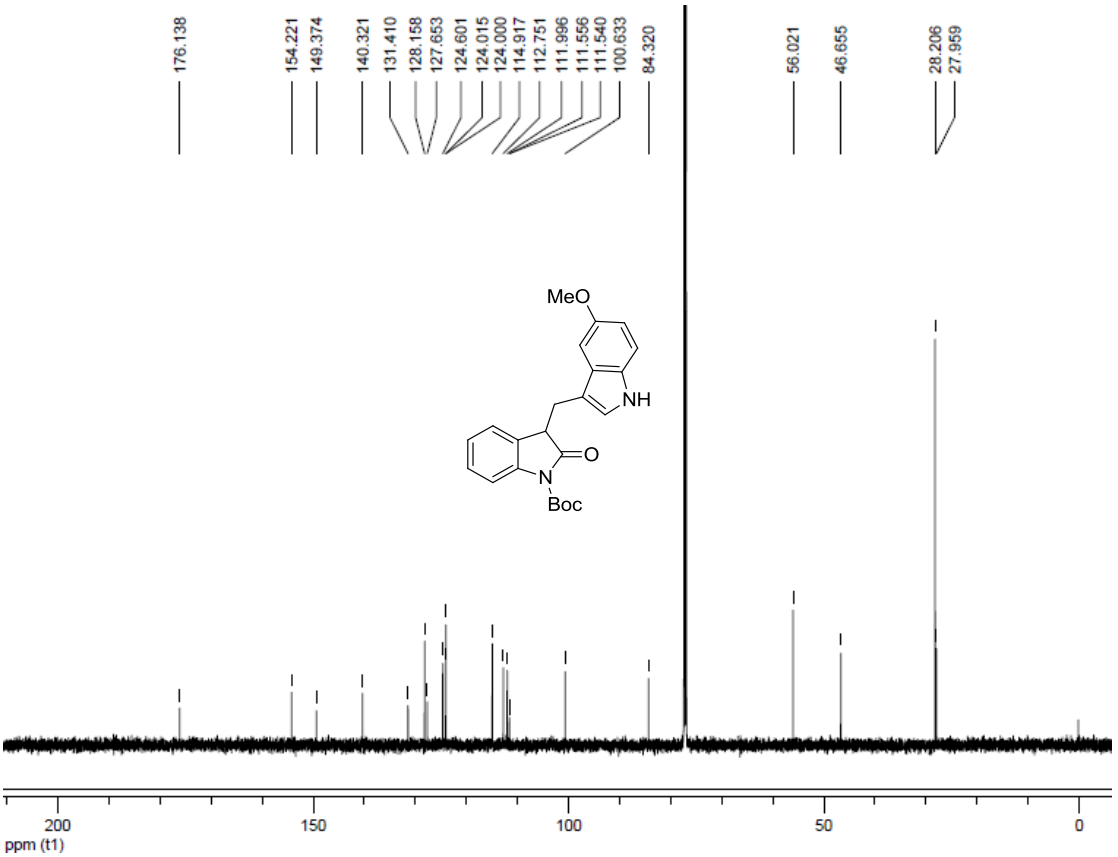
7.731
7.242
7.227
7.217
7.029
7.026
7.012
6.999
6.987
6.875
6.863
6.851
6.847
6.836
6.832
3.913
3.905
3.898
3.891
3.837
3.601
3.594
3.577
3.569
3.182
3.167
3.157
3.143
1.607
MeO
NH
O
N
Boc
1.01
1.01
2.00
2.05
3.01
1.03
1.02
9.03
10.0
5.0
0.0
ppm (t1)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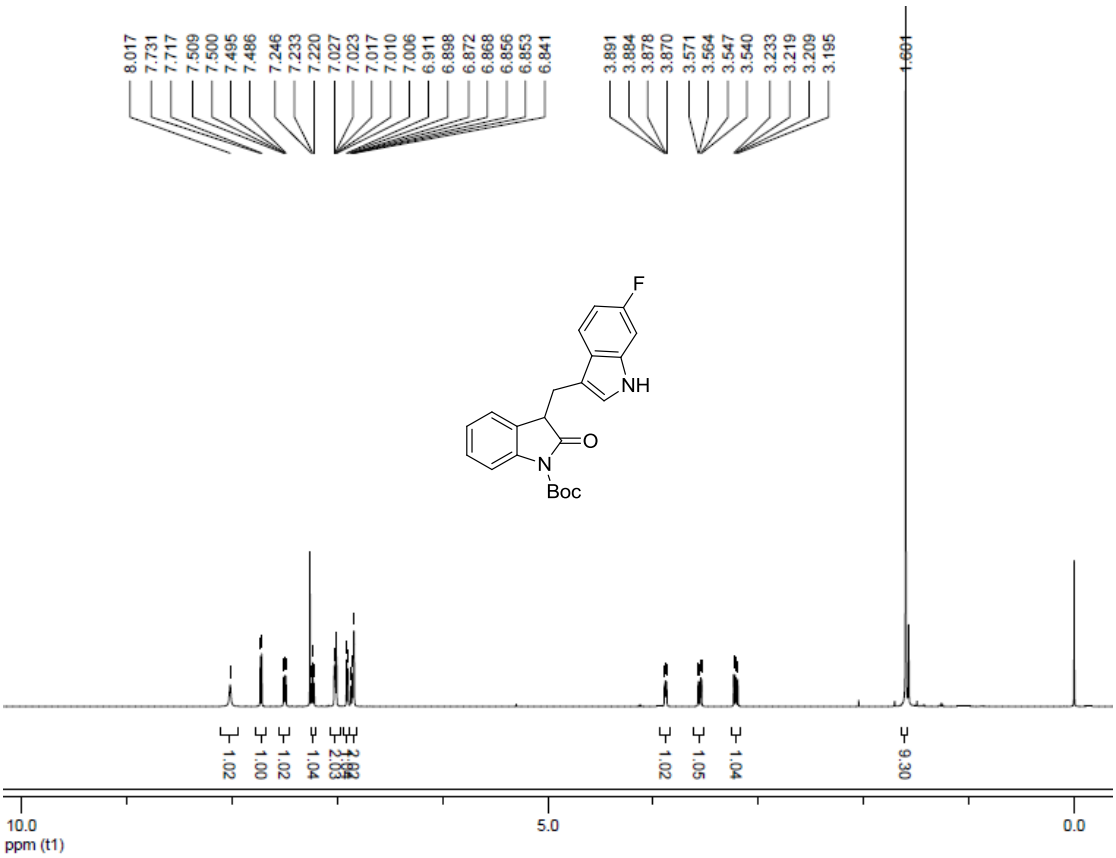
149.374
140.321
131.410
128.158
127.653
124.601
124.015
124.000
114.917
112.751
111.996
111.556
111.540
100.633
84.320
56.021
46.655
28.206
27.959
MeO
NH
O
N
Boc
200
150
100
50
0
ppm (t1)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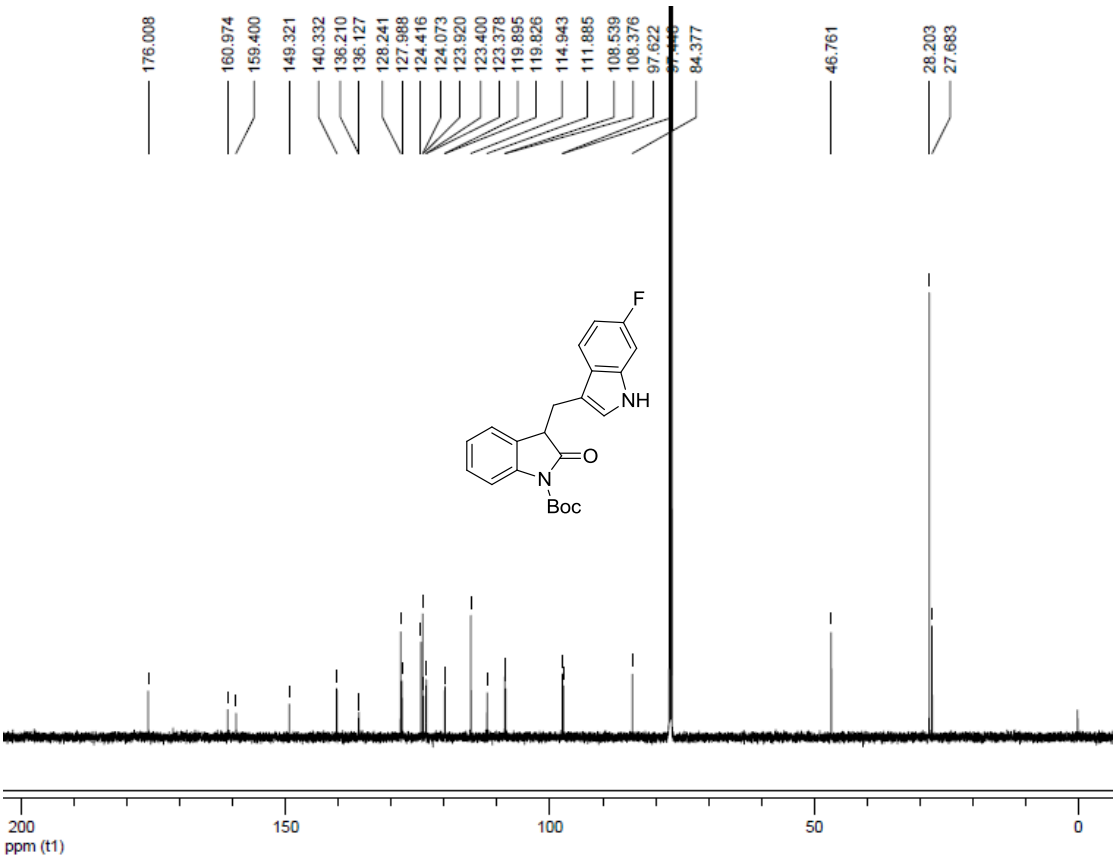
7.731
7.717
7.509
7.500
7.495
7.486
7.246
7.233
7.220
7.027
7.023
7.017
7.010
7.006
6.911
6.898
6.872
6.868
6.856
6.853
6.841
3.891
3.884
3.878
3.870
3.571
3.564
3.547
3.540
3.233
3.219
3.209
3.195
1.601
F
NH
O
N
Boc
1.02
1.00
1.02
1.04
2.84
2.03
1.02
1.05
1.04
9.30
10.0
ppm (t1)
5.0
0.0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159.400
149.321
140.332
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136.127
128.241
127.988
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124.073
123.920
123.400
123.378
119.895
119.826
114.943
111.885
108.539
108.376
97.622
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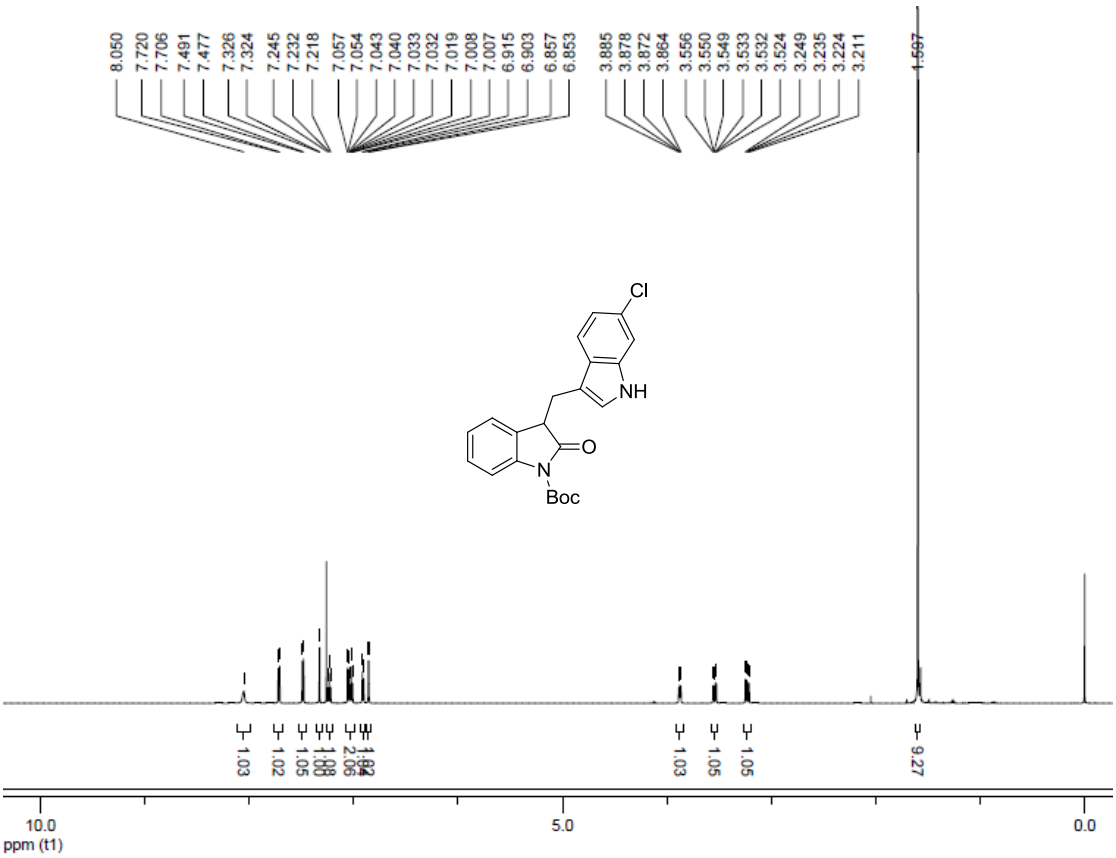
46.761
28.203
27.683
F
NH
O
N
Boc
200
ppm (t1)
150
100
50
0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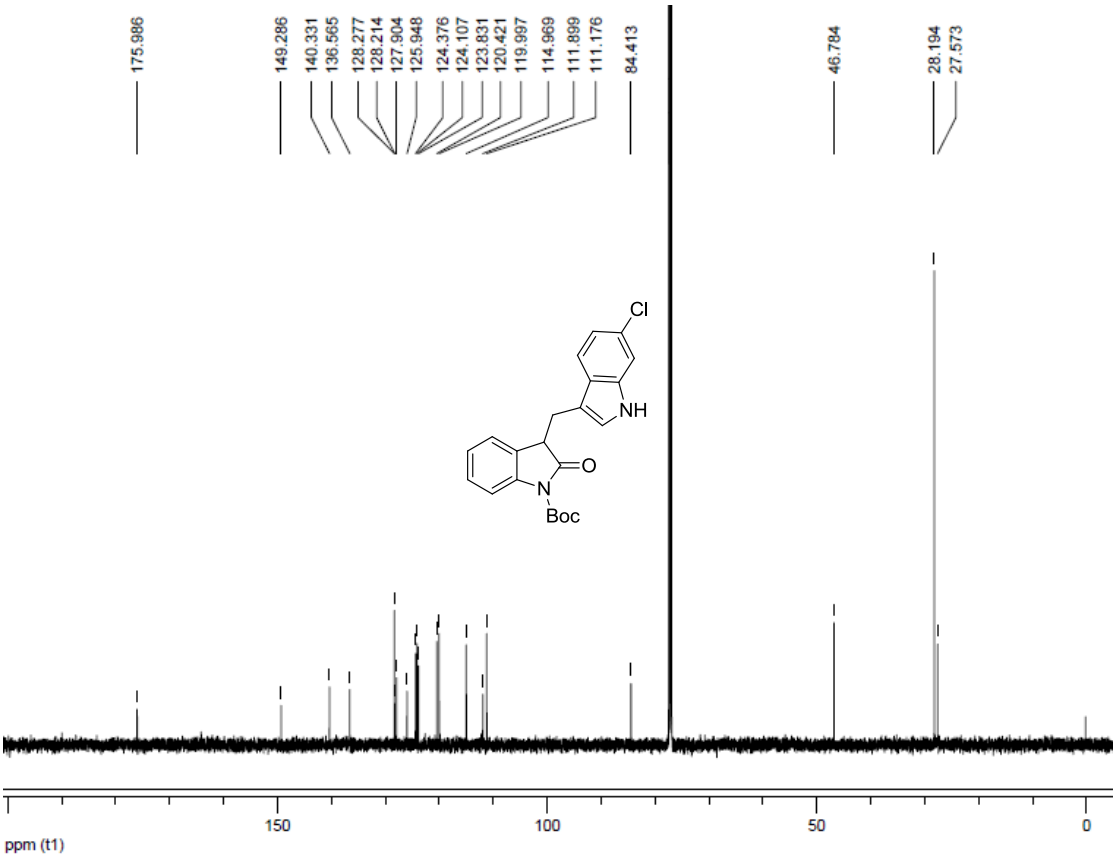
7.720
7.706
7.491
7.477
7.326
7.324
7.245
7.232
7.218
7.057
7.054
7.043
7.040
7.033
7.032
7.019
7.008
7.007
6.915
6.903
6.857
6.853
3.885
3.878
3.872
3.864
3.556
3.550
3.549
3.533
3.532
3.524
3.249
3.235
3.224
3.211
1.597
Cl
NH
O
N
Boc
1.03
1.02
1.05
1.00
2.06
9.27
1.03
1.05
1.05
10.0
5.0
0.0
ppm (t1)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140.331
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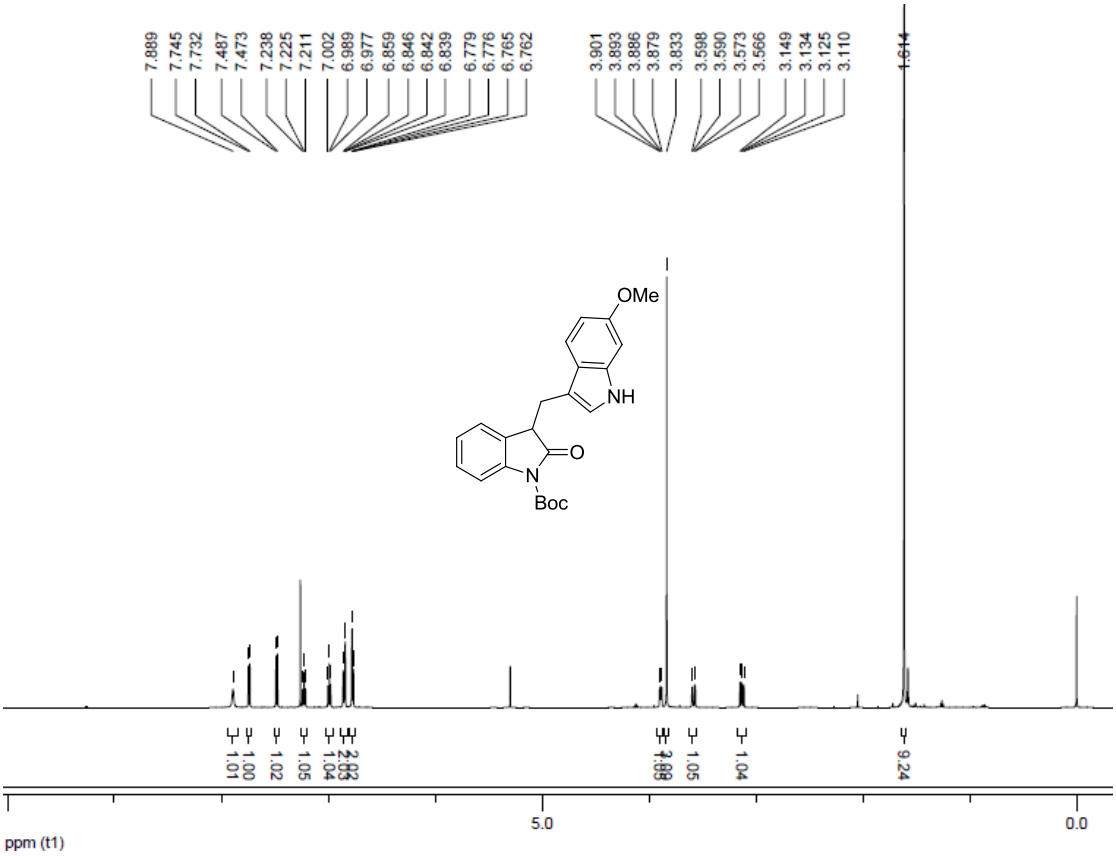
128.277
128.214
127.904
125.648
124.376
124.107
123.831
120.421
119.997
114.969
111.899
111.176
84.413
46.784
28.194
27.573
Cl
NH
O
N
Boc
150
100
50
0
ppm (t1)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7.487
7.473
7.238
7.225
7.211
7.002
6.989
6.977
6.859
6.846
6.842
6.839
6.779
6.776
6.765
6.762
3.901
3.893
3.886
3.879
3.833
3.598
3.590
3.573
3.566
3.149
3.134
3.125
3.110
1.614
OMe
NH
O
N
Boc
1.01
1.00
1.02
1.05
1.04
2.03
2.03
3.09
1.05
1.04
9.24
5.0
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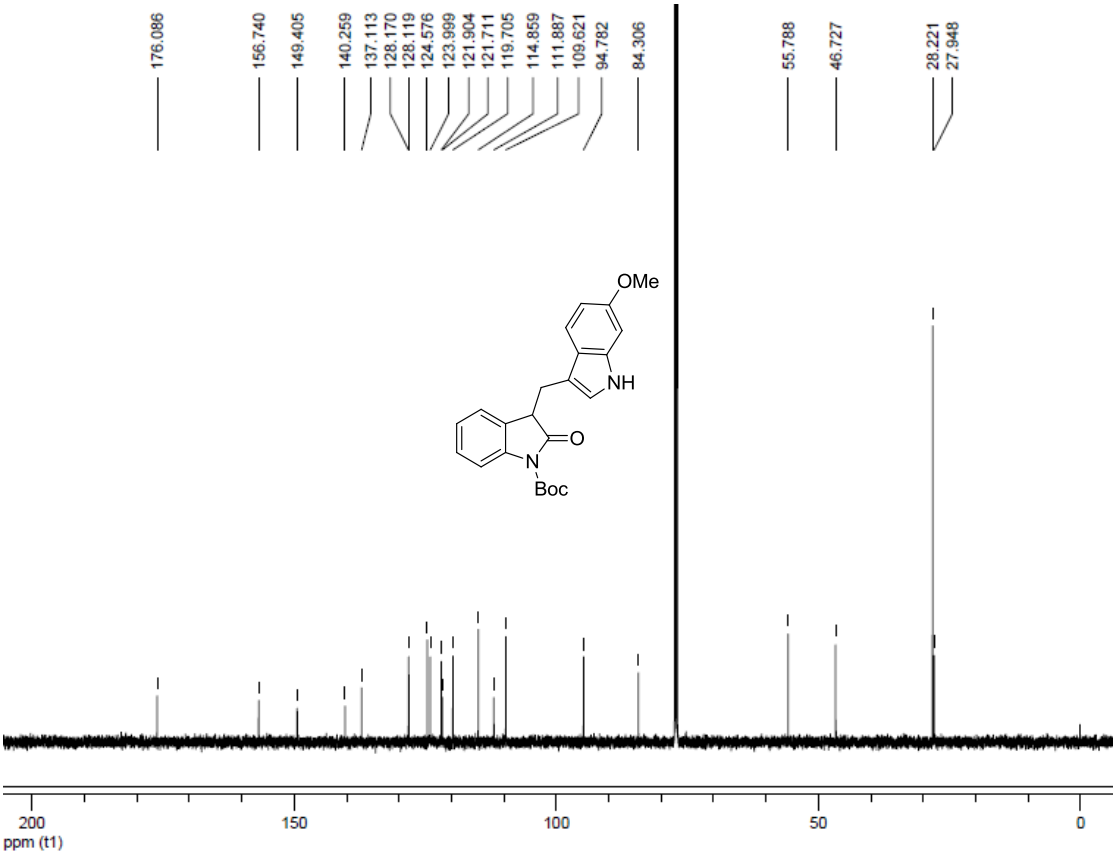
ppm (t1)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149.405
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137.113
128.170
128.119
124.576
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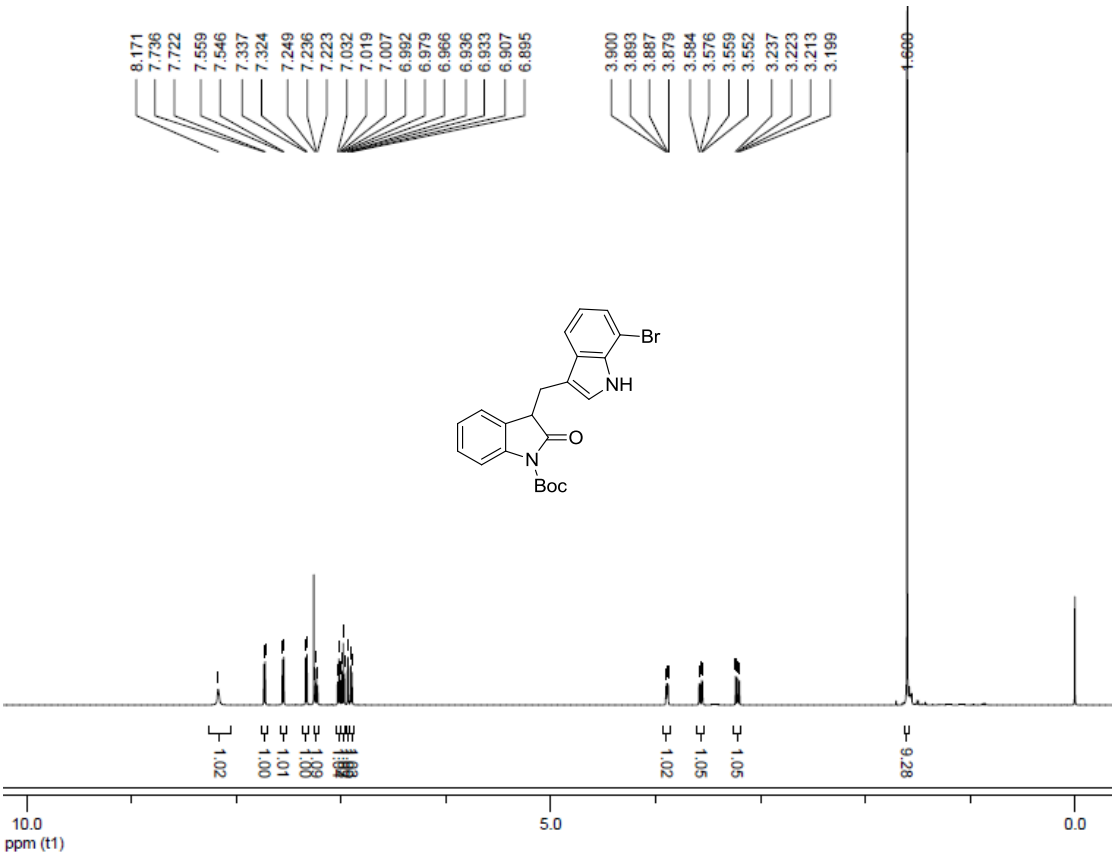
121.904
121.711
119.705
114.859
111.887
109.621
94.782
84.306
55.788
46.727
28.221
27.948
OMe
NH
O
N
Boc
200
150
100
50
0
ppm (t1)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7.722
7.559
7.546
7.337
7.324
7.249
7.236
7.223
7.032
7.019
7.007
6.992
6.979
6.966
6.936
6.933
6.907
6.895
3.900
3.893
3.887
3.879
3.584
3.576
3.559
3.552
3.237
3.223
3.213
3.199
1.000
Br
NH
O
N
Boc
1.02
1.00
1.01
1.00
1.09
9.28
1.02
1.05
1.05
10.0
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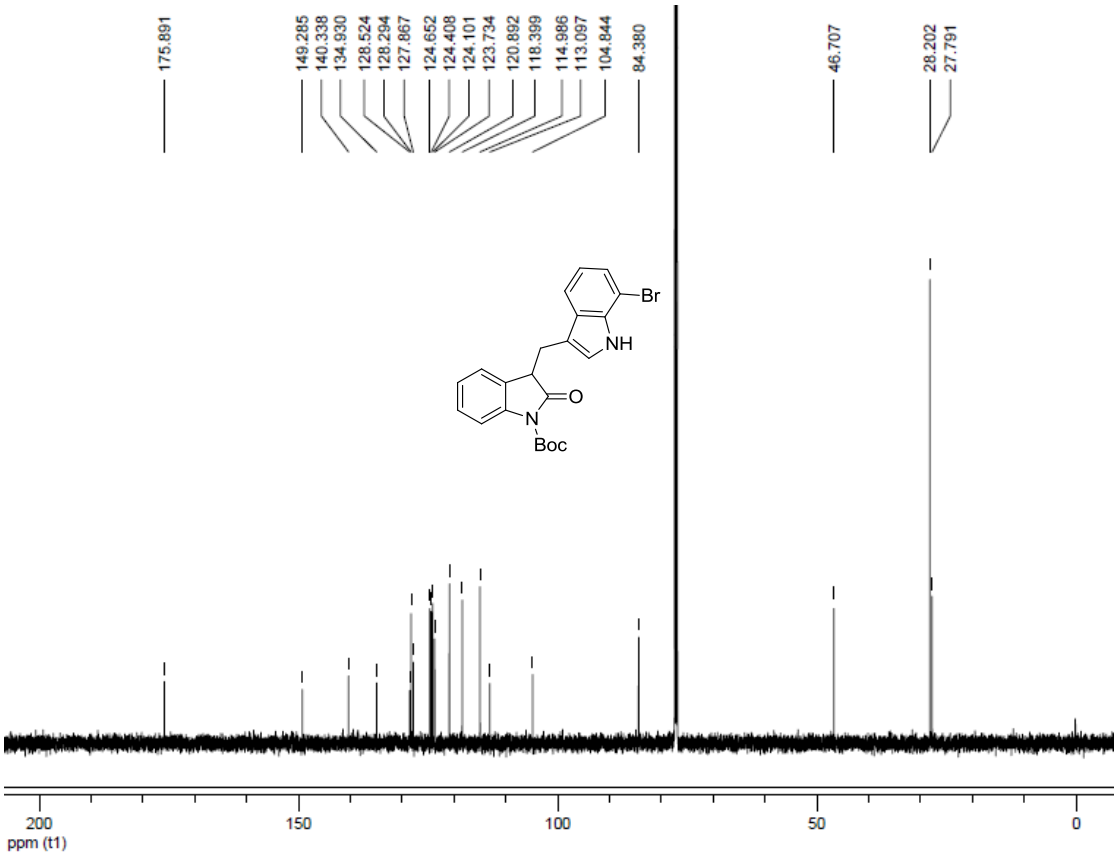
ppm (t1)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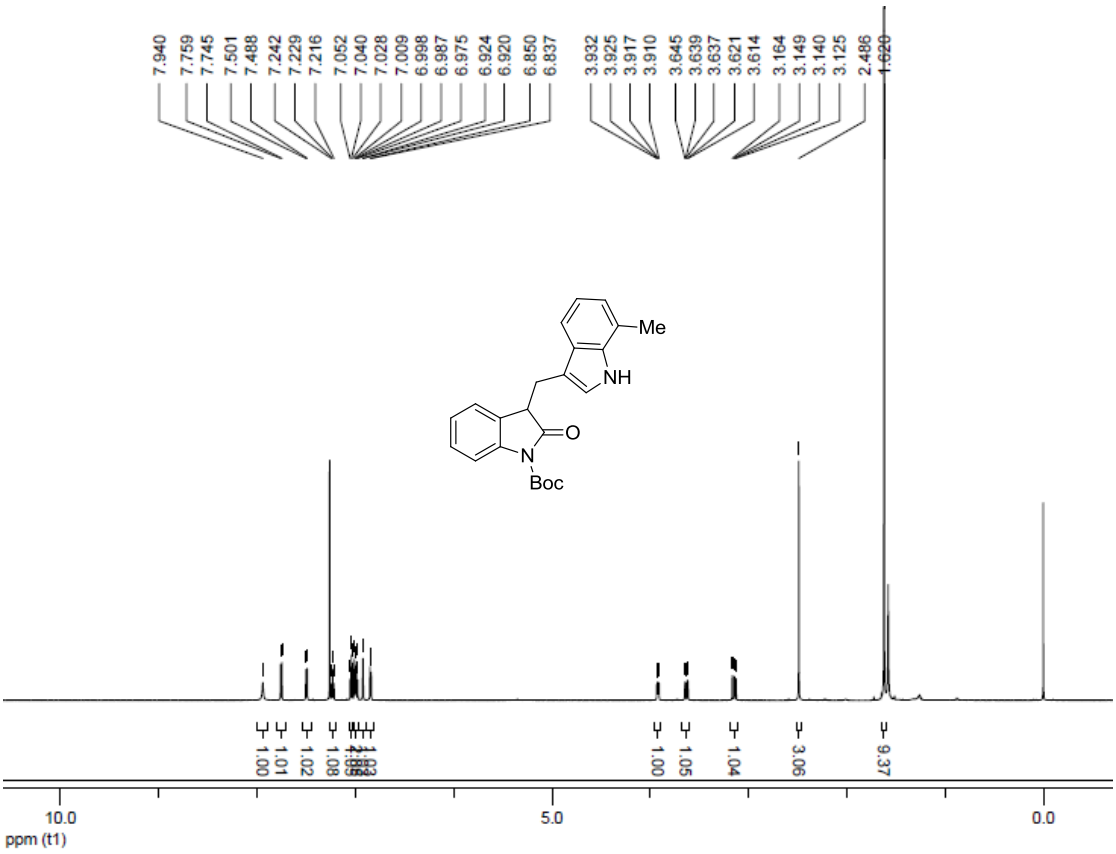
128.294
127.867
124.652
124.408
124.101
123.734
120.892
118.399
114.986
113.097
104.844
84.380
46.707
28.202
27.791
Br
NH
O
N
Boc
200
150
100
50
0
ppm (t1)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7.242
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7.216
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7.040
7.028
7.009
6.998
6.987
6.975
6.924
6.920
6.850
6.837
3.932
3.925
3.917
3.910
3.645
3.639
3.637
3.621
3.614
3.164
3.149
3.140
3.125
2.486
1.620
Me
NH
O
N
Boc
1.00
1.01
1.02
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1.00
1.05
1.04
3.06
9.37
10.0
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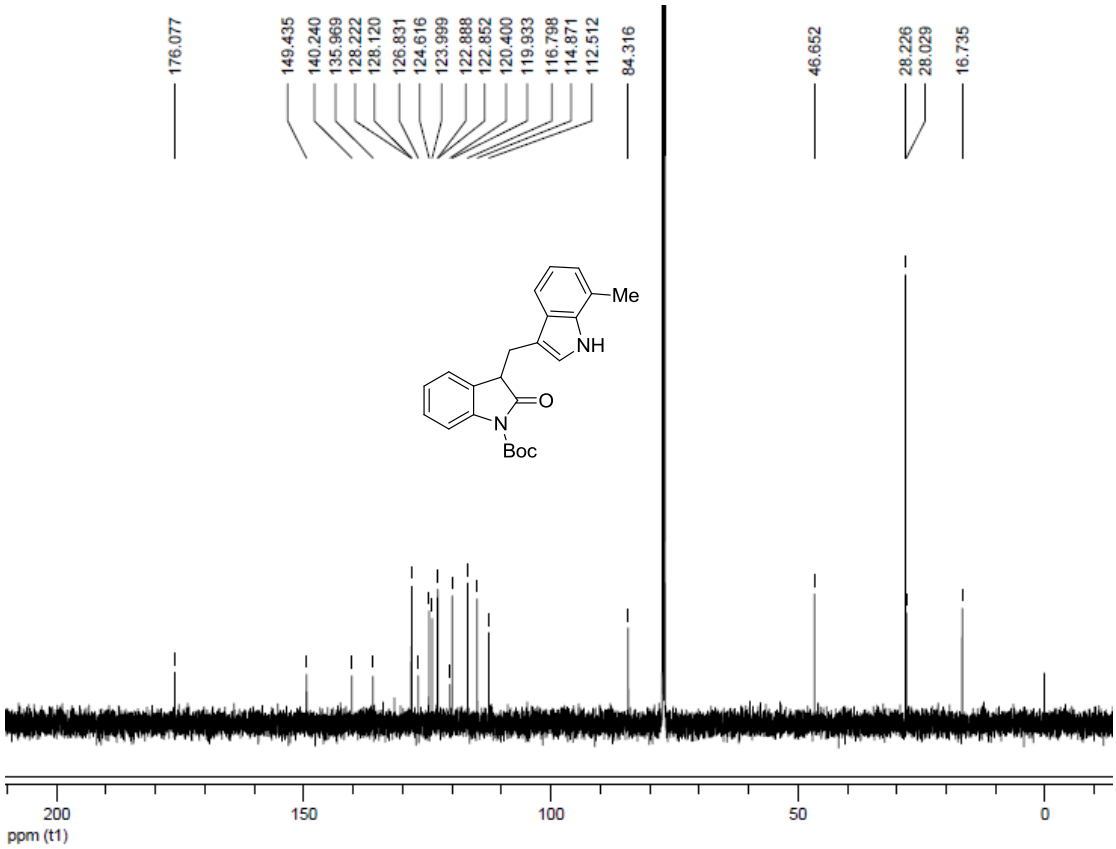
ppm (t1)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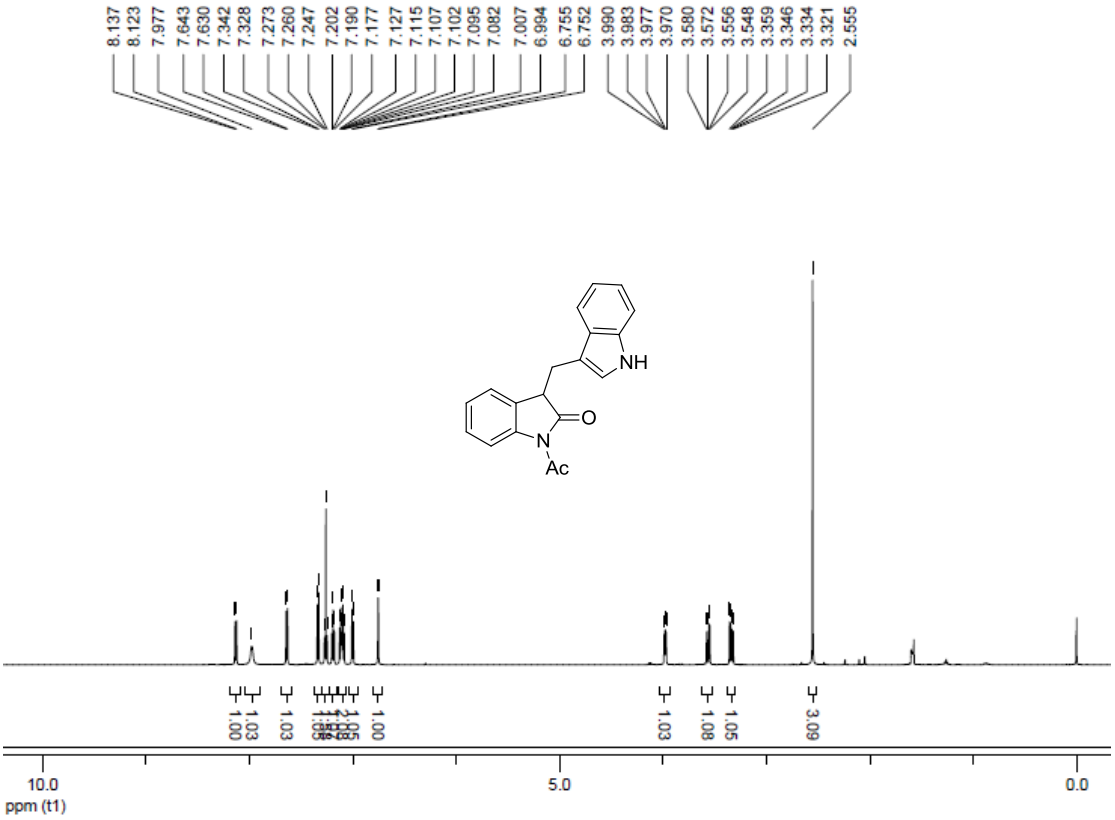
128.120
126.831
124.616
123.999
122.888
122.852
120.400
119.933
116.798
114.871
112.512
84.316
46.652
28.226
28.029
16.735
Me
NH
O
N
Boc
200
150
100
50
0
ppm (t1)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7.342
7.328
7.273
7.260
7.247
7.202
7.190
7.177
7.127
7.115
7.107
7.102
7.095
7.082
7.007
6.994
6.755
6.752
3.990
3.983
3.977
3.970
3.580
3.572
3.556
3.548
3.359
3.346
3.334
3.321
2.555
NH
O
N
Ac
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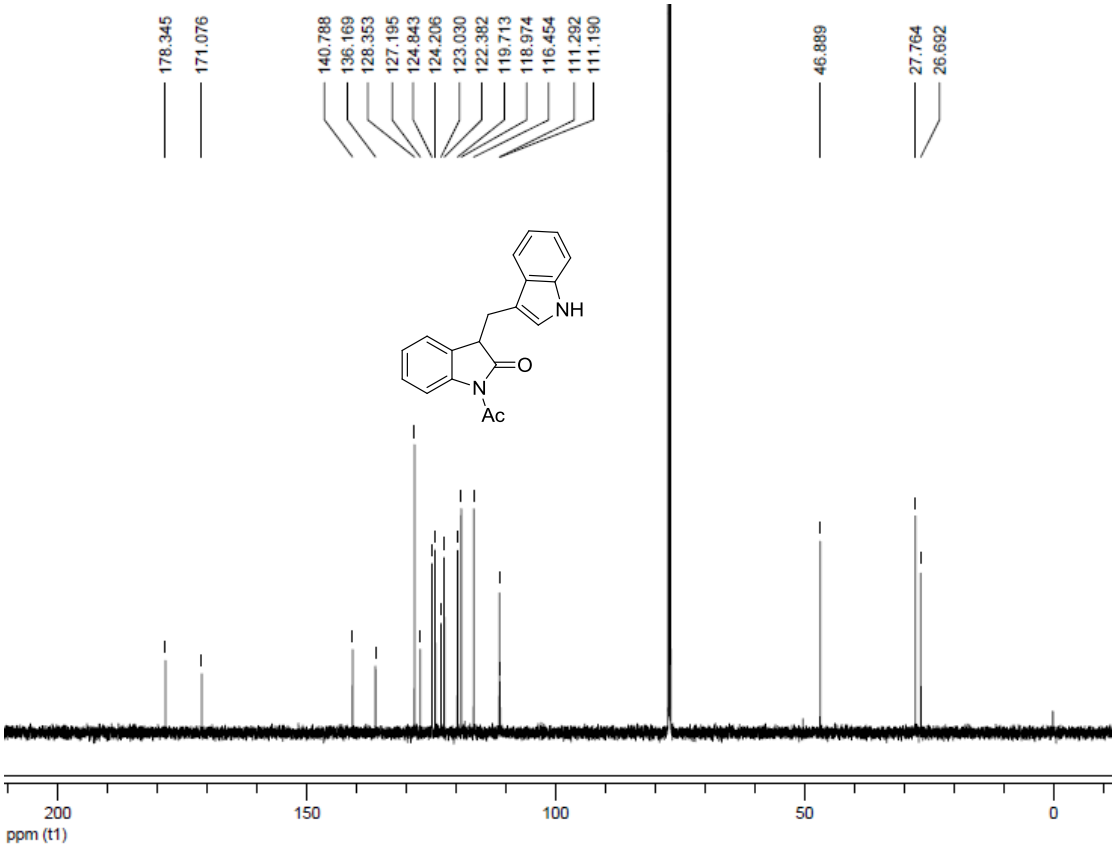
1.03
1.03
1.00
1.03
1.08
1.05
3.09
10.0
5.0
0.0
ppm (t1)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136.169
128.353
127.195
124.843
124.206
123.030
122.382
119.713
118.974
116.454
111.292
111.190
46.889
27.764
26.692
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O
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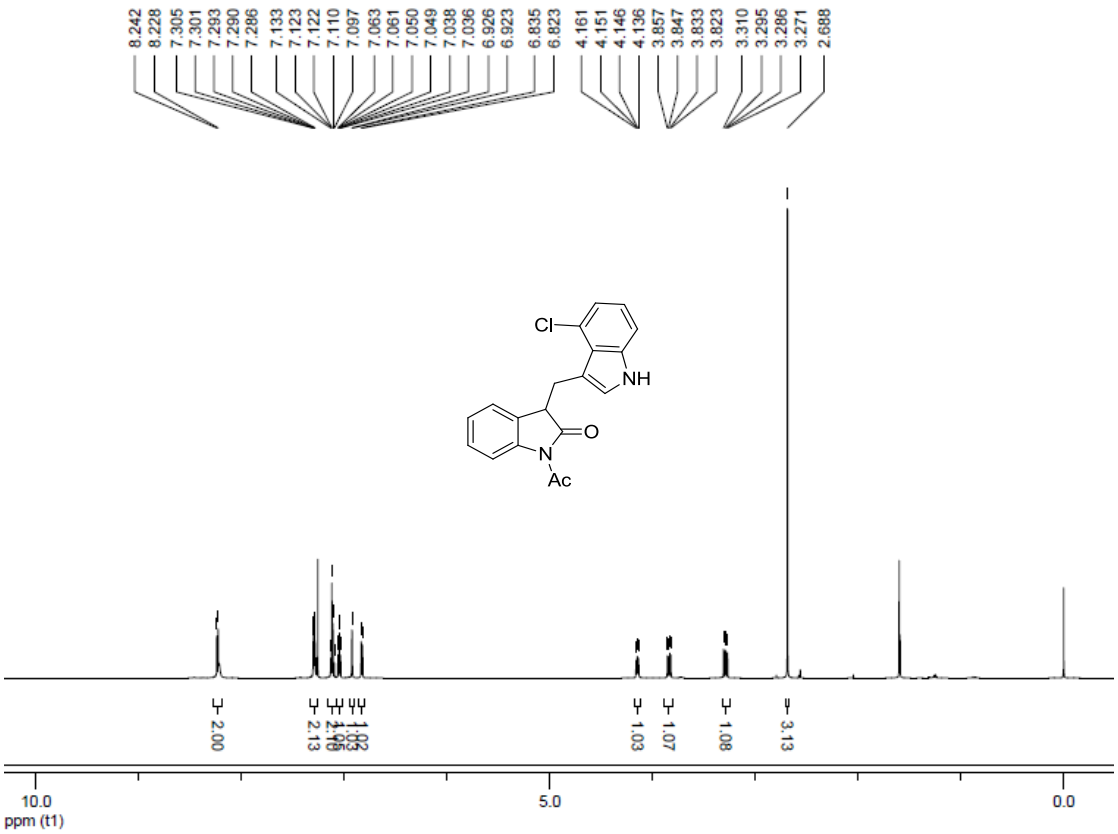
Ac
200
150
100
50
0
ppm (t1)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7.122
7.110
7.097
7.063
7.061
7.050
7.049
7.038
7.036
6.926
6.923
6.835
6.823
4.161
4.151
4.146
4.136
3.857
3.847
3.833
3.823
3.310
3.295
3.286
3.271
2.688
Cl
NH
O
N
Ac
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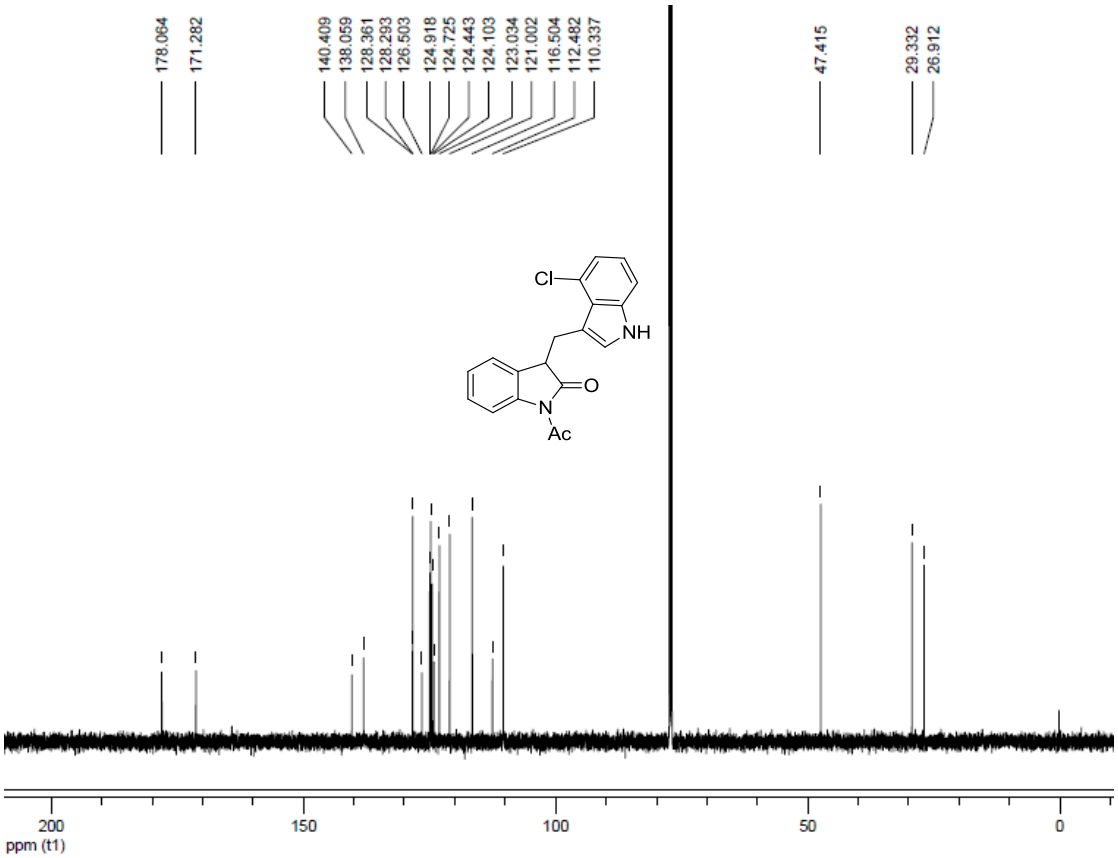
2.13
1.03
1.07
1.08
3.13
10.0
5.0
0.0
ppm (t1)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128.293
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124.918
124.725
124.443
124.103
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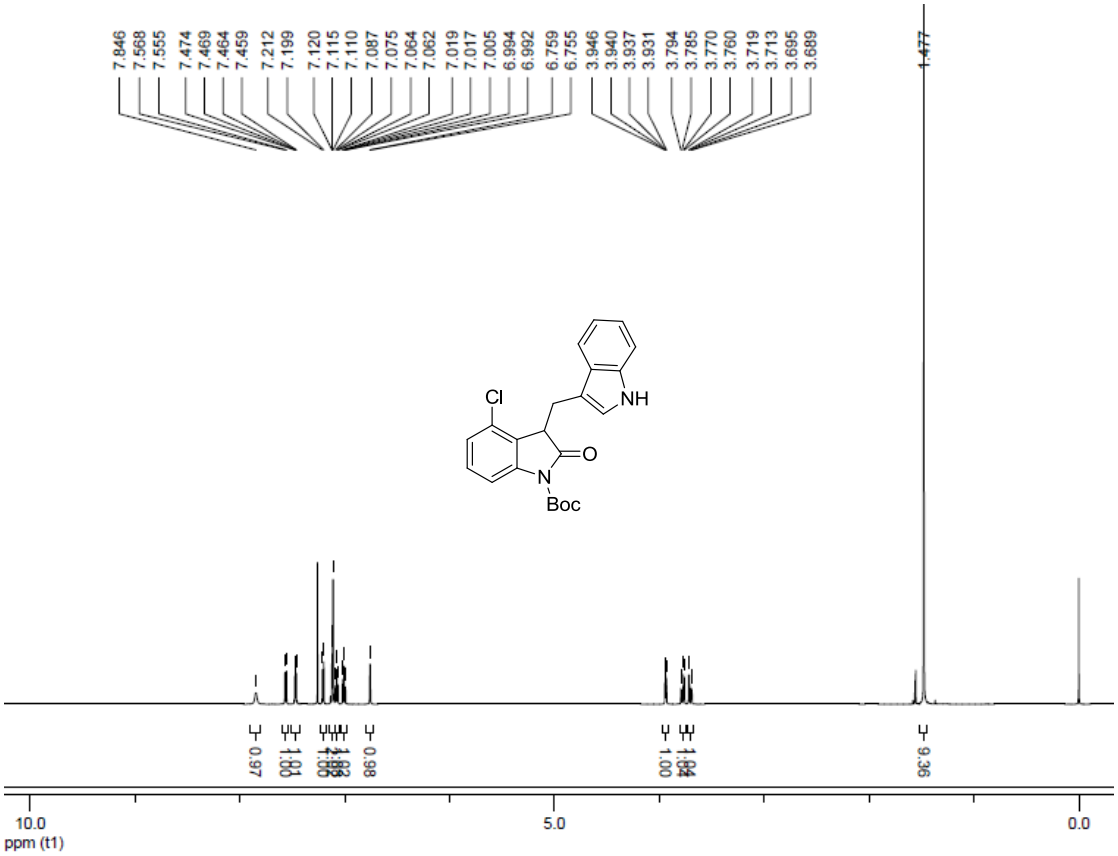
121.002
116.504
112.482
110.337
47.415
29.332
26.912
Cl
NH
O
N
Ac
200
150
100
50
0
ppm (t1)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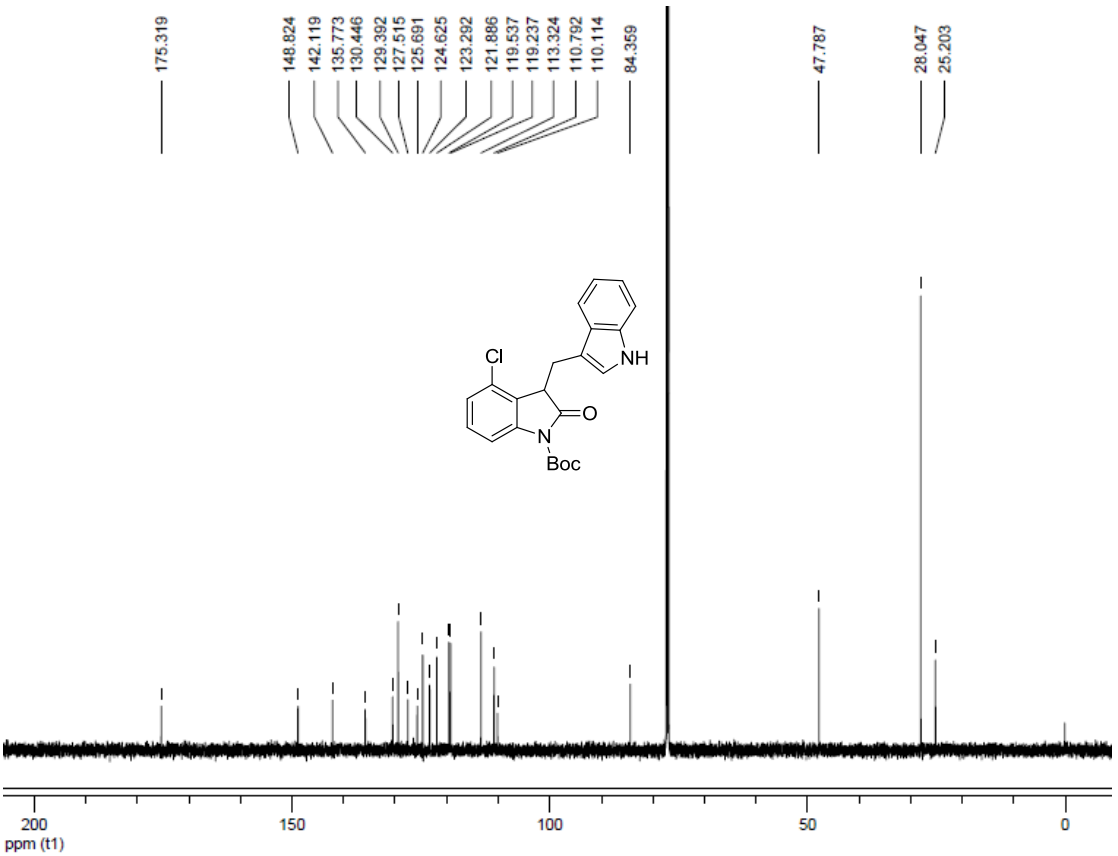
7.120
7.115
7.110
7.087
7.075
7.064
7.062
7.019
7.017
7.005
6.994
6.992
6.759
6.755
3.946
3.940
3.937
3.931
3.794
3.785
3.770
3.760
3.719
3.713
3.695
3.689
1.477
Cl
NH
O
N
Boc
0.97
1.00
0.98
1.00
9.36
10.0
ppm (t1)
5.0
0.0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127.515
125.691
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123.292
121.886
119.537
119.237
113.324
110.792
110.114
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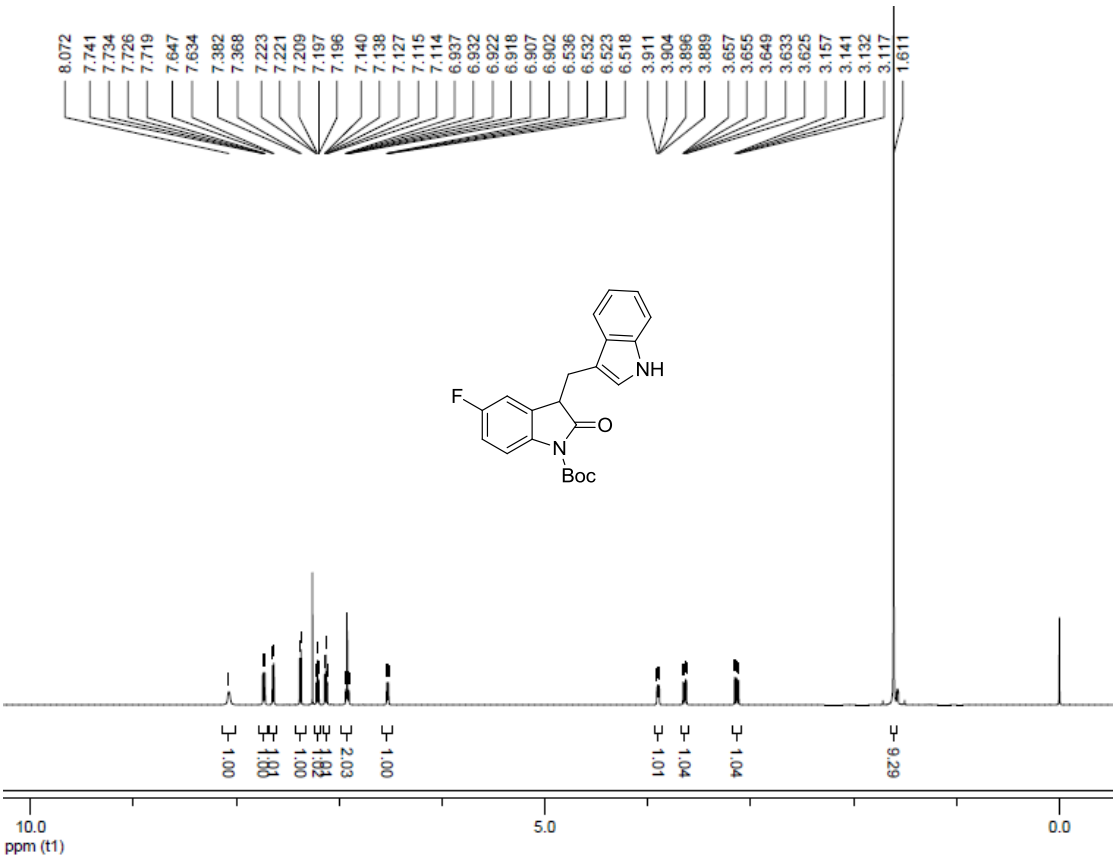
47.787
28.047
25.203
Cl
NH
O
N
Boc
200
ppm (t1)
150
100
50
0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7.634
7.382
7.368
7.223
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7.209
7.197
7.196
7.140
7.138
7.127
7.115
7.114
6.937
6.932
6.922
6.918
6.907
6.902
6.536
6.532
6.523
6.518
3.911
3.904
3.896
3.889
3.657
3.655
3.649
3.633
3.625
3.157
3.141
3.132
3.117
1.611
NH
F
O
N
Boc
1.00
1.00
1.00
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1.00
1.01
1.04
1.04
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10.0
ppm (t1)
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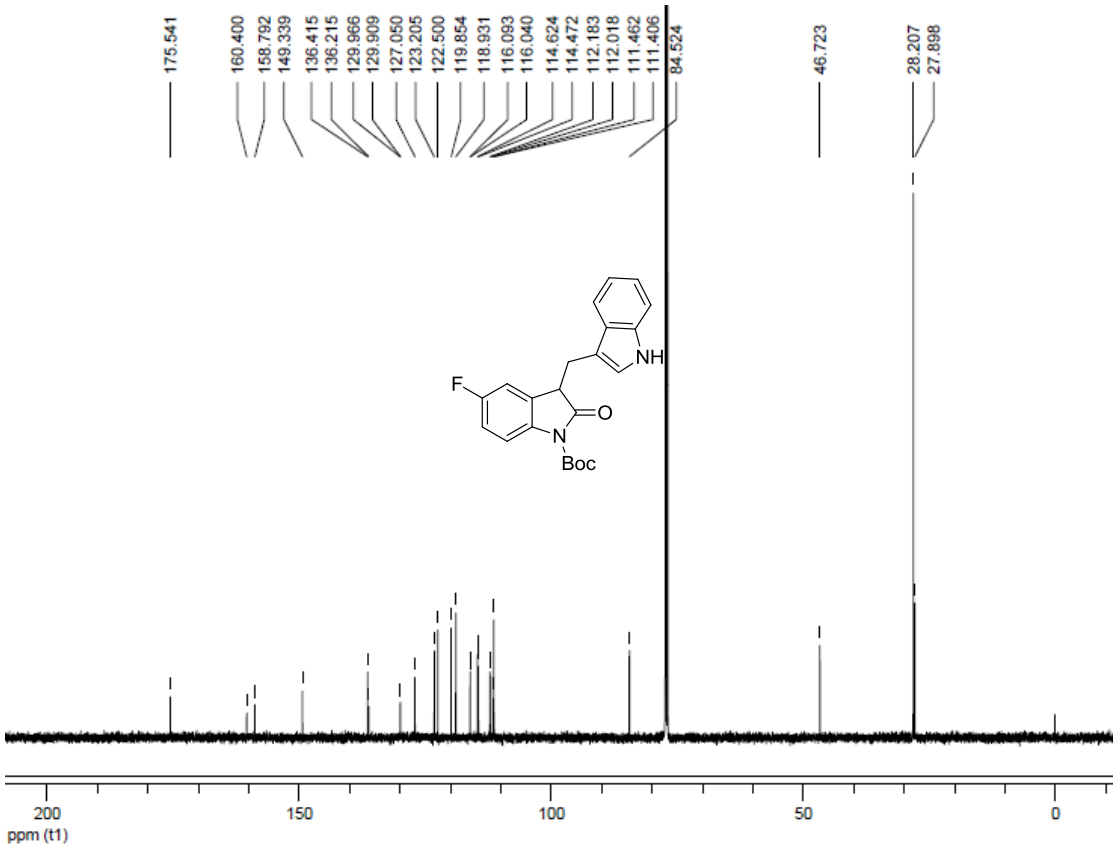
0.0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158.792
149.339
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136.215
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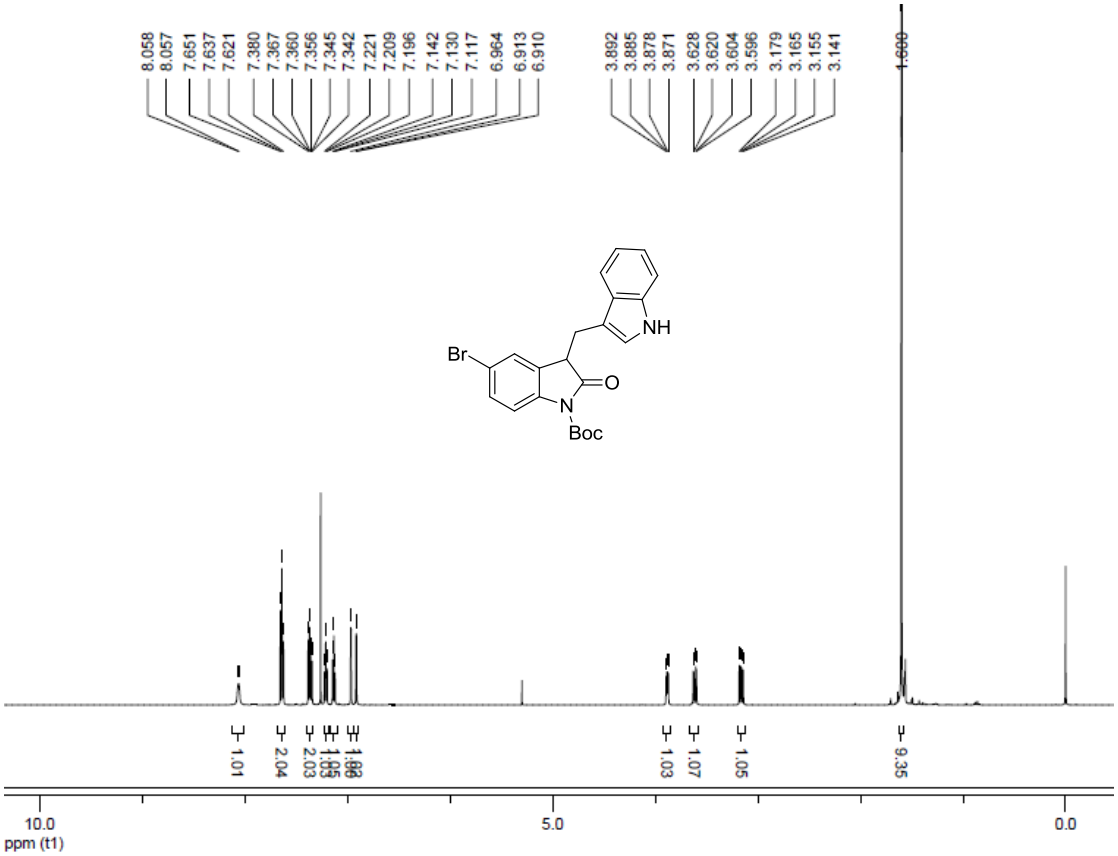
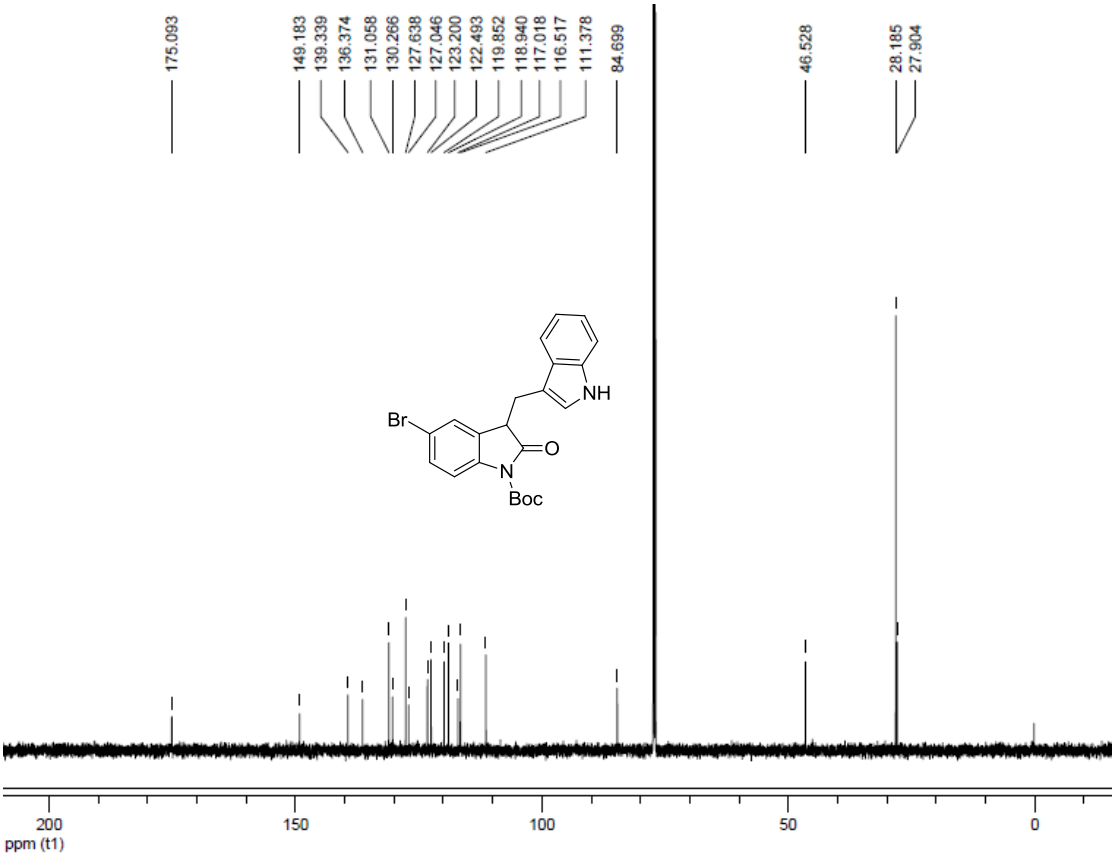
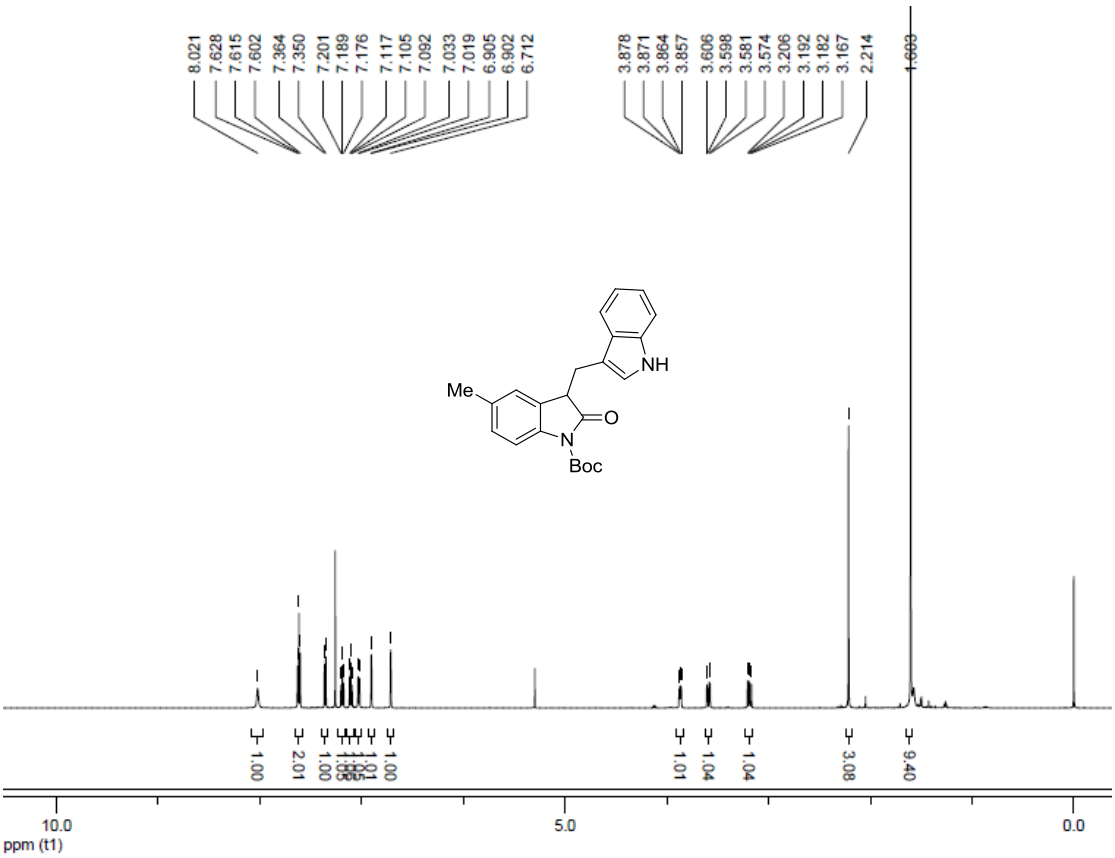
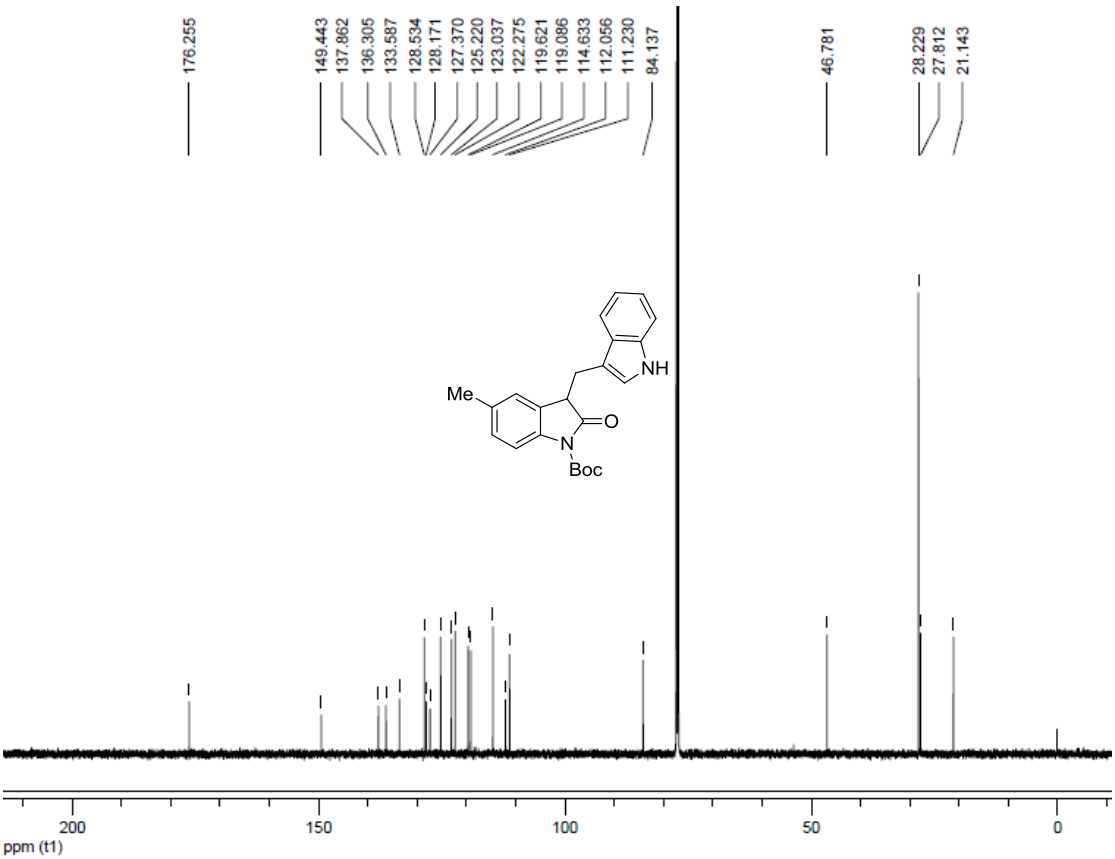
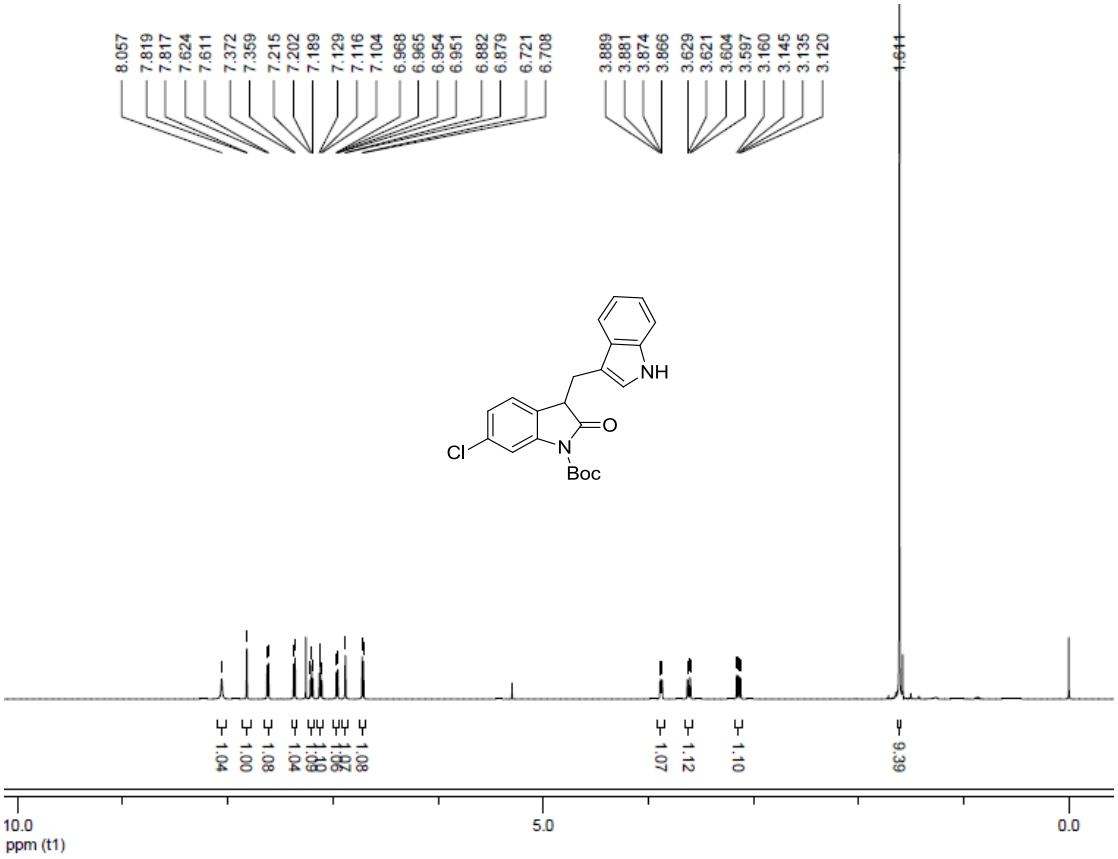
127.050
123.205
122.500
119.854
118.931
116.093
116.040
114.624
114.472
112.183
112.018
111.462
111.406
84.524
46.723
28.207
27.898
NH
F
O
N
Boc
200
ppm (t1)
150
100
50
0

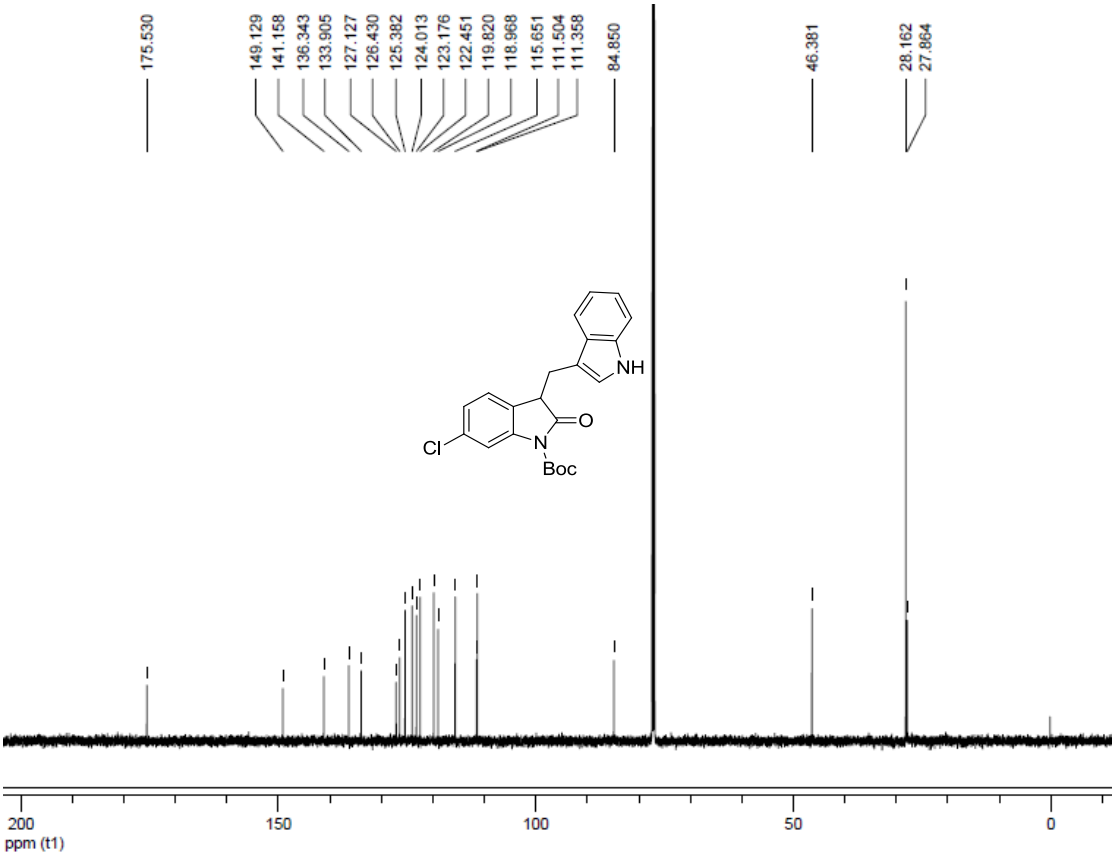

8.058
8.057
7.651
7.637
7.621
7.380
7.367
7.360
7.356
7.345
7.342
7.221
7.209
7.196
7.142
7.130
7.117
6.964
6.913
6.910
3.892
3.885
3.878
3.871
3.628
3.620
3.604
3.596
3.179
3.165
3.155
3.141
1.000
1.01
2.04
2.03
1.03
1.07
1.06
9.35
Br
NH
O
N
Boc
10.0
5.0
0.0
ppm (t1)

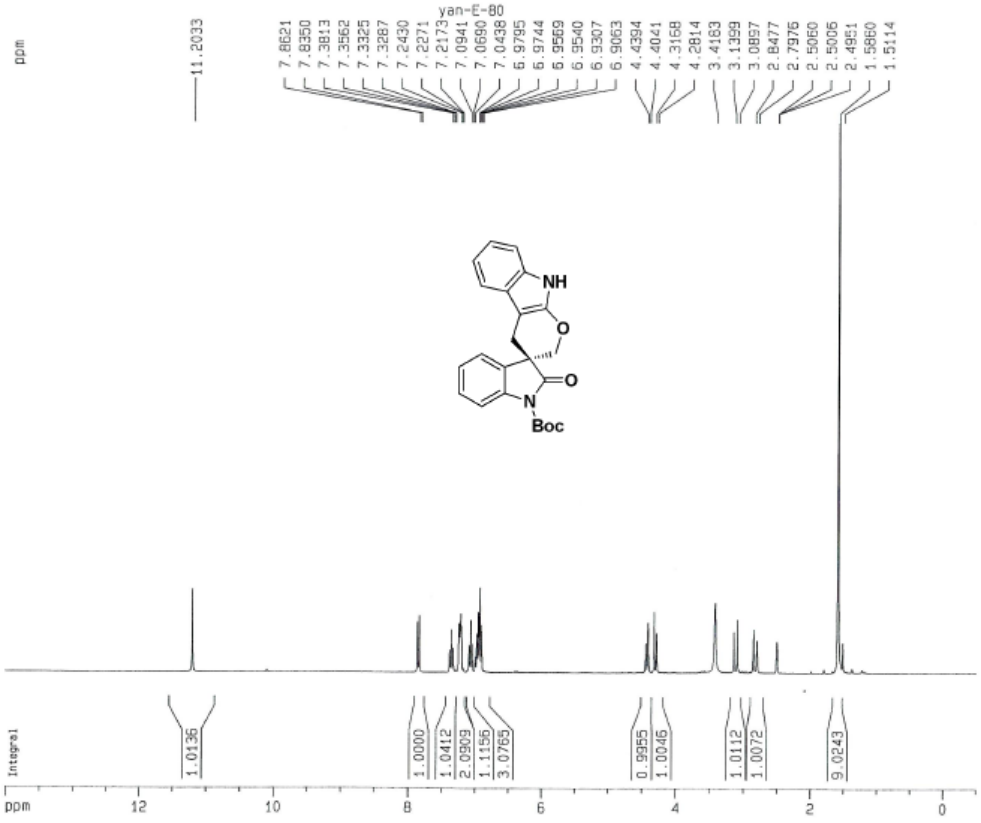

175.093
149.183
139.339
136.374
131.058
130.266
127.638
127.046
123.200
122.493
119.852
118.940
117.018
116.517
111.378
84.699
46.528
28.185
27.904
Br
NH
O
N
Boc
200
150
100
50
0
ppm (t1)

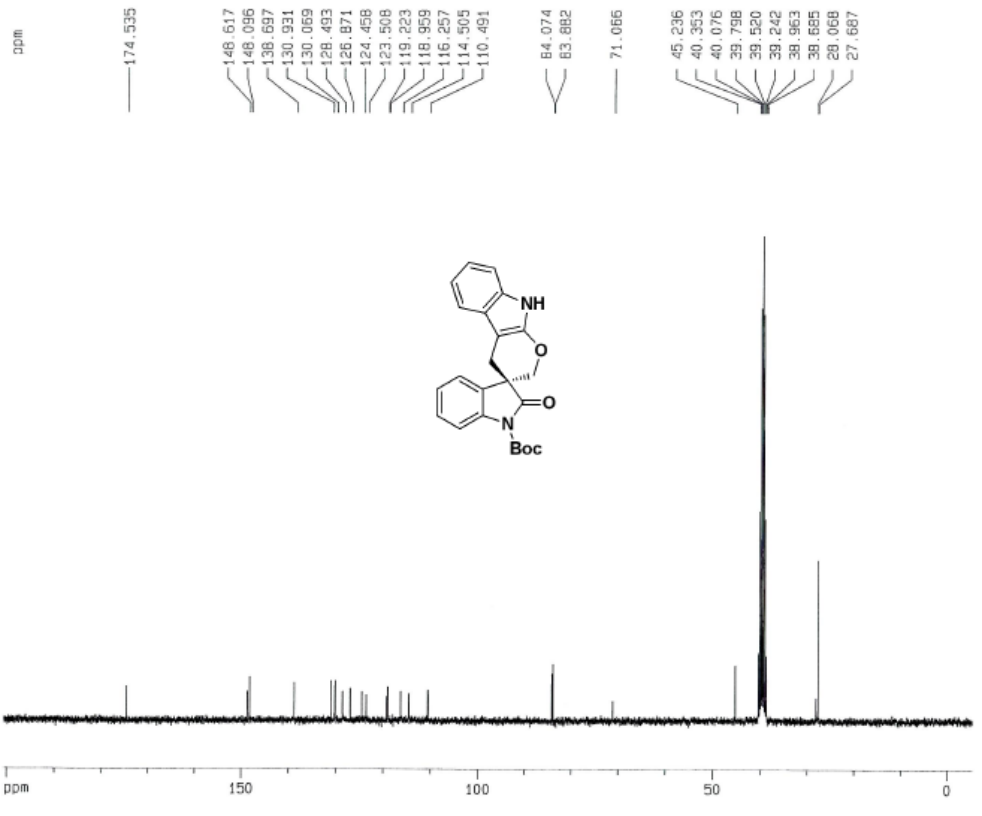

8.021
7.628
7.615
7.602
7.364
7.350
7.201
7.189
7.176
7.117
7.105
7.092
7.033
7.019
6.905
6.902
6.712
3.878
3.871
3.864
3.857
3.606
3.598
3.581
3.574
3.206
3.192
3.182
3.167
2.214
1.603
NH
Me
O
N
Boc
1.00
2.01
1.00
1.00
1.01
1.04
1.04
3.08
9.40
10.0
5.0
0.0
ppm (t1)


176.255
149.443
137.862
136.305
133.587
128.534
128.171
127.370
125.220
123.037
122.275
119.621
119.086
114.633
112.056
111.230
84.137
46.781
28.229
27.812
21.143
NH
Me
O
N
Boc
200
150
100
50
0
ppm (t1)

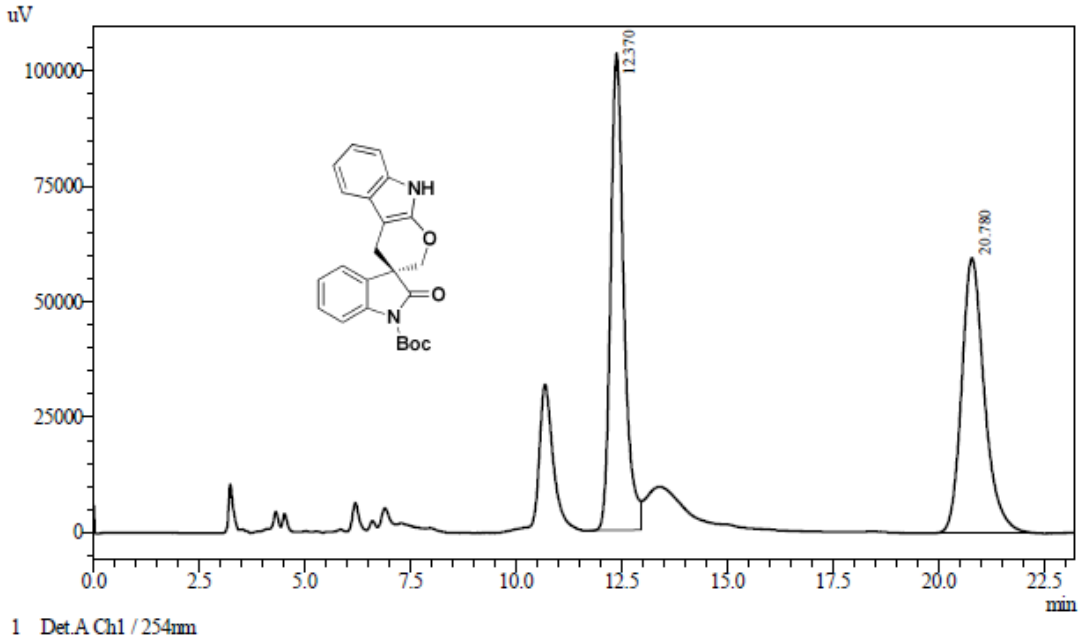

8.057
7.819
7.817
7.624
7.611
7.372
7.359
7.215
7.202
7.189
7.129
7.116
7.104
6.968
6.965
6.954
6.951
6.882
6.879
6.721
6.708
3.889
3.881
3.874
3.866
3.629
3.621
3.604
3.597
3.160
3.145
3.135
3.120
1.611
NH
O
N
Cl
Boc
1.04
1.00
1.08
1.04
1.09
1.08
1.07
1.12
1.10
9.39
10.0
ppm (t1)
5.0
0.0


175.530
149.129
141.158
136.343
133.905
127.127
126.430
125.382
124.013
123.176
122.451
119.820
118.968
115.651
111.504
111.358
84.850
46.381
28.162
27.864
NH
O
N
Cl
Boc
200
ppm (t1)
150
100
50
0


yan-E-80
ppm
11.2033
7.8621
7.8350
7.3813
7.3562
7.3325
7.3287
7.2430
7.2271
7.2173
7.0941
7.0690
7.0438
6.9795
6.9744
6.9569
6.9540
6.9307
6.9063
4.4394
4.4041
4.3168
4.2814
3.4183
3.1399
3.0897
2.8477
2.7976
2.5060
2.5006
2.4951
1.5860
1.5114
NH
O
O
N
Boc
Integral
1.0136
1.0000
1.0412
2.0909
1.1156
3.0765
0.9955
1.0046
1.0112
1.0072
9.0243
ppm
12
10
8
6
4
2
0


ppm
174.535
148.617
148.096
138.697
130.931
130.069
128.493
126.871
124.458
123.508
119.223
118.959
116.257
114.505
110.491
84.074
83.882
71.066
45.236
40.353
40.076
39.798
39.520
39.242
38.963
38.685
28.068
27.687
NH
O
O
N
Boc
ppm
150
100
50
0

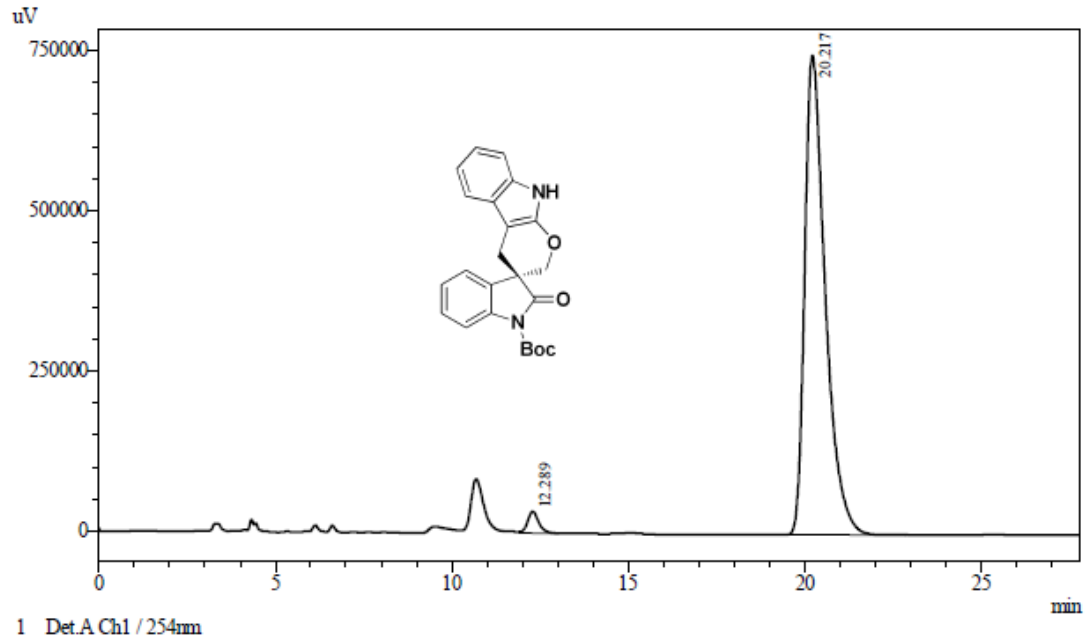
2a: Racemic



Detector A Ch1 254nm

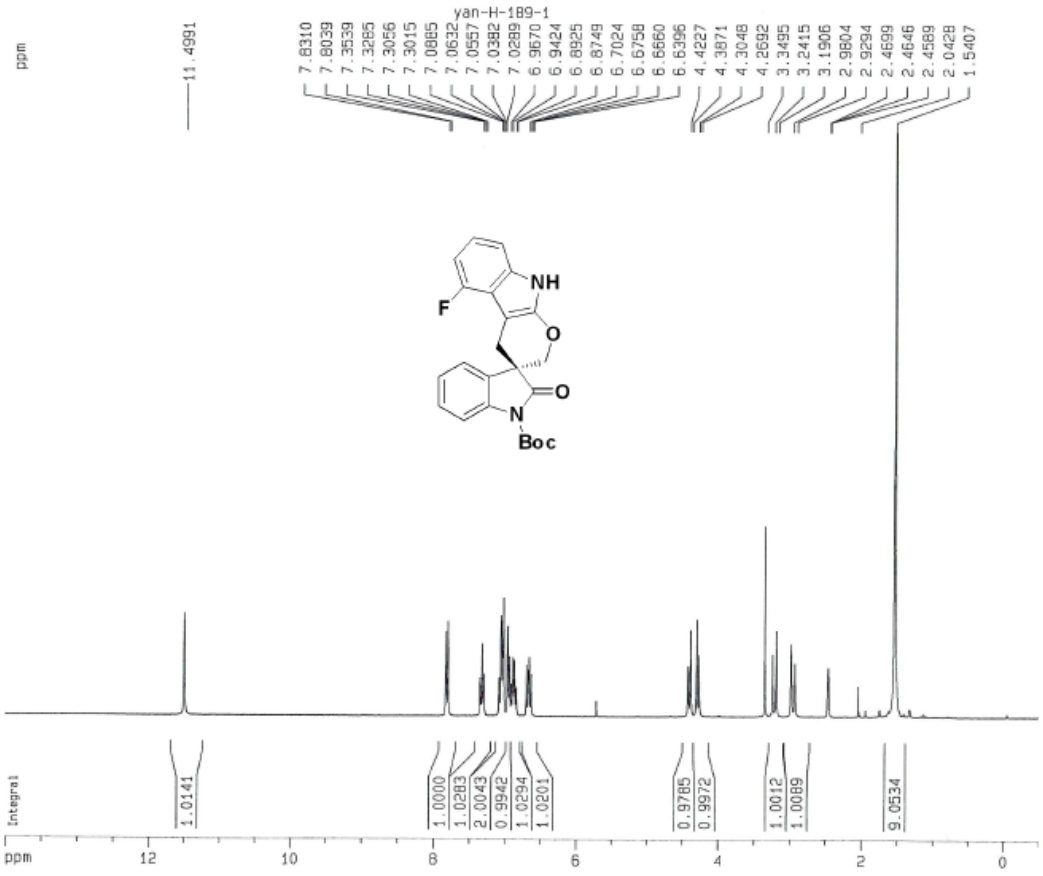
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.370	2252472	103354	50.121	63.417
2	20.780	2241623	59622	49.879	36.583
Total		4494095	162976	100.000	100.000

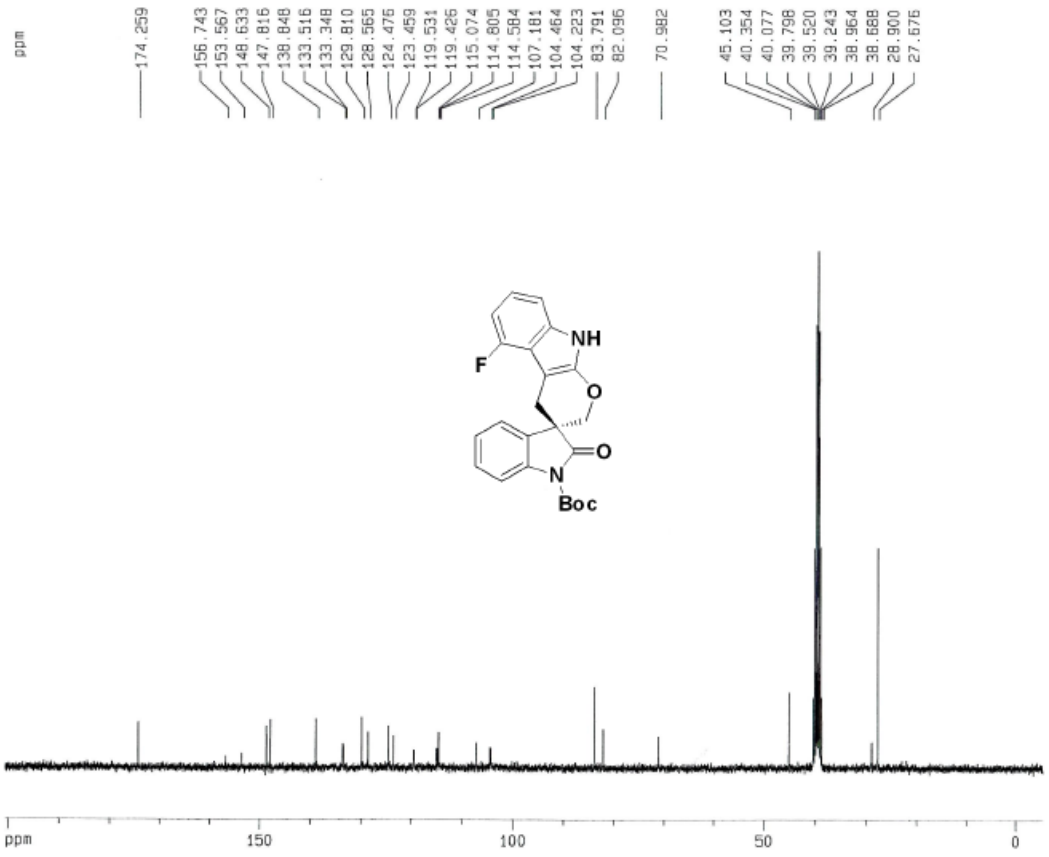
2a: Chiral



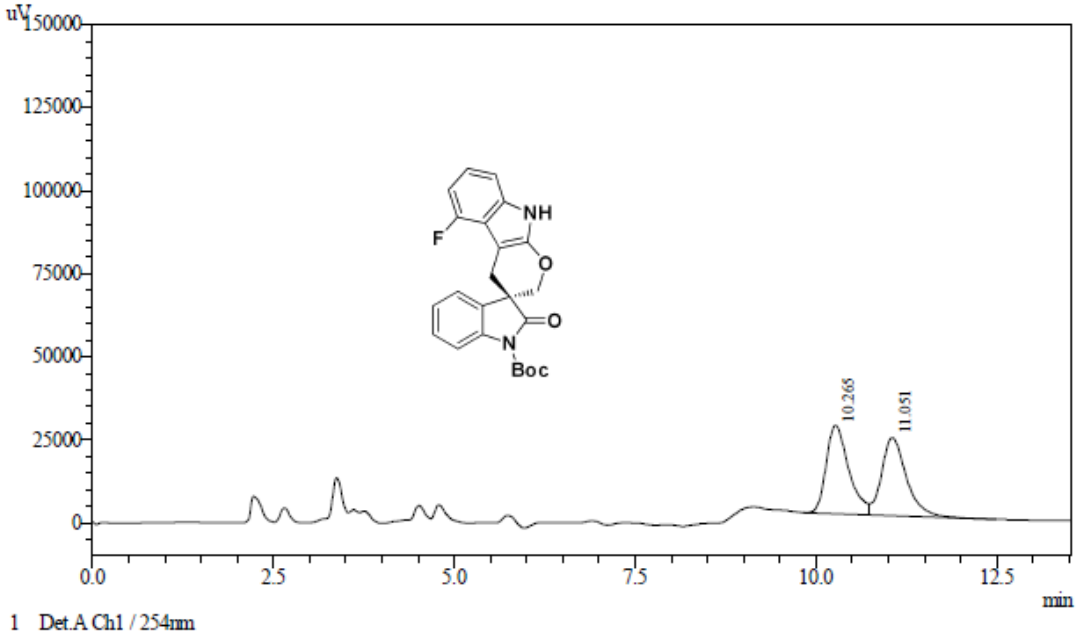
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.289	756008	33856	2.436	4.333
2	20.217	30274276	747487	97.564	95.667
Total		31030283	781343	100.000	100.000


yan-H-189-1
ppm
11.4991
7.8310
7.8039
7.3539
7.3285
7.3056
7.3015
7.0885
7.0632
7.0557
7.0382
7.0289
6.9670
6.9424
6.8925
6.8749
6.7024
6.6758
6.6660
6.6396
4.4227
4.3871
4.3048
4.2692
3.3495
3.2415
3.1906
2.9804
2.9294
2.4699
2.4646
2.4589
2.0428
1.5407
NH
F
O
O
N
Boc
Integral
1.0141
1.0000
1.0283
2.0043
0.9942
1.0294
1.0201
0.9785
0.9972
1.0012
1.0089
9.0534
ppm
12
10
8
6
4
2
0


ppm
174.259
156.743
153.567
148.633
147.816
138.848
133.516
133.348
129.810
128.565
124.476
123.459
119.531
119.426
115.074
114.805
114.584
107.181
104.464
104.223
83.791
82.096
70.982
45.103
40.354
40.077
39.798
39.520
39.243
38.964
38.688
28.900
27.676
NH
F
O
O
N
Boc
ppm
150
100
50
0

2b: Racemic

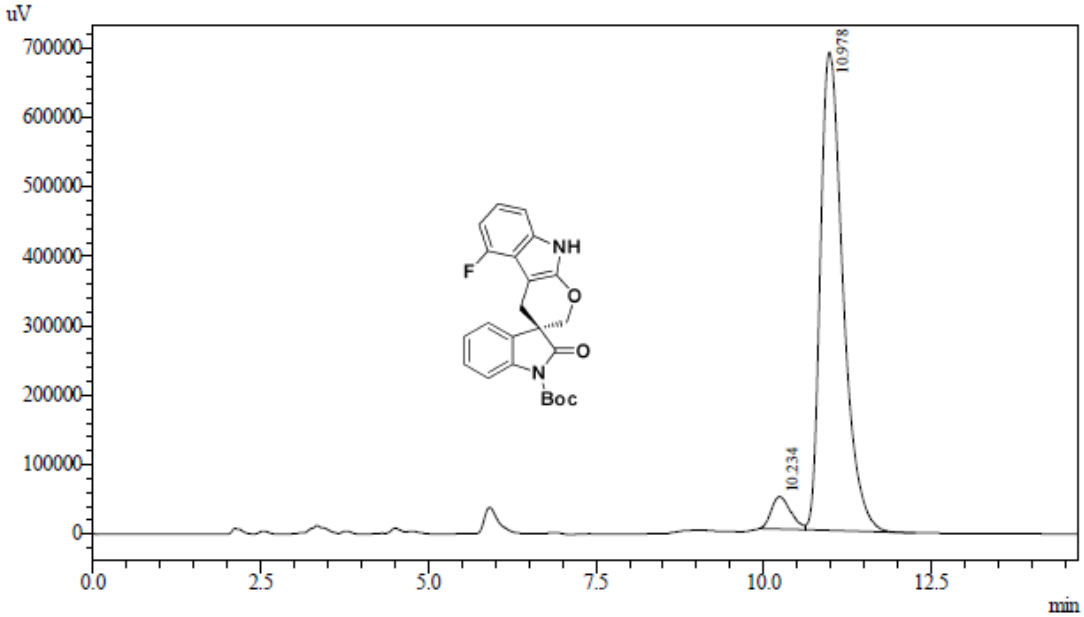


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.265	583403	26595	50.837	53.084
2	11.051	564185	23505	49.163	46.916
Total		1147588	50100	100.000	100.000

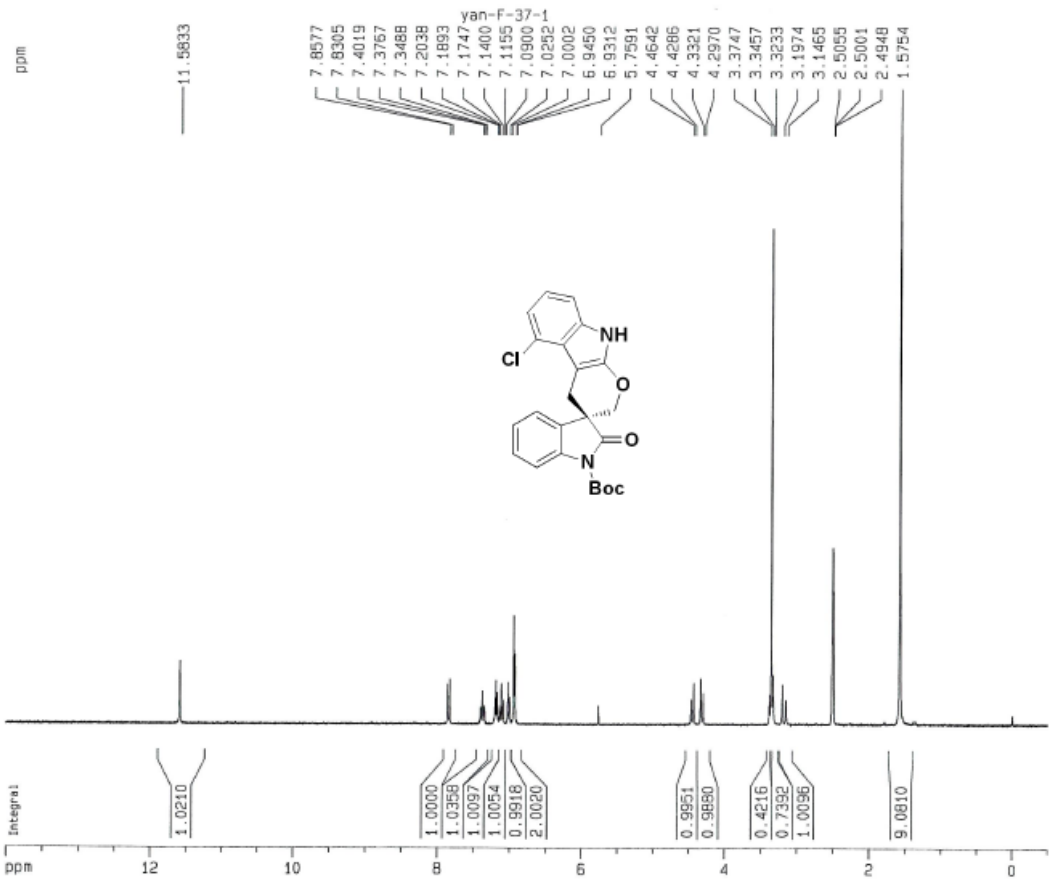
2b: Chiral

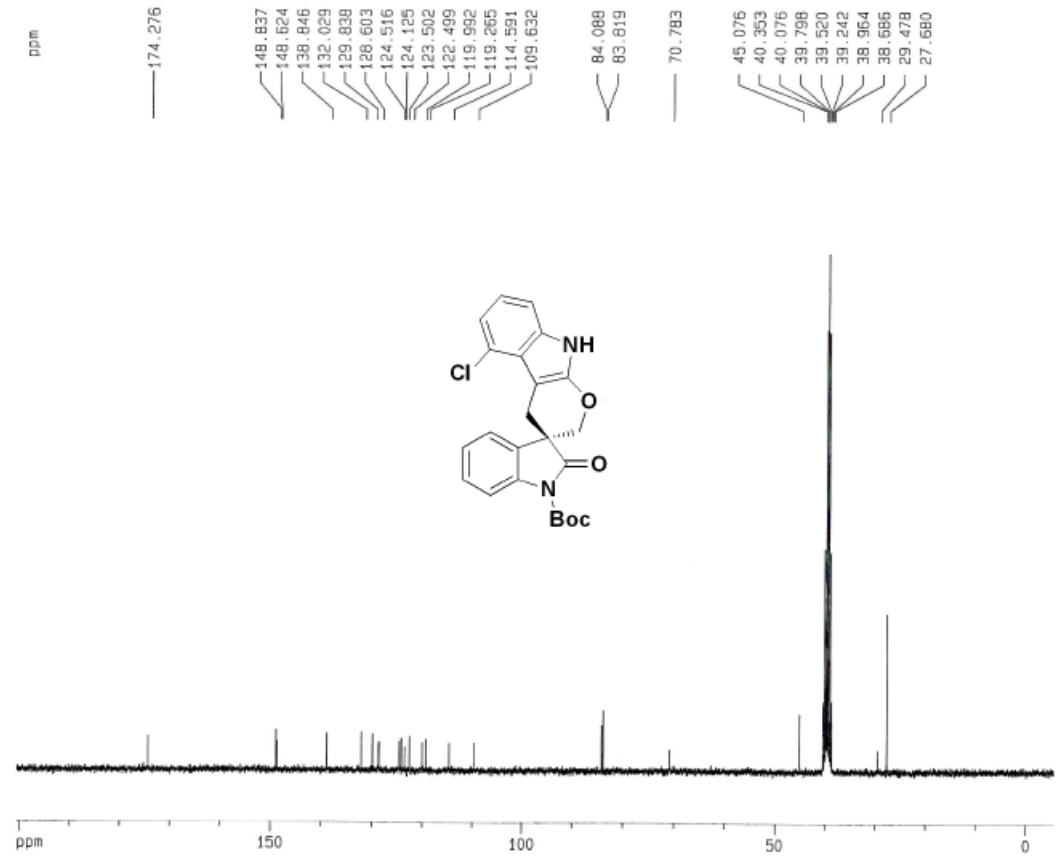


1 Det.A Ch1 / 254nm

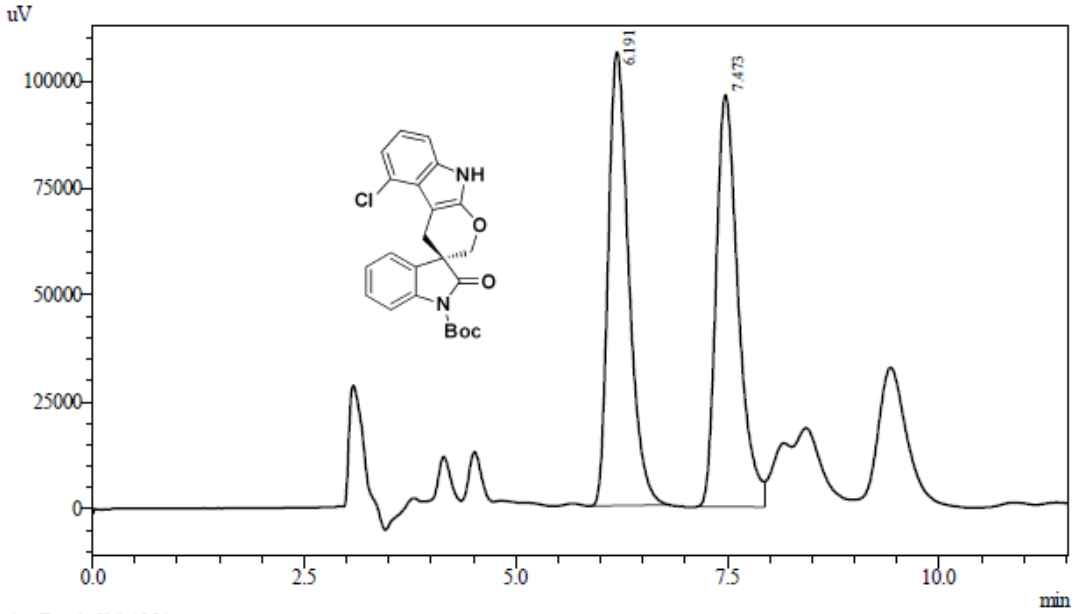
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.234	943058	46744	5.549	6.352
2	10.978	16052791	689142	94.451	93.648
Total		16995849	735887	100.000	100.000


yan-F-37-1
ppm
11.5833
7.8577
7.8305
7.4019
7.3767
7.3488
7.2038
7.1893
7.1747
7.1400
7.1155
7.0900
7.0252
7.0002
6.9450
6.9312
5.7591
4.4642
4.4286
4.3321
4.2970
3.3747
3.3457
3.3233
3.1974
3.1465
2.5055
2.5001
2.4948
1.5754
Cl
NH
O
O
N
Boc
Integral
1.0210
1.0000
1.0358
1.0097
1.0054
0.9918
2.0020
0.9951
0.9880
0.4216
0.7392
1.0096
9.0810
ppm
12
10
8
6
4
2
0


ppm
174.276
148.837
148.624
138.846
132.029
129.838
128.603
124.516
124.125
123.502
122.499
119.992
119.265
114.591
109.632
84.088
83.819
70.783
45.076
40.353
40.076
39.798
39.520
39.242
38.964
38.686
29.478
27.680
Cl
NH
O
O
N
Boc
ppm
150
100
50
0

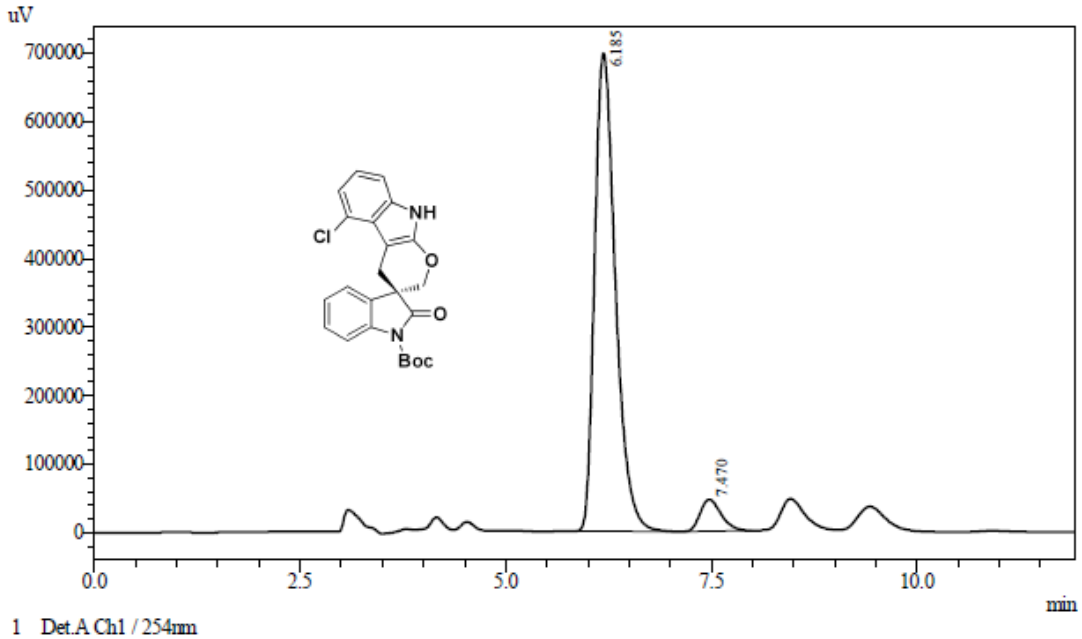
2c: Racemic



Detector A Ch1 254nm

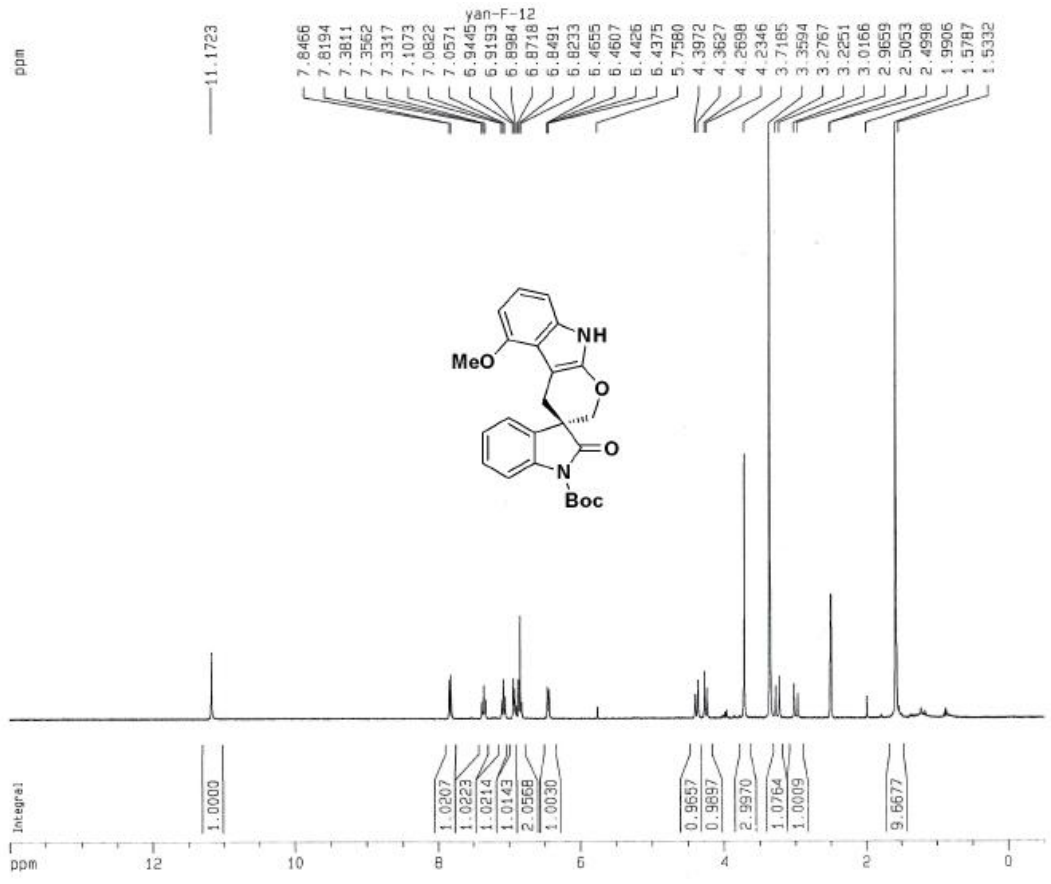
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.191	1793175	106138	50.571	52.430
2	7.473	1752707	96300	49.429	47.570
Total		3545882	202438	100.000	100.000

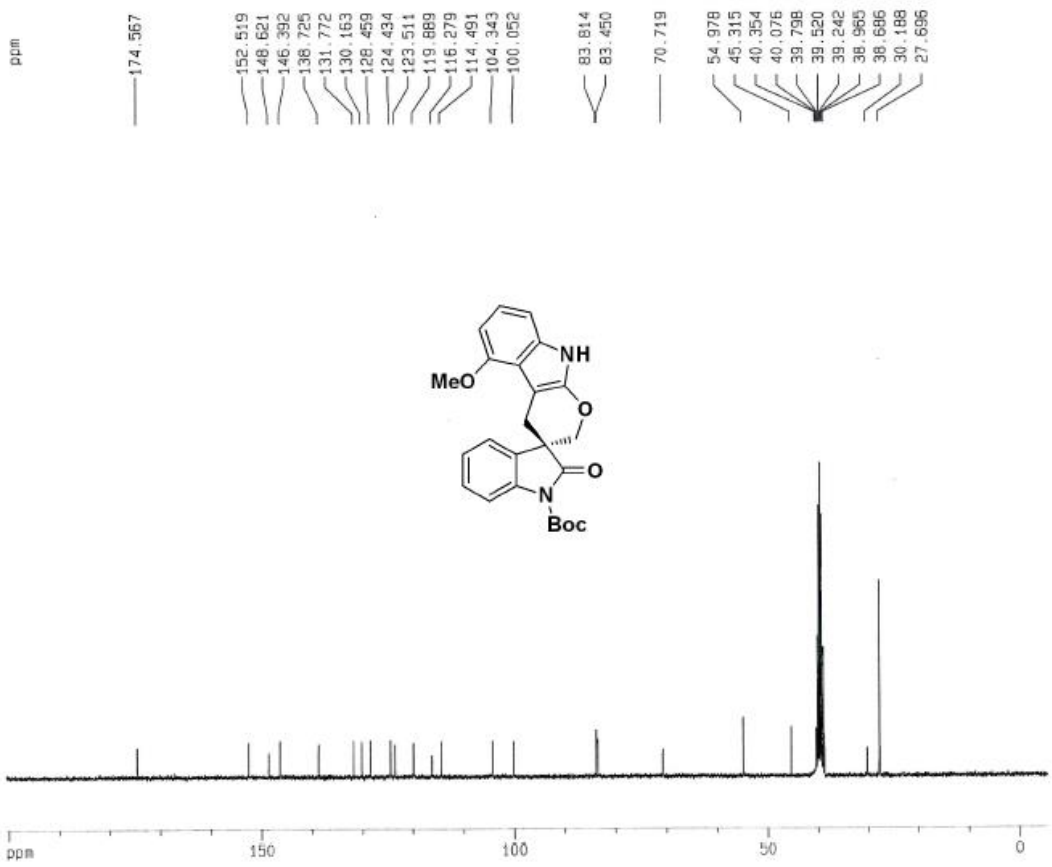
2c: Chiral



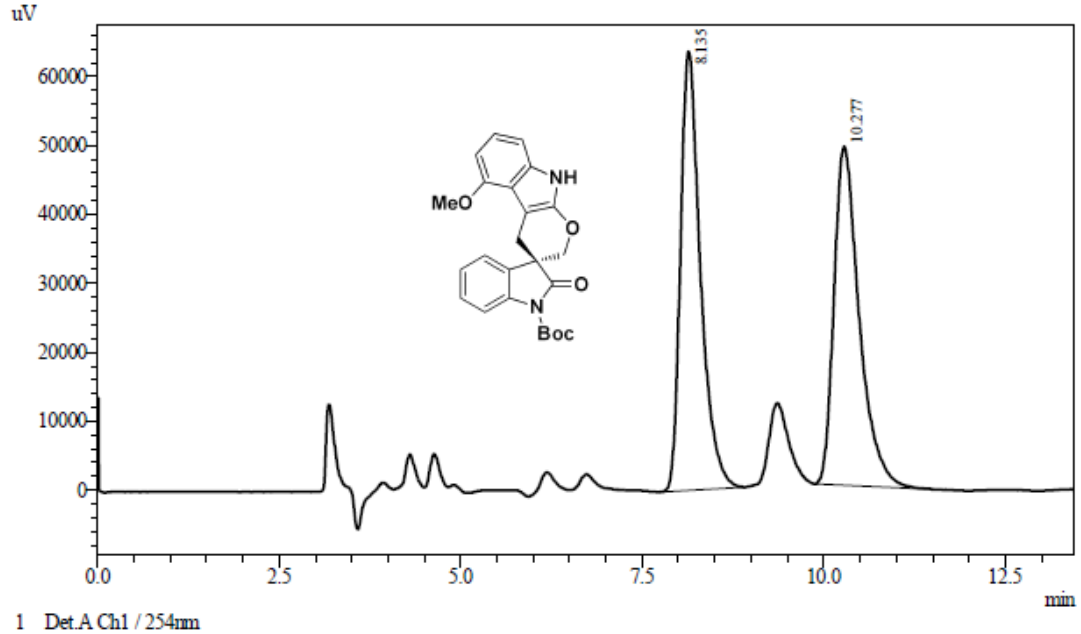
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.185	12272943	697819	93.683	93.767
2	7.470	827618	46389	6.317	6.233
Total		13100561	744208	100.000	100.000


yan-F-12
ppm
11.1723
7.8466
7.8194
7.3811
7.3562
7.3317
7.1073
7.0822
7.0571
6.9445
6.9193
6.8984
6.8718
6.8491
6.8233
6.4655
6.4607
6.4426
6.4375
5.7580
4.3972
4.3627
4.2698
4.2346
3.7185
3.3594
3.2767
3.2251
3.0166
2.9659
2.5053
2.4998
1.9906
1.5787
1.5332
MeO
NH
O
O
N
Boc
Integral
1.0000
1.0207
1.0223
1.0214
1.0143
2.0568
1.0030
0.9557
0.9897
2.9970
1.0764
1.0009
9.6677
ppm
12
10
8
6
4
2
0


ppm
174.567
152.519
148.621
146.392
138.725
131.772
130.163
128.459
124.434
123.511
119.889
116.279
114.491
104.343
100.052
83.814
83.450
70.719
54.978
45.315
40.354
40.076
39.798
39.520
39.242
38.965
38.686
30.188
27.696
MeO
NH
O
O
N
Boc
ppm
150
100
50
0

2d: Racemic

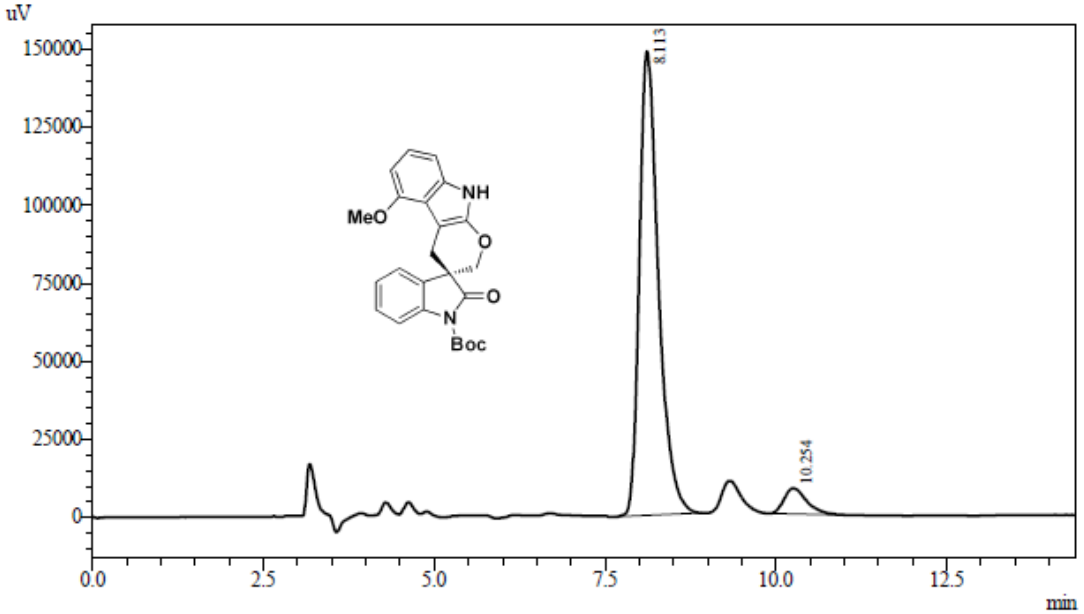


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.135	1216168	63640	50.575	56.447
2	10.277	1188520	49103	49.425	43.553
Total		2404688	112743	100.000	100.000

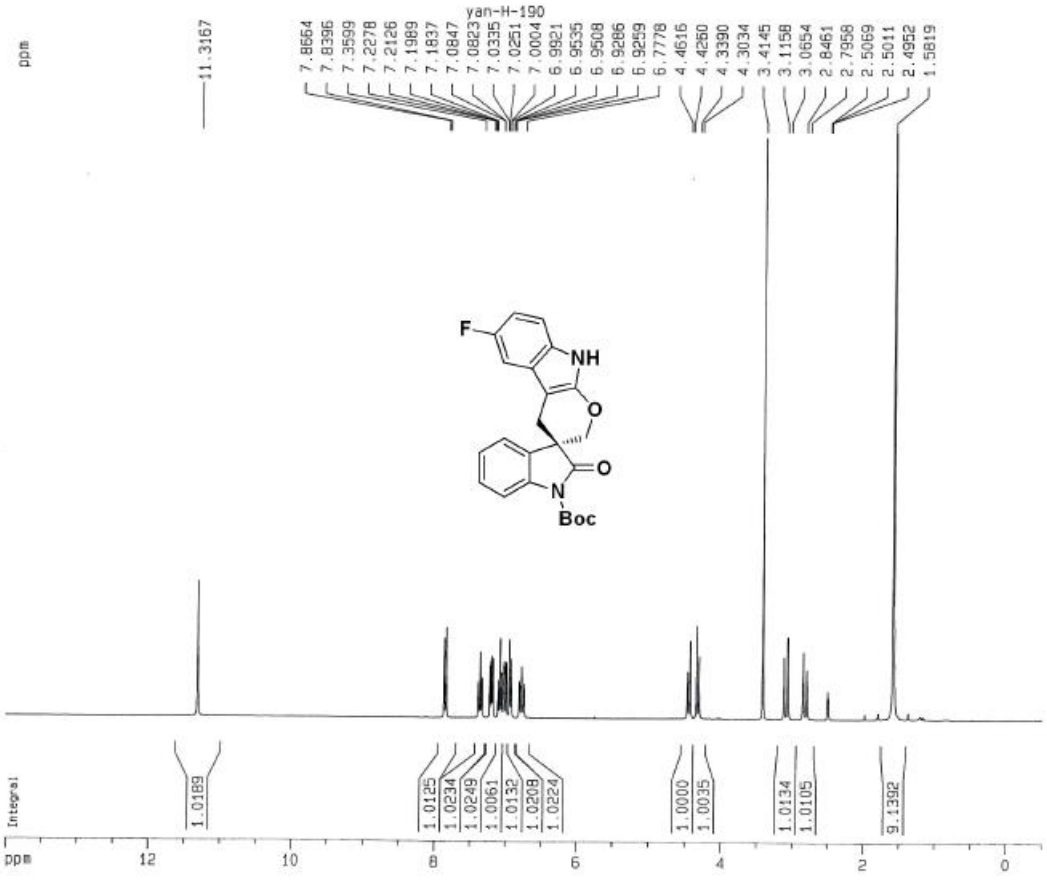
2d: Chiral

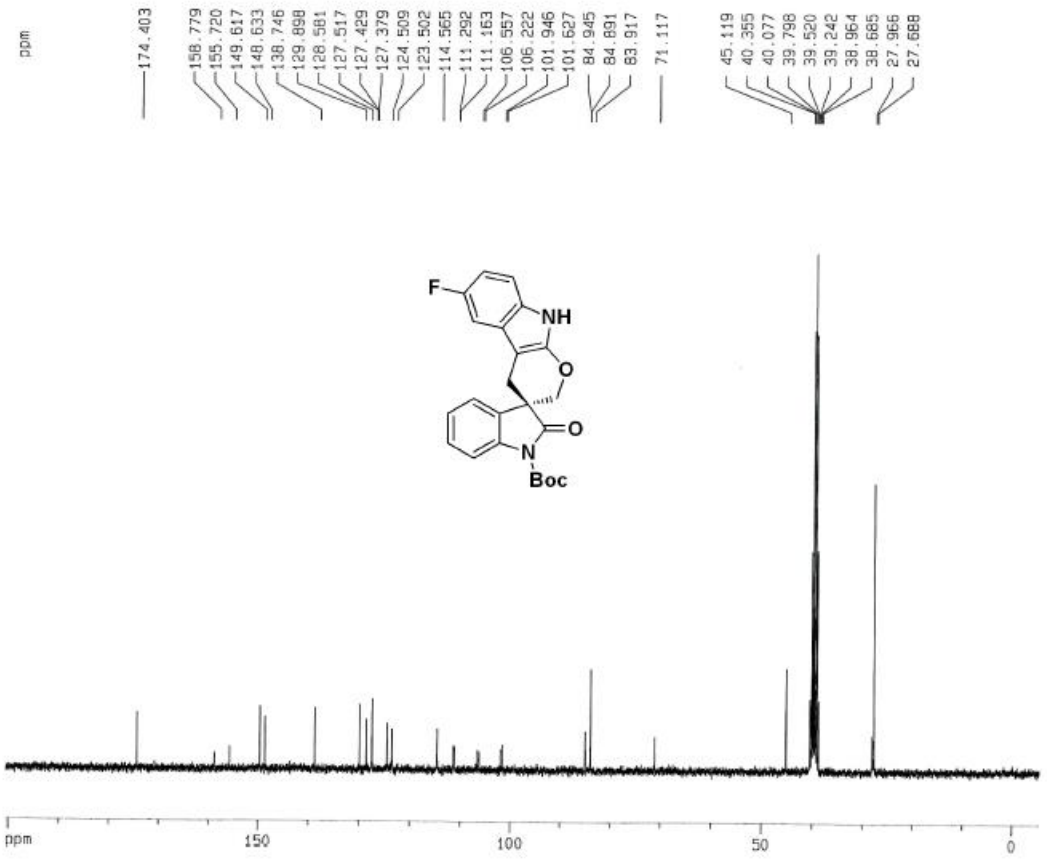


1 Det.A Ch1 / 254nm

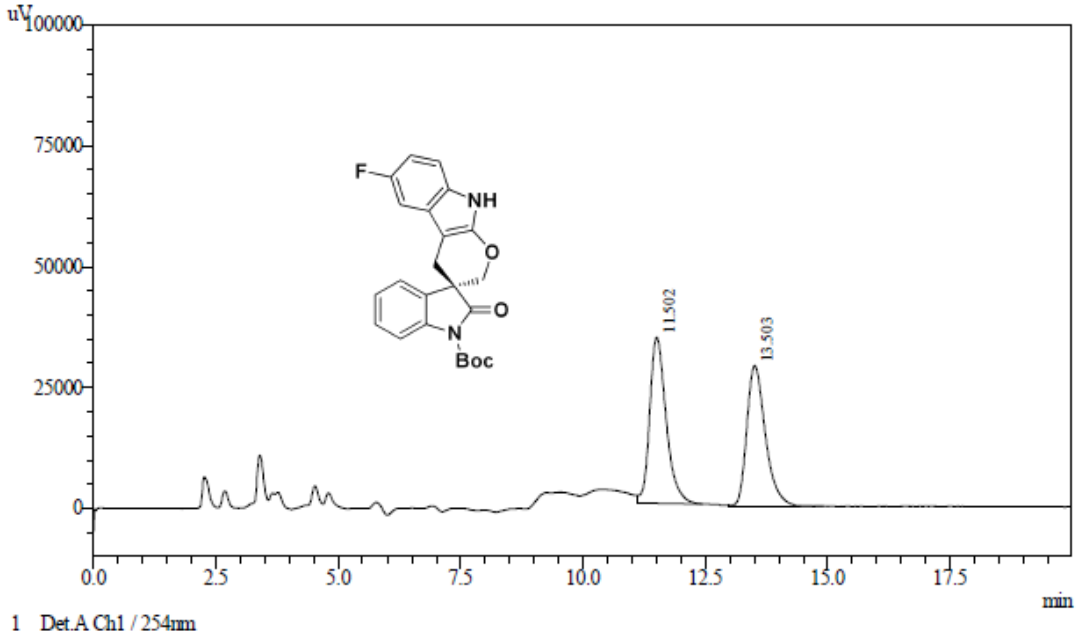
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.113	2901862	148628	93.877	94.770
2	10.254	189283	8202	6.123	5.230
Total		3091145	156830	100.000	100.000


yan-H-190
ppm
11.3167
7.8664
7.8396
7.3599
7.2278
7.2126
7.1989
7.1837
7.0847
7.0823
7.0335
7.0251
7.0004
6.9921
6.9535
6.9508
6.9286
6.9259
6.7778
4.4616
4.4260
4.3390
4.3034
3.4145
3.1158
3.0654
2.8461
2.7958
2.5069
2.5011
2.4952
1.5819
F
NH
O
O
N
Boc
Integral
1.0189
1.0125
1.0234
1.0249
1.0061
1.0132
1.0208
1.0224
1.0000
1.0035
1.0134
1.0105
9.1392
ppm
12
10
8
6
4
2
0


ppm
174.403
158.779
155.720
149.617
148.633
138.746
129.898
128.581
127.517
127.429
127.379
124.509
123.502
114.565
111.292
111.163
106.557
106.222
101.946
101.627
84.945
84.891
83.917
71.117
45.119
40.355
40.077
39.798
39.520
39.242
38.964
38.685
27.966
27.688
F
NH
O
O
N
Boc
ppm
150
100
50
0

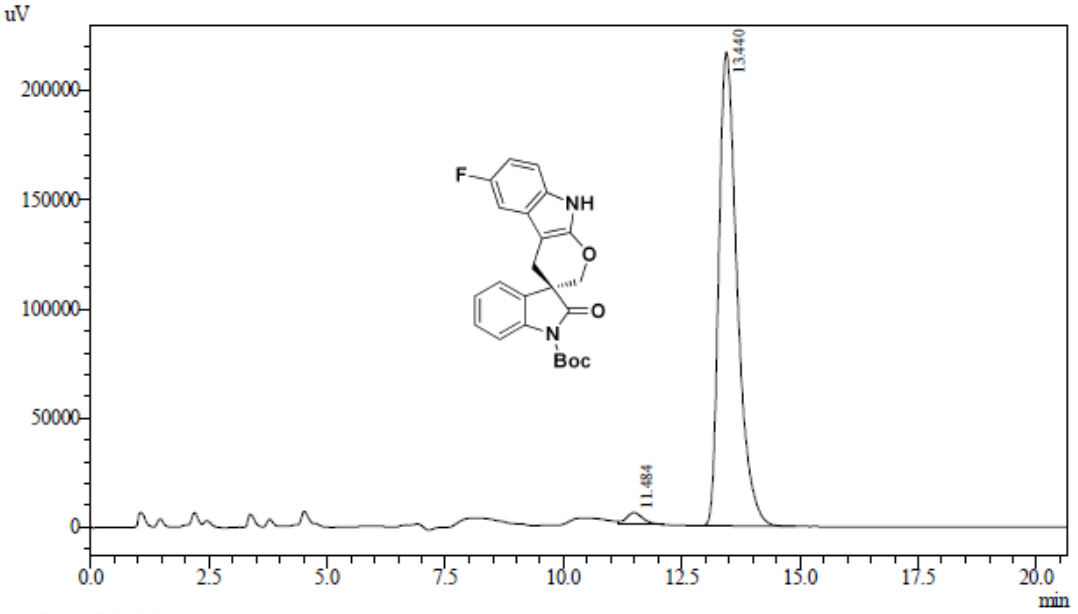
2e: Racemic



Detector A Ch1 254nm

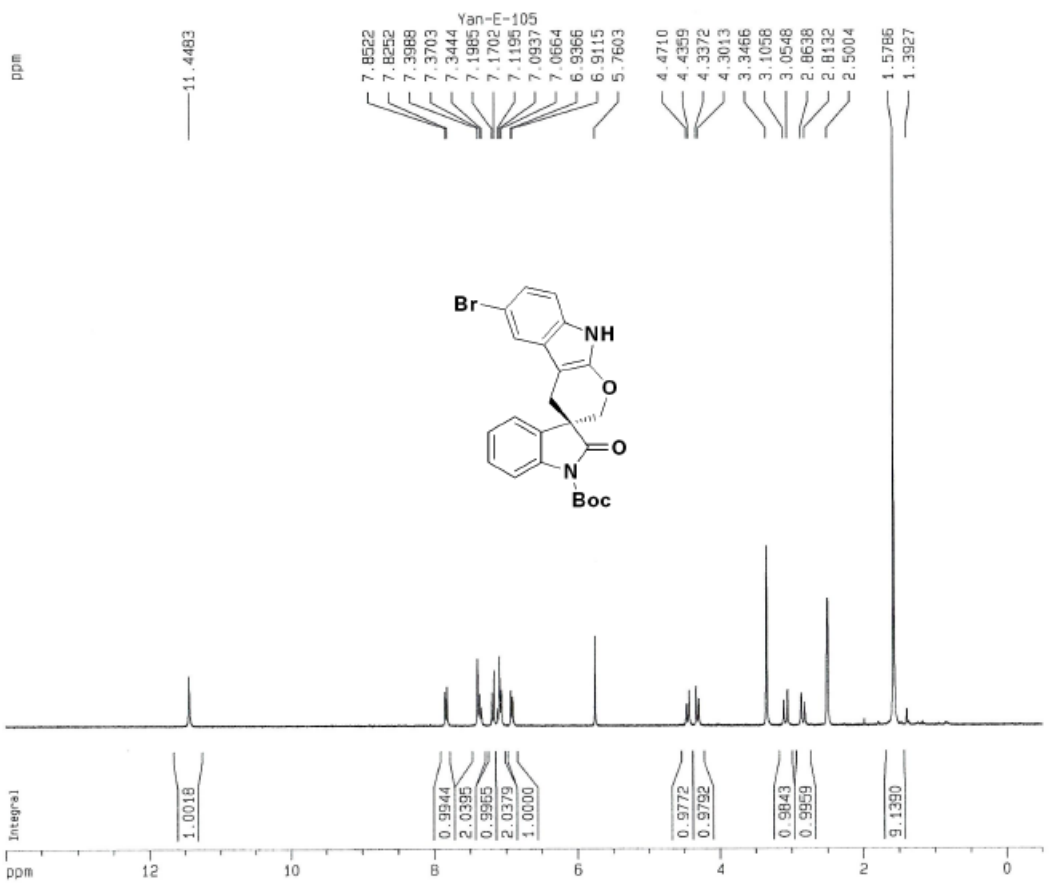
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.502	801927	34285	50.871	54.073
2	13.503	774458	29121	49.129	45.927
Total		1576385	63406	100.000	100.000

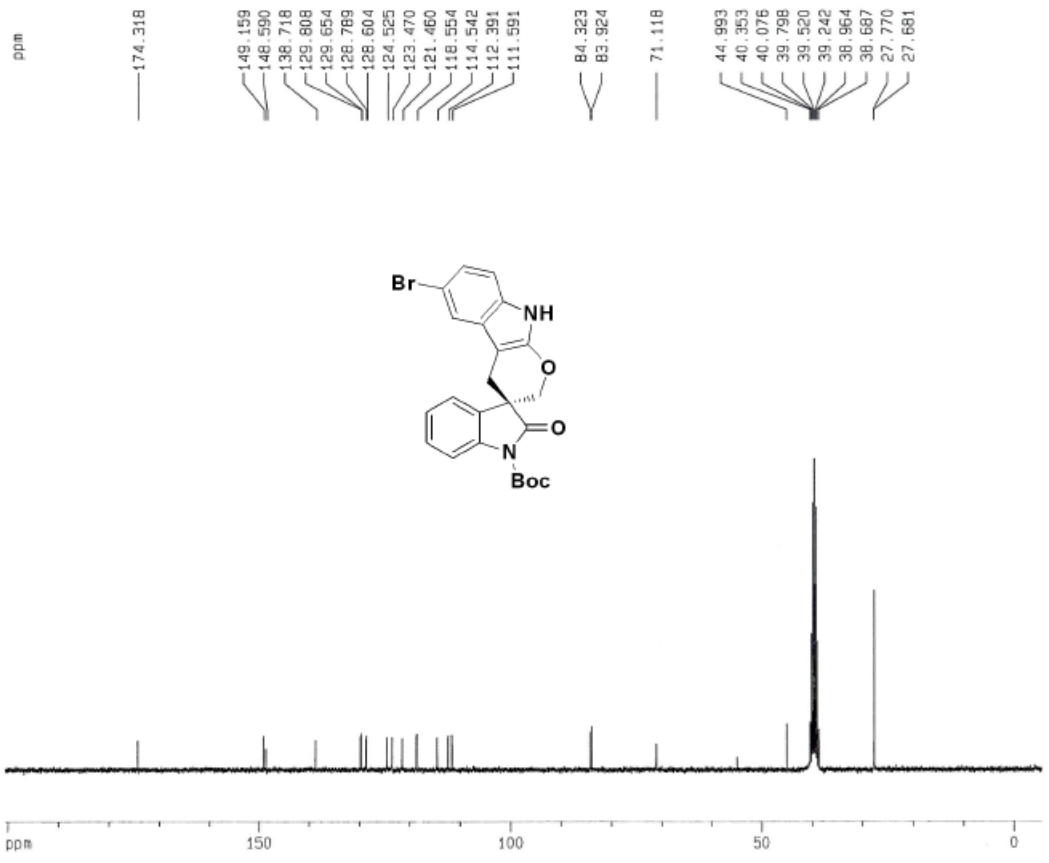
2e: Chiral



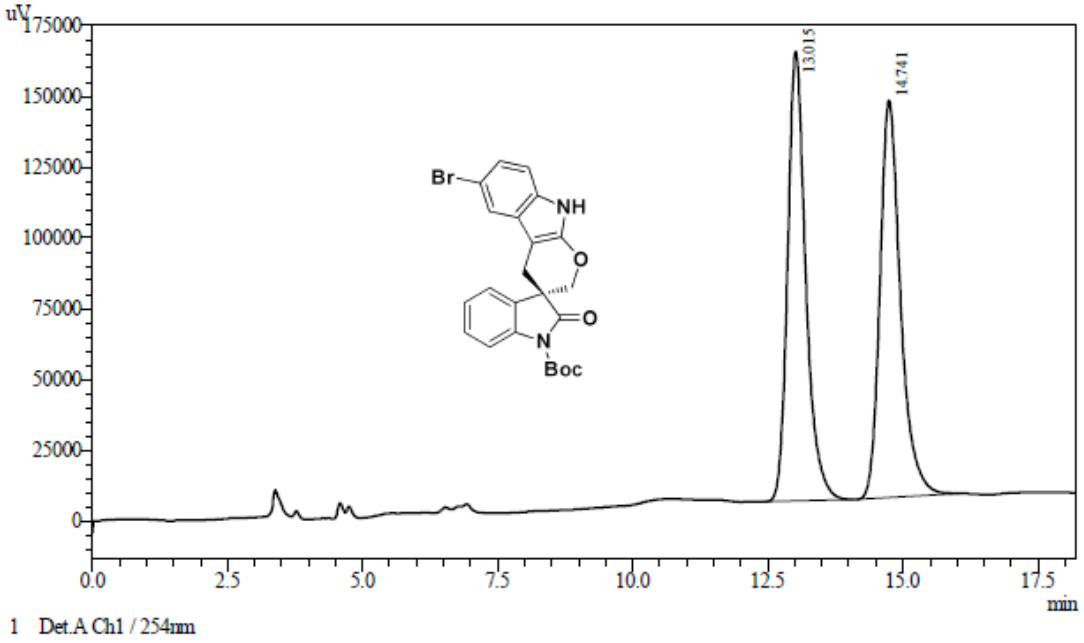
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.484	138159	5474	2.299	2.460
2	13.440	5870080	217000	97.701	97.540
Total		6008239	222474	100.000	100.000


Yan-E-105
ppm
11.4483
7.8522
7.8252
7.3988
7.3703
7.3444
7.1985
7.1702
7.1195
7.0937
7.0664
6.9366
6.9115
5.7603
4.4710
4.4359
4.3372
4.3013
3.3466
3.1058
3.0548
2.8638
2.8132
2.5004
1.5786
1.3927
Br
NH
O
O
N
Boc
Integral
1.0018
0.9944
2.0395
0.9965
2.0379
1.0000
0.9772
0.9792
0.9843
0.9959
9.1390
ppm
12
10
8
6
4
2
0


ppm
174.318
149.159
148.590
138.718
129.808
129.654
128.789
128.604
124.525
123.470
121.460
118.554
114.542
112.391
111.591
84.323
83.924
71.118
44.993
40.353
40.076
39.798
39.520
39.242
38.964
38.687
27.770
27.681
Br
NH
O
O
N
Boc
ppm
150
100
50
0

2f: Racemic

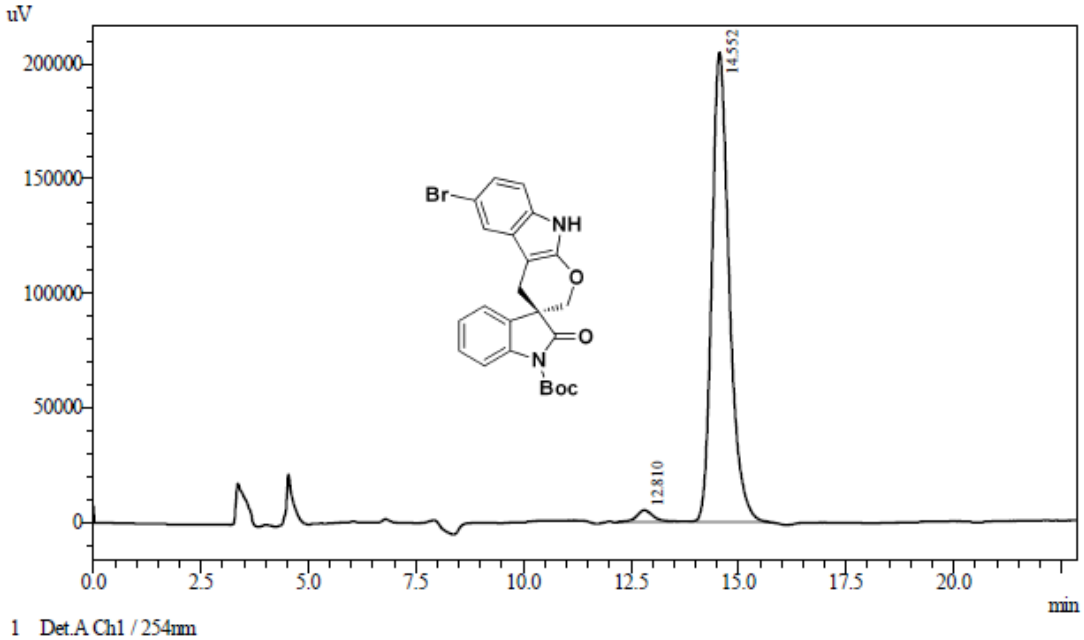


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.015	3708730	158892	49.822	53.104
2	14.741	3735170	140316	50.178	46.896
Total		7443900	299209	100.000	100.000

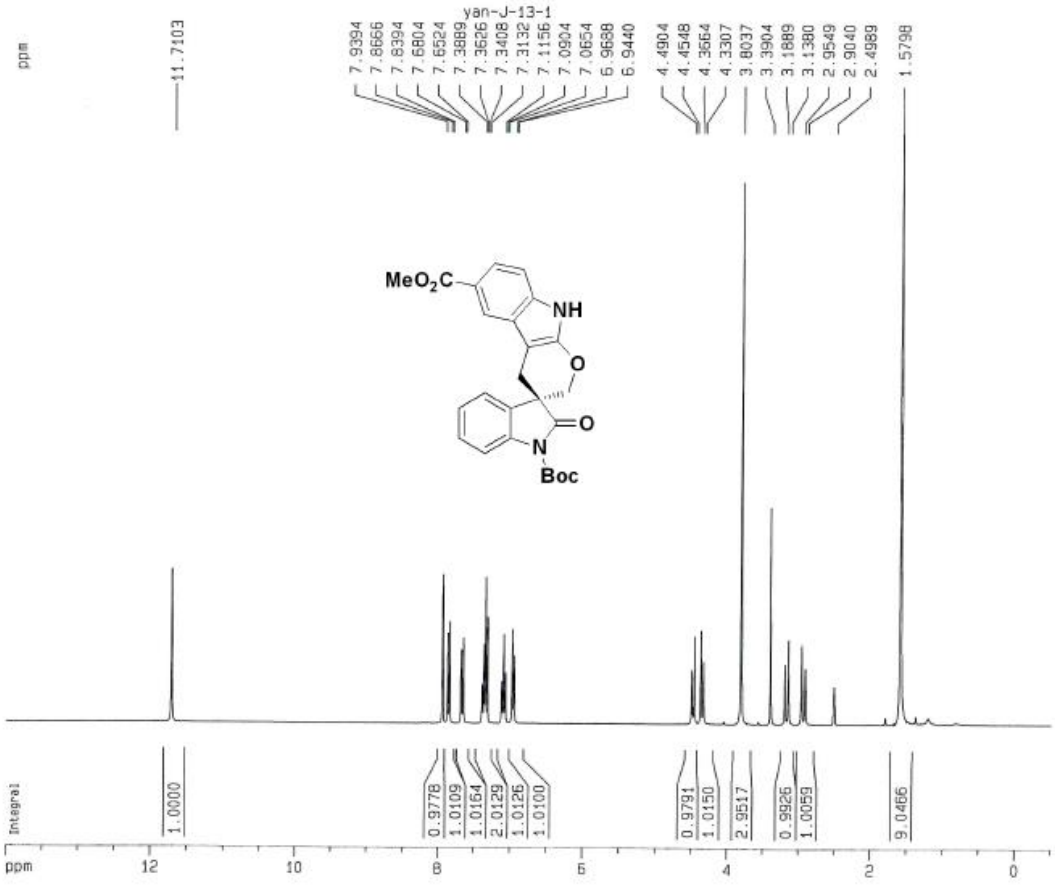
2f: Chiral

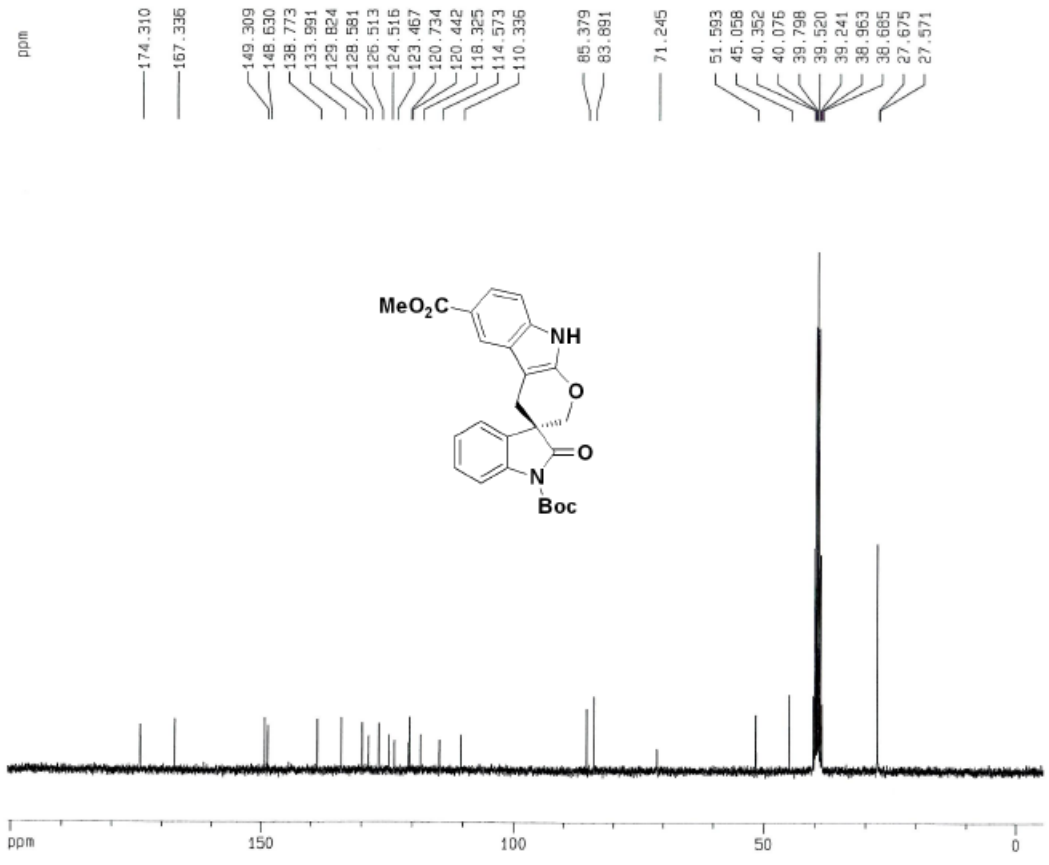


1 Det.A Ch1 / 254nm

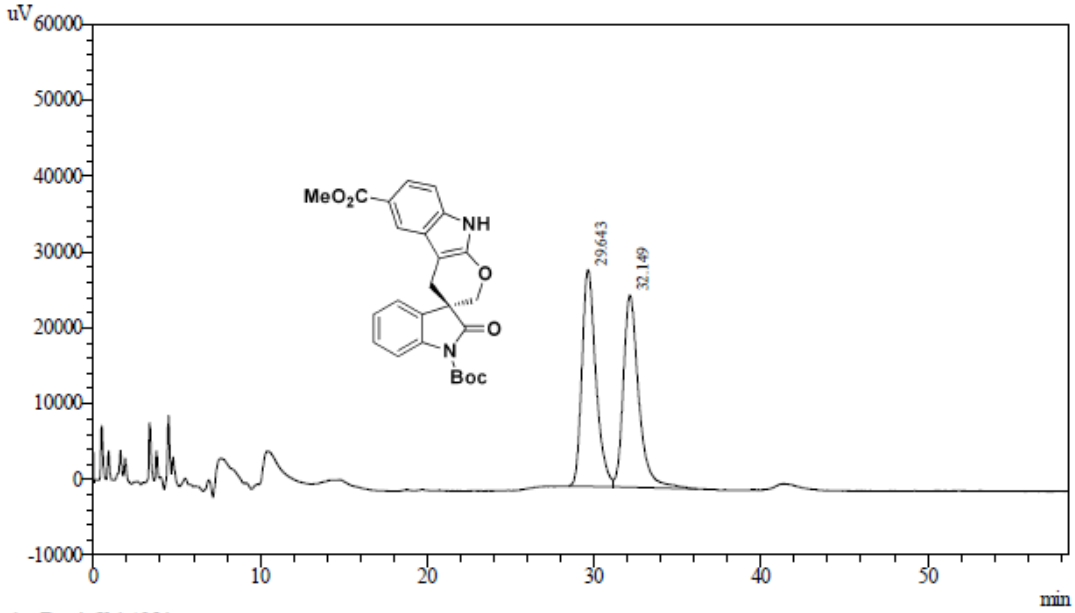
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.810	138135	5111	2.340	2.434
2	14.552	5764087	204880	97.660	97.566
Total		5902222	209991	100.000	100.000


yan-J-13-1
ppm
11.7103
7.9394
7.8666
7.8394
7.6804
7.6524
7.3889
7.3626
7.3408
7.3132
7.1156
7.0904
7.0654
6.9688
6.9440
4.4904
4.4548
4.3664
4.3307
3.8037
3.3904
3.1889
3.1380
2.9549
2.9040
2.4989
1.5798
MeO2C
NH
O
O
N
Boc
Integral
1.0000
0.9778
1.0109
1.0164
2.0129
1.0126
1.0100
0.9791
1.0150
2.9617
0.9926
1.0059
9.0466
ppm
12
10
8
6
4
2
0


ppm
174.310
167.336
149.309
148.630
138.773
133.991
129.824
128.581
126.513
124.516
123.467
120.734
120.442
118.325
114.573
110.336
85.379
83.891
71.245
51.593
45.058
40.352
40.076
39.798
39.520
39.241
38.963
38.685
27.675
27.571
MeO2C
NH
O
O
N
Boc
ppm
150
100
50
0

2g: Racemic

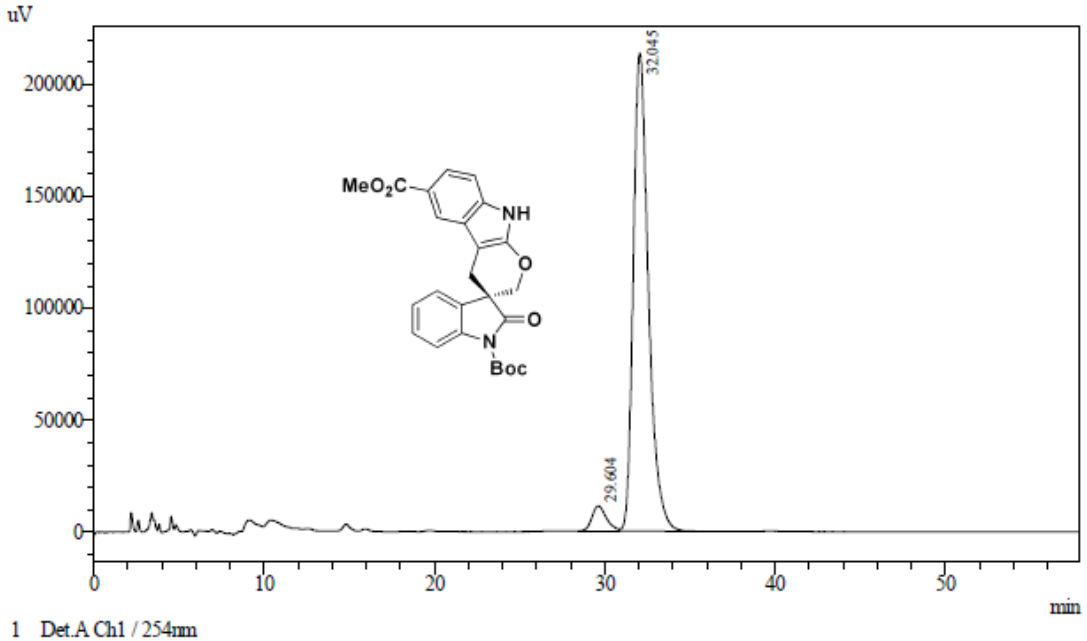


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.643	1658835	28572	50.457	52.987
2	32.149	1628783	25350	49.543	47.013
Total		3287618	53922	100.000	100.000

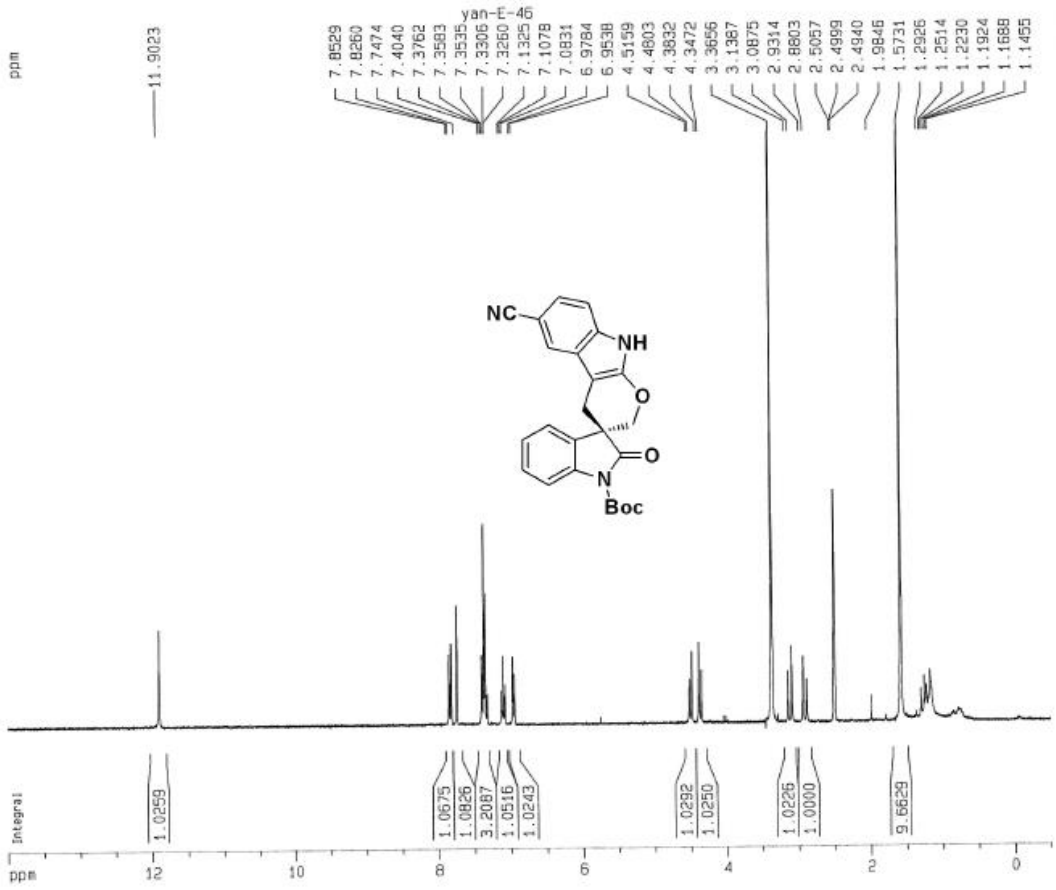
2g: Chiral

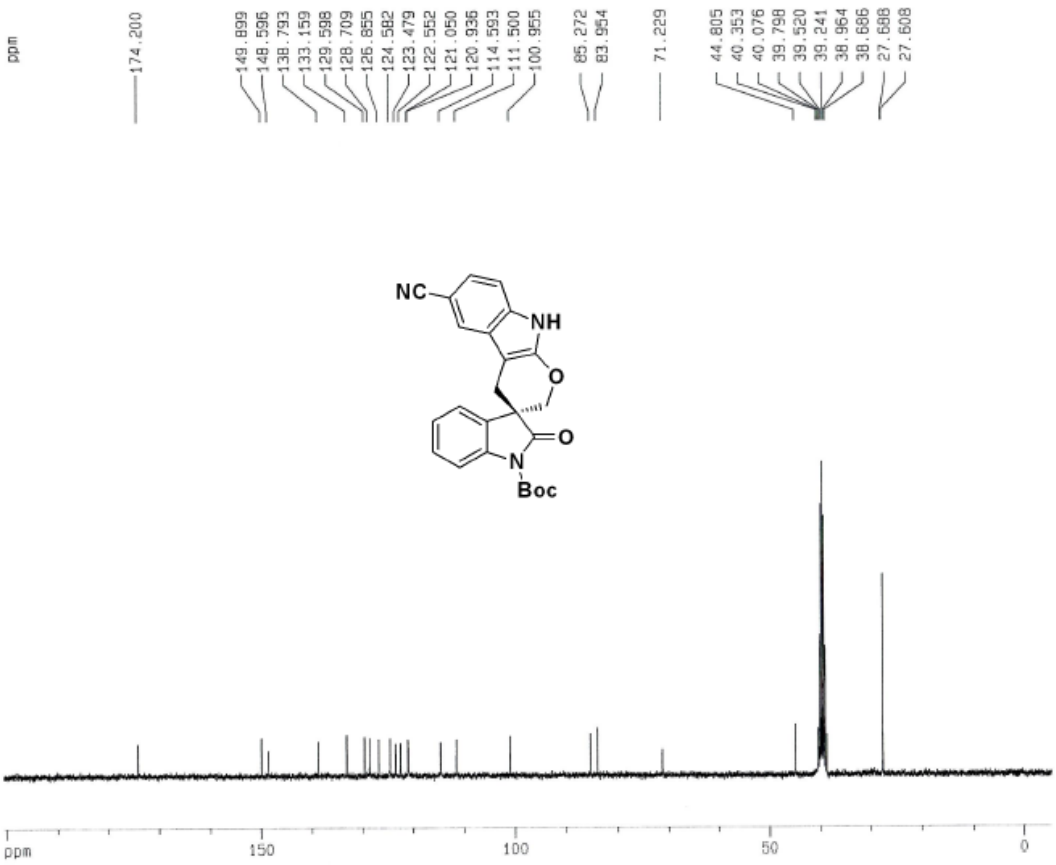


1 Det.A Ch1 / 254nm

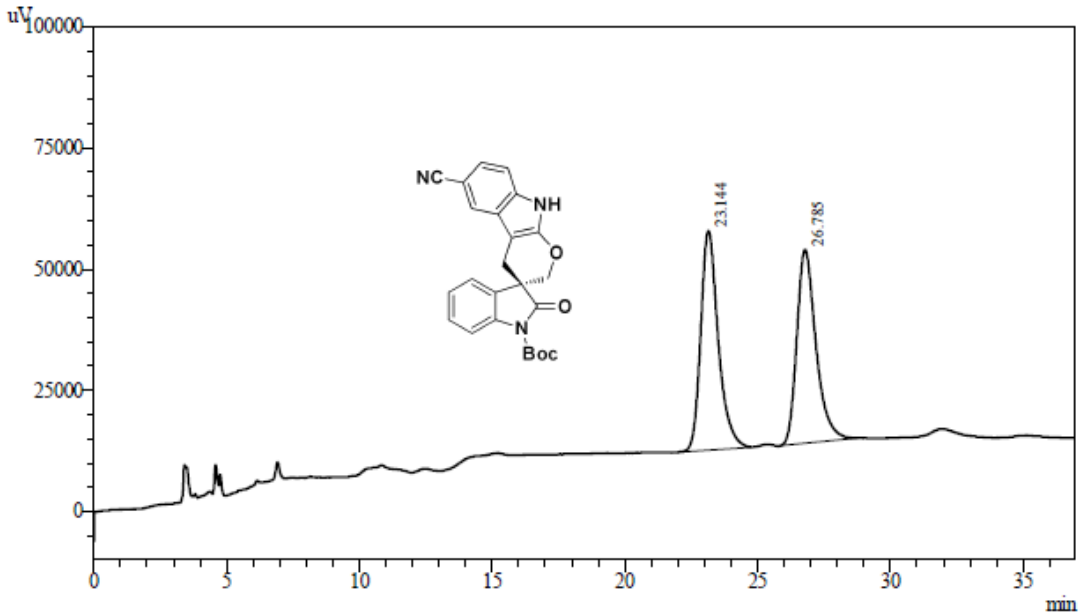
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.604	653155	11174	4.716	4.975
2	32.045	13195861	213434	95.284	95.025
Total		13849016	224608	100.000	100.000


yan-E-46
ppm
11.9023
7.8529
7.8260
7.7474
7.4040
7.3762
7.3583
7.3535
7.3306
7.3260
7.1325
7.1078
7.0831
6.9784
6.9538
4.5159
4.4803
4.3832
4.3472
3.3656
3.1387
3.0875
2.9314
2.8803
2.5057
2.4999
2.4940
1.9846
1.5731
1.2926
1.2514
1.2230
1.1924
1.1688
1.1455
NC
NH
O
O
N
Boc
Integral
1.0259
1.0675
1.0826
3.2087
1.0516
1.0243
1.0292
1.0250
1.0226
1.0000
9.6629
ppm
12
10
8
6
4
2
0


ppm
174.200
149.899
148.596
138.793
133.159
129.598
128.709
126.855
124.582
123.479
122.552
121.050
120.936
114.593
111.500
100.955
85.272
83.954
71.229
44.805
40.353
40.076
39.798
39.520
39.241
38.964
38.686
27.688
27.608
NC
NH
O
O
N
Boc
ppm
150
100
50
0

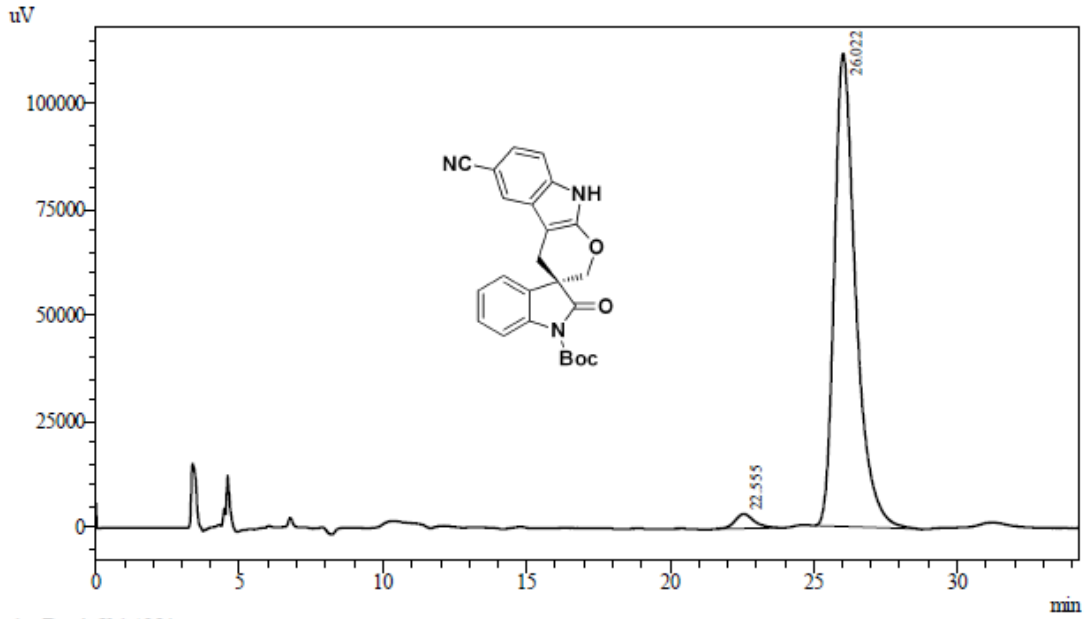
2h: Racemic



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.144	2071714	45208	50.814	53.080
2	26.785	2005366	39961	49.186	46.920
Total		4077080	85169	100.000	100.000

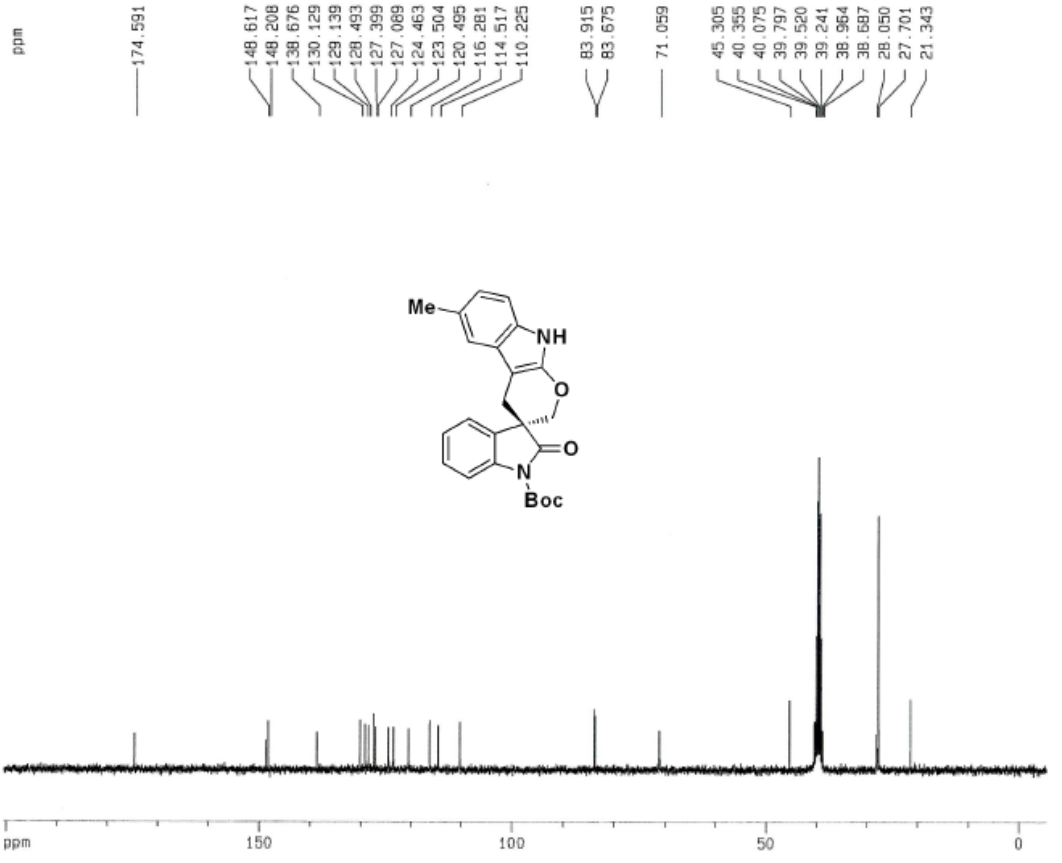
2h: Chiral



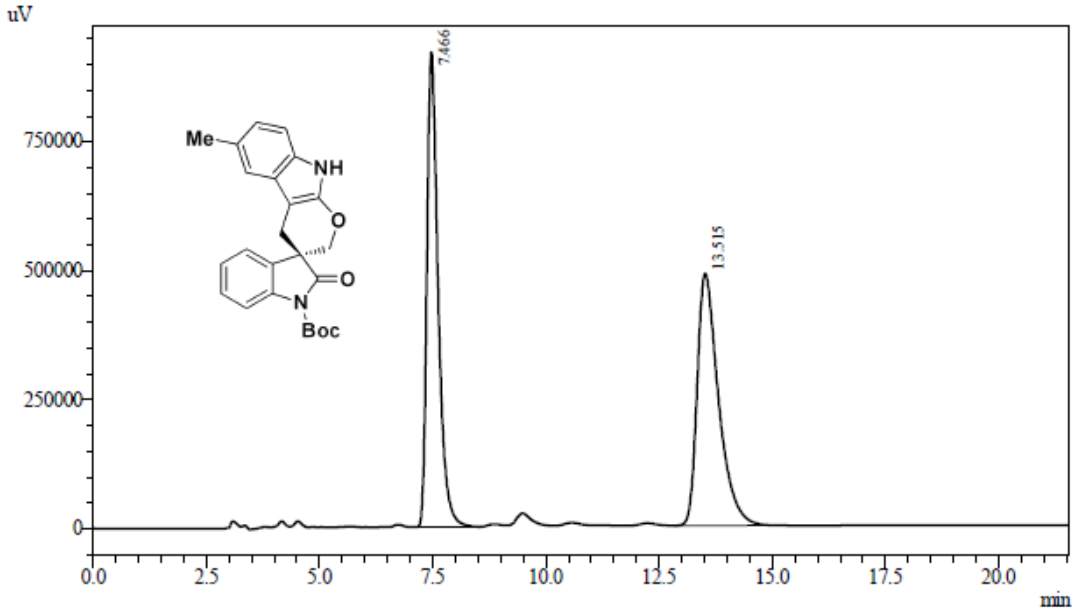
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.555	153002	3360	2.566	2.922
2	26.022	5810450	111624	97.434	97.078
Total		5963452	114984	100.000	100.000


Yan-E-52
ppm
10.9969
7.8100
7.7833
7.3192
7.0725
7.0575
7.0459
7.0326
6.9667
6.8532
6.8273
6.7597
6.7329
5.7235
4.3432
4.2492
4.2136
3.3237
3.0676
3.0169
2.7657
2.7144
2.4698
2.4639
2.4581
2.2736
2.0472
1.5454
1.4763
1.4561
1.3567
Me
NH
O
O
N
Boc
Integral
1.0000
1.0220
1.1796
2.2518
1.0409
1.0716
1.0954
1.9824
1.0002
1.1401
3.2315
9.9143
ppm
14
12
10
8
6
4
2
0


ppm
174.591
148.617
148.208
138.676
130.129
129.139
128.493
127.399
127.089
124.463
123.504
120.495
116.281
114.517
110.225
83.915
83.675
71.059
45.305
40.355
40.075
39.797
39.520
39.241
38.964
38.687
28.050
27.701
21.343
Me
NH
O
O
N
Boc
ppm
150
100
50
0

2i: Racemic

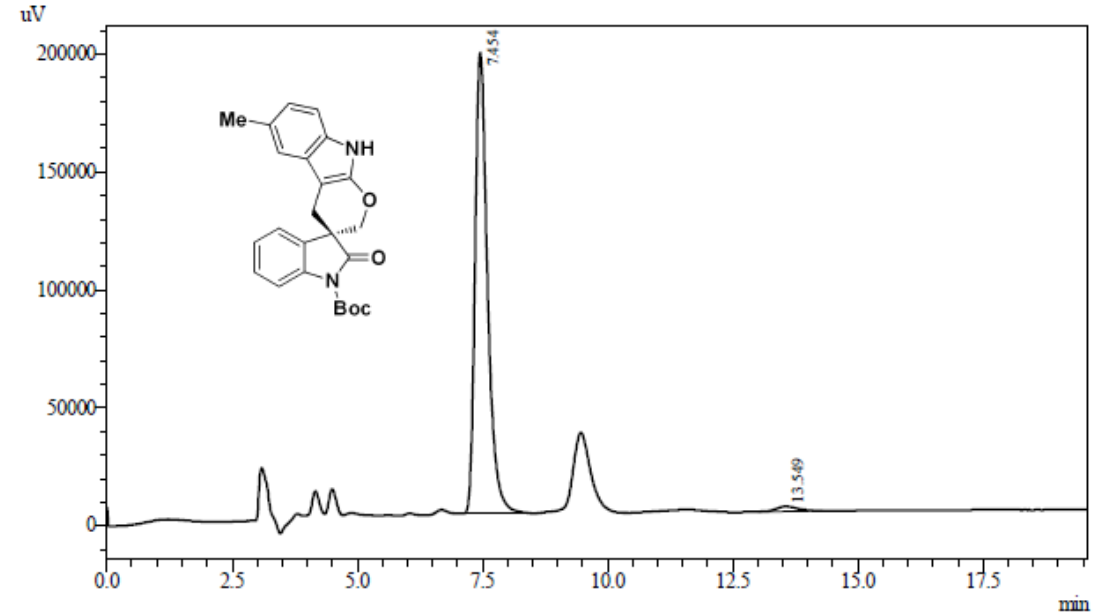


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.466	15855168	920666	49.656	65.309
2	13.515	16075112	489041	50.344	34.691
Total		31930280	1409708	100.000	100.000

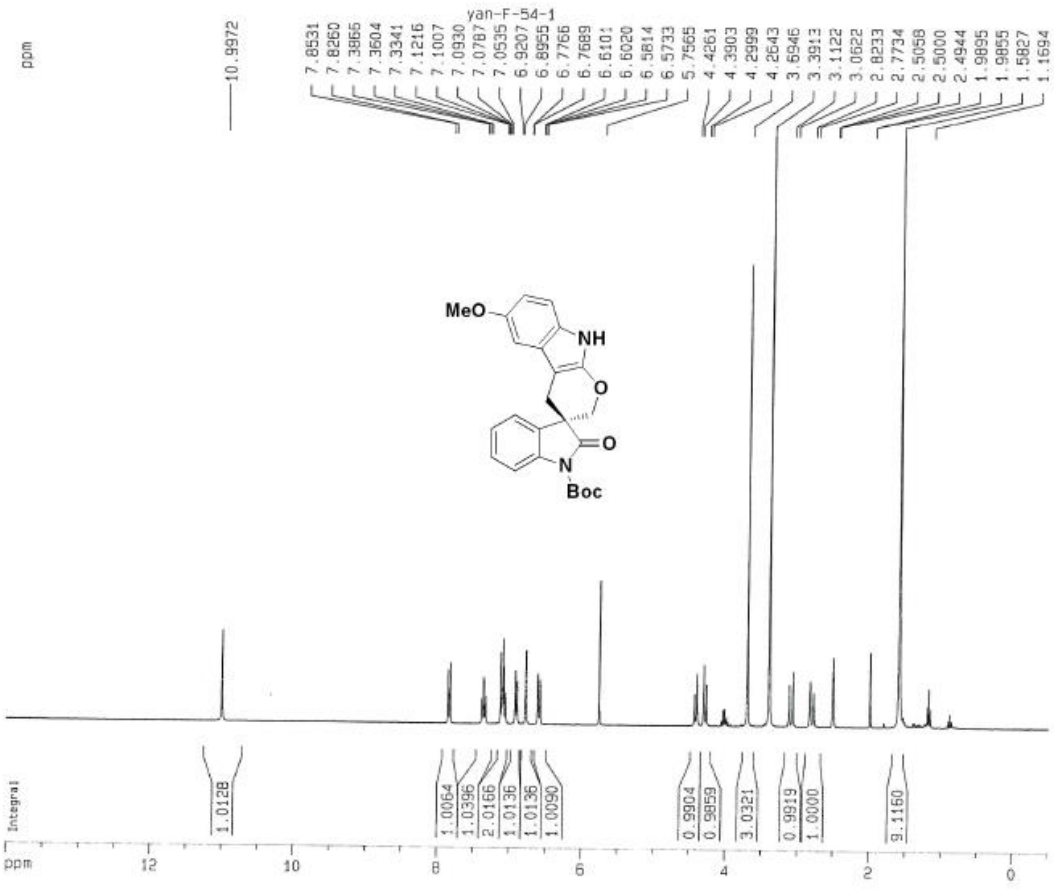
2i: Chiral

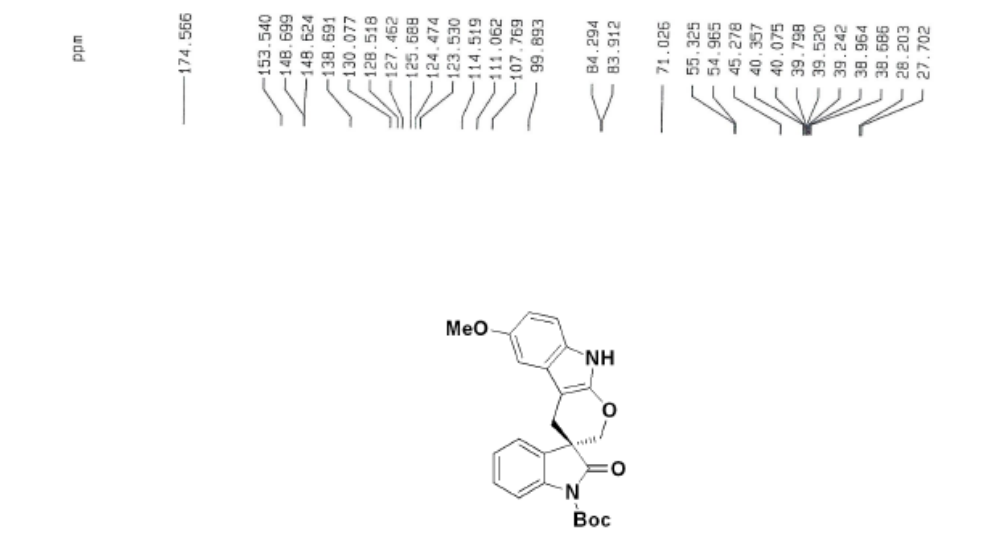


1 Det.A Ch1 / 254nm

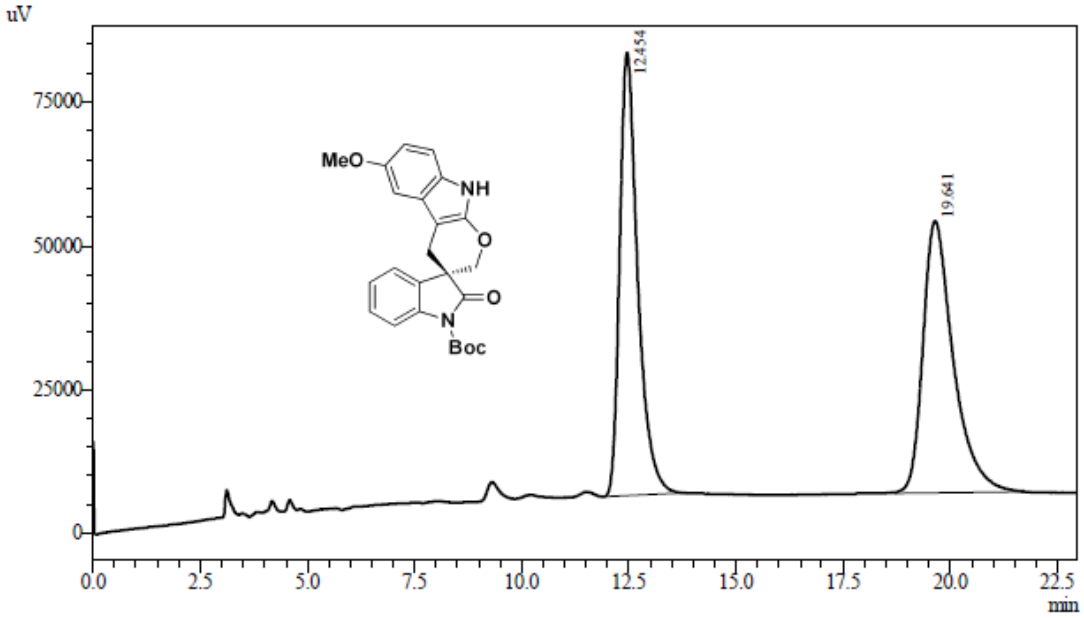
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.454	3402720	195444	98.189	98.962
2	13.549	62766	2049	1.811	1.038
Total		3465486	197493	100.000	100.000


yan-F-54-1
ppm
10.9972
7.8531
7.8260
7.3866
7.3604
7.3341
7.1216
7.1007
7.0930
7.0787
7.0535
6.9207
6.8955
6.7766
6.7689
6.6101
6.6020
6.5814
6.5733
5.7565
4.4261
4.3903
4.2999
4.2643
3.6946
3.3913
3.1122
3.0622
2.8233
2.7734
2.5058
2.5000
2.4944
1.9895
1.9855
1.5827
1.1694
MeO
NH
O
O
N
Boc
Integral
1.0128
1.0064
1.0396
2.0166
1.0136
1.0136
1.0090
0.9904
0.9859
3.0321
0.9919
1.0000
9.1160
ppm
12
10
8
6
4
2
0


ppm
174.566
153.540
148.699
148.624
138.691
130.077
128.518
127.462
125.688
124.474
123.530
114.519
111.062
107.769
99.893
84.294
83.912
71.026
55.325
54.965
45.278
40.357
40.075
39.798
39.520
39.242
38.964
38.686
28.203
27.702
MeO
NH
O
O
N
Boc
ppm
150
100
50
0

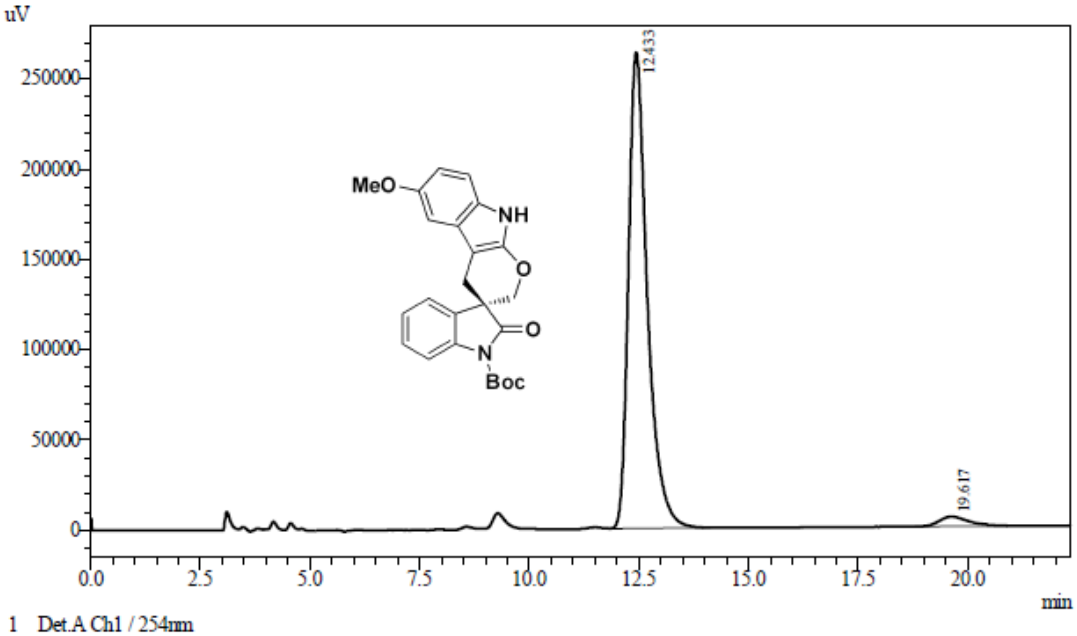
2j: Racemic



Detector A Ch1 254nm

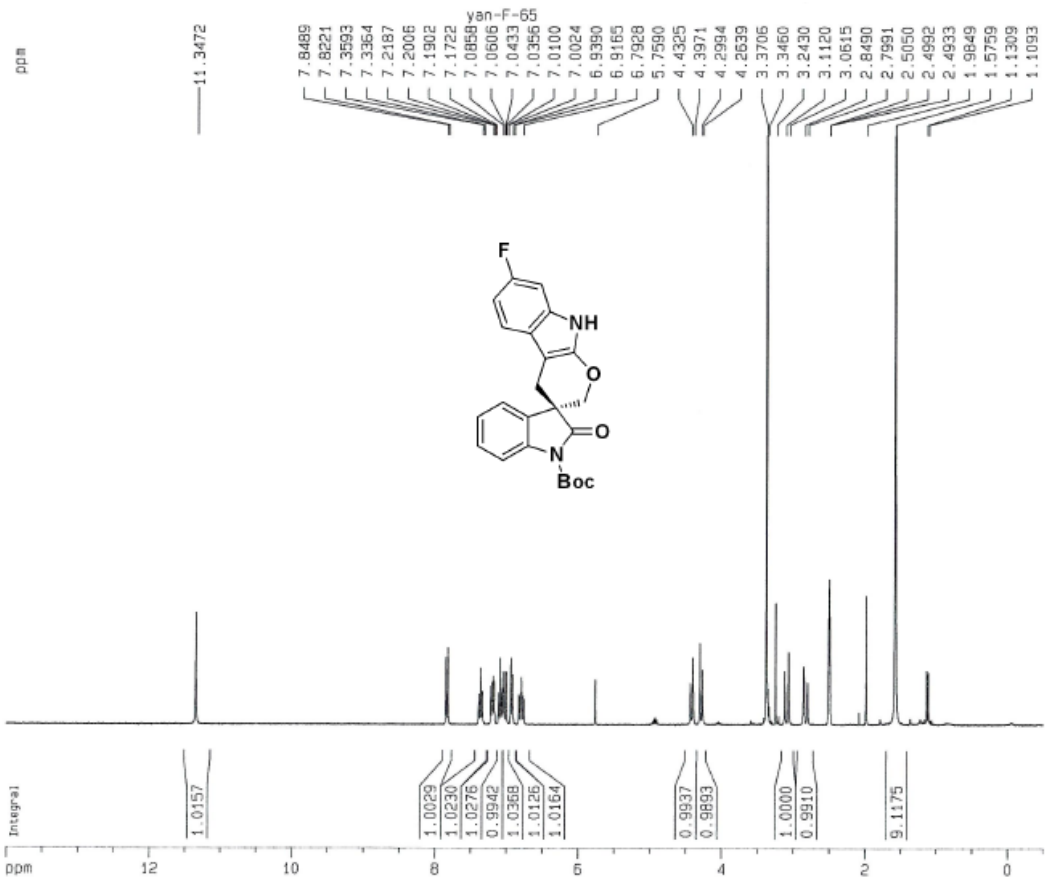
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.454	2261388	77022	49.293	61.998
2	19.641	2326243	47210	50.707	38.002
Total		4587632	124232	100.000	100.000

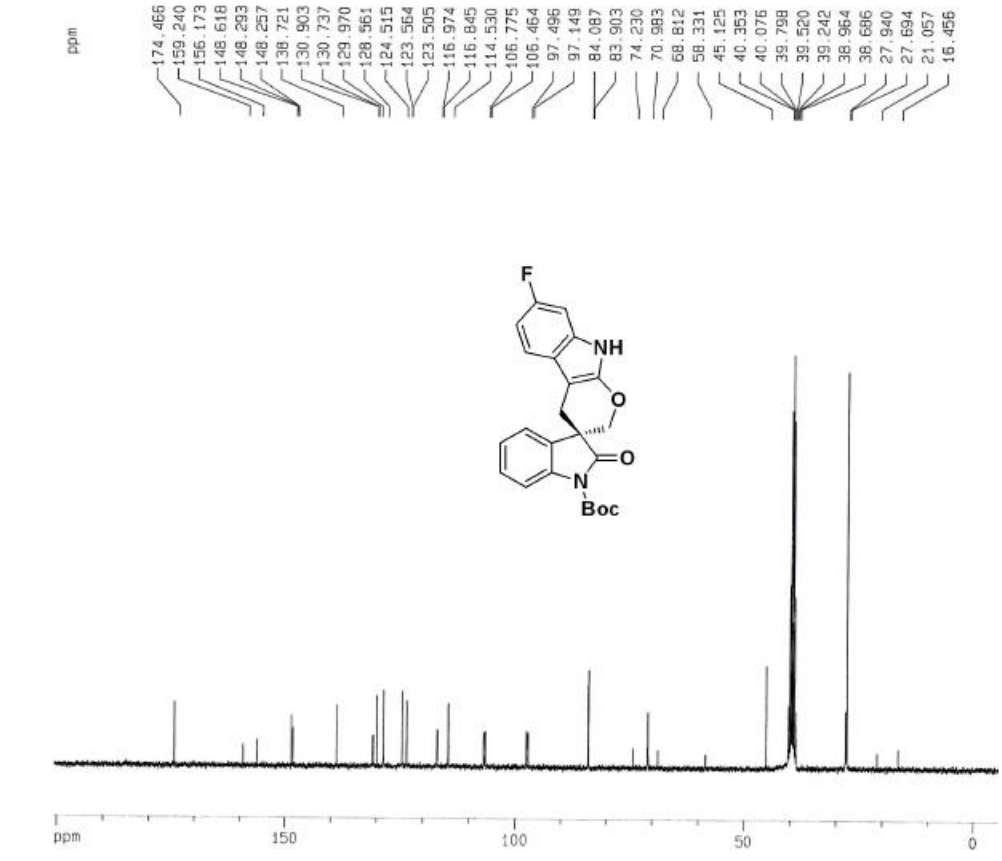
2j: Chiral



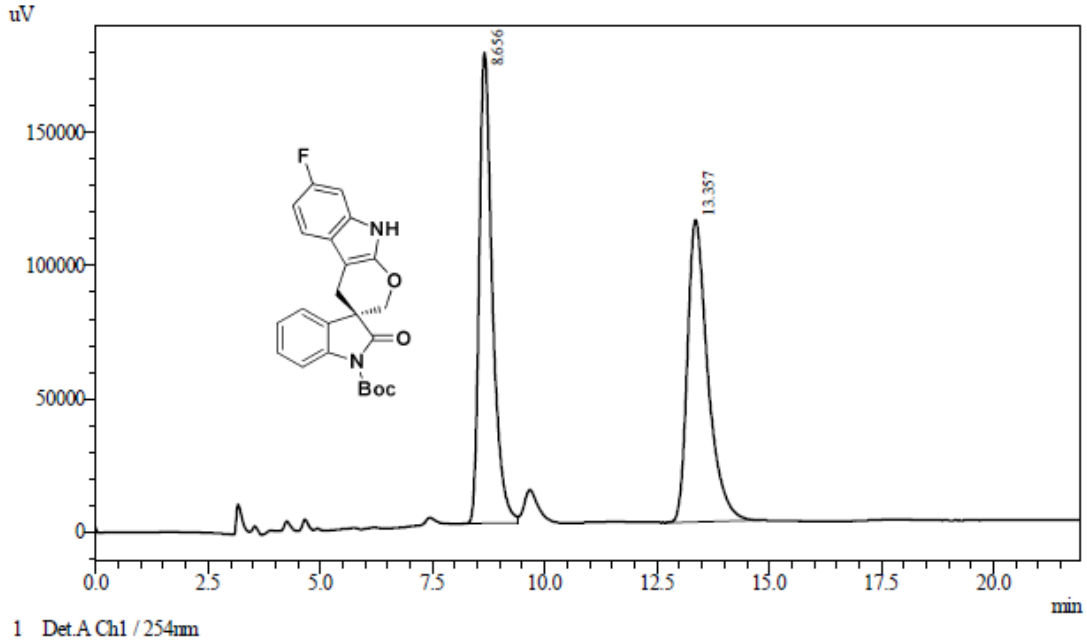
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.433	7872148	263600	96.937	98.019
2	19.617	248704	5328	3.063	1.981
Total		8120852	268928	100.000	100.000


yan-F-65
ppm
11.3472
7.8489
7.8221
7.3593
7.3364
7.2187
7.2006
7.1902
7.1722
7.0858
7.0606
7.0433
7.0356
7.0100
7.0024
6.9390
6.9165
6.7928
5.7590
4.4325
4.3971
4.2994
4.2639
3.3706
3.3460
3.2430
3.1120
3.0615
2.8490
2.7991
2.5050
2.4992
2.4933
1.9849
1.5759
1.1309
1.1093
F
NH
O
O
N
Boc
Integral
1.0157
1.0029
1.0230
1.0276
0.9942
1.0368
1.0126
1.0164
0.9937
0.9893
1.0000
0.9910
9.1175
ppm
12
10
8
6
4
2
0


ppm
174.466
159.240
156.173
148.618
148.293
148.257
138.721
130.903
130.737
129.970
128.561
124.515
123.564
123.505
116.974
116.845
114.530
106.775
106.464
97.496
97.149
84.087
83.903
74.230
70.983
68.812
58.331
45.125
40.353
40.076
39.798
39.520
39.242
38.964
38.686
27.940
27.694
21.057
16.456
F
NH
O
O
N
Boc
ppm
150
100
50
0

2k: Racemic

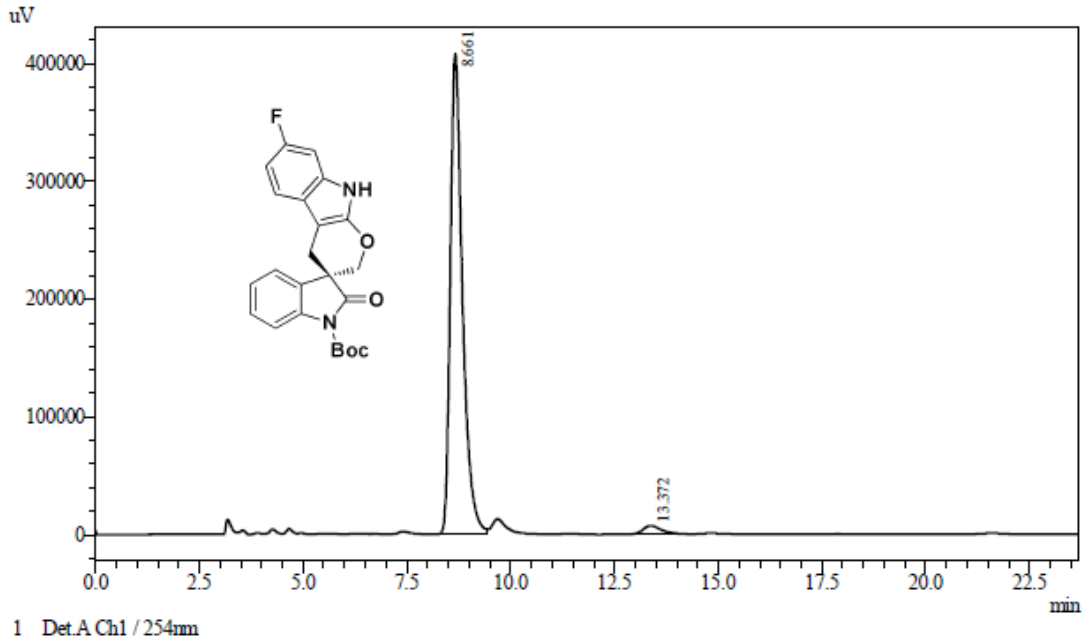


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.656	3613396	176537	50.180	60.923
2	13.357	3587439	113232	49.820	39.077
Total		7200835	289769	100.000	100.000

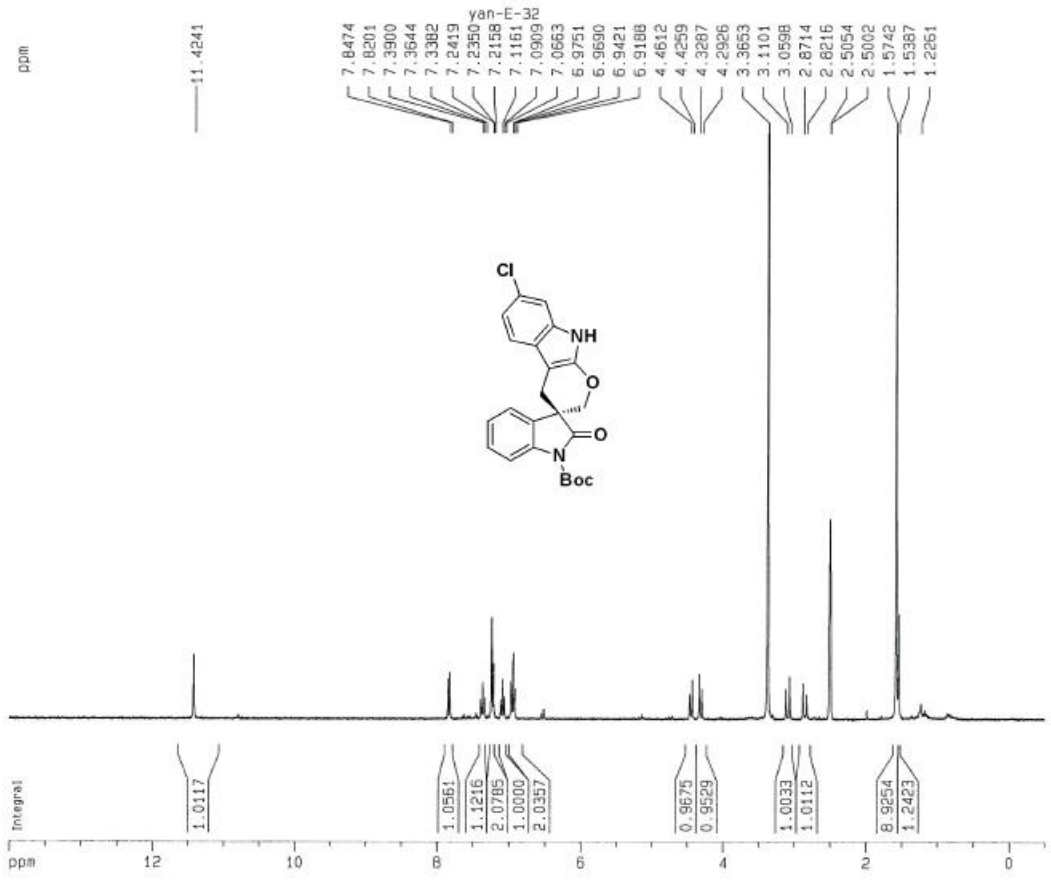
2k: Chiral

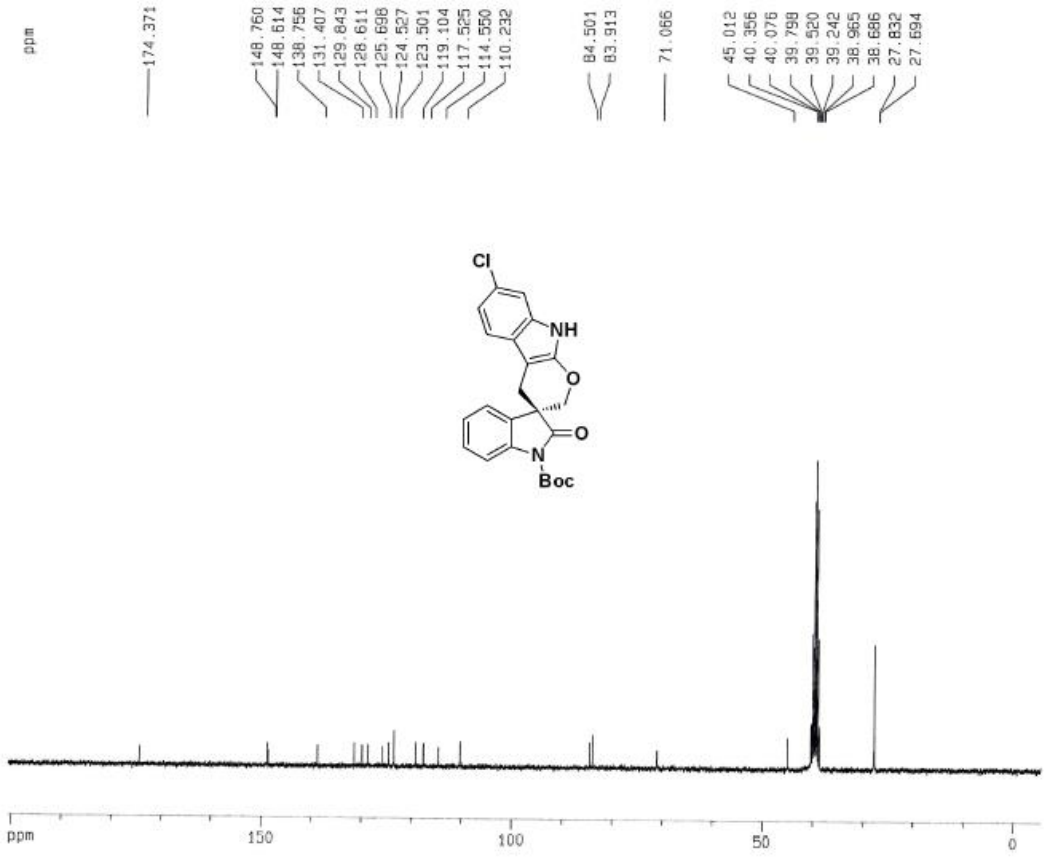


1 Det.A Ch1 / 254nm

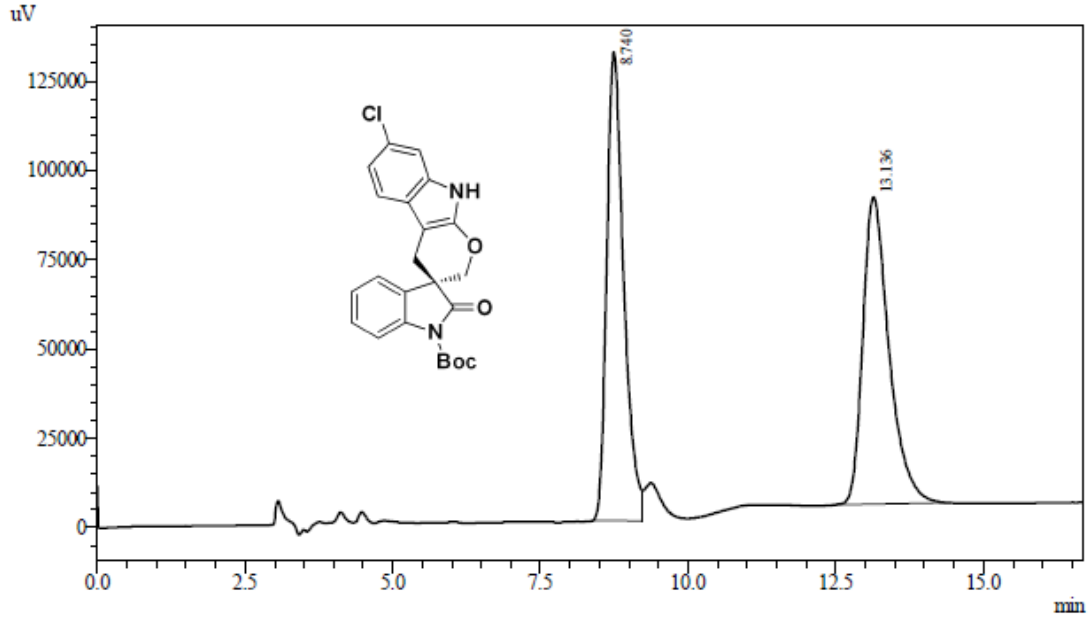
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.661	8299995	407951	97.322	98.254
2	13.372	228353	7251	2.678	1.746
Total		8528348	415202	100.000	100.000


yan-E-32
ppm
11.4241
7.8474
7.8201
7.3900
7.3644
7.3382
7.2419
7.2350
7.2158
7.1161
7.0909
7.0663
6.9751
6.9690
6.9421
6.9188
4.4612
4.4259
4.3287
4.2926
3.3653
3.1101
3.0598
2.8714
2.8216
2.5054
2.5002
1.5742
1.5387
1.2261
Cl
NH
O
O
N
Boc
Integral
1.0117
1.0561
1.1216
2.0785
1.0000
2.0357
0.9675
0.9529
1.0033
1.0112
8.9254
1.2423
ppm
12
10
8
6
4
2
0


ppm
174.371
148.760
148.614
138.756
131.407
129.843
128.611
125.698
124.527
123.501
119.104
117.525
114.550
110.232
84.501
83.913
71.066
45.012
40.356
40.076
39.798
39.520
39.242
38.965
38.686
27.832
27.694
Cl
NH
O
O
N
Boc
ppm
150
100
50
0

2l: Racemic

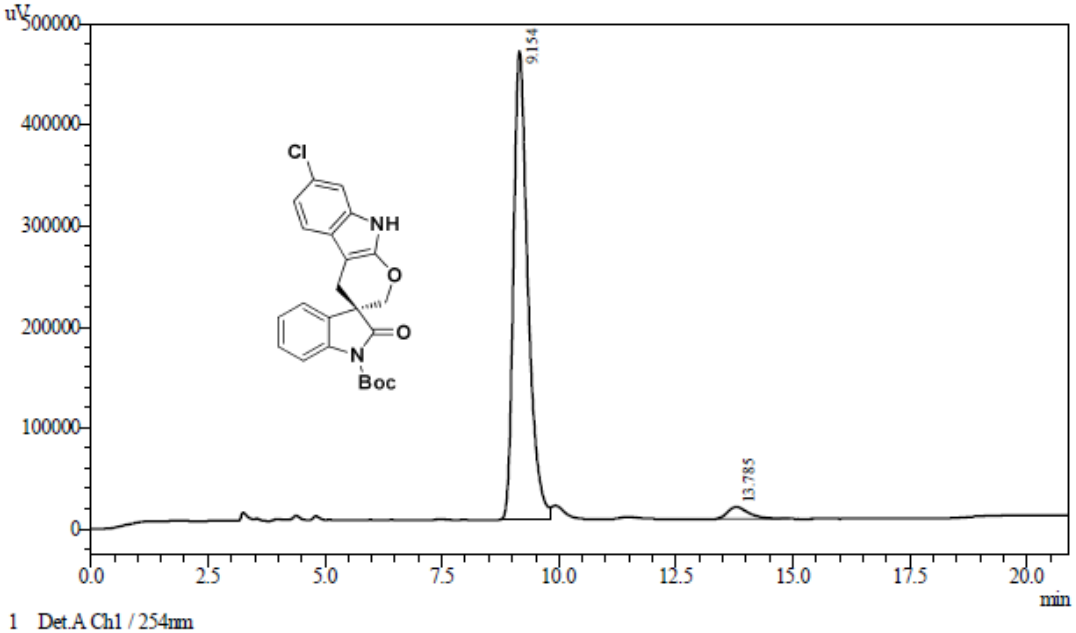


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.740	2631616	131131	49.801	60.400
2	13.136	2652663	85972	50.199	39.600
Total		5284279	217103	100.000	100.000

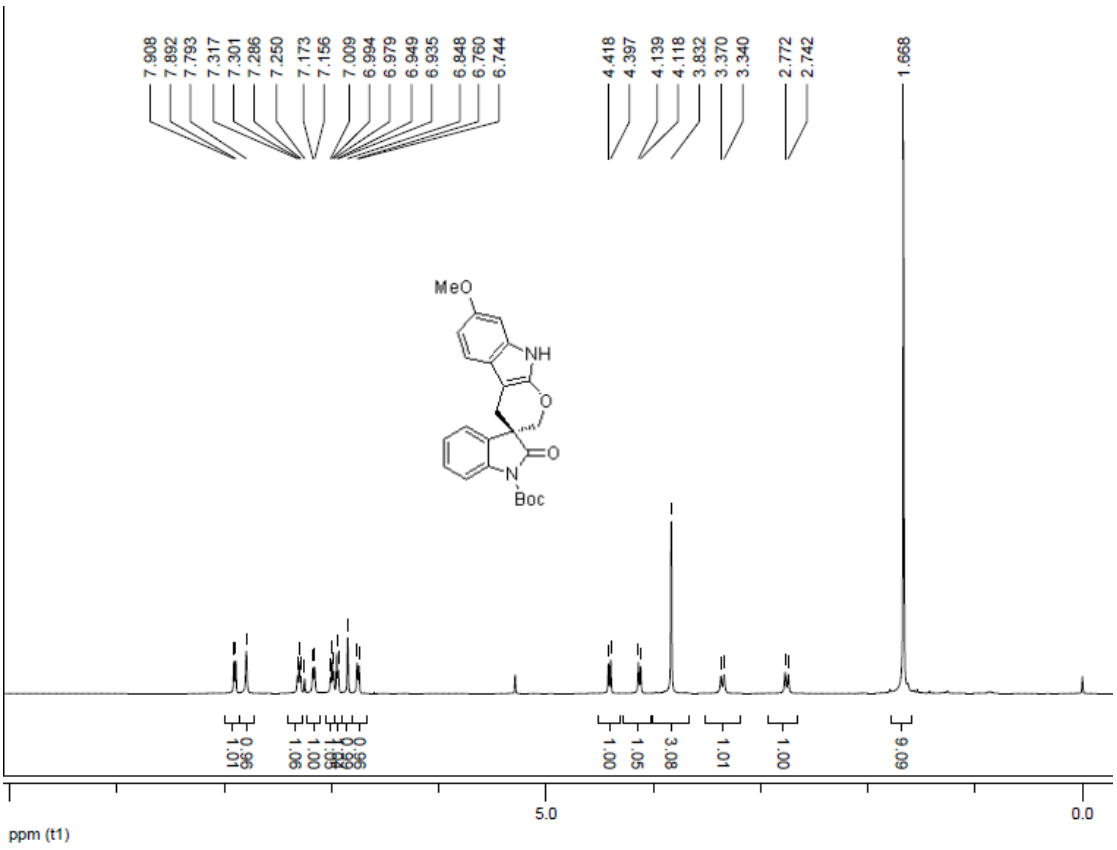
2l: Chiral

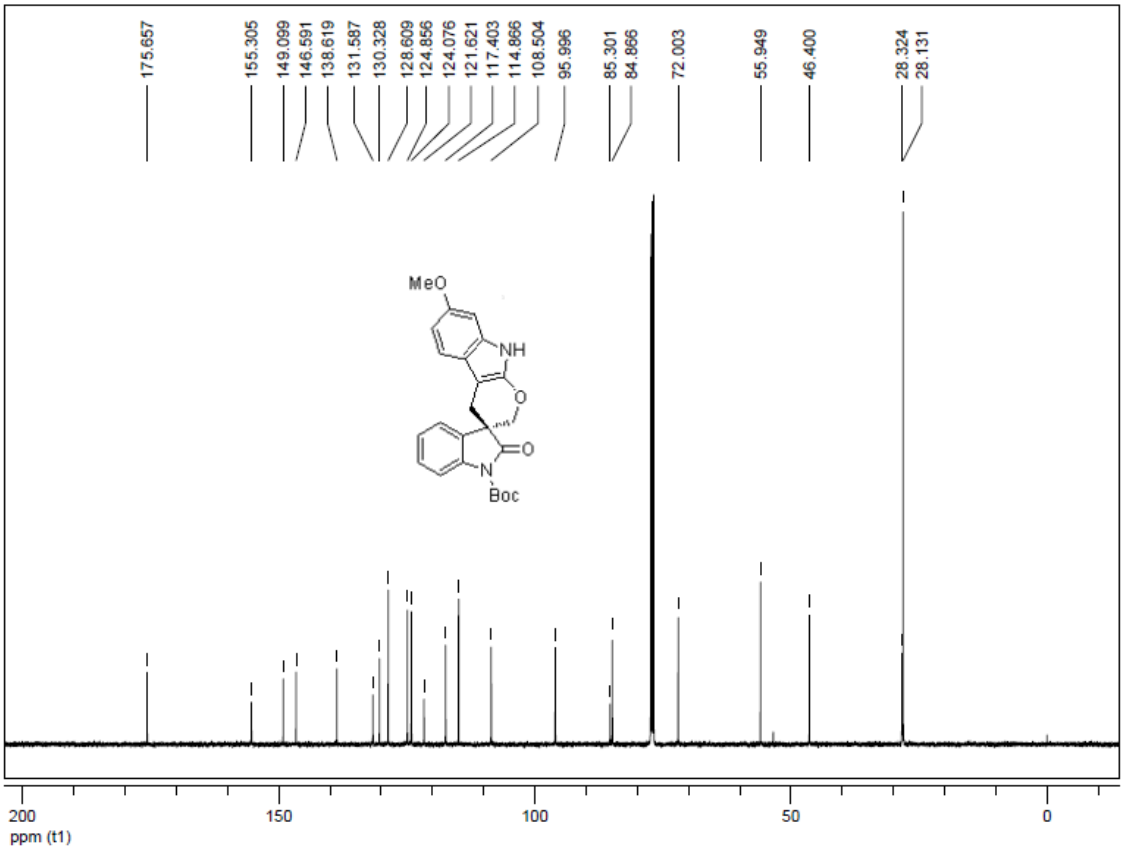


1 Det.A Ch1 / 254nm

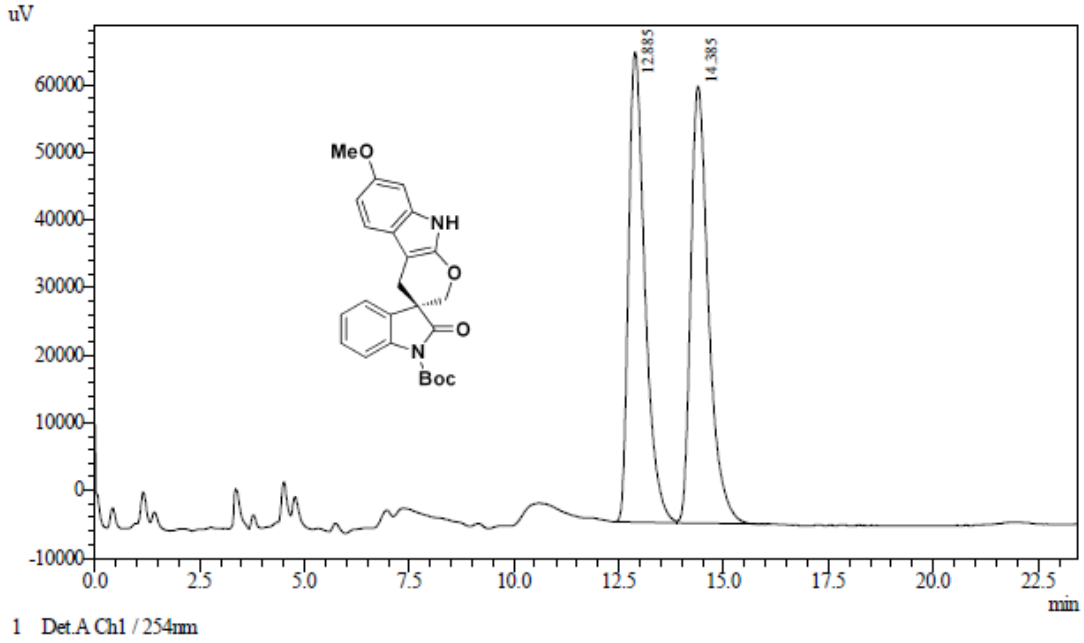
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.154	9925194	464145	96.259	97.476
2	13.785	385746	12019	3.741	2.524
Total		10310940	476164	100.000	100.000


7.908
7.892
7.793
7.317
7.301
7.286
7.250
7.173
7.156
7.009
6.994
6.979
6.949
6.935
6.848
6.760
6.744
4.418
4.397
4.139
4.118
3.832
3.370
3.340
2.772
2.742
1.668
MeO
NH
O
O
N
Boc
1.01
0.96
1.06
1.00
1.00
1.00
1.05
3.08
1.01
1.00
9.09
5.0
0.0
ppm (t1)


175.657
155.305
149.099
146.591
138.619
131.587
130.328
128.609
124.856
124.076
121.621
117.403
114.866
108.504
95.996
85.301
84.866
72.003
55.949
46.400
28.324
28.131
MeO
NH
O
O
N
Boc
200
150
100
50
0
ppm (t1)

2m: Racemic

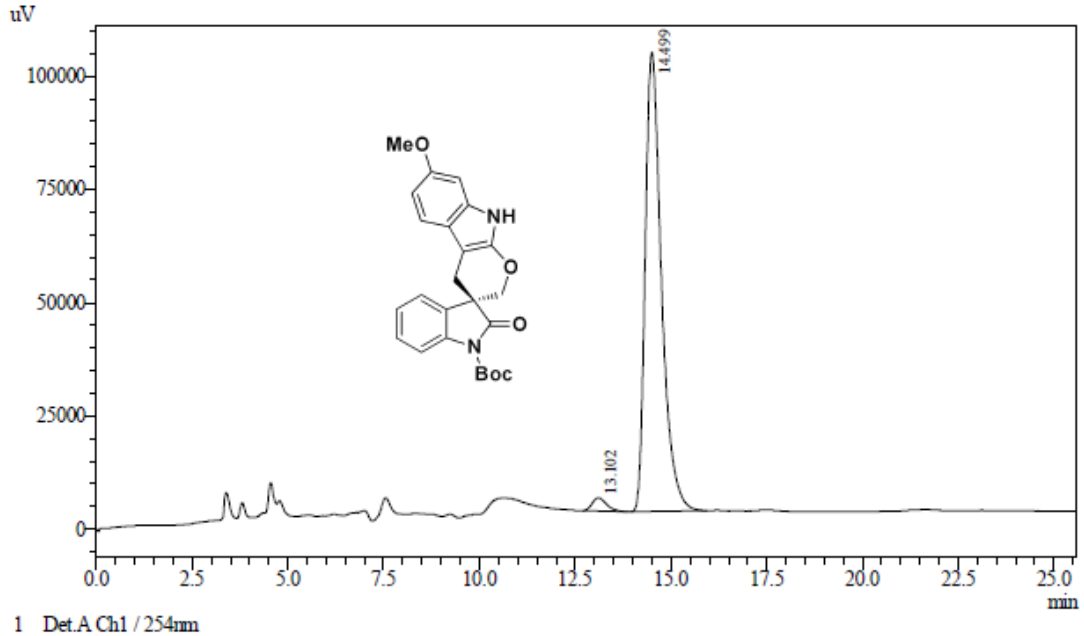


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.885	1887428	69486	49.760	51.826
2	14.385	1905668	64589	50.240	48.174
Total		3793096	134075	100.000	100.000

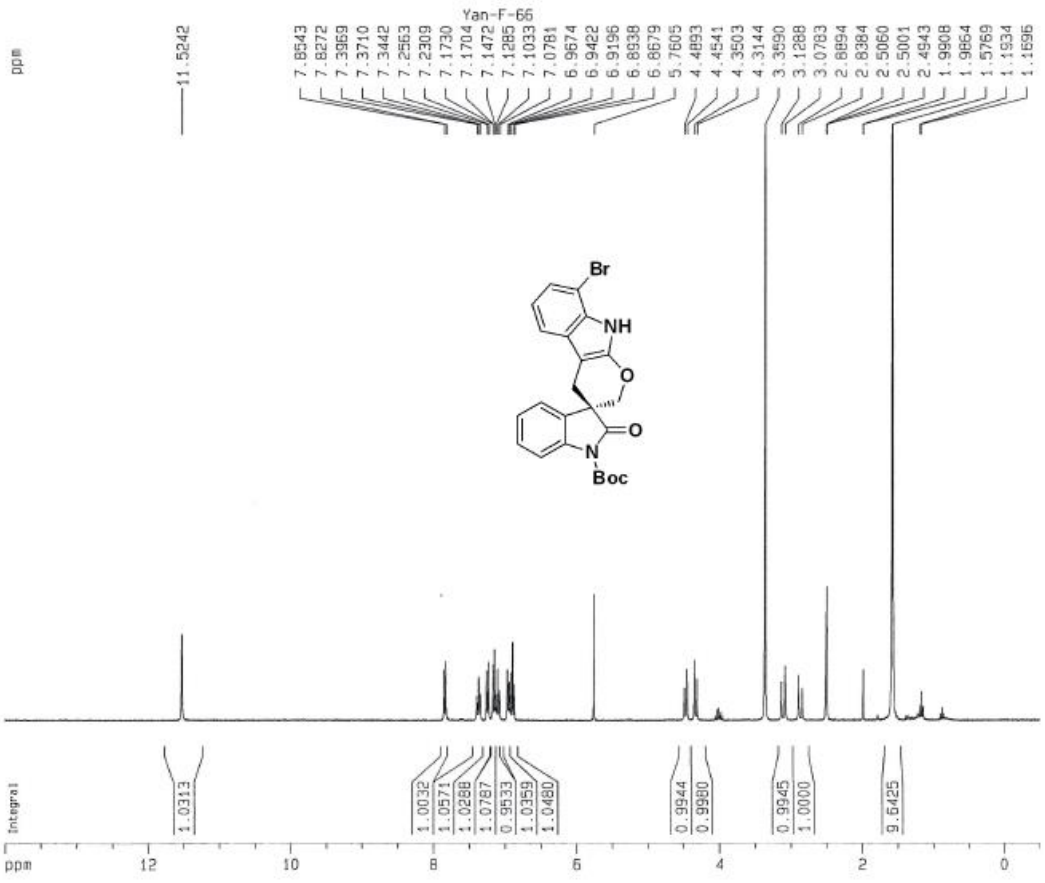
2m: Chiral

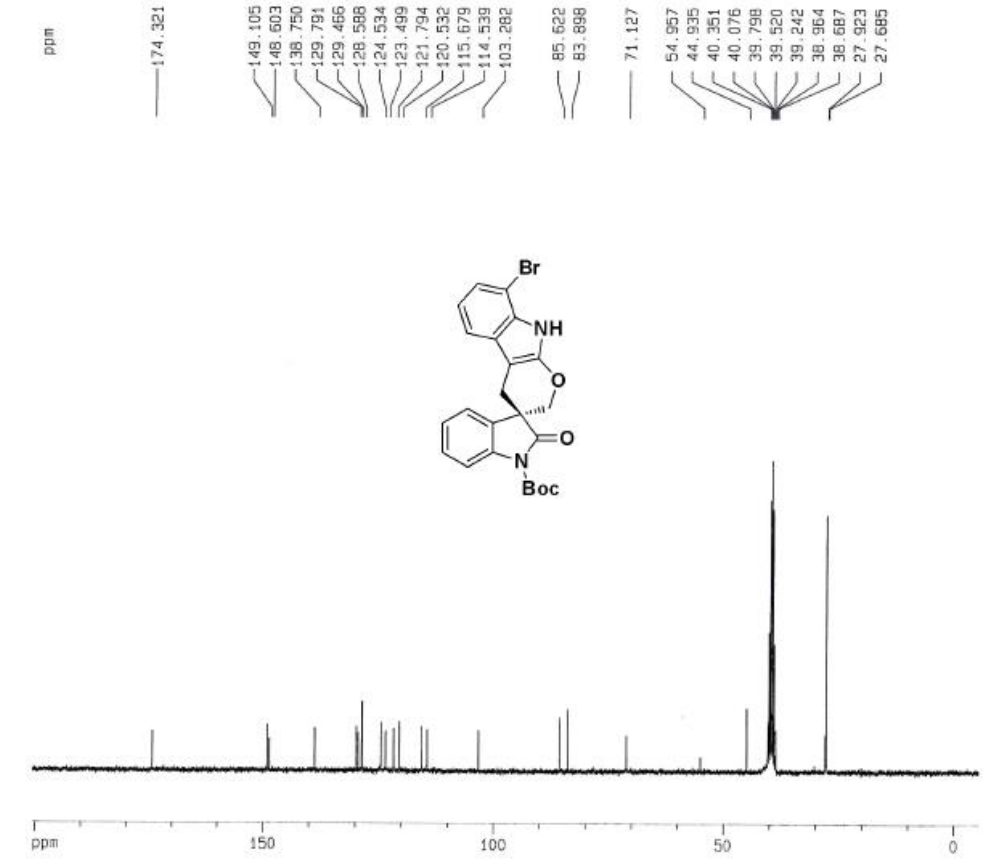


1 Det.A Ch1 / 254nm

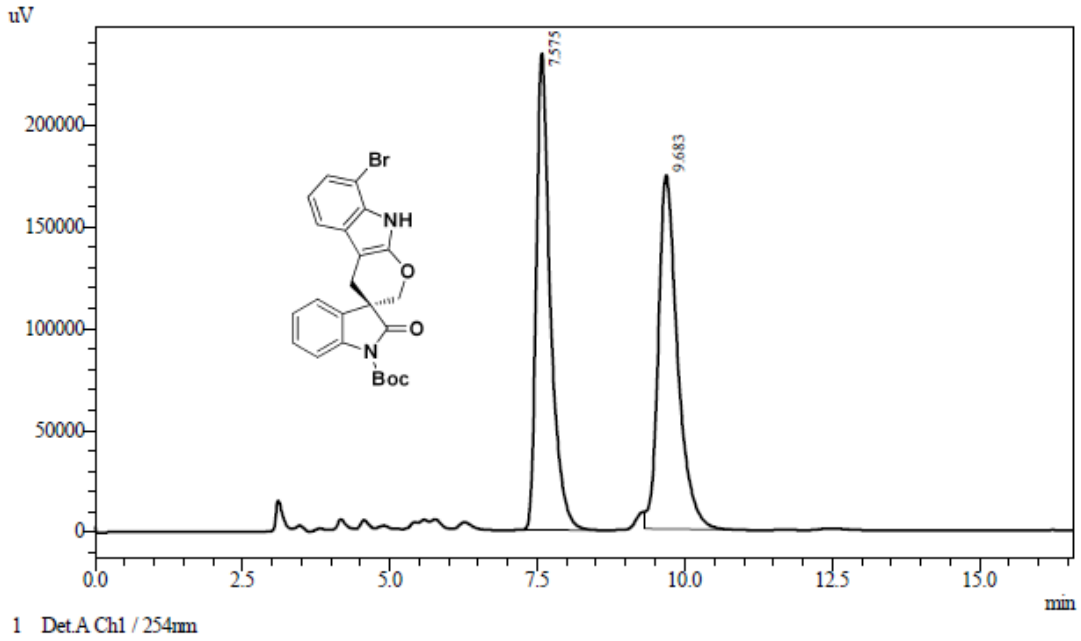
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.102	76980	2925	2.504	2.804
2	14.499	2997909	101379	97.496	97.196
Total		3074889	104304	100.000	100.000


Yan-F-66
ppm
11.5242
7.8543
7.8272
7.3969
7.3710
7.3442
7.2563
7.2309
7.1730
7.1704
7.1472
7.1285
7.1033
7.0781
6.9674
6.9422
6.9196
6.8938
6.8679
5.7605
4.4893
4.4541
4.3503
4.3144
3.3590
3.1288
3.0783
2.8894
2.8384
2.5060
2.5001
2.4943
1.9908
1.9864
1.5769
1.1934
1.1696
Br
NH
O
O
N
Boc
Integral
1.0313
1.0032
1.0571
1.0288
1.0787
0.9533
1.0359
1.0480
0.9944
0.9980
0.9945
1.0000
9.6425
ppm
12
10
8
6
4
2
0


ppm
174.321
149.105
148.603
138.750
129.791
129.466
128.588
124.534
123.499
121.794
120.532
115.679
114.539
103.282
85.622
83.898
71.127
54.957
44.935
40.351
40.076
39.798
39.520
39.242
38.964
38.687
27.923
27.685
Br
NH
O
O
N
Boc
ppm
150
100
50
0

2n: Racemic

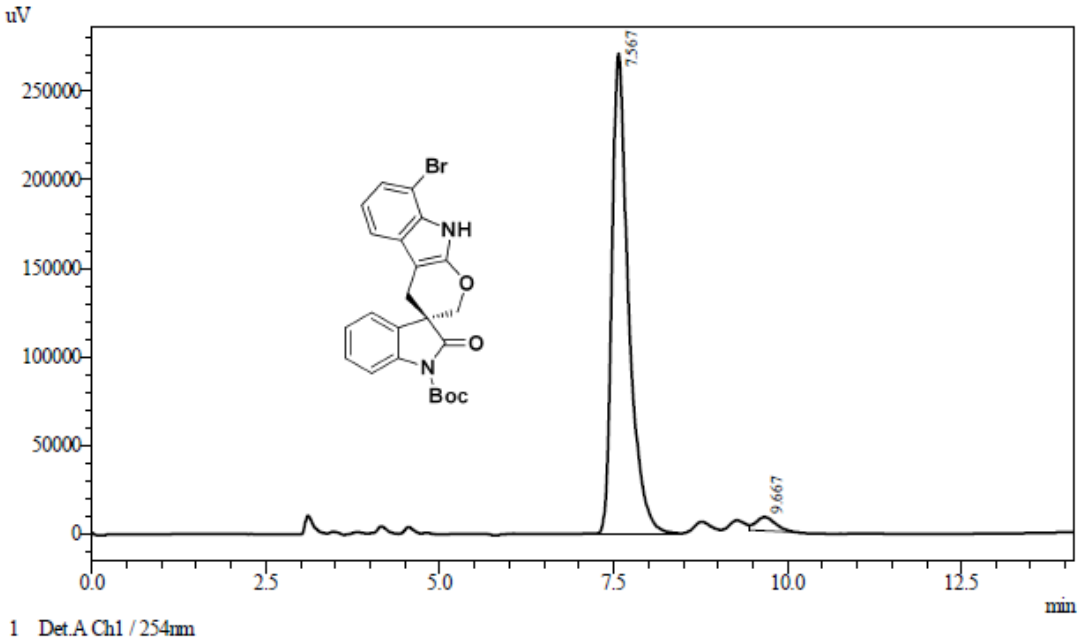


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.575	3882755	233855	49.586	57.395
2	9.683	3947621	173595	50.414	42.605
Total		7830376	407450	100.000	100.000

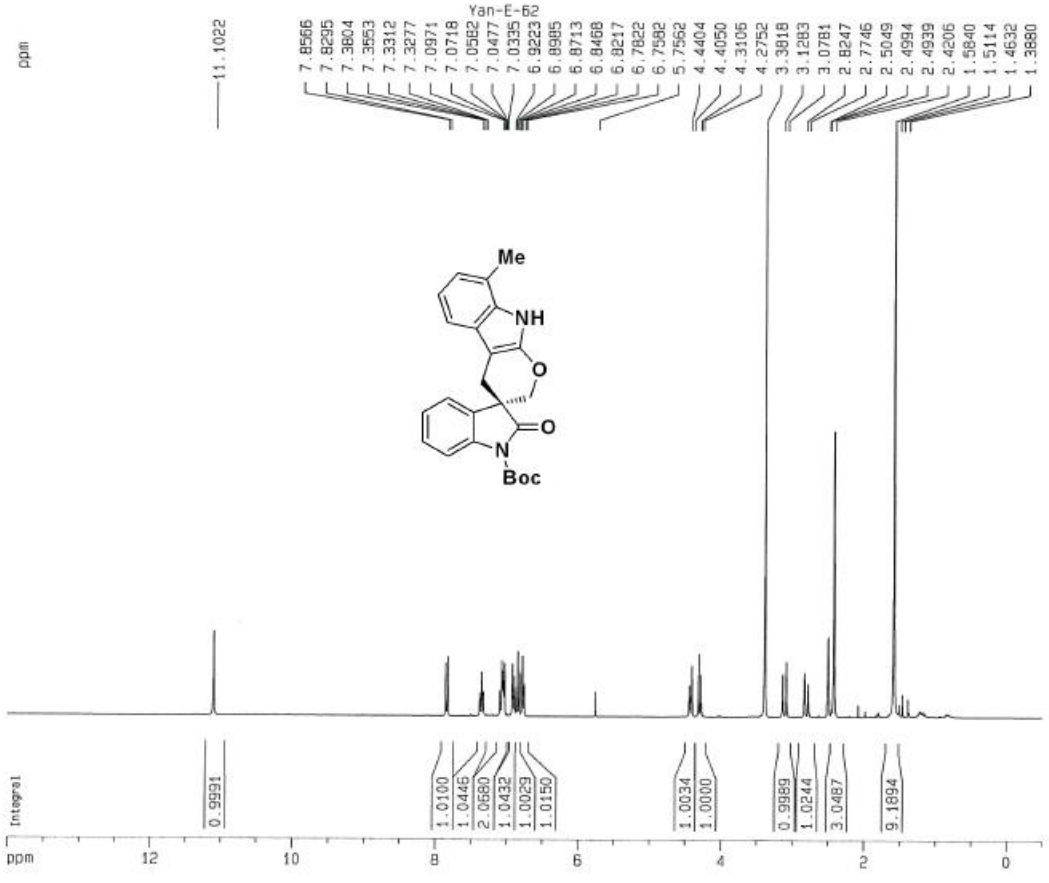
2n: Chiral

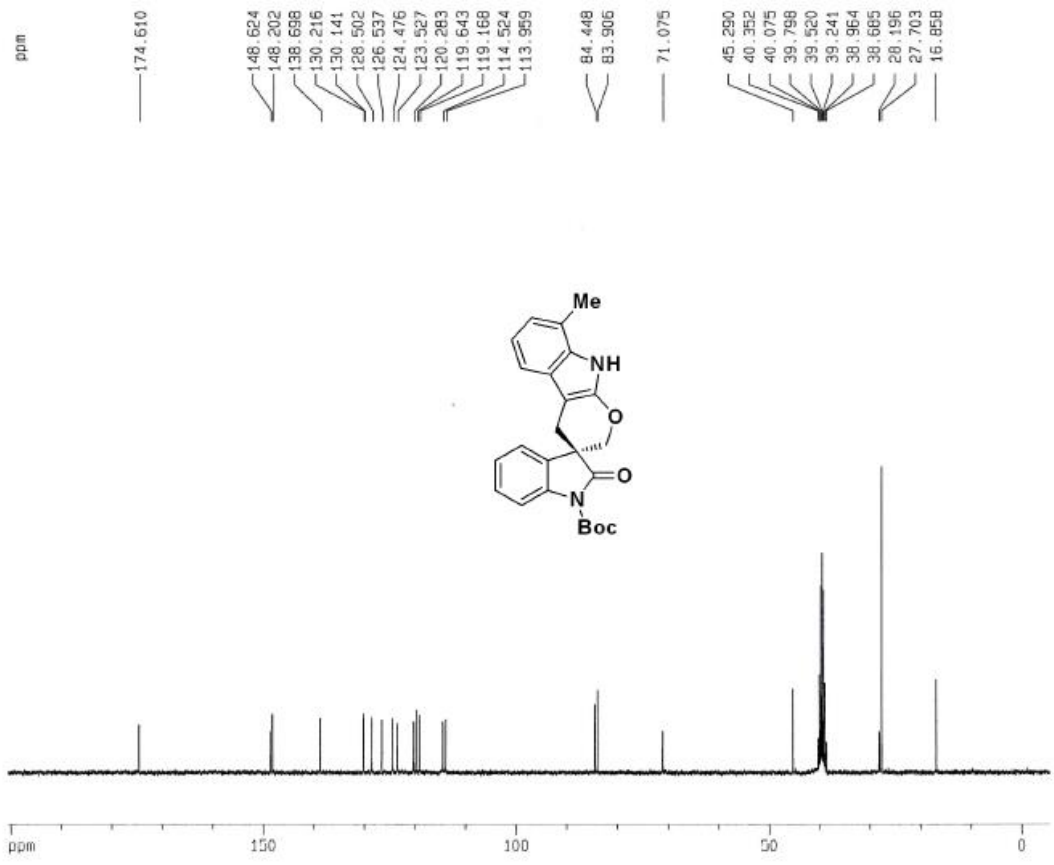


1 Det.A Ch1 / 254nm

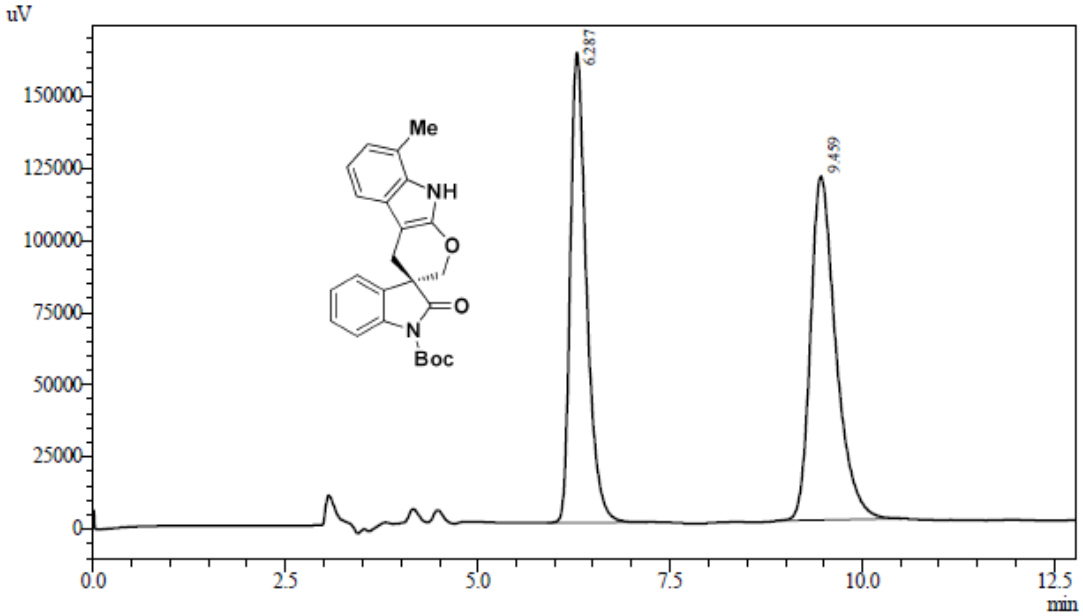
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.567	4491032	270323	96.700	97.217
2	9.667	153269	7739	3.300	2.783
Total		4644301	278062	100.000	100.000


Yan-E-62
ppm
11.1022
7.8566
7.8295
7.3804
7.3553
7.3312
7.3277
7.0971
7.0718
7.0562
7.0477
7.0335
6.9223
6.8985
6.8713
6.8468
6.8217
6.7822
6.7582
5.7562
4.4404
4.4050
4.3106
4.2752
3.3818
3.1283
3.0781
2.8247
2.7746
2.5049
2.4994
2.4939
2.4206
1.5840
1.5114
1.4632
1.3880
Me
NH
O
O
N
Boc
Integral
0.9991
1.0100
1.0446
2.0680
1.0432
1.0029
1.0150
1.0034
1.0000
0.9989
1.0244
3.0487
9.1894
ppm
12
10
8
6
4
2
0


ppm
174.610
148.624
148.202
138.698
130.216
130.141
128.502
126.537
124.476
123.527
120.283
119.643
119.168
114.524
113.959
84.448
83.906
71.075
45.290
40.352
40.075
39.798
39.520
39.241
38.964
38.685
28.196
27.703
16.858
Me
NH
O
O
N
Boc
ppm
150
100
50
0

2o: Racemic

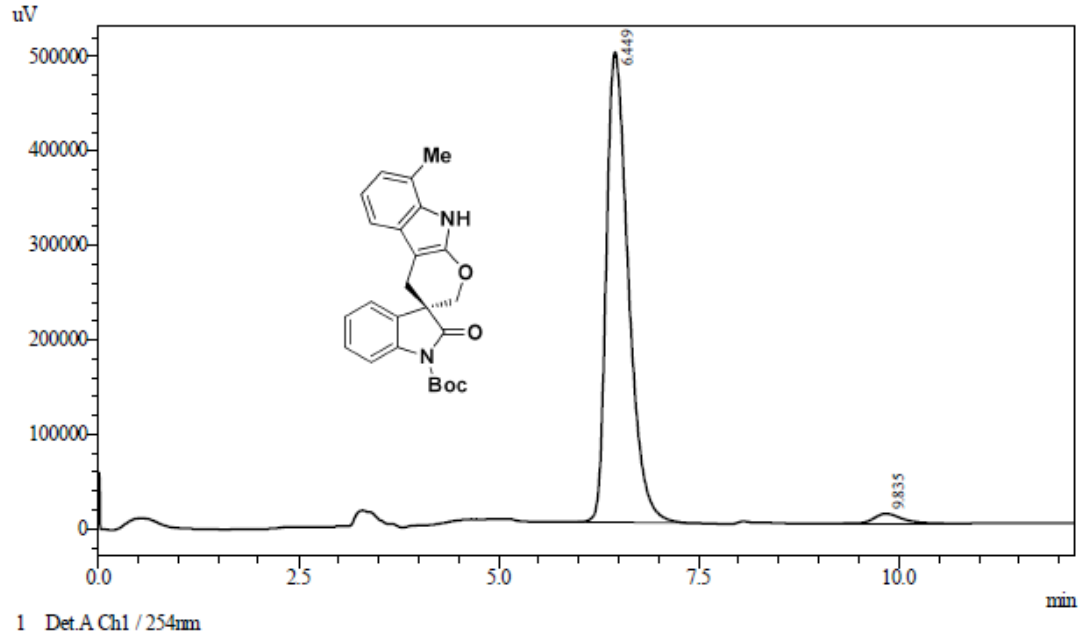


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.287	2391233	163018	46.555	57.785
2	9.459	2745164	119092	53.445	42.215
Total		5136397	282110	100.000	100.000

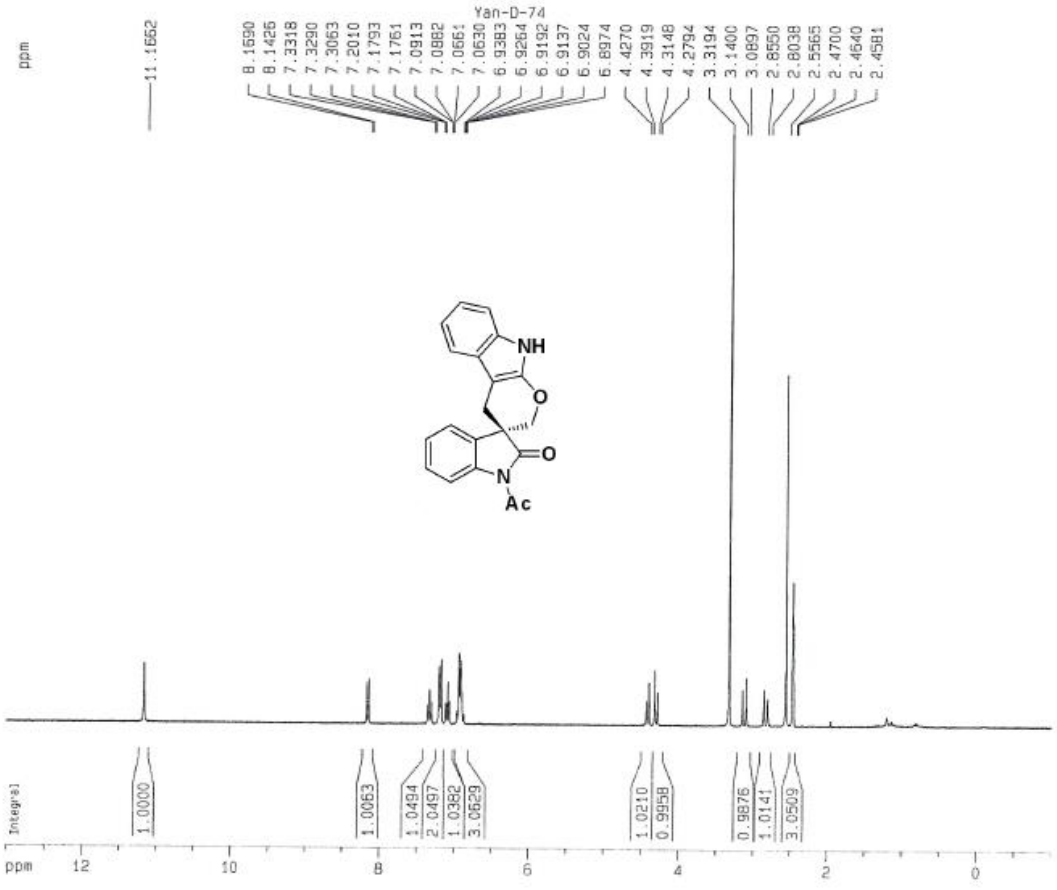
2o: Chiral

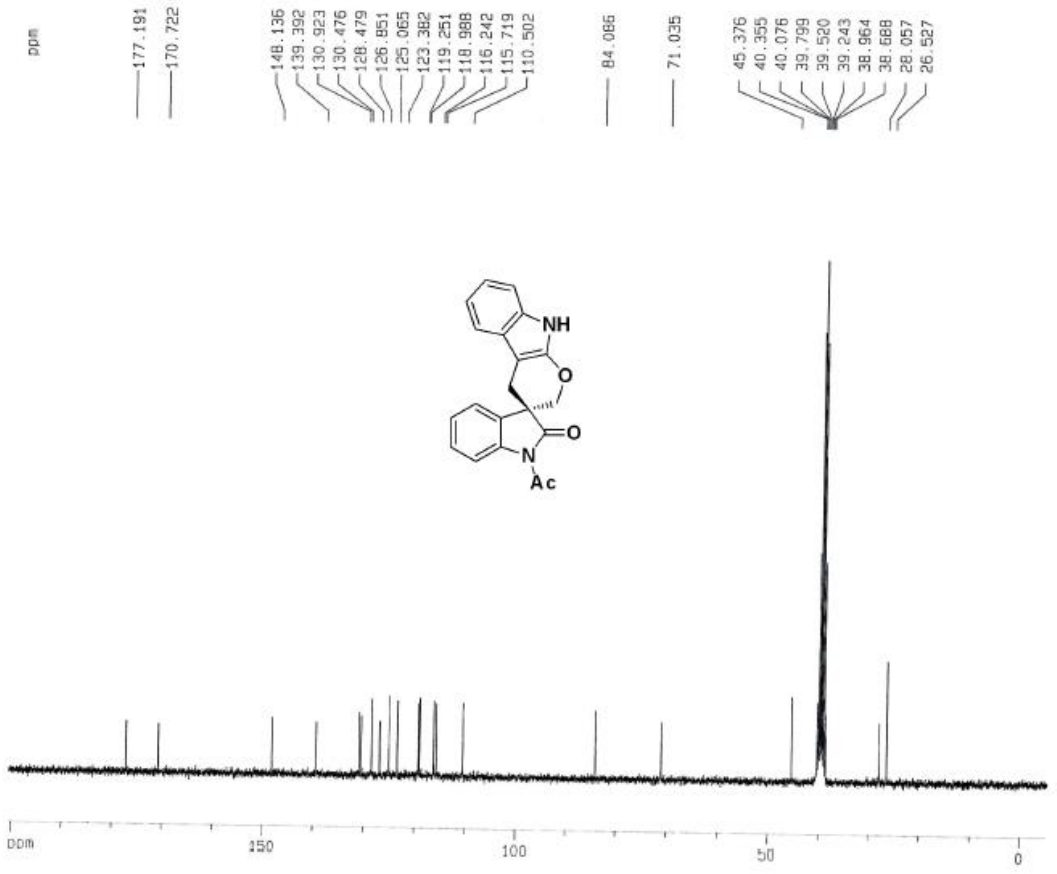


1 Det.A Ch1 / 254nm

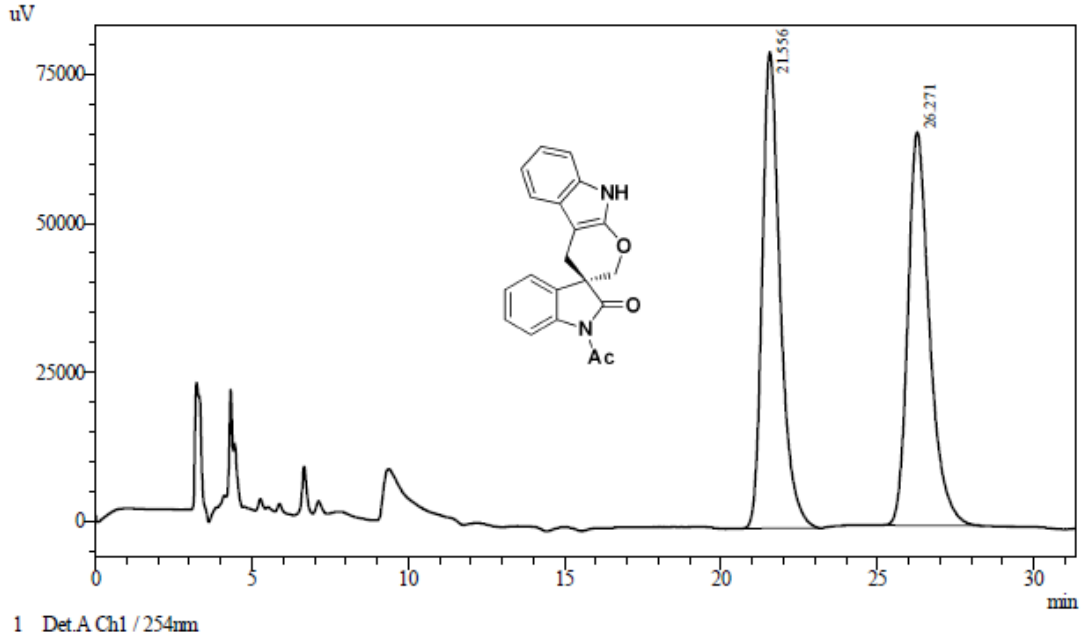
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.449	9532034	497230	97.502	97.974
2	9.835	244244	10281	2.498	2.026
Total		9776278	507511	100.000	100.000


Yan-D-74
ppm
11.1652
8.1590
8.1425
7.3318
7.3290
7.3063
7.2010
7.1793
7.1761
7.0913
7.0882
7.0661
7.0630
6.9383
6.9264
6.9192
6.9137
6.9024
6.8974
4.4270
4.3919
4.3148
4.2794
3.3194
3.1400
3.0897
2.8550
2.8038
2.5565
2.4700
2.4640
2.4581
NH
O
O
N
Ac
Integral
1.0000
1.0063
1.0494
2.0497
1.0382
3.0629
1.0210
0.9958
0.9876
1.0141
3.0509
ppm
12
10
8
6
4
2
0


ppm
177.191
170.722
148.136
139.392
130.923
130.476
128.479
126.851
125.065
123.382
119.251
118.988
116.242
115.719
110.502
84.066
71.035
45.376
40.355
40.076
39.799
39.520
39.243
38.964
38.688
28.057
26.527
NH
O
O
N
Ac
ppm
150
100
50
0

2p: Racemic

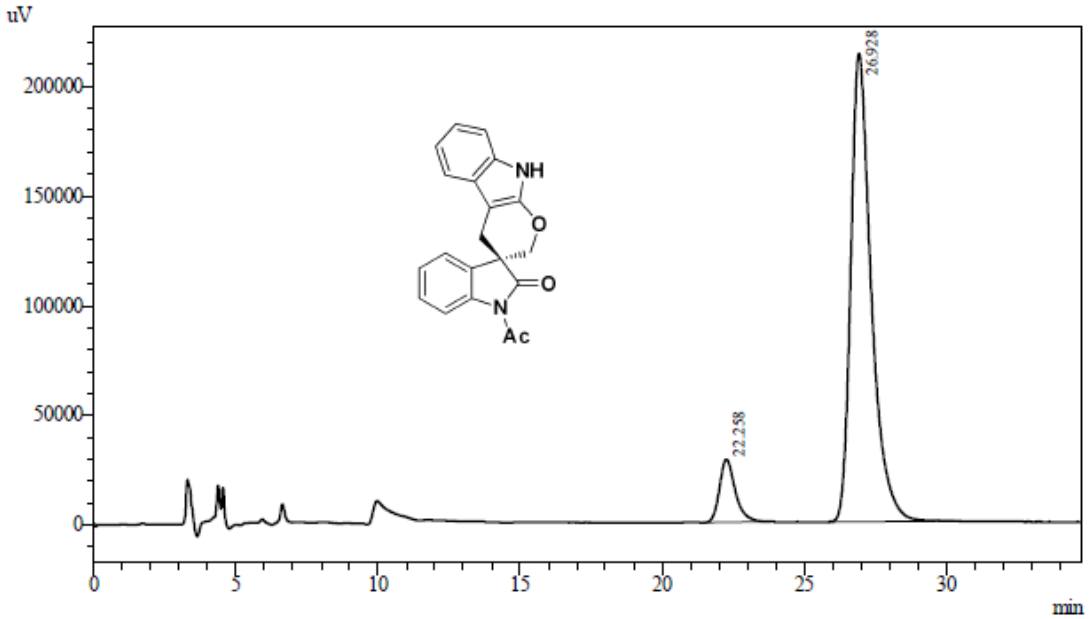


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.556	3199847	79897	50.025	54.776
2	26.271	3196685	65963	49.975	45.224
Total		6396532	145859	100.000	100.000

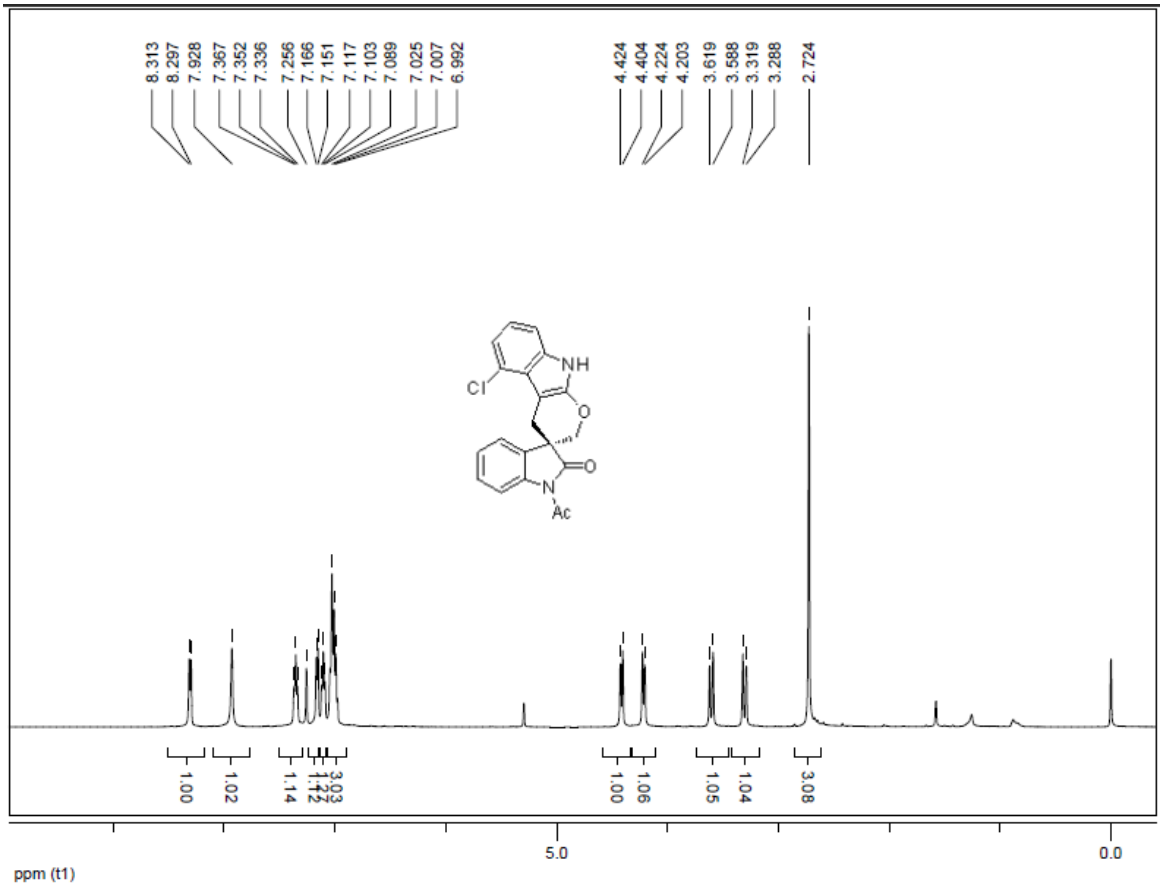
2p: Chiral

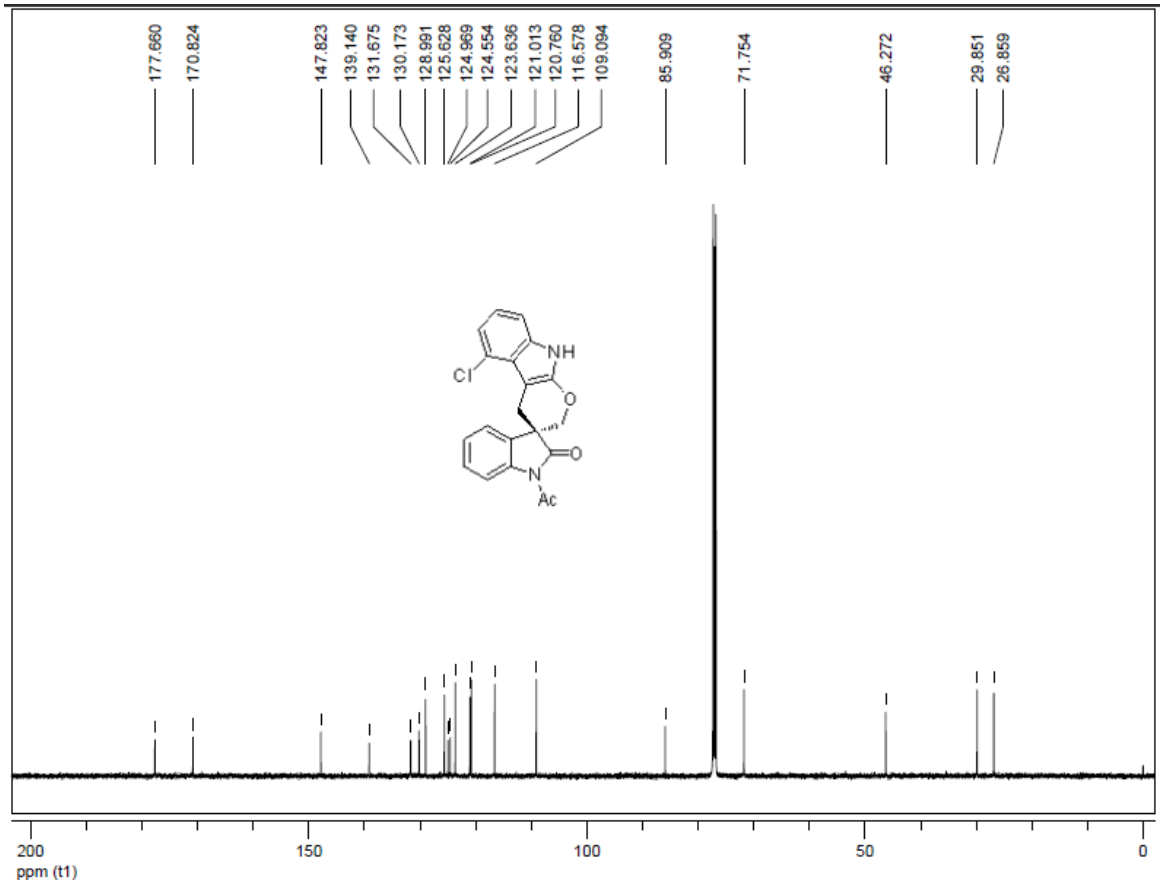


1 Det.A Ch1 / 254nm

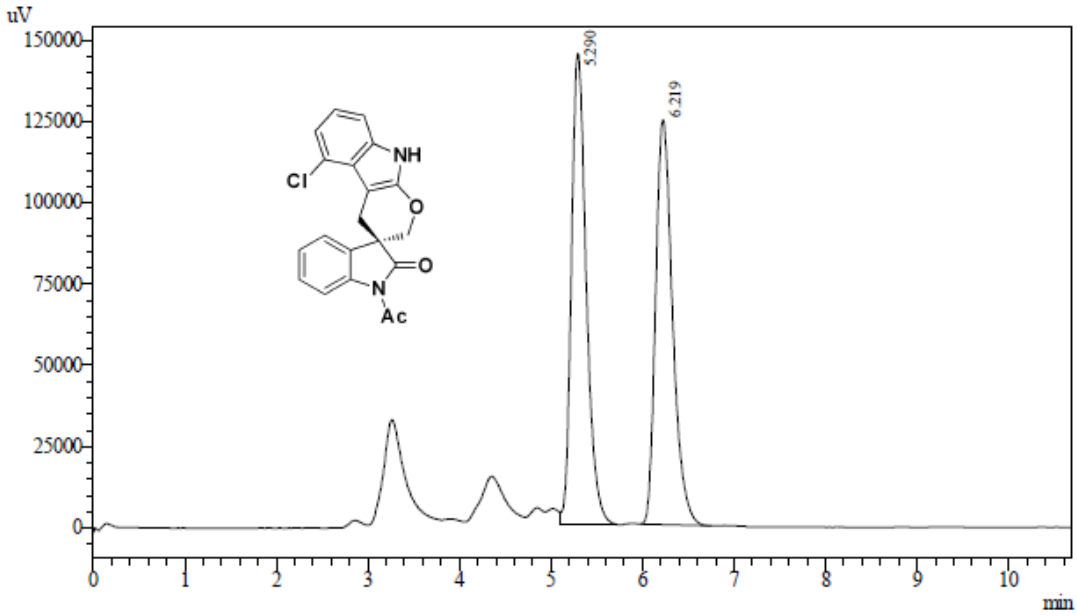
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.258	1117662	28657	9.450	11.829
2	26.928	10709754	213613	90.550	88.171
Total		11827415	242270	100.000	100.000


8.313
8.297
7.928
7.367
7.352
7.336
7.256
7.166
7.151
7.117
7.103
7.089
7.025
7.007
6.992
4.424
4.404
4.224
4.203
3.619
3.588
3.319
3.288
2.724
Cl
NH
O
O
N
Ac
1.00
1.02
1.14
1.42
1.22
3.03
1.00
1.06
1.05
1.04
3.08
5.0
0.0
ppm (t1)


177.660
170.824
147.823
139.140
131.675
130.173
128.991
125.628
124.969
124.554
123.636
121.013
120.760
116.578
109.094
85.909
71.754
46.272
29.851
26.859
Cl
NH
O
O
N
Ac
200
150
100
50
0
ppm (t1)

2q: Racemic

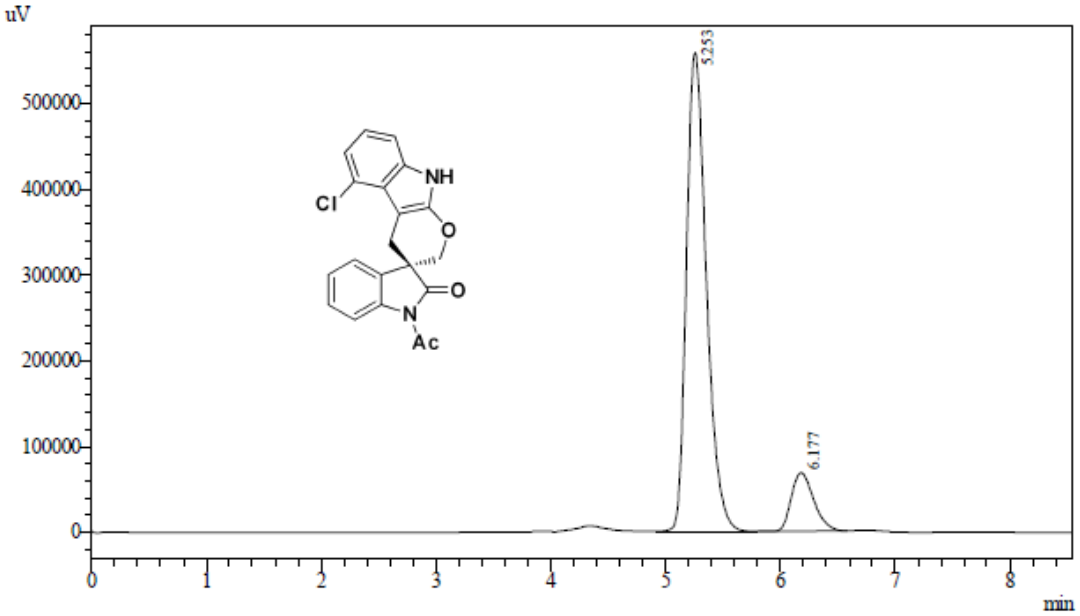


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.290	1629156	144821	50.379	53.761
2	6.219	1604623	124557	49.621	46.239
Total		3233779	269378	100.000	100.000

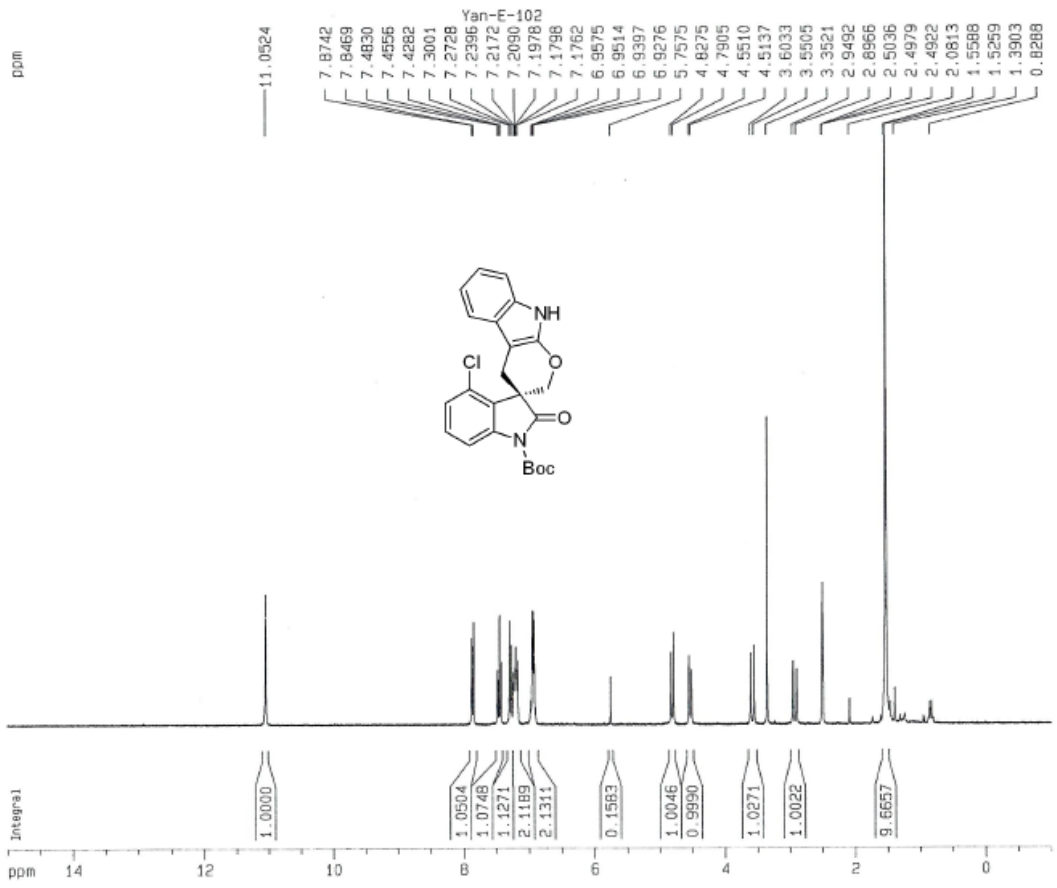
2q: Chiral

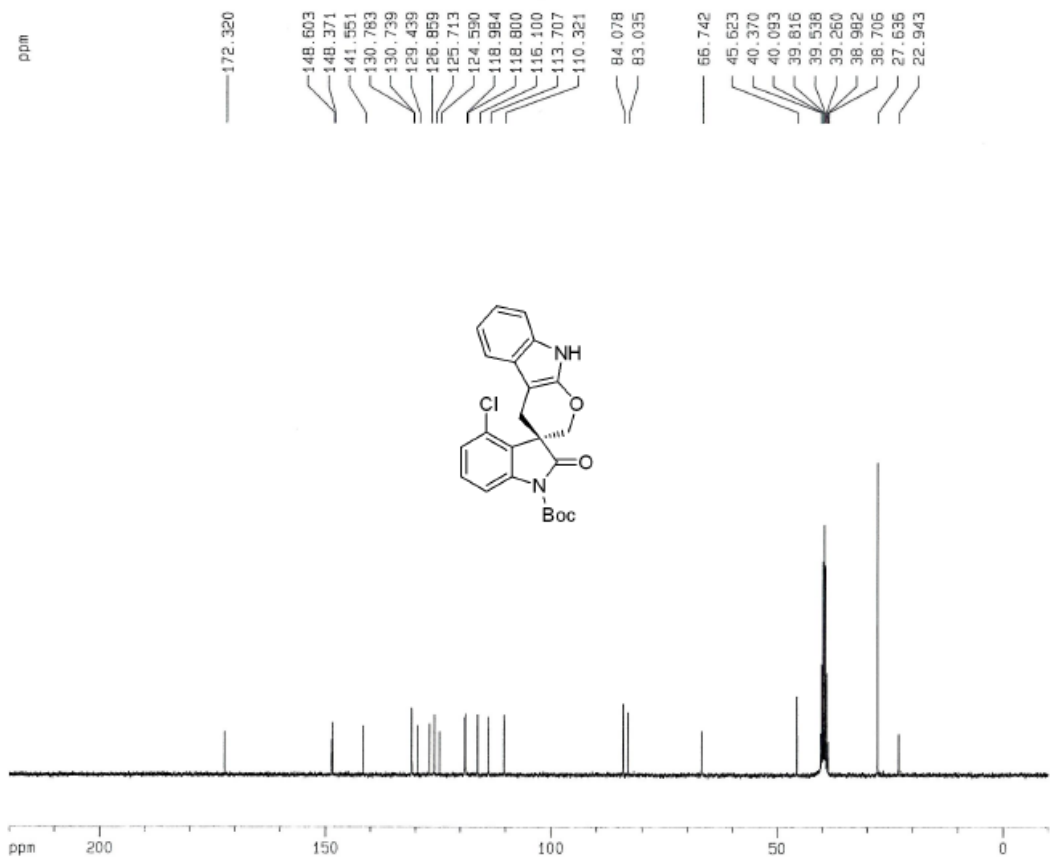


1 Det.A Ch1 / 254nm

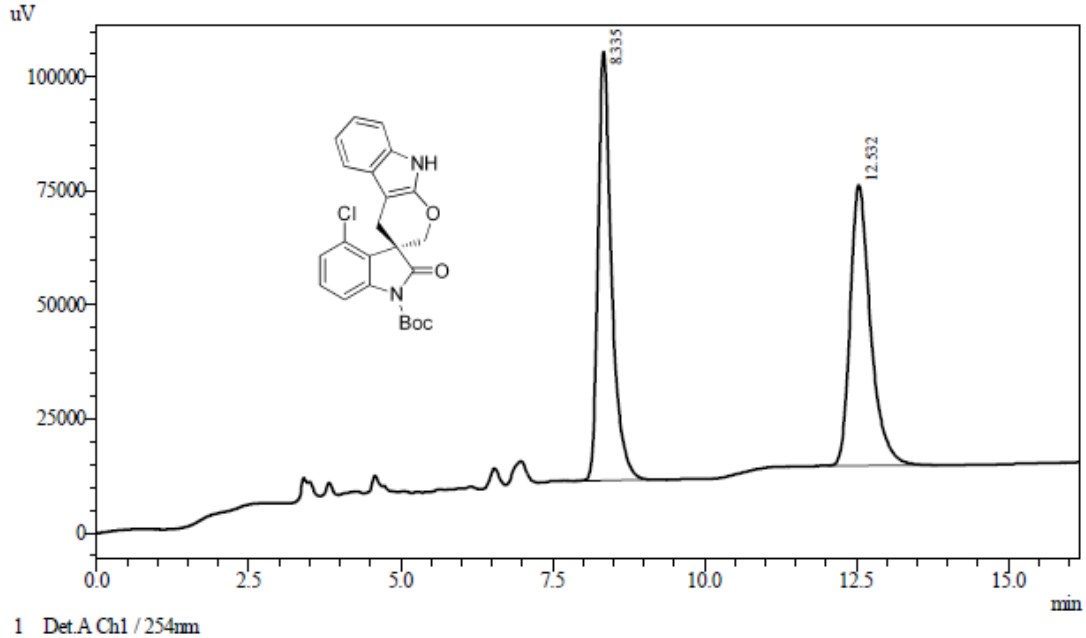
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.253	6754407	558641	87.871	89.106
2	6.177	932344	68301	12.129	10.894
Total		7686750	626942	100.000	100.000


Yan-E-102
ppm
11.0524
7.8742
7.8469
7.4830
7.4556
7.4282
7.3001
7.2728
7.2396
7.2172
7.2090
7.1978
7.1798
7.1762
6.9575
6.9514
6.9397
6.9276
5.7575
4.8275
4.7905
4.5510
4.5137
3.6033
3.5505
3.3521
2.9492
2.8966
2.5036
2.4979
2.4922
2.0813
1.5588
1.5259
1.3903
0.8288
NH
Cl
O
O
N
Boc
Integral
1.0000
1.0504
1.0748
1.1271
2.1189
2.1311
0.1583
1.0046
0.9990
1.0271
1.0022
9.6657
ppm
14
12
10
8
6
4
2
0


ppm
172.320
148.603
148.371
141.551
130.783
130.739
129.439
126.859
125.713
124.590
118.984
118.800
116.100
113.707
110.321
84.078
83.035
66.742
45.623
40.370
40.093
39.816
39.538
39.260
38.982
38.705
27.636
22.943
NH
Cl
O
O
N
Boc
ppm
200
150
100
50
0

2r: Racemic

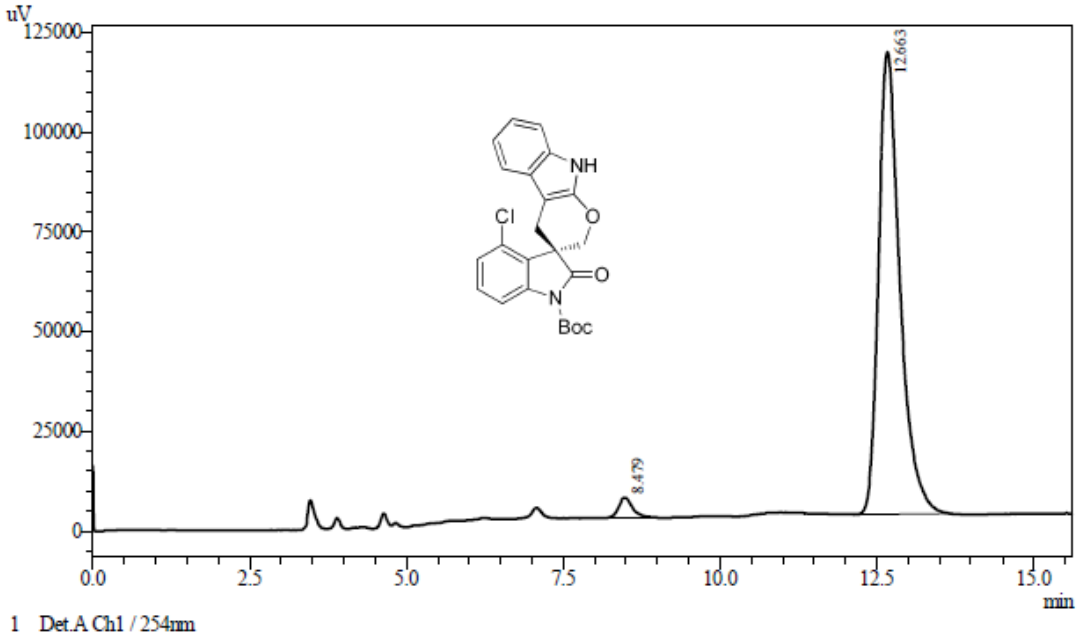


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.335	1459981	94001	50.315	60.448
2	12.532	1441692	61505	49.685	39.552
Total		2901673	155506	100.000	100.000

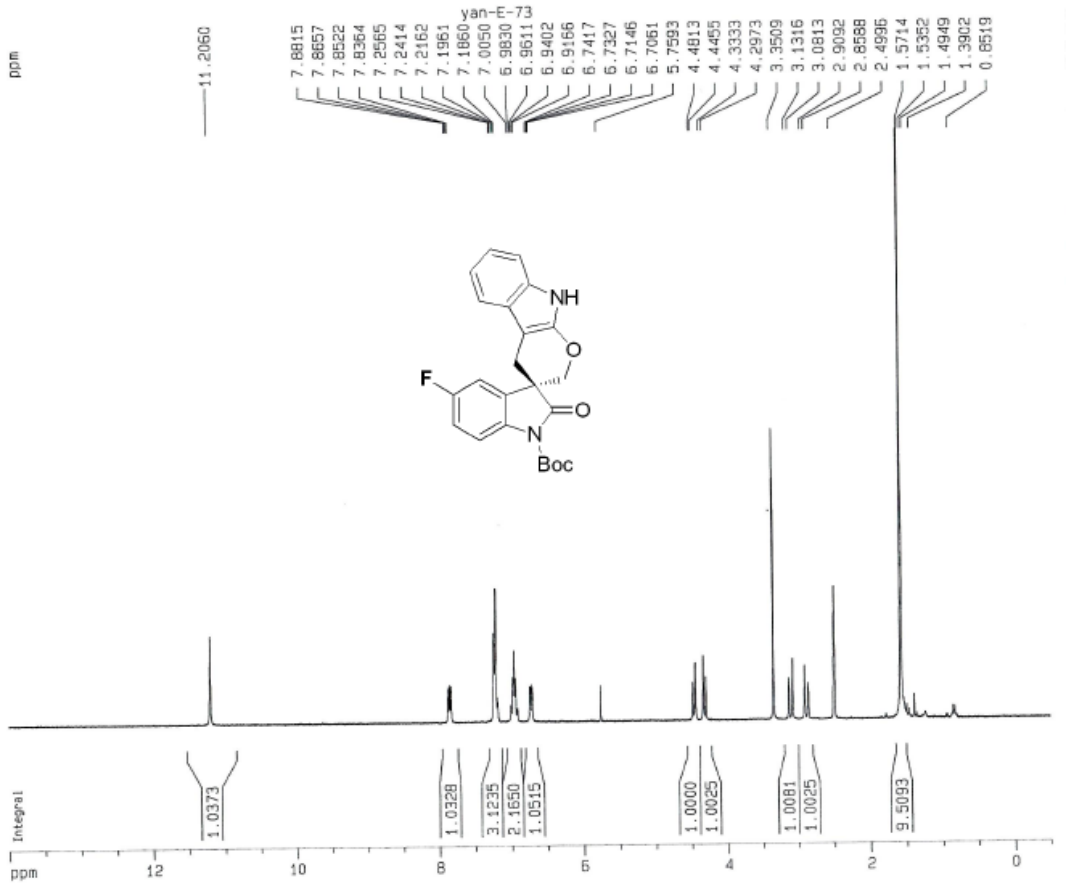
2r: Chiral

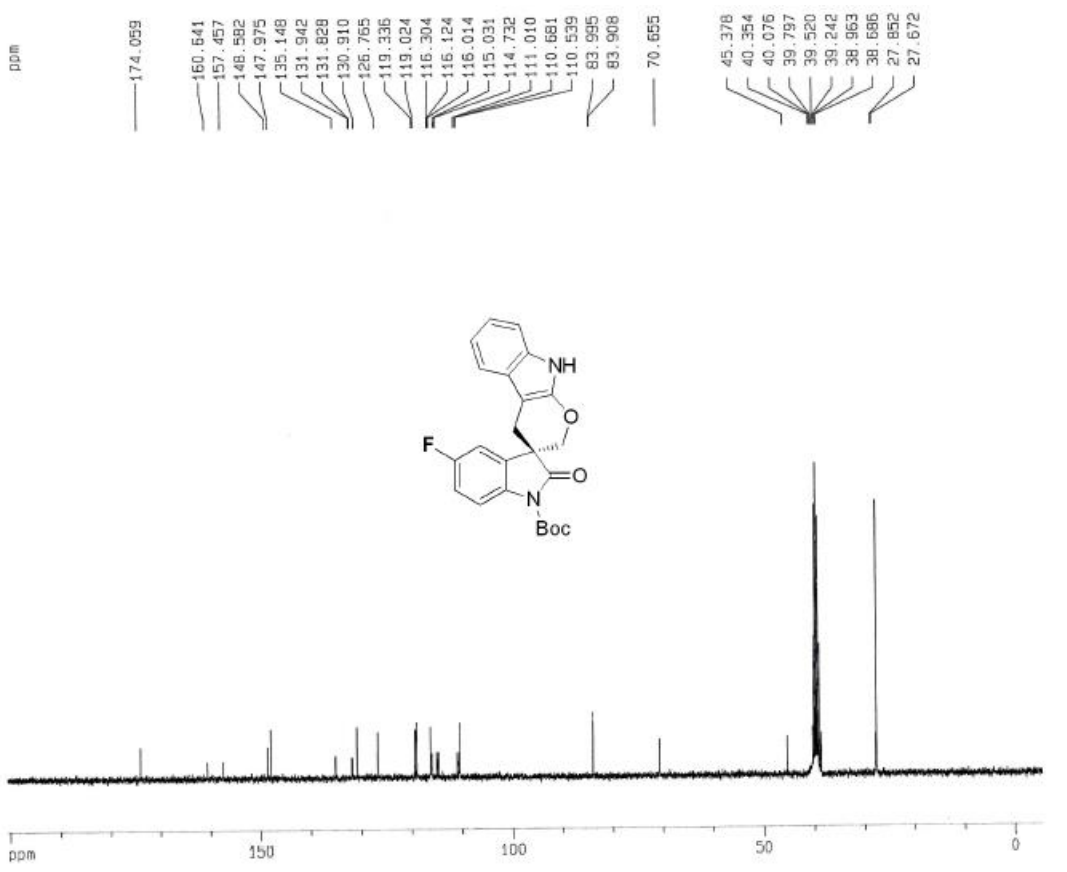


1 Det.A Ch1 / 254nm

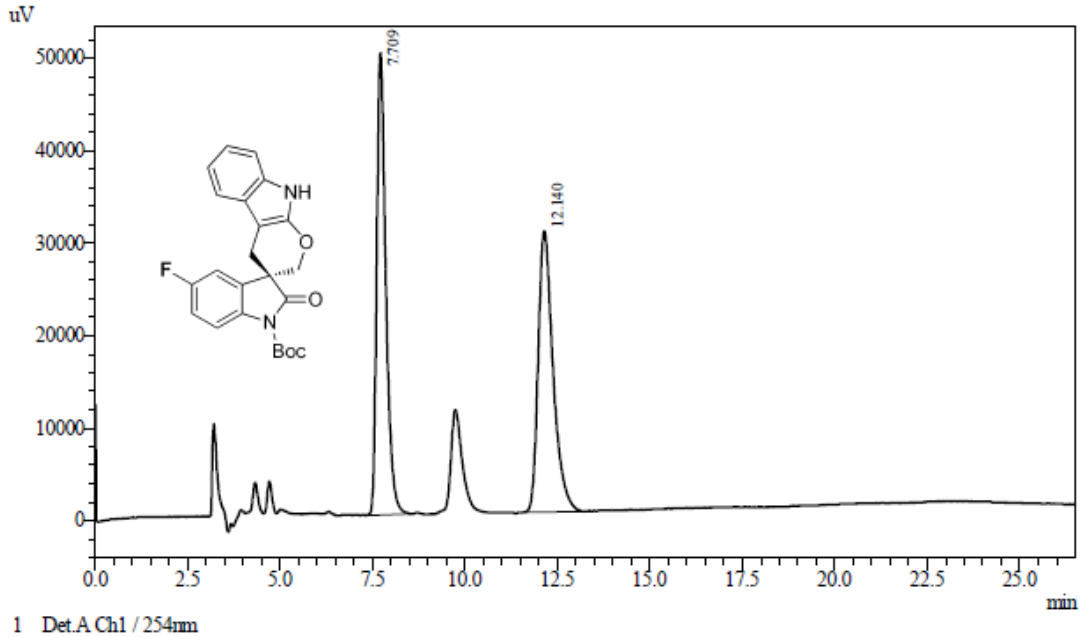
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.479	79715	5101	2.815	4.218
2	12.663	2751807	115822	97.185	95.782
Total		2831522	120923	100.000	100.000


yan-E-73
ppm
11.2060
7.8815
7.8657
7.8522
7.8364
7.2565
7.2414
7.2162
7.1961
7.1860
7.0050
6.9830
6.9611
6.9402
6.9166
6.7417
6.7327
6.7146
6.7061
5.7593
4.4813
4.4455
4.3333
4.2973
3.3509
3.1316
3.0813
2.9092
2.8588
2.4996
1.5714
1.5352
1.4949
1.3902
0.8519
NH
O
F
O
N
Boc
Integral
1.0373
1.0328
3.1235
2.1650
1.0515
1.0000
1.0025
1.0081
1.0025
9.5093
ppm
12
10
8
6
4
2
0


ppm
174.059
160.641
157.457
148.582
147.975
135.148
131.942
131.828
130.910
126.765
119.336
119.024
116.304
116.124
116.014
115.031
114.732
111.010
110.681
110.539
83.995
83.908
70.655
45.378
40.354
40.076
39.797
39.520
39.242
38.963
38.686
27.852
27.672
NH
O
F
O
N
Boc
ppm
150
100
50
0

2s: Racemic

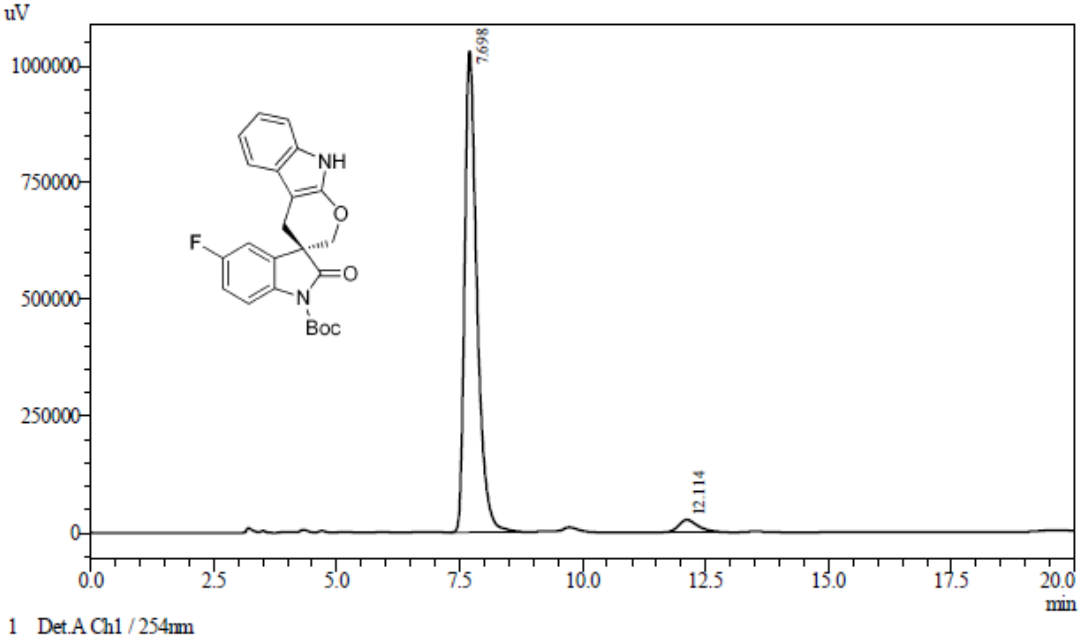


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.709	853343	49944	50.088	62.165
2	12.140	850348	30397	49.912	37.835
Total		1703691	80341	100.000	100.000

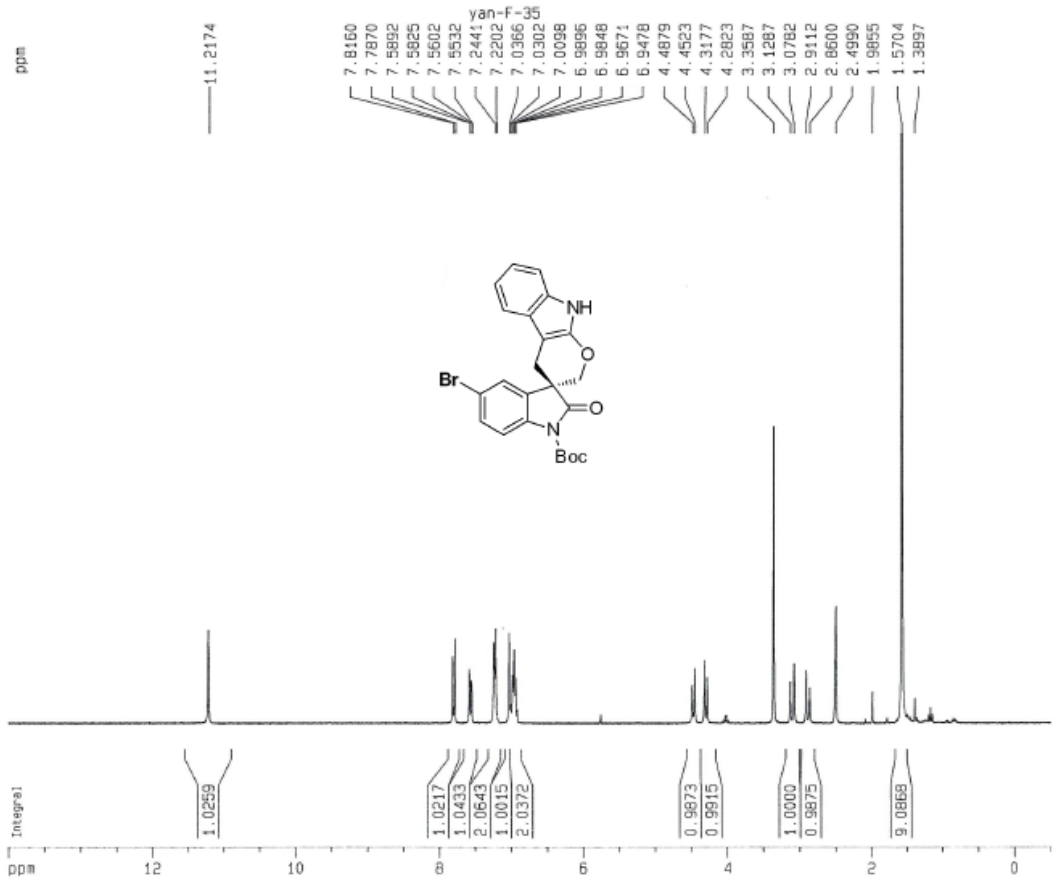
2s: Chiral

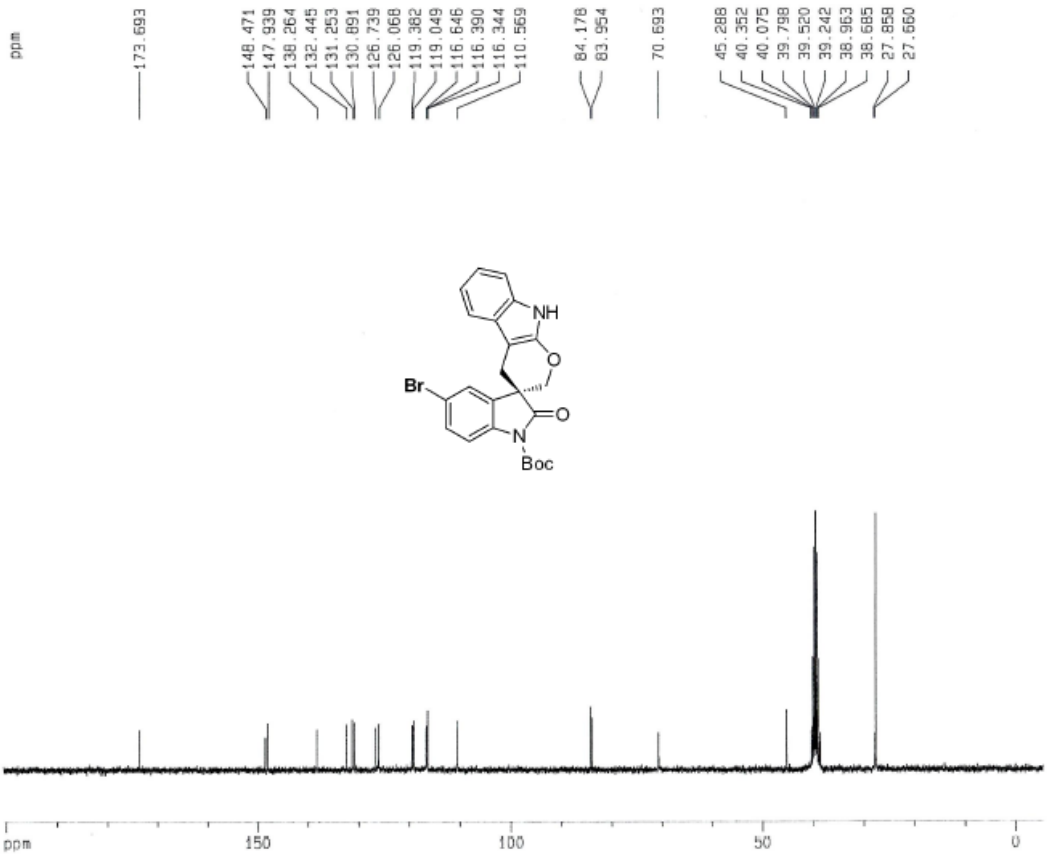


1 Det.A Ch1 / 254nm

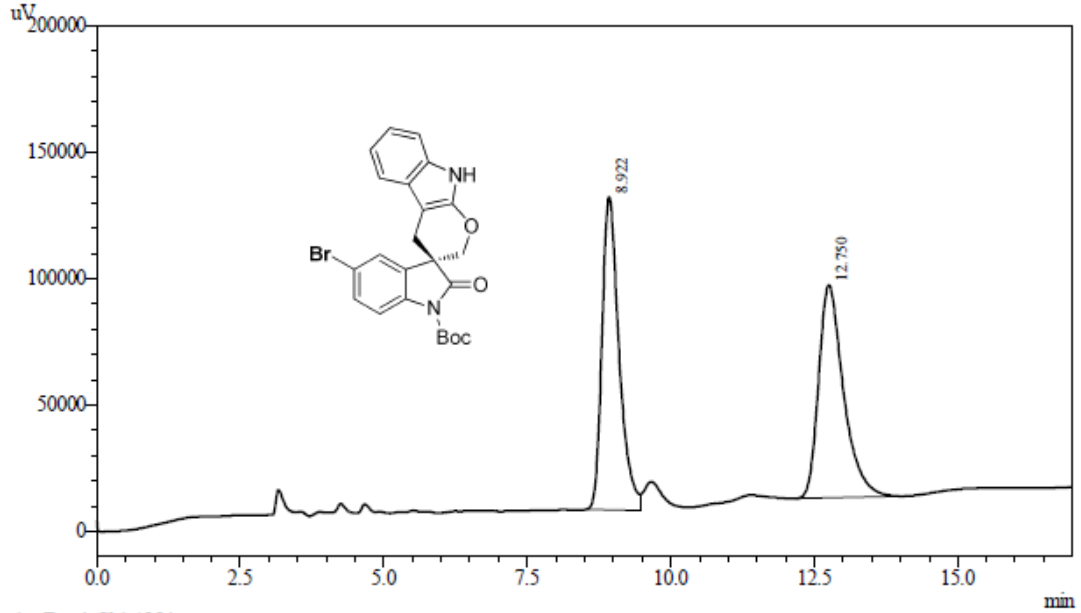
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.698	17886645	1029860	95.922	97.470
2	12.114	760448	26732	4.078	2.530
Total		18647093	1056591	100.000	100.000


yan-F-35
ppm
11.2174
7.8160
7.7870
7.5892
7.5825
7.5602
7.5532
7.2441
7.2202
7.0366
7.0302
7.0098
6.9896
6.9848
6.9671
6.9478
4.4879
4.4523
4.3177
4.2823
3.3587
3.1287
3.0782
2.9112
2.8600
2.4990
1.9855
1.5704
1.3897
NH
O
Br
O
N
Boc
Integral
1.0259
1.0217
1.0433
2.0643
1.0015
2.0372
0.9873
0.9915
1.0000
0.9875
9.0868
ppm
12
10
8
6
4
2
0


ppm
173.693
148.471
147.939
138.264
132.445
131.253
130.891
126.739
126.068
119.382
119.049
116.646
116.390
116.344
110.569
84.178
83.954
70.693
45.288
40.352
40.075
39.798
39.520
39.242
38.963
38.685
27.858
27.660
NH
O
Br
O
N
Boc
ppm
150
100
50
0

2t: Racemic

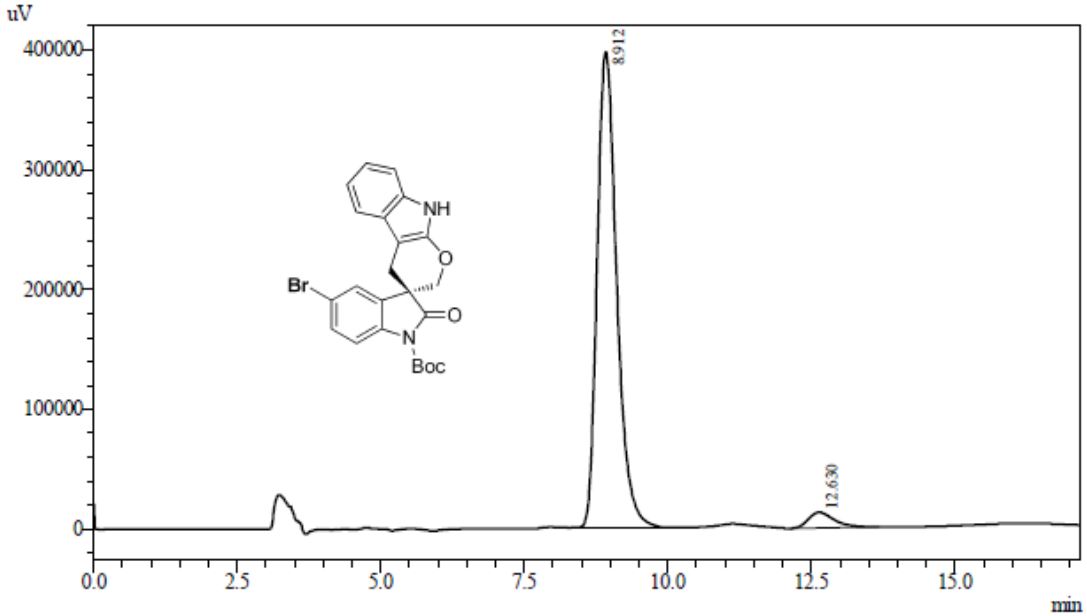


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.922	2563643	123684	50.312	59.564
2	12.750	2531820	83966	49.688	40.436
Total		5095463	207650	100.000	100.000

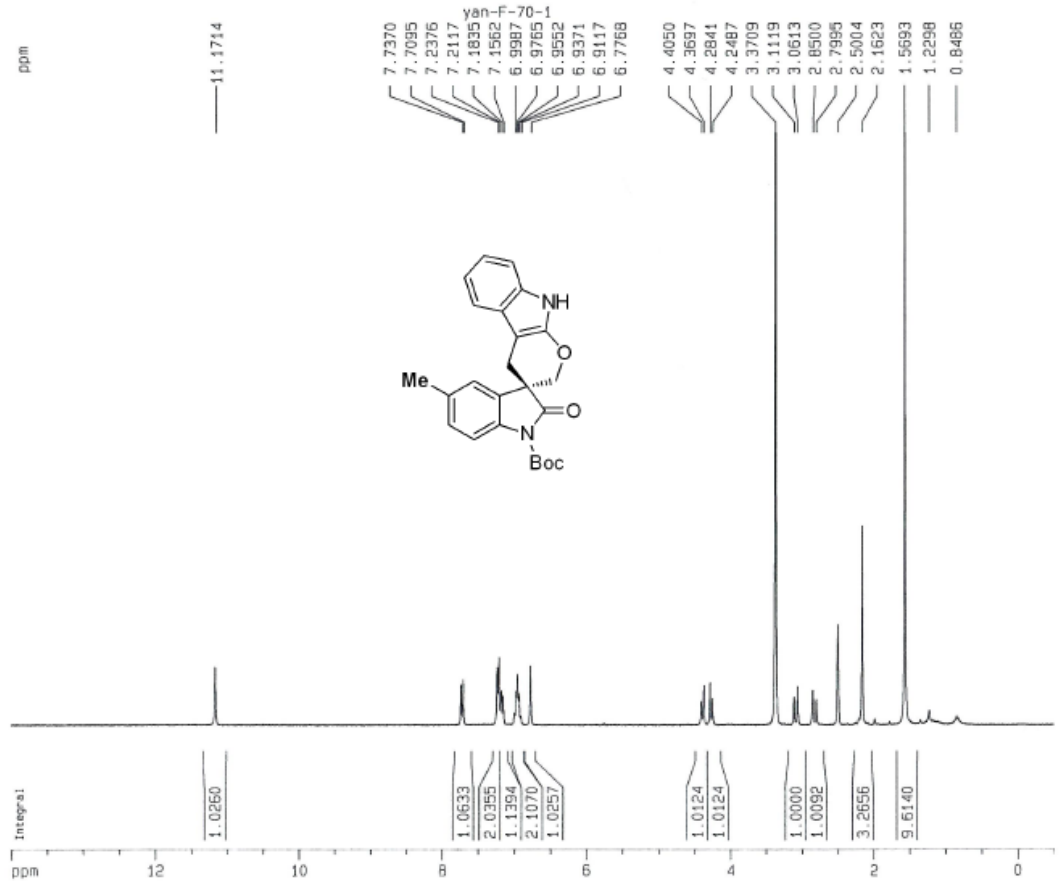
2t: Chiral

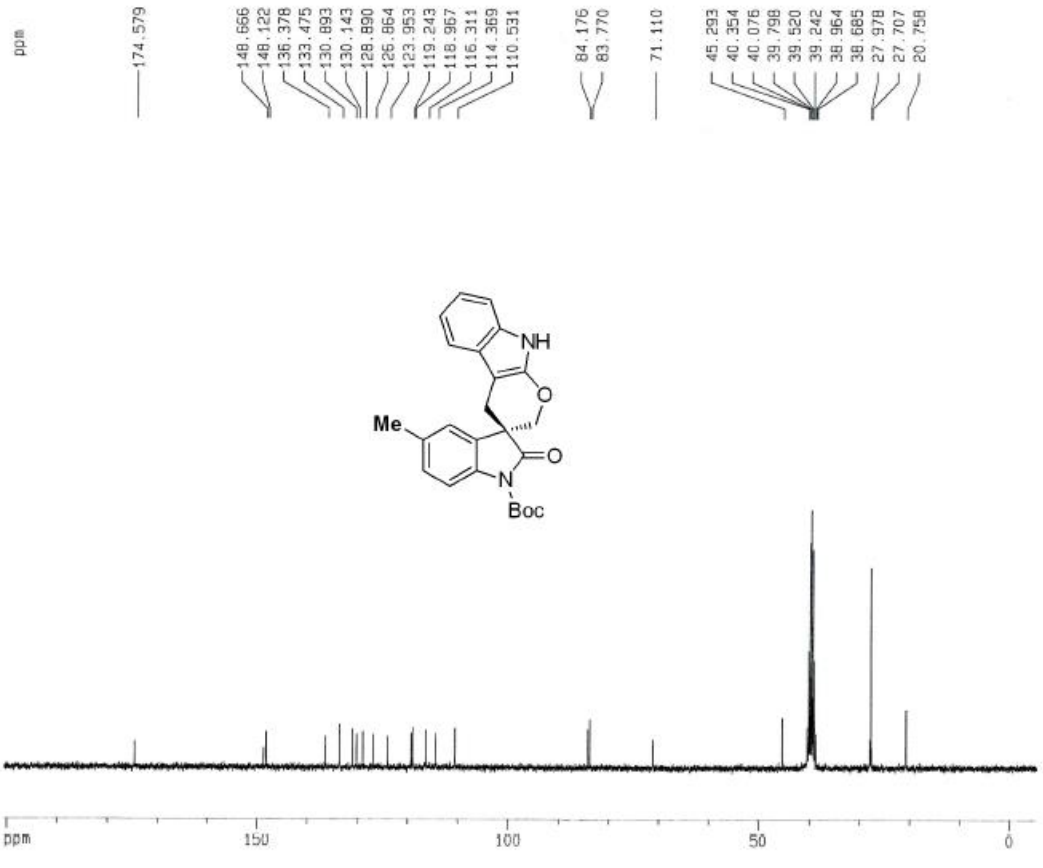


1 Det.A Ch1 / 254nm

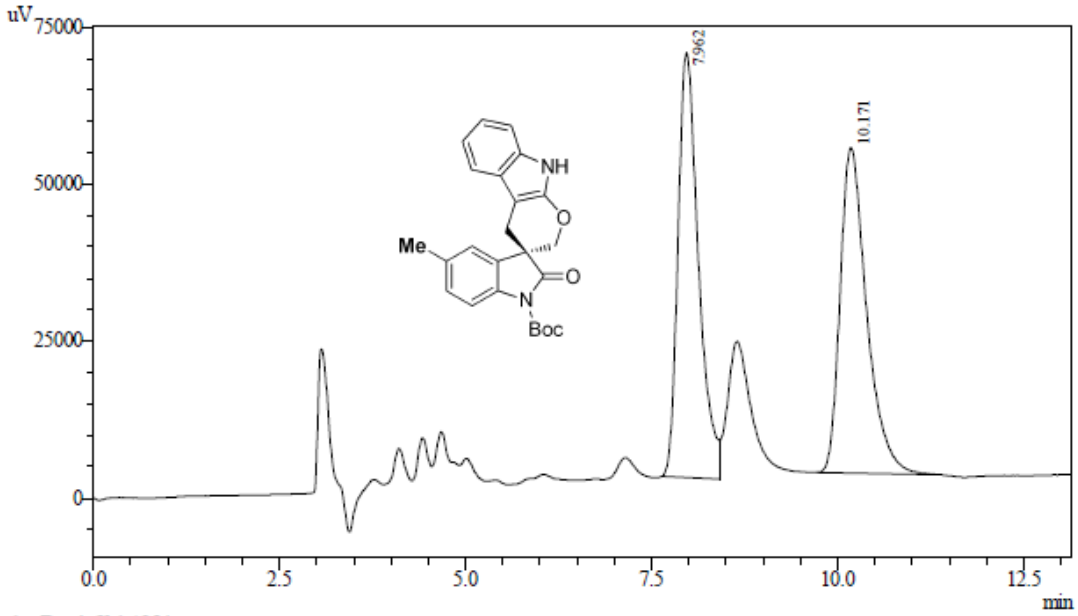
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.912	9410314	397038	95.819	96.836
2	12.630	410588	12974	4.181	3.164
Total		9820902	410012	100.000	100.000


yan-F-70-1
ppm
11.1714
7.7370
7.7095
7.2376
7.2117
7.1835
7.1562
6.9987
6.9765
6.9552
6.9371
6.9117
6.7768
4.4050
4.3697
4.2841
4.2487
3.3709
3.1119
3.0613
2.8500
2.7995
2.5004
2.1623
1.5693
1.2298
0.8486
NH
O
Me
O
N
Boc
Integral
1.0260
1.0633
2.0355
1.1394
2.1070
1.0257
1.0124
1.0124
1.0000
1.0092
3.2656
9.6140
ppm
12
10
8
6
4
2
0


ppm
174.579
148.666
148.122
136.378
133.475
130.893
130.143
128.890
126.864
123.953
119.243
118.967
116.311
114.369
110.531
84.176
83.770
71.110
45.293
40.354
40.076
39.798
39.520
39.242
38.964
38.685
27.978
27.707
20.758
NH
O
Me
O
N
Boc
ppm
150
100
50
0

2u: Racemic

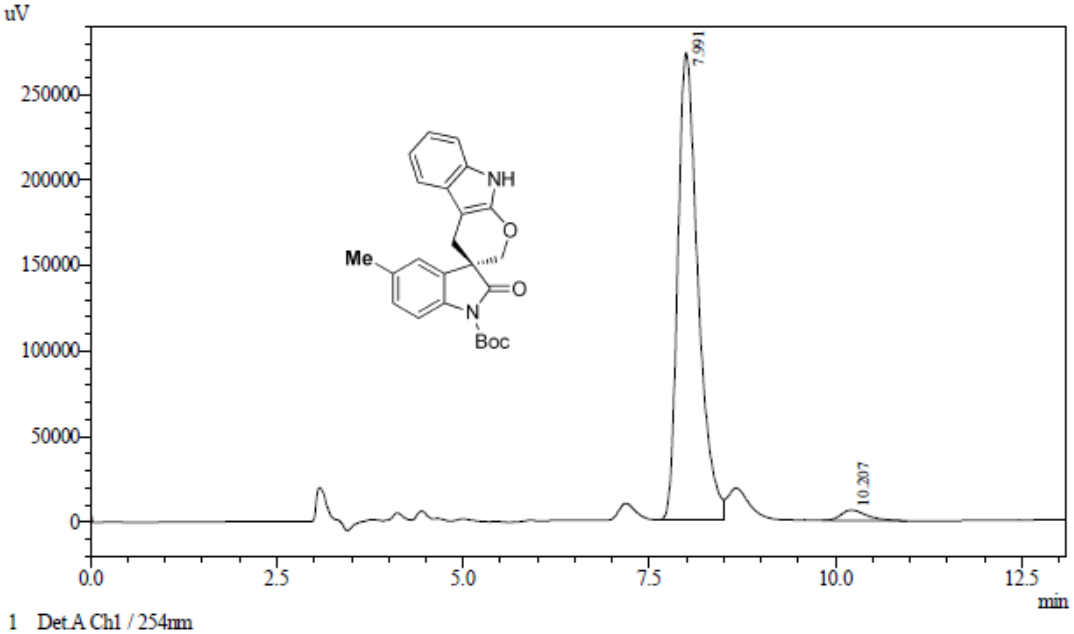


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.962	1296102	67681	50.161	56.606
2	10.171	1287764	51884	49.839	43.394
Total		2583866	119565	100.000	100.000

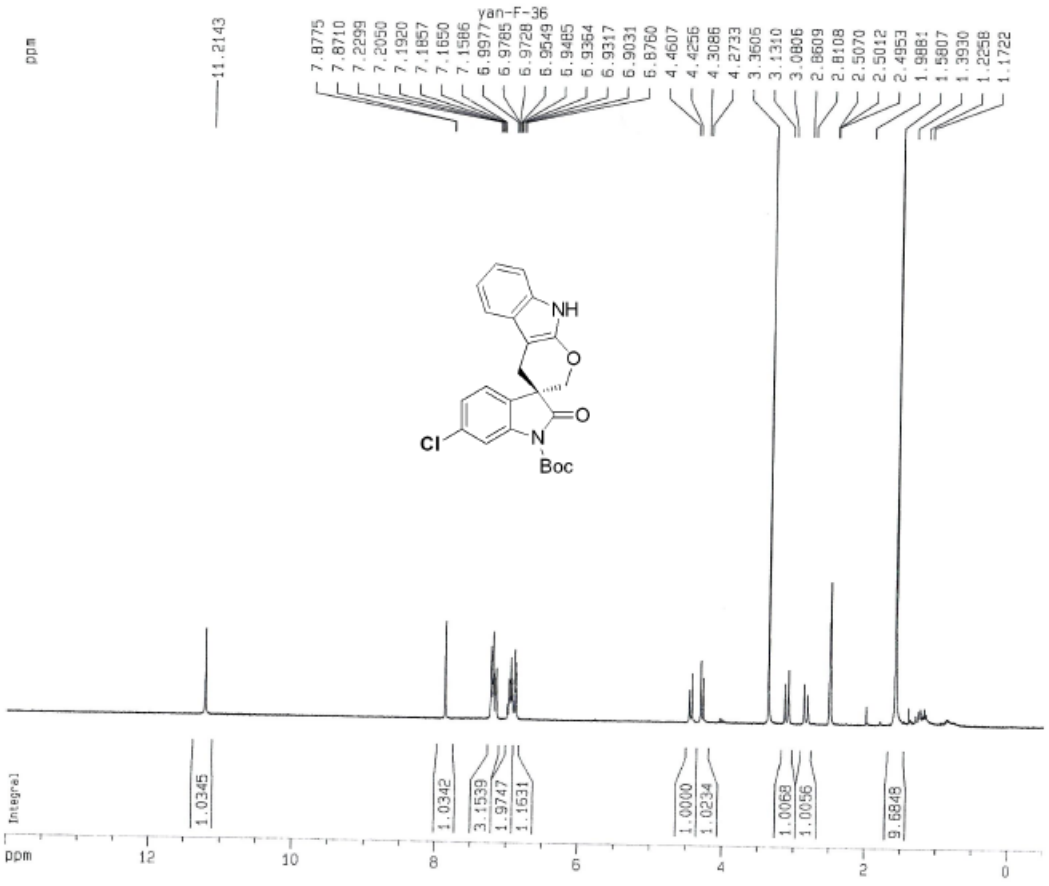
2u: Chiral



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.991	5173853	273210	97.226	97.813
2	10.207	147595	6109	2.774	2.187
Total		5321449	279319	100.000	100.000


yan-F-36
ppm
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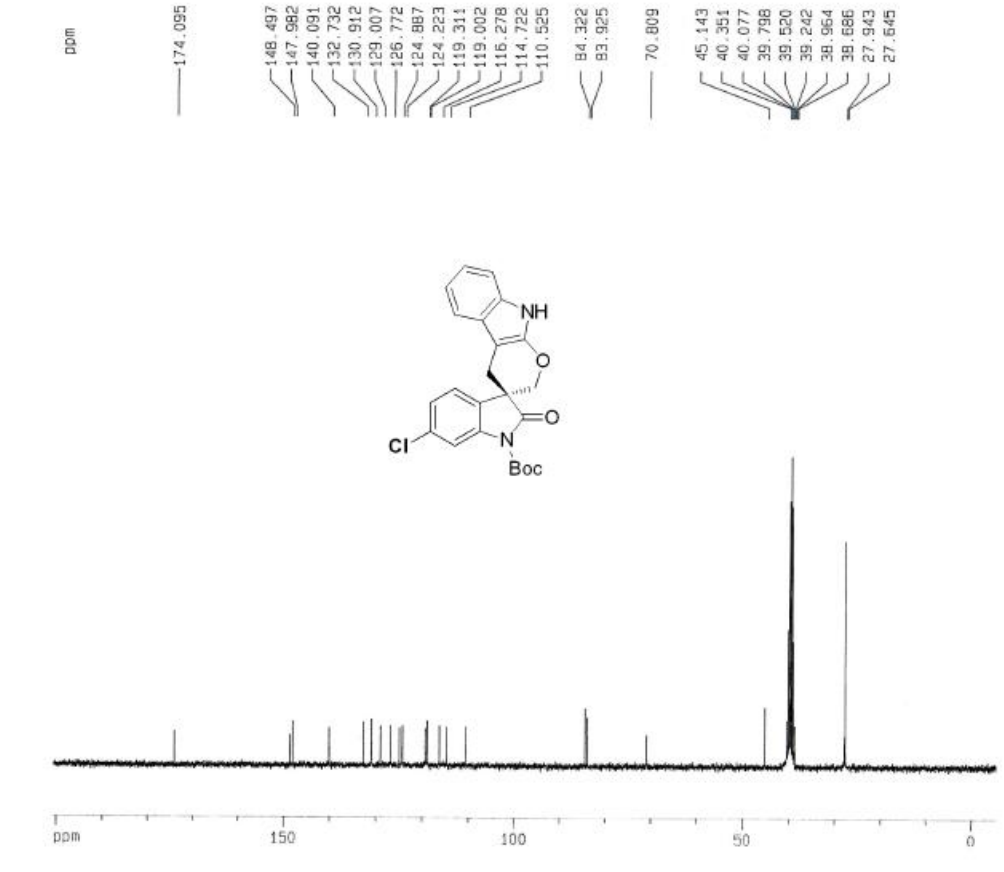
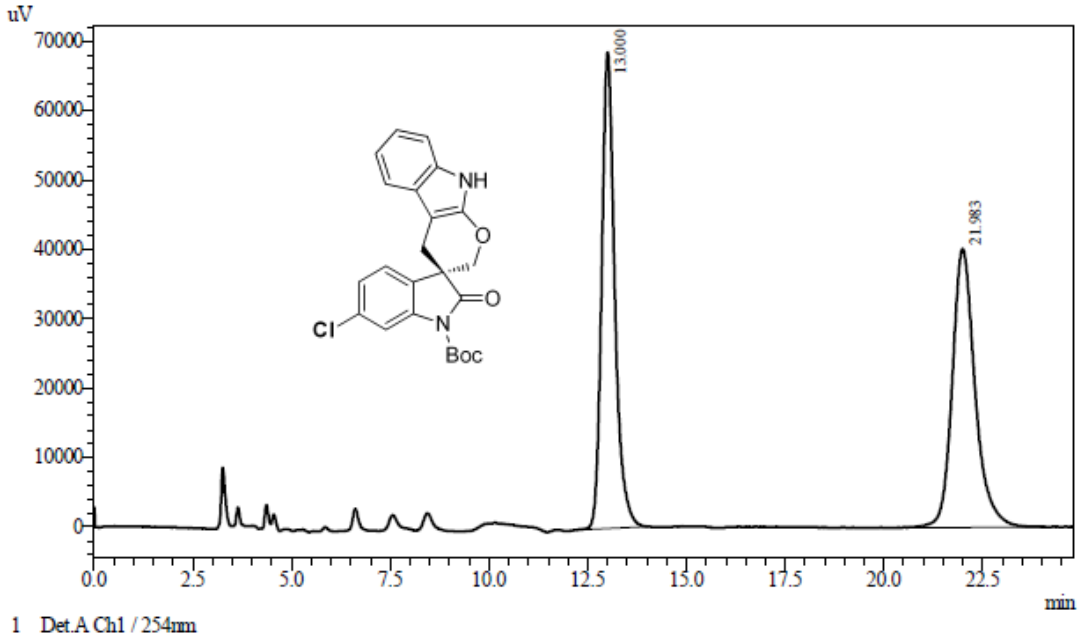
7.8775
7.8710
7.2299
7.2050
7.1920
7.1857
7.1650
7.1586
6.9977
6.9785
6.9728
6.9649
6.9485
6.9364
6.9317
6.9031
6.8760
4.4607
4.4256
4.3086
4.2733
3.3605
3.1310
3.0806
2.8609
2.8108
2.5070
2.5012
2.4953
1.9881
1.5807
1.3930
1.2258
1.1722
NH
O
O
N
Cl
Boc
Integral
1.0345
1.0342
3.1539
1.9747
1.1631
1.0000
1.0234
1.0068
1.0056
9.6848
ppm
12
10
8
6
4
2
0


ppm
174.095
148.497
147.982
140.091
132.732
130.912
129.007
126.772
124.887
124.223
119.311
119.002
116.278
114.722
110.525
84.322
83.925
70.809
45.143
40.351
40.077
39.798
39.520
39.242
38.964
38.686
27.943
27.645
NH
O
O
N
Cl
Boc
ppm
150
100
50
0

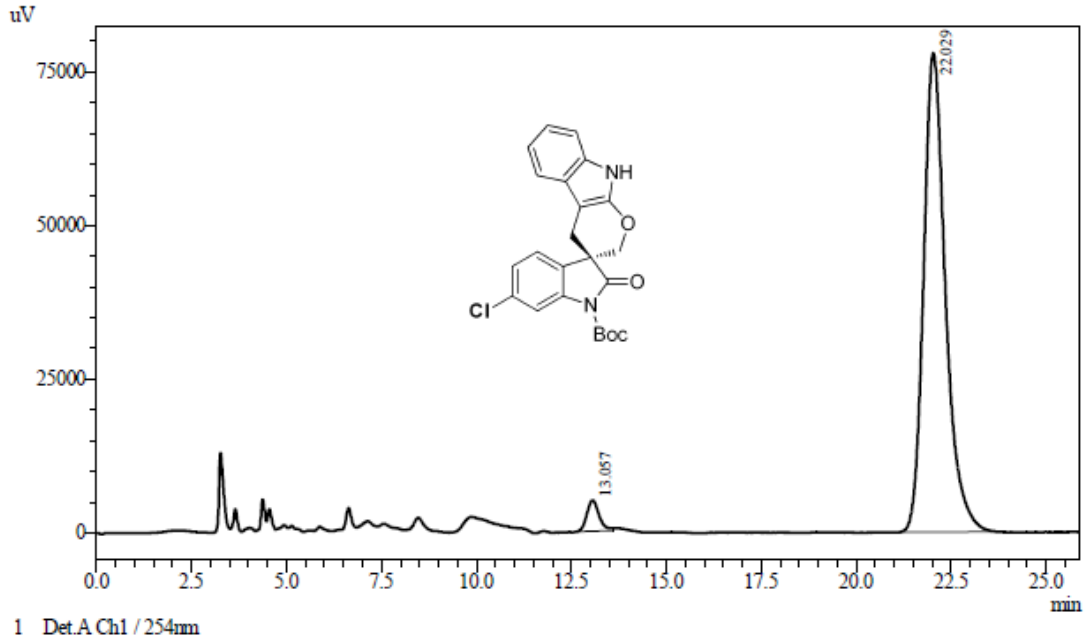
2v: Racemic



Detector A Ch1 254nm

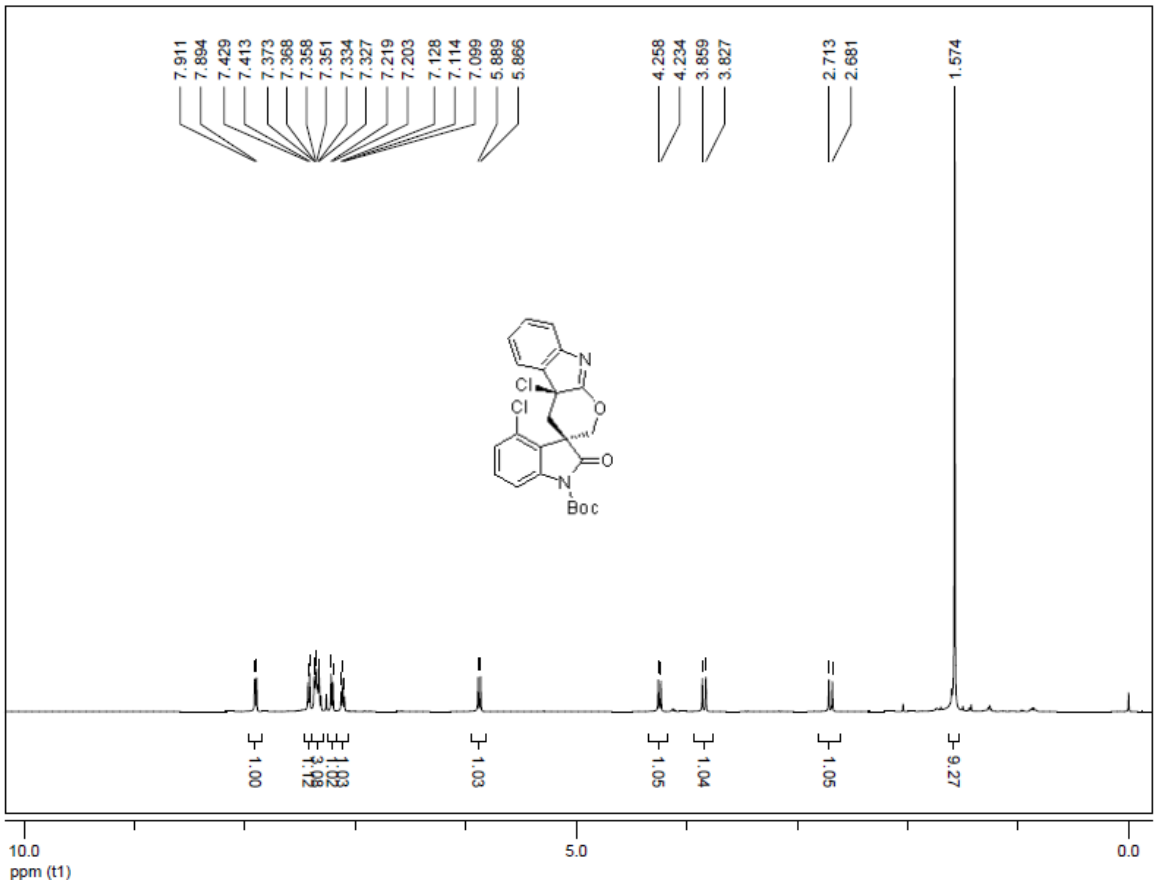
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.000	1588612	68633	49.593	63.123
2	21.983	1614674	40096	50.407	36.877
Total		3203287	108729	100.000	100.000

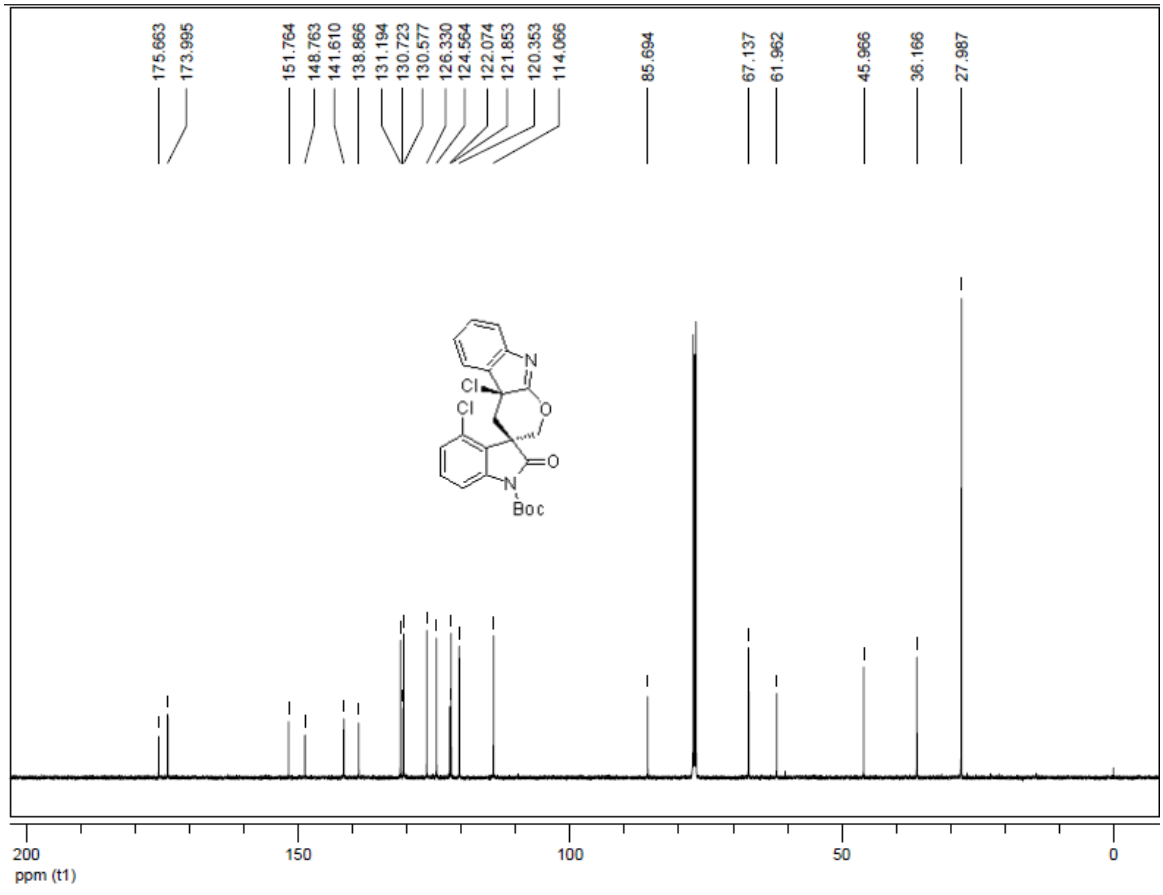
2v: Chiral

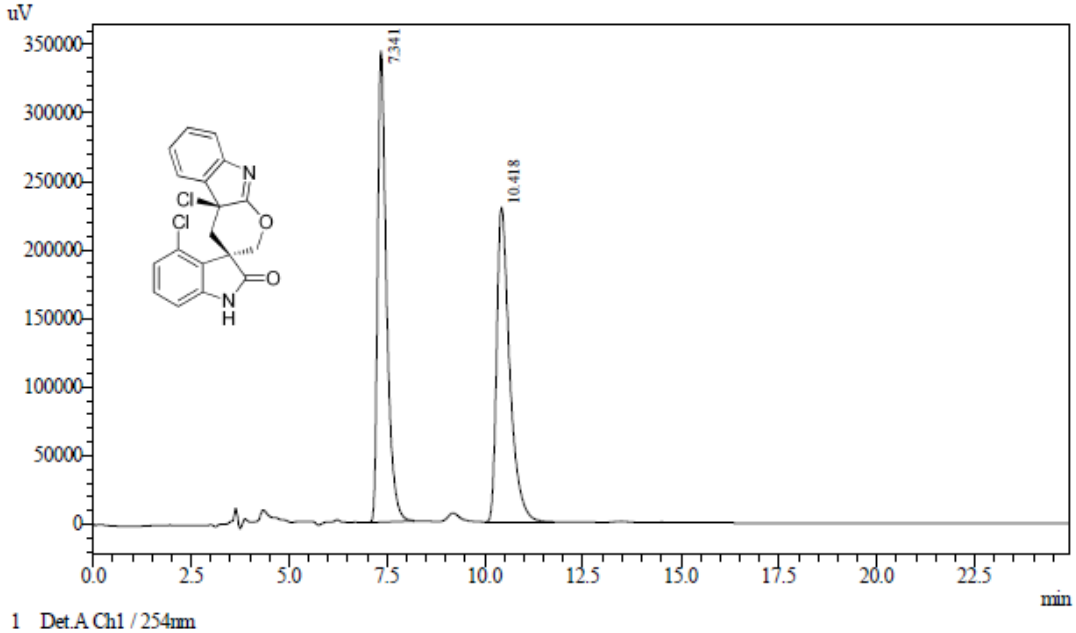


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.057	113758	5074	3.514	6.112
2	22.029	3123665	77937	96.486	93.888
Total		3237423	83011	100.000	100.000


7.911
7.894
7.429
7.413
7.373
7.368
7.358
7.351
7.334
7.327
7.219
7.203
7.128
7.114
7.099
5.889
5.866
4.258
4.234
3.859
3.827
2.713
2.681
1.574
Cl
Cl
N
O
O
N
Boc
1.00
1.03
1.05
1.04
1.06
9.27
10.0
5.0
0.0
ppm (t1)

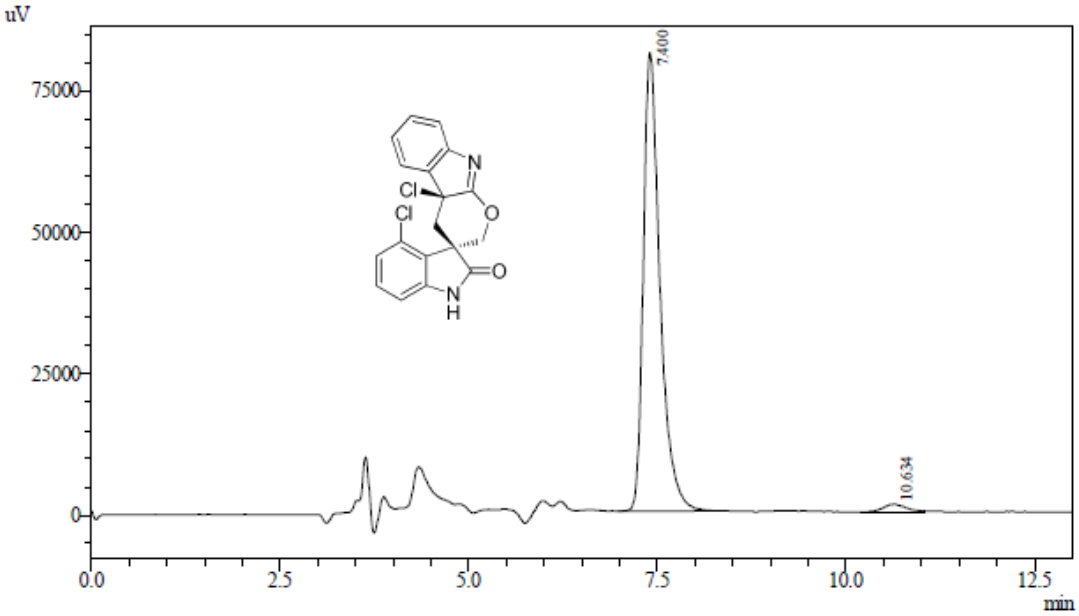

175.663
173.995
151.764
148.763
141.610
138.866
131.194
130.723
130.577
126.330
124.564
122.074
121.853
120.353
114.066
85.694
67.137
61.962
45.966
36.166
27.987
Cl
Cl
N
O
O
N
Boc
200
150
100
50
0
ppm (t1)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

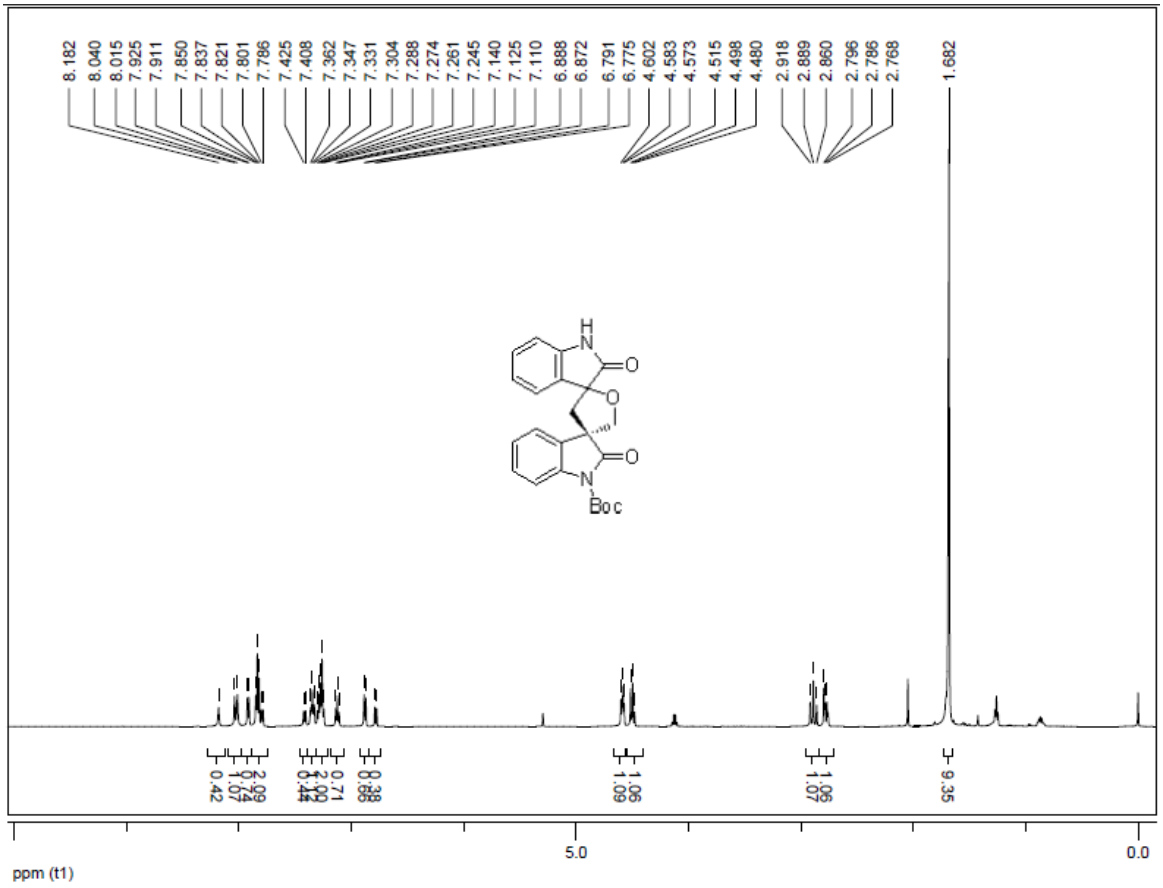
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.341	5425213	343513	50.624	59.960
2	10.418	5291504	229395	49.376	40.040
Total		10716717	572908	100.000	100.000

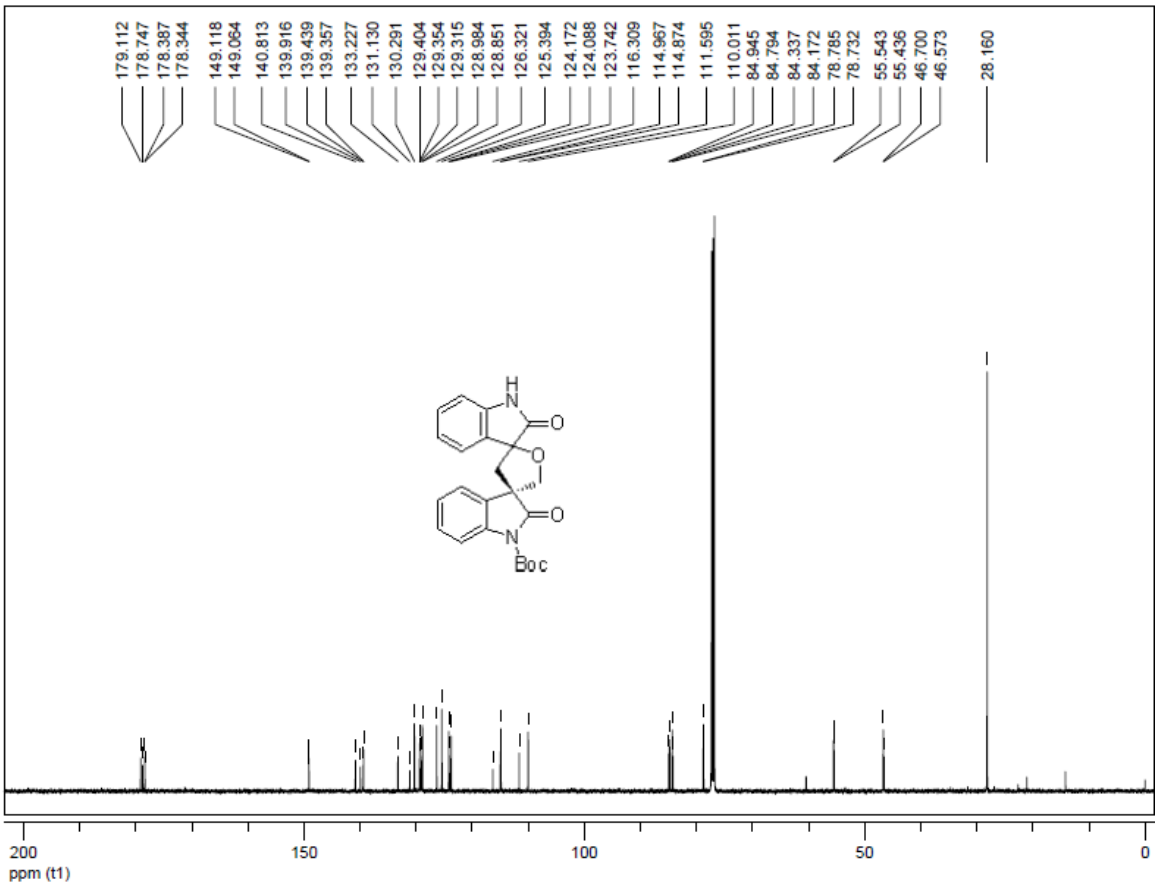


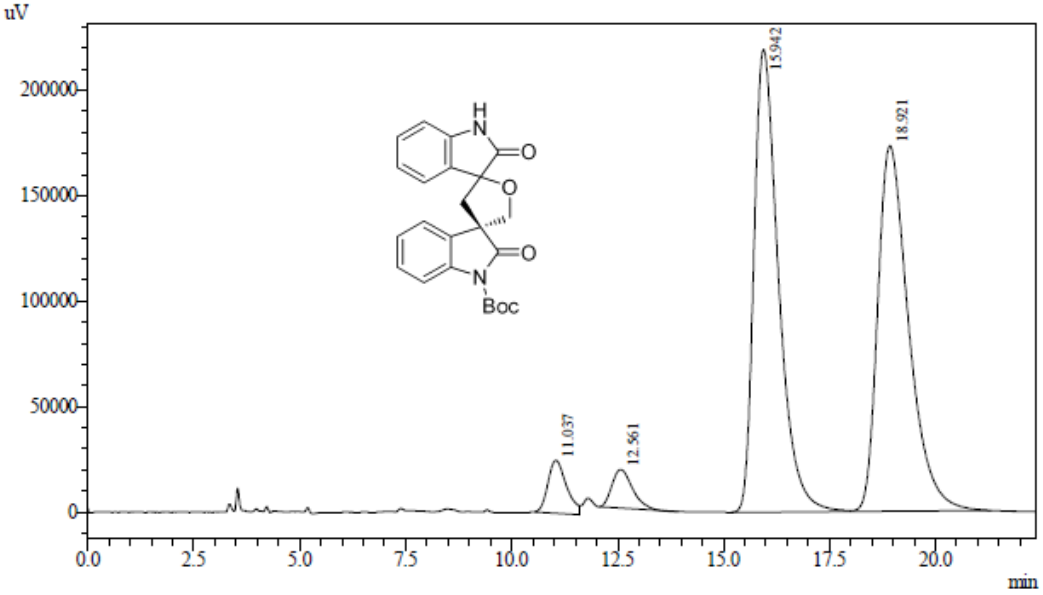
1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.400	1252039	81166	97.657	98.361
2	10.634	30041	1352	2.343	1.639
Total		1282079	82519	100.000	100.000


8.182
8.040
8.015
7.925
7.911
7.850
7.837
7.821
7.801
7.786
7.425
7.408
7.362
7.347
7.331
7.304
7.288
7.274
7.261
7.245
7.140
7.125
7.110
6.888
6.872
6.791
6.775
4.602
4.583
4.573
4.515
4.498
4.480
2.918
2.889
2.860
2.796
2.786
2.768
1.682
Boc
5.0
0.0
ppm (t1)

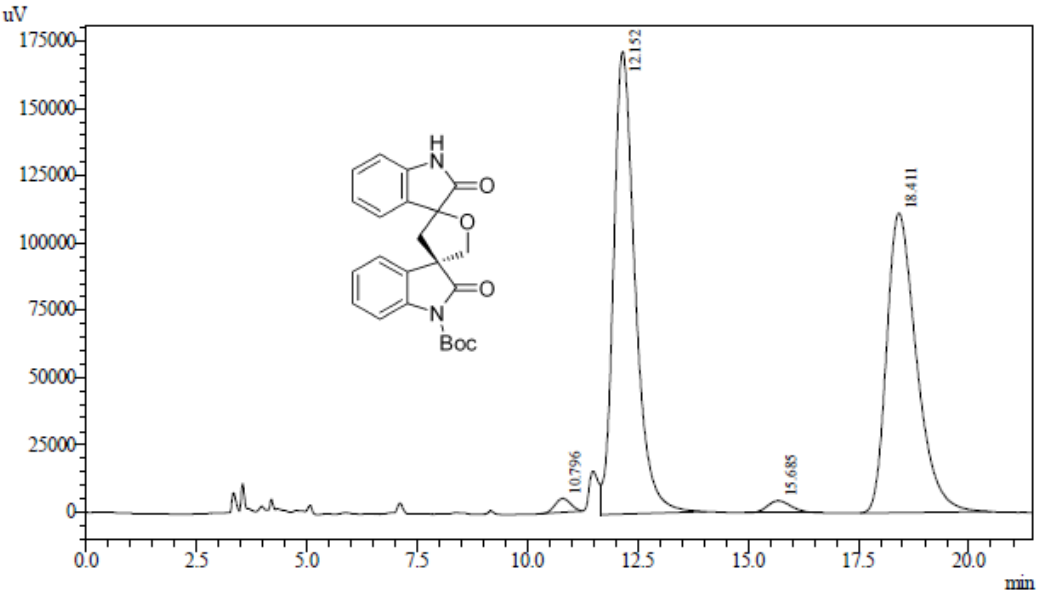

179.112
178.747
178.387
178.344
149.118
149.064
140.813
139.916
139.439
139.357
133.227
131.130
130.291
129.404
129.354
129.315
128.984
128.851
126.321
125.394
124.172
124.088
123.742
116.309
114.967
114.874
111.595
110.011
84.945
84.794
84.337
84.172
78.785
78.732
55.543
55.436
46.700
46.573
28.160
Boc
200
150
100
50
0
ppm (t1)



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

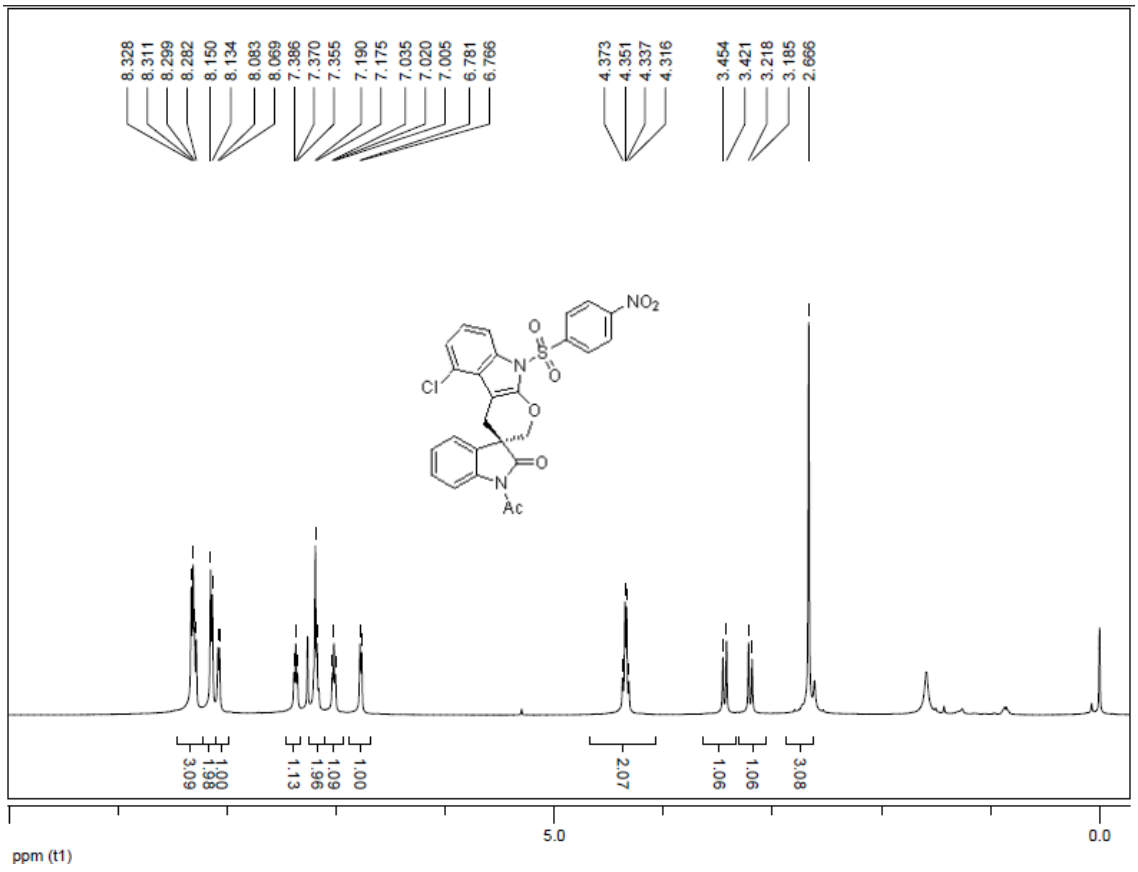
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.037	768259	24996	4.038	5.739
2	12.561	617506	18309	3.246	4.204
3	15.942	8848889	219183	46.515	50.323
4	18.921	8789014	173067	46.200	39.735
Total		19023668	435556	100.000	100.000

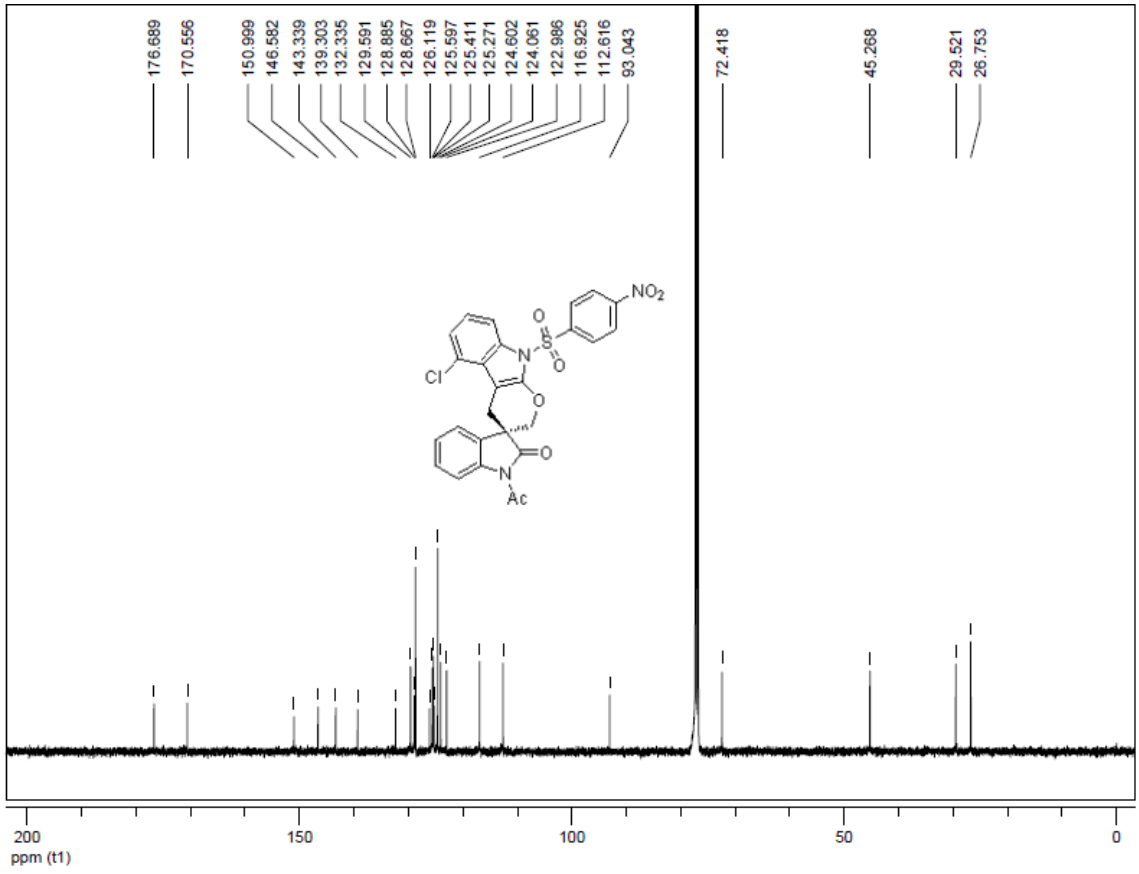


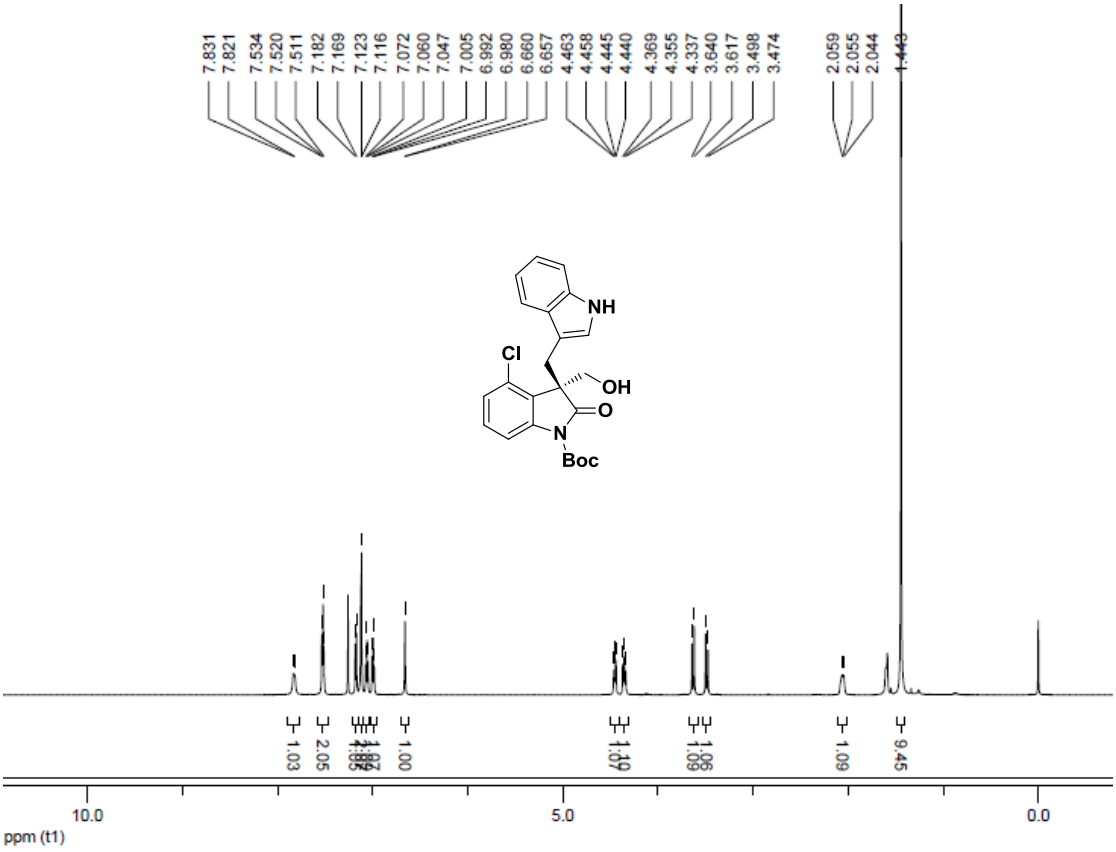
1 Det.A Ch1 / 254nm

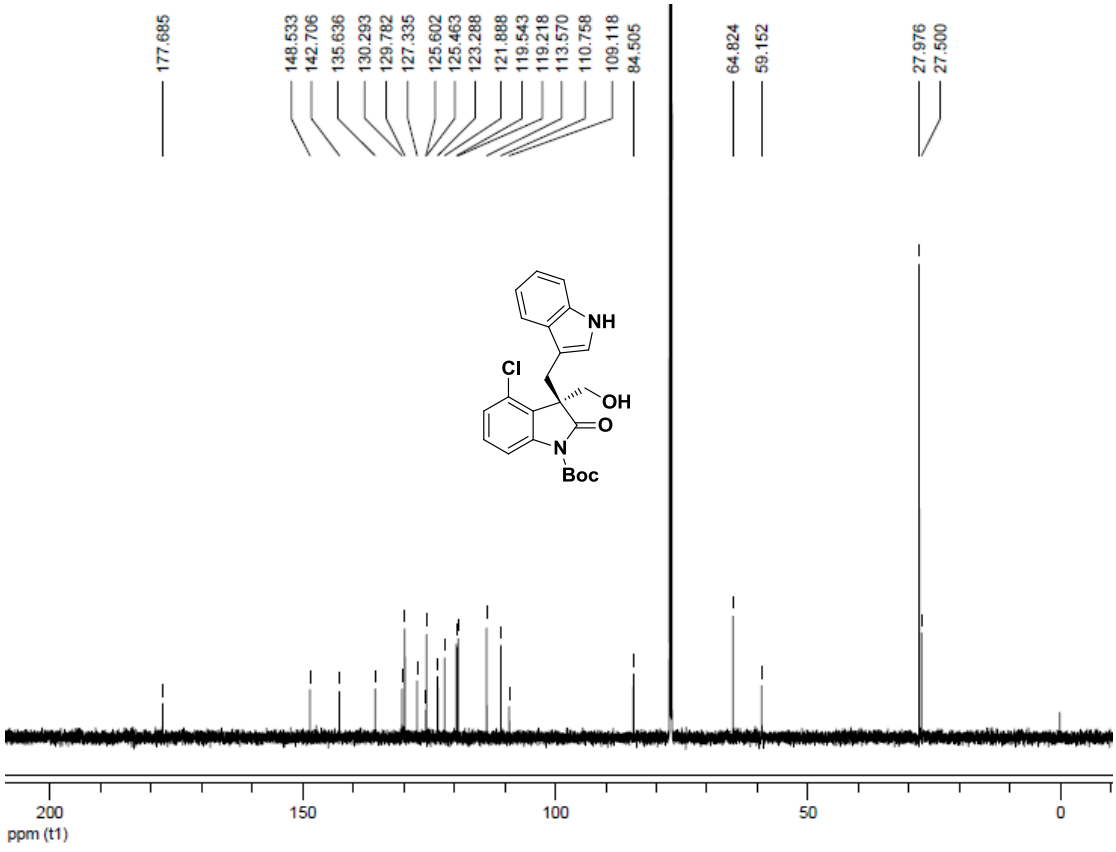
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.796	126404	5143	1.110	1.756
2	12.152	5855419	171959	51.416	58.719
3	15.685	167361	4483	1.470	1.531
4	18.411	5239105	111267	46.004	37.994
Total		11388288	292852	100.000	100.000

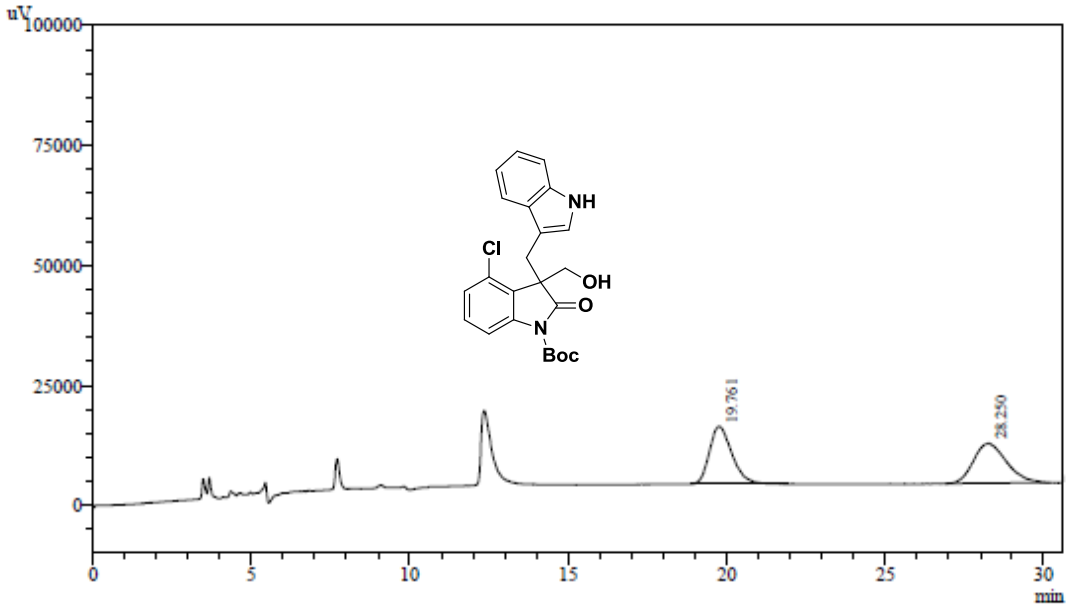

8.328
8.311
8.299
8.282
8.150
8.134
8.083
8.069
7.386
7.370
7.355
7.190
7.175
7.035
7.020
7.005
6.781
6.766
4.373
4.351
4.337
4.316
3.454
3.421
3.218
3.185
2.666
NO2
Cl
O
S
N
O
O
O
N
Ac
3.09
1.98
1.00
1.13
1.96
1.09
1.00
2.07
1.06
1.06
3.08
5.0
0.0
ppm (t1)


176.689
170.556
150.999
146.582
143.339
139.303
132.335
129.591
128.885
128.667
126.119
125.597
125.411
125.271
124.602
124.061
122.986
116.925
112.616
93.043
72.418
45.268
29.521
26.753
NO2
Cl
O
S
N
O
O
O
N
Ac
200
150
100
50
0
ppm (t1)


7.831
7.821
7.534
7.520
7.511
7.182
7.169
7.123
7.116
7.072
7.060
7.047
7.005
6.992
6.980
6.660
6.657
4.463
4.458
4.445
4.440
4.369
4.355
4.337
3.640
3.617
3.498
3.474
2.059
2.055
2.044
1.443
NH
Cl
OH
O
N
Boc
1.03
2.05
1.00
1.10
1.09
1.09
9.45
10.0
5.0
0.0
ppm (t1)


177.685
148.533
142.706
135.636
130.293
129.782
127.335
125.602
125.463
123.288
121.888
119.543
119.218
113.570
110.758
109.118
84.505
64.824
59.152
27.976
27.500
NH
Cl
OH
O
N
Boc
200
150
100
50
0
ppm (t1)

Racemic: 1r a

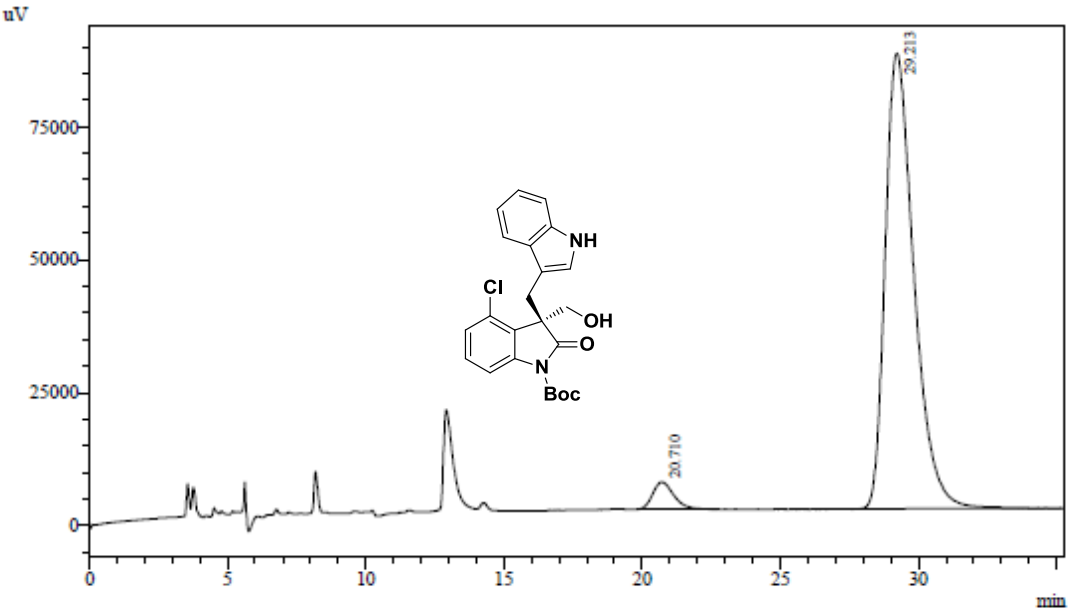


1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.761	593726	11976	49.544	59.055
2	28.250	604654	8303	50.456	40.945
Total		1198380	20279	100.000	100.000

Chiral



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.710	272238	5155	4.209	5.682
2	29.213	6196414	85574	95.791	94.318
Total		6468651	90729	100.000	100.000